2-[(4-Chlorophenyl)iminomethyl]hydroquinone

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The title compound, $C_{13}H_{10}ClNO_2$, exists in the phenol–imine form in the crystal, and the aromatic rings are oriented at a dihedral angle of 2.82 (9)°. An intramolecular O—H⋯N hydrogen bond results in the formation of a planar six-membered ring. In the crystal structure, intermolecular O—H⋯O hydrogen bonds link the molecules into chains.

Related literature

For general background to *o*-hydroxy Schiff bases, see: Calligaris *et al.* (1972); Hadjoudis *et al.* (1987); Hökelek *et al.* (2004); Maslen & Waters (1975); Moustakali-Mavridis *et al.* (1980); Xu *et al.* (1994). For related structures, see: Filarowski *et al.* (2003); Karadayı *et al.* (2003); Yıldız *et al.* (1998).
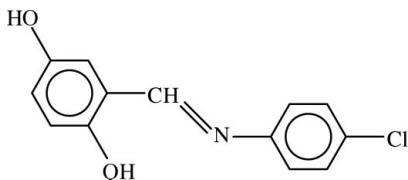
Experimental

Crystal data

$C_{13}H_{10}ClNO_2$	V = 1110.78 (12) Å³
M_r = 247.67	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 20.3347 (14) Å	μ = 0.33 mm⁻¹
b = 4.5848 (2) Å	T = 296 K
c = 12.0383 (9) Å	0.80 × 0.40 × 0.06 mm
β = 98.231 (6)°	

Data collection

Stoe IPDS-II diffractometer	15373 measured reflections
Absorption correction: integration (X-$RED32$; Stoe & Cie, 2002)	2185 independent reflections
	1575 reflections with $I > 2\sigma(I)$
T_{min} = 0.819, T_{max} = 0.978	R_{int} = 0.069

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	154 parameters
$wR(F^2)$ = 0.091	H-atom parameters constrained
S = 0.95	$\Delta\rho_{max}$ = 0.13 e Å⁻³
2185 reflections	$\Delta\rho_{min}$ = −0.25 e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N1	0.82	1.90	2.6270 (18)	147
O2—H2⋯O2ⁱ	0.82	2.04	2.7631 (13)	147

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-RED32* (Stoe & Cie, 2002); data reduction: *X-RED32*; program(s) used to solve structure: *SHELXS97* (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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supporting information

2-[(4-Chlorophenyl)iminomethyl]hydroquinone

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S1. Comment

o-Hydroxy Schiff bases derived from the reactions of *o*-hydroxyaldehydes with aniline have been examined extensively (Calligaris *et al.*, 1972; Maslen & Waters, 1975). In general, *o*-hydroxy Schiff bases exhibit two possible tautomeric forms, namely, phenol-imine and keto-amine. Naphthaldimine and salicylaldimine can also exist in the phenol-imine and keto-amine forms, respectively depending on the stereochemistry of the molecule and the type of nitrogen substituents in naphthaldimine and salicylaldimine Schiff bases (Hökelek *et al.*, 2004). Schiff base compounds display interesting photochromic and thermochromic features and can be classified in terms of these (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).

In the title compound (Fig. 1), the phenol-imine form is favored over the keto-amine form, as indicated by C13-O1 [1.356 (2) Å] and C7-N1 [1.280 (2) Å] bonds, which are in accordance with the corresponding values in a similar compound [C-O = 1.352 (3) and C-N = 1.280 (4) Å; Karadayı *et al.*, 2003]. As a common feature of *o*-hydroxysalicyl-idene systems, the title compound displays a strong hydrogen bond between atoms N1 and O1 (Filarowski *et al.*, 2003; Yıldız *et al.*, 1998).

It is known that Schiff bases may exhibit thermochromism or photochromism, depending on the planarity or non-planarity of the molecule, respectively. Therefore, one can expect thermochromic properties in the title compound caused by planarity of the molecule; the dihedral angle between rings A (C1-C6) and B (C8-C13) is 2.82 (9)°. Intramolecular O-H⋯N hydrogen bond (Table 1) results in the formation of a planar six-membered ring C (O1/N1/C7/C8/C13/H1), which is oriented with respect to rings A and B at dihedral angles of A/C = 2.97 (8) and B/C = 1.35 (8) °. So, they are nearly coplanar.

In the crystal structure, intermolecular O-H⋯O hydrogen bonds (Table 1) link the molecules into chains (Fig. 2), in which they may be effective in the stabilization of the structure.

S2. Experimental

The title compound was prepared by refluxing a mixture of a solution containing 2,5-dihydroxybenzaldehyde (0.034 g 0.246 mmol) in ethanol (20 ml) and a solution containing 4-chloroaniline (0.031 g 0.246 mmol) in ethanol (20 ml). The reaction mixture was stirred for 1 h under reflux. Crystals suitable for X-ray analysis were obtained from ethylalcohol by slow evaporation (yield; 69%; m.p. 439-441 K).

S3. Refinement

H atoms were positioned geometrically, with O-H = 0.82 Å (for OH) and C-H = 0.93 Å for aromatic H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,O)$, where x = 1.5 for OH H and x = 1.2 for aromatic H atoms.
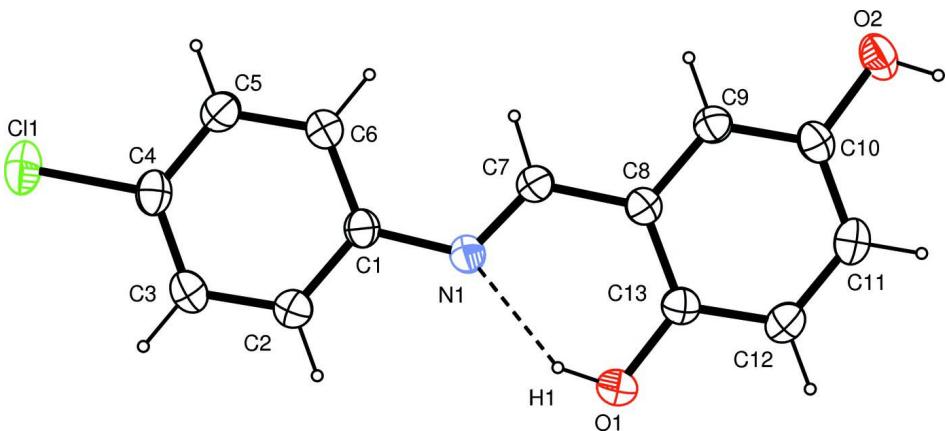
Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.
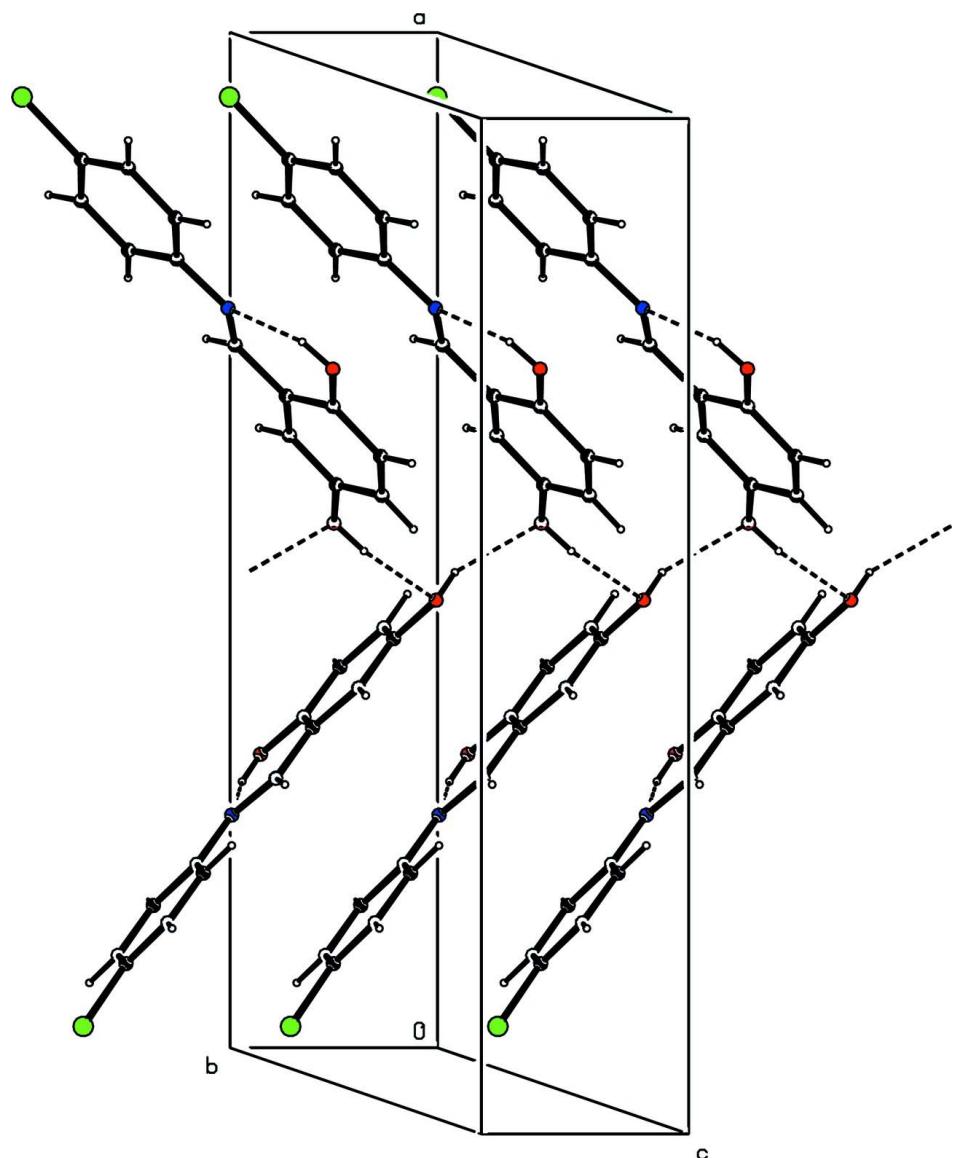
Figure 2
A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

2-[(4-Chlorophenyl)iminomethyl]hydroquinone

Crystal data

$C_{13}H_{10}ClNO_2$	$F(000) = 512$
$M_r = 247.67$	$D_x = 1.481$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 13223 reflections
$a = 20.3347$ (14) Å	$\theta = 1.7–27.2°$
$b = 4.5848$ (2) Å	$\mu = 0.33$ mm^{-1}
$c = 12.0383$ (9) Å	$T = 296$ K
$\beta = 98.231$ (6)°	Plate, brown
$V = 1110.78$ (12) Å^3	$0.80 \times 0.40 \times 0.06$ mm
$Z = 4$	

Data collection

Stoe IPDS-II diffractometer	15373 measured reflections
Radiation source: fine-focus sealed tube	2185 independent reflections
Graphite monochromator	1575 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.069$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
Absorption correction: integration (X-$RED32$; Stoe & Cie, 2002)	$h = -25 \rightarrow 25$ $k = -5 \rightarrow 5$
$T_{min} = 0.819$, $T_{max} = 0.978$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.091$	
$S = 0.95$	H-atom parameters constrained
2185 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
154 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.13$ e Å^{-3} $\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. 370 frames, detector distance = 120 mm

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cl1	0.46483 (2)	1.40871 (10)	0.33464 (4)	0.06076 (18)
O1	0.21937 (7)	0.2322 (3)	0.60021 (10)	0.0600 (4)
H1	0.2441	0.3500	0.5759	0.090*
O2	0.03814 (6)	−0.1943 (3)	0.25297 (11)	0.0554 (3)
H2	0.0127	−0.3115	0.2757	0.083*
N1	0.26643 (6)	0.5541 (3)	0.44912 (11)	0.0404 (3)
C1	0.31206 (7)	0.7617 (3)	0.41651 (14)	0.0390 (3)
C2	0.35972 (8)	0.8701 (4)	0.50029 (14)	0.0469 (4)
H2A	0.3599	0.8079	0.5739	0.056*
C3	0.40681 (8)	1.0686 (4)	0.47659 (15)	0.0491 (4)
H3	0.4388	1.1380	0.5334	0.059*
C4	0.40585 (8)	1.1623 (3)	0.36807 (15)	0.0445 (4)
C5	0.35838 (9)	1.0629 (4)	0.28379 (15)	0.0499 (4)
H5	0.3578	1.1304	0.2108	0.060*
C6	0.31162 (8)	0.8628 (4)	0.30758 (14)	0.0480 (4)

H6	0.2796	0.7954	0.2504	0.058*
C7	0.22399 (8)	0.4302 (3)	0.37519 (13)	0.0409 (4)
H7	0.2238	0.4777	0.3000	0.049*
C8	0.17625 (7)	0.2186 (3)	0.40433 (13)	0.0384 (3)
C9	0.13019 (8)	0.1001 (3)	0.31857 (14)	0.0421 (4)
H9	0.1312	0.1561	0.2446	0.051*
C10	0.08364 (8)	−0.0975 (3)	0.34244 (14)	0.0427 (4)
C11	0.08231 (9)	−0.1840 (4)	0.45228 (16)	0.0510 (4)
H11	0.0504	−0.3164	0.4686	0.061*
C12	0.12807 (9)	−0.0745 (4)	0.53729 (15)	0.0530 (4)
H12	0.1274	−0.1360	0.6107	0.064*
C13	0.17529 (8)	0.1273 (4)	0.51433 (13)	0.0436 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0545 (3)	0.0499 (3)	0.0821 (4)	−0.0131 (2)	0.0244 (2)	−0.0049 (2)
O1	0.0675 (8)	0.0733 (8)	0.0374 (7)	−0.0226 (7)	0.0010 (6)	0.0007 (6)
O2	0.0450 (7)	0.0519 (7)	0.0651 (8)	−0.0090 (5)	−0.0062 (6)	−0.0033 (6)
N1	0.0395 (7)	0.0397 (7)	0.0417 (7)	−0.0030 (6)	0.0047 (6)	−0.0009 (6)
C1	0.0380 (8)	0.0355 (7)	0.0436 (9)	−0.0002 (6)	0.0065 (7)	−0.0012 (7)
C2	0.0499 (9)	0.0477 (9)	0.0426 (9)	−0.0046 (7)	0.0049 (7)	−0.0003 (7)
C3	0.0448 (9)	0.0481 (9)	0.0527 (11)	−0.0080 (8)	0.0012 (7)	−0.0062 (8)
C4	0.0402 (9)	0.0367 (8)	0.0590 (11)	−0.0017 (6)	0.0148 (8)	−0.0036 (7)
C5	0.0546 (10)	0.0507 (9)	0.0457 (10)	−0.0048 (8)	0.0115 (8)	0.0037 (8)
C6	0.0469 (9)	0.0514 (10)	0.0446 (10)	−0.0094 (7)	0.0025 (7)	0.0003 (8)
C7	0.0436 (8)	0.0408 (8)	0.0383 (9)	−0.0014 (7)	0.0062 (7)	0.0019 (7)
C8	0.0380 (8)	0.0371 (8)	0.0400 (9)	0.0013 (6)	0.0050 (7)	−0.0007 (6)
C9	0.0445 (9)	0.0414 (8)	0.0398 (9)	0.0004 (7)	0.0036 (7)	0.0026 (7)
C10	0.0360 (8)	0.0390 (8)	0.0514 (10)	0.0006 (7)	0.0008 (7)	−0.0037 (7)
C11	0.0454 (10)	0.0472 (9)	0.0622 (12)	−0.0074 (7)	0.0141 (8)	0.0023 (8)
C12	0.0591 (11)	0.0559 (10)	0.0458 (10)	−0.0076 (9)	0.0138 (8)	0.0056 (8)
C13	0.0444 (9)	0.0474 (9)	0.0391 (9)	−0.0027 (7)	0.0060 (7)	−0.0019 (7)

Geometric parameters (Å, º)

O1—H1	0.8200	C7—N1	1.280 (2)
O2—H2	0.8200	C7—C8	1.451 (2)
C1—C2	1.387 (2)	C7—H7	0.9300
C1—C6	1.390 (2)	C8—C13	1.392 (2)
C1—N1	1.4229 (19)	C8—C9	1.401 (2)
C2—C3	1.380 (2)	C9—C10	1.370 (2)
C2—H2A	0.9300	C9—H9	0.9300
C3—C4	1.373 (3)	C10—C11	1.384 (2)
C3—H3	0.9300	C10—O2	1.3883 (19)
C4—C5	1.374 (2)	C11—C12	1.376 (3)
C4—Cl1	1.7365 (16)	C11—H11	0.9300
C5—C6	1.381 (2)	C12—C13	1.389 (2)

C5—H5	0.9300	C12—H12	0.9300
C6—H6	0.9300	C13—O1	1.3557 (19)
C13—O1—H1	109.5	N1—C7—C8	122.44 (14)
C10—O2—H2	109.5	N1—C7—H7	118.8
C7—N1—C1	120.41 (14)	C8—C7—H7	118.8
C2—C1—C6	118.42 (15)	C13—C8—C9	119.06 (15)
C2—C1—N1	117.03 (14)	C13—C8—C7	122.16 (14)
C6—C1—N1	124.55 (14)	C9—C8—C7	118.78 (14)
C3—C2—C1	121.29 (16)	C10—C9—C8	120.75 (15)
C3—C2—H2A	119.4	C10—C9—H9	119.6
C1—C2—H2A	119.4	C8—C9—H9	119.6
C4—C3—C2	119.16 (16)	C9—C10—C11	119.88 (15)
C4—C3—H3	120.4	C9—C10—O2	116.90 (15)
C2—C3—H3	120.4	C11—C10—O2	123.20 (15)
C3—C4—C5	120.78 (15)	C12—C11—C10	120.16 (16)
C3—C4—Cl1	120.53 (13)	C12—C11—H11	119.9
C5—C4—Cl1	118.69 (14)	C10—C11—H11	119.9
C4—C5—C6	119.93 (16)	C11—C12—C13	120.54 (16)
C4—C5—H5	120.0	C11—C12—H12	119.7
C6—C5—H5	120.0	C13—C12—H12	119.7
C5—C6—C1	120.39 (15)	O1—C13—C12	118.99 (15)
C5—C6—H6	119.8	O1—C13—C8	121.41 (14)
C1—C6—H6	119.8	C12—C13—C8	119.59 (15)
C8—C7—N1—C1	−179.65 (13)	N1—C7—C8—C9	178.06 (15)
C2—C1—N1—C7	−175.30 (14)	C13—C8—C9—C10	1.7 (2)
C6—C1—N1—C7	5.2 (2)	C7—C8—C9—C10	−179.12 (14)
C6—C1—C2—C3	−1.5 (2)	C8—C9—C10—C11	−0.7 (2)
N1—C1—C2—C3	178.92 (14)	C8—C9—C10—O2	177.31 (14)
C1—C2—C3—C4	0.7 (3)	C9—C10—C11—C12	−0.7 (3)
C2—C3—C4—C5	0.6 (3)	O2—C10—C11—C12	−178.57 (15)
C2—C3—C4—Cl1	−179.27 (12)	C10—C11—C12—C13	1.1 (3)
C3—C4—C5—C6	−1.1 (3)	C11—C12—C13—O1	179.57 (16)
Cl1—C4—C5—C6	178.81 (13)	C11—C12—C13—C8	−0.1 (3)
C4—C5—C6—C1	0.2 (3)	C9—C8—C13—O1	179.08 (14)
C2—C1—C6—C5	1.1 (2)	C7—C8—C13—O1	−0.1 (2)
N1—C1—C6—C5	−179.43 (15)	C9—C8—C13—C12	−1.3 (2)
N1—C7—C8—C13	−2.7 (2)	C7—C8—C13—C12	179.54 (15)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.90	2.6270 (18)	147
O2—H2···O2ⁱ	0.82	2.04	2.7631 (13)	147

Symmetry code: (i) −x, y−1/2, −z+1/2.