Study of Geometrical Optimization and Some Electronic Properties of D-B-A Molecular System

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Abstract

This work deals with designing donor - bridge - acceptor molecular system depending on Aviram – Ratner model and calculating the geometrical parameters and energies for the D- B-A and it is components. Benzene ring is the basic part for all the components of such molecular system. The LUMO-HOMO energy gap for the studied structures showed that the D-B-A molecular system has a suitable small energy gap. The results showed that this new molecular system is more reactive in charge transfer process and has good semiconductor properties.

Keywords:B3LYP , DFT, , energy gap, HOMO ,LUMO and polarizability.

Introduction

This study deals with designing 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 GAUSSIAN 09 suite of programs.

Results and Discussion

The molecular structures in figure 1 are optimized at the ground state by employing the density functional theory at hybrid B3 LYP level with 6-31G (d, p) basis sets. In present donor- bridge- acceptor molecular system, we use benzene ring as a bridge between the donor and the acceptor.

The molecular structures in chart 1 are optimized at the ground state by employing the density functional theory at hybrid B3 LYP level with 6-31G (d, p) basis sets. The molecular structures in chart 1 are optimized at the ground state by employing the density functional theory at hybrid B3 LYP level with 6-31G (d, p) basis sets. The molecular structures in chart 1 are optimized at the ground state by employing the density functional theory at hybrid B3 LYP level with 6-31G (d, p) basis sets.

The geometrical optimized parameters (bond lengths in Angstroms, bond angles and dihedral angles in degrees) of donor, bridge, acceptor and D-B-A molecular system are illustrated in tables (1- 4), respectively. In donor, the presence of NH_2 subgroup in benzene ring has small effect on the values of bonds between atoms, C-C and C-H bonds in benzene are (1.482 A$^{\circ}$) and (1.084 A$^{\circ}$), respectively, they become (1.487 A$^{\circ}$) and (1.081-1.087) A$^{\circ}$ in donor, respectively. The convergence between the atomic numbers for carbon and nitrogen atoms gave good convergence between C-C and C-N bonds in the donor. The results in table 1 are in good agreement with those in ref.[Robert Thornton Morrison and Robert Neilson Boyd] . As we see in table 2, the calculated values of bonds in benzene using the theoretical method are in good agreement with experimental data. Table 2 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.

The values of the bonds in table 3 for the acceptor showed that the C-C and C-H bonds equal to(1.395 A$^{\circ}$) and(1.083 A$^{\circ}$), respectively, and C-C-C and C-C-H bonds are (120.14^0) and (119.65^0), respectively. Adding the hydoxide and cyano substituents in phenyl ring effect on the geometrical parameters of the ring. In general, the results of B3LYP/DFT calculations are in good agreement with the results in ref.[Robert Thornton Morrison and Robert Neilson Boyd]. In table 4, the bonds C-N and C-C from the link between the donor and acceptor still in the same range of bonds in aromatic species.

The results of the ground state total energy E_T in (a.u), virial ratio (-V/T) and molecular symmetry for donor, acceptor and D-B-A molecular system are shown in table 5. The level of theory B3LYP density functional theory used for the optimization of these structures gave high accuracy for all optimum structures without any imaginary frequency, and these optimized structures have (-V/T) ratio in the range of the molecular structures. This an indicates to good relaxation these structures have.

Table 5 declares 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:

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

The molecular symmetry in table 5 showed that the donor has high symmetry 2-fold axis of rotation and two vertical mirror planes, it has C_{2V} symmetry. Adding the substituents in the terminal ends of benzene ring make the acceptor has low symmetry C_s in which it contains only the identity and a plane of reflection. B3LYP hybrid functional employed for geometrical optimization for the π – bridge (benzene ring) gave the same molecular point group for benzene (D_6h)[Peter Atkins]. The D – B – A molecular system is a (C_1) Point group, it has only 1- fold proper axis of rotation symmetry operation.

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[A. Aviram, M. A. Ratner]. Figure 2 shows the total energy of D-B-A molecular system and it is components.

Table 6 shows the values of E_{HoMo} , E_{LuMo} and energy gap Eg in eV for donor, acceptor and D – B – A molecular system. As we see, the energy gap for D – B – A is smaller than for donor and acceptor. The $\pi -$ bride linking between the donor and the acceptor is a suitable to construct D – B – A molecular system has new electronic properties. B3LYP/ DFT calculations gave (Eg= 6.57eV) for $\pi -$bridge, this value is agree with experimental data. The results of energy gap of donor, acceptor and D-B-A molecular system are shown in figure 3.

As we know, the charge distribution in π – aromatic bridge (benzene ring) is symmetric in the plane of the molecule, means, the total dipole moment of benzene equals zero, adding the substituents to this ring leads to a new structure may have non – polarity and a symmetry in charge distribution (change in the polarity of the molecule). In table 7, the total dipole moment of the donor and the acceptor structures are (4.124 and 3.505) Debye, these values are independent on the number of atoms or subgroups ((substituents)) added to the original molecule but depend on the positions of these substituents in the molecule. The complex compound (D – B – A) have large value of dipole moment (15.235 Debye) corresponds to its C_1 molecular point group. This large value indicates to that this localized system is much better on electrophilic system, while the donor presents nucleophilic delocalized system in which it has small value of electric dipole moment in comparison with the D–B–A molecular system. This conclusion corresponds to the values of maximum charge transfer obtained for each system. As we see the relationship of D.M with ΔN_{max} in figure 6

Table 7 showed good result of exact polarizability, the polarizability components are distributed in the order that α_{zz} is greater than α_{yy} and α_{xx} in each structure (D, A and D – B – A), α_{xx} is the smaller one. The results of average polarizability for donor, acceptor and D – B –A molecular system refer to that the π – bridge used to intract both donor and acceptor gave reactive D – B – A molecular system has high value of average polarizability, it is approximately three times that for donor and acceptor. The results of $< \alpha >$ for D – B – A molecular system and its conponents are agree with their results of electric dipole moment.

Conclusions

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), but it requires a large time compared with other small basis sets. 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 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. NH_2-benzene 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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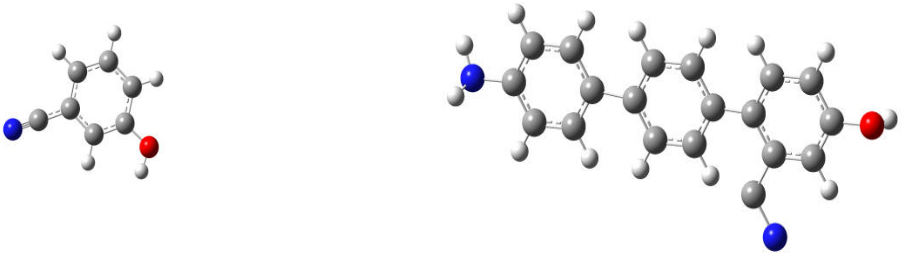
Donor (D) Bridge (B)



Acceptor (A) Donor-Bridge-Acceptor (D-B-A)

Figure 1: The structures under study

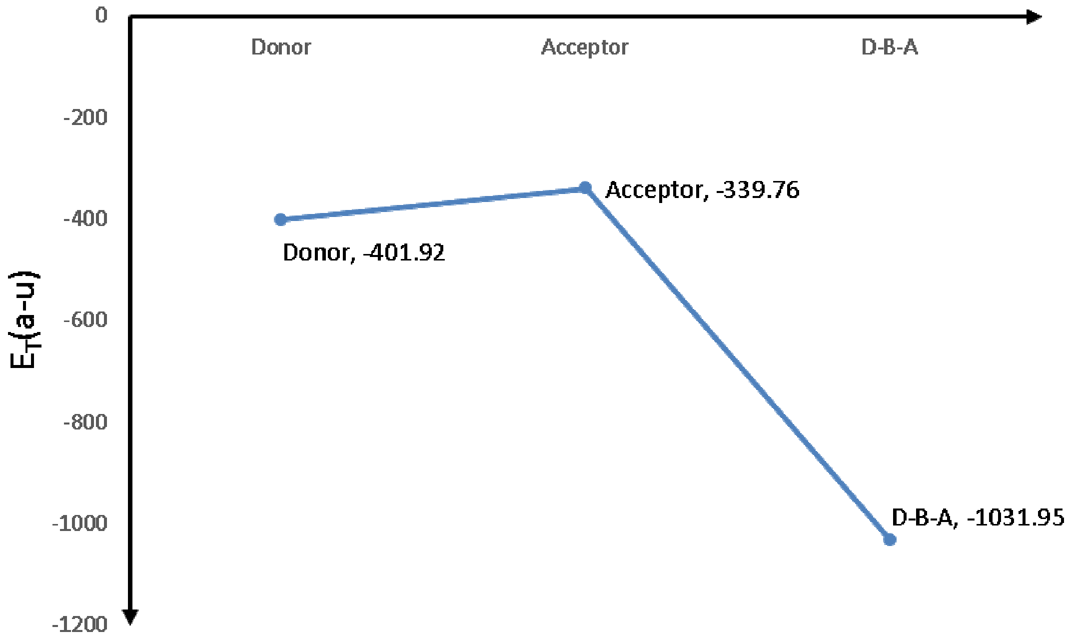


Figure 2: The total energy for donor, acceptor and D-B-A molecular system.

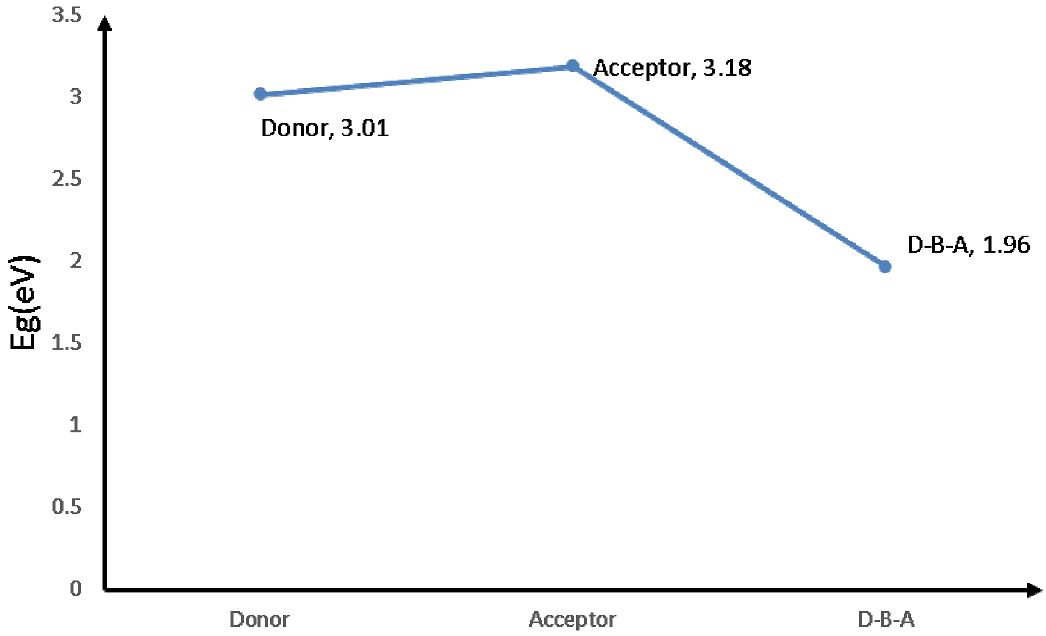


Figure 3: The E_g of the D-B-A molecular system and it is components

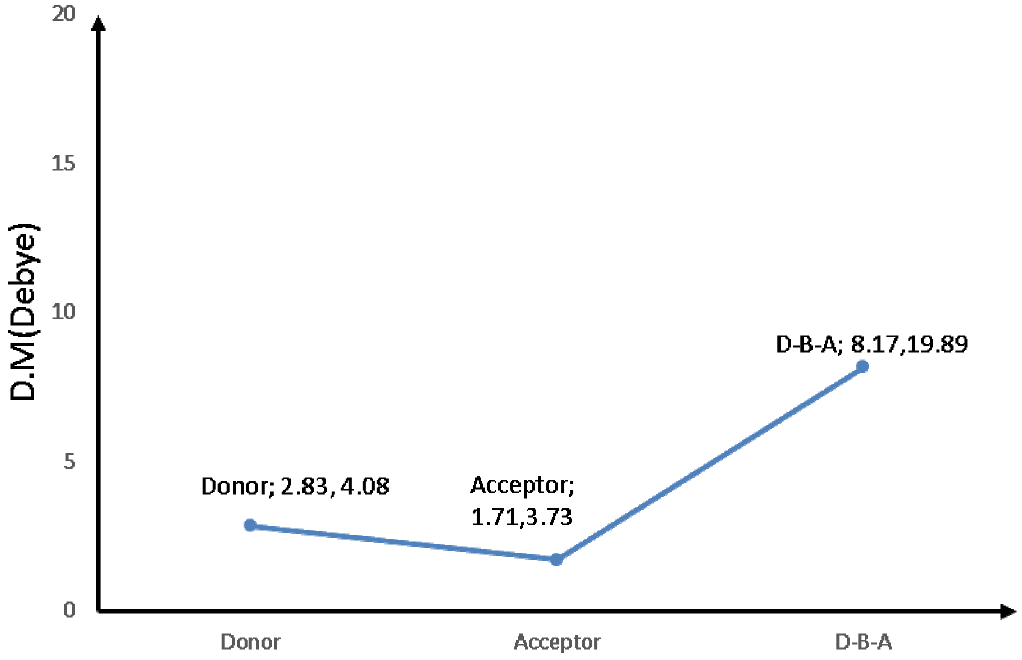


Figure 4: The relationship of D.M with ΔN_{max} for studied structures

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

Bond length(A°)		Bond angle (deg)		Dihedral angle (deg)	
Bond	value	Bond	Value	Bond	value
C-C	1.484-1.486	C-C=C	126.45-128.12	C=C-C=C	0.0009
C=C	1.38	C=C-C	107.5	C-C=C-C	-0.0011
C∸C	1.402-1.404	C∸C-C	126.45	H-C-C-H	0.0000
C - H	1.081-1.087	H-C-C	116.05	H-C-C=C	0.00738
C-N	1.350	H-C=C	128.827	C-C∸N∸H	0.00652
N-H	1.435	C∸N∸H	105.5	N∸C-C=C	179.889

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

(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

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

Bond length(A°)		Bond angle (deg)		Dihedral angle (deg)	
Bond	value	Bond	Value	Bond	value
C-C	1.395	C-C=C	120.14	C-C=C-C	0.0006
C=C	1.401	C-C-H	119.65	C=C-C=C	-0.0017
C-H	1.083	C=C-H	120.125	H-C=C-H	0.0005
C≡N	1.159	C=C-C	120.08	H-C-C=C	-179.99
C- O	1.365	C-C≡N	179.97	C-C=C-H	179.99
O-H	0.963	C-C-O	117.24	C-C-C≡N	0.145
		C-O-H	110.04	N≡C-C=C	-179.85
				H-C=C-O	-0.00027
				O-C=C-C	-179.99

Table 4: B3LYP/6-31G (d, p) optimized parameters of (D-B-A) system

Bond length(A°)		Bond angle (deg)		Dihedral angle (deg)	
Bond	value	Bond	Value	Bond	value
C-C	1.388	C-C=C	128.49	H-C=C-H	-0.106
C=C	1.40-1.40	C=C-C	119.33	C-C=C-H	179.86
C-H	1.081-1.081	H-C-C	115.97-116.27	C-C=C-C	-0.458
C-N	1.36	C=C-H	120.60	H-C=C-C	-179.22
N≡C	1.15	C-N-C	124.62	C-C=C-N	179.15
C-O	1.35	C-C≡N	179.10	C-N-C-C	-139.28
O-H	0.963	C-C-O	116.76	C=C-C≡N	-2.113
		C-O-H	110.82	H-C=C-O	-0.459
				H-O-C=C	179.70
				C-C-O-H	-0.105

Table 5: Results of geometry optimization for studied molecules

Structures	Total Energy (a.u)	-V/T	Symmetry
Donor	-401.922	2.0078	C_{2V}
Acceptor	-399.762	2.0080	C_s
D-B-A	-1031.956	2.0077	C_1

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

Structure	HOMO (eV)	LUMO (eV)	E_g (eV)
Donor	-5.781	-2.765	3.015
Acceptor	-7.033	-4.846	3.186
D – B – A	-8.997	-7.035	1.962

Table 7: Total dipole moment, maximum amount of charge transfer and Polarizability for donor, acceptor and D – B – A molecular system.

Structure	Total dipole moment (Debye)	ΔN_{max}	Polarizability (a.u)			
			$\alpha\ xx$	$\alpha\ yy$	αzz	$< \alpha >$
Donor	4.124	2.833	63.559	128.787	181.604	124.65
Acceptor	3.502	1.711	52.820	98.997	128.651	93.48
D –B – A	15.235	8.171	191.782	232.729	619.479	347.99