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A Theoretical Study of Geometry Optimization and Energies for Donor-π bridge-Acceptor Molecular System: B3LYP/DFT Calculations

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Abstract : B3LYP/6-31G (d , p) density functional theory has been employed to calculate the geometry optimization and energies of donor- π bridge-acceptor molecular system. The electronic state 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 systems in which that satisfy important property for the D-B-A system as a molecular electronics.

Keywords: DFT, Koopmanns theorem, Energy gap, HOMO and LUMO, Molecular System: B3LYP/DFT.

Introduction

The first concrete idea for an electronic component consisting of a single molecule was the molecular rectifier described by Aviram , Ratner and others[1,2]. The molecular rectifier that they considered consisted of an electron donating moiety, tetrathiafulvalene, which was connected to an electron-accepting group, tetracyanoquinodimethane, by an ‘‘insulating’’ σ-bonded spacer. This molecule can be considered as an analog of p–n junctions common to the design of traditional solid-state rectifiers. Quantum mechanical calculations suggested that this molecule should indeed exhibit rectifying behavior. After this landmark proposal, it took another 25 years until such behavior was experimentally confirmed for the related donor–acceptor molecule by Metzger *et al*. and others[3-6].

A more recent approach to realize a single-molecule rectifier, reported by the group of Dekker and others[7,8], is more akin to its macroscopic equivalent. It consists of single-walled nanotubes that can be either metallic or semiconducting depending on their diameter and helicity. An intramolecular junction between a metallic and a semiconducting nanotube section can be realized by introducing a pentagon and a heptagon into the hexagonal carbon lattice. Electrical transport measurements on a single carbon nanotube intramolecular metal–semiconductor junction have been performed[7]. It was shown that the transport characteristics were strongly asymmetric with respect to the bias polarity, thus exhibiting the behavior of a rectifying diode. The disadvantage of using carbon nanotubes is that there is no synthetic control over the construction of the molecules and the realization relies on coincidence during the synthesis of carbon nanotubes. Present work deals with the calculating the relaxation of donor- π bridge-acceptor molecular system and calculating the electronic states and charge transfer for such system and it is components.

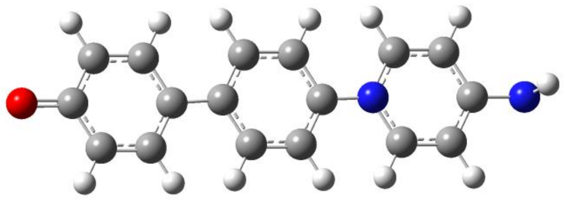
Computational Details

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[9,10] (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[11-13]. 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. 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[14]. 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[15-16].

Results and Discussion

Figure(1) shows the optimized structures for the phenolate as a donor and 3, NH- pyridine as an acceptor connected by the benzene as a π- bridge at B3LYP/6-31G (d, P) density functional theory.

Donor **Acceptor**



Donor-π bridge-Acceptor

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

Table (1&2) shows that the optimized bond lengths of the bridge backbone linking between donor and acceptor are having double bond less than 1.42 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 of the compound.

Table 1: B3LYP/6-31G (d ,p) optimized parameters of the (a) donor and (b) acceptor

(a)

Bond Length (A^0)		**Bond Angle (deg)**		**Dihedral angle (deg)**	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c-c)	1.396	A(c-c=c)	120.265	D(c=c-c=c)	-0.045
R(c-H)	1.091	A(c-c-H)	119.752	D(H-c-c=c)	179.925
R(c=c)	1.402	A(c=c-H)	120.001	D(H-c-c-H)	-0.246
R(O-C)	1.202	A(c=c-c)	119.484	D(c-c=c-c)	0.102
		A(c=c-O)	120.342	D(c-c=c-O)	178.87
		A(c-H-c)	119.602	D(H-c=c-O)	-2.542
		A(c-O-c)	117.56	D(O-c-c=c)	-179.095
(b)				D(O-c-c-H)	2.551
Bond Length (A^0)		**Bond Angle (deg)**		**Dihedral angle (deg)**	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c=c)	1.396	A(c=c-c)	119.855	D(c-c=c-c)	0.015
R(c-H)	1.089	A(c=c-H)	120.917	D(c-c=c-H)	180.003
R(c-N)	1.474	A(c-c-H)	119.78	D(H-c=c-c)	180.01
R(N-H)	1.352	A(c=c-c)	120.101	D(H-c=c-H)	0.014
		A(c-c=c)	121.365	D(c-c-c-c)	-0.0081
		A(c-c-N)	118.905	D(c=c-c=c)	-0.001
		A(c-N-c)	119.725	D(c=c-c-N)	-180.009
		A(N-c-c)	121.55	D(H-c-c-c)	179.989

Table (2): B3LYP/6-31G (d, p) optimized parameters of (D-πB-A) system

Bond Length (A^0)		**Dihedral angle (deg)**		**Dihedral angle (deg)**	
Bond	**Value**	**Bond**	**Value**	**Bond**	**Value**
R(c=c)	1.413	D(c=c-c-H)	-179.92	D(c-c-c=c)	0.158
R(c-H)	1.092	D(H-c-c-H)	0.402	D(c-c=c-H)	0.018
R(c-N)	1.395	D(c-c=c-c)	-0.052	D(c-c=c-c)	0.035
R(N-H)	1.012	D(c-c=c-N)	-178.126	D(N-c=c-H)	-0.057
R(c-c)	1.405	D(H-c=c-N)	2.633	D(c-c-c-O)	-0.055
R(c-O)	1.345	D(H-c=c-c)	-0.045	D(c=c-c-c)	0.052
Bond Angle (deg)		D(c=c-c=c)	-178.54		
A(c-c-H)	119.936	D(c=c-c-N)	179.458		
A(c-c=c)	122.027	D(H-c-c-N)	-2.567		
A(c=c-c)	116.925	D(c=c-N-H)	-21.5		
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		

Table (3) shows the results of geometry optimization included the total energy $E_{T,}$ virial ratio (-V/T), symmetry and number of imaginary frequency for donor (D), bridge, acceptor and D-B-A system.

Table (4) clears that the total energy for D-B-A system is less than the total energy of mentioned 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 (D-B-A system) ≈ E_T (donor) + E_T (bridge) +E_T (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, donor is a planar and has a low symmetry contain only the plane of reflection, 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. This change in molecular symmetry comes from the presence of the substituent in the ring. 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 donor with the 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 3.022 eV.

Table(3): Results of geometry optimization for studied molecules

Species	ET(a,u)	-V/T	Symmetry	NO. Of imaginary frequency
Donor (D)	-228.144	2.006	C_S	0
Bridge (B)	-232.158	2.005	D_{6h}	0
Acceptor (A)	-325.925	2.008	C_{2v}	0
Molecular System (D-B-A)	-786.227	2.0065	C_1	0

Table (4): E_{HOMO} , E_{LUMO} and energy gap E_g for studied molecules

Species	$E_{HMO(}$ev)	E_{LUMO}(ev)	Eg(ev)
Donor (D)	-7.858	-2.843	5.015
Acceptor (A)	-5.563	-1.509	4.054
Molecular System (D-B-A)	-5.001	-1.979	3.022

The interaction between the donor and the acceptor 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.

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.

The HOMO and LUMO for the acceptor are more stable in comparison with donor. The HOMO and LUMO for donor are situated (-7.858, -2.843) eV, the ionization energy for donor is higher than that for acceptor, this an indicates for that the donor can be easily donating it is electron. The HOMO and LUMO for acceptor are situated (-5.563, -1.509)eV, but (LUMO-HOMO) difference between donor and acceptor is approximately one eV. 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 levels 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. Adding the subgroups to the terminal ends of benzene rings leads to reducing the separation LUMO-HOMO[16] and π -bridge has very high energy gap in which this indicates that π -bridge can acts as a suitable barrier. The (LUMO-HOMO) for the D-B-A molecular system is small (3.022eV) in compared to it is components (donor, bridge and acceptor).

The results of absorption analysis calculated from the CIS calculations showed that the D-B-A molecular system absorbs at maximum wave length λmax = 515 nm corresponds to absorption energy ΔEge =2.27 eV. The oscillation strength f_{ge} = 0.88 for this absorption is strong strength. The difference of dipole moment from ground to excited states $\Delta\mu_{ge}$ =24.25 refers to that a very large amount of charge transfer ΔN_{max} during excitation process. This excitation of the high occupied molecular orbital and lower unoccupied molecular orbital is corresponding with the amount of charge transfer from the donor to acceptor. The large value of hyperpolarizability for D-B-A molecular system ||b|| = 542.56 is a reflection result to the other parameters calculated for the system and agree with the model of the two systems.

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 keeps under the connection donor part and acceptor part through the π-bridge.
- Phenyl ring with adding group was truly predicted to be a better semiconducting material because of its suitable 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 systems in which that satisfy important property for the D-B-A system as a molecular electronics.
- Good value of absorption energy and oscillation strength for D-B-A, and agree with it is hyperpolarizability and the amount of charge transfer.

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