SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL STUDIES OF TRIPHENYLSILANOL-PIPERAZINE ADDUCT

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ABSTRACT

The solid-state structure of triphenylsilanol-piperazine adduct was reported from optimized reaction conditions. The molecular composition was further supported by elemental analysis, FT-IR, multinuclear NMR (¹H and ¹³C) and TGA. In solid-state, the four triphenylsilanols are associated in tetrameric form with one piperazine molecule through intra and intermolecular hydrogen bonds that lead to the new type of hydrogen bonding. The molecule represents one of the rare examples of triphenylsilanol-amine derivatives with a new hydrogen-bonding pattern.

Keywords: Organosilicon, Triphenylsilanol, Piperazine, Hydrogen bond, Co-crystal, Crystal Structure.

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INTRODUCTION

Stabilization of organosilanol in basic medium assumes importance, in presence of their use in the rational synthesis of metasilicates.¹⁻⁵ Recently the organic amine stabilized organosilanol have been used as potential catalysts in organic transformations.^{6,7} Among various structurally rich organo silanol-amine co-crystals,⁸⁻¹⁰ the sterically crowded triphenyl silanol has been extensively studied. However, the structural understanding of triphenyl silanol with dinitrogen donor ligand is one of the most challenging task.¹¹ For example, the reaction between triphenylsilanol and 4,4'-bipyridyl in methanol resulted in both 1:1 and 2:1 adducts.^{12,13} In both adducts, triphenyl silanol and 4,4'-bipyridyl are linked through intermolecular hydrogen bond.^{14,15} In 2:1 adduct the two silanol units are linked by an intramolecular hydrogen bond. Later the reactions between triphenylsilanol and different dinitrogen donor ligands such as 1,4-diazabicyclo[2.2.2]octane, 1,2-bis(4-pyridyl)ethene, N,N'-dimethylpiperazine, 1,2-bis(4'-bipyridyl)ethane and 4,4'-bipyridyl were investigated.^{16,17} Several attempts were made to obtain co-crystals^{18,19} of triphenylsilanol with piperazine.²⁰ However, the attempts to isolate the triphenylsilanol-piperazine adduct in dry methanol failed. We herein report the triphenylsilanol-piperazine adduct. The 4:1 adduct of triphenylsilanol and piperazine was isolated in quality yield from 1:1 mixture of 1,4-dioxane: methanol solvents.

EXPERIMENTAL

All manipulations were carried out under ambient conditions. The solvents were purchased from commercial sources and purified according to standard procedures.²¹ Unless otherwise stated, the

chemicals were purchased from commercial sources. FT-IR measurement was carried out on a Bruker Alpha-P Fourier transform spectrometer. Thermogravimetric analysis (TGA) was performed using a TA-SDT Q600, Tzero-press. Elemental analyses were performed by the Euro EA Elemental Analysis. The crystal structure of **1** was measured on an Oxford Xcalibur 2 diffractometer. Suitable single crystal for X-ray structural analysis of **1** was mounted at 298 K in inert oil under an argon atmosphere. The crystal was kept at 298 K during data collection. Using Olex2²² the structure was solved with the ShelXS²³ structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization. CCDC 1488282 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Synthesis of **1**

A solution of piperazine (500 mg, 5.80 mmol) in 1,4-dioxane/methanol (1:1, 2 ml) was added to a solution of Ph₃SiOH (140 mg, 0.51 mmol) in 1,4-dioxane/methanol (1:1, 2 mL) under stirring condition at room temperature. The clear reaction mixture was stirred for 20 minutes then stored at 25 °C to isolate the colorless crystals of **1**. Yield: 93% (based on Ph₃SiOH). M.p.: 96-98 °C (dec.). Elemental analysis calcd. (%) for C₇₆H₇₄N₂O₄S₄ (1191.75): C, 76.59; H, 6.26; N, 2.35; Found: C, 76.6; H, 6.2; N, 2.4. FT-IR (neat): $\bar{\nu}$ = 3376(w), 3212(w), 1425(m), 1259(w), 1112(s), 1032(w), 997(w), 886(w), 855(m), 828(s), 741(m), 697(vs) cm⁻¹. ¹H NMR (DMSO-d₆, 400 MHz): δ 7.50 (d) and 7.33-7.28 (m, 15H, ArH), 2.50 (s, 8H, CH) ppm; ¹H NMR (CDCl₃, 400 MHz): δ 7.64 (d) and 7.44-7.36 (m, 15H, ArH), 2.53 (s, 8H, CH), 2.17 (s, 2H, NH) ppm. ¹³C NMR (DMSO-d₆, 100.68 MHz): δ 136.1, 134.0, 129.1, 127.3 (ArC), 46.2 (CH₂) ppm; ¹³C NMR (CDCl₃, 100.68 MHz): δ 135.8, 135.7, 135.0, 129.9, 127.8, (ArC), 46.0, 45.9, 45.8 (CH₂) ppm.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

Until now the attempts to isolate triphenylsilanol and piperazine adduct under different reaction conditions were not successful. In this paper we report the 4:1 adduct of triphenylsilanols and piperazine co-crystal, 4Ph₃Si(OH):[HN(CH₂)₂]₂ (**1**) (Scheme-1). In contrast to the literature, we treated the triphenylsilanols with a large excess of piperazine. However, only 4:1 adduct of triphenylsilanols and piperazine was isolated. The Crystal structure of **1** was obviously or Experimentally determined by the single-crystal X-ray diffraction technique.

Scheme-1: Synthesis of **1**

The suitable single crystals of **1** for the X-ray analysis were obtained from the mixed solutions of 1,4-dioxane/methanol. **1** crystallized in the triclinic space group, *P* $\bar{1}$ with three triphenylsilanol and one piperazine molecule. The asymmetric unit of **1** consists of 0.5 piperazine and two triphenylsilanols. The molecular structure of **1** is depicted in Fig.-1. The crystallographic data for **1** is provided in Table-1 and

the significant Geometric parameters are listed in Table-2. Molecule **1** represents one of the rare examples of triphenylsilanol-amine derivatives with a new hydrogen-bonding pattern (Fig.-1(II)).

Molecule **1** consists of four triphenylsilanols and one piperazine molecules, in which two triphenylsilanol dimers are hydrogen-bonded through O-H $\cdots$ O hydrogen bond and two such dimers are hydrogen-bonded through N-H $\cdots$ O hydrogen bond. The O-H $\cdots$ O hydrogen bond (Si(2)-O(2) $\cdots$ H(1)-O(1), 2.373 Å) is much stronger than the N-H $\cdots$ O hydrogen bond (O(2) $\cdots$ H(1a)-N(1), 2.856 Å). The O(2) $\cdots$ H(1a)-N(1) bond angle (119.8°) is slightly wider than the Si(2)-O(2) $\cdots$ H(1) bond angle (109.9°). Thus, O(2) oxygen act as acceptor which results in two different types of hydrogen bonds, while O(1) oxygen and N(1) nitrogen act as a donor. As shown in molecular packing, the 4:1 triphenylsilanol and piperazine adduct is packed in a zig-zag manner thus providing nearly no space for additional piperazine to participate in the hydrogen bond. The existence of O $\cdots$ H-N and O $\cdots$ H-O hydrogen bonds in **1** are confirmed by the corresponding FT-IR (Fig.-2) stretching frequency observed at 3376 and 3212 cm⁻¹, respectively. As it is clearly shown in the ¹H and ¹³C NMR studies, the molecular association is sensitive to the solvents. The ¹H NMR (Fig.-3) chemical shift parameters of **1** in CDCl₃ is significantly different from that in DMSO-*d*₆. Similarly, the notable ¹³C NMR (Fig.-4) chemical shift changes were observed between CDCl₃ and DMSO-*d*₆. Thus, the dynamic nature of chemical shift values in different solvents indicate that kinetically stable nature of co-crystal **1**.

Fig.-1: Molecular Structure of **1**

Structural Comparison

Molecule **1** consists of four triphenylsilanol and one piperazine molecule, in which two triphenylsilanol dimers are hydrogen-bonded through O-H $\cdots$ O hydrogen bond and two such dimers are hydrogen-bonded through N-H $\cdots$ O hydrogen bond (Fig. 1(II)). The O-H $\cdots$ O hydrogen bond (O(2) $\cdots$ H(1)-O(1), 2.373 Å) is much stronger than the N-H $\cdots$ O hydrogen bond (O(2) $\cdots$ H(1a)-N(1), 2.856 Å). The O(2) $\cdots$ H(1a)-N(1) bond angle (119.8°) is slightly wider than the Si(2)-O(2) $\cdots$ H(1) bond angle (109.9°). Thus, O(2) oxygen act as acceptor which results in two different types of hydrogen bonds, while O(1) oxygen and N(1) nitrogen act as a donor. As shown in molecular packing, the 4:1 triphenylsilanol and piperazine adduct is packed in a zig-zag manner thus providing nearly no space for additional piperazine to participate in the hydrogen bonding (Fig.-5). The hydrogen-bonding pattern of **1** is not comparable with that of triphenylsilanol and 1,4-diazabicyclo[2.2.2]octane or 1,2-bis(4-pyridyl)ethene (Scheme-2). The striking difference between piperazine vs 1,4-diazabicyclo[2.2.2]octane and 1,2-bis(4-pyridyl)ethene is C-H $\cdots$ π interaction. The C-H $\cdots$ π interaction is absent in **1**. As a result, the packing pattern of **1** is new. Moreover, the D $\cdots$ A bond distance of O-H $\cdots$ O in **1** is considerably a strong interaction compared to triphenylsilanol and 1,4-diazabicyclo[2.2.2]octane (2.727, 2.729, 2.736 and 2.701 Å) or 1,2-bis(4-pyridyl)ethene (2.641 and 2.801 Å). Similarly, the O-H $\cdots$ N hydrogen bond interaction in **1** is much weaker than that of triphenylsilanol and 1,4-diazabicyclo[2.2.2]octane (2.642, 2.620 and 2.633 Å) or 1,2-bis(4-pyridyl)ethene (2.753 and 2.791 Å). The H-bond parameters: the H...A distances H(1a) $\cdots$ O(2) (2.374 Å) and O(2) $\cdots$ H(1) (2.857 Å) indicates that the bonds are weaker compared to that in triphenylsilanol-DABCO and triphenylsilanol-1,2-bis(4-pyridyl)ethene adducts; $\angle$ D-H $\cdots$ A (donor-H $\cdots$ acceptor) bond angle $\angle$ O(1)-H(1a) $\cdots$ O(2) is 109.78° and $\angle$ H(2)-O(2) $\cdots$ H(1) is 78.47° clearly shows that the structure is not a favorable structure. This could also be a reason that 2:1 adduct is not formed unlike the diamine, N,N'-dimethylpiperazine.

The reactions between triphenylsilanol and different dinitrogen donor ligands such as 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,2-bis(4-pyridyl)-ethene 1,2-bis(4-pyridyl)ethene, N,N'-dimethylpiperazine, 1,2-bis(4'-bipyridyl)ethane and 4,4'-bipyridyl were investigated (Bowes et al., 2003). In the cases of diamines DABCO and 1,2-bis(4-pyridyl)ethene, the reaction with triphenylsilanol uniformly yielded 1:4 adduct as the only crystalline product irrespective of the molar ratios (diamine:triphenylsilanol) 1:1, 1:2 or 1:4 in methanol. The reaction of triphenylsilanol with N,N'-dimethylpiperazine in methanol yielded 2:1 adduct, whereas that with 1,2-bis(4'-bipyridyl)ethane yielded hydrated 2:1 adduct. In this study we obtained 4:1 adduct of triphenylsilanol-piperazine using mixture of solvents 1,4-dioxane: methanol in the ratio 1:1. Thus, the structural comparison of triphenylsilanol-piperazine adduct with triphenylsilanol-DABCO and triphenylsilanol-1,2-bis(4-pyridyl)ethene adducts would be significant. The Si-O bond lengths (Table S1a) in all the three adducts are comparable. However, the torsion angles (Table S1b) differ considerably (Table-2). ~~Hydrogen bond parameters are given in Tables S1e.~~ Hence the molecular packing of each system (triphenylsilanol-DABCO, triphenylsilanol-1,2-bis(4-pyridyl)ethene and **1**) is unique.

Fig.-2: FT-IR Spectrum of **1** (neat)

Fig.-3: ^1H NMR Spectra of **1** at 25 °C Fig.-4: ^{13}C NMR Spectra of **1** at 25 °CTable-1: Structural Parameters of **1**

Empirical Formula	$\text{C}_{19}\text{H}_{18.5}\text{N}_{0.5}\text{OSi}$
Formula weight	595.89
T (K)	298
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	9.2524(5)
$b/\text{\AA}$	12.0651(5)
$c/\text{\AA}$	15.0585(9)
$\alpha/^\circ$	85.945(4)
$\beta/^\circ$	79.275(5)
$\gamma/^\circ$	86.635(4)
$V (\text{\AA}^3)$	1645.72(15)
Z	2
$\rho_{\text{calc}}/\text{mg mm}^{-3}$	1.2024
$\mu (\text{mm}^{-1})$	1.235
$F(000)$	634.7
Data collected	6221
Unique data	393
R_{int}	0.0284

GOF on F^2	1.072
R_1 ($I > 2\sigma(I)$)	0.0685
wR_2 ($I > 2\sigma(I)$)	0.1850
R_1 values (all data)	0.0865
wR_2 values (all data)	0.2076

Fig.-5: Molecular Packing of **1** View along (i) X-axis and (ii) Y-axisTable-2: Selected Bond Lengths and Angles of **1**.

Bond Lengths [Å]			
Si(1)-O(1)	1.638(2)	Si(2)-O(2)	1.637(2)
Si(1)-C(1)	1.863(3)	Si(2)-C(19)	1.870(3)
Si(1)-C(7)	1.868(3)	Si(2)-C(25)	1.864(3)
Si(1)-C(13)	1.870(3)	Si(2)-C(31)	1.866(3)
Bond Angles[°]			
C(7)-Si(1)-O(1)	109.59(13)	C(19)-Si(2)-O(2)	111.09(13)
C(1)-Si(1)-O(1)	110.63(12)	C(25)-Si(2)-O(2)	106.31(13)
C(13)-Si(1)-O(1)	110.63(12)	C(31)-Si(2)-O(2)	111.07(13)
C(1)-Si(1)-C(7)	109.61(13)	C(19)-Si(2)-C(25)	107.42(13)
C(13)-Si(1)-C(7)	110.24(13)	C(19)-Si(2)-C(31)	109.59(13)
C(13)-Si(1)-C(1)	109.03(14)	C(25)-Si(2)-C(31)	111.28(13)

Scheme-2: The comparison of hydrogen bonding modes in co-crystals of (i) triphenylsilanol:piperazine, (ii) triphenylsilanol:1,4-diazabicyclo[2.2.2]octane and (iii) triphenylsilanol:1,2-bis(4-pyridyl)ethene

TGA Analysis

To understand the thermal decomposition pathway of **1**, thermogravimetric analysis (TGA) ($10\text{ }^{\circ}\text{C min}^{-1}$, $30\text{--}1000\text{ }^{\circ}\text{C}$, under N_2 atmosphere) was carried out on **1** (Fig.-6).

Fig.-6: TGA Curve of **1** from $30\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$ with $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate under N_2 atmosphere.

Compound **1** depicted a gradual decrease in weight loss to $500\text{ }^{\circ}\text{C}$ with 94% weight loss. The gradual weight loss of the molecule can be attributed to the decomposition of organic moieties (decomposition of phenyl group of the silanol and amine group). The residual weight is around 6%.

CONCLUSION

The 4:1 adduct of triphenylsilanol and piperazine was isolated under new reaction conditions. The hydrogen bond patterns in **1** are completely different from that of triphenylsilanol and 1,4-diazabicyclo[2.2.2]octane or triphenylsilanol and 1,2-bis(4-pyridyl)ethane adducts. Adduct **1** is different in its molecular packing due to the absence of $\text{C-H}\cdots\pi$ interaction in the extended network. The adduct **1** is thermally stable and sensitive to solvents. Future studies on the application of **1** and related adducts toward organic transformations are undertaken in our laboratory.

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