



**Table 17.2** Infrared stretching frequencies of some phosphoryl compounds

Compound	$\bar{\nu}_{\text{PO}}$ (cm <sup>-1</sup> )	$\Sigma_{\text{ZM}}$
F <sub>3</sub> PO	1404	11.70
F <sub>2</sub> ClPO	1358	10.75
Cl <sub>3</sub> PO	1295	8.85
Cl <sub>2</sub> BrPO	1285	8.52
ClBr <sub>2</sub> PO	1275	8.19
Br <sub>3</sub> PO	1261	7.86
$\phi$ <sub>3</sub> PO	1190	(7.2)
Me <sub>3</sub> PO	1176	(6.0)

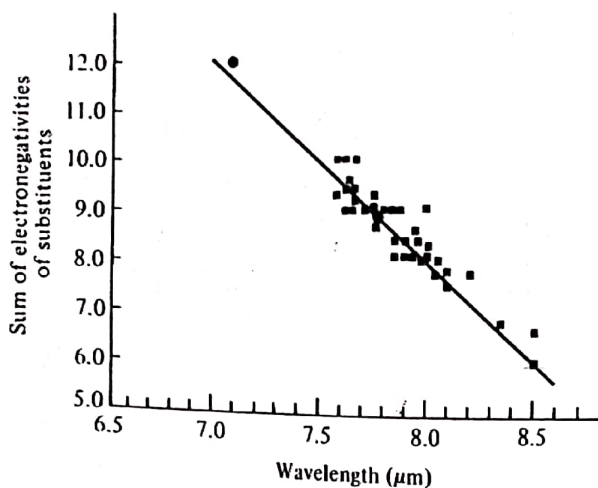
The double bond character introduced by the latter strengthens the bond and accounts for the extraordinary stability of the phosphorus oxygen linkage. Note that this extra stability cannot be attributed to ionic resonance energy (*a priori* a reasonable suggestion since the difference in electronegativity is greater in P—O than N—O) because the dipole moment of the *nitrogen* compound is greater than that of the phosphorus compound, a result completely unexpected on the basis of electronegativities, unless consideration is taken of canonical form 17.19 (II), which would be expected to lead to a reduced moment.

✓ A comparison of the bond energies also supports the above interpretation. The dissociation energies of P=O bonds in a variety of compounds lie in the range of 500–600 kJ mol<sup>-1</sup> compared with values for N→O of about 200–300 kJ mol<sup>-1</sup>.<sup>10</sup> The value for the latter is typical of what we might expect for a single bond, but 600 kJ mol<sup>-1</sup> is stronger than any known single bond (see Chapter 6, p. 263). A closer examination of the strengths of various P=O bonds in terms of infrared stretching frequencies shows some interesting trends. For a series of similar molecules, such as the phosphine oxides, the stretching frequency provides an indication of the strength of the bond (Table 17.2).<sup>11</sup> The highest stretching frequency among the phosphoryl compounds is that of F<sub>3</sub>PO, and the lowest of the halides is that of Br<sub>3</sub>PO (the iodo compound is unknown). When the stretching frequencies (in the form of wavelength,  $\lambda = 1/\bar{\nu}$ ) are plotted as a function of the sum of the electronegativities of the substituents, a straight line is obtained (Fig. 17.1). This relationship has been used to obtain group electronegativities from the stretching frequencies of phosphine oxides, for example, which are internally self-consistent and which agree with those obtained by other means (see Table 3.13) except in the case of groups such as —NH<sub>2</sub> which can compete in the  $\pi$  bonding.<sup>12</sup>

<sup>10</sup> R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, 1965, pp. 67–70.

<sup>11</sup> Note that the dissociation energy, R<sub>3</sub>PO → R<sub>3</sub>P + O, is not a sensitive measure of the P=O bond energy since the remaining three bonds may be strengthened or weakened in the dissociation process. The IR stretching frequency is a function of the force constant, *k*, and the reduced mass,  $\mu$ , of the molecule. If the molecule is assumed to be a light oxygen atom vibrating on a "fixed" larger mass of the R<sub>3</sub>P group, the reduced mass is constant, and so changes in frequency will reflect corresponding changes in the force constant. For similar molecules the force constant will be related to the total bond energy.

<sup>12</sup> J. V. Bell et al., *J. Am. Chem. Soc.*, 1954, 76, 5185. See also M. A. Davis, *J. Org. Chem.*, 1967, 32, 1161, and papers cited therein.



**Fig. 17.1** The relation between the stretching frequency (expressed as wavelength) and the electronegativity of the substituents. Circles represent halides, squares other substituted  $P=O$  compounds. [From J. V. Bell et al., *J. Am. Chem. Soc.*, 1954, 76, 5185. Reproduced with permission.]

The correlation between the electronegativity of substituent groups and the strength of the  $P=O$  bond provides support for a  $\pi$ -bonding model but not for the alternative dative  $\sigma$ -only model. The latter might be expected to be destabilized as electron density is removed from the phosphorus, requiring it to withdraw electrons from the  $P \rightarrow O$  bond, weakening it. In contrast, if the oxygen can back bond to the phosphorus through a  $d-p$   $\pi$  bond, the induced charge on the phosphorus can be diminished and the  $P=O$  bond strengthened.

The bond lengths in phosphoryl compounds are in accord with the concept of double bond character.<sup>13</sup> In the simplest case, that of  $P_4O_{10}$ , there are two  $P-O$  bond lengths. There are 12 relatively long ones (163 pm) within the cage framework proper and 4 shorter ones (139 pm) between the phosphorus atoms and the oxygen atoms external to the cage. It is interesting to note that the ratio of these two bond lengths ( $\sim 0.85$ ) is about the same as  $C=C$  to  $C-C$  or  $C=O$  to  $C-O$ .

Isoelectronic with the phosphine oxides are the phosphonium ylids,  $R_3PCH_2$ .<sup>14</sup> Like the oxides, two resonance forms



contribute to the stability of the phosphonium ylids but not the corresponding ammonium ylids,  $R_3N^+-C^-H_2$ . This difference is reflected in the reactivity. The ammonium ylids are generally quite basic and quite reactive; the phosphonium ylids are much less so,

<sup>13</sup> The complete discussion, including partial ionic character, is too long to present here. See R. F. Hudson, *Adv. Inorg. Chem. Radiochem.*, 1963, 5, 347, and K. A. R. Mitchell, *Chem. Rev.*, 1969, 69, 157.

<sup>14</sup> The nomenclature is unfortunate since the "-onium" name used with the ylids focuses attention on the polar nature (resonance structure (I)) whereas the "-ine oxide" name seems to focus more on the covalent nature (resonance structure (II)). Electronically, both types of molecules are resonance hybrids of (I) and (II).

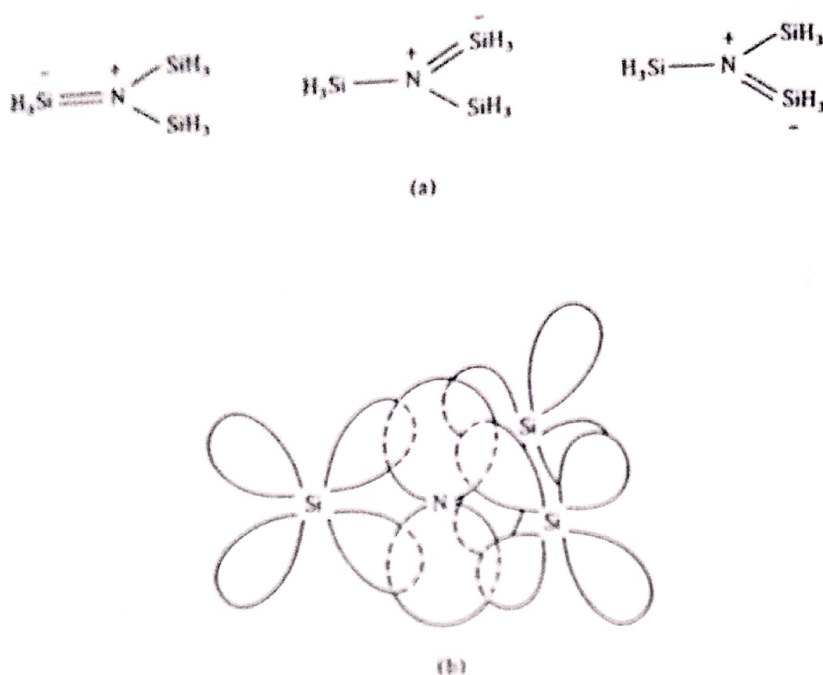


Fig. 17.2 Delocalization of the lone pair in trisilylamine. (a) Resonance structures. (b) Overlap of  $d_{\text{Si}}$  and  $p_{\text{N}}$  orbitals.

many not being sufficiently basic to abstract a proton from water and, in fact, not dissolving in water unless strong acids are present.<sup>13</sup>

#### Evidence from bond angles

The trimethylamine molecule has a pyramidal structure much like that of ammonia with a  $\text{CH}_3\text{—N—CH}_3$  bond angle of  $107.8^\circ \pm 1^\circ$ . In contrast, the trisilylamine molecule is planar. Although steric effects of the larger silyl groups might be expected to open up the bond angles, it seems hardly possible that they could force the lone pair out of a fourth "tetrahedral" orbital and make the molecule perfectly planar (even  $\phi_3\text{N}$  has bond angles of  $116^\circ$ ). It seems more likely that the lone pair adopts a pure  $p$  orbital on the nitrogen atom because orbitals on the three silicon atoms can overlap with it and delocalize the lone pair over the entire system (Fig. 17.2).

Rather similar results are obtained by comparing the bond angles in the silyl and methyl ethers (Fig. 17.3) and isothiocyanates (Fig. 17.4). In the former the oxygen is hybridized approximately  $sp^3$  with two lone pairs on the oxygen atom in dimethyl ether as compared to an approximate  $sp^2$  hybrid in disiloxane with  $\pi$  bonding. In the same way the methyl isothiocyanate molecule,  $\text{CH}_3\text{N=C=S}$ , has a lone pair localized on the nitrogen atom, hence is bent ( $\text{N} \sim sp^2$ ), but the delocalization of this lone pair into a back-bonding  $\pi$  orbital to the silicon atom of  $\text{H}_3\text{SiN=C=S}$  leads to a linear structure for this molecule.

The hypothesized delocalization of lone pair electrons in the above silicon compounds is supported by the lowered basicity of the silyl compounds as compared to the

<sup>13</sup> A. W. Johnson, "Ylid Chemistry," Academic Press, New York, 1966.

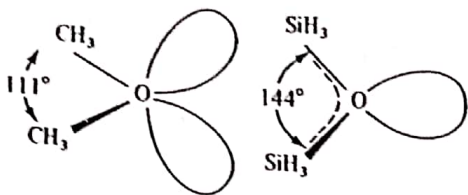


Fig. 17.3 Comparison of the molecular structure of dimethyl ether and disiloxane.

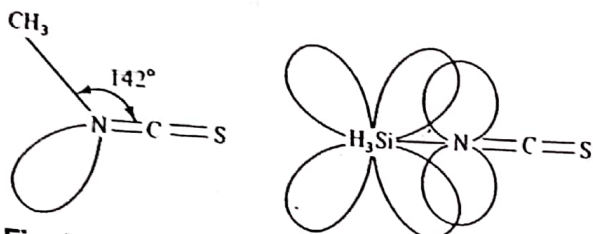
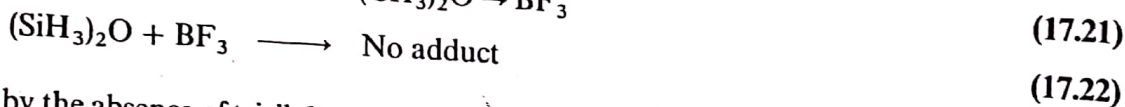
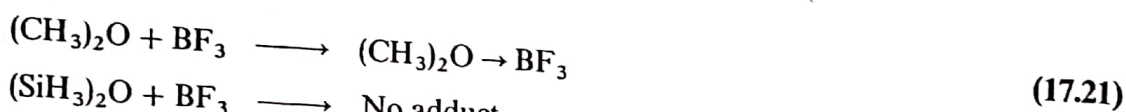
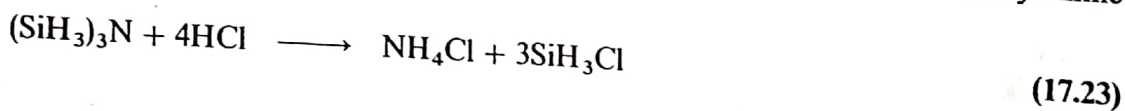


Fig. 17.4 Comparison of the molecular structure of methyl isothiocyanate and silyl isothiocyanate.

corresponding carbon compounds. This reduced basicity is contrary to that expected on the basis of electronegativity effects operating through the  $\sigma$  system since silicon is less electronegative than carbon. It is consistent with an "internal Lewis acid-base" interaction between the nitrogen and oxygen lone pairs and empty acceptor  $d$  orbitals on the silicon. Experimentally this reduced basicity is shown by the absence of disiloxane adducts with  $\text{BF}_3$  and  $\text{BCl}_3$ :

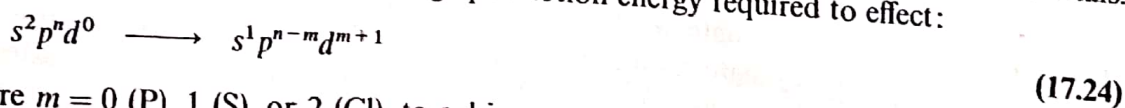


and by the absence of trisilylammonium salts. Instead of onium salt formation trisilylamine is cleaved by hydrogen chloride:



Theoretical arguments against  $d$  orbital participation in nonmetals

Several workers have objected to the inclusion of  $d$  orbitals in bonding in nonmetals. The principal objection is to the large promotion energy required to effect:



where  $m = 0$  (P), 1 (S), or 2 (Cl), to achieve a maximum multiplicity and availability of electrons for bonding. A second factor which does not favor the utilization of  $d$  orbitals is the poor overlap that they make with the orbitals of neighboring atoms. The  $3d$  orbitals of the free sulfur atoms, for example,<sup>16</sup> are shielded completely<sup>17</sup> by the lower-lying

<sup>16</sup> These same general arguments apply to the other nonmetals as well.

<sup>17</sup> In the simplified Slater scheme (p. 36) the  $d$  orbitals are assumed to be shielded to the extent of 1.0 electronic unit for each electron lying "below" them.