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STRUCTURAL AND MOLECULAR ORBITAL STUDIES OF CARBORANES

A thesis presented

by

Thomas Frederick Koetzle

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

November 1969

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STRUCTURAL AND MOLECULAR ORBITAL STUDIES OF CARBORANES

(a Summary)

Research Director: Thomas F. Koetzle

Professor W. N. Lipscomb November 1969

The crystal and molecular structures of $1,6\text{-}B_7H_7C_2(CH_3)_2$ and $1,6\text{-}B_8H_8C_2(CH_3)_2$ have been determined by three-dimensional X-ray diffraction studies at low temperatures. In each case, atomic positions are elucidated by application of direct methods of phase determination. The resulting molecular geometries provide the basis for theoretical investigations by both the extended Hückel and non-empirical molecular orbital methods.

The desire for better carborane wavefunctions has led us to perform accurate minimum basis set SCF calculations for the two isomers of $B_4C_2H_6$. Parameters from these SCF results have been used in the calculation of non-empirical molecular orbitals for several carboranes in the series $B_NC_2H_{N+2}$. Energies, ionization potentials, charge distributions, and dipole moments are tabulated.

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Acknowledgments

I am indebted to Professor William N. Lipscomb for his advice and encouragement throughout the course of this work. In addition, I would like to thank Irving Epstein, Jean Hartsuck, George Reeke, Frank Scarbrough, and Eugene Switkes for their help and cooperation.

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Chapter I

Introduction

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Since the pioneering work of Alfred Stock, who prepared the first boron hydrides early in this century,[1] boron chemistry has experienced tremendous growth, and large numbers of novel compounds have been produced. Among these are the polyhedral carboranes in the series $B_NC_2H_{N+2}$. At present, eight members of the series are known for N = 3-10.[2] These carboranes are interesting because of their unusual closed cage structures and aromatic character, both of which contribute to their great chemical stability. A great many C-substituted derivatives have been prepared, particularly in the case of the icosahedral carboranes, $B_{10}C_2H_{12}$. Smaller numbers of B-substituted products are also known.[3]

Carboranes, along with boron hydrides and other related compounds, are "electron deficient" in the sense that these molecules do not possess enough electrons to form normal covalent bonds between each pair of neighboring atoms. In the past, theoretical descriptions of electron deficient molecules have

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developed as knowledge of molecular structures became available.[4] This close relationship between theory and structure is apparent in the studies of polyhedral carboranes which comprise this thesis. In the work presented here, structure determinations have been made by the techniques of X-ray diffraction.[5] Molecular orbital (MO) calculations, performed using experimentally determined geometries as a starting point, provide information on total energies, charge distributions, dipole moments, and reactivities.

X-ray Crystallography, Direct Methods

We have reported the molecular and crystal structures of 1,6-$B_7H_7C_2(CH_3)_2$ and of 1,6-$B_8H_8C_2(CH_3)_2$ in Chapters II and III, respectively. Both structures were solved by mathematical methods in which the phases of the structure factors are obtained directly from the X-ray diffraction data. A brief discussion of such "direct methods" of phasing for centrosymmetric structures is provided in this section.

In 1948 Harker and Kasper first pointed out the existence of certain inequality relationships among

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structure factors which could be used to determine signs for large reflections.[6] Methods based on inequalities were the first direct methods to be used in crystallography.[7] More powerful methods for centric structures currently in use are based upon a modified form of Sayre's equation[8]

$$s(E_h) = s(\sum_k E_{h-k} E_k).$$

Here s means "sign of." The calculation of normalized structure factors E_h, which serve to emphasize high-order reflections, is described elsewhere.[5c]

All methods which use Sayre's equation begin by assuming definite signs for certain of the largest reflections. Fortunately, in most space groups up to three reflections may be given arbitrary signs which serve to specify the choice of origin.[9] One of two possible approaches is usually adopted to provide additional starting signs.

In the symbolic addition method of Karle and Karle,[10] the first step is to prepare a list of the terms in Sayre's equation for the reflections with

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the highest values of E_h. The number of reflections included should be small enough to keep the size of the list manageable. With the aid of this list of terms, phasing is performed by hand starting from the signs of the origin determining reflections, and making use of the fact that Sayre's equation will very probably indicate the correct sign, even if only one term is included in the summation, provided that all three E's involved are sufficiently large.[11] During the phasing, unknown symbols are introduced as necessary for the signs of a small number of key reflections (hence the name symbolic addition). These reflections should be carefully chosen to contribute to as many terms as possible. As the phase determination progresses, it is usually possible to reduce the number of symbols or to eliminate them entirely. For example, many indications of the type a = a.a or a = b.b may appear, showing that the sign of symbol a is likely to be plus.

Once enough reflections have been properly

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phased, the correct structure will emerge from a Fourier map computed with values of E_h as coefficients (E-map). If any symbols remain undetermined, it may be necessary to compute several E-maps before finding the correct structure. Given sufficient work, the required number of signs can be obtained by hand.[12] Happily, a computer program is now available which will perform the phase determination automatically if the first 40 or so signs are supplied.[13] A set of phases obtained in less than a day with the aid of this program yielded the structure of 1,6-$B_8H_8C_2(CH_3)_2$ (Chapter III).

The second type of approach, which has been more completely automated than has symbolic addition, is the multiple solutions method. In this method, the signs of three or four reflections are allowed to take on all possible values, giving eight or sixteen different starting sets, respectively. Additional signs are determined by the iterative application of Sayre's equation until all reflections with E_h

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greater than a certain minimum value have been phased.[14] Each starting set produces a different solution. The most probably correct solution is that possessing the most internal consistency among the various terms in Sayre's equation for all reflections. Sometimes the correct solution is not the most consistent one, in which case less consistent solutions must be examined by trial and error. The structure of 1,6-$B_7H_7C_2(CH_3)_2$ (Chapter II) was solved by the multiple solutions method.

In general, there does not seem to be much to choose between the symbolic addition method and the multiple solutions method. Both methods have a proven record of success in many centric structures,[15] yet neither is without possible pitfalls, nor do they eliminate the need for skill and intuition on the part of the investigator. Together, the two direct methods have made possible the solution of many complicated structures possessing no heavy atoms, which could probably not have been solved

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using vector methods based on the Patterson function.

Molecular Orbital Methods

The appearance of accurate self-consistent field (SCF) wavefunctions for small polyatomic molecules has stimulated the development of an approximate non-empirical molecular orbital (NEMO) method.[16] The idea of the NEMO method is to remain within the basic framework of Roothaan's LCAO SCF approximation to Hartree-Fock MO's,[17] while at the same time circumventing the need to calculate all of the integrals which arise in the theoretical formulation for large molecules. The required approximations are accomplished using parameters transferred from SCF results on small related molecules.

The recent development of new mathematical methods, along with improvements in computer technology, has made feasible accurate minimum basis set SCF calculations for molecules containing as many as 40 electrons.[18] NEMO wavefunctions based

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on parameters taken from SCF results for molecules of intermediate size should be improved over those using parameters taken from small molecules, which in general provide less representative atomic environments. In addition, comparisons between NEMO and SCF results for larger molecules may provide a more accurate assessment of the capabilities of the NEMO method.

In Chapter IV we have reported SCF calculations for 1,2-$B_4C_2H_6$ and 1,6-$B_4C_2H_6$. Parameters taken from these SCF results have been used in Chapter V to calculate NEMO wavefunctions for several carboranes in the series $B_NC_2H_{N+2}$. Unfortunately, in both $B_4C_2H_6$ isomers the energies and charge distributions obtained by the NEMO method fail to reproduce the SCF results very well. It is difficult to judge our NEMO results for carboranes other than $B_4C_2H_6$, because very few experimental data exist for these molecules. Certain consistent trends are apparent in the NEMO charge distributions, and it is hoped that the conclusions drawn from these trends will help to correlate future

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experimental information.

Remarks

The author wishes to acknowledge the collaboration of F. E. Scarbrough on the crystallographic study of $B_7H_7C_2(CH_3)_2$ described in Chapter II, and of I. R. Epstein on the SCF computations of Chapter IV.

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(11) The probability that the sign of E_h is positive for a structure with N equal atoms in the unit cell was estimated by Woolfson to be

$$P_+(h) = 1/2 + 1/2\tanh(N^{-1/2}|E_h|\sum_k E_k E_{h-k}).$$

See ref. (7), p. 89.

(12) This process is especially tedious for large structures. Karle and Karle recommend that ten to fifteen reflections be phased per atom in the asymmetric unit.

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Chapter II

Molecular and Crystal Structure of 1,6-$B_7H_7C_2(CH_3)_2$

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Chapter III

Molecular and Crystal Structure of 1,6-$B_8H_8C_2(CH_3)_2$

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Molecular and Crystal Structure of Dimethyl-1,6-dicarbaclovodecaborane (10)

By Thomas F. Koetzle and William N. Lipscomb

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Abstract

A three-dimensional single crystal X-ray diffraction study shows the molecule of dimethyl-1,6-dicarbaclovodecaborane (10), $B_8H_8C_2(CH_3)_2$, to have C_s symmetry. The B_8C_2 unit is a square antiprism only slightly distorted from full D_{4d} symmetry. The charges on the B atoms, determined by LCAO-MO methods, increase in the order B8 (attached to no C atoms) < B10,B7,B9,B3,B4 (attached to one C) < B2,B5 (attached to two C atoms). The compound crystallizes in the orthorhombic space group P_{bca} with eight molecules in a cell of dimensions a = 11.36, b = 11.81, and c = 14.74 Å. The 1615 observed X-ray reflections were refined to $R = \Sigma||F_o|-|F_c||/\Sigma F_o = 0.084$.

[end of Abstract]

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The 1,6 isomer of $B_8H_8C_2(CH_3)_2$ is produced,[1] along with $B_6H_6C_2(CH_3)_2$ and $B_7H_7C_2(CH_3)_2$, when $B_7C_2H_{11}(CH_3)_2$ is pyrolized near 200° in the presence of diphenyl ether. The ^{11}B nuclear magnetic resonance spectrum[1] of this molecule at 19.3 Mc shows two peaks: a doublet of area 1 at low field and a complex peak of area 7 at high field. The doublet at low field was assigned[1] to an apical BH position, like that previously assigned[2] for $B_{10}H_{10}^{-2}$, and all others to equatorial positions on a square antiprism cage. Our X-ray study,as described below, proves that the C atoms are in the non-adjacent 1 and 6 positions, not in the adjacent 1 and 2 positions which would also be consistent with the ^{11}B NMR spectrum. Thus, the 1 and 6 assignment for C atoms, considered more plausible on chemical grounds, has been confirmed by our study. In addition, a detailed molecular geometry which is suitable for theoretical study is established below.

Experimental Section

Liquid 1,6-$B_8H_8C_2(CH_3)_2$ (mp 1.0-1.6°) was sealed into pyrex capillaries having uniform wall thickness and inside diameter about 0.7 mm. The sample size was regulated to yield crystals, grown in a cold stream of N_2,[3] which were roughly equal in all dimensions.

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Crystals were stable for periods of up to four months when maintained at a temperature between -20° and -35°, and all X-ray data were collected from two crystals. Reciprocal lattice symmetry D_{2h} and systematic absences of $0k\ell$ for k odd, $h0\ell$ for ℓ odd, and hk0 for h odd indicated that the space group is P_{bca}. Unit cell parameters of a = 11.36±0.01, b = 11.81±0.01, and c = 14.74±0.01 Å were obtained from Weissenberg photographs calibrated by the superposition of a powder diffraction pattern of Al. The cell dimensions were refined by a previously described least-squares procedure[4] using as data 2θ values for 50 reflections. Assuming eight molecules in the unit cell, a reasonable density of 0.997 g/cm^3 was calculated. No attempt was made to measure the density experimentally, but the related compound $B_7C_2H_{11}(CH_3)_2$ has a density[5] of 0.92 g/cm^3. Thus, there is one molecule in the asymmetric unit, and all atoms are expected to be in general positions.

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Data were taken on a Weissenberg camera using Ni-filtered Cu K_α radiation. Some 1615 reflections (Table I) were indexed on levels hKℓ for $0 \leq K \leq 9$ and Hkℓ for $0 \leq H \leq 3$. Of these, 647 were below the observational limits. Intensities were estimated by comparison with an intensity scale prepared from the same substance. Corrections were applied for Lorentz and polarization factors and for oblique incidence of X-rays on the upper level films. A standard deviation was assigned to each intensity reading using the function

$$\sigma(I) = \left[\frac{I_{min}}{3} + bI + \frac{0.1\ I^2}{(I_{max}-I)^2} \right] \left[1+0.25\ \exp\left\{-50(0.5-\sin^2\theta)^2\right\}\right]$$

where I_{min} and I_{max} are the maximum and minimum values on the intensity scale. The fractional parameter b was determined during film-to-film scaling by an analysis of the consistency of intensities for reflections read on more than one film. Actual values of b were 0.091 for the a axis data and 0.096 for the b axis data. The use of this error function, which attempts to reproduce the uncertainties in estimating intensities visually, has been

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described.[6,7]

The intensities were placed upon a common scale by a least squares procedure minimizing

$$\sum_{\substack{hij \\ i \neq j}} w_{hij} (\ln(s_i I_{hi}) - \ln(s_j I_{hj}))^2$$

where s_i is the scale factor for the i'th set, I_{hi} is the measurement of reflection h on set i, and $1/w_{hij} = \sigma^2(I_{hi})/I_{hi}^2 + \sigma^2(I_{hj})/I_{hj}^2$. Weights were assigned to the final scaled intensities based upon the input deviations which were propagated through the scaling calculations. These weights were used in all subsequent refinements.

No attempt was made to introduce an absorption correction. The magnitude of absorption effects was estimated at less than 3% from the calculated value of $\mu = 2.91$ cm^{-1} for Cu K_α radiation and the radius of our crystals (0.035 cm).

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Structure Determination and Refinement

The structure was solved by application of the symbolic addition procedure of Karle and Karle.[8] Initially, signs were arbitrarily chosen for three reflections in order to fix the origin. Introduction of unknown symbols as the signs of four other reflections and application by hand of the Σ_2 formula[8] led to determination of signs for 49 of the 55 reflections having normalized structure factors[9] $|E| \geq 2.2$ and $\rho = \sin^2\theta/\lambda^2 \leq 0.34$. During this procedure it became possible to introduce definite signs for the four unknown symbols. Using a program for the IBM 7094 computer written in this laboratory[10,11] the 49 signs determined by symbolic addition were extended with Sayre's equation[12] to yield signs for the 302 reflections having $|E| \geq 1.3$, all of which ultimately proved correct in the final refinement. An E map made from these reflections readily showed the locations of the twelve B and C atoms, and a structure factor calculation based upon the unrefined

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model gave a value of $R_F = \Sigma||F_o|-|F_c||/\Sigma F_o = 0.205$. The eight cage H atoms were next located from a difference map, and two cycles of least-squares refinement were carried out varying position and isotropic thermal parameters[13] for B and C atoms. The quantity minimized in these refinements was $\Sigma w^2(k^2|F_o|^2-|F_c|^2)^2$, where $w = 1/\sigma(F_o^2)$. At this stage the agreement had improved such that $R_F = 0.136$. In order to locate methyl H atoms, a new difference map was computed, and sections normal to the two C-C bonds were plotted. Five of the six methyl H atoms were fairly well resolved in these sections and the sixth was fitted to the others. Introduction of anisotropic temperature factors for the heavy atoms and two further cycles of refinement gave $R_F = 0.084$. In the last cycle no parameter changed by more than its standard deviation, so the refinement was judged complete. Attempts to refine isotropic temperature parameters for the cage H atoms gave unrealistically low values, so in the final refinement these thermal parameters for all H atoms

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were set equal to 4.2, the average obtained for the heavy atoms in the earlier refinement. Coordinates were refined only for cage H atoms; the methyl H atoms were kept fixed. A final difference map showed no peaks greater than 0.29 $e/\text{Å}^3$.

Geometrical Results

The molecule, shown in Figure 1, has the two C atoms with attached methyl groups located in the 1 and 6 positions as previously suggested.[1] The thermal ellipsoids, calculated according to the method of Waser,[14] describe a motion which is quite isotropic. Tables II and III give atomic coordinates and thermal parameters which in turn yield the bond distances and angles of Tables IV and V. Figure 2 displays the packing of the eight molecules within one unit cell. A calculation of intermolecular contacts showed the closest approaches to be 2.71 Å (methyl H to cage H) and 2.77 Å (methyl H to methyl H).

The molecular structure of 1,6-$B_8H_8C_2(CH_3)_2$ shows only slight distortions of the square antiprism cage from the full D_{4d} symmetry reported for the isoelectronic

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$B_{10}H_{10}^{=}$ unit in $Cu_2B_{10}H_{10}$.[15] Atoms B2, B3, B4 and B5 lie in a plane, as do C6, B7, B8 and B9, to the limits of experimental accuracy. The B-C bonds in the molecule are between 0.05 and 0.10 Å shorter than B-B bonds of equivalent type. Among the six bonds between equatorial B atoms, the smallest differs from the largest by only 0.041 Å. The three types of B-B bonds in $Cu_2B_{10}H_{10}$ have average distances 1.73±0.02 (apical), 1.815±0.015 (equatorial), and 1.86±0.03 Å (basal).[15] These agree fairly well with the corresponding distances for 1,6-$B_8H_8C_2(CH_3)_2$, which are 1.69, 1.805, and 1.83 Å, respectively. It is worth noting that bond B2-B5, between B atoms bonded to both C's, is the longest bond in the molecule. The distance of 1.861±0.007 Å compares well with 1.89±0.01 Å in the related compound $B_6H_6C_2(CH_3)_2$,[7] 1.89±0.04 Å in m-$B_{10}Br_2H_8C_2H_2$,[16] and 1.89±0.06 Å in m-$B_{10}Cl_{10}C_2H_2$[17] for the same type of distance. However, no abnormal lengthening of this bond was observed for $B_7H_7C_2(CH_3)_2$,[4] where the distance is 1.76±0.03 Å.

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Molecular Orbital Studies

Molecular orbital (MO) calculations were carried out using both the extended Hückel[18,19] and non-empirical molecular orbital (NEMO) methods.[20,21] To simplify matters somewhat, the calculations were performed for 1,6-$B_8C_2H_{10}$, where the CH_3 groups are replaced by H atoms. Otherwise, the geometry was taken directly from the X-ray study with slight adjustments in the somewhat uncertain H positions. The B-H distance was fixed at 1.196 Å, the terminal B-H distance in B_2H_6 as determined by gas phase electron diffraction.[22] The H atoms attached to C were positioned to give a C-H distance of 1.102 Å, the value calculated from infrared and Raman spectra of C_2H_6.[23] The complete adjusted coordinates are given in Table VI.

Previous MO studies of various $B_8C_2H_{10}$ and $B_{10}C_2H_{12}$ isomers led[24] to a simple rule for predicting the relative charges of different B atoms in these systems. The rule gives in order of increasing positive charge those B atoms bonded to (a) no C atoms, (b) one C atom, and (c) two C atoms. Within a given category a four coordinated apical

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B is predicted to be more negative than a five coordinated equatorial B atom. The net Mulliken atomic charges[25] for 1,6-$B_8C_2H_{10}$ are given in Table VIII for each of the six MO calculations. In the extended Hückel results, the relative order is that predicted by the rule given above, B8 < B10 < B7,B9,B3,B4 < B2,B5, also in agreement with the earlier calculations[24] which were based on the geometry of the $B_{10}H_{10}^{2-}$ ion. The same order holds for the charges calculated by the NEMO method, except that the apical B atom, B10, is very slightly more positive than B7 and B9. The net framework charges (Table IX) follow the same general order as the atomic charges. Dipole moments have been calculated from the NEMO wavefunctions using Ruedenberg's invariant method of partitioning,[26] and are included in Table VIII along with point charge dipoles calculated from the net Mulliken charges alone. The direction of the dipole makes the side of the molecule containing the C atoms positive.

Earlier NEMO calculations on $B_6H_6C_2(CH_3)_2$[7] and $B_7H_7C_2(CH_3)_2$[4] were based upon self-consistent field (SCF)

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results for B_4H_4[27] and C_2H_6,[28] and used Slater exponents except for Hls which was assigned an exponent of 1.2. Results were obtained with the one-center 2s-2p zero-overlap constant[21] set equal to $K^{ZO} = 0.229$, the value from B_4H_4, and again with $K^{ZO} = 0$. For purposes of comparison, calculations were performed in the same manner for 1,6-$B_8C_2H_{10}$. Two additional calculations used parameters (Table VII) derived from SCF results for B_5H_9,[29] with optimized exponents for B and C taken from B_2H_6[30] and C_2H_6,[31] respectively. A further refinement in the method based upon newly available SCF results for the two isomers of $B_4C_2H_6$[32] is currently being pursued. More representative α's will be introduced for the cage C atoms replacing the values from C_2H_6 used here. It is hoped that better wavefunctions and more accurate charges will result.

In the present calculations B7(B9) are more negative than B3(B4) even though these four equatorial B atoms bonded to one C should be equivalent according to the simple rule. We await electrophilic substitutions on the molecule to determine if these positions are, in fact, chemically distinguishable.

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Acknowledgment. We wish to thank M. F. Hawthorne for providing the sample, H. V. Hart for sealing it into capillaries, G. N. Reeke for the use of his phasing program, the Office of Naval Research and the Advanced Research Projects Agency for support, and the National Institutes of Health for a fellowship to T.F.K.

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Figure 1. Stereo Drawing Showing the Molecule and Numbering Scheme for 1,6-$B_8H_8C_2(CH_3)_2$.

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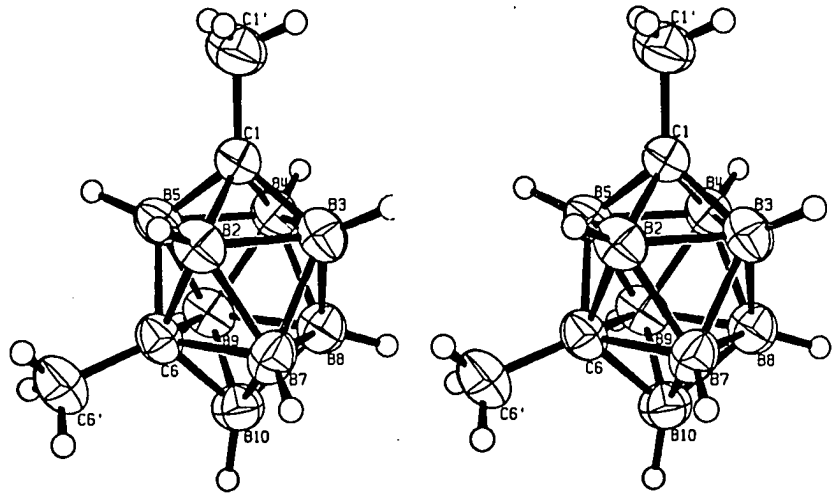

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Figure 2. Stereo View of the Unit Cell in the 0kℓ Projection. The origin is at the lower left with $\vec{c}$ pointing up and $\vec{b}$ across.

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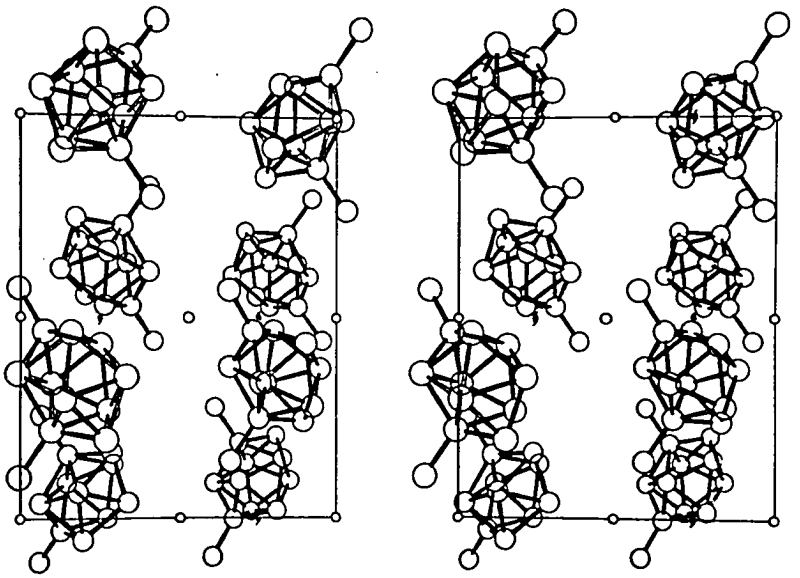

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Table I. Observed and Calculated Structure Factors for $1,6\text{-}B_8H_8C_2(CH_3)_2$.[a,b]

[a] The three columns contain, from left to right, values of K, F_{obs} and F_{calc}. Reflections designated by an asterisk were assigned zero weight in the refinements. A minus sign before F_o indicates a reflection that was too weak to be observed.

[b] Multiply by 0.25 to place on an absolute scale with $F_{ooo} = 624$.

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Table II. Coordinates and Anisotropic Thermal Parameters[a] ($\times 10^4$)

for Non-Hydrogen Atoms

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	0.3234(3)	0.1528(3)	0.0257(2)	75(4)	62(4)	37(2)	-3(6)	-11(5)	1(5)
B2	0.2654(4)	0.1644(4)	0.1239(3)	67(5)	83(5)	42(2)	-3(8)	2(6)	8(6)
B3	0.3001(4)	0.2819(5)	0.0499(3)	73(5)	82(6)	44(3)	2(8)	-13(6)	18(6)
B4	0.4456(5)	0.2221(4)	0.0261(3)	73(5)	81(5)	40(2)	-2(8)	9(6)	7(5)
B5	0.4126(4)	0.1025(5)	0.0992(3)	76(5)	81(5)	33(2)	6(8)	8(5)	2(6)
C6	0.3828(3)	0.1747(3)	0.2004(2)	70(4)	75(4)	37(2)	12(7)	9(5)	10(5)
B7	0.3037(5)	0.2991(4)	0.1712(3)	84(5)	59(5)	53(3)	14(8)	8(6)	-4(5)
B8	0.4311(4)	0.3421(5)	0.1035(3)	80(5)	75(5)	48(3)	-20(8)	1(6)	5(6)
B9	0.5102(4)	0.2115(4)	0.1369(3)	57(4)	102(6)	42(2)	-11(8)	6(6)	5(6)
B10	0.4435(5)	0.2992(4)	0.2118(3)	94(6)	78(5)	46(3)	-25(9)	4(7)	-15(6)
C1'	0.2726(4)	0.0883(4)	-0.0532(3)	113(6)	103(5)	51(2)	15(7)	-47(6)	-15(6)
C6'	0.3749(4)	0.1013(4)	0.2855(3)	119(5)	108(5)	41(2)	-1(8)	11(6)	28(5)

[a] Anisotropic temperature parameters are calculated by the expression

$$\exp[-(h^2\beta_{11}+k^2\beta_{22}+\ell^2\beta_{33}+hk\beta_{12}+h\ell\beta_{13}+k\ell\beta_{23})].$$

Table III. Coordinates of Hydrogen Atoms

Atom	x	y	z
H2	0.183(4)	0.120(3)	0.144(3)
H3	0.239(4)	0.331(4)	0.009(2)
H4	0.502(4)	0.223(3)	-0.039(3)
H5	0.441(4)	0.011(4)	0.103(3)
H7	0.232(4)	0.341(4)	0.212(3)
H8	0.458(4)	0.427(4)	0.080(3)
H9	0.600(4)	0.184(4)	0.150(3)
H10	0.475(4)	0.332(4)	0.275(3)
$H1'_a$	0.307	0.040	-0.073
$H1'_b$	0.203	0.067	-0.047
$H1'_c$	0.246	0.133	-0.097
$H6'_a$	0.437	0.068	0.300
$H6'_b$	0.318	0.050	0.282
$H6'_c$	0.341	0.141	0.334

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Table IV. Complete Bond Distances[a]

	Bond	Bond Length, Å	Bond	Bond Length, Å
		B-C, Apical C		
Type I	C1-B2	1.596(6)	C1-B5	1.598(6)
Type II	C1-B3	1.588(7)	C1-B4	1.611(6)
		B-B at Base of C Apex		
Type I	B2-B5	1.861(7)		
Type II	B2-B3	1.808(7)	B4-B5	1.815(7)
Type III	B3-B4	1.831(7)		
		Equatorial B-C		
	B2-C6	1.750(6)	B5-C6	1.752(6)
		Equatorial B-B		
Type I	B2-B7	1.790(7)	B5-B9	1.787(7)
Type II	B3-B7	1.800(6)	B4-B9	1.795(7)
Type III	B3-B8	1.828(7)	B4-B8	1.827(7)
		B-C, at Base of B Apex		
	C6-B7	1.774(7)	C6-B9	1.777(6)
		B-B, at Base of B Apex		
	B7-B8	1.830(7)	B8-B9	1.851(7)
		B-C, Apical B		
	C6-B10	1.632(7)		
		B-B, Apical B		
Type I	B7-B10	1.696(8)	B9-B10	1.692(7)
Type II	B8-B10	1.681(7)		
		C-C		
Type I	C1-C1'	1.505(6)		
Type II	C6-C6'	1.527(6)		

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Table IV (cont'd.)

	Bond	Bond Length, Å	Bond	Bond Length, Å
		Apical B-H		
	B10-H	1.08(4)		
		Equatorial B-H		
Type I	B2-H	1.11(4)	B5-H	1.13(5)
Type II	B3-H	1.09(4)	B4-H	1.15(4)
Type III	B7-H	1.13(4)	B9-H	1.08(4)
Type IV	B8-H	1.10(5)		
		C-H		
	$C1'-H1'_a$	0.74		
	$C1'-H1'_b$	0.83		
	$C1'-H1'_c$	0.89		
	$C6'-H6'_a$	0.83		
	$C6'-H6'_b$	0.89		
	$C6'-H6'_c$	0.93		

[a] Assumption of C_s symmetry leads to three pairs of equivalent atoms: B2 and B5, B3 and B4, B7 and B9.

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Table V. Complete Bond Angles

	Angle	Degrees	Angle	Degrees
		Around Apical C		
Type I	B2-C1-B3	69.2(3)	B4-C1-B5	68.9(3)
Type II	B2-C1-B5	71.3(3)		
Type III	B3-C1-B4	69.8(3)		
		B-B-B Angles at Base of C Apex		
Type I	B3-B2-B5	89.3(3)	B2-B5-B4	89.8(3)
Type II	B2-B3-B4	90.9(3)	B3-B4-B5	90.0(3)
		C-B-B Angles at Base of C Apex		
Type I	C1-B2-B3	55.2(3)	C1-B5-B4	55.9(3)
Type II	C1-B2-B5	54.4(2)	C1-B5-B2	54.3(2)
Type III	C1-B3-B2	55.6(3)	C1-B4-B5	55.2(2)
Type IV	C1-B3-B4	55.7(3)	C1-B4-B3	54.5(3)
		Equatorial B-B-B		
Type I	B3-B2-B7	60.0(3)	B4-B5-B9	59.8(3)
Type II	B2-B3-B7	59.5(3)	B5-B4-B9	59.3(3)
Type III	B7-B3-B8	60.6(3)	B8-B4-B9	61.5(3)
Type IV	B4-B3-B8	59.9(3)	B3-B4-B8	60.0(3)
Type V	B2-B7-B3	60.5(3)	B4-B9-B5	60.9(3)
Type VI	B3-B7-B8	60.5(3)	B4-B9-B8	60.1(3)
Type VII	B3-B8-B7	59.0(3)	B4-B8-B9	58.4(3)
Type VIII	B3-B8-B4	60.1(3)		
		Equatorial C-B-B		
Type I	C6-B2-B5	57.9(2)	C6-B5-B2	57.9(2)
Type II	C6-B2-B7	60.1(3)	C6-B5-B9	60.3(3)
Type III	C6-B7-B2	58.8(3)	C6-B9-B5	58.9(2)
		Equatorial B-C-B		
Type I	B2-C6-B5	64.2(3)		
Type II	B2-C6-B7	61.0(3)	B5-C6-B9	60.8(3)

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Table V (Cont'd.)

	Angle	Degrees	Angle	Degrees
	B-B-B at Base of B Apex			
Type I	B7-B8-B9	90.4(3)		
Type II	B7-B8-B10	57.6(3)	B9-B8-B10	57.0(3)
Type III	B8-B7-B10	56.8(3)	B8-B9-B10	56.4(3)
	C-B-B at Base of B Apex			
Type I	C6-B7-B8	87.8(3)	C6-B9-B8	87.1(3)
Type II	C6-B7-B10	56.0(3)	C6-B9-B10	56.0(3)
	B-C-B at Base of B Apex			
Type I	B7-C6-B9	94.7(3)		
Type II	B7-C6-B10	59.6(3)	B9-C6-B10	59.3(3)
	Around Apical B			
Type I	C6-B10-B7	64.4(3)	C6-B10-B9	64.6(3)
Type II	B7-B10-B8	65.6(3)	B8-B10-B9	66.6(3)
	Angles Including Apical Methyl C			
Type I	C1'-C1-B2	125.9(4)	C1'-C1-B5	125.4(4)
Type II	C1'-C1-B3	126.6(3)	C1'-C1-B4	126.1(3)
	Angles Including Equatorial Methyl C			
Type I	C6'-C6-B2	116.4(3)	C6'-C6-B5	115.8(3)
Type II	C6'-C6-B7	129.7(3)	C6'-C6-B9	128.3(4)
Type III	C6'-C6-B10	116.8(3)		

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Table VI. Orthogonal Coordinates in Å for $B_8C_2H_{10}$ [a]

Atom	x	y	z
C1	3.673	1.804	0.379
B2	3.014	1.941	1.826
B3	3.408	3.329	0.736
B4	5.061	2.622	0.384
B5	4.686	1.210	1.462
C6	4.347	2.063	2.954
B7	3.449	3.532	2.524
B8	4.896	4.039	1.525
B9	5.794	2.497	2.018
B10	5.037	3.533	3.121
H1	3.251	1.246	-0.473
H2	2.007	1.379	2.141
H3	2.644	3.964	0.072
H4	5.721	2.637	-0.613
H5	5.024	0.064	1.514
H6	4.283	1.438	3.859
H7	2.589	4.060	3.166
H8	5.230	5.126	1.154
H9	6.917	2.143	2.225
H10	5.432	3.969	4.162

[a] As adjusted to give an idealized model for the purposes of MO calculations.

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Table VII. NEMO Parameters

A. α's and Exponents

B_5H_9			C_2H_6		
Orbital	Exponent	α,au	Orbital	Exponent	α,au
B_{1s}	4.680	-7.4988	C_{1s}	5.680	-11.2078
B_{2s}	1.443	-1.1748	C_{2s}	1.730	-1.5312
B_{2p}	1.477	-0.2770	C_{2p}	1.760	-0.2957
H_{1s}	1.147	-0.4183	H_{1s}	1.160	-0.5239

B. Mulliken Approximation Coefficients

One-center		Two-center	
K_{1s-2s}	=0.6599	K_{2s-2s}	=1.0603
		K_{2s-2p}	=1.1071
Two-center		K_{2s-H}	=1.0167
K_{1s-1s}	=1.0000	$K_{2p\sigma-2p\sigma}$	=1.1249
K_{1s-2s}	=0.7939	$K_{2p\pi-2p\pi}$	=1.0085
K_{1s-2p}	=0.8050	K_{2p-H}	=0.8792
K_{1s-H}	=0.8118	K_{H-H}	=0.8643

C. Zero-overlap Coefficient

$$K^{ZO} = 0.3902$$

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Table VIII. Atomic Charges and Dipole Moments[a]

Atom	Net Mulliken Charge I	II	III	IV	V	VI
C6 (equatorial)	-0.53	-0.48	0.50	0.31	0.10	-0.06
C1 (apical)	-0.63	-0.61	0.48	0.29	0.05	-0.07
B2,B5 (bonded to both C's)	0.57	0.57	0.25	-0.05	0.39	0.15
B3,B4 (bonded to one C, equatorial)	0.34	0.35	0.17	-0.12	0.24	0.03
B7,B9 (" " " " ")	0.31	0.32	0.10	-0.17	0.15	-0.04
B10 (bonded to one C, apical)	0.25	0.23	0.12	-0.15	0.17	-0.01
B8 (bonded to no C's)	0.14	0.13	-0.02	-0.24	-0.03	-0.16
(C)H	0.05	0.04	-0.14	-0.01	-0.03	-0.06
(B)H	-0.22	-0.23	-0.23	0.06	-0.22	-0.02
Dipole Moments (Debyes)						
Total Dipole Moment[b]			5.88	5.89	5.96	5.98
Point Charge Dipole Moment			5.30	4.29	4.54	3.55

[a] I- Extended Hückel: α's - B_{2s} = -15.02, B_{2p} = -8.55, C_{2s} = -20.78, C_{2p} = -11.31, H_{1s} = -13.60 ev; optimized exponents from Table VII.
II- Extended Hückel: α's - B_{2s} = -15.36, B_{2p} = -8.63, C_{2s} = -21.4, C_{2p} = -11.4, H_{1s} = -13.61 ev; Slater exponents except 1.2 for H_{1s}.
III- NEMO with parameters from Table VII and K^{ZO} = 0.3902.
IV- NEMO with parameters from Table VII and K^{ZO} = 0.0.
V- NEMO with parameters from reference 7 and K^{ZO} = 0.229.
VI- NEMO with parameters from reference 7 and K^{ZO} = 0.0.

[b] Calculated as $\int \psi^* \vec{r} \psi \, d\tau$.

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Table IX. Framework Charges[a]

Type	I	II	III	IV	V	VI
C-H equatorial (C6)	-0.48	-0.44	0.38	0.30	0.08	0.02
C-H apical (C1)	-0.58	-0.57	0.32	0.28	0.01	0.00
B-H bonded to both C's (B2,B5)	0.35	0.34	0.01	0.01	0.15	0.13
B-H bonded to 1C (B3,B4)	0.12	0.11	-0.07	-0.07	0.00	-0.01
B-H bonded to 1C (B7,B9)	0.10	0.10	-0.10	-0.09	-0.05	-0.02
B-H bonded to 1C, apical (B10)	0.03	0.02	-0.13	-0.08	-0.05	-0.01
B-H bonded to no C's (B8)	-0.09	-0.10	-0.23	-0.19	-0.25	-0.19

[a] Defined as the sum of the atomic charges for a B-H or C-H unit.

Chapter IV

Self-Consistent Field Wavefunctions for $1,2\text{-}B_4C_2H_6$ and $1,6\text{-}B_4C_2H_6$

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Self-Consistent Field Wavefunctions for $1,2\text{-}B_4C_2H_6$ and $1,6\text{-}B_4C_2H_6$[1]

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Abstract

Accurate SCF molecular orbital wavefunctions for the two isomers of $B_4C_2H_6$ have been obtained from a minimum basis set of Slater type atomic orbitals. Ionization potentials of 9.90 ev and 9.25 ev, and atomization energies of -1.363 au and -1.387 au are predicted, respectively, for the 1,2 and the 1,6 isomers. The 1,6 isomer is computed to be more stable than the 1,2 isomer by about 15 kcal/mole.

Charge densities are presented in certain sections of these isomers. In $1,2\text{-}B_4C_2H_6$, atom B3 (attached to two C atoms) is expected to be slightly less reactive towards electrophiles than atom B4 (attached to one C atom). The calculated dipole moment of 2.95 D makes the carbon side of the 1,2 isomer positive, but the value is expected to be too large by about a factor of two.

[end of abstract]

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The polyhedral carboranes are a series of extremely stable compounds, for which a quite extensive chemistry has grown up in recent years.[3-6] They have been the subject of much theoretical investigation by molecular orbital (MO) techniques which has provided insight into their interesting properties. Both the extended Hückel method[7] and the non-empirical molecular orbital (NEMO) method[8] have been used previously to calculate approximate wavefunctions for molecules in the series.[9] In this paper we report accurate self-consistent field (SCF) wavefunctions for the two isomers of $B_4C_2H_6$. In the following paper[10] parameters from these calculations are used to generate NEMO wavefunctions for other carboranes.

Both 1,2- and 1,6-$B_4C_2H_6$ are distorted octahedra assumed to possess C_{2v} and D_{4h} symmetry, respectively. Coordinates for the unique atoms are given in Table I and the molecules are drawn in Figs. 1 and 2. The geometry of the 1,2 isomer was taken from a recent microwave spectroscopic study.[11] Average B-B and B-C bond lengths from this structure were then used to construct approximate coordinates for the 1,6 isomer. The H atoms

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were positioned to give B-H and C-H bond lengths of 1.196 and 1.102 Å, respectively.

The SCF calculations utilized a modified form of Stevens' program[12] for the IBM 7094 computer. Computations, in which each unique integral was calculated to five decimal places, required about 200 min. for the 1,2 isomer and 150 min. for the more symmetrical 1,6 isomer. The minimum basis set of Slater orbitals had optimized exponents (Table II) taken from B_2H_6[13] for B and from C_2H_6[12] for C. In Tables III and IV we show the wavefunctions and SCF energies. Agreement with the virial theorem is quite good for both molecules and only slightly worse than that obtained in the optimized calculation for B_2H_6.[13]

Molecular energies and ionization potentials

First ionization potentials, from the energies of the least stable filled orbitals, are 9.90 ev for 1,2-$B_4C_2H_6$ and 9.25 ev for 1,6-$B_4C_2H_6$. No experimental results are available for comparison, but in a series of SCF calculations on boron hydrides,[14] calculated ionization potentials differed from the observed values by as

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much as 15 per cent.

Atomization energies, using Clementi's best single-zeta atomic energies[15] as a reference, are calculated to be -1.363 and -1.387 au for the 1,2 and 1,6 isomers, respectively. From the difference in total energies, we predict the symmetric 1,6 isomer to be the more stable of the two by 15 kcal/mole, in agreement with qualitative observations.[16]

Population Analysis

The Mulliken charges and bonded overlap populations[17] for the two isomers are presented in Tables V and VI, respectively. The charge distribution confirms our expectations that carbon is more electronegative than boron, and that framework charges are small. Charges and overlap populations are in good agreement with those found in SCF calculations on boron hydrides[13,14] and hydrocarbons.[12]

The overlap populations do not correlate well with bond distances, particularly for B-B bonds. We find in the 1,6 isomer that the B-B overlap population is somewhat

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smaller and the B-C population somewhat larger than the average values in the 1,2 isomer. If an overlap population *versus* bond distance correlation existed and were transferable between molecules, we should expect the actual B-B distance in 1,6-$B_4C_2H_6$ to be slightly longer than the value of 1.735 Å used in the present calculation, while the B-C distance should be shorter than our average value.[18] This optimistic assumption about the value of overlap populations is probably unwarranted, however, especially for B-B bonds in the same polyhedron as B-C bonds (and C-C bonds if the C atoms are adjacent). An extreme example is the anomalously low overlap population for either normal or lengthened B-B bonds in 1,5-$B_3C_2H_5$ in our approximate (NEMO) calculations.[10] Thus, the small difference between the B2-B3 population in 1,6-$B_4C_2H_6$ and the average B-B population in 1,2-$B_4C_2H_6$ could easily be due to this effect, rather than to an abnormally long B-B bond.

The fact that B-H bonds have greater overlap populations than C-H bonds is disturbing at first sight. However, one should not ordinarily compare overlap

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populations for pairs of atoms using different basis sets. The carbon atomic orbitals are far more contracted than their boron counterparts, giving lower overlap integrals even though the C-H distance is about 0.1 Å shorter than the B-H distance. The questionable significance of overlap or bond populations in view of ambiguities in partitioning the charge density has been discussed elsewhere.[14,19] Perhaps a more reliable comparison of B-H and C-H bonds is given by the electron densities at the midpoints of the bonds. This electron density is, of course, a property of the total wavefunction, and therefore invariant with respect to partitioning procedures. These midpoint values, shown in Table VI, clearly indicate that C-H bonds are, as expected, stronger than B-H bonds. Overlap populations within sets of B-B or B-C bonds generally follow the order of the midpoint densities, since within each set we use the same basis orbitals.

The total electron density also enables us to study in more detail some of the other aspects of bonding in

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these molecules. In Figs. 3-7 we present contour maps of the total density in several planes of interest. Fig. 3 shows the four boron plane of the 1,6 isomer. The B-H bonds are clearly visible, as is the "hole," or region of low electron density in the center of the molecule. Fig. 4 shows the plane perpendicular to that of Fig. 3, and includes the apical carbon. We see, first, that carbon has a far greater electron density than boron, as indicated by the greater extent of the C-H bond contour. Secondly, we note the non-spherical shape of the "hole," which follows the geometry of the molecule, extending further across the longer B-B diagonal than across the shorter C-C distance. The total density in the B-C-B face of the 1,6 isomer (Fig. 5) clearly indicates the effect of the carbon's greater electronegativity.

The total density in the B-B-C-C plane of 1,2-$B_4C_2H_6$ is drawn in Fig. 6a. We again find higher electron density in C-H than in B-H bonds and a central "hole." In addition, there is a large overlap between the two C atoms. In order to determine whether this

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effect represents a true single bond in this electron deficient molecule, we have calculated the difference density. This density, shown in Fig. 6b, was derived by subtracting from our molecular density the contributions from non-interacting spherical B, C and H atoms at the same positions and with the same Slater exponents used in the molecular calculation. The results indicate that the major contribution to the C-C overlap is from the overlap of spherical atomic electron densities rather than from any great molecular concentration of bond density. Difference density calculations also show that the "holes" are truly molecular phenomena. The difference densities at the centers of the holes are about -0.03 electrons/au^3 while the positive difference densities at the midpoints of the bonds vary from 0.006 to 0.035 electrons/au^3, depending on the type of bond. Even the difference density map does not distinguish among the many 2-center and 3-center resonance structures which may be drawn. Perhaps some slight preference for certain resonance structures may be made when localized orbitals for this molecule are determined.

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In Fig. 7 we show the densities on the faces of the distorted octahedron of 1,2-$B_4C_2H_6$. Again, no conclusions about 2-center or 3-center bonding can be drawn, although the greater overlap of C-C as compared to B-C and B-B bonds is clearly seen. Fig. 7b is nearly identical to Fig. 5 except for a very slight asymmetry between B4 and B5 in the 1,2 isomer. This strong resemblance illustrates the similarity of the bonding in the face planes of the two isomers. All maps of total electron density have been drawn using the same set of contours in order to facilitate comparisons between different planes.

Reactivity

The first molecular orbital calculations of carborane charge distributions and reactivities were undertaken by Hoffmann and Lipscomb[7] because the polyhedral carboranes afforded "an opportunity to overcome the ex post facto character usually present in reactivity predictions." At the time of writing, the $B_4C_2H_6$ isomers still provide such an opportunity.

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The net atomic charges suggest that in electrophilic substitution B4 is expected to react in very slight preference to B3 in 1,2-$B_4C_2H_6$. This order of boron reactivity is in keeping with the observations of Potenza and Lipscomb,[20] who found that Friedel-Crafts type bromination of o-$B_{10}C_2H_{12}$ occurred first at those boron atoms furthest removed from the carbons, i.e., electrophilic substitution takes place more easily at borons bonded to one carbon than at borons bonded to two carbons.

Except in comparing the two non-equivalent borons in the 1,2 isomer, consideration of frontier orbital populations gives little information about reactivity, since the different nuclear charges on the atoms make straightforward comparisons between boron and carbon impossible. Even in the less ambiguous case of B3 versus B4 in 1,2-$B_4C_2H_6$, consideration of only the highest filled or lowest unfilled MO reverses the order of reactivity

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predicted by the net atomic charges. Inclusion of the highest three filled or lowest three virtual MO's, however, restores the order given by the charges. Consideration of three frontier orbitals rather than only one is justified by the relatively small energy differences (Tables III and IV) between the first three orbitals compared to the large gaps between the third and fourth orbitals (ϵ_4 = 0.452 au for 1,2-$B_4C_2H_6$, = 0.445 au for 1,6-$B_4C_2H_6$) in both the occupied and virtual orbital sets.

Free valence calculations[14,21] indicate that in the 1,2 isomer, B3 should be somewhat more reactive than B4 toward free radical substitutions. Comparison between the two molecules shows that B2 in the symmetric isomer has a free valence identical to that of B3 in the 1,2 isomer. Also, the C atoms of the more stable symmetric isomer should be less susceptible to free radical attack than those of the 1,2 isomer.

Since experimental determinations of reactivities of these isomers in various types of reactions are

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nonexistent, our admittedly tentative reactivity predictions remain untested. Mechanisms involving several stages or rearrangements[22] will make interpretation of experiments difficult in the absence of a detailed pathway. In addition, steric considerations may also play a role in determining reactivity in these molecules. The slightly more contracted configuration near carbon in the 1,2 isomer should make B4 somewhat more accessible than B3 to attack by larger reagents. However, we hope that a projected study by one of the authors (I.R.E.) of boron hydride and carborane reactivities using more rigorous theoretical methods will soon be complemented by definitive experimental investigations of these reactivities, and mechanistic studies.

Dipole Moments

The dipole moment of the less symmetric 1,2 isomer was calculated by the origin-invariant partitioning method of Ruedenberg[23] to be 2.95 D. The direction of the moment makes the side of the molecule containing the C atoms positive. This dipole moment, like those calculated for the boron hydrides,[14] is probably about twice the

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experimental value, which has not yet been determined.

The Ruedenberg method was also used to analyze the atomic and bond components of the dipole moment in both isomers. These results are shown in Table VII. The net contributions to the 1,2-$B_4C_2H_6$ dipole moment were 1.49 D for atomic moments, 0.32 D for bond moments, and 1.15 D for the formal (Mulliken charge) moment. The fact that the net bond moment points in the same direction as does the total moment, rather than opposing it as in the boron hydrides,[14] is due to the absence of bridge hydrogens in 1,2-$B_4C_2H_6$. As found in previous calculations,[12,14] B-H and C-H bond moments appear to be almost independent of local environment, while other types of bond and atomic moments are far more sensitive.

Conclusion

We should like to emphasize once more the unreliability of all basis-set dependent indices in comparing different types of atoms. Thus, we avoid most possible comparisons between B and C atoms using charges, overlap populations, free valences, dipole

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moment components, or frontier orbital populations. This approach greatly limits the range of our conclusions. Nevertheless, by stressing the solid theoretical framework of such partitioning-invariant quantities as the total electron density, we hope to minimize the arbitrary and/or ex post facto interpretations often given to approximate molecular orbital calculations of this type.

Acknowledgment

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The total dipole moment was calculated as $\int \psi^* \vec{r} \psi d\tau$.

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Figure Captions

Figure 1. 1,2-$B_4C_2H_6$.

Figure 2. 1,6-$B_4C_2H_6$.

Figure 3. Total electron density (electrons/au^3) in the B2-B3-B4-B5 plane of 1,6-$B_4C_2H_6$. Atomic centers are indicated by x's.

Figure 4. Total electron density (electrons/au^3) in the C1-B2-B4-C6 plane of 1,6-$B_4C_2H_6$.

Figure 5. Total electron density (electrons/au^3) in the C1-B2-B3 plane of 1,6-$B_4C_2H_6$.

Figure 6. Electron density (electrons/au^3) in the C1-C2-B4-B6 plane of 1,2-$B_4C_2H_6$.

a. Total density.

b. Difference density. Contours are: solid line, 0.009; dotted line, 0.0; dashed line, -0.009.

Figure 7. Total electron densities (electrons/au^3) in the face planes of 1,2-$B_4C_2H_6$.

a. B3-B4-B6 plane.

b. C1-B3-B4 plane.

c. C1-C2-B5 plane.

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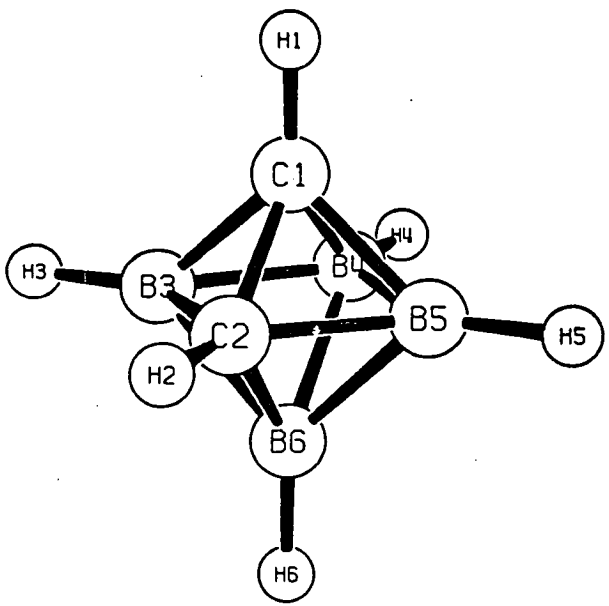

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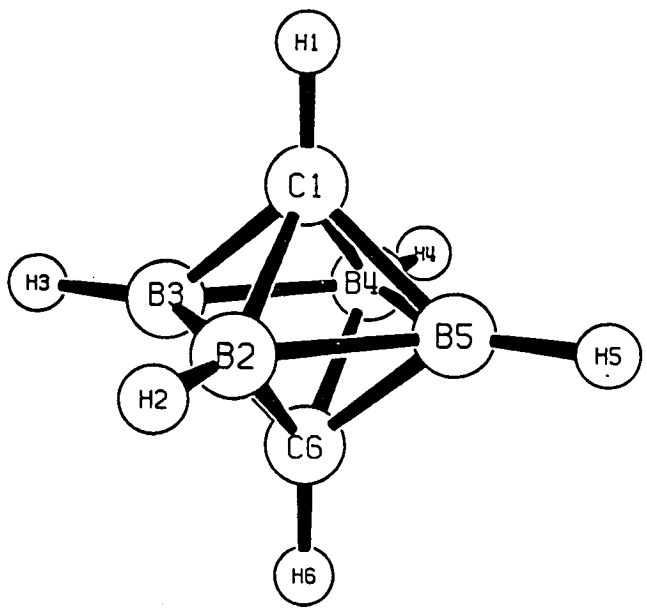

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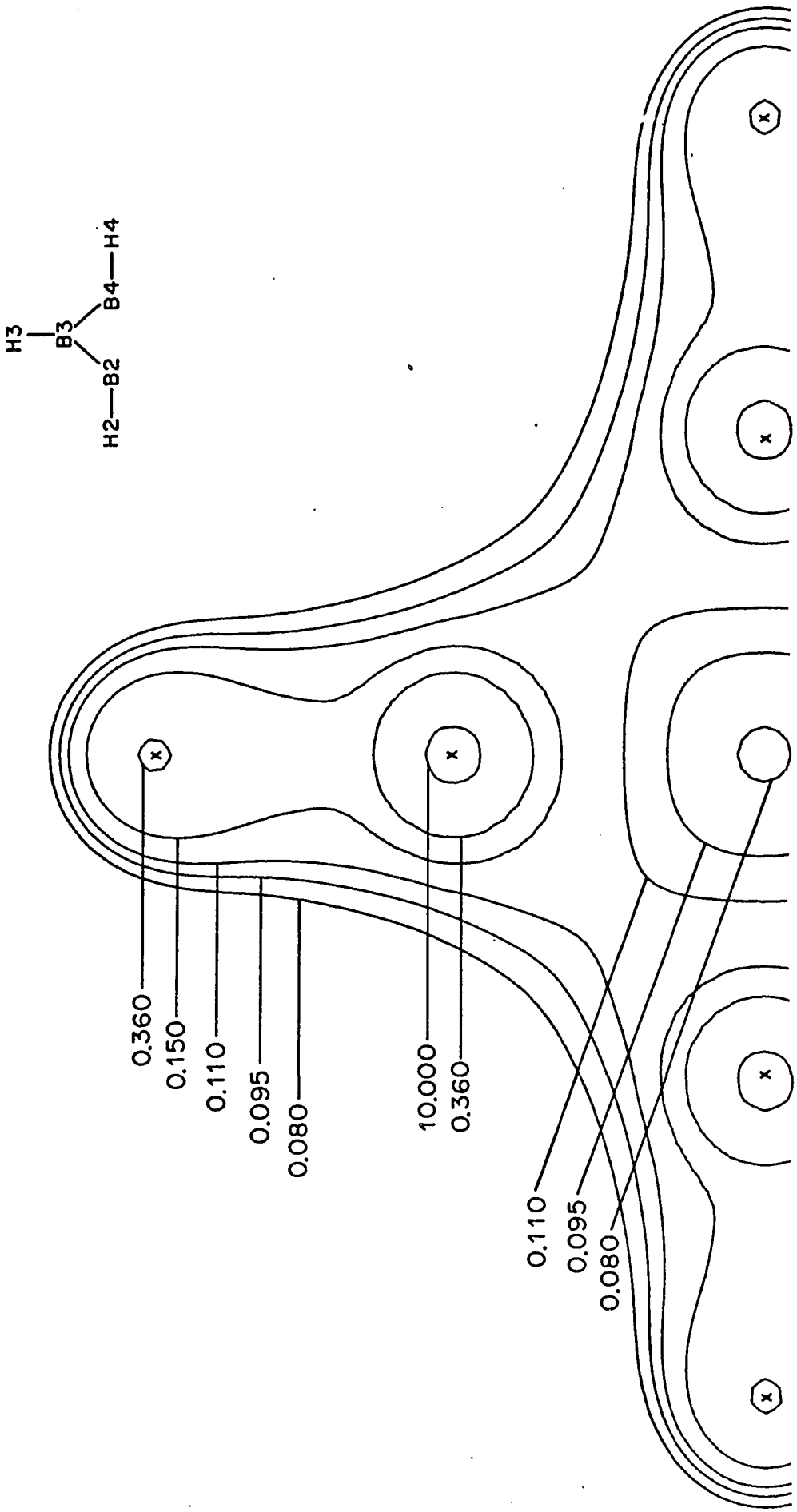

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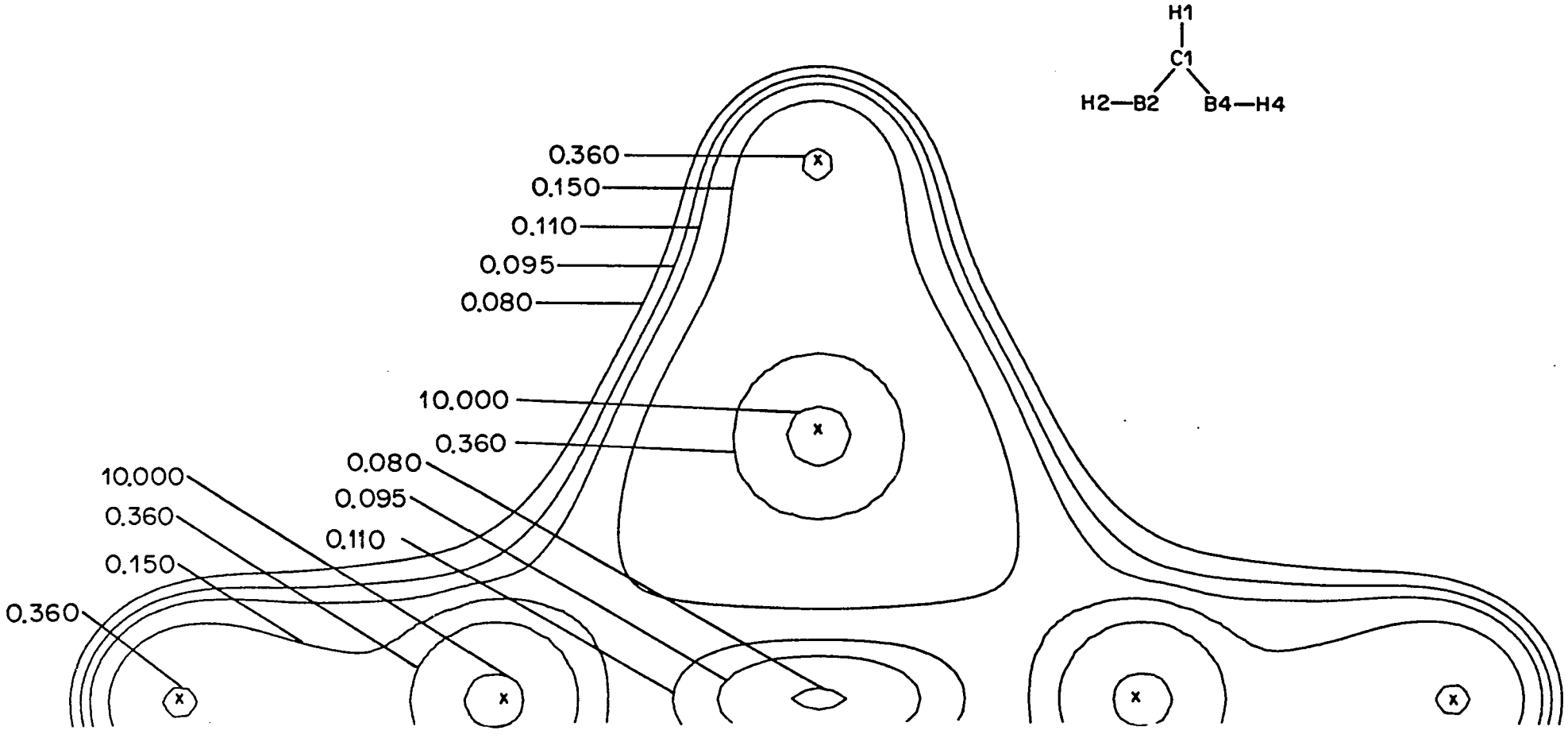

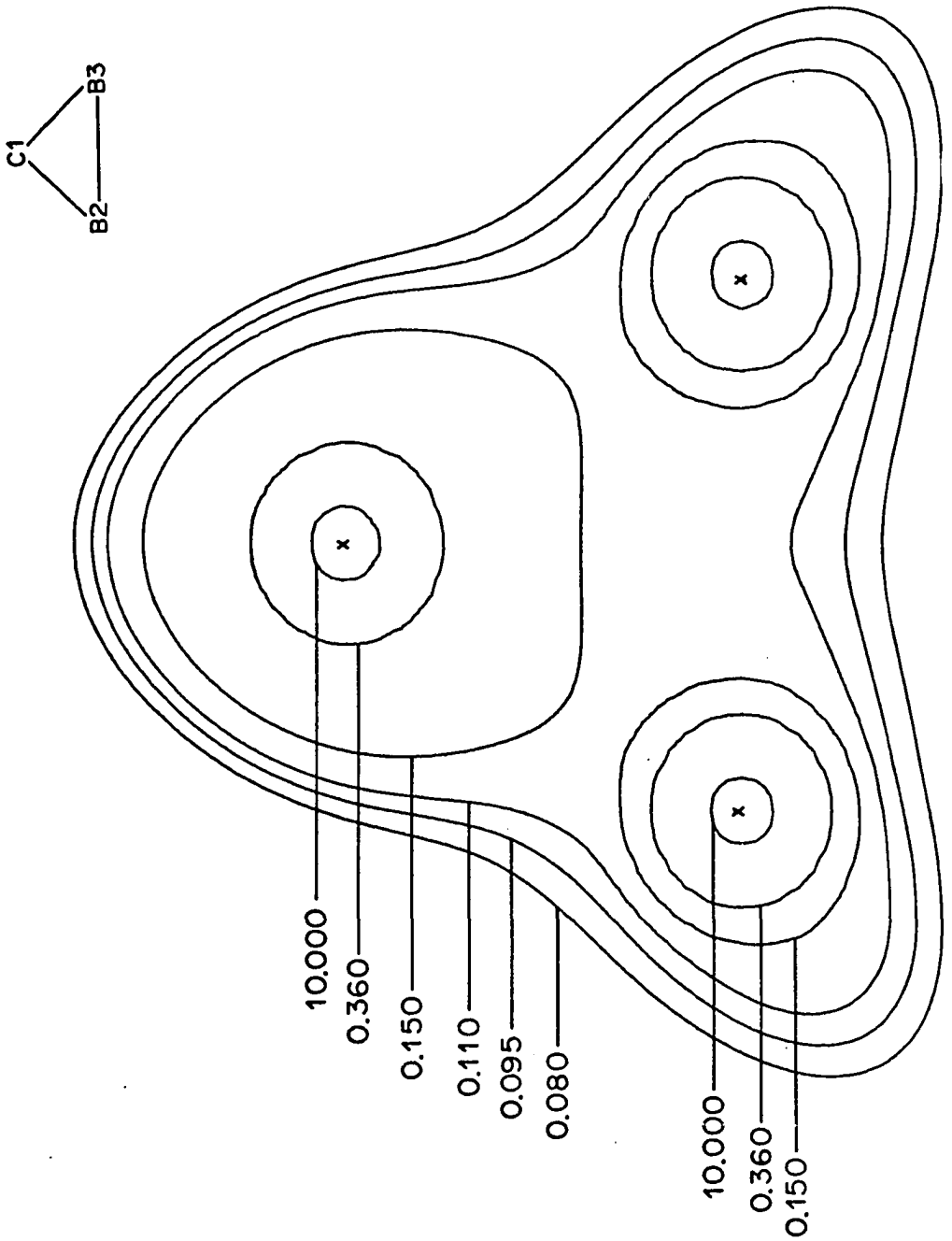

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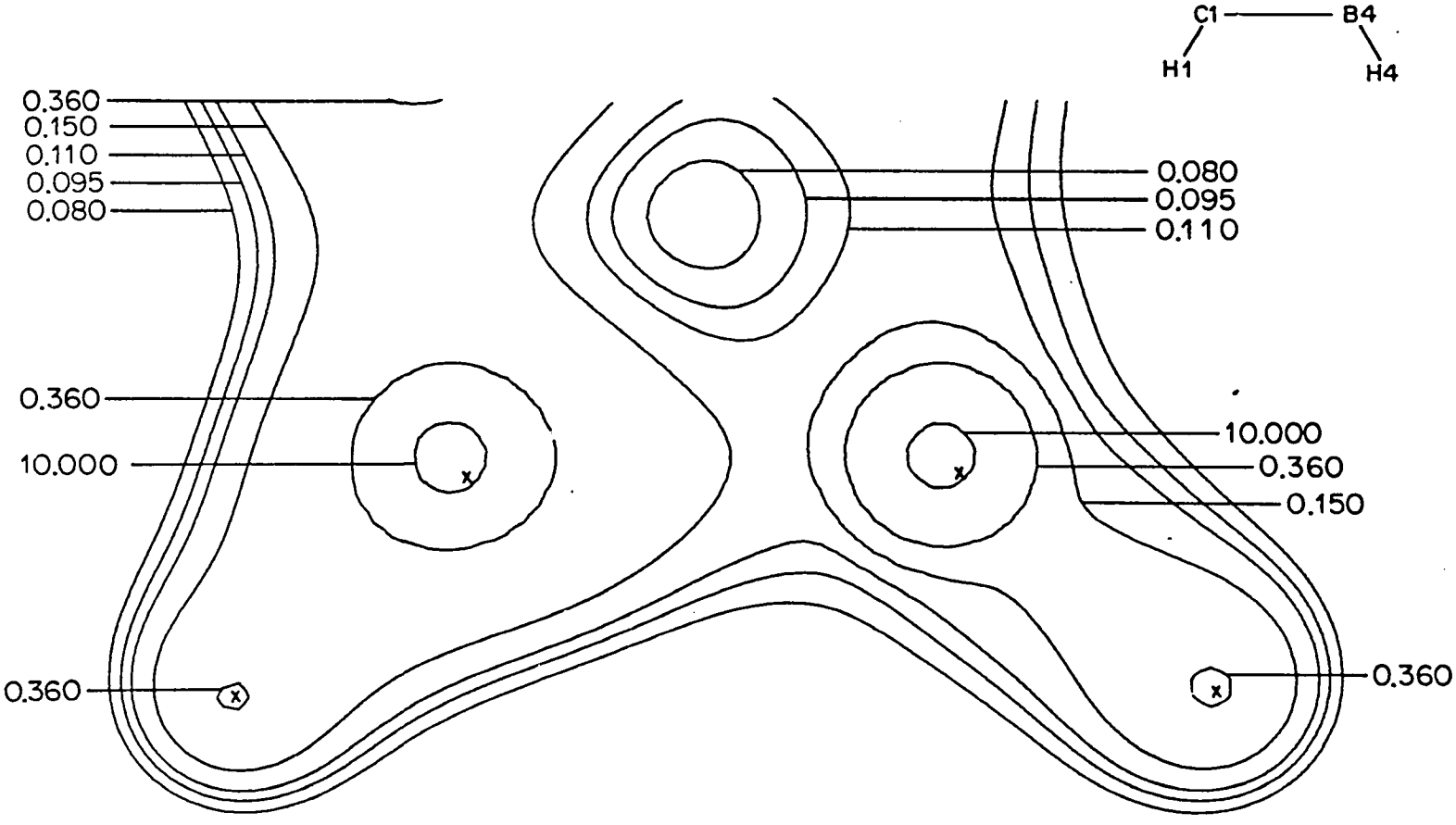

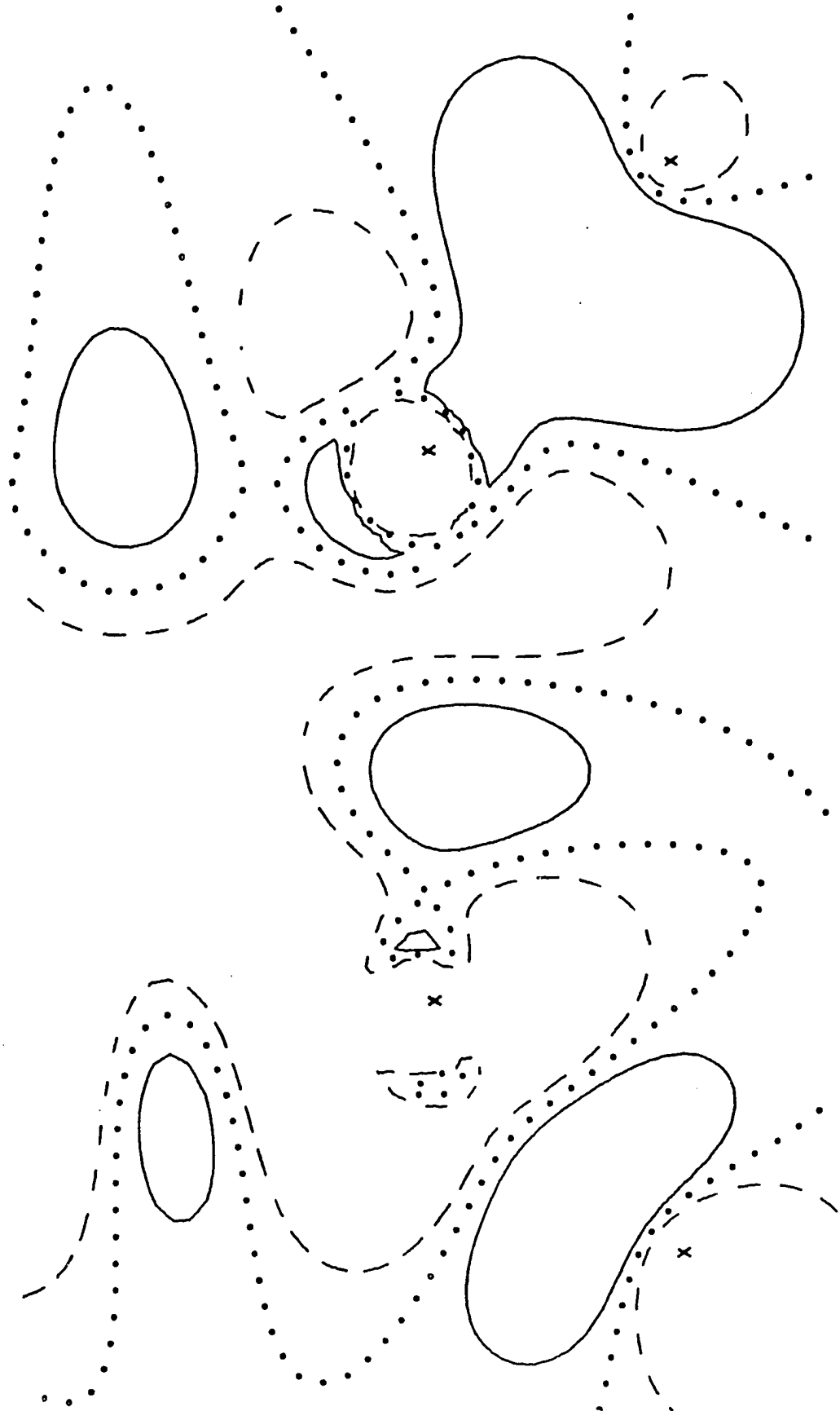

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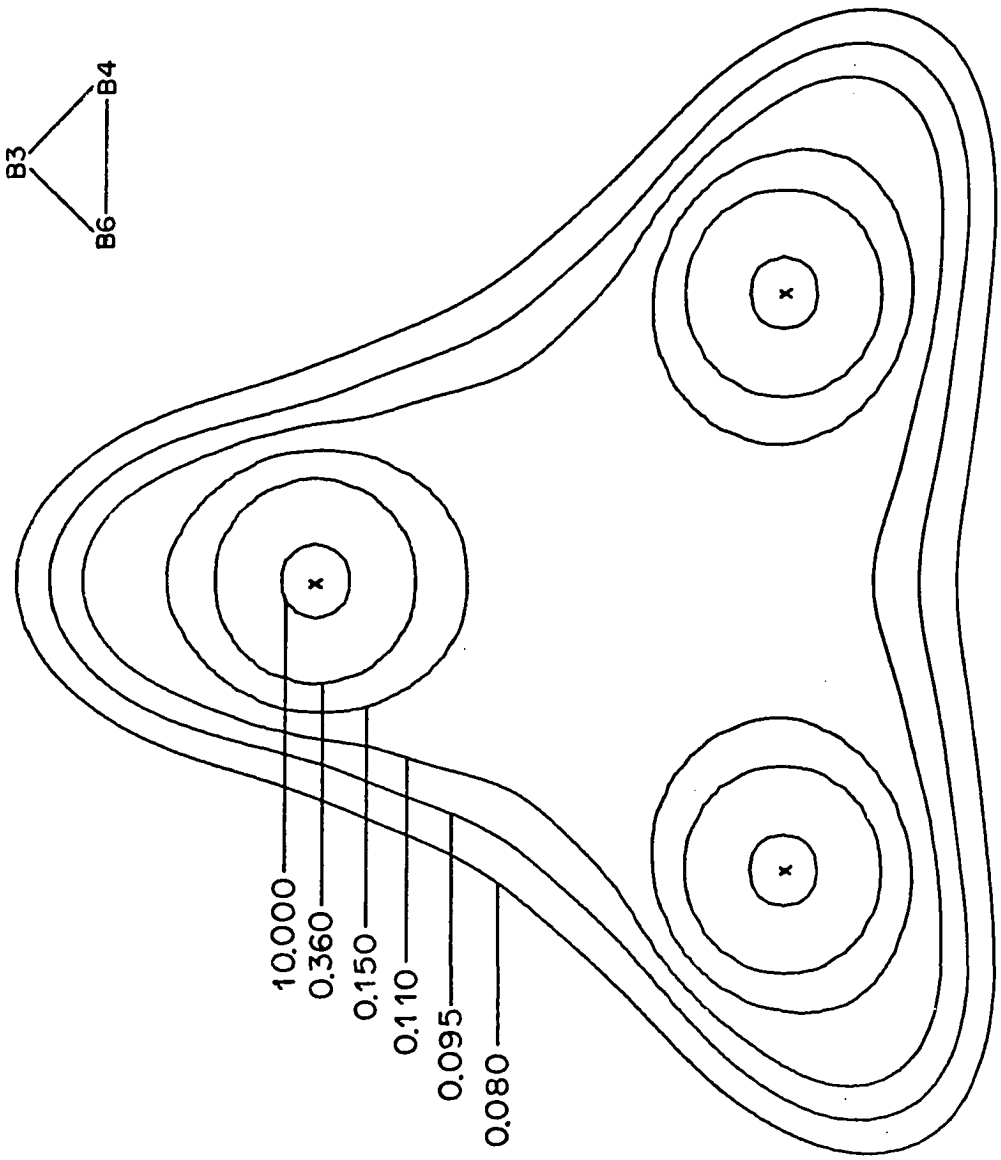

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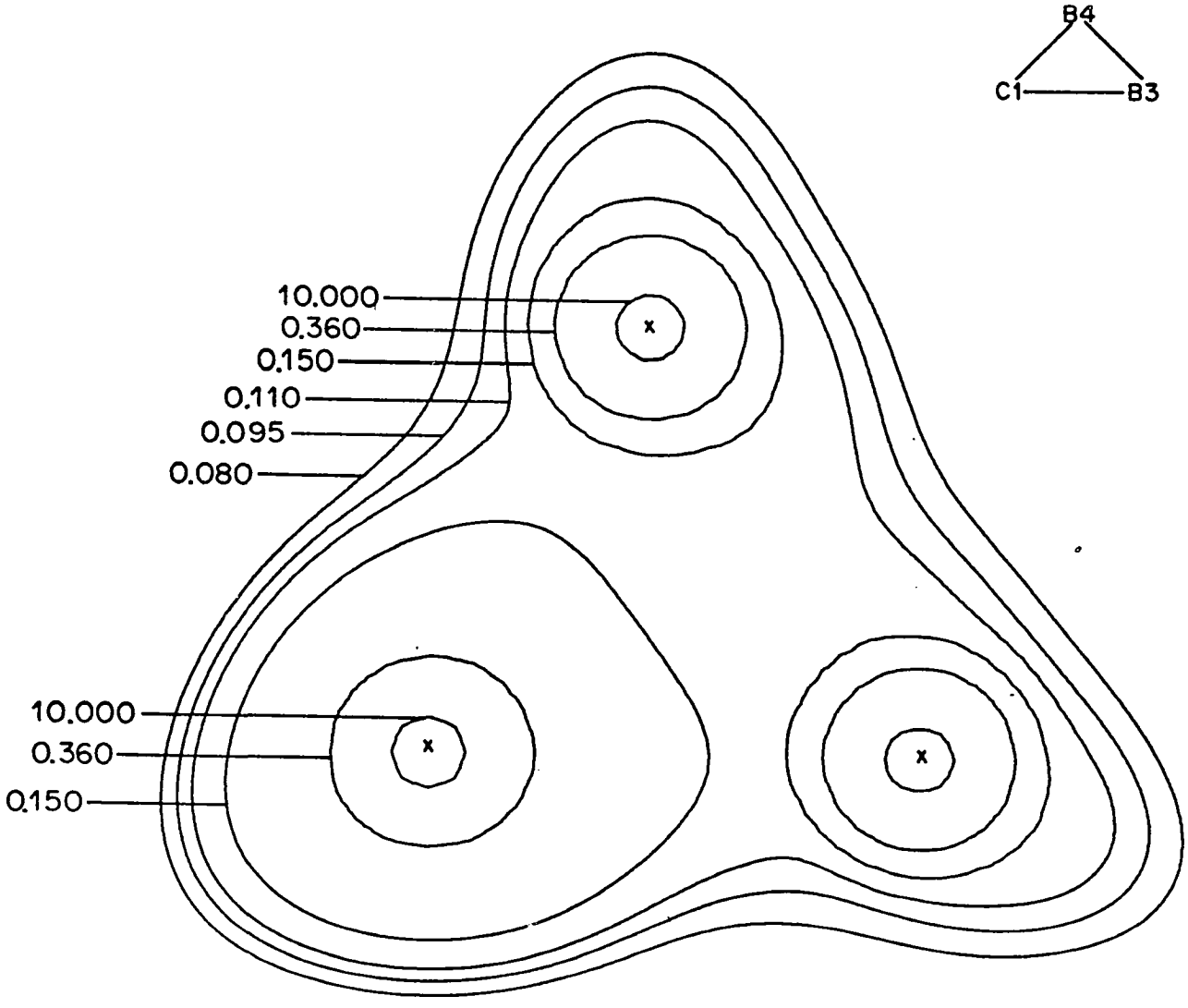

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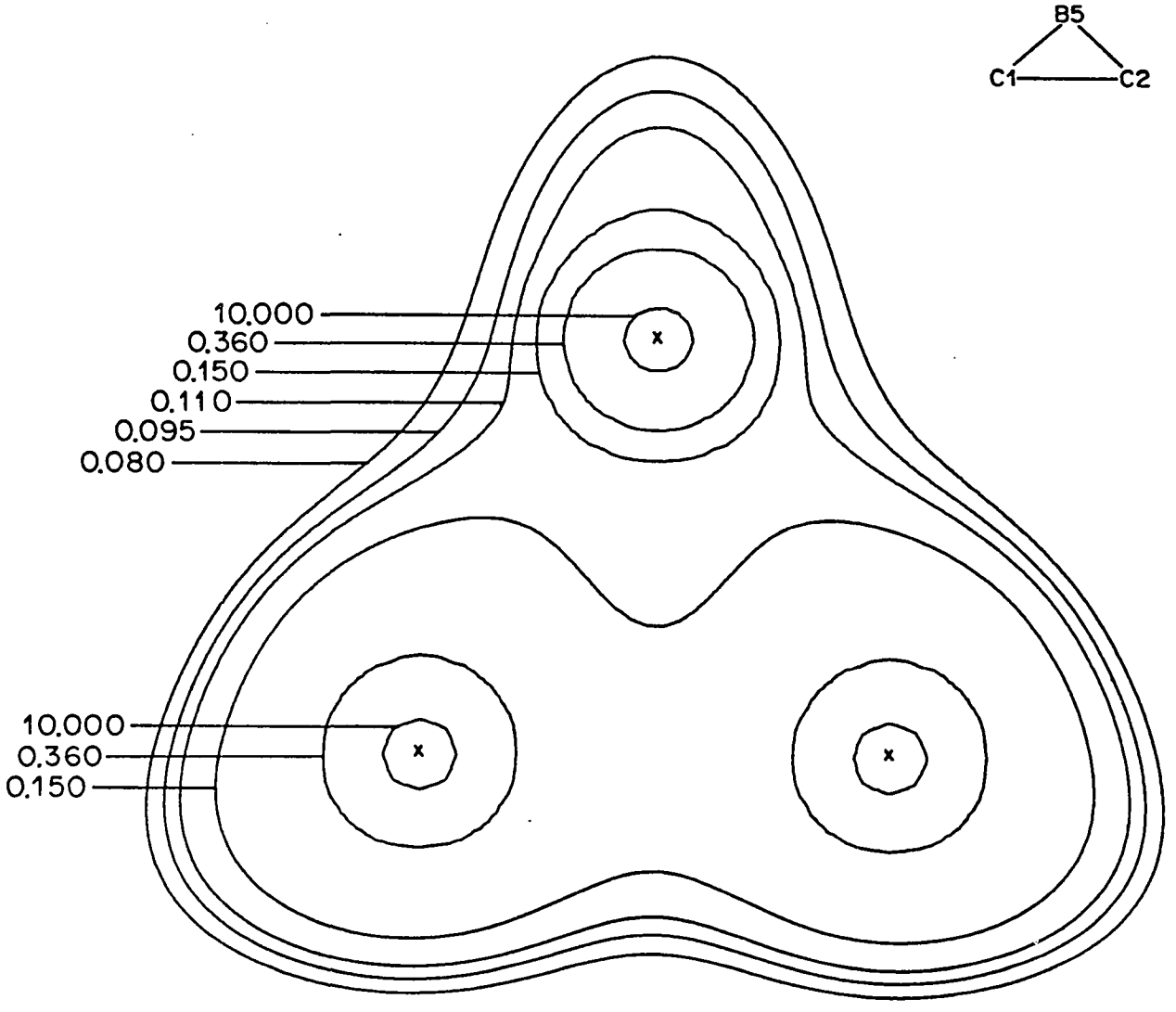

Table I

Unique Coordinates for $B_4C_2H_6$ (au)

	Atom	x	y	z
1,2 Isomer[a]	C1	1.455	-1.436	0.0
	B3	0.0	0.0	2.301
	B4	1.655	1.595	0.0
	H1	2.938	-2.898	0.0
	H3	0.0	0.0	4.561
	H4	3.283	3.163	0.0
1,6 Isomer[b]	C1	0.0	0.0	1.990
	B2	2.320	0.0	0.0
	H1	0.0	0.0	4.073
	H2	4.581	0.0	0.0

[a] 2-fold axis along y.

[b] 4-fold axis along z.

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Table II

Optimized Exponents

From B_2H_6		From C_2H_6	
Orbital	Exponent	Orbital	Exponent
B1s	4.680	C1s	5.680
B2s	1.443	C2s	1.730
B2p	1.477	C2p	1.760
H1s	1.147	H1s	1.160

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Table III 1,2-$B_4C_2H_6$ Occupied and three lowest unoccupied molecular orbitals and energies (in a. u.'s)

		-11.272	-11.272	-7.572	-7.572	-7.554	-7.553	-1.206	-0.853	-0.797	-0.733	-0.654	-0.603	-0.553	-0.503	-0.497	-0.495	-0.411	-0.408	-0.364	0.266	0.280	0.298
H1	1S	-0.003	0.003	0.000	0.000	0.000	0.000	0.046	0.200	0.210	0.000	0.240	0.296	0.096	0.113	0.000	-0.168	-0.116	0.000	0.000	0.000	-0.058	-0.009
H2	1S	-0.003	-0.003	0.000	0.000	0.000	-0.000	0.046	-0.200	0.210	0.000	0.240	-0.296	0.096	0.113	0.000	0.168	-0.116	0.000	0.000	0.000	0.058	-0.009
H3	1S	-0.000	0.000	-0.003	0.003	-0.000	0.000	0.022	0.000	-0.016	-0.146	0.081	0.000	-0.387	0.043	-0.388	0.000	0.024	0.000	-0.115	0.000	0.000	-0.033
H4	1S	0.000	0.000	0.000	-0.000	0.003	0.003	0.017	0.039	-0.061	0.000	0.160	-0.202	0.046	-0.341	0.000	-0.369	0.148	0.000	0.000	0.000	-0.026	0.039
H5	1S	-0.000	0.000	0.003	0.003	-0.000	0.000	0.022	0.000	-0.016	0.146	0.081	0.000	-0.387	0.043	0.388	0.000	0.024	0.000	0.115	0.000	0.000	-0.033
H6	1S	0.000	-0.000	0.000	-0.000	0.003	-0.003	0.017	-0.039	-0.061	0.000	0.160	0.202	0.046	-0.341	0.000	0.369	0.148	0.000	0.000	0.000	0.026	0.039
C1	1S	0.704	-0.703	0.000	-0.000	0.000	0.000	-0.136	-0.141	-0.083	0.000	-0.002	-0.018	-0.016	0.004	0.000	-0.029	-0.022	0.000	0.000	0.000	-0.009	0.006
	2S	0.016	-0.019	0.000	0.005	0.002	0.002	0.349	0.464	0.299	0.000	-0.003	0.045	0.042	-0.042	0.000	0.125	0.105	0.000	0.000	0.000	0.045	-0.047
	2PZ	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	-0.289	0.000	0.000	0.000	0.000	0.247	0.000	0.000	-0.415	-0.213	-0.570	0.000	0.000
	2PX	0.000	0.003	0.000	-0.001	0.001	0.001	-0.124	0.122	-0.001	0.000	0.339	0.108	0.113	0.294	0.000	-0.057	0.132	0.000	0.000	0.000	-0.325	0.248
	2PY	0.002	-0.001	0.000	0.001	0.001	0.002	0.086	0.049	-0.234	0.000	-0.095	-0.303	0.027	0.136	0.000	0.244	0.323	0.000	0.000	0.000	-0.314	0.226
C2	1S	0.704	0.703	0.000	-0.000	0.000	-0.000	-0.136	0.141	-0.083	0.000	-0.002	0.018	-0.016	0.004	0.000	0.029	-0.022	0.000	0.000	0.000	0.009	0.006
	2S	0.016	0.019	0.000	0.005	0.002	-0.002	0.349	-0.464	0.299	0.000	-0.003	-0.045	0.042	-0.042	0.000	-0.125	0.105	0.000	0.000	0.000	-0.045	-0.047
	2PZ	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	-0.289	0.000	0.000	0.000	0.000	0.247	0.000	0.000	0.415	-0.213	0.570	0.000	0.000
	2PX	-0.000	0.003	0.000	0.001	-0.001	0.001	0.124	0.122	0.001	0.000	-0.339	0.108	-0.113	-0.294	0.000	-0.057	-0.132	0.000	0.000	0.000	-0.325	-0.248
	2PY	0.002	0.001	0.000	0.001	0.001	-0.002	0.086	-0.049	-0.234	0.000	-0.095	0.303	0.027	0.136	0.000	-0.244	0.323	0.000	0.000	0.000	0.314	0.226
B3	1S	0.000	0.000	0.703	-0.703	0.014	0.000	-0.082	0.000	0.042	0.147	-0.019	0.000	0.095	-0.021	0.027	0.000	0.008	0.000	-0.027	0.000	0.000	-0.009
	2S	-0.004	0.000	0.020	-0.020	0.006	0.000	0.114	0.000	-0.080	-0.398	0.062	0.000	-0.276	0.044	-0.052	0.000	-0.017	0.000	0.094	0.000	0.000	0.056
	2PZ	0.002	0.000	-0.004	0.004	-0.002	0.000	-0.102	0.000	0.063	0.079	0.084	0.000	-0.240	0.001	-0.338	0.000	0.034	0.000	-0.144	0.000	0.000	-0.018
	2PX	0.000	0.002	0.000	0.000	0.000	0.003	0.000	0.108	0.000	0.000	-0.000	-0.108	0.000	0.000	0.000	0.101	0.000	-0.369	0.000	0.123	0.609	0.000
	2PY	0.002	0.000	-0.000	0.000	0.002	0.000	-0.018	0.000	-0.109	0.046	0.090	0.000	0.048	0.057	-0.050	0.000	-0.150	0.000	0.385	0.000	0.000	-0.630
B4	1S	0.000	-0.000	0.000	-0.015	-0.703	-0.703	-0.067	-0.064	0.101	0.000	-0.084	0.107	-0.035	0.035	0.000	0.038	0.022	0.000	0.000	0.000	-0.004	0.003
	2S	-0.002	0.002	0.000	0.005	-0.018	-0.023	0.085	0.156	-0.231	0.000	0.246	-0.301	0.090	-0.097	0.000	-0.090	-0.070	0.000	0.000	0.000	-0.002	-0.010
	2PZ	0.000	0.000	-0.004	0.000	0.000	0.000	0.000	0.000	0.000	-0.127	0.000	0.000	0.000	0.000	0.023	0.000	0.000	-0.218	0.346	0.592	0.000	0.000
	2PX	-0.000	-0.000	0.000	-0.001	0.001	0.004	-0.050	0.012	0.112	0.000	0.026	-0.082	-0.006	-0.151	0.000	-0.166	0.388	0.000	0.000	0.000	-0.246	-0.318
	2PY	0.002	-0.002	0.000	-0.002	0.003	0.002	-0.067	-0.099	0.038	0.000	0.052	0.043	-0.024	-0.250	0.000	-0.263	-0.149	0.000	0.000	0.000	0.258	0.319
B5	1S	0.000	0.000	-0.703	-0.703	0.014	0.000	-0.082	0.000	0.042	-0.147	-0.019	0.000	0.095	-0.021	-0.027	0.000	0.008	0.000	0.027	0.000	0.000	-0.009
	2S	-0.004	0.000	-0.020	-0.020	0.006	0.000	0.114	0.000	-0.080	0.398	0.062	0.000	-0.276	0.044	0.052	0.000	-0.017	0.000	-0.094	0.000	0.000	0.056
	2PZ	-0.002	0.000	-0.004	-0.004	0.002	0.000	0.102	0.000	-0.063	0.079	-0.084	0.000	0.240	-0.001	-0.338	0.000	-0.034	0.000	-0.144	0.000	0.000	0.018
	2PX	0.000	0.002	0.000	0.000	0.000	0.003	0.000	0.108	0.000	0.000	0.000	-0.108	0.000	0.000	0.000	0.101	0.000	0.369	0.000	-0.123	0.609	0.000
	2PY	0.002	0.000	0.000	0.000	0.002	0.000	-0.018	0.000	-0.109	-0.046	0.090	0.000	0.048	0.057	0.050	0.000	-0.150	0.000	-0.385	0.000	0.000	-0.630
B6	1S	0.000	0.000	0.000	-0.015	-0.703	0.703	-0.067	0.064	0.101	0.000	-0.084	-0.107	-0.035	0.035	0.000	-0.038	0.022	0.000	0.000	0.000	0.004	0.003
	2S	-0.002	-0.002	0.000	0.005	-0.018	0.023	0.085	-0.156	-0.231	0.000	0.246	0.301	0.090	-0.097	0.000	0.090	-0.070	0.000	0.000	0.000	0.002	-0.010
	2PZ	0.000	0.000	-0.004	0.000	0.000	0.000	0.000	0.000	0.000	-0.127	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.218	0.346	-0.592	0.000	0.000
	2PX	0.000	-0.000	0.000	0.001	-0.001	0.004	0.050	0.012	-0.112	0.000	-0.026	-0.082	0.006	0.151	0.000	-0.166	-0.388	0.000	0.000	0.000	-0.246	0.318
	2PY	0.002	0.002	0.000	-0.002	0.003	-0.002	-0.067	0.099	0.038	0.000	0.052	-0.043	-0.024	-0.250	0.000	0.263	-0.149	0.000	0.000	0.000	-0.258	0.319

Electronic energy = -353.919 Two-electron energy = 232.177
Nuclear repulsion = 176.318 Kinetic energy = 178.005
Total energy = -177.601 -E/T = 0.99773

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Table IV 1,6-$B_4C_2H_6$ Occupied and three lowest unoccupied molecular orbitals and energies (in a.u.'s)

		-11.244	-11.244	-7.576	-7.576	-7.576	-7.575	-1.184	-0.886	-0.727	-0.727	-0.696	-0.581	-0.544	-0.509	-0.492	-0.492	-0.442	-0.442	-0.340	0.271	0.271	0.302
H1	1S	0.003	-0.003	-0.000	0.000	0.000	0.000	0.039	0.179	0.000	0.000	0.349	-0.079	0.000	0.383	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2	1S	0.000	0.000	-0.002	-0.003	0.000	-0.002	0.024	0.000	0.155	0.000	0.017	0.262	-0.297	0.000	0.398	0.000	0.000	0.000	0.000	0.092	0.000	0.000
H3	1S	0.000	0.000	-0.002	0.000	0.003	0.002	0.024	0.000	0.000	-0.155	0.017	0.262	0.297	0.000	0.000	-0.398	0.000	0.000	0.000	0.000	-0.092	0.000
H4	1S	0.000	0.000	-0.002	0.003	0.000	-0.002	0.024	0.000	-0.155	0.000	0.017	0.262	-0.297	0.000	-0.398	0.000	0.000	0.000	0.000	-0.092	0.000	0.000
H5	1S	0.000	0.000	-0.002	0.000	-0.003	0.002	0.024	0.000	0.000	0.155	0.017	0.262	0.297	0.000	0.000	0.398	0.000	0.000	0.000	0.000	0.092	0.000
H6	1S	0.003	0.003	-0.000	0.000	0.000	0.000	0.039	-0.179	0.000	0.000	0.349	-0.079	0.000	-0.383	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C1	1S	-0.703	0.703	-0.000	0.000	0.000	0.000	-0.123	-0.160	0.000	0.000	-0.071	0.037	0.000	0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2S	-0.018	0.017	-0.006	0.000	0.000	0.000	0.307	0.516	0.000	0.000	0.248	-0.114	0.000	-0.164	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PZ	0.002	-0.001	0.002	0.000	0.000	0.000	-0.135	0.005	0.000	0.000	0.336	-0.004	0.000	0.437	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PX	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.003	0.254	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PY	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	0.000	0.000	-0.197	0.000	0.000	0.471	0.000	0.518	0.000
H2	1S	-0.000	0.000	0.497	0.703	0.000	0.497	-0.086	0.000	-0.151	0.000	0.019	-0.066	0.077	0.000	-0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2S	0.004	0.000	0.010	0.020	0.000	0.018	0.124	0.000	0.408	0.000	-0.028	0.198	-0.215	0.000	0.018	0.000	0.000	0.000	0.000	0.036	0.000	0.000
	2PZ	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	-0.162	0.000	0.000	0.000	0.000	0.362	0.000	0.000	0.000
	2PX	-0.003	0.000	-0.001	-0.004	0.000	-0.004	-0.111	0.000	-0.078	0.000	0.077	0.180	-0.168	0.000	0.367	0.000	0.000	0.000	0.000	0.000	0.000	0.601
	2PY	0.000	0.000	0.000	0.000	-0.004	0.000	0.000	0.000	0.000	0.154	0.000	0.000	0.000	0.000	0.000	-0.100	0.000	0.000	-0.415	0.000	-0.653	0.000
B3	1S	-0.000	0.000	0.497	0.000	-0.703	-0.497	-0.086	0.000	0.000	0.151	0.019	-0.066	-0.077	0.000	0.000	0.016	0.000	0.000	0.000	0.000	-0.006	0.000
	2S	0.004	0.000	0.010	0.000	-0.020	-0.018	0.124	0.000	0.000	-0.408	-0.028	0.198	0.215	0.000	0.000	-0.018	0.000	0.000	0.000	0.000	-0.004	0.000
	2PZ	0.000	-0.003	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.162	0.000	0.000	-0.362	0.000	0.000	0.000	0.601
	2PX	0.000	0.000	0.000	-0.004	0.000	0.000	0.000	0.154	0.000	0.000	0.000	0.000	0.000	-0.100	0.000	0.000	0.000	0.000	0.415	-0.653	0.000	0.000
	2PY	0.003	0.000	0.001	0.000	-0.004	-0.004	0.111	0.000	0.000	-0.078	-0.077	-0.180	-0.168	0.000	0.000	0.367	0.000	0.000	0.000	0.000	-0.027	0.000
B4	1S	-0.000	0.000	0.497	-0.703	0.000	0.497	-0.086	0.000	0.151	0.000	0.019	-0.066	0.077	0.000	0.016	0.000	0.000	0.000	0.000	-0.006	0.000	0.000
	2S	0.004	0.000	0.010	-0.020	0.000	0.018	0.124	0.000	-0.408	0.000	-0.028	0.198	-0.215	0.000	-0.018	0.000	0.000	0.000	0.000	-0.004	0.000	0.000
	2PZ	0.000	-0.003	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	0.000	-0.162	0.000	0.000	0.000	-0.362	0.000	0.000	0.000	0.601
	2PX	0.003	0.000	0.001	-0.004	0.000	0.004	0.111	0.000	-0.078	0.000	-0.077	-0.180	0.168	0.000	0.367	0.000	0.000	0.000	0.000	-0.027	0.000	0.000
	2PY	0.000	0.000	0.000	0.000	-0.004	0.000	0.000	0.000	0.154	0.000	0.000	0.000	0.000	0.000	0.000	-0.100	0.000	0.000	0.415	0.000	-0.653	0.000
B5	1S	-0.000	0.000	0.497	0.000	0.703	-0.497	-0.086	0.000	0.000	-0.151	0.019	-0.066	-0.077	0.000	0.000	-0.016	0.000	0.000	0.000	0.000	0.006	0.000
	2S	0.004	0.000	0.010	0.000	0.020	-0.018	0.124	0.000	0.000	0.408	-0.028	0.198	0.215	0.000	0.000	0.018	0.000	0.000	0.000	0.000	0.004	0.000
	2PZ	0.000	-0.003	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	0.000	-0.162	0.000	0.000	0.000	0.362	0.000	0.000	0.000	-0.601
	2PX	0.000	0.000	0.000	-0.004	0.000	0.000	0.000	0.154	0.000	0.000	0.000	0.000	0.000	-0.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PY	-0.003	0.000	-0.001	0.000	-0.004	0.004	-0.111	0.000	-0.078	0.000	0.077	0.180	0.168	0.000	0.000	0.367	0.000	0.000	-0.415	-0.653	0.000	0.000
C6	1S	-0.703	-0.703	-0.000	0.000	0.000	0.000	-0.123	0.160	0.000	0.000	-0.071	0.037	0.000	-0.034	0.000	0.000	0.000	0.000	0.000	0.000	-0.027	0.000
	2S	-0.018	-0.017	-0.006	0.000	0.000	0.000	0.307	-0.516	0.000	0.000	0.248	-0.114	0.000	0.164	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PZ	-0.002	-0.001	-0.002	0.000	0.000	0.000	0.135	0.005	0.000	0.000	-0.336	0.004	0.000	0.437	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PX	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	0.000	0.000	0.000	-0.197	0.000	0.000	0.000	0.000	0.000	0.000
	2PY	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	0.000	0.000	-0.197	-0.471	0.000	0.000	0.000	0.518	0.000

Electronic energy = -354.126 Two-electron energy = 232.423
Nuclear repulsion = 176.501 Kinetic energy = 178.006
Total energy = -177.625 -E/T = 0.99786

Table V

Net Mulliken Atomic Charges

	Atom	Charge
1,2 Isomer	C1	-0.08
	B3	0.09
	B4	0.08
	H1	0.07
	H3	-0.07
	H4	-0.08
1,6 Isomer	C1	-0.10
	B2	0.10
	H1	0.05
	H2	-0.07

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Table VI

Bond Overlap Populations and Electron Densities

	Bond	Distance (Å)	OP	Density[a]
1,2 Isomer	C1-C2	1.54	0.52	0.207
	C1-B3	1.63	0.46	0.157
	C1-B4	1.61	0.52	0.170
	B3-B4	1.72	0.46	0.123
	B4-B6	1.75	0.50	0.122
	C1-H1	1.10	0.77	0.265
	B3-H3	1.20	0.81	0.170
	B4-H4	1.20	0.82	0.168
1,6 Isomer	C1-B2	1.62	0.52	0.166
	B2-B3	1.74	0.40	0.115
	C1-H1	1.10	0.77	0.266
	B2-H2	1.20	0.81	0.170

[a] Evaluated at bond midpoint in e/au^3.

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Table VII

Atomic and Bond Moments (Debyes)

	1,2 Isomer		1,6 Isomer	
	y Component	Total		Total
Cl	-0.24	0.27	Cl	0.22
B3	-0.26	0.36	B2	0.29
B4	-0.25	0.25	Cl-B2	0.56
Cl-C2	-0.59	0.59	B2-B3	0.63
Cl-B3	0.27	0.63	Cl-Hl	1.05
Cl-B4	0.14	0.52	B2-H2	1.21
B3-B4	0.43	0.60		
B4-B6	0.50	0.50		
Cl-Hl	0.78	1.01		
B3-H3	0.11	1.23		
B4-H4	-0.81	1.24		

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Chapter V

Approximate Wavefunctions for Carboranes

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Approximate Wavefunctions for Carboranes Parametrized from SCF Model Calculations[1]

by Thomas F. Koetzle and William N. Lipscomb

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Abstract

Molecular orbitals have been obtained by a non-empirical method for carboranes in the series $B_NC_2H_{N+2}$, using parameters from exact minimum basis set SCF calculations for $B_4C_2H_6$. Molecular energies, ionization potentials, charge distributions, and dipole moments have been calculated, and certain predictions made concerning relative reactivities of B atoms in these systems.

[End of Abstract]

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In the past, the carboranes have been the subject of many theoretical studies utilizing molecular orbitals (MO) expressed as a linear combination of atomic orbitals (LCAO). Approximate wavefunctions have been calculated by both the extended Hückel method,[2] and the non-empirical molecular orbital (NEMO) method,[3,4] in which matrix elements are transferred from self-consistent field (SCF) results on small related molecules. All 1s orbitals are included specifically, and overlap and kinetic energy integrals are calculated exactly.

In the preceding paper we have presented SCF results for the two isomers of $B_4C_2H_6$.[5] These are the first such calculations available for a compound containing both B and C atoms. Here we use the results for the $B_4C_2H_6$ isomers as a model in the calculation of new NEMO wavefunctions for several other carboranes. We also discuss the accuracy to which the NEMO method is capable of reproducing the SCF results for these $B_4C_2H_6$ isomers. Of course, some sizable errors do arise in the NEMO results, but in spite of these errors the new wavefunctions

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show some improvement over those from previous studies[6,7] in which parameters were taken from SCF results for boron hydrides[8,9] for B and from C_2H_6[8,10] for C.

Calculations

Calculations were performed using Newton, Boer, and Lipscomb's NEMO program[4] for the IBM 7094 computer. One isomer of each of the seven carboranes studied is shown in Fig. 1, from which H atoms are omitted for the sake of clarity. The assumed molecular symmetries and coordinates for unique atoms are given in Table I. These geometries were obtained from microwave spectroscopic studies for 1,5-$B_3C_2H_5$,[11] 1,2- and 1,6-$B_4C_2H_6$,[12] and 2,4-$B_5C_2H_7$.[13] The distorted icosahedra of the three $B_{10}C_2H_{12}$ isomers were constructed to have B-B and B-C bond lengths of 1.77 and 1.72 Å, respectively. These are average values from X-ray diffraction studies of four halogenated derivatives of the 1,2 isomer.[14,15] Coordinates for 1,7-$B_6C_2H_8$, 1,6-$B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ were taken from X-ray structures of their dimethyl derivatives[7] without imposing any additional molecular symmetry, and are not shown in Table I. In all of the above molecules, H atoms

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were placed to give bond lengths of 1.196 Å for B-H and 1.102 Å for C-H.[16]

A fundamental assumption behind the NEMO method is the transferability of diagonal elements (α) of the F-matrix between related molecules. In Table II we give values of α from our SCF model calculations[5] for the $B_4C_2H_6$ isomers, and we also include the exponents of our minimum Slater basis set for these SCF wavefunctions. It is encouraging to note that corresponding α's from the two isomers agree to within 0.03 au. Also, the two unique B atoms of the asymmetric 1,2 isomer are remarkably similar: their α's differ by no more than 0.02 au. On the other hand, large anisotropies are observed in all 2p orbitals. For example, in symmetric 1,6-$B_4C_2H_6$, the 2p orbital on B perpendicular to the plane of the four B atoms ($2p_z$) has α = -0.511 au, while the two 2p orbitals in the plane have α's of -0.171 and -0.185 au. A serious error in our method results from our present requirement that the same α be employed for the three 2p orbitals on each center. These α's are to be used to generate

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matrix elements for atoms in molecules of different geometry, and are therefore required to be invariant under transformations among the 2p orbitals of the basis set. Methods for transferring anisotropic atoms, or of allowing the local environment to generate anisotropy in these α's have not been introduced into our present programs.

The off-diagonal elements of the potential energy term in the NEMO Hamiltonian are obtained according to a modified Mulliken approximation[17]

$$U_{ij} = K_{ij}S_{ij}(U_{ii} + U_{jj})/2. \qquad (1)$$

In Table III we give Mulliken coefficients K_{ij}, which have been calculated by substituting into eq. 1 values of overlap and potential energy integrals, S_{ij} and U_{ij}, all taken from the SCF results for $B_4C_2H_6$.[5] Also shown are values of the zero-overlap parameter K^{ZO}. One-center 2s-2p elements, which correspond to a vanishing overlap integral, are evaluated as follows

$$U_{2s-2p} = K^{ZO}\sum_k S_{2sk}S_{2pk}\alpha_k \qquad (2)$$

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where the summation runs over basis orbitals.[18] Table III gives three sets of K_{ij} and K^{ZO}, one from the asymmetric, and two from the symmetric isomer. The agreement among them is quite good. In order to maintain consistency, all of our NEMO calculations were performed using input parameters taken from the asymmetric isomer, with the exception of calculations on symmetric $B_4C_2H_6$ itself, in which we used α's and K's (B-C interaction) from that isomer.

One limitation of the NEMO method is its failure to give either the total molecular energy or the energy of atomization directly. Here we have used the approximate relations for these energies in terms of eigenvalues obtained by Boer, Newton, and Lipscomb[19]

$$E_{tot} = (\Sigma \epsilon_i^m + \Sigma E_i^a)/2. \quad (3)$$

$$A = (\Sigma \epsilon_i^m - \Sigma \epsilon_i^a)/2. \quad (4)$$

Sums are taken over all electrons i, and ϵ_i and E_i are molecular (m) or atomic (a) orbital eigenvalues and core (kinetic plus electron-nuclear attraction) energies, respectively. Atomic parameters were taken from

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Clementi's best single-zeta atoms.[20] The major assumption leading to Eqs. 3 and 4 is that the internuclear repulsion cancels against half of the difference between molecular and atomic core energies. The SCF results for $B_4C_2H_6$[5] show that this cancellation holds within 0.05 au for both isomers.

Results

Results of our carborane LCAO MO studies are outlined in Tables IV-VI. Energies are given in Table IV, net Mulliken atomic[21] and framework charges in Table V, and non-zero dipole moments, calculated according to Ruedenberg's origin-invariant method of partitioning,[22] in Table VI. Throughout, calculation I refers to the SCF results of ref. 5, while calculation II is the NEMO method with one-center 2s-2p zero-overlap elements included. Calculation III neglects zero-overlap elements ($K^{ZO} = 0$), but is otherwise the same as calculation II.

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A. $B_4C_2H_6$

Until very recently, no experimentally determined geometry was available for 1,6-$B_4C_2H_6$. Our SCF calculation used an approximate geometry based upon average bond distances taken from the 1,2 isomer. In order to estimate the resulting errors, we have included here NEMO results for a new geometry determined by microwave spectroscopy.[12] For both calculations II and III, the charge distribution (Table V) obtained from the revised geometry is quite similar to that from the geometry assumed for the SCF calculation. For example, the net Mulliken charges differ by only about 0.03 electrons. The total energy (Table IV) increases by 0.12 au in going from the SCF to the revised geometry. This small change is in the opposite direction from that expected, but may be associated with the limitation to a minimum basis set. Hence, optimizations based upon our approximate NEMO total energies would probably be unreliable. However, our calculations do show that the SCF wavefunction for symmetric $B_4C_2H_6$ is not likely to be in serious error due to choice of geometry.

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A detailed comparison (not shown) of NEMO and SCF eigenvalues for $B_4C_2H_6$ indicates differences of up to 0.14 au (symmetric isomer) or 0.19 au (asymmetric isomer) in the energies of corresponding MO's as well as some inversions in the order of eigenvalues which are similar in energy.[23] These changes produce sizable deviations between the SCF and NEMO methods in the molecular energies of Table IV. Similar differences were observed in B_4H_{10}, B_5H_9, and B_5H_{11},[9] although better agreement was obtained for the smaller boron hydrides BH_3 and B_2H_6.[19] Finally, we note that the NEMO results appear to satisfy the virial theorem almost as well as do those from the SCF calculations.

The Mulliken atomic charges (Table V) obtained by the NEMO method for $B_4C_2H_6$ do not agree well with those from the SCF method. The NEMO charge distribution is sensitive to the choice of K^{ZO}. As had previously been observed in boron hydrides,[19] the effect of including zero-overlap elements is to transfer charge out to the terminal H atoms. Framework charges (Table V) tend to

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show less dependence on K^{ZO} than do atomic charges, and may be a more reliable index for comparison of non-equivalent B atoms in these systems. In asymmetric $B_4C_2H_6$, B4 (bonded to one C atom) is predicted to be more negative than B3 (bonded to two C's) in all three calculations. Turning to the calculated dipole moments for this isomer given in Table VI, we note that, as usual, the charge separation is exaggerated in the NEMO results as compared with the SCF results. The direction of the dipole is, however, the same in both methods.

The most important source of the differences between the NEMO and SCF results for both $B_4C_2H_6$ isomers is probably to be found in NEMO's failure to account for anisotropies in the 2p orbitals, as noted above. One other possible source of error may lie in the neglect of one-center 2p-2p zero-overlap elements. In the SCF Hamiltonian for the asymmetric isomer, these elements are as large as 0.16 au, or roughly the same size as the 2s-2p zero-overlap elements which are included in calculation II.

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B. Other Carboranes

It is difficult to judge our NEMO results for carboranes other than $B_4C_2H_6$, because there are so few experimentally measured quantities available for comparison. Among the energies and ionization potentials (Table IV), the extremely low energy of atomization calculated for 1,7-$B_6C_2H_8$ may be significant. From the calculated total energies for $B_{10}C_2H_{12}$ we might predict the meta (or 1,7) isomer to be most stable, followed by the ortho (1,2) and para (1,12) isomers, in that order. However, these predictions are in contradiction with experiments, which show the para isomer to be comparable in stability to the meta isomer.[24] Thus, the total energies obtained from our NEMO results are clearly not accurate enough to reliably predict the small differences between isomers.

Some consistent trends do emerge from the atomic and framework charges of Table V. In each molecule, B atoms become more positive as the number of C atoms to which they are bonded increases. From this order of charges, which was also found in earlier NEMO studies,[7]

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we predict the most reactive B atoms in electrophilic substitution to be those furthest removed from C. Conversely, the B atoms bonded to two C's should be most susceptible to nucleophilic attack. These predictions agree with the observed positions of Friedel-Crafts bromination in 1,2-$B_{10}C_2H_{12}$.[25] On the other hand, our results show no generally valid relationship between the charges of four and five-coordinated B's bonded to the same number of C atoms.[26] We have also calculated Mulliken overlap populations[21] (not shown) for all pairs of atoms in the molecules studied. Here we merely note that the extremely low overlap populations (0.10 in calculation II and 0.17 in calculation III) obtained for the B-B bond in 1,5-$B_3C_2H_5$, in addition to the long distance (1.86 Å),[11] indicate very weak bonding in the plane of the three B atoms in this molecule. When a more normal B-B distance of 1.74 Å was used, the B-B overlap populations increased only slightly to 0.11 and 0.20 in calculations II and III, respectively.

The dipole moments of Table VI are probably all about two and one-half times too large, as are those

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for 1,2- and 1,7-$B_{10}C_2H_{12}$, which have been measured experimentally.[27] In every case, the direction of the dipole makes the side of the molecule containing the C atoms positive. Although the total dipoles from calculations II and III agree to 10 per cent, the partitioning into classical (point charge), atomic, and bond terms again illustrates the sensitivity of charge distributions to zero-overlap elements.

In conclusion, we look forward to future measurements of ionization potentials, energies of atomization, dipole moments, and reactivities for carboranes, with the hope that our MO results may prove useful in correlating this experimental information.

Acknowledgment

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Figure 1. Carborane Geometries.

a. 1,5-$B_3C_2H_5$, b. 1,2-$B_4C_2H_6$, c. 2,4-$B_5C_2H_7$,

d. 1,7-$B_6C_2H_8$, e. 1,6-$B_7C_2H_9$, f. 1,6-$B_8C_2H_{10}$,

g. 1,2-$B_{10}C_2H_{12}$.

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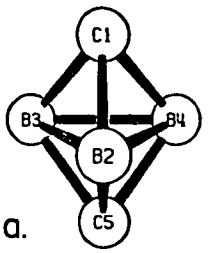

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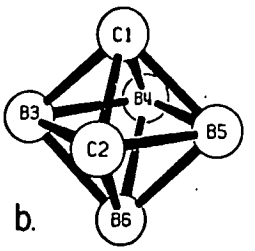

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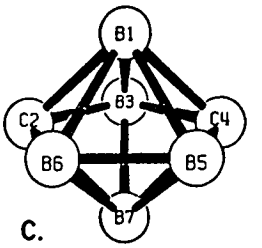

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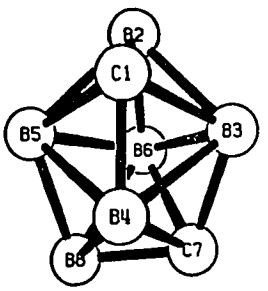

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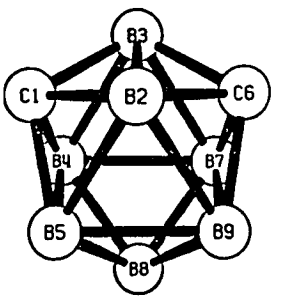

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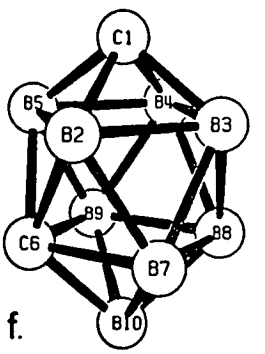
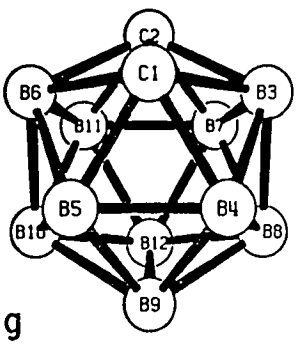


f.



g

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Table I. Coordinates of Unique Atoms for Carboranes (in Å)

	Assumed Symmetry[a]	Atom	x	y	z
$1,5\text{-}B_3C_2H_5$	D_{3h}	C1	0.0	0.0	1.159
		B2	1.074	0.0	0.0
		H1	0.0	0.0	2.261
		H2	2.270	0.0	0.0
$1,2\text{-}B_4C_2H_6$	C_{2v}	C1	0.770	0.0	0.760
		B3	0.0	1.218	0.0
		B4	0.876	0.0	-0.844
		H1	1.555	0.0	1.534
		H3	0.0	2.414	0.0
		H4	1.737	0.0	-1.674
$1,6\text{-}B_4C_2H_6$[b]	D_{4h}	C1	0.0	0.0	1.053
		B2	1.228	0.0	0.0
		H1	0.0	0.0	2.155
		H2	2.424	0.0	0.0
$1,6\text{-}B_4C_2H_6$[c]	D_{4h}	C1	0.0	0.0	1.026
		B2	1.195	0.0	0.0
		H1	0.0	0.0	2.128
		H2	2.391	0.0	0.0
$2,4\text{-}B_5C_2H_7$	C_{2v}	B1	1.154	0.0	0.135
		C2	0.0	-1.210	0.328
		B3	0.0	0.0	1.388
		B5	0.0	0.825	-1.120
		H1	2.342	0.0	0.273
		H2	0.0	-2.264	0.649
		H3	0.0	0.0	2.584
		H5	0.0	1.554	-2.069

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Table I (cont'd.)

	Assumed Symmetry	Atom	x	y	z
1,2-$B_{10}C_2H_{12}$	C_{2v}	Cl	0.0	0.833	-1.348
		B3	1.432	0.0	-0.885
		B4	0.885	1.432	0.0
		B8	1.432	0.0	0.885
		B9	0.0	0.885	1.432
		H1	0.0	1.412	-2.285
		H3	2.449	0.0	-1.514
		H4	1.514	2.449	0.0
		H8	2.449	0.0	1.514
		H9	0.0	1.514	2.449
1,7-$B_{10}C_2H_{12}$	C_{2v}	Cl	0.0	1.348	-0.833
		B2	0.885	0.0	-1.432
		B4	-1.432	0.885	0.0
		B5	0.0	1.432	0.885
		B9	-0.885	0.0	1.432
		H1	0.0	2.285	-1.412
		H2	1.514	0.0	-2.449
		H4	-2.449	1.514	0.0
		H5	0.0	2.449	1.514
		H9	-1.514	0.0	2.449
1,12-$B_{10}C_2H_{12}$	D_{5d}	Cl	0.0	0.0	1.584
		B2	1.506	0.0	0.753
		H1	0.0	0.0	2.686
		H2	2.576	0.0	1.288

[a] The symmetry axis is along z.

[b] Geometry used in the SCF calculations in ref. 5.

[c] Revised geometry.

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Table II. Exponents and α's

Orbital[a]	Exponent	α,a u 1,2-$B_4C_2H_6$	1,6-$B_4C_2H_6$
(C-)Hls	1.160	-0.560	-0.543
(1B-)Hls	1.147	-0.445	
(2B-)Hls	1.147	-0.457	-0.459
Cls	5.680	-11.269	-11.241
C2s	1.730	-1.643	-1.619
C2p	1.760	-0.405	-0.378
1Bls	4.680	-7.551	
1B2s	1.443	-1.171	
1B2p	1.477	-0.261	
2Bls	4.680	-7.569	-7.573
2B2s	1.443	-1.195	-1.195
2B2p	1.477	-0.288	-0.289

[a] 1B and 2B denote B atoms bonded to one or two C atoms, respectively. In the 1,6 isomer, all four B atoms are equivalent.

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Table III. Mulliken Coefficients

		$1,2\text{-}B_4C_2H_6$	$1,6\text{-}B_4C_2H_6$	
		1B-1B[a]	B-C[b]	B-B
One-center	$K_{1s\text{-}2s}$	0.66	0.66	0.66
Two-center	$K_{1s\text{-}1s}$	1.0[c]	1.0[c]	1.0[c]
	$K_{1s\text{-}2s}$	0.79	0.79	0.79
	$K_{1s\text{-}2p}$	0.80	0.80	0.80
	$K_{1s\text{-}H}$	0.81	0.83	0.81
	$K_{2s\text{-}2s}$	1.07	1.04	1.08
	$K_{2s\text{-}2p}$	1.11	1.07	1.12
	$K_{2s\text{-}H}$	1.02	1.04	1.02
	$K_{2p\text{-}2p,\sigma}$	1.10	1.06	1.14
	$K_{2p\text{-}2p,\pi}$	1.10	0.99	1.11
	$K_{2p\text{-}H}$	0.89	0.91	0.88
	$K_{H\text{-}H}$	0.96	0.99	0.95
Zero overlap	K^{ZO}	0.41	0.36	0.35

[a] For the interaction between B atoms bonded to one C.

[b] Interactions involving H taken from C-H; one-center $K_{1s\text{-}2s}$ and K^{ZO} taken from C.

[c] Set at 1.0; the overlap is too small to obtain meaningful results from eq. 1.

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Table IV. Energies and Ionization Potentials (in au)

		$-1/2\sum_i \epsilon_i^m$	-A	$-E_{tot}$	T	-I.P.
1,2-$B_4C_2H_6$	I	60.871	1.363	177.601	178.005	0.364
	II	61.321	1.811	178.047	177.413	0.420
	III	61.463	1.953	178.189	178.187	0.423
1,6-$B_4C_2H_6$	I	60.852	1.387	177.625	178.006	0.340
(SCF geometry)	II	61.139	1.629	177.865	178.018	0.444
	III	61.249	1.739	177.975	178.528	0.429
1,6-$B_4C_2H_6$	II	61.017	1.507	177.743	178.405	0.431
(revised geometry)	III	61.126	1.616	177.852	178.769	0.413
1,5-$B_3C_2H_5$	II	52.740	1.792	153.030	152.826	0.459
	III	52.842	1.894	153.132	153.402	0.484
2,4-$B_5C_2H_7$	II	70.080	2.008	203.242	202.952	0.396
	III	70.227	2.155	203.389	203.728	0.392
1,7-$B_6C_2H_8$	II	78.693	0.059	228.291	228.161	0.384
	III	78.850	0.216	228.448	228.998	0.385
1,6-$B_7C_2H_9$	II	87.454	2.258	253.488	253.172	0.396
	III	87.617	2.421	253.651	254.079	0.401
1,6-$B_8C_2H_{10}$	II	96.159	2.401	278.629	278.234	0.399
	III	96.337	2.579	278.807	279.233	0.407
1,2-$B_{10}C_2H_{12}$	II	113.562	2.680	328.904	328.094	0.376
	III	113.755	2.873	329.097	329.240	0.382
1,7-$B_{10}C_2H_{12}$	II	113.589	2.707	328.931	328.296	0.375
	III	113.781	2.899	329.123	329.430	0.380
1,12-$B_{10}C_2H_{12}$	II	113.464	2.582	328.806	328.311	0.368
	III	113.654	2.772	328.996	329.435	0.372

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Table V. Charge Distributions

		Net Mulliken Charge			Framework Charge[a]		
	Atom	I	II	III	I	II	III
$1,2\text{-}B_4C_2H_6$	C1	-0.08	0.25	-0.02	-0.01	0.13	0.07
	B3	0.09	0.31	-0.05	0.01	0.00	-0.01
	B4	0.08	0.21	-0.05	0.00	-0.13	-0.06
	H1	0.07	-0.11	0.09			
	H3	-0.07	-0.31	0.04			
	H4	-0.08	-0.34	-0.01			
$1,6\text{-}B_4C_2H_6$ (SCF geometry)	C1	-0.10	0.05	-0.13	-0.05	-0.05	-0.06
	B2	0.10	0.28	-0.04	0.03	0.02	0.03
	H1	0.05	-0.10	0.07			
	H2	-0.07	-0.25	0.07			
$1,6\text{-}B_4C_2H_6$ (revised geometry)	C1		0.05	-0.14		-0.09	-0.09
	B2		0.34	0.00		0.05	0.05
	H1		-0.14	0.05			
	H2		-0.29	0.05			
$1,5\text{-}B_3C_2H_5$	C1		-0.15	-0.30		-0.20	-0.18
	B2		0.40	0.03		0.14	0.12
	H1		-0.05	0.12			
	H2		-0.26	0.09			
$2,4\text{-}B_5C_2H_7$	B1		0.38	0.03		0.04	0.02
	C2		0.03	-0.18		-0.05	-0.09
	B3		0.45	0.09		0.12	0.11
	B5		0.25	0.02		-0.05	0.00
	$(B\text{-})H_{ave}$		-0.32	0.00			
	H2		-0.08	0.08			
$1,7\text{-}B_6C_2H_8$	C1		-0.02	-0.22		-0.09	-0.13
	B2		0.35	0.09		0.03	0.07
	B3		0.44	0.12		0.11	0.09
	B5		0.28	0.03		-0.05	-0.03
	H1		-0.07	0.09			
	$(B\text{-})H_{ave}$		-0.33	-0.03			

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Table V (cont'd.)

		Net Mulliken Charge			Framework Charge	
	Atom	I	II	III	I	II	III
1,6-$B_7C_2H_9$	C1		0.02	-0.17		-0.03	-0.07
	B2		0.46	0.14		0.15	0.13
	B4		0.30	0.04		0.01	0.01
	B8		0.00	-0.15		-0.27	-0.17
	H1		-0.05	0.10			
	(B-)H_{ave}		-0.29	-0.02			
1,6-$B_8C_2H_{10}$	C1		-0.02	-0.22		-0.08	-0.12
	B2		0.41	0.12		0.11	0.10
	B3		0.36	0.10		0.05	0.05
	C6		0.05	-0.14		0.03	-0.05
	B7		0.27	0.03		0.00	0.01
	B8		0.06	-0.12		-0.22	-0.16
	B10		0.27	0.02		-0.04	0.00
	(C-)H_{ave}		-0.04	0.10			
	(B-)H_{ave}		-0.29	-0.03			
1,2-$B_{10}C_2H_{12}$	C1		0.25	0.07		0.22	0.17
	B3		0.36	0.10		0.07	0.07
	B4		0.32	0.08		0.02	0.03
	B8		0.13	-0.08		-0.16	-0.14
	B9		0.12	-0.09		-0.17	-0.16
	H1		-0.03	0.09			
	(B-)H_{ave}		-0.29	-0.05			
1,7-$B_{10}C_2H_{12}$	C1		0.06	-0.10		0.04	-0.01
	B2		0.38	0.12		0.09	0.10
	B4		0.32	0.08		0.02	0.03
	B5		0.31	0.07		0.01	0.02
	B9		0.10	-0.10		-0.19	-0.16
	H1		-0.02	0.09			
	(B-)H_{ave}		-0.29	-0.05			

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Table V (cont'd.)

		Net Mulliken Charge			Framework Charge	
	Atom	I	II	III	II	III
1,12-$B_{10}C_2H_{12}$	C1		0.04	-0.13	0.02	-0.05
	B2		0.29	0.06	0.00	0.01
	H1		-0.02	0.09		
	H2		-0.30	-0.05		

[a] Defined as the sum of the atomic charges for a B-H or C-H unit.

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Table VI. Dipole Moments (in Debyes)

		$\mu_{expt'l}$	μ_{total}[a]	$\mu_{classical}$	μ_{atomic}	μ_{bond}
1,2-$B_4C_2H_6$	I		2.95	1.15	1.49	0.32
	II		5.46	3.88	0.51	1.07
	III		4.50	1.77	1.79	0.94
2,4-$B_5C_2H_7$	II		2.18	1.49	0.30	0.39
	III		2.21	0.94	0.97	0.29
1,7-$B_6C_2H_8$	II		2.68	1.69	0.34	0.65
	III		2.42	0.60	1.27	0.56
1,6-$B_7C_2H_9$	II		5.05	4.23	0.29	0.53
	III		4.64	2.83	1.31	0.51
1,6-$B_8C_2H_{10}$	II		4.31	3.14	0.49	0.72
	III		4.46	2.22	1.64	0.61
1,2-$B_{10}C_2H_{12}$	II	4.31	11.47	9.90	0.66	0.91
	III		10.75	7.92	1.81	1.02
1,7-$B_{10}C_2H_{12}$	II	2.78	6.94	5.84	0.53	0.58
	III		6.58	4.67	1.22	0.69

[a] Calculated as $\int \psi^* \vec{r} \psi d\tau$.

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Appendix I

The Unit Cell and Molecular Weight of a Compound Containing Both B and S Atoms

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Recent research has explored the use of boron compounds in brain tumor therapy.[1] If tissue containing B^{10} nuclei is irradiated with thermal neutrons, a well known reaction occurs

$$_0n^1 + {}_5B^{10} = {}_3Li^7 + {}_2He^4 + 2.4 \text{ Mev.}$$

The α particle and Li^7 nucleus are released with high kinetic energy, but travel only a very short distance, so the destructive effects are confined to the area immediately surrounding the original site of the B^{10} nucleus. If a boron compound were absorbed preferentially by tumor tissue compared to normal brain tissue or the blood, it should be effective in therapy.

Some encouraging results have been observed with material resulting from the reaction of H_2S with the acid of $B_{12}H_{12}^{-2}$. One compound was separated from the complex product as the Cs salt by Dr. A. H. Soloway, who provided a sample to the author. This sample gave a rather unsatisfactory elemental analysis: Cs-52.79, B-28.49, H-2.99, and S-5.06 %

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(total 89.33%).

The salt was recrystallized from hot H_2O and formed large plates several millimeters square. A crystal was mounted on the Picker four-circle diffractometer, and the 2θ values of 45 reflections were measured. A least squares refinement based on these 2θ values indicated that the unit cell is orthorhombic with dimensions a = 14.739, b = 9.580, and c = 10.284 Å. The space group was not determined with certainty, but was tentatively assigned from extinctions observed on precession photographs as $P2_12_12_1$.

The density of several crystals was determined by flotation in a mixture of C_2H_5I and $CHBr_3$. All crystals gave a density close to the mean value of 2.143 g/cc. Assuming eight molecules per unit cell, the molecular weight is calculated to be 457.1 .

One chemically reasonable formula for this salt, $Cs_2B_{12}H_{11}SH.H_2O$, gives a molecular weight of 457.7, in good agreement with the value obtained above. On the other hand, the weight percentages

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calculated from this formula are: Cs-58.07, B-28.34, H-3.08, S-7.01, O-3.50%. These values do not agree with the elemental analysis.

If there are eight molecules per unit cell and two Cs atoms per B_{12} unit, our density rules out any dimer structure containing a disulfide bond.

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References

(1) A. H. Soloway, in "Progress in Boron Chemistry," Vol. 1, ed. H. Steinberg and A. L. McCloskey, The Macmillan Co., New York, 1964, p. 203.

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Appendix II

Listing of Model Building Program

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```
$IBFTC DRILL   FULIST,DD,DECK
CDRILL
C A FORTRAN IV PROGRAM TO DETERMINE DRILL SETTINGS NECESSARY TO MAKE A
C BALL AND STICK MODEL OF THE UNIT CELL OF A CRYSTAL STRUCTURE. WRITTEN
C BY THOMAS F KOETZLE ON THE MODEL OF AN EARLIER PROGRAM BY JACK Z
C GOUGOUTAS. THIS PROGRAM ACCEPTS AS INPUT THE REFINED FRACTIONAL COOR-
C DINATES PUNCHED BY EITHER FLS OR CRYRM. IT WILL PRODUCE A MODEL PRO-
C JECTED IN THE PLUS OR MINUS X, Y, OR Z DIRECTIONS FOR ORTHOGONAL UNIT
C CELLS. FOR TRICLINIC OR MONOCLINIC UNIT CELLS, ONLY PLUS OR MINUS Y IS
C ALLOWED.
      DIMENSION ISUPRT(16,100),SI(3),X(16,100,3),NT(100,20),AL(3),CO(3)
      DIMENSION IDEN(8),RAD(8),T8(16,3),T7(16,3),J6(16,3),NO(100)
      DIMENSION LFF(100),C(36,3),DIS(36),R(3),U(3),GG(3),NBA(100)
      DIMENSION AXIS(3),VECTR1(3),VECTR2(3),NJ(20),VIP(16)
      DIMENSION PROD(16),SUPORT(3)
      COMMON P
      DATA (AXIS(I),I=1,3)/1HX,1HY,1HZ/
      DO 3001 I=1,100
      DO 3001 J=1,20
 3001 NT(I,J)=0
      P=180./3.1416
      ONE=1.
      SMIN=0.
      DMIN=1000.
      REWIND 1
C READ TITLE AND WRITE TITLE ON OUTPUT TAPE
      READ(5,113)(NT(I,1),I=1,14)
  113 FORMAT(13A6,A2)
      WRITE(6,114)(NT(I,1),I=1,14)
  114 FORMAT(1H1,13A6,A2)
C READ CELL CONSTANTS AND WRITE THEM ON THE OUTPUT TAPE.
      READ(5,76)(AL(I),I=1,3),(CO(I),I=1,3),ICELTP
   76 FORMAT(6F9.3,I3)
      DO 270 I=1,3
  270 SI(I)=SQRT(1.-CO(I)**2)
      WRITE(6,7600)(AL(I),I=1,3),(CO(I),I=1,3)
 7600 FORMAT(//5H A = ,F7.3,10H ANGSTROMS,4X,4HB = ,F7.3,10H ANGSTROMS,4
     1X,4HC = ,F7.3,10H ANGSTROMS/13H COS ALPHA = ,F8.5,4X,11HCOS BETA =
     2 ,F8.5,4X,12HCOS GAMMA = ,F8.5/)
C READ FIRST CONTROL CARD
      READ(5,1000)T1,T2,SFIN,REC,ORG,K,NK,NSY
 1000 FORMAT(5F5.0,3I3)
C TEST TYPE OF UNIT CELL AND WRITE APPROPRIATE MESSAGE
      IF(ICELTP)220,221,222
  220 WRITE(6,223)
  223 FORMAT(27H THE UNIT CELL IS TRICLINIC)
      GO TO 224
  221 WRITE(6,225)
  225 FORMAT(28H THE UNIT CELL IS ORTHOGONAL)
      GO TO 224
  222 WRITE(6,226)
  226 FORMAT(28H THE UNIT CELL IS MONOCLINIC)
  224 WRITE(6,227)NK
  227 FORMAT(33H THE MODEL IS PROJECTED ALONG THE,I3,5H AXIS)
C WRITE INFORMATION ON FIRST CONTROL CARD
      RECIN=REC/2.54
      WRITE(6,230)K,T1,T2,SFIN,RECIN,NSY
  230 FORMAT(/I3,6H ATOMS/22H ALL DISTANCES BETWEEN,F7.4,4H AND,F7.4,31H
     1 ANGSTROMS ARE BONDED DISTANCES/27H THE SCALE OF THIS MODEL IS,F7.
     23,17H CM. PER ANGSTROM/23H HOLES EXTEND TO WITHIN,F6.3,34H INCHES
```

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```
     30F THE CENTER OF EACH BALL/I3,20H SYMMETRY OPERATIONS)
C READ BALL IDENTITIER CARD AND BALL RADIUS CARD
      READ(5,113)(IDEN(I),I=1,8)
      READ(5,760)(RAD(I),I=1,8)
  760 FORMAT(8F9.3)
C CALCULATE VECTOR FROM ANY ATOM TO BASE OF MODEL. THIS WILL FIX THE
C DIRECTION OF ALL SUPPORTS
      NS=IABS(NK)
      SIGN=NK/NS
      DO 2760 L=1,3
 2760 SUPORT(L)=0.
      SUPORT(NS)=-SIGN
C IF MODEL IS ALONG A - AXIS SET XCO=0. IF MODEL IS ALONG A + AXIS, SET
C XCO = 1000. XCO WILL CONTAIN VERTICAL COORDINATE OF BALL CLOSEST TO
C THE BASE OF THE MODEL
      IF(SIGN)2002,2002,2003
 2002 XCO=0.
      GO TO 2004
 2003 XCO=1000.
 2004 WRITE(6,592)
  592 FORMAT(//20H SYMMETRY OPERATIONS)
      DO 520 J=1,NSY
C READ SYMMETRY CARDS AND WRITE THEIR CONTENTS ON OUTPUT TAPE
C ALSO PRINT OUT WHICH MOLECULES ARE RIGHT-HANDED, AND WHICH ARE LEFT-
C HANDED.
      READ(5,521)(T8(J,I),T7(J,I),J6(J,I),I=1,3)
      PROD(J)=T7(J,1)*T7(J,2)*T7(J,3)
      IF(PROD(J))710,710,1710
  710 WRITE(6,521)(T8(J,I),T7(J,I),J6(J,I),I=1,3),J
      GO TO 520
 1710 WRITE(6,711)(T8(J,I),T7(J,I),J6(J,I),I=1,3),J
  521 FORMAT(3(2F9.3,I2),11H  MOLECULE ,I2,16H IS LEFT-HANDED.)
  711 FORMAT(3(2F9.3,I2),11H  MOLECULE ,I2,17H IS RIGHT-HANDED.)
  520 CONTINUE
C WRITE HEADER FOR ATOMIC COORDINATES ON OUTPUT TAPE
      WRITE(6,120)
  120 FORMAT(23H1  INPUT PEAK POSITIONS/4X,2HNO,3X,3HLFF,1X,6HISUPRT,14X
     1,1HX,8X,1HY,8X,1HZ///)
C READ FIRST CARD OF ATOMIC DECK FOR FORMAT CONTROL
      READ(5,231)IFORM
  231 FORMAT(I1)
C READ ATOMIC DECK IN APPROPRIATE FORMAT
      DO 4 J=1,K
      IF(IFORM)232,233,232
  232 READ(5,235)NO(J),LFF(J),ISUPRT(1,J),(X(1,J,I),I=1,3)
  235 FORMAT(3X,I3,3X,I2,3X,I2,3F9.7)
      GO TO 234
  233 READ(5,5)NO(J),LFF(J),ISUPRT(1,J),(X(1,J,I),I=1,3)
    5 FORMAT(3X,I3,3X,I2,3X,I2,11X,3F9.3)
C WRITE COORDINATES ON OUTPUT TAPE
  234 WRITE(6,5)NO(J),LFF(J),ISUPRT(1,J),(X(1,J,I),I=1,3)
      DO 2005 I=1,3
 2005 X(1,J,I)=X(1,J,I)*AL(I)
    4 CONTINUE
C CALCULATE COORDINATES OF SYMMETRY EQUIVALENT ATOMS IN ANGSTROMS
      DO 240 J=1,NSY
      DO 240 I=1,K
      DO 241 L=1,3
      MQS=J6(J,L)
  241 X(J,I,L)=X(1,I,MQS)*T7(J,L)+T8(J,L)*AL(L)
```

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```
  240 ISUPRT(J,I)=ISUPRT(1,I)
C ORTHOGONALIZE COORDINATES
      CONST1=(CO(2)-CO(1)*CO(3))/SI(3)
      CONST2=SQRT((1.-CO(1)**2-CO(2)**2-CO(3)**2+2.*CO(1)*CO(2)*CO(3))/S
     1I(3)**2)
      DO 2236 J=1,NSY
      DO 236 I=1,K
      X(J,I,2)=X(J,I,2)+X(J,I,1)*CO(3)+X(J,I,3)*CO(1)
      X(J,I,1)=X(J,I,1)*SI(3)+X(J,I,3)*CONST1
      X(J,I,3)=X(J,I,3)*CONST2
C CALCULATE VERTICAL COORDINATE OF BALL CLOSEST TO BASE
      IF(SIGN)244,245,245
  244 XCO=AMAX1(XCO,X(J,I,NS))
      GO TO 236
  245 XCO=AMIN1(XCO,X(J,I,NS))
  236 CONTINUE
 2236 CONTINUE
C WE ARE READY TO BEGIN CALCULATING DRILLING ANGLES
      DO 8 JX=1,K
      DO 3002 I=1,36
      DIS(I)=0.
      DO 3002 J=1,3
 3002 C(I,J)=0.
      NBA(JX)=0
      DO 6 M=1,K
      IF(M-JX)7,6,7
    7 DO 73 J=1,3
C GET DISTANCE BETWEEN ATOM JX AND ATOM M
   73 R(J)=X(1,M,J)-X(1,JX,J)
      XE=DOT(R,R)
      D=SQRT(XE)
C IF THIS IS A BONDED DISTAMCE INCREASE COUNTER BY 1
      IF(D-T1)79,79,6
   79 IF(D-T2)250,3,3
  250 IF(D-DMIN)2021,2020,2020
C THE SMALLEST DISTANCE YET ENCOUNTERED IS DMIN
 2021 DMIN=D
      IMIN=NO(JX)
      MMIN=NO(M)
      GO TO 2020
    3 NBA(JX)=NBA(JX)+1
 2020 CONTINUE
C CALCULATE MINIMUM OVERALL SCALE FACTOR WHICH WILL ALLOW THE BALLS
C CORRESPONDING TO ATOMS JX AND M TO CLEAR ONE ANOTHER. ACCUMULATE THE
C MINIMUM SCALE WHICH ALLOWS ALL BALLS IN THE MODEL TO CLEAR AS SMIN.
      JKL=LFF(JX)
      JKG=LFF(M)
      XSFA=(RAD(JKL)+RAD(JKG))/D
      SMIN=AMAX1(SMIN,XSFA)
      ME=NBA(JX)
      DIS(ME)=D
      PROD(ME)=XE
      NT(JX,ME)=M
      DO 3006 I=1,3
 3006 C(ME,I)=R(I)
    6 CONTINUE
C IF NO ATOMS ARE BONDED TO JX, WE CAN HAVE ONLY A REFERENCE HOLE IN THE
C BALL FOR JX. THIS HOLE WILL BE FOR THE SUPPORT ROD
      IF(NBA(JX)-1)8,400,400
C IF ONE OR MORE ATOMS ARE BONDED TO JX, WE MUST CALCULATE THETA AND CHI
```

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```
C THE DRILLING COORDINATES FOR THE BONDS.
  400 K1=NT(JX,1)
      WRITE(1)NO(K1),DIS(1)
      IF(NBA(JX)-1)8,8,1400
 1400 DO 974 L=1,3
      R(L)=C(2,L)
  974 U(L)=C(1,L)
      DISU=PROD(1)
      DO 27 L1=2,ME
      DO 82 K1=1,3
   82 GG(K1)=C(L1,K1)
C CALCULATE THE COORDINATE THETA FOR THE BOND POINTING IN
C THE DIRECTION OF VECTOR C(L1). THETA =0 IS FIXED BY THE FIRST BOND IN
C THE DIRECTION OF VECTOR C(1).
      DISGG=PROD(L1)
      THE=THETA(U,GG,DISU,DISGG)
C NOW WE DETERMINE CHI, THE SECOND DRILLING COORDINATE. THE CIRCLE CHI=0
C IS DEFINED BY THE DIRECTION OF THE SECOND BOND, THE VECTOR C(2).
      IF(L1-2)309,309,604
  309 CHI=0.
      GO TO 609
  604 CHI=DETCHI(U,R,GG,DISU)
  609 IG=NT(JX,L1)
   27 WRITE(1)NO(JX),NO(IG),THE,CHI,DIS(L1)
    8 CONTINUE
C NOW WE HAVE THE DRILLING COORDINATES THETA AND CHI STORED ON TAPE 1 IN
C THE FOLLOWING ORDER- 1ST.-THE IDENTIFYING NUMBER OF THE FORST ATOM TO
C WHICH JX IS BONDED AND THE BOND DISTANCE. 2ND THE IDENTIFIER NUMBERS
C OF JX AND OF EACH OF THE OTHER ATOMS TO WHICH JX IS BONDED FOLLOWED BY
C THETA, CHI FOR THIS BOND AND THE BOND DISTANCE.
C IF THERE WAS A BOND DISTANCE BELOW THE MINIMUM, PRINT IT OUT.
      IF(DMIN-1000.)2022,2023,2023
 2022 WRITE(6,2024)IMIN,MMIN,DMIN
 2024 FORMAT(///7H  BOND ,I2,3H - ,I2, 3H = ,F7.3,46H ANGSTROMS LIES BEL
     1OW THE MINIMUM BOND LENGTH.)
 2023 CONTINUE
C IF THE SPECIFIED SCALE IS NOT LARGE ENOUGH TO ALLOW ALL BALLS TO CLEAR
C PRINT ERROR MESSAGE AND CALL EXIT
      IF(SFIN-SMIN)253,254,254
  253 WRITE(6,255)SMIN
  255 FORMAT(///79H THE SCALE DOES NOT ALLOW ALL BALLS TO CLEAR. THE MIN
     1IMIM SATISFACTORY SCALE IS,F7.4,17H CM PER ANGSTROM.)
      GO TO 252
  254 CONTINUE
C CHECK TO SEE IF ANY OF THE ATOMS IN THE MODEL WILL BE ABOVE ONE ANOTH-
C ER, MAKING SUPPORT OF THE UPPER ATOM IMPOSSIBLE.
      DO 2260 J=1,NSY
      DO 2260 I=1,K
      DO 2260 JPRIME=J,NSY
      DO 260 IPRIME=I,NSY
      IF(J.EQ.JPRIME.AND.I.EQ.IPRIME)GO TO 260
      VECTOR=0.
      DO 262 L=1,3
      IF(L-NS)263,262,263
  263 VECTOR=VECTOR+(X(J,I,L)-X(JPRIME,IPRIME,L))**2
  262 CONTINUE
      VECTOR = SQRT(VECTOR)
      IF(SIGN*(X(J,I,NS)-X(JPRIME,IPRIME,NS)))264,260,265
  264 INDEX=LFF(I)
      JSAVE=J
```

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```
      ISAVE=I
      GO TO 266
  265 INDEX=LFF(IPRIME)
      JSAVE=JPRIME
      ISAVE=IPRIME
  266 RADIUS=RAD(INDEX)
      IF(VECTOR*SFIN-RADIUS-0.5)267,260,260
  267 IF(NBA(I).EQ.0.AND.NBA(IPRIME).EQ.0)GO TO 2270
      IF(NBA(I))272,271,272
  271 ISAVE=I
      JSAVE=J
      GO TO 268
  272 IF(NBA(IPRIME))268,273,268
  273 ISAVE=IPRIME
      JSAVE=JPRIME
      GO TO 268
 2270 WRITE(6,274)NO(I),J,NO(IPRIME),JPRIME
  274 FORMAT(//5H BALL,I3,12H OF MOLECULE,I3,9H AND BALL,I3,12H OF MOLEC
     1ULE,I3,44H ARE NOT BONDED AND LIE ONE ABOVE THE OTHER.)
      GO TO 260
  268 IF(ISUPRT(JSAVE,ISAVE))260,275,269
  275 ISUPRT(JSAVE,ISAVE)=-1
      GO TO 260
  269 ISUPRT(JSAVE,ISAVE)=-2
  260 CONTINUE
 2260 CONTINUE
C A SUPPORT MUST MAKE NO ANGLE LESS THAN 30 DEGREES WITH ANY BOND, OR
C THERE WILL BE INTERFERENCE. CHECK EACH SUPPORTABLE POSITION AGAINST
C THIS CRITERION
      DO 700 J=1,NSY
      DO 701 I=1,K
      IF(ISUPRT(J,I))701,1702,1702
 1702 LIMIT=NBA(I)
      DO 702 JPRIME=1,LIMIT
      INDEX=NT(I,JPRIME)
      DO 703 L=1,3
  703 U(L)=X(J,INDEX,L)-X(J,I,L)
      DISU=DOT(U,U)
      ANGLE=THETA(U,SUPORT,DISU,ONE)
      IF(ANGLE-30.)704,702,702
  702 CONTINUE
      GO TO 701
  704 IF(ISUPRT(J,I))701,706,707
  706 ISUPRT(J,I)=-1
      GO TO 701
  707 ISUPRT(J,I)=-2
  701 CONTINUE
  700 CONTINUE
C NOW, FOR EACH OF THE ATOMS FOR WHICH SUPPORT WAS INDICATED BUT NOT
C POSSIBLE (ISUPRT=-2) WE FIND AN ALTERNATE SUPPORT SITE.
      DO 2280 J=1,NSY
      DO 280 I=1,K
      IF(ISUPRT(J,I)+1)281,280,280
  281 LIMIT=K/2
      DO 282 L=1,LIMIT
      INDEX=I+L
      IF(ISUPRT(J,INDEX))283,284,283
  284 ISUPRT(J,INDEX)=1
      GO TO 280
  283 INDEX=I-L
```

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```
      IF(ISUPRT(J,INDEX))282,284,282
  282 CONTINUE
  280 CONTINUE
 2280 CONTINUE
C NOW WE PROCEED TO PRINT OUT THE DRILLING COORDINATES FOR EACH BALL
      REWIND 1
      AL(2)=(AL(2)+AL(1)*CO(3)+AL(3)*CO(1))*SFIN
      AL(1)=(AL(1)*SI(3)+AL(3)*CONST1)*SFIN
      AL(3)=SFIN*CONST2*AL(3)
C MULTIPLY COORDINATES IN ANGSTROMS BY SCALE FACTOR
      DO 3010 J=1,NSY
      DO 3010 I=1,K
      DO 3010 L=1,3
 3010 X(J,I,L)=X(J,I,L)*SFIN
      XCO=XCO*SFIN
      INDEX1=NS+1
      INDEX2=NS+2
      IF(INDEX1-3)290,291,292
  292 INDEX1=INDEX1-3
  291 INDEX2=INDEX2-3
  290 IF(SIGN)293,294,294
  294 ICARRY=INDEX1
      INDEX1=INDEX2
      INDEX2=ICARRY
  293 WRITE(6,994)AXIS(INDEX1),AL(INDEX1),AXIS(INDEX2),AL(INDEX2)
  994 FORMAT (32H1 THE BASE OF THE MODEL WILL BE ,A1,1H=,F8.3,15H CM. AC
     1ROSS BY ,A1,1H=,F8.3,9H CM. DOWN)
      IF(ICELTP-1)295,296,295
  296 BETA =P*ARCOS(CO(2))
      WRITE(6,297)BETA
  297 FORMAT(87H0 THE ORIGINAL A AXIS POINTS ALONG ORTHOGONAL X. THE ORI
     1GINAL C AXIS MAKES AN ANGLE OF ,F7.3,16H DEGREES WITH A.)
  295 WRITE(6,298)AXIS(NS),AL(NS)
  298 FORMAT(24H0 THE UNIT CELL WILL BE ,A1,1H=,F8.3,9H CM HIGH.)
      IF(SIGN)3005,3005,2006
 3005 HIT=ORG-(AL(NS)-XCO)
      GO TO 2007
 2006 HIT=ORG-XCO
 2007 WRITE(6,576)HIT
  576 FORMAT(/22H  ORIGIN OF MODEL LIES,F7.3,18H CM ABOVE THE BASE)
      WRITE(6,445)
  445 FORMAT(///16H  DRILL SETTINGS)
      DO 402 I=1,K
C COMPUTE LENGTH OF SUPPORT ROD FOR EACH ATOM EQUIVALENT TO I BY
C SYMMETRY.
      DO 528 LD=1,NSY
      IF(SIGN)2010,2010,2011
 2010 VIP(LD)=ORG+(XCO-X(LD,I,NS))
      GO TO 528
 2011 VIP(LD)=HIT+X(LD,I,NS)
  528 CONTINUE
      JA=LFF(I)
      WRITE(6,407)NO(I),IDEN(JA)
  407 FORMAT(6H1 BALL,I5,10X,7HUSE A ,A6,11H  INCH BALL//)
      J=NBA(I)
      IF(J)890,890,836
  836 DO 805 MY=1,J
      IG=NT(I,MY)
  805 NJ(MY)=NO(IG)
      WRITE(6,112)(NJ(MY),MY=1,J)
```

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```
  112 FORMAT(18H  BONDED TO BALLS ,20(I3,1H,))
      GO TO 2012
  890 WRITE(6,877)
  877 FORMAT(34H0 DRILL ONLY ONE HOLE IN THIS BALL)
      WRITE(6,889)(LD,(X(LD,I,LX),LX=1,3),VIP(LD),LD=1,NSY)
  889 FORMAT(9H0MOLECULE,I3,31H. ORTHOGONALIZED COORDINATES X=,F8.3,7H C
     1M, Y=,F8.3,7H CM, Z=,F8.3,28H CM. LENGTH OF SUPPORT ROD =,F8.3,3H
     2CM)
      GO TO 402
 2012 WRITE(6,712)
  712 FORMAT(1H0,37X,5HRIGHT,5X,4HLEFT)
      ME=NBA(I)+NSY
      DO 868 K1=1,ME
      IF(K1-1)866,866,865
  866 READ(1)JX,AN2
      AN2=SFIN*AN2-2.*REC
      IF(NO(I)-JX)213,213,214
  214 AN2=0.
  213 WRITE(6,855)NO(I),JX,AN2
  855 FORMAT(25H0 DRILL REFERENCE HOLE AT,6X,3H0.0,6X,3H0.0,6X,13H0.0  F
     1OR BOND,I4,2H -,I4,10X,12HROD LENGTH =,F9.2)
      GO TO 868
  865 ICD=K1-NBA(I)
      IF(ICD)847,847,848
  847 READ(1)JX,JA,THE,CHI,AN2
      AN2=SFIN*AN2-2.*REC
      IF(JX-JA)215,215,216
  216 AN2=0.
  215 CHILFT=360.-CHI
      IF(CHI)1215,1216,1215
 1216 CHILFT=CHI
 1215 CONTINUE
      WRITE(6,845)THE,CHI,CHILFT,JX,JA,AN2
  845 FORMAT(25H0 DRILL  ANOTHER  HOLE AT,3F9.1,10H  FOR BOND,I4,2H -,I4
     1,10X,12HROD LENGTH =,F9.2)
      GO TO 868
  848 WRITE(6,849)ICD,(X(ICD,I,LX),LX=1,3)
  849 FORMAT(//10H  MOLECULE,I3,31H. ORTHOGONALIZED COORDINATES X=,F8.3,
     17H CM, Y=,F8.3,7H CM, Z=,F8.3,4H CM.)
      IF(ISUPRT(ICD,I))868,868,850
C CALCULATE DRILLING COORDINATES OF SUPPORT HOLES ON THOSE ATOMS CHOSEN
C AS FINAL SUPPORT POSITIONS.
  850 INDEX1=NT(I,1)
      INDEX2=NT(I,2)
      DO 1850 L=1,3
      VECTR1(L)=X(ICD,INDEX1,L)-X(ICD,I,L)
 1850 VECTR2(L)=X(ICD,INDEX2,L)-X(ICD,I,L)
      DISTC1=DOT(VECTR1,VECTR1)
      THE=THETA(VECTR1,SUPORT,DISTC1,ONE)
      CHI=DETCHI(VECTR1,VECTR2,SUPORT,DISTC1)
      WRITE(6,804)THE,CHI,VIP(ICD)
  804 FORMAT (23H0 DRILL SUPPORT HOLE AT,2F9.1,5X,20HSUPPORT ROD LENGTH
     1=,F9.2,4H CM.)
  868 CONTINUE
  402 CONTINUE
  252 RETURN
      END
```

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```
$IBFTC DOTX     FULIST,DD,DECK
       FUNCTION DOT(V,W)
C TAKE DOT PRODUCT OF VECTOR V AND W
       DIMENSION V(3),W(3)
       COMMON P
       DP=0.
       DO 500 MX=1,3
  500  DP=V(MX)*W(MX)+DP
       DOT=DP
       RETURN
       END
```

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```
$IBFTC THETAX  FULIST,DD,DECK
      FUNCTION THETA(V,W,DISV,DISW)
C ROUTINE TO FIND THE ANGLE BETWEEN TWO VECTORS V AND W.
      DIMENSION V(3),W(3)
      COMMON P
      XE=DOT(V,W)
      CA=XE/SQRT(DISV*DISW)
      THETA=P*ARCOS(CA)
      RETURN
      END
$IBFTC DETCHX  FULIST,DD,DECK
      FUNCTION DETCHI(U,R,W,DISU)
C ROUTINE TO FIND THE ANGULAR COORDINATE CHI OF A VECTOR  W. THE ORIGIN
C DETERMINING VECTORS ARE U AND R.
      DIMENSION U(3),R(3),GG(3),R1(3),W(3)
      COMMON P
      QQ=DISU
      QB=DOT(R,U)
      DO 313 L=1,3
      GG(L)=W(L)
  313 R1(L)=R(L)-(QB/QQ)*U(L)
      QB=DOT(R1,R1)
      TOT=(R(2)*U(3)-U(2)*R(3))*GG(1)+(R(3)*U(1)-U(3)*R(1))*GG(2)+(R(1)*
     1U(2)-U(1)*R(2))*GG(3)
      IF(TOT)766,766,768
  766 SUP=2.
      GO TO 769
  768 SUP=0.
  769 AN2=DOT(GG,U)/QQ
      DO 614 LP=1,3
  614 GG(LP)=GG(LP)-AN2*U(LP)
      AN2=DOT(GG,GG)*QB
      AN3=DOT(GG,R1)
      CA=AN3/SQRT(AN2)
      DETCHI=SUP*180.+(1.-SUP)*ARCOS(CA)*P
      RETURN
      END
```

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Appendix III

Listing of Error Estimating Program

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```
CSIGMA
C A1620 PROGRAM TO CALCULATE STANDARD DEVIATIONS IN BOND DISTANCES AND
C BOND ANGLES FROM THE STANDARD DEVIATIONS IN FRACTIONAL COORDINATES
C OBTAINED FROM A LEAST SQUARES REFINEMENT. PROGRAMMED BY THOMAS F.
C KOETZLE, JUNE 22, 1967.
      COMMON NATOMS,DMAX
      DEFINE DISK (10,1660)
      CALL QXDATA
      CALL QXDIST
      CALL QXCALC
      CALL QXANGL
      CALL EXIT
      END
```

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```
      SUBROUTINE QXDATA
      DIMENSION N(49),X(49),Y(49),Z(49),SIGX(49),SIGY(49),SIGZ(49)
      COMMON NATOMS,DMAX
      LOC1=1
      FIND(LOC1)
      PRINT 1
    1 FORMAT(/35H   DISTANCES AND ANGLES CALCULATION)
C READ TITLE CARD AND PUNCH IT.
      READ 10
   10 FORMAT (72H
     1                    )
      PUNCH 10
C GET UNIT CELL PARAMETERS AND PRINT THEM
      READ 2,A,B,C,ALPHA,BETA,GAMMA
    2 FORMAT (6F10.4)
      PRINT 3,A,B,C,ALPHA,BETA,GAMMA
    3 FORMAT (4H  A=,F7.3,4H  B=,F7.3,4H  C=,F7.3,8H  ALPHA=,F8.4,7H  BE
     1TA=,F8.4,8H  GAMMA=,F8.4)
C CONVERT ALPHA, BETA, AND GAMMA TO RADIANS.
      ALPHA=ALPHA/57.296
      BETA=BETA/57.296
      GAMMA=GAMMA/57.296
C CALCULATE QUANTITIES NEEDED TO ORTHOGONALIZE COORDINATES.
      CALPHA=COSF(ALPHA)
      CBETA=COSF(BETA)
      CGAMMA=COSF(GAMMA)
      SGAMMA=SINF(GAMMA)
      QUANT1=(CBETA-CALPHA*CGAMMA)*C/SGAMMA
      QUANT2=SQRTF((1.-CALPHA**2-CBETA**2-CGAMMA**2+2.*CALPHA*CBETA*
     1CGAMMA)/SGAMMA**2)*C
      SGAMMA=SGAMMA*A
      CGAMMA=CGAMMA*A
      CALPHA=CALPHA*C
C READ CONTROL CARD
      READ 4,NATOMS,DMAX
    4 FORMAT(I3,F10.7)
      PRINT 100,NATOMS,DMAX
  100 FORMAT(/11H    NATOMS=,I3,8H   DMAX=,F6.3)
C READ IN COORDINATES AND DEVIATIONS
      DO 5 I=1,NATOMS
    5 READ 6,N(I),X(I),SIGX(I),Y(I),SIGY(I),Z(I),SIGZ(I)
    6 FORMAT(I3,6F10.7)
C CONVERT TO ORTHOGONALIZED COORDINATES
      DO 7 J=1,NATOMS
      Y(J)=Y(J)*B+X(J)*CGAMMA+Z(J)*CALPHA
      X(J)=X(J)*SGAMMA+Z(J)*QUANT1
      Z(J)=Z(J)*QUANT2
      SIGY(J)=SQRTF((SIGY(J)*B)**2+(SIGX(J)*CGAMMA)**2+(SIGZ(J)*CALPHA)
     1**2)
      SIGX(J)=SQRTF((SIGX(J)*SGAMMA)**2+(SIGZ(J)*QUANT1)**2)
    7 SIGZ(J)=SIGZ(J)*QUANT2
      PRINT 8
    8 FORMAT(/40H   READY TO PUNCH DISTANCE OUTPUT HEADER)
C PUNCH HEADING FOR DISTANCE OUTPUT
      PUNCH 9
    9 FORMAT(34H   BOND    DISTANCE,A  DEVIATION,A)
      RECORD(LOC1)(N(I),X(I),Y(I),Z(I),SIGX(I),SIGY(I),SIGZ(I),
     1I=1,NATOMS)
      RETURN
      END
```

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```
      SUBROUTINE QXDIST
      DIMENSION N(49),X(49),Y(49),Z(49),SIGX(49),SIGY(49),SIGZ(49),
     1DISTIJ(49)
      COMMON NATOMS,DMAX
C CALCULATE BOND DISTANCES
      LOC1=1
      LOC2=51
      FETCH(LOC1)(N(I),X(I),Y(I),Z(I),SIGX(I),SIGY(I),SIGZ(I),
     1I=1,NATOMS)
      DO 10 I=1,NATOMS
      FIND(LOC2)
      DO 11 J=1,NATOMS
C IF BOND IS BETWEEN AN ATOM AND ITSELF, SET BOND DISTANCE = 0.
      IF(I-J)13,12,13
   12 DISTIJ(J)=0.
      GO TO 11
C AS WE BUILD UP THE SQUARE OF THE BOND DISTANCE, TEST IT TO SEE IF IT
C IS GREATER THAN DMAX SQUARED. IF IT IS,SET IT =0.
   13 DMAX2=DMAX**2
      COMP1=(X(I)-X(J))**2
      IF(COMP1-DMAX2) 20,20,15
   20 COMP1=COMP1+(Y(I)-Y(J))**2
      IF(COMP1-DMAX2) 21,21,15
   21 COMP1=COMP1+(Z(I)-Z(J))**2
      IF(COMP1-DMAX2) 22,15,15
   15 DISTIJ(J)=0.
      GO TO 11
   22 DISTIJ(J)=SQRTF(COMP1)
   14 SIGDIJ=SQRTF(((X(I)-X(J))**2)*(SIGX(I)**2+SIGX(J)**2)+((Y(I)-
     1Y(J))**2)*(SIGY(I)**2+SIGY(J)**2)+((Z(I)-Z(J))**2)*(SIGZ(I)**2+
     2SIGZ(J)**2))/DISTIJ(J)
C IF I IS LESS THAN J, PUNCH THE BOND DISTANCE AND THE DEVIATION
      IF(I-J,16,11,11
   16 PUNCH 17,N(I),N(J),DISTIJ(J),SIGDIJ
   17 FORMAT(3X,I2,1H-,I2,5X,F7.4,5X,F7.4)
   11 CONTINUE
C STORE DISTANCES AND DEVIATIONS ON THE DISK
      RECORD(LOC2)(DISTIJ(J),J=1,NATOMS)
   10 CONTINUE
C PRINT MESSAGE TO OPERATOR
      PRINT 18
   18 FORMAT(/74H  CALCULATION OF DISTANCES NOW COMPLETE. READY TO PUNCH
     1 HEADER FOR ANGLES.)
C PUNCH HEADER FOR BOND ANGLES
      PUNCH 19
   19 FORMAT(38H  BOND ANGLE     DEGREES       DEVIATION)
      RETURN
      END
```

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```
      SUBROUTINE QXCALC
      DIMENSION N(49),X(49),Y(49),Z(49),SIGX(49),SIGY(49),SIGZ(49),
     1DISTIJ(49)
      COMMON NATOMS,DMAX
      LOC1=1
      LOC2=51
      LOC3=351
      FETCH(LOC1)(N(I),X(I),Y(I),Z(I),SIGX(I),SIGY(I),SIGZ(I),
     1I=1,NATOMS)
C RECALL DISTANCES FROM DISC
      DO 20 I=1,NATOMS
      FETCH(LOC2)(DISTIJ(J),J=1,NATOMS)
      FIND(LOC3)
C DECIDE WHICH ANGLES INVOLVING N(I) AS THE CENTRAL ATOM ARE BOND ANGLES
      LIMITP=NATOMS-1
      DO 21 K=1,LIMITP
      IF(DISTIJ(K)-0.)22,21,22
   22 LIMIT=K+1
      DO 23 L=LIMIT,NATOMS
      IF(DISTIJ(L)-0.)24,23,24
C WE NOW HAVE AN ANGLE. CALCULATE THE LENGTH OF THE THIRD SIDE OF THE
C TRIANGLE.
   24 C=SQRTF((X(K)-X(L))**2+(Y(K)-Y(L))**2+(Z(K)-Z(L))**2)
      A=DISTIJ(K)
      B=DISTIJ(L)
C CALCULATE THE BOND ANGLE IN DEGREES.
      CTHETA=(A**2+B**2-C**2)/(2.*A*B)
      STHETA=SQRTF(1.0-CTHETA**2)
      THETA=57.296*ATANF(STHETA/CTHETA)
      RECORD(LOC3)THETA,STHETA,N(I),X(I),Y(I),Z(I),SIGX(I),SIGY(I),
     1SIGZ(I),N(K),X(K),Y(K),Z(K),SIGX(K),SIGY(K),SIGZ(K),N(L),X(L),
     2Y(L),Z(L),SIGX(L),SIGY(L),SIGZ(L),A,B,C
   23 CONTINUE
   21 CONTINUE
   20 CONTINUE
      ZERO=0.
      RECORD(LOC3) ZERO
      RETURN
      END
```

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```
      SUBROUTINE QXANGL
      DIMENSION THETA(50),SIGTH(50),I(50),K(50),L(50)
      COMMON NATOMS,DMAX
C DEFINE ARITHMETIC FUNCTIONS
      FIRSTF(ARG1,ARG2,ARG3)=QA*(B*(ARG1-ARG2)/A+A*(ARG1-ARG3)/B)+QB
     1*(ARG2+ARG3-2.*ARG1)
      SECNDF(DUMMYA,DUMMYB,DUMMYC,DUMMYD,DUMMYE)=QA*DUMMYE*(DUMMYB-
     1DUMMYA)/DUMMYD+QB*(DUMMYA-DUMMYC)
      LOC3=351
  200 CONTINUE
      DO 1 J=1,50
      FETCH(LOC3) THETA(J),STHETA,I(J),XI,YI,ZI,SIGXI,SIGYI,SIGZI,K(J),
     1XK,YK,ZK,SIGXK,SIGYK,SIGZK,L(J),XL,YL,ZL,SIGXL,SIGYL,SIGZL,A,B,C
      FIND(LOC3)
C TEST FOR END OF FILE MARK, AND FOR NEGATIVE VALUES OF THETA. ADD 180
C DEGREES TO NEGATIVE VALUES OF THETA.
      IF(THETA(J)) 2,3,4
    2 THETA(J)=180.+THETA(J)
      GO TO 4
    3 NANGLS=J
      GO TO 5
    4 CONTINUE
C CALCULATE THE DEVIATION IN THE BOND ANGLE IN DEGREES.
      QA=(A**2+B**2-C**2)/(2.*(A*B)**2*STHETA)
      QB=1./(A*B*STHETA)
      DX1=FIRSTF(XI,XK,XL)
      DY1=FIRSTF(YI,YK,YL)
      DZ1=FIRSTF(ZI,ZK,ZL)
      DX2=SECNDF(XI,XK,XL,A,B)
      DY2=SECNDF(YI,YK,YL,A,B)
      DZ2=SECNDF(ZI,ZK,ZL,A,B)
      DX3=SECNDF(XI,XL,XK,B,A)
      DY3=SECNDF(YI,YL,YK,B,A)
      DZ3=SECNDF(ZI,ZL,ZK,B,A)
      SIGTH(J)=57.296*SQRTF((DX1*SIGXI)**2+(DX2*SIGXK)**2+(DX3*SIGXL)**2
     1+(DY1*SIGYI)**2+(DY2*SIGYK)**2+(DY3*SIGYL)**2+(DZ1*SIGZI)**2+
     2(DZ2*SIGZK)**2+(DZ3*SIGZL)**2)
    1 CONTINUE
C PUNCH THE BOND ANGLE AND DEVIATION
      PUNCH 25,(K(J),I(J),L(J),THETA(J),SIGTH(J),J=1,50)
   25 FORMAT(3X,I2,1H-,I2,1H-,I2,F10.3,5X,F10.3)
      GO TO 200
    5 PUNCH 25,(K(J),I(J),L(J),THETA(J),SIGTH(J),J=1,NANGLS)
      RETURN
      END
```

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