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X-Ray Photoelectron Spectroscopic (ESCA) Study of Bonding in Pentacoordinate Silicon Compounds

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The Si 2p and N 1s binding energies have been measured for a series of pentacoordinate silicon compounds and compared with Si 2p binding energies for other organosilicon compounds. A correlation was observed between the N 1s and Si 2p chemical shifts indicative of strong Si–N bonding. For aliphatic derivatives, the chemical shifts can be explained on the basis of inductive effects between silicon and the attached group. For aromatic systems, π conjugation is significant to the extent of transmitting effects from the functional group of the aromatic ring to the coordinated nitrogen atom.

Frye et al.[1] have synthesized an interesting series of organosilicon compounds involving a trialkoxyamine ligand and a series of groups attached to silicon. These compounds have the structure X–Si(OCHRCH$_2$)$_3$N, where X is the functional group and R is either H or CH$_3$. Considerable data have been amassed which indicate the presence of a dative bond between nitrogen and silicon,[2] involving the lone electron pair of nitrogen and a d orbital of silicon. X-ray crystallography[3] has confirmed that the nitrogen atom is within bonding distance (2.1–2.2 Å) of silicon. Also, the Si–N bond length shortens as a more electronegative X group is substituted on the silicon, corresponding to strengthening the Si–N bond.

Table I. Experimental Si 2p and N 1s Binding Energies for Pentacoordinate Silicon Compounds (eV)

Compd no.	X group	Si 2p E_B (exptl)	Si 2p E_B (calcd)[a]	N 1s E_B (exptl)
1	F	102.8	103.21	400.4
2	Cl	103.0	102.89	400.7
3	Br	102.4	102.51	399.9
4	H	102.5	102.21	400.0
5	CH$_3$	102.3	102.11	399.7
6	Ph	102.2	102.28	400.0
7	OSi(CH$_3$)$_2$Ph	102.6	102.52	400.2
8	PhNO$_2$ (*-m*)	102.1	(102.28)[b]	400.3
9	PhN(CH$_2$CH$_3$)$_2$ (*-p*)	102.3	(102.28)[b]	399.7

[a] Calculated as (CH$_3$CH$_2$O)$_3$Si-X, from group shifts. [b] Calculated as X = C$_6$H$_5$

Experimental Section

ESCA spectra were obtained using an AE1 ES-100 electron spectrometer with either an aluminum (1486.6 eV) or magnesium (1253.6 eV) anode. The samples were pressed into a brass mesh on the spectrometer probe. Chemical shifts were referenced to carbon contamination taken as C 1s = 285.0 eV. Preparation of compounds has been described.[1]

Results and Discussion

The ESCA spectra of nine pentacoordinate silicon compounds have been measured; the results are presented in Table I. Binding energies were estimated for silicon by the group shift method, using data reported previously.[4] Group shift calculations assumed three ethoxys and one hetero group attached to silicon with no contribution to the silicon chemical shift from the Si–N bond. This was to determine if Si–N bonding could be detected by consistent deviations from a plot of calculated vs. experimental silicon binding energies. A plot of binding energies for these compounds is shown in Figure 1, along with data for selected silicon compounds from ref 4. Although there is considerable scatter of the data from the pentacoordinate silicon compounds about the 45° correlation line, the points appear to be randomly scattered. Of all of the compounds studied, only the compound having X = F falls outside of the experimental error lines (±0.15 eV). Therefore one may conclude that this type of plot cannot be used to detect Si–N bonding in pentaccordinate silicon compounds.

If there were no interaction between the nitrogen and silicon atoms in these compounds, one would expect the N 1s binding energy to remain essentially constant for all compounds, because the nitrogen is too far removed from the X group to be affected by changing the X group electronegativity. This would hold true both for through-bond and long-range inductive effects. Careful examination of Table I, however, shows there is a relationship between the N 1s and Si 2p binding energies. This is illustrated in Figure 2. With the exception of **6** and **8**, the chemical shift of nitrogen correlates exactly with that of silicon. In fact the agreement is exceptionally good. Points **6**, **8**, and **9** form a separate correlation line (dashed line) in Figure 2. These compounds have an aromatic ring attached to the silicon and represent a special case as will be discussed below. The important point is that the correlation between the N 1s and Si 2p binding energies constitutes strong evidence for an Si–N interaction in these compounds. Thus the type of plot in Figure 2 may be used to confirm the presence of Si–N bonding.

The slope of the main correlation line in Figure 2 is positive; i.e., as silicon becomes more positive, so does nitrogen. This can be readily explained by simple inductive effects. The X–Si–N bond system will have the resonance forms X–Si–N $\leftrightarrow$ X$^-$[Si–N]$^+$ where the positive charge will be distributed over both Si and N. Therefore as X becomes more electronegative, both silicon and nitrogen should shift to higher binding energies. Although this is qualitatively true, the data do not correlate exactly with electronegativities. For example, the chemical shift for X = Cl is greater than the chemical shift for X = F. Although group shift calculations as done for Figure 1 compensate for molecular potential corrections, they do not allow for changes in final state relaxation. Because the point for fluorine falls outside the experimental error line in Figure 1 and also is anomalous in Figure 2, this effect may be due to a difference in relaxation energies between **1** and other compounds. If this is the case, it is interesting that relaxation affects Si and N in the same way. An alternate explanation may be more extensive π-bonding effects in the Si–F bond than in the Si–Cl bond, reducing the effective electronegativity of fluorine. This correlates with the smaller Lewis acid strength of BF$_3$ relative to BCl$_3$.

Another interesting feature of the pentacoordinate silicon data is that **1**, **2**, and **7** must have a high partial positive charge on the nitrogen atom. In fact the binding energies reported here are comparable to those reported for some quaternary ammonium salts.

Correlations between ESCA chemical shifts (E_B) and partial atomic charges (q) are usually done by the electrostatic potential model

$$E_B = kq + V + R + l$$

where V is the molecular potential, R the relaxation energy,

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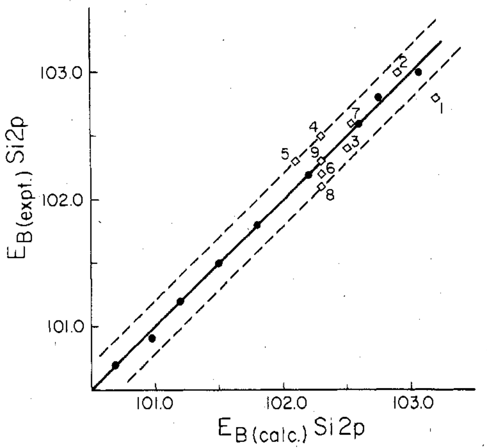

Figure 1. Correlation between experimental Si 2p binding energies and binding energies calculated by the group shift method: ●, data from ref 4; □, pentacoordinate silicon compounds (numbers refer to Table I). Dashed lines correspond to ±0.15 eV from the line of slope 1.

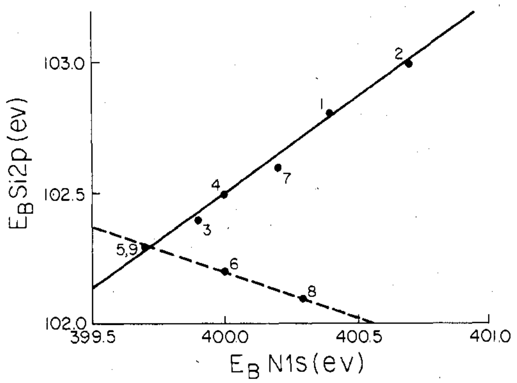

Figure 2. Correlation between Si 2p and N 1s binding energies of the pentacoordinate silicon compounds (numbers refer to Table I): —, least-squares line excluding points 6 and 8; ---, line for points 6, 8, 9.

and l a reference energy. One can estimate k as $k \simeq \langle 1/r \rangle e^2$ where $\langle 1/r \rangle$ is the expectation value of $1/r$ of the valence shell atomic orbital.[5] Good correlations have been observed between $\langle 1/r \rangle e^2$ and k for a number of elements,[6] derived from plots of $(E_B - V)$ vs. q. These correlations assume that changes in relaxation energy are negligible. This is a reasonable assumption usually applied to homologous series.

The slope of the main correlation line in Figure 2 is 0.71. Values for k derived from relativistic Hartree–Fock calculations[7] are 13.8 and 26.9 for Si and N, respectively. This would predict a slope of 0.51 for the plot shown in Figure 2, fairly close to the observed value. This assumes equal charge distribution between Si and N in the $X^-[Si-N]^+$ system. Such an assumption is unreasonable considering that a Si–N bond is 30% polar based on Pauling electronegativities. Because Si is the more electropositive element, it will get a greater portion of the positive charge, which will tend to increase the slope relative to that calculated by the ratio of k's.

Compounds **6**, **8**, and **9** form an interesting set. In each case X is an aromatic ring; **8** has an electron-withdrawing substituent, **9** an electron-donating substituent, and **6** an unsubstituted benzene. Clearly there must be an effect operating that is absent in the nonaromatic compounds. The dashed line in Figure 2 has a small negative slope, −0.3, indicating the effect we are seeing is more important for nitrogen than for silicon.

The above effects can be explained by π bonding between Si and the aromatic ring. The effect of π bonding will be to induce a slight negative charge on silicon due to bonding between the π orbitals of the ring and the d orbitals of silicon. This will tend to decrease the negative charge on nitrogen, shifting the ESCA binding energy to a higher value. Such an effect is seen when comparing **5** and **6**. Similarly, adding an electron-donating group to the ring should cause a shift to even higher values for N, **9**, and an electron-withdrawing group should cause a shift to lower values, **8**. However, our simple charge considerations do not predict the small shifts observed for silicon. They should be at least 50% those of nitrogen. The multiple interactions in the σ bonds (including oxygens) probably act to obscure the shift on silicon.

The results of our ESCA study and the interpretation agree with the chemical behavior of the aromatic compounds. Frye has reported that the preparation of **8** proceeds exothermally and rapidly, heating is required to prepare **6**, and even more vigorous conditions are required to prepare **9**. Frye attributed this behavior to the strength of the Sn–N bond increasing in the order **9** < **6** < **8**, a sequence which has been established on the basis of Si–N bond lengths by x-ray crystallography. This is exactly the behavior one would predict on the basis of the ESCA data. The transfer of charge from N is greatest in the compound of highest binding energy (**8**) and least in the compound of lowest binding energy (**9**). Thus one would predict a shorter Si–N bond length and higher heat of formation as the coupling between the N and Si and the aromatic ring increases.

There are several things we may conclude from this study. First, chemical shifts of N and Si correlate with each other, providing evidence for a strong Si–N interaction in pentacoordinate silicon compounds. Second, there is considerable transfer of charge from N when the X group is very electronegative. Third, inductive effects are operative in nonaromatic systems and can adequately explain the observed shifts. Fourth, in aromatic Si systems, π bonding permits transfer of charge from a para functional group to the pentacoordinate nitrogen atom.

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Registry No. **1**, 62415-54-7; **2**, 62415-61-6; **3**, 62415-60-5; **4**, 22761-51-9; **5**, 23908-48-7; **6**, 20645-69-6; **7**, 62415-53-6; **8**, 50725-35-4; **9**, 62415-49-0.

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