

Three (*E*)-2-[(bromophenyl)iminomethyl]-4-methoxyphenols

Arzu Özek,^{a*} Çiğdem Albayrak,^b Mustafa Odabaşoğlu^b
and Orhan Büyükgüngör^a

^aDepartment of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, and

^bDepartment of Chemistry, Ondokuz Mayıs University, TR-55139 Samsun, Turkey
Correspondence e-mail: arzuozek@omu.edu.tr

Received 29 September 2006

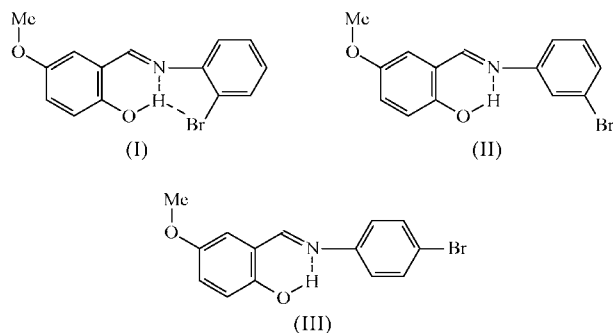
Accepted 20 January 2007

Online 17 February 2007

The title compounds, (*E*)-2-[(2-bromophenyl)iminomethyl]-4-methoxyphenol, C₁₄H₁₂BrNO₂, (I), (*E*)-2-[(3-bromophenyl)iminomethyl]-4-methoxyphenol, C₁₄H₁₂BrNO₂, (II), and (*E*)-2-[(4-bromophenyl)iminomethyl]-4-methoxyphenol, C₁₄H₁₂BrNO₂, (III), adopt the phenol–imine tautomeric form. In all three structures, there are strong intramolecular O—H...N hydrogen bonds. Compound (I) has strong intermolecular hydrogen bonds, while compound (III) has weak intermolecular hydrogen bonds. In addition to these intermolecular interactions, C—H... π interactions in (I) and (III), and π – π interactions in (I), play roles in the crystal packing. The dihedral angles between the aromatic rings are 15.34 (12), 6.1 (3) and 39.2 (14)° for (I), (II) and (III), respectively.

Comment

Although Schiff bases have been widely used as ligands in the formation of transition metal complexes and structurally characterized, a relatively small number of free Schiff bases have been similarly characterized (Calligaris & Randaccio,



1987). Schiff bases, however, play an important role in many fields of chemistry and biochemistry (Lozier *et al.*, 1975; Garnovskii *et al.*, 1993). The overall behaviour of these compounds has been defined as a proton-transfer reaction between the phenol–imine and keto–amine tautomers. It is known that the phenol–imine tautomer is dominant in salicylaldimine, while the keto–amine form is preferred in naph-

thaldimine Schiff bases, depending on the solvent polarities. Moreover, in the solid state, the keto–amine tautomer is present in naphthaldimines (Hökelek *et al.*, 2000; Odabaşoğlu *et al.*, 2003), while the phenol–imine form exists in salicylaldimine Schiff bases (Kaitner & Pavlovic, 1996; Yıldız *et al.*, 1998). As part of a general study of the crystal chemistry of dyes, and to provide templates for molecular-modelling studies, the crystal structures of the title compounds, *viz.* (I), (II) and (III) (see scheme), have been determined.

The molecular structures of (I), (II) and (III), with the atom-labelling schemes, are shown in Figs. 1, 2 and 3, respectively, and selected bond lengths and angles are given in Table 1. In all three molecules, the phenol–imine tautomer is favoured over the keto–amine form, as indicated by the C6—O1, C8—N1, C1—C8 and C1—C6 bond lengths (Figs. 1–3 and Table 1). A similar situation was observed for 2-(3-methoxysalicylideneamino)-1*H*-benzimidazole monohydrate [C—O = 1.357 (2) Å and C—N = 1.285 (2) Å; Albayrak *et al.*, 2005]. The H atom in all three compounds is located on atom O1, thus confirming a preference for the phenol–imine tautomer in the solid state. The O1—C6 bond lengths are approximately the same, indicating single-bond character, whereas the C8—N1 bond lengths are indicative of significant double-bond character in (I), (II) and (III).

It is known that Schiff bases may exhibit thermochromism or photochromism, depending on the planarity or non-planarity of the molecule, respectively. This planarity of the

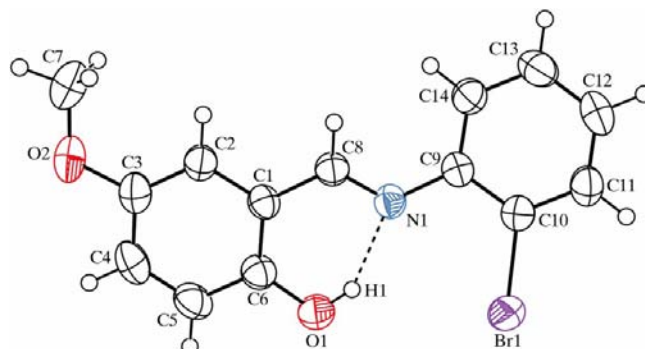


Figure 1
A view of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond. H atoms are represented as small spheres of arbitrary radii.

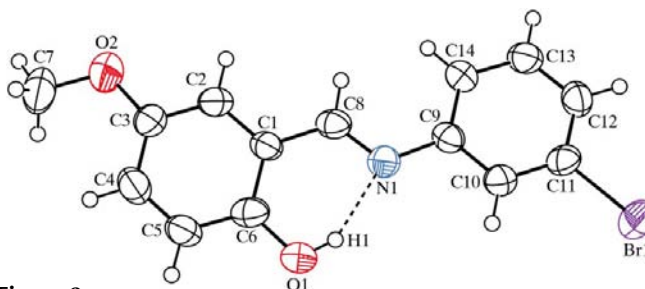


Figure 2
A view of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond. H atoms are represented as small spheres of arbitrary radii.

molecule allows the H atom to be transferred through the hydrogen bond in the ground state with a low energy requirement (Hadjoudis *et al.*, 1987). Therefore, one can expect thermochromic properties in (I) and (II) caused by planarity of the molecules: the dihedral angles between rings *A* (atoms C1–C6) and *B* (C9–C14) are 15.34 (12) and 6.1 (3)°, respectively. One can also expect photochromic properties in (III) caused by the non-planarity of the molecule: the dihedral angle between rings *A* and *B* is 39.2 (14)°.

These differences in planarity are also reflected in the C14–C9–N1–C8 torsion angles (Table 1) and are certainly related to the occurrence of intermolecular C–H···O and C–H··· π interactions observed in compounds (I) and (III) (Tables 2 and 4), which influence the packing of the molecules of (I) and (III), as shown in Figs. 4–6. Indeed, in compound (II), there is only an intramolecular O–H···N hydrogen bond (Table 3). The higher value of the torsion angle observed in compound (III) [–31.1 (4)°] compared with the lower values observed in (I) and (II) [–20.9 (3) and –6.6 (9)°] may result from the occurrence of three C–H··· π interactions in (III) (Table 4 and Fig. 7), whereas only one is present in compound (I) (Table 2 and Fig. 5). In (II), there are no C–H··· π and π – π interactions, and the only interactions playing a role in the

packing are intermolecular van der Waals interactions, resulting in a rather low torsion angle of –6.6 (9)°.

The occurrence of C–H···O hydrogen bonds results in the formation of *C*(5) and *C*(8) chains (Bernstein *et al.*, 1995) developing parallel to the *c* axis in (I) and (III), respectively (Tables 2 and 4, and Figs. 4 and 6). In addition to these interactions, only compound (I) presents π – π stacking (Fig. 5). This slipped π – π interaction occurs between *Cg*1 (the centroid of the C1–C6 ring) and its symmetry equivalent at (1 – *x*, 1 – *y*, 1 – *z*), with a centroid-to-centroid distance of 3.851 Å and a plane-to-plane separation of 3.486 Å, resulting in an offset angle of 25.2°.

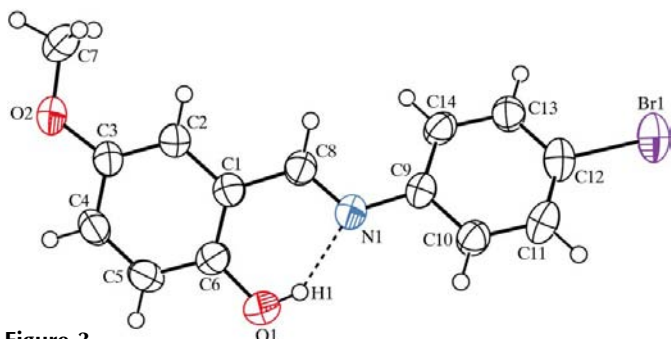


Figure 3
A view of (III), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond. H atoms are represented as small spheres of arbitrary radii.

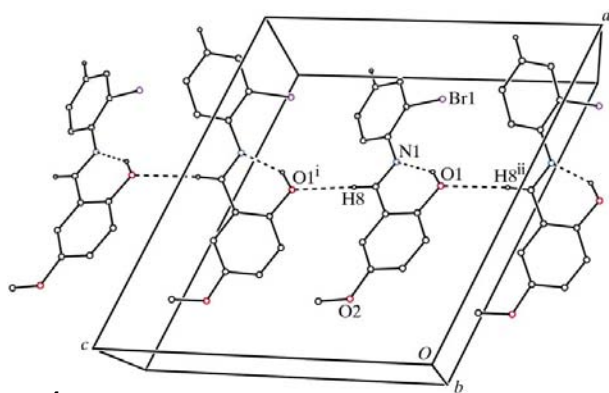


Figure 4
A partial packing view of (I), showing the formation of the *C*(5) chain through C–H···O hydrogen bonds (dashed lines). H atoms are represented as small spheres of arbitrary radii and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, \frac{3}{2} - y, z + \frac{1}{2}$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$]

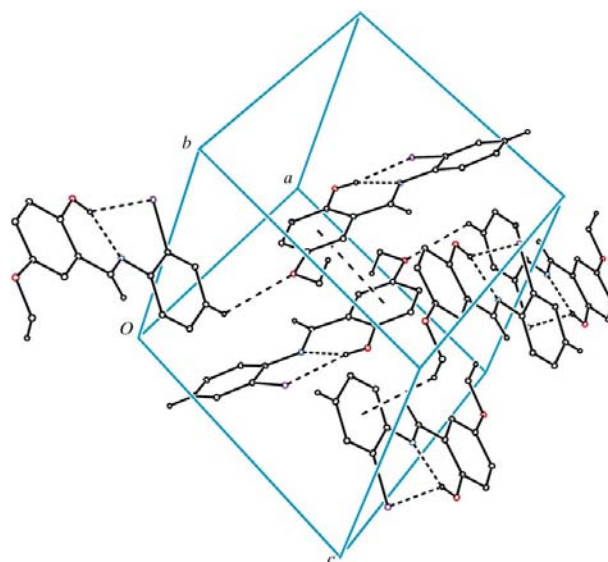


Figure 5
A partial packing view of (I), showing the C–H··· π and π – π interactions. Dashed lines indicate hydrogen bonds. H atoms are represented as small spheres of arbitrary radii and H atoms not involved in hydrogen bonding have been omitted for clarity.

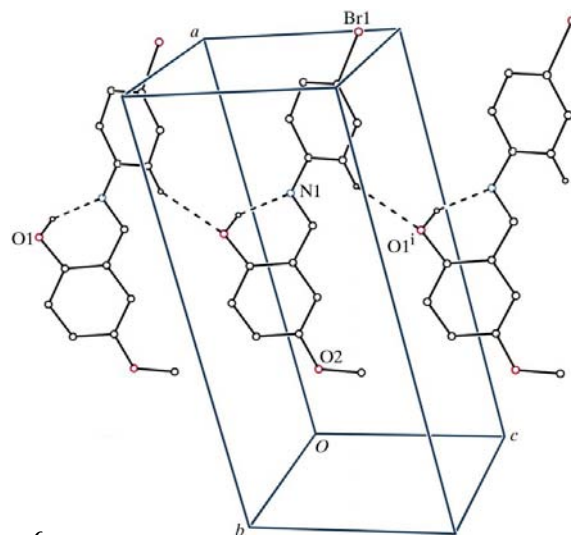


Figure 6
A partial packing view of (III), showing the formation of the *C*(8) chain through C–H···O hydrogen bonds (dashed lines). H atoms are represented as small spheres of arbitrary radii and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $x, y, 1 + z$.]

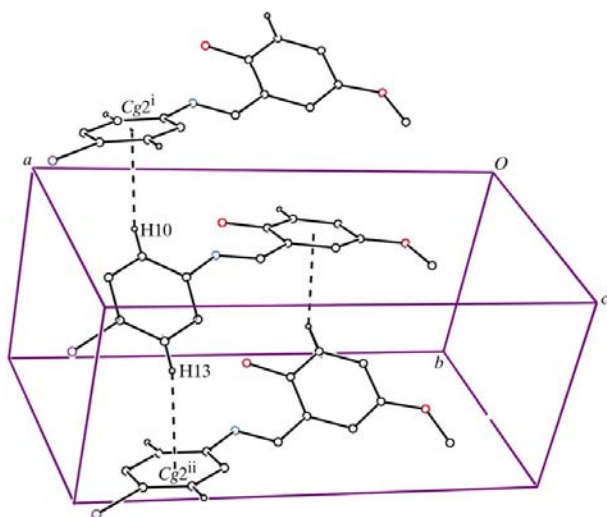


Figure 7

A partial packing view of (III). Dashed lines indicates C10—H... π and C13—H... π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity. Cg2 is the centroid of the C9—C14 ring. [Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $x, y + \frac{1}{2}, z + \frac{1}{2}$.]

Experimental

The title compounds were prepared according to reported procedures (Odabaşoğlu *et al.*, 2005), using 2-, 3- and 4-bromoaniline and 5-methoxysalicylaldehyde as starting materials. Well shaped crystals of (I), (II) and (III) were obtained by slow evaporation of ethanol solutions [for (I), yield 72% and m.p. 399–400 K; for (II), yield 86% and m.p. 367–368 K; for (III), yield 78% and m.p. 396–397 K].

Table 1

Selected geometric parameters (Å, °) for (I), (II) and (III).

| | (I) | (II) | (III) |
|---------------|-------------|------------|------------|
| C1—C6 | 1.399 (3) | 1.417 (9) | 1.397 (4) |
| C1—C8 | 1.443 (3) | 1.444 (8) | 1.442 (4) |
| C3—O2 | 1.374 (3) | 1.373 (8) | 1.364 (5) |
| C6—O1 | 1.360 (3) | 1.352 (7) | 1.358 (4) |
| C8—N1 | 1.280 (3) | 1.278 (6) | 1.287 (4) |
| C10—Br1 | 1.896 (2) | | |
| C11—Br1 | | 1.915 (5) | |
| C12—Br1 | | | 1.897 (4) |
| C6—C1—C8 | 121.74 (19) | 121.9 (6) | 121.3 (3) |
| C2—C1—C8 | 119.24 (19) | 119.5 (5) | 119.9 (3) |
| C2—C3—O2 | 125.5 (2) | 116.1 (6) | 126.3 (4) |
| O1—C6—C1 | 122.0 (2) | 120.8 (6) | 122.0 (3) |
| N1—C8—C1 | 121.20 (19) | 123.2 (5) | 120.9 (3) |
| C14—C9—N1 | 124.50 (19) | 124.5 (5) | 123.7 (3) |
| C10—C9—N1 | 118.35 (18) | 116.2 (5) | 117.0 (3) |
| C9—C10—Br1 | 119.72 (16) | | |
| C10—C11—Br1 | | 118.7 (4) | |
| C13—C12—Br1 | | | 119.4 (3) |
| C8—N1—C9 | 122.19 (18) | 120.6 (4) | 121.7 (3) |
| C8—C1—C2—C3 | −178.8 (2) | 178.1 (6) | 172.1 (3) |
| C1—C2—C3—O2 | −179.5 (2) | −178.6 (6) | −177.9 (3) |
| C8—C1—C6—O1 | −0.1 (3) | −0.1 (10) | 5.7 (4) |
| C6—C1—C8—N1 | 6.2 (3) | 2.9 (9) | −4.4 (4) |
| C2—C1—C8—N1 | −175.8 (2) | −177.8 (5) | −178.8 (3) |
| N1—C9—C10—C11 | 179.2 (2) | −179.1 (5) | 176.2 (3) |
| N1—C9—C10—Br1 | −1.6 (3) | | |
| C1—C8—N1—C9 | 177.96 (19) | 178.1 (5) | 170.4 (2) |
| C14—C9—N1—C8 | −20.9 (3) | −6.6 (9) | −31.1 (4) |
| C10—C9—N1—C8 | 162.1 (2) | 172.7 (5) | 153.5 (3) |
| C2—C3—O2—C7 | 2.0 (4) | 175.7 (7) | −169.8 (3) |

Compound (I)

Crystal data

C₁₄H₁₂BrNO₂
M_r = 306.16
 Monoclinic, *P*2₁/*c*
a = 13.3255 (8) Å
b = 8.7090 (5) Å
c = 11.9743 (6) Å
 β = 113.845 (4)°
V = 1271.02 (12) Å³

Z = 4
D_x = 1.600 Mg m^{−3}
 Mo *K* α radiation
 μ = 3.23 mm^{−1}
T = 296 K
 Prism, red
 0.66 × 0.35 × 0.17 mm

Data collection

Stoe IPDS2 diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.264, *T_{max}* = 0.603

17760 measured reflections
 2500 independent reflections
 2041 reflections with *I* > 2 σ (*I*)
R_{int} = 0.043
 θ_{\max} = 26.0°

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.027
wR(*F*²) = 0.057
S = 1.05
 2500 reflections
 163 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 0.369P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 2

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

Cg2 is the centroid of the C9—C14 ring.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1...N1 | 0.82 | 1.88 | 2.603 (2) | 146 |
| O1—H1...Br1 | 0.82 | 2.97 | 3.6368 (17) | 139 |
| C12—H12...O2 ⁱ | 0.93 | 2.84 | 3.377 (3) | 118 |
| C8—H8...O1 ⁱⁱ | 0.93 | 2.56 | 3.478 (3) | 171 |
| C7—H7B...Cg2 ⁱⁱⁱ | 0.96 (1) | 2.98 (1) | 3.763 (4) | 140 (1) |

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

Compound (II)

Crystal data

C₁₄H₁₂BrNO₂
M_r = 306.16
 Monoclinic, *Pc*
a = 12.6852 (19) Å
b = 4.5157 (4) Å
c = 12.1383 (18) Å
 β = 113.915 (11)°
V = 635.62 (15) Å³

Z = 2
D_x = 1.600 Mg m^{−3}
 Mo *K* α radiation
 μ = 3.23 mm^{−1}
T = 296 K
 Prism, red
 0.75 × 0.33 × 0.11 mm

Data collection

Stoe IPDS2 diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.279, *T_{max}* = 0.723

8350 measured reflections
 1259 independent reflections
 1105 reflections with *I* > 2 σ (*I*)
R_{int} = 0.086
 θ_{\max} = 26.0°

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.051
wR(*F*²) = 0.101
S = 1.37
 2504 reflections
 164 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.2013P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 with 1245 Friedel pairs
 Flack parameter: 0.467 (16)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------|------|-------|-----------|---------|
| O1—H1...N1 | 0.82 | 1.91 | 2.638 (7) | 148 |

Compound (III)

Crystal data

C₁₄H₁₂BrNO₂ *Z* = 2
M_r = 306.16 *D_x* = 1.603 Mg m⁻³
 Monoclinic, *Pc* Mo *K*α radiation
a = 14.0683 (12) Å *μ* = 3.23 mm⁻¹
b = 6.9497 (7) Å *T* = 296 K
c = 6.5553 (6) Å Prism, red
β = 98.264 (7)° 0.36 × 0.27 × 0.11 mm
V = 634.26 (10) Å³

Data collection

Stoe IPDS2 diffractometer 8753 measured reflections
ω scans 2785 independent reflections
 Absorption correction: integration 2225 reflections with *I* > 2σ(*I*)
 (*X-RED*; Stoe & Cie, 2002) *R_{int}* = 0.075
T_{min} = 0.287, *T_{max}* = 0.732 *θ_{max}* = 27.5°

Refinement

Refinement on *F*² $w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.0074P]$
 $R[F^2 > 2\sigma(F^2)] = 0.034$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.075$ (Δ/σ)_{max} < 0.001
S = 1.04 $\Delta\rho_{max} = 0.18 \text{ e \AA}^{-3}$
 2785 reflections $\Delta\rho_{min} = -0.23 \text{ e \AA}^{-3}$
 167 parameters Absolute structure: Flack (1983),
 H atoms treated by a mixture of with 1325 Friedel pairs
 independent and constrained refinement Flack parameter: 0.015 (9)

Table 4
Hydrogen-bond geometry (Å, °) for (III).

Cg1 and Cg2 are the centroids of the C1–C6 and C9–C14 rings, respectively.

| D—H...A | D—H | H...A | D...A | D—H...A |
|-----------------------------|----------|----------|-----------|---------|
| O1—H1...N1 | 0.80 (6) | 1.85 (6) | 2.577 (4) | 151 (6) |
| C14—H14...O1 ⁱ | 0.93 | 2.44 | 3.270 (5) | 148 |
| C7—H7C...O2 ⁱⁱ | 0.96 | 2.76 | 3.604 (6) | 148 |
| C5—H5...Cg1 ⁱⁱⁱ | 0.93 | 2.89 | 3.538 (3) | 129 |
| C10—H10...Cg2 ^{iv} | 0.93 | 2.85 | 3.569 (4) | 135 |
| C13—H13...Cg2 ^v | 0.93 | 2.85 | 3.572 (2) | 136 |

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

For all three compounds, all H atoms were refined using a riding model, with C—H distances of 0.93 Å for aromatic H atoms and 0.96 Å for methyl H atoms, O—H distances of 0.82 Å, and *U_{iso}*(H) = 1.5*U_{eq}*(C) for the methyl H atoms or 1.2*U_{eq}*(C,O) for the remaining H atoms. For (II), there is a twin by inversion (racemic twin), as suggested by the value of the Flack (1983) parameter of 0.47 (2).

For all three compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (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, 1998).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-2 diffractometer (purchased under grant F.279 of the University Research Fund).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3025). Services for accessing these data are described at the back of the journal.

References

Albayrak, Ç., Odabaşoğlu, M. & Büyükgüngör, O. (2005). *Acta Cryst.* **E61**, o423–o424.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Calligaris, M. & Randaccio, L. (1987). Editors. *Comprehensive Coordination Chemistry* (Series Editor: G. Wilkinson), Vol. 2, pp. 715–738. London: Pergamon Press.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1998). *WinGX*. University of Glasgow, Scotland.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–69.
 Hadjoudis, E., Vitterakis, M. & Maviridis, I. M. (1987). *Tetrahedron*, **43**, 1345–1360.
 Hökelek, T., Kılıç, Z., Işıklan, M. & Toy, M. (2000). *J. Mol. Struct.* **523**, 61–69.
 Kaitner, B. & Pavlovic, G. (1996). *Acta Cryst.* **C52**, 2573–2575.
 Lozier, R., Bogomolni, R. A. & Stoekenius, W. (1975). *Biophys. J.* **15**, 955–962.
 Odabaşoğlu, M., Albayrak, Ç. & Büyükgüngör, O. (2005). *Acta Cryst.* **E61**, o425–o426.
 Odabaşoğlu, M., Albayrak, Ç., Büyükgüngör, O. & Goemann, H. (2003). *Acta Cryst.* **C59**, o234–o236.
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
 Yıldız, M., Kılıç, Z. & Hökelek, T. (1998). *J. Mol. Struct.* **441**, 1–10.