Crystal and Molecular Structure and Bonding in Methylfluorocyclotetraphosphonitriles

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Summary The molecular structures of *gem*-$N_4P_4F_6Me_2$ and *gem*-$N_4P_4F_4Me_4$ show bond length variations which are interpretable in terms of a delocalised π-system.

THE ring bond-lengths in homogeneously substituted cyclic phosphonitriles are normally all equal within experimental error. Systematic inequalities occur in the six-membered rings of $N_3P_3Cl_4Ph_2$,[1] $N_3P_3Cl_2Ph_4$,[2] and $N_3P_3F_4Ph_2$,[3] but, although the observed variations are as expected by π-electron theory, they do not provide a decisive test. Alternation in the lengths of the ring bonds is found in two octamethylcyclophosphonitrilium ions,[4] but the transmission of the effect of the proton to the fourth bond, although evident, may be partly obscured by conformational effects. We have determined the crystal structures of two geminally substituted methylfluorocyclotetraphosphonitriles,[5] so as to provide further information on the effect of ligand electronegativity on the geometry of the rings.

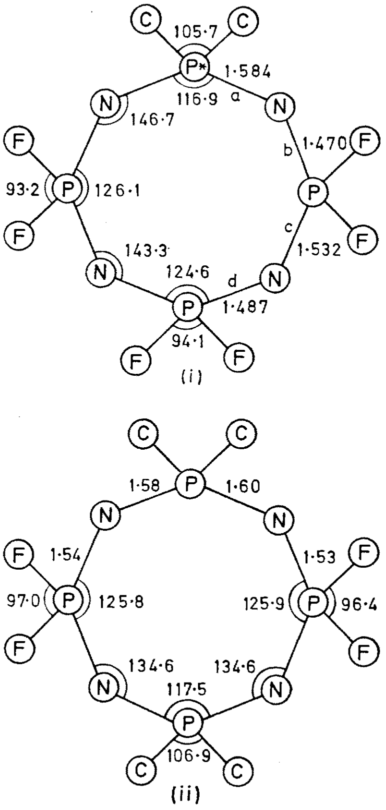

FIGURE 1. *Bond lengths* (Å) *and angles* (*degrees*) *in* (*i*) $N_4P_4F_6Me_2$ [σ(P–N) = 0·006 Å], (*ii*) $N_4P_4F_4Me_4$ [σ(P–N) = 0·01 Å].

Crystals of 1,1,3,3,5,5-hexafluoro-7,7-dimethylcyclotetraphosphonitrile, $N_4P_4F_6Me_2$, are monoclinic, a = 9·355(5), b = 12·400(5), c = 11·132(5) Å, β = 113·75(3)°, Z = 4, space group $I2/a$, and of 1,1,5,5-tetrafluoro-3,3,7,7-tetramethylcyclotetraphosphonitrile, $N_4P_4F_4Me_4$, are monoclinic, a = 12·910(5), b = 9·236(4), c = 12·329(5) Å, β = 117·13(3)°, Z = 4, space group $C2/c$. Both structures were determined with Cu-K_α diffractometer data from Patterson and Fourier syntheses; full-matrix least-squares refinement reduced R to 0·067 for 621 observed reflections ($N_4P_4F_6Me_2$) and to 0·081 for 444 observed reflections ($N_4P_4F_4Me_4$). Both molecules have a crystallographic C_2 symmetry axis, passing through the P(Me_2) group in the first molecule and through the P(F_2) groups in the second, so that the phosphorus atoms in each molecule lie in a plane. The conformation of both molecules is of the limiting "saddle" type,[6] though, since the ring angles at nitrogen are large in $N_4P_4F_6Me_2$, the nitrogen atoms deviate only slightly (± 0·15 Å) from the phosphorus plane. The effect of decreasing mean ligand electronegativity on the mean lengths of the ring bonds (and, in parentheses, the mean ring angles at nitrogen) is shown by the series: $N_4P_4F_8$, 1·51 Å (147°);[7] $N_4P_4F_6Me_2$, 1·518 (145°); $N_4P_4F_4Me_4$, 1·56 (135°); $N_4P_4Me_8$, 1·596 (132°).[8] The bonding system in phosphonitriles is evidently highly polarisable, the range of variation of bond lengths being much greater than in organic compounds for similar changes in substituent. The more detailed geometry is shown in Figure 1. As in the phenylcyclotriphosphonitriles,[1-3] the longer bonds in the tetrafluoro-tetramethyl compound meet in the phosphorus atom carrying the less electronegative substituent. The bonds in the dimethyl compound show the further feature that a highly significant alternation of bond length occurs away from the perturbing methyl groups, the second bond (1·470 Å) being the shortest so far found in a phosphonitrilic

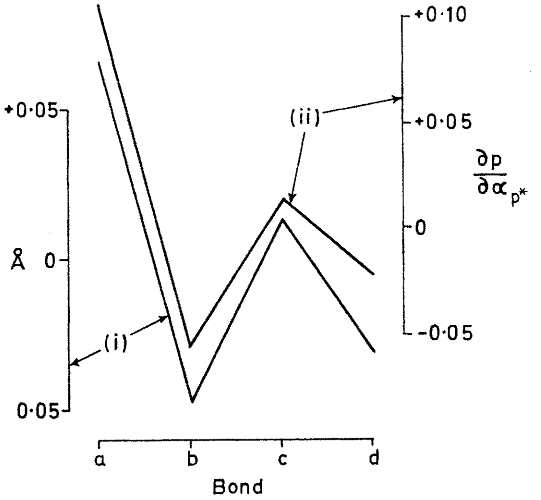

FIGURE 2. *Comparison of* (*i*) *deviations of individual* P–N *bond lengths from the mean in* $N_4P_4F_6Me_2$ (*lower curve, l.h. scale*) *and* (*ii*) *Bond–atom polarisabilities, HMO,* $\alpha_N = \alpha_P + \beta$ (*upper curve, r.h. scale*).

molecule. The large variation in the individual values, as of the mean values, is to be attributed to the polarisability of the bonding system, and shows that structural influences are propagated through the whole molecule. Since the molecular framework is nearly planar, the conditions for the application of simple Hückel theory are satisfied, and the effect of a π-inductive perturbation at phosphorus has therefore been estimated through the calculation of bond–atom polarisabilities[9] $\pi_{rs,t} = \frac{\partial p_{rs}}{\partial \alpha_t}$ for a delocalised π-system based on an 8-membered ring. They are shown in Figure 2, in comparison with the observed deviations of individual bond lengths from the mean, for the four successive distinct bonds in $N_4P_4F_6Me_2$. The close correspondence in pattern, like the pattern of ionisation potentials[10] in $(NPF_2)_n$, seems very direct evidence for electronic delocalisation in these molecules.

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