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The Electrical Properties of Biphenylenes

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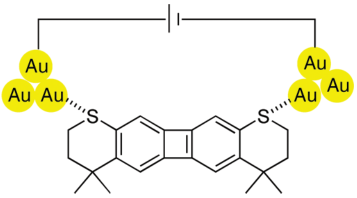
ABSTRACT



The effect of the partial antiaromaticity of biphenylene on its substitution chemistry, its oxidation potential, and its single-molecule conductance is explored. Biphenylene and fluorene molecules with linkers of two amino groups or two cyclic thioether groups were synthesized and their conduction properties were investigated using scanning tunneling microscopy (STM) break-junction techniques and DFT calculations. Despite the partial antiaromaticity of biphenylene, which causes the biphenylenes to be much more easily oxidizable, no significant increase in molecular conductance was found.

Understanding the relationship between the electronic properties of single molecule devices and the molecular structures from which they are constructed is fundamental to the advancement of nanoscience toward making functional nanoscaled devices.[1,2] Many different molecular systems have been proposed to function as highly conducting molecular wires bridging gaps between two metal electrodes, including oligo(phenylene-ethinylene), oligo(phenylene-vinylene), polyphenyls, and polythiophenes.[3−8] These molecules form extended conjugated systems, where the delocalization of the electrons through the molecular backbone decreases the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Electron transport measurements through such molecules bonded to metal electrodes with various different chemical link groups including thiols and amines have been performed, primarily through either the mechanically controlled break-junction technique or the STM-based break-junction technique.[9−11]

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(1) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.
(2) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384.
(3) Kushmerick, J. G.; Naciri, J.; Yang, J. C.; Shashidhar, R. *Nano Lett.* **2003**, *3*, 897.
(4) Blum, A. S.; Yang, J. C.; Shashidhar, R.; Ratna, B. *Appl. Phys. Lett.* **2003**, *82*, 3322.
(5) Wu, S. M.; González, M. T.; Huber, R.; Grunder, S.; Mayor, M.; Schönenberger, C.; Calame, M. *Nature Nanotechnol.* **2008**, *3*, 569.
(6) Kim, B.; Beebe, J. M.; Jun, Y.; Zhu, X. Y.; Frisbie, C. D. *J. Am. Chem. Soc.* **2006**, *128*, 4970.
(7) Widawsky, J. R.; Kamenetska, M.; Klare, J.; Nuckolls, C.; Steigerwald, M. L.; Hybertsen, M. S.; Venkataraman, L. *Nanotechnology* **2009**, 434009.
(8) Lu, Q.; Liu, K.; Zhang, H.; Du, Z.; Wang, X.; Wang, F. *ACS Nano* **2009**, *3*, 3861.
(9) Xu, B. Q.; Tao, N. J. J. *Science* **2003**, *301*, 1221.

10.1021/ol1017036

Earlier work on diaminoacenes had shown that 9,10-diaminoanthracene was more conducting than 1,4-diaminonaphthalene, which was a better conductor than 1,4-diaminobenzene. In this series, the trends in the HOMO−LUMO gap correlated with the conductance. In addition, since the N in these molecules could form partial π-bonds with the adjacent C when bonded in a junction, developing some quinoid character in the ring, it was interesting to note that the conductance of these diamino-acenes correlated with the stability of the corresponding quinones relative to their hydroquinones.[12] This result suggests the possibility of increased conductance in antiaromatic compounds,[13] where the equivalent of a quinoid form with diminished antiaromaticity could be favorable.[14−16] Furthermore, the HOMO−LUMO gap is generally smaller in antiaromatic rings than in aromatic ones, and thus, one would expect a higher conductance for antiaromatic compounds.

Antiaromatic cyclobutadienes would provide ideal test molecules for this study, but simple cyclobutadienes perform Diels−Alder reactions on themselves so rapidly that they cannot be handled under normal room temperature conditions. Thus, we focused first on the more stable biphenylene system **1**, with the cyclobutadiene ring fused with benzene rings. The proposed antiaromatic effect on conductivity could be considerably smaller in biphenylene, reflecting the greatly diminished cyclobutadiene character in the central ring. Only one resonance form out of four has both double bonds in the four-membered ring (Figure 1), and that one is a minor contributor.

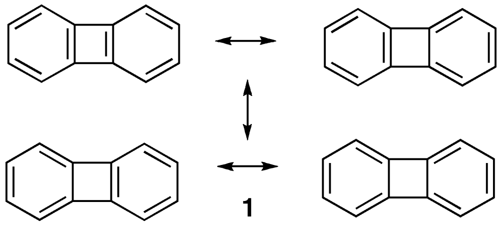
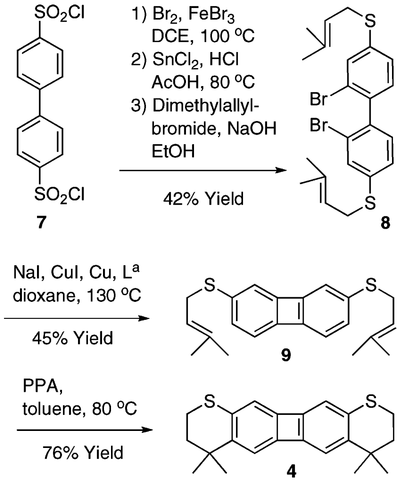


Figure 1. Resonance forms of biphenylene.

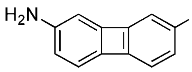
For this study, we synthesized biphenylenes with two different terminal chemical groups for linking to gold electrodes: amines and cyclic thioethers, which couple well to the π-systems in these molecules and bind selectively to undercoordinated gold.[17] We compared the conductance of the biphenylene backbone with that of a fluorene backbone.

Scheme 1. Synthesis of Biphenylene **4**[a]

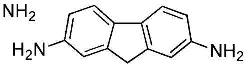


[a] L = *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine. DCE is 1,2-dichloroethane.

2,7-Diaminobiphenylene **2** is a known compound, and we synthesized it following the published procedure.[18] 2,7-Diaminofluorene **3** was purchased from Sigma-Aldrich and used without further purification. In ref 18, the authors reported a melting point and a low-resolution mass spectrum for **2**, but no NMR spectra. We were able to obtain a ^{1}H NMR spectrum of an impure sample of **2** (see the Supporting Information). The authors of ref 18 reported that solid **2** turned color on standing in air, while we find that oxidation occurs instantly in air with solutions of **2**. We attempted cyclic voltammetry and conductivity measurements on reasonably pure solutions of **2** in an inert atmosphere, but the CV curves were not reversible and the conductivity was ill-defined at best. Thus, we turned to a biphenylene derivative and its fluorene analogue with contacts that were less electron-donating, the thioether groups in compounds **4** and **5**.[17] They were synthesized as outlined in Schemes 1 and 2.



biphenylene **2**



fluorene **3**

We brominated commercial biphenyldisulfonyl chloride **7** and then reduced it in situ to the bis thiol to which we attached two dimethylallyl units. The resulting bis-bromobiphenyl **8** was then converted into the diiodide following a methodology developed by Buchwald and Klapars,[19] and under the reaction conditions the biphenylene compound **9** was formed directly in an Ullman-type coupling. Finally, we then cyclized **9** under acidic conditions to **4**. In principle, **9** might cyclize to either carbon 1 or carbon 3, and at the other end to carbon 8 or carbon 6, but

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(10) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458.

(11) Li, C.; Pobelov, I.; Wandlowski, T.; Bagrets, A.; Arnold, A.; Evers, F. *J. Am. Chem. Soc.* **2008**, *130*, 318.

(12) Quinn, J. R.; Foss, F. W.; Venkataraman, L.; Breslow, R. *J. Am. Chem. Soc.* **2007**, *129*, 12376.

(13) Breslow, R.; Foss, F. W. *J. Phys.: Condens. Matter* **2008**, *20*, 374104.

(14) Breslow, R.; Murayama, D. R.; Murahash, S.; Grubbs, R. *J. Am. Chem. Soc.* **1973**, *95*, 6688.

(15) Roberts, J. D. *Chem. Soc., Spec. Publ.* **1958**, *12*, 111.

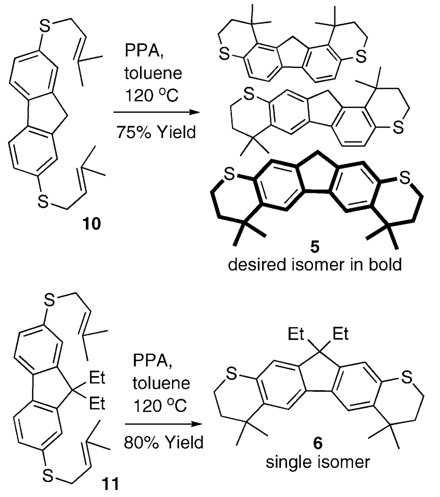
(16) Manatt, S. L.; Roberts, J. D. *J. Org. Chem.* **1959**, *24*, 1336.

(17) Park, Y. S.; Widawsky, J. R.; Kamenetska, M.; Steigerwald, M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L. *J. Am. Chem. Soc.* **2009**, *131*, 10820.

(18) Larkem, A.; Larkem, H. *Indian J. Chem., Sec. B* **2002**, *41*, 175.

(19) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844.

Scheme 2. Synthesis of Fluorene Derivatives



the cyclization reaction was completely regioselective, cyclizing only onto carbons 3 and 6.

This selectivity reflects the result of antiaromaticity in the four-membered ring.[20,21] Biphenylenes preferentially substitute on the β carbon,[22] in contrast with naphthalenes that substitute on the α carbon.[23] In naphthalene, the attachment to carbon 1 is used in order to produce reasonable stabilization of a cation without disrupting the aromaticity of the second benzene ring. The preference to go to the β carbon in the biphenylene system reflects the fact that disrupting the antiaromaticity of the four-membered ring is desirable and occurs in two of the resonance forms for β-attack (Figure 2). Only one favorable resonance form can be drawn for α-attack, making β-substitution preferred.

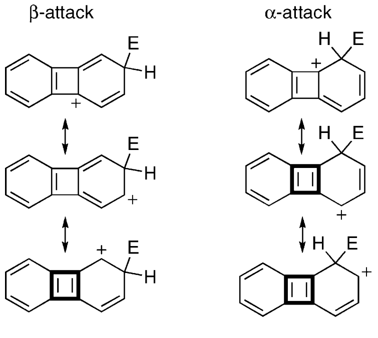


Figure 2. Major resonance forms of the intermediate for α and β electrophilic attack on biphenylene (left ring fixed). Destabilizing cyclobutadiene parts are shown in bold.

The synthesis of the fluorene derivatives **5** and **6** followed a route similar to that for the synthesis of biphenylene **4**. Compounds **10** and **11** were prepared as described in the Supporting Information and then again cyclized under acidic conditions (Scheme 2). As expected, the cyclization reaction of **10** gave a mixture of isomers, which we separated with preparative HPLC. We were able to avoid the problem of an unselective synthesis by attaching two ethyl groups to the methylene carbon of the fluorenyl system in compound **11**, which by steric hindrance promoted only the cyclization onto carbons 3 and 6 of the fluorenyl compounds.

Biphenylene **4** was much easier to handle than the diamino analogue **2** and did not oxidize in air. The reversible oxidation potential of **4** measured by cyclic voltammetry was lower by about 120 mV than the oxidation potentials of the fluorenyl analogues **5** and **6** (see Table 1). This indicates that the cyclobutadiene system in biphenylene **4** still promoted oxidation, as it did in **2**. Biphenylene **2** gave an irreversible oxidation peak (see the Supporting Information) by cyclic voltammetry at −1045 mV, explaining its reactivity with air. In the past, we have seen that more easily oxidized derivatives of benzene had higher conductivities, suggesting that in the conducting state the ring becomes partially p-doped as some electron density is withdrawn by the anode before electrons could be fed in from the cathode.[12]

Table 1. Experimental Conductance and First Oxidation Potentials

compd	conductance ($G_0 \times 10^{-3}$)[a]	$E_{1/2}$ (V) vs Ag/Ag^{+}[b]
2	undefined	irreversible
3	1.7 ± 0.2[c]	−0.037[c]
4	3.6 ± 0.2	0.509
5	3.5 ± 0.3	0.633
6	4.4 ± 0.3	0.627

[a] Most probable molecular conductance, determined with break junction measurements. Error bars represent standard deviations of measured peak positions determined from a Lorentzian fit to the conductance histogram. [b] First oxidation potential determined with CV. [c] Values from ref 8.

We measured the conductance of all four molecules using a scanning tunneling microscope-based break-junction technique.[9,10] 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.[10] 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 3 shows conductance histograms generated (without any data selection) from over 5000 measured traces with each molecule. Measurements of **2** were carried out in an argon atmosphere due to its instability in air, but even so it gave a broad conductance range that could not be identified with a single value. From the position of these peaks for all other molecules, we obtain a conductance value, listed in Table 1. We see that the conductance values for the biphenylenes are not significantly different from those of the fluorenes.

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(20) Eckert-Maksic, M.; Fabian, W. M. F.; Janoschek, R.; Maksic, Z. B. *THEOCHEM* **1995**, *338*, 1.

(21) Wang, D. Z.; Streitwieser, A. *Theor. Chem. Acc.* **1999**, *102*, 78.

(22) Blatchly, J.; Taylor, R. *J. Chem. Soc. B* **1968**, 1402.

(23) Field, L. D.; Sternhell, S.; Wilton, H. V. *J. Chem. Educ.* **1999**, *76*, 1246.

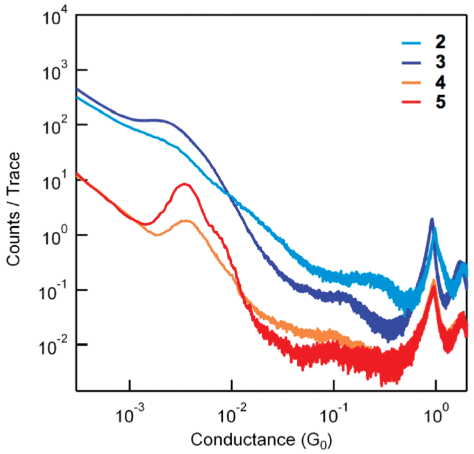

Figure 3. Conductance histograms for compounds **2**−**5** generated using a linear bin size of 0.0001 G_0.

To gain a better understanding of these results, in particular, the reason that oxidation potentials did not correlate with conductivities, we performed density functional theory calculations[24−26] for the two diamines (**2**, **3**) and the two cyclic thioether compounds (**4**, **5**). In each case, the geometry was fully optimized. In agreement with overall expectations, the calculated HOMO−LUMO gaps for the biphenylene species are about 20% smaller than those for the fluorene species. However, the calculated vertical ionization potentials are very similar, with the biphenylene species showing values 0.1 eV smaller, at most. The tunnel coupling was estimated using a single gold atom to model the attachment point of each linker to its respective electrode. The tunnel coupling is proportional to the splitting between the symmetric and antisymmetric combinations of the Au−molecule−Au frontier orbitals. This general method to assess tunnel coupling and conductance[27,28] has been shown to correctly predict the trends in low-bias conductance of single gold−diamine−molecule junctions.[29] The predicted ratio of the conductance through the amine-linked biphenylene **2** to that through the amine-linked fluorene **3** was 1.3, and the predicted ratio for the methylsulfide-linked **4** to that for **5** was 1.2. These modest changes in conductance follow the trend suggested by the HOMO−LUMO gap trends, and they are consistent with the measured values.

The possible higher conductivity of antiaromatic wires is not seen in these studies, even though the biphenylenes are indeed more easily oxidized than are the fluorenyl compounds. It is not clear whether this lack of a higher conductivity simply reflects the greatly diminished antiaromaticity of biphenylenes compared with true cyclobutadienes. Thus, our goal is now to prepare sterically protected cyclobutadiene derivatives that are not compromised by fusion with benzene rings to see if we can measure conductivities in a purely antiaromatic system. These studies are underway.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(25) Jaguar v7.5; Schrodinger, L.L.C., New York, NY, 2008.

(26) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(27) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

(28) Nitzan, A. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681.

(29) Hybertsen, M. S.; Venkataraman, L.; Klare, J. E.; Whalley, A. C.; Steigerwald, M. L.; Nuckolls, C. *J. Phys.: Condens. Matter* **2008**, *20*, 374115.