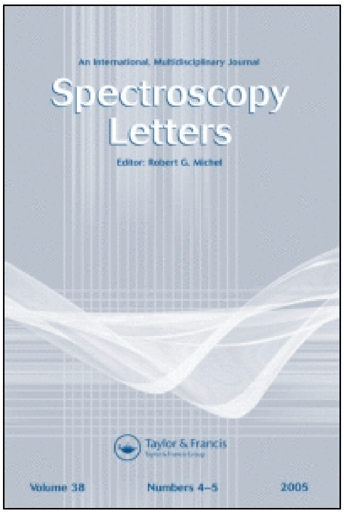

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Tautomerism in Solution and Solid State, Spectroscopic Studies and Crystal Structure of (*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)methylene]-1,8a-dihydronaphthalen-2(3*H*)-one

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Tautomerism in Solution and Solid State, Spectroscopic Studies and Crystal Structure of (*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)methylene]-1,8a-dihydronaphthalen-2(3*H*)-one

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ABSTRACT A new Schiff base compound—(*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)methylene]-1,8a-dihydronaphthalen-2(3*H*)-one—was synthesized by the reaction of 2-hydroxy-1-naphthaldehyde with 2,3,5,6-tetramethyl-p-phenylenediamine. It was investigated by using elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, UV-Visible-spectroscopy, and X-ray-crystallography techniques. Its UV-Visible spectra were examined in polar and nonpolar solvents. The Schiff base studied exists in enol-imine ↔ keto-amine form in DMSO ethanol, chloroform, and benzene solution. The keto-amine tautomer was found to be dominant in both the phases. The (*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)methylene]-1,8a-dihydronaphthalen-2(3*H*)-one molecule is not planar. It contains a strong intramolecular N-H...O hydrogen bond between the amine and oxo group [N1 and O1 = 2.591(2) Å], the H atom being essentially bonded to the N1 and O1 atoms.

KEYWORDS crystal structure, intramolecular hydrogen bond, Schiff base, spectroscopy, tautomerism

INTRODUCTION

Proton tautomerism plays an important role in many fields of chemistry and especially biochemistry.[1–3] The ortho hydroxy Schiff bases form the intramolecular hydrogen bonds, which reveal very interesting properties like photochromism and thermochromism in the solid state,[4–6] attributed to the intramolecular proton transfer reaction. It suggests that the proton transfer state is comparatively easily accessible and that the energy of keto and enol forms should not be very different.[7] Photochromism is produced by an intramolecular proton transfer associated with a change in the π-electron configuration. The presence of ortho hydroxyl group, for

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instance, has been regarded as one of the importance elements that favor the existence of intramolecular hydrogen bonding (O-H...N and O...H-N) and also the tautomerism that accounts for the formation of either enol-imino or keto-amino tautomer.[8–12] The proton transfer process has shown that the position of the tautomeric equilibrium depends not only on the electronic structure of the molecule but also on its conformation.[13] The interactions between the nonbonded atoms in molecules, leading to the strengthening of the hydrogen bond, and the intermolecular interactions in the solid state, stabilizing the planar structure of the molecule, shift the equilibrium toward the keto-amine form.[14,7]

In the field of coordination chemistry, this type of ortho hydroxylated Schiff bases has received overwhelming attention particularly in the study of complex formation.[15–16] Recently, the liquid crystals researchers have also made a significant revelation: The introduction of lateral polar hydroxyl group will enhance the molecular polarizability as well as stabilize the liquid crystalline compounds.[17–19]

In this work, we synthesized the Schiff base (*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)methylene]-1,8a-dihydronaphthalen-2(3*H*)-one and investigated its structure by using FT-IR, UV-VIS, NMR, HETCOR, and X-ray crystallographic techniques in order to study the hydrogen bonding and tautomeric equilibrium in both the solution and the solid states (Fig. 1).

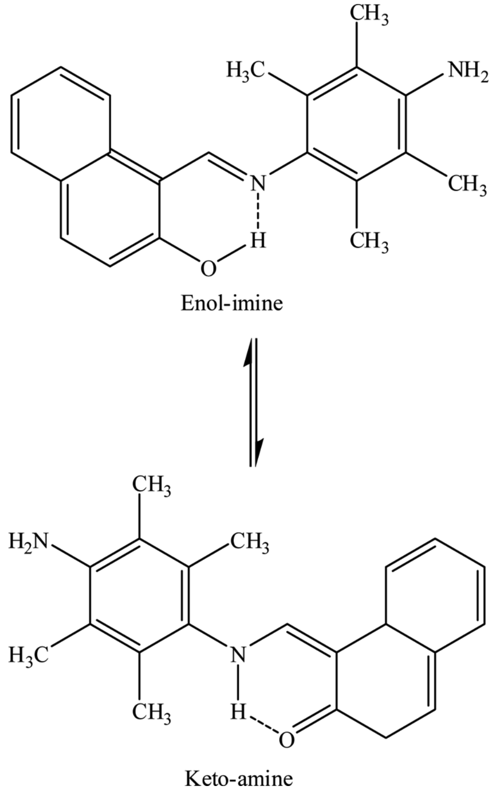

FIGURE 1 Tautomerism of the title compound.

MATERIALS AND METHODS

Reagents and Techniques

The ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer (Bruker AXS, Inc.; United States) operating at 400 and 101.6 MHz. The ^{1}H-NMR and ^{13}C-NMR chemical shifts were measured using $SiMe_4$ as an internal standard. Infrared absorption spectra were obtained from a PerkinElmer BX II spectrometer (PerkinElmer; United States) in KBr discs and were reported in cm^{-1} units. The UV-Visible spectra were measured using a SHIMADZU 1208 series spectrometer (SHIMADZU, Japan). Carbon, nitrogen, and hydrogen analyses were performed on a LECO CHNS-932 analyzer (LECO, USA). Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. 2,3,5,6-Tetramethyl-p-phenylenediamine, 2-hydroxy-1-naphthaldehyde, THF, $CHCl_3$, DMSO, ethanol, benzene, and n-heptane were purchased from Merck (Germany).

Synthesis of (*Z*)-1-[(4-amino-2,3,5,6-tetramethylphenylamino)-methylene]-1,8a-dihydronaphthalen-2(3*H*)-one

Tetramethyl-p-phenylenediamine (0.82 g; 5×10^{-3} mol) was added to a dry THF (100 mL) solution of 2-hydroxy-1-naphthaldehyde (0.86 g; 5×10^{-3} mol). The mixture was stirred and heated for 2 hr. Compound was obtained from the evaporation of THF. It was crystallized from chloroform/n-heptane as yellow crystals, m.p. 229°C, 1.35 g (85%) yields. Found: C, 79.01; H, 6.90; N, 8.67. Calcd.: For $C_{21}H_{22}N_2O$: C, 79.25; H, 6.92; N, 8,81% IR (KBr, cm^{-1}); (Ar-NH_2 and NH; 3423–3357 m, νAr-H; 3058–3030 w, νAliphatic-H; 2924–2862 w, νArC=O; 1617 s, νC=C; 1543 s, νC-N; 1352 m. ^{1}H-NMR(DMSO); δ ppm, 15.64(d, 1H, Ar-N$\underline{H}$-CH=Ar, $^3J_{\underline{H}CN\underline{H}} = 7.00$ Hz); 8.20 (d, 1H, Ar=C$\underline{H}$-N-Ar, $^3J_{\underline{H}NC\underline{H}} = 7.00$ Hz); 7.87–6.92 (m, 6H, Ar-$\underline{H}$); 4.60 (s, 2H, Ar-NH_2), 2.08 (s, 6H, Ar-C$\underline{H_3}$); 2.01 (s, 6H, Ar-CH_3).

X-Ray Crystallographic Details

The structure of the title compound was determined by single-crystal X-ray diffraction. A single deep plate light yellow crystal with approximate dimensions of $0.8 \times 0.3 \times 0.15\,mm^3$ was mounted inside a glass fiber capillary. Data were collected on a Bruker Smart CCD Diffractometer (Bruker AXS, Inc.; United States)[20] at 293 K using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and ω-2θ-scans technique in the range of $2.69^\circ < \theta < 38.56^\circ$C. Empirical absorption correction was applied. A total of 25566 (9244 unique, $R_{int} = 0.0352$) reflections were measured. The structure was solved by direct methods using the program SHELXS-97[21] and refined by full-matrix least squares methods on F^2 using the SHELXL-97[22] program package. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions, and those attached to nitrogen atoms were not located. The hydrogen atoms attached to nitrogen atom (N1) was found from difference Fourier map calculated at the refinement process as a small positive electron density. The details of the X-ray data collection, structure solution, and structure refinements are given in Table 1. The final fractional atomic coordinates and thermal parameters are given in Table 2. Selected bond distances and angles are listed in Table 3. The molecular structure with the atom-numbering scheme is shown in Fig. 2.[23] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 639794.[24]

TABLE 1 Crystal and Experimental Data for the Title Compound

Compound	$C_{21}H_{22}N_2O$
Color/shape	Light Yellow/Plate
Formula weight	318.41
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.0189(2)$ Å
	$b = 8.9642(1)$ Å
	$\beta = 107.742(1)^\circ$
	$c = 14.8644(2)$ Å
Volume	1652.23(4) $Å^3$
Z	4
Density (calculated)	1.280 $g\,cm^{-3}$
Absorption coefficient	0.079 mm^{-1}
$F(0\ 0\ 0)$	680
Crystal size	$0.8 \times 0.3 \times 0.15\,mm^3$
θ Range for data collection	2.69 to 38.56°
Index ranges	$-21 \leq h \leq 22;$ $-15 \leq k \leq 15;$ $-26 \leq l \leq 22$
Reflections collected	25556
Independent reflections	9244
Reflections observed ($I > 2\sigma(I)$)	5894
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5894/0/221
Goodness-of-fit on F^2	1.027
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0588$; $wR_2 = 0.1683$
R indices (All Data)	$R_1 = 0.0952$; $wR_2 = 0.1888$
Largest diff. peak and hole	0.751 and −0.423 $e \cdot Å^{-3}$

RESULTS AND DISCUSSION

Spectroscopic Studies

The FT-IR spectrum of the compound is given in synthetic procedures. The Ar-NH_2 and N-H bond was observed at 3423–3357 cm^{-1} (Fig. 3). The absorption bands assignable to the stretching of

TABLE 2 Fractional Atomic Coordinates and Isotropic Temperature Factors ($Å^2$), with Standard Deviations in the Least Significant Digits in Parentheses for Non-Hydrogen Atoms

Atom	x/a	y/b	z/c	U ($Å^2$)
C1	0.33079(7)	0.58384(10)	0.15471(6)	0.01892(16)
C2	0.42382(8)	0.50873(12)	0.21711(7)	0.02341(19)
C3	0.47966(8)	0.40547(12)	0.18453(7)	0.02354(19)
C4	0.44920(7)	0.36332(10)	0.08659(7)	0.01904(16)
C5	0.50935(8)	0.25548(12)	0.05518(8)	0.02378(19)
C6	0.48130(8)	0.21344(12)	−0.03838(8)	0.02471(19)
C7	0.39071(8)	0.27939(11)	−0.10302(7)	0.02364(19)
C8	0.33039(8)	0.38555(11)	−0.07387(7)	0.02055(17)
C9	0.35840(7)	0.43176(10)	0.02146(6)	0.01637(15)
C10	0.29953(7)	0.54510(9)	0.05591(6)	0.01590(15)
C11	0.21497(7)	0.62388(10)	−0.00800(6)	0.01655(15)
N1	0.15574(6)	0.72611(8)	0.01702(5)	0.01731(14)
C12	0.08022(7)	0.81983(9)	−0.05020(6)	0.01531(15)
C13	−0.02907(7)	0.81492(10)	−0.05423(6)	0.01660(15)
C14	−0.10277(7)	0.90685(10)	−0.11922(6)	0.01775(16)
C15	−0.06553(7)	1.00280(10)	−0.17765(6)	0.01816(16)
C16	0.04339(7)	1.00243(10)	−0.17531(6)	0.01833(16)
C17	0.11780(7)	0.91328(10)	−0.10900(6)	0.01611(15)
C18	−0.06555(8)	0.70889(11)	0.00861(8)	0.02376(19)
C19	−0.22220(8)	0.90182(12)	−0.12964(8)	0.0253(2)
C20	0.07838(9)	1.10030(13)	−0.24338(8)	0.0285(2)
C21	0.23660(7)	0.92632(11)	−0.09962(7)	0.02122(17)
N2	−0.13764(7)	1.09807(10)	−0.24217(6)	0.02395(17)
O1	0.28039(6)	0.68200(9)	0.18764(5)	0.02536(16)

TABLE 3 **Some Selected Bond Lengths (Å), Bond Angles (°) and Torsion Angles (°) for the Title Compound**

C1 O1	1.2806(11)	C11 N1	1.3220(11)
C1 C10	1.4418(13)	N1 C12	1.4395(11)
C1 C2	1.4477(13)	C15 N2	1.4078(12)
C9 C10	1.4564(12)	C12 C17	1.4020(12)
C10 C11	1.4057(12)	C12 C13	1.4064(12)
C1 C10 C9	120.72(8)	C16 C15 C14	121.09(8)
N1 C11 C10	124.19(8)	C16 C15 N2	118.42(9)
O1 C1 C10	122.44(8)	N2 C15 C14	120.46(8)
O1 C1 C2	120.05(8)	C17 C12 C13	122.20(8)
C10 C1 C2	117.50(8)	C17 C12 N1	119.15(7)
C11 C10 C1	119.16(8)	C13 C12 N1	118.65(8)
C2 C1 C10 C9	1.49(13)	C1 C10 C11 N1	−4.97(13)
O1 C1 C2 C3	−179.32(10)	C9 C10 C11 N1	178.48(8)
C4 C9 C10 C11	174.62(8)	C10 C11 N1 C12	170.88(8)
C8 C9 C10 C1	178.23(9)	N1 C12 C17 C21	−4.11(13)
N2 C15 C16 C17	177.32(8)	C11 N1 C12 C13	120.62(9)
C3 C4 C9 C10	0.97(13)	N1 C12 C13 C14	179.57(8)
O1 C1 C10 C11	4.06(14)	N1 C12 C13 C18	−2.20(12)
N2 C15 C16 C20	−1.66(13)	C13 C14 C15 N2	−178.82(8)
N1 C12 C17 C16	179.00(8)	C19 C14 C15 N2	2.84(13)

C=O bond for compound was observed at frequencies of 1617 cm^{-1}, and this value is less than that reported in the IR spectrum for substituted aromatic Schiff base that possesses the formulation of *o*-OH-$C_{10}H_6CH{=}NC_6H_5R$.[11] The O-H stretch at 4000–3500 cm^{-1} region was not observed in the IR spectrum for compound. This observation implies that the H atom from the O-H group in compound migrates to azomethine N atom via the N-H…O intramolecular hydrogen bonding in the solid state. The C=N bond that is accountable partially for the existence of keto-amine form can also be inferred from the IR spectra of compound.

The ^1H NMR data for compound show that the tautomeric equilibrium favors the keto-amine in DMSO (Fig. 4). The NH_2 proton of the compound gave a singlet at $\delta = 4.60$ ppm. The NH and azomethine proton are observed as doublet 15.64 and 9.56 ppm ($^3J_{\underline{H}NC\underline{H}} = 7.00$ Hz) for ligand. The naphthyl protons resonate at $\delta = 7.87$–6.92 ppm multiplet, respectively, for compound. The $ArC\underline{H}_3$ proton of the compound gave a singlet at $\delta = 2.08$ ppm and $\delta = 2.01$ ppm, respectively.

According to the ^{13}C NMR spectra, compound has 17 signals (Fig. 5). ^{13}C-NMR data δ ppm, 173.97 ($\underline{C}9$ ipso, ArC=O), 161.23 ($\underline{C}7$, Ar = CH-NH), 143.43 ($\underline{C}4$ipso, Ar-NH_2) 137.05 ($\underline{C}11$), 134.11 ($\underline{C}1$ ipso, Ar-N=CH), 132.60 ($\underline{C}16$), 129.38 ($\underline{C}12$), 128.53 ($\underline{C}14$), 126.72 ($\underline{C}17$), 126.43 ($\underline{C}3$-$\underline{C}3'$), 124.03 ($\underline{C}15$), 123.25 ($\underline{C}13$), 119.68 ($\underline{C}10$), 118.09 ($\underline{C}2$-$\underline{C}2'$), 107.56 ($\underline{C}8$ ipso,

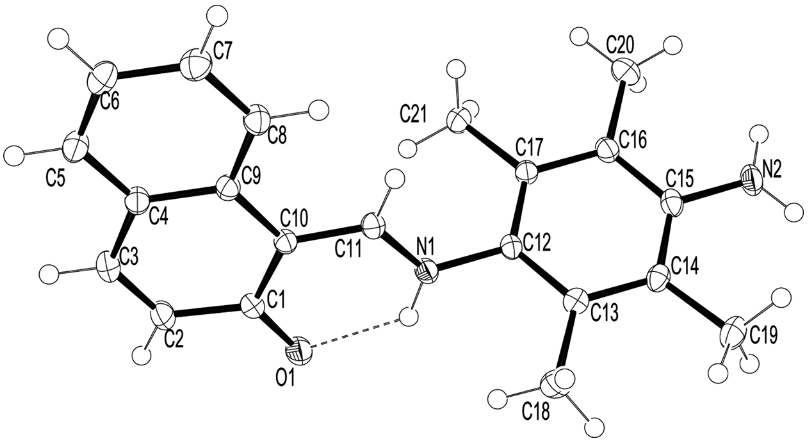

FIGURE 2 **The molecular structure of the title molecule. Displacement ellipsoids are plotted at the 50% probability level.[23]**

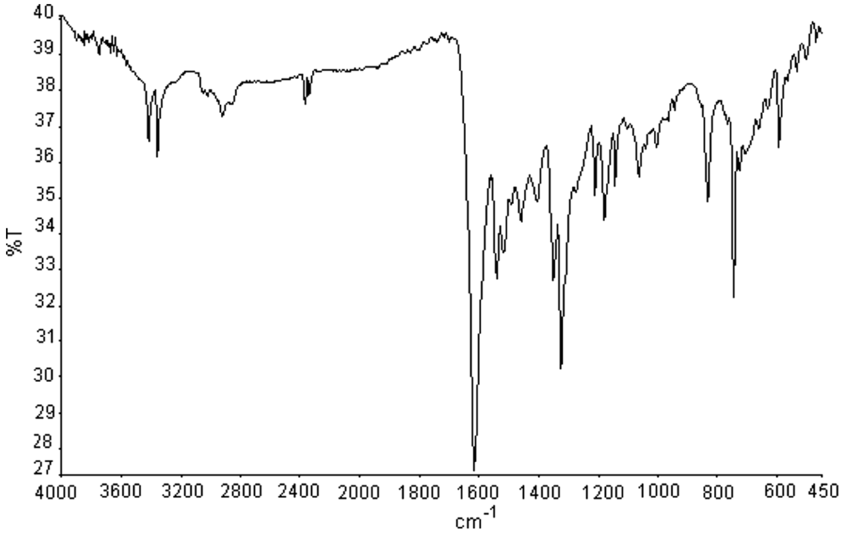

FIGURE 3 FT-IR spectrum of the title molecule.

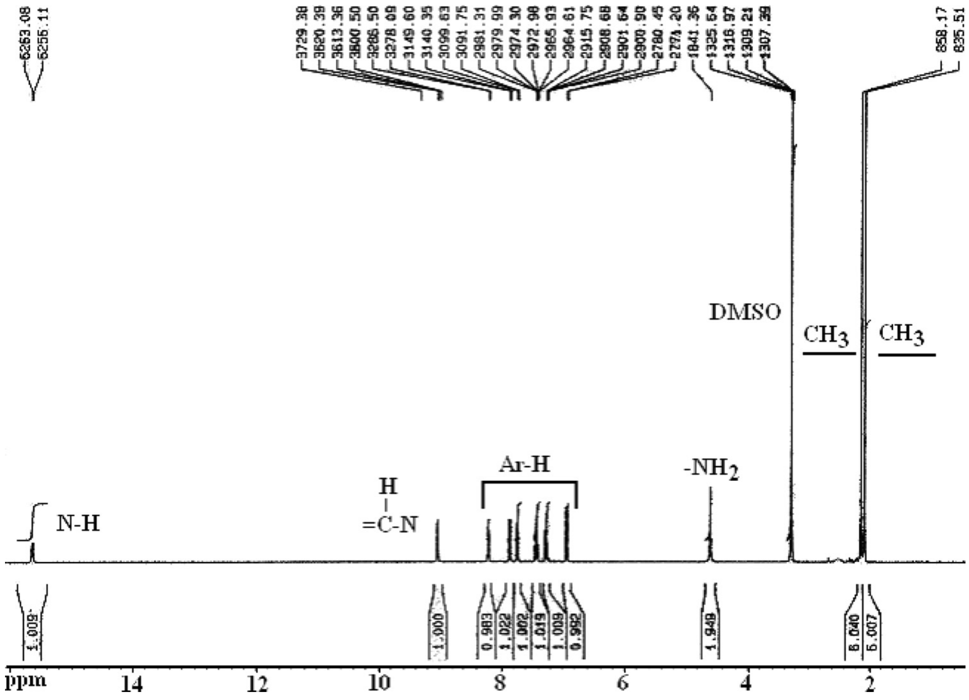

FIGURE 4 ^{1}H-NMR spectrum of the title molecule.

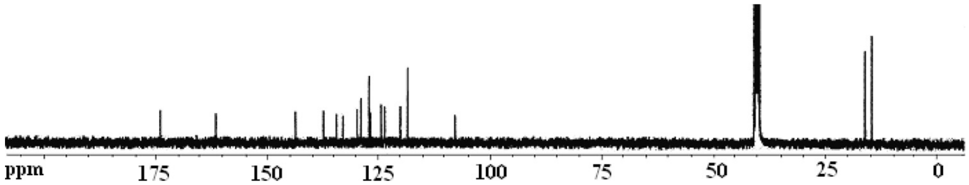

FIGURE 5 ^{1}H-NMR spectrum of the title molecule.

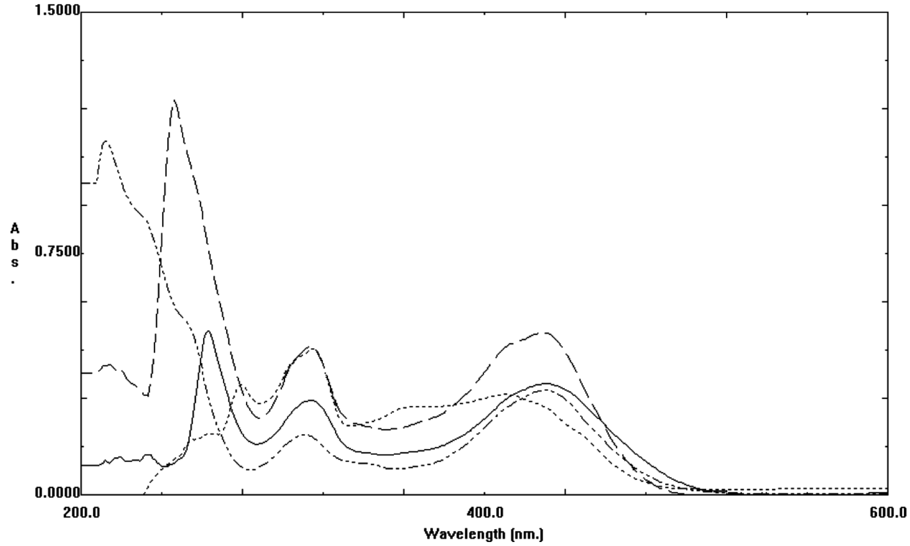

FIGURE 6 Solvent effect on UV spectra of the compound, DMSO (————), ethanol (–··–), CHCl$_3$ (——), benzene (--------).

Ar = CH), 15.82 (C5-C5′), and 14.27 (C6-C6′) (-ArCH$_3$) has been observed for compound. Assignments of the protons and carbons were made by two-dimensional hetero-nuclear-correlated experiments (HETCOR) using delay values that correspond to ^{1}J(C, H), between the carbons and protons (Fig. 7). From HETCOR data, Ar = O and = CH-NH carbons were assigned unambiguously.

The UV-VIS spectra of the compound were studied in polar and nonpolar solvents. The Schiff bases show absorption in the range greater than 400 nm in polar and nonpolar solvents.[9–12,25] We point out that the new band belongs to the keto-amine form of the Schiff bases with OH group in ortho position to the imino group in polar and nonpolar solvents in both acidic and basic media.[9–12] The compound showed absorption above 400 nm in polar (DMSO, ethanol, and chloroform) and nonpolar (benzene) solvents (Fig. 6). The keto-amine tautomer is dominant only in DMSO, ethanol, chloroform and benzene for compound. The calculated keto-amine form is given in Table 4.

TABLE 4 Effect of Solvent on the UV Spectra of Compound

Solvent	Keto-amine tautomer (%)
DMSO	91
EtOH	88
CHCl$_3$	87
Benzene	67

In conclusion, UV-VIS, ^{1}H NMR, and ^{13}C NMR results show that in DMSO solution, the compound exists in the keto-amine form.

Crystallographic Study

Two types of intramolecular hydrogen bonds—N-H . . . O (keto-amine form) and N . . . O-H (enol-imine form)—can exist in 2-hydroxy 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.[26] In the compounds derived from 2-hydroxy-1-naphthaldehyde, both types of hydrogen bonds were found.[27] The title molecule contains a strong intramolecular hydrogen bond between the O1 and N1 atoms [2.591(2) Å], the H atom being essentially bonded to the N1 and O1 atoms as seen in Fig. 1. The sum Van der Waals radius of the O and N atoms (3.07 Å) is significantly longer than intramolecular hydrogen bond lengths.[28]

The title compound is not planar. The molecules **I** [O1, C1-C11; planar with a maximum deviation of 0.0804(7) Å for the C11 atom] and **II** [N1, C12-C21, N2; planar with a maximum deviation of 0.0981(9) Å for the C20 atom] are inclined at an angle of 68.72(1)°. The phenyl rings show small distortions from ideal geometry with the C=C distances for the phenyl rings close to the expected value for aromatic rings [1.394(5) Å].[28] X-ray structure determinations reveal that the keto tautomer is favored over the enol tautomer. This is evident from the observed bond

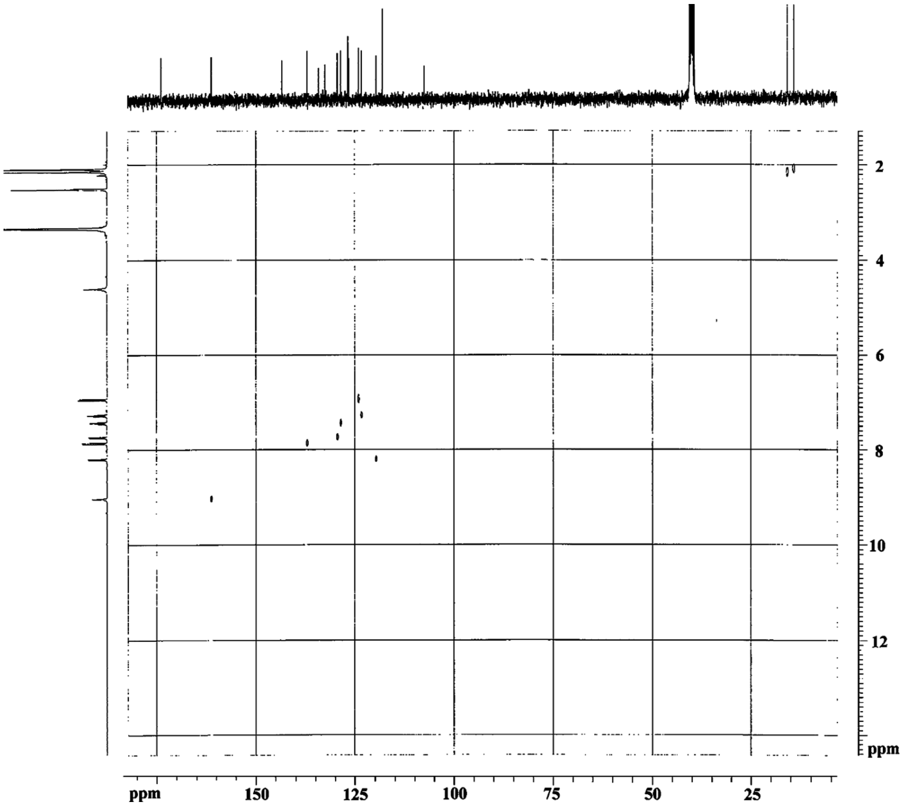

FIGURE 7 HETCOR spectrum of the title molecule.

distance of 1.281(1) Å for O1=C1 atoms, which is consistent with the O=C double bond. Similarly, the C11-N1 distance of 1.322(1) Å is consistent with the C-N single bond.

Thus, crystal structure and molecular structure have been investigated by using IR, ^{1}H-NMR, ^{13}C-NMR, UV-Visible spectroscopy and X-ray crystallography techniques. The IR, electronic, ^{1}H, and, ^{13}C NMR spectra indicate that the keto form is favored in both solution and the solid state. The X-ray structure determination also confirms that the keto tautomer is favored over the enol tautomer in the title compound.

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REFERENCES

1. Peng, B. H.; Liu, G. F.; Liu, L.; Jia, D. Z. Studies on solid-state proton transfer along hydrogen bond of pyrazolone-ring. *Tetrahedron* **2005**, *61*(24), 5926–5932.
2. Garnovskii, A. D.; Vasil'chenko, I. S. Tautomerism and various coordination modes of typical chelating agents with metals. *Usp. Khim.* **2005**, *74*(3), 211–234.
3. Raczynska, E. D.; Kosinska, W.; Osmialowski, B.; Gawinecki, R. Tautomeric equilibria in relation to pi-electron delocalization. *Chem. Rev.* **2005**, *105*(10), 3561–3612.
4. Cohen, M. D.; Schmidt, G. M. J.; Flavian, S. Topochemistry: VI. Experiments on photochromy and thermochromy of crystalline anils of salicylaldehydes. *J. Chem. Soc.* **1964**, 2041–2051.
5. Moustakalimavridis, I.; Hadjoudis, E.; Mavridis, A. Structure of thermochromic Schiff-bases: 2. Structures of n-salicylidene-3-aminopyridine and n-(5-methoxysalicylidene)-3-amiinopyridine. *Acta Crystallogr., Sect. B: Struct. Sci.* **1980**, *36*, 1126–1130.
6. Hadjoudis, E.; Vitterakis, M.; Moustakalimavridis, I. Photochromism and thermochromism of Schiff-bases in the solid-state and in rigid glasses. *Tetrahedron* **1987**, *43*(7), 1345–1360.
7. Filarowski, A.; Glowiaka, T.; Koll, A. Strengthening of the intramolecular O···H···N hydrogen bonds in Schiff bases as a result of steric repulsion. *J. Mol. Struct.* **1999**, *484*, 75–89.
8. Elmalı, A.; Kabak, M.; Kavlakoglu, E.; Elerman, Y.; Durlu, T. N. Tautomeric properties, conformations and structure of N-(2-hydroxy-5-chlorophenyl) salicylaldimine. *J. Mol. Struct.* **1999**, *510*, 207–214.
9. Yıldız, M.; Kılıç, Z.; Hökelek, T. Intramolecular hydrogen bonding and tautomerisim in Schiff bases: Part I. Structure of 1,8-di[N-2-oxyphenyl-salicylidene]-3,6-dioxaoctane. *J. Mol. Struct.* **1998**, *441*, 1–10.
10. Nazır, H.; Yıldız, M.; Yılmaz, H.; Tahir, M. N.; Ülkü, D. Intramolecular hydrogen bonding and tautomerisim in Schiff bases: Structure of N-(2-pyridil)-2-oxo-1-naphthylidenemethylamine. *J. Mol. Struct.* **2000**, *524*, 241–250.
11. Ünver, H. Synthesis and spectroscopic studies in some new Schiff bases. *Spectrosc. Lett.* **2001**, *34*, 783–791.
12. Yıldız, M. Synthesis and spectroscopic studies of some new polyether ligands of Schiff base type. *Spectrosc. Lett.* **2004**, *37*, 367–381.

13. Schilf, W.; Kamienski, B.; Dziembowska, T. Intramolecular hydrogen bond investigations in Schiff bases derivatives of 2-hydroxy-1-naphthaldehyde and 2-hydroxy-1-acetonaphthone in $CDCl_3$ solution and in the solid state by NMR methods. *J. Mol. Struct.* **2002**, *602*, 41–57.
14. Dziembowska, T. Resonance assisted intramolecular hydrogen bond in Schiff bases. *Pol. J. Chem.* **1998**, *72*, 193–209.
15. Yeap, G. Y.; Teoh, S. G.; Teo, S. B.; Loh, C. S.; Fun, H. K. Inner sphere complexes derived from the coordinate interactions of tin(IV) isothiocyanate moieties with 1-[(4-methylphenylimino)methyl]-2-phenol: Crystal structure of diisothiocyanatodimethylbis {1-[(4-methylphenylimino) methyl]-2-phenol}tin(IV), Me(2)Sn(NCS)(2)center dot[HOC_6H_4CH:$NC_6H_4CH_3$](2). *Polyhedron* **1996**, *15*, 3941–3946.
16. Popovic, Z.; Roje, V.; Pavlovic, G.; Calogovic, D. M.; Giester, G.; Rajic, M. Preparation and characterization of the 1:1 adducts of mercury(II) halides with N-benzyl- and N-p-tolyl-2-oxo-1-naphthylideneamine: The crystal and molecular structures of two isostructural di-mu-halo-bis[halo(N-benzyl-2-oxo-1-naphthylideneamine)-mercury(II)] adducts (halo = chloro, bromo). *Inorg. Chim. Acta* **2001**, *322*, 65–73.
17. Caruso, U.; Roviello, A.; Sirigu, A. Thermotropic mesomorphism in some Cu(II) and Pd(II) metallorganic complexes. *Liq. Cryst.* **1988**, *3*, 1515–1523.
18. Rao, N. V. S.; Singha, D.; Das, M.; Paul, M. K. Synthesis and mesomorphic properties of N(4-n-alkyloxy salicylidene)4′-n-alkylanilines and their copper complexes: I. *Mol. Cryst. Liq. Cryst.* **2002**, *373*, 105–117.
19. Prajapati, A. K.; Vora, R. A.; Pandya, H. M. Effect of lateral hydroxy/alkoxy group on mesomorphism of azobenzene derivatives. *Mol. Cryst. Liq. Cryst.* **2001**, *369*, 37–46.
20. Bruker AXS, Inc. *Smart CCD Diffractometer* Version 5.054; Bruker AXS, Inc.: Madison, Wisconsin, United States, 1998.
21. Sheldrick, G. M. Phase annealing in Shelx-90: Direct methods for larger structures. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467–473.
22. Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
23. Farrugia, L. J. *ORTEP*-3 for Windows - a version of *ORTEP*-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **1997**, *30*, 565.
24. Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC 639794 E-mail: deposit@ccdc.cam.ac.uk.
25. Salman, S. R.; Shawkat, S. H.; Al-Obaidi, G. M. Tautomerism in ortho-hydroxy Schiff-bases – effect of alkyl group. *Can. J. Anal. Sci. Spectros.* **1990**, *35*, 25–27.
26. Gavranic, M.; Kaitner, B.; Mestrovic, E. Intramolecular N-H O hydrogen bonding, quinoid effect, and partial pi-electron delocalization in N-aryl Schiff bases of 2-hydroxy-1-naphthaldehyde: The crystal structures of planar N-(alpha-naphthyl)- and N-(beta-naphthyl)-2-oxy-1-naphthaldimine. *J. Chem. Crystallogr.* **1996**, *26*, 23–28.
27. Kaitner, B.; Pavlovic, G. A reinvestigation of the quinoidal effect in N-n-propyl-2-oxo-1-naphthylidenemethylamine. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 2573–2575.
28. Bondi, A. Wan Der Waals Volumes + Radii. *J. Phys. Chem.* **1964**, *68* (3), 441.