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## VIBRATIONAL SPECTRAL STUDIES (UV) AND FRONTIER MOLECULAR ORBITAL ANALYSIS OF 1,5-DIFLUORO-2,4-DINITROBENZENE BASED ON DENSITY FUNCTIONAL CALCULATION

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### Abstract

The theoretical ground state geometry and electronic structure of the 1,5-Difluoro-2,4-DiNitroBenzene (DFDNB) were optimized by B3LYP/6-311++G(d,p) method. The first order hyper polarizability is comparable with that of similar derivatives of the standard NLO material urea. Natural Bond Orbital (NBO) analysis has been carried out to analyze the stability of the molecule arising from hyper-conjugative interactions and charge delocalization. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule.

**Keywords:** B3LYP, NLO, NBO, HOMO and LUMO.

### INTRODUCTION

Nitrobenzene is used as a flavouring or perfume additive, highly toxic in large quantities. In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents. Aromatic compound such as benzene derivative of fluoronitrobenzene is commonly used in pharmaceutical products. Benzene undergoes nitration and halogenations, then the reactions of the benzene slow down. Nitrofluorobenzene are produced for industrial uses such as dyes, drugs, pesticides, shoe polish, spray paint, and synthetic rubber [1].

Fluorine substituent can greatly increase the fat solubility of molecules, which is particularly important in pharmaceuticals where it can increase their bioavailability. Molecules including more

fluorine, amplifies the effect and have regular feature in both drug and agrochemical actives. Numerous common fungicides also contain fluorine atoms. Fluorine is a common element in antibiotic molecules, too. Fluorine has become a popular feature in drugs and agrochemicals because of the effects it exerts in molecules. Nitrobenzene can cause a wide variety of harmful health effects to exposed persons. Repeated exposures to a high concentration of nitrobenzene can result in a blood condition called methemoglobinemia (a form of anemia).

In the present study, electronic absorption spectrum for optimized molecule calculated with Time Dependent Density Functional Theory (TD-DFT) at B3LYP/6-311++G(d,p) level. Molecular geometry, optimized parameters and Non-Linear Optical (NLO)

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properties calculated by same method. Natural Bond Orbital (NBO) analysis, HOMO (Highest Occupied Molecular Orbital) LUMO (Lowest Unoccupied Molecular Orbital) energies and frontier orbital energy gap also performed.

### EXPERIMENTAL DETAILS

The fine polycrystalline samples of a 1,5-Difluoro-2,4-dinitrobenzene (DFDNB) was used for the spectral measurements. The UV absorption spectrum is registered in ethanol on Shimadzu UV-1800 PC spectro-photometer in the spectral region 800–100 nm.

### COMPUTATIONAL DETAILS

The entire calculations were performed at DFT/B3LYP levels with 6-311++G(d,p) basis set using Gaussian 09W [2] program. B3LYP represents Becke's three parameter hybrid functional method [3] with Lee-Yang-Parr correlation functional (LYP) [4, 5] is the best predicting results for molecular geometry and vibrational wavenumbers for moderately larger molecule. Furthermore, in order to show nonlinear optical (NLO) activity of DFDNB molecule, the dipole moment, linear polarizability and first hyperpolarizability were obtained from molecular polarizabilities based on theoretical calculations. The natural bonding orbital (NBO) calculation was

performed using NBO 3.1 program [6] and was carried out in the Gaussian 09W package at the DFT/B3LYP level. The hyperconjugative interaction energy was deducted from the second order perturbation approach. UV-Vis spectrum, electronic transition, vertical excitation energies, absorbance and oscillator strengths were computed with the time-dependent DFT method.

### RESULTS AND DISCUSSION

The optimized geometry structure of the title compound is shown in Figure 16.1. The molecular structure of the DFDNB belongs to a C<sub>1</sub> point group of symmetry. The optimized structure parameter for this compound calculated by B3LYP with 6-311++G(d,p) basis set is listed in Table 1. The calculated geometric parameters can be used as the foundation to calculate the other parameters for the compound. To the best of our knowledge exacts experimental data of the geometrical parameter of DFDNB are not available in literature. The molecule contains two fluorine groups in the benzene ring at 1 and 5 positions. The calculated C–F bond length in varies from 1.382 to 1.392 for HF and 1.327 to 1.082 for B3LYP. The other optimized bond lengths are shorter with the electron donating substituent on benzene ring, the symmetry of the ring distorted, yielding ring angles smaller than 120° at the point of substitution and slightly larger than 120° at other position.

**Table 1. Bond Lengths, Bond Angles and Dihedral Angles for 1,5-Difluoro-2,4-Dinitrobenzene (DFDNB) calculated by B3LYP/6-311++G(d,p)**

Bond Lengths	Values	Bond Angles	Values	Dihedral Angles	Values
C1–F7	1.327	C2–C1–F7	117.829	C6–C1–C2–N8	178.241
C2–N8	1.082	C6–C1–F7	121.649	F7–C1–C2–C3	–179.241
C4–N12	1.477	C3–C2–N8	120.279	F7–C1–C2–N8	0.318
C5–F15	1.082	C2–C3–H11	117.854	C2–C1–C6–H16	179.326
N8–O9	1.219	C4–C3–H11	121.626	F7–C1–C6–C5	177.531
N8–O10	1.222	C3–C4–N12	122.304	F7–C1–C6–H16	–2.831
N12–O13	1.223	C5–C4–N12	118.084	C1–C2–C3–H11	179.234
N12–O14	1.225	C4–C5–F15	119.853	N8–C2–C3–C4	–178.242
		C6–C5–F15	11.841	N8–C2–C3–H11	–0.324
		C2–N8–O9	118.076	C2–C3–C4–N12	–179.319
		C2–N8–O10	116.678	H11–C3–C4–N12	2.843
		O9–N8–O10	125.836	N12–C4–C5–C6	177.686
		C4–N12–O13	116.687	N12–C4–C5–F15	–2.269
		C4–N12–O14	117.493	C3–C4–N12–O13	25.734
		O13–N12–O14	125.811	C5–C4–N12–O14	–153.904

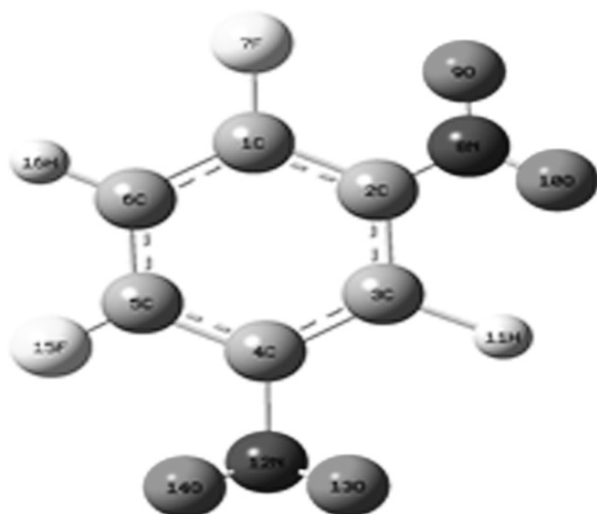


Figure 16.1: Molecular Structure of DFDNB

## ABSORPTION SPECTRUM

All the molecular structure allows strong  $\pi-\pi^*$  and  $\sigma-\sigma^*$  transition in the UV-vis region with a high extinction coefficient. The lowest singlet-singlet spin-allowed excited states were taken into account to investigate the properties of electronic absorption. The UV-vis spectrum of DFDNB was recorded in ethanol solution as shown in Figure 16.2. To support experimental observations, TD-DFT calculation electronic absorption spectra of the title compound in ethanol solution was performed. The experimental and computed electronic features such as the absorption wavelength (nm), excitation energies (E in eV) and oscillator strengths (f) major contributions of the transitions and assignments of electronic transitions are listed in Table 2 TD-DFT methods are computationally more expensive than semi-empirical methods but allow easily studies of medium-size molecules [7, 8]. Test calculations have shown that the inclusion of extra polarization functions does not affect the excitation energies, besides the addition of diffuse functions lead to an increase in computation time. The maximum absorption values obtained at 486.00, 343.64, 326.29, 310.03, 287.75 and 273.59 nm shows good agreement experimental absorption values are 450 nm and 280 nm. These excitations correspond to  $\pi-\pi^*$  transition.

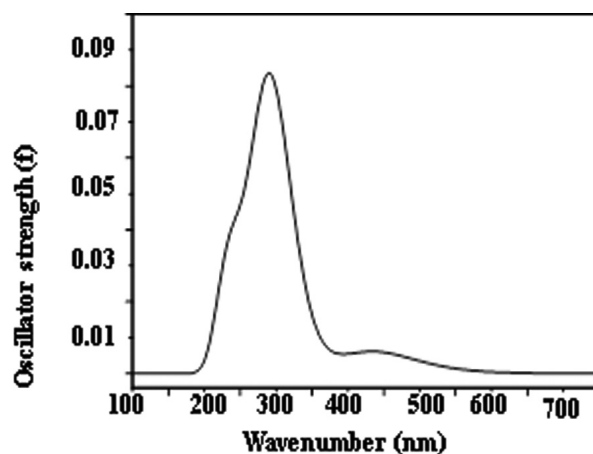


Figure 16.2: UV-Vis Spectrum of DFDNB

Table 2. Experimental and calculated absorption wavelength (nm), excitation energies (E in eV), oscillator strength (f) of DFDNB by TD-B3LYP/6-311++G(d,p) method.

Excitation States	Excitation Energies (E in eV)	Wavelength (nm)		Oscillator (f)
		Experimental	Theoretical	
S1	2.5511	450	486.00	0.0072
S2	3.6080		343.64	0.0874
S3	3.7998		326.29	0.0093
S4	3.9992		310.03	0.0061
S5	4.3087	280	287.75	0.0337
S6	4.5318		273.59	0.0065

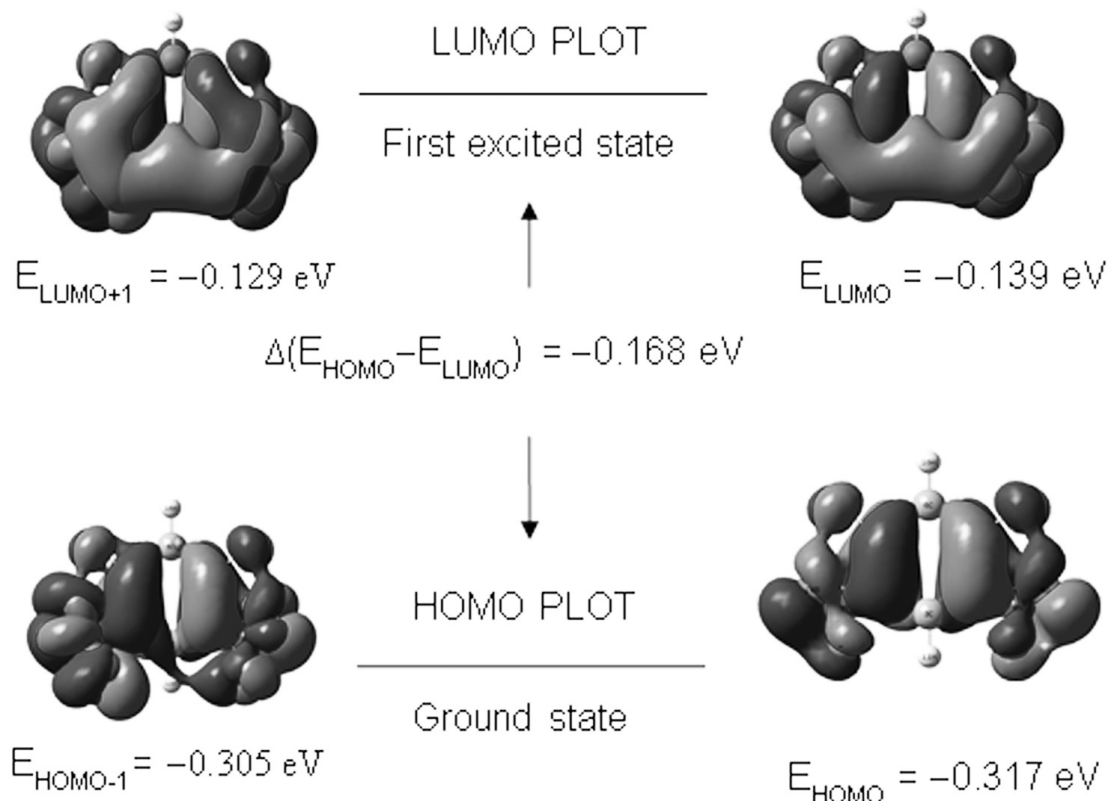
## FRONTIER MOLECULAR ORBITAL ANALYSIS

Many organic molecules that contain conjugated  $\pi$  electrons are characterized as hyper-polarizabilities and are analyzed by vibrational spectroscopy [9, 10]. According to the TD-DFT calculated electronic absorption spectra, the maximum absorption wavelength corresponding to the electronic transition is from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). We examine the four important molecular orbitals of DFDNB molecule, the highest and second highest occupied molecular orbitals and the lowest and second lowest unoccupied molecular orbitals which we denote HOMO, HOMO-1, LUMO and LUMO-1, respectively in Figure 16.3. The lowest singlet $\rightarrow$ singlet spin-allowed excited states were taken into account for

the TD-DFT calculation to investigate the properties of electronic absorption.

The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties because it is measure of electron conductivity. The lowest unoccupied molecular orbital (LUMO) energy  $-0.139$  eV and the highest occupied molecular orbital (HOMO) energy is  $-0.317$  eV. The

energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, and the frontier orbital energy gap of DFDNB is found to be  $-0.168$  eV. The HOMO is located over the benzene ring and amino group, the HOMO–LUMO transition implies an electron density transfer to C–F group from the benzene ring.



**Figure 16.3: The Frontier Molecular Orbitals of Dfdnb**

### NON-LINEAR OPTICAL (NLO) PROPERTIES

The potential application of the DCDNB in the field of non-linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement. For calculating hyperpolarizability, the geometry of the investigated molecule is treated as an isolated molecule. The optimization has been carried out in the unrestricted open-shell B3LYP level. The geometries are fully optimized without any constraint with the help of analytical gradient procedure implemented within Gaussian 09W program [2]. The electric dipole moment and dispersion free first hyperpolarizability

are calculated using finite field method. The finite field method offers a straight forward approach to the calculation of hyperpolarizability [11].

In the presence of an applied electric field, first order hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry [12]. The matrix can be given in the lower tetrahedral format. It is obvious that the lower part of the  $3 \times 3 \times 3$  matrixes is a tetrahedral.

The total static dipole moment ( $\mu$ ), the average polarizability ( $\alpha_0$ ), the anisotropy polarizability ( $\Delta\alpha$ ), first hyperpolarizability ( $\beta_0$ ) and vector hyperpolarizability ( $\beta_{vec}$ ) using the x, y, z components they are defined as follows:

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

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2]^{1/2} \quad (3)$$

$$\beta_0 = [(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{zzz} + \beta_{xxx})^2 + (\beta_{zzz} + \beta_{xxx} + \beta_{yyy})^2]^{1/2} \quad (4)$$

$$\beta_{vec} = \frac{3}{5} [(\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}] \quad (5)$$

The  $\beta_0$  components of Gaussian output are reported in atomic units and therefore the calculated values are converted into esu units (1 a.u.=8.3693×10<sup>-33</sup> esu). The calculated values of hyperpolarizability and polarizability are tabulated in Table 3. According to the present calculations, the total molecular dipole moment ( $\mu$ =11.729 Debye), the anisotropy of the polarizability ( $\Delta\alpha$ =12.314×10<sup>-24</sup> esu), polarizability ( $\alpha_0$ =41.468×10<sup>-24</sup> esu) and the first hyperpolarizability ( $\beta_0$ =0.196×10<sup>-24</sup> esu), vector hyperpolarizability ( $\beta_{vec}$ =4.218×10<sup>-24</sup> esu) for DCDNB molecule by using B3LYP methods with 6-31++G(d,p) basis set.

**Table 3. The electric dipole moment  $\mu$  (Debye), average polarizability  $\alpha_0$  (×10<sup>-24</sup>esu), anisotropy polarizability  $\Delta\alpha$  (×10<sup>-24</sup> esu), first hyperpolarizability  $\beta_0$  (×10<sup>-24</sup> esu) and vector hyperpolarizability  $\beta_{vec}$  (×10<sup>-24</sup> esu) for DFDNB calculated by B3LYP levels with 6-311++G(d,p) basis set.**

Parameters	B3LYP	Parameters	B3LYP
$\mu_x$	0.024	$\beta_{xxx}$	0.055
$\mu_y$	3.280	$\beta_{xyy}$	21.536
$\mu_z$	-0.268	$\beta_{yyy}$	0.011
$\mu$	11.729	$\beta_{yyy}$	12.294
$\alpha_{xx}$	-103.238	$\beta_{xxz}$	38.555
$\alpha_{xy}$	3.547	$\beta_{yyz}$	-12.638
$\alpha_{yy}$	-78.834	$\beta_{yyz}$	-0.005
$\alpha_{xz}$	-0.009	$\beta_{xzz}$	5.141
$\alpha_{yz}$	0.072	$\beta_{yzz}$	0.007
$\alpha_{zz}$	-75.38	$\beta_{zzz}$	1.738
$\alpha_0$	-41.468	$\beta_0$	-0.196
$\Delta\alpha$	12.314	$\beta_{vec}$	4.218

## NBO ANALYSIS

NBO analysis provides the most accurate possible 'natural Lewis structure' and all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and inter molecular interactions.

The second-order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis [13]. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy  $E^{(2)}$  associated with the delocalization  $i \rightarrow j$  is estimated as (6)

$$E^{(2)} = -n_{\sigma} \frac{\langle \sigma | F | \sigma^* \rangle}{\epsilon_{\sigma^*} - \epsilon_{\sigma}} = -n_{\sigma} \frac{F_{ij}^2}{\Delta E}$$

where  $\langle \sigma | F | \sigma^* \rangle$  or  $F_{ij}^2$  is the Fock matrix element between the i and j NBO orbital,  $\epsilon_{\sigma^*}$  and  $\epsilon_{\sigma}$  are the energies of  $\sigma$  and  $\sigma^*$  NBO's and  $n_{\sigma}$  is the population of the donor  $\sigma$  orbital.

NBO analysis has been carried out to explain the charge transfer or delocalization of charge due to the intramolecular interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from

the second order micro disturbance theory is reported [14, 15]. The larger the stabilization energy value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system.

Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO calculation is performed using Gaussian 09W package program at the DFT/B3LYP level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyperconjugation. The corresponding results have been tabulated in Tables 4 and 5.

The intramolecular interactions are observed as increase in electron density (ED) in (C-F) anti-bonding orbital that weakens the respective bonds. The electron density of conjugated bond of substitution (1.997 a.u) clearly demonstrates strong delocalization. The occupancy of  $\pi$  bonds is lesser than  $\sigma$  bonds which lead more delocalization.

The intramolecular hyperconjugative interaction of distribute to  $\sigma$  electrons of BD (C2-N8) to the anti BD\*(N8-O10) bond in the ring leads to stabilization of some part of the ring as evident from Table 6. The intramolecular hyperconjugative interaction of the BD (C2-N8) to the anti BD\*(N8-O10) bond in the ring leads to stabilization of 19.67 kcal/mol. This enhanced further conjugate with bonding orbital of BD (C2-N8) and anti-bonding orbital of BD\*(N8-O9) which leads to strong delocalization of 19.55 kcal/mol.

**Table 4. Selected NBO Results Showing Formation of Lewis and Non-Lewis Orbitals for DCDNB using B3PW91/6-31++G(d,p) Level of Theory**

Bond (A B)	ED/Energy (a.u)	ED <sub>A</sub> (%)	ED <sub>B</sub> (%)	NBO	S (%)	P (%)
BD(C1 F7)	1.997	27.49	72.52	0.524(sp <sup>2.95</sup> )C+ 0.851(sp <sup>0.94</sup> )F	25.26 51.40	74.46 48.45
BD(C3 H11)	1.996	27.60	72.40	0.525(sp <sup>2.92</sup> )C+0.851(sp <sup>0.96</sup> )H	25.42 50.95	74.30 48.89
BD(C4 N12)	1.965	37.29	62.71	0.610(sp <sup>2.05</sup> )C+0.791(sp <sup>1.62</sup> )N	32.75 38.07	67.24 61.74
BD(C6 H16)	1.965	36.61	63.39	0.605(sp <sup>2.23</sup> )C+0.796(sp <sup>1.47</sup> )H	30.95 40.41	59.24 69.24
BD(N8 O9)	1.982	49.53	50.47	0.703(sp <sup>2.25</sup> )N+0.710(sp <sup>1.44</sup> )O	30.71 40.95	69.12 58.87
BD(N8 O10)	1.983	49.58	50.42	0.704(SP <sup>2.23</sup> )N+0.710(SP <sup>1.44</sup> )O	30.92 40.97	68.90 58.84
BD(N14 O16)	1.972	48.62	51.38	0.697(SP <sup>2.30</sup> )N+0.716(SP <sup>1.90</sup> )O	30.19 34.48	69.52 65.36
BD(C6 H16)	0.069	63.39	36.61	0.796(SP <sup>2.23</sup> )C+0.605(SP <sup>1.47</sup> )H	30.95 40.41	69.00 59.24
BD(N12 O13)	0.668	62.21	37.79	0.788(SP <sup>1.00</sup> )N+-0.614(SP <sup>1.00</sup> )O	0.00 0.00	99.47 99.85
BD(N12 O14)	0.099	50.62	49.38	0.711(SP <sup>2.52</sup> )N+0.702(SP <sup>1.90</sup> )O	28.34 34.9	71.36 65.45
BD(C5 F15)	0.019	72.41	27.60	0.850(SP <sup>2.92</sup> )C+-0.525(SP <sup>0.96</sup> )F	25.42 50.95	74.30 48.39

**Table 5. Second Order Perturbation Theory Analysis of Fock Matrix in Nbo Basis for Dfdnb Using B3lyp Method With 6-311++G(D,P)Basis Set.**

Donor NBO (i)	Acceptor NBO (j)	E(2) <sup>a</sup> (Kcal/mol)	E(i)-E(j) <sup>b</sup> (a.u)	F(i,j) <sup>c</sup> (a.u)
BD(C1-F7)	BD*(C1-C2)	2.09	2.05	0.059
BD(C1-F7)	BD*(C1-C6)	1.43	2.04	0.049
BD(C1-F7)	BD*(C5-C6)	0.85	2.07	0.038
BD(C2-N8)	BD*(N8-O9)	19.55	2.12	0.183
BD(C2-N8)	BD*(N8-O10)	19.67	2.12	0.184
BD(C5-F15)	BD*(C6-H16)	1.48	1.38	0.041
BD(C5-F15)	BD*(N12-O13)	1.41	1.31	0.039
BD(C6-H16)	BD*(N12-O14)	17.38	1.95	0.167
BD(C6-H16)	BD*(C6-C5)	13.23	2.00	0.073
BD(N12-O13)	BD*(C4-N12)	17.25	2.32	0.183
BD(N12-O14)	BD*(N12-O13)	11.54	2.49	0.153

<sup>a</sup>E<sup>(2)</sup> means energy of hyper conjugative interactions (stabilization energy).

<sup>b</sup>Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup>F(i,j) is the Fock matrix element between i and j NBO orbital.

## CONCLUSION

The non-linear optical properties were calculated theoretically. The predicted first hyperpolarizability values 10 times greater than those of urea. A deep insight of the charge transfer was elucidated by NBO analysis. UV-Vis spectral analyses of DFDNB have been done by experimental and theoretical calculations are compared. Molecular orbital coefficient analyses suggest that the electronic spectrum corresponds to the electronic transition. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule.

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