
Latha Venkataraman,*† Young S. Park,‡ Adam C. Whalley,‡ Colin Nuckolls,‡ Mark S. Hybertsen,§⊥ and Michael L. Steigerwald‡

Department of Physics, Department of Chemistry, Department of Applied Physics and Applied Mathematics, and Center for Electron Transport in Molecular Nanostructures, Columbia University, New York, New York

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ABSTRACT

We measure the low bias conductance of a series of substituted benzene diamine molecules while breaking a gold point contact in a solution of the molecules. Transport through these substituted benzenes is by means of nonresonant tunneling or superexchange, with the molecular junction conductance depending on the alignment of the metal Fermi level to the closest molecular level. Electron-donating substituents, which drive the occupied molecular orbitals up, increase the junction conductance, while electron-withdrawing substituents have the opposite effect. Thus for the measured series, conductance varies inversely with the calculated ionization potential of the molecules. These results reveal that the occupied states are closest to the gold Fermi energy, indicating that the tunneling transport through these molecules is analogous to hole tunneling through an insulating film.

Understanding the transport characteristics of molecules bonded between metal electrodes is of fundamental importance for molecular scale electronics. It is well-known that these transport characteristics are influenced by the intrinsic properties of the molecules, including their length, conformation, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the alignment of this gap to the metal Fermi level. Experiments measuring the two-terminal conductance of single molecules between metal electrodes have been performed by employing a variety of different techniques. Although some insight into the transport mechanism has been demonstrated in experiments on devices formed with a large number of molecules in the junction, probing the details of the transport mechanism through single-molecule devices has proven difficult, primarily due to the large variability in the conductance measurements of such devices. Using amine—gold link chemistry, we have previously demonstrated that we can measure the conductance of single molecules reliably and reproducibly and relate the measured conductance to molecular conformations. Here we use chemical substituents to provide new insight to the nature of electron transport through single-molecule devices. By studying a series of substituted 1,4-diaminobenzene molecules that have the same length and conformation, we probe the details of the Fermi level alignment to the molecular orbitals.

We measure the conductance of single-molecule junctions by breaking Au point contacts in a 1,2,4-trichlorobenzene solution of molecules (See refs 10 and 11 for a detailed description.) Conductance traces measured as a function of tip—sample displacement reveal quantized conductance steps observed at multiples of $G_0 (2e^2/h)$, the fundamental quantum of conductance. In addition, many of the traces reveal steps at molecule-dependent conductance values below $G_0$. Figure 1B shows the conductance histograms for two molecules: 2-chloro-1,4-diaminobenzene and 2-methoxy-1,4-diaminobenzene constructed from thousands of consecutively measured conductance traces without any data selection or processing. These histograms show clear peaks both at multiples of $G_0$ and at a molecule dependent value below $G_0$. 

* Corresponding author. E-mail: latha@phys.columbia.edu.
† Department of Physics.
‡ Department of Chemistry.
§ Department of Applied Physics and Applied Mathematics.
⊥ Center for Electron Transport in Molecular Nanostructures.
Current Address: Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973.

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The shift in the peak positions in Figure 1B shows the change in the conductance of the two molecules, differing only in their substituents on the benzene ring. We have performed the same experiment with nine other substituted 1,4-diaminobenzenes (listed in Table 1) and find that their conductance depends on the nature of the substituent. For all of the substituents tested, we have also performed control experiments on molecules with the substituent groups at the 1 and 4 positions (for example, with 1,4-dicyanobenzene) to ensure that the substituent groups do not bind to broken gold point contacts. For all of the substituents listed in Table 1, the histograms measured with the 1,4-disubstituted benzenes do not differ from the control histograms in solvent alone. However, for the carboxylic group (COOH) and the nitro group (NO2), we find that the histograms measured with the 1,4-disubstituted benzenes differ considerably from the control histograms in clean solvent, indicating that these groups bind to gold, and hence we do not include these in our measurements. For the 1,4-diaminobenzene molecules with substituents, we measure an increase in molecular junction conductance with electron-donating substituents (for example with a methoxy or methyl group) as listed in Table 1. For electron-withdrawing substituents (for example, with a chlorine or a cyano group), we measure a decrease in molecular junction conductance. To determine the ultimate physical reason for this increased conductance, it is useful to look at the physical changes in the 1,4-diaminobenzene system that accompany the replacement of the ring H atoms with other chemical functional groups.

The highest occupied molecular orbital in 1,4-diaminobenzene is best described as a combination of the lone pairs on each of the N atoms and some component of p-density on each of the two C atoms to which the N atoms are bonded. As electron-donating substituents replace H atoms on the ring, the energy of the HOMO orbital increases. When an H is replaced by a methoxy group (OCH3), the O(2pπ) lone pair delocalizes into the benzene π space, thereby raising the energy of the HOMO. Similarly, when electron-withdrawing substituents replace H atoms, the energy of the HOMO is lowered. When H is replaced by Cl, the more...
electron-withdrawing substituents increase IP.

To explore this further, we plot in Figure 2A the measured molecular conductance for the series tested against the vertical IP calculated for the isolated molecules based on density functional theory (DFT)\(^{13-15}\) (See Supporting Information for details). There is very limited experimental data available across the series of molecules under study for a comparison. The DFT calculations moderately underestimate the measured IP, as also observed for other aromatics\(^{16}\) but represent the trends. For example, the measured IP is 6.87 ± 0.05 eV for the unsubstituted 1,4-diaminobenzene and 6.43 eV for tetramethyl-1,4-diaminobenzene,\(^{17}\) while the calculated adiabatic IPs are 6.39 and 5.96 eV for the two molecules, respectively. We see in Figure 2A that the molecular junction conductance decreases with increasing ionization potential, thus for molecules with a more deeply bound HOMO, the conductance is reduced.

We have demonstrated previously\(^{12}\) that the low bias conductance through polyphenyls attached to gold electrodes amine end groups is through a nonresonant tunneling process or superexchange. Two different models are frequently used to describe this process when the voltage applied across the junction is much smaller than the HOMO–LUMO gap of the bridging molecule. The molecule can be thought of as a tunnel barrier, and the transport details can be understood in terms of Simmons’ model,\(^{8,9,18,19}\) as illustrated in Figure 3A. Equivalently, conductance can be related to the electron-transfer rate between a donor electrode and an acceptor electrode through a molecular bridge (a model introduced by McConnell\(^{20}\)), as illustrated in Figure 3B.\(^{21,22}\) As long as the metal Fermi level or, equivalently, the donor and acceptor levels are far enough from the molecular levels (HOMO and LUMO), the electron-tunneling rates decrease exponentially with increasing molecule length (\(L\)) with the measured low bias conductance \(G\) scaling as \(e^{-\beta L}\). Here, the decay constant \(\beta\) depends on the intrinsic electronic properties of the molecule in the junction. For example, \(\beta\) is 0.77 Å\(^{-1}\) for fully saturated diaminoalkanes measured between gold electrodes,\(^{11}\) while it is 0.4 Å\(^{-1}\) for conjugated diaminopolyphenyls.\(^{12}\)

The tunneling process is dominated by the molecular level that is closest to the metal Fermi level, for example, the HOMO, as shown in Figure 3A and B. In this case, the tunneling decay rate \(\beta\) depends on the energy separation \(\Phi_B = E_{\text{Fermi}} - E_{\text{HOMO}}\). Although the details of the relation between \(\beta\) and \(\Phi_B\) differ for the two models (\(\beta \propto \Phi_B^{1/2}\) in Simmons’ model while \(\beta \propto \log(\Phi_B)\) in the McConnell model\(^{20}\)), both models predict an increase in the measured conductance with a decrease in \(\Phi_B\).\(^{23}\) Our measurements show that electron-donating substituents, which shift the HOMO level up (decreasing IP), increase the junction conductance, hence they must decrease \(\Phi_B\). Similarly, electron-withdrawing substituents must increase \(\Phi_B\). These results therefore show that the HOMO is the molecular level that is closest to the Au Fermi level in these molecular junctions. With reference to the Simmons model, transport in these junctions is equivalent to hole tunneling through an insulating film.

This picture is further supported by quantum chemistry calculation\(^{13-15}\) for all molecules studied, with the amine link groups coupled to Au clusters representing the contacts.\(^{11,12}\) The binding of an Au atom to each amine results in frontier orbitals that are predominantly of Au-s, N lone pair antibonding character. These frontier orbitals are tunnel coupled through the molecular backbone, resulting in a symmetric and antisymmetric pair with a splitting, \(2\tau\). In the cases with a single substituent, the molecule has a built-in dipole that breaks the symmetry between the two Au contact atoms. However, the dipole is oriented nearly orthogonal to the junction (the Au–Au contact line) and the degree of asymmetry is small, as judged from the frontier molecular orbitals.\(^{24}\) In Figure 2B, we plot \(4\tau^2\), which is proportional to the tunnel conductance\(^{11,12,20,25}\) against the ionization potential (also listed in Table 1). A comparison of Figure 2A and B indicates that the trends in the measured conductance are accounted for by the changes in the tunnel coupling of the frontier orbitals across the molecular backbone induced by the substituents. Furthermore, we find a close correspondence in the isosurface plot of the frontier orbital (Figure 3D) and the HOMO level for the isolated molecule (Figure 3C). This provides additional evidence that it is indeed the HOMO that is the molecular orbital that is closest to the Fermi level.
We have shown that the conductance of diaminobenzene is altered by having substituents on the benzene ring. It is well-known that reaction rates can be affected by substituents. These effects are often quantified by use of substituent constants, an idea that was first introduced by L. P. Hammett. Reaction rates for a substituted molecule relative to the rate for an unsubstituted molecule are plotted against the Hammett substituent constant in order to gain insight into the reaction mechanism. In organic reactions, the logarithm of the reaction rate is proportional to the activation energy for the reaction, and the Hammett equation is an example of a linear free energy relation. Extending this idea to electron tunneling, we can relate the molecular conductance to the Hammett constants as the logarithm of conductance is a function of the tunneling barrier height.

In Figure 4, we plot the log of the ratio of the measured conductance for the substituted \((G_X)\) and unsubstituted \((G_H)\) molecule scaled by the number of substituents on the ring against the Hammett parameter \(\sigma_{para}\) from ref 27. We have made three major assumptions here. First, the choice of Hammett constant \(\sigma_{para}\) may not represent the effect of the substituent fully. Second, we assume that the effect of multiple substituents is additive, even though it is clear from the methyl and fluorine substituted data that this is not so. Third, we know that the logarithm of the conductance is not linear in the tunnel barrier, although for small conductance changes measured here, the deviation from a linear relation is within our error bar. Nonetheless, Figure 4 shows a clear trend, that the conductance decreases as the Hammett constant is made more positive. This negative slope indicates that the transition state in this tunneling “reaction” is positively charged. Quite remarkably, this is consistent with the picture of hole tunneling described above.
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Supporting Information Available: Synthetic procedure, theoretical procedure, references. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(24) The largest asymmetry is observed for the single methoxy substitution where the potential difference between the contact Au atoms is estimated to be less than 0.03 eV, which has a negligible impact on the estimated tunnel coupling.