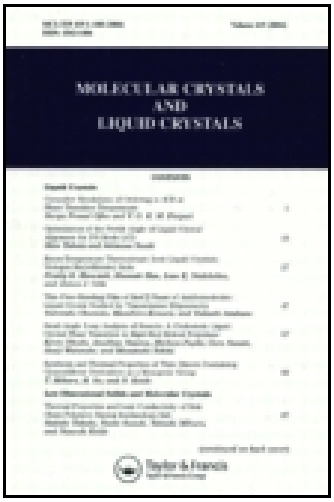

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Synthesis, Crystal Structure, and Spectroscopic Studies of N-(4-Bromobenzylidene)-N′-(2-Pyridyl) Hydrazine Schiff Base Molecule

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Synthesis, Crystal Structure, and Spectroscopic Studies of N-(4-Bromobenzylidene)-N′-(2-Pyridyl) Hydrazine Schiff Base Molecule

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A new Schiff base complex N-(4-bromobenzylidene)-N′-(2-pyridyl) hydrazine, $C_{12}H_{10}N_3Br$, has been synthesized and characterized by elemental analyses, mass, ^1H NMR, ultraviolet–visible (UV–VIS), and IR spectroscopy and single-crystal X-ray determination. The p-Br-benzene and pyridine rings are almost planar and the dihedral angle between the planes is 11.1(3)°. The crystal structure is stabilized by intermolecular N—H . . . N—Py hydrogen bonding interaction. X-ray diffraction analyses show that N-(4-bromobenzylidene)-N′-(2-pyridyl) hydrazine Schiff base molecule crystallizes in the monoclinic system, $P2_1/c$ space group, $a = 5.611(5)$ Å, $b = 19.566(5)$ Å, $c = 10.715(5)$ Å, $\beta = 98.766(5)°$, and $V = 1162.60(12)$ Å^3.

Keywords Condensation reaction; crystal structure; hydrazone; Schiff base; X-ray diffraction

Introduction

Schiff base complexes are often used as ligands in coordination chemistry related to catalysis and enzymatic reactions. Schiff base ligands and their metal complexes have been extensively studied over the past few decades. In particular, hydrazones are useful for the synthesis of formazans. Formazans form tetrazolium salt when they are oxidized [1]. Tetrazolium salts are reduced back to formazans by the enzymes in the cell and stain the tissue. The tetrazolium-formazan system is classified as a marker of vitality [2]. Hydrazones are also useful for the synthesis of metal complexes as they easily form stable complexes with most transition metal ions [3,4]. Hydrazones and their metal complexes have gained a special attraction for widespread application in technology and analytical chemistry.

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Hydrazones are formed when hydrazines condense with aldehydes and ketones by the condensation of aldehydes (or substituted aldehydes) with phenylhydrazine (or substituted phenylhydrazine) and typically are crystalline compounds with sharp melting points [5,6]. These compounds can therefore be used to identify the aldehydes and ketones from which the hydrazones have been formed. Hydrazide and hydrazones' ligands, owing to their structural flexibility, are quite diverse in their chelating ability and can act as a neutral or mononegative ligand and as a bidentate or tridentate unit, though they have the potential to act as bridging tetradentate ligands [7]. Aroylhydrazone complexes of transition metal ions are known to provide useful models for elucidation of the mechanism of enzyme inhibition by hydrazine derivatives [8]. Hydrazone Schiff bases and their metal complexes exhibit a wide variety of biological activities such as antimycobacterial, anticancer, antiviral, and antifungal agents [9–12]. Moreover, they have been the subjects of extensive investigation due to their versatile chelating behavior, for which they are widely used in analytical chemistry as a selective metal extracting agent, as well as in spectroscopic determination of certain transition metals [13].

In our previous studies, the synthesis and characterization of aroylhydrazone compounds were achieved [14,15]. In the present study, the compound N-(4-bromobenzylidene)-N′-(2-pyridyl)hydrazine (BrPyH) Schiff base had been synthesized and its structure was determined by the use of elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction techniques and characterized with spectroscopic techniques.

The goal of this study is to develop the spectral and crystal structure determination of the new Schiff base for the using fields, which are medical, analytical, drug applications, the dye industry, and new organic synthesis. It is also hoped that this compound will be more suitable for using fields than the known other substituted Schiff bases.

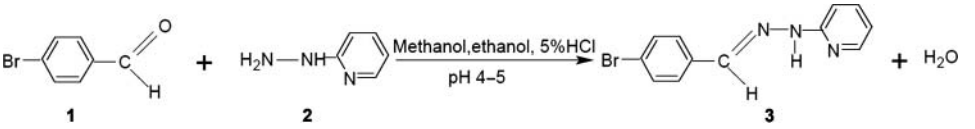
Experimental Details

General Procedures and Materials

2-hydrazinopyridine and 4-bromobenzaldehyde were purchased from Aldrich and used without further purification. Organic solvents and all the other chemical substances used were purchased from Carlo Erba. The IR spectra were recorded on a Thermo Nicolet 6700 ATR spectrophotometer by using KBr disks in the range 4000–400 cm^{-1}. The electronic spectra in the range of 200–900 nm were obtained on a Shimadzu UV-1240 spectrophotometer. Elemental analyses for C, H, and N were performed using a LECO CHNS 932 elemental analyzer. ^{1}H-NMR spectra were performed on a Bruker AVANCE DPX-300 MHz and mass spectra were recorded using an Agilent 1100 MSD mass spectrometer.

Synthesis of BrPyH

The title compound, BrPyH, was prepared as shown in Scheme 1. A solution of 4-bromobenzaldehyde (**1**) (4.623 g, 0.025 mol) in hot methanol (20 ml) was gradually added



Scheme 1. Synthetic pathway for the synthesis of BrPyH Schiff base.

to a solution of 2-hydrazinopyridine (**2**) (2.72 g, 0.025 mol) in hot ethanol–dioxane mixture (100:20 ml, 5% HCl) with constant stirring. Since condensation reaction is carried out in acidic conditions, synthesis was made at about pH 4–5 [5]. The procedure was completed in approximately 30 min. The resulting pale yellow Schiff base (**3**) was left on the bench for 4 days and was then filtered. The pale yellow precipitate formed was dissolved in hot methanol under the reflux for 3 hr and was kept in a cupboard for 2 days for recrystallization and was then filtered [5,6]. Also, unsubstituted N-benzlidene-N′-phenyl hydrazine (BPH) was synthesized in the same way for clarification of substituent effects of BrPyH. Experimental data of Schiff base are given in Table 1.

X-Ray Diffraction Study

The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 2. Diffraction measurements were performed at room temperature on a four-circle Rigaku R-AXIS RAPID-S diffractometer [equipped with a two-dimensional (2D) area image plate (IP) detector]. The graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta\omega = 5^\circ$ for one image were used for data collection. 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., The Woodlands, TX) software [16]. The structures were solved by direct methods using SHELXS-97 [17] and refined by a full matrix least-squares procedure using the program SHELXL-97 [18]. All nonhydrogen atoms were refined using anisotropic displacement parameters and hydrogen atoms were included in their idealized positions and refined isotropically, except for H7 and H2N. An ORTEP (Oak Ridge Thermal-Ellipsoid Plot Program) [19] drawing of the molecule with 40% probability displacement thermal ellipsoids and atom-labeling scheme is shown in Fig. 1. Except for H7 and H2N, the H atoms were positioned geometrically, with C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2\ U_{eq}(C)$.

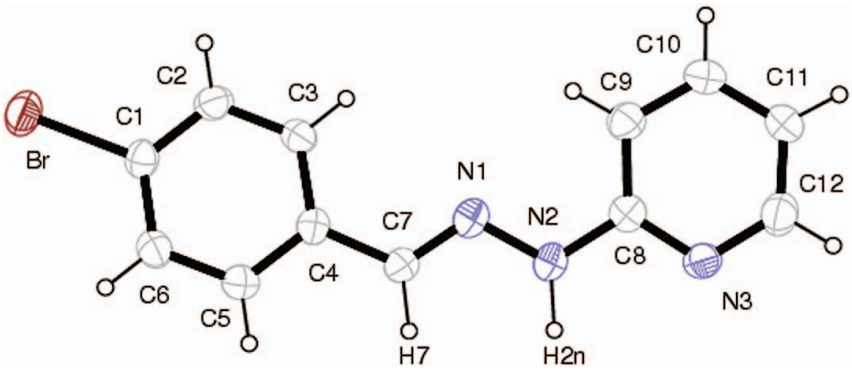


Figure 1. ORTEP drawing of the title compound, represented with displacement ellipsoids, is drawn at 50% probability level and showing the labeling scheme.

Table 1. Experimental data of the BrPyH

Abbreviation	Molecular formula	Molecular weight calculated (found)	Color	Yield (%)	MP (°C)	Elemental analysis					
						%C		%N		%H	
						Calculated	Found	Calculated	Found	Calculated	Found
BPH	$C_{13}H_{12}N_2$	196.25 (197.02)	Pale Yellow	84	154–155	79.563	79.502	14.274	14.302	6.163	5.696
BrPyH	$C_{12}H_{10}N_3Br$	276.14 (279.01)	Orange	75.4	189–190	52.195	52.132	15.217	15.173	3.650	3.617

Table 2. Crystal data and structural refinement details for the complex

Chemical formula	$C_{12}H_{10}Br\,N_3$
Formula weight	276.14
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
Crystal color	Pale yellow
a, b, c	5.611(5), 19.566(5), 10.715(5) Å
β	98.766(5)°
V	1162.60(12) Å^3
D_x	1.58 g cm^{-3}
Radiation, λ	MoKα, 0.71073 Å
μ	3.510 mm^{-1}
T	293(2) K
T_{min}, T_{max}	0.496, 0.501
Scanning mode	$\omega/2\theta$
Scan range	$-6 \le h \le 8$, $-27 \le k \le 27$, $-15 \le l \le 15$
Crystal size	0.20 × 0.20 × 0.20 mm
θ_{min}, θ_{max}	2.19°, 30.56°
Number of measured/independent reflections, R_{int}	31,939/3539, 0.1466
Number of reflections with $I > 2\sigma(I)$	2774
Number of refined parameters	151
S	1.422
Final R indices [$I > 2\sigma(I)$]	0.1131
wR (I)	0.1447
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.562, −0.315 e Å^{-3}

Results and Discussion

Spectral Properties

The selected IR spectral data of Schiff base are given in Table 3 and the spectrum of BrPyH is shown in Fig. 2(a). Pyridine and phenyl rings with Br substituent are attached to BrPyH Schiff base. Owing to this structure, the IR spectrum of Schiff base BrPyH is different according to BPH (Fig. 2(b)). In the IR bands of BrPyH, N−H and aromatic C−H bands were observed at 3189–2850 cm^{-1} weak and broad bands. Stretching N−H band exhibits a great broadening and low frequency shift when it forms strong intermolecular bonds and overlapped with aromatic C−H bands [20,21]. Therefore, in this study, the multiplet bands at 3189–2850 cm^{-1} could be N−H stretching mode forming hydrogen bond, and aromatic C−H groups overlapped with the N−H mode. The H of N−H forms strong intermolecular hydrogen bonds with unpaired electrons of N pyridine of other molecules. These values confirmed X-ray results (Fig. 3). Furthermore, strong sharp bands were observed in the IR spectrum of Schiff base for C=C at 1436 cm^{-1} and at 1592 cm^{-1} for C=N. The band in the IR spectrum at approximately 811 cm^{-1} can be assigned to the C−Br stretching mode [21,22]. In the IR spectra, three intensity bands appear at 1539, 1087–1060, and 765 cm^{-1}, which are assigned to vibration frequency v (Py ring), v (Py ring bending), and v (Py ring

Table 3. Selected IR spectral data of the hydrazones (KBr, ν cm^{-1})

Abbreviation	N—H	Ar—H	CH=N	Py (ring)	Ar. C=C	N—N	Py bending	C—Br	CNNC skeleton (fingerprint)
BPH	3300	3500–3000	1600	–	1500	1250	–	–	930–500
BrPyH	3189	3143–2850	1592	1539	1436	1130	1087–1060	904–678	904–678

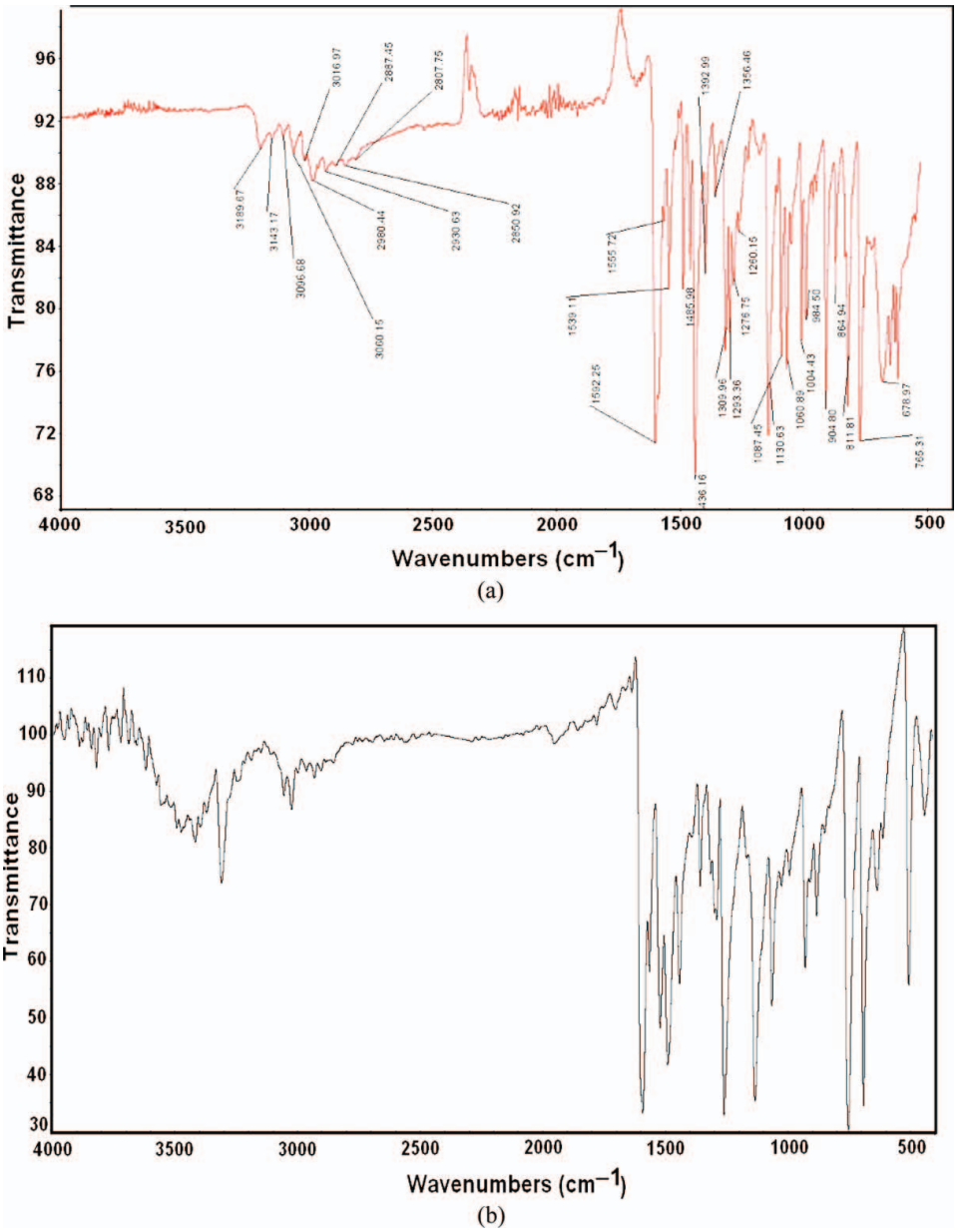


Figure 2. The experimental FTIR spectrum of the (a) BrPyH Schiff base (b) BPH Schiff base.

outside the plan), respectively (outside the plan is into fingerprint region [21–23]). These values verified the structures of the synthesized Schiff base, which were elucidated by elemental analysis and X-ray results.

As seen from Table 4 and Fig. 3, the ^{1}H-NMR data showed that the δ values of BrPyH shifted to a lower field compared with those of unsubstituted BPH. For instance, δ values for C—H_{arom} (C_6H_5) appeared as a multiplet in the region of δ 6.91–7.70 ppm in BPH (Fig. 3(a)), shifting to the lower field to the region of δ 6.79–8.17 ppm in BrPyH (Fig. 3(b)). Also, at

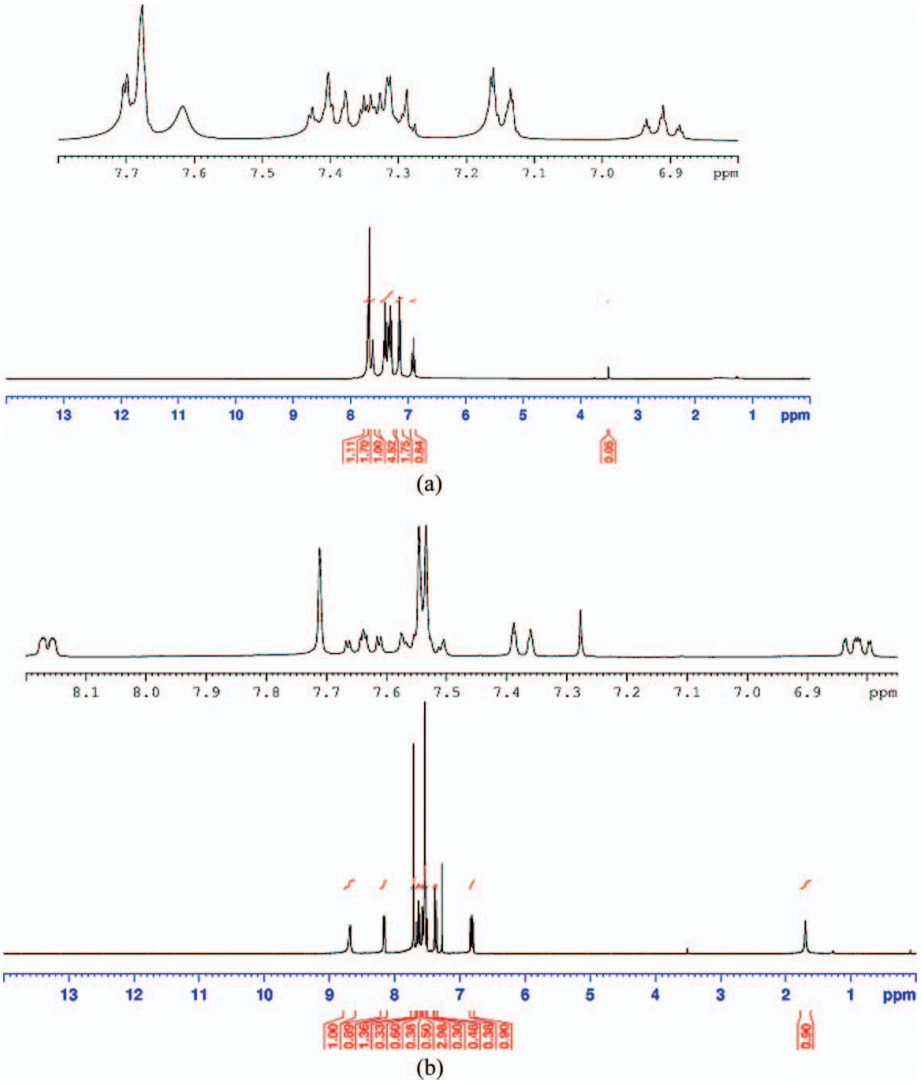


Figure 3. ^{1}H-NMR spectrum of (a) BPH Schiff base (b) BrPyH Schiff base.

δ 7.62 ppm, the observed N—H signal shifted to δ 8.17 ppm and at δ 7.13 ppm, the observed HC=N proton signal was observed at δ 8.15 ppm on the spectrum of BrPyH. These results are justifiable because there are electron-withdrawing groups such as *p*-Br (Hammett substituent coefficients for *p*-Br, $\sigma_p = 0.26$) and pyridine in the structure of

Table 4. ^{1}H-NMR data of the hydrazones (in $CDCl_3$)

Abbreviation	H_{arom}, $H_{pyridine}$ δ (ppm)	N—H δ (ppm)	HC=N δ (ppm)
BPH	7.70–6.91	7.62	7.13
BrPyH	8.17–6.79	8.17	8.15

BrPyH. Also, the downfield shift of the N−H signal indicates intermolecular hydrogen bonding. Hydrogen bonding decreases electron density around the proton of amine group and thus moves the proton absorption to a lower field. On the other hand, the assignment of the Z-configuration to the HC=N hydrazone double bond was performed considering literature data [6]. In fact, the chemical shift due to the −CH= hydrogen atom in the Z-isomer is usually upfield with respect to the E-isomer, appearing in substituted pyridine hydrazone derivatives at the range 7.45–8.30 ppm in the ^{1}H NMR spectrum [6].

UV–VIS Absorption λ_{max} Values of the BrPyH

Substituent Effect. The ultraviolet–visible (UV–VIS) absorption λ_{max} peaks values of Schiff bases are generally observed at 250–450 nm depending upon the structures. These peaks originate from the π–$\pi^*$and n–π^* transitions that correspond to HC=N and aromatic C=C groups in the molecule [3,23,24]. As seen in Table 5 and Fig. 4(a), in this study, when UV–VIS absorption λ_{max} values are observed 350 nm for BPH, it is 335 nm for BrPyH in CH_3OH. Therefore, the absorption λ_{max} value of compound BrPyH shows a slight shift toward the lower wavelength according to BPH. There is a total of two effects shifting λ_{max} value to the lower wavelength. The first one, Br, is inductively electron withdrawing, but by the resonance, electron-donating effects impose opposing direction effects on each other. As known, inductively electron-withdrawing effect is deflated from *o*-position to *p*-position. Consequently, substitute Br at *p*-position to effect only a little electron-withdrawing effect (Hammett substituent coefficients $\sigma_p = 0.26$). The second one, i.e., on pyridine ring the unpaired electron of N atom, is not acted on as electron-donating groups by the resonance. Because of unpaired electrons of N, pyridine forms strong intermolecular hydrogen bonds, and the electron-donating effect is deflated at *o*-position. Consequently, both *p*-Br and *o*-Py substituents in total exert a hypsochromic effect on the λ_{max} values, and hence, the λ_{max} values shift toward the blue direction [24]. This result reveals that the energy difference between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) is left over in the system. Thereupon, absorption λ_{max} value could be shifted to the lower λ_{max} value (hypsochromic effect).

Solvent Effect. Absorption spectra of the BrPyH were recorded in three different solvents with the aim of clarifying the effects of solvents. For this purpose, solvents of different types were selected: the polar nonprotic solvent, dimethyl sulfoxide (DMSO), the polar protic solvent, methanol, and the apolar solvent, toluene. Generally, in many dye molecules, the ground state is less polar than the excited state so that polar protic or aprotic solvents will tend to stabilize the excited state more than the ground state. Therefore, λ_{max} values shift to the bathochromic region. This case is seen in solvent DMSO. However, this is not seen in methanol. As seen from Table 6 and Fig. 4(b), in the apolar solvent toluene, λ_{max} values

Table 5. UV–VIS absorption maxima λ_{max} of the hydrazones (in methanol 10^{-6} M)

Abbreviation	λ_{max1} (nm)	Absorbance	λ_{max2} (nm)	Absorbance
BPH	350	0.473	245	1.363
BrPyH	335	2,554	240	1,694

Note: Between screen 780 nm and 200 nm.

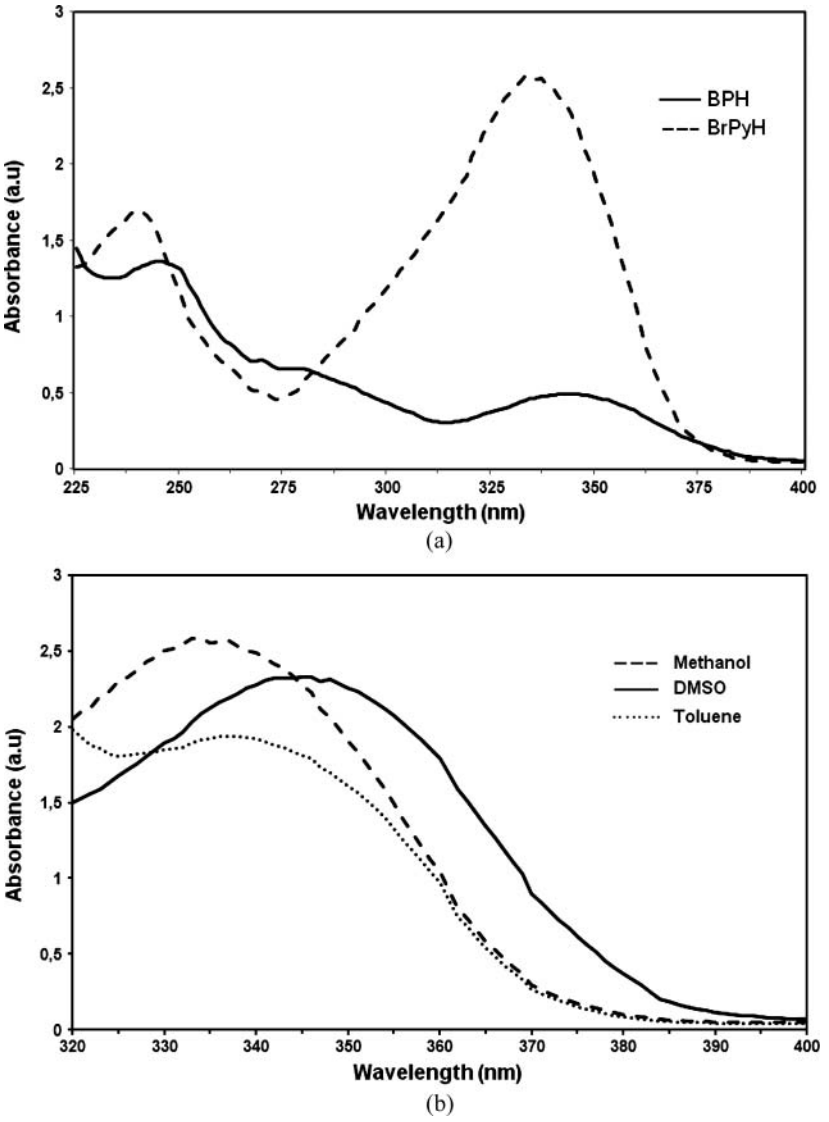


Figure 4. (a) UV–VIS spectra of BPH and BrPyH Schiff bases (in CH_3OH, 10^{-6} M) and (b) UV–VIS spectra of BrPyH Schiff base in various solvents.

shifted more toward the bathochromic region (λ_{max} 337 nm) than in the case of solvent methanol (λ_{max} 335 nm). This might be due to the formation of a strong hydrogen bond between the dye BrPyH and methanol molecule. Thus, the ground state will tend to stabilize more than the excited state. Consequently, the energy difference between the HOMO and LUMO increases. Thereupon, absorption λ_{max} value could be shifted to the lower λ_{max} value than toluene as $\Delta\lambda = 2$ nm. In addition, at around 320 nm, the absorbance decreases with the increase of wavelength only in the case of toluene. This can be attributed to the nonformation of hydrogen bond between dyes BrPyH with the nonprotic apolar molecule toluene [22]. BrPyH in the excited state has basic hydrazo and imino nitrogen atoms. The

Table 6. UV–VIS absorption maxima λ_{max} of the BrPyH in various solvents

Abbreviation	Toluene λ_{max} (nm) absorbance	Methanol λ_{max} (nm) absorbance	DMSO λ_{max} (nm) absorbance
BrPyH	337 (1.937)	335 (2.554)	346 (1.788)

basic property of hydrazo and imino nitrogen is increased by successive introduction of electron-donating groups by resonance and weak electron-withdrawing groups, such as Br, at the *p*-position of the benzene ring. Furthermore, Br stabilizes the excited state by donating nonbonding electrons [25]. Consequently, as seen from Table 6 and Fig. 4(b), the more the solvent polarity increases, the more shifting happens to the absorption λ_{max} value to the bathochromic region/area.

Description of the Crystal Structure. The structure of BrPyH crystallizes into a monoclinic lattice with space group $P2_1/c$. An ORTEP view of the asymmetric unit is shown in Fig. 5 and selected bond distances and angles are presented in Table 7. The asymmetric unit contains one Schiff base molecule. In the molecule, the benzene and pyridine rings and

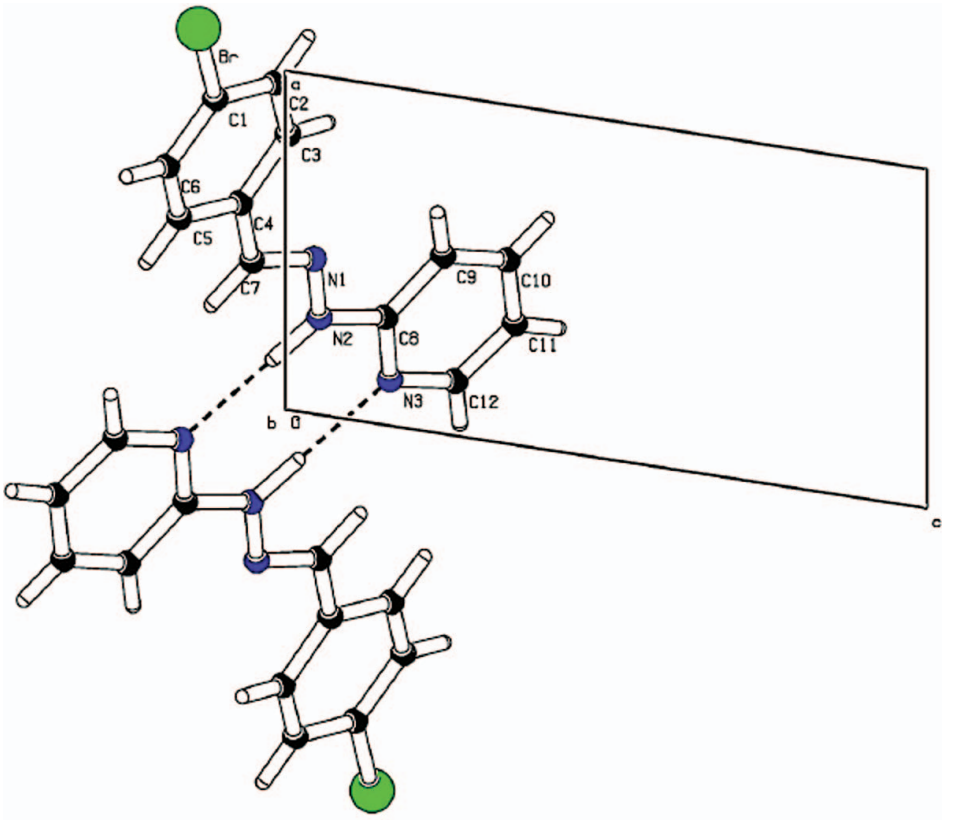


Figure 5. View of the crystal packing of the title compound, along the *b*-axis. Hydrogen bonds are indicated by dashed lines.

Table 7. Selected bond distances (Å), angles (°), and torsion angles (°)

Bond distance (Å)	
Br−C1	1.894(5)
N2−N1	1.393(5)
N2−C8	1.382(6)
N1−C7	1.272(6)
N3−C8	1.333(6)
N3−C12	1.356(7)
Bond angles (°)	
N1−C7−C4	121.9(5)
C2−C1−Br	120.3(4)
N1−N2−N8	118.6(4)
C7−N1−N2	116.9(4)
Torsion angles (°)	
C3−C4−C7−N1	11.0(8)
N1−N2−C8−C9	−4.5(7)

the hydrazone bridge are practically coplanar. Molecules of the title compound adopt an E-configuration about the azomethine C=N double bond, with an N2-N1-C7-C4 torsion angle of 178.5(4)°. For the molecule of BrPyH (Fig. 5), the benzene and pyridine rings intersect at an 11.1(3)°. The N2−C8 and N1−N2 bond distances are between 1.382(6) Å and 1.393(5) Å, respectively. The N1−C7 double bond is 1.272(6) Å.

As shown in Fig. 5, each enantiomer forms head-to-tail molecular pairs. An intermolecular hydrogen bond was observed between the H atom attached to the N atom (N2) of the hydrogen bridge and the N atom (N3) of the pyridine rings of the adjacent molecule [N2−H2···N3]. Intermolecular hydrogen bond distances and bond angles are listed in Table 8. Also, π–π interactions can be seen from the packing diagram (Fig. 6). Intermolecular π–π and hydrogen bonding interactions link the molecules and these interactions play an important role in the stabilization of the crystal structure.

Similarly, the structure of BPH crystallizes into a monoclinic lattice with space group $P2_1/c$ [26,27]. The molecule of BPH takes up E-configuration and the angle between the two benzene rings is 8.1(1)° [26]. In BPH molecule, the bond distances corresponding to N2−C8 and N1−N2 bonds and C7−N1 double bond are 1.435(10), 1.330(8), and 1.312(9) Å, respectively [26]. While the C7−N1−N2 and N1−N2−C8 bond angles in BrPyH molecule are 116.9(4)° and 118.6(4)°, bond angles corresponding to them in BPH

Table 8. The hydrogen bond distances (Å) and angles (°)

D−*H*... *A*	d(*D*−*H*) (*Å*)	d(*H* ··*A*) (*Å*)	d(*D* ··*A*) (*Å*)	*D*−*H* ··*A* (°)
N2−H2N ··N3^{i}	1.05	2.02	3.066(2)	172

Note: Symmetry code: (i) = –*x*, –*y*, –*z*.

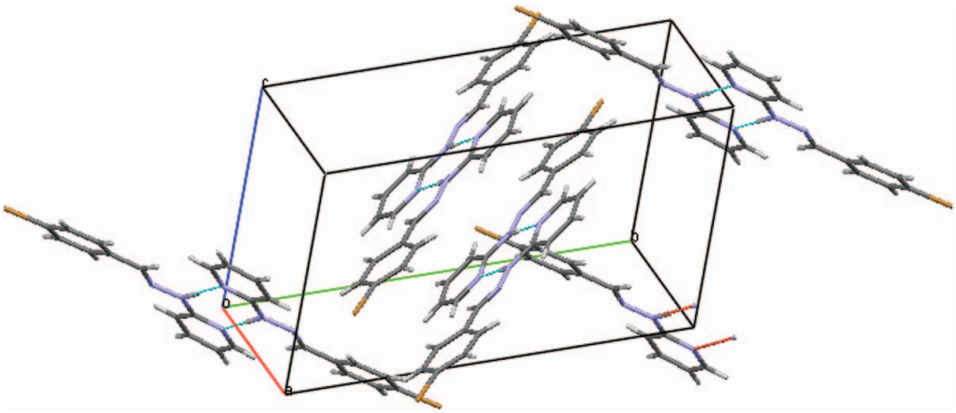


Figure 6. The crystal packing of the compound viewed along *a*-axis. Intermolecular N—H···N hydrogen bonds are shown as dashed lines.

are 114.9(7)° and 120.8(7)°. Also, there is no intermolecular hydrogen bonding in BPH molecule [26,27].

An interesting comparison can be made with the structure of N-(4-methoxybenzylidene)-N′-(2-pyridyl) hydrazine (MtPyH) [28], which contain a methoxy group different from BrPyH molecule. The structure of MtPyH crystallizes into a monoclinic lattice with space group $P2_1/c$. The molecule of MtPyH takes up E-conformation and the dihedral angle between the planes of the pyridine and methoxyphenyl rings is 6.19(12)° [28]. In MtPyH molecule, the bond distances corresponding to N2—C8, N1—N2 bonds, and C7—N1 double bond are 1.374(2), 1.367(2), and 1.270(2) Å, respectively. Also, in MtPyH molecule, the bond angles corresponding to C7—N1—N2 and N1—N2—C8 are 118.18(18)° and 118.12(19)°, respectively [28]. While C8—N2—N1—C7 torsion angle of the hydrazone bridge in BrPyH molecule is 178.5(4)°, it is −179.54(19)° in MtPyH molecule. Moreover, centrosymmetrically related molecules are linked into discrete pairs by pairwise N2—H2···N3^{i} [symmetry code: (i) 2-x, 2-y, 2-z] hydrogen bonds in MtPyH molecule. The bond distances, bond angles, and hydrogen bonding are comparable with the literature [14,15,26–30].

Conclusions

In this study, BrPyH was synthesized by the condensation reaction of 4-bromobenzaldehyde and 2-hydrazinopyridine. Also, unsubstituted BPH was synthesized for clarification of substituents' effects on BrPyH. Analysis of spectral data shows that both *p*-Br and *o*-Py substituents in total exert a hypsochromic effect on the λ_{max} values and thus the λ_{max} values shift toward the blue direction. Furthermore, solvent effect on the UV–VIS absorption behavior was investigated and it was noted that the more the solvent polarity increases, the more shifting happens to the absorption λ_{max} value to the bathochromic region. On the other hand, all the bond distances and bond angles are within normal ranges and comparable with those of similar compounds. The crystal structure is stabilized by the intermolecular N—H···N hydrogen bonding interaction. This result is confirmed via both spectral and X-ray values.

Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 798670. Copies of this data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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