



Synthesis, Characterization and Reactivity of Novel Bis(2,4-dinitrophenoxy)diethoxysilane

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ABSTRACT

The hypervalent complex of Silicon with composition $[(DNP)_2SiR_2]$ (3), ($R = C_2H_5O-$, DNP = anion of 2,4-dinitrophenol) has been synthesized by the reaction of diethoxydichlorosilane with 2,4-dinitrophenol in tetrahydrofuran. The reactivity of (3) was studied with dipicolinic acid and Schiff base of hydrazine and salicylaldehyde and the products obtained has composition $[(DNP)_2SiX]$, ($X = -OOC_5H_3NCOO-$ (6) and $-OC_7H_5NNC_7H_5O-$ (7)). The structures of the (3,6 and 7) were established by DFT studies and were correlated with 1H , ^{13}C NMR and elemental analysis.

Keywords: Dinitrophenoxysilane, diethoxydichlorosilane, dipicolinic acid, Schiff's base, hypervalent complexes

INTRODUCTION

Bis(2,4-dinitrophenoxy)diethoxysilane, in which the silicon atom incorporates in a six-membered ring containing two 2,4-dinitrophenoxy groups is a hypervalent compound reported here for the first time. A number of publications have appeared which put light on various structural aspects of the hypervalent organosilicon compounds including the distorted trigonal bipyramidal geometry at the silicon atom of the silatranes [1-7]. Phenoxide derivatives have been known for a long time to possess anti-inflammatory activity and have also been considered of interest from structural point of view [8]. Their complexes have been found to have biological activity and exhibited antimicrobial activity stronger than that of the free ligand [9-10]. It is known that the electronic effect of the nitro substituent at para-position influences the intermolecular coordination behaviour of the nitrophenols as ligands. Also the phenolic ligands containing a second donor atom incorporated at the ortho position are known to exhibit a unique intramolecular bonding behaviour [11] (Figure 1).

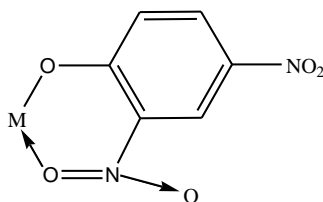


Figure 1: Bidentate mode of bonding of 2, 4-dinitrophenol

To the best of our knowledge none of the silicon complex with phenoxide derivative containing nitro group at the ortho and para position has been reported. This has prompted us to choose 2,4-dinitrophenol as an ancillary ligand for the synthesis of novel organosilicon hypervalent complexes with the aim to study its coordination chemistry and to gain an insight into the structure and behaviour of these complexes.

MATERIALS AND METHODS

All syntheses were carried out under dry nitrogen atmosphere using vacuum glassline. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen atmosphere. 2, 4-Dinitrophenol (Himedia), Silicon tetrachloride (Merck), Absolute ethanol (CYC China), Dipicolinic acid (SDFCL) were used as supplied. ^1H NMR and ^{13}C NMR spectra were recorded on a Jeol AC 300 FT-NMR spectrometer (in $\text{DMSO-d}_6/\text{CDCl}_3$). Chemical shifts were reported in ppm relative to internal $\text{DMSO-d}_6/\text{CDCl}_3$ and external tetramethylsilane (TMS).

Synthesis of bis(2,4-dinitrophenoxy)diethoxysilane (3) : To the stirred solution of potassium salt of 2,4-dinitrophenol (46.4g, 209.0 mmol) (potassium salt used here was prepared by dissolving equal moles of 2,4-dinitrophenol and potassium hydroxide in ethanol and potassium salt precipitated out) in tetrahydrofuran (30 mL), dichlorodiethoxysilane (19.7 mL, 104.2 mmol) was added drop wise and the mixture was stirred for overnight at room temperature. Thereafter KCl formed was removed from the reaction mixture by filtration. Solvent was removed from the filtrate under vacuum and this gave the solid product of bis(2,4-dinitrophenol) diethoxysilane. It was purified from tetrahydrofuran. m.p.=108-110°C (Yield 20 g ,39%). Anal. Calc. For $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_{12}\text{Si}$ (Molar mass 484): C, 39.6; H, 3.3; N, 11.5. Found: C, 39.3; H, 3.6; N, 11.9. ^1H NMR ($\text{DMSO-d}_6/\text{CDCl}_3$): δ 1.10 (t, 6H, CH_3), 2.51 (q, 4H, OCH_2), 7.23 (d, 2H, DNP-H), 8.33 (d, 2H, DNP-H), 8.67 (s, 2H, DNP-H). ^{13}C NMR ($\text{DMSO-d}_6/\text{CDCl}_3$): δ 24.18 (CH_3), 63.51 (OCH_2), 87.72-89.50 (DNP-C), 106.30 (C- NO_2), 125.49 (C-O).

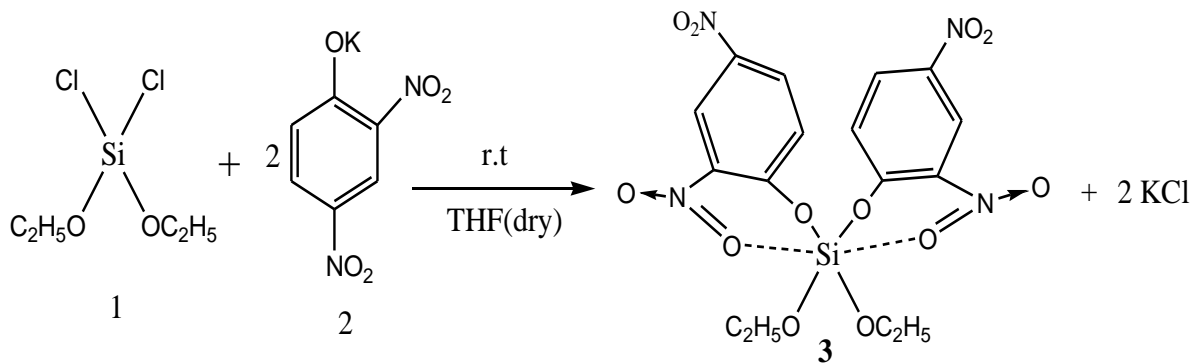
Synthesis of $[\text{Si}(\text{dipic})(\text{DNP})_2]$ (dipic = dipicolinate ion, DNP = 2,4 dinitrophenolate ion) (6) : The solution of (3) (0.7 g, 1.44 mmol) and dipicolinic acid (0.24 g, 1.44 mmol) in tetrahydrofuran (30 mL) was stirred and refluxed for 3h. Solvent was removed by vacuum evaporation. The addition of 2mL hexane to the resulting solution resulted in the separation of a solid which was again purified from tetrahydrofuran-hexane. m.p.=186- 188 °C(decomposition) (yield 0.6 g , 75%). Anal. Calc. For $\text{C}_{19}\text{H}_9\text{N}_5\text{O}_{14}\text{Si}$ (Molar mass 574): C, 40.8; H, 1.6; N, 12.5. Found: C, 40.8; H, 1.5; N, 12.6. ^1H NMR ($\text{DMSO-d}_6/\text{CDCl}_3$): 7.25 (d, 2H, DNP-H), 7.96 (d, 2H, DNP-H), 8.11 (t, 1H, Picolinic-H), 8.26 (d, 2H, Picolinic-H), 8.63 (s, 2H, DNP-H). ^{13}C NMR ($\text{DMSO-d}_6/\text{CDCl}_3$): δ 120.12-129.48 (DNP-C), 133.97-146.16 (Picolinic-C), 157.73 (C-O), 164.18 (C=O).

Synthesis of $[\text{Si}(\text{SB})(\text{DNP})_2]$ (SB = Schiff base of salicylaldehyde with hydrazine, DNP = 2,4 dinitrophenolate ion) (7) : To the stirred solution of (3) (1 g, 2.0 mmol) in tetrahydrofuran (70 mL), schiff's base (5) (0.5 g, 2.0 mmol) was added and the contents were refluxed for 3h. Solvent was removed by vacuum evaporation. The addition of 2 mL hexane to the resulting solution resulted in the separation of a solid which was again purified from tetrahydrofuran-hexane. m.p.186- 187°C (decomposition) (yield 1 g, 77%). Anal. Calc. For $\text{C}_{26}\text{H}_{16}\text{N}_6\text{O}_{12}\text{Si}$ (molar mass 632) : C, 49.4; H, 2.6; N, 13.3. Found: C, 49.3; H, 2.6;

N, 13.2. ^1H NMR (DMSO- d_6 /CDCl $_3$): 6.92 (t, 2H, Ar-H), 6.96 (t, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.35 (d, 2H, Ar-H), 8.29 (s, 2H, =C-H), 8.32 (d, 2H, DNP-H), , 8.70 (d, 2H, DNP-H), 8.89 (s, 2H, DNP-H). Due to the partial solubility of the compound in the solvent ^{13}C NMR could not be recorded.

RESULTS AND DISCUSSION

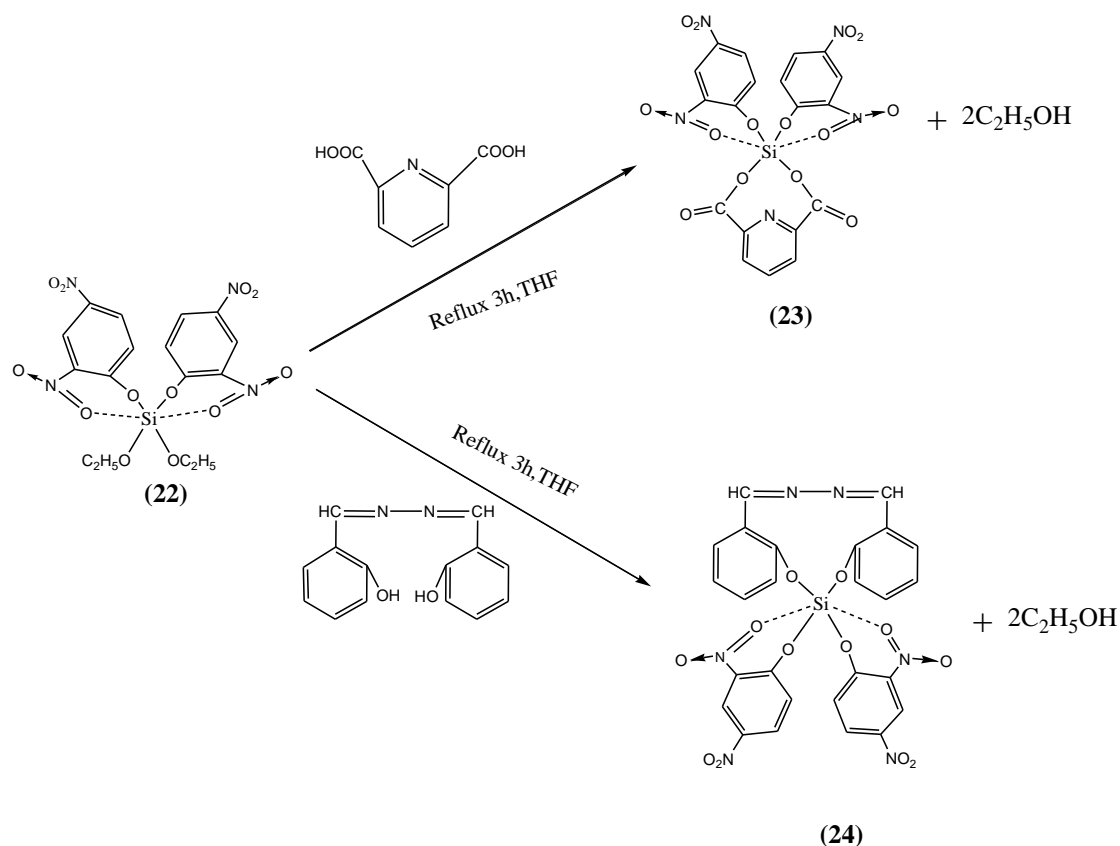
Bis(2,4-dinitrophenoxy)diethoxysilane (3) was synthesized from organosilane and 2,4 dinitrophenol as a light brown complex which was soluble in common organic solvents such as tetrahydrofuran, dimethylsulfoxide. It was characterised by ^1H NMR, ^{13}C NMR and elemental analysis. The general reaction scheme for the synthesis of (3) is given below in Scheme 1.



Scheme 1: Synthesis of silane (3)

The reactions of bis(2,4-dinitrophenoxy)diethoxysilane with dipicolinic acid and Schiff's base were carried out under nitrogen atmosphere in tetrahydrofuran to yield corresponding compounds(6 and 7) and the routes followed are summarized in Scheme 2. Compounds were characterised by ^1H NMR, ^{13}C NMR and elemental analysis.

Computational Study: The limited literature on computational studies of silatranes is due to the large size of these molecules which restricts largely these studies to semi empirical methods, but a few reports using Ab Initio methods have appeared in the last decade [12-15]. The optimized geometrical parameters of Bis(2,4-dinitrophenoxy)silanes and its derivatives with various levels of RHF methods are summarized in table 1. The Hartree-Fock calculations were performed at 3-21+G* basis sets for (3), (6), (7) and the results were compared with experimental data. The most important geometrical parameter i.e. N=O→Si bond distance was examined with RHF method at 3-21+G* and it was interesting to compare the results of (3) with that of related 2, 4-dinitrophenoxy silatrane (6), (7). It was found that the oxygen atom of nitro group coordinate to the Si atom in (3) and O→Si is 1.92Å, while the bond distance decreases to 1.84Å and 1.79 Å in (6) and (7) respectively. From the comparison shown in Table 1, it was apparent that in going from a Bis(2,4-dinitrophenoxy)diethoxysilanes to their derivatives both energy and O-Si distance decrease. This was attributed to the decrease in the size of ring.



Scheme 2 : Reactions of silane (3) with ligands (4) and (5)

Table 1 : HF studies of Bis(2,4-dinitrophenoxy)Silanes and their derivatives

	Compound (3)	Compound (6)	Compound (7)
Energy (a.u.)	-2019.31959719	-2320.69725980	-2493.52230343
N=O→Si (Å)	1.92	1.84	1.79

APPLICATIONS

Silatrane are valuable objects for medicinal chemistry [16,17] owing to the broad spectrum of biological activities they possess. They find applications as bactericides [18,19] and fungicides [20], as anticancer [21] and antitumour [22] agents and are also useful for immobilizations of DNA [23].

CONCLUSIONS

The bis(2,4-dinitrophenoxy)diethoxy silane has unique structural properties with respect to the bidentate bonding between Si and O of nitro group as observed from the computational studies. The stability of derivatives (6, 7) is more towards hydrolysis than silane (3) because of more electron density on Si atom in derivatives than the parent silane.

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