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

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Abstract

This work deals with structural and electronic properties of trifluoroborane-carbonyl BF_3-CO 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 and electrophilic index. The results show that 6-31G (d, p) level of theory gave good agreement values of geometrical parameters with experimental data in compared with other levels.

Key words: DFT, energy gap, ionization potential, hardness and IR- spectrum.

الخصائص التركيبية والإلكترونية لنظام جزيئي مانح – متقبل :حسابات نظرية دالة الكثافة

ناهدة حسن

الخلاصة:

يتناول هذا العمل مع الخصائص التركيبية والإلكترونية لثلاثي فلوروبورين- كاربونيل كنظام جزيئي مانح- متقبل.

نظرية دالة الكثافة مع مختلف مجموعات أساس أستخدمت لحساب بعض الخصائص التركيبية والإلكترونية B3LY. لهذا النظام. وتشمل الحسابات طول الاواصر والزوايا بين الذرات، وتمت دراسة بعض الخصائص الإلكترونية للمركبات تحت الدراسة تتضمن الطاقة الكلية، الحالات الألكترونية ، والألفة الإلكترونية، وصلابة الكيميائية، ليونة ومؤشرألكتروفلك . بينت النتائج أن 6- ج31(دي –بي) مستوى النظرية أعطى اتفاق جيد لقيم المعلمات هندسية مع البيانات التجريبية في مقارنة مع المستويات الأخرى.

كلمات مفتاحية: نظرية دالة الكثافة ، فجوة الطاقة ، جهد التأين ،الصلابة وطيف الأشعة تحت الحمراء

Introduction

Charge transfer has long been recognized as the key process in many fields of chemistry, physics, and biology [1–7] monographs [8–10] . This work stand on the design of donor-acceptor and then can in future contact the donor and acceptor by a either Π or δ bridges to determine the quantity of charge transfer. 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) [11- 17]. 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. Extensive studies emphasized the role of different factors controlling the charge transport mechanism of donor-bridge- acceptor systems including inter-site electronic coupling , electronic energies and electronic - nuclear coupling. present work focuses on calculating the structural and electronic properties of BF_3-CO 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.

Theory and Computational Details

In this work, density functional theory has been used to calculate the electronic properties of the studied molecules at (B3LYP) functional with various basis sets. The geometry optimization, energies and IR-spectrum have been done using Gaussian 09 program [18] .

According to the density functional theory, the total energy can be written as [19] :

$$E_o = E_v(\rho_o) = T[\rho_o] + \int V_{en}(r)\,\rho_o(r)\,dr + J[\rho_o] + E_{NC}(\rho_o) \quad \ldots\ldots(1)$$

For a normalized wave function Ψ, the particle density is given by ρ (r) :

$$\rho(r) = \sum_i^{ni}[\psi_i(r)]^2 \quad \ldots\ldots\ldots\ldots(2)$$

Where ni is the number of electrons in orbital (i), and the summation is over the occupied molecular orbital. The kinetic energy of the system is [20]:

$$T[\rho] = T_S[\rho] + J[\rho] + V_{en}[\rho] + E_{XC}[\rho] \quad \ldots(3)$$

Where $T_S[\rho]$, J [ρ], $V_{en}[\rho]$ and E_{XC} [ρ] are the kinetic energy of non interacting electron system, classical coulomb energy, and exchange–correlation energy, respectively.

$$E_{XC}[\rho] = \int (\rho)\, E_{XC}[\rho]\, dr \quad \ldots\ldots\ldots\ldots(4)$$

$$T_S[\rho] = -\frac{1}{2}\sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle \quad \ldots\ldots\ldots(5)$$

$$J[\rho_o] = \frac{1}{2}\iint \frac{\rho_o(r_1)\,\rho_o(r_2)}{|r_1 - r_2|}\, dr_1 dr_2 \quad \ldots\ldots(6)$$

$$V_{en}[\rho_o] = \frac{1}{2}\iint \frac{\rho_o(r_1)\,\rho_o(r_2)}{|r_1 - r_2|}\, dr_1 dr_2 + E_{XC}[\rho] \quad \ldots.(7)$$

According to B3LYP function, the exchange correlation energy E_{XC}^{B3LYP} is given by [21]:

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + a_o(E_X^{HF} - E_X^{LDA}) + a_X(E_X^{GGA} - E_X^{LDA}) + a_C(E_C^{GGA} - E_C^{LDA}) \quad \ldots\ldots(8)$$

Where the three parameters : $a_o = 0.20$, $a_x = 0.72$ and $a_c = 0.81$.

The ionization potential (IP) and the electron affinity (EA) of the molecule are calculated according to the following relations (Koopman's theorem) [21]:

$$IP = -E_{HOMO} \quad \ldots\ldots\ldots\ldots(9)$$

$$EA = -E_{LUMO} \quad \ldots\ldots\ldots\ldots(10)$$

Where E_{HOMO} and E_{LUMO} are the high occupied molecular orbital and lower unoccupied molecular orbital energies, respectively. The electronic chemical potential (χ), the chemical hardness (η) and the softness (s) are given by [21]:

$$\chi = \frac{IP + EA}{2} \quad \text{….. ……(11)}$$

$$\eta = \frac{IP - EA}{2} \quad \text{……(12)}$$

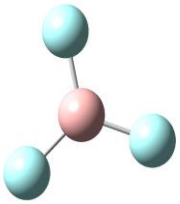
$$S = \frac{1}{2\eta} \quad \text{…….....….(13)}$$

And the electrophlicity index (ω) of the molecular is given by [21]:

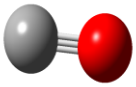
$$\omega = \frac{\chi^2}{2\eta} \quad \text{……...(14)}$$

Results and Discussion

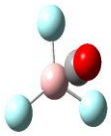
Figure (1) shows the geometrical structure of BF_3 (acceptor), CO (donor) and BF_3-CO (acceptor-donor) optimized at B3LYP density functional theory. The total energy in (a.u), symmetry and total dipole moment in (Debye) for studied molecules computed by B3LYP/6-31G(d, p) are presented in Table (1).



BF_3 (A)



CO (D)



BF_3-CO (A-D)

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 molecule is a planar with inversion center and it has D_{3h} symmetry (high symmetry) with low total dipole moment (0.0004 Debye), while the carbon monoxide molecule has infinity C_{infv} symmetry (low symmetry) and the donor-acceptor system has C_{3v} symmetry with dipole moment equals to (0.6040 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)
CO (D)	-113.325536206	C_{infv}	0.0580
BF_3 (A)	-324.589333620	D_{3h}	0.0004
BF_3-CO	-437.917864584	C_{3v}	0.6040

Table (2) declare the results of geometrical parameters included the bond length (in Angstrom) and bond angles in (degree). The computational levels of theory used in this work give good results of length linking between donor and acceptor, the bond B-C obtained from 6-31G(d,p) equals (2.887Å) in a good agreement with experimental value (2.886 Å), F-B-F bond equals 120^{o} [15]. Other levels of theory gave approximately values of these parameters nearly to experimental results.

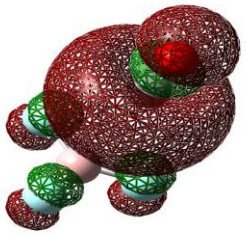
Table (2): Bond lengths in Angstrom and angles in degree for donor-acceptor system.

Species	Bond	STO-3G	3-21G	4-21G	6-31G	6-31G (d)	6-31G (d, p)	6-311G	Exp. [15]
CO	C-O	1.142	1.129	1.128	1.129	1.115	1.126	1.122	1.128
BF_3	B-F	1.310	1.326	1.318	1.315	1.309	1.307	1.308	1.307
	F-B-F	119.990	120.0	119.880	119.980	120.0	120.0	119.988	120.0
BF_3-CO	B-F	1.308	1.320	1.315	1.312	1.307	1.305	1.306	1.305
	B-C	2.835	2.585	2.602	2.625	2.965	2.887	2.895	2.886
	C-O	1.145	1.125	1.228	1.123	1.118	1.128	1.122	1.128
	F-B-F	119.990	120.0	119.880	119.980	120.0	120.0	119.988	120.0

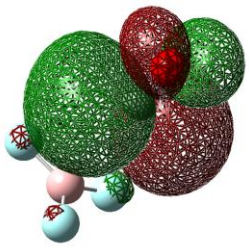
Table (3) shows the values of the electronic states (HOMO and LUMO) and the energy gap ($E_{LUMO} - E_{HOMO}$) of trifluoroborane-carbonyl BF_3-CO as a donor-acceptor system calculated by B3LYP density functional theory with many levels of theory. The energy gap for the new structure is take place in the range about (8.5-11.0) eV and the differences in the value of energy gap depend on the level used in calculation. Table (3) tells us that STO-3G give more larger value for band gap, this may be come from that level of theory is a small to describe the donor-acceptor systems in compared with large basis sets, such as, 6-31G(d) and 6-31G(d, p) levels of theory. Figure (2) shows the shapes of HOMO and LUMO drawn from the calculations of 6-31G (d, p) basis sets, these shapes come from the distribution of electrons according to the linear combination atomic orbital-molecular orbital, the high value of electro-negativity of fluorine atoms has the large contribution in HOMO and LUMO energies.

Table (3): HOMO, LUMO and energy gap for donor-acceptor system.

Property	STO-3G	3-21G	4-21G	6-31G	6-31G (d)	6-31G (d, p)	6-311G
HOMO (eV)	-12.6805	-12.0211	-9.3365	-11.1159	-11.05584	-11.07691	-11.7858
LUMO (eV)	-1.2269	-1.0065	-0.9885	-0.99854	-1.322479	-1.517773	-1.2258
Energy Gap (eV)	11.4536	11.01464	8.34801	10.11738	9.733361	9.559137	10.56



HOMO



LUMO

Figure (2) : HOMO and LUMO of BF_3-CO structure.

The results of ionization potential (IP), electron affinity (EA), chemical potential (χ), electrophlicity index (ω) and charge transfer (ΔN) are presented in

Table (4). As we see from the above 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 high ionization potential value (11.07691 eV). This level of theory give good result for electrophlicity index (ω = 4.148 eV), this may help to interact this system with effective surrounding molecular system. The amount of charge transfer in BF_3 - CO 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	6-31G (d)	6-31G (d, p)	6-311G
IP (eV)	12.6805	12.0211	9.3365	11.1159	11.05584	11.07691	11.7858
EA (eV)	1.2269	1.0065	0.9885	0.99854	1.322479	1.517773	1.2258
χ (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 obtained from the calculations for donor, acceptor and donor- acceptor system using B3LYP density functional theory with 6-31G (d, p). High polarizability means high chemical reactivity. The donor - acceptor system has more reactivity than other species 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 that the tensors of polarizability in three dimensions are $\alpha_{xx} < \alpha_{yy} < \alpha_{zz}$.

Table (5): Average polarizability for donor-acceptor system.

Species	Polarizability (a. u)			
	α_{xx}	α_{yy}	α_{zz}	α_{ave}
BF_3	13.542	17.507	17.509	16.186
CO	11.908	11.908	15.420	12.968
BF_3 - CO	27.742	27.743	32.843	29.442

Figure (3) represents the IR spectrum for BF_3-CO 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 bending of B-C bond lies at (650.29 cm^{-1}). For B-F bond, the stretching of B-F bond lies at (873.83cm^{-1}) and the bending is at (1436.83 cm^{-1}) in which it corresponds to intensity (398.9994 Km/mol). The large value of frequency (2222.75 cm^{-1}) for the stretching of C-O bond and it corresponds to (77.999 Km/mol) infrared intensity.

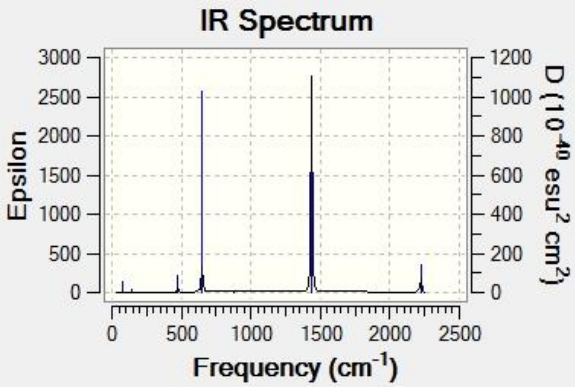


Figure (3): The IR spectrum of BF_3-CO donor - acceptor system.

Conclusions

The density functional theory used in this study is a powerful method 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 with experimental data. The geometric structures, symmetry and total energies

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. The results obtained in this work help us to select a type of bridges to interact the donor and acceptor to calculate the physical properties of donor-bridge-acceptor.

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