ORGANOGERMANIUM-NITROGEN AND ORGANOSILICON-NITROGEN COMPOUNDS
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Organogermanium- and Organosilicon-Nitrogen Compounds

A thesis presented

by

Alan Hunt Bates

to

The Department of Chemistry

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

in the subject of

Chemistry

Harvard University

Cambridge, Massachusetts

May, 1970

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ORGANOSILICON- AND ORGANOGERMANIUM-NITROGEN COMPOUNDS

May, 1970

Alan H. Bates
E.G. Rochow, Advisor

Summary

Organosilicon chemistry has been refined until it has become possible to generalize somewhat and predict the behavior of the silicon-oxygen or silicon-nitrogen bond under different circumstances. Such thorough study has not characterized organogermanium chemistry. Particularly within the much neglected area of organogermanium-nitrogen chemistry, too few compounds have been prepared to permit well-founded generalization about bonding.

In this research, a number of new organogermanium-nitrogen compounds were characterized, primarily for purposes of comparison with related silazanes and silylamines. A consistent goal was to prepare compounds with low moisture sensitivity. Characterization of N-phenyl and N-cyclohexyl organogermazanes by NMR, IR, mass spectrometry, and elemental analysis added to what little had been known, particularly spectroscopically, about organogermanium-nitrogen compounds. One noted some differences in the reactions of dimethyldichlorosilane and dimethyldichlorogermane with aromatic amines like aniline. The germazane products were monomers or six- and eight-membered heterocycles, rather than linear polymers.

New linear silylamine and cross-linked germylamine polymers were prepared by reaction of dimethyldichlorosilane and dimethyldichlorogermane with the three isomeric xylylenediamines. The NMR spectra of these materials furnished readily interpretable contrasts with the spectra of the previously known ethylenediamine compounds.[1] The N,N'-bis-(trimethylsilyl) and N,N'-bis-(trimethylgermyl) derivatives of o-, m-, and p-xylylenediamine were also characterized fully.

The bis-(trimethylsilyl) derivative of 2,3-dihydrophthalazine-1,4-dione has been tentatively shown to involve Si-N rather than Si-O bonding. NMR spectra suggested that at room temperature rotation of the trimethylsilyl groups is hindered in this compound. Low molecular weight polymers formed from 2,3-dihydrophthalazine-1,4-dione and dimethyldichlorosilane or dimethyldichlorogermane have been characterized.

[1] D. Kummer and E.G. Rochow, Inorg. Chem., 4, 1450(1965).
F.A. Henglein and K. Lienhard, Makromol. Chem., 32, 218(1959).

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To Lyn and My Parents

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I am very pleased to express my thanks to Professor Rochow for his kindness and steadfast assistance during my period of graduate research. His willingness to help with any developing problem without at the same time exerting pressure has made him an ideal advisor for me. Freedom of choice and action, accompanied by the ready availability of assistance when it was needed surely speeded my development as a chemist. During my term as teaching fellow in Natural Sciences 3, I benefited from Professor Rochow's example as an unusually fine undergraduate teacher.

As an individual who has a well-balanced interest in industrial chemistry, academic chemical research and university teaching, Professor Rochow has provided excellent periods of instruction and association for numerous undergraduate, predoctoral, and postdoctoral students. His students are particularly conscious of his contributions to their training and outlook on chemistry as his term as research advisor now approaches its end. Most of all his students remember his kindness and sincere concern for their interests.

One of the most pleasant aspects of my years in the Rochow group was my association with some five graduate students and seven postdoctoral fellows. I surely value the discussions which led to solutions of both chemical and world problems. Lasting friendships were the best results obtained

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from our association.

During 1968-69, I enjoyed working with Professor Nash and his alert students in Chemistry 6. I learned just how successful an energetic professor and enthusiastic students can be in educational processes.

I wish to thank the Chemistry Department for efficient provision of material, services, and working space. Those who endeavor to keep the department functioning smoothly are most adept in their work. In particular, Peggy Carr has skillfully contributed to the preparation of this thesis.

I wish to thank Harvard University for a fellowship supporting my first year of graduate study, and the Chemistry Department for repeated teaching assistantships. Principal support for my thesis research (1966-1969) came from the National Institutes of Health in the form of a Predoctoral Fellowship.

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Fig. 2.30 $(CH_3)_3Si\text{-}(hydrazide)\text{-}Si(CH_3)_3$, 10% in CCl_4, TMS internal standard.

Fig. 2.31 $(CH_3)_3Si\text{-}(hydrazide)\text{-}Si(CH_3)_3$, 2% in CCl_4.

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INTRODUCTION

Clemens A. Winkler's preparation[1] of the first organogermanium compound, tetraethylgermane, trailed his discovery and isolation of the element in 1886[2] by only a single year. This compound, seemingly prepared primarily to test Mendeleef's prediction[3] of its boiling point, was of roughly the same vintage as the first organosilicon (tetraethylsilane, 1863),[4] organotin (diethyltin, 1852),[5] and organolead (probably impure hexaethyldilead, 1853)[6] compounds. Though the organic chemistry of silicon and tin developed steadily during succeeding years, tetraethylgermane remained the solitary known organogermanium compound until 1922.[7] Because early research indicated that the chemical properties of germanium placed it so neatly between silicon and tin, and because of the sparse occurrence and the expense of the element, only about 250 organic derivatives of germanium had been prepared before O.H. Johnson presented the first review article in 1951.[8] A recent upsurge in research

1. C.A. Winkler, J. Prakt. Chem., 36(2), 177 (1887).
2. C.A. Winkler, ibid., 34(2), 188 (1886); Chem. Ber., 19, 210 (1886).
3. D.I. Mendeleef, Justus Liebigs Ann. Chem., 8(2), 196(1871).
4. (a) C. Friedel and J.M. Crafts, Ann. Chem., 127, 31(1863).
   (b) E. Krause and A. von Grosse, Die Chemie der Metallorganischen Verbindungen, Borntraeger, Berlin, 1937, p. 260.
5. C. Löwig, Ann. Chem., 84, 320(1852).
6. (a) C. Löwig, ibid., 88, 318(1853).
   (b) L.C. Willemsens and G.J.M. Van der Kerk, Investigations in the Field of Organolead Chemistry, International Lead Zinc Research Organization, Utrecht, 1965, p. 1.
7. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, p. 4.
8. O.H. Johnson, Chem. Rev., 48, 259(1951).

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has resulted from increased commercial availability of germanium metal, the dioxide, and the tetrahalides; from examination of publications by Mirovov and Gar[9] and by Glockling,[10] one estimates that 2500 organogermanium compounds are now known.[11] Because of rather low thermal stability of lead-carbon and lead-hydrogen bonds, organolead chemistry is now surprisingly less well developed than organogermanium chemistry, in spite of the massive use of organolead compounds as antiknock agents in gasoline.[12]

The research reported here was begun as a result of the following observations. Organosilicon chemistry has been expanded and refined until it has become possible to generalize somewhat and predict the behavior of the silicon-oxygen or silicon-nitrogen bond under different circumstances. Enough compounds have been prepared and studied so that infrared absorption frequencies and NMR chemical shifts observed for new compounds may usually be correlated with those of previously-known compounds. Examination of the three volumes compiled by Bažant, Chvalovsky,

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9. V.F. Mirovov and T.K. Gar, Organic Compounds of Germanium (in Russian), Acad. Sciences USSR, Moscow, 1967.

10. F. Glockling, The Chemistry of Germanium, Academic Press, N.Y., 1969.

11. Other recent reviews of organogermanium chemistry:
(a) D. Quane and R.S. Bottei, Chem. Rev., 63, 403(1963); (through 1962).
(b) M. Dub and R.W. Weiss, Organometallic Compounds, 2nd Ed., Vol. II, Springer-Verlag, N.Y., 1967; (covers 1937-1964).

12. L.C. Willemsens and G.J.M. Van der Kerk, Investigations in the Field of Organolead Chemistry, International Lead Zinc Research Organization, Utrecht, 1965, p. 2.

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and Rathouský,[13] or of the first volume of the currently-growing series edited by MacDiarmid,[14] reveals that few, if any, gaping holes exist in the fabric of organosilicon chemistry.

Such thorough study has not characterized organogermanium chemistry. Particularly within the highly-neglected area of organogermanium-nitrogen (and phosphorus) chemistry, too few compounds have been prepared to permit well-founded generalization about bonding; interpretation and correlation of spectroscopic data are difficult because so few data have been published. In 1960, twenty germylamines and germazanes were known;[15] the papers related to those compounds describe preparations but little else. Chapter 3 of the monograph by Rijkens and Van der Kerk[16] presents the first real estimation of Ge-N bond properties, primarily a study of cleavage of the bond by reagents of variable acidic and nucleophilic strength. Though organogermanium-nitrogen chemistry has grown more rapidly in the last few years, four pages in Glockling's book suffice to review the research of the last five years.[17] Notably, that same book omits reference to the Ge-N bond in tables of bond energies

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13. V. Bažant, V. Chvalovský, and J. Rathouský, Organosilicon Compounds (English trans.), Czechoslovak Academy of Science, Prague, 1965.

14. A. MacDiarmid, Ed., Organometallic Compounds of the Group IV Elements, Vol. 1, Part 1, Marcel Dekker, N.Y., 1968.

15. F. Rijkens, Organogermanium Compounds, Germanium Research Committee, Utrecht, 1960, pp. 73-74.

16. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, pp. 35-52.

17. F. Glockling, The Chemistry of Germanium Academic Press, N.Y., 1969, pp. 95-98.

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and bond length, and to all organogermanium-nitrogen compounds in discussions of infrared and NMR spectra.[18]

Coupled with this investigator's interest in acquiring information about organogermanium-nitrogen compounds that might lead to greater knowledge of trends (and dislocations) among the elements in Group IVA was an almost purely practical interest in the nature of polymeric materials. Numerous efforts, with little success, have been made to prepare silazane or silylamine polymers which would improve upon the properties of the silicones (for example, at high temperature). Basically, hopes for attainment of novel properties rested upon the presence of three blocking groups, two on silicon and one on nitrogen, in an Si-N polymer (in contrast with the two silicon substituents in a silicone). Though the individuals who have previously conducted research in this area deserve specific mention, attention is instead here directed to B.J. Aylett's comprehensive review and assessment of the field.[19] Scarcely from belief that organogermanium-nitrogen polymers would prove superior to the silylamines and silazanes, but mostly from curiosity about how the former would differ from the latter, the present author directed most of his attention to the preparation and characterization of cyclic and linear polymeric germazanes and germylamines.

The report by Yoder and Zuckerman[20] of germyl-ethylenediamine and

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18. F. Glockling, The Chemistry of Germanium, Academic Press, N.Y., 1969, pp. 10, 13, 15-21.

19. B.J. Aylett, Organometal. Chem. Rev., 3, 151(1968).

20. C.H. Yoder and J.J. Zuckerman, J.A.C.S., 88, 4831(1966).

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germyl-piperazine polymers is the only significant previous reference to germylamine or germazane polymers.

From the standpoint of simplicity in thoroughly characterizing a germazane system, logical choices for study originally centered around the products of dimethyl- or diethyldichlorogermane with ammonia and methylamine. For example, infrared and NMR spectra of these products would be expected to be the simplest possible for germazane and germylamine systems. Two reactions of diethyldichlorogermane with NH_3 and one of dimethyldichlorogermane with methylamine were conducted during the early stages of this research.

In glassware thoroughly dried at 130°C and under a constantly-maintained dry N_2 atmosphere, the ammonia reactions were performed at 0-5°C by bubbling NH_3 gas (dried by passage through a KOH tower) through a dilute solution of diethyldichlorogermane in sodium-dried diethylether. As anticipated from a previous study of the reaction of diethyldibromogermane with NH_3[21] and from numerous silazane studies,[22] the reactions yielded neither anything approaching high polymer nor, apparently, a single cyclic or linear oligomeric species. During fractional vacuum distillation of the liquid crude product, following removal of solvent at

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21. E.A. Flood, J.A.C.S., 54, 1663(1932).

22. For example, with Et_2SiCl_2:
W. DeMan, J. van Steenis, and H.I. Waterman, Rec. Trav. Chim. Pay-Bas, 67, 864(1948); Chem. Abst. 43, 6971(1949).
With R_2SiCl_2(R=Me, Et):
S.D. Brewer and C.P. Haber, J.A.C.S., 70, 3888(1948).

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atmospheric pressure, the head temperature rose steadily. Most discouragingly, samples for elemental analysis, molecular weight determination, and IR and NMR study could not be prepared, even in a thoroughly flushed glove bag, with any confidence that extensive hydrolysis had not occurred. Sample flasks and capillary pipettes quickly showed deposits of white solid hydrolysis products in the glove-bag atmosphere. No pure discrete products (e.g. cyclic trimer, cyclic tetramer, or diethyldiaminogermane) could be characterized.

The reaction of dimethyldichlorogermane with methylamine was then performed as nearly as possible after the procedure described by I. Ruidisch and M. Schmidt.[23] The yield of nonamethylcyclotrigermazane was about 50% based on dimethylgermanium, on the low side of the range of 50-80% reported by the foregoing authors. The NMR chemical shifts of -18.0 Hz (vs. TMS as internal standard) for the Ge-CH_3 protons, and -157.5 Hz for the N-CH_3 protons, agreed reasonably well with the reported values of -19.0 Hz and -159.0 Hz.[24] This cyclic trimer, presumably a candidate for attempts to prepare higher polymers by catalytic ring opening, was again observed to be inconveniently sensitive to moisture. Though, as reported in the following chapter, the diethylgermanium-ammonia system was used in transamination reactions (without isolation if intermediate products), neither ammonia nor methylamine products were studied further. In retrospect, one would think that the dimethylgermanium-methylamine system was,

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23. I. Ruidisch and M. Schmidt, Angew. Chem., 76, 686(1964).

24. I. Schumann-Ruidisch and B. Jutzi-Mebert, J. Organometal. Chem., 11, 77(1968).

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and is, worthy of further study. However, as a beginning for research which might lead to a thesis, a more tractable system was needed.

The reaction of diethyldichlorogermane with aniline provided the first series of tractable and interesting products obtained in this research. Following characterization of those products, the analogous ones derived from the rather parallel reaction of cyclohexylamine with diethyldichlorogermane were obtained. At a much later date, the reactions of dimethyldichlorogermane with aniline and cyclohexylamine were conducted and the products were analyzed. Chapter I of this thesis treats in detail these four reaction systems.

During the early stages of research, the writer was attracted by the three isomers (ortho, meta and para) of α,α'-diaminoxylene (more commonly named xylylenediamine) as sources of possible interesting monomeric, cyclic oligomeric, and linear polymeric germylamines. Reactions of dimethyldichlorogermane with all three isomers, and of trimethylbromogermane with the para isomer, were performed and the products characterized. Since compounds of xylylenediamine with Group IV elements had been previously unreported, dimethyldichlorosilane and trimethylchlorosilane also were reacted with all three xylylenediamine isomers. The organogermanium- and organosilicon- xylylenediamine reactions, demonstrating interesting differences between the two metalloids, are treated in detail in Chapter II.

Finally, the process of preparation of the o- and p- xylylenediamines yielded large quantities of 2,3-dihydrophthalazine-1,4-dione (also named phthalylhydrazide). This rather curious organic compound (mp 349°C!)

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itself suggested a possible new system of organogermanium and organosilicon monomers and polymers, containing either the metal-nitrogen or metal-oxygen bond, or perhaps both. Chapter III considers the trimethylsilyl, dimethylsilyl, and dimethylgermyl derivatives of 2,3-dihydrophthalazine-1,4-dione.

In Chapter IV, the investigator briefly summarizes the principal observations that have been made about germazanes and germylamines, as compared with silazanes, in this research. Appendix I lists in tabular form the non-organogermanium reagents used in this research, indicates their source, and describes their purification prior to reaction. The bulk of the di- and triorganohalogermanes used were prepared and purified by the investigator. Appendix II briefly describes the (previously known) methods of preparation and delineates the means by which the starting materials, Ge metal and GeO_2, were utilized with nearly 100% efficiency.

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CHAPTER I

First-order considerations in efforts to prepare germazanes and germylamines which are relatively moisture-insensitive dictate that the Lewis basicity of the nitrogen be made low, in order that the nitrogen "unshared" electron pair be made inaccessible to electrophilic attack by water or another proton donor. Previous research[25] has indicated that electrophilic attack on nitrogen is important in hydrolysis of the Ge-N (Si-N) bond, unlike many other displacement reactions of silanes and germanes; some limited evidence has suggested that attack at silicon is also important. Rijkens and Van der Kerk[26] found that phenol, ethanol, tert-butanol, phenylacetylene, and octylamine (in decreasing order of acidity) show decreasing reactivity in the same order with compounds of the type $(n\text{-}C_4H_9)_3GeNR_2$ (in benzene solution). Reactivity does not follow the order of increasing nucleophilic character; while nucleophilic attack at the germanium atom is necessarily involved in the reaction, that attack is evidently less important than the protonation of nitrogen. The foregoing authors suggested the following scheme for such reactions:

$$ROH + \equiv Ge\text{-}N= \longrightarrow RO(-) + \equiv Ge\text{-}\overset{(+)}{N}H=$$

$$\equiv Ge\text{-}\overset{(+)}{N}H= \longrightarrow \equiv Ge(+) + HN= \qquad \text{(rate-determining)}$$

$$\equiv Ge(+) + RO(-) \longrightarrow ROGe\equiv$$

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25. (a) K.A. Andrianov and G. Rumba, Zh. Obshch. Khim., 31, 4038(1961). (b) K.A. Andrianov, V.P. Bazov, G.V. Kotrelev, Dokl. Akad. Nauk SSSR, 176, 579(1967).

26. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, pp. 47-52.

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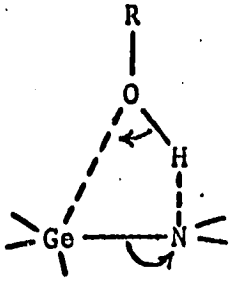
If the first step is assumed to be fast, as is usually the case for protonations, and if departure of the amine group is indeed rate-determining, one would not expect to observe correlations of reactivity with increasing acidity of the attacking agent. Particularly in solvents of low polarity there is probably no distinct protonating step. The same authors noted that formation of completely separated charges may not occur, and that reaction may occur nearly concertedly in a transition state involving a weak interaction between germanium and oxygen:



Breakage of the O-H bond within such a four-center transition state should be favored by the same factors which increase the acidity of the protonic reagent. If such bond breakage were involved in the rate-controlling step, one would expect the observed rate differences.

Rijkens and Van der Kerk observed that triphenyl- and tributylgermyl derivatives of pyrrole and indole, in which the "unshared" electron pair participates strongly in the aromatic π-system, resist electrophilic attack (no appreciable reaction of tri-n-butylgermyl derivative upon heating with equivalent amount of water in a Carius tube at 180°C for 4 1/2 hours).

Similarly, derivatives of succinimide and phthalimide, in which delocalization of electron density over the nitrogen and carbonyl groups reduce the basicity of the nitrogen, show very low reactivity toward phenol

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and ethanol.

Much evidence supports the statement that the basicity of an amino nitrogen atom may also be reduced by participation of the nitrogen "lone" pair in pπ-dπ bonding between nitrogen and germanium (4d orbitals employed) or silicon (3d orbitals). Two research groups[27] have reported decreasing basicity, with increasing dπ-pπ bonding, in the series Me_3GeNMe_2, $(Me_3Ge)_2NH$, and $(Me_3Ge)_3N$. However, all of these compounds are readily attacked by water; distinctions in reactivity occur only with weaker acids such as phenylacetylene, diphenylphosphine, and octylamine. More striking π-bonding effects, with much more extensive documentation, are found in organosilicon chemistry. The low basicity and planar structure of trisilylamine derive from participation of the nitrogen "lone" pair in extensive pπ-dπ bonding between nitrogen and the silicon atoms.[28] In the series $N(CH_3)_3$, $(SiH_3)N(CH_3)_2$, $(SiH_3)_2N(CH_3)$, and $(SiH_3)_3N$, as silyl groups replace methyl groups, as π-bonding and delocalization of the nitrogen "unshared" pair increase, the stabilities of Lewis acid-base complexes with trimethylboron decrease. The last two compounds in the series, in fact, form no such complexes.[29] The infrared, Raman, and NMR spectra of silylamines and silazanes have been thoroughly investigated

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27. (a) F. Rijkens, M.J. Jansen, G.J.M. Van der Kerk, Rec. Trav. Chim., 84, 1597(1965).
    (b) J. Satgé and M. Baudet, Compt. Rend., 265, 435(1966).

28. K. Hedberg, J.A.C.S., 77, 6491(1955).

29. (a) A.B. Burg and E.S. Kuljian, ibid., 72, 3103(1950).
    (b) S. Sujishi and S. Witz, ibid., 76, 4631(1954).

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and, in many cases, have been used to estimate the degree of π-bonding in various Si-N compounds. Spectroscopic data indicate that the force constant of the Si-N bond in hexamethylcyclotrisilazane[30] and hexamethyldisilazane[31] is greater than that for a single Si-N bond. Measurements of dipole moment[32] on Me_3SiNMe_2 and $Me_2Si(NMe_2)_2$ have shown the polarity of the Si-N bond to be decreased, in reflection of some transfer of nitrogen electron density toward silicon. No attempt has been made here to list fully the many studies of Si-N dπ-pπ bonding. Attention is instead directed to the discussion and more thorough documentation in the reviews of Wannagat[33] and of Bažant, Chvalovsky, and Rathouský.[34]

One must strongly modify the foregoing electronic considerations by indicating that steric effects are also observed in the hydrolysis and alcoholysis of Si-N and Ge-N compounds. The extent and rate of reaction are dependent on hindrance about the Si atom and about the hydroxyl group of an alcohol, less so on hindrance at the N atom.[35] Pike has reported decreasing reactivity of silylamines ($R_3SiNR'_2$) with silanols in

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30. H. Kriegsmann, Z. Anorg. Allg. Chem., 298, 223(1959).

31. H. Kriegsmann, Z. Elektrochem., 61, 1088(1957).

32. K. Schaarschmidt, Z. Anorg. Allg. Chem., 310, 78(1961).

33. U. Wannagat, Advan. Inorg. Chem. Radiochem., 6, 225(1964).

34. V. Bažant, V. Chvalovsky, and J. Rathouský, Organosilicon Compounds (English trans.), Czechoslovak Academy of Sciences, Prague, 1965, p. 76.

35. (a) R.M. Pike, J. Org. Chem., 26, 232(1961).
(b) R. Fessenden and J.S. Fessenden, Chem. Rev., 61, 361(1961).
(c) K.A. Andrianov, S.A. Golubtsov, and E.A. Semenova, Izvest. Akad. Nauk. S.S.S.R., Otdel, Khim. Nauk., 47(1958); Chem. Abst., 52, 11734(1958).

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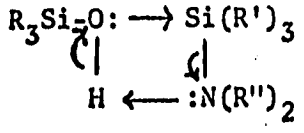
the order R = Me > Et > N-Bu. Notably, however, he interprets his entire series of reactions in terms of nucleophilic displacement at silicon; i.e. the oxygen of the silanol attacks the silicon of the silylamine, and deprotonation of the silanol follows. Pike also notes that his results support a four-center mechanism:



There may not be much to distinguish such a four-center array from that suggested by Rijkens and Van der Kerk (see above)[26] in their postulation of electrophilic attack on nitrogen. In the series described by Pike, triphenylsilanol reacts more rapidly than triethylsilanol (K_A of former greater than that of latter). Without specific knowledge of the relative nucleophilicity of the two species, one cannot decide between nucleophilic and electrophilic attack; presumably triethylsilanol would be the stronger nucleophile. Parenthetically, the best kinetic studies of reactions about silicon (those of exchange of labelled chloride ion with $SiCl_4$ or of hydrolysis of $SiCl_4$) indicate nucleophilic attack in the given cases.[36]

Breed and Elliott[37] have attributed the decreasing hydrolytic stability in the order tris(N-ethyl)-hexamethylcyclotrisilazane > nonamethylcyclotrisilazane > hexamethylcyclotrisilazane to the steric effect of the N-methyl and N-ethyl groups. A statement by the same

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36. C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960, pp. 103-113.

37. L.W. Breed and R.L. Elliott, Inorg. Chem., 3, 1622(1964).

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authors that phenyl substitution on silicon appears to decrease hydrolytic stability (trimethyltriphenylcyclotrisilazane hydrolyzed 1.2 times as fast as hexamethylcyclotrisilazane) agrees poorly with the fact that hexaphenylcyclotrisilazane is quite moisture insensitive (water precipitates it from moist acetone).[38] Attempts to distinguish steric from electronic effects in the hydrolysis of phenyl silazanes had best wait for more experimental results. One notes that the $(C_6H_5)_3Si$ group clearly withdraws electrons inductively and that the phenyl group conjugates effectively with silicon (using the silicon d-orbitals)[39]; both effects, if paralleled by the $(C_6H_5)_2Si$ group in silazanes, should stabilize the Si-N bond against hydrolysis.

In organogermanium-nitrogen chemistry, there have been no extensive studies of steric influences on the hydrolysis and alcoholysis of germazanes. Satgé and Baudet found that the trimethylgermylamines react more readily with n-octylamine than do germylamines with heavier alkyl groups on germanium.[27b] In all considerations of steric influence of alkyl groups on germanium or silicon, one must remember that, particularly among the smaller alkyl groups, increase in size results in greater inductive donation of electrons. Transfer of electrons to the metal, simply by decreasing the effective electronegativity difference between Ge or Si and N, should reduce moisture sensitivity. A most pronounced effect would result if attack were nucleophilic. Even if attack were most significantly electrophilic, increases in electron density at the metal should influence

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38. E. Larsson and Lars Bjellerup, J.A.C.S., 75, 995(1953).

39. C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960, pp. 97-103.

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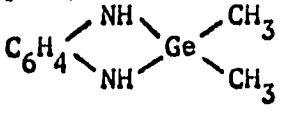
the basicity of the nitrogen in systems well tied together with σ and dπ-pπ bonding.

1. N-phenyl germazanes

Discussion

In this research, the first compounds synthesized which demonstrated relatively good hydrolytic stability were N-phenylated amino derivatives of diethylgermaniumdichloride. In the immediately following sections these products, and the reactions producing them, are considered in detail.

One previously-prepared N-phenylated organogermanium-nitrogen compound shows striking moisture insensitivity. The hydrazine derivative $(C_6H_5)_3GeN(C_6H_5)NH(C_6H_5)$, prepared in THF by addition of triphenylgermyllithium to azobenzene or azoxybenzene, was isolated in yields of 51-79% after hydrolysis of $(C_6H_5)_3GeN(C_6H_5)NLi(C_6H_5)$ with water or a saturated NH_4Cl solution.[40] This compound and the previously-mentioned[26] pyrrole and indole derivatives of tributyl- and triphenylgermane are the only known organogermanium-nitrogen compounds which survive in the presence of water for extended periods of time.

Wieber and Schmidt[41] have isolated an o-phenylenediamine derivative of dimethylgermanium in 30% yield by reaction of $(CH_3)_2GeCl_2$ with o-phenylenediamine in the presence of triethylamine. This compound  , with a five-membered Ge-containing ring, is similar

40. M.V. George, P.B. Talukdar, C.W. Gerow, and H. Gilman, J.A.C.S., 82, 4562(1960).

41. M. Wieber and M. Schmidt, Z. Naturforsch., B, 18, 849(1963).

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to catechol, o-aminophenol, and o-aminothiophenol derivatives reported in the same paper. The analogous silicon compounds have been prepared. Notably, the o-phenylenediamine-dimethylgermanium compound is both moisture sensitive and oxygen sensitive (or, at least, the hydrolysis products are rapidly darkened in air). Early in this research one reaction of Et_2GeCl_2 (Et = ethyl) with o-phenylenediamine (purified by repeated sublimation) was conducted; the outstanding products were tar and o-phenylenediamine.

I. Haiduc and H. Gilman[42] have recently reported the preparation of an N-pentafluorophenyl cyclodigermazane (and several silazanes) by reaction of N-dilithiopentafluoroaniline with diphenyldichlorogermane (and dimethyl- and diphenyldichlorosilane). The molecular weight of the high melting (331-332°C) germazane was determined by mass spectrometry.

Three series of reactions (direct aminolysis of Et_2GeCl_2, reaction of the dilithioanilide with Et_2GeCl_2, and transamination by aniline of the crude product resulting from an ammonia-Et_2GeCl_2 reaction) yielded N-phenylated diethylgermazanes. Because of the low basicity of aniline, triethylamine promoted aminolysis by accepting the evolved HCl in all direct reactions of aniline with the organochlorogermanes. The three synthetic reactions are described by the following schematic, oversimplified equations:

$$x\ Et_2GeCl_2 + x\ C_6H_5NH_2 + 2x\ Et_3N \xrightarrow[\text{ethyl ether}]{\text{benzene or}} \frac{x}{y}\ (Et_2GeNC_6H_5)_y + 2x\ Et_3NH^+Cl^- \quad (1)$$

42. I. Haiduc and H. Gilman, J. Organometal. Chem., 18, P5, (1969).

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$$2x\ n\text{-BuLi} + x\ C_6H_5NH_2 \xrightarrow{\text{hexane}} x\ Li_2NC_6H_5 + 2x\ C_4H_{10} \quad (2a)$$

$$x\ Et_2GeCl_2 + x\ Li_2NC_6H_5 \xrightarrow[\text{n-heptane}]{\text{hexane +}} \frac{x}{y}\ (Et_2GeNC_6H_5)_y + 2x\ LiCl \quad (2b)$$

$$x\ Et_2GeCl_2 + 3x\ NH_3 \xrightarrow[\text{low boiling}]{\text{pet. ether,}} \frac{x}{y}\ (Et_2GeNH)_y + 2x\ NH_4Cl \quad (3a)$$

or,

$$x\ Et_2GeCl_2 + 3x\ NH_3 + Z\ Et_3N \xrightarrow{\text{benzene}} \frac{x}{y}\ (Et_2GeNH)_y + (2x-Z)NH_4Cl + Z\ Et_3NH^+Cl^- \quad (3b)$$

$$\frac{x}{y}\ (Et_2GeNH)_y + x\ C_6H_5NH_2 \xrightarrow[\text{or benzene}]{\text{pet. ether}} \frac{x}{y}\ (Et_2GeNC_6H_5)_y + x\ NH_3 \quad (3c)$$

The formula $(Et_2GeNC_6H_5)_y$ refers to linear oligomeric materials, which of course bear either amine or chlorine terminal groups, or to a cyclic tetramer. The crude products obtained were, without exception, mixtures of the two types. Omission of dianilinodiethylgermane from these equations reflects the results of these experiments; no such species was isolated and spectroscopic results indicate its absence even in impure distillation fractions. All preparative details for these products are contained in the following Experimental section.

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Of the three general reaction types, direct aminolysis, even in the presence of triethylamine, was least satisfactory for the production of chlorine-free N-phenylated germazanes, whether cyclic or linear oligomeric. Such, of course, is not surprising; because of the low basicity and nucleophilicity of aniline, reaction of this amine with organochlorogermanes should be more difficult than the reaction with ammonia or alkylamines. Even with the latter relatively strong bases, aminolysis of organochlorogermanes is not easily driven to completion under some conditions. Complete aminolysis of dimethyldichlorogermane has been shown[43] to be difficult compared with the corresponding reaction of dimethyldichlorosilane. At 0°C in benzene, dimethylamine replaces only one chlorine atom on germanium to produce chloro(dimethylamino)dimethylgermane.[43a] The unassisted reaction of aniline with organohalogermanes, though unreported and untried in this research, must be slight. Germanium tetrachloride does undergo aminolysis more easily; Rijkens and Van der Kerk[44] report that Davidson prepared $ClGe(NHC_6H_4)_3$ by direct aminolysis in boiling benzene.

In contrast, aminolysis of organochlorosilanes generally proceeds easily. H.H. Anderson[45] indicated no real difficulty in preparing alkyltrianilinosilanes, dialkyldianilinosilanes, and trialkylanilinosilanes

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43. (a) C.H. Yoder and J.J. Zuckerman, J.A.C.S., 88, 4831(1966).
    (b) I. Ruidisch and M. Schmidt, Angew. Chem., 76, 229(1964).

44. (a) F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, p. 38.
    (b) W.E. Davidson, Thesis, Braunschweig, 1961.

45. H.H. Anderson, J.A.C.S., 73, 5802(1951).

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in 70-80% yields by direct aminolysis. Aniline was usually present in 15-20 mole % excess; the trialkylanilinosilanes only formed well in the absence of solvent. In addition to preparing dimethyldianilinosilane by reaction of dimethyldichlorosilane and aniline in 1:4 molar ratio in CCl_4, Larsson and Smith[46] isolated a small quantity of $[(CH_3)_2SiNC_6H_5]_3$ from a 1:3 molar reaction. The cyclic trimer (3.5% yield) was separated from a chlorine-free solid assumed to be (not fully characterized) mostly dimethyldianilinosilane. These foregoing results indicate a pronounced tendency of organosilicon compounds to form the dianilino derivative, essentially regardless of the amount of aniline present. Surprisingly, however, Andrianov and Rumba[47] reported isolation of tris(N-phenyl)-hexamethylcyclotrisilazane in 39% yield from a 1:4 molar reaction of $(CH_3)_2SiCl_2$ and aniline. That report does not agree with other investigators' experience; in the same paper, Andrianov and Rumba in fact emphasized the value of preparing the cyclic trimer by transamination from $[(CH_3)_2SiNH]_4$, though they cited yields of 10-15%.[48] In the direct aminolysis, they did not indicate the solvent and reaction conditions used. One must emphasize that no reasonably strong base assisted in any of these direct aminolyses.

Five reactions of aniline and Et_2GeCl_2 [see equation (1) above] conducted with different proportions of the two reagents, with different

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46. E. Larsson and B. Smith, Acta Chem. Scand., 3, 487(1949).

47. K.A. Andrianov and G. Rumba, Zh. Obshch. Khim., 32, 1993(1962); English trans. 32, 1974(1962).

48. W. Fink maintains [Angew. Chem. Internat. Ed., 5, 760(1966)] that the transamination product (mp 247-248°C) is identical with cyclodisilazane $[(CH_3)_2SiNC_6H_5]_2$ (mp 252.5°C) which he has characterized.

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amounts of Et_3N, with different reaction temperatures, and with different treatment of the crude products, have defined the products and product yields obtainable by direct aminolysis. In the first reaction, with stoichiometry reflecting equation (1), 0.102 mole of aniline was added to a dilute benzene solution of 0.102 mole of diethyldichlorogermane and 0.200 mole of triethylamine. During four hours of stirring at 0-5°C, only a small amount of amine hydrochloride separated from solution. Considerable precipitation of triethylamine hydrochloride occurred during stirring at room temperature overnight. With no more forcing conditions than these, however, the aminolysis was quite incomplete. Two low-boiling (near 35°C at 0.4mm Hg) fractions, obtained by vacuum distillation of the product after benzene and Et_3N had been removed at atmospheric pressure, were nearly 1:1 mixtures of unreacted aniline and Et_2GeCl_2. The two most prominent N-H stretching bonds of aniline, appearing normally at about 3350 cm^{-1} and 3420 cm^{-1}, were shifted, in the mixture, to 3370 cm^{-1} and 3440 cm^{-1}, respectively. That shift to higher energy suggested that Et_2GeCl_2 helped break down whatever intermolecular hydrogen bonding existed in aniline and did not itself hydrogen bond with aniline. No significant shifts occurred in other regions of the spectra of the mixtures. For both fractions, a weak infrared band at 855-860 cm^{-1} suggested the presence of minute amounts of Ge-O or Ge-N containing material. Approximately twenty-five percent by weight of the aniline and diethyldichlorogermane starting material remained unreacted.

The major portion of this first aminolysis product, a heavy yellow-white oil collected over a wide distillation temperature range (105°-165°C at 0.2 mm Hg), was not thoroughly characterized because of the incompleteness

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of reaction. An infrared spectrum of liquid boiling at the low end of the range showed that germanium-chlorine bonds were still present. A negative test with $AgNO_3$ and another infrared spectrum indicated that the higher-boiling oil (140-165°C) did not contain chlorine. With recurring formation of such oils in succeeding reactions, the materials were more thoroughly characterized.

After the distillation head temperature had exceeded 165°C at 0.15 mm Hg, white crystalline solid formed rapidly in the air-cooled condenser. That solid, distilling along with a small amount of yellow oil in the range of 165-175°C at 0.15 mm, comprised the topmost fraction obtained from the first reaction. By twice dissolving the solid in hot, sodium-dried heptane and cooling the resulting solution in ice, purified crystals (mp 152-153°C) in 14% yield based on the germanium starting material were obtained. Chemical analysis and infrared, NMR, and mass spectra characterized this solid as the cyclic tetramer $(Et_2GeNC_6H_5)_4$, tetrakis-(N-phenyl)-octaethylcyclotetragermazane. The analytical results[49] are as follows:

Found:	C, 53.43%	H,	6.95%	Ge,	32.45%
Calc'd:	C, 54.14%	H,	6.83%	Ge,	32.72%

The tetramer demonstrated surprising insolubility at room temperature in common organic solvents. One observed negligible solubility in CCl_4,

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49. The carbon-hydrogen analysis was performed by Mr. Herbert Markatz, Inst. f. Anorg. Chem. der Tech. Hochsh., Graz, Austria. The germanium analysis was performed in this laboratory by titration of the mannitol-germanate complex after oxidation of the compound with Na_2O_2 and $KClO_4$ in a Parr bomb (analytical method described in Experimental section).

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cyclohexane, petroleum ether, dimethylformamide, tetrahydrofuran, diethyl-ether, and aniline. Low concentrations, insufficient to permit recording of well-developed NMR spectra, were obtained in benzene, chloroform, and dichloromethane. Surprisingly, the solid dissolved easily in pyridine. When suspended in distilled water, the last crystals disappeared only after about one hour. The tetramer outwardly showed signs of hydrolysis, and its infrared spectrum changed significantly, only after exposure to air for about an hour. After standing in air for one week, the infrared spectrum of the solid was that of a diethylgermanium oxide, and evidonces of aniline were gone.

Since determination of molecular weight by cryoscopic and vapor pressure osmometric methods in the usual solvents were impossible or uncertain, the writer attempted to determine the molecular weight in pyridine using a vapor pressure osmometer (Hewlett-Packard Mechrolab Osmometer Model 104A). Pyridine is a difficult solvent to use with that apparatus. In contrast with the two-minute reading times normally required with solvents like benzene and CCl_4, reproducible measurements on pyridine solutions of the calibrant benzil and of the cyclic tetramer were obtained only after fifteen minute equilibration times before each reading. The average molecular weight obtained from measurements on three solutions was 198 ± 7 (theory for tetramer = 887.3). The value found lies within 14% of the weight (221.8) of the theoretical monomeric unit. The unusually high solubility in pyridine might suggest that pyridine dissolves the tetramer by breaking it into monomeric units. However, one cannot suggest a solvated species which would not involve

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improbable multiple Ge-N bonding. Though the pyridine was carefully dried before use, the hygroscopic solvent probably absorbed enough water in the osmometer block in fifteen minutes to hydrolyze the tetramer. One would expect a drift in determined molecular weights if hydrolysis were occurring in solutions of different concentration. The 30% total variation in concentration among the three solutions was perhaps insufficient to produce a noticeable drift. Mass spectrometry, discussed later, provided the best evidence for the tetrameric nature of the compound.

The infrared spectrum (Fig. 1.5, Appendix A)[50] of the solid clearly characterizes this material as an N-phenylated diethylgermazane. Table I lists the prominent IR bands by wave number and qualitative intensity, and makes probable assignments where possible. Most bands, except those attributable to Ge-N stretching and to ring modes, were assigned by comparison with the previously interpreted spectra of Et_2GeCl_2 and aniline (Fig. 1.1 and Fig. 1.3, respectively). For purposes of comparison, Table I lists the prominent bands and assignments for the latter two compounds.

If the discussion by Colthup, Daly, and Wiberly[51b] of aromatic amines

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50. All infrared spectra indicated by number in this thesis appear in Appendix A. All numbered NMR spectra appear in Appendix B.

51. (a) L.J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, New York, 1958, pp. 65-83, 249-251.
(b) N. B. Colthup, L.H. Daly, and S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, pp. 220-230.
(c) E.W. Randall, J.J. Ellner, and J.J. Zuckerman, Inorg. Nucl. Chem. Letters, 1, 109(1966).

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Table I[52,53]

Aniline		Et_2GeCl_2		$(Et_2GeNC_6H_5)_4$	
cm^{-1}	assignment[51]	cm^{-1}	assignment[54]	cm^{-1}	assignment
3425(s) 3350(s)	ν N-H				
3205(m)	2x δ N-H				
3020(m) 3060(m)	ν C-H aromatic (major peaks of complex group)				
		2970(s) 2935(m) 2920(m) 2880(m)	ν C-H(Et)	3060(m)	ν C-H aromatic
					see footnote 53

52. All infrared spectra reported in this thesis were recorded on a Perkin-Elmer Model 337 Grating Spectrophotometer. Wave number error in first range (4000-1200 cm^{-1}) is approximately ±5 cm^{-1} (with calibration with polystyrene film); in second range (1330-400 cm^{-1}), ±2 cm^{-1}. The following standard symbols are used in all infrared tables: ν = stretch, δ = angle deformation, ρ = rock, s = strong, m = medium, w = weak, v = very, sh = shoulder.

53. In Kadol mull spectra, overlapping bands in the range 2825-2975 cm^{-1} (s), a band at 1450-1460 cm^{-1} (s), a band at 1365 cm^{-1} (s), and a band at 720 cm^{-1} (w) derive from the hydrocarbon mulling agent and obscure sample peaks in those regions.

54. (a) K. M. MacKay and R. Watt, J. Organometal. Chem., 6, 336(1966).
(b) R.J. Cross and F. Glockling, J. Organometal. Chem., 3, 146(1965).

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Table I, Contd.

Aniline		Et_2GeCl_2		$(Et_2GeNC_6H_5)_4$		
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment	
1615(s)	δ N-H					
1590(s), 1480(s), 1460(w)	benzene ring stretching			1580(s), 1560(sh), 1530(sh), 1475(s)	benzene ring stretching	
		1460(s)	$\delta_{asym}(CH_3)$			
		1425(m)	$\delta_{asym}(CH_2)$	1410(w)	$\delta_{asym}(CH_2)$	(?) see footnote 53
		1385(m)	$\delta_{sym}(CH_3)$			
		1230(m)	$\delta_{sym}(CH_2)$	1225(w)	$\delta_{sym}(CH_2)$	
1278(s)	ν C-N			1300(s)	ν C-N	
1178(s), 1156(m), 1027(m)	C-H aromatic (in plane) bending			1180(m), 1154(m), 1028(sh)	C-H aromatic (in plane) bending	
		1027(sh), 1020(s)	ν C-C	1024(m), 1015(m)	ν C-C(Et)	
				1080	unassigned	
997(m)	benzene ring mode			992(m)	benzene ring mode	
		973(m)	δ C-H	966(m)	δ C-H(Et)	
878(s)	unassigned			888(s)	ν_{asym} Ge-N-Ge	

Table I, Contd.

Aniline		Et_2GeCl_2		$(Et_2GeNC_6H_5)_4$	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
				857(m)	unassigned
				788(s)	unassigned
750(s)	C-H aromatic (out of plane) bending			744(s)	C-H aromatic (out of plane) bending
		708(vs)	ρ (CH_2)	694(m)	ρ (CH_2) (Et)
690(s)	benzene ring mode			684(s)	benzene ring mode
		604(s)	ν_{asym} Ge-C	585(m)	ν_{asym} Ge-C
		560(s)	ν sym Ge-C	547(m)	ν sym Ge-C
502(s)	benzene ring mode			507(m)	benzene ring mode

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and monosubstituted benzenes is assumed correct, one can assign most prominent aniline infrared bands in excellent agreement with that description. Two assigned bands of medium intensity, at 1120 cm^{-1} and 1053 cm^{-1}, are not of significance in the study of the spectrum of $(Et_2GeNC_6H_5)_4$. Their absence in the spectrum of the latter compound suggests their involvement with motions of the N-H group. The low, broad absorption between 550 cm^{-1} and 800 cm^{-1} in the aniline spectrum, and absent from the germazane spectrum, is assigned to NH_2 wagging by Colthup, Daly, and Wiberly.[55] Of the major aniline absorbances, only the 878 cm^{-1} band remains uninterpreted. Unfortunately, that strong band lies in the region where one expects the asymmetric Ge-N-Ge stretching band for $(Et_2GeNC_6H_5)_4$. For that reason, the $(Et_2GeNC_6H_5)_4$ bands observed at 888, 857, and 788 cm^{-1} possess uncertain assignments. The rather weak band at 857 cm^{-1} presumably cannot correspond to the ν_{asym} Ge-N-Ge mode. Of the two remaining strong absorbances, one tentatively assigns the 888 cm^{-1} band to the asymmetric mode. That band clearly disappears on hydrolysis of the tetramer; the 788 cm^{-1} band apparently does not disappear. For the N-methylsilazanes, Breed and Elliott[37] reported an increase in ν_{asym}Si-N-Si in passing from linear oligomers such as $CH_3N[Si(CH_3)_2NHCH_3]_2$ ($\sim$900 cm^{-1}) to the cyclic $[(CH_3)_2SiNCH_3]_3$ ($\sim$940 cm^{-1}).[56] In anticipation of results discussed later in this thesis, one

55. N.B. Colthup, L.H. Daly, and S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, p. 387.

56. The ν_{asym} Si-N-Si assignment for the cyclic trimer is subject to some disagreement. E.W. Abel and R.P. Bush (J. Inorg. Nucl. Chem., 26, 1685(1964)) assign a strong 915 cm^{-1} band to that mode. Those authors also list a very strong band at 945 cm^{-1}.

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notes that linear oligomeric N-phenylated germazanes show a very intense, broad Ge-N-Ge stretching band at 850 cm^{-1}. The cyclic tetramer may be expected to absorb at higher energy than the linear oligomer.

For the compound $[(CH_3)_2GeNC_6H_5]_3$ described later in this thesis, intense bands at 906 cm^{-1} and 870 cm^{-1} both disappear in hydrolysis. An intense, broad absorbance at 803 cm^{-1} persists with hydrolysis and probably derives from methyl group rocking.

However, the Ge-N-Ge asymmetric stretching band for $(Et_3Ge)_2NH$[57] occurs at 805 cm^{-1}. Although not specified as such, that band probably appears at 819 cm^{-1} for $[(CH_3)_3Ge]_2NH$ and at 817 cm^{-1} for $[(CH_3)_3Ge]_3N$.[58] Therefore there is some precedent for assignment of ν_{asym} Ge-N-Ge to a band nearer to 800 cm^{-1} than to 900 cm^{-1}. The dearth of Ge-N infrared information hampers assignment of Ge-N-Ge stretching frequencies. For $(Et_2GeNC_6H_5)_4$, the 888 cm^{-1} band probably corresponds to ν_{asym} Ge-N-Ge, but the 788 cm^{-1} band is not excluded.

The Ge-N-Ge symmetric stretching mode cannot confidently be assigned for the cyclic tetramer. One or both of the weak bands found between 610 and 620 cm^{-1} might correspond to that mode. The absorption may quite possibly occur below 400 cm^{-1},

In the spectrum of $(Et_2GeNC_6H_5)_4$, the C-N stretching frequency (1300 cm^{-1}) is higher than that for aniline (1278 cm^{-1}). In agreement with that observation, Randall and Zuckerman have reported[59] C-N frequencies

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57. J. Satgé and M. Baudet, Compt. Rend. (Paris), Ser. C., 265, 435 (1966).

58. I. Ruidisch and M. Schmidt, Angew. Chem., 76, 229(1964).

59. E.W. Randall and J.J. Zuckerman, J.A.C.S., 90, 3167(1968).

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of 1294 cm^{-1}, 1295 cm^{-1}, and 1292 cm^{-1} for $(CH_3)_5MNHC_6H_5$ in the series M=Si, Ge, Sn, as compared with 1276 cm^{-1} for aniline. Replacement of hydrogen on nitrogen by the much heavier metal atoms results in stiffening of the adjacent C-N bond. The constancy of that mode in passing from silicon to tin is not so easily explained. A roughly four-fold increase in mass of the metal atom surprisingly produces no significant shift of the C-N stretching frequency. Changing the $(CH_3)_3M$ substituent presumably alters the degree of π-bonding of the metal with nitrogen, the stereochemistry of bonding about nitrogen, and the inductive release of electrons to nitrogen. However, collectively, and perhaps coincidentally, these modifications do not significantly shift the C-N frequency.

Both the asymmetric and symmetric Ge-C stretching frequencies decrease in passing from Et_2GeCl_2 to $(Et_2GeNC_6H_5)_4$. Similar reductions in frequency occur in moving from Et_2GeCl_2 to Et_2GeBr_2 (604 cm^{-1}, 560 cm^{-1}) to Et_2GeI_2 (590 cm^{-1}, 547 cm^{-1}).[54a] The decrease can seemingly result from decreasing polarity of the C-Ge bond with substitution of less electronegative atoms (N,Br,I) on Ge, or from compression of the C-Ge-C angle, or from both. Model building demonstrates that this sterically crowded molecule must be globular in form. Open "chair" and "boat" forms, such as are known[60] for $[(CH_3)_2SiNH]_4$, are not possible for this molecule. The bulky phenyl substituents perhaps compress the C-Ge-C angle. No X-ray structural analyses have been done on Ge-N heterocycles. One therefore has no real basis for predicting large N-Ge-N angles and

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60. G.S. Smith and L.E. Alexander, Acta Crystallogr., 16, 1015(1963).

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small C-Ge-C angles (with Ge-C bonds high in p-character).

In moving from $(CH_3)_2SiCl_2$[61] to $[(CH_3)_2SiH]_3$,[62] one finds a similar decrease in metal-carbon stretching frequencies. The ν_{asym} Si-C mode drops from 804 cm^{-1} to 788 cm^{-1}, the ν_{sym} Si-C mode[63] from 691 cm^{-1} to 677 cm^{-1}. In $[(CH_3)_2SiNH]_3$ and in the two forms of $[(CH_3)_2SiNH]_4$, the N-Si-N angles (110°-113°) are scarcely larger than the tetrahedral angle.[60,64] The C-Si-C angles (109°-114°) of $[(CH_3)_2SiNH]_4$ are not compressed.[60] In both the silazanes and germazanes, replacement of chlorine by the less electronegative nitrogen probably produces the lowered metal-carbon stretching frequencies.

In considering the nuclear magnetic resonance (NMR) spectrum of $(Et_2GeNC_6H_5)_4$, one notes that the spectra of Et_4Ge[65], Et_3GeCl, Et_2GeCl_2, and $EtGeCl_3$[54a] have previously been reported and the theoretical spectra (second order A_3B_2 type) calculated. For purposes of comparison, the 60 MHz spectra[66] of $EtGeCl_3$ (Fig. 2.1, Appendix B) and Et_2GeCl_2 (Fig. 2.2), recorded using 10% CCl_4 solutions, are included in this thesis. One finds excellent agreement with the chemical shift values reported by Narasimhan and Rogers for the most intense spectral peak (usually denoted A_6), the central methyl proton resonance. For Et_2GeCl_2 this peak appears at -76 Hz

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61. M.C. Tobin, J.A.C.S., 75, 1788(1953).

62. H. Kriegsmann, Z. Anorg. Allg. Chem., 298, 223(1959).

63. In this mode the carbon atoms move out of phase.[62] The completely symmetric mode appears in the Raman at 712 cm^{-1}.

64. M. Yokoi and K. Yamasaki, J.A.C.S., 75, 4139(1953).

65. P.T. Narasimhan and M.T. Rogers, J.A.C.S., 82, 5983(1960).

66. Unless otherwise noted, NMR spectra have been recorded using a Varian A-60 spectrometer.

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(-76.1 Hz reported); for $EtGeCl_3$, at -82 Hz (-82.3 Hz). Essentially the complicated Et_2GeCl_2 spectrum results from the similarity in magnitude of the internal chemical shift $\Delta = \delta(CH_3) - \delta(CH_2)$ and the coupling constant J(AB). (The letters A and B refer to the methyl and methylene protons, respectively.) For Et_2GeCl_2, Δ=+16.1 Hz (the plus sign indicating that the methyl resonance is at higher field than the methylene resonance) and J(AB)=7.7 Hz. In $EtGeCl_3$, where one can see a more usual "ethyl" spectrum, Δ=+39.4 Hz and J(AB)=7.9 Hz. Notably, for Et_3GeCl (Δ=-1.5 Hz) and Et_4Ge (Δ= -18.4Hz), the methylene protons are more highly shielded than the methyl protons.

Because of the previously-mentioned insolubility in common solvents, the writer could not obtain well-resolved, integrable spectra of $(Et_2GeNC_6H_5)_4$ in CCl_4, benzene, $CHCl_3$, and CH_2Cl_2. In $CHCl_3$, resolution of the ethyl resonance was sufficient to determine that the most intense resonance appeared at -69.6 ±0.1 Hz (-1.16 ±0.01$). However, the feeble concentration of $(Et_2GeNC_6H_5)_4$ was comparable to that of the ethanol used as stabilizer. The methyl resonance of ethanol was mixed with the ethyl resonance of the germazane. More importantly, the concentration of ethanol was probably sufficient to have destroyed a significant amount of $(Et_2GeNC_6H_5)_4$. For the benzene and $CHCl_3$ solution, where concentrations of $(Et_2GeNC_6H_5)_4$ were largest, integration of the phenyl resonance was obviously not possible because of solvent resonance.

Ultimately, good NMR spectra of $(Et_2GeNC_6H_5)_4$ were obtained from pyridine-d_5 solutions. Figures 2.3 and 2.4 are spectra (approx. 10% in pyridine-d_5) of $(Et_2GeNC_6H_5)_4$. At the RF power and amplitude settings

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used in recording these spectra, one could not detect undeuterated pyridine in the solvent. The most intense resonance, assumed to be the central methyl peak, appeared at -69.2±0.1 Hz (-1.15±0.01δ).[67] The observed agreement with the chemical shift found in $CHCl_3$ demonstrated that the methyl group resonance is not greatly subject to solvent shifts. Surprisingly, the writer could not discern a significant methyl peak upfield from that most intense resonance. In $CHCl_3$ solution, strong peaks at -1.04δ and -1.12δ were found upfield from the most intense peak. Since the upper two methyl proton peaks of ethanol appear at -1.10δ and -1.22δ, at least the -1.04δ peak should have been produced by ethyl groups on germanium. In light of the questionable nature of the species in $CHCl_3$, however, the observed differences may not be meaningful.

In pyridine-d_5, other ethyl resonances appeared at -1.02δ, -1.22δ, -1.24δ, -1.27δ, -1.29δ, -1.34δ, -1.44δ, and -1.49δ; all ten apparent peaks occurred within 0.47δ. In Et_2GeCl_2, ten peaks also were observed, but within a range of 0.70δ. Except for the striking difference in intensity of the peak at highest field, the ethyl spectra of Et_2GeCl_2 and $(Et_2GeNC_6H_5)_4$ seemed much alike, at first glance. In passing from Et_2GeCl_2 to $(Et_2GeNC_6H_5)_4$, however, the most prominent peak moved upfield from -1.27δ to -1.15δ. Perhaps more significantly, the lower field peaks, presumably deriving largely from methylene protons, were shifted relatively more toward low field in Et_2GeCl_2 than in $(Et_2GeNC_6H_5)_4$. The outgrowth of that shifting was the greater total breadth of the ethyl spectrum for Et_2GeCl_2. One surmises

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67. For all NMR spectra, error bounds are estimations, not standard deviations.

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that the internal chemical shift $\delta(CH_3)-\delta(CH_2)$ is greater for Et_2GeCl_2 than for $(Et_2GeNC_6H_5)_4$. In replacing chlorine by the less electronegative nitrogen, one expects such a result. In earlier studies on ethyl compounds of the type $(C_2H_5)_nM$, an approximately linear relationship between Δ and the electronegativity X of M was found.[68,54a] Deviations from that equation ($X = 0.62\Delta(ppm) + 2.07$) for compounds of the type $(C_2H_5)_{m-n}MX_n$ have been attributed to magnetic anisotropy of the M-X bond, M atom, or X atoms.[54a] For Et_2GeCl_2 and $(Et_2GeNC_6H_5)_4$, the change in solvent from CCl_4 to pyridine-d_5 places in doubt the consideration of changes in Δ with substituent electronegativity. Pyridine, if it so easily dissolved $(Et_2GeNC_6H_5)_4$ by somehow coordinating to the Ge atom, would have been expected to influence the methylene chemical shift in particular. The shift of the A_6 peak from -1.27δ to -1.15δ, in apparent independence of solvent, probably did result from the replacement of chlorine by nitrogen. In the series Et_2GeCl_2, Et_2GeBr_2, and Et_2GeI_2, the methyl shift decreases from -76.1 Hz, to -72.5 Hz, to -68.3 Hz. However, in that series some of the trend to higher field derives from increasing shielding of the methyl group as it comes in actual contact with the large bromine and iodine atoms.[54a] In rough analogy with this latter effect, the methyl groups in $(Et_2GeNC_6H_5)_4$ would experience greater shielding if placed above the face of the phenyl ring.

The complex set of phenyl resonances for $(Et_2GeNC_6H_5)_4$ appeared between -6.46δ and -7.26δ in the pyridine-d_5 solvent. In Fig. 2.4, the

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68. (a) B.P. Dailey and J.N. Shoolery, J.A.C.S., 77, 3977(1955).
(b) P.T. Narasimhan and M.T. Rogers, ibid, 82, 34(1960).

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phenyl spectrum was offset 204 Hz to higher field.

From the integration found in Fig. 2.3, the ratio of ethyl to phenyl protons was 2.0/1.0, in excellent agreement with the theoretical 2/1 ratio for $(Et_2GeNC_6H_5)_4$.

Mass spectrometry provided good evidence for the tetrameric nature of the ethyl germazane solid. Mass spectroscopic study of organogermanium compounds is complicated by the penta-isotopic nature of the element. In his recent review[69] of germanium mass spectra, Glockling lists the following isotopic abundances: ^{70}Ge, 20.56%, ^{72}Ge, 27.42%; ^{73}Ge, 7.79%; ^{74}Ge, 36.47%; ^{76}Ge, 7.76%, These five iosotopes, all in appreciable abundance, produce characteristic patterns for each germanium-containing ion. For example, a species containing three germanium atoms can be distinguished readily from a four-germanium ion. On the other hand, when more than one germanium atom occurs in each sample molecule, determination of relative ion abundances is difficult (or hopeless) without computer assistance, unless the envelope of peaks for a given ion is completely separated from other such envelopes. When overlapping of patterns for two species occurs, one must either perform exact mass measurements at high resolution or program a computer to analyze and simulate that spectral region.

Though the primary concern at this point is the evidence for the tetrameric nature of $(Et_2GeNC_6H_5)_4$, the investigator first considers the manner in which the mass spectra have been obtained[70] and interpreted.

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69. F. Glockling, The Chemistry of Germanium, Academic Press, New York, 1969, pp. 21-27.

70. All spectra were recorded on an A.E.I. M.S.-9 instrument at a 70 eV accelerating potential. All solid samples, and several liquids, were introduced with a direct insertion probe. Oven temperatures at insertion are indicated for each sample.

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These conditions apply not only to the $(Et_2GeNC_6H_5)_4$ mass spectrum, but to additional mass spectral results which are scattered throughout the remainder of this thesis. In this research, the principal use of mass spectrometry was for molecular weight determination. For relatively heavy molecules like $(Et_2GeNC_6H_5)_4$ (integral molecular weight = 888) and $(Et_2GeNC_6H_{11})_4$ (integral molecular weight = 912) exact mass determination of the high mass "peaks"[71] was not possible. The molecular weight of the customarily used perfluorotri-n-butylamine is 671, considerably below the aforementioned weights. For masses above 700 it is difficult to find standards with known, reproducible fragmentation patterns. In addition, above mass 800 or 850, manual counting of peaks to obtain molecular weights usually became difficult because background peaks were absent. Only under extraordinary conditions could one count as far as mass 900 with confidence. Since the M.S.-9 spectrum is nonlinear with increasing mass, extrapolations and interpolations based on length measurement were subject to doubt. For $(Et_2GeNC_6H_5)_4$, no molecular ion "peak" was recorded. The estimation of molecular weight for this heavy species then rests upon interpretation of "peaks" somewhat below the molecular ion trace. The evidence obtained denied parent molecules smaller than the tetramer. The pentamer and larger types were deemed unlikely because no "peaks" above the tetrameric mass were recorded. For compounds with molecular weights less than approximately 700, direct

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71. The expression "peak" in this thesis refers to the entire envelope of peaks for a given germanium-containing species.

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counting was sufficient to identify the molecular ion "peak" or a nearby, reasonable fragmentation "peak" and to provide a measure of the molecular weight. Exact mass measurements were then not essential.

In the high m/e region of the spectrum and in the absence of overlap (the case for the ethyl-germanium derivatives), the fingerprint pattern of a germanium-containing species removed ambiguities of the type that one encounters in interpreting organic mass spectra. Frequently only one ion type could have produced a given envelope. In the spectrum of heavy molecules, the low mass regions (<300) were extremely complicated. Peaks deriving from one-germanium species were interspersed with peaks from purely organic fragments and from background. In these regions, where intense peaks were found near every integral mass, interpretation without exact mass measurements was impossible. For the purposes of this research, such low mass regions for heavy molecules were nearly ignored. Even for lighter molecules like $Et_2Ge(NHC_6H_{11})_2$ attention was directed to the higher mass "peaks". In the higher mass regions, one could follow apparent fragmentation routes (e.g. successive losses of ethylene and Et·). Suggestion of fragmentation routes on the basis of such observation does not constitute proof of the mechanisms, but simply indicates high probability for those routes.

Computer simulation of the mass-abundance distribution for a given germanium-containing species, particularly for one containing more than one germanium atom, has assisted in the interpretation of spectral envelopes. Carrick and Glockling[69,72] have described a sophisticated program

72. (a) A. Carrick and F. Glockling, J. Chem. Soc., A, 632(1966).
(b) A. Carrick and F. Glockling, J. Chem. Soc., A, 40(1967).

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for calculating the mass-abundance pattern for ions containing up to ten atoms of up to four polyisotopic elements. For example, patterns and masses for ions containing Fe_2Mo_2Sn or Mo_2Ge_2 can be calculated. A second part of the program combines, C, H, N, O, and P with the pattern of the heavy polyisotopic atoms to give mass-abundance data for molecular and fragment ions. The program permits correction for up to two heavy isotopes each of C, H, N, and O. Calculation employs exact isotopic masses rounded to six decimal places. However, in the Friden "Flexowriter" graphic output which presents the simulated mass-abundance envelopes of given ions, masses are rounded to integral values. In simulation, a single spike appears exactly at an integral value. The height of that spike indicates the total abundance of ions which in a high resolution measured spectrum would produce lines extending perhaps 25 p.p.m. on either side of the integral mass value. Notably, at the resolution used to record spectra photographically, these closely-spaced ion peaks appear as a single peak, effectively placed at an integral mass. The graphic output, with rounding of masses, then represents the photographically recorded spectrum quite well. In a graphic simulation, the accurately calculated relative abundances are similarly rounded because of limitation in the fineness of the plotting grid. Disappointingly, the program "is written in the Elliott 8 channel dialect of ALGOL 60 ... Copies of the mnemonic tape in either the Elliott 8 hole telecode, or an English Electric-Leo KDF 9 coded version of the Elliott program, are available from the University Computer Unit."[72b] That coding would have been unintelligible to the primarily FORTRAN-handling computers available to

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this investigator.

In this research, a FORTRAN program, actually conceived prior to knowledge of the Carrick and Glockling programs, has been employed to simulate mass spectral envelopes on a somewhat more simplified basis. A form of this program, designed to handle species containing four germanium atoms, comprises Appendix C. Madeleine Bates kindly did the actual FORTRAN programming. In its present form, this program permits one to calculate mass-abundance patterns for ions containing up to four germanium atoms, any number of carbons (with correction for ^{13}C), and any number of hydrogens and heteroatoms (N, O, P, etc., but without heavy isotope correction). Failure to correct for heavy isotopes of H, N, O, or P means that the calculated relative abundances are not accurate. Moreover, integral isotopic masses, rather than exact masses, have been used in all calculations. The program therefore provides no calculation of the spread of masses which would actually contribute to an apparent single spectral peak. The Calcomp plotter output from this program cannot be visually distinguished from similar output obtained by Carrick and Glockling.[69] The comparison was made by using the simplified program to calculate the envelope of $(C_{21}H_{49}Ge_4O_4)^+$. For purposes of studying low resolution, photographically recorded spectra, the simplified program provides excellent simulation. Parenthetically, use of exact masses rather than integral values would not require great modification of the simplified program. With graphic presentation of the output, however, the additional calculation would not produce significant changes in the envelope. Correction for ^{2}D, ^{15}N, and other heavy isotopes would greatly multiply the amount

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of required computing time. The departmental IBM 1620 performed the four-germanium, forty-carbon calculation in under thirty minutes, a one-germanium calculation in five minutes.

For one-germanium ions of a given type, the most intense peak in the spectral envelope naturally derives primarily from that species which contains ^{74}Ge, the most abundant isotope. For ions containing more than one germanium atom, the position of the most intense peak in an envelope is not so intuitively obvious. Computer calculation indicated that for two- or four- germanium species the most intense peak occurs near the integral value obtained if one calculates the ion mass using H = 1, C = 12, N = 14, and Ge = 73. Rather surprisingly, a calculation using H = 1, C = 12, N = 14, and Ge = 72 2/3 yields the position of the most intense peak in the envelope for a three-germanium ion type. Performance of such calculations ignores the detailed contributions of various combinations of isotopes to the peak of greatest intensity and simply allows one to correlate the position of that peak with the number of germanium atoms in the ion. These simple rules are based entirely on the empirical observations of Glockling[69] and of this investigator. For example, the most intense peak in the envelope of $[C_{18}H_{42}Ge_3O_3]^+$ occurs at m/e 524. To reproduce that m/e value one performs the following calculation: (18 x 12) + (42 x 1) + (3 x 72 2/3) + (3 x 16) = 524. Another example indicates the usefulness of these rules of thumb. Near what integral value would one expect the most intense peak in the molecular ion envelope of $[(CH_3)_2GeNC_6H_{11}]_3$? Use of Ge = 73 yields a calculated value of 600 for that peak; in accordance with

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the foregoing rules, use of Ge = 72 2/3 produces a value of 599. In the actual mass spectrum, the most intense peak appeared at 599. Interpretation of this envelope as deriving from the molecular ion, rather than from the molecular ion minus a hydrogen atom, is dictated by the foregoing rules, is in agreement with the "nitrogen rule," and is supported by successive fragmentation.

The mass spectrum of $(Et_2GeNC_6H_5)_4$ was to some extent puzzling. The molecular ion "peak" expected at m/e 888 was absent from the spectrum. That absence is consistent with the view that a bonding electron is removed on ionization.[69] The frequently observed low abundance of organogermanium molecular ions relative to analogous organosilicon species may reflect the lower bond energy of germanium with carbon (Ge-Et, 56.7 kcal/mole; Si-Et, ~63 kcal/mole).[73]

Regardless of the oven temperature at insertion, the base "peak" appeared at m/e 444, the mass of the dimer $(Et_2GeNC_6H_5)_2^+$. Intense "peaks", corresponding to successive losses of ethyl groups from that dimer, occurred at m/e 415, 386, 357, and 328. At an insertion temperature of 100°C, the relative abundances of these "peaks" were as follows:

Table II

m/e	rel. abund.
444	100.0
415	69.0
386	54.2
357	8.5
328	45.3

73. F. Glockling, The Chemistry of Germanium, Academic Press, New York, 1969, p. 12.

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"Peaks" at m/e 222 and 192, with respective relative abundances of 13.6 and 17.5 corresponded to monomeric ($Et_2GeNC_6H_5^+$) and the monomer minus ethane. At low mass, one found peaks at m/e 77 ($C_6H_5^+$), 78 ($C_6H_6^{+\cdot}$), and 93 ($C_6H_5NH_2^+$), with respective abundances of 2.3, 1.2, and 3.9. In the range of m/e 70-76, peak intensities did not directly correlate with the abundances of the Ge isotopes. In keeping with those abundances, an alternation in peak intensity occurred, but with highest intensity at m/e 75, 73, and 71 rather than m/e 74, 72, and 70. Germanium hydrides such as GeH^+ and GeH_3^+, rather than free metallic ions, therefore predominated as the lowest mass germanium-containing species. Such hydrides have been observed previously in the fragmentation of alkylgermanes.[74] The predominant portion of the ion current derived from germanium-containing species and particularly from those species above m/e 328.

At 100°C, well-defined, low intensity "peaks" appeared above m/e 444. Table III lists those "peaks" and their relative abundances, where freedom from overlap permitted abundance measurements. At oven temperatures between 100°C and 250°C, the positions of these "peaks", except for occasional appearance of a "peak" at m/e 636 instead of m/e 634, were completely reproducible. The relative abundances, however, changed significantly with insertion temperature and with time after insertion. For example, at 195°C, the m/e 851 "peak" was more intense than the m/e 705 "peak". For all spectra run in the range 100°-250°C, "peaks" above m/e 444 were not observed until sample pressures were high, at about five minutes after

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74. F. Glockling, The Chemistry of Germanium, Academic Press, New York, 1969, p. 24.

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Table III

m/e	rel. abund.
444	100.0
486	5.2
501	--
515	--
529	--
559	27.5
634	1.8
663	--
705	2.3
851	0.9

insertion. At 330°C, one did not find well-defined "peaks" recorded above m/e 444.

One cannot very plausibly interpret the highest mass "peak" at m/e 851. The implied loss of 37 mass units (C_3H) from the molecular ion seems unlikely. That fragment could presumably only be lost from the phenyl ring; such fragmentation has not been observed for benzene.[75] Moreover, elimination of a neutral C_3H species from a phenyl substituent of $(Et_2GeNC_6H_5)_4^+$, with necessary breakage of an even number of bonds, would produce another odd-electron ion, but at odd-numbered m/e. On the reasonable assumption that the m/e 851 species still contained four nitrogen atoms, elimination of neutral C_3H would violate the "nitrogen rule";

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75. F.W. McLafferty, Interpretation of Mass Spectra, W.A. Benjamin, Inc., New York, 1966, p. 44.

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"An odd-electron ion will be at an even-numbered m/e unless it contains an odd number of nitrogen atoms."[76] The possibility remains that an ion-molecule reaction, particularly at high sample pressures, yielded the species with m/e 851, but one cannot easily suggest a reasonable reaction.

The occurrence of the highest m/e "peak" at 851 and the lack of well-defined traces in the interval m/e 851-705 made interpretation of successively lower "peaks" difficult. The species with m/e 851 and 705 were shown to contain four germanium atoms. The form of the experimental "peaks" agreed well with the computer-simulated mass-abundance patterns for m/e 888 (Fig. 1), 851 (Fig. 2), and 705 (Fig. 3). Fig. 3a below shows the experimental spectral envelope for m/e 705. One notes that the patterns shown in Figs. 1-3 are essentially identical, that the detailed form of the envelope is dictated by the presence of four germanium atoms.

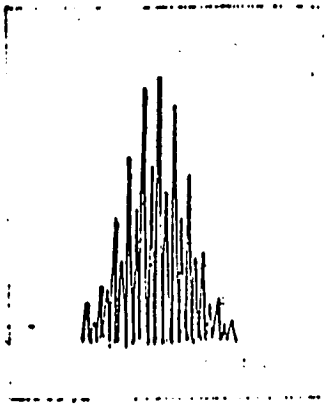

Fig. 3a

76. F.W. McLafferty, Interpretation of Mass Spectra, W.A. Benjamin, Inc., New York, 1966, p. 32.

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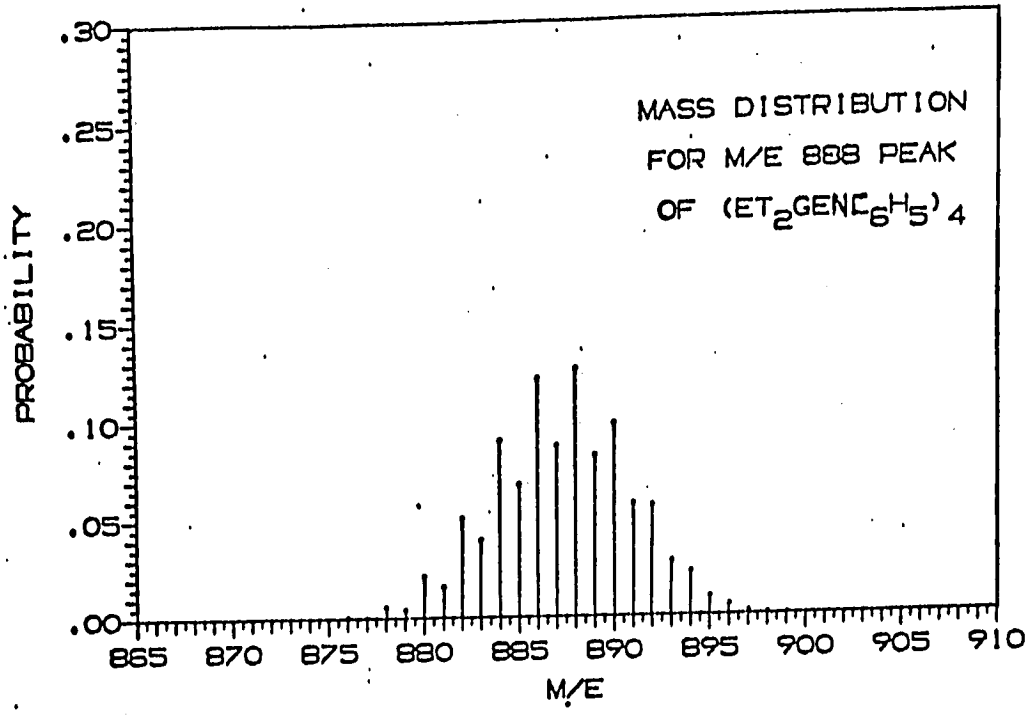

Figure 1

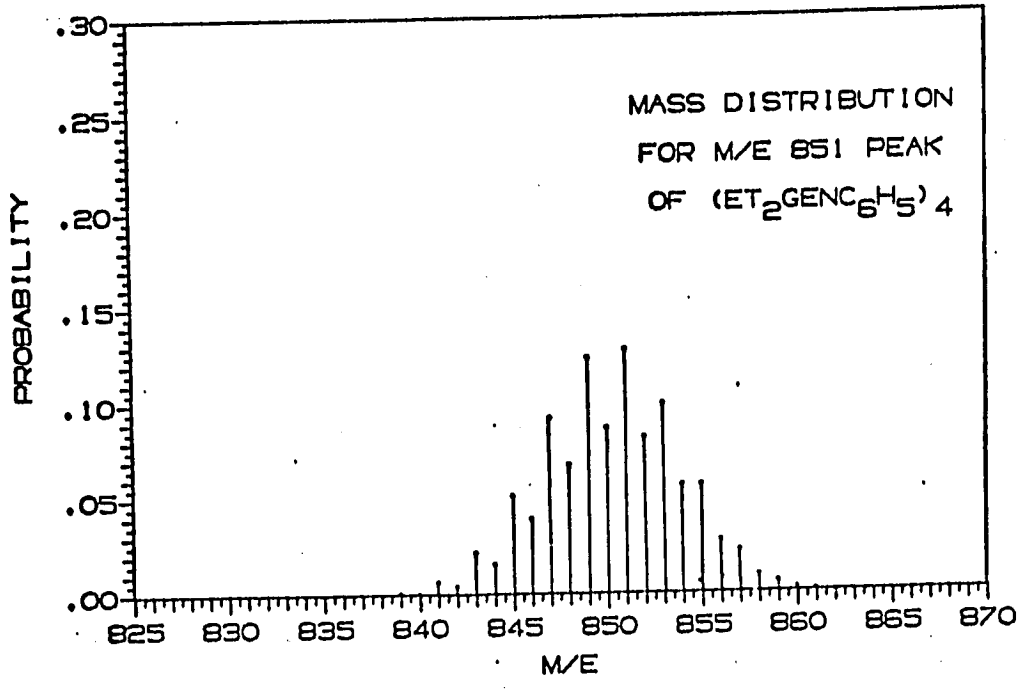

Figure 2

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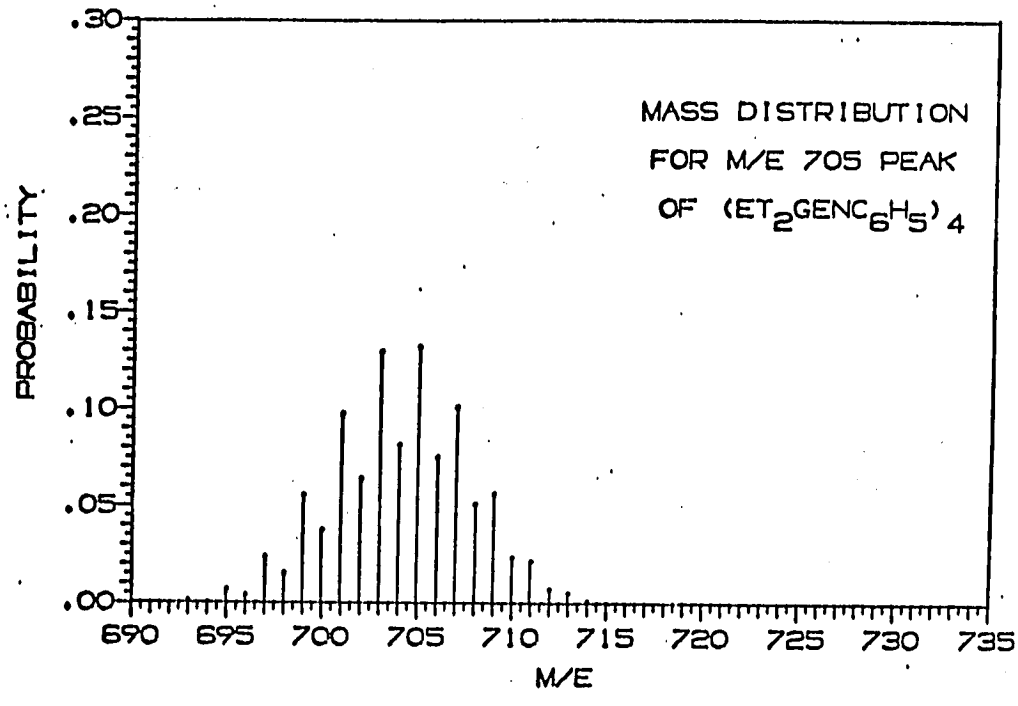

Figure 3

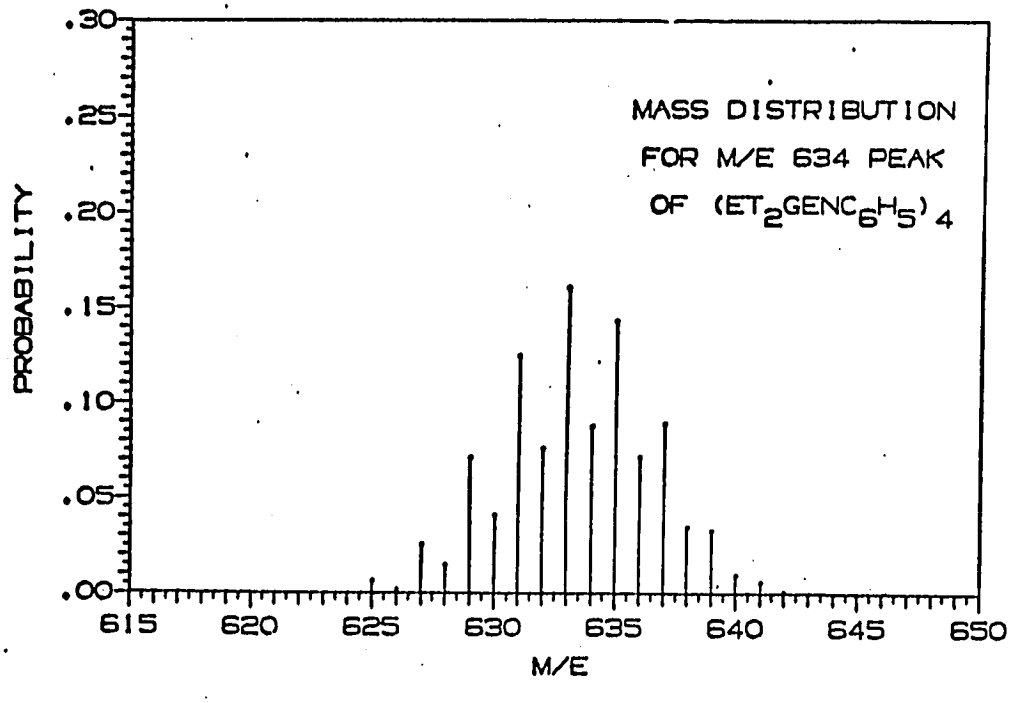

Figure 4

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The pattern for m/e 851 was calculated with an assumed loss of C_3H from $(Et_2GeNC_6H_5)_4$, despite the previous considerations. The m/e 705 "peak" might have effectively resulted from loss of two phenyl groups and an ethyl group (183 mass units) from $(Et_2GeNC_6H_5)_4^+$ or of four ethyl and two methyl radicals (146 mass units) from the m/e 851 species. The simulation shown in Fig. 3, using 4 germanium, 4 nitrogen, 26 carbon, and 45 hydrogen atoms, was based on the former alternative. A decision between the two possibilities would have required exact mass measurements.

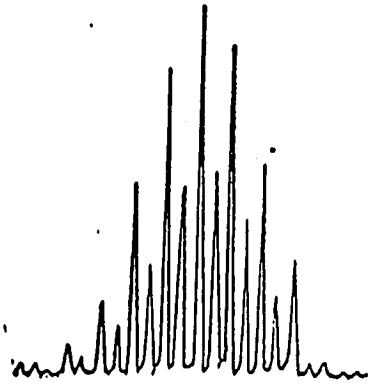

Fig. 4a

Comparison of the experimental (Fig. 4a) and simulated (Fig. 4) envelopes for the m/e 634 "peak" shows that this "peak" derived from a three-germanium species. A loss of one germanium atom or germanium hydride species occurred in passing from m/e 705 to m/e 634. Since simple loss of a germanium atom would have produced a "peak" at m/e 631, the fragmenting species seemingly gained several hydrogen atoms while losing one germanium. An observed lack of reproducibility in the form of the m/e 634 "peak" under various conditions suggested that the envelopes of two or more species with different numbers of hydrogen atoms and with slightly

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different (1-3 integral units) m/e values overlapped in this region.

The reproducible, strong m/e 599 "peak" derived from a three germanium ion. Fragmentation of the four-germanium m/e 705 species, with a loss of Et_2Ge and a nitrogen atom or methylene group, perhaps produced this three-germanium ion. Weak "peaks" at m/e 529, 515, and 501 suggested successive losses of ethane and methylene groups or nitrogen atoms. Exact mass measurements would have provided information about the elemental composition of these various ions; even with that knowledge, however, one could not have chosen definite fragmentation paths from the numerous possibilities that exist for such a complicated molecule. This spectrum and those of other germazanes demonstrated that losses of small molecules (ethane, ethylene, methylene) occurred more frequently than did losses of small hydrocarbon radicals (methyl, ethyl). The even-electron ions which predominated in this spectrum tended to produce new even-electron species on fragmentation.[77]

Observation of the previously considered "peaks" at m/e greater than 444 and 666 indicated, but did not prove, the tetrameric nature of the N-phenylated diethylgermazane. A reproducible, broad, metastable peak centered near m/e 776-778 also provided evidence for this molecular weight. A calculation using the well-known equation[78] for the position of metastable peaks, $m^* = (m_2)^2/m_1$, suggested that a loss of two ethyl groups

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77. F. Glockling, The Chemistry of Germanium, Academic Press, New York, 1969, p. 23.

78. F.W. McLafferty, Interpretation of Mass Spectra, W.A. Benjamin, Inc., New York, 1966, p. 65.

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or two ethylene molecules from the molecular ion $(Et_2GeNC_6H_5)_4^+$ occurred during acceleration. The much more clearly substantiated tetrameric nature of $(Et_2GeNC_6H_{11})_4$, reported later in this chapter, further supported the assumed form of $(Et_2GeNC_6H_5)_4$.

This report of the cyclic tetramer $(Et_2GeNC_6H_5)_4$ (mp. 152-153°C) may or may not conflict with the recent report[42] of the compound bis-(N-pentafluorophenyl)-tetraphenylcyclodigermazane (mp. 331-332°C). The high melting point of the latter agrees well with the melting points reported[79] for the cyclodisilazanes $[(CH_3)_2SiNC_6H_5]_2$ (252.5°C) and $[(C_6H_5)_2SiNC_6H_5]_2$ (355.5°C). While assuming that Haiduc and Gilman did isolate a cyclodigermazane, one would nevertheless like to know the insertion temperature(s) used by those investigators in their mass spectrometric molecular weight determination. As mentioned previously, in this research one observed a diminution and eventual disappearance of "peaks" above the dimeric mass with increasing temperature. Similarly, Fink has noted[80] the tendency of N-trimethylsilylated and N-phenylated cyclotrisilazanes to undergo ring contraction at 400-425°C. Though other means of preparing cyclodisilazanes are known, (e.g. reactions of dilithium derivatives of amines with diorganodichlorosilanes), the best yields are obtained from pyrolyses and thermal rearrangements.[80] In this research, mass spectrometry at low temperatures did not indicate dimeric character for any of

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79. W. Fink, Helv. Chim. Acta, 47, 498(1964).

80. W. Fink, Angew. Chem. Internat. Ed., 5, 760(1966).

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the several cyclopolygermazanes studied.

Though the room-temperature reaction of Et_2GeCl_2 and aniline in the presence of a stoichiometric amount of triethylamine produced a significant yield of $(Et_2GeNC_6H_5)_4$, the aminolysis was decidedly incomplete. A second reaction, performed by heating essentially the same reagent quantities at 58°C for 0.5 hour and at 68°C for 7 hours, produced a slightly larger quantity of triethylamine hydrochloride. Nevertheless, about 15% by weight of the aniline and diethyldichlorogermane starting material was recovered in low-boiling vacuum distillation fractions. A small amount of white solid sublimed into an ice-cooled receiving flask during initial stages of distillation and was shown to be aniline hydrochloride. These distillations demonstrated just how difficult the direct reaction of diethyldichlorogermane with aniline was. Based on the quantity of Et_2GeCl_2 starting material, the reaction at 68°C produced an 8.8% yield of $(Et_2GeNC_6H_5)_4$ and a 42.2% yield of oily oligomer. The boiling range of that oil, 165-180°C at 0.25mm Hg, was quite like that for the apparently chlorine-free oil from the first reaction.

Fig. 1.6 shows the infrared spectrum of the yellow, oily oligomer from the second reaction. The single N-H stretching band at 3380 cm^{-1} indicated that at least some $-NHC_6H_5$ groups were present in the material, probably as terminal groups for the low oligomers. As with $(Et_2GeNC_6H_5)_4$, the aniline N-H deformation band near 1615 cm^{-1} was missing from the spectrum. However, the intense band at 1585 cm^{-1}, deriving at least partly from benzene ring stretching, perhaps masked a weaker N-H band. The aromatic C-N stretching mode at approximately 1297 cm^{-1}, while at lower

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energy than for $(Et_2GeNC_6H_5)_4$, was still above the aniline ν C-N mode (1278 cm^{-1}). No reasonable assignment could be made for the strong band near 1225 cm^{-1}. The very strong, broad band centered at approximately 850 cm^{-1} likely derived from germanium-nitrogen asymmetric stretching. Since the low polymers presumably contained germanium in at least two distinct environments (attached only to bridging nitrogens or attached to one bridging and one terminal amino nitrogen), the broad peak was to have been expected. The report by Yoder and Zuckerman[81] of asymmetric N-Ge-N stretching modes in the 930-870 cm^{-1} region suggested that one would not observe significant differences between Ge-N-Ge and N-Ge-N(HC_6H_5) stretching in polymers containing those structures. The Ge-C stretching bands at 597 and 558 cm^{-1} were closer to those of Et_2GeCl_2 than to those of $(Et_2GeNC_6H_5)_4$. These results suggested that the Ge-C bond was more polar in the linear oligomers than in $(Et_2GeNC_6H_5)_4$, that less electron density resided at the germanium atoms, and that the nitrogen atoms were slightly more basic in the linear oligomers. The oily polymers underwent rapid hydrolysis on exposure to air. The cyclic tetramer did not show signs of hydrolysis, nor did its infrared spectrum change significantly, until it had been exposed to air for about an hour. Model building indicated, however, that steric hindrance in the globular $(Et_2GeNC_6H_5)_4$ molecule might slow hydrolysis. In Fig. 1.6, the remaining infrared bands were common to the oligomeric material and to $(Et_2GeNC_6H_5)_4$ and need no further discussion.

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81. C.H. Yoder and J.J. Zuckerman, Inorg. Chem., 5, 2055(1966).

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The yellow, oily polymers were easily soluble in common solvents like CCl_4 and benzene. Integration of the ethyl and phenyl resonances in the NMR spectra of several polymer samples (from first and second reaction) yielded ethyl/phenyl ratios varying from 1.8/1 to 3.5/1 (theoretical ratio for a four-germanium polymer terminated by $-NHC_6H_5$ groups = 1.6/1). Since the writer did not detect chlorine in these polymers, he suspected that almost all polymer distillation fractions were hydrolyzed to some extent. No molecular weight determinations were performed on these materials. Later studies on similar cyclohexylamino polymers suggested that the polymers contained 3-5 germanium atoms.

The most complete aminolysis of Et_2GeCl_2 by aniline occurred when triethylamine present in large excess was the only solvent. Triethylamine provided a basic medium for reaction and permitted refluxing at 85°-89°C. Addition of Et_2GeCl_2 to triethylamine produced some white solid (an adduct of the two species?), but without significant evolution of heat. A definitely exothermic reaction then occurred when aniline was added to the Et_2GeCl_2- triethylamine mixture. Reaction of aniline and Et_2GeCl_2 in a 1:1 molar ratio produced a 15% yield of $(Et_2GeNC_6H_5)_4$ and a 60% yield of oily oligomer. Smaller amounts of aniline and Et_2GeCl_2 were recovered then in the reactions in benzene. Rather interestingly, approximately one half (49%) of the aniline used in another reaction of aniline and Et_2GeCl_2 in a 2:1 molar ratio was recovered unreacted. The products from the 2:1 reaction were essentially like those from the 1:1 reaction; one did not detect any bis-(phenylamino)diethylgermane. NMR spectra of the liquid (oily) fractions always indicated ethyl/phenyl

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ratios of at least 2/1. That ratio for bis-(phenylamino)diethylgermane would be 1/1. The use of triethylamine as sole solvent for reaction seemingly increased the total degree of aminolysis, but did not signif-cantly increase the yield of $(Et_2GeNC_6H_5)_4$.

A reaction of 0.05 mole of Et_2GeCl_2 with 0.05 mole of aniline in the presence of 0.10 mole of triethylamine and 175 milliliters of benzene was used to study the nature of the aminolysis product before high temperature vacuum distillation. After heating for two hours at 60°C, stirring overnight at room temperature, and filtering of the precipitated triethylamine hydrochloride, the investigator used a rotary evaporator to remove benzene and triethylamine. Some additional hydrochloride was sublimed (or swept by the solvents) from the product flask. With occasional heating of the flask at 40-50°C, the product was then evacuated under oil pump vacuum for seven days. Aniline gradually collected in a trap cooled in a dry ice-acetone bath. After that lengthy evacuation, an infrared spectrum looked almost exactly like Fig. 1.6, except that one found two additional weak bands at 3250 cm^{-1} and 3450 cm^{-1} and a shoulder of medium intensity (probably a δ N-H band) at 1615 cm^{-1}. The relative intensities and positions of the two new bands were different from the 3425 cm^{-1} (ν N-H) and 3205 cm^{-1} (2 x δ N-H) bands of aniline, but perhaps still indicated the presence of dissolved aniline in the product. With an additional four day period of heating and evacuation, one detected aniline hydrochloride in the evacuation adapter. Though only a single ν N-H band then appeared in the infrared spectrum of the evacuated material, one also observed intense, broad Ge-O bands at 800 cm^{-1} and in the region

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1000-1100 cm^{-1}. Hydrolysis therefore denied further investigation of the product. Crystallization of $(Et_2GeNC_6H_5)_4$ from the crude product was never detected.

The second route to N-phenylated diethylgermazanes, outlined by the previously mentioned equations (2a) and (2b), involved the dilithio derivative of aniline. In a first series of reactions, slightly more than 0.2 mole of n-butyl lithium, prepared by reaction of butyl chloride with a hexane suspension of lithium sand, was allowed to react vigorously with 0.1 mole of aniline. The resulting white solid, $Li_2NC_6H_5$, was extremely reactive; a small portion turned brown instantly on exposure to air. Under a constantly maintained atmosphere of argon, 0.1 mole of Et_2GeCl_2 reacted readily with the dilithioanilide. After separation of the rather brown-colored, impure LiCl by protracted filtration, one removed most of the hexane solvent by distillation at atmospheric pressure and vacuum distilled the oily crude product. Even with use of the organolithium reagent, one recovered about one gram of impure aniline (about 10% of the starting material). Such was formed by hydrolysis of $Li_2NC_6H_5$ or of the germazane product. The rather violent reaction of $Li_2NC_6H_5$ and Et_2GeCl_2 was not likely incomplete. The writer isolated 2.90 grams (14% yield) of the cyclic tetramer (mp 152°C) and about 13 grams (59% yield) of polymer much like that obtained previously. Considering the difficulty in washing the rather heavy mass of LiCl free of product, these yields probably reflected increased success in gaining aminolysis of the Et_2GeCl_2. The absolute masses of isolated products were no better, however. The infrared spectrum of the solid product agreed exactly with those obtained

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for $(Et_2GeNC_6H_5)_4$ in earlier reactions.

A second organolithium reaction was performed with a commercially available (Alpha Inorganics) 22.1% by weight solution of n-butyl lithium in hexane. In contrast with the previous experiment, the $Li_2NC_6H_5$ appeared here as a bright yellow solid which turned to tan on standing.[82] The color probably derived from impurities in the organolithium reagent. Before addition of 0.1 mole of Et_2GeCl_2 to 0.27 mole of $Li_2NC_6H_5$ (170% in excess), 250 ml of sodium-dried heptane were added to the hexane solution. When the exothermic reaction had subsided, the flask contents were heated at 75°C for eleven hours. Since $Li_2NC_6H_5$ was a solid, seemingly rather insoluble in the hydrocarbon solvents, the investigator made no deliberate effort to destroy the excess organolithium reagent and simply filtered in an inert atmosphere. The filtered solid gradually turned brown with slow exposure to oxygen and atmospheric moisture. Vacuum distillation of the yellow-brown product produced oily polymer in 60% yield, but only a few tenths of a gram of crystalline cyclic tetramer. One had no explanation for this disappointing outcome, except that the rather intractable mass of filtered solid must have trapped much product. In summary then, the dilithioanilide reagent, which held much promise because of its great reactivity, was not of particular value because the polymeric products were not easily separated from the muck of impure LiCl. Preparations of monomeric trimethylsilyl-, trimethylgermyl-, and trimethylstannylanilines were apparently easier to perform.[82] In this research,

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82. E.W. Randall and J.J. Zuckerman reported a yellow-green color for their $LiNHC_6H_5$ preparation. [J.A.C.S., 90, 3167(1968)].

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one preferred to deal with the more tractable amino hydrochlorides.

Equations (3a), (3b), and (3c) roughly outline the third procedure followed in preparing N-phenylated diethylgermazanes. Relatively few syntheses of cyclic and polymeric N-substituted silazanes and germazanes by transamination have been reported. Larsson and Bjellerup[83] reported formation of diphenyldianilinosilane in a direct reaction, without solvent, of hexaphenylcyclotrisilazane with aniline. Andrianov and Rumba claimed[84] formation of $[(CH_3)_2SiNC_6H_5]_3$ (mp 247-248°C) in a 45.5 hour (327°C!) reaction of four moles of aniline with three moles of $[(CH_3)_2SiNH]_4$, but did not discuss product yields. Fink asserted[85] that the material obtained by the Russian authors was actually the cyclodisilazane $[(CH_3)_2SiNC_6H_5]_2$ (mp 252.5°C). Andrianov and coworkers[86] obtained polymer of low molecular weight by cleavage of $[(CH_3)_2SiNH]_3$ with an aromatic diamine. Morgunova and his associates[87] synthesized cross-linked polymers by transamination of hexamethylcyclotrisilazane with aliphatic diamines. Henglein and Lienhard[88] prepared polymers stable below 300°C according to the following equation:

$$(CH_3)_2Si(NEt_2)_2 + NH_2(CH_2)_nNH_2 \rightarrow \frac{1}{x}[-(CH_3)_2SiNH(CH_2)_nNH-]_x + \text{diamine}\cdot 2HCl$$

$(n = 2,4,6)$

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83. E. Larsson and L. Bjellerup, ibid, 75, 995(1953).

84. K.A. Andrianov and G. Rumba, Zh. Obshch. Khim., 32, 1993(1962); Eng. transl. in J. Gen. Chem. USSR, 32, 1974(1962).

85. W. Fink, Angew. Chem. Internat. Ed., 5, 760(1966).

86. K.A. Andrianov, G.A. Kurakov, L.M. Khananashvili, and T.A. Lomonosova, Chem. Abstr., 59, 10105(1963).

87. M.M. Morgunova, D. Zhinkin, and M.V. Sobolevskii, Chem. Abstr., 59, 11674(1963); Chem. Abstr., 60, 5664(1964).

88. F.A. Henglein and K. Lienhard, Makromol. Chem., 32, 218(1959).

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And finally, Yoder and Zuckerman[89] prepared monomeric sila- and germa-imidazolidines and polymeric germyl- and silylamines by transamination of $(CH_3)_2Ge(NEt_2)_2$ and $(CH_3)_2Si(NEt_2)_2$ by N,N'-dimethylethylenediamine, ethylenediamine, and piperazine. An examination of the literature, particularly of the research of Andrianov and Rumba,[84] conveyed the distinct impression that transamination of such as octamethylcyclotetrasilazane by amines (aniline) did not provide a very satisfactory route to discrete N-substituted cyclic species, but that transamination might lead to low molecular weight linear polymers. In the research by the Russian authors, most of the product weight evidently lay in oily polymer rather than in crystalline cyclic material.

In an initial transamination reaction, ammonia gas, after passing through a tower filled with potassium hydroxide, was bubbled into a petroleum ether solution of 0.1 mole of Et_2GeCl_2 for four hours. Following filtration of the precipitated ammonium chloride, ammonia was again passed through the solution and an additional small amount of NH_4Cl formed. One obtained a stoichiometric amount of NH_4Cl from the ammonolysis reaction. Without isolating the diethylgermazane products, one introduced 0.1 mole of aniline. During four hours of stirring at room temperature and an additional four hours of stirring and heating at 60°C (solvent changed to benzene), evolved NH_3 was collected in a trap containing a known amount of HCl. Finally, dry N_2 was bubbled into the flask to sweep any residual NH_3 into the acid trap. Titration of excess HCl indicated 96%

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89. C.H. Yoder and J.J. Zuckerman, J.A.C.S., 88, 4831(1966); Inorg. Chem., 4, 116(1965).

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recovery of the ammonia (0.1 mole) theoretically obtainable from the diethylgermazane. Following removal of most of the benzene, an infrared spectrum of the yellow-brown crude product, corrected for the presence of a small amount of benzene, looked strikingly like Fig. 1.6. Only a very weak hump at 3450 cm^{-1} and a low intensity shoulder at 1615 cm^{-1} suggested the presence of free amine or ammonia. Refrigeration of the crude product induced no crystallization over several weeks. Vacuum distillation ultimately yielded a few drops of aniline and nearly 18 grams of yellow oily polymer, the latter in two distillation fractions at 180°-190°C and 195°-210°C (0.2-0.3 mm Hg). In the topmost fraction one could discern traces of white solid. The 81% yield (based on germanium starting material) of high boiling polymer was the best so far encountered. No cyclic tetramer was isolated, though the traces of white solid indicated its presence. The outcome of this reaction seemingly denied the experimenter's previous suspicion that $[Et_2GeNC_6H_5]_4$ was a thermally induced product of the high temperature vacuum distillations and not a species present in the crude direct aminolysis or organolithium products. An infrared spectrum of the larger 180°-190°C fraction, after the material had stood in a glass-stoppered flask for four weeks, showed the presence of a small amount of aniline; otherwise the spectrum again looked like Fig. 1.6. Oil pump evacuation of the liquid polymer for eight days successfully removed the aniline. Sizable amounts of white gooey material were found adhering to the sides of the product flask. An infrared spectrum, quite different from that of the yellow, liquid polymer, characterized this white material as polymeric diethylgermanium oxide. Evidences

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of aniline, even the normally intense 1590 cm^{-1} peak, were weak; two intense, very broad peaks were centered at 1020 cm^{-1} and 1100 cm^{-1}. Another strong, broad peak, always found in the diethylgermanium hydrolysis products, appeared at approximately 800-810 cm^{-1}. The latter band undoubtedly derived from asymmetric Ge-O-Ge stretching. The two higher energy bands, also observed previously, were at too high energy to derive from Ge-O-Ge stretching. Glockling[90] cited germanium-oxygen stretching vibrations for discrete alkyl germanium oxides between 855 cm^{-1} and 926 cm^{-1}. However, alkoxygermanes[90] show a band at 1040 cm^{-1}. The 1020 cm^{-1} and 1100 cm^{-1} bands observed in this research then undoubtedly derived from O-Ge-O asymmetric stretching, perhaps in uncondensed germanols. Though the infrared spectrum of the liquid polymer was strongly different from that of the diethylgermanium oxide, NMR spectra, with ethyl/phenyl ratios varying from 3.5/1 to 4.2/1 indicated that considerable hydrolysis had occurred. Aniline formed in hydrolysis had been thoroughly evacuated.

A second transamination reaction, beginning with 0.1 mole of Et_2GeCl_2 dissolved in benzene, differed from the first in that 0.25 mole of triethylamine was present during reaction (see equation (3b)). Ammonia was bubbled into the solution during an eight hour period of refluxing at 80°C. Rather surprisingly, a quantitative yield of ammonium chloride was obtained, and no detectable triethylamine hydrochloride, in spite of the fact that the reported[91] basicity constants are $K_b(Et_3N) = 5.50 \times 10^{-4}$ and $K_b(NH_3) = 1.82 \times 10^{-5}$. Those constants were determined in

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90. F. Glockling, The Chemistry of Germanium, Academic Press, New York, 1969, p. 16.

91. H.K. Hall, Jr., J. Phys. Chem., 60, 63(1956).

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aqueous solution. After addition of 0.2 mole of aniline (100% excess for formation of polymeric germazanes) and essentially quantitative evolution of ammonia, the product was treated as in the first reaction. Again no crystallization occurred with refrigeration of the yellow-brown, oily product. Vacuum distillation yielded 8.20 g of quite pure aniline and a 4.3 g fraction containing aniline. Therefore, approximately half of the aniline originally added remained unreacted. In a distillation fraction boiling over the wide range of 145°-165°C (0.04 mm Hg), one obtained 17.5 g of liquid polymer (79% yield). That fraction contained a little aniline, but with a redistillation the infrared spectrum was quite like Fig. 1.6 of the oligomeric germazanes obtained by direct aminolysis. The infrared spectrum of the topmost of three fractions obtained from that redistillation in fact contained only a rather weak ν N-H band at 3375 cm^{-1}.

In the interval 175°-180°C (0.04 mm Hg), the investigator obtained 3.0 g of heavy yellow oil and white solid. The approximately 1 g of solid was again found to be $(Et_2GeNC_6H_5)_4$. Fig. 1.7 is the infrared spectrum of the heavy, light-yellow, oily filtrate from that white solid. That spectrum, of the heaviest, presumably linear oligomeric diethylgermazanes obtained by transamination is in many respects like Fig. 1.6. The two scarcely resolved bands near 1590 cm^{-1} appeared because some cyclic tetramer remained dissolved in the liquid (see also the sharp peak at 888 cm^{-1}). The ν N-H band in Fig. 1.7 is weak and somewhat broadened compared with that band in Fig. 1.6. That result probably indicated that some of the polymers from transamination were terminated

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by $-NH_2$ groups, and not that the polymers were of significantly higher molecular weight than those from direct aminolysis. The ethyl/phenyl ratio obtained from the NMR spectrum of the highest boiling polymer was 2.2/1, reasonably close to the theoretical value of 2/1 for a N-phenylated diethylgermazane polymer of infinite length. Analytical results for the highest boiling fraction obtained in redistillation of the main portion (17.5 g) of polymer were as follows:

Found:	C, 56.90%	H, 6.81%	N, 7.26%
Calc'd:	C, 53.43%	H, 6.83%	N, 6.32%

(for a polymer of infinite length or for a cyclopolygermazane)

Calc'd:	C, 57.00%	H, 6.93%	N, 7.39%

(for a three-germanium polymer terminated by aniline)

The C, H, N, and Si analyses reported here and in the remainder of this thesis were performed by Schwarzkopf Microanalytical Laboratory.

All of the N-phenylated diethylgermazane polymers obtained by direct aminolysis, reaction of $Li_2NC_6H_5$, and transamination were quickly hydrolyzed on exposure to air. These low molecular weight liquids were obtained in highest yield by transamination.

The reaction of $(CH_3)_2GeCl_2$ with aniline was less extensively studied in this research. The products obtained by direct aminolysis in the presence of triethylamine were more easily characterized than the diethylgermazane materials. Equation (4), only a slight modification of the previously presented equation(1), essentially describes the reactions that were performed:

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$$x(CH_3)_2GeCl_2 + xC_6H_5NH_2 + 2xEt_3N \xrightarrow{\text{benzene}} \frac{x}{y}[(CH_3)_2GeNC_6H_5]_y + 2xEt_3NH^+Cl^- \quad (4)$$

In anticipation of the results to be described in greater detail below, one notes that the heavily predominating product in this series of reactions was the cyclic trimer $[(CH_3)_2GeNC_6H_5]_3$, that limited amounts of liquid polymer were isolated, and that bis(phenylamino)dimethylgermane was not encountered. Most preparative details for these products are contained in the following Experimental section.

In a first reaction, 0.1 mole of $(CH_3)_2GeCl_2$ was combined with 0.1 mole of aniline in the presence of 0.3 mole (50% excess) of Et_3N and 150 ml of sodium-dried benzene. The reaction flask was initially cooled in an ice bath, but the system was allowed to warm to room temperature during stirring overnight. Following removal of a stoichiometric amount of triethylamine hydrochloride and of benzene and excess Et_3N, vacuum distillation yielded some slightly impure aniline (about 11% of the starting material), 3.22 g of a liquid boiling at 108°-120°C (0.05 mm Hg), and a large amount of yellow-white solid. That solid formed rather awkwardly in the distillation head and condenser when the head temperature had exceeded about 140°C (0.05 mm Hg). The solid was somewhat soluble in all the common, weakly acidic solvents which were tried. Benzene, carbon tetrachloride, chloroform, dichloromethane, diethylether, and hexane rather easily dissolved the material. The solid was recrystallized by dissolving it in a minimal amount of n-heptane at room temperature and filtering the crystals which formed with refrigeration. The yield of recrystallized solid was 10.3 g, 53.2% based on the $(CH_3)_2GeCl_2$ starting

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material. Because of losses in recrystallization, the actual yield of solid was somewhat greater. Chemical analysis, infrared and NMR spectroscopy, and mass spectrometry characterized this material, with mp 130°-132°C, as tris(N-phenyl)-hexamethylcyclotrigermazane, $[(CH_3)_2GeNC_6H_5]_3$. Rather surprisingly, a similar reaction performed with 0.055 mole of $(CH_3)_2GeCl_2$ and 0.11 mole of aniline (i.e. seemingly designed to produce bis(phenylamino)dimethylgermane) produced relatively even more cyclic trimer, in 74.5% yield. One recovered most of the excess aniline in the latter reaction and obtained about one gram of yellow liquid polymer over the boiling range 120°-140°C at 0.035 mm Hg. Therefore, the reactions of aniline with both $(CH_3)_2GeCl_2$ and Et_2GeCl_2 showed a great tendency to form cyclic and polymeric germazanes, but not the bis(phenylamino)dialkylgermane.

The analytical results obtained for the solid $[(CH_3)_2GeNC_6H_5]_3$ were as follows:

Found:	C, 49.23%	H, 5.90%	Ge, 37.2%
Calc'd:	C, 49.58%	H, 5.71%	Ge, 37.46%

Fig. 1.8 shows the Kadol mull infrared spectrum of $[(CH_3)_2GeNC_6H_5]_3$, and Fig. 1.9 the spectrum of the liquid polymer from the second reaction. The two scans in Fig. 1.8, range 2, simply derived from mulls of different thicknesses. A good spectrum, free from signs of hydrolysis, was not easily obtained for the solid trimer unless the sample was prepared quickly inside a glove bag. Therefore this cyclic material was much more moisture sensitive than the previously reported $(Et_2GeNC_6H_5)_4$. Table IV lists the prominent infrared bands of $(CH_3)_2GeCl_2$, $[(CH_3)_2GeNC_6H_5]_3$, and the oligomeric dimethylgermazane polymer, with assignments where such could reasonably

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Table IV[52,53]

$(CH_3)_2GeCl_2$		$[(CH_3)_2GeNC_6H_5]_3$		Oligomeric N-phenylated Dimethylgermazane[93]	
cm^{-1}	assignment[92]	cm^{-1}	assignment	cm^{-1}	assignment
				3421(m)	ν N-H
		3040(sh)	ν C-H aromatic	3100(m) 3061(m) 3041(m)	ν C-H(aromatic)
3000(m)	ν_{asym}C-H	see footnote 53			
				3021(m)	ν_{asym}C-H(CH_3)
2922(m)	ν_{sym}C-H			2936(w)	ν_{sym}C-H(CH_3)
		1585(m)	benzene ring stretching	1601(vs)	δ N-H and benzene ring stretching
		1470(s)	see footnote 53	1496(s) 1471(s)	benzene ring stretching
1406(m)	$\delta_{asym}(CH_3)$			1401(w)	$\delta_{asym}(CH_3)$
				1376(m)	unassigned

92. The assignments for $(CH_3)_2GeCl_2$ used here are those reported by (a) J.E. Griffiths, Spectrochimica Acta, 20, 1335(1964); (b) D.F. Van de Vondel and G.P. Van der Kelen, Bull. Soc. Chim. Belges, 74, 453(1965).

93. Note that in Fig. 1.9, range 1, a correction of +21 cm^{-1} must be made to locate the correct band positions. The polystyrene calibration peak correctly appears at 1944.0 cm^{-1}.

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Table IV, Contd.

$(CH_3)_2GeCl_2$		$[(CH_3)_2GeNC_6H_5]_3$		Oligomeric N-phenylated Dimethylgermazane[93]	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
		1274(m)	νC-N	1290(s)	νC-N
		1256(m)	unassigned		
1252(s)	$\delta_{sym}(CH_3)$	1240(s)	$\delta_{sym}(CH_3)$	1244(s)	$\delta_{sym}(CH_3)$
				1230(m)	unassigned
1197(w)	unassigned	1175(m) 1170(m) 1150(w)	C-H aromatic (in plane) bending	1176(m) 1150(w)	C-H aromatic (in plane) bending
		1075(sh) 1070(m)	unassigned	1072(m)	unassigned
		1028(m) 1021(m)	C-H aromatic bending	1026(m)	C-H aromatic bending
		992(m)	benzene ring mode	990(m)	benzene ring mode
		906(m) 875(s)	ν_{asym} Ge-N-Ge and	920(w) 870(sh)	ν_{asym} Ge-N-Ge and
850(s) 826(s) 766(m)	$\rho(CH_3)$	~830(m) 800(s)	$\rho(CH_3)$	850(s) 802(s)	$\rho(CH_3)$

Table IV, Contd.

$(CH_3)_2GeCl_2$		$[(CH_3)_2GeNC_6H_5]_3$		Oligomeric N-phenylated Dimethylgermazane[93]	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
		746(sh)	C-H aromatic bending	747(s)	C-H aromatic (out of plane) bending
		734(m)	?		
		699(s), 688(m)	benzene ring modes	689(s)	benzene ring modes
640(m)	ν_{asym}Ge-C	613(m)	ν_{asym}Ge-C	620(m)	ν_{asym}Ge-C
		610(sh)	unassigned	610(sh)	unassigned
594(m)	ν_{sym}Ge-C	578(m)	ν_{sym}Ge-C	585(m)	ν_{sym}Ge-C
		508(m)	benzene ring mode	509(m)	benzene ring mode
400(m)	ν_{asym}Ge-Cl				

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be made. The aniline infrared bands listed in Table I were again useful in analysis of these dimethylgermazane spectra.

Only rather tentative interpretation of the two dimethylgermazane spectra was possible. In the regions of greatest interest, i.e. 1200-1300 cm^{-1}, 700-900 cm^{-1}, and 550-650 cm^{-1}, bands so overlapped that assignment of peaks to distinct modes was difficult. Evidences of NH groups were clearly absent in the trimer spectrum and present in that of the polymer. Of the three peaks in both spectra in the region 1200-1300 cm^{-1}, the highest energy band (1274; 1290) was assigned to C-N stretching, in accord with the spectra of aniline and $(Et_2GeNC_6H_5)_4$. Assignment of bands to the strong $\delta_{sym}(CH_3)$ mode was made on intensity grounds and by comparison with reported values for other methylgermazanes. I. Ruidisch and M. Schmidt listed[94] the following values for that mode in several compounds: 1234 cm^{-1}, hexamethyldigermazane; 1235 cm^{-1}, tris(trimethylgermyl)amine; 1247 cm^{-1}, $[(CH_3)_2GeCl)]_3N$. Similarly, Scherer and Schmidt[95] assigned a band at 1243 cm^{-1} (vs) to the $\delta_{sym}(CH_3)$ mode of $[(CH_3)_3Si]_2$-$NGe(CH_3)_3$. However, the third band, appearing at 1256 cm^{-1} (Fig. 1.8) and 1230 cm^{-1} (Fig. 1.9), remained unassigned. Though splitting of the $\delta_{sym}(CH_3)$ band would explain the presence of the two lower energy bands, such could not be confirmed without some knowledge of the molecular symmetry. The overlap of $\rho(CH_3)$ and ν_{asym}Ge-N-Ge bands in the region 750-900 cm^{-1} made assignment of peaks in that region almost impossible.

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94. I. Ruidisch and M. Schmidt, Angew. Chem., 76, 229(1964).

95. O.J. Scherer and M. Schmidt, J. Organometal. Chem., 1, 490(1964).

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Disappearance of the strong peaks at 875 cm^{-1} (Fig. 1.8) and 870 cm^{-1} (Fig. 1.9) with complete hydrolysis to dimethylgermanium oxide, suggested that these were Ge-N-Ge stretching bands. For $[(CH_3)_2GeNC_6H_5]_3$, the weaker, sharp peak at 906 cm^{-1} also decreased with hydrolysis. The strong, broad bands between 800 and 850 cm^{-1} were best assigned to methyl rocking modes. In these germazane spectra (Figs. 1.5 and 1.6), one observed a lowering in energy of the antisymmetric and symmetric Ge-C stretching modes relative to those of $(CH_3)_2GeCl_2$. The earlier explanation in terms of changing effective electronegativity of the germanium substituents applies here as well.

The NMR spectrum of $[(CH_3)_2GeNC_6H_5]_3$, shown in Figs. 2.5 and 2.6, was of course much simpler than the $(Et_2GeNC_6H_5]_4$ spectrum. A single resonance for the dimethylgermanium protons occurred at -0.49δ, compared with -1.18δ for $(CH_3)_2GeCl_2$.[96] There are few references to the NMR spectra of dimethylgermazanes. Schumann-Ruidisch and Jutzi-Mebert[97] reported a chemical shift of -19.0 Hz (-0.32δ) for the methylgermanium protons of $[(CH_3)_2GeNCH_3]_3$. The value given by Satgé and Baudet[98] for $[(CH_3)_3Ge]_3N$ was -0.3δ. Yoder and Zuckerman[99] listed proton chemical shifts of -0.29δ and -0.34δ for dimethylgermanium groups in imidazolidine rings and linking such rings, respectively. The chemical shift of the protons in $[(CH_3)_2GeCl)]_3N$ is -63.5 Hz (-1.06δ).[100] For purposes of comparison,

96. K. Moedritzer, J. Organometal. Chem., 6, 282(1966).

97. I. Schumann-Ruidisch and B. Jutzi-Mebert, J. Organometal. Chem., 11, 77(1968).

98. J. Satgé and M. Baudet, Compt. Rend. (Paris), Ser. C, 265, 435(1966).

99. C.H. Yoder and J.J. Zuckerman, J.A.C.S., 88, 483(1966).

100. I. Ruidisch and M. Schmidt, Angew. Chem., 76, 229(1964).

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the proton chemical shift for hexamethyldigermoxane is -18.5 Hz (-0.31δ).[101] The methyl proton chemical shift for $[(CH_3)_2GeNC_6H_5]_3$ is therefore quite high for a methylgermazane compound. The phenyl resonances appeared as expected between -6.5 and -7.5δ. Integration of the methyl and phenyl resonances for several NMR samples, the methyl/phenyl ratio varied from 1.17/1 to 1.21/1 (theory 1.20/1).

The NMR spectra of the liquid, N-phenylated dimethylgermazane polymers were considerably more complicated. For example, the polymer (bp 120°-140°C; 0.035 mm) from the second reaction showed methyl resonances (unnormalized intensities in parentheses) at -0.48δ (10.2), -0.59δ (7.0), -0.68δ (1.0), and -0.82δ (2.2). These different chemical shifts of course simply indicated that the polymer contained germanium in at least four different environments. The two peaks with largest chemical shift strongly indicated that these liquids contained some chlorine or oxygen. Chemical analysis unfortunately was not obtained for these very moisture-sensitive materials.

For $[(CH_3)_2GeNC_6H_5]_3$, mass spectrometry provided an unambiguous molecular weight determination. The molecular weight calculated from atomic weights is 581.39. The expected position for the most intense peak in the molecular ion envelope, as calculated with the previously stated rule for three germanium atoms, is m/e 581. In a mass spectrum obtained at 70 ev with an 140°C insertion temperature, the topmost envelope was centered at 581. Table V lists other prominent envelopes in the spectrum, with relative abundances where overlap did not deny such

101. H. Schmidbauer and I. Ruidisch, Inorg. Chem., 3, 599(1964).

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measurement. Overlapping of envelopes was of course more serious here than in the diethylgermazane spectra. The envelope of the base "peak", at m/e 195, was so intense that an abundance measurement could not be made. Abundances are normalized with respect to the molecular ion envelope. The loss of a methyl group in passing from m/e 581 to m/e 566 was supported by the presence of a metastable "peak" centered at approximately m/e 551. Figures 5, 6, and 7 are computer simulations of the m/e 581, m/e 566, and m/e 388 envelopes; agreement with the experimental envelopes was excellent.

Table V

m/e		Abundances
581		1.0
566	$-(CH_3)$	2.1
388	(dimer)	0.48
373		0.89
358		1.3
195	(base peak; monomer)	--

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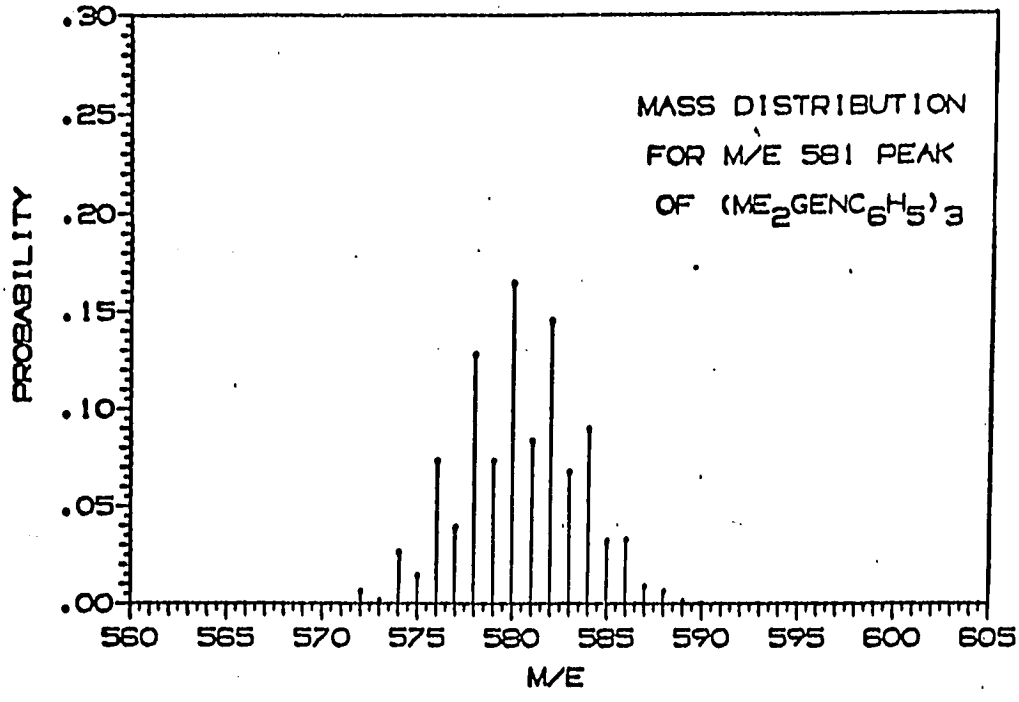

Figure 5

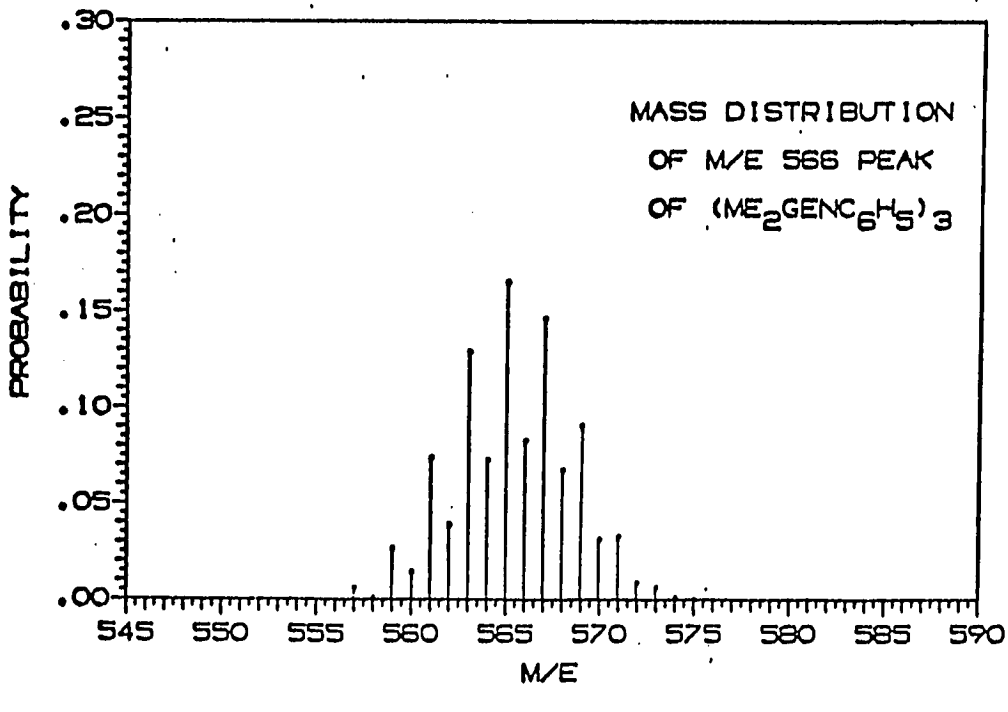

Figure 6

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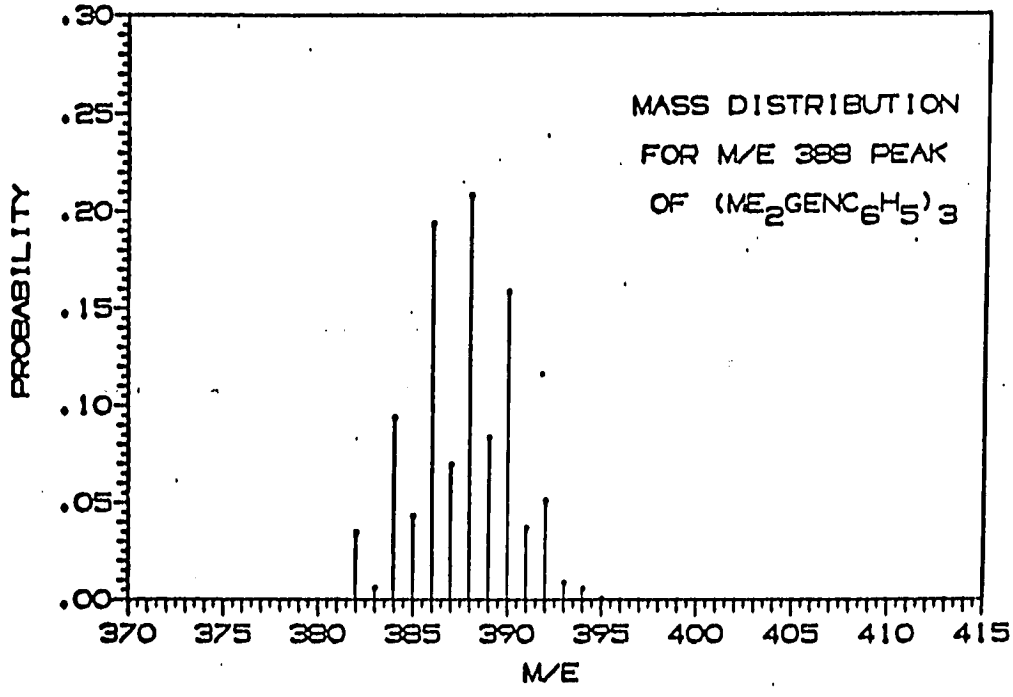

Figure 7

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2 N-cyclohexylgermazanes

Discussion

The reactions of the moderately strong organic base cyclohexylamine with Et_2GeCl_2 and $(CH_3)_2GeCl_2$ were conducted in parallel with the studies involving aniline. The much greater basicity of cyclohexylamine (cyclohexylammonium ion pK_a (H_2O) = 10.79)[91] indicated both that reaction with the organochlorogermanes would be easier than with aniline (anilinium ion pK_a (H_2O) = 4.60)[91] and that the properties of the resulting germazanes would be different from the N-phenylated germazanes. It was expected that the steric effects of the cyclohexyl and phenyl groups on the properties of the germazanes would be similar. Thorough study of the cyclohexylamino products was hindered by a shortage of spectroscopic information about the amine itself. NMR has been used[102] with several different techniques to study the conformational equilibria of cyclohexylamine and its derivatives, but full analysis and simulation of the cyclohexylamine NMR spectrum has not been performed. For cyclohexane itself, the rapid interconversion of equivalent chair conformations converts axial protons into equatorial and vice versa so that one observes a single resonance at -1.5δ in benzene solution. In cyclohexylamine, deshielding of the α-proton, the proton on the carbon to which $-NH_2$ is attached, by the amino group causes the α-proton resonance to appear at lower field than the other ring-proton resonances. In addition, the β, γ, and δ protons are differently shielded so that the NMR spectrum shows

102. a) G. Ransbotyn, J.C. Celotti, R. Ottinger, J. Reisse, and G. Chuirdoglu, Tetrahedron, 24, 3647(1968).
b) W.C. Neikam and B.P. Dailey, J. Chem. Phys., 38, 445(1963).
c) H. Feltkamp and N.C. Franklin, Liebigs Ann. Chem., 683, 55(1965).

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a broad resonance for those ring protons. In benzene, the sharp amino proton resonance appears at -0.96; the α-proton envelope is centered at -2.486.[103] Fig. 2.7 shows the NMR spectrum of cyclohexylamine in CCl_4. The sharp, amino proton resonance appears at -0.876 and the α-proton envelope approximately at -2.556. The small chemical shift of the amino group compared with that for aniline (-3.176; Fig. 2.8) provides one bit of indirect evidence for the greater basicity of the cyclohexylamino nitrogen. Little more can be said about this complicated spectrum.

Interpretation of the infrared spectrum of cyclohexylamine was also more uncertain than for aniline. Using CCl_4 solutions of cyclohexylamine, Feltkamp and Thomas[104] assigned bands at 3385 cm^{-1} and 3319 cm^{-1} to N-H stretching and a band at 1610 cm^{-1} to N-H deformation. Stewart's assignment,[105] from liquid film spectra, of a band at 1038 cm^{-1} to C-N stretching and of bands at 830 cm^{-1} and 778 cm^{-1} to antisymmetric and symmetric NH_2 bending, respectively, agrees well with the positions of bands in Fig. 1.4. Other infrared bands, deriving mostly from C-H and C-C vibrational modes, are listed in Table VII.

In the immediately following sections, the products obtained by reaction of cyclohexylamine with Et_2GeCl_2 are discussed. Thereafter, products from several $(CH_3)_2GeCl_2$ reactions are reported. Direct

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103. H. Booth, N.C. Franklin, and G.C. Gidley, Tetrahedron, 2, 1077(1965).

104. H. Feltkamp and K.D. Thomas, Liebigs Ann. Chem., 683, 49(1965).

105. J.E. Stewart, J. Chem. Phys., 30, 1259(1959).

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aminolysis of both chlorogermanes, though it proceeded easily without assistance from Et_3N, was an unsatisfactory route for preparing germazanes. The cyclohexylamine hydrochloride produced in such aminolyses was so soluble in the germazane products themselves that it became an all-pervading pest. Most vacuum distillation fractions, even those obtained at high temperature, contained some hydrochloride. In spite of this inconvenience, however, direct aminolyses were used in preparations of the germylamines bis(cyclohexylamino)diethylgermane and bis(cyclohexylamino)dimethylgermane. For cyclohexylamine, in contrast with aniline, good yields of the diamino derivative were obtained from reactions in which the cyclohexylamino/germane molar ratio was at least 4/1. Linear and cyclic germazanes were the primary products in 1:1 reactions. The presence of cyclohexylamine hydrochloride was so disturbing that in the very first reaction run the preparation of bis(cyclohexylamino)diethylgermane was overlooked, though later experience indicated that compound must have been present. Organolithium reactions, as outlined in equations (2a) and (2b), with simple substitution of cyclohexylamine for aniline, were used to prepare cyclic and linear oligomeric diethylgermazanes.

In a typical preparation, following filtration of lithium chloride from the hexane solution of the products of reaction of 0.1 mole of Et_2GeCl_2 with 0.1 mole $Li_2NC_6H_{11}$, almost all solvent was removed by distillation at atmospheric pressure. Vacuum distillation yielded several liquid oligomer fractions with increasing boiling ranges:

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		Mass	%Yield Based on Germanium
1.	76-90°C (0.04 mm Hg)	3.76 g	16.5%
2.	91-100°C (0.04 mm Hg)	1.11 g	4.9%
3.	120-140°C (0.04 mm Hg)	1.63 g	7.1%
4.	160-185°C (0.04 mm Hg)	4.12 g	18.0%
	Total =	10.62 g	Total = 46.5%

Along with the highest boiling liquid fraction, when the boiling point was near 170°C (0.04 mm Hg), one obtained crystalline solid, mp 93-95°C (2.2 g after recrystallization) which was characterized as $(Et_2GeNC_6H_{11})_4$. Heavy, yellow, oily liquid continued to distil after the solid had been melted with application of heating tapes and conducted into a receiving flask. Finally, brown, rather viscous polymer (8.2 g) remained in the distilling pot at temperatures exceeding 250°C (0.04 mm Hg). The total yield of products, based on the Et_2GeCl_2 starting material, was 92.3%. The outcome of a second reaction of this type was virtually identical. All of the N-cyclohexyl germazane compounds, even the solid tetramer $(Et_2GeNC_6H_{11})_4$, were extremely moisture sensitive. Detectable hydrolysis of the liquids occurred with exposure to atmospheric moisture for about fifteen seconds. Crystals of the cyclic tetramer became mushy after about five minutes in air.

Characterization of the four liquid fractions by infrared and NMR spectroscopy was difficult. The NMR spectra, formed essentially by superposition of the separately complex diethylgermanium and cyclohexylamine spectra, were scarcely interpretable and nearly identical in appearance. The infrared spectra of the 76-90°C and 91-100°C fractions were

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distinctly different from the spectrum of $Et_2Ge(NHC_6H_{11})_2$ presented as Fig. 1.11 and discussed later. However, since the boiling ranges of the first two fractions were comparable to the boiling point of $Et_2Ge(NHC_6H_{11})_2$, 117.5-118°C (0.25 mm), these fractions perhaps contained some of the diamino compound. A mass spectrum (direct insertion at 100°C) of the 76-90°C fraction contained a two-germanium "peak" at m/e 555 which suggested the presence of $C_6H_{11}NHGeEt_2N(C_6H_{11})GeEt_2NHC_6H_{11}$ (integral molecular weight = 555). The mass spectrum (direct insertion at 145°C) of the 120-140°C fraction showed four-germanium "peaks" at some of the same m/e values (748, 721, 693) found for the solid $(Et_2GeNC_6H_{11})_4$. The higher boiling liquid fractions were probably comprised of oligomers containing three or four germanium atoms and of dissolved $(Et_2GeNC_6H_{11})_4$. The most intense "peaks" in the spectrum of fraction 3 occurred at m/e 456 (mass of the dimer), 427 (dimer minus an ethyl group), and 413 (m/e 427 minus N or CH_2).

In the infrared, small and not easily explained changes were observed in moving from lower to higher boiling liquid fractions. The single N-H stretching band at 3375 cm^{-1}, while never strong in any of the spectra, seemed to decrease in intensity as the boiling point increased. A relative decrease in the number of terminal $-NHC_6H_{11}$ groups for the heavier oligomers explained that result. In the C-H stretching region (2825-2950 cm^{-1}), the spectra of the polymers differed from Fig. 1.11 ($Et_2Ge(NHC_6H_{11})_2$) in that a high intensity, nearly resolved shoulder appeared at 2950 cm^{-1} and peaks of equal intensity occurred at 2845 cm^{-1} and 2870 cm^{-1}. The intensity of a strong band at 1105 cm^{-1}, assignable

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at least partly to N-Ge-N stretching (carbon-carbon stretching in the cyclohexane ring occurs in the same region), decreased in moving to the heavier oligomers. For the 91-100°C and 120-140°C fractions, a strong band, significantly broader than in Figs. 1.10 and 1.11, occurred at 845 cm^{-1} and probably derived from asymmetric Ge-N-Ge stretching. This broadening of the ν_{asym}Ge-N-Ge band in low linear oligomers had been observed earlier for the N-phenylated germazanes. The Ge-C stretching bands for the oligomers appeared at 550 cm^{-1} and 575-580 cm^{-1}, at energies higher than for $(Et_2GeNC_6H_{11})_4$. The analytical results shown below confirmed the description of the polymers outlined above.

For fraction(1) Found: C, 55.04% H, 10.49%

fraction(2) Found: C, 53.53% H, 9.92%

fraction(3) Found: C, 53.20% H, 10.03%

Calc'd: C, 52.72% H, 9.29% N, 6.15% Ge, 31.84%
(for a polymer of infinite length or a cyclic polygermazane)

Calc'd: C, 55.24% H, 9.80% N, 7.16% Ge, 27.80%
(for a three-germanium polymer terminated by $-NHC_6H_{11}$)

Calc'd: C, 58.75% H, 10.48% N, 8.57% Ge, 22.20%
(for $Et_2Ge(NHC_6H_{11})_2$)

The carbon analyses in particular showed the composition approaching that of the infinite polymer as the boiling ranges increased.

The most attractive product for investigation obtained from the reaction of Et_2GeCl_2 with $Li_2NC_6H_{11}$ was, of course, the crystalline cyclic tetramer. The compound dissolved easily in benzene, cyclohexane, $CHCl_3$, and CH_2Cl_2, but less well in CCl_4. Analytical results for the tetramer

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were as follows:

Found: C, 52.64% H, 9.01% N, 6.10% Ge, 31.6 %

Calc'd: C, 52.75% H, 9.29% N, 6.15% Ge, 31.86%

Molecular weight evidence was more easily obtained for $(Et_2GeNC_6H_{11})_4$ than for $(Et_2GeNC_6H_5)_4$. The molecular weight as determined by freezing point depression was 870 (theory for $(Et_2GeNC_6H_{11})_4$ = 911.28). Table VI lists several prominent high mass "peaks" in the mass spectrum (direct insertion at 150°C) of that compound. Abundances are scaled relative to the base peak at m/e 427.

Table VI

m/e	relative abundance
855±5	0.1
748	1
721	19
693	2
521	2
492	20
456	69
427	100
413	45
397	82

The molecular ion "peak" was not observed at m/e 912. The position of the highest mass envelope was estimated from extrapolation based on length measurement and is therefore questionable. That highest mass envelope seemingly resulted from loss of two ethyl groups, two ethylene molecules,

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or, more probably, an ethyl group and ethylene from the molecular ion. The well-developed, four-germanium m/e 748 "peak" was seemingly produced by loss of two cyclohexene molecules from the molecular ion. The envelope at m/e ∿855, 748, 721, and 693 derived from four-germanium species; 521 and 492 from three germanium species; and 456 (dimer), 427, 413, and 397 from two-germanium species. At lower mass, strong peaks appeared at m/e 98 ($C_6H_{11}NH^+$) and 83 ($C_6H_{11}^+$). As previously observed for $(Et_2GeNC_6H_5)_4$, peaks at m/e 71, 73, and 75 were more intense than the peaks at the masses of the more abundant germanium isotopes (m/e 70, 72, 74).

Fig. 2.10 shows a Varian HA-100 spectrum of the tetramer at low concentration in CCl_4. Though the complicated spectrum could neither be integrated nor interpreted in detail, in the interval (-0.8δ)-(-1.2δ), one can see the sharp diethylgermanium proton resonances extending above the broad envelope from the cyclohexyl ring protons. The chemical shift of the most intense ethyl resonance in the spectrum, assumed to be the A_6 peak (the central methyl resonance), was -1.15δ, exactly the same as that reported earlier for $(Et_2GeNC_6H_5)_4$. A hint of the broad cyclohexyl α-proton resonance appears between -2.5δ and -3.0δ.

The infrared spectrum of $(Et_2GeNC_6H_{11})_4$ shown in Fig. 1.11 is apparently not completely authentic. The peak at 1620 cm^{-1}, only interpretable as an N-H deformation band, was present without much variation in intensity in spectra of three different samples prepared in a glove bag. Though that peak indicated that hydrolysis had occurred, only a hint of an N-H stretching band appeared near 3350 cm^{-1}. The small band

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at 812 cm^{-1} was perhaps the first trace of the broad, intense ν_{asym}Ge-O-Ge band always found in an extensively hydrolyzed germazane. Fig. 1.11 clearly presents the essentials of the tetrakis(N-cyclohexyl)-octaethyl-cyclotetragermazane infrared spectrum, in spite of that small amount of hydrolysis. The difficulty in obtaining an authentic mull spectrum provided a good estimation of the moisture sensitivity of this compound. Table VII lists the prominent infrared bands of cyclohexylamine, of $(Et_2GeNC_6H_{11})_4$, and of $Et_2Ge(NHC_6H_{11})_2$, discussed below.

As Table VII indicates, interpretation of the $(Et_2GeNC_6H_{11})_4$ spectrum was quite incomplete. Most of the difficulty resulted from the presence of the aliphatic amino group because assignments for aliphatic amines are uncertain. The matter of greatest importance was the assignment of Ge-N-Ge modes, and those assignments unfortunately remained in doubt. One of the two strong bands at 892 cm^{-1} and 846 cm^{-1} perhaps derived from that mode. However, the presence of the same (?) two bands in Fig. 1.10 of $Et_2Ge(NHC_6H_{11})_2$, and probably also in Fig. 1.4 of cyclohexylamine placed such an assignment in question. Because the origin of these bands was unknown, the assumption that similarly placed peaks in the different spectra had the same source was equally questionable. On intensity grounds alone, the peak most likely deriving from Ge-N-Ge asymmetric stretching appeared at 760 cm^{-1}, at very low energy. Quite simply, the ν_{asym}Ge-N-Ge assignment could not be made. One observed the same lowering of Ge-C stretching energies reported earlier for $(Et_2GeNC_6H_5)_4$ and $[(CH_3)_2GeNC_6H_5]_3$.

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Table VII[52]

Cyclohexylamine		$(Et_2GeNC_6H_{11})_4$		$Et_2Ge(NHC_6H_{11})_2$	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
3340(m)	ν_{asym}N-H			3360(w)	ν N-H
3275(m)	ν_{sym}N-H				
3170(w)	2x δ N-H				
2930(vs)	ν_{asym}C-H	See footnote 53		2920(vs)	ν C-H
				2860(m)	ν C-H
2850(vs)	ν_{asym}C-H			2840(s)	ν C-H
2660(w), 2580(w)	overtone or combination	2640(w), 2620(w), 2570(w)	overtone or combination	2650(w), 2580(w)	overtone or combination
1600(m)	δ N-H	(1620)(m)	(δ N-H)	1600(vw)	δ N-H
				1460(sh)	$\delta_{asym}(CH_3)$(Et)
1450(vs)	δ CH_2	See footnote 53		1450(s)	δ CH_2
		1420(m)	$\delta_{asym}(CH_2)$(Et)	1425(m)	$\delta_{asym}(CH_2)$(Et)
				1400(m)	
1380(m), 1370(m), 1350(m), 1313(m)	unassigned	See footnote 53			
		1360(m), 1345(m), 1306(m), 1288(m)	unassigned	1350(m), 1285(m)	unassigned

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Table VII, Contd.

Cyclohexylamine		$(Et_2GeNC_6H_{11})_4$		$Et_2Ge(NHC_6H_{11})_2$	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
1264(m)	ν C-C skeleton[106]	1256(m)	ν C-C skeleton	1255(m)	ν C-C skeleton
1244(w)	unassigned	1233(w)	$\delta_{sym}(CH_2)(Et)$	1230(m)	$\delta_{sym}(CH_2)(Et)$
1208(m)					
1180(w)		1165(sh)	unassigned	1140(m)	unassigned
1152(m)		1145(s)		1130(m)	
				1102(vs)	ν_{asym}N-Ge-N
1105(s)					
1092(s)		1095(m)			
		1075(m)			
1038(m)	ν C-N[105] and C-C skeletal vibrations[106]	1020(sh)	ν C-N, ν C-C skeletal, and ν C-C(Et)	1014(m)	ν C-N, C-C skeletal, and ν C-C(Et)
		1012(s)			
975	C-C skeletal vibrations[106]	985(m)	unassigned	978(m)	C-C skeletal vibrations[106]
		958(m)			
		935(w)	unassigned		
926(m)	unassigned	924(m)			
895(m)		900(m)			
842(s)					

106. L.J. Bellamy, The Infra-red Spectra of Complex Molecules, John Wiley and Sons, New York, 1958, p. 31.

Table VII, Contd.

Cyclohexylamine		$(Et_2GeNC_6H_{11})_4$		$Et_2Ge(NHC_6H_{11})_2$	
cm^{-1}	assignment	cm^{-1}	assignment	cm^{-1}	assignment
		892(s)	ν_{asym}Ge-N-Ge(?)	884(m)	unassigned
830(s)	asym. NH_2 bending[105]	846(s)	ν_{asym}Ge-N-Ge(?)	842(m)	unassigned
		(812)(m)			
778(m)	sym NH_2 bending[105]	785(m)	unassigned	784(w)	unassigned
		760(s)	ν_{asym}Ge-N-Ge(?)		
		698(s)	ρ (CH_2)(Et)	695(m)	ρ (CH_2)(Et)
		652(m)	unassigned	674(m)	unassigned
		628(m)	ν_{sym}Ge-N-Ge(?)		
		568(s)	ν_{asym}Ge-C	583(s)	ν_{asym}Ge-C
555(m)	unassigned	555(s)	unassigned		
		538(s)	ν_{sym}Ge-C	554(s)	ν_{sym}Ge-C
464(m)	unassigned	495(m) 434(m)	unassigned; perhaps ν_{sym}Ge-N-Ge		

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When direct aminolysis of Et_2GeCl_2 by cyclohexylamine was performed with a 4:1 molar ratio of amine to germane, one obtained a 64% yield of $Et_2Ge(NHC_6H_{11})_2$. Equation (5) describes the reaction as it was performed at room temperature with dry n-hexane as solvent.

$$Et_2GeCl_2 + 4C_6H_{11}NH_2 \xrightarrow{\text{hexane}} Et_2Ge(NHC_6H_{11})_2 + 2C_6H_{11}NH_3^+Cl^- \quad (5)$$

With slow addition of cyclohexylamine to a solution of Et_2GeCl_2, one observed only slight warming of the reaction flask contents. Along with the diamino compound one obtained small amounts of liquids with infrared spectra essentially like those for the liquid germazanes from the 1:1 Et_2GeCl_2-$Li_2NC_6H_{11}$ reaction. Purification of these products, in fact only pursued fully for $Et_2Ge(NHC_6H_{11})_2$, was tedious. Cyclohexylamine hydrochloride was only removed fully, as shown by infrared spectra, by repeated cooling and filtration in conjunction with double redistillation under vacuum. In another reaction, one surprisingly isolated $Et_2Ge(NHC_6H_{11})_2$ in 35.2% yield based on germanium, low boiling oligomer in 38.6% yield, and $(Et_2GeNC_6H_{11})_4$ in 8.2% yield when approximately 0.03 mole of cyclohexylamine (3.0 g) was added to a reaction mixture of 0.1 mole Et_2GeCl_2 and 0.1 mole $Li_2NC_6H_{11}$. The latter, seemingly haphazard, procedure actually permitted the easiest isolation of $Et_2Ge(NHC_6H_{11})_2$.

Bis(cyclohexylamino)diethylgermane, with bp 117.5-118°C at 0.25 mm Hg, is a very moisture sensitive liquid. Analytical results obtained for the compound were as follows:

Found:	C, 58.66%	H, 10.52%			
Calc'd:	C, 58.75%	H, 10.48%	N, 8.57%	Ge, 22.20%	

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A molecular weight determination in cyclohexane by freezing point depression yielded a value of 311 (mw of $Et_2Ge(NHC_6H_{11})_2$ = 327.04).

In the mass spectrum of $Et_2Ge(NHC_6H_{11})_2$ (direct insertion at 145°C), one did not observe a molecular ion "peak". An intense one-germanium "peak", appearing at m/e 299, resulted from loss of an ethyl group from the molecular ion (m/e 328) to produce $EtGe^+(NHC_6H_{11})_2$. The base peak of the spectrum occurred either at m/e 229 or 228; two envelopes, resulting from loss of $C_6H_{11}NH_2$ and $C_6H_{11}NH$- from the molecular ion overlapped at those values. In contrast with the results obtained for $(Et_2GeNC_6H_{11})_4$, only a weak "peak" appeared at m/e 246 and indicated loss of cyclohexene. Other weak, one-germanium "peaks" occurred at m/e 285, 271, and 257 and were easily interpreted as resulting from successive losses of CH_2 groups from the m/e 299 ion. A strong "peak" at m/e 200 probably corresponded to the $Et(H)Ge^+NHC_6H_{11}$ ion. "Peaks" at m/e 186 and 172 indicated losses of CH_2 groups from the m/e 200 ion, leading finally to the $H_2Ge^+NHC_6H_{11}$ ion. At low mass, the m/e 98 peak ($C_6H_{11}NH^+$) was intense. Once again, relative strong peaks were observed at m/e 71, 73, and 75, at the masses of germanium hydride ions. Fig. 8 shows the computer simulation of the m/e 299 envelope; that simulation agreed excellently with the experimental envelope.

A Varian HA-100 spectrum of $Et_2Ge(NHC_6H_{11})_2$ in CCl_4 comprises Fig. 2.9. In that spectrum, the ethyl group A_6 peak (central methyl resonance) appeared at -1.04±0.01δ, with a chemical shift less than that for the A_6 peaks (-1.15δ) of $(Et_2GeNC_6H_5)_4$ and $(Et_2GeNC_6H_{11})_4$. A sound theoretical basis for explaining the apparently greater shielding of the methyl protons in

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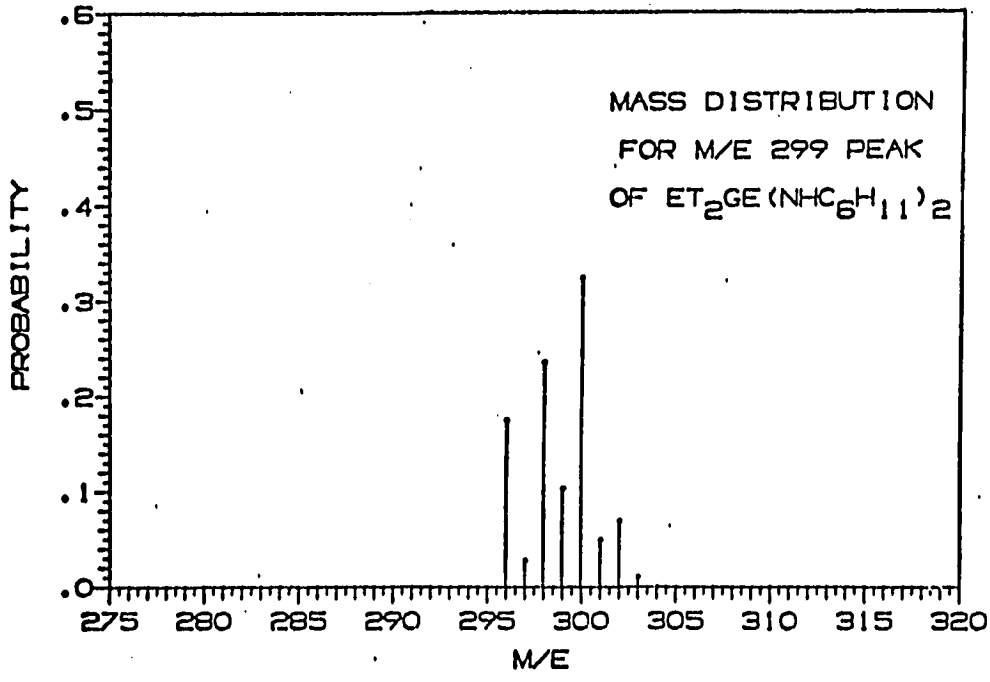

Figure 8

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$Et_2Ge(NHC_6H_{11})_2$ was not available. While somewhat different germanium orbital hybridization presumably existed in the diaminogermane and germazanes, one could not even begin to access the effect of those unknown hybridization changes on electron density in the methyl groups. In Fig. 2.9, the α-proton resonance of the cyclohexyl group was distinct and centered at approximately -2.60δ. One could see fine structure in the α-proton envelope resulting from the coupling of that spin with ring protons on the adjacent carbons and perhaps with the N-H proton. Such splitting has been discussed by Feltkamp and Franklin.[102c]

The most common method for preparing N-substituted cyclotrisilazanes, generally not obtainable by direct aminolysis of organochlorosilanes, is the ammonium sulfate-catalyzed self-condensation of alkylamino and arylamino diorganosilanes.[37] The following equation presents one example of this type of reaction:

$$3(CH_3)_2Si(NHEt)_2 \xrightarrow[150\text{-}200^\circ C]{NH_4SO_4} [(CH_3)_2SiNEt]_3 + 3EtNH_2$$

The reaction mixtures are usually heated until the stoichiometric quantity of amine distils from the system. In this research, a rather different but not fully characterized type of reaction was encountered when ammonium chloride and $Et_2Ge(NHC_6H_{11})_2$ were allowed to react in benzene at room temperature overnight or heated in refluxing benzene for more than 0.5 hour. In a first experiment, at room temperature, reaction of 0.0153 mole of $Et_2Ge(NHC_6H_{11})_2$ with 0.0153 mole of NH_4Cl produced 0.0132 mole of cyclohexylamine hydrochloride in an initial filtration. From vacuum distillation, one obtained fractions with boiling ranges of 80-110°C

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(0.08 mm Hg) and 110-130°C (0.08 mm Hg). Though these fractions contained additional cyclohexylamine hydrochloride which confused analysis, infrared spectra indicated that condensation of the germylamine into low germazane polymers had occurred. A strong, broad, Ge-N-Ge stretching band appeared at 845 cm^{-1}. The ν N-H and δ N-H bands were weak, but readily discernible. The spectrum of the 110-130°C fraction was much like that of the 91-100°C and 120-140°C fractions of liquid N-cyclohexyl-diethylgermazane polymer reported earlier. In a second experiment, 0.00964 mole of $Et_2Ge(NHC_6H_{11})_2$ and 0.00412 mole of previously oven-dried (3 hours at 110°C) NH_4Cl were heated together in refluxing benzene. After about 0.5 hour, one observed a definite increase in the volume of white solid suspended in the benzene. After four hours of heating, the solid filtered from the reaction mixture was largely cyclohexylamine hydrochloride. From infrared spectroscopy, one could not determine whether solid NH_4Cl was still present. The liquid products from the second reaction were quite like those from the first experiment.

In two final experiments, the writer attempted to estimate the role of NH_4Cl in this type of reaction. In a reaction performed overnight at 95°C in n-heptane, 0.0111 mole of $Et_2Ge(NHC_6H_{11})_2$ and 0.0108 mole of NH_4Cl produced 0.085 mole of cyclohexylamine hydrochloride. Use of the n-heptane permitted higher reaction temperature and reduced, but by no means eliminated, the problem with solubility of cyclohexylamine hydrochloride. One assumed that the actual yield of cyclohexylamine hydrochloride was not far from one mole for each reacting mole of $Et_2Ge(NHC_6H_{11})_2$. To the utter disgust of the experimenter, each distillation fraction, on standing, delivered up small amounts of hydrochloride. No really accurate

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weighing of precipitated hydrochloride was obtained from any reaction because of the tendency of this material to disperse itself in minute amounts throughout all distillation fractions. An infrared spectrum of a 80-110°C (0.05 mm Hg) fraction from this third reaction showed a moderately strong, sharp ν N-H band at 3275 cm^{-1}. In other respects, the spectrum was like that from other products. NMR spectra shed light on the nature of the third reaction products. The methyl A_6 resonance appeared regularly at -1.16δ, as for $(Et_2GeNC_6H_5)_4$, $(Et_2GeNC_6H_{11})_4$, and germazane polymers, and not at the $Et_2Ge(NHC_6H_{11})_2$ value of -1.04δ. There was a distinction, however, between low boiling (e.g. 70-90°C at 0.04 mm Hg) and higher boiling (e.g. 110-130°C at 0.04 mm Hg) product fractions. In the former, the ethyl portion of the spectrum was intense, but the broad cyclohexyl envelope was not strong. For the higher boiling fraction, the spectrum was much like that for $(Et_2GeNC_6H_{11})_4$. These results suggested that, excluding hydrolysis, ammonia replaced some cyclohexylamino groups in the condensed products. Absence of Ge-O-Ge and O-Ge-O stretching bands in the infrared spectra indicated that hydrolysis of the low boiling fractions was not significant.

In a final experiment performed at 95°C in n-heptane, reaction of 0.00714 mole of $Et_2Ge(NHC_6H_{11})_2$ and 0.00720 mole of NH_4Cl yielded 0.00384 mole of initially filtered cyclohexylamine hydrochloride. More importantly, dry nitrogen swept gently through the system during reaction carried some ammonia into a trap containing a known amount of hydrochloric acid. Titration of the excess acid indicated that 37.5% of the ammonia originally available from ammonium chloride had been delivered to the trap.

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That ammonia, and not cyclohexylamine, had reacted with the acid was shown by quick addition of concentrated sodium hydroxide to a portion of the trap contents; the odor of ammonia was readily detected upon swirling of the solution. At any rate, it was expected that a reflux condenser interposed between the reaction flask and the acid trap would have held back most free cyclohexylamine, if such were present.

In summary, it is believed that the reaction was more complicated than originally expected. The ammonium chloride caused condensation of the germylamine, but without acting as a true catalyst. Some free ammonia was evolved, and some NH or NH_2 groups were seemingly incorporated into low-boiling liquid oligomers. Cyclohexylamine hydrochloride was formed in amounts approaching one mole for each mole of reacting $Et_2Ge(NHC_6H_{11})_2$. The reactions were never performed at temperatures high enough to permit removal of cyclohexylamine by distillation.

The final series of reactions investigated in this area of research involved the direct aminolysis of $(CH_3)_2GeCl_2$ by cyclohexylamine. Since cyclohexylamine and triethylamine possess similar basicities ($pK_a(H_2O)$ of cyclohexylammonium ion = 10.79; $pK_a(H_2O)$ of triethylammonium ion = 10.74),[91] no triethylamine was used in these reactions. Isolation of cyclohexylamine hydrochloride in 76% yield immediately indicated that formation of cyclic and polymeric germazanes, rather than germylamines, had not occurred completely. The products obtained from the reaction of 0.0814 mole of $(CH_3)GeCl_2$ with 0.244 mole of cyclohexylamine were bis-(cyclohexylamino)dimethylgermane, tris(N-cyclohexyl)-hexamethylcyclotrigermazane, and low boiling oligomeric dimethylgermazanes which contained some chlorine. Only the first two materials received much further

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attention.

Bis(cyclohexylamino)dimethylgermane, with a boiling point of 46±1°C at 0.07 mm Hg, was found to be a very moisture sensitive liquid. Chemical analyses were not performed on this compound because NMR spectra (Fig. 2.11 and 2.12) indicated that the material was not pure. In Fig. 2.11, apparent impurity peaks appeared at -0.46δ, -0.51δ, and -0.92δ. The high field (-0.46δ and -0.51δ) impurity peaks were nearly gone in Fig. 2.12, but the -0.92δ peak remained. For both spectra, integration, exclusive of the -0.46δ and -0.51δ impurity peaks, yielded cyclohexylamino/dimethylgermanium proton ratios of 24/6, exactly in keeping with that ratio for $(CH_3)_2Ge(NHC_6H_{11})_2$. The fascinating possibility existed that the -0.92δ peak derived not from impurity, but from NH proton resonance. Though precise integration confirming that hypothesis could not be performed, it was estimated that the intensity of the dimethylgermanium proton peak at -0.73δ was correct relative to the peak at -0.92δ. That interpretation was reinforced by the fact that the rather sharp cyclohexylamine NH_2 resonance occurs at -0.87δ (see footnote 103 and Fig. 2.7). Such a sharp NH proton resonance would require rapid intramolecular (or, less likely, intermolecular) exchange of the NH protons. Such exchange-narrowing is observed in amines like ethylenediamine or the three isomeric xylylenediamines discussed in the next chapter, but very broad NH resonances, if detected at all, have been observed for most silylamines and silazanes. In the next chapter, such broad NH resonances are reported for the silyl and germyl derivatives of the xylylenediamines. Quite simply, the broadness results from the combined effect of the I = 1 spin

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value for ^{14}N (causing an attached proton to show three equally intense peaks) and the electrical quadrupole moment of the ^{14}N nucleus. If exchange is rapid, the NH proton is decoupled from the nitrogen atom. The cyclohexyl α-proton resonance was centered at approximately -2.75δ, compared with -2.60δ for $Et_2Ge(NHC_6H_{11})_2$ and -2.55δ for cyclohexylamine. The dimethylgermanium proton chemical shift of -0.73δ, as expected, was significantly greater than that reported earlier for $[(CH_3)_2GeNC_6H_5]_3$ (-0.49δ). In $(CH_3)_2Ge(NHC_6H_{11})_2$, more electron density resided at the more basic nitrogen atoms; inductive withdrawal of electrons by the two cyclohexylamino groups deshielded the methyl protons relative to those in $[(CH_3)_2GeNC_6H_5]_3$. Table VIII lists only the most prominent infrared bands of $(CH_3)_2Ge(NHC_6H_{11})_2$ and $[(CH_3)_2GeNC_6H_{11}]_3$. The spectrum of $(CH_3)_2Ge(NHC_6H_{11})_2$ comprises Fig. 1.12.

In making the assignments presented in Table VIII, one used references mentioned earlier in connection with other dimethylgermanium[92] and cyclohexylamine[104,105,106] derivatives. The spectrum of $(CH_3)_2Ge(NHC_6H_{11})_2$ is as much like that of $Et_2Ge(NHC_6H_{11})_2$ as can be expected for the different organogermanium derivative.

The crystalline solid $[(CH_3)_2GeNC_6H_{11}]_3$ was hydrolyzed quickly by atmospheric moisture. Through an oversight, the melting point of this compound was not obtained before preparation of this thesis. Analytical results for the compound were as follows:

Found:	C, 47.96%	H, 8.40%		Ge, 36.3%
Calc'd:	C, 48.08%	H, 8.60%	N, 7.00%	Ge, 36.32%

Fig. 1.13, in two scans, shows a mull spectrum and dilute CCl_4 solution

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Table VIII[52]

$(CH_3)_2Ge(NHC_6H_{11})_2$		$[(CH_3)_2GeNC_6H_{11}]_3$	
cm^{-1}	assignment	cm^{-1}	assignment
3340(m)	ν N-H		
2970(sh)	ν C-H	2960(sh)	ν C-H
2920(vs)	ν_{asym}C-H	2920(s)	ν_{asym}C-H
2840(s)	ν_{asym}C-H	2840(s)	ν_{sym}C-H
			solution values; for mull, see footnote 53.
1600(vw)	δ N-H		
1440(m)	δ CH_2	1440(s)	δ CH_2
			solution value; for mull, see footnote 53.
1400(m)	$\delta_{asym}(CH_3)$	1400(m)	$\delta_{asym}(CH_3)$
		1370(s)	unassigned; solution value; for mull, see footnote 53.
1340(w)	unassigned	1340(m)	solution value
1258(sh)	ν C-C skeleton[106]	1257(sh)	ν C-C skeleton solution value
1245(s)	$\delta_{sym}(CH_3)$	1236(s)	$\delta_{sym}(CH_3)$ solution value
1100(s)	ν_{asym}N-Ge-N	1110(sh) 1090(s) 1075(sh)	unassigned; strong band perhaps ν N-Ge-N
1024(m)	ν C-N[105] and C-C skeletal vibrations[106]	1025(m)	ν C-N[105] and C-C skeletal vibrations[106]
904(m) 887(m)	unassigned	903(s) 888(m)	unassigned, but one perhaps ν_{asym}Ge-N-Ge
845(s) 814(s)	ρ (CH_3)	845(s) 800(s)	ρ (CH_3) and/or ν_{asym}Ge-N-Ge
630(s) 590(s)	ν_{asym}Ge-C ν_{sym}Ge-C	625(s) 593(s) 570(s)	ν_{asym}Ge-C and ν_{sym}Ge-C
		492(m) 450(m)	one band perhaps ν_{sym}Ge-N-Ge

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spectrum of the trimer. Assignments, when they could be made, are listed in Table VIII. In the solution spectrum, the region between 720 cm^{-1} and 810 cm^{-1} was not meaningful; strong CCl_4 absorption in both sample and reference cells yielded a "dead region" in the spectrum. Definite assignment of a band to the ν_{asym}Ge-N-Ge mode was not possible because of the certain proximity of methyl rocking bands.

The NMR spectrum of $[(CH_3)_2GeNC_6H_{11}]_3$ in dilute CCl_4 solution is shown in Fig. 2.13. The methyl proton resonance occurred at -0.44δ, in reasonable accord with the value of -0.49δ found for $[(CH_3)_2GeNC_6H_5]_3$. The dimethylgermanium proton chemical shift for both of these compounds was large compared with that reported[97] (and confirmed by this investigator) for $[(CH_3)_2GeNCH_3]_3$ (-0.32δ). In Fig. 2.13, the peak at -0.60δ seemingly derived from an impurity.

The mass spectrum (direct insertion at 145°C) contained a distinct three-germanium molecular ion "peak" at m/e 599. Mass spectroscopy then provided a satisfactory molecular weight determination. The molecular weight calculated from atomic weights is 599.55, but the integral value expected in the mass spectrum is 599. The computer simulation of the m/e 599 envelope, shown in Fig. 9, agreed exactly with the experimental envelope.

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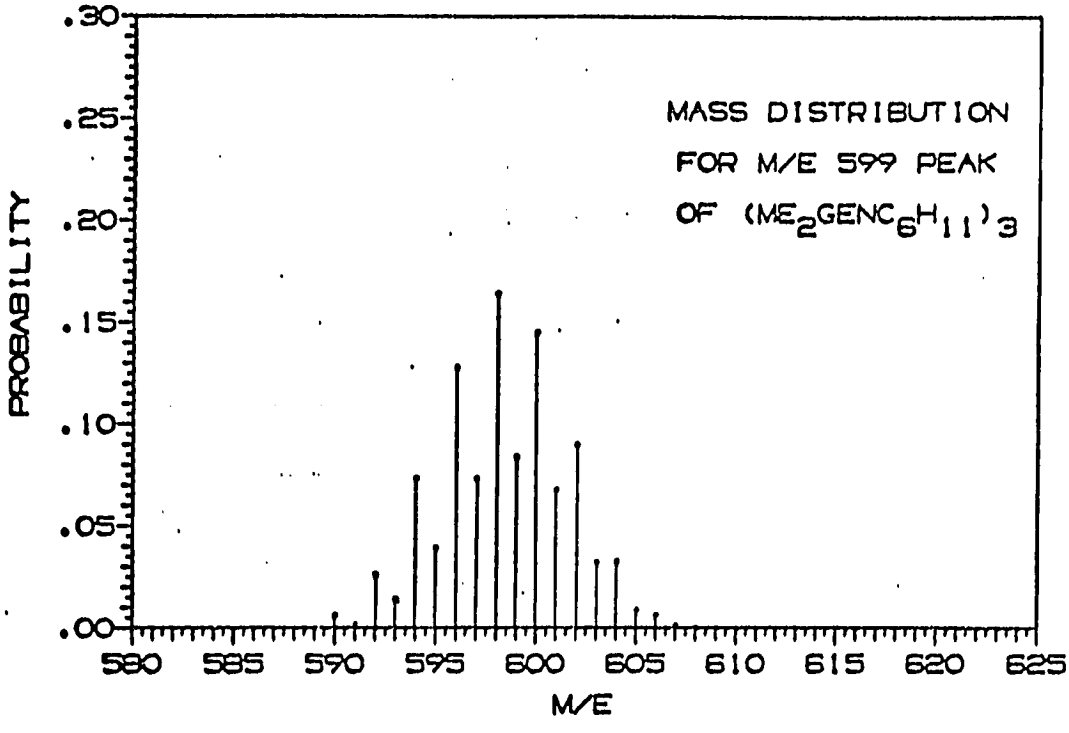

Figure 9

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3. Experimental: Preparations of N-phenyl and N-cyclohexyl diethyl- and dimethylgermazanes; preparation of bis(cyclohexylamino)dimethyl- and diethylgermanes.

A. N-phenylated diethylgermazanes by direct aminolysis.

In an initial procedure, 200 ml of sodium-dried benzene (Fisher) and 20.24 g (0.2000 mole) of triethylamine (Eastman) were transferred to a one liter, three-necked flask equipped with a 50 ml dropping funnel, Teflon paddle stirrer, and reflux condenser. All glassware had been oven-dried for 12 hours at 120°C prior to assembly of the apparatus. The system was swept with argon, dried by passage through a tower containing Drierite, before addition of the benzene and Et_3N and during the entire reaction period. With addition of 20.53 g (0.1018 mole) of Et_2GeCl_2[107] to the flask no formation of a solid Et_3N-Et_2GeCl_2 adduct was observed. After the flask had been cooled thoroughly in ice, 9.4 g (0.102 mole) of aniline (Baker) was dripped into the reaction mixture over 0.5 hour. During four hours of stirring in the ice bath, only limited formation of triethylamine hydrochloride was observed. With stirring at room temperature overnight, considerable solid precipitated. The amine hydrochloride was removed quite completely by filtration in an argon-flushed, oven-dried, inert-atmosphere filtration apparatus. Additional benzene (3 x 50 ml) was then used to wash the filtered solid. The weight of $Et_3NH^+Cl^-$ obtained in this first reaction was not determined. Benzene was removed by distillation at atmospheric pressure until the head temperature dropped. No crystallization occurred from the condensed

107. The Et_2GeCl_2 used in all reactions was prepared by the copper-catalyzed direct reaction of ethyl chloride with germanium metal. That preparation is discussed in Appendix II.

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crude product during standing for two weeks under an argon atmosphere. With vacuum distillation in oven-dried Minilab apparatus, including a 10 cm, unjacketed Vigreux column, the following fractions were obtained:

1. 33-37°C, 0.4 mm Hg; 3.5 g
2. 41-45°C, 0.5 mm Hg; 4.0 g
3. 65-70°C, 0.35 mm Hg; 0.1 g
4. 105-130°C 0.25 mm Hg; 2.3 g
5. 140-165°C, 0.20 mm Hg; 6.6 g
6. 165-175°C, 0.15 mm Hg; 7.2 g

During distillation of fraction (6), solid formed in the condenser; the material was melted with application of heating tapes and conducted into a receiving flask. The solid was recrystallized by dissolving it in dry n-heptane at 80°C in an oil bath and then cooling in ice to force crystallization. A second crop was obtained in a similar manner after removal of some n-heptane. The total yield of the solid was 3.1 g, 14% based on the Et_2GeCl_2 starting material. As indicated in the discussion section, chemical analysis and infrared, NMR, and mass spectra characterized the solid, with mp 152-153°C, as $(Et_2GeNC_6H_5)_4$.

Infrared spectroscopy showed that fractions (1) and (2) above contained both aniline and Et_2GeCl_2. Because of the incompleteness of aminolysis in this reaction, fractions (3), (4), (5), and (6) were not extensively studied. Following dissolution of a portion of fraction (4) in ethanol, addition of 0.1 N $AgNO_3$ indicated that the material contained chlorine; the same test was negative for fraction (5).

As indicated in the discussion section, the solubility of $(Et_2GeNC_6H_5)_4$

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in various weakly acidic organic solvents was determined. The concentrations obtainable (<2%) in solvents like cyclohexane and benzene denied molecular weight determination with the cryoscopic apparatus (equipped with Beckmann thermometer) available to the investigator. With discovery that the solid was easily soluble in pyridine, a molecular weight determination in that solvent was begun with the departmental vapor pressure osmometer (Hewlett-Packard Mechrolab Osmometer Model 104A). Five solutions of the calibrant benzil, varying from 0.00503 molar to 0.1024 molar, were used to prepare a calibration curve. It was found that the waiting periods (2 minutes) usually used with the instrument were insufficient to produce reproducible readings for benzil solutions. Reproducibility was attained with fifteen minute waiting between deposition of the sample drop on the thermistor bead and measurement. The pyridine (Fisher) used for all stages of the determination had been dried for more than a month over molecular sieves and then distilled from fresh molecular sieves. The molecular weight value obtained from measurements on three samples containing from 0.0446 g to 0.0506 g of solid in 5 ml of pyridine was 198±7 (theory for tetramer = 887.3).

A mass spectral study of the solid tetramer, as indicated in the discussion section, was performed with the A.E.I. M.S.-9 instrument, with 70 eV accelerating voltage, and with insertion temperatures listed in the discussion of individual spectra. Most of the mass spectra were run by Mr. Fred Kerst.

The germanium analysis for $(Et_2GeNC_6H_5)_4$, and for certain other compounds reported in this thesis, was performed by titration of the

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mannitol-germanate complex after oxidation of the compound with Na_2O_2 and $KClO_4$ in a Parr bomb. The full analytical procedure is described in the last section of this Experimental.

In a second procedure, 9.45 g (0.1015 mole) of aniline was dripped into a solution of 20.76 g (0.1030 mole) of Et_2GeCl_2 and 20.24 g (0.2000 mole) of Et_3N in 225 ml of sodium-dried benzene. The apparatus used was that used in the first experiment, except that a thermometer, extending into the reaction mixture, was supported in an adapter along with the reflux condenser. Before addition of the aniline, the temperature of the flask contents was 58°C; a slight rise in temperature to 60°C was observed during the 0.5 hour addition of aniline. A large quantity of triethylamine hydrochloride formed during 7 hours of stirring at 68°C. The weight of hydrochloride, measured after filtering in an inert atmosphere apparatus, washing with 3 x 50 ml of benzene, and thorough suctioning of the solid under oil pump vacuum, was 21.25 g (0.1543 mole), 77.3% of the expected amount. Most of the benzene was removed by atmospheric pressure distillation and 50 ml of dry n-heptane was added in an effort to induce crystallization from the condensed crude product. When no such crystallization occurred, vacuum distillation of the yellow-brown crude product in the apparatus previously described, yielded the following fractions:

1.	35-43°C,	1.3 mm Hg;	2.16 g
2.	50-75°C,	1.5 mm Hg;	3.51 g
3.	110-140°C,	1.5 mm Hg;	0.27 g
4.	165-180°C,	1.5 mm Hg;	4.42 g
5.	190-220°C, (solid and yellow oil)	1.5 mm Hg;	6.86 g

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Upon filtration of the solid from fraction (5) and recrystallization from n-heptane, 1.95 g of $(Et_2GeNC_6H_5)_4$ was obtained, an 8.8% yield based on 0.1030 mole of Et_2GeCl_2 starting material. The total weight of yellow oily oligomer obtained from fractions (4) and (5) was 9.35 g, a 42.4% yield based on Et_2GeCl_2. As before, fractions (1) and (2) contained aniline and Et_2GeCl_2. Infrared and NMR spectra of fractions (4) and (5) and of the solid tetramer were recorded and analyzed, as outlined in the discussion section.

In oven-dried argon-flushed apparatus like that previously described, one combined 54.7 g (0.540 mole) of Et_3N and 20.16 g (0.1000 mole) of Et_2GeCl_2. During addition of the Et_2GeCl_2 to the Et_3N, small amounts of white solid formed. It was surmised that a weak adduct of the two materials had formed. No stable adduct of Et_3N and Et_2GeCl_2 has been characterized.[108] With addition of 18.6 g (0.200 mole) of aniline and 36.5 g (0.360 mole) of Et_3N to the Et_2GeCl_2 solution over 45 minutes, one noted a rise in temperature to 40°C. After an additional 0.5 hour, the reaction mixture was stirred at 85-89°C for 15 hours. After filtration of the amine hydrochloride and removal of Et_3N, fractional vacuum distillation yielded the following fractions:

1.	77-81°C,	10 mm Hg;	4.26 g
2.	83-100°C,	10 mm Hg;	4.86 g
3.	80-90°C,	2.8 mm Hg;	0.55 g
4.	174-180°C,	2.8 mm Hg;	1.45 g
5.	185-195°C,	2.5 mm Hg;	7.05 g
6.	200-205°C, (solid and oil)	2.0 mm Hg;	8.00 g

108. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, pp 36-42.

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The first two fractions were almost entirely aniline. From filtration and recrystallization (n-heptane) of the solid in fraction (6), one obtained 3.30 g of $(Et_2GeNC_6H_5)_4$, in 14.8% yield. A 60% yield, 13.30 g, of yellow oily oligomer was obtained from fractions (4), (5) and (6). NMR spectra of fractions (3)-(5) indicated that no bis(phenylamino)diethylgermane was obtained from this 2:1 molar reaction. As before, infrared and NMR spectroscopy were used for product analysis. Finally, in an experiment designed to determine the nature of the aminolysis product before high temperature vacuum distillation, 10.08 g (0.0501 mole) of Et_2GeCl_2 and 4.66 g (0.500 mole) of aniline were allowed to react as before in the presence of 10.12 g (0.1000 mole) of Et_3N and 150 ml of sodium-dried benzene. In the absence of an ice bath, the reaction temperature rose to 38°C. After heating for 2 hours at 60°C, stirring overnight at room temperature, and filtering the precipitated triethylamine hydrochloride, benzene and triethylamine were removed with a rotary evaporator. Then with a dry ice-acetone and liquid nitrogen trap placed between the oil pump and product flask, the flask was evacuated under oil pump vacuum for seven days. For this evacuation the rotary evaporator was not used because it was suspected that the apparatus would have permitted much moist air to be pulled through the system and over the product. The flask was heated occasionally for intervals of several hours at 40-50°C. During that evacuation, no crystallization of solid occurred from the crude. A considerable amount of aniline was collected in the dry ice-acetone trap. Infrared spectra were used to characterize the crude product. With an additional four days of heating and evacuation, infrared spectra indicated

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that hydrolysis had occurred. Prior to hydrolysis, the infrared spectra of the product strongly resembled those obtained for earlier oligomic distillation fractions.

B. N-phenylated diethylgermazanes by reaction with $Li_2NC_6H_{11}$.

In one experiment, n-butyl lithium was first prepared from lithium and n-butyl chloride, and unreacted lithium and lithium chloride were removed by filtration. Addition of aniline to a portion of the pentane-hexane solution of n-butyl Li produced $Li_2NC_6H_5$ with evolution of butane.

The source of lithium was a hexane dispersion of lithium sand (50% by weight; Foote Mineral Co.). In an argon-filled glove bag, 13.8 g of lithium dispersion (assumed to contain about 1.0 mole (6.9 g) of lithium) was weighed out. To the same 500 ml, three-necked flask, equipped with Teflon paddle stirrer and two glass stoppers, there was added 200 ml of dry hexane (Fisher). Outside the glove bag, an oven-dried 250 ml dropping funnel was used to add 46.28 g (0.2000 mole) of n-butyl chloride (Eastman) and 60 ml of hexane. Addition was made over 0.5 hour with thorough cooling of the flask in ice; stirring was continued for three hours.

$$2\ Li + n\text{-}BuCl \xrightarrow[0\text{-}10^\circ C]{\text{hexane}} n\text{-}BuLi + LiCl$$

In an inert atmosphere filtration apparatus, thoroughly flushed with argon and set up so that the pressure in both reaction and receiver flasks could be finally equalized with argon, lithium chloride was slowly (6-7 hours) removed, along with traces of unreacted lithium. In a glove bag,

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a serum cap was attached to one neck of the receiver flask. Following careful hydrolysis of two 2 ml aliquots of the n-butyl lithium solution, titrations with standard acid indicated that the solution was 1.18 molar in n-butyl lithium.

A 100 ml syringe was used to transfer 175 ml of n-butyl lithium solution to a dry, argon-flushed, 500 ml three-necked flask. To that solution of 0.206 mole of n-butyl lithium one added 9.31 g (0.1000 mole) of aniline over a one hour period. The reaction flask became warm even with constant cooling in an ice bath. The butane which was formed was conducted to a hood through tubing connected to the reflux condenser. Stirring continued for one hour after addition of the aniline. In this reaction, large quantities of quite white solid precipitated. When the dropping funnel was removed for a few seconds to dislodge a large chunk of solid, the material in the end of the dropping funnel immediately turned brown. Et_2GeCl_2 (20.16 g; 0.1000 mole), diluted with hexane, was dripped into the $Li_2NC_6H_5$ suspension. Immediate reaction was observed, with formation of yellow-brown oil or solid. Shortly after complete addition of the Et_2GeCl_2 the flask contents turned green (olive drab). That color persisted for ten or fifteen minutes, and then the color changed again to yellow-brown. The solid was allowed to settle overnight while argon slowly passed through the system. Filtration of the heavy mass of lithium chloride, even after such settling, required five hours. The filtered solid was finally washed with 4 x 50 ml of hexane; that filtrate was combined with the original orange-brown filtrate. An accurate weighing of the LiCl was not accomplished; the material stood in air for some time and picked up considerable water

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before weighing was attempted. A broad water band in the infrared spectrum of the halide indicated that significant hydration had occurred. Hexane was distilled from the product and the condensed, rather brown crude liquid was fractionally vacuum distilled to produce the following fractions:

1.	39-55°C,	1.7 mm Hg;	0.25 g
2.	75-80°C,	1.7 mm Hg;	0.75 g
3.	90-96°C,	1.6 mm Hg;	1.40 g
4.	120-130°C,	1.6 mm Hg;	0.10 g
5.	190-215°C,	1.6 mm Hg;	9.37 g
6.	215-230°C,	2.0 mm Hg;	6.64 g (white solid and heavy yellow oil)

From fractions (4), (5), and (6), one isolated 13 g (59% yield) of oily polymer and 2.90 g (14% yield) of recrystallized cyclic tetramer, mp 152-153°C.

A second, essentially identical $Li_2NC_6H_5$ reaction was performed with a commercially available (Alpha Inorganics) 22.1% by weight solution of n-butyl lithium in hexane. The solution was diluted with 250 ml of sodium-dried benzene. In contrast with the previous experiment, the $Li_2NC_6H_5$ appeared as a yellow solid which turned to tan on standing. Et_2GeCl_2 (20.16 g; 0.1000 mole) in additional benzene was dripped into the $Li_2NC_6H_5$ suspension over one hour. When the exothermic reaction had subsided, the flask contents were heated at 75°C for eleven hours. The product was worked up as in the first reaction, and 13.3 g (60% yield) of oily polymer was obtained, but only a few tenths of a gram of solid tetramer.

The products of both organolithium reactions were characterized by

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infrared and NMR spectroscopy and have been considered in the discussion section.

C. N-phenylated diethylgermazanes by transamination.

Diethyldichlorogermane (20.16 g; 0.1000 mole) was placed in a 500 ml, three-necked flask with 150 ml of sodium-dried, low boiling petroleum ether. The flask was equipped with a Teflon stirring paddle, a gas inlet tube extending to within about 2 centimeters of the solution surface, and a reflux condenser. Tygon tubing led from the reflux condenser to a mineral oil bubbler and drying tower and then to a hood. Ammonia gas (Matheson) was passed for four hours directly from a lecture bottle, through a tower filled with potassium hydroxide, and into the Et_2GeCl_2 solution. Following filtration of the precipitated ammonium chloride, ammonia was again passed through the solution for an hour and an additional small amount of NH_4Cl precipitated. There was obtained 10.7 g (100% yield) of NH_4Cl from that reaction. Without isolating the mixed diethylgermazane products, 9.31 g (0.1000 mole) of aniline was introduced. During four hours of stirring at room temperature and an additional four hours of stirring and heating at 60°C (solvent changed to benzene), evolved NH_3 was collected in a trap containing a known amount of HCl. Finally, dry N_2 was bubbled into the flask to sweep any residual NH_3 into the acid trap. Titration of excess HCl indicated 96% recovery of the ammonia (0.1 mole) theoretically obtainable from the diethylgermazane. Refrigeration of the crude product induced no crystallization over several weeks. Fractional vacuum distillation then yielded the following fractions:

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1.	35-40°C,	0.3 mm Hg;	1.7 g
2.	75-90°C,	0.3 mm Hg;	0.2 g
3.	100-130°C,	0.3 mm Hg;	0.6 g
4.	140-175°C,	0.25-0.3 mm Hg;	6.5 g
5.	180-190°C,	0.2-0.3 mm Hg;	4.0 g
6.	195-210°C, (only traces of solid)	0.2 mm Hg;	6.7 g

Fraction (1) was entirely aniline. The 17.8 g (81% yield) of liquid polymer obtained from fractions (3)-(6) was the best yield thus far encountered in this research. No cyclic tetramer was isolated, though the traces of white solid indicated its presence. The various polymer fractions were analyzed by infrared and NMR spectroscopy.

A second transamination reaction differed from the first in that the 0.100 mole of Et_2GeCl_2 was dissolved in 150 ml of benzene and that 25.3 g (0.250 mole) of Et_3N was present. Ammonia was bubbled into the solution during an eight hour period of refluxing at 80°C. One filtered off 10.6 g (99% yield) of ammonium chloride, rather than the expected 27.5 g of $Et_3NH^+Cl^-$. After addition of 18.6 g (0.200 mole) of aniline and essentially quantitative evolution of ammonia, the product was treated as in the first reaction. Vacuum distillation yielded the following fractions:

1.	28-30°C,	0.05 mm Hg;	7.50 g
2.	32-50°C,	0.04 mm Hg;	0.70 g
3.	94-96°C,	0.04 mm Hg;	4.3 g
4.	145-165°C,	0.04 mm Hg;	17.5 g
5.	175-180°C,	0.04 mm Hg;	3.0 g

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Fractions (1) and (2) were quite pure aniline; fraction (3) contained some aniline. The 17.5 g (79% yield) of polymer from fraction (4) and an additional small amount (about 1.5 g) from fraction (5) paralleled the result from the first reaction. About one gram of $(Et_2GeNC_6H_5)_4$ was also isolated. Infrared and NMR spectra were used to characterize the polymers from transamination. C, H, and N analyses, performed by Schwarzkopf Microanalytical Laboratory on some of the higher boiling polymer, indicated that at least that portion of the product contained three-germanium polymer species terminated by aniline.

D. N-phenylated dimethylgermazanes by direct aminolysis.

In a first reaction, 9.31 g (0.1000 mole) of aniline, 150 ml of sodium-dried benzene, and 30.36 g (0.3000 mole; 50% excess) of Et_3N were placed in a 500 ml three-necked flask equipped with reflux condenser and dropping funnel. Tho materials were stirred magnetically and cooled thoroughly in ice. $(CH_3)_2GeCl_2$ (17.36 g; 0.1000 mole) was then dripped into the flask. With stirring overnight, the system was allowed to warm to room temperature. With filtration, one obtained 27.2 g (nearly 100% yield) of $Et_3NH^+Cl^-$. Vacuum distillation yielded the following fractions:

1. 40-50°C, 0.07 mm Hg; 0.34 g
2. 75-100°C, 0.07 mm Hg; 1.00 g
3. 108-120°C, 0.05 mm Hg; 3.22 g
4. 125- °C, 0.05 mm Hg; 11.9 g
   (yellow-white solid melted into receiver)

Fractions (1) and (2) contained mostly aniline. From fractions (3) and

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(4), one obtained the 3.22 g of heavy liquid and 10.3 g (53.2% yield) of recrystallized $[(CH_3)_2GeNC_6H_5]_3$, mp 130-132°C. The products were characterized by infrared, NMR, and mass spectroscopy. The C, H analysis for the solid was performed by Schwarzkopf; the germanium analysis was performed in this laboratory.

In a second reaction, performed exactly as above, aniline (10.32 g; 0.1110 mole) was combined with 9.62 g (0.0554 mole) of $(CH_3)_2GeCl_2$ and 15.18 g (0.1500 mole; 50% excess) of Et_3N. Vacuum distillation of the product yielded the following products:

1. 33-40°C, 0.04 mm 4.95 g (aniline)
2. 120-140°C, 0.035 mm; 1.00 g
3. 140- °C, 0.035 mm; 8.4 g
   (yellow-white solid melted into receiver flask)

With recrystallization of fraction (3), one obtained 7.93 g (74.5% yield) of $[(CH_3)_2GeNC_6H_5]_3$. One isolated no bis(phenylamino)dimethylgermane.

E. N-cyclohexyl diethylgermazanes from $Li_2NC_6H_{11}$.

An oven-dried 50 ml hypodermic syringe was used to transfer 83 ml of a 22.3% by weight hexane solution (Alfa Inorganics) of n-butyllithium to a 500 ml three-necked flask through a serum cap. Additional hexane (100 ml) was added to dilute the organolithium reagent. Cyclohexylamine (9.92 g; 0.1000 mole) was dripped into the thoroughly cooled solution of 0.2 mole of butylLi. During the vigorous reaction which produced white $Li_2NC_6H_{11}$, stirring was performed magnetically for 30 minutes and the flask was swept continuously with argon. Et_2GeCl_2 (20.16 g; 0.1000 mole) was then added along with 25 ml of dry hexane. The latter step was performed

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at room temperature. Though the reaction was vigorous, the temperature never rose above 40°C. With destruction of the organolithium reagent, a Teflon paddle stirrer was substituted for the magnetic stirrer and stirring was continued overnight under an argon atmosphere. Following filtration of lithium chloride from the hexane solution in an inert atmosphere, solvent was removed in an atmospheric pressure distillation. The following fractions were obtained by vacuum distillation:

1. 40-60°C, 0.04 mm Hg; 0.22 g
2. 60-75°C, 0.04 mm Hg; 0.55 g
3. 80-90°C, 0.04 mm Hg; 3.76 g
4. 91-100°C, 0.04 mm Hg; 1.11 g
5. 120-140°C, 0.04 mm Hg; 1.63 g
6. 160-185°C, 0.04 mm Hg; 4.12 g

Along with the highest boiling liquid fraction, when the boiling point was near 170°C (0.04 mm Hg), there was obtained a crystalline solid, mp 93-95°C (2.2 g after recrystallization from n-heptane) which was characterized as $(Et_2GeNC_6H_{11})_4$. Yellow liquid continued to distil after the solid had been conducted into a receiving flask. Brown, rather viscous polymer (8.2 g) remained in the distilling pot at temperatures exceeding 250°C (0.04 mm Hg). Fractions (1) and (2) contained impure cyclohexylamine. The total weight of liquid product, from fractions (3)-(6) and from filtration of $(Et_2GeNC_6H_{11})_4$, was 11.09 g (48.7%). Those liquids were characterized by NMR, infrared, and mass spectroscopy and by C, H elemental analysis. The total yield of products, including the polymeric residue, was 21.02 g (92.3% yield). The characterization of $(Et_2GeNC_6H_{11})_4$ is reported in the

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discussion section.

F. N-cyclohexyl dimethylgermazanes and bis(cyclohexylamino)dimethylgermane by direct aminolysis.

Direct aminolyses of $(CH_3)_2GeCl_2$ by cyclohexylamine, performed without Et_3N, yielded $(CH_3)_2Ge(NHC_6H_{11})_2$, $[(CH_3)_2GeNC_6H_{11}]_3$, and low boiling oligomeric dimethylgermazanes which contained chlorine. Typically, $(CH_3)_2GeCl_2$ (14.13 g; 0.0814 mole) was added to an ice-cooled mixture of 24.40 g (0.2442 mole) of cyclohexylamine and 150 ml of dry heptane. Following stirring at room temperature overnight, filtration in an inert atmosphere yielded 16.7 g (76% of the 22.0 g expected from complete aminolysis) of cyclohexylamine hydrochloride. Fractional vacuum distillation yielded the following fractions:

1. 45-48°C, 0.07 mm Hg; 0.8 g
2. 55-70°C, 0.05 mm Hg; 1.4 g
3. 115-140°C, 0.59 mm Hg; 1.28 g
4. 140-150°C, 0.50 mm Hg; 3.4 g
5. 160-185°C, 0.48 mm Hg; 4.2 g
6. 190-210°C, 0.45 mm Hg; 0.86 g
   (solid in condenser, melted into receiver)

Fraction (1) was found by NMR and infrared spectroscopy to be nearly pure bis(cyclohexylamino)dimethylgermane; fraction (2) contained some of the same. Fractions (3)-(5) were not significantly investigated because a $AgNO_3$ test performed in the 95% ethanol solution of the liquids indicated that the polymers contained chlorine. The crystalline solid from fraction (6) was shown to be $[(CH_3)_2GeNC_6H_{11}]_3$ by chemical analysis and infrared,

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NMR, and mass spectroscopy.

G. Bis(cyclohexylamino)diethylgermane by direct aminolysis.

When 20.16 g (0.1000 mole) of Et_2GeCl_2 was added to a solution of 39.67 g (0.4000 mole) of cyclohexylamine in 150 ml of n-heptane, rapid precipitation of cyclohexylamine hydrochloride and a slight warming of the flask were observed. The weight of hydrochloride, determined after thorough suctioning of the solid, was 26.4 g (97% of expected 27.13 g). With vacuum distillation, it became clear that the small additional amount of hydrochloride was dissolved in the products. The following fractions were noticeably contaminated with hydrochloride:

1.	65-73°C,	0.18 mm Hg;	1.03 g
2.	85-110°C,	0.24 mm Hg;	1.55 g
3.	110-118°C,	0.25-0.27 mm Hg;	9.39 g
4.	117.5-118°C,	0.25 mm Hg;	11.51 g
5.	118-130°C,	0.24 mm Hg;	3.02 g
6.	130-150°C,	0.24 mm Hg;	2.56 g

From infrared, NMR, and mass spectroscopy, fraction (4) was shown to be quite pure $Et_2Ge(NHC_6H_{11})_2$ after hydrochloride had been removed by repeated filtration and double distillation. Fraction (3) was mostly the diamino compound. The total yield of $Et_2Ge(NHC_6H_{11})_2$ was about 64%, based on the Et_2GeCl_2. Carbon and hydrogen analyses on the compound were performed by Schwarzkopf. The molecular weight was determined by freezing point depression in cyclohexane. The apparatus used employed a Beckmann thermometer in an insulated glass well. Agitation during

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freezing was provided by a magnetically operated glass plunger in the same well. The moisture-sensitive liquid (0.2760 g in one sample) was drawn quickly into a thin glass bulb that had been warmed in a burner flame and the bulb was then sealed. The bulb itself was blown from a disposable capillary pipet. The sample bulb was placed in the insulated well with 25.00 ml of cyclohexane and then crushed with the magnetic plunger. The solution was agitated for 15 minutes to assure homogeneity before lowering the temperature. The weight of cyclohexane was calculated from a separate measurement of the density of cyclohexane at the prevailing room temperature. Then, quite straight-forwardly, the molecular weight was calculated from the known molality, freezing point depression, and cryoscopic constant of cyclohexane. From two samples, identical values of 311 were obtained (mw of $Et_2Ge(NHC_6H_{11})_2$ = 327.04.). The error inherent in this method was probably about 5%.

Analytical technique for determination of Ge in organogermanium-nitrogen compounds.

At the beginning of this research, the investigator experienced some difficulty in getting good commerical analyses for germanium. Seeking a reliable method for analysis on the premises, a sodium peroxide semimicro bomb[109] was purchased from the Parr Instrument Company, Moline, Illinois. The bomb was equipped with rubber gaskets which probably served about as well as the available lead gaskets. The technique then used for

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109. R.M. Lincoln, A.S. Carney, and E.C. Wagner, Ind. Eng. Chem., Anal. Ed., 13, 358(1941).

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the analysis, with variations cited here, was that described by Rijkens and Van der Kerk.[110] The method was first tested by analysis of pure Et_2GeCl_2; the liquid was introduced into the bomb in a frail glass vial which was broken by concussion with the bomb lid as the bomb was closed. After considerable practice, a value of 36.2% Ge (theory, 36.0%) was obtained. Solid samples, most commonly analyzed, were treated more easily by weighing directly into the bomb cup. Fisher $KClO_4$ (0.2 g) and 0.15 g of sucrose (Fisher) were transferred to the bomb cup. The sample, containing 0.5-1.0 mmole of germanium, was weighed into the cup. Then 4.0 ± 0.1 g of Na_2O_2 (Merck) was quickly placed on top of the charge and the bomb was tightly closed with the wrench provided. The firing stage was crucial in the analysis, particularly for the stable N-phenylated germazanes. The bomb was suspended on a silica triangle behind an iron plate and heated directly with a gas-O_2 torch. Prolonged heating was required, but most satisfactory results were obtained (with a minimum of charring of the gasket) when the bomb was heated for three-minute periods at intervals of several hours. After final cooling, the bomb was opened and placed in a 150 ml stainless steel beaker. Five milliliters of water were placed in the cup and the beaker was covered with a watchglass. The excess of peroxide was decomposed and the fused material dissolved by gentle heating on a hot plate for about an hour. Heating was not allowed to force visible gas evolution. The sample was then washed quantitatively into a 200 ml glass beaker with about 120 ml of water. The beaker was

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110. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, Utrecht, 1964, p. 117.

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covered with a watchglass with a central hole. With magnetic stirring of the sample solution, concentrated sulfuric acid was added slowly through that central hole until the slightly yellow color of bromcresol purple indicator (pH about 5) was observed. Residual carbon dioxide was removed by boiling for a few minutes.

After cooling, the equivalence point for excess acid was determined graphically from a potentiometric titration (Leeds and Northrup pH Meter) with standard 0.1 N sodium hydroxide from approximately pH 5 to 7.5 (no higher!). Then about 10 g (0.6-0.7 g/10 ml) of mannitol (Eastman) was added, resulting in a drop of the pH to about 4 from formation of the mannitol-germanate complex. Another potentiometric titration determined the equivalence point for that weak acid. The amount of sodium hydroxide consumed between both equivalence points is a measure of the germanium present; i.e. the germanate complex is titrated as a monoprotic acid. All germanium analyses reported in this research were obtained by this method.

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Chapter II

Discussion

1. The Three Xylylenediamine Isomers

The ortho, meta, and para isomers of xylylenediamine, $NH_2CH_2(C_6H_4)CH_2NH_2$, have received very limited attention in chemical research. No Group IV derivatives of these amines have been reported. While o-xylylenediamine, in particular, is potentially an interesting bridging and bidentate chelating ligand for transition metals, a single paper describes copper, nickel, and zinc complexes with that ligand.[111] Most published research with these amines, and that heavily concentrated in Soviet journals, has involved the preparation of polyamides by reaction with dicarboxylic acids such as adipic, phthalic, and sebacic acids. For example, the one-to-one molar reaction of m-xylylenediamine and terephthalic acid in boiling water produced a transparent, amorphous polymer which was insoluble in organic solvents.[112] Most research has involved the meta isomer.

There are reasons for the dearth of research involving these amines. One American company, Aldrich, has recently advertised the availability of tonnage quantities of m-xylylenediamine, but no American company makes the ortho and para isomers. The Japanese chemical firm Showa Denko, K.K. (Tokyo), which provided the investigator with a kilogram of mixed m- and

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111. R.C. Brasted, T.D. O'Brien, and W.L. Heino, Inorg. Chem., 3, 503 (1964).

112. B.A. Zhubanov, S.R. Rafikov, K.Z. Gumargalieva, and L.V. Pavlitenko, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., 2, 88(1962); Chem. Abstr., 58, 14098b(1963).

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p-xylylenediamine, markets that mixture for the preparation of polyamides and polyurethanes. The meta and para isomers are prepared commercially by hydrogenation of nitriles over supported metal catalysts. In a typical laboratory preparation, terephthalonitrile was reduced in a rotary autoclave over nickel and cobalt alloy catalysts. A methanol solution of the nitrile was saturated with ammonia and heated at 100°C with 90 atmospheres of hydrogen.[113] Ammonia is mentioned in almost all reports of reduction of nitriles. The ammonia prevents or minimizes the formation of secondary or tertiary amines [114] by removing an imine intermediate from the reaction mixture:

$$RCN \xrightarrow{H_2} RCH{=}NH \overset{NH_3}{\rightleftharpoons} \underset{\displaystyle NH_2}{\overset{\displaystyle |}{RCHNH_2}} \xrightarrow{H_2} RCH_2NH_2 + NH_3$$

Catalytic reduction of the ortho nitrile, however, yields 91-98% o-xylyleneimine, $o\text{-}C_6H_4(CH_2)_2NH$, even with ammonia present.[115] The difficulty in preparing o-xylylenediamine by reduction partly explains the limited study of this amine. In addition it became apparent during this research that o-xylylenediamine is not very stable. Amine which was vacuum distilled twice at 85°C (0.25 mm Hg) and stored under argon turned brown and evolved ammonia upon standing in darkness for several weeks. The decomposition clearly occurred more rapidly with exposure to

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113. N.I. Shcheglov, D.V. Sokol'skii, A.A. Andreeva, V.P. Ruidire, and P.N. El'chishchev, Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR, 14, 167(1966); Chem. Abstr., 67, 53975c(1967).

114. P.N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967, p. 208.

115. L.K. Freidlin and T.A. Sladkova, Izvest. Akad. Nauk SSR, Otdel. Khim. Nauk, 1859(1959); Chem. Abstr., 50, 12021f(1956).

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light. In contrast, the meta and para isomers were not yellowed by exposure to light for several weeks. The meta and para isomers decompose at 250-270°C to yield ammonia and secondary (meta) and tertiary (para) amines.[116]

In necessary connection with studies of organosilicon and organogermanium derivatives of the three xylylenediamines in this research, the writer attempted to prepare p- and o-xylylenediamine, particularly the latter, by several methods. The immediately following sections report those efforts and also discuss some of the physical, chemical, and spectroscopic properties of the xylylenediamines. The infrared and NMR spectra of the xylylenediamines have not been discussed in published papers.

Several attempted catalytic reductions with hydrogen at atmospheric pressure were fruitless. The procedures recommended by Rylander[117] for reduction of nitriles failed with phthalonitrile. In one experiment, performed at 60°C for 23 hours, hydrogen was diffused into a solution of 5.09 g (0.0398 mole) of phthalonitrile, 4.6 ml of concentrated H_2SO_4 (about 0.08 mole), and 30 ml of water in 200 ml of ethanol. The catalyst was one gram of 10% by weight palladium on carbon. Following removal of the catalyst and adjustment of the pH to 10, a vacuum distillation was conducted until solid phthalonitrile separated from solution. Five grams

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116. S.R. Rafikov, V.P. Derevyanchenko, V.A. Zhubanov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., 15, 30(1965); Chem. Abstr., 63, 8233b(1965).

117. P.N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967, pp. 203-226.

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of unreacted phthalonitrile was recovered, and no high boiling amine was obtained.

Roughly following a method patented by Quin[118] for hydrogenation of 1,4-dicyanobenzene, the writer attempted the catalytic hydrogenation of phthalonitrile in ammonia-saturated toluene and ethanol. Phthalonitrile (2 g) was partially dissolved in 100 ml of a 1:1 solution of toluene and ethanol. The solution-suspension was added to a mixture of 1 g of 10% palladium on carbon and 150 ml of toluene which had been flushed with ammonia and hydrogen for several hours. During heating and stirring at 70°C, hydrogen was passed into the solution for 22 hours. Once again, vacuum distillation of the product yielded only phthalonitrile.

The writer also attempted a lithium aluminum hydride reduction of phthalonitrile in tetrahydrofuran. A solution of phthalonitrile (0.040 mole) in THF was dripped slowly into an ice-cooled solution of $LiAlH_4$ (0.54 mole; 13 times the amount theoretically required) in 150 ml of THF. Immediate reaction occurred with formation of a reddish-purple product. After several hours, excess hydride was consumed by addition of ethyl acetate. Following final destruction of the aluminum hydride adducts with water and filtration of the mixed hydroxides, an attempted vacuum distillation at 0.4 mm Hg yielded no high boiling distillable liquid. Although the product remained uncharacterized, it is surmised that this reduction produced o-xylyleneimine or a similar heterocyclic species.

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118. D.C. Quin, British Patent 814,631, June 10, 1959; Chem. Abstr., 54, 9851e(1960).

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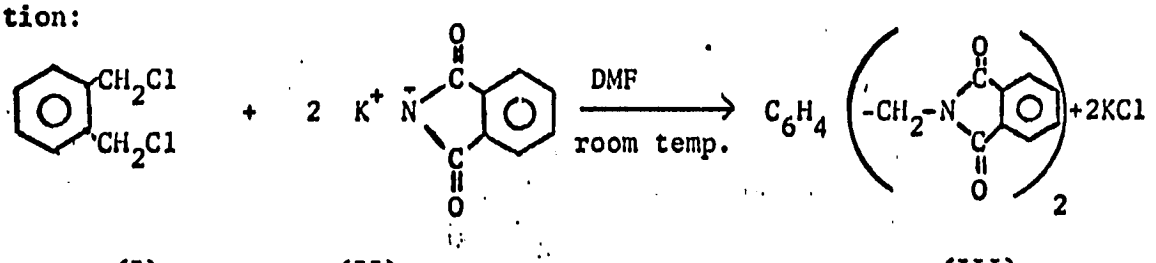
The one successful preparation of both o- and p-xylylenediamine involved the long-known Gabriel phthalimide synthesis of primary amines.[119] Strassman[119b] and Gabriel and Pinkus[119c] in fact prepared o-xylylenediamine by the original, forceful version of the phthalimide synthesis, but described the amine only as a liquid smelling strongly of ammonia. They isolated derivatives (dihydrochloride, dipicrate, diphthalimide, and diacetyl and dibenzoyl derivatives) of the amine, but never even determined the boiling point of the amine itself. Lustig[120] obtained the dihydrochloride of p-xylylenediamine from the Gabriel synthesis. The procedure used in this research, described in the Experimental Section, was a combination of the methods described by Ing and Manske[119d] and by Sheehan and Bolhofer.[119e] The following equations,[121] applying as well to the para isomer, outline the preparation:



(I) (II) (III)

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119. a) S. Gabriel, Chem. Ber., 20, 2224(1887).
b) H. Strassmann, Chem. Ber., 21, 576(1888).
c) S. Gabriel and G. Pinkus, Chem. Ber., 26, 2210(1893).
d) H.R. Ing and R.H.F. Manske, J. Chem. Soc., 2348(1926).
e) J.C. Sheehan and W.A. Bolhofer, J.A.C.S., 72, 2786(1950).
f) H. Ing and H. Manske, J. Chem. Soc., 203(1952).

120. F. Lustig, Chem. Ber., 28, 2992(1895).

121. H.L. Barber and W.R. Wragg, J. Chem. Soc., 1331(1947).

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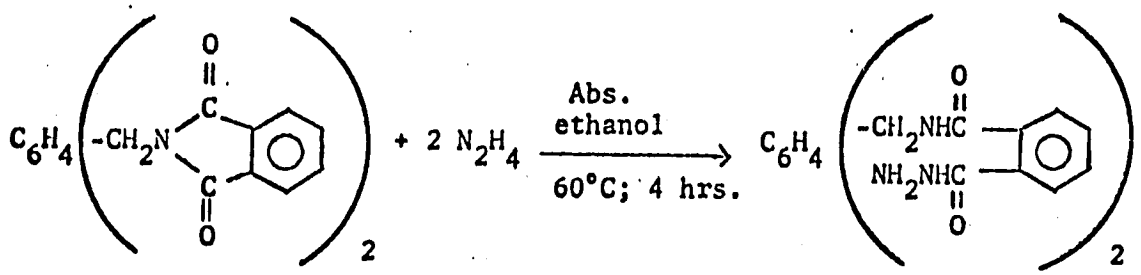
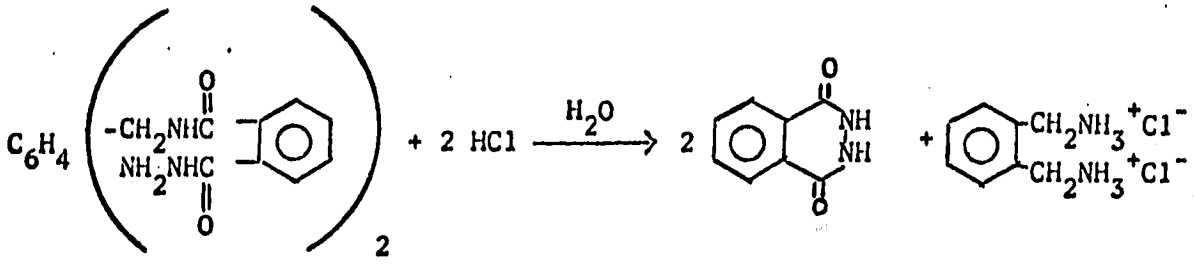
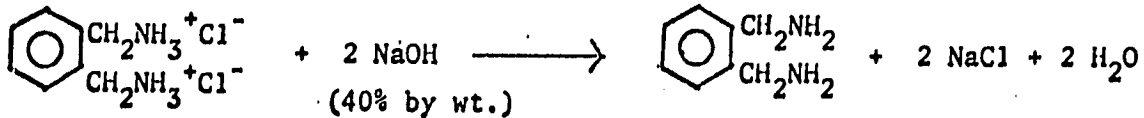


(III) (IV)



(IV) (V) (VI)



(VI) (VII)

Overall yields of xylylenediamine obtained from the α,α'-dichloroxylene (I) in this sequence of reactions were in the range 65-75%. An advantage of this synthetic route was the formation of two moles of 2,3-dihydrophthalazine-1,4-dione (V) for each mole of α,α'-dichloroxylene used. In Chapter III of this thesis, organosilicon and organogermanium derivatives of 2,3-dihydrophthalazine-1,4-dione are discussed.

The boiling points of the three xylylenediamines are closer together than reported previously. The boiling range found for m-xylylenediamine

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(140-143°C at 13 mm Hg; 84-85°C at 0.2 mm Hg) agreed approximately with that reported (140°C, 14 mm Hg).[122] The boiling range for o-xylylenediamine, previously unreported, is 85-87°C (0.2 mm Hg). While the reported[123] melting point (37°C) for p-xylylenediamine is correct, the boiling point[123,124] (230°C at 10 mm Hg) must be wrong; the writer found a boiling point of 84.5-85°C (0.24 mm Hg). Because of uncertainty in the pressure during vacuum distillation, the boiling points of the three isomers must be considered essentially identical. At 10 mm Hg pressure, the boiling point of p-xylylenediamine must be in the range 130-140°C, rather than near 230°C. Testimony for the similarity of the boiling points of m- and p-xylylenediamine also came from attempts to separate the two isomers (about 30% para) in the Showa Denko, K.K. product "Sho-Amine-X". The 76 cm distillation column packed with stainless steel helices (see Appendix II for description) was used in an extremely slow, five-day distillation of "Sho-Amine-X". Fig. 1.17 shows how unsuccessful that distillation was. The three isomers may be distinguished from the pattern of their infrared overtone and combination bands, characteristic of different benzene ring substitution, which appear in the interval

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122. Beilsteins Handbuch der Organischen Chemie, Ersten Ergänsungswerk, Band XIII, Verlag v. Julius Springer, Berlin, 1930, p. 186.

123. I.P. Losev, O. Ya. Fedotova, and M.L. Kerber, J. Gen. Chem. USSR, 26, 585(1956).

124. I. Heilbron, A.H. Cook, H.M. Burbary, and D.H. Hey, Eds., Dictionary of Organic Compounds, vol. 2, Oxford Univ. Press, New York, 1965, p. 882.

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1750-1950 cm^{-1}. In Fig. 1.17, scan A shows the infrared spectrum of the undistilled Japanese product. Since the infrared spectra of the xylylenediamines are discussed later in this chapter, the writer simply indicates here that the sharp band at 1900 cm^{-1} derives from p-xylylenediamine, and the 1880 cm^{-1} and 1940 cm^{-1} bands derive from m-xylenediamine. Scan B, of a fraction taken near the end of the distillation, indicates that the writer had attained slight enrichment in p-xylylenediamine in that fraction. The slight changes in composition which occurred during distillation denied the existence of an azeotrope, but indicated great similarity in the boiling points for the two isomers.

Nearly quantitative isolation of pure p-xylylenediamine from the m-xylylenediamine in "Sho-Amine-X" was accomplished through direct application of the method patented by Ferstandig.[125] Following conversion of both amines to their dihydrochlorides with excess concentrated (37% by weight) HCl, 97% of the p-xylylenediamine dihydrochloride was filtered from the acidic mixture while all the m-xylylenediamine dihydrochloride (and a little p-xylylenediamine dihydrochloride) remained dissolved. Standard procedures were then used to isolate p-xylylenediamine from the hydrochloride. Following vacuum distillation, the distillate crystallized quickly and completely (mp 37°C). In contrast, the product from the Gabriel synthesis was about 90% solid and clearly somewhat impure. The latter product yellowed somewhat on standing, suggesting the presence of o-xylylenediamine. NMR spectra also showed that o-xylylenediamine was present as an impurity from the starting material α,α'-dichloroxylene.

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125. L.L. Ferstandig, California Research Corp., U.S. Patent 2,884,457, April 28, 1958.

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All three xylylenediamines are strong organic bases, at least as strong or stronger than ethylenediamine. The thermodynamic acidity constants[111] pK_1° (7.35±0.04) and pK_2° (9.87±0.05) for o-xylylenediamine dihydrochloride indicate that this amine is slightly stronger than ethylenediamine (pK_1°=6.80±0.06; pK_2°=9.80±0.06) in water. As previously reported for p-xylylenediamine,[123] all three isomers react readily with CO_2 on contact with the atmosphere and form water-insoluble white carbonates. The amines must therefore be stored in a tightly closed flask, preferably under an inert atmosphere.

Figures 2.14, 2.15, and 2.16 show the simple NMR spectra of o-, p-, and m-xylylenediamine, respectively. Because the chemical shifts of the NH_2 and CH_2 resonances are rather dependent upon concentration and solvent, comparison of the spectra of the three isomers was only possible by study of dilute solutions of identical concentration. Table IX lists the chemical shifts and integration found with CCl_4 solutions of the indicated concentration.

Table IX

	Chem. Shift (Integration in parentheses)		
	NH_2	CH_2	C_6H_4
o-xylylenediamine (3.5% by wt)	-1.33 δ(1.0)	-3.80 δ(1.0)	-7.15 δ(1.0)
p-xylylenediamine (3.6% by wt)	-1.12 δ(1.0)	-3.74 δ(1.0)	-7.15 δ(1.0)
m-xylylenediamine (3.6% by wt)	-1.14 δ(1.0)	-3.73 δ(1.0)	-7.03δ, -7.13δ (1.0) (complex)

The sharpness of the NH_2 resonances, particularly for o-xylylenediamine, resulted from the assumed intramolecular (and to a much smaller extent,

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intermolecular) exchange of CH_2 protons with NH_2 protons and of NH_2 protons with NH_2 protons. Such exchange narrowing of an NH_2 resonance has been discussed in Chapter I in connection with consideration of $(CH_3)_2Ge(NHC_6H_{11})_2$. For the xylylenediamines, as with ethylenediamine, coupling with the CH_2 protons was removed so that both the CH_2 and NH_2 resonances appeared as singlets at room temperature. The NH_2 resonance for p-xylylenediamine was noticeably broader than for the other two isomers. Intramolecular exchange of protons between different NH_2 groups was excluded for the para isomer and led to a broadened signal. In addition, as the ease of exchange increased in the series para<meta<ortho, the NH_2 protons apparently became less well shielded and the chemical shift increased.

In the phenyl region of the NMR spectra, fine structure clearly appeared only for m-xylylenediamine. Only a slight broadening of the o-xylylenediamine resonance reflected the presence of nonequivalent phenyl protons.

The complicated infrared spectra of the three xylylenediamines could only be superficially interpreted. As shown in Figure 1.14, 1.15, and 1.16, the overlapping of broad bands between 700 cm^{-1} and 1000 cm^{-1} made definite assignment impossible. In all three figures, scan B was recorded with CCl_4 solutions of sufficient concentration (about 10%) so that the overtone and combination bands between 1750 cm^{-1} and 1950 cm^{-1} were well defined. Table X lists some prominent infrared bands with assignments made by comparison with Colthup, Daly, and Wiberley's analysis[126] of the spectra of substituted benzenes. The only consequential

126. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, pp 220-230, 195-198.

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Table X[52]

m-xylylenediamine		o-xylylenediamine		p-xylylenediamine	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
3360(s)	ν_{asym}N-H	3355(s)	ν_{asym}N-H	3350(s)	ν_{asym}N-H
3280(s)	ν_{sym}N-H	3270(s)	ν_{sym}N-H	3280(s)	ν_{sym}N-H
3180(sh)	2xδN-H	3175(sh)	2xδN-H	3175(sh)	2xδN-H
3040(m), 3010(m)	νC-H aromatic	3055(m), 3010(m)	νC-H aromatic	3040(m), 3005(m)	νC-H aromatic
2905(s)	$\nu_{asym}CH_2$	2905(s)	$\nu_{asym}CH_2$	2900(s)	$\nu_{asym}CH_2$
2845(s)	$\nu_{sym}CH_2$	2855(s)	$\nu_{sym}CH_2$	2850(s)	$\nu_{sym}CH_2$
1945(w), 1880(w), 1805(vw)	overtone and combination bands (solution)	1950(w), 1920(w), 1880(vw), 1840(vw), 1810(w)	overtone and combination bands (solution)	1925(vw), 1900(w), 1870(vw), 1785(w), 1740(vw)	overtone and combination bands (solution)
1600(s), 1590(sh)	δN-H and benzene ring stretching	1595(s)	δN-H and benzene ring stretching	1595(s)	δN-H and benzene ring stretching
1505(w), 1480(m)	benzene ring modes	1480(m)	benzene ring mode	1505(m), 1475(w), 1415(m)	benzene ring modes
1410(m)	unassigned				
1440(m)	δCH_2	1445(s)	δCH_2 and benzene ring mode	1445(m)	δCH_2
1375(m), 1340(w)	unassigned	1375(m), 1340(vw)	unassigned	1380(m), 1340(w)	unassigned

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Table X Contd.

m-xylylenediamine		o-xylylenediamine		p-xylylenediamine	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
1270(vw)	In-plane hydrogen bending on benzene ring	1270(w)	In-plane hydrogen bending on benzene ring	1262(m)	In-plane hydrogen bending on benzene ring
1157(m)		1160(w)		1150(w)	
		1215(w)	unassigned	1215(w)	unassigned
		1185(w)			
1060(m)	νC-N(?) and in-plane hydrogen bending on benzene ring	1040(m)	νC-N(?) (in complex region)	∿1055(m)	νC-N(?) (part of broad absorption)
				1018(m)	In-plane hydrogen bending on benzene ring
980(m)	unassigned	975(m)	unassigned		
885(sh)	very broad overlapping bands; NH_2 bending modes and out-of-plane hydrogen bonding on benzene ring	∿860(s)	very broad overlapping extending from 800-900 cm^{-1}; NH_2 bending	885(s)	very broad overlapping extending from 800-900 cm^{-1}; NH_2 bending and out-of-plane hydrogen bending on benzene ring
845(s)		825(sh)		815(sh)	
		810(sh)		800(vs)	
788(s)					
		758(vs)	out-of-plane hydrogen bending on benzene ring		
725(m)	unassigned	725(sh)	unassigned	725(m)	unassigned
700(s)	benzene ring mode			700(w)	unassigned
		604(m)	unassigned		
575(w)	broad; unassigned	580(w)		595(w)	broad; unassigned
				555(w)	

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distinction among the three spectra of course resulted from different substitution of the benzene ring.

Assignment of an infrared band to the C-N stretching mode, in approximate agreement with Stewart's report[105] of 1079 ± 11 cm^{-1} for primary amines, was only unambiguous for m-xylylenediamine (1060 cm^{-1}). For the ortho and para isomers, several bands occurred near 1060 cm^{-1} and denied assignment of the νC-N mode.

In regions where one expected either bands from benzene ring stretching or from carbon-hydrogen (aromatic and aliphatic) stretching, bending, and deformation, the writer found nearly perfect correlation with Colthup, Daly, and Wiberley's assignments.[126] While unambiguous assignments could not always be made, the writer always found bands in the positions expected of the three isomeric disubstituted benzenes. The three strongest bands which reflected the different benzene ring substitution resulted from in-phase, out-of-plane hydrogen bending on the benzene ring. The three adjacent ring hydrogens in the meta isomer produced a strong band at 788 cm^{-1}; the four adjacent hydrogens in o-xylylenediamine, a very strong band at 758 cm^{-1}; the two adjacent hydrogens in p-xylylenediamine, a very strong band at 800 cm^{-1}.

Between 1750 cm^{-1} and 1950 cm^{-1}, the patterns of overtone and combination bands found for the three isomers looked almost exactly like the patterns drawn by Colthup, Daly, and Wiberley,[126] but were without exception shifted 20-50 cm^{-1} to higher energy. These finger-printing patterns provided the principal means of assessing the content of isomeric mixtures, particularly of the meta and para isomers.

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Though NMR spectroscopy provided evidence for differences in intramolecular exchange of amino protons in the three isomers, the N-H infrared bands with their practically identical positions, did not reveal significant differences in hydrogen bonding and did not uniquely characterize the isomers. In contrast, striking shifts of the N-H stretching bands were observed for the three isomeric dihydrochlorides, in Kadol mull spectra:

Table XI

	o-xylylene-diamine·2HCl	m-xylylene-diamine·2HCl	p-xylylene-diamine·2HCl
ν_{asym}N-H	3475 cm^{-1} (s)	3340 cm^{-1} (s)	∿3175 cm^{-1} shoulder on C-H bands
ν_{sym}N-H	3440 cm^{-1} (s)	3305 cm^{-1} (m)	

In amine hydrohalides, the principal hydrogen bonding involves the halide anion ($I^- < Br^- < Cl^-$); stronger hydrogen bonding lowers the N-H stretching frequencies as with other hydrogen bonded compounds.[127] The results obtained for the xylylenediamine dihydrochlorides then indicated that the strongest hydrogen bonding occurred with the para isomer. For o-xylylenediamine dihydrochloride, both N-H stretching bands occurred at higher energy than that usually observed (∿3200 cm^{-1}) for the ν_{asym}N-H band of primary amine hydrohalides.[127] Though intramolecular hydrogen bonding between two ortho amino groups did not greatly affect the frequency of N-H stretching, interaction of the ortho (ammonium) groups did seemingly weaken hydrogen bonding with the chloride anions. It is surmised that the strikingly facile separation of the para and meta hydrochlorides on

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127. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, p 282.

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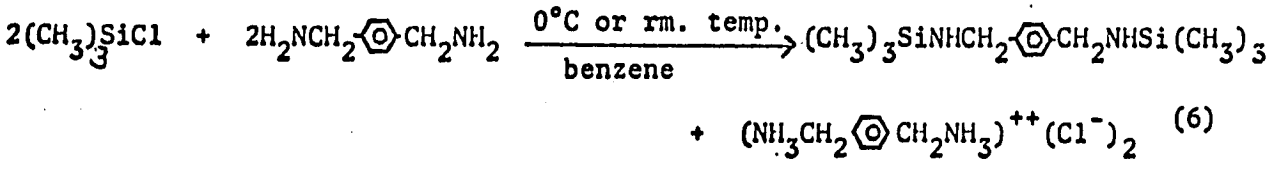
the basis of their different solubilities in concentrated hydrochloric acid resulted, in some fashion, from stronger hydrogen bonding and greater association in p-xylylenediamine·2HCl.

2. Trimethylsilyl and trimethylgermyl derivatives of the xylylenediamines

Since Group IV derivatives of the xylylenediamines had not been reported, the writer prepared and characterized several organosilyl and organogermyl xylylenediamines. This section discusses the N,N'-bis-trimethylsilyl and N,N'-bis-trimethylgermyl compounds. In the next section, the polymers prepared by reaction of dimethyldichlorosilane and dimethyldichlorogermane with the xylylenediamines are discussed. Because of their relationship to the silylethylenediamine polymers prepared earlier[128] and to the NMR study of Kummer and Baldeschwieler,[129] the polymeric compounds were of somewhat greater interest to the investigator than the monomeric species.

The N,N'-bis-trimethylmetallated xylylenediamines were prepared easily by direct aminolysis, unassisted by Et_3N, in benzene. The preparative details are contained in the following Experimental section. Equation (6), while showing the reaction of trimethylchlorosilane with p-xylylenediamine, outlines as well all of the aminolyses performed:



$$2(CH_3)_3SiCl + 2H_2NCH_2C_6H_4CH_2NH_2 \xrightarrow[\text{benzene}]{0^\circ C \text{ or rm. temp.}} (CH_3)_3SiNHCH_2C_6H_4CH_2NHSi(CH_3)_3 + (NH_3CH_2C_6H_4CH_2NH_3)^{++}(Cl^-)_2 \quad (6)$$

128. a) R. Minné and E.G. Rochow, J.A.C.S., 82, 5625, 5628(1960).
b) D. Kummer and E.G. Rochow, Z. Anorg. Allg. Chem., 321, 21(1963).
c) F.A. Henglein and K. Lienhard, Makromol. Chem., 32, 218(1959).
d) D. Kummer and E.G. Rochow, Inorg. Chem., 4, 1450(1965).

129. D. Kummer and J.D. Baldeschwieler, J. Phys. Chem., 67, 98(1963).

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The bis-trimethylsilyl derivatives of all three isomers were characterized. Because the writer possessed only a small amount of $(CH_3)_3GeBr$, prepared from bromination of tetramethylgermane, only N,N'-bis-(trimethylgermyl)-p-xylylenediamine was prepared. All four products were moisture sensitive, colorless liquids.

N,N'-bis(trimethylsilyl)o-xylylenediamine (VIII), with a boiling range of 91-92.5°C at 0.075 mm Hg, was obtained in 72% yield by vacuum distillation of the product of aminolysis of $(CH_3)_3SiCl$ by freshly distilled o-xylylenediamine. Approximately 95% of the expected weight of o-xylylenediamine dihydrochloride was removed by filtration prior to distillation. Figure 2.26 shows the rather simple NMR spectrum of N,N'-bis-(trimethylsilyl)-o-xylylenediamine. The writer observed the trimethylsilyl proton resonance at -0.06δ. A doublet appearing at -3.83δ and -3.96δ (centered at -3.90δ), resulting from coupling of the methylene protons with the single adjacent NH proton, may be observed. Though scarcely visible in the spectrum, a very broad NH resonance approximately at -0.5δ was readily detected by integration. While the methylene and NH proton resonance of the free amine were exchange-narrowed to single sharp peaks, exchange of the NH protons in VIII was slow enough that coupling of the methylene and NH protons occurred. The extreme broadness of the NH resonance resulted from the combined effect of the I=1 spin value and the electric quadrupole moment of ^{14}N. No splitting of the NH resonance by the methylene protons or by the ^{14}N nucleus was apparent. Phenyl resonances appeared at -7.14δ and -7.18δ. From integration, the trimethylsilyl, methylene, and phenyl protons were found to be in the ratio 4.5:1.0:1.0, in exact agreement with theoretical values for VIII.

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In a higher boiling fraction (95-105°C at 0.075 mm), the writer obtained in 8.5% yield a mixture of VIII with trimethylsilyl-o-xylylenediamine and/or free o-xylylenediamine. Integration of the NMR spectrum of this fraction revealed a deficiency of trimethylsilyl groups compared with VIII; the ratio of trimethylsilyl protons to methylene protons was 3.5:1 compared with the value of 4.5:1 for VIII. Appearance of a methylene resonance at -3.80δ in the spectrum of the mixture suggested the presence of o-xylylenediamine. However, another peak at -3.91δ, between the two peaks for VIII, indicated that trimethylsilyl-o-xylylenediamine was perhaps present, i.e. that a doublet (-3.80δ and -3.91δ) for one type of methylene group (coupled with a single NH proton) overlapped the methylene resonance (-3.80δ) of the un-trimethylsilylated groups. One would have expected free o-xylylenediamine (boiling range 68-71°C at 0.05 mm) to boil slightly below, rather than above, compound VIII. However, the existence of trimethylsilyl-o-xylylenediamine was problematical. The monosubstituted derivative of ethylenediamine does not exist for any significant time, but readily disproportionates; with a deficiency of trimethylsilyl groups in a product, one isolates only bis-(trimethylsilyl)ethylenediamine and ethylenediamine.[130]

The limited quantity of the high boiling mixture denied attempts to isolate and purify the monosubstituted amine. Chemical analysis, molecular weight determination, and infrared, NMR, and mass spectroscopy would have been of no assistance in proving the existence of trimethylsilyl-o-xylylenediamine in the mixture. The results of a brief chromatographic investigation on an F & M Flame Ionization Gas Chromatograph

130. a) Personal communication from Mr. C.H. Kim, Harvard University Chemistry Department.
b) C.G. Pitt and M.S. Habercom, J. Organometal. Chem., 12, 397(1968).

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were inconclusive. Using a silicone rubber column heated at 260-265°C, a rather sharp peak with a nearly resolved, prominent shoulder was obtained. No columns or column conditions were found which permitted better resolution of these peaks. A third peak was not discerned in any chromatogram. The retention time of o-xylylenediamine was close to, but usually slightly less than, that of the compound producing the shoulder. It is suspected that even if the monosubstituted amine were present in the mixture, the high injection port and column temperatures would have forced a redistribution reaction. In summary, the NMR spectra hinted at the presence of trimethylsilyl-o-xylylenediamine, but no proof of that presence was obtained.

N,N'-bis-(trimethylsilyl)-m-xylylenediamine (IX), with a surprisingly high boiling point of 139-141°C at 0.03 mm Hg, was obtained in 78% yield by vacuum distillation of the aminolysis product. The pressure reading in this distillation was perhaps in error. The dihydrochloride was isolated in essentially 100% yield as the reaction by-product. The NMR spectrum of the compound, shown in Fig. 2.27, was as simple as for the ortho derivative; Table XII summarizes the NMR results. Since the chemical shift of cyclohexane vs TMS is correctly -1.43δ, it was necessary in interpreting Fig. 2.27 to add -0.05δ to the apparent chemical shift of each resonance.

Table XII

Proton Type	Chem. Shift	Integration
$(CH_3)_3Si$-	-0.06δ	9.0
-NH-	-0.6δ (broad)	∿1
-CH_2-	-3.78δ (doublet) -3.91δ	2.0
-m-C_6H_4-	-7.04δ (∿3:1) -7.11δ	2.0

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The integration shown in Fig. 2.27 is incomplete; a separate Varian T-60 spectrum was used to assess the full integration. Again the splitting of the methylene resonance by coupling with the amino proton was observed. As with the ortho derivative, the chemical shift of the doublet was 0.10δ greater than the methylene shift for the free amine.

From the reaction of p-xylylenediamine with $(CH_3)_3SiCl$, the writer obtained N,N'-bis-(trimethylsilyl)-p-xylylenediamine (X) (boiling range 97-99°C at 0.05 mm) in 77% yield. Quantitative formation of p-xylylenediamine·2HCl was observed. The NMR spectrum of the compound, obtained from a CCl_4 solution with TMS as internal standard, is shown in Fig. 2.28. The NMR results are presented in Table XIII.

Table XIII

Proton Type	Chem. Shift	Integration
$(CH_3)_3Si$-	-0.05δ	9.0
-NH-	∿0.5-0.6δ	∿1
$-CH_2-$	-3.79δ (doublet) -3.92δ	2.0
$-p-C_6H_4-$	-7.07δ -7.14δ	2.0

The split phenyl resonance was unexpected for this compound. The integration of the $(CH_3)_3Si$, methylene, and phenyl resonances agreed so well with the expected integration that it was suspected that the broad hump at -7.07δ was anomalous; a similar, but smaller, hump appeared in the spectrum of p-xylylenediamine. With the great similarity of this spectrum to those of compounds VIII and IX, no further discussion is necessary here. For all three compounds, the coupling constant $J_{CH_2,NH}$ for the amino and methylene protons was 7.8 Hz. That constant is about the same as that

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usually observed for amines and ammonium salts (5-7 Hz).[131]

The mass spectrum of N,N'-bis-(trimethylsilyl)-p-xylylenediamine (integral molecular weight = 280) was recorded after direct insertion at 145°C. While the molecular ion peak was prominent at m/e 280, the strongest high mass peak occurred at m/e 279. An even-electron ion, formed by loss of a single hydrogen atom, was evidently favored over the molecular ion. In this rather complicated spectrum, one never observed an isolated pattern characteristic of a species containing two silicon atoms, but instead found overlapping silicon patterns. The writer did not engage in the extensive arithmetic necessary in making heavy-isotope corrections and in determining the relative abundance of species with overlapping envelopes. Prominent high mass peaks occurred in the spectrum at m/e 280, 279, 265, 249, 236, 207, 191, 178, 176, 162, and 148. The most intense peak in the base envelope appeared at m/e 176. The "peak" at m/e 207 resulted from loss of a trimethylsilyl group from the molecular ion. Peaks resulting from doubly-charged ions and metastable species were much more common than in the previously discussed germazane spectra. Prominent "doubly-charged" peaks appeared at m/e 132.5, 125.5, 110.5, 98.5, and 73.5.

The infrared spectra of the three N,N'-bis-trimethylsilylated xylylenediamines are presented in Figures 1.24 (ortho), 1.25 (meta), and 1.26 (para). Table XIV lists the salient infrared bands and some assignments for those compounds. Assignments were made by comparison with the spectra of the three xylylenediamine isomers (see Table X) and with the

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131. R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, Second Ed., John Wiley and Sons, New York, 1967, pp 123-124.

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Table XIV[52]

N,N'-bis-(trimethylsilyl)-o-xylylenediamine		N,N'-bis-(trimethylsilyl)-m-xylylenediamine		N,N'-bis-(trimethylsilyl)-p-xylylenediamine	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
3395(m)	νN-H	3395(m)	νN-H	3395(m)	νN-H
∿3325(sh)	2xδN-H(?)	3300(sh)	2xδN-H(?)	3300(sh)	2xδN-H(?)
3060(m)	νC-H aromatic	3050(m)	νC-H aromatic	3050(m)	νC-H aromatic
3015(m)		3015(m)		3010(m)	
2950(s)	$\nu_{asym}(CH_3)$	2950(s)	$\nu_{asym}(CH_3)$	2950(s)	$\nu_{asym}(CH_3)$
2885(m)	$\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_3)$	2885(m)	$\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_3)$.	2885(m)	$\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_3)$
2835(m)	$\nu_{sym}(CH_2)$	2840(m)	$\nu_{sym}(CH_2)$	2840(m)	$\nu_{sym}(CH_2)$
1595(vw)	δN-H and benzene ring stretching	1605(w) 1590(sh)	δN-H and benzene ring stretching	1605(w) 1590(sh)	δN-H and benzene ring stretching
1470(sh)	benzene ring mode	1480(w)	benzene ring mode	1505(w)	benzene ring mode
1440(m)	$\delta(CH_2)$	1445(m)	$\delta(CH_2)$	1445(m)	$\delta(CH_2)$
1380(s)	$\delta_{asym}(CH_3)$ (?)	1390(s)	$\delta_{asym}(CH_3)$ (?)	1400(s)	$\delta_{asym}(CH_3)$ (?)

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Table XIV Contd.

N,N'-bis-(trimethylsilyl)-o-xylylenediamine		N,N'-bis-(trimethylsilyl)-m-xylylenediamine		N,N'-bis-(trimethylsilyl)-p-xylylenediamine	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
1260(sh)	$\delta_{sym}(CH_3)$	1260(sh)	$\delta_{sym}(CH_3)$	1260(sh)	$\delta_{sym}(CH_3)$
1250(vs)		1250(vs)		1250(vs)	
1205(w)	unassigned			1215(w)	broad; unassigned
1180(w)					
1126(s)	In-plane hydrogen bending on ring or δNH	1152(s)	In-plane hydrogen bending on ring and δNH	1152(s)	In-plane hydrogen bending on ring or δN-H
		1108(s)	unassigned	1105(sh)	unassigned
				1088(s)	unassigned
1080(s)	νC-N (?)	1078(s)	νC-N (?)	1078(sh)	νC-N (?)
1070(sh)	unassigned				
1046(m)	unassigned				
				1015(w)	unassigned
935(w)	unassigned				
875(vs)	broad; νSi-N	870(vs)	broad; νSi-N	870(vs)	broad; νSi-N
835(vs)	$\rho(CH_3)$	835(vs)	$\rho(CH_3)$	835(vs)	$\rho(CH_3)$

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Table XIV Contd.

N,N'-bis-(trimethylsilyl)-o-xylylenediamine		N,N'-bis-(trimethylsilyl)-m-xylylenediamine		N,N'-bis-(trimethylsilyl)-p-xylylenediamine	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
758(s)	Out-of-plane hydrogen bending on benzene ring	774(m)	Out-of-plane hydrogen bending on benzene ring	774(m)	Out-of-plane hydrogen bending on benzene ring
746(sh)	ν_{asym}Si-C (?)	745(m)	ν_{asym}Si-C (?)	745(m)	ν_{asym}Si-C (?)
		695(m)	ν_{sym}Si-C (?)	695(m)	ν_{sym}Si-C (?)
682(m)	ν_{sym}Si-C (?)	680(m)	ν_{sym}Si-C (?)	680(m)	ν_{sym}Si-C (?)
620(w)	unassigned	618(w)	unassigned	615(w)	unassigned

papers of A. Lee Smith[132] (general discussion of organosilicon infrared spectra), H. Kriegsmann[30], and M.C. Tobin.[61] The N-H stretching and angle deformation bands at 3395 cm^{-1} and near 1600 cm^{-1} were rather weak in all three spectra. As with other trimethylsilylated compounds, the methyl symmetric deformation peak at 1250 cm^{-1} was strong and sharp. The 1200-1500 cm^{-1} region was deceptively simple. Though only four bands were apparent in each of the spectra, those bands necessarily had multiple origins. To generalize, methyl group deformations, methylene deformations, benzene ring stretching modes, and in-plane hydrogen bending modes contributed to those bands.

In the lower wave number range of each of the three spectra, the C-N stretching band probably occurred at 1078-1080 cm^{-1}, though a fully resolved band in that region appeared only for the ortho compound. The nearby bands appearing in the meta (1108 cm^{-1}) and para (1088, 1105 cm^{-1}) spectra might instead have resulted from C-N stretching. For the free xylylenediamines, the C-N stretching band occurred in the interval 1040-1060 cm^{-1}. From the results for N-phenyl and N-cyclohexyl organogermazanes reported earlier and from the observations of Randall, Ellner, and Zuckerman,[133] one expected trimethylsilyl substitution to raise the C-N stretching frequency. The nitrogen pyramid was presumably somewhat flattened with the bonding of nitrogen to silicon, with the presence of Si-N $d\pi$-$p\pi$ bonding. The C-N bond probably possessed increased s character and was therefore stronger.

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132. A. Lee Smith, Spectrochim. Acta, 16, 87(1960).

133. E.W. Randall, J.J. Ellner, and J.J. Zuckerman, Inorg. Nucl. Chem. Letters, 1, 109(1966).

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The very strong infrared band at 835 cm^{-1} undoubtedly resulted from methyl group rocking. The broad, strong band between 870 and 875 cm^{-1} probably derived mostly from Si-N(-C) stretching. Randall, Ellner, and Zuckerman[133] reported a value of 899 cm^{-1} for Si-N stretching in $(CH_3)_3$-$SiNHC_6H_5$. In the 800-900 cm^{-1} region the intense νSi-N and $\rho(CH_3)$ bands greatly overshadowed the aromatic C-H bending bands expected in the same interval. As shown in Table XIV, the positions of the asymmetric and symmetric Si-C stretching bands were uncertain. In his frequently quoted paper[132] on the infrared spectra of organosilicon compounds, A.L. Smith indicated that the ν_{asym}Si-C band occurs near 13.1μ (765 cm^{-1}) for the trimethylsilyl group. Tobin[61] reported a ν_{asym}Si-C band at 760 cm^{-1} for $(CH_3)_3SiCl$. However, Kriegsmann reported[30] ν_{asym}Si-C bands for hexamethyldisilazane and heptamethyldisilazane at 685 and 682 cm^{-1}, respectively. Kriegsmann apparently based those assignments on correlations with spectra of compounds like $(CH_3)_3SiCl$; in the cited paper, he showed the ν_{asym}Si-C band of $(CH_3)_3SiCl$ near 700 cm^{-1}. In Fig. 1.24-1.26, bands appeared which correlated with either Smith's or Kriegsmann's assignment. Because of the conflicting interpretations, definite assignments could not be made for the xylylenediamine derivatives.

The analytical results obtained for two of the N,N'-bis-trimethylsilylated xylylenediamines were as follows:

	%C	%H	%Si	%N
N,N'-bis-(trimethylsilyl)-m-xylylenediamine	60.16	9.91	20.15	
N,N'-bis-(trimethylsilyl)-p-xylylenediamine	59.95	10.06	20.35	
Theoretical values for both compounds	59.91	10.08	20.02	9.99

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N,N'-bis-(trimethylgermyl)-p-xylylenediamine (XI), with a boiling range of 123.5-125°C at 0.04 mm Hg, was prepared by aminolysis of $(CH_3)_3GeBr$ with p-xylylenediamine in a reaction of the same form as that outlined in equation (6). Compound XI was initially isolated in relatively pure condition in only 43% yield. NMR spectra indicated that unreacted p-xylylenediamine and probably some trisubstituted amine were present in distillation fractions boiling below and above compound XI. All but the lowest distillation fraction (78-85°C at 0.05 mm Hg) contained XI, but fractional distillation did not permit complete separation of the disubstituted amine. In addition, it was found that about six grams of germanium-containing product were trapped in the filtered p-xylylenediamine-•2HBr. The weight of hydrobromide obtained after refluxing a benzene suspension of the initially impure solid for three hours was 89% of the weight expected from the reaction. The aminolysis reaction had evidently been somewhat incomplete. Distillation of the material extracted from the hydrobromide raised the yield of XI to 58%, still considerably below the yields obtained from the organosilicon reactions.

Analytical results obtained for N,N'-bis-(trimethylgermyl)-p-xylylenediamine were as follows:

	%C	%H	%Ge	%N
Found:	45.21	7.59	40.2	
Calc'd for disubstituted	45.49	7.66	39.26	7.59
Calc'd for trisubstituted	41.98	7.48	44.78	5.76

These results suggested that the product contained a small amount of the trisubstituted amine, N,N,N'-tris-(trimethylgermyl)-p-xylylenediamine.

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The mass spectrum of XI, obtained with direct insertion at 145°C, showed a well-defined, two-germanium envelope at m/e 370 (molecular ion). A second "peak", resulting from loss of a methyl group from the molecular ion, appeared at m/e 355. Because one-germanium envelopes overlapped through much of the spectrum, determination of relative ion abundances required extensive calculation. Those calculations were not performed. The base "peak" in the spectrum apparently occurred at m/e 253, at the mass of the molecular ion minus a trimethylgermyl group. Under the conditions required to observe a well-developed molecular ion "peak", extremely faint higher mass "peaks" were observed in the most sensitive galvanometer scan. The species producing these "peaks" necessarily comprised a minor portion of the total ion current.

The NMR spectrum of XI, shown in Fig. 2.29, indicated that impurity was present in the disubstituted amine. The complicated phenyl resonances, in particular, were not expected for XI. The resonance observed at -3.75δ probably derived from the methylene protons of un-trimethylgermylated groups; the methylene resonance for p-xylylenediamine occurred at -3.74δ. One could not exclude the presence of mono- or tri-substituted amine, however. Finally, the small impurity peaks at -0.29δ and -0.39δ suggested that partial hydrolysis had occurred. The chemical shift of the trimethylgermyl protons in hexamethyldigermoxane is -0.31δ (-18.5 Hz at 60 MHz).[134] In its essentials, the spectrum was much like that of the organosilicon derivatives. However, with the assumption that the resonances at -3.86 and -4.12δ comprised a simple doublet, one obtained the unacceptably large $J_{CH_2,NH}$ coupling constant of 15.6±1.2 Hz (normally 5-8 Hz). For

134. H. Schmidbaur and I. Ruidisch, Inorg. Chem., 3, 599(1964).

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this compound, for all dimethylgermyl derivatives of the xylylenediamines discussed later in this chapter, and for one dimethylsilyl-o-xylylenediamine compound, simple interpretation of the NMR spectra led to unusually large $J_{CH_2,NH}$ values. The observed splitting probably did not result from simple methylene and amino proton coupling. The matter is discussed generally in Chapter IV. Table XV summarizes the NMR results. Because of the probable impurity of the sample, the good agreement of the integration with expected values was fortuitous.

Table XV

Proton Type	Chem. Shift	Integration
$(CH_3)_3Ge$	-0.21δ -0.29δ] impurity -0.39δ]	4.4_5
-NH-	∿-0.7δ	
$-CH_2-$	-3.86δ] apparent -4.12δ] doublet -3.75δ impurity	1.0
$-p-C_6H_4-$	-7.15δ strongest peak of complex multiplet	1.0

The infrared spectrum of compound XI is shown in Fig. 1.28. Fig. 1.27, of a fraction distilling just below that of the disubstituted amine, was virtually identical to Fig. 1.28 and indicated that infrared spectroscopy was unsatisfactory for characterizing the impurities in the disubstituted amine. Table XVI lists several prominent infrared bands in the N,N'-bis-(trimethylgermyl)-p-xylylenediamine spectrum with tentative assignments. Assignments for the trimethylgermyl group were made with the assistance of previously cited papers by Cross and Glockling[54b] and Van de Vondel and Van der Kelen.[92b]

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The close positioning of the intense, broad νGe-N and $\rho(CH_3)$ bands made individual assignments to those modes impossible. The band at 820 cm^{-1} was probably the methyl rocking band. As with all the germazane and germylamine compounds discussed earlier, the Ge-C stretching bands at 598 cm^{-1} and 564 cm^{-1} were at lower energy than for $(CH_3)_2GeCl_2$ (640 cm^{-1} and 594 cm^{-1}).

In anticipation of more extensive discussions in the next section, this section is concluded by comparing the NMR spectroscopic properties of the bis-trimethylmetallated xylylenediamines with the properties of the well-known ethylenediamine compounds. Table XVII lists the proton chemical shifts[128d] for bis-(trimethylsilyl)ethylenediamine:

Table XVII

Proton Type	Chemical Shift
$(CH_3)_3Si$-	-0.01δ
-NH-	-0.58δ (broad)
$-CH_2CH_2-$	-2.62δ (unsymmetrical "triplet")

For the substituted xylylenediamines, the $(CH_3)_3Si$ proton resonance at (-0.05)-(-0.06δ) indicated slight deshielding of the organosilyl protons compared with the ethylenediamine derivative. The chemical shift of the methylene protons in the xylylenediamine compounds (centered between -3.84δ and -3.90δ) was considerably greater than the -2.62δ value for bis-(trimethylsilyl)ethylenediamine. The phenyl ring, by inductive withdrawal of electrons, clearly deshielded the methylene protons in the xylylenediamine compounds. In turn, that electron withdrawal seemingly reduced the donation of nitrogen electron density to silicon and resulted in slight deshielding of the organosilyl protons. The relative

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basicities of the nitrogen atoms in the xylylenediamine and ethylenediamine compounds were not determined, but should be measured in future research. From consideration of all information obtained in this research, it appears that the nitrogen basicities are greater, although perhaps only slightly, in the xylylenediamines and their derivatives.

The most noticeable effect of the interposition of the phenyl ring was simplification of the methylene resonance in the NMR spectra of the organosilyl and organogermyl xylylenediamines. The previously discussed simple doublets contrasted with the complex methylene resonance for bis(trimethylsilyl)ethylenediamine. Kummer and Baldeschwieler[129] have analyzed the methylene resonance of the latter compound in terms of mutual coupling of the methylene and NH proton spins in an $XA_2A_2'X'$ or XABA'B'X' spin system. For the xylylenediamine compounds, coupling of the phenyl protons with the methylene (and NH) protons was negligible (over a minimum of four bonds) and resulted in no visible splitting of the methylene resonance. Coupling between a pair of methylene protons and the immediately adjacent NH proton yielded the observed simple spectrum. Interaction of the amino proton with the ^{14}N nucleus of course produced a broad, unstructured NH resonance.

3. Dimethylsilyl and dimethylgermyl derivatives of the xylylenediamines

As previously mentioned, the products prepared by reaction of dimethyldichlorosilane and dimethyldichlorogermane with the three xylylenediamine isomers presented opportunities for comparison with the well-characterized silylethylenediamine[128,129] and germylethylenediamine[20] polymers. A brief review of the research with ethylenediamine is necessary

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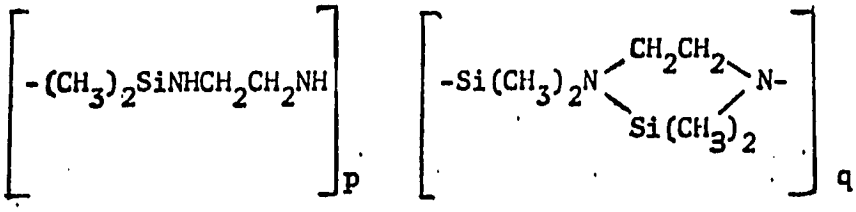
here. Although the detailed nature of the products obtained from $(CH_3)_2SiCl_2$ and ethylenediamine depended somewhat on the reaction conditions, Minné[128a], Henglein and Lienhard[128c], and Kummer and Rochow[128b,d] all obtained polymers with molecular weights of about 2000. By transamination of $(CH_3)_2Si(NEt_2)_2$ with ethylenediamine, Henglein and Lienhard obtained polymers with slightly higher molecular weight (3000). Extensive studies by Kummer and Baldeschwieler[129] and Kummer and Rochow[128d] demonstrated, primarily by analysis of NMR spectra, that the polymers were not linear $[-(CH_3)_2SiNHCH_2CH_2NH-]_x$ and that large rings (e.g. ten-membered) were not present. Analytical results and IR and NMR spectra were interpreted in terms of polymers containing different ratios of linear and five-membered cyclic units:



When freshly prepared, Minné's material had a higher percentage of linear units than the Henglein-Lienhard polymer, but on standing, or more rapidly with heating, the ratio q:p increased for both polymers. With heating at 300-350°C for several hours in vacuo, Kummer and Rochow observed formation of a polymer incorporating only the more stable five-membered ring units.[128d] None of the products were particularly stable thermally or hydrolytically. Wide-line NMR spectra showed that there was less freedom of movement of the polymer chains, particularly between -100°C and 0°C, than in the linear polysiloxanes and polysilazanes.[135] The simple monomeric

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135. J.R. Barrante and E.G. Rochow, J. Organometal. Chem., 1, 273(1964).

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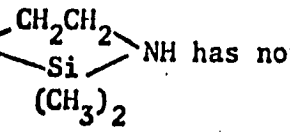
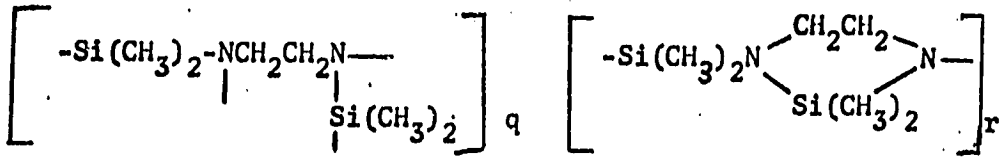
compound  has not been isolated.

More recently, Yoder and Zuckerman[20] prepared dimethylsilyl- and dimethylgermylethylenediamine polymers by transamination of bis-(diethylamino)dimethylsilane (catalyzed by ammonium sulfate) and bis-(diethylamino)dimethylgermane. In the silicon case, these authors proposed the following structure with a high ratio of q to r:



These resinous white solids (mol. wt = 5200) possessed different properties from those of the mixed ring and chain polymers (viscous oils) prepared by Kummer and Rochow.[128b,d] In the germanium case, a facile transamination at 120°C produced a pasty polymer (mol wt > 1000) which was reported by Yoder and Zuckerman to contain mostly five-membered germaimidazolidine rings. From NMR and IR spectra, the latter authors notably found no evidence for N-H bonds in any of the polymers.

In comparison with the xylylenediamine compounds, the ethylenediamine polymers are most interesting on NMR spectroscopic grounds. The investigation by Kummer and Baldeschwieler[129] of the NMR spectra of numerous monomeric linear and cyclic silyl ethylenediamine compounds paved the way for the studies of polymeric materials. Polymers which contained some linear dimethylsilylethylenediamine units showed a single broad NH resonance at 9.24τ (-0.76δ); the single broad NH resonance for N,N'-bis-(trimethylsilyl)-ethylenediamine appeared at 9.42τ (-0.58δ). Chemical shifts of 9.87τ (-0.13δ), 9.91τ (-0.08δ), and 9.97τ (-0.03δ) were assigned to $(CH_3)_2Si$

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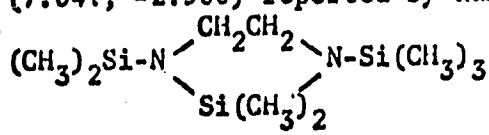
groups within five-membered rings, linking five-membered rings, and linking rings and linear units, respectively.

The resonance of the methylene groups in five-membered rings was a sharp singlet at 7.03τ (-2.97δ), in agreement with the result (7.04τ; -2.96δ) reported by Kummer and Baldeschwieler for



For both the monomeric and polymeric ring units, the single methylene resonance meant that the five-membered ring was planar, and that the nitrogen atoms were either trigonally hybridized or underwent rapid inversion. Without planarity of the five-membered ring, the non-equivalent protons on the two CH_2 groups would lead to a complex CH_2 resonance. In addition, if the $Si(CH_3)_3$ groups or ring-linking $Si(CH_3)_2$ groups were fixed above or below the plane of the ring, the CH_2 protons would again be non-equivalent and <u>cis</u> and <u>trans</u> arrangements of the organosilicon groups with respect to the plane of the ring might be expected. For linear polymeric units, which retained a single proton on each nitrogen, and for the linear monomer $(CH_3)_3SiNHCH_2$ - $CH_2NHSi(CH_3)_3$, the methylene resonance was a complex, unsymmetrical "triplet" at 7.37τ (-2.63δ) and 7.38τ (-2.62δ), respectively. That spectrum, resulting from coupling of the NH protons with the bridge methylene groups, was analyzed and simulated by considering the spin system to be of an $XA_2A_2'X'$ or XABA'B'X' type. A and A' refer to protons which are chemically equivalent, but magnetically non-equivalent. A and B refer to chemically non-equivalent CH_2 protons. Finally, the compounds $[(CH_3)_3Si]_2NCH_2CH_2N$-$[Si(CH_3)_3]_2$ and $(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$ showed single, sharp CH_2 resonances without the possibility of coupling with NH protons.[129,128d]

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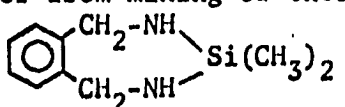
For their dimethylgermanium polymers made up mostly of linked five-membered rings, Yoder and Zuckerman reported[20] a broad CH_2 resonance at 7.01τ (-2.99δ), a ring $Ge(CH_3)_2$ resonance at 9.71τ (-0.29δ), and two overlapping resonances for linking $Ge(CH_3)_2$ at 9.66τ (-0.34δ). In the absence of NH protons, the unsymmetrical "triplet" structure was, of course, not found for the methylene resonance.

The three xylylenediamines resulted from interposition of a phenyl ring between the two methylene groups of ethylenediamine. One expected that meta and para xylylenediamine would form polymers with dimethylsilyl and dimethylgermyl groups, and that those polymers would possess noticeably different properties from the ethylenediamine materials. For both the meta and para isomers, formation of small rings from one amine molecule and one dimethylsilyl or dimethylgermyl group (i.e. analogous with the silaimidazolidines) was impossible. The question remained whether the polymers obtained would be linear or highly cross-linked through nitrogen; one surmised that the phenyl group would discourage cross-linking. Ortho xylylenediamine, with its amino groups directed so that seven-membered-ring formation with silicon or germanium was tenable, presented several possibilities for compound formation. Polymers might result from linking of seven-membered rings, from polymerization of linear units, from cross-linking of linear units, or from mixing of these possibilities. Finally, the monomeric compound  was perhaps isolable, though the ethylenediamine compound[2] did not escape polymerization.

The polymers formed by reaction of $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ with

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meta and para xylylenediamine were thoroughly investigated in this research. Primarily because of the facile oxidation and discoloration of o-xylylenediamine and its dimethylsilyl and dimethylgermyl derivatives, characterization of the limpid liquid obtained from $(CH_3)_2SiCl_2$ and o-xylylenediamine and of the resinous white solid from $(CH_3)_2GeCl_2$ and o-xylylenediamine was difficult and ultimately uncertain. The o-xylylenediamine products were somewhat different from the derivatives of the other two isomers.

Several slightly different methods were used in conducting the reactions of m-xylylenediamine with $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$, but pure products were obtained most straight-forwardly by simple aminolysis in benzene. Only the procedure adhering to the stoichiometry of equation 7 is described in detail in the Experimental section. In that procedure, a slight excess of amine, varying from 0.8 mole % to 5.0 mole %, based on

$$(CH_3)_2MCl_2 + 2\ H_2NCH_2(m\text{-}C_6H_4)CH_2NH_2 \xrightarrow[0°C]{\text{benzene}} \quad (7)$$

$$\frac{1}{x}\left[(CH_3)_2MNHCH_2(m\text{-}C_6H_4)CH_2NH\right]_x + NH_3CH_2(m\text{-}C_6H_4)CH_2NH_3^{++}(Cl^-)_2$$

M = Si, Ge

the amine, was always added to provide amine terminal groups for the polymers and to assure complete substitution for chlorine. With diethylether as solvent, temperatures varying from -78°C to room temperature made no observable difference in the nature of the polymeric product. Ether was an unsatisfactory solvent for reaction because m-xylylenediamine dihydrochloride was much more soluble in it than in benzene. With benzene, an inert atmosphere filtration and brief distillation of the solvent at atmospheric pressure was sufficient for complete removal of the dihydrochloride.

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Because of the high basicity of the diamine, addition of Et_3N was unnecessary. The presence of triethylamine in fact unduly complicated the reaction, for then triethylamine hydrochloride and the m-xylylenediamine mono- and dihydrochlorides all formed. From reaction, for example, of 0.1 mole of $(CH_3)_2SiCl_2$ with 0.1 mole of m-xylylenediamine in the presence of 0.2 mole of Et_3N, one obtained approximately equal amounts (as determined only from infrared spectra) of triethylamine hydrochloride and m-xylylenediamine dihydrochloride. Aminolysis of the chlorosilane was then incomplete. From reaction of excess m-xylylenediamine with the organochlorosilane and -germane (e.g. in a 4:1 molar ratio), the writer obtained almost entirely m-xylylenediamine monohydrochloride, a small amount of dihydrochloride, and a polymeric product quite indistinguishable from the product obtained from a reaction following equation 7.

Room-temperature addition of 12.91 g (0.1000 mole) of $(CH_3)_2SiCl_2$ to a solution of 28.60 g (0.2099 mole; 5.0 mole % excess) of m-xylylenediamine in 250 ml of benzene resulted in a gently exothermic reaction. Following fourteen hours of stirring at room temperature and one hour of refluxing at 80°C, a filtration separated m-xylylenediamine dihydrochloride in 98.5% yield. A small additional amount of halide remained dissolved in the benzene, but was swept away from the product by distillation of the solvent at atmospheric pressure. Vacuum distillation yielded 1.25 g of m-xylylenediamine (bp 68.5°C at 0.05 mm Hg) but no other distillable material. The yield of residual, viscous, yellow-white polymer (XII) was 18.5 g (96%, assuming complete aminolysis but ignoring terminal amino groups). At room temperature (25-30°C), the viscous polymer flowed slowly

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about the inside of its container with rotation of the flask. With insertion of a spatula into the polymer, the material could be drawn out into long strings. At 0°C, the polymer did not distort or flow in an inverted flask over a one hour period. At 70°C, the polymer was of about the same consistency as the silicone oil (e.g. Dow Corning 710) used in laboratory heating baths.

The polymer dissolved readily in benzene (4.1 g of polymer in 50.00 ml of solution at room temperature), CCl_4, $CHCl_3$, and CH_2Cl_2. Not enough polymer to obtain a 3.2% by weight solution could be dissolved in cyclohexane. With benzil as calibrant, the writer attempted to use a Hewlett-Packard Mechrolab Model 301A vapor pressure osmometer for a molecular weight measurement on the polymer. For the polymer itself, the customary plot of $\Delta R/C$ vs C (ΔR in ohms, C in grams/liter) was erratic, perhaps reflecting hydrolysis of the polymer in solution on the thermistor beads, and denied determination of the molecular weight. From cryoscopic measurements on two benzene solutions of the polymer, the number average molecular weight was found to be 2580±40. Assuming equivalence of a weight average molecular weight for the polymer with this number average value, the polymer species comprising the largest weight fraction of the polymer would contain 13-14 linear units.[136] The molecular weight was comparable to that for the heaviest ethylenediamine polymer prepared by Henglein and Lienhard;[128c] the Minné[128a] and Kummer and Rochow[128d] polymers contained about the same number of polymer units.

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136. A. Rudin, J. Chem. Ed., 46, 595(1969).

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Analytical results for the m-xylylenediamine-organosilicon polymer were as follows:

	%C	%H	%Si	%N
Found:	62.91	8.61	13.90	
Calc'd: (for infinite linear polymer)	62.43	8.40	14.61	14.56
Calc'd: (for 12 unit polymer terminated by xylylenediamine groups)	62.86	8.38	13.87	14.89

The Si and C analyses agreed adequately with the previous report of a molecular weight of 2500-2600.

In a similar reaction, performed with 8.68 g (0.0500 mole) of $(CH_3)_2GeCl_2$ and 14.30 g (0.1050 mole; 5.0 mole % excess) of m-xylylenediamine, aminolysis was essentially complete. The dihydrochloride was isolated in 98.5% yield after lengthy benzene extraction was employed to remove trapped germanium-containing material. With attempted vacuum distillation, 2.24 g of unreacted amine distilled from the product. With recovery of only the added excess of amine, that mass would have been 0.72 g. The yield of residual white polymer (XIII) was 11.25 g (95%, assuming complete aminolysis, but ignoring terminal amino groups). While the silicon polymer had been a liquid in agitated motion during high temperature vacuum distillation, the white germanium polymer existed as a gum-like, immobile plug even at elevated temperature (> 200°C). The pot temperature was raised until an increase in pressure indicated that decomposition, with formation of materials not condensable in a dry ice-acetone trap, had commenced. Slight charring of the polymer that was in direct contact with the bottom of the pot was noted. Both the silicon

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and germanium polymers had been subjected in vacuo to temperatures of about 250°C. The silicon polymer exhibited greater apparent thermal stability because agitation of the liquid avoided localized over-heating. Heat was definitely not distributed as effectively in the immobile germanium polymer. At room temperature, the material was intractable. The preparation of infrared and NMR samples was difficult because the polymer could not easily be cut or pulled apart with a spatula.

The germanium polymer was only slightly soluble in CCl_4, $CHCl_3$, CH_2Cl_2, cyclohexane, and benzene. NMR spectra deriving from dilute solutions (containing small amounts of suspended material) in these solvents are discussed later in this section. The polymer dissolved readily in dry acetone (3.4 g of polymer in 50.00 ml of solution at room temperature). A cryoscopic molecular weight determination could not be made because of low solubility in usable solvents.

Analytical results obtained for the m-xylylenediamine dimethylgermanium polymer were as follows:

	%C	%H	%Ge	%N
Found:	45.00	6.46	33.0	
Calc'd: (for infinite linear polymer)	50.70	6.83	30.64	11.83
Calc'd: (for a fully cross-linked polymer, $[-Ge(CH_3)_2-NCH_2C_6H_4CH_2N]_n$ with $(CH_3)_2Ge$ bridging)	42.57	6.26	42.89	8.28

The low percentage found for carbon, the high %Ge value, the macroscopic properties of the polymer, and the NMR spectra indicated significant cross-linking. However, the C,H results derived from a single determination.

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The standard technique for C,H analysis used by Schwartzkopf involves mixing divanadium pentoxide with a sample to ensure complete combustion. With the germanium polymer, an intimate mixture could not have been made. Complete oxidation of some of the organogermanium compounds required quite forceful conditions. Combustion may have been incomplete for the m-xylylenediamine polymer, and so the C,H values may be low. The germanium and carbon analyses suggested 20-30% cross-linking in the polymers.

The study of infrared and NMR spectra permitted interesting comparison of the organosilicon and organogermanium polymers m-xylylenediamine. Infrared analysis did not clearly point to reasons for the strikingly different physical properties of the two materials. The differences between Figures 1.18 and 1.19 (organosilicon polymer, XII) and Figure 1.23 (organogermanium polymer, XIII) were those largely expected from replacement of silicon by germanium. The NH stretching band at 3395 cm^{-1} for XIII (recorded with a dilute CCl_4 solution) was weak compared with the prominent band at 3395 cm^{-1} for XII (thin film between KBr discs). However, the strong band at 1650 cm^{-1} for XIII was presumably due to NH deformation. In Figures 1.18 and 1.19, a relatively weak band appeared at 1635-1640 cm^{-1} for the organosilicon polymer. Quite simply, the intensities of the characteristic νNH and δNH bands did not reveal much about the relative abundance of NH groups in the two polymers. For XIII, a resolved low intensity hump was apparent at 3290 cm^{-1}; for XII a shoulder occurred at about the same position.

In Table XVIII the principal infrared bands for the m-xylylenediamine polymers are listed with their tentative assignments. The organosilicon

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Table XVIII[52]

$[-(CH_3)_2Si-(m)-NHCH_2C_6H_4CH_2NH-]_x$		$[-(CH_3)_2Ge-(m)-NHCH_2C_6H_4CH_2NH-]_x$	
cm^{-1}	Assignment	cm^{-1}	Assignment
3395(s)	νN-H	3395(w)	νN-H
~3325(sh)	2xδN-H (?)	3290(w)	2xδN-H (?)
3085(w), 3045(m), 3010(m)	νC-H aromatic	3085(w), 3050(m), 3010(m)	νC-H aromatic
2950(vs)	$\nu_{asym}(CH_3)$	2975(vs)	$\nu_{asym}(CH_3)$
2880(s)	$\nu_{asym}(CH_2)$ and $_{sym}(CH_3)$	2905(vs)	$\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_3)$
2835(s)	$\nu_{sym}(CH_2)$	2835(vs)	$\nu_{sym}(CH_2)$
1940(w), 1870(w), 1785(w)	overtone and combination bands	1945(w), 1870(w), 1800(w)	overtone and combination bands
1640(m)	δN-H	1650(s)	δN-H
1600(s), 1585(m)	benzene ring stretching	1610(s), 1590(sh)	benzene ring stretching
1505(w), 1480(m)	benzene ring modes	1485(m)	benzene ring mode
1440(s)	$\delta(CH_2)$	1445(s)	$\delta(CH_2)$
		1415(m)	$\delta_{asym}(CH_3)$

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Table XVIII Contd.

$[-(CH_3)_2Si-(m)-NHCH_2C_6H_4CH_2NH-]_x$		$[-(CH_3)_2Ge-(m)-NHCH_2C_6H_4CH_2NH-]_x$	
cm^{-1}	Assignment	cm^{-1}	Assignment
1395(vs)	$\delta_{asym}(CH_3)$ (?)	1385(m)	
1350(w)	unassigned	1350(m)	unassigned
1330(w)		1330(m)	
		1262(sh)	
1255(vs)	$\delta_{sym}(CH_3)$	1240(vs)	$\delta_{sym}(CH_3)$
1220(m)	unassigned		
1152(s)	In-plane hydrogen bending on benzene ring	1142(m)	In-plane hydrogen bending
1110(vs)			
1095(sh)	ν_{asym}N-Si-N, $_{asym}$Si-N-C, or νC-N	1095(vs)	ν_{asym}N-Ge-N or νC-N
1078(vs)		1070(vs)	
1025(m)	unassigned	1020(sh)	unassigned
983(w)		1010(vs)	
880(sh)	ν_{asym}Si-N-Si	720-880 (very broad vs)	νGe-N and $\rho(CH_3)$
850(vs; bd)	$\rho(CH_3)$		
782(vs)	out-of-plane hydrogen bending		
740(m)	ν_{asym}Si-C		
697(s)	benzene ring mode	695(s)	benzene ring mode
650(m)	ν_{sym}Si-C	610(s)	ν_{asym}Ge-C
∿575(w)	unassigned	585(s)	ν_{sym}Ge-C

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spectra were recorded with films of the polymer between KBr discs, the organogermanium spectrum with a dilute CCl_4 solution in NaCl cells. The assignment of bands deriving from the m-xylylenediamino moiety was made by reference to the spectrum of the parent amine (Fig. 1.14; Table X). Several previously cited papers, listed here only by author, were consulted in correlating bands with organosilicon, organogermanium, and metal-nitrogen vibrations: A. Lee Smith;[132] H. Kriegsmann;[30] M.C. Tobin;[61] R. Cross and F. Glockling;[54b] D.F. Van de Vondel and G.P. Van der Kelen;[92b] C.H. Yoder and J.J. Zuckerman;[81] and E.W. Randall, J.J. Ellner, and J.J. Zuckerman;[133] and finally, the infrared spectra reported in Chapter I for several dimethylgermazanes and germylamines (N-phenyl and N-cyclohexyl derivatives) were compared with the spectra of the polymers.

The same uncertainties existed in interpretation of these spectra as were countered with the trimethylsilyl- and trimethylgermyl- substituted xylylenediamines (see Tables XIV and XVI and the corresponding spectra). Particularly in the interval from 800-1100 cm^{-1}, a number of broad, overlapping bands, with several possible origins, appeared. On the other hand, the polymer spectra were pleasingly consistent with the spectrum of bis-(trimethylsilyl)-m-xylylenediamine (IX). For the organosilicon polymer (XII) and for IX, the νNH band appeared at 3395 cm^{-1}, 35 cm^{-1} higher than for m-xylylenediamine. There are several interconnected reasons why this increased stretching frequency might have been expected. With substitution of hydrogen by the organosilicon group, both a decrease in the basicity of nitrogen and the introduction of steric restrictions

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probably led to a reduction in the amount and strength of intermolecular hydrogen bonding. Such a reduction would lead to a higher νNH frequency. Decreased nitrogen basicity of the organosilyl ethylenediamines and hydrazines, in fact of silylamines in general, relative to the free amines has been well established.[130b,137] Second, with the existence of some Si-N dπ-pπ bonding, the nitrogen pyramid was probably somewhat flattened and the NH bond somewhat strengthened (relatively more s character). Third, the organosilicon group, with its positive inductive character, seemingly increased the sigma bonding electron density between nitrogen and hydrogen. In actual fact, an attempt to separate these strongly interrelated causes either in theory or by experiment, may not be meaningful.

The peak appearing at 1635-1650 cm^{-1}, most strongly for the organogermanium polymer, was clearly an NH deformation band. For uncertain reasons, that frequency was higher than for m-xylylenediamine (~1600 cm^{-1}) and (IX). The two sharp peaks, or a peak and a shoulder, near 1600 cm^{-1} were expected from benzene ring "quadrant stretching."[138] In the parent amine, the δNH and benzene ring bands were unresolved.

For most dimethylsilyl compounds, the $\delta_{asym}(CH_3)$ band at 1390-1410 cm^{-1} is weak compared with the $\delta_{sym}(CH_3)$ band at 1250-1260 cm^{-1}. The latter intense band is the most striking feature of dimethylsilyl and trimethylsilyl spectra.[29,30] In Figures 1.18 and 1.19, the very strong peak at

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137. a) E.W. Abel, D.A. Armitage, and G.R. Willey, Trans. Faraday Soc., 60, 1257(1964).
b) E.W. Abel, D.A. Armitage, and D.B. Brady, ibid., 62, 3459(1966).

138. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, p. 224.

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1395 cm^{-1} was probably mostly an $\delta_{asym}(CH_3)$ band, though other absorbances (C-H deformations) perhaps contributed. For the dimethylgermyl polymer, the $\delta_{asym}(CH_3)$ band appeared with the expected moderate strength at 1415 cm^{-1} (compared with 1410 cm^{-1} for N,N'-bis-(trimethylgermyl)-p-xylylenediamine. For both XII and XIII the characteristic $\delta_{sym}(CH_3)$ bands appeared at their expected frequencies.

The overlapping, intense bands between 1070 cm^{-1} and 1110 cm^{-1} for both the organosilyl and organogermyl polymers had uncertain origins. The νC-N absorbance, near 1060 cm^{-1} for m-xylylenediamine and at 1078 cm^{-1} for IX, probably occurred in this interval. The nearly identical positioning of the bands for the silicon and germanium compounds pointed to principal involvement of the C-N mode. The bands near 1100 cm^{-1} were weak or absent in the spectra of m-xylylenediamine, $(CH_3)_2GeCl_2$, and $(CH_3)_2SiCl_2$. One or more of the bands perhaps resulted from mixing of Si-N (Ge-N) and C-N stretching modes. Similar, though weaker, bands occurred in the spectrum of IX. Earlier in this thesis, it was asserted that ν_{asym}N-Ge-N bands occurred near 1100 cm^{-1} for $(CH_3)_2Ge(NHC_6H_{11})_2$ and $Et_2Ge(NHC_6H_{11})_2$. However, Yoder and Zuckerman reported lower frequency ν_{asym}N-Si-N and ν_{asym}N-Ge-N bands at 970-930 cm^{-1} and 930-870 cm^{-1}, respectively, for bis(diethylamino)dimethylsilane, bis(diethylamino)-dimethylgermane, and the 1,2,2,3-tetramethylsila(germa) imidazolidines.[81]

The important Si-N and Ge-N Stretching bands, expected in the region 750-900 cm^{-1}, could not be specifically located because of the proximity of broad $\rho(CH_3)$ bands. Since for dimethylsilyl and trimethylsilyl compounds the strongest $\rho(CH_3)$ band occurs regularly at 850 cm^{-1}, the νSi-N band comprised the broad shoulder near 880 cm^{-1}. In the organogermanium

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spectrum, overlapping denied any distinction of stretching and rocking bands.

In Figures 1.18 and 1.19, the bands at 740 cm^{-1} and 650 cm^{-1} seemingly derived from ν_{asym}Si-C and ν_{sym}Si-C vibrations. Those assignments agreed with Smith's[132] and Tobin's[61] interpretation of the ν_{asym}Si-C mode and contradicted Kriegsmann's[30] assessment. (See the foregoing discussion of the infrared spectra of the N,N'-bis-(trimethylsilyl)xylylenediamines.) In Figure 1.23 the νGe-C bands at 610 cm^{-1} and 585 cm^{-1} were comparable to those of $[(CH_3)_2GeNC_6H_5]_3$ (613 and 578 cm^{-1}), $[(CH_3)_2GeNC_6H_{11}]_3$ (625 and 593 cm^{-1}), and $[(CH_3)_2Ge(NHC_6H_{11})_2]$ (630 and 590 cm^{-1}). Reasons for the observed shifts in νGe-C frequencies were not obvious. Since m-xylylenediamine and cyclohexylamine are strong aliphatic bases, one would have expected these bands for the m-xylylenediamine derivatives to be closer to those of the cyclohexylamine compounds than to those of the aniline derivative; that was curiously not the case.

Infrared spectra indicated that both the organosilicon and organogermanium polymers were quite moisture sensitive. When an organosilicon polymer film on KBr infrared discs had been exposed to moist air for fifteen minutes, the broad bands between 1050-1100 cm^{-1} characteristic of Si-O-Si asymmetric stretching in dimethylpolysiloxanes were intense. The ν_{asym}Si-N-Si band between 850-880 cm^{-1}, strong and broad for the unhydrolyzed polymer, was much reduced in intensity. With exposure of a film of the organogermanium polymer to the air for fifteen minutes, the infrared spectrum was like that expected from superposition of the spectra of m-xylylenediamine and octamethylcyclotetragermoxane.[139] Even the

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139. M.P. Brown, R. Okawara, and E.G. Rochow, Spectrochimica Acta, 16, 595(1960).

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normally weak ν_{sym}Ge-O-Ge bands between 490 and 530 cm^{-1} quickly became apparent.

Contrasts of the dimethylsilyl and dimethylgermyl polymers were more apparent from NMR spectroscopy than from infrared analysis. The organosilicon polymer dissolved quite easily to form a 10% by weight solution in CCl_4. Figures 2.17 and 2.18 show the spectra of material from two different preparations, with different internal standards. Table XIX shows the chemical shifts and integration measured for the peaks in those spectra; the relative integration values expected for a linear polymer are shown in parentheses. The measured integration was then as expected. The integration of the broad NH resonance "sagged" somewhat relative to the others because of the greater time required to pass over the peak. Chemical shifts were most meaningful when cyclohexane was used as the standard. The resonance of the rather acidic CH_2Cl_2 was evidently shifted ($\sim$0.15δ) from its normal position in CCl_4 by interaction with the basic sites of the silylamine.

The dimethylsilyl proton chemical shift of -0.03δ was identical with that reported by Kummer and Rochow[128d] for groups linking linear units and five-membered rings in the ethylenediamine polymers. For the ethylenediamine polymers, that resonance was, of course, only one of three for the dimethylsilyl group. With m-xylylenediamine, formation of eight-membered rings containing the dimethylsilyl group was made impossible by interposition of a vertex of the benzene ring between the two nitrogen-bearing groups. As the accompanying drawing suggests, ring formation would require extremely close approach of the dimethylsilyl group and

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Table XIX

Cyclohexane Internal Standard[140]

Proton Type	Chem. Shift	Integration	
$-(CH_3)_2Si-$	-0.03δ	3.1	(3.0)
-NH-	-0.85δ (center of triplet)	1.0	(1.0)
$-CH_2-$	-3.66δ -3.81δ] doublet -3.94δ]	2.0	(2.0)
$-m-C_6H_4-$	-7.07δ (∿3:1) -7.12δ	2.0	(2.0)

CH_2Cl_2 Internal Standard[141]

Proton Type	Chem. Shift	Integration	
$-(CH_3)_2Si-$	-0.18δ	3.2	(3.0)
-NH-	-1.02δ (center of triplet)	1.0	(1.0)
$-CH_2-$	-3.85δ -3.97δ] -4.10δ] doublet	2.1	(2.0)
$-m-C_6H_4-$	-7.22δ (∿3:1) -7.28δ	2.1	(2.0)

140. Chemical shifts were corrected to refer them to the normal position of cyclohexane at -1.43δ.

141. Chemical shifts were corrected to refer them to the normal position of CH_2Cl_2 at -5.30δ.

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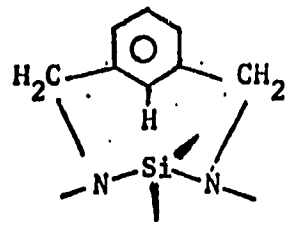
the ring proton:



Chemical analysis, the gross physical properties, and the single $(CH_3)_2Si$ resonance indicated that the polymer was linear.

Figures 2.17 and 2.18 revealed the first structured NH resonance encountered in this research. From the triplet centered at -0.85δ, one obtained a coupling constant of 7.8-8.4 Hz. That constant, like that measured from the methylene resonances in Figures 2.17 and 2.18 (7.8±1.2 Hz) or from the spectra of the bis(trimethylsilyl)xylylenediamines (7.8 Hz) was $J_{CH_2,NH}$. Rather surprisingly, no splitting of the proton resonance by the nitrogen nucleus (J∿50 Hz) was observed. Amine salts, for which protons exchange slowly, sometimes show structured NH resonances. There, however, the principal splitting is produced by the ^{14}N nucleus (J∿50 Hz); only with good resolution is it possible to observe splitting of the three equivalent humps by the protons on adjacent carbon atoms (J∿7 Hz).[131]

The methylene doublet appeared at -3.81δ and -3.94δ, compared with -3.78δ and -3.91δ for IX. A small singlet at -3.66δ, present in the spectra of all reaction products with slightly variable intensity, evidently derived from CH_2 adjacent to un-dimethylsilylated (i.e. terminal) amino groups. The chemical shift was not greatly different from that for m-xylylenediamine itself (-3.73δ). The resonance was not reduced after a four day evacuation of the polymer at 80°C and 0.03 mm Hg.

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Figures 2.19 and 2.20 show NMR spectra of the organogermyl polymer in CCl_4 and acetone-d_6, respectively. As previously indicated, the germanium polymer was only slightly soluble in CCl_4. The first spectrum was obtained with a sample containing small amounts of suspended polymer. The resonance at -0.06δ was rather puzzling. That small chemical shift was atypical of methyl protons in dimethylgermazanes. The peak perhaps derived from methyl groups in undispersed polymer, but, if that were the case, the peak was surprisingly narrow. The three somewhat broadened resonances between -0.25 and -0.47δ occurred as expected for dimethylgermanium protons in organogermanium nitrogen moieties; cf. -0.44δ in $[(CH_3)_2GeNC_6H_{11}]_3$, -0.49δ in $[(CH_3)_2GeNC_6H_5]_3$, -0.21δ in $(CH_3)_3Ge$-(p)-$NHCH_2C_6H_4CH_2NHGe(CH_3)_3$. The multiple dimethylgermanium proton resonances were interpretable in two ways. Protons in dimethylgermanium groups attached to tertiary nitrogens (bonded to one carbon and two germanium atoms) were expected to have greater chemical shifts, by about 0.1δ, than those in groups attached to secondary nitrogens (bonded to one hydrogen, one carbon, and one germanium atom).[142,100] In other words, with partial cross-linking through nitrogen, two broadened dimethylgermanium resonances were expected in the NMR spectrum. However, that cross-linking did not explain the appearance of a third broadened resonance and the sharp resonance at -0.06δ. Chlorine content of the polymer was certainly too slight to allow a noticeable resonance for methyl groups on germanium atoms with attached chlorine. A definite integration of the resonances in Fig. 2.19 was not obtained. However, the ratio of dimethylgermyl to phenyl (or methylene) protons was definitely larger than the

142. C.R. Kruger and E.G. Rochow, J. Polym. Sci., Part A, 2, 3179(1964).

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Table XX

Proton Type	Solvent CCl_4 Chem. Shift	Integration
$-(CH_3)_2Ge-$	-0.06δ -0.25δ -0.38δ -0.47δ	2.3 (uncertain)
-NH-	-1.1δ	?
$-CH_2-$	-3.76δ -4.16δ -4.72δ	1.0
$-m-C_6H_4-$	-7.06δ	1.0

Proton Type	Solvent acetone-d_6 Chem. Shift	Integration
$-(CH_3)_2Ge-$	-0.48δ	2.5-3.0 (uncertain)
-NH-	?	?
$-CH_2-$	-4.37δ	0.9
$-m-C_6H_4-$	-7.16δ	1.0

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value of 1.5/1 expected for a linear polymer. Integration of a Varian T-60 spectrum reproduced the value of 2.3/1. The integration indicated that the polymer was approximately 50% cross-linked through nitrogen, that about 50% of the m-xylylenediamine in a linear polymer had been "split out," presumably thermally, to yield cross-linked material. That estimation of cross-linking conflicted with the values of 20-25% estimated from elemental analysis and with the fact that only 16% of the initially added m-xylylenediamine was recovered. With change to the mixed "solvent" system of $CHCl_3$ and CCl_4, in which the polymer was slightly more soluble, the pattern of resonances was the same, but the methylgermanium resonances appeared at -0.31, -0.48, and -0.60δ, the methylene resonances at -3.84, -4.24, and -4.81δ, and the phenyl resonance at -7.19δ. The shifts which occurred with change of solvent were far from uniform. Finally, with benzene as "solvent" the pattern of dimethylgermanium resonances was much more complicated; six distinct resonances appeared between -0.24 and -0.58δ. The pattern of the methylene and phenyl resonances was the same in all solvents. Spectra in benzene and $CHCl_3/CCl_4$ suggested that the resonances at -3.84 and -4.24δ comprised a doublet and that the -4.81δ peak was an isolated singlet. However, assessment of the -3.84 and -4.24δ resonances as a doublet implied an unacceptably large $J_{CH_2,NH}$ coupling 24.0±1.2 Hz. That constant was 7.8 Hz for the m-xylylenediamine-dimethylsilyl polymer. The broadened, multiple dimethylgermanium proton resonances and the three methylene resonances observed in CCl_4, $CHCl_3/CCl_4$, and benzene perhaps resulted primarily from the presence of undissolved polymer. In the solid material, some germanium atoms probably existed with

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coordination greater than four. Lewis-base coordination of m-xylylenediamino nitrogen atoms with nearby, but non-adjacent germanium atoms would increase the germanium coordination number, result in complicated, broadened NMR resonances, and increase the rigidity of the bulk polymer through effective cross-linking. The principal cross-linking, however, obviously occurred through tertiary nitrogens.

The organogermanium m-xylylenediamine polymer dissolved readily in acetone-d_6. As shown in Fig. 20 and Table XX, a single sharp dimethylgermanium resonance appeared at -0.48δ. A single, somewhat broadened methylene resonance occurred at -4.37δ. But for the fact that the ratio of dimethylgermanium and methylene resonances was approximately 2.5-3.0/1, this spectrum would have suggested a linear polymer. Additional experimental work must be done to determine why the acetone produced such simplification of the polymer NMR spectrum.

Observation of a single methylene resonance seemingly indicated that exchange of the amino hydrogen was more rapid in the basic ketonic solvent than in CCl_4 or benzene and that coupling of the methylene and amino proton spins was small. Insertion of the ketone carbonyl group into the Ge-N bond, if it occurred, would at least at low resolution remove the chemical shift distinction between dimethylgermanium groups which had been bonded to secondary and tertiary nitrogens. However, no precedence exists for such insertion of the carbonyl group of a simple ketone. Satge, Lesbre, and Baudet[143] reported insertion of CO_2, CS_2,

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143. J. Satgé, M. Lesbre, and M. Baudet, Compt. Rend. (Paris), Ser. C, 259, 4733(1964).

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C_6H_5NCO, and C_6H_5NCS into the Ge-N bond of dialkylaminotrialkylgermanes to form dialkylcarbamates, dialkyldithiocarbamates, substituted ureas, and substituted thioureas. E. Abel[144] observed insertion of the carbonyl group of hexafluoroacetone into the silicon-phosphorus and silicon-sulfur bond; e.g.

$$(CH_3)_3SiP(C_6H_5)_2 \longrightarrow (CH_3)_3SiOCP(C_6H_5)_2 \quad \text{and}$$

$$(CH_3)_3SiCOP(C_6H_5)_2$$

$$(CH_3)_3SiSSi(CH_3)_3 \longrightarrow (CH_3)_3SiOC\text{-}S\text{-}C\text{-}OSi(CH_3)_3$$

No reaction was found with acetone and hexachloroacetone. Ketones react[145] with organosilyl-substituted alkali metal amides, but without insertion into the silicon-nitrogen bond; e.g.

$$C_6H_5CC_6H_5 + Na^{\oplus}N^{\ominus}(SiR_3)_2 \longrightarrow C_6H_5\text{-}C(ONa)(SiR_3)\text{-}N(C_6H_5)(SiR_3) \longrightarrow$$

$$Na^{\oplus}O^{\ominus}SiR_3 + (C_6H_5)_2C{=}N\text{-}SiR_3$$

144. E. Abel (University of Bristol, England), "Organometallic Bases", Inorganic Seminar, Massachusetts Institute of Technology, July 3, 1967.

145. U. Wannagat, Advan. Inorg. Chem. Radiochem., 6, 225(1964).

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In summary, NMR spectra and elemental analysis showed that the m-xylylenediamine-dimethylgermanium polymer was significantly cross-linked through tertiary nitrogen. The NMR analysis indicated approximately 50% cross-linking and chemical analysis approximately 25%. That cross-linking was responsible for the much greater rigidity of the germanium polymer as compared with the organosilicon compound.

The polymers obtained from $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ with p-xylylenediamine were so much like the derivatives of the meta isomer that less extensive discussion is necessary here. Dimethyldichlorosilane and dimethyldichlorogermane were each added slowly to a benzene solution of p-xylylenediamine held near 0°C by an ice bath. Following ten hours of stirring at room temperature under an argon atmosphere, the direct aminolysis was completed by refluxing near 80°C for four hours. In all reactions, the diamine was present in small excess (1-5 mole %) of the amount dictated by equation 7. With an inert atmosphere filtration of the by-product p-xylylenediamine dihydrochloride and brief washing with benzene, the weight of the halides was found to be about 10% too high. The polymeric material trapped in the halides was removed by repeated washing with sodium-dried benzene. The yield of hydrochloride was then 95-100%. When no more than a 1% excess of p-xylylenediamine had been used in the organosilicon reaction, no distillable liquid was obtained in an attempted vacuum distillation of the product. The polymer, with essentially the same gross properties as observed for the meta isomer, was obtained in 95% yield (assuming complete aminolysis but ignoring terminal groups). With $(CH_3)_2GeCl_2$, 6% of the original p-xylylenediamine (added in 1 mole% excess) was recovered in vacuum distillation. Above 100°C, a milky white,

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viscous, scarcely mobile organogermanium polymer existed in the distillation flask. At room temperature, the polymer formed an immobile plug with a rather slippery surface. As with the m-xylylenediamine polymer, this material was inelastic and intractable (not easily pulled apart or cut). The polymer was obtained in 85-95% yield from several reactions. Areas of the polymer which were in direct contact with a glass surface charred significantly with heating above 250°C in vacuum.

Analytical results for the organosilyl and organogermyl polymers were as follows:

$(CH_3)_2Si$: p-xylylenediamine

	%C	%H	%Si	%N
Found:	62.61	8.49	13.75	
Calc'd: (for infinite linear polymer)	62.43	8.40	14.61	14.56
Calc'd: (for 10 unit polymer terminated by xylylenediamine groups)	63.00	8.39	13.64	14.97

$(CH_3)_2Ge$: p-xylylenediamine

	%C	%H	%Ge	%N
Found:	47.12	6.31	34.6	
Calc'd: (for infinite linear polymer)	50.70	6.83	30.64	11.83
Calc'd: (for a fully cross-linked polymer, $[-Ge(CH_3)_2-NCH_2C_6H_4CH_2N]_n$ with $(CH_3)_2Ge-$ on the N)	42.57	6.26	42.89	8.28

For the organosilicon polymer, the analytical results resembled those for the m-xylylenediamine polymer and supported an assumption that the polymer was linear. A single cryoscopic molecular weight determination

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in benzene provided a value of 2475, similar to that (2580) for the m-xylylenediamine polymer. Once again, the analytical results spoke for partial cross-linking of the organogermanium polymer. The germanium and carbon analyses suggested 32% and 56% cross-linking, respectively. With the likelihood that the carbon analysis was the more accurate of the two, cross-linking appeared to be significantly greater for the p-xylylenediamine polymer than for that involving the meta isomer.

The infrared spectrum of the p-xylylenediamine-organosilicon polymer, shown in Fig. 1.21, was scarcely distinguishable from that of the m-xylylenediamine polymer (Fig. 1.18 and 1.19; Table XVIII). In Fig. 1.21, two bands at 1510 and 1480 cm^{-1} resulted from the stretching of the para-substituted benzene ring; the meta-substituted ring showed the expected[126] sharp band at 1485 cm^{-1}. A band at 1018 cm^{-1} was much sharper in Fig. 1.21 than in Fig. 1.18. Since the origins of this band were unknown, the observed distinction was unexplained.

The infrared spectrum of the p-xylylenediamine-organogermanium polymer (Fig. 1.22) was slightly different from that of the m-xylylenediamine polymer (Fig. 1.23; Table XVIII). In the 4000-1300 cm^{-1} region, the better, more reproducible spectrum was obtained with a CCl_4 solution. That spectrum permitted direct comparison with Fig. 1.23. The single, broadened absorbance near 1600 cm^{-1} in Fig. 1.22 resulted from overlap of the δN-H band and at least one benzene-ring stretching band. As noted previously, the δN-H and benzene-ring bands were partly resolved for the meta polymer, with the δN-H band occurring at quite high energy (1650 cm^{-1}). Recording of satisfactory thin film spectra of the organogermanium polymer was difficult. In Fig. 1.22, scan 1A indicated that

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considerable hydrolysis had occurred though the sample was prepared in a glove bag. The three high wave-number bands (νN-H and 2xδN-H) of p-xylylenediamine were observed. Between 500 and 600 cm^{-1}, a ν_{sym}Ge-O-Ge band (525 cm^{-1}) and a Ge-C stretching band (600 cm^{-1}) characteristic of dimethylgermoxanes were apparent. Scan 2A of Fig. 1.22 derived from a film in which hydrolysis was minimal or absent. Except for small differences in relative peak intensity, the spectra of the meta and para polymers between 400 and 1300 cm^{-1} were the same. The broad ν_{asym}Ge-N-Ge and $\rho(CH_3)$ bands between 750-850 cm^{-1} seemingly obliterated some bands (out-of-plane hydrogen bending) which usually distinguish meta and para substituted benzene rings.[126]

NMR spectroscopy provided further evidence for the similarity of the m- and p-xylylenediamine polymers. Spectra of the organosilicon material are shown in Figs. 2.21 and 2.22 and of the organogermanium product in Figs. 2.23-2.24. Data on chemical shift and integration are listed in Table XXI. The relative integration values expected for a linear polymer are shown in parentheses.

For the easily-soluble organosilicon compound, the chemical shifts of the dimethylsilyl, amino, and methylene protons were the same as for the meta product within experimental error. As in the previously considered case, evacuation did not reduce the size of the methylene resonance at -3.67δ. This writer had no satisfactory explanation for the unexpectedly complicated phenyl resonances. A broadened peak at -7.05δ was partly resolved on the high field side of the sharp resonance at -7.10δ. The high field peak seemed too prominent to derive from phenyl

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Table XXI

CCl_4 Solution; Cyclohexane Internal Standard[146]

Proton Type	Chem. Shift	Integration
$-(CH_3)_2Si-$	-0.04δ	3.0 (3.0)
-NH-	-0.85δ (center of triplet)	0.9_7 (1.0)
$-CH_2-$	-3.67δ -3.80δ] doublet -3.93δ]	1.9 (2.0)
$-p-C_6H_4-$	-7.05δ -7.10δ	2.0 (2.0)

CCl_4 Solution-Suspension; TMS Internal Standard

Proton Type	Chem. Shift[147]		Integration
$-(CH_3)_2Ge-$	-0.22δ] sharp -0.23δ]		
	-0.28δ] broadened -0.40δ] "triplet" -0.48δ]	-0.27δ] -0.39δ] -0.48δ]	2.1
-NH-	-1.1δ	?	
$-CH_2-$	-3.78δ] apparent -4.20δ] doublet -4.74δ	-3.77δ] -4.20δ]	1.0
$-p-C_6H_4-$	-7.11δ -7.19δ	-7.06δ	1.0

Acetone-d_6 Solution; TMS Internal Standard

Proton Type	Chem. Shift	Integration
$-(CH_3)_2Ge-$	-0.50δ	2.1

146. Chemical shifts were corrected to refer them to the normal position of cyclohexane at -1.43δ.

147. The first column of chemical shift data derived from Fig. 2.24 and the second from Fig. 2.25 (T-60 spectrum). The estimated error in the T-60 data is about ±0.03δ.

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Table XXI Contd.

Acetone-d_6 Solution; TMS Internal Standard

Proton Type	Chem. Shift	Integration
-NH-	-	-
$-CH_2-$	-4.37δ	0.9
$-p-C_6H_4-$	-7.17δ	1.0

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protons in terminal groups. At any rate, one would not have expected such a sizeable chemical shift difference between phenyl protons in terminal and nonterminal groups. The reader is reminded that the same complicated phenyl resonance was reported earlier for N,N'-bis-(trimethylsilyl)-p-xylylenediamine (compound X). In the phenyl region, Figs. 2.21, 2.22, and 2.28 are virtually identical. Within experimental error, overall integration of the organosilicon polymer spectrum indicated that the polymer was linear.

For the organogermanium polymer, Figs. 2.24 and 2.25 demonstrated that the details of the spectrum in CCl_4 depended on the degree of dissolution of the polymer. When the sample had remained in an NMR tube for two hours (Fig. 2.25), a seemingly obvious methylene doublet was present. With the freshly prepared sample (Fig. 2.24), the structure of the methylene was less apparent. The coupling constant $J_{CH_2,NH}$ obtained from Fig. 2.25 was 25.8±1.2 Hz, in fair agreement with the value of 24.0±1.2 Hz suggested tentatively for the m-xylylenediamine-dimethylgermyl polymer. These constants are unacceptably large for coupled amino and methylene protons. Discussion follows in Chapter IV.

The chemical shifts listed for the para polymer were in approximate but not perfect agreement with those given in Table XX for the meta polymer. The dimethylgermyl proton resonances were perhaps the same in Figs. 2.24 and 2.25 in spite of the apparent differences. Resolution with the Varian HA-100 was much better than with the T-60. (In Figs. 2.25, the peaks at -0.99δ, -1.26δ, and -2.59δ were artifacts.)

As in the meta case, the p-xylylenediamine-dimethylgermyl polymer

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dissolved readily in acetone-d_6 to produce a simple NMR spectrum (Fig. 2.23). Within experimental error, chemical shifts were the same as in Fig. 2.20. The integration shown in Figs. 2.23 and 2.25 was consistent. It suggested 40% cross-linking of the polymer through tertiary nitrogen.

When the mixture of xylylenediamine isomers (about 70% meta and 30% para) marketed by the Japanese firm Showa Denko, K.K. was combined with $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$, the polymeric products obtained were quite indistinguishable from those made with each of the pure isomers. The infrared and NMR spectra of the three product types were so similar that at least at low resolution, it was not possible to discover differences among the materials. These similarities made the different characteristics of the products with o-xylylenediamine even more striking.

The writer's association with the reaction products of $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ with o-xylylenediamine was not pleasant. He quickly learned that the liquid organosilicon products were extremely moisture sensitive, the resinous organogermanium pro..cts less so. Earlier in this chapter, the striking instability of the amine itself was mentioned. Particularly with exposure to light (and presumably in the presence of traces of oxygen), the amine first yellowed, then turned brown-black, and evolved easily-detectable amounts of ammonia. The reagent used with the organochlorometalloids was made "water white" by fractional distillation immediately prior to reaction. However, the distillable liquid products yellowed during vacuum distillation and turned orange with standing in an inert atmosphere. Products which underwent partial hydrolysis quickly blackened, probably from decomposition of the freed amine. While the organogermanium products seemed less sensitive, their resinous character

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and low solubility in common organic solvents made characterization difficult. For the foregoing reasons, the description of the o-xylylenediamine products is rather tentative.

The direct aminolysis of 0.05 mole $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$ by 0.1 mole of o-xylylenediamine were performed in diethylether either at 0°C or room temperature. With the assumption that one mole of o-xylylenediamine dihydrochloride formed for each mole of reacting organochlorometalloid, yields of the dihydrochloride were about 90-95% after fifteen-hour reaction periods. Following vacuum distillation of the organosilicon crude product, distillable liquids and a nonvolatile brown polymeric residue amounted to 85% of the product weight (9.62 g) obtainable from complete aminolysis. Just under half (47.5%) of the product was volatile and was obtained in three liquid fractions:

1) 70-80°C, 0.04 mm Hg, 1.19 g
2) 81.5-90°C, 0.05 mm Hg, 2.42 g
3) 90-115°C, 0.04 mm Hg, 0.96 g

The brown residue was not characterized. In the organogermanium case, the total product weight after distillation was 10.70 g (91% of theory), but only 29% of this was obtained in two volatile fractions:

1) 100-105°C, 0.45 mm Hg, 0.72 g
2) 105-110°C, 0.45 mm Hg, 2.35 g

Though initially viscous liquids, the volatile organogermylamine fractions shortly solidified to give orange, brittle resins. Most of the product existed as a nonvolatile, dark brown, brittle resin, the properties of which were not investigated.

Figure 1.20 shows the infrared spectrum of the middle distillation

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fraction from the organosilicon reaction. The principal absorption bands with their tentative assignments are listed in Table XXII. Such broad bands occurred between 700 and 1100 cm^{-1} that definite assignments could not be made in that important finger-printing region. Assignments were made with reference to the spectrum of the parent amine (Fig. 1.15, Table X), the previously listed papers on organosilicon infrared spectra,[30,61,132] and the spectra of the m- and p-xylylenediamine polymers. In this spectrum, the principal νN-H band at 3375 cm^{-1} possessed rather low intensity relative to the shoulder at 3290 cm^{-1}. More importantly, both of these bands occurred at about 20 cm^{-1} lower frequency than for the m- and p-xylylenediamine polymers, but at higher frequency (by about 20 cm^{-1}) than for o-xylylenediamine. Presumably because of intramolecular hydrogen bonding, the νN-H bands for o-xylylenediamine are normally at lower energy than for the meta and para isomers (see Table X). For the compound currently under consideration, the frequency lowering relative to the absorbances for the m- and p- compounds perhaps implied some residual intramolecular hydrogen bonding. On the other hand, it perhaps meant that less Si-N dπ-pπ bonding existed in this compound, that the nitrogen pyramid was less flattened, and that the nitrogen basicity was relatively high. Notably, the νN-H frequencies for N,N'-bis-(trimethylsilyl)-o-xylylenediamine were just as high as for the m- and p- compounds. Systematic measurements of the nitrogen basicities within these series of analogous compounds should be made in future research.

The identifiable bands in the infrared spectrum were those expected of a polymer containing dimethylsilyl and o-xylylenediamino moieties. The

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Table XXII

Oil from $(CH_3)_2SiCl_2$ and o-xylylenediamine

cm^{-1}	Assignment
3375(m) 3290(sh)	νN-H
3050(m) 3005(m)	νC-H aromatic
2940(s)	$\nu_{asym}(CH_3)$
2880(m)	$\nu_{asym}(CH_2)$ and $\nu_{sym}(CH_3)$
2840(m)	$\nu_{sym}(CH_2)$
1595(bd,m)	δN-H
1475(m)	benzene ring mode
1445(m)	$\delta(CH_2)$ and benzene ring mode
1390(s)	$\delta_{asym}(CH_3)$
1265(vs)	$\delta_{sym}(CH_3)$
1180(m)	unassigned
1124(s) 1078(vs) 1044(s)	ν_{asym}N-Si-N, ν_{asym}Si-N-C, and νC-N
1025(sh)	unassigned
965(m) 936(m)	unassigned
∿880(sh)	ν_{asym}Si-N-Si
845(vs,bd)	$\rho(CH_3)$
795(vs,bd)	$\rho(CH_3)$
765(vs) 750(sh)	out-of-plane hydrogen bending on benzene ring and ν_{asym}Si-C

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Table XXII Contd.

cm^{-1}	Assignment
680(m)	unassigned
646(m)	ν_{sym}Si-C
607(m)	unassigned

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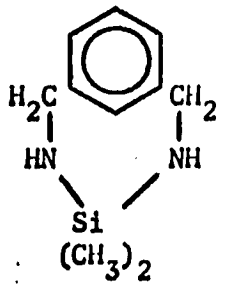
broad bands between 750 and 1100 cm^{-1} seemingly favored a polymeric material. However, from the infrared, the monomeric compound



was not excluded. The fact that the material was a volatile liquid or mixture of liquids further suggested monomeric character. The infrared spectra of the fractions preceeding and following the 81.5-90°C fraction were virtually identical with Fig. 1.20 though the boiling points were different. Infrared spectroscopy then neither identified the main fraction nor provided an index of purity.

The NMR chemical shift and integration data for the 81.5-90°C fraction are shown in Table XXIII. The integration values expected for a 1:1 o-xylylenediamine-dimethylsilyl compound are in parentheses.

Table XXIII

Oil from $(CH_3)_2SiCl_2$ and o-xylylenediamine

Proton Type	Chem. Shift		Integration	
$(CH_3)_2Si$	-0.06δ		3.1	(3.0)
NH	-1.10δ		?	(1.0)
CH_2	-3.73δ -3.97δ	apparent doublet	2.0	(2.0)
o-C_6H_4	-6.94δ -7.09δ	~1:1	2.0	(2.0)

Integration clearly demonstrated that the middle fraction contained 1:1 product; the results for the topmost fraction were nearly identical. Two

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aspects of these spectra were puzzling. An apparent doublet occurred at -3.73 and -3.97δ, though some very low intensity fine structure suggested that the assumed doublet might be an oversimplification. One consequence of the assumption was an unusually large $J_{CH_2,NH}$ coupling constant of 14.4±1.2 Hz. This was the first case of apparent variation of $J_{CH_2,NH}$ from 7.8 Hz for the organosilyl derivatives of the xylylene-diamines; as for the organogermanium compounds, the splitting probably did not result from methylene and amino proton coupling. The NH resonance was considerably more narrow in these spectra than in Figs. 2.17, 2.18, and 2.21, indicating that exchange of the amino protons was rapid and that coupling of amino and methylene protons should have been weak or absent. The writer notes that a nearly resolved, strong shoulder existed on the high field side of each of the -3.73 and -3.97δ resonances. This situation is discussed along with the previously cited organogermyl examples in Chapter IV.

Since neither infrared nor NMR spectroscopy adequately identified these liquid fractions, mass spectrometry was employed to assess the molecular weight of the species. The liquids were inserted "directly" on the tip of a ceramic probe, at 120°C and 140°C. Though the m/e 192 peak (mass of the monomeric, seven-membered ring) was present for the 81.5-90°C fraction, the peak was less intense than several at higher mass (m/e 207, 222, 253, 311). For that fraction, the highest mass peak occurred at m/e 384, at the mass of the molecule:

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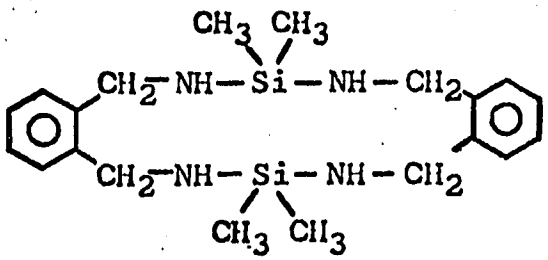

Since exact mass measurements were not made, the presence of that species was not proven and is merely suggested here. For the 90-115°C distillation fraction, prominent high mass peak appeared at m/e 207, 222, 249, 264, 281, 296, 325, 355, 370, 383, 399, 429, 502, and 576. The highest mass peak (m/e 576) perhaps derived from the cyclic species $[-Si(CH_3)_2NHCH_2\text{-}o\text{-}C_6H_4CH_2NH-]_3$ with a molecular weight of 576. Determination of the relative abundances of various species in these spectra was not possible. The writer did not observe the simple pattern characteristic of species with several silicon atoms (an intense peak from species containing only ^{28}Si followed by minor "heavy isotope peaks"). The envelopes of species differing by only a few mass units (different numbers of hydrogens) overlapped considerably. The mass spectra indicated that the volatile organosilicon material was at least not primarily the cyclic monomer, but more likely a mixture of cyclic, polymeric species. The o-xylylenediamine product was then not so different from the meta and para products. The ortho isomer apparently more easily formed low molecular weight cyclic materials. Resinous, nonvolatile polymer, which was less tractable than the m- and p- polymers, comprised much of the

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product. The facile decomposition of the o-xylylenediamine made investigation of the dark brown polymer undesirable.

The orange resin which had been obtained from the organogermylamine crude product by vacuum distillation was freed of most of the coloration and left as a yellow-white gum by washing with sodium-dried benzene and ether. The resin itself was not soluble enough in such solvents as benzene, CCl_4, $CHCl_3$, CH_2Cl_2, cyclohexane, and pyridine to permit measurement of an NMR spectrum. The texture of the material was like that of the p- and m-xylylenediamine-dimethylgermanium polymers. The infrared spectrum was much like that for the polymer involving m-xylylenediamine (Fig. 1.23). Three rather sharp bands occurred between 1575 and 1650 cm^{-1}. The most intense of these, at 1635 cm^{-1}, was undoubtedly the δN-H band, and the others were benzene ring stretching bands. Moderately strong $\delta_{asym}(CH_3)$ and $\delta_{sym}(CH_3)$ absorbances for the methyl group on germanium appeared at 1415 cm^{-1} and 1240 cm^{-1}, respectively. The $\delta_{sym}(CH_3)$ band was unusually broad, perhaps suggesting that dimethylgermyl groups existed in several different environments in the polymer. Three strong, broad bands between 750 and 900 cm^{-1} were well-defined for this compound. At 760 cm^{-1}, one found the band characteristic of out-of-plane hydrogen bending on an ortho substituted ring. In this polymer, that band did not overlap the absorbances at 805 cm^{-1} (probably $\rho(CH_3)$) and 860 cm^{-1} (probably ν_{asym}Ge-N-Ge). The Ge-C asymmetric and symmetric stretching bands occurred at 624 and 590 cm^{-1}.

Because of the unstable character of free o-xylylenediamine, the investigator attempted reaction of o-xylylenediamine dihydrochloride

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with $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ in triethylamine. Reaction proceeded approximately according to the following equation:

$$(CH_3)_2MCl_2 + H_3NCH_2(o\text{-}C_6H_4)CH_2NH_3^{++}(Cl^-)_2 + 4Et_3N \xrightarrow{\Delta}$$

$$\frac{1}{x}[(CH_3)_2MNHCH_2(o\text{-}C_6H_4)CH_2NH]_x + 4Et_3NH^+Cl^- \qquad M=Si, Ge$$

The method was only semi-satisfactory because of difficulty in preparing completely dry dihydrochloride. With addition of 0.05 mole of $(CH_3)_2SiCl_2$ to a solution-suspension of o-xylylenediamine dihydrochloride in Et_3N, aminolysis occurred rather easily. Following heating of the reaction mixture at 64°C for 13 hours, triethylamine hydrochloride, containing only traces of the xylylenediamine dihydrochloride, was isolated in 94% yield. Even before investigation of the products was commenced, the recovery of over one gram of o-xylylenediamine in vacuum distillation indicated that considerable hydrolysis had occurred. The infrared spectrum of the small amount of volatile dimethylsilylamine product was like that discussed previously (Fig. 1.20). The fact that aminolysis occurred at all was fascinating. When o-xylylenediamine dihydrochloride was refluxed with excess Et_3N for twelve hours the o-xylylenediamine dihydrochloride was recovered quantitatively. That result simply confirmed previous reports that o-xylylenediamine was a stronger base than Et_3N. Given the stability of the dihydrochloride in its solid lattice, the driving force for aminolysis would not seem to be as great as in simple aminolysis. Except for the difficulty in obtaining an anhydrous reagent, the method would be more efficient than simple aminolysis for the preparation of derivatives of o- and p-xylylenediamine. The Gabriel synthesis of the amines involves initial preparation of the hydrochlorides.

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4. Experimental

A. Preparation of o- or p-xylylenediamine by a modified Gabriel synthesis[119]

The equations outlining the procedure are listed near the beginning of this Chapter. The small scale preparation described here was scaled up without difficulty to produce several hundred grams of product. Without prior purification, the organic dihalide α,α'-dichloro-o-xylene or α,α'-dichloro-p-xylene (25.0 g, 0.143 mole) (Matheson, Coleman, and Bell) was dissolved in 350 ml of dimethylformamide. Potassium phthalimide (54.4 g, 0.294 mole, 2.8 mole% excess) (Eastman) was added to the halide solution in a 500 ml, three-necked flask equipped with a reflux condenser and paddle stirrer. In the case of the ortho dihalide, reaction began almost immediately with mild evolution of heat. For the para dichloride, heating to about 50°C induced reaction. The reaction mixtures were heated at 60°C and stirred vigorously for 18 hours. The large quantity of white solid α,α'-(diphthalimido)xylene was washed with 6x50 ml of water and 6x50 ml of chloroform to remove potassium chloride, unreacted potassium phthalimide, and soluble organic impurities (xylenols, etc.). The diphthalimide derivative was almost completely insoluble in chloroform. The solid (54.4-55.3 g, 97-98% yield) was dried superficially by suctioning on a fritted glass filter and then heated for several hours at about 50°C in a drying oven.

The diphthalimide solid was suspended in 300 ml of absolute ethanol in a 1 liter, three-necked flask equipped with paddle stirrer, reflux condenser, and dropping funnel. Hydrazine hydrate, about 95% hydrazine

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(9.5 g, small excess), was then added through the dropping funnel. The reaction had a lengthy induction period. During vigorous stirring and heating at 60°C for about 1/2 hour, nothing seemingly happened. Then stirring abruptly became difficult as reaction with the hydrazine occurred. Even without watching the flask, one could hear the performance of the stirrer change suddenly. The amount of ethanol in the flask was approximately doubled, and the reaction mixture was stirred and refluxed near 78°C for 10 hours. Experience showed that, particularly in the case of the para reaction, additional hydrazine hydrate (arbitrarily again 9.5 g) was needed to drive the reaction to completion.

Assuming complete reaction in the previous step, approximately 0.3 mole (5.4 g) of water, with an acid catalyst, was required to destroy the hydrazine adduct. That amount of water was added along with 0.28 mole of hydrochloric acid (23.3 ml of 12 M HCl), sufficient acid to convert all of the freed amine to the dihydrochloride. An immediate rise in temperature from room temperature to about 40°C was observed. The mixture was refluxed at 78°C for three hours. The precipitated 2,3-dihydrophthalazinedione ("hydrazide"), completely insoluble in the alcohol, was suction filtered and washed with copious amounts of water to remove all xylylenediamine dihydrochloride. Infrared spectroscopy showed that the hydrazide was easily freed of the dihydrochloride.

Water pump vacuum distillation (7-10 mm Hg) of the considerable volume (500-1000 ml) of water wash was then performed until the dihydrochloride began to crystallize. A first crop of dihydrochloride was obtained by refrigeration and then rapid filtration. Acetone was then added to the aqueous filtrate to force out additional dihydrochloride. All crops of

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the dihydrochloride were dried for at least a day in a round-bottomed flask under oil pump vacuum. Gentle heating (not over about 80°C; decomposition occurred at higher temperatures) of the flask assisted in that evacuation. Although the latter crops of dihydrochloride were likely not as pure as the initial crop, the infrared spectra of all crops were the same. The yield of hydrazide by-product from the reactions was usually 93-95%. The yield of dry o- or p-xylylenediamine dihydrochloride from the last reaction was 81-89%. A gravimetric chloride determination demonstrated, with only 0.1% error, that the halide was in fact the dihydrochloride. With addition of the dihydrochloride to excess 40% aqueous sodium hydroxide, most of the p-xylylenediamine separated from the aqueous layer. From this point on in the purification, exclusion of carbon dioxide was vital to avoid irreversible formation of carbonates. Extraction of the water layer with benzene or dichloromethane allowed quite complete separation of p-xylylenediamine. The ortho isomer was surprisingly soluble in the concentrated hydroxide solution; repeated extraction with benzene was necessary to gain anything approaching quantitative isolation of o-xylylenediamine. Vacuum distillation of the combined, dried (anhydrous Na_2SO_4) benzene and CH_2Cl_2 extracts yielded the free amines.

B. Preparation of N,N'-bis-(trimethylsilyl) and N,N'-bis(trimethylgermyl) derivatives of o-, m-, and p-xylylenediamine.

The general method of preparation of the N,N'-bis-trimethylmetallated xylylenediamines is outlined here. No significant variation from this procedure was necessary in individual cases. Trimethylchlorosilane

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(General Electric) was purified by a single, one-plate distillation. Trimethylbromogermane, prepared as outlined in Appendix II, was purified by fractional distillation with a four-inch Mini-Lab column filled with stainless-steel helices.

All reactions were performed in glassware which had been oven-dried at 130°C at least overnight. The o-, m-, or p-xylylenediamine (13.62 g, 0.1000 mole) was dissolved in 100 ml of sodium-dried benzene in a 300 ml, three-necked flask equipped with a reflux condenser and dropping funnel. Stirring was performed magnetically. Trimethylchlorosilane (10.86 g, 0.1000 mole) or trimethylbromogermane (19.76 g, 0.1000 mole) was dripped slowly into the ice-cooled amine solution. Before and during the reaction the system was swept thoroughly with argon. Reaction proceeded approximately according to equation 6 presented earlier in this Chapter. The reaction mixture was refluxed near 80°C for 4-10 hours. The minimum refluxing period was seemingly adequate to force complete aminolysis by these strongly basic amines. The finely dividied xylylenediamine dihydrochloride was usually allowed to settle somewhat before filtration in an inert atmosphere apparatus. Except in the preparation of N,N'-bis-(trimethylgermyl)-p-xylylenediamine, the yields of the xylylenediamine dihydrochlorides from these aminolyses were essentially quantitative. Most of the benzene was removed in distillation at atmospheric pressure. Fractional vacuum distillation, under oil pump vacuum, then yielded the following specific fractions from typical reactions:

a) $(CH_3)_3SiCl$ + m-xylylenediamine (the pressure reading in this distillation was perhaps erroneous).

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1) 135.5-136°C, 0.03 mm Hg, 0.74 g

2) 137-139°C, 0.03 mm Hg, 6.69 g

3) 139-141°C, 0.03 mm Hg, 3.55 g

All three fractions contained primarily N,N'-bis-(trimethylsilyl)-m-xylylenediamine, characterized as stated in the discussion section.

b) $(CH_3)_3SiCl$ + o-xylylenediamine

1) 84-91°C, 0.09 mm 0.86 g

2) 91-92.5°C, 0.075 mm, 10.02 g

3) 95-105°C, 0.075 mm, 0.33 g

Quite pure N,N'-bis-(trimethylsilyl)-o-xylylenediamine was obtained in fraction 2. Characterization of the top two fractions is considered in the discussion section.

c) $(CH_3)_3SiCl$ + p-xylylenediamine

1) 85-89°C, 0.05 mm, 0.87 g (contained some suspended dihydrochloride and also free amine)

2) 95-97°C, 0.05 mm, 3.30 g

3) 97-99°C, 0.05 mm, 6.65 g

The purest N,N'-bis-(trimethylsilyl)-p-xylylenediamine was obtained in fraction 3. The characterization of this material is discussed earlier in this Chapter.

d) $(CH_3)_3GeBr$ + p-xylylenediamine

1) 78-85°C, 0.05 mm, 0.50 g

2) 111-120°C, 0.04 mm, 1.00 g

3) 123.5-125°C, 0.04 mm, 8.05 g

4) 130-140°C, 0.04 mm, 0.60 g

The purest N,N'-bis-(trimethylgermyl)-p-xylylenediamine was obtained

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in fraction 3. The yield of this material was raised to 10.80 g by vacuum distillation of an additional benzene extract of the dihydrobromide. Characterization of the main product is discussed earlier in this Chapter.

C. Preparation of polymers form $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$ and o-, m-, or p-xylylenediamine.

Polymers were formed from $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$ and m- and p-xylylenediamine by simple aminolysis in benzene (see equation 7). For no particular reason, diethylether was used as the solvent for the o-xylylenediamine reactions. Dimethyldichlorosilane (General Electric) was purified by single plate distillation. Dimethyldichlorogermane, prepared by one of the methods discussed in Appendix II, had been previously purified by fractional distillation and sealed in glass vials.

The specific procedure for one reaction of $(CH_3)_2SiCl_2$ with m-xylylenediamine is given here. With no significant variations, all reactions were run in the same fashion. The m-xylylenediamine (28.60 g, 0.2099 mole, 5% excess) was dissolved in 300 ml of sodium-dried benzene in a 1 liter, three-necked flask equipped with a dropping funnel and reflux condenser. All glassware had been oven-dried at 110-130°C at least overnight. Stirring was performed magnetically in a system which was constantly flushed with argon. The $(CH_3)_2SiCl_2$ (12.91 g, 0.1000 mole) was dripped slowly into the ice-cooled amine solution. The reaction mixture was refluxed at 80°C for one hour and then stirred at room temperature overnight. The finely divided dihydrochloride was allowed to settle before filtration in an inert atmosphere apparatus.

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In all polymer preparations, repeated washing of the hydrochlorides with sodium-dried benzene (e.g. 4x50 ml) was essential to remove the polymer from the filtered solid. The dimethylgermanium polymers, in particular, were not very soluble in benzene. Refluxing of the hydrochlorides with 250-500 ml of benzene usually sufficed to remove most of the polymer. Yields of the dihydrochlorides were without exception 95-100%.

Most of the benzene was removed by distillation at atmospheric pressure. An oil pump vacuum distillation then yielded the following specific results:

a) $(CH_3)_2SiCl_2$ + m-xylylenediamine

Distillation yielded 1.25 g of unreacted m-xylylenediamine. Viscous, yellow-white polymer (18.5 g) remained in the distillation pot. Decomposition did not occur up to about 250°C. The characterization of this material is given in the discussion section.

b) $(CH_3)_2GeCl_2$ + m-xylylenediamine

Distillation yielded 2.24 g of unreacted m-xylylenediamine. A rather rigid plug of white organogermylamine polymer (11.25 g) remained in the distillation pot. Above approximately 250°C that portion of the polymer in contact with the bottom of the flask charred slightly. The properties and apparent structure of the polymer are described earlier in this Chapter.

c) $(CH_3)_2SiCl_2$ + p-xylylenediamine

No distillable liquid was isolated in a one-plate vacuum distillation. A few droplets of liquid (probably free amine) were

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present in the distillation head at high pot temperature (> 100°C), but not enough to pass over into a receiving flask. The polymer, much resembling that from the m-xylylenediamine reaction, was isolated in 95% yield (13.7 g). Again, this polymer is characterized earlier in the Chapter.

d) $(CH_3)_2GeCl_2$ + p-xylylenediamine

Free p-xylylenediamine (1.10 g, 6% of the originally added 0.151 mole) was recovered in vacuum distillation. In one reaction, polymer with character much like that described in b) above was isolated in 85% yield (15.0 g).

e) $(CH_3)_2SiCl_2$ + o-xylylenediamine

Infrared spectra indicated that the dihydrochloride was free of product only with repeated washing with benzene and low boiling petroleum ether. The product was strongly trapped in the hydrochloride. With removal of most of the solvent, the crude product was dark brown. In vacuum distillation, one obtained three liquid fractions:

1) 70-80°C, 0.04 mm Hg, 1.19 g
2) 81.5-90°C, 0.05 mm Hg, 2.42 g
3) 90-115°C, 0.04 mm Hg, 0.96 g

The latter two fractions are discussed in more detail earlier in this Chapter. A brittle, brown-black residue (5.05 g) comprised over half of the total product. That material was not characterized.

f) $(CH_3)_2GeCl_2$ + o-xylylenediamine

As in e) above, the writer experienced great difficulty in

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washing the product from the dihydrochloride. From vacuum distillation he obtained two heavy, orange, oily fractions between 100-110°C (0.45 mm Hg) (total 3.07 g). On standing these oils solidified to give orange, brittle resins. Most of the product (7.63 g) existed as a brown-black, brittle resin, the properties of which were not investigated.

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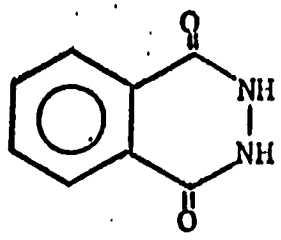
CHAPTER III

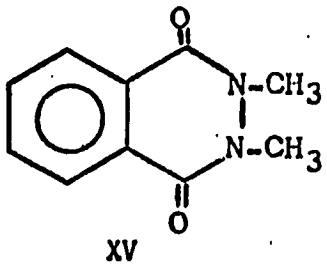
The organic compound 2,3-dihydrophthalazine-1,4-dione, shown below as it is usually written, possesses rather unusual properties. A melting



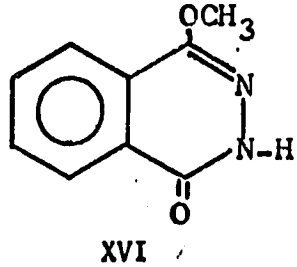
XIV

point of 349°C (without decomposition) and extremely low solubility in almost all organic solvents indicate the presence of strong intermolecular hydrogen bonding in the solid. The material dissolves easily in pyridine but only slightly in other common amines. Concentrations high enough to permit UV studies are possible in alcohol.[143]

Primarily as a result of comparisons of the infrared spectra of 2,3-dihydrophthalazine-1,4-dione (XIV), 2,3-dimethylphthalazine-1,4-dione (XV), and 1-methylphthalazone-4 (XVI), Cheinker and his coworkers[143]



XV



XVI

demonstrated that 2,3-dihydrophthalazine-1,4-dione in fact exists as

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143. J.U.N. Cheinker, T.V. Gortinskaia, and T.P. Sycheva, J. Chim. Phys., 55, 217(1958).

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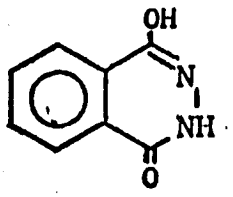
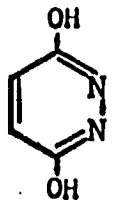
1-hydroxyphthalazone-4 (XVII) in the solid phase. The infrared spectrum

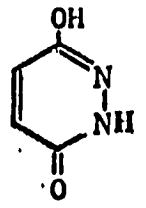


XVII

of XVII, particularly in the carbonyl and N-H stretching regions, is much like that of XVI, but unlike that of the dione (XV). Similarly, the compound commonly written as 1,4-dihydroxypyridazine (XVIII) actually exists as 1-hydroxypyridazone-4 (XIX) in the solid phase. For XIX, intimate -OH···O=C and NH··N hydrogen bonding evidently occurs between closely

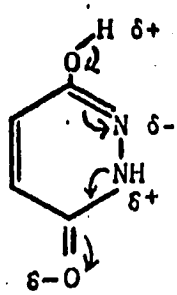


XVIII



XIX

overlapped rings and leads to formation of long molecular chains. No strong carbonyl stretching band appears in the usual region (1630-1660 cm^{-1}) of the infrared spectrum of XIX but a band at 1556 cm^{-1} was assigned to that mode. The authors suggested that in the following "polarized" structure (XX), in the hydrogen-bonded solid, the strength of the carbonyl



XX

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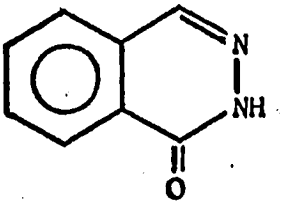
bond approaches that of a C-O single bond.

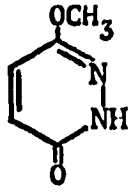
For XVII, the presence of the second ring prohibits the kind of close overlapping possible for XIX and probably leads to somewhat different hydrogen bonding. Cheinker surmised that the bonding was similar to that for phthalazone (XXI). In the infrared spectrum of XVII, an intense



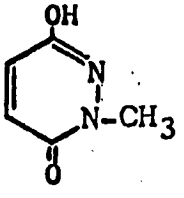
XXI

carbonyl band at 1660 cm^{-1} perhaps indicates that a highly polarized structure (after XX) does not exist in the solid. Since one does not observe infrared bands characteristic of free N-H (3200-3400 cm^{-1}) and O-H (3400-3700 cm^{-1}) groups, but only those of hydrogen-bonded species (3050-3200 cm^{-1}), it is clear that hydrogen bonding does contribute to the stability of the solid lattice.

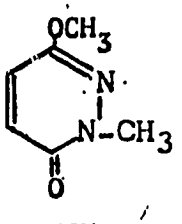
From comparative ultraviolet studies of XVIII (XIX), 1-methoxypyridazone-4 (XXII), 1-hydroxy-3-methylpyridazone-4 (XXIII), 1-methoxy-3-methylpyridazone-4 (XXIV), and 2,3-dimethylpyridazine-1,4-dione (XXV),



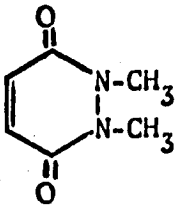
XXII



XXIII



XXIV



XXV

Cheinker and his coworkers concluded[143] that 1,4-dihydroxypyridazine

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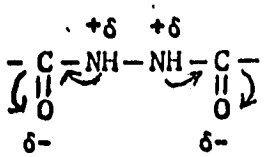
(XVIII) exists primarily as 1-hydroxypyridazone-4 (XIX) in solution as well as in the solid. However, for the compound of immediate interest here, 2,3-dihydrophthalazine-1,4-dione, ultraviolet spectra did not allow distinction between the dioxo and hydroxy-oxo forms. The spectra of XIV (XVII), 1-methoxyphthalazone-4 (XVI), and 2,3-dimethylphthalazine-1,4-dione (XV) were so similar that the authors could not decide between structures XIV and XVII for 2,3-dihydrophthalazine-1,4-dione in solution. In most recent publications about the dione and its chemiluminescing derivatives (e.g. luminol), the structures of the phthalylhydrazides in solution have been represented as involving an equilibrium between the isomers XIV and XVII.[144]

Cheinker postulated[143] that the relative Bronsted acidities of the various possible isomers (dihydroxy, hydroxy-oxo, and dioxo) of 2,3-dihydrophthalazine-1,4-dione define which form occurs in the solid and, particularly, in solution. The dihydroxy form would be more acidic (and less stable) than the dioxo form (K_a for phenols is $\sim 10^{-10}$ and for amides $\sim 10^{-16}$ in aqueous solution). However, in a structure such as



the adjacent positioning of the -C(=O)-NH- groups should enhance the acidity of both groups. The neighboring partial positive charges on the two nitrogens would facilitate departure of protons. The acidity of the dioxo isomer is probably then greater than for the hydroxy-oxo form

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144. E.H. White and D.F. Roswell, Accts. Chem. Research, 3, 54(1970).

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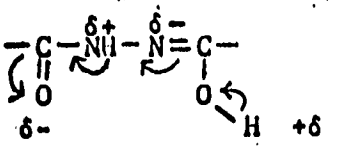
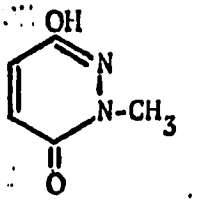
where adjacent positive charges would not be present:



Simply from considerations of acidity, the hydroxy-oxo form would appear to be the most stable of the three isomers. In the solid, the formation of strong hydrogen bonds apparently stabilizes the hydroxy-oxo form.

In a potentiometric acid-base titration of 1-methoxyphthalazone-4 (XVI) in alcohol, Cheinker observed no significant acidity for the compound. With the first addition of base, the pH changed abruptly as it did with addition of base to the pure solvent. In contrast, 1-hydroxy-3-methylpyridazone-4 (XXVI), was titrated as a moderately strong acid with an equivalence point at about pH 8.5. In other words, hydrogen



XXVI

attached to nitrogen was weakly acidic, but that attached to oxygen was easily titrated. The titration curve for 2,3-dihydrophthalazine-1,4-dione was like that for XXVI. The compound reacted as a moderately strong monoprotic acid; addition of a second equivalent of base produced no detectable inflection in the titration curve. These results then suggested that 2,3-dihydrophthalazine-1,4-dione exists as 1-hydroxyphthalazone-4 (XVII) in solution as well as in the solid phase. (The second ionization constant for 2,3-dihydrophthalazine-1,4-dione and its derivatives, e.g. luminol, was found to be no greater than 10^{-13}. The reaction leading to

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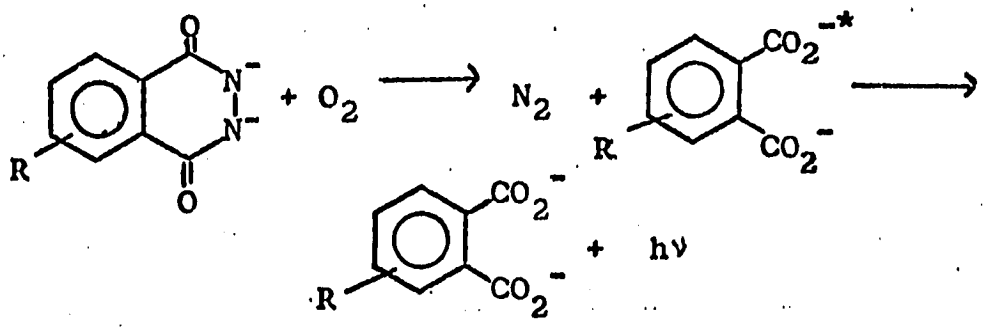
chemiluminescence evidently involves a dinegative ion, but only a low concentration of the ion is present in the reaction mixture.[145] For



most purposes, the compounds may be considered to be monoprotic acids.)

As a basis for the characterization of several organosilyl and organogermyl derivatives of the hydrazide, a study of the infrared spectrum of the parent hydrazide was essential. No thoroughgoing infrared analysis of the hydrazide and its organic derivatives has been performed. Cheinker and coworkers[143] confined their attention to the region between 1500 and 1700 cm^{-1} and even then only discussed the carbonyl bands. The complicated spectrum of 2,3-dihydrophthalazine-1,4-dione is shown in Figures 1.29 and 1.30. Table XXIV is a listing of only those principal infrared bands for which assignments could be tentatively made. In making those assignments, the writer relied upon the discussions of amides and hydrazides by Bellamy,[146] Colthup, Daly, and Wiberley,[147] and Silverstein and Bassler.[148]

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145. F.H. Stross and G.E.K. Branch, J. Org. Chem., 3, 385(1938).

146. L.J. Bellamy, The Infra-red Spectra of Complex Molecules, John Wiley and Sons, New York, 1958, pp. 203-223.

147. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, pp. 223-230, 262-268.

148. R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 1967, pp. 93-99.

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Table XXIV[52,53]

2,3-dihydrophthalazine-1,4-dione

cm^{-1}	Assignment
3155(m) 3120(m) 3055(sh) 3000(s) 2960(sh) 2880(vs)	νN-H (or OH) bonded or νC-H aromatic; in lower region probably νC-H
1655(vs)	νC=O
1610(sh) 1598(m)	νC=O and benzene ring mode
1548(w)	CNH (amide II) band (?) or benzene ring mode
1485(vs)	δN-H (?) or benzene ring modes
1460(w) 1440(w)	benzene ring modes
1310(m) 1300(sh)	C-H deformation (?) (or CNH band, largely νC-N)
1220(m)	CNH band (?)
1267(m) 1160(w) 1020(m)	In-plane hydrogen bending
1085(m)	νC-N (?)
793(m) 782(m)	Out-of-plane hydrogen bending (?)
684(m)	Out-of-plane δN-H
651(w) 629(w)	Amide bands of unknown origin

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The infrared band at 3155 cm^{-1}, first assumed to be a νN-H or νO-H absorption, persisted in all of the organosilyl and organogermyl derivatives without undergoing a significant shift, and therefore was undoubtedly a νC-H band. Any N-H and O-H stretching bands were seemingly buried among the broad absorbances occurring between 2900 and 3100 cm^{-1}. The intense band at 1655 cm^{-1} and probably one of the scarcely resolved bands near 1600 cm^{-1} derived from carbonyl stretching (in-phase and out-of-phase, respectively). The second slightly resolved band likely resulted from benzene ring stretching.

The rather weak band at 1548 cm^{-1} had a puzzling origin. A similar absorbance (1540 cm^{-1}) in the spectrum of a bis(trimethylsilyl) derivative (discussed below) indicated a lack of involvement with N-H bonds, though an N-H deformation (or the "amide II" mode involving the entire CNH group) was expected in that region for the hydrazide. Again, in anticipation of a later discussion, one notes that for the dimethylsilyl polymeric material (see Fig. 1.35) a very sharp, strong absorbance at 1540 cm^{-1} gradually disappeared with exposure of a mull to moist air and, after 18 hours, was replaced by the weak 1548 cm^{-1} absorbance characteristic of the parent hydrazide. That particular striking change did not occur in the spectrum of the bis-(trimethylsilyl) compound, though other evidences of hydrolysis appeared. This difference suggested that the dimethylsilyl and trimethylsilyl compounds possessed somewhat different structures and bonding. For the polymer, the dynamic behavior with hydrolysis indicated a change in the system of CNH bonding (e.g. disappearance of C=N bonds and formation of N-H bonds). The static situation for the bis(trimethylsilyl) derivative suggested that the 1548 cm^{-1} band

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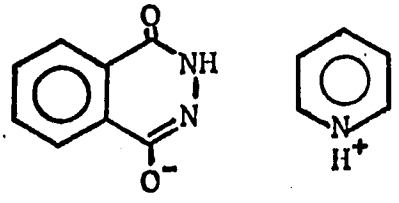
at least partly involved a benzene ring mode. It is possible that the 1540-1548 cm^{-1} band did not have a single origin, but was formed from overlap of several absorbances.

As Table XXIV indicates, the assignment of bands possibly involving the C-N bond were highly uncertain. Colthup, Daly, and Wiberley[147] have noted that in cyclic amides, where the carbonyl and N-H groups are held in a cis relationship, not much interaction of the νC-N and δN-H modes occurs. For such structures, one expects a definite cis δN-H band near 1480 cm^{-1} and a νC-N band near 1300 cm^{-1}. In Figs. 1.29 and 1.30 prominent bands fit that description; whether the description really applies to phthalylhydrazide is a good question.

The NMR spectrum of phthalylhydrazide, recorded with pyridine-d_5 as solvent, comprised only a series of phenyl resonances near -7.0δ. At room temperature the NH proton resonance was evidently too broad for detection at a reasonable spectrum amplitude. The broadness indicated that protons are resident on the nitrogen, but not the oxygen, atoms of phthalylhydrazide; the rate of exchange of the NH protons must be slow. In pyridine, phthalylhydrazide perhaps exists at the soluble pyridinium salt.



In light of the somewhat unusual properties and structure of 2,3-dihydrophthalazine-1,4-dione (henceforth referred to as phthalylhydrazide or the hydrazide), this investigator was interested in what

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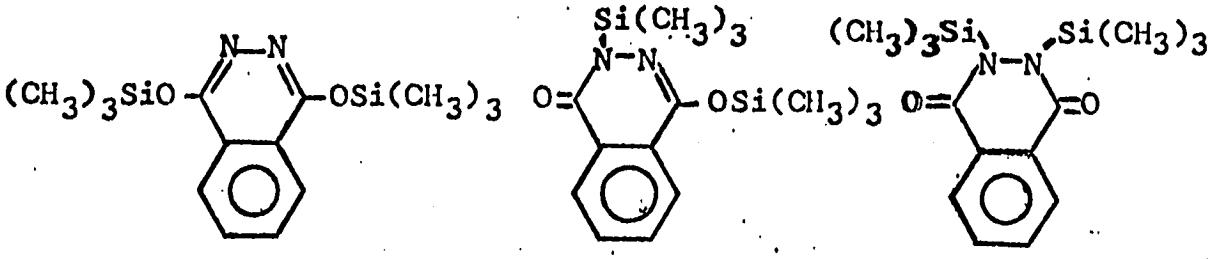
organosilyl and organogermyl derivatives of this compound might be prepared. In a bis-(trimethylsilyl) compound, the hydrazide might be substituted N,N'; O,O'; or N,O. Of the following three structures, the first two seemed most probable for several reasons. For compounds XXVII



XXVII XXVIII XXIX

and XXVIII, the trimethylsilyl groups would be sterically uncrowded. Considerable driving force for the formation of XXVII would seemingly result from formation of a ring possessing some aromatic character. At the same time, formation of two Si-O bonds would release more energy than formation of two Si-N bonds. Since the hydroxy-oxo form of the hydrazide (XVII) is apparently stable, the bis-(trimethylsilyl) derivative of that isomer (XXVIII) might be expected.

For N,N'-bis(trimethylsilyl)phthalazine-1,4-dione (XXIX), the trimethylsilyl groups would necessarily be rather crowded. Figure 10 shows two views of a model of this compound built with space-filling Fisher-Hershfelder models. The models indicated that the compound might be tenable, but that the heterocyclic ring would be distorted and not in the plane of the benzene ring. The symmetry point group of the molecule appeared to be C_2 rather than C_{2v}. Rotation of the trimethylsilyl groups about the Si-N bonds would definitely be restricted. Were this compound to exist, the NMR spectrum would probably not contain a single sharp

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Figure 10. N,N'-bis(trimethylsilyl)phthalazine-1,4-dione

Two views, "side" and "top." Grey = Si; black = C; dark blue = N; light blue = O; orange = H.

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trimethylsilyl resonance even at room temperature, but resonances reflecting the different environments of the methyl protons.

Along with preparation and characterization of a bis-(trimethylsilyl) derivative of phthalylhydrazide, dimethyldichlorosilane and dimethyldichlorogermane were combined with the hydrazide to form low molecular weight solid polymers.

The preparation of the bis-(trimethylsilyl) compound was accomplished by slowly adding 0.10 mole of $(CH_3)_3SiCl$ to an ice-cooled solution of the hydrazide in dry pyridine and triethylamine. The strong organic base Et_3N accepted the HCl evolved in reaction. When the preparation was attempted with a suspension of the hydrazide in Et_3N alone, reaction did not occur. In the homogeneous system, reaction occurred so vigorously that cautious addition of $(CH_3)_3SiCl$ was necessary. The yield of thoroughly dried triethylamine hydrochloride was 13.55 g (98.5%). After removal of the pyridine and excess triethylamine by distillation at atmospheric pressure, one obtained the following three distillation fractions:

1. 110-113°C, 0.08 mm Hg, 4.24 g
2. 114-116°C, 0.08 mm Hg, 7.18 g (primarily at 114-114.5°C)
3. 116-120°C, 0.08 mm Hg, 1.97 g

Total 13.39 g

The total yield of isolated product was 87.5% of theory. The first two fractions were initially "water-white" liquids, but the third solidified in the condenser and receiving flask during distillation. Most of the white solid was loosened from the condenser wall after distillation and transferred to the receiver flask. The first two fractions remained

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liquid for three hours, but with standing overnight the flask contents solidified totally. One obtained no well-formed crystals, but a single, hard block of white solid which could be broken with a spatula only with difficulty.

In a sealed, evacuated capillary melting point tube, melting of fractions 1,2, and 3 occurred at 64-65°C. However, the liquid initially formed was milky white. In a more gradual transition, the liquid cleared completely at about 105°C. With cooling to room temperature, the liquids did not solidify within four hours.

Infrared spectra indicated that fraction 3 was rather unlike the first two fractions. Most of the impurity peaks in the spectrum of fraction 3 matched up well with the spectrum of the hydrazide. The final fraction then probably contained some phthalylhydrazide or the mono-substituted compound and was not given further attention.

Chemical analysis of the material in fraction 2

	%C	%H	%Si	%N	%O
Found:	54.91	7.21	18.29		
Calc'd: (for bis-(trimethylsilyl)phthalazine-1,4-dione)	54.87	7.24	18.32	9.14	10.43

demonstrated that the principal product was a bis-(trimethylsilyl) derivative of the hydrazide. Since the infrared spectra of the first two fractions were the same, at least 85% of the total product was this compound.

In contrast with the parent hydrazide, the new compound dissolved readily in common solvents like CCl_4, $CHCl_3$, and benzene. No reason

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existed why a cryoscopic molecular weight determination could not have been made in a solvent like benzene. Instead, a mass spectrometric study of the compound was undertaken. The molecular weight of bis-(trimethylsilyl)phthalazine-1,4-dione is 306.56; the highest mass strong peak expected in a mass spectrum was m/e 306. Table XXV lists the prominent high mass peaks in the spectrum. "Envelopes" of peaks are recorded with the strongest peak listed first, and the relative abundances of the very highest envelopes are given.

Table XXV

bis-(trimethylsilyl)phthalazine-1,4-dione

m/e	Rel. Abundance	m/e	Rel. Abundance
305		147	
306	7.9		
307		138	
308			
		133	
291			
292	8.9	132	
293			
294		131	
233		130	
234	0.5		
235		99	
219		73	3.0
220	1.0		
221			

In contrast with most of the organogermanium mass spectra considered earlier, the molecular ion envelope was intense in this case. The strongest peak appeared at m/e 305 rather than 306, but the 306 peak was strong. For the molecular ion, the expected ratio of peaks at m/e 306 and 307 would be approximately 18.9/1 (considering combinations of ^{28}Si and

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^{29}Si but ignoring ^{13}C). In other words, the heavy isotope peaks would be much smaller than the peak deriving from species containing only ^{28}Si. Since the ratio of peak heights at m/e 305 and 306 was actually 1.6/1, it was clear that the patterns for at least two different species (differing in the numbers of hydrogens) overlapped to form the envelope near m/e 305. The molecular ion and a species with one less hydrogen reached the detector. The mass spectrum then left no doubt of the molecular weight. The base peak in the spectrum occurred at m/e 291 (molecular ion $-CH_3$). The envelope at m/e 233 undoubtedly resulted from loss of $(CH_3)_3Si\cdot$ from the molecular ion. The envelopes at m/e 305, 291, 233, and 219 and the single peak at m/e 73 [$(CH_3)_3Si^{\oplus}$] were decidedly the most prominent features of the spectrum. Evidences of doubly charged ions were common in the spectrum, the most obvious occurring at m/e 66.5, 122.5, 123.5, 130.5, and 138.5. Metastable ion peaks appeared near m/e 165 and 274. The latter seemingly resulted from the loss of 16 mass units (CH_4 or O) from the molecular ion.

Below m/e 150, the mass spectrum was too complicated to permit estimation of fragmentation patterns without exact mass and abundance measurements. The spectrum of the hydrazide itself was complicated. The surprising feature of the latter was that, while the base peak appeared at m/e 162 (molecular ion), abundant higher mass peaks (203, 214, 231, 233, 248, 279, 310, 330) were recorded. Some of the strongly associated molecular species remained together even to the spectrometer detector.

The information given up to this point has not defined which of the three possible isomers was actually obtained. Evidence derived from

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infrared and NMR spectroscopy indicated that the product was N,N'-bis(trimethylsilyl)phthalazine-1,4-dione, the isomer originally least expected. The infrared spectrum of the new compound is shown in Fig. 1.31. Infrared data with tentative assignments are presented in Table XXVI. Assignments were made by consideration of the spectrum of the hydrazide, the references listed in footnotes 146-148, and the previously cited organosilicon papers by Kriegsmann,[30] Tobin,[61] and Smith.[132]

On the assumption that the intense band at 1655 cm^{-1} derived from carbonyl stretching, the existence of O,O'-bis-(trimethylsilyl)phthalazine-1,4-dione (XXVII) was certainly impossible. The band at 1590 cm^{-1}, considerably more intense in Fig. 1.31 than for the hydrazide itself, probably also resulted from carbonyl stretching (out-of-phase). While νC=N absorptions might be expected in the same general region, this intensity would be less than for the 1655 and 1590 cm^{-1} bands. The growth of the 1590 cm^{-1} band perhaps followed from conversion of the hydrazide from its hydroxy-oxo form to the dioxo form in N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione.

In Fig. 1.31, either or both of the bands at 866 cm^{-1} and 880 cm^{-1} (and perhaps the shoulder at 900 cm^{-1}) probably derived from Si-N stretching. Silicon-oxygen stretching bands occur between 920-1000 cm^{-1} when the oxygen is bonded to an aromatic ring, and between 1000-1110 cm^{-1} when the oxygen is bonded to an aliphatic group.[132,149] If considerable double-bond character remained in the C-O bond, the frequency of the Si-O mode might be lowered, however. Simply on the basis of correlation with previously

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149. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964, p 297.

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Table XXVI[52,53]

N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione

cm^{-1}	Assignment
3155(w) 3050(w) 3010(w)	νC-H aromatic
2950(m)	ν_{asym}C-H(CH_3)
2885(m)	ν_{sym}C-H(CH_3)
1655(s)	νC=O (in phase)
1590(s)	νC=O (out-of-phase) and/or benzene ring mode (?) (or νC=N)
1552(sh) 1540(m)	benzene ring mode and/or νC=N
1490(m)	benzene ring mode
1395(vs)	δ_{asym}(CH_3)
1350(m) 1320(m)	unassigned
1312(sh)	δC-H (?)
1260(sh) 1160(m) 1020(m)	In-plane hydrogen bending
1250(vs)	δ_{sym}(CH_3)
1205(m) 1186(m)	unassigned
1090(m)	νC-N (?)
1053(w)	unassigned
900(sh)	unassigned
880(vs)	broad; νSi-N (?)
866(vs)	broad; νSi-N (?)

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Table XXVI Contd.

cm^{-1}	Assignment
845(vs)	$\rho(CH_3)$; broad
825(sh)	unassigned
790(m) 772(m)	out-of-plane hydrogen bending (?)
756(s)	ν_{sym}Si-C
716(w)	unassigned
687(w)	unassigned
678(m)	ν_{sym}Si-C (?)
660(m)	ν_{sym}Si-C (?)
638(w) 630(w)	amide bands of unknown origin

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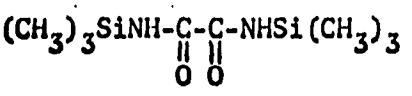
known compounds, the bands between 850 and 880 cm^{-1} were assigned to silicon-nitrogen stretching. Pump and Wannagat[150] reported νSi-N absorbances near 850 cm^{-1} for compounds such as N,N'-bis-(trimethylsilyl)oxalamide XXX, N,N'-bis-(trimethylsilyl)urea XXXI, and N-(trimethylsilyl)acetamide. Though bonding in the substituted acyclic amides is presumably different



XXX

XXI

from that in the heterocyclic phthalazinedione ring, the effect of the carbonyl group may be about the same. In XXX, one might expect the νSi-N band to be lower in energy than for N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione because of the combined electron-withdrawing effect of the adjacent carbonyl groups; i.e. electron density would be removed from the Si-N bond.

Certain other characteristics of the infrared spectrum of N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione deserve mentioning. The intense band (1485 cm^{-1}) assigned primarily to N-H deformation for the parent hydrazide was greatly reduced in Fig. 1.31. The residual small band perhaps derived from benzene ring stretching. For the hydrazide, the strong band at 1085 cm^{-1} was assigned to carbon-nitrogen stretching. In Fig. 1.31, that band remained intense and was shifted slightly to 1090 cm^{-1}. The methyl group deformation and rocking bands at 1395, 1250, and 845 cm^{-1} appeared as expected; the $\delta_{sym}(CH_3)$ band was unusually intense. Though the absorbance at 756 cm^{-1} was assigned to ν_{asym}Si-C, the peak perhaps

150. J. Pump and U. Wannagat, Monatsh. Chemie, 93, 352(1962).

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was another methyl rocking band. Because several bands appeared between 600 and 750 cm^{-1}, the Si-C stretching bands could not be assigned with confidence.

As demonstrated in Figs. 1.32 and 1.33, exposure of a Kadol mull of the bis-(trimethylsilyl) compound to moisture for twenty minutes (and two hours) produced noticeable changes in the spectrum. Even after several hours the hydrolysis was not complete. Though the resistance to hydrolysis perhaps spoke in favor of Si-O bonding in the compound, one is reminded of the necessarily crowded structure of N,N-bis-(trimethylsilyl)phthalazine-1,4-dione. Both the trimethylsilyl groups and the protruding oxygen atoms perhaps inhibited hydrolysis of the Si-N bond. After twenty minutes, the δN-H band at 1485 cm^{-1} had grown significantly. At 1085 cm^{-1}, the writer found some evidence for the band (νC-N?) at that position for the hydrazide. The decrease of the 790 cm^{-1} band with hydrolysis remained unexplained. Bands at 684 cm^{-1} (out-of-plane N-H for the parent hydrazide) and 629 cm^{-1} (unassigned) grew considerably as hydrolysis proceeded. After two hours, the carbonyl band at 1590 cm^{-1} had noticeably decreased in magnitude. In contrast with the dimethylsilyl polymers to be discussed below, the resistance of N,N'-bis-(trimethylsilyl)-phthalazine-1,4-dione to hydrolysis was striking.

The NMR spectrum of the bis-(trimethylsilyl) compound at two different concentrations in CCl_4 is shown in Figures 2.30 and 2.31. Chemical shifts and integration data are presented in Table XXVII (theory for integration in parentheses). Simple consideration of chemical shifts did not define which of the three possible isomers (O,O'; N,O; N,N') had been obtained. Depending on the form of hybridization at oxygen, nitrogen,

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Table XXVII

N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione

Proton Type	Chem. Shift	Integration
(10% CCl_4 soln.):		
$(CH_3)_3Si$	+0.05δ -0.03δ -0.08δ	1.0
	-0.34δ -0.40δ -0.43δ	8.6-9.5
		4.5 (4.5)
$-C_6H_4-$	(-7.5δ)-(-8.1δ)	1.0 (1.0)
(2% CCl_4 soln.):		
$(CH_3)_3Si-$	-0.03δ -0.08δ	
	-0.34δ -0.40δ -0.44δ	
$-C_6H_4-$	(-7.5δ)-(-8.0δ)	

carbon, and silicon, the trimethylsilyl proton chemical shift varies considerably in siloxanes and silazanes. Simply on the basis of electronegativity, shielding of the methyl protons would seemingly be less for siloxanes than for silazanes. Yet trimethylsilyl proton chemical shift data (in Hz relative to TMS) such as the following have been recorded:[151,24]

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151. H. Schmidbaur, J.A.C.S., 85, 2336(1963).

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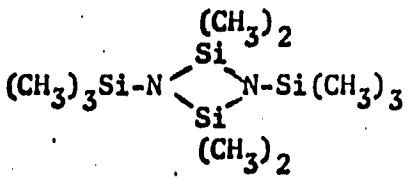
$(CH_3)_3SiOSi(CH_3)_3$ δ = -3.5 Hz

$[(CH_3)_3Si]_2NCH_3$ δ = -3.0 Hz

$[(CH_3)_3Si]_3N$ δ = -10.7 Hz



= 0.0 Hz

For a number of siloxanes and silazanes, Schmidbaur observed[151] that chemical shifts generally increased as pπ-dπ bonding of silicon with a heteroatom decreased. Prominent π-bonding between silicon and oxygen explained the unusually small chemical shift for hexamethyldisiloxane. For $[(CH_3)_3Ge]_2NH$ (δ = -13 Hz)[44b] and $[(CH_3)_3Ge]_2O$ (δ = -18.5 Hz),[134] where π-bonding is less significant, chemical shifts increase with electronegativity of the heteroatom.

Several features of Figures 2.30 and 2.31 are striking. The writer did not find a single trimethylsilyl resonance, but multiple resonances. The most intense resonances occurred between -0.34δ (-20.4 Hz) and -0.44δ (-26.4 Hz), with unusually large chemical shifts for either siloxanes or silazanes. Except for a weak resonance at +0.05δ in the 10% CCl_4 solution, resonances occurred at the same chemical shifts for both the 2% and 10% solutions, but the relative intensities (i.e. appearance) of the resonances changed with concentration. In 2% solution, the -0.03δ and -0.08δ peaks seemed to comprise a doublet; in 10% solution, the +0.05δ, -0.03δ, and -0.08δ resonances looked like a triplet, though the peak spacing was not correct. The writer had no explanation for the observed variation with concentration. The overall ratio of trimethylsilyl to phenyl protons

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(18/4 = 4.5/1) was correct for a bis-(trimethylsilyl) compound. For the O,O' derivative, one would have expected a single high field resonance. For the N,O derivative, two resolved peaks of equal intensity were probable. Yet one actually found a minimum of five peaks. From Fig. 2.30, the ratio of intensities of the two distinctly separated groups of high field resonances was 8.6-9.5/1, and perhaps meant that about two of eighteen methyl protons were more highly shielded than the rest. Neither Fig. 2.30 nor 2.31 suggested that two different derivatives (e.g. N,O and O,O') were present simultaneously. In light of the infrared data, the NMR spectra best corresponded to N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione, where the rotation of trimethylsilyl groups was hindered. Because of a shortage of both time and starting materials, measurements of the organosilicon spectrum at various temperatures or preparation of the bis-(trimethylgermyl) compound were not attempted. Real proof of the structure of the bis-(trimethylsilyl) compound requires some such additional research.

Preparation of low molecular weight, solid polymers from $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$ and 2,3-dihydrophthalazine-1,4-dione was accomplished easily by the method already outlined for the bis-(trimethylsilyl) compound. With slow addition of 0.1 mole of $(CH_3)_2SiCl_2$ or $(CH_3)_2GeCl_2$ to a pyridine/Et_3N solution of the hydrazide, vigorous reaction occurred. The $Et_3NH^+Cl^-$ formed in the organosilicon reaction was easily freed of polymeric product and obtained in 97% yield. In the organogermanium case, the hydrochloride was initially badly contaminated with polymeric product. Refluxing of the solid with benzene only partially removed the polymer.

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Following removal of solvent at atmospheric pressure, the writer obtained amorphous, white solid products from both reactions. Unreacted hydrazide was removed by suspending the solids in carefully dried and purified refluxing pyridine. Only trace amounts of the organosilicon and organogermanium polymers were found to dissolve in pyridine, CCl_4, $CHCl_3$, benzene, and dimethylsulfoxide.

Carbon, hydrogen, and silicon analyses on the dimethylsilyl polymer yielded the following results (2 determinations):

%C	%H	%Si
55.3±0.4	4.45±0.05	10.4±0.5

Though the deviation of the individual results from their mean was large, the tabulated values notably lie between the calculated values for 1:2 and 1:1 dimethylsilyl-hydrazide products:

Calc'd for $(CH_3)_2Si$(phthalylhydrazide-H)$_2$

%C	%H	%Si
56.8	4.24	7.4

Calc'd for $(CH_3)_2Si$(phthalylhydrazide-2H)

%C	%H	%Si
55.0	4.63	12.8

Calc'd for XXXII

%C	%H	%Si
55.8	4.44	10.3

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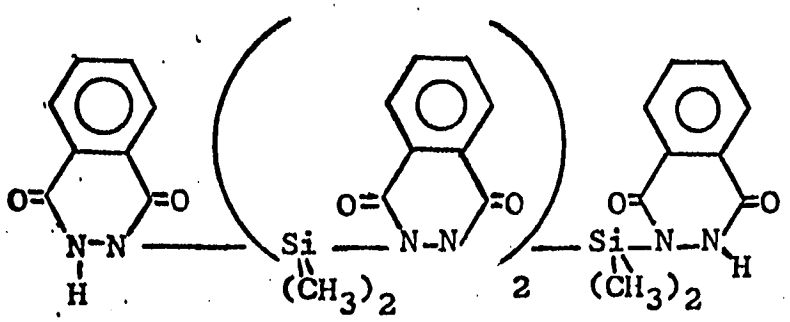

XXXII

The analytical results agreed rather well with the theoretical values for structure XXXII (molecular weight = 817.09). Because of the general insolubility of the polymer, a cryoscopic molecular weight determination was not possible. With direct insertion of the solid into the MS-9 mass spectrometer at 150°C, well-developed envelopes characteristic of organosilicon species appeared up to m/e 732. Poorly-developed envelopes were recorded up to approximately m/e 800. Though the mass spectrum was extremely complicated, envelopes separated by 15 mass units (CH_3^+) were unmistakable.

In similar fashion, analytical results for the organogermanium product lay between the values for 1:1 and 1:2 dimethylgermyl-hydrazide products:

	%C	%H	%Ge
Found:	48.8	3.7	19.1
Calc'd for $(CH_3)_2$Ge(phthalylhydrazide-2H):	45.7	3.83	27.6
Calc'd for $(CH_3)_2$Ge(Phthalylhydrazide-H)$_2$:	51.1	3.34	17.2

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The highest mass spectral envelope for this polymer, with a pattern characteristic of a species with an odd number of germanium atoms, occurred at m/e 803. The species reaching the detector probably contained three germanium atoms. From chemical analysis and mass spectrometry, the organosilicon and organogermanium products evidently had much in common.

Because of the feeble solubility of both materials in common organic solvents, NMR spectroscopy shed no light on the problem of determining the structure of the polymers. Benzene was seemingly the best solvent for the organosilicon product; an intense $(CH_3)_2Si$ proton resonance appeared at -0.24δ, but minor resonances also were found at -0.16δ and -0.35δ. In other solvents ($CDCl_3$, pyridine) multiple resonances occurring between -0.2δ and -0.4δ were somewhat irreproducible and remained uninterpreted.

A series of infrared spectra of the dimethylsilyl-hydrazide polymer are shown in Figures 1.34-1.40. On the assumption that this material would be no more moisture sensitive than the monomeric N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione, spectrum 1.34 was first recorded with a Kadol mull prepared in moist air. At a later time, the investigator prepared a sample in an argon-filled glove bag and obtained a quite different spectrum (Fig. 1.35). Fig. 1.35 is the fully reproducible spectrum of the unhydrolyzed organosilicon polymer. In Table XXVIII, the principal bands of that spectrum are listed with tentative assignments where reasonable interpretation could be made. Some similarities existed between the spectrum of N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione and Fig. 1.35, but there were also several prominent differences not simply

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Table XXVIII[52,53]

$[(CH_3)_2Si$-(hydrazide)-$]_x$		$[(CH_3)_2Ge$-(hydrazide)-$]_x$	
cm^{-1}	Assignment	cm^{-1}	Assignment
3155(m)	νC-H aromatic	3150(m)	νC-H aromatic
1750(w) 1700(w)	unassigned	1700(w)	unassigned
1655(vs)	νC=O (in phase)	1655(vs)	νC=O (in phase)
1590(vs)	νC=O (out-of-phase) or benzene ring mode or νC=N (?)	1585(s)	νC=O (out-of-phase) or benzene ring mode or νC=N (?)
1540(vs)	primarily νC=N (?)		
1490(m)	benzene ring mode	1495(s)	benzene ring mode
1395(vvs)	$\delta_{asym}(CH_3)$	1400(m)	$\delta_{asym}(CH_3)$
1330(s)	unassigned	1355(s) 1330(m)	unassigned
1255(vs)	$\nu_{sym}(CH_3)$	1263(m)	$\nu_{sym}(CH_3)$
1205(m)	unassigned	1210( )	unassigned
1260(sh) 1164(s) 1020(m)	In-plane hydrogen bending	1157(w) 1022(m)	In-plane hydrogen bending
		1100(sh)	unassigned
1093(vs)	νC-N (?)	1085(s)	νC-N
1070(sh) 1055(m)	unassigned	1070(m) 1030(m)	unassigned
895(vvs;broad)	νSi-N		
864(vs)	νSi-N or $\rho(CH_3)$	860(sh) 841(vs) 803(s)	νGe-N and $\rho(CH_3)$
810(vs)	$\rho(CH_3)$		
792(vs) 775(s)	out-of-plane hydrogen bending (?)	776(s)	out-of-plane hydrogen bending

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Table XXVIII Contd.

$[(CH_3)_2Si\text{-(hydrazide)-}]_x$		$[(CH_3)_2Ge\text{-(hydrazide)-}]_x$	
cm^{-1}	Assignment	cm^{-1}	Assignment
722(m) 702(m) 679(m)	unassigned	715(m) 700(s) 682(s) 651(m)	unassigned
663(vs)	νSi-C		
643(m)	unassigned	605(m) 592(m)	ν_{asym}Ge-C
591(w)	νSi-C (?)	567(s)	ν_{sym}Ge-C
568(m)	unassigned		

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attributable to replacement of $(CH_3)_3Si-$ by $-(CH_3)_2Si-$. Changes in Fig. 1.35 with exposure to moisture occurred much more quickly and more strikingly than for the monomeric compound.

As for the monomeric compound, the intense bands at 1655 and 1590 cm^{-1} were assumed to be carbonyl absorbances. The strong, sharp band at 1540 cm^{-1} has been mentioned previously in this Chapter. In the sequence of spectra 1.36-1.39, one can follow the complete disappearance of that band with exposure to air for 1.5-2.5 hours. The 1540 cm^{-1} band is probably either a third carbonyl band or a $\nu C=N$ absorbance. If in the polymer the hydrazide were bonded in the hydroxy-oxo form, such a $\nu C=N$ band might be expected. That absorbance indicated some difference between the bonding of the monomer and polymer, but definite interpretation of the band was not possible. The greater ease of hydrolysis for the polymer than for N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione perhaps resulted from bonding of the hydrazide in the less hindered hydroxy-oxo form. As shown in Fig. 1.40, exposure of the Kadol mull to moist air for a long time (18 hours) led to major reduction of the 1590 cm^{-1} peak and growth of the hydrazide peak at 1540 cm^{-1}. After 18 hours, the spectrum between 1500-1650 cm^{-1} was that of the hydrazide. A question not directly considered during the discussion of the monomeric compound is whether the N-N bond of the hydrazide might have been cleaved in synthesis of the bis-(trimethylsilyl) compound; i.e. whether the compound was actually N,N'-bis-(trimethylsilyl)diphthalamide. For the polymer, the regeneration of 2,3-dihydrophthalazine-1,4-dione with hydrolysis was completely obvious. Cleavage of the N-N bond definitely had not occurred.

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Though more striking in Figs. 1.36-1.40 than for the monomer, most other alterations of the polymer spectrum with hydrolysis had their parallel in Figs. 1.32 and 1.33. Bands at 1490 cm^{-1} (δN-H) and 680 cm^{-1} (out-of-plane δN-H) grew considerably with time. The intense $\delta_{asym}(CH_3)$ band at 1390 cm^{-1} decreased in intensity; initially it was the most intense absorbance in the spectrum. The shrinking of the broad bands between 860 and 900 cm^{-1} reflected destruction of the Si-N (or Si-O?) bonds. At 663 cm^{-1}, a band most likely resulting from Si-C stretching decreased strikingly. The hydrazide band assumed to involve carbon-nitrogen stretching (1080 cm^{-1}) grew with time while the band at 1090 cm^{-1} (perhaps also νC-N) decreased. After 18 hours, the presence of 2,3-dihydrophthalazine-1,4-dione was unmistakable.

The infrared spectrum of the dimethylgermyl polymer is shown in Fig. 1.41 and the principal bands are tabulated in Table XXVIII. Figs. 1.41 and 1.42 (the latter of partly hydrolyzed polymer) require little comment because of their similarity to the organosilicon spectra. The most striking difference was the total absence of the sharp band at 1540 cm^{-1} for the unhydrolyzed organogermanium polymer. Unfortunately, these spectra are so complicated and the possibilities for different bonding so numerous that much more information about the polymers must be accumulated before their structures can be defined. They are clearly made up of only a few (3 or 4) repeating units; their great insolubility perhaps inhibits the formation of higher polymers.

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Experimental

A. Preparation of N,N'-bis-(trimethylsilyl)phthalazine-1,4-dione

In an oven-dried, 500 ml, 3-necked flask equipped with dropping funnel, reflux condenser, and Teflon-paddle stirrer, 8.11 g (0.0500 mole) of 2,3-dihydrophthalazine-1,4-dione was partly suspended and partly dissolved in a solution of 100 ml dry pyridine and 100 ml dry Et_3N. Over half of the solid, which had previously been vacuum-dried (oil pump) at 70°C for ten hours, dissolved in that amount of solvent. The entire system was flushed with argon before and during the reaction. When the solution had been thoroughly cooled in an ice-bath, 10.86 g (0.1000 mole) of $(CH_3)_3SiCl$ was dripped slowly into the reaction flask. Vigorous reaction, requiring continuous cooling in ice, commenced immediately. The reaction mixture was stirred overnight. After the precipitated $Et_3NH^+Cl^-$ had been allowed to settle somewhat, the hydrochloride was removed by filtration in an inert atmosphere and washed with 3 x 25 ml of sodium-dried benzene. The yield of vacuum-dried hydrochloride was 13.55 g (98.5% of theory). After removal of solvent at atmospheric pressure, the writer obtained the following three distillation fractions:

1. 110-113°C, 0.08 mm Hg, 4.24 g
2. 114-116°C, 0.08 mm Hg, 7.18 g
   (primarily at 114-114.5°C)
3. 116-120°C, 0.08 mm Hg, 1.97 g

Total 13.39 g

The total product yield was 87.5% of theory, with the bis-(trimethylsilyl) compound comprising all of the first two fractions. Characterization of

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the main component is discussed earlier in the Chapter; the third fraction was not characterized.

B. Preparation of dimethylsilyl and dimethylgermyl derivatives of 2,3-dihydrophthalazine-1,4-dione

In apparatus exactly like that described in Part A, 8.68 g (0.0500 mole) of $(CH_3)_2GeCl_2$ or 6.46 g (0.0500 mole) of $(CH_3)_2SiCl_2$ was combined with 8.11 g (0.0500 mole) of the hydrazide in 100 ml each of pyridine and Et_3N. Again, vigorous reaction occurred with formation of by-product $Et_3NH^+Cl^-$. The reaction mixture was stirred overnight. In the organosilicon case, the filtered halide (98% yield) was freed of product by washing (or better, refluxing) with sodium-dried benzene. Solvent was removed at atmospheric pressure to leave a white solid which did not soften with heating to 220°C (0.05 mm Hg). The solid residue (9.68 g) was washed with 3 x 50 ml of dry pyridine and/or refluxed with benzene to remove unreacted hydrazide. The characterization of the low molecular weight solid polymer is discussed earlier in the Chapter. Work-up of the organogermanium product different only in that repeated washing was required to remove polymer from the halide; even then, about 3 g of polymer never was removed from the hydrochloride. The yield of isolated organogermanium product was 10.96 g (77.5%).

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Chapter IV: Conclusion

The principal concern in conducting this research has been to characterize some new organogermanium-nitrogen compounds and to gain some knowledge of the Ge-N bond. With either monomeric or polymeric materials, a consistent goal was to prepare compounds with low moisture sensitivity. Germylamine polymers were synthesized for purposes of comparison with the known silylamine (e.g. dimethylsilylethylenediamine) polymers and to add to the information reported by Yoder and Zuckerman.[20] As the research progressed, particularly with the systems involving 2,3-dihydrophthalazine-1,4-dione and the xylylenediamine isomers, the writer increasingly relied upon knowledge of parallel Si-N compounds for leverage in characterizing the Ge-N species. Except for the derivatives of aniline and cyclohexylamine, the organogermanium-nitrogen polymers were uniformly less tractable than their organosilicon-nitrogen analogues. The dimethylgermyl-xylylenediamine polymers were all extensively cross-linked; interpretation of their structure was eased by prior investigation of the relatively simple, linear Si-N polymers.

In light of the discussion early in Chapter I of factors contributing to the moisture insensitivity of the Si-N and Ge-N bonds, efforts to prepare hydrolytically stable germazanes and germylamines were only marginally successful. Donation of electron density to germanium by two ethyl groups and withdrawal from nitrogen by a phenyl substituent apparently

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stabilized $(Et_2GeNC_6H_5)_4$ (scarcely hydrolyzed in air after one hour). Since low molecular weight, linear N-phenyl germazanes were quickly destroyed in air, electronic effects did not unambiguously define the stability of the cyclic tetramer. The molecule was perhaps sufficiently crowded for steric restrictions to slow hydrolysis. The considerable moisture sensitivity of the similar compound $(Et_2GeNC_6H_{11})_4$, however, indicated that the phenyl group did stabilize $(Et_2GeNC_6H_5)_4$. The only germanium compound of comparable stability obtained in this research was the polymeric dimethylgermyl derivative of 2,3-dihydrophthalazine-1,4-dione. If germanium was indeed bonded to nitrogen in the latter compound, the hydrolytic stability followed naturally from the undoubted low basicity of nitrogen in that species. No compounds were prepared with stability as great as that of N,N'-diphenyl-N-triphenylgermylhydrazine,[40] the tributylgermyl and triphenylgermyl derivatives of pyrrole,[26] and the diphenylpolysilazanes,[38] all of which can be isolated from mixtures containing water. Placement of moderately bulky substituents (ethyl, phenyl, and cyclohexyl) on germanium and nitrogen and of an electron-withdrawing group (phenyl) on nitrogen did not strikingly reduce the rate of hydrolysis.

The major cross-linking of the dimethylgermyl xylylenediamine polymers, in contrast with the linearity of the dimethylsilyl compounds, was somewhat surprising since the preparation and treatment of both types of products was the

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same. The dimethylgermyl polymers evidently possessed lower thermal stability than did the organosilicon compounds, perhaps because the Ge-N bond was weaker than the Si-N bond. (No Ge-N bond energy has been published, but the bond is generally assumed to be weaker than the Si-N bond.) The cross-linking perhaps proceeded thermally, with evolution of free xylylenediamine. As suggested previously, some of the rigidity of the organogermanium products probably resulted from existence of germanium in higher than four coordination. The intractable nature of the organogermyl-xylylenediamine polymers was, of course, disappointing; only the dimethylsilyl products held some promise as useful polymeric materials.

The pronounced tendency of dimethyl- and diethyldichlorogermane to form 1:1 products (cyclogermazanes and low linear polymers) with aniline contrasted sharply with the reactions of organohalosilanes. Direct aminolysis even with a 3:1 molar ratio of aniline to diorganodichlorogermane always yielded 1:1 polymeric products. With $(CH_3)_2SiCl_2$, direct aminolysis yields only $(CH_3)_2Si(NHC_6H_5)_2$.[46] Even the familiar $(NH_4)_2SO_4$-catalyzed rearrangement of the diamino compound to cyclic silazanes does not proceed easily with the aniline system.[37] The writer encountered no difficulty in obtaining dicyclohexylamino derivatives of dimethyl- and diethyldichlorogermane. One most tentative explaination for the distinction observed with aniline is as follows. With the organosilicon compounds, $d\pi$-$p\pi$ bonding between silicon

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and the weakly basic nitrogen of aniline is likely strongest when the nitrogen is only attached to one silicon atom. The molecules are seemingly most stable with that $d\pi$-$p\pi$ bonding at a maximum. Such π-bonding is generally assumed to be less significant or negligible between germanium and nitrogen. Stability of the Ge-N bond perhaps depends on the strength of a highly ionic bond, on the polarity of the bond. That polarity is probably greater (the nitrogen more negative with respect to germanium) with two electropositive germanium atoms attached to nitrogen than with one germanium and one hydrogen.

A problem encountered in the interpretation of the NMR spectra of one dimethylsilyl and all organogermyl derivatives of the xylylenediamines has not been solved. For N,N'-bis-(trimethylsilyl)xylylenediamine (o-, m-, and p-) and the dimethylsilyl-xylylenediamine (m- and p-) polymers, the writer observed coupling of methylene and NH protons with an expected coupling constant $J_{CH_2,NH} = 7.8$ Hz. Apparently anomalous $J_{CH_2,NH}$ coupling constants for three organogermyl compounds and one dimethylsilyl compound are summarized below:

	$J_{CH_2,NH}$ (Hz)
N,N'-bis-(trimethylgermyl)-p-xylylenediamine (see Fig. 2.29 and Table XV)	15.6 ± 1.2
$[-(CH_3)_2Ge-(m)-NHCH_2C_6H_4CH_2NH-]$ (see Fig. 2.19 and Table XX)	24.0 ± 1.2
$[-(CH_3)_2Ge-(p)-NHCH_2C_6H_4CH_2NH-]$ (see Fig. 2.24 and 2.25 and Table XXI)	25.8 ± 1.2
Oil from $(CH_3)_2SiCl_2$ and o-xylylenediamine	14.4 ± 1.2

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For the two dimethylgermyl polymers (see particularly Figs. 2.19 and 2.25) the resonances comprising the apparent doublet might have derived from two different types of methylene groups; i.e. methylene protons adjacent to a nitrogen bonded to two germaniums or to one germanium. The chemical shift differences arising from such bonding differences were not expected to be as large as the observed 23-27 Hz. However, the assumption of two different types of methylene groups gained support from the appearance of the polymer spectra in acetone-d_6 (Figs. 2.20 and 2.23). Single methylene resonances suggested that for completely dissolved germylamine polymers coupling of CH_2 and NH protons was removed. In the presence of nitrogen with basicity greater than that in the silylamines and more like that in a free amine, the exchange of NH protons would be rapid and the coupling of CH_2 and NH protons removed.

The preceeding explanation did not permit rationalization of the form of the spectra of N,N'-bis-(trimethylgermyl)-p-xylylenediamine and the dimethylsilyl derivative of o-xylylenediamine. If real doublets in fact existed in these spectra, they surely did not derive from coupling of CH_2 and NH spins. With an asymmetric center at nitrogen, i.e. if inversion about nitrogen did not occur readily, the two methylene protons might not be chemically equivalent and might show an AB spectrum. From failure to observe small outer peaks in such spectra, the two prominent inner peaks

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are sometimes mistaken for a doublet.[152] However, such a situation seems most improbable; one would not expect inversion about nitrogen to be inhibited in these compounds. Because of a time shortage, decoupling experiments designed to determine the source of splitting of the methylene resonance were not attempted. Such experiments would help considerably in characterizing the dimethylgermyl polymers, in particular.

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152. R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 1967, p. 129.

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Appendix I

Non-organogermanium Reagents and Solvents

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The non-organogermanium reagents and solvents used in this research are listed here in alphabetical order. The commercial source of the reagent follows in parentheses. Methods of purification and drying are specified.

1. Aluminum bromide (anhydrous) (Fisher)
2. Aluminum chloride (anhydrous) (Fisher)
3. Ammonia gas (Matheson Lecture Bottle) Passed through one foot tower containing KOH pellets.
4. Aniline (Baker) Stored for several weeks over KOH pellets. Fractionally distilled from fresh KOH just prior to use. Stored out of light under argon.
5. Argon (Med-Tech Cylinder Gases) Passed through one foot tower containing Drierite ($CaSO_4$).
6. Benzene (Fisher) Pressed sodium wire into bottle. Let stand for several days. Added fresh sodium wire when shiny sodium surface was no longer visible.
7. Bromine (Fisher)
8. n-Butyl chloride (Eastman reagent)
9. n-Butyl lithium (Alfa Inorganics, 22% by wt.)
10. Carbon tetrachloride (Eastman Spectro Grade) Dried over Linde 4A Molecular Sieves.
11. Chlorine gas (Matheson Lecture Bottle)
12. Chloroform (Fisher) Dried over Linde 4A Molecular Sieves. Encountered some difficulty with formation of $COCl_2$ on standing for lengthy period. Molecular sieves evidently took up much of ethanol stabilizer.

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13. Cyclohexylamine (Fisher) Purified as for aniline.
14. Dichloromethane (Fisher)
15. α,α'-Dichloro-o-xylene (Matheson, Coleman, and Bell)
16. α,α'-Dichloro-p-xylene (Matheson, Coleman, and Bell)
17. Diethylether (Mallinckrodt Anhydrous Reagent) Immediately after opening pressed in sodium wire.
18. Diglyme (Ansul Ether) Stored one week over CaH_2. Refluxed 24 hours with fresh CaH_2. Vacuum distilled at 12 mm Hg from fresh CaH_2.
19. Dimethyldichlorosilane (General Electric) One plate distillation.
20. N,N'-Dimethylformamide (Eastman Spectro Grade)
21. D_2O (Bio-Rad, 99.90 mole %)
22. Deuterochloroform (Merck, Sharpe, and Dohme, Ltd.)
23. Ethanol (anhydrous) (Gold Seal)
24. Ethyl chloride (Matheson Cylinder Gas) Passed through one foot tower containing Drierite ($CaSO_4$)
25. n-Heptane (Phillips 66) Dried as with benzene.
26. n-Hexane (Phillips 66) Dried as with benzene.
27. Hydrazine hydrate (95+%) (Eastman)
28. Lithium metal (50% by wt dispersion in hexane) (Foote Mineral Co.)
29. Lithium aluminum hydride (Ventron Metal Hydrides)
30. Mannitol (Eastman reagent)
31. Methylamine (Matheson Lecture Bottle) Passed through tower containing KOH pellets.

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32. Nitrogen (prepurified gas) (Med-Tech Cylinder Gases) Passed through one foot tower containing Drierite.

33. Pentane (Phillips 66) Dried as with benzene.

34. Phosphorus pentoxide (Baker Granusic)

35. Phthalonitrile (Fisher)

36. Potassium hydroxide (pellets) (Fisher)

37. Potassium perchlorate (Fisher)

38. Potassium phthalimide (Eastman)

39. Pyridine (Fisher) Dried initially over Linde 4A Molecular Sieves. Refluxed with CaH_2. Fractionally distilled from fresh CaH_2. Stored over CaH_2 chunks.

40. Sodium hydroxide pellets (Fisher)

41. Sodium hydroxide (N/10 solution) (Fisher)

42. Sodium peroxide (Merck)

43. Sucrose (Fisher)

44. Triethylamine (Eastman) Purified as for aniline.

45. Trimethylchlorosilane (General Electric) One plate distillation.

46. m-Xylylenediamine (Aldrich) Purified as for aniline.

47. m- and p-Xylylenediamine mixed (Sho-Amine-X) (Showa Denko, K.K.) Purified as for aniline.

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Appendix II

Organogermanium Reagents

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Three organogermanium reagents, Et_2GeCl_2, $(CH_3)_3GeCl_2$, and $(CH_3)_3GeBr$, were used extensively in this research. A researcher who enters the field of germanium chemistry encounters the problem of obtaining rather expensive germanium reagents in sufficient quantities. In recent years, the Germanium Research Committee, formed by an international group of germanium producers, has fostered investigation by providing information and germanium materials for research purposes. The writer wishes to thank the Committee for providing, at various times, 100 g of GeO_2, 200 g of powdered Ge metal, and about 100 g of Ge metal in ingot form. During this research, considerable efforts were made to convert the inorganic germanium materials into the three previously mentioned organohalogermanes and to recover impure, unreacted, germanium metal and compounds. The procedures involved were all previously known and extensively documented. No attempt will be made here to cite all directly or loosely related references; the review articles mentioned in the Introduction provide easy access to the original papers.

Finely powdered Ge metal was obtained from GeO_2 by reduction with H_2 gas in a Vycor combustion tube at 480-490°C. When 23 g of GeO_2 was placed in a tube of one-inch diameter in a tube furnace, reduction at 490°C for two successive seven hour periods quantitatively yielded dark grey germanium metal. Unreacted hydrogen gas was burned

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at the exit port of the system. An exit tube (5 mm internal diameter) was bent downward about 10° from the horizontal to allow facile removal of water.

Germanium metal in ingot form was first crushed in a diamond mortar and then ground to pass a 100-mesh sieve. Without use of the diamond mortar, the metal shattered and flew in all directions.

Dimethyldichlorogermane and diethyldichlorogermane were initially produced by the copper-catalyzed direct reaction of methyl chloride with germanium metal. For production of diethyldichlorogermane, the procedure used was close to that described by E.G. Rochow.[153] In one reaction sequence, about 25 g of fine, granular copper metal (electrolytic grade) was reduced with hydrogen gas at 350°C for 3.5 hours. Freshly reduced copper (20.77 g) was then thoroughly mixed with 118.07 g of Ge metal powder. The mixture was interwoven with thin strips of glass wool in a Pyrex tube 2.5 cm in internal diameter and 40 cm long. The exit tube (5 mm internal diameter) led to a one-foot water condenser and 500 ml round-bottomed receiving flask. An exit tube from the latter flask led to a dry ice-acetone trap, a $CaCl_2$ drying tube, and finally a KOH trap. Ethyl chloride was passed slowly through the reaction tube for about one hour while the temperature, as monitored by a thermocouple and

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153. E.G. Rochow, J.A.C.S., 72, 198(1950).

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Barber-Coleman Pyrometer Apparatus, was raised to 365°C; this operation removed adsorbed water from the germanium-copper mixture. With a flow rate of 5-6 bubbles/second through a mineral oil bubbler and with an oven temperature of 365°C, droplets of product appeared at the exit from the reaction tube. The receiving flask was constantly cooled in ice to keep the crude product from being swept into the dry ice-acetone trap. Some ethyl chloride also condensed in the receiving flask, but most of the halide condensed in the dry ice-acetone trap. When the cold trap had filled with ethyl chloride at various stages of the reaction, the reagent was recycled through the reaction tube. During a 39.5 hour reaction period at 355-360°C, evolution of product was quite constant. After 50 hours, about 500 ml of crude product (organogermanium halides and ethyl chloride) had been collected. At this stage the charge, particularly at the center of the tube, had become blackened by deposition of carbon. The solid mixture, much decreased in mass, was stirred with a glass rod and concentrated near the center of the tube. With an additional reaction period (total time 94 hours) 150 additional milliliters of crude product were obtained. Following removal of most of the ethyl chloride in a fractional distillation, the weight of residual crude product was 263 g.

In order to separate the various organochlorogermanes by fractional distillation, the author built a jacketed

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column, packed with stainless-steel helices, which was shown (by the McCabe-Thiele graphic method involving measurement of refractive indices of CCl_4-benzene solutions)[154] to have about 22 theoretical plates under total reflux. Briefly described, the column involved a central shaft of Pyrex tubing (8 mm internal diameter and 86 cm length) filled with 3/32" stainless-steel helices and equipped with 19/38 joints. Two thermometers fastened to the central shaft permitted temperature measurement. A Pyrex tube (1" internal diameter and 89 cm length), wound with nichrome ribbon in two 25-turn sections, surrounded the central shaft and provided insulation. Electrical leads were connected so that the column could be heated in two sections; two 360°C thermometers permitted temperature measurement on the heated jacket. Finally, a Pyrex tube (2" in internal diameter and 96 cm in length) provided a second insulating jacket for the system. This outer tube projected well above the top of the two inner tubes; with appropriate placement of glass wool, the region of the column just below the head was well insulated. The three glass tubes were spaced apart and held in position by machined Teflon rings at the top and bottom of the column. The entire mass of glass tubing was supported on a wooded block; the fractionating column passed through a 3/4" central hole in the block. The functioning central

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154. T.P. Carney, Laboratory Fractional Distillation, MacMillan Co., 1949, pp. 13-14, 28, 32, 142.

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column, with its attached Teflon rings, could be removed and replaced by a different type of fractionating medium (e.g. spiral wire). The column was, of course, not vacuum jacketed; instead, dead-air spaces provided some insulation. This column was usually used in conjunction with the variable-takeoff distillation head pictured in Fig. 11. An electrical on-off timer controlled the current in a wire coil (solenoid), and this in turn moved a glass plunger (with soft iron core) in and out of a Teflon seal. This automatic distillation head, made by cutting into an existing piece of glassware, was considerably less expensive than commercially available apparatus.

By repeated fractional distillation of the product from the previously described direct reaction, the writer obtained 58.5 g (0.281 mole) of $EtGeCl_3$ and 189.0 g (0.939 mole) of Et_2GeCl_2. The molar ratio of products (3.34/1) was better than that (2.58/1) originally reported by Rochow.[152] Based on the pure isolated products, the conversion of Ge metal was about 75%.

After two such direct reactions had been run, much of the $EtGeCl_3$ was converted to Et_4Ge in a Grignard reaction (EtGeBr) in diethyl ether. In the presence of excess Grignard reagent, the yield of Et_4Ge was about 85%. Much of that Et_4Ge was then used, in conjunction with $GeCl_4$, in a

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redistribution reaction catalyzed by anhydrous $AlCl_3$.[155] In a procedure like that described by Rijkens and Van der Kerk,[155] approximately 50 ml, heavy-walled Carius tubes were charged with 20.0 g Et_4Ge (0.106 mole), 18.8 g (0.088 mole) $GeCl_4$, and 2.38 g (0.0179 mole) anhydrous $AlCl_3$. Usually three such tubes were wrapped in glass wool and placed in a steel autoclave bomb. Reaction occurred for 24 hours at 200°C in a rocker autoclave. The writer experienced no difficulty with rupturing of the tubes (nine in all) during heating. Yields of Et_2GeCl_2 from the redistribution reactions were regularly near 96%, based on the germanium. Some of the $GeCl_4$ involved in these reactions was purchased from Alfa Inorganics, but much was obtained by chlorination of the impure germanium in residues from the direct reaction. The chlorination reaction proceeded easily with passage of chlorine gas over the solid residues in a tube heated at 200-300°C. Molecular chlorine dissolved in the crude product was removed by reaction with Hg_2Cl_2 (either with standing or brief heating). A single fractional distillation then yielded reasonably pure $GeCl_4$.

Dimethyldichlorogermane was prepared by the copper-catalyzed direct reaction of methyl chloride with germanium. The apparatus and procedure were much like that described above for the ethylchlorogermanes, except that the writer

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155. F. Rijkens and G.J.M. Van der Kerk, Organogermanium Chemistry, Germanium Research Committee, 1964, pp. 17-34.

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followed certain recommendations made by Moedritzer.[156] Higher methyl chloride flow rates (400 cc/min vs about 150 cc/min) and higher reaction temperatures (375-400°C vs 320-360°C) than customarily used[157] led to more rapid conversion of the germanium. The molar ratio of germanium to copper catalyst was 2.25/1. At the high flow rates, considerable amounts of methyl chloride passed through the reaction zone without reacting and condensed in the cold trap; that methyl chloride was easily recycled through the reaction tube. NMR spectroscopy was used to analyze the crude products from two direct reactions. The average composition of the products was as follows:

	Mole %
CH_3Cl	14.3
$(CH_3)GeCl_3$	23.2
$(CH_3)_2GeCl_2$	60.5
$(CH_3)_3GeCl$	2.0

Traces of such species as $(CH_3)GeHCl_2$ were also apparently present. In one reaction, the conversion of germanium to methylchlorogermanes was 86.2%, but near the end of the reaction CH_3GeCl_3 was the principal product.

All $GeCl_4$ obtained by chlorination of the impure germanium in the direct reaction residues and most of the

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156. K. Moedritzer, J. Organometal. Chem., 6, 282(1966).

157. E.G. Rochow, J.A.C.S., 69, 1729(1947).

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CH_3GeCl_3 were converted to $(CH_3)_4Ge$ in a Grignard reaction. Excess Grignard reagent (CH_3MgI) was formed in carefully dried and purified di-n-butylether. With thorough cooling in ice, vigorous reaction occurred with slow addition of the $GeCl_4$-CH_3GeCl_3 mixture. The yield of $(CH_3)_4Ge$ from this reaction was 79% based on germanium.

Finally, $(CH_3)_3GeBr$ was prepared by reaction of 34.65 g (0.261 mole) of $(CH_3)_4Ge$ with 41.75 g (0.261 mole) of Br_2 in the solvent 1,2-dibromoethane. Small amounts of $(CH_3)_2GeCl_2$ also formed. The yield of $(CH_3)_3GeBr$ from a single fractional distillation of the crude product was 69%.

The writer wishes to thank Mr. John McLaughlin, a student in Natural Sciences 3 (Spring, 1968) for his considerable assistance in preparing some of the methylchlorogermane reagents and in recovering impure germanium as $GeCl_4$.

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Appendix A

Infrared Spectra

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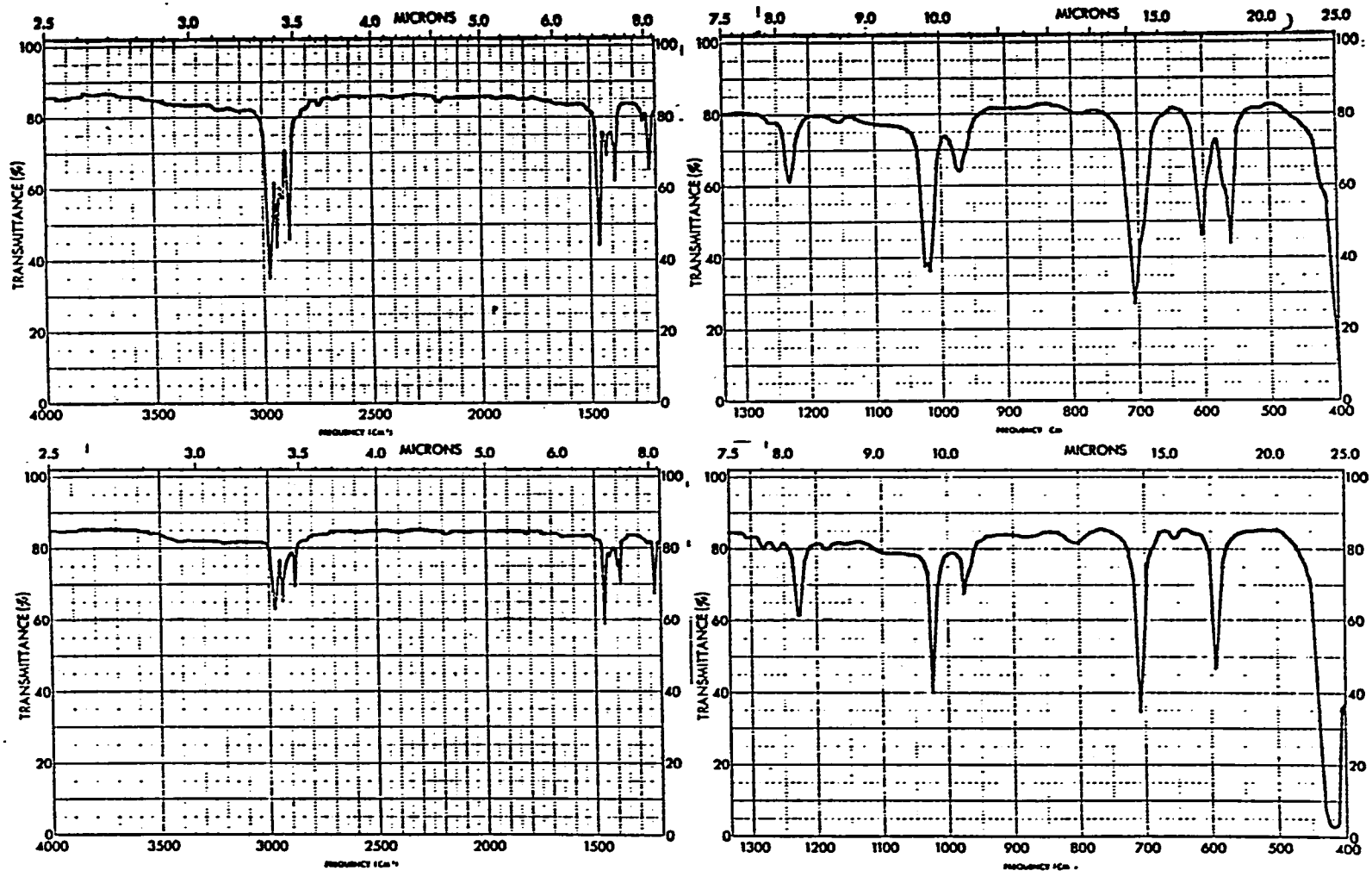

Fig. 1.1(top; 2 ranges): Et_2GeCl_2, liquid film between KBr discs.

Fig. 1.2(bottom; 2 ranges): $EtGeCl_3$, liquid film between KBr discs.

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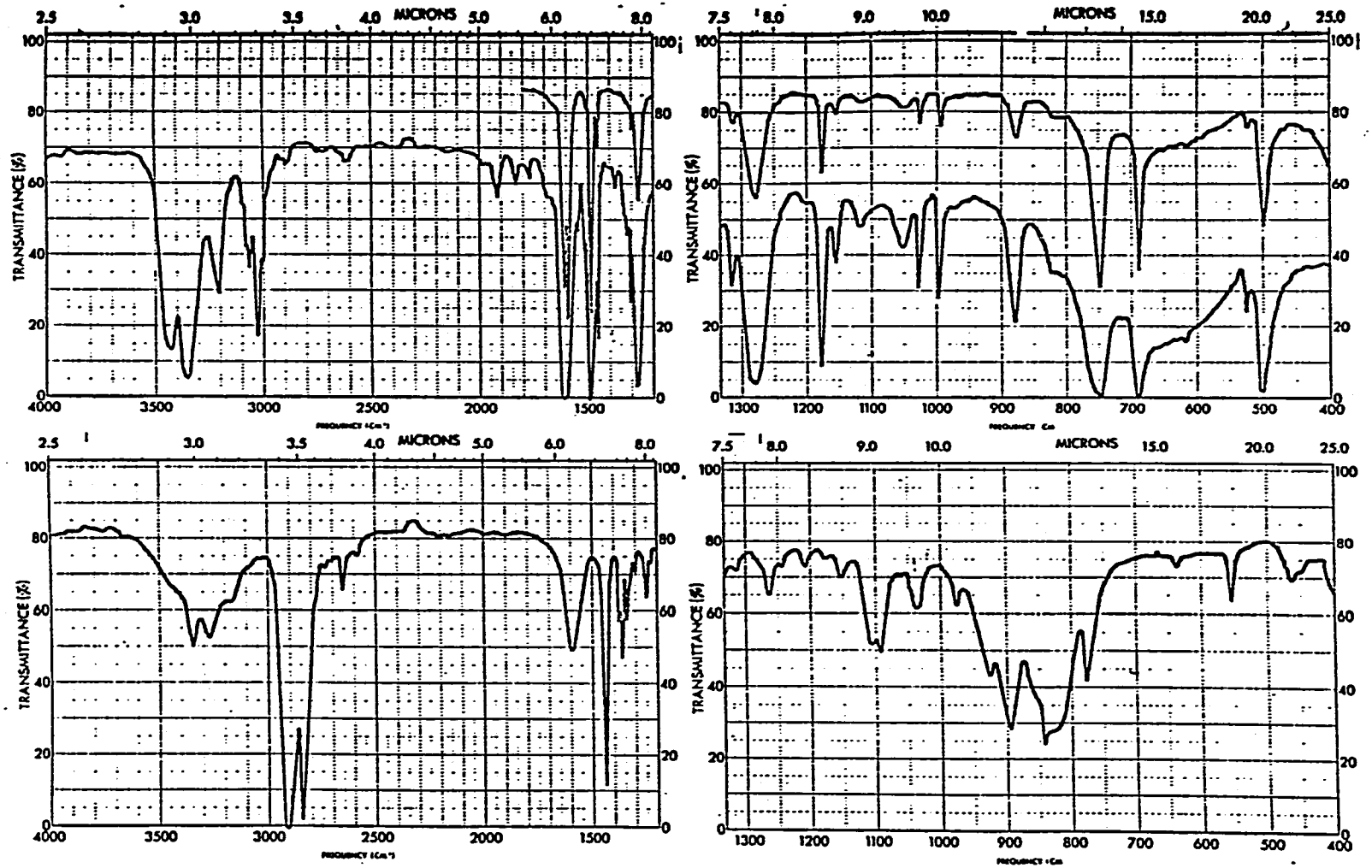

Fig. 1.3(top; 2 ranges): Aniline, liquid film between KBr discs.

Fig. 1.4(bottom; 2 ranges): Cyclohexylamine, liquid film between KBr discs.

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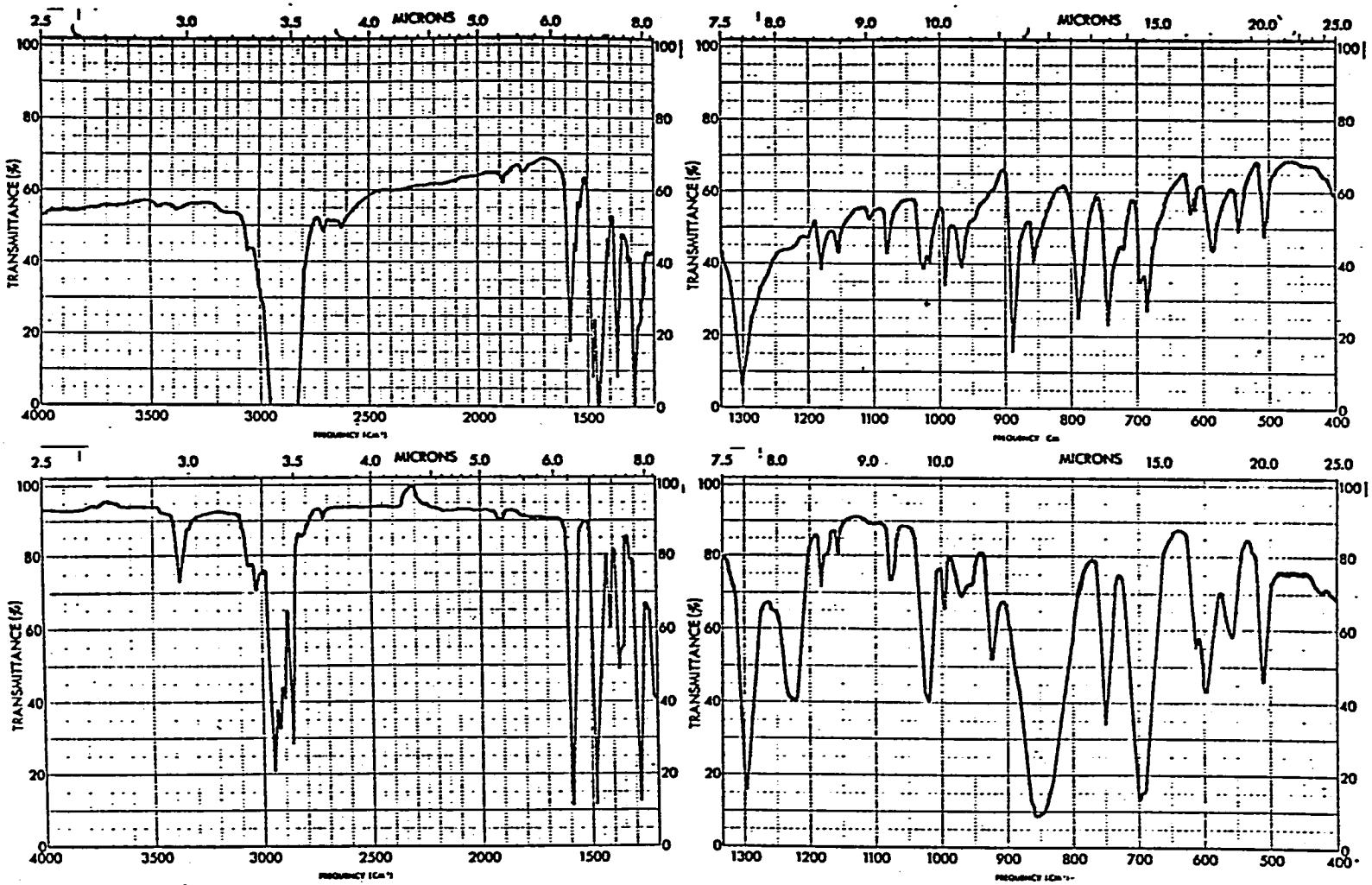

Fig. 1.5(top; 2 ranges): $(Et_2GeNC_6H_5)_4$, Kadol mull of solid between KBr discs.

Fig. 1.6(bottom; 2 ranges): linear oligomeric N-phenylated diethylgermazane, liquid film between KBr discs.

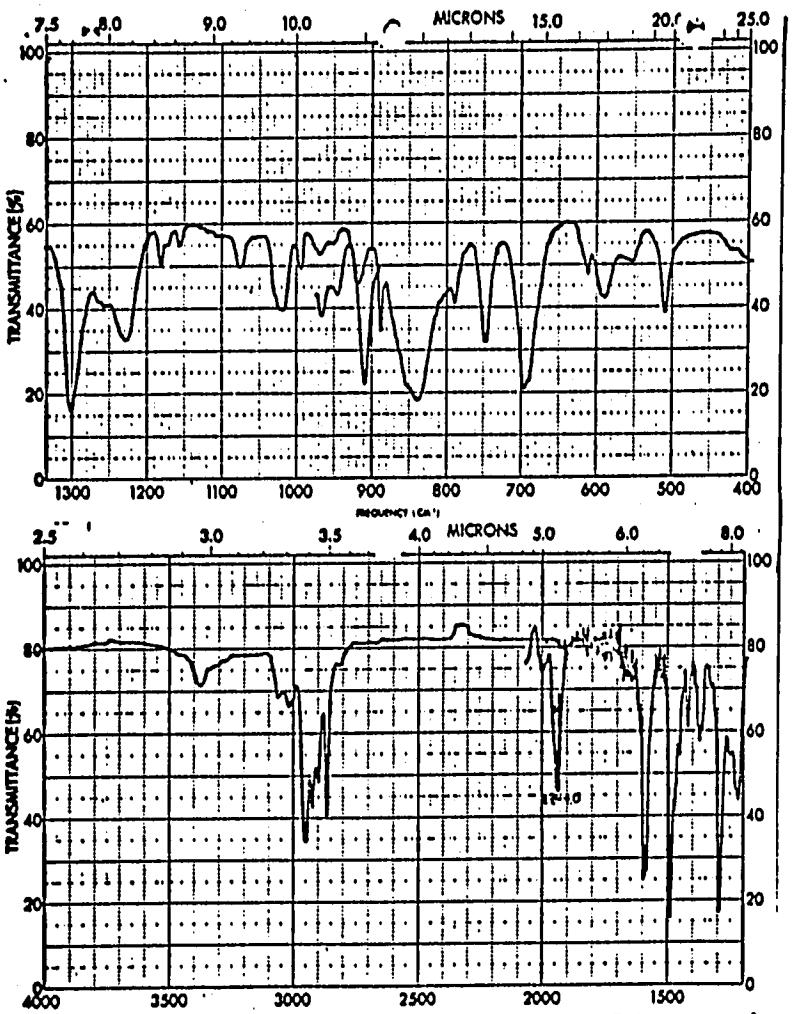

Fig. 1.7(2 ranges): linear oligomeric N-phenylated diethylgermazanes, from transamination, liquid film between KBr discs.

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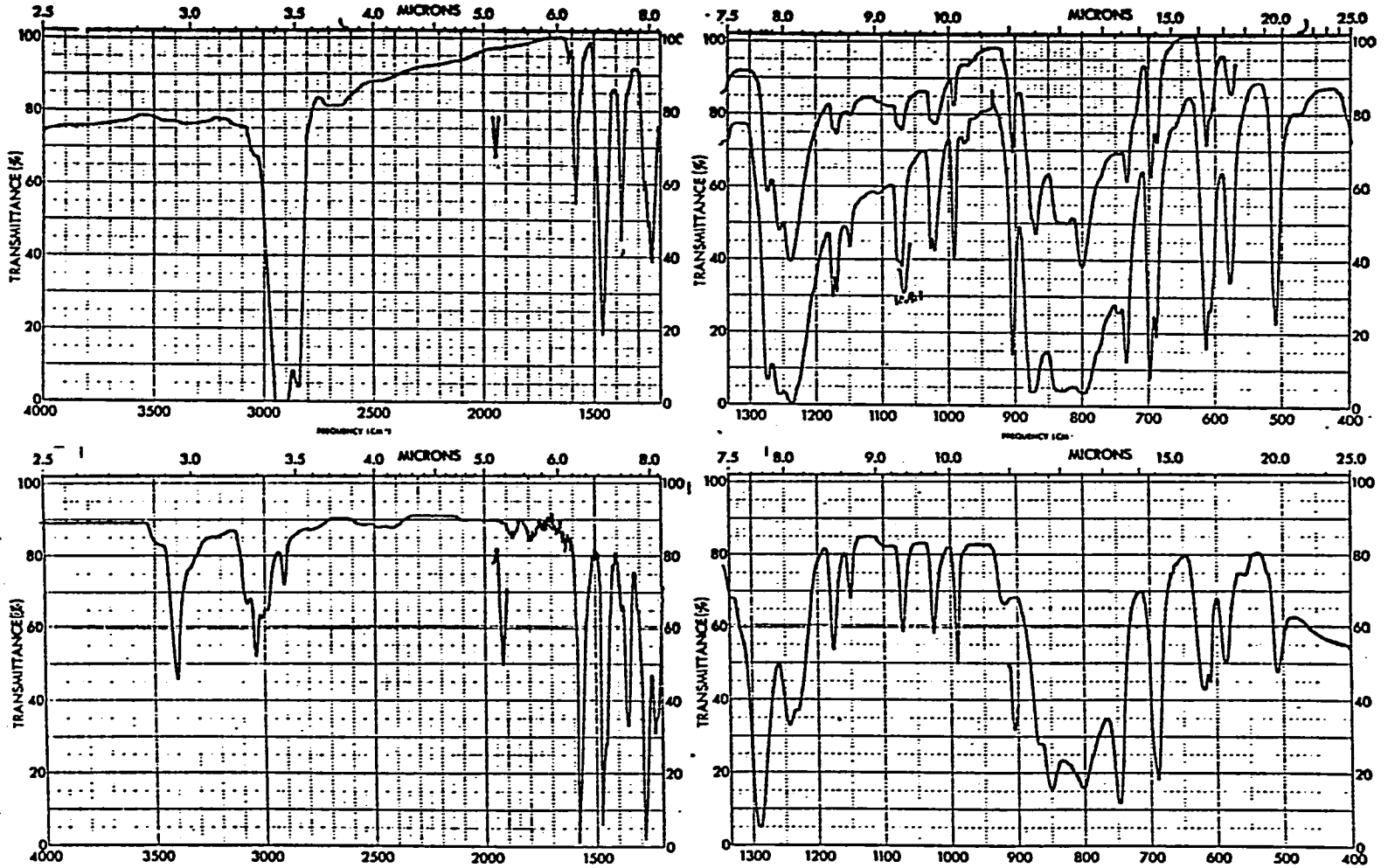

Fig. 1.8(top; 2 ranges): $[(CH_3)_2GeNC_6H_5]_3$, Kadol mull between KBr discs.

Fig. 1.9(bottom; 2 ranges): linear oligomeric N-phenylated dimethylgermazanes, liquid film between KBr discs.

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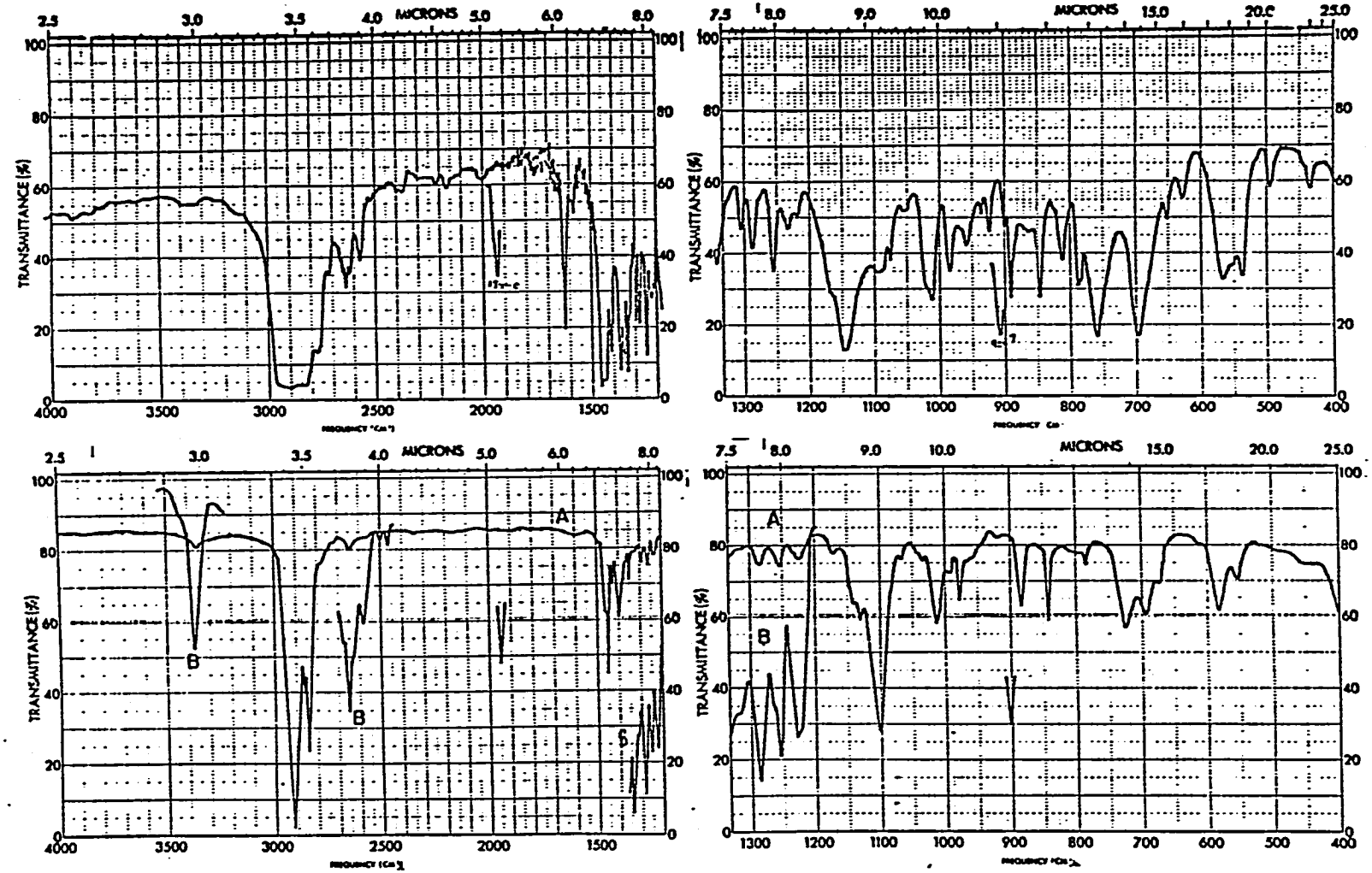

Fig. 1.10(top; 2 ranges): $(Et_2GeNC_6H_{11})_4$, Kadol mull between KBr discs.

Fig. 1.11(bottom; 2 ranges): $Et_2Ge(NHC_6H_{11})_2$, liquid film between KBr discs, scan B thicker film than A.

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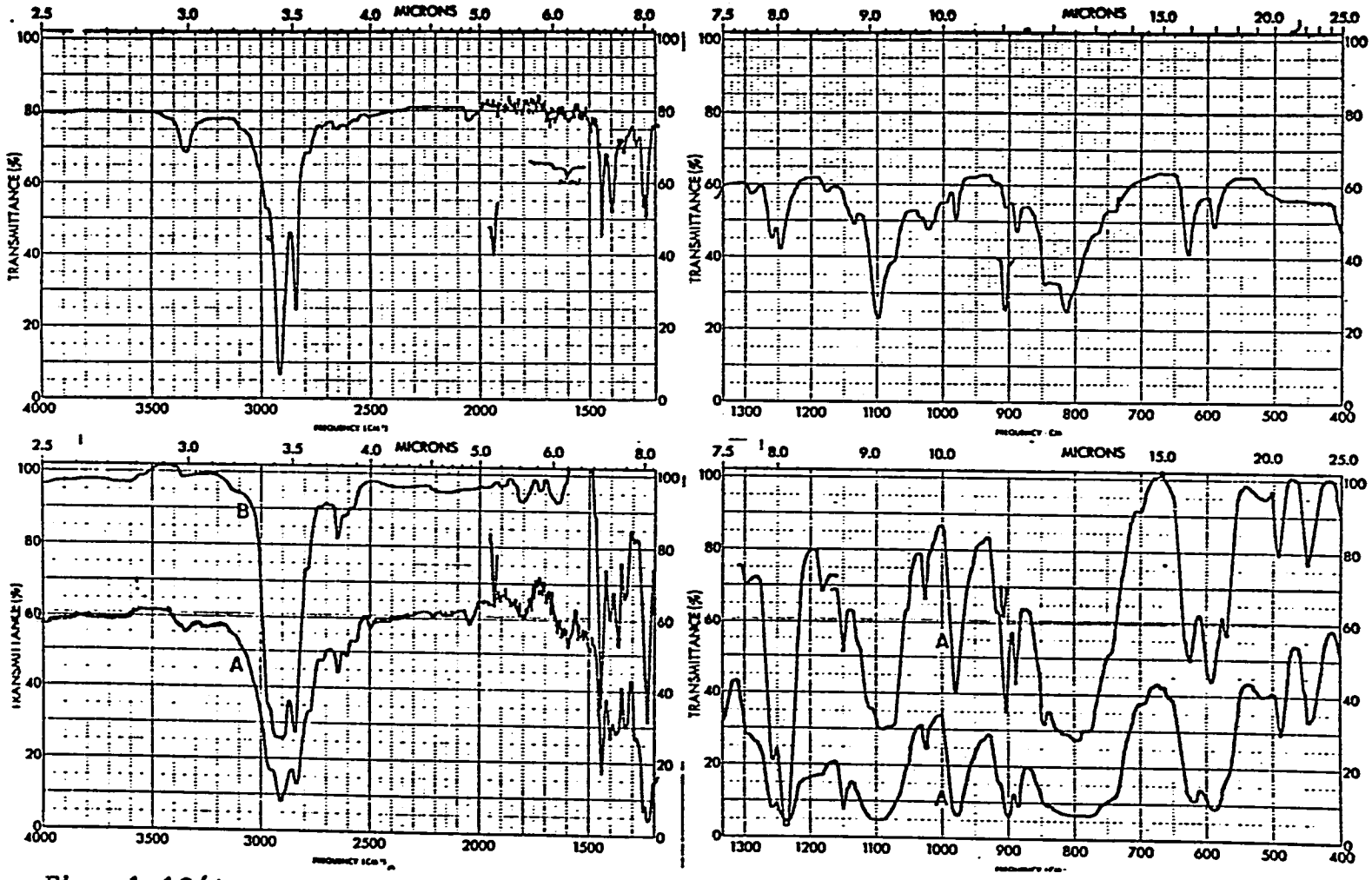

Fig. 1.12(top; 2 ranges): $(CH_3)_2Ge(NHC_6H_{11})_2$, liquid film between KBr discs

Fig. 1.13(bottom; 2 ranges): $[(CH_3)_2GeNC_6H_{11}]_3$; scan A, Kadol mull between KBr discs; scan B, 5% soln. in CCl_4, NaCl matched cells.

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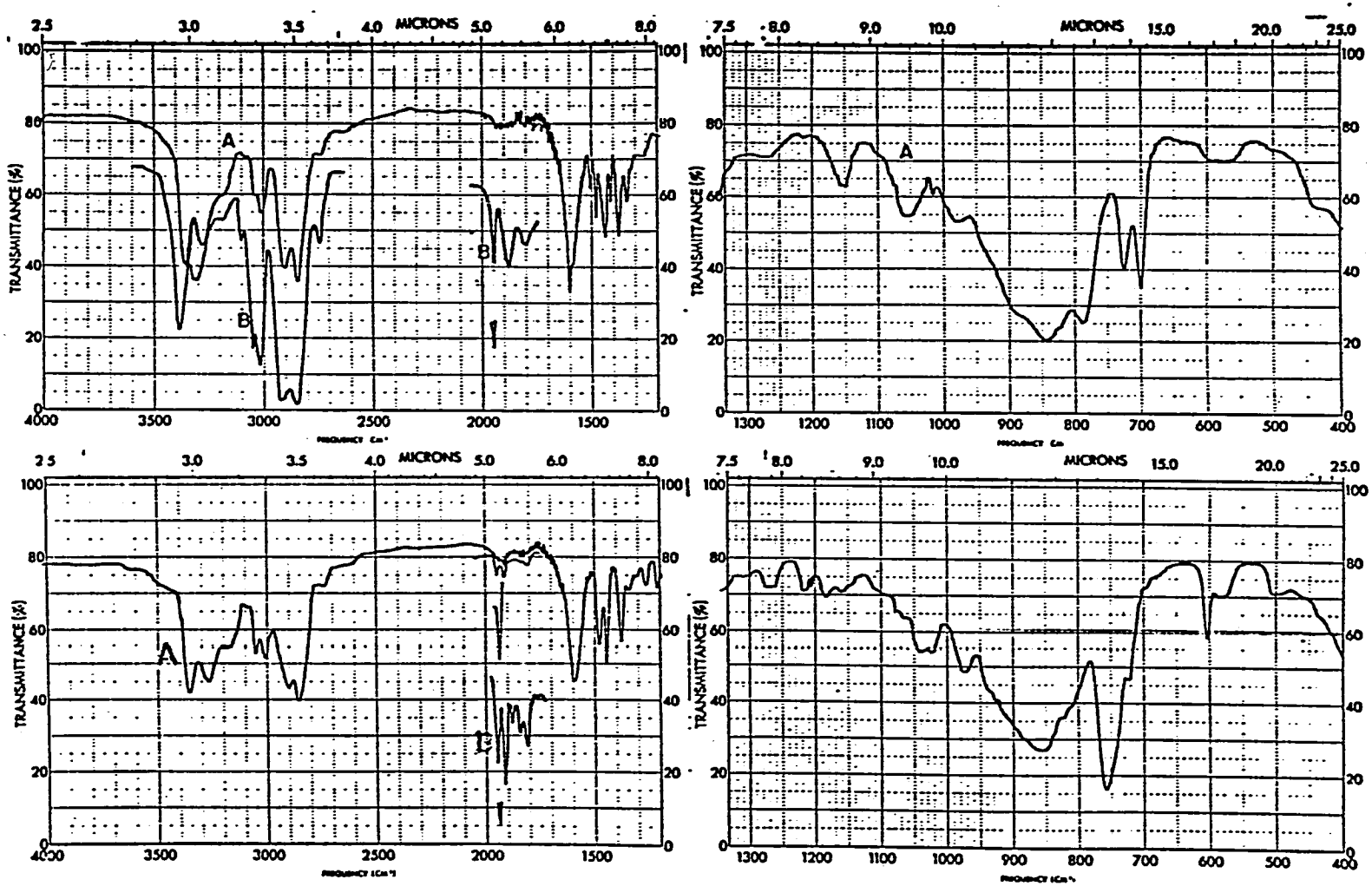

Fig. 1.14(top; 2 ranges): m-xylylenediamine; scan A, liquid film between KBr discs; scan B, 10% CCl_4 solution.

Fig. 1.15(bottom; 2 ranges): o-xylylenediamine; scan A, liquid film between KBr discs; scan B, 10% CCl_4 solution.

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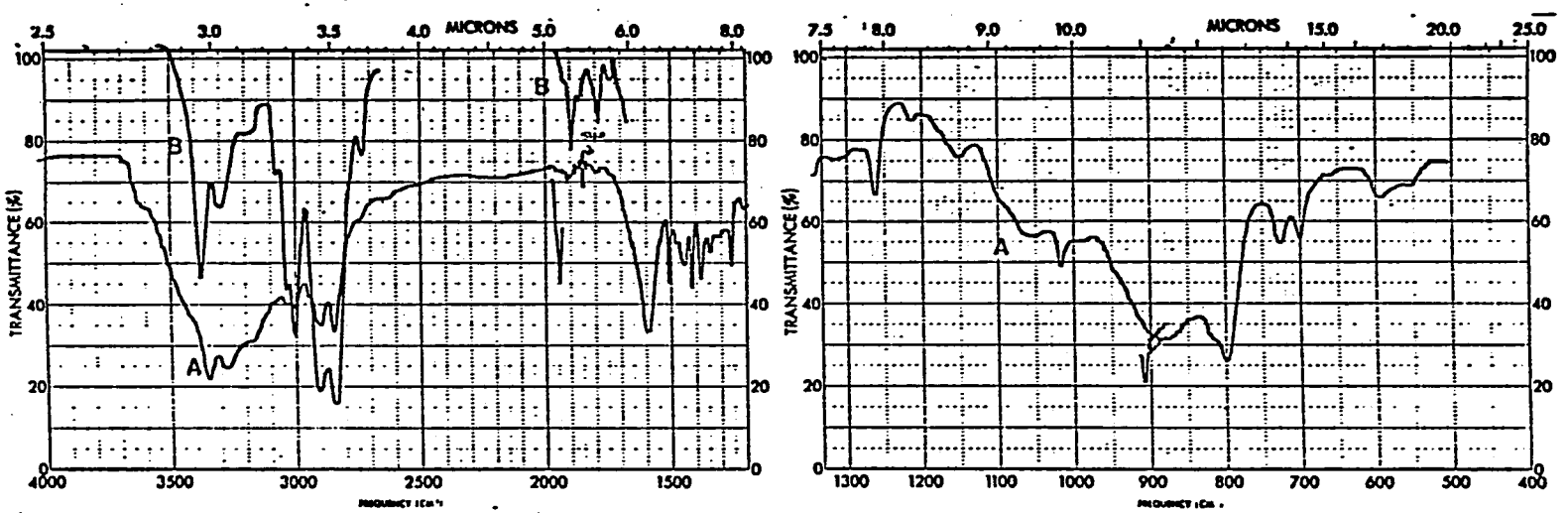

Fig. 1.16(2 ranges): p-xylylenediamine; scan A, film between KBr discs; scan B, 10% CCl_4 solution.

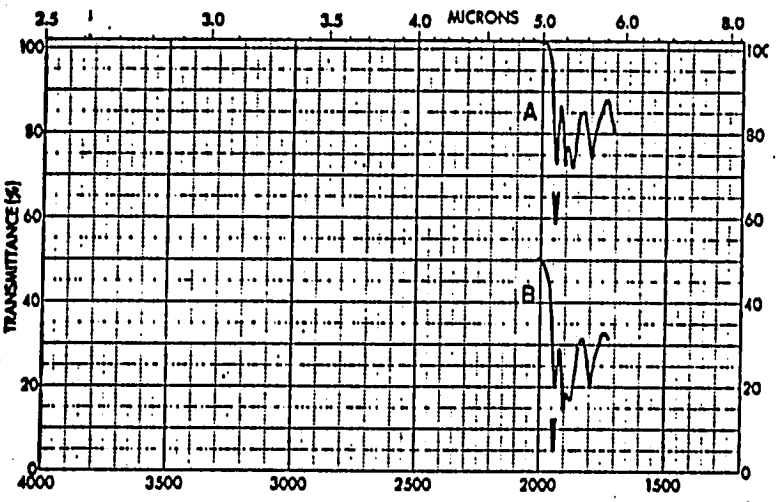

Fig. 1.17: scan A, mixed m- and p-xylylenediamines, Sho-Amine-X (Showa Denko K.K.); scan B, enrichment in p-xylylenediamine with fractional distillation.

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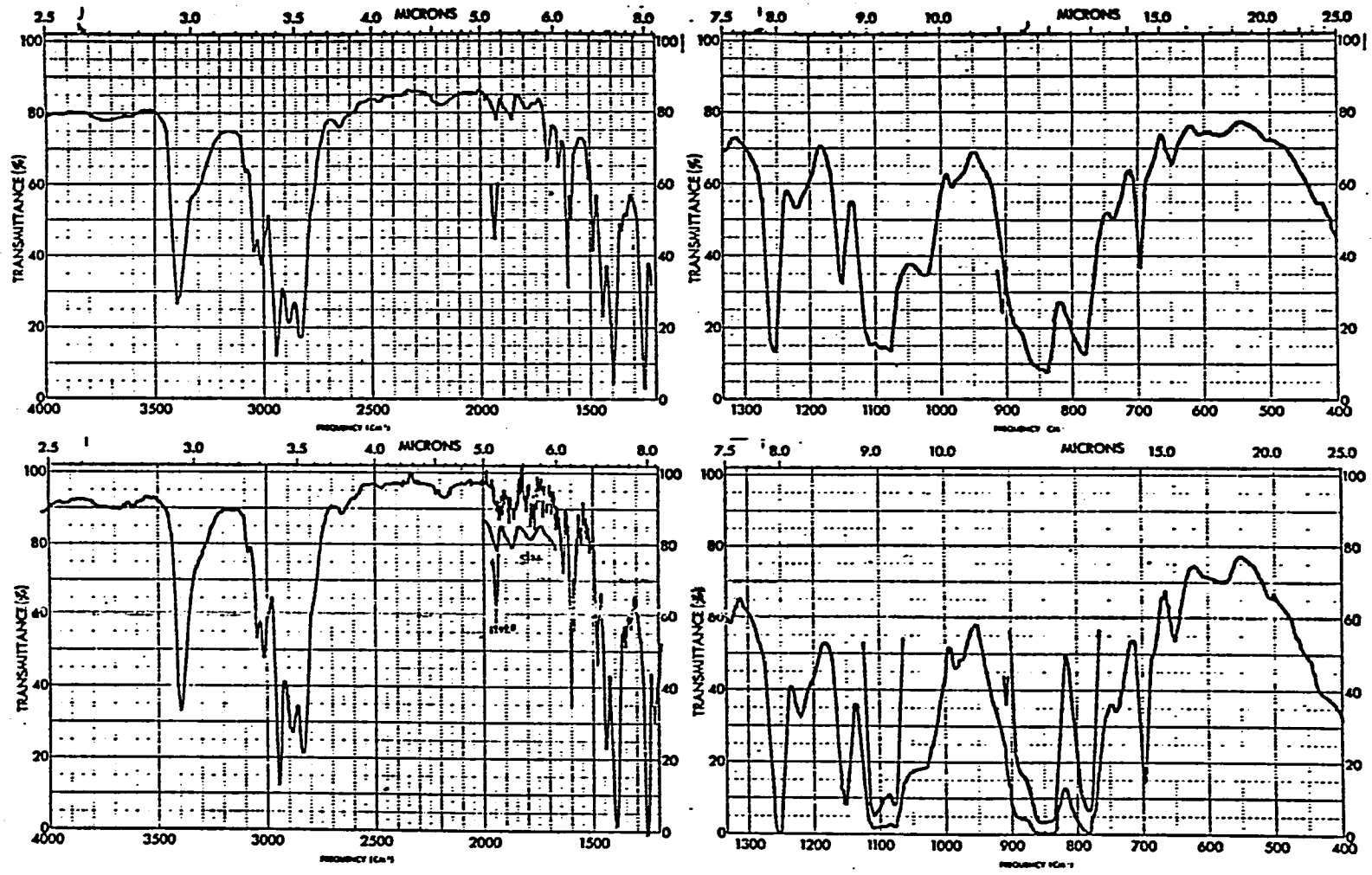

Fig. 1.18(top; 2 ranges): $[(CH_3)_2Si\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, first reaction, film between KBr discs.

Fig. 1.19(bottom; 2 ranges): $[(CH_3)_2Si\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, third reaction, film between KBr discs.

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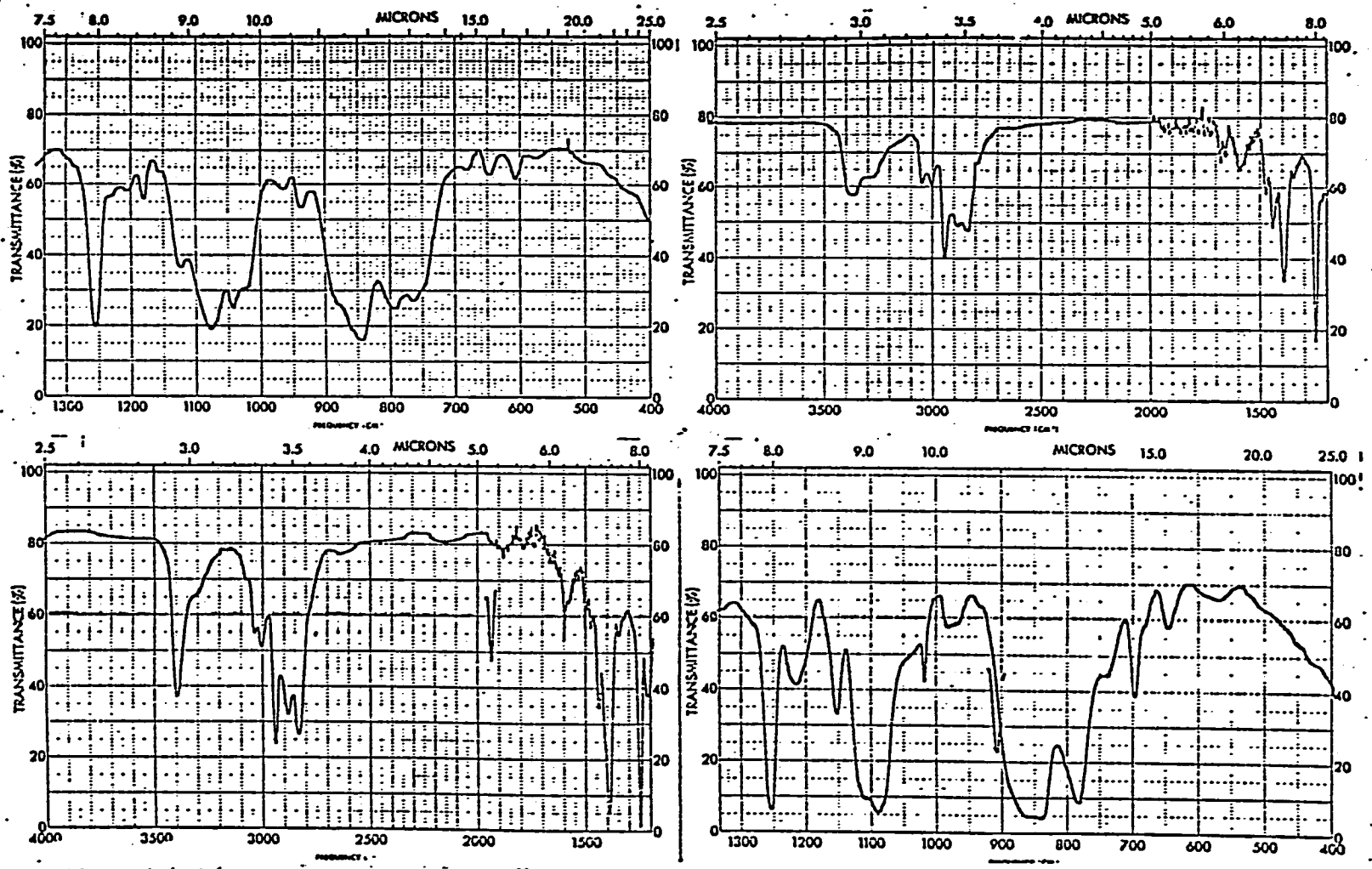

Fig. 1.20(top; 2 ranges): oil from $(CH_3)_2SiCl_2$ + o-xylylenediamine, 81.5°-90°C at 0.05 mm Hg, liquid film between KBr discs.

Fig. 1.21(bottom; 2 ranges): $[(CH_3)_2Si\text{-}(p)\text{-}NHCH_2C_6H_4CH_2NH]_x$, film between KBr discs.

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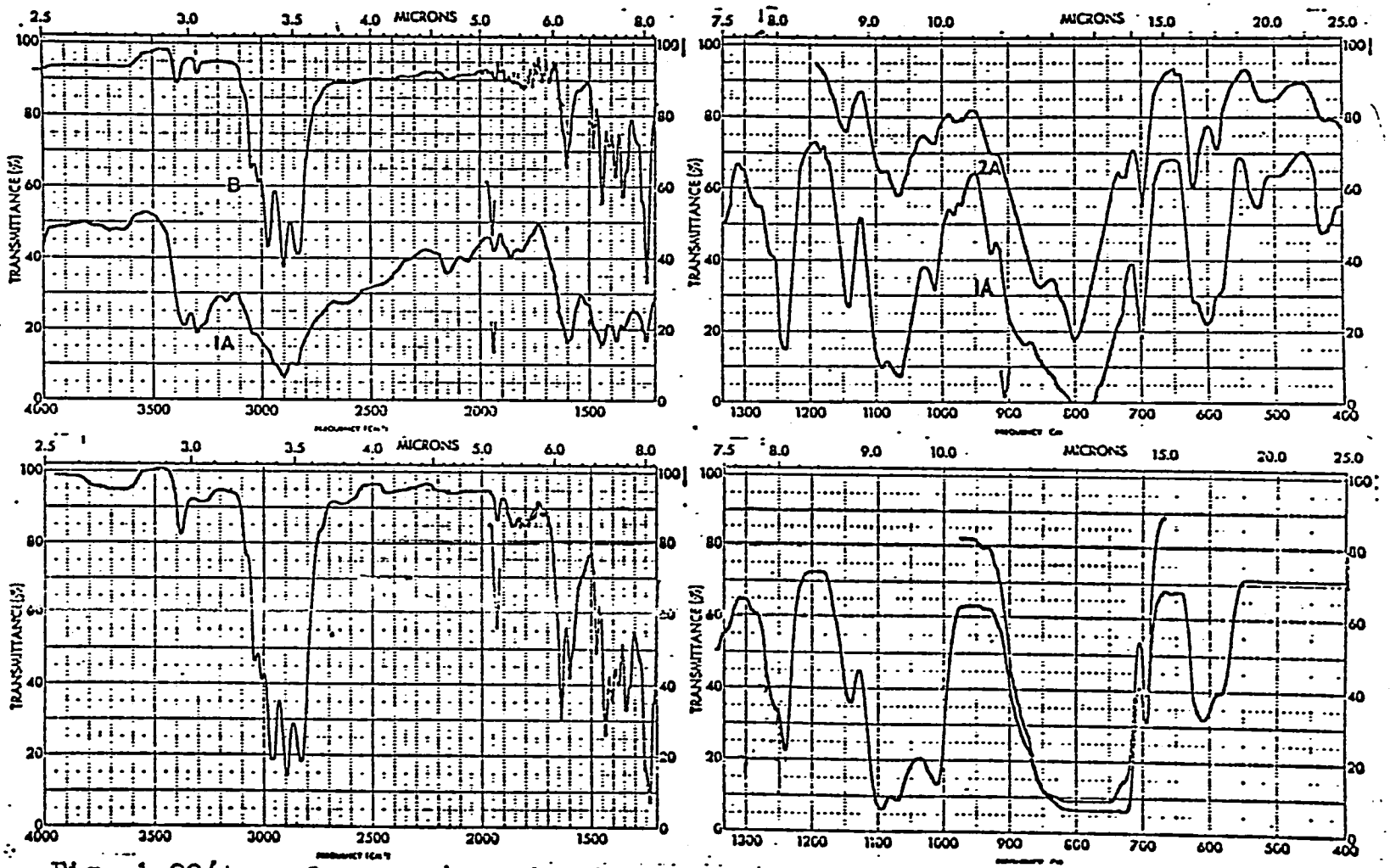

Fig. 1.22(top; 2 ranges): $[(CH_3)_2Ge\text{-}(p)\text{-}NHCH_2C_6H_4CH_2NH]_x$; scan A, film between KBr discs; scan B, dilute CCl_4 solution in NaCl matched cells.

Fig. 1.23(bottom; 2 ranges): $[(CH_3)_2Ge\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, dilute CCl_4 solution in NaCl matched cells.

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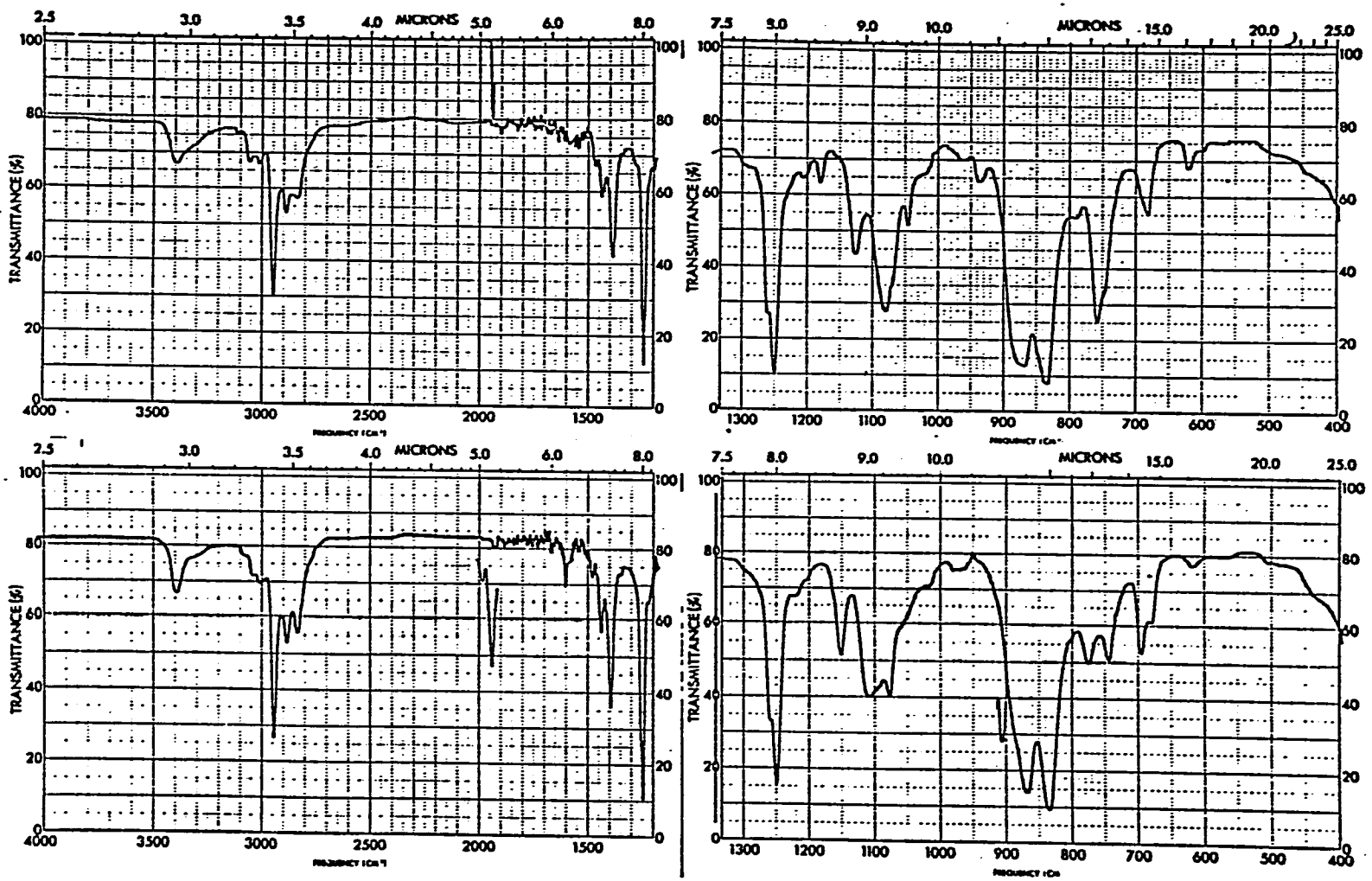

Fig. 1.24(top; 2 ranges): $(CH_3)_3SiCl$ + o-xylylenediamine; fraction 91°-92.5°C at 0.075mm; liquid film between KBr discs.

Fig. 1.25(bottom; 2 ranges): $(CH_3)_3Si$-(m)-$NHCH_2C_6H_4CH_2NHSi(CH_3)_3$, liquid film between KBr discs.

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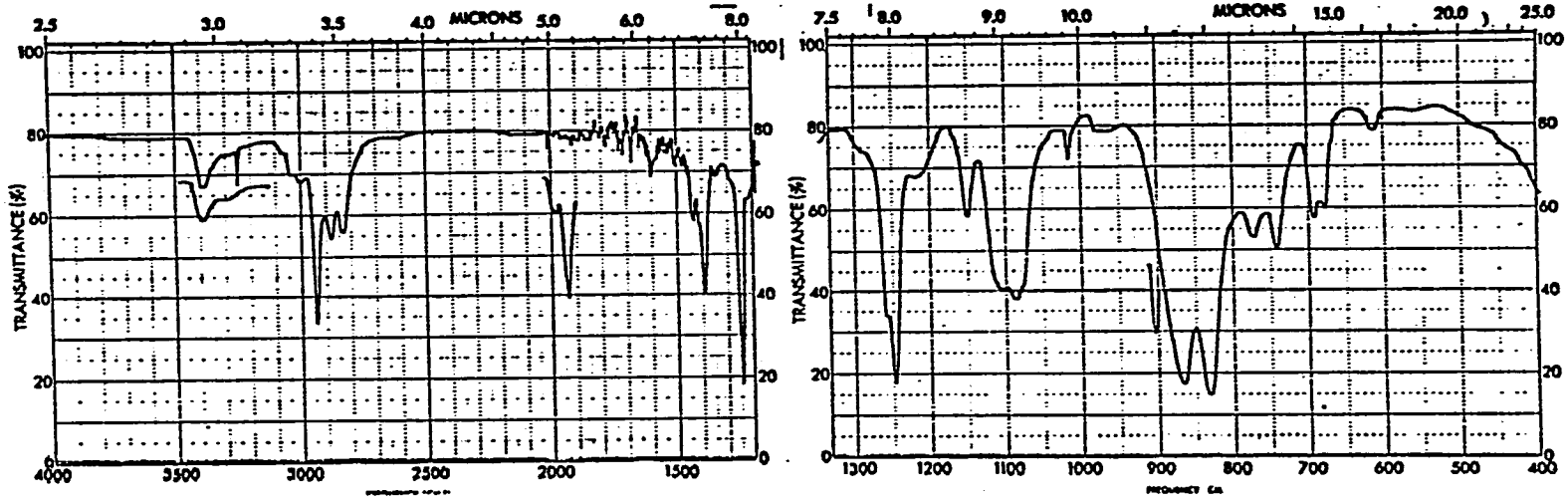

Fig. 1.26(2 ranges): $(CH_3)_3Si$-(p)-$NHCH_2C_6H_4CH_2NHSi(CH_3)_3$, liquid film between KBr discs.

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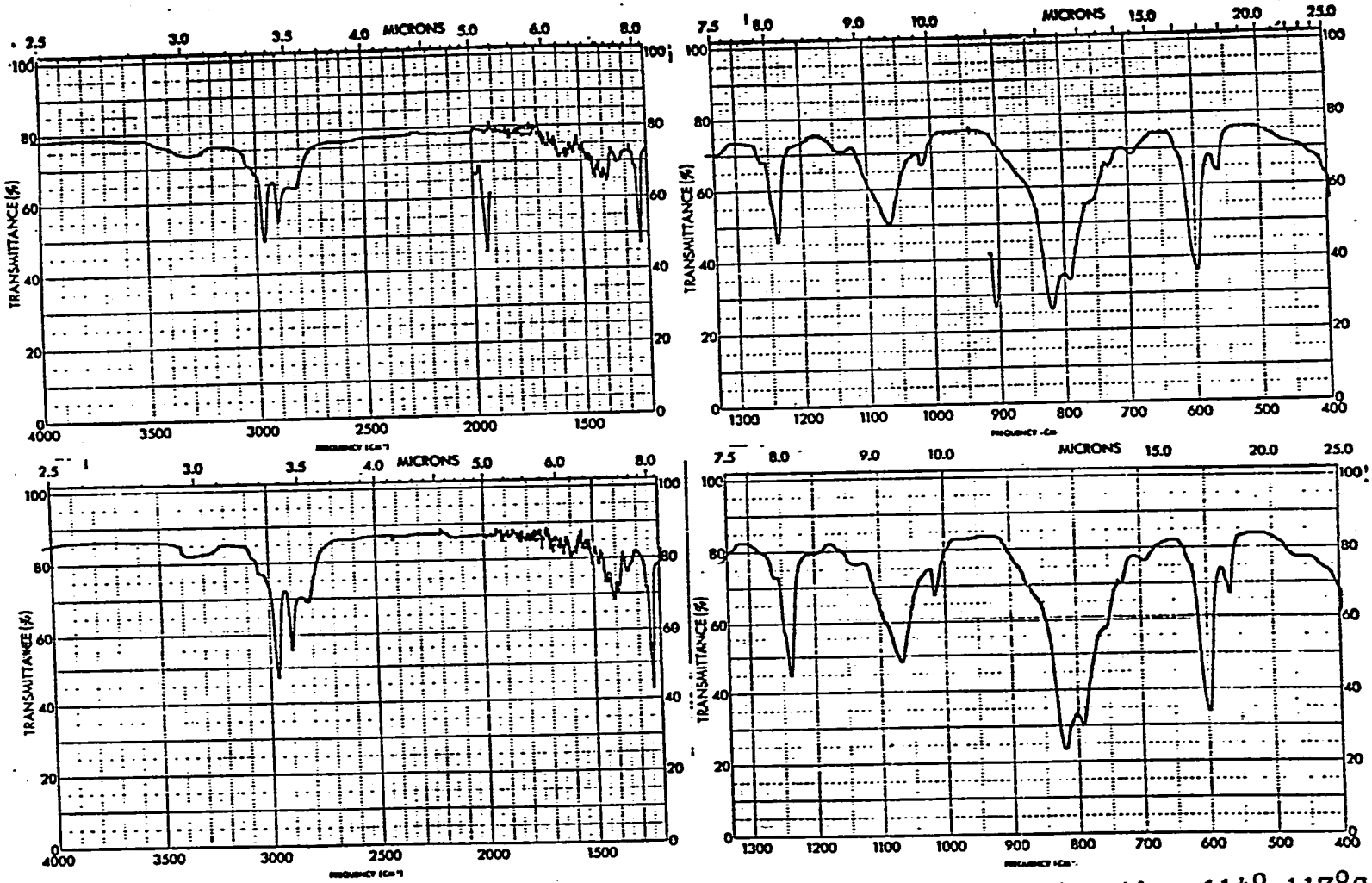

Fig. 1.27(top; 2 ranges): $(CH_3)_3GeBr$ + p-xylylenediamine; fraction 114°-117°C at 0.04 mm; liquid film between KBr discs.

Fig. 1.28(bottom; 2 ranges): $(CH_3)Ge$-(p)-$NHCH_2C_6H_4CH_2NHGe(CH_3)_3$, liquid film between KBr discs.

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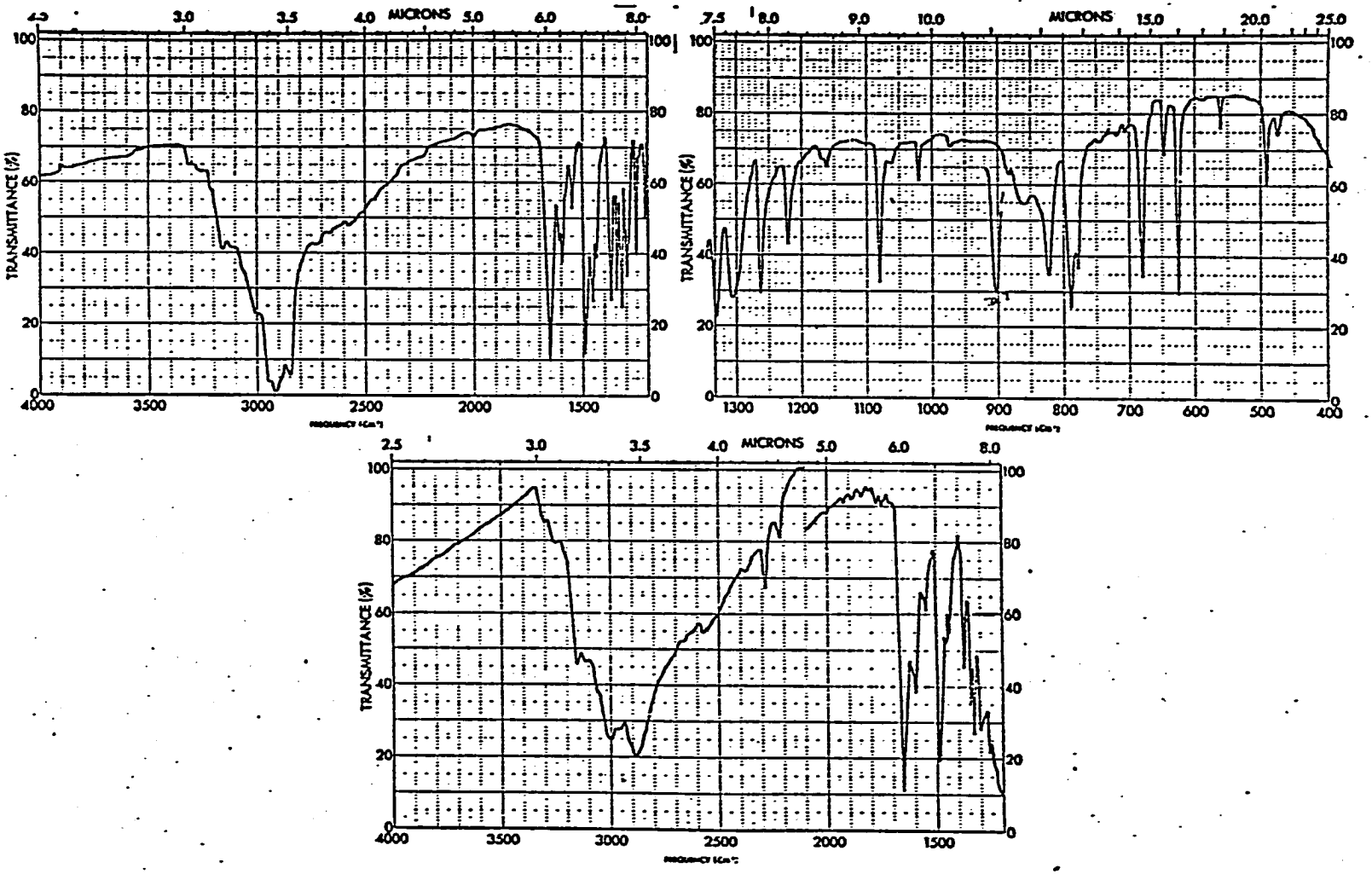

Fig. 1.29(top; 2 ranges): 2,3-dihydrophthalazine-1,4-dione, Kadol mull between KBr discs.

Fig. 1.30(bottom): 2,3-dihydrophthalazine-1,4-dione, Fluorolube mull between KBr discs.

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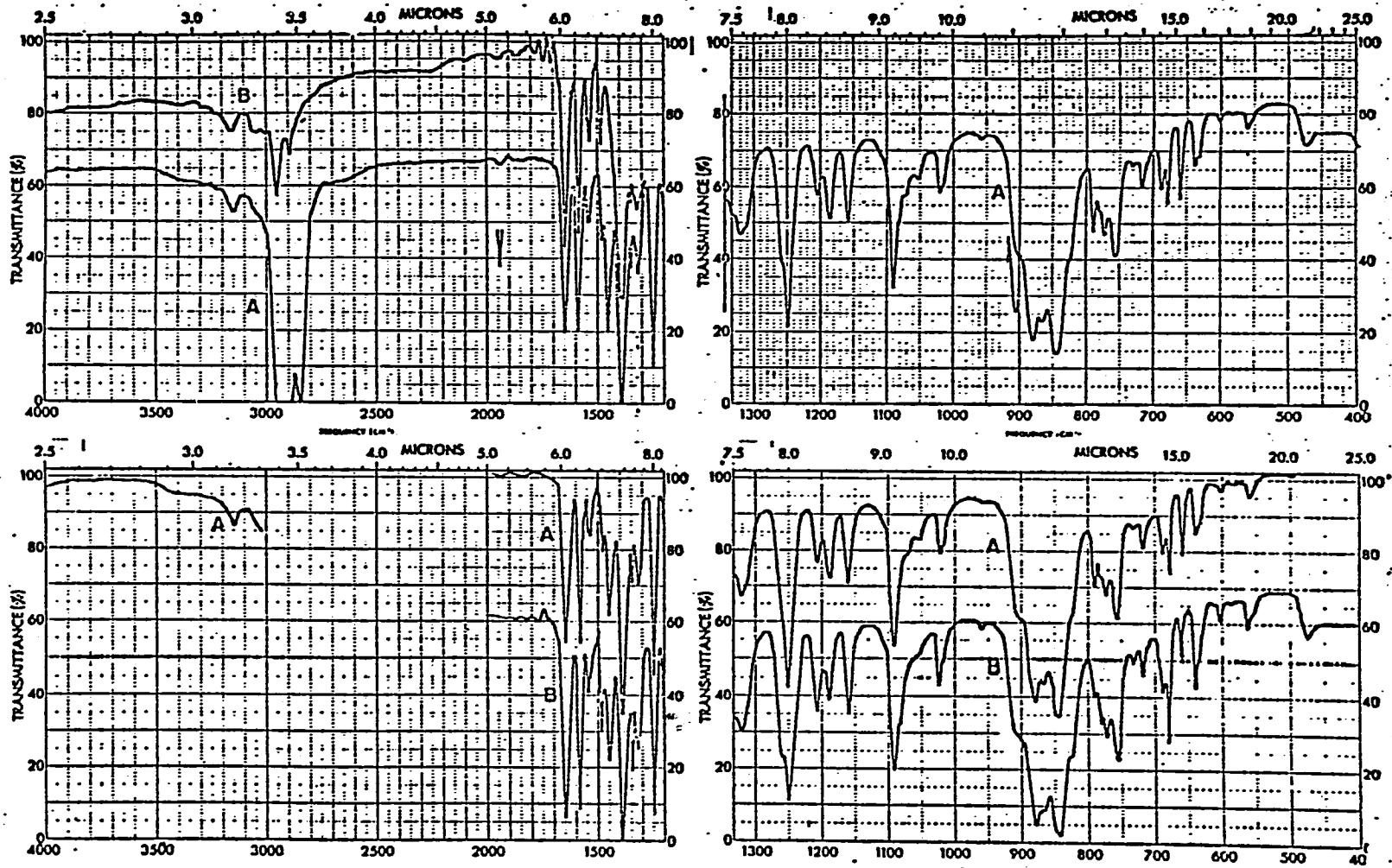

Fig. 1.31(top; 2 ranges): $(CH_3)_3Si$-(hydrazide)-$Si(CH_3)_3$; scan A, Kadol mull between KBr discs; scan B, Fluorolube mull between KBr discs.

Fig. 1.32(bottom; 2 ranges): $(CH_3)_3Si$-(hydrazide)-$Si(CH_3)_3$; scan A, Kadol mull exposed to air 1 minute; scan B, Kadol mull exposed to air 20 minutes.

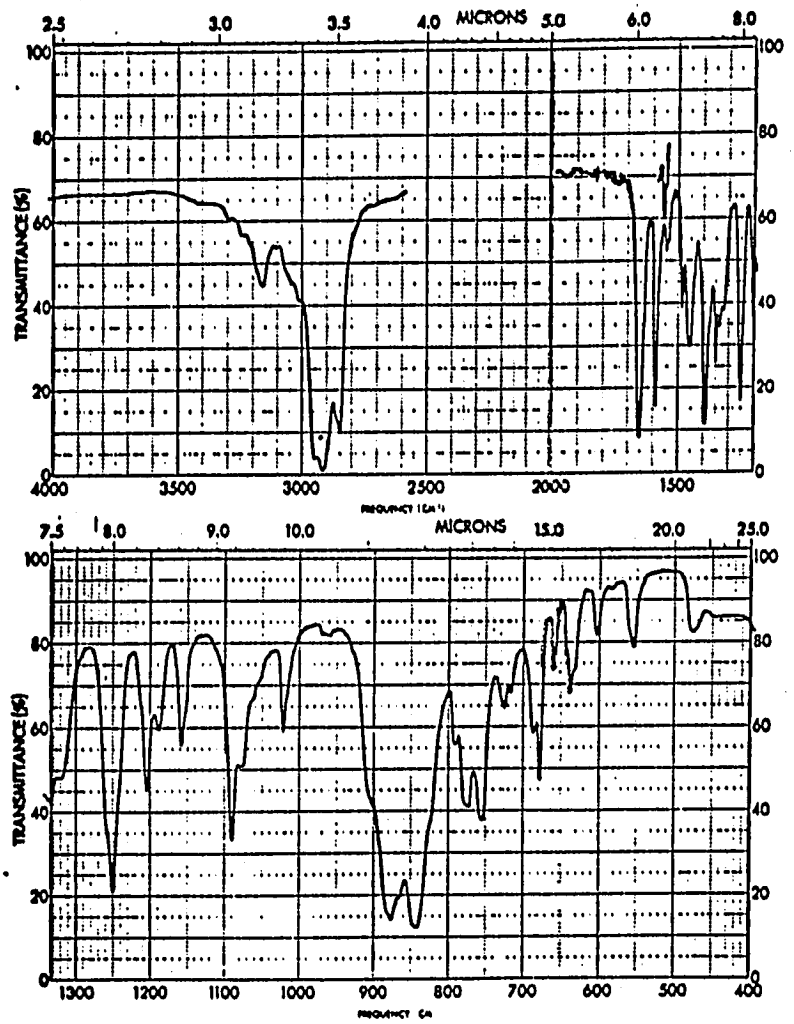

Fig. 1.33(2 ranges): $(CH_3)_3Si$-(hydrazide)-$Si(CH_3)_3$; Kadol mull exposed to air 2 hours.

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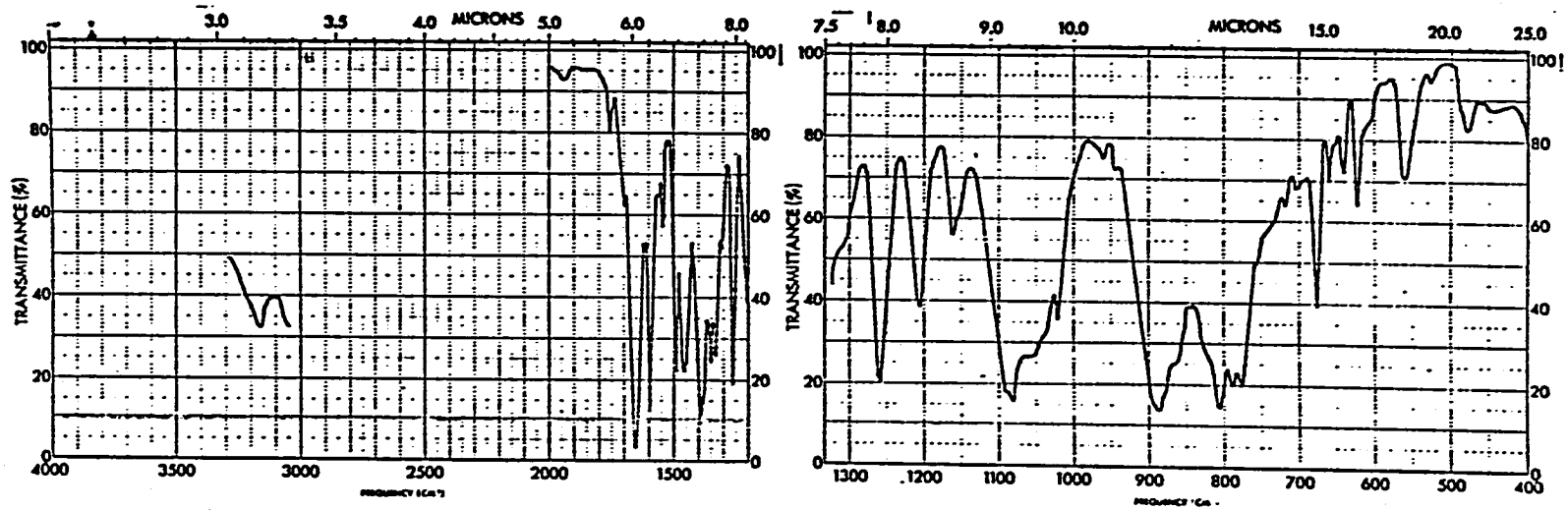

Fig. 1.34(2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$, Kadol mull between KBr discs, prepared in air.

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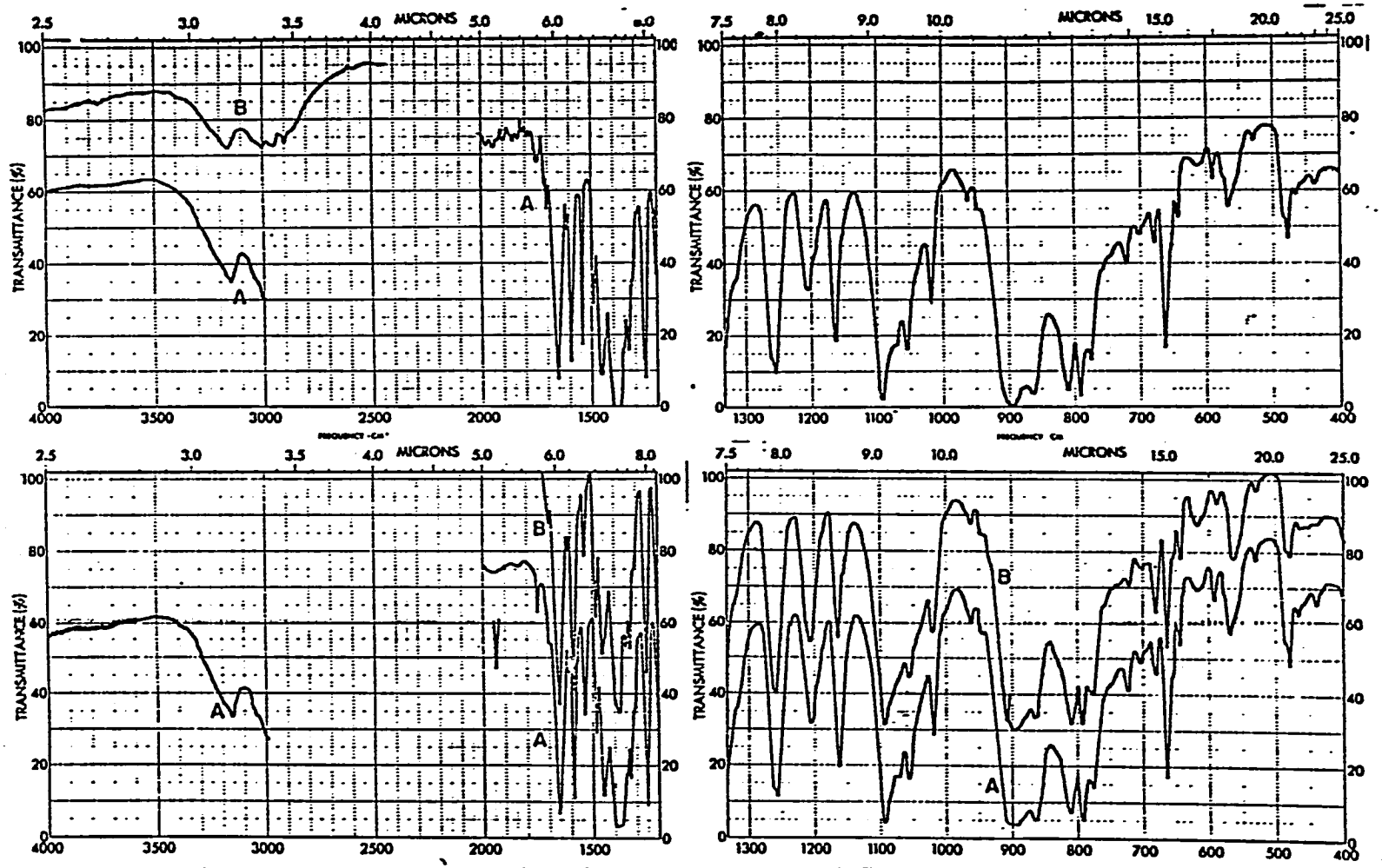

Fig. 1.35(top; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; scan A, Kadol mull between KBr discs, prepared in glove bag; scan B, Fluorolube mull, prepared in glove bag.

Fig. 1.36(bottom; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; scan A, Kadol mull exposed to air 1 minute; scan B, Kadol mull exposed to air 2 minutes.

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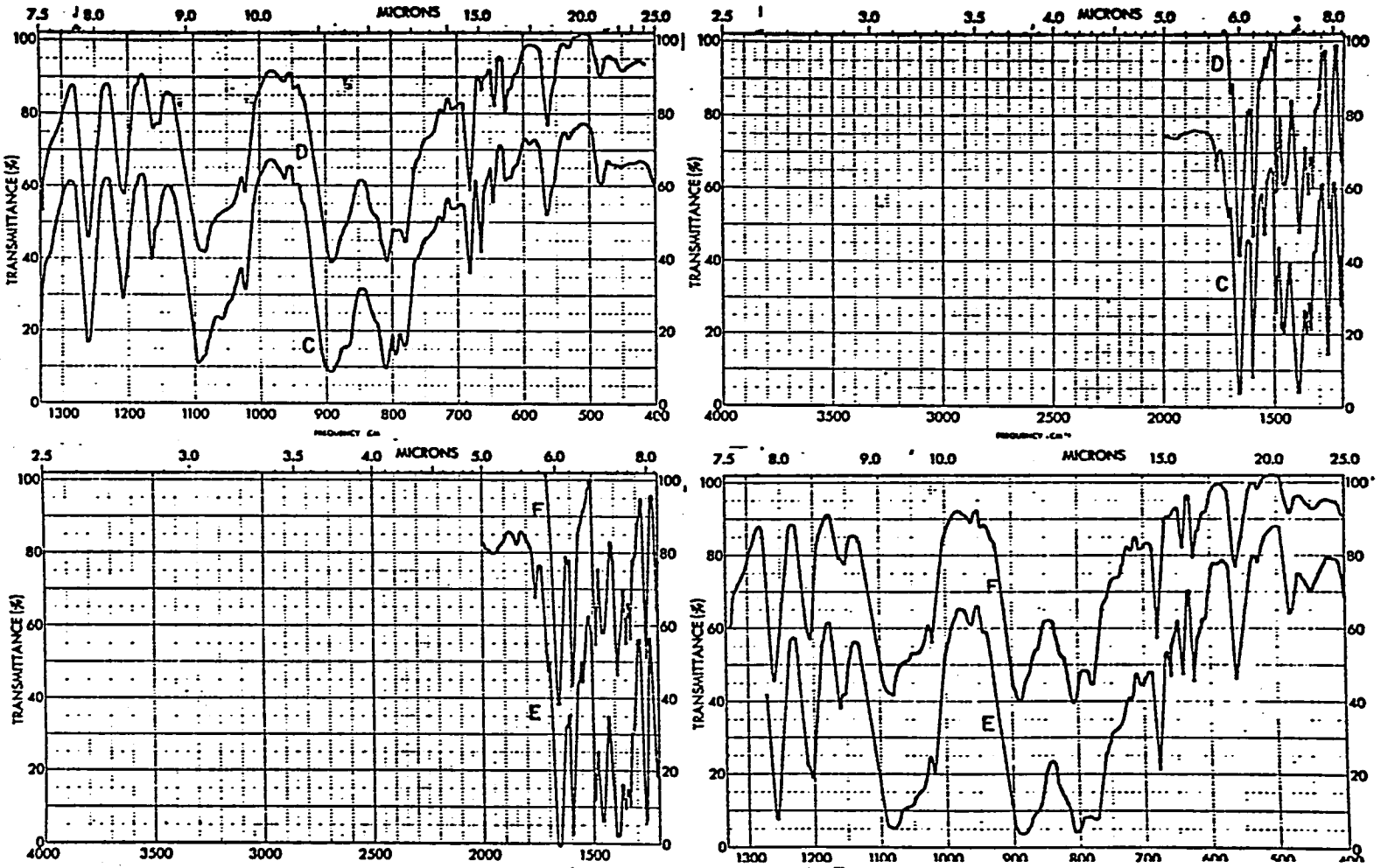

Fig. 1.37(top; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; scan C, Kadol mull exposed to air 5 minutes; scan D, Kadol mull exposed to air 7 minutes.

Fig. 1.38(bottom; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; scan E, Kadol mull exposed to air 15 minutes; scan F, Kadol mull exposed to air 30 minutes.

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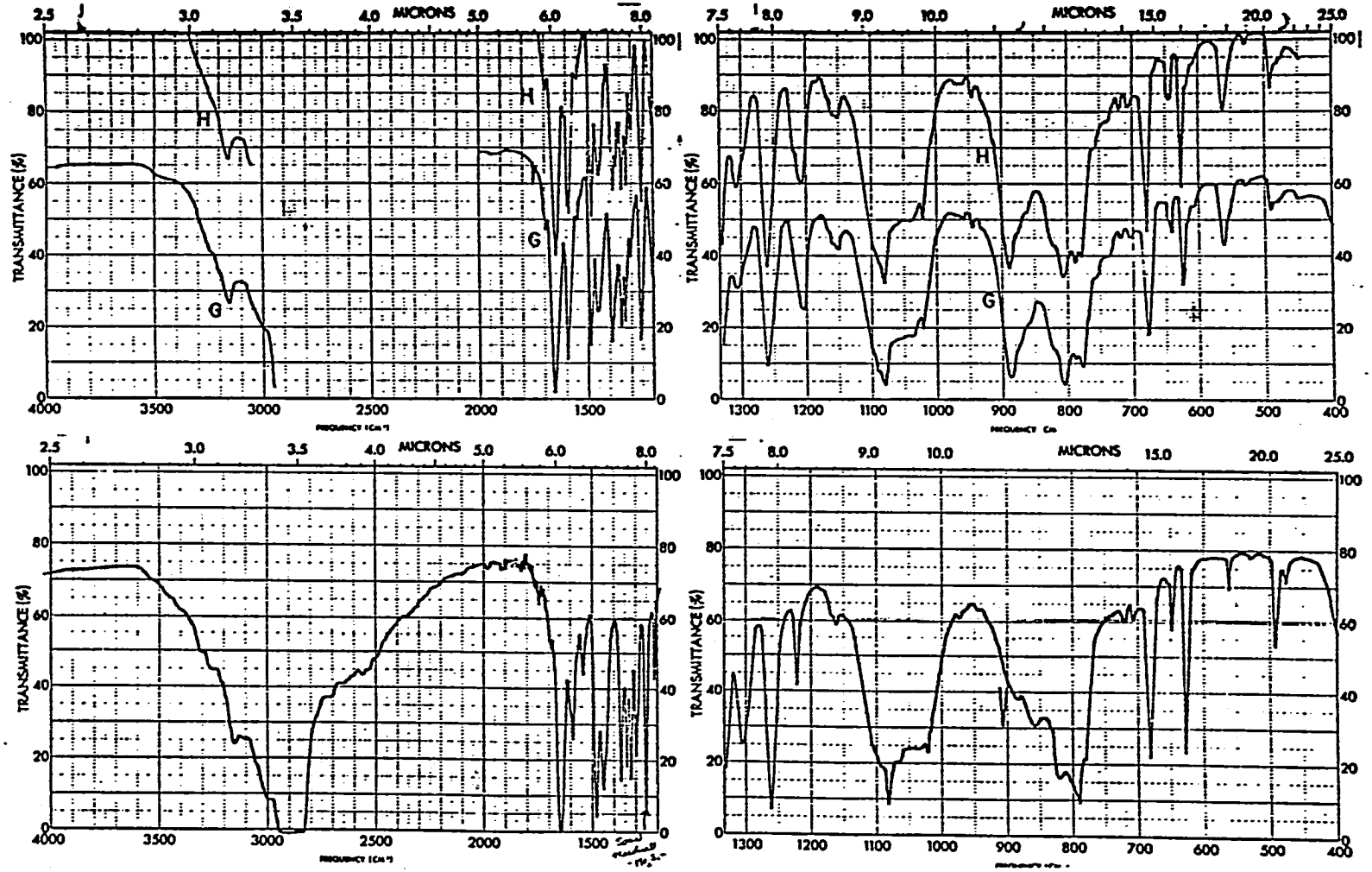

Fig. 1.39(top; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; scan G, Kadol mull exposed to air 1.5 hours; scan H, Kadol mull exposed to air 2.5 hours.

Fig. 1.40(bottom; 2 ranges): $[(CH_3)_2Si\text{-(hydrazide)-}]_x$; Kadol mull exposed to air 18 hours.

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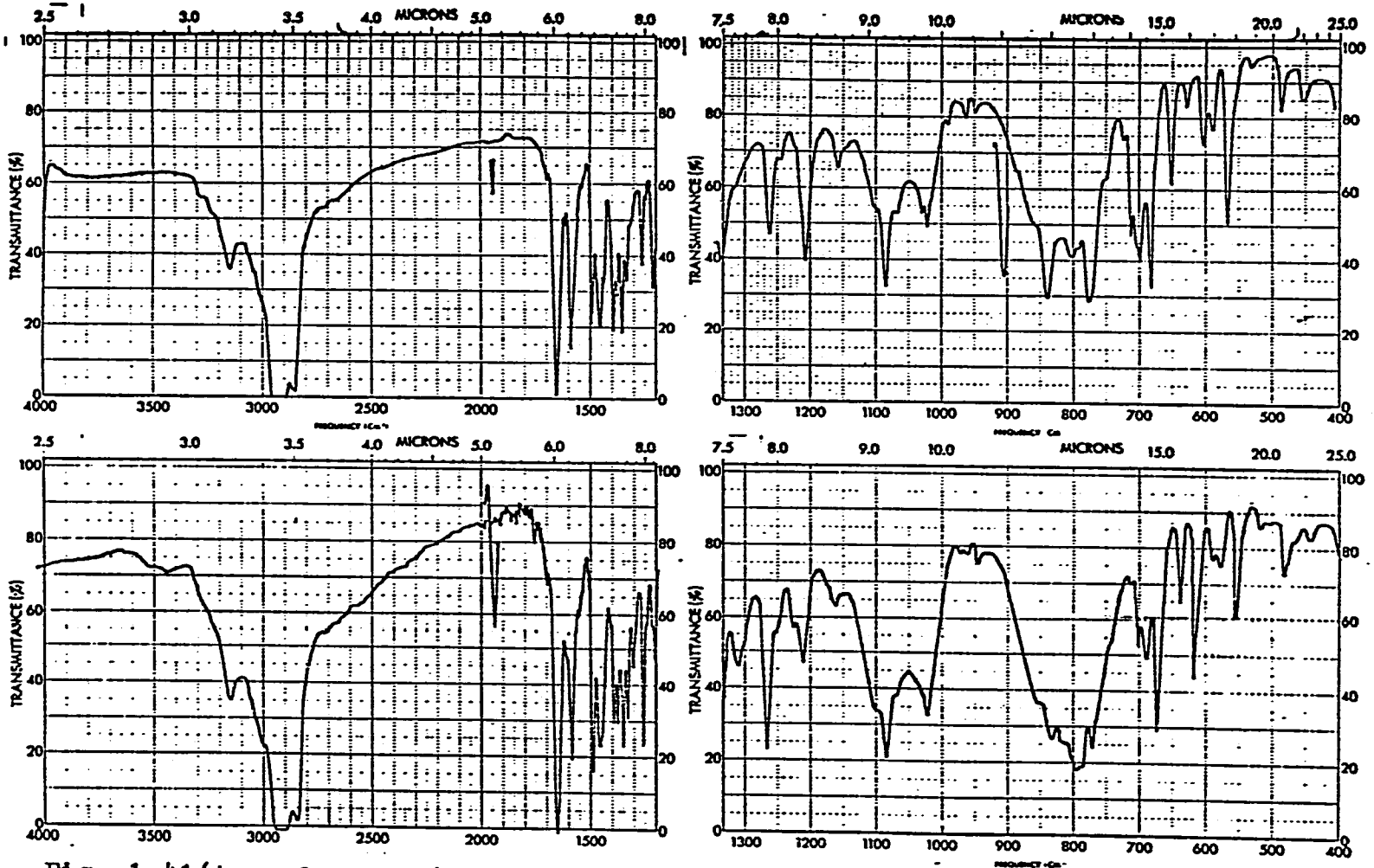

Fig. 1.41(top; 2 ranges): $[(CH_3)_2Ge\text{-(hydrazide)-}]_x$, Kadol mull between KBr discs, prepared in glove bag.

Fig. 1.42(bottom; 2 ranges): $[(CH_3)_2Ge\text{-(hydrazide)-}]_x$, Kadol mull exposed to air 1 hour.

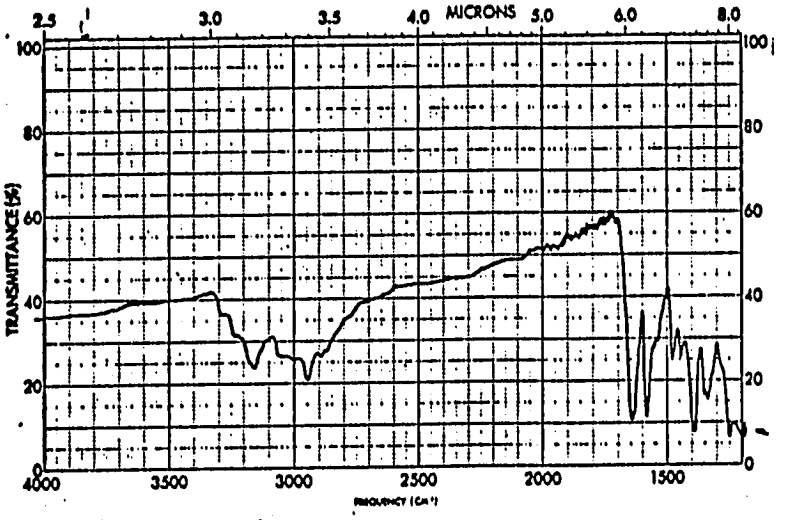

Fig. 1.43: $[(CH_3)_2Ge\text{-(hydrazide)-}]_x$, Fluorolube mull between KBr discs, prepared in glove bag.

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Appendix B

NMR Spectra

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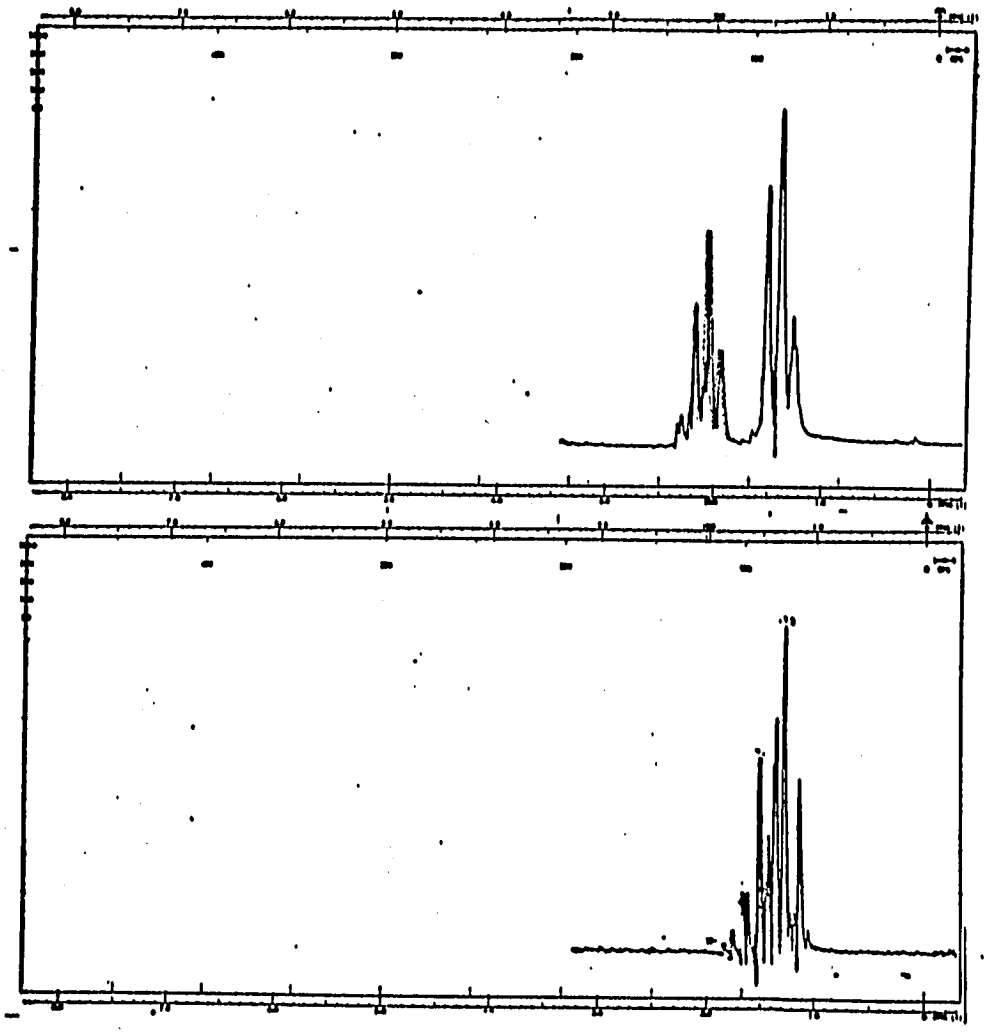

Fig. 2.1(top): $EtGeCl_3$, 10% by volume in CCl_4, TMS internal standard.

Fig. 2.2(bottom): Et_2GeCl_2, 10% by volume in CCl_4, TMS internal standard.

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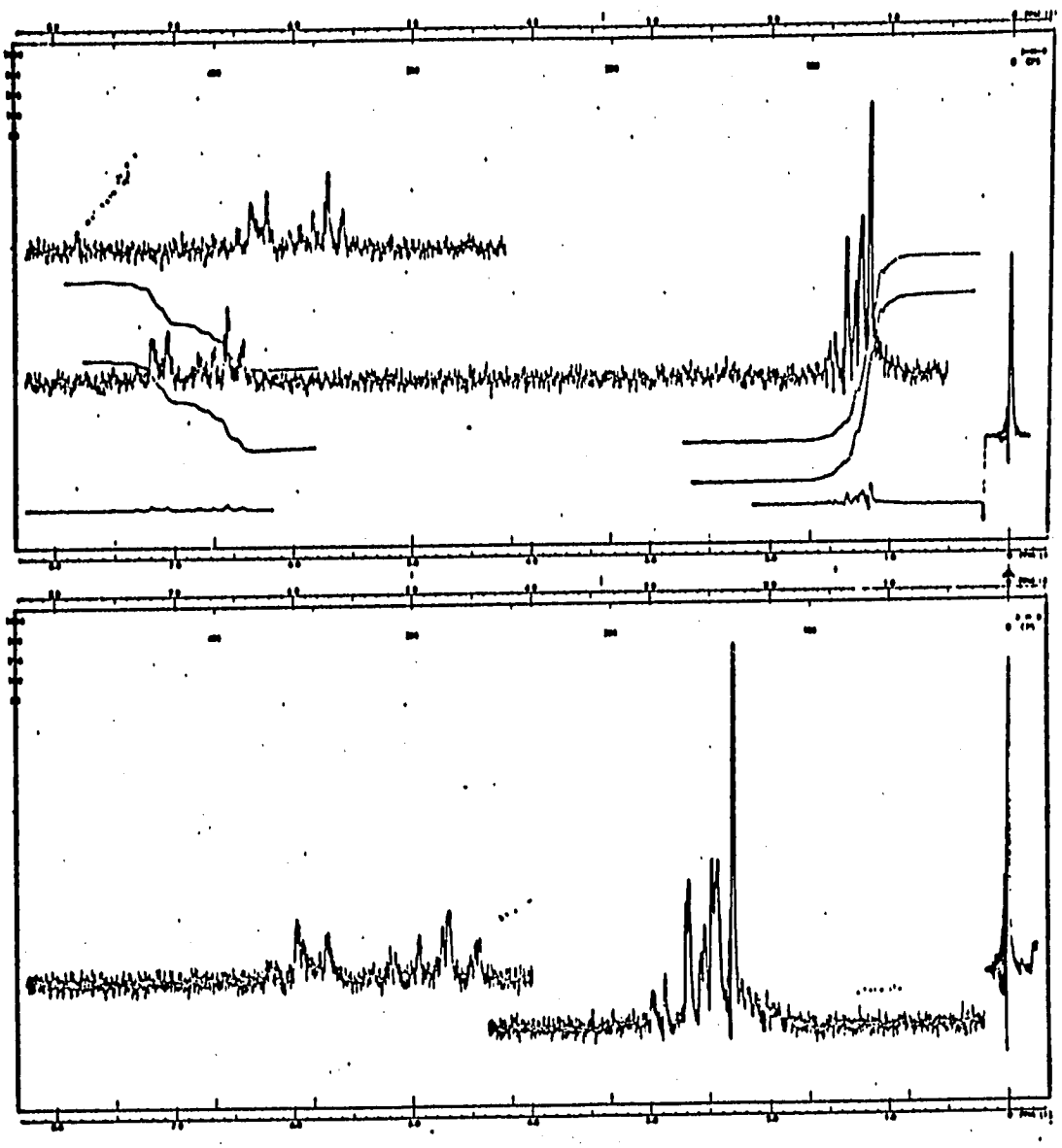

Fig. 2.3(top): $(Et_2GeNC_6H_5)_4$, 10% by volume in pyridine-d_5, TMS internal standard, 500 Hz scan.

Fig. 2.4(bottom): $(Et_2GeNC_6H_5)_4$, 10% by volume in pyridine-d_5, TMS internal standard, 250 Hz scan.

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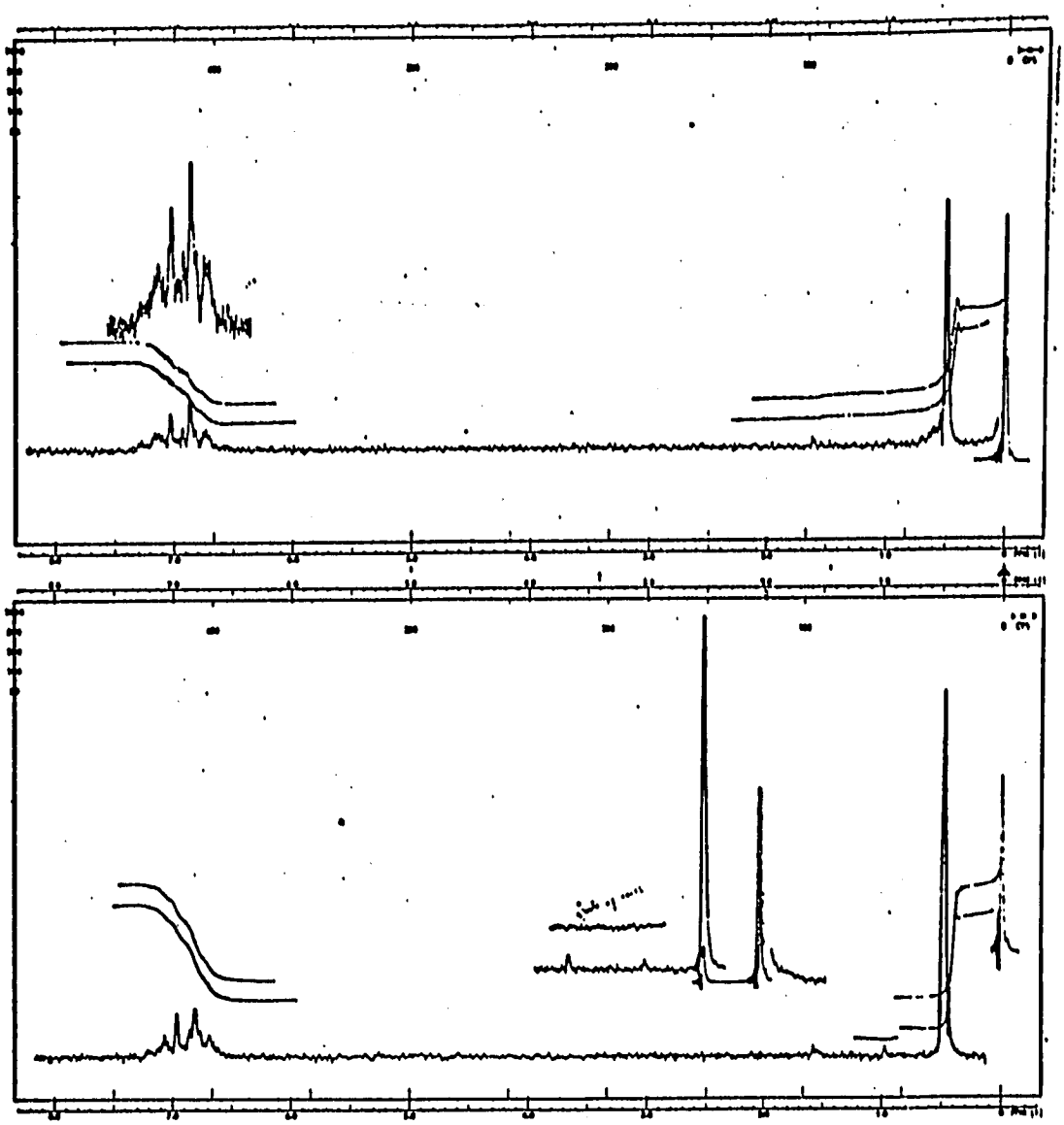

Fig. 2.5(top): $[(CH_3)_2GeNC_6H_5]_3$, 10% by volume in $CDCl_3$, TMS internal standard.

Fig. 2.6(bottom): $[(CH_3)_2GeNC_6H_5]_3$, 10% by volume in CCl_4, TMS internal standard.

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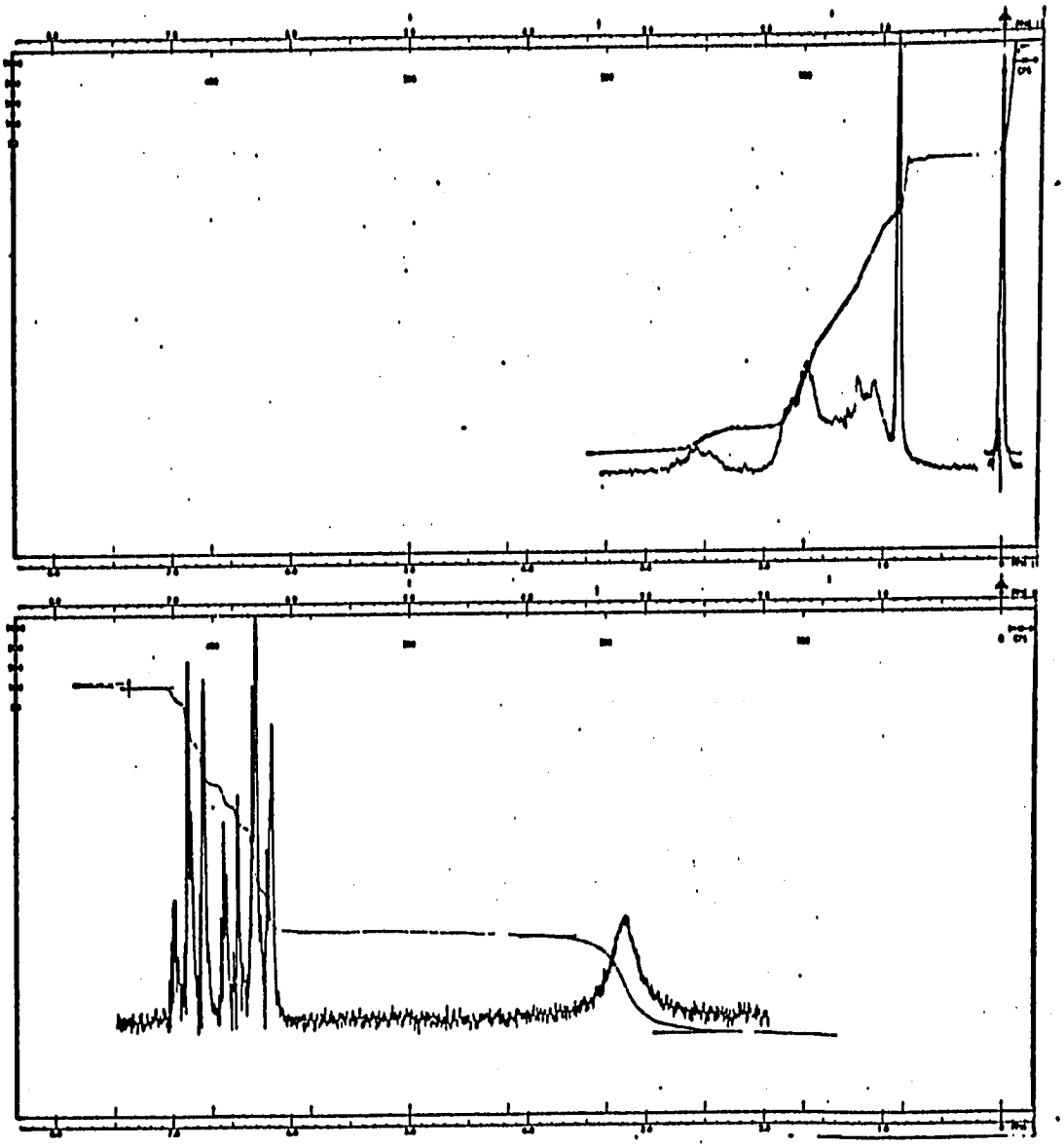

Fig. 2.7(top): cyclohexylamine, 10% in CCl_4, TMS internal standard.

Fig. 2.8(bottom): aniline, 10% in CCl_4, TMS internal standard.

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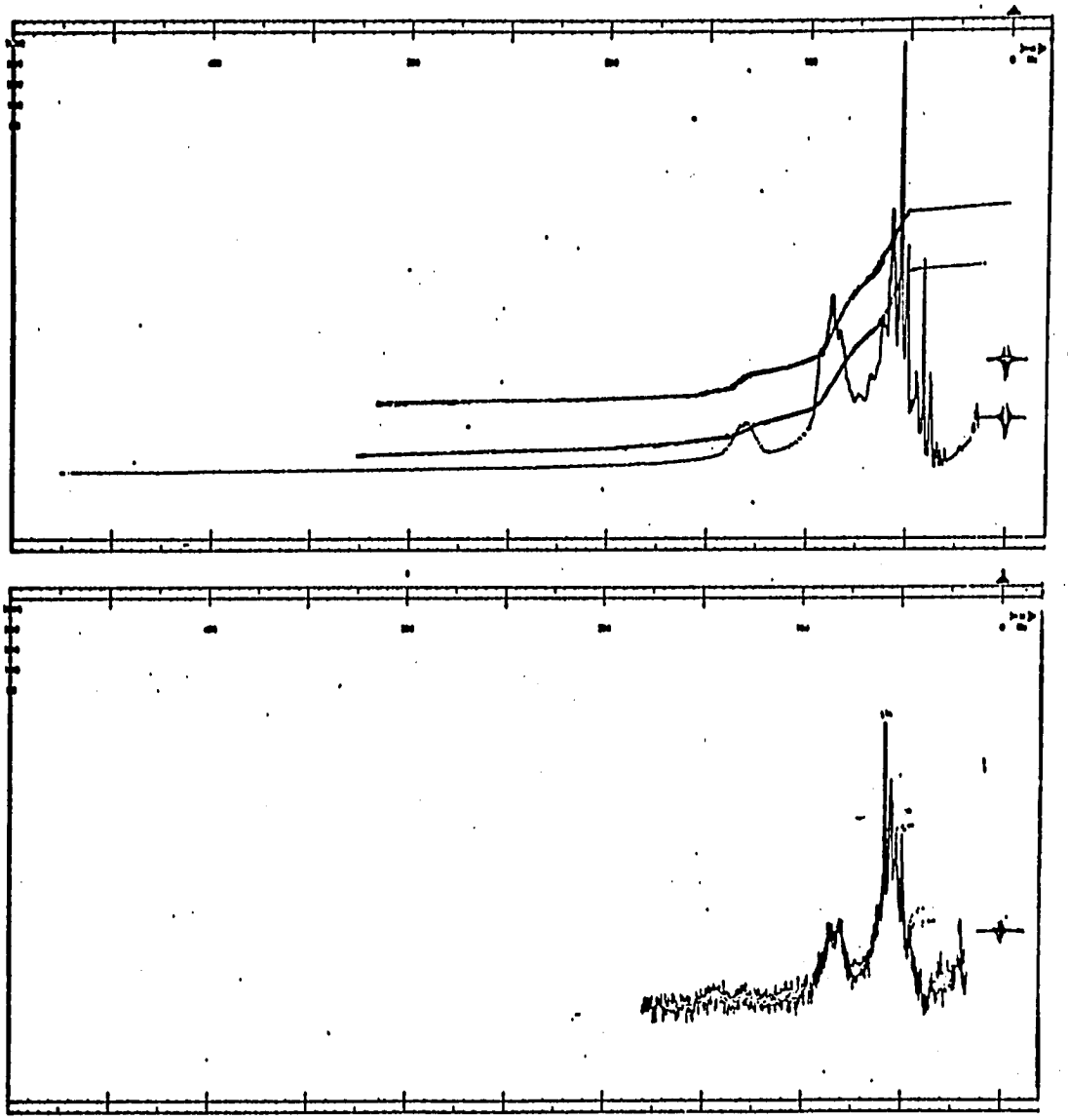

Fig. 2.9(top): $Et_2Ge(NHC_6H_{11})_2$, 10% in CCl_4, TMS internal standard; HA-100 spectrum.

Fig. 2.10(bottom): $(Et_2GeNC_6H_{11})_4$, 2% in CCl_4, TMS internal standard, HA-100 spectrum.

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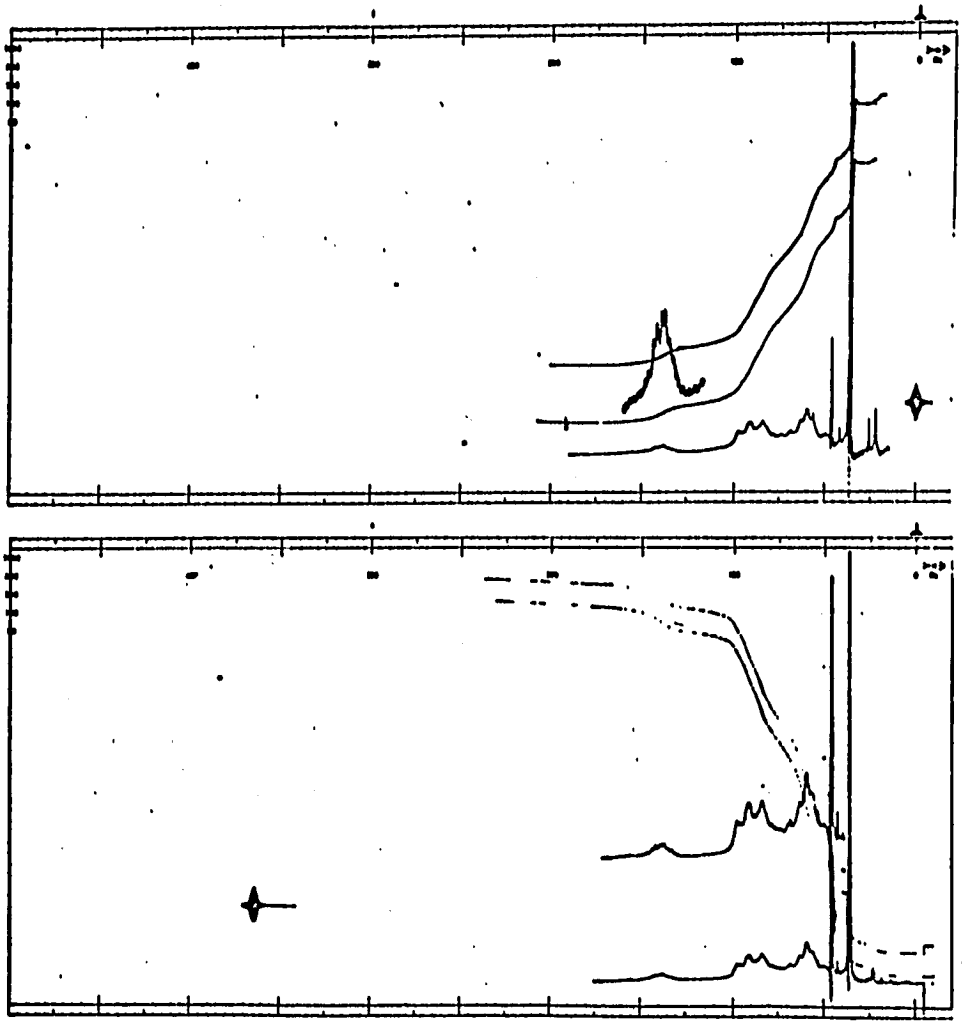

Fig. 2.11(top): $[(CH_3)_2Ge(NHC_6H_{11})_2]$, 10% in CCl_4, TMS internal standard, HA-100 spectrum.

Fig. 2.12(bottom): $[(CH_3)_2Ge(NHC_6H_{11})_2]$, 10% in CCl_4, benzene internal standard, HA-100 spectrum.

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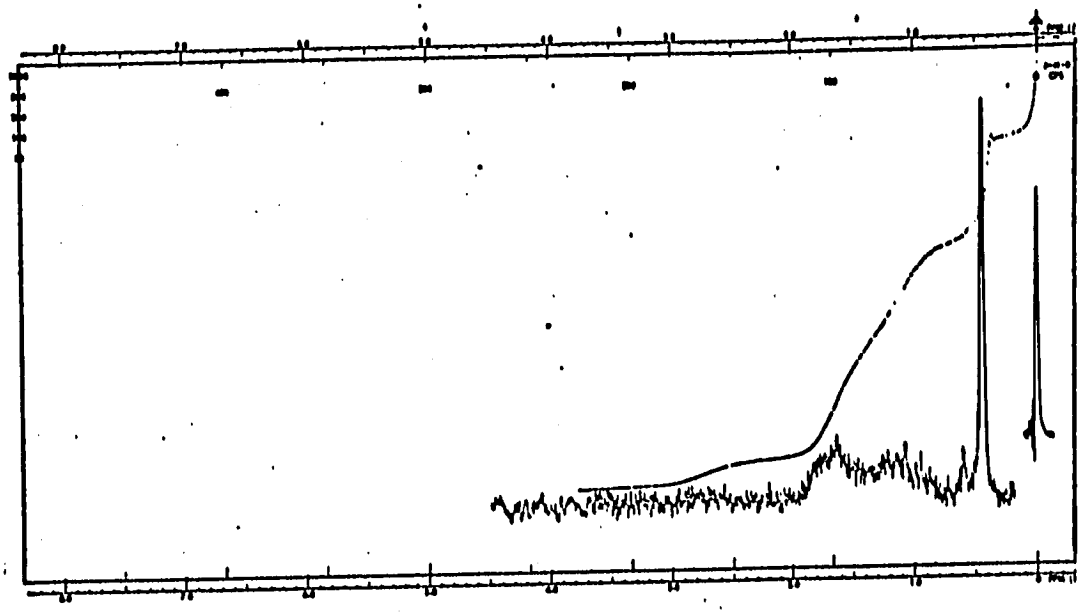

Fig. 2.13: $[(CH_3)_2GeNC_6H_{11}]_3$, 5% in CCl_4, TMS internal standard.

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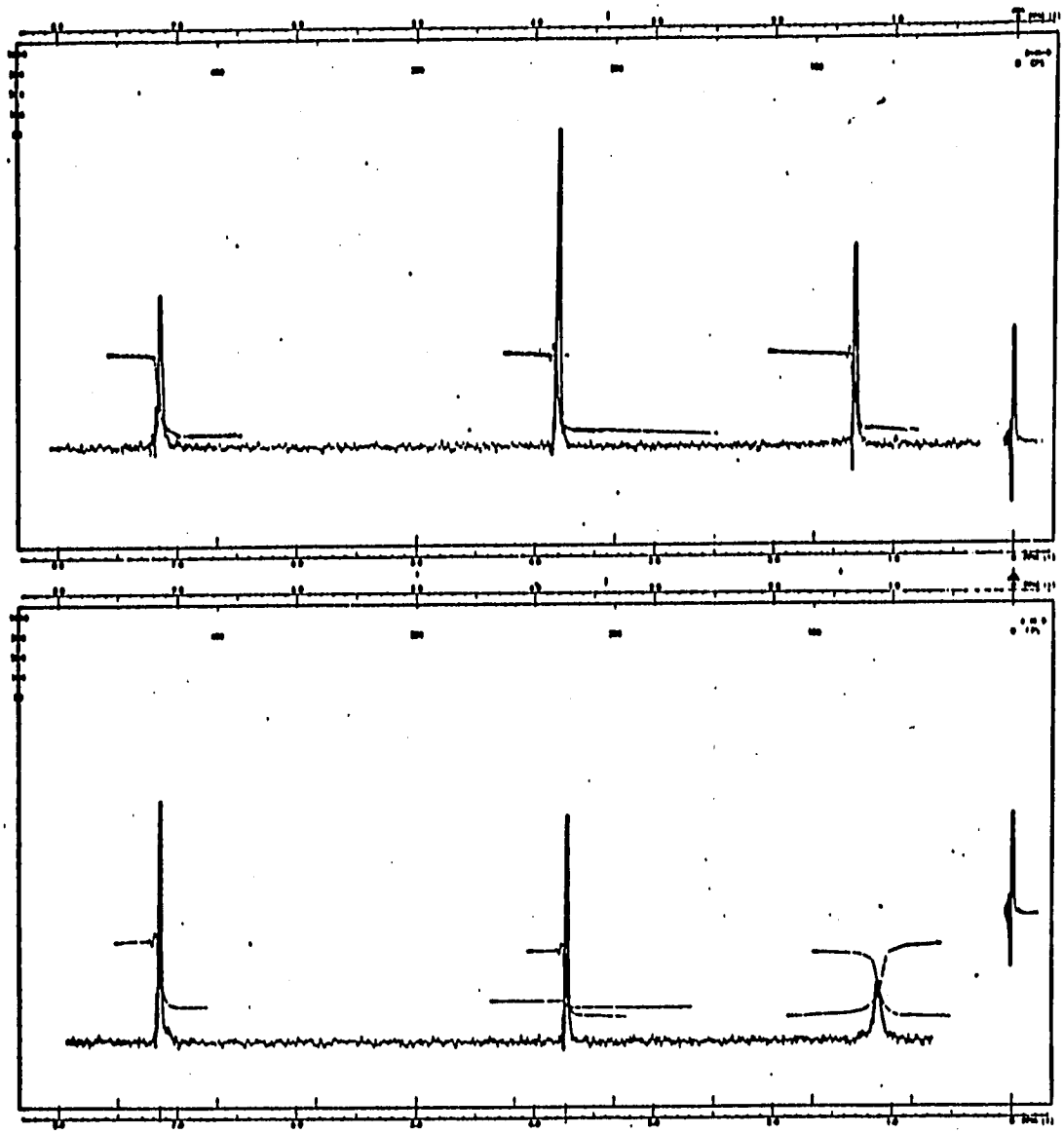

Fig. 2.14(top): o-xylylenediamine, 3.5% by wt. in CCl_4, TMS internal standard.

Fig. 2.15(bottom) p-xylylenediamine, 3.6% by wt. in CCl_4, TMS internal standard.

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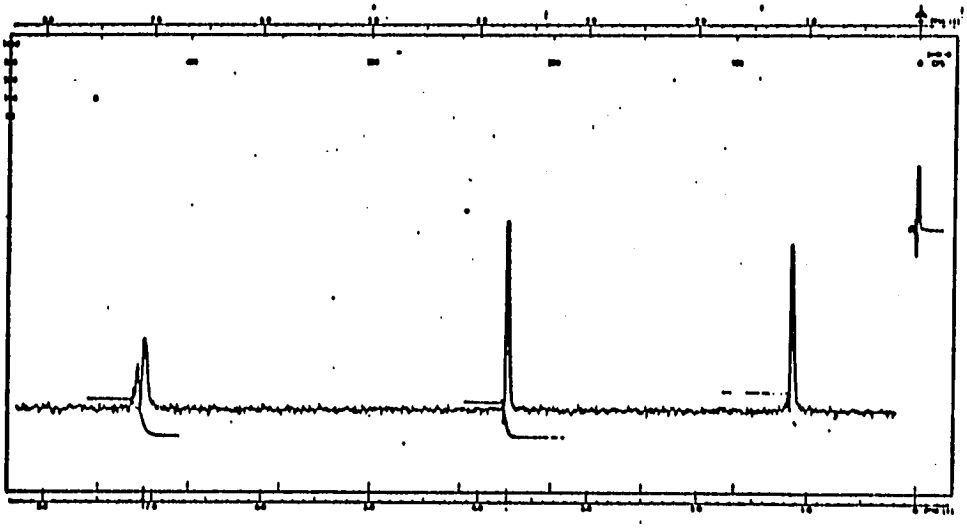

Fig. 2.16: m-xylylenediamine, 3.5% by wt. in CCl_4, TMS internal standard.

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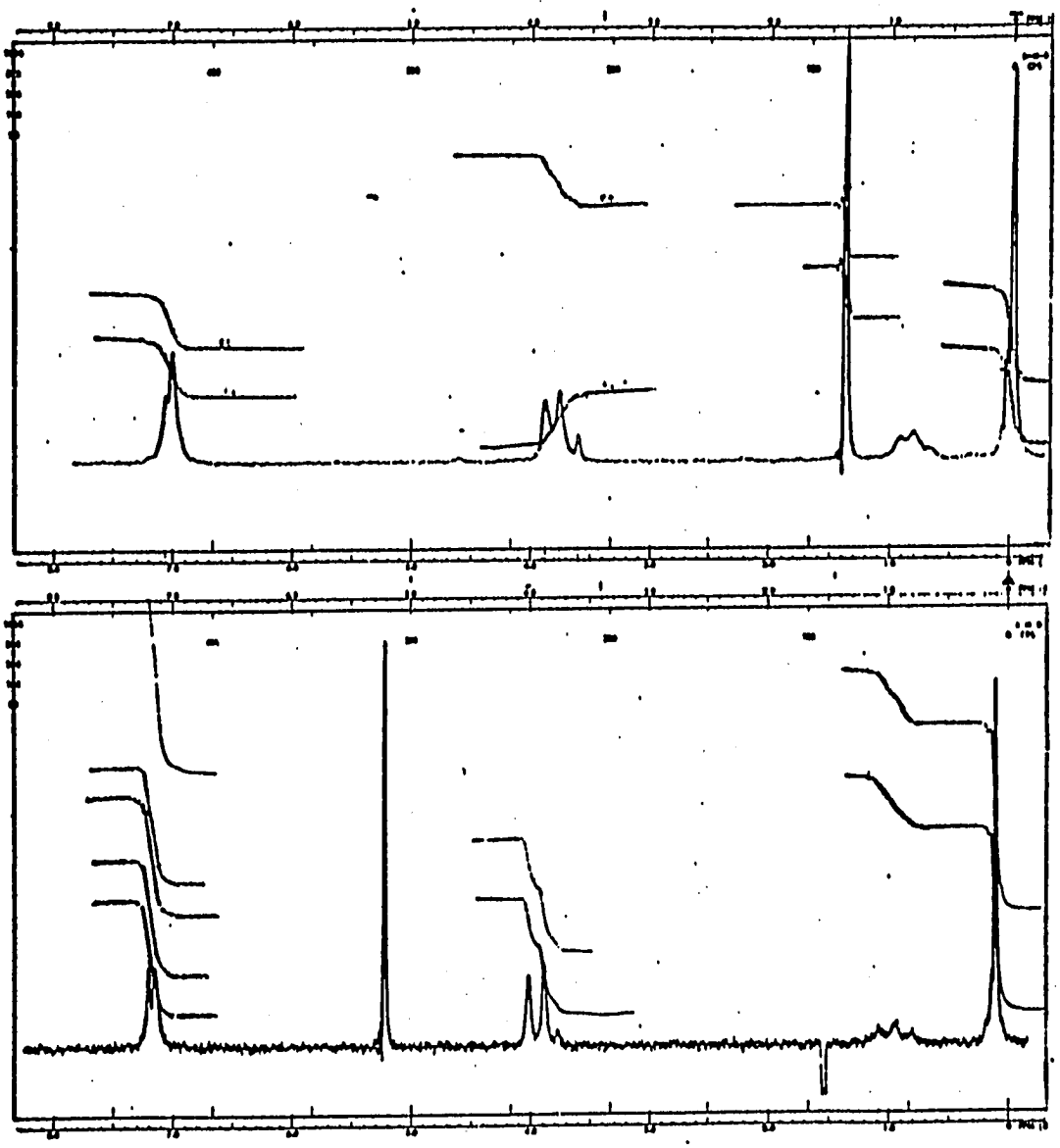

Fig 2.17(top): $[(CH_3)_2Si\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, 10% in CCl_4, cyclohexane internal standard.

Fig. 2.18(bottom): $[(CH_3)_2Si\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, 10% in CCl_4, CH_2Cl_2 internal standard.

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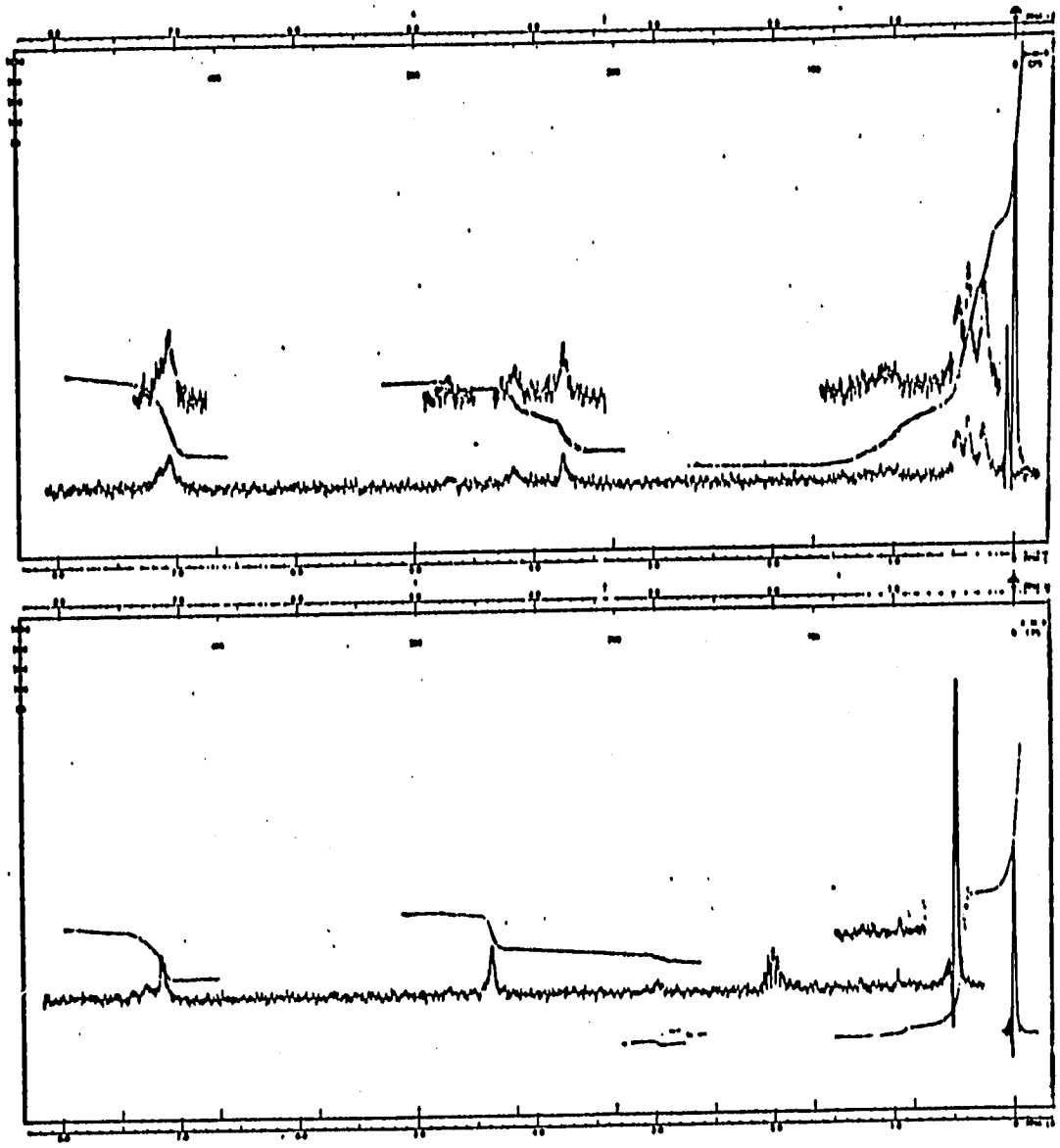

Fig. 2.19(top): $[(CH_3)_2Ge\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, suspension in CCl_4, TMS internal standard.

Fig. 2.20(bottom): $[(CH_3)_2Ge\text{-}(m)\text{-}NHCH_2C_6H_4CH_2NH]_x$, 5% in acetone-$d_6$, TMS internal standard.

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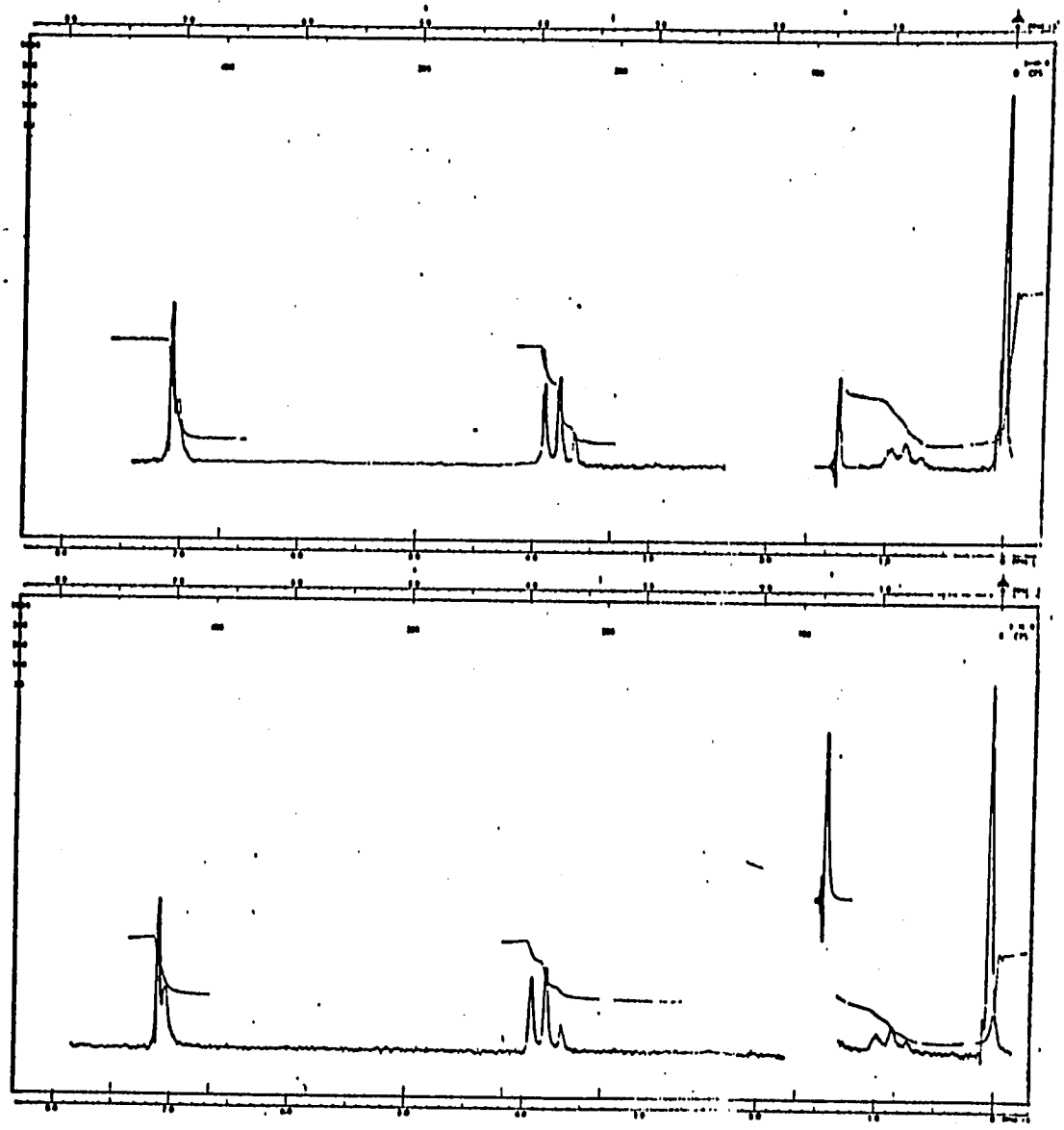

Fig. 2.21(top): $[(CH_3)_2Si$-(p)-$NHCH_2C_6H_4CH_2NH]_x$, 10% in CCl_4, cyclohexane internal standard.

Fig. 2.22(bottom): $[(CH_3)_2Si$-(p)-$NHCH_2C_6H_4CH_2NH]_x$, 10% in CCl_4, cyclohexane internal standard, after 10 hr. heating (70°C) and evacuation of polymer.

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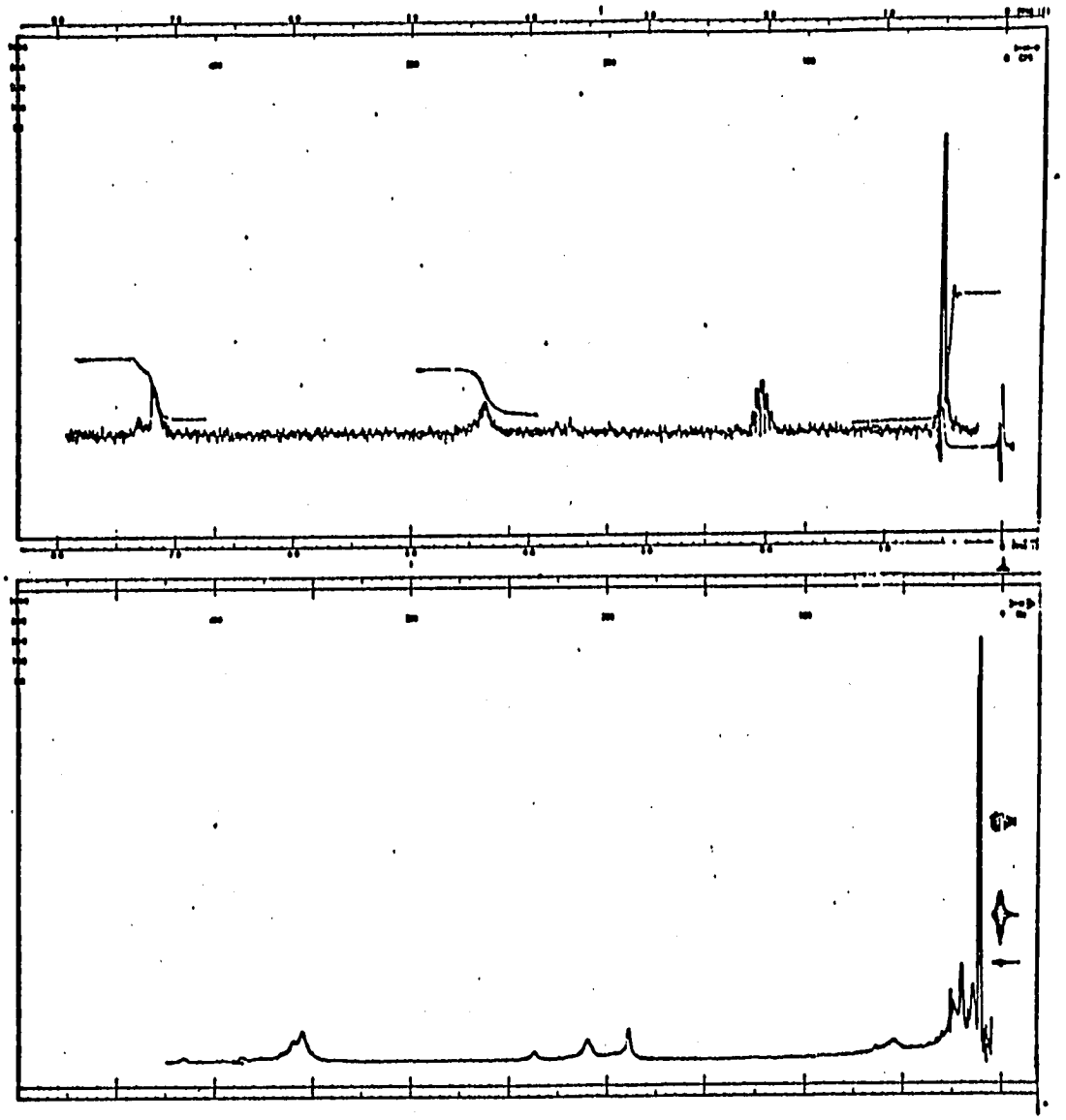

Fig. 2.23(top): $[(CH_3)_2Ge\text{-}(p)\text{-}NHCH_2C_6H_4CH_2NH]_x$, 5% in acetone-$d_6$, TMS internal standard.

Fig. 2.24(bottom): $[(CH_3)_2Ge\text{-}(p)\text{-}NHCH_2C_6H_4CH_2NH]_x$, suspension in CCl_4, TMS internal standard, HA-100 spectrum.

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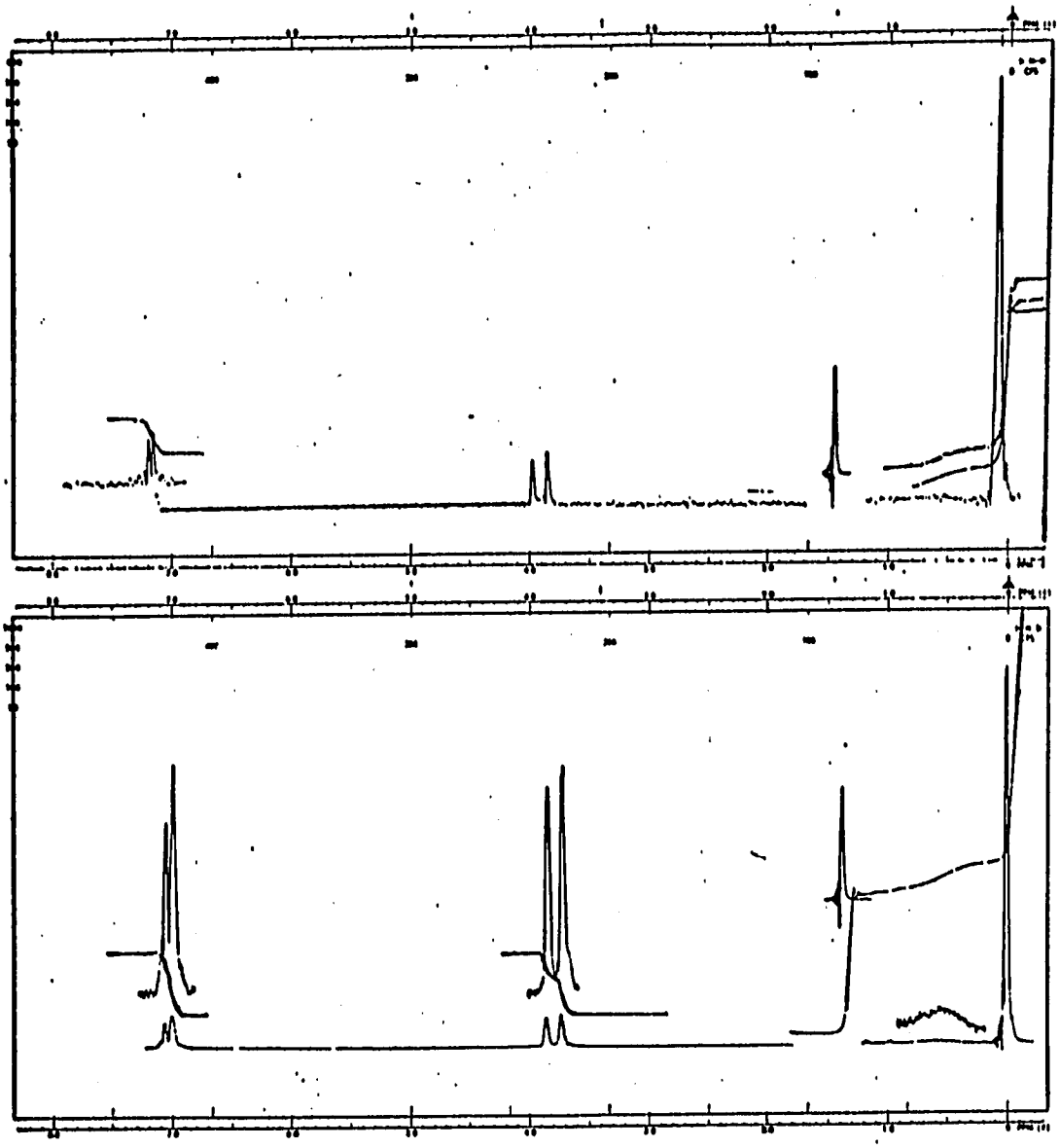

Fig. 2.26(top): $(CH_3)_3Si$-(o)-$NHCH_2C_6H_4CH_2NHSi(CH_3)_3$, 10% in CCl_4, cyclohexane internal standard.

Fig. 2.27(bottom): $(CH_3)_3Si$-(m)-$NHCH_2C_6H_4CH_2NHSi(CH_3)_3$, 10% in CCl_4, cyclohexane internal standard.

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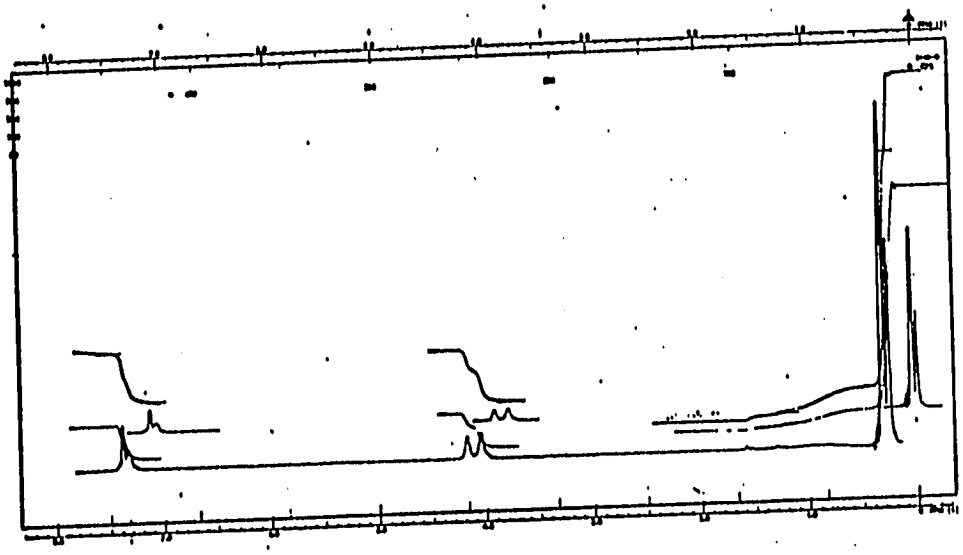

Fig. 2.28: $(CH_3)_3Si$-(p)-$NHCH_2C_6H_4CH_2NHSi(CH_3)_3$, 10% in CCl_4, TMS internal standard.

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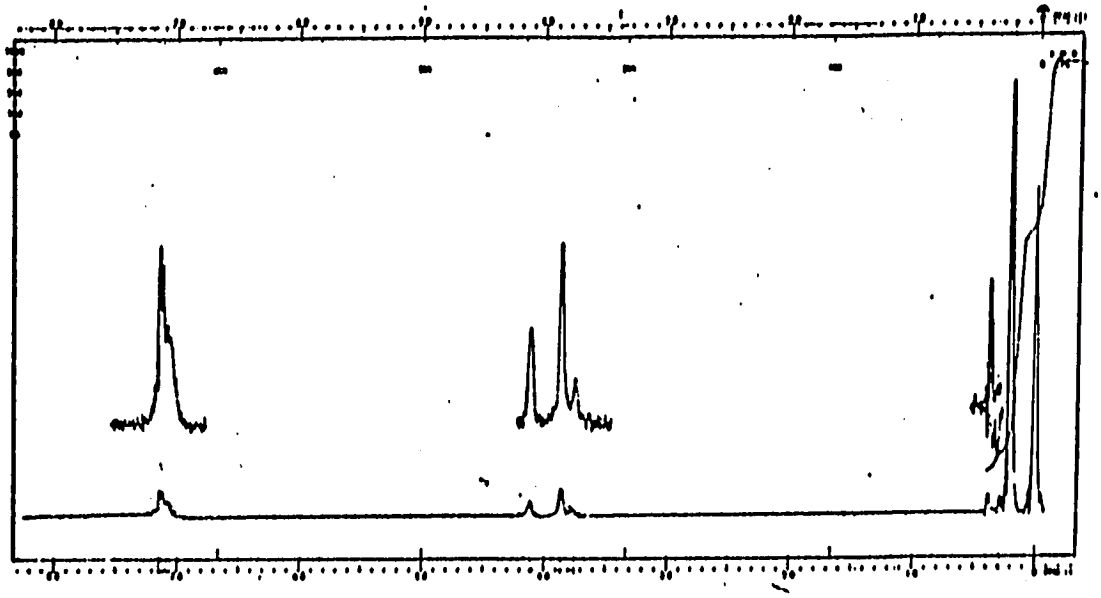

Fig. 2.29: $(CH_3)_3Ge$-(p)-$NHCH_2C_6H_4CH_2NHGe(CH_3)_3$, 5% in CCl_4, TMS internal standard.

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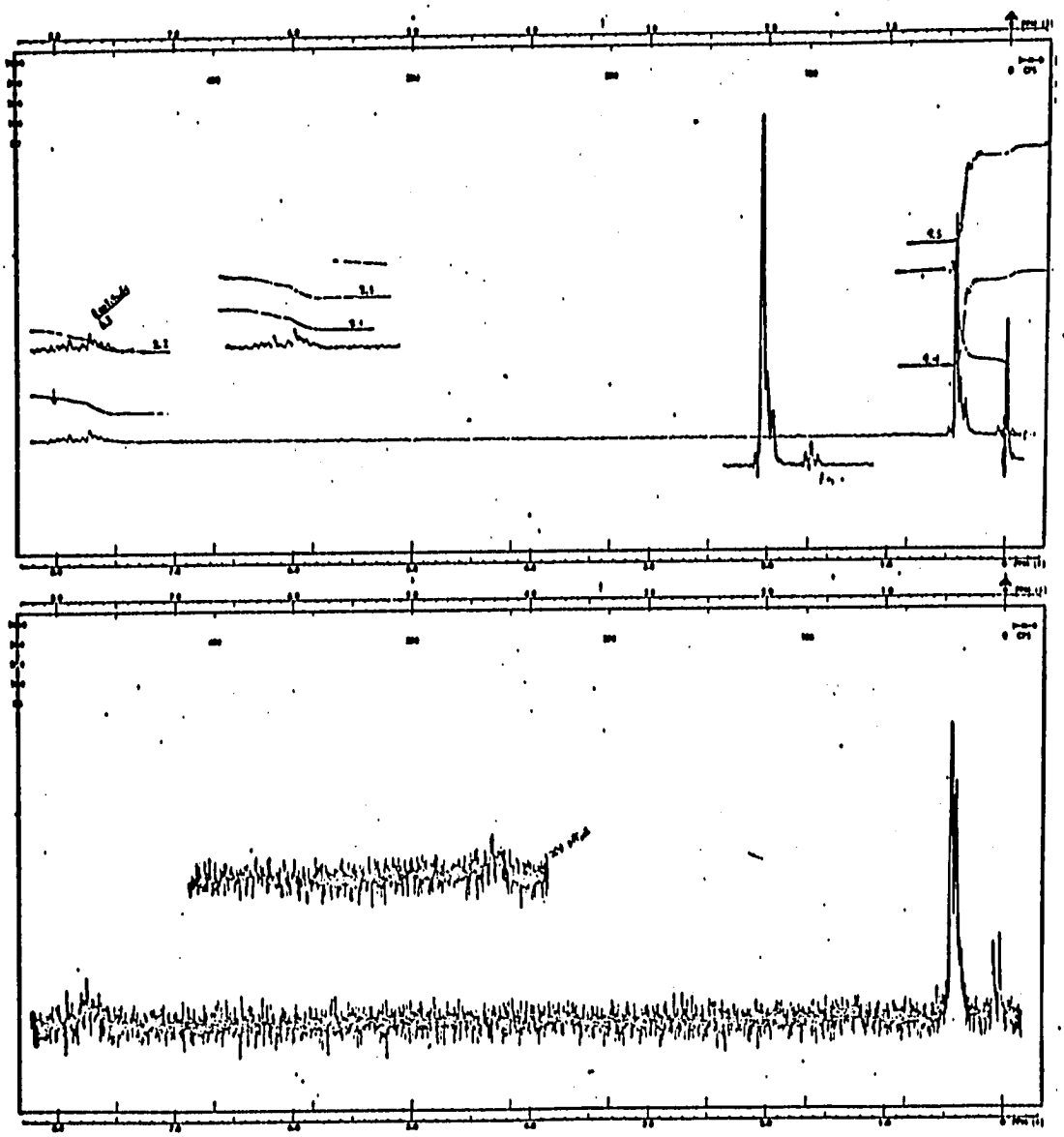

Fig. 2.30(top): $(CH_3)_3Si$-(hydrazide)-$Si(CH_3)_3$, 10% in CCl_4, TMS internal standard.

Fig. 2.31(bottom): $(CH_3)_3Si$-(hydrazide)-$Si(CH_3)_3$, 2% in CCl_4.

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Appendix C

FORTRAN Program for Simulating Mass Spectral Mass-Probability Distribution for Four-Germanium Species

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```
      DIMENSION APROB(100)
      DO 2 I=1,100
    2 APROB(I)=0.0
   10 READ 11, ICARB
      READ 12, ICONST
      READ 12, IDIFF
      IT=0
   51 IU=ICARB-IT
      IF(IU-IT) 6,6,7
    6 IT1=IFACT(IU)
      IUF=IT
      GO TO 8
    7 IT1 = IFACT(IT)
      IUF = IU
    8 T1 = IT1
      A = ICARB
      B= IUF
      FF=1.0
   81 IF (A-B) 82,82,83
   83 FF = FF*A
      A=A-1.
      GO TO 81
   82 UN2=FF/T1
      DO 111 IIV=1,5
      IV=IIV-1
      DO 111 IIW=1,5
      IW=IIW-1
      IF (IV+IW-4) 30,30,111
   30 DO 111 IIX=1,5
      IX=IIX-1
      IF (IV+IW+IX-4) 40,40,111
   40 DO 111 IIY=1,5
      IY=IIY-1
      IF(IV+IW+IX+IY-4) 50,50,111
   50 DO 111 IIZ=1,5
      IZ=IIZ-1
      IF(IV+IW+IX+IY+IZ-4) 111,115,111
  115 UN1=IFACT(IV)*IFACT(IW)*IFACT(IX)*IFACT(IY)*IFACT(IZ)
      UN1=24.0/UN1
      MOLWT=(70*IZ)+(72*IY)+(73*IX)+(74*IW)+(76*IV)+(12*IU)+(13*IT)
     /+ICONST-IDIFF
      PROBAB=UN1*UN2*(.205**IZ)*(.274**IY)*(.078**IX)*(.365**IW)
     /*(.078**IV)*(.9889**IU)*(.0111**IT)
      APROB(MOLWT)=APROB(MOLWT)+PROBAB
  111 CONTINUE
      IF(IT-19) 53,54,54
   53 IT=IT+1
      GO TO 51
   54 DO 88 I=1,100
   88 PUNCH 13,I,APROB(I)
      GO TO 10
   11 FORMAT(I2)
   12 FORMAT(I3)
   13 FORMAT(I3,1X,E14.7)
      END
```

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