

# Designing The Molecular System(Donor-Nanobridge-Acceptor) Employing the Aviram-Ratner Model

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## ABSTRACT

Present study depends on Aviram – Ratner model to designing molecular electronic system as a donor -nanobridge - acceptor and calculating the geometrical parameters and energies for the D- NB-A molecular system and its components by B3LYP/DFT Calculations. 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-NB-A molecular system has a suitable small energy gap. The results showed that the new D-NB-A molecular system is more reactive in charge transfer processes compared with its components.

**Keywords :** Donor-NanoBridge-Acceptor Molecular System, energy gap, HOMO, LUMO, B3LYP/DFT Calculations and polarizability

## I. INTRODUCTION

This work stands on the design of donor- Nanobridge-acceptor to determine the quantity of charge transfer CT. The main process in many fields of chemistry, physics, and biology [1–7] monographs [8–10] is the charge transfer. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [3, 4]. 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 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 [23].

## II. METHODS AND MATERIAL

The calculations of the electronic properties of the donor – bridge – acceptor molecular system and its components are carried out using the density functional theory DFT methods at the hybrid functional B3LYP with 6-31G level of theory [ ]. In this investigation, the more relevant electronic ionization energy IE, electron affinity EA, electronegativity  $\chi$ , electrochemical hardness H, electronic softness S and electrophilic index W and the electric polarizability  $\alpha$  were calculated.

The electronic states HOMO and LUMO energies were used to evaluate the IE and EA in the basis of the orbital energy method as called Koopman's theorem :

$$IE = -E_{\text{HOMO}} \text{ and } EA = -E_{\text{LUMO}}$$

The chemical potential of the molecule  $\mu$  is the measure of the escaping tendency of an electronic cloud and the difference approximation to chemical potential gives.

$$\mu = -\chi = -(IE + EA)/2$$

Where  $\chi$  is the electronegativity of the molecule. The theoretical definition of the electrochemical hardness has

been provided by the density functional theory and it is calculated as.

$$H=(IE-EA/2)$$

The electronic softness of the molecule is given by :

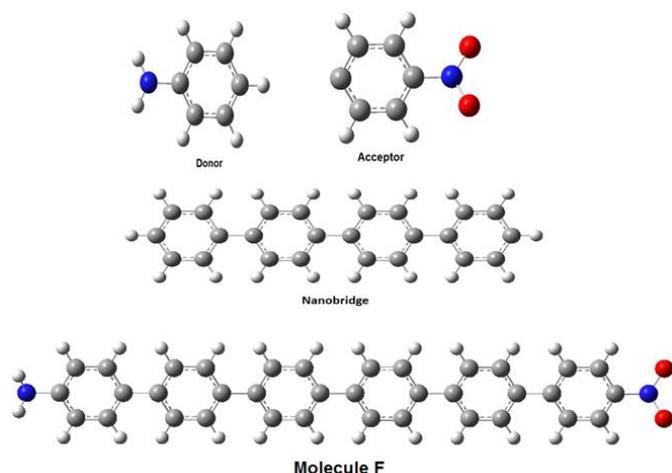
$$S=1/2H$$

The electrophilic index is a measure of energy lowering due to maximal electron flow between the donor and acceptor . the electrophilic index  $W$  is defined as :

$$W=\mu^2/2H$$

### III. RESULTS AND DISCUSSION

Chart 1 shows the optimized structures studied in present work . here, we use  $\pi$ - conjugated nanobridge as spacer connecting between aminobenzene as a donor and nitrobenzene as an acceptor. These molecular structures are optimized at ground state by employing the hybrid functional B3LYP density functional theory with 6-31G basis set .



**Chart 1 :** The optimized structures from B3LYP/6-31G density functional theory

Table 1 illustrate the geometrical optimized parameters (bond length in nm, bond angles and dihedral angles in degree) of donor, nonabridge, acceptor and donor – nanobridge – acceptor molecular system, respectively . In table 1 (donor), the subgroup (amino) adding to phenyl ring has a small effect on the values of bonds

between atoms, C-C, C=C and C-H bond in benzene are (0.1421 nm) , (0.1398 nm) and (0.198 nm), respectively. Convergence between the atomic numbers of carbon and nitrogen atoms gave a good convergence between C-C and C-N bonds in the donors .

One can see that , a minor deviation in the bridge bond angle and dihedral angle between the two plnes containing the end substitutes , in which , this deviation can be expected due to stringent contact coming from the presence of phenyl groups at the terminal position of the molecular structure.

**Table 1 :** The optimized parameters of molecule under study

Bond type	Bond length (nm)	Bond angle (deg)	Dihedral angle (deg)
R(C-C)	0.14092- 0.14839	117.075- 121.461	-179.986 – 179.838
R(C=C)	0.13921- 0.13977	119.900- 121.765	-179.971 – 179.972
R(C-H)	0.10049- 0.10866	118.780- 121.625	-179.455 – 179.249
R(C-N)	0.13836 – 0.14601	119.224 – 120.966	-179.981
R(N-O)	0.126628	118.163	-0.1537 – 179.845
R(N-H)	0.100492	121.032	-179.642 - 0.4088

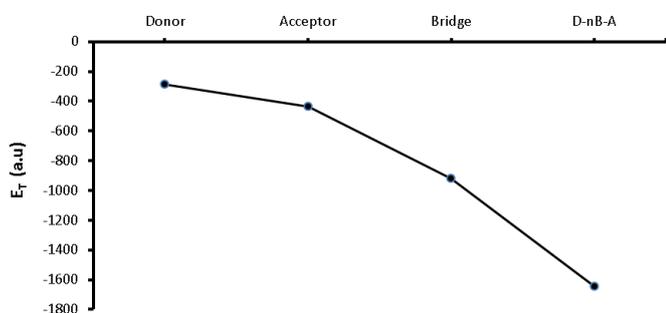
**Table 2 :**  $E_T$  in a.u,  $-V/T$ , symmetry and the number of imaginary frequency of the donor, acceptor and D-nB-A molecular system.

Species	$E_T$ (a.u)	$-V/T$	Symmetry	No. of imaginary frequency
Donor	-287.5376	2.0057	$C_{2v}/C_1$	0
Acceptor	-436.6185	2.0053	$C_{2v}/C_1$	0
Bridge	-920.3335	2.0088	$C_2/C_1$	0
D-nB-A (Mol)	-1646.9893	2.0055	$C_2/C_1$	0

Table 2 the results we produced in this study showed that the optimized structures have good relaxation and the functional used for this optimized is a suitable with 6-31G basis set , it is found that the optimization of the structures together with the linear combination keep on the aromaticity of phenyl ene rings , also the ratio of the potential to kinetic energy of all structures under study ( $-V/T$ ) is remain in the same rande of these structures

(2.0053- 2.0088). One of the important resultant of the relaxation is that no imaginary frequency appears for the IR-spectra of donor, acceptor and donor – nanobridge – acceptor molecular system.

Figure 2 shows the total energy of the studied molecular system and it is three components as result of relaxation of the structures at the ground state by employing the three parameters B3LYP density functional theory. figure 2 declare that the total energy of the donor – nanobridge – acceptor molecular system is less than that for donor and acceptor , the nanobridgr used for connecting the donor and acceptor leads to construct a new molecular structure has more stability in comparison with the donor and acceptor .



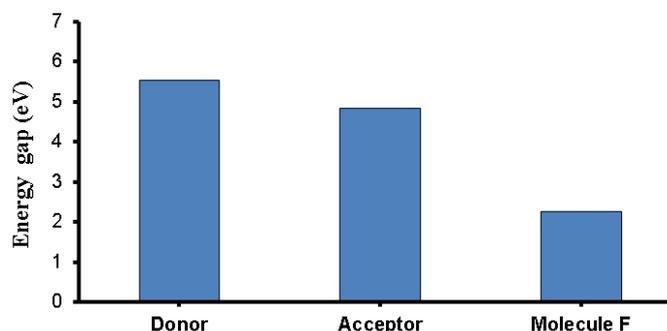
**Figure 2 :** The total energy  $E_T$  in a.u of the studied structures .

Table 3 : Electronic states and energy gap in eV of the studied structures.

Species	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_{gap}$ (eV)
Donor	-5.1545	0.37442	5.529
Acceptor	-7.7483	-2.9086	4.839
Molecule	-5.0819	-2.8248	2.257

Table 3 illustrates the electronic states (HOMO and LUMO ) end energy gap  $E_g$  of the donor ,acceptor and donor – nanobridge – acceptor molecular system. As we know , benzene molecule is an insulator material , it has energy gap (6.7eV) , adding the substituents (amino and nitro )in the terminal ends of benzene gave the phenyl a semiconducting behavior with suitable energy gaps ( 5.529 eV for donor and 4.839 eV for acceptor ). The interacting between the donor and acceptor by ( four rings) as nanobridge leads to construct the molecular system ( donor – nanobridge – acceptor ) as Aviram Ratner model has small energy (2.257 eV) in comparison with the donor and acceptor , as we see in figure 3 . Aviram-Ratner model considered that the construction principle of an organic rectifier is based an

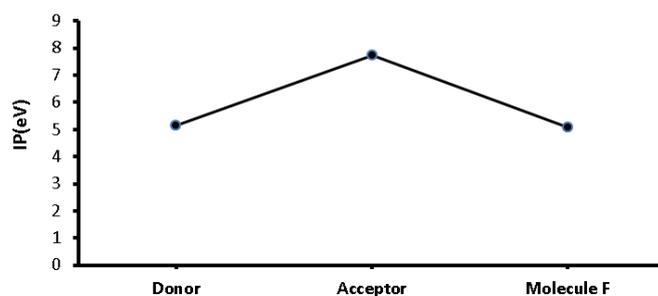
the insulating bridge that connect the donor and the acceptor .



**Figure 3 :** the energy gap of the molecular system and it is components .

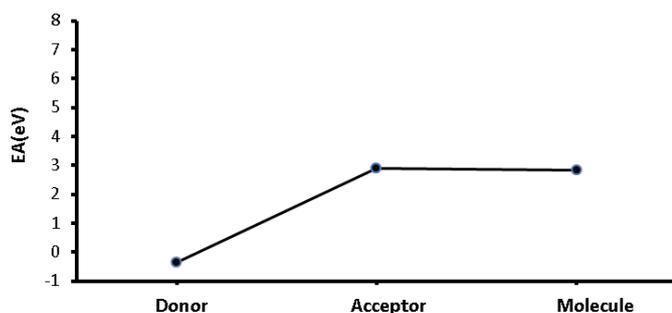
Figure 4 shows the results of ionization energy IE in eV of the donor, acceptor and donor – nanobridge – acceptor molecular system. These results declare that the donor have low ionization energy in comparison to the acceptor. As a requirement to donating it is electron easily. The donor – nanobridge – acceptor molecular system have abest value ionization energy (5.08 eV) gave this molecular system the ability of rectification when it is aligned between two metallic electrodes.

We know that the strength of an acceptor molecule is measured by it is electron affinity in which the energy released when adding one electron to the LUMO. An acceptor must have a high electron affinity.



**Figure 4 :** The ionization energy of the molecular system and it is components .

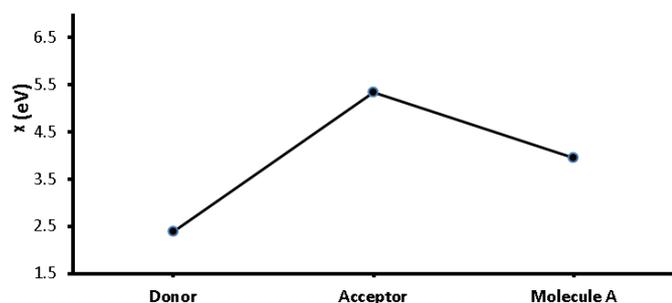
Figure 5 declare that the acceptor has to exhibit a high electron affinity EA . the results of electron affinity are (2.9 eV for acceptor and 0.37 eV for donor) .



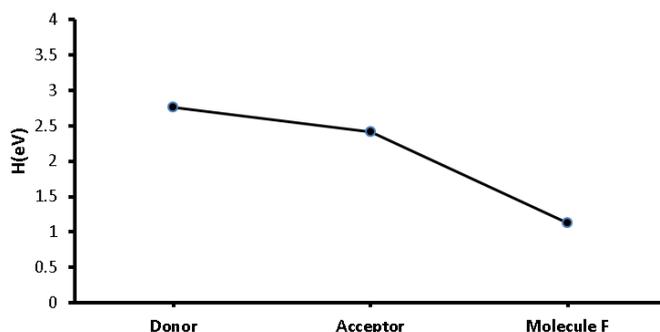
**Figure 5 :** The electron affinity of the molecular system and its components .

Interesting observations have been made from the results that are shown in figures 6 ,7 ,8 and 9 obtained through the orbital-vertical method , it has been found that for almost the commonly used exchange–correlation functional such as B3LYP , the koopman’s theorem is satisfied accurately. The results obtained by the calculation of the electronegativity in figure 6 was agreed very well with the employing for these donor – nanobridge–acceptor molecular system. This could be the reason for the low electrochemical hardness values obtained from this method, as we see in figure7. therefore the koopman’s theorem is a best useful and fast approach.

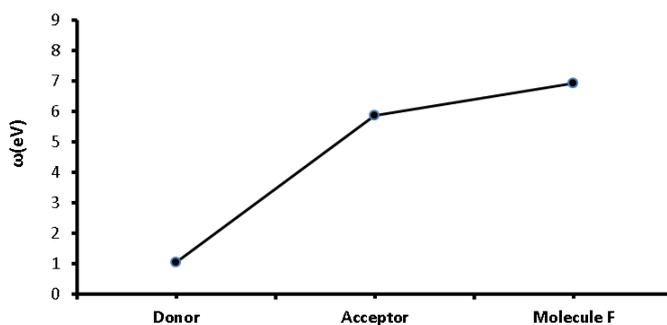
The behavior of electronegativity, softness and electrophilic index for the studied donor–nanobridge–acceptor molecular system and its components shows the magnitude large than these for the original phenyl ring, adding the substituents to the terminal end of benzene molecule gave the molecule more softness. In general , the results of softness in figure 8 are of the order of ( Molecule >Acceptor >Donor) and the results of electrophilic index of the studied structures are the order of(Molecule >Acceptor >Donor) , as in figure 9 . These results refer to that this molecular system is more soft and more reactive to interacting with other species or the surrounding molecules.



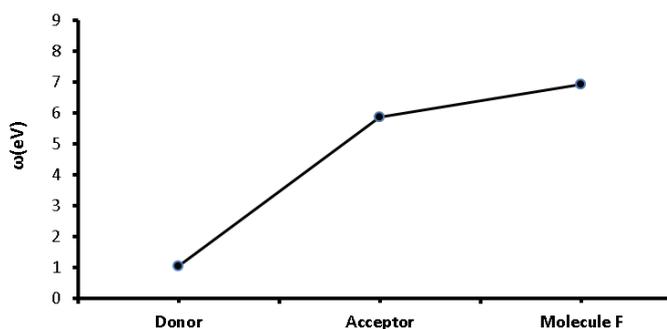
**Figure 6 :** The electronegativity of the donor – nanobridge – acceptor and its components .



**Figure 7:** The electrochemical hardness of the donor – nanobridge – acceptor and its components.



**Figure 8 :** The softness of the donor – nanobridge – acceptor and its components.



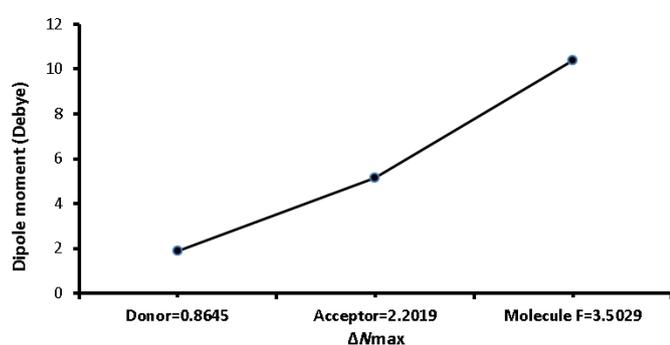
**Figure 9 :** The electrophilic index of the donor – nanobridge – acceptor and its components.

Table 4: The total dipole moment and polarizability of the donor – nanobridge – acceptor and its components

Species	Total dipole moment(Debye)	$\Delta N_{\max}$	Polarizability (a.u)			
			$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{ave}$
Donor	1.9077	0.8645	20.760	75.294	91.059	62.371
Acceptor	5.1512	2.2019	22.789	86.085	102.359	70.411
Molecule	10.3814	3.5029	228.154	261.944	1054.818	514.972

Table 4 shows the results of the dipole moment in Debye and the polarizability in atomic units of donor , acceptor and donor – nanobridge – acceptor molecular system. As we know the benzene molecule is aplanar has  $D_{6h}$  high symmetry and total dipole moment equals zero. Adding the substituents (amino and nitro ) leads to change the distribution of charge , therefore effects on the symmetry of the molecule and its polarity. In other words the donor and the acceptor have total dipole moments (1.907 and 5.15) Debye , respectively .

these values are depend on the position of the substituents in the benzene ring and independent on the number of atoms or subgroups adding to the ring . the donor – nanobridge – acceptor molecular system have the largest value of dipole moment and this may be a sign to that this molecular system have electrophilic behavior . the results of dipole moments of the studied structures are correspond to the a moment of charge transfer  $\Delta N_{\max}$  obtained for each structure , as we see the relationship between the total dipole moment and  $\Delta N_{\max}$  in figure 10. The results of exact polarizability of all studied structures is agree with the molecular polarizability theories in which it is components are of order of  $\alpha_{xx} < \alpha_{yy} < \alpha_{zz}$  . the donor – nanobridge – acceptor molecular system has high value of average polarizability , it is more reactive molecular system .



**Figure 10 :** The relationship between the dipole moment and  $\Delta N_{\max}$  of donor – nanobridge – acceptor and it is components

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