

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  $\text{NH}_3\text{PO}_3^-$  (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  $\text{C}\cdots\text{Cl}$ , 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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### The Crystal Structure of *trans*-1,3-Dimethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazene, $[\text{PhP}(\text{S})\text{NMe}]_2$

BY T. S. CAMERON

*Chemistry Department, University of Ulster, Coleraine, N. Ireland*

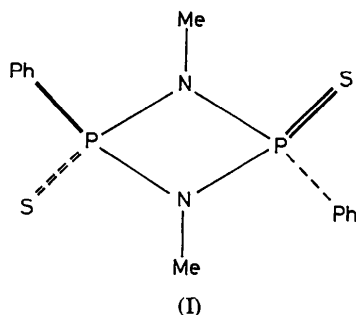
AND C. K. PROUT AND K. D. HOWLETT

*Chemical Crystallography Department, 9 Parks Road, Oxford OX2 3QR, England*

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**Abstract.**  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{P}_2\text{S}_2$ , monoclinic,  $P2_1/a$ ,  $a=6.87(1)$ ,  $b=9.43(1)$ ,  $c=13.54(2)$  Å;  $\gamma=108.10(5)^\circ$ ,  $Z=2$ ,  $D_c=1.34$ ,  $D_m=1.28$  g cm $^{-3}$ ,  $\mu(\text{Mo } K\alpha)=4.90$  cm $^{-1}$ ,  $\lambda=0.7107$  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  $^1\text{H}$  n.m.r., infrared and Raman spectra and from the sequence of isomers eluted in column chromatography (Flint, Ibrahim, Shaw, Smith & Thakur, 1971).



The compound was provided by Professor R. A. Shaw. The crystal system and approximate cell dimensions were determined from Weissenberg photographs. Systematic extinctions  $hk0$ ,  $h = 2n + 1$ ;  $00l$ ,  $l = 2n + 1$  uniquely indicated space group  $P2_1/a$  ( $C_{2h}^5$ , No. 14, non-standard setting; equivalent positions  $\pm(x, y, z) \pm(\frac{1}{2} + x, \frac{1}{2} - y, z)$ , unique axis  $c$ ). The cell dimensions were refined from high-angle axial reflexions on a Hilger and Watts linear diffractometer. With Mo K radiation and balanced filters 1003 independent reflexions with  $I > 3\sigma$  were measured from layers  $hk0$ – $hk11$  with the Bragg angle restricted to a maximum of  $32^\circ$ . The data were corrected for Lorentz and polarization effects but no absorption correction was applied.

The measured density indicated only two molecules in the unit cell; thus it was thought that the molecules, centrosymmetric themselves, would each be found at a symmetry centre.

The positions of the phosphorus and sulphur atoms were determined from a three-dimensional Patterson function sharpened to 'point atoms at rest' (Buerger, 1959) and those of the other non-hydrogen atoms were found from the  $F_o$  map phased on the positions of these two heavier atoms. After four cycles of full-matrix least-squares refinement with individual isotropic temperature factors on all atoms followed by four cycles with anisotropic temperature factors  $R$  was 0.084 and the refinement had converged.

The scattering factors used were those of Cromer & Waber (1965) and Rollett & Ford's *NOVTAPE* (1967, unpublished) was used for all the calculations.

The interatomic distances and interbond angles are given in Table 2. The diagram of the packing of the molecules in the unit cell is given in Fig. 1.\*

\* 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 31059 (8 pp.). 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, England (K. D. Howlett, D. Phil. Thesis; Catalogue No. D. Phil. M. S. C1172; p. 64 and Appendix 5, Part 2: 7 pp.).

Table 1. Fractional coordinates (*e.s.d.*'s in parentheses)  $\times 10^4$

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	1125 (3)	1326 (2)	106 (2)
S(1)	3523 (4)	2161 (3)	924 (2)
N(1)	1021 (9)	–145 (7)	–617 (6)
C(1)	2030 (15)	–236 (12)	–1557 (9)
C(11)	435 (11)	2659 (8)	–612 (7)
C(12)	1771 (12)	4160 (8)	–711 (7)
C(13)	1153 (13)	5152 (9)	–1256 (8)
C(14)	–732 (14)	4808 (9)	–1698 (8)
C(15)	–2079 (14)	3352 (9)	–1600 (8)
C(16)	–1525 (13)	2313 (9)	–1045 (8)

Table 2. Interatomic distances (Å) and interbond angles ( $^\circ$ ) (*e.s.d.*'s in parentheses)

P(1)–S(1)	1.938 (6)		
P(1)–N(1)	1.680 (9)	C(11)–C(16)	1.410 (12)
P(1)–N(1')	1.695 (7)	C(12)–C(13)	1.359 (14)
P(1)–C(11)	1.767 (10)	C(13)–C(14)	1.371 (13)
N(1)–C(1)	1.464 (16)	C(14)–C(15)	1.404 (11)
C(11)–C(12)	1.434 (9)	C(15)–C(16)	1.379 (15)
S(1)–P(1)–N(1)	118.7 (3)		
S(1)–P(1)–N(1')	119.4 (5)	P(1)–C(11)–C(12)	121.5 (6)
N(1)–P(1)–N(1')	83.7 (4)	P(1)–C(11)–C(16)	120.8 (5)
N(1)–P(1)–C(11)	108.4 (5)	C(12)–C(11)–C(16)	117.5 (8)
N(1')–P(1)–C(11)	108.8 (4)	C(11)–C(12)–C(13)	119.3 (8)
S(1)–P(1)–C(11)	114.0 (3)	C(12)–C(13)–C(14)	123.2 (7)
P(1)–N(1)–P(1')	96.3 (5)	C(13)–C(14)–C(15)	118.5 (9)
P(1)–N(1)–C(1)	130.9 (6)	C(14)–C(15)–C(16)	120.2 (9)
P(1')–N(1)–C(1)	130.3 (6)	C(11)–C(16)–C(15)	121.1 (7)

(') atom at equivalent position  $-x, -y, -z$ .

**Discussion.** The two molecules are each situated about centres of symmetry at  $(0, 0, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$  (Fig. 1) and consequently the four-membered phosphazene ring is

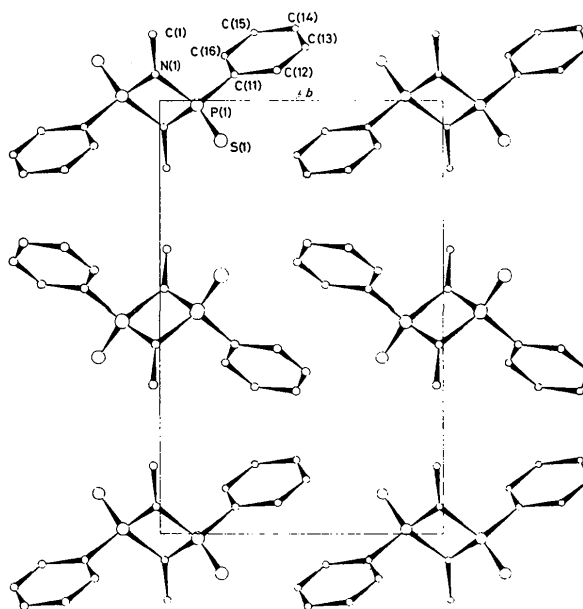


Fig. 1. Projection along [100].

planar. The two sulphur atoms, one bonded to each P atom are *trans* with respect to the plane of the phosphazene ring as are the two phenyl groups.

The torsional angle between the plane of the phenyl group and the P–N bond about the P–C (phenyl) bond is  $59^\circ$  so that the angle between the planes of the phenyl group and the cyclodiphosphazene ring is  $108^\circ$ .

The nitrogen atoms deviate by  $0.14 \text{ \AA}$  from the plane through the three atoms bonded to each of them and the two P–N bond lengths,  $1.681(9) [\text{N}(1)]$  and  $1.695(7) [\text{N}(1')]$ , are effectively equivalent.

This, in the context of the planar  $(\text{PN})_2$  group, suggests that there may be significant  $\pi$  electron delocalization in the ring. The length of a P–N single bond has been reported as  $1.759 \text{ \AA}$  from the ion  $\text{NH}_3\text{PO}_3^-$  (Cruickshank, 1964) where the nitrogen atom is four coordinate and the P–N bond length in cyclotriphosphazenes where there is extensive delocalization of the nitrogen lone pair throughout the ring is in the range  $1.57\text{--}1.60 \text{ \AA}$  (Corbridge, 1974). The mean P–N bond length in this compound  $1.688(6) \text{ \AA}$  is thus much longer than those found in cyclotriphosphazenes and the increase may be the result of an expansion of the whole ring to prevent too close an approach of the opposite phosphorus and of the opposite nitrogen atoms. The P...P and N...N contact distances are  $2.52$  and  $2.25 \text{ \AA}$  and compare with van der Waals contact distances of  $3.60$  and  $3.10 \text{ \AA}$  respectively. The inter-bond angles within the ring N–P–N  $83.7^\circ$ , P–N–P  $96.3^\circ$  are probably a compromise between the optimum relative contact distances across the ring, and the normal valence angles. Thus the small N–P–N angle, reduced from the tetrahedral value of  $109^\circ$ , allows the two phosphorus atoms to be further apart than the two nitrogen atoms where the larger P–N–P angle has been reduced from an  $sp^2$  value of  $120^\circ$ . The mean P–N bond length is similar to those found in *cis*- and *trans*- $[\text{PhP}(\text{S})\text{NEt}]_2$ ,  $1.687(10)$  and  $1.685(7) \text{ \AA}$  respectively (Ibrahim *et al.*, 1971) and though this

bond length [ $1.695(1) \text{ \AA}$ ] in *trans*- $[\text{PhNP}(\text{S})\text{Ph}]_2$  is somewhat longer (Peterson & Wagner, 1973) the difference is within the experimental error of the present compound. The P–C(phenyl) bond length [ $1.767(10) \text{ \AA}$ ] however is probably significantly shorter than that [ $1.796(6) \text{ \AA}$ ] in *trans*- $[\text{PhP}(\text{S})\text{NPh}]_2$ . The difference may be attributed to the superior electron-donating power of the *N*-methyl group compared to the *N*-phenyl groups which increase the electron density within the phosphazene ring thus causing some contraction of the P–N and P–C bonds. The N–C(methyl) bond length of  $1.464(16) \text{ \AA}$  is typical and longer than the N–C(phenyl), a result of the different hybridization states in aliphatic and aromatic carbon atoms (Coulson, 1961).

The structure contains no unusually short intermolecular contacts.

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