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Intramolecular hydrogen bonding and tautomerism in Schiff bases. Structure of *N*-(2-pyridil)-2-oxo-1-naphthylidenemethylamine

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Abstract

N-(2-pyridil)-salicylidene (**1**) and *N*-(2-pyridil)-2-oxo-1-naphthylidene-methylamine (**2**) were studied by elemental analysis, IR, ^{1}H NMR and UV–visible techniques and the structure of compound (**2**) was examined crystallographically. The UV–visible spectra of 2-hydroxy Schiff bases are investigated in different solvents, acidic and basic media. Compound (**2**) is in tautomeric equilibrium (phenol–imine, O–H···N ⇌ keto–amine, O···H–N forms) in polar and non-polar solvents. These tautomers are not observed in polar and non-polar solvents for (**1**) as also supported by ^{1}H NMR and UV–visible data. The keto–amine form of compound (**2**) was observed in basic solutions of DMSO, ethanol, chloroform, benzene, cyclohexane and in acidic solutions of chloroform and benzene, but not in acidic solutions of DMSO and ethanol. On the contrary, this form for compound (**1**) was not observed in the same solutions. The asymmetric unit of compound (**2**) contains two independent molecules of ($C_{16}H_{12}N_2O$) which constitute a tautomeric pair. The observed differences in the related C=N (1.317(4) and 1.330(4) Å) and C–O (1.279(4) and 1.263(4) Å) bond lengths in the two crystallographically independent molecules indicate that the phenol–imine and the keto–amine forms coexist in the solid state. Intramolecular hydrogen bond lengths (O–H···N) are 2.586(4) Å and 2.518(4) Å for the two individual tautomers. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.837(2)$, $b = 17.476(2)$, $c = 24.295(3)$ Å, $\beta = 91.95(4)°$, $V = 2476.9(6)$ Å^3, $Z = 4$ and $D_x = 1.3315$ g cm^{-3}.

Keywords: Crystal structure; Schiff bases; Tautomerism; Spectroscopic and crystallographic studies; Intramolecular hydrogen bond

1. Introduction

2-Hydroxy Schiff base ligands and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with amines have been extensively studied [1–6] and a number of them were used as models for biological systems [7–11]. The Schiff base complexes have also been used in the catalytic reactions [12]. A series of the Schiff base complexes display interesting structural and electronic properties [5,9,13]. Tautomerism in 2-hydroxy Schiff bases both in solution and in solid state were investigated using IR [1,14,15], UV [1,15–24], ^{15}N NMR [25], ^{1}H NMR [26–29], ^{13}C NMR [30,31] and X-ray crystallography techniques [32,33]. 2-Hydroxy Schiff base ligands are of interest mainly due to the existence of (O–H···N) and (O···H–N) type hydrogen bonds and tautomerism between phenol–imine and keto–amine forms [9,16,34]. In these compounds,

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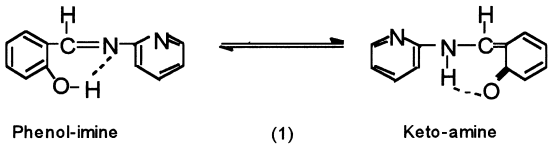
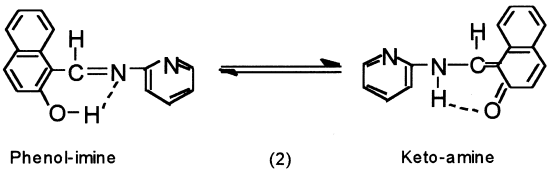


Scheme 1.



Scheme 2.

short hydrogen bonds were observed between the 2-hydroxy group and the imine nitrogen. In some instances the hydrogen from the phenol group is completely transferred to the imine nitrogen. In other words, Phenol–imine ⇌ keto–amine equilibrium shifts predominantly to the keto–amine side [28,32,33,35]. The hydrogen bond type depends neither on the stereochemistry of the molecule nor on the sort of the substituent to the imine (N) atom, but on the kind of aldehyde used [32]. The UV–visible spectra of some 2-hydroxy Schiff bases were also studied in polar and non-polar solvents [1,16]. In polar solvents, a new band at >400 nm was observed, which is not found in non-polar solvents. The results indicate that the absorption band at 400 nm belongs to the keto–amine form of the Schiff base. The keto–amine tautomer is always observed when the Schiff base is derived from 2-hydroxy naphthaldehyde and aniline. For Schiff bases derived from salicylaldehyde and aniline, the keto–amine form was not observed in polar and non-polar solvents, but was noted after acid addition [1,16]. We report here the spectroscopic studies of Schiff bases and the crystal structure of the Schiff base formed by 2-aminopyridine and 2-hydroxy-1-naphthaldehyde in order to compare the hydrogen bonding and tautomerism (Schemes 1 and 2) in those compounds. As can be seen from Fig. 4 the asymmetric unit includes both the tautomeric forms at 50% abundance in the crystalline state.

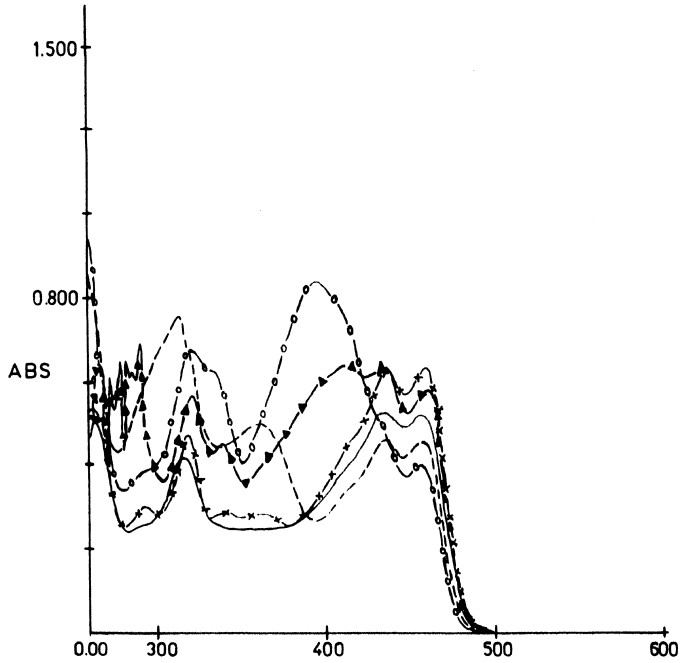


Fig. 1. Solvent effect on compound (**2**). DMSO —, ethanol - - -;, chloroform -×-×-, benzene -▲-▲, cyclohexane -○-○-, Schiff base concentration 5×10^{-5} mol dm^{-3}.

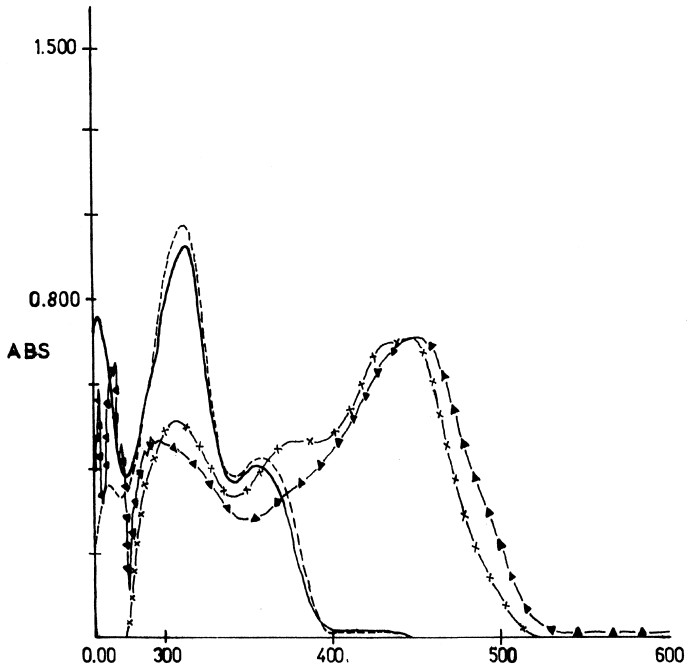


Fig. 2. Acid effect on compound (**2**). DMSO —, ethanol - - -, chloroform -×-×-, benzene -▲-▲, CF_3COOH, pH: 2.

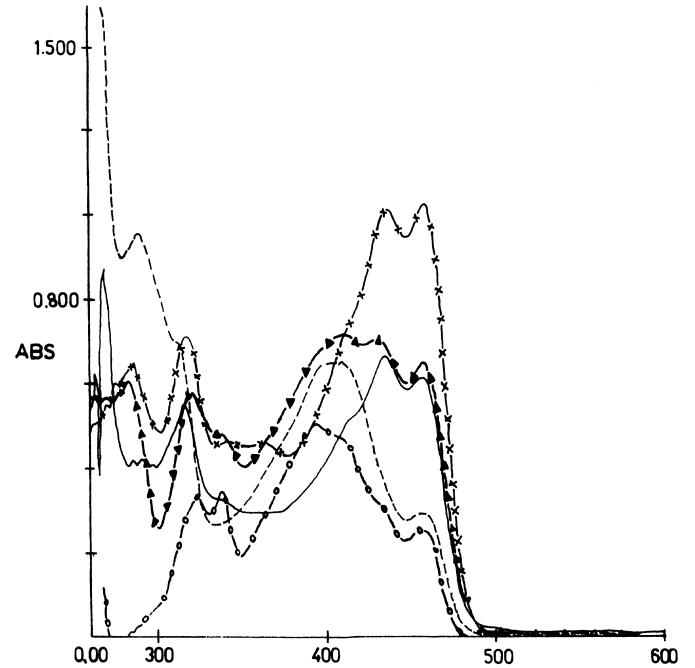


Fig. 3. Base effect on compound (**2**). DMSO —, ethanol - - -, chloroform -×-×-, benzene -▲-▲, cyclohexane -○-○-, $(C_2H_5)_3N$, pH: 9.

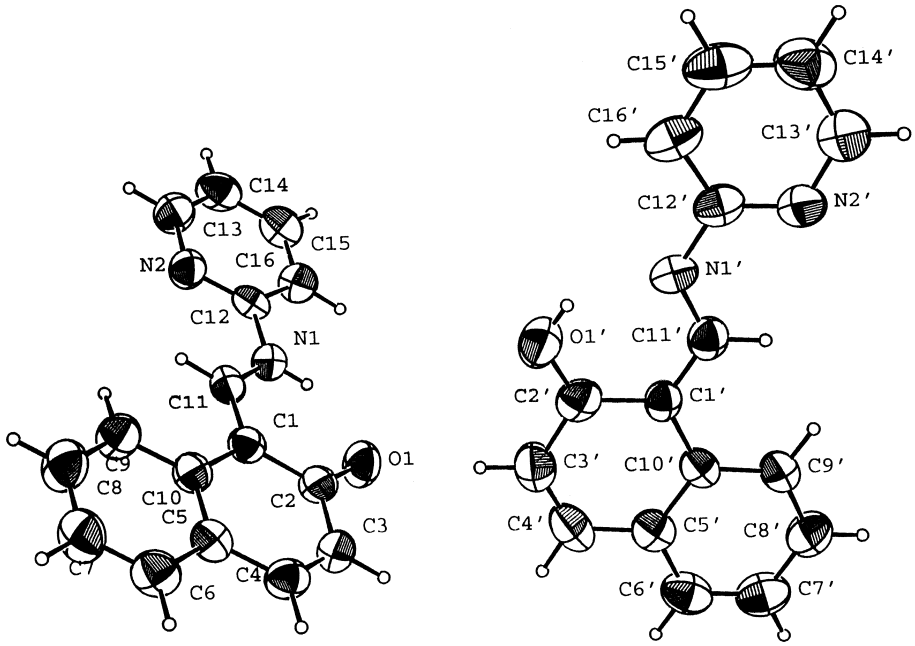


Fig. 4. An ORTEP [41] drawing of the title molecule with the atom-numbering scheme.

2. Experimental

2.1. Reagents and techniques

The ^{1}H NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer operating at 400 MHz. The proton shifts were measured using $SiMe_4$ as an internal standard. Infrared absorption spectra were obtained from a Mattson 1000-FTIR spectrometer in KBr discs and were reported in cm^{-1} units. UV–visible spectra were measured using a UNICAM UV2-100 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed on a LECO CHNS-932 C-, H-, N- analyzer. Melting points were measured on a Gallonkamp apparatus using a capillary tube, chloroform, THF, Benzene, EtOH, cyclohexane, DMSO, light petroleum ether (b.p. 50–70°C) were purchased from Merck (Germany).

2.2. Synthetic procedures

2.2.1. N-(2-pyridil)-salicylidene) (1)

Salicylaldehyde (1.22 g, 0.01 mol) was added to a dry THF (100 ml) solution of 2-amino pyridine (0.94 g, 0.01 mol). The mixture was stirred and heated for 1 h. Compound (**1**) was obtained after the evaporation of THF, as a yellow solid m.p. 65°C, 1.50 g (76%) yield. Found: C, 72.94; H, 5.11; N, 14.16; calc. for $C_{12}H_{10}N_2O$; C, 72.72; H, 5.05; N, 14,14%. IR (KBr, cm^{-1}): ν (Ar–H) 3059 m, ν (C–H)2929 w), ν(O–H) 2719 w, ν (C=N) 1612 s, ν (C=C) 1600 s. ^{1}H NMR ($CDCl_3$): δ ppm; 13.44(s, 1H, OH), 9.45 (s, 1H, –CH=N=), 7.79–6.94 (m, 8H, Arom-H).

2.2.2. Synthesis of N-(2-pyridil)-2-oxo-1-naphthylidenemethylamine (2)

2-Hydroxy-1-naphthaldehyde (1.72 g, 0.01 mol) was added to a dry THF (100 ml) solution of 2-amino-pyridine (0.94 g, 0.01 mol). The mixture was stirred and heated for 1 h. Compound (**2**) was obtained from the evaporation of THF [36]. It was crystallized from ($CHCl_3$/petroleum ether (50–70)) by the slow-diffusion method as a yellow solid, m.p. 174°C, 2.0 g (81%) yield. Found: C, 76.90; H, 4.97; N, 11.32. $C_{16}H_{12}ON_2$; C, 77.42; H, 4.84; N, 11.29%. IR (KBr, cm^{-1}): ν (Ar–H) 3061 m, ν (C=N) 1620 s, ν (C=C) 1600, ν (C–O) 1473 s, 1321 s. ^{1}H NMR ($CDCl_3$); δ ppm, 15.41 (s, 1H, OH); 15.45 (broad, OH) [36]; 9.95(d, 1H, CH=N, $^3J_{NHCH} = 7.04$ Hz); 9.99(d,

Table 1
Experimental data

Compound	$C_{32}H_{24}N_4O_2$
Color/shape	Dark brown/needle
For. Wt.	496.57
Space group	Monoclinic, $P2_1/n$
Temperature (K)	295
Cell constants	$a = 5.837(2)$, $b = 17.476(2)$, $c = 24.295(3)$ Å, $\beta = 91.95(4)°$
Cell volume (Å^3)	2476.9(6)
Formula units/unit cell	4
D calc (mg m^{-3})	1.332
μ calc (mm^{-1})	0.079
Diffractometer/scan	Enraf-nonius CAD-4/w-2θ
Radiation used, graphite monochromator	MoKα ($\lambda = 0.71073$ Å)
Max. crystal dimen. (mm)	$0.35 \times 0.15 \times 0.10$ mm^3
Standard reflections	3
Decay of standard	−0.59
Reflections measured	3844
θ (max) (°)	23.57
Range of h, k, l	$0 < h < 6$; $0 < k < 19$; $-27 < l < 27$
No. of reflections with $I > 1/s(I)$	2118
Corrections applied	Lorentz-polarization
Computer programs	MoIEN[37]ORTEP(II)[41]
Source of atomic scattering factor	Ref. [42]
Structure solution	Direct method
Treatment of hydrogen atoms	calculated geometrically and a riding model was used
No. of parameters var.	343
GOF	1.33
$R = \|\|Fo\| - \|Fc\|\|/\|Fo\|$	0.054
Rw	0.049
(Δ/ρ) max (e Å^{-3})	0.247
(Δ/ρ) min (e Å^{-3})	−0.195

CH=N, $^3J_{NHCH} = 7.0$ Hz) [36]; 8.50–6.87 (m, 10H, Arom-H).

2.3. Crystallography

The crystals suitable for X-ray analysis were obtained by recrystallization from ($CHCl_3$/petroleum ether (50–70)) by slow-diffusion method. Probably due to the fact that the crystallization medium was a mixture and that the rates of evaporation of the two liquids were different, a careful control of the crystallization process has proven to be difficult. The result was minute crystals not perfectly suitable for X-ray studies and attempts to grow better sizes failed. Experimental data, methods and the procedures used to elucidate the structure and other related parameters are given in Table 1. The structure was solved by the Direct method, Simpel-MoIEN [37]. All non-H atoms were refined with anisotropic thermal parameters. H atoms were placed in naphthyl geometrically at 0.95 Å from their corresponding C atoms. For all H atoms a riding model was used with $U_{iso}(H) = 1.3U_{eq}(C, N, O)$.

3. Results and discussion

3.1. IR and ^{1}H NMR spectroscopies

The ν (C=N) absorbtion bands were observed at 1612 and 1620 cm^{-1} for compounds (**1**) and (**2**) as in ArCH=NAr [32,38]. The observation of phenolic ν (C–O) at 1321 cm^{-1} for (**2**) is the evidence for the existence of the keto–amine form (N–H···O) intramolecular hydrogen bonding only in the solid state. The stretching frequency observed at 2719 cm^{-1} in (**1**) shows the presence of O–H···N intramolecular hydrogen bond, which is in agreement with the reported values in the literature [38]. ^{1}H NMR data for compound (**1**) shows that the tautomeric equilibrium favors the phenol–imine in $CDCl_3$ ($\delta =$ 13.44 ppm, singlet for OH; $\delta = 9.45$ ppm, singlet for –CH=N–). The compound (**2**) shifts to the keto–amine form in the $CDCl_3$ ($\delta = 15.41$ ppm, singlet for OH; $\delta = 9.95$ ppm, doublet, $^3J_{NHCH} = 7.04$ Hz).

3.2. UV–visible spectroscopy

The UV–visible spectra of compounds (**1**) and (**2**) were studied in polar and non-polar solvents both in acidic and basic media. Table 2 gives the calculated keto–amine form. Figs. 1–3 show the UV spectra of compound (**2**) in different solvents both in acidic and basic media. Compound (**1**) did not show any absorption above 400 nm in DMSO, EtOH, chloroform, benzene and cyclohexane. However, for compound (**2**), a new band was observed at >400 nm in the same solvents (Fig. 1). The band was observed at >400 nm in acidic (CF_3COOH, pH = 2) solutions of chloroform and benzene and basic ($(C_2H_5)_3N$, pH = 9) solutions of DMSO, EtOH, chloroform, benzene and cyclohexane for compound (**2**) (Figs. 2 and 3) but it is not observed in acidic and basic solutions

Table 2
Effect of solvent, acid and base on the UV spectra of compounds (**1**) and (**2**)

Compound	Solvent	λ, nm (ε, M^{-1} cm^{-1})	Keto–amine isomer (%)		
			Solvent media	Acidic media[a]	Basic media[b]
(**1**)	DMSO	256(3200),270(3500) 308(3900),346(3400)	–	–	–
	EtOH	226(550),272(240) 304(300),346(250)	–	–	–
	$CHCl_3$	240(5600),270(5700) 306(6600),350(5700)	–	–	–
	Benzene	224(4700),234(6400, 270(6300),306(8200), 354(7700)	– –	– –	– –
	Cyclohexane	228(4200),268(3800) 304(5000),352(4400)	–	–	–
(**2**)	DMSO	316(3100),436(3900) 458(3800)	63	–	67
	EtOH	314(800),434(110) 458(110)	63	–	68
	$CHCl_3$	318(5300),436(7700) 458(7800)	62	68	72
	Benzene	322(700),412(900) 434(520)	57	75	61
	Cyclohexane	322(5100),396(6300) 458(3000)	52	Not measured[c]	70

[a] CF_3COOH, pH:2.
[b] $(C_2H_5)_3N$, pH:9.
[c] Not mixtured cyclohexane and acid.

of the same solvents for compound (**1**). In Schiff bases derived from salicylaldehyde and aniline this new band at >400 nm was observed only in acidic media [1,16].

The molar extinction (ε) coefficients of the bands in the range of 222–354 nm for compound (**1**) can be ordered as EtOH < DMSO < cyclohexane < chloroform < benzene. However, for compound (**2**), the extinction coefficients are ordered as ethanol < benzene < cyclohexane < DMSO < chloroform for bands above 400 nm and as benzene < EtOH < DMSO < chloroform < cyclohexane for bands in the range of 318–396 nm. The bathochromic shifts both above and below 400 nm in all of the solvents studied (DMSO, EtOH, chloroform, benzene and cyclohexane) do not depend on solvent polarities for compound (**1**) and (**2**). Phenol–imine tautomer is dominant only in the acidic solutions of DMSO and ethanol for compound (**2**), while for compound (**1**) it is dominant in both acidic and basic solutions of DMSO, EtOH, chloroform, benzene and cyclohexane. On the contrary, keto–amine tautomer was increased by 6, 7, 8, 16, 57% and 6, 32%, respectively in the basic solutions of DMSO, benzene, EtOH, chloroform, cyclohexane and in the acidic solutions of chloroform and benzene with respect to the pure solvent media. Absence of keto–amine form in the acidic solutions of DMSO and ethanol may be explained by the hydrogen bonding to CF_3COOH.

3.3. Crystal study

Single crystal X-ray structure of compound (**2**) is reported to further corroborate the structure assignments. The final coordinates and equivalent isotropic displacement parameters are given in Table 1. The molecular structure with the atom-numbering scheme is shown in Fig. 4. The atomic coordinates and equivalent isotropic displacement parameters are

Table 3
Atomic coordinates and equivalent isotropic displacement parameters with e.s.d.s in parentheses (starred atoms were refined isotropically). Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a2 \times B(1,1) + b2 \times B(2,2) + c2 \times B(3,3) + ab(\cos gamma) \times B(1,2) + ac(\cos beta) \times B(1,3) + bc(\cos alpha) \times B(2,3)]$

Atom	X	Y	Z	B (Å^2)
O1	0.4177(4)	0.0652(1)	1.04873(9)	4.92(6)
O1′	0.8327(5)	0.0929(1)	1.2131(1)	5.92(7)
N1	0.6662(5)	0.1379(2)	0.9798(1)	3.84(7)
N1′	1.0960(5)	0.0545(2)	1.2926(1)	4.01(7)
N2	0.8906(5)	0.2062(2)	0.9197(1)	4.22(7)
N2′	1.3427(5)	0.0226(2)	1.3672(1)	5.36(8)
C1	0.3531(6)	0.1956(2)	1.0259(1)	3.30(8)
C1′	0.7760(6)	−0.0217(2)	1.2641(1)	3.52(8)
C2	0.3024(6)	0.1256(2)	1.0547(1)	3.82(8)
C2′	0.7117(7)	0.0337(2)	1.2227(1)	4.57(9)
C3	0.1115(6)	0.1270(2)	1.0905(1)	4.09(9)
C3′	0.5034(7)	0.0234(2)	1.1905(1)	5.2(1)
C4	−0.0185(6)	0.1893(2)	1.0960(1)	4.15(8)
C4′	0.3713(7)	−0.0381(2)	1.1987(1)	5.1(1)
C5	0.0235(6)	0.2594(2)	1.0675(1)	3.54(8)
C5′	0.4305(6)	−0.0964(2)	1.2377(1)	3.96(8)
C6	−0.1198(7)	0.3231(2)	1.0735(1)	4.67(9)
C6′	0.2910(7)	−0.1608(2)	1.2430(1)	5.01(9)
C7	−0.0791(7)	0.3897(2)	1.0468(1)	5.4(1)
C7′	0.3514(7)	−0.2187(2)	1.2790(1)	5.5(1)
C8	0.1062(7)	0.3942(2)	1.0127(2)	5.4(1)
C8′	0.5492(7)	0.2123(2)	1.3104(2)	5.3(1)
C9	0.2468(7)	0.3328(2)	1.0056(1)	4.60(9)
C9′	0.6897(7)	−0.1496(2)	1.3062(1)	4.62(9)
C10	0.2096(6)	0.2634(2)	1.0327(1)	3.56(8)
C10′	0.6335(6)	−0.0896(2)	1.2700(1)	3.61(8)
C11	0.5336(6)	0.1976(2)	0.9908(1)	3.60(8)
C11′	0.9676(6)	−0.0068(2)	1.2980(1)	4.05(9)
C12	0.8531(6)	0.1407(2)	0.9449(1)	3.50(8)
C12′	1.2870(6)	0.0703(2)	1.3268(1)	4.17(9)
C13	1.0745(6)	0.2083(2)	0.8883(1)	4.96(9)
C13′	1.5318(7)	0.0406(2)	1.3978(2)	6.5(1)
C14	1.2190(7)	0.1476(2)	0.8807(1)	5.00(9)
C14′	1.6615(7)	0.1056(2)	1.3904(2)	6.4(1)
C15	1.1723(7)	0.0803(2)	0.9070(1)	4.82(9)
C15′	1.5976(7)	0.1534(2)	1.3484(2)	6.2(1)
C16	0.9857(6)	0.0760(2)	0.9394(1)	4.11(9)
C16′	1.4097(7)	0.1366(2)	1.3157(2)	5.2(1)
H1	0.635	0.099	0.995	4.5*
H1′	0.938	0.104	1.237	7.4*
H3	0.079	0.082	1.111	5.3*
H3′	0.459	0.060	1.163	6.9*
H4	−0.145	0.187	1.120	5.5*
H4′	0.231	−0.042	1.178	6.6*
H6	−0.248	0.319	1.096	6.1*
H6′	0.152	−0.165	1.222	6.5*
H7	−0.176	0.433	1.051	7.0*
H7′	0.257	−0.263	1.282	7.1*
H8	0.136	0.441	0.994	7.2*
H8′	0.591	−0.252	1.336	7.0*
H9	0.372	0.338	0.982	6.0*

Table 3 (*continued*)

Atom	X	Y	Z	B (Å^2)
H9′	0.827	−0.147	1.328	6.1*
H11	0.569	0.244	0.973	4.9*
H11′	1.005	−0.043	1.326	5.1*
H13	1.106	0.225	0.870	6.6*
H13′	1.578	0.007	1.427	8.6*
H14	1.348	0.152	0.858	6.4*
H14′	1.792	0.116	1.414	8.3*
H15	1.269	0.037	0.903	6.2*
H15′	1.684	0.198	1.342	8.3*
H16	0.948	0.030	0.957	5.2*
H16′	1.364	0.169	1.286	6.8*

Table 4
Bond lengths (Å), bond angles (°) and torsion angles (°)

O1′–C2′	1.279(4)	C12′–C16′	1.394(5)
N1–C11	1.330(4)	C13–C14	1.372(5)
N1–C12	1.406(4)	C13′–C14′	1.380(6)
N1′–C11′	1.317(4)	C3–C4	1.336(5)
N1′–C12′	1.395(4)	C4–C5	1.432(4)
N2–C12	1.320(4)	C4′–C5′	1.426(5)
N2–C13	1.338(5)	C5–C6	1.403(5)
N2′–C12′	1.320(4)	C5–C10	1.401(5)
N2′–C13′	1.347(5)	C5′–C6′	1.397(5)
C1–C2	1.445(4)	C5′–C10′	1.403(5)
C1–C10	1.463(5)	C6′–C7′	1.376(5)
C1–C11	1.380(5)	C6–C7	1.358(5)
C1′–C2′	1.436(5)	C7′–C8′	1.367(5)
C1′–C10′	1.459(5)	C7–C8	1.386(6)
C1′–C11′	1.392(5)	C8–C9	1.365(5)
C2–C3	1.438(5)	C8′–C9′	1.375(5)
C2′–C3′	1.434(5)	C14–C15	1.372(5)
C3′–C4′	1.341(5)	C14′–C15′	1.361(5)
C9′–C10′	1.402(5)	C15–C16	1.367(5)
C9–C10	1.400(5)	C15′–C16′	1.364(5)
C11′–N1′–C12′	123.2(3)	C3′–C4′–C5′	122.9(3)
C12–N2–C13	115.9(3)	C4–C5–C6	121.0(3)
C12′–N2′–C13′	116.1(3)	C4–C5–C10	118.9(3)
C2–C1–C10	120.3(3)	C6–C5–C10	120.1(3)
C2–C1–C11	119.6(3)	C4′–C5′–C6′	120.5(3)
C10–C1–C11	120.1(3)	C4′–C5′–C10′	119.4(3)
C2′–C1′–C10′	118.7(3)	C6′–C5′–C10′	120.1(3)
C2′–C1′–C11′	118.4(3)	C5′–C6′–C7′	120.9(3)
C10′–C1′–C11′	122.9(3)	C5–C6–C7	121.0(3)
O1–C2–C1	122.3(3)	C6′–C7′–C8′	119.2(3)
O1–C2–C3	120.8(3)	C5–C10–C9	117.5(3)
C1–C2–C3	117.0(3)	N1′–C11′–C1′	122.7(3)
O1′–C2′–C1′	122.7(3)	N1–C11–C1	124.5(3)

Table 4 (*continued*)

O1′–C2′–C3′	117.7(3)	N1–C12–N2	117.0(3)
C1′–C2′–C3′	119.6(3)	N1–C12–C16	118.7(3)
C2′–C3′–C4′	120.0(3)	N2–C12–C16	124.3(3)
C6–C7–C8	119.2(3)	N1′–C12′–N2′	119.3(3)
C7–C8–C9	121.0(3)	N1′–C12′–C16′	117.1(3)
C7′–C8′–C9′	121.2(3)	N2′–C12′–C16′	123.6(3)
C8′–C9′–C10′	121.1(3)	N2–C13–C14	124.4(3)
C8–C9–C10	121.2(3)	N2′–C13′–C14′	124.3(4)
C1′–C10′–C5′	119.2(3)	C13–C14–C15	117.8(3)
C1′–C10′–C9′	123.3(3)	C13′–C14′–C15′	117.7(4)
C5′–C10′–C9′	117.5(3)	C14–C15–C16	119.3(3)
C1–C10–C5	119.1(3)	C14′–C15′–C16′	120.0(4)
C1–C10–C9	123.4(39)	C12–C16–C15	118.2(3)
C2–C3–C4	122.0(3)	C12′–C16′–C15′	118.3(3)
C3–C4–C5	122.8(3)		
C12–N1–C11–C1	−178.53(0.29)		
C11–N1–C12–N2	−3.18(0.44)		
C11–N1–C12–C16	176.28(0.30)		
C12′–N1′–C11′–C1′	179.39(0.31)		
C11′–N1′–C12′–N2′	−0.95(0.48)		
C11′–N1′–C12′–C16′	178.92(0.31)		
C10–C1–C2–O1	177.84(0.29)		
C11–C1–C2–O1	−0.29(0.49)		
C10′–C1′–C2′–O1	−176.67(0.31)		
C11′C1′C2′O1′	5.45(0.50)		

given in Table 3 and the bond lengths and angles with some selected torsion angles are given in Table 4. The structure of the Schiff base ligand (**2**) is the same both in solid state and in solution. Phenol–imine and keto–amine forms do exist in the solid state. When the phenol–imine form is transformed into the keto–amine form, an appreciable increase in the C=N distance is observed ((C11′=N1′ 1.317(4) Å versus C11–N1:1.330(4) Å). However, in naphthaldimine derivatives, only the keto–amine form is dominant as in (*N*-(α-naphtyl)-2-oxo-1-naphthaldimine) (N–O: 2.536, N–H: 0.851) [32] and (*N*-*n*-propyl-2-oxo-1-naphthylidenemethylamine) (N–O: 2.578(2), N–H: 0.775, H···O: 1.936 Å) [33]. A concomitant decrease in the C–O distance is also noted ((C2′–O1′: 1.279(4) Å; C2–O1: 1.263(4) Å). The corresponding bond lengths in ($C_{14}H_{15}NO$) and ($C_{15}H_{17}NO$) are 1.23(1) and 1.254(8) Å, respectively [39,40]. In the solid state, the shortening in the C–O bond length can be explained by the quinoidal structure (keto–amine form) as in the 2-hydroxy-1-naphthaldimine derivatives [32]. The C=N imine bond and C–N–C bond angles are (1.317(4) Å; 1.330(4) Å) and (124.2(3)°; 123.2(3)°) compared with 1.313(8) Å and 122.5(6)° values in ($C_{14}H_{15}NO$) [39]. The degrees of planarity for the two molecules in the asymmetric unit are different. Least squares plane calculations show that the keto–amine type molecule as a whole is practically planar. In contrast, the phenol–imine structure is not quite as planar with a maximum dihedral angle of 5.5(9)° between the moieties of the molecule. The intramolecular hydrogen bonds between (N···H–O; N–H···O) for the two different forms are rather short as expected (N1–O1: 2.586(4) Å and N1′–O1′: 2.518(4) Å) with respective angles of 137.09(4) and 136.06(4)°.

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