



## Computational characterization of (*E*)-N-(3-bromo-4-fluorobenzylidene)-4-nitrobenzenamine compound

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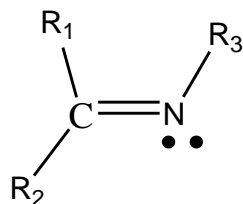
### ABSTRACT

Schiff bases are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group. In this work, (*E*)-N-(3-bromo-4-fluorobenzylidene)-4-nitrobenzenamine have been synthesized and characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies. Density functional theory (DFT) has been used to optimize geometrical parameters, atomic charges, vibrational wavenumbers and intensity of vibrational bands. The molecular properties HOMO-LUMO, NBO were calculated using B3LYP/6-311G (d, p) basis set. The polarizability and first order hyperpolarizability of the title Compound was calculated and interpreted.

**Keywords:** Schiff base, IR and Raman spectra, DFT, HOMO-LUMO and NBO

### 1. INTRODUCTION

Schiff bases, named after Hugo Schiff<sup>1</sup>, are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) (**Scheme - 1**), is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group.



R<sub>1</sub>, R<sub>2</sub> and (or) R<sub>3</sub> = Alkyl / Aryl

### Scheme - 1

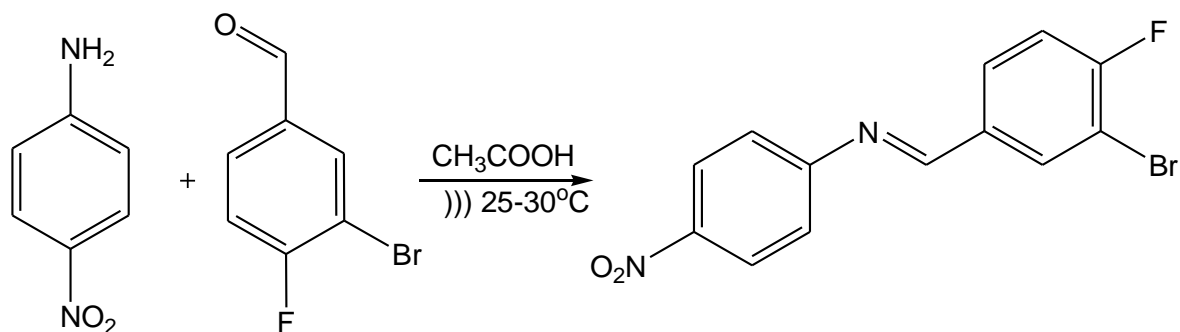
The chemistry of  $>C=N$  is studied extensively because of its high synthetic flexibility, varied coordinating ability and medicinal utility. The compounds containing  $>C=N$  include mainly the products of reaction between aldehyde or ketonic components and primary aliphatic or aromatic amines, ammonia, hydrazine, N-phenylhydrazine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide and their substituted derivatives. Schiff bases have recently assumed greater importance in view of the fact that several of them have been found to be biologically active and have found used in biology, medicine as well as in industry. Schiff bases exhibit a broad range of biological activities including antimicrobia<sup>2</sup>, anti-inflammatory<sup>3</sup>, analgesic<sup>4</sup>, anti-tubercular<sup>5</sup>, anti-mycobacterial<sup>6</sup>, antioxidant<sup>7</sup>, antiviral<sup>8</sup> and inhibitors<sup>9</sup>, antifungals<sup>10</sup>, antitumor<sup>11</sup>, insecticides<sup>12</sup>, antihelminthics<sup>13</sup> and antiemetics<sup>14</sup>. Schiff bases have good electronic, linear and non-linear optical properties (Several theoretical analyses have been carried out for isomeric forms of these Schiff bases).

The present investigation is focused on the synthesis and theoretical investigation of the molecular structures and their vibrational frequencies analysis and charges of newly synthesized Schiff bases derived from 3-bromo-4-fluoro benzaldehyde having extended conjugation. HOMO-LUMO energies, dipole moments, polarizabilities and first hyperpolarizabilities were determined by density functional theory (DFT) method.

## 2. EXPERIMENTAL

### General Procedure for Preparation of (*E*)-N-(3-bromo-4-fluorobenzylidene)-4-nitrobenzenamine (4NBA)

An appropriate equimolar quantity of the 4-nitroaniline (0.01mol) with 3-bromo-4-fluoro benzaldehyde (0.01 mol) and absolute ethanol (10 ml) were taken in 150 ml conical flask. To this mixture, glacial acetic acid (1 drop) was added. The mixture was partially submerged in the sonic bath<sup>15</sup> at room temperature at 25-30 °C for 50-60 min (**Scheme - 2**). The completion of the reaction was monitored by TLC and the mixture was cooled at room temperature. The resulting precipitate was filtered and washed with cold water. The product appeared as pale yellow solids. Then this was recrystallized using ethanol to obtain pale yellow glittering solid which melts at 112-113 °C. m.f: C<sub>13</sub>H<sub>8</sub>BrFN<sub>2</sub>O<sub>2</sub>; Yield 86%.



Scheme-2

**Table 1.** IR spectral characterization of (*E*)-N-(3-bromo-4-fluorobenzylidene)-4-nitrobenzenamine (4NBA).

Type	Vibration mode	Observed Frequency value (cm <sup>-1</sup> )	Reported frequency value
Aromatic	C-H ( <i>stretching</i> )	3064.89	3080 – 3010 (cm <sup>-1</sup> ) <sup>16,17</sup>
	C-H ( <i>in-plane deformation</i> )	1082.07	1300-1000 (cm <sup>-1</sup> ) <sup>18,19</sup>
	C-H ( <i>out of plane deformation</i> )	823.60	950-809 (cm <sup>-1</sup> ) <sup>20,21</sup>
Ar-N=CH-Ar	-N=C ( <i>stretching</i> )	1622.13	1640 –1580 (cm <sup>-1</sup> ) <sup>22,23</sup>
C-Br	C-Br ( <i>stretching</i> )	677.01	650–485 (cm <sup>-1</sup> ) <sup>22,23</sup>
C-F	C-F ( <i>stretching</i> )	1265.30	1270-1100 (cm <sup>-1</sup> ) <sup>24,25</sup>
C-NO <sub>2</sub>	C-NO <sub>2</sub> ( <i>asymmetric stretching</i> )	1564.27	1570-1485 (cm <sup>-1</sup> ) <sup>26</sup>
	C-NO <sub>2</sub> ( <i>symmetric stretching</i> )	1365.60	1370-1320 (cm <sup>-1</sup> ) <sup>26</sup>

## 2. 1. Spectral measurements

The UV spectra were recorded on SHIMADZU-1650 SPECTROMETER in spectral grade methanol. IR spectra of all Schiff base compounds were recorded on AVATAR – NICOLET 330 FT-IR spectrophotometer. The sample was mixed with KBr and pellet technique was adopted to record the spectra. The <sup>1</sup>H and <sup>13</sup>C NMR Spectra of all synthesised Schiff base compounds were recorded using BRUKER AVIII 5000, 500 MHz for <sup>1</sup>H NMR spectra and 125.46 MHz for <sup>13</sup>C NMR spectra model Spectrometer. RAMAN spectra were recorded on BRUKER:RFS27 spectrometer operating at Laser 100 mW in Sophisticated Analytical Instrument Facility(SAIF).

## 2. 2. Computational studies

All calculations were done at density functional theory (DFT) level on a personal computer using Gaussian-06 package using B3LYP/6-31G (d,p) basis set. The polarizabilities and hyperpolarizabilities were determined from the DFT optimized structure by finite field approach using B3LYP/6-31 G (d, p) basis set. Vibrational frequencies are characterized using the B3LYP/6-31 G (d, p) available in Gaussian-06 package.

## 3. RESULTS AND DISCUSSION

### 3. 1. Molecular geometry

The optimized structural parameters such as bond lengths, bond angle and dihedral angle of **4NBA** was determined at B3LYP level theory with 6-31G (d,p) basis set and are presented in Table - 2. Optimized structure of **4NBA** shown in Fig. 1. Overall, the C21-N20-C3 bond angles ( $120.2^\circ$ ) of compound **4NBA** illustrate the double bond character and the  $sp^2$  hybridization of the imine carbon atom. The bond angle in title compound, indicate an almost planar E-configuration with respect to the imine C=N bond. As a result from optimized structural parameters such as bond lengths, bond and dihedral angles, we can conclude the E-configuration with respect to the imine C=N bond is more stable compound.

### 3. 2. Vibrational assignments

The vibrational analysis of **4NBA** is performed on the basis of the characteristic vibrations of nitro and imine modes. The molecule under consideration belongs to the C1 point group. It has 27 atoms, so 75 normal modes of fundamental vibrations. The computed vibrational wavenumbers, their IR and Raman activities corresponding to the different normal modes are used for identifying the vibrational modes. The harmonic vibrational frequencies calculated for **4NBA** at B3LYP level using the 6-31G(d,p) basis set have been summarized in Table 3.

#### (a) C=N Vibrations

The assignment band due to the C=N stretching vibration in Ar-N=C-Ar type of compounds expected in the region  $1640-1580\text{ (cm}^{-1}\text{)}$ <sup>27</sup>. Mohan *et.al.*<sup>28</sup> have identified the stretching frequency of C=N bond in benzimidazole at  $1617\text{ cm}^{-1}$ . The C=N stretching vibration of the **4NBA** compound are identified at  $1622\text{ cm}^{-1}$  in FT-IR and  $1627\text{ cm}^{-1}$  in FT-Raman. These observed frequencies value shows good agreement with the theoretically calculated wave number  $1639\text{ cm}^{-1}$  (mode no: 9). The above result is in close agreement with the literature values<sup>29-31</sup>.

#### (b) C-F vibration

The Aromatic fluorine compounds give stretching bands in the region  $1270-1100\text{ (cm}^{-1}\text{)}$ <sup>32</sup>. In our compound **4NBA**, mostly stretching vibrations of C-F is observed in this region. Since the vibration is easily influenced by adjacent atoms or groups. The C-F stretching vibration shows a peak at  $1265\text{ cm}^{-1}$  in FT-IR and peak at  $1283\text{ cm}^{-1}$  in FT-Raman, respectively and its corresponding DFT calculated vibration coincides well at  $1257\text{ cm}^{-1}$  (mode no: 24). The in-plane bending and out-of-plane bending vibrations are observed

in lower range frequency below  $500\text{ cm}^{-1}$ . The C-F in-plane bending vibrations are expected in the range  $420\text{-}254\text{ (cm}^{-1}\text{)}^{33}$ . The band observed at  $362\text{ cm}^{-1}$  in FT-Raman is assigned to C-F in-plane bending vibration. The computed C-F in-plane bending vibration for 4NBA observed at  $479,445,375$  and  $214\text{ cm}^{-1}$  (mode numbers: 56,57,61,66). The C-F out-of-plane bending vibrations were observed in the range  $520\text{-}101\text{ (cm}^{-1}\text{)}^{34}$ . The computed out-of-plane bending vibrations are observed at  $576$ , and  $232\text{ cm}^{-1}$ . (mode numbers: 52,65)

### (c) C- Br vibrations

The C-Br bond shows lower absorption frequencies as compared to C-H bond due to the decreased force constant and increase in reduced mass. The calculated C- Br stretching vibrations of the 4NBA compound are observed at  $247\text{ cm}^{-1}$  (mode no: 64). These stretching vibration agree with the literature data<sup>35</sup>. The corresponding vibration in experimental FT-Raman band appearing at  $241\text{ cm}^{-1}$ . The C-Br out-of-plane bending and in-plane bending vibrations are assigned  $232$  (mode no: 65) and  $173\text{ cm}^{-1}$  (mode no: 67), respectively. This is in agreement with the literature data<sup>35</sup>.

### (d) NO<sub>2</sub> Vibrations

Aromatic nitro compounds have strong absorption due to the asymmetric and symmetric stretching vibration of the NO<sub>2</sub> group at  $1570\text{-}1485\text{ cm}^{-1}$  and  $1370\text{-}1320\text{ cm}^{-1}$  respectively. In the present study, FT-Raman bands at  $1507\text{ cm}^{-1}$  and FT-IR band at  $1564\text{ cm}^{-1}$  are assigned to asymmetric stretching. The FT-IR band appearing at  $1365\text{ cm}^{-1}$  and the FT-Raman band appearing at  $1338\text{ cm}^{-1}$  are assigned to NO<sub>2</sub> symmetric stretching. The theoretically calculated frequencies for the NO<sub>2</sub> asymmetric stretching vibration is calculated at  $1597$  and  $1543\text{ cm}^{-1}$  (mode no: 10,14) and NO<sub>2</sub> symmetric stretching vibrations is calculated at  $1338\text{ cm}^{-1}$  (mode no:20) respectively. The theoretically calculated wave number shows good agreement with the experimental values. This is in agreement with the literature data<sup>36</sup>.

The deformation vibration of NO<sub>2</sub> group (scissoring, wagging, rocking and twisting) contributes to several modes in the low frequency region<sup>37</sup>. The NO<sub>2</sub> scissoring mode of vibration occurs in the region  $815\text{ cm}^{-1}$  (mode no: 43) in theoretically computed (DFT/B3LYP) methods is well supported by  $814\text{ cm}^{-1}$  in FT-IR. For the present compound wagging mode of NO<sub>2</sub> assigned at  $732\text{ cm}^{-1}$  (mode no:46) in B3LYP/6-31G(d,p) methods coincides with  $723\text{ cm}^{-1}$  in FT-IR experimental spectra. The frequency computed theoretically by B3LYP/6-31G(d,p) methods at  $527,511\text{ cm}^{-1}$  (mode numbers: 54,55) is assigned to rocking mode of NO<sub>2</sub> group. The corresponding rocking mode of NO<sub>2</sub> group observed at  $501\text{ cm}^{-1}$  in FT-IR. The scissoring, wagging, rocking mode of 4NBA shows very good agreement with the literature data<sup>38</sup>.

### (e) C-H Vibrations

In the aromatic compounds, the C-H stretching vibrations normally occur at  $3100\text{ - }3000\text{ (cm}^{-1}\text{)}^{27}$ . The aromatic C-H stretching vibration shows a signal at  $3005\text{ cm}^{-1}$  and  $3064\text{ cm}^{-1}$  in FT-IR and band observed at  $3075\text{ cm}^{-1}$  in FT-Raman also corresponds to the same vibration mode. The C-H in plane bending ring vibrations<sup>39</sup> normally are shown as a number of strong to weak sharp bands in the region  $1300\text{-}1000\text{ cm}^{-1}$ . The C-H in plane bending vibrations of the 4NBA compound are identified at  $1014$ ,  $1082$  and  $1130\text{ cm}^{-1}$  in FT-IR and  $1108$ ,  $1179$ ,  $1195\text{ cm}^{-1}$  in FT-Raman, respectively. The theoretically calculated frequencies

for the C-H in-plane bending vibrations are calculated at 1265, 1243, 1149, 1104, 1085 and 1021  $\text{cm}^{-1}$  (mode numbers: 23, 25, 28, 29, 31, 32). The theoretically calculated wave number shows good agreement with the experimental values. The out-of-plane bending vibrations<sup>40</sup> are strongly coupled vibrations and normally observed in the region 950-809  $\text{cm}^{-1}$ . In the present study, the C-H out-of-plane bending bands are observed at 908, 862 and 823  $\text{cm}^{-1}$  in FT-IR and 863  $\text{cm}^{-1}$  in FT-Raman. The theoretically calculated wavenumber are 946, 881, 840, 817, 815 and 809  $\text{cm}^{-1}$  (mode numbers: 36, 39, 41, 42, 43, 44) shows well agreement with the experimental values.

### 3. 3. Frontier molecular orbital analysis

The MOs for gas phase are outlined in **Figure 3**. The positive phase is red and the negative one is green. The HOMO is located all over the molecule and the energy is = 6.7387 eV. The LUMO is located all over the nitro group phenyl ring whereas in halogens containing phenyl ring LUMO is located over carbon atoms and the energy is = 2.6629 eV. The energy gap of 4NBA is about = -4.0763 eV.

$$\begin{aligned} \text{HOMO energy} &= 6.7387 \text{ eV,} \\ \text{LUMO energy} &= 2.6629 \text{ eV,} \\ \text{HOMO-LUMO energy gap} &= 4.0758 \text{ eV} \end{aligned}$$

In addition, the energy gap of HOMO-1 LUMO+1 is 5.3708 eV and the HOMO-2 LUMO+2 is 6.5182 eV. Moreover, the lower in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. Chemical hardness is related with the stability and reactivity of a chemical system, it measures the resistance to change in the electron distribution or charge transfer. In this sense, chemical hard-ness corresponds to the gap between the HOMO and LUMO. The larger the HOMO–LUMO energy gap, the harder and more stable/less reactive the molecule. The higher value of  $\Delta E$  represents more hardness or less softness of a compound, thus compound 4NBA referred as hard molecule.

### 3. 4. Natural Bond Orbital (NBO) Analysis of 4NBA

The delocalization effects or donar-acceptor charge transfers (CTs) can be estimated of the Fock matrix in the NBO basis. The stabilization energy  $E^{(2)}$  connected with electron delocalization between donor NBO(i) and acceptor NBO(j) were estimated as following equation (1),

$$E^{(2)} = \Delta E_{ij} = qi \frac{F(i,j)x^2}{\epsilon_j - \epsilon_i} \quad \dots (1)$$

The results of second-order perturbation theory analysis of the Fock matrix and the stabilization energies larger than 3  $\text{kcal mol}^{-1}$  are presented in **Table 4**. Some strong intramolecular interactions, which are formed by the overlap between  $\sigma(\text{C-C})$ ,  $\sigma^*(\text{C-C})$  and  $\pi(\text{C-C})$ ,  $\pi^*(\text{C-C})$  bond orbital in the aromatic ring, which leads intramolecular charge transfer (ICT) causing stabilization of the system have revealed by the NBO analysis. The strong intramolecular hyperconjugative interaction of the  $\sigma$  and  $\pi$  electrons of C–C to the anti C–C bond of the aromatic rings results to stabilization of some part of the rings as evident from

**Table 4.** The orbital interaction energy between  $\pi(\text{C1-C6}) \rightarrow \pi^*(\text{C4-C5})$ ,  $\pi(\text{C2-C3}) \rightarrow \pi^*(\text{C4-C5})$  and  $\pi(\text{C12-C13}) \rightarrow \pi^*(\text{C14-C15})$ ,  $\pi^*(\text{C11-C16})$  and shows larger stabilization E(2) energies of about are 210.51, 222, 96.66, 126.49 respectively. The higher interaction energies are due to strong interactions in phenyl rings leading to the stabilization of the molecule.

### 3. 5. Non linear optical Properties of 4NBA

The mean polarizability ( $\alpha_0$ ), the total static dipole moment ( $\mu$ ) and the first order hyper polarizability ( $\beta_0$ ) are calculated by using x, y, z components and are shown in equations (2) to (5),

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad \dots (2)$$

$$\alpha_0 = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \dots (3)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad \dots (4)$$

$$\beta_0 = [(\beta_{XXX} + \beta_{XYY} + \beta_{XZZ})^2 + (\beta_{YYY} + \beta_{YXX} + \beta_{YZZ})^2 + (\beta_{ZZZ} + \beta_{ZXX} + \beta_{ZYY})^2]^{1/2} \quad \dots (5)$$

The total molecular dipole moment ( $\mu$ ) and the first-order hyperpolarizability ( $\beta$ ) were calculated for the present compound by B3LYP method with 6-31G(d,p) basis set. The calculated values of the  $\mu_{\text{tot}}$ , and  $\beta_{\text{tot}}$  are listed in **Table 5**. The  $\alpha$  and  $\beta$  values of the Gaussian 06 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) ( $\alpha : 1 \text{ a.u} = 0.1482 \times 10^{-24} \text{ esu}$ ; for  $\beta : 1 \text{ a.u} = 8.639 \times 10^{-33} \text{ esu}$ ; ). To study the NLO properties of molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison.

It is well known that the higher values of dipole moment and the hyperpolarizabilities ( $\beta$ ) are important for more active NLO properties. The first hyperpolarizabilities of the present molecule ( $5.3223 \times 10^{-30}$ ) is found to be fourteen times greater than the urea ( $\mu$  and  $\beta$  of urea are 1.3732 Debye and  $0.3728 \times 10^{-30} \text{ cm}^5/\text{esu}$ )<sup>41</sup> and from the resultant values we identify the present compound 4NBA as a good NLO material. By knowing the dipole moment in a molecule we can study the dipole-dipole interactions which occur inside the atoms of that molecule and the inter-molecular interactions are getting stronger when the dipole moment is high.

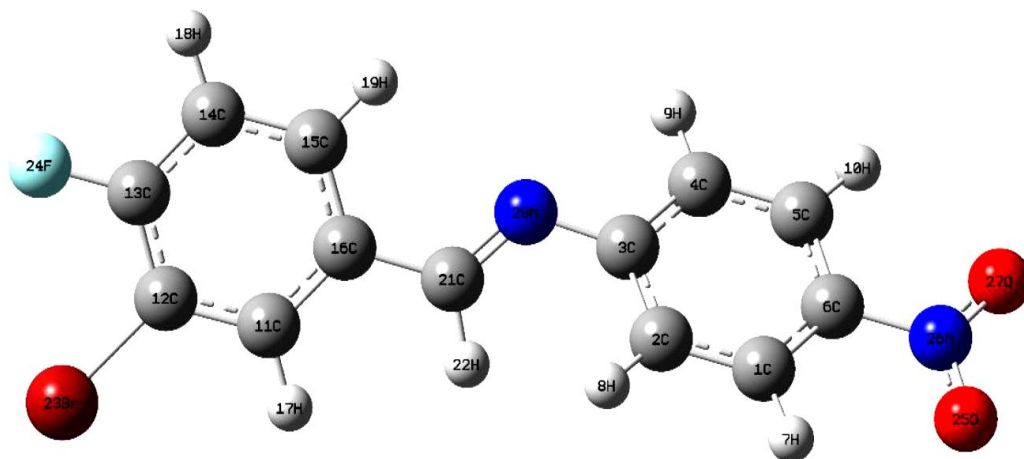
**Table 2.** Selected Bond Lengths, Bond Angles and Dihedral Angles of 4NBA

Parameter	Bond length (Å)	Parameter	Bond Angle (°)	Parameter	Dihedral Angle (°)
C2-C1	1.3894				
C3-C2	1.4088	C3-C2-C1	120.47		
C4-C3	1.4076	C4-C3-C2	119.21	C4-C3-C2-C1	-1.546



C5-C4	1.3871	C5-C4-C3	120.62	C5-C4-C3-C2	2.3319
C6-C1	1.3939	C6-C1-C2	118.97	C6-C1-C2-C3	-0.032
H7-C1	1.0827	H7-C1-C2	121.68	H7-C2-C2-C3	179.67
H8-C2	1.085	H8-C2-C1	119.84	H8-C2-C1-C6	-178.1
H9-C4	1.0844	H9-C4-C3	118.57	H9-C4-C3-C2	-178.4
H10-C5	1.0826	H10-C5-C4	121.74	H10-C5-C4-C3	179.06
C11-C3	4.7942	C11-C3-C2	98.827	C11-C3-C2-C1	161.45
C12-C11	1.3909	C12-C11-C3	153.37	C12-C11-C3-C2	139.79
C13-C12	1.3947	C13-C12-C11	119.26	C13-C12-C11-C3	1.2908
C14-C13	1.3943	C14-C13-C12	121.11	C14-C13-C12-C11	-0.019
C15-C14	1.3876	C15-C14-C13	119.49	C15-C14-C13-C12	-0.042
C16-C11	1.4027	C16-C11-C3	32.933	C16-C11-C3-C2	141.73
H17-C11	1.0851	H17-C11-C3	87.382	H17-C11-C3-C2	-39.17
H18-C14	1.0845	H18-C14-C13	118.64	H18-C14-C13-C12	-180
H19-C15	1.0841	H19-C15-C14	120.95	H19-C15-C14-C13	179.96
N20-C3	1.3998	N20-C3-C2	122.89	N20-C3-C2-C1	-178.6
C21-N20	1.2814	C21-N20-C3	120.2	C21-N20-C3-C2	-42.69
H22-C21	1.0998	H22-C21-N20	121.8	H22-C21-N20-C3	-4.067
Br23-C12	1.8976	Br23-C12-C11	120.92	Br23-C12-C11-C3	-178.7
F24-C13	1.3385	F24-C13-C12	119.85	F24-C13-C12-C11	180
O25-C6	2.3133	O25-C6-C1	90.947	O25-C6-C1-C2	-179.7
N26-O25	1.232	N26-O25-C6	34.131	N26-O25-C6-C1	-179.9
27-N26	1.2318	O27-N26-O25	124.54	O27-N26-O25-C6	-179.8





**Figure 2.** Optimized structure of (*E*)-*N*-(3-bromo-4-fluorobenzylidene)-4-nitrobenzenamine (4NBA)

**Table 3.** The Experimental and calculated frequencies of 4NBA using B3LYP /6-31 G(d,p) level of basis set.

Modes	Calculated Frequencies (cm <sup>-1</sup> )		Observed Frequencies (cm <sup>-1</sup> )		Reduced mass	Force constant	Intensity		<sup>d</sup> Assignments TED ≥10%
	Unscaled	<sup>a</sup> Scaled	FT-IR	FT-Raman			<sup>b</sup> IR	<sup>c</sup> Raman	
1	3247	3120			1.09	6.79	1.02	114.07	νC5H10(95)
2	3245	3118			1.09	6.78	1.04	82.6	νC1H7(97)
3	3230	3104			1.1	6.73	2.03	113.2	νC14H18(27) + νC15H19(72)
4	3217	3091			1.09	6.65	2.51	62.59	νC4H9(95)
5	3217	3091			1.09	6.64	0.99	98.34	νC14H18(71)
6	3208	3083			1.09	6.62	0.4	25.31	νC11H17(98)
7	3207	3081	3064w	3075m	1.09	6.6	4.18	34.43	νC2H8(97)

8	3032	2913	3005w		1.09	5.88	29.27	40.81	vC21H22(100)
9	1706	1639	1622vs	1627s	7.85	13.47	179.88	2541.57	vN20C21(68)
10	1662	1597			9.8	15.96	133.01	57.9	vasO25N26(22) + vC6C5(13)
11	1652	1587			6.48	10.42	4.98	56.83	vC15C14(23)
12	1638	1574			6.07	9.59	270.76	4202.64	vC2C1(21)
13	1617	1554			7.95	12.25	116.16	803.36	vC13C12(31) + βC15C14C13(13)
14	1606	1543	1564vs	1507m	9.7	14.73	81.98	17.99	vasO27N26(20) + vC6C5(21)
15	1543	1482			3.38	4.74	124.7	78.99	βH17C11C16(14) + βH18C14C15(17)
16	1527	1467			2.45	3.37	7.59	175.09	βH8C2C1(16) + βH9C4C5(14) + βH10C5C6(13)
17	1455	1398			3.19	3.97	2.61	17.21	vC5C4(23)
18	1444	1387			2.47	3.03	11.65	169.94	βH22C21N20(21)
19	1406	1351			2.29	2.67	30.07	7.64	βH22C21N20(23)
20	1393	1338	1365m	1338s	13.51	15.44	665.46	1296.99	vsO25N26(39) + vO27N26(39)
21	1365	1312			7.82	8.59	5.37	31.97	vC4C3(26)
22	1347	1294			6.5	6.94	8.98	21.95	vC16C11(24)
23	1316	1265			1.38	1.41	4.74	26.43	βH7C1C2(18) + βH9C4C5(19) + βH10C5C6(18)
24	1309	1257	1265w	1283vs	4.54	4.59	114.11	88.77	vF24C13(34)
25	1294	1243			1.6	1.58	2.33	2.69	βH17C11C16(13)
26	1262	1212		1195m	2.13	1.99	29.94	84.77	vN20C3(22) + βH17C11C16(25)
27	1220	1172			2.67	2.34	145.55	1272.87	vN20C3(14) + vC21C16(17)
28	1196	1149	1130s	1179w	1.37	1.15	34.56	241.23	βH8C2C1(24) + βH9C4C5(24)
29	1149	1104		1108s	1.23	0.96	32.98	65.37	βH19C15C16(33)
30	1130	1086			2.72	2.05	107.92	398.83	vC1C6(18) + βC6C5(18) + βH10C5C6(10)

31	1129	1085	1082s		1.24	0.93	12.32	3.68	$\beta$ H7C1C2(21) + $\beta$ H8C2C1(13) + $\beta$ H10C5C6(18)
32	1063	1021	1014s		2.84	1.89	17.28	14.55	$\beta$ H17C11C16(12) + $\beta$ C15C14C13(28) + $\beta$ C13C12C11(21)
33	1027	987			2.56	1.59	4.76	6.65	$\beta$ C1C6C5(17)
34	1017	977			1.63	0.99	17.92	204.15	$\beta$ C22C21N20
35	991	952			1.31	0.76	0.27	5.52	$\tau$ H10C5C6N26(53)
36	984	946			1.31	0.75	0.39	5.02	$\tau$ H19C15C16C11(54)
37	982	944			1.32	0.75	0.23	9.05	$\tau$ H7C1C6N26(57)
38	923	887			3.82	1.92	38.06	23.56	$\beta$ C14C13C12(20)
39	917	881	908w		1.46	0.72	8.54	8.89	$\tau$ H17C11C16C15(61) + $\tau$ C16C11C12C13(17)
40	889	854			4.96	2.31	36.19	12.9	$\beta$ C1C6C5(12)
41	874	840	862w	863s	2.33	1.05	58.76	12.21	$\tau$ H9C4C5C6(21) + $\tau$ H10C5C6N26(14)
42	850	817	823m		1.48	0.63	23.21	7.78	$\tau$ H18C14C15C16(54) + $\tau$ H19C15C16C11(20)
43	848	815	814w		2.72	1.15	5.8	104.5	$\delta$ O27N26O25(20) + $\tau$ H9C4C5C6(16) + $\tau$ H10C5C6N26(11)
44	842	809			1.63	0.68	0.88	3.56	$\tau$ H7C1C6N26(19) + $\tau$ H8C2C1C6(34)
45	800	769			5.41	2.04	0.16	32.3	$\beta$ C16C11C12(17)
46	762	732	723w		5.95	2.03	13.67	4.39	$\tau$ C6C5C4C3(19) + $\Gamma$ N26C5C1C6(12) + $\omega$ O27C6O25N26(26)
47	733	704			4.28	1.35	6.91	3.42	$\tau$ C15C14C13C12(16) + $\tau$ C16C11C12C13(21)
48	710	682			5.02	1.49	33.04	1.21	$\tau$ C6C5C4C3(16)
49	703	675			5.47	1.59	23.55	3.02	$\tau$ C6C5C4C3(16) + $\Gamma$ O27C6O25N26(13)
50	669	643			7.74	2.04	9.43	6.44	$\beta$ C13C12C11(11)
51	646	620			7.09	1.74	0.34	9.44	$\beta$ C6C5C4(30)
52	600	576			3.74	0.79	6.25	6.88	$\Gamma$ F24C12C14C13(14)
53	570	548			7.6	1.45	9.25	0.73	$\tau$ C16C11C12C13(10)

54	548	527			4.57	0.81	2.87	6.31	$\rho\text{O25N26C6(28)}$
55	532	511	501		4.28	0.71	1.66	10.51	$\rho\text{O25N26C6(28)}$ + $\tau\text{C5C4C3N20(10)}$
56	498	479			5.12	0.75	7.92	1.72	$\beta\text{F24C13C14(34)}$
57	463	445			7.44	0.94	6.03	1.04	$\beta\text{C4C3N20(18)}$ + $\beta\text{F24C13C14(20)}$
58	459	441			3.36	0.42	1.2	1.13	$\tau\text{C16C11C12C13(24)}$
59	428	411			3.17	0.34	1.76	21.96	$\tau\text{C6C5C4C3(13)}$
60	405	389			8.35	0.81	10.18	2.97	$\nu\text{N26C6(21)}$
61	390	375		362m	5.51	0.49	2.3	5.62	$\beta\text{F24C12C14(10)}$ + $\Gamma\text{C21C11C15C16(12)}$
62	344	331			5.65	0.39	3.02	36.65	$\Gamma\text{C21C11C15C16(12)}$
63	316	304			7.58	0.45	2.72	5.6	$\tau\text{C5C4C3N20(21)}$ + $\Gamma\text{N26C5C1C6(15)}$
64	257	247		241w	8.21	0.32	3.5	9.23	$\nu\text{Br23C12(13)}$ + $\beta\text{O25N26C6(12)}$ + $\beta\text{N26C6C1(35)}$
66	223	214			13.06	0.38	3.12	4.44	$\beta\text{F24C13C14(12)}$ + $\beta\text{N26C6C1(16)}$
67	180	173			9.37	0.18	4.22	15.09	$\beta\text{C3N20C21(12)}$ + $\beta\text{Br23C12C13(29)}$
69	144	139			5.01	0.06	0.2	15.12	$\tau\text{C14C13C12C11(39)}$
70	124	120			8.54	0.08	2.44	16.18	$\beta\text{C21C16C15(11)}$ + $\beta\text{Br23C12C13(10)}$
71	91	87			7.96	0.04	0.21	3.91	$\beta\text{C21C16C15(13)}$
72	68	65			7.15	0.02	0.08	0.68	$\tau\text{O25N26C6C5(84)}$
73	37	36			9.41	0.01	1	1.79	$\beta\text{C3N20C21(16)}$ + $\tau\text{C3N20C21C16(25)}$ + $\Gamma\text{C21C11C15C16(14)}$
74	32	31			9.23	0.01	0.62	3.54	$\tau\text{C5C4C3N20(29)}$ + $\tau\text{C3N20C21C16(20)}$
75	28	27			7.03	0	0.66	9.45	$\tau\text{N20C21C16C11(34)}$ + $\tau\text{C4C3N20C21(41)}$

vw - very weak, w- week, s- strong, vs- very strong, m-medium,  $\tau$ - torsion;  $\Gamma$  - out of plane bending,  $\beta$ - in plane bending,  $\rho$ - rocking,  $\delta$ - scissoring,  $\nu$ - stretching,  $\nu_s$ - symmetric stretching,  $\nu_{as}$ - asymmetric stretching, w- wagging, <sup>a</sup>Scaling factor 0.960842, <sup>b</sup>Relative IR absorption intensities normalized with highest peak absorption equal to 100, <sup>c</sup>Relative Raman intensities calculated by equation and normalized to 100. <sup>d</sup>Total energy distribution calculated at B3LYP/6-31G(d,p) level.

**Table 4.** Second order perturbation theory analysis of the Fock matrix in NBO basis for 4NBA.

Type	Donor NBO (i)	ED/e	Acceptor NBO (i)	ED/e	<sup>a</sup> E <sup>(2)</sup> kcal/mol	<sup>b</sup> E(j)-E(i) a.u	<sup>c</sup> F(i,j) a.u
$\sigma - \sigma^*$	C1-C2	1.97	C1-C6	0.02	3.07	1.26	0.056
			C3-N20	0.02	3.75	1.13	0.058
			C6-N26	0.09	4.61	1.01	0.062
$\sigma - \sigma^*$	C1-C6	1.98	C5-C6	0.02	4.74	1.27	0.069
$\pi - \pi^*$	C1-C6	1.64	C2-C3	0.38	17.27	0.28	0.062
			C4-C5	0.27	20.37	0.29	0.07
			N26-O27	0.67	35.58	0.12	0.064
$\sigma - \sigma^*$	C2-C3	1.98	C3-C4	0.02	3.72	1.25	0.061
$\pi - \pi^*$	C2-C3	1.61	N20-C21	0.15	8.43	0.27	0.045
			C4-C5	0.27	16.12	0.28	0.062
			C1-C6	0.39	24.9	0.27	0.073
$\sigma - \sigma^*$	C3-C4	1.97	C2-C3	0.03	3.48	1.24	0.059
$\sigma - \sigma^*$	C3-N20	1.98	C16-C21	0.03	3.23	1.26	0.057
$\sigma - \sigma^*$	C4-C5	1.97	C5-C6	0.02	3.04	1.26	0.055
			C3-N20	0.02	3.21	1.13	0.054
			C6-N26	0.09	4.64	1.01	0.062
$\pi - \pi^*$	C4-C5	1.67	C1-C6	0.39	19.1	0.27	0.065
			C2-C3	0.38	21.89	0.27	0.07
			C1-C6	0.39	19.1	0.27	0.065

$\sigma - \sigma^*$	C5-C6	1.98	C1-C6	0.02	4.76	1.27	0.069
$\sigma - \sigma^*$	C11-C12	1.98	C11-C16	0.02	3.09	1.29	0.056
		1.98	C12-C13	0.04	3.88	1.28	0.063
			C11-C16	0.02	3.09	1.29	0.056
$\sigma - \sigma^*$	C11-C16	1.98	C11-C12	0.02	3.26	1.26	0.057
			C11-C12	0.02	3.26	1.26	0.057
			C15-C16	0.02	3.56	1.25	0.06
$\pi - \pi^*$	C11-C16	1.63	N20-C21	0.15	19.65	0.27	0.069
			C12-C13	0.43	20.2	0.25	0.064
			C14-C15	0.29	19.95	0.28	0.068
$\sigma - \sigma^*$	C12-C13	1.98	C11-C12	0.02	3.75	1.31	0.063
			C13-C14	0.03	3.82	1.31	0.063
$\pi - \pi^*$	C12-C13	1.67	C14-C15	0.29	15.84	0.31	0.063
			C11-C16	0.38	20.39	0.31	0.071
$\sigma - \sigma^*$	C13-C14	1.98	C12-C13	0.04	4.77	1.27	0.07
$\sigma - \sigma^*$	C14-C15	1.97	C16-C21	0.03	3.23	1.18	0.055
$\pi - \pi^*$	C14-C15	1.67	C12-C13	0.43	25.43	0.25	0.073
			C11-C16	0.38	18.45	0.27	0.064
$\sigma - \sigma^*$	C15-C16	1.97	C11-C16	0.02	3.78	1.25	0.061
$n - \sigma^*$	C16-C21	1.97	C3-N20	0.02	4.21	1.1	0.061
$n - \pi^*$	N20-C21	1.91	C11-C16	0.38	8.56	0.35	0.053
			C2-C3	0.38	9.96	0.35	0.057

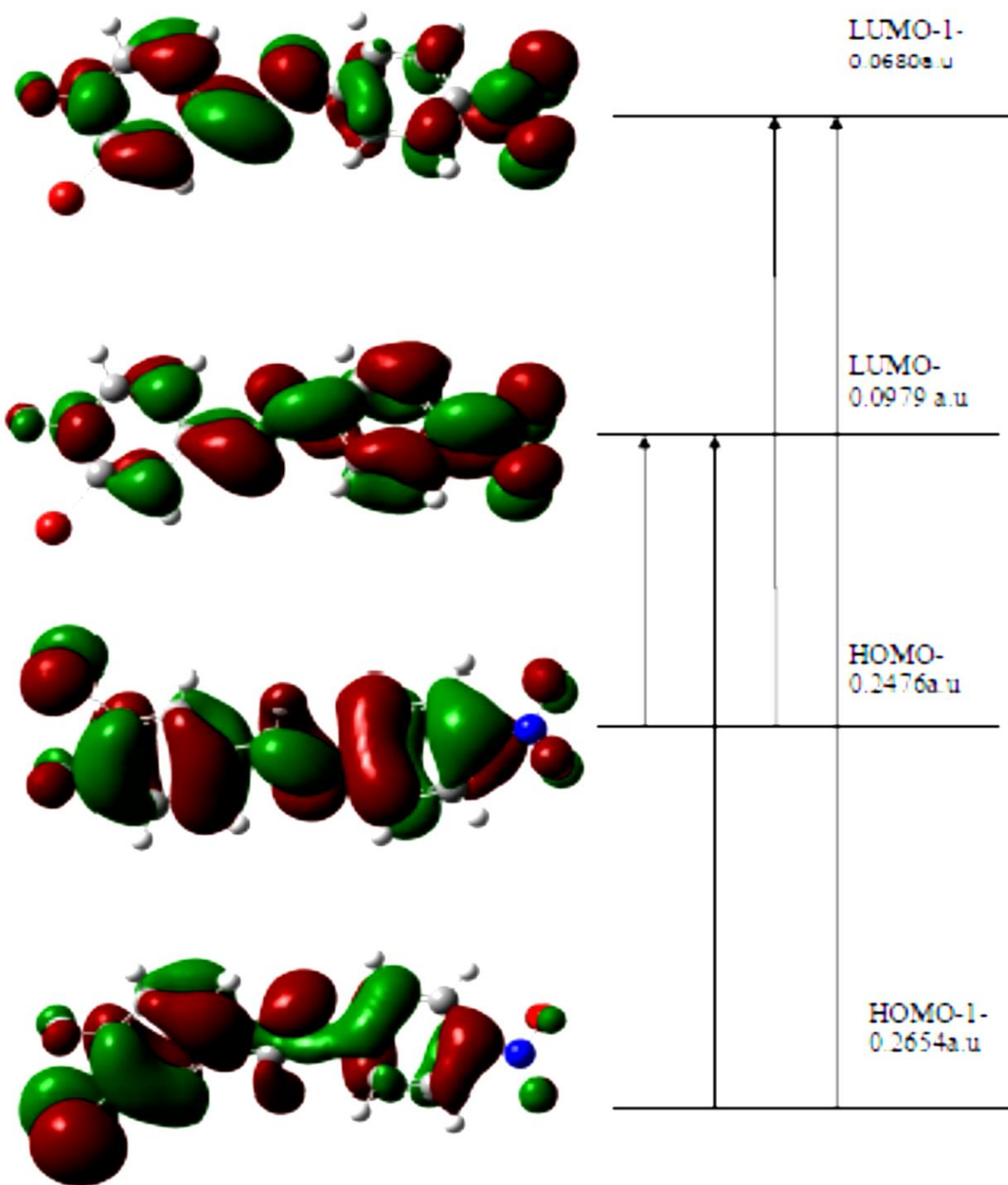
$\pi - \pi^*$	N26-O27	1.98	C1-C6	0.39	4.92	0.44	0.046
			N26-O27	0.67	9.1	0.28	0.055
			C1-C6	0.39	4.92	0.44	0.046
			N26-O27	0.67	9.1	0.28	0.055
$n - \pi^*$	N20	1.87	C2-C3	0.38	6.71	0.34	0.046
$n - \sigma^*$	N20	1.87	C21-H22	0.04	12.35	0.74	0.088
			C2-C3	0.03	6	0.87	0.066
$n - \pi^*$	Br23	1.97	C12-C13	0.43	9.95	0.27	0.052
$n - \sigma^*$	F24	1.97	C13-C14	0.03	5.5	0.94	0.064
		1.92	C12-C13	0.43	19.97	0.38	0.086
$n - \sigma^*$	O25	1.98	C6-N26	0.09	3.79	1.1	0.059
		1.91	C6-N26	0.09	10.07	0.58	0.068
			N26-O27	0.06	18.48	0.62	0.097
		1.44	N26-O27	0.67	174.13	0.11	0.128
$n - \sigma^*$	O27	1.98	C6-N26	0.09	3.79	1.1	0.059
		1.91	C6-N26	0.09	10.08	0.58	0.068
			O25-N26	0.06	18.51	0.62	0.097
$\pi - \pi^*$	C1-C6	1.64	C4-C5	0.27	210.51	0.01	0.08
$\pi - \pi^*$	C2-C3	1.61	C4-C5	0.27	222	0.01	0.079
$\pi - \pi^*$	C12-C13	1.67	C14-C15	0.29	96.66	0.03	0.082
$\pi - \pi^*$	C12-C14	1.67	C11-C16	0.38	126.49	0.03	0.08



a -  $E^{(2)}$  means energy of hyper conjugative interactions.  
 b - Energy difference between donor and acceptor i and j NBO orbitals.  
 c -  $F_{ij}$  is the Fock matrix element between i and j NBO orbitals.  
 ED- Electron Density.

**Table 5.** Non Linear Optical properties of 4NBA.

<b>Parameters</b>	<b>Dipole Moment</b>
$\mu_x$	-4.2639
$\mu_y$	0.9697
$\mu_z$	0.1143
$\mu$ (Debye)	4.3743
<b>Parameters</b>	<b>Hyperpolarizability</b>
$\beta_{xxx}$	-507.2959
$\beta_{yyy}$	-20.8323
$\beta_{zzz}$	-6.5526
$\beta_{xyy}$	-67.2734
$\beta_{xxy}$	43.0915
$\beta_{xxz}$	2.5728
$\beta_{xzz}$	-41.4105
$\beta_{yzz}$	-14.0797
$\beta_{yyz}$	-3.3776
$\beta_{xyz}$	-6.3277
$B_0$ (e.s.u)	$5.3223 \times 10^{-30}$



**Figure 3.** Frontier molecular orbital of 4NBA

#### 4. CONCLUSIONS

Structures of 4NBA was analyzed by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. In addition, molecular geometry and NBA analysis predicts the most reactive parts in the molecule. The electronic transitions and states were investigated computationally and show good agreement with the experimental data. The calculated HOMO and LUMO energies were used to analyze the charge transfer within the molecule. The calculated dipole moment and first order hyperpolarizability results indicate that the molecule has a reasonably good nonlinear optical behavior.

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