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π Bonding in Trisilylamine and Related Compounds

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The very weak Lewis basicity[1] and the planarity of the skeletal atoms[2] of trisilylamine, as contrasted with the strong Lewis basicity and pyramidal structure of trimethylamine, are usually attributed to $N(p\pi) \rightarrow Si(d\pi)$ bonding.[1-4] However, these anomalous properties of trisilylamine have also been ascribed to nonbonded interactions of the SiH_3 groups[5] and to electrostatic repulsions of the positively charged silicon atoms.[6]

In principle, the nitrogen $2p\pi$ orbital of trisilylamine can be both *stabilized* by interaction with empty higher lying orbitals of the SiH_3 groups and *destabilized* by repulsive interaction with the bonding electrons of the SiH_3 groups. In this research, we have used a method[7] involving both core and valence ionization potentials to determine whether the combination of these interactions results in a net stabilization or destabilization of the nitrogen $2p\pi$ orbital in trisilylamine. We have also used this method to study analogous interactions in other molecules for which $p\pi \rightarrow Si(d\pi)$ bonding has been proposed, viz. tris(trimethylsilyl)amine, bis(trimethylsilyl)amine, disilyl ether, disilyl sulfide, and disilyl selenide.

The required core and lone-pair ionization potentials are given in Table I. The core ionization potentials for trisilylamine and tris(trimethylsilyl)amine are new, and the experimental details are given in the Experimental Section.

Table I. Core and Lone-Pair Ionization Potentials (eV) for Silyl Compounds and Related Compounds and the Derived Lone-Pair Stabilization Energies

	E_B(N 1s, O 1s, S $2p_{3/2}$, Se 3d)	IP(N $2p\pi$, O $2p\pi$, S $3p\pi$, Se $4p\pi$)	LOIP(N 2p, O 2p, S 3p, Se 4p)	lone-pair stabilizn energy, IP − LOIP
planar NH_3 [a]	405.3	9.8	9.8	0.0
$N(SiH_3)_3$	403.91[b]	9.7[c]	8.7	1.0
$N[Si(CH_3)_3]_3$	402.72[b]	8.60[d]	7.7	0.9
$NH[Si(CH_3)_3]_2$	403.32[e]	8.66[d]	8.2	0.5
H_2O	539.90[e]	12.62[f]	12.62	0.00
$(CH_3)_2O$	538.6[e]	10.04[g]	11.58	−1.54
$(SiH_3)_2O$	538.60[e]	11.17[g]	11.58	−0.41
H_2S	170.20[h]	10.47[f]	10.47	0.00
$(CH_3)_2S$	169.05[e]	8.71[g]	9.55	−0.84
$(SiH_3)_2S$	168.60[i]	9.70[g]	9.19	0.51
H_2Se	62.62[i]	9.90[f]	9.90	0.00
$(CH_3)_2Se$	61.52[i]	8.40[g]	9.02	−0.62
$(SiH_3)_2Se$	61.91[i]	9.18[g]	9.33	−0.15

[a] Reference 10. [b] This work. [c] Cradock, S.; Ebsworth, E. A. V.; Savage, W. J.; Whiteford, R. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 934. [d] Starzewski, K. A. O.; tom Dieck, H.; Bock, H. *J. Organomet. Chem.* 1974, *65*, 311. [e] Reference 12. [f] Rosenstock, H. M.; Sims, D.; Schroyer, S. S.; Webb, W. J. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1980**, *NSRDS-NBS 66*, part 1. [g] Reference 13. [h] Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werme, L. O.; Manne, R.; Baer, Y. "ESCA Applied to Free Molecules"; North-Holland Publishing Co.: Amsterdam, 1969. [i] Drake, J. E.; Riddle, C.; Henderson, H. E.; Glavincevski, B. *Can. J. Chem.* 1977, *55*, 2957.

We assume that the nitrogen $p\pi$ lone pair of planar ammonia is strictly nonbonding. Using a procedure described and justified in previous work,[7-10] we subtract from the lone-pair ionization potential of planar ammonia eight-tenths of the difference in the N 1s binding energies of planar ammonia and trisilylamine to obtain the "localized orbital ionization potential" (LOIP) for the N 2p orbital of trisilylamine. This LOIP value is the ionization potential that the N 2p orbital of trisilylamine *would have* it it were strictly nonbonding. Of particular interest is the difference between the actual N $2p\pi$ ionization potential and the LOIP value, given in the last column of Table I. In the case of trisilylamine we see that the nitrogen lone pair is stabilized, relative to the hypothetical nonbonding state, by 1.0 eV. Similar calculations for tris(trimethylsilyl)amine and bis(trimethylsilyl)amine show that the nitrogen lone pairs in these molecules are stabilized by 0.9 and 0.5 eV, respectively.

We also assume that the $p\pi$ lone pairs of the chalcogen atoms in H_2O, H_2S, and H_2Se are strictly nonbonding. By procedures analogous to those used for the nitrogen compounds, we have calculated the lone-pair stabilization energies for $(SiH_3)_2O$, $(SiH_3)_2S$, and $(SiH_3)_2Se$ given in Table I. Only in the case of $(SiH_3)_2S$ was a net positive lone-pair stabilization energy found. However, each of the dimethyl chalcogenides shows a very marked destabilization, which we ascribe to repulsive interaction of the lone pairs with the bonding electrons of the CH_3 groups. The lone pairs of $(SiH_3)_2O$ and $(SiH_3)_2Se$ show weaker net destabilizations.

Only the CH_3 and SiH_3 bonding orbitals of $(CH_3)_2O$ and $(SiH_3)_2O$ with the same symmetry as the oxygen lone pairs (b_1) can interact with the oxygen lone pairs. We can calculate the stabilization of the b_1 CH_3 and SiH_3 orbitals using the same general method used to calculate the destabilization of the lone-pair orbitals. We use the t_2 ionization potentials of CH_4 and SiH_4 as reference ionization potentials, corresponding to no interaction of the MH_3 groups.[11] We use the C 1s ionization potentials of CH_4 and $(CH_3)_2O$ and the Si 2p ionization potentials of SiH_4 and $(SiH_3)_2O$ to calculate LOIP values of 15.4 eV for the b_1 CH_3 orbital of $(CH_3)_2O$ and 13.2 eV for the b_1 SiH_3 orbital of $(SiH_3)_2O$.[12] The b_1 CH_3 orbital of $(CH_3)_2O$ has not been unequivocally assigned in the UPS spectrum.[13,14] However, it seems likely that the peak corresponding to this orbital lies in a band at 16.2 eV (or at even higher ionization potential), corresponding to a net stabilization of at least 0.8 eV. Likewise, there is no consensus regarding the b_1 SiH_3 orbital of $(SiH_3)_2O$.[13,14] However, we believe the peak corresponding to this orbital lies in a band at 14.5 eV (or possibly higher), corresponding to a net stabilization of at least 1.3 eV. The UPS spectra of the sulfur and selenium compounds are not well enough resolved in the region of the MH_3 bond orbital bands to allow analogous interpretations.[13] However, at least for $(CH_3)_2O$ and $(SiH_3)_2O$, the data are consistent with significant stabilization of the b_1 MH_3 bonding orbitals by interaction with the oxygen lone pairs. Of course,

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(1) Burg, A. B.; Kuljian, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 3103.
(2) Hedberg, K. *J. Am. Chem. Soc.* **1955**, *77*, 6491.
(3) Sujishi, S.; Witz, S. *J. Am. Chem. Soc.* **1954**, *76*, 4631.
(4) For a review of the use of d orbitals in main-group elements, see: Brill, T. B. *J. Chem. Educ.* **1973**, *50*, 392.
(5) Glidewell, C. *Inorg. Chim. Acta* **1975**, *12*, 219.
(6) Noodleman, L.; Paddock, N. L. *Inorg. Chem.* **1979**, *18*, 354.
(7) Jolly, W. L. *Acc. Chem. Res.* **1983**, *16*, 370.
(8) Jolly, W. L. *J. Phys. Chem.* **1981**, *85*, 3792.
(9) Jolly, W. L.; Eyermann, C. J. *J. Phys. Chem.* **1982**, *86*, 4834.
(10) Eyermann, C. J.; Jolly, W. L. *J. Phys. Chem.* **1983**, *87*, 3080.
(11) Potts, A. W.; Price, W. C. *Proc. R. Soc. London, Ser. A* **1972**, *326*, 165.
(12) Jolly, W. L.; Bomben, K. D.; Eyermann, C. J. *At. Data Nucl. Data Tables*, in press.
(13) Cradock, S.; Whiteford, R. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 281.
(14) Bock, H.; Mollere, P.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1973**, *61*, 113.

0020-1669/84/1323-4774$01.50/0

a destabilization of the lone pairs is associated with the stabilization of the b_1 MH_3 bonding orbitals. We believe the small *net* destabilizations of the lone pairs of $(SiH_3)_2O$ and $(SiH_3)_2Se$ are caused by the stabilizing interactions being less than the destabilizing interactions.

A question remains: What orbital interactions are responsible for the lone-pair stabilizations observed for $N(SiH_3)_3$, $N[Si(CH_3)_3]_3$, $NH[Si(CH_3)_3]_2$, and $(SiH_3)_2S$ (and believed likely for $(SiH_3)_3O$ and $(SiH_3)_2Se$)? The traditional opinion, toward which we are inclined, is that the empty $d\pi$ orbitals of the silicon atoms interact with the $p\pi$ lone-pair orbital, causing the stabilization of the latter orbital and an effective drift of the electron density to the silicon atoms. However, it has been suggested that the lone-pair stabilization in compounds of the type $R_2N–SiX_3$ and $RO–SiX_3$ is due to interaction of the lone pair with the σ^* orbitals of the Si–X bonds.[15,16] Even though the unperturbed lone pair is assumed to be closer in energy to the σ level than to the σ^* level of the Si–X bonds, it is argued that, because of the $Si^+–X^-$ polarization of the Si–X bonds, the p-orbital coefficient of silicon is greater in the σ^* orbital than in the σ orbital. The resultant greater overlap with the σ^* orbital is believed to overcome the greater energy difference and to account for the stabilization of the lone pair. It is difficult if not impossible to refute this argument with experimental data. However, we believe that the small Pauling electronegativity difference between silicon and carbon ($\Delta\chi = 0.7$), and especially between silicon and hydrogen ($\Delta\chi = 0.3$), would not cause the silicon coefficient to be much greater in σ^* than in σ. Our conclusion is that the lone pairs in the silyl compounds of this study are stabilized by interaction with the silicon d orbitals and destabilized by interaction with the σ Si–H or σ Si–C orbitals, although a significant stabilization by interaction with the σ^* Si–H or σ^* Si–C orbitals cannot be ruled out.

Experimental Section

Trisilylamine was prepared by the reaction of SiH_3Br and NH_3.[17] The vapor pressure (109 mm at 0 °C) and infrared spectrum of the product agreed with the literature.[17,18] Tris(trimethylsilyl)amine was obtained commercially (Petrarch) and was sublimed before use.

Vapor-phase X-ray photoelectron spectra were obtained with a GCA McPherson ESCA-36 spectrometer with a Mg anode. The method used for obtaining and calibrating spectra has been described previously.[19] The flow of trisilylamine vapor into the spectrometer was regulated with a needle valve. Tris(trimethylsilyl)amine was not sufficiently volatile to flow through a needle valve and was introduced into the spectrometer through a large-diameter (1.5 cm) inlet system from a reservoir held at −20 °C.

The following data were obtained but not reported in Table I: full widths at half-maximum (fwhm) of the N 1s lines, 1.33 (9) eV for $N(SiH_3)_3$ and 1.47 (9) eV for $N[Si(CH_3)_3]_3$; Si 2p binding energies, 107.47 (3) eV with a fwhm of 1.63 (7) eV for $N(SiH_3)_3$ and 106.34 (3) eV with a fwhm of 1.66 (8) eV for $N[Si(CH_3)_3]_3$; C 1s binding energy, 289.60 (3) eV with a fwhm of 1.61 (9) eV for $N[Si(CH_3)_3]_3$.

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Registry No. $N(SiH_3)_3$, 13862-16-3; $N[Si(CH_3)_3]_3$, 1586-73-8; $NH[Si(CH_3)_3]_2$, 999-97-3; $(SiH_3)_2O$, 13597-73-4; $(SiH_3)_2S$, 16544-95-9; $(SiH_3)_2Se$, 14939-45-8.

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(15) Michl, J., private communication, 1984. For a relevant discussion of this concept, see ref 16.

(16) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49.

(17) Ward, L. G. L. *Inorg. Synth.* **1968**, *11*, 159.

(18) Ebsworth, E. A. V.; Hall, J. R.; Mackillop, M. J.; McKean, D. C.; Sheppard, N.; Woodward, L. A. *Spectrochim. Acta* **1958**, *13*, 202.

(19) Chen, H. W.; Jolly, W. L.; Kopf, J.; Lee, T. H. *J. Am. Chem. Soc.* **1979**, *101*, 2607.

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Does Coordination Activate Heterocycles toward Nucleophilic Attack? The Importance of π Interactions between Metal Ion and Ligand

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Transition-metal complexes containing coordinated nitrogen heterocycles have been prominent in the chemical literature for a variety of reasons including their photochemical properties, substitution inertness, and stabilization of low oxidation states. The interest in these complexes has resulted in much, and often lively, debate in the chemical literature on whether or not metal ions activate coordinated heterocycles toward nucleophilic attack.[1–7] Evidence for covalent hydration and pseudobase formation in many chemical processes, including nucleophilic substitution, has been collected.[1,4] Two recent reviews[2,3] have evaluated this evidence and concluded that, in general, alternative explanations are more appropriate, although controversy still remains for some systems.[4] The purpose of this note is to question the chemical basis for whether coordination may be considered in the same way as quaternization with regard to activation of heterocycles (which is the basis of Gillard's[1,4] mechanisms). This fundamental question has been largely ignored in the considerable discussion in this area.

The fundamental difference between quaternization of a nitrogen heterocycle by an alkyl group and coordination by a metal ion is the interaction of metal d orbitals with the ligand π systems. In essence, the metal ion acts not only as an electron-withdrawing σ group (as does R^+) but also as a π donor and a π acceptor (resonance effects) through its d orbitals. Reduction of electron density within the heterocycle by σ acceptance and π acceptance by the metal ion will polarize the N=C bonds, activating them toward nucleophilic attack. Opposing this process is metal ion π donation, which deactivates the ligand. Clearly, a predominance of one of these factors will result in activation or deactivation of covalent hydration or pseudobase formation. In order to set a background for discussion, the factors which affect π bonding and π back-bonding will be briefly outlined below.

(i) The π-donating and π-accepting abilities of a given metal ion depend on the relative energies of the metal d orbitals as compared to the lowest lying interacting π^* and highest energy interacting π orbital.

(ii) Both interactions are increased as the extent of orbital overlap increases.

(iii) Electronic configurations with six or more outer-shell d electrons will be good π donors while π acceptance by the metal ion will increase as the outer-shell d-electron density decreases.

We will initially consider point i. As the difference in energy of the π^* and d orbitals decreases, their interaction increases, leading to stronger π donation by the metal ion and weaker π acceptance.[8,9] Therefore, π back-bonding is more favored as you go down a transition-metal triad and as you decrease the oxidation state. In consideration of point ii, a factor overlooked is that geometrical orbital overlap is inherently greater for interactions involving π^* orbitals (I) than for those involving π orbitals (II) (as shown for pyridine). Therefore, π back-bonding is more favored than is π bonding. Secondly, the strengths of interaction for both I and II will increase with

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