The Crystal Structure of Violanthrone (Dibenzanthrone)

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Violanthrone, $C_{34}H_{16}O_2$, is a vat dye of the quinonoid series much used as a model substance for coal in carbonization experiments for which its crystal structure was required. The monoclinic unit cell has dimensions $a = 15·26$, $b = 33·60$, $c = 3·827$ Å, $\beta = 90·5°$ and the space group is $P2_1$. A three-dimensional approach to the transform fitting helped greatly in unravelling the structure which was unusually complicated by having two independent molecules per asymmetric unit in a non-centrosymmetric space group.

The planar molecules are stacked parallel to each other at 26° to (001) with inter-planar spacings of 3·45 Å. Viewed down the plane normal, molecules in both independent stacks superpose very much like the macromolecular layers of the graphite structure. The molecular packing represents a departure from the arrangements in related compounds and can best be compared with alternations of stacked ploughshares.

Introduction

Violanthrone, or 2:2′:Bz-1:Bz-1′-dibenzanthrone, is an anthraquinone vat dye with the configurational formula (I) (Scholl & Seer, 1912). Apart from its com-
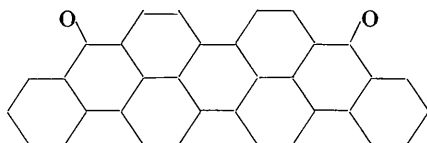
(I) $C_{34}H_{16}O_2$

mercial value as a dye, its main interest lies in its extensive use as a model compound for bituminous coals. Blayden, Gibson & Riley (1945) established that there is a close resemblance in the carbonization behaviour of carbonaceous materials such as pitch or coal and the dyes violanthrone and its isomer iso-violanthrone. The carbonization of these dyes was subsequently studied by Adamson & Blayden (1959), Akamatsu, Mrozowski & Wobschall (1959) and Brown, Brooks & Shannon (1958), but it was essential for the understanding of the complex structural changes taking place during the carbonization in the solid state that the structure of the starting material should be known.

Experimental

The commercial samples, for which we are indebted to I. C. I. Dyestuffs Division and to E. I. Du Pont de Nemours and Co., were purified by vatting with sodium hydrosulphite solution (Lüttringhaus & Neresheimer, 1929) to free them from the insoluble iso-dibenzanthrone, followed by reoxidation with air. Aci-

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cular crystals were then obtained by sublimation in a slow stream of nitrogen at low pressure. The cell dimensions of the monoclinic crystals are:

$a = 15·26$ Å $\quad D_x = 1·53$ g.cm^{-3}
$b = 33·60$ $\quad D_m = 1·50$
$c = 3·827$ $\quad Z = 4$.
$\beta = 90·50°$

The systematic absences of $0k0$ for odd k leave a choice of spacegroups $P2_1/m$ or $P2_1$. A special feature of the intensity pattern was a pronounced pseudo-halving of $hk0$ for odd h, but for low values of k only (Fig. 1).

All intensity photographs had to be taken about the c axis, the needle axis of the crystals, since their ready cleavage along this direction made it impossible to cut pieces suitable for intensity photographs about other axes. Zero to third layer equi-inclination Weissenberg photographs were therefore used to record the
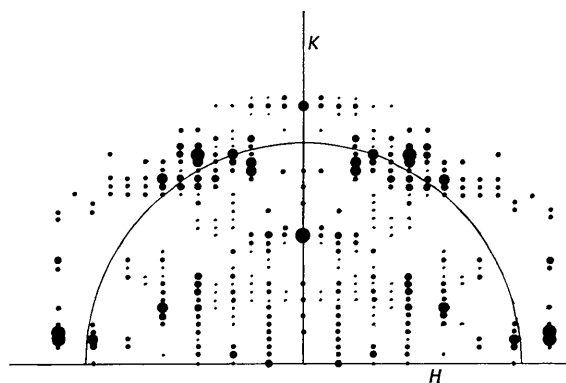

Fig. 1. The $(hk0)$ weighted reciprocal lattice of violanthrone. The pseudo-halving is evident from the weak or absent reflexions with odd h and low k but disappears with increasing k. Transform benzene peaks lie on the full circle.

intensities on multiple film packs. The different lay-
ers were correlated by means of double slit Weissen-
berg photographs (Stadler, 1950) and put on an ap-
proximately absolute scale by comparison with a
flavanthrone photograph (Stadler, 1953) taken with a
crystal of similar dimensions.

The structure determination

It was decided to attempt a solution of the structure
by the use of Fourier transform methods. For this
purpose an idealized dibenzanthrone molecule was
assumed to consist of stationary point atoms of equal
weight at the corners of a regular hexagonal network.
Such a transform will have a periodicity determined
by the regular network. For dibenzanthrone the trans-
form, G, has a real and an imaginary part. These are
readily expressed in a form suitable for evaluation
by Beevers–Lipson strips, as was done for flavan-
throne (Stadler, 1953). The modulus of G was plotted
and used for the subsequent transform fitting on the
weighted reciprocal lattice, with due allowance for
the simplifying assumptions made for the idealized
model. In the real molecule the bond lengths will, of
course, be unequal, but this only introduces minor
distortions into the transform; the electron distribu-
tion in the atoms and their thermal vibration can be
allowed for by multiplying this idealized transform of
point atoms by the temperature-corrected scattering
factor. The dominant feature of the resulting trans-
form will still be the six 'benzene peaks' arranged
hexagonally around the central origin peaks which are
common to all benzenoid structures (Lipson & Coch-
ran, 1953; Lipson & Taylor, 1951). It is also worth
noting that the cross-section of each peak will be of
a shape reciprocal to that of the molecule, since such
knowledge may often be used to eliminate pseudo-
homometric solutions without a full calculation of the
transform. The benzene peaks in Fig. 1 are clearly
compressed in the b^* direction, so that the long axis
of the molecule must be approximately along this
axis.

Intensity statistics applied to the three-dimensional
intensities (Howells, Phillips & Rogers, 1950) suggested
a centre of symmetry. It was therefore assumed
on the basis of this and the transform fit evidence
that there were two independent molecules in the
space group $P2_1/m$ with their planes of symmetry at
$y=\frac{1}{4}$, as demanded by the space group and with a
separation very close to $\frac{1}{2}a$ to account for the observed
pseudo-halving for all orders of h. This, in turn, al-
lowed the x coordinate of the molecular centre, x_c, to
be determined by finding the fringe function which
produced the best match between the observed struc-
ture amplitudes and the summed transform values
(Taylor, 1954). In this case, $F(h00)=\pm 4A(h00)$
$\cos 2\pi hx_c$ for even h, with $A(h00)$ the real part of the
molecular transform sampled at the reciprocal lat-
tice points, $h00$. The value $x_c=0.195$, obtained from

the first seven even $F(h00)$, gave good general agree-
ment for all $F(hk0)$ with h even, thus showing that
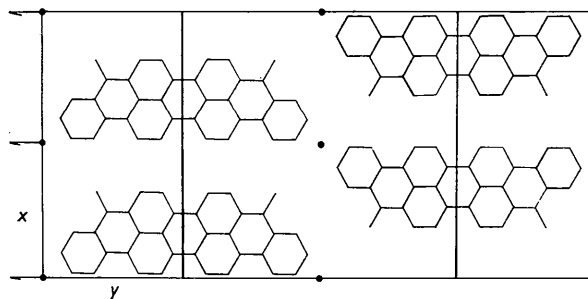this arrangement of the molecules (Fig. 2) was essen-

Fig. 2. The trial structure of violanthrone molecules in the
(wrong) space group $P2_1/m$ found from considering the
fringe function at $(h00)$.

tially correct, but it was apparent that the breakdown
of the pseudo-halving of h at high values of k (Fig. 1)
was incompatible with the presence of a mirror-plane
perpendicular to b, and that the space-group $P2_1/m$
had to be abandoned. The lower symmetry require-
ments of $P2_1$, on the other hand, would permit small
relative displacements of the molecules in the b direc-
tion, or differences in foreshortening of the two pro-
jected molecules due to different tilts, which would
account for the emergence of reflexions at high k
values for odd h. They would also permit a small
rotation of the projected molecules, by approximately
equal amounts, as suggested by the $hk0$ transform fit,
without upsetting the pseudo-halving. The possibility
of slight lateral displacements would impose a fringe
function on the $0k0$ intensities and was excluded by
trial calculation of the $F(0k0)$. The axes of tilt of the
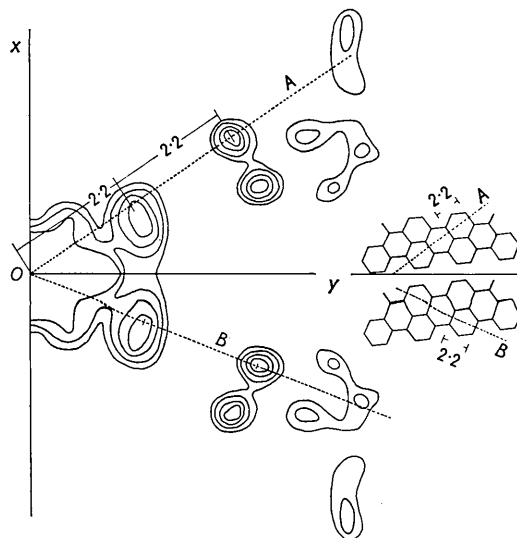molecules, viz. their intersections with (001), could be

Fig. 3. The Patterson section at $z=0$. The two sets of collinear
vector peaks could be interpreted to mean that the un-
related molecules were tilted about A and B as shown.

ascertained from the $xy0$ Patterson section (Fig. 3) which also confirmed that the molecules were rotated about 4° away from the mirror plane in the trial structure. The two lines of tilt shown must, however, be transferred to different quadrants of the Patterson section to account for the increase with k of the $hk0$ intensities for odd h (Fig. 1). The direction of tilt was immediately apparent from an inspection of upper layers of the weighted reciprocal lattice, which reveal four origin peaks (Stadler, Bolton & Maitland, 1964) fixing the direction and magnitude of tilt of both molecules (Fig. 4).

An $hk0$ structure factor calculation with the molecules in these orientations gave an R value of 0·34. After refinement by Fourier syntheses and least squares this reduced to 0·13.

To solve the structure completely, only the z coordinates of the molecular centres were now needed. In order to find these, a method similar to Taylor & Morley's (1959) was used on some $(h0l)$ structure factors. factors. Since the $(h0l)$ projection is centrosymmetric so that the four molecular centres are at $\pm (x_1, z_1)$ and $\pm (x_2, z_2)$ with x_1 and x_2 known, $\Sigma ||G| - |F||$ could be evaluated and plotted as a function of z_1 and z_2 only.

Table 1. *Violanthrone: atomic coordinates*

|	x (Å)	y (Å)	z (Å)		x (Å)	y (Å)	z (Å)
O(1)	1·8852	−·34487	3·8474	O(1′)	−4·5781	−13·9031	−2·1966
O(2)	3·0646	−14·2345	1·1051	O(2′)	−5·8653	−3·0786	0·5199
C(1)	5·7486	−7·4486	1·4913	C(1′)	−1·8716	−7·6965	0·6259
C(2)	5·8953	−8·8306	1·1272	C(2′)	−1·7491	−9·1147	0·2937
C(3)	3·5100	−7·9526	2·4172	C(3′)	−4·1911	−7·7187	−0·4226
C(4)	3·6850	−9·3781	2·1191	C(4′)	−3·9973	−9·1633	−0·7648
C(5)	6·7099	−6·5206	1·1857	C(5′)	−0·8865	−6·9731	1·2918
C(6)	6·5664	−5·1531	1·5054	C(6′)	−1·0246	−5·6272	1·5333
C(7)	6·2845	−2·4166	2·3948	C(7′)	−1·2871	−2·7906	2·1495
C(8)	7·0643	−9·3445	0·5366	C(8′)	−0·5663	−9·8353	0·6509
C(9)	7·2075	−10·7083	0·2401	C(9′)	−0·4105	−11·1741	0·3697
C(10)	7·5799	−13·5900	−0·3740	C(10′)	−0·1304	−14·0162	−0·2925
C(11)	4·5505	−7·0409	2·1279	C(11′)	−3·0994	−6·9999	0·2511
C(12)	4·8382	−9·8022	1·4803	C(12′)	−2·7960	−9·7989	−0·4112
C(13)	4·3642	−5·6581	2·4741	C(13′)	−3·2193	−5·6255	0·5748
C(14)	5·0114	−11·1624	1·1091	C(14′)	−2·6480	−11·1558	−0·6915
C(15)	4·0765	−2·9026	3·1486	C(15′)	−3·5583	−2·8718	1·3125
C(16)	5·2946	−13·9289	0·4207	C(16′)	−2·3856	−13·9980	−1·1811
C(17)	3·9380	−1·5037	3·4935	C(17′)	−3·7163	−1·5303	1·6731
C(18)	5·4476	−15·2695	0·0693	C(18′)	−2·3004	−15·3823	−1·4766
C(19)	5·3915	−4·6940	2·1787	C(19′)	−2·1882	−4·9255	1·2193
C(20)	6·2289	−11·6128	0·5196	C(20′)	−1·4276	−11·8747	−0·3054
C(21)	5·2700	−3·3383	2·5189	C(21′)	−2·3448	−3·5078	1·5776
C(22)	6·3810	−13·0267	0·1660	C(22′)	−1·2976	−13·3046	−0·6118
C(23)	3·1636	−5·2382	3·0580	C(23′)	−4·4845	−4·9855	0·2648
C(24)	3·9621	−12·0885	1·4341	C(24′)	−3·7093	−11·9010	−1·3716
C(25)	2·9466	−3·7755	3·3640	C(25′)	−4·7175	−3·6008	0·7222
C(26)	4·0739	−13·4976	0·9656	C(26′)	−3·6262	−13·3009	−1·6039
C(27)	4·9263	−0·5637	3·2986	C(27′)	−2·6660	−0·8027	2·1932
C(28)	6·6284	−15·7480	−0·4948	C(28′)	−1·1066	−16·0309	−1·1814
C(29)	6·1336	−1·0752	2·6962	C(29′)	−1·4662	−1·4539	2·4954
C(30)	7·6800	−14·9114	−0·6861	C(30′)	−0·0267	−15·3070	−0·5984
C(31)	2·1979	−6·0929	3·3414	C(31′)	−5·4848	−5·6962	−0·4425
C(32)	2·8620	−11·6241	2·0839	C(32′)	−4·8390	−11·1837	−1·7089
C(33)	2·3855	−7·4831	3·0668	C(33′)	−5·3321	−7·0225	−0·7656
C(34)	2·7291	−10·2785	2·4450	C(34′)	−4·9735	−9·8145	−1·4740
H(27)	4·8500	0·4700	3·4800	H(27′)	−2·7800	0·2500	2·3540
H(29)	0·9000	−0·4000	2·4930	H(29′)	−0·6100	−0·8500	2·9220
H(7)	7·2700	−2·7000	0·9430	H(7′)	−0·3700	−3·3000	2·9220
H(6)	7·3000	−4·4500	1·3660	H(6′)	−0·1500	−5·0200	2·0000
H(5)	7·7100	−6·8500	0·7250	H(5′)	0·1000	−7·5500	1·4540
H(8)	7·8500	−8·6500	0·3770	H(8′)	0·3000	−9·2000	1·1170
H(9)	8·2000	−11·1000	−0·1920	H(9′)	0·5100	−11·6500	0·6110
H(10)	8·4500	−13·0000	−0·5280	H(10′)	0·7400	−13·4500	0·1300
H(30)	8·6500	−15·3000	−1·1730	H(30′)	0·9000	−15·8000	−0·4300
H(28)	6·7000	−16·8000	−0·6480	H(28′)	−0·9800	−17·1000	−1·3830
H(18)	4·6000	−15·9200	0·2400	H(18′)	−3·1600	−15·8600	−1·9400
H(32)	2·0700	−12·3500	2·2540	H(32′)	−5·7700	−11·7000	−2·1580
H(34)	1·7400	−10·0000	2·8850	H(34′)	−6·0200	−9·2500	−1·6680
H(33)	1·6200	−8·1300	3·2300	H(33′)	−6·2000	−7·6100	−1·2380
H(31)	1·2500	−5·8000	3·8200	H(31′)	−6·4500	−5·2000	−0·6530
H(17)	3·0000	−1·1500	3·9180	H(17′)	−4·6600	−1·0000	1·4530
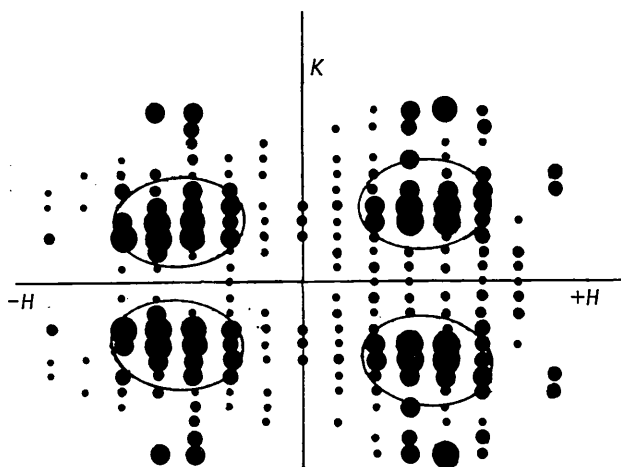
Fig. 4. The transform origin peaks on the $(hk2)$ weighted reciprocal lattice of violanthrone. Their positions fix the magnitude and direction of tilt of the molecules with respect to (001).

Fig. 5. The plot of $\Sigma||G|-|F||$ for selected $(h0l)$ structure factors as a function of the z coordinates of the molecular centres of unrelated molecules (z_1, z_2). The steep minimum near $(0, -0\cdot5)$ is the correct solution.

Several false minima were obtained (Fig. 5) but these were eliminated by packing considerations and calculations of the agreement index.

The three-dimensional refinement of the structure was carried out on a Ferranti Pegasus computer, Cruickshank's (1958) diagonal matrix least-squares program being used. Hughes's (1941) weighting scheme was used and hydrogen atoms in fixed positions were included in the final refinements. The agreement residual for 1832 observed reflexions was 12·4% in the
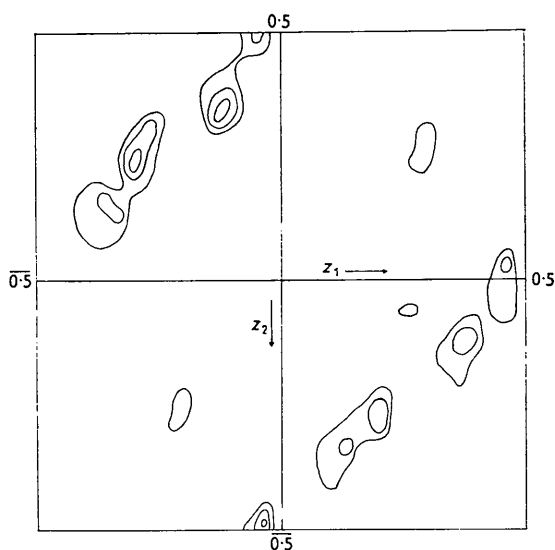
last calculation. The refinement was not carried to completion because of the considerable time needed to refine atomic and thermal parameters of 72 atoms in the non-centrosymmetric space group (18 hours per cycle) and because accurate molecular dimensions were not the main aim of the analysis.
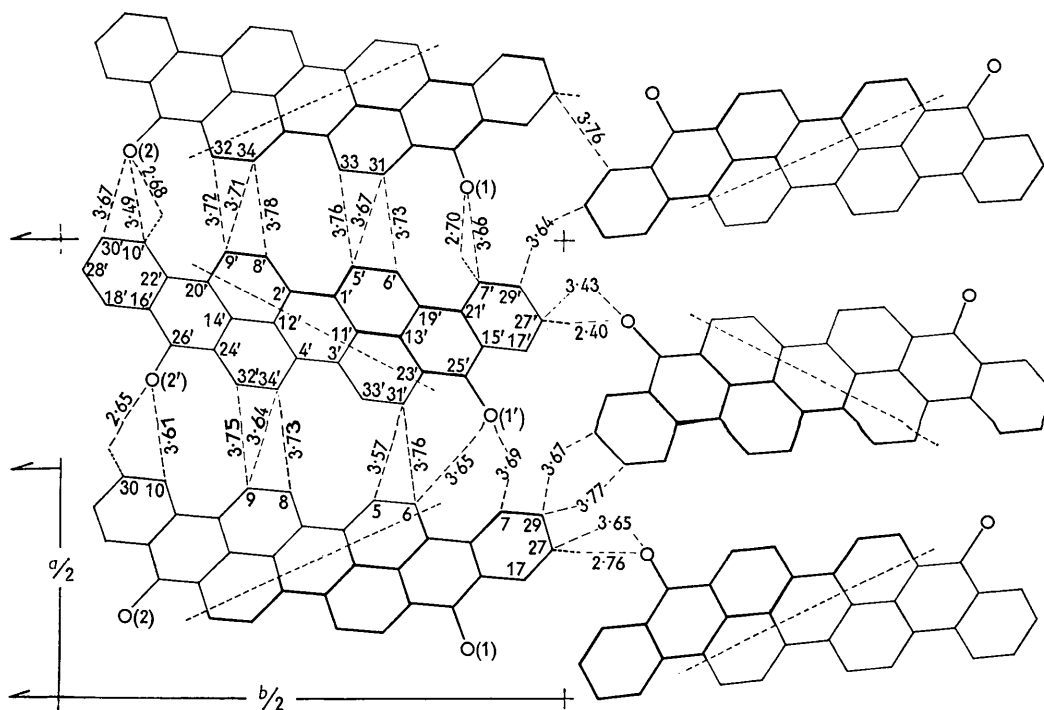
The final atomic coordinates and isotropic thermal

Fig. 6. The structure of violanthrone projected on (001).

parameters are shown in Table 1. The estimated standard deviations are

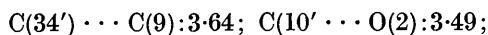$$\sigma(x) = \sigma(y) = 0\cdot011 \text{ Å}, \quad \sigma(z) = 0\cdot012 \text{ Å}$$

and

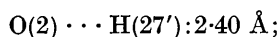$$\sigma(B) = 0\cdot22 \text{ Å}^2 .$$

A copy of the final F_c and F_o table may be obtained from the authors.

Description of the structure

The crystal structure projected on (001) with the closest intermolecular contacts is shown in Fig. 6. The smallest intermolecular distances are

$$C(34') \cdots C(9):3\cdot64; \quad C(10' \cdots O(2):3\cdot49;$$

and

$$O(2) \cdots H(27'):2\cdot40 \text{ Å};$$

which are larger than the sums of the van der Waals radii (Pauling, 1960) and are close to the corresponding values in the related compounds α-indanthrone (Bailey, 1955), flavanthrone (Stadler, 1953) and pyranthrone (Maitland & Stadler, 1963).

The periodicity along the c axis produces two stacks in each of which the molecules are parallel to each other with normals at 26° to c, and with interplanar spacings of 3·45 Å. Viewed along their normals the superposition of the molecules is identical, within the accuracy of this determination, in the two space-group
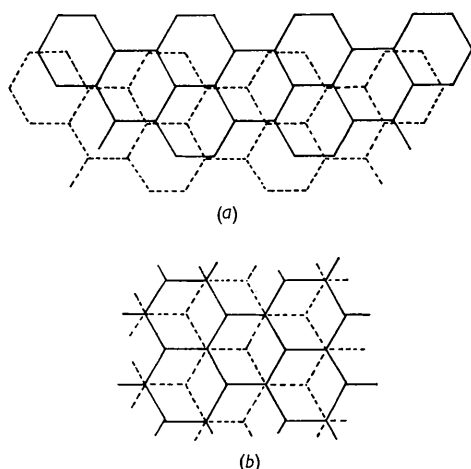
(a)

(b)

Fig. 7. (a) The superposition of violanthrone molecules along the plane normals which is closely similar to (b) the stacking in graphite.

unrelated stacks (Fig. 7(a)), and shows close similarity to that in graphite (Fig. 7(b)).

The compound exhibits a novel type of molecular packing compared with the other polynuclear aromatic quinones α-indanthrone, flavanthrone and pyranthrone, whose structures are known. In violanthrone the molecules are packed together like stacked plough-
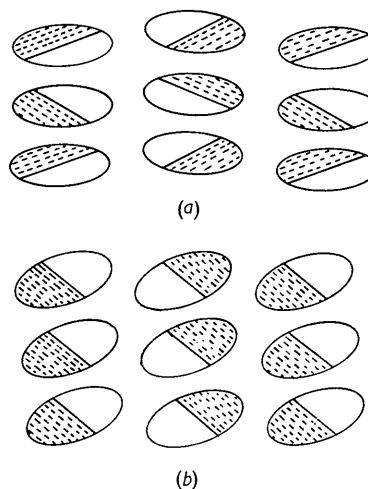
(a)

(b)

Fig. 8. (a) The type of packing of violanthrone molecules compared with (b) the arrangement in flavanthrone and some other vat dyes.

shares with ridges pointing in different directions (Fig. 8(a)) whereas in the other structures the axes of tilt of the molecules are almost parallel forming zigzags like the roofs of houses with parallel ridges (Fig. 8(b)).

The bond lengths in the two independent molecules are shown in Table 2. The standard deviations lie between 0·018 and 0·014 Å. If the dibenzanthrone molecule is assumed to have a mirror plane perpendicular to its long axis and crystal field effects on the dimensions of the two molecules are neglected each row in Table 2 represents four determinations of the same bond length. The observed differences are thought to be due to incomplete refinement of the structure and do not warrant discussion.

Table 2. *Violanthrone: bond lengths*

		(Å)	(Å)	(Å)	(Å)
C(1) –C(5);	C(2) –C(8);				
C(7')–C(5');	C(2')–C(8')	1·371	1·407	1·393	1·429
C(1) –C(11);	C(2) –C(12)	1·416	1·476	1·462	1·432
C(3) –C(11);	C(4) –C(12)	1·413	1·385	1·468	1·405
C(3) –C(33);	C(4) –C(34)	1·381	1·352	1·380	1·372
C(5) –C(6);	C(8) –C(9)	1·412	1·403	1·373	1·379
C(11)–C(13);	C(12)–C(14)	1·439	1·421	1·417	1·394
C(31)–C(33);	C(32)–C(34)	1·430	1·401	1·375	1·394
C(25)–C(23);	C(24)–C(26)	1·509	1·488	1·476	1·423
C(13)–C(19);	C(14)–C(20)	1·440	1·426	1·403	1·417
C(6) –C(19);	C(9) –C(20)	1·430	1·362	1·394	1·407
C(13)–C(23);	C(14)–C(24)	1·400	1·437	1·450	1·464
C(31)–C(23);	C(32)–C(24)	1·320	1·359	1·416	1·382
C(19)–C(21);	C(20)–C(22)	1·410	1·466	1·471	1·470
C(21)–C(15);	C(22)–C(16)	1·418	1·436	1·395	1·41₀
C(15)–C(25);	C(16)–C(26)	1·444	1·406	1·490	1·484
C(21)–C(7);	C(22)–C(10)	1·379	1·430	1·400	1·398
C(7) –C(29);	C(10)–C(30)	1·382	1·361	1·393	1·334
C(27)–C(29);	C(28)–C(30)	1·444	1·358	1·398	1·424
C(17)–C(27);	C(18)–C(28)	1·381	1·393	1·382	1·392
C(15)–C(17);	C(16)–C(18)	1·446	1·391	1·401	1·418
C(1)–C(2)		1·436	—	1·461	—
C(3)–C(4)		1·466	—	1·497	—
C(25)–O(1);	C(26)–O(2)	1·210	1·257	1·274	1·274

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The Crystal Structure of Isoviolanthrone (Isodibenzanthrone)

BY W. BOLTON*

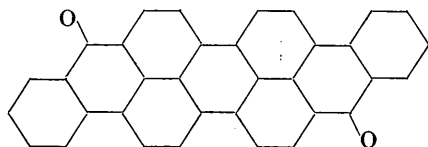*School of Chemistry, The University, Newcastle upon Tyne, 1, England*

The crystal structure of the vat dye isoviolanthrone (isodibenzanthrone), $C_{34}H_{16}O_2$, has been solved from three-dimensional photographic data and refined by least squares. The space group is $P2_1/c$ with $a = 15\cdot21$, $b = 3\cdot825$, $c = 33\cdot12$ Å, and there are two independent molecules in the asymmetric unit. Their orientations and relative positions have been found by the application of Fourier transform considerations to the whole weighted reciprocal lattice. The structure is remarkably similar to that of the isomeric violanthrone (reported in the preceding paper) and in particular the molecular packing is of the stacked ploughshare type. There are significant deviations of the molecule from planarity and the low value of formally single C–C bonds, with a mean of $1\cdot45 \pm 0\cdot01$ Å, suggests appreciable contributions from excited canonical forms.

Introduction

In connection with their use as model substances in carbonization experiments the crystal structures of several vat dyes have been studied. The preceding paper gives an account of the crystal structure of one of these, violanthrone. The crystal structure of its isomer isoviolanthrone (I), which is of equal importance in this relation, is reported here.

(I) $C_{34}H_{16}O_2$

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Crystals of isoviolanthrone can be obtained from specially purified samples (kindly supplied for this work by E. I. Du Pont de Nemours & Co.) by the sublimation method used for violanthrone. These are needle shaped about [*b*] and, generally, twinned about [001]. The unit cell was found to be monoclinic with the dimensions:

$$a = 15\cdot21 \text{ Å} \qquad D_m = 1\cdot53 \text{ g.cm}^{-3}$$
$$b = 3\cdot825 \qquad D_x = 1\cdot52$$
$$c = 33\cdot12 \qquad Z = 4$$
$$\beta = 90\cdot8°$$

As the $h0l$ reflexions with l odd and the only two observable $0k0$ reflexions with k odd were missing, even on very strong photographs, the space group was assumed to be $P2_1/c$.

All intensity data were recorded by the equi-inclina-