SHORT STRUCTURAL PAPERS

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Acta Cryst. (1975). B**31**, 2331

6-Chloro-2,5,7,10-tetramethyl-6-thio-6,7-dihydro-5*H*,12*H*-dibenzo[*d*,*g*]-1,3,2-diazaphospholine

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(*Received* 9 *January* 1975; *accepted* 27 *February* 1975)

Abstract. $C_{17}H_{20}N_2PSCl$, monoclinic, $P2_1/b$, $a=11{\cdot}14(1)$, $b=12{\cdot}67(1)$, $c=15{\cdot}44(1)$ Å, $\gamma=125{\cdot}58(10)°$, $Z=4$, $D_c=1{\cdot}30$, $D_m=1{\cdot}29$ g cm^{-3}. The structure has been determined by direct methods and refined to $R=0{\cdot}05$ for 2261 independent reflexions. The proposed molecular structure was confirmed and its conformation is similar to that of the analogous structure where an oxygen atom replaces the sulphur atom.

Introduction. The compound was provided by Professor R. A. Shaw and the crystals were grown by slow evaporation from carbon tetrachloride. The crystal system and approximate cell dimensions were determined from Weissenberg photographs. Systematic extinctions $hk0$, $k=2n+1$; $00l$, $l=2n+1$, uniquely indicated space group $P2_1/b$ (C^5_{2h}, No. 14, first setting). The cell dimensions were refined on a Hilger and Watts four-circle diffractometer by the unpublished method of Dobler and Duerr. 2261 independent reflexions with $I>4\sigma$ were measured ($\omega/2\theta$ scan) on the diffractometer by the ordinate analysis procedure (Watson, Shotton, Cox & Muirhead, 1970), balanced filters were used for reflexions in the range $0<\theta<25°$ and the β filter for $25°<\theta<75°$. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (North, Phillips & Matthews, 1968). μ for Cu $K\alpha$ is 37·4 cm^{-1}.

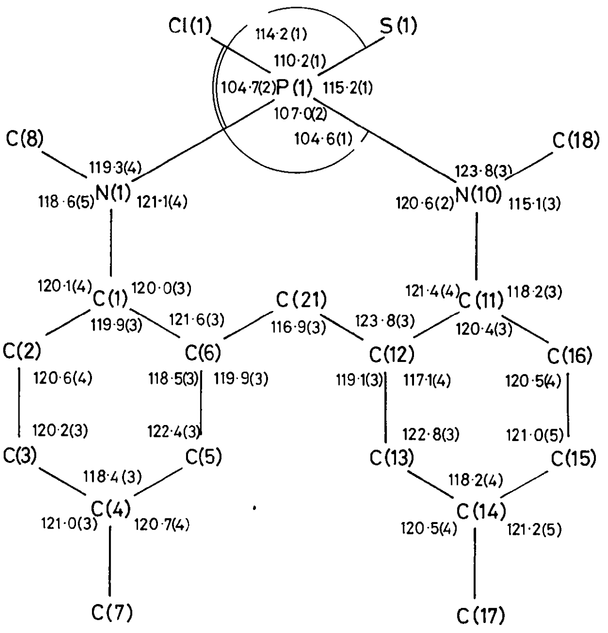

Fig. 1. Interbond angles (°).

Table 1. *Fractional coordinates* (× 10⁵) *with e.s.d.'s in parentheses*

Hydrogen atoms follow directly the carbon atoms to which they are bonded.

	x	y	z
Cl(1)	−27479 (12)	4121 (11)	52046 (6)
P(1)	−15467 (10)	13128 (9)	41016 (5)
S(1)	3444 (12)	28686 (11)	43945 (8)
N(1)	−25915 (39)	15578 (32)	35224 (18)
N(10)	−14924 (28)	2028 (25)	36016 (15)
C(1)	−33827 (38)	7636 (33)	27830 (20)
C(2)	−49247 (41)	−774 (41)	27990 (24)
H(2)	−54340 (468)	−1030 (412)	32914 (283)
C(3)	−56994 (40)	−8532 (39)	20932 (24)
C(4)	−49492 (36)	−8168 (34)	13599 (22)
C(5)	−34213 (36)	274 (32)	13536 (20)
H(5)	−29193 (379)	328 (330)	8519 (235)
C(6)	−26197 (34)	8239 (30)	20550 (19)
C(7)	−57769 (56)	−16766 (50)	5868 (33)
C(8)	−29510 (107)	24303 (77)	38521 (39)
C(11)	−2929 (32)	5664 (30)	30217 (19)
C(12)	−874 (31)	12254 (29)	22461 (18)
C(13)	10322 (33)	14419 (32)	16952 (21)
H(13)	11644 (368)	18499 (338)	11976 (235)
C(14)	19272 (34)	10491 (33)	18933 (22)
C(15)	17070 (39)	4278 (36)	26687 (24)
H(15)	23342 (478)	2060 (415)	28724 (294)
C(16)	6127 (37)	1870 (35)	32293 (22)
H(16)	5129 (401)	−2331 (359)	37894 (255)
C(17)	31145 (52)	13033 (56)	12714 (35)
H(171)	36124 (598)	20894 (550)	9456 (348)
H(172)	40227 (793)	14673 (655)	15668 (423)
H(173)	27326 (792)	8110 (725)	7812 (507)
C(18)	−26997 (47)	−11804 (38)	36120 (31)
C(21)	−9519 (33)	17533 (33)	19999 (21)
H(211)	−6515 (446)	24812 (423)	23403 (288)
H(212)	−6975 (380)	21086 (337)	14017 (241)

Normalized structure factors (E) were calculated with an estimated temperature factor $U=0{\cdot}08$. The signs of the 522 largest E's were determined by means of the tangent formula with a restriction on the phases to 0 or π. The subsequent E map showed the positions of all the non-hydrogen atoms in the structure with the exception of one N-methyl carbon atom which was located from an F_o synthesis phased on the positions of the other atoms. After four cycles of full-matrix least-squares refinement with individual isotropic temperature factors on all atoms followed by two cycles with anisotropic temperature factors the R value was 0·07. A difference map revealed the positions of ten hydrogen atoms, and when these were included with isotropic temperature factors the refinement converged after three more cycles at $R=0{\cdot}05$.* The scattering factors used were those of Cromer & Waber (1965) and Sheldrick's (1972) system was used for all calculations.

A list of atomic coordinates is given in Table 1. The bond lengths are given in Table 2 and the interbond angles are shown in Fig. 1.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

P(1)—Cl(1)	2·053 (2)	C(4)—C(5)	1·387 (5)
P(1)—S(1)	1·922 (2)	C(14)-C(7)	1·514 (6)
P(1)—N(1)	1·634 (5)	C(5)—C(6)	1·393 (4)
P(1)—N(10)	1·636 (4)	C(6)—C(21)	1·517 (4)
N(1)—C(1)	1·435 (4)	C(11)-C(12)	1·400 (5)
N(1)—C(8)	1·496 (3)	C(11)-C(16)	1·384 (7)
N(10)-C(11)	1·443 (4)	C(12)-C(13)	1·399 (5)
N(10)-C(18)	1·462 (4)	C(12)-C(21)	1·506 (7)
C(1)—C(2)	1·399 (5)	C(13)-C(14)	1·383 (7)
C(1)—C(6)	1·384 (5)	C(14)-C(15)	1·374 (5)
C(2)—C(3)	1·383 (5)	C(14)-C(17)	1·510 (7)
C(3)—C(4)	1·392 (6)	C(15)-C(16)	1·377 (6)

Discussion. The conformation and dimensions of the molecule are not substantially different from those reported by Cameron (1972) for the analogue of this compound where the sulphur atom is replaced by oxygen. The P–Cl bond length [2·053(2) Å, *cf.* 2·069(3) Å in the oxide] reverses the usual trend where chlorine atoms attached to thiophosphoryl groups have longer bond lengths than those attached to phosphoryl groups. The nitrogen atoms deviate by 0·09 Å [N(1)] and 0·06 Å [N(10)] from the plane through the three atoms bonded to them. The angle between the plane through the three atoms bonded to a nitrogen atom and the plane through the associated phenyl group has the values 62° for N(1) and 68° for N(10) (mean 66°). The mean N–C (phenyl) bond length of 1·439(4) Å can be compared with 1·418(3) Å in $[PhP(S)NPh]_2$ where the angle between the planes is 8° (Peterson & Wagner, 1973), and with 1·473(7) Å in $Cl_2P(O)N(Ph)P(S)Cl_2$ where the angle is 88° (Cameron, Howlett & Prout, 1975). It is probable that there is some $p\pi$–$d\pi$ interaction along the P–N bond. This

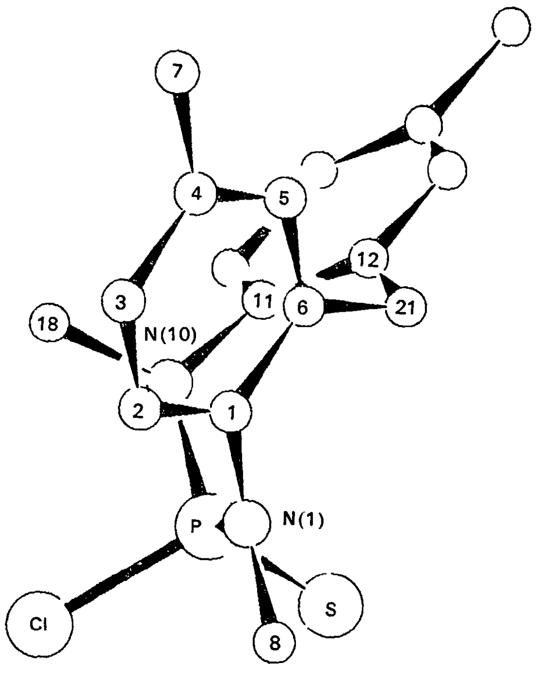

Fig. 2. Detail of the molecule.

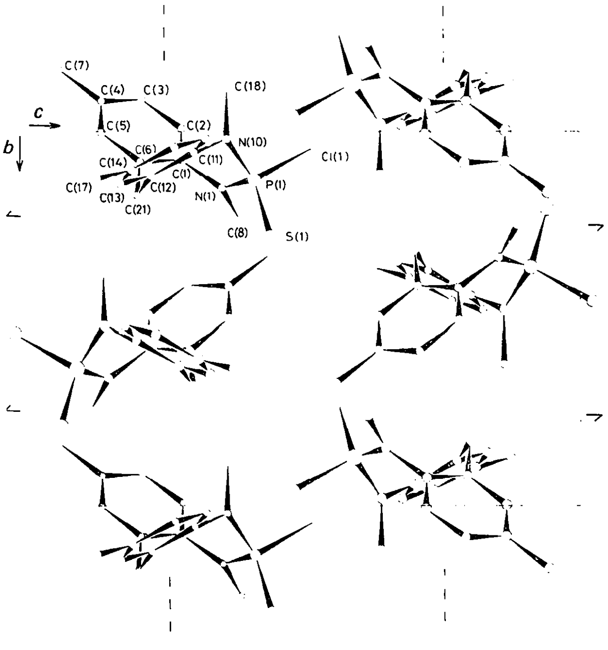

Fig. 3. Projection along a.

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* The observed amplitudes and structure factors calculated from the final atomic coordinates listed in Table 1 and a table of the thermal parameters used have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31072 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England. Photocopies may also be obtained without reference to the author from Oxford University, Radcliffe Science Library, Oxford (K. D. Howlett, D. Phil. Thesis; Catalogue No. D. Phil. M. S. C1172; p. 137 and Appendix 5, Part 7: 15 pp.).

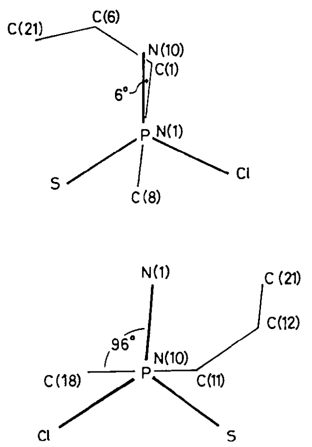

Fig. 4. Newman projection along the P–N bonds.

bond length [1·635(3) Å] is much shorter than the P–N single-bond length (1·759 Å) in the ion $NH_3PO_3^-$ (Cruickshank, 1964), and is within the range of bond lengths (1·50–1·68 Å) found (Corbridge, 1974) in the cyclophosphazenes where there is extensive delocalization within the rings. The interaction along the P–N bond in this compound probably extends through the nitrogen atom to the phenyl group.

The configuration adopted by the molecule is thought to be the result of two steric interactions (Fig. 4); one between the chlorine atom and the two *N*-methyl groups, the relevant distances being 3·3 Å [C(8)] and 3·2 Å [C(18)] which are much shorter than the van der Waals contact distances for C···Cl, and the other between the methyl group at carbon atom C(8) and the chlorine and sulphur atoms where the distances are both 3·4 Å. As a consequence the sulphur atom comes close to the bridging methylene group (Fig. 2) and is 3·79 and 3·92 Å from carbon atoms C(12) and C(21) respectively. This close but efficient packing of the atoms of the molecule protects the phosphorus atom and probably explains its surprising chemical inertness.

Figs. 2 and 3 show details of the molecular structure and the packing of the molecules in the unit cell and Fig. 4 shows the Newman projections along the two P–N bonds. There are no intermolecular distances less than the expected van der Waals separations.

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Acta Cryst. (1975). B**31**, 2333

The Crystal Structure of *trans*-1,3-Dimethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazene, $[PhP(S)NMe]_2$

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(*Received* 21 *February* 1975; *accepted* 7 *April* 1975)

Abstract. $C_{12}H_{16}N_2P_2S_2$, monoclinic, $P2_1/a$, $a=6{\cdot}87(1)$, $b=9{\cdot}43(1)$, $c=13{\cdot}54(2)$ Å; $\gamma=108{\cdot}10(5)$°, $Z=2$, $D_c=1{\cdot}34$, $D_m=1{\cdot}28$ g cm^{-3}, μ(Mo $K\alpha$) = 4·90 cm^{-1}, $\lambda=0{\cdot}7107$ Å. The structure was solved by the heavy-atom method and refined to R 0·08. The compound is a cyclic diphosphazene, and its *trans* configuration had been correctly predicted from spectroscopic and chromatographic evidence.

Introduction. In an investigation to establish non-crystallographic criteria to distinguish between *cis* and *trans* isomers in cyclodiphosphazenes, this present structure was determined to see if it had the *trans* configuration (I) predicted both from ^{1}H n.m.r., infrared and Raman spectra and from the sequence of isomers eluted in column chromatography (Flint, Ibrahim, Shaw, Smith & Thakur, 1971).