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ORIGINAL PAPER

Spectroscopic Studies and Crystal Structure of 3-[(2-morpholinoethylimino)methyl]benzene-1,2-diol

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Abstract Schiff base 3-[(2-morpholinoethylimino)methyl] benzene-1,2-diol has been synthesized from the reaction of 4-(2-aminoethyl)morpholine with 2,3-dihydroxybenzaldehyde. The title compound has been characterized by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and UV–visible techniques. The structure of the compound also has been examined crystallographically. For the compound exist as dominant form of enol-imines in both the solutions and solid state. The crystal structure has been solved by direct methods and refined by full-matrix least squares. The title compound crystallize in the monoclinic space group $P2_1/n$ with $a = 12.085(1)$, $b = 8.256(1)$, $c = 13.650(1)$ Å, $\beta = 108.56(1)°$, $V = 1291.1(2)$Å^3, $D_x = 1.288$ g cm^{-3}, respectively ($R_1 = 0.0336$ and w$R_2 = 0.0922$ for 2117 reflections [$I > 2\sigma(I)$].

Keywords Schiff base · Spectroscopy · Crystal structure · FT-IR · ^{1}H-NMR

Introduction

Many salicylidene anilines being relatively simple in structure and exhibiting intramolecular proton transfer, have, therefore, attracted considerable attention from both experimental [1–3] and theoretical points of view [4–8]. Schiff bases derived from the condensation of salicylaldehyde with aniline and with substituted aniline and naphthaldehyde with aniline and exists as enol-imine [9–17], keto-amine [18], or enol-imine/keto-amine form [19–23] in all solvents.

The UV–visible spectrum of *ortho* hydroxylated Schiff bases which exists mainly as enol-imine structure indicate the presence of a band at <400 nm, while compounds exists either as keto-amine or as mixture of enol-imine/keto-amine forms show a new band, especially in polar solvents at >400 nm. Different methods were used to show the presence of the enol-imine and keto-amine forms, amongst them are UV–visible, IR, MS, ^{1}H-, ^{13}C-, ^{14}N-NMR spectroscopy and X-ray crystallographically [13–20]. *N*-salicylideneaniline derivatives have been shown to exist as tautomeric forms due to intramolecular proton shifts between the phenol–oxygen and the imine–nitrogen, via intramolecular hydrogen bonding O–H···N or O···H–N [13, 24–34]. These prototropic shifts in solution and in the crystal. Some crystals of such internally hydrogen bonded Schiff bases exhibit thermochromism by a thermally induced intramolecular proton shift to the keto-amine tautomer, or photochromism, by an irradiation-induced proton migration [35, 36].

In this study, we have synthesized new Schiff base and investigated by using IR, ^{1}H-NMR, ^{13}C-NMR, UV–visible and X-ray crystallographic techniques in order to study the hydrogen bonding and tautomeric equilibrium in both the solution and solid states (Scheme 1).

Experimental

Reagents and Techniques

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400 and

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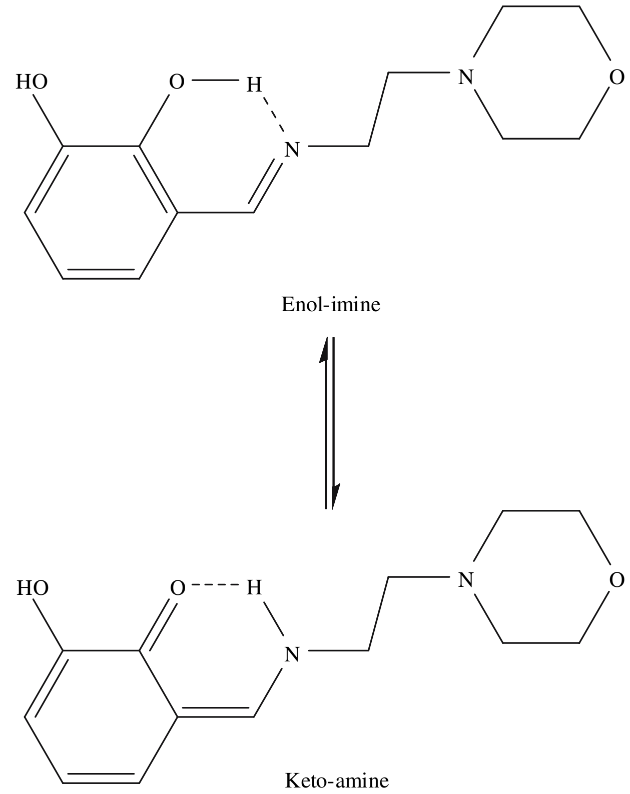


Scheme 1 Tautomerisim of the title compound

101.6 MHz. The ^{1}H- and ^{13}C-NMR chemical shifts were measured using SiMe$_4$ as an internal standard. Infrared absorption spectra were obtained from a Perkin Elmer BX II spectrometer in KBr discs and were reported in cm^{-1} units. The UV–visible spectra were measured using a SHIMADZU 1208 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed on a LECO CHNS-932 analyzer. Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. 4-(2-aminoethyl) morpholine, 2,3-dihydroxybenzaldehyde, THF, CHCl$_3$, EtOH, benzene, DMSO were purchased from Merck (Germany).

Synthesis of 3-[(2-morpholinoethylimino)methyl] benzene-1,2-diol

4-(2-aminoethyl) morpholine (1.30 g; 1 × 10^{-2} mol) was added to a dry THF (100 mL) solution of 2,3-dihydroxybenzaldehyde (1.38 g; 1 × 10^{-2} mol). The mixture was stirred and heated for 2 h. Compound was obtained from the evaporation of THF. It was crystallized from chloroform/*n*-heptane as a yellow crystal, m.p. 135 °C, 2.13 g (85 %) yield. Found: C, 62.18; H, 7.13; N, 11.10. Calc. For $C_{13}H_{18}N_2O_3$; C, 62.40; H, 7.20; N, 11.20%. IR (KBr, cm^{-1}); νO–H; 3,448 m, νAr–H; 3,057 w, νC–H; 2,971–2,933–2,872 m, νO–H···N; 2,821 m, νC=N; 1,630 s, νC=C; 1,468 s, νC–N; 1,374 m, νC–O; 1,320 m, 1,271 s, νC–O–C; 1,259 s, 1,230 s, 1,115 s, 1,071 m.

Crystallography

The data were collected on a STOE IPDS II imaging plate diffractometer [37] using plane graphite monochromated MoK$_\alpha$ radiation. Preliminary cell constants were obtained from 165 narrow frame (frame wide = 1° in w) data. Final cell parameters were obtained by global refinement of reflections obtained from integration of all frame data. A total of 331 frames were collected with a frame wide of 1° in w and a counting time of 1 min. per frame at a crystal-to-detector distance of 10 cm. The multiple pinhole method of scanning was used to exclude any noise. The collected frames were integrated using the preliminary cell orientation matrix. The integration process yielded a total of 16,281 reflections of which 2,527 were independent reflections. Data collections and cell refinement were made by using the program STOE X-AREA [37]. Data reduction and absorption correction by integration method was carried out by using STOE X-RED [37] program. The structure was solved by direct methods using SHELXS-97 [38] and refined by full-matrix least squares using SHELXL-97 [39]. All hydrogen atoms were located from a difference Fourier map and refined isotropically. $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1413P]$ where $P = (F_o^2 + 2F_c^2)/3$. The details of the X-ray data collection, structure solution and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. The molecular structure with the atom-numbering scheme is shown in Fig. 1 [40]. Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 264162 [41].

Result and Discussion

FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV–visible Spectroscopic Studies

The IR spectra of the compounds are given in synthetic procedures. Vibration bands with the wave numbers of 3,448 (ν_{O-H}), 3,054 cm^{-1} (ν_{C-H}, Ar–H), 1,630 cm^{-1} ($\nu_{C=N}$), 1,468 cm^{-1} ($\nu_{C=C}$), 1,374, 1,271 cm^{-1} (ν_{C-O}, Ar–O) and 1,259, 1,230, 1,115, 1,071 cm^{-1} (ν_{C-O-C}, Csp^3–O–Csp^3) were observed for compound, respectively Fig. 2. The stretching frequency observed at 2,849 and 2,821 cm^{-1} in compound shows the presence of O–H···N intramolecular

Table 1 Crystal and experimental data

Compound	$C_{13}H_{18}N_2O_3$
Compound weight	250.29
CCDC deposit No.	264162
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal dimension	0.25 × 0.33 × 0.42 mm^3
Unit cell parameters	
a	12.0850(10) Å
b	8.2563(5) Å
c	13.6500(12) Å
β	108.564(6)°
V	1291.10(17) $Å^3$
Z	4
D_c (g cm^{-3})	1.288 g cm^{-3}
μ(MoKα)	0.092 mm^{-1}
$F(000)$	536
$2\theta_{max}$	59.30°
h, k, l range	$-14 \leq h \leq 14$
	$-10 \leq k \leq 10$
	$-16 \leq l \leq 16$
Maximum and minimum transmission	0.9880 and 0.9349
Goodness of fit on F^2	1.069
No. of reflections used	2527
Final R indices[$I > 2\sigma(I)$]	R_1 = 0.0336 and wR_2 = 0.0922
R indices (all data)	R_1 = 0.0436 and wR_2 = 0.0977
Measurement	STOE IPDS 2
Program system	STOE X-AREA
Structure determination	SHELXS-97
	Refinement: full matrix
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	0.178, −0.127e $Å^{-3}$

Table 2 Some selected bond lengths (Å), bond angles (°) and torsion angles (°)

O1 C1	1.337(1)	C3 C2 C1	119.8(1)
N2 C9	1.468(1)	N1 C8 C9	109.5(1)
N1 C7	1.276(2)	N1 C8 H8A	108.4(8)
N1 C8	1.461(1)	N1 C8 H8B	107.4(8)
C6 C1	1.403(2)	C5 C4 C3	120.2(1)
C6 C7	1.450(2)	C8 N1 C7 C6	176.9(1)
C1 C2	1.406(2)	C5 C6 C7 N1	−179.5(1)
O2 C2	1.357(2)	C1 C6 C7 N1	−1.3(2)
C1 O1 H1	101.8(1)	C5 C6 C1 O1	−179.7(1)
C7 N1 C8	119.9(1)	C7 C6 C1 O1	2.1(2)
C1 C6 C7	120.0(1)	C5 C6 C1 C2	1.6(2)
N1 C7 C6	122.1(1)	C7 C6 C1 C2	−176.7(1)
N1 C7 H7	120.6(1)	O1 C1 C2 O2	−1.0(2)
O1 C1 C6	122.4(1)	C6 C1 C2 O2	177.8(1)
O1 C1 C2	118.3(1)	O1 C1 C2 C3	178.7(1)
C6 C1 C2	119.2(1)	C6 C1 C2 C3	−2.5(2)
C2 O2 H2	114.0(1)	O2 C2 C3 C4	−178.6(1)
O2 C2 C3	119.3(1)	C7 N1 C8 C9	108.3(1)
O2 C2 C1	121.0(1)		

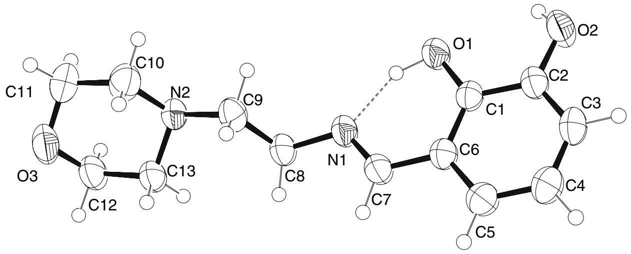


Fig. 1 The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level [40]

hydrogen bond [13, 14]. The C=N bond which is accountable partially for the existence enol-imine form can also be inferred from the IR spectra of compound. The compound with strong band at 1,271 cm^{-1} possesses highest percentage of enol-imino tautomer due to the stabilization of phenolic C–O bond [42].

^{1}H-NMR spectra of some Schiff bases were measured in a range of solvents, and the presence of a $^3J_{(C\underline{H}N\underline{H})}$ coupling between the exchangeable and the olefinic proton, confirmed by decoupling, was interpreted as being due to the presence of the keto-amine tautomer. This coupling and $^1J_{(N\underline{H})}$ were measured in a range of solvents and, with a good reference value for this in a non-tautomeric situation of 96 Hz; it is then possible to deduce a value for $^3J_{(C\underline{H}N\underline{H})}$ for pure keto-amine tautomer of 11.6 Hz [43]. The ^{1}H-NMR data for compound show that the tautomeric equilibrium favours the enol-imine in DMSO. The OH and azomethine protons are observed as singlets δ = 13.75 and δ = 8.87 ppm, and δ = 8.20 ppm, respectively for compound. The phenyl protons resonate at δ = 6.45–6.72 ppm multiplet, the OC$\underline{H_2}$ protons of the compound gave a triplet at δ = 3.59 ppm (4H, OC$\underline{H_2}$, $^3J_{HH}$ = 5.40 Hz). The Ar–C=N–C$\underline{H_2}$– and –N–C$\underline{H_2}$CH$_2$O– protons are equivalent for compound. These protons are observed as triplets 3.46 ppm (6H, $^3J_{HH}$ = 5.45 Hz) for compound. Ar–C=N–CH$_2$C$\underline{H_2}$–N protons of the compound gave a triplet at δ = 2.48 ppm (2H, $^3J_{HH}$ = 5.45 Hz).

According to the proton de-coupled ^{13}C-NMR spectra compound has 10 signals Fig. 3. The compound seems to have symmetric carbon atoms (10, 10′ and 11, 11′) in solution (Scheme 2). The aliphatic –ArC=N–$\underline{C}$(8)– and –N–$\underline{C}$–CH$_2$O(10 and 10′) carbons are found to be equivalent for compound. The C=N–$\underline{C}$(8)– and –N–$\underline{C}$–(10 and 10′) carbons are observed at δ = 58.79 ppm for compound. The chemical shifts δ ppm; 166.9 (s, 1C, C7, –$\underline{C}$H=N–), 154.2 (s, 1C, C2, $\underline{C}$ipso–, OH), 146.87 (s, 1C3, $\underline{C}$ipso, –OH), 122.31 (s, 1C6), 117.77 (s, 1C1), 117.47 (s, 1C5),

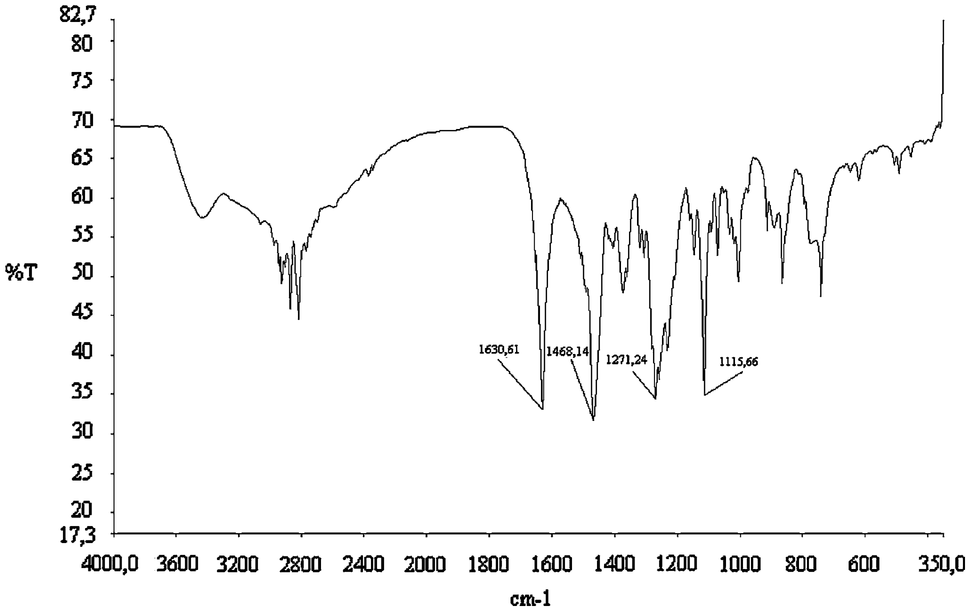


Fig. 2 FT-IR spectra of compound in the solid state (KBr)

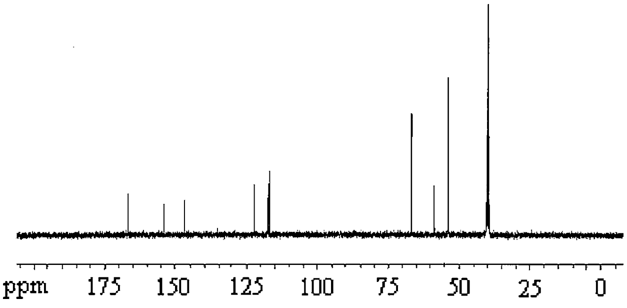


Fig. 3 ^{13}C-NMR spectra of the compound

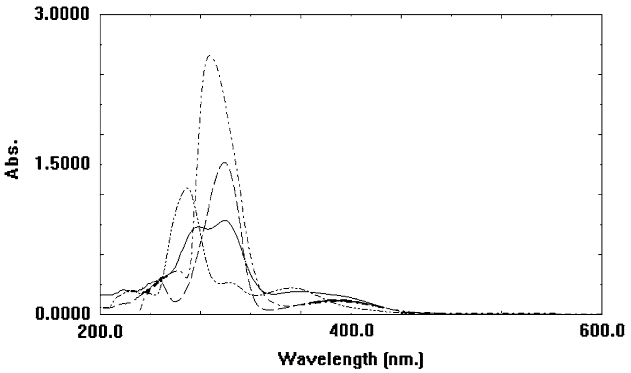
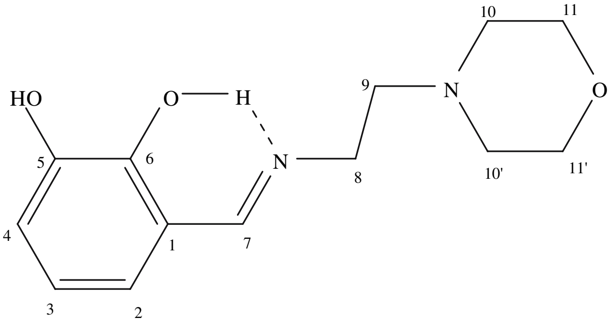


Fig. 4 Solvent effect on compound. DMSO ——, Ethanol –·–·–, $CHCl_3$ - - - - -, Benzene – – – –, Schiff base concentration 5 × 10^{-5} mol dm^{-3}



Scheme 2 Numerous carbon atoms of the title compound. Molecular structure of the title compound which is numbered for ^{13}C NMR identification

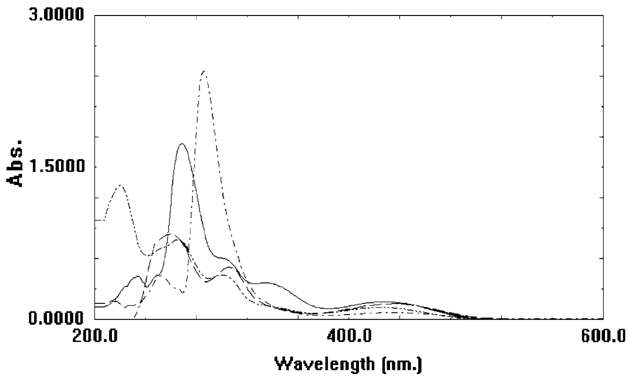


Fig. 5 Acid effect on compound. DMSODMSO ——, Ethanol –·–·–, $CHCl_3$ - - - - -, Benzene – – – –, Schiff base concentration 5 × 10^{-5} mol dm^{-3}

117.12 (s, 1C4) and 66.66 (s, 2C11 and 11′, –O$\underline{C}H_2$), 53.75 (s, 1C9, ArC=N–$CH_2\underline{C}$–).

The UV–visible spectra of the compound were studied in polar (DMSO, ethanol and chloroform) and non-polar (benzene) solvents both in acidic and basic media (Figs. 4–6). The Schiff bases show absorption in the range greater than

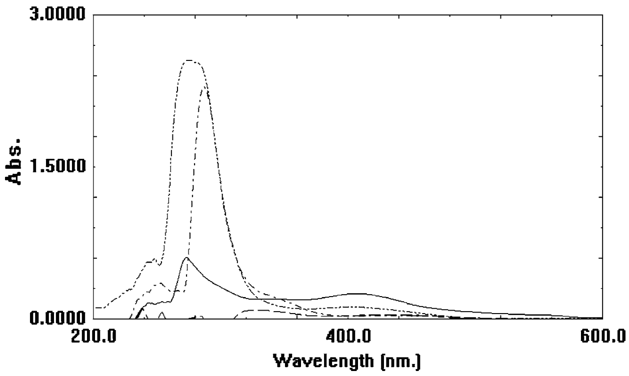


Fig. 6 Base effect on compound. DMSO ——, Ethanol –·–·–, $CHCl_3$ - - - - -, Benzene – – – –, Schiff base concentration 5 × 10^{-5} mol dm^{-3}

400 nm in polar and non-polar solvents [9–16]. It is pointed 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 non-polar solvents in both acidic and basic media [9–16, 28]. The calculated keto-amine form is given in Table 3. The compound showed absorption above 400 nm in polar (DMSO, ethanol and chloroform) and non-polar (benzene) solvents and acidic (CF_3COOH, pH = 2) chloroform and benzene and basic ($[C_2H_5]_3N$, pH = 9) DMSO, ethanol, chloroform and benzene solutions. The band was not observed with value greater than 400 nm in acidic solutions of DMSO and ethanol for compound (Figs. 3–5). The enol-imine tautomer is dominant in the all-pure solvents, in acidic and basic solutions for compound. The keto-amine tautomer ratio was increased by 85% and 216%, respectively in the acidic chloroform and benzene solutions and 133% and 96% in the basic DMSO and ethanol solutions with respect to the pure solvent media, while it was not changed in the basic chloroform and benzene solutions [14–16]. The absence of keto-amine form in the acidic DMSO and ethanol solutions may be explained by the hydrogen bonding to acid (CF_3COOH) [13].

In conclusion; UV–visible, ^{1}H-NMR and ^{13}C-NMR results show that the compound exists in the enol-imine form in DMSO solution.

Crystallographic Study

The title molecule is not planar. The plane through the C atoms of the morpholine ring makes a dihedral angle of 56.98(4)° with the Schiff base moieties (O1, O2, C1, C2, C3, C4, C5, C6, C7, and N1). The morpholine ring adopts a chair conformation, with a total puckering amplitude of Q_T = 0.576(2) Å [44]. In the morpholine ring, bond lengths and angles conform to those found previously [45].

There is a strong intramolecular hydrogen bond between O1 and N1 atom while H···N distance is 1.68(2) Å. The O1···N1 distance of 2.575(1) Å is clearly indicative of strong intramolecular hydrogen bonding; a criterion for hydrogen bonding between oxygen and nitrogen atoms is considered to be that the distance O···N should be shorter than the sum, 3.07 Å, of the van der Waals radii [46]. The intramolecular O1···N1 hydrogen bond length can be compared with N-(2-hydroxy-1-naphtylidene)4-aminomorpholine [44] 2.573(3) Å, 2-(3-methoxy-2-hydroxyphenyl) benzimidazole [47] 2.577(6) Å and 3,3′-dimethoxybenzydine(2-hydroxybenzal)diimine [48] 2.568(3) Å.

C–H···X hydrogen bonds have been postulated to stabilize the geometries of many organic compounds in the solid state [49, 50]. The crystal structure is stabilized by a strong intermolecular hydrogen bond between O2···N2^i [O2···N2^i 2.849(1) Å, O2–H2 0.90(2) Å, H2···N2^i 2.01(2) Å, O2–H2···N2^i 154.5(2)°; symmetry code: (i) −x, −y + 2, −z].

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 1.337(1) Å, which is consistent with the O–C single bond; similarly the N1–C7 distance of 1.276(2) Å is also consistent with the N=C double bonding.

Table 3 Effect of solvent, acid, and base on the UV spectra of compound

	Solvent	λ, nm (ε, M^{-1} cm^{-1})	Keto-amine tautomer (%)		
			Solvent media	Acidic media^a	Basic media^b
Compound	DMSO	425(34409), 334(7180), 269(34640)	15	–	40
	EtOH	425(2360), 300(8760) 266(15760), 220(26740)	13	–	25
	$CHCl_3$	434(3080), 306(10280) 259(16780)	10	17	9
	Benzene	432(1300), 286(49320)	3	13	3

[a] CF_3COOH

[b] $[(C_2H_5)_3N]$

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