

5-Hydroxyindole

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(Received 18 January 1991; accepted 25 September 1991)

Abstract. C_8H_7NO , $M_r = 133.1$, trigonal, $P3_1$, $a = 17.729$ (2), $c = 5.6242$ (6) Å, $V = 1530.9$ (4) Å³, $Z = 9$, $D_x = 1.300$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.081$ mm⁻¹, $F(000) = 630$, $T = 210$ K, $R = 0.0342$, $wR = 0.0324$ for 1395 unique reflections. There are three independent molecular stacks, each centred on a threefold screw axis, with the molecules O—H...O hydrogen bonded. The polar orientation of one stack is inverted with respect to the other two.

Introduction. Black human skin pigments or eumelanins are derived from polymerization of 5,6-dihydroxyindole (DHI) and related precursors. The idea of forming ordered synthetic melanins by controlled solid-state reaction of the precursor molecules has led us to a study of their crystal structures and solid-state packing arrangements. The structure of 1-methyl-5,6-dihydroxyindole (1-Me-DHI) has been reported (Parvez, Kurtz & Williams, 1990). This belongs to the polar rhombohedral space group $R3c$. Preferred darkening of one of the end [001] faces for 1-Me-DHI needles indicates the influence of the crystal structure on the solid-state reactivity. The related compound 5-hydroxyindole was also found to crystallize as trigonal needles, but preferred darkening is less pronounced, so we have determined its structure for comparison.

Experimental. 5-Hydroxyindole was purchased from Sigma Chemical Co. (St Louis, MO) and crystallized from ethanol–ethyl acetate at room temperature. A brownish-white needle fragment was selected with dimensions 0.20 [010] \times 0.34 [$1\bar{1}0$] \times 0.70 [001] mm. A reversible phase transition was found to occur at 195 K. No major change in the c axis was found but peak broadening occurred so that data were collected outside of this temperature regime at 210 K. The unit cell was refined from the setting angles at 210 K of 25 reflections with $23 < 2\theta < 30^\circ$. Measurements were taken on a Siemens R3m/V diffractometer using graphite-monochromated Mo $K\alpha$ radiation in the 2θ range 4.0 – 50.0° ; $0 \leq h \leq 21$, $-21 \leq k \leq 18$, $-6 \leq l \leq$

6. The ω -scan technique was employed with a scan width of 1.2° and variable scan speeds of 2.44 – 29.3° min⁻¹. A total of 5608 reflections were collected, with 1809 independent ($R_{\text{int}} = 2.56\%$) and 1395 observed [$F > 4\sigma(F)$]. A numerical absorption correction was applied following indexing of the crystal faces; the maximum/minimum transmission coefficients were 0.989/0.963. All computations were carried out using the Siemens *SHELXTL-Plus* system (Sheldrick, 1990) with neutral-atom scattering factors for C, N and O (Cromer & Waber, 1974) and H (Stewart, Davidson & Simpson, 1965). The structure was successfully solved by direct methods in the enantiomorphic space group $P3_1$, compatible with Laue symmetry of $\bar{3}$ and the systematic absences $00(l), l \neq 3n$. Three crystallographically independent molecules were revealed. All H atoms were located by difference Fourier. Refinement was by full-matrix least squares on F minimizing $\sum w(|F_o| - |F_c|)^2$, with the weights $w = 1/[\sigma^2(F) + 0.0001F^2]$. The final discrepancy indices were $R = 4.82\%$, $wR = 3.53\%$ for all data, $R = 3.42\%$, $wR = 3.24\%$ for observed data alone; the goodness of fit was 1.47. A total of 301 parameters were refined with all non-H atoms refined anisotropically and H atoms constrained to a riding model, with the exception of the hydroxyl H atoms which were isotropically refined. The data-to-parameter ratio was low, 4.6:1. Although a better ratio could be obtained with unmerged data, the indeterminacy of the enantiomorph (*i.e.* $P3_1$ versus $P3_2$) led to refinement based on merged data rather than individual hkl . The mean Δ/σ in the final cycle was 0.047 with the largest Δ/σ 0.445 for the z coordinate of hydroxyl atom H(5b). The largest difference peak and hole were $\pm 0.10 e \text{ \AA}^{-3}$. Final atomic positional and thermal parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54690 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic displacement coefficients (\AA^2)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor. z coordinate of atom O(5a) fixed to define origin.

Molecule A	x	y	z	U_{eq}
N(1a)	0.0642 (3)	0.3535 (2)	0.3886 (8)	0.081 (2)
C(2a)	0.1239 (3)	0.4059 (3)	0.2255 (10)	0.088 (3)
C(3a)	0.1291 (3)	0.3576 (3)	0.0476 (8)	0.076 (2)
C(4a)	0.0452 (2)	0.1889 (2)	-0.0094 (7)	0.056 (2)
C(5a)	-0.0150 (2)	0.1138 (2)	0.1001 (7)	0.056 (2)
C(6a)	-0.0543 (2)	0.1144 (3)	0.3137 (7)	0.064 (2)
C(7a)	-0.0336 (2)	0.1915 (3)	0.4238 (8)	0.068 (2)
C(8a)	0.0690 (2)	0.2689 (2)	0.0996 (8)	0.057 (2)
C(9a)	0.0285 (2)	0.2686 (3)	0.3166 (8)	0.061 (2)
O(5a)	-0.0419 (2)	0.0322 (2)	0	0.068 (1)
H(5a)	-0.0120 (36)	0.0354 (33)	-0.1254 (84)	0.109 (18)
Molecule B				
N(1b)	0.9558 (2)	0.7386 (2)	0.2034 (8)	0.078 (2)
C(2b)	1.0092 (3)	0.7529 (3)	0.0119 (10)	0.081 (2)
C(3b)	0.9761 (3)	0.6815 (3)	-0.1260 (8)	0.072 (2)
C(4b)	0.8338 (3)	0.5318 (2)	-0.0742 (8)	0.061 (2)
C(5b)	0.7649 (3)	0.4881 (2)	0.0755 (8)	0.060 (2)
C(6b)	0.7549 (3)	0.5265 (3)	0.2803 (8)	0.073 (2)
C(7b)	0.8151 (3)	0.6112 (3)	0.3379 (9)	0.073 (2)
C(8b)	0.8965 (2)	0.6175 (2)	-0.0180 (7)	0.059 (2)
C(9b)	0.8856 (2)	0.6554 (2)	0.1894 (8)	0.063 (2)
O(5b)	0.7021 (2)	0.4030 (2)	0.0230 (8)	0.081 (2)
H(5b)	0.6881 (63)	0.3799 (62)	-0.0952 (161)	0.227 (32)
Molecule C				
N(1c)	0.5070 (3)	0.4584 (2)	-0.3169 (9)	0.089 (2)
C(2c)	0.5717 (4)	0.4854 (3)	-0.1500 (11)	0.091 (3)
C(3c)	0.5578 (3)	0.5299 (3)	0.0245 (9)	0.078 (2)
C(4c)	0.4358 (2)	0.5704 (2)	0.0687 (7)	0.061 (2)
C(5c)	0.3633 (2)	0.5606 (2)	-0.0422 (8)	0.063 (2)
C(6c)	0.3332 (3)	0.5154 (3)	-0.2555 (8)	0.074 (2)
C(7c)	0.3769 (3)	0.4779 (3)	-0.3611 (8)	0.078 (2)
C(8c)	0.4813 (3)	0.5321 (2)	-0.0361 (8)	0.064 (2)
C(9c)	0.4502 (3)	0.4866 (2)	-0.2499 (8)	0.072 (2)
O(5c)	0.3145 (2)	0.5956 (2)	0.0512 (7)	0.077 (2)
H(5c)	0.3449 (25)	0.6299 (26)	0.1652 (70)	0.075 (13)

Table 2. Bond lengths (\AA) angles ($^\circ$) and intermolecular contacts (\AA)

	Mol. A	Mol. B	Mol. C
N(1)—C(2)	1.357 (6)	1.372 (7)	1.370 (8)
N(1)—C(9)	1.370 (6)	1.377 (4)	1.382 (8)
C(2)—C(3)	1.349 (8)	1.344 (7)	1.356 (8)
C(3)—C(8)	1.420 (5)	1.430 (5)	1.418 (7)
C(4)—C(5)	1.368 (4)	1.362 (6)	1.359 (6)
C(5)—C(6)	1.392 (6)	1.394 (7)	1.393 (6)
C(5)—O(5)	1.395 (5)	1.395 (5)	1.394 (6)
C(6)—C(7)	1.373 (7)	1.376 (5)	1.383 (8)
C(7)—C(9)	1.393 (5)	1.377 (6)	1.378 (8)
C(8)—C(4)	1.403 (6)	1.399 (5)	1.417 (7)
C(8)—C(9)	1.414 (6)	1.406 (6)	1.399 (6)
Angles ($^\circ$)			
C(2)—N(1)—C(9)	109.1 (4)	108.8 (4)	108.7 (5)
N(1)—C(2)—C(3)	110.1 (4)	110.1 (3)	109.6 (6)
C(2)—C(3)—C(8)	107.4 (4)	107.1 (4)	107.2 (4)
C(5)—C(4)—C(8)	118.8 (4)	118.5 (4)	118.5 (4)
C(4)—C(5)—C(6)	122.1 (4)	122.1 (3)	122.3 (5)
C(4)—C(5)—O(5)	121.6 (3)	119.4 (4)	121.9 (4)
C(6)—C(5)—O(5)	116.3 (3)	118.6 (4)	115.8 (4)
C(5)—C(6)—C(7)	120.8 (3)	120.5 (4)	120.1 (5)
C(6)—C(7)—C(9)	117.9 (4)	117.8 (4)	118.3 (4)
C(3)—C(8)—C(4)	135.2 (4)	134.3 (4)	134.0 (4)
C(3)—C(8)—C(9)	106.3 (4)	106.9 (3)	107.3 (4)
C(4)—C(8)—C(9)	118.5 (3)	118.8 (3)	118.6 (4)
N(1)—C(9)—C(8)	107.2 (3)	107.1 (3)	107.1 (4)
N(1)—C(9)—C(7)	130.9 (4)	130.7 (4)	130.7 (4)
C(7)—C(9)—C(8)	121.9 (4)	122.3 (3)	122.2 (5)
Intermolecular contacts (\AA)			
Mol. A	Mol. B	Mol. C	
O(5a)—H—O(5a')	O(5b)—H...O(5b ^m)	O(5c)—H...O(5c')	2.724 (4)
O(5a)...	O(5b)...	O(5c)...	2.724 (4)
O(5a)...	O(5b)...	O(5c)...	2.634 (4)
O(5a)...	O(5b)...	O(5c)...	2.634 (4)
O(5a)...	O(5b)...	O(5c)...	2.710 (4)
O(5a)...	O(5b)...	O(5c)...	2.710 (4)

Symmetry code: (i) $y - x, -x, z - \frac{1}{2}$; (ii) $-y, x - y, z + \frac{1}{2}$; (iii) $1 + y - x, 1 - x, z - \frac{1}{2}$; (iv) $1 - y, x - y, z + \frac{1}{2}$; (v) $1 - y, 1 + x - y, z + \frac{1}{2}$; (vi) $y - x, 1 - x, z - \frac{1}{2}$.

Discussion. The three independent molecules (*A*, *B* and *C*) of the asymmetric unit are shown (50% probability thermal ellipsoids) with labeling scheme in Fig. 1, with the c axis vertical. Each molecule associates through O—H...O hydrogen bonds with molecules which are translated by a threefold

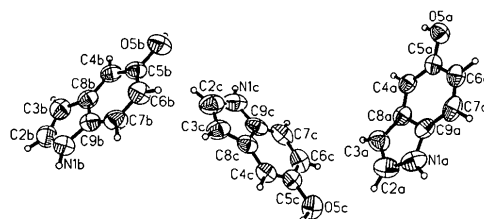
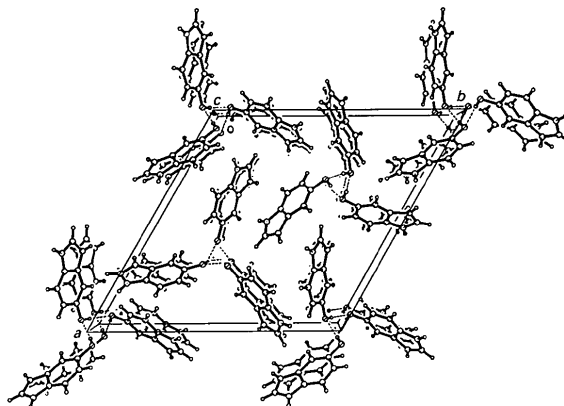
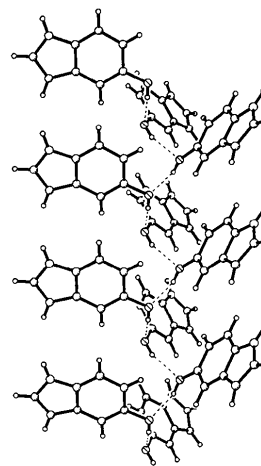


Fig. 1. 5-Hydroxyindole. Atomic labeling scheme and 50% probability thermal ellipsoids.

Fig. 2. Unit-cell packing diagram viewed down the c axis.Fig. 3. Molecular stack *A*, showing the 3_1 helix of O—H...O bonding.

screw axis. Thus three molecular stacks are formed about the three independent 3₁ axes of the unit cell, a packing diagram of which is shown in Fig. 2. Two of the stacks (from molecules *A* and *B*) have the same effective polarity with the O—H...O bonds directed along negative *c* (of the arbitrarily chosen *P*₃, enantiomorph), whereas molecular stack *C* has the reverse orientation. The stack composed of molecules *A* is shown in Fig. 3. In 1-Me-DHI the packing is again dictated by hydrogen bonds and the molecules also associate in trigonal stacks with the hydrophilic groups at the center. In this case all 5-OH groups are linked to each other around a pure threefold axis and 6-OH...5-OH contacts link the molecules along the *c* glide. All molecules have the same polar orientation and the [001] and [00 $\bar{1}$] faces are more readily chemically differentiated.

Bond lengths, angles and intermolecular contacts for 5-hydroxyindole are given in Table 2. No significant differences are found between the three independent molecules, with the exception of the exocyclic C—C—O angles which are influenced by the intermolecular hydrogen bonds. A deviation of more than 2.0° is found for molecule *B*, with C(6)—C(5)—O(5)

greater and C(4)—C(5)—O(5) smaller than in molecules *A* or *C*. The average molecular dimensions for 5-hydroxyindole were not found to be significantly different from 1-Me-DHI or the mean values for 17 other indole structures in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983).

We are grateful to University of Waterloo and NSERC of Canada for partial support of this work. IDW acknowledges a grant from the DARPA (order No. 6614).

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Acta Cryst. (1992). **C48**, 726–728

Structure of Ursolic Acid Ethanol Solvate

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(Received 2 July 1991; accepted 21 October 1991)

Abstract. C₃₀H₄₈O₃·C₂H₆O, *M_r* = 502.78, orthorhombic, *P*2₁2₁2₁, *a* = 7.199 (1), *b* = 12.157 (2), *c* =

33.888 (2) Å, *V* = 2966 Å³, *Z* = 4, *D_x* = 1.13 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 5.3 cm⁻¹, *F*(000) = 1112, *T* = 298 K, *R* = 0.050 for 1632 reflections with *I* > 3σ(*I*). The rings adopt chair conformations. Crystal

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