

Acta Crystallographica Section C

Crystal Structure  
Communications

ISSN 0108-2701

Bis[4-(salicylideneamino)phenyl]-  
methaneHenrik Birkedal<sup>a,\*</sup> and Philip Pattison<sup>a,b</sup><sup>a</sup>Laboratory of Crystallography, École Polytechnique Fédérale de Lausanne, BSP Dorigny, CH-1015 Lausanne, Switzerland, and <sup>b</sup>Swiss–Norwegian Beam Line, ESRF, BP 220, F-38043 Grenoble Cedex, France  
Correspondence e-mail: [hbirkedal@chem.au.dk](mailto:hbirkedal@chem.au.dk)

Received 4 January 2006

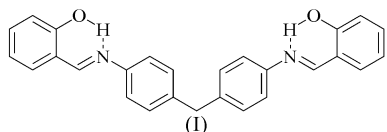
Accepted 26 January 2006

Online 21 February 2006

The crystal structure of the title Schiff base {systematic name: 2,2′-[methylenedi-*p*-phenylenebis(nitrilomethylidene)]-diphenol}, C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>, consists of intramolecularly hydrogen-bonded molecules interlinked by C–H···O hydrogen bonds [C···O = 3.426 (2) Å and C–H···O = 152.7 (17)°]. The molecule is in the enol form and is located on a twofold axis. The central methane C atom of the diphenylmethane motif is displaced from the aromatic ring planes. This effect is compared with previous results, which display an inverse correlation between the out-of-plane displacement and the C–C–C angle around the central methane C atom. In the title compound, the displacement is 0.124 (2) Å and the C–C–C angle is 110.18 (19)°.

## Comment

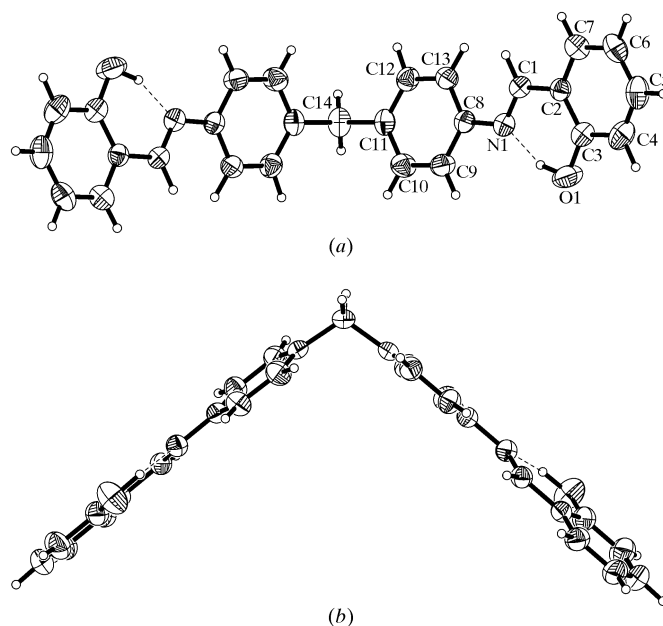
Bis-bidentate Schiff base ligands have attracted significant interest as building blocks in metallo-supramolecular chemistry, especially in the synthesis of helicates (see, for example, Kruger *et al.*, 2001; Yoshida & Ichikawa, 1997; Yoshida *et al.*, 2000; Franceschi *et al.*, 2001; Albrecht, 2001). The title compound, (I), has been shown to form helicate supramolecular complexes of the form [M<sub>2</sub>L<sub>2</sub>] with transition metals (Yoshida & Ichikawa, 1997; Yoshida *et al.*, 2000; Kruger *et al.*, 2001). Free *N*-salicylideneanilines are often thermochromic (Ogawa *et al.*, 1998; Filarowski *et al.*, 2002; Popović *et al.*, 2002; Ogawa & Harada, 2003) due to a temperature-dependent equilibrium between the keto–amine and enol–imino forms.



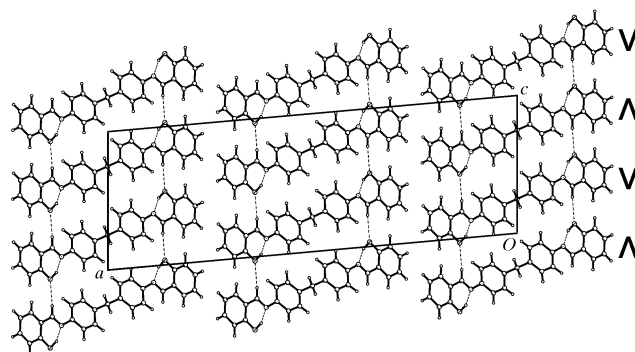
The location of the H atoms showed unequivocally that (I) occurs in the enol–imino form in the crystalline state, in agreement with previous IR results (Kruger *et al.*, 2001; Pui *et*

\* Present address: Department of Chemistry, University of Aarhus, 140 Langelandsgade, DK-8000 Århus C, Denmark.

*et al.*, 2001). This is also the form found in CHCl<sub>3</sub> solution (Yoshida *et al.*, 2000; Kruger *et al.*, 2001). The factors determining whether a given molecule will occur in the keto–amine or enol–imino form are manifold. It has been shown to depend on the substitution on the benzene rings (Filarowski *et al.*, 2002; Popović *et al.*, 2002) and intermolecular hydrogen bonding (Ogawa *et al.*, 1998; Ogawa & Harada, 2003), and aggregation (packing) of the molecules plays an important role for the equilibrium in solution (Ogawa *et al.*, 2001; Ogawa & Harada, 2003). It has been reported that (I) undergoes a



**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. Dashed lines indicate the intramolecular O–H···N hydrogen bonds. (a) A projection of (I) on to the mean plane. The molecule is situated on a twofold axis (through atom C14); unlabelled atoms are related to labelled atoms by the symmetry operator  $(1 - x, y, -z + \frac{1}{2})$ . (b) A view of (I) perpendicular to the least-squares plane of the C8–C13 aromatic ring. Note the twist of the molecule at the N atom.

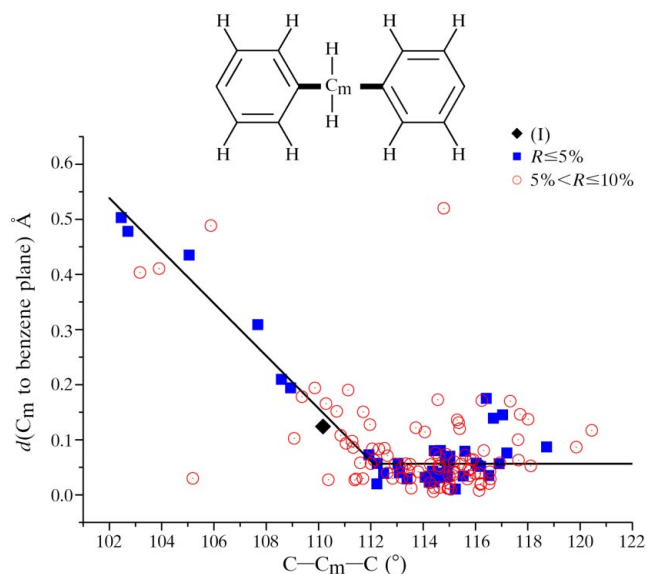


**Figure 2** A packing diagram for (I), in projection along (010). The 'V' symbols on the right-hand side indicate the orientation of the molecular shapes in the columns along (010) (*i.e.* perpendicular to the plane of view). Dashed lines indicate intra- and intermolecular hydrogen bonds.

colour change from yellow to red at 373 K (Zhu *et al.*, 2001), but it is unclear whether this colour change is related to the keto–enol tautomerism.

The molecules of (I) are V-shaped, with atom C14 coinciding with a crystallographic twofold axis. The angle between the two symmetry-related C8–C13 benzene rings is 78.87 (5)°. The C2–C7 phenol ring (ring 1) is not coplanar with the C8–C13 benzene ring (ring 2), the interplanar angle being 12.99 (7)° (Fig. 1*b* and Table 1). The imino plane is almost coplanar with ring 1 [interplanar angle = 1.66 (11)°]. It is, however, twisted significantly out of the plane of ring 2; the C1–N1–C8–C9 torsion angle differs significantly from 180° (Table 1) and the interplanar angle is 14.86 (13)°. This lack of coplanarity is presumably caused by steric hindrance between the H atoms on atoms C1 and C13. Indeed, the H1A···H13 distance [2.07 (3) Å] is significantly shorter than the sum of the van der Waals radii (2.40 Å; Gilli, 1992).

Surprisingly, atom C14 is significantly out of the mean plane of ring 2 [0.124 (2) Å]. In order to determine whether this phenomenon is particular to the structure of (I) or reflects a general effect, we examined the Cambridge Structural Database (CSD, Version 5.27 of November 2005, 355064 entries; Allen, 2002). Fig. 3 shows the search fragment, diphenylmethane, together with the relation between the average distance of the methane C atom ( $C_m$ ) to the planes of the benzene rings and the methane C– $C_m$ –C bond angle. Below a given onset angle, there is an inverse linear correlation between the angle and displacement of the  $C_m$  atom out of the aromatic plane. The data with  $R < 0.05$  (38 structures, 44 angles) were fitted to the relation  $d = d_0 + \alpha(a - a_c)$  for  $a < a_c$ ,



**Figure 3**

The relation between the C– $C_m$ –C bond angle around the methylene group in diphenylmethane and the average distance between the methane  $C_m$  atom and the aromatic ring planes, as extracted from the CSD. The search fragment is shown at the top, with the C– $C_m$ –C bond angle marked in bold. Closed solid squares represent CSD data with  $0.05 < R < 0.10$  and open circles are data with  $R < 0.05$ . The black diamond represents (I).

and  $d = d_0$  otherwise. The fit, with  $R^2 = 0.919$ , resulted in  $a_c = 112.1$  (4)°,  $d_0 = 0.057$  (6) Å and  $\alpha = -0.048$  (3) Å/degree. The value found in (I) (black diamond in Fig. 3) is in excellent agreement with the overall correlation. Structures of lesser quality, *viz.*  $0.05 < R < 0.10$  (61 structures, 93 angles), show a larger spread than the lower  $R$  factor data set but the trends are similar. The displacement is towards the interior of the V shape formed by the two aromatic rings. This effect is likely to be related to  $\pi$ – $\pi$  interactions between the two benzene rings. However, in (I) and several, but not all, of the CSD structures with significant out-of-plane displacements, the two benzene rings are not coplanar. This suggests that a more complicated mechanism may be responsible for the observed behaviour.

The V-shaped molecules pack into chevron-like columns that extend along (010) (Fig. 2) *via* van der Waals contacts. These columns are connected to their inverted neighbouring stacks along the  $c$  axis by C–H···O hydrogen bonds between the enol O atom and the H atom on atom C1.

## Experimental

A sample of (I), synthesized by Franceschi & Floriani (2000), was kindly provided by Dr F. Franceschi of the Department of Chemistry of the École Polytechnique Fédérale de Lausanne, Switzerland. A plate-shaped yellow crystal with well developed faces was selected and mounted on a glass needle. The structure of (I) was determined using synchrotron radiation data collected at the Swiss–Norwegian Beam Line at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

### Crystal data

$C_{27}H_{22}N_2O_2$	Synchrotron radiation
$M_r = 406.47$	$\lambda = 0.80000$ Å
Monoclinic, $C2/c$	Cell parameters from 1586 reflections
$a = 36.496$ (7) Å	$\theta = 4.3$ – $28.5^\circ$
$b = 4.6030$ (9) Å	$\mu = 0.08$ mm <sup>−1</sup>
$c = 12.231$ (2) Å	$T = 293$ (2) K
$\beta = 95.06$ (3)°	Platelet, yellow
$V = 2046.7$ (7) Å <sup>3</sup>	$0.40 \times 0.15 \times 0.05$ mm
$Z = 4$	
$D_x = 1.319$ Mg m <sup>−3</sup>	

### Data collection

MAR345 diffractometer	$\theta_{\max} = 29.9^\circ$
$\varphi$ scans	$h = -44 \rightarrow 45$
5072 measured reflections	$k = -5 \rightarrow 5$
1954 independent reflections	$l = -15 \rightarrow 15$
1820 reflections with $I > 2\sigma(I)$	
$R_{\text{int}} = 0.022$	

**Table 1**

Selected geometric parameters (Å, °).

O1–C3	1.344 (3)	C1–C2	1.450 (2)
N1–C1	1.280 (2)	C2–C3	1.410 (3)
N1–C8	1.418 (2)		
C11–C14–C11 <sup>1</sup>	110.17 (19)		
C9–C8–N1–C1	−165.97 (17)	O1–C3–C2–C1	−0.2 (3)
C1–N1–C8–C9	−165.97 (17)	C10–C11–C14–C11 <sup>1</sup>	82.96 (16)
C2–C1–N1–C8	179.92 (15)		

Symmetry code: (i)  $-x + 1, y, -z + \frac{3}{2}$ .

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.168$   
 $S = 1.12$   
 1954 reflections  
 174 parameters  
 Only H-atom coordinates refined

$$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 1.25P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ N1	1.02 (3)	1.63 (3)	2.595 (2)	155 (3)
C1—H1A $\cdots$ O1 <sup>ii</sup>	0.97 (2)	2.53 (2)	3.426 (2)	152.7 (17)

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

All H atoms were clearly visible in the final difference electron-density map. They were initially included using a riding model. Subsequent refinement including the H-atom positions led to significant reduction in residuals. Thus, the positions of all H atoms were refined freely in the final model [ $C-H = 0.94$  (3)– $1.00$  (2)  $\text{\AA}$ ]. The atomic displacement parameters of the H atoms were constrained according to  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *MAR345 Software* (Marresearch, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2000); data reduction: *CrysAlis RED* and *XPREP* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1996); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Federico Franceschi for the kind gift of the sample of the title compound and for helpful discussions. We thank the staff of the Swiss–Norwegian Beam Line for their support during the measurements. The Swiss–Norwegian Beam Line is funded by the Swiss National Science Foundation and the Norwegian Research Council. HB is a

Steno Research Assistant Professor funded by the Danish Natural Science Research Council and the Danish Research Council for Production and Technology Sciences and gratefully acknowledges this support. HB also thanks the Danish Research Training Council for additional financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1307). Services for accessing these data are described at the back of the journal.

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