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(*E*)-2-Ethoxy-6-[(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 = 0.035
wR factor = 0.068
Data-to-parameter ratio = 14.2

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

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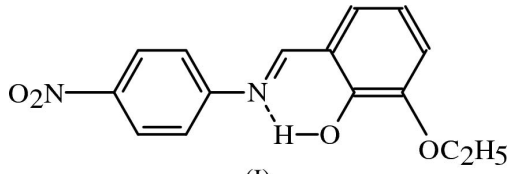
The title compound, $C_{15}H_{14}N_2O_4$, exists as an enol–imine tautomer, in which a strong intramolecular O—H···N hydrogen bond is formed. This work verifies the preference for the enol–imine tautomeric form in the solid state.

Comment

O-Hydroxy Schiff bases derived from the reaction of *o*-hydroxy aldehydes with aniline have been extensively examined (Stewart & Lingafelter, 1959; Calligaris *et al.*, 1972; Maslen & Waters, 1975). Schiff base compounds display interesting photochromic and thermochromic features and can be classified by them (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, namely keto-amine (N—H···O) and enol–imine (N···H—O) tautomeric forms. The present X-ray investigation shows that the title compound, (I), prefers the enol–imine tautomeric form rather than the keto-amine tautomeric form.

The molecular structure of (I) is shown, with the atom-numbering scheme, in Fig. 1. Selected bond lengths and angles

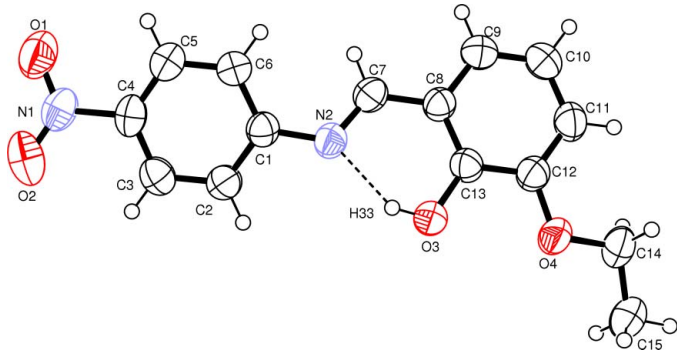


Figure 1
A view of the molecule of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

are listed in Table 1. The C13—O3 and C7—N2 bond lengths verify the enol–imine tautomeric form. These distances agree with the literature [1.352 (3) and 1.280 (4) Å; Karadayı *et al.*, 2003], which also show the enol–mine tautomeric form. The C4—N1 bond length in (I) is also in a 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 compounds which contain a nitro group.

As is a common feature of *o*-hydroxysalicylidene systems, compound (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 (I).

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

Experimental

Compound (I) was prepared by refluxing a mixture of a solution containing 3-ethoxysalicylaldehyde (3.5 mmol) and 4-nitroaniline (3.5 mmol) in ethanol (10 ml). The reaction mixture was stirred for 1 h under reflux and left to cool. Crystals of (I) were obtained by slow evaporation of a solution in tetrahydrofuran (yield 60%; m.p. 400–402 K).

Crystal data

$C_{15}H_{14}N_2O_4$
M_r = 286.28
Monoclinic, $C2/c$
a = 27.883 (2) Å
b = 7.1237 (7) Å
c = 14.7975 (10) Å
β = 111.524 (4)°
V = 2734.2 (4) Å^3
Z = 8
D_x = 1.391 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11318 reflections
θ = 1.5–26.1°
μ = 0.10 mm^{-1}
T = 293 (2) K
Prism, dark red
0.42 × 0.30 × 0.11 mm

Data collection

Stoe IPDS 2 diffractometer
ω rotation scans
Absorption correction: integration *X-RED32* (Stoe & Cie, 2002)
T_{min} = 0.966, T_{max} = 0.989
16558 measured reflections
2693 independent reflections
1289 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 26.0°
$h = -34 \rightarrow 34$
$k = -8 \rightarrow 8$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.069
S = 0.81
2693 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.08 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N2—C7	1.2825 (17)	N1—O2	1.2197 (18)
C4—N1	1.469 (2)	N1—O1	1.2246 (18)
C13—O3	1.3496 (16)		
O2—N1—O1	124.06 (18)		

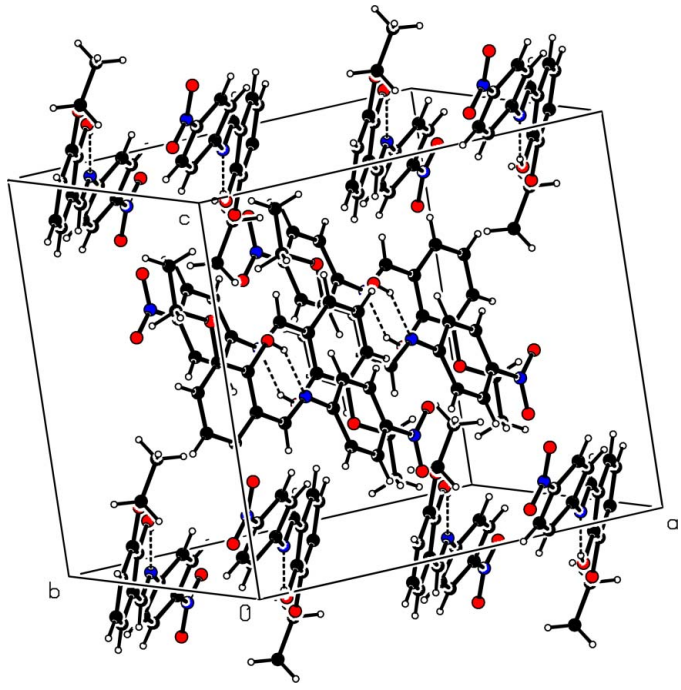


Figure 2
A packing diagram for (I). Dashed lines indicate intermolecular hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H33···N2	0.82	1.88	2.6043 (16)	147

All H atoms were refined using a riding model, with C—H = 0.93, 0.97 (for CH_2) or 0.96 Å (for CH_3) and O—H = 0.82 Å, and with U_{iso}(H) = 1.2 or 1.5U_{eq}(C) and 1.5U_{eq}(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: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

Acta Cryst. (2005). E**61**, o2109–o2111 [https://doi.org/10.1107/S1600536805018167]

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$c = 14.7975$ (10) Å
$\beta = 111.524$ (4)°
$V = 2734.2$ (4) Å^3
$Z = 8$
$F(000) = 1200$
$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 11318 reflections
$\theta = 1.5$–$26.1°$
$\mu = 0.10$ mm^{-1}
$T = 293$ K
Prism, dark red
0.42 × 0.30 × 0.11 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation scans
Absorption correction: integration X-RED32 (Stoe & Cie, 2002)
$T_{min} = 0.966$, $T_{max} = 0.989$
16558 measured reflections
2693 independent reflections
1289 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.6°$
$h = -34 \rightarrow 34$
$k = -8 \rightarrow 8$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.069$
$S = 0.81$
2693 reflections
190 parameters
28 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.08$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N2	0.19145 (5)	0.01499 (17)	0.46671 (9)	0.0541 (3)
O4	0.08969 (4)	0.23344 (16)	0.66700 (8)	0.0698 (3)
C4	0.30980 (6)	−0.1273 (2)	0.37268 (13)	0.0582 (4)
C1	0.23027 (6)	−0.0365 (2)	0.43092 (11)	0.0514 (4)
C13	0.11459 (6)	0.1315 (2)	0.54012 (12)	0.0524 (4)
O3	0.16196 (4)	0.10675 (15)	0.60865 (7)	0.0647 (3)
H33	0.1818	0.0709	0.5829	0.097*
C7	0.14488 (6)	0.0428 (2)	0.40868 (12)	0.0552 (4)
H7	0.1369	0.0269	0.3424	0.066*
C8	0.10437 (6)	0.0979 (2)	0.44210 (11)	0.0502 (4)
C12	0.07507 (6)	0.1970 (2)	0.56943 (12)	0.0560 (4)
C11	0.02645 (6)	0.2202 (2)	0.50197 (13)	0.0638 (5)
H11	0.0002	0.2614	0.5216	0.077*
N1	0.35282 (7)	−0.1742 (2)	0.34188 (15)	0.0774 (5)
O1	0.34245 (6)	−0.2107 (2)	0.25592 (12)	0.1027 (5)
C6	0.22042 (6)	−0.1233 (2)	0.34157 (11)	0.0617 (4)
H2	0.1867	−0.1510	0.3015	0.074*
O2	0.39643 (5)	−0.1736 (2)	0.40282 (12)	0.1021 (5)
C2	0.28053 (6)	0.0002 (2)	0.49074 (12)	0.0576 (4)
H6	0.2872	0.0559	0.5510	0.069*
C5	0.26057 (7)	−0.1681 (2)	0.31272 (12)	0.0646 (5)
H3	0.2543	−0.2256	0.2530	0.078*
C9	0.05420 (6)	0.1236 (2)	0.37502 (12)	0.0613 (4)
H13	0.0469	0.0999	0.3095	0.074*
C3	0.32096 (6)	−0.0450 (2)	0.46198 (13)	0.0618 (5)
H5	0.3549	−0.0203	0.5021	0.074*
C10	0.01584 (6)	0.1830 (2)	0.40447 (13)	0.0670 (5)
H12	−0.0174	0.1986	0.3593	0.080*
C15	0.07949 (7)	0.3888 (2)	0.80025 (12)	0.0752 (5)
H15A	0.0555	0.4539	0.8220	0.113*
H15B	0.1077	0.4707	0.8051	0.113*
H15C	0.0924	0.2800	0.8401	0.113*
C14	0.05272 (7)	0.3293 (2)	0.69640 (12)	0.0685 (5)
H14A	0.0241	0.2467	0.6906	0.082*
H14B	0.0394	0.4383	0.6555	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0539 (8)	0.0602 (8)	0.0524 (8)	0.0010 (7)	0.0243 (7)	0.0011 (6)

O4	0.0651 (8)	0.0940 (8)	0.0551 (7)	0.0220 (6)	0.0277 (6)	−0.0012 (6)
C4	0.0603 (12)	0.0553 (10)	0.0701 (12)	0.0049 (8)	0.0371 (10)	0.0057 (9)
C1	0.0529 (11)	0.0525 (10)	0.0528 (11)	−0.0005 (8)	0.0240 (9)	0.0044 (8)
C13	0.0472 (10)	0.0586 (10)	0.0511 (10)	0.0030 (8)	0.0175 (9)	0.0064 (8)
O3	0.0545 (7)	0.0896 (8)	0.0499 (7)	0.0129 (6)	0.0190 (6)	0.0009 (6)
C7	0.0618 (11)	0.0574 (10)	0.0505 (10)	0.0001 (8)	0.0254 (9)	0.0038 (8)
C8	0.0518 (10)	0.0541 (9)	0.0474 (10)	0.0014 (7)	0.0213 (9)	0.0039 (8)
C12	0.0551 (11)	0.0631 (10)	0.0516 (11)	0.0050 (8)	0.0217 (9)	0.0039 (9)
C11	0.0533 (11)	0.0756 (12)	0.0662 (12)	0.0102 (9)	0.0265 (10)	0.0022 (9)
N1	0.0757 (12)	0.0687 (10)	0.1041 (14)	0.0020 (9)	0.0521 (12)	0.0055 (10)
O1	0.1157 (12)	0.1109 (12)	0.1132 (12)	−0.0056 (9)	0.0795 (11)	−0.0205 (10)
C6	0.0559 (11)	0.0757 (11)	0.0537 (11)	0.0016 (9)	0.0204 (9)	−0.0062 (9)
O2	0.0640 (9)	0.1167 (12)	0.1357 (13)	0.0112 (8)	0.0486 (10)	0.0047 (10)
C2	0.0589 (11)	0.0617 (10)	0.0533 (10)	−0.0021 (9)	0.0218 (9)	−0.0038 (8)
C5	0.0671 (12)	0.0730 (11)	0.0602 (11)	0.0043 (10)	0.0310 (10)	−0.0054 (9)
C9	0.0583 (11)	0.0689 (11)	0.0531 (10)	0.0030 (9)	0.0162 (9)	0.0017 (8)
C3	0.0522 (11)	0.0645 (11)	0.0687 (12)	−0.0024 (8)	0.0223 (9)	0.0029 (9)
C10	0.0535 (11)	0.0802 (12)	0.0612 (12)	0.0099 (9)	0.0138 (9)	0.0030 (10)
C15	0.0869 (13)	0.0782 (12)	0.0733 (13)	0.0012 (10)	0.0444 (11)	−0.0095 (10)
C14	0.0707 (11)	0.0747 (11)	0.0723 (12)	0.0106 (10)	0.0409 (10)	0.0002 (10)

Geometric parameters (Å, º)

N2—C7	1.2825 (17)	C11—H11	0.9300
N2—C1	1.4168 (18)	N1—O2	1.2197 (18)
O4—C12	1.3734 (18)	N1—O1	1.2246 (18)
O4—C14	1.4310 (17)	C6—C5	1.374 (2)
C4—C5	1.365 (2)	C6—H2	0.9300
C4—C3	1.373 (2)	C2—C3	1.381 (2)
C4—N1	1.469 (2)	C2—H6	0.9300
C1—C2	1.380 (2)	C5—H3	0.9300
C1—C6	1.393 (2)	C9—C10	1.362 (2)
C13—O3	1.3496 (16)	C9—H13	0.9300
C13—C8	1.393 (2)	C3—H5	0.9300
C13—C12	1.404 (2)	C10—H12	0.9300
O3—H33	0.8200	C15—C14	1.502 (2)
C7—C8	1.443 (2)	C15—H15A	0.9600
C7—H7	0.9300	C15—H15B	0.9600
C8—C9	1.399 (2)	C15—H15C	0.9600
C12—C11	1.367 (2)	C14—H14A	0.9700
C11—C10	1.388 (2)	C14—H14B	0.9700
C7—N2—C1	120.97 (14)	C1—C6—H2	120.0
C12—O4—C14	116.15 (13)	C1—C2—C3	120.62 (16)
C5—C4—C3	122.38 (16)	C1—C2—H6	119.7
C5—C4—N1	119.38 (17)	C3—C2—H6	119.7
C3—C4—N1	118.23 (17)	C4—C5—C6	119.24 (16)
C2—C1—C6	119.57 (15)	C4—C5—H3	120.4

C2—C1—N2	116.50 (14)	C6—C5—H3	120.4
C6—C1—N2	123.93 (15)	C10—C9—C8	120.80 (16)
O3—C13—C8	121.99 (14)	C10—C9—H13	119.6
O3—C13—C12	118.31 (14)	C8—C9—H13	119.6
C8—C13—C12	119.69 (14)	C4—C3—C2	118.27 (16)
C13—O3—H33	109.5	C4—C3—H5	120.9
N2—C7—C8	122.68 (15)	C2—C3—H5	120.9
N2—C7—H7	118.7	C9—C10—C11	119.95 (16)
C8—C7—H7	118.7	C9—C10—H12	120.0
C13—C8—C9	119.04 (15)	C11—C10—H12	120.0
C13—C8—C7	121.12 (14)	C14—C15—H15A	109.5
C9—C8—C7	119.80 (15)	C14—C15—H15B	109.5
C11—C12—O4	125.26 (15)	H15A—C15—H15B	109.5
C11—C12—C13	119.67 (15)	C14—C15—H15C	109.5
O4—C12—C13	115.07 (14)	H15A—C15—H15C	109.5
C12—C11—C10	120.81 (16)	H15B—C15—H15C	109.5
C12—C11—H11	119.6	O4—C14—C15	107.62 (14)
C10—C11—H11	119.6	O4—C14—H14A	110.2
O2—N1—O1	124.06 (18)	C15—C14—H14A	110.2
O2—N1—C4	118.41 (18)	O4—C14—H14B	110.2
O1—N1—C4	117.52 (18)	C15—C14—H14B	110.2
C5—C6—C1	119.90 (16)	H14A—C14—H14B	108.5
C5—C6—H2	120.0		

C7—N2—C1—C2	157.85 (14)	C3—C4—N1—O2	14.4 (2)
C7—N2—C1—C6	−23.4 (2)	C5—C4—N1—O1	15.4 (2)
C1—N2—C7—C8	−179.14 (13)	C3—C4—N1—O1	−165.29 (16)
O3—C13—C8—C9	179.02 (13)	C2—C1—C6—C5	−1.4 (2)
C12—C13—C8—C9	−2.3 (2)	N2—C1—C6—C5	179.93 (14)
O3—C13—C8—C7	−2.9 (2)	C6—C1—C2—C3	1.3 (2)
C12—C13—C8—C7	175.74 (13)	N2—C1—C2—C3	−179.95 (14)
N2—C7—C8—C13	2.8 (2)	C3—C4—C5—C6	0.9 (2)
N2—C7—C8—C9	−179.18 (14)	N1—C4—C5—C6	−179.73 (14)
C14—O4—C12—C11	−9.9 (2)	C1—C6—C5—C4	0.3 (2)
C14—O4—C12—C13	169.91 (14)	C13—C8—C9—C10	0.8 (2)
O3—C13—C12—C11	−178.77 (14)	C7—C8—C9—C10	−177.29 (15)
C8—C13—C12—C11	2.5 (2)	C5—C4—C3—C2	−1.1 (2)
O3—C13—C12—O4	1.4 (2)	N1—C4—C3—C2	179.61 (13)
C8—C13—C12—O4	−177.31 (14)	C1—C2—C3—C4	−0.1 (2)
O4—C12—C11—C10	178.64 (15)	C8—C9—C10—C11	0.5 (2)
C13—C12—C11—C10	−1.2 (2)	C12—C11—C10—C9	−0.4 (3)
C5—C4—N1—O2	−164.98 (16)	C12—O4—C14—C15	−168.97 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H33···N2	0.82	1.88	2.6043 (16)	147