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Structure of 3-Chlorotropolone

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Abstract. $C_7H_5ClO_2$, $M_r = 156{\cdot}6$, monoclinic, $P2_1/c$, $a = 8{\cdot}476\,(2)$, $b = 12{\cdot}241\,(2)$, $c = 8{\cdot}170\,(2)$ Å, $\beta = 126{\cdot}47°$, $V = 681{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}525$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 44{\cdot}63$ cm^{-1}, $F(000) = 320$, $T = 293$ K, $R = 0{\cdot}046$ for 833 reflections with $I > 3\sigma(I)$. The hydroxylic proton forms a bifurcated hydrogen bond with carbonyl O atoms, one branch intramolecular and the other intermolecular. The latter intermolecular branches form a hydrogen-bonded dimer, which is roughly planar.

Introduction. The structures of tropolone and some tropolone derivatives have been studied. It has been shown that 5-isopropyltropolone (Berg, Karlasson, Pilotti & Wiehager, 1976) as well as tropolone (Shimanouchi & Sasada, 1973) forms a bifurcated hydrogen bond with the carbonyl O atoms, one branch being intramolecular and other intermolecular. On the other hand, 4-isopropyltropone does not form a dimer, but O···O hydrogen bonds of 2·8 Å link the molecules in a chain (Derry & Hamor, 1972).

Very recently, we have measured the electronic spectra of the isolated 3-chlorotropolone (Tsuji, Sekiya, Nishimura, Mori & Takeshita, 1991) and 3-bromotropolone (Sekiya, Sasaki, Nishimura, Mori & Takeshita, 1990). The observation of tunnel splitting provides conclusive evidence for the delocalization of the proton. We have found that the hydroxylic proton is delocalized in 3-chlorotropolone, whereas the proton is localized in 3-bromotropolone. It has been suggested that the localization of the hydroxylic proton strongly depends on the planarity of the molecule. In order to examine the effect of the substitution of a Cl atom on the molecular and crystal structure, an X-ray analysis has been performed for crystalline 3-chlorotropolone.

Experimental. 3-Chlorotropolone was synthesized following a known method (Nozoe, Seto, Ito, Sato & Katano, 1953). 3-Chlorotropolone crystals were prepared in a sealed Pyrex tube by heating at about 393 K with a coiled heater followed by gradual cooling. A crystal of 0·12 × 0·12 × 0·12 mm was sealed in a thin-walled Lindemann glass tube to minimize loss by sublimation. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters from setting of 15 reflections with $13{\cdot}52 \le \theta \le 17{\cdot}57°$. ω–2θ scan technique used to collect intensities of 1107 independent reflections with $2 \le \theta \le 60°$ $(-9 \le h \le 9,\ 0 \le k \le 13,\ 0 \le l \le 9)$, 833 of which were considered as observed $[I > 3\sigma(I)]$. Three standard reflections monitored every 3600 s, no significant variation in intensity during data collection; intensities not corrected for absorption. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); H-atom positions determined by difference Fourier synthesis. Refinement by full-matrix least-squares method on F. C, O and Cl atoms anisotropic, H atoms isotropic and fixed at 4·0 Å^2. Final conventional $R = 0{\cdot}046$, $wR = 0{\cdot}084$, $w = 4F_o^2/[\sigma(F_o^2)]^2$; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·60; final difference Fourier height maximum (absolute value) 0·21 e Å^{-3}, refined secondary extinction value $g = 2{\cdot}9931 \times 10^{-5}$. Atomic scattering factors from Cromer & Waber (1974). Computation on PDP11/23 computer using Enraf–Nonius *SDP-Plus* (Frenz, 1985) and *ORTEP*II (Johnson, 1976) programs.

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Discussion. Fig. 1 shows the structure of the hydrogen-bond dimer and the numbering of the atoms. The final atomic coordinates and isotropic temperature factors are given in Table 1. Bond lengths and angles are listed in Table 2.* The formal single bonds C(1)—C(2) and C(2)—C(3) are significantly longer than the formal single bonds C(4)—C(5) and C(6)—C(7). The formal double bonds are longer than the pure double-bond length of 1·337 Å (Weast, 1987), yet they are shorter than the formal single bonds. The bond angle C(2)—C(3)—Cl is smaller than the bond angle C(4)—C(3)—Cl. This suggests that the steric repulsion between the O(2) atom and the Cl atom is insignificant, although the interatomic distance between O(2) and Cl is shorter than the sum of the respective van der Waals radii (Pauling, 1942). The maximum deviation of the C atom from the least-squares plane is less than 0·01 Å. Thus the deviation of the molecular structure of 3-chlorotropolone from that of tropolone is very small.

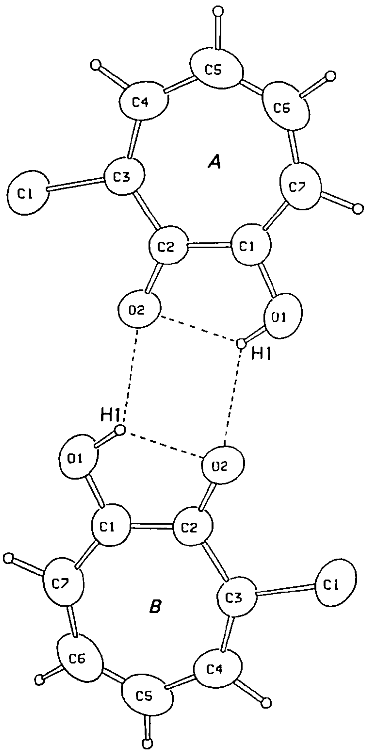

Fig. 1. Structure of the dimer with atomic numbering. Hydrogen bonds are indicated by broken lines.

Table 1. *Final atomic coordinates and equivalent anisotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = 3/4(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta).$$

	x	y	z	B_{eq}
C(1)	0·3951 (4)	0·0102 (3)	1·1924 (4)	4·54 (8)
C(2)	0·2734 (4)	0·0824 (3)	1·0209 (4)	4·03 (7)
C(3)	0·3574 (4)	0·1687 (3)	0·9753 (4)	4·22 (7)
C(4)	0·5455 (4)	0·2019 (3)	1·0680 (4)	5·06 (8)
C(5)	0·7184 (4)	0·1604 (4)	1·2240 (5)	6·0 (1)
C(6)	0·7381 (5)	0·0756 (3)	1·3614 (5)	6·0 (1)
C(7)	0·5940 (4)	0·0076 (3)	1·3374 (5)	5·38 (9)
Cl	0·1796 (1)	0·24384 (8)	0·7619 (1)	6·24 (3)
O(1)	0·2914 (3)	−0·0657 (2)	1·2101 (3)	6·28 (7)
O(2)	0·0926 (3)	0·0668 (2)	0·9147 (3)	5·17 (6)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(2)—C(1)	1·446 (4)	C(7)—C(6)	1·392 (6)
C(2)—C(3)	1·442 (5)	C(6)—C(5)	1·356 (6)
C(2)—O(2)	1·248 (3)	C(5)—C(4)	1·403 (4)
C(1)—C(7)	1·368 (4)	C(4)—C(3)	1·458 (4)
C(1)—O(1)	1·345 (5)	C(3)—Cl	1·742 (3)
C(1)—C(2)—C(3)	121·4 (2)	C(7)—C(6)—C(5)	129·0 (3)
C(1)—C(2)—O(2)	117·0 (3)	C(6)—C(5)—C(4)	128·1 (4)
C(3)—C(2)—O(2)	121·6 (2)	C(5)—C(4)—C(3)	129·0 (4)
C(2)—C(1)—C(7)	130·9 (4)	C(2)—C(3)—C(4)	132·3 (3)
C(2)—C(1)—O(1)	113·0 (2)	C(2)—C(3)—Cl	112·3 (2)
C(7)—C(1)—O(1)	116·0 (3)	C(4)—C(3)—Cl	115·6 (3)
C(1)—C(7)—C(6)	129·4 (4)		

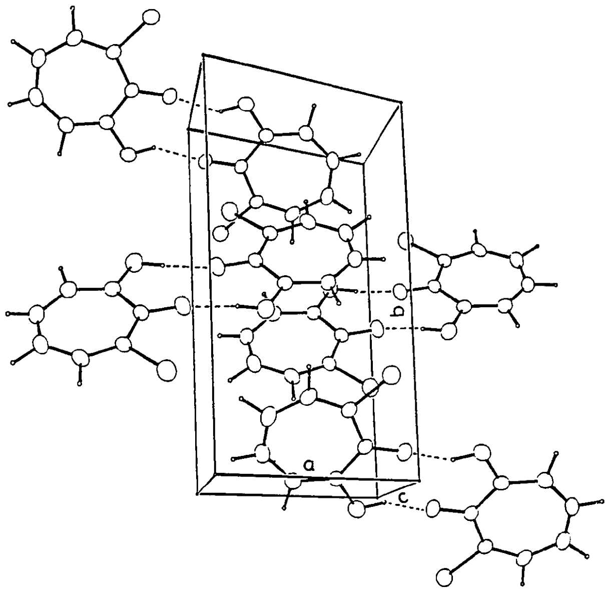

Fig. 2. Crystal packing. The broken lines indicate the intermolecular hydrogen bonds.

The crystal packing is shown in Fig. 2. The hydroxyl group forms a bifurcated hydrogen bond with carbonyl O atoms as shown in Fig. 1. The intermolecular hydrogen bonds form a dimer, in which two molecules are roughly planar. A similar dimer has been found in crystalline tropolone (Shimanouchi & Sasada, 1973) and 5-isopropyltropolone (Berg, Karlasson, Pilotti & Wiehager, 1976). The distances O(1)(*A*)—O(2)(*B*) and H(1)(*A*)—

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54299 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(2)(*B*) are 2·773 and 2·175 Å, respectively. These values are somewhat larger than the coresponding values of 2·754 and 1·98 Å and 2·775 and 1·980 Å for the tropolone dimer and the 5-isopropyltropolone dimer, respectively. This implies that the substitution of a Cl atom in the 3-position of the ring has slightly weakened the strength of the intermolecular hydrogen bond.

The hydroxylic proton has been found to be delocalized in the isolated 3-chlorotropolone (Tsuji, Sekiya, Nishimura, Mori & Takeshita, 1991) and tropolone (Tomioka, Mikami & Ito, 1983), whereas the hydroxylic proton is localized on the O atom in crystalline 3-chlorotropolone and tropolone (Shimanouchi & Sasada, 1973). The localization of the hydroxylic proton in crystalline tropolone and 3-chlorotropolone suggests that the effective potential energy barrier to proton tunneling has increased due to the formation of the intermolecular hydrogen bonds.

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Structure of 1-Ethyl-5-nitroimidazole Hydrochloride Monohydrate at 100 K

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Abstract. $C_5H_8N_3O_2^+.Cl^-.H_2O$, $M_r = 195{\cdot}60$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}436\,(3)$, $b = 11{\cdot}023\,(7)$, $c = 12{\cdot}482\,(7)$ Å, $V = 885{\cdot}6\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}46$, $D_x = 1{\cdot}467$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}403$ mm^{-1}, $F(000) = 408$, $T = 100$ K, final $R = 0{\cdot}020$ for 1038 unique observed $[F \geq 4\sigma(F)]$ reflections. Protonation of N3 is responsible for the opening of the N3 ring angle relative to the corresponding average angle of the unprotonated 5-nitroimidazoles or to N3 in imidazole. The influence of the N3 proton substituent on the unsubstituted C2 and C4 *ortho* ring angles is opposite to its influence on the *ipso* angle. The nitro group makes an angle of 13·9° to the imidazole ring. The intermolecular hydrogen bonds build up a helix parallel to the *a* axis.

Introduction. Nitroimidazoles are generally known as antiprotozoic and antibiotic drugs (Edwards, 1981). The investigation of 1-ethyl-5-nitroimidazole hydrochloride monohydrate is part of an extensive structure–activity study including conformational

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