Table 7. *Hydrogen-bonding parameters*

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	∠D–H···A (°)
N(16)–H(161)···O(W)^{i}	2·889 (14)	1·11	1·81	163·3
O(W)–H(OW)···O′^{ii}	2·936 (14)	1·06	2·02	142·6
N(16′)–H(161′)···O^{iii}	2·748 (11)	1·01	1·95	133·9

Symmetry code

(i) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$
(ii) $\frac{3}{2}-x, -y, -\frac{1}{2}+z$
(iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

Table 8. *Comparison of* N(1)···N(16) *distances in various sparteine derivatives*

Compound	N(1)···N(16) (Å)	Reference
11-Cyano-α-isolupanine	2·883 (4)	(1)
13-β-Hydroxy-α-isolupanine	2·870 (5)	(2)
13-α-Hydroxy-α-isolupanine	2·895 (6)	(3)
Multiflorine perchlorate	2·896 (11) [molecule (I*a*)]	(4)
hemihydrate	2·947 (12) [molecule (I*b*)]	(4)

References: (1) Rychlewska & Wiewiórowski (1980); (2) Pyżalska & Borowiak (1980); (3) Pyżalska, Gawron & Borowiak (1980); (4) this work.

Struchkov, 1973) indicates that the structural modifications introduced into ring *A* in the case of multiflorine perchlorate hemihydrate do not cause any long-range conformational effects in the sparteine skeleton for the *C*/*D* fragment. The conformation is the same in all these cases.

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The Structure of an Optically Active Form of *O*-Tetramethylhaematoxylin

By C. De Martinis and M. F. Mackay

Department of Physical Chemistry, La Trobe University, Bundoora, Victoria 3083, *Australia*

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Abstract

Crystals of (+)-*O*-tetramethylhaematoxylin, $C_{20}H_{22}O_6$, are orthorhombic, space group $P2_12_12_1$, with a = 8·545 (2), b = 8·838 (1), c = 24·022 (11) Å, Z = 4. Refinement with 1430 diffractometer data converged to R = 0·053. The tetracyclic molecule has an approximate propeller shape with the aromatic rings mutually inclined at 61·7 (4)°. The dihydropyran ring has a skewed conformation with four adjacent atoms coplanar within ±0·004 Å and the other two 0·418 (5) and 0·307 (5) Å above and below the plane respectively. The cyclopentene ring is an envelope with the out-of-plane atom 0·503 (5) Å from the mean plane of the other four. The cyclopentene and dihydropyran rings are *cis* fused.

Introduction

(+)-*O*-Tetramethylhaematoxylin (I), $C_{20}H_{22}O_6$, is a derivative of the naturally occurring (+)-haematoxylin, $C_{16}H_{14}O_6$, isolated by Chevreul (1810) from Logwood which occurs in *Haematoxylon campechianum* (family

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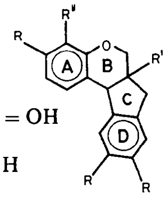
Caesalpiniaceae). Together with the related substance, (+)-brazilin, $C_{16}H_{14}O_5$, isolated from Brazil wood (Chevreul, 1808), haematoxylin has been the subject of extensive chemical study for more than a hundred years (Robinson, 1958). The structures of haematoxylin (II) and brazilin (III) as polyhydroxybenzindenopyrans are known (Perkin & Robinson, 1907; Robinson, 1958, 1977), whilst the *cis* fusion of rings *B* and *C* was established by NMR spectral studies (Craig, Naik, Pratt, Johnson & Bhacca, 1965). An X-ray analysis of (±)-bi-*O*-trimethylbrazilane (Isaacs & Mackay, 1976), an intermediate in a recent synthesis of (±)-haematoxylin and (±)-brazilin (Morsingh & Robinson, 1970; Chatterjea, Robinson & Tomlinson, 1974), established conformational detail in the dimeric molecule. The present analysis has defined the relative molecular structure of a monomeric haematoxylin derivative. The absolute configuration was not established and is not implied in the figures.



(I) $R = R'' = OCH_3, R' = OH$
(II) $R = R' = R'' = OH$
(III) $R = R' = OH, R'' = H$

Experimental

The compound has a specific rotation, $[\alpha]^{20\,^{\circ}\mathrm{C}}_{589}$ of +106° ($c = 0{\cdot}07$ g dm^{-3}, water:ethanol = 1:1). Weissenberg photographs indicated that the irregular prismatic crystals were orthorhombic, space group $P2_12_12_1$. Cell parameters were determined by least squares from 2θ values measured for 25 strong reflections on a four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The density was determined by flotation in a carbon tetrachloride/heptane mixture.

Crystal data

$C_{20}H_{22}O_6$, $M_r = 358{\cdot}4$, orthorhombic, space group $P2_12_12_1$, $a = 8{\cdot}545\ (2)$, $b = 8{\cdot}838\ (1)$, $c = 24{\cdot}022\ (11)$ Å, $U = 1814\ (1)$ Å^3, $D_m = 1{\cdot}31\ (1)$, $D_c = 1{\cdot}31$ Mg m^{-3}, $F(000) = 760$, $Z = 4$; $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}71$ mm^{-1}.

Intensities were measured on a Rigaku-AFC four-circle diffractometer with Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1{\cdot}5418$ Å). The intensities were recorded by an ω–2θ scan of 2° min^{-1} and 10 s stationary background counts from a crystal $0{\cdot}58 \times 0{\cdot}20 \times 0{\cdot}15$ mm, aligned with the longest crystal axis (a) approximately parallel to the diffractometer φ axis. Three reference reflections monitored every 50 reflections showed no significant variation in intensity. Of the 1754 unique reflections measured to a 2θ maximum of 128°, 1430 had $|F_o| > 3\sigma|F_o|$ and were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization factors but not for absorption or extinction. The scattering factors for C and O were from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections, f' and f'', were made for the non-hydrogen atoms (Cromer & Liberman, 1970).

The structure was solved by direct methods. The $|E|$ terms were derived from a modified K curve (Karle, Hauptman & Christ, 1958), and phases for 311 terms with $|E| > 1{\cdot}20$ were generated by application of the tangent formula (Karle & Karle, 1966). The E map calculated with 161 terms for which $|E| > 1{\cdot}50$ had thirteen maxima which could be assembled to form a partial structure corresponding to the two aromatic rings in the molecule and the bridging C atom. The remaining non-hydrogen atoms were located on two successive Fourier maps, and refinement with anisotropic temperature factors yielded $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}085$. Apart from one benzene-ring H atom, the non-methyl H atoms were located on difference maps. Those not located were included with calculated coordinates assuming C—H = 1·08 Å. The H-atom coordinates were not refined but the methyl and non-methyl H atoms were given refined isotropic temperature factors $U = 0{\cdot}094$ and $0{\cdot}060$ Å^2 respectively. Refinement converged to $R = 0{\cdot}053$ and $R_w = 0{\cdot}062 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

The direct-methods calculations and the least-squares refinements were made with *SHELX*76 (Sheldrick, 1976). In the latter, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the terms weighted according to $w = 1/(\sigma^2|F_o| + 0{\cdot}017|F_c|^2)$. Final atomic coordinates are given in Tables 1 and 2.* Bond lengths and angles are given in Table 3, while some short intermolecular distances are given in Table 5, see also Fig. 2. Fig. 1 has been prepared from the output of *ORTEP* (Johnson, 1965).

Description of the structure

The atom numbering is given in Fig. 1. Ring-*A* atoms and the associated O(3), O(4), O(5), C(11) lie close to one plane (Table 4), while ring-*D* atoms and the associated O(1), O(2), C(9), C(11) lie close to another. The two planes are oriented to give the molecule an approximate propeller shape with the dihedral angle

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35177 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates of the non-hydrogen atoms* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
C(1)	4098 (6)	267 (6)	5135 (2)
C(2)	5467 (6)	715 (6)	5386 (2)
C(3)	5409 (5)	1685 (6)	5843 (2)
C(4)	3988 (6)	2234 (5)	6034 (2)
C(5)	2583 (6)	1810 (6)	5780 (2)
C(6)	2650 (6)	819 (6)	5334 (2)
C(7)	−123 (6)	562 (8)	5273 (3)
C(8)	5419 (8)	−1278 (9)	4484 (2)
C(9)	6736 (6)	2261 (6)	6196 (2)
C(10)	5887 (6)	2791 (5)	6727 (2)
C(11)	4245 (5)	3294 (5)	6526 (2)
C(12)	3062 (6)	3266 (5)	6989 (2)
C(13)	3394 (5)	2573 (5)	7499 (2)
C(14)	5706 (6)	1473 (5)	7124 (2)
C(15)	2315 (6)	2581 (5)	7927 (2)
C(16)	882 (6)	3333 (6)	7869 (2)
C(17)	541 (6)	4041 (6)	7367 (2)
C(18)	1642 (6)	3997 (6)	6938 (2)
C(19)	3445 (8)	2601 (7)	8830 (2)
C(20)	−1604 (7)	3892 (9)	8259 (2)
O(1)	4003 (5)	−692 (5)	4688 (2)
O(2)	1369 (4)	267 (5)	5052 (1)
O(3)	4785 (4)	1870 (4)	7605 (1)
O(4)	2627 (4)	1785 (4)	8412 (1)
O(5)	−75 (4)	3292 (5)	8319 (1)
O(6)	6706 (4)	3903 (4)	7031 (1)

Table 2. *Final atomic coordinates of the hydrogen atoms* ($\times 10^3$)

The atoms are given the same numbering as the atoms to which they are bonded.

	x	y	z
H(2)*	653	19	524
H(5)*	147	249	586
H(7*A*)	−100	7	501
H(7*B*)	−21	7	568
H(7*C*)	−31	177	530
H(8*A*)	519	−201	413
H(8*B*)	617	−36	435
H(8*C*)	599	−192	481
H(9*A*)*	723	320	600
H(9*B*)*	748	140	626
H(11)*	432	453	638
H(14*A*)*	668	85	735
H(14*B*)*	516	58	696
H(17)	−56	462	731
H(18)*	123	448	657
H(19*A*)	363	188	919
H(19*B*)	456	297	867
H(19*C*)	276	358	895
H(20*A*)	−223	379	865
H(20*B*)	−154	507	814
H(20*C*)	−222	327	794
H(O6)*	672	489	682

* These atoms were located by a difference map.

between the perpendiculars to the aromatic rings, *A* and *D*, 61·7 (4)°. This conformation differs from the conformations of the brazilanyl moieties in bi-*O*-trimethyl-*cis*-brazilane (Isaacs & Mackay, 1976) which are butterfly, with a dihedral angle between the aromatic rings of 45·7° (mean value). The conformation of the dihydrobenzindenopyran system with the *cis*-*B*/*C* ring junction is staggered as in the brazilanyl moiety, and the torsion angle, O(3)|C(14),C(10)|C(11), is 60·4 (4)°.

Apart from C(19), the methoxy C atoms are *pseudo* coplanar with their respective aromatic rings (deviations range from 0·016 to 0·253 Å) as noted in comparable structures, for example sceletium (Luhan & McPhail, 1972) and cryptostyline I (Westin, 1972). Ring *C* is envelope with the four atoms C(3), C(4), C(9), C(11) planar within ±0·012 Å and C(10) −0·503 (5) Å out of plane. Ring *B* adopts a skewed conformation with O(3), C(13), C(12), C(11) planar within ±0·004 Å and C(14), C(10) +0·418 (5) and −0·307 (5) Å above and below the plane respectively. In the brazilanyl moiety (Mackay & Isaacs, 1980), ring

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·374 (7)	C(12)—C(13)	1·399 (7)
C(2)—C(3)	1·394 (7)	C(13)—C(15)	1·381 (7)
C(3)—C(4)	1·386 (7)	C(15)—C(16)	1·400 (7)
C(4)—C(5)	1·398 (7)	C(16)—C(17)	1·389 (7)
C(5)—C(6)	1·385 (7)	C(17)—C(18)	1·396 (7)
C(6)—C(1)	1·413 (7)	C(12)—C(18)	1·380 (7)
C(1)—O(1)	1·370 (7)	C(15)—O(4)	1·387 (5)
C(6)—O(2)	1·377 (6)	C(16)—O(5)	1·356 (6)
O(1)—C(8)	1·404 (8)	O(4)—C(19)	1·420 (6)
O(2)—C(7)	1·405 (6)	O(5)—C(20)	1·417 (7)
C(3)—C(9)	1·505 (7)	C(11)—C(12)	1·503 (7)
C(4)—C(11)	1·524 (7)	C(13)—O(3)	1·365 (6)
C(9)—C(10)	1·540 (7)	C(14)—O(3)	1·441 (6)
C(10)—C(11)	1·549 (7)	C(10)—C(14)	1·513 (6)
C(10)—O(6)	1·410 (6)		

C(6)—C(1)—C(2)	119·8 (5)	C(18)—C(12)—C(13)	117·4 (4)
C(6)—C(1)—O(1)	115·3 (5)	C(18)—C(12)—C(11)	121·2 (4)
C(2)—C(1)—O(1)	124·9 (5)	C(11)—C(12)—C(13)	121·3 (4)
C(1)—C(2)—C(3)	119·5 (5)	C(12)—C(13)—C(15)	121·0 (4)
C(2)—C(3)—C(4)	120·5 (5)	C(12)—C(13)—O(3)	122·6 (4)
C(2)—C(3)—C(9)	128·7 (5)	O(3)—C(13)—C(15)	116·4 (4)
C(4)—C(3)—C(9)	110·8 (4)	C(10)—C(14)—O(3)	112·0 (4)
C(3)—C(4)—C(5)	120·9 (5)	C(13)—C(15)—C(16)	120·8 (4)
C(3)—C(4)—C(11)	110·2 (4)	C(13)—C(15)—O(4)	119·6 (4)
C(5)—C(4)—C(11)	128·8 (4)	O(4)—C(15)—C(16)	119·5 (4)
C(4)—C(5)—C(6)	118·1 (5)	C(15)—C(16)—C(17)	118·9 (5)
C(1)—C(6)—C(5)	121·1 (5)	O(5)—C(16)—C(15)	115·8 (4)
C(1)—C(6)—O(2)	114·0 (4)	O(5)—C(16)—C(17)	125·3 (5)
O(2)—C(6)—C(5)	124·9 (5)	C(16)—C(17)—C(18)	119·1 (5)
C(3)—C(9)—C(10)	102·4 (4)	C(12)—C(18)—C(17)	122·7 (5)
C(9)—C(10)—C(11)	104·8 (4)	C(4)—C(11)—C(12)	117·8 (4)
C(9)—C(10)—C(14)	109·6 (4)	C(10)—C(11)—C(12)	112·0 (4)
C(9)—C(10)—O(6)	114·0 (4)	C(1)—O(1)—C(8)	116·8 (5)
C(11)—C(10)—C(14)	108·9 (4)	C(6)—O(2)—C(7)	118·0 (4)
C(11)—C(10)—O(6)	114·3 (4)	C(13)—O(3)—C(14)	115·9 (4)
C(14)—C(10)—O(6)	105·1 (4)	C(15)—O(4)—C(19)	115·5 (4)
C(4)—C(11)—C(10)	101·3 (4)	C(16)—O(5)—C(20)	117·7 (4)

Table 4. *Equations of least-squares planes in which X, Y and Z are expressed in* Å, *and distances of atoms from the planes* (Å × 10^3)

The e.s.d.'s are in parentheses.

Plane *A*: $-0{\cdot}4097X-0{\cdot}8457Y-0{\cdot}3420Z+9{\cdot}2619=0$
Plane *B*: $-0{\cdot}3699X-0{\cdot}8604Y-0{\cdot}3506Z+9{\cdot}3404=0$
Plane *C*: $0{\cdot}0969X+0{\cdot}7789Y-0{\cdot}6196Z+7{\cdot}1006=0$
Plane *D*: $0{\cdot}0684X+0{\cdot}7794Y-0{\cdot}6227Z+7{\cdot}2552=0$

Plane *A*		Plane *B*	
C(12)	+6 (5)	C(11)	−2 (4)
C(13)	−11 (4)	C(12)	+4 (5)
C(15)	+9 (5)	C(13)	−4 (4)
C(16)	−3 (5)	O(3)	+2 (3)
C(17)	−1 (5)	C(10)*	−307 (5)
C(18)	−1 (5)	C(14)*	+418 (5)
C(11)*	−48 (4)		
O(3)*	−60 (3)		
O(4)*	+96 (3)		
O(5)*	−8 (4)		

Plane *C*		Plane *D*	
C(3)	+12 (5)	C(1)	−3 (5)
C(4)	−12 (5)	C(2)	+10 (5)
C(9)	−7 (5)	C(3)	−9 (5)
C(11)	+7 (5)	C(4)	+1 (5)
C(10)*	−503 (5)	C(5)	+6 (5)
		C(6)	−5 (5)
		O(1)*	−3 (5)
		O(2)*	−38 (4)
		C(9)*	−62 (5)
		C(11)*	+10 (5)

* These atoms were not included in the plane calculation.

Table 5. *Intermolecular distances* ≤3·65 Å

E.s.d.'s range from 0·01 to 0·02 Å.

C(3)···C(7^{I})	3·65	O(2)···C(3^{VI})	3·54
C(2)···C(19^{II})	3·46	O(3)···O(6^{II})	3·05
C(5)···C(20^{III})	3·57	O(4)···O(6^{II})	2·82
C(13)···C(14^{IV})	3·64	O(5)···C(8^{VII})	3·33
O(1)···C(19^{V})	3·38	O(6)···C(13^{IV})	3·44
O(1)···O(4^{V})	3·50	O(6)···C(15^{IV})	3·36

Symmetry code

(I)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	(V)	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$
(II)	$1-x$	$-\frac{1}{2}+y$	$1\frac{1}{2}-z$	(VI)	$-\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$
(III)	$-x$	$-\frac{1}{2}+y$	$1\frac{1}{2}-z$	(VII)	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
(IV)	$1-x$	$\frac{1}{2}+y$	$1\frac{1}{2}-z$				

C also is envelope with C(10) −0·31 Å (mean value) out of plane, but ring *B* adopts a severely distorted boat conformation with C(14), C(10) the same side of the plane of the other four atoms at mean distances +0·79 and +0·17 Å respectively. Apparently the dimerization has caused the benzopyran system to adopt a conformation significantly different from that in the haematoxylin derivative.

All the bond lengths are normal (Table 3). As expected the C(sp^3)—O bonds are significantly longer than the C(aromatic)—O bonds, the respective mean values being 1·416 Å (mean deviation 0·011 Å) and 1·371 Å (mean deviation 0·009 Å). About the exocyclic attachments of the methoxy groups substituted at C(1), C(6) and C(16), the angle enclosed by the methyl group is larger than the other, the mean values being 125·0° (mean deviation 0·2°) and 115·0° (mean deviation 0·7°) respectively. Similar features have been noted in other structures including the alkaloids sceletium (Luhan & McPhail, 1972) and cryptostyline I (Westin, 1972). The analogous angles at C(15), however, do not deviate significantly from the regular trigonal value.

The molecules are orientated in the unit cell with their long molecular axes extending along [001], see Fig. 2. The dihedral angles between the perpendiculars to the aromatic rings *A* and *D* and the (010) plane are 32·2 (3) and 38·8 (3)° respectively. There is an intermolecular hydrogen bond in which the hydroxyl O(6) acts as the donor to a methoxy O(4) of a molecule symmetry-related by the twofold screw axis along [010]. The O(4)···O(6) distance of 2·82 (1) Å and the

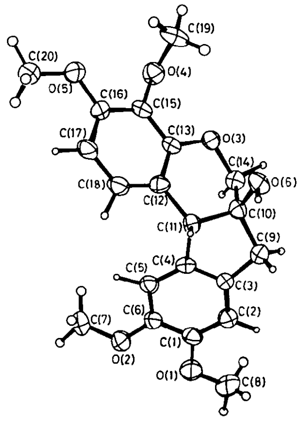

Fig. 1. A perspective view of the molecule with thermal ellipsoids scaled to 50% probability.

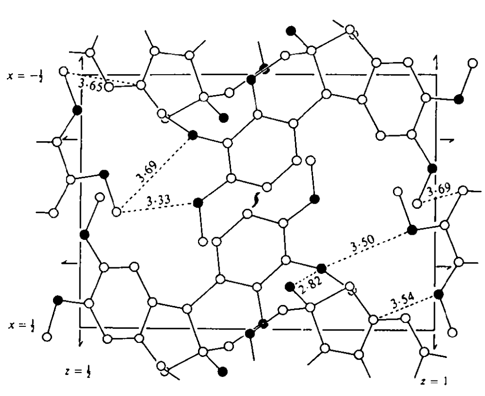

Fig. 2. Projection of the structure along [010].

O(6)—H(6) and O(4)···H(6) distances 1·00 and 1·86 Å with the O(4)···H(6)—O(6) angle 160° are normal. Although the participation of O(4) in the hydrogen bond appears to preserve the symmetry of the exocyclic angles at C(15), O(4) is forced +0·96 (3) Å from the plane of ring *B* with C(19) of the attached methyl group +1·143 (6) Å from the plane. The shortest intermolecular approaches (Table 5) indicate that along [100] and [001] the molecules are held together by van der Waals interactions only.

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Electron-Density Distribution in Urea. A Multipolar Expansion

BY D. MULLEN

Fachrichtung 17.3 *Kristallographie, Universität des Saarlandes, D*-6600 *Saarbrücken,*
Federal Republic of Germany

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Abstract

A multipole deformation density refinement for urea is presented. Deformation-density maps (model maps) so obtained are compared with a pseudo-atom model, as well as with theoretically calculated densities. An analysis is made of errors arising from attributing phases from $F_{c,N}$ to the observed structure amplitudes.

Introduction

The electron-density distribution in urea has been reported in a previous paper (Scheringer, Mullen, Hellner, Hase, Schulte & Schweig, 1978), in which a pseudo-atom model of the valence density was refined.

A multipolar expansion of the valence density (Hirshfeld, 1971) has now been carried out and a comparison will be made between the two models and also with the theoretical densities described by Scheringer *et al.* (1978).

The same X-ray data set (at 123 K) has been used for all refinements.

Multipole refinement

(*a*) *Description of the model*

The expansion of the charge density in the stationary molecule is described by Hirshfeld (1971). The charge density (ρ_{mol}) is expressed in terms of the spherical-

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