Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 12 (4) 349-357: Winter 2016
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

FT-IR and NMR Spectroscopic Investigation and Hybrid Computational DFT/HF Analysis on the Molecular Structure of NSPD

Mohammad Mahdi Akbarzadeh[1,]*, Khirollah Mehrani[2], Shahriar Ghammamy[3]and Vahideh Hadigheh Rezvan[4]

[1] Building Chemical Engineering, Setoodeh Bana Co., Jomhori St., P.O. Box 13187-63715, Tehran, Iran
[2] Department of Chemistry, Ardabil Branch, Islamic Azad University, P.O. Box 56157-31567, Ardabil, Iran
[3] Faculty of Sciences, Science and Research Branch, Islamic Azad University, P.O. Box 14778-93855, Tehran, Iran
[4] Department of Chemistry, Imam Khomeini International University, P.O. Box 34148 - 96818 Qazvin, Iran

Received October 2015; Accepted January 2016

ABSTRACT

Compound (N,N-bis (salicylidene) 1,2-diaminophenylene) was prepared by condensation of ethanol solution of 2-Hydroxybanzaldehyde and 1,2-diaminophenylene. The compound was characterized by ^{1}H NMR, infrared spectroscopy (FT-IR) data and analytical data. The geometrical parameters and energies have been obtained from Density Functional Theory (DFT) B3LYP method and Hartree-Fock (HF) method with 3-21G* (6D, 7F) basis sets calculations. In the first instance, the full geometry optimization of the studied molecule was performed at the gradient corrected density functional level of theory using the hybrid B3LYP method based on Becke's three parameters functional of DFT and Gauge Including Atomic Orbital (GIAO). HF/3-21G* (6D, 7F) calculations on B3LYP geometries were done for all the reactants and HOMO-LUMO energy gaps. The force fields calculated with the B3LYP functional yield infrared spectra in very good agreement with the experiment. All of these calculations were performed using Gaussian 03 program.

Keywords: 2-Hydroxybanzaldehyde; Proton-Proton Coupling; DFT; HOMO-LUMO; GIAO

INTRODUCTION

Salicylaldehydes are two indent ligands and have good ability to form many transition metal ion complexes [1]. Many attempts have been made to evaluate different factors affecting the stability of the metal chelates along with their stability constants [2 - 4]. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry [5 - 9]. Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system.

They are used, e.g., in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectivity and sensitivity [10 - 12].

THEORETICAL METHODS

The geometric optimization and harmonic vibrational frequencies analysis were calculated using Density Functional Theory (DFT) methods. In this work, we employed B3LYP (the three-parameter fit of the exchange-correlation potential suggested by Becke in conjunction with the LYP exchange potential) with the

---

*Corresponding author: mehdiakbarzadeh10@yahoo.com

Standard basis: 3-21G* (6D, 7F) (Fig. 1) [13 - 17].

EXPERIMENTAL

IR spectra were recorded from KBr disk using a FT-IR NEXUS 670 instrument. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker 250 MHz Avance instruments using deuterochloroform (CDCl$_3$) as the solvent with tetra methyl silane (TMS) as the internal standard.

All theoretical calculations were performed using the Becke's three parameter exchange functional combined with the LYP correlation functional (B3LYP) [18]. The B3LYP functional is known to yield molecular geometries similar to those afforded by MP2 calculations [19 - 25].

Synthesis of compound nspd

To 2-Hydroxybanzaldehyde (1.88 g, 15 mmol) dissolved in ethanol (15 mL) was added to substituted 1,2-diaminophenylene (1.67 g, 15 mmol) in ethanol (15 mL) and contents were refluxed for 12 h at 70 °C. This product was washed with ethanol; solvent was evaporated, dried and recrystallized with ethanol. The yield ranged from 70 – 85 % and the melting points of compound was above 162 °C (Fig. 2).

RESULTS AND DISCUSSION

The reaction of 2-Hydroxybenzaldehyde with 1,2diaminophenylene afforded N,N- bis (salicylidene) 1, 2-diphenylenediamine according to Figure 2.

Infrared spectral data

There is strong coupling among the IR bands of ternary complexes and hence, quantitative interpretation of the band in the IR spectra is not possible without normal coordinate analysis. Important IR frequencies of the complexes are listed in (Table 1) along with their suggested assignments.

The spectrum of compound NSPD shows bands at 3432, 2854, 2712 and 1613 cm^{-1} that may be attributed to the υ (OH), υ (=C-H) and υ (C=N) respectively (Fig. 3).

^{1}H NMR spectral data

The ^{1}H NMR spectrum of the compound NSPD was recorded in CDCl$_3$.

The spectrum shows characteristic signals of the compound δ (ppm). A signal at 6 - 8.68 is due to (S, 2H, aldehyde protons), A signal at δ 12 - 14 (S, 2H,-OH).

In the spectra showed aromatic signals for Ha protons at δ 7.350, 7.372, 7.411, 7.438 as doublet of doublets (Fig. 4). The data of NMR also was taken from SDBS [26].

High-order splitting pattern

High-order splitting pattern takes place when chemical shift difference in hertz is much less or the same that order of magnitude as the j coupling.

$$\frac{\Delta\nu}{J} \leq 8$$

The second order pattern is observed as leaning of a classical pattern. The inner peaks are taller and the outer peaks are shorter in case of AB system (Fig. 5, 6). This is called the "roof effect."

Vicinal proton-proton coupling ($^3J_{HH}$)

Vicinal coupling occurs though three bonds (Fig. 7). The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules. Vicinal coupling constant always has the positive value and is affected by the dihedral angle (H-C-C-H), the valence angle (H-C-C), the bond length of carbon-carbon, and the effects of electronegative atoms.

$^3J = 7.0 – 0.5\cos\phi + 4.5\cos^2\phi$

Split (spin-spin) the aromatic protons are as follows: Proton resonance of (H_a) is a double ($^3J_{HH}$) of doublets data ($^4J_{HH}$) and the proton resonance (H_b) is a triple ($^3J_{HH}$) of doublet data ($^4J_{HH}$) is (Fig. 7). The proton resonance (H_c) is a double ($^3J_{HH}$) and the proton resonance (H_d) is a triplet ($^3J_{HH}$) (Fig. 7).

Multiple skewing the cleavage of several branches of spin - spin of the proton (H_a) is shown in Fig. 7.

Molecular geometry

Calculations of the molecular orbital geometry show that the absorption maxima of this molecule correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. The optimized structural parameters of compound NSPD calculated by ab-initio/HF levels with the standard 3-21G*(6D, 7F) basis set are listed in Table 2. Figure 8 shows the atomic orbital composition calculated for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NSPD. Both orbitals are of π nature, as expected.

The energy gap between the HOMO and LUMO (Δ (E_{LUMO} - E_{HOMO})), for spin non-polarized, is also shown in Figure 8.

To understand the reactivity of amines and establish a relationship with MOs, the amine sets, namely those aliphatic, aromatic, and heterocyclic, were classified according to their Frontier MOs.

Table 1. Infrared spectral data of compound NSPD

	υ OH	υ =C-H	$\upsilon_{C-H}^{SP^2}$	$\upsilon_{C-H}^{SP^3}$	$\upsilon_{C-H}^{Inplane}$	υ_{C-H}^{OPP}
Compound NSPD	3432(w)	2854/14(w)	3052/93(w)	-	1107/78 Sh (w)	756/17 Sh (s)
			2986/22(w)			
		2712/25(w)	2925/18(w)			

Table 2. Theoretical and experimental IR spectral data (cm^{-1}) of compound NSPD at the HF/3-21G*(6D, 7F)

Bond lengths	HF/3-21G*(6D,7F)	Bond angles	HF/3-21G*(6D,7F)
C1-C2	1.39516	C1-C2-C3	120.00862
C2-C3	1.39471	C6-C11-N23	122.22492
C3-C4	1.39543	C11N23C13	116.4408
C4-C5	1.39482	C13-C15-C18	119.99397
C5-C6	1.39514	C13-C14-C16	120.00864
C6-C11	1.54	C14-C16-C19	119.99842
C11-N23	1.22732	C15-N24-C35	122.22486
N23-C13	1.67733	N24-C35-C25	115.20147
C13-C14	1.39471	C35-C25-C26	135.09941
C14-C16	1.39516	C25-C26-C28	119.99843
C16-C19	1.39483	C26-C28-C31	119.99998
C19-C18	1.39514	C31-C30-C27	119.99998
C18-C15	1.39483	C27-C25-C35	94.24317
C15-C13	1.39543	O38-C27-C25	120.01279
C15-N24	1.54	O38-C27-C30	119.99302

Tabel 2. Continued

N24-C35	1.22732	O37-C5-C6	119.9839
C35-C25	1.74314	O37-C5-C4	120.01137
C25-C26	1.39516	-	-
C26-C28	1.39483	-	-
C28-C31	1.39514	-	-
C31-C30	1.39482	-	-
C30-C27	1.39543	-	-
C27-C25	1.39471	-	-
C27-O38	1.47	-	-
C5-O37	1.47	-	-

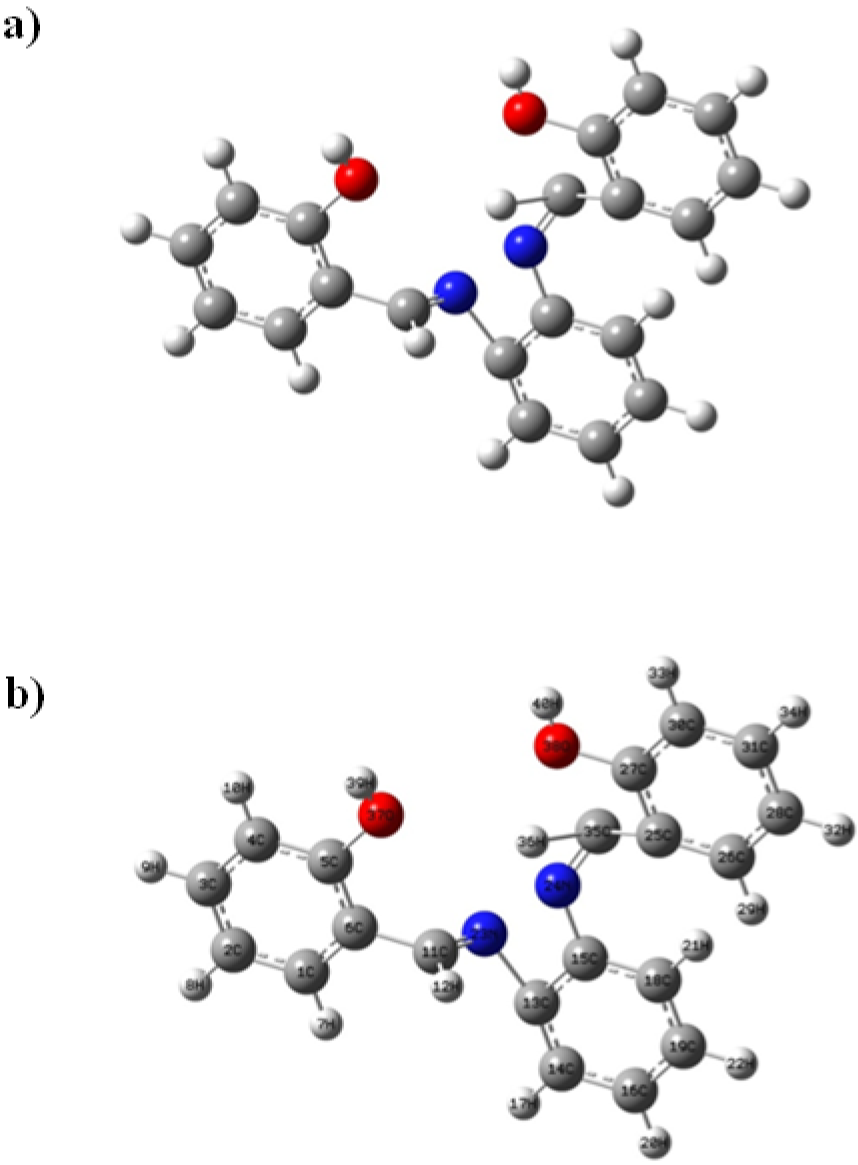

Fig. 1. a) System adopted in the theoretical study for compound NSPD **b**) Numbering system adopted in the theoretical study for compound NSPD using HF/3-21G*(6D,7F) level.

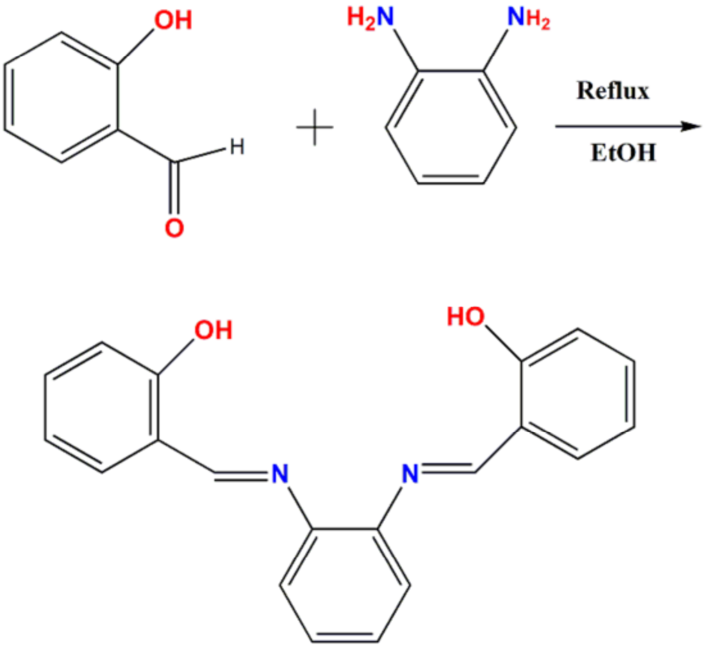

Fig. 2. Chemical structure of compound NSPD.

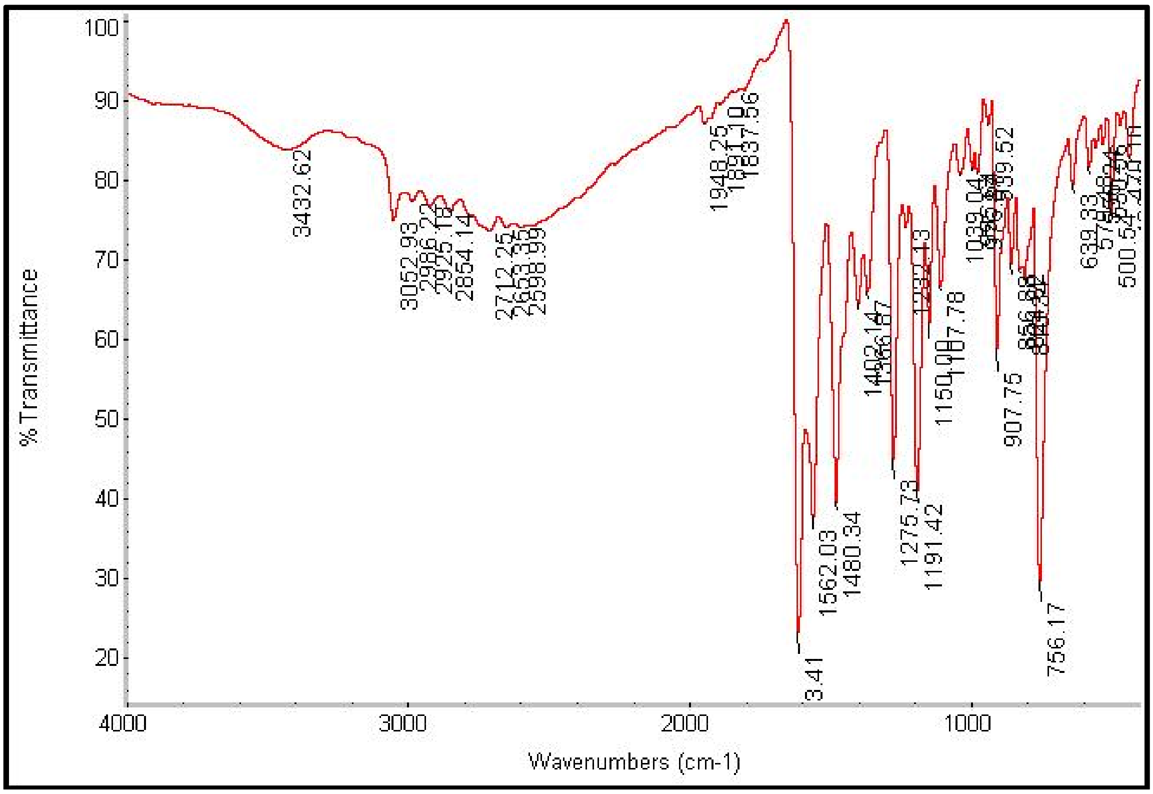

Fig. 3. FT-IR spectrum of compound NSPD.

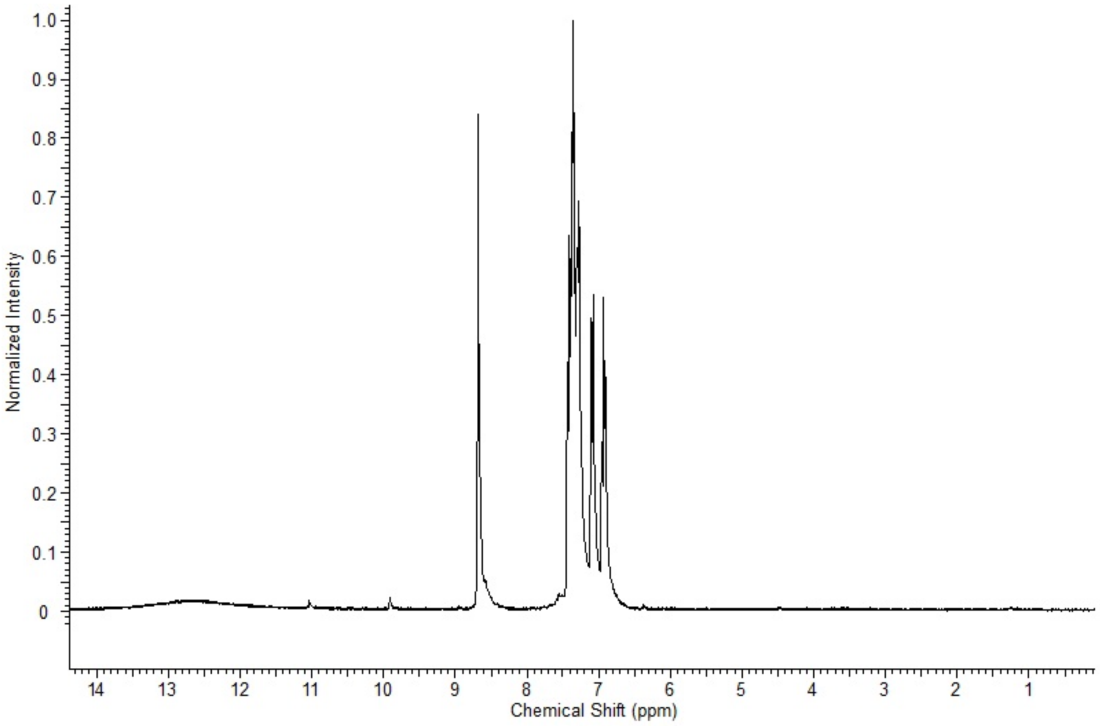

Fig. 4. ^{1}HNMR spectrum of the compound **NSPD**.

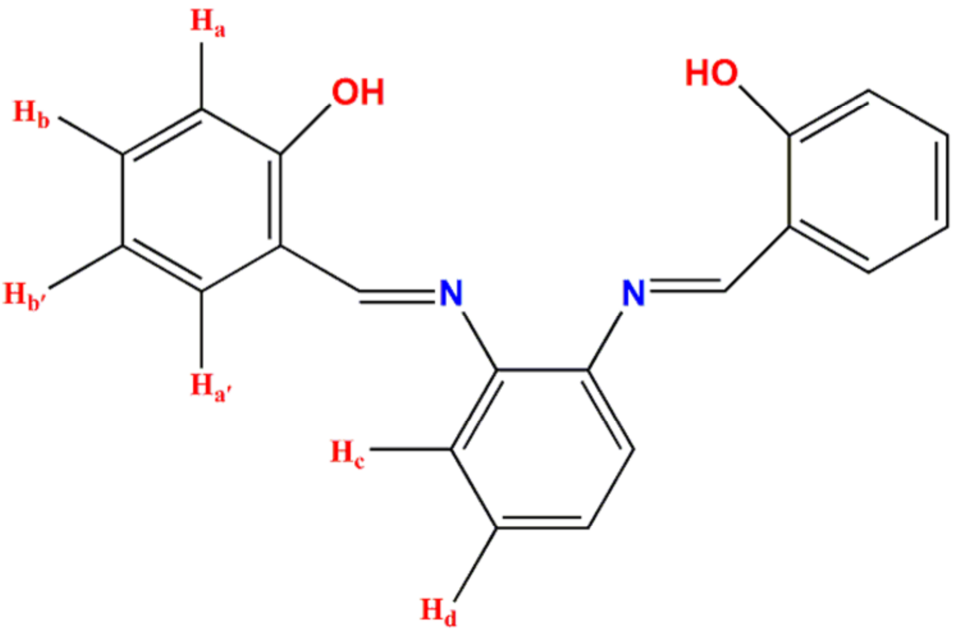

Fig. 5. Chemical structure of compound NSPD with bonds hydrogen atoms.

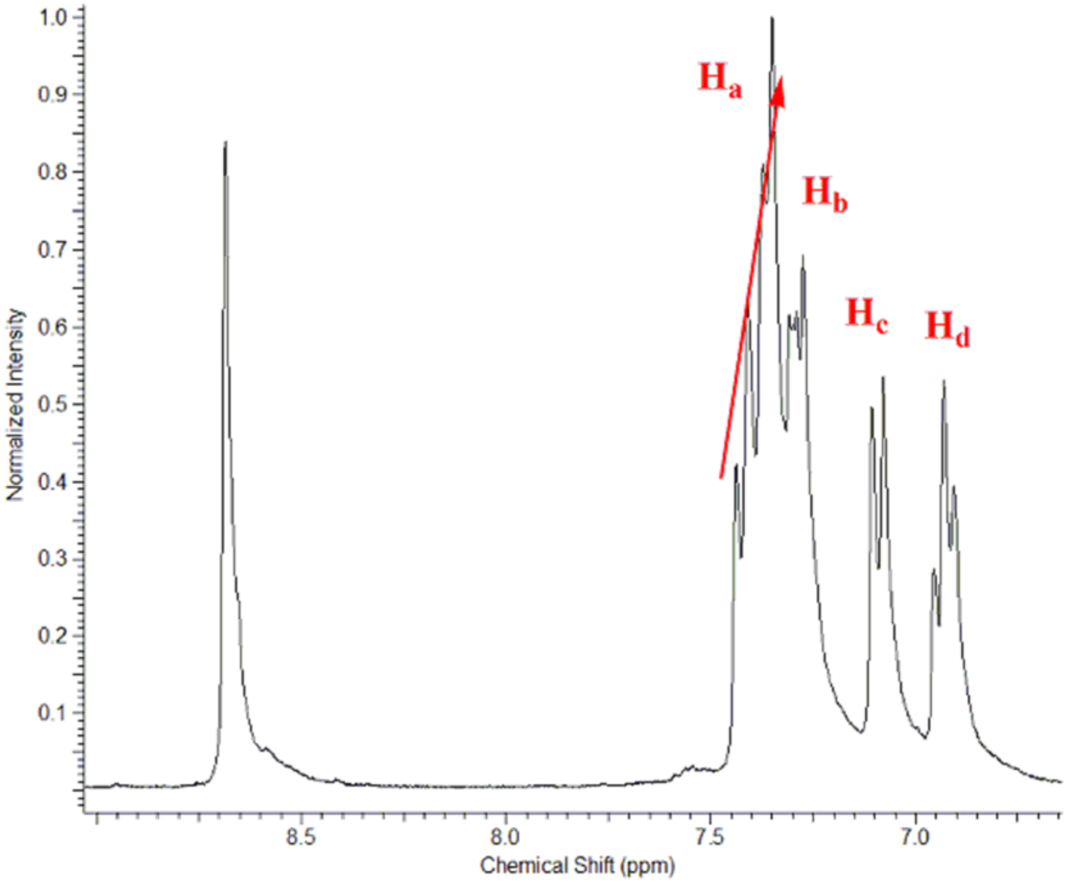

Fig. 6. Multiple skewing the cleavage of several branches of spin - spin of the proton (H_a).

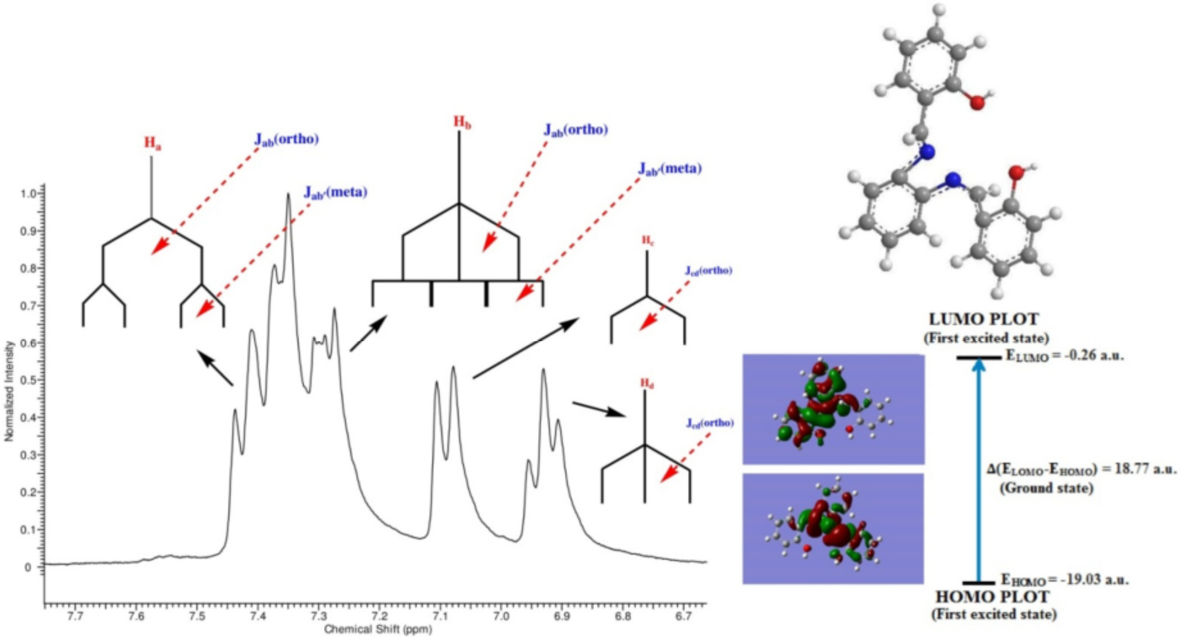

Fig. 7. Graphical analysis of ^{1}HNMR spectrum of compound NSPD.

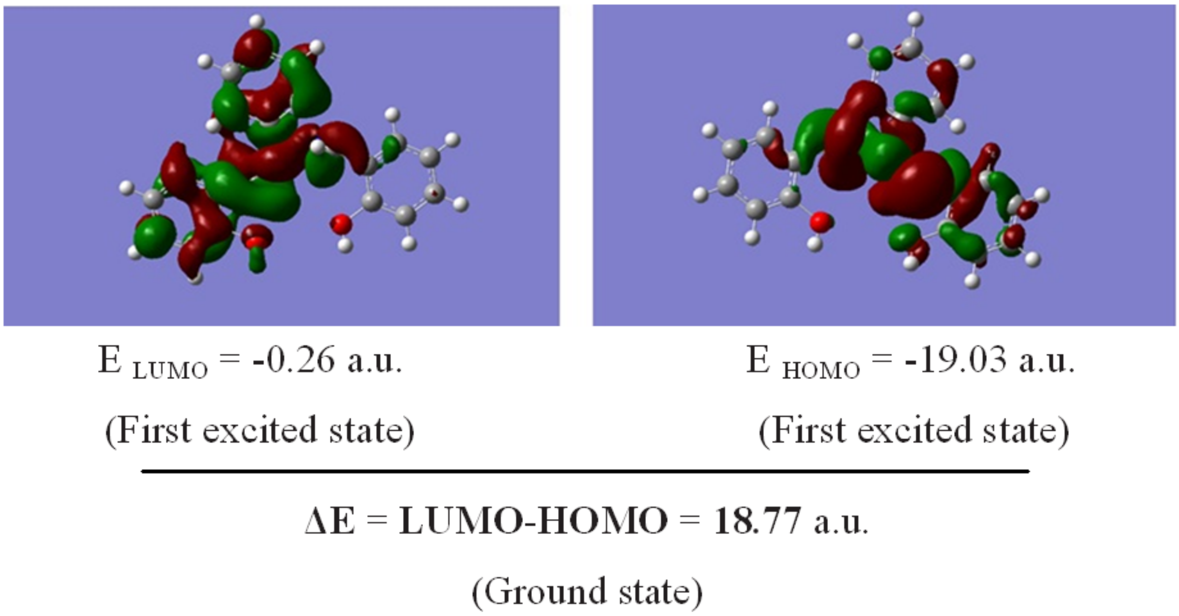

Fig. 8. The atomic orbital compositions of the frontier molecular orbital for compound NSPD at the HF/3-21G* (6D, 7F).

CONCLUSION

Schiff base were prepared in this work through condensation of 2-Hydroxy banzaldehyde derivatives and 1,2-diamino phenylene derivatives, The IR and NMR spectral data confirmed their molecular structure.

In this work, we have shown calculations of NSPD performed using Hartree-Fock and density functional methods at 3-21G* (6D, 7F) basis set level. These results allowed us to characterize the different reactive sites within the molecules. Total energies as a measure of stability, and an evaluation of electro negativities and chemical hardness's and as a measure of the HOMO-LUMO gap useful for the design of low-band gap NSPD had been accomplished. All the experimental reports of NSPD were evaluated by comparing theoretical calculations of the NSPD. The molecular structure optimization and corresponding vibrational harmonic frequencies of NSPD were calculated using ab-intio HF and DFT calculations.

REFERENCES

[1]. K. K. Narang, A. Aggarwal, Inorganica Chimica Acta., 9 (1974) 137.
[2]. Henry Freiser, Anal. Chem., 77 (1952) 830.
[3]. *H. Irving, R. J. P. Williams, J. Chem. Soc*. (1953) 3192.
[4]. Kazuo. Nakamoto, Paul J. Mc Carthy, E. Martell. Arthur, J. Am. Chem. Soc., 83 (1961) 1272.
[5]. Venukrishnan Komanduri, Michael J. Krische, J. Am. Chem. Soc., 128 (2006) 16448.
[6]. Lillian S. De. Bruin, P. David Josephy, Janusz B. Pawliszyn, Anal. Chem., 70 (1998) 1986.
[7]. Qi. Liu, Yitzhak Tor, Org. Lett., 5 (2003) 2571.
[8]. Karine Barral, Adam D. Moorhouse, John E. Moses, Org. Lett., 9 (2007) 1809.
[9]. Marco. Bandini, Giorgio Cozzi Pier, Paolo. Melchiorre, Stefano Morganti, Achille Umani-Ronchi, Org. Lett., 3 (2001) 1153.

[10]. Eric. Bakker, Yu. Qin, Anal. Chem., 78 (2006) 3965.

[11]. Jay W. Grate, Steven N. Kaganove, Samuel J. Patrash, Richard Craig, Mary Bliss, Chem. Mater., 9 (1997) 1201.

[12]. *K.* Bodenhöfer, A. Hierlemann, J. Seemann, G. Gauglitz, B. Koppenhoefer, W. Gpel, Nature., 387 (1997) 577.

[13]. R. DitchfieldJ. Chem. Phys., 56 (1972) 5688.

[14]. K. Wolinski, J. F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.

[15]. Anthony P. Scott, Leo. Radom, J. Phys. Chem., 100 (1996) 16502.

[16]. Guntram Rauhut, Peter Pulay, J. Phys. Chem., 99 (1995) 3093.

[17]. Hong Ju, Zhen-Peng Kai, Yan Li, Corrosion Science., 50 (2008) 865.

[18]. Axel D. J. Becke, Chem. Phys., 98 (1993) 1372.

[19]. Mareike Gerenkamp, Stefan Grimme, Chemical Physics Letters., 392 (2004) 229.

[20]. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, J. M. Frisch, J. Phys. Chem., 98 (1994) 11623.

[21]. Annegret Hille, Ingo Ott, Ana Kitanovic, Igor. Kitanovic, Hamed Alborzinia, Elke Lederer, Stefan Wölfl, Nils Metzler-Nolte, Sven Schäfer, William S. Sheldrick, Caroline Bischof, Ulrich Schatzschneider, Ronald Gust, JBIC Journal of Biological Inorganic Chemistry., 14 (2009) 725.

[22]. Jian-ning Liu, Bo-wan Wu, Bing Zhang, Yongchun Liu, Turk. J. Chem., 30 (2006) 41.

[23]. *M.* N. Patel, S. H. Patil, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry., 12 (1982) 203.

[24]. Krunoslav Užarević, Mirta Rubčić, Vladimir Stilinović, Branko Kaitner, Marina Cindrić, Journal of Molecular Structure., 984 (2010) 232.

[25]. A. Z. El-Sonbati, A. A. El-Bindary, M. A. Diab, S. A. Mazrouh, Monatshefte für Chemie/Chemical Monthly., 124 (1993) 793.

[26]. SDBS Web: http://sdbs.riodb.aist.go.jp/ National Institute of Advanced Industrial Science and Technology, Japan 2013.