Crystal Structure of Compounds with (N–P)$_n$ Rings. Part XI.[1] 1,2,3,4-Tetraphenyl-2,4-dithiocyclodiphosphazane, [PhNP(S)Ph]$_2$

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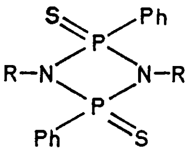
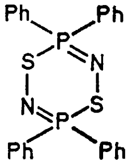
The crystal structure of the title compound (I; R = Ph) has been determined from 5873 three-dimensional *X*-ray intensity data collected on a diffractometer. The structure was solved by the symbolic addition method and refined by block-diagonal least-squares to *R* 7·5%.

The triclinic unit-cell, space group $P\bar{1}$ [(a = 9·510(2), b = 14·195(2), c = 9·866(2) Å, α = 85·43(1), β = 94·30(1), γ = 59·77(1)°] contains two molecules, which lie on inversion centres at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $\frac{1}{2}$,0,0. Owing to the inversion symmetry the molecules have a planar (N–P)$_2$ ring and the substituents at the phosphorus atoms are *trans*. The P–N bonds are equal and the bonding arrangement around the nitrogen atoms is planar. Around the phosphorus atoms the arrangement is distorted tetrahedral. The approximate molecular symmetry is C_{2h}. Mean values (and individual standard deviations) of bond lengths and valence angles are: P–N 1·695(4), P–S 1·913(2), P–C 1·796(6), N–C 1·418(6), and C–C 1·386(8) Å; P–N–P 98·1(4), P–N–C 130·9(4), N–P–N 81·9(2), S–P–C 114·8(2), and C–C–C 120·0(6)°.

THERMAL condensation reactions of phenylphosphonothioic diamides PhP(S)(NHR)$_2$ (R = H, alkyl, or Ph) have been studied by Ibrahim and Shaw.[2] The alkyl derivatives gave products which were characterized as cyclic diphosphazanes [(I); R = alkyl]. With the phenyl substituted diamide PhP(S)(NHPh)$_2$ a different product was obtained, the structure of which was formulated as (II) on the basis of chemical analysis, molecular-weight determination, u.v., i.r., and ^{1}H n.m.r. spectroscopy, and, in particular, hydrolytic degradation which gave diphenylphosphinic acid. Structure (II) would involve a novel six-membered P–N–S ring system.


(I)


(II)

Later hydrolytic degradation experiments failed to give the diphenylphosphinic acid and yielded aniline instead.[3] These results cast doubt on the correctness of the originally suggested structure (II) and suggested that (I; R = Ph) after all might be the correct structure. We have therefore carried out an *X*-ray structure determination of a sample of the compound N$_2$P$_2$S$_2$Ph$_4$ (m.p. 265 °C), in order to solve the ambiguity regarding the molecular structure.

EXPERIMENTAL

Crystals of N$_2$P$_2$S$_2$Ph$_4$ are colourless and triclinic. Accurate unit-cell dimensions were determined from zero-level Weissenberg photographs around the *a*, *b*, and *c* axes taken with Cu-K_α radiation. Unit-cell constants were calculated from the measured θ values by a least-squares procedure.

Crystal Data.—C$_{24}$H$_{20}$N$_2$P$_2$S$_2$, M = 462·4, Triclinic, a = 9·510(2), b = 14·195(2), c = 9·866(2) Å, α = 85·43(1), β = 94·30(1), γ = 59·77(1)°, U = 1136·9 Å^3, D_m = 1·30, Z = 2, D_c = 1·35 g cm^{-3}, $F(000)$ = 480. No systematically absent reflexions. Space group $P\bar{1}$, from distribution of normalized structure factors. Cu-K radiation, $\lambda(\alpha_1)$ = 1·5405, $\lambda(\alpha_2)$ = 1·5443 Å; Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 3·2 cm^{-1}.

A crystal with the shape of a parallelepiped and with dimensions *ca.* 0·1 × 0·2 × 0·1 mm was cemented to a glass fibre and used for the collection of the three-dimensional intensity data on a Nonius automatic three-circle single-crystal diffractometer. The crystal was mounted with c^* parallel to the ϕ axis of the goniometer. The θ—2θ scan technique was employed with a scan angle of 1·5—2·1° in 2θ, a scan speed of 2·4° min^{-1} in 2θ, and stationary background measurements. 6585 Independent reflexions up to $(\sin\theta)/\lambda = 0{\cdot}7$ Å^{-1} were measured with zirconium-filtered Mo radiation. One of a set of three standard reflexions was measured every 47 reflexions. The long-range variation in the intensities of the standard reflexions was $<8\%$. After subtraction of the background, only the 5873 reflexions with a positive net intensity were considered further. Structure factor amplitudes $|F_o|$ were derived by applying Lorentz and polarization factors and the weights were calculated on the basis of the counting rate uncertainties. No absorption corrections were applied.

Structure Analysis.—The structure was solved by application of the symbolic addition method.[4] The observed structure factors were brought on the absolute scale with the aid of the statistical method of Wilson [5] and the normalized structure factor amplitudes $|E|$ were computed. Statistical averages for the normalized structure factors are listed in Table 1, together with the percentages of reflexions with $|E| > 1$, 2, or 3. Comparison of the experimental values with theoretical values calculated for crystals with randomly distributed atoms shows the centrosymmetric space group $P\bar{1}$ to be the most probable.

TABLE 1

Characteristic quantities of the normalized structure factor amplitudes $|E|$

	Obs.	Calc. Centrosym.	Calc. Non-centrosym.
$\langle\lvert E\rvert\rangle$	0·822	0·798	0·886
$\langle\lvert E\rvert^2\rangle$	0·973	1·000	1·000
$\langle\lvert E\rvert^2 - 1\rangle$	0·895	0·968	0·736
$\lvert E\rvert > 1$ (%)	31·8	32·0	36·8
$\lvert E\rvert > 2$ (%)	3·4	5·0	1·8
$\lvert E\rvert > 3$ (%)	0·1	0·3	0·01

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[1] Part X, J. G. Hartsuiker and A. J. Wagner, *J.C.S. Dalton*, 1972, 1069.

[2] E. H. M. Ibrahim and R. A. Shaw, *Chem. Comm.*, 1967, 244.

[3] R. A. Shaw, personal communication.

[4] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[5] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

The basis set in the phase-determining process (Table 2) was determined by giving positive signs to the reflexions $\bar{6},\bar{4},1$, $\bar{3},3,1$, and 3,12,10, thus specifying the origin, and by giving symbolic signs to four other reflexions. In applying the Σ_2 relation, first by hand, in later stages with the help of a computer-program (written by Dr. van der Spek), a sign was accepted only when the probability of the corresponding relation was at least 99%, corresponding to the value 13·7 for the triple product $E_H E_{H'} E_{H+H'}$. In this way a real or symbolic sign could be determined for 294 reflexions, *i.e.* for all reflexions with $|E| \geqslant 1{\cdot}9$, except five. Using the sign indications for the symbols with the highest probability ($a = b = c$, $d = ab$) an E map was calculated with d positive and with $a = b = c$ all negative. This map proved to be the correct one. In the E map, indications for the atomic positions of the phosphorus, sulphur, nitrogen, and carbon atoms were observed. The unit-cell appeared to contain two independent molecules lying at inversion centres.

Refinement.—The crystal structure was refined by block-diagonal least-squares analysis. In the initial cycles the scale factor, the atomic co-ordinates, and the isotropic thermal parameters of the phosphorus, sulphur, carbon, and nitrogen atoms were refined, using 639 reflexions. Later, the thermal parameters were refined anisotropically and more reflexions, finally all 5873 observed independent reflexions except four which were omitted because of suspected

TABLE 2

Basis set in phase-determining process

h	k	l	$\|E\|$	Sign
$\bar{6}$	$\bar{4}$	1	3·20	+
$\bar{3}$	3	1	2·90	+
3	12	10	3·08	+
5	0	4	3·21	a
2	$\bar{7}$	2	3·26	b
0	2	8	3·31	c
0	$\bar{2}$	3	2·81	d

TABLE 3

Final fractional co-ordinates with standard deviations in parentheses

Atom	x	y	z
	Molecule (1)		
P(1)	0·3637(1)	0·5521(1)	0·4192(1)
S(1)	0·2407(1)	0·4986(1)	0·3249(1)
N(1)	0·5677(2)	0·4937(2)	0·4108(2)
C(1)	0·2729(3)	0·6988(2)	0·3914(3)
C(2)	0·3673(4)	0·7450(2)	0·4278(3)
C(3)	0·2986(4)	0·8580(3)	0·4085(4)
C(4)	0·1356(5)	0·9260(3)	0·3542(4)
C(5)	0·0425(4)	0·8799(3)	0·3165(5)
C(6)	0·1090(4)	0·7667(3)	0·3338(4)
C(7)	0·6535(3)	0·4904(2)	0·2981(2)
C(8)	0·8240(3)	0·4311(2)	0·3163(3)
C(9)	0·9077(3)	0·4289(3)	0·2052(3)
C(10)	0·8222(4)	0·4821(3)	0·0766(3)
C(11)	0·6525(4)	0·5400(3)	0·0596(3)
C(12)	0·5669(3)	0·5454(2)	0·1708(3)
	Molecule (2)		
P(2)	0·4430(1)	0·0862(1)	0·0597(1)
S(2)	0·2380(1)	0·1661(1)	0·1295(1)
N(2)	0·5548(3)	−0·0526(2)	0·1008(2)
C(13)	0·5780(3)	0·1391(2)	0·0854(3)
C(14)	0·5573(4)	0·2063(2)	0·1860(3)
C(15)	0·6682(5)	0·2414(3)	0·2091(3)
C(16)	0·7941(5)	0·2130(3)	0·1314(4)
C(17)	0·8134(5)	0·1474(3)	0·0323(4)
C(18)	0·7066(4)	0·1097(3)	0·0072(3)
C(19)	0·6280(3)	−0·1189(2)	0·2300(2)
C(20)	0·6294(3)	−0·0694(2)	0·3456(3)
C(21)	0·6963(4)	−0·1333(3)	0·4735(3)
C(22)	0·7606(4)	−0·2453(3)	0·4848(3)
C(23)	0·7619(4)	−0·2948(2)	0·3696(3)
C(24)	0·6956(3)	−0·2316(2)	0·2411(3)

TABLE 4

Parameters ($\text{Å}^2 \times 10^{-4}$) of the anisotropic temperature factors * with standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
			Molecule (1)			
P(1)	318(3)	434(4)	303(3)	−384(6)	−52(5)	52(5)
S(1)	526(4)	693(5)	454(4)	−793(8)	−167(7)	−20(6)
N(1)	317(10)	471(12)	312(10)	−343(18)	−57(17)	91(15)
C(1)	375(13)	463(14)	407(13)	−399(23)	35(21)	134(21)
C(2)	477(16)	513(17)	651(19)	−503(28)	−142(28)	64(27)
C(3)	676(22)	497(18)	930(26)	−638(33)	−97(34)	90(36)
C(4)	715(24)	534(20)	1077(30)	−527(37)	26(39)	495(42)
C(5)	422(19)	602(22)	1354(37)	−194(33)	556(45)	94(40)
C(6)	378(16)	614(20)	914(25)	−446(29)	371(34)	−36(30)
C(7)	406(13)	370(12)	348(12)	−446(22)	−159(19)	167(19)
C(8)	395(13)	482(15)	387(13)	−397(24)	−127(22)	117(21)
C(9)	430(15)	674(19)	455(15)	−568(28)	−289(26)	240(23)
C(10)	588(18)	757(21)	445(15)	−845(33)	−252(28)	370(26)
C(11)	604(18)	806(22)	361(14)	−802(34)	52(27)	56(25)
C(12)	415(14)	581(17)	375(13)	−491(26)	26(23)	43(21)
			Molecule (2)			
P(2)	394(3)	328(3)	296(3)	−343(5)	−172(5)	104(5)
S(2)	449(4)	568(4)	584(4)	−379(7)	−443(7)	352(7)
N(2)	457(12)	309(10)	316(10)	−352(18)	−125(15)	35(17)
C(13)	487(14)	386(13)	355(12)	−471(23)	−144(20)	59(21)
C(14)	802(22)	532(17)	498(16)	−845(33)	−371(26)	255(29)
C(15)	963(27)	679(21)	661(21)	−1135(41)	−432(33)	98(37)
C(16)	794(24)	691(24)	928(27)	−1095(40)	−251(37)	19(39)
C(17)	703(23)	883(26)	1008(28)	−1111(43)	−571(43)	537(40)
C(18)	643(20)	729(22)	718(21)	−890(36)	−591(34)	489(32)
C(19)	360(12)	405(13)	336(12)	−417(21)	−104(19)	80(19)
C(20)	497(15)	460(14)	330(12)	−492(25)	−167(21)	114(21)
C(21)	560(17)	628(18)	348(13)	−532(30)	−75(24)	46(23)
C(22)	497(17)	660(19)	427(15)	−505(30)	281(26)	−93(24)
C(23)	546(17)	407(15)	586(17)	−416(27)	157(25)	−43(27)
C(24)	537(16)	408(14)	493(15)	−503(26)	−131(23)	49(25)

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \cdots]$.

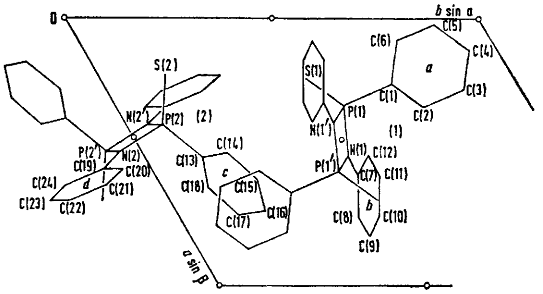
TABLE 5

Calculated atomic co-ordinates of the hydrogen atoms and refined parameters (Å^2) of the isotropic temperature factors $\exp[-B \sin^2 \theta/\lambda^2]$, with standard deviations in parentheses. Hydrogen atoms are numbered according to the corresponding carbon atom to which they are bonded

Atom	x	y	z	B
		Molecule (1)		
H(2)	0·494	0·691	0·471	5·7(8)
H(3)	0·373	0·893	0·438	7·6(7)
H(4)	0·083	1·014	0·340	6·8(7)
H(5)	−0·084	0·934	0·274	8·0(7)
H(6)	0·035	0·731	0·305	7·1(7)
H(8)	0·891	0·388	0·416	5·0(7)
H(9)	1·041	0·383	0·219	6·0(8)
H(10)	0·887	0·479	−0·009	6·1(8)
H(11)	0·584	0·583	−0·040	6·3(8)
H(12)	0·435	0·591	0·157	5·4(7)
		Molecule (2)		
H(14)	0·458	0·229	0·246	6·9(9)
H(15)	0·654	0·293	0·288	6·7(8)
H(16)	0·876	0·244	0·151	7·2(8)
H(17)	0·911	0·126	−0·030	7·5(8)
H(18)	0·721	0·059	−0·071	5·2(7)
H(20)	0·577	0·019	0·336	3·9(6)
H(21)	0·696	−0·094	0·563	5·9(8)
H(22)	0·811	−0·295	0·585	5·6(7)
H(23)	0·813	−0·382	0·379	6·6(8)
H(24)	0·695	−0·230	0·152	5·3(7)

extinction, were incorporated in the refinement. The hydrogen atoms were placed at calculated positions assuming C–H 1·08 Å. Their positions were coupled with those of the corresponding carbon atoms, and their thermal motions were refined isotropically. The function minimized was $\Sigma w[|F_o| - K|F_c|]^2$, where the weight w is given by $w = \{w_c^{-1} + p|F_o|^2\}^{-1}$. In this expression w_c is the weight calculated from counting statistics and p is a constant, chosen so as to make $w(\Delta F)^2$, averaged over groups of reflexions, as far as possible independent of $|F_o|$. For p the value 0·0005 was taken. Atomic scattering factors were taken from ref. 6. The final value of R was 7·5% and of R' 6·8% $\{R' = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$.

The final atomic co-ordinates of the non-hydrogen atoms with their standard deviations as calculated by the least-squares program are given in Table 3. The thermal parameters and their standard deviations are listed in Table 4. Analysis of the thermal motion showed that the molecules cannot be considered as rigid bodies and, accordingly, no libration corrections were applied to the atomic co-ordinates. The co-ordinates and the isotropic thermal parameters of the hydrogen atoms are given in Table 5. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20511 (32 pp., 1 microfiche).*



Projection of the crystal structure on a plane perpendicular to the c axis

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The present structure determination has confirmed that the molecular structure is based on a four-membered phosphorus–nitrogen ring, with phenyl groups attached to the nitrogen atoms and with sulphur atoms and phenyl groups bonded to the phosphorus atoms. Thus the thermal condensation of PhP(S)(NHPh)$_2$ leads to a product with structure (I), just as in case of the analogous alkyl compounds.

In the crystal, the molecules are located on inversion centres at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $\frac{1}{2}$,0,0 of the triclinic unit-cell. The Figure shows a projection of the crystal structure on a plane perpendicular to the c axis, showing the contents of one unit-cell. Owing to the inversion symmetry of the molecules, only half of each molecule is crystallographically independent, the (N–P)$_2$ rings are planar, and the sulphur atoms and phenyl groups bonded to the phosphorus atoms are *trans*.

The approximate molecular symmetry conforms to the point group C_{2h} and involves, in addition to the inversion centre required crystallographically, a mirror plane through the phosphorus atoms perpendicular to the (N–P)$_2$ ring and a two-fold axis through the nitrogen atoms. The pseudo-symmetry C_{2h} is obeyed by the positions of the phosphorus, nitrogen, and sulphur atoms, and by the overall positions of the phenyl groups. Further, it is reasonably well obeyed by the orientations of the phenyl groups, as can be seen from the torsion angles of these groups around the P–C and N–C bonds. In molecule (1), the torsion angle of phenyl group (*a*) with respect to the plane through P(1)–C(1) parallel to N(1) · · · N(1′) is 105·6° (ideal value 90°) and the torsion angle of group (*b*) with respect to the plane through N(1)–C(7) parallel to P(1) · · · P(1′) [which is virtually the same as the plane of the (N–P)$_2$ ring] is 5·8° (ideal value 0°). In molecule (2), these angles are 110·4 and 9·7°, respectively. Corresponding torsion angles in molecules (1) and (2) have to a high extent the same value, suggesting that the overall molecular structure is affected only very little by the crystal forces.

Bond lengths and valence angles are given in Table 6,

TABLE 6

Bond lengths and valence angles. The standard deviations are based on the inverse least-squares matrix and are given in parentheses

(*a*) Bond lengths (Å)

Molecule (1)		Molecule (2)	
P(1)–N(1)	1·695(2)	P(2)–N(2)	1·696(2)
P(1)–N(1′)	1·702(2)	P(2)–N(2′)	1·688(2)
P(1)–S(1)	1·912(1)	P(2)–S(2)	1·913(1)
P(1)–C(1)	1·794(3)	P(2)–C(13)	1·797(3)
N(1)–C(7)	1·418(3)	N(2)–C(19)	1·418(3)
C(1)–C(2)	1·395(4)	C(13)–C(14)	1·387(4)
C(2)–C(3)	1·383(4)	C(14)–C(15)	1·388(5)
C(3)–C(4)	1·381(5)	C(15)–C(16)	1·373(5)
C(4)–C(5)	1·387(6)	C(16)–C(17)	1·363(5)
C(5)–C(6)	1·389(5)	C(17)–C(18)	1·382(5)
C(6)–C(1)	1·396(4)	C(18)–C(13)	1·394(4)
C(7)–C(8)	1·388(4)	C(19)–C(20)	1·389(3)
C(8)–C(9)	1·396(4)	C(20)–C(21)	1·391(4)
C(9)–C(10)	1·384(4)	C(21)–C(22)	1·378(5)
C(10)–C(11)	1·382(4)	C(22)–C(23)	1·381(5)
C(11)–C(12)	1·399(4)	C(23)–C(24)	1·393(4)
C(12)–C(7)	1·381(3)	C(24)–C(19)	1·382(4)

(*b*) Valence angles (°)

P(1)–N(1)–P(1′)	98·2(2)	P(2)–N(2)–P(2′)	98·0(1)
P(1)–N(1)–C(7)	130·7(2)	P(2)–N(2)–C(19)	130·6(2)
(P1′)–N(1)–C(7)	131·0(2)	P(2′)–N(2)–C(19)	131·3(2)
N(1)–C(7)–C(8)	119·8(2)	N(2)–C(19)–C(20)	119·4(2)
N(1)–C(7)–C(12)	119·8(2)	N(2)–C(19)–C(24)	120·3(2)
N(1)–P(1)–N(1′)	81·8(1)	N(2)–P(2)–N(2′)	81·9(1)
N(1)–P(1)–S(1)	120·0(1)	N(2)–P(2)–S(2)	118·6(1)
N(1′)–P(1)–S(1)	118·6(1)	N(2′)–P(2)–S(2)	119·6(1)
N(1)–P(1)–C(1)	108·1(1)	N(2)–P(2)–C(13)	108·3(1)
N(1′)–P(1)–C(1)	109·0(1)	N(2′)–P(2)–C(13)	109·0(1)
S(1)–P(1)–C(1)	114·7(1)	S(2)–P(2)–C(13)	114·9(1)
P(1)–C(1)–C(2)	119·6(2)	P(2)–C(13)–C(14)	119·9(2)
P(1)–C(1)–C(6)	120·5(2)	P(2)–C(13)–C(18)	119·9(2)
C(1)–C(2)–C(3)	120·3(3)	C(13)–C(14)–C(15)	119·0(3)
C(2)–C(3)–C(4)	120·2(3)	C(14)–C(15)–C(16)	120·8(3)
C(3)–C(4)–C(5)	119·4(3)	C(15)–C(16)–C(17)	119·9(3)
C(4)–C(5)–C(6)	121·4(3)	C(16)–C(17)–C(18)	121·0(3)
C(5)–C(6)–C(1)	118·7(3)	C(17)–C(18)–C(13)	119·2(3)
C(6)–C(1)–C(2)	119·9(3)	C(18)–C(13)–C(14)	120·1(3)
C(7)–C(8)–C(9)	119·5(3)	C(19)–C(20)–C(21)	119·9(2)
C(8)–C(9)–C(10)	120·5(3)	C(20)–C(21)–C(22)	119·8(2)
C(9)–C(10)–C(11)	119·4(2)	C(21)–C(22)–C(23)	120·4(2)
C(10)–C(11)–C(12)	120·7(3)	C(22)–C(23)–C(24)	121·3(3)
C(11)–C(12)–C(7)	119·4(2)	C(23)–C(24)–C(19)	119·4(3)
C(12)–C(7)–C(8)	120·5(2)	C(24)–C(19)–C(20)	120·3(2)

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

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with their standard deviations as derived from the inverse least-squares matrix. The least-squares standard deviations, however, should be considered as a lower limit to the errors in the molecular parameters. A better measure of the accuracy of the structure is provided by the root-mean-square standard deviations calculated from the internal consistency of the parameters of the phenyl rings. The root-mean-square standard deviations of the C–C bond lengths and C–C–C angles are 0·008 Å and 0·6° respectively, *i.e.* twice as large as the least-squares standard deviations. Therefore, the standard deviations given in Table 7 are the doubled least-squares values; these have been added to the mean values of the bond lengths and valence angles, in terms of which the molecular structure will be discussed.

TABLE 7

Mean values of bond lengths and valence angles in $[PhNP(S)Ph]_2$. The standard deviations are twice the least-squares standard deviations and are given in parentheses

(*a*) Bond lengths (Å)			
P–N	1·695(4)	N–C	1·418(6)
P–S	1·913(2)	C–C	1·386(8)
P–C	1·796(6)		
(*b*) Valence angles (°)			
P–N–P	98·1(4)	N–P–C	108·6(2)
P–N–C	130·9(4)	S–P–C	114·8(2)
N–C–C	119·8(4)	P–C–C	120·0(4)
N–P–N	81·9(2)	C–C–C	120·0(6)
N–P–S	119·2(2)		

TABLE 8

Structural data for the $(N–P)_2$ rings of cyclic diphosphazanes

Compd.	Formula	P–N (Å)		P–N–P (°)	N–P–N (°)	P···P (Å)	N···N (Å)
(1)	$(MeNPF_3)_2$ [a]	1·60	1·74	102	78	2·59	2·09
(2)	$(MeNPF_2Ph)_2$ [b]	1·64(2)	1·78(2)	99·4	80·6	2·61	2·21
(3)	$(MeNPCl_3)_2$ [c]	1·629(10)	1·776(10)	98·3(5)	81·7(5)	2·577	2·230
	[d]	1·635(7)	1·769(7)	99·5(4)	80·5(4)	2·599	2·202
(4)	$(NMe)_6P_4Cl_8$ [e]	1·66	1·74	100	80	2·61	2·19
(5)	$[MeNP(S)Cl]_2$ [f]	1·67		96	84	2·48	2·23
(6)	*trans*-$[MeNP(S)Ph]_2$ [g]	1·69(1)		96·0(3)	84·0(3)	2·50	2·26
(7)	*trans*-$[EtNP(S)Ph]_2$ [g]	1·686(6)		96·7(2)	83·4(3)	2·518	2·241
(8)	*cis*-$[EtNP(S)Ph]_2$ [g]	1·687(10)		95·2(5)	84·2(5)	2·491	2·261
(9)	*trans*-$[PhNP(S)Ph]_2$ [h]	1·695(4)		98·1(3)	81·9(2)	2·562	2·221

[a] Ref. 7. [b] Ref. 8. [c] Ref. 9. [d] Ref. 10. [e] Ref. 11. [f] Ref. 12. [g] Ref. 13. [h] This work.

In order to discuss the P–N bond length and the angles P–N–P and N–P–N it is helpful to compare also the structures of other cyclic diphosphazanes. The structural data (Table 8) are from *X*-ray diffraction studies, except for compound (1) where the structure was determined by electron diffraction. Not all structures have been determined with equal accuracy; the more accurate results are those for compounds (3) (two independent studies) and (7)—(9).

The cyclic diphosphazanes belong to the group of phosphorus–nitrogen compounds with three-co-ordinate nitrogen atoms. The nitrogen atoms in these compounds have a lone electron-pair available in a $2p$ orbital which may to some extent be delocalized into suitable $3d$ orbitals of neighbouring phosphorus atoms to form a d_π–p_π bond system. This is reflected in the lengths of the P–N bonds which vary for the compounds listed in Table 8 from 1·60 to 1·78 Å.

The group of phosphorus–nitrogen compounds with three-co-ordinate nitrogen may be considered as intermediate between the phosphoramidate anion $NH_3PO_3^-$ on the one hand and the group of (cyclic and linear) phosphazenes on the other. The $NH_3PO_3^-$ anion is the only phosphorus–nitrogen species with known structure having a four-co-ordinate nitrogen atom and the P–N bond length observed [14] (1·76 Å) may be taken as the single bond value. In the phosphazenes the nitrogen atoms are two-co-ordinated and the molecules are characterized by a dual system of delocalized d_π–p_π bonds composed of mutually perpendicular components in each P–N bond. Accordingly, the P–N bonds in the phosphazenes are short, varying from 1·51 to 1·62 Å.[15]

In compounds (1)—(4) of Table 8 the phosphorus atoms are five-co-ordinated in a trigonal bipyramidal arrangement. Two types of P–N bonds are observed: short equatorial bonds and long axial bonds. After Rundle,[16] the difference in bond length may be explained in terms of a MO treatment of the σ bonding, for which the use of $3d$ orbitals of the phosphorus atoms is not needed. Alternatively, the different P–N bond lengths may be explained according to Gillespie's VSEPR theory,[17] in which bonding and molecular shape are treated in terms of the repulsive interactions between electron pairs in the valence shell of a central atom.

In compounds (5)—(9) the phosphorus atoms are four-co-ordinated, the arrangement is more or less tetrahedral, and the σ bonds may be considered to be based on an sp^3 type hybridization. Thus, in these compounds all P–N bonds in a $(N–P)_2$ ring are expected to have the same length.

It is seen in the last two columns of Table 8 that the

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diagonals of the $(N-P)_2$ rings have very much the same values in different cyclodiphosphazanes. The mean distances (P · · · P 2·55, N · · · N 2·22 Å) are considerably less than the corresponding van der Waals distances [18] (3·60 and 3·10 Å). The ratio of observed diagonal to van der Waals distance is the same for P · · · P and N · · · N, *viz.* 0·71 and 0·72 respectively.

From these data it may be inferred that there are appreciable repulsions between diametrically placed atoms in the $(N-P)_2$ ring and, undoubtedly, these repulsions have a dominant effect on the shape of the ring. This is expressed most clearly by the values of the ring angles P–N–P and N–P–N which are very much the same in all the compounds listed in Table 8, irrespective of the type of co-ordination of the phosphorus atoms.

The role of atom–atom repulsions between non-bonded atoms as a factor determining molecular geometry has been discussed by Bartell,[19] in particular with reference to organic compounds. The general idea is that non-bonded repulsions are always present in principle, but play a dominant role only in crowded molecules, when many (large) ligands are packed around a (small) central atom. In the case of the cyclodiphosphazanes there is only a ' local crowdedness ' arising from the phosphorus and nitrogen atoms being bonded in a four-membered ring.

The length of the P–N bond in compound (9) is the same as in compounds (6)—(8). The P–N bond in these compounds is much longer than the equatorial P–N bond in those listed in the first half of Table 8. The difference is *ca.* 0·06 Å, much larger than may be expected on the basis of hybridization differences at the phosphorus atoms, or on the basis of electronegativity effects of the substituents. It is likely that in compounds (6)—(9) the P · · · P and N · · · N repulsions are responsible for the long P–N bonds. Calculation of the diagonals of a hypothetical $(N-P)_2$ ring, having P–N–P and N–P–N angles of 96 and 84° and a short P–N bond of 1·63 Å, gives 2·42 and 2·18 Å for P · · · P and N · · · N, respectively. Comparison with the values in Table 8 suggests that cross-ring repulsions have stretched the P–N bonds in compounds (6)—(9) to a length greater than would occur in a corresponding open ring structure.

The N–C bond length in $[PhNP(S)Ph]_2$ is 1·418(6) Å, a value in agreement with the N–C bond lengths in acetanilide [20] [1·413(3) Å] and thioacetanilide-*S*-oxide [21] (1·42 Å). A similar N–C bond length has been found in triphenylamine [22] [1·42(4) Å].

The N–C bond in $[PhNP(S)Ph]_2$ is shorter than that in $[MeNP(S)Ph]_2$ and $[EtNP(S)Ph]_2$, mean [13] 1·46(1) Å. Part of the difference of 0·04 Å may be ascribed to the different hybridization states of the carbon atoms involved, the hybridization being trigonal (tr) in the former molecule and tetrahedral (te) in the latter ones. An estimate of the effect of hybridization on bond length may be obtained from the difference between C(te)–C(te) and C(te)–C(tr) bonds, for which Lide [23] gives the value 0·025 Å, and from the corresponding difference between O–C(te) and O–C(tr) bonds, which may be derived as 0·029 Å from data for the compounds $N_3P_3(OPh)_6$, $N_6P_6(OMe)_{12}$, and $N_8P_8(OMe)_{16}$,[24] and for $N_4P_4(OMe)_8$.[25]

If, similarly, 0·027 Å of the N–C bond-length difference in $[Me,EtNP(S)Ph]_2$ and $[PhNP(S)Ph]_2$ is accounted for by hybridization differences of the carbon atoms, the remaining difference of *ca.* 0·013 Å indicates some conjugation between the nitrogen lone-pair orbital and the π bonding system of phenyl rings (*b*) or (*d*) in $[PhNP(S)Ph]_2$. The small angle between the plane of a phenyl ring and the plane of the $(N-P)_2$ ring [5·8 and 9·7° in molecules (1) and (2) respectively] is in agreement with this.

The sum of the three valence angles around nitrogen is 359·9° indicating a planar configuration. A planar environment at three-co-ordinated nitrogen has been observed in many phosphorus–nitrogen compounds (see *e.g.* ref. 26) and can be taken as evidence for a delocalized π bonding system over the P–N–P fragment involved. For $[PhNP(S)Ph]_2$ this means that half the $(N-P)_2$ ring and the phenyl group bonded to nitrogen form one continuous conjugated system.

Although all compounds represented in Table 8 have a planar nitrogen environment, it should be noted that the exocyclic angles P–N–C are equal in those with four-co-ordinated phosphorus atoms and unequal (*ca.* 135 and 125°) in those with five-co-ordinated phosphorus atoms. The difference can be understood, according to the VSEPR theory, in terms of the electron densities of the P–N bonds in the respective types of compounds.

The P–S bond length [1·913(2) Å] is typical for a terminal P–S bond.[27] The P–C bond length [1·796(6) Å] is the same as the mean (1·796 Å) of such bonds in four phenyl-substituted cyclotriphosphazenes.[28,29]

The valence angles around the phosphorus atom show that the bonding arrangement at this atom is distorted compared with a regular tetrahedral one. The main origin of the distortion is the inclusion of the phosphorus atom in the four-membered $(N-P)_2$ ring. Comparison with the corresponding valence angles in related compounds, *e.g.* Et_3PS,[30] $N_3P_3Ph_xCl_{6-x}$,[28] shows that the small ring angle N–P–N is compensated for by somewhat larger values of all the exocyclic angles.

The C–C bond lengths [mean 1·386(8) Å] and the angles C–C–C in the phenyl rings [mean 120·0(6)°] are as expected.[31]

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All intermolecular contacts are in accord with the appropriate van der Waals distances.

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