



## Structural and Electronic Properties of Donor-Acceptor Molecular System: Dft Calculations

### KEYWORDS

DFT, energy gap, IR spectrum, chemical potential and charge transfer

Musa Kadhim Mohsin Al-Oujani

Physics Dept.- College of Science - Babylon University-Iraq

### ABSTRACT

This work deals with structural and electronic properties of trifluoroborane-ammonia  $BF_3-NH_3$  as a donor-acceptor molecular system. B3LYP density functional theory was employed with various basis sets to calculate some structural and electronic properties for this system. The calculations include the bond length and angles between atoms. And some electronic properties of the studied compound were investigated include the total energy, electronic states, electron affinity, chemical hardness, softness, electrophilic index and amount of charge transfer. The results show that 6-31G (d, p) level of theory gave good agreement values of geometrical parameters in compared with experimental data, and few amount of charge was transfer in this system.

### Introduction

Charge transfer (CT) has long been recognized as the key process in many fields of chemistry physics, and biology (see, e.g., reviews, [1–7] monographs, [8–10] and references therein). Current interest in characterization of this process on the nanoscale (1-100 nm) has been driven by further progress in such areas of practical interest as artificial solar-energy conversion [11] nonlinear optics [12] molecular electronics [13,14] and oxidative damage of DNA. [15] A convenient model system often used to probe the mechanism of CT in molecular objects with nanoscale dimensions comprises a donor (D) and an acceptor (A) of electrons or holes connected by molecular bridge (B); for details see, e.g., refs [11]. The number and variety of such donor-bridge-acceptor (D-B-A) systems have grown explosively in recent years. Molecular bridges linking between an electron donor and an electron acceptor are known to control charge transport in molecular systems. [1-7]. Extensive studies emphasized the role of different factors controlling the charge transport mechanism of donor-bridge-acceptor systems including intersite electronic coupling, electronic energies and electronic - nuclear coupling. The nuclear parameters of the molecular bridge have been shown to control the charge transport process by changing the transport rate [8-10], switching between different transport mechanisms [11,12] and selecting the pathway for charge transport [13-15]. present work focuses on calculating the structural and electronic properties of  $BF_3-NH_3$  as a donor-acceptor system and compute the amount of charge transport as a measure the maximum electronic charge that saturates the system, it is a measure of the electronic transfer that a system may accept.

### Molecular models and computational details

B3LYP density functional theory is employed in present work as it is proper for studying the structural and electronic properties of donor-acceptor system and comparison with experimental results. The geometries of donor, acceptor and donor-acceptor were fully optimized with B3LYP/6-31G(d, p) method, followed by optimization + frequency at the same level to validate the optimized structural stability as in figure 1. The calculations of energies were performed at seven different basis set levels, they are STO-3G, 3-21G, 4-21G, 6-31G, 6-31G(d), 6-31G(d, p) and 6-311G, to find a suitable basis set for calculating the total energy.

### Results and Discussion

Figure 1 shows the geometrical structure of  $BF_3$  (acceptor),  $NH_3$  (donor) and  $BF_3-NH_3$  (acceptor -donor) optimized at B3LYP density functional theory. The total energy in (a. u),

symmetry and total dipole moment in ( Debye) for studied molecules computed by B3LYP/6-31G(d, p) are presented in table 1.

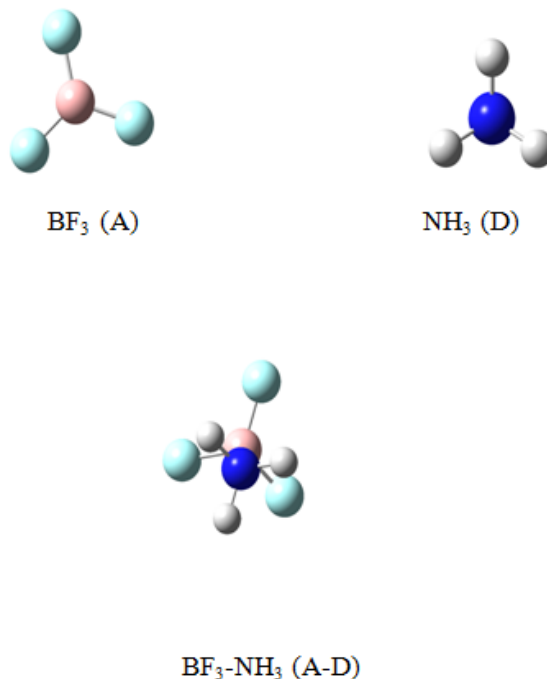


Figure (1): The optimized structure of donor - acceptor system

It is clear that from table 1, the total energy for each molecule depends on the number of atoms in the molecule, it is decreasing with the increase of atoms number that the molecule included. Table (1) shows also the symmetry of studied structures, the trifluoroborane structure is a planar with inversion center and it has  $D_{3h}$  symmetry (high symmetry) with low total dipole moment (0.0004 Debye), while the ammonia molecule has  $C_{3v}$  symmetry and the donor-acceptor system has also  $C_{3v}$  symmetry with large value of dipole moment equals to (6.0973 Debye). All donor, acceptor and acceptor-donor have not imaginary frequencies, this may refers to good geometrical optimization obtained from the best B3LYP with large 6-31G(d, p) level of theory.

**Table 1: Total energy, symmetry and total dipole moment for structures**

Species	Total Energy (a.u)	Symmetry	Total D. M (Debye)
NH <sub>3</sub> (D)	-56.5742362490	C <sub>3v</sub>	1.5348
BF <sub>3</sub> (A)	-324.589333620	D <sub>3h</sub>	0.0004
BF <sub>3</sub> -NH <sub>3</sub> (A-D)	-381.195585542	C <sub>3v</sub>	6.0973

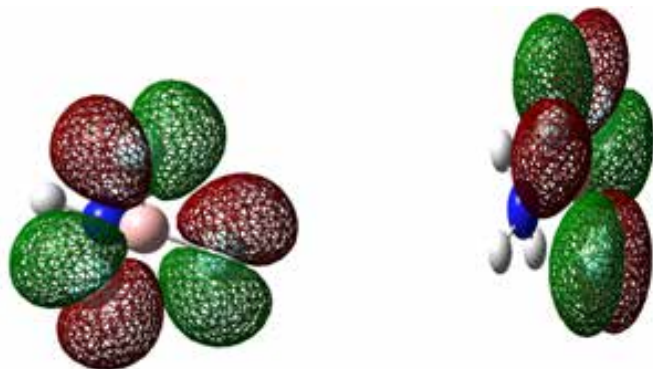
Table 2 declare the results of geometrical parameters included the bond length (in Angstrom) and bond angles in (degree). The seven computational levels of theory used in this work give good results of length linking between donor and acceptor, but 6-31G (d, p) is the best method for computation these parameters, the bond B-N obtained from 6-31G(d, p) equals (1.60Å) is in a good agreement with experimental value (1.60Å), the two bonds F-B-F and N-H-N computed by 6-31G (d, p) level are 111.50 and 109.50, respectively, these results are agree with reference [15]. Other levels of theory gave values of geometrical parameters are approximately nearly to experimental results.

**Table 2: Bond lengths in Angstrom and angles in degree for donor-acceptor system**

Species	Bond	STO-3G	3-21G	4-21G	6-31G	6-31G (d)	6-31G (d, p)	6-311G	Exp. (15)
NH <sub>3</sub>	N-H	1.142	1.129	1.128	1.129	1.115	1.012	1.122	1.012
	N-H-N	112.5	112.0	118.5	108.0	111.2	106.5	108.3	106.7

**Table 3: HOMO, LUMO and energy gap for donor-acceptor system**

Property	STO-3G	3-21G	4-21G	6-31G	631G (d)	6-31G (d, p)	6-311G
HOMO (eV)	-12.4064	-12.0211	-10.564	-11.5559	-11.8344	-9.98008	-11.4576
LUMO (eV)	-1.3259	-1.0065	-0.8798	-0.9985	-1.7762	-1.265265	-1.5223
Energy Gap (eV)	11.1825	11.0146	9.6845	10.5574	10.0582	8.714815	9.9353

**HOMO****Figure 2 : HOMO and LUMO of BF<sub>3</sub>-NH<sub>3</sub> structure**

The results of ionization potential (IP), electron affinity (EA), chemical potential (K), electrophilicity index (w) and charge transfer (ΔN) are presented in table 4. As we see from this table, the largest value of charge transfer (0.65877) between two systems (donor - acceptor) was results by employing B3LYP/6-31G (d, p), this value corresponding to small ioniza-

**LUMO**

tion potential value (9.98008 eV). This level of theory give good result for electrophilicity index (w = 4.148 eV), this may help to interact this system with effective surrounding molecular system. The amount of charge transfer in BF<sub>3</sub> - NH<sub>3</sub> donor - acceptor system results from other basis sets gave approximately the same few lower value.

**Table 4: Electronic properties for donor-acceptor system**

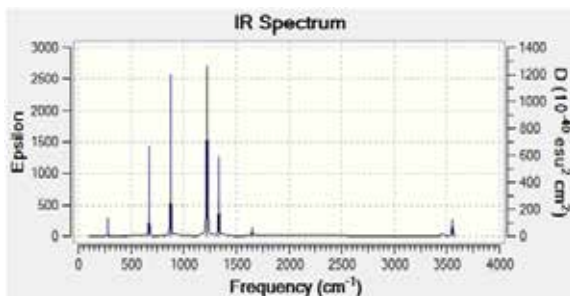
Property	STO-3G	3-21G	4-21G	6-31G	631G (d)	6-31G (d, p)	6-311G
IP (eV)	12.4064	12.0211	10.564	11.5559	11.8344	9.98008	11.4576
EA (eV)	1.3259	1.0065	0.8798	0.9985	1.7762	1.265265	1.5223
K (eV)	-6.9537	-6.5138	-5.1625	-6.05722	-6.189159	-6.297341	-6.5058
W (eV)	4.221724	3.852108	3.192546	3.626424	3.935504	4.148544	4.00809
ΔN	0.607119	0.591376	0.618410	0.598694	0.635870	0.65877	0.61607

The results of exact polarizability in (a. u) obtained from the calculations for donor, acceptor and donor- acceptor system using B3LYP density functional theory with 6-31G (d, p) are shown in table 5. The  $\text{BF}_3\text{-NH}_3$  donor-acceptor system has high polarizability in compared with donor and acceptor. High polarizability means high chemical reactivity. The donor - acceptor system has more reactivity than others in which the polarizability of this system is approximately twice the polarizability of the donor and acceptor, as we see in table 5. So the results satisfy the polarizability tensors calculations in three dimensions, where  $\alpha_{xx} < \alpha_{yy} < \alpha_{zz}$ .

**Table 5: Average polarizability for donor-acceptor system**

Species	Polarizability ( a. u)			
	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{avg}$
$\text{BF}_3$	13.542	17.507	17.509	16.186
$\text{NH}_3$	12.922	12.922	14.724	13.522
$\text{BF}_3\text{-NH}_3$	27.275	27.281	30.217	28.257

Figure 3 represents the IR spectrum for  $\text{BF}_3\text{-NH}_3$  donor-acceptor system. The number of modes was calculated by the relation  $3N-6$ , where N is the number of atoms in the structure, the stretching of N-H bond lies in the range (3441.45-3554.40)  $\text{cm}^{-1}$ , while the bending of N-H bond lies in the range (1334.66-1654) $\text{cm}^{-1}$ . For B-F bond, the bending of B-F bond lies at (876.04 $\text{cm}^{-1}$ ), the stretching is at (1221.12  $\text{cm}^{-1}$ ) in which it corresponds to intensity (386.6319  $\text{Km/mol}$ ). The stretching of N-B bond lies at 439.62 $\text{cm}^{-1}$  and it corresponds to very low infrared intensity (0.7953  $\text{Km/mol}$ ).



**Figure 3: The IR spectrum of  $\text{BF}_3\text{-NH}_3$  donor - acceptor system**

### Conclusions

The density functional theory used in this study is a powerful method with high accuracy but it is a cost in compared with ab initio and semi-empirical methods, and B3LYP functional is a suitable and an efficient function for studying the electronic properties of these structures. 6-31G (d, p) give a good agreement results for geometrical parameters comparing with experimental data. The geometric structures, symmetry and total energies for donor - acceptor system show that this structure is more stable and has high symmetry. The donor - acceptor system has large average polarizability comparing with donor and acceptor and this system has high reactivity than others.

### REFERENCE

- Schleyer P. v. R., (2001), "Aromaticity (Editorial)", Chemical Reviews, Vol.101, P.1115-1118.
- Balaban A. T., Schleyer P. v. R. & Rzepa H. S.,(2005), Crocker, Armit and Robinson, Chemical Reviews, Vol.105, P.3436-3447.
- Scheiner S.,(1974), Hydrogen Bonding: a Theoretical Perspective, Oxford University Press, Oxford.
- Hobza P., Havlas Z., (2000), Chem. Rev. 100 4253.
- Desiraju G. R, Steiner T., (1997), The Weak Hydrogen Bond, Oxford University Press, Oxford.
- Sadasivam K., Kumaresan R.,(2011), Computational and Theoretical Chemistry 963 227-235.
- Ravi P., Gory G. M., Tewari S. P. & Sikder A. K.,(2011), Journal of Energetic Materials, 29 209-227.
- Denniston K. J., Topping J. & Dwyer T. M.,(2007), "General Organic and Biochemistry", 5th Edition, Towson University.
- Santos J. C., Andres J., Aizman A., Fuentealba P., Chem J., (2005), Theory Comput, 183.
- Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y.,(1994), Aromaticity and Antiaromaticity: Electronic and Structural Aspects; Wiley: New York.
- Levine Ira N., (2009), " Quantum Chemistry ", 6th Edition, Chemistry Department, Brooklyn College, City University of New York.
- Ali A.M.,(2009), " Theoretical Study of Nitrides Molecules : Investigation of DNA Using Density Function Theory ", Ph.D Thesis, Basrah University.
- David R. Lide, (2005), " CRC Handbook of Chemistry and Physics ", National Institute of Standards and Technology, CRC Press LLC, USA.
- Scuseria G. E. & Staroverov V.N.,(2005), Progress in the development of exchange - correlation functional, Elsevier, Amsterdam.
- Hutter J.,(2005), Lecture notes in computational chemistry; electronic structure theory, Physical chemistry Institute, University of Zurich 190, 8057.