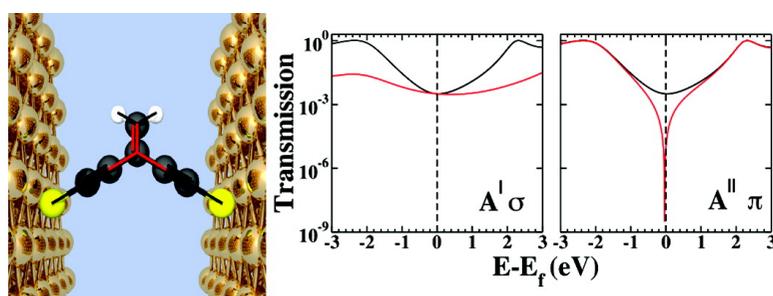


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Quantum Interference in Acyclic Systems: Conductance of Cross-Conjugated Molecules

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Abstract: We calculate that significant quantum interference effects can be observed in elastic electron transport through acyclic molecules. Interference features are evident in the transmission characteristics calculated for cross-conjugated molecules; significantly, these effects dominate the experimentally observable conduction range. The unusual transport characteristics of these molecules are highlighted through comparison with linearly conjugated and nonconjugated systems. The cross-conjugated molecules presented here show a large dynamic range in conductance. These findings represent a new motif for electron transfer through molecules that exhibit both very high and very low tunneling conductance states accessible at low bias without nuclear motion. In designing single molecule electronic components, a large dynamic range allows a high on/off ratio, a parameter of fundamental importance for switches, transistors, and sensors.

1. Introduction

The pioneering work of Marcus^{1,2} and Hush^{3,4} paved the way for today's understanding of molecular electron transfer. Understanding electron transfer and biological mimics led to the proposal that single molecules could be utilized in the design of components for electronic devices.⁵ Nature's ingenuity in generating and controlling so many different biological processes through electron transfer suggests that the vast dimensions of chemical space would yield promising candidates for molecular electronics. The inspiration that can be drawn directly from nature is somewhat limited, however, as synthetic variants of the large protein structures which regulate electron transfer may not be a feasible design architecture for electronic devices. To date, investigations of molecules for electronic applications have predominantly focused on a small subset of conjugated molecules and comparisons with their saturated counterparts. The rationale for using conjugated molecules is that the high rates of electron transfer they are known to facilitate in donor-bridge-acceptor systems will lead to high currents when they are bound in transport junctions. This is borne out in the measurements made on such systems: relatively high conductance is observed over the measurable range.⁶ For electronic functionality such as switching, logic, memory, or sensing, however, it is necessary to have both high and low conductance states. Large perturbations are required—for example, conformational change^{7–10}—to shift conjugated molecules to a low conductance state, resulting

in slow switching times. For many applications, the device performance could be improved if the switching could be induced by electronic changes alone.¹¹ Without looking to the complex molecules nature uses to achieve fast and slow rates of electron transfer, we can instead look to alternative chemical functionalities with more complex conductance characteristics.

1.1. Barrier Tunneling Models. Despite the complex quantum nature of electron transport through molecules, previous studies have suggested that charge transport in the off-resonant Landauer-Imry regime can be described by modeling the molecule as a tunneling barrier. There has been considerable success using a simple Simmons model,^{12–16} where the barrier height can be controlled by the energy separation between the Fermi energy of the electrode and the closest molecular energy level. So long as the barrier tunneling model holds, it is necessary to utilize other physical processes to induce any sort of diversity in a molecule's transport properties.^{17–19} Recent interest in this area has focused on conformational change,

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vibrational motion, and electron correlation to induce more dynamic conductance characteristics in molecules. This is not to suggest that the barrier tunneling model encompasses all of the complexities of these systems; indeed, there has been extensive work to examine the subtleties of molecular conduction and the processes it comprises. The success of the single-barrier tunneling model does, however, provide a metric for determining when a molecule's conduction characteristics are simply another example of the behavior already observed in simple conjugated and saturated molecules. In this article we will use this metric and will infer from the breakdown of the barrier tunneling model that a new motif in molecular electron transfer is being accessed.

1.2. Quantum Interference. In mesoscopic systems, a diverse range of conductance characteristics have been predicted and observed. The quantum nature of transport in these systems is readily apparent, exemplified by the prediction^{20,21} and observation^{22–24} of Aharonov–Bohm oscillations in the transport through a variety of systems. Quantum interference is not limited to cyclic structures and has been seen in T-shaped semiconductor nanostructures^{25–27} and predicted in arrays of quantum dots.^{28–31} The observation of these distinctly quantum phenomena in mesoscopic systems requires electron coherence lengths that are much greater than the molecular scale; nonetheless, this has not resulted in analogous effects being readily observed in molecular electron transport. At the nanoscale, the conditions required for the observation of quantum interference have been described in terms of the spatial requirements on the wave function;³² however, it is not clear what sorts of chemical functionality will lead to these conditions being met in the experimentally observable range.

Quantum interference has been predicted in the transmission characteristics of Hückel models, designed to represent molecular systems.^{33–43} In such models, the interference features are dramatic and in many cases dominate the spectrum; however,

when density functional theory calculations are employed, the results may not be nearly so stark as the model systems might suggest.^{38,41} The model system calculations seem to predict many interference features where none are observed, bringing into question which sorts of chemical functionalities really will exhibit measurable interference effects. The best known exception to this is the marked differences in the transmission characteristics of derivatives of benzene depending upon whether the connection to the electrodes is through the meta or para positions. These differences have been seen experimentally^{44,45} and have been discussed theoretically.^{37,39,44,46,47}

In this article, we take inspiration from the quantum interference observed in mesoscopic systems and present a class of acyclic molecules with properties distinctly different from those previously investigated. Previous descriptions of quantum interference in cyclic molecules focused on the idea that different spatial paths were responsible for the interference features,^{37,39,43} suggesting that such interference would be unlikely in acyclic structures. Here we show that interference features in acyclic molecules can be understood with reference to two different concepts: first, the descriptions developed for alternant hydrocarbons provide a natural basis to understand zeros in the coupling in both cyclic and acyclic structures; second, the concept of nonspanning nodes in the wave function,³² while inapplicable for cyclic molecules, provides a very useful description for acyclic molecules.

We show that there is a low-bias regime where the simple Simmons model breaks down and transmission through the molecule can no longer be correlated simply with the relative positions of the molecular resonances. Consequently, very striking conductance characteristics are obtained through coherent tunneling alone, not by geometric changes, stochastic motion, or vibronic effects. Molecular devices that function through the modulation of coherent transport are highly desirable, as they will have fast and reproducible performance characteristics. We show that the interference features arise from antiresonances (not from a simple break in conjugation), that they are robust to thermal motions, and that they provide very strong switching behavior with increasing voltage.

1.3. Calculation Details. All molecular geometries were obtained by optimizing the isolated molecule in the gas phase using Q-Chem 3.0⁴⁸ with density functional theory using the B3LYP functional^{49,50} and 6-311G** basis. The gas-phase molecules were chemisorbed (terminal hydrogens removed) to the face-centered cubic hollow site of a Au(111) surface with the Au–S bond length taken from the literature.⁵¹ All transport calculations shown here were performed using gDFTB^{52–54} unless otherwise stated. No gold atoms were included in the extended molecule so that the symmetry of the molecule could

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be used to separate the transmission into σ and π components.⁵⁵ The electrode comprised a 4×4 atom unit cell with six layers in the transport direction, and periodic boundary conditions were used. Transport calculations were also performed using density functional theory (ATK)^{56–59} and Hückel-IV 3.0,⁶⁰ giving similar results (included in the Supporting Information).

Throughout this paper we will focus on zero-bias transmission, as this is where the interference features are most evident and the most straightforward to interpret. Naturally, such interference features are of significant interest only if their effects can be seen in observable quantities such as current and conductance. The importance of cross-conjugated molecules is that the interference features seen in the transmission have a considerable impact on the low-bias current. In the Landauer–Imry limit, the current is given by^{61–64}

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE \text{Tr}[\Gamma_L(E)G^r(E)\Gamma_R(E)G^a(E)](f_L(E, V) - f_R(E, V)) \quad (1)$$

where $G^{r(a)}$ are the retarded (advanced) Green's functions for the molecule or extended molecule, $\Gamma_{L(R)}$ are twice the imaginary component of the self-energies for the left (right) electrodes, and $f_{L(R)}$ are the Fermi functions for the left (right) electrodes. The zero-bias transmission is given by the trace in eq 1, computed with no applied bias. These results are based on Landauer conductance calculations, ignoring electron correlation, and may fail when resonances are approached.

2. Cross-Conjugated Molecules

Early work⁶⁵ provides a definition of a cross-conjugated compound: “a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other.” Molecules containing this functionality are well known,^{66–68} and electronic delocalization in these systems has been studied.^{69,70} Whether a molecule is cross-conjugated or linearly conjugated can simply be a matter of where the connections to the source and drain (or donor and acceptor) are made. Figure 1 shows that the manner in which a central ethylene unit is connected to the source and drain can change if the bridge between the two is viewed as cross-

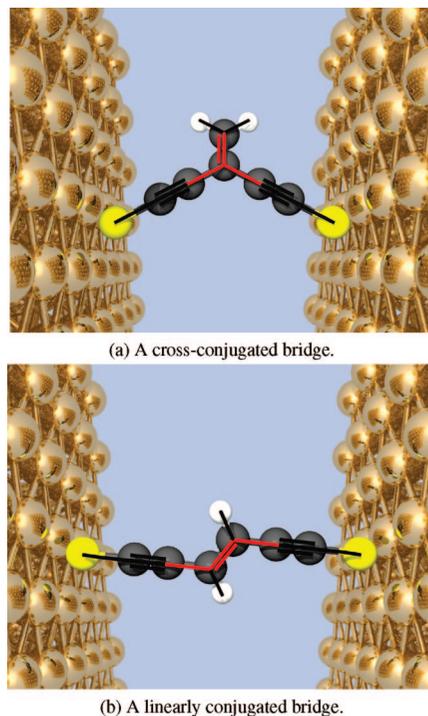


Figure 1. The bonding geometry of a molecule bridging source and drain electrodes controls whether the bridge is cross-conjugated (a) or linearly conjugated (b).

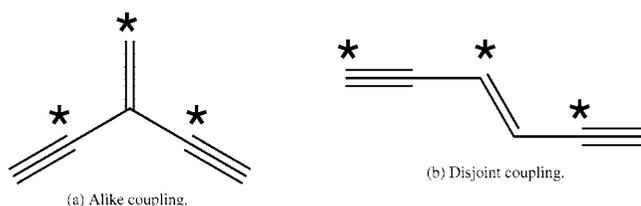


Figure 2. Assignment of atoms to starred and unstarred sets for the basic cross-conjugated and linearly conjugated units: (a) alike and (b) disjoint coupling.

conjugated or linearly conjugated. Figure 1a can be interpreted in terms of the definition above by considering the two triple-bonded ethynylene units as the two unsaturated groups not conjugated to each other; the third unsaturated group is simply the central ethylene unit.

The electronic coupling through these molecules can be understood in simple chemical terms, as they are both even alternant hydrocarbons and there has been extensive work on the properties of such systems.⁷¹ Alternant hydrocarbons are molecules in which each neighboring conjugated carbon atom can be marked with or without a star and no two starred or unstarred atoms are bonded to each other. This assignment is shown in Figure 2 for the two basic units underlying the cross-conjugated and linearly conjugated systems. When these molecules are bound to two electrodes, as shown in Figure 1, the essential difference between linear conjugation and cross-conjugation arises because of the different character of the resulting points of attachment. Figure 2 shows that, for cross-conjugated systems, there is alike coupling (the attachment is made to two unstarred atoms). For the linearly conjugated system, the coupling is disjoint (the attachment is made to one

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starred and one unstarred atom), although this will not always be the case with multiple even numbers of subunits.

From early work on even alternant hydrocarbons, it is known that there is orbital pairing.^{72–74} That is, for every occupied orbital there is a matching virtual orbital; these form symmetric pairs above and below the midpoint of the HOMO–LUMO gap (midgap), and the forms of these orbitals differ only in the phase on the starred atoms. The coupling through a molecule can be related to the molecular orbital coefficients,⁷⁵ and it can be deduced that the midgap coupling is zero for alike coupling.^{76–78} Cross-conjugated paths always involve alike coupling, and linearly conjugated paths always involve disjoint coupling; consequently, it is anticipated that the midgap π coupling through cross-conjugated paths will go to zero, while it will be nonzero for linearly conjugated paths.

This approach can also be used to explain the different properties of meta (alike)- and para (disjoint)-substituted benzene,⁷⁷ and similarly for larger aromatic structures. It suggests that the symmetry in the electronic structure, orbital pairing, is responsible for zeros in the electronic coupling of organic molecules rather than spatially separated transmission paths. It also provides a link to other descriptions of quantum interference which focused on orbital^{46,79,80} or wave function-type³² components, leading to the cancelation responsible for the interference features.

Low electronic coupling has been observed experimentally for cross-conjugated molecules,^{81,82} calculated for cyclic cross-conjugated systems,⁸³ and reported in our recent work on the transport of acyclic systems.⁸⁴ This previous work has focused on the behavior of these systems close to the midgap, where it is simply concluded that cross-conjugated systems had very low coupling and linearly conjugated systems had high coupling. Here, we continue from that work and elucidate some of the consequences of the distinctly different electronic properties of cross-conjugated and linearly conjugated systems as an applied voltage allows us to probe the behavior away from midgap.

2.1. Transmission through Small Molecules. At the simplest level, the effects of the cross-conjugated functionality can be seen by comparing the transmission through 3-methylenepenta-1,4-diyne-1,5-dithiol (**1**, cross-conjugated) with that through (*E*)-hexa-3-ene-1,5-diyne-1,6-dithiol (**2**) and (*Z*)-hexa-3-ene-1,5-diyne-1,6-dithiol (**3**), both linearly conjugated. Figure 3 shows

the transmission through these three molecules separated by symmetry into the σ and π components.⁵⁵ In each case, the red curve gives the σ or π component and the black curve shows the total transmission (given by the sum of the σ and π transmissions). The cross-conjugated orientation of **1** introduces the distinct antiresonance near the Fermi energy in the π component of the transmission, resulting in a number of interesting consequences.

First, at the Fermi energy, the transmission through a shorter five-carbon chain (**1**) is only a small fraction (~6%) of the transmission through the six-carbon chains (**2** and **3**). This occurs despite the fact that all are conjugated molecules and is in stark contrast with the usual trend that transmission decreases with increasing bridge length. Second, the transmission resonances occur at approximately the same energy in all three molecules, yet there is a substantial difference in the transmission at energies between the resonances, again contrasting with the usual trend that transmission at the Fermi energy can be correlated with the energy gap between molecular orbitals. Finally, in fully conjugated molecules, it is generally assumed that, at low bias, conduction is dominated by transport through the π system; however, in the case of **1**, it is in fact the σ system which dominates the transport close to the Fermi energy. Barrier tunneling models assume¹⁵ that the energetically proximate molecular resonances will dominate the transmission, but this is clearly incorrect when the σ transmission is the dominant component at the energies closer to the π orbitals of the system. These unusual features in the zero-bias transmission lead to a large difference in the calculated current/voltage characteristics. Throughout the low-bias region, the current through **1** is substantially lower than in either of the two linearly conjugated systems. This is again an unexpected result, given that all three molecules are conjugated and **1** is shorter than the linearly conjugated molecules. The unusually low transmission and current for **1** are consistent with the weak coupling reported when cross-conjugated systems are used to bridge between electron donor and acceptor moieties.⁸² Together, the unusual transport characteristics of **1** point to a new motif for molecular electronics: conjugated molecules with low conductance near the Fermi energy due to an antiresonance.

The attribution of these unusual conductance characteristics to quantum interference needs to be addressed in more detail. The interference feature, an antiresonance, exists here only in the π system transmission close to the Fermi energy. Antiresonances can be viewed as the opposite of a transmission resonance, with the transmission coefficient going to zero. One condition for the appearance of antiresonances in transmission is the presence of nonspanning nodes in the wave function.³² That is, the number of nodes in the wave function will increase with increasing energy, but in 2D or 3D systems the number of nodes found along the path between the electrodes (or the donor and acceptor in chemical systems) need not increase. In the case of cross-conjugated molecules, this is exactly what happens between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as shown in Figure 4. In all cases, the number of nodes in the system increases from two to three; however, the new node is a nonspanning node for **1** alone. Importantly, this condition will not be met in the experimentally observable range for branched linearly conjugated systems, as is evident in the transmission calculations in previous work.³⁸ Further, this condition cannot

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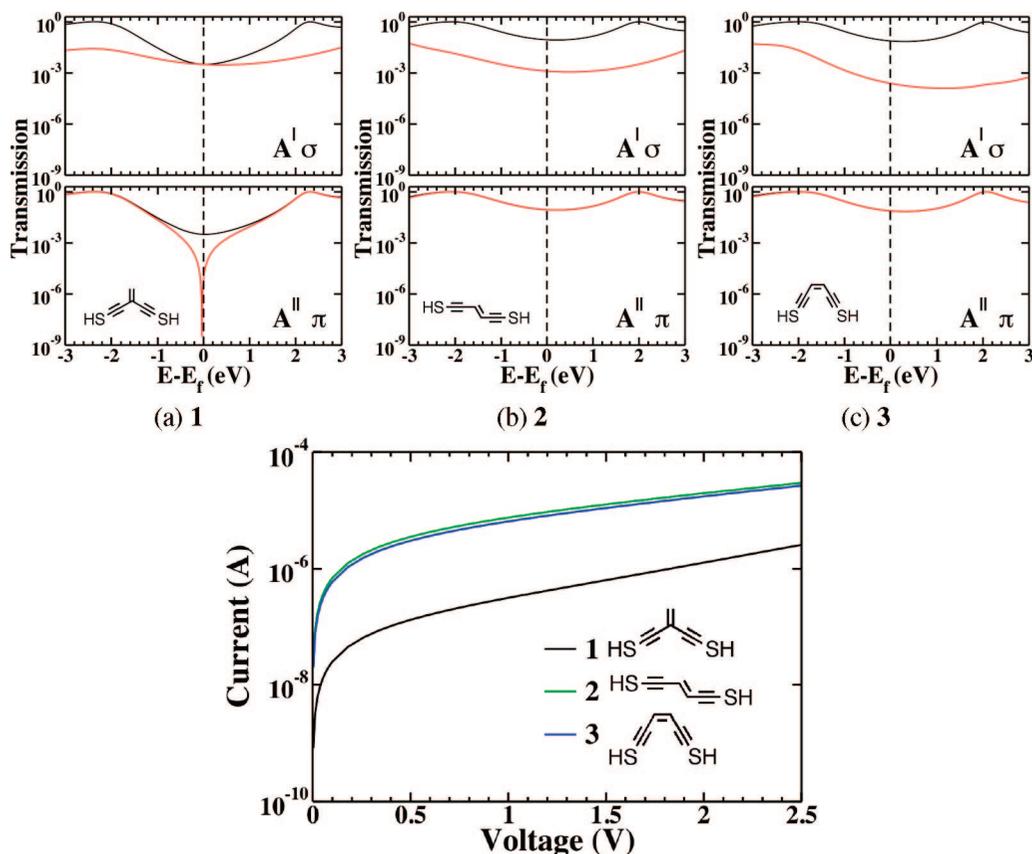


Figure 3. Transmission and current through a cross-conjugated molecule (**1**) compared with its linearly conjugated counterparts (**2** and **3**). In each case, the total transmission is shown in black and the component through either the σ or π system is shown in red. The cross-conjugated system has an antiresonance in the π transmission near the Fermi energy, providing a local minimum in the transmittance, in contrast with the high level of transmission through the linearly conjugated systems.

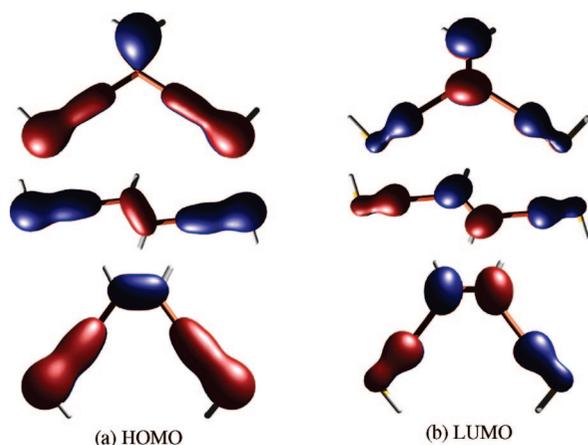


Figure 4. HOMO (left) and LUMO (right) for **1** (top), **2** (middle), and **3** (bottom), showing that a nonspanning node in the π system is introduced only in the case of the cross-conjugated species.

be used to describe the interference features in phenyl rings,^{37,39,44–47} as all nodes are “spanning nodes” in a cyclic system.

It is interesting to note how these results relate to Hückel model calculations on branched structures. In these calculations, only the π system is considered, and **1** would be considered to be a branched structure with five sites in the backbone and one in a side chain. Model system calculations have not readily provided the distinction between cross-conjugated and linearly conjugated bridges but rather suggested there was a dependence

on whether the length of the side chain was odd or even.³⁴ This result can be recovered with the observation that it is possible to have a fully conjugated molecule with an odd-length side chain only when the path between the electrodes is cross-conjugated or the molecule is a radical. Model system calculations can also predict that interference features will be observed where none occur in the real molecule calculations, as detailed in the Supporting Information.

In a real molecule, in contrast to a model system where only the π system is described, the total transmission will not go to zero at an antiresonance unless the antiresonance exists in all symmetry components of the transmission. In the case of cross-conjugated molecules, the antiresonance close to the Fermi energy is in the π system, which would otherwise be the majority component of the total transmission. Consequently, the minority component of the transmission close to the Fermi energy, the σ component, then dominates and defines the “floor” of the dip in the total transmission. The antiresonance arises from the unusual transport characteristics coming from the central ethylene unit (shown in the Supporting Information); the ethynylene groups simply act as conjugated spacers. Significantly, this means that the ethylene unit can be connected to any number of spacer groups and still maintain its function: it is a local effect.

2.2. Larger Systems. The effect of the antiresonance is mitigated in **1** due to the magnitude of the σ transport near the Fermi energy. This can, however, be reduced by increasing the length of the molecule, and numerous extended cross-conjugated systems⁶⁸ are suitable candidates. One such class of molecules

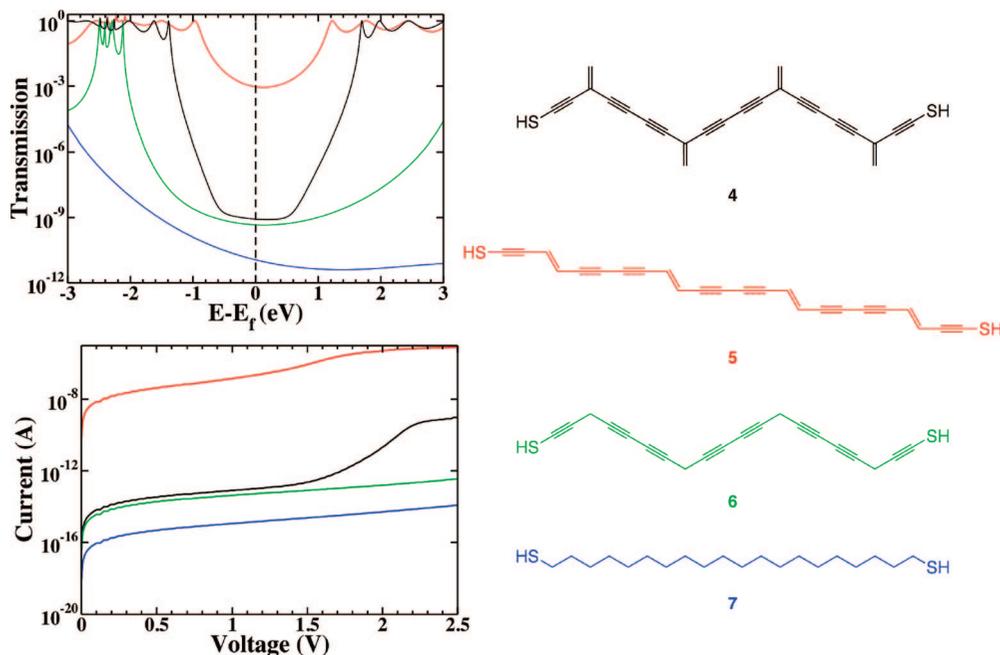


Figure 5. Zero bias transmission as a function of energy, and current as a function of voltage, for a group of comparable molecules, illustrating the unusual transport characteristics of a cross-conjugated system. Specifically, an extended cross-conjugated molecule (**4**) is compared with its linearly conjugated counterpart (**5**) and with a partially conjugated (**6**) and a saturated (**7**) system of the same length.

are the iso-polytriacylenes:⁶⁶ these molecules are rigid, conjugated systems of variable length comprising multiple cross-conjugated units. Reducing the transmission through the σ system is critical in order to make the dramatic effects of interference experimentally observable.

To illustrate just how unusual the transmission characteristics of cross-conjugated molecules can be, we compare **4** with its linearly conjugated counterpart **5**, the partially conjugated **6**, and the nonconjugated **7**, as shown in Figure 5. These molecules were selected to facilitate the comparison of their transport characteristics: **4**, **6**, and **7** all have the same number of carbon atoms in the backbone (20), and **5** is a structural isomer of **4**.

The linearly conjugated system, **5**, has the highest transmission close to the Fermi energy, despite having the longest backbone. This result would be expected from the conventional wisdom in a comparison with **6** and **7** alone. What is unexpected, however, is the 6 orders of magnitude difference in the transmission at the Fermi energy between **5** and **4**, both fully conjugated molecules. In the region exceeding 1.5 eV above and below the Fermi energy, the molecular resonances in **4** are most similar to those in **5** because both have dominant π system transport that is strongly coupled to the electrodes. But close to the Fermi energy, the transmission in **4** resembles that in **6**, where the conjugation is broken with saturated groups throughout the backbone. The comparison with **7** illustrates how the low-voltage transmission through **4** is, in fact, closer to a fully saturated alkane than it is to a linearly conjugated molecule such as **5**. The substantially longer length of these molecules compared with those shown in Figure 3 results in the σ system transport being orders of magnitude lower at the Fermi energy. Consequently, the “floor” of the dip in transmission at the π system antiresonance in **4** is dramatically lower than it was for smaller systems, and a much greater dynamic range in transmission is accessible.

While these results might appear more dramatic if the transmission through the cross-conjugated species dropped below that of the comparable alkane, the fact that it does not is

an important result from a practical standpoint. Measuring the conductance of one molecule, or even a small number of molecules, is a very difficult experiment, and the signal-to-noise ratio will always be an important consideration. Alkanedithiols of varying lengths have been studied extensively in this area and exhibit measurable conductance.⁶ For a given cross-conjugated molecule, the characteristics of an alkane of the same length will constitute a lower bound to its conductance, providing a simple metric to determine whether it is expected to be within the measurable range.

The potential applications for cross-conjugated molecules can be envisaged from the dramatic current/voltage features also shown in Figure 5. Over the 2.5 V range considered, the current through **4** increases by ~ 5 orders of magnitude; in particular, between 1.5 and 2.0 V, the current increases by 2 orders of magnitude. Such dramatic changes in the current over such a modest voltage range make this a promising candidate for a molecular switch, with a potentially low operating bias and a large on/off ratio. Further, the breadth of the class of cross-conjugated molecules⁶⁸ means that the position and depth of the antiresonance feature can be tuned by chemical substitution, leading to even more promising characteristics. By varying the switching mechanism, cross-conjugated molecules could become promising candidates for many electronic devices.⁸⁵

2.3. Cross-Conjugation versus Broken Conjugation. It is important to note that the effects of cross-conjugation (**4**) are not simply the same as those of breaking conjugation (**6**), despite the similarity in their representation as two adjacent single bonds in the conduction path. The single bonds in the cross-conjugated system, **4**, are still part of a conjugated path whereas the single bonds in **6** are not, and this has a significant impact on the transport characteristics. The transmissions through **4** and **6** are shown in Figure 6, and the character of the π system transport highlights the difference between these two systems. The

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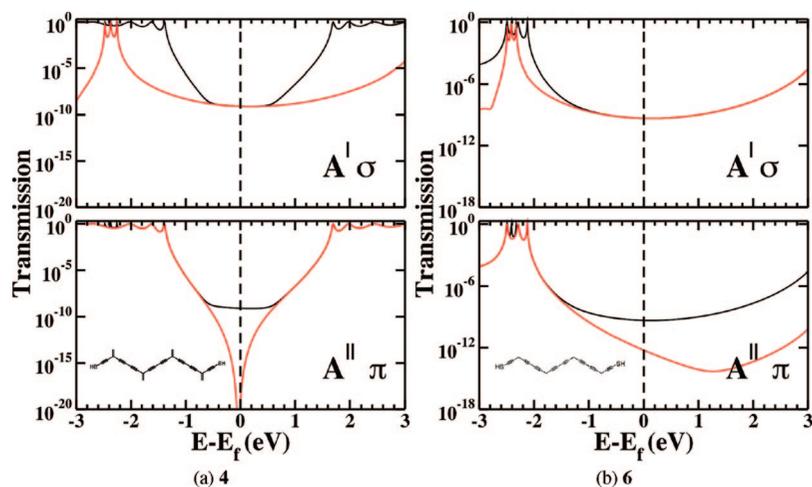


Figure 6. Transmission through **4** compared with **6**, both separated into their σ and π system transport by symmetry. In each case the total transmission is shown in black and the component through either the σ or π system is shown in red. The cross-conjugated system has an antiresonance in the π transmission near the Fermi energy, providing a local minimum in the transmission, in contrast with the low, broad transmission through the π system of **6**.

antiresonance in the cross-conjugated system is absent in **6** and is replaced with low transmission over a much larger range. Without the abrupt transition from low transmission to high transmission seen for cross-conjugated molecules, a molecule such as **6** does not have the same potential for diverse range of electronic functions.

The symmetry-separated transmission shown in Figure 6 also makes evident the similarity between the features in **4** and **1**. In both cases an interference feature exists in the π system transport close to the Fermi energy, and consequently the σ system transport dominates. It is clear that the general features of the transmission are common among all the cross-conjugated molecules discussed here; however, the magnitude of the σ system transport dramatically changes what can be seen in the total transmission.

3. Stability

The feasibility of molecular quantum interference devices rests in part on the stability of the conductance characteristics. Two modes might be envisaged by which thermal effects could destroy the interference; however, in both instances this is precluded by the small size of the functional component, the ethylene unit, and the resulting locality of the effect. First, previous work has shown that, if sufficiently fast, pure local dephasing is capable of destroying interference.^{86–88} However, the effects of dephasing are dependent on the length scale of the system. The strongest indications that dephasing will not be a problem in cross-conjugated molecules are the room-temperature experimental measurements of the low level of electronic communication through meta-substituted benzene, a comparably sized system whose transmission is dominated by a large destructive interference feature.^{44,45}

Second, conformational flexibility could affect the conductance characteristics, as a real measurement will not be made on the perfectly symmetric optimized geometries. The antiresonance in molecule **4** is present when thermal motion is accounted for by using the geometries obtained from a molecular dynamics

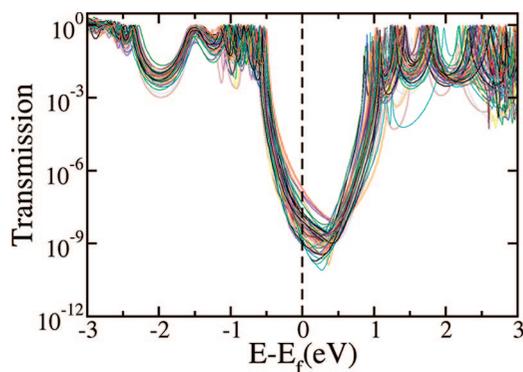


Figure 7. Transmission through **4** for 50 different geometries obtained from molecular dynamics calculations. Importantly, the antiresonance is present in all cases.

simulation completed using Tinker.⁸⁹ The last 50, 1-ps snapshots of the 1-ns simulation are used as input files for Hückel IV. Figure 7 shows the transmission obtained from the 50 molecular geometries. In the geometric space sampled through molecular dynamics, the antiresonance remains. Again, as the interference feature arises solely from each small, rigid ethylene unit, the antiresonance should be stable at ambient temperature.

4. Conclusions

The conductance characteristics of cross-conjugated molecules are distinctly different from those of both the linearly conjugated and saturated systems that have been explored to date. This difference can be seen clearly, as the properties of cross-conjugated molecules cannot be explained with the barrier tunneling models which previously afforded so much success. These properties arise from the fundamental nature of the central ethylene unit in a cross-conjugated path and the prediction of a zero in the through-molecule π -coupling in the HOMO–LUMO gap. When cross-conjugated molecules are bound to metallic electrodes, instead of donor and acceptor units, the rich transport properties of these systems can be uncovered. Linearly conjugated systems exhibit high conductance throughout the measurable range, and saturated systems exhibit low conductance.

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Cross-conjugated systems display low conductance at low bias voltages (near midgap) but then transition to high conductance with increasing voltage. Cross-conjugated molecules owe their high conductance state to the π system transport, characterized by broad transmission resonances, as this system couples strongly with the electrodes. The low conductance state arises from σ system transport, which is characteristically low at the Fermi energy and dominates the transmission spectrum only because quantum interference nearly destroys transmission in the π component. Cross-conjugated functionalities represent the first class of substituents that follow the predicted spatial requirements on the wave function for the observation of interference features³² in acyclic systems, in the experimentally observable range. The properties of cross-conjugated molecules are controlled by local interactions at the central ethylene unit, allowing them to be seen in systems with a variety of different substituents and making them stable under geometric fluctua-

tions. The crossover from low to high conductance as a result of electronic changes alone represents a new transport motif in single molecule electronics.

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Supporting Information Available: Calculation details, transmission through the basic cross-conjugated unit, a comparison of three transport codes, the differences between calculations on model systems and real molecules, and complete ref 48. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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