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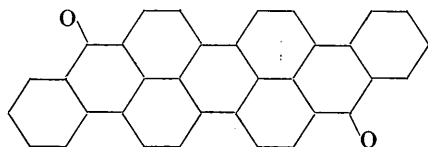
The Crystal Structure of Isoviolanthrone (Isodibenzanthrone)

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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 trans-form 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 impor-tance 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-

tion Weissenberg method with Cu $K\alpha$ radiation and the crystal mounted about the b axis. This was necessary because easy cleavage along this axis prevented the cutting of crystals of suitable dimensions for other orientations. The $h0l$ to $h3l$ zones, comprising 89% of the accessible data, were recorded, visually estimated and correlated with the double-slit method (Stadler, 1950).

The structure determination

The unit-cell dimensions are very close to the violanthrone values, and suggested a possible similarity between the two structures despite the different space groups. This was strengthened by the very similar distribution of groups of strong reflexions (undoubtedly corresponding to transform peaks) in the weighted reciprocal lattice. Moreover the $(h0l)$ intensity pattern (Fig. 2) had pronounced pseudo-halving for odd h and low values of l (see preceding paper). In view of these similarities it seemed reasonable to try and solve the structure by the three-dimensional Fourier transform considerations which had led to an understanding of the violanthrone structure.

Since the violanthrone molecule has a centre of symmetry, its transform, G, is everywhere real and readily evaluated. This transform could be adjusted against the $(h0l)$ weighted reciprocal lattice section to give superposition of the high peaks in six different orientations. These were caused by the sixfold pseudo-symmetry of the high transform peaks.

However, all but one of the resulting molecular orientations could be excluded by packing and by a detailed comparison of the shape of the transform peaks, which are roughly elliptical, with their images in the weighted reciprocal lattice.

The molecules themselves are centrosymmetrical and were expected to lie on space-group centres of symmetry. With four molecules per unit cell, this meant there were two unrelated half molecules in the asymmetric unit, centred on $(0, 0, 0)$ and $(\frac{1}{2}, 0, 0)$ or $(\frac{1}{2}, \frac{1}{2}, 0)$. However, a single orientation had been found in the transform fit of the $(h0l)$ projection. This, like the pseudo-halving, was analogous to the behaviour of violanthrone (see preceding paper) in which two independent molecules gave the same orientation in projection but were tilted out of the plane about different lines. This should show in the weighted reciprocal lattice as two separate transform origin peaks on each (hnl) section as in violanthrone, and this proved to be so. The origin peaks can be seen in Fig. 1, which also shows the orientation of the molecular planes inferred from the origin peak positions. These make angles of 26° with (010). The positions of the origin peaks are consistent with two orientations for each molecule corresponding to the up-down tilting out of the (010) plane (Fig. 1), because of the symmetry of the weighted reciprocal lattice, but these appear the same in projection.

It was now possible to derive the plane transforms of the foreshortened molecules as they appear in projection by expanding the scale of the transform by
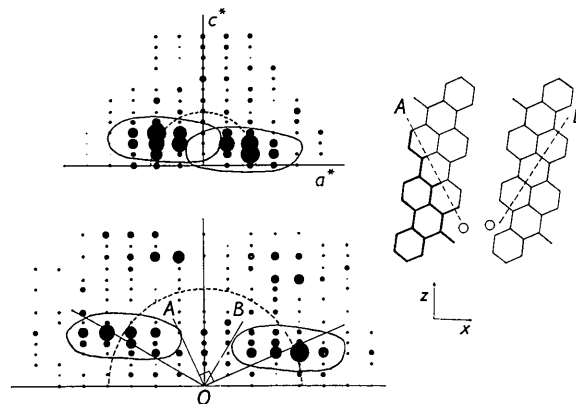

Fig. 1. The transform origin peaks on the $(h1l)$ and $(h2l)$ weighted reciprocal lattice sections of isoviolanthrone. If the direction of tilt of one molecule out of the plane (about OA) is fixed then the second molecule may be tilted up or down about OB. Both possibilities give origin peaks in the same positions.
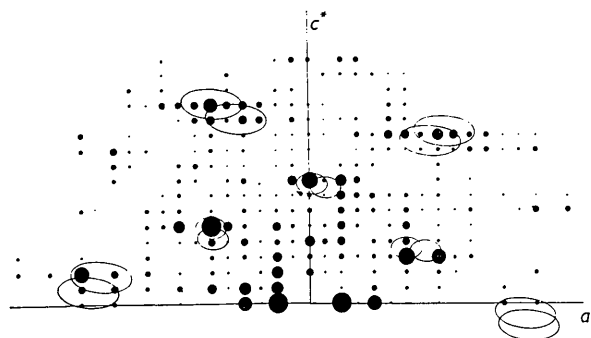
Fig. 2. The $(h0l)$ weighted reciprocal lattice of isoviolanthrone. The transform peaks from two unrelated molecules overlap because, although they are in the same orientation in projection, they are tilted out of the plane about different lines.

$(\cos 26°)^{-1}$ along OA or OB (Fig. 1). These were matched as accurately as possible against the $(h0l)$ weighted reciprocal lattice (Fig. 2) and the magnitudes of G_1 and G_2, the transform values at the reciprocal lattice points, were read off. The expression for F_c in terms of these is formulated by adding the contributions of each molecule to a particular structure factor multiplied by the appropriate fringe function (e.g. Taylor & Morley, 1959; Bolton, 1963).

In this case it reduces to:

$$F(h0l) = 2G_1 + 2G_2 \quad \text{for } h = \text{even}$$
$$= 2G_1 - 2G_2 \quad \text{for } h = \text{odd}$$

This was evaluated to allocate signs unambiguously

to 78 high F_o. The resulting Fourier synthesis (Fig. 3) confirmed the structure as it showed the atoms of both molecules clearly and there was little spurious density. Atomic coordinates from this gave an R value of 0·335 for observed $h0l$ reflexions which reduced to 0·142 after cyclical least-squares refinements.

Fig. 3. The Fourier synthesis on (010) with signs obtained from the ($h0l$) transform fit.

Assuming a molecule (I) at (000) in a fixed inclination it remained only to find the height of the second molecule (II) above the plane of pro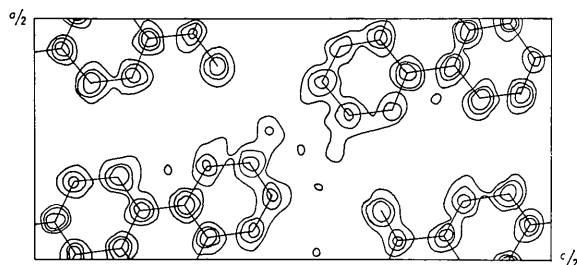jection and its relative tilt to solve the structure three-dimensionally. Each of the possible arrangements gives the same distribution of peaks in the weighted reciprocal lattice sections. However, it is found by summing the transform contributions with the appropriate fringe functions that for $(h1l)$ structure factors with odd l, irrespective of tilt,

$$F = (G_1 + G_1') - (G_2 + G_2') \quad (1) \text{ for II on } \tfrac{1}{2}\tfrac{1}{2}0$$
or
$$F = (G_1 + G_1') + (G_2 + G_2') \quad (2) \text{ for II on } \tfrac{1}{2}00$$

where G_1, G_1' and G_2, G_2' are the contributions of molecules I and II and their space-group related mates. These are read off directly from the transform fitted against the $(h1l)$ weighted reciprocal lattice sections (Stadler, Bolton & Maitland, 1964). Consistent agreement for several reflexions was only possible with I showing that molecule II was on ($\tfrac{1}{2}\tfrac{1}{2}0$).

In a similar way, the expression for $F(h1l)$ with l even can be written:

$$F = (G_1 - G_1') - (G_2 - G_2') \quad (3)$$
or
$$= (G_1 - G_1') + (G_2 - G_2') \quad (4)$$

depending on the relative tilts of the molecules alone. Only (4) agreed consistently with $F(h1l)$ and therefore fixed the relative tilts of the molecular planes.

By considering the overlap of the two origin peaks only, this result was subsequently confirmed by the much simpler method given in Fig. 3 of Stadler, Bolton & Maitland (1964).

With the unrelated molecules tilted in this manner and centred on (000) and ($\tfrac{1}{2}\tfrac{1}{2}0$) atomic y coordinates were allocated assuming a strictly planar configuration. The agreement index for the first structure factor calculation was about 0·32 (not all (hkl) structure factors were included in the first calculations). This

Table 1. *Atomic positional and isotropic thermal parameters*

	Molecule I					Molecule II			
Atom	x (Å)	y (Å)	z (Å)	B (Å²)	Atom	x (Å)	y (Å)	z (Å)	B (Å²)
O(1)	−1·490	2·123	5·418	3·85	O(2)	9·098	1·299	−5·788	3·50
C(1)	−2·498	0·435	−2·769	2·90	C(18)	8·288	1·513	−3·640	2·41
C(2)	−1·211	0·378	−0·702	2·45	C(19)	7·471	1·571	−1·391	1·88
C(3)	0·172	0·304	1·401	2·56	C(20)	6·597	1·612	0·931	2·60
C(4)	1·551	0·213	3·478	2·42	C(21)	5·781	1·659	3·209	2·40
C(5)	2·875	0·257	5·591	3·15	C(22)	5·584	1·283	1·860	2·04
C(6)	−2·314	0·724	−1·405	2·20	C(23)	6·417	1·234	−0·453	2·20
C(7)	−1·050	0·679	0·698	2·58	C(24)	7·228	1·249	−2·763	2·10
C(8)	0·361	0·586	2·777	2·47	C(25)	8·127	1·144	−5·043	2·62
C(9)	1·722	0·579	4·895	3·05	C(26)	6·933	0·515	−5·504	2·62
C(10)	3·034	1·566	6·936	3·42	C(27)	6·022	0·617	−3·240	2·15
C(11)	−2·045	1·358	1·423	2·50	C(28)	5·240	0·640	−0·961	2·24
C(12)	−0·742	1·226	3·427	2·17	C(29)	6·774	0·167	−6·848	3·11
C(13)	0·682	1·142	5·585	3·05	C(30)	5·872	0·273	−4·611	2·94
C(14)	1·950	1·167	7·573	4·30	C(31)	5·080	0·310	−2·302	2·62
C(15)	−1·856	1·611	2·759	2·95	C(32)	5·590	−0·337	−7·358	3·28
C(16)	−0·557	1·498	4·877	3·50	C(33)	4·672	−0·273	−5·150	3·13
C(17)	0·782	1·444	6·904	3·56	C(34)	4·520	−0·596	−6·498	3·24
H(1)	−3·40	0·77	−3·42		H(21)	5·04	1·38	3·95	
H(5)	3·70	−0·30	5·08		H(22)	4·56	0·81	1·75	
H(6)	−3·10	1·15	−0·80		H(28)	4·43	0·41	−0·22	
H(10)	4·00	0·30	7·37		H(29)	7·60	0·50	−7·52	
H(11)	−2·92	1·48	0·85		H(31)	4·15	−0·17	−2·63	
H(14)	2·00	1·30	8·60		H(32)	5·20	−0·44	−8·40	
H(15)	−2·65	1·98	3·36		H(33)	3·85	−0·44	−4·22	
H(17)	0·01	1·93	7·48		H(34)	3·52	−1·04	−6·90	

reduced to 0·182 after least-squares refinement and further to 0·137 when hydrogen atoms at 1·09 Å from carbon atoms in the mean molecular plane were included in the calculations. Refinement of the 144 non-hydrogen atom coordinate and isotropic temperature parameters was continued with Cruickshank's diagonal least-squares program for the Ferranti Pegasus computer using Hughes's(1941) weighting scheme. The terminal R value was 0·125 for all observed reflexions. The mean estimated standard deviations are $\sigma(x) = \sigma(y) = \sigma(z) = 0\cdot009$ Å and $\sigma(B) = 0\cdot18$ Å^2, but these are probably underestimated since in the final two cycles there were atomic shifts of as much as 0·013 Å in one direction. The atomic positional and thermal parameters are shown in Table 1. A copy of the final F_o and F_c tables may be obtained from the author on request.

Discussion of the structure

The projected crystal structure is shown in Fig. 4. The roughly planar molecules are 3·42 Å 'thick' (for molecules I and II) and stack parallel to one another in the **b** direction. This makes angles of 27·9° and 26·8° with the plane normals and adjacent molecules are held together by van der Waals forces as there are no abnormally close approaches.

The molecules are not quite planar as certain atoms, namely C(5), (10), (14) and C(33), (34), (32), O(2), in molecules I and II are relatively large distances from the least-squares planes. The equations to the molecular planes with these atoms omitted are:

$$-0\cdot409x - 0\cdot883y + 0\cdot229z = 0$$

$$0\cdot414x - 0\cdot893y + 0\cdot175z - 1\cdot430 = 0$$

The displacements from these planes are given in Table 2. In terms of the standard deviations several of these are significant but the only common systematic feature is the bending of the ends of the mole-

Table 2. *Distances of atoms from the mean planes*

Molecule I		Molecule II	
Atom	Δ (Å)	Atom	Δ (Å)
C(1)	−0·010	C(18)	0·024
C(2)	−0·002	C(19)	0·015
C(3)	−0·011	C(20)	0·009
C(4)	−0·008	C(21)	0·023
C(5)	−0·093	C(22)	0·042
C(6)	−0·021	C(23)	0·038
C(7)	−0·006	C(24)	−0·031
C(8)	−0·015	C(25)	0·048
C(9)	−0·069	C(26)	0·037
C(10)	−0·140	C(27)	−0·048
C(11)	−0·029	C(28)	−0·005
C(12)	0·024	C(29)	0·005
C(13)	0·020	C(30)	−0·035
C(14)	−0·054	C(31)	−0·004
C(15)	−0·017	C(32)	−0·070
C(16)	0·049	C(33)	−0·140
C(17)	0·022	C(34)	−0·140
O(1)	0·004	O(2)	0·140

Fig. 4. The crystal structure of isoviolanthrone projected on (010).

cules represented by the large negative displacements of C(5), (10), (14) and C(34), (33), (32). There does not appear to be a simple reason for the significant non-planarity of such atoms as C(9) and O(2). Viewed down the plane normals, the molecules superpose like the layers of atoms in the graphite structure or molecules of violanthrone (cf. Fig. 6(b) of the preceding paper).

The molecular packing is of the stacked ploughshare type found in violanthrone (Fig. 8(a) of the preceding paper) and the two structures are remarkably similar. Indeed, if the asymmetric units are superimposed, with the molecular centres coincident, all the atoms in the configuration common to both molecules coincide. This close similarity between the two offers an explanation why it was not possible to make single crystals of either compound unless it was first thoroughly purified from the isomer, because co-crystallization of even a small amount of one isomer with the other would cause considerable local disturbance of the crystal lattice.

Of the 22 pairs of bonds in the two crystallograph-

ically different molecules (shown in Fig. 4) only two are significantly different in terms of the mean standard deviation of 0·017 Å. The mean bond lengths are, with certain notable exceptions, in reasonable agreement with those derived from Pauling's (1960) bond order–bond length curve by giving equal weight to the 21 possible Kekulé-like structures (Table 3). The largest discrepancies are for resulting single bonds, which lie on the steepest part of the curve. These are all shorter than predicted and have from 10% (C(12)–C(11), C(25)–C(18)) to 22% (C(2)C(7), C(23)–C(20)) observed double bond character. Also they are much shorter than the corresponding carbon (sp^2)–carbon (sp^2) single bonds in quaterrylene (Shrivastava & Speakman, 1960) which have an average length of 1·53 Å.

This shortening indicates that excited structures, presumably with $> C-O^-$ bonds, make important contributions to the ground state of the molecule which is in accord with its strong colour.

Table 3. Observed and estimated bond lengths

Bond	Double bond character	Calc. (Å)	Obs. (Å)	Δ (Å)
C(2) –C(7); C(23)–C(20)	0	1·504	1·443	0·061
C(4) –C(9); C(27)–C(30)		1·504	1·447	0·057
C(16)–C(13); C(25)–C(26)		1·504	1·450	0·054
C(12)–C(16); C(25)–C(18)		1·504	1·474	0·030
C(7) –C(3); C(19)–C(20')	0·333	1·423	1·444	0·021
C(3) –C(2); C(19)–C(23)		1·423	1·438	0·015
C(1) –C(6); C(31)–C(28)		1·423	1·397	0·026
C(8) –C(4); C(24)–C(27)		1·423	1·436	0·013
C(3) –C(8); C(24)–C(19)		1·423	1·425	0·002
C(11)–C(15); C(22)–C(21)		1·423	1·394	0·029
C(8) –C(12); C(18)–C(24)		1·423	1·416	0·007
C(5) –C(9); C(30)–C(33)	0·500	1·394	1·405	0·011
C(9) –C(13); C(26)–C(30)		1·394	1·388	0·006
C(13)–C(17); C(29)–C(26)		1·395	1·378	0·016
C(14)–C(17); C(32)–C(29)		1·394	1·378	0·016
C(10)–C(14); C(32)–C(34)		1·394	1·396	0·002
C(5) –C(10); C(33)–C(34)		1·394	1·391	0·003
C(2) –C(6); C(28)–C(23)	0·667	1·371	1·382	0·011
C(4) –C(1'); C(27)–C(31)		1·371	1·358	0·013
C(7) –C(11); C(20)–C(22)		1·371	1·410	0·039
C(12)–C(15); C(18)–C(21')		1·371	1·381	0·010

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