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Crystal structure and conformational analysis of 1-[*N*-(2-bromophenyl)]naphthaldimine

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Abstract

1-[*N*-(2-bromophenyl)]naphthaldimine (C₁₇H₁₂NOBr) (1) was synthesised and its crystal structure was determined. The compound 1 is orthorhombic, space group $P_{2_12_12_1}$ with a = 12.653(2), b = 13.7311(14), c = 7.9799(12) Å, V = 1386.4(4) Å³, Z = 4, $D_c = 1.563$ g cm⁻³, μ (Mo K_{α}) = 2.959 mm⁻¹, R = 0.032 for 499 reflections $I > 2\sigma(I)$]. There is an intramolecular hydrogen bond of distance 2.473(3) Å between the hydroxyl oxygen atom and imine nitrogen atom, the hydrogen atom essentially being bonded to the oxygen atom. Minimum energy conformation was calculated as a function of torsion angle θ (C10–C11–N1–C12) varied every 5 degrees. The optimized geometry of the crystal structure corresponding to the non-planar conformation is the most stable conformation in all calculations. The results strongly indicate that the minimum energy conformation is primarily determined by hydrogen–hydrogen repulsions between the ortho-hydrogen atoms on the aldehyde rings. Complementary IR, ¹H NMR and UV measurements in solution and in the solid state were carried out. © 2003 Elsevier B.V. All rights reserved.

Keywords: Schiff base; Photochromism; Conformational analysis; Crystal structure; Intramolecular hydrogen bonding

1. Introduction

Schiff bases from 2-hydroxy-1-naphthaldehyde have often been used as chelating ligands in the field coordination chemistry [1]. The Schiff base compounds can be classified by their photochromic and thermochromic characteristics [2]. Photochromism is produced by intramolecular proton transfer associated with a change in the π -electron configuration [3–8]. Studies on the photochromic compounds have been increased ever since the potential applications of photochromic materials were realised in various areas such as the control and measurement of radiation intensity, optical computers and display systems [9]. The Schiff base complexes have also been used in catalytic reactions [10] are used as models for biological systems [11,12].

There are two types of intramolecular hydrogen bonds [either N–H···O (keto form) or N···H–O (enol form), Fig. 1] in Schiff bases. 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) [13–17] (Table 1). In the aldimine compounds derived from 2-hydroxy-1naphthaldehyde, both types of hydrogen bonds were

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Fig. 1. Enol and keto tautomerism of 1.

found [18–27] (Table 2). In this study, we investigated the structure of the title compound in order to reveal the presence of either the enol or keto forms related with hydrogen bonding by using IR, ¹H NMR, UV and X-ray crystallographic techniques in the solution and solid states, respectively. The tautomerism of the title compound has also been investigated by AM1 semi-empirical quantum mechanical method.

2. Experimental

2.1. Reagents and techniques

2-Hydroxy-1-naphthaldehyde and 2-bromoaniline were purchased from Merck (Germany). Melting points were measured on a Gallonkamp apparatus using a capillary tube. Infrared absorption spectra were obtained from a Mattson 1000 FTIR spectrometer in KBr discs and reported in cm⁻¹. UV-vis spectra were measured using a Perkin Elmer Lambda 2 series spectrometer. ¹H NMR (400 MHz) were recorded with a Bruker DPX FT-NMR spectrometer (CDCl₃ as internal standard).

Table 1				
Bond lengths (Å) and	bond angles ((deg) in salicy	laldehyde	ligands

	O–H	$H \! \cdots \! N$	$O{\cdots}N$	С-О	C=N	$O-H\cdots N$
I ^a	0.95(5)	1.73(5)	2.577(6)	1.353(4)	1.325(5)	151(3)
Π^{b}	0.95(3)	1.73(3)	2.604(2)	1.346(3)	1.276(2)	150(2)
III ^c	0.84(4)	1.83(4)	2.604(3)	1.354(3)	1.281(3)	154(3)
IV^d	0.97(3)	1.71(3)	2.607(3)	1.351(2)	1.287(2)	153(2)
V ^e	1.154(3)	1.488(3)	2.578(3)	1.356(3)	1.270(3)	

^a 2-(3-Methoxy-2-hydroxyphenyl)benzimidazole [13].

^b *N*-(2,5-methylphenyl)salicylaldimine [14].

^c N-(2-methyl-5-chlorophenyl)salicylaldimine [15].

^d 4-([(1*E*)-(2-hydroxyphenyl)methylidene]amino(-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one [16].

^e 1,8-di[*N*-2-oxyphenyl-salicylidene]-3,6-dioxaoctane [17].

Table 2
Bond lengths (Å) and bond angles (deg) in naphthaldehyde ligands

	$O{\cdots}H$	H–N	$O{-}H{\cdot}{\cdot}{\cdot}N$	C=O	C-N	$O{\cdots}N$
Ia	1 846(8)	0.827(9)	2 544(2)	1 310(8)	1 319(6)	141
II ^b	1.852(3)	1.00(3)	2.583(3)	1.260(4)	1.329(4)	127(3)
III ^c	1.83(3)	0.91(3)	2.532(3)	1.281(4)	1.322(4)	133(3)
IV^d	1.96(5)	0.66(4)	2.530(4)	1.303(5)	1.30(4)	146(6)
V ^e	1.759(4)	0.90(4)	2.572(4)	1.274(4)	1.345(4)	150(3)
	O-H	$H{\cdots}N$	$O-H\!\cdot\cdot\cdot N$	C–O	C=N	O−H···N
VI^{f}	1.130	1.534	2.547(3)	1.337(4)	1.273(4)	145
VII ^g	0.95(3)	1.70(3)	2.540(2)	1.334(2)	1.290(2)	146.3
$VIII^h$	0.97	1.71	2.553(4)	1.321(5)	1.291(4)	143.2
IX^i	0.83		2.570(3)	1.323(3)	1.290(3)	152
$\mathbf{X}^{\mathbf{j}}$	0.88(4)	1.76(4)	2.574(3)	1.357(3)	1.294(3)	153(4)
VI ^k	4.04(0)	1 ((()	0 (50)		1 200 (5)	10((0))

^a 1-[*N*-(4-bromophenyl)]aminomethylidene-2(1*H*)naphthalenone [8].

[18]. ^b 1-[N-(6-metyl-2-pyridyl)]aminomethylidene-2(1H)naphthalenone [19].

^c 1-[*N*-(4-metyl-2-pyridyl)]aminomethylidene-2(1*H*)naphthalenone [20].

^d 1-[*N*-(4-iodophenyl)]aminomethylidene-2(1*H*)naphthalenone [21].

^e 1-[*N*-(2-pyridyl)]aminomethylidene-2(1*H*)naphthalenone [22].

^f 1-[*N*-(4-fluorophenyl)]naphthaldimine [23].

^g N-(2-aminophenyl)]naphthaldimine [24].

^h N-(2-bromo-4-methylphenyl)]naphthaldimine [25].

ⁱ N-(3,5-dichlorophenyl)]naphthaldimine [26].

^j 4-Ethyl-2-(2-hydroxynaphthymethylidene)-amino-5-methyl-3-thiophenecarbonitrile [27].

^k Present study [1-[N-(2-bromophenyl)]naphthaldimine].

2.2. Synthesis of compound 1

Compound **1** was prepared by addition of 100 ml hot ethanol solution of 0.001 mol of 2-bromoaniline (0.172 g) to 75 ml hot ethanol solution of 0.001 mol of 2-hydroxy-1-naphthaldehyde (0.172 g). The mixture was refluxed for 5 h and during reflux process brown coloured prismatic crystals were formed [28], m.p. 145 °C, 0.312 g (91%) yields. Found: C, 62.43; H, 3.82; N, 4.20. Calcd for C₁₇H₁₂NOBr; C, 62.60; H, 3.71; N, 4.29%. UV/vis (C₂H₅OH): λ_{max} (log ε) = 344 nm (4.90). IR (KBr, cm⁻¹): ν (C=N) 1623s, ν (C=C) 1421–1619, ν (C–O) 1321s, ν (C–H) 3069–3071, ν (O–H) 3402vwb. ¹H NMR (CDCl₃): δ = 15.18 (s, 1H, NH), 9.26 (s, 1H, CH=N), 6.84– 8.18 (m, 10H).

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2.3. X-ray structure determination

The data collection was performed on a RIGAKU AFC7-S diffractometer employing graphite-monochromatized Mo K_{α} radiation ($\lambda = 0.71073$ Å) [29]. The details of the X-ray data collection, structure solution and structure refinements are given in Table 3. Data reduction and corrections for absorption and crystal decomposition (1.1%) were carried out using the TEXSAN Single Crystal Structure Analysis Software [30]. The structure was solved by SHELXS-97 [31] and refined with SHELXL-97 [32]. The positions of H atoms bonded to C atoms were calculated (C-H distances 0.93 Å), and included in the structure factor calculation using a riding model (except HO1). The hydrogen atom HO1 riding on the O1 atom was found from a difference map at the end of the refinement process as a small positive electron

Table 3			
Crystal data	and	structure	refinement

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Compound	C ₁₇ H ₁₂ NOBr
Color/shape	Brown/prismatic
Formula weight	326.19
Crystal system	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
Cell constants	a = 12.653(2) Å
	b = 13.7311(14) Å
	c = 7.9799(12) Å
Cell volume	1386.4(4) Å ³
Formula units/unit cell	4
D_x	1.563 g cm^{-3}
μ (Mo K _{α})	2.959 mm^{-1}
Diffractometer/Scan	Rigaku AFC7-S/ ω -2 θ
λ (Mo K _{α})	0.71073 Å
Crystal size	$0.10 \times 0.15 \times 0.05 \text{ mm}^3$
Т	293 K
F(000)	656
Index ranges	$0 \le h \le 15$
	$0 \le k \le 19$
	$0 \le l \le 11$
Number of reflections measured	1871
Number of reflections used	499
Number of parameters	185
R	0.032
$R_{ m w}$	0.055
Goodness-of-fit	1.002
$(\Delta(\sigma)_{\max})$	0.004
$(\Delta(ho)_{\rm max})$	$0.356 \text{ e}\text{\AA}^{-3}$
$(\Delta(ho)_{\min})$	$-0.390 \text{e} \text{\AA}^{-3}$

density. H atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given for in Table 4. Bond distances and bond angles for **1** are listed in Table 5 and an ORTEP view of the molecular structure is given in Fig. 2. [33].

2.4. Conformation analyses

Theoretical calculations were carried out with the standard parameters using a locally modified version of the MOPAC 6.0 program package [34] which includes the AM1 Hamiltonian [35] running on a Pentium II PC starting with the optimized X-ray crystallographic coordinates [36] of **1**. The geometry optimizations of the crystal structure of **1** were carried out by using the Fletcher–Powell–Davidson algorithm [37,38], which is implemented in the MOPAC 6.0 package, and the PRECISE option was used to improve the convergence criteria. To determine

Table 4

Atomic coordinates (×10⁻⁴) and equivalent isotropic displacement parameters (×10⁻³ Å²) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	Y	Ζ	$U^a_{ m eq}$
01	3276(3)	2821(2)	3631(5)	73(2)
C1	2544(4)	2126(3)	3617(6)	53(2)
C2	1528(4)	2377(3)	4308(7)	65(2)
C3	788(4)	1741(4)	4268(6)	78(2)
C4	918(4)	776(4)	3604(6)	55(2)
C5	73(4)	100(4)	3544(6)	70(2)
C6	195(4)	-816(4)	2900(6)	72(2)
C7	1183(4)	-1073(4)	2236(6)	64(2)
C8	2008(3)	-444(3)	2252(6)	53(2)
C9	1915(3)	516(3)	2922(6)	43(2)
C10	2753(4)	1203(4)	2961(6)	42(2)
C11	3812(3)	994(3)	2421(6)	38(2)
N1	4535(3)	1635(3)	2436(4)	51(1)
C12	5588(4)	1384(3)	1994(6)	45(2)
C13	6064(3)	515(4)	2421(6)	57(2)
C14	7111(4)	323(3)	2054(7)	64(2)
C15	7724(4)	1018(4)	1262(7)	72(2)
C16	7258(3)	1873(4)	823(6)	65(2)
C17	6240(4)	2068(3)	1221(6)	47(2)
Br1	5612(1)	3273(1)	586(1)	76(1)
HO1	385(2)	268(2)	273(4)	46

 $U_{\rm eq}^a = (1/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$





Table 5 Bond lengths (Å) and angles (deg)

O1-C1	1.331(5)	C1-C10	1.406(6)
C1-C2	1.432(6)	C2-C3	1.285(6)
C3-C4	1.432(6)	C4-C5	1.413(7)
C4-C9	1.423(6)	C5-C6	1.369(7)
C6-C7	1.407(7)	C7-C8	1.366(6)
C8-C9	1.431(6)	C9-C10	1.422(6)
C10-C11	1.416(6)	C11-N1	1.280(5)
N1-C12	1.444(5)	C12-C13	1.373(6)
C12-C17	1.397(6)	C13-C14	1.387(6)
C14-C15	1.389(7)	C15-C16	1.352(7)
C16-C17	1.342(6)	C17-Br1	1.901(4)
O1-HO1	1.01(3)	HO1···N1	1.66(3)
O1-C1-C10	122.0(4)	O1-C1-C2	118.6(4)
C10-C1-C2	119.4(4)	C3-C2-C1	119.8(5)
C2-C3-C4	124.2(5)	C5-C4-C9	119.2(5)
C5-C4-C3	122.5(4)	C9-C4-C3	118.3(4)
C6-C5-C4	122.5(5)	C5-C6-C7	118.2(5)
C8-C7-C6	121.4(5)	C7-C8-C9	121.5(4)
C10-C9-C4	117.7(4)	C10-C9-C8	125.2(4)
C4-C9-C8	117.1(4)	C1-C10-C11	118.5(5)
C1-C10-C9	120.6(4)	C11-C10-C9	120.8(5)
N1-C11-C10	122.2(4)	C11-N1-C12	124.5(4)
C13-C12-C17	117.9(5)	C13-C12-N1	121.2(4)
C17-C12-N1	120.7(4)	C12-C13-C14	120.2(5)
C13-C14-C15	120.5(5)	C15-C16-C17	122.1(5)
C16-C17-Br1	121.3(4)	C12-C17-Br1	117.6(3)
O1-HO1···N1	136(3)		

the conformation energy profiles, heat of formation energies were calculated as a function of the torsion angle θ (C10-C11-N1-C12) varied from 0 to 360°, for every 5°.

3. Results and discussion

3.1. Spectroscopic study

Absorption bands were observed of 1623 cm^{-1} ($\nu_{\text{C}=\text{N}}$), 3071 cm^{-1} , ($\nu_{\text{C}-\text{H}}$, Ar–H), 1605 cm^{-1} ($\nu_{\text{C}=\text{C}}$). Observation of a phenolic $\nu_{\text{C}-\text{O}}$ at 1321 cm^{-1} is evidence for the existence of the enol form (N···H–O) intramolecular hydrogen bonding only in the solid state.

The UV-visible spectra of the compound were studied in polar, non-polar solvents and with the addition acid and base. Absorption in the range above 400 nm is observed in DMSO, ethanol, chloroform, benzene and cyclohexane [17]. The new band (above 400 nm) belongs to the keto form was observed in polar (DMSO, ethanol and chloroform) and non-polar (benzene and cyclohexane) solvents and in acidic (CF₃COOH) solutions of chloroform and benzene and basic [(C₂H₅)₃N] solutions of DMSO, ethanol, chloroform, benzene and cyclohexane but it is not observed in acidic solutions of DMSO and ethanol [17].

The enol tautomer is dominant only in the acidic solutions of DMSO and ethanol, while it is dominant in polar and non-polar solvents and in both acidic solutions of chloroform and benzene and basic solutions of DMSO, ethanol, chloroform, benzene and cyclohexane [17,21,28]. Absence of the keto form in the acidic solutions of DMSO and ethanol may be explained by the hydrogen bonding to CF₃COOH.

The phenolic function in compound 1 was neutralized with NaOH (Fig. 3). According to this result compound 1 is in the enol tautomer as expected.



Fig. 2. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.



Fig. 3. Chemical reactions in enol tautomeric form.



3.2. Crystallographic studies

The title molecule is not planar; Schiff base moieties A[C1-C11, O1; planar with a maximum deviation of 0.0798 (0.0018) Å for the O1 atom] and **B**[N1, C12, C13, C14, C15, C16, C17, Br1; planar with a maximum deviation of -0.0353(0.0003) Å for the N13 atom] are inclined at angle of $41.67(2)^{\circ}$ reflecting mainly the twist about N1-C12 [C11-N1-C12–C13, $38.1(2)^{\circ}$]. The title molecule contains an intramolecular hydrogen bonds (O-H···N) [O1-H1 1.01(3) Å, H1···N1 1.66(3) Å, O···N 2.473(3) Å, O1-HO1···N1 136(3)°]. X-ray structure determinations reveal that the enol tautomer is favoured over the keto tautomer. This is evident from the observed O1-C1 bond distance of 1.331(5) which is consistent with the O-C single bond, similarly the N1-C11 distance of 1.280(5) Å is also consistent with the N=C double bonding.

3.3. Conformation analyses

Semi-empirical AM1 calculations were carried out to complement the experimental investigations and to clarify the tautomerism of **1**. Results are shown in Fig. 4. The theoretical calculations were performed on the torsion angles θ (C10-C11-N1-C12) (Fig. 4), that control the planarity of **1**. In order to find the most stable conformation in the solid state, we studied



Fig. 4. AM1 conformation energies of the enol and keto form as a function of the θ (C10–C11–N1–C12) torsion angle (\bullet) enol, (\blacksquare) keto.

the molecular model of the enol and keto tautomeric form.

The heat of formation energy profile shows that the minimum energy value is 56.42 kcal/mol for keto tautomeric form while 41.46 kcal/mol for enol form (Fig. 4). The energy profile of keto and enol forms of **1** as a function of θ show maximum near 190 and 250°, respectively, due to the steric interaction between H13 and HO1. Besides, the interactions of the hydrogen atom H8 attached to the C8 on the naphthaldehyde ring and the hydrogen atom (H11) on the 'bridge' carbon atom of C11 is repulsive in conformation analysis in the planar conformation, but it is reduced with increasing the non-planarity for the enol form. The results confirm the X-ray data so the most stable non-planar conformation of **1** is the enol form.

Bürgi and Dunitz [39] carried out an extensive theoretical and experimental study on the nonplanar conformation of N-benzylideneaniline and related compounds. Their explanation for the nonplanarity of N-benzylideneaniline involves a competition between two principal factors: (i) the interaction of the ortho hydrogen on the aniline ring and the hydrogen on the bridge carbon is repulsive in the planar conformation but reduced with increasing non-planarity, (ii) the π -electron system, itself divisible into two components, including, on the one hand, delocalisation between the -HC=N- double bond and the aniline phenyl ring (which is maximised for a planar conformation) and, on the other hand, delocalisation of the nitrogen lone pair of electrons into the aniline ring which is essentially zero for the planar conformation but increases with increasing nonplanarity (where the lone pair density on the nitrogen may interact with the π systems of the ring).

In summary, the AM1 optimized geometry of the crystal structure of the investigated compound corresponding to non-planar conformation is the most stable conformation in all considered calculations. The results strongly indicate that the most stable conformation is primarily determined by non-bonded hydrogen-hydrogen repulsions. The interaction between the *N*-lone pair and the π electrons of the rotated naphthaldehyde ring, however, might also contribute to the conformational energy of the title compound.

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