

1-((*E*)-{(1*R*,2*R*)-2-[(*E*)-(2-Hydroxy-1-naphthyl)methyleneamino]cyclohexyl}imino)methyl)naphthalen-2-olate: a Schiff base compound having both OH and NH character

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The title Schiff base compound, C₂₈H₂₆N₂O₂, possesses both OH and NH tautomeric character in its molecular structure. While the OH side of the compound is described as an intermediate state, its NH side adopts a predominantly zwitterionic form. The molecular structure of the compound is stabilized by both N⁺—H···O[−] and O—H···N intramolecular hydrogen bonds. There are two weak C—H···O hydrogen bonds leading to polymeric chains of topology C(5) and C(13) running along the *b* axis of the unit cell. In addition, intermolecular C—H···π interactions serve to stabilize the extended structure.

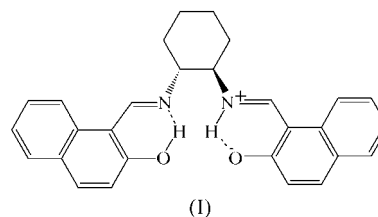
Comment

The structures of aromatic Schiff base compounds have received much attention due to their keto–enol (or NH–OH) tautomerism. Depending on the type of tautomer, two types of intramolecular hydrogen bond involving a photochemically or thermochemically induced proton are possible, namely O···H—N in keto (NH) and O—H···N in enol (OH) tautomers. Although the proton-transfer reaction is seemingly straightforward, it causes a change in the π electronic system and induces large-scale in-plane and out-of-plane skeletal deformations. In the solid state, while OH tautomeric forms of Schiff bases are predominant in salicylaldimines (Kaitner & Pavlovic, 1996; Yıldız *et al.*, 1998), both NH and OH forms have been found in naphthaldimine Schiff bases (Nazır *et al.*, 2000; Popović *et al.*, 2004). These imply that the type of tautomer does not depend only on the parent aromatic aldehyde used in the synthesis, but on the stereochemistry of the molecules themselves.

Although Schiff bases exhibit two possible tautomeric forms, OH and NH, another structural form, the zwitterion, is

also observed. Zwitterionic forms of Schiff bases are regarded as a variant of their NH forms, but they can easily be distinguished from canonical keto (NH) tautomers by their N⁺—H bond distances. Zwitterionic forms of Schiff bases have an intramolecular ionic hydrogen bond (N⁺—H···O[−]), and their N⁺—H bonds are longer than the standard interatomic separations observed in neutral N—H bonds (0.87 Å). The other ionic bonds in the zwitterions, C=N⁺ and C—O[−], are not as distinctive as indicators as is the N⁺—H bond, because the NH form of Schiff bases in the solid state can be regarded as a resonance hybrid of two canonical structures, namely the keto tautomer and the zwitterionic form (Ogawa & Harada, 2003). However, the predominance of the zwitterionic over the NH canonical form of Schiff bases can be discerned from details of their molecular geometry.

Although naphthaldimine Schiff bases are commonly found in the NH form (Hökelek *et al.*, 2000; Ünver *et al.*, 2001), the OH and NH forms may co-exist in the same crystal structure, although heretofore they have not been observed in the same molecule (Nazır *et al.*, 2000). The title Schiff base compound, (I), possesses both OH and NH tautomers.



Heteroatom bonds are most affected by molecular self-isomerization. In this regard, the C9—O1 and N1—C7 bonds are the most sensitive indicators of the tautomeric form on the OH side of the molecule of (I) (Table 1). The heteroatom bond lengths on the OH side of the compound are intermediate between single and double C—O (1.362 and 1.222 Å, respectively) and C—N bond lengths (1.339 and 1.279 Å, respectively) (Allen *et al.*, 1987). In particular, C9—O1 is significantly shorter than its expected value. Although the chelate ring atoms N1, C7, C8, C9, O1 and H1 all lie roughly in the same plane (r.m.s. deviation 0.029 Å), atoms O1 and H1 show greater deviations of 0.04 (1) and −0.05 (2) Å, respectively. It is a well known fact that H atoms participating in intramolecular hydrogen bonds in Schiff bases are rather mobile. The geometry of the OH side of the molecule of (I) indicates that the transfer of atom H1 is not complete. Thus, the OH side of the molecule can be regarded as having an intermediate state between its canonical OH and NH forms, and therefore the O1—H1 bond remains somewhat longer than its expected value (Table 2). Here, the term ‘intermediate state’ means that its structure can be regarded as neither the canonical NH tautomeric form nor the canonical OH form with respect to its covalent topology, and does not mean that atom H1 is disordered between the OH and NH forms.

On the other side of the molecule, the N2—H2 bond is longer than the distance observed in neutral N—H bonds (Table 2). Therefore, it can be concluded that the NH side

adopts a predominantly zwitterionic form. Although the N2—C18 bond length (NH side) is comparable with those found in zwitterionic Schiff bases (Petek *et al.*, 2006; Ogawa & Harada, 2003), it is shifted slightly towards the value expected for canonical NH tautomers. Furthermore, the O2—C20 bond length is in the range found for the structures of the ketoamine naphthylideneamines [1.277 (2)–1.302 (3) Å; Elerman *et al.*, 1998; Gavrančić *et al.*, 1996; Pizzala *et al.*, 2000] and possesses appreciable keto character.

It is worth noting the shortening and elongation of some C—C bond distances in the naphthalene rings on both the NH and OH sides. There is a significantly short C10—C11 bond length on the OH side (C21—C22 on the NH side). At the same time, C8—C17, C8—C9 and C9—C10 on the OH side (C21—C20, C20—C19 and C19—C28 on the NH side) are considerably lengthened. Similar tendencies are found for other canonical NH tautomers of naphthylideneamines (Friščić *et al.*, 1998; Popović *et al.*, 2004). These distortions observed in the naphthalene fragments on both sides of (I) can be explained by a possible through-resonance effect between canonical NH and zwitterionic forms on the NH side of the compound, in accordance with the Ogawa & Harada (2003) conjecture.

In order to investigate quantitatively the differences between the aromaticities of the two naphthalene fragments of (I), their harmonic oscillator model of aromaticity (HOMA) indices (Krygowski, 1993) were calculated. The HOMA index is equal to unity for purely aromatic systems and zero for non-aromatic systems. The calculated HOMA indices for the OH and NH naphthalene fragments of (I) are 0.722 and 0.684, respectively. Comparing these values with the HOMA index calculated for canonical naphthalene (0.779; Matito *et al.*, 2005), it can be stated that the aromaticities of the naphthalene fragments on both sides of (I) are diminished and that the deviation from full aromaticity of the naphthalene fragment on the NH side is more pronounced than that on the OH side,

since the canonical NH tautomer character on the predominantly zwitterionic side of the compound is not completely negligible. The aromaticity of the naphthalene fragment on the OH side is also diminished, since this side of the compound is in an intermediate state between NH and OH tautomers. Although the C—N, C—O and C—C distances are very similar on both sides of the molecule, C7—C8 is longer than C18—C19, indicating less double-bond character in the former. This observed distribution of geometric parameters indicates that there is significant charge separation towards a zwitterionic configuration on both sides but, in the absence of other considerations, in particular when the position of the tautomeric atom H1 on the OH side is considered, the separation of charge on that side cannot be sufficient to qualify it as a zwitterionic form. Therefore, the chemical diagram is drawn with predominantly zwitterionic character on the NH side of the molecule. However, it is not surprising that both sides have similar C—N, C—O and C—C bond distances, since zwitterionic forms of Schiff base compounds are also accepted as an intermediate state between their two possible canonical tautomers.

This inference is substantiated by the difference in orientations of the C=N bridges linked to the cyclohexane ring of (I), which adopts an almost perfect chair conformation [puckering parameters $Q = 0.555$ (2) Å, $\theta = 1.8$ (2)° and $\varphi = 58$ (6)°; Cremer & Pople, 1975]. The C7—N1—C6—C1 and C18—N2—C1—C6 torsion angles are 139.1 (2) and 118.3 (2)°, respectively, and the C8—C7—N1—C6 and C19—C18—N2—C1 torsion angles are 169.3 (2) and 175.7 (2)°, respectively. Delocalization of the π electrons in the chelate ring on the OH side is slightly different from that of the NH side, due to the presence of a protonated imine bond (C18—N2). The difference in the degree of delocalization of the π electrons in the two chelate rings explains the orientational difference

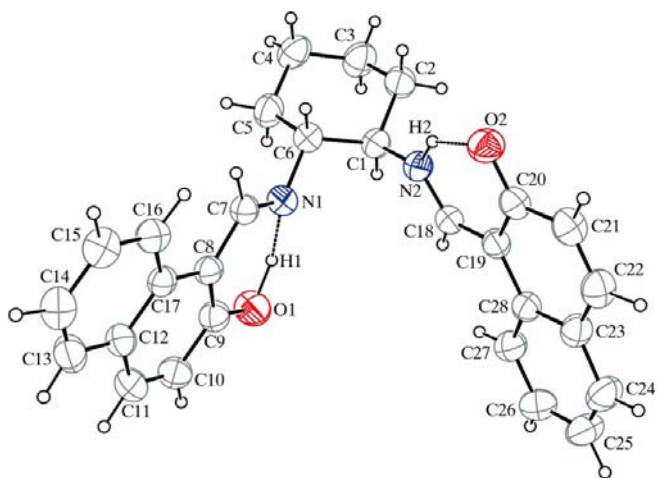


Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is depicted by a dashed line.

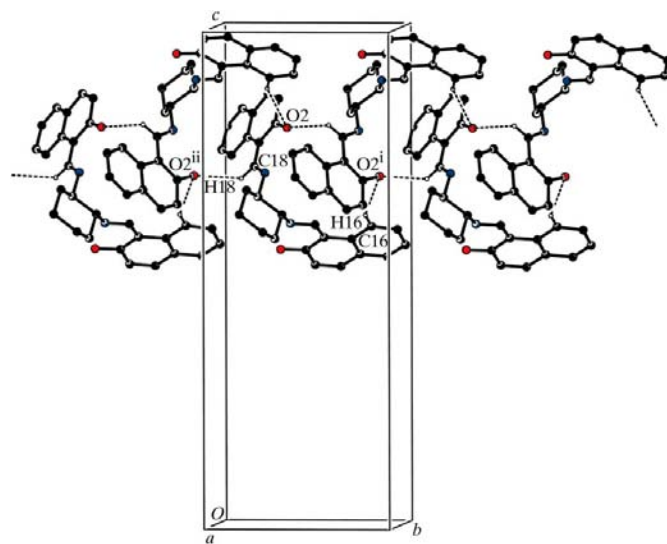


Figure 2

The C(5) and C(13) polymeric chains of (I). For the sake of clarity, only H atoms participating in weak intermolecular hydrogen bonds are shown. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$.]

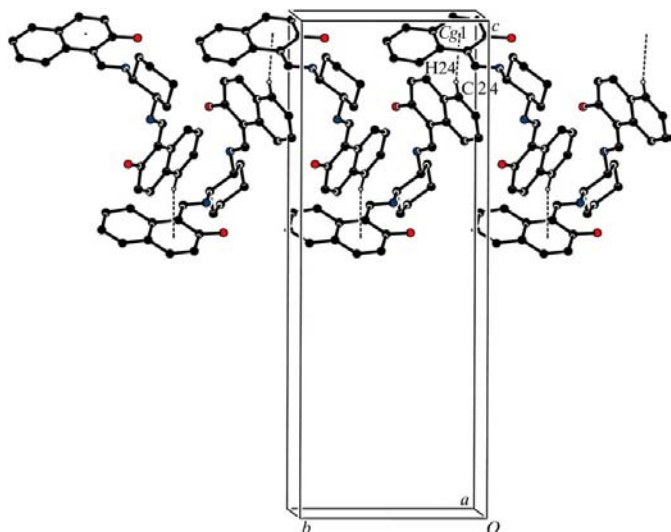


Figure 3

C—H $\cdots\pi$ interactions in the crystal structure of (I). Only H atoms participating in these interactions have been plotted. (Symmetry code for the interaction: $-x, -\frac{1}{2} + y, \frac{3}{2} - z$.)

mentioned above. In addition, both N atoms are linked to the ring equatorially. There are no distance anomalies within the ring.

There are two strong intramolecular hydrogen bonds, one of which has ionic character, N2⁺—H2 \cdots O2⁻ (Table 2 and Fig. 1), and each of them serves to stabilize the geometry and tautomeric character on its respective side of the molecule. According to graph-set notation (Bernstein *et al.*, 1995), the molecules of (I) are packed into C(13) one-dimensional polymeric arrangements generated by translation along the *b* axis of the unit cell with the aid of weak C16—H16 \cdots O2⁻ⁱ hydrogen bonds [symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$] (Fig. 2 and Table 3). At the same time, weak C18—H18 \cdots O2⁻ⁱⁱ intermolecular hydrogen bonds [symmetry code: (ii) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$] also generate C(5) chains running collinear with the *b* axis of the unit cell. The intersection of these C(5) and C(13) chains can be described as an R₂²(18) dimeric aggregate. Consequently, both weak intermolecular hydrogen bonds can be seen as charge-assisted non-covalent interactions. A noteworthy intermolecular C—H $\cdots\pi$ interaction (Fig. 3) involving the ring through atoms C8—C12/C17 (centroid Cg1), Cg1 \cdots Cg1ⁱⁱⁱ [symmetry code: (iii) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$], supplies a principal contribution to the molecular packing. Atom O2⁻ participates in both inter- and intramolecular interactions as acceptor due to its excess negative charge. Thus, the molecular structure of the title compound is stabilized by intramolecular hydrogen bonds, while the extended structure is stabilized by weak charge-assisted C—H \cdots O hydrogen bonds and C—H $\cdots\pi$ intermolecular interactions.

Experimental

An ethanol solution (20 ml) of 2-hydroxy-1-naphthaldehyde (0.20 g, 1.65 mmol) was added dropwise, at room temperature, to a solution of (*R,R*)-1,2-diaminocyclohexane (0.59 g, 3.40 mmol) in ethanol

(20 ml), yielding a large amount of yellow precipitate. The mixture was stirred for 30 min at room temperature and filtered under vacuum. Crystallization from dichloromethane gave the spectroscopically pure product as a yellow crystalline compound (yield 89%; m.p. 496 K). Elemental analysis calculated for C₂₈H₂₆N₂O₂: C 79.59, H 6.20, N 6.63%; found: C 79.52, H 6.24, N 6.59%; ¹H NMR (CDCl₃, 400 MHz): δ 14.0, 13.6 (s, 2H, OH), 8.3, 8.2 (s, 2H, NCH), 7.4–7.1 (m, 4H, Ar—H), 6.6–6.2 (m, 8H, Ar—H), 3.1 (t, 2H, —CH), 1.9–1.4 (m, 8H, CH₂). FT-IR (KBr, ν , cm⁻¹): 3550–3200 (br, Ar—OH), 3020 (w, H—CN), 2951, 2937, 2889 (w, —CH₂—), 1598 (s, Ar).

Crystal data

C ₂₈ H ₂₆ N ₂ O ₂	<i>V</i> = 2295.21 (15) Å ³
<i>M_r</i> = 422.51	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 9.4829 (4) Å	μ = 0.08 mm ⁻¹
<i>b</i> = 9.5307 (4) Å	<i>T</i> = 296 (2) K
<i>c</i> = 25.3955 (8) Å	0.58 × 0.54 × 0.42 mm

Data collection

Stoe IPDSII diffractometer	37222 measured reflections
Absorption correction: integration (<i>X-AREA</i> ; Stoe & Cie, 2002)	2922 independent reflections
<i>T</i> _{min} = 0.954, <i>T</i> _{max} = 0.967	2186 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.089

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.033	$\Delta\rho_{\max}$ = 0.15 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.082	$\Delta\rho_{\min}$ = -0.12 e Å ⁻³
<i>S</i> = 0.92	Absolute structure: assigned from known absolute configuration of starting material
2922 reflections	
355 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected bond lengths (Å).

C1—N2	1.458 (2)	C10—C11	1.338 (3)
C6—N1	1.465 (2)	C18—N2	1.301 (2)
C7—N1	1.286 (2)	C18—C19	1.410 (2)
C7—C8	1.440 (2)	C19—C20	1.418 (2)
C8—C9	1.404 (2)	C19—C28	1.452 (2)
C8—C17	1.436 (2)	C20—O2	1.291 (2)
C9—O1	1.311 (2)	C20—C21	1.428 (2)
C9—C10	1.429 (3)	C21—C22	1.342 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N1	1.11 (4)	1.54 (4)	2.531 (2)	146 (3)
N2 ⁺ —H2 \cdots O2 ⁻	1.07 (3)	1.64 (3)	2.566 (2)	142 (2)

Table 3

Geometric details of the intermolecular C—H $\cdots\pi$ interaction and weak C—H \cdots O hydrogen bonds (Å, °).

Cg1 is the centroid of the C8—C12/C17 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C16—H16 \cdots O2 ⁻ⁱ	1.00 (2)	2.50 (2)	3.330 (2)	140 (2)
C18—H18 \cdots O2 ⁻ⁱⁱ	0.97 (2)	2.60 (2)	3.153 (2)	117 (1)
C24—H24 \cdots Cg1 ⁱⁱⁱ	0.95 (2)	2.78 (2)	3.711 (3)	167 (2)

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

H atoms linked to the cyclohexane ring were positioned geometrically and refined using a riding model, fixing the bond lengths at 0.97 Å for CH₂ groups and at 0.98 Å for methine CH groups, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. Other H atoms were found in a difference Fourier map and refined freely. In the absence of significant anomalous scattering, the absolute structure parameter (Flack, 1983) could not be refined. The absolute structure was established on the basis of the known absolute configuration of the chiral centres in the starting material, which were not altered by the synthetic procedure.

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: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3062). Services for accessing these data are described at the back of the journal.

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