

The Crystal and Molecular Structure of *trans*-1,3-Diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane

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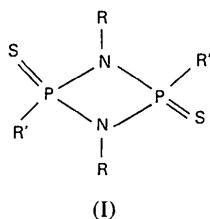
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Crystals of *trans*-1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane [NEtP(S)Ph]₂ are triclinic, $a = 8.06$, $b = 9.34$, $c = 13.13$ Å, $\alpha = 93.6$, $\beta = 104.2$, $\gamma = 99.2^\circ$, space group $P\bar{1}$, 2 molecules in the unit cell. The atomic positions have been determined by least-squares refinement from X-ray diffractometer intensity data, the final R being 0.095 for 3101 reflexions. The two molecules in the unit cell lie on centres of symmetry at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and in consequence the phosphazane ring is planar. These molecules, although not mutually related by symmetry, differ in shape only by the position of the terminal carbon atom of the ethyl group. Mean bond lengths and angles are: P–N 1.688, P–S 1.928, P–C 1.807, N–C 1.47 Å, N–P–N 83.25°, and P–N–P 96.75°. The geometry of the molecule is discussed in terms of steric factors.

Introduction

Thermolysis of phenylphosphonothioic diamides PhPS(NHR)₂ generally yields the cyclic dimers I (R' = Ph) which contain four-membered phosphorus–nitrogen rings.



If R=H the corresponding trimers are obtained. The possibility of geometric isomerism in the cyclodiphosphazanes (I) has been discussed by Trippett (1962) but in the majority of systems studied only one isomer has been isolated (Ibrahim *et al.*, 1971). However, in the case of 1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane (I: R = Et, R' = Ph) two isomers, with melting points 134 and 142°C, have been separated and assigned *cis* and *trans* configurations respectively on the basis of their infrared, Raman, and ¹H n.m.r. spectra (Flint, Ibrahim, Shaw, Smith & Thakur, 1971). Their crystal structures have been studied in this laboratory and in this paper we present the results for the *trans* isomer; the structure of the *cis* isomer will be published shortly. Our results can be compared with the crystal structures of two other closely related *trans*-cyclodiphosphazanes, [NMeP(S)Ph]₂ (I: R = Me, R' = Ph) (Ibrahim *et al.*, 1971) and [NPhP(S)Ph]₂ (I: R = R' = Ph) (Peterson & Wagner, 1973), which have been studied simultaneously in other laboratories and with the known structures of trimeric and tetrameric cyclic phosphazanes.

Experimental

The crystals of *trans*-[NEtP(S)Ph]₂ are triclinic parallelepipeds, elongated along *a* but roughly equidimensional in cross-section and showing the forms {011}, {0 $\bar{1}$ 1}, and {101}. The unit-cell dimensions were measured from precession photographs. Crystal data are given in Table 1.

Table 1. Crystal data

<i>trans</i> -[NEtP(S)Ph] ₂ , m.p. 144°C*	$V = 959$ Å ³
Triclinic	$Z = 2$
$a = 8.06 \pm 0.03$ Å	$D_m = 1.27$ g cm ⁻³
$b = 9.34 \pm 0.03$	(by flotation)
$c = 13.13 \pm 0.04$	$D_c = 1.26$ g cm ⁻³
$\alpha = 93.6 \pm 0.5^\circ$	$F(000) = 384$
$\beta = 104.2 \pm 0.5$	$\lambda(\text{Mo } K\alpha) = 0.7107$ Å
$\gamma = 99.2 \pm 0.5$	$\mu(\text{Mo } K\alpha) = 4.1$ cm ⁻¹
	Space group $P\bar{1}$ (No. 2)

* Our measurement. Flint *et al.* (1971) report 142°C.

X-ray intensities of the 11 layers of reflexions 0–10,*k*,*l* were measured at 22–25°C on a Philips PAILRED diffractometer using monochromated Mo *K*α radiation. 3273 reflexions with reliable intensities [*i.e.* with $I > 2\sigma(I)$] were obtained by measuring all reflexions with $\sin \theta/\lambda \leq 0.70$ Å⁻¹. The intensities were corrected for Lorentz and polarization effects but not for absorption, the linear absorption coefficient being small (see Table 1).

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, using a computer program written by O. S. Mills, L. I. Hodgson and F. S. Stephens. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Structure determination

The positions of the phosphorus and sulphur atoms were deduced from the three-dimensional Patterson function. This contained 24 strong peaks, corresponding to a centrosymmetric arrangement of the eight phosphorus and sulphur atoms in the unit cell (double-weight vectors only), indicating the space group $P\bar{1}$. From the positions of the atoms it was clear that the unit cell contains two centrosymmetric molecules located at the special positions $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In consequence this is a structure in which the asymmetric unit comprises two half-molecules. The carbon and nitrogen atoms were located from a subsequent Fourier

Table 2. Fractional atomic coordinates ($\times 10^3$ for H atoms, $\times 10^4$ for all other atoms) with estimated standard deviations

Molecule (1)	x/a	y/b	z/c
S(1)	39 (3)	3117 (2)	-16 (2)
P(1)	-160 (2)	1192 (2)	432 (1)
N(1)	1414 (7)	202 (5)	420 (4)
C(11)	-682 (8)	1118 (6)	1687 (5)
C(12)	-608 (9)	2388 (7)	2323 (6)
C(13)	-1003 (12)	2313 (9)	3286 (7)
C(14)	-1486 (12)	982 (9)	3630 (7)
C(15)	-1554 (17)	-263 (10)	3004 (8)
C(16)	-1157 (15)	-218 (8)	2047 (7)
C(17)	3059 (10)	260 (9)	1203 (7)
C(18)	4416 (14)	1511 (16)	1102 (12)
H(12)*	-24 (14)	334 (12)	213 (8)
H(13)	-77 (14)	312 (12)	373 (8)
H(14)	-158 (14)	113 (11)	441 (8)
H(15)	-203 (14)	-106 (12)	319 (8)
H(16)	-95 (13)	-113 (12)	161 (8)
H(17a)	351 (15)	-54 (12)	114 (8)
H(17b)	290 (14)	11 (11)	200 (8)
H(18a)	465 (15)	151 (12)	43 (9)
H(18b)	538 (16)	145 (12)	162 (9)
H(18c)	356 (15)	238 (11)	133 (8)
Molecule (2)			
S(2)	1878 (3)	6155 (2)	4124 (2)
P(2)	4070 (2)	5527 (2)	4251 (1)
N(2)	4342 (7)	3876 (6)	4627 (4)
C(21)	4921 (9)	5752 (7)	3111 (5)
C(22)	3843 (10)	6025 (8)	2152 (5)
C(23)	4511 (11)	6153 (9)	1282 (6)
C(24)	6205 (11)	6003 (8)	1348 (6)
C(25)	7278 (10)	5750 (8)	2289 (6)
C(26)	6615 (10)	5606 (8)	3163 (6)
C(27)	4009 (11)	2481 (9)	3962 (6)
C(28)	3347 (17)	1245 (10)	4521 (9)
H(22)	260 (15)	616 (11)	208 (8)
H(23)	349 (14)	630 (11)	54 (8)
H(24)	662 (14)	598 (11)	66 (8)
H(25)	835 (15)	562 (12)	230 (8)
H(26)	773 (14)	547 (11)	391 (8)
H(27a)	295 (14)	278 (11)	306 (8)
H(27b)	512 (15)	228 (11)	388 (8)
H(28a)	403 (15)	122 (12)	524 (9)
H(28b)	210 (15)	149 (11)	456 (8)
H(28c)	352 (14)	45 (12)	396 (8)

* The hydrogen atoms are given the same number as the carbon atom to which they are attached.

synthesis phased on the heavier atoms. Two cycles of full-matrix least-squares refinement using isotropic temperature factors reduced R to 0.15. The hydrogen atoms were then inserted, the positions of those in the phenyl and methylene groups being calculated from the molecular geometry assuming a C-H bond length of 1.08 Å and those in the methyl groups being located from a difference-Fourier synthesis. They were assigned fixed isotropic temperature factors with $B = 5.0 \text{ \AA}^2$.

Least-squares refinement was continued, using anisotropic temperature factors for all atoms except hydrogen. The conditions used were: (i) only those reflexions, 3101 in number, having $|F_o| \geq 4.0$ (on absolute scale) were included; (ii) the weighting scheme $w = (1.37 - 0.065|F_o| + 0.006|F_o|^2)^{-1}$, which made the average $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) for groups of reflexions fairly constant over the whole range of $|F_o|$ and $\sin \theta/\lambda$; (iii) because for full-matrix refinement the size of the normal matrix is so large, the parameters were split into three blocks, one for each symmetry-independent half-molecule and the third containing just the overall scale and temperature factors; (iv) in the final cycle of refinement, 67 reflexions having $3|F_c| < |F_o|$ were excluded (almost all of these were weak, with $|F_o| < 6$); (v) in the later cycles coordinates of hydrogen atoms were also refined. The final R is 0.095 for 3101 reflex-

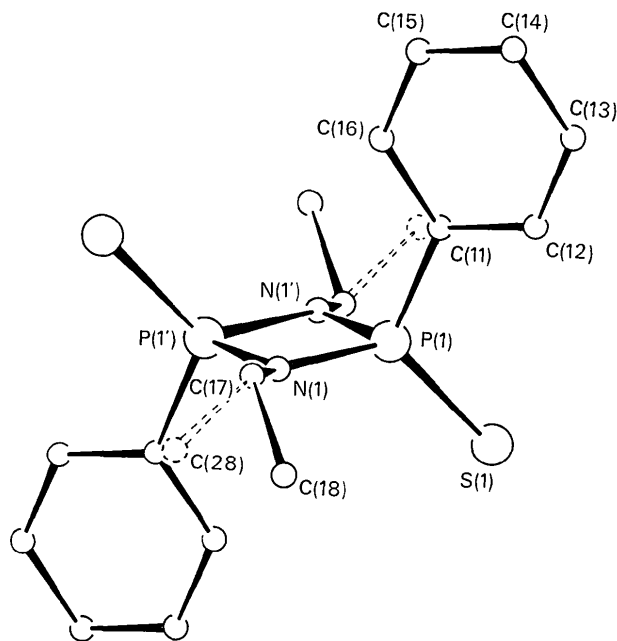


Fig. 1. Molecular shape and labelling of the atoms. The shapes of molecule (1) (at $0,0,0$) and molecule (2) (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) differ only by the position of the terminal carbon of the ethyl group. The atom labelling shown here is for molecule (1); for molecule (2) P(1) becomes P(2), and C(11) becomes C(21) etc. A primed atom is related to the corresponding unprimed atom by inversion through the molecular centre. The terminal carbon in molecule (2), C(28), is shown by the broken lines.

ions and $R' [= (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}]$ is 0.121. In the last cycle of refinement all parameter changes, other than those of hydrogen atoms, were less than 0.22σ . For hydrogen the maximum change was 0.86σ . An attempt to refine the structure in the space group $P1$ led to insignificant parameter changes.

The final atomic coordinates and thermal parameters with estimated standard deviations are listed in Tables 2 and 3. The molecular shape and the numbering of the atoms are shown in Fig. 1. A list of observed and calculated structure factors is available.* Bond lengths and bond angles with their estimated standard deviations are listed in Tables 4 and 5. The orientation and magnitudes of the principal axes of the vibration ellipsoids are given in Table 6. The anisotropic thermal parameters were analysed in terms of

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30079 (18 pp., 1 microfiche): copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

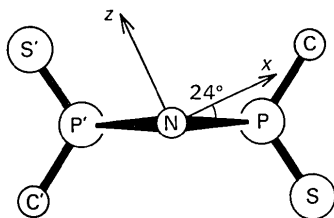


Fig. 2. Molecular axes chosen for the rigid-body vibration analysis. X and Z are in the plane of the P , S , and C atoms with X at 24° to the plane of the phosphazane ring. Y is perpendicular to X and Z and is directed towards N' .

a rigid-body motion for the central part of the molecule comprising the phosphazane ring and those atoms directly bonded to it, e.g. $S(1)$, $C(11)$, and $C(17)$ for molecule 1. The remaining carbon atoms were not included because it was thought unlikely that the whole

Table 4. Bond lengths (\AA) with estimated standard deviations

The C-H bond lengths lie in the range 0.86–1.35 \AA , mean 1.03 \AA .

(a) From the least-squares refinement

P(1)—N(1)	1.687 (5)	P(1)—C(11)	1.801 (6)
P(1)—N(1')	1.676 (5)	P(2)—C(21)	1.804 (6)
P(2)—N(2)	1.678 (5)	C(11)—C(12)	1.391 (9)
P(2)—N(2')	1.694 (5)	C(12)—C(13)	1.381 (10)
P(1)—S(1)	1.922 (2)	C(13)—C(14)	1.379 (11)
P(2)—S(2)	1.921 (3)	C(14)—C(15)	1.367 (12)
N(1)—C(17)	1.456 (9)	C(15)—C(16)	1.373 (11)
N(2)—C(27)	1.470 (9)	C(16)—C(11)	1.392 (9)
C(17)—C(18)	1.504 (13)	C(21)—C(22)	1.407 (9)
C(27)—C(28)	1.502 (12)	C(22)—C(23)	1.381 (9)
Mean	1.503 (9)	C(23)—C(24)	1.377 (11)
		C(24)—C(25)	1.382 (11)
		C(25)—C(26)	1.385 (9)
		C(26)—C(21)	1.379 (9)
		Mean	1.383 (10)

(b) Corrected for molecular oscillations

P(1)—N(1)	1.692 (5)	P(1)—C(11)	1.806 (6)
P(1)—N(1')	1.681 (5)	P(2)—C(21)	1.808 (6)
P(2)—N(2)	1.682 (5)	Mean	1.807 (5)*
P(2)—N(2')	1.698 (5)		
Mean	1.688 (5)*	N(1)—C(17)	1.461 (9)
		N(2)—C(27)	1.474 (9)
P(1)—S(1)	1.928 (2)	Mean	1.468 (6)
P(2)—S(2)	1.927 (3)		
Mean	1.928 (4)*		

* These standard deviations have been enlarged to allow for possible error in the unit-cell parameters.

Table 3. Anisotropic thermal parameters ($\times 10^4$) with estimated standard deviations in parentheses

The temperature factor is in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	223 (4)	84 (2)	79 (1)	40 (2)	56 (2)	30 (1)
P(1)	125 (3)	64 (2)	48 (1)	18 (2)	27 (1)	6 (1)
N(1)	136 (9)	81 (6)	48 (3)	12 (5)	13 (4)	-6 (3)
C(11)	136 (11)	88 (7)	57 (4)	10 (7)	37 (5)	10 (4)
C(12)	173 (13)	97 (8)	70 (5)	29 (8)	48 (7)	3 (5)
C(13)	259 (18)	123 (9)	74 (6)	38 (10)	72 (8)	0 (6)
C(14)	279 (20)	143 (11)	77 (6)	28 (11)	74 (9)	13 (6)
C(15)	468 (32)	125 (11)	94 (7)	1 (15)	128 (13)	26 (7)
C(16)	465 (30)	91 (8)	82 (6)	22 (12)	129 (11)	10 (6)
C(17)	135 (12)	144 (10)	80 (6)	50 (9)	4 (7)	18 (6)
C(18)	148 (18)	304 (24)	138 (12)	-42 (16)	10 (12)	41 (14)
S(2)	162 (3)	167 (3)	64 (1)	62 (2)	35 (2)	15 (1)
P(2)	138 (3)	101 (2)	38 (1)	22 (2)	24 (1)	13 (1)
N(2)	151 (9)	99 (6)	36 (3)	13 (6)	14 (4)	11 (3)
C(21)	171 (12)	105 (8)	48 (4)	43 (8)	34 (6)	22 (4)
C(22)	178 (14)	149 (10)	51 (4)	41 (9)	29 (6)	32 (5)
C(23)	210 (16)	177 (12)	46 (4)	39 (11)	33 (7)	30 (6)
C(24)	231 (16)	132 (9)	50 (4)	28 (9)	48 (7)	20 (5)
C(25)	176 (14)	142 (10)	69 (5)	35 (9)	54 (7)	24 (6)
C(26)	172 (13)	144 (10)	57 (4)	50 (9)	41 (6)	33 (5)
C(27)	199 (15)	132 (10)	63 (5)	30 (10)	18 (7)	-9 (5)
C(28)	362 (28)	115 (10)	90 (7)	36 (13)	24 (11)	25 (7)

molecule behaves as a rigid body. The analysis was first carried out using a molecular axial system in which the normal to the phosphazane ring was Z and the $P' \cdots P$ line was X . This gave for both the molecules a librational tensor ω in which ω_{13} was fairly large. The molecular axes were therefore modified to those shown in Fig. 2 in which X makes an angle of 24° with the $P' \cdots P$ line. This gave translational and librational tensors (Table 7) whose off-diagonal elements are small in comparison with their standard deviations, so that the molecular axes chosen may be regarded as principal axes. Presumably the molecular X axis does not coincide with the $P' \cdots P$ line because of the greater mass of the phenyl group compared with the sulphur atom. Within experimental error ω is the same for molecule 1 and molecule 2. Bond lengths corrected for the effect of the molecular oscillations (Cruickshank, 1956, 1961) are given in Table 4(b). The corrections are of importance particularly for the P-S bonds and marginally for the P-N bonds. The correction to the sulphur atom positions was also taken into account in calculating the S \cdots S intermolecular distance (Fig. 3).

Discussion

Molecular geometry

Our analysis confirms that the isomer of 1,3-diethyl-2,4-diphenyl-2,4-dithiocyclophosphazane with melting point 144°C has the *trans* configuration as proposed by Flint *et al.* (1971). The two molecules in the unit cell lie on centres of symmetry at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 3) and, in consequence, the four-membered phosphazane rings are planar. There is in this a close similarity to the crystal structure of *trans*-[NPhP(S)Ph]₂ (Peterson & Wagner, 1973) which also has two centrosymmetric molecules located on special positions in a triclinic unit cell [though with the cell chosen the posi-

Table 5. Bond angles ($^\circ$) with estimated standard deviations

N(1)-P(1)-N(1')	83.3 (3)	P(1)-N(1)-C(17)	129.0 (5)
N(2)-P(2)-N(2')	83.2 (3)	P(1')-N(1)-C(17)	130.0 (5)
		P(2)-N(2)-C(27)	128.5 (5)
P(1)-N(1)-P(1')	96.7 (3)	P(2')-N(2)-C(27)	128.3 (5)
P(2)-N(2)-P(2')	96.8 (3)		
		P(1)-C(11)-C(12)	121.0 (5)
S(1)-P(1)-C(11)	113.0 (2)	P(1)-C(11)-C(16)	120.5 (6)
S(2)-P(2)-C(21)	114.0 (2)	P(2)-C(21)-C(22)	120.2 (6)
		P(2)-C(21)-C(26)	120.2 (5)
N(1)-P(1)-S(1)	120.4 (2)	C(11)-C(12)-C(13)	120.3 (6)
N(1')-P(1)-S(1)	118.7 (2)	C(12)-C(13)-C(14)	120.7 (7)
N(2)-P(2)-S(2)	120.6 (2)	C(13)-C(14)-C(15)	118.8 (8)
N(2')-P(2)-S(2)	117.4 (2)	C(14)-C(15)-C(16)	121.6 (8)
		C(15)-C(16)-C(11)	120.1 (7)
N(1)-P(1)-C(11)	108.5 (3)	C(16)-C(11)-C(12)	118.5 (6)
N(1')-P(1)-C(11)	109.4 (3)	C(21)-C(22)-C(23)	119.2 (7)
N(2)-P(2)-C(21)	107.4 (3)	C(22)-C(23)-C(24)	120.5 (7)
N(2')-P(2)-C(21)	110.4 (3)	C(23)-C(24)-C(25)	120.7 (6)
		C(24)-C(25)-C(26)	119.2 (7)
N(1)-C(17)-C(18)	111.8 (8)	C(25)-C(26)-C(21)	120.8 (7)
N(2)-C(27)-C(28)	110.7 (7)	C(26)-C(21)-C(22)	119.6 (6)

Table 6. Root-mean-square amplitudes of thermal vibration (\AA) along the principal axes of the vibrational ellipsoids

The direction of each principal axis is specified by the angles it makes with the orthogonal axes a' , b' and c , where b' lies in the bc plane.

	a'	b'	c		a'	b'	c		
S(1)	0.274	38	79	54	S(2)	0.273	62	28	89
	0.231	128	72	43		0.228	70	102	23
	0.173	88	22	111		0.198	35	115	113
P(1)	0.203	44	92	46	P(2)	0.209	74	20	78
	0.182	134	91	44		0.203	17	107	90
	0.165	89	2	88		0.169	94	101	12
N(1)	0.216	111	109	31	N(2)	0.224	40	125	107
	0.206	33	122	83		0.201	53	37	91
	0.172	67	40	60		0.169	76	100	17
C(11)	0.224	47	100	45	C(21)	0.237	35	60	74
	0.201	103	29	65		0.202	125	45	65
	0.177	46	63	124		0.179	89	120	30
C(12)	0.251	48	99	43	C(22)	0.261	72	28	69
	0.213	51	50	116		0.228	19	104	103
	0.190	114	42	58		0.184	84	114	25
C(13)	0.292	28	98	64	C(23)	0.278	80	16	77
	0.238	69	34	116		0.250	10	99	93
	0.195	108	57	39		0.178	89	103	13
C(14)	0.302	25	101	68	C(24)	0.265	11	97	81
	0.248	82	11	82		0.240	85	14	77
	0.216	113	94	24		0.179	100	102	16
C(15)	0.393	21	103	75	C(25)	0.261	52	56	56
	0.255	89	39	51		0.236	119	34	107
	0.190	111	126	43		0.192	129	95	40
C(16)	0.388	19	99	74	C(26)	0.264	59	40	66
	0.198	90	30	60		0.213	33	123	93
	0.192	109	118	35		0.188	100	111	24
C(17)	0.271	103	83	15	C(27)	0.263	61	57	133
	0.251	65	25	90		0.242	35	124	83
	0.180	29	114	75		0.209	72	52	44
C(18)	0.398	101	31	62	C(28)	0.343	27	99	115
	0.324	84	118	28		0.271	63	73	33
	0.198	13	77	90		0.213	89	19	109

tions are $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The geometries of the two symmetry-independent molecules in *trans*-[NETP(S)Ph]₂ are virtually identical with the exception of the orientation of the ethyl groups (see Fig. 1), it being possible to superpose the atoms of molecule 1 on those of molecule 2 with differences in position of at most 0.18 \AA . The ethyl groups adopt staggered conformations with P-N-C-C torsion angles of 80° (molecule 1) and 145° (molecule 2), so giving satisfactory separation of C(18) and C(28) from the neighbouring phosphorus atoms.

The coordination of phosphorus is distorted tetrahedral and that of nitrogen is approximately planar, the sum of the three bond angles at nitrogen being 356° (molecule 1) and 354° (molecule 2) (see also Table 8 for deviations of the atoms from planarity). In *trans*-

It seems more likely to us that the difference arises from two effects. In the cyclic tri- and tetraphosphazanes, where the ring is larger, the non-bonded contacts across the ring are not as close as in (II) and yet the P-N bonds are still some 0.03 Å longer than the equatorial bonds in (II). A difference of this order can therefore be attributed to the different coordination of the phosphorus atom, leaving the cross-ring repulsions to account for only some 0.03 Å, the difference between the bond length in the di- and higher phosphazanes.

The mean P=S bond length (1.928 Å) does not differ greatly from those found in the cyclodiphosphazanes [NMeP(S)Cl]₂ and trans-[NPhP(S)Ph]₂ or from the terminal P=S bonds in P₄S₅, P₄S₇ and P₄S₁₀ (Vos, Olthof, van Bolhuis & Botterweg, 1965). It is however, significantly shorter than the P=S bonds in diphosphine disulphides, e.g. 1.95–1.97 Å in (III): R = R' = Me (Lee & Goodacre, 1971a). The estimate for P=S corrected for electronegativity difference is 1.92 Å (Pauling, 1960).

The mean P-C bond length (1.807 Å), although similar to that reported in cyclophosphazenes (Bullen & Mallinson, 1972; Ahmed, Singh & Barnes, 1969) and the other cyclodiphosphazanes with phenyl groups attached to phosphorus (Ibrahim *et al.*, 1971; Peterson & Wagner, 1973), is rather shorter than the Schomaker-Stevenson estimate for a P-C single bond (1.83 Å). Since the P-C lengths in the phosphinoborines [(Ph₂P)BH₂]₃ (1.823 Å, Bullen & Mallinson, 1973) and [(Me₂P)BH₂]₃ (1.837 Å, Hamilton, 1955) agree with

this estimate, it is probable that the shorter bonds found in phosphazanes and phosphazenes result from the phosphorus here being bonded to more electro-negative nitrogen.

The mean N-C length (1.468 Å) is similar to that usually found but the C-C bond in the ethyl group (mean 1.50 Å) is short for a single bond. This may to some extent be due to the lack of a correction for libration of the ethyl group.

In the four-membered ring the N-P-N angles are considerably smaller than the P-N-P angles. This is found to be so in the other four cyclodiphosphazanes, trans-[NMeP(S)Ph]₂, cis-[NEtP(S)Ph]₂ (Ibrahim *et al.*, 1971), trans-[NPhP(S)Ph]₂, and [NMeP(S)Cl]₂, in which the N-P-N angles all lie in the range 81.9–84.2° and the P-N-P angles 95.2–98.1°. This inequality is most probably caused by non-bonded repulsions across the ring, the phosphorus atoms being forced further apart than the nitrogen atoms because of their greater size. As Peterson & Wagner (1973) point out for trans-[NPhP(S)Ph]₂ the P...P and N...N distances are both about the same proportion (70%) of their usual respective van der Waals distances (3.6 Å for phosphorus and 3.1 Å for nitrogen). The small N-P-N angles are balanced by larger exocyclic bond angles at phosphorus, particularly those involving the P=S bond. This permits the exocyclic non-bonded contacts to approach more closely the van der Waals distance, e.g. the ratio of the observed contact to the van der Waals distance is 0.93 for S...N, 0.89 for C...S, and 0.87

Table 7. Translational (T , Å²) and librational (ω , deg²) tensors for the central part of the two molecules (referred to the molecular axes defined in Fig. 2)

Molecule (1)		
$T = \begin{pmatrix} 0.045 & & \\ & 0.004 & \\ & & 0.007 \end{pmatrix}$	$\omega = \begin{pmatrix} 16 & -2 & 1 \\ & 6 & 2 \\ & & 7 \end{pmatrix}$	
Molecule (2)		
$T = \begin{pmatrix} 0.038 & & \\ & 0.005 & \\ & & 0.000 \end{pmatrix}$	$\omega = \begin{pmatrix} 13 & 0 & 0 \\ & 6 & -1 \\ & & 6 \end{pmatrix}$	

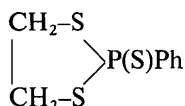
Table 8. Equations of mean planes through sets of atoms and distances (Å) of atoms from the plane (in square brackets)

Coordinates in Å are referred to orthogonal axes a' , b' , and c , where b' lies in the bc plane.

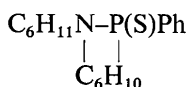
Molecule (1)	
Plane (i): P(1), N(1), P(1'), N(1')	0.214X + 0.432Y - 0.876Z = 0
Plane (ii): P(1), N(1), P(1'), C(17)	0.364X + 0.427Y - 0.828Z = 0.039
[P(1) - 0.038, N(1) 0.136, P(1') - 0.039, C(17) - 0.059]	
Plane (iii): C(11)-C(16)	-0.959X + 0.183Y - 0.217Z = 0.213
[C(11) 0.002, C(12) 0.001, C(13) - 0.003, C(14) 0.002, C(15) 0.001, C(16) - 0.003, P(1) - 0.002]	
Molecule (2)	
Plane (iv): P(2), N(2), P(2'), N(2')	-0.692X + 0.148Y + 0.706Z = 1.658
Plane (v): P(2), N(2), P(2'), C(27)	-0.766X - 0.022Y + 0.643Z = 0.419
[P(2) - 0.048, N(2) 0.169, P(2') - 0.048, C(27) - 0.073]	
Plane (vi): C(21)-C(26)	0.294X + 0.946Y + 0.135Z = 5.897
[C(21) 0.002, C(22) 0.001, C(23) 0.002, C(24) - 0.007, C(25) 0.008, C(26) - 0.006, P(2) - 0.049]	

for C...N. It is interesting to note that in [NMeP(O)OMe]₃, where the larger ring removes the necessity for distortion, the above ratio is 0.84 for all the O...N and O...O contacts.

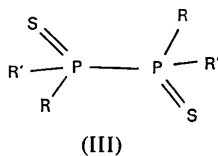
The phenyl groups are planar to within experimental error [Table 8, planes (iii) and (vi)]. In molecule 1 the phosphorus atom is coplanar with the attached phenyl group but in molecule 2 there is a small displacement (0.05 Å) from the plane. In both molecules the phenyl ring adopts a conformation almost eclipsed with the P=S bond, the S-P-C-C torsion angles being only 11° in molecule 1 and 13° in molecule 2. This conformation is surprising in that it produces close intramolecular non-bonded contacts between the phenyl ring and the sulphur atom, C(12)...S(1) 3.33 Å and C(22)...S(2) 3.36 Å, which could easily be avoided by twisting the ring about the P-C bond. Nevertheless the eclipsed conformation occurs in a number of other molecules containing the Ph-P=S grouping: *trans*-[NMeP(S)Ph]₂, *trans*-[NPhP(S)Ph]₂, and



(Lee & Goodacre, 1971*b*). It is therefore unlikely to have been caused merely by intermolecular forces. A staggered conformation is however found in the diphosphine disulphide (III) with R = Me and R' = Ph (Wheatley, 1960) and in the bicyclic compound



(Healy *et al.*, 1971).



Intermolecular distances

The shortest intermolecular distance (excluding hydrogen atoms) is the S...S contact of 3.51 Å between molecules related by the **b** lattice translation (Fig. 3). This gives a van der Waals radius for sulphur close to the 1.75 Å favoured by Bondi (1964) and larger than the 1.72–1.73 Å preferred by Lee & Goodacre (1971*a*, *b*). There are six symmetry-independent S...C contacts between 3.82 and 3.88 Å, which are shown in Fig. 3. The orientation of the ethyl groups, different in molecules 1 and 2, is related to the packing of molecules in the crystal. In the direction of the **a** lattice translation the molecules are arranged so that the terminal methyl groups of molecules 1 and 2 lie opposite the phenyl group in molecule 1, respectively 3.77 and

3.68 Å away from its plane. The shortest contacts between the ethyl groups of molecules 1 and 2 are 3.90–3.91 Å (Fig. 3).

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