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The Crystal and Molecular Structure of 1,1,3,3,5,5-Hexaphenyl-1,3-diphospha-5-arsatriazene

BY M. J. BEGLEY, D. B. SOWERBY AND R. J. TILLOTT

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

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$Ph_6P_2AsN_3$ is triclinic, $P\bar{1}$, with $a = 9{\cdot}601$ (1), $b = 13{\cdot}015$ (1), $c = 15{\cdot}309$ (1) Å, $\alpha = 106{\cdot}8$ (1), $\beta = 93{\cdot}5$ (1), $\gamma = 119{\cdot}0$ (1)°, $Z = 2$. The structure was solved by Patterson and Fourier methods from 4624 diffractometer data and refined to a final R of 0·051. The compound contains a planar six-membered AsNPNPN ring with pairs of phenyl groups attached to the As and P atoms. The structure is, however, disordered with the As atom occupying the P positions in *ca* 49% of the molecules. The ring bond lengths which vary between 1·636 and 1·700 Å are thus not meaningful but it is possible to correct for the effects of disorder from the refined values for the population parameters of the heavier atoms. This leads to two As–N distances of 1·790 Å and two pairs of P–N distances of 1·635 and 1·557 Å. In a similar way it is possible to obtain values of 1·91 and 1·79 Å for the As–C and P–C distances. The molecular parameters are discussed in relation to the possibility of delocalized multiple bonding within the ring.

Introduction

Structural information on a variety of compounds containing P_3N_3 or P_4N_4 ring systems is now available (Corbridge, 1974) and supports the presence of ring π bonding, but the exact nature of this bonding is still a matter for discussion. Although far fewer results have been obtained for the analogous As–N species, bond shortening within As_3N_3 (Krannick, Thewalt, Cook, Jain & Sisler, 1973) and As_4N_4 (Begley, Sowerby & Tillott, 1974) rings has been observed pointing to a broadly similar bonding picture to that above. Compounds have recently been prepared (Sowerby & Tillott, 1977) in which one of the P atoms in the P_3N_3 system is replaced by As and it was of interest to determine the molecular parameters of such a mixed ring. The compound chosen for investigation was $Ph_6P_2AsN_3$ as the presence of identical substituents at the P and As atoms would minimize exocyclic effects.

Experimental

The compound was prepared from diphenylarsenic trichloride and $[Ph_2(NH_2)PN(NH_2)Ph_2]Cl$ (Sowerby & Tillott, 1977). Suitable crystals were grown from hot acetonitrile, and a single crystal was loaded into a capillary in a dry box. Oscillation and Weissenberg photographs gave the cell dimensions and indicated that the compound was triclinic with the space group $P1$ or $P\bar{1}$. The data were then refined on a Hilger & Watts four-circle diffractometer with Mo $K\alpha$ radiation.

Crystal data

$C_{36}H_{30}AsN_3P_2$, $M_r = 641{\cdot}3$, triclinic, $a = 9{\cdot}601$ (1), $b = 13{\cdot}015$ (1), $c = 15{\cdot}309$ (1) Å, $\alpha = 106{\cdot}8$ (1), $\beta = 93{\cdot}5$ (1), $\gamma = 119{\cdot}0$ (1)°, $U = 1555{\cdot}1$ Å^3, $Z = 2$, $D_c = 1{\cdot}37$ g cm^{-3}, $F(000) = 660$, space group $P\bar{1}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}57$ cm^{-1}. The crystal was 0·2 × 0·5 × 0·7 mm.

The intensities of 4624 reflexions with $I > 3{\cdot}0\sigma$ were measured in the range $0° \le \theta \le 30°$. The structure was solved with the 1990 strongest reflexions on the University of Nottingham ICL 1906A computer but subsequent refinement used all the observed reflexions and the University of Manchester CDC 7600 computer. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974); data reduction and subsequent calculations used the X-RAY 70 package.

Structure determination

The structure was solved by the heavy-atom method. Block-diagonal, isotropic, least-squares refinement led to an R of 0·103 and further refinement with anisotropic thermal parameters gave $R = 0{\cdot}090$. A difference synthesis revealed approximate positions for 30 H atoms and refinement with the H atoms reduced R to 0·083. The positions of several of the H atoms were uncertain and refinement was unsatisfactory.

The difference map had also shown two strong peaks in the P atom positions and a large region of negative electron density near the As atom, suggesting that the crystal is disordered with the As atom occupying in some instances the positions ascribed to P.

The initial approach to this problem was to add two new atoms, As(2) and As(3), with the coordinates of P(1) and P(2) respectively and a new P(3) with the coordinates of As(1). It would then be possible to carry out further cycles of refinement allowing variation in the population parameters of all six atoms in addition to the usual atomic coordinates and thermal parameters. During these attempts it was assumed that the N, C and H parameters remained constant. Many variations in the refinement procedure were attempted in which different combinations of the possible variables were allowed to refine but in most cases there was no improvement in R. A final R of 0·08 was achieved after refinement in which the only variables were the coordinates and isotropic thermal parameters of As(2), As(3), and P(3) and the population parameters of all six heavy atoms.

Table 1. *Fractional coordinates* (×10⁴) *with estimated standard deviations*

	x	y	z
As(1)	3586 (1)	103 (0)	2533 (0)
P(1)	6296 (1)	2174 (1)	4107 (1)
P(2)	6349 (1)	2208 (1)	2243 (1)
N(1)	4589 (4)	793 (3)	3680 (2)
N(2)	7098 (4)	2885 (3)	3384 (2)
N(3)	4539 (4)	869 (3)	1820 (2)
C(1)	7799 (5)	1993 (4)	4726 (3)
C(2)	9360 (6)	3017 (4)	5168 (4)
C(3)	10514 (6)	2882 (5)	5636 (4)
C(4)	10063 (6)	1709 (5)	5667 (4)
C(5)	8517 (6)	703 (5)	5255 (4)
C(6)	7370 (5)	823 (4)	4774 (3)
C(7)	6001 (5)	3244 (4)	5025 (3)
C(8)	5030 (6)	2804 (5)	5625 (3)
C(9)	4798 (7)	3599 (6)	6330 (4)
C(10)	5544 (7)	4846 (6)	6446 (4)
C(11)	6498 (9)	5298 (5)	5857 (6)
C(12)	6751 (7)	4502 (5)	5140 (4)
C(13)	6198 (5)	3332 (4)	1819 (3)
C(14)	7536 (6)	4549 (4)	2081 (4)
C(15)	7430 (7)	5426 (5)	1778 (4)
C(16)	5989 (7)	5096 (5)	1221 (4)
C(17)	4643 (7)	3882 (5)	963 (4)
C(18)	4753 (6)	2996 (4)	1254 (3)
C(19)	7853 (5)	1957 (4)	1681 (3)
C(20)	7338 (5)	1013 (4)	821 (3)
C(21)	8491 (6)	858 (5)	373 (3)
C(22)	10112 (6)	1633 (5)	803 (4)
C(23)	*10638 (6)*	*2584 (5)*	*1659 (4)*
C(24)	9514 (5)	2748 (4)	2115 (3)
C(25)	1535 (5)	−74 (4)	2474 (3)
C(26)	1380 (6)	839 (4)	3128 (3)
C(27)	−151 (7)	717 (6)	3093 (4)
C(28)	−1497 (6)	−285 (6)	2417 (5)
C(29)	−1361 (6)	−1196 (5)	1754 (4)
C(30)	177 (5)	−1085 (4)	1780 (3)
C(31)	3173 (5)	−1525 (4)	2064 (3)
C(32)	2651 (6)	−2271 (5)	2618 (4)
C(33)	2228 (7)	−3516 (5)	2239 (5)
C(34)	2298 (10)	−4018 (6)	1336 (6)
C(35)	2821 (12)	−3277 (7)	797 (5)
C(36)	3254 (9)	−2025 (6)	1156 (4)

Before alternative approaches were considered, it was desirable to obtain the atomic coordinates from the full data set. This was corrected for Lorentz and polarization effects and an anomalous dispersion correction for As was included. Block-diagonal, anisotropic, least-squares refinement of the parameters for As(1), P(1) and P(2) and the N and C atoms obtained above reduced R to 0·123.

A weighting scheme, $W = \{1 + [(F_o - 14{\cdot}0)/21{\cdot}9]^2\}^{-1}$, was introduced but led to only a marginal reduction of R to 0·122. However, when the three extra heavy atoms As(2), As(3) and P(3) were introduced as described above, refinements of the positions, thermal parameters and population parameters led to a reduction of R to 0·073. At this stage it was found that the refinement could be improved if the three additional atoms were removed and refinement continued in the usual manner except that the population parameters of the three heavy atoms were also included as variables. After block-diagonal, least-squares refinement with anisotropic thermal parameters, an R of 0·063 was achieved. The

Table 2. *Fractional coordinates of hydrogen atoms* (×10³) *and thermal parameters* (×10³) *with estimated standard deviations*

	x	y	z	U
H(2)	965 (8)	380 (6)	512 (4)	72 (21)
H(3)	1166 (7)	374 (5)	598 (4)	54 (17)
H(4)	1083 (5)	168 (7)	614 (5)	90 (23)
H(5)	815 (8)	−5 (6)	528 (5)	74 (22)
H(6)	630 (6)	10 (5)	438 (4)	38 (15)
H(8)	454 (8)	200 (6)	554 (4)	65 (19)
H(9)	413 (7)	324 (5)	680 (4)	60 (18)
H(10)	541 (8)	539 (6)	690 (6)	76 (21)
H(11)	719 (10)	622 (7)	594 (6)	117 (29)
H(12)	738 (7)	491 (6)	461 (4)	62 (18)
H(14)	861 (7)	482 (6)	254 (4)	60 (18)
H(15)	836 (8)	623 (7)	202 (5)	88 (23)
H(16)	577 (7)	571 (5)	100 (4)	57 (18)
H(17)	352 (7)	370 (5)	51 (4)	49 (17)
H(18)	391 (6)	220 (4)	106 (3)	31 (14)
H(20)	619 (7)	42 (5)	61 (4)	57 (18)
H(21)	*803 (7)*	*18 (5)*	*−34 (4)*	*58 (17)*
H(22)	1105 (9)	168 (7)	53 (5)	89 (24)
H(23)	1182 (9)	312 (7)	203 (5)	102 (26)
H(24)	976 (7)	333 (5)	273 (4)	54 (18)
H(26)	237 (5)	158 (4)	365 (3)	26 (12)
H(27)	−21 (6)	142 (5)	357 (4)	52 (16)
H(28)	−258 (9)	−21 (7)	250 (5)	101 (26)
H(29)	−237 (8)	−213 (6)	115 (4)	73 (15)
H(30)	31 (7)	−164 (5)	133 (4)	47 (16)
H(32)	249 (7)	−193 (5)	325 (4)	50 (16)
H(33)	201 (8)	−394 (6)	264 (5)	76 (22)
H(34)	190 (9)	−487 (7)	103 (5)	105 (26)
H(35)	266 (12)	−363 (9)	8 (6)	151 (37)
H(36)	358 (8)	−147 (6)	75 (4)	74 (21)

30 H atoms were readily found from a difference synthesis and after further refinement with isotropic thermal parameters for the H atoms R converged at 0·051. No further changes occurred after one cycle of full-matrix refinement and a final difference synthesis showed no peaks greater than 0·3 e Å^{-3}.

The atomic coordinates for the heavier atoms are given in Table 1, those for the H atoms in Table 2.*

Results and discussion

Description of the structure

Bond distances and angles are in Table 3. Fig. 1 shows the numbering of the atoms and Fig. 2 a view of the molecule emphasizing the orientation of the phenyl groups. A measure of the randomness is given by the final values of the refined population parameters which are: As(1) 0·727 (2), P(1) 1·248 (5) and P(2) 1·342 (5).

The P_2AsN_3 ring is essentially planar (Fig. 2); the deviations from the mean plane are shown in Fig. 3(*a*). The equation of this plane in orthogonal ångström space is:

$$-0{\cdot}882x + 0{\cdot}470y - 0{\cdot}033z = -2{\cdot}880.$$

The slight puckering of the ring is not sufficiently regular to be described in terms of, for example, the chair conformation found in $[Ph_2PN]_3$ (Ahmed, Singh & Barnes, 1969). The torsion angles of the ring bonds

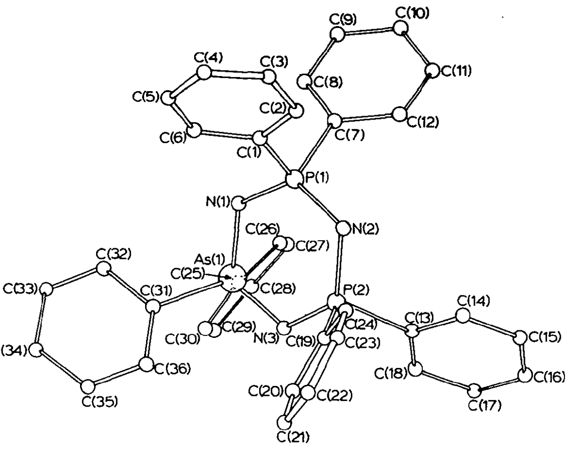

Fig. 1. Numbering of the atoms in $Ph_6P_2AsN_3$.

Table 3. *Bond distances* (Å) *and bond angles* (°) *with estimated standard deviations*

(See text for distances corrected for disorder.)

P(1)–N(1)	1·636 (3)	P(1)–C(1)	1·825 (5)
P(1)–N(2)	1·637 (4)	P(1)–C(7)	1·815 (5)
P(2)–N(2)	1·640 (3)	P(2)–C(13)	1·823 (6)
P(2)–N(3)	1·659 (3)	P(2)–C(19)	1·830 (5)
As(1)–N(1)	1·691 (3)	As(1)–C(25)	1·862 (5)
As(1)–N(3)	1·700 (4)	As(1)–C(31)	1·853 (5)
N(1)–P(1)–N(2)	118·4 (2)	N(1)–As(1)–N(3)	116·0 (2)
N(1)–P(1)–C(1)	107·4 (2)	N(1)–As(1)–C(25)	107·4 (2)
N(1)–P(1)–C(7)	109·2 (2)	N(1)–As(1)–C(31)	109·4 (2)
N(2)–P(1)–C(1)	109·4 (2)	N(3)–As(1)–C(25)	109·4 (2)
N(2)–P(1)–C(7)	107·5 (2)	N(3)–As(1)–C(31)	108·6 (2)
C(1)–P(1)–C(7)	104·0 (2)	C(25)–As(1)–C(31)	105·6 (2)
N(2)–P(2)–N(3)	118·8 (2)		
N(2)–P(2)–C(13)	108·1 (2)	As(1)–N(1)–P(1)	122·7 (2)
N(2)–P(2)–C(19)	109·2 (2)	P(1)–N(2)–P(2)	122·3 (2)
N(3)–P(2)–C(13)	107·2 (2)	P(2)–N(3)–As(1)	120·9 (2)
N(3)–P(2)–C(19)	108·4 (2)		
C(13)–P(2)–C(19)	104·2 (2)		
C(1)–C(2)	1·378 (5)	C(7)–C(8)	1·390 (7)
C(2)–C(3)	1·391 (10)	C(8)–C(9)	1·376 (9)
C(3)–C(4)	1·387 (10)	C(9)–C(10)	1·366 (10)
C(4)–C(5)	1·356 (6)	C(10)–C(11)	1·372 (11)
C(5)–C(6)	1·384 (9)	C(11)–C(12)	1·399 (10)
C(6)–C(1)	1·397 (7)	C(12)–C(7)	1·381 (7)
P(1)–C(1)–C(2)	120·2 (4)	P(1)–C(7)–C(8)	120·2 (4)
P(1)–C(1)–C(6)	120·4 (3)	P(1)–C(7)–C(12)	120·5 (4)
C(6)–C(1)–C(2)	119·4 (5)	C(12)–C(7)–C(8)	119·4 (5)
C(1)–C(2)–C(3)	120·4 (5)	C(7)–C(8)–C(9)	121·2 (5)
C(2)–C(3)–C(4)	119·1 (4)	C(8)–C(9)–C(10)	119·5 (6)
C(3)–C(4)–C(5)	120·9 (7)	C(9)–C(10)–C(11)	120·3 (7)
C(4)–C(5)–C(6)	120·3 (6)	C(10)–C(11)–C(12)	120·9 (6)
C(5)–C(6)–C(1)	119·8 (4)	C(11)–C(12)–C(7)	118·7 (6)
C(13)–C(14)	1·385 (5)	C(19)–C(20)	1·373 (6)
C(14)–C(15)	1·393 (10)	C(20)–C(21)	1·403 (8)
C(15)–C(16)	1·376 (9)	C(21)–C(22)	1·357 (6)
C(16)–C(17)	1·386 (7)	C(22)–C(23)	1·371 (7)
C(17)–C(18)	1·396 (10)	C(23)–C(24)	1·388 (8)
C(18)–C(13)	1·383 (7)	C(24)–C(19)	1·396 (5)
P(2)–C(13)–C(14)	119·7 (4)	P(2)–C(19)–C(20)	120·5 (3)
P(2)–C(13)–C(18)	121·0 (3)	P(2)–C(19)–C(24)	119·9 (3)
C(18)–C(13)–C(14)	119·3 (5)	C(24)–C(19)–C(20)	119·6 (5)
C(13)–C(14)–C(15)	120·4 (5)	C(19)–C(20)–C(21)	120·4 (4)
C(14)–C(15)–C(16)	120·4 (4)	C(20)–C(21)–C(22)	119·5 (4)
C(15)–C(16)–C(17)	119·4 (7)	C(21)–C(22)–C(23)	120·9 (6)
C(16)–C(17)–C(18)	120·3 (6)	C(22)–C(23)–C(24)	120·4 (4)
C(17)–C(18)–C(13)	120·2 (4)	C(23)–C(24)–C(19)	119·2 (4)
C(25)–C(26)	1·392 (7)	C(31)–C(32)	1·403 (8)
C(26)–C(27)	1·396 (10)	C(32)–C(33)	1·385 (8)
C(27)–C(28)	1·366 (6)	C(33)–C(34)	1·369 (11)
C(28)–C(29)	1·387 (10)	C(34)–C(35)	1·381 (13)
C(29)–C(30)	1·410 (9)	C(35)–C(36)	1·388 (11)
C(30)–C(25)	1·386 (5)	C(36)–C(31)	1·379 (8)
As(1)–C(25)–C(26)	119·2 (3)	As(1)–C(31)–C(32)	119·0 (4)
As(1)–C(25)–C(30)	120·9 (4)	As(1)–C(31)–C(36)	120·2 (5)
C(30)–C(25)–C(26)	120·0 (5)	C(36)–C(31)–C(32)	120·6 (5)
C(25)–C(26)–C(27)	119·8 (4)	C(31)–C(32)–C(33)	118·8 (5)
C(26)–C(27)–C(28)	120·5 (6)	C(32)–C(33)–C(34)	120·9 (7)
C(27)–C(28)–C(29)	120·5 (6)	C(33)–C(34)–C(35)	120·3 (7)
C(28)–C(29)–C(30)	119·7 (4)	C(34)–C(35)–C(36)	120·6 (7)
C(29)–C(30)–C(25)	119·6 (5)	C(35)–C(36)–C(31)	119·2 (7)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32533 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

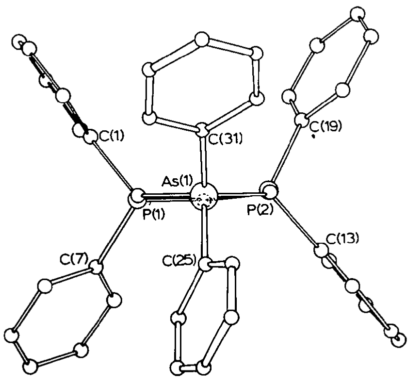


Fig. 2. Structure of $Ph_6P_2AsN_3$ showing the orientation of the phenyl groups.

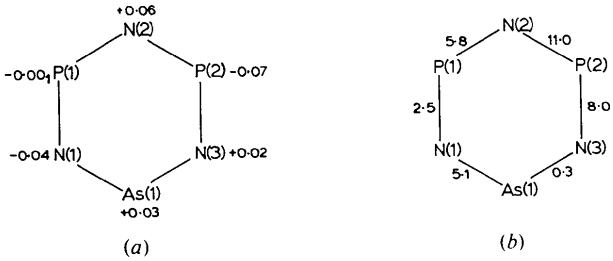


Fig. 3. (a) Deviations (Å) of the ring atoms from the mean ring plane. (b) Torsion angles (°) of the ring bonds.

[Fig. 3(b)] also imply near planarity for the ring; the largest torsion angles are associated with P(2) which is also the atom furthest displaced from the plane.

The ring bond lengths range between 1·636 and 1·700 Å with mean As–N and P–N distances of 1·696 and 1·643 Å respectively. These results should be compared with 1·758 and 1·597 Å found in $Ph_6As_3N_3$ and $Ph_6P_3N_3$ respectively. The large deviations from these latter values are a result of the randomness and the distances given in Table 3 are thus not true measures of the As–N and P–N distances. The other molecular parameters most likely to be affected by the disorder are the As–C and P–C distances which have mean values of 1·86 and 1·82 Å respectively. Again, as expected, the As–C distance is shorter than in $Ph_6As_3N_3$ (mean 1·923 Å) and the P–C is longer than in $Ph_6P_3N_3$ (mean 1·804 Å). An attempt to derive more realistic bond distances is described later.

The endocyclic angles at P (mean 118·6°) and As (116·0°) will also be subject to some error from the non-random values but the effect is considered to be less serious than in the bond distances. The angle at As is smaller than in $Ph_6As_3N_3$ (122°) but this may be a consequence of being associated with P in a mixed ring. The P angles have values close to 118° as is generally observed in trimeric phosphazenes.

The six phenyl groups are planar within experimental error with C–C lengths varying from 1·357 to 1·410 Å (mean 1·384 Å) and C–C–C angles between 118·8 and 121·2°. C–H lengths range between 0·87 and 1·13 Å (mean 1·00 Å). The exocyclic angles at P between geminal phenyl groups are 104·0 and 104·2° for P(1) and P(2) respectively while the analogous C–As–C angle is 105·6°. These angles are similar to those found in the corresponding trimeric and tetrameric phosphazenes and arsazenes (Ahmed, Singh & Barnes, 1969; Begley, Sowerby & Tillott, 1974). The phenyl groups attached to a given heavy atom are not oriented in exactly the same way with respect to the P_2AsN_3 ring, which leads to differences of 1–2° in the angles made with the two associated ring N atoms.

The orientations of the phenyl groups with respect to the mean P_2AsN_3 ring are given by the torsion angles in Table 4 and, because of the near planarity of the ring, the angles relating orientation to the local NMN segment are similar to these. The four phenyl groups attached to P are in very similar orientations, the mean torsion angle, 54·3°, being comparable with those found in $P_3N_3Ph_6$ (Ahmed, Singh & Barnes, 1969), $P_3N_3Ph_2Cl_4$ and $P_3N_3Ph_4Cl_2$ (Mani, Ahmed & Barnes, 1965, 1966). The orientations of the two phenyl groups attached to As on the other hand are greatly different

Table 4. *Torsion angles (°) of the planes of the phenyl groups with the* P_2AsN_3 *ring*

Phenyl group	Torsion angle with mean ring plane	Torsion angle with local NMN segment
C(1)–C(6)	56·9	55·4
C(7)–C(12)	52·3	52·3
C(13)–C(18)	51·9	58·5
C(19)–C(24)	55·9	48·6
C(25)–C(30)	71·8	71·8
C(31)–C(36)	45·8	48·9

Table 5. *Torsion angles (°) of the planes of the phenyl groups with each other*

	Phenyl group	Phenyl group	Torsion angle
(*a*) *gem*	C(1)–C(6)	C(7)–C(12)	83·4
	C(13)–C(18)	C(19)–C(24)	77·2
	C(25)–C(30)	C(31)–C(36)	83·6
(*b*) *cis*	C(1)–C(6)	C(19)–C(24)	72·0
	C(1)–C(6)	C(31)–C(36)	77·1
	C(7)–C(12)	C(25)–C(30)	64·5
	C(7)–C(12)	C(13)–C(18)	86·5
	C(13)–C(18)	C(25)–C(30)	61·4
	C(19)–C(24)	C(31)–C(36)	74·6
(*c*) *trans*	C(1)–C(6)	C(25)–C(30)	56·3
	C(1)–C(6)	C(13)–C(18)	5·2
	C(7)–C(12)	C(19)–C(24)	58·9
	C(7)–C(12)	C(31)–C(36)	21·7
	C(13)–C(18)	C(31)–C(36)	74·7
	C(19)–C(24)	C(25)–C(30)	16·1

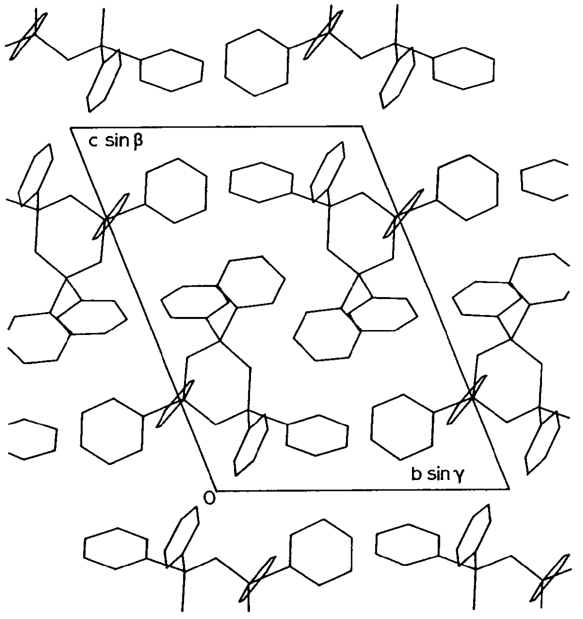


Fig. 4. Unit cell of $Ph_6P_2AsN_3$ projected along **a**.

with angles of 71·8 and 45·8° with respect to the mean ring plane, but here as in the PPh_2 groups the two phenyl groups are almost normal to each other (Table 5). The data in Table 5 also include values for the torsion angles between phenyl groups which are *cis* to each other (mean value 72·6°) while the *trans* oriented rings, C(1)–C(6) and C(13)–C(18), are almost parallel. Low torsion angles (16·1 and 21·7°) are also found for two other pairs of *trans* phenyl groups but the overall conformation probably results from the minimization of steric interactions between phenyl groups both within the molecule and with groups in neighbouring molecules. No short intermolecular contacts were observed; a view of the two molecules in the unit cell is shown in Fig. 4.

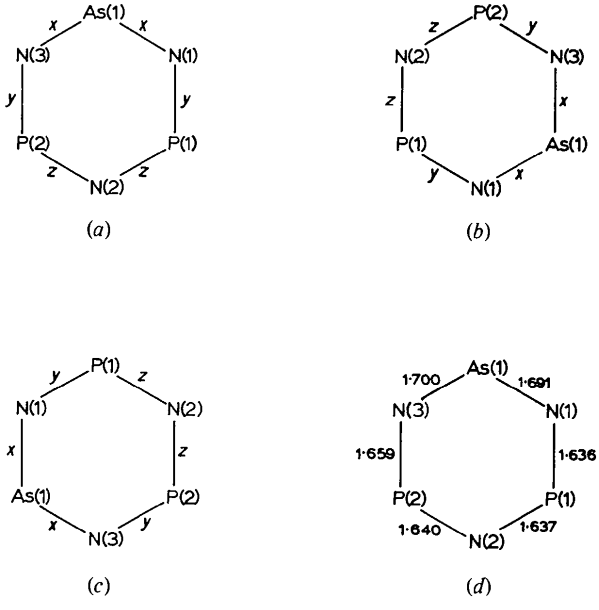
Disorder in the structure

The refined values of the population parameters for As(1), P(1), and P(2) point to the presence of disorder in the structure which can be explained in terms of the three possible molecular orientations shown in Fig. 5(*a*–*c*). The electron density at the As position is 23·99, *i.e.* 0·727 × 33, while at the P(1) and P(2) positions it is 18·72 and 20·13 respectively. By considering the actual electron density at the two 'phosphorus' atoms in (*a*), the fraction (r_1) of molecules in orientation (*b*) and the fraction (r_2) in orientation (*c*) can be evaluated as 0·21 and 0·28 respectively. Similarly, from the electron density at the 'arsenic' position in (*a*), the sum of r_1 and r_2 can be confirmed as 0·49. Thus only 51% of the molecules are oriented in the direction defined in the structure but the alternative orientations are not equally favoured, *i.e.* 21% of the molecules have the As atom at the approximate coordinates of P(1) and 28% at the P(2) position. This disorder clearly reduces the value of the skeletal bond lengths in the originally defined structure but it is possible to derive more meaningful distances as the nature and extent of the disorder are now known.

As $Ph_6P_2AsN_3$ is symmetrically substituted it can be assumed that the ring contains three pairs of ring bonds, the As–N (length x) and two pairs of P–N bonds (lengths y and z) (Fig. 5). In any one instance the observed length can be considered as being the overall effect of the three bond lengths x, y and z, the proportion of each being directly related to the fraction of molecules in the respective orientation. This leads to six equations

$$\begin{aligned}
0{\cdot}51x + 0{\cdot}28y + 0{\cdot}21z &= 1{\cdot}700\\
0{\cdot}51x + 0{\cdot}21y + 0{\cdot}28z &= 1{\cdot}691\\
0{\cdot}21x + 0{\cdot}51y + 0{\cdot}28z &= 1{\cdot}636\\
0{\cdot}21x + 0{\cdot}28y + 0{\cdot}51z &= 1{\cdot}637\\
0{\cdot}28x + 0{\cdot}21y + 0{\cdot}51z &= 1{\cdot}640\\
0{\cdot}28x + 0{\cdot}51y + 0{\cdot}21z &= 1{\cdot}659
\end{aligned}$$

which yield 20 values for x, y and z. The mean value for As–N is 1·790 Å which, although significantly longer than the lengths found in the trimeric (Krannick, Thewalt, Cook, Jain & Sisler, 1973) and tetrameric (Begley, Sowerby & Tillott, 1974) phenylarsazenes (1·739 and 1·758 Å respectively), is still shorter than the accepted value for a single bond (1·87 Å)



(*a*) (*b*)

(*c*) (*d*)

Fig. 5. Disorder in the structure; (*a*), (*b*), (*c*) bond distances for the three possible orientations of the molecule; (*d*) observed bond distances.

(Krannick, Thewalt, Cook, Jain & Sisler, 1973). The calculated P—N lengths are 1·635 Å for the two closest to As and 1·557 Å for the remote pair. Values of 1·597 and 1·590 Å have been reported for P—N in the trimeric (Ahmed, Singh & Barnes, 1969) and tetrameric (Begley, Sowerby & Tillott, 1974) phenylphosphazenes. The standard deviation from the mean of these calculated dimensions is 0·04 Å but the difference in the two sets of P—N distances is considered to be real.

The lengths of the As—C and P—C bonds are also affected by the disorder in the structure but the approach used for correction is less rigorous than that used above. The mean M—C length for each pair of phenyl groups is used as a basis and if v is the 'true' As—C and w the 'true' P—C distance the three equations below can be written

$$\begin{aligned} 0{\cdot}51v + 0{\cdot}49w &= 1{\cdot}857 \\ 0{\cdot}21v + 0{\cdot}79w &= 1{\cdot}820 \\ 0{\cdot}28v + 0{\cdot}72w &= 1{\cdot}827. \end{aligned}$$

Solution leads to 1·92, 1·92 and 1·90 Å (mean 1·91 Å for v and 1·79, 1·79, and 1·80 Å (mean 1·79 Å) for w in good agreement with previously observed values of 1·92 and 1·81 Å.

Bonding in $Ph_6P_2AsN_3$

Although some uncertainty is necessarily attached to the exact values of the corrected ring bond distances, their general values are likely to be correct. On this basis some comment is required on the increase in the As—N distance over that in $Ph_6As_3N_3$ and $Ph_8As_4N_4$ and on the two different P—N distances.

Bonding in the P_2AsN_3 ring is likely to be analogous to that in P_3N_3 systems and, although recent calculations support the formation of P—N—P islands of π-electron density with substantial interaction between the formally non-bonded P atoms (Armstrong, Longmuir & Perkins, 1972), the following comments are based on the qualitatively simpler approach of a σ framework supplemented by two π systems (Paddock, 1964). Incorporation of an As in place of a P atom into a P_3N_3 ring will have an effect in both the σ and π_a systems owing to reduced electronegativity which will account, at least in part, for the longer As—N distance. The major influence is expected, however, in the in-plane (π_s) system, where the shorter P(1)—N(2) and P(2)—N(2) bonds imply that the lone pair formally associated with N(2) is strongly delocalized into the π_s system. The lone pairs associated with N(1) and N(3), on the other hand, must be considered more strongly localized on the basis of the bond distances to both As and respectively P(1) and P(3). It is not possible to cite a specific cause for this observation. The variation in bond lengths in the P_2AsN_3 ring, however, provides some information on the protonation site in the monohydrochloride, $Ph_6P_2AsN_3.HCl$ (Sowerby & Tillott, 1977). This will be most probably at the equivalent N(1) or N(3) atoms which appear to be more basic than the alternative N(2) site.

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