

Three isomeric forms of hydroxyphenyl-2-oxazoline: 2-(2-hydroxyphenyl)-2-oxazoline, 2-(3-hydroxyphenyl)-2-oxazoline and 2-(4-hydroxyphenyl)-2-oxazoline

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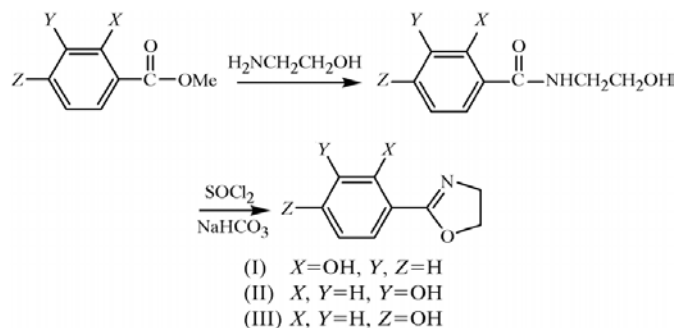
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Crystal structures are reported for three isomeric compounds, namely 2-(2-hydroxyphenyl)-2-oxazoline, (I), 2-(3-hydroxyphenyl)-2-oxazoline, (II), and 2-(4-hydroxyphenyl)-2-oxazoline, (III), all C₉H₉NO₂ [systematic names: 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol, (I), 3-(4,5-dihydro-1,3-oxazol-2-yl)phenol, (II), and 4-(4,5-dihydro-1,3-oxazol-2-yl)phenol, (III)]. In these compounds, the deviation from coplanarity of the oxazoline and benzene rings is dependent on the position of the hydroxy group on the benzene ring. The coplanar arrangement in (I) is stabilized by a strong intramolecular O—H...N hydrogen bond. Surprisingly, the 2-oxazoline ring in molecule *B* of (II) adopts a ³T₄ (^{C2}T_{C3}) conformation, while the 2-oxazoline ring in molecule *A*, as well as that in (I) and (III), is nearly planar, as expected. Tetramers of molecules of (II) are formed and they are bound together *via* weak C—H...N hydrogen bonds. In (III), strong intermolecular O—H...N hydrogen bonds and weak intramolecular C—H...O hydrogen bonds lead to the formation of an infinite chain of molecules perpendicular to the *b* direction. This paper also reports a theoretical investigation of hydrogen bonds, based on density functional theory (DFT) employing periodic boundary conditions.

Comment

Cyclic imino ethers, among them 2-oxazolines, are important intermediates in organic synthesis. The title compounds, (I)–(III), were prepared in the course of our research focused on cyclic imino ethers and their utilization in polymer chemistry (Kronek *et al.*, 1998), as hydroxyphenyl-2-oxazolines are known to produce poly(ether-amides) on heating of the

monomer (Wörner *et al.*, 1995). Although the syntheses of these compounds have already been reported [(I): Cwik *et al.* (2002), Black & Wade (1972) and Peterson *et al.* (1980); (II):



Kalle (1969); (III): Nonnenmacher & Plieninger (1982)], their crystal structures have not been published until now. Among 87 matches from the Cambridge Structural Database (CSD, February 2005 update, Version 5.26; Allen, 2002) for (I), only 15 structures were relevant (*i.e.* having a 4,5-unsubstituted 2-oxazoline ring and a 3,4,5,6-unsubstituted 2-hydroxyphenyl moiety), but in all these compounds the 2-(2-hydroxyphenyl)-2-oxazoline has been reported only as a ligand in several complexes with metals such as Fe, Mn, Ni, V, Zn, Al, In and Re (*e.g.* Qian *et al.*, 2004; Kooijman *et al.*, 2002; Miller *et al.*, 1999; Melchior *et al.*, 1999). For compounds (II) and (III), a CSD search revealed only one and 13 similar structures, respectively, but none of them had a relevant hydroxy group in the *meta* or *para* position of the benzene ring.

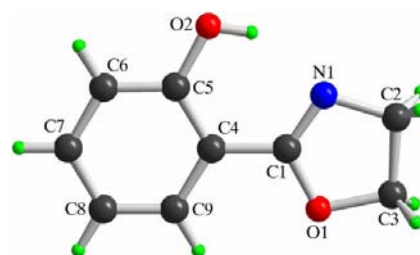


Figure 1

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

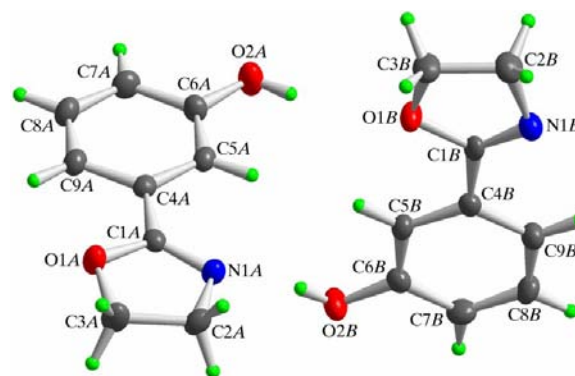


Figure 2

The atom-numbering scheme for (II), with atomic displacement ellipsoids drawn at the 50% probability level.

Selected geometric parameters for (I), (II) and (III) are compared in Table 1. The numbering schemes, together with the corresponding atomic displacement ellipsoid plots, are shown in Figs. 1–3, respectively. The crystal packings of (I) and (II) are depicted in Figs. 4 and 5, respectively. The hydrogen-bonding schemes for (II) and (III) are shown in Figs. 6 and 7, respectively. The hydrogen-bonding geometries for (I), (II) and (III) are compared in Table 2. The 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 density functional theory (DFT) with periodic boundary conditions (Jones & Gunnarsson, 1989).

The 2-oxazoline ring in (I) and (III) is nearly planar. Surprisingly, in the case of compound (II), with two molecules, *A* and *B*, in the asymmetric unit, the values of the relevant dihedral angles (Table 1) and puckering parameters (Cremer & Pople, 1975), $Q = 0.108$ (3) Å and $\varphi = 310.3$ (17)°, indicate that this ring in molecule *B* deviates significantly from planarity (twisting about the C3*B*–C2*B* bond) and adopts a 3T_4 (${}^2T_{C3}$) conformation, while the 2-oxazoline ring in molecule *A* is again nearly planar. This difference may be due to

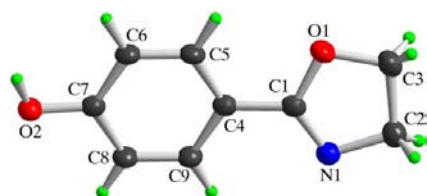


Figure 3
The atom-numbering scheme for (III), with atomic displacement ellipsoids drawn at the 50% probability level.

the arrangement of molecule *B* in the tetramer, as well as hydrogen bonding.

As seen from the values of the acute angles between the planes of the oxazoline and benzene rings [0.74 (4)° for (I), 4.75 (16) and 3.49 (17)° for molecules *A* and *B* of (II), respectively, and 11.22 (6)° for (III)], the mutual position of these rings reflects the location (*ortho*, *meta* or *para*, respectively) of the hydroxy group on the benzene ring. In this respect, the coplanarity of both rings in the *o*-hydroxy derivative, (I) (Fig. 1), and the most evident deviation from coplanarity in the *p*-hydroxy derivative, (III), is observed. We assume that the coplanar arrangement of the rings and the synperiplanar orientation of atom O2 (*ortho*-hydroxy group) with respect to the C1–N1 bond in (I) is stabilized by the strong intramolecular O2–H2···N1 hydrogen bond (Table 2). In this regard, free rotation about the sp^2 – sp^2 C1–C4 bond could be sufficiently restricted, leading to possible atropisomerism, and this is probably responsible for the chirality because, although there is no chiral atom in (I), optical activity of $[\alpha]_D^{20} = 3.0$ ($c = 1$, CHCl₃) was observed for this compound. The synperiplanar arrangement of atom N1 relative to the C4–C5 bond, with atom N1 directed slightly below the benzene ring plane, is observed for both molecules *A* and *B* of the *m*-hydroxy derivative, (II) (Fig. 2). In the case of molecule *A*, similar to the C5–O2 and C1–N1 bonds in (I), the C6–O2 and C1–N1 bonds are oriented *cis* with respect to the plane perpendicular to the plane of the benzene and oxazoline rings across the C1–C4 bond. In contrast, the orientation of the C6–O2 and C1–N1 bonds is *trans* in the case of molecule *B*. For the *p*-hydroxy derivative, (III), shown in Fig. 3, the C1–N1 and C4–C5 bonds are oriented antiperiplanar, with atom N1 directed slightly above the plane of the benzene ring.

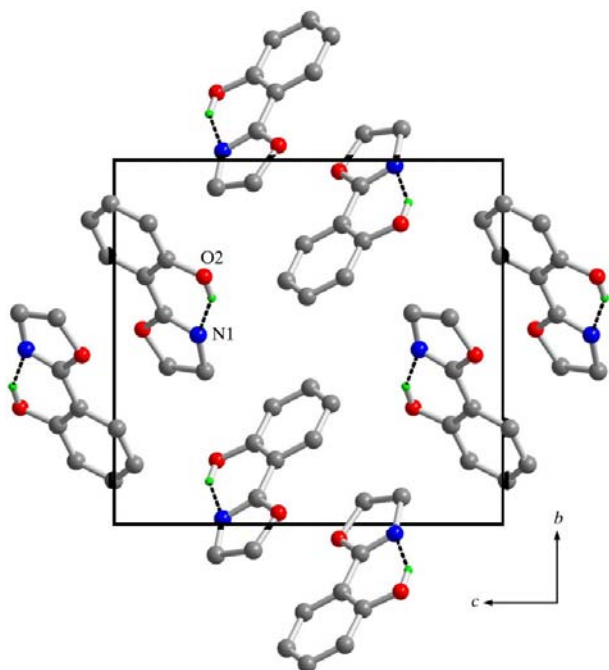


Figure 4
The unit-cell contents of (I) in projection along the *a* axis. H atoms not involved in hydrogen bonding have been omitted for clarity.

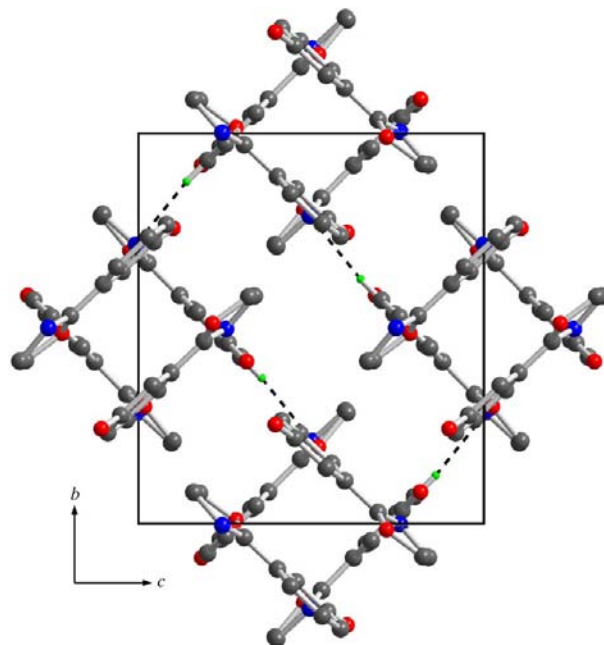


Figure 5
A projection of the structure of (II) along the *a* axis. The tetramers are bound together *via* weak hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

The C1–C4 bonds (Table 1) in compounds (I)–(III) indicate a weak conjugation between the 2-oxazoline ring substituted at the C-2 position (C1) and the benzene ring.

The hydrogen-bonding patterns can be described using graph-set theory (Bernstein *et al.*, 1995; Grell *et al.*, 1999). For (I), there is just one intramolecular hydrogen bond of the O–H···N type, which is, on the first-level graph-set, described as

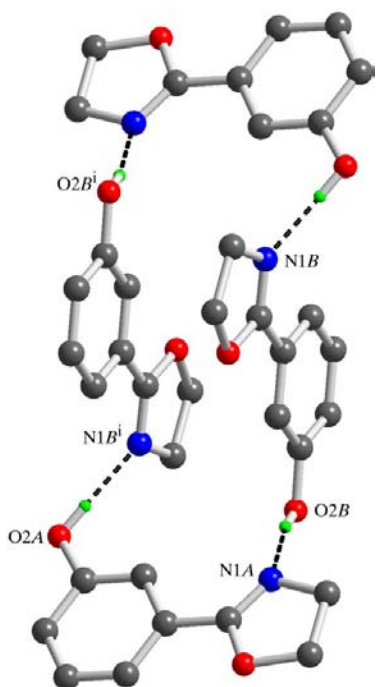


Figure 6
A tetramer of molecules of (II) formed *via* hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

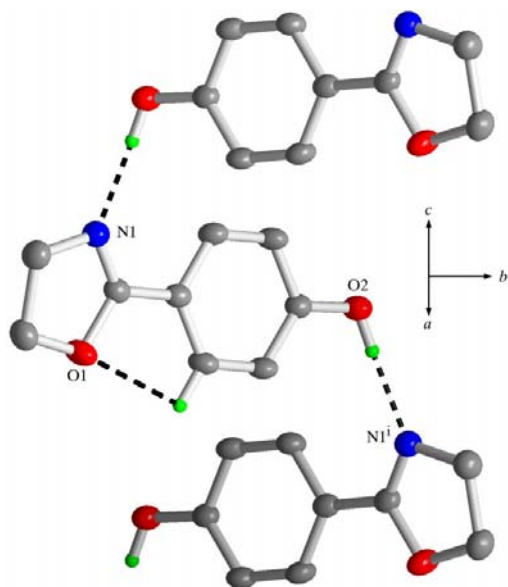


Figure 7
The hydrogen-bonding pattern in the crystal lattice of (III). H atoms not involved in hydrogen bonding have been omitted for clarity.

an $S(6)$ string. For (II), there are two strong hydrogen bonds of the O–H···N type, two weak intramolecular bonds of the C–H···O type and one weak intermolecular interaction of the C–H···N type. On the first-level graph-set, the hydrogen-bonding pattern can be classified as $D(2)$ for hydrogen bonds (IIa) and (IIb), as $S(5)$ for (IIc) and (Iie), and as a $C(7)$ chain for hydrogen bond (IId) (Table 2). On the second-level graph-set, the above-mentioned tetramer is described as an $R_4^4(28)$ ring formed by hydrogen bonds (IIa) and (IIb), apart from $D_3^3(14)$ and $D_2^2(10)$ for bonds (IIa) and (IId), and (IIb) and (IId), respectively. The first-level graph-set descriptors for (III) are $C(8)$ for the strong hydrogen bond (IIIa) and $S(5)$ for the weak intramolecular hydrogen bond (IIIb). The molecules thus form an infinite chain along [101]. 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 as defined in Table 2.

Experimental

Compound (I) was prepared according to the procedure of Kobayashi *et al.* (1984). In the first step, methyl 2-hydroxybenzoate was reacted with an excess of ethanolamine at 413 K to give the corresponding hydroxyamide. This, in the next step, upon treatment with thionyl chloride, afforded the required compound, (I). Compounds (II) and (III) were prepared analogously starting from the methyl 3-hydroxybenzoate and methyl 4-hydroxybenzoate, respectively. The analytical data of all three title compounds were in accordance with those published previously. Colourless single crystals of adequate quality for diffraction analysis [with the exception of (II)] were obtained by slow crystallization from nearly saturated solutions in ethanol under moderate cooling in a refrigerator.

Compound (I)

Crystal data

$C_9H_9NO_2$
 $M_r = 163.17$
 Monoclinic, $P2_1/n$
 $a = 5.7562(1) \text{ \AA}$
 $b = 11.2464(1) \text{ \AA}$
 $c = 12.1365(1) \text{ \AA}$
 $\beta = 98.162(1)^\circ$
 $V = 777.72(2) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.394 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 8192 reflections
 $\theta = 2.5\text{--}33.0^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
 Block, colourless
 $0.80 \times 0.42 \times 0.40 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
 $T_{\min} = 0.724$, $T_{\max} = 0.961$
 13125 measured reflections

2785 independent reflections
 2451 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 33.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -16 \rightarrow 17$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.119$
 $S = 1.03$
 2785 reflections
 120 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 0.1146P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL* (Bruker, 2001)
 Extinction coefficient: 0.051 (7)

Compound (II)

Crystal data

C₉H₉NO₂ $D_x = 1.360 \text{ Mg m}^{-3}$
 $M_r = 163.17$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/c$ Cell parameters from 8192 reflections
 $a = 11.3650 (2) \text{ \AA}$ $\theta = 2.4\text{--}25.0^\circ$
 $b = 12.5867 (1) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $c = 11.2966 (2) \text{ \AA}$ $T = 173 (2) \text{ K}$
 $\beta = 99.534 (1)^\circ$ Needle, colourless
 $V = 1593.63 (4) \text{ \AA}^3$ $0.58 \times 0.18 \times 0.16 \text{ mm}$
 $Z = 8$

Data collection

Siemens SMART CCD area-detector diffractometer 2663 independent reflections
 ω scans 2167 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002) $R_{\text{int}} = 0.056$
 $T_{\text{min}} = 0.816$, $T_{\text{max}} = 0.985$ $\theta_{\text{max}} = 25.0^\circ$
 14444 measured reflections $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 2.9545P]$
 $R[F^2 > 2\sigma(F^2)] = 0.068$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.175$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.00$ $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 2663 reflections $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
 237 parameters
 H-atom parameters constrained

Compound (III)

Crystal data

C₉H₉NO₂ $D_x = 1.394 \text{ Mg m}^{-3}$
 $M_r = 163.17$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/n$ Cell parameters from 6730 reflections
 $a = 4.7778 (1) \text{ \AA}$ $\theta = 2.3\text{--}33.1^\circ$
 $b = 14.9883 (2) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $c = 10.9194 (1) \text{ \AA}$ $T = 173 (2) \text{ K}$
 $\beta = 95.945 (1)^\circ$ Plate, colourless
 $V = 777.74 (2) \text{ \AA}^3$ $0.60 \times 0.32 \times 0.06 \text{ mm}$
 $Z = 4$

Data collection

Siemens SMART CCD area-detector diffractometer 2784 independent reflections
 ω scans 2064 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002) $R_{\text{int}} = 0.038$
 $T_{\text{min}} = 0.710$, $T_{\text{max}} = 0.994$ $\theta_{\text{max}} = 33.1^\circ$
 13219 measured reflections $h = -7 \rightarrow 7$
 $k = -22 \rightarrow 22$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.2076P]$
 $R[F^2 > 2\sigma(F^2)] = 0.047$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.133$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.02$ $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 2784 reflections $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
 119 parameters
 H-atom parameters constrained

The sample of (II) used for data collection was not a single crystal. Nevertheless, it was possible to resolve one set of diffractions from one domain. As a result, there were overlapping reflections; 118 reflections were omitted from the data set due to severe F_o/F_c discrepancies ($F_o \gg F_c$). H atoms for all three compounds were refined isotropically and constrained to ideal geometry using an appropriate riding model. For aromatic H atoms, the C—H distance was kept fixed at 0.95 Å, and for secondary H atoms, C—H was fixed at 0.99 Å. For the hydroxy groups, the O—H distances (0.84 Å) and

Table 1

Comparison of selected interatomic parameters (Å, °) for compounds (I)–(III).

	(I)	(IIa)	(IIb)	(III)
C1—C4	1.4619 (10)	1.466 (4)	1.467 (4)	1.4654 (16)
C1—O1	1.3481 (9)	1.356 (3)	1.359 (3)	1.3575 (13)
C1—N1	1.2832 (10)	1.281 (4)	1.276 (4)	1.2775 (14)
C2—N1—C1—O1	0.07 (10)	−2.1 (4)	−2.8 (4)	2.11 (14)
C3—O1—C1—N1	−1.64 (10)	−2.4 (4)	−4.7 (4)	1.25 (14)
C1—N1—C2—C3	1.43 (8)	5.5 (3)	8.7 (3)	−4.32 (13)
C1—O1—C3—C2	2.32 (8)	5.6 (3)	9.5 (3)	−3.83 (13)
N1—C2—C3—O1	−2.27 (8)	−6.6 (3)	−10.9 (3)	4.86 (13)
N1—C1—C4—C9	−179.65 (7)	173.1 (3)	−6.2 (5)	−9.22 (18)
O1—C1—C4—C9	0.06 (10)	−5.2 (4)	174.9 (3)	172.50 (11)
N1—C1—C4—C5	0.40 (11)	−6.9 (4)	173.9 (3)	168.38 (12)
O1—C1—C4—C5	−179.89 (6)	174.8 (2)	−5.0 (4)	−9.90 (16)

Table 2

Comparison of hydrogen-bonding geometry (Å, °) for compounds (I)–(III) and results of density functional theory (DFT) calculations.

Notation	$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
(I)	O2—H2···N1 DFT	0.84 1.052	1.88 1.513	2.6238 (9) 2.481	148 150.22
(IIa)	O2A—H2A···N1B ⁱ DFT	0.84 1.028	1.92 1.619	2.732 (3) 2.637	164 169.2
(IIb)	O2B—H2B···N1A DFT	0.84 1.05	1.88 1.582	2.709 (3) 2.615	167 166.97
(IIc)	C5B—H5B···O1B DFT	0.95 1.083	2.43 2.384	2.764 (4) 2.767	100 98.9
(IId)	C7A—H7A···N1A ⁱⁱ DFT	0.95 1.097	2.60 2.375	3.540 (4) 3.467	171 175.94
(IIe)	C9A—H9A···O1A DFT	0.95 1.083	2.45 2.388	2.767 (4) 2.769	100 98.84
(IIIa)	O2—H2···N1 ⁱⁱⁱ DFT	0.84 1.043	1.86 1.480	2.6997 (13) 2.522	178 177.43
(IIIb)	C5—H5···O1 DFT	0.95 1.032	2.46 2.474	2.7874 (15) 2.830	100 99.31

Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

C—O—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting positions based on the circular Fourier synthesis.

For all compounds, 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: DN1097). Services for accessing these data are described at the back of the journal.

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