

Theoretical Interpretation of Switching in Experiments with Single Molecules

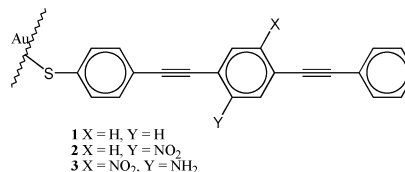
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Thus far, two mechanisms have been determined to be responsible of the changes in impedance of single molecules: the relative motion of the molecule internal structures,^{1,2} and changes in the molecule charge states.^{2,3} Recently, an experiment involving scanning tunneling microscopy (STM), to which we refer hereafter as the experiment, reported conductance switching in phenylene ethynylene oligomers isolated in matrices of dodecanethiolate monolayers.⁴ The oligomers analyzed in the experiment are shown in Scheme 1. The molecules were inserted into a self-assembled dodecanethiolate matrix on a Au surface. The three oligomers showed conductance bistability, and it was reported that the substituents in molecules **2** and **3** were not a determining factor in their conductance switching. The molecule environment within the matrix is considered to play a critical role in the switching. The experiment suggests that restricting conformational changes through environmental arrangements reduces switching between the on and off states, since a well-ordered matrix reduces the rate at which switching occurs, while a poorly ordered matrix yields a much more frequent switching. We suggest that rotations of the oligomers take place by a mechanism similar to earlier nanopore studies featuring devices with almost linear behavior.^{1,2} This is a mechanism different from charge transfer, which is the main mechanism for switching indicated in recent nanopore studies featuring devices with nonlinear characteristics.^{2,3,5} However, the experimental evidence demonstrates that the switching behavior of these molecules persists on a much longer time scale (a few hours) than that expected from the predicted rotation barrier.⁶ According to earlier calculations,^{1,3,7} the rotational barrier of one ring with respect to another adjacent in the oligomer is ~ 1 kcal/mol. When this barrier is used in molecular dynamics simulations of these molecules assembled on Au surfaces at 300 K, we obtain rotational frequencies of 390.6 GHz, corresponding to a switching cycle of only 2.56 ps (picoseconds) for a molecule isolated from its neighbors. Our argument is that longer switching rates are expected because steric effects when neighbor molecules are very close to each other forming a complex. To show quantitatively this argument, we calculated the rotational barrier of one ring with respect to the other in tolane, when it is forming a complex with an undecane. We find that the torsional barrier increases from 1 kcal/mol for the isolated tolane molecule to 38 kcal/mol for the tolane–undecane complex. Therefore, considering an exponential relation of the transition rate, $\tau \propto \exp(\Delta E/kT)$, with respect to the energy barrier, ΔE , the switching time is predicted to be ~ 50 million years for the rotation on one ring with respect to the other in the complex tolane–undecane. This supporting calculation should be used just to understand how rapidly the rotation (switching) period changes with changes in the barrier height yielding a range from picoseconds to millions of years for the possible switching rates when the monomers are totally separated and when they are forming a complex, respectively. Therefore, we can say that the packing density of the SAM affects the switching rates by several orders of magnitude and effectively

Scheme 1



explain the much longer scales observed in the experiment. On the other hand, the height of the STM tip above the molecule was an indicator of the conductance; since the STM was operated at constant-current mode, the height of the tip is directly related to the molecule conductance. The height occurrence distributions showed bimodal behavior in the conductance, making it possible to estimate on/off ratios. Both experimental and theoretical studies concur in that high conductance is only possible when all the rings in the molecule are aligned. Yet, this condition by itself does not warrant high conductance. On the other hand, a change in the charge state does not necessarily yield switching and cannot be observed unambiguously above the top benzene ring. We use the B3PW91/LANL2DZ level of theory in Gaussian 98,⁸ to calculate the electronic density and the molecular electrostatic potentials (MEP) to explain the relationship between theoretical and experimental results. The MEP is a well-proven tool for the analysis of several aspects of molecular systems,^{9–11} and recently it has been proposed as a medium for information coding in molecular circuits.^{12,13} Figure 1 shows 2.2 V MEP isosurfaces for **3** at three charge states. The MEP isosurface was chosen to be almost the minimum potential in the neutral state. The volume inside this surface increases as the charge increases but not uniformly, being the increase more pronounced in the perpendicular direction rather than along the molecular axis.

Table 1 shows that the net charge on the anion and dianion concentrates mainly on the NO₂ and SAu groups, practically not affecting the H at the top of the molecule. This is confirmed from Figure 2, where the MEP is color-coded on an isodensity surface, chosen to intersect the small surface of isopotential (Figure 1) close

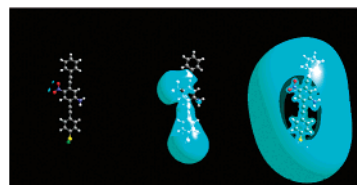


Figure 1. MEP isosurfaces at $V = 2.2$ V for **3** when $Q = 0$ (left), $Q = -1$ (center), and $Q = -2$ (right).

Table 1. Mulliken Populations on Selected Groups of **3**

state	S-Au	NO ₂	NH ₂	top H
neutral	0.1	-0.4	0.0	0.2
anion	-0.4	-0.5	-0.1	0.2
dianion	-0.7	-0.8	-0.1	0.2

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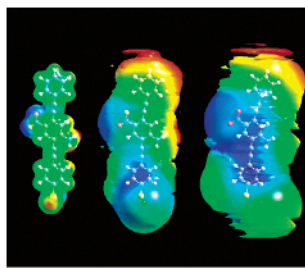


Figure 2. MEP color-coded on constant ρ isosurfaces of **3**. (Left) $Q = 0$, $\rho = 0.02$, MEP from -2.2 (blue) to 3.2 (red). (Center) $Q = -1$, $\rho = 10^{-5}$, MEP from -2.5 (blue) to 3.3 (red). (Right) $Q = -2$, $\rho = 10^{-6}$, MEP from -3.7 (blue) to -2.0 (red). MEP in V, ρ and Q in au.

to the NO_2 of the neutral. This is not precisely accomplished for the dianion since the electron density values needed are below the calculation threshold, but an isosurface at 10^{-6} e/Bohr³ already shows the indicated trend.

Frontier MOs (HOMO, LUMO, and a few in their neighborhood) fully delocalized along the whole molecule, make the molecule conductive.^{2,14} On the other hand, localized frontier orbitals yield lower conductance. Charge states rendering a nonconductive molecule show most of the frontier orbitals localized; however, some of them can show slight delocalization, leading to a low but nonzero current. However, a perpendicular conformation of at least one ring with respect to another results in the impossibility of having fully delocalized MOs, yielding a very low conduction state.

Molecules **1** and **2** were found to conduct in their neutral charge state when theoretically analyzed.^{2,3} Since the bias voltage range used in the experiment makes both molecules remain uncharged during the whole experiment, only conformational changes intervene in the switching process. In this way, either molecule **1** or **2** switches to the low conductance state when the rings become perpendicular, and the conductance switches to high when the rings are parallel.

The experiment also reveals that **2** can be turned off when the applied voltage is increased to 3 or 4 V, and theory shows that it is nonconductive when its charge is -1 ; thus, when a high voltage is applied, **2** gets charged and stops conducting. However, **1** does not show switching, and it is always conducting as long as its rings are parallel; therefore, according to our theoretical analysis, a higher applied voltage would not have yielded switching in **1**.

Theoretical calculations³ and other experimental results⁵ showed that **3** is nonconductive when neutral, and conductive when charged. The observed switching for this molecule in the experiment is due to changes from the nonconductive (when compare to its anion) planar conformation to the perpendicular conformation, which is even less conductive than the nonconductive planar. MO analysis shows that the HOMO for the neutral is mostly localized in the central ring but with slight contribution from the external ring, rendering a low but nonzero conductance.^{2,3} Rotating the central ring fully localizes all the frontier orbitals.^{2,3}

Although the STM can track the changes in the molecular conductance of the oligomers, whether the reason for the switching is a change in conformation or a change in the charge state cannot be unambiguously established, because the STM is not able to determine a change in charge state, except when a simultaneous change of molecule conductance occurs. The electron density and the electrostatic potential along the direction of the top CH bond in the upper ring for the three charge states shows no significant differences between themselves when compared to their corresponding charge density and MEP along the NO_2 directions, suggesting that charging the molecule does not necessarily change, the position of the tip, which remains at the same height, regardless of the charge state of the molecule.

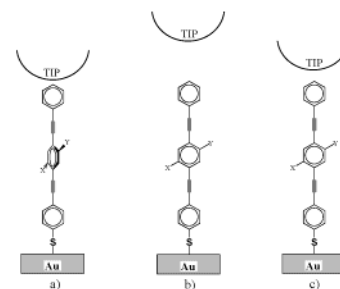


Figure 3. Conductance states: (a) Rotated conformation, the STM tip is in its lowest position, high impedance. (b) Parallel conformation and low impedance charge state; the STM tip is on its largest height. (c) Parallel conformation with high impedance charge state, the STM tip could be in an intermediate point. One Au atom on each end is used to represent the interface to the bulk surface and STM tip. Notice that, when we mention molecule conductance, we imply the extended molecule, i.e., the molecule and one or more atoms from the contacts, thus actually dealing with the junction.

The three cases shown in Figure 3 correspond to the possible cases that can be identified and distinguished with the technique used in the experiment: (a) rings in a nonplanar conformation, whereby irrespective of the charge state, the molecule keeps a low conductance since charging can change the shape of the MOs but it is not able to delocalize them; thus, the STM tip is at its lowest height; (b) rings in a planar conformation and low impedance charge state (the molecule has its largest possible conductance, and the tip is at its highest point); (c) rings in a parallel conformation and high impedance charge state so that the conductance for the molecule can be as low as case (a) or higher, depending on how many MOs remain delocalized and what are their energies with respect to the energy of the injected electrons. Certain molecules in (c) are of intermediate conductance, and switching between (a) and (b) can be observed.

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