Crystal and Molecular Structure of 2,3,6-Triphenylarsenin

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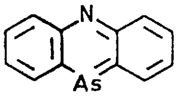
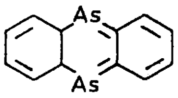
Crystals of the title compound are monoclinic, space group $C2/c$, with a = 31·768, b = 10·456, c = 10·543 Å, β = 94·58°, Z = 8. Diffractometer data for 1648 planes were used to solve the structure by Patterson methods and were refined by least squares to a final R of 0·085. The arsenin ring shows no significant departures from $mm2$ (C_{2v}) symmetry and exhibits only two different bond lengths: As–C 1·872(14) and C–C 1·405(20) Å.

It has been shown [1-3] that the compounds described as phenarsazin (I) [4] and arsanthrene (II) [5] are in fact dimeric, (III) and (IV), and do not contain a heterocyclic aromatic ring. Successful syntheses of such rings have now finally been accomplished. Arsenin (V),[6] the arsenic analogue of pyridine, 10-phenyl-9-arsa-anthracene (VI),[7] and aromatically substituted arsenins (VII) [8] have all been prepared recently. Their spectral properties (u.v., n.m.r., and i.r.) are consistent with the presence of an aromatic ring system, but the exact nature of the bonding, such as the possible involvement of the arsenic d orbitals and the existence of ring current, remains unclear. To establish the geometric features of the novel heterocyclic ring we have determined the structure of 2,3,6-triphenylarsenin [(VII); R = Ar = Ph]; a brief report has appeared.[9]



(I)



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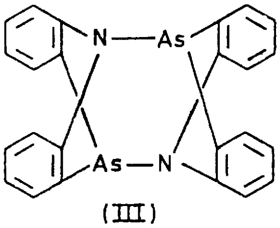

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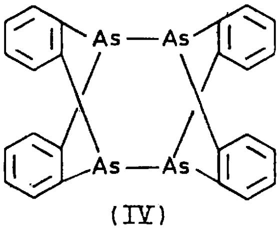

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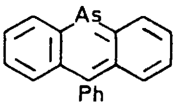

(VI)

(VII)

EXPERIMENTAL

Crystal Data.—$C_{23}H_{17}As$, M = 368·3, Monoclinic, a = 31·768(22), b = 10·456(4), c = 10·543(7) Å, β = 94·58(8)°, U = 3490·8 Å^3, D_m = 1386, Z = 8, D_c = 1401. Space group C_2/c. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 2050 m^{-1}.

Cell dimensions were obtained by a least-squares process from ($h0l$) and ($0kl$) precession photographs and the standard deviations quoted contain no allowance for systematic error.

The systematic extinctions, (hkl) for $h + k = 2n + 1$ and ($h0l$) for $l = 2n + 1$, are consistent with the space groups Cc and $C2/c$. An $N(z)$ test showed somewhat better agreement with the centrosymmetric case and the distribution of the As · · · As and As · · · C vectors in the three-dimensional Patterson function was consistent with the $C2/c$ space group which was accordingly adopted and used throughout the analysis.

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[1] H. Vermeer and F. Bickelhaupt, *Tetrahedron Letters*, 1970, 1007.

[2] C. Jongsma and H. van der Meer, *Tetrahedron Letters*, 1970, 1323.

[3] H. Vermeer, R. Lourens, and F. Bickelhaupt, *Tetrahedron Letters*, 1970, 3255, ref. 10.

[4] H. Weiland and W. Rheinheimer, *Annalen*, 1921, **423**, 1.

[5] L. Kalb, *Annalen*, 1921, **423**, 39.

[6] A. J. Ashe, *J. Amer. Chem. Soc.*, 1971, **93**, 3294.

[7] H. Vermeer and F. Bickelhaupt, *Tetrahedron Letters*, 1970, 3255.

[8] G. Märkl, H. Hauptmann, and J. Advena, *Angew. Chem.*, 1972, **84**, 440.

[9] F. Sanz and J. J. Daly, *Angew. Chem.*, 1972, **84**, 679.

Intensity measurements were carried out on a Hilger and Watts linear diffractometer equipped with a graphite monochromator. The crystal used was needle-shaped with cross-section *ca.* 0·05 × 0·1 mm^2 and the data were collected about *c*, the needle axis. A total of 1648 reflections with intensities $>1\cdot5\sigma$ were used for the analysis. The effects of absorption were ignored.

The positions of all non-hydrogen atoms were found from a three-dimensional Patterson function and this trial structure was refined by a block-diagonal 3 × 3 and 1 × 1 or 6 × 6 least-squares procedure first with isotropic and then with anisotropic temperature factors till R was reduced to 0·095. At this stage a difference-Fourier synthesis was calculated and from it the hydrogen atom positions were found. Further least-squares refinement of the atomic positional parameters converged with R 0·085 and R' $(= \Sigma w\Delta^2/\Sigma wF_o^2)$ 0·0166. A modified Cruickshank[10] weighting scheme was used with $w_1^{-1} = 2^{-3}\,(24\cdot5 + |F_o| + 0\cdot081|F_o^2|)$ for $|F_o| > 24\cdot5$ and $w_2^{-1} = w_1^{-1}\,(24\cdot5/|F_o|)^2$ for $|F_o| < 24\cdot5$. The hydrogen atoms were all given a fixed isotropic temperature factor of U 0·06 Å^2.

RESULTS AND DISCUSSION

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20582 (11 pp., 1 microfiche).* Tables 1—3 give the co-ordinates, the thermal parameters of the heavy atoms, and the more important bond lengths and angles. Table 4 lists some important planes in the molecule. The Figure shows the molecule projected on the least-squares plane of the arsenin ring and the labelling of the atoms.

The most interesting part of the molecule is the arsenin ring which shows no significant deviations from *mm*2 (C_{2v}) symmetry. Although this symmetry allows two different carbon–carbon bond lengths in the ring, all four of these bonds are equal to the mean length within experimental error. The ring is then planar with As–C 1·872 and C–C 1·405 Å just as would be expected in a delocalised 6π-electron system. The As–C bond length is less than the sum of the single-bond radii[11] (1·98 Å) and the standard[12] single-bond length (1·96 Å). More recent measurements[2,13] of bonds from arsenic to carbon give values of *ca.* 1·95 Å, but a few shorter distances have been reported.[14] The C–C bond

TABLE 1

Final co-ordinates (Å) with standard deviations

	X	Y	Z
As	5·6893(15)	0·4817(14)	2·6684(17)
C(1)	6·821(13)	−0·886(14)	3·394(15)
C(2)	6·543(16)	−2·257(15)	3·078(15)
C(3)	5·467(15)	−2·664(14)	2·283(14)
C(4)	4·406(13)	−1·956(12)	1·615(14)
C(5)	4·385(14)	−0·517(13)	1·688(15)
C(6)	7·994(14)	−0·440(15)	4·268(15)
C(7)	7·914(16)	0·627(14)	5·128(16)
C(8)	9·087(19)	0·988(20)	5·930(18)
C(9)	10·267(17)	0·286(17)	5·876(17)
C(10)	10·375(17)	−0·758(16)	5·097(18)
C(11)	9·186(14)	−1·116(16)	4·223(17)
C(12)	3·380(13)	−2·731(12)	0·794(17)
C(13)	2·993(14)	−2·384(15)	−0·535(16)
C(14)	2·153(16)	−3·177(16)	−1·343(17)
C(15)	1·624(16)	−4·354(15)	−0·794(18)
C(16)	1·923(16)	−4·690(15)	0·490(19)
C(17)	2·835(17)	−3·889(16)	1·279(19)
C(18)	3·237(13)	0·299(11)	1·100(14)
C(19)	3·453(17)	1·254(12)	0·132(17)
C(20)	2·443(18)	2·069(14)	−0·392(19)
C(21)	1·155(17)	1·923(15)	0·026(17)
C(22)	0·899(15)	0·981(16)	0·991(17)
C(23)	1·936(16)	0·137(14)	1·514(17)
H(2)	7·02(19)	−3·24(19)	3·47(20)
H(3)	5·36(18)	−3·91(20)	2·21(19)
H(7)	6·79(19)	1·20(20)	5·03(20)
H(8)	8·94(18)	1·76(20)	6·63(20)
H(9)	11·10(19)	0·56(19)	6·74(20)
H(10)	11·21(18)	−1·66(20)	4·95(20)
H(11)	9·38(18)	−1·90(19)	3·70(19)
H(13)	3·21(19)	−1·68(20)	−0·94(20)
H(14)	1·71(18)	−2·95(19)	−2·20(20)
H(15)	0·98(19)	−4·83(19)	−1·45(20)
H(16)	1·48(19)	−5·67(19)	1·09(20)
H(17)	2·89(18)	−4·11(20)	2·11(20)
H(19)	4·39(19)	1·31(20)	−0·17(19)
H(20)	2·58(18)	2·69(19)	−0·98(19)
H(21)	0·49(18)	2·54(19)	−0·45(19)
H(22)	−0·04(19)	0·93(20)	1·18(20)
H(23)	1·78(19)	−0·54(19)	2·20(20)

TABLE 2

Thermal parameters (Å^2 × 10^4 for As, × 10^3 for C) *

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
As	436(8)	275(7)	593(10)	−26(14)	−38(15)	−8(13)
C(1)	35(7)	37(7)	44(8)	13(11)	34(13)	16(12)
C(2)	70(10)	44(9)	30(9)	−22(15)	18(14)	−2(14)
C(3)	57(9)	40(8)	34(9)	34(14)	50(13)	8(13)
C(4)	47(7)	22(6)	37(8)	−11(11)	20(11)	15(12)
C(5)	52(8)	29(7)	43(9)	7(14)	−0(13)	14(12)
C(6)	44(8)	51(9)	45(9)	−39(15)	7(15)	29(13)
C(7)	62(9)	30(7)	45(9)	4(13)	−7(13)	−3(13)
C(8)	78(12)	83(13)	43(11)	−65(21)	−3(19)	4(16)
C(9)	72(11)	52(10)	46(10)	−34(17)	−12(16)	23(15)
C(10)	67(10)	41(9)	68(12)	15(15)	55(16)	22(17)
C(11)	41(8)	48(9)	59(10)	−24(14)	10(16)	9(14)
C(12)	40(7)	10(5)	74(11)	−10(10)	−19(13)	11(13)
C(13)	39(8)	40(8)	53(10)	28(12)	1(14)	−26(13)
C(14)	52(9)	55(10)	56(10)	28(16)	−15(16)	−38(14)
C(15)	53(9)	34(7)	70(12)	−11(13)	−45(15)	−12(15)
C(16)	49(9)	38(8)	86(13)	2(15)	−47(18)	1(16)
C(17)	60(10)	39(9)	80(13)	10(15)	−18(17)	50(17)
C(18)	36(7)	12(6)	52(9)	8(10)	−4(11)	−15(11)
C(19)	82(11)	7(6)	71(11)	−18(13)	−24(13)	22(17)
C(20)	83(12)	20(7)	72(11)	11(15)	12(15)	11(18)
C(21)	71(11)	37(8)	55(11)	9(16)	−33(15)	−17(16)
C(22)	44(8)	49(9)	61(11)	4(14)	−43(16)	10(14)
C(23)	51(9)	30(7)	69(12)	4(13)	−6(14)	24(15)

* In form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klc^*b^*U_{23} + 2hla^*c^*U_{13})]$.

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

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TABLE 3

Bond lengths (Å) and angles (°) with standard deviations

(*a*) Arsenin ring

(i) Bond lengths		(ii) Bond angles	
As–C(1)	1·884(14)	C(1)–As–C(5)	100·8(6)
As–C(5)	1·859(14)	As–C(1)–C(2)	120·8(10)
C(1)–C(2)	1·430(21)	As–C(5)–C(4)	123·4(10)
C(2)–C(3)	1·349(21)	C(2)–C(3)–C(4)	131·9(14)
C(3)–C(4)	1·400(20)	C(1)–C(2)–C(3)	123·4(14)
C(4)–C(5)	1·442(19)	C(3)–C(4)–C(5)	119·6(12)
Mean C–H	1·21(20)	Mean	120·0
		Mean C–C–H	116(13)

(*b*) Ph-Arsenin ring

(i) Bond lengths	
C(6)–C(1)	1·474(20)
C(12)–C(4)	1·481(19)
C(18)–C(5)	1·491(19)
Mean	1·482

(ii) Angles	
As–C(1)–C(6)	115·7(10)
C(1)–C(2)–C(6)	123·5(13)
As–C(5)–C(18)	113·5(10)
C(4)–C(5)–C(18)	122·8(12)
C(3)–C(4)–C(12)	117·8(12)
C(5)–C(4)–C(12)	122·6(12)
C(1)–C(6)–C(7)	121·4(13)
C(1)–C(6)–C(11)	118·9(13)
C(4)–C(12)–C(13)	121·6(13)
C(4)–C(12)–C(17)	121·2(13)
C(5)–C(18)–C(19)	119·6(12)
C(5)–C(18)–C(23)	121·5(12)
Mean	120·0

(*c*) Phenyl groups

(i) Bond lengths		(ii) Angles	
C(6)–C(7)	1·378(21)	C(6)–C(7)–C(8)	117·7(15)
C(7)–C(8)	1·414(25)	C(7)–C(8)–C(9)	121·5(17)
C(8)–C(9)	1·377(26)	C(8)–C(9)–C(10)	122·7(17)
C(9)–C(10)	1·313(24)	C(9)–C(10)–C(11)	116·6(16)
C(10)–C(11)	1·463(23)	C(10)–C(11)–C(6)	121·7(14)
C(11)–C(6)	1·374(22)	C(11)–C(6)–C(7)	119·7(14)
C(12)–C(13)	1·399(20)	C(12)–C(13)–C(14)	121·8(14)
C(13)–C(14)	1·371(22)	C(13)–C(14)–C(15)	118·8(15)
C(14)–C(15)	1·419(23)	C(14)–C(15)–C(16)	121·2(15)
C(15)–C(16)	1·338(23)	C(15)–C(16)–C(17)	118·8(16)
C(16)–C(17)	1·408(24)	C(16)–C(17)–C(12)	122·3(15)
C(17)–C(12)	1·384(22)	C(17)–C(12)–C(13)	117·0(14)
C(18)–C(19)	1·389(20)	C(18)–C(19)–C(20)	121·7(14)
C(19)–C(20)	1·370(23)	C(19)–C(20)–C(21)	119·5(15)
C(20)–C(21)	1·394(24)	C(20)–C(21)–C(22)	120·5(15)
C(21)–C(22)	1·386(23)	C(21)–C(22)–C(23)	119·7(15)
C(22)–C(23)	1·405(23)	C(22)–C(23)–C(18)	119·5(14)
C(23)–C(18)	1·406(20)	C(23)–C(18)–C(19)	118·9(13)
Mean C–C	1·388	Mean C–C–C	120·0
Mean C–H	1·10(20)	Mean C–C–H	120(12)

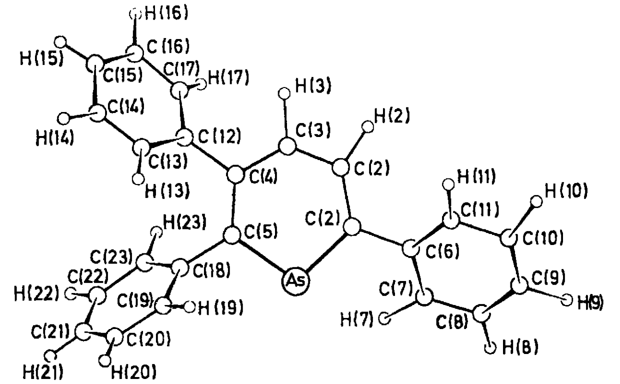
TABLE 4

Equations of some important least-squares (w = atomic no.) planes in the molecule in the form: $lX' + mY' + nZ' = p$ where $X' = X + Z \cos \beta$, $Y' = Y$, and $Z' = Z \sin \beta$. Deviations (Å) of constituent atoms from the planes are given in square brackets

l	m	n	p
0·5953	0·0581	−0·8014	1·1540
[As 0·002, C(1) −0·017, C(2) 0·005, C(3) 0·013, C(4) −0·011, C(5) −0·003]			
−0·3323	−0·6129	0·7169	0·7762
[C(6) 0·000, C(7) 0·010, C(8) −0·007, C(9) −0·008, C(10) 0·019, C(11) −0·014]			
0·8007	−0·5260	−0·2869	3·8517
[C(12) 0·008, C(13) −0·019, C(14) 0·009, C(15) 0·012, C(16) −0·022, C(17) 0·012]			
0·1618	0·6678	0·7265	1·4956
[C(18) 0·011, C(19) −0·005, C(20) 0·002, C(21) −0·005, C(22) 0·011, C(23) −0·013]			

lengths in this ring are slightly, but not significantly, longer than those found in benzene,[12] pyridine,[12] and 2,4-dimethyl-4-phenylphosphorin.[15]

The ring angles show large deviations from 120° but, for a ring of *mm*2 symmetry, they are subject to geometrical constraints and if two are known the other two may be calculated if the sides of the hexagon are also known. Table 5 shows how the ring angles are related when the angles at C(1) and C(2) are allowed to vary from 100 to 140°. A comparison with the corresponding Table for a phosphorin ring[15] is illuminating. The increased length of As–C as opposed to P–C decreases the ring angle at As by about 2·4—4·3° and increases the C(3) ring angle of the arsenin ring by about the same amount. This difference is observed experimentally, at least qualitatively, but the C(3) angle in the arsenin ring is larger than predicted from the two Tables. This increase is compensated for by a decrease in the ring angle at C(2). Two particular hypothetical C_5As rings are of special interest, the first has essentially the carbon skeleton found in benzene with C–C 1·405 Å and C–C–C 120° and if As–C is 1·872 Å, interpolation in Table 6 gives C–As–C 81·1 and As–C–C 139·5°. The second case has C–As–C 120°, As–C 1·872, and C–C 1·405 Å; here the



The molecule projected on the least-squares plane (w = atomic number) of the arsenin ring, and the labelling of the atoms

TABLE 5

Calculated values of the angles at As(ϕ_{As}) and C(3) (ϕ_3) in a C_5As ring of *mm*2 symmetry with As–C 1·872 Å and C–C 1·405 Å. The angles at C(1) (ϕ_1) and C(3) (ϕ_2) are given the values 100, 110, 120, 130, and 140°. Observed angles ϕ_A 100·8, ϕ_1 122·1, ϕ_2 121·5, and ϕ_3 131·9°

ϕ_{As}

ϕ_2 \ ϕ_1	100	110	120	130	140
100	133·8	121·4	109·5	98·0	86·7
110	133·4	120·3	107·8	95·8	84·0
120	131·1	117·7	104·9	92·5	80·4
130	127·5	113·9	100·9	88·4	76·1
140	123·0	109·3	96·3	83·6	71·2

ϕ_3

ϕ_2 \ ϕ_1	100	110	120	130	140
100	186·2	178·6	170·5	162·0	153·3
110	166·6	159·7	152·2	144·2	136·0
120	148·9	142·3	135·1	127·5	119·6
130	132·5	126·1	119·1	111·6	103·9
140	117·1	110·7	103·7	96·4	88·8

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[15] J. C. J. Bart and J. J. Daly, *Angew. Chem.*, 1968, **80**, 843; *J. Chem. Soc.* (*A*), 1970, 567.

remaining angles are not fixed but they are restricted to a few values. The angle at C(1) is close to 110° while that at C(2) may be 110 or *ca.* 140°; the resulting angles for C(3) are then 160 or *ca.* 110°. Thus even with some physically acceptable angles in the ring, geometrical constraints can give very unfavourable values for the other ring angles.

The phenyl groups have their usual geometry with C–C 1·388 Å and C–C–C 120° as mean values. The bonds joining these rings to the arsenin ring have a mean of 1·482 Å. The phenyl rings are all twisted in the same sense about their bonds to the heterocyclic ring, the interplanar angles being 36·1, 47·5, and 63·4° for the rings containing C(6), C(12), and C(18).

Non-bonded intramolecular and the van der Waals' contacts exhibit no unusual features.

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[2/1955 *Received, 17th August,* 1972]