Struct Chem (2010) 21:153–157
DOI 10.1007/s11224-009-9554-5

ORIGINAL RESEARCH

Synthesis, characterization, crystal structure, and theoretical studies on Schiff-base compound 6-[(5-Bromopyridin-2-yl)iminomethyl]phenol

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Received: 31 August 2009 / Accepted: 10 November 2009 / Published online: 21 November 2009

Abstract The title Schiff-base compound, 6-[(5-Bromopyridin-2-yl)iminomethyl]phenol (**1**), has been synthesized and characterized by elemental analyses, FT-IR, UV–Vis and ^{1}H-NMR spectroscopy, and X-ray single crystal diffraction. In the gas phase four isomers were found for title compound. Density functional (DFT) calculations have been carried out and it was found that the **A** isomer is the most stable one. The protonated imine N atom is involved in intra- and inter-molecular hydrogen bonds with the phenoxide group and H aromatic atoms, respectively. The title compound displays a *trans* configuration about the C=N double bond.

Keywords Schiff-base compound · Single crystal · Monoclinic · Spectroscopy · DFT

Introduction

Schiff-base compounds exhibit a wide range of biological activities [1], anti-HIV [2, 3], anti-tumor activities [4], and they play an important role in the synthesis of transition metal complexes [5–8]. This activity increases by coordinating a ligand to the metal ion, such as catalyst [9] and interaction with DNA [10, 11]. Among the variety of Schiff-base ligands, Salen derivatives have been studied widely [5, 11–13]. In this article, we have succeeded in the synthesis of new Schiff-base compound 6-[(5-Bromopyridin-2-yl)iminomethyl]phenol (**1**) and its characterization by elemental analyses, FT-IR, UV–Vis and ^{1}H-NMR spectroscopy, and X-ray single crystal diffraction (Fig. 1).

Experimental

Physical techniques and materials

All reagents and solvents for synthesis and spectroscopic studies were commercially available and used as received without further purification. ^{1}H-NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in δ units downfield from TMS. The infrared spectrum was recorded on a JASCO 680 plus FT-IR spectrophotometer as a KBr pellet.

Synthesis of 6-[(5-Bromopyridin-2-yl)iminomethyl]phenol (1)

Salicylaldehyde (36.6 mg, 0.3 mmol) and 5-bromo-2-aminopyridine (51.9, 0.3 mmol) were dissolved in methanol (10 mL). The mixture was stirred at room temperature for 30 min to give a clear yellow solution. Suitable crystals of the title compound for X-ray study were formed by slow evaporation of the solvent over 3 days at room temperature (63 mg, yield 76%). Yellow crystals. IR (KBr pellet,

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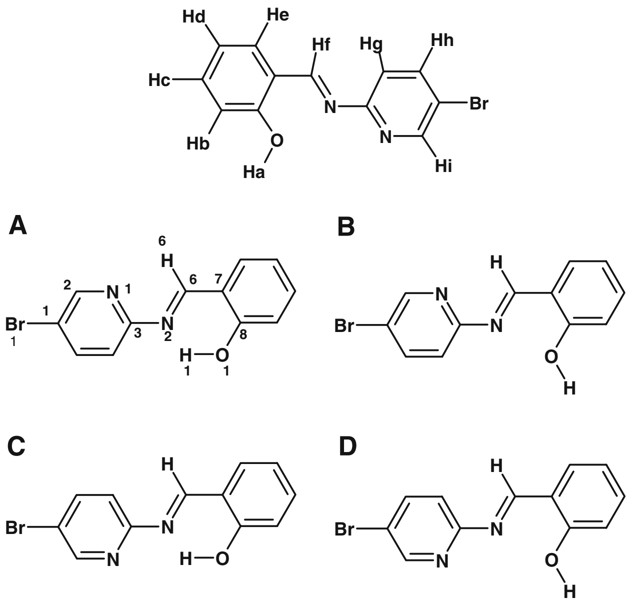

Fig. 1 Chemical structure and selected numbering of four conformers considered in the gas phase of the title compound **1** with its labeling

cm^{-1}): 2850–3080 (m, C–H aromatic and aliphatic), 1605 (s, C=N), 1490–1570 (m, C=C and C=N aromatic). ^{1}H-NMR (CDCl$_3$, δ(ppm)): 6.94–6.97 (1H, t, Hd), 7.01–7.03 (1H, d, Hb), 7.20–7.21 (1H, d, Hf), 7.26 (CDCl$_3$), 7.39–7.43 (1H, td, He), 7.47–7.49 (1H, dd, Hc), 7.85–7.87 (1H, dd, Hh), 8.53 (1H, d, Hg), 9.39 (1H, s, Hi), 13.20 (1H, s, Ha).

X-ray data collection and structure determination

Crystallographic measurements were done with four circle CCD diffractometer Geminy of Oxford diffraction, Ltd., with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structures was solved by direct methods using program SIR2002 [14] and refined with the Jana2006 program package [15] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by using the ORTEP III [16]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. Selected bond distances and angles are listed in Table 2.

Computational details

Density functional theory (DFT) [17] calculations were performed using Gaussian 98 program [18]. Geometries of all species were optimized using 6-31G(d) and 6-31+G(d) basis sets at the HF and DFT levels. Vibrational frequency calculations were used to characterize all stationary points as minima (the number of imaginary frequencies (NIMAG = 0). All calculations were performed on a Pentium IV Processor personal computer without any constraint on the geometry.

Table 1 Crystallographic and structure refinement for **1**

Empirical formula	$C_{12}H_9BrN_2O$
Formula weight	277.1
Crystal system, space group	Monoclinic, $P2_1/c$
T (K)	120
a (Å)	5.7979(2)
b (Å)	8.5662(5)
c (Å)	21.7821(9)
β (deg)	91.584(3)
V (Å^3)	1081.42(9)
Z	4
μ (mm^{-1})	3.78
Crystal size (mm^3)	0.28 × 0.16 × 0.10
$T_{\min}$	0.502
$T_{\max}$	0.690
Measured reflections	4843
Independent reflections	1822
Reflection with $I > 3\sigma(I)$	1445
Parameters	149
R_{int}	0.028
S	1.33
$R[F^2 > 3\sigma(F^2)]$	0.031
$wR(F^2)$	0.076
$\Delta\rho_{\max}$ (e Å^{-3})	0.56
$\Delta\rho_{\min}$ (e Å^{-3})	−0.40

Table 2 Selected bond lengths (Å) and angles (°) optimized and experimental of conformers **1** in the gas phase obtained at the DFT/6-31+G(d) level of theory

	DFT/6-31+G(d)				Exp
	A	**B**	**C**	**D**	
N2–C3	1.405	1.406	1.402	1.399	1.423
N2–C6	1.299	1.287	1.293	1.280	1.296
C6–C7	1.445	1.461	1.447	1.464	1.433
C7–C8	1.425	1.419	1.425	1.417	1.411
C8–O1	1.344	1.359	1.343	1.357	1.352
O1–H1	0.998	0.971	0.996	0.971	0.820[a]
C3–N1	1.342	1.345	1.342	1.344	1.338
N1–C2	1.333	1.332	1.333	1.333	1.333
C2–C1	1.398	1.398	1.397	1.397	1.398
C1–Br1	1.900	1.902	1.899	1.901	1.896
H1–N2	1.756	–	1.773	–	1.873
C3–N2–C6	120.2	118.7	121.4	119.4	119.1
N2–C3–N1	120.4	121.6	115.0	115.8	119.1

[a] Restrained to 0.82 A

Results and discussions

Synthesis and spectroscopy

The title compound **1** was obtained in yields 76%. It is air-stable in the solid state for about 3–5 months. The stability of dissolved compound is much shorter than in the solid state and depends on the nature of the solvent. The title compound is stable in methanol and acetonitrile solution at room temperature for about 4 days and at 273 K for 9 days. Also, it remains unchanged in chloroform and dichloromethane for about 1 day at room temperature and 3 days at 273 K. The title compound is slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane.

The strong bands at 1,605 cm^{-1} FT-IR spectra is assigned to the C=N stretching vibration. The spectrum of **1** also shows several weak bands corresponding to aromatic and aliphatic C–H stretching (2,850–3,080 cm^{-1}), and aromatic C=C or C=N stretching (1,490–1,570 cm^{-1}). The ^{1}H-NMR spectra of **1** is shown in Fig. 2, and display nine different signals for nine hydrogen ($\mathbf{H}_a$ to $\mathbf{H}_i$) (see "Experimental" section and Fig. 2).

Crystal structure

The title compound **1** crystallizes in the monoclinic system with space group $P2_1/c$. The molecular structure of **1** with the atom numbering scheme is given in Fig. 3. All bond distances and angles are normal and in good agreement with those reported in similar Schiff-base compounds [19, 20]. The bond angles C7–C6–N2 and C6–N2–C3 are 121.9(3)° and 119.1(3)°, respectively, which is consistent with the sp^2 hybrid character of C6 and N2 atoms. The two aromatic rings in the roughly planar molecule of **1** (Fig. 3) are bridged by the –C=N– fragment double bonds, with the distance between aromatic rings of ca 3.687 Å. The title compound **1**, exhibits intramolecular O1–H1o–N2 hydrogen bond (Table 3).

Theoretical studies

In the gas phase the four conformers for the compound **1** were found. The structure and selected numbering of these isomers are presented in the Fig. 1. In the conformer **A** the hydroxyl group and imine nitrogen participate in an inter-molecular hydrogen bonding and pyridine nitrogen is in the other side of the N1–C7 bond. Isomer **B** was obtained with rotation of hydroxyl group around C4–O5 bond while rotation around N1–C7 yields the rotamer **C**. In this isomer internal hydrogen bonding between hydroxyl hydrogen and imine nitrogen is clear. With a rotation of hydroxyl group around C4–O5 bond isomer **D** was obtained.

The results of calculated total energies and relative stabilities of four conformers of title compound are presented in the Table 4. In consistence with results obtained in the solid state, DFT calculations predict that in the gas phase isomer **A** is the most stable ones. It is clear that hydrogen bonding stabilizes the isomer of **A** but similar stabilization for the isomer **C** has not been confirmed. The order of stability predicted by DFT methods was found as: **A** > **C** > **B** > **D**. In addition, based on DFT results a planar structure for the conformers was found.

Fig. 2 ^{1}H-NMR spectra of **1** in $CDCl_3$

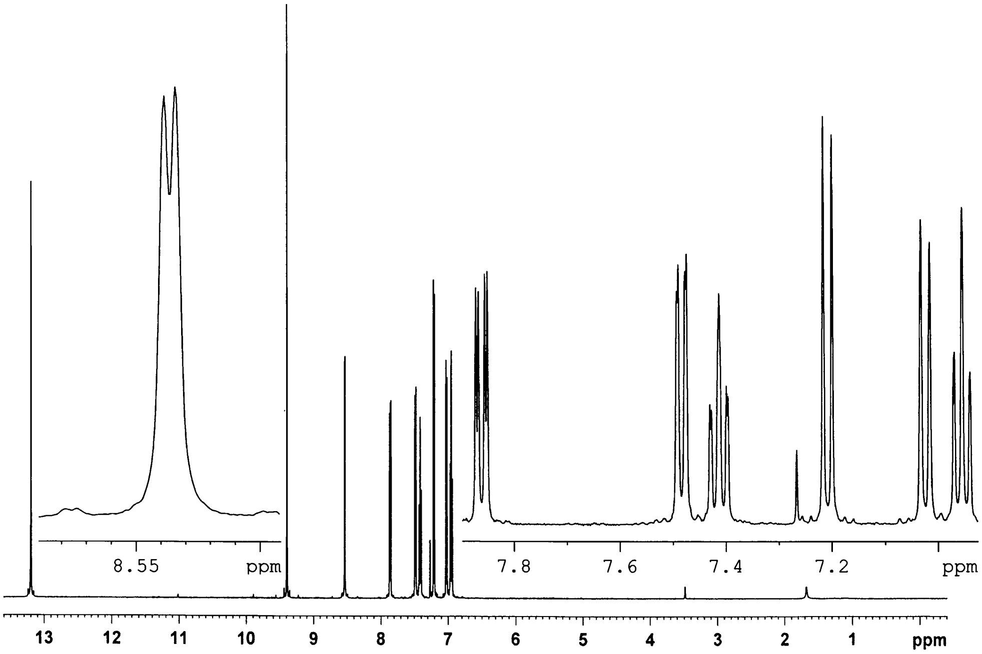

Fig. 3 ORTEP view of **1**, showing the crystallographic numbering scheme

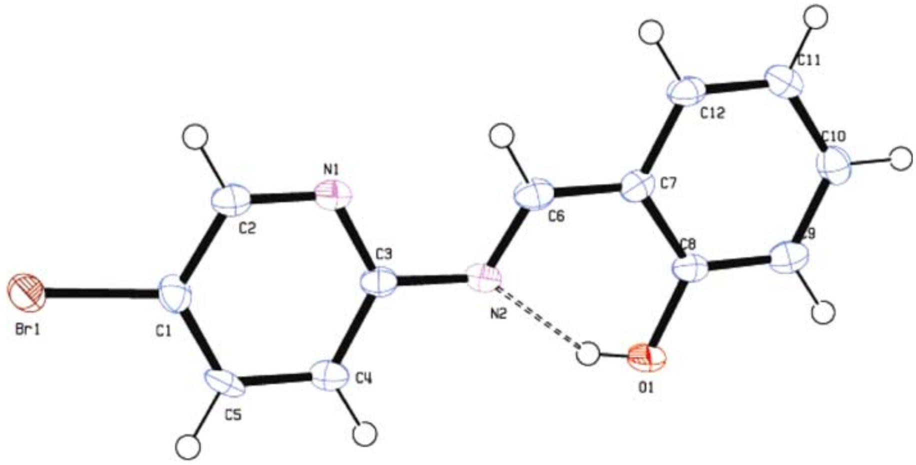

Table 3 Hydrogen-bond geometry (Å, °)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H10···N2	0.820	1.873	3.974	149.690

Table 4 Calculated total energies and relative stabilities of four conformers of the title compound at various levels of the theory

	A	B	C	D
DFT/6-31G(d)	−3219.1316623[a]			
	0[b]	13.93	4.29	17.85
DFT/6-31+G(d)	−3219.1805441			
	0	13.22	4.27	17.39

[a] Total energies in Hartree

[b] Relative stabilities in kcal/mol

The optimized bond lengths and selected bond angles for the preferred geometries of conformers **A–D** determined at B3LYP/6-31+G(d) levels are presented in Table 2 in accordance with the atom numbering scheme of the molecule shown in Fig. 3. A close looked at shows that the results of DFT calculation are in good agreement with those obtained from experimental data. For example DFT calculated N2–C3 bond length differs from the experimental value by 0.0179. In addition for N2–C6 bond length in the isomer **A**, difference between DFT calculation with experimental data was found as 0.0026.

It was observed that the influence of the internal hydrogen bonding on the molecular parameters, particularly in the C–C bond distance in phenyl rings, seems to be negligibly small except for C7–C8. The results of calculated bond angles of four isomers of the title compound are collected in the Table 2. It is clear that there is very good agreement between calculated and experimental data. In addition, the calculations show that hydroxyl group in the all isomers is located in the plane of the phenyl ring. Moreover, the pyridine ring in the isomers **A** and **B** is planar with C6=N2 bond, while in the isomer **D** pyridine ring and phenyl rings were deviated by 132.7 (DFT) degrees from each other. Interestingly DFT calculation predict that pyridine ring is deviated by 145.0 degree from C=N bond.

Conclusion

In summary, the new Schiff-base compound **1** was synthesized and single crystals were successfully characterized. FT-IR and ^{1}H-NMR spectroscopy confirms the functional groups, particularly –**H**C=N imine groups, of the compound. The single crystal X-ray diffraction has revealed a monoclinic structure, space group $P2_1/c$. The molecules form 3D network via weak C–H···O, C–H···Br, and C–H···π interactions. In the gas phase, four isomers of the title compound **1** were found. Density functional (DFT) calculations have been carried. They have confirmed the **A** isomer being the most stable one.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 739030. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgments We thank Golestan University (GU) and Yasouj University (YU) for partial support of this work. The institutional research plan No. AVOZ10100521 of the Institute of Physics and the project Praemium Academiae of the Academy of Sciences of the Czech Republic is also gratefully acknowledged.

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