International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 - 5161

Research Article

Theoretical Study of Geometry Optimization And Energies For Donor-Nanobridge-Acceptor Molecular System:B3LYP/DFT Calculations

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Accepted 05 January 2014, Available online 01 February 2014, **Vol.4, No.1 (February 2014)**

Abstract

B3LYP/6-31G (d , p) density functional theory has been employed to calculate the geometry optimization and energies of donor-nanobridge-acceptor molecular system. The electronic states of the system has been calculated depend 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. The energy level diagram shows that 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 as a molecular electronics.

Keywords:*B3LYP , DFT, total energy , energy gap, HOMO and LUMO*

Introduction

The main process in many fields of chemistry, physics, and biology monographs is the charge transfer. This work stand on the design of donor- bridge-acceptor 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). 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 of the studied structures and energies of 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. Aromatic compounds are important in industry and play key roles in the biochemistry of all living things. The organic semiconductor materials, such as, conjugated organic molecules have been widely used as active materials for optoelectronic devices such as light emitting diodes, field effect transistor, and photovoltaic and solar cells. In this work, we use the original aromatic molecule (benzene) to design a donor-bridge-acceptor molecular system depends on Aviram-Ratner model.

Computational Details

Full geometry optimizations of amino-benzene as a donor, nitrobenzene as an acceptor, benzene as a bridge and donor-bridge-acceptor were performed with Berny optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates. The gradient corrected density functional methodology was employed: Becke’s exchange functional (B) and Becke’s three-parameter adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee–Yang–Parr correlation functional B3LYP. While the BLYP methodology is a ‘pure DFT’ one (itincludes 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. 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. 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 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 GAUSSIAN09 suite of programs.

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Results and Discussion

Figure 1 shows the optimized structures for the amino-benzene as a donor and nitrobenzene as an acceptor connected by the benzene as a bridge at B3LYP/6-31G (d, P) density functional theory.

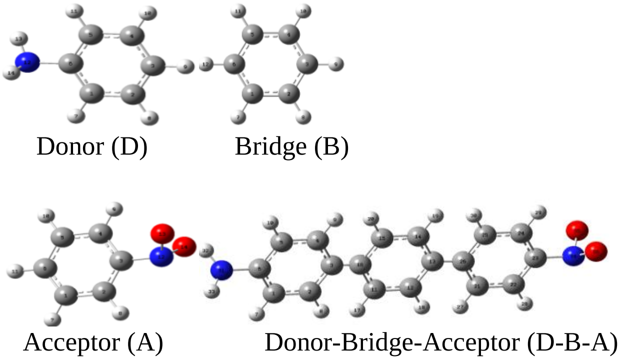


Figure 1: B3LYP/6-31G (d, p) optimized structures under study

Table 1: B3LYP/6-31G (d ,p) optimized parameters of amino-benzene (D)

Bond Length (A^0)		Bond Angle (deg)		Dihedral angle (deg)	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c-c)	1.392	A(c-c=c)	120.765	D(c=c-c=c)	0.069-
R(c-H)	1.084	A(c-c-H)	119.232	D(H-c-c=c)	179.911
R(c=c)	1.403	A(c=c-H)	120.002	D(H-c-c-H)	0.366-
R(N-H)	1.009	A(c=c-c)	118.694	D(c-c=c-c)	0.142
		A(c=c-N)	120.617	D(c-c=c-N)	177.1
		A(c-N-H)	114.584	D(H-c=c-N)	2.622-
		A(H-N-H)	111.19	D(N-c-c=c)	177.099-
				D(N-c-c-H)	2.611
				D(c=c-N-H)	156.683

Table 2: B3LYP/6-31G (d ,p) optimized parameters of benzene (B)

(Bond or Angle) Label	Value	Experimental Value
R(c=c)	1.396	1.39
R(c-H)	1.086	1.1
A(c=c-c)	120	120
A(c-c-H)	120	120

Tables 1, 2, 3 and 4 show the optimized geometric parameters (bond lengths in Angstrom, bond angles in degree and dihedral angles in degree) of donor, bridge, acceptor and donor- bridge- acceptor structures, respectively, calculated at the same level of theory. It is clear from table 5 that the geometrical parameters calculations by B3LYP method are in good agreement with experimental data for amino-benzene (donor) molecule. Also, the bonds calculated in this work for benzene (bridge) are in good agreement with experimental results, as we see in table 2. The difference of atomic numbers for the conjugated atoms effect on the bond length between these atoms, the convergence between the bonds C-C and C-N comes from the convergence between their atomic numbers, and this reason explains the difference of C-H bond.

Table 3: B3LYP/6-31G (d, p) optimized parameters of nitrobenzene (A)

Bond Length (A^0)		Bond Angle (deg)		Dihedral angle (deg)	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c=c)	1.392	A(c=c-c)	118.443	D(c-c=c-c)	0.01
R(c-H)	1.08	A(c=c-H)	121.917	D(c-c=c-H)	180.005
R(c-N)	1.476	A(c-c-H)	119.64	D(H-c=c-c)	180.01
R(N-O)	1.227	A(c=c-c)	120.206	D(H-c=c-H)	0.004
		A(c-c=c)	122.365	D(c-c-c-c)	0.0091-
		A(c-c-N)	118.819	D(c=c-c=c)	0.001-
		A(c-N-O)	117.746	D(c=c-c-N)	180.009-
		A(O-N-O)	124.5	D(H-c-c-c)	179.989

It is clear from table 1 that the geometrical parameters calculations in present study are in a good agreement with experimental data.

Table 4 shows that the optimized bond lengths of the bridge backbone linking between donor and acceptor are having double bond less than 1.45 A^0 , 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: B3LYP/6-31G (d, p) optimized parameters of (D-B-A) system

Bond Length (A^0)		Dihedral angle (deg)		Dihedral angle (deg)	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c=c)	1.403	D(c=c-c-H)	-179.89	D(c-c-c=c)	0.158
R(c-H)	1.084	D(H-c-c-H)	0.322	D(c-c=c-H)	0.018
R(c-N)	1.391	D(c-c=c-c)	-0.082	D(c-c=c-c)	0.035
R(N-H)	1.009	D(c-c=c-N)	-177.26	D(N-c=c-H)	-0.057
R(c-c)	1.411	D(H-c=c-N)	2.53	D(c-c-N-O)	-0.065
R(N-O)	1.23	D(H-c=c-c)	-0.049	D(c=c-c-c)	0.062
Bond Angle (deg)		D(c=c-c=c)	-178.1		
Bond	**Value**	D(H-c=c-H)	-0.534		
A(c-c-H)	119.936	D(c=c-c-N)	177.268		
A(c-c=c)	122.027	D(H-c-c-N)	-2.567		
A(c=c-c)	116.925	D(c=c-N-H)	-23.5		
A(c-c-c)	123.969	D(c-c-N-H)	24.217		
A(c-N-H)	115.917	D(c-c=c-H)	0.53		
R(H-N-H)	112.505	D(c=c-c-c)	2.279		
A(c-c=c)	127.559	D(H-c-c=c)	1.841		
A(o-N-o)	124.162	D(c-c-c-H)	0.315		

Table 5: Results of geometry optimization for studied molecules

Species	ET(a,u)	-V/T	Symmetry	NO. Of imaginary frequency
Donor (D)	-287.647	2.008	C_S	0
Bridge (B)	-232.158	2.005	D_{6h}	0
Acceptor (A)	-436.803	2.007	C_{2v}	0
Molecular System (D-B-A)	-956.336	2.006	C_1	0

Table 5 shows the results of geometry optimization included the total energy $E_T$varial ratio (-V/T), symmetry and number of imaginary frequency for amino-benzene (D),

Table 5 clears that the total energy for D-B-A system is less than the total energy ofmentioned molecules in this work, the total energy of D-B-A system is approximately the summation of total energy for all donor, bridge and acceptor molecules, it can be found an equation associates the total energy E_T for the donor- bridge –acceptor molecular system with its components:

$$E_T \text{ (D-B-A system)} \approx E_T \text{ (donor)} + E_T \text{ (bridge)} + E_T \text{ (acceptor)}$$

The 6-31G (d, p) functional is a suitable level of theory used for optimization geometry of these structures, in which all the studied structures have no imaginary frequency. Table 5 shows also the symmetry of studied molecules, amino-benzene (donor) is a planar and has a low symmetry, nitrobenzene (acceptor) has high symmetry, benzene (bridge) is a planar with D_{6h} high symmetry and the donor- bridge- acceptor molecular system has C_1 point group symmetry and this means that only a rotation of 360^0 leaves it apparently unchanged.

The high occupied molecular orbital energy E_{HOMO} , lower unoccupied molecular orbital energy $E_{LUMO}$and energy gap $_{Eg}$for donor, acceptor, and donor- bridge –acceptor structures are shown in table 6. It has been found that the benzene (bridge) used to link the amino-benzene aa donor with nitrobenzene as an acceptor gave a new structure (donor- bridge –acceptor) system has a small energy gap in compared with it is components, the energy gap for D-B-A system is 3.045 eV.

The interaction between amino-benzene (D) and nitrobenzene (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. Figure 3 show the shapes of HOMO and LUMO for these structures, drawn by Gaussian View 5.0.8 using B3LYP/6-31G (d, p) method.

In the system under study, the donor part and acceptor part are coupled through π-bridge to result the molecular system. As we know that the structural construction principle of organic molecular electronic is based on acceptor part and donor part connected through an insulating bridge, these three (donor, acceptor and bridge) can be considered as components in bringing out the molecular electronic.

The optimization of donor, acceptor, π -bridge and D-B-A molecular system has been carried out at B3LYP/6-31 G(d, p) level along with the population analysis and donor for comparison analysis of the energy level arrangements in these components and the system.

Table 6: E_{HOMO} , E_{LUMO} and energy gap E_g for studied molecules

Species	E_{HMO}(ev)	E_{LUMO}(ev)	Eg(ev)
Donor (D)	-5.768	-0.353	5.415
Acceptor (A)	-7.863	-2.857	5.006
Molecular System (D-B-A)	-5.799	-2.754	3.045

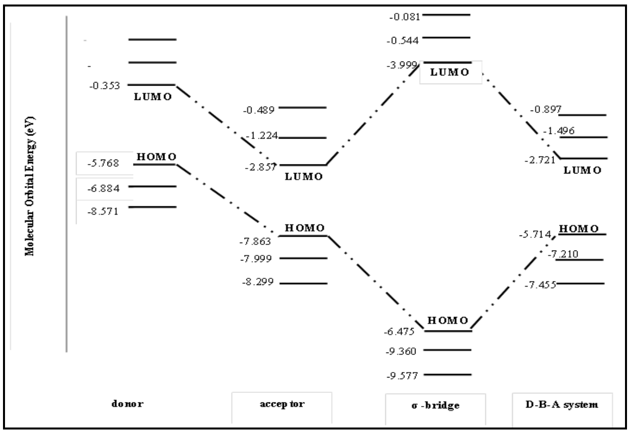
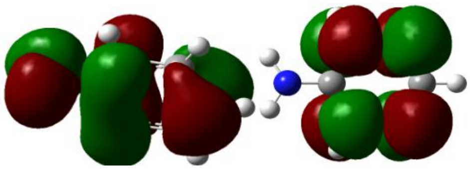


Figure 2: Energy level diagram for donor, bridge, acceptor and D-B-A.

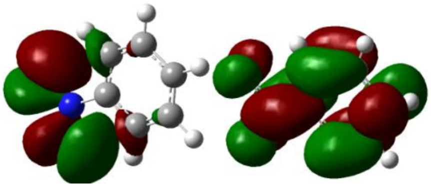
Figure 2 shows the energy level diagram for the three highest occupied and three lowest unoccupied molecular orbitals for the donor, bridge, acceptor and D-B-A system. From this diagram, one can see that the HOMO and LUMO for the acceptor are more stable in comparison with donor. The HOMO and LUMO for donor are situated (-5.768, -0.353) eV, higher than the HOMO and LUMO for acceptor, but (LUMO-HOMO) for both donor and acceptor is approximately the same (5.415 eV for donor and 5.006 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 energy level diagram shows that the HOMO of π -bridge (-6.475 eV) is more stable like the HOMO of the acceptor and the LUMO (-3.999 eV) is unstable like the LUMO of the donor, and π -bridge has very high energy gap in which this indicate that π -bridge can acts as a suitable barrier. The (LUMO-HOMO) for the D-B-A is small (3.045eV) in compared to donor, bridge and acceptor.



LUMO HOMO

Donor



LUMO HOMO

Acceptor

Figure 3: The shapes of HOMO and LUMO for studied structures

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) and studying the spectra analysis for the studied molecular electronics, but it requires a large time compared with other small basis sets.
- The presence of substituent 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 π-bridge.
- Phenyl ring with amino 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 as a molecular electronics.

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