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(*E*)-4-Methoxy-2-[(4-nitrophenyl)iminomethyl]phenol

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.104
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{14}H_{12}N_2O_4$, exists as an enol–imine tautomer, in which a strong intramolecular O—H···N hydrogen bond is formed. This study verifies the preference of the enol–imine tautomeric form in the solid state.

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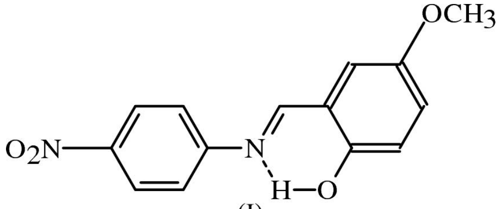
Comment

o-Hydroxy Schiff bases derived from the reaction of *o*-hydroxyaldehydes with aniline have been examined extensively (Stewart & Lingafelter, 1959; Calligaris *et al.*, 1972; Maslen & Waters, 1975). Schiff base compounds display interesting photochromic and thermochromic features and can be classified in terms of these (Cohen *et al.*, 1964; Moustakali-Mavridis *et al.*, 1980; Hadjoudis *et al.*, 1987). Photo- and thermochromism arise *via* H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994).



(I)

There are two possible types of intramolecular hydrogen bonds in Schiff bases, *viz*. the keto–amine (N—H···O) and enol–imine (N···H—O) tautomeric forms. X-ray investigation shows that (I) prefers the enol–imine tautomeric form.

o-Hydroxy Schiff bases have been found in the keto form (Ünver, Kabak *et al.*, 2002; Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003; Kǫsar *et al.*, 2004; Ersanlı *et al.*, 2004) or in the enol form (Karadayı *et al.*, 2003; Leardini *et al.*,

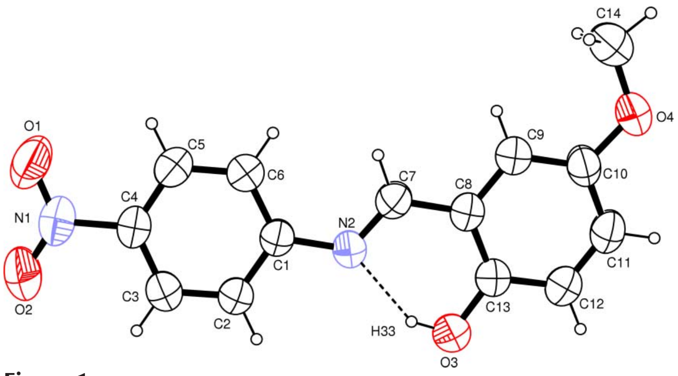


Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

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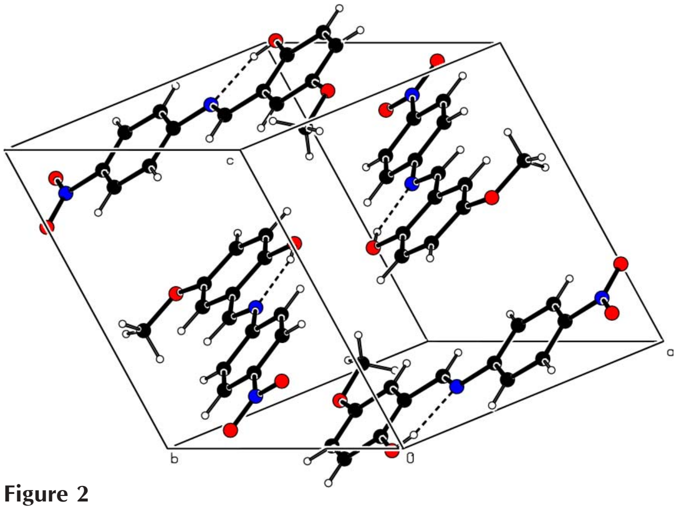

Figure 2
Packing diagram of (I). Intramolecular hydrogen bonds are shown as dashed lines.

1998; Ünver, Yıldız *et al.*, 2002; Elmalı *et al.*, 1998) or as enol/keto mixtures (Nazır *et al.*, 2000).

The molecular structure of (I) is shown with the atom-numbering scheme in Fig. 1. Selected bond lengths and angles are listed in Table 1. The C13—O3 and C7—N2 bond lengths verify the presence of the enol–imine tautomeric form. These distances agree with the corresponding distances in *N*-(2-fluoro-3-methoxy)salicylaldimine [1.347 (3) and 1.280 (3) Å; Ünver, Kendi *et al.*, 2002] and *N*-[3,5-bis(trifluoromethyl)phenyl]-3-methoxysalicylaldimine [1.352 (3) and 1.280 (4) Å; Karadayı *et al.*, 2003], which also show the enol–imine tautomeric form. The same bond distances can be compared with the corresponding distances in 2-{[tris-(hydroxymethyl)methyl]amino-methylene}cyclohexa-3,5-dien-1(2*H*)-one [1.3025 (16) and 1.2952 (18) Å; Odabaşoğlu, Albayrak, Büyükgüngör & Lönnecke, 2003] and 3-[(2-oxo-1-naphthylidene)methylamino]benzoic acid [1.290 (2) and 1.319 (3) Å; Pavlović & Sosa, 2000], which show the keto–amine tautomeric form. The C4—N1 bond length in the title compound is also in good agreement with the corresponding distances in the literature [1.4671 (18) Å (Zeller & Hunter, 2004) and 1.456 (4) Å (Glidewell *et al.*, 2004)] for related compounds that contain a nitro group.

As a common feature of *o*-hydroxysalicylidene systems, (I) displays a strong hydrogen bond between atoms N2 and O3 (Filarowski *et al.*, 2003; Yıldız *et al.*, 1998). The bond lengths and angles of this hydrogen bond are listed in Table 2.

For a closely related compound, (*E*)-2-ethoxy-6-[(4-nitrophenylimino)methyl]phenol, see Koşar *et al.* (2005).

Experimental

Compound (I) was prepared by refluxing a mixture of a solution containing 5-methoxysalicylaldehyde (3.5 mmol) in ethyl alcohol (10 ml) and a solution containing 4-nitroaniline (3.5 mmol) in ethyl alcohol (10 ml). The reaction mixture was stirred for 1 h under reflux. The solution was left to cool. The powder product was recrystallized from ethyl alcohol. Appropriate single crystals were grown from methyl alcohol (yield 70%, m.p. 461–462 K).

Crystal data

$C_{14}H_{12}N_2O_4$
$M_r = 272.26$
Monoclinic, $P2_1/n$
$a = 8.9769$ (9) Å
$b = 14.3789$ (13) Å
$c = 10.0589$ (10) Å
$\beta = 101.755$ (8)°
$V = 1271.2$ (2) Å^3
$Z = 4$

$D_x = 1.423$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9989 reflections
$\theta = 1.4$–27.8°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.27 × 0.18 × 0.11 mm

Data collection

Stoe IPDS-II diffractometer
ω rotation scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.977$, $T_{\max} = 0.989$
19135 measured reflections
3049 independent reflections

1230 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\max} = 28.1$°
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.104$
$S = 0.82$
3049 reflections
181 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N2—C7	1.277 (2)	N1—O2	1.214 (2)
O3—C13	1.351 (2)	N1—O1	1.223 (2)
C4—N1	1.465 (2)		
O2—N1—O1	123.43 (18)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H33···N2	0.82	1.89	2.6102 (19)	146

All H atoms were refined using a riding model, with C—H = 0.96 Å (for CH_3), C—H = 0.93 Å (for other CH), O—H = 0.82 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm C_{methyl}},{\rm O})$.

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).

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