

Single-Molecule Conductance through Multiple π - π -Stacked Benzene Rings Determined with Direct Electrode-to-Benzene Ring Connections

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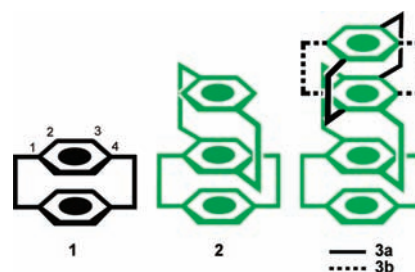
S Supporting Information

ABSTRACT: Understanding electron transport across π - π -stacked systems will help to answer fundamental questions about biochemical redox processes and benefit the design of new materials and molecular devices. Herein we employed the STM break-junction technique to measure the single-molecule conductance of multiple π - π -stacked aromatic rings. We studied electron transport through up to four stacked benzene rings held together in an eclipsed fashion via a paracyclophane scaffold. We found that the strained hydrocarbons studied herein couple directly to gold electrodes during the measurements; hence, we did not require any heteroatom binding groups as electrical contacts. Density functional theory-based calculations suggest that the gold atoms of the electrodes bind to two neighboring carbon atoms of the outermost cyclophane benzene rings in η^2 fashion. Our measurements show an exponential decay of the conductance with an increasing number of stacked benzene rings, indicating a nonresonant tunneling mechanism. Furthermore, STM tip-substrate displacement data provide additional evidence that the electrodes bind to the outermost benzene rings of the π - π -stacked molecular wires.

Understanding electron transport at the molecular level is crucial for the design and construction of functional nanoscale devices¹ and will also help to elucidate the mechanisms of biological redox processes.² One area of particular interest is how π - π -stacked aromatic rings conduct electricity, since electron transport through stacked DNA base pairs³ and amino acid residues⁴ plays a key role in xenobiotic metabolism,⁵ photosynthesis,⁶ and DNA repair.⁷ Inspired by how π - π stacking is efficiently used by nature to achieve directed long-range electron transport, it is believed that synthetic molecular wires incorporating π - π stacking will be useful as new electronic materials⁸ or as components in molecular devices.⁹ Furthermore, rigid synthetic molecular wires represent model systems for their biological counterparts, for which it is often difficult to obtain reproducible conductance data due to the large size and the increased flexibility.¹⁰

Measurements of molecular layers incorporating a paracyclophane scaffold¹¹ and conductance between molecules held together by spontaneous π - π stacking¹² have provided evidence for transport across two π -systems. However, the important question of how the electron transport properties of multiple π -stacked systems differ from those of saturated or conjugated chains has not been addressed

Chart 1. Molecular Wires with up to Four π - π -Stacked Benzene Rings Used in the Gold STM Break-Junction Conductance Measurements^a



^a Compound 3 was isolated and measured as a mixture (1.35:1.00) of the isomers 3a (with solid black bonds) and 3b (with dashed black bonds).

experimentally at the single-molecule level. Herein we are, for the first time, able to experimentally determine the single-molecule conductance of synthetic molecular wires with multiple, tightly π - π -stacked aromatic rings. The benzene rings in our synthetic molecular wires (compounds 1–3, Chart 1) are held together in eclipsed fashion via ethylene bridges as in [2.2]-paracyclophane (1).

Electron transport measurements of single molecules are carried out using the STM-based break-junction technique.¹³ While in our previous work heteroatom-attached groups such as amines,^{13b} phosphines,¹⁴ or alkylsulfides¹⁵ were needed to connect organic molecules to metal electrodes, we herein find that simple hydrocarbons with strained aromatic rings can directly contact two gold electrodes, as has been shown for C₆₀.¹⁶ Since heteroatom linker groups can destabilize molecular wires,¹⁷ employing simple hydrocarbons as linkers could allow access to conductance studies of less stable structures.

Single-molecule junctions were created by repeatedly forming and breaking gold point contacts in a solution of the molecules in 1,2,4-trichlorobenzene, in a home-built setup.^{13b} While compounds 2 and 3 were measured under an argon atmosphere, all other compounds were measured in air. For each molecule studied, the measured conductance traces reveal steps at molecule-dependent conductance values less than the quantum of conductance, $G_0 = 2e^2/h$; these are due to conduction through a molecule bonded in the gap between the two Au point contacts. Figure 1A shows conductance

Received: December 15, 2010

Published: January 25, 2011

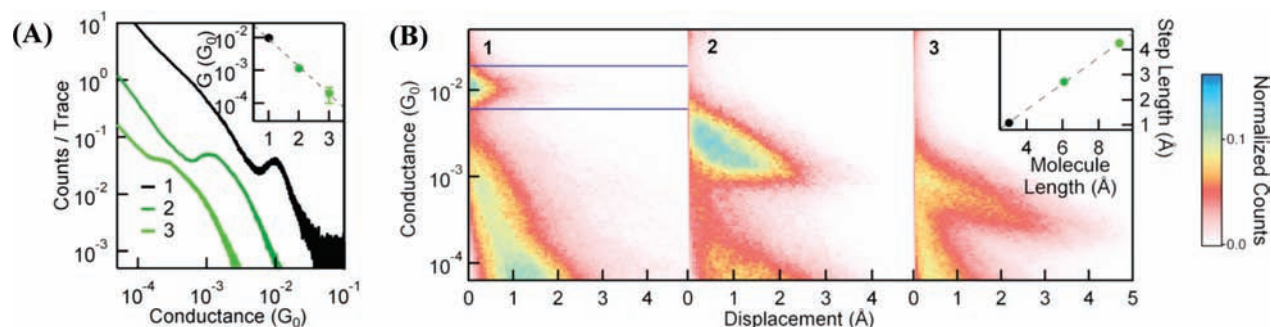


Figure 1. (A) Conductance histograms of compounds 1–3 generated using a linear bin size of $10^{-5}G_0$ for compounds 1 and 2 and $10^{-6}G_0$ for compound 3. Inset: Conductance histogram peak versus number of paracyclophane units shown on a semilog scale. The dotted line represents an exponential fit to the data with a decay constant β of $(1.94 \pm 0.25)/(\text{stacked benzene unit})$. Error bars capture the variability in peak position. (B) Two-dimensional histograms showing molecular conductance as a function of STM tip–sample displacement for compounds 1–3 generated using a logarithmic binning with 10 bins/decade. The displacement dimension was binned linearly with a bin size of 0.072 Å. The color scale indicates the average number of counts per trace in a given conductance–displacement bin. The tip–sample displacement is proportional to the length of the molecule in the break-junction.^{14,18} The horizontal blue lines in the 2D histogram for compound 1 mark the section of the plot used to determine the step length.¹⁴ Inset: Measured step length plotted against the distance between the outermost benzene rings. The dashed line represents a linear least-squares fit with slope ~ 0.5 .

histograms generated (without any data selection) from over 5000 measured traces for compounds 1–3.

Compound 1 was obtained from Acros Organics, while compounds 2 and 3 were prepared, according to known procedures, by reductive desulfuration reactions with $P(\text{OEt})_3$ under UV light from the corresponding dithia[3.3]-paracyclophane derivatives.¹⁹ Compound 3 was isolated as a 1.35:1.00 mixture of the two isomers 3a and 3b shown in Chart 1. The isomers were not separated for this experiment, which might explain the broader peak observed for 3.

The inset in Figure 1A shows the position of the histogram peaks determined from Lorentzian fits to the data. We see that the molecular conductance decreases exponentially with increasing number of stacked aromatic rings. This finding is consistent with a nonresonant tunneling mechanism of the electron transport through these π -stacked molecules and strongly suggests that each gold electrode contacts the outermost benzene rings in compounds 1–3, rather than the bridging ethylene groups. Further evidence for this conclusion is obtained by analyzing two-dimensional histograms¹⁸ showing molecular conductance as a function of STM tip–sample displacement (Figure 1B). Briefly, 2D histograms are generated using an automated algorithm by setting the rupture of the G_0 contact as the origin of the displacement axis on each trace; conductance and displacement relative to zero are then binned to generate 2D maps out of thousands of traces, as shown in Figure 1B.¹⁸ The inset of Figure 1B shows that the most probable step length increases linearly with the number of stacked benzene rings. The fact that the slope is ~ 0.5 could indicate that the molecules on average bind at an angle or that they often desorb from the junction while the tip–substrate separation is still small enough to allow the molecule to remain bound. While more investigation is needed, the linear dependence of step length on molecule length indicates that the metal electrodes bind to the outermost benzene rings of the paracyclophanes and transport has a component along the molecular axis which lengthens as the number of stacked benzene units is increased. From an exponential fit to the conductance data shown in Figure 1A, we were able to determine the decay constant β with $G \sim e^{-\beta N}$, as $(1.94 \pm 0.25)/(\text{stacked benzene unit})$. Using a ring spacing of 3.07 ± 0.02 Å (average \pm standard deviation of all possible benzene centroid distances in compounds 1–3, obtained from B3LYP/LACVP** structures of compounds 1–3 bound to

two gold electrodes modeled as Au_2 -clusters) between layers of stacked benzene rings, this converts to a β of $(0.63 \pm 0.09)/\text{Å}$. This is smaller than the value observed for alkanes, which show a β of about $0.8/\text{Å}$.^{13a,20,15} In fact, if we consider the σ through-bond channel for this series of molecules, we see that it would increase by at least four C–C bonds with the addition of each benzene layer (including one bond between carbons 3 and 4 in the benzene ring in Chart 1). The resulting β would be $\sim 0.5/(\text{C–C bond})$, which is significantly lower than previously measured values of $\sim 1/(\text{C–C bond})$ ^{13b,14} and cannot be accounted for purely by conductance through the σ channel. Therefore, the significant difference between the decay constant of the π - π -stacked paracyclophanes 1–3 and that of alkyl chains indicates that the conductance channel in which electrons tunnel between the contacting π - π -stacked layers has indeed a major contribution to the overall conductance in [2.2]-paracyclophane-type structures, as has been predicted in a computational study as well.^{11a}

It is well known that the strained benzene rings in [2.2]-paracyclophanes can form complexes with transition metals that are in general significantly more stable than the corresponding complexes involving normal, unstrained benzene rings.²¹ To better understand the role of strain in facilitating the binding of hydrocarbons to gold electrodes, we measured the unstrained [4.4]-paracyclophane (4, Chart 2, obtained from Sigma-Aldrich's rare chemical library). We found that 4 did not show any molecular conductance plateaus in traces or conductance peak in the histogram to within the measurement limit of our experiment (Figure 2), indicating that it probably did not bind to gold electrodes. If compound 4 had bound to the gold electrodes, one would expect to see molecular conductance traces with low, but still detectable, conductance as commonly observed for alkanes of similar length.²⁰

Further insight into the nature of the direct gold–electrode carbon contacts observed herein was obtained by studying substituted versions of [2.2]-paracyclophane (1). In general, electron-withdrawing substituents such as fluorines lower the Lewis basicity of the paracyclophane benzene rings and therefore reduce the binding affinity for gold electrodes. On the other hand, electron-donating substituents such as methoxy should lead to stronger binding to the electrodes. To test this hypothesis, we synthesized fluorine- and methoxy-substituted versions of

Chart 2. π - π -Stacked Molecular Wires without Strain (4), with an Electron-Donating Substituent (5), and with Electron-Withdrawing Substituents (6)

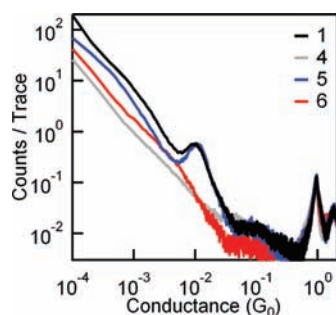
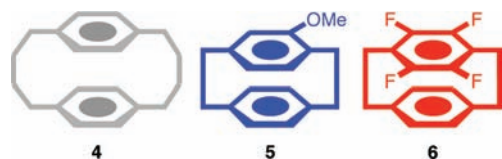


Figure 2. Conductance histograms of compounds 1, 4, 5, and 6 generated using a linear bin size of $10^{-4}G_0$.

[2.2]-paracyclophane (compounds 5 and 6) following known procedures.²² Analogous to the synthesis of compounds 2 and 3,^{19a} we obtained the substituted [2.2]-paracyclophanes 5 and 6 in good yield via a reductive desulfuration reaction of the corresponding dithia[3.3]-paracyclophane derivatives under UV light. While we found that compound 6, with four fluorine substituents, did not bind to gold electrodes and conduct electricity, results with the methoxy-substituted compound 5 were very similar to those of the unsubstituted [2.2]-paracyclophane (1, Figure 2).

To understand the relative gold binding affinities of compounds 1–6 in a more quantitative fashion, we carried out DFT-based calculations of the molecular binding energy to gold dimers, making the assumption that a linear chain of gold atoms links the molecule to the electrode. All binding energy calculations were performed at the spin-unrestricted B3LYP/LACV3P**+//B3LYP/LACVP** level²³ with the Jaguar²⁴ software package. The pseudospectral method²⁵ was employed to speed up the SCF cycles. Default grids and convergence criteria were employed. We note here that binding energies calculated with gold dimers cannot be compared directly with those of single gold atoms due to an odd/even effect on the binding energy.²⁶ However, our focus here is on the trends in calculated binding energies, which are robust. Calculations with larger gold clusters, which will be necessary to get more accurate gold binding energies of the compounds studied herein but are beyond the scope of this work, are in progress and will be reported elsewhere.

We find two stable binding geometries for the gold dimers bound to compound 1. The first has the gold coordinating the C_1 – C_2 “double” bond in η^2 -fashion, and the second has the gold attached in η^1 -fashion to C_1 of [2.2]-paracyclophane (with C_1 and C_2 defined in Chart 1). These calculated gold binding affinities of 0.74 eV (17 kcal/mol) are very similar to that reported for C_{60} (0.67 eV) with a gold dimer electrode model.²⁶

To compare these gold dimer binding energies of cyclophane compounds 1–6 to those of traditional Lewis basic heteroatom link groups, we also calculated the gold dimer binding affinity of

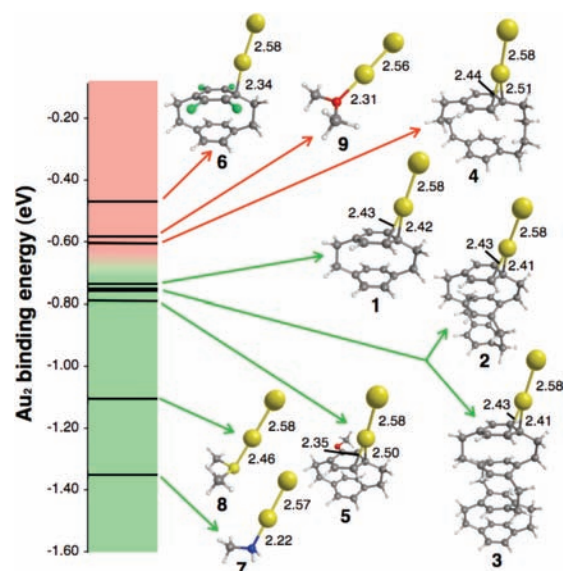


Figure 3. Optimized structures (B3LYP/LACVP** level) of compounds 1–9 bound to a single gold dimer (bond distances in Å). The most stable binding configurations are shown for all compounds. The green gold dimer binding energy range represents compounds that successfully bind to gold electrodes in STM break-junction conductance measurements.

methylamine (7) and dimethylsulfide (8), which are known to bind to undercoordinated Au in the experiments, and of dimethyl ether (9), which does not bind to Au in the experiments. For the amine-terminated molecule 7, the calculated gold dimer binding energy is significantly larger than those reported with either a single gold atom or larger gold clusters.^{15,18} Nonetheless, these gold dimer binding affinities serve as a guide for the relative gold binding strengths of the various compounds studied here.

Figure 3 shows the calculated gold dimer binding energies for compounds 1–9. We see that all molecules with gold dimer binding energies above 0.7 eV actually bind to gold electrodes in STM break-junction measurements, allowing conductance measurements. Compounds with lower gold dimer binding energies do not show any peaks in conductance histograms, consistent with the understanding that these do not bind to undercoordinated Au on the electrodes. Finally, these calculations show that paracyclophanes bind through their outer π system to the C_1 carbon or to the C_1 – C_2 bond.

Frontier molecular orbitals determined by analyzing the molecular Hartree–Fock orbitals (at the RHF/LACVP** // UB3LYP/LACVP** level, computed with Gamess²⁷) are shown in Figure 4 for molecule 1 bound to two gold dimers. We see that the frontier molecular orbitals are mainly localized on the benzene rings and on the gold atoms, indicating that the Au is indeed coupled to the molecular π system. This provides further evidence that, during electron transport through the π - π -stacked systems studied herein, transport is through the π system rather than the σ -type molecular orbitals of the ethylene link groups.

In summary, we were able to study the single-molecule conductance of strained paracyclophanes with up to four π - π -stacked benzene rings. We find that the hydrocarbons studied form direct electrical contacts with gold electrodes in STM break-junction conductance measurements. The observed exponential decay of molecular conductance with increasing number of stacked benzene rings confirms that the gold electrodes bind to the outermost

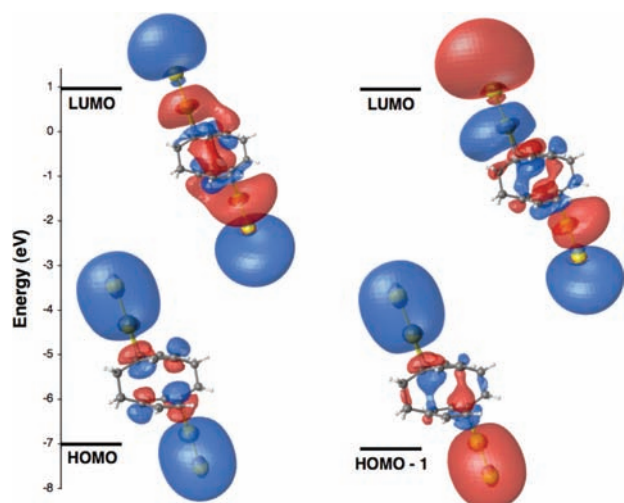


Figure 4. Isosurface plots (contour value = 0.01) of the frontier molecular orbitals of [2.2]-paracyclophane (1) bound to two gold dimers. The two LUMOs shown are degenerate. Orbitals with bonding character between the gold dimers and the benzene rings are lower in energy and are not shown in this plot.

benzene rings of the paracyclophane derivatives. DFT calculations suggest that stable electrical contacts are formed via coordination of the gold electrodes to C–C “double” bonds of the outermost benzene rings in η^2 -fashion. It is likely that many other unsaturated strained hydrocarbons can be employed to form direct Au–C bonds with gold electrodes as well. This possibility is currently being explored in our laboratories and will be reported in due time.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C NMR spectra showing the purity of all compounds; Cartesian coordinates of all optimized structures as well as total energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was supported in part by the Nanoscale Science and Engineering Initiative of the NSF (Award CHE-0641523), the New York State Office of Science and Technology, and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy (Grant DE-FG02-90ER14162). L.V. also thanks the Packard Foundation for support, and S.T.S. thanks the Guthikonda family for an Arun Guthikonda Memorial graduate fellowship. The cover was designed by Severin Schneebeli.

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