# Crystal and Molecular Structure of 6-Chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo[d,g][1,3,2]diazaphosphocine 6-Oxide

By T. S. Cameron,*† Chemical Crystallography Laboratory, Oxford University, South Parks Road, Oxford OX1 3QS

The structure of the title compound has been determined by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 9.151 \pm 0.003$, $b = 9.610 \pm 0.003$, $c = 13.801 \pm 0.004$ Å, $\alpha = 96.10$, $\beta = 126.12$, $\gamma = 106.25°$, all $\pm 0.01°$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 0.082 for 2381 independent reflections. The eight-membered ring is constructed from three planar groups of atoms and the environment of the nitrogen atoms is also planar.

As part of a structural investigation into compounds containing phosphorus–nitrogen bonds, the crystal structure of the phosphorus heterocycle (I) has been examined.

(I)
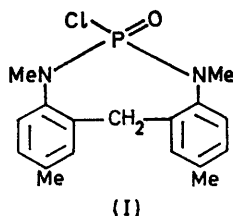
RESULTS AND DISCUSSION

The structure analysis showed that the crystals contained only molecules of $C_{17}H_{20}ClN_2OP$. Details of the crystal packing are given in Figure 1 and the interatomic distances and interbond angles, with estimated standard deviations, in parentheses are recorded in Figure 2.

† *Present address*: The Chemistry Department, The New University of Ulster, Coleraine, County Londonderry, Northern Ireland.

The four atoms bonded to the phosphorus atom are in essentially tetrahedral positions, and the phosphorus atom together with the two nitrogen atoms form part of an eight-membered ring. This ring is constructed from the three planar groups: N(2), C(21), C(22), and C(18); C(18), C(16), C(11), and N(1); and C(11), N(1), P(1), and N(2). Table 1 shows the deviation of the atoms of the ring from the least-squares best plane through each of these groups.

The mean P–N bond length of 1.644 Å is longer than that in some cyclophosphazines, *e.g.* 1.58 Å for $N_3P_3Cl_6$ [1] and for $N_4P_4(NMe_2)_8$,[2] but is similar to the corresponding length in 4-nitroso-5-triphenylphosphoranylideneamino-benzo[1,2-c:3,4-c']difurazan.[3] The N–C(methyl) mean bond length of 1.510 Å compared with a distance of 1.474 in methylamine [4] and 1.498 Å in NN-dimethyl-p-nitroaniline,[5] while the mean N–C(phenyl) bond length

[1] A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 1960, 2548.
[2] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.
[3] T. S. Cameron and C. K. Prout, *J. Chem. Soc. (C)*, 1969, 2285.
[4] D. R. Lide, *J. Chem. Phys.*, 1959, **27**, 343.
[5] T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68.

of 1·444 compares with a distance of 1·43 Å in the similar bond [6] in acetanilide.

The nitrogen atoms deviate by only 0·014 [N(1)] and 0·089 Å [N(2)] from the plane of the three atoms bonded
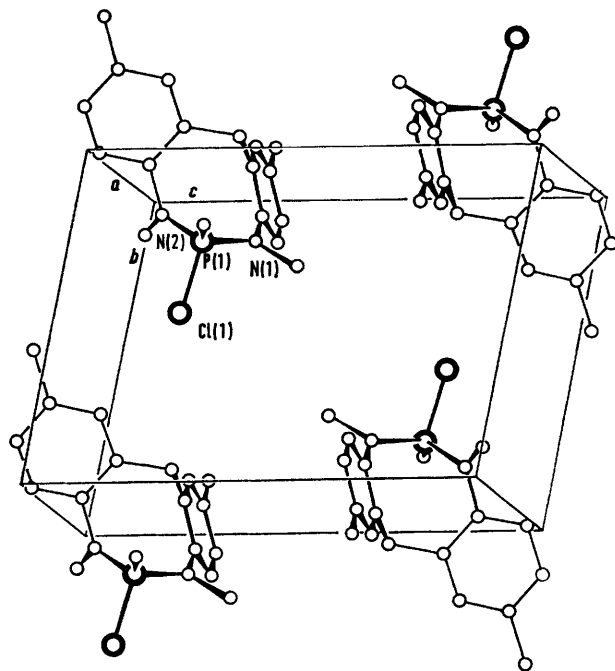

FIGURE 1 Clinographic drawing of the contents of the unit cell. Axis *a* makes an angle of 28·5° to the normal to the paper
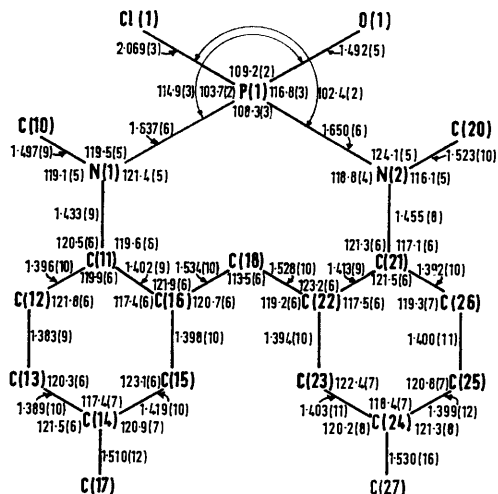

FIGURE 2 Interatomic distances and interbond angles

to them, indicating sp^2 hybridisation. However since the torsional angles between the plane of the three atoms bonded to each nitrogen atom and that of the adjacent phenyl group about the N–C(phenyl) bond are 58·6

[6] C. J. Brown, *Acta Cryst.*, 1966, **21**, 442.
[7] R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlen, *Chem. and Ind.*, 1971, 151.
[8] (*a*) T. S. Cameron and C. K. Prout, *Acta Cryst.*, to be published; (*b*) T. S. Cameron, K. D. Howlett, and C. K. Prout, to be published.

[N(1)] and 64·5° [N(2)], there can be little interaction between the phenyl π system and the lone-pair of electrons on the nitrogen atom.

TABLE 1

Distances (Å) of atoms from least-squares planes. Parenthesis denote atoms not in the calculation of that plane

N(1)	0·029	0·015	(0·545)
P(1)	−0·026	(1·263)	(1·166)
N(2)	0·013	(2·398)	−0·013
C(21)	(−1·232)	(2·463)	0·029
C(22)	(−2·313)	(1·359)	−0·028
C(18)	(−2·323)	−0·014	0·013
C(16)	(−1·099)	0·030	(−1·050)
C(11)	−0·017	−0·031	(−0·741)

The phosphoryl P=O bond length of 1·492 Å is very similar to the mean phosphoryl bond length of 1·50 Å in the three independent molecules in the crystal lattice of tri-*o*-tolylphosphine oxide.[7] It is longer than the corresponding length in triethyl phosphate [8a] (1·45 Å) and triphenyl phosphate [9] (1·43 Å).

It is suggested [8b] that there is some p_π–d_π interaction involving the phosphorus and the two nitrogen atoms which causes a shortening of the P–N single bond and a lengthening of the phosphoryl P=O bond.

The two N–C(methyl) bonds make torsional angles of 51·6 [N(1)] and 119·4° [N(2)] with the phosphoryl P=O bond about the corresponding N–P bond. Consequently the distances between the phosphoryl oxygen atom and the *N*-methyl carbon atoms are significantly different [3·21 and 4·08 Å for C(10) and C(20) respectively]. The ^1H n.m.r. spectrum [10] shows that the *N*-methyl groups are also nonequivalent in solution, but it is not yet clear whether this is due to the same cause as in the crystal.

The bonds about the methylene carbon atom [C(18)] which bridges the two phenyl groups are not significantly distorted. The least-squares best planes through the two phenyl groups are inclined at an angle of 107·8° and the methylene carbon atom is 0·152 Å from the line of intersection of these two planes. The angle C(16)–C(18)–C(22) of 113·5° and the bond lengths C(16)–C(18), C(18)–C(22) of 1·534 and 1·528 Å are within the range of values found in the supposedly undistorted structures of long-chain aliphatic acids, *e.g.* DL-2-methyl-7-oxododecanoic acid.[11]

EXPERIMENTAL

Crystal Data: $C_{17}H_{20}ClN_2OP$, Triclinic, $a = 9·151 \pm 0·003$, $b = 9·610 \pm 0·003$ $c = 13·801 \pm 0·004$ Å, $\alpha = 96·10° \pm 0·01$, $\beta = 126·12° \pm 0·01$ $\gamma = 106·25° \pm 0·01$, $U = 880·76$ Å³, $D_m = 1·294$, $Z = 2$, $D_c = 1·304$, $F(000) = 352$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α radiation, $\lambda = 1·54178$ Å, $\mu(Cu-K_\alpha) = 22·14$ cm⁻¹.

The unit-cell dimensions were determined first from calibrated Weissenberg photographs and later refined on a

[9] G. W. Svetich and C. N. Caughlan, *Acta Cryst.*, 1965, **19**, 645.
[10] C. Y. Cheng, R. A. Shaw, T. S. Cameron, and C. K. Prout, *Chem. Comm.*, 1968, 616.
[11] A. M. O'Connell, *Acta Cryst.*, 1968, **24B**, 1399.

Picker four-circle diffractometer. The intensities of 2381 non-zero independent reflections were estimated from equi-inclination, multiple-film Weissenberg photographs about the a axis (layers 0—$7kl$). The visually estimated data were corrected for Lorentz and polarisation effects but not for absorption. The data were placed on a common scale by comparison with data measured about the b axis (layers $h0l$—$h2l$).

The intensity statistics of an $N(z)$ plot clearly indicated

least-squares with anisotropic temperature factors for all atoms except hydrogen. Neither the temperature factors, nor the positional parameters of the hydrogen atoms were refined. After three cycles with a weight w, where $w = \{1 + [(|F_o|_{abs} - 150)/100]^2\}^{-1}$, R was 0·082 and the refinement had converged. The block-diagonal least-squares refinement was calculated on a Data Saab D 21 computer using the programs of ref. 12. The atomic scattering factors for the isotropic refinement were taken from ref. 13; the

TABLE 2

Atom parameters * ($\times 10^4$)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
P(1)	1224(1)	2937(1)	3138(1)	281(6)	376(6)	427(7)	138(5)	245(6)	125(5)
Cl(1)	1484(2)	5110(2)	3022(2)	697(10)	440(8)	757(10)	250(7)	489(9)	193(7)
O(1)	2938(5)	2707(4)	3372(4)	296(19)	629(23)	580(23)	93(19)	291(19)	184(17)
N(1)	1145(6)	2944(5)	4292(4)	306(22)	477(24)	446(24)	99(19)	259(20)	92(18)
N(2)	−1025(6)	1796(5)	1768(4)	308(22)	447(23)	419(23)	71(23)	181(24)	123(23)
C(10)	2968(8)	3967(6)	5638(5)	391(29)	468(29)	428(29)	145(20)	247(22)	163(20)
C(11)	−620(7)	1957(5)	4048(5)	313(26)	401(25)	401(26)	171(23)	351(26)	210(22)
C(12)	−1557(8)	2585(6)	4357(5)	421(30)	393(26)	573(31)	247(26)	417(29)	297(26)
C(13)	−3320(8)	1670(6)	4071(5)	518(33)	513(29)	577(32)	221(24)	292(25)	180(24)
C(14)	−4235(8)	84(6)	3436(5)	398(29)	500(29)	469(29)	198(21)	282(24)	188(21)
C(15)	−3245(8)	−547(5)	3153(5)	437(29)	384(25)	415(25)	160(20)	241(22)	201(20)
C(16)	−1432(7)	353(5)	3469(4)	378(26)	363(24)	361(24)	327(36)	513(36)	166(32)
C(17)	−6150(9)	−948(8)	3120(7)	519(37)	752(42)	859(46)	160(18)	219(19)	170(18)
C(20)	−2845(9)	2141(8)	1180(6)	423(33)	718(40)	702(40)	284(32)	272(31)	344(30)
C(21)	−1415(7)	238(6)	1189(4)	286(25)	436(26)	386(26)	103(21)	197(22)	141(21)
C(22)	−1209(7)	−834(5)	1835(4)	335(27)	426(26)	408(26)	128(21)	252(23)	191(21)
C(23)	−1692(8)	−2321(6)	1189(5)	473(32)	496(30)	552(32)	136(25)	331(28)	231(26)
C(24)	−2352(9)	−2764(7)	−54(6)	512(35)	654(36)	515(33)	41(28)	324(29)	224(29)
C(25)	−2530(9)	−1669(8)	−661(5)	416(32)	838(44)	421(31)	46(29)	272(27)	166(30)
C(26)	−2055(8)	−164(7)	−42(5)	402(31)	706(36)	411(29)	175(26)	279(26)	200(27)
C(27)	−2851(14)	−4409(9)	−717(8)	1168(70)	789(50)	766(50)	−50(40)	589(50)	389(47)
C(18)	−362(8)	−408(7)	3221(5)	503(31)	457(27)	427(27)	218(22)	329(25)	303(23)

				U_{iso}
H(1)	1124	342	3817	399
H(2)	−448	−1369	3466	399
H(3)	−928	3755	4804	390
H(4)	−3977	2146	4321	432
H(5)	−3888	−1705	2684	376
H(6)	−1543	−3112	1653	478
H(7)	−3041	−1981	−1583	576
H(8)	−2315	392	−681	497

* Anisotropic coefficients have the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}kha^*b^*)]$

the centrosymmetric space group $P\bar{1}$, and the positions of the phosphorus and chlorine atoms in this space group were established from a three-dimensional Patterson function 'sharpened to point-atoms-at-rest.' The 20 light-atom positions were determined from an F_o synthesis phased on the phosphorus and chlorine atom positions. The trial structure with individual isotropic temperature factors for all atoms was refined by full-matrix least-squares using the program of Rollett and Hodder. After four cycles, with unit weights, R was 0·129. The positions of the non-methyl hydrogen atoms were calculated assuming C–H 1·01 Å. The hydrogen atoms were assigned the isotropic temperature factor of the carbon atom to which they were attached and refinement was continued by block-diagonal

* For details of Supplementary Publications see Notice to Authors, No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

curves for neutral phosphorus and chlorine were not corrected for the real part of the anomalous dispersion effect.

The structure amplitudes and structure factors are listed in Supplementary Publication No. SUP 20271 (13 pp., 1 microfiche).*

12 S. Abrahamsson and K. Larsson, *Arkiv Kemi*, 1965, **24**, 383; S. Abrahamsson, *Arkiv Kemi*, 1965, **24**, 389; S. Aleby, *Arkiv Kemi*, 1965, **24**, 395.
13 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.