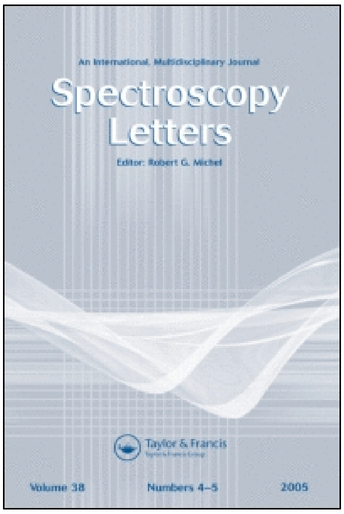

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THE CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF N,N′-*BIS*(5-BROMO-2-HYDROXY-BENZYLIDENE)ETHYLENEDIAMINE

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ABSTRACT

The Schiff base ligand, [$C_{16}H_{14}N_2O_2Br_2$], has been synthesized and its crystal structure has been investigated by X-ray analysis and PM3 method. The compound crystallizes in monoclinic space group $P2_1/a$ with $a = 6.119(4)$, $b = 7.179(8)$, $c = 18.124(8)$ Å, $\beta = 93.56(4)°$, $V = 794.6(1)$ Å^{-3}, $Z = 2$ and $D_{calc} = 1.781$ Mg m^{-3}. In the crystal structure of the free Schiff base ligand, the existence of a strong intramolecular O-H···N hydrogen bonding [O1-H1 0.82(9), H1···N1 1.834(8), O1···N1 2.613(8) Å, O1-H1···N1 157.3(7)°] is observed. The C=N imine bond and C-N-C bond angle are 1.259(8) Å and 119.1(5)°, respectively. The energy profile of the compound was calculated by PM3 method as a function of q[N1′-C8′-C8-N1].

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Key Words: N,N′-*bis*(5-Bromo-2-hydroxybenzylidene)ethylenediamine; Imine; X-ray structure; Conformation

INTRODUCTION

Schiff bases and their biologically active complexes have been studied during the last decade. Schiff bases have often been used as chelating ligands in the field of coordination chemistry[1] for obtaining thermotropic liquid crystalline polymers[2,3] and their metal complexes have been used as radiopharmaceuticals for cancer targeting[4], as dioxygen carriers[5] and as model systems for biological macromolecules[6,7]. Although a series of Schiff base complexes have been investigated crystallographically, there are only a very limited number of reports about the free Schiff bases in the literature[8–13]. Aldimine Schiff base ligands may have two types of intramolecular hydrogen bonds (N-H $\cdots$O or N $\cdots$H-O). In aldimine Schiff base ligands prepared from 2-hydroxy-1-napthaldehyde, both types of hydrogen bonds are found[11–17]. 2-Hydroxy Schiff base ligands are of interest mainly due to the existence of (O-H$\cdots$N and O$\cdots$H-N) type hydrogen bonds and tautomerism between the phenol-imine and keto-amine forms[8,18–19]. In these types of ligands, short hydrogen bonds are observed between 2-hydroxy group and the imine nitrogen atom. The hydrogen from the phenol group is completely transferred to the imine nitrogen in some instances[9,20]. Hydrogen bonding depends neither on the stereochemistry of the molecule nor on the sort of the substituent on the imine atom, but on the kind of aldehyde used[20].

The tautomerism in the Schiff base ligands plays an important role in distinguishing their photochromic[21–24] and thermochromic[25,26] characteristics. Structural and conformational analyses of free Schiff bases are important in view of intramolecular hydrogen bonding. For this reason, the synthesis, structural and conformational studies of the title compound were undertaken in comparison with the structures of the reported free Schiff base ligands.

EXPERIMENTAL

Reagents and Techniques

5-Bromo-2-hydroxybenzaldehyde (BDH), ethylenediamine (Aldrich), methanol and ethanol (Carlo Erba) were used in this study. Infrared spectrum was recorded using a SHIMADZU FTIR-8101 spectrophotometer as KBr discs, in the range of 400–4000 cm^{-1}. UV-visible spectrum was measured using a UNICAM UV/VIS spectrophotometer in CH_3OH solvent, in the range of 190–600 nm. Melting point was measured on the Gallencamp apparatus using a capillary tube.

Synthesis of N,N′-*bis*(5-Bromo-2-hydroxybenzylidene)ethylenediamine

5-Bromo-2-hydroxybenzaldeyde (1 g, 4.97 mmol) was dissolved in ethanol (50 mL). Ethylenediamine (0.16 mL, 2.48 mmol) in ethanol was then added and the solution was stirred at room temperature for 3 h. The yellow precipitate was filtered and crystallized in methanol, 0.87 g (83%) yield, m.p. 193°C. IR (KBr, cm^{-1}); 2800–2900 ($\surd_{\text{C-H}}$ aliphatic), 3080 ($\surd_{\text{C-H}}$ aromatic), 3400–3500 ($\surd_{\text{O-H}}$), 1275 ($\surd_{\text{C-O}}$). 1634 ($\surd_{\text{C=N}}$). λ_{max}($CHCl_3$, nm); 330, 415.

Crystallography

The experimental data, methods and procedures used to elucidate the structure and other related parameters are given in Table 1. The structure was solved by direct methods, SHELXS86[27].The difference synthesis clarified the positions of H atoms. The structure was refined by SHELXL97[28] and the figures were drawn by ORTEP[29].

Method of Calculation

Semiempirical calculations were performed at the restricted Hartree-Fock level (RHF) using PM3[30] method in the MOPAC 7.0 package[31]. All calculations were carried out with the complete geometry optimization at precise level, and the conformers located at minima were characterized by the vibrational frequencies.

IR Spectroscopy

In the IR spectrum of the title compound, the broadening and shifting to lower frequency of O-H at 3400–3500 cm^{-1} shows the hydrogen bond formation. The sharp peak at 1634 cm^{-1} is assigned to $\surd_{\text{C=N}}$. The phenolic $\surd_{\text{C-O}}$ is observed at 1275 cm^{-1}, which is the evidence for the existence of the phenol-imine form in the solid state, in agreement with the reported values in the literature[13].

Table 1. Experimental Data and Structure-Refinement Parameters

Compound	$C_{16}H_{14}N_2O_2Br_2$
Colour/shape	Yellow/plate
Formula weight	426.11
Space group	$P2_1/a$
Temperature (K)	294
Cell constants	$a = 6.119(4)$, $b = 7.179(8)$ $c = 18.124(8)$ Å, $\beta = 93.56(4)°$
Cell volume (Å^3)	794.6(1)
Formula units/unit cell	2
D_{calc} (Mg m^{-3})	1.781
μ_{calc} (mm^{-1})	0.654
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
Radiation used, graphite monochromator	Cu K_α ($\lambda = 1.54184$ Å)
Maximum crystal dimension(mm)	$0.20 \times 0.25 \times 0.30$
Standard reflection	3
Decay of standard	$< 1\%$
Reflections measured	1915
θ (max) (°)	61.24
Range of h, k, l	$0 \leq h \leq 6$, $0 \leq k \leq 8$, $-20 \leq l \leq 20$
Number of reflections	904 with $I > 2.0\sigma(I)$
Corrections applied	Lorentz-polarization
Computer programs	SHELXS86[27], SHELXL97[28], ORTEP[29], MolEN[32]
Source of atomic scattering factors	Int. Table for X-ray Cryst. Vol. IV, 1974 [33]
Structure solution	Direct methods
Treatment of hydrogen atoms	Hydrogen atoms were obtained from difference map and refined isotropically
No. of parameters var.	120
Weight	$w = 1/[\sigma^2(F_O^2) + (0.1520P)^2 + 0.3953P]$ where $P = (F_O^2 + 2F_C^2)/3$
GOF	0.951
R	0.0656
R_w	0.1823
$(\Delta/\sigma)_{max}$ (e Å^{-3})	1.103
$(\Delta/\sigma)_{min}$ (e Å^{-3})	−0.658

Crystal Study

Single crystal X-ray structure of the title compound is reported to further corroborate the structure assignments. The final coordinates and the equivalent isotropic displacement parameters are given in Table 2. The molecular structure with the atom-numbering scheme is shown in Figure 1. The molecular packing is shown in Figure 2. The packing of the molecules in the unit cell is purely due to van der Waals force of interaction. The molecule is in the staggered conformation and directed in parallel to the c-axis of the unit cell. The bond lengths and angles with some selected torsion angles are given in Table 3. The asymmetric unit contains only one half molecule. The strong intramolecular O-H···N hydrogen bonding [O1-H1 0.82(9), H1···N1 1.834(8), O1···N1 2.613(8) Å, O1-H1···N1 157.3(7)°] shows that the title compound is in the phenol-imine form. The existence of intramolecular hydrogen bonding of O-H···N type is predicted by IR but unequivocally is established crystallographically. However, in naphthaldimine derivatives, only keto-amine form is dominant as in [N-n-propyl-2-oxo-1-naphthylidenemethylamine] [N···O 2.578(2), N-H 0.775, H···O 1.936 Å] and [N-(α-naphthyl)-2-oxo-1-naphthaldimine] [N···O 2.536, N-H 0.851][9,20]. C5-O1 bond length is 1.320(7) Å. The corresponding bond lengths in [$C_{14}H_{15}NO$] and [$C_{16}H_{17}NO$] are 1.23(1) and 1.254(8) Å, respectively[11,12]. In the solid state, the reason for shortening in the C1-O1 bond length can be

Table 2. Atomic Coordinates and Equivalent Displacement Parameters with e.s.d.'s in Parentheses (Anistropically Refined Atoms Are Given in the Form of Isotropic Equivalent Displacement Parameters Defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

Atom	x	y	z	U_{iso}
Br1	0.80227(11)	0.06345(11)	0.56387(4)	0.0798(5)
O1	0.4314(7)	−0.0702(5)	0.8591(3)	0.0578(11)
C1	0.8083(8)	0.0669(6)	0.7204(3)	0.0436(12)
C5	0.5149(8)	−0.0366(6)	0.7950(3)	0.0404(11)
C6	0.7294(7)	0.0361(6)	0.7891(3)	0.0399(11)
C3	0.4746(8)	−0.0477(6)	0.6609(3)	0.0472(12)
C7	0.8659(8)	0.0735(6)	0.8558(3)	0.0429(12)
N1	0.8030(8)	0.0500(5)	0.9200(3)	0.0517(12)
C8	0.9576(11)	0.0859(7)	0.9841(4)	0.0607(16)
C2	0.6823(9)	0.0263(7)	0.6560(3)	0.0503(13)
C4	0.3910(8)	−0.0781(6)	0.7284(3)	0.0452(13)

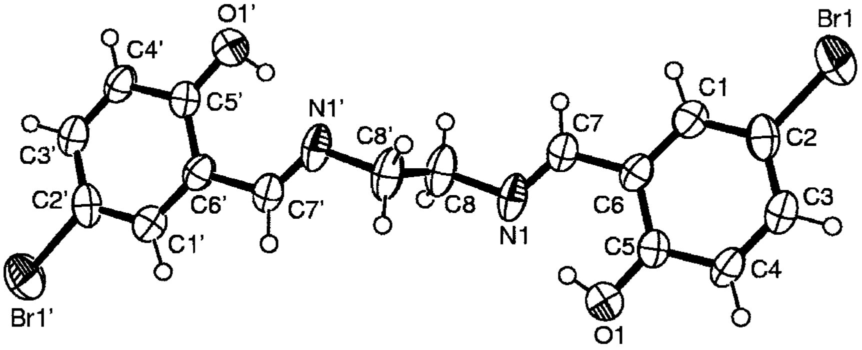

Figure 1. An ORTEPII[29] drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

explained by the quinoidal structure (keto-amine form) as in 2-hydroxy-1-napthaldimine derivatives[9].

The C=N imine bond and C-N-C bond angle are 1.259(8) Å and 119.1(5)°, compared with 1.313(8) Å and 122.5(6)° in $[C_{14}H_{15}NO]$[11] and 1.270(3) Å and 123.5(2)° in $[C_{32}H_{32}O_6N_2]$[8]. As expected, benzene ring, (C6, C7, N1, C8) moiety and (N1, C7, C6, C5, O1, H1) are planar.

Computational Study

The geometry data was taken from X-ray structure and PM3 calculation was performed. In the optimized geometry N1′-C8′-C8-N1 is 179.7° which shows that imine moieties are in the anti conformation. The calcu-

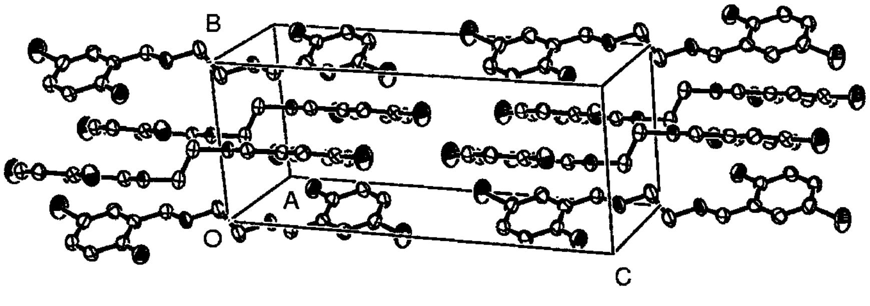

Figure 2. Packing diagram.

Table 3. The Bond Lengths (Å) and Angles (°) with Some Selected Torsion Angles (°)

Br1-C2	1.885(6)	C6-C7	1.452(7)
O1-C5	1.320(7)	C3-C4	1.373(9)
C1-C6	1.381(8)	C3-C2	1.386(8)
C1-C2	1.388(8)	C7-N1	1.259(8)
C5-C4	1.417(7)	N1-C8	1.475(6)
C5-C6	1.422(6)	C8-C8′	1.445(11)
C6-C1-C2	121.1(5)	N1-C7-C6	123.5(5)
O1-C5-C4	119.7(5)	C7-N1-C8	119.1(5)
O1-C5-C6	122.9(4)	C8′-C8-N1	111.2(5)
C4-C5-C6	117.4(5)	C3-C2-C1	119.4(6)
C1-C6-C5	120.2(4)	C3-C2-Br1	121.3(4)
C1-C6-C7	120.4(4)	C1-C2-Br1	119.2(4)
C5-C6-C7	119.4(5)	C3-C4-C5	121.1(5)
C4-C3-C2	120.8(5)		
C2-C1-C6-C5	−0.6(6)	C7-N1-C8-C8′	−103.1(9)
C2-C1-C6-C7	177.9(4)	C4-C3-C2-C1	1.1(7)
O1-C5-C6-C1	179.5(4)	C4-C3-C2-Br1	178.5(4)
C4-C5-C6-C1	1.1(6)	C6-C1-C2-C3	−0.5(7)
O1-C5-C6-C7	0.9(6)	C6-C1-C2-Br1	−177.9(3)
C4-C5-C6-C7	−177.5(4)	C2-C3-C4-C5	−0.6(7)
C1-C6-C7-N1	179.3(4)	O1-C5-C4-C3	−178.9(4)
C5-C6-C7-N1	−2.1(7)	C6-C5-C4-C3	−0.5(6)
C6-C7-N1-C8	177.8(4)		

lated angles for N1-C7-C6-C5[-0.62°], N1-C7-C6-C1[179.45°], C7-C6-C5-O18[0.07°] and C6-C5-O1-H1[0.34°] indicate that the non-hydrogen phenyl, the conjugated imine group atoms and hydroxy group are almost planar (Table 4). The O1-H1···N1 distance, 1.836 Å, is clearly indicative of strong intramolecular hydrogen bonding. This intramolecular O1-H1···N1 distance is in comparable to those observed for 2-hydroxy-N-n-propyl-1-naphthaldimine [H···N 2.403(7) Å][11] and 1,5-di(N-2-oxyphenyl-salicylidene)-3-oxapentane [H1···N1 1.863(3) and H5···N2 1.603(4) Å][16].

In order to define the conformational flexibility of the title compound, semi-empirical calculations using PM3 method were carried out as a function of the torsion angle of [N1′-C8′-C8-N1]. Figure 3 depicts the PM3 stable structures corresponding to the three conformers of the title compound at angles of 80, 180 and 280°. According to the gas phase PM3 energies, gauche conformations at 80 and 280° are energetically favorable conformers besides the anti conformation at 180°. The eclipsed

Table 4. Calculated Bond Lengths (Å) and Angles (°) with Some Selected Torsion Angles (°)(PM3)

Br1-C2	1.866	C6-C7	1.462
O1-C5	1.354	C3-C4	1.383
C1-C6	1.404	C3-C2	1.387
C1-C2	1.374	C7-N1	1.297
C5-C4	1.412	N1-C8	1.464
C5-C6	1.414	C8-C8′	1.532
C6-C1-C2	118.7	N1-C7-C6	119.3
O1-C5-C4	115.5	C7-N1-C8	122.1
O1-C5-C6	123.6	C8′-C8-N1	109.2
C4-C5-C6	120.8	C3-C2-C1	123.8
C1-C6-C5	118.6	C3-C2-Br1	117.9
C1-C6-C7	118.3	C1-C2-Br1	118.2
C5-C6-C7	122.9	C3-C4-C5	119.6
C4-C3-C2	118.4		
C2-C1-C6-C5	0.0	C7-N1-C8-C8′	−134.01
C2-C1-C6-C7	179.9	C4-C3-C2-C1	0.0
O1-C5-C6-C1	179.9	C4-C3-C2-Br1	179.9
C4-C5-C6-C1	0.0	C6-C1-C2-C3	0.0
O1-C5-C6-C7	0.0	C6-C1-C2-Br1	−179.9
C4-C5-C6-C7	−179.9	C2-C3-C4-C5	0.0
C1-C6-C7-N1	179.4	O1-C5-C4-C3	−179.9
C5-C6-C7-N1	−0.6	C6-C5-C4-C3	0.0
C6-C7-N1-C8	−179.0		

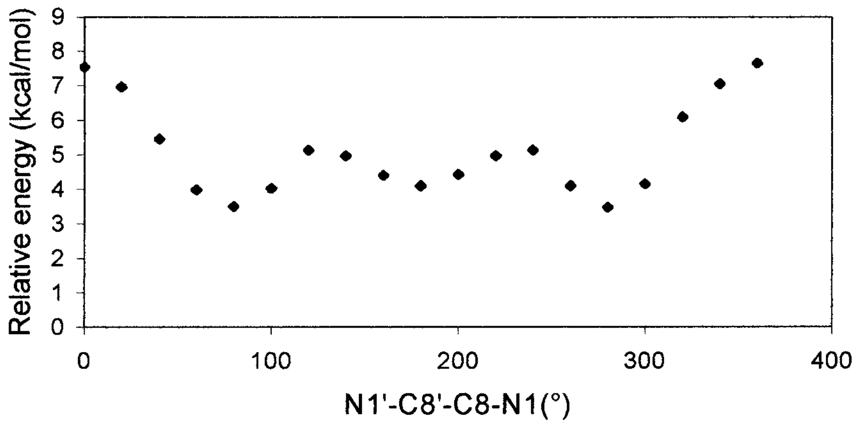

Figure 3. PM3 calculated conformation energy profile of θ[N1′-C8′-C8-N1] torsion angle (°).

conformation (at 0°) is approximately 4.0 Kcal mol^{-1} unstable than the gauche conformations.

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