

Racemic 3,5-dichloro-2-[[*(1-phenylethyl)imino*]methyl]phenol

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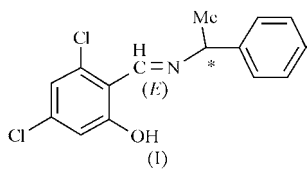
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The title compound, (*RS*)-3,5-dichloro-2-[[*(1-phenylethyl)imino*]methyl]phenol, C₁₅H₁₃Cl₂NO, was synthesized from racemic 1-phenylethylamine and 3,5-dichlorosalicylaldehyde. The π -conjugate system around the imine group is essentially planar in the phenol–imine tautomer. Intramolecular O \cdots N hydrogen-bond and intermolecular C–H \cdots π interactions are present in the crystal structure.

Comment

Schiff bases are used extensively as ligands in the field of coordination chemistry (Yamada, 1999). The complexes formed are interesting, for example in structural phase transitions (Akitsu & Einaga, 2004), as homogeneous catalysts (Akitsu *et al.*, 2004), and for their other chemical and physical properties. They have potential as sophisticated chiral building blocks in the synthesis of optical materials (Evans & Luneau, 2002), as well as in conventional stereochemistry (Sakiyama *et al.*, 1990). In order to clarify the relationship between structure and function in these organic ligands, which exhibit both tautomerism and photochromism (Hadjoudis *et al.*, 1987) in their metal complexes, an X-ray structure determination of the title compound, (I), has been carried out.



The molecule of (I) adopts an *E* configuration with respect to the imine C=N double bond, with a C6–C7–N1–C8 torsion angle of 176.2 (3) $^\circ$ (Fig. 1). Thus, the π -conjugate system around the imine group is essentially planar. This is a common feature in related compounds, such as 2-benzylamino-3-(2-hydroxybenzylidene)aminobenzofuran, which have stereochemically bulky groups (Bossio *et al.*, 1991). The maximum deviation from the least-squares mean plane of atoms O1/C1/C6/C7/N1, incorporating the bidentate chelate sites, is only 0.018 (4) Å for atom C7.

In general, Schiff base compounds exhibit tautomerism between keto–amine and phenol–imine tautomers by H-atom transfer, with the C–O bond being longer in the latter form. The C1–O1 bond distance in (I) is 1.347 (3) Å, and the C7=N1 and N1–C8 bond distances are 1.271 (5) and 1.478 (4) Å, respectively. The geometric parameters for (I) (Table 1) agree with the corresponding values for analogous Schiff base compounds containing the 1-phenylethylamine moiety, with the usual C=N and C–N bond distances being around 1.27 and 1.45 Å, respectively (Senn & Nowacki, 1977; Antonov *et al.*, 1995; Liu *et al.*, 1997). Compound (I) is therefore in the stable phenol–imine tautomeric form with insignificant changes in the intramolecular geometry, even in the presence of an electron-withdrawing Cl group.

As (I) crystallizes in a (racemic) centrosymmetric space group, there is no spontaneous resolution. The two six-membered aromatic rings, C1–C6 and C9–C14, form a dihedral angle of 76.11 (9) $^\circ$.

The molecular planarity of (I) is stabilized by an intramolecular N1 \cdots O1 hydrogen bond of 2.601 (3) Å (Table 2), with the parent N1 \cdots O1 distance being shorter than the sums of the relevant van der Waals radii (Bondi, 1964). The corresponding distances are in the range 2.58–2.62 Å for other *N*-salicylideneanilines (Inabe *et al.*, 1989, 1991, 1994). Unfor-

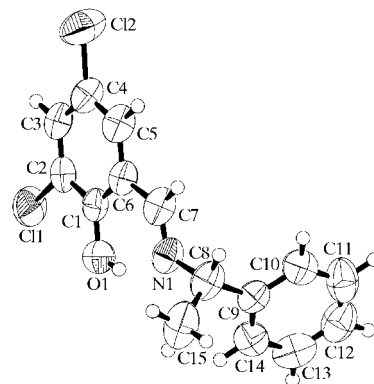


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

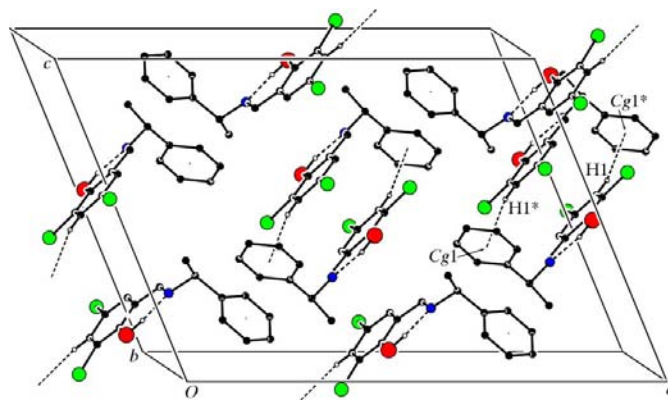


Figure 2

A molecular packing diagram for (I), showing the centrosymmetric dimers. Atoms marked with an asterisk (*) are at the symmetry position (2 - *x*, 2 - *y*, 1 - *z*).

tunately, we could not assign the hydroxyl H atom (H13) bonded to atom O1 directly from the difference Fourier map, so we located it at a reasonable position (O—H = 0.99 Å) and constrained it using a riding model.

The crystal packing of (I) (Fig. 2) involves a weak C—H... π intermolecular C3—H1...Cg1 interaction, yielding centrosymmetric dimers, with H1...Cg1 = 2.82 Å, C3...Cg1 = 3.752 (3) Å and C3—H1...Cg1 = 167° [Cg1 is the centroid of ring C9—C14 at (2 - x, 2 - y, 1 - z)].

We also observed photochromism of (I) in the solid state at 8 K. The imine band of the IR spectrum appeared initially at 1635 cm⁻¹. Irradiation with UV light resulted in a shift of this band to 1630 cm⁻¹, and the spectroscopic features were recovered after irradiation with visible light.

Experimental

Reaction of equimolar quantities of 1-phenylethylamine and 3,5-dichlorosalicylaldehyde in methanol at room temperature overnight gave rise to a brown compound, (I). Prismatic crystals were grown from the resulting solution over a period of several days. IR (KBr): 1635 cm⁻¹ (imine band).

Crystal data

C ₁₅ H ₁₃ Cl ₂ NO	$D_x = 1.357 \text{ Mg m}^{-3}$
$M_r = 294.16$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
$a = 21.395 (8) \text{ \AA}$	$\theta = 10.0\text{--}12.3^\circ$
$b = 9.463 (5) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$c = 15.571 (7) \text{ \AA}$	$T = 298 (1) \text{ K}$
$\beta = 113.99 (3)^\circ$	Prismatic, brown
$V = 2880 (2) \text{ \AA}^3$	$0.60 \times 0.50 \times 0.50 \text{ mm}$
$Z = 8$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.030$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -25 \rightarrow 27$
$T_{\text{min}} = 0.768, T_{\text{max}} = 0.802$	$k = 0 \rightarrow 12$
3867 measured reflections	$l = -20 \rightarrow 8$
3323 independent reflections	3 standard reflections
1468 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 0.5%

Table 1

Selected geometric parameters (Å, °).

Cl1—C2	1.714 (2)	N1—C7	1.271 (5)
Cl2—C4	1.726 (2)	N1—C8	1.478 (4)
O1—C1	1.347 (3)		
C7—N1—C8	117.8 (3)	N1—C7—C6	121.3 (3)
O1—C1—C6	121.6 (2)	N1—C8—C9	108.0 (3)
C5—C6—C7	118.1 (2)	N1—C8—C15	108.4 (3)
O1—C1—C6—C7	2.3 (4)	C7—N1—C8—C9	-111.1 (4)
N1—C7—C6—C1	1.3 (5)	C7—N1—C8—C15	123.6 (4)
C6—C7—N1—C8	176.2 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1—H13...N1	0.99	1.71	2.601 (3)	148

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 1.9396P]$
$R(F) = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.180$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
1468 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
149 parameters	
H-atom parameters constrained	

H atoms were placed in calculated positions, with C—H = N—H = 0.95 Å and O—H = 0.99 Å, and included in the final cycles of refinement using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. The C atoms of the phenyl groups (C1—C6 and C9—C14) were treated as rigid groups of anisotropic atoms.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1070). Services for accessing these data are described at the back of the journal.

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