

(Z)-6-[[1,3-Dihydroxy-2-(hydroxymethyl)propan-2-yliminio]methyl]-2-ethoxyphenolate, (Z)-6-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yliminio]methyl]-4-nitratocyclohexa-2,4-dienone monohydrate and (R,E)-2-[(1-hydroxybutan-2-ylimino)methyl]phenol

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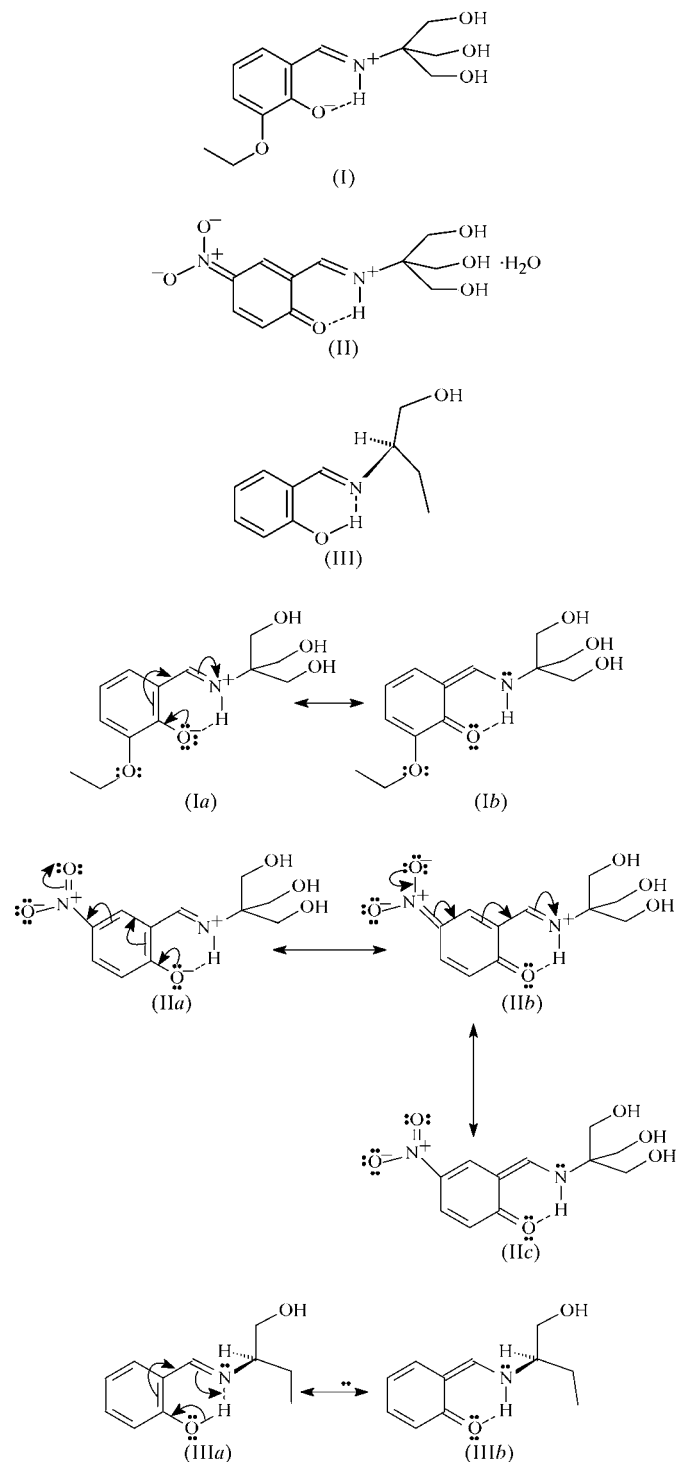
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The title compounds $C_{13}H_{19}NO_5$, $C_{11}H_{14}N_2O_6 \cdot H_2O$ and $C_{11}H_{15}NO_2$, respectively, have been derived from 3-ethoxysalicylaldehyde, 5-nitrosalicylaldehyde and salicylaldehyde, respectively. The C—O and N—C bond distances, and three hydrogen bonds formed by the phenolate O atom, show that the zwitterionic form exists in the first compound. The second compound is transformed to the quinoid form as a result of resonance between the zwitterionic form and the nitro group. The third compound exists in the phenol-imine form, with appropriate C—N and C—O bond distances.

Comment

There is considerable interest in Schiff base ligands and their complexes because of their striking antitumour activities (Zhou *et al.*, 2000). Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxy O atom to the imine N atom (Cohen *et al.*, 1964), *i.e.* phenol-imine/keto-amine tautomerism. It is known that the phenol-imine tautomer is dominant in salicylaldehyde, while the keto-amine form is preferred in the naphthaldehyde Schiff bases depending on the solvent polarities. Moreover, *o*-hydroxy Schiff bases can exist in different tautomeric forms. The configurations of these compounds are controlled by steric and electronic effects (Filarowski *et al.*, 2002), and the phenol-imine (molecular or phenol) and keto-amine (or keto) tautomeric forms are the most common. The substituents on the phenol ring affect the tautomeric equilibrium. The existence of electron-attracting groups on the *ortho* and *para* positions to the OH group increase the acidity

and the stability of the keto-amine form with the mesomeric and inductive effects (Filarowski *et al.*, 2002). Studies made so far show that *o*-hydroxy Schiff bases with electron-attracting groups such as Cl and NO_2 at the *ortho* or *para* position exhibit the keto-amine form (Wozniak *et al.*, 1995). The zwitterionic form is rarely seen in the solid state (Krygowski *et al.*, 1997).



We report here the structures of the title compounds, (I), (II) and (III). In (I), as shown in Fig. 1, there are two molecules in the asymmetric unit. Fig. 2 shows (II), with a water

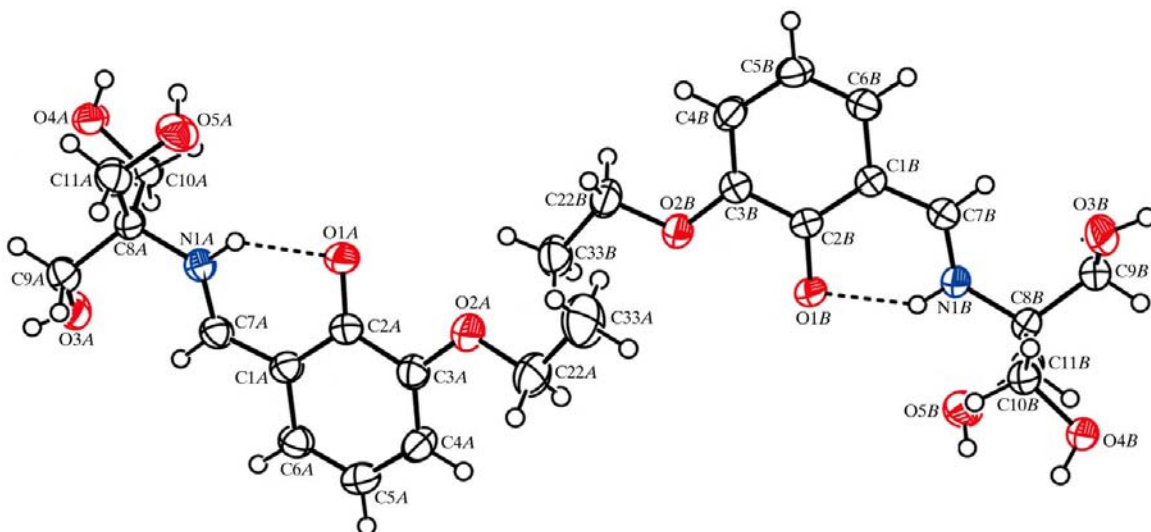


Figure 1
A view of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

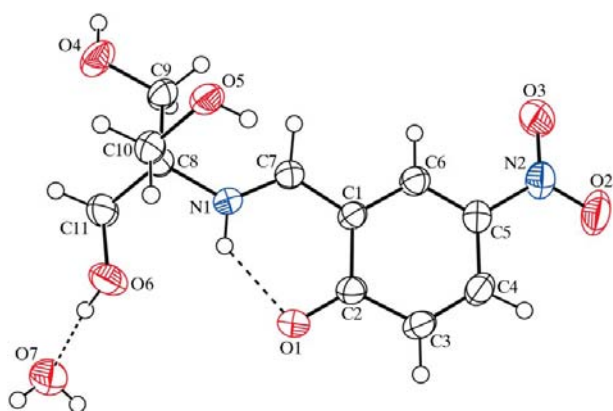


Figure 2
A view of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

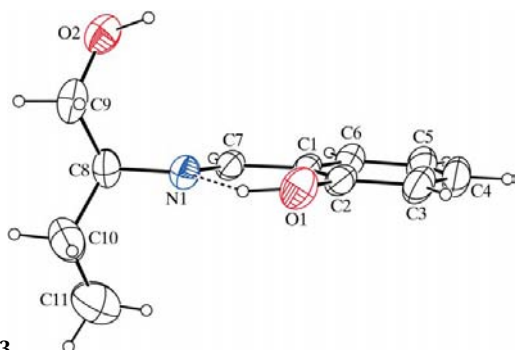


Figure 3
A view of (III), showing the atom-numbering scheme and 30% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

molecule of crystallization in the asymmetric unit, and Fig. 3 shows (III). Selected geometric parameters are given in Tables 1, 3 and 5. From Table 8, it can be seen that the C1–C2 bond

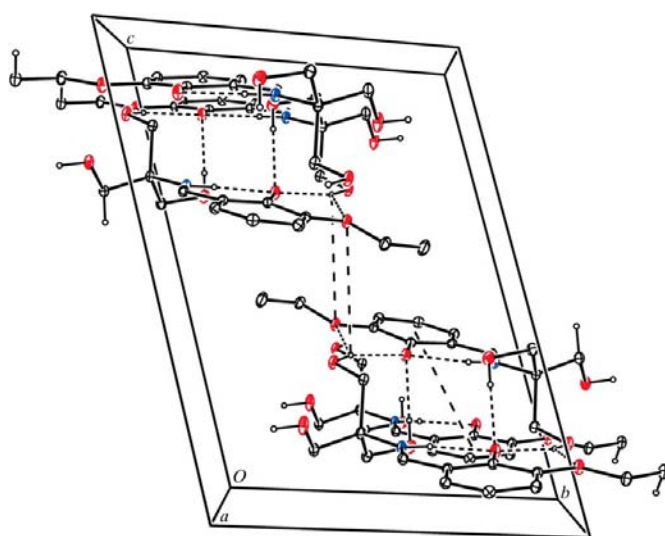


Figure 4
The packing of (I). Dashed lines indicate hydrogen bonds and C–H... π and π – π interactions. H atoms not involved in hydrogen bonding or C–H... π interactions have been omitted for clarity.

lengths in (I) and (II) are longer than that in (III), whilst the C2–O1 bond length in (II) is longer than those in other two compounds. The longest C1–C7 bond is in (III), and those of (I) and (II) are nearly equal. The C7–N1 bond lengths in all three compounds indicate that these bonds are C=N double bonds. For compound (I), the comparisons of the C–O and N–C bond distances with the corresponding values of Allen *et al.* (1987), and also the existence of three hydrogen bonds formed by the negative O1 atom, show that the zwitterionic form (Ia) is very important. In (II), by evaluating the N–C and C–O bonds, it can be concluded that the zwitterionic form (IIb) is important; this form arises from the resonating

effect of the nitro group. In the solid state, the phenol–imine tautomeric form exists in salicylaldehyde Schiff bases (Kaitner & Pavlovic, 1996; Yildiz *et al.*, 1998). In addition, the position of atom H1, and the C–N and C–O bond distances, indicate that compound (III) is in the phenol–imine tautomeric form, (IIIa).

In compound (I), each molecule in the asymmetric unit has an intramolecular N–H···O hydrogen bond. In addition, molecules *A* and *B* in the asymmetric unit are linked by intermolecular O–H···O hydrogen bonds (Table 2) forming a three-dimensional network, as shown in Fig. 4; this figure also shows the two five-membered pseudo-rings formed by intermolecular hydrogen bonds (O4A–H4A···O1Bⁱⁱⁱ, O4A–H4A···O2Bⁱⁱⁱ, O4B–H4B···O1A^{iv} and O4B–H4B···O2A^{iv}; symmetry codes as in Table 2). In (II), there are two intramolecular hydrogen bonds, N1–H1···O1 and O6–H6···O7,

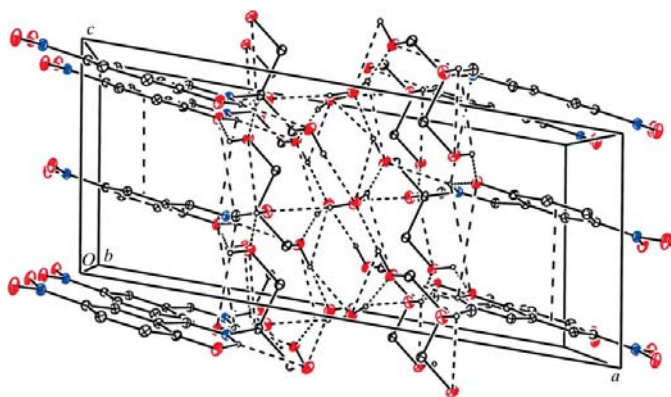


Figure 5
The packing of (II). Dashed lines indicate hydrogen bonds and π – π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

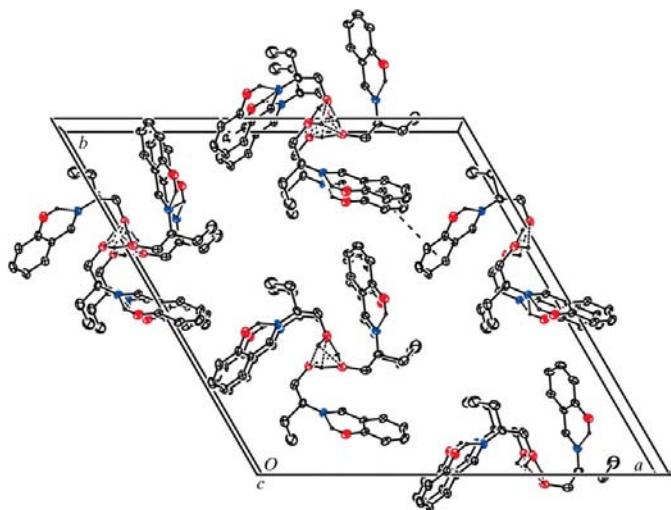


Figure 6
The packing of (III). Dashed lines indicate hydrogen bonds and π – π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

and the water molecules form intermolecular hydrogen bonds with atoms O4 and O6 (Table 4 and Fig. 5). Compound (III) has one intramolecular hydrogen bond, O1–H1···N1, which is shown in Fig. 3, and there is also an intermolecular hydrogen bond, O2–H2···O2 (Table 6 and Fig. 6). In all three compounds, in addition to the intermolecular hydrogen bonds, there are π – π interactions (Table 7), leading to a three-dimensional network.

Experimental

The three title compounds were prepared as described by Odabaşoğlu *et al.* (2003) using as starting materials 3-ethoxysalicylaldehyde and tris(hydroxymethyl)aminomethane for (I) (yield 92%, m.p. 437–439 K), 5-nitrosalicylaldehyde and tris(hydroxymethyl)aminomethane for (II) (yield 95%, m.p. 508–510 K), and salicylaldehyde and (*R*)-(–)-2-amino-1-butanol for (III) (yield 85%, m.p. 329–331 K).

Compound (I)

Crystal data

C₁₃H₁₉NO₅
M_r = 269.29
 Triclinic, *P* $\bar{1}$
a = 9.7424 (8) Å
b = 10.6073 (8) Å
c = 14.4820 (11) Å
 α = 102.592 (6)°
 β = 104.459 (6)°
 γ = 105.840 (6)°

V = 1326.7 (2) Å³
Z = 4
D_x = 1.348 Mg m^{−3}
 Mo *K* α radiation
 μ = 0.10 mm^{−1}
T = 296 K
 Prism, yellow
 0.43 × 0.31 × 0.19 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.946, *T_{max}* = 0.988

22555 measured reflections
 6080 independent reflections
 3597 reflections with *I* > 2 σ (*I*)
R_{int} = 0.051
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.039
wR (*F*²) = 0.095
S = 0.88
 6080 reflections
 361 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

C8A–N1A	1.4695 (18)	C8B–N1B	1.4726 (18)
N1B–C7B–C1B	123.48 (14)	N1B–C8B–C10B	105.30 (12)
N1A–C8A–C9A	111.76 (12)	O2A–C22A–C33A	108.00 (15)
N1A–C8A–C11A	106.66 (12)	O2B–C22B–C33B	107.19 (13)
N1A–C8A–C10A	105.68 (12)	C7A–N1A–C8A	128.68 (13)
N1B–C8B–C9B	112.15 (12)	C7B–N1B–C8B	128.84 (13)
N1B–C8B–C11B	107.17 (12)		
C7A–C1A–C2A–O1A	−5.9 (2)	C6A–C1A–C7A–N1A	177.53 (14)
C6A–C1A–C2A–O1A	174.57 (14)	C6B–C1B–C7B–N1B	−179.21 (14)
C7B–C1B–C2B–O1B	−1.5 (2)	C2B–C1B–C7B–N1B	3.5 (2)
C6B–C1B–C2B–O1B	−178.79 (14)	C9A–C8A–N1A–C7A	22.5 (2)
O1A–C2A–C3A–O2A	3.9 (2)	C11A–C8A–N1A–C7A	141.16 (16)
C1B–C2B–C3B–O2B	179.89 (13)	C10A–C8A–N1A–C7A	−100.12 (17)
C2A–C1A–C7A–N1A	−2.0 (2)		

Table 2

Hydrogen-bond geometry (Å, °) for (I).

Cg_1 and Cg_2 are the centroids of the $C1A-C6A$ and $C1B-C6B$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3A-H3A\cdots O4B^i$	0.861 (16)	1.845 (16)	2.7011 (15)	173 (2)
$O3B-H3B\cdots O4A^{ii}$	0.841 (16)	1.863 (16)	2.6994 (16)	173 (2)
$O4A-H4A\cdots O1B^{iii}$	0.831 (15)	1.977 (18)	2.7300 (15)	150 (2)
$O4A-H4A\cdots O2B^{iii}$	0.831 (15)	2.430 (19)	3.0894 (15)	137 (2)
$O4B-H4B\cdots O1A^{iv}$	0.860 (15)	1.921 (17)	2.7205 (15)	154 (2)
$O4B-H4B\cdots O2A^{iv}$	0.860 (15)	2.523 (19)	3.1811 (15)	133.9 (18)
$O5A-H5A\cdots O1B^{iii}$	0.839 (15)	1.927 (16)	2.7548 (16)	169 (2)
$O5B-H5B\cdots O1A^{iv}$	0.845 (15)	1.998 (16)	2.8351 (16)	171 (2)
$N1A-H1A\cdots O1A$	0.878 (19)	1.898 (19)	2.6331 (17)	140.3 (15)
$N1B-H1B\cdots O1B$	0.887 (19)	1.876 (19)	2.6210 (17)	140.4 (16)
$C9A-H9A\cdots Cg_1^v$	0.97	2.84	3.7045 (17)	149
$C33B-H33F\cdots Cg_2^{vi}$	0.96	2.97	3.628 (2)	127

Symmetry codes: (i) $x+1, y+2, z$; (ii) $x-1, y-2, z$; (iii) $x+1, y+1, z$; (iv) $x-1, y-1, z$; (v) $-x+1, -y+2, -z+1$; (vi) $-x+2, -y+2, -z$.

Compound (II)

Crystal data

$C_{11}H_{14}N_2O_6 \cdot H_2O$
 $M_r = 288.26$
 Monoclinic, $P2_1/c$
 $a = 16.9205$ (11) Å
 $b = 10.7034$ (6) Å
 $c = 7.2308$ (5) Å
 $\beta = 99.518$ (5)°
 $V = 1291.52$ (14) Å³

$Z = 4$
 $D_x = 1.482$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 296$ K
 Plate, yellow
 $0.38 \times 0.25 \times 0.08$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 ($X-RED32$; Stoe & Cie, 2002)
 $T_{min} = 0.955, T_{max} = 0.989$
 11553 measured reflections

2877 independent reflections
 1898 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.059$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.107$
 $S = 0.93$
 2877 reflections
 214 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.30$ e Å⁻³
 $\Delta\rho_{min} = -0.32$ e Å⁻³
 Extinction correction: $SHELXL97$
 Extinction coefficient: 0.053 (4)

Table 3

Selected geometric parameters (Å, °) for (II).

$C5-N2$	1.437 (2)	$C8-N1$	1.4673 (18)
$O1-C2-C1$	121.75 (13)	$N1-C8-C11$	106.98 (13)
$C6-C5-N2$	119.57 (14)	$N1-C8-C9$	110.47 (12)
$N1-C7-C1$	123.18 (14)	$N1-C8-C10$	106.61 (12)
$C6-C1-C7-N1$	-178.96 (16)	$C10-C8-N1-C7$	-89.06 (19)
$N1-C8-C9-O4$	-179.39 (14)		

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O4-H4A\cdots O5^i$	0.82	1.97	2.6801 (15)	145
$O5-H5A\cdots O1^{ii}$	0.82	2.03	2.6661 (15)	134
$O7-H7A\cdots O6^{iii}$	0.819 (17)	1.961 (18)	2.765 (2)	167 (3)
$O7-H7B\cdots O4^{iv}$	0.829 (18)	2.037 (19)	2.855 (2)	169 (3)
$N1-H1\cdots O1$	0.86 (2)	1.95 (2)	2.6221 (17)	134.6 (18)
$O6-H6\cdots O7$	0.88 (3)	1.77 (3)	2.649 (2)	173 (2)

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

Compound (III)

Crystal data

$C_{11}H_{15}NO_2$
 $M_r = 193.24$
 Trigonal, $R\bar{3}$
 $a = 23.561$ (4) Å
 $c = 5.7823$ (8) Å
 $V = 2779.8$ (8) Å³
 $Z = 9$

$D_x = 1.039$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 296$ K
 Prism, yellow
 $0.50 \times 0.37 \times 0.23$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 ($X-RED32$; Stoe & Cie, 2002)
 $T_{min} = 0.967, T_{max} = 0.982$
 2997 measured reflections

1209 independent reflections
 646 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.039$
 $\theta_{max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.093$
 $S = 0.81$
 1209 reflections
 134 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.08$ e Å⁻³
 $\Delta\rho_{min} = -0.10$ e Å⁻³

Table 5

Selected geometric parameters (Å, °) for (III).

$C8-N1$	1.468 (4)		
$N1-C7-C1$	122.0 (3)	$N1-C8-C10$	109.8 (3)
$N1-C8-C9$	107.5 (3)	$C7-N1-C8$	119.2 (3)
$C7-C1-C2-O1$	-1.7 (4)	$C1-C7-N1-C8$	179.6 (3)
$N1-C8-C9-O2$	65.7 (4)		

Table 6

Hydrogen-bond geometry (Å, °) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O2^i$	1.04 (5)	1.65 (5)	2.675 (4)	170 (4)
$O1-H1\cdots N1$	1.04 (7)	1.67 (7)	2.591 (3)	145 (5)

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

Table 7Observed π - π interaction distances (\AA) for (I), (II) and (III). C_{g1} is the centroid of the C1A–C6A ring in (I) and the C1–C6 ring in (II) and (III); C_{g2} is the centroid of the C1B–C6B ring.

Compound	C_{g1} – C_{g2}	$d_{\text{centroids}}$	$d_{\text{perpendicular}}$
(I)	C_{g1} – C_{g2}^i	4.056 (10)	3.243
(II)	C_{g1} – C_{g1}^{ii}	3.684 (10)	3.508
(III)	C_{g1} – C_{g1}^{iii}	4.951 (3)	4.929
(III)	C_{g1} – C_{g1}^{iv}	5.971 (3)	4.012

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-y + \frac{1}{3}, x - y - \frac{1}{3}, z - \frac{1}{3}$; (iv) $-x + y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{2}{3}$.**Table 8**Observed bond distances (\AA) for (I), (II) and (III).

Compound	C1–C2	C2–O1	C1–C7	C7–N1
(IA)	1.417 (2)	1.2936 (16)	1.414 (2)	1.2983 (18)
(IB)	1.420 (2)	1.2952 (16)	1.418 (2)	1.2960 (18)
(II)	1.443 (2)	1.2666 (19)	1.423 (2)	1.284 (2)
(III)	1.397 (4)	1.347 (4)	1.448 (4)	1.263 (4)

For (I), H atoms attached to N atoms were refined freely. The positions of O-bound H atoms were refined and the $U_{\text{iso}}(\text{H})$ values were fixed at 0.082 \AA^2 . All other H atoms were refined using a riding model, with C–H distances of 0.93–0.97 \AA and U_{iso} values equal to 1.5 (methyl H atoms) or 1.2 (other H atoms) times U_{eq} of the parent atom. For (II), the H atoms bonded to atoms C9–C11, O4 and O5 were refined as riding [C–H = 0.97 \AA , O–H = 0.82 \AA , and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$]. All other H atoms were refined freely, with C–H distances in the range 0.93 (2)–0.98 (2) \AA . For (III), O-bound H atoms were refined freely; all other H atoms were refined using a riding model, with C–H distances of 0.93–0.98 \AA and U_{iso} values

equal to 1.5 (methyl H atoms) or 1.2 (other H atoms) times U_{eq} of the parent atom.

For all three compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1092). Services for accessing these data are described at the back of the journal.

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