Structure of 5-Chloro-3-hydroxy-3-methyl-2(3*H*)-indolone, C₉H₈ClNO₂

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Abstract. $M_r = 197.6$, monoclinic, $P2_1/c$, $a = 7.625$ (5), $b = 9.968$ (7), $c = 11.652$ (8) Å, $\beta = 91.61$ (6)°, $V = 885$ (2) Å³, $D_x = 1.482$, $D_m = 1.400$ Mg m⁻³, $Z = 4$, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.391$ mm⁻¹, $F(000) = 408$, $T = 300$ K, $R = 0.029$ for 1227 observed reflections. The molecule is not planar. The structure is stabilized by the formation of dimers. The $-$OH group is engaged in an intermolecular hydrogen bond with the carbonyl O [O⋯O 2.667 (2) Å, $\angle$O–H⋯O 162 (2)°], and the $-$NH group with the hydroxyl O [N⋯O 2.874 (3) Å, $\angle$N–H⋯O 170 (2)°]. Alternating layers of oppositely oriented molecules are piled in stacks along the a axis.

Introduction. Indole and its various substituted products have long been known for their interesting chemical and physiological activities. Recently, indole chemistry has received special attention and a number of substituted indole compounds have been synthesized for the investigation of their physicochemical and biological activities. However, the characterization of these compounds sometimes poses special problems.

The title compound was synthesized by Chatterjee, Pandit & Sarkar (1982) and various methods of characterization were employed. The study of this compound by ¹H NMR spectroscopy cannot conclusively prove the existence of $-$OH and $-$NH, because their signals are absent due to the high rate of the proton-exchange reaction in deuterated solvents. One of our aims in the present study is to establish the presence of such groups in this compound, which will help in its complete characterization. Also, there are no X-ray data available in the literature for halogen-substituted oxindole compounds.

The present study also complements the interpretation offered for the biological activities of various substituted indoles (Sundberg, 1970), since these activities are dependent both on the substituent groups and on the stereochemical arrangement. X-ray crystal-

lographic analysis of the title compound will therefore be of importance to biochemists in helping to explain biochemical reactions of substituted indoles.

Experimental. Colourless crystals (m.p. 513 K) were obtained by slow evaporation of a solution of the substance in acetone. Crystal 0.4 × 0.3 × 0.175 mm. CAD-4 diffractometer, ω–2θ scan, $4° \leq 2\theta \leq 50°$, graphite-monochromatized Mo $K\alpha$ radiation. Density measured by flotation using a mixture of tribromomethane and bromoform. Cell constants obtained from a least-squares fit to the setting angles of 25 reflections taken from all octants in reciprocal space. Range of h,k,l: $h -9 \rightarrow +9$, $k\, 0 \rightarrow 11$, $l\, 1 \rightarrow 13$. The observed systematic absences uniquely determined the space group as $P2_1/c$. 1552 measured reflections; 325 with $I < 4\sigma(I)$ classed as unobserved and excluded from subsequent refinement. Lorentz and polarization corrections applied; no absorption correction. The position of the Cl atom was obtained from a Patterson map and a three-dimensional Cl-phased Fourier map then revealed the positions of all the non-hydrogen atoms. A few cycles of isotropic refinement gave $R = 0.124$. The positions of three H atoms associated with the benzene ring were generated from the known geometry around C atoms; the other H atoms were located from the difference map, and given the same isotropic temperature factors as the atoms to which they are bonded. After a few cycles of anisotropic full-matrix least-squares refinement of non-hydrogen atoms (H atoms isotropic) final $R = 0.029$ for 150 parameters; $wR = 0.020$; $S = 0.81$. Function minimized during refinement was $\sum w(\Delta F)^2$, with $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0.38$, $(\Delta/\sigma)_{ave} = 0.04$. Max. and min. heights in final difference map ± 0.2 e Å⁻³. No correction for secondary extinction. Scattering factors of the heavy atoms taken from *International Tables for X-ray Crystallography* (1962), for H atoms from Stewart, Davidson & Simpson (1965). Programs used from *X-RAY ARC* (Vickery, Bright & Mallinson, 1973), modified for the B 6700 computer.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Cl	8771 (1)	1649 (1)	2986 (1)	3·6
O(1)	5205 (2)	−4090 (1)	6389 (1)	3·0
O(2)	5359 (2)	−3295 (1)	3935 (1)	2·3
N(1)	6117 (2)	−1910 (1)	6539 (1)	2·1
C(1)	8042 (2)	624 (2)	4094 (2)	2·3
C(2)	7730 (2)	1190 (2)	5146 (2)	2·5
C(3)	7098 (2)	410 (2)	6030 (2)	2·3
C(4)	6808 (2)	−927 (2)	5802 (1)	1·9
C(5)	7123 (2)	−1500 (2)	4745 (1)	1·9
C(6)	7764 (2)	−730 (2)	3871 (1)	2·3
C(7)	5892 (2)	−3095 (2)	5991 (1)	2·1
C(8)	6664 (2)	−2977 (2)	4789 (1)	2·0
C(9)	8248 (3)	−3893 (2)	4723 (2)	3·1

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–Cl	1·749 (2)	O(1)–C(7)	1·220 (2)
C(1)–C(2)	1·377 (3)	O(2)–C(8)	1·423 (2)
C(2)–C(3)	1·388 (3)	C(8)–C(9)	1·518 (3)
C(3)–C(4)	1·376 (3)	N(1)–C(7)	1·351 (2)
C(4)–C(5)	1·385 (2)	C(7)–C(8)	1·539 (2)
C(5)–C(6)	1·375 (2)	C(8)–C(5)	1·514 (3)
C(4)–N(1)	1·415 (2)	C(1)–C(6)	1·390 (3)
C(6)–C(1)–C(2)	122·3 (2)	C(8)–C(5)–C(6)	130·9 (2)
C(1)–C(2)–C(3)	120·2 (2)	N(1)–C(4)–C(3)	127·9 (2)
C(2)–C(3)–C(4)	117·2 (2)	Cl–C(1)–C(2)	119·0 (1)
C(3)–C(4)–C(5)	122·7 (2)	Cl–C(1)–C(6)	118·7 (1)
C(4)–C(5)–C(6)	120·2 (2)	O(1)–C(7)–C(8)	126·0 (2)
C(5)–C(6)–C(1)	117·4 (2)	O(2)–C(8)–C(7)	109·9 (1)
C(4)–N(1)–C(7)	111·3 (1)	O(2)–C(8)–C(9)	111·8 (1)
N(1)–C(7)–C(8)	108·5 (1)	C(5)–C(8)–C(9)	113·5 (1)
C(7)–C(8)–C(5)	101·5 (1)	C(7)–C(8)–C(9)	109·0 (1)
C(5)–C(4)–N(1)	109·3 (1)	O(1)–C(7)–N(1)	125·6 (2)
C(8)–C(5)–C(4)	108·9 (1)	O(2)–C(8)–C(5)	110·5 (1)
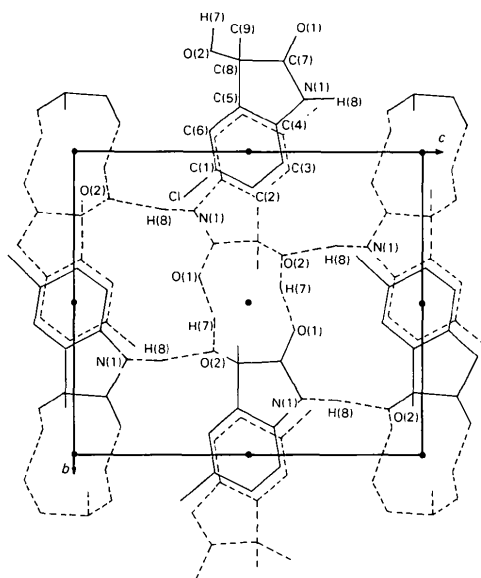
Fig. 1. Projection of the structure on the bc plane. For clarity, only the H atoms involved in hydrogen bonds are shown.

Discussion. The atomic coordinates are listed in Table 1 and interatomic distances and angles in Table 2.* The weighted average of the bond lengths within the benzenoid ring is 1·382 (3) Å. The Cl attached to the benzene ring lies almost in the same plane with a deviation of 0·0611 (6) Å.

The interesting feature of the structure is that the five-membered ring of the oxindole nucleus is a little puckered. The N(1),C(4),C(5) and N(1),C(7),C(8) least-squares planes make a dihedral angle of 5·6 (2)°. The C(4),N(1),C(7),O(1) system is planar as a result of the delocalized π-electron system of the benzenoid ring which extends over atoms N(1), C(7) and O(1). The bond distance N(1)–C(7) = 1·351 (2) Å is shorter than a single bond (1·47 Å). This shortening is caused by the resonance conjugation of the N electron pair with the carbonyl group (James & Williams, 1972). N(1) is only 0·026 (2) Å out of the ring plane indicating that it is sp^2- hybridized.

The interesting feature of the molecular packing is that the −OH group is engaged in an intermolecular hydrogen bond [O(2)–H(7)$\cdots$O(1) = 2·667 (2) Å and $\angle$O(2)–H(7)$\cdots$O(1) = 162 (2)°] which links the molecules to form dimers about centres of symmetry (see Fig. 1). Packing of the dimers is determined by the hydrogen bond N(1)–H(8)$\cdots$O(2) = 2·874 (3) Å, $\angle$N(1)–H(8)$\cdots$O(2) = 170 (2)°.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances involving H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42263 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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