

Effect of Bond-Length Alternation in Molecular Wires

James G. Kushmerick,^{*,†,§} David B. Holt,[†] Steven K. Pollack,[†] Mark A. Ratner,[‡] John C. Yang,[†] Terence L. Schull,[†] Jawad Naciri,[†] Martin H. Moore,[†] and Ranganathan Shashidhar^{*,†}

Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, D.C. 20375, and Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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In this communication, we report experimental and theoretical current–voltage (*I*–*V*) characteristics which demonstrate that bond-length alternation plays an important role in determining the conductance of molecular wires. Charge transport across organic molecules as a function of molecular structure has previously been investigated with a variety of experimental measurements including electrochemical,¹ scanning probe,² donor–bridge–acceptor,³ and mercury drop electrode,⁴ as well as theoretical calculations.⁵ Two particular classes of molecular wires oligo(phenylene ethynylene) (OPE) and oligo(phenylene vinylene) (OPV) have been the focus of much study.^{1b,d,e,2a,b,3d} While it has previously been argued that the higher planarity of OPV makes it a better molecular wire than OPE, the measurements and theoretical calculations presented here highlight a second important contribution to molecular wire conductance: the extent of bond-length alternation along the π -conjugated molecular backbone.

The *I*–*V* characteristics of self-assembled monolayers (SAMs) of the three molecules investigated (Table 1) are measured with a crossed-wire tunnel junction (Figure 1). The crossed-wire tunnel junction is formed from two 10 μm Au wires, one modified with a SAM of the molecule of interest. The wires are mounted to a custom built test-stage so that they are crossed, and the wire spacing is controlled by the Lorentz force: dc current in one wire deflects it in a magnetic field (**B**). This deflection current is slowly increased to bring the wires gently together, forming a junction at the contact point. By comparison to other charge transport measurements, we calculate that the junction contains $\sim 10^3$ molecules.^{2c,4} We have previously used this experimental configuration to investigate the role that metal–molecule contacts play in charge transport across monolayers.⁶

Figure 2A shows the experimental *I*–*V* characteristics for junctions formed from monolayers of the three classes of molecules studied. The error bars associated with the measurements are attributed to variations in junction area between independent junctions. Multiple measurements on the same junction show a much smaller deviation. As would be expected, there is a clear difference in the magnitude of charge transport across monolayers of the electrically insulating σ -bonded alkane (C12) and that of the π -conjugated oligo(phenylene ethynylene) (OPE) and oligo(phenylene vinylene) (OPV) molecular wires. The difference in conductance for OPE and OPV is discussed below.

To better understand the physical basis for the measurements, we calculated the *I*–*V* characteristics for the junctions studied using extended Hückel theory (EHT) and Green's functions (GF)

Table 1. Molecular Structures, Calculated HOMO–LUMO Gap (E_g), Calculated (G_{calc}) and Measured (G_{meas}) Relative Junction Conductance at 0.5 V

compound	molecular structure	E_g (eV) ^a	G_{calc} ^b	G_{meas} ^b
C12	AcS(CH ₂) ₁₂ SAc	7.11	1	1
OPE		3.51	10	15
OPV		3.12	78	46

^a E_g is the HOMO–LUMO gap calculated from density-functional theory at the B3LYP/6-31G* level. ^b Junction conductance (*I*/*V*) at 0.5 V normalized to the conductance of the C12 junction.

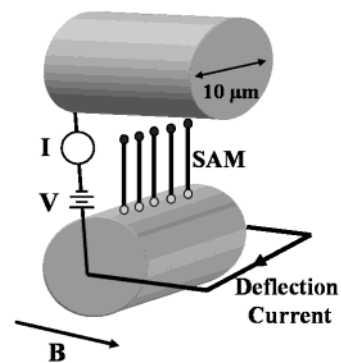


Figure 1. Schematic representation of the crossed-wire tunnel junction (not to scale). All measurements were made in a nitrogen purged Faraday cage at room temperature.

techniques under the approximation that the entire potential drop occurs at the metal–molecule interfaces. The details of the theoretical methods used here have been reported previously.^{6,7} Briefly, the EHT/GF treatment allows the calculation of the transmission function, which is then implemented within the Landauer–Buttiker formalism to calculate the *I*–*V* characteristics.⁸ While we have previously shown that junctions with asymmetric metal–molecule contacts can have unequal voltage drops at the two metal–molecule interfaces, resulting in asymmetric *I*–*V* characteristics, all of the junctions in this study have symmetric metal–molecule attachments, and thus the voltage drop is expected to be split equally at both interfaces.⁶

The calculated *I*–*V* characteristics are in excellent qualitative agreement with the experimental measurements (Figure 2B). Both experiment and theory show the same trend in molecular conductance, C12 < OPE < OPV (Table 1).⁹ Now we turn our attention to the differences in charge transport for OPE and OPV. It has previously been argued that the higher coplanarity and thus better

* To whom correspondence should be addressed. E-mail: J.G.K., kushmerick@nrl.navy.mil; R.S., rshashidhar@cbmse.nrl.navy.mil.

[†] Naval Research Laboratory.

[‡] Northwestern University.

[§] Also at Geo-Centers Inc., Fort Washington, MD 20749.

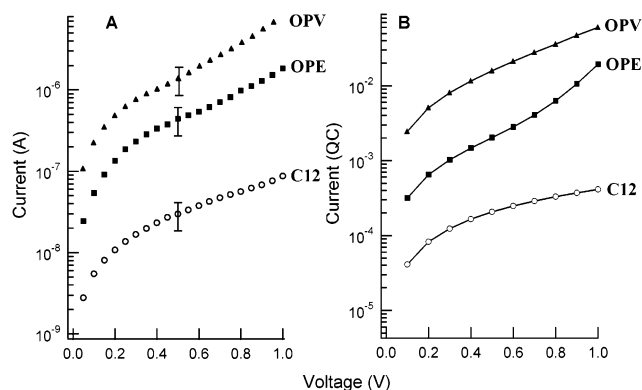


Figure 2. Experimental (A) and theoretical (B) plots of current (logarithmic scale) as a function of the applied bias voltage for junctions formed from the three compounds studied. The theoretical traces are given in units of the quantum of current ($2e^2/h$ V).

π -conjugation of OPV systems as compared to that of OPE (in which the phenylene rings are freely rotating at room temperature) explain the more facile charge transport in OPV.^{1b,d,e,10} Charge transport calculations as a function of coplanarity demonstrate that conductance is reduced when the rings of an OPE system are perpendicular to each other.¹¹ While we do not dispute that the increased coplanarity of OPV should enhance its conductivity relative to OPE (at least in isolated molecules), our calculations indicate a second important contribution. Because the transport calculations reported in Figure 2B were performed for individual molecules rigidly fixed at their energy minimized structures (approximately planar for both molecules), the differences in conductance cannot be attributed to disruption of π -conjugation from phenylene ring rotation. Instead, the higher conductivity is due to the smaller bond-length alternation in OPV as compared to that in OPE.

If we consider the molecules as one-dimensional crystals, we see that the short (1.218 Å) ethynylene linkage in OPE disrupts the periodicity of the π -conjugated molecular backbone (1.41 ± 0.01 Å) more drastically than the vinylene linkage in OPV (1.352 Å, backbone = 1.41 ± 0.03 Å) (see Supporting Information). We also know, from studies of conducting polymers, the size of the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap) is directly related to the extent of bond-length alternation,¹² and thus the greater bond-length alternation in OPE causes a larger HOMO–LUMO gap relative to the OPV system (Table 1). Because, at low applied bias, transport is dominated by charge carrier tunneling inside the HOMO–LUMO gap, the smaller gap of OPV leads to higher conductance. In the language of solid-state physics, OPV can be thought of as having a smaller Peierls distortion than OPE and thus acts more like a one-dimensional metal.¹³

In summary, we have measured the I–V characteristics of three classes of molecules with a crossed-wire tunnel junction. The measured I–V characteristics are in good agreement with I–V characteristics calculated from extended Hückel theory coupled with a Green's function approach and point out that the degree of bond-length alternation needs to be considered to fully understand

differences in charge transport across π -conjugated molecular wires. We are currently adding low-temperature capabilities to our crossed-wire molecular electronics test-bed to further unravel the relative importance of internal rotations and bond-length alternation in molecular wires.

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Supporting Information Available: Synthesis of compounds, SAM preparation, and bond lengths for OPE and OPV (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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