# Crystal Structure of 1, *trans*-3, *cis*-5, *trans*-7-Tetrakis(dimethylamino)-1,3,5,7-tetrafluorotetraphosphonitrile

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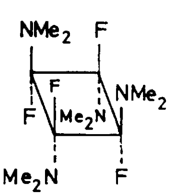
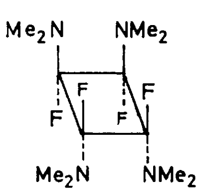
Crystals of the title compound are monoclinic with $a$ = 15·97, $b$ = 9·27, $c$ = 27·34 Å and β = 102°, space group $C2/c$ with $Z$ = 8. The atomic positions have been determined by Patterson and Fourier methods and refined by least squares to $R$ 0·046 (1640 reflexions) from $X$-ray data. The conformation of the eight membered ring is close to a saddle with a mean P–N ring bond length of 1·557 Å. The PNP angles are in the range 132·7—137·4°. The dimethylamino-groups and fluorine atoms are arranged alternately above and below the mean ring plane with P–N (amine) bonds of 1·621 Å and P–F bonds of 1·566 Å. Possible factors influencing the ring conformation adopted in tetrasubstituted compounds of this type are discussed.

THE relationship between the ring conformation adopted by a tetraphosphonitrile and the properties of the substituents at the phosphorus atoms is currently of interest. In this connexion non-geminally substituted compounds of the type $P_4N_4X_4Y_4$ are as important as homogeneously substituted phosphonitriles. A number of such compounds has been examined previously [1-4] including one of the isomeric dimethylaminofluoro-compounds.[5] In this paper we report the results of a crystal structure determination on a second non-geminally substituted tetrakis(dimethylamino)tetrafluoro-derivative. Spectroscopic data have been used to assign tentatively a 1, *trans*-3, *cis*-5, *trans*-7 structure (I) to the present compound; the previously examined isomer was the 1, *cis*-3, *trans*-5, *trans*-7 compound (II). As the electronic effects of the substituents are expected to be broadly similar, any differences (particularly in ring conformation) can, in the absence of strong intermolecular interactions, be directly correlated with the stereochemical arrangement of the groups attached to the phosphorus atoms.



(I)



(II)

## EXPERIMENTAL

The compound (m.p. 109°) was obtained by fractional crystallization from light petroleum of the isomer mixture obtained by treating $P_4N_4Cl_4(NMe_2)_4$ with antimony trifluoride.[6]

*Crystal Data.*—$C_8H_{24}F_4N_8P_4$, $M$ = 432, Monoclinic, $a$ = 15·974 ± 0·007, $b$ = 9·271 ± 0·005, $c$ = 27·238 ± 0·014 Å, β = 101·97° ± 0·03°, $U$ = 3946 Å$^3$, $Z$ = 8, $D_c$ = 1·45, $F(000)$ = 1792. Space group $C2/c$ from systematic absences, $hkl$ when $h + k = 2n + 1$ and $h0l$ when $l = 2n + 1$ and subsequent refinement, Mo-$K_\alpha$ radiation, λ = 0·7107 Å, μ = 4·33 cm$^{-1}$.

The unit cell parameters and space group were determined initially from oscillation and Weissenberg photographs and later refined on a Hilger and Watts Four Circle Diffractometer using Mo-$K_\alpha$ radiation. 1640 Reflexions with net counts $> 3\sigma$ were considered observed and measured in the range $0° \leqslant \theta \leqslant 30°$. The intensities were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and crystallographic calculations used the N.R.C. (Ottawa) programs [7] and atomic scattering factors were taken from ref. 8.

The positions of the phosphorus atoms were readily deduced from a three-dimensional sharpened Patterson map.

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[1] G. J. Bullen and P. R. Mallinson, *J.C.S. Dalton*, 1972, 1412.

[2] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 1651.

[3] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

[4] G. J. Bullen, P. R. Mallinson, and A. H. Burr, *Chem. Comm.*, 1969, 691.

[5] D. Millington, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1973, 396.

[6] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, **1973**, **2649**.

[7] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, N.R.C. (Ottawa), Crystallographic Programs.

[8] 'International Tables for $X$-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

Since the molecule contains an eight membered P–N ring, it was anticipated that the four phosphorus atoms in one molecule would lie approximately at the corners of a square of side *ca.* 2·8 Å. This would give rise to a set of four coplanar vectors within 3—5 Å of the origin in known geometry, and these were observed. The large ring–ring vector between phosphorus atoms in molecules related by a centre of symmetry, and its surrounding pattern of vectors similar to those near the origin, were found and used to locate the four phosphorus atoms in the asymmetric unit.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| P(1) | 0·3084(1) | 0·5795(2) | 0·0911(1) |
| P(2) | 0·3801(1) | 0·3733(2) | 0·1679(1) |
| P(3) | 0·2134(1) | 0·2537(2) | 0·1617(1) |
| P(4) | 0·1508(1) | 0·4170(2) | 0·0728(1) |
| N(1) | 0·3585(4) | 0·5249(7) | 0·1427(2) |
| N(2) | 0·3119(4) | 0·2520(7) | 0·1637(2) |
| N(3) | 0·1509(4) | 0·3538(8) | 0·1265(2) |
| N(4) | 0·2285(4) | 0·5006(7) | 0·0612(2) |
| N(5) | 0·2901(4) | 0·7501(7) | 0·0967(2) |
| C(1) | 0·2245(6) | 0·8290(10) | 0·0602(3) |
| C(2) | 0·3592(7) | 0·8423(10) | 0·1233(4) |
| F(1) | 0·3734(3) | 0·5736(5) | 0·0547(2) |
| N(6) | 0·4651(4) | 0·3034(7) | 0·1541(2) |
| C(3) | 0·5345(5) | 0·3927(11) | 0·1437(3) |
| C(4) | 0·4935(5) | 0·1585(10) | 0·1722(4) |
| F(2) | 0·4063(3) | 0·4130(5) | 0·2250(2) |
| N(7) | 0·1928(4) | 0·2684(8) | 0·2172(2) |
| C(5) | 0·2483(6) | 0·1974(13) | 0·2611(3) |
| C(6) | 0·1041(6) | 0·2944(14) | 0·2246(4) |
| F(3) | 0·1872(3) | 0·0984(6) | 0·1437(2) |
| N(8) | 0·1218(4) | 0·2972(7) | 0·0290(2) |
| C(7) | 0·1348(6) | 0·3213(11) | −0·0228(3) |
| C(8) | 0·0487(6) | 0·2014(12) | 0·0307(4) |
| F(4) | 0·0759(3) | 0·5296(6) | 0·0654(2) |

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$) with estimated standard deviations in parentheses

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{23}$ | $b_{13}$ | $b_{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 44(1) | 104(3) | 12(1) | −1(2) | 9(1) | −32(3) |
| P(2) | 34(1) | 124(3) | 12(1) | 5(2) | 9(1) | −10(3) |
| P(3) | 36(1) | 125(3) | 16(1) | 5(2) | 19(1) | −19(3) |
| P(4) | 36(1) | 142(3) | 12(1) | −1(2) | 8(1) | 1(3) |
| N(1) | 55(3) | 135(10) | 15(1) | 6(5) | 1(3) | −28(10) |
| N(2) | 37(3) | 132(9) | 22(1) | 19(6) | 21(3) | 0(9) |
| N(3) | 37(3) | 232(13) | 13(1) | 13(6) | 11(3) | −4(10) |
| N(4) | 45(3) | 155(10) | 13(1) | 4(5) | 5(3) | −53(10) |
| N(5) | 65(4) | 121(9) | 16(1) | −6(6) | 5(3) | −30(10) |
| C(1) | 78(6) | 141(13) | 23(2) | 8(8) | 5(5) | 68(14) |
| C(2) | 92(6) | 169(16) | 26(2) | −15(10) | −13(6) | −82(17) |
| F(1) | 60(2) | 209(8) | 19(1) | −6(4) | 29(2) | −28(7) |
| N(6) | 33(3) | 154(10) | 17(1) | −4(6) | 11(3) | −20(9) |
| C(3) | 40(4) | 275(19) | 26(2) | 40(10) | 25(4) | −56(15) |
| C(4) | 54(4) | 152(14) | 29(2) | −24(9) | 20(5) | 1(13) |
| F(2) | 73(3) | 219(8) | 14(1) | −3(4) | 10(2) | 36(8) |
| N(7) | 49(3) | 215(12) | 15(1) | 29(6) | 18(3) | 10(11) |
| C(5) | 67(5) | 377(25) | 18(1) | 88(11) | 12(5) | 25(19) |
| C(6) | 65(5) | 361(25) | 25(2) | 47(12) | 45(5) | 105(19) |
| F(3) | 66(3) | 185(8) | 39(1) | −31(5) | 42(3) | −65(8) |
| N(8) | 52(3) | 183(11) | 14(1) | −1(6) | 9(3) | −63(10) |
| C(7) | 79(5) | 211(16) | 13(1) | −23(8) | 16(4) | −39(15) |
| C(8) | 72(6) | 243(20) | 29(2) | 9(11) | 8(6) | −161(17) |
| F(4) | 64(3) | 282(10) | 21(1) | 20(5) | 17(2) | 90(9) |

* In the form: $\exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)$.

The positions of the other non-hydrogen atoms were revealed by a three dimensional Fourier synthesis. Four cycles of block-diagonal least-squares refinement reduced $R$ to 0·09 and with anisotropic temperature factors, $R$ converged at 0·046 after eight further cycles of refinement. The hydrogen atoms could not be located from a difference Fourier and were thus considered to be rotating.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20977 (7 pp.).* The final atomic co-ordinates and temperature factors are listed in Tables 1 and 2 respectively and Figure 1 shows the numbering of the atoms.

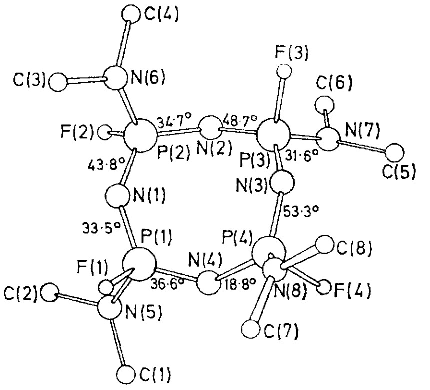

FIGURE 1 Diagram showing numbering of atoms and the dihedral angles of the ring bonds

## DISCUSSION

As expected from the method of preparation and n.m.r. data,[6] compound (I) is a non-geminal isomer in which each phosphorus atom carries a fluorine atom and a dimethylamino-group as substituents. As these are arranged alternately above and below the mean ring plane, it can be designated as the 1, *trans*-3, *cis*-5, *trans*-7 isomer. Bond distances and angles together with estimated standard deviations are given in Tables 3 and 4 respectively and the molecular configuration is shown in Figure 2.

TABLE 3

Bond lengths/Å with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| P(1)–N(1) | 1·552(6) | P(2)–N(6) | 1·617(6) |
| P(2)–N(1) | 1·570(7) | N(6)–C(3) | 1·460(11) |
| P(2)–N(2) | 1·553(6) | N(6)–C(4) | 1·467(11) |
| P(3)–N(2) | 1·563(6) | P(2)–F(2) | 1·568(5) |
| P(3)–N(3) | 1·544(7) | | |
| P(4)–N(3) | 1·574(6) | P(3)–N(7) | 1·617(6) |
| P(4)–N(4) | 1·551(6) | N(7)–C(5) | 1·486(12) |
| P(1)–N(4) | 1·548(6) | N(7)–C(6) | 1·492(12) |
| | | P(3)–F(3) | 1·550(6) |
| P(1)–N(5) | 1·621(7) | | |
| N(5)–C(1) | 1·477(11) | P(4)–N(8) | 1·627(7) |
| N(5)–C(2) | 1·464(12) | N(8)–C(7) | 1·483(10) |
| P(1)–F(1) | 1·576(5) | N(8)–C(8) | 1·476(12) |
| | | P(4)–F(4) | 1·568(6) |

Mean distances

| | |
|---|---|
| P–N (ring) | 1·557 |
| P–N (amine) | 1·621 |
| P–F | 1·566 |
| N–C | 1·476 |

The eight atoms forming the ring are alternately in pairs above and below the mean plane (see Table 5), thus the conformation is that of a tub (with *ca.* $S_4$ symmetry). The deviations of the four phosphorus atoms

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. Items less than 10 pp. are sent as full-size copies.

from the plane, however, are relatively small and the conformation is close to the ' saddle '. Ideally this would have coplanar phosphorus atoms with the nitrogen atoms being displaced alternately above and below this plane. The overall symmetry would be $D_{2d}$.

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| N(4)–P(1)–N(1) | 122·4(3) | F(1)–P(1)–N(5) | 104·4(3) |
| N(1)–P(2)–N(2) | 121·9(3) | F(2)–P(2)–N(6) | 105·1(3) |
| N(2)–P(3)–N(3) | 122·9(4) | F(3)–P(3)–N(7) | 106·3(3) |
| N(3)–P(4)–N(4) | 121·9(3) | F(4)–P(4)–N(8) | 105·5(3) |
| P(1)–N(1)–P(2) | 135·6(4) | P(1)–N(5)–C(1) | 122·5(6) |
| P(2)–N(2)–P(3) | 132·9(4) | P(1)–N(5)–C(2) | 118·9(6) |
| P(3)–N(3)–P(4) | 132·7(4) | P(2)–N(6)–C(3) | 121·7(5) |
| P(4)–N(4)–P(1) | 137·4(4) | P(2)–N(6)–C(4) | 120·4(5) |
| | | P(3)–N(7)–C(5) | 120·8(6) |
| F(1)–P(1)–N(1) | 105·9(3) | P(3)–N(7)–C(6) | 121·7(6) |
| F(1)–P(1)–N(4) | 103·3(3) | P(4)–N(8)–C(7) | 121·3(5) |
| F(2)–P(2)–N(1) | 102·3(3) | P(4)–N(8)–C(8) | 119·6(6) |
| F(2)–P(2)–N(2) | 106·4(3) | | |
| F(3)–P(3)–N(2) | 101·8(3) | C(1)–N(5)–C(2) | 113·7(7) |
| F(3)–P(3)–N(3) | 105·3(3) | C(3)–N(6)–C(4) | 113·0(6) |
| F(4)–P(4)–N(3) | 102·8(3) | C(5)–N(7)–C(6) | 112·7(7) |
| F(4)–P(4)–N(4) | 105·3(3) | C(7)–N(8)–C(8) | 112·9(7) |
| N(5)–P(1)–N(1) | 107·7(3) | | |
| N(5)–P(1)–N(4) | 111·5(3) | | |
| N(6)–P(2)–N(1) | 112·2(3) | | |
| N(6)–P(2)–N(2) | 107·6(3) | | |
| N(7)–P(3)–N(2) | 111·6(3) | | |
| N(7)–P(3)–N(3) | 107·5(3) | | |
| N(8)–P(4)–N(3) | 111·8(3) | | |
| N(8)–P(4)–N(4) | 108·2(3) | | |

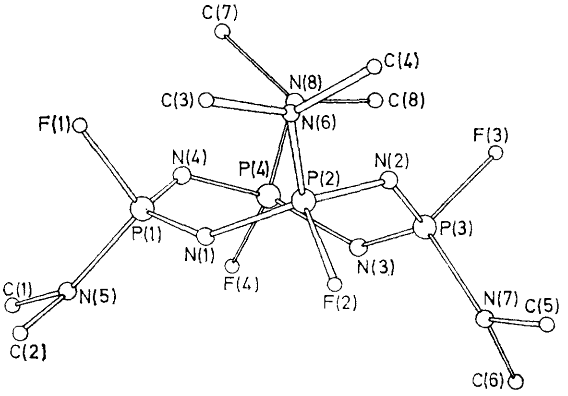

FIGURE 2 Molecular configuration

The deviation of the present ring from $D_{2d}$ symmetry can be assessed by considering the dihedral angles associated with the ring bonds. For perfect symmetry, these should be equal to 45° but here the spread is from 18·8 to 53·3° (average, 37·6°). On this criterion, the ring is similar to that in $P_4N_4(OMe)_8$.[9] An alternative description of puckered ring systems of the type considered here is in terms of the ratio $\Delta P{:}\,\Delta N$. Here $\Delta P$ and $\Delta N$ are respectively the displacements of the phosphorus and nitrogen atoms from the mean ring plane. For $D_{2d}$ symmetry the ratio is zero and tends toward unity as the conformation tends to $S_4$. The ratio for compound (I) is 0·30 and the conformation falls between that for $P_4N_4(OMe)_8$ (0·20) and $P_4N_4(NMe_2)_8$ (0·35).[10]

TABLE 5

Equations of mean planes and distances of atoms from the plane

| Atoms in plane | Equation | Distances/Å |
|---|---|---|
| P(1)—(4)<br>N(1)—(4) | $0{\cdot}414x - 0{\cdot}650y - 0{\cdot}637z = -3{\cdot}100$ | P(1) −0·115, P(2) +0·119<br>P(3) −0·142, P(4) +0·176<br>N(1) −0·451, N(2) +0·481<br>N(3) −0·478, N(4) +0·410 |
| P(1), C(1), C(2) | $0{\cdot}676x + 0{\cdot}082y - 0{\cdot}732z = 1{\cdot}643$ | N(5) −0·197 |
| P(2), C(3), C(4) | $-0{\cdot}217x - 0{\cdot}249y - 0{\cdot}944z = -6{\cdot}194$ | N(6) +0·197 |
| P(3), C(5), C(6) | $-0{\cdot}314x - 0{\cdot}932y - -0{\cdot}184z = -3{\cdot}765$ | N(7) −0·195 |
| P(4), C(7), C(8) | $-0{\cdot}692x - 0{\cdot}654y - 0{\cdot}306z = 0{\cdot}544$ | N(8) −0·221 |

The eight P–N distances in the ring are equal within experimental error (mean, 1·557 Å) as expected for a symmetrically substituted molecule of this type and are equal to those found previously for the 1, *cis*-3, *trans*-5, *trans*-7 isomer (II).[5] The ring angles at nitrogen vary between 132·7 and 137·4° and fall into two groups, N(2)–N(3) and N(1)–N(4), with the smaller angles for the former being associated with greater displacement from the mean ring plane.

The P–N (amine) bonds are short but, contrary to the situation in (II), all four are equal (mean 1·621 Å); the P–F bond distances, similarly do not differ significantly. The shortening of the exocyclic P–N bonds is associated with delocalisation of amine lone pairs and the extent to which this occurs will be shown by (a) the small deviation of the nitrogen atom from the appropriate PCC plane (see Table 5) and (b) the closeness of the sum of the angles at that atom to 360°. The values here are *ca.* 355° and in all cases this reflects a value of *ca.* 113° for the CNC angle. The orientation of the dimethylamino-groups is the same with respect to the mean plane of the four phosphorus atoms as found for isomer (II) and carries the same implications in terms of nitrogen–phosphorus $p\pi \longrightarrow d\pi$ bonding.[5]

Comparison of the molecular parameters indicates a close similarity for compounds (I) and (II) and the relationships to the structures of $P_4N_4(NMe_2)_8$ and $P_4N_4F_8$, discussed previously[5] for compound (II), are equally applicable here. Similarities between (I) and (II) are not unexpected as in each case the substituents at phosphorus are the same and those parameters which depend primarily on the electronic effects of the fluorine and dimethylamino-groups should be almost identical. The major difference occurs in the ring conformation which is markedly different from that found for isomer (II) and must be basically a function of the steric arrangement (configurational symmetry) of the substituents. Similar changes in ring conformation have been noted for two non-geminal isomers with the stoicheiometry

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[9] G. B. Ansell and G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 2498.

[10] M. J. Begley, T. J. King, and D. B. Sowerby, unpublished results.

$P_4N_4Cl_4Ph_4$.[2,4] In these cases, the steric requirements of the bulky phenyl groups might be expected to play a more dominant role in determining ring conformation than in the dimethylaminofluoro-species discussed here where less bulky substituents are involved.

For the non-geminally tetrasubstituted compounds examined thus far by *X*-ray methods, there appears to be a correlation between the substituent orientation and the ring conformation adopted. For example, a $C_{2h}$* arrangement of substituents (*cis–cis–trans–trans*) is, with one exception,[3] associated with a chair ring conformation [1,4,5] (ideal symmetry, $C_{2h}$), while the $D_{2d}$ arrangement of exocyclic groups (*cis–trans–cis–trans*) in the structure reported here and in the chlorine analogue [10] gives a ring conformation close to the saddle (ideal symmetry, $D_{2d}$). The one example of a $C_{4v}$ substituent arrangement is associated with a crown conformation (ideal symmetry, $C_{4v}$). Although at present the number of examples is small, the correlation may have value in predicting the ring conformation for a given substituent orientation, particularly where one substituent is larger than the second. The relationship is probably a consequence of the fact that, in general, the ring conformation adopted will be a compromise between that which on the one hand allows strong ring π-bonding and on the other minimises steric interactions of substituents. Some examples of the operation of these factors follow.

In *cis*-$P_4N_4Cl_4Ph_4$, the configurational symmetry is $C_{4v}$ and steric interactions between phenyl groups are minimised by these groups occupying equatorial positions in a crown ring conformation. π-Bonding here would be weak and interactions might be expected between the four chlorine atoms which occupy axial positions. The molecule, in fact, has a flattened crown conformation ($C_{2v}$ symmetry) which may be rationalised as there is now the possibility for both increased π-bonding and smaller chlorine repulsions. Although π-bonding would be greater with either the chair or saddle ring conformation, neither is expected for a molecule with $C_{4v}$ configurational symmetry as steric repulsions would be too great. A $C_{2h}$ configuration of substituents in conjunction with a chair ring conformation gives the possibility of both low steric interactions and reasonable ring π-bonding, while the alternative crown or saddle conformations would bring larger steric effects into play as the pairs of substituents on adjacent atoms would be eclipsed. For substituents with $D_{2d}$ configurational symmetry, steric effects are small as groups in *cis* positions are on distant (1,5) phosphorus atoms; the saddle conformation also allows relatively strong π-bonding.[11]

These examples presuppose that crystal packing effects are of minimal importance. That this is not always the case is shown by the $C_s$ (crown–saddle) ring conformation found for the 1, *cis*-3, *trans*-5, *trans*-7 isomer of $P_4N_4Cl_4(NMe_2)_4$ when a chair conformation might be expected.[3] This observation is all the more surprising when one notes that the related 1, *trans*-3, *cis*-5, *trans*-7 isomer has a saddle conformation in agreement with prediction on the basis of the configurational symmetry.[10]

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* This designates the maximum possible symmetry of the substituent arrangement and does not consider the symmetry of the ring system.

[11] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.