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B3LYP/DFT Calculations of Donor-πbridge-Acceptor Molecular System

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Abstract: - Present study deals with designing donor -π bridge - acceptor molecular system depending on Aviram–Ratner model and calculating the geometrical parameters and energies for the D-π B-A and it is components. The LUMO-HOMO energy gap for the studied structures showed that the substituents adding to the phenyl ring lead to a new electronic materials and the D-πB-A molecular system has a suitable small energy gap. The results of polarizability showed that this new molecular system is more reactive in charge transfer process.

Keywords: *- B3LYP, DFT,, energy gap, HOM , LUMO and polarizability.*

I. 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.

II. COMPUTATIONAL DETAILS

All calculations were performed with the GAUSSIAN09 suite of programs.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.

III. RESULTS AND DISCUSSION

In present donor- bridge- acceptor molecular system, we use benzene ring (C_6H_6) as π-bridge between nitro-azolene (C_9H_8N) as a donor and 1-cyano,3-hydroxy phenyl (C_6H_3OHCN) as an acceptor. The molecular structures in chart 1 are optimized at the ground state by employing the density functional theory at hybrid B3LYP level with 6-31G (d, p) basis sets.

Donor (D) Bridge (B)

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

Chart 1:The optimized structures under study at B3LYP/6-31G (d, p) / DFT

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 nitrogen atom in azolene ring has small effect on the values of bonds between atoms, C-C and C-H bonds in azolene are (1.482 A°) and (1.084 A°), respectively, they become (1.487 A°) and (1.081-1.087)A° 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°) and(1.083 A°), 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 parameter of the ring. In general, the results of B_3 LYP/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.

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	1.487	C-C=C	128.08-130.66	C=C-C=C	0.0009
C=C	1.38-1.39	C=C-C	104.199	C-C=C-C	-0.0011
C$\overset{\cdot}{-}$C	1.406	C$\overset{\cdot}{-}$C-C	128.201	H-C-C-H	0.0000
C - H	1.081-1.087	H-C-C	115.962-116.04	H-C-C=C	0.00738
C-N	1.350	H-C=C	126.827	C-C$\overset{\cdot}{-}$N$\overset{\cdot}{-}$C	-0.0341
		C$\overset{\cdot}{-}$N$\overset{\cdot}{-}$C	107.469	N$\overset{\cdot}{-}$C-C=C	179.981
		H-C$\overset{\cdot}{-}$N	121.107	C-C=C$\overset{\cdot}{-}$N	0.0195

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

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: 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 5 declares 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 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 symmetryC_S in which it contains only the identity and aplane 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.

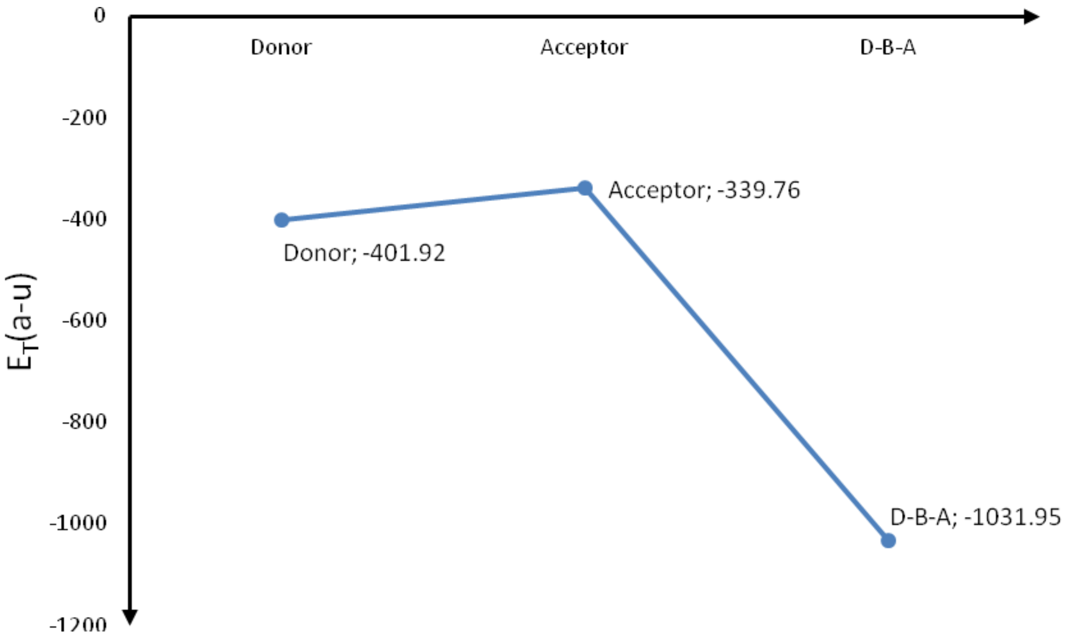


Figure 2:The total energy for donor, acceptor and D-B-A molecular system.

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 asuitable to construct D – B – A molecular system has new electronic properties. B_3LYP/ 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.

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

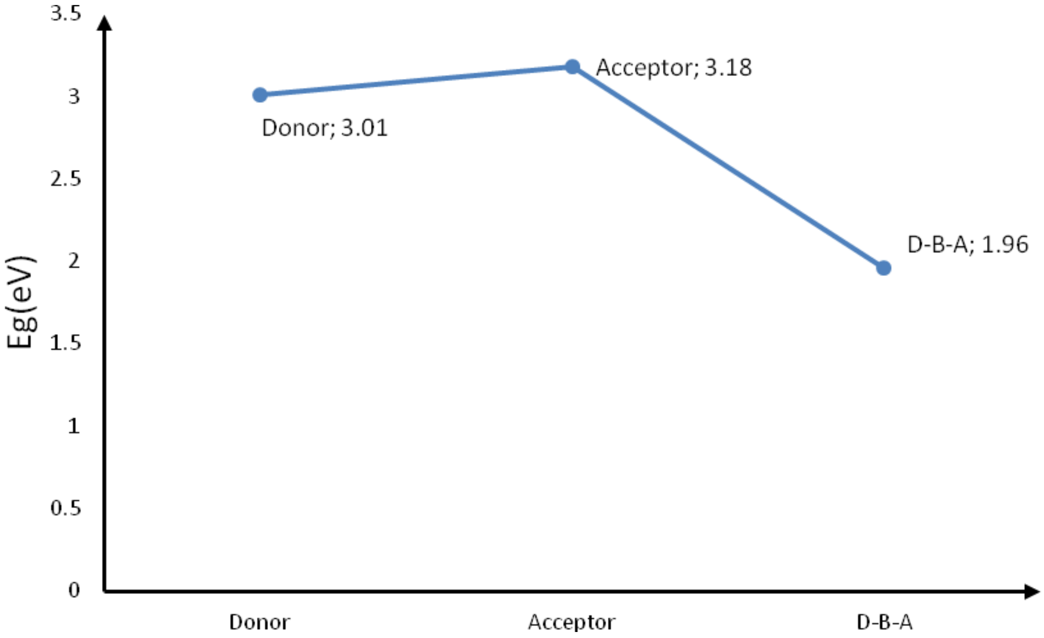
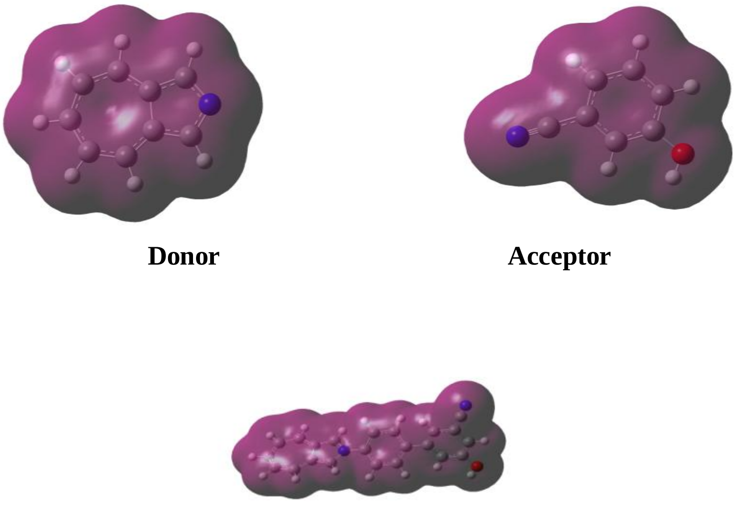


Figure 3: The E_g of the D-B-A molecular system and it is components

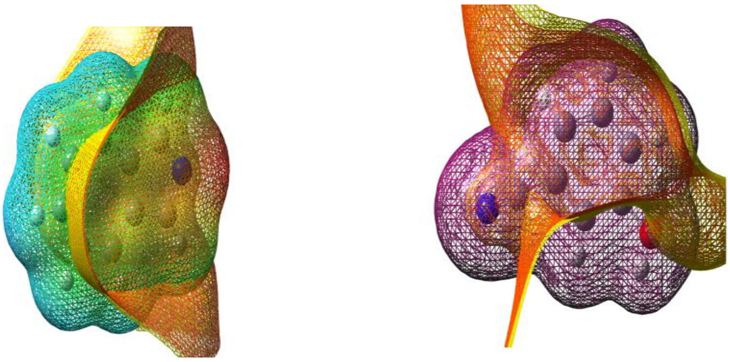
The electron density and the molecular electrostatic potential ESP calculations of donor, acceptor, and D-B-A molecular system were carried out at the same B3LYP level of theory from the self-consistent field density. The 3-D electron density and ESP for D-B-A molecular system and its components are shown in figures 4 and 5, respectively. As we Know, the electron density provides formations on the location of the electrons in a molecule.The square of the wave function at a point is interpreted as the probability of finding an electron at that point, if a summation is taken over all occupied molecular orbitals for all space surrounding the nuclei in a molecule, the electron density of that molecule can be found. Electron density indicates the most probable location of electrons in a molecule and is useful for understanding bonding and reactivity, so it can provide an indication of molecular size. The aromatic ring (benzene molecule) was drawn with localized double bonds and the π–electron are actually delocalized through the ring, the substituents added to the ring changes the electron density surface. The area on nitrogen atoms represents an area of high electron density with partially negative charge, and the area on carbon and hydrogen atoms represents an area of low electron density with partially positive charge.



Donor **Acceptor**

D-B-A

Figure4:The electron density distribution for donor, acceptor and D-B-A molecular system.



Donor **Acceptor**

D-B-A

Figure5:The ESP for donor, acceptor and D-B-A molecular system.

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 anew 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 (4.087 and 3.732) 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 (19.896 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: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	4.087	2.833	63.559	128.787	181.604	124.65
Acceptor	3.732	1.711	52.820	98.997	128.651	93.48
D –B – A	19.896	8.171	191.782	232.729	619.479	347.99

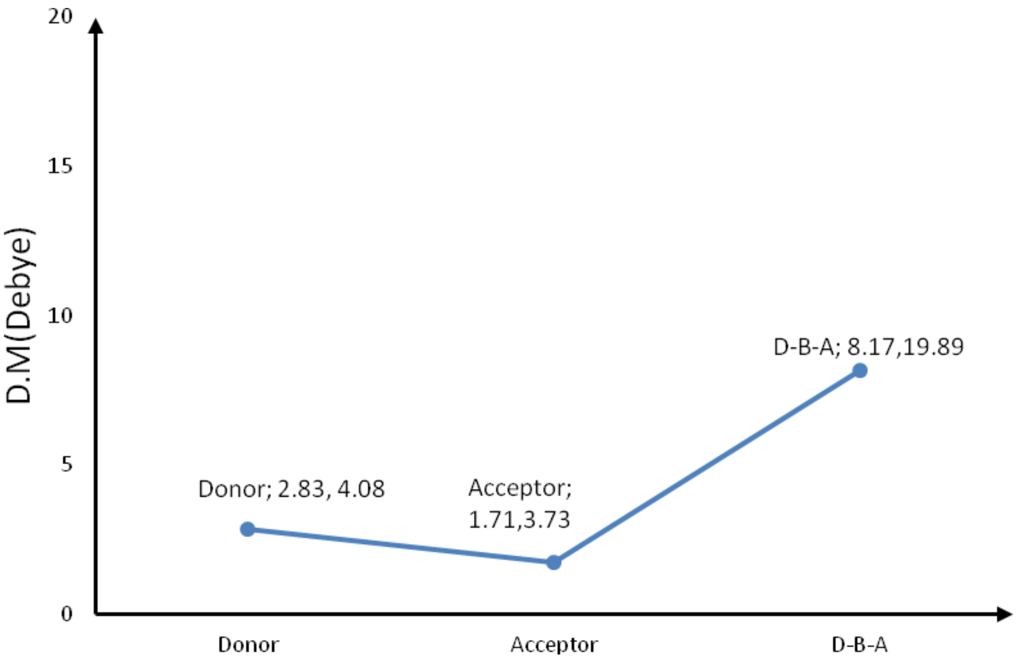


Figure 6: The relationship of D.M with ΔN_{max} for studied structures

Table 7 showed good result of exact polarizability, the polarizability components are distributed in the order that $\alpha_{zz}$is greater than α_{yy} and α_{xx} in each structure (D, A and D – B – A),$\alpha_{xx}$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.

IV. 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) and studying the spectra analysis for the studied molecular electronics, 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.Nitro-azolene 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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