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2-(4-Hydroxyphenyl)-4,4-dimethyl-2-oxazoline: X-ray and density functional theory study

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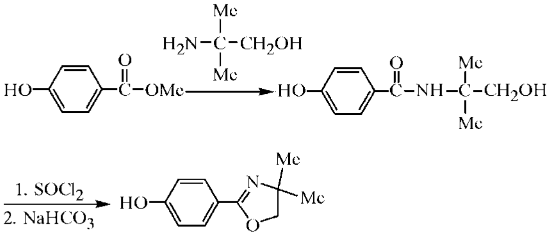
In the crystal structure of the title compound, $C_{11}H_{13}NO_2$, there are strong intermolecular O—H···N hydrogen bonds which, together with weak intramolecular C—H···O hydrogen bonds, lead to the formation of infinite chains of molecules, held together by weak intermolecular C—H···O hydrogen bonds. A theoretical investigation of the hydrogen bonding, based on density functional theory (DFT) employing periodic boundary conditions, is in agreement with the experimental data. The cluster approach shows that the influence of the crystal field and of hydrogen-bond formation are responsible for the deformation of the 2-oxazoline ring, which is not planar and adopts a $^4T_3$ ($^{C3}T_{C2}$) conformation.

Comment

In a previous paper (Langer *et al.*, 2005), we reported the crystal structures for three isomers of hydroxyphenyl-2-oxazoline, namely 2-(2-hydroxyphenyl)-2-oxazoline, 2-(3-hydroxyphenyl)-2-oxazoline and 2-(4-hydroxyphenyl)-2-oxazoline. All these compounds polymerize rapidly at around 473 K. On the other hand, it has been observed that polymerization of 2-(4-hydroxyphenyl)-4,4-dimethyl-2-oxazoline, (I), is restricted under similar conditions (Lustoň *et al.*, 2006). This confirmed the observation of Bassiri *et al.* (1967) that 4- and 5-substituted 2-oxazolines have low reactivity in the course of cationic polymerization. Therefore, it was of interest to determine the crystal structure of (I) as a contribution to the understanding of low reactivity in both ring-opening polyaddition reactions and in cationic polymerization.

The atom-numbering scheme, together with the corresponding atomic displacement ellipsoid plot for (I), are shown in Fig. 1. Selected geometric parameters for (I) are listed in Table 1. The C1—C4 bond length in (I) indicates weak conjugation between the 2-oxazoline ring substituted at the C-2 position (C1) and the benzene ring. The angle between the planes of the oxazoline and benzene rings is 5.84 (8)°. Surprisingly, the 2-oxazoline ring in (I) is not planar, as it is, for example, in 2-(2-hydroxyphenyl)-2-oxazoline and 2-(4-hydroxyphenyl)-2-oxazoline (Langer *et al.*, 2005). The values of the relevant dihedral angles (Table 1) and puckering parameters [Cremer & Pople (1975); $Q = 0.142$ (2) Å and $\varphi = 134.4$ (6)°] indicate that this ring deviates significantly from planarity (twisting about C2—C3) and adopts a $^4T_3$ ($^{C3}T_{C2}$) conformation slightly distorted towards the ^4E (^{C3}E) conformation. This is similar to what was found for one of the symmetry-independent molecules in the structure of 2-(3-hydroxyphenyl)-2-oxazoline (Langer *et al.*, 2005), but in that case a $^3T_4$ conformation of the 2-oxazoline ring was observed. We assume that the presence of two 4-methyl substituents is responsible for the observed deviation from planarity and hence the observed low reactivity in the course of both thermally initiated polyaddition and cationic polymerization of the title compound.



(I)

Density functional theory (DFT) calculations at the B3LYP/6-31G** level of theory using *GAUSSIAN98* (Frisch *et al.*, 1998) were used in an attempt to explain the non-planarity of the 2-oxazoline ring in (I). An isolated molecule of (I) was optimized first and, surprisingly, the molecule with a planar 2-oxazoline ring was the stable configuration. In order to simulate the influence of nearest neighbours on the molecular geometry, a methanol molecule was positioned to allow formation of the O2—H2···N1 hydrogen bond. In this case, the molecular geometry remains very close to that found in the crystal structure. The calculated O2—H2···N1 hydrogen bond (1.89 Å) and *D*—H···*A* angle (173°) agree well with the experimental data (1.88 Å and 174°). A trial with the molecule having a planar oxazoline ring and a methanol molecule in the

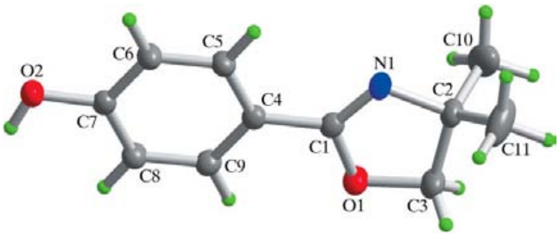


Figure 1
The atom-numbering scheme of (I), with atomic displacement ellipsoids drawn at the 50% probability level.

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neighbourhood also resulted in the deformation of the oxazoline ring. The calculated O2—H2···N1 hydrogen-bond energy of a molecule of (I) with a methanol molecule, corrected for the basis set superposition error (BSSE) using a standard procedure (Boys & Bernardi, 1970), was estimated to be approximately −13 kJ mol^{-1}. This value falls within the range for weak hydrogen bonds (Jeffrey, 1997). Despite the simplicity of such simulations, we propose that it is the influence of the crystal field and hydrogen-bond formation which are responsible for the deformation of the oxazoline ring. Llamas-Saiz *et al.* (1992) published a statistical survey of the intermolecular R—O—H···Nsp^2 interaction in organic crystals. The calculated geometric parameters presented in this work (Table 2) agree with their published mean values (in parentheses) [O—H = 1.06 Å (0.97 Å), O···N = 2.62 Å (2.80 Å), H···N = 1.56 Å (1.87 Å) and O—H···N = 173° (175°)].

The hydrogen-bonding geometry for (I) is listed in Table 2. A theoretical investigation of hydrogen bonds was performed using the Vienna *ab initio* simulation package *VASP* (Kresse & Furthmüller, 1996; Kresse & Hafner, 1993). The calculations were based on DFT with periodic boundary conditions (Jones & Gunnarsson, 1989) using a generalized gradient approximation (GGA) in an exchange-correlation function (Perdew *et al.*, 1992). The interactions between ions and electrons were described using the projector-augemented wave method (PAW; Kresse & Joubert, 1999) with a plane wave cut-off of 400 eV. The optimizations of the structure were carried out using the conjugated gradient method in 4κ points (Teter *et al.*, 1989; Bylander *et al.*, 1990). The results of the calculations are in agreement with the experimental data.

The hydrogen-bonding pattern can be described using graph theory (Bernstein *et al.*, 1995; Grell *et al.*, 1999). For (I), there is just one intermolecular hydrogen bond, *a*, of the O—H···N type, which is described as a $C(8)$ chain in the first-level graph set (Fig. 2). There are also two weak hydrogen bonds of C—H···O type, one intramolecular, *b*, described as an $S(5)$ string, and one intermolecular, *c*, described as a $C(5)$ chain. On the second-level of graph-set theory, $C_2^2(7)$ and $C_2^2(13)$ chains, formed by hydrogen bonds *a* and *c*, are recognized. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999), and the notation of the hydrogen bonds here is that given in Table 2.

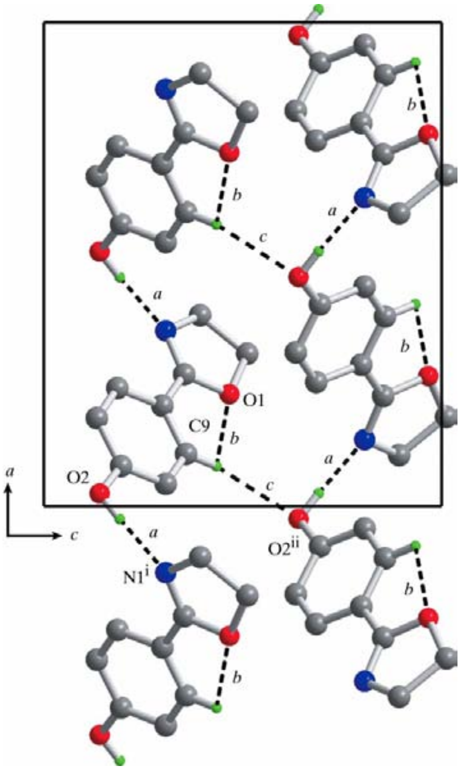

Figure 2
The hydrogen-bonding pattern in the crystal structure of (I), viewed along the *b* axis. H atoms not involved in hydrogen bonding and methyl C atoms have been omitted for clarity. See Table 2 for symbols and symmetry codes.

Experimental

For the preparation of compound (I) (see scheme), methyl 4-hydroxybenzoate (7.61 g, 0.05 mol) and 2-amino-2-methylpropan-1-ol (4.46 g, 0.05 mol) were stirred under argon at 423 K for 6 h and evolved methanol was collected in a Dean–Stark trap. The product, *N*-(1,1-dimethyl-2-hydroxyethyl)-4-hydroxybenzamide, which is a brown viscous material, was diluted with CH_2Cl_2 (50 ml) and cyclized in the next step with thionyl chloride (11.2 g, 0.1 mol, added dropwise at 273 K). The reaction mixture was then left for 48 h at room temperature. A brown solid was isolated, washed with CH_2Cl_2 and dried. It was then dispersed in water and solid $NaHCO_3$ was added in small portions until the pH was neutral. The resulting white solid, which appeared after several minutes, was recrystallized from toluene. Colourless crystals of compound (I) (m.p. 494–496 K) were obtained (yield 8.02 g, 83.9%). ^{1}H NMR (DMSO-d_6): δ 10.04 (*s*, 1H, OH), 7.66 (*d*, 2H, aromatic), 6.80 (*d*, 2H, aromatic), 4.03 (*s*, 2H, OCH_2), 1.24 (*s*, 6H, CH_3).

Crystal data

$C_{11}H_{13}NO_2$
M_r = 191.22
Orthorhombic, $Pca2_1$
a = 12.1590 (2) Å
b = 8.5666 (1) Å
c = 9.9999 (1) Å
V = 1041.60 (2) Å^3
Z = 4
D_x = 1.219 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 173 (2) K
Block, colourless
0.80 × 0.40 × 0.26 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.936, T_{max} = 0.978
11104 measured reflections
1962 independent reflections
1776 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 32.9°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.105
S = 1.05
1962 reflections
138 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.0539P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3640 (17)	C1—C4	1.4652 (18)
N1—C1	1.2826 (17)	O2—C7	1.3566 (16)
C2—N1—C1—O1	2.42 (17)	N1—C1—C4—C9	177.18 (14)
C3—O1—C1—N1	7.33 (18)	O1—C1—C4—C9	−2.97 (19)
C1—N1—C2—C3	−10.43 (16)	N1—C1—C4—C5	−2.2 (2)
C1—O1—C3—C2	−13.26 (17)	O1—C1—C4—C5	177.61 (13)
N1—C2—C3—O1	14.24 (17)		

Table 2
Comparison of hydrogen-bonding and short-contact geometry (Å, °) for compound (I) with the results of theoretical calculations.

Notation	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
a	O2—H2···N1^{i}	0.84	1.88	2.7175 (16)	174
	calculated	1.06	1.56	2.621	173
b	C9—H9···O1	0.95	2.42	2.7637 (17)	101
	calculated	1.09	2.39	2.753	99
c	C9—H9···O2^{ii}	0.95	2.54	3.4638 (17)	163
	calculated	1.09	2.40	3.449	162

Symmetry codes: (i) $-\frac{1}{2}+x, 1-y, z$; (ii) $-x, 1-y, \frac{1}{2}+z$.

H atoms were allowed for isotropically and were constrained to ideal geometry using an appropriate riding model. The C—H distance was kept fixed at 0.95 Å for aromatic H atoms and at 0.99 Å for secondary H atoms. For the hydroxyl group, the O—H distance (0.84 Å) and C—O—H angle (109.5°) were kept fixed, while the torsion angle was allowed to refine, with the starting position based on the circular Fourier synthesis. For methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on the threefold averaged circular Fourier synthesis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); 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: FG3022). Services for accessing these data are described at the back of the journal.

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