

Fig. 2. Projection of the structure of (*p*-methylphenoxy)acetic acid on the (001) plane. Short contacts of less than 3.5 Å are shown.

acetic acid (Smith, Kennard & White, 1976) and 90° in 3-indolylacetic acid (Karle, Britts & Gum, 1964). In the COOH group, the differences in the two C—O bond lengths and the values of the C—C—O angles are similar to those observed in other substituted phenoxyacetic acids, where double- and single-bond characters distinctly exist, but it is different from the case of (*p*-nitrophenoxy)acetic acid where occupational disorder of the H atom of the COOH group exists, leading to

near equality in C—O bond lengths and C—C—O angles.

The carboxylic group takes part in dimer formation across centres of symmetry situated halfway along the *x* axis. Fig. 2 shows the packing arrangement of these dimers consisting of two stacks of hydrogen-bonded molecule pairs related to each other by the glide plane $c(0\frac{1}{2}0)$.

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Structure of 6-Nitro-2,3-dihydroxyquinoxaline* Hydrate

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Abstract. $C_8H_5N_3O_4 \cdot H_2O$, monoclinic, $P2_1/c$, $a = 7.489$ (1), $b = 11.949$ (2), $c = 12.066$ (2) Å, $\beta = 120.43$ (2)°, $Z = 4$. 732 independent and non-zero reflexions were measured on a single-crystal diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (173 parameters) to a final $R = 0.052$. The compound exists in crystals in the keto form only (the average C—O bond distance is 1.229 Å). The carbon ring is aromatic (average C—C bond distance of 1.386 Å). The molecules are linked by a three-dimensional set of strong N—H...O and O—H...O hydrogen bonds.

* Alternative name: 6-nitro-2,3(1*H*,4*H*)-quinoxalinedione.

Introduction. Structure investigations of substituted quinoxalines have been undertaken in our department (Stępień, Grabowski, Cygler & Wajsman, 1976; Grabowski, Stępień, Cygler & Wajsman, 1977; Stępień, 1977). The results presented here are a continuation of this work. Crystals of 6-nitro-2,3-dihydroxyquinoxaline hydrate were obtained from the Center for Research and Development of Dyes in Zgierz, Poland.

The light-yellow crystals were recrystallized from ethanol at room temperature. The crystals used for the X-ray measurements had average dimensions of 0.2 × 0.2 × 0.3 mm. The intensities were measured on a Syntex $P2_1$ diffractometer, by the θ - 2θ scan method,

up to the limit 114° in 2θ (Cu $K\alpha$ radiation). The cell constants were refined by the least-squares method. 920 independent reflexions were measured. Of these, 732 had intensities greater than $1.96\sigma(I)$; the remaining reflexions were treated as unobserved. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way.

The crystal structure was solved by the symbolic addition procedure using 158 reflexions with $E > 1.56$. Three symbols were chosen and two of them were given signs unequivocally. 360 reflexions with $E > 1.14$ were phased on the basis of the Σ_2 relationship. From the two variants of the E map, one gave approximate parameters of all the non-H atoms. 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).

After anisotropic refinement a difference synthesis was calculated which revealed all H-atom positions in the quinoxaline molecule as well as in the water molecule. In the next four cycles of least squares, positional and anisotropic thermal parameters of non-H atoms and positional parameters of the H atoms were refined. The individual isotropic thermal parameters of the H atoms were assumed to be the same as those of the atoms to which they are attached. The final parameters are listed in Table 1 together with

Table 1. Fractional coordinates ($\times 10^4$; for H $\times 10^3$) with standard deviations resulting from the least-squares refinement and B_{iso} values

$$B_{\text{iso}} = \frac{1}{3}[(4\beta_{11}/a^2) + (4\beta_{22}/b^2) + (4\beta_{33}/c^2)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (\AA^2)
O(1)	9035 (7)	1452 (4)	-255 (4)	4.8 (2)
O(2)	9087 (6)	2488 (3)	1762 (4)	4.4 (2)
O(3)	6483 (8)	6131 (4)	-4570 (4)	7.0 (3)
O(4)	5770 (7)	7567 (4)	-3779 (5)	6.3 (2)
O(5)	8384 (8)	5144 (4)	2771 (4)	5.4 (3)
N(1)	8171 (7)	3088 (4)	-1358 (4)	3.1 (2)
N(2)	8028 (7)	4105 (4)	624 (4)	3.0 (2)
N(3)	6268 (8)	6581 (5)	-3739 (5)	4.7 (3)
C(1)	8612 (8)	2446 (5)	-323 (5)	3.1 (3)
C(2)	8573 (8)	3024 (5)	767 (5)	3.1 (3)
C(3)	6927 (9)	5843 (5)	-565 (6)	3.6 (3)
C(4)	6506 (8)	6452 (5)	-1643 (6)	3.7 (3)
C(5)	6633 (8)	5925 (5)	-2612 (5)	3.2 (3)
C(6)	7156 (8)	4817 (5)	-2582 (5)	3.2 (3)
C(7)	7591 (7)	4204 (4)	-1488 (5)	2.8 (2)
C(8)	7503 (8)	4722 (4)	-481 (5)	2.8 (3)
H(11)	823 (10)	283 (6)	-192 (6)	3.0
H(21)	810 (10)	450 (5)	127 (6)	2.7
H(31)	686 (10)	620 (5)	20 (6)	3.7
H(41)	609 (10)	733 (5)	-170 (6)	4.1
H(61)	719 (10)	447 (5)	-321 (6)	3.2
H(51)	900 (12)	576 (7)	307 (8)	5.2
H(52)	831 (14)	491 (7)	331 (8)	5.2

Table 2. Distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Intramolecular			
C(1)—O(1)	1.221 (9)	C(3)—C(8)	1.395 (8)
C(2)—O(3)	1.237 (7)	C(4)—C(5)	1.374 (9)
C(1)—N(1)	1.357 (8)	C(5)—C(6)	1.376 (8)
C(2)—N(2)	1.340 (7)	C(6)—C(7)	1.396 (8)
C(1)—C(2)	1.499 (9)	C(7)—C(8)	1.395 (9)
C(7)—N(1)	1.387 (7)	C(5)—N(3)	1.470 (9)
C(8)—N(2)	1.394 (7)	N(3)—O(3)	1.218 (9)
C(3)—C(4)	1.380 (9)	N(3)—O(4)	1.229 (7)
N(1)—H(11)	0.76 (8)	C(4)—H(41)	1.09 (7)
N(2)—H(21)	0.89 (7)	C(6)—H(61)	0.87 (8)
C(3)—H(31)	1.04 (8)	O(5)—H(51)	0.84 (7)
		O(5)—H(52)	0.73 (9)
Mean C—O = 1.229 (8)			
Mean C—C in aromatic ring = 1.386 (4)			
O(1)—C(1)—N(1)	123.1 (6)	N(2)—C(8)—C(3)	120.3 (6)
O(1)—C(1)—C(2)	120.6 (6)	N(2)—C(8)—C(7)	118.9 (5)
N(1)—C(1)—C(2)	116.3 (5)	C(3)—C(8)—C(7)	120.8 (5)
O(2)—C(2)—N(2)	123.3 (6)	C(8)—C(3)—C(4)	119.3 (6)
O(2)—C(2)—C(1)	118.5 (5)	C(3)—C(4)—C(5)	118.7 (5)
N(2)—C(2)—C(1)	118.1 (5)	C(4)—C(5)—C(6)	124.0 (6)
C(1)—N(1)—C(7)	124.4 (6)	C(5)—C(6)—C(7)	117.2 (6)
C(2)—N(2)—C(8)	123.6 (5)	N(3)—C(5)—C(4)	118.8 (5)
N(1)—C(7)—C(6)	121.4 (6)	N(3)—C(5)—C(6)	117.1 (6)
N(1)—C(7)—C(8)	118.6 (5)	O(3)—N(3)—C(5)	119.0 (5)
C(6)—C(7)—C(8)	120.0 (5)	O(4)—N(3)—C(5)	117.3 (6)
O(3)—N(3)—O(4)	123.7 (6)		
C(1)—N(1)—H(11)	120 (5)	C(8)—C(3)—H(31)	119 (4)
C(7)—N(1)—H(11)	116 (5)	C(3)—C(4)—H(41)	120 (4)
C(2)—N(2)—H(21)	122 (4)	C(5)—C(4)—H(41)	122 (4)
C(8)—N(2)—H(21)	115 (4)	C(5)—C(6)—H(61)	125 (4)
C(4)—C(3)—H(31)	122 (4)	C(7)—C(6)—H(61)	118 (4)
H(51)—O(5)—H(52)	103 (8)		

Intermolecular

O(5)—N(2)	2.761 (8)	N(2)—H(2)—O(5)	171 (5)
O(5)—H(2)	1.87 (7)		
O(1)—O(5 ⁱ)	2.894 (8)	O(1)—H(52 ⁱ)—O(5 ⁱ)	150 (10)
O(1)—H(52 ⁱ)	2.24 (9)		
O(2)—O(5 ⁱⁱ)	3.266 (7)	O(2)—H(51 ⁱⁱ)—O(5 ⁱⁱ)	159 (9)
O(2)—H(51 ⁱⁱ)	2.46 (9)		
O(2)—N(1 ⁱⁱⁱ)	2.770 (9)	O(2)—H(11 ⁱⁱⁱ)—N(1 ⁱⁱⁱ)	162 (7)
O(2)—H(11 ⁱⁱⁱ)	2.03 (9)		

Symmetry code: (i) $x, 0.5 - y, -0.5 + z$; (ii) $2 - x, -0.5 + y, 0.5 - z$; (iii) $x, 0.5 - y, 0.5 + z$.

standard deviations.* The interatomic distances and bond angles are listed in Table 2 (the values have not been corrected for thermal motion). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

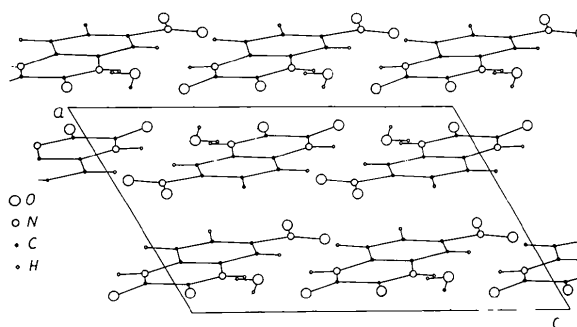
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP35893 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Deviations of atoms from the least-squares planes (Å)

Carbon ring		Heterocyclic ring	
C(3)	-0.009 (2)	C(1)	-0.020 (2)
C(4)	0.001 (2)	C(2)	0.008 (2)
C(5)	0.005 (2)	N(1)	0.016 (2)
C(6)	-0.002 (2)	N(2)	0.008 (2)
C(7)	-0.005 (2)	C(7)	0.001 (2)
C(8)	0.010 (2)	C(8)	-0.013 (2)
N(3)	0.008 (2)	O(1)	-0.063 (2)
O(3)	0.141 (2)	O(2)	0.059 (2)
O(4)	0.055 (2)		

Discussion. The carbon and heterocyclic rings of the molecule are planar but inclined at an angle of 1.5° . The deviations from the 'best' planes, given by the equations $6.49222x + 3.10129y - 0.87021z = 6.36680$ (carbon ring) and $6.56884x + 3.13793y - 1.18283z = 6.48469$ (heterocyclic ring), are listed in Table 3 (x, y, z are the crystallographic parameters of the atoms). N(3) of the NO_2 group lies (within experimental error) in the plane of the carbon ring but the NO_2 group is not coplanar with the latter (3.7°). This torsion is probably caused by the mutual interaction of the close NO_2 groups of two molecules of the compound. Such location of the NO_2 groups and the deviations of their planes from the carbon-ring plane were also observed in 5-chloro-7-nitro-2,3-dihydroxyquinoxaline (Grabowski *et al.*, 1977).

The mean C—O bond length (1.229 Å) indicates a double-bond character and the keto form of the compound in the crystalline state. The C—C distances (average value 1.386 Å) in the carbon ring and planarity of the ring show the aromatic character of that ring. In the heterocyclic ring there is a system of conjugated double bonds $\text{O}=\text{C}-\text{C}=\text{O}$. The C—C distance of this system is 1.499 Å; this exceeds the 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. In other 2,3-dihydroxy derivatives of quinoxaline studied so far a similar shortening of C—C bonds was observed. In 2-hydroxyquinoxaline, where there is no interaction between identically charged C atoms, the shortening is the same as that in butadiene (1.545 Å) (Stępień *et al.*, 1976).

Fig. 1. The projection of the structure along the y' axis. Hydrogen bonds are marked by dotted lines.

There is a three-dimensional system of hydrogen bonds in the structure. The molecules of 6-nitro-2,3-dihydroxyquinoxaline form dimers due to a strong hydrogen bond of type $\text{N}-\text{H}\cdots\text{O}$ ($\text{H}\cdots\text{O}$ 2.03 Å, $\text{N}-\text{H}-\text{O}$ 162°), each of which is bonded to three water molecules by one strong hydrogen bond of type $\text{N}-\text{H}\cdots\text{O}$ and two weaker bonds of type $\text{O}-\text{H}\cdots\text{O}$.

O(2) takes part in two hydrogen bonds and O(1) in only one which causes a difference in the C—O distances (0.018 Å) of the carbonyl groups.

The arrangement of the molecules and the hydrogen bonds are given in the projection of the structure along the y axis (Fig. 1).

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