

Aromaticity Decreases Single-Molecule Junction Conductance.

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Supporting Information

ABSTRACT: We have measured the conductance of single-molecule junctions created with three different molecular wires using the scanning tunneling microscope-based break-junction technique. Each wire contains one of three different cyclic five-membered rings: cyclopentadiene, furan, or thiophene. We find that the single-molecule conductance of these three wires correlates negatively with the resonance energy of the five-membered ring; the nonaromatic cyclopentadiene derivative has the highest conductance, while the most aromatic of this series, thiophene, has the lowest. Furthermore, we show for another wire structure that the conductance of furan-based wires is consistently higher than for analogous thiophene systems, indicating that the negative correlation between conductance and aromaticity is robust. The best conductance would be for a quinoid structure that diminishes aromaticity. The energy penalty for partly adopting the quinoid structure is less with compounds having lower initial aromatic stabilization. An additional effect may reflect the lower HOMOs of aromatic compounds.

Conjugated organic oligomer wires have formed the building blocks of organic electronics and photovoltaics.¹ One basic component in these wires is an aromatic unit, such as a benzene or thiophene unit.² From a chemical perspective, these ring systems are more stable than noncyclic analogues due to the delocalization of electrons within the ring. This additional stability of the aromatic system is measured by resonance energy or aromatic stabilization energy. The greater the resonance energy for a unit, the more stable the system is. For example, a benzene ring gains a (negative) resonance energy of 36 kcal/mol, as the electron cloud of benzene is more delocalized than that of a noncyclic system with three single and double bonds.³ Previous measurements with acenes had shown that the central ring of anthracene was a better conductor than one ring of naphthalene, which was a better conductor than a benzene ring.⁴ One explanation for this finding was that the central ring of anthracene was the least aromatic, while benzene was the most aromatic. However, these acenes also had different numbers of electrons in the π -systems, so a direct correlation between conductance and aromatic character of the molecular wires was not unambiguous.

Here we study the correlation between conductance and aromaticity in a single-molecule junction containing five-atom

cyclic units and use resonance energy as a measure of its aromatic character. We compare conductance through a thiophene, furan, and cyclopentadiene species. Cyclopentadiene has 4π electrons in a conjugated system and is nonaromatic. Furan and thiophene both have 6π electrons cyclically delocalized. Because the cyclopentadiene does not have a cyclic conjugated system, it is nonaromatic, while the furan and thiophene are both aromatic with resonance energies of 16 and 29 kcal/mol, respectively.^{3,5} We expect that the conductance will be greatest for the five-membered unit that is least aromatic as it can most easily acquire a quinoid structure, as illustrated in Figure 1A.⁶ In this form, a better coupling between the Au

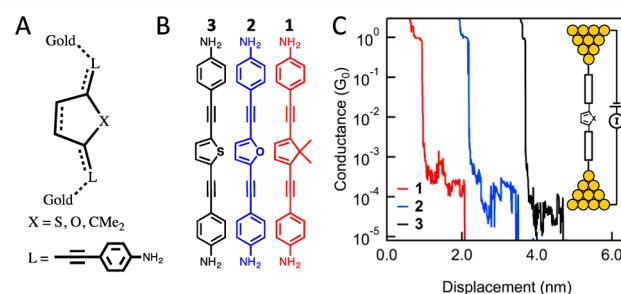


Figure 1. (A) Illustration of the quinoid structure that maximizes conductance across a five-membered ring. (B) Structure of the three molecular wires investigated. (C) Sample conductance traces measured for 1, 2, and 3 at a bias voltage of 225 mV. Inset: Schematic of a single-molecule junction.

electrodes and the cyclic unit is achieved (the dashed double C–C bond is shortened as shown in Figure 1A). With the nonaromatic cyclopentadiene, achieving the quinoid structure does not cost any stabilization energy, in contrast to furan or thiophene where such increased external π -character decreases aromaticity.

We use the scanning tunneling microscope-based break-junction (STM-BJ) technique⁷ to measure the conductance of a series of three molecular wires (Figure 1B) that have a cyclic five-member unit built into backbones. These three amine-terminated molecular wires (Figure 1B): 1,4-bis(4-aminophenylethynyl)-5,5-dimethylcyclopenta-1,3-diene (1), 2,5-bis(4-aminophenylethynyl)furan (2), and 2,5-bis(4-aminophenylethynyl)thiophene (3) are synthesized following procedures detailed in the Supporting Information document

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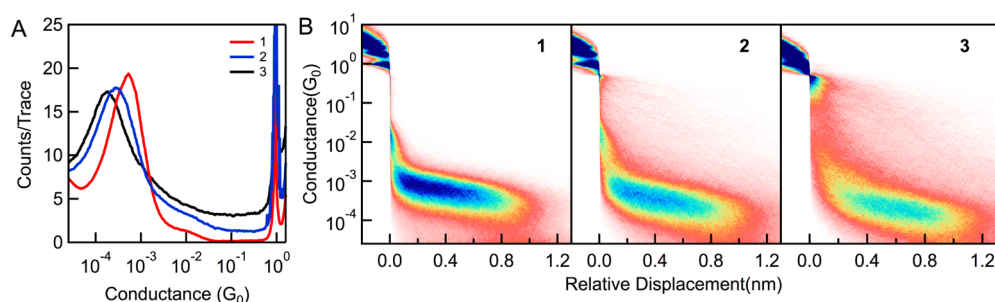


Figure 2. Log-binned one-dimensional conductance histograms for molecules 1, 2, and 3 generated without any data selection, from 10000 traces, using a bin size of 100/decade. B Two-dimensional histograms for 1, 2, and 3 showing conductance peaks extending over a distance of ~ 1 nm relative to the break of the G_0 contact.

(SI). These wires vary only in their aromatic character; they have the same length and internal torsion angle, due to the triple bonds and linker groups, which allows us to compare conductance directly from aromaticity (or specifically resonance energies). The amine terminations bind selectively to under-coordinate gold in order to form a single-molecule junction between two gold electrodes, thus enabling the STM-BJ conductance measurements.^{7,8}

We measure the molecular conductance of these molecules by repeatedly forming and breaking Au point contacts in the presence of molecules using a modified STM-BJ setup that has been described in detail previously.⁹ We use an Au/mica substrate with an Au wire tip (Alfa-Aesar, 99.998% purity) for these measurements. The STM operates in ambient conditions at room temperature and the junctions are broken in a 0.2 mM solution of the molecules in 1,2,4-trichlorobenzene (Alfa-Aesar 99% purity). Each conductance measurement starts by moving the tip into the substrate to create a metal point-contact with a conductance of at least $5G_0$.¹⁰ This ensures that a new electrode structure is created for each measurement. The tip is then withdrawn from the substrate at a speed of about 16 nm/s while the current is recorded at a fixed applied bias voltage of 225 mV at a 40 kHz data acquisition rate. This yields a conductance (current/voltage) versus displacement trace. In all measurements reported here, 10,000 traces were collected with each molecule to allow for detailed statistical analysis. Figure 1C shows three sample traces measured with molecules 1–3. These show conductance plateaus at integer multiples of $G_0 = 2e^2/h$, the quantum of conductance, as well as a molecular dependent conductance feature between $10^{-3}G_0$ and $10^{-5}G_0$. These illustrative traces show that the conductance of 1 is the largest, while that of 3 is the smallest.

To determine the conductance of each molecule in a statistically significant manner, we create one-dimensional and two-dimensional histograms of all 10000 traces measured. One-dimensional histograms show the frequency of conductance values measured averaged over all traces while two-dimensional histograms reveal the junction conductance evolution as a function of elongation.¹¹ Figure 2A shows one-dimensional conductance histograms of molecules 1–3 created using logarithm bins. We find that the peak of these histograms shifts systematically to lower conductance as the aromaticity of the central unit is enhanced. Specifically, the cyclopentadiene derivative has the highest conductance, while the thiophene derivative has the lowest. We show, in Figure 2B, two-dimensional conductance histograms generated from the same traces used to create the histograms in Figure 2A. These illustrate clearly that in all cases we are measuring conductance

across the entire molecular backbone, as the lengths of the features seen in these 2D histograms are roughly the same for all three.

To show that the correlation between the aromaticity and conductance is robust, we also synthesized and measured another simpler series of three molecules: 1,4-bis(4-aminophenyl)-5,5-dimethylcyclopenta-1,3-diene (4), 2,5-bis(4-aminophenyl)furan (5), and 2,5-bis(4-aminophenyl)thiophene (6). Figure 3A shows the structures of these molecules, and

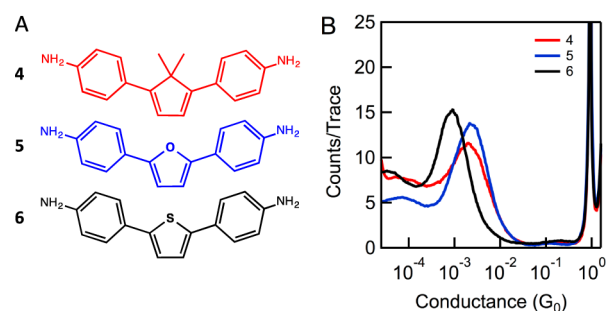


Figure 3. (A) Structures of molecules 4, 5, and 6. (B) Log-binned one-dimensional conductance histograms for molecules 4, 5, and 6 generated from 10000 conductance traces using a bin size of 100/decade.

Figure 3B shows one-dimensional conductance histograms for this series (see SI for 2D histograms). We again see a decreasing conductance due to enhanced aromaticity; however, for molecule 4 (the cyclopentadiene derivative), we do not see a clear increase in conductance when compared with that for the furan derivative (5). We attribute this to the internal torsion angle of 4, determined from its X-ray structure, which is $\sim 16^\circ$ (see SI Figure S1). Without the acetylene bridging within the molecular wire, the two methyls on the cyclopentadiene ring interfere with the ortho hydrogens on the aniline rings, resulting in larger internal torsion angles and a lower conductance.^{8,12}

We plot, in Figure 4, the conductance values for molecules 1–3 obtained by fitting a Gaussian function to the histogram peaks shown in Figure 2A against the resonance energy of the five-membered ring units. We see that conductance correlates negatively with resonance energy, i.e. the more aromatic the molecule is, the lower the conductance. The best structures for conductivity would have π bonds external to the rings, quinoid structures, while the best structures for the aromatic rings themselves would not have such external π bonds. The compromise structures adopted would have a larger energy

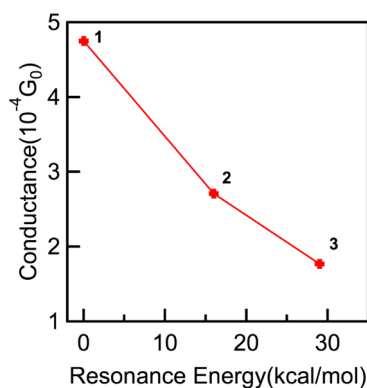


Figure 4. Conductance values for molecules 1, 2, and 3 as a function of resonance energy of the aromatic component in the molecular wire.

penalty for systems with larger initial aromatic stabilization. Another consideration is that the HOMOs for aromatic compounds are lower in energy than those for nonaromatic compounds, and conductivity in these electron-rich amine-terminated systems depends on the location of the HOMOs relative to the gold electrode Fermi energy.¹³

In conclusion, we have studied the relationship between aromaticity and conductance of a single-molecule junction in ambient conditions. We are able to attain a series of molecular structures where the change in conductance would only come from the different aromatic components that we are studying. This work thus provides an experimental guide to building active elements for organic photovoltaics using nonaromatic components, as our results show that stronger aromaticity leads to lower conductance at the single-molecule level.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic and measurement details and the crystal structure of 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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