



A Mechanism for Conductance Switching in Carbon-Based Molecular Electronic Junctions

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A molecular junction formed by a 10-15 Å organic monolayer between carbon and mercury contacts exhibited conductance switching for several monolayer structures. When the carbon potential was scanned to a sufficiently negative voltage relative to the mercury, the junction resistance suddenly decreased by at least an order of magnitude, and high resistance could be restored by a positive voltage scan. The high and low conductance states were persistent, and conductance switching was repeatable at least 100 cycles for the case of a terphenyl junction. The switching behavior is consistent with phenyl ring rotation and formation of a planar, quinoid structure as a consequence of electron injection into the monolayer. A unique feature of the junction structure is the strong electronic coupling between the monolayer π system and the graphitic carbon through a quinoid double bond. Not only does this interaction lead to high conductivity and possible practical applications as a molecular switch, it also combines the electronic properties of the conjugated monolayer with those of the graphitic substrate. The switching mechanism reported here is an example of "dry electrochemistry" in which a redox process appears to occur under the influence of a high electric field in the absence of solvent or electrolyte.

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Conductance switching is the basis of many potential molecular electronic devices, and has been the focus of numerous research efforts in recent years.¹⁻⁸ If a single molecule or an assembly of molecules can be switched between high and low conductance states by an electrical or optical stimulus, molecular scale memory and logic elements become possible, and molecular electronic components may be integrated with conventional microelectronics or assembled into true molecular circuits.⁹⁻¹² A range of molecular structures which exhibit conductance switching has been reported, including self-assembled monolayers (SAMs) of phenylethynyl oligomers^{2,7,13,14} and rotaxanes oriented between two conductors by Langmuir-Blodgett assembly.^{5,6} The phenomenon of negative differential resistance (NDR) is notable as an example of a small collection of molecules changing from high to low resistance state in an applied electric field, then back to a high resistance state as the field increased further.^{2,7,13} In several cases the states of the molecule are persistent and controllable, and may be repeatedly cycled between "On" (low resistance) and "Off" (high resistance) states.

Although several examples of conductance switching have been investigated extensively, the switching mechanism in most cases is unknown and is the subject of some controversy. NDR was originally attributed to redox reactions involving a nitro and/or amino group in the monolayer molecule,² but switching was subsequently observed without such groups present.^{4,14} NDR was also attributed to shifts in molecular orbital energies in response to an applied electric field, resulting in resonant tunneling at certain applied field magnitudes.¹⁵ Switching by isolated phenylethynyl molecules surrounded by aliphatic SAMs was observed to be stochastic by scanning tunneling microscopy (STM), and was attributed to conformation changes, possibly involving interactions with the monolayer surrounding the active molecules.⁴ Of course, any mechanism established to explain conductance switching also bears directly on the broader issue of which factors control electronic conductivity in organic molecules, a topic of wide interest in the areas of conducting polymers, optoelectronic materials, and energy conversion, in addition to molecular electronics.^{9,10,12}

We report here a completely new approach to fabricating mo-

lecular junctions which exhibit conductance switching and which provide critical insights into the switching mechanism. Shown schematically in Fig. 1, the carbon-based molecular junction⁸ consists of a covalently bonded monolayer on a very flat (rms roughness <5 Å) graphitic carbon substrate made by pyrolysis of a photoresist film (PPF).^{16,17} Spectroscopy of the monolayer/PPF interface has established that the bonding is covalent and stable to at least 400°C in vacuum,¹⁸ and that the phenyl rings of the monolayer are rotationally disordered relative to the graphitic aromatic rings.^{19,20} The junction is completed by a suspended Hg drop placed on the monolayer which defines a junction area of approximately 0.78 mm². Conductance switching of nitrobiphenyl and biphenyl molecular junctions is apparent in the current/voltage (*i/V*) curves of Fig. 2. The initial junction resistance varies for different junctions, but in the case shown was 25 k Ω for nitrobiphenyl and 13 k Ω for biphenyl ($V = \pm 50$ mV).

If the voltage applied to the PPF relative to the Hg is scanned in a range of approximately ± 0.5 V, the *i/V* curve is nonlinear, invariant with scan rate (for 0.01 to 1000 V/s), shows no observable hysteresis, and exhibits weak rectification. When the voltage was scanned more negative than approximately -0.8 V, a sudden increase in current was observed, which occasionally occurred in several steps. Upon the return scan near zero voltage, the junction resistance had decreased to <1 k Ω , and this high conductance state persisted for at least several minutes with $V = 0$. Upon scanning to a positive voltage of greater than approximately $+0.9$ V, the junction resistance returned to its initial value. The complete cycle of turning the junction On at negative voltage and Off at positive voltage was repeatable many times before apparent degradation resulted in a nonswitching junction resistance between the On and Off values. The number of switching repetitions before failure varies with the sample and molecular structure, but several examples are listed in Table I.

Eight monolayer structures were investigated to probe the switching mechanism, including a polynuclear aromatic hydrocarbon (chrysene) and a molecule which includes an aliphatic spacer (4-(phenylmethylene)phenyl). Repetitive conductance switching was observed for the first four molecules listed in Table I, with the observed Off/On resistance ratio indicated. Not all junctions of a given molecule exhibited switching, and the percentage of active junctions (*i.e.*, those exhibiting at least three successive switching cycles) is listed as well. Junctions made with the second group of four molecules occasionally exhibited conductance switching, but with a shorter lifetime. A few junctions which exhibited conductance switching were examined over a range of temperatures, and switch-

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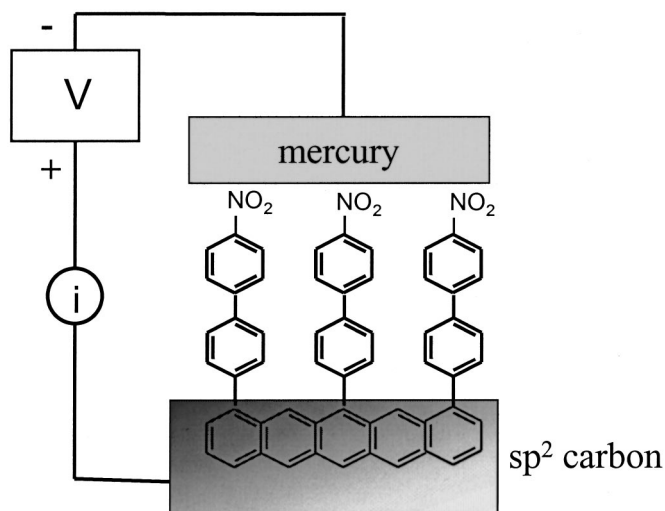


Figure 1. Carbon-based molecular junction with nitro-biphenyl as the monolayer spacer. Nitro-biphenyl was bonded to a flat sp^2 carbon substrate (on polished silicon 100) by electrochemical reduction of 4'-nitro-biphenyl 4-diazonium ion in acetonitrile. Applied voltages are stated as the carbon potential relative to the mercury top contact. Phenyl rings in shaded area are intended to represent a graphitic sheet.

ing was observed to cease at low temperature. For example, nitroazobenzene stopped switching below 0°C , but switching was restored when the junction was heated to above 20°C .

Structural properties shared by the "switchers" in Table I are not initially obvious. Several switchers contain nitro groups, but robust

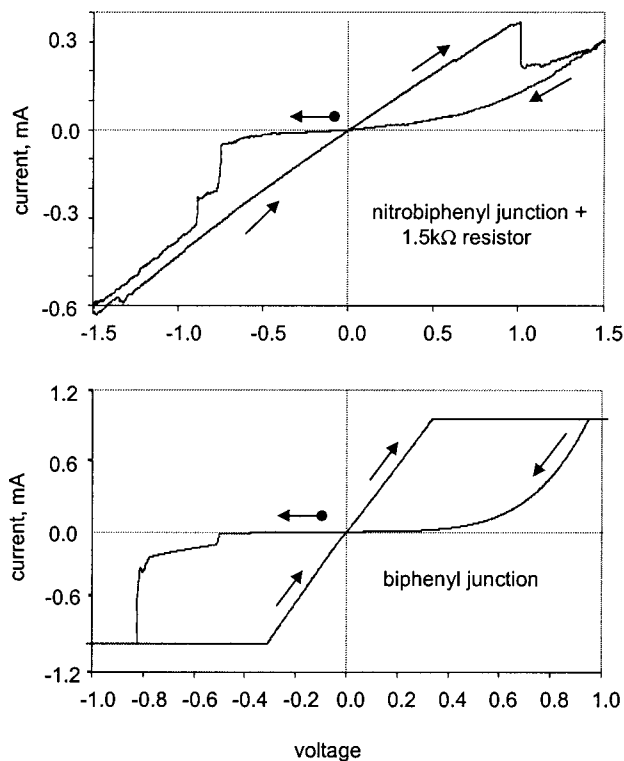


Figure 2. Room-temperature current/voltage behavior of nitro-biphenyl (top) and biphenyl (bottom) molecular junctions, scanned at 0.1 V/s. Arrow with circle indicates initial scan direction. The nitro-biphenyl junction had a 1.5 k Ω resistor in series to prevent overcurrent damage, and the biphenyl junction was limited to 1 mA by the potentiostat. Scan rate was 0.1 V/s.

switching was also observed in biphenyl and terphenyl, without a nitro group. A mechanism that is common to all switching molecules is shown in Fig. 3, illustrated for the case of nitro-biphenyl. The phenyl rings in free nitro-biphenyl are nonplanar, with a dihedral angle between 30 and 40° . Furthermore, a monolayer of nitroazobenzene is rotationally disordered when bonded to the edge plane of highly ordered pyrolytic graphite.¹⁹ All the molecules listed in Table I as switchers are likely to have one or more phenyl rings which are out of the plane of the graphitic rings when the molecules are initially bonded to the PPF substrate.

Past spectroscopic and electrochemical observations indicate that the electronic coupling between the carbon substrate and monolayer is strong, as might be expected for a symmetric, conjugated C—C bond.^{19,20} As the PPF surface becomes more negative in response to an applied voltage, one would expect electron transfer into the monolayer. This electron transfer is analogous to an electrochemical reduction of the monolayer molecule, except there are no counterions or solvent, and the molecule is strongly coupled to the substrate. A similar charge transfer has been considered for STM experiments, in which an electric field is imposed on an adsorbate, and interactions between the electric field and the surface dipole were proposed.²¹ Predicted electric fields in junctions such as that of Fig. 1 are 5-10 MV/cm when switching occurs, certainly adequate to partially polarize the electron distribution between the monolayer molecule and the PPF. The structure shown in the right side of Fig. 3 results from transfer of one electron into the nitro-biphenyl molecule. We refer to the right hand structure as the "quinoid" form, which includes several resonance forms in addition to that shown. It is important to note that the quinoid form is planar, the anion is delocalized over the entire structure, and has significant bond length changes relative to the original nitro-biphenyl. In fact, strong electronic coupling between the quinoid structure and the graphitic π system may result in a large, delocalized electronic system which combines contributions from both the monolayer molecule and the carbon substrate. The ring rotation and bond length changes from the phenyl to quinoid forms result in activation barriers which are presumably the origin of the temperature dependence. The electron transfer is expected to be governed by Marcus theory, with the activation barrier representing the reorganization energy associated with ring rotation and nuclear rearrangement.

It is useful to consider the structural changes associated with electron transfer from PPF to a monolayer molecule in more detail. Rather than attempt to analyze graphite fragments theoretically, we used model structures based on nitro-biphenyl and its quinoid form. The case shown in Fig. 3 was modeled by nitro-biphenyl, its anion, and 4-nitro-biphenyl-4'-methide to force the nitro-biphenyl to assume the quinoid form. Bond lengths and charge distributions were calculated with Gaussian 98 using density functional theory (B3LYP/6-31G(d) level) for nitro-biphenyl, free nitro-biphenyl anion, and nitro-biphenyl methide. The calculated structures and selected bond lengths are shown in Fig. 4. The methide is planar, as opposed to a 38° dihedral angle in nitro-biphenyl. The bridging C—C bond shortens by 0.023° in the anion and 0.051° in the quinoid form. These observations support the changes in conjugation shown in Fig. 3, with the nitro-biphenyl/PPF bond taking on double bond character and the two rings in nitro-biphenyl becoming coplanar with the graphite plane of the PPF.

In addition to increased conjugation and planarity, there are several reasons why the anion or quinoid structures would be expected to have higher conductivity than the biphenyl form. The highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO-LUMO) gap decreases from the phenyl to the quinoid forms of all the "switching" molecules (Table II), and the polarizability of the quinoids is much higher. The bond lengths in the methide skeleton are closer to each other in magnitude, and the molecular orbitals of the methide are more delocalized. It is generally accepted that bond length alternation is a primary determinant of the bandgap in polyacetylene, with the limit of equal length bonds yielding zero gap and metallic conduction.²²⁻²⁴ For polyphenylenes

Table I. Observed switching characteristics of carbon-based molecular junctions.

Junction molecule ^a	R_{off} , $k\Omega$	$R_{\text{off}}/R_{\text{on}}$	No. of repetitive switches ^b	No. of junctions studied	Percentage switched ^c	t ($^{\circ}\text{C}$) ^d
<i>para</i> -Terphenyl	23.7	8.8	>100	11	82	5-70
4'-Nitrobiphenyl ^e	23.9	8.5	60	10	80	50
<i>para</i> -Biphenyl	13.6	24.4	17	12	83	50
4'-Nitroazobenzene	17.3	5.7	33	14	14	20-50
4-Azobenzene	9.4	105	8	13	15	20-50
2-Chrysenes	0.27	-	0	21	0	20-50
4-Stilbene	8.1	-	0	10	0	20-50
4-(Phenyl methylene)phenyl	3.1	-	0	17	0	50

^a All junctions formed with 10 derivatization scans in diazonium salt solution (1 mM) in acetonitrile except for nitroazobenzene, which used four scans.

^b Maximum number of switching cycles observed for a single junction.

^c Exhibited three successive On/Off switching cycles.

^d Temperature range studied for each molecule.

^e 4' indicates the ring position farthest from the graphitic substrate, unprimed numbers refer to the ring position bonded to the substrate.

and poly(*p*-phenylene vinylene), however, the bandgap is a function more of quinoid character than bond alternation, and charge injection is predicted to increase quinoid character.^{25,26} The switching observed in Fig. 2 is likely to be a direct measure of molecular conductivity, with high conductance associated with the extended π system in the quinoid form of nitrobiphenyl. The activation barrier associated with the structural rearrangement shown in Fig. 3 is responsible not only for the activation barrier but also for the switching hysteresis. The quinoid form is apparently the higher energy form in the absence of an electric field, but is the favored form in a high field. The reorganization energy is sufficiently large that the quinoid form survives after the field is removed, at least for several minutes to several hours.

A mechanism similar to that shown in Fig. 3 is likely for nitroazobenzene, but does not obviously apply to the other switchers, biphenyl and terphenyl. A useful model for the biphenyl case is shown in Fig. 5 and Table II, using a biphenyl monomethide to represent chemisorbed biphenyl after injection of an electron. Note

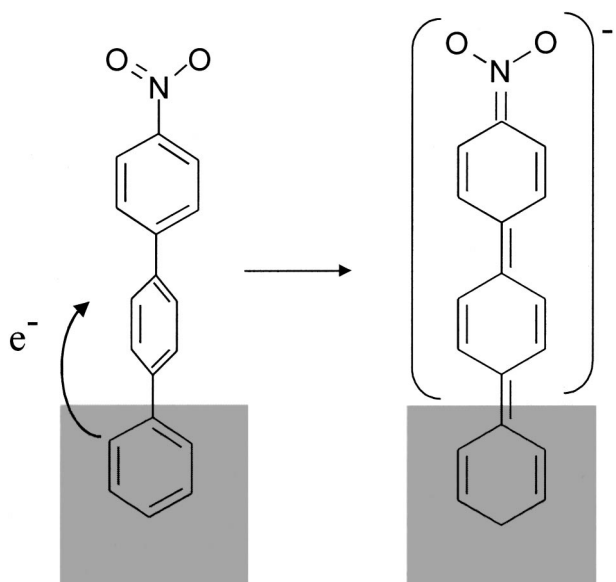


Figure 3. Mechanism for conductance switching based on electron transfer from the carbon substrate to the nitrobiphenyl monolayer, resulting in formation of a planar quinoid structure. The dihedral angle between the biphenyl rings and the graphite plane is expected to be 30-40 $^{\circ}$ initially, but decreases to near zero in the On state. Shaded region represents the extended graphitic π system.

that electron injection to form an anion creates a more planar structure, and decreases the bridging bond length from 1.486 to 1.439. The negative charge is distributed over the entire biphenyl anion, implying extensive electron delocalization. These bond length changes are similar to the $\sim 0.04^{\circ}$ predicted theoretically when charge is injected into a *p*-phenylvinylene oligomer.²⁶ The theoretical predictions imply that electron injection into biphenyl and presumably terphenyl promotes formation of a more conductive quinoid species. In all of the switching molecules listed in Table II, there is a transition from a rotationally disordered phenylene species to a planar, quinoid species. Accompanying this transition are significant changes in bond length, an increase in quinoid character and shortening of the bridging C—C or C—N bonds. The extent of charge transfer from the graphitic π system into the monolayer and the involvement of the graphite-monolayer bond determine whether the free anion or the methide anion is a more accurate representation of the junction, but both structures are more planar and have more quinoid character than the initial monolayer structure. It should be emphasized that the structures in Fig. 3-5 represent a few of many possible resonance forms. Spectroscopic experiments are currently in progress to more precisely define the structural changes accompanying switching conductance.

Electron injection into a monolayer was originally proposed to explain NDR,² but was criticized due to the requirement for a coun-

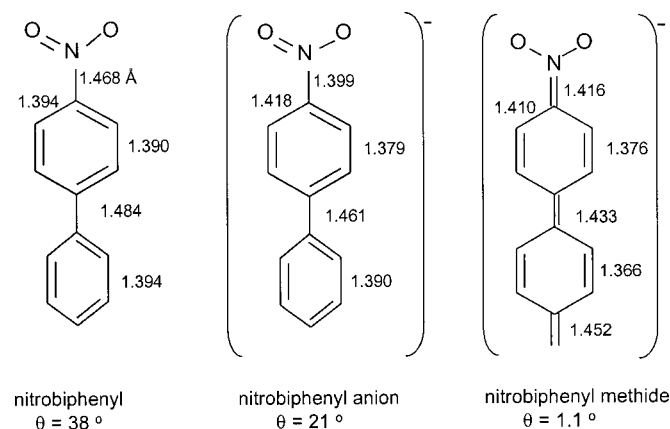


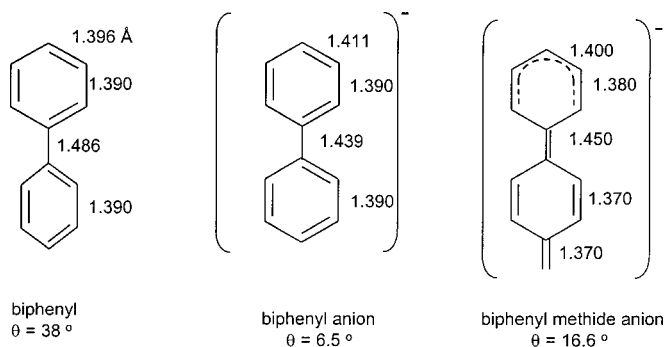
Figure 4. Calculated bond lengths and dihedral angles for nitrobiphenyl, its anion, and a methide form designed to force formation of the quinoid structure. Results are for free molecules determined with Gaussian 98 using density functional theory, and bonding shown represents one of several resonance forms.

Table II. Calculated^a structural parameters and HOMO-LUMO gaps.

Structure	HOMO-LUMO, eV	Bridging bond length, ^b Å	Dihedral angle ^c
Terphenyl	4.75	1.484	38°
Terphenyl anion	2.08	1.440	15.6°
Terphenyl dimethide	1.39	1.422	0.0°
Nitrobiphenyl	4.26	1.484	34°
Nitrobiphenyl anion	2.23	1.461	21°
Nitrobiphenyl 4'-methide anion	1.96	1.433	1.1°
Biphenyl	5.37	1.486	38°
Biphenyl anion	1.62	1.439	6.5°
Biphenyl monomethide anion	2.94	1.450	16.6°
Biphenyl dimethide	2.24	1.406	0.0°
Nitroazobenzene (NAB)	3.62	1.419	0.0°
NAB anion	2.16	1.360	0.0°
NAB methide	2.11	1.365	0.0°

^a Gaussian 98, B3LYP/6-31G(d).^b C-N_{azo} for NAB, phenyl-phenyl bond in other cases.^c Between phenyl rings.

terion to neutralize the resulting space charge. The mechanism of Fig. 3-5 would also generate a negative space charge in the monolayer, and the question arises of how that space charge is compensated. Compensation may not be necessary in the presence of a large static field, as shown by an estimate of space charge effects in the monolayer. A parallel plate capacitor with a thickness of 15 Å and a dielectric constant of 2 has a predicted capacitance of 1.1 μF/cm². If 10% of the molecules in the junction are turned On, the resulting potential is 0.17 V for a coverage of 2 × 10⁻¹⁰ mol/cm². As more charge is injected, this space charge potential will increase, and the voltage required for charge injection will increase. While space charge effects are undoubtedly important at some point, they do not appear to prevent switching a minority of the molecules in the absence of counterions.

**Figure 5.** Calculated bond lengths and dihedral angles for free biphenyl, its anion, and its monomethide.

A conductance switching mechanism based on field induced molecular rearrangement explains the observations for the carbon-based molecular junctions studied here. A similar rearrangement is possible for the phenyl-ethynyl monolayers which exhibit NDR, although there is less experimental support. The fact that NDR is observed below 100 K implies that any reorganization is very small, with a small activation barrier. However, changes in structure in high fields is likely in many molecular junctions, and may have significant practical applications, such as nonvolatile memory or programmable logic elements. A more general and fundamental implication of the mechanism is the consideration of a molecular junction as a form of dry electrochemistry. Electron transfer and nuclear reorganization apparently occur in molecular junctions in a manner analogous to redox reactions in solutions or solid electrolytes. However, the absence of solvent and counterions, and the orientation of molecules within the junction permit some unusual experiments, particularly the effect of high electric fields on oriented organic molecules.

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