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The Crystal Structure of 10-Bromoanthrone

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Crystals of 10-bromoanthrone are triclinic, space group $P\bar{1}$, with $a=7{\cdot}304$ (1), $b=7{\cdot}768$ (1), $c=11{\cdot}358$ (1) Å, $\alpha=90{\cdot}33$ (1), $\beta=104{\cdot}58$ (1), $\gamma=116{\cdot}83$ (1)°, $Z=2$. Approximately 2300 intensities were collected on a Pailred diffractometer from a crystal mounted along **a**. The structure was derived by direct phasing methods and refined by full-matrix least-squares calculations. Final refinement led to an R of 0·061 and standard deviations in the range 0·003–0·006 Å in the positions of the heavy atoms. The molecule, whose symmetry is very close to m, exhibits a 'butterfly' shape: the planes of the two outer rings make a dihedral angle of 164°. The most salient details of the molecular geometry are the long C(10)–Br distance of 2·032 (4) Å and the boatlike configuration of the central ring, the atoms C(10) and C(9) being displaced by 0·19 and 0·12 Å respectively from the plane of the other four carbon atoms.

Introduction

The molecular conformation of complexes in electrophilic aromatic substitution reactions has been the subject of several recent investigations. Rys, Skrabal & Zollinger (1972) have pointed out the need for accurate determinations of the structures of such intermediates to improve the understanding of the mechanism of heterolytic aromatic substitutions. In line with this interest, the X-ray analysis of 10-bromoanthrone, which corresponds to the σ-complex of the bromination of 9-anthrol, has been carried out.

Experimental

Crystals of 10-bromoanthrone, obtained from Professor Zollinger, were clear, pale-yellow prisms. Weissenberg and oscillation photographs, used for the initial alignment and to verify crystal quality, indicated the crystals were triclinic. Accurate cell dimensions were obtained from a least-squares treatment of 63 measurements on zero-level Weissenberg photographs about **a**, **b** and **c**, taken at 20 (1)°C; the films were held in the asymmetric position, following the Straumanis technique. No corrections for eccentricity or absorption were included in least-squares calculations, and weights were assigned as inversely proportional to $\sin^2 2\theta$. The density was measured by flotation in a mixture of benzene and methylene iodide. Crystallographic data are given in Table 1.

Table 1. *Crystal data*

$C_{14}H_9OBr$	F.W. 273·14
Triclinic	Space group $P\bar{1}$
$a=$ 7·304 (1) Å	$Z=2$
$b=$ 7·768 (1)	$V=551{\cdot}2$ Å^3
$c=$ 11·358 (1)	$F(000)=272$
$\alpha=$ 90·33 (1)°	$D_m=1{\cdot}61$ g cm^{-3}
$\beta=104{\cdot}58$ (1)	$D_x=1{\cdot}645$ g cm^{-3}
$\gamma=116{\cdot}83$ (1)	$\lambda(\mathrm{Cu}\ K\alpha_1)=1{\cdot}54051$ Å
$\mu(\mathrm{Cu}\ K\alpha)=52{\cdot}59$ cm^{-1}	$\lambda(\mathrm{Cu}\ K\alpha_2)=1{\cdot}54433$
$\mu(\mathrm{Mo}\ K\alpha)=38{\cdot}35$ cm^{-1}	$\lambda(\mathrm{Cu}\ K\alpha)=1{\cdot}5418$

Intensities were collected on a Philips equi-inclination linear diffractometer (Pailred) in the automatic mode, with the ω-scan technique. Mo $K\alpha$ radiation [monochromated by a graphite (0001) single crystal], and a scintillation detector with pulse-height analyser were used. The scan range varied from ± 1° to ± 1·5°, the larger values being used in the higher layers for low values of the Υ angle. The scanning rate was 2·5° min^{-1}; background was counted for 24 sec at each end of the scan. Reflexions within the limit of the Cu sphere for the layers 0 to 7 about **a** were collected from a crystal 0·25 × 0·30 × 0·20 mm in size. Five $0kl$ reflexions were monitored before the collection of each layer; a general downward trend in the intensities of these reflexions was observed. At the end of the data collection, all zero-layer reflexions were measured again; the average intensity drop amounted to 12%.

A second set of data was obtained from a crystal 0·20 × 0·20 × 0·20 mm in size, mounted along **b**; the layers 0 to 3, including only reflexions within the limits of the first set, were collected.

Intensity data of the two sets were corrected for background and for the Lorentz and polarization effects. An approximate absorption correction was applied assuming the two crystals to be spherical with $\mu R_{\max}=0{\cdot}7$ and 0·4 respectively. Observational variances $\sigma^2(I)$ included, besides counting statistics for the scan and backgrounds, a term $(0{\cdot}03S)^2$, where S is the scan count.

The intensity variation for the reflexions within a single layer was assumed to be negligible and the two sets were processed together. The evaluation of relative scale factors for each layer was performed according to the method of Rollett & Sparks, modified to account for the dependence of the weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). Intensity data of the first set were then corrected, while those of the second set were disregarded.

Reflexions for which the scaled background counts exceeded the scan counts (227 in number) were given

Table 2. *Observed and calculated structure factors* (× 10)

The reflexions with $F_o=0$ were measured as having net intensities less than zero; they were given zero weight in the least-squares refinement.

K	L	FO	FC
H = 0			
1	0	133	-128
2	0	142	-143
3	0	337	-314
4	0	233	-237
5	0	277	-281
6	0	56	-44
7	0	10	10
8	0	35	44
1	1	345	-329
2	1	459	-455
2	-1	178	166
3	1	387	-362
3	-1	462	458
4	1	171	-178
4	-1	192	194
5	1	119	122
5	-1	45	-57
6	1	274	213
6	-1	90	-78
7	1	178	179
7	-1	115	-129
8	1	32	34
8	-1	103	-108
0	2	448	-439
1	2	141	-144
1	-2	93	71
2	2	25	12
2	-2	1314	-1336
3	2	324	324
3	-2	287	283
[illegible]	[illegible]	[illegible]	[illegible]
1	-12	57	46
2	12	49	-30
2	-12	36	-42
3	12	0	1
3	-12	94	91
4	-12	88	93
5	-12	28	13
0	13	30	-17
1	13	17	-5
1	-13	96	-86
2	13	50	33
2	-13	[illegible]	-16
3	-13	41	-28
4	-13	45	61
0	14	27	14
1	-14	0	21
2	-14	0	-5
H = 1			
1	0	638	-646
2	0	113	108
-2	0	371	-358
3	0	239	257
-3	0	41	-45
4	0	119	129
-4	0	208	233
5	0	150	159
-5	0	397	399
[illegible]	[illegible]	[illegible]	[illegible]

zero intensity and weight. The final set consisted of 2311 independent intensities.

Determination and refinement of the structure

The data were placed on an approximate absolute scale by Wilson's (1942) method. The normalized structure factors, $|E|$ (Hauptman & Karle, 1953), were calculated with an overall temperature factor of 3·6 Å^2.

The process of sign determination for 285 reflexions with $|E| \geq 1{\cdot}5$ was performed by means of a computer program (Long, 1965). The origin was specified by assigning + signs to 203, $\bar{6}11$ and $10\bar{2}$. An E map (Karle, Hauptman, Karle & Wing, 1958) was computed with the set of signs leading to the second highest consistency index (0·99), since the set containing all + signs (consistency index = 1·0) was obviously incorrect. The positions of the bromine, oxygen and carbon atoms were clearly evident in this map, which showed a single spurious peak of comparable height.

Preliminary refinement of atomic parameters was based on the 1310 reflexions with $I \geq 3\sigma_{c.s.}(I)$, where $\sigma_{c.s.}$ refers to counting statistics only. A block-diagonal least-squares process, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, was performed. During the first cycles, weights of the form $w = 1/f^2$ were used, where f is the average scattering factor for all the atoms at the calculated value of $\sin\theta/\lambda$. Five refinement cycles of the coordinates and isotropic temperature factors led to an R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·15.

At this point a difference map clearly indicated the positions of all nine hydrogen atoms, and the model was complete. Weights were then changed to $w = 1/\sigma^2(F)$, where $\sigma^2(F)$ was taken as $\sigma^2(F^2)/4F^2$ (see Experimental section). In the next stage of refinement, anisotropic temperature factors were assigned to the heavier atoms and the hydrogen atoms included only in structure-factor calculations. R dropped to 0·047. A modified version of the *ORFLS* program (Busing, Martin & Levy, 1962) was used to carry out the final full-matrix least-squares refinement for this data set; the coordinates and isotropic temperature factors of the hydrogen atoms were introduced as further variables. After two cycles R was 0·038 for the 1310 reflexions.

A secondary extinction coefficient g (Larson, 1967, equation (3); Zachariasen, 1963) was added to the previous set of parameters, which were then refined through four full-matrix least-squares cycles based on the whole set of data. At the end of this process, no parameter shift was as much as 10% of its standard deviation, and convergence was assumed. A final difference map showed no unusual features. The final R was 0·061; the goodness-of-fit, $[\sum w(|F_o| - |F_c|)^2/(m-s)]^{1/2}$, where $m = 2084$ reflexions of non-zero weight and $s = 182$ parameters, was 1·13. The final value of the secondary extinction parameter g was $1{\cdot}5\ (2) \times 10^{-6}$.

Atomic form factors were from Cromer & Waber (1965), except for H which was from Stewart, Davidson & Simpson (1965). The Br form factor was decreased by 0·21 to take into account the real component of anomalous dispersion (Cromer, 1965). The observed and calculated structure factors are listed in Table 2. The final parameters of the heavier atoms and their standard deviations as calculated from the diagonal elements of the least-squares inverse matrix are given in Table 3, and those of the hydrogen atoms in Table 4.

Table 4. *Final parameters for the hydrogen atoms*

Values of x, y and z are multiplied by 10^3 and those of B by 10. Estimated standard deviations are in parentheses.

	x	y	z	B
H(1)	−39 (5)	316 (4)	12 (3)	50 (8)
H(2)	−42 (6)	164 (5)	−164 (3)	52 (11)
H(3)	205 (5)	86 (5)	−194 (3)	58 (9)
H(4)	495 (5)	181 (5)	−18 (3)	51 (9)
H(5)	949 (5)	568 (5)	390 (3)	56 (8)
H(6)	993 (5)	790 (5)	540 (3)	45 (8)
H(7)	733 (6)	860 (5)	555 (4)	65 (11)
H(8)	412 (5)	705 (4)	409 (3)	36 (8)
H(10)	727 (5)	389 (4)	179 (3)	41 (7)

Table 3. *Heavy atom final parameters and their standard deviations* (*in parentheses*)

All the values have been multiplied by 10^4. The temperature factor is in the form

$$T_i = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\right].$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	693 (6)	2856 (6)	−11 (4)	217 (12)	231 (11)	121 (5)	127 (9)	54 (7)	57 (6)
C(2)	580 (8)	1929 (7)	−1066 (5)	302 (16)	252 (13)	110 (6)	93 (12)	18 (8)	43 (7)
C(3)	2186 (7)	1510 (6)	−1144 (5)	379 (16)	240 (11)	96 (5)	137 (11)	65 (8)	25 (6)
C(4)	3924 (7)	2040 (6)	−135 (4)	301 (14)	221 (11)	112 (6)	144 (10)	77 (7)	43 (6)
C(5)	8289 (6)	5961 (6)	3921 (4)	226 (12)	205 (10)	110 (5)	113 (9)	48 (6)	44 (6)
C(6)	8626 (7)	7316 (7)	4829 (4)	235 (13)	239 (12)	121 (6)	76 (11)	19 (7)	35 (7)
C(7)	7007 (7)	7759 (6)	4888 (5)	383 (17)	181 (11)	99 (5)	96 (11)	66 (8)	20 (6)
C(8)	5083 (8)	6839 (6)	4026 (4)	321 (15)	216 (11)	108 (5)	165 (11)	93 (7)	52 (6)
C(9)	2609 (5)	4522 (5)	2132 (3)	240 (11)	240 (10)	99 (5)	169 (9)	70 (6)	67 (5)
C(10)	5978 (5)	3560 (5)	2037 (3)	181 (10)	188 (9)	104 (4)	119 (8)	66 (6)	52 (5)
C(11)	2460 (5)	3425 (5)	1023 (3)	166 (10)	177 (9)	91 (4)	81 (8)	47 (5)	53 (5)
C(12)	4090 (5)	3003 (5)	952 (3)	172 (9)	158 (8)	86 (4)	88 (7)	47 (5)	45 (5)
C(13)	6333 (5)	5022 (5)	3033 (3)	180 (10)	167 (9)	93 (4)	86 (8)	51 (5)	50 (5)
C(14)	4702 (5)	5460 (5)	3091 (3)	240 (11)	170 (9)	90 (4)	125 (8)	71 (5)	51 (5)
O	1087 (4)	4699 (4)	2254 (3)	293 (8)	481 (10)	139 (4)	286 (8)	72 (4)	42 (5)
Br	5601 (1)	1104 (1)	2799 (1)	313 (1)	214 (1)	125 (1)	182 (1)	40 (1)	48 (1)

Discussion of the structure

(i) *Bond distances and angles*

A diagram of the molecule, showing the bond distances and angles between heavy atoms, is shown in Fig. 1. Estimated standard deviations are in the range 0·005–0·008 Å in the bond distances and 0·3–0·5° in the bond angles. A comparison between chemically equivalent bond distances and angles suggests that these e.s.d.'s are reasonable.

The carbon–bromine distance [2·032 (4) Å] is significantly longer than the average paraffinic carbon–bromine distance [1·938 (5) Å] reported by Sutton (1965). A rather similar value (2·048 Å) was found for one of the two C–Br distances in 10,10′-dibromoanthrone (Silverman & Yannoni, 1963), the other one being 1·978 Å. However, a comparison between our molecule and the latter is perhaps not fully adequate, since that structure, according to the authors, was not completely refined.

Distances and angles in the present determination can be better compared (Tables 5 and 6) with those of 10,10′-dianthronyl (Ehrenberg, 1967) and 10-(dicyanomethylene)anthrone (Silverman & Yannoni, 1967); anthrone itself cannot be considered, owing to its structural disorder (Srivastava, 1964). In general, the bond distances of 10-bromoanthrone (BA) are in good agreement with the values found in 10,10′-dianthronyl (DA). The most significant discrepancies are in the C(3)–C(4) and C(12)–C(10) bond distances, in their chemically equivalent C(5)–C(6) and C(13)–C(10), and in the C(9)–O distance, for which the values found in DA are greater than our values by more than three times the pooled standard deviations. Still larger are the differences between our values and those of 10-(dicyanomethylene)anthrone (DCA) for the C(2)–C(3) and C(3)–C(4) distances; the values of the other bond lengths in DCA differ by less than three times their e.s.d.'s (0·013–0·016 Å) from BA values.

Table 5. *Comparison of bond lengths of* 10-*bromoanthrone with those found in two similar compounds*

DCA has a crystallographic *m* symmetry. E.s.d.'s are in the range 0·004–0·006 Å for DA and 0·013–0·016 Å for DCA.

	BA	DA	DCA
C(1)—C(2)	1·359 (8)Å	1·367Å	1·39Å
C(7)—C(8)	1·355 (8)	1·379	
C(2)—C(3)	1·374 (8)	1·394	1·45
C(6)—C(7)	1·389 (7)	1·384	
C(3)—C(4)	1·373 (7)	1·395	1·46
C(5)—C(6)	1·363 (7)	1·395	
C(4)—C(12)	1·389 (6)	1·387	1·37
C(5)—C(13)	1·384 (6)	1·398	
C(12)–C(11)	1·389 (5)	1·398	1·43
C(13)–C(14)	1·395 (5)	1·401	
C(11)–C(1)	1·399 (6)	1·402	1·41
C(14)–C(8)	1·387 (6)	1·392	
C(11)–C(9)	1·469 (6)	1·476	1·48
C(14)–C(9)	1·484 (6)	1·479	
C(9)—O	1·220 (5)	1·238	1·24
C(12)–C(10)	1·486 (5)	1·506	1·48
C(13)–C(10)	1·485 (5)	1·508	
C(10)–Br	2·032 (4)		

BA = 10-bromoanthrone, this structure
DA = 10,10′-dianthronyl (Ehrenberg, 1967)
DCA = 10-(dicyanomethylene)anthrone (Silverman & Yannoni, 1967)

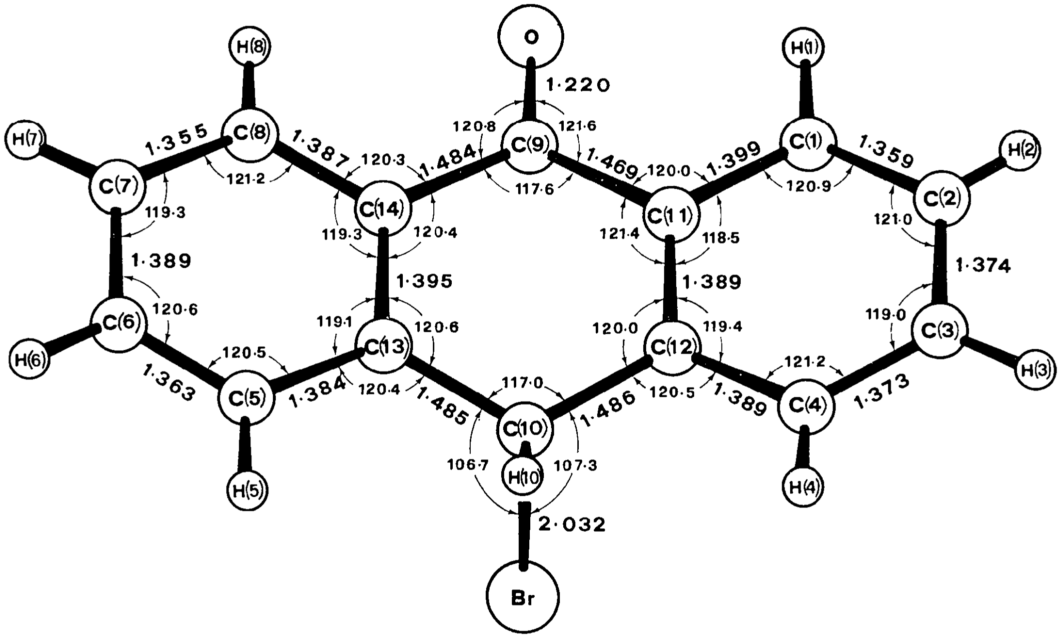

Fig. 1. Bond distances and angles involving the heavy atoms. Standard deviations are in the range 0·005–0·008 Å in the bond distances and 0·3–0·5° in the bond angles.

Table 6. *Bond angles of* 10-*bromoanthrone compared with those found in two similar compounds*

For symbols BA, DA and DCA see Table 5. E.s.d.'s are in the range 0·3–0·4° for DA and 0·6–1·2° for DCA.

	BA	DA	DCA
C(11)–C(1)—C(2)	120·9 (4)°	121·0°	121°
C(14)–C(8)—C(7)	121·2 (5)	121·0	
C(1)—C(2)—C(3)	121·0 (5)	119·5	119
C(8)—C(7)—C(6)	119·3 (5)	119·6	
C(2)—C(3)—C(4)	119·0 (5)	119·7	119
C(7)—C(6)—C(5)	120·6 (5)	120·0	
C(3)—C(4)—C(12)	121·2 (4)	121·1	120
C(6)—C(5)—C(13)	120·5 (4)	120·9	
C(4)—C(12)–C(11)	119·4 (4)	118·5	120
C(5)—C(13)–C(14)	119·1 (4)	118·3	
C(12)–C(11)–C(1)	118·5 (4)	119·9	121
C(13)–C(14)–C(8)	119·3 (4)	120·0	
C(11)–C(9)—C(14)	117·6 (3)	118·7	119
C(12)–C(11)–C(9)	121·4 (3)	120·1	119
C(13)–C(14)–C(9)	120·4 (3)	120·9	
C(10)–C(12)–C(11)	120·0 (3)	121·6	119
C(10)–C(13)–C(14)	120·6 (3)	120·3	
C(12)–C(10)–C(13)	117·0 (3)	115·1	115
C(4)—C(12)–C(10)	120·5 (4)	119·8	121
C(5)—C(13)–C(10)	120·4 (4)	121·3	
C(1)—C(11)–C(9)	120·0 (4)	119·9	120
C(8)—C(14)–C(9)	120·3 (4)	119·0	
C(11)–C(9)—O	121·6 (4)	120·2	121
C(14)–C(9)—O	120·8 (4)	121·1	
Br–––C(10)–C(13)	106·7 (3)		
Br–––C(10)–C(12)	107·3 (3)		

Comparison of the bond angles of the three compounds (Table 6) shows that the most significant differences concern the values of some bond angles of the BA and DA molecules, particularly the central ring angles at C(11), C(12) and C(10), where the discrepancies amount to four to six times the e.s.d.'s.

It is perhaps interesting to notice that in 10-bromoanthrone the central ring angles at C(10) and C(9) are almost coincident in value, 117·0 (3) and 117·6 (3)° respectively, in spite of the different coordination of the two atoms. On the other hand, in tricyclic molecules

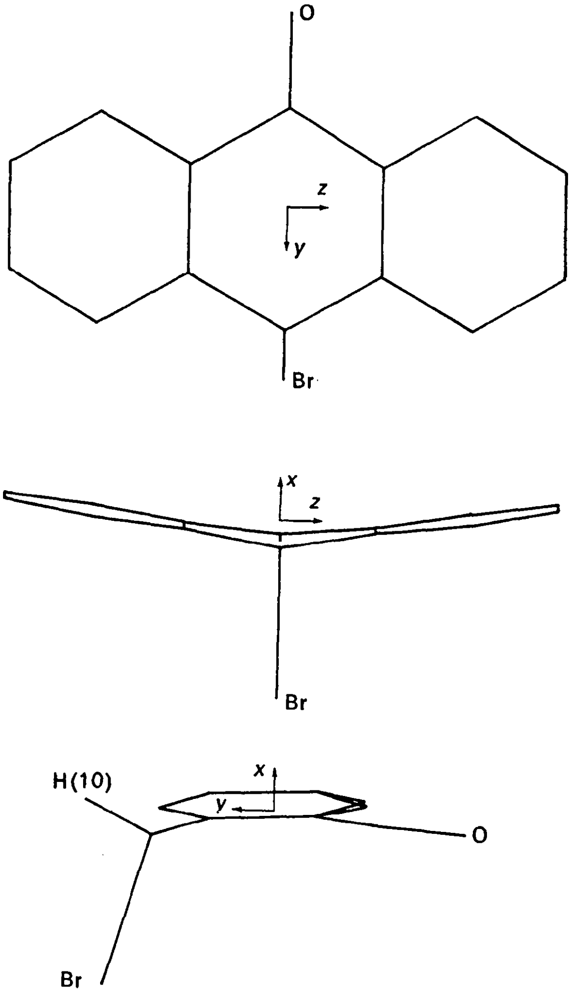

Fig. 2. Three different views of the molecule of 10-bromoanthrone. The directions *XYZ* correspond to the principal moments of inertia of the molecule without the bromine atom.

Table 7. *Deviations* (Å) *from least-squares planes*

The equatons are referred to the triclinic axes and fractional coordinates; the distance is the origin-to-plane distance. Atoms marked with an asterisk were omitted from the least-squares calculations; the remaining atoms were given equal weights. The planes were calculated according to the method of Schomaker, Waser, Marsh & Bergman (1959).

Plane *A*		Plane *B*		Plane *C*		Plane *D*		Plane *E*	
	Δ		Δ		Δ		Δ		Δ
C(11)	−0·004	C(1)	−0·004	C(5)	−0·005	C(9)	−0·002	C(9)	−0·009
C(12)	0·004	C(2)	0·002	C(6)	0·003	C(10)	0·001	C(11)	0·002
C(13)	−0·004	C(3)	0·003	C(7)	0·001	O	0·001	C(14)	0·002
C(14)	0·004	C(4)	−0·004	C(8)	0·001	Br	0·000	O	0·002
*C(9)	−0·122	C(11)	0·002	C(13)	0·004				
*C(10)	−0·189	C(12)	0·001	C(14)	−0·002				
*O	−0·287								

Plane *A*: $1{\cdot}1916x+5{\cdot}5206y-6{\cdot}6829z=1{\cdot}5048$
Plane *B*: $1{\cdot}2768x+5{\cdot}8549y-5{\cdot}3432z=1{\cdot}7711$
Plane *C*: $1{\cdot}1118x+5{\cdot}0570y-7{\cdot}8812z=0{\cdot}8502$
Plane *D*: $0{\cdot}9737x+2{\cdot}5379y+8{\cdot}6625z=3{\cdot}2498$
Plane *E*: $0{\cdot}1426x+6{\cdot}1551y-6{\cdot}2111z=1{\cdot}5057$

Dihedral angles: $A\wedge B$ 171·7° $A\wedge C$ 171·8° $A\wedge D$ 89·8° $A\wedge E$ 171·7°

with two outer benzene rings the internal angles at the central sp^3 carbon atoms are usually greater than the tetrahedral value: in 9,9,10,10-tetrachloro-9,10-dihydroanthracene, for instance, values of 116·7 and 119·1° were found for such angles (Yannoni & Silverman, 1966).

Because of the implications in the study of the mechanism of electrophilic substitution reactions (Rys, Skrabal & Zollinger, 1972) and in relation to the large value of the angle C(13)–C(10)–C(12), it would be interesting to know precisely the value of the angle H(10)–C(10)–Br, and, more particularly, those of the angles made by the bonds H(10)–C(10) and Br–C(10) with the plane defined by the atoms C(10), C(12) and C(13). The values obtained from our X-ray analysis are 101, 45 and 56° respectively, but the accuracy of the first two measurements is obviously low.

(ii) *Molecular conformation*

As shown in Fig. 2, the most evident features of the 10-bromoanthrone molecule, whose symmetry (non-crystallographic) is very close to *m*, are the boatlike middle ring and the butterfly shape, arising from two planes intersecting at the common atoms C(9) and C(10). In Table 7 some least-squares planes of interest are reported.

The boatlike conformation of the central ring is also present in DA and DCA molecules. The four atoms C(11), C(12), C(13) and C(14) are coplanar within 0·018 Å in DA and exactly coplanar in DCA; the displacements of C(10), C(9) and O from that plane are 0·228, 0·071 and 0·146 Å respectively in DA and 0·36, 0·16 and 0·38 Å respectively in DCA.

In all three cases the displacement of C(10) from the plane helps to lengthen the contacts between the substituent group at C(10) and the atoms C(4) and C(5); in 10-bromoanthrone the intramolecular distances Br–C(4) and Br–C(5) are 3·451 and 3·423 Å respectively.

The other feature, which is common to all three of these compounds, is the butterfly shape of the anthracene skeleton, another possible way of relieving the crowding mentioned. The two outer benzene rings of BA are planar within experimental uncertainty (maximum deviation 0·005 Å); their planes, *B* and *C* in Table 7, both make a dihedral angle of about 172° with the central ring plane. In DCA the plane of the outer benzene ring is folded out of the central ring plane by 14°; in DA smaller values were found, the two benzene rings being folded by about 4 and 6° respectively.

(iii) *Molecular packing and thermal librations*

Assuming as intermolecular radii for bromine, carbon and oxygen the values of 1·95, 1·8 and 1·4 Å respectively (Kitaigorodskii, 1961), the intermolecular distances less than or corresponding to the van der

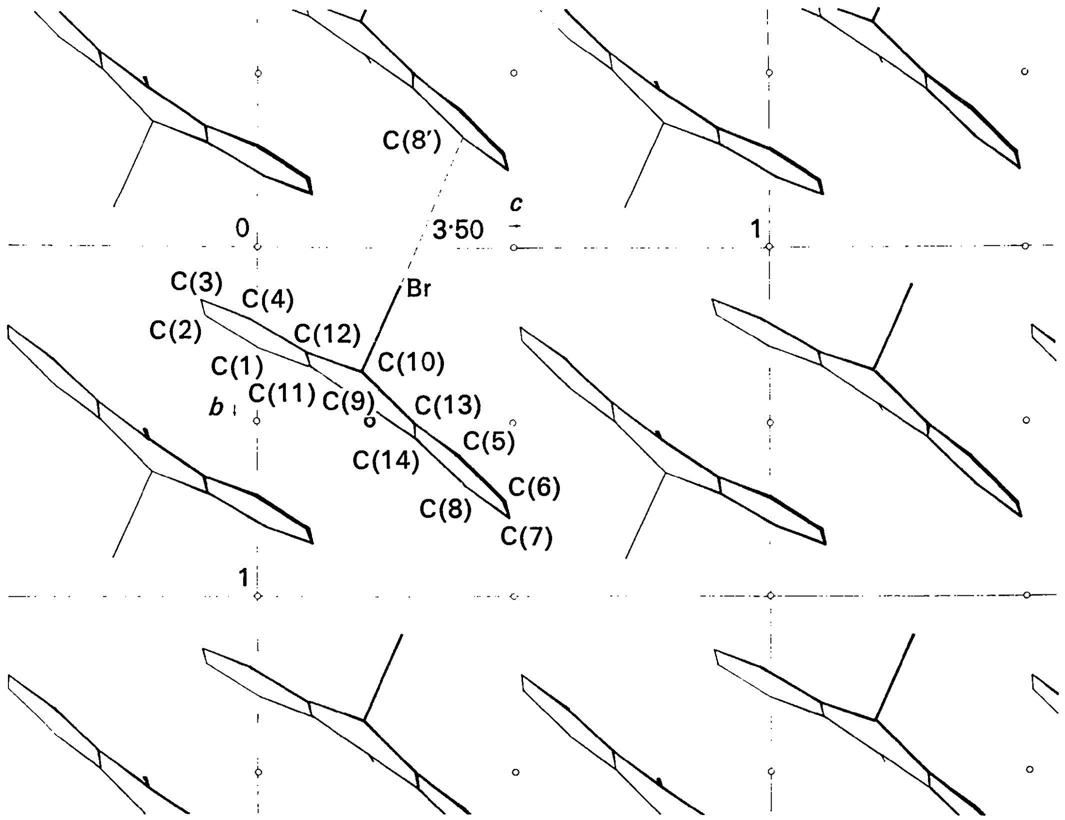

Fig. 3. Molecular packing seen along **a**.

Waals distance are reported in Table 8. It should be noticed (see Fig. 3) that the atom C(8) involved in the very short contact of 3·50 Å [Br···C(8)] lies on the straight line passing through the Br and C(10) atoms. The anomalous length of the C(10)–Br bond cannot therefore be ascribed to intermolecular effects.

Table 8. *Intermolecular contact distances* (Å)

C(1)–C(3)	$-x$,	$-y$,	$-z$	3·56
C(3)–C(13)	$1-x$,	$1-y$,	$-z$	3·41
C(7)–C(8)	$1-x$,	$1-y$,	$1-z$	3·56
C(7)–C(14)	$1-x$,	$1-y$,	$1-z$	3·43
Br—C(8)	x,	$-1+y$,	z	3·50

For each pair of atoms, the coordinates of the second atom are transformed as shown.

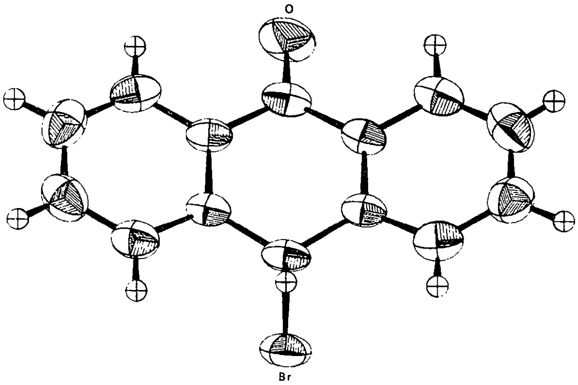

Fig. 4. Perspective view of the molecule. The thermal ellipsoids are drawn at 50% probability level (Johnson, 1965).

The precise positions of the hydrogen atoms should be particularly interesting for packing considerations; from their coordinates (Table 4) it is found that the shortest values for C–H, O–H, Br–H and H–H intermolecular distances are 3·1, 2·5, 3·1 and 2·7 Å respectively.

The anisotropic temperature factors of the heavy atoms (see Fig. 4) were examined with the rigid-body treatment of Schomaker & Trueblood (1968); a program written for this purpose by Filippini & Gramaccioli (1969) was employed. When all 16 atoms were included, the fit to a rigid-body model was unsatisfactory. Deletion of the bromine and oxygen atoms led to a considerably improved but not entirely satisfactory fit; although the quantity $[\sum(\Delta U_{ij})^2/n-s]^{1/2}$ had the relatively low value of 0·004, four of the individual values of ΔU_{ij} were greater than three times their standard deviations. The lengths of principal axes of the L tensor were 15, 12 and 6 $(°)^2$, and implied corrections to the interatomic distances were in the range 0·004–0·006 Å. We have ignored these corrections.

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