

Research Article

Density Function Theory B3LYP/6-31G**Calculation of Geometry Optimization and Energies of Donor-Bridge-Acceptor Molecular System

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Accepted 25 May 2014, Available online 01 Aug 2014, Vol.4, No.4 (Aug 2014)

Abstract

Theoretical B3LYP/6-31G (d , p) density functional theory has been employed to examine the electronic properties of donor-bridge-acceptor molecular system and determine the energies. The electronic states of the system has been calculated depends on Koopman's theorem under the orbital-vertical theory. The results show that the functional used in the description of the studied molecular system has been proved its validity in calculating the HOMO and LUMO energies and it is a suitable for studying the geometry optimization for the organic molecular system, there are localized orbitals in different parts of the D-B-A molecular system in which that satisfy important property for the D-B-A system to show model new electronic properties as an Aviram-Ratner.

Keywords: Density Function Theory, Donor-Bridge-Acceptor Molecular System etc.

Introduction

The main process in many fields of chemistry, physics, [Marcus and Sutin ,1985; Barbara *et.al*,1996 Bixon and Jortner 1999; Berlin *et.al*, 2004; Matyushov and Voth,2002; Adamset *et.al*,2003; Weiss *et.al*,2005] monographs [Kuznetsov,1995; Kuznetsov and Ulstrup,1999; Balzani *et.al*,2001] is the charge transfer. This work aims to design of donor-bridge-acceptor molecular system to determine the quantity of charge transfer CT. 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) [Wasielewski,1992; Schuddeboom *et.al*,1991; Ratner *et.al*,1997; Lindsay and Ratner,2007; See and Schuster, 2004; Jordan and Paddon,1992; Warman *et.al*,1999]. 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 optimization and energies of the components and the donor-bridge-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. The system under study was designed depends on Aviram-Ratner model [A. Aviram, M. A. Ratner, 1974]

Computational Details

The geometry optimizations of carboxy benzene as a donor, thiophene iso indene as an acceptor and donor-bridge-acceptor molecular system were performed with Berny's optimization algorithm by (calculating the energy derivatives with respect to nuclear coordinates analytically [H.B.Schlegel, J. Comput, 1982], in redundant internal coordinates. The gradient corrected density functional methodology was employed: Becke's exchange functional (B) [A.D. Becke 1988] and Becke's three-parameter adiabatic connection (B3) hybrid [A.D. Becke 1993] exchange functional were used in combination with the Lee–Yang–Parr correlation functional B3LYP [C. Lee, W. Yang, R.G. Parr 1988]. Note that while the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP one contains an admixture of HF exchange (i.e. is of hybrid form). The B3 functional, in fact, contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange [A.D. Beck 1993]. The standard 6-31G(d,p) basis set of DZP quality was used for orbital expansion to solve the Kohn– Sham equations in all cases. Numerical harmonic vibrational analyses were performed for the stationary points found on the potential energy hyper surface, in order to test their character and to compute the harmonic vibration frequencies. The number of imaginary frequencies served as a test whether the stationary points correspond to real minima, or to first-order saddle points. The computed stationary points for which the structures and force fields are presented

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correspond to real minima on the molecular potential energy hyper surfaces. The DFT (LUMO-HOMO) energy for the donor-bridge-acceptor molecular system studied here was calculated at the same level of theory. All calculations were performed with the GAUSSIAN 09 suite of programs.

Results and Discussion

Geometries

Figure 1 shows the B3LYP/6-31G (d, P) optimized structures under study. It can be seen from this figure, carboxy benzene as a donor and thiophene iso- indene as an acceptor are connected by (CH)₂ as a bridge.

Tables 1, 2 and 3 show the optimized geometric parameters (bond lengths in Angstrom, bond angles in degree and dihedral angles in degree) of donor, acceptor and donor- bridge- acceptor structures, respectively, calculated by B3LYP/6-31G (d, P) The difference of atomic numbers for the conjugated atoms effect on the measurements of the bond length between these atoms.

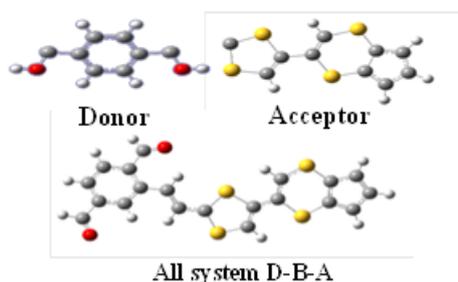


Figure1. The optimized geometric structures of studied molecules obtained from B3LYP/6-31G (d, p).

Table 1: The optimized geometric parameters (lengths in angstrom , angles in degree and dihedral angles in degree) carboxybenzene (D) using B3LYP/6-31G** (d,p).

Bond Length (Å)		Bond Angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C-C)	1.418	A(C-C-C)	120	D(C-C-C-C)	0.008
R(C-H)	1.084	A(C-C-H)	120	D(H-C-C-C)	-179
R(H-O)	0.975	A(C-C-O)	108	D(C-C-C-O)	0.0019
R(C-O)	1.362	A(C-O-H)	111	D(C-C-O-H)	179

Table 2: The optimized geometric parameters (lengths in angstrom , angles in degree and dihedral angles in degree) of thiophene isoindene (A) using B3LYP/6-31G** (d,p).

Bond Length (Å)		Bond Angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C=C)	1.341	A(C-C-C)	116	D(S-C=C-H)	- 179
R(C-S)	1.834	A(C-C-H)	126	D(S-C-C-S)	-0.015
R(C-H)	1.081	A(C-C-S)	127	D(H-C=C-H)	0.065
R(S-S)	2.922	A(H-C-S)	115	D(H-C-S-S)	-0.728

Table 1 declare that the convergence between the bonds C-C and C-O comes from the convergence between their atomic numbers, and this reason explains the difference of C-H bond.

Table 3: The optimized geometric parameters (lengths in angstrom , angles in degree and dihedral angles in degree) of all system(D-B-A) using B3LYP/6-31G** (d,p).

Bond Length (Å)		Bond Angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C=C)	1.369	A(C-C-S)	118	D(S-C-C-C)	-178
R(C-S)	1.703	A(C-C-H)	123	D(H-C-C-C)	-1.84
R(C-H)	1.080	A(S-C-S)	113	D(C-C-C-O)	-0.054
R(C=O)	1.109	A(C-C=O)	124	D(H-C-S-S)	-179

Table (3) shows that the optimized bond lengths of the bridge backbone linking between donor and acceptor are having double bond less than 1.35 Å , and it can be seen that a minor deviation in the bridge bond angle and dihedral angle between the two planes containing the end substituent's. This deviation can be expected due to strict interaction coming from the presence of phenyl groups at the terminal positions.

Table (4) shows the results of total energy , symmetry and number of imaginary frequency for carboxy benzene (D), thiophene iso-indene (A), (CH)₂ (B) and D-B-A molecules obtained from B3LYP/6-31G (d, p) calculations.

Table 4: Total energy in (a.u), symmetry and number of imaginary frequency for studied molecules from B3LYP/6-31G (d, p) functional.

Species	E_T (a.u)	Symmetry	No. of imaginary frequency
Donor (D)	-1976.966	C _{2v}	0
Bridge (B)	-77.3196	C ₁	0
Acceptor (A)	- 458.6187	C ₁	0
Molecular System (D-B-A)	-2512.5414	C ₁	0

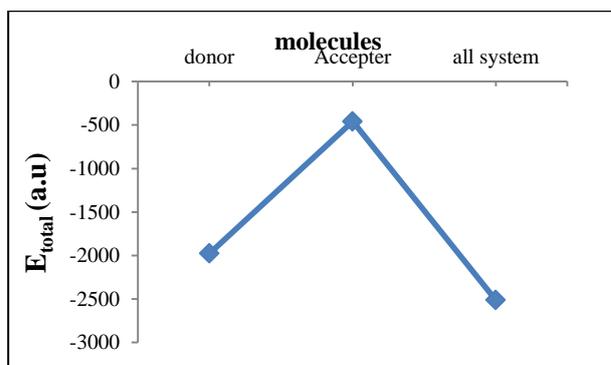


Figure 2: The total energy for donor, acceptor and donor-bridge- acceptor system by B3LYP/ 6-31G (d, p).

It is obvious from Table 4 that the total energy for D-B-A system is less than the total energy of mentioned molecules in this study, the total energy of D-B-A system

is approximately the summation of total energy for all donor, bridge and acceptor molecules, as illustrated in figure 2. From table 4, one can see that all structures have not imaginary frequency, this may refer to that 6-31G (d, p) is a suitable level of theory used in optimization geometry for this type of structures. Table 4 shows also the symmetry of studied molecules, carboxybenzene (donor) is a planar and has a high symmetry, thiophene iso-indene (acceptor) and the donor- bridge- acceptor molecular system has C_1 symmetry and this means these structures have one point of rotation to leaves them apparently unchanged.

Electronic States and Energy Gap

Table (5) shows the high occupied molecular orbital energy and lower unoccupied molecular orbital energy, and energy gap for donor, acceptor, and donor- bridge – acceptor molecules. It has been found that the bridge used to link the carboxy benzene as a donor with thiophene iso-indene as an acceptor gave a new structure as a donor-bridge –acceptor system has a small energy gap in compared with donor and acceptor, the energy gap for D-B-A system is 0.6 eV. Figure 3 shows the energy gap for studied molecules.

Table 5: E_{HOMO} , E_{LUMO} and energy gap for donor, acceptor and donor –bridge –acceptor molecular system.

Species	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
Donor (D)	-6.1	-3.3	2.8
Acceptor (A)	-6.4	-4.6	1.8
Molecular System (D-B-A)	-4.5	-3.9	0.6

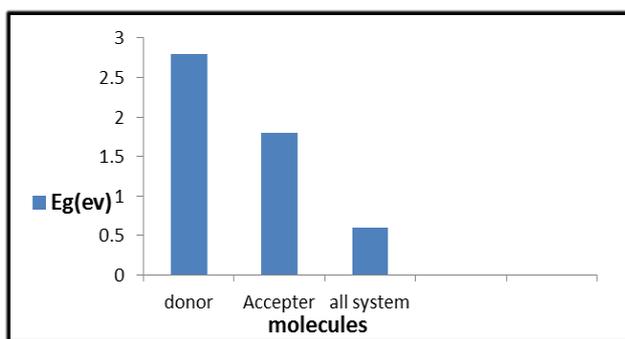


Figure 3: Energy gap for donor, acceptor, and donor-bridge- acceptor molecular system.

The interaction between carboxy benzene (D) and thiophene+iso-indene (A) through the bridge affected on HOMO and LUMO of these molecules, the main change occurs at LUMO of the donor and HOMO of the acceptor and this change depends on the type of bridge used in linking donor and acceptor. Figures 4, 5 and 6 show the LUMO- HOMO for donor, acceptor and D-B-A system, respectively. And figure 7 shows the shapes of HOMO and LUMO for these structures, drawn by Gaussian View 5.0.8 using B3LYP/6-31G (d, p) method.

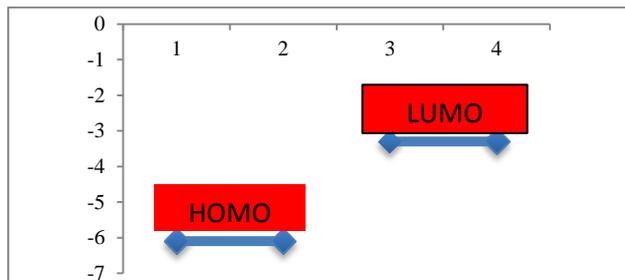


Figure 4: LUMO-HOMO energy for carboxybenzene (D)

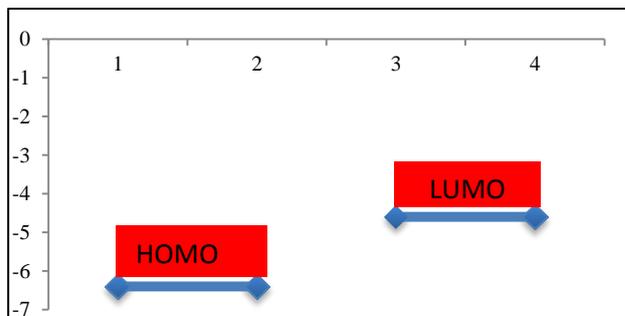


Figure 5: LUMO-HOMO energy for thiophene iso-indene (A)

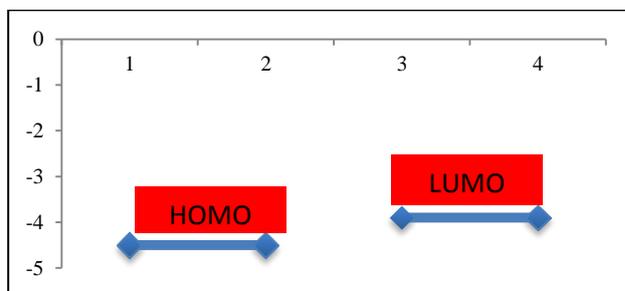


Figure 6: LUMO-HOMO energy for D-B-A system.

In this system, the donor part and acceptor part are coupled through σ -bridge to result the molecular system. As we know that the structural construction principle of organic molecular semiconductor is based on acceptor part and donor part connected through a bridge, these three (donor, acceptor and bridge) can be considered as components in bringing out the rectifier.

Figure (8) shows the energy level diagram for the three highest occupied and three lowest unoccupied molecular orbitals for the donor, acceptor and D-B-A system. From this diagram, one can see that the HOMO and LUMO for the acceptor are more stable in comparison with donor. The HOMO and LUMO for donor are situated (-6.1, -3.3) eV, while the HOMO and LUMO for acceptor, but (LUMO- HOMO) for both donor and acceptor is approximately the same (2.8 eV for donor and 1.8 eV for acceptor). The electron injection of an electron to the LUMO of the acceptor will be a lower energy process compared to the donor because the LUMO of the acceptor is more stable in compared to donor. On the other hand, removal of one electron from the HOMO of the donor will be a less energetic process compared to the acceptor

because the HOMO of the donor is less stable in compared to HOMO of the acceptor. The (LUMO-HOMO) for the D- B-A is small (0.6 eV) in compared to donor, bridge and acceptor.

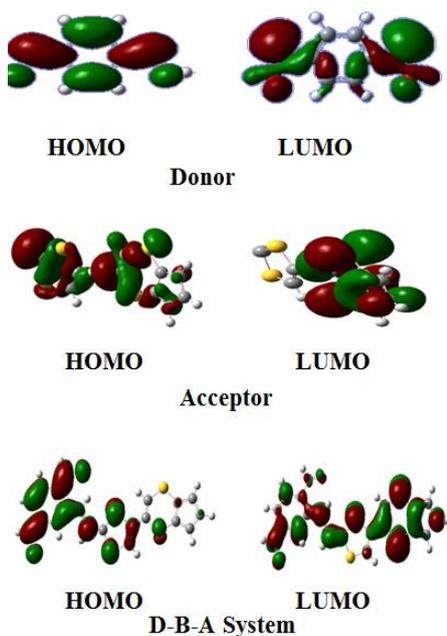


Figure 7: The shapes of HOMO and LUMO for studied structures.

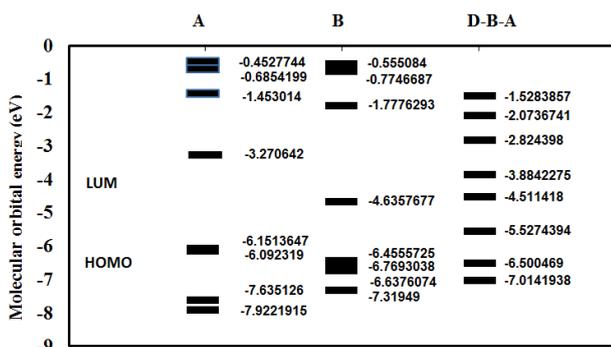


Figure 8: Energy level diagram for donor, bridge, acceptor and D-B-A molecular system.

Conclusions

B3LYP/6-31 G(d, p) density functional theory has been proved its validity in studying the geometry optimization and calculating the geometrical parameters. Therefore, density functional theory presented good results in calculation of total energy for the D-B-A molecular system comes from the summation of total energies for all donor, bridge and acceptor parts.

The large 6-31 G(d, p) basis set used to describe the studied structures with B3LYP functional level is a significant theory for calculating the electronic states (HOMO and LUMO) for the studied molecular electronics, but it requires a large time compared with other small basis sets. The presence of substituents in

phenyl rings at the donor and the acceptor did not have effect on the aromaticity of these organic molecules. So, the aromaticity of phenylenes keep under the connection donor part and acceptor part through the σ -bridge. Phenyl ring with carboxy group was truly predicted to be a better semiconducting material because of its lower oxidation potential, it is good electron donating group.

Small value of (LUMO-HOMO) for the D-B-A molecular system compared with their individual components. For device application with these structures connected to two electrodes, a decrease in (LUMO-HOMO) value is play an important role in electron injection. From the molecular orbital distribution, there are localized orbitals in different parts of the D-B-A molecular system in which that satisfy important property for the D-B-A system to show rectification.

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