Structural and Electronic Properties of Donor-Acceptor Molecular System: B3LYP/ DFT Calculations

Basim Abdullattif Ghalib   Falah Hassan Hanon
Afrah Abdulameer Mohammed   Hamid Ibrahim Abbood

Abstract

Present work deals with the structural and electronic properties of trifluorocarbon-nitro CF3-NO as a donor-acceptor molecular system. Density functional theory at the three parameters B3LYP level of theory was employed with various basis sets to determine and calculate some structural and electronic properties for this molecular system. The calculations include the geometrical parameters of the studied structures. And some electronic properties of these were investigated include the total energy, electronic states, ionization potential, electron affinity, electro chemical hardness, softness and electrophilic index. The results showed 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.*

حسابات الخواص التركيبية والالكترونية لثلاثي فلوريد كاربون – نيترو كنظام جزيئي واهب قابل

باسم عبد اللطيف غالب   فلاح حسن حنون   افراح عبد الامير محمد   حامد ابراهيم عبود

الخلاصة

البحث الحالي يهدف الى معالجة الخواص التركيبية والالكترونية لثلاثي فلوروكاربون–نيترو كنظام جزيئي واهب–قابل. تم تطبيق نظرية دالة الكثافة عند مستوي المعاملات الثلاث B3LYP وبدوال اساس مختلفة لتحديد وحساب بعض الخواص التركيبية و الالكترونية للنظام الجزيئي المذكور. تضمنت الحسابات المعاملات الهندسية للتراكيب قيد الدراسة. الخواص الالكترونية المحسوبة في هذا البحث تضمنت الطاقة ألكلية الحالات الالكترونية، جهد التأين، الالفة الالكترونية الصلادة الكهرو كيميائية، المرونة ومعامل التآلف مع الوسط. تبين النتائج ان المستوي (d, p) G‏31–6 قد أعطى نتائج تتفق بشكل جيد مع النتائج العملية للمعاملات الهندسية مقارنة مع المستويات والدوال الاساس الاخرى.

Introduction

The researches based on the charge transfer has long been recognized as the key process in many fields of chemistry(1), physics(2-4), and biology (5–7) monographs(8–10) . This work stands on the design of donor-acceptor and then can in future contact the donor and acceptor by a either π or σ bridges to determine the quantity of charge transfer. A convenient model system often used to probe the mechanism of charge transfer in molecular objects with nanoscale dimensions comprises a donor (D) and an acceptor (A) of electrons or holes connected by molecular bridge (B) (11- 14). The number and variety of such donor-bridge acceptor (D-B-A) systems have grown explosively in recent years (15-17). 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 CF3-NO 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.

Computational Details

Density functional theory has been used in this work 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).

For a normalized wave function Ψ, the particle density is given by $\rho(r)$

$$\rho(r) = \sum_i^{ni} [\Psi_i(r)]^2$$

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

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

Where $T_s[\rho]$, $J[\rho]$, $V_{en}[\rho]$ and $E_{XC}[\rho]$ are the kinetic energy of non interacting electron system, classical coulomb energy, and exchange–correlation energy, respectively, can be written as:

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

$$T_s[\rho] = -\frac{1}{2} \sum_i \langle \emptyset_i | \nabla^2 | \emptyset_i \rangle$$

$$J[\rho_0] = \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$

$$V_{en}[\rho_0] = \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 + E_{XC}[\rho]$$

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

$$E_{xc}^{B3LYB} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

Where the three parameters: $a_0 = 0.20$, $a_x = 0.72$ 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) (22):

$$IP = E_{HOMO}$$

$$EA = E_{LUMO}$$

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 (23):

$$\chi = \frac{IP+EA}{2}$$

$$\eta = \frac{IP-EA}{2}$$

$$S = \frac{1}{2\eta}$$

And the electrophlicity index (ω) of the molecular is given by (23, 24):

$$\omega = \frac{\chi^2}{2\eta}$$

Results and Discussion

In figure 1, CF_3 molecule is an acceptor and NO is a donor molecule, this choice is due to the electronic distribution of the two structures. The geometrical structure of CF_3-NO as a acceptor-donor molecular system was optimized at B3LYP density functional theory. Table 1 represents the B3LYP/6-31G(d, p) calculations of total energy in (a. u), symmetry and total dipole moment in (Debye) for donor, acceptor and donor-acceptor molecular systems. 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 the studied structures, the trifluorocarbon molecule is a planar with inversion center and it has D_{3h} symmetry (high symmetry), and this is the reason that this molecule has not dipole moment as seen in table 1, while the nitro monoxide molecule has infinity C_{infv} symmetry (low symmetry) and the donor-acceptor system has C_1 symmetry with dipole moment equals to (0.1458 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.
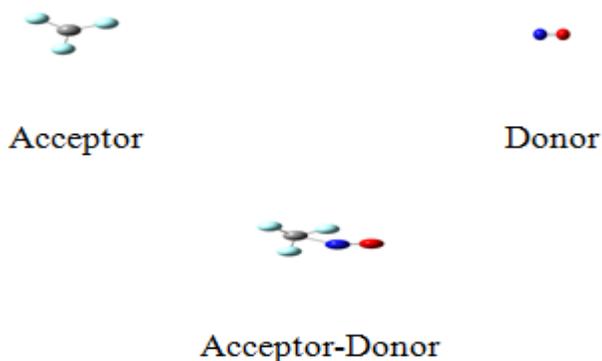

Acceptor   Donor

Acceptor-Donor

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

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

Species	Total Energy (a.u)	Symmetry	Total D. M(Debye)
NO (D)	-129.45296	C_{infv}	0.5570
CF$_3$ (A)	-337.10016	D_{3h}	0.0000
CF$_3$-NO (A-D)	-467.35868	C_1	0.1458

The results of geometrical parameters included the bond length (in Angstrom) and bond angles in (degree) are declare in table 2. The computational levels of theory used in this work give good results of length linking between donor and acceptor, the bond C-N obtained from 6-31G(d, p) equals (1.457A^0) in a good agreement with experimental value (1.452 A^0), F-C-F bond equals 120^0 (15).Other levels of theory gave approximately values of these parameters nearly to experimental results.

Table 2: Geometrical parameters 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)
NO	N-O	1.242	1.229	1.228	1.229	1.215	1.226	1.222	1.225
CF$_3$	C-F	1.365	1.355	1.368	1.382	1.379	1.370	1.380	1.370
	F-C-F	119.99	120.0	119.99	120.0	120.0	120.0	119.99	120.0
CF$_3$-NO	C-F	1.361	1.370	1.365	1.362	1.366	1.371	1.362	1.375
	C-N	1.802	1.581	1.600	1.550	1.565	1.547	1.595	1.542
	N-O	1.245	1.225	1.228	1.223	1.228	1.225	1.222	1.225
	F-C-F	119.99	120.0	119.89	119.98	120.0	120.0	119.99	120.0

The HOMO, LUMO and the energy gap ($E_{LUMO} - E_{HOMO}$)of trifluorocarbon-nitro CF3-NO as a donor-acceptor system in table 3 are 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 (3.558-6.688) 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 orbitals -

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)	-11.0208	-10.2116	-11.336	-11.1255	-11.0976	-8.168470	-10.5255
LUMO (eV)	-4.3328	-5.6401	-4.9809	-4.9986	-5.3287	-4.609543	-5.02115
Energy Gap (eV)	6.688	4.5715	6.3551	6.1269	5.7689	3.558927	5.50435

HOMO   LUMO
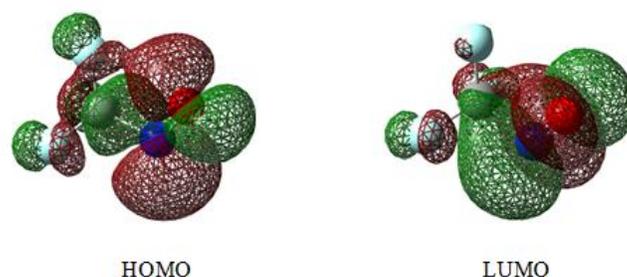
Figure 2: HOMO and LUMO of CF$_3$-NO structure

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 the above table, the largest value of charge transfer (0.97745) between two systems (donor - acceptor) was results by employing B3LYP/6-31G (d, p), this value corresponding to high ionization potential value (11.0976 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 CF$_3$ - NO donor - acceptor system results from other basis sets gave approximately the same few lower value. 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 four times the value of polarizability for acceptor, as we see in table 5. So the results satisfy that the tensors of polarizability in three dimensions are $α_{xx} < α_{yy} < α_{zz}$.

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)	11.0208	10.2116	11.336	11.1255	11.0976	8.168470	10.5255
EA (eV)	4.3328	5.6401	4.9809	4.9986	5.3287	4.609543	5.02115
K (eV)	7.6768	7.92585	8.15845	8.06205	8.21315	6.3890065	7.773325
W (eV)	2.6649	3.24592	1.60380	3.626424	3.935504	4.148544	4.00809
ΔN	0.80325	0.80042	0.678895	0.80056	0.97745	0.955676	0.89545

Table 5: Average polarizability for donor-acceptor system

Species	Polarizability (a. u)			
	α_{xx}	α_{yy}	α_{zz}	α_{ave}
CF_3	5.142	13.268	13.269	10.559
NO	3.987	3.987	9.457	5.81033
CF_3 - NO	15.988	18.098	26.415	20.167

The results of IR spectrum for CF_3-NO donor-acceptor system are illustrated in table 5. The number of modes was calculated by the relation 3N-5, where N is the number of atoms in the structure, the bending of C-N bond lies at (745.55 cm^{-1}). For C-F bond, the stretching of B-F bond lies at (1086.15 cm^{-1}) and the bending is at (1436.83 cm^{-1}) in which it corresponds to intensity (415.9089 Km/mol). The large value of frequency (1560.35 cm^{-1}) for the stretching of N-O bond and it corresponds to (75.015 Km/mol) infrared intensity.
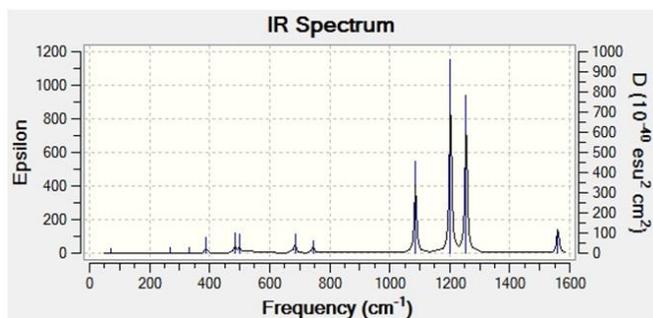
Figure 3: The IR spectrum of CF_3-NO donor - acceptor system. Epsilon: intensity in (Km/mol)

Conclusions

As we see from the results in this paper, 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. The total energy for donor – acceptor molecular system declare 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, this idea came from the results of the energy gap for the structure, 6-31G (d, p) showed small energy gap in comparison with other used levels.

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