

degrees with it. The temperature factors of the remaining atoms all show some anisotropy, but the orientations of their principal axes do not appear to bear a simple relationship to the structure. Further interpretation seems to require an understanding of the dynamics of the infinite aluminum-oxygen network.

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## The Crystal Structures of Some Anthracene Derivatives. II. 9:10-Dibromoanthracene

BY JAMES TROTTER\*

*Division of Pure Physics, National Research Council, Ottawa, Canada*

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The crystal structure of 9:10-dibromoanthracene has been determined from Patterson and Fourier projections along two crystallographic axes, and values of the bond lengths and valency angles in the molecule and intermolecular distances are given.

### Introduction

The first molecule which was examined in the present series of investigations of anthracene derivatives (Trotter, 1958) was 9:10-dibromoanthracene. The structure of this molecule has been investigated previously (Kitajgorodskij, 1946a; *Structure Reports*, 1945-46) but as no details of the structure or coordinates of the atoms are given, a full analysis by X-ray diffraction methods has been carried out.

### Experimental

Crystals of 9:10-dibromoanthracene were obtained by crystallization from petroleum ether. They are greenish-yellow in colour, and consist of prisms elongated along the *a*-axis with (010) and (001) faces developed. The density was determined using a Berman balance (Berman, 1939) with carbon tetrachloride as displacement liquid. The unit-cell dimen-

sions and space group were determined from rotation and oscillation films about the *a*-axis, *Ok*l and *l*kl Weissenberg films, and *h*0*l*, *h*1*l*, *h*k0 and *h*kl precession films.

### Crystal data

9:10-dibromoanthracene, C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>; *M* = 336.0; m.p. 226 °C. Triclinic,

*a* = 4.06 ± 0.01, *b* = 8.88 ± 0.02, *c* = 16.15 ± 0.04 Å,  
α = 98° 50' ± 10', β = 97° 05' ± 10', γ = 100° 21' ± 10'.

Volume of the unit cell = 559.3 Å<sup>3</sup>.

Density, calculated (*Z* = 2) = 1.983 g.cm.<sup>-3</sup>,  
measured = 1.981 g.cm.<sup>-3</sup>.

Absorption coefficient for X-rays,

λ = 1.542 Å, μ = 92.7 cm.<sup>-1</sup>;

λ = 0.7107 Å, μ = 78.2 cm.<sup>-1</sup>.

Total number of electrons per unit cell = *F*(000) = 324.

\* National Research Laboratories Postdoctorate Fellow.

No systematic absences; space group is either  $P1-C_1^1$  or  $P\bar{1}-C_1^1$ .

The intensities of the  $0kl$  reflexions were recorded on moving film exposures for a crystal rotating about the  $a$ -axis, using  $\text{Cu } K\alpha$  radiation. The multiple-film technique (Robertson, 1943) was used to correlate strong and weak reflexions. The range of intensities measured was about 6000 to 1, the estimates being made visually. The cross-section of the crystal, normal to the rotation axis, was  $0.06 \times 0.04$  mm.; no absorption corrections were applied. The  $h0l$  intensities were recorded on multiple-exposure precession films, using  $\text{Mo } K\alpha$  radiation. The range of intensities measured was about 2000 to 1, and again no corrections were made for absorption.

Of 361 independent  $0kl$  reflexions observable with  $\text{Cu } K\alpha$  radiation, 315 were observed (87%). On the  $h0l$  precession films ( $\text{Mo } K\alpha$ ), 83 reflexions of a possible 132 were observed (63%).

The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal; the absolute scale was established later by correlation with the calculated structure factors.

### Structure analysis

The unit-cell dimensions determined by Kitajgorodskij (1946a) are referred to an  $A$ -centred cell. The original communication does not quote values for the unit-cell volume or calculated density, and the values in *Structure Reports* (1945-46) ( $U = 1340 \text{ \AA}^3$ ,  $D_x = 1.665 \text{ g.cm.}^{-3}$ ) are in error, since this volume does not correspond to the unit-cell dimensions. Direct computation of the volume from the unit-cell edges and angles gives  $U = 1090 \text{ \AA}^3$ .

The cell given in the crystal data above is the reduced cell, and it may be transformed to an end-centred cell for comparison with Kitajgorodskij's data (Table 1). Throughout the present investigation all measurements are referred to the reduced cell.

Table 1. *Unit-cell data*

	Reduced	End-centred	Kitajgorodskij
$a$	4.06 $\text{\AA}$	16.82 $\text{\AA}$	16.90 $\text{\AA}$
$b$	8.88	4.06	4.03
$c$	16.15	17.50	17.24
$\alpha$	$98^\circ 50'$	$87^\circ 03'$	$89^\circ 05'$
$\beta$	$97^\circ 05'$	$110^\circ 13'$	$110^\circ 00'$
$\gamma$	$100^\circ 21'$	$91^\circ 36'$	$98^\circ 40'$
$U$	$559.3 \text{ \AA}^3$	$1118.6 \text{ \AA}^3$	$1090.0 \text{ \AA}^3$
$Z$	2	4	4

The space group is of course either  $P1$  or  $P\bar{1}$ , and since the unit cell contains two molecules, the latter is more likely, with the two molecules probably related by a centre of symmetry. Best resolution of the atoms is probably in the projection down the short  $a$ -axis, and the  $0kl$  zone was examined first.

### [100] projection

A Patterson projection down the  $a$ -axis was computed, and four large peaks corresponding to Br-Br vectors were easily picked out. Two of these peaks were double the height of the other two, and so the four peaks represent vectors between two pairs of bromine atoms related by a centre of symmetry. The space group is therefore  $P\bar{1}$ . The bromine positions were found, and an  $F_o$  synthesis was computed with signs based on the Br atom contributions only. All the carbon atoms were reasonably well resolved, and coordinates were obtained for all the atoms in the molecule (except of course hydrogen atoms).

When the Br positions were obtained from the Patterson synthesis, it did not seem possible to fit an anthracene nucleus between two bromine atoms which were not related by a centre of symmetry, as these atoms were too close together in the projection, so that it appeared that the cell contains two independent molecules, situated on non-related symmetry centres. This was borne out by the carbon positions obtained from the  $F_o$  synthesis, so that each molecule lies on a centre of symmetry, the two molecules in the cell occupy independent centres, and the asymmetric unit is two half-molecules. This type of arrangement was predicted by Kitajgorodskij (1946a) on the basis of his theory of the packing of molecules in crystals of organic compounds (Kitajgorodskij, 1946b).

Structure factors were calculated for the  $0kl$  reflexions, and the value of  $R$ , the usual discrepancy factor, was 23.0% (calculated over the observed reflexions). The scattering curve used for bromine was that of Thomas & Umeda (1957), corrected for anomalous dispersion of the  $\text{Cu } K\alpha$  radiation, using values  $\Delta f'$  and  $\Delta f''$  given by Dauben & Templeton (1955).

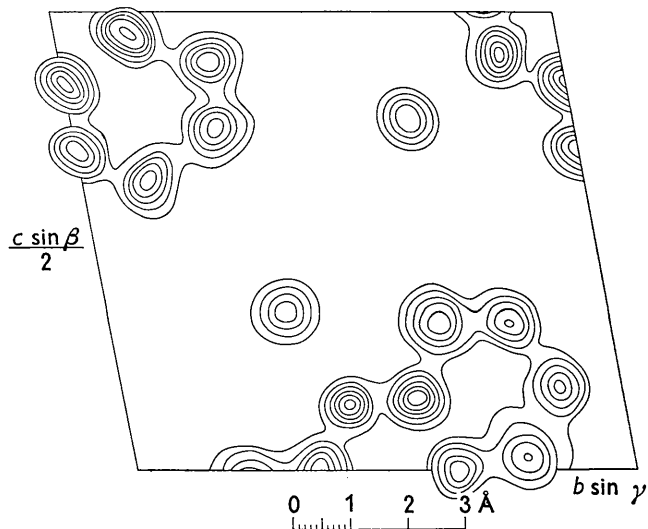


Fig. 1. Electron-density projection down [100]. Contours at intervals of  $1 \text{ e.\AA}^{-2}$ , starting at  $2 \text{ e.\AA}^{-2}$ , except at the bromine atoms where the lowest contour is  $10 \text{ e.\AA}^{-2}$  and the interval  $10 \text{ e.\AA}^{-2}$ .

McWeeny's curve was used for carbon. Both curves were corrected for thermal vibration as usual, taking  $B = 4.8 \text{ \AA}^2$ .

A second Fourier synthesis was then computed, using as coefficients observed structure factors with calculated signs. New atomic centres were chosen, and structure factors recalculated. The value of the temperature parameter  $B$  was retained at  $4.8 \text{ \AA}^2$  for the bromine atoms and for carbons  $A$  and  $G$ , but was taken as  $4.2 \text{ \AA}^2$  for all the other carbon atoms. The value of  $R$  dropped to  $15.9\%$ . Observed and calculated structure factors are listed in Table 4, and a final  $F_o$  synthesis, computed with measured  $F_o$  values and the signs of the calculated structure factors is shown in Fig. 1.

Finally, to correct for series termination errors, an  $(F_o - F_c)$  synthesis was computed, and some of the carbon atoms were shifted by small amounts to minimize the slopes at the atomic centres. The structure factors were not recalculated.

### [010] projection

On the  $h0l$  Patterson projection, the four Br-Br peaks were easily distinguished, bromine coordinates were obtained, and a  $F_o$  synthesis was computed with signs based on the bromine contributions only. There were a few large structure factors whose signs were not determined by the Br atoms, and these were of course omitted from the synthesis. On the resulting map, the bromine atoms were well resolved, but the positions of the carbon skeletons could not be fixed unambiguously. After a few trials a structure was obtained with  $R = 26.6\%$ . The scattering factors used were the same as those for the  $0kl$  reflexions, except

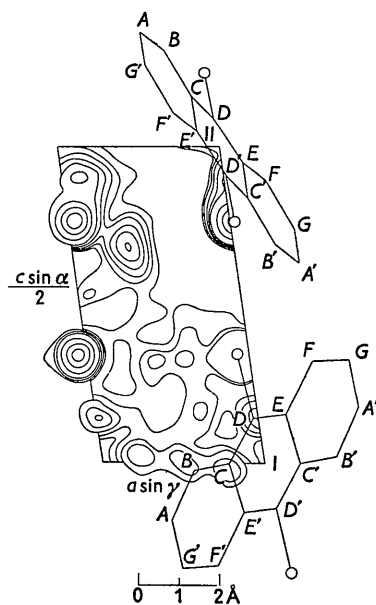


Fig. 2. Electron-density projection down [010]. Contours at intervals of  $2 \text{ e.}\text{\AA}^{-2}$ , except on the bromine atoms where contours above 10 are at intervals of  $10 \text{ e.}\text{\AA}^{-2}$ .

that the anomalous dispersion correction of the Br curve was that for Mo  $K\alpha$  radiation.

A second  $F_o$  synthesis was then computed, and this map revealed that one of the anthracene nuclei had been incorrectly positioned, although some of its atoms were, by chance, close to true atomic positions. Structure factors were recalculated with the new coordinates, and the value of  $R$  (observed reflexions) was  $18.3\%$ . There were no sign changes from the previous structure with one of the molecules in an incorrect position.

An  $(F_o - F_c)$  synthesis was computed and some of the carbon atoms shifted by small amounts. On recalculating structure factors,  $R$  dropped to  $12.6\%$ . Observed and calculated structure factors are listed in Table 4, and the final  $F_o$  synthesis is shown in Fig. 2.

### Coordinates and molecular dimensions

The final coordinates of the atoms are listed in Table 2, expressed as fractions of the unit-cell edges, the labelling of the atoms being shown in Fig. 2.

Table 2. Coordinates of the atoms in the asymmetric unit

Molecule I			
Atom	$x/a$	$y/b$	$z/c$
Br	-0.0671	0.3517	0.1722
A'	0.6305	0.8757	0.0896
B'	0.4508	0.7765	0.0089
C'	0.2242	0.6414	0.0007
D	-0.0270	0.4420	0.0730
E	0.1791	0.5805	0.0786
F	0.3863	0.6570	0.1614
G	0.6050	0.7951	0.1621
Molecule II			
Atom	$x/a$	$y/b$	$z/c$
Br'	0.0268	0.6700	0.3811
A'	0.3850	0.1365	0.3130
B'	0.2567	0.0009	0.3457
C'	0.1283	0.0005	0.4227
D'	0.0155	0.8676	0.4511
E	0.1283	0.1532	0.4743
F	0.2567	0.2922	0.4448
G	0.3850	0.2796	0.3711

The coordinates of the atoms can be fitted to equations of the form

$$lX + mY + nZ + p = 0,$$

where  $X, Y, Z$  are coordinates expressed in  $\text{\AA}$  units and referred to the triclinic crystal axes.

Table 3. Bond lengths in anthracene and 9:10-dibromoanthracene

Bond	Anthracene	9:10-Dibromoanthracene
A-B	1.37 $\text{\AA}$	1.41 $\text{\AA}$
B-C	1.43	1.42
C-D	1.40	1.37
A-G'	1.42	1.46
C-E'	1.44	1.47
Br-D	—	1.93



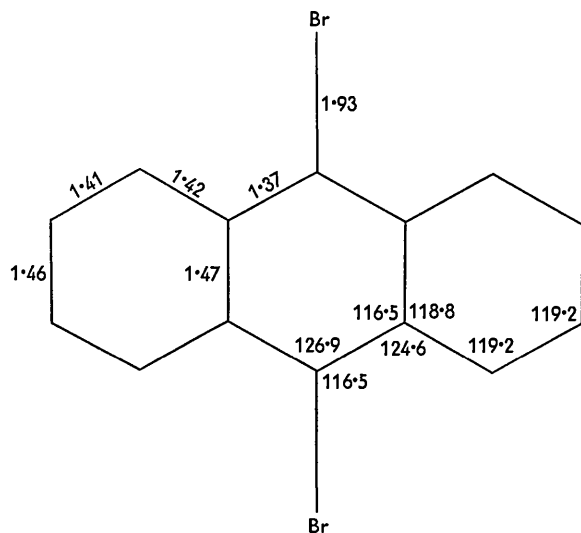


Fig. 3. Bond lengths and valency angles.

carbon atoms, so that the standard deviations of the mean bond lengths are about 0.025 Å for a Br-C bond, and 0.03 Å for a C-C bond.

The molecule is completely planar within the limits of experimental error, the Br-C distance (1.93 Å) corresponds to a single bond, and the C-C bond lengths (Table 3) do not differ significantly from the corresponding bond lengths in anthracene (Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956).

All the intermolecular distances correspond to normal van der Waals interactions. The mean perpendicular distance between the planes of molecules related by translation  $a$  is 3.55 Å. The shorter lateral contacts are illustrated in Fig. 4.

The author wishes to thank Dr W. H. Barnes for his interest in this problem and for much helpful discussion, Mrs M. E. Pippy for assistance with some

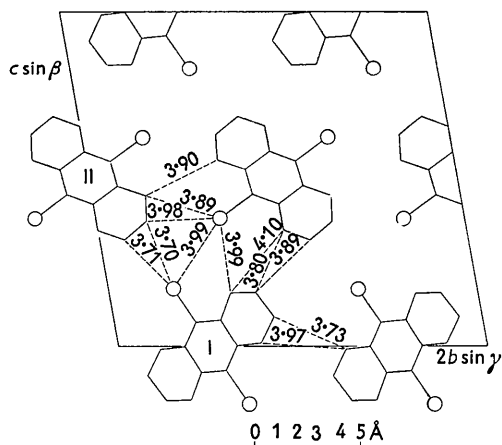


Fig. 4. Projection of the structure down [100], showing the shorter intermolecular contacts.

of the calculations and Dr F. R. Ahmed for computing some of the Fourier series and structure factors.

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