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1,3-Bis[2-(2-hydroxybenzylideneamino)phenoxy]propane

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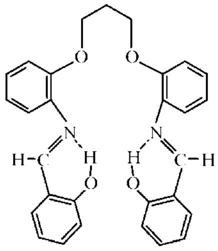
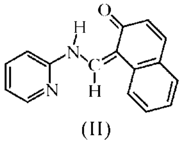
The title compound {systematic name: 2,2′-[1,3-propanediyldioxydi-*o*-phenylenebis(nitrilomethylidyne)]diphenol}, $C_{29}H_{26}N_2O_4$, exists as the phenol–imine form in the crystal, and there are strong intramolecular O—H···N hydrogen bonds, with O···N distances of 2.545 (2) and 2.579 (2) Å. The C=N imine bond distances are in the range 1.276 (2)–1.279 (2) Å and the C=N—C bond angles are in the range 123.05 (16)–124.64 (17)°. The configurations about the C=N bonds are *anti* (1*E*).

Comment

Tautomerism and intramolecular hydrogen bonds in 2-hydroxy Schiff bases in solution and in the solid state have been investigated using IR and UV spectroscopies (Hayvalı *et al.*, 2003), ^{1}H, ^{13}C and ^{15}N NMR spectroscopies (Salman *et al.*, 1991; Pizzala *et al.*, 2000; Gilli *et al.*, 2000), and X-ray crystallography techniques (Kaitner & Pavlovic, 1996). A good review of hydrogen bonds has been published by Steiner (2002). Tautomerism in Schiff bases plays an important role in distinguishing their photochromic (Hadjoudis, 1981; Dürr, 1989) and thermochromic (Moustakali-Mavridis *et al.*, 1980) characteristics.

In solution, the existence of tautomeric equilibria [phenol–imine (O—H···N) and keto–amine (O···H—N) forms] in polar and non-polar solvents, depending on the formation of intermolecular hydrogen bonding, is observed (Costamagna *et al.*, 1992). This tautomerism depends strongly on the polarity of the solvent and its ability to form hydrogen bonds, as reported by Hayvalı *et al.* (2003). It is claimed that the phenol–imine form is dominant in salicylaldimine, with the keto–amine form dominant in naphthaldimine derivatives, depending on the solvent polarities (Salman *et al.*, 1993). However, in the solid state, it is generally specified by X-ray analysis that the keto–amine form is observed in naphthaldimine, while the phenol–imine form is observed in salicylaldimine Schiff bases (Gavranic *et al.*, 1996; Kaitner & Pavlovic, 1996), although it is claimed that both keto–amine and phenol–imine forms are present in the crystalline state, based on NMR studies (Pizzala *et al.*, 2000).


(I)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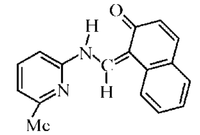
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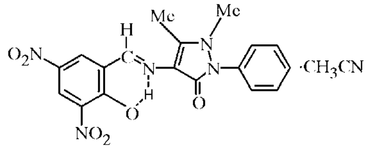
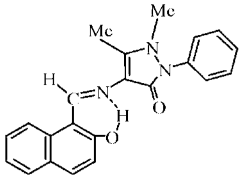
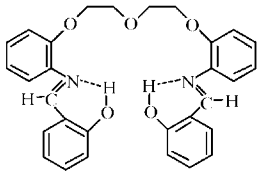
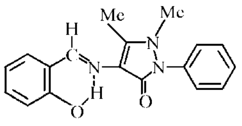
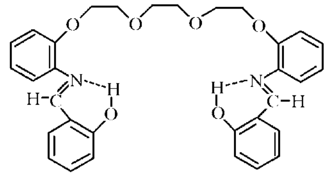


(IV)


(V)


(VI)


(VII)


(VIII)

The structures of naphthaldimine and salicylaldimine Schiff base derivatives with different substituents have been the subject of much interest in our laboratory. Examples include compounds (II) (Hökelek, Kılıç *et al.*, 2000), (III) (Hökelek, Işıklan, & Kılıç, 2000), (IV) (Hökelek, Kılıç, Işıklan, Dal & Nazır, 2002), (V) (Hökelek, Kılıç, Işıklan &

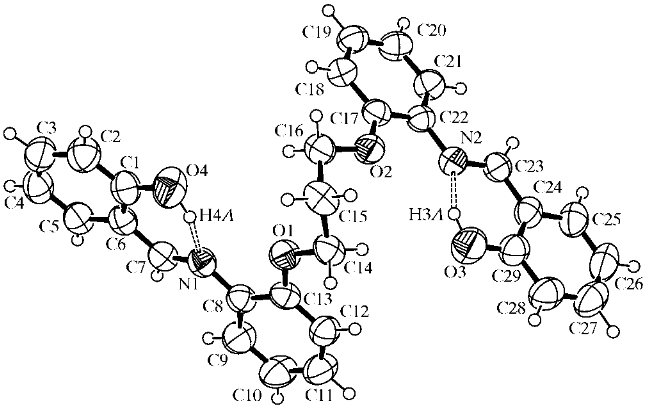


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The broken lines indicate the intramolecular hydrogen bonds.

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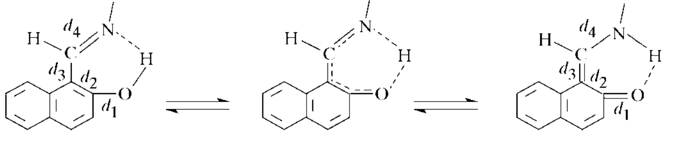
Hayvalı, 2002), (VI) (Hökelek, Akduran *et al.*, 2000), (VII) (Hökelek *et al.*, 2001) and (VIII) (Yıldız *et al.*, 1998). Our crystallographic studies have shown a phenol–imine form in (V) and (VII), which are naphthaldimine and salicylaldimine Schiff bases, respectively. Compound (IV) is also a salicylaldimine Schiff base, having nitro groups at the 3- and 5-positions of the phenyl ring. The molecular structure observed in (IV) corresponds to the situation where symmetric hydrogen bonds occur between the two forms (Scheme 2), which might be an artifact due to the disorder caused by H-atom transfer. The nitrogen substituents in (IV), (V) and (VII) are the same, but in (IV) and (V), the aldehyde parts are different. It was once claimed that the hydrogen-bond type depends neither on the stereochemistry of the molecule nor on the type of substituent bonded to the imino N atom, but on the type of aldehyde used (Gavranic *et al.*, 1996), with only an intramolecular O—H···N (phenol–imine form) type of hydrogen bond being observed in salicylaldimines, and an O···H—N (keto–amine form) type in naphthaldimines (Kaitner & Pavlovic, 1996; Elerman *et al.*, 1998). However, compound (V) indicates that the naphthaldimine can also exist in the phenol–imine form. These crystallographic results clearly reflect the importance of the stereochemistry of the molecule and the type of nitrogen substituents in salicylaldimine and naphthaldimine Schiff bases. In this paper, the structure of the title compound, (I), has been determined and is compared with those reported previously.

The molecule of (I) is in the phenol–imine form (Fig. 1). In $CDCl_3$ solution, ^1H NMR data for (I) also show the existence of only the phenol–imine form (δ = 13.97 p.p.m., singlet for OH; δ = 8.67 p.p.m., singlet for HC═N). The C═N imine bond distances and C—N—C bond angles (Table 1) are comparable with the corresponding values of 1.270 (3) Å and 123.5 (2)° in (VIII), and those of 1.288 (4) Å and 121.3 (3)°, and 1.277 (4) Å and 124.3 (3)° in (VI).

There are short intramolecular O—H···N hydrogen bonds in the structure of (I) (Table 2). The dihedral angles between the best planes of the salicylidenes and the nitrogen-substituted benzene rings are 6.09 (6) and 9.30 (5)°. The C6—C7—N1—C8 and C22—N2—C23—C24 torsion angles (Table 1) show that the configurations about the C7—N1 and N2—C23 bonds are *anti* (1*E*), while the O1—C14—C15—C16 and C14—C15—C16—O2 torsion angles correspond to the *gauche* conformation (Hilgenfeld & Saenger, 1982). The dihedral angle between the two nitrogen-substituted benzene rings is 86.72 (6)°.



Scheme 2

For all compounds (I)–(VIII), the salicylidene and naphthylidene groups are characterized by short N···O distances (Table 3). On the basis of studies of intramolecular hydrogen bonds (Gilli *et al.*, 1989), a short hydrogen bond associated with a charge flow through the system of conjugated double bonds (Scheme 2) is denoted 'resonance-assisted hydrogen bonding' and a delocalization parameter, $Q = (d_1 - d_4) + (d_3 - d_2)$, is defined (distances d_1 to d_4 are as defined in Scheme 2). In general, the Q values (Table 3) have negative and positive signs in the naphthaldimine and salicylaldimine derivatives, respectively, and there is no clear relationship between the corresponding Q and N···O values. In the extreme case of a symmetric position of the H atom, Q is nearly zero, as in the salicylaldimine derivative (IV). In contrast, the Q value is positive in the naphthaldimine derivative (V), due to the strongly electron-withdrawing nitrogen substituent group.

Experimental

A solution of 1,3-propanedioxybis(2-aminophenyl ether) (0.50 g, 1.94 mmol) in dry MeOH (25 ml) was added dropwise to a stirred solution of salicylaldehyde (0.47 g, 3.88 mmol) in dry MeOH (75 ml) over a period of 1 h. The mixture was refluxed for 4 h and then cooled. The precipitated orange solid of (I) was filtered off and crystallized from ethanol (yield 0.73 g, 81%; m.p. 406 K).

Crystal data

$C_{29}H_{26}N_2O_4$
M_r = 466.52
Orthorhombic, *Pbca*
a = 14.3665 (10) Å
b = 17.1608 (18) Å
c = 19.762 (3) Å
V = 4872.1 (10) Å^3
Z = 8
D_x = 1.272 Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 10–22°
μ = 0.69 mm^{-1}
T = 293 (2) K
Block, orange
0.35 × 0.25 × 0.15 mm

Table 1
Selected geometric parameters (Å, °).

O1—C13	1.362 (2)	C3—C4	1.374 (3)
O1—C14	1.433 (2)	C5—C6	1.397 (3)
O2—C16	1.424 (2)	C6—C7	1.445 (3)
O2—C17	1.366 (2)	C8—C13	1.403 (2)
O3—C29	1.346 (3)	C14—C15	1.504 (3)
O4—C1	1.356 (2)	C15—C16	1.508 (3)
N1—C7	1.276 (2)	C17—C22	1.388 (2)
N1—C8	1.412 (2)	C23—C24	1.445 (3)
N2—C22	1.417 (2)	C24—C25	1.399 (3)
N2—C23	1.279 (2)	C24—C29	1.403 (3)
C1—C2	1.388 (3)	C27—C28	1.371 (4)
C1—C6	1.402 (3)	C28—C29	1.393 (3)
C2—C3	1.375 (3)		
C13—O1—C14	117.93 (15)	C1—C6—C7	121.12 (17)
C17—O2—C16	118.66 (15)	N1—C7—C6	120.06 (18)
C7—N1—C8	124.64 (17)	C9—C8—N1	125.60 (18)
C23—N2—C22	123.05 (16)	C13—C8—N1	115.41 (16)
O4—C1—C2	118.9 (2)	C17—C22—N2	116.39 (15)
O4—C1—C6	121.30 (18)	C21—C22—N2	124.52 (17)
C2—C1—C6	119.8 (2)	O3—C29—C28	118.5 (2)
C5—C6—C1	118.37 (19)	O3—C29—C24	121.68 (18)
C5—C6—C7	120.40 (18)	C28—C29—C24	119.8 (2)
O1—C14—C15—C16	−62.1 (2)	C8—N1—C7—C6	174.92 (16)
O2—C16—C15—C14	−59.0 (2)	C22—N2—C23—C24	−178.86 (16)
C1—C6—C7—N1	3.5 (3)	C23—C24—C29—O3	0.4 (3)
C5—C6—C7—N1	−172.73 (18)	C25—C24—C23—N2	174.22 (18)
C7—C6—C1—O4	4.4 (3)	C29—C24—C23—N2	−5.6 (3)
C7—C6—C1—C2	−176.50 (19)		

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.814$, $T_{\max} = 0.902$
4900 measured reflections
4893 independent reflections
3296 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.051$
$\theta_{\max} = 74.2°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 21$
$l = -24 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.136$
$S = 1.06$
4893 reflections
420 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.4634P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N2	0.96 (3)	1.69 (3)	2.579 (2)	154 (3)
O4—H4A···N1	0.98 (2)	1.61 (3)	2.545 (2)	158 (3)

Table 3
Q values (Å) and N···O distances (Å) for compounds (I)–(VIII).

Compound	Q	N···O
(I)	0.123 (3)/0.109 (3)	2.579 (2)/2.545 (2)
(II)	−0.135 (5)	2.572 (4)
(III)	−0.121 (4)	2.583 (3)
(IV)	−0.009 (3)/−0.005 (3)	2.525 (3)/2.555 (3)
(V)	0.122 (6)	2.527 (4)
(VI)	0.114 (5)/0.098 (5)	2.587 (4)/2.542 (4)
(VII)	0.120 (2)	2.607 (3)
(VIII)	0.142 (3)	2.578 (3)

H atoms were located in difference syntheses and refined isotropically [C—H = 0.93 (2)–1.04 (2) Å and O—H = 0.96 (3)–0.985 (18) Å].

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1202). Services for accessing these data are described at the back of the journal.

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