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Nature of the Si–N Bond in Silatranes

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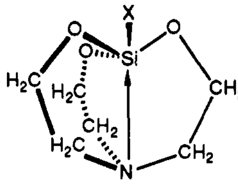
Both ab initio and semiempirical calculations are used to investigate the structure and bonding in substituted silatranes. In agreement with gas-phase experiments, which find Si–N distances that are 0.25–0.35 Å longer than those in the crystal phase, the Si–N distance (for example, in methylsilatrane) is predicted to be much larger than that observed in the crystal. Nonetheless, a bond critical point is found between Si and N, suggesting the existence of an Si–N bond in these compounds. It is found that the energy cost for constraining the Si–N distance in hydroxysilatrane to a value similar to that observed in the crystal is less than 6 kcal/mol. This suggests that crystal forces may be responsible for the much shorter Si–N distance in the solid.

I. Introduction

There has been an increasing number of papers, both experimental and theoretical, on anionic hypervalent silicon compounds,[1] with regard to their role as intermediates in S_N2 reactions[2] at silicon centers, in discussions of the fundamental nature of bonding in hypervalent compounds,[3] with regard to their role in silanol polymerization,[4] and in detailed discussions of pseudorotational motion.[5] Considerably less attention, especially on the theoretical side, has been paid to neutral hypervalent silicon compounds.

Voronkov et al.,[6] Corriu et al.,[7] and Kummer[8] have performed a great number of beautiful experiments, which demonstrate the existence of neutral penta-, hexa-, and even heptacoordinated silicon species. Among the most interesting of these compounds are the silatranes



in which the central silicon is bonded to a nitrogen, both through three oxo bridges as well as (apparently) via a dative bond to the nitrogen lone pair. Many of these compounds have been demonstrated to exhibit biological activity.[9] An important observation regarding the structural characteristics of these compounds is the relationship between the SiX and SiN distances: A longer SiX bond length (implying a weaker SiX bonding interaction) generally results in a shorter SiN distance (suggesting a stronger SiN bonding interaction). This is consistent with the notion that the axial bonding in pentacoordinated silicon compounds may be described in terms of four-electron three-center bonding.

In early theoretical papers on neutral pentacoordinated compounds, Cheyhaber and co-workers[10] and Marsden[11] used minimal basis and double-ζ ab initio calculations, respectively, to study the adduct formed between ammonia and SiF_4 and predicted stabilization energies of 10.0 and 8.6 kcal/mol, respectively. Both studies concluded that the most stable adduct is trigonal bipyramidal, with the NH_3 in the axial position. Using matrix isolation techniques, Ault[12] found direct evidence for an adduct of SiF_4 with ammonia. The infrared spectrum suggested a trigonal bipyramidal structure with the ammonia axial. An SCF/6-31G(d)[13,14] investigation of silicon-containing amines provides evidence for neutral species with pentacoordination at silicon.[15]

In a systematic probe of the stability of neutral pentacoordinated compounds containing a silicon–nitrogen bond, molecules with the general formula $Y_3SiX–NH_3$, with X and NH_3 in the axial positions, were recently investigated.[16] It was found in that paper that two factors help to stabilize the pentacoordinated system relative to separated $SiXY_3 + NH_3$. Since the NH_3 is fairly weakly bound and since the species in the axial positions share a three-center, four-electron bond, the ammonia is most

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[1] (a) Davis, L. P.; Burggraf, L. W., Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056. (b) Damrauer, R.; Davis, L. P.; Burggraf, L. W.; Gordon, M. S. **1988**, *110*, 6601. (c) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *Top. Phys. Organomet. Chem.* **1989**, *3*, 75.

[2] (a) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. **1984**, *106*, 7711. (b) Davis, L. P.; Burggraf, L. W.; Gordon, M. S.; Baldridge, K. K. *J. Am. Chem. Soc.* **1985**, *107*, 4415. (c) Gordon, M. S.; Davis, L. P.; Burggraf, L. W. Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889. (d) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686, 1692. (e) van der Wel, H.; Nibbering, N. M. M.; Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 5823.

[3] Deiters, J. A.; Holmes, R. R.; Holmes, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 7673.

[4] (a) Burggraf, L. W.; Davis, L. P. *Chemically Modified Surfaces*; Gordon and Breach Science: New York, 1986; pp 157–187. (b) Davis, L. P.; Burggraf, L. W. *Science of Chemical Ceramic Processing*; John Wiley and Sons: New York, 1986; pp 400–411. (c) Burggraf, L. W.; Davis, L. P. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 529. (d) Davis, L. P.; Burggraf, L. W. *Ultrastructure Processing of Advanced Ceramics*; John Wiley and Sons: New York, 1988; pp 367–368.

[5] Windus, T. L.; Gordon, M. S.; Davis, L. P.; Burggraf, L. W. *J. Am. Chem. Soc.* **1990**, *112*, 7167.

[6] Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

[7] (a) Corriu, R. J. P.; Royo, G.; de Saxce, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892. (b) Boyer, J.; Corriu, R. J. P.; Kopoton, A.; Mazhar, M.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *301*, 131.

[8] Kummer, D., private communication.

[9] Tandura, S. N.; Voronkov, M. G.; Alekseev, N. Y. *Curr. Top. Chem.* **1986**, *131*, 99.

[10] Cheyhaber, J. M.; Nagy, S. T.; Lin, C. S. *Can. J. Chem.* **1984**, *62*, 27.

[11] Marsden, C. J. *Inorg. Chem.* **1983**, *22*, 3177.

[12] Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.

[13] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *67*, 2257.

[14] Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. Standard polarization functions were used: H (p = 1.1), C (d = 0.8), N (d = 0.8), O (d = 0.8), Si (d = 0.395).

[15] Julian, M. M.; Gibbs, G. V. *J. Phys. Chem.* **1988**, *92*, 1444.

[16] Gordon, M. S.; Davis, L. P.; Burggraf, L. W. *Chem. Phys. Lett.* **1989**, *163*, 371.

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tightly bound when a weak ligand (e.g., Cl) is in the opposite axial position. (Note that this is consistent with the experimental observations of silatrane structures discused above). In addition, since increasing the positive charge on silicon increases the electrostatic attraction of this atom for the nitrogen lone pair, placing electronegative substituents (e.g., F) in the equatorial (Y) positions also enhances the Si–N bonding.

Of particular interest in the present paper is the nature of the Si–N bond in silatranes. It is pertinent in this regard to contrast the observed Si–N distances in the solid and gas phases. For typical X substituents (e.g., OH, CH_3), the X-ray Si–N distances are in the range 2.1–2.2 Å. In contrast, Shen and Hilderbrandt[17] found (using gas-phase electron diffraction) that the Si–N distance in methyl silatrane (X = CH_3) is 2.45 Å. These authors concluded from this observation that there may be no actual Si–N bond in the gas phase and that the silicon and nitrogen are held more tightly together in the solid due to crystal forces.

There have been a few semi-empirical studies of silatrane species,[18,19] but to our knowledge there have to date been no ab initio calculations on these species. In the present work, the structure and bonding in hydroxysilatrane (X = OH) and related compounds are investigated, using a combination of ab initio and semiempirical electronic structure methods. In order to analyze the Si–N bonding, the hydroxysilatrane molecule is "constructed" in a series of steps, starting with $Si(OH)_4$–NH_3. Then, each of three hydroxyl hydrogens is sequentially replaced by a CH_2CH_2 bridge to the nitrogen. These latter three compounds will be referred to as the singly, doubly, and triply bridged species, respectively. The triply bridged species is, of course, hydroxysilatrane.

II. Computational Methods

All structures have been fully optimized with the semiempirical AM1 method,[20] using the MOPAC[21] suite of programs. For all of the pentacoordinated silicon compounds, the nitrogen was placed in one of the axial positions, and no symmetry constraints were imposed during these optimizations. In addition, the structures of both $Si(OH)_4$–NH_3 and the singly bridged species were optimized with the 6-31G(d) basis set[14] at the self-consistent field (SCF) level of theory, using the analytical gradient code in the GAMESS (General Atomic and Molecular Electronic Structure System) suite of programs.[22] Again, no symmetry constraints were imposed during the geometry optimization. The $Si(OH)_4$–NH_3 structure was verified as a minimum by establishing that its hessian (matrix of analytically determined energy second derivatives) is positive definite. Because of the size of the singly bridged species, the 6-31G(d) hessian was not calculated for it. However, since no symmetry constraints were imposed, any imaginary frequencies that may exist for this compound will correspond to internal rotations, and these are not likely to alter the qualitative discussions of bonding. In addition, in order to analyze the bonding in each of the structures on an equal basis, single-point SCF/6-31G(d) calculations were performed at each of the AM1 geometries.

To analyze the Si–N bonding, the electron density analysis developed by Bader[23] has been utilized. According to this method, the existence of a bond is indicated by the presence of a bond critical point, $\mathbf{r}_b$; that is, a saddle point in the electron density distribution $\rho(\mathbf{r})$ between the two atoms. At such a point the hessian (second-derivative matrix) of the electron density has one positive eigenvalue along the bond axis and two negative eigenvalues orthogonal to the bond axis. The existence of a bond critical point implies the existence of a bond path (path of maximum electron density passing through $\mathbf{r}_b$), and the two atoms are said to be bonded.

Table I. AM1 (ab Initio) Structural Parameters for $HOSi(OCH_2CH_2)_n(OH)_{3-n}NH_{3-n}$ Compounds[a,b]

	n			
	0	1	2	3
R(Si–N)	2.277 (2.066)	2.325 (2.175)	2.459	2.527
R(Si–O_{ax})	1.750 (1.709)	1.747 (1.685)	1.739	1.736
R(Si–OC)		1.764 (1.671)	1.761	1.763
R(Si–OH)	1.752 (1.665)	1.749 (1.660)	1.745	
R(N–C)		1.447 (1.391)	1.448	1.449
R(N–H)	1.000 (1.003)	1.000 (1.001)	1.000	
α(N–Si–OC)		82.0 (81.6)	80.0	78.6
α(N–Si–OH)$_{eq}$	83.5 (82.6)	83.1 (81.9)	81.4	
α(N–Si–OH)$_{ax}$	176.1 (177.5)	177.5 (177.7)	173.1	174.8
α(Si–N–C)		103.5	100.8	100.0
α(Si–N–H)	107.9 (110.1)	107.2 (108.2)	110.7	

[a] Ab initio values are given in parentheses. [b] Bond lengths in angstroms, angles in degrees; where there are several parameters that are similar, but not necessarily related by symmetry (e.g., R(N–H)), the value given is the average value.

III. Results and Discussion

The key structural parameters for the compounds $HOSi(OCH_2CH_2)_n(OH)_{3-n}NH_{3-n}$ are listed in Table I for n = 0, 1, 2, 3. Both ab initio and AM1 structures have been determined for n = 0 and 1, and for these two compounds an interesting structural trend already emerges: The Si–N bond length increases (by 0.05 Å for AM1, by 0.11 Å for 6-31G(d)) when one of the OH groups is replaced by an OCH_2CH_2 bridge to the nitrogen. For the AM1 calculations, this trend continues as n is increased to 3, so that for the full hydroxysilatrane, R(Si–N) = 2.527 Å. To provide a more direct comparison with experiment, the AM1 geometry was also obtained for methylsilatrane (i.e., with X = CH_3). In this case, an even longer Si–N distance of 2.609 Å is predicted. This latter value may be compared with the experimental Si–N distance of 2.45 Å obtained by Shen and Hilderbrandt.[17] We have previously noted[16] the difficulty of predicting Si–N distances for this weak type of interaction in unconstrained complexes. The constrained structure in the present case reduces the overestimation to 0.15 Å. Despite the overestimation of the Si–N distance by AM1, the computational results are in agreement with the experimental[17] evidence that the Si–N distance in the gas phase is much longer than that in the crystal.

The ab initio and semiempirical calculations also both predict a steady decrease in the axial Si–O bond length as n increases. This reflects the balance in the axial three-center, four-electron bonding as the Si–N interaction apparently weakens.

As a probe of the amount of energy required to constrain the Si–N distance to a value similar to that observed in the crystal, a series of AM1 geometry optimizations was performed in which the Si–N distance was held fixed at several intermediate values between 2.15 and 2.53 Å. As the Si–N distance is decreased from the AM1 fully optimized value, both the AM1 and 6-31G(d) energies steadily increase. At a distance of 2.15 Å, the AM1 (ab initio)

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(17) Shen, Q.; Hilderbrandt, R. L. *J. Mol. Struct.* **1980**, *64*, 257.

(18) Sidorkin, V. F.; Pestunovich, V. A.; Voronkov, M. G. *Dokl. Akad. Nauk. SSSR* 1977, *235*, 1363.

(19) Hencsei, P.; Csonka, G. *Acta Chim. Acad. Sci. Hung.* 1981, *106*, 285.

(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(21) Stewart, J. J. P. Quantum Chemistry Program Exchange; Program 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(22) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(23) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

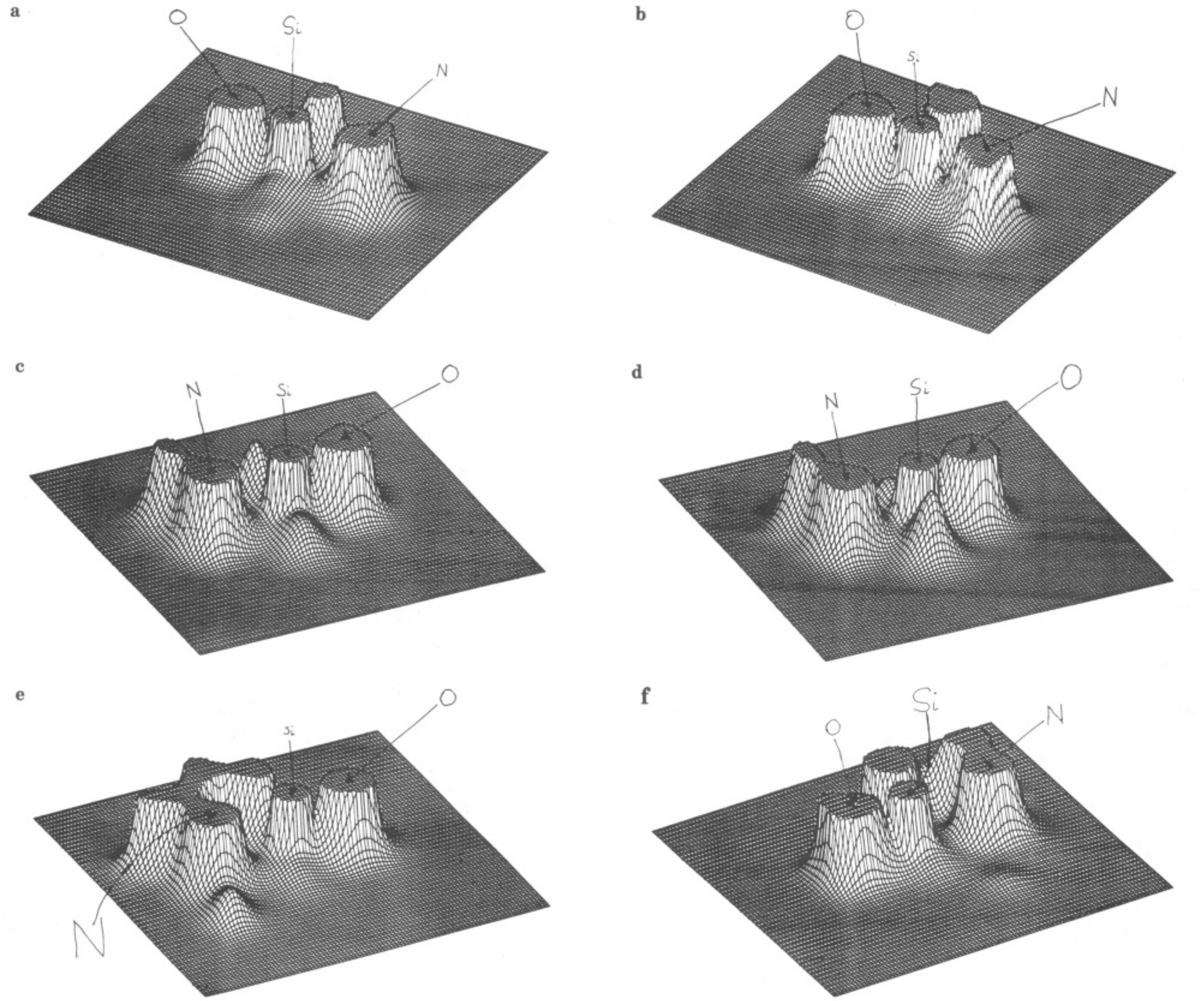

Figure 1. Relief maps of the electron density of silatranes in planes containing Si, N, and O_{ax} atoms. In all figures, the electron density cutoff is set to 0.16 au. All figures are drawn to the same scale and the center of the maps is at the silicon nuclei. (a) $n = 0$ with electron density generated from 6-31G(d)//AM1; (b) $n = 0$ with electron density generated from 6-31G(d)//6-31G(d); (c) $n = 1$ with electron density generated from 6-31G(d)//AM1; (d) $n = 1$ with electron density generated from 6-31G(d)//6-31G(d); (e) $n = 2$ with electron density generated from 6-31G(d)//AM1; (f) $n = 3$ with electron density generated from 6-31G(d)//AM1.

energy has increased by 5.3 (5.9) kcal/mol. This relatively small value predicted by both ab initio and semiempirical methods suggests that crystal packing forces may be sufficient to cause the Si–N distance to shorten considerably as compared with that in the gas-phase structure.

In order to more carefully analyze the nature of the Si–N interaction, the electron density analysis introduced by Bader has been utilized. Despite the fact that the Si–N bond length increases steadily as the number of CH_2CH_2 bridges increases from zero to three, a bond critical point is found for all four compounds, as illustrated in Table II and Figure 1 for 6-31G(d) single-point calculations of the AM1 structures. In fact, it is somewhat surprising that the electron density ρ at the bond critical point undergoes only a slight decrease with increasing n. Indeed, the value of $\rho(\mathbf{r}_b)$ for the $n = 3$ structure is still 79% of the corresponding value for the $n = 0$ structure!

The polarity of the Si–N bonds is illustrated by the values of d_{Si}, the ratio of the distance of the bond critical point from the Si atomic center, to R(Si–N) (Table II). Since the bond critical point is in each case much closer to the Si atom, the bonds are clearly highly polarized toward the nitrogen. With increasing n, the bond critical point moves progressively away from the Si atomic center, implying that Si becomes less electropositive relative to N as the number of bridges increases.

Table II. Analysis of SiN Bond Critical Points ($\boldsymbol{r}_b$) in Silatranes[a]

n[b]	R(Si–N), Å	$\rho(\mathbf{r}_b)$, au	$\nabla^2\rho(\mathbf{r}_b)$, au	d_{Si},[c] %
0	2.277 (2.066)	0.0380 (0.0550)	0.0978 (0.2403)	37.8 (37.9)
1	2.325 (2.175)	0.0375 (0.0465)	0.0557 (0.1474)	39.0 (38.0)
2	2.459	0.0315	0.0361	40.7
3	2.527	0.0301	0.0351	41.7

[a] For $n = 0$, 1 the values enclosed in parentheses arise from 6-31G(d)//6-31G(d) calculations. All other values are 6-31G(d)//AM1. [b] n = number of CH_2CH_2 bridges. [c] d_{Si} = (distance of $\mathbf{r}_b$ from Si atomic center)/R(Si–N).

Also shown in Table II is the Laplacian of the electron density at the bond critical point, $\nabla^2\rho(\mathbf{r}_b)$. A positive value of the Laplacian indicates that the interaction between the centers is a closed shell, or ionic, interaction. In the case of the silatranes, the size of this interaction decreases dramatically when the first CH_2CH_2 bridge is added and then remains essentially constant as the next two bridges are added. This is also a reflection of the closed-shell

Table III. Analysis of SiO_{ax} Bond Critical Points (r_b) in Silatranes[a]

n[b]	$R(Si–O_{ax})$, Å	$\rho(\mathbf{r}_b)$, au	$\nabla^2\rho(\mathbf{r}_b)$, au	d_{Si},[c] %
0	1.750 (1.709)	0.1021 (0.1096)	0.6737 (0.8216)	39.9 (40.2)
1	1.747 (1.685)	0.1034 (0.1177)	0.6774 (0.9063)	39.9 (40.2)
2	1.739	0.1063	0.6944	39.9
3	1.736	0.1090	0.6989	39.9

[a] For n = 0, 1 the values enclosed in parentheses arise from 6-31G(d)//6-31G(d) calculations. All other values are 6-31G(d)//AM1. [b] n = number of CH_2CH_2 bridges. [c] d_{Si} = (distance of $\mathbf{r}_b$ from Si atomic center)/$R(Si–O_{ax})$.

nature of the interaction, since such interactions are long range and fall off rather slowly.

Although the preceeding analysis is based for consistency on structures obtained with the AM1 method, similar results are obtained with the 6-31G(d) structures for n = 0, 1. As n increases in the 6-31G(d) structures, $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ decrease and d_{Si} increases (Table II). The $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ values are larger for these structures compared to the AM1 values because the SiN bond lengths are shorter in the 6-31G(d) structures. (Compare part b with a and d with c in Figure 1). Because of this shortening, it is expected that the 6-31G(d) n = 2, 3 structures will have shorter Si–N bond lengths and larger $\rho(\mathbf{r}_b)$ values than the corresponding AM1 structures.

An examination of the bonding in the $Si–O_{ax}$ bond in the silatranes allows the findings of Voronkov and coworkers[6,18] (as the Si–X bond weakens, the Si–N bond strengthens) to be tested. It has been shown that for a given bond, the value of $\rho(\mathbf{r}_b)$ increases with increasing bond order and bond strength.[24] For the AM1 structures, as n increases, $R(Si–O_{ax})$ decreases and $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ increase (Table III). The values of the ratio [$\rho(\mathbf{r}_b)$ for $Si–O_{ax}$]/[$\rho(\mathbf{r}_b)$ for Si–N] are 2.69, 2.76, 3.38, and 3.62 for n = 0, 1, 2, 3, respectively. Consequently, as n increases, more charge is accumulated in the $Si–O_{ax}$ bonding region and less in the Si–N bonding region. Thus, as n decreases from 3 to 0, the $Si–O_{ax}$ bond weakens and the Si–N bond strengthens, in agreement with the findings of Voronkov and co-workers.[6,18] An analysis of the $Si–O_{ax}$ and Si–N bonds in the 6-31G(d) structures (n = 0, 1) yields the same general conclusions as those found for the AM1 structures.

It is noteworthy that even though $\rho(\mathbf{r}_b)$ in the $Si–O_{ax}$ bond increases as n increases, the corresponding d_{Si} values remain constant (Table III). The electropositivity of Si relative to O_{ax} therefore appears to be insensitive to the number of CH_2CH_2 bridges in the system.

IV. Conclusions

The main findings of this study are the following:

(i) Even though the gas-phase silatrane Si–N internuclear distance is at least 0.25 Å longer than the corresponding distance in the solid, an Si–N bond critical point still exists in the gas phase. Thus, Si and N are directly bonded in the gas phase even for the n = 3 structure.

(ii) Only a small amount of energy is required to decrease the Si–N distance in hydroxysilatrane from the gas-phase value down to a value that is typical of silatrane crystal structures. Thus, it is easy to see how crystal forces are able to contract the Si–N distance.

(iii) As the number of bridges increases, the Si–N bond length increases and the $Si–O_{ax}$ bond length decreases. Concomitantly, $\rho(\mathbf{r}_b)$ in the Si–N bond decreases and $\rho(\mathbf{r}_b)$ in the $Si–O_{ax}$ bond increases. Therefore, the Si–N bond weakens and the $Si–O_{ax}$ bond strengthens.

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(24) (a) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. (b) Kraka, E. Ph.D. Thesis, University of Koln, 1984. (c) Carroll, M. T. Ph.D. Thesis, McMaster University, 1989.

Deuterium Substitution of Thiophenes by D_2: Catalytic Role of a Hydrosulfido-Bridged Molybdenum Complex

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The cationic complex $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1; Cp′ = MeCp = $C_5H_4CH_3$) catalyzed the deuterium substitution of thiophene, methylthiophenes, and benzothiophene in dichloromethane solution at D_2 pressures of 3–4 atm and temperatures of 25–70 °C. Substitution patterns were similar to those observed for deuteration reactions carried out over sulfided molybdenum surfaces. Possible roles for 1 in the homogeneous catalytic reaction have been investigated. Evidence has been observed for the activation of D_2 by 1; when 1 was stirred under a mixture of H_2/D_2, HD was produced. However, no evidence for the interaction of 1 with thiophenes has been observed. A mechanism has been proposed for the thiophene deuteration, which involves the conversion of D_2 to D^+ by 1, followed by the electrophilic aromatic substitution of D^+ on thiophenes. Substitution patterns and kinetic information are consistent with an acid-exchange pathway. Implications of this mechanism for the surface-catalyzed reactions are discussed.

Introduction

An important characteristic of the tetrasulfur-bridged cyclopentadienylmolybdenum complexes is their ability to activate molecular hydrogen.[1-9] In some cases these reactions with hydrogen have resulted in the isolation of complexes with S–H ligands.[1-5] This reactivity appears

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(1) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

(2) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(3) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.