

Table 6. *Internal rotation angles*

Internal rotation angle $A-B-C-D$, is defined as the angle between the projections of $A-B$ and $C-D$, when the projection is taken along the $B-C$ bond. The positive angle is taken in the same sense as that of the turning direction of a right handed screw advancing along the $B-C$ bond. To make the definition concordant with that defined by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966), the angle is taken as 0° in the case of exact *trans* conformation.

	Molecule I	Molecule II
Cl-C α -C'-N (ψ)	178.7°	165.8°
Cl-C α -C'-O	0.3	12.4
C α -C'-N-C	1.8	3.0
O-C'-N-C	180.1	181.1

The projection of the crystal structure along the a axis is shown in Fig. 1, in which the intermolecular contacts less than 3.8 \AA are indicated. It is seen that two kinds of molecules I and II form different layers I and II, respectively, and they stack together along the b axis. The orientations and the packings of the molecules in the layers I and II are almost identical as shown in Fig. 2. Within each layer, the molecules are bound together in the c direction through N-H...O hydrogen bonds which must stabilize the close contacts between the chlorine atom and the α -carbon atom of the neighbouring in the same layer.

There are three kinds of interlayer interactions as shown in Fig. 3. The following Cl...C distances are distinctly short and may be responsible for the difference in the conformations of the two kinds of molecules.

- Cl (layer I) to C' (layer I, related by a centre of symmetry), 3.62 \AA ,
- Cl (layer I) to C α (layer II), 3.62 \AA ,
- Cl (layer II) to C' (layer II, related by a glide plane), 3.61 \AA .

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The Crystal Structure of Anthanthrone

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The crystal structure of anthanthrone ($C_{22}H_{10}O_2$) has been solved by molecular transform methods using room temperature photographic data, and refined to a residual of 13.7% with the standard deviations of the atomic coordinates about 0.03 \AA . The space group is $P2_1/c$ with $a = 20.9$, $b = 3.86$, $c = 33.2 \text{ \AA}$, $\beta = 92^\circ$, and $Z = 8$. The three independent molecules are planar and are arranged in stacks with different superpositions and interplanar spacings of 3.46 , 3.54 , 3.50 \AA . Some recurring structural features are discussed.

The crystal structure of anthanthrone

Anthanthrone $C_{22}H_{10}O_2$ (Kalb, 1914) and similar compounds have been used as models in the study of the carbonization of coal. Knowledge of the crystal structure of these compounds is essential to a more com-

plete understanding of the mechanism of carbonization and the structure of a number of aromatic quinones have been determined in this laboratory.

We are indebted to I.C.I. Dyestuffs Division for a sample of the material. This was further purified and recrystallized by sublimation under partial vacuum, in

As will be understood from Fig. 1, the chlorine atom of molecule II would be located too close to the C' atom of molecule II in the neighbouring layer if molecule II took a planar conformation of $\psi = 180^\circ$.

It is to be noted that the molecules take the *cis* conformation in spite of the strong intramolecular steric hindrance between the chlorine and nitrogen atoms. This fact suggests that the internal rotation potential inherent to the C α -C' axis has one of the minima at $\psi = 180^\circ$ and takes an important role in stabilizing the *cis* conformation.

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a stream of dry nitrogen at about 350°C. Only small crystals were obtained; the one chosen for intensity work measured $4 \times 0.05 \times 0.08$ mm and was only suitable for photographs about the needle axis.

As the crystal was small, even very long exposure times with unfiltered Cu *K* radiation only allowed observations of reflexions up to 1.5 r.l.u.

The crystals were found to be monoclinic with

$$\begin{aligned} a &= 20.9 (\pm 0.1) \text{ \AA} \\ b &= 3.86 (\pm 0.02), \beta = 92 (\pm 0.5)^\circ \\ c &= 33.2 (\pm 0.1) \end{aligned}$$

$$\rho(\text{obs}) = 1.52 \text{ g.cm}^{-3} \quad Z = 8 \quad \rho(\text{calc}) = 1.518 \text{ g.cm}^{-3}.$$

Zero to third layer equi-inclination Weissenberg photographs were taken using a multiple film technique, and the intensities estimated by visual comparison with a prepared chart. The layers were correlated by scaling the observed to the calculated structure factors.

Systematic absences for $h0l$ with l odd indicated space groups $P2/c$ or $P2_1/c$. The possible space groups project into plane groups $p2$ down the short b axis and this projection was investigated first. It should be reasonably well resolved since comparison of the b dimension with the benzene ring 'thickness' of 3.42 Å indicates a tilt of only 27° out of the plane with no possibility of overlap.

Molecular Fourier transform methods which had proved successful in solving crystal structures of related compounds (Stadler, 1953), were applied. Two sets of benzene transform peaks of equivalent height, about 30° apart, could be distinguished in the weighted reci-

procal lattice. This implied that the four molecules in the projected unit cell would have two independent orientations but the near sixfold symmetry of the molecular transform afforded little indication of the molecular orientations, as opposed to the benzene ring orientation, which dominates the transform.

The $h0l$ reflexions were weak for h odd. This pronounced pseudohalving of the a axis could be caused by having the molecules either at $\pm a/4$ from the twofold axis in $p2$ to give them a separation of $a/2$; or on the twofold axes, $a/2$ apart, in similar orientations. Packing considerations showed that both these possibilities were, in fact, utilized: of the four molecules in the projected unit cell, two were on twofold axes $a/2$ apart, and two more approximately at $\pm a/4$ from the other twofold axes. It remained to determine which set belonged to each set of transform peaks, and to choose molecular orientations which gave no overlap. This eliminated all but eight of the large number of pseudo-homometric sets and these eight were tested by refinement using the *SFLS* program, written by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), for the Pegasus computer. Only one gave good agreement between observed and calculated structure factors and this was refined to a residual of 19% (Fig. 1.)

To extend the projection into a three-dimensional structure, exact angles and axes of tilt of the molecules had to be determined as well as their y levels. Two independent methods for estimating axes and angles of tilt – the foreshortening of the benzene rings in projection, and the position of the 'origin peak' on the upper layers of the weighted reciprocal lattice (Stadler, Bolton & Maitland, 1964) – gave good agreement.

With this knowledge of tilts it was then possible to construct the transform superposition for an upper layer as shown in Fig. 2. The pattern of the principal benzene peaks in the $h1l$ layer of the reciprocal lattice was constructed on this basis taking all the molecules into account (Fig. 3). Each A peak is composite, corresponding to the centrosymmetrically related pairs of molecules.

The vector separations of the molecular centres could be ascertained from a study of overlap regions of the benzene transform peaks, by a method similar to that described for origin peaks in the paper last referred to. The fringe function in the overlap region BC in Fig. 4 indicates a separation of $\frac{1}{2}$, 0, $\frac{1}{2}$ and this fixes the tilt and the molecular centre of C_1 relative to B_2 . Similarly, the overlap of origin peaks AC indicates the vector separation and relative tilts of these molecules. These relationships were confirmed for the overlap regions on $h1l$ and other layers. The y coordinates of the molecular centres were partially space-group dependent, so, by applying the above relationships, the number of possible solutions reduced to two, one belonging to $P2/c$ and the other to $P2_1/c$. Trial calculations confirmed the previous choice of space group $P2_1/c$.

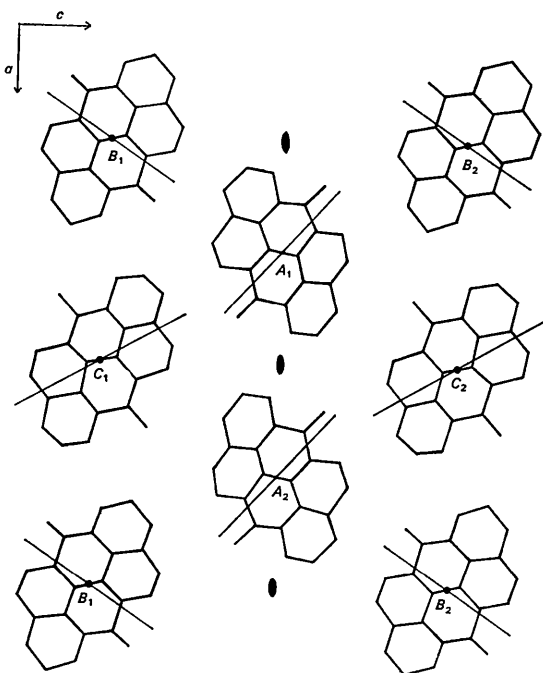


Fig. 1. ($h0l$) projection of anthanthrone. Molecules in the half-cell are shown with axes of tilt derived from the foreshortening. A , B , and C are the three unrelated molecules.

Because of the large number of parameters and the uncertainty of the layer scale factors, least-squares refinement tended to shift atomic positions away from reasonable values and a program was therefore written (Edwards, 1968) to refine the molecular positions treating the molecule as a rigid unit. This produced rapid convergence and a basis for conventional atomic refinement.

Individual atomic refinement using the Glasgow *SFLS* program, with anisotropic temperature factors and including the hydrogen atoms at 'theoretical' positions (with C-H=1.0 Å) produced good agreement, with a final residual for all observed reflexions of 13.7%. The weighting scheme used was

$$w = (1 - \exp(-p_1 S^2)) / (1 + p_2 F + p_3 F^2 + p_4 F^3),$$

with the parameters (p) chosen to equalize the average values of $w\Delta F^2$ for ranges of $\sin \theta$ and $|F|$.

The unobserved reflexions were calculated, and all were found to have structure factors below the minimum observed. The structure viewed along the b axis is shown in Fig. 5, and the final parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2. Details of the molecular planes and the superposition of the molecules along their normals are given in Table 3.

Table 1. Final atomic parameters with standard deviations in brackets

The numbering corresponds to Fig. 5.

	x	y	z
O(1)	0.1492 (8)	-0.0989 (57)	0.0664 (5)
C(1)	-0.1871 (14)	0.4546 (73)	0.0496 (9)
C(2)	-0.1752 (13)	0.3431 (70)	0.0099 (9)
C(3)	-0.1167 (10)	0.2115 (62)	0.0012 (7)
C(4)	-0.1411 (13)	0.4388 (74)	0.0776 (8)
C(5)	-0.0779 (11)	0.3059 (63)	0.0690 (7)
C(6)	-0.0663 (11)	0.1874 (61)	0.0296 (7)
C(7)	-0.0048 (11)	0.0603 (60)	0.0193 (6)
C(8)	-0.0245 (13)	0.2889 (77)	0.0972 (8)
C(9)	0.0307 (13)	0.1677 (69)	0.0897 (8)
C(10)	0.0421 (10)	0.0536 (60)	0.0495 (7)
C(11)	0.1052 (12)	-0.0831 (69)	0.0388 (7)
O(2)	0.6353 (9)	0.9059 (58)	0.0609 (6)
C(12)	0.3047 (11)	0.2810 (69)	0.0570 (8)
C(13)	0.3218 (13)	0.2108 (81)	0.0170 (9)
C(14)	0.3834 (11)	0.3100 (71)	0.0045 (7)
C(15)	0.3455 (12)	0.4379 (71)	0.0840 (8)
C(16)	0.4090 (11)	0.5174 (67)	0.0720 (7)
C(17)	0.4266 (11)	0.4634 (70)	0.0321 (7)
C(18)	0.4917 (11)	0.5325 (68)	0.0207 (7)
C(19)	0.4541 (13)	0.6774 (81)	0.0987 (8)
C(20)	0.5136 (12)	0.7584 (77)	0.0881 (8)
C(21)	0.5329 (11)	0.6751 (72)	0.0476 (7)
C(22)	0.5985 (12)	0.7746 (78)	0.0359 (8)
O(3)	0.1003 (8)	0.1768 (51)	0.3151 (5)
O(4)	0.4039 (8)	0.3175 (58)	0.1981 (5)
C(23)	0.4356 (14)	0.7370 (80)	0.3131 (9)
C(24)	0.4287 (11)	0.6122 (74)	0.2753 (8)
C(25)	0.3698 (11)	0.4614 (77)	0.2621 (8)
C(26)	0.3844 (12)	0.7433 (67)	0.3403 (7)
C(27)	0.3234 (12)	0.5962 (69)	0.3271 (7)
C(28)	0.3160 (11)	0.4539 (64)	0.2887 (6)
C(29)	0.2554 (11)	0.3239 (65)	0.2757 (7)
C(30)	0.2714 (13)	0.6004 (79)	0.3535 (8)

Table 1 (cont.)

	x	y	z
C(31)	0.2149 (12)	0.4657 (72)	0.3389 (7)
C(32)	0.2053 (11)	0.3182 (65)	0.3012 (7)
C(33)	0.1444 (12)	0.1816 (75)	0.2891 (7)
C(34)	0.0673 (14)	-0.2292 (75)	0.1988 (8)
C(35)	0.0756 (11)	-0.0972 (71)	0.2376 (8)
C(36)	0.1333 (11)	0.0327 (70)	0.2494 (6)
C(37)	0.1191 (12)	-0.2383 (77)	0.1724 (8)
C(38)	0.1790 (12)	-0.0956 (70)	0.1844 (7)
C(39)	0.1858 (11)	0.0406 (66)	0.2228 (7)
C(40)	0.2464 (10)	0.1708 (65)	0.2356 (6)
C(41)	0.2312 (12)	-0.0949 (77)	0.1581 (7)
C(42)	0.2887 (11)	0.0270 (72)	0.1712 (7)
C(43)	0.2981 (11)	0.1594 (72)	0.2095 (7)
C(44)	0.3601 (13)	0.3164 (87)	0.2228 (7)

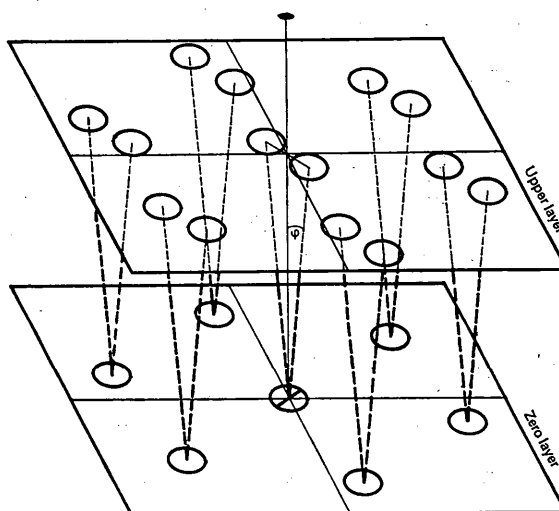


Fig. 2. Construction of transform peaks in an upper layer for one pair of molecules related by a twofold axis. The molecules tilt by an angle ϕ about a line (axis of tilt) indicated on the origin peak.

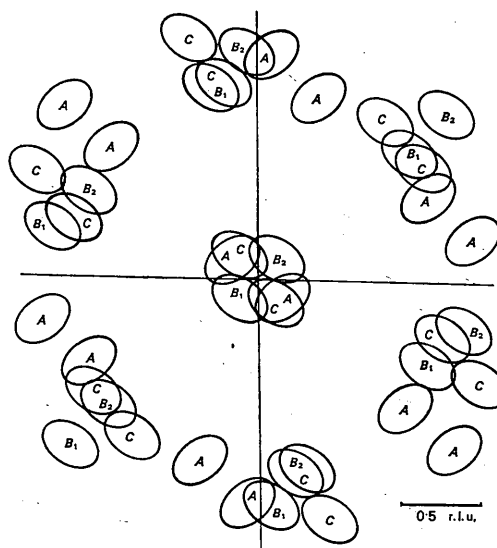


Fig. 3. Pattern of principal benzene peaks for the $(h1l)$ layer. The peaks are labeled as in Fig. 1. The choice of the direction of tilt of molecule B_1 corresponds to arbitrarily choosing the origin.

Discussion

The bond lengths of corresponding bonds are not significantly different. The variations in bond lengths within

the molecule are however significant, and theoretical calculations taking only the Kekulé and first excited structures into account have shown good agreement with the observed values. The bond angles are not sig-

Table 2. Observed and calculated structure factors

Values for the unobserved reflexions are primed.

h	k	l	Observed	Calculated	Observed	Calculated	Observed	Calculated
0	0	0	100	100	0	0	0	0
0	0	1	100	100	0	0	0	0
0	1	0	100	100	0	0	0	0
0	1	1	100	100	0	0	0	0
1	0	0	100	100	0	0	0	0
1	0	1	100	100	0	0	0	0
1	1	0	100	100	0	0	0	0
1	1	1	100	100	0	0	0	0
2	0	0	100	100	0	0	0	0
2	0	1	100	100	0	0	0	0
2	1	0	100	100	0	0	0	0
2	1	1	100	100	0	0	0	0
3	0	0	100	100	0	0	0	0
3	0	1	100	100	0	0	0	0
3	1	0	100	100	0	0	0	0
3	1	1	100	100	0	0	0	0
4	0	0	100	100	0	0	0	0
4	0	1	100	100	0	0	0	0
4	1	0	100	100	0	0	0	0
4	1	1	100	100	0	0	0	0
5	0	0	100	100	0	0	0	0
5	0	1	100	100	0	0	0	0
5	1	0	100	100	0	0	0	0
5	1	1	100	100	0	0	0	0
6	0	0	100	100	0	0	0	0
6	0	1	100	100	0	0	0	0
6	1	0	100	100	0	0	0	0
6	1	1	100	100	0	0	0	0
7	0	0	100	100	0	0	0	0
7	0	1	100	100	0	0	0	0
7	1	0	100	100	0	0	0	0
7	1	1	100	100	0	0	0	0
8	0	0	100	100	0	0	0	0
8	0	1	100	100	0	0	0	0
8	1	0	100	100	0	0	0	0
8	1	1	100	100	0	0	0	0
9	0	0	100	100	0	0	0	0
9	0	1	100	100	0	0	0	0
9	1	0	100	100	0	0	0	0
9	1	1	100	100	0	0	0	0
10	0	0	100	100	0	0	0	0
10	0	1	100	100	0	0	0	0
10	1	0	100	100	0	0	0	0
10	1	1	100	100	0	0	0	0
11	0	0	100	100	0	0	0	0
11	0	1	100	100	0	0	0	0
11	1	0	100	100	0	0	0	0
11	1	1	100	100	0	0	0	0
12	0	0	100	100	0	0	0	0
12	0	1	100	100	0	0	0	0
12	1	0	100	100	0	0	0	0
12	1	1	100	100	0	0	0	0
13	0	0	100	100	0	0	0	0
13	0	1	100	100	0	0	0	0
13	1	0	100	100	0	0	0	0
13	1	1	100	100	0	0	0	0
14	0	0	100	100	0	0	0	0
14	0	1	100	100	0	0	0	0
14	1	0	100	100	0	0	0	0
14	1	1	100	100	0	0	0	0
15	0	0	100	100	0	0	0	0
15	0	1	100	100	0	0	0	0
15	1	0	100	100	0	0	0	0
15	1	1	100	100	0	0	0	0
16	0	0	100	100	0	0	0	0
16	0	1	100	100	0	0	0	0
16	1	0	100	100	0	0	0	0
16	1	1	100	100	0	0	0	0
17	0	0	100	100	0	0	0	0
17	0	1	100	100	0	0	0	0
17	1	0	100	100	0	0	0	0
17	1	1	100	100	0	0	0	0
18	0	0	100	100	0	0	0	0
18	0	1	100	100	0	0	0	0
18	1	0	100	100	0	0	0	0
18	1	1	100	100	0	0	0	0
19	0	0	100	100	0	0	0	0
19	0	1	100	100	0	0	0	0
19	1	0	100	100	0	0	0	0
19	1	1	100	100	0	0	0	0
20	0	0	100	100	0	0	0	0
20	0	1	100	100	0	0	0	0
20	1	0	100	100	0	0	0	0
20	1	1	100	100	0	0	0	0
21	0	0	100	100	0	0	0	0
21	0	1	100	100	0	0	0	0
21	1	0	100	100	0	0	0	0
21	1	1	100	100	0	0	0	0
22	0	0	100	100	0	0	0	0
22	0	1	100	100	0	0	0	0
22	1	0	100	100	0	0	0	0
22	1	1	100	100	0	0	0	0
23	0	0	100	100	0	0	0	0
23	0	1	100	100	0	0	0	0
23	1	0	100	100	0	0	0	0
23	1	1	100	100	0	0	0	0
24	0	0	100	100	0	0	0	0
24	0	1	100	100	0	0	0	0
24	1	0	100	100	0	0	0	0
24	1	1	100	100	0	0	0	0
25	0	0	100	100	0	0	0	0
25	0	1	100	100	0	0	0	0
25	1	0	100	100	0	0	0	0
25	1	1	100	100	0	0	0	0
26	0	0	100	100	0	0	0	0
26	0	1	100	100	0	0	0	0
26	1	0	100	100	0	0	0	0
26	1	1	100	100	0	0	0	0
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27	0	1	100	100	0	0	0	0
27	1	0	100	100	0	0	0	0
27	1	1	100	100	0	0	0	0
28	0	0	100	100	0	0	0	0
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28	1	0	100	100	0	0	0	0
28	1	1	100	100	0	0	0	0
29	0	0	100	100	0	0	0	0
29	0	1	100	100	0	0	0	0
29	1	0	100	100	0	0	0	0
29	1	1	100	100	0	0	0	0
30	0	0	100	100	0	0	0	0
30	0	1	100	100	0	0	0	0
30	1	0	100	100	0	0	0	0
30	1	1	100	100	0	0	0	0
31	0	0	100	100	0	0	0	0
31	0	1	100	100	0	0	0	0
31	1	0	100	100	0	0	0	0
31	1	1	100	100	0	0	0	0
32	0	0	100	100	0	0	0	0
32	0	1	100	100	0	0	0	0
32	1	0	100	100	0	0	0	0
32	1	1	100	100	0	0	0	0
33	0	0	100	100	0	0	0	0
33	0	1	100	100	0	0	0	0
33	1	0	100	100	0	0	0	0
33	1	1	100	100	0	0	0	0
34	0	0	100	100	0	0	0	0
34	0	1	100	100	0	0	0	0
34	1	0	100	100	0	0	0	0
34	1	1	100	100	0	0	0	0
35	0	0	100	100	0	0	0	0
35	0	1	100	100	0	0	0	0
35	1	0	100	100	0	0	0	0
35	1	1	100	100	0	0	0	0
36	0	0	100	100	0	0	0	0
36	0	1	100	100	0	0	0	0
36	1	0	100	100	0	0	0	0
36	1	1	100	100	0	0	0	0
37	0	0	100	100	0	0	0	0
37	0	1	100	100	0	0	0	0
37	1	0	100	100	0	0	0	0
37	1	1	100	100	0	0	0	0
38	0	0	100	100	0	0	0	0
38	0	1	100	100	0	0	0	0
38	1	0	100	100	0	0	0	0
38	1	1	100	100	0	0	0	0
39	0	0	100	100	0	0	0	0
39	0	1	100	100	0	0	0	0
39	1	0	100	100	0	0	0	0
39	1	1	10					

Table 2 (cont.)

Table 2 (cont.) contains a large number of rows of data, each representing a different crystallographic plane. Each row consists of a series of characters (likely '0' and '1') arranged in a grid-like pattern, representing the presence or absence of atoms at specific lattice points. The rows are organized into several groups, with some groups starting with a small number (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100) indicating the plane number. The data is presented in a dense, repetitive format typical of crystallographic tables.

Table 3. Molecular planes

The equation of the plane is $m_1u^* + m_2v + m_3w = p$, with u^* , v and w in Å - coordinates along the orthogonal axes a^* , b , c . The shifts are the displacement of the molecules at right angles to the axis of tilt (as seen along the normals to the molecules).

Molecule	m_1	m_2	m_3	p	Angle of tilt	Inter-planar spacing	Shift
A_1	-0.284	0.897	-0.337	-3.43	26.2	3.46	1.69
B_1	0.291	0.919	-0.266	0.00	23.2	3.54	1.51
C_1	-0.371	0.908	-0.275	-1.46	24.8	3.50	1.60

nificantly different from 120° . The intermolecular distances are similar to those observed in other structures (Table 4) and the number of intermolecular contacts below 3.8 \AA is comparable with those found in structures with larger molecules.

The three independent molecules are all planar to within 0.02 \AA . For such planar molecules the structure factors are very sensitive to molecular orientation. The angles of tilt of the molecules are therefore known with considerable accuracy and so are the interplanar spacings which are directly derived from them (Table 3). It is of particular interest therefore to compare the space group independent molecules, *A* and *B*, which tilt about the same molecular axis (*i.e.* parallel to the C=O bond as shown in Fig. 5), but tilt by different amounts and therefore have different interplanar separations and exhibit different superpositions when viewed along their normals. Of these, the one with the bonds more nearly eclipsed (*A*) unexpectedly shows the lower interplanar spacing. This would indicate a 'smooth' interactive potential between molecules in a

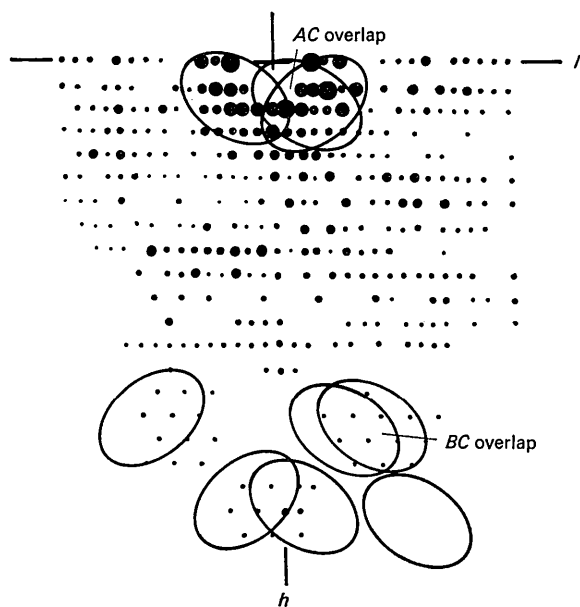


Fig. 4. Overlap regions on the $(h1l)$ layer of the w.r.l. used in determining y levels and tilt directions of molecules *A* and *C* relative to *B* (*cf.* Fig. 3).

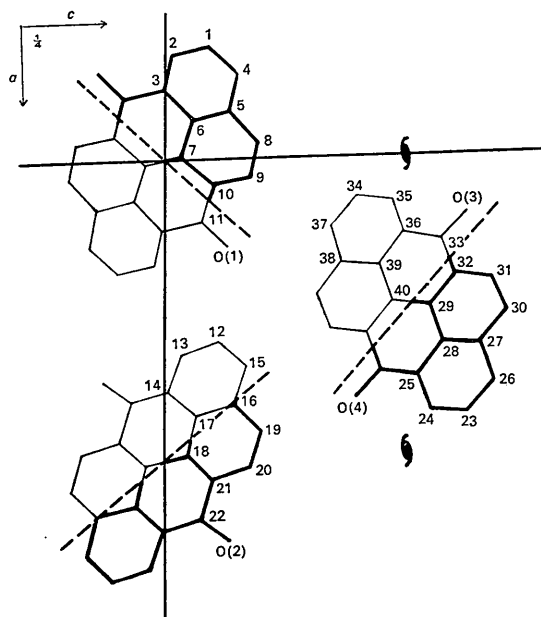


Fig. 5. Final structure viewed along the b axis. The portions in heavy outline are tilted upwards. The molecular centres are B_1 $(0, 0, 0)$, C_1 $(0.5, 0.5, 0)$ and A_1 $(0.252, 0.249, 0.256)$.

stack, with the arrangement mainly determined by lateral forces between stacks.

The *C* molecules tilt about an axis almost perpendicular to the C=O bond thus giving an entirely different superposition – as had previously been observed in pyranthrone (Stadler, 1964). Another feature in common with that structure is that both contain molecules in different orientations tilted about almost parallel axes of tilt (in this case *A* and *C*). On the other hand, anthanthrone also contains molecules (*B* and *C*) which are practically parallel in projection – and give rise to pronounced pseudohalving in the relevant zone – but with large angles between their axes of tilt, a feature previously observed in dibenzanthrone (Bolton & Stadler, 1964) and isodibenzanthrone (Bolton, 1964). In none of these dye structures previously reported have there been more than two symmetry unrelated molecules,⁷ and the overall packing is therefore correspondingly more complex in anthanthrone than has been observed hitherto.

Table 4. Shortest intermolecular distances for anthanthrone and related compounds

	Short axis	C---C	C---O	Interplanar	Reference
Anthanthrone	3.86 \AA	3.54 \AA	3.38 \AA	(3.46 \AA) (3.54) (3.50)	Edwards (1968)
Dibenzanthrone	3.83	3.56	3.31	(3.44) (3.45)	Bolton & Stadler (1964)
Isodibenzanthrone	3.83	3.76	3.57	3.42	Bolton (1964)
Flavanthrone	3.80	3.55	3.28	3.44	Stadler (1953)
Pyranthrone	3.84	3.60	3.23	(3.44) (3.46)	Stadler (1964)
Indanthrone	3.83	3.83	3.34	3.44	Bailey (1955)

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The Crystal Structure of 1,3-Bis-(8-theophylline)propane

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The crystal structure of 1,3-bis-(8-theophylline)propane (BTP, $C_{17}H_{20}N_8O_4 \cdot H_2O$) has been determined by direct methods. BTP possesses anti-tumor activity. It crystallizes in orthorhombic space group *Pcca*; $a=13.28(2)$, $b=10.60(1)$, $c=13.49(1)$ Å, $Z=4$, $D_x=1.44$ g.cm $^{-3}$ and $D_m=1.43$ g.cm $^{-3}$. The integrated intensities of 1920 independent reflections were measured on a diffractometer with Cu $K\alpha$ radiation. The bifunctional molecule crystallizes in a folded conformation. The propane moiety is disordered in the crystal in such a manner as to provide a statistical twofold axis of molecular symmetry utilized by the space group. While the theophylline moieties of BTP depart significantly from planarity all bond lengths and angles, with the exception of bonds C(5)–N(7) and N(7)–C(8), are within 2.5σ of those found in theophylline itself. The water molecule occupies a position on a twofold axis and participates in a hydrogen bonding system which cross links columns of stacked BTP molecules. The hydrogen bonding network accounts for the high melting point, slight solubility and cleavage characteristics of BTP. Trial coordinates were refined by block-diagonal least-square techniques. The final *R* value was 0.059.

Introduction

Theophylline possesses no known anti-tumor activity. Of a series of bifunctional theophylline compounds connected at the C(8) position by methylene bridges of different lengths, only the 1,3-bis-(8-theophylline)propane (BTP) has been found to possess such activity (Beech, 1963).

The distinctive activity spectrum of the bis-theophylline series (Fig. 1), indicative of the importance of the amount of separation and relative orientations of the theophylline moieties, was one reason for doing the complete crystal structure analysis of BTP. In addition, a comparison of bond lengths and angles of the theophylline moiety with those of theophylline (Sutor, 1958a) was expected to yield information concerning the effects of a substituent on the dimension of the imidazole ring. It was also hoped that complete structure analysis would delineate the relationship between the hydrogen bonding scheme, bifunctionality of the compound and the considerably higher melting point of BTP relative to theophylline.

Experimental

Synthesized according to the method of Beech (1963), BTP in powder form was generously provided by Dr

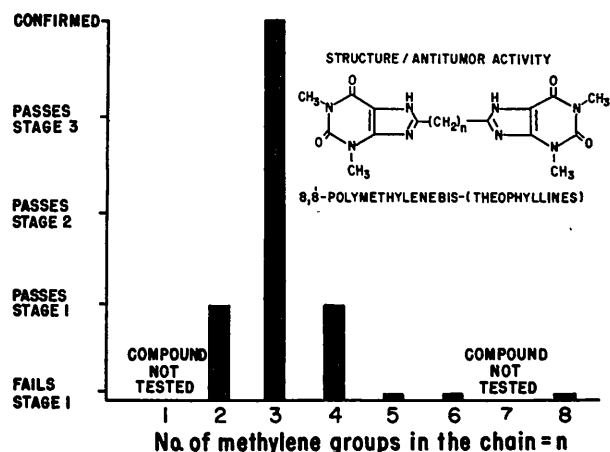


Fig. 1. Anti-tumor activity versus methylene chain length in the polymethylenebis-theophyllines.