The basic lead carbonate crystals had a disordered layer-lattice-type structure and gave extensive spot patterns at all angles of tilt. The 'untilted' $hk0$ spot pattern had hexagonal symmetry. This pattern was used in conjunction with one obtained with a tilt of approximately $17\frac{1}{2}°$, as deduced from the dimensions of the pattern. Instead of normal Patterson projections, modified Patterson projections (Cowley, 1956*b*) were calculated, since these contained more information on the details of the structure. The modified Patterson maps are reproduced in Fig. 2(*a*) and (*b*).

The three-dimensional Patterson function was assumed to have a sixfold symmetry about the c axis, so that six equivalent points on each of the two maps were compared. Sections for a number of values of z were derived. The section $z = 0$ is reproduced in Fig. 2(*c*), and the section $z = 0{\cdot}13$ (= 3·2 Å) in Fig. 2(*d*).

The interpretation of these maps is discussed in the report of the structure analysis (Cowley, 1956*a*). However, it can be clearly seen that the major peaks of the projection, Fig. 2(*a*), have been separated into two groups with differing z coordinates. No indication was found that any of the features of the sections which were of sufficient importance to be considered in the course of a structure analysis were spurious. Comparison with the structure eventually found for the crystals showed that all the main features of the sections and most of the details were real.

References

Cowley, J. M. (1953). *Acta Cryst.* **6**, 516.
Cowley, J. M. (1956*a*). *Acta Cryst.* **9**, 391.
Cowley, J. M. (1956*b*). *Acta Cryst.* **9**, 397.
Moodie, A. F. (1956). Unpublished.

Acta Cryst. (1956). **9**, 401

Crystallographic Study of an Arsonium Bromide, $(C_{21}H_{19}As_2)Br$

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(*Received* 15 *October* 1954 *and in revised form* 5 *October* 1955)

The investigation of an arsonium bromide by X-ray crystallographic methods distinguished between three possible molecular structures. The molecule is correctly described as di-*o*-phenylene-*o*-xylylene-diarsine monomethobromide.

Introduction

The evidence from chemical work proved insufficient to distinguish between structural formulae (Fig. 1) for the compound with which this investigation was concerned. As this arsonium bromide was one of several compounds involved in a series of chemical investigations it was important to find its actual structure. In Fig. 1(*a*) the arsenic atom is common to the arsanthren ring structure (Kalb, 1921; Chatt & Mann, 1940) and to that of *iso*-arsindoline (Lyon & Mann, 1945); hence the value of independent physical evidence for the structure of the bromide or the corresponding iodide. It was therefore decided to examine

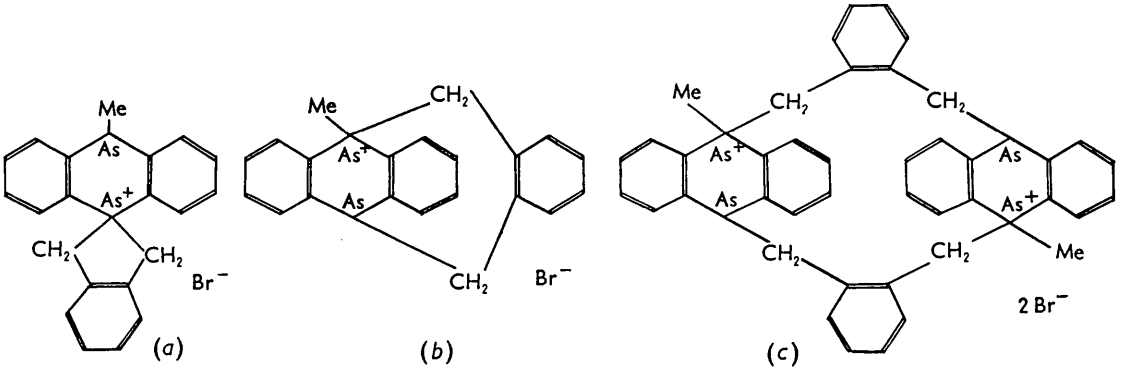


Fig. 1.

crystals of this compound by X-ray diffraction methods. The aim was to find the approximate structure so as to decide between the three chemical possibilities, rather than to attempt an accurate determination of bond lengths and angles which would have taken too long and delayed the chemical investigations.

The bromide, when heated in a vacuum, decomposed to form a glass, from which no definite product could be isolated: these conditions, however, normally cause ready dissociation of an alkyl arsonium halide, e.g. $R_3MeAsBr \rightarrow R_3As+MeBr$. This dissociation should therefore apply to the structures of Fig. 1(*b*) and (*c*). The chemical evidence, although not decisive, thus appears to favour the structure of Fig. 1(*a*). On the other hand, Cochran (1954), investigating a closely related arsonium dibromide (1:4-dimethyl-*o*-phenylene-*o*-xylylene-diarsine dimethobromide), found crystallographic evidence for a structure analogous to that of Fig. 1(*b*).

Experimental measurements

The crystals were white with well developed faces. Oscillation photographs were taken, using Cu $K\alpha$ radiation, and were used to determine the axial cell dimensions. Series of Weissenberg photographs were then taken about the *a* and *b* axes. Optical measurement of the angles between faces gave results in agreement with the X-ray measurements, which showed the unit cell to be triclinic with

$$a = 12{\cdot}4,\ b = 7{\cdot}8,\ c = 12{\cdot}0\ \text{Å};$$
$$\alpha = 107,\ \beta = 96,\ \gamma = 92°;$$
$$a^* = 0{\cdot}127,\ b^* = 0{\cdot}205,\ c^* = 0{\cdot}132;$$
$$\alpha^* = 72,\ \beta^* = 83,\ \gamma^* = 86°\ .$$

These measurements are correct to within 2%. The volume of the unit cell is thus 1110 Å^3. The arsonium bromide used had been crystallized from a mixture of methyl and ethyl alcohols, containing also some water. Analysis of the crystals (Mann, 1954) gave C = 48·9%, H = 4·9%. These figures correspond to either $C_2H_5OH+H_2O$ or else $2CH_3OH$ per $(C_{21}H_{19}As_2)Br$. Assuming two formula units per unit cell, one finds $D_c = 1{\cdot}69$ g.cm.$^{-3}$, which agrees with $D_o = 1{\cdot}67 \pm 0{\cdot}01$ g.cm.$^{-3}$.

Intensities from the (*h*0*l*) zone were used in the Wilson statistical test (Howells, Phillips & Rogers, 1950). The results agreed very well with those expected for a centrosymmetric crystal. Taken together with the results reported below, and the fact that $Z = 2$, space group $P\bar{1}$ is established beyond reasonable doubt.

Determination of heavy-atom positions

A Patterson projection on (100) did not give a clear indication of the heavy-atom positions and it was decided to try direct methods of determining the signs of the *F*'s. Unitary structure factors were calculated for both (100) and (010) projections. Some of them were found to be very large, and inequalities and probability relations were therefore used. The Harker–Kasper inequality

$$\{|U(h)|+|U(h')|\}^2 \leqslant \{1+s(h)s(h')U(h+h')\} \times \{1+s(h)s(h')U(h-h')\}$$

was used to prove that in a number of cases the sign relation

$$s(h)s(h') = s(h+h') \qquad (1)$$

was certainly satisfied for (0*kl*) structure factors. In other cases this result, although not proved, was strongly indicated. The signs of two structure factors were taken as positive, and the signs of three others were denoted by the letters *a*, *b* and *c*. The signs of some 51 (0*kl*) structure factors were then determined in terms of *a*, *b* and *c* by applying equation (1). No relations between *a*, *b* and *c* were indicated. In the notation of Cochran & Douglas (1953) it follows that there are $2^3 = 8$ ways in which signs may be chosen so as to give a maximum possible value of $\chi = \sum_h \sum_{h'} U(h)U(h')U(h+h')$. It was decided to investigate these eight sets of signs before any others were considered. A second criterion which Cochran & Douglas (unpublished) have suggested is the value of $\psi = \sum_h |\sum_{h'} U(h')U(h+h')|$, the first sum being over those values of *h* for which $U(h) = 0$. It can be shown that the correct set of signs may be expected to give a smaller value of ψ than most other sets of signs would give. In evaluating ψ, all relevant signs found previously were used, and the first sum was taken over some 16 terms for which $|U(h)|$ was very small. To save time, and as the correctness of the set of signs chosen was eventually tested by other criteria, all $|U(h')|$ and $|U(h+h')|$ used were taken to be equal. Results obtained are shown in Table 1. Set No. 3 of signs was therefore used to calculate a Fourier synthesis, with values of $U(0kl)$ as coefficients. This gave a map in which three large and approximately equal peaks could be taken to represent the two arsenic and one bromine atoms in one half of the unit cell. From these positions of the heavy atoms, structure factors were calculated and a number of additional signs were obtained. It was not found necessary to change any of the signs found by the direct method described

Table 1

Set No.	Signs of *a*, *b*, *c*	ψ
1	+ + +	220
2	− + +	83
3	+ − +	65
4	− − +	106
5	+ + −	94
6	− + −	78
7	+ − −	118
8	− − −	120

above. A new Fourier synthesis was then made using values of $F(0kl)$ as coefficients. This of course showed the heavy atoms in the same positions as before (Fig. 2(*a*)); individual carbon atoms were not resolved.

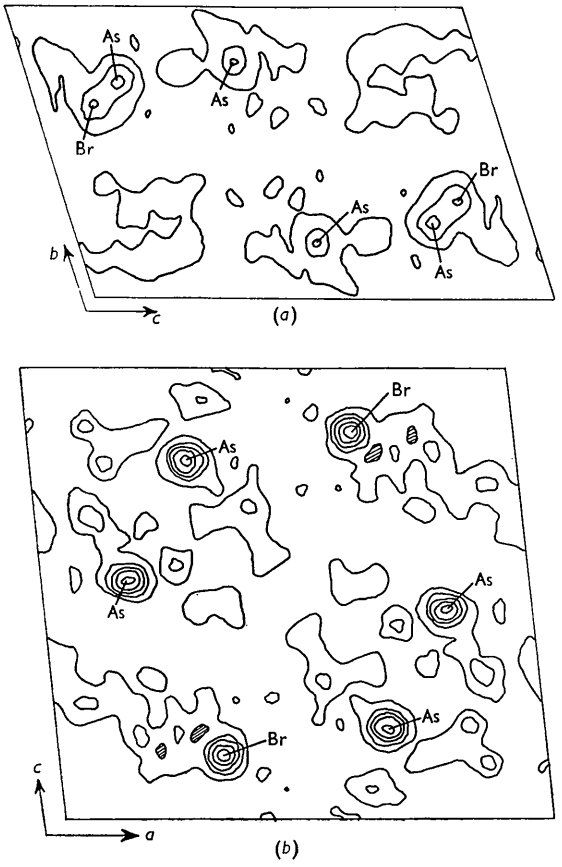


Fig. 2. (*a*) (100) Fourier projection; (*b*) (010) Fourier projection. Contour scale arbitrary.

The data for the (010) projection were treated in a similar way to those used for the (100) projection. The first electron-density map, using signs obtained by the direct method, clearly showed the positions of the three heavy atoms. Their common z coordinates in the two projections agreed very closely, thus establishing the validity of the procedure used and incidentally confirming that the space group was indeed $P\bar{1}$. The distance in three dimensions between two of the heavy atoms agreed closely with the distance between the As atoms expected from stereochemistry. This was additional confirmation, and served to distinguish As from Br. A second refinement was made of the electron density projected on (010) (Fig. 2(*b*)).

Distinction between three possible structures

A difference synthesis was calculated for the (010) projection, the Fourier coefficients being the amplitudes calculated from the heavy atoms subtracted from the observed structure factors, terms of doubtful sign being omitted. The resulting density map (Fig. 3) appeared to show the benzene rings on either side of the As–As axis of the molecule, but further work made it clear that the measured structure factors were not sufficiently accurate for the structure to be determined unambiguously in this way.

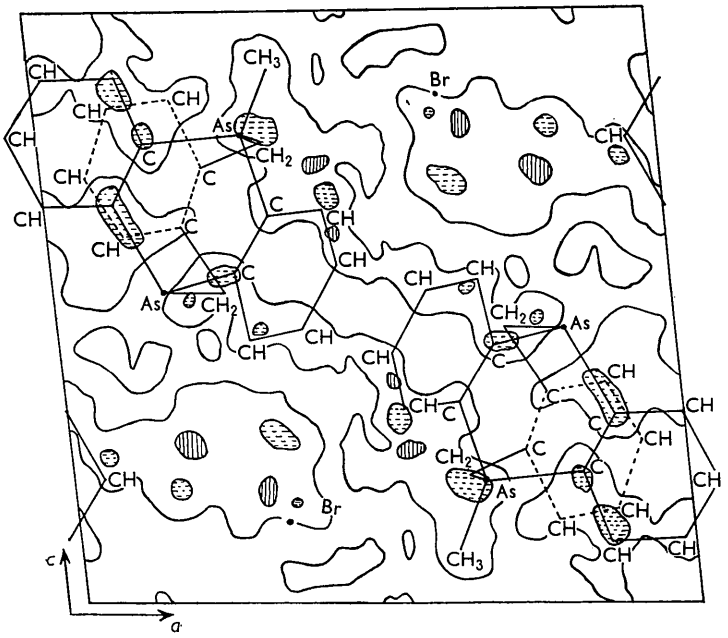
A model of the structure consisting of several unit cells was built, each of the three structures considered possible on chemical grounds being tried in turn. In each case models of the postulated molecule were made of copper wire and mounted with the As atoms correctly placed, the Br ions being separately mounted. The model molecules were then turned about the As–As axis in order to get satisfactory packing, bearing in mind the indications of the (010) difference map. It was immediately clear that the dimer structure of Fig. 1(*c*) was ruled out, as the distance between As atoms could not be bridged without severe distortion of bond angles and even of bond lengths. The structure of Fig. 1(*a*) was then tried, as it was the most likely from chemical evidence available at the time. No position of the molecules could be found which gave acceptable separation of carbon atoms from one another and from the bromine ions. The structure of Fig. 1(*b*), however, was found to give a plausible set of distances between atoms of neighbouring molecules, and there was fair agreement with the (010) difference map, most of the carbon atoms projecting into peaks or on to areas of considerable density. A 'hole' remained which was large enough to accommodate two molecules of CH_3OH.

Coordinates for the atoms of the arsonium molecule are given in Table 2. There was not enough evidence to justify postulating coordinates for the remaining atoms—$2CH_3OH$ or $C_2H_5OH+H_2O$. It is not claimed that these coordinates are exact, except for the heavy atoms, but merely that they indicate correctly the general position and orientation of the molecule. Comparison of observed and calculated ($h0l$) structure factors, based on the postulated structure, showed an

Table 2. *Atomic coordinates*

	x/a	y/b	z/c		x/a	y/b	z/c
Br	0·342	0·667	0·133	C	0·117	0·267	0·675*
As	0·183	0·200	0·533	C	0·000	0·300	0·675*
As	0·333	0·267	0·792	C	−0·050	0·350	0·792*
CH_3	0·383	0·150	0·908	C	0·017	0·367	0·892*
CH_2	0·225	0·433	0·533	C	0·142	0·342	0·900*
CH_2	0·367	0·500	0·783	C	0·175	0·300	0·775*
C	0·358	0·083	0·658*	C	0·225	0·575	0·642*
C	0·450	−0·050	0·667*	C	0·125	0·667	0·625*
C	0·460	−0·200	0·567*	C	0·075	0·800	0·725*
C	0·400	−0·217	0·467*	C	0·125	0·817	0·842*
C	0·308	−0·083	0·450*	C	0·225	0·733	0·858*
C	0·300	0·067	0·558*	C	0·267	0·600	0·742*

* Benzene ring.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