# The Crystal and Molecular Structure of 2-Hydroxyquinoxaline

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2-Hydroxyquinoxaline crystallizes in the orthorhombic system, space group $P2_12_12_1$ with $a = 4\cdot356$ (3), $b = 7\cdot336$ (7), $c = 21\cdot29$ (2) Å, $Z = 4$. The intensities were estimated by photographic methods. The crystal structure was solved by the direct method and refined by full-matrix least squares; the final $R$ is 0·110. The compound exists in crystals in the keto form only (the C–O bond distance is 1·23 Å). The carbon ring is aromatic (the average C–C bond distance is 1·386 Å), while the heterocyclic ring is not. The molecules are linked by strong non-linear hydrogen bonds $N-H\cdots O$.

## Introduction

Some of the quinoxaline derivatives exhibit different properties (*e.g.* reactivity, solubility) from those that one might expect on the basis of chemical formula (Wojciechowski, 1972). To elucidate the differences the crystal structure investigations of these compounds were undertaken. The crystals of 2-hydroxyquinoxaline were obtained from the Centre for Research and Development of Dyes in Zgierz, Poland.

## Experimental

Crystals chosen for X-ray analysis were ground into a cylindrical shape ($r = 0\cdot1$ mm). The accurate cell constants were obtained by least-squares methods from Weissenberg photographs (Table 1).

Intensity data were collected using an integrated Weissenberg goniometer with Cu $K\alpha$ radiation. The intensities of 638 non-zero, independent reflexions were estimated visually. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way.

## Determination of the structure

The crystal structure was solved by symbolic addition and tangent methods. With symbolic addition, the phases of 60 reflexions with $E > 2\cdot1$ were determined. These formed the basis for the determination of the phases of 260 reflexions with $E > 1\cdot5$ by the tangent

Table 1. *Crystal data*

| Space group $P2_12_12_1$ | $D_m = 1\cdot443$ g cm$^{-3}$ |
|---|---|
| $a = 4\cdot356$ (3) Å | $D_x = 1\cdot426$ |
| $b = 7\cdot336$ (7) | Systematic absences: |
| $c = 21\cdot29$ (2) | $h00$  $h = 2n+1$ |
| $V = 680\cdot34$ Å$^3$ | $0k0$  $k = 2n+1$ |
| $Z = 4$ | $00l$  $l = 2n+1$ |

Table 2. *Progress of refinement*

| | $R$ |
|---|---|
| $E$ map | 0·224 |
| Four cycles of least squares with isotropic temperature factors | 0·173 |
| Four cycles with anisotropic temperature factors | 0·127 |
| Two cycles including hydrogen atoms | 0·110 |

Table 3. *Final coordinates and anisotropic thermal parameters $\beta_{ij}$ with standard deviations resulting from the least-squares refinement*

The $\beta_{ij}$ ($\times 10^4$) values are defined by the temperature factor: exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ or $B_{iso}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | −0·5493 (13) | 0·2720 (7) | 0·2517 (3) | 501 (46) | 158 (11) | 24 (1) | 9 (18) | −44 (7) | 0 (3) |
| N(1) | −0·2424 (14) | 0·4579 (7) | 0·3069 (3) | 286 (39) | 150 (11) | 20 (1) | 13 (20) | −15 (6) | −6 (3) |
| N(2) | −0·0418 (15) | 0·1567 (8) | 0·3771 (3) | 363 (47) | 160 (13) | 25 (1) | 7 (21) | −14 (7) | 7 (4) |
| C(1) | −0·3589 (16) | 0·2925 (9) | 0·2936 (3) | 275 (44) | 142 (14) | 17 (1) | 1 (20) | −4 (7) | 0 (4) |
| C(2) | −0·2386 (18) | 0·1425 (10) | 0·3306 (4) | 386 (57) | 137 (13) | 26 (2) | 18 (25) | −9 (9) | 3 (4) |
| C(3) | 0·2590 (19) | 0·3580 (13) | 0·4412 (3) | 338 (50) | 252 (19) | 22 (2) | 15 (30) | −23 (8) | −3 (5) |
| C(4) | 0·3697 (20) | 0·5294 (14) | 0·4560 (4) | 346 (53) | 295 (22) | 23 (2) | −42 (31) | −21 (8) | −2 (6) |
| C(5) | 0·2686 (18) | 0·6781 (11) | 0·4218 (4) | 329 (48) | 210 (18) | 28 (2) | −18 (26) | 3 (9) | −19 (5) |
| C(6) | 0·0787 (18) | 0·6580 (10) | 0·3710 (3) | 316 (49) | 173 (15) | 23 (2) | 28 (22) | 6 (8) | −13 (5) |
| C(7) | −0·0364 (14) | 0·4857 (9) | 0·3569 (3) | 179 (42) | 147 (12) | 17 (1) | 6 (18) | 8 (6) | 1 (4) |
| C(8) | 0·0650 (15) | 0·3324 (10) | 0·3905 (3) | 156 (36) | 186 (15) | 18 (1) | 8 (20) | 7 (6) | 3 (4) |
| H(1) | −0·3126 (259) | 0·5322 (130) | 0·2790 (47) | 2·91 | | | | | |
| H(2) | −0·3540 (294) | 0·0361 (135) | 0·3365 (42) | 3·35 | | | | | |
| H(3) | 0·3198 (261) | 0·2419 (147) | 0·4631 (42) | 3·57 | | | | | |
| H(4) | 0·5761 (312) | 0·5106 (131) | 0·4926 (45) | 4·00 | | | | | |
| H(5) | 0·4928 (235) | 0·7633 (144) | 0·4274 (46) | 3·81 | | | | | |
| H(6) | −0·0416 (259) | 0·7717 (125) | 0·3427 (41) | 3·41 | | | | | |

method. *E* maps of four possible variants were obtained. One gave positions of all non-hydrogen 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). The first four cycles included isotropic thermal parameters and the next four, anisotropic parameters. At this stage a $W^2$-$\beta$ synthesis (Ramachandran & Raman, 1959) was calculated which revealed all hydrogen atom positions. The next two cycles of refinement included hydrogen atoms and the individual isotropic thermal parameters for them were assumed to be the same as the average anisotropic parameters of the atom to which they are attached. The thermal parameters of the hydrogen atoms were not refined. The progress of the refinement is shown in Table 2.
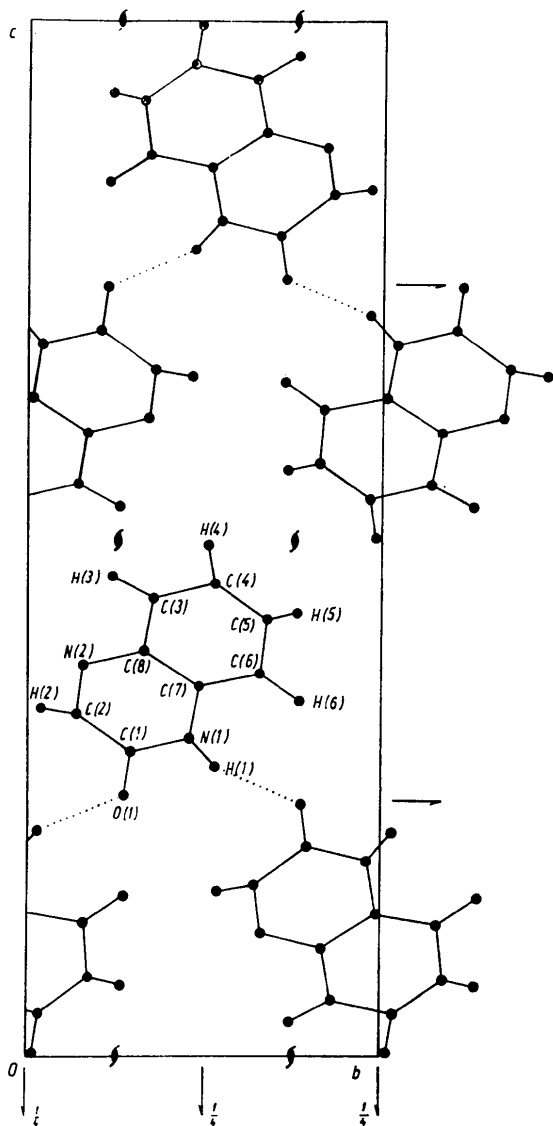


Fig. 1. The projection of the structure down the *x* axis. Hydrogen bonds are marked by dotted lines.

The final parameters are listed in Table 3 along with the standard deviations. The interatomic distances and bond angles are listed in Table 4 (the values have not been corrected for thermal motion). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

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

The superscript marks the position:

|  | (I) | $-1-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
|---|---|---|---|---|

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·227 (8) | C(3)–C(4) | 1·384 (13) |
| N(1)–C(1) | 1·345 (8) | C(4)–C(5) | 1·384 (12) |
| N(1)–C(7) | 1·408 (9) | C(5)–C(6) | 1·371 (11) |
| N(2)–C(2) | 1·313 (10) | C(6)–C(7) | 1·392 (10) |
| N(2)–C(8) | 1·400 (9) | C(7)–C(8) | 1·404 (9) |
| C(1)–C(2) | 1·451 (10) | C(8)–C(3) | 1·383 (10) |
| N(1)–H(1) | 0·86 (10) | C(3)–H(3) | 1·01 (11) |
| C(2)–H(2) | 0·94 (11) | C(4)–H(4) | 1·20 (12) |
| | | C(5)–H(5) | 1·17 (10) |
| | | C(6)–H(6) | 1·15 (10) |

Mean C–C distance in aromatic ring 1·386
Mean C–H distance in aromatic ring 1·09

| | | | |
|---|---|---|---|
| N(1)–O(1$^{\rm I}$) | 2·774 (8) | O(1$^{\rm I}$)–H(1) | 1·97 (10) |

| | | | |
|---|---|---|---|
| O(1)–C(1)–C(2) | 123·1 (6) | C(1)–N(1)–H(1) | 107 (7) |
| O(1)–C(1)–N(1) | 121·3 (6) | C(7)–N(1)–H(1) | 131 (7) |
| N(1)–C(1)–C(2) | 115·7 (6) | C(1)–C(2)–H(2) | 121 (7) |
| C(1)–C(2)–N(2) | 125·8 (7) | N(2)–C(2)–H(2) | 108 (7) |
| C(1)–N(1)–C(7) | 122·1 (6) | C(4)–C(3)–H(3) | 125 (6) |
| C(2)–N(2)–C(8) | 116·4 (6) | C(8)–C(3)–H(3) | 114 (6) |
| N(1)–C(7)–C(6) | 121·6 (6) | C(3)–C(4)–H(4) | 108 (5) |
| N(1)–C(7)–C(8) | 118·0 (6) | C(5)–C(4)–H(4) | 132 (5) |
| C(7)–C(8)–N(2) | 121·9 (6) | C(4)–C(5)–H(5) | 96 (5) |
| N(2)–C(8)–C(3) | 119·2 (6) | C(6)–C(5)–H(5) | 130 (5) |
| C(8)–C(3)–C(4) | 121·0 (8) | C(5)–C(6)–H(6) | 127 (5) |
| C(3)–C(4)–C(5) | 119·0 (8) | C(7)–C(6)–H(6) | 112 (5) |
| C(4)–C(5)–C(6) | 121·6 (8) | | |
| C(5)–C(6)–C(7) | 119·0 (7) | N(1)–H(1)–O(1$^{\rm I}$) | 155 (7) |
| C(6)–C(7)–C(8) | 120·3 (6) | | |
| C(7)–C(8)–C(3) | 118·7 (7) | | |

## Description of the structure

The carbon and heterocyclic rings of the molecule are planar but make an angle of 2° with each other. The deviations from the 'best' planes given by the equations:

$$-0{\cdot}7778x + 0{\cdot}1243y + 0{\cdot}6161z - 5{\cdot}2240 = 0$$

for the carbon ring and

$$-0{\cdot}7531x + 0{\cdot}1282y + 0{\cdot}6453z - 5{\cdot}4667 = 0$$

for the heterocyclic ring, are listed in Table 5. $x, y, z$ are given in Å. One of the hydrogen atoms is out of the plane by as much as 0·59 Å, but since the coordinates of the hydrogen atoms are not accurate, this deviation may not be significant.

Table 5. *Deviations from the best planes* (Å)

| O(1) | 0·05 | C(3) | 0·01 |
|------|------|------|------|
| N(1) | −0·02 | C(4) | −0·01 |
| N(2) | 0·00 | C(5) | 0·02 |
| C(1) | 0·02 | C(6) | −0·02 |
| C(2) | −0·01 | C(7) | 0·01 |
| H(1) | −0·11 | C(8) | 0·00 |
| H(2) | 0·35 | H(3) | −0·01 |
|      |      | H(4) | 0·25 |
|      |      | H(5) | −0·59 |
|      |      | H(6) | 0·11 |

The C–O bond length (1·227 Å) indicates typical double bond character and keto form of the compound in the crystalline state. This is confirmed by H(1) being linked to N(1). The bond lengths in the carbon ring are as expected (mean value 1·386 Å). In the heterocyclic ring there is a system of conjugated double bonds O=C–C=N. C(1)–C(2) shows the characteristic shortening for this system (1·451 Å). C(1)–N(1) is also appropriately shortened (1·345 Å).

The molecules are linked by two strong (2·774 Å) non-linear (155°) hydrogen bonds. The numbering of atoms, the arrangement of molecules and hydrogen bonds are given in the projection of the structure down *x* (Fig. 1). It seems that the deviation from coplanarity of the molecule may be caused by the net of strong hydrogen bonds.

### References

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# A Comparative Analysis of Structural Parameters Obtained by Diffractometer and Scanning-Densitometer Measurements

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The structure of cytosine monohydrate has been redetermined with reflexion data obtained from automatic digital scanning of Weissenberg films. The previous determination with diffractometer data [McClure & Craven, *Acta Cryst.* (1973), B29, 1234–1238] converged to an *R* of 0·037, with average estimated standard deviations of 0·002 Å and 0·15° in derived bond lengths and angles. The photographic data set converged to an *R* of 0·0672 with e.s.d.'s of 0·004–0·005 Å and 0·3–0·4°. Normal probability plots showed that the positional (and the derived geometric) parameters were very comparable; the vibrational parameters were rather less so, some systematic error being apparent. The overall conclusion from the study is that the two data sets have given essentially the same positional description of the structure.

## Introduction

The past few years have seen the advent of reliable digitizing scanning densitometers, as a means of rapidly estimating reflexion intensities from single-crystal film data. These instruments have found especial use in the field of protein crystallography (Matthews, Klopfenstein & Colman, 1972), and have been used for scanning precession, both screened and screenless (Xuong & Freer, 1971), and oscillation photographs (Arndt, Champness, Phizackerley & Wonacott, 1973). In general, a sensitive indication of systematic errors in measurement is given by comparison of symmetry-related reflexions, and of reflexions recorded on successive films in a film pack; it has been found that careful scanner measurements can compare favourably on this basis with diffractometer intensity measurement.

The scanner method has also been applied to estimation of Weissenberg-geometry film intensities for small-molecule crystal structures, albeit on a much more restricted basis, and some structures have been solved with data collected in this manner (for example: Werner, Linnros & Leijonmarck, 1971; Sussman & Wodak, 1973; Sjölin, Olsson & Lindqvist, 1975). A centralized service has recently been set up by the (British) Science Research Council to provide such scanning facilities. As mentioned above, it is straightforward to assess the reliability (and reproducibility) of scanner measurement; our experience, paralleled by that of others (Machin & Elder, 1975), is that a scanning densitometer can indeed measure intensities from Weissenberg films with an accuracy sometimes approaching diffractometer results, in agreement with experience in the protein field.

Comparison of intensities measured from films, and