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Synthesis, spectral studies of salicylidine-pyridines: Crystal and molecular structure of 2-[(1*E*)-2-aza-2-(5-methyl (2-pyridyl)ethenyl)]-4-bromobenzen-1-ol

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Abstract

Schiff bases derived from different *meta*-substituted salicylaldehyde and 5-methylaminopyridine have been synthesized and characterized by elemental analysis, FT-IR, NMR and UV–vis techniques. NMR assignments were made using ^{1}H, ^{13}C NMR and aided by 2D HETCOR and HMBC heteronuclear correlation techniques. The UV–vis spectra of the compounds were found useful in understanding the existence of tautomeric equilibria [phenol-imine (O–H···N) and keto-amine (O···H–N) forms] in polar and non-polar solvents. In order to rationalize the stabilization of tautomer in solid state, X-ray structure of 2-[(1*E*)-2-aza-2-(5-methyl(2-pyridyl)ethenyl)]-4-bromobenzen-1-ol (**6**) was determined. According to our crystallographic result, it has enol-imine tautomeric form.

Keywords: Schiff bases; Tautomerism; HETCOR; HMBC; Crystal structure

1. Introduction

Schiff bases are a class of important compounds with medical and pharmaceutical applications. They show antibacterial [1–3] antifungal [4,5] and herbicidal [6] activities. Introduction of a hydroxyl group enhances molecular polarizability and stabilize the liquid crystalline compounds [7,8]. The presence of *ortho*-hydroxyl group, for instance, has been regarded as one of the important elements which favours for the existence of intramolecular hydrogen bonding (O–H···N and O···H–N) and also the tautomerism which accounts for the formation of either enol-imino or keto-amino tautomer [9]. Tautomerism in shiff bases, with an OH group in ortho position to the imino group both in solution and in solid state, have been investigated using spectroscopy and X-ray crystallography techniques [10–12].

In these compounds short hydrogen bonds between the OH group and the imine nitrogen are formed. In some instances the hydrogen atom of the OH is completely transferred to the imine nitrogen. In other words, enol-imine keto-amine equilibrium shifts predominantly to the keto-amine side [10–15].

In the present work, we report: (i) the synthesis of Schiff bases obtained from the reaction of salicylaldehydes and aminopyridines and (ii) structural and spectroscopic characterization of these compounds. Total assignments of ^{1}H and ^{13}C NMR spectra for the structure are made with the help of H–H correlation spectroscopy (H–H COSY), as well as heteronuclear chemical shift correlation (HETCOR) and heteronuclear multiple-bond correlation (HMBC). The effects attributed to the emergence of the tautomeric conformers in crystal and liquid phases were studied by spectroscopic methods and X-ray diffraction analysis.

2. Experimental

2.1. Reagents and techniques

2-Hydroxybenzaldehyde, 2-hydroxy-5-bromobenzaldehyde, 2-hydroxy-5-chlorobenzaldehyde, aminopyridine and 5-methylaminopyridine were purchased from Fluka and used without further purification. Tetrahydrofuran, *n*-hexane, chloroform and methanol were dried by standard methods prior to use and kept under argon atmosphere. All experimental

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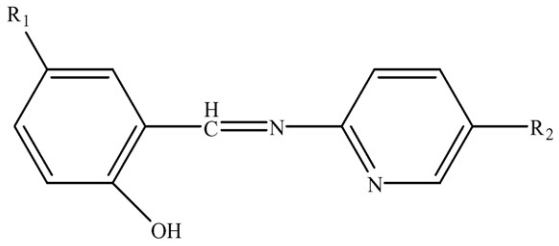


Compound	IUPAC Name	R_1	R_2
1	2-[(1E)-2-aza-2-(2-pyridyl)ethenyl]benzen-1-ol	H	H
2	2-[(1E)-2-aza-2-(2-pyridyl)ethenyl]-4-chlorobenzen-1-ol	Cl	H
3	2-[(1E)-2-aza-2-(2-pyridyl)ethenyl]-4-bromobenzen-1-ol	Br	H
4	2-[(1E)-2-aza-2-(5-methyl(2-pyridyl)ethenyl]benzen-1-ol	H	CH_3
5	2-[(1E)-2-aza-2-(5-methyl(2-pyridyl)ethenyl]-4-chlorobenzen-1-ol	Cl	CH_3
6	2-[(1E)-2-aza-2-(5-methyl(2-pyridyl)ethenyl]-4-bromobenzen-1-ol	Br	CH_3

Scheme 1.

manipulations were carried out under argon atmosphere. Melting points were measured on a Gallenkamp apparatus using a capillary tube. Elemental analysis (C, H and N) were performed using a Vario EL III CHNS elemental analyzer. UV spectra were measured with Shimadzu 3150 a spectrophotometer using 1 cm Quartz cell, slit fixed at 2 nm. ^{1}H, ^{13}C, HMBC and HETCOR spectra were obtained on a Bruker 500 MHz ultrashield spectrometer equipped with a 5 mm PABBO BB-inverse gradient probe. The concentration of solute molecules was 150 mg in 1.0 mL $CDCl_3$. Standard Bruker pulse programs [16] were used the entire experiment. FT-IR spectra were recorded on a Jasco 300E FT-IR spectrometer in KBr discs and were reported in cm^{-1} units. Microanalyses were carried out by Medicinal Plants and Medicine Research Center of Anadolu University Eskişehir (Turkey).

2.2. Synthesis of Schiff bases

The Schiff bases have been obtained using a method in which salicylaldehyde and the appropriate aminopyridines are refluxed for 5 h in MeOH (50 mL) [17,18]. The solid residue was crystallized from absolute THF/*n*-hexane and dried under reduced pressure. The general formulate of the Schiff bases with numbering and IUPAC names are shown in Scheme 1. Experimental and analytical data are listed in Table 1.

2.3. X-ray data collection, structure solution and refinement for 2-[(1E)-2-aza-2-(5-methyl(2-pyridyl)ethenyl)]-4-bromobenzen-1-ol (**6**)

For the crystal structure determination, the single-crystal of the compound $C_{13}H_{11}N_2O_1Br$ (**6**) was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The cylindrically shaped imaging plate covers the two-theta angular range between −60° and 140° with a crystal-film distance of 127.4 mm. The graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Images for **6** were taken successfully by varying ω with three sets of different χ and φ values, and 216 images for six different runs covering about 99.8% of the Ewald spheres were performed. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc., 2005) software [19]. The structure of **6** was solved by the direct method using SIR92 [20] and SHELXS [21]. The positional and atomic displacement parameters (ADPs) were refined by the full-matrix least-squares method using SHELXL [21]. In all, 3665 independent reflections with $R_{int} = 0.070$ were retrieved from 29,418 measured reflections

Table 1
Experimental and analytical data

Compound	Formula	MW	Yield (%)	mp (°C)	Calculated (found) (%)		
					C	H	N
1	$C_{12}H_{10}N_2O$	198	92	73	72.71 (72.38)	5.08 (4.98)	14.13 (14.05)
2	$C_{12}H_9ClN_2O$	232	88	138	61.94 (61.65)	3.89 (3.46)	12.04 (11.95)
3	$C_{12}H_9BrN_2O$	277	86	150	52.01 (51.44)	3.27 (3.06)	10.10 (9.75)
4	$C_{13}H_{12}N_2O$	212	94	105	73.56 (72.69)	5.69 (5.72)	13.19 (13.06)
5	$C_{13}H_{11}ClN_2O$	246	78	108	63.29 (64.44)	4.49 (3.37)	11.35 (11.62)
6	$C_{13}H_{11}BrN_2O$	291	81	126	53.63 (53.44)	3.80 (3.39)	9.62 (9.58)

Table 2
Crystal data and structure refinement for **6**

Chemical formula	$C_{13}H_{11}N_2O_1Br$
Formula weight	291.1
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pc*21*n*
Unit cell dimensions	
a (Å)	4.3794(2)
b (Å)	11.4357(2)
c (Å)	24.2864(5)
Volume (Å^3)	1216
Z	4
Density (calculated) (mg/m^3)	1.59
Absorption coefficient	3.364
F(0 0 0)	584
Crystal size (mm^3)	0.30 × 0.17 × 0.15
Theta range for collection (°)	3.4–30.5
Index ranges	$-6 \le h \le 5$, $-16 \le k \le 16$, $-34 \le l \le 34$
Reflections collected	29,418
Independent reflections	3665 ($R_{int} = 0.070$)
Observed reflections	3089 ($I > 2\sigma I$)
Parameters	156
Goodness-of-fit on F^2	1.367
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.081$, $wR_2 = 0.108$
R indices (all data)	$R_1 = 0.092$, $wR_2 = 0.113$
Largest diff. peak and hole (Å^{-3})	0.399 and 0.312

$R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$,

$wR_2 = \left\{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \right\}^{1/2}$

CCDC 605541 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge crystallographic data center via http://www.ccdc.cam.ac.uk/data_request/cif.

and used for structure determination and the refinement procedure. The positional and isotropic atomic displacement parameters of hydrogen atoms were refined together with other structural parameters by the full-matrix least-squares procedure based on the squared value of the structure factors. The weighting scheme $\omega = 1/[\sigma^2(F_o^2) + (0.0114P)^2 + 0.6112P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used. The final difference Fourier maps showed no peaks of chemical significance. The details of the data collection and final refinement parameters are listed in Table 2.

3. Results and discussion

3.1. IR spectroscopy

Selected FT-IR frequencies of various diagnostic bands for the compounds **1**–**6** are given in Table 3. The IR spectra show characteristic bands, which were assigned in accordance with literature data [18]. The absorption bands assignable to the ν(C=N) strectching vibration for compounds **1**–**6** were observed in the 1608–1613 cm^{-1} range, in agreement with values reported in the literature for pyridine-derived Schiff bases [22]. A band assignable to the ν(OH) vibration was found as a broad absorption at 3426–3445 cm^{-1} region. This observation implies that

Table 3
Infrared frequencies (cm^{-1}) of compounds **1**–**6** in the solid state (KBr)

Compound	ν(OH)	ν(C=N)	ν(C=C)	ν(C–O)
1	3437 m	1608 vs	1586 vs	1278 s
2	3445 m	1610 s	1586 vs	1277 s
3	3427 vs	1610 vs	1584 vs	1276 vs
4	3427 s	1612 s	1563 s	1278 s
5	3426 m	1613 s	1555 s	1277 s
6	3426 s	1610 s	1587 s	1280 s

s, strong; m, medium; v, very.

the H atom from the O–H in compounds have intramolecular hyrogen bonding as that observed for 1-[*N*-(6-methyl-2-pyridyl)aminomethylidene]-2(1*H*)-naphthalenone in the solid state [23].

The characteristic feature is that there are bands corresponding to the stretching of phenolic C–O bonds in different intensity

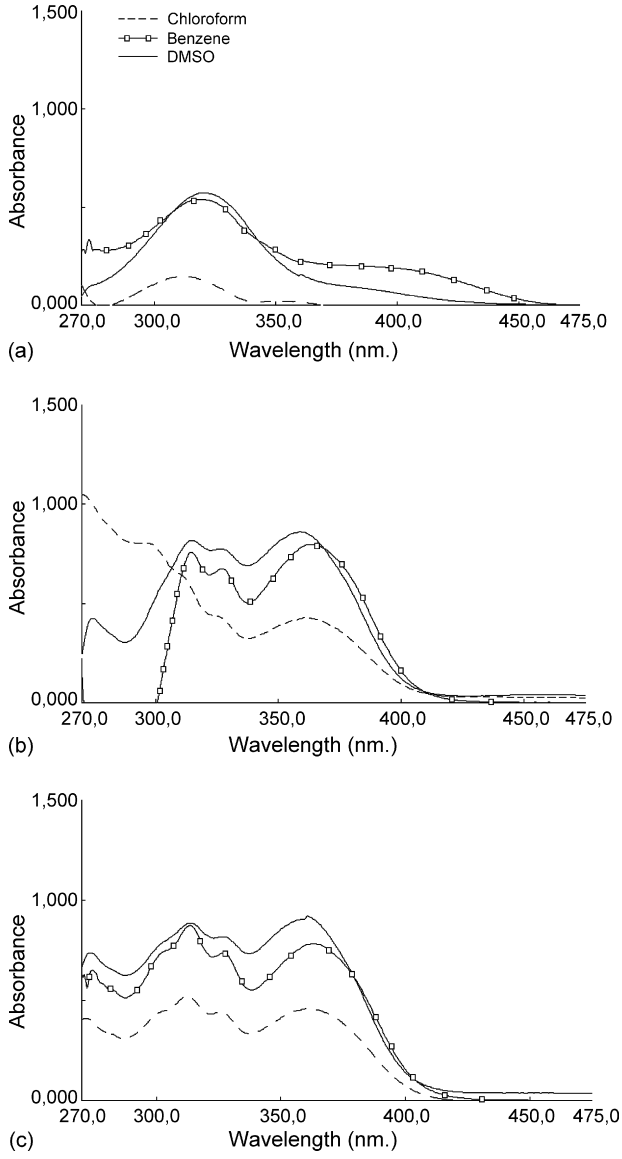
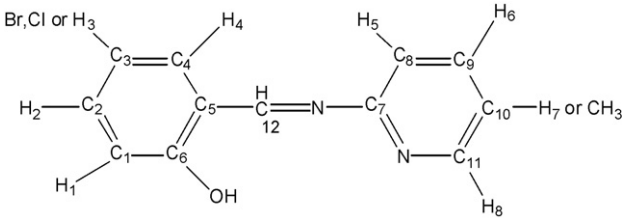


Fig. 1. The UV–vis spectra of compound **6** in (a) acidic, (b) neutral and (c) basic media.

Table 4
^{1}H and ^{13}C NMR spectral data in $CDCl_3$



	Compounds		
	1	**2**	**3**
H1	7.43 (dd, 1H) [$^{2}J_{H1–H2}$ = 8.44]	6.91 (d, 1H) [$^{2}J_{H1–H2}$ = 8.82]	6.90 (d, 1H) [$^{2}J_{H1–H2}$ = 8.84]
H2	7.39 (td, 1H) [$^{3}J_{H1,3–H2}$ = 8.28]	7.35 (m)	7.48 (dd, 1H) [$^{3}J_{H1–H2}$ = 8.8], [$^{4}J_{H2–H4}$ = 2.5]
H3	6.69 (t, 1H) [$^{3}J_{H2,4–H3}$ = 7.80]	–	–
H4	7.58 (dd, 1H) [$^{3}J_{H3–H4}$ = 8.12], [$^{4}J_{H2–H4}$ = 2.51]	7.55 (d, 1H) [$^{4}J_{H2–H4}$ = 2.63]	7.61 (d, 1H) [$^{4}J_{H2–H4}$ = 2.64]
H5	7.34 (d, 1H) [$^{3}J_{H4–H5}$ = 7.55]	7.35 (m)	7.34 (d, 1H) [$^{3}J_{H4–H5}$ = 7.91]
H6	7.24 (td, 1H) [$^{3}J_{H6–H5,7}$ = 7.43], [$^{4}J_{H6–H8}$ = 2.06]	7.24 (td, 1H) [$^{3}J_{H6–H5,7}$ = 7.32], [$^{4}J_{H6–H8}$ = 1.81]	7.26 (td, 1H) [$^{3}J_{H6–H5,7}$ = 7.49], [$^{4}J_{H6–H8}$ = 1.32]
H7	7.81 [$^{3}J_{H5,6–H8}$ = 7.65], [$^{4}J_{H4–H8}$ = 1.72]	7.80 [$^{3}J_{H5,6–H8}$ = 7.67], [$^{4}J_{H4–H8}$ = 1.61]	7.80 (td, 1H) [$^{3}J_{H5,6–H8}$ = 7.62], [$^{4}J_{H4–H8}$ = 1.93]
H8	8.49 (dd, 1H)	8.51 (dd, 1H) [$^{4}J_{H6–H8}$ = 1.82]	8.35 (dd, 1H)
CH	9.44 (s, 1H)	9.45 (s, 1H)	
CH_3	–	–	–
OH	13.48	13.55	
C1	119.2	118.9	119.5
C2	133.4	133.6	136.4
C3	118.1	123.7	110.6
C4	132.9	132.3	135.3
C5	118.5	119.7	119.7
C6	161.2	160.4	160.9
C7	155.2	157.0	157.0
C8	119.5	120.6	120.9
C9	138.8	138.6	138.6
C10	123.4	123.7	123.2
C11	149.2	148.8	149.3
C12	163.5	163.5	163.4
CH_3	–	–	–

	Compounds		
	4	**5**	**6**
H1	7.44 (dd, 1H) [$^{2}J_{H1–H2}$ = 8.37]	6.99 (d, 1H) [$^{2}J_{H1–H2}$ = 8.81]	6.93 (d, 1H) [$^{2}J_{H1–H2}$ = 8.83]
H2	7.41 (td, 1H) [$^{3}J_{H1,3–H2}$ = 8.37]	7.35 (dd, 1H) [$^{3}J_{H1–H2}$ = 8.6], [$^{4}J_{H2–H4}$ = 2.7]	7.55 (dd, 1H) [$^{3}J_{H1–H2}$ = 8.8], [$^{4}J_{H2–H4}$ = 2.5]
H3	6.65 (t, 1H) [$^{3}J_{H2,4–H3}$ = 7.43]	–	–
H4	7.59 (dd, 1H) [$^{3}J_{H3–H4}$ = 8.07], [$^{4}J_{H2–H4}$ = 2.34]	7.61 (d, 1H) [$^{4}J_{H2–H4}$ = 2.35]	7.50–7.60 (m, 2H)
H5	7.24 (d, 1H) [$^{3}J_{H4–H5}$ = 7.99]	7.34 (d, 1H) [$^{3}J_{H4–H5}$ = 7.91]	7.30 (d, 1H) [$^{3}J_{H4–H5}$ = 8.0]
H6	7.50 (dd, 1H) [$^{3}J_{H6–H5}$ = 7.67], [$^{4}J_{H6–H8}$ = 1.59]	7.26 (d, 1H) [$^{3}J_{H6–H5}$=]	7.50–7.60 (m, 2H)
H7	–	–	–
H8	8.32 (d, 1H) [$^{4}J_{H6–H8}$ = 1.6]	8.35 (d, 1H) [$^{4}J_{H6–H8}$ = 3.0]	8.34 (d, 1H) [$^{4}J_{H6–H8}$ = 2.2]
CH	9.45 (s, 1H)	9.42 (s, 1H)	9.50 (s, 1H)
CH_3	2.40 (s, 3H)	2.40 (s, 3H)	2.40 (s, 3H)
OH	13.58	13.61	13.60
C1	119.2	118.8	119.4
C2	133.6	133.3	136.1
C3	117.2	123.7	110.6
C4	133.3	132.1	135.3
C5	118.9	119.8	120.5
C6	161.8	160.4	160.8
C7	155.4	154.9	154.8
C8	119.9	120.1	120.0
C9	139.0	139.0	138.9
C10	132.4	132.9	132.9
C11	149.2	149.3	149.3
C12	163.8	162.4	162.4
CH_3	18.1	18.2	18.2

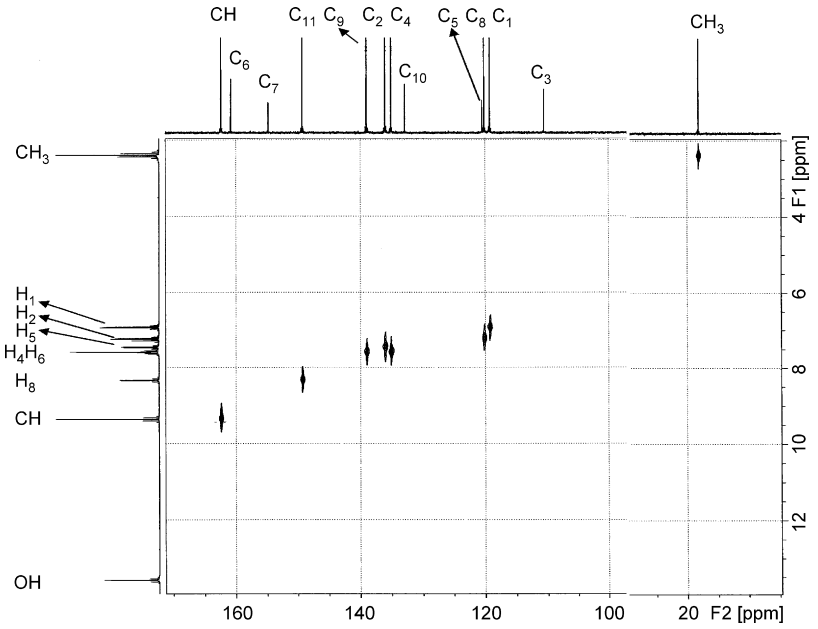


Fig. 2. HETCOR spectrum of **6**.

at 1280–1276 cm^{-1} for the compounds (**1**–**6**). Compound **6** with strong band at 1280 cm^{-1} possesses highest percentage of enol-imino tautomer due to the stabilization of phenolic C–O bond.

3.2. UV–vis spectroscopy

In solution, the existence of tautomeric equilibria [phenol-imine (O–H···N) and keto-amine (O···H–N) forms] in polar and non-polar solvents, depending on the formation of intermolecular hydrogen bonding, is observed [24]. This tautomerism depends strongly on the polarity of the solvent and its ability to form hydrogen bonds, as reported in the literature [25].

In the UV–vis spectra of Schiff bases with the OH group in ortho position to the imino group a new band at wavelengths greater than 400 nm, attributable to the keto-amine form are not observed in polar and non-polar solvents, acidic, neutral and basic media. The absorption band that was attributes to the phenol-imine form is about −325 nm (Fig. 1). It is claimed that in Schiff bases derived from salicylaldehyde and aromatic amine, the keto-amine form is not observed in polar and non-polar solvents, but it is observed in acidic media [10,11]. The UV–vis spectra of all the compounds (**1**–**6**) are recorded in different solvents and the phenol-imine forms are observed. The UV–vis spectra of **6** are depicted in Fig. 1, as representative. Fig. 1(a) indicates that phenol-imine form of **6** is present in benzene solution.

3.3. NMR spectroscopy

The ^{1}H and ^{13}C NMR data recorded in $CDCl_3$ solutions are shown in Table 4. In the ^{1}H NMR spectrum of **6**, the peaks at 6.93 ppm (d, 1H), 7.55 ppm (dd, 1H), 7.50–7.60 ppm (m, 1H) and 7.30 ppm (d, 1H) are assigned to be H1, H2, H4–H6 and H5, respectively, which have H–H correlation in H–H COSY spectrum. A signal at $\delta = 13.60$ ppm (s, 1H) which showed no hydrogen–hydrogen correlation in the COSY spectrum was attributed to the proton of hydroxyl group. Assignments of the protons and carbons were made by two-dimensional heteronuclear-correlated experiments (HETCOR) using delay values which corresponding to ^{1}J(C, H), HMBC using delay values which corresponding to ^{2}J(C, H) or ^{3}J(C, H) between the carbons and protons (Figs. 2 and 3). A signal appeared as a singlet at $\delta = 9.50$ ppm can be ascribed to CH=N. Both of the singlets indicated that the tautomeric equilibrium favors the enol-imine form in $CDCl_3$ as that reported in the literature [26]. The phenomenon has further been supported by NMR techniques [27]. A singlet assignable to the chemically and magnetically equivalent protons in 5-methoxy group of pyridine ring was observed at $\delta = 2.40$ ppm. Compounds **2**–**6** show similar characteristics as those discussed in compound **6**. H1, H2, H3(Cl, Br), H4, H5, H6, H7(CH_3) and H8 protons of all the compounds are easily distinguishable and assigned by using HMBC methods (Table 5) (Fig. 3).

Table 5
2D ^{1}H–^{13}C HETCOR and HMBC correlations for **6**

Atom	HETCOR	HMBC [J(C, H)]			
	^{1}J	^{2}J	^{3}J	^{4}J	$^{intra}J$
H1	C1	C6, C2	C3	–	–
H5	C8	C9	C10	CH	C3
H2	C2	–	C4	–	–
H6	C9	C10	C11, C7	CH_3	C3
H4	C4	C3	C2	–	C7
H8	C11	C10	C9, C7	–	–
CH	C12	C5	C4, C7, C6	C8	–
OH	–	C6	C11	C2	–

intra, intramolecular interaction.

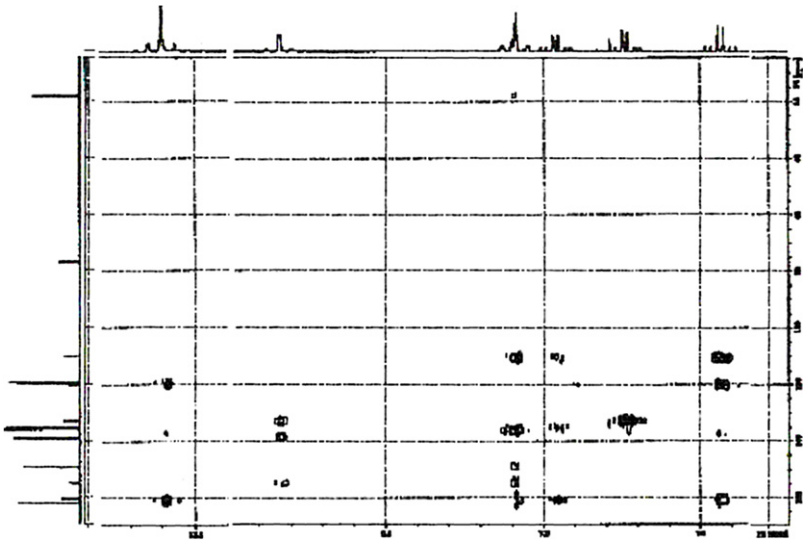


Fig. 3. HMBC spectrum of **6**.

Assignments of protonated carbons were made by two 2D ^{13}C–^{1}H HETCOR experiment using delay values which corresponds to ^{1}J(C, H) [28]. From HETCOR data CH_3 and CH carbons were assigned unambiguously. Heteronuclear multiple-bond correlation (^{1}H–^{13}C HMBC), a modified version of HETCOR was applied on **6** in order to determine the long range ^{1}H–^{13}C connectivities. The long range ^{1}H–^{13}C correlations for **6** and its two-dimensional spectra are shown in (Fig. 3), as an example. Observation from HMBC experiment showed that the hydroxyl proton (O–H) correlated with C1, C6 and C5 atoms, but did not correlate any pyridine carbon atoms. The imine CH proton was located near to C7 rather than hydroxyl proton (O–H) owing to the relationship observed CH proton correlated with C4, C5 C7 and C8 atoms. In compounds **4**, **5** and **6** the chemical shifts of C3 carbon atoms are observed at 117.2, 123.7 and 110.6 ppm, respectively. Consequently, according to the NMR results, the probable conformation of compound **6** in $CDCl_3$ solution are depicted in Fig. 4.

3.4. Crystal structures of **6**

The crystallographic data are summarized in Table 2 and selected bond distances and angles are given in Table 6. A perspective view of **6**, including the atom-numbering schemes are illustrated in Fig. 5. The skeleton is essentially planar. The dihedral angle between the phenyl and pyridine rings is 4.1(4)°.

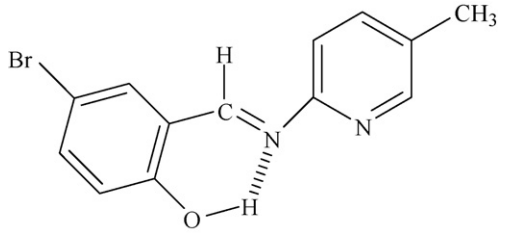


Fig. 4. The stereoisomer structure of compound **6** at ambient temperature in $CDCl_3$.

Table 6
Selected bond lengths (Å), and bond for compound **6**

C(1)–C(2)	1.368(7)	N(1)–C(8)	1.417(4)
C(1)–C(6)	1.402(7)	N(2)–C(12)	1.336(5)
C(2)–C(3)	1.381(5)	O(1)–H(10)	0.820(4)
C(3)–C(4)	1.376(8)	O(1)–C(5)	1.344(4)
C(4)–C(5)	1.389(7)	Br(1)–C(2)	1.894(4)
C(5)–C(6)	1.406(7)	O(1)–C(5)–C(6)	122.0(5)
C(6)–C(7)	1.448(4)	O(1)–C(5)–C(4)	118.2(5)
C(8)–N(2)	1.335(4)	C(6)–C(7)–N(1)	121.8(5)
C(13)–C(11)	1.508(4)	C(8)–N(1)–C(7)	120.2(4)
N(1)–C(7)	1.283(4)		

As mentioned before, similar compounds [29–31] generally include two type of intramolecular hydrogen bonds, either N–H···O or N···H–O and these hydrogen bonds cause to reversible proton transfer between the amino N atom and the hydroxyl O atom. The C–O bond can have a single bond character in the enol-imine tautomer compared to those in phenols [1.362(3) Å] or possess a significant double bond character in quinines [1.220(5) Å] [32]. According to our crystallographic results, compound **6** has enol-imine tautomeric form. Phenolic H atom in **6** was positioned at the distance not favourable for

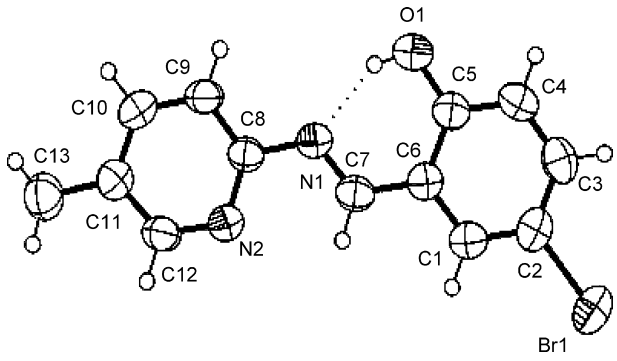


Fig. 5. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level.

the formation of keto-imine tautomer. The compound **6** has a short intramolecular N···H–O hydrogen bond [O1–H10; 0.820, H10···N1; 1.873, N1···O1; 2.600(4) Å, N1···H10-O1 147.1(4)°] which means that it is in enol-imine form. In addition C5–O1 bond length [1.344(4) Å] is comparable to the single bond values in enols [1.333(7) Å] [33]. In the structure of 1-{(4-methylphenyl-imino)methyl}-2-hydroxy-3-methoxyphenol and 1-{(4-methylphenylimino)-methyl}-2-hydroxyphenol [26] the O–H···N hydrogen bonds are established as 2.611(6) and 2.624(4) Å, respectively.

For compound **6** maximum deviation from mean plane C7/C6/C5/O1/H is 0.003 Å for atom O1. The N1–C7 bond of 1.283(4) Å for compound **6** is estimated to have remarkable double bond character similar as in the C_{ar}–C=N–C_{ar} moiety [1.279(5) Å] [33].

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