

495. *The Crystal Structure of Bromodiphenylarsine.*

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Crystals of bromodiphenylarsine, Ph_2AsBr , are monoclinic, with four molecules in a unit cell of dimensions $a = 11.00$, $b = 8.56$, $c = 12.03$ Å, $\beta = 93.0^\circ$. The structure has been determined from projections along the a - and b -crystal axes. The mean values of the bond lengths and valency angles (with estimated standard deviations) are: $\text{As-Br} = 2.40 \pm 0.01$, $\text{As-C} = 1.99 \pm 0.04$, $\text{C-C} = 1.39 \pm 0.03$ Å, $\angle \text{Br-As-C} = 95^\circ \pm 1^\circ$, $\angle \text{C-As-C} = 105^\circ \pm 2^\circ$, $\angle \text{As-C-C} = 120^\circ \pm 2^\circ$, $\angle \text{C-C-C} = 120^\circ \pm 2^\circ$. The closest intramolecular contacts between phenyl groups are $\text{C} \cdots \text{C}$ 3.4 and $\text{H} \cdots \text{H}$ 2.8 Å. One phenyl ring is rotated $\sim 90^\circ$ and the other about 30° from their positions in an ideal model, with maximum overlap between both sets of aromatic π -orbitals and the arsenic lone pair, suggesting that only one ring is able to interact with the lone pair. All the intermolecular contacts correspond to normal van der Waals interactions.

A DETAILED X -ray analysis of the crystal and molecular structure of bromodiphenylarsine Ph_2AsBr has been undertaken as part of a series of investigations of the structures and stereochemistry of arsenic compounds. The structure has been determined from projections along two crystal axes, and molecular geometry and dimensions, and intermolecular separations, have been obtained.

EXPERIMENTAL

Almost colourless crystals of bromodiphenylarsine, suitable for X -ray work, were obtained by crystallization from 95% ethanol. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of crystals rotating about the a - and the b -axis, and $0kl$, $h0l$, and $h1l$ Weissenberg films. An approximate value of the density was determined by flotation in aqueous silver nitrate.¹

Crystal Data.—Bromodiphenylarsine, $C_{12}H_{10}AsBr$; M , 309.0; m. p. 55°. Monoclinic, $a = 11.00 \pm 0.04$, $b = 8.56 \pm 0.03$, $c = 12.03 \pm 0.04$ Å, $\beta = 93.0^\circ \pm 0.5^\circ$. Volume of the unit cell = 1131 Å³; d calc. (with $Z = 4$) = 1.803, measured ~ 1.8 g. cm.⁻³. Absorption coefficient for X -rays, $\lambda = 1.542$ Å, $\mu = 81.2$ cm.⁻¹. Total number of electrons per unit cell = $F(000) = 600$. Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd. Space group: $C_{2h}^{2h}-P2_1/a$.

The intensities of the $0kl$ and $h0l$ reflexions were recorded on Weissenberg films for a crystal rotating in turn about the a - and the b -axis, with $Cu-K_\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. The range of intensities measured was about 10,000 to 1, the estimates being made visually. The crystal was approximately cubic in shape with edge 0.4 mm., and absorption corrections were applied for each zone by assuming cylindrical cross-sections with radius 0.2 mm. The structure amplitudes were derived by the usual formulæ for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 117 independent $0kl$ reflexions and 118 $h0l$ reflexions were observed, representing 85% and 68%, respectively, of the possible number observable under the experimental conditions.

Structure Analysis.—[010] *Projection.* The heavy-atom vectors on the b -axis Patterson map were easily distinguished, but were rather poorly resolved because of overlapping. However, co-ordinates were derived for the arsenic and bromine atoms, although it was not possible at this stage to distinguish between them. Structure factors were calculated for all the $h0l$ reflexions, with the heavy-atoms given equal weight, and a Fourier series was then summed by using as coefficients the measured structure amplitudes and the calculated signs for those reflexions whose signs were well established. On the resulting electron-density map the heavy-atoms were well resolved, but still indistinguishable, and their positions had changed by about 0.1–0.2 Å from the previous estimate. The rest of the map could not be interpreted in terms of any chemically reasonable structure. Structure factors were therefore recalculated with the revised heavy-atom co-ordinates, and a second Fourier series was summed; some signs were changed, and it was possible to include more terms. Further small shifts in heavy-atom positional parameters were indicated, and in addition all six atoms of one of the phenyl groups were clearly resolved. The second ring was also clearly defined although only one atom was separately resolved. New co-ordinates were obtained for the arsenic and the bromine atoms, which, although their peak heights were approximately identical, could now be distinguished by their different environments, and co-ordinates were also read off from the map for all twelve carbon atoms in the molecule. Structure factors were calculated for all the $h0l$ reflexions, with the scattering curve for bromine of Thomas and Umeda,² corrected for anomalous dispersion of the $Cu-K_\alpha$ radiation, by using values of $\Delta f'$ and $\Delta f''$ given by Dauben and Templeton;³ the scattering factors of Berghuis *et al.*⁴ were used for arsenic and carbon, that for arsenic being corrected for anomalous dispersion.³ An overall temperature factor $B = 7.5$ Å² was determined from a plot of $\ln \{|F_c|/|F_0|\}$ against $\sin^2 \theta/\lambda^2$. This is a rather high value of B , but it is not unrealistic in view of the relatively low melting point. Refinement proceeded by difference syntheses until there were no further significant changes in positional parameters, the discrepancy between measured and calculated structure factors, for the observed reflexions, then being 13.8%. The structure factors are listed in Table 2, and a final F_0 synthesis, computed with measured structure amplitudes and calculated signs, is shown in Fig. 1.

[100] *Projection.* Co-ordinates for the arsenic and bromine atoms were derived from the Patterson projection, and further analysis then proceeded as for the $h0l$ zone. Final measured

¹ Cullen and Trotter, *Canad. J. Chem.*, 1961, **39**, 2602.

² Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

³ Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

⁴ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

and calculated $0kl$ structure factors are included in Table 2 (discrepancy factor 11.8%) and an electron-density projection along the a -axis is shown in Fig. 2.

Co-ordinates and molecular dimensions. The final positional parameters of the arsenic, bromine, and carbon atoms are listed in Table 1, x , y , and z being co-ordinates referred to the monoclinic crystal axes and expressed as fractions of the unit cell edges, and X' , Y , and Z' co-ordinates in Å referred to orthogonal axes a' , b , and c .

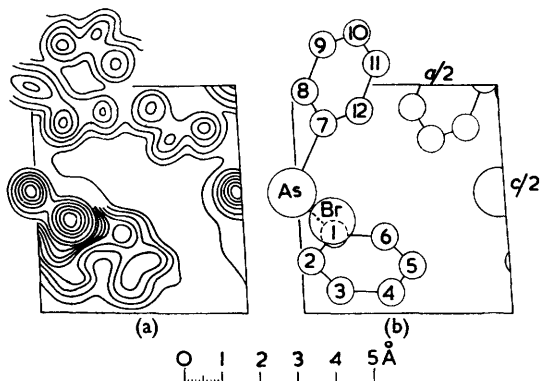


FIG. 1. (a) Electron-density projection along the b -axis. Contours at intervals of $1 \text{ e}\text{\AA}^{-2}$, starting at $2 \text{ e}\text{\AA}^{-2}$, but with contours above $10 \text{ e}\text{\AA}^{-2}$ at intervals of $5 \text{ e}\text{\AA}^{-2}$. (b) Projection of the structure on to (010) .

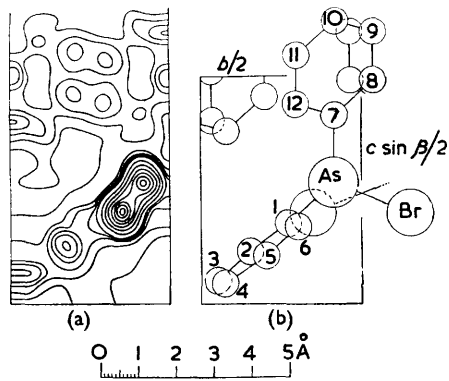


FIG. 2. (a) Electron-density projection along the a -axis. Contours at intervals of $2 \text{ e}\text{\AA}^{-2}$, except at the As and Br atoms, where contours above $10 \text{ e}\text{\AA}^{-2}$ are at intervals of $5 \text{ e}\text{\AA}^{-2}$. (b) Projection of the structure along $[100]$.

TABLE I.

Final positional parameters, and deviations (Δ) from the mean aromatic planes.

Atom	x	y	z	X'	Y	Z'	Δ_1 (Å)	Δ_2 (Å)
As	-0.0140	0.1636	0.2652	-0.154	1.400	3.198	+0.02	-0.14
Br	0.0793	0.4000	0.2033	0.871	3.424	2.400	—	—
C 1	0.082	0.024	0.175	0.900	0.202	2.059	+0.02	—
2	0.023	-0.098	0.114	0.256	-0.842	1.363	-0.01	—
3	0.090	-0.200	0.051	0.989	-1.712	0.558	0	—
4	0.213	-0.176	0.046	2.337	-1.504	0.427	+0.01	—
5	0.267	-0.049	0.105	2.936	-1.419	1.111	0	—
6	0.204	0.051	0.168	2.241	0.440	1.903	-0.01	—
7	0.073	0.167	0.418	0.801	1.428	4.988	—	0
8	0.031	0.286	0.488	0.344	2.452	5.850	—	0
9	0.082	0.286	0.593	0.899	2.452	7.086	—	+0.01
10	0.167	0.167	0.619	1.838	1.428	7.352	—	-0.01
11	0.210	0.047	0.550	2.305	0.400	6.497	—	0
12	0.161	0.047	0.444	1.767	0.400	5.251	—	+0.01

The bond distances and valency angles in the molecule, calculated from the co-ordinates of Table 1, are shown in Fig. 3. The closest intramolecular $C \cdots C$ contacts between phenyl groups are: $C_1-C_{12} = 3.31$; $C_6-C_{12} = 3.38$; $C_6-C_7 = 3.54$ Å. The distance between the hydrogen atoms attached to C_6 and C_{12} (assumed to lie on the ring diagonals with $C-H = 1.08$ Å) is 2.76 Å.

The equations of the planes of the aromatic rings are:

$$C_1-C_6: 0.1729 X' - 0.5965 Y + 0.7838 Z' - 1.6290 = 0.$$

$$C_7-C_{12}: 0.7330 X' + 0.5986 Y - 0.3232 Z' + 0.1693 = 0.$$

The deviations of the atoms from these planes are listed in the final columns of Table 1. The angle between the planes is 61° .

Standard deviations. The standard deviations of the atomic positions, calculated from

TABLE 2.
Measured and calculated structure factors.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
0	0	1	not obs	-1	6	0	II	6	+9	0	5	1	37	+33	0	5	1	37	+33
		2	133	-142			8	57	+61			2	12	-12			2	12	-12
		3	116	-124			9	<6	0			3	24	-29			3	24	-29
		4	67	+63			10	18	-20			4	13	+13			4	13	+13
		5	59	+52			II	6	+9			5	22	+25			5	22	+25
		6	53	-54			IO	14	-15			6	14	-19			6	14	-19
		7	8	-8			9	21	-23			7	18	-20			7	18	-20
		8	9	-10			8	21	+24	0	1	1	134	-137			8	10	+11
		9	13	-10			7	43	+46			2	<3	+4			9	3	+7
		10	8	+9			6	<6	-6			3	153	+162			10	3	-2
		11	16	+15			5	75	-71			4	53	+50			11	<3	-2
		12	6	-4			4	12	+9			5	53	-56			12	3	+4
		13	10	-10			3	79	+67			6	8	-1			0	6	0
		14	2	+2			2	15	+20			7	7	+3			1	10	-11
		15	5	+7			I	41	-45			8	5	-6			2	10	-6
2	0	II	5	+6			0	6	-24			9	4	-3			3	37	+30
		IO	<3	-2			1	11	-21			10	8	+10			4	11	+11
		II	12	-12			2	26	-14			11	4	-4			5	24	-22
		III	<5	+3			3	21	+32			12	11	-10			6	15	-20
		IV	11	+18			4	35	+38			13	<3	-1			7	21	+15
		V	7	+7			5	28	-30			14	5	+6			8	10	+12
		VI	48	-43			6	35	-30			15	1	0			9	12	-12
		VII	<5	-10			7	17	+16			0	17	-8			10	7	-8
		VIII	43	+42			8	30	+31	0	2	0	17	-8			11	3	+4
		IX	14	+14			9	6	-8			1	27	+33			12	4	+5
		X	8	+12			10	19	-18			2	20	-14			0	7	1
		XI	7	+21			11	<5	+2			3	78	-73			1	3	+2
		XII	54	-44			12	8	+8			4	30	-24			2	15	+12
		XIII	56	-40			8	7	+13			5	42	+38			3	3	<4
		XIV	99	+93			7	16	+13			6	36	+40			4	15	-12
		XV	166	+153			6	18	-30			7	8	-8			5	4	-6
		XVI	114	-119			5	49	-39			8	26	-23			6	20	+16
		XVII	242	-245			4	20	+19			9	26	+20			7	9	+8
		XVIII	<3	+3			3	62	+55			10	6	+6			8	11	-11
		XIX	170	+167			2	27	-21			11	<3	-1			9	6	-8
		XX	10	+4			I	44	-43			12	5	-7			10	3	+3
		XXI	87	-78			0	<6	-8			0	82	-89			11	4	+4
		XXII	36	-28			1	38	+38			1	27	-33			0	8	0
		XXIII	46	+42			2	<6	+12			2	43	+49			1	6	-7
		XXIV	9	+12			3	13	-14			3	58	+59			2	<3	+2
		XXV	<6	+2			4	10	+11			4	14	-14			3	3	-2
		XXVI	<6	-2			5	13	-17			5	62	-54			4	5	-2
		XXVII	<5	-1			6	<6	+4			6	20	-19			5	<3	-1
		XXVIII	4	-4			7	12	+10			7	12	+13			6	4	+4
		XXIX	6	+3			8	13	+9			8	12	+13			7	5	+4
		XXX	4	+4			9	7	-10			9	26	+26			8	4	+4
		XXXI	8	-13			10	10	-11			10	<3	+2			9	3	-3
		XXXII	3	+4			0	<6	-8			11	7	-7			10	3	-2
		XXXIII	18	+23			5	17	-8			12	<3	-4			0	8	0
		XXXIV	4	-8			4	19	+19			0	75	-74			1	3	+2
		XXXV	32	-35			3	20	+18			1	13	-19			2	<3	+1
		XXXVI	<6	+5			2	20	-18			2	78	+76			3	4	-2
		XXXVII	46	+54			I	27	-22			3	15	+12			4	3	-4
		XXXVIII	8	+13			0	18	+15			4	25	-33			5	6	-1
		XXXIX	68	-79			1	27	+25			5	18	-22			6	2	+2
		XXXX	11	-22			2	10	-6			6	10	+13			7	<2	+2
		XXXXI	12	+20			3	13	-18			7	7	+11			8	2	-2
		XXXXII	<4	+12			4	<5	-1			8	3	-2			0	10	0
		XXXXIII	57	+55			5	10	+8			9	4	+1			1	3	+2
		XXXXIV	65	+54			6	3	+1			10	5	-5			2	3	+2
		XXXXV	55	-76			7	<3	-2			11	3	-3			3	4	-1
		XXXXVI	78	-76			8	5	+2			12	5	+4			4	4	-3
		XXXXVII	24	+27			9	3	+4			13	3	+4			5	<2	-1
		XXXXVIII	100	+102			4	3	+4			14	2	-2			6	3	+3
		XXXXIX	45	-36			5	8	+3			0	4	+4			0	10	0
		XXXXX	68	-69			6	3	-6			1	3	-2			1	3	+2

Cruickshank's formulae,⁵ are $\sigma(x) = \sigma(y) = \sigma(z) = 0.005 \text{ \AA}$ for arsenic and bromine, and 0.06 \AA for carbon.

Cruickshank's method of assessing accuracy is not strictly applicable to poorly resolved atoms, and thus the accuracy of the positions of the overlapped carbon atoms may not be as high as suggested by the above values. The standard deviations of the bond distances (0.007 \AA for As-Br, 0.06 \AA for As-C, and 0.085 \AA for C-C) might then be a little optimistic.

In comparing the lengths of bonds which are crystallographically different but chemically similar, we find that the maximum values of $\delta l / \sqrt{(\sigma_1^2 + \sigma_2^2)}$ are only 0.8 and 0.7 for As-C and C-C bonds, respectively, so that none of the differences between chemically equivalent bonds is significant. This conclusion is still valid even if the method of assessment is underestimating

⁵ Cruickshank, *Acta Cryst.*, 1949, 2, 65.

the errors by a factor of three, and this is not very likely, particularly for those atoms which are well resolved. No significance can be attached then to the variations of the bond distances in the aromatic rings; the mean C-C length is 1.39 Å (the standard deviation of this mean value being $0.085/\sqrt{12} = 0.025$ Å).

Similar considerations apply to chemically equivalent valency angles.

Intermolecular distances. The intermolecular distances correspond to van der Waals interactions. The shortest contact is a C-C distance of 3.24 Å, but this is not significantly shorter than the usual separation of this type. The shorter contacts are illustrated in Fig. 4, which also shows that the arsenic lone pair occupies a considerable volume.

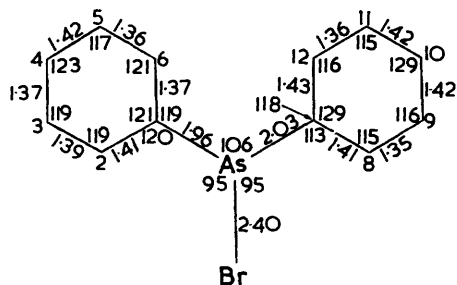


FIG. 3. Measured bond lengths (Å) and valency angles (degrees).

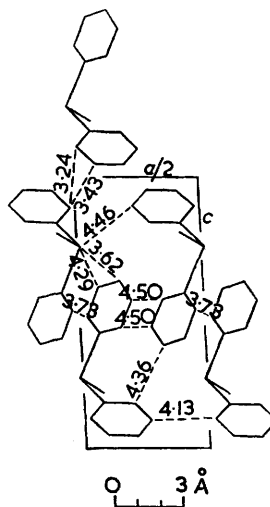


FIG. 4. Projection of the structure on to (010), showing the shorter intermolecular distances.

DISCUSSION

On the basis of the estimated standard deviations, differences between chemically equivalent bond lengths and valency angles are not significant. The mean values, with standard deviations, are:

$$\begin{aligned} \text{As-Br} &= 2.40 \pm 0.01 \text{ \AA} \\ \text{As-C} &= 1.99 \pm 0.04 \text{ \AA} \\ \text{C-C} &= 1.39 \pm 0.03 \text{ \AA} \end{aligned}$$

$$\begin{aligned} \angle \text{Br-As-C} &= 95^\circ \pm 1^\circ \\ \angle \text{C-As-C} &= 105^\circ \pm 2^\circ \\ \angle \text{As-C-C} &= 120^\circ \pm 2^\circ \\ \angle \text{C-C-C} &= 120^\circ \pm 2^\circ \end{aligned}$$

These values are in good agreement with the dimensions of the few other arsenic derivatives whose structures have been determined, chiefly by electron-diffraction.⁶ In trimethylarsine,⁷ $\text{As-C} = 1.98 \pm 0.02$ Å and $\angle \text{C-As-C} = 96^\circ \pm 5^\circ$; the significantly larger angle in bromodiphenylarsine is not surprising in view of the presence of the bulkier phenyl substituents. In an electron-diffraction investigation of bromodimethylarsine,⁸ Me_2AsBr , the dimensions $\text{As-Br} = 2.34 \pm 0.04$ Å and $\angle \text{Br-As-C} = 96^\circ \pm 3^\circ$ were derived by assuming As-C and $\angle \text{C-As-C}$ identical with those in Me_3As . The $\angle \text{Br-As-C}$ angle in bromodiphenylarsine is almost identical with that given for Me_2AsBr , but the As-Br bond is a little longer than the corresponding bond in the methyl derivative. The

⁶ Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

⁷ Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996.

⁸ Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

As-Br distance in arsenic tribromide has been reported as 2.31,⁹ 2.33,¹⁰ and 2.36 Å,¹¹ and again the bond distance in Ph₂AsBr is slightly greater than these values.

The angle between the planes of the aromatic rings is about 60°, and in this particular configuration the closest inter-ring C···C and H···H contacts are about 3.4 and 2.8 Å, respectively, these distances being exactly equal to the sums of the corresponding van der Waals radii. These approaches may be compared with the H···H distance of rather less than 1 Å which would pertain in a model with the rings coplanar and in the C₁-As-C₇ plane. Such a model is not very satisfactory for a more general description of the molecular configuration, and probably the most useful comparison is with an "ideal" model in which there is maximum interaction between the aromatic π-electrons and the arsenic lone pair, that is, in which there is maximum overlap between the π-orbitals and the lone pair.

In setting up such an ideal model it was necessary to define the direction of the lone pair, since this is not determined, as that direction which makes equal angles with the As-Br, As-C₁, and As-C₇ bonds; these angles were calculated to be 119°. The phenyl groups were then oriented so that the ring normals lay in the planes defined by the lone pair and the As-C bonds. In the true structure ring I (C₁-C₆) is rotated about the As-C₁ bond by 80° from its position in this idealized structure, and ring II (C₇-C₁₂) by 33° about bond As-C₇. These figures are of course only qualitative, since the exact location of the arsenic lone pair cannot be determined, but they do indicate that ring I is twisted by about π/2 from the ideal model, and is therefore in a position where interaction with the lone pair is negligible, while ring II, which is rotated only by about 30°, will interact to a considerable extent.

The molecular configuration is, of course, influenced by steric interferences other than those between the phenyl groups; the minimum distances between the bromine atom and the aromatic rings are Br···C₆ = 3.32 Å and Br···H₆ = 2.84 Å, and these could probably not be reduced further because of steric repulsion. In addition, since the energies involved in rotating the rings are not very large, intermolecular forces could possibly influence the molecular configuration.

It is possibly significant however that for diphenyltrifluoromethylarsine, Ph₂As·CF₃, a very similar configuration, that is, with one ring interacting strongly and the other only weakly with the arsenic lone pair, has been proposed to explain the spectroscopic properties in solution.¹²

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⁹ Hassel and Sandbo, *Z. phys. Chem.*, 1938, **B**, **41**, 75.

¹⁰ Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

¹¹ Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393.

¹² Cullen and Hochstrasser, *J. Mol. Spectroscopy*, 1960, **5**, 118