# Cyclic Inorganic Compounds. Part XIV.[1] Crystal and Molecular Structure of 1,*cis*-3,*trans*-5,*trans*-7-Tetrakis(dimethylamino)-1,3,5,7-tetrafluorotetraphosphonitrile

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Crystals of the title compound are monoclinic with $a = 10{\cdot}18 \pm 0{\cdot}02$ $b = 9{\cdot}00 \pm 0{\cdot}02$, $c = 13{\cdot}04 \pm 0{\cdot}02$ Å, and $\beta = 123{\cdot}1° \pm 0{\cdot}1°$, space group $P2_1/c$ with $Z = 2$. The atomic positions have been determined by Patterson and Fourier methods and refined by least-squares to $R$ 0·073 (1281 reflexions) from *X*-ray diffraction data. The molecule has a centre of symmetry and the eight-membered $P_4N_4$ ring has a chair conformation. The mean P–N ring bonds are 1·55 Å and the mean P–N–P and N–P–N angles are 139·5 and 121·3°. The four phosphorus atoms are coplanar with two pairs of non-equivalent nitrogen atoms displaced 0·40 and 0·19 Å from the plane. The mean P–N(amine) bond is 1·61 Å implying a high π-bond order.

*X*-RAY diffraction studies of a variety of homogeneously substituted tetraphosphonitriles[2-9] have shown that the conformation adopted by the $P_4N_4$ ring system depends intimately on the nature of the groups attached to the phosphorus atoms. It is clear that in compounds carrying different substituents, the relative influences of the groups can in some measure be assessed by the resulting ring conformation. From this point of view, it was interesting to examine the structure of a tetraphosphonitrile non-geminally substituted by both strongly electron-withdrawing fluorine groups and dimethylamino-groups which are capable of strongly back-π-bonding to phosphorus.

## EXPERIMENTAL

Crystals of the compound (m.p. 140°) were obtained by fractional crystallization from light petroleum (b.p. 60—80 °C) of the mixture resulting from the fluorination of $P_4N_4Cl_4(NMe_2)_4$ with antimony trifluoride.[10,11]

*Crystal Data.*—$C_8H_{24}F_4N_8P_4$, $M = 432$, Monoclinic, $a = 10{\cdot}18 \pm 0{\cdot}02$, $b = 9{\cdot}00 \pm 0{\cdot}02$, $c = 13{\cdot}04 \pm 0{\cdot}02$ Å, $\beta = 123{\cdot}1° \pm 0{\cdot}1°$, $U = 1000$ Å$^3$, $Z = 2$, $D_c = 1{\cdot}43$, $F(000) = 448$. Space group $P2_1/c$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$.

The cell parameters and space group were determined initially from oscillation and Weissenberg photographs and later refined on a Hilger–Watts linear diffractometer. The layers 0—12*kl* were explored and 1281 reflexions with net counts $>3\sigma$ were considered observed. No account was taken of anomalous dispersion and no corrections were made for absorption or secondary extinction. Data reduction and crystallographic calculations used the National Research Council (Ottawa) programs of ref. 12. Atomic scattering factors were taken from ref. 13.

The two independent phosphorus atoms were located from a three-dimensional Patterson synthesis and a three-dimensional Fourier synthesis phased by these two atoms revealed the other non-hydrogen atom positions. Block-diagonal least-squares refinement finally using anisotropic temperature factors for all atoms converged at $R$ 0·073.* A difference-Fourier synthesis did not reveal

TABLE 1

Atomic co-ordinates with standard deviations in parentheses

| Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| P(1) | 0·2205(2) | 0·4016(2) | 0·0919(1) |
| P(2) | 0·0958(2) | 0·6741(2) | 0·1166(1) |
| N(1) | 0·0875(7) | 0·3520(7) | −0·0373(5) |
| N(2) | 0·2091(7) | 0·5428(7) | 0·1515(5) |
| F(1) | 0·3533(6) | 0·4378(6) | 0·0677(5) |
| F(2) | 0·1339(8) | 0·7897(5) | 0·0520(5) |
| N(3) | 0·2945(7) | 0·2691(7) | 0·1884(5) |
| C(1) | 0·4014(13) | 0·2956(14) | 0·3199(8) |
| C(2) | 0·3059(15) | 0·1150(10) | 0·1459(13) |
| N(4) | 0·1321(7) | 0·7564(7) | 0·2398(5) |
| C(3) | 0·2861(12) | 0·7471(13) | 0·3551(7) |
| C(4) | 0·0283(12) | 0·8637(13) | 0·2377(10) |

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20578 (15 pp. 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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the hydrogen atom positions. Atomic co-ordinates and the thermal parameters are listed in Tables 1 and 2 respectively.

TABLE 2

Thermal parameters * (× $10^4$)

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 149 | 122 | 84 | 3 | 82 | 41 |
| P(2) | 184 | 107 | 73 | −49 | 116 | −25 |
| N(1) | 209 | 225 | 123 | −107 | 83 | 39 |
| N(2) | 201 | 203 | 124 | −98 | 94 | 38 |
| F(1) | 309 | 271 | 219 | 22 | 363 | 32 |
| F(2) | 643 | 194 | 250 | −48 | 627 | −185 |
| N(3) | 250 | 181 | 125 | 60 | 92 | 25 |
| C(1) | 346 | 432 | 115 | 146 | 83 | 99 |
| C(2) | 470 | 170 | 264 | 44 | 218 | 161 |
| N(4) | 233 | 269 | 100 | −137 | 147 | −39 |
| C(3) | 309 | 464 | 96 | −187 | 82 | −14 |
| C(4) | 325 | 400 | 225 | −314 | 300 | 40 |

* In the form:

$$[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)].$$

## DISCUSSION

*Description of the Structure.*—The compound is one of the four possible completely nongeminally substituted tetraphosphonitriles in which each phosphorus atom carries as substituents a fluorine atom and a dimethylamino-group. As the molecule is centrosymmetric, two of the fluorine atoms occupy *cis*-positions on one side of the phosphorus–nitrogen ring while the other pair of *cis*-fluorines are disposed on the opposite side of the ring. Bond distances and angles, together with estimated standard deviations are summarised in Table 3. The numbering of atoms is shown in Figure 1 while the structure is illustrated in Figure 2.

The four phosphorus atoms are coplanar and the ring system adopts a chair-type structure in which there are two pairs of non-equivalent nitrogen atoms. The nitrogen atoms N(1) and N(1′) are displaced 0·40 Å vertically from the plane of the phosphorus atoms while the pair N(2),N(2′) are displaced by 0·19 Å. There is therefore the possibility of conformational isomerism resulting from the arrangement of the *cis*-groups with respect to the two types of nitrogen atoms. The conformer examined is that in which the fluorine atoms are *cis* across each of the least displaced nitrogen atoms; the displacement is away from the fluorine atoms. A plane can also be drawn through the four ring nitrogen atoms from which two of the phosphorus atoms [P(1) and P(1′)] deviate by 0·18 and the other two [P(2) and P(2′)] by 0·45 Å.

TABLE 3

Intramolecular distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| P(1)–N(1) | 1·542(6) | P(2)–N(2) | 1·536(7) |
| P(1)–N(2) | 1·526(6) | P(2)–N(1′) | 1·581(8) |
| P(1)–N(3) | 1·592(6) | P(2)–N(4) | 1·617(6) |
| P(1)–F(1) | 1·581(7) | P(2)–F(2) | 1·515(7) |
| N(3)–C(1) | 1·46(1) | N(4)–C(3) | 1·42(2) |
| N(3)–C(2) | 1·52(1) | N(4)–C(4) | 1·47(1) |

(*b*) Angles

| | | | |
|---|---|---|---|
| N(1)–P(1)–N(2) | 122·1(4) | N(1′)–P(2)–N(2) | 120·4(4) |
| N(1)–P(1)–N(3) | 113·6(4) | N(1′)–P(2)–N(4) | 105·4(4) |
| N(1)–P(1)–F(1) | 100·2(3) | N(1′)–P(2)–F(2) | 107·9(4) |
| N(2)–P(1)–N(3) | 110·9(4) | N(2)–P(2)–N(4) | 109·3(4) |
| N(2)–P(1)–F(1) | 104·0(3) | N(2)–P(2)–F(2) | 108·3(4) |
| P(1)–N(1)–P(2′) | 140·9(5) | P(1)–N(2)–P(2) | 138·0(5) |
| P(1)–N(3)–C(2) | 119·5(7) | P(2)–N(4)–C(4) | 121·9(6) |
| P(1)–N(3)–C(1) | 122·1(7) | P(2)–N(4)–C(3) | 121·9(7) |
| C(1)–N(3)–C(2) | 114·8(8) | C(3)–N(4)–C(4) | 115·2(8) |
| N(3)–P(1)–F(1) | 103·0(3) | N(4)–P(2)–F(2) | 104·4(4) |

Six of the P–N ring bonds are equal (mean, 1·534 Å) while two are longer (1·581 Å). There is, however, no indication that this implies any alternation in bond lengths round the ring. The mean value of the bond length (1·55 Å) is in agreement with the relationship [7,14] established with the electronegativity of the substituents and as expected, falls between the values for $P_4N_4(OMe)_8$ and $P_4N_4F_6Me_2$.

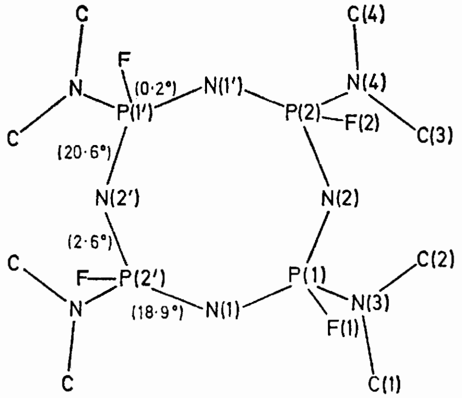

FIGURE 1 Schematic diagram showing numbering of atoms and the dihedral angles of ring bonds

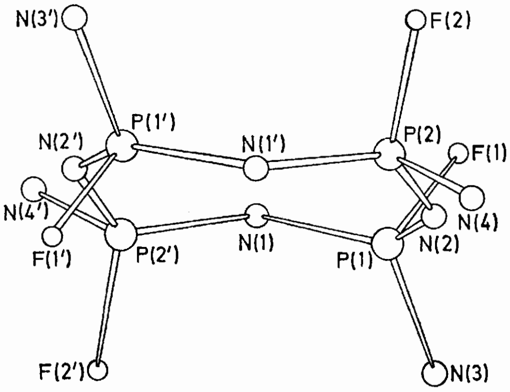

FIGURE 2 Molecular configuration (the carbon atoms have been omitted)

The endocyclic angles at phosphorus are close to 120° as generally found for phosphonitriles, but there are two different ring nitrogen angles (138 and 141°). The larger ring angles are found at the nitrogen atoms most highly displaced from the plane of the phosphorus atoms.

The P–N exocyclic bond lengths (1·59 and 1·62 Å) are short compared with the accepted P–N single-bond length (1·77 Å). Further, the angles at the amine nitrogen atoms all fall between 114·8 and 122·1° and

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[14] A. J. Wagner, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3988.

their sum is 356·4 for N(3) and 359·0° for N(4). The closeness to 360° implies that hybridization at both these atoms is close to $sp^2$. The amine groups are, however, non-equivalent and this is confirmed by deviations of 0·17 and 0·08 Å for atoms N(3) and N(4) respectively from the appropriate P,C,C plane. In both cases, the projection of the phosphorus–amine bond on the plane of the four phosphorus atoms is almost colinear with the bisector of the N–P–N ring angle. More important, from the point of view of bonding, the orientation of the $Me_2N$ system is such that the filled nitrogen $p$ orbital can overlap with an empty phosphorus $d_{x^2-y^2}$ orbital,[15] thus providing a system through which delocalization of the lone pair might occur.

TABLE 4

Bond lengths (Å) and angles (°) in $P_4N_4F_4(NMe_2)_4$ and related molecules

| | $P_4N_4F_4(NMe_2)_4$ | $P_4N_4(NMe_2)_8$ [a] | $P_4N_4F_8$ [b] | $P_4N_4Cl_8(T)$ [c] | $P_4N_4Ph_4Cl_4$ [d] | $P_4N_4Ph_4(NHMe)_4$ [e] |
|---|---|---|---|---|---|---|
| P–N(ring | 1·55 | 1·58 | 1·51 | 1·56 | 1·57 | 1·59 |
| P–N(amine) | 1·59, 1·62 | 1·68 | | | | 1·67 |
| P–F | 1·58, 1·52 | | 1·51 | | | |
| N–P–N | 121·3° | 120 | 122·7 | 121 | 120 | 119·5 |
| P–N–P | 138·0, 140·9 | 133 | 147·2 | 134, 138 | 132, 139 | 124·6, 131·3 |
| Ring conformation | Chair | Saddle | Planar | Chair | Chair | Chair |

[a] Ref. 4. [b] Ref. 2. [c] Ref. 6. [d] Ref. 16. [e] Ref. 17.

The fluorine substituents also constitute two non-equivalent pairs with P–F bond lengths of 1·58 and 1·52 Å.

Valid comparisons can be made between the structure of this molecule and $P_4N_4F_8$ [2] and $P_4N_4(NMe_2)_8$ [4] on the one hand and the series, $P_4N_4Cl_8$ ($T$-form),[6] $P_4N_4Ph_4Cl_4$,[16] and $P_4N_4Ph_4(NHMe)_4$ [17] on the other. The latter molecules all have centrosymmetric structures similar to that described here. Relevant molecular parameters are given in Table 4.

In many respects, the aminofluoro-compound falls between the extremes set by the octafluoro- and the octakis(dimethylamino)-derivatives. This is particularly apparent in the P–N ring bond lengths and the angles at the ring nitrogen atoms. This is in spite of the variation in the ring conformation from $D_{4h}$ in the fluoride to $D_{2d}$ for the dimethylamino-compound. On average, the P–F bond lengths are longer than those in $P_4N_4F_8$ but, significantly, the mean P–N(amine) bond is considerably shorter than in $P_4N_4(NMe_2)_8$.

The alternative comparison shows that there are two types of ring nitrogen atoms in all species which contain a ring system in the chair conformation, including the homogeneously substituted tetrameric chloro-compound. Further, the mean value of the angle at the ring nitrogen atoms in the mixed aminofluoro-compound is one of the largest found for a centrosymmetric structure.

There are no short distances between non-bonded atoms except F(2) · · · C(2) 3·28 Å. This may have a slight effect on the orientation of that amine group.

*Bonding.*—Exocyclic groups have a marked influence on the electron distribution in the P–N ring system of phosphonitriles and consequently on the ring conformation adopted. In this case, it will be greatly affected by the presence of equal numbers of strongly electron-withdrawing fluorine atoms and strongly electron-donating dimethylamino-groups in the same molecule.

Bonding in phosphonitriles in general is discussed in terms of supplementation of a $\sigma$ framework by the $\pi_a$ and $\pi_s$ system.[18-20] In octafluorotetraphosphonitrile, the high electronegativity of fluorine promotes extensive delocalization of nitrogen lone pairs (strong $\pi_s$ bonding), and a planar ring system ($D_{4h}$) with large nitrogen ring angles results.[2] The ring conformation in the octakis(dimethylamino)-derivative, is close to a saddle ($D_{2d}$) which is compatible with donation of the lone pairs on the exocyclic nitrogen atoms into empty phosphorus $d$ orbitals. This prevents delocalization of lone pairs on the ring nitrogen atoms and the $\pi_s$ system is thus greatly weakened over that in the octafluoro-compound.

In nongeminal $P_4N_4F_4(NMe_2)_4$, the competition between the exocyclic groups more nearly equalizes the $\pi_a$ and $\pi_s$ systems and a chair form of the $P_4N_4$ ring is obtained,[18] in which steric interactions between exocyclic groups are small. The conformation ($C_i$) deviates from an idealized chair ($C_{2h}$) as shown by the dihedral angles of the ring bonds (see Figure 1). These should be equal in pairs, but here the differences are 16 and 20°.

The mean ring angle at nitrogen is large and is compatible with a moderately high degree of delocalization of the nitrogen lone pairs. The size of the nitrogen angle is, however, affected by the ring conformation and it is significant that the nitrogen angles in the tetrameric chloro-compound are greater in the $T$-form [6] than in the $K$-form ($S_4$ 131°).[5]

The amine substituents also possess lone pairs which can be used in $\pi$ bonding to phosphorus. This is consistent with the shortness of the P–N(amine) bonds and the near planarity of the $PNC_2$ systems. Thus the situation in this compound is unique in that the phosphorus atoms are accepting substantial electron density from lone pairs on both the ring nitrogen atoms and the amine groups. The longer P–F bond is found at the phosphorus atom attached to the more nearly planar amine nitrogen, implying that back-co-ordination from the amine is favoured here.

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The shortness of the exocyclic P–N bonds compared with those in $P_4N_4(NMe_2)_8$ is not unexpected, since in $P_4N_4F_4(NMe_2)_4$ the absence of geminal amine groups means that there is less competition for phosphorus *d* orbitals. Moreover, the inductive effect of fluorine will strengthen exocyclic $\pi$ bonding in the same way as it promotes $\pi$ bonding in the ring system.

Exocyclic bonding between phosphorus and the amine groups will involve the phosphorus $d_{z^2}$ orbital, though the amine lone pair is also orientated for interaction with the $d_{x^2-y^2}$ orbital.[15] With increasing deviations from planarity, the $d_{x^2-y^2}$ orbital becomes less well orientated for interaction with the ring nitrogen lone pair and significant overlap becomes possible with the $d_{xz}$ orbital.[15] This provides a mechanism for the delocalization of the ring nitrogen lone pairs into orbitals which are relatively unaffected by the amine groups.

We thank the S.R.C. for the award of a Research Studentship (to D. M.).

[2/1777 *Received, 28th July,* 1972]