Crystal Structures of *cis*-2,4,6-Trichloro- and *cis*-2,4,6-Tribromo-2,4,6-trifluorocyclotri(phosphazene)

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The crystal structures of (I), 2,*cis*-4,*cis*-6-trichloro-, and (II), 2,*cis*-4,*cis*-6-tribromo-2,4,6-trifluorocyclotri(phosphazene), have been determined by Patterson and Fourier methods and refined by least squares to R 0·028 [(I) 534 reflexions] and 0·071 [(II), 539 reflexions]. Crystals of both compounds are orthorhombic, space group *Cmc* 21, with $Z = 4$. The ring conformation for (I) is a slight boat while in (II) it is an irregular slight chair. These deviations from planarity together with small differences in some of the chemically equivalent bond distances and angles are attributed to crystal packing effects. Crystal data: (I), $a = 12{\cdot}575(1)$, $b = 9{\cdot}654(1)$, $c = 7{\cdot}75(1)$; (II), $a = 12{\cdot}514(2)$, $b = 10{\cdot}144(1)$, $c = 7{\cdot}987(1)$ Å.

DETAILED structures are available [1-7] for a number of homogeneously substituted triphosphazenes, $P_3N_3X_6$, but only $P_3N_3Cl_3(NMe_2)_3$,[8] which has the substituents arranged non-geminally in the *cis*-configuration, has been investigated. We report the structures of two further compounds of this type, (I), $P_3N_3Cl_3F_3$, and (II), $P_3N_3Br_3F_3$, and assess the influence of different halogen

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atoms in specific orientations on the structure adopted. Of the non-geminal bromo- and chloro-fluorotriphosphazenes, these two are the only ones which are solids at room temperature.

EXPERIMENTAL

The compounds were prepared as described previously[9] and crystals were obtained by sublimation at room temperature, at *ca.* 20 mmHg (I) and *ca.* 0·01 mmHg (II). Because of their reactivity and volatility, the colourless needles (elongated along the b axis) were sealed in silica capillaries.

Structure of (I).—*Crystal data.* $Cl_3F_3N_3P_3$, $M = 298·4$, Orthorhombic, $a = 12·575(1)$, $b = 9·654(1)$, $c = 7·751(1)$ Å, $U = 941·4$ Å^3, $Z = 4$, $D_c = 2·105$ g cm^{-3}, $F(000) = 576$. Space group $Cmc2_1$, from systematic absences: hkl ($h + k \neq 2n$), $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$). Mo-K_α radiation, $\lambda = 0·7107$ Å, μ(Mo-K_α) $= 14·7$ cm^{-1}.

Oscillation and Weissenberg photographs gave the unit-cell parameters initially and these were subsequently refined on a Hilger and Watts four-circle diffractometer. The original photographs clearly indicated that all available crystals were twinned but it was possible to separate the reflexions on the diffractometer. Of 762 independent reflexions measured, 228 had $I < 3\sigma(I)$ and were rejected as being unobserved. Data were corrected for Lorentz and polarization effects but no account was taken of anomalous dispersion and no corrections were made for absorption or secondary extinction. Data reduction and subsequent calculations used the '*X*-Ray '70' programs and atomic scattering factors were obtained from ref. 10.

Determination of the structure. The molecule lies on a mirror plane and the asymmetric unit consists of eight atoms. The positions of the chlorine and phosphorus atoms were obtained from a three-dimensional Patterson map and after two cycles of full-matrix refinement R was 0·323. The two nitrogen and two fluorine atoms were then located from a Fourier synthesis phased by the phosphorus and chlorine atoms. Four cycles of full-matrix refinement reduced R to 0·123 and two further cycles with anisotropic temperature factors gave convergence at R 0·030. A weighting scheme of the form: $w = [1 + (F_0 - B)^2/A]^{-1}$, with $A = 33·6$ and $B = 27·8$ was introduced and after two further cycles of refinement, in which five reflexions having $w\Delta F > 2$ were omitted, final convergence was achieved at 0·028.

Structure of (II).—*Crystal data.* $Br_3F_3N_3P_3$, $M = 431·7$, Orthorhombic, $a = 12·514(2)$, $b = 10·144(1)$, $c = 7·987(1)$ Å, $U = 1014·2$ Å^3, $Z = 4$, $D_c = 2·828$ g cm^{-3}, $F(000) = 792$. Space group $Cmc2_1$, from absences as for (I). μ(Mo-K_α) $=$ 131·1 cm^{-1}.

Preliminary photographs indicated this compound to be isostructural with (I). The intensities of 829 independent reflexions were measured of which 539 were considered observed (as before). The bromine atom positions were determined from a Patterson map and after three cycles of full-matrix isotropic least-squares refinement R was 0·290. A Fourier synthesis phased by these atoms gave the phosphorus and fluorine positions and a difference Fourier allowed location of the nitrogen atoms. After three cycles of isotropic refinement R converged at 0·123 and with anisotropic temperature factors convergence to R 0·083 was achieved after three further cycles of refinement. An absorption correction was then applied assuming that the crystal was cylindrical and R was reduced to 0·072 after three cycles. A parabolic weighting scheme as for (I) with $A = 26·5$ and $B = 31·0$ gave a final reduction of R to 0·071.

Observed and calculated structure factors for the two compounds are listed in Supplementary Publication No. SUP 21080 (9 pp., 1 microfiche).* Final atomic parameters and thermal parameters for (I) are summarized in Tables 1 and 2 and those for (II) in Tables 3 and 4. The numbering of the atoms is shown in Figure 1.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for (I)

Atom	x/a	y/b	z/c
P(1)	1084(1)	1924(1)	4904(4)
P(2)	0	3303(2)	2389(4)
N(1)	0	1427(6)	5683(7)
N(2)	1069(3)	2926(4)	3303(7)
F(1)	1721(2)	2638(3)	6327(5)
F(2)	0	4869(5)	2040(8)
Cl(1)	2009(1)	330(1)	4439(3)
Cl(2)	0	2631(2)	0

TABLE 2

Thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses, for (I)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	382(4)	611(5)	481(5)	2(4)	−39(5)	47(6)
P(2)	551(9)	446(8)	489(4)	0	0	70(8)
N(1)	498(3)	715(3)	473(3)	0	0	184(3)
N(2)	443(18)	734(25)	714(25)	−37(18)	61(19)	180(22)
F(1)	688(18)	1033(22)	777(18)	−144(16)	221(17)	46(18)
F(2)	1018(25)	492(19)	1026(39)	0	0	158(24)
Cl(1)	683(7)	818(9)	943(11)	278(6)	119(8)	100(8)
Cl(2)	1283(17)	903(13)	474(9)	0	0	17(13)

* In the form: $[\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

TABLE 3

Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for (II)

Atom	x/a	y/b	z/c
P(1)	1093(3)	2028(4)	4932(8)
P(2)	0	3381(5)	2535(10)
N(1)	0	1560(22)	5753(28)
N(2)	1073(10)	3057(14)	3440(24)
F(1)	1781(10)	2662(14)	6346(19)
F(2)	0	4840(13)	2108(27)
Br(1)	2056(2)	362(2)	4271(5)
Br(2)	0	2594(3)	0

TABLE 4

Thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses, for (II)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	355(15)	444(17)	402(18)	−26(15)	−43(17)	16(20)
P(2)	392(26)	287(21)	498(31)	0	0	68(24)
N(1)	494(100)	602(115)	459(102)	0	0	279(108)
N(2)	423(60)	515(72)	529(77)	−81(58)	26(66)	59(67)
F(1)	662(57)	850(75)	640(69)	−161(58)	155(59)	181(66)
F(2)	973(106)	202(68)	975(163)	0	0	218(76)
Br(1)	636(10)	565(9)	737(13)	161(8)	116(10)	98(11)
Br(2)	928(21)	738(16)	479(13)	0	0	−35(17)

* See footnote to Table 2.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

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RESULTS AND DISCUSSION

Bond length and angle data are given in Tables 5 and 6 and confirm the previous identification[9] of the compounds by spectroscopic methods as the *cis* non-geminally substituted isomers.

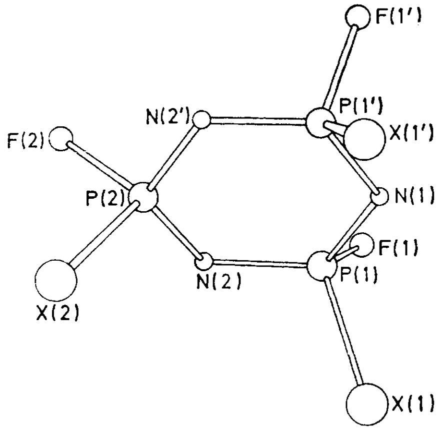

FIGURE 1 Diagram showing numbering of atoms in (I; X = Cl), and (II; X = Br)

The standard deviations for the molecular parameters of (II) are considerably larger than those for (I), but as all the changes in the final cycle of refinement were smaller than the standard deviations, no further improvement is possible. The number of reflexions per parameter is slightly smaller in the case of (II), and this will have some effect, but the major reason is associated with the large scattering power of the bromine atoms.

TABLE 5

Intramolecular distances (Å) and angles (°) for (I)

(*a*) Distances			
P(1)–N(1)	1·567(3)	P(1)–Cl(1)	1·962(2)
P(1)–N(2)	1·573(5)	P(2)–F(2)	1·536(5)
P(2)–N(2)	1·562(5)	P(2)–Cl(2)	1·962(5)
P(1)–F(1)	1·527(4)		
(*b*) Angles			
N(1)–P(1)–N(2)	118·8(3)	P(1)–N(1)–P(1′)	121·0(4)
P(1)–N(2)–P(2)	120·7(3)	F(1)–P(1)–Cl(1)	100·1(2)
N(2)–P(2)–N(2′)	118·7(3)	F(2)–P(2)–Cl(2)	99·2(3)
N(2)–P(2)–Cl(2)	110·5(2)	N(2)–P(2)–F(2)	108·0(2)
N(2)–P(1)–F(1)	107·4(2)	N(2)–P(1)–Cl(1)	110·2(2)
N(1)–P(1)–F(1)	108·4(3)	N(1)–P(1)–Cl(1)	110·2(2)

TABLE 6

Intramolecular distances (Å) and angles (°) for (II)

(*a*) Distances			
P(1)–N(1)	1·589(12)	P(1)–Br(1)	2·141(4)
P(1)–N(2)	1·586(18)	P(2)–F(2)	1·519(15)
P(2)–N(2)	1·559(15)	P(2)–Br(2)	2·177(8)
P(1)–F(1)	1·559(15)		
(*b*) Angles			
N(1)–P(1)–N(2)	119·5(9)	P(1)–N(1)–P(1′)	118·8(14)
P(1)–N(2)–P(2)	120·1(9)	F(1)–P(1)–Br(1)	101·2(6)
N(2)–P(2)–N(2′)	118·8(10)	F(2)–P(2)–Br(2)	98·5(9)
N(2)–P(2)–Br(2)	110·8(7)	N(2)–P(2)–F(2)	108·0(7)
N(2)–P(1)–F(1)	106·3(8)	N(2)–P(1)–Br(1)	110·1(6)
N(1)–P(1)–F(1)	107·4(10)	N(1)–P(1)–Br(1)	110·5(8)

The P_3N_3 ring in both compounds is slightly puckered (see Figure 2) to give a slight boat conformation for (I) and an irregular slight chair for (II). In each case the angle between the planes containing respectively the phosphorus and nitrogen atoms is *ca.* 3·8°. The equations for the mean ring plane and a number of other important planes are given in Table 7.

TABLE 7

Equations of planes * and, in square brackets, deviations (Å) of relevant atoms from them

(*a*) Compound (I)	
Plane (1): P(1), P(2), N(1), N(2)	$0{\cdot}807Y + 0{\cdot}591Z = 3{\cdot}742$
[P(1) 0·002, P(2) −0·075, N(1) −0·028, N(2) 0·050]	
Plane (2): P(1), P(2)	$0{\cdot}826Y + 0{\cdot}564Z = 3{\cdot}677$
[N(1) −0·056, N(2) 0·099]	
Plane (3): N(1), N(2)	$0{\cdot}787Y + 0{\cdot}617Z = 3{\cdot}802$
[P(1) 0·005, P(2) −0·151]	
Plane (4): Cl(1), Cl(2)	$0{\cdot}840Y + 0{\cdot}542Z = 2{\cdot}134$
Plane (5): F(1), F(2)	$0{\cdot}839Y + 0{\cdot}544Z = 4{\cdot}805$
(*b*) Compound (II)	
Plane (1): P(1), P(2), N(1), N(2)	$0{\cdot}739Y + 0{\cdot}610Z = 4{\cdot}058$
[P(1) −0·025, P(2) −0·105, N(1) −0·001, N(2) 0·078]	
Plane (2): P(1), P(2)	$0{\cdot}831Y + 0{\cdot}582Z = 3{\cdot}967$
[N(1) −0·004, N(2) 0·156]	
Plane (3): N(1), N(2)	$0{\cdot}772Y + 0{\cdot}635Z = 4{\cdot}142$
[P(1) −0·050, P(2) −0·207]	
Plane (4): Br(1), Br(2)	$0{\cdot}833Y + 0{\cdot}553Z = 2{\cdot}193$
Plane (5): F(1), F(2)	$0{\cdot}837Y + 0{\cdot}546Z = 5{\cdot}032$

* In each plane symmetry-related atoms are included. Equations are in terms of orthogonal (Å) co-ordinates.

There are differences in a number of the chemically equivalent bond distances and angles, *e.g.* in (I) F(2)–P(2)–Cl(2) is smaller by 0·9° than F(1)–P(1)–Cl(1), while in (II) the corresponding difference is 2·7°. In addition there is a significant difference between the two P–Br distances and although the standard deviations are larger, the difference in the P–F bond lengths is also probably significant. The cumulative effect of these differences and the slight puckering of the rings is to make the planes containing the fluorine atoms and those containing the chlorine or bromine atoms almost parallel. The angles between the planes are 0·11 (I) and 0·43° (II);

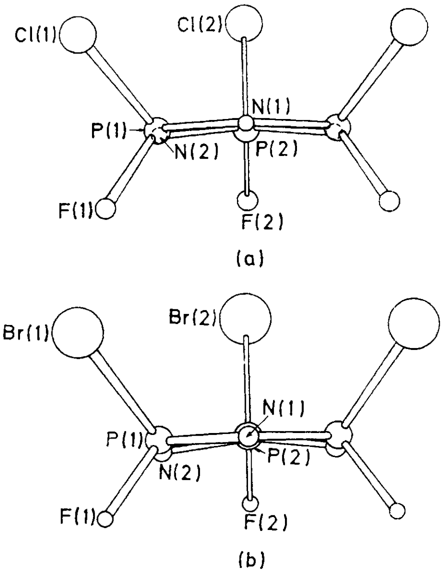

FIGURE 2 Diagram showing the ring conformation (a) in (I) and (b) in (II)

thus it seems likely that crystal-packing effects are the driving force and there is no significance from the point of view of bonding. There is no spectroscopic evidence from solutions of these compounds that would imply non-equivalence between the various segments of the molecules.

With the exception of the fluoro-compound, all the trimeric compounds for which *X*-ray data are available have puckered ring systems and in this general respect there is a similarity with the analogous tetramers. However the physical restraints imposed by a six-membered ring system leads to only slight deviations from planarity in comparison with those observed for tetramers. In the latter, ring puckering seems to be associated with both the electronic and steric requirements of the exocyclic groups and takes place so as to maximize ring π-bonding while minimizing steric interactions between groups on neighbouring phosphorus atoms.[11,12] With trimeric compounds, on the other hand, the small deviations observed seem to be governed primarily by factors associated with crystal packing.

In phosphazenes of the type $(PNXY)_n$ ($n = 3$ or 4) there is evidence from bond lengths for the transfer of charge from X to Y, *e.g.* in *cis*-2,4,6-tris(dimethylamino)-trichlorocyclotriphosphazene, the P–N(amine) bond is shorter than in the hexa-amide while the P–Cl bond is longer than in $P_3N_3Cl_6$. The extent of such charge transfer in the mixed halogen compounds considered here will be much less, but as expected the P–Cl bond distance (1·062 Å) is shorter than that in $P_3N_3Cl_6$ (1·985 Å).[2] The corresponding increase in the P–F bond length is not observed but this may be due to the small size of the expected effect. Certainly in other situations, *e.g.* the non-geminally substituted $P_4N_4F_4(NMe_2)_4$ isomers,[11,13] the expected increase is observed. Although more extensive charge transfer is expected in (II), the large standard deviations associated with the P–Br distances make it difficult to show this conclusively.

The change in P–N ring bond lengths in trimeric compounds has been correlated with the electronegativity of the exocyclic groups,[5] where an increase in electronegativity leads to a shorter bond presumably as a result of increased in-plane π-bonding. This effect seems to be observed in the present compounds where the mean ring bond length decreases from 1·580 in (II) to 1·567 Å in (I), though the former is subject to a high standard deviation. Similar correlations have also been suggested between electronegativity and the ring angles at phosphorus and nitrogen, but when the data for the larger number of compounds now available are included neither the correlation with P–N distance nor with ring angles is as systematic as appeared previously.

[4/637 *Received*, 28*th March*, 1974]

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