The Electronic Structure of Donor-Bridge-Acceptor: Density Functional Theory Calculations.

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Abstract

Aviram-Ratner model was used to designing donor-nanobridge-acceptor D-NB-A molecular electronic system. Geometrical parameters and energies for the D-NB-A molecular system were investigated by the three parameters Lee-Yang-Parr density functional theory B3LYP/DFT Calculations. The LUMO-HOMO energy gap for the D-NB-A showed that the substituents adding to the phenyl ring lead to a new electronic material 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 it is components (donor and acceptor).

Keywords*:* Aviram-Ratner model, D-NB-A, energy gap, HOMO-LUMO, B3LYP/DFT.

الخلاصة

تم استخدام أنموذج Ratner – Aviram في تصميم نظام الكتروني جزيئي(واهب-جسر نانوي-قابل) . تم تحقيق المعاملات الهندسية وطاقات النظام الجزيئي بالاعتماد على حسابات نظرية دالية الكثافة لي-يانغ-بار ذات المعاملات الثلاثة. ان فجوة الطاقة المحسوبة للنظام تبين ان الاضافات الى حلقة الفنيل أدت الى تصميم مادة الكترونية تمتلك فجوة طاقة مناسبة. تبين النتائج ان النظام الجزيئي له فعالية عالية في عمليات نقل الشحنة بالمقارنة مع مكوناته (الواهب والقابل).

كلمات مفتاحية: موديل Ratner – Aviram , واهب-جسر نانوي- قابل , فجوة الطاقة, المستوي الجزيئي العلوي المشغول-المستوي الجزيئي السفلي غير المشغول, نظرية دالية الكثافة.

1. Introduction

Charge transfer (CT) is the main process in many fields of chemistry, physics, and biology [1–7] monographs [8–10]. 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 D-B-A systems including inter-site electronic coupling, electronic energies and electronic-nuclear coupling. This work stand on Aviram-Ratner model to design of donor- Nanobridge-acceptor and determine the quantity of charge transfer (CT). All calculations were viewed at the GaussView 5.0.8 program and performed with the Gaussian 09 package of programs [23].

2. Theoretical Background

The calculations were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 package of programs [12]. The molecular properties of the structure have been calculated by DFT using the standard 6-31G basis set. In the DFT calculations the Lee, Yang and Parr correlation functional [13] is used together with Becke's three parameters[14]exchange functional B3LYP.

The molecular relax was performed at the B3LYP/DFT with the same basis set [12, 15]. Harmonic vibration frequencies were computed at the same level of theory. The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and vibration analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface [20].

The DFT partitions the electronic energy as[19, 20]:

(1)
$$E = E_T + E_V + E_J + E_{XC}$$

where E_T, E_V and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms, respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the anti-symmetry of the quantum mechanical wave function and the dynamic correlation in the motion of individual electrons, it makes DFT dominant over the conventional Hartree - Fock (HF) procedure [19].

The more relevant electronic ionization energy (IE), electron affinities (EA), chemical potential μ, it is the negative of electro negativity χ, Fermi

energy E_F, electronic softness S, electrophilic index ω and the electric dipole polarizability α were calculated in this investigation.

The high occupied molecular orbital (HOMO) and the lower unoccupied molecular orbital (LUMO) energies were used to calculate the energy gap Eg, where (Eg = LUMO-HOMO) estimate the IE and EA according to Koopmans' theorem[22]:

$$IP = -\varepsilon_{HOMO} \qquad (2)$$
$$EA = -\varepsilon_{LUMO}$$

Within the framework of the (DFT), the chemical potential μ, which is measures the escaping tendency of an electronic cloud, and calculated from the relationship[23]:

$$\mu \approx -\chi = -(IP + EA)/2 \quad (3)$$

Where χ is the electronegativity EN of the molecule [23].
Fermi energy E_F is half of the energy gap, E_F is the electrochemical hardness H[22]:

$$H= E_F = (IP- EA) / 2 \qquad (4)$$

And the electronic softness is given by the relationship[22]:

(5)
$$S= 1/2E_F$$

The electrophilic index is a measure of energy lowering due to maximal electron flow. Electrophilic index (ω) is defined as[19]:

$$W=\mu^2 / 2E_F \qquad (6)$$

One of the other global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, the mean polarizability$< \alpha >$ is evaluated using the equation[19,23] :

$$< \alpha >= \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

where $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$are the eigenvalues of the polarizability tensor.

3. Results and Discussion

The optimized structure in fig.1 showed the π- conjugated nanobridge as spacer connecting between the donor (aminobenzene) and the acceptor (nitrobenzene). This molecular structure was optimized at the ground by employing the hybrid functional B3LYP/DFT with 6-31G basis sets.
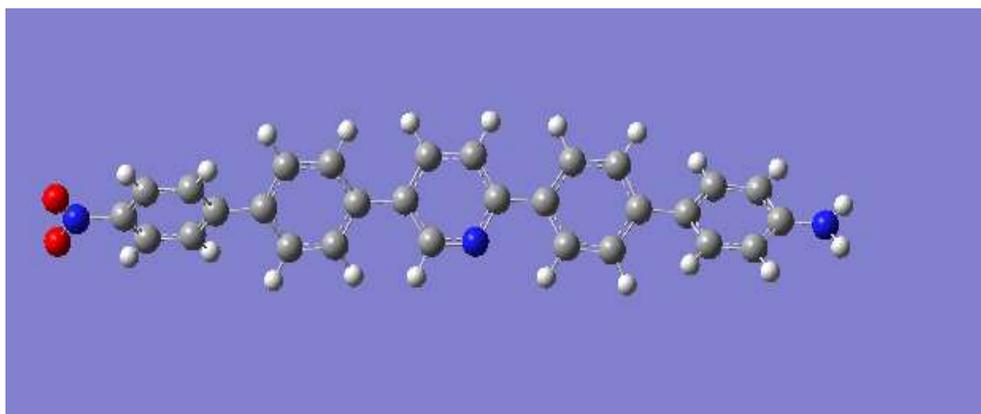
Fig. 1 : B3LYP/DFT optimized structure.

The geometrical optimized parameters (bond length in nm , bond angles in degree) of the donor–nanobridge–acceptor molecular system are illustrated in Table 1. As shown, the subgroups adding to phenyl ring in the terminal ends of the molecular system has a small effect on the values of bonds between atoms, C-C, C=C and C-H bond in benzene are are in the same range of those for benzene ring. Convergence between the atomic numbers of carbon and nitrogen atoms gave a good convergence between C-C and C-N bonds in the structure. We can see that, a deviation in the bridge bond angle between the two phenyl containing the end substitutes, in which, this deviation can be expected due to string contact coming from the presence of phenyl groups at the terminal positions of the molecular structure.

Table 1: The structural parameters of the studied molecule.

Bond length		Bond angle	
Bond	**Value (nm)**	**Bond**	**Value (deg)**
C-C	0.1401-0.1403	**C=C-C**	119.368
C=C	0.1410-0.1417	**C=C-N**	119.614
C-H	0.1082-0.1086	**O=N=O**	123.316

C-N	0.1442	C=C-N	119.623
N=O	0.1275	C-C-H	121.041
N-H	0.1005		

Table 2 showed the optimized structure has good relax and B3LYP functional used for this optimization is a suitable with 6-31G basis set, it is found that the optimization of the structure together with the linear combination keeps the aromaticity of phenyl rings, also the virial ratio (the ratio of the potential to kinetic energy) of the studied D-NB-A molecular system and it is components (-V/T) is remain in the same range of these structures (2.0053- 2.0057). So, there is no imaginary frequency appears for the IR-spectra of donor, acceptor and donor-nanobridge-acceptor molecular system.

Table 2: Total energy E_T in a.u, -V/T, symmetry and the number of imaginary frequency of the studied molecule.

Structure	E_T (a.u)	-V/T	Symmetry	No. of imaginary frequency
Donor	-287.5376	2.0057	C_{2v}	0
Acceptor	-436.6185	2.0053	C_{2v}	0
D-NB-A	-1432.0057	2.0055	C_2	0

Fig.2 shows the total energy of the studied molecular system and it is as result of relaxation of the structures at the ground state from the B3LYP/DFT. Fig.2 declare that the total energy of the D-NB-A 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 both the donor and acceptor.
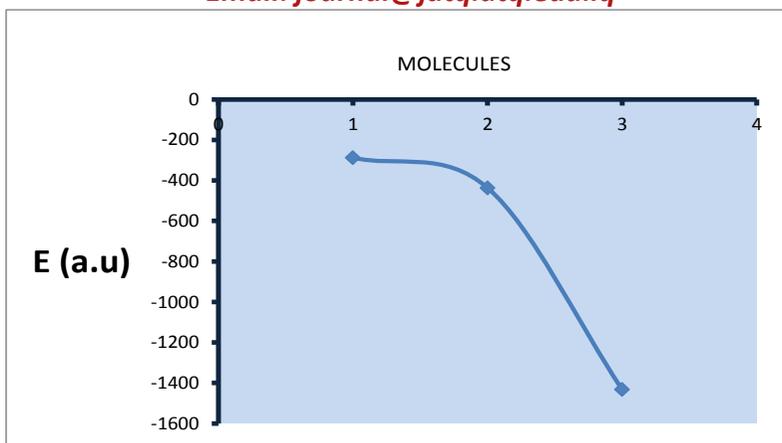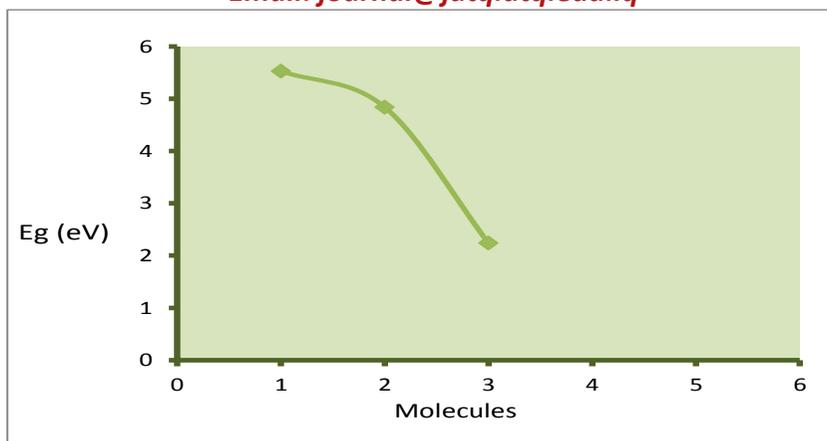
Fig. 2: Total energy of the molecular system and it is components.

The electronic states (HOMO and LUMO) and energy gap E_g of the donor, acceptor and D-NB-A molecular system are illustrated in Table 3. As known, benzene ring has an insulator behavior with energy gap equals 6.7eV, adding the substituents 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). Due to Aviram-Ratner model, the interacting between the donor and acceptor by a nanobridge leads to construct the D-NB-A molecular system with energy gap (2.240 eV), in which it is small gap in comparison with the donor and acceptor, as shown in fig.3.

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

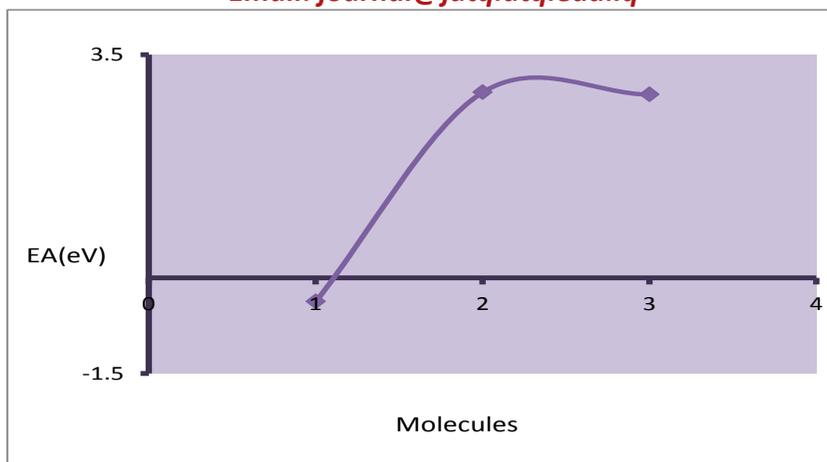| Species	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
Donor	-5.1545	0.37442	5.529
Acceptor	-7.7483	-2.9086	4.839
Molecule	-5.1148	-2.8748	2.240

Fig. 3: The energy gap of the molecular system and it is components.

Fig.4 illustrates the ionization energy IE in eV of the donor, acceptor and D-NB-A molecular system. These results declare that the donor has a low ionization energy in comparison with the acceptor, as a requirement to donating an electron easily. The D-NB-A molecular system have a suitable value ionization energy (5.114 eV) gave this molecular system the ability of rectification when it is aligned between two metallic electrodes.

The strength of an acceptor molecule is measured by it is electron affinity in which the energy released when adding an electron to the LUMO. An acceptor must have a high electron affinity. Fig.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) .
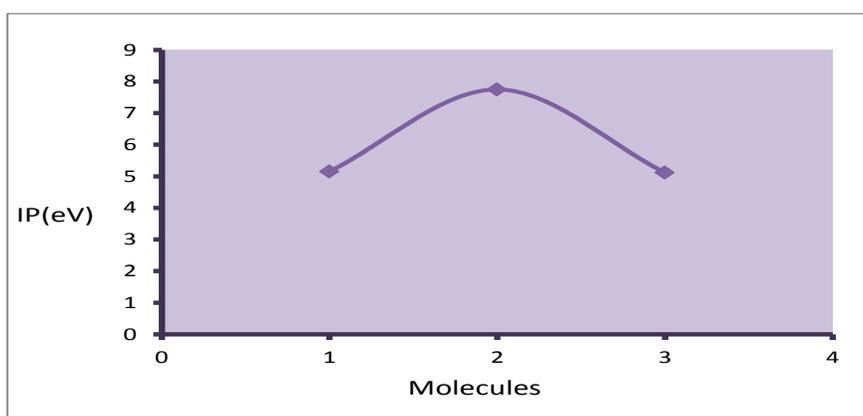
Fig.4: The ionization energy of the molecular system and it is components.

Fig.5: The electron affinity of the molecular system and it is components.

Interesting observations have been made from the results that are shown in figures 6 - 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 satisfy accurately. The results obtained by the calculation of the electronegativity in fig.6 was agreed very well with the employing for the D-NB-A molecular system. This could be the reason for the low electrochemical hardness values obtained from this method, as we see in fig.7. The koopman's theorem is a best, useful and fast approach.

The behavior of electronegativity, softness and electrophilic index for the studied D-NB-A 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 and electrophilic index in fig.8 and fig.9, respectively are of the order of (Molecule >Acceptor >Donor). These results refer to that this molecular system is more soft and more reactive to interacting with other species or the surrounding molecules.
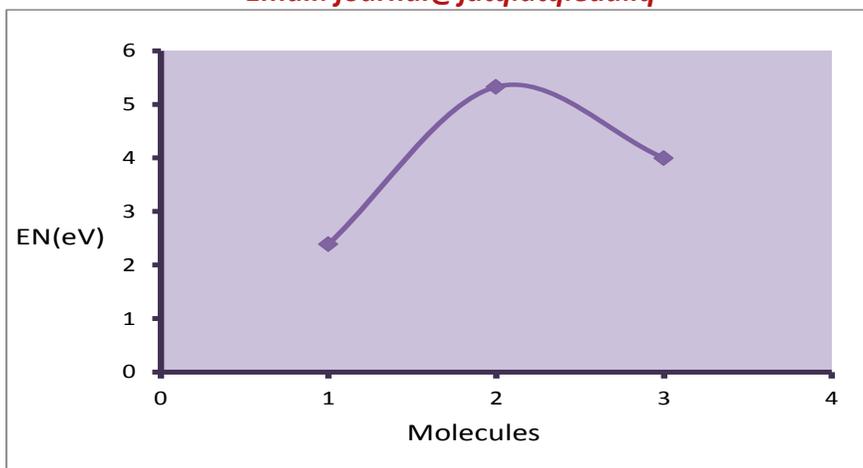
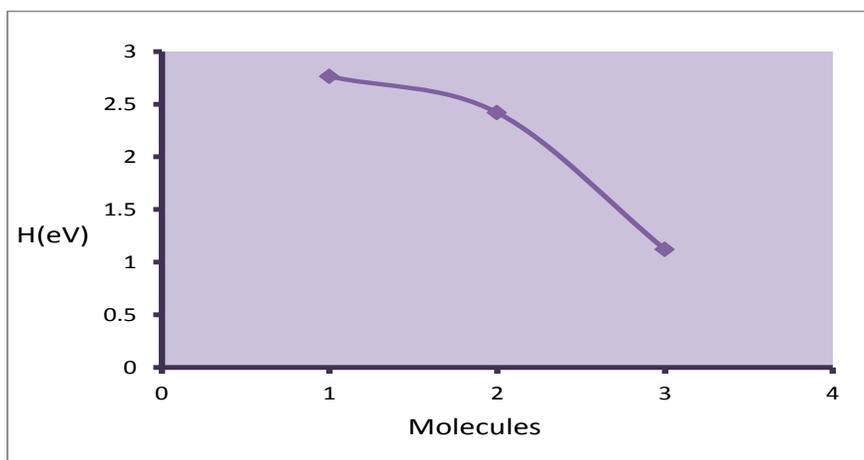**Fig.6: The electronegativity of the D-NB-A and its components .**

Fig.7: The electrochemical hardness of the D-NB-A and its components.
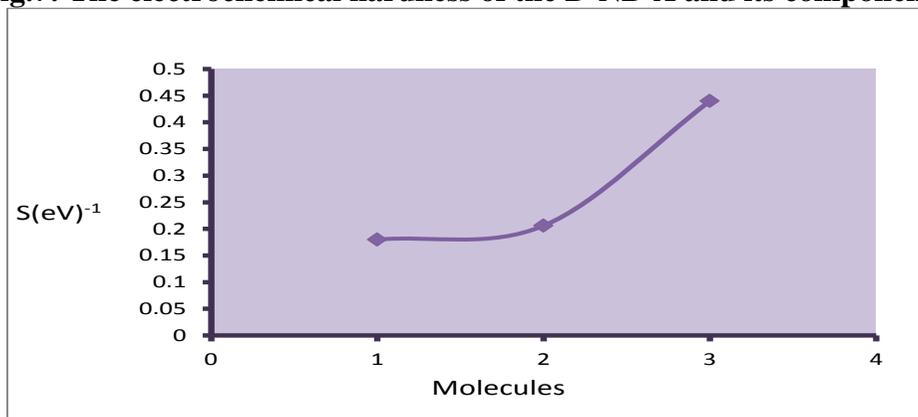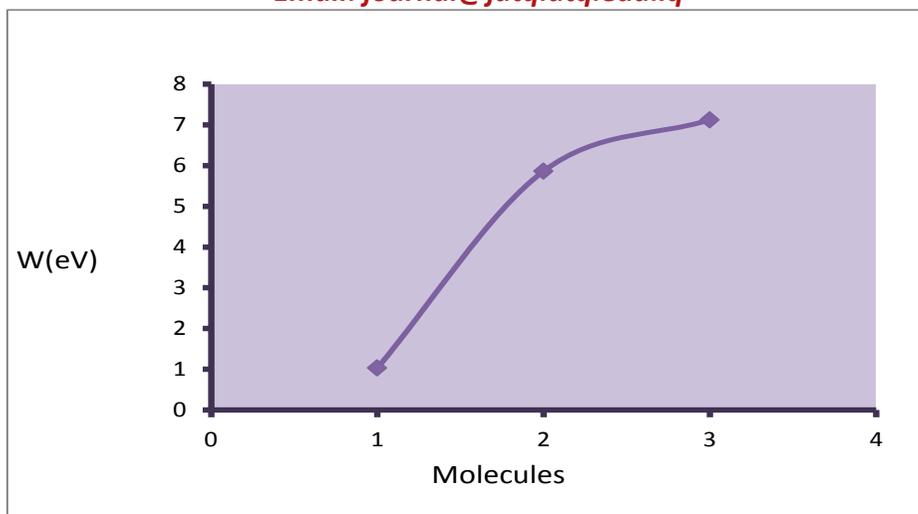

Fig.8: The softness of the D-NB-A and its components.

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Fig.9: The electrophilic index of the D-NB-A and its components.

Table 4 shows the results of the dipole moment in Debye and the polarizability in atomic units of donor, acceptor and D-NB-A molecular system. As we know the benzene molecule is a planar has D_{6h} high symmetry with total dipole moment equals zero. Adding the substituents leads to change the distribution of charge, therefore effects on the symmetry and polarity of the molecule. 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 D-NB-A molecular system has the largest value of dipole moment and this may be a sign to this molecular system has electrophilic behavior. The results of exact polarizability of all studied structures are agree with the molecular polarizability theories in which it is components are of order of $\alpha_{xx} < \alpha_{yy} < \alpha_{zz}$, the D-NB-A molecular system has high value of average polarizablitiy, D-NB-A is more reactive molecular system compared with both donor and acceptor.

Table 4: The molecular polarizability of the D-NB-A and it is components.

Species	Total dipole moment(Debye)	ΔN_{max}	Polarizability (a.u)			
			α_{xx}	α_{yy}	α_{zz}	α_{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	9.2568	3.6042	173.999	234.522	905.936	514.972

4. Conclusions

From the results obtained in the present work, one can conclude that:

The total energy of the structure depends on the number of atoms in each structure and the atomic number for all atoms in the species, the total energy was decreased with increasing the number of atoms in the structure. The designed donor-nanobridge-acceptor molecular system has low value of energy gap.

The donor-nanobridge-acceptor has low value of ionization potential and high value of electron affinity in comparison with it is components (donor and acceptor), in which it has small energy to donating an electron and becomes cation. The donor-nanobridge-acceptor molecular system is more soft and more reactive than both the donor and acceptor to interacting with other species or the surrounding molecules.

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