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Molecular Resistance in a Molecular Diode: A Case Study of the Substituted Phenylethynyl Oligomer

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Theoretical calculations are carried out to understand the geometric and electronic properties of the 4-nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine molecule, which has been demonstrated to behave like a resonant tunneling diode under an external bias voltage. Results from density functional and Hartree−Fock theory show conflicting planar and nonplanar ground-state geometries, respectively. To underscore the effect of the molecular conformation on the electronic structure of the molecular devices, the potential energy surface of this molecule was calculated under the rigid rotor model. The results suggest that even a small perturbation can lead to a significant increase in the energy gaps between the highest occupied and lowest unoccupied energy levels. The electronic transport behavior in this molecule is analyzed from the electronic structure and spatial orientations of the molecular orbitals.

Introduction

The field of molecular electronics, for which electron transfer is controlled from an external electric field, has been indisputably one of the most rapidly developing areas of the past decade. A number of groups have synthesized structures proposed as molecular wires and have also demonstrated their ability to conduct electricity.[1−6] The extraordinarily small size of molecular devices offers advantages beyond the simple ability to pack more of them into a small area. Certain quantum mechanical phenomena arising from electrons confined to the space of atoms or molecules can be exploited in specially designed molecules to perform desired functions. For example, to construct a molecular wire, we need an elongated molecule through which electrons can flow easily from one end to the other. The incoming electrons move through an unoccupied orbital that is dispersed throughout the molecule. A typical empty, low-energy electron orbital is the π-orbital. Normally, a conjugated system provides a path where electron clouds overlap between molecular components so that electrons can hop from one to another. A molecular wire can thus be constructed by combining π-conjugated molecular units.

The task of a molecular electronics engineer is to design a molecule whose orbital characteristics achieve the desired electronic control. For example, when the orbital overlaps are disturbed by twisting the molecule or by doping the molecules with electron-withdrawing or electron-donating groups, the smooth electron flow is blocked. The molecule can then be used as a switch. Two types of molecular-scale electronic diode switches, molecular rectifying diodes[7−8] and molecular resonant diodes,[9] have been demonstrated experimentally. A diode is a two-terminal switch consisting of a source and a drain where current can be turned on or off depending on the direction of the flow. A rectifying diode adopts electronic structures that allow the currents to flow in one direction while preventing flow in the other. In a resonant tunneling diode, current can flow equally in both directions. However, the process of switching the current “on and off” could take place due to the alignment of the quantized energy levels or a change in the molecular conformation under an external bias.

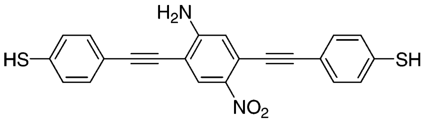

Figure 1. Molecular structure of the molecular diode discussed in this work. The central benzene ring is substituted by -NH$_2$ and -NO$_2$ groups.

Recently, Chen et al.[10] have shown through experiment that a single molecule (shown in Figure 1) can behave as a resonant tunneling diode or a device with negative differential molecular impedance. The resonance effect for electron tunneling has been observed at a 2.1 V bias with a peak current of 1 nA. The molecule consists of three benzene rings connected to each other by acetylene groups. The central benzene ring is substituted by -NO$_2$ and -NH$_2$ groups on opposite sides. This asymmetrical configuration makes the molecule susceptible to change in its configuration under an external field. Seminario et al.[11] calculated the electronic structure of this molecule by density functional theory. However, details of the conformational analysis and energetics were not reported.

Various theoretical investigations of conjugated organic molecules have demonstrated the importance of correlation effects. The traditional method of accurately calculating the electronic properties of a molecule is to first perform a Hartree−Fock (HF) calculation followed by computation of electron correlation effects by many-body perturbation theory.[12] Alternatively, density functional theory (DFT) has provided another way of estimating the correlation effects at a lower computational cost.[13]

In the present work we have performed a systematic theoretical study of this molecular diode starting from its smallest subunit benzene and building to the complete molecule. The results are arranged as follows. First, to set the background, we present the results for the individual benzene, aniline, and

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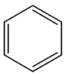
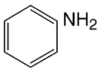
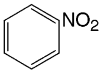
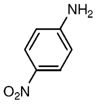
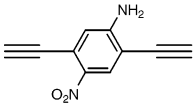
TABLE 1: HOMO, LUMO, and HLG (HOMO − LUMO) Energy States of the Small Molecular Subunits of the Molecule Shown in Figure 1

	HOMO (eV)	LUMO (eV)	HLG (eV)
Benzene 	-6.97	-0.25	-6.72
Aniline 	-5.57	-0.35	-5.22
Nitrobenzene 	-7.95	-2.91	-5.04
4-nitro-phenylamine 	-6.54	-2.39	-4.14
2,5 diethynyl–4-nitro-phenylamine 	-6.58	-2.76	-3.82

nitrobenzene molecules. In the second part we show the results for the properties of 4-nitrophenylamine and 2,5-diethynyl-4-nitrophenylamine, which represent the central part of the molecular diode shown in Figure 1. The effects of the different substituent groups are discussed. Geometry optimization of the complete 4-nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine is discussed in the next section. We compare Hartree−Fock, density functional, and second-order perturbation theory results for this molecule. In section 4, we discuss the molecular resistance with respect to different conformations. This is calculated from the potential energy surface by use of the rigid rotor model. Finally, the electronic transport behavior of this molecule is illustrated from the electronic structure and the spatial shape of the frontier molecular orbitals.

Computation Details

All of the calculations described in this work were performed with the Gaussian 98 program.[14] The geometries of all small systems were optimized at the density functional level by use of the B3PW91 hybrid functional[15−17] and the 6-311G all-electron valence triple-ζ basis set augmented with polarization functions on all atoms. Some calculations also include additional diffuse functions. To understand the correlation effects on the ring torsion angles, optimizations of the complete molecular diode were performed at the HF, post-HF, and DFT levels.

Results

1. Electronic Structures of Benzene, Aniline, and Nitrobenzene. The geometries of benzene, aniline, and nitrobenzene were optimized to understand the effect of the substituent groups on the benzene rings. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, as well as the HOMO−LUMO gaps, are shown in Table 1. The effect on the molecular energy levels of benzene depends on the type of substituent attached. For example, in the case of the -NH_2 group, the energy levels increase, and for the -NO_2 group, the energy levels decrease as compared to benzene. This effect is attributed to the increase or decrease in the electron density as an electron-donating (-NH_2) or electron-withdrawing (-NO_2) group is attached. Interestingly, in both cases the HOMO−LUMO gap (HLG) decreases. This decrease in the HLG is important, as the midpoint of the HLG is assumed to be aligned with the Fermi levels of the metal contacts. Therefore, it can be anticipated that substitution by electron-donating or electron-withdrawing groups can reduce the molecular impedance of benzene. The bond lengths and the angles between the ring carbon atoms adjacent to the substituent groups are distorted. The optimized geometries and the energetics of these three molecules were compared with experiment[18] and the good agreement reflects the reliability of these calculations.

Structural optimization of these molecules at the HF level does not lead to significantly different geometries. The HOMO−LUMO gaps, however, are aphysically large because the HF LUMOs tend to be unbound. This has also been seen in other molecular diode calculations[19] and is typical of HF theory.

2. Structural Analysis of 4-Nitrophenylamine and 2,5-Diethynyl-4-nitrophenylamine. To address the detailed electronic structure of 4-nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine, we have first optimized the geometries of 4-nitrophenylamine and 2,5-diethynyl-4-nitrophenylamine. In the equilibrium structure of 4-nitrophenylamine all atoms from the substituents (-NH_2 and -NO_2) occupy the same plane as the molecular backbone. Small changes in the geometry of the adjacent carbon atoms of the substituent groups occur depending on the nature of the functional groups attached. The bond lengths of the carbon atoms (C−C = 1.41 Å) attached to the -NH_2 group are more elongated than the carbon atoms (C−C = 1.39 Å) adjacent to the -NO_2 group as well as the C−C bond (1.38 Å) without a substituent. The C−N bonds are 1.36 and 1.45 Å for carbon attached to the -NH_2 and -NO_2 groups, respectively. The corresponding C−N bond lengths in aniline and nitrobenzene are 1.38 and 1.47 Å, respectively.

Table 1 summarizes the energetics of this molecule. Substitution of donor and acceptor groups further decreases the difference between the HOMO and LUMO energy levels compared to benzene and the monosubstituted molecules. The dipole moment of the disubstituted molecule is significantly higher than those of the monosubstituted molecules. For example, while nitrobenzene and aniline have dipole moments of 4.90 and 1.82 D, respectively, 4-nitrophenylamine has a dipole moment of 8.32 D. The higher dipole moment reflects greater asymmetry in the charge distribution of the disubstituted molecule, thereby making it more susceptible to change in its electronic structure under an external field.

Extending the molecule by the addition of two acetylene groups does not affect the molecular structure of the central ring. The C−C bond distance between two C atoms of the acetylene group is 1.2 Å. As seen in Table 1, the HLG is reduced to 3.82 eV.

3. Electronic Structure of 4-Nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine. The geometry of 4-nitro-2,5-bis-(4-mercaptophenylethynyl)phenylamine was optimized by the HF and DFT methods. Interestingly, while HF calculations lead to a twisted geometry for the ground-state structure, DFT calculations result in a planar configuration. In HF the end ring close to the -NH_2 group is twisted by about 33°, while the DFT planar configuration is consistent with that obtained by Seminario et al.[11] This twist is quite important because the HOMO level of the twisted configuration does not span the length of the molecule and thus would not be conducting. Supposing that the difference in the geometrical configuration is most likely due to correlation effects, we performed Møller−Plesset second-order perturbation (MP2) calculations on the HF and DFT optimized geometries. The results show that the DFT geometry is 1.76 kcal/mol (0.075 eV) more stable than the HF geometry. Further optimization of the HF structure at the MP2 level results in a more planar configuration, in which the central ring is rotated 17° from the end phenyl ring closer to the -NH_2 group and 9° from the other ring. Because of the difference between the HF and MP2 results, we cannot say that the post-HF structure is converged with respect to correlation effects; time-consuming calculations including higher orders of perturbation would be required to confirm this. The present results, however, do demonstrate the importance of including correlation to predict the correct ground-state configuration of this kind of system. This can be done most efficiently with hybrid functionals.

4. Conformational Analysis of the Molecular Diode. In this section we discuss the molecular resistance from the variation in the HOMO and LUMO energies when one of the terminal phenyl rings is rotated. The difference in the HOMO and LUMO energies (HLG) is used as a parameter to define the molecular resistance. It is known that for tolane systems the rotational energy barrier is significantly small; however, such small barriers can produce large resistance by increasing the HLG in the twisted configuration.[20] For the tolane molecule the HLG for the planar configuration is 4.44 eV while the rotated one has a HLG of 5.45 eV. This indicates a significant change in the conduction characteristics by a small perturbation in the total energy.[21]

These results further prompted us to investigate the potential energy surface of the 4-nitro-2,5-bis(4-mercaptophenylethynyl)-phenylamine molecule by use of a rigid rotor model under density functional theory. These calculations were done in two parts. In the first case we have rotated the end phenyl ring closer to the -NH_2 group. The step size for the rotation was 15°. In the second set we have rotated the other end ring closer to the -NO_2 group with the same step size. Figure 2 shows the total energy variation as a function of the rotation angle. From this figure it is clear that the rotational energy barrier is higher for rotation of the phenyl rings closer to the -NO_2 group than the -NH_2 group. While the planar configuration of atoms represents the most stable structure, the highest potential barrier is found for the perpendicular configurations; however, the rotational energy barrier is very small. The maximum energies required for the rotation of the phenyl rings closer to the -NH_2 and -NO_2 groups are 0.752 and 2.65 kcal/mol, respectively.

Further, we have estimated the molecular gain with respect to the rotation of one phenyl ring closer to the -NH_2 or -NO_2 group. The gain is defined as the ratio between the difference in HLG values of two states and the difference in their corresponding total energies. Figure 3 shows that the gain is higher when the phenyl ring closer to the -NH_2 group is rotated, signifying increasing resistance from a small perturbation in energy.

5. Electron Transport. To understand the electronic transport through this molecule we have analyzed the shape of the frontier molecular orbitals calculated under a DFT framework. We assume that the molecular admittance is the highest for the lowest unoccupied orbital that spans the entire length of the molecule. It is found that the lowest unoccupied orbital that is delocalized over the molecule is the LUMO+2 level. Figure 4 shows the spatial orientation of the frontier molecular orbitals. To a first approximation it is assumed that the chemical potential of the molecular diode attached with a metal electrode is aligned at the half between the HOMO and LUMO energy levels of the free molecular diode.[11] Therefore, the threshold energy for electron transport in these molecules can be calculated from the difference between HOMO and the lowest unoccupied orbital connected across the molecule. The difference between LUMO+2 and HOMO is 4.95 eV and therefore an applied voltage of 2.48 V is estimated for electronic transport. The corresponding experimental value is 2.1 V.[9] The difference between the experimental and theoretical values can be attributed to the fact that the theoretical system is ideal and the electronic structure corresponds to the ground-state geometry at 0 K, and the molecule is not attached to a substrate. Moreover, it has been observed that the presence of metal electrodes can change

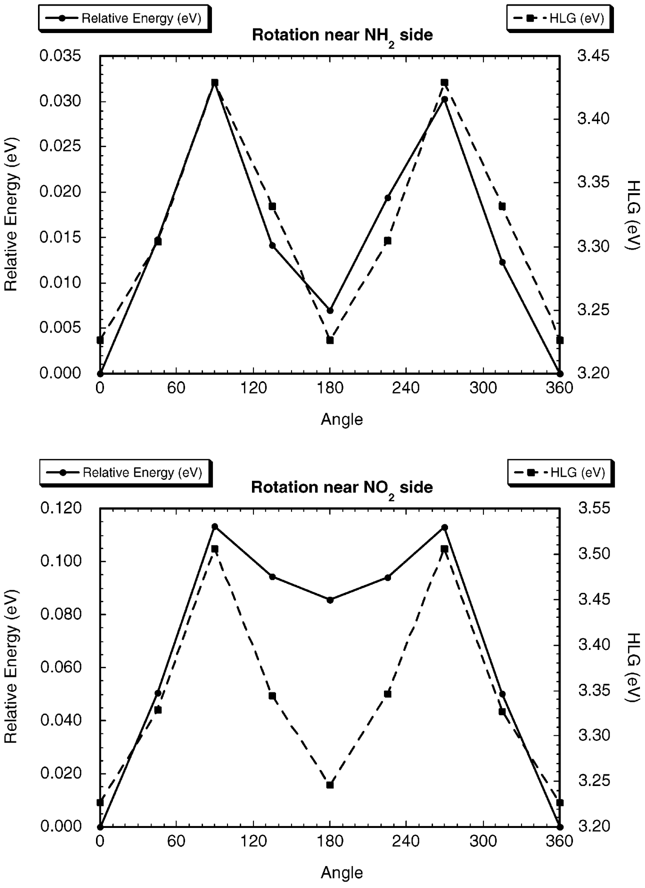


Figure 2. Potential energy surface of the molecular diode as a function of rotation angle of the phenyl rings.

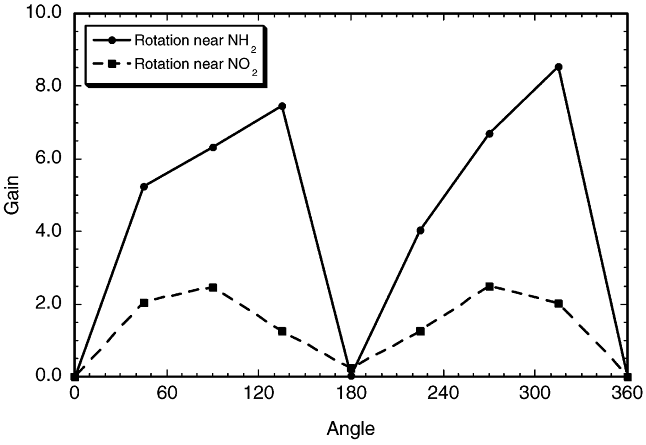


Figure 3. Gain curve of the molecular diode as a function of rotation angle of the phenyl rings.

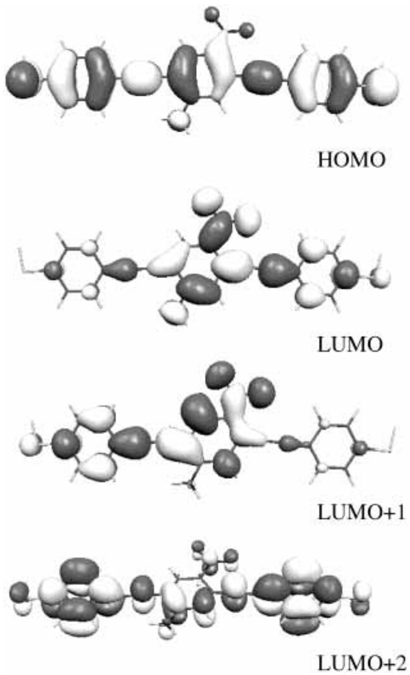


Figure 4. Spatial orientations of the HOMO and LUMO energy states of the molecular diode.

the energetics for such molecules with large dipole moments.[22] Therefore, further studies are required to understand the electron transport of this molecule considering experimental conditions.

Conclusions

Systematic geometric and electronic structure calculations were carried out for the 4-nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine molecule at the HF, post-HF, and DFT levels of theory. From the results the following conclusions can be made:

1. Significant differences between HF and DFT results for the ground-state structure of the 4-nitro-2,5-bis(4-mercaptophenylethynyl)phenylamine molecule were obtained. While HF predicts a twisted structure, more planar configurations were found from the MP2 and DFT calculations. This indicates exchange-correlation energies play an important role in the equilibrium structure.
2. The potential energy surface calculated from the rigid rotor model indicates a small perturbation can lead to significant increase in the HLG. This leads to higher molecular resistance or increasing threshold energy for conduction.
3. The electron transport through this molecule calculated from the orbital orientation shows reasonable agreement with experiment.

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