

## 2-Chloro-(3-methoxysalicylidene)aniline

Savarimuthu Francis,  
Packianathan Thomas Muthiah,\*  
Galmari Venkatachalam and  
Rengan Ramesh

Department of Chemistry, Bharathidasan  
University, Tiruchirappalli 620 024, Tamil  
Nadu, India

Correspondence e-mail:  
tomtrichy@yahoo.co.in

## Key indicators

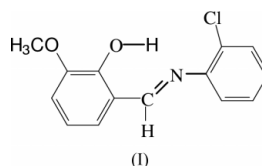
Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$   
R factor = 0.050  
wR factor = 0.144  
Data-to-parameter ratio = 7.5

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

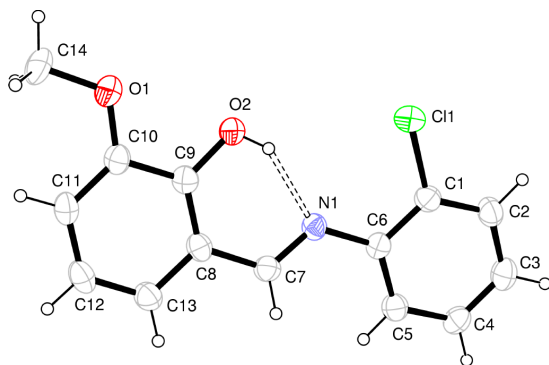
An almost planar conformation exhibited by the title molecule,  $\text{C}_{14}\text{H}_{12}\text{ClNO}_2$ , is stabilized by an intramolecular  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bond, which forms a ring of graph-set motif  $S(6)$ . In the crystal structure,  $\pi-\pi$  and  $\text{C}-\text{H}\cdots\pi$  interactions involving both the aromatic rings form two-dimensional networks.

## Comment

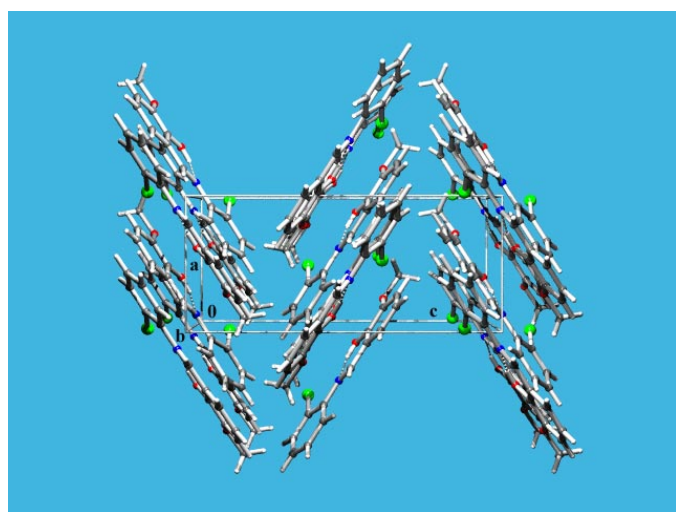
The title compound, (I), was obtained by condensing *o*-vanillin with *o*-chloroaniline. Vanillin occurs naturally in vanilla, in potato parings, in Siam benzoin *etc.* Vanillin is used as a flavoring agent in confectionery, beverages, foods *etc.* and as a reagent in analytical chemistry. Vanillin is of current interest due to its non-linear optical properties (Singh *et al.*, 1991). The crystal structures of vanillin-I (Velavan *et al.*, 1995), the polymorphic forms of isovanillin (Iwasaki, 1973), *o*-vanillin (Iwasaki *et al.*, 1976) and other vanillin derivatives (Usman *et al.*, 2002; Li *et al.*, 1999) have been reported. A study on the condensation of aniline and its derivatives with salicylaldehyde has been reported (Khera *et al.*, 1983). The Schiff base ligands of *o*-vanillin derivatives with aniline and *o*-, *m*- and *p*-toluidine have also been reported (Viswanathamurthy & Natarajan, 2000). In order to gain more structural information on these systems, compound (I) was investigated.



The title molecule (Fig. 1) is slightly distorted from a planar arrangement. The dihedral angle between the two aromatic rings is  $7.8 (2)^\circ$  and the torsion angle  $\text{C}6-\text{N}1-\text{C}7-\text{C}8$  is  $-179.1 (3)^\circ$ . The almost planar conformation exhibited by the molecule is stabilized by an intramolecular  $\text{O}2-\text{H}2\cdots\text{N}1$  hydrogen bond, which forms a ring of graph-set motif  $S(6)$ . The methoxy group is coplanar with the attached benzene ring. The bond distances observed in the molecule (Table 1) are comparable with those reported for related structures (Usman *et al.*, 2002; Sethuraman & Muthiah, 2002). In the crystal structure, the molecules translated by one unit along the *a* axis are arranged such that the two aromatic rings are stacked with a centroid-to-centroid distance of  $3.724 (3) \text{ \AA}$ , indicating weak  $\pi-\pi$  interactions. Adjacent symmetry-related stacks are linked by  $\text{C}-\text{H}\cdots\pi$  interactions (Desiraju, 2002), involving the two phenyl rings (Table 2), to form two-dimensional networks (Fig. 2).



**Figure 1**  
The structure of the title compound, showing 50% probability displacement ellipsoids and the intramolecular hydrogen bond.



**Figure 2**  
The molecular packing in the unit cell, viewed down the *b* axis.

## Experimental

Methanol solutions of *o*-vanillin (152 mg, Merck) and *o*-chloroaniline (127 mg, Merck) were mixed in 1:1 molar ratio and refluxed for 1 h, yielding the title compound. Recrystallization from methanol gave orange plate-like crystals suitable for X-ray study.

### Crystal data

$C_{14}H_{12}ClNO_2$   
 $M_r = 261.70$   
Orthorhombic,  $Pn2_1a$   
 $a = 6.409$  (1) Å  
 $b = 13.062$  (1) Å  
 $c = 14.842$  (1) Å  
 $V = 1242.5$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.399$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 4.5$ – $69.9^\circ$   
 $\mu = 2.67$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Plate, orange  
 $0.6 \times 0.6 \times 0.2$  mm

### Data collection

Enraf–Nonius CAD-4 four-circle diffractometer  
 $\omega$ – $2\theta$  scans  
Absorption correction: none  
1220 measured reflections  
1220 independent reflections  
1136 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 69.9^\circ$

$h = 0 \rightarrow 7$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 18$   
1 standard reflection every 100 reflections  
frequency: 60 min  
intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.144$   
 $S = 1.06$   
1220 reflections  
163 parameters  
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1185P)^2 + 0.0697P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.64$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.32$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|            |           |            |           |
|------------|-----------|------------|-----------|
| Cl1–C1     | 1.731 (4) | O2–C9      | 1.337 (5) |
| O1–C10     | 1.346 (6) | N1–C7      | 1.275 (5) |
| O1–C14     | 1.428 (6) | N1–C6      | 1.410 (4) |
| C10–O1–C14 | 116.9 (4) | N1–C7–C8   | 120.9 (4) |
| C6–N1–C7   | 122.4 (4) | O2–C9–C8   | 123.3 (4) |
| Cl1–C1–C2  | 118.8 (3) | O2–C9–C10  | 117.1 (3) |
| Cl1–C1–C6  | 118.7 (3) | O1–C10–C11 | 126.6 (4) |
| N1–C6–C1   | 118.0 (3) | O1–C10–C9  | 114.7 (4) |
| N1–C6–C5   | 124.7 (3) |            |           |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| <i>D</i> –H··· <i>A</i>     | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2–H2···N1                  | 0.82        | 1.86          | 2.585 (4)             | 146                     |
| C3–H3···Cg1 <sup>i</sup>    | 0.93        | 3.01          | 3.819 (5)             | 146                     |
| Cl1–H11···Cg2 <sup>ii</sup> | 0.93        | 2.85          | 3.656 (5)             | 145                     |

Symmetry codes: (i)  $\frac{1}{2} + x, y, -\frac{1}{2} - z$ ; (ii)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ . Cg1 and Cg2 are the centroids of rings C1–C6 and C8–C13, respectively.

H atoms were treated as riding atoms, with C–H distances in the range 0.93–0.96 Å and O–H distance of 0.82 Å, with isotropic displacement parameters of 1.2 (1.5 for O2 and methyl) times  $U_{eq}$  of the parent atom. As the intensities of Friedel opposites were not measured, the absolute configuration could not be established. Since the crystal belongs to a non-centrosymmetric space group and intensities for Friedel opposites were not measured, the r:p ratio (7.48) is poor. The ratio of  $T_{\max}/T_{\min}$  expected is 2.2, but we were unable to apply an absorption correction as the  $\psi$  scan data were not collected.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1997); software used to prepare material for publication: *PLATON*.

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