Stereochemistry of Phosphorus Compounds. Part I. The Crystal and Molecular Structure of 1,3-Di-t-butyl-2-*trans*-4-dichloro-2,4-dioxocyclodiphosphazane †

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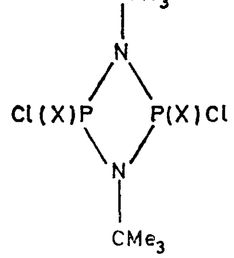
The structure of the title compound has been determined from 841 *X*-ray intensity data measured on a diffractometer. Crystals are tetragonal, space group $P4_2/n$, $a = 13{\cdot}428(5)$, $c = 8{\cdot}152(3)$ Å, $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to R 0·036. The crystals are built of discrete monomeric molecules, which exhibit exact C_i symmetry. The chlorine atoms thus adopt a mutually *trans*-configuration. Selected bond lengths are: P–Cl 2·007(2), P–O 1·448(3), mean P–N 1·661(5), mean N–C 1·507(5) Å.

THE oxidation of phosphorus(III) compounds by dimethyl sulphoxide is now a well established route to phosphorus(V) oxides.[1-3] Thus the title compound, (I), was obtained by oxidation of (II) in methylene chloride solution at —78 °C.[4] To obtain an insight into the stereochemistry of this reaction we have determined the crystal and molecular structure of (I) by *X*-ray diffraction methods. A preliminary account has been published.[4] The molecular structure of (II) has been established earlier.[5]



(I) X = O

(II) X = lone pair

EXPERIMENTAL

The crystals were transparent needles, slowly decomposing in air. The crystal used in this analysis was *ca.* 0·02 × 0·03 × 0·06 cm.

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† No reprints available.

[1] H. H. Szmant and O. Cox, *J. Org. Chem.*, 1966, **31**, 1595.

[2] E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 4296.

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[4] R. Keat, Lj. Manojlović-Muir, and K. W. Muir, *Angew. Chem. Internat. Edn.*, 1973, **12**, 311.

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

Crystal Data.—$C_8H_{18}Cl_2N_2O_2P_2$, M = 307·1, Tetragonal, a = 13·428(5),* c = 8·152(3) Å, U = 1469·9 Å^3, Z = 4, D_c = 1·383 g cm^{-3}, $F(000)$ = 640. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 6·4 cm^{-1}. Space group $P4_2/n$.

The space group was determined from systematic absences of reflexions on Weissenberg photographs. Unit-cell constants were initially obtained from oscillation and Weissenberg photographs, and were later adjusted by a least-squares treatment of the setting angles of 12 reflexions centred on a Hilger and Watts' Y 290 four-circle diffractometer, controlled by a PDP 8 computer.

Intensity Measurements.—The intensities of all independent reflexions with θ(Mo-K_α) $\leqslant$ 30° were measured on a Y 290 diffractometer, by use of molybdenum radiation in conjunction with a graphite monochromator and a pulse-height analyser. The orientation of the crystal was such as to make the crystallographic c axis approximately coincident with the ϕ axis of the diffractometer. The θ—2θ scan technique was used; the scan step in θ was 0·02° and the counting time for each step was 2·5 s. Each reflexion was scanned through a 2θ range of 1·4°, and the local background was counted for 25 s at each end of the scan range. The intensities of four strong reflexions, monitored periodically throughout the experiment, dropped by *ca.* 20% during data collection.

The integrated intensities, I, and their variances, $\sigma^2(I)$, were calculated from the relationships $I = P - (B_1 + B_2)p/2b$ and $\sigma^2(I) = P + (B_1 + B_2)p^2/4b^2 + (qI)^2$, where P is the peak count, B_1 and B_2 the background counts, p the time spent counting the peak, and b the time spent counting each background. The empirical factor, q, was assigned a value of 0·04. The I and $\sigma(I)$ values so derived were corrected for Lorentz, polarisation, and crystal decomposition effects, but not for absorption.

841 Reflexions having $I \geqslant 3\sigma(I)$ were used in the subsequent analysis.

Structure Analysis.—The positions of the phosphorus and chlorine atoms were determined from a Patterson synthesis, and those of the other non-hydrogen atoms from the subsequent difference synthesis.

The structure was refined by the method of full-matrix least-squares. The function minimised was $\Sigma w\Delta^2$, where $\Delta = ||F_o| - |F_c||$ and the weights, w, were derived from the variances of F_o^2 as described earlier.[6] Atomic scattering factors for non-hydrogen atoms were taken from ref. 7, that for hydrogen from ref. 8. Corrections for anomalous scattering of chlorine and phosphorus ($\Delta f'$, $\Delta f''$) were taken from ref. 9.

The refinement of the scale factor and of the positional and isotropic thermal parameters of all non-hydrogen atoms gave R of 0·099 and R' of 0·124 [$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. Allowance for the anisotropic thermal vibrations of all non-hydrogen atoms decreased R to 0·053 and R' to 0·071. The positions of all hydrogen atoms were then determined from a difference synthesis, and these atoms were assigned isotropic temperature factors and included in further refinement. The refinement finally converged at R 0·036 and R' 0·042.

In the last cycle of refinement all parameters shifted by $<0·6\sigma$. The standard deviation of an observation of unit weight was 1·5. The adequacy of the weighting scheme was confirmed by an analysis of the mean $w\Delta^2$ as a bivariant function of $|F_o|$ and sin θ/λ. The function values in the final difference synthesis ranged from −0·24 to 0·27 eÅ^{-3}, and the minimum peak height of a carbon atom in the final synthesis of electron density was 5·3 eÅ^{-3}. Final atomic parameters are shown in Table 1. Observed structure amplitudes and the calculated structure factors are listed in Supplementary Publication No. SUP 21119 (7 pp., 1 microfiche).†

TABLE 1

Final fractional co-ordinates and thermal parameters of atoms

Atom	x	y	z	$U_{iso}(\times 10^2)$/Å^2
P	0·05608(7)	0·01593(7)	0·1147(1)	*
Cl	0·0874(1)	0·16001(9)	0·1552(2)	*
O	0·1093(2)	−0·0451(2)	0·2319(3)	*
N	−0·0656(2)	0·0058(2)	0·0858(3)	*
C(1)	−0·1552(3)	0·0333(3)	0·1876(5)	*
C(2)	−0·2352(4)	−0·0440(5)	0·1549(9)	*
C(3)	−0·1238(5)	0·0284(6)	0·3679(6)	*
C(4)	−0·1883(5)	0·1370(5)	0·1433(11)	*
H(21)	−0·213(4)	−0·119(4)	0·184(6)	9(2)
H(22)	−0·255(4)	−0·033(4)	0·041(8)	10(2)
H(23)	−0·291(5)	−0·025(5)	0·211(8)	11(2)
H(31)	−0·191(6)	0·042(6)	0·436(10)	19(3)
H(32)	−0·072(5)	0·088(5)	0·375(8)	13(2)
H(33)	−0·097(5)	−0·037(5)	0·386(9)	12(3)
H(41)	−0·249(4)	0·147(4)	0·194(7)	9(2)
H(42)	−0·212(4)	0·132(4)	0·035(9)	10(2)
H(43)	−0·134(5)	0·184(6)	0·186(10)	14(3)

* These atoms were assigned anisotropic temperature factors of the form $\exp(-2\pi^2 \times 10^{-4}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*h_ih_j)$. The U_{ij} parameters are:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	449(6)	492(6)	333(4)	27(4)	−15(5)	−22(5)
Cl	833(8)	597(7)	701(8)	−107(6)	−39(6)	−163(6)
O	669(20)	759(21)	434(17)	126(16)	−122(14)	65(15)
N	423(16)	552(18)	305(17)	26(13)	36(14)	−22(13)
C(1)	473(22)	615(25)	443(24)	98(19)	127(19)	−4(19)
C(2)	557(31)	950(43)	962(50)	−49(28)	257(32)	−106(37)
C(3)	869(40)	1092(49)	490(31)	140(38)	176(27)	−68(34)
C(4)	824(40)	810(37)	977(56)	384(32)	274(41)	64(36)

The computer programs used were the Univac 1108 version of J. M. Stewart's '*X*-Ray '70 System,' and the Hilger and Watts software package for the Y 290 diffractometer fitted with a DF 32 magnetic disc unit.

DISCUSSION

The crystal structure is built of discrete monomeric molecules. A calculation of all intermolecular distances <3·8 Å revealed none less than the sum of the appropriate van der Waals radii.

The molecular structure of (I) is shown in the Figure, and bond lengths and valency angles in Table 2. Differences between chemically equivalent bond lengths are within the limits expected from the standard deviations calculated from the inverse least-squares matrix. Between equivalent interbond angles statistically sig-

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* Throughout the paper limits of error (in parentheses) are estimated standard deviations, derived either from the appropriate least-squares matrix or, in the case of mean values, from the range of individual measurements.

† 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).

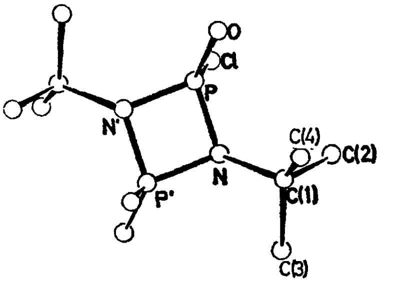
[6] Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796; K. W. Muir, *ibid.*, p. 2663.

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

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

nificant differences do occur, but these are small in absolute magnitude. Accordingly, the mean bond lengths and interbond angles (Table 2) are used in the subsequent discussion.



Molecular structure of (I); hydrogen atoms are omitted for clarity

TABLE 2

Molecular geometry

(*a*) Bond lengths (Å)

P–Cl	2·007(2)	C(2)–H(22)	0·98(6)
P–O	1·448(3)	C(2)–H(23)	0·91(6)
P–N	1·656(3)	C(3)–H(31)	1·08(8)
P–N′	1·665(3)	C(3)–H(32)	1·06(7)
N–C(1)	1·507(5)	C(3)–H(33)	0·96(7)
C(1)–C(2)	1·517(7)	C(4)–H(41)	0·92(6)
C(1)–C(3)	1·530(7)	C(4)–H(42)	0·95(7)
C(1)–C(4)	1·506(8)	C(4)–H(43)	1·03(8)
C(2)–H(21)	1·08(5)		

(*b*) Bond angles (°)

Cl–P–O	109·5(1)	C(1)–C(2)–H(23)	107(4)
Cl–P–N	108·0(1)	C(1)–C(3)–H(31)	105(4)
Cl–P–N′	108·3(1)	C(1)–C(3)–H(32)	102(4)
O–P–N	122·3(2)	C(1)–C(3)–H(33)	107(4)
O–P–N′	120·7(2)	C(1)–C(4)–H(41)	107(4)
N–P–N′	85·5(2)	C(1)–C(4)–H(42)	105(3)
P–N–C(1)	133·6(2)	C(1)–C(4)–H(43)	106(4)
P′–N–C(1)	130·1(2)	H(21)–C(2)–H(22)	116(4)
P–N–P′	94·5(2)	H(21)–C(2)–H(23)	112(5)
N–C(1)–C(2)	107·5(4)	H(22)–C(2)–H(23)	102(5)
N–C(1)–C(3)	107·3(4)	H(31)–C(3)–H(32)	113(6)
N–C(1)–C(4)	109·3(4)	H(31)–C(3)–H(33)	113(6)
C(2)–C(1)–C(3)	109·6(5)	H(32)–C(3)–H(33)	116(5)
C(2)–C(1)–C(4)	112·4(5)	H(41)–C(4)–H(42)	97(5)
C(3)–C(1)–C(4)	110·6(5)	H(41)–C(4)–H(43)	113(6)
C(1)–C(2)–H(21)	114(3)	H(42)–C(4)–H(43)	127(6)
C(1)–C(2)–H(22)	105(3)		

(*c*) Mean values of chemically equivalent bond lengths (Å) and angles (°)

P–N	1·661(5)	P–N–C	131·9(18)
C–C	1·518(7)	N–C–C	108·0(7)
C–H	1·00(2)	C–C–C	110·9(8)
Cl–P–N	108·2(2)	C–C–H	106(1)
O–P–N	121·5(8)	H–C–H	112(3)

Primed atoms are related to corresponding unprimed atoms by the transformation $\bar{x}, \bar{y}, \bar{z}$.

The space group requires each molecule of (I) to possess exact C_i symmetry. Consequently the [P–N]$_2$ ring is strictly planar, the equation of the ring plane being $0·732x - 13·186y + 1·474z = 0$. The displacement of C(1) from this plane is 0·28 Å, indicating that the bonds from each nitrogen atom are disposed in a pyramidal fashion. In dithiocyclodiphosphazane molecules, such as *trans*-[PhNP(S)Ph]$_2$, the three bonds involving each nitrogen atom are usually found to be coplanar.[10] However, in [Bu^{t}NPCl]$_2$ the two nitrogen atoms adopt different configurations, one being pyramidal and the other planar.[5] We consider that in these molecules the difference in energy between the two arrangements is unlikely to be large, and that crystal-packing forces may be sufficient to determine which co-ordination geometry a particular nitrogen atom will adopt.

The bond lengths at the phosphorus atom indicate that the phosphorus *d* orbitals accept *p* electrons mainly from the oxygen and nitrogen atoms rather than from the chlorine atom. The mean P–N bond length [1·661(5) Å] is much shorter than that (1·76 Å) in $H_3NPO_3^-$,[11] where the P–N bond is formally single in character; however, it is not as short as those in phosphazenes, where values between 1·51 and 1·62 Å have been found.[12] The P–O [1·448(3) Å] and P–Cl [2·007(2) Å] bond lengths in (I) agree excellently with the corresponding values in gaseous $POCl_3$ [1·447(2) and 1·991(1) Å], determined by electron diffraction.[13] An *ab initio* SCFMO calculation on $POCl_3$ indicates that p_π–d_π donation to phosphorus is extensive from oxygen, but not from chlorine.[14]

Of the valency angles at the phosphorus atom only O–P–Cl [109·5(1)°] and N–P–Cl [108·2(2)°] are close to the tetrahedral value. The acute N–P–N angle [85·5(2)°] is a consequence of the participation of the phosphorus atom in a four-membered [P–N]$_2$ ring. The rather large mean N–P–O angle [121·5(8)°] may be rationalised in terms of VSEPR theory,[15] since both bonds involved possess multiple character and the electron pairs in such bonds are thought to occupy more space than the one electron pair of a single bond. The valency angles at phosphorus thus appear to be consistent with the suggested bonding scheme. In dithiocyclodiphosphazanes the interbond angles at phosphorus display a pattern similar to that in (I). Thus, in *trans*-[PhNP(S)Ph]$_2$ [12] the mean N–P–S angle [119·2(2)°] is comparable with the mean N–P–O angle in (I) and may presumably be interpreted similarly.

The dimensions of [P–N]$_2$ rings have recently been discussed by Peterson and Wagner.[10] In the dithiocyclophosphazane compounds [RNP(S)Ph]$_2$ (R = Me, Et, or Ph) the rings are either planar or only slightly puckered, and the P–N bond lengths lie between 1·686(6) and 1·695(4) Å. The P · · · P separations, which lie in the range 2·49—2·56 Å, and the N · · · N separations, ranging between 2·22 and 2·26 Å, are nearly constant, and they are very much shorter than the van der Waals diameters of phosphorus (3·8 Å) and nitrogen (3·0 Å). These authors [10] suggested that repulsions between diametrically placed atoms have a dominant effect on the shape of the [P–N]$_2$ ring. This view is

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

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

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

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

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

supported by our results. The P–N bond length in (I) [1·661(5) Å] is somewhat shorter than those in the dithiocyclophosphazanes,[10] presumably because of the presence of more electronegative substituent atoms on phosphorus. An additional factor may be the strong electron-releasing inductive effect of the t-butyl group to the nitrogen atom in (I). The N · · · N separation in (I) (2·255 Å) is comparable to that in the dithiocyclophosphazanes. Hence, the shorter P–N bond length leads mainly to a reduction of the P · · · P separation to 2·439 Å, with a consequent opening of the N–P–N angles by 1—2°, compared with the dithiocyclophosphazanes, and a closure of the P–N–P angles by a corresponding amount. The similarity of the N · · · N distances in these molecules appears surprising, since in (I) it leads to a P · · · P separation only 0·22 Å greater than the P–P single bond length (2·22 Å) in P_2H_4.[16]

In (I) the chlorine atoms are *trans*, whereas in the parent phosphorus(III) compound (II) they are mutually *cis*.[5] It thus appears that the formation of (I) is stereospecific, and that it proceeds with an inversion, as well as a retention of configuration, at the phosphorus atoms. This mechanism is somewhat unexpected, since in the oxidation of cyclic phosphites by nitric acid and by dinitrogen tetroxide retention of configuration at the phosphorus atom occurs with both oxidants.[17]

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