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Reinvestigation of the Structure of 2-Hydroxyquinoxaline

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Abstract. $C_8H_6N_2O$, $M_r = 146{\cdot}15$, orthorhombic, $P2_12_12_1$, $a = 4{\cdot}354\,(1)$, $b = 7{\cdot}348\,(1)$, $c = 21{\cdot}320\,(1)$ Å, $V = 682{\cdot}13$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$, $D_m = 1{\cdot}41$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}6$ mm^{-1}, $F(000) = 304$, room temperature, $R = 0{\cdot}041$ for 771 observed reflections [$I > 3\sigma(I)$]. A reinvestigation of the structure of 2-hydroxyquinoxaline based on diffractometer data has yielded more precise structural parameters (bond-length and angle e.s.d.'s of 0·004 Å, 0·2°) than the photographic results of Stępień, Grabowski, Cygler & Wajsman [(1976). *Acta Cryst.* B**32**, 2048–2050] ($R = 0{\cdot}110$, bond-length and angle e.s.d.'s 0·01 Å, 0·7°). The compound exists in the keto form in the crystal with C=O = 1·239 (3) Å. The quinoxaline rings are essentially planar (inter-ring dihedral angle = 1·6°) including the exocyclic atoms. The large deviation of H(5) from the ring plane (0·59 Å) reported earlier is not observed here. The crystal structure is stabilized by strong intermolecular hydrogen bonds: N···O = 2·782 (6) Å, N—H···O = 162°.

Experimental. Crystals obtained from Regional Research Laboratory (CSIR), Jorhat, Assam, India. Brown plate-like crystal of size 0·5 × 0·25 × 0·18 mm. The density was measured by flotation in CCl_4/*n*-hexane. Cell parameters were derived from least-squares analysis of 25 high-angle reflections, $12{\cdot}83 \le \theta \le 54{\cdot}52°$, on an Enraf–Nonius CAD-4 diffractometer. Intensity data collected for $(\sin\theta)/\lambda \le 0{\cdot}626$ Å^{-1} with ω–2θ scans using Ni-filtered Cu $K\alpha$ radiation. Three reflections monitored at regular intervals, crystal stable to X-rays. Analytical absorption correction (North, Phillips & Mathews, 1968) was applied, transmission factor varied from 0·965 to 0·999. Index range for unique data $-5 \le h \le 5$, $0 \le k \le 9$, $0 \le l \le 26$. A total of 1654 reflections collected from the octants *hkl* and $\bar{h}kl$. The symmetry-related reflections were averaged with a merging R factor on F_o's of 0·020. Of 891 unique reflections 771 were considered to be observed [$I > 3\sigma(I)$]. Structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). All hydrogen atoms located from difference Fourier map. Final full-matrix least-squares refinement on F's using *SHELX*76 (Sheldrick, 1976) with non-hydrogen atoms refined anisotropically and hydrogen atoms isotropically converged at $R = 0{\cdot}041$. Individual weights, $w \propto 1/\sigma^2(F)$, $wR = 0{\cdot}05$, maximum $\Delta/\sigma = 0{\cdot}08$; $\Delta\rho$ in the final difference map within $\pm 0{\cdot}17$ e Å^{-3}. The atomic scattering factors as supplied in *SHELX*76 and initial calculations performed using the Enraf–Nonius (1979) *Structure Determination Package* on a PDP11/44 computer.

Table 1. *Final fractional coordinates and temperature factors of the atoms, with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}(Å^2)
O(1)	−0·5464 (5)	0·2725 (2)	0·2512 (1)	0·0536 (6)
N(1)	−0·2427 (6)	0·4589 (2)	0·3079 (1)	0·0438 (6)
N(2)	−0·0450 (6)	0·1594 (3)	0·3768 (1)	0·0537 (7)
C(1)	−0·3553 (7)	0·2941 (3)	0·2936 (1)	0·0452 (7)
C(2)	−0·2384 (8)	0·1430 (3)	0·3315 (1)	0·0524 (8)
C(3)	0·2615 (8)	0·3574 (4)	0·4412 (1)	0·0542 (9)
C(4)	0·3653 (8)	0·5267 (5)	0·4565 (1)	0·0613 (10)
C(5)	0·2750 (7)	0·6779 (4)	0·4208 (1)	0·0572 (9)
C(6)	0·0774 (7)	0·6583 (3)	0·3711 (1)	0·0490 (8)
C(7)	−0·0389 (7)	0·4858 (3)	0·3561 (1)	0·0418 (7)
C(8)	0·0578 (6)	0·3331 (3)	0·3910 (1)	0·0430 (7)
H(1)	−0·331 (9)	0·537 (4)	0·287 (1)	0·047 (8)
H(2)	−0·314 (12)	0·032 (5)	0·317 (2)	0·078 (11)
H(3)	0·277 (9)	0·250 (5)	0·466 (1)	0·064 (8)
H(4)	0·472 (13)	0·574 (6)	0·488 (2)	0·093 (14)
H(5)	0·323 (10)	0·792 (5)	0·429 (1)	0·063 (9)
H(6)	0·022 (8)	0·768 (5)	0·351 (2)	0·066 (9)

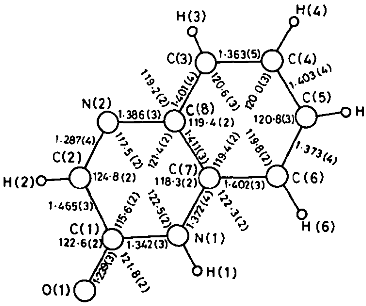

Fig. 1. Atomic numbering scheme for the 2-hydroxyquinoxaline molecule along with bond lengths (Å) and bond angles (°).

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The final positional and thermal parameters for the atoms are given in Table 1.* Bond lengths and bond angles are shown in Fig. 1 along with the atomic numbering scheme for the 2-hydroxyquinoxaline molecule.

Related literature. The quinoxaline moiety, present in peptide antibiotics such as echinomycin and triostin A (Ughetto, Wang, Quigley, van der Marel, van Boom & Rich, 1985) and TANDEM (Viswamitra *et al.*, 1981), is known to intercalate bifunctionally into DNA. Hence it is of interest to obtain accurate structural parameters of the quinoxaline moiety and its chemical modifications.

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44127 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of the Product Formed by Reaction of (±)-Synthanecine A with Thionyl Chloride

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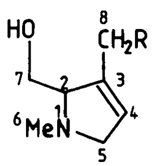
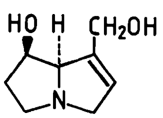
Abstract. (1): 3-Chloromethyl-2,5-dihydro-1-methyl-1*H*-pyrrole-2-methanol hydrochloride, $C_7H_{13}ClNO^+.Cl^-$, $M_r = 198.1$, monoclinic, $P2_1/c$, $a = 7.005$ (2), $b = 8.685$ (2), $c = 15.904$ (3) Å, $\beta = 91.85$ (2)°, $V = 967.0$ Å^3, $Z = 4$, $D_x = 1.36$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 6.24$ cm^{-1}, $F(000) = 416$, $T = 291$ K, final $R = 0.068$ for 1201 observed reflections. The X-ray structure analysis of the title compound has established that treatment of synthanecine A (2) with thionyl chloride produced an allylic chloride (1) apparently by reaction of the less nucleophilic hydroxy group in (2). The Cl^- anion is chelated *via* hydrogen bonds to N and O atoms; Cl(1)···N = 3.056 (5), Cl(1)···O = 3.106 (6) Å with respective H-bond angles of 174 (4) and 172 (5)°. The stabilization due to chelation may help to account for the formation of (1) in preference to the alternative 7-chloro compound.

Experimental. Treatment of synthanecine A (2) with thionyl chloride (Barbour & Robins, 1987) gave a chloro compound (1) isolated as the hydrochloride.



(1) R = Cl, HCl salt
(2) R = OH



(3)

Colourless, cube-shaped crystals were grown by slow evaporation from an ethanol–acetone mixture, crystal *ca* 0.4 × 0.4 × 0.3 mm used in data collection, CAD-4 diffractometer. Systematic absences from Weissenberg photographs indicated the crystals to be monoclinic $P2_1/c$. 1897 independent intensities, θ limit 26°, $\omega/2\theta$ scan. Although crystal colour changed from colourless

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