

The Crystal and Molecular Structure of 1,4-Dihydro-2,3-quinoxalinedione

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The crystal and molecular structure of 1,4-dihydro-2,3-quinoxalinedione, $C_8H_6N_2O_2$, has been determined using single crystal X-ray diffractometer data. The crystals are monoclinic, $P2_1/n$, with a unit cell $a = 8.068(1)$, $b = 4.275(1)$, $c = 20.911(2)$ Å, $\beta = 100.42(1)^\circ$, $Z = 4$. The final R -factor was 0.043 for 1028 observed reflexions. In the crystal the molecules exist as diones connected in two dimensions *via* N—H...O hydrogen bonds.

In solution 1,4-dihydro-2,3-quinoxalinedione is in equilibrium with the tautomers with one and two hydroxyl groups. This amide-iminol tautomerism involves a fast hydrogen transfer between nitrogen and oxygen. It has generally been found that compounds capable of this tautomerism usually exist predominantly in the amide form. This is so even in cases where the iminol has larger aromatic stabilization, *e.g.* 2-pyridone.^{1,2} Kvik ³ has recently studied the crystal structures of some substituted 2-pyridones and found the iminol in two cases, *viz.* 6-chloro-2-hydroxypyridine and 6-bromo-2-hydroxypyridine. Cheeseman *et al.*^{4,5} have studied the UV- and IR-spectra of the title compound and its *O*- and *N*-methyl derivatives. They found that the dione is the predominant tautomer both as solid and in chloroform solution. This X-ray crystallographic study confirms their results and gives a more detailed knowledge of the bonding situation.

EXPERIMENTAL

Commercial 2,3-dihydroxyquinoxaline (Fluka) in the form of long needles was recrystallized from ethanol. The crystals obtained were colourless prisms. Weissenberg photographs showed monoclinic symmetry and, from

systematic extinctions, space group $P2_1/c$, or the equivalent $P2_1/n$, could be deduced. A crystal of approximate dimensions $0.12 \times 0.20 \times 0.05$ mm³ was mounted on an automatic Enraf-Nonius CAD4 diffractometer with $CuK\alpha$ radiation. The unit-cell dimensions were determined from the θ -values of 36 intensities measured in the range $\theta = 38$ to 48° , using $\lambda(CuK\alpha_1) = 1.54051$ Å.

Three-dimensional intensity data were collected at 22 °C by the ω - 2θ scan technique with $\Delta\omega = 0.8^\circ + 0.5^\circ \tan \theta$. The background was measured with stationary crystal-stationary counter for 1/4 of the time spent on the scan. Double scans were made for each reflexion for a net count of 2000 within a maximum time of 4 minutes. Two standard reflexions were measured at regular intervals. Their intensities showed no systematic variation. Data were collected to $\theta = 70^\circ$. After data reduction, including Lp -correction but no absorption correction, 1028 observed structure amplitudes were left. 419 intensities with $I < 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics, were considered unobserved.

Phases for the structure amplitudes were determined by the symbolic addition method using program GAASA.⁶ The coordinates of all atoms except the hydrogens were found from a subsequent E -map. Minimizing $\sum w_i (|F_o| - |F_c|)^2$, the positional parameters and anisotropic temperature factors together with an overall scale factor were refined. The weights were calculated from

$w_i^{-1} = \sigma^2(|F_o|^2) / 4|F_o|^2 + 0.001|F_o|^2$. The resulting R -factors were $R = 0.072$ and $R_w = 0.115$. A difference map now revealed all hydrogen atom positions. Including them with isotropic temperature factors in a refinement resulted in $R = 0.043$ and $R_w = 0.067$. The form factors were those of Stewart, Davidson and Simpson⁸ for hydrogen and of Hansson, Herman, Lea and Skillman⁷ for the other atoms. The final parameters are listed in Table 1. Lists of observed and calculated structure amplitudes can be obtained on request.

Table 1. Positional and thermal parameters. The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The β_{ij} -values have been multiplied by 10^5 . Standard deviations are given in parentheses. R_1 , R_2 and R_3 are the root-mean-square displacements (Å) along the principal axes of the thermal vibration ellipsoids.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	
O(1)	-0.17951(18)	1.03404(33)	0.43634(6)	For β_{ij} , see below	
O(2)	-0.30928(17)	0.81867(36)	0.31338(6)		
C(1)	-0.10232(23)	0.83765(42)	0.41013(8)		
C(2)	-0.17287(23)	0.72138(43)	0.34182(8)		
N(1)	0.04666(19)	0.71670(35)	0.43861(7)		
N(2)	-0.07729(20)	0.51915(35)	0.31589(7)		
C(3)	0.14291(23)	0.50837(39)	0.40948(8)		
C(4)	0.08028(23)	0.40821(39)	0.34638(8)		
C(5)	0.29926(25)	0.40414(47)	0.44148(9)	4.0(5)	
C(6)	0.17454(27)	0.20471(47)	0.31528(9)		
C(7)	0.39322(28)	0.20719(49)	0.41023(11)		
C(8)	0.33074(29)	0.10932(51)	0.34705(11)		
H(N1)	0.0875(34)	0.7730(50)	0.4802(12)		
H(N2)	-0.1133(32)	0.4453(54)	0.2767(12)		3.5(5)
H(C5)	0.3385(28)	0.4803(49)	0.4872(11)		3.0(5)
H(C6)	0.1254(30)	0.1307(47)	0.2700(12)		3.6(5)
H(C7)	0.5032(38)	0.1363(50)	0.4302(13)	4.3(5)	
H(C8)	0.3974(38)	-0.0437(59)	0.3262(14)	5.4(6)	

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
O(1)	1197(24)	6290(97)	148(3)	756(38)	-7(7)	-249(14)	0.267	0.166	0.177
O(2)	1104(25)	7180(108)	129(3)	769(37)	-46(7)	51(13)	0.268	0.145	0.201
C(1)	927(31)	4358(109)	110(4)	63(44)	24(9)	9(16)	0.201	0.151	0.177
C(2)	912(29)	4269(111)	103(4)	-51(44)	9(8)	71(16)	0.201	0.144	0.176
N(1)	995(27)	4217(95)	104(4)	194(37)	-39(8)	-92(13)	0.210	0.137	0.182
N(2)	1015(27)	4399(94)	94(3)	-22(39)	-23(7)	-56(14)	0.203	0.134	0.191
C(3)	933(29)	3289(97)	133(4)	-51(43)	11(9)	-31(16)	0.186	0.158	0.176
C(4)	869(29)	3459(101)	125(4)	-116(42)	15(8)	28(15)	0.186	0.155	0.171
C(5)	1012(34)	4763(121)	180(5)	104(48)	-74(10)	-92(19)	0.231	0.156	0.204
C(6)	1288(36)	4344(117)	153(5)	-27(49)	89(10)	-90(17)	0.205	0.176	0.202
C(7)	1007(36)	5042(129)	258(6)	344(52)	-34(12)	-91(22)	0.254	0.169	0.212
C(8)	1247(38)	4907(130)	240(6)	422(53)	147(12)	-112(21)	0.234	0.178	0.222

CRYSTAL DATA

1,4-Dihydro-2,3-quinoxalinedione, C₈H₆N₂O₂F.W. 162.2 g mol⁻¹Monoclinic, space group *P*2₁/*n* $a = 8.068(1)$, $b = 4.275(1)$, $c = 20.911(2)$ Å, $\beta = 100.42(1)^\circ$ $V = 709.3$ Å³ $Z = 4$, $F(000) = 336$ $D_x = 1.518$ g cm⁻³ $\mu(\text{CuK}\alpha) = 8.4$ cm⁻¹

DISCUSSION

Bond distances and angles for a molecule of 1,4-dihydro-2,3-quinoxalinedione in the crystal are given in Fig. 1, which also shows the labelling of the atoms. The question of which tautomer is predominant in the solid state is clearly answered by the C-O distances of 1.23 Å and the localization of the hydrogen atoms bonded to nitrogen. Obviously the molecule is a dione. There is no evidence that more than one tautomer is present in the crystal.

Chemically equivalent distances and angles are very similar and so are the thermal vibrations of corresponding atoms (Table 1). In the

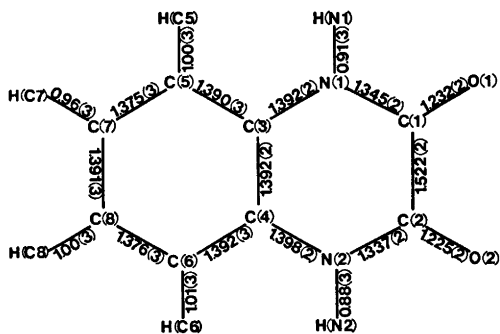


Fig. 1. Bond distances (Å) and angles (°) in 1,4-dihydro-2,3-quinoxalinedione.

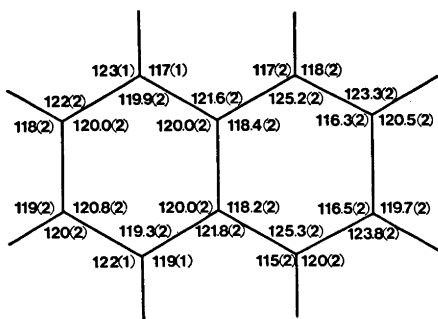


Fig. 2. A stereoview down [010] of the crystal structure showing the packing of the molecules and the hydrogen bonding. Hydrogen bonds are drawn as single lines.

Table 2. Deviations (Å) from a least-squares plane through the molecule. All atoms except hydrogens were included and given equal weight in the calculation.

Atom	Deviation (Å)	Atom	Deviation (Å)
O(1)	0.070	C(6)	0.011
O(2)	0.004	C(7)	0.024
C(1)	0.004	C(8)	0.050
C(2)	-0.015	H(N1)	-0.085
N(1)	-0.040	H(N2)	-0.040
N(2)	-0.025	H(C5)	-0.055
C(3)	-0.036	H(C6)	-0.001
C(4)	-0.019	H(C7)	0.062
C(5)	-0.028	H(C8)	0.030

crystalline form the molecule is not completely planar, *cf.* Table 2. Atom O(1) has the largest deviation, 0.07 Å, from the least-squares plane fitted to all non-hydrogen atoms. The conformation can be described as a very flattened boat as is the case for one of the two independent molecules in the crystal structure of 2,3-*t*-butyl-quinoxaline.⁹ Probably the molecule is planar, of symmetry C_{2v} , in solution and distorted by intermolecular forces in the solid state.

Tinland¹⁰ has calculated bond distances in quinoxaline using a modified semi-empirical Pariser-Parr-Pople method. His values are in

Table 3. Intermolecular distances and angles describing the hydrogen bonding.

Atoms	Distance (Å)	Atoms	Angle (°)
O(1)–N(1)	2.847(2)	C(1)–O(1)–H(N1)	123.0(8)
O(1)–H(N1)	1.95(2)	O(1)–H(N1)–N(1)	170(2)
O(2)–N(2)	2.826(2)	C(2)–O(2)–H(N2)	131.7(8)
O(2)–H(N2)	1.95(2)	O(2)–H(N2)–N(2)	175(2)

good agreement with the bond distances found in 2,3-*t*-butyl-quinoxaline⁹ except the distance C(1)–C(2) (numbering according to Fig. 1), which is 0.06 Å longer, possibly because of the bulky *t*-butyl groups. Tinland's calculation predicted a shortening of 0.02 Å in the distances C(5)–C(7) and C(6)–C(8) and a similar elongation of the other bonds in that ring relative to the benzene carbon-carbon distances. In 1,4-dihydro-2,3-quinoxalinedione the shortening of the two bonds prevails while the other distances in the aromatic ring, around 1.39 Å, are unaffected. The distances in the hetero atom ring (*cf.* Fig. 1) are approximately 1.52, 1.34 and 1.40 Å compared to 1.48, 1.32 and 1.36 Å, respectively, in 2,3-*t*-butyl-quinoxaline. The distances C(3)–N(1) and C(4)–N(2) are only slightly shorter than the C–N distances in 1,2-diaminobenzene (1.41 Å).¹¹

The diamide part of the molecule has dimensions very similar to those of oxamide, (NH₂CO)₂, with the distances C–C 1.542(6), C–O 1.243(4), and C–N 1.315(4) Å.¹² Oxamide is planar and in the *trans* conformation in the crystals. The distance C(1)–C(2) of 1.522(2) Å in the present compound indicates essentially σ -bonding. On the other hand there is a considerable double bond character in the C–N bonds just as in oxamide. This π -overlap is only possible with an approximately planar hetero atom ring.

Fig. 2 shows the packing of the molecules. The only short intermolecular contacts are *via* hydrogen bonds N–H...O, *cf.* Table 3. One of the amide parts in a molecule is hydrogen bonded over an inversion centre to another molecule. The other amide part is hydrogen bonded to two other molecules along a 2₁-axis. The hydrogen bonds connect the molecules to infinite zig-zag layers, parallel to [010], which are stacked with normal van der Waals contacts.

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