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Single molecule conductance of aromatic, nonaromatic, and partially antiaromatic systems



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ABSTRACT

We describe the syntheses of thiophene, cyclopentadienone and dimethylketalcyclopentadienone derivatives and their single molecule electrical conductivities. The ketone had the lowest conductivity of the three, although it has some antiaromaticity. The carbonyl group is electron attracting and its ionization potential outweighs any conductivity increase that the antiaromaticity effect might bring. © 2015 Published by Elsevier Ltd.

Introduction

Miniaturization of photovoltaics and organic electronics is advancing towards the molecular level.^{1,2} The goal is to replace the interconnecting wires between transistors in electronics with a conducting material as small as a single molecule or more likely short oligomers, molecular wires.^{3–6} Conjugated organic oligomers such as polythiophenes and polyaniline are a few examples of highly conducting molecular systems that have been used in nanoscaled devices.^{7,8}

We have described evidence that the aromaticity of such common components of molecular wires as thiophene rings diminishes their electrical conductivity.⁹ The reason is that the aromatic systems comprise six pi electrons cyclical delocalized in the rings, while when the ring has connections to an anode and a cathode the preferred electron distribution for maximum electrical conductivity has some pi electron density external to the ring. In a sense, in order to maximize the conductivity of the system an aromatic benzene ring in 1,4-diaminobenzene would shorten the external C–N bonds and develop more quinoid character if the two amino groups were placed between electrodes across a potential gap. This diminishes the aromaticity, so there is an energy price compared with similar nonaromatic systems.

Our first example of this effect was seen comparing the conductivity of a thiophene ring, an oxazole ring, and a

1,1-dimethylcyclopentadiene ring with attached *p*-aminophenylacetylene (Fig. 1) leads that then contacted gold electrodes in a gold scanning tunneling microscope break-junction (STM-BI) experiment.⁹ We saw that the poorest conductor was the thiophene ring, somewhat better was the oxazole ring (oxazole has less aromatic stabilization than thiophene) and the best was the nonaromatic dimethylcyclopentadiene ring. This raises the question of whether the aromatic polythiophenes, commonly used as molecular wires, are poorer electrical conductors than polymers of less aromatic or anti aromatic compounds would be. It also raises the question of whether an antiaromatic compound would be a better electrical conductor. As we described,⁹ when aromatic molecules are placed between electrodes there is a distortion of the electronic structure of the aromatic system since the molecules adopt a nonaromatic structure to some extent in which a benzene ring partially resembles a quinone-like structure. Thus aromaticity fights conductivity. However, antiaromatic systems diminish cyclic conjugation as far as possible, for instant by making cyclobutadiene an elongated rectangle, not a square. Thus antiaromatic compounds should prefer the distortion that conductivity also prefers, and become better conductors as a result.¹⁰

Results and discussion

We wanted to examine the conductivity of a cyclopentadienone ring, which is partially antiaromatic. Since such rings are very reactive unless they have tetra-substitution, reflecting their partial antiaromaticity, we have constructed three molecules





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Figure 1. Structures of thiophene, oxazole, and cyclopentadiene molecular wires.



Figure 2. Structures of three molecular wires investigated.



Scheme 1. Syntheses of compounds **1** and **2**. Reagents and conditions: (a) *tert*-butylacetylene, Pd(PPh₃)₄, CuI, *i*Pr₂NH, rt, 12 h; (b) 4-aminophenylacetylene, Pd(PPh₃)₄, CuI, Et₃N, THF, 50 °C, 12 h; (c) CF₃COOH (5%), CH₂Cl₂, H₂O, 0 °C-rt, 30 min.



Scheme 2. Syntheses of compound **3**. Reagents and conditions: (a) 4-aminopheny-lacetylene, Pd(PPh₃)₄, Cul, iPr_2NH , THF, 0 °C–rt, 3 h; (b) *tert*-butylacetylene, Pd(PPh₃)₄, Cul, Et₃N, THF, 50 °C, 12 h.

Table 1

Molecular structures and their conductance

Molecule number	Conductance $(G_0 \times 10^{-4})^a$	Relative conductance
1	1.25	0.50
2	3.16	1.26
3	2.51	1.00

^a G_0 is the quantum of conductance, $2e^2/h$.

2,5-bis((4-aminophenyl)ethynyl)-3,4-bis(3,3-dimethylbut-1-yn-1yl)cyclopenta-2,4-dien-1-one (**1**), 4,4'-((4,5-bis(3,3-dimethylbut-1-yn-1-yl)-2,2-dimethoxycyclopenta-3,5-diene-1,3-diyl)bis(ethyne-2, 1-diyl))dianiline (**2**), and 4,4'-((3,4-bis(3,3-dimethylbut-1-yn-1yl)thiophene-2,5-diyl)bis(ethyne-2,1-diyl))dianiline (**3**) with *p*-aminophenylacetylene conducting links on carbons 2 and 5 and with *tert*butylacetylene groups on positions 3 and 4 (Fig. 2).

In the synthesis (Scheme 1) we started with the known 1,2,3, 4-tetrabromo-5,5-dimethoxy cyclopentadiene 5,^{11,12} prepared from a modified literature procedure using hexabromocyclopentadiene (**4**) as described in experimental section and coupled it with two equivalents of *tert*-butylacetylene under Sonogashira coupling conditions¹³ to afford intermediate **6**. This was then coupled with *p*-aminophenylacetylene to afford **2**, the dimethylketal that has a non-aromatic cyclopentadiene system. Aqueous acid catalyzed hydrolysis of **2** afforded the ketone **1**, the potentially antiaromatic compound. For comparison we also synthesized the thiophene derivative **3**, with an aromatic central ring. Starting with commercially available tetraiodothiophene **7**, intermediate diiodo compound **8** was synthesized by coupling with two equivalents of aminophenylacetylene. Intermediate **8** was then coupled with *tert*-butylacetylene to yield thiophene derivative **3** (see Scheme 2).

We then used the scanning tunneling microscope break-junction (STM-BJ) technique^{3,9} to determine the electrical conductance of these three molecules. The conductance for the molecules **1**, **2**, and **3** are given in Table 1 and their Log-binned one/two dimensional histograms are shown in Figure 3. The comparison of molecule **2** having a non-aromatic central core with molecule **3** having an aromatic thiophene center shows 26% better conductance by the non-aromatic species than the aromatic species. In our previous work the dimethylcyclopentadiene derivative was somewhat better, ~175% a better conductor than the thiophene. However, the proposed anti-aromatic compound **1** was the poorest conductor.

The poor conductance of **1** is related to the previous Letter¹⁴ that the diaminofluorenone derivative **9** is a poorer electrical conductor than its oxime ether derivative **10** (Fig. 4). Our 'antiaromatic' molecule **1** also has a strong electron-attracting carbonyl group.



Figure 4. Structures of diaminofluorenone and its oxime derivative.



Figure 3. (A) Log-binned one-dimensional conductance histograms for molecules 1, 2, and 3 generated without any data selection, from 10,000 traces, using a bin size of 100/ decade. (B) Two-dimensional histograms for 1, 2, and 3 showing conductance peaks extending over a distance of 1 nm relative to the break of the *G*₀ contact.

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Figure 5. Structures of compounds 11, 12, and 13.

The lower conductivity of the cyclopentadienone systems apparently reflects the fact that with electron-rich systems, such as those amines of the present and previous cases, placing the compounds between anodes and cathodes will result in some partial electron transfer to the anode (p-doping) to generate a better conducting system. The conductivity is lower if the ionization potential for partial p-doping is more positive. Since the carbonyl groups in compounds **1** and **9** are electron attracting, their effect on the ionization potentials of the molecules outweigh anyhypothetical increase in conductivity that the antiaromaticity effect might bring.

We have seen such counterbalancing effects previously.¹⁵ Few years ago we synthesized compounds 11 and 12, (Fig. 5) and determined their single-molecule conductivities. We found that they had essentially the same conductivity. Since the X-ray structure for biphenylene 13 shows strong distortions (alternating short and long lengths) induced by the antiaromaticity of biphenylene itself in order to diminish any double-bond character in the fourmembered ring (but **12** had no distortion) we proposed that this distortion should have decreased the conductivity of 11, so some other effect (e.g., antiaromaticity) should have made a conductivity-increasing contribution.^{10,15} That is related to our proposal for the current case, where any conductivity increase because of antiaromaticity was overwhelmed by the electron-withdrawing effect of the carbonyl group. If aromaticity decreases conductivity. as we have shown here and previously, the argument that antiaromaticity should increase it seems reasonable. However, the proposed effect remains to be demonstrated.

Conclusion

This work confirms the fact that aromaticity diminishes electrical conductivity in single molecule conjugation, but it does not yet furnish support for the idea that antiaromaticity should enhance conductivity. This remains a challenge for future work.

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Supplementary data

Supplementary data (experimental procedures and ¹H, ¹³C NMR and MS) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.06.076.

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