769. *The Crystal Structure of Tetramethylarsonium Bromide.*

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Tetramethylarsonium bromide crystallises in the hexagonal space group $P6_3mc$ with two molecules in the unit cell a 7·04 Å, c 9·94 Å. The arsenic atom is surrounded tetrahedrally by its four methyl groups at about 1·9 Å; the bromine atom makes van der Waals contacts with thirteen methyl groups at about 4 Å. Arsenic and bromine atoms are approximately tetrahedrally co-ordinated as in the ZnS (wurtzite) pattern.

The main features of the structure appear to be determined by packing considerations, and no information is obtained, from the interatomic distances, about the contact distance which would correspond to purely ionic bonding between the arsenic and the bromine.

The object of this investigation was to determine the normal distance between the arsenic atom and the halogen atom in a quaternary arsonium salt of type $[R_4As]Br$. No examples of the measurement of this ionic distance have apparently been recorded. Since this distance must be affected by the size and nature of the group R, tetramethylarsonium bromide was chosen because it has the simplest possible arsonium cation.

Experimental.—Tetramethylarsonium bromide. This salt was readily obtained by the action of methyl bromide on trimethylarsine in di-n-butyl ether, but it was not pure even after recrystallisation from methanol or from methanol–acetone. The solution of trimethylarsine was therefore treated with methyl iodide; the precipitated tetramethylarsonium iodide, when collected, twice recrystallised from methanol, and dried, was pure (Found: C, 18·4; H, 4·4. Calc. for $C_4H_{12}AsI$: C, 18·3; H, 4·6%); when this salt was heated, either in an open capillary tube or in a tube which had been evacuated and sealed, it dissociated at 340° and was re-formed in the cooler upper portion of the tube.

An excess of freshly prepared silver bromide was added to a cold aqueous solution of the iodide, which was shaken for 3 hr. and then filtered. The filtrate was evaporated to dryness in a desiccator, and the residue, when recrystallised from ethanol and dried at 75°/0·1 mm., afforded the pure deliquescent tetramethylarsonium bromide (Found: C, 22·2; H, 5·4. Calc. for $C_4H_{12}AsBr$: C, 22·35; H, 5·6%); the salt when heated as above dissociated at 370°.

Crystal data. $C_4H_{12}AsBr$, $M = 215·0$, hexagonal, a 7·04 Å, c 9·94 Å, $U = 426·6$ Å^3. $D_m = 1·62 \pm 0·02$ (by flotation; trichloroethylene and bromoform); $Z = 2$, $D_c = 1·67$, $F(000) = 208$. Space group $P6_3mc$ (C_{6v}^4, No. 186), Laue symmetry $6/mmm$. Mo-K_α radiation, $\mu_{\text{linear}} = 94$ cm.$^{-1}$.

The unit-cell dimensions were measured on oscillation photographs. For intensity measurements, $hki0$ and $0k\bar{k}l$ reflexions were recorded on Weissenberg photographs, by the multiple-film technique with nickel foil interleaving the films. No corrections were applied for absorption or extinction.

Space Group and Approximate Structure.—The approximate structure, and the space-group symmetry, were deduced directly from considerations of the Laue symmetry, the number of molecules in the unit cell, the axial lengths, and the probable nature of the As–Br and As–CH_3 co-ordination groupings and contact distances (as suggested by the structure of tetraphenylarsonium iodide[1]). These deductions were confirmed by the observation of only a few weak reflexions contravening the systematic absences which would correspond to the heavy-atom positions in the suggested structure ($hh\overline{2h}l$ for $l = 2n + 1$, and $hkil$ for $h - k = 3n, l = 2n + 1$), and by comparison of the sharpened Patterson functions $hki0$ and $0k\bar{k}l$ with those corresponding to the postulated structure and normal interatomic distances.

In this structure the arsenic atom, the bromine atom, and one methyl group, represented by carbon atom C(1), of a molecule lie on a triad axis, the other three methyl groups, carbon atoms C(2), C(3), C(4), of the molecule lying on mirror planes in such positions that the four methyl groups are located at the corners of a tetrahedron with the arsenic atom at its centre. The positions of arsenic and bromine atoms correspond approximately to those of zinc and sulphur in wurtzite, each being tetrahedrally co-ordinated by the other. The line joining arsenic to bromine is nearly normal to a face of the tetrahedron of methyl groups, which thus "shields" the arsenic atom from the four surrounding bromine atoms.

TABLE 1.

Atomic co-ordinates and isotropic temperature factors.

Atom	x	y	z	B (Å^2) (from $0k\bar{k}l$)	B (Å^2) (from $hki0$)
As	$\frac{1}{3}$	$\frac{2}{3}$	0·4090	5·6	4·6
Br	$\frac{1}{3}$	$\frac{2}{3}$	0·0058	5·8	4·6
C(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·600	6·2	6·2
C(2)	0·188	0·812	0·354	5·1	5·1

Notes: (1) The atomic co-ordinates are referred to the hexagonal unit cell and space group $P6_3mc$. (2) Carbon atoms C(3) and C(4) of the molecule are symmetry-related to the type atom C(2) in the Table: their actual (x, y, z) co-ordinates (for the same molecule) are C(3) 0·188, 0·376, 0·354, and C(4) 0·624, 0·812, 0·354.

Refinement of the Atomic Parameters.—The least-squares refinement process (by J. S. Rollett's programme[2]), leading to the atomic parameters and temperature factors listed in Table 1, was not pressed very far since it was already clear that information about the length of a pure ionic bond As–Br would not be obtained from the structure. For arsenic and bromine Thomas and Umeda's[3] scattering factors were used, for carbon those

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[1] Mooney, *J. Amer. Chem. Soc.*, 1940, **62**, 2955.

[2] Mills and Rollett, in "Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman. Pergamon Press, Oxford, 1960, p. 108.

[3] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

of Berghuis *et al.*[4] Non-observed reflexions were given zero weight; all others were assigned equal weights. Six cycles of least-squares refinement were computed for each projection, giving final R factors 4·2% for *hki*0 and 9·1% for $0k\bar{k}l$, at which stage shifts in the z-co-ordinates of the heavy atoms were of the same order of magnitude as the standard deviations. Examination of difference maps calculated after four cycles of least-squares refinement (*i.e.*, before the completion of refinement) gave no indication of anisotropy of thermal vibration for the heavy atoms; the existence of large diffraction ripples round arsenic, at this stage, was presumably an indication of the need for further refinement of the isotropic temperature factor.

TABLE 2.

Observed and calculated structure amplitudes for reflexions *hki*0 and $0k\bar{k}l$.

(*a*) Reflexions *hki*0.

hkl	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c
010	720	−681	110	1020	1100	220	735	756	330	330	337
020	660	−643	120	375	−371	230	270	−262			
030	720	732	130	330	−324	240	180	−174			
040	270	−301	140	420	423	250	195	192			
050	150	−139	150	135	−135						
060	210	244									

(*b*) Reflexions $0k\bar{k}l$.

hkl	$\lvert F_o \rvert$	F_c	α(°)	*hkl*	$\lvert F_o \rvert$	F_c	α(°)	*hkl*	$\lvert F_o \rvert$	F_c	α(°)	*hkl*	$\lvert F_o \rvert$	F_c	α(°)
002	1106	1063	320	017	245	261	260	030	641	684	0	047	144	156	260
004	118	129	250	018	93	106	230	031	51	67	220				
006	160	193	71	01.10	59	78	210	032	557	509	340	050	118	109	180
008	194	207	40					033	59	53	112	051	68	65	168
00.10	127	136	28	020	616	628	180	034	152	177	300	052	101	109	174
				021	110	155	114	036	84	61	108	053	144	165	130
010	549	676	180	022	371	379	142	038	144	149	59	055	152	166	103
011	380	340	5	023	397	391	134	03.10	84	114	24	057	84	88	76
012	439	448	156	024	51	54	84								
013	777	703	310	025	532	502	111	040	245	272	180	060	211	192	0
014	93	116	119	026	59	75	250	041	59	81	320	062	127	132	330
015	615	582	280	027	253	289	77	042	160	181	146	064	59	31	290
016	42	54	270	028	84	85	220	043	228	219	310				
								045	270	263	290				

Notes: (1) The F values listed should be divided by 10 to correspond to $F(000) = 208$. (2) In calculating F_c the atomic co-ordinates, and the *appropriate* B values of Table 1 are used.

The final atomic co-ordinates and isotropic temperature factors are listed in Table 1, and in Table 2 two sets of reflexions are tabulated. Reflexions *hki*0, relatively few in number, show excellent agreement (R 4·2%) between the scaled F_o values and F_c values which depend only upon one variable atomic parameter and the appropriate isotropic B values of Table 1. Reflexions $0k\bar{k}l$ show less close agreement (R 9·1%), as might be expected since five variable atomic parameters are involved, as well as the appropriate isotropic B values (Table 1). It is to be noted that the two sets of reflexions, measured with different crystals, were treated separately in the refinement process; the atomic (positional) co-ordinates finally selected are quoted in Table 1; the differences in the separate B values given for the two sets of reflexions for arsenic and bromine may represent real anisotropy of thermal vibration for these heavy atoms or they may arise from differences in absorption effects (for which no correction was applied) in the two sets of experimental measurements. The differences in the values of F_o for the reflexions 010—060, common to both sets of reflexions quoted in Table 2, are due in part to real differences in the measured values, in part to the scaling of F_o to match F_c; the differences in F_c for these reflexions arise from the choice of different B values.

The standard deviations in atomic co-ordinates, calculated from the weighted residuals from the least-squares refinement, are $\sigma(z) = 0{\cdot}0167$ Å for As, 0·0159 Å for Br, 0·114 Å for C, and $\sigma(x) = \sigma(y) = 0{\cdot}130$ Å for C(2), C(3), C(4).

Table 3 lists bond lengths and angles, and all contacts less than 5 Å involving a heavy atom, together with their standard deviations.

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

TABLE 3.

Bond lengths and angles, and intermolecular distances.

(*a*) Tetramethylarsonium ion

Bond	Length (Å)	Standard deviation (Å)
As–C(1) ...	1·90	0·13
As–C(2) ...	1·85	
As–C(3) ...	1·85	
As–C(4) ...	1·85	

Bond	Length (Å)	Standard deviation (Å)
C(1)–C(2) ...	3·02	0·17
C(1)–C(3) ...	3·02	
C(1)–C(4) ...	3·02	
C(2)–C(3) ...	3·07	
C(2)–C(4) ...	3·07	
C(3)–C(4) ...	3·07	

Angle	Size	Standard deviation
C(1)–As–C(2)	107°	8½°
C(1)–As–C(3)	107	
C(1)–As–C(4)	107	
C(2)–As–C(3)	112	
C(2)–As–C(4)	112	
C(3)–As–C(4)	112	

(*b*) As–Br contacts

Contact	Length (Å)	Standard deviation (Å)
As–Br	4·01	0·02
As–Br′..................	4·18	
As–Br″	4·18	
As–Br‴	4·18	

Angle	Size	Standard deviation
Br–As–Br′	103·3°	0·6°
Br–As–Br″	103·3	
Br–As–Br‴	103·3	
Br′–As–Br″	114·9	
Br′–As–Br‴	114·9	
Br″–As–Br‴.........	114·9	

(*c*) Br–CH_3 contacts

Co-ordinates of methyl group		Length of contact (Å)
(x, y, z)	C(2)	3·89
	C(3)	3·89
	C(4)	3·89
$(-x, y, -1 + z)$	C(1)	4·03

Co-ordinates of methyl group		Length of contact (Å)
$(-x, 1 - y, -\frac{1}{2} + z)$	C(1)	4·17
	C(2)	3·84
	C(3)	3·84
$(1 - x, 1 - y, -\frac{1}{2} + z)$	C(1)	4·17
	C(3)	3·84
	C(4)	3·84
$(1 - x, 2 - y, -\frac{1}{2} + z)$	C(1)	4·17
	C(2)	3·84
	C(4)	3·84

Standard deviation 0·13 Å for all Br–CH_3 contacts.

Notes: (1) In (*b*), co-ordinates of bromine atoms are Br (xyz), Br′ $(-x, 1 - y, \frac{1}{2} + z)$, Br″ $(1 - x, 1 - y, \frac{1}{2} + z)$, and Br‴ $(1 - x, 2 - y, \frac{1}{2} + z)$. (2) In (*c*), contacts are for reference atom Br at (xyz).

Description of the Crystal Structure.—The structure is seen in projection along *a* in Fig. 1, and the stereochemical arrangement about the arsenic atom is shown in Fig. 2.

If arsenic and bromine atoms formed an undistorted wurtzite pattern, all As–Br contacts would be equal in length and all Br–As–Br angles would correspond to regular tetrahedral co-ordination. The tests of Cruickshank and Robertson[5] show that the differences [Table 3(*b*)] in bond lengths (4·01 and 4·18 Å) and in bond angles (103·3° and 114·9°) are significant; these departures from regular tetrahedral co-ordination are in the direction to be expected from a small increase in the length of the *a*-axis relative to that in the ideal wurtzite structure. The difference in length of the As–Br contacts is reminiscent of differences in the pairs of arsenic–halogen contacts in the dibromide and di-iodide of 5,10-dihydro-5,10-dimethylarsanthren[6] (2·59, 2·66 Å in the dibromide, 2·80, 2·98 Å in the di-iodide); in these compounds folding of the molecule, resulting in some steric hindrance, is at least partly responsible for the inequality.

Within the tetramethylarsonium ion, however, the departures from regular tetrahedral co-ordination shown in Table 3(*a*) are not significant, either in regard to C–As–C angles (107° and 112°) or in regard to As–C bond lengths (1·85 and 1·90 Å) which are also not significantly different from other published values, *e.g.*, 1·98 ± 0·02 Å in trimethylarsine[7] and 1·95 Å in tetraphenylarsonium iodide.[1]

The bromine atom makes close contacts with 13 methyl groups, of which 12 are at the corners of the 4 tetrahedrally disposed faces of the tetramethylarsonium ions; the

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[5] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.

[6] Sutor and Harper, *Acta Cryst.*, 1959, **12**, 585.

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

remaining group is C(1) on the same triad axis but in the cell below. Conversely, each methyl group is associated with 3 bromine atoms, except C(1) which has contacts with 4 bromine atoms. The length of the bromine–methyl contact ranges from 3·84 to 4·17 Å, with average 3·94 Å, in good agreement with 3·95 Å for the sum of the van der Waals radii. The significance to be attached to the differences in the lengths of these contacts is not clear at the present stage of refinement of the structure. The closest methyl–methyl intermolecular contacts are 3·97 and 4·34 Å.

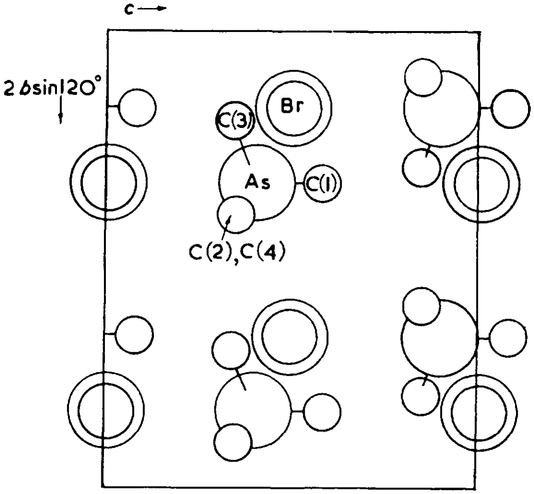

FIG. 1. Projection of the structure along *a*.

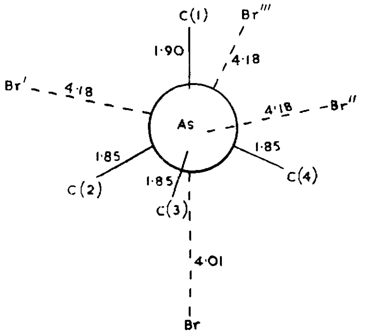

FIG. 2. Arrangement of groups about an arsenic atom. Distances in Å.

We thank Dr. W. H. Taylor for much valuable advice during this work, which was started in Cambridge (by E. C.), supported by a D.S.I.R. joint research award (to F. G. M. and W. H. T.), and completed at Birkbeck College during the tenure (by D. J. S.) of an I.C.I. Fellowship awarded by the University of London. We are also indebted to Dr. M. V. Wilkes, of the Mathematical Laboratory, Cambridge, for permission to use EDSAC, and to Mr. O. S. Mills and Dr. J. S. Rollett for making available their programmes for London University's Ferranti Mercury Computer.

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[*Received, January 24th,* 1963.]