The $(p \rightarrow d)$ π-Bond in Trisilylamine

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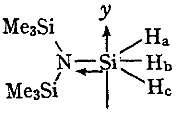
RECENTLY the question of $(p \rightarrow d)$ π-bonding in compounds containing the M–N bond (where M is Si, Ge, or Sn) has been re-examined.[1,2] On the one hand the effect does not appear to manifest itself in n.m.r. measurements on nitrogen-substituted silyl-, germyl-, and stannyl-anilines[1] whilst, on the other, the planarity of trisilylamine (for example) argues the existence of fairly strong d_π–p_π Si–N bonds. Moreover these bonds are expected only to be modified and not destroyed when the Si–N moiety forms part of a pyramidal system.[2] The latter situation is analogous to that which obtains in a "re-organised" boron halide.[3]

This Communication presents the principal results of an investigation of the π-electronic system of trisilylamine by the Pariser–Parr–Pople SCF method. The purpose of the calculation is to help resolve the above problem by determining to what extent the pair of electrons in the nitrogen p_x orbital are delocalised into the d-orbitals of the three peripheral silicon atoms and, further, to estimate the energy of the resulting Si–N $(p \rightarrow d)$ π-bond.

In the silyl group itself the three hydrogen 1s orbitals may be formed into three orthogonal molecular orbitals (See Table). One of these is σ-type and bonds with an atomic orbital of suitable symmetry on the silicon atom. With respect to $Si(H_3)$ as a *diatomic unit* the other two have the symmetry of a doubly degenerate pair of π-type group orbitals which interact with both the two d_π- and two p_π-orbitals on silicon. However in the context of the *whole molecule* the second of these interacts only with σ-type orbitals on silicon and nitrogen. The overall result is that, at the outset, the silicon d_π- orbital which does have the correct symmetry for interaction with the nitrogen p_x orbital is not independent of the Si–H bonding. In discussions of the d_π–p_π bond this feature is generally ignored and indeed it is difficult to

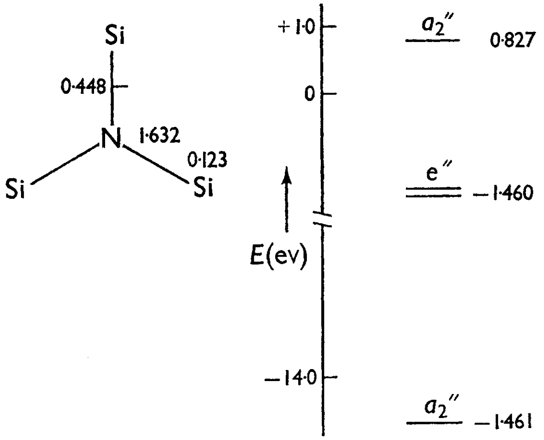
TABLE



Obital Mixing in N–Si–H_3

Nitrogen orbital	can mix with	Silicon orbital	can mix with H_3 orbital
trigonal (σ)		$3s,3p_z,3d_{z^2}$	$(a + b + c)$
$2p_x(\pi)$		$3p_x,3d_{xz}$	$(2a - b - c)$
$2p_y(\sigma)$		$3p_y,3d_{yz}$	$(b - c)$
nil		$3d_{xy},3d_{x^2-y^2}$	nil

incorporate it quantitatively into calculations. What is certain, however, is that as a consequence of the 'saturation' theorem,[4] the SiH_3 group as a whole cannot transfer π-electron density to the nitrogen p_x-orbital. Hence the only effect the attached H atoms can have is to modify the electron acceptor characteristics of the silicon atoms. The Si–N bond length[7] is 1·738 Å and appropriate values of the core Hamiltonian matrix elements for silicon and nitrogen have been derived previously.[5,6] The one-centre repulsion integral for silicon, with an electron in a d_π-orbital has not been obtained previously and it was derived from the work of Zauli.[8] Its value was 3·59 ev. Polarisation of the Si–N σ-electron core was then allowed for and the input data scaled accordingly.[9] The π-charge distribution throughout the molecule is illustrated in the Figure, as also is the one-electron energy correlation diagram. The self-consistent 'vertical' π-electron energy (*i.e.*, the energy difference between the delocalised system and a localised model having the same bond lengths) is 4·26 ev. With regard to the latter, it must be recognised that it results from a calculation employing 'excited state' parameters; energies calculated from 'ground state' parameters are generally about half the former.[10] On this basis, it seems clear that Si–N ($d \rightarrow p$) π-bonding exists in trisilylamine, with each Si–N bond having a mean energy $\sim$ 16 kcal.mole^{-1}. This amount certainly seems sufficient to maintain the planarity of the molecule. The drift of π-electrons from the nitrogen to the three silicon atoms is perhaps slightly overestimated because the calculation should really be made self-consistent to the electronegativity of the nitrogen atom, which will vary with the π-electron migration. However the *order* of the effect is reasonable and its magnitude stems from the weak mutual repulsions of electrons in silicon $3d_\pi$-orbitals.



FIGURE

The situation becomes immediately more complex if the planar Si–N skeleton is distorted in the direction of a pyramidal structure. This is because, under the resulting C_{3v} symmetry, π-bonding to the nitrogen p_x-orbital is not destroyed but merely somewhat reduced. However, because of the loss of the mirror plane inherent in planar trigonal molecules, the distinction between σ and π molecular orbitals (the σ–π separability condition) vanishes. This means that the linear combinations of *both* (*a*) the silicon orbitals directed towards the central atom and (*b*) the original silicon d_π-orbitals, transform as the irreducible representations $a_1 + e$. Thus mixing of the 'σ' and 'π' sets must ensue and 'σ–π' interactions will now assume considerable importance. Hence, although the original π-bonding does not vanish on skeletal deformation, it becomes inextricably mixed with the σ-bonding and cannot be simply related by a phase factor to its strength in the plane unless the σ–π separability condition is ignored.

Randall and Zuckermann[1] state that, whereas the ^{15}N–H coupling constants in aniline remain unaffected by substitution of *e.g.*, Me_3Si on nitrogen, substitution of NO_2 in the phenyl nucleus *increases* $J(^{15}N–H)$. They attribute the latter phenomenon to increased $p_\pi–p_\pi$ interaction between the phenyl ring and the nitrogen atom which brings about a flattening of the pyramid. However it must be borne in mind that *N*-substitution (of Me_3Si) is not directly comparable with simple substitution in the phenyl ring because, in the former case, the silicon atom *competes* with the phenyl group for the nitrogen lone-pair. This happens because the empty d_π-orbital of silicon is similar in energy to the empty e_{2u} acceptor orbitals of benzene and means that $d_\pi–p_\pi$ bonding to silicon could take place resulting in a stereochemical change and a more flattened pyramid at nitrogen whilst retaining essentially the same electron distribution around that atom. This would then leave $J(^{15}N–H)$ virtually unchanged. Finally, it has been noted[10] that the strength of a $p_\pi–p_\pi$ bond *does not* decrease markedly down Group III and hence by analogy we might expect that the situation in Si could also obtain for Ge and Sn.

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[1] E. W. Randall and J. J. Zuckerman, *Chem. Comm.*, 1966, 732.
[2] E. A. V. Ebsworth, *Chem. Comm.*, 1966, 530.
[3] P. G. Perkins, *Chem. Eng. News*, 1965, 90.
[4] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.
[5] D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta.*, 1966, **5**, 69.
[6] P. G. Perkins and D. H. Wall, *J. Chem. Soc.*, 1966, 235.
[7] "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, 1958, No. 11.
[8] C. Zauli, *Boll. sci. Fac. Chim. ind. Bologna*, 1957, **17**, 74.
[9] D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, 1966, **4**, 352.
[10] D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.*, to be published.