

## Structure of 3,5,7-Trichloro-3-methyl-2(3H)-indolone, C<sub>9</sub>H<sub>6</sub>Cl<sub>3</sub>NO

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**Abstract.**  $M_r = 250.5$ , monoclinic,  $P2_1/c$ ,  $a = 10.069$  (1),  $b = 10.064$  (3),  $c = 11.405$  (3) Å,  $\beta = 113.75$  (2)°,  $V = 1058$  (1) Å<sup>3</sup>,  $D_x = 1.572$ ,  $D_m = 1.540$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 8.26$  cm<sup>-1</sup>,  $F(000) = 504$ ,  $T = 303$  K,  $R = 0.037$  for 1591 observed reflections. The molecule is nearly planar [dihedral angle between the planes of the two rings 1.2 (1)°] and the structure is stabilized by the formation of dimers through centrosymmetric pairs of intermolecular hydrogen bonds [N—H...O 2.847 (3) Å,  $\angle \text{N—H...O } 169$  (3)°].

**Introduction.** Indole and its various substituted products are known for their interesting chemical and biological activities. Electrophilic substitution of 3-methylindole (skatole) with sulfuryl chloride in the presence of acetic acid produces a series of oxindole compounds (Chatterjee, Pandit & Sarkar, 1982). We describe here the second compound found. The crystal structure of the first compound, 5-chloro-3-hydroxy-3-methyl-2(3H)-indolone, has already been reported (Chakraborty, Talapatra & Chatterjee, 1985) and the work on others is in progress.

The study of the title compound by <sup>1</sup>H NMR spectroscopy cannot conclusively prove the existence of the —NH group because its signals are absent due to the high rate of the proton-exchange reaction in deuterated solvents. One of our aims is to establish the presence of such a group in this compound, which will help in its complete characterization. Another aim is to provide X-ray data on halogen-substituted oxindole compounds, as these data are not available in the literature.

Since the chemical and biological activities of the compound (Sundberg, 1970) are dependent both on the substituent groups and on the stereochemical arrangement of them, the X-ray crystallographic analysis of the title compound will be of importance to biochemists for explaining biochemical reactions.

**Experimental.** Single crystals of this compound were obtained by slow evaporation of a solution of the substance in acetone. Crystal 0.3 × 0.2 × 0.15 mm. Intensities measured by  $\omega$ - $2\theta$  scan in the range  $4^\circ \leq 2\theta \leq 50^\circ$  on a CAD-4 diffractometer with

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  $h, k, l$ :  $h -11 \rightarrow 10$ ,  $k 0 \rightarrow 11$ ,  $l 0 \rightarrow 13$ . The observed systematic absences uniquely determine the space group  $P2_1/c$ . Out of 1852 reflections 261 had intensities less than  $4\sigma(I)$  and were classed as unobserved and excluded from subsequent refinement. Lorentz and polarization corrections were applied but no absorption or extinction corrections were made. The H atoms associated with the benzene ring were generated from the known geometry around C atoms. The other H atoms were located from a difference map and given the same isotropic temperature factors as the atoms to which they are bonded. Structure solved, after various trials, by direct methods using the program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The refinement was carried out first with isotropic and then with anisotropic temperature factors until  $R = 0.037$  and  $wR = 0.035$  with 151 parameters.  $S = 0.63$ . Function minimized during refinement was  $\sum w(\Delta F)^2$ , with  $w = \{1 + [(F_o - 50.)/50]^2\}^{-1}$ .  $(\Delta/\sigma)_{\text{max}} = 0.49$ ,  $(\Delta/\sigma)_{\text{ave}} = 0.12$ . Max. and min. heights in final difference map  $\pm 0.5 e \text{ \AA}^{-3}$ . Scattering factors of non-hydrogen atoms taken from *International Tables for X-ray Crystallography* (1968) and for H atoms from Stewart, Davidson & Simpson (1965). Programs from *X-RAYARC* (Vickery, Bright & Mallinson, 1973), modified for the B 6700 computer.

**Discussion.** The atomic coordinates, bond lengths and bond angles with their estimated standard deviations are given in Tables 1 and 2.†

The relevant point of the structure is that the five-membered ring is almost planar, unlike the first compound, 5-chloro-3-hydroxy-3-methyl-2(3H)-indolone (Chakraborty *et al.*, 1985). Here the angle

† 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 42270 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

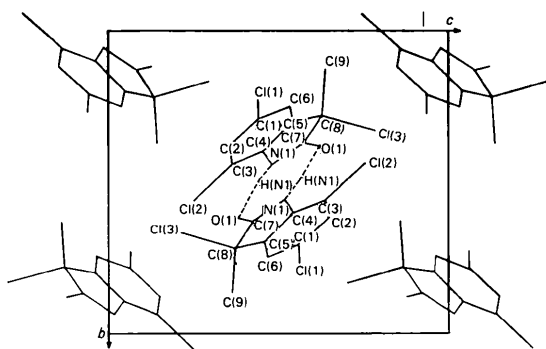
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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors
$$B_{eq} = \frac{4}{3} \sum_i \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cl(1)	2583 (1)	2284 (1)	4420 (1)	6.4
Cl(2)	5485 (1)	5517 (1)	2491 (1)	5.3
Cl(3)	8639 (1)	3324 (1)	7931 (1)	5.5
O(1)	10477 (2)	3800 (2)	6253 (2)	5.4
N(1)	8176 (3)	4350 (2)	4811 (2)	4.2
C(1)	4206 (3)	2900 (3)	4458 (3)	4.3
C(2)	4180 (3)	3820 (3)	3547 (3)	4.3
C(3)	5480 (3)	4345 (3)	3603 (3)	4.0
C(4)	6764 (3)	3944 (3)	4558 (3)	3.7
C(5)	6777 (3)	2995 (3)	5448 (3)	3.8
C(6)	5500 (3)	2464 (3)	5408 (3)	4.4
C(7)	9171 (3)	3692 (3)	5826 (3)	4.1
C(8)	8318 (3)	2745 (3)	6338 (3)	4.0
C(9)	8840 (4)	1289 (3)	6390 (4)	5.4

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

C(1)—C(2)	1.383 (4)	C(4)—N(1)	1.394 (4)
C(1)—Cl(1)	1.733 (3)	N(1)—C(7)	1.360 (4)
C(1)—C(6)	1.389 (4)	C(7)—C(8)	1.546 (4)
C(2)—C(3)	1.389 (4)	C(5)—C(8)	1.496 (4)
C(3)—C(4)	1.374 (4)	O(1)—C(7)	1.209 (4)
C(4)—C(5)	1.389 (4)	C(8)—C(9)	1.550 (4)
C(5)—C(6)	1.376 (4)	C(3)—Cl(2)	1.733 (3)
		C(8)—Cl(3)	1.809 (3)
C(2)—C(1)—C(6)	121.7 (3)	C(5)—C(4)—N(1)	109.9 (3)
C(1)—C(2)—C(3)	119.1 (3)	N(1)—C(4)—C(3)	129.4 (3)
C(2)—C(3)—C(4)	119.6 (3)	O(1)—C(7)—C(8)	125.6 (3)
C(3)—C(4)—C(5)	120.7 (3)	O(1)—C(7)—N(1)	127.5 (3)
C(4)—C(5)—C(6)	120.6 (3)	Cl(1)—C(1)—C(2)	119.1 (3)
C(1)—C(6)—C(5)	118.3 (3)	Cl(1)—C(1)—C(6)	119.1 (3)
C(4)—N(1)—C(7)	112.0 (3)	Cl(2)—C(3)—C(4)	120.1 (2)
N(1)—C(7)—C(8)	106.9 (3)	Cl(2)—C(3)—C(2)	120.3 (3)
C(5)—C(8)—C(7)	102.8 (3)	C(7)—C(8)—C(9)	111.4 (3)
C(4)—C(5)—C(8)	108.4 (3)	C(5)—C(8)—C(9)	115.4 (3)
C(6)—C(5)—C(8)	131.1 (3)	Cl(3)—C(8)—C(7)	106.2 (2)
		Cl(3)—C(8)—C(9)	110.3 (2)
		Cl(3)—C(8)—C(5)	110.2 (2)

Fig. 1. Projection of the structure on the  $bc$  plane. Hydrogen bonds are indicated by dotted lines.

between the N(1),C(7),C(8) and N(1),C(4),C(5) least-squares planes is  $1.51 (1)^\circ$ , compared to  $5.6 (2)^\circ$  for the first compound. The dihedral angle between the planes through the two rings, *i.e.*  $[C(1)C(2)C(3)C(4)C(5)-C(6)] \wedge [N(1)C(4)C(5)C(7)C(8)]$  is  $1.2 (1)^\circ$ , which indicates that the indole nucleus is almost planar.

The C(4),N(1),C(7),O(1) least-squares plane shows that these atoms and H(N1) do not deviate from it by more than  $0.03 \text{ \AA}$ . This planarity and the shortening of N(1)—C(7) [ $1.360 (4) \text{ \AA}$ ] is due to the delocalized  $\pi$ -electron system of the benzenoid ring which extends over atoms N(1), C(7) and O(1) (James & Williams, 1972). The bond distance O(1)—C(7) [ $1.209 (4) \text{ \AA}$ ] clearly shows double-bond character, but this is not in agreement with a  $\pi$  delocalization of the benzenoid electrons to O(1). The C(8)—Cl(3) distance is longer than C(1)—Cl(1) and C(3)—Cl(2), because C(8) is an  $sp^3$  carbon, while C(1) and C(3) are  $sp^2$ .

The interesting feature of the molecular packing is that the —NH group of the five-membered ring is engaged in an intermolecular hydrogen bond with the carbonyl moiety (see Fig. 1). The molecular packing clearly shows that the molecules dimerize about a centre of symmetry and are linked by a pair of hydrogen bonds with N(1)—H(N1)...O(1)  $2.847 (3) \text{ \AA}$  and  $\angle N(1)—H(N1)...O(1) 169 (3)^\circ$ .

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