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# Theoretical Study of a Molecular Resonant Tunneling Diode

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**Abstract:** Density functional theory calculations are performed to explain the electrical behavior of a $\pi$-conjugated oligo(phenylene ethynylene) resembling a resonant tunneling diode. Results of this theoretical study are compatible with the assumptions that electron transport occurs through the lowest unoccupied molecular orbital, that the conduction barrier is determined by the molecule chemical potential, and that the molecule becomes charged as the external potential increases. We are able to explain the nonlinear character of the current−voltage characteristic of the molecule and its temperature dependence. The intrinsic controlled-amplification feature of these molecules is indicated.

## Introduction

Recent experimental results obtained from a small group of molecules (ca. 1000) forming a nanopore showed a behavior that resembles a resonant tunneling diode (RTD)[1] or a device with a negative differential molecular impedance. At a temperature of 60 K the current peaks at 2.1 V and reaches a peak current of 1 nA while the valley current is around 1−4 pA. The form of the peak is shown schematically in Figure 1. Also, as the temperature increases, the voltage at which the current is maximum decreases monotonically at a rate of 9 mV/K. After the resonance effect, a sharp decrease of the current takes place. The molecule in the nanopore can be represented as indicated in Figure 2, where a small portion of the actual measured nanopore is shown. In the nanopore, the molecules are self-assembled on the gold surface. Sulfur atoms served as *alligator clips*[2] to connect the surface. The top terminal was constructed by gold vapor deposition to the H-terminated molecules. The exact nature of the bonding to the gold terminals has not been characterized experimentally, especially at the vapor deposited side. However, preliminary quantum chemistry calculations predict[3] that the gold atoms attach to carbon atoms, while their H atoms remain bonded to the ring (Figure 2). The curve shown in Figure 1 was obtained when a potential difference between the two gold ends was applied with the higher potential (positive) applied to the self-assembled monolayer (SAM) side. The application of a negative bias (i.e., when the negative potential is applied to the SAM side) yields practically no current; the whole system behaves as a standard diode. We refer to this system as a molecular resonant tunneling diode (MRTD).

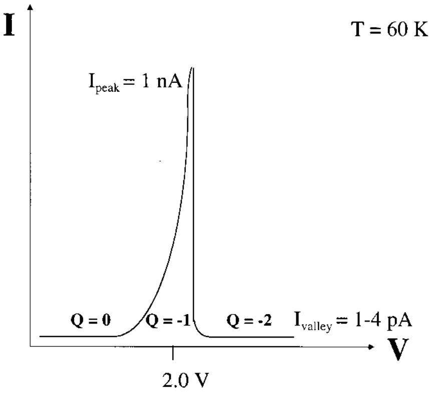

**Figure 1.** Experimental current−voltage characteristics of the MRTD (shown in Figure 2). The charge Q (in electrons) determines distinct conduction channels (shown in Figure 4) triggered by the bias voltage (in V).

Electroactive substituents, the injection or withdrawal of electrons in oligomers and polymers and the effects of ring torsion have been studied theoretically using mainly semiempirical methods,[4−6] and provided excellent ways to understand transport in polymers. It is known, for instance, that the HOMO-LUMO gap (HLG) is a critical parameter for the molecular admittance because it is a measure of the hardness[7,8] of the electron density. The larger the HLG, the more stable the molecule, and therefore the harder it is to rearrange its electron density under the presence of an external electron. Thus the

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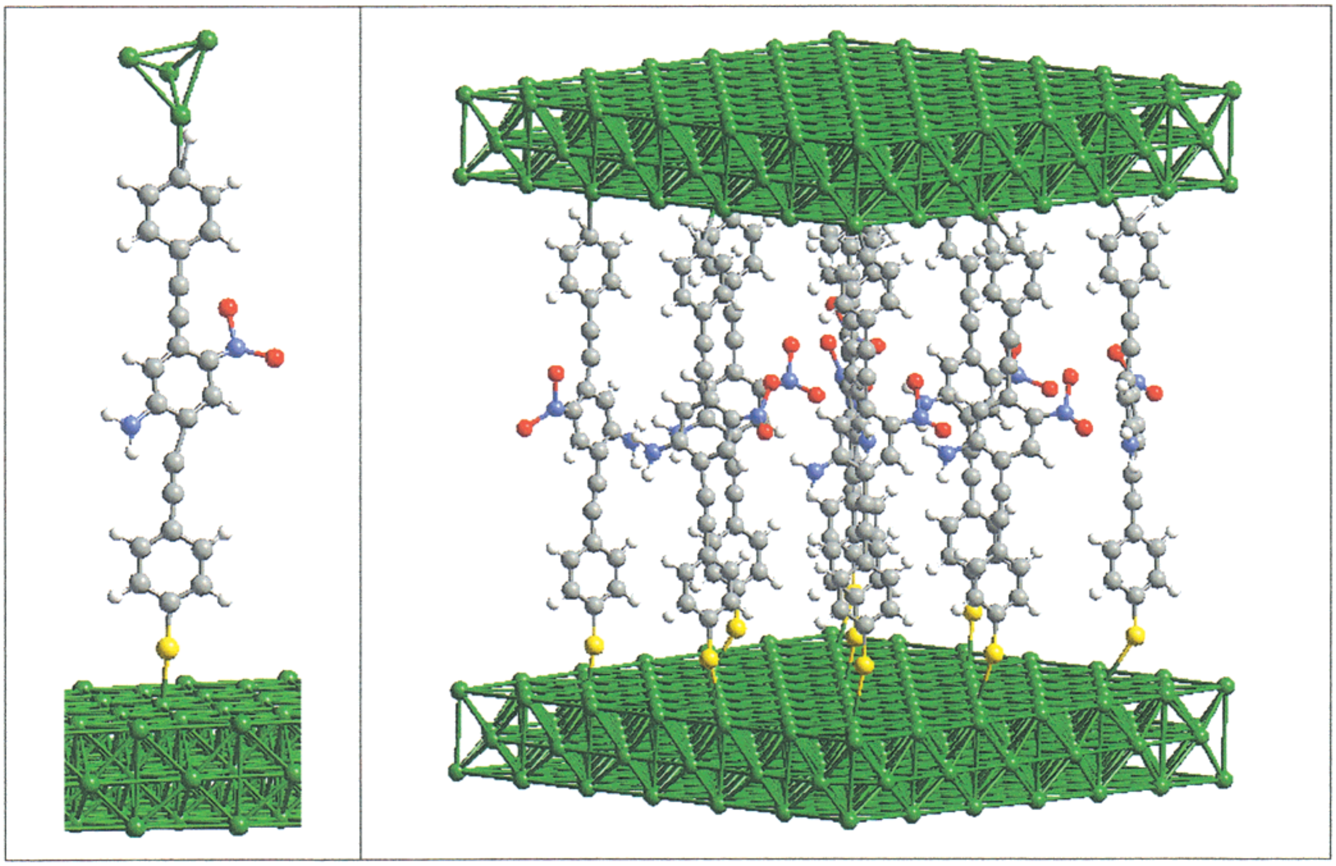

**Figure 2.** A small portion of the nanopore containing one (left) and several (right) MRTD molecules. The molecules are connected to the lower surface through the sulfur atoms by a SAM process. The top surface was created by vapor deposited gold. The resonant effects occur when electrons are injected from the vapor deposited side to the SAM side.

molecule presents lesser admittance to the incoming electron. On the other hand, due to the electronegativity equalization theorem,[8−10] the Fermi level of the metal aligns within the HLG as can be explicitly explained theoretically for extended structures,[11−13] therefore the barrier for electron transfer is proportional, in a first approximation, to the HLG.

## Theoretical Approach

We use quantum density functional theory (DFT)[8,14−18] techniques to investigate the sources of the resonance, the peak voltage, and the temperature effect on the behavior of the whole system. DFT is a ground state theory (formally valid for neutral as well as ionic species) and it is also equally valid for the lowest state of each electronic symmetry.[19−21] The analysis of the MRTD and related compounds was performed using the DFT methods as provided by the program Gaussian-94.[22] Two basis sets were used: the 6-31G* for all systems, and the 6-311G** for selected systems. We have used the hybrid functional B3PW91, which combines the Becke exchange (B) functional,[23] and the Perdew-Wang-91 correlation functional,[24] both of which are nonlocal generalized gradient-approximated functionals.[24−26] In addition, the B3 indicates a three-parameter functional where a portion of the exchange contribution has been calculated in the same fashion as in the Hartree−Fock (HF)

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procedure,[27] but using the Kohn−Sham noninteractive wave function instead of the HF wave function. All cases were treated first with a Hartree−Fock approach to have a good starting point for the DFT calculations.

Changes in the molecular orbitals are excellent indicators of the molecular electron transport. We analyze small molecular units to determine what groups are responsible for the observed behaviors. This helps us to determine the effects that are intrinsic to the molecules of the nanopore. We also want to analyze the temperature effects on the electron transport, since these effects are connected to the temperature dependence of the torsional properties of the molecule.[28] In this context, by torsion we mean the rotation of one aromatic ring with respect to an adjacent ring.

Conduction in molecules cannot be treated using mesoscopic or macroscopic models since they fail even for mesoscopic systems.[11,12] It is necessary to perform a molecular level study using the well-established tools of quantum chemistry.[8,29,30] It is important to understand the electronic molecular transport of a charged molecule, i.e., when electrons are occupying *unoccupied* orbitals of the neutral system due to the action of an external voltage. In this context, the HLG energy and the spatial extent of the LUMO are respectively the logical candidates for a quantitative and qualitative prediction of the transport characteristics. The present analysis is based on the ansatz that, in a first approximation, transport occurs through the LUMO orbital and other unoccupied orbitals, and as the molecule becomes charged, its chemical potential adapts to the local levels of the macroscopic electrodes addressing the molecule.

Notice that the HLG of a single molecule cannot be associated with an optical band gap; however, this does not affect our results since we are calculating the corresponding ions to assess electron transfer. In addition, the number of molecules in the nanopore is small enough (ca. 1000) to have an acceptable discrete spectrum rather than a band. This of course will take us to more elaborated questions such as, How can conduction exist if there is no band? However, conduction does indeed take place in single molecules as several experiments have already demonstrated (see, for instance, ref 31 and papers therein), and the mechanism of conduction can be associated with a path that uses one or more of the single-molecule frontier orbitals.[32]

We need to quantify two effects regarding the transport of electrons in molecules to investigate their electrical properties. First, the LUMO effect needs to be quantified because the molecular admittance (or the inverse of the molecular impedance) between two ends of a molecule increases when the LUMO is extended (delocalized) over the two ends. This yields a spatial contribution to the molecular admittance. The second effect is due to a directly quantifiable property, the HLG. When this gap decreases, the molecular admittance increases. In a first-order approximation, it is the midgap that will be pinned to the Fermi energy levels of the connecting terminals. The HLG is tremendously affected when an electron crosses a molecule. This is dramatically different from bulk devices. In bulk systems, barriers are formed because of the interaction of a large number of atoms, so single particle effects such as electron transfer do not significantly affect the rigid barriers. In molecules, however, barriers are very flexible. Therefore, real Hamiltonians and many-electron techniques have to be used to obtain meaningful results. To the best of our knowledge, this is the first time that the HLG and the shape of the LUMO are used to determine qualitative features of conduction in single molecules. While HLGs and frontier orbital considerations are used often for torsional barriers and chemical problems in bulk polymers (see for instance refs 33−37 among others), most previous work on single-molecule conductance uses the orbital energetics without considering the spatial extent of the conduction channels (see review papers in ref 31).

## Background Studies

To set the stage for the analysis on the MRTD, it is necessary to briefly discuss key findings on the electronic properties of related single molecules. We noticed that the molecular energy levels decrease in value when electrons are transferred from one side of a molecule to the other by action of an external field. In the special case of benzene connected in *para* positions by two Au atoms,[38] the HOMO energy is lowered by 1.66 and 3.28 eV after one and two electrons, respectively, have been transferred from one Au atom to the other. These energy drops may not be relevant since the midpoint of the HLG is located between the Fermi local levels of the metal contacts. This is why our attention is focused on the HLG, which decreases after one electron has been transferred and slightly increases when a second electron is transferred. Although the shapes of the orbitals are not strongly changed, the relative values of the gaps are due to the nonrigid character of the molecular orbitals under external effects. Therefore, they can be used to explain the complex behavior obtained in current−voltage characteristics of single molecules and single layers of few molecules. An analogous phenomenon can be observed by analysis of the HLG when an extra electron is present in the molecule. For neutral benzene, the HLG is 6.78 eV, which decreases to 3.82 eV for the positive ion and to 3.81 eV for the negative ion. The large HLG of benzene resembles its high ionization potential of 9.14 eV. However its electron affinity is negative, i.e., the ground state of the negative ion is embedded in the continuum of the neutral. Therefore, the effect of both electron-withdrawing and electron-donating groups is similar with respect to the HLG, in both cases shortening the gap. An OH group in the ring decreases the gap to 5.94 eV. This gap gets further reduced when the system loses or gains one electron to 3.79 and 3.65 eV, respectively. There is a static inertia to the molecular impedance, which is decreased as soon as the molecule is charged. The presence of a CN substituent for instance reduces the HLG of benzene by 0.9 eV.

These values can be contrasted with results for the tolane molecule[28] where the HLG for planar tolane is 4.44 eV while the rotated one has a HLG of 5.45 eV. This 1 eV increase in the HLG has considerable effect on the transport properties of the tolane molecule,[28] which are also strongly dominated by the shape of the LUMO of the planar and rotated configurations of tolane. The torsional barrier in this case is less than 1 kcal/mol. The HLG energy in the tolane dimer (1.18 eV) is enhanced with respect to the monomer (1.01 eV).[28] Therefore, the effect

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of the collective behavior is 0.17 eV when two molecules are interacting. This effect may be relevant for a group of nonbonded similar tolanes in the nanopore. However, the sole effect of the torsion in single molecules is a plausible explanation for the change of impedance with temperature, since temperature strongly affects the torsional angles. Indeed, small torsional energies are able to control the large HLG energies thereby providing the possibility of designing molecular amplifiers. The LUMO of the planar conformation is practically delocalized covering the whole molecule; however, the LUMO of the perpendicular conformation is localized in one of the rings thereby not permitting connection to the other ring.[28] These two conformations are energetically close to each other because the torsional barrier is small. Unoccupied orbitals near the LUMO are also localized for the rotated tolane, ensuring the insulator-like behavior of the rotated structure. The effect of temperature in the current−voltage characteristics of the MRTD can be attributed to the rotational (torsional) nature of these molecules. As an illustration, for instance, the HLG energy in the staggered and eclipsed ethane is 10.99 and 10.94 eV, respectively. This is an indication that rotations of the $CH_3$ groups in ethane with a torsional barrier of about 2.7 kcal/mol do not produce any significant change (a mere 0.05 eV) in the HLG. A totally different effect is observed in nitramide[39] where the torsional barrier is about 11.5 kcal/mol with a change in the HLG of about 0.99 eV.

This preliminary study suggests that one way to determine the transport characteristics of single molecules is to determine their HLG, then to study the spatial extent of the unoccupied orbitals to see if there is enough delocalization to allow the transport of electrons between two end points. The following step is to determine the effect of the incoming electrons on the shape of the unoccupied orbitals. The LUMO can become localized or delocalized due to the presence of an extra electron in the molecule.

## Results on the MRTD System

To study the molecule in question, we must first consider S atoms used for adhesion to the metallic probes. One S atom at the termini of the molecules is needed for the connection to the metallic atoms during the self-assembly process. However, its presence does not seem to have a significant impact on the HLG of the MRTD, nor on the shape of its molecular orbitals. This is demonstrated in the characteristics of the frontier orbitals of the molecules with and without the sulfur. The shapes of the HOMO and LUMO are practically identical (not shown) and their HLGs (Figure 3) are 3.48 (**c**), 3.37 (**e**), and 3.29 eV (**f**) for the MRTD with no sulfur, one sulfur, and two sulfur-ended, respectively. In addition, the torsion of the central ring in (**c**) does not dramatically affect the form of the LUMO orbital, but the HLG increases in 0.53 eV with the torsion of the central ring (from **c** to **d**). However, for the unsubstituted molecule, the torsion increases the HLG in 1 eV (from **a** to **b**), and the shape of LUMO changes radically (from delocalized to localized).

The torsional angles are precisely 0° and 90° for **a** and **b**, respectively. However, in the substituted molecules, the rings are not perfectly planar or perpendicular to each other. The torsion angle for (**c**) is 0.4° on the nitro side and 2.8° on the amine side. For the rotated case (**d**), the angles are 89.9° and 89.7° on the nitro and amine sides, respectively. The torsional angles are kept practically unmodified by the presence of the SH groups. The larger torsional angle on the amine side is due to the tetrahedral nature of its N, which is different than the planar N in the $NO_2$ group. The torsional effects of the nitro and amine groups are minimum and indistinguishable from each other in the rotated configuration (**d**). Charging systems **a** and **b** to −1 does not affect the torsional angles; however, it tends to slightly reduce the torsion of (**c**) to 0.2° on the nitro side and to 1.9° on the amine side. These torsions are further reduced to 0.1° and 1.7°, respectively, when the molecule gets charged to −2. The charging of the rotated configuration (**d**) to −1 or −2 forces the molecule back to the planar configuration (**c**).

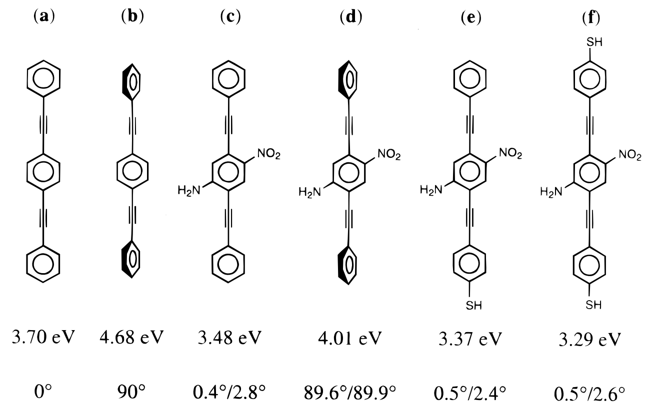

**Figure 3.** Several of the systems and conformations studied in this work corresponding to the optimized geometries at the B3PW91/6-31G* level of theory. The HOMO-LUMO gap (in eV) for each case is indicated, as well as the torsion angle (deg) between the top and the central rings followed by the angle between the central and the bottom rings (only one angle is shown when both are identical).

Evidently, the increase of the number of units in the oligomers also reduces the HLG. It is known experimentally that the band gap of the $\pi$-conjugated oligo(phenylene ethynylene)s with 13 units is approximately 3.0 eV,[40] which coincides with the theoretical trend of values for the smallest oligomers of that family: 6.78 eV for benzene, 4.76 eV for *p*-diethynylbenzene, 4.44 eV for tolane (diphenylethyne),[28] and 3.70 eV for 1,4-(ethynylphenyl)phenylene (**a**).

The very small molecular admittance of the MRTD at low voltages can be easily explained by the frontier orbitals (Figure 4) where, for charge $Q = 0$, there is clearly no connection of the LUMO between the two terminals of the molecule (**c**). This is very different than the case of the planar unsubstituted (**a**) where the LUMO provides the connection to the two terminals. This was also the case of the tolane molecule[28] and this is the case for these types of unsubstituted oligomers. The presence of the $NO_2$ and $NH_2$ substituents in the central ring modifies the characteristic admittance of the molecule. Figure 4 shows that the torsion of the central ring of the MRTD (**c**) does not affect the localized nature of its LUMO. On the other hand, (**c**) bends in the direction of its dipole moment created by the opposite position and function (push−pull) of the nitro and amine substituents. Note that all molecules, both planar and rotated, as well as their neutral and their negative ion forms, were fully optimized without any geometrical constraints, using the built-in defaults in the program Gaussian-94. For the molecules reported here, the geometry optimization of the planar

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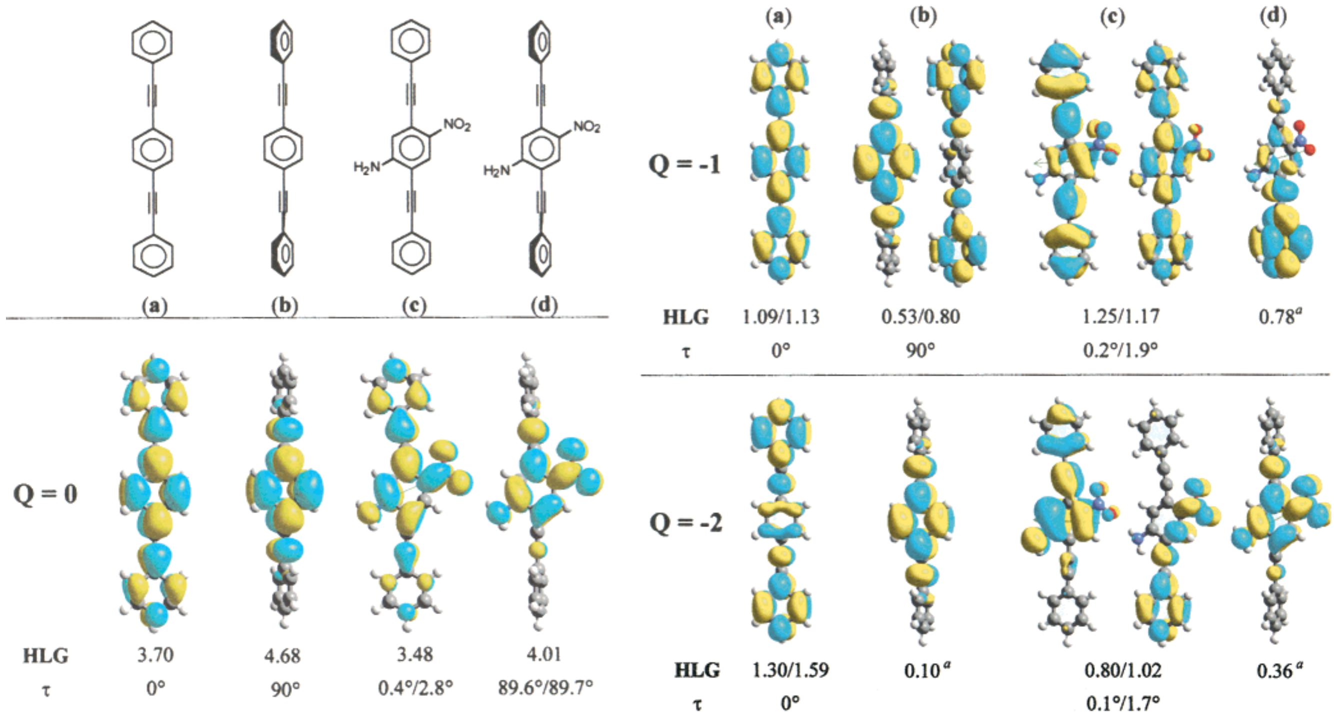

**Figure 4.** LUMO plots, HLG energies (in eV), and torsion angles for the optimized neutral and for the vertical and adiabatic structures of the anions. Only one LUMO is shown if the vertical and adiabatic shapes are similar. The torsion angle ($\tau$) between the top and the central rings is indicated first followed by the angle between the central and the bottom rings (only one angle is shown when both are identical) for all optimized structures. For those structures designated with a super *a*, only verticle HLG is shown because the structure becomes planar during the optimization.

and rotated structures was initiated with dihedral angles of approximately 20° and 110°, respectively. Local minima were found around 0° and 90°, respectively. In all cases, it was found that the planar structures were more stable than the rotated ones.

The most interesting feature, observed in the experiment,[1] was the sudden decrease in current at a given voltage. An explanation of the complex behavior of this system (MRTD) follows. Figure 4 shows the four cases studied: the unsubstituted (**a** and **b**) and substituted (**c** and **d**) molecules, planar (**a** and **c**) and rotated (**b** and **d**), for charges 0, $-1$, and $-2$, their corresponding HLG energies, and their LUMO orbitals. For the negative ions, we show the corresponding vertical and adiabatic results. When two LUMOs are showed, the first one corresponds to the vertical case, i.e., the LUMO obtained using the geometry of the optimized neutral, and the second one corresponds to the adiabatic case, i.e., the LUMO obtained using the optimized geometry of the negative ion. The cases where the perpendicular structures for the ions did not converge and the geometry ended up in the corresponding planar structures are indicated in Figure 4. This is the case of the molecule (**b**) with charge $-2$, and molecule (**d**) with charges $-1$ and $-2$. The torsional angles $\tau$ for the fully optimized structures are also indicated. The first one corresponds to the angle between the top and central rings, and the second one corresponds to the angle between the central and bottom ring. If the two torsion angles are identical only one value is shown.

In the unsubstituted molecule (**a**), the HLG changes as it becomes charged, having the lowest gap for charge $-1$. However in the rotated (**b**) case, the lowest gap occurs for charge $-2$. In both cases the gap is maximum for 0 charge. For the unsubstituted case, the charge of the molecule does not change the shape of the LUMO orbital. As seen, the LUMO is totally delocalized for the planar configuration (**a**) and connects the two ends of the molecule. In the case of the rotated configuration (**b**), the LUMO is localized in the central ring and therefore it is not connecting both ends of the molecule. Similar to the case of the tolane molecule,[28] the rotated molecule (**b**) can be catalogued as an insulator and the planar (**a**) as a conductor. The geometry optimizations indicated that as (**b**) gets charged to $-2$, it becomes planar. The presence of the $NO_2$ and $NH_2$ substituents totally changes some of these features. Now the planar case (**c**) has some degree of localization; its LUMO does not cover the lower ring for 0 charge. In this case, we expect a partially conducting system with high molecular impedance. However, as the MRTD (**c**) becomes charged to $-1$, the LUMO orbital extends over the two ends of the molecule, yielding maximum transport. When **c** becomes charged to $-2$, again its LUMO does not connect both ends. Actually, one of the rings gets totally disconnected, bringing the molecular admittance to zero. Although the LUMO shapes are different for the vertical and adiabatic cases of both charged species of (**c**), the nature from localized to delocalized or vice versa does not change. The three regions for charge 0, $-1$, and $-2$ are indicated in Figure 1. Figure 4 also shows the rotated substituted molecule (**d**) where the LUMO never connects the two ends of the molecule. When uncharged, the LUMO localizes in the central ring, as in the case of the unsubstituted molecule. With charge $-1$, the LUMO localizes in one of the external rings, and with charge $-2$ the LUMO again localizes in the central ring. Notice also that the rotated structure (**d**) for charges $-1$ and $-2$ tends to become planar during the geometry optimization. This was also the case for the unsubstituted (**b**) with charge $-2$, suggesting that charging the molecules will tend to planarize them.

The above discussion agrees entirely with our original proposal that the conduction is through the LUMO, thus conduction depends on the LUMO spatial extent and on the HLG. In a first approximation, the barrier for transport of electrons will be half of the HLG. Therefore, we can predict that at 0 K the molecule will not conduct for voltages smaller than 1.74 V, which is the barrier corresponding to charge 0 in the molecule. Once the molecule becomes charged by one electron upon reaching 1.74 V, the LUMO extends over the whole molecule and the conduction will occur, increasing the current until the molecule becomes charged with two electrons. The charge of −2 in the molecule will take place when the input voltage increases another 0.63 V, which corresponds to half the HLG of the molecule charged to −1. At this voltage, 2.37 V, the LUMO corresponding to charge −2 in the molecule gets localized, thereby becoming disconnected from the lower ring, as indicated in Figure 4, with a concomitant current drop to practically zero.

Since the presence of the sulfur atom does not affect either the HLG or the LUMO, on the basis of the results in Figure 4, we can speculate on the temperature dependence of the peak voltage. Notice that the relative rotation of the rings on the neutral molecule tends to increase the gap by about the same amount that the relative rotations reduce the gap when the molecule is charged to −1. These values, using the vertical energies, are +0.53 and −0.47 eV, respectively, for a 90° torsion of the central ring with respect to the other two rings. The torsional barrier from the neutral (**c**) to the neutral (**d**) is 3.4 kcal/mol; therefore, we expect the relative rotations to be only a few degrees at most. Therefore, as temperature increases, we expect a decrease of the HLG if the molecule is charged to −1. Consequently, a reduction of the peak voltage is expected. This explains qualitatively the peak found around 2.1 V at a temperature of 60 K and it is also consistent with the experimentally observed reduction in peak voltage. This is important because it provides us an avenue to produce amplification using single molecules, i.e., the ability to control the peak voltage or barrier (on the order of eV) using small torsional energies (on the order of meV). On the other hand, to make devices able to work at higher temperatures, all that is needed are similar molecules with higher torsional barriers, which can be imposed intra- or intermolecularly.

## Conclusions

We have performed an ab initio molecular study to explain a resonant behavior of a molecule when an external voltage between its two ends is applied. These studies require knowledge of the precise geometry of the system, which can be determined by quantum chemistry techniques. The principal assumptions taken in this study are that the conduction is through the LUMO, and that the HLG determines the conduction barrier. Under these assumptions, the MRTD behavior of the molecule can be quantitatively explained and the temperature effect on the voltage at the current peak can be qualitatively rationalized. A quantitative temperature study will require molecular dynamics simulations, which must be based on a sound description of the atomistic geometry of the nanopore. Finally, this study provides a straightforward use of well-developed ab initio techniques for the nascent field of molecular electronics. These results could have a tremendous impact because of the large variety of molecules available and the ability to tailor specific characteristics, resulting in a practically infinite number of distinct possible molecular electronic devices.

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