When Things Are Not as They Seem: Quantum Interference Turns Molecular Electron Transfer "Rules" Upside Down

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A variety of acyclic cross-conjugated molecules[1] have been synthesized,[2] and they have physical properties that differ from their linearly conjugated counterparts.[3] Here, we address another consequence of this difference: the breakdown of the conventional trends in molecular electron transfer.

In the last half-century, understanding of molecular electron transfer[4] has advanced significantly. From this body of knowledge, three "rules of thumb" for trends in rates of electron transfer can be deduced: (1) Increasing molecular length leads to decreasing rate. (2) Transport through a fully conjugated bridge is greater than through a saturated bridge. (3) A larger energy difference between the donor and acceptor energy levels and the bridge levels leads to decreased electron transfer rates. These rules of thumb are not universal; however, significant deviations are not widespread and provide insight into novel phenomena.

This understanding of electron transport is also applied more generally to predict the behavior of molecules bound to electrodes in place of the donor and acceptor. The link between theories that describe these two regimes has been documented.[5] Importantly, chemical trends are common among these methods. We proceed in the electron transport regime; however, the conclusions that are made apply equally to intramolecular electron transfer. These results are based on Landauer conductance calculations, ignoring electron correlation, and may fail when resonances are approached.

We calculate the transport through three systems shown in Figure 1. We consider two different binding orientations either through the red group (the "short" system) or through the green group (the "long" system). These systems are compared with 1,5-dithiopentane (dtp), a saturated molecule with the same length carbon chain as the short system. Using the rules of thumb for electron transport we would expect that conductance would scale as dtp < long < short.

The molecular geometries were obtained by optimizing the isolated molecule in the gas phase using Q-Chem 3.0[6] with density functional theory using B3LYP,[7,8] and 6-311G**. The molecules were chemisorbed (terminal hydrogens removed) to the fcc hollow site of a Au(111) surface with the Au−S bond length taken from the literature.[9] The electronic structure and transport calculations were performed using gDFTB.[10–12]

The molecular orbital spectrum of the isolated molecules is shown in Figure 2, with the gold Fermi energy at −5 eV. The short and long molecules have a conductance point group[13] of C_s and dtp of C_{2v}, allowing the molecular orbitals to be separated into A′ and A″ symmetry groups, shown in black and red, respectively. The A″ orbitals constitute the π-system of the short/long system. The striking disparity between the conjugated and saturated systems is the size of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The fully delocalized HOMO and LUMO common to the short and long systems are also shown in Figure 2, with no indication of a difference in the electronic character of the two paths.
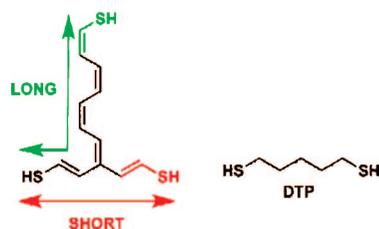

Figure 1. The "long" and "short" systems are defined as two different methods of attaching the molecule on the left to two gold electrodes. In both cases one electrode is attached to the thiol group shown in black; the long system utilizes the thiol shown in green, and the short system uses the thiol shown in red. These are compared with dtp (right).
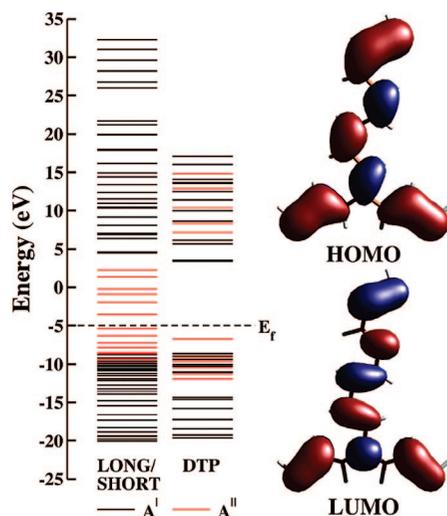

Figure 2. The molecular orbital eigenenergies for the isolated molecules (left) show the large band gap typical in the saturated system and the much smaller gap in the conjugated systems. The gold Fermi energy is shown for comparison. The HOMO and LUMO of the short/long system (right) show delocalization across all three arms, giving no indication that there should be any difference between the different paths beyond their differing length.

Figure 3 shows the transmission and current through these three systems, the important feature to note is the dip in the transmission through the short system (red) close to the Fermi energy, controlling the low bias current. These unexpected results show that near the Fermi level the transport scales as dtp < short < long. The expectation is that transport through a conjugated molecule will be dominated by high levels of transmission through the π-system (A″). This is not the case for the short system, as a consequence of a large (destructive) interference feature near the Fermi energy. In fact, the σ-system transport dominates in the trough created by this interference feature.[14]

Interference features have been documented for other molecules[15] and in model system calculations.[16–18] What is unusual about the
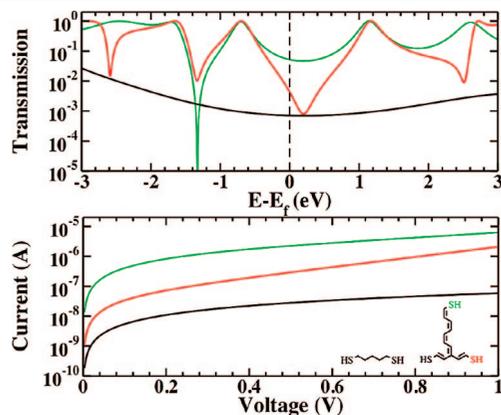
Figure 3. The transmission (above) and current (below) through the long system (green), short system (red), and dtp (black). The dramatic differences between the long system and the short system cannot be predicted from conventional understanding of molecular electron transfer.

short system, and similar molecules, is that there is an interference feature close to the Fermi energy and it is broad and deep. Interference features will not always occur as predicted by model system calculations and in almost all other molecules occur outside the measureable range. The only other documented systems to exhibit a similar destructive interference features are cyclic systems: meta-substituted benzene rings[19–23] and cyclic cross-conjugated systems.[24]

The implications of these results can be clarified by an examination of each of the three rules of thumb. First, there are different path lengths through a similar molecule: the short and long paths through the same conjugated molecule. Conventional understanding would suggest that transmission through the short system should be much higher than that through the long system; however, the opposite trend is observed. Here, increasing length results in increasing current.

Second, the differences in transmission through conjugated and saturated bridges can be examined. Unexpectedly, close to the Fermi energy the transmission through the short system is only slightly greater than the transmission through dtp. Indeed, there are cross-conjugated molecules that have lower transmission than molecules of the same length with saturated groups in the conduction path.[25] While in this case dtp does have lower transmission than the short system, the difference between the two is not nearly so large as would be expected. Further, if the Fermi energy of the electrodes occurred in the trough of the interference feature, as in other cases,[14] the two systems would exhibit very similar behavior at low voltage.

Finally, there is a comparison of the transmission through two systems with the same energy gap, the long and short systems. By virtue of comprising the same molecule, the molecular resonances for the long and short systems are energetically very close. Dtp on the other hand has a much larger energy gap. Usually, this would indicate that the transmission through the long and short systems would be similar. Again, this is not the case. The energy of the frontier molecular orbitals fails to predict the difference in the current and transmission through the short and long systems.

These results clearly show how the established rules of thumb for understanding patterns in molecular electron transfer will not always hold. Quantum interference is often present in transport through molecules; however, it is rarely manifest as the dramatic destructive interference features seen here. The critical difference between the two paths is that the short system is cross-conjugated[1,2] and the long system is linearly conjugated. Cross-conjugated molecules represent an interesting class of molecules where interference effects are dominant and persist even in the presence of the geometric changes anticipated under ambient conditions.[25]

The rules of thumb will continue to be of primary importance for understanding the properties of the great majority of systems. It is important to realize, however, how they can fail. Quantum interference, can have a substantial and unexpected effect both on the electron transfer properties of systems and the breakdown of conventional understanding from a simple barrier tunneling picture.[26] The vast dimensions of chemical space may yet yield more surprises to challenge our understanding of molecular electron transfer and, thereby, show us new opportunities for both understanding nature and building electronic devices of the future.

Supporting Information Available: Complete ref 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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