

## The Crystal and Molecular Structure of 5-Chloro-7-nitro-2,3-dihydroxyquinoxaline

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5-Chloro-7-nitro-2,3-dihydroxyquinoxaline crystallizes in the triclinic system, space group  $P\bar{1}$ , with  $a = 9.280$  (2),  $b = 12.870$  (3),  $c = 8.503$  (2) Å,  $\alpha = 90.95$  (2),  $\beta = 97.08$  (2),  $\gamma = 118.48$  (2)°. 3085 independent reflexions were measured on a single-crystal diffractometer. The structure was solved by direct methods and refined by full-matrix least squares to a final  $R$  of 0.046. The compound exists as crystals in the keto form only (the average C—O bond distance is 1.215 Å). The carbon ring is aromatic with an average C—C bond distance of 1.387 Å; the heterocyclic ring is not aromatic. The molecules are linked by strong N—H...O hydrogen bonds.

### Introduction

Structure investigations of derivatives of hydroxyquinoxaline have been undertaken in our Department (Stępień, Grabowski, Cygler & Wajsman, 1976; Stępień, 1977); this paper is a continuation of this work.

### Experimental

A sample provided by the Centre for Research and Development of Dyes in Zgierz, Poland, was recrystallized from ethanol. The crystals obtained were light yellow. The crystals chosen for X-ray analysis had average dimensions of 0.2 mm and the intensities were measured on a Philips PW 1100 single-crystal diffractometer (Cu  $K\alpha$  radiation). The accurate cell constants (Table 1) were refined by the least-squares method. 3085 independent reflexions were measured. Of these, intensities of 2063 were greater than  $3\sigma(I)$ ; the remaining 1022 reflexions were treated as unobserved. The intensities were corrected for Lorentz-polarization effects but not for absorption.

Table 1. *Crystal data*

Space group $P\bar{1}$	$\alpha = 90.95$ (2)°
$a = 9.280$ (2) Å	$\beta = 97.08$ (2)
$b = 12.870$ (3)	$\gamma = 118.48$ (2)
$c = 8.503$ (2)	$D_m = 1.772$ g cm <sup>-3</sup>
$V = 882.53$ Å <sup>3</sup>	$D_x = 1.818$
$Z = 4$	$\mu r(\text{Cu } K\alpha) = 0.39$

### Determination of the structure

The crystal structure was solved by direct methods. The phases of 168 reflexions with a normalized factor  $E > 1.96$  were determined by the symbolic addition

procedure, where four symbols were used. For two of these the phases were determined unequivocally on the basis of the  $\Sigma_2$  relationship. Thus, four variants of phase distribution were obtained and the following procedure was applied. The set of reflexions was increased to 416 by including those with  $E > 1.4$ . Their phases were assigned by applying the tangent formula and four  $E$  maps were obtained. One of these revealed interpretable positions for all the Cl, N and C atoms and half the O atoms. The approximate parameters of the two remaining O atoms were obtained from the electron density map.

The structure was refined by full-matrix least squares. In the refinement Cruickshank's weighting scheme,  $w^{-1} = A + BF_o + CF_o^2$ , was used with  $A, B, C$  calculated after each cycle by the method of Lee (1974). The progress of the refinement is shown in Table 2.

At this stage a difference synthesis was calculated which revealed all H atom positions. The final cycles of refinement were performed with anisotropic thermal parameters for the non-hydrogen atoms, and positional parameters for the H atoms. The individual isotropic thermal parameters for the H atoms were assumed to be the same as the average anisotropic parameters of the atom to which they are attached.

The final positional parameters are listed in Table 3 along with the standard deviations. Interatomic dis-

Table 2. *Progress of the refinement*

	$R$
$E$ map	0.338
Fourier synthesis	0.189
Four cycles of least squares with isotropic temperature factors	0.122
Four cycles with anisotropic temperature factors	0.060
Four cycles including hydrogen atoms	0.046

Table 3. The fractional coordinates ( $\times 10^4$ ) with standard deviations resulting from the least-squares refinement

	x	y	z
Molecule 1			
Cl(1)	802 (1)	9405 (1)	1419 (1)
O(1)	6134 (4)	9431 (3)	770 (3)
O(2)	6908 (3)	8339 (3)	3127 (3)
O(3)	926 (5)	7653 (3)	8179 (4)
O(4)	-720 (4)	8257 (3)	7079 (4)
N(1)	3970 (4)	9286 (3)	1913 (4)
N(2)	5015 (4)	8448 (3)	4485 (4)
N(3)	477 (4)	8103 (3)	7097 (4)
C(1)	5318 (5)	9148 (3)	1851 (4)
C(2)	5823 (4)	8596 (3)	3224 (4)
C(3)	1607 (4)	9051 (3)	3137 (4)
C(4)	767 (5)	8800 (3)	4428 (5)
C(5)	1401 (5)	8438 (3)	5746 (4)
C(6)	2795 (5)	8323 (3)	5808 (4)
C(7)	3641 (4)	8598 (3)	4509 (4)
C(8)	3066 (4)	8991 (3)	3166 (4)
H(1)	3694 (57)	9539 (41)	1185 (58)
H(2)	5187 (59)	8146 (43)	5172 (58)
H(3)	-278 (59)	8800 (40)	4413 (54)
H(4)	3058 (56)	8058 (40)	6638 (58)
Molecule 2			
Cl(1')	2353 (1)	6154 (1)	2103 (1)
O(1')	4701 (4)	3660 (2)	4459 (3)
O(2')	4332 (4)	1986 (2)	2227 (3)
O(3')	1553 (4)	4046 (3)	-4771 (3)
O(4')	1602 (4)	5686 (3)	-4067 (3)
N(1')	3563 (4)	4412 (3)	2619 (4)
N(2')	3405 (4)	2823 (3)	312 (4)
N(3')	1696 (4)	4793 (3)	-3763 (4)
C(1')	4099 (4)	3638 (3)	3086 (4)
C(2')	3944 (4)	2733 (3)	1836 (4)
C(3')	2446 (4)	5270 (3)	613 (4)
C(4')	2011 (5)	5389 (3)	-952 (4)
C(5')	2071 (4)	4636 (3)	-2088 (4)
C(6')	2482 (4)	3756 (3)	1729 (4)
C(7')	2942 (4)	3672 (3)	-133 (4)
C(8')	2973 (4)	4447 (3)	1044 (4)
H(1')	3593 (54)	4999 (41)	3356 (54)
H(2')	3356 (57)	2344 (43)	-388 (57)
H(3')	1625 (54)	5953 (41)	-1296 (53)
H(4')	2534 (54)	3291 (40)	-2573 (55)

tances and angles (uncorrected for thermal motion) are given in Table 4. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).\*

### Description of the structure

There are two molecules (unprimed and primed in Fig. 1) in the asymmetric unit. The differences between

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32591 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

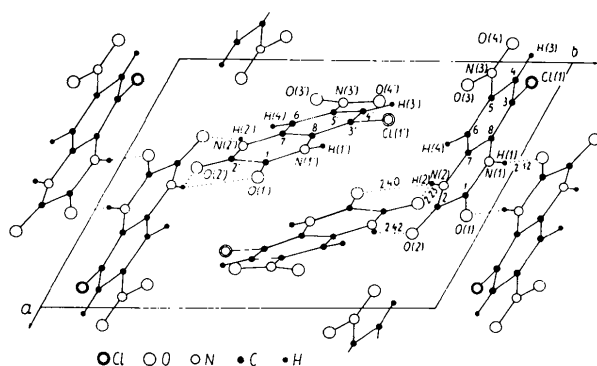
Table 4. Distances (Å) and angles (°) with estimated standard deviations

Intramolecular distances and angles			
C(1)—O(1)	1.212 (6)	C(3)—C(4)	1.378 (6)
C(2)—O(2)	1.210 (5)	C(3)—C(8)	1.391 (6)
C(1)—C(2)	1.515 (6)	C(4)—C(5)	1.391 (6)
C(1)—N(1)	1.352 (6)	C(5)—C(6)	1.366 (7)
C(2)—N(2)	1.348 (5)	C(6)—C(7)	1.387 (7)
C(7)—N(2)	1.380 (6)	C(3)—Cl(1)	1.726 (4)
C(8)—N(1)	1.383 (5)	C(5)—N(3)	1.465 (5)
C(7)—C(8)	1.404 (5)	N(3)—O(4)	1.217 (6)
		N(3)—O(3)	1.229 (6)
N(1)—H(1)	0.78 (5)	C(4)—H(3)	0.97 (6)
N(2)—H(2)	0.75 (6)	C(6)—H(4)	0.85 (5)
C(1')—O(1')	1.225 (5)	C(3')—C(4')	1.374 (5)
C(2')—O(2')	1.215 (6)	C(3')—C(8')	1.399 (6)
C(1')—C(2')	1.506 (6)	C(4')—C(5')	1.382 (6)
C(1')—N(1')	1.354 (6)	C(5')—C(6')	1.385 (7)
C(2')—N(2')	1.358 (5)	C(6')—C(7')	1.393 (5)
C(7')—N(2')	1.394 (6)	C(3')—Cl(1')	1.727 (4)
C(8')—N(1')	1.393 (5)	C(5')—N(3')	1.464 (5)
C(7')—C(8')	1.389 (6)	N(3')—O(4')	1.223 (6)
		N(3')—O(3')	1.225 (5)
N(1')—H(1')	0.96 (5)	C(4')—H(3')	0.99 (6)
N(2')—H(2')	0.83 (6)	C(6')—H(4')	0.95 (5)
C—O (mean) 1.215 (4)			
C—C (mean) in aromatic ring 1.387 (4)			
N(1)—C(1)—O(1)	124.2 (4)	C(3)—C(4)—C(5)	117.4 (4)
N(1)—C(1)—C(2)	117.3 (3)	C(4)—C(5)—C(6)	123.2 (4)
O(1)—C(1)—C(2)	118.5 (4)	C(5)—C(6)—C(7)	118.7 (4)
N(2)—C(2)—O(2)	125.2 (4)	C(6)—C(7)—C(8)	120.1 (4)
N(2)—C(2)—C(1)	115.7 (4)	C(7)—C(8)—C(3)	119.0 (3)
O(2)—C(2)—C(1)	119.1 (4)	C(8)—C(3)—C(4)	121.6 (4)
C(1)—N(1)—C(8)	124.2 (3)	Cl(1)—C(3)—C(4)	119.5 (3)
C(2)—N(2)—C(7)	124.8 (3)	Cl(1)—C(3)—C(8)	118.9 (3)
N(2)—C(7)—C(6)	121.0 (4)	N(3)—C(5)—C(6)	118.4 (4)
N(2)—C(7)—C(8)	118.9 (3)	N(3)—C(5)—C(4)	118.3 (4)
N(1)—C(8)—C(3)	122.8 (3)	O(4)—N(3)—C(5)	118.6 (4)
N(1)—C(8)—C(7)	118.2 (4)	O(4)—N(3)—O(3)	123.0 (4)
		O(3)—N(3)—C(5)	118.4 (4)
H(1)—N(1)—C(1)	117 (4)	H(3)—C(4)—C(3)	123 (3)
H(1)—N(1)—C(8)	119 (4)	H(3)—C(4)—C(5)	120 (3)
H(2)—N(2)—C(2)	120 (5)	H(4)—C(6)—C(5)	117 (4)
H(2)—N(2)—C(7)	114 (5)	H(4)—C(6)—C(7)	125 (4)
N(1')—C(1')—O(1')	122.5 (4)	C(3')—C(4')—C(5')	117.1 (4)
N(1')—C(1')—C(2')	117.4 (3)	C(4')—C(5')—C(6')	123.7 (3)
O(1')—C(1')—C(2')	120.1 (4)	C(5')—C(6')—C(7')	117.6 (4)
N(2')—C(2')—O(2')	123.7 (4)	C(6')—C(7')—C(8')	120.5 (4)
N(2')—C(2')—C(1')	117.1 (4)	C(7')—C(8')—C(3')	119.0 (3)
O(2')—C(2')—C(1')	119.2 (3)	C(8')—C(3')—C(4')	121.8 (4)
C(1')—N(1')—C(8')	123.2 (4)	Cl(1')—C(3')—C(4')	119.8 (4)
C(2')—N(2')—C(7')	123.6 (4)	Cl(1')—C(3')—C(8')	118.4 (3)
N(2')—C(7')—C(6')	120.7 (4)	N(3')—C(5')—C(6')	118.5 (4)
N(2')—C(7')—C(8')	118.7 (3)	N(3')—C(5')—C(4')	117.8 (4)
N(1')—C(8')—C(3')	121.3 (4)	O(4')—N(3')—C(5')	117.7 (3)
N(1')—C(8')—C(7')	119.7 (4)	O(4')—N(3')—O(3')	124.1 (3)
		O(3')—N(3')—C(5')	118.2 (4)
H(1')—N(1')—C(1')	123 (3)	H(3')—C(4')—C(3')	124 (3)
H(1')—N(1')—C(8')	115 (3)	H(3')—C(4')—C(5')	119 (3)
H(2')—N(2')—C(2')	118 (4)	H(4')—C(6')—C(5')	119 (3)
H(2')—N(2')—C(7')	119 (4)	H(4')—C(6')—C(7')	123 (3)

Table 4 (cont.)

## Intermolecular distances and angles

Symmetry code		(i)	1 - x,	2 - y,	-z
(ii)		1 - x,	1 - y,	1 - z	
(iii)		1 - x,	1 - y,	-z	
(iv)		x,	y,	-z	
N(1)—O(1) <sup>i</sup>	2.858 (5)	N(1)—H(1)—O(1) <sup>j</sup>	160 (4)		
H(1)—O(1) <sup>i</sup>	2.12 (5)	N(2)—H(2)—O(2') <sup>ii</sup>	151 (6)		
N(2)—O(2') <sup>ii</sup>	2.908 (4)	N(2)—H(2)—O(1') <sup>iii</sup>	137 (5)		
H(2)—O(2') <sup>ii</sup>	2.23 (5)	N(2') <sup>iii</sup> —H(2') <sup>iii</sup> —O(2)	153 (5)		
N(2)—O(1') <sup>iii</sup>	2.990 (4)	N(1')—H(1')—O(3') <sup>iv</sup>	111 (3)		
H(2)—O(1') <sup>iii</sup>	2.40 (6)				
N(2') <sup>iii</sup> —O(2)	3.179 (5)				
H(2') <sup>iii</sup> —O(2)	2.42 (5)				
N(1')—O(3') <sup>iv</sup>	2.974 (5)				
H(1')—O(3') <sup>iv</sup>	2.49 (5)				

Fig. 1. The projection of the structure down the *z* axis. Hydrogen bonds are marked by dotted lines.

comparable bond lengths and angles in each molecule are not significant. Slight differences are probably caused by different intermolecular bonding.

The carbon and heterocyclic rings of the molecules are planar but make angles of 4.3 and 4.4° with each other (for unprimed and primed molecules respectively). The deviations from the 'best' planes given by the equations  $0.60146x + 10.01520y + 2.50079z = 9.96337$  (for the unprimed molecule) and  $6.92176x + 2.92250y - 1.80425z = 3.14295$  (for the primed molecule) for the carbon rings and  $1.22649x + 9.39768y + 2.65086z = 9.70632$  (for the unprimed molecule) and  $6.91010x + 2.81100y - 2.44043z = 3.07152$  (for the primed molecule) for the heterocyclic rings are listed in Table 5 (*x*, *y* and *z* are the parameters of the atoms). The planes of the nitro groups are non-coplanar with the carbon rings of both molecules. The nitro groups of the adjacent molecules face each other. Such a configuration ensures the formation of the maximum number of hydrogen bonds. The deviation of the planes of the NO<sub>2</sub> groups from the planes of the aromatic rings is due to the electrostatic repulsion of the O atoms of these groups. In such an

Table 5. Deviations of atoms from the least-squares planes (Å)

Carbon rings			
C(3)	-0.017	C(1)	-0.060
C(4)	0.004	C(2)	0.034
C(5)	0.009	C(7)	0.016
C(6)	-0.008	C(8)	-0.041
C(7)	-0.006	N(2)	0.037
C(8)	0.018	N(1)	0.014
Cl(1)	-0.141	O(2)	-0.193
N(3)	-0.045	O(1)	-0.026
O(3)	-0.198	H(2)	-0.04
O(4)	0.034	H(1)	0.03
H(3)	-0.06		
H(4)	0.05		
Heterocyclic rings			
C(3')	-0.020	C(1')	-0.026
C(4')	-0.004	C(2')	0.031
C(5')	0.022	C(7')	0.026
C(6')	-0.015	C(8')	-0.022
C(7')	-0.009	N(2')	-0.002
C(8')	0.026	N(1')	-0.008
Cl(1')	-0.095	O(2')	-0.063
N(3')	0.111	O(1')	0.117
O(3')	-0.025	H(1')	0.00
O(4')	0.362	H(2')	0.00
H(3')	0.04		
H(4')	-0.04		

orientation the minimum distance between O atoms of neighbouring nitro groups is 2.858 Å (the van der Waals radius is 1.40 Å), with the remainder exceeding 3.1 Å. The angles between the planes of the NO<sub>2</sub> groups and those of the aromatic rings are 7.17 and 11.83° for the unprimed and primed molecules respectively. Such an arrangement of the molecules (Fig. 1) elucidates the existence of the plane of cleavage (100).

The mean C—O bond length (1.215 Å) indicates a double-bond character and the keto form of the compound in the crystalline state. The planarity of the carbon ring and also the C—C distances (mean 1.387 Å) show the aromatic character of that ring. In the heterocyclic ring there is a system of conjugated double bonds O=C—C=O. The mean C—C distance in this configuration is 1.511 Å; this exceeds the mean distance in typical conjugated double-bond systems (*e.g.* butadiene 1.461 Å). The elongation of the bond is due to the identity of fractional charges on both the C(carbonyl) atoms — as in oxalic acid, where the distance is 1.538 Å (Delaplane & Ibers, 1969). In 5-chloro-7-amino-2,3-dihydroxyquinoxaline hydrochloride the analogous bond distance is 1.515 Å (Stępień, 1977). If one of the electronegative O atoms in such a system is replaced by a neutral atom, the elongation of the bond does not take place, *e.g.* in 2-

hydroxyquinoxaline where the C—C distance is 1.451 Å (Stępień, Grabowski, Cygler & Wajsman, 1976).

The molecules are linked by N—H...O hydrogen bonds. The arrangement of the molecules and hydrogen bonds is given in the projection of the structure down the *z* axis (Fig. 1). The primed molecule is linked by hydrogen bonds to two unprimed molecules, related by translation along the *z* axis: to one by a single hydrogen bond (H...O 2.42 Å), and to the other by a bifurcated hydrogen bond (H...O 2.23 and 2.40 Å). Such an arrangement forms a chain directed along the *z* axis. The unprimed molecule is linked to the centrosymmetric one by two strong hydrogen bonds (H...O 2.12 Å) joining the two chains.

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#### References

- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* B25, 2423–2437.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 LEE, J. D. (1974). Loughborough Univ. X-ray system. Loughborough Univ. of Technology, England.  
 STĘPIEŃ, A. (1977). *Acta Cryst.* B33, 2854–2857  
 STĘPIEŃ, A., GRABOWSKI, M. J., CYGLER, M. & WAJSMAN, E. (1976). *Acta Cryst.* B32, 2048–2050.

*Acta Cryst.* (1977). B33, 2854–2857

## The Crystal and Molecular Structure of 5-Chloro-7-amino-2,3-dihydroxyquinoxaline Hydrochloride

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Crystals of  $C_8N_3O_2H_6Cl \cdot 0.52HCl$  are orthorhombic, space group *Pbca*, with  $a = 8.554$  (2),  $b = 16.639$  (3),  $c = 13.402$  (3) Å,  $Z = 8$ . 1430 independent reflexions were measured on a single-crystal diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (159 parameters) to a final  $R = 0.040$ . The compound exists as crystals in the keto form only (the average C—O bond distance is 1.226 Å). The carbon ring is aromatic with an average C—C bond distance of 1.391 Å; the heterocyclic ring is not aromatic. The molecules are linked by strong N—H...O hydrogen bonds.

#### Introduction

The structures of derivatives of hydroxyquinoxaline had not been studied, in spite of their interesting features. Such studies were, therefore, started in our Department (Stępień, Grabowski, Cygler & Wajsman, 1976; Grabowski, Stępień, Cygler & Wajsman, 1977). This paper is a continuation of this work. Crystals of 5-chloro-7-amino-2,3-dihydroxyquinoxaline were obtained from the Centre for Research and Development of Dyes in Zgierz, Poland. The preparation of the pure amine is difficult; what is commonly obtained is a mixture of the amine with some of its hydrochloride. It was found in this work that the hydrochloride is joined to the amine not ionically, but by hydrogen bonds. This explains why the chemical analysis for Cl in the hydrochloride was unsatisfactory. In this investigation the fractional occupancy value of this Cl atom was refined in addition to its remaining parameters.

#### Experimental

The crystals used in the X-ray measurements had average dimensions of 0.3 mm. The intensities were measured on a CAD-4 diffractometer in Jagellonian University, Regional Laboratory of Physicochemical Analysis and Structure Research, by the  $\theta$ - $2\theta$  scan

Table 1. *Crystal data*

Space group <i>Pbca</i>	$D_m = 1.603 \text{ g cm}^{-3}$
$a = 8.554$ (2) Å	$D_x = 1.604$
$b = 16.639$ (3)	Systematic absences
$c = 13.402$ (3)	$hk\cdot: h = 2n + 1$
$V = 1907.51 \text{ Å}^3$	$h0l: l = 2n + 1$
$Z = 8$	$0kl: k = 2n + 1$
$\mu r(\text{Cu K}\alpha) = 0.71$	$h00: h = 2n + 1$
	$0k0: k = 2n + 1$
	$00l: l = 2n + 1$