Bond Angles in Silyl Compounds and ($p \rightarrow d$) π-Bonding

By E. A. V. EBSWORTH

(*University Chemical Laboratory, Lensfield Road, Cambridge*)

IT is well known that replacement of methyl groups bound to nitrogen by silyl (SiH_3) groups leads to a widening of the valence angles at the nitrogen atom. Thus whereas trimethylamine is pryamidal,[1] trisilylamine is planar;[2] the heavy-atom skeletons of methyl isocyanate[3] and methyl isothiocyanate are both bent at nitrogen,[4] whereas the heavy-atom skeletons of silyl isocyanate and silyl isothiocyanate are both linear.[5,6] Similar effects have been observed in silyl–oxygen[7] and silyl–phosphorus[8] derivatives. The explanation usually offered invokes ($p \rightarrow d$) π-bonding from the nitrogen, oxygen, or phosphorus atom to silicon. It is argued that if the lone pair at, say, nitrogen is in a pure p-orbital, it can overlap a π-type d-orbital of silicon, with resulting formation of a π-bond. This argument implies that such π-bonding will be much less important in the pyramidal or bent configuration; indeed, it is sometimes assumed[9] that changes in σ-bond angles afford a reliable index of the occurrence of such π-bonding in these compounds. The purpose of this Communication is to challenge any such assumption.

It is clear that overlap between a π-type d-orbital and a lone-pair orbital is maximal for a given set of energies and orbital exponents if the lone-pair orbital is also of π-symmetry relative to the σ-bond joining the two atoms. If we consider a silicon atom bound to a nitrogen atom in which the lone pair is in a tetrahedral (sp^3) hybrid orbital, a simple calculation shows that with axes chosen as in Figure 1(b) the lone-pair orbital could be written $[\frac{1}{2}s - (1/\sqrt{12})p_x + \sqrt{(\frac{2}{3})}\cdot p_z]$. Thus, other things being equal, the overlap integral $S(d_\pi sp^3)$ may be as great as $\sqrt{(\frac{2}{3})}.S(d_\pi p_\pi)$. Of course, other things are not equal; changes in the s-character of the lone-pair orbital will influence the σ-bond energies, the energy of the lone-pair orbital itself,

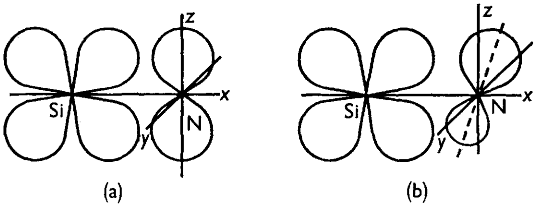

FIGURE 1

and the appropriate exponent. None the less, it seems clear that substantial π-bonding is at least possible in pyramidal or nonlinear systems; thus while it is still probably reasonable to associate the planarity of trisilylamine and trisilylphosphine with substantial ($p \rightarrow d$) π-bonding from nitrogen or phosphorus to silicon, it does not follow that because the skeleton of trigermylphosphine is non-planar[10] any ($p \rightarrow d$) π-interactions between germanium and phosphorus are necessarily negligible.

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