Stereochemistry of Phosphorus Compounds. Part II.[1] Crystal and Molecular Structure of 1,3-Di-t-butyl-2,4-dichlorodiazadiphosphetidine †

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The crystal and molecular structure of the title compound has been determined by *X*-ray analysis. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$ in a cell of dimensions a = 15·818(7), b = 15·742(6), c = 11·608(6) Å. The structure was solved by direct methods and refined to R 0·098 by the method of full-matrix least-squares, by use of 926 intensity data measured on a diffractometer. The crystals contain discrete molecules of almost exact C_s symmetry. The $[P-N]_2$ ring is slightly puckered and the chlorine atoms are mutually *cis*. There are no significant differences between chemically equivalent bond lengths, and mean values are P–N 1·689(4), P–Cl 2·105(9), N–C 1·498(11), and C–C 1·564(8) Å.

STRUCTURAL studies have been carried out on many molecules containing four-membered $[P-N]_2$ rings in which the phosphorus atoms are formally in the +v oxidation state and four- or five-co-ordinate.[1,2] The recent discovery of synthetic routes to the unusual diazadiphosphetidine molecules (I)[3] and (II)[4] now

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† No reprints available.

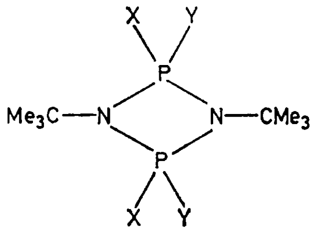
[1] Part I, Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 239.

[2] M. B. Peterson and A. J. Wagner, *J.C.S. Dalton*, 1973, 106, and refs. therein.

[3] O. J. Scherer and P. Klusmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 752.

[4] J. F. Nixon and B. Wilkins, *Z. Naturforsch.*, 1970, **25b**, 649.

permits the extension of these studies to systems containing $[P-N]_2$ rings in which the phosphorus atoms are three-co-ordinate and in the +III oxidation state. Accordingly, the crystal-structure analysis of the title compound (I) has been undertaken. The results of this work, briefly reported earlier,[5] permit the bonding and ring conformation in (I) to be compared with the



(I) X = lone pair, Y = Cl
(II) X = lone pair, Y = F
(III) X = O, Y = Cl

corresponding features of the dioxocyclodiphosphazane molecule (III), the structure of which was described in Part I.[1]

EXPERIMENTAL

Crystals of (I) decompose in the atmosphere and melt at 42 °C. For the X-ray measurements a crystal of dimensions 0·38 × 0·34 × 0·57 mm was selected from a freshly sublimed sample and sealed in a Lindemann glass capillary in an atmosphere of dry nitrogen.

Crystal Data.—$C_8H_{18}Cl_2N_2P_2$, $M = 275·1$, Orthorhombic, $a = 15·818(7)$, $b = 15·742(6)$, $c = 11·608(6)$ Å, $U = 2890·5$ Å^3, $D_m = 1·22$ (by flotation), $Z = 8$, $D_c = 1·264$ g cm^{-3}, $F(000)$ 1152, Mo-K_α radiation, $\lambda = 0·71096$ Å, μ(Mo-K_α) = 6·4 cm^{-1}. Space group *Pbca*.

TABLE 1

Fractional co-ordinates (× 10^4), and vibrational parameters

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	4561(3)	4556(3)	2535(5)	119(3)	64(2)	211(9)	−6(2)	−57(4)	−37(3)
Cl(2)	2570(3)	2891(3)	2418(5)	102(3)	93(3)	275(11)	4(2)	95(4)	42(4)
P(1)	4396(2)	4032(2)	874(4)	50(2)	38(1)	140(6)	−6(1)	−6(3)	6(3)
P(2)	3158(2)	3012(2)	808(4)	47(2)	43(2)	168(6)	−7(1)	1(3)	5(3)
N(1)	4194(5)	2996(5)	1123(10)	55(5)	36(4)	89(14)	−1(4)	−15(6)	12(6)
N(2)	3332(5)	4069(6)	705(11)	50(5)	43(5)	141(17)	−1(4)	−16(7)	4(7)
C(1)	4771(8)	2293(7)	1493(18)	59(7)	38(7)	192(31)	11(5)	−12(10)	−8(10)
C(2)	4421(9)	1470(8)	870(20)	101(9)	39(6)	296(35)	12(6)	−67(14)	−47(13)
C(3)	5654(7)	2505(9)	924(17)	55(7)	93(9)	171(27)	21(7)	3(11)	24(13)
C(4)	4777(10)	2235(11)	2840(17)	144(13)	119(14)	40(28)	21(9)	−23(11)	28(13)
C(5)	2825(8)	4714(9)	56(17)	66(8)	57(8)	144(28)	24(6)	−25(11)	13(11)
C(6)	3090(8)	5597(8)	502(15)	90(9)	44(7)	175(27)	11(6)	18(10)	−6(10)
C(7)	1880(8)	4540(9)	385(15)	52(8)	90(10)	176(28)	7(6)	−18(9)	−30(11)
C(8)	2975(11)	4623(11)	−1251(21)	161(16)	108(13)	117(35)	68(11)	−10(14)	17(14)

The form of the anisotropic temperature factor was $\exp[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Weissenberg and precession photographs allowed the space group to be determined and yielded preliminary values of the unit-cell parameters. Final values of these parameters were obtained by a least-squares method from the setting angles of twelve reflexions manually centred on a Hilger and Watts Y 290 diffractometer.

Intensity Measurements.—The intensities of all independent reflexions with θ(Mo-K_α) ⩽ 25° were measured on the diffractometer, by use of zirconium-filtered molybdenum radiation in conjunction with a pulse-height analyser. The crystal was deliberately mis-set so that the crystallographic c axis made an angle of *ca.* 10° with the diffractometer ϕ axis. The θ—2θ scan technique was used; the scan step in θ was 0·01° and the counting time for each step was 1·3 s. Each reflexion was scanned through a range of 0·60° in θ, and the local background was counted for 15 s at each end of the scan. The intensities of two strong reflexions, measured periodically during the experiment, showed only random fluctuations of <3% of their mean values.

The integrated intensities, I, and their standard deviations, $\sigma(I)$, were calculated as described previously,[1] the value of the factor q being taken as 0·04. Lorentz and polarisation factors were applied, but no correction was made for absorption by the crystal and the capillary. Of the 2452 reflexions for which intensities measurements were made only 956, having $I \geqslant 2\sigma(I)$, were used in the subsequent analysis. At a late stage in the refinement it was discovered that the last 30 reflexions measured, all of which had $h = 0$, were in error because of diffractometer malfunction. Remeasurement proved impossible and the analysis was finally carried out with 926 reflexions.

Structure Analysis.—The structure was solved by direct methods, by use of Long's program REL in which the phases are determined by reiterative application of Sayre's equation.[6] A total of 212 reflexions with $E \geqslant 1·9$ were used. In addition to the three reflexions which define the origin, a further four were assigned symbolic phases. Of the sixteen possible solutions, the most self consistent proved to be correct and all the non-hydrogen atoms, with the exception of three methyl carbon atoms, were located in the resulting E map. The positions of the three missing carbon atoms were obtained from a subsequent difference synthesis.

The structure was refined by the method of full-matrix least-squares. The function minimised was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$. The weights, w, were derived from the standard deviations of $|F_o|$.[7] Atomic scattering factors were taken from ref. 8. No allowance was made for the anomalous scattering of the chlorine and phosphorus atoms.

The refinement of a scale factor and the positional and isotropic thermal parameters of the non-hydrogen atoms brought R to 0·26. When allowance was made for aniso-

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[5] K. W. Muir and J. F. Nixon, *Chem. Comm.*, 1971, 1405.

[6] R. E. Long, Doctoral Dissertation, University of California, Los Angeles, 1965.

[7] K. W. Muir, *J. Chem. Soc.* (*A*), 1971, 2663.

[8] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

tropic vibrational motion of all the non-hydrogen atoms the refinement converged with R 0·098 and R' 0·092. In the last cycle none of the 127 parameters altered by $>0·07\sigma$. The adequacy of the weighting scheme was confirmed by an analysis of mean values of $w\Delta^2$, taken as a bivariant function of $|F_0|$ and $\sin\theta/\lambda$. In the final difference synthesis the function values ranged from 0·37 to $-0·34$ eÅ^{-3} whereas the minimum peak-height of a carbon atom in the final synthesis of electron density was 3·2 eÅ^{-3}. A low-angle difference synthesis, calculated with the final F_o and F_c values, did not show clearly the positions of the hydrogen atoms. Extinction corrections did not appear to be necessary. Final atomic parameters, and a selection of functions derived from them, are presented in Tables 1 and 2. Observed structure amplitudes and calculated structure factors are listed in Supplementary Publication No. SUP 21166 (7 pp., 1 microfiche).*

TABLE 2

Molecular dimensions

(*a*) Bond lengths (Å)			
P(1)–Cl(1)	2·114(7)	P(2)–Cl(2)	2·096(7)
P(1)–N(1)	1·687(9)	P(2)–N(1)	1·681(9)
P(1)–N(2)	1·695(8)	P(2)–N(2)	1·691(9)
N(1)–C(1)	1·498(15)	N(2)–C(5)	1·497(15)
C(1)–C(2)	1·584(18)	C(5)–C(6)	1·541(18)
C(1)–C(3)	1·581(18)	C(5)–C(7)	1·567(18)
C(1)–C(4)	1·566(23)	C(5)–C(8)	1·543(24)
Means			
P–Cl	2·105(9)	N–C	1·498(11)
P–N	1·689(4)	C–C	1·564(8)
(*b*) Interbond angles (°)			
Cl(1)–P(1)–N(1)	104·1(5)	Cl(2)–P(2)–N(1)	103·7(4)
Cl(1)–P(1)–N(2)	102·4(4)	Cl(2)–P(2)–N(2)	103·0(5)
N(1)–P(1)–N(2)	82·3(4)	N(1)–P(2)–N(2)	82·6(4)
P(1)–N(1)–P(2)	97·6(5)	P(1)–N(2)–P(2)	96·9(5)
P(1)–N(1)–C(1)	130·5(7)	P(1)–N(2)–C(5)	127·8(9)
P(2)–N(1)–C(1)	131·9(7)	P(2)–N(2)–C(5)	128·0(9)
N(1)–C(1)–C(2)	105·1(11)	N(2)–C(5)–C(6)	107·3(12)
N(1)–C(1)–C(3)	105·2(12)	N(2)–C(5)–C(7)	105·7(12)
N(1)–C(1)–C(4)	109·5(12)	N(2)–C(5)–C(8)	110·5(12)
C(2)–C(1)–C(3)	107·0(14)	C(6)–C(5)–C(7)	109·6(12)
C(2)–C(1)–C(4)	114·2(14)	C(6)–C(5)–C(8)	111·9(15)
C(3)–C(1)–C(4)	115·1(13)	C(7)–C(5)–C(8)	111·7(14)
Means			
Cl–P–N	103·3(4)	C–N–P	129·6(10)
N–P–N	82·5(3)	P–N–P	97·3(4)
N–C–C	107·2(9)	C–C–C	111·6(12)
(*c*) Intramolecular non-bonded distances (Å)			
P(1) · · · P(2)	2·53	N(1) · · · N(2)	2·23
P(1) · · · C(1)	2·89	P(2) · · · C(1)	2·90
P(1) · · · C(5)	2·87	P(2) · · · C(5)	2·87
P(1) · · · C(3)	3·12	P(2) · · · C(2)	3·15
P(1) · · · C(6)	3·24	P(2) · · · C(7)	3·18
Cl(1) · · · C(4)	3·69	Cl(2) · · · C(4)	3·67
Cl(1) · · · Cl(2)	4·10		
(*d*) Intermolecular contacts <4 Å			
C(3) · · · Cl(2^{I})	3·64	Cl(1) · · · C(2^{IV})	3·89
C(7) · · · C(2^{II})	3·71	C(4) · · · N(1^{III})	3·94
C(4) · · · C(3^{III})	3·86	C(6) · · · C(3^{V})	3·95

Roman numerals refer to the following transformations of the co-ordinates in Table 1:

I $\frac{1}{2} + x, y, \frac{1}{2} - z$
II $\frac{1}{2} - x, \frac{1}{2} + y, z$
III $x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $1 - x, 1 - y, -z$

(*e*) Deviations (Å) of atoms from least-squares plane through P(1), P(2), N(1), and N(2)

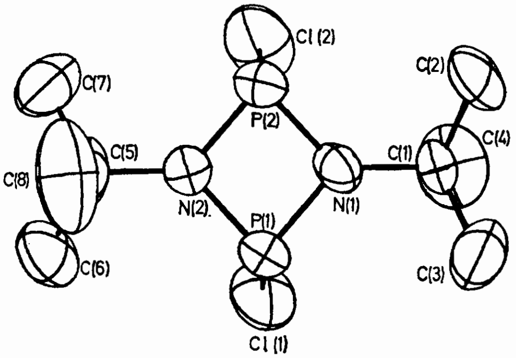
P(1) 0·045, P(2) 0·045, N(1) $-$ 0·045, N(2) $-0·044$, Cl(1) $-1·919$, Cl(2) $-1·900$, C(1) $-0·151$, C(5) 0·409

The computer programs used were those of the '*X*-Ray '63' and '*X*-Ray '70' systems of J. M. Stewart, R. E. Long's REL direct-methods program, C. Johnson's ORTEP thermal ellipsoid plotting program, and the Hilger and Watts software package for the Y 290 diffractometer.

DISCUSSION

The crystal is built of discrete $[\mathrm{Bu^tNPCl}]_2$ molecules (Figure) which possess almost exact C_s point symmetry. Both nitrogen atoms lie on the mirror plane, which is perpendicular to the $[\mathrm{P–N}]_2$ ring. There are no anomalously short contacts between atoms of different molecules (Table 2).

The P–N bond lengths are equal, mean is 1·689(4) Å, 0·028(6) Å longer than the corresponding distance [1·661(5) Å] in (III).[1] Both values are somewhat shorter than that [1·769(19) Å] in $[\mathrm{H_3NPO_3}]^-$,[9] where the P–N bond is thought to be single in character. It therefore appears likely that there is some delocalisation of the nitrogen lone-pairs onto the phosphorus atoms in both (I) and (III), and that its extent may be slightly greater in (III). In cyclic phosphazenes, where such delocalisation is believed to be considerable, P–N distances as short as 1·51 Å have been observed.[10] The mean P–N distance in (I) agrees well with the values for the open-chain compounds $\mathrm{Me_2NPCl_2}$ [1·69(3) Å][11] and $(\mathrm{Me_2N})_3\mathrm{P}$ [1·700(5) Å][12] obtained by gas-phase electron diffraction. Hence the P–N bonds in (I) do not appear to lengthen in order to decrease P · · · P and N · · · N non-bonded repulsions across the ring. In dithiocyclodiphosphazane molecules, which contain $[\mathrm{P–N}]_2$ rings with dimensions similar to those in (I) (*vide retro*), it has been suggested that an extension of the P–N bonds by 0·06 Å may be attributed to such repulsions.[2]



The molecule viewed down the normal to the $[\mathrm{P–N}]_2$ ring; thermal ellipsoids enclose 50% probability. Hydrogen atoms are omitted

The mean P–Cl bond length is 2·105(9) Å. Correction

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

[9] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671.

[10] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

[11] L. V. Vilkov and L. S. Khaikin, *Doklady Akad. Nauk S.S.S.R.*, 1966, **168**, 810.

[12] L. V. Vilkov, L. S. Khaikin, and V. V. Evdokimov, *J. Struct. Chem.*, 1969, **10**, 978.

for the effects of thermal motion, based on the assumption that the chlorine atoms ride on the phosphorus atoms,[13] increases this value to 2·149(5) Å, [P(1)–Cl(1) 2·152(7), P(2)–Cl(2) 2·146(7) Å]. The P–Cl bonds in (I) are the longest so far observed in a tervalent phosphorus compound. Comparable values (obtained by microwave spectroscopy or gas-phase electron diffraction) are 2·043(3) in PCl_3,[14] 2·085(5) in $(Me_2N)PCl_2$,[11] and 2·105(7) and 2·093(9) Å, respectively, in the chlorophosphite compounds $Cl\overline{PO(CR_2)_2O}$ where R = H or Me.[15,16] Replacement of chlorine by other functional groups in tervalent phosphorus compounds thus leads to substantial lengthening of the remaining P–Cl bonds. Since nitrogen and oxygen are more electronegative than chlorine it may be argued that the lengthening of the P–Cl bonds reflects an increase in their ionic character.* This view is supported by spectroscopic studies on chlorocyclophosphazenes, where a decrease in ^{35}Cl n.q.r. frequency was found to be associated with an increase in P–Cl bond length, and it was concluded that both effects could be ascribed to an increase in the degree of ionic character of the P–Cl bond.[18] However, it is in conflict with the Schomaker–Stephenson rule [19] which predicts that increased ionic character leads to bond shortening. In this connection it should be pointed out that the mean P–Cl bond length in $POCl_3$ [1·993(3) Å] [20] is much shorter than that in PCl_3 and that *ab initio* MO calculations indicate the P–Cl bonds to be appreciably more polar in $POCl_3$ than in PCl_3.[21]

The four-membered ring is slightly puckered, successive atoms being displaced by 0·045 Å alternately above and below the mean $[P–N]_2$ plane. The chlorine atoms adopt a *cis*-configuration with respect to the ring. They are displaced from it by *ca.* 1·9 Å in the same direction as the nitrogen atoms. In *cis*-$[EtNP(S)Ph]_2$ the $[P–N]_2$ ring was also found to be slightly puckered,[22] whereas in *trans*-dithiocyclodiphosphazanes [2] and in (III), which also has a *trans*-configuration,[1] the rings are exactly planar. The mean P–N–P, N–P–N, and Cl–P–N angles in (I) [97·3(4), 82·5(3), and 103·3(4)°] differ only slightly from the corresponding values [1] [94·5(2), 85·5(2), and 108·2(2)°] in (III). The presence of a lone pair rather than an oxygen atom on phosphorus leads, as predicted by VSEPR theory,[23] to a small decrease in the valency angles at phosphorus, with a consequent increase in the internal ring angle at nitrogen. The P ··· P separation in (I) (2·53 Å) is somewhat greater than that of 2·44 Å in (III), whereas the N ··· N distances (2·23 and 2·26 Å) are rather similar. In dithiocyclodiphosphazanes the P ··· P and N ··· N distances lie in the respective ranges 2·48—2·56 and 2·22—2·26 Å.[2] The similarity of the dimensions of the $[P–N]_2$ ring in (I) with those found in cyclodiphosphazanes suggests that they are determined by similar factors. We concur with the view of Peterson and Wagner [2] that the most important of these factors is the strong repulsion between diametrically placed pairs of phosphorus and nitrogen atoms.

The atoms N(1) and N(2) show a small but significant difference in their co-ordination. The displacement of N(1) from the plane through the atoms P(1), P(2), and C(1) is only 0·006 Å, whereas N(2) deviates by 0·247 Å from the plane through P(1), P(2), and C(5). Furthermore, the mean P–N–C angle [131·2(7)°] at N(1) is rather larger than the corresponding value [127·9(6)°] at N(2). These differences may be caused by crystal-packing forces, since the energy separation between planar and pyramidal configurations of a trivalent nitrogen atom is believed to be small.[17]

The mean C–C bond length [1·564(8) Å] in (I) is significantly longer than the corresponding distance [1·518(7) Å] in (III), but this may be due to the lack of allowance for the scattering of the hydrogen atoms in (I). Other bond lengths and valency angles in the tertiary butyl groups of (I) and (III) are in excellent agreement.

I thank Dr. J. F. Nixon for bringing this problem to my attention, for a gift of crystals, and for helpful discussions.

[4/1268 *Received*, 26*th June*, 1974]

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* It has been recently shown, by *ab initio* MO calculations, that in H_2NPH_2 inductive electron release from phosphorus to nitrogen more than counterbalances p_π–d_π donation in the opposite direction.[17]

[13] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

[14] P. Kislink and C. H. Townes, *J. Chem. Phys.*, 1950, **18**, 1109.

[15] V. A. Naumov, N. M. Zaripov, and V. G. Dashevskij, *Doklady Akad. Nauk S.S.S.R.*, 1969, **188**, 1062.

[16] V. A. Naumov and N. M. Zaripov, *J. Struct. Chem.*, 1970, **11**, 1030.

[17] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1972, 1147; 1974, 432.

[18] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648.

[19] V. Schomaker and D. P. Stephenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[20] T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344.

[21] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 1510.

[22] E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, C. P. Thakur, G. J. Bullen, J. S. Rutherford, P. A. Tucker, T. S. Cameron, K. D. Howlett, and C. K. Prout, *Phosphorus*, 1971, **1**, 153.

[23] R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.