A DFT approach to analyze charge transfer path through *trans* and *cis* isomers of azobenzene

C Karthika[a], R Praveena[b] & K Sadasivam[c,]*

[a]Department of Physics, Kongu Engineering College (Autonomous), Perundurai, Erode, Tamil Nadu 638 060, India

[b]Department of Chemistry & [c]Department of Physics, Bannari Amman Institute of Technology (Autonomous), Sathyamangalam, Erode, Tamil Nadu 638 401, India

*E-mail: dftsada@gmail.com

The influence of external electrical field (EF) over the *trans* and *cis* isomers of azobenzene is investigated upto molecular orbital level with the aid of density functional theory. The frontier molecular orbital analysis and electrostatic potential (ESP) mapping are used to figure out the response of the molecules (*trans* and *cis* isomers of azobenzene) to the applied EF. The variation in dipole moment gives the extent of polarization in the molecule due to EF. With the aid of natural bond orbital analysis (NBO) the possible charge transfer path through the molecule can be predicted. ESP and NBO analysis clearly shows that drastic charge redistribution takes place for the EF strength of 0.15 V/Å. Hence the EF strength above 0.15 V/Å can be considered as threshold filed strength for organic molecular conductance. All these theoretical investigations provide a basic knowledge about the influence of molecular conformation over the conductivity of a molecule in the presence of EF.

Keywords: DFT, Azobenzene, Molecular orbitals, Charge distribution, NBO

During the past decade, an interdisciplinary group of physicists, chemists and engineers are performing a series of experimental and theoretical studies in molecular electronics to measure and control the charge transport through a single molecule[1-3]. Compared to experimental studies, theoretical investigations give an insight into the electronic structure of molecules which paves the way for the better understanding of the molecule's behaviour under various circumstances[4-6]. In this aspect density functional theory (DFT) is widely employed to find out the electron transport through single molecule sandwiched between two electrodes through a linking agent[7-9].

In this article *trans* and *cis* isomers of azobenzene, the simplest structure among azo- group, is considered for the study. Azo-compounds are well known for their photo-switching between *trans* and *cis* conformations in ultra violet range which makes it suitable to be used in molecular photoelectric switches, electrical data storage devices and logical devices with appropriate fictionalization[10-14]. Actual molecular circuits are established through chemical bonds without any macroscopic interface. But in most of the experimental methods like STM and AFM a single molecule is precisely positioned in between a metal substrate and a metal tip for measuring the electrical conductance of the molecule. Thus, it is necessary to represent such metal-molecule connection in theoretical study also. In this aspect, *trans* and *cis* isomers of azobenzene are connected to gold atoms (Au) through the linking agent nitrogen N. The purpose of including linking agent is to enhance the connection between the metal (Au) and organic molecule. This extended *trans* and *cis* isomers of azobenzene (with N and Au atoms) are named as M-I and M-II, respectively.

The study mainly focuses on the response of M-I and M-II to the applied electric field (EF). The information obtained from these analyses will be useful to tune azo-group of molecules for various applications in molecular electronics. Also the extent of the effect of molecular conformation over the electrical conductivity of a molecule is analyzed.

Materials and Methods
Computational details

All the calculations are carried out as implemented in Gaussian 09 software package[15] through DFT[16] with B3LYP hybrid functional. Since heavy atoms

(gold) are involved in this system, LANL2DZ basis set[17-19] has been used in order to minimize the computational cost with the usage of effective core potential. Initially the geometries *trans* and *cis* isomers of azobenzene are optimized followed by the bonding of two Au atoms to represent the bulk metal electrode on both the ends of the molecule with N as linking agent. The reason for using N-atom as linking agent instead of sulfur atom (conventional) is to bring the HOMO energy level of the molecule in accordance with Fermi level of bulk Au electrode leading to enhancement of the conductance of the molecules.[20] All the geometries are optimized in gas phase and confirmed to have no imaginary frequency of Hessian. Then the optimized structure of M-I and M-II are subjected to the external EF in three steps (0.05, 0.10 and 0.15 V/Å) along the molecular axis. The molecular orbitals (MOs) and electrostatic potential (ESP) mappings are plotted using GView program[21] density of states (DOS) is calculated using GaussSum program[22] and NBO analysis as implemented in Gaussian 09W suite of program is carried out.

Results and Discussion

Bond length

The molecule under study must exhibit a strong structural stability even under the influence of EF. Hence the structural analysis is carried out for M-I and M-II. The bond formation of azobenzene (*trans* and *cis)* with N and Au atoms does not have any significant variations over the molecular geometry. The optimized geometries with atom numbering and bond lengths of M- I and M-II are depicted Fig. 1a, 1b

and Table 1, respectively. Since azobenzene is symmetric, bond length values are given only for the first half of the structure. The C2−C3, C4−C5 and N−Au bond lengths are 1.39, 1.42 and 2.06 Å in both the molecules. The N=N bond length is 1.31 Å in M-I and 1.29 Å in M-II. All these bond length values are in good agreement with the reported value of 1.2589 Å for N−N bond length and 1.392 Å, 1.406 Å for C−C bond length in $C_6H_{11}N_3O_2$ molecule optimized under B3LYP/6-31G(d,p) level of theory by Cojocaru et al.[23].The *trans* conformation M-I is planar with the dihedral angle of C4−N7−N8−C9 as 180°. Whereas M-II (*cis* conformation) is twisted with the dihedral angle 18° for C4−N7−N8−C9.
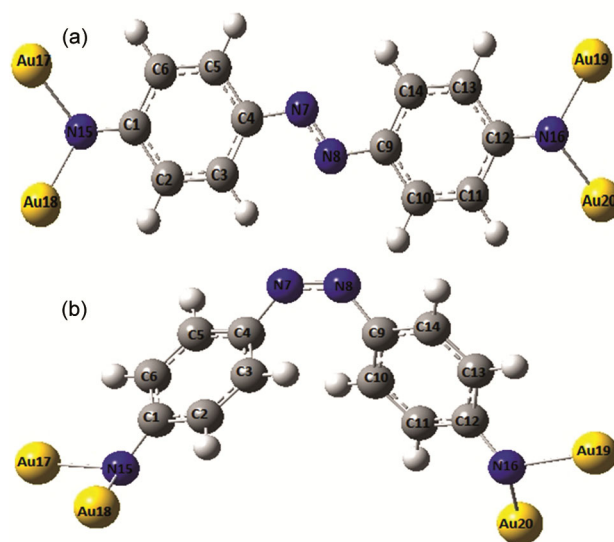

Fig. 1 — Optimized Structure and atom numbering of (a) M-I and (b) M-II

Table 1 — Bond length (Å) of M-I and M-II under various EF

Bond	M-I with EF strength (V/Å)				M-II with EF strength (V/Å)			
	0	0.05	0.1	0.15	0	0.05	0.1	0.15
C(1)-C(2)	1.44	1.44	1.44	1.44	1.43	1.43	1.43	1.44
C(2)-C(3)	1.39	1.39	1.39	1.38	1.39	1.39	1.39	1.39
C(3)-C(4)	1.43	1.43	1.43	1.43	1.42	1.42	1.43	1.43
C(4)-C(5)	1.42	1.42	1.42	1.43	1.42	1.42	1.42	1.42
C(5)-C(6)	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39
C(6)-C(1)	1.43	1.43	1.43	1.44	1.43	1.43	1.43	1.44
C(4)-N(7)	1.41	1.41	1.40	1.39	1.43	1.43	1.42	1.41
N(7)-N(8)	1.31	1.31	1.31	1.32	1.29	1.29	1.29	1.29
C(1)-N(15)	1.40	1.40	1.39	1.38	1.40	1.40	1.40	1.39
C(12)-N(16)	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
N(15)-Au(17)	2.06	2.05	2.04	2.03	2.06	2.06	2.05	2.04
N(15)-Au(18)	2.06	2.06	2.05	2.03	2.07	2.06	2.05	2.04
N(16)-Au(19)	2.06	2.07	2.08	2.09	2.07	2.08	2.09	2.11
N(16)-Au(20)	2.06	2.07	2.09	2.10	2.06	2.07	2.07	2.09

There is no significant change is observed over the geometry of the azobenzene due to EF. At the same time the bond length of N−Au on the left side gradually decreases whereas on the right side it increases gradually, which is attributed to the field direction. These bond length variations are reversed when the field direction is reversed. Also there is no significant change in the bond angle of both the molecules even under the influence of EF. Hence it become clear the structural stability of both M-I and M-II is well preserved even after the EF application.

Frontier molecular orbital analysis

The frontier orbitals are highly significant among the molecular orbital (MO), as it contributes much to the charge transfer. Fully delocalized orbitals along the molecular backbone are considered as a good channel for charge transfer. Hence the spatial distribution of frontier and its nearest orbitals of molecule I and II are examined under the influence of EF. In both M-I and M-II Highest occupied molecular orbitals (HOMO) and HOMO-1 are completely delocalized compared to lowest unoccupied molecular orbital (LUMO) and LUMO+1orbital and also HOMO is very close to the Fermi energy level (FL) of bulk gold electrode(-5.31 eV)[24]. Hence in azobenzene hole transfer will be dominating the electron transfer and there is no observable changes in the spatial distribution of the MOs due to the application of EF.

Density of state is a measure of number of available energy state in a molecule per unit energy. Fig. 2 depicts the DOS of M-I and M-II at 0 EF. The blue line represents the FL of bulk Au electrode. HOMO of M-I is in exact alignment with FL of bulk Au electrode owing to better conductance. The HOMO-LUMO gap is 1.361 eV for both M-I and M-II.

Fig. 3 and 4 represents the evolution of energy levels of M-I and M-II, respectively, in response to the applied EF. The red, green and blue line represents the HOMO, LUMO and FL of the molecule. The lengthy blue colored dotted line represents FL bulk Au material. Comparing M-I and M-II the LUMO+ energy states are almost similar for both the molecules, but the distribution of HOMO-energy states are widely spread out in M-II. In both M-I and M-II, LUMO and LUMO + energy levels remains very rigid and only slight shifting takes place in HOMO and HOMO- energy levels with the application of EF. Because of which the HOMO-
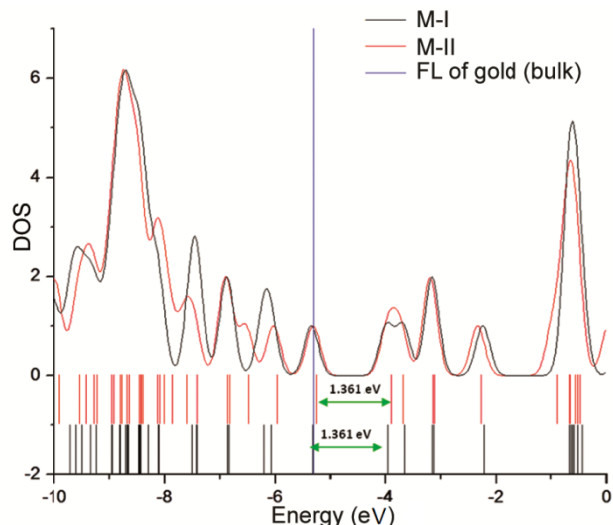

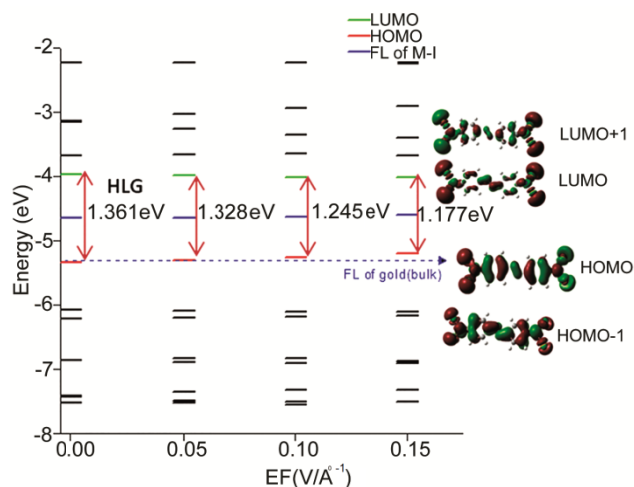Fig. 2 — Plot of density of states of M -I and M-II

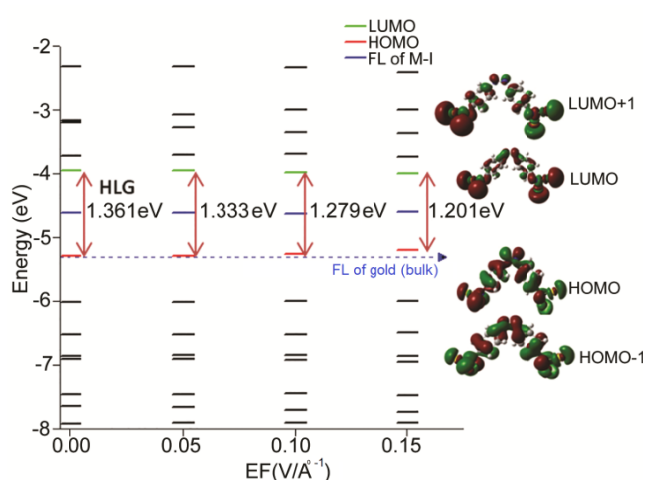Fig. 3 — Energy distribution in M-I for various EF strength

Fig. 4 — Energy distribution in M-II for various EF strength

LUMO gap gradually decreases from 1.361 eV to 1.177 eV and 1.201 eV in M-I and M-II, respectively.

Natural bond orbital analysis

In natural bond orbital (NBO) analysis by second order perturbation theory inter and intra molecular interactions can be estimated[25]. As a result of these interactions charge transfer takes place from Lewis (donor) to non-Lewis (acceptor) orbitals. Hence the stabilization energy associated with such conjugative interactions between Lewis and non-Lewis NBOs are analyzed to identify the bonds which contribute much to the charge transfer. In M-I the π(C-C) $\longrightarrow$ π*(N-N) interaction shows high stabilization energy of the order 26 kcal/mol (Table 2). When EF is applied the stabilization energy for π(C1–C6) $\longrightarrow$ π*(C4–C5), π(C9–C10) $\longrightarrow$ π*(C11–C12) and π(C4–C5) $\longrightarrow$ π*(N7-N8) gradually increases. At the same time stabilization energy for π(C9–C10) $\longrightarrow$ π*(N7–N8) , π(C4–C5) $\longrightarrow$ π*(C1–C6) and π(C11–C12) $\longrightarrow$ π*(C9–C10) interactions decreases. These changes in the stabilization energy due to the EF are useful in predicting the possible path of the charge flow through the molecules.

In M-II π(C1–C6) $\longrightarrow$ π*(C4–C5) and π(C12–C13) $\longrightarrow$ π*(C9–C14) interactions shows high stabilization energy of the around 25 kcal/mol (Table 3). Further the application of EF increases the stabilization energy for π(C9–C14) $\longrightarrow$ π*(N7–N8), π(C12–C13) $\longrightarrow$ π*(C9–C14), π(C4–C5) $\longrightarrow$ π*(C1–C6), π(C9–C14) $\longrightarrow$ π*(C10–C11), π(C2–C3) $\longrightarrow$ π*(C4–C5) and π(C10–C11) $\longrightarrow$ π*(C12–C13) interactions. But the other interactions in M-II experiences reduction in the stabilization energy. From these variations in stabilization energy with respect to EF it is clear that the charges are getting redistributed only within the ring and there is no significant charge flow through M-II. This is clearly picturised as arrow marks in graphical abstract. At the EF strength of 0.15 V/Å older interactions disappear with the incoming of new interactions between the bonds involving N (linking agent) and Au atoms with very high stabilization energy ranging from 200 to 130 kcal/mol. This is attributed to the strong EF which drift away most of the charges leading to instability around the contact between azobenzene and Au atoms.

Dipole moment, electrostatic potential and electrical resistance

Dipole moment indicates the extent of asymmetric charge distribution in a molecule and can also be described as the first derivative of energy with respect

Table 2 — Stabilization energy for NBO in M-I

Donor	Acceptor	Stabilization energy (kcal/mol)			
		0 V/Å	0.05 V/Å	0.1 V/Å	0.15 V/Å
π (C9-C10)	π*(N7-N8)	26.55	25.21	24.74	24.91
	π*(C11-C12)	21.88	22.72	23.56	24.43
π (C4-C5)	π*(N7-N8)	26.38	28.23	30.57	_
	π*(C1-C6)	22.03	21.18	20.68	_
π (C11-C12)	π*(C9-C10)	25.14	24.14	23.61	23.35
π (C1-C6)	π*(C4-C5)	24.99	26.04	27.32	_
σ(N15-Au18)	π*(C1-N15)	_	_	_	160.3
σ(N15-Au17)	π*(C1-N15)	_	_	_	151.63

Table 3 — Stabilization energy for NBO in M-II

Donor	Acceptor	Stabilization energy (kcal/mol)			
		0 V/Å	0.05 V/Å	0.1 V/Å	0.15 V/Å
π(C1-C6)	π*(C5-C4)	25.61	24.62	24.98	_
π(C12-C13)	π*(C9-C14)	25.37	27.57	26.25	29.77
π(C4-C5)	π*(C1-C6)	21.33	22.89	22.07	_
	π*(C2-C3)	19.43	18.25	18.93	_
π(C9-C14)	π*(C12-C13)	21.17	19.94	20.46	_
	π*(C10-C11)	19.15	19.91	19.55	_
	π*(N7-N8)	16.94	23.61	19.75	_
π(C2-C3)	π*(C1-C6)	18.77	18.02	18.51	_
	π*(C5-C4)	17.64	18.15	18.05	_
π(C10-C11)	π*(C12-C13)	18.54	18.77	18.72	18.8
σ(N15-Au17)	π*(C1-N15)	_	_	_	200.22
	σ*(N15-Au18)	_	_	_	138.56
σ(N15-Au18)	π*(C1- N15)	_	_	_	136.76
	σ*(N15-Au17)	_	_	_	131.86
π(C1- N15)	σ*(N15-Au17)	_	_	_	113.01

to applied field. As a response to EF the dipole moment increases in M-I and M-II from 0.02 to 18.06 D and 2.82 to 13.824 D, respectively. Thus, presence of EF leads to high degree of polarization of M-I compared with M-II which can be clearly visualized in Fig. 5 of electrostatic potential (ESP) mapping[26]. At zero EF the charge distribution is symmetric in M-I and M-II. As the EF strength increases more charges accumulates near the right terminal of both the molecules. This is due to the field direction. Comparatively charge accumulation is high in M-I than in M-II.

Electrical resistance (R) of M-I and M-II are calculated from the Landauer formula[27],

$$R = \frac{h}{2e^2 T_l T_r T_m}$$

where, $\frac{h}{2e^2}$ is quantum of resistance, T_l and T_r are charge transport efficiency along left and right

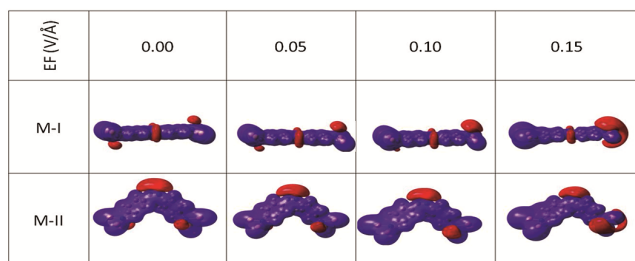| EF (V/Å)	0.00	0.05	0.10	0.15
M-I				
M-II				

Fig. 5 — ESP mapping of M-I and M-II for various EF showing electropositive (blue) and electronegative (red) regions

electrodes, respectively, T_m is the charge transmission through the molecule (azobenzene). The calculated R-value of M-I at various EF strengths (0, 0.05, 0.10 and 0.15 V/Å) is 325, 286, 207 and 157 MΩ, respectively. Similarly, R of M-II at various EF strengths (0, 0.05, 0.10 and 0.15 V/Å) is 539, 498, 397 and 285 MΩ, respectively. Hence the resistance of M-II is nearly twice that of M-I. In other words linear conductance (R^{-1}) of M-I is twice than that of M-II.

Conclusions

These electronic structure calculations are helpful in revealing the behaviour of *trans* and *cis* conformation azobenzene in the presence of EF. The geometry of azo benzene is very rigid even under the influence of EF. From FMO analysis, it is clear that the contribution to the charge transfer is high for HOMO compared to LUMO, since HOMO is in exact alignment with FL of bulk gold. The complete delocalization of HOMO, HOMO-1, LUMO and LUMO+1 orbitals are good sign for electrical conductance in M-I and M-II. The HOMO-LUMO gap decreases to 1.177 eV and 1.201 eV in M-I and M-II, respectively. NBO analysis is very useful in predicting the path followed by the charge flow through the azobenzene. The flow of charge take place in M-I from left to right direction without any hindrance, whereas in M-II there is no specific direction for the flow of charges. M-I exhibits high polarization with dipole moment 18.06 D and also ESP shows high charge accumulation compared to M-II. As sudden increase in charge redistribution occurs at 0.15 V/Å, it could be considered as the threshold filed strength for molecular conductance. Landauer formula is useful in calculating the conductance of the molecule. The conductivity of M-I is almost two times higher than that of M-II. All these theoretical information clearly illustrate the reason for low conductance of *cis* isomer M-I compared to *trans* isomer M-II. This basic information about the redistribution of electron density in response to EF will provide a better way to tune an azo-compound with appropriate functional groups as molecular switches or logical devices with *trans* and *cis* confirmations as on and off state of operation.

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