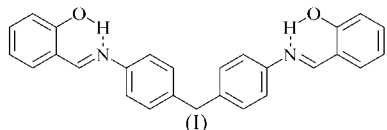


Bis[4-(salicylideneamino)phenyl]-
methaneHenrik Birkedal^{a,*} and Philip Pattison^{a,b}^aLaboratory of Crystallography, École Polytechnique Fédérale de Lausanne, BSP Dorigny, CH-1015 Lausanne, Switzerland, and ^bSwiss–Norwegian Beam Line, ESRF, BP 220, F-38043 Grenoble Cedex, France
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The crystal structure of the title Schiff base [systematic name: 2,2′-[methylenedi-*p*-phenylenebis(nitrilomethylidene)]-diphenol], C₂₇H₂₂N₂O₂, 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 [M₂L₂] 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*

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et al., 2001). This is also the form found in CHCl₃ 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

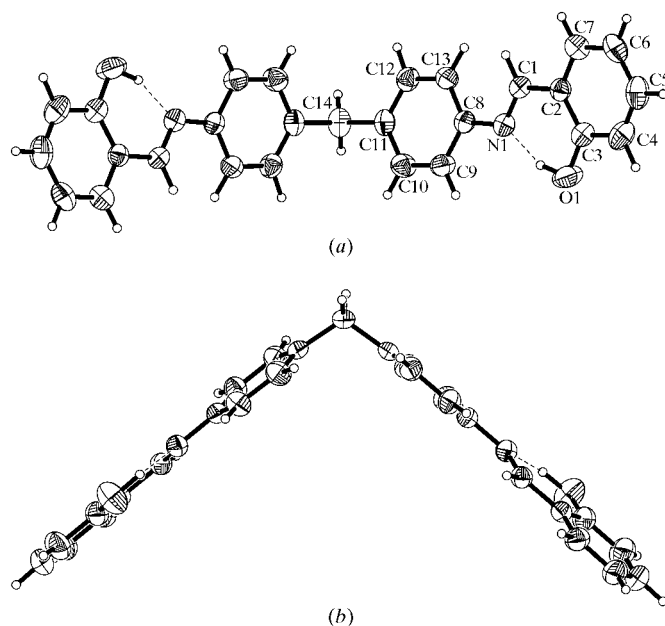


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the intramolecular O–H···N hydrogen bonds. (a) A projection of (I) on to the mean 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.

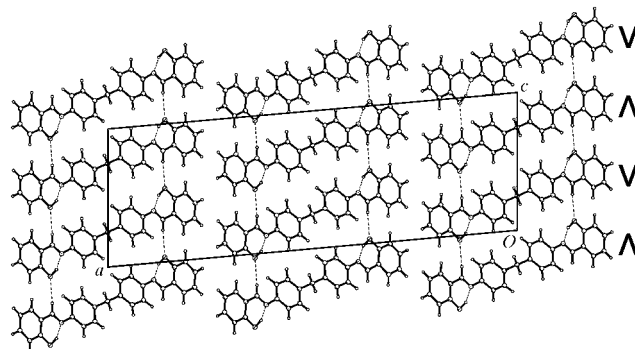


Figure 2
A packing diagram for (I), in projection along (010). The 'V' symbols on the right-hand side indicate the orientation of the molecular shapes in the columns along (010) (*i.e.* perpendicular to the plane of view). Dashed lines indicate intra- and intermolecular hydrogen bonds.

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 $a < a_c$,

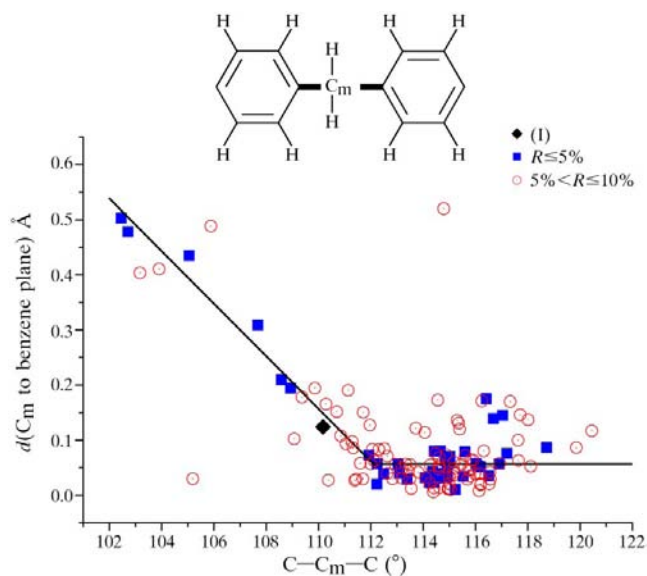


Figure 3

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 π – π 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°
$b = 4.6030$ (9) Å	$\mu = 0.08$ mm ^{−1}
$c = 12.231$ (2) Å	$T = 293$ (2) K
$\beta = 95.06$ (3)°	Platelet, yellow
$V = 2046.7$ (7) Å ³	$0.40 \times 0.15 \times 0.05$ mm
$Z = 4$	
$D_x = 1.319$ Mg m ^{−3}	

Data collection

MAR345 diffractometer	$\theta_{\max} = 29.9^\circ$
φ 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 ¹	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 ¹	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 (\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 ⁱⁱ	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) \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*.

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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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