

754. *The Crystal Structure of the Complex $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$.*

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A crystal-structure determination, by two-dimensional Fourier methods, of the complex formed by aluminium bromide with benzene, confirms that the aluminium bromide exists in the dimeric form in the complex and establishes the composition of the solid as $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$. The bromine atoms in the structure form overlapping, approximately close-packed bands extending infinitely along the *b* crystal axis. The benzene molecules lie in spaces between these bands with their planes parallel to the mean planes of the bands. The components seem to be held together by van der Waals forces but the possibility of charge-transfer interaction, between the π -electrons of the benzene rings and the bridge-bromine atoms, is not excluded.

THE binary system aluminium bromide–benzene has been studied by many workers but the conclusions about complex formation have not been in agreement. After the earlier formulation ¹ of the complex in terms of the aluminium bromide monomer, $\text{AlBr}_3\cdot\text{C}_6\text{H}_6$, recent work led to one or other of the formulæ $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$ ² and $\text{Al}_2\text{Br}_6\cdot 2\text{C}_6\text{H}_6$. ³ Previous diffraction studies have given little detailed information. The earlier suggestion by Plotnikov *et al.* ¹ that crystals of the complex were face-centred cubic was refuted by Fairbrother and Field ⁴ who obtained powder photographs indicating a low crystal symmetry (probably triclinic). Dallinga, ⁵ studying X-ray diffraction by solutions of aluminium bromide in benzene, concluded that the diffraction pattern was in reasonable agreement with the Al_2Br_6 bridge structure obtained by Palmer and Elliott ⁶ by electron-diffraction studies of aluminium bromide vapour.

Two difficulties probably account for the differing suggestions about the composition of the complex. The first is the readiness with which the complex is attacked by traces of atmospheric moisture producing the ionic complex $[\text{C}_6\text{H}_7]^+[\text{Al}_2\text{Br}_7]^-$. The second is the ease with which the complex loses benzene. In the present investigation these difficulties were overcome by preparing very pure complex by vacuum-line techniques and by sealing crystals of the complex into thin Pyrex capillary tubes with drops of mother-liquor, where they remain stable under the equilibrium vapour pressure of benzene. The aims of the investigation were to establish the composition of the solid complex, to confirm the dimeric form of aluminium bromide in the complex, and to obtain structural information which might indicate the nature of the intermolecular forces in the crystal.

EXPERIMENTAL

Preparation of the Complex.—Pure aluminium bromide was first prepared by passing bromine vapour in a stream of dry nitrogen over aluminium turnings at 300°. The product was sublimed twice *in vacuo* over aluminium turnings and resublimed *in vacuo* a further 8–10 times until it was pure white. Benzene was shaken with sulphuric acid, sodium carbonate solution, and water, frozen 3 times (with the rejection of the liquid phase, about 20% of the whole, on each occasion), dried (CaCl_2), refluxed over P_2O_5 , and distilled; the middle fraction was collected in a trap containing more P_2O_5 and the liquid was degassed, frozen, evacuated,

¹ Plotnikov and Gratsianskii, *Mem. Inst. Chem., Ukrain. Acad. Sci.*, 1938, **5**, 213; *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1947, 101; *Chem. Abs.*, 1939, **33**, 2432; 1948, **42**, 4480; Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287.

² Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6265; Sang Up Choi, *Diss. Abs.*, 1958, **19**, 38.

³ Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 3619.

⁴ Fairbrother and Field, *J.*, 1956, 2614.

⁵ Dallinga, *Internat. Union Pure & Appl. Chem.*, 1953, Abs., p. 172; *Proc. Symp. Co-ordination Chemistry*, Danish Chem. Soc., 1954, p. 134.

⁶ (a) Palmer and Elliott, *J. Amer. Chem. Soc.*, 1938, **60**, 1852; (b) Akishin, Rambidi, and Zasorin, *Kristallografiya*, 1959, **4**, 186.

and sealed off. The benzene was then further purified with the aid of aluminium bromide as follows. An evacuated bulb containing some resublimed aluminium bromide was broken inside the vacuum system by a magnetically operated hammer. The seal of the trap containing benzene was similarly broken and the benzene was cold-distilled on to the aluminium bromide, the first and the last fraction being rejected. The resulting yellow solution was cold-distilled on to lithium aluminium hydride (only the middle fraction being collected) and, after agitation for several hours and removal of the hydrogen produced, the dry benzene was cold-distilled twice. This benzene was found to give a colourless solution with pure aluminium bromide.

The complex was prepared by distilling pure benzene on to pure aluminium bromide in a vacuum system until, on warming, a homogeneous solution was obtained which deposited crystals of the complex when cold. Crystals and mother liquor were transferred to a trap to which was attached about 5 cm. of thin-walled Pyrex glass tubing of internal diameter 0.1—0.2 mm. Lengths of 1—2 cm. of this tubing were sealed off, each containing small quantities of liquid and solid. Single crystals were caused to grow in these capillaries by warming them on a microscope stage with an electrically heated wire loop. In this way, cylindrical crystals filling the whole width of the tube were obtained. They were fairly stable to small temperature changes, but the capillaries had to be handled with extreme care because the heat of the hand was sufficient to cause the crystals to dissolve in the drop of mother liquor. Powder diffraction photographs could be obtained from the capillaries used for single crystal photographs by warming the contents and then cooling them rapidly with liquid air to obtain a microcrystalline mass of complex. (The lines observed on such powder photographs were in good agreement with those reported by Fairbrother and Field,⁴ indicating that the complex was the same as that studied by these authors.)

Intensity Data.—It was found possible to crystallise the complex in the capillary tubes so as to obtain either the *a* or the *b* crystallographic axis or the [10 $\bar{1}$] diagonal of the unit cell parallel to the length of the tube. This allowed Weissenberg photographs to be taken with the crystals oscillating about these three directions. Cu- K_{α} radiation was used. Intensities of the $0kl$ and $h0l$ reflections were measured by Wallwork and Standley's photometric method⁷ which makes some allowance for the background intensity, which was rather higher than usual. Intensities of the hkh reflections, used only in confirmatory syntheses at the end of the structure determination, were obtained by visual comparison. Because the crystals completely filled the widths of the capillary tubes of known dimensions, the simple absorption corrections for cylindrical specimens could be applied. The intensity data were corrected in this way, with $\mu = 190$.

Unit Cell and Composition.— $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_6$. $M = 611.5$. Triclinic. $a = 6.85$, $b = 6.91$, $c = 9.00$ (all ± 0.02) Å. $\alpha = 104.6^\circ$, $\beta = 103.1^\circ$, $\gamma = 90.0^\circ$ (all $\pm 0.5^\circ$). $U = 401$ Å³. $Z = 1$. $D_c = 2.53$. Space group, $P\bar{1}$ [since the $N(z)$ test indicated centrosymmetry], implying that both the Al_2Br_6 and the C_6H_6 components are centrosymmetric.

A reliable density measurement could not be made because of decomposition of the complex, and the above formulation and value of Z were adopted tentatively at first on the basis of the comparison of effective volumes. From the cell dimensions and contents for the pure crystalline components, the effective volumes are $\text{Al}_2\text{Br}_6 = 269$,^{8a} $\text{C}_6\text{H}_6 = 127$ ^{8b} Å³. The sum of these, 396 Å³, is in good agreement with the cell volume for the complex. These conclusions were borne out by the subsequent structure analysis.

Structure Determination.—Application of the usual corrections to the $0kl$ and $h0l$ intensity data led to values of F_o^2 which were used in calculating the Patterson projections shown in Fig. 1. These suggested two alternative orientations for the Al_2Br_6 molecule; a decision between them was then made by an application of inequalities.⁹ From this point refinement proceeded first by Fourier methods, with F_o , $(F_o - F_{\text{Br}})$, and $(F_o - F_{\text{Br}} - F_{\text{Al}})$ syntheses, where F_{Br} and F_{Al} represent the contributions of the bromine and aluminium atoms. In the later stages, some of the larger structure factors were corrected for extinction by the method of Pinnock, Taylor, and Lipson¹⁰ and structure factors for unobserved reflections were included in the syntheses by assuming them to have a value one-half of the minimum observable value

⁷ Wallwork and Standley, *Acta Cryst.*, 1954, **7**, 272.

⁸ (a) Renes and MacGillavry, *Rec. Trav. chim.*, 1945, **64**, 275; (b) Cox, Cruickshank, and Smith, *Proc. Roy. Soc.*, 1958, **A**, 247, 1.

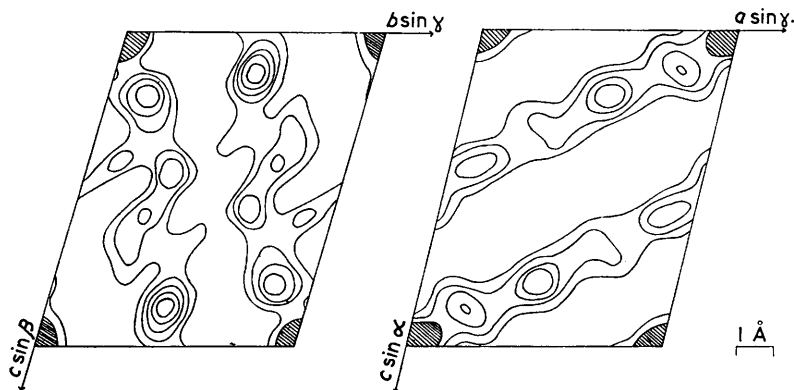
⁹ Gillis, *Acta Cryst.*, 1948, **1**, 174.

¹⁰ Pinnock, Taylor, and Lipson, *Acta Cryst.*, 1956, **9**, 173.

at the appropriate Bragg angle θ . After several cycles of refinement the disagreement factors R for the $0kl$ and $h0l$ reflections were both 0.14 if allowance was made for extinction or 0.25 and 0.23, respectively, without this correction. At this stage some evidence for the positions of the carbon atoms was obtained from the $(F_o - F_{\text{Br}} - F_{\text{Al}})$ syntheses and it was considered that the refinement could best proceed by the least-squares method.¹¹

Least-squares refinement and final structure. The 104 $0kl$ and the 107 $h0l$ F_o values (not corrected for extinction) were combined for a least-squares refinement of the atomic co-ordinates and thermal parameters, the facilities of the University of Leeds Electronic Computing Laboratory being used. The Hughes weighting scheme was employed and the shifts

FIG. 1. Patterson $0kl$ and $h0l$ projections (contours at arbitrary equal intervals).



made at the end of each cycle were reduced in the earlier stages to $\frac{2}{3}$ of the values indicated and, in the last two cycles, to 0.3 of the indicated values. Anisotropic thermal parameters were derived for the bromine atoms, but only isotropic parameters were derived for the aluminium and carbon atoms. After six cycles, R had fallen to 0.12 and the maximum co-ordinate shift indicated was less than one standard deviation. This was considered a satisfactory state of refinement in view of the rather limited data.

TABLE 1. *Final atomic co-ordinates in Å (e.s.d. in parentheses).*

Atom	x	y	z
Br(1)	0.865 (0.006)	6.108 (0.006)	1.274 (0.005)
Br(2)	2.703 (0.009)	2.059 (0.012)	0.565 (0.009)
Br(3)	6.719 (0.009)	2.918 (0.009)	2.514 (0.007)
Al	1.026 (0.019)	1.440 (0.020)	0.925 (0.015)
C(1)	4.41 (0.112)	0.94 (0.113)	4.02 (0.080)
C(2)	3.78 (0.081)	5.63 (0.116)	4.20 (0.087)
C(3)	4.48 (0.090)	6.30 (0.086)	3.76 (0.066)

TABLE 2. *Final thermal parameters and their e.s.d. (in Å²). (U is the isotropic mean square vibration amplitude; U_{ij} correspond to $f = f_o \exp -[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{23}klb^*c^* + U_{13}hla^*c^*]$.)*

Atom	U	Atom	U	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Al	0.051	C(2)	0.093	Br(1)	0.058	0.047	0.050	0.005	0.041	0.020
(e.s.d....)	0.003		0.025)	(e.s.d....)	0.003	0.003	0.002	—	0.005	0.004)
C(1)	0.107	C(3)	0.077	Br(2)	0.085	0.104	0.102	0.011	0.083	0.062
(e.s.d....)	0.024		0.018)	(e.s.d....)	0.005	0.007	0.006	—	0.012	0.010)
				Br(3)	0.084	0.074	0.068	0.009	0.011	0.052
				(e.s.d....)	0.005	0.005	0.003	—	0.008	0.007)

The final atomic co-ordinates and their estimated standard deviations (e.s.d.) are shown in Table 1 and the thermal parameters and estimated standard deviations are shown in Table 2. Fourier syntheses showing the electron density projected along the a and b axes were calculated

¹¹ Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737; Cruickshank, *Acta Cryst.*, 1950, **3**, 10; 1952, **5**, 511.

from F_o (some of the large values having been corrected for extinction) and from the signs calculated in the sixth least-squares cycle. These electron density maps are shown in Fig. 2.

Confirmation of the structure from a projection along the $[10\bar{1}]$ cell diagonal. Since one Al-Br bond appeared to be unusually short, a check of the structure from an independent set of intensities was desirable. For this, the hkh intensities were measured and converted into F_o values in the usual way. Comparison of these with the corresponding F_c values gave a dis-

FIG. 2. Final Fourier $0kl$ and $h0l$ projections [contours at 0 (broken line), 5, 10, 20, . . . $e\text{\AA}^{-2}$; crosses indicate the final atomic positions].

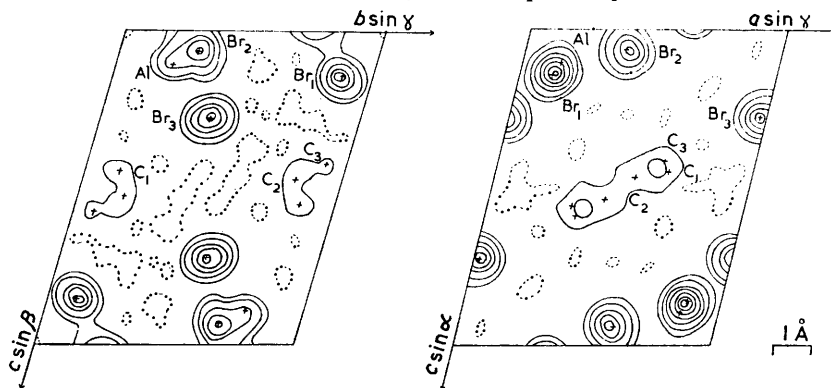
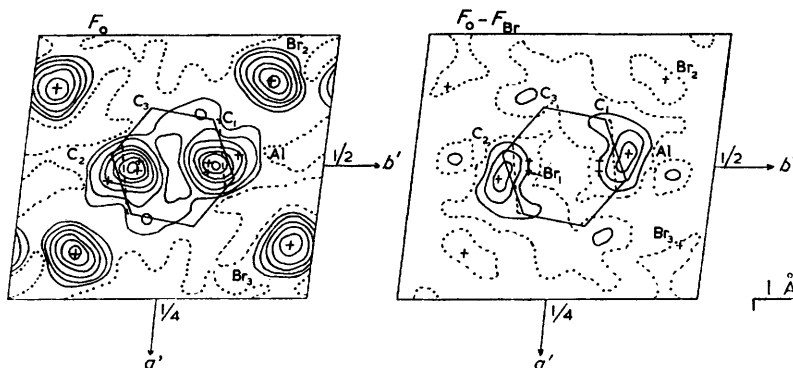


FIG. 3. F_o and $(F_o - F_{Br})$ Fourier projections along the $[10\bar{1}]$ cell diagonal (contours as in Fig. 2). Crosses indicate the final Al and Br positions. The benzene molecule is shown according to the final "least-squares" positions (broken lines) and as a regular hexagon in a similar orientation (full lines).



agreement factor R of 0.21 (53 reflections, no correction for extinction). The F_o synthesis and the $(F_o - F_{Br})$ synthesis for this projection gave the electron-density maps shown in Fig. 3. The positions of the atoms derived from the least-squares refinement are also shown on these maps and the agreement can be seen to be quite satisfactory.

RESULTS AND DISCUSSION

Composition of the Complex.—The refinement of the structure confirms the formula $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$ for the complex. The monomeric formula¹ $\text{AlBr}_3\cdot\text{C}_6\text{H}_6$ is shown to be incorrect by the appearance of Al_2Br_6 molecules in the electron-density maps. Equally, the formula³ $\text{Al}_2\text{Br}_6\cdot 2\text{C}_6\text{H}_6$ may be rejected because there are no vacant spaces in the structure where a second benzene molecule could be accommodated.

Molecular Dimensions.—The dimensions calculated from the observed atomic positions are given in Table 3 in comparison with dimensions for Al_2Br_6 previously obtained by

electron diffraction⁶ and X-ray studies.⁸ The approximate standard deviations for interatomic distances (calculated from the e.s.d. of atomic co-ordinates) are $\sigma_{\text{Br-Br}}$ 0.02, $\sigma_{\text{Al-Br}}$ 0.03, and $\sigma_{\text{C-C}}$ 0.2 Å. The agreement of the Al_2Br_6 dimensions with those previously published is, therefore, satisfactory apart from the short bond Al-Br(2). It is difficult

TABLE 3. *Molecular dimensions in the complex compared with previously published dimensions for Al_2Br_6 (in Å). (Values in parentheses are calculated from data of other authors.)*

	Complex	Al_2Br_6 vapour ^{6a}	Al_2Br_6 vapour ^{6b}	Al_2Br_6 solid ⁸
Al-Br(1)	2.37	2.33 ± 0.04	2.38 ± 0.02	2.34
Al-Br(2)	1.93	2.21 ± 0.04	2.22 ± 0.02	2.23
Al-Br(3)	2.39	2.21 ± 0.04	2.22 ± 0.02	2.33
Al-Br(1')	2.50	2.33 ± 0.04	2.38 ± 0.02	2.42
Al-Al'	3.39	3.39 ± 0.10	(3.59)	3.14
Br(1)-Br(2)	3.68	3.78 ± 0.03	(3.84)	3.80
Br(2)-Br(3)	3.78	3.72 ± 0.03	(3.81)	3.84
Br(1)-Br(3)	3.75	3.78 ± 0.03	(3.84)	3.85
Br(1')-Br(2)	3.70	3.78 ± 0.03	(3.84)	3.84
Br(1')-Br(3)	3.91	3.78 ± 0.03	(3.84)	3.86
Br(1')-Br(1)	3.50	3.20 ± 0.10	(3.12)	3.59
C(1)-C(2)	1.7			
C(1)-C(3)	1.5			
C(2)-C(3)	1.2			
Br(1)AlBr(1')	91.3°	(87°)	82 ± 3°	(98°)
Br(1)AlBr(2)	118.4	(113)	(113)	(112)
Br(1)AlBr(3)	107.0	(113)	(113)	(111)
Br(2)AlBr(3)	121.4	(115)	118 ± 3	(115)
Br(1')AlBr(2)	112.0	(113)	(113)	(111)
Br(1')AlBr(3)	100.0	(113)	(113)	(109)
AlBr(1)Al	88.7	(93)	(98)	(82)

to see why this should differ so much from the bond Al-Br(3) which has a similar environment in the structure and the most probable explanation is that the errors in the atomic positions have been underestimated. This is particularly likely in the case of the alu-

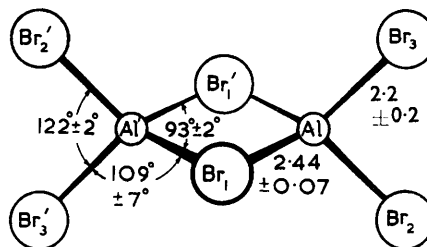


FIG. 4. *Dimensions for the "averaged" molecule Al_2Br_6 .*

minium atom, partly because it is almost completely eclipsed by a bromine atom in each of the three projections and partly because diffraction errors from the surrounding bromine atoms will tend to accumulate at the position of the aluminium atom. In view of this, dimensions for an "averaged" molecule of symmetry mmm (D_{2h}) have been calculated and are shown in Fig. 4. The deviations of the benzene molecule from the usual regular hexagonal structure of side 1.4 Å are insignificant.

Relative Positions and Bonding of the Components.—Fig. 5 shows layers of atoms in several adjacent unit cells of the structure seen in projection along the $[10\bar{1}]$ axis. It can be seen that the atoms Br(1), Br(2), and Br(3) of the infinite set of molecules related by unit cell translations along b , together with atoms Br(1'), Br(2'), and Br(3') of a second identical infinite set of molecules related to the first set by the unit cell translation a , form an approximately close-packed band of bromine atoms all nearly in the plane of projection. This band (whose atoms are represented by broken circles) is infinitely extended along b but is limited in width to that of two Al_2Br_6 molecules. In a plane parallel to this band but about 3.2 Å above it are two further bands of close-packed bromine atoms (represented

by full circles). These two bands are identical with the first and they are so arranged that the bromine atoms of one of them lie approximately above the interstices in the first band, as they would if continuing a three-dimensional close-packed structure of bromine atoms. In the appropriate number of tetrahedral holes in the region of overlap are the aluminium atoms, linking the overlapping bromine atoms to form the Al_2Br_6 molecules.

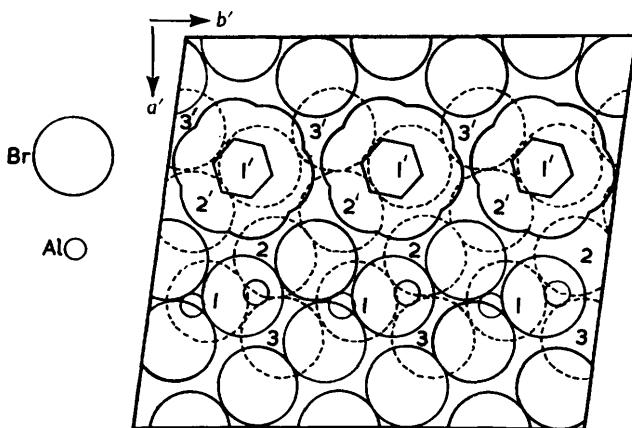
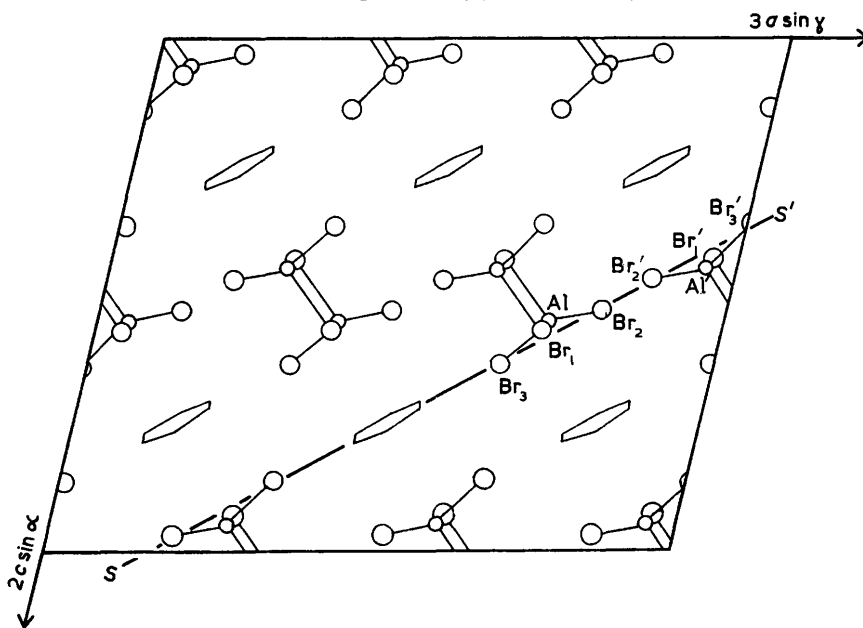


FIG. 5. Atomic and molecular packing diagram showing sections perpendicular to the $[10\bar{1}]$ axis. A band of approximately close-packed bromine atoms (broken lines) has superimposed on it similar bands of bromine atoms and benzene molecules (full lines) all approximately in the same plane (SS' of Fig. 6). Aluminium atoms in approximately tetrahedral sites link the superimposed bands to form Al_2Br_6 molecules.

FIG. 6. The interleaving of bands of bromine atoms and benzene molecules as seen in the $h0l$ projection. Section SS' is that represented by full lines in Fig. 5.



The benzene molecules shown in Fig. 5 are also in the same plane as the bands of bromine atoms represented by full circles. They are therefore also separated perpendicularly by about 3.2 \AA from the mean plane of the band of bromine atoms represented by broken circles. Because of the centre of symmetry at the centre of the benzene ring there must be a further parallel band of bromine atoms 3.2 \AA away on the other side of the benzene molecules. This is not indicated in Fig. 5 but it can be seen in Fig. 6, which shows the contents of several adjacent unit cells projected along the b axis.

One way of considering the bonding of the benzene molecules is to regard them as being held in channels between the overlapping bands of bromine atoms. This is not really justified, however, because the sides of the channels are themselves not a continuous structure but are largely held together by van der Waals forces. Instead, the benzene molecules are better considered as contributing to the bonding of the whole structure by their perpendicular and sideways interactions with neighbouring bromine atoms. Of these, the perpendicular interactions would seem to be the more significant in view of the 3.2 Å separation from the mean plane of adjacent bromine atoms. However, the shortest interatomic distance in this direction is 3.7 Å [Br(1)-C(1)] and this is approximately a normal van der Waals distance. All the other distances between carbon and bromine atoms (perpendicular or sideways) are 4.0 Å or more. The conclusion is that solid $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$ is probably a lattice complex, the components being held together by van der Waals forces. There is some possibility of charge-transfer interaction between Br(1) and the π -electrons of the benzene ring, after the manner of the complex between bromine and benzene.¹² If this is the case, it is not clear which component is the donor and which the acceptor, in view of the tendency for the bromine atoms generally and the bridge bromine atoms in particular to bear a partial negative charge.¹³ The weak intermolecular forces of a lattice complex would be consistent with the low heat of formation from the molecular components² and with the low incongruent melting point.¹

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¹² Hassel and Stromme, *Acta Chem. Scand.*, 1958, **12**, 1146.

¹³ Barnes and Segel, *J. Chem. Phys.*, 1956, **25**, 180.
