

## 2-(2-Oxazolin-2-yl)benzene-1,4-diol: X-ray and density functional theory studies

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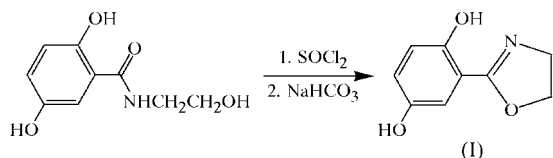
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In the crystal structure of the title compound, C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>, there are strong intramolecular O—H···N and intermolecular O—H···O hydrogen bonds which, together with weak intermolecular C—H···O hydrogen bonds, lead to the formation of infinite chains of molecules. The calculated intermolecular hydrogen-bond energies are  $-11.3$  and  $-2.7$  kJ mol<sup>-1</sup>, respectively, showing the dominant role of the O—H···O hydrogen bonding. A natural bond orbital analysis revealed the electron contribution of the lone pairs of the oxazoline N and O atoms, and of the two hydroxy O atoms, to the order of the relevant bonds.

### Comment

The present study of the title compound, (I), is a continuation of our previous studies of bifunctional monophenols (Langer *et al.*, 2005, 2006), which are monomers of the AB type that provide linear poly(etheramide)s in a thermally initiated polymerization (Lustoň *et al.*, 2006). According to Flory (1952), analogous compounds containing two phenolic groups, hence compounds of the AB<sub>2</sub> type, provide hyperbranched polymers during thermal treatment (Lustoň & Kronek, 2007; Huber *et al.*, 1999). Therefore, it was of interest to study also the crystal structure of these monomers, *viz.* compounds with two phenolic groups and a 2-oxazoline ring. In this paper, we present the results for (I), one of the six possible isomers.



The atom-numbering scheme, together with the corresponding atomic displacement ellipsoid plot for (I), are shown

in Fig. 1. Selected geometric parameters are listed in Table 1. The C1—C4 bond length indicates weak conjugation between the 2-oxazoline ring substituted at the C-2 position (C1) and the benzene ring. The acute angle between the planes of the oxazoline and benzene rings is 2.76 (15)°. The 2-oxazoline ring in (I) is almost planar [ $\chi^2 = 63.5$ , maximum deviation 0.012 (2) Å], as it is, for example, in 2-(2-hydroxyphenyl)-2-oxazoline and 2-(4-hydroxyphenyl)-2-oxazoline (Langer *et al.*, 2005).

A natural bond orbital (NBO) analysis (Foster & Weinhold, 1980) reveals that the electrons of the lone pairs of atoms N1, O1, O5 and O8 participate in the electron density within the N1=C1, O1—C1, O5—C5 and O8—C8 bonds. The Wiberg indices illustrated in Fig. 2 show bond orders in the molecule of (I).

There are strong hydrogen bonds in the structure of (I), of the O—H···N (intramolecular) and O—H···O (intermolecular) types, as well as weak hydrogen bonds of the C—H···O type (intermolecular) (Fig. 3 and Table 2). Calculations using the GAUSSIAN98 program package (Frisch *et al.*, 1998) confirmed the experimental data, with more realistic H···A distances and D—H···A angles (Table 2).

The hydrogen-bonding pattern can be described using graph theory (Bernstein *et al.*, 1995; Grell *et al.*, 1999). On the first-level graph set, S(6) intramolecular strings formed by

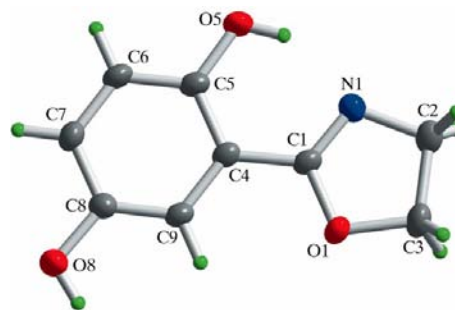


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small spheres of arbitrary radii.

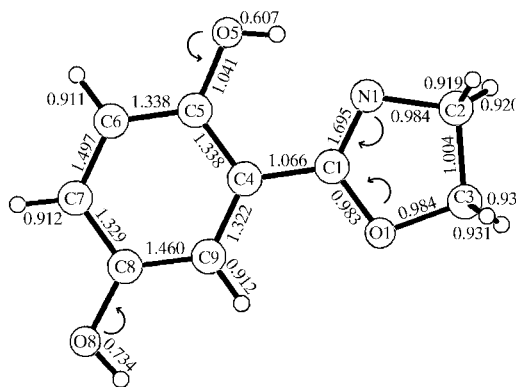
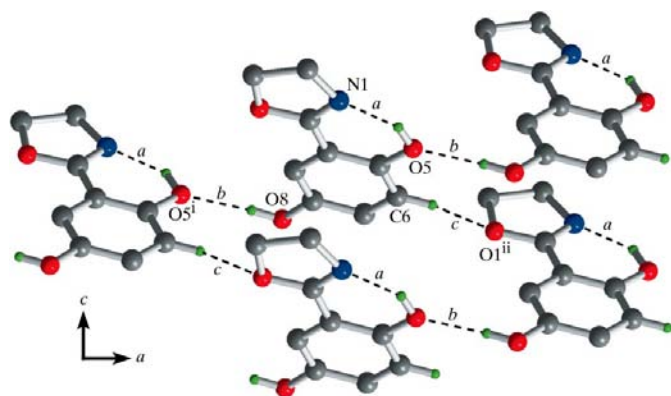


Figure 2

Wiberg bond orders calculated for an isolated molecule of (I) using NBO formalism. Arrows indicate predicted transfers of electron density from lone pairs.


**Figure 3**

The hydrogen-bonding pattern in the crystal structure of (I); see Table 2 for definitions of symbols and symmetry codes.

hydrogen bonds *a*,  $C(7)$  chains formed by hydrogen bonds *b* and  $C(6)$  chains formed by hydrogen bonds *c* were identified (see Fig. 3 for definitions of hydrogen bonds). On the second-level graph set,  $C_2^2(11)$  chains and  $R_4^4(22)$  rings, formed by hydrogen bonds *b* and *c*, could be recognized.

The energy of the intermolecular hydrogen bonds was calculated and corrected to basis set superposition error (BSSE) using a standard procedure (Boys & Bernardi, 1970). The energy of hydrogen bond *b* was estimated to be approximately  $-11.3 \text{ kJ mol}^{-1}$ , and that of hydrogen bond *c* to be  $-2.7 \text{ kJ mol}^{-1}$ . Hydrogen bond *b* plays a dominant role in the intermolecular interactions in the structure of (I) (Fig. 3).

## Experimental

The relevant data for the synthetic and analytical methods, as well as a description of the instruments and materials used for the preparation and characterization of 2-(2-oxazolin-2-yl)benzene-1,4-diol, have been reported previously (Lustoň & Kronek, 2007). After recrystallization from toluene, well developed yellow needles of (I) were obtained (m.p. 388–389 K).

### Crystal data

$C_9H_9NO_3$	$Z = 16$
$M_r = 179.17$	$D_x = 1.383 \text{ Mg m}^{-3}$
Orthorhombic, <i>Fdd2</i>	Mo $K\alpha$ radiation
$a = 24.4297(3) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 31.7167(7) \text{ \AA}$	$T = 173(2) \text{ K}$
$c = 4.4409(1) \text{ \AA}$	Needle, yellow
$V = 3440.94(12) \text{ \AA}^3$	$1.00 \times 0.06 \times 0.04 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	9919 measured reflections
$\omega$ scans	1010 independent reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)	840 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.513$ , $T_{\max} = 0.996$	$R_{\text{int}} = 0.073$
	$\theta_{\max} = 26.4^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 2.545P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
1010 reflections	$\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
129 parameters	
H-atom parameters constrained	

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O1—C1	1.348 (3)	O5—C5	1.361 (3)
N1—C1	1.277 (3)	O8—C8	1.375 (3)
C1—C4	1.451 (3)		
C2—N1—C1—O1	−1.9 (4)	N1—C1—C4—C9	−178.0 (3)
C3—O1—C1—N1	0.7 (3)	O1—C1—C4—C9	3.4 (4)
C1—N1—C2—C3	2.2 (3)	N1—C1—C4—C5	1.2 (4)
C1—O1—C3—C2	0.7 (3)	O1—C1—C4—C5	−177.5 (3)
N1—C2—C3—O1	−1.7 (3)		

**Table 2**

Comparison of experimental and calculated hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for compound (I).

Notation	$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
<i>a</i>	O5—H5 $\cdots$ N1	0.84	1.80	2.548 (3)	147
	Calculated	1.006	1.642	2.549	147.7
<i>b</i>	O8—H8 $\cdots$ O5 <sup>i</sup>	0.84	1.92	2.756 (3)	175
	Calculated	0.975	1.781	2.755	176.0
<i>c</i>	C6—H6 $\cdots$ O1 <sup>ii</sup>	0.95	2.53	3.284 (3)	136
	Calculated	1.084	2.442	3.282	133.3

Symmetry codes: (i)  $-\frac{1}{4} + x, \frac{1}{4} - y, -\frac{1}{4} + z$ ; (ii)  $\frac{1}{4} + x, \frac{1}{4} - y, -\frac{3}{4} + z$ .

H atoms were constrained to ideal geometry using an appropriate riding model and were refined isotropically. For the hydroxyl groups, the O—H distances (0.84  $\text{\AA}$ ) and C—O—H angles ( $109.5^\circ$ ) were kept fixed, while the torsion angles were allowed to refine, with the starting positions based on the circular Fourier synthesis.

In the absence of significant anomalous scattering, the absolute configuration could not be reliably determined and the Friedel pairs were therefore merged.

The theoretical investigation of the hydrogen bonds was performed using the *GAUSSIAN98* program package (Frisch *et al.*, 1998) at the B3LYP/6-31G\*\* level of theory (Becke, 1993). A cluster (66 atoms) consisted of three neighbouring molecules of (I), which represented hydrogen bonds existing in this compound. Only partial optimization of the positions of the H atoms participating in the hydrogen bonds was carried out. Natural bond orbital (NBO) calculations were carried out by means of the *NBO* program (Glendening *et al.*, 1993) included in the *GAUSSIAN98* package.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN2121). Services for accessing these data are described at the back of the journal.

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