

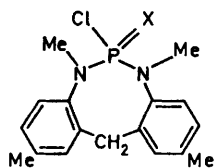
Aromatic Amines and their Derivatives. Part 1. The Reactions of 4-Methyl-2-[*N*-(*p*-toluidinyl)methyl]aniline with Phosphorus Oxychloride and Thiophosphoryl Chloride. Spectroscopic Investigations of the Heterocyclic Products, and the Crystal Structure of 2-Chloro-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-Oxide

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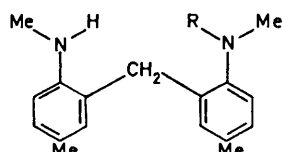
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4-Methyl-2-[*N*-(*p*-toluidinyl)methyl]aniline, (3), reacts with phosphorus oxychloride or thiophosphoryl chloride to give 2-chloro-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-oxide, (5a), or 2-{4-methyl-2-[*N*-(*p*-toluidinyl)methyl]anilino}-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-sulphide, (5c), respectively. Under more forcing conditions the diamine (3) and thiophosphoryl chloride give the pentacycle, 3,11-dimethyl-6,14-di-*p*-tolyl-5,6,13,14-tetrahydro[1,3,2,4]diazadiphospheto[1,2-*a*;3,4-*a'*]-{bis[1,3,2]benzodiazaphosphorine} 7,15-disulphide, (6). The ^1H n.m.r. spectra of the above compounds are discussed. A crystal structure determination of the compound (5a) shows it to consist of hydrogen-bonded dimers. The heterocyclic rings are not planar. A tentative relation between dihedral angles, P-N-C-H, and spin-spin coupling constants, $J(\text{P-N-C-H})$, is drawn for compounds (5a) and (6).

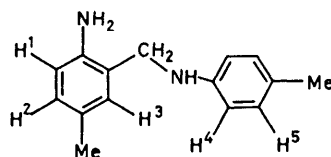
In an extension of our work on ambident nucleophiles,¹ novel eight-membered phosphorus-containing heterocycles, (1), were isolated and their structures elucidated



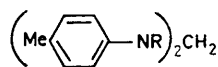
(1) a: X = O
b: X = S



(2) a: R = H
b: R = Me



(3)



(4) a: R = H
b: R = Me

by spectroscopic and crystallographic techniques.^{2,3} Studies to ascertain the mechanism of formation of compounds (1) were undertaken, and the preliminary results have been published elsewhere.³

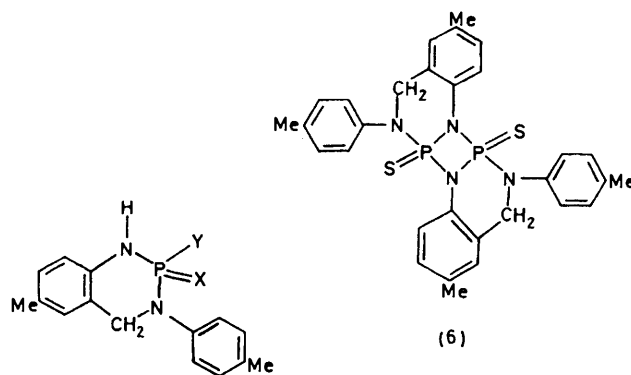
It was shown that the bidentate amine (2a), or more likely (2b) (formed in the reaction medium), reacts with phosphorus oxychloride, $\text{P}(\text{O})\text{Cl}_3$, or thiophosphoryl chloride, $\text{P}(\text{S})\text{Cl}_3$, to give the heterocycles (1a) and (1b) respectively. The diamine (2a) was synthesised by a two-stage acid-catalysed rearrangement⁴ of compound (4b). Compound (3) comes from the rearrangement of bis-(*p*-toluidinyl)methane, (4a), in the presence of acid.

RESULTS AND DISCUSSION

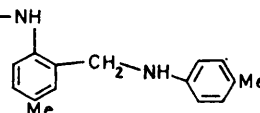
The diamine (3) cyclises under mild conditions with phosphorus oxychloride, $\text{P}(\text{O})\text{Cl}_3$, in the presence of an

organic base to form the diazaphosphorine, (5a). This crystallises from benzene or carbon tetrachloride with a molecule of the solvent, which is readily removed by heating *in vacuo*. Compound (5a) is a stable solid, although it decomposes in solution on prolonged standing.

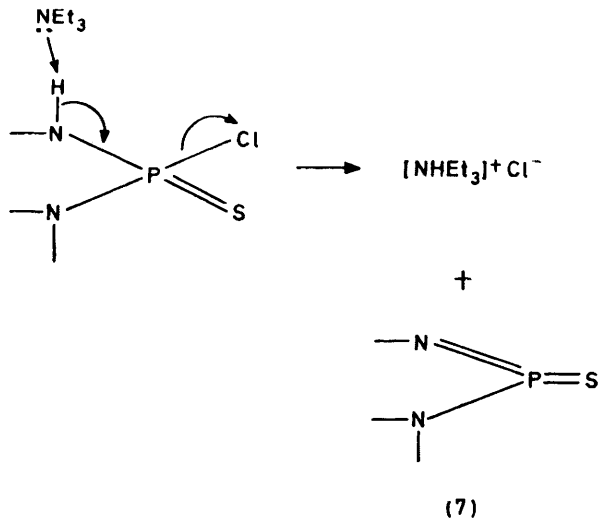
A similar reaction of the diamine (3) with thiophosphoryl chloride, $\text{P}(\text{S})\text{Cl}_3$, in the presence of 2 equiv. triethylamine, gives two products under mild conditions (one in trace quantities) in benzene or chloroform. The major product is not, however, the diazaphosphorine (5b), but its derivative, (5c). We were unable to isolate compound (5b) under any of the various conditions investigated. The formation of the derivative (5c) might be due to the presence of a metathiophosphoramidate type of intermediate (7), with triethylamine acting as a proton abstractor (see top of p. 2).



(5) a: X = O, Y = Cl
b: X = S, Y = Cl
c: X = S, Y = -NH



Such a monomeric metathiophosphoramidate $[(R_3C)(R_3Si)N]P(S)(NCR_3)$ ($R = Me$) has recently been isolated by Scherer and Kuhn.⁵ The intermediate, (7), suggested above, could then react with another molecule of diamine



(3) to form the amino-derivative, (5c). When the reaction is carried out with four equivalents of triethylamine in boiling toluene, the only product is the pentacycle (6). This compound is identical with the trace product of the same reaction when carried out under mild conditions. It may be formed by the dimerisation of the metathiophosphoramidate intermediate, (7), or by the reaction of (7) with (5c) [or transient (5b)].

Such a dimerisation process has been shown to give, in related compounds, similar four-membered P-N ring systems, $[(R_2N)P(NR)_2] \rightarrow [(R_2N)(RN)PNR]_2$ ($R = Me_3Si$).⁶

Spectroscopy.—The 1H n.m.r. spectrum of the diamine (3) (in CCl_4) shows a complicated phenyl region, with signals that approximate to: (a) a singlet for H^3 (δ 6.79); (b) an AB quartet for H^1 and H^2 (with little coupling to H^3) [H^1 at δ 6.42, H^2 at 6.92, $J(H^1H^2)$ 8.5 Hz]; and (c) a second AB quartet for H^4 and H^5 [H^4 at δ 6.47, H^5 at 6.92, $J(H^4H^5)$ 8.5 Hz]. Singlets for the methylene group (δ 4.03), for the NH protons (δ 3.6), and for both *p*-methyl groups (δ 2.21) were also observed. The i.r. spectrum showed a secondary N-H band at 3 440 cm^{-1} and two primary N-H bands at 3 330 and 3 260 cm^{-1} . The 1H n.m.r. spectrum of the diazaphosphorine, (5a), shows several interesting features. The ring NH proton gives a signal considerably downfield from its diamine precursor [δ 7.7, $J(PH)$ 7.0 Hz]. This suggests that this proton may be involved in hydrogen-bonding in solution, probably by an intermolecular interaction with the phosphoryl oxygen.⁷ The methylene protons give rise to an eight-line signal which can be approximated to the AB part of an ABX pattern (Figure 1). One of the protons couples very strongly (Table 1) with the phosphorus nucleus. The coupling constant, $J(PH_A)$, is large (25.5 Hz in nitrobenzene, 23.5 Hz in deuteriochloroform). Such strong coupling may be interpreted

TABLE I
 1H N.m.r. data for (5a), (5c), and (6) (solvent $CDCl_3$)

Compound	CH ₂		<i>p</i> -CH ₃ δ
	δ	J/Hz	
(5a)	H _A 4.57	$J(H_A H_B)$ 15.0	2.26
	H _B 4.92	$J(PH_A)$ 23.5	2.33
(5c)	H _A 4.13	$J(H_A H_B)$ 15.0	2.21
	H _B 4.50	$J(PH_A)$ 19.0	2.26
		$J(PH_B)$ 13.0	
(6)	H _A 4.16	$J'(H_A H_B)$ 15.0 *	2.32
	H _B 5.46	$J'(PH_A)$ 27.5 *	2.34
		$J'(PH_B)$ 8.0 *	

* Apparent spin-spin coupling constants.

as the C-H_A bond and the N-P bond lying nearly in the same plane; in other words, the dihedral angle between P-N and C-H_A could be unusually small (see X-ray crystallographic section).

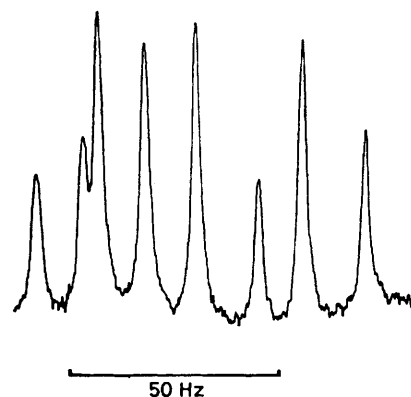


FIGURE 1 The methylene proton n.m.r. spectrum of compound (5a) in nitrobenzene at 100 MHz (sweep-width 270 Hz)

The i.r. spectrum of compound (5a) displays a rather broad N-H stretching band at 3 180 cm^{-1} . The N-H band appears at a very low frequency, which is in good agreement with the frequency range postulated by Bellamy^{8a} for a hydrogen-bonded *cis*-N-H stretching band for secondary amides. The broad P=O band is also within the range for hydrogen-bonded phosphoryl frequencies put forward by the same author,^{8b} as well as by Thomas and Chittenden.⁹ The observed values are also in good agreement with those reported by Edmundson¹⁰ for similar compounds.

The 1H n.m.r. spectrum of compound (5c) also exhibits an eight-line signal for the CH₂ protons of the diazaphosphorine ring, though neither of these protons is as strongly coupled to the phosphorus nucleus (Table 1) as H_A is in compound (5a). Signals from only two NH protons were directly observed, C-NH (δ 3.3) and P-NH [δ 5.8, $J(PH)$ 9.0 Hz]. The third NH proton signal, another P-NH, was obscured by those of the aromatic protons (δ 6.3–7.2) and detected by integration before and after D₂O treatment.

The methylene signals of compound (6) (Table 1 and Figure 2) also give rise to a spectrum of the ABX (tending to an AMX) type. In addition to the eight sharp lines, humps characteristic of long range virtual

coupling are observed. This phenomenon, which involves parameters such as the chemical-shift differences between the phosphorus nuclei and their spin-spin interactions, has been observed in aminocyclophosphazenes,¹¹ alkoxy-cyclophosphazenes,¹² and some acyclic phosphorus compounds.^{7a}

X-Ray Crystallography.—In order to obtain further structural information on these diazaphosphorines an X-ray crystallographic investigation of compound (5a) was undertaken. The interatomic distances and inter-bond angles are given in Table 2. Figure 3 shows the asymmetric unit and Figure 4 shows the packing of the molecules in the unit cell.

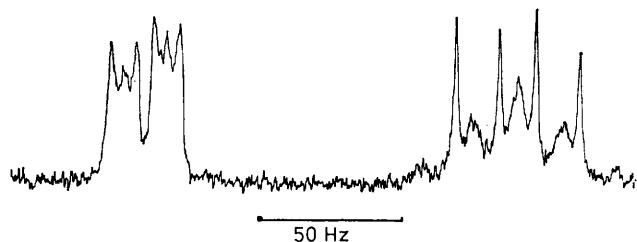


FIGURE 2 The methylene proton n.m.r. spectrum of compound (6) in CDCl_3 at 100 MHz (sweep-width 270 Hz)

The crystal is constructed from isolated hydrogen-bonded dimers of (5a). The dimer is made up of two unique molecules which are not related by any cell symmetry operation. The two molecules, however, are practically identical. Each molecule consists of an aromatic six-membered ring fused with a 1,2-linkage to a heterocyclic, formally saturated, six-membered ring, which contains the N-P-N grouping. The atoms of the aromatic ring are, within experimental error, co-planar, but the heterocyclic ring is not planar. Table 3 gives the torsional angles around this ring, from which it can be seen that in both molecules the atoms of the groups P(1)-N(11)-C(21)-C(26)-C(1) (equation to ring plane:

$-14.901x + 7.506y - 7.182z = 0.219$) and P(2)-N(21)-C(41)-C(46)-C(2) ($16.448x - 9.069y + 4.389z = -0.930$) are practically co-planar, and that N(1) and N(2) are respectively well out of the planes. The mean deviations from the least-squares best plane through each group are 0.031 and 0.035 Å, and the sixth atoms of the rings are 0.563 and 0.600 Å from the corresponding planes. As can be seen in Figure 3, and confirmed in Table 3, the two molecules are almost centrosymmetrically related.

The compound is closely analogous to the 6-chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo[*d,g*]-[1,2,3]diazaphosphocine 6-oxide, and the corresponding 6-sulphide.^{13a,b} The structure of the 6-oxide, however, was determined from visual data and refined by block-diagonal least squares,^{13a} so that the dimensions reported for it must be treated with some caution. In compound (5a) the P-Cl, P-N, and P=O bond lengths are all shorter than those observed in the 6-oxide, and the former two also, than in the 6-sulphide. The P-Cl bond lengths [mean 2.031(2) Å] compare with 2.069(3) Å and 2.053(2) Å; the P-N bond lengths [mean 1.618(2) Å] compare with 1.635(3) and 1.643(4) Å respectively. The P=O bond lengths [mean 1.451(3) Å] compare with 1.492(5) Å in the 6-oxide. The P-N and P-Cl bond lengths are within the range of acceptable values,¹⁴ but the P=O bond length is much shorter than that normally observed in compounds with the $\text{N}_2\text{XP=O}$ grouping.^{15a,b} The two hydrogen bonds are not equivalent; O(1) \cdots N(21) is 2.767(6) with an N(21)-H(2) bond length of 0.822(6) Å, and O(2) \cdots N(11) is 2.893(6) with N(11)-H(1) 1.003(6) Å. These lengths represent reasonably strong hydrogen bonds.¹⁶ As predicted from the solution n.m.r. (see above), one of the hydrogen atoms of the methylene groups in the heterocyclic rings is close to the plane through the P-N-C atoms. The torsional angle (for e.s.d.s see Table 3) P(1)-N(1)-C(1)-H(112) is -174.6° , just 5.4° away from complete co-planarity, and

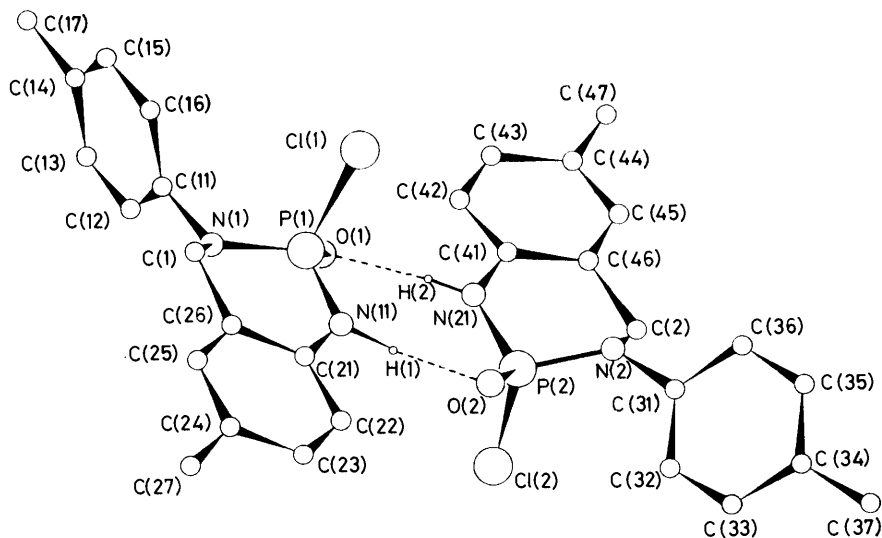


FIGURE 3 Projection of the asymmetric unit viewed along *b*

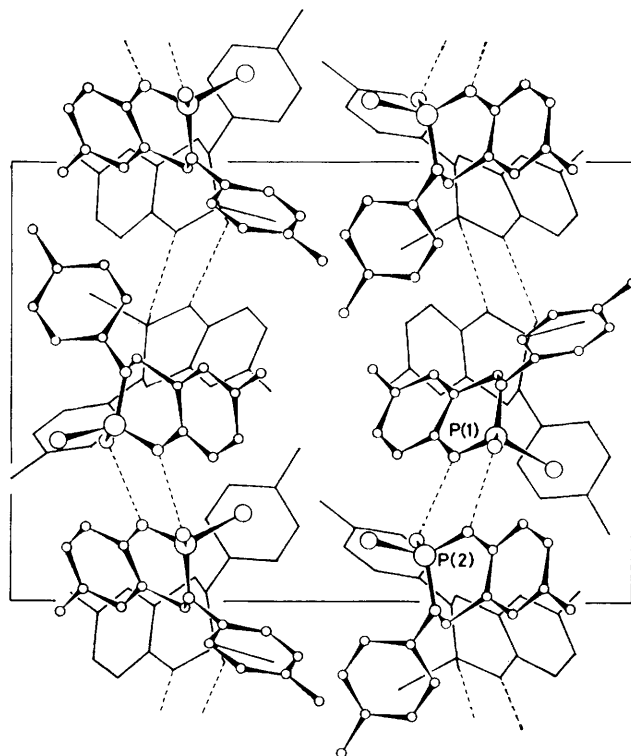
TABLE 2

Interatomic distances and bond angles

P(1)—Cl(1)	2.026(2)	P(2)—Cl(2)	2.035(3)
P(1)—N(1)	1.625(4)	P(2)—N(2)	1.627(4)
P(1)—N(11)	1.608(4)	P(2)—N(21)	1.613(4)
P(1)—O(1)	1.456(4)	P(2)—O(2)	1.446(3)
N(1)—C(1)	1.485(7)	N(2)—C(2)	1.492(9)
N(1)—C(11)	1.451(5)	N(2)—C(31)	1.447(5)
N(11)—C(21)	1.402(6)	N(21)—C(41)	1.396(5)
N(11)—H(1)	1.003(6)	N(21)—H(2)	0.822(6)
C(1)—C(26)	1.501(6)	C(2)—C(46)	1.530(11)
C(11)—C(12)	1.379(8)	C(31)—C(32)	1.376(6)
C(11)—C(16)	1.366(8)	C(31)—C(36)	1.388(7)
C(12)—C(13)	1.373(7)	C(32)—C(33)	1.378(7)
C(13)—C(14)	1.381(10)	C(33)—C(34)	1.375(8)
C(14)—C(15)	1.374(11)	C(34)—C(35)	1.378(7)
C(14)—C(17)	1.513(10)	C(34)—C(37)	1.509(8)
C(15)—C(16)	1.376(8)	C(35)—C(36)	1.372(7)
C(21)—C(22)	1.385(6)	C(41)—C(42)	1.370(6)
C(21)—C(26)	1.399(7)	C(41)—C(46)	1.386(7)
C(22)—C(23)	1.365(8)	C(42)—C(43)	1.374(6)
C(23)—C(24)	1.384(9)	C(43)—C(44)	1.382(8)
C(24)—C(25)	1.384(6)	C(44)—C(45)	1.378(6)
C(24)—C(27)	1.508(8)	C(44)—C(47)	1.488(7)
C(25)—C(26)	1.365(6)	C(45)—C(46)	1.381(6)
O(1)···H(2)	1.97	O(2)···H(1)	1.90
Cl(1)—P(1)—N(1)	105.7(2)	Cl(2)—P(2)—N(2)	106.8(2)
Cl(1)—P(1)—N(11)	106.5(2)	Cl(2)—P(2)—N(21)	105.3(2)
Cl(1)—P(1)—O(1)	107.5(2)	Cl(2)—P(2)—O(2)	108.2(2)
N(1)—P(1)—N(11)	103.9(2)	N(2)—P(2)—N(21)	103.2(2)
N(1)—P(1)—O(1)	116.7(2)	N(2)—P(2)—O(2)	116.7(2)
N(11)—P(1)—O(1)	115.7(2)	N(21)—P(2)—O(2)	115.7(2)
P(1)—N(1)—C(1)	117.0(3)	P(2)—N(2)—C(2)	114.5(4)
P(1)—N(1)—C(11)	115.1(3)	P(2)—N(2)—C(31)	121.8(3)
C(1)—N(1)—C(11)	116.6(4)	C(2)—N(2)—C(31)	114.5(5)
P(1)—N(11)—C(21)	125.4(4)	P(2)—N(21)—C(41)	125.4(3)
P(1)—N(11)—H(1)	118.3(5)	P(2)—N(21)—H(2)	127.2(5)
C(21)—N(11)—H(1)	116.2(5)	C(41)—N(21)—H(2)	107.3(6)
N(1)—C(1)—C(26)	111.7(4)	N(2)—C(2)—C(46)	111.3(8)
N(1)—C(11)—C(12)	118.3(5)	N(2)—C(31)—C(32)	122.1(4)
N(1)—C(11)—C(16)	122.0(5)	N(2)—C(31)—C(36)	118.5(4)
C(12)—C(11)—C(16)	119.6(4)	C(32)—C(31)—C(36)	119.4(4)
C(11)—C(12)—C(13)	120.0(5)	C(31)—C(32)—C(33)	120.7(5)
C(12)—C(13)—C(14)	121.3(6)	C(32)—C(33)—C(34)	120.7(4)
C(13)—C(14)—C(15)	117.2(5)	C(33)—C(34)—C(35)	117.8(5)
C(13)—C(14)—C(17)	121.3(7)	C(33)—C(34)—C(37)	121.6(5)
C(15)—C(14)—C(17)	121.4(7)	C(35)—C(34)—C(37)	120.5(5)
C(14)—C(15)—C(16)	122.3(6)	C(34)—C(35)—C(36)	122.6(5)
C(11)—C(16)—C(15)	119.4(6)	C(31)—C(36)—C(35)	118.7(4)
N(11)—C(21)—C(22)	119.7(5)	N(21)—C(41)—C(42)	120.6(4)
N(11)—C(21)—C(26)	120.9(4)	N(21)—C(41)—C(46)	120.2(4)
C(22)—C(21)—C(26)	119.4(4)	C(42)—C(41)—C(46)	119.2(4)
C(21)—C(22)—C(23)	119.9(5)	C(41)—C(42)—C(43)	120.8(4)
C(22)—C(23)—C(24)	122.2(5)	C(42)—C(43)—C(44)	121.7(4)
C(23)—C(24)—C(25)	116.6(5)	C(43)—C(44)—C(45)	116.4(4)
C(23)—C(24)—C(27)	120.9(5)	C(43)—C(44)—C(47)	122.5(4)
C(25)—C(24)—C(27)	122.5(5)	C(45)—C(44)—C(47)	121.0(5)
C(24)—C(25)—C(26)	123.2(5)	C(44)—C(45)—C(46)	123.1(5)
C(1)—C(26)—C(21)	121.2(4)	C(2)—C(46)—C(41)	120.8(4)
C(1)—C(26)—C(25)	120.1(4)	C(2)—C(46)—C(45)	119.6(5)
C(21)—C(26)—C(25)	118.6(4)	C(41)—C(46)—C(45)	118.7(4)
N(11)—H(1)—O(2)	169	N(21)—H(2)—O(1)	163

the torsional angle P(2)—N(2)—C(2)—H(221) is 155.8°, which is 24.2° away (Table 3) (for relationship to spin-spin coupling constants, see below). There is no obvious reason why the two molecules of the dimer are crystallographically non-equivalent, though presumably this is a consequence of crystal-packing force requirements since the two tolyl groups bonded at the nitrogen atoms have different conformations [torsional angle P(1)—N(1)—C(11)—C(12) is 83.4°; P(2)—N(2)—C(31)—C(32) is 38.4°]. The dimensions of the rest of the molecule are unexceptional and the final difference-Fourier synthesis shows no unusual features.

The structure of the related compound, (6), has recently been determined by Cameron *et al.*¹⁷ The sulphur atoms were shown to be in a *trans* relation. Insufficient diffraction data was obtained on compound (6) for a meaningful comparison with structure (5a).

FIGURE 4 The unit cell projected down *b*

Dihedral Angles and Coupling Constants.—It is likely that in solution the two halves of the dimer (5a) are similar. If the preferred orientations of the *p*-tolyl groups are related to the ones in the crystal, that

TABLE 3

Torsional angles (e.s.d.s 0.7–0.9°) in the heterocyclic rings and adjacent atoms

N(11)—P(1)—N(1)—C(1)	43.7
P(1)—N(1)—C(1)—C(26)	—53.0
N(1)—C(1)—C(26)—C(21)	32.3
C(1)—C(26)—C(21)—N(11)	—6.0
C(26)—C(21)—N(11)—P(1)	0.0
C(21)—N(11)—P(1)—N(1)	—16.7
O(1)—P(1)—N(1)—C(11)	—45.2
O(1)—P(1)—N(11)—H(1)	30.6
P(1)—N(1)—O(11)—C(12)	83.4
P(1)—N(1)—C(1)—H(111)	68.8
P(1)—N(1)—C(1)—H(112)	—174.6
N(21)—P(2)—N(2)—C(2)	—49.1
P(2)—N(2)—C(2)—C(46)	55.4
N(2)—C(2)—C(46)—C(41)	—33.9
C(2)—C(46)—C(41)—N(21)	13.7
C(46)—C(41)—N(21)—P(2)	—11.6
C(41)—N(21)—P(2)—N(2)	27.7
O(2)—P(2)—N(2)—C(31)	37.8
O(2)—P(2)—N(21)—H(2)	—28.2
P(2)—N(2)—C(31)—C(32)	38.4
P(2)—N(2)—C(2)—H(222)	—91.7
P(2)—N(2)—C(2)—H(221)	155.8

hydrogen atom of the methylene group which has the small dihedral angle will come under the influence of the aromatic shielding cone. This would allow a tentative assignment of this proton as H_A , and hence to it being involved in the larger spin-spin coupling constant $J(PH_A)$. A similar reasoning applies to proton H_A and $J'(PH_A)$ in compound (6).

EXPERIMENTAL

Crystals of (5a) were prepared as below, preliminary space-group data were determined from Weissenberg photographs, and accurate unit-cell dimensions were obtained by least-squares refinement of the setting angles of 12 reflections measured on an automatic diffractometer.

Crystal Data.— $C_{30}H_{32}Cl_2N_4O_2P_2$, $M = 614.5$, Monoclinic, $a = 19.338(10)$, $b = 13.195(5)$, $c = 12.815(4)$ Å, $\gamma = 111.88(2)^\circ$, $U = 3\,034.39$ Å³, $Z = 4$, $D_c = 1.344$ g cm⁻³, $F(000) = 1\,280$, space group $P2_1/a$, (C_2^h , No. 14), from systematic absences ($hk0$ for h odd, $h00$ for h odd, and $00l$ for l odd). Cu- K_α radiation, $\lambda = 1.540\,51$ Å, $\mu(\text{Cu-}K_\alpha) = 30.64$ cm⁻¹. Intensities of 3 153 reflections (97% of those observable) were measured on a Picker FACS I four-circle diffractometer in the range $2 \leq \theta \leq 59^\circ$. Of these, 2 359 reflections had $I > 3\sigma(I)$ and were considered observed. Lorentz and polarisation, but not absorption, corrections were applied.

Structure Analysis.—The structure was solved using the Sheldrick X -ray system.¹⁸ The positions of the phosphorus and chlorine atoms were determined from a three-dimensional sharpened Patterson function. Most of the light atoms were located in the Fourier synthesis phased on the positions of the phosphorus and chlorine atoms. The positions of the remaining light atoms were found in successive Fourier syntheses. The structure was refined by large-block least squares (minimising $\sum \omega \Delta F^2$) with isotropic temperature factors on all atoms. This refinement converged at R 0.11 and the positions of all the hydrogen atoms were detected in a difference-Fourier synthesis. The refinement continued with anisotropic temperature factors on all but the hydrogen atoms, and it converged at R 0.046. The weighting scheme was $w = [\sigma^2 |F_o| + 0.000\,3 F_o^2]^{-1}$ where σ is the individual e.s.d. for each reflection and was calculated from the diffractometer counting statistics. The final atomic co-ordinates are given in Table 4; observed structure amplitudes, calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22519 (24 pp.).* The atomic scattering factors were those of ref. 19 and were corrected for the real part of the anomalous dispersion effect.

Chemicals and Spectroscopic Techniques.—Phosphorus oxychloride (May and Baker Ltd.), thiophosphoryl chloride (Alfa Inorganics Inc.), triethylamine, and *p*-toluidine (Koch-Light Ltd.) were purified by conventional methods. ¹H N.m.r. spectra were obtained from Varian Associates Model A60 and JEOL Model JNM-MH-100 spectrometers (SiMe₄ as internal standard). I.r. spectra were recorded (KBr disc) on a Perkin-Elmer Model 457 grating i.r. spectrometer. Mass spectra were obtained from an A.E.I. MS9 spectrometer, PCMU, Harwell. Microanalyses were carried out by Dr. Kolbe Laboratories, Mülheim, Ruhr, Germany.

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

TABLE 4
Atomic parameters ($\times 10^4$, hydrogen $\times 10^3$)

Atom	x	y	z
P(1)	2 189(1)	8 166(1)	3 732(1)
Cl(1)	1 264(1)	8 199(1)	3 015(1)
N(1)	2 118(2)	8 475(3)	4 944(8)
N(11)	2 878(2)	9 197(3)	3 296(3)
O(1)	2 224(2)	7 100(3)	3 532(2)
C(1)	2 179(3)	9 611(4)	5 165(4)
C(11)	1 578(3)	7 617(4)	5 556(3)
C(12)	1 793(3)	6 821(4)	5 982(4)
C(13)	1 290(4)	5 974(5)	6 534(5)
C(14)	561(4)	5 888(5)	6 661(6)
C(15)	369(3)	6 710(6)	6 253(6)
C(16)	867(3)	7 571(5)	5 706(4)
C(17)	7(5)	4 954(6)	7 269(9)
C(21)	3 177(3)	10 225(4)	3 775(4)
C(22)	3 787(3)	11 037(4)	3 334(4)
C(23)	4 096(3)	12 027(5)	3 816(5)
C(24)	3 820(3)	12 258(4)	4 746(4)
C(25)	3 202(3)	11 438(4)	5 158(4)
C(26)	2 875(3)	10 436(4)	4 704(4)
C(27)	4 184(4)	13 352(5)	5 270(6)
P(2)	3 325(1)	7 557(1)	1 036(1)
Cl(2)	4 238(1)	7 203(1)	1 374(1)
N(2)	3 157(2)	7 316(3)	-202(3)
N(21)	2 636(3)	6 606(3)	1 587(3)
O(2)	3 463(2)	8 657(2)	1 388(2)
C(2)	2 983(7)	6 157(6)	-514(6)
C(31)	3 543(3)	3 112(3)	-990(3)
C(32)	4 287(3)	8 757(4)	-907(4)
C(33)	4 643(3)	9 485(4)	-1 687(5)
C(34)	4 267(3)	9 560(4)	-2 629(4)
C(35)	3 519(3)	8 920(5)	-2 639(4)
C(36)	3 146(3)	8 215(4)	-1 859(4)
C(37)	4 651(4)	10 323(5)	-3 454(5)
C(41)	2 239(3)	5 581(3)	1 159(3)
C(42)	1 751(2)	4 767(4)	1 759(4)
C(43)	1 348(3)	3 764(4)	1 335(4)
C(44)	1 410(3)	3 537(4)	293(4)
C(45)	1 905(3)	4 367(4)	-293(4)
C(46)	2 382(3)	5 375(4)	118(4)
C(47)	987(3)	2 451(5)	-177(5)
H(1)	314(4)	910(6)	265(6)
H(2)	247(3)	661(5)	218(5)
H(111)	173(2)	973(4)	488(4)
H(112)	217(4)	967(5)	595(2)
H(12)	230(2)	683(5)	583(5)
H(13)	140(3)	534(3)	681(4)
H(15)	-16(2)	665(6)	624(6)
H(16)	71(3)	813(3)	536(4)
H(17)	-34(3)	518(6)	770(4)
H(18)	25(2)	458(4)	771(4)
H(19)	-31(3)	441(4)	673(4)
H(22)	397(2)	1 083(3)	268(2)
H(23)	451(2)	1 263(3)	348(4)
H(25)	296(2)	1 153(3)	581(2)
H(27)	474(1)	1 362(6)	518(6)
H(28)	402(3)	1 390(4)	492(4)
H(29)	407(4)	1 335(6)	603(2)
H(221)	268(4)	618(8)	-118(3)
H(222)	339(3)	584(5)	-77(5)
H(32)	459(2)	873(3)	-30(2)
H(33)	517(4)	994(4)	-156(4)
H(35)	320(2)	896(4)	-325(2)
H(36)	262(1)	772(4)	-191(4)
H(37)	477(2)	1 115(2)	-341(3)
H(38)	525(1)	1 041(3)	-318(3)
H(39)	475(2)	1 011(3)	-418(2)
H(42)	172(3)	493(4)	251(2)
H(43)	102(3)	317(4)	181(4)
H(45)	202(2)	422(4)	-102(2)
H(47)	473(2)	210(5)	121(4)
H(48)	94(3)	252(6)	-95(2)
H(49)	124(3)	192(5)	-6(5)

4-Methyl-2-[N-(*p*-toluidinyl)methyl]aniline (3).—Bis-*p*-toluidinylmethane (4a) (11.3 g, 0.05 mol) and *p*-toluidine hydrochloride (7.17 g, 0.05 mol) were dissolved in *p*-

toluidine (133.75 g, 1.25 mol). The mixture was stirred at 60–80 °C (4 h) under nitrogen. After cooling to room temperature, it was neutralised with sodium hydroxide solution and then steam distilled to remove *p*-toluidine. The oily product solidified on cooling and was repeatedly recrystallised (charcoal treatment) from light petroleum (b.p. 60–80 °C) to obtain (3), m.p. 88 °C (lit.,²⁰ 88 °C), yield 8.2 g (73%) (Found: C, 79.6; H, 8.0; N, 12.4%; M^+ , 226.147 1. $C_{15}H_{16}N_2$ requires C, 79.6; H, 8.0; N, 12.4%; M , 226.147 1).

2-Chloro-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-Oxide (5a).—Compound (3) (2 g, 0.009 mol) and triethylamine (1.8 g, 2.48 ml, 0.018 mol) were dissolved in benzene (NaH dried) (100 ml). Phosphorus oxychloride (1.36 g, 0.82 ml, 0.009 mol) was added dropwise, with stirring, at room temperature. After 24 h triethylamine hydrochloride was filtered off and the solvent reduced to half the original volume. Compound (5a) crystallised out on standing, and was filtered off and dried *in vacuo*, m.p. 158–163 °C (with decomposition), yield 1.3 g (47%) (Found: C, 58.7; H, 5.25; N, 9.1; P, 10.1; Cl, 11.5%; M^+ , 306.068 5. $C_{15}H_{16}N_2ClOP$ requires C, 58.5; H, 5.2; N, 9.1; P, 10.1; Cl, 11.6%; M , 306.068 9).

2-{4-Methyl-2-[N-(*p*-toluidinyl)methyl]anilino}-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-Sulphide (5c).—Compound (3a) (4.52 g, 0.02 mol) and triethylamine (2.1 g, 0.04 mol) were dissolved in benzene (NaH dried) (150 ml). Thiophosphoryl chloride (3.38 g, 0.02 mol) was added dropwise under nitrogen and the mixture was heated under reflux (5 h). Triethylamine hydrochloride was filtered off, the solvent removed and the residual oil eluted through a silica column [benzene–ethyl acetate (85:15)]. The first component eluted (in minute amount) was compound (6). (5c) was eluted next and was recrystallised from cyclohexane, m.p. 161 °C, yield 1.4 g (22%) (Found: C, 71.2; H, 7.6; N, 10.4; P, 5.8; S, 5.0%; M^+ , 512.214 8. $C_{30}H_{33}N_4PS$ requires C, 70.3; H, 6.4; N, 10.9; P, 6.0; S, 6.3%; M , 512.216 3).

3,11-Dimethyl-6,14-*di-p*-tolyl-5,6,13,14-tetrahydro[1,3,2,4]-diazadiphospho[1,2-*a*:3,4-*a'*]bis[1,3,2]benzodiazaphosphorine 7,15-Disulphide (6).—Compound (3) (1 g, 0.004 4 mol) and triethylamine (1.8 g, 0.017 mol) were dissolved in toluene (NaH dried) (50 ml). While the mixture was refluxed under nitrogen, thiophosphoryl chloride (0.7 g, 0.004 4 mol) was added dropwise and the resultant mixture kept under reflux (6 h). Triethylamine hydrochloride was filtered off while the mixture was still hot and the solvent was reduced to one-third its original volume. The crystals which separated were filtered off, and recrystallised from

acetonitrile to give colourless needles, m.p. 273 °C, yield 0.45 g (43%) (Found: C, 63.0; H, 5.2; N, 9.75; P, 10.85; S, 11.2%; M^+ , 572.138 0. $C_{30}H_{30}N_4S_2P_2$ requires C, 62.9; H, 5.2; N, 9.8; P, 10.8; S, 11.2%; M , 572.137 1).

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