

| | |
|---------------------|-------------|
| C22D—C23D—N2D—C19D | 56.97 (18) |
| N2D—C24D—C25D—C26D | 128.03 (15) |
| C24D—C25D—C26D—C27D | 116.0 (2) |

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N,N'-Bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine

Table 2. Hydrogen-bonding geometry (Å, °)

| D—H...A | H...A | D...A | D—H...A |
|--------------------------------|----------|-----------|---------|
| O3A—H43A...O2A | 2.37 | 2.736 (2) | 107 |
| O3D—H43D...O2D | 2.27 | 2.728 (2) | 115 |
| O4D—H44D...O6D | 2.40 | 2.698 (2) | 102 |
| O1A—H41A...O61 ⁱ | 1.74 | 2.564 (2) | 165 |
| O3A—H43A...O5A ⁱⁱ | 2.07 | 2.861 (2) | 158 |
| O4A—H44A...O4D ⁱ | 1.92 | 2.747 (2) | 166 |
| O1D—H41D...O6A | 1.66 | 2.488 (2) | 167 |
| O18A—H48A...O3A ⁱⁱⁱ | 2.12 | 2.872 (2) | 149 |
| O18A—H48A...O4A ⁱⁱⁱ | 2.49 | 3.165 (2) | 138 |
| N2A—H52A...O4A | 2.38 | 2.997 (2) | 126 |
| N2A—H52A...O5A | 1.95 | 2.817 (2) | 160 |
| N2D—H52D...O6D | 1.80 | 2.740 (2) | 162 |
| O18D—H48D...O5D ⁱ | 1.83 | 2.657 (2) | 171 |
| O61—H61A...O5D ⁱⁱ | 1.93 (3) | 2.720 (2) | 156 (3) |
| O61—H61B...O6D | 1.86 (3) | 2.725 (2) | 166 (3) |

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $x, 1 + y, z$; (iii) $x, y - 1, z$.

The data reduction was performed with the *DREDD* programs (Blessing, 1989). Direct methods failed to provide a solution and Patterson search methods (*PATSEE*; Egert & Sheldrick, 1985) were employed instead. Cinchonidine without substituents was used as a search model and gave the positions of the cations. The refinement of the structure was performed with *SHELXL93* (Sheldrick, 1993) and in the final stages with *SHELXL97* (Sheldrick, 1997). The H atoms, shown clearly in the difference electron-density map, were fixed in idealized positions, each with an isotropic displacement parameter of $1.5U_{eq}$ of the attached atom.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1012). Services for accessing these data are described at the back of the journal.

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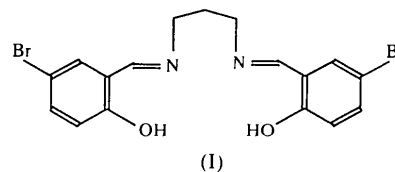
Abstract

The title compound {alternative name for this Schiff base: 4,4'-dibromo-2,2'-[propanediylbis(nitrilomethylidene)]diphenol; C₁₇H₁₆Br₂N₂O₂} displays two strong intramolecular N...H—O hydrogen bonds within each salicylideneimine unit. The molecule is not planar and the two aromatic rings are inclined at an angle of 69.8 (1)°.

Comment

Schiff bases and their biologically active complexes have been studied extensively over the past decade. Although numerous transition metal complexes of Schiff bases have been structurally characterized, relatively few free Schiff bases have been similarly characterized (Garnovskii *et al.*, 1993). *N*-Salicylideneaniline and its derivatives show photochromism and thermochromism in the solid state (Cohen *et al.*, 1964). These effects are produced by intramolecular proton transfer associated with a change in the π -electron configuration (Hadjoudis *et al.*, 1987).

In the course of a structural investigation of Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997, 1998; Elmali *et al.*, 1995; Elmali & Elerman, 1997, 1998; Elmali, Elerman & Zeyrek, 1998), the structure of the tetradentate Schiff base ligand, (I), was determined.



Several non-planar tetradentate Schiff bases similar to (I) have been reported (Pahor *et al.*, 1976, 1978; Subrahmanyam *et al.*, 1982; Cimerman *et al.*, 1992; Senn & Nowacki, 1977; Elerman *et al.*, 1991, 1994; Corden *et al.*, 1996). The title molecule is also not planar. The

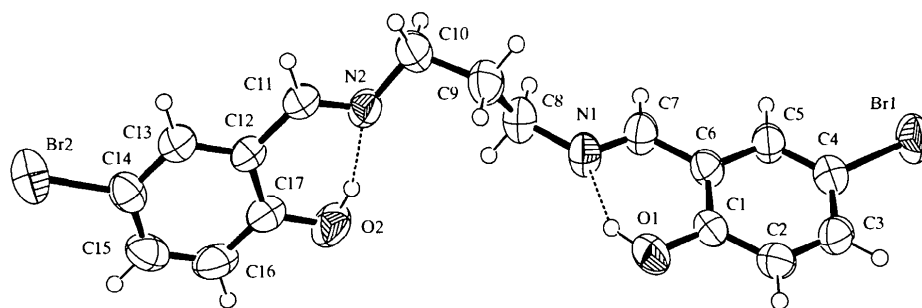


Fig. 1. The molecular structure and atomic labelling scheme of the title compound. Displacement ellipsoids are plotted at the 50% probability level (ORTEP; Johnson, 1976).

least-squares planes through the two aromatic rings are inclined at an angle of 69.8 (1)°. The values of the torsion angles C11—N2—C10—C9 [139.8 (4)°] and C7—N1—C8—C9 [−115.7 (5)°] also indicate that the molecule is not planar. The conformation of the free ligand in the solid state is of particular interest in relation to that required in a metal complex (Corden *et al.*, 1996). Clearly, this conformation is not suitable for direct coordination to a metal ion.

Intramolecular hydrogen bonds occur between O1 and N1 [N1···H1O 1.69 (6), N1···O1 2.537 (5) Å and N1···H1O—O1 146 (5)°], and between O2 and N2 [N2···H2O 1.77 (6), N2···O2 2.584 (5) Å and N2···H2O—O2 158 (6)°]. Two types of intramolecular hydrogen bond (either N—H···O or N···H—O) can exist in Schiff bases (Garnovskii *et al.*, 1993). The Schiff bases derived from salicylaldehyde always form the N···H—O type of hydrogen bonding, regardless of the nature of the N-substituent (alkyl or aryl) (Gavranic *et al.*, 1996). Clearly, the enolimine tautomer is favoured over the ketamine form. This is evident from the observed O1—C1 and O2—C17 bond distances of 1.342 (5) and 1.341 (5) Å, respectively, which are consistent with O—C single bonds; similarly the N1—C7 and N2—C11 distances of 1.265 (5) and 1.273 (5) Å, respectively, are consistent with N=C double bonding.

Experimental

A solution of 5-bromosalicylaldehyde (0.002 mol, 0.402 g) in pure ethanol (50 ml) was prepared and to it was added a solution of 1,3-diaminopropane (0.001 mol, 0.074 g) in pure ethanol (10 ml). A mixture of the two solutions was then refluxed for 3 h. Crystals of (I) formed during the reflux operation and were washed twice with ethanol.

Crystal data

C₁₇H₁₆Br₂N₂O₂
M_r = 440.14

Mo K α radiation
 λ = 0.71069 Å

Monoclinic
P2₁/n
a = 11.438 (2) Å
b = 8.902 (1) Å
c = 17.189 (3) Å
 β = 96.35 (1)°
V = 1739.5 (5) Å³
Z = 4
D_x = 1.681 Mg m^{−3}
D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\theta/2\theta$ scans
Absorption correction:
 ψ scan (North *et al.*,
1968)
T_{min} = 0.272, T_{max} = 0.627
6580 measured reflections
3405 independent reflections

Refinement

Refinement on F²
R[F² > 2 σ (F²)] = 0.037
wR(F²) = 0.097
S = 0.980
3403 reflections
214 parameters
H atoms not refined
w = 1/[\sigma²(F_o²) + (0.0364P)²
+ 0.324P]
where P = (F_o² + 2F_c²)/3

Cell parameters from 25
reflections
 θ = 3.41–12.30°
 μ = 4.670 mm^{−1}
T = 300 (2) K
Prism
0.25 × 0.15 × 0.10 mm
Yellow

1674 reflections with
I > 2 σ (I)
R_{int} = 0.079
 θ_{max} = 25.98°
h = −14 → 11
k = −10 → 0
l = −21 → 21
3 standard reflections
frequency: 120 min
intensity decay: 2.7%

(Δ/σ)_{max} = 0.006
 $\Delta\rho_{max}$ = 0.444 e Å^{−3}
 $\Delta\rho_{min}$ = −0.467 e Å^{−3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|-----------|-----------|-------------|-----------|
| O1—C1 | 1.342 (5) | C10—N2 | 1.460 (5) |
| C4—Br1 | 1.897 (4) | N2—C11 | 1.273 (5) |
| C7—N1 | 1.265 (5) | C14—Br2 | 1.892 (4) |
| N1—C8 | 1.461 (5) | C17—O2 | 1.341 (5) |
| O1—C1—C2 | 119.3 (4) | N2—C10—C9 | 111.3 (4) |
| O1—C1—C6 | 121.0 (4) | C11—N2—C10 | 118.1 (3) |
| C5—C4—Br1 | 120.7 (3) | N2—C11—C12 | 122.5 (4) |
| C3—C4—Br1 | 119.0 (3) | C13—C14—Br2 | 119.8 (3) |
| N1—C7—C6 | 121.2 (4) | C15—C14—Br2 | 120.2 (3) |
| C7—N1—C8 | 120.2 (4) | O2—C17—C16 | 119.8 (4) |
| N1—C8—C9 | 109.9 (4) | O2—C17—C12 | 121.2 (4) |

Diffraction intensities from the crystals were generally weak and only 49% of the reflections were observed with $I > 2\sigma(I)$, as evidenced by the high R_{int} value. All H-atom positions (except for H1O and H2O) were calculated using a riding model and were considered with fixed isotropic displacement parameters in all refinements. The H1O and H2O atoms were found in the difference Fourier maps calculated at the end of the refinement process as small positive electron densities and were not refined.

Data collection: *Nonius Diffractometer Control Software* (Nonius, 1993). Cell refinement: *Nonius Diffractometer Control Software*. Data reduction: *REDU4* (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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2,4-Cl₂-6,9-*exo,endo*-(PMe₂Ph)₂-*arachno*-B₁₀H₁₀

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Abstract

The title compound, 2,4-dichloro-6-*exo*-9-*endo*-bis(dimethylphenylphosphino)-*arachno*-decaborane(10) [(PMe₂Ph)₂B₁₀H₁₀Cl₂ or C₁₆H₃₂B₁₀Cl₂P₂], has a typical *arachno* ten-vertex cluster geometry, with one of the phosphine ligands bound *exo*-polyhedrally and the other in an uncommon *endo* configuration.

Comment

Ten years ago, Fontaine & Kennedy (1987) reported the identification by NMR spectroscopy of the previously unknown *exo,endo*-isomer, (I), of [6,9-(PMe₂Ph)₂-*arachno*-B₁₀H₁₂], formed concomitantly with the corresponding conventional *exo,exo*-isomer, (II). We have recently (Dörfler *et al.*, 1997) confirmed the structures of (I) and (II) by single-crystal X-ray diffraction studies, and also confirmed the structure of (III), the 2-bromo-substituted analogue of (I). These structural studies suggested some differential perturbation of the cluster that arises from the presence of an *endo*-P versus *exo*-P substituent. However, in (III), there are some deviations in structure that may be due to the presence of the single boron-bound halogen and this substituent might equally contribute to apparent *exo* versus *endo* perturbation. To examine further for patterns of structure flexing which might be attributable to *exo/endo* substitution, and for any effect of a halogen substituent upon this, we have determined the structure of the symmetrically dichloro-substituted title compound, (IV).