

(E)-2-[(2-Chlorophenyl)iminomethyl]-4-methylphenol

Özlem Deveci,^a Şamil Işık,^a Ferda Erşahin^b and Erbil Açar^{b*}

^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey, and ^bDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

Correspondence e-mail: odeveci@omu.edu.tr

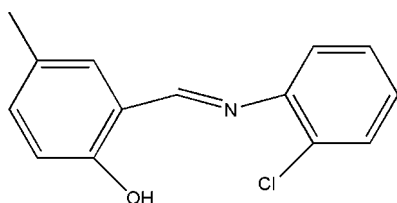
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.073; wR factor = 0.233; data-to-parameter ratio = 18.3.

The molecule of the title compound, $\text{C}_{14}\text{H}_{12}\text{ClNO}$, adopts the enol-imine tautomeric form, with an intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond. In the molecule, the two benzene rings are twisted with respect to each other by $30.6(2)^\circ$. The crystal structure is stabilized by intermolecular $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For general background, see: Cohen *et al.* (1964); Hadjoudis *et al.* (1987); Williams (1972); Garnovski *et al.* (1993); Zhou *et al.* (2000); Dürr & Bouas-Laurent *et al.* (1990). For related structures, see: Ünver *et al.* (2002); Karadayı *et al.* (2003); Filarowski *et al.* (2003); Yıldız *et al.* (1998); Odabaşoğlu *et al.* (2003).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{ClNO}$
 $M_r = 245.70$
 Orthorhombic, $Pbca$
 $a = 7.5121(7)$ Å
 $b = 11.9190(15)$ Å
 $c = 27.500(3)$ Å

$V = 2462.3(5)$ Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.29$ mm⁻¹
 $T = 296(2)$ K
 $0.8 \times 0.23 \times 0.09$ mm

Data collection

Stoe IPDS II diffractometer
 Absorption correction: none
 14292 measured reflections

2428 independent reflections
 833 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.133$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.233$
 $S = 0.81$
 2428 reflections
 133 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the $\text{C1}-\text{C6}$ ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H9}\cdots\text{N1}$	0.82	1.89	2.622 (5)	147
$\text{C14}-\text{H15B}\cdots\text{Cg1}^{\text{i}}$	0.93	2.83	3.849 (6)	174

Symmetry code: (i) $-\frac{1}{2} + x, y, \frac{1}{2} - z$

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area*; data reduction: *X-Red32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXL97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2392).

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supporting information

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(E)-2-[(2-Chlorophenyl)iminomethyl]-4-methylphenol**Özlem Devenci, Şamil Işık, Ferda Erşahin and Erbil Ağar****S1. Comment**

Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic properties (Williams, 1972). In addition, Schiff bases have been used extensively as ligands in the field of coordination chemistry (Garnovski *et al.*, 1993). There is considerable interest in Schiff base complexes due to their striking anti-tumour activities (Zhou *et al.*, 2000). Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl O atom to the imine N atom (Cohen *et al.*, 1964; Hadjoudis *et al.*, 1987). Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems (Dürr & Bouas-Laurent *et al.*, 1990).

There are two possible types of intramolecular hydrogen bonds in Schiff bases, *viz.* the keto-amine (N—H \cdots O) and enol-imine (O—H \cdots N) tautomeric forms. X-ray investigation shows that (I) prefers the enol-imine tautomeric form. The molecular structure of (I) is shown in Fig. 1, with the atom-numbering scheme. Selected bond lengths and angles are listed in Table 1. The C13—O1 and C7—N1 bond lengths verify the enol-imine form. The same bonds can be compared with the corresponding distances in (*E*)-*N*-(2-fluoro-3-methoxy)-salicylaldehyde [1.347 (3) Å and 1.280 (3) Å; Ünver *et al.*, 2002] and (*E*)-*N*-(3,5-bis(trifluoromethyl)phenyl)-3-methoxysalicylaldehyde [1.352 (3) Å and 1.280 (4) Å; Karadayı *et al.*, 2003], which exist in the enol-imine tautomeric form. The dihedral angle between the two benzene rings is 30.6 (2)°. The title molecule has a strong intramolecular O—H \cdots N hydrogen bond between atoms N1 and O1 (Table 2). This type of strong intramolecular hydrogen bond is a common feature of *o*-hydroxysalicylidene systems (Filarowski *et al.*, 2003; Yıldız *et al.*, 1998; Odabaşoğlu *et al.*, 2003). The O—H \cdots N hydrogen-bonded ring is almost coplanar with the adjacent ring, with an N1—C7—C8—C13 torsion angle of 3.4 (6)°. In the crystal there are also C—H \cdots π interactions between C14-methyl group and C1ⁱ-containing benzene ring [symmetry code: (i) $-1/2 + x, y, 1/2 - z$] (Fig. 2), C14—H15B—Cg1ⁱ = 174°, H15B \cdots Cg1ⁱ = 2.83 and C14 \cdots Cg1ⁱ = 3.849 (6) Å (Cg1 is centroid of the C1-containing benzene ring).

S2. Experimental

The title compound was prepared by reflux a mixture of a solution containing 5-methylsalicylaldehyde (0.05 g, 0.367 mmol) in 20 ml ethanol and a solution containing 2-kloranilin (0.0447 g, 0.367 mmol) in 20 ml ethanol. The reaction mixture was stirred for 2 h under reflux. The crystals suitable for X-ray analysis were obtained from an ethanol solution by slow evaporation (yield % 80).

S3. Refinement

H atoms were positioned geometrically and treated using a riding model with C—H = 0.93, 0.96, 0.82 and 0.93 Å for CH, CH₃, OH and CH (aromatic), respectively. $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl or $1.2U_{\text{eq}}(\text{C}, \text{N})$ for others.

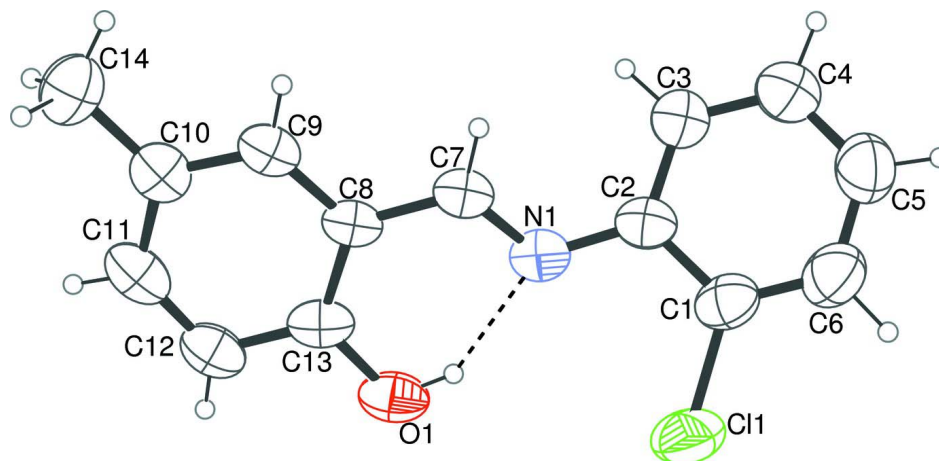


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability.

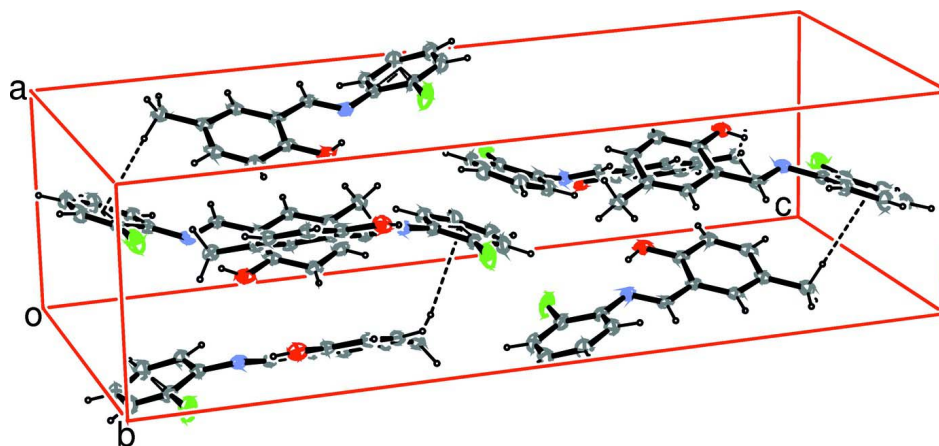


Figure 2

A perspective view of the molecular packing of compound (I). Dashed lines indicate hydrogen bonds and C—H... π interactions.

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Crystal data

$C_{14}H_{12}ClNO$

$M_r = 245.70$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 7.5121 (7) \text{ \AA}$

$b = 11.9190 (15) \text{ \AA}$

$c = 27.500 (3) \text{ \AA}$

$V = 2462.3 (5) \text{ \AA}^3$

$Z = 8$

$F(000) = 1024$

$D_x = 1.325 \text{ Mg m}^{-3}$

Melting point = 356–358 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5622 reflections

$\theta = 27.1\text{--}2.2^\circ$

$\mu = 0.29 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, yellow

$0.8 \times 0.23 \times 0.09 \text{ mm}$

Data collection

Stoe IPDS-2 diffractometer	2428 independent reflections
Radiation source: fine-focus sealed tube	833 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.133$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
rotation method scans	$h = -9 \rightarrow 8$
14292 measured reflections	$k = -14 \rightarrow 14$
	$l = -33 \rightarrow 33$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.073$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.233$	$w = 1/[\sigma^2(F_o^2) + (0.1247P)^2]$
$S = 0.81$	where $P = (F_o^2 + 2F_c^2)/3$
2428 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
133 parameters	$\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0007 (7)	0.3349 (5)	0.43397 (19)	0.0948 (15)
C2	-0.0462 (6)	0.2701 (4)	0.39300 (17)	0.0767 (12)
C3	-0.0457 (7)	0.1562 (4)	0.39911 (19)	0.0942 (15)
H3	-0.0826	0.1102	0.3737	0.113*
C4	0.0080 (9)	0.1088 (5)	0.4419 (2)	0.1153 (18)
H4	0.0088	0.0310	0.4449	0.138*
C5	0.0600 (9)	0.1724 (6)	0.4798 (2)	0.122 (2)
H5	0.0990	0.1388	0.5084	0.146*
C6	0.0550 (9)	0.2868 (6)	0.4761 (2)	0.1143 (19)
H6	0.0888	0.3313	0.5023	0.137*
C7	-0.0567 (6)	0.2814 (4)	0.30913 (17)	0.0722 (11)
C8	-0.0967 (5)	0.3344 (4)	0.26359 (17)	0.0738 (7)
C9	-0.0565 (5)	0.2805 (4)	0.21962 (17)	0.0738 (7)
C10	-0.0914 (5)	0.3263 (3)	0.17485 (16)	0.0738 (7)
C11	-0.1683 (6)	0.4315 (4)	0.1750 (2)	0.0911 (7)
H11	-0.1943	0.4636	0.1450	0.109*
C12	-0.2100 (6)	0.4931 (4)	0.21632 (18)	0.0911 (7)

H12	-0.2614	0.5639	0.2146	0.109*
C13	-0.1696 (6)	0.4417 (4)	0.2609 (2)	0.0911 (7)
C14	-0.0490 (7)	0.2641 (5)	0.12922 (18)	0.1075 (17)
H15A	0.0380	0.3053	0.1109	0.161*
H15B	-0.1553	0.2557	0.1102	0.161*
H15C	-0.0025	0.1914	0.1372	0.161*
Cl1	-0.0042 (3)	0.47953 (13)	0.42906 (6)	0.1482 (9)
N1	-0.0919 (5)	0.3258 (3)	0.35040 (15)	0.0780 (10)
O1	-0.2054 (4)	0.5014 (2)	0.30200 (12)	0.0911 (7)
H9	-0.1766	0.4645	0.3259	0.137*
H1	0.011 (5)	0.210 (4)	0.3066 (13)	0.083 (12)*
H2	-0.010 (5)	0.211 (3)	0.2174 (13)	0.072 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.093 (4)	0.096 (3)	0.095 (3)	-0.001 (3)	0.022 (3)	-0.020 (3)
C2	0.057 (3)	0.077 (3)	0.096 (3)	0.005 (2)	0.012 (2)	-0.006 (3)
C3	0.099 (4)	0.080 (3)	0.103 (4)	-0.006 (3)	-0.007 (3)	-0.005 (3)
C4	0.145 (5)	0.090 (4)	0.112 (4)	-0.003 (4)	-0.002 (4)	0.008 (3)
C5	0.147 (6)	0.125 (5)	0.093 (4)	0.008 (5)	0.010 (4)	0.005 (4)
C6	0.131 (5)	0.120 (5)	0.092 (4)	-0.011 (4)	0.010 (3)	-0.014 (4)
C7	0.053 (3)	0.064 (3)	0.099 (3)	-0.001 (2)	0.003 (2)	-0.006 (3)
C8	0.0491 (12)	0.0711 (17)	0.1013 (18)	-0.0093 (12)	-0.0077 (14)	0.0037 (13)
C9	0.0491 (12)	0.0711 (17)	0.1013 (18)	-0.0093 (12)	-0.0077 (14)	0.0037 (13)
C10	0.0491 (12)	0.0711 (17)	0.1013 (18)	-0.0093 (12)	-0.0077 (14)	0.0037 (13)
C11	0.0687 (12)	0.0733 (13)	0.1313 (19)	0.0018 (10)	0.0032 (12)	0.0041 (11)
C12	0.0687 (12)	0.0733 (13)	0.1313 (19)	0.0018 (10)	0.0032 (12)	0.0041 (11)
C13	0.0687 (12)	0.0733 (13)	0.1313 (19)	0.0018 (10)	0.0032 (12)	0.0041 (11)
C14	0.092 (4)	0.132 (4)	0.098 (3)	-0.019 (3)	-0.006 (3)	-0.015 (3)
Cl1	0.240 (2)	0.0908 (10)	0.1138 (11)	-0.0054 (12)	0.0417 (12)	-0.0294 (8)
N1	0.065 (2)	0.074 (2)	0.095 (3)	-0.0028 (19)	0.016 (2)	-0.009 (2)
O1	0.0687 (12)	0.0733 (13)	0.1313 (19)	0.0018 (10)	0.0032 (12)	0.0041 (11)

Geometric parameters (Å, °)

C1—C6	1.354 (7)	C8—C13	1.393 (6)
C1—C2	1.410 (6)	C8—C9	1.402 (6)
C1—Cl1	1.730 (6)	C9—C10	1.372 (6)
C2—C3	1.368 (6)	C9—H2	0.91 (4)
C2—N1	1.390 (5)	C10—C11	1.380 (6)
C3—C4	1.366 (7)	C10—C14	1.491 (6)
C3—H3	0.9300	C11—C12	1.389 (6)
C4—C5	1.348 (7)	C11—H11	0.9300
C4—H4	0.9300	C12—C13	1.403 (6)
C5—C6	1.368 (8)	C12—H12	0.9300
C5—H5	0.9300	C13—O1	1.364 (6)
C6—H6	0.9300	C14—H15A	0.9600

C7—N1	1.280 (5)	C14—H15B	0.9600
C7—C8	1.434 (6)	C14—H15C	0.9600
C7—H1	0.99 (4)	O1—H9	0.8200
C6—C1—C2	121.8 (5)	C10—C9—C8	123.4 (5)
C6—C1—C11	119.6 (4)	C10—C9—H2	112 (2)
C2—C1—C11	118.5 (4)	C8—C9—H2	124 (2)
C3—C2—N1	125.3 (4)	C9—C10—C11	116.0 (5)
C3—C2—C1	116.4 (5)	C9—C10—C14	121.1 (4)
N1—C2—C1	118.3 (4)	C11—C10—C14	122.8 (5)
C4—C3—C2	121.2 (5)	C10—C11—C12	125.2 (5)
C4—C3—H3	119.4	C10—C11—H11	117.4
C2—C3—H3	119.4	C12—C11—H11	117.4
C5—C4—C3	121.3 (6)	C11—C12—C13	115.8 (5)
C5—C4—H4	119.4	C11—C12—H12	122.1
C3—C4—H4	119.4	C13—C12—H12	122.1
C4—C5—C6	119.6 (6)	O1—C13—C8	120.8 (5)
C4—C5—H5	120.2	O1—C13—C12	117.0 (4)
C6—C5—H5	120.2	C8—C13—C12	122.2 (5)
C1—C6—C5	119.6 (6)	C10—C14—H15A	109.5
C1—C6—H6	120.2	C10—C14—H15B	109.5
C5—C6—H6	120.2	H15A—C14—H15B	109.5
N1—C7—C8	123.3 (5)	C10—C14—H15C	109.5
N1—C7—H1	122 (2)	H15A—C14—H15C	109.5
C8—C7—H1	115 (2)	H15B—C14—H15C	109.5
C13—C8—C9	117.3 (5)	C7—N1—C2	119.9 (4)
C13—C8—C7	122.2 (5)	C13—O1—H9	109.5
C9—C8—C7	120.4 (4)		
C6—C1—C2—C3	4.4 (7)	C8—C9—C10—C11	0.7 (6)
C11—C1—C2—C3	-178.0 (4)	C8—C9—C10—C14	-178.7 (4)
C6—C1—C2—N1	-176.8 (5)	C9—C10—C11—C12	0.7 (7)
C11—C1—C2—N1	0.8 (6)	C14—C10—C11—C12	-179.8 (4)
N1—C2—C3—C4	177.4 (5)	C10—C11—C12—C13	-0.3 (7)
C1—C2—C3—C4	-3.8 (8)	C9—C8—C13—O1	-177.2 (4)
C2—C3—C4—C5	1.0 (9)	C7—C8—C13—O1	0.3 (6)
C3—C4—C5—C6	1.6 (10)	C9—C8—C13—C12	3.0 (6)
C2—C1—C6—C5	-2.0 (9)	C7—C8—C13—C12	-179.5 (4)
C11—C1—C6—C5	-179.6 (5)	C11—C12—C13—O1	178.5 (4)
C4—C5—C6—C1	-1.0 (10)	C11—C12—C13—C8	-1.7 (7)
N1—C7—C8—C13	3.4 (6)	C8—C7—N1—C2	-178.9 (4)
N1—C7—C8—C9	-179.2 (4)	C3—C2—N1—C7	-33.4 (6)
C13—C8—C9—C10	-2.5 (6)	C1—C2—N1—C7	147.9 (4)
C7—C8—C9—C10	179.9 (4)		

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—H9 \cdots N1	0.82	1.89	2.622 (5)	147
C14—H15 <i>B</i> \cdots Cg1 ⁱ	0.93	2.83	3.849 (6)	174

Symmetry code: (i) $x-1/2, y, -z+1/2$.