Effect of Torsion Angle in Molecular Devices: An Investigation on Electron Transport Properties of Borazine Dimer

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Abstract— Using Extended Huckle Theory (EHT) combined with nonequilibrium Green's functions (NEGF), the effect of torsion angle on electron transport properties of borazine dimer-based molecular devices have been investigated.The electron transport characteristics of the borazine dimer system for different torsional angles were analyzed through current–voltage characteristics, transmission spectra and density of states. By changing the torsion angle between two borazine rings, namely changing the magnitude of the intermolecular coupling effect, a different transport behavior can be observed in these systems. Our results show that the torsional angle plays a crucial role in determining the overall conductivity of the molecular devices.

Index Terms—Molecular Devices, Extended Huckle theory, Nonequilibrium Green's function, Electron Transport, Torsional angle, Transmission Spectra, I-V characteristics, Density of states.

1 INTRODUCTION

Over the past decade, molecular devices have received significant attention owing to their great potential practical applications in atomic-scale circuits[1]. Many interesting physical properties of molecular devices have been predicted theoretically and verified experimentally, such as single electron characteristics [2] negative differential resistance (NDR) [3],[4] molecular rectification [5], and field-effect characteristics [6], etc. An important objective in molecular electronics is to study and control electron transport through a molecule attached between two electrodes. At present, a number of theoretical models concentrating on the sandwich structure of an individual molecule between metallic electrodes using semiempirical [7], [8], [9] and first principle [10], [11], [12] theory are developed to provide quantitative description of molecular conduction. The semi-empirical method is computationally flexible compared to ab initio method and it is able to capture several quantitative descriptions of molecules of moderate size [13], [14], [15]. From the semi empirical calculations, it is clear that the chemical nature of the metal electrodes may have strong effect on the conductance of a molecular junction. Bai and co-workes [16], [17] studied the electron transport of thiolated borazine and benzene using ab initio method and they demonstrated that the magnitude of benzene is much higher than borazine due to less delocalization. Also they observed Negative differential resistance (NDR) behavior for borazine in lower bias. Based on break junction experiment Xia et al. [18] recently analyzed the transport behavior of borazine molecule with different metal-molecule interface and reported that the enhancement of current is more for the bridge sited molecule. Recently Kala et al. [19] studied the electron transport of borazine and bcn systems for different terminal groups using semi empirical method and they predicted Negative differential resistance (NDR) behavior in borazine-CN system.

But, in an experimental environment, the performance of a device will be affected by external factors during operation. Therefore the structure of the molecular device, including the torsion angle, the length of molecular bonds, the site where molecule is bonded on the metal surface, etc., may be influenced by these factors which may also have effects on the electronic transport properties of a molecular device. Recently, wang et al., theoretically demonstrate that the effect of torsion angle on electronic transport through different anchoring groups in molecular junction [20].

In this study, we apply nonequilibrium Green's function (NEGF) formalism coupled with the extended Huckel theory (EHT) to investigate the effect of torsional angle on the electron transport through borazine dimers sandwiched between gold electrodes through anchoring group sulfur S, by changing the torsion angels between two borazine rings. We investigate the transmission function (TF), current- voltage (I-V) characteristics and density of states (DOS), to understand the influence of torsional angles between two borazine rings. The theoretical results predict that the intermolecular interaction deeply depends on the torsion angles and plays an important role in the electronic transport of molecular devices.

2 COMPUTATIONAL METHOD

2.1 Model

In this work, the computational scheme is carried out in two parts. First part is the geometry optimization of borazine dimer molecule. This employment is done by using Gaussian

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03 suit of program with B3LYP method and 6–311++G** basis set. Second part is the calculation of transport properties of the optimized borazine dimer molecules inserted between two gold electrodes through thiol group. The transport calculations are carried out using the Atomistix Toolkit (ATK 11.2.3 version) [21] program which combines extended huckle theory (EHT) and Non-equilibrium Green's functions (NEGF) method to simulate the transport properties of two-probe systems. In NEGF theory, the molecular wire junction is divided into three regions: left electrode (L), contact region (C), and right electrode (R). The contact region contains parts of the electrodes include the screening effects in the calculations. For the left and right electrodes, we used 3 × 3 unit cell in the x and y directions to avoid the interaction between the molecules and the mirror image. The adsorption geometry is such that the molecules are located symmetrically at the top site of Au (111) surface.The semi-infinite electrodes are calculated separately to obtain the bulk self-energy. In our calculations, single-zeta plus polarization (SZP) basis set for Au atoms and double-zeta plus polarization (DZP) basis set for N and B atoms are adopted [19]. The Brillouin zone of the leads is sampled by 1 × 1 × 100 k points in the directions of x, y and z (z is the electron transport direction), which is enough to produce the results.

In the present work, we consider the tor torsion angleseffects on the electronic transport properties by keeping one borazine ring fixed and twisting the other borazine ring with different torsion angles related to the first ring. The models of borazine dimer molecular sytem for different torsional angles, say 0^0, 45^0 and 90^0, which is referred to as models A, B, and C respectively, are shown in Fig. 1.

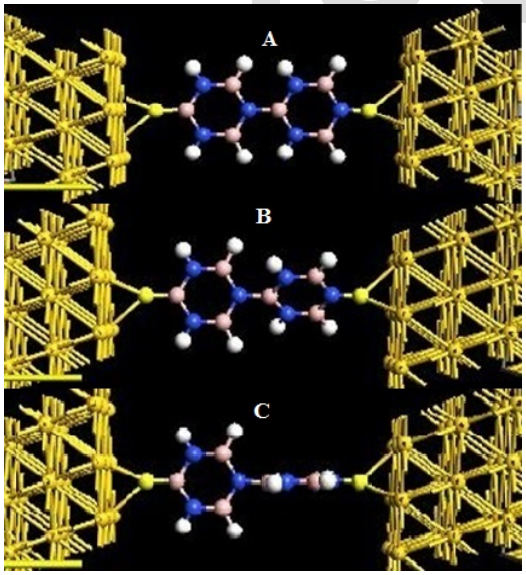

Fig. 1. Molecular Systems with borazine dimer molecule sandwiched between two gold electrodes through thiol end groups, for different torsional angles say 0^0, 45^0 and 90^0, which is referred to as models A, B, and C respectively.

2.2 Methodology

In the NEGF theory, the transmission function T (E, V) of the system is the sum of transmission probabilities of all channels available at energy E under external bias voltage V:

$$T(E,V) = Tr\left[\Gamma_L(E,V)G^R(E,V)\Gamma_R(E,V)G^A(E,V)\right] \quad (1)$$

where GR/A are the retarded and advanced Green's function and coupling functions ΓL/R are the imaginary parts of the left and right self-energies, respectively. Self-energy depends on the surface Green's functions of the electrode regions and comes from the nearest-neighbour interaction between the extended molecule region and the electrodes.

The I-V characteristics of the two probe system can be obtained by using the Landauer–Buttier formula [22], the current is the integration of the transmission function over the bias window around the Fermi level:

$$I = \frac{2e}{h}\int_{\mu_1}^{\mu_2} T(E,V)[f(E-\mu_1) - f(E-\mu_2)]dE \quad (2)$$

where T (E, V) is the transmission function through the device at energy E and funcion f (E – μ1/2) are the Fermi distribution functions of electrons in the left / right electrodes.

$$\mu_{1,2} = E_f \pm \frac{eV}{2} \quad (3)$$

are the chemical potentials of the left/right electrodes, with μ the Fermi level of the electrodes in equilibrium and V the bias applied to the device.

3 Result & Dicussions:

3.1 Transmission Function (TF)

Transmission functions (TF) are the main factor to decide the electron transport properties of the whole system. The Transmission function (TF) as a function of the electronic energy for different torsion angles between two borazine rings at zero bias are plotted as shown in Fig. 2.

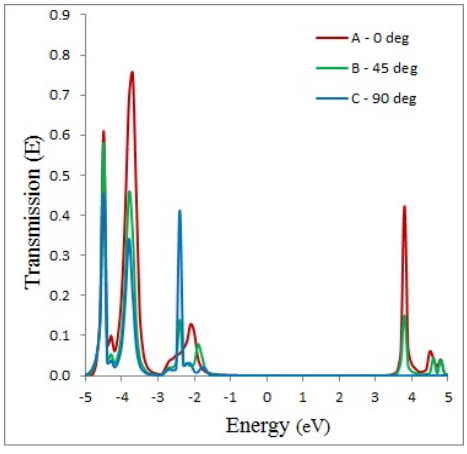

Fig. 2. Transmission Spectra of borazine dimer molecule sandwiched between two gold electrodes through thiol end groups, for different torsional angles say 0^0, 45^0 and 90^0 respectively at zero bias.

In our calculation, the average Fermi level, which is the average value of the chemical potential of the left and right electrodes, is set as zero. As can be seen from Fig. 2, magnitude of the transmission function is large for molecular

system A with torsional angle 0^0, closely followed by transmission fuction of a sytem B with torsional angle 45^0 in the lower and higher energy channel. Molecular system C with torsional angle as 90^0 between two borazine rings, the transmission function is small. This means that the conductance of molecular system A is higher than system B and C. The transmission peak can be related with the molecular orbitals of the molecule, which has been modified by the electrodes. It can be concluded that the electron transmission will be greatly affected by torsional angles as the transmission funtions were changed which has been confirmed in similar type of work [20].

3.2 Device Density of States (DDOS)

In order to further understand the difference in the transmission functions, device density of states (DDOS) for three systems are calculated under zero bias and shown in Fig. 3. We notice in particular sytem A and B, the DDOSs are rather large and for system C the DDOS is understandably small. The higher conductance of system A is the result of a higher density of states, than B and C systems. These are effects imposed by the torsional angles.

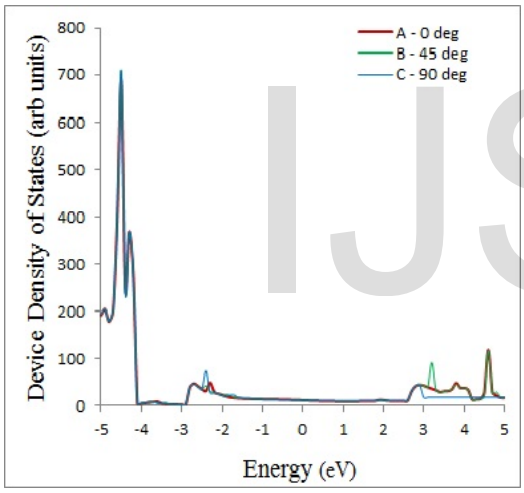

Fig. 3. Device densit of states for borazine dimer molecule sandwiched between two gold electrodes through thiol end groups, for different torsional angles 0^0, 45^0 and 90^0 respectively at zero bias.

3.3 Current – Voltage Characteristics (I-V)

Finally, we calculate the I-V characteristics of all three molecular systems containing borazine dimer molecules sandwiched between gold electrodes for torsional angles 0^0, 45^0 and 90^0, respectively, in bias voltage region (−1.5 V, 1.5 V), are calculated and presented in Fig. 4. The I-V characteristics of all three molecular systems, exihibit negative differential resistance (NDR) effect. As it can be seen from Fig. 4, when the torsion angle is equal to 0^0, i.e., the two borazine rings are coplanar, the current of system A is 10 times larger than that of sytem C whose torsional angle is 90^0. By changing the torsion angle between two borazine rings, namely changing the magnitude of the intermolecular interaction [20], a different transport behavior can be found in these three systems. As shown in Fig. 4, when the torsion angle smaller, the differences in I–V curves are small too. With the torsion angle increasing, i.e., the torsion angle is larger than 45^0, the current decreases obviously and reaches its minimum at 90^0.

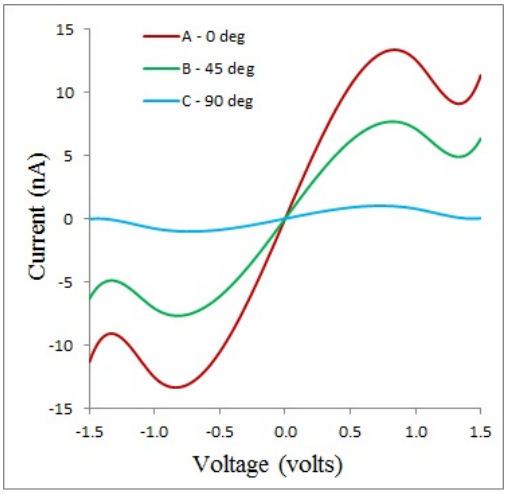

Fig. 4. I-V Characteristics of borazine dimer molecule sandwiched between two gold electrodes through thiol end groups, for different torsional angles 0^0, 45^0 and 90^0 respectively.

The results of I-V characteristics demonstrate that the torsional angle between the two borazine rings offer the possibility of modifying their electron transport behavior in a controlled way.

4 Conclusion

In summary, the effect of the torsion angle on electronic transport has been theoreticaly simulated using the non-equilibrium Green's function (NEGF) formalism coupled with the extended Huckel theory (EHT) for borazine dimer based molecular devices. We showed that the reason for the variable conductance was not simply the difference in the molecule electrode coupling strengths but also in the intermolecular coupling effect. The torsion angle plays a critical role in determining the electronic transport of borazine dimer based molecular device. The results will be helpful to understand further the possible situation in experiments and design molecular electronic devices with specific properties.

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