Crystal Structure of 4,4,6,6-Tetrachloro-2,2-di-t-butylaminocyclotriphosphazene

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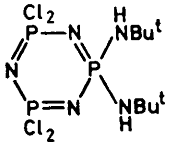
Crystals of the title compound are orthorhombic, with *a* = 20.41(1), *b* = 11.96(1), and *c* = 15.97(1) Å, space group *Pna*2_1, and *Z* = 8. The atomic positions have been determined by direct methods from *X*-ray diffractometer data and refined by full-matrix least squares to *R* 0.062 for 2 139 observed reflections. The two t-butylamino-groups are attached to the same phosphorus atom and the compound is thus the geminal isomer. The asymmetric unit consists of two independent molecules with similar molecular parameters which are linked together by two hydrogen bonds. The P_3N_3 rings both have a slight boat conformation with P–N(ring) bonds of 1.61 Å for the amine-substituted phosphorus atoms and 1.56 Å for those carrying chlorine substituents. Bond angles in the ring also vary. Mean values for other parameters are P–N(amine) 1.609, P–Cl 2.001 Å, N–P–N(*exo*) 104.0 and Cl–P–Cl 99.3°.

SUBSTITUTION reactions of hexachlorotriphosphazene, $N_3P_3Cl_6$, with amines can follow either a geminal path, in which a second substitution step takes place at the phosphorus atom already carrying an amine substituent, or a non-geminal path where the second step occurs preferentially at a PCl_2 centre. In general terms, the nature of the amine has a dominant influence on the reaction path adopted but, in some cases, the course of the reaction can be modified by a change in solvent.

Reactions of t-butylamine with $N_3P_3Cl_6$ are known to give good yields of the disubstituted compound $N_3P_3Cl_4(NBu^tH)_2$ which was shown,[1] on the basis of the ^1H n.m.r. spectrum of the product of exhaustive dimethylaminolysis, to have the geminal structure:



The ^1H n.m.r. spectrum of the compound itself in CCl_4 solution shows a strong singlet at δ 1.2 and a weak doublet centred on δ 2.4 due respectively to the equivalent methyl groups and the NH protons. In the NH stretching region of the i.r. spectrum, however, there are two sharp peaks at 3 440 and 3 280 cm^{-1}; two similar bands occur for the corresponding di-isopropylamine derivative while one broad band is found for the methylamine and ethylamine analogues which have the alternative non-geminal structure. This information points to the possible differentiation of the amine hydrogen atoms for the t-butylamine and isopropylamine derivatives by, perhaps, intra- or inter-molecular hydrogen-bond formation, and to investigate this the crystal structure of $N_3P_3Cl_4(NBu^tH)_2$ has been determined.

EXPERIMENTAL

Tetrachlorodi-t-butylaminotriphosphazene.—t-Butylamine (17 g, 0.23 mol) in diethyl ether (20 cm^3) was added slowly over 1 h to a well stirred solution of resublimed hexachlorotriphosphazene (20 g, 0.06 mol) in ether (500 cm^3) at −78 °C. After allowing the mixture to warm to room temperature, the precipitated t-butylamine hydrochloride was filtered off and the solvent was removed from the mother liquor. The residue was fractionally crystallized from light petroleum (b.p. 60—80 °C) to give pure samples of the mono- and di-substituted compounds, with melting points of 110 (lit.,[1] −10 to −11) and 121 °C (lit.,[1] 120—122 °C) respectively (Found: C, 12.8; H, 2.5; N, 13.8. Calc. for $C_4H_{10}Cl_5N_4P_3$: C, 12.6; H, 2.6; N, 14.7. Found: C, 22.7; H, 5.3; N, 16.4. Calc. for $C_8H_{20}Cl_4N_5P_3$: C, 22.9; H, 4.7; N, 16.9%).

Crystal Data.—$C_8H_{20}Cl_4N_5P_3$, M = 420.8, Orthorhombic, a = 20.41(1), b = 11.96(1), c = 15.97(1) Å, U = 3 898.3 Å^3, Z = 8, D_c = 1.433 g cm^{-3}, $F(000)$ = 1 728, space group *Pna*2_1 from systematic absences and subsequent refinement, Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 8.4 cm^{-1}.

The unit-cell parameters and space group originally obtained from oscillation and Weissenberg photographs were refined by a least-squares procedure on the positions of 12 strong reflections accurately measured on a Hilger and Watts four-circle diffractometer. Intensity data were then collected for *ca.* 3 900 reflections of which 2 139 with $I > 3\sigma(I)$ were considered observed. Corrections were applied for Lorentz and polarization effects, but not for absorption and secondary extinction. Atomic scattering factors were taken from ref. 2.

The ambiguity in the space group, *Pna*2_1 or *Pnma*, was resolved by analysis of the intensity statistics. This clearly indicated the absence of a centre of symmetry with mean $|E|$ 0.914 and $|E^2 - 1|$ 0.646, compared with the theoretical values $|E|$ 0.886, $|E^2 - 1|$ 0.736 for non-centrosymmetric and $|E|$ 0.798, $|E^2 - 1|$ 0.968 for centrosymmetric structures. The structure was then solved by direct methods by use of the MULTAN programs.[3] An E map based on the best set of phases revealed possible positions for six phosphorus, eight chlorine, and three nitrogen atoms. Refinement of these positions and all subsequent calculations used the CRYSTALS package.[4] One cycle of full-matrix least-squares refinement reduced R to 0.267 and a difference-Fourier synthesis revealed positions for another six nitrogen and ten carbon atoms. After a further cycle of refinement R was 0.189 and a difference map produced positions for the missing nitrogen and six carbon atoms. Refinement with isotropic thermal parameters converged at R 0.138 after two additional cycles and at 0.069 after three cycles with anisotropic thermal parameters. Although a difference-Fourier synthesis at this stage showed a number of peaks with intensities between 0.3 and 0.5 e Å^{-3} they could not be

TABLE 1

Fractional co-ordinates ($\times 10^3$), with estimated standard deviations in parentheses

	x/a	y/b	z/c
Cl(1)	220.2(2)	983.4(5)	914.9
Cl(2)	368.4(3)	1 006.5(5)	923.1(3)
Cl(3)	231.8(4)	593.5(5)	853.8(5)
Cl(4)	381.1(4)	600.5(5)	833.1(5)
P(1)	300.0(2)	919.2(3)	861.2(2)
P(2)	303.1(3)	700.2(3)	819.7(3)
P(3)	299.9(2)	857.6(3)	692.0(2)
N(1)	307.3(13)	794.1(13)	887.7(9)
N(2)	293.6(6)	731.7(8)	727.6(7)
N(3)	301.3(6)	949.7(9)	765.8(6)
N(4)	239.3(6)	875.6(9)	626.8(9)
N(5)	364.1(6)	885.5(11)	637.3(9)
C(1)	170.8(6)	836.9(12)	630.8(9)
C(2)	165.6(8)	724.7(14)	586.3(12)
C(3)	130.6(9)	923.5(15)	581.8(13)
C(4)	144.8(7)	831.2(17)	719.4(12)
C(5)	393.0(8)	830.0(14)	564.1(12)
C(6)	455(2)	795(6)	587(4)
C(7)	401(4)	908(3)	502(3)
C(8)	354(1)	744(3)	527(2)
Cl(11)	450.1(3)	1 322.3(4)	899.8(3)
Cl(12)	557.7(2)	1 419.7(4)	789.9(4)
Cl(13)	589.9(2)	1 045.7(4)	663.7(4)
Cl(14)	505.3(2)	943.6(4)	801.3(4)
P(11)	492.8(2)	1 295.6(3)	788.8(2)
P(12)	511.6(2)	1 084.2(3)	734.8(3)
P(13)	410.0(1)	1 213.2(2)	665.1(2)
N(11)	531.8(6)	1 183.4(11)	794.5(10)
N(12)	448.5(5)	1 097.5(8)	680.4(7)
N(13)	443.4(5)	1 313.3(8)	716.7(6)
N(14)	407.9(6)	1 254.5(9)	569.3(7)
N(15)	335.6(5)	1 189.4(10)	687.0(7)
C(11)	456.3(7)	1 311.9(13)	518.1(8)
C(12)	438.6(10)	1 294.9(17)	427.1(10)
C(13)	453.0(10)	1 437.2(15)	535.9(12)
C(14)	526.3(9)	1 271.2(19)	534.1(10)
C(15)	277.7(6)	1 258.3(11)	697.4(12)
C(16)	287.5(9)	1 372(2)	667(2)
C(17)	261(2)	1 271(2)	787(2)
C(18)	221(1)	1 204(2)	664(4)

associated with the hydrogen atoms of the t-butyl groups and these were therefore placed at the calculated positions. Four cycles of refinement with fixed hydrogen co-ordinates and a weighting scheme of the type $w = 1/\{1 + [(F_o - 16)/11]^2\}$ gave final convergence at R 0.062.

Table 1 contains the atomic co-ordinates, while the calculated hydrogen positions, anisotropic thermal parameters for the heavy atoms, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22531 (20 pp.).* The numbering of the atoms is shown in Figure 1.

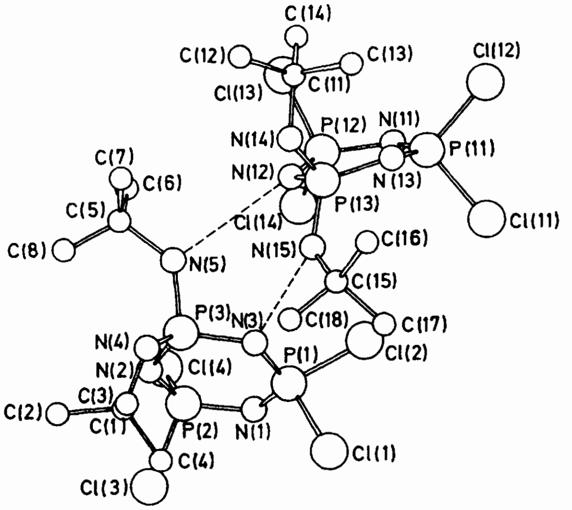


FIGURE 1 Numbering of the atoms

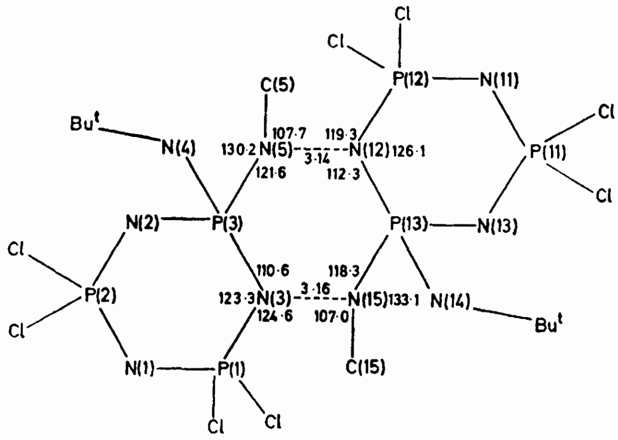


FIGURE 2 Bond distances and angles in the double hydrogen-bond system

RESULTS AND DISCUSSION

This crystallographic determination confirms that the two t-butylamine groups are arranged geminally, but it also shows that the two crystallographically independent molecules in the asymmetric unit are probably linked by two hydrogen bonds. As mentioned above, it was not possible to locate any hydrogen-atom positions convincingly from a final difference map, but the structure contains two short intermolecular contacts (see Figure 1). In each case these are between an amine nitrogen atom of one molecule and a ring nitrogen atom of the second, *i.e.* N(5) $\cdots$ N(12) 3.14 and N(15) $\cdots$ N(3) 3.16 Å. In addition, the general geometry about the two potential hydrogen bonds (see Figure 2) is completely appropriate. The hydrogen-bond distances found here are similar to those found in the structure of $N_3P_3F_5(NH_2)$.[5] In this compound both hydrogen atoms of the NH_2 group are bound to ring nitrogen atoms of two different neighbours. In contrast, there are no apparent hydrogen bonds formed in the analogous geminally substituted diamine, $N_3P_3F_4(NH_2)_2$.[6] In the present compound, there are no intermolecular contacts of <4.2 Å to either N(4) or N(14), the t-butylamine nitrogens not involved in the intermolecular hydrogen bonds.

Molecular dimensions for the two molecules in the asymmetric unit are very similar as shown by the bond distances and angles in Table 2. The mean P–Cl distance (2.001 Å) is little different from that in $N_3P_3Cl_6$ (1.993 Å),[7] but the exocyclic Cl–P–Cl angle with a mean of 99.3° is closer to that in the geminally substituted $N_3P_3Cl_3(NMe_2)_3$ (99.6°)[8] than in $N_3P_3Cl_6$ (101.4°).[7] The exocyclic P–N distances (mean 1.609 Å) are, as expected, much shorter than the single-bond value with the usual implication in this type of compound of back co-ordin-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 2

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

P(1)–Cl(1)	1.993(6)	P(11)–Cl(11)	2.000(5)
P(1)–Cl(2)	2.005(6)	P(11)–Cl(12)	1.989(5)
P(2)–Cl(3)	2.011(9)	P(12)–Cl(13)	2.014(6)
P(2)–Cl(4)	2.000(8)	P(12)–Cl(14)	1.993(5)
P(3)–N(4)	1.631(12)	P(13)–N(14)	1.609(11)
P(3)–N(5)	1.611(13)	P(13)–N(15)	1.583(11)
P(1)–N(1)	1.56(2)	P(11)–N(11)	1.56(1)
P(1)–N(3)	1.57(1)	P(11)–N(13)	1.55(1)
P(2)–N(1)	1.57(1)	P(12)–N(11)	1.58(1)
P(2)–N(2)	1.53(1)	P(12)–N(12)	1.56(1)
P(3)–N(2)	1.61(1)	P(13)–N(12)	1.61(1)
P(3)–N(3)	1.61(1)	P(13)–N(13)	1.60(1)
N(4)–C(1)	1.47(2)	N(14)–C(11)	1.45(2)
C(1)–C(2)	1.52(2)	C(11)–C(12)	1.51(2)
C(1)–C(3)	1.53(2)	C(11)–C(13)	1.53(2)
C(1)–C(4)	1.51(2)	C(11)–C(14)	1.53(2)
N(5)–C(5)	1.47(2)	N(15)–C(15)	1.45(2)
C(5)–C(6)	1.37(4)	C(15)–C(16)	1.46(2)
C(5)–C(7)	1.37(4)	C(15)–C(17)	1.48(4)
C(5)–C(8)	1.43(3)	C(15)–C(18)	1.43(3)
N(1)–P(1)–N(3)	119.0(7)	N(11)–P(11)–N(13)	119.6(6)
N(1)–P(2)–N(2)	119.8(7)	N(11)–P(12)–N(12)	118.4(6)
N(2)–P(3)–N(3)	112.4(6)	N(12)–P(13)–N(13)	110.9(5)
P(1)–N(1)–P(2)	119.6(9)	P(11)–N(11)–P(12)	118.5(8)
P(2)–N(2)–P(3)	123.9(7)	P(12)–N(12)–P(13)	125.1(6)
P(1)–N(3)–P(3)	123.4(7)	P(11)–N(13)–P(13)	123.8(6)
Cl(1)–P(1)–Cl(2)	99.0(3)	Cl(11)–P(11)–Cl(12)	99.4(3)
Cl(1)–P(1)–N(1)	109.3(9)	Cl(11)–P(11)–N(11)	107.9(7)
Cl(1)–P(1)–N(3)	110.1(5)	Cl(11)–P(11)–N(13)	110.8(4)
Cl(2)–P(1)–N(1)	107.4(8)	Cl(12)–P(11)–N(11)	107.5(6)
Cl(2)–P(1)–N(3)	110.3(5)	Cl(12)–P(11)–N(13)	109.8(5)
Cl(3)–P(2)–Cl(4)	99.8(4)	Cl(13)–P(12)–Cl(14)	99.1(2)
Cl(3)–P(2)–N(1)	107.9(9)	Cl(13)–P(12)–N(11)	107.8(6)
Cl(3)–P(2)–N(2)	108.9(5)	Cl(13)–P(12)–N(12)	111.4(5)
Cl(4)–P(2)–N(1)	108.1(9)	Cl(14)–P(12)–N(11)	109.2(6)
Cl(4)–P(2)–N(2)	110.6(6)	Cl(14)–P(12)–N(12)	109.2(4)
N(4)–P(3)–N(5)	104.1(8)	N(14)–P(13)–N(15)	103.9(6)
N(4)–P(3)–N(2)	106.7(6)	N(14)–P(13)–N(12)	114.9(6)
N(4)–P(3)–N(3)	112.9(6)	N(14)–P(13)–N(13)	105.7(6)
N(5)–P(3)–N(2)	116.7(7)	N(15)–P(13)–N(12)	106.3(6)
N(5)–P(3)–N(3)	103.9(6)	N(15)–P(13)–N(13)	115.4(6)
C(1)–N(4)–P(3)	130.6(11)	C(11)–N(14)–P(13)	131.5(9)
C(2)–C(1)–N(4)	108.9(12)	C(12)–C(11)–N(14)	108.4(13)
C(3)–C(1)–N(4)	105.9(12)	C(13)–C(11)–N(14)	108.8(15)
C(4)–C(1)–N(4)	112.7(12)	C(14)–C(11)–N(14)	113.0(12)
C(2)–C(1)–C(3)	108.6(12)	C(12)–C(11)–C(13)	107.5(14)
C(2)–C(1)–C(4)	111.9(14)	C(12)–C(11)–C(14)	110.0(14)
C(3)–C(1)–C(4)	108.7(14)	C(13)–C(11)–C(14)	108.8(15)
C(5)–N(5)–P(3)	131.6(10)	C(15)–N(15)–P(13)	134.8(10)
C(6)–C(5)–N(5)	107.0(20)	C(16)–C(15)–N(15)	112.3(11)
C(7)–C(5)–N(5)	108.1(17)	C(17)–C(15)–N(15)	110.0(15)
C(8)–C(5)–N(5)	115.9(15)	C(18)–C(15)–N(15)	111.0(15)
C(6)–C(5)–C(7)	107(4)	C(16)–C(15)–C(17)	105(2)
C(6)–C(5)–C(8)	114(3)	C(16)–C(15)–C(18)	114(2)
C(7)–C(5)–C(8)	105(3)	C(17)–C(15)–C(18)	103(3)

ation of the amine lone pairs of electrons into phosphorus orbitals. For comparison, values of 1.628—1.642 Å were found in *gem*-$N_3P_3Cl_3(NMe_2)_3$,[8] 1.652 Å in $N_3P_3(NMe_2)_6$,[9] and 1.600 Å in both $N_3P_3F_5(NH_2)$ [5] and $N_3P_3F_4(NH_2)_2$.[6] The shortness of the exocyclic P–N bonds is strong evidence against any participation of the amine lone pair itself in hydrogen-bond formation; a further implication is that in this geminally substituted compound the most basic centres are the ring nitrogen atoms flanking the $P(NBu^tH)_2$ group, rather than the nitrogen atoms of the amine groups. This would be in general agreement with the accepted electronic nature of this type of compound. The basicity however is not high since the pK_a' value in nitrobenzene is below the lower limit of the experimental method.[10] In passing it may be noted that there is a possible inequality in the P–N(amine) distances, the shorter being that involved in hydrogen bonding. The exocyclic N–P–N angles of 104° should be compared with values of 102.4 in $N_3P_3F_4(NH_2)_2$,[6] 103.7° in $N_3P_3Cl_3(NMe_2)_3$,[8] and 101.8° (mean) in $N_3P_3(NMe_2)_6$.[9]

Although the two chlorine atoms in each PCl_2 group are very similarly orientated with respect to the local NPN ring segment as shown by the closeness of the two angles with the flanking ring nitrogen atoms, this is not so with the amine nitrogen atoms at P(3) and P(13). For the former, N(5) is distorted toward N(3), *i.e.* the angle N(5)–P(3)–N(3) is 103.9° while N(5)–P(3)–N(2) is 116.7° whereas N(4) is orientated toward N(2). In the second molecule, the angle N(15)–P(13)–N(12) (106.3°) is smaller than the corresponding angle to N(13) (115.4°), while with N(14) the effect is opposite and this atom is distorted toward N(13).

The relative orientations of the amine groups will be influenced by two factors. The first, which is steric, will lead to staggering of the distorted-tetrahedral arrangements at P(3) and (13) to accommodate better the amine residues and promote better π-back bonding to phosphorus. The second is a result of geometrical constraints imposed by the presence of the hydrogen bonds. Differences in the relative orientations of the t-butylamine groups are also emphasized by the torsion angles given in Table 3.

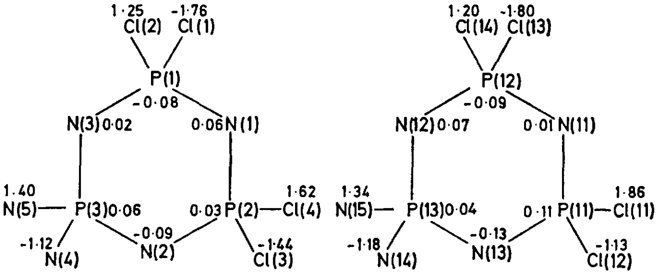

FIGURE 3 Deviation (Å) of specific atoms from the mean ring plane

TABLE 3

Torsion angles (°) of P–N (amine) bonds

N(2)–P(3)–N(4)–C(1)	38.6
N(3)–P(3)–N(4)–C(1)	−85.4
N(5)–P(3)–N(4)–C(1)	162.2
N(2)–P(3)–N(5)–C(5)	53.0
N(3)–P(3)–N(5)–C(5)	177.0
N(4)–P(3)–N(5)–C(5)	−64.2
N(13)–P(13)–N(14)–C(11)	41.3
N(12)–P(13)–N(14)–C(11)	−81.2
N(15)–P(13)–N(14)–C(11)	164.0
N(13)–P(13)–N(15)–C(15)	46.0
N(12)–P(13)–N(15)–C(15)	169.3
N(14)–P(13)–N(15)–C(15)	−69.7

Both the P_3N_3 rings have slight boat conformations (see Figure 3) with mean deviations of the ring atoms from the appropriate best plane of 0.057 and 0.075 Å respectively for the P(1) and P(11) molecules. Figure 4 includes the torsion angles of the ring bonds and shows again that the deviation from planarity is slightly greater for the P(11) molecule. These deviations, of course, are small in comparison with those found in derivatives of the more flexible tetrameric compound, $N_4P_4Cl_8$.

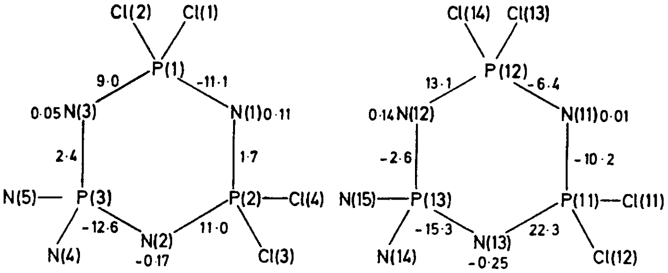

FIGURE 4 Deviation (Å) of the ring nitrogen atoms from the plane through the appropriate phosphorus atoms; torsion angles of the ring bonds are also shown

The unsymmetrical substitution in the present compound does however have substantial structural consequences, similar to those observed previously for $N_3P_3F_4(NH_2)_2$.[6] For example, the P–N ring bonds involving P(3) and P(13), *i.e.* those carrying the t-butylamine substituents, average 1.61 Å compared with a mean value of 1.56 Å for bonds to the PCl_2 groups. Endocyclic angles are also affected with those at P(3) and P(13) being smaller (111.7°) than those at the chlorine-substituted phosphorus atoms (119.2°). Similarly, the endocyclic angles at the nitrogen atoms flanking P(3) and P(13) (124.1°) are larger than those at N(1) and N(11) (119.1°) which are flanked by two PCl_2 groups. The major reason for these structural differences is the acceptance by P(3) and P(13) of π-electron density from the t-butylamine groups, and the consequent reduced tendency to accept electron density from the flanking ring nitrogen atoms.

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