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Structure–property relationships in molecular wires

Ronald Breslow [*], Severin T. Schneebeli

Columbia University, Department of Chemistry, New York, NY 10027, United States

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ABSTRACT

Molecular electrical conductivities between gold electrodes have been measured at the single molecule level through a variety of systems. The results show that the aromaticity of molecules is partly disrupted by passage of electricity, leading to increased resistance. The possibility of the opposite effect resulting from the disruption of antiaromaticity was explored in biphenylene derivatives. When gold atoms terminate benzene or polymethylene molecules they incorporate into the electrodes, greatly diminishing the resistance from other terminating atoms. In paracyclophanes with two, three, and four benzenes in stacks the gold electrodes can directly contact them, and thus measure conductivity directly through the stacks.

Gilbert Stork

This is an article in recognition of the remarkable career of Gilbert Stork, with whom I have had a very long connection. I first met him when he was a young Assistant Professor at Harvard and I was an undergraduate chemistry major. I took one graduate course with him, but more importantly I did undergraduate research with Gilbert, working on the structure of cedrene. We used the then new tool of infrared spectroscopy to determine the ring size of the anhydride of a dicarboxylic acid from the oxidative degradation of cedrene, and the surprising result led to two JACS communications (Tetrahedron was not then in existence). In one we proposed the structure of cedrene itself, and in the other we described the rearrangement that must have occurred in the degradation path. Gilbert treated me as a knowledgeable colleague, and started me on the road to a research career.

After I graduated from Harvard I came to Columbia for a summer to work with Gilbert before starting my Ph.D. with Bob Woodward, and this may have helped me see that Columbia was an interesting place. Thus after my Ph.D. and a postdoc with Alex Todd I went on the job market, applying for various academic positions. I asked Gilbert to write supporting letters for me, and at one point received a telegram from him telling me that Columbia would offer me an instructorship. I accepted it, and when Gilbert told the Columbia chair Louis Hammett that I had accepted the position, Hammett replied ‘what position?’ It got straightened out, and I joined Columbia as Gilbert’s junior colleague in 1956.

In the succeeding 55 years it has been my great pleasure to continue as Gilbert’s colleague, resisting various opportunities to move. He is a wonderful colleague and role model, continuing his creative approach to organic synthesis up until this day. Gilbert is a fount of information, and of inspiration, and I have enjoyed helping him build what has become a world-class chemistry department. He has trained and educated a remarkable group of alumni of the Stork School of Chemistry. I happily congratulate him on his career, which we are all celebrating in this issue of Tetrahedron.

Ronald Breslow.

1. Electrical conduction in organic molecules

About 10 years ago Columbia University obtained one of the first grants from the National Science Foundation to start a study of nanoscale chemistry and physics. At the time Ronald Breslow was the Director of the Chemistry Section of the group and Nobel Laureate Horst Stormer was the co-Director in charge of the Physics parts of the work. It was a collaborative effort in which we chemists made interesting new molecules and did some measurements on them, including electrochemistry, and the physicists did some theory and as well measured the electrical conducting properties of the species we made.

1.1. Conjugated molecular wires

One of the areas that had interested many chemists and solid-state physicists concerns the properties of molecular wires, in

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[*] Corresponding author. E-mail address: rb33@columbia.edu (R. Breslow).

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which a number of well-defined units are linked together to make a conjugated and electrically-conducting system. A promising class of such molecules comprises polythiophenes, which needed a contact at each end in order to be able to connect with electrodes for conduction. We synthesized a group of these polythiophenes with well-defined lengths and discovered several interesting features.[1] In order to make contact with platinum electrodes, we put isocyanide groups on each end of the wires.

In the first work we characterized these wires by spectroscopy and were able to show that they did indeed bind to platinum surfaces with their isocyanide groups. Ultra-violet spectra indicated that there was conjugation up to a certain length as the UV signal moved to longer and longer wavelengths, but after that length there was no further increase in the position of the UV signal as the wires were made longer. The wires were at some point twisted, and not fully conjugated through their entire length of up to 16-mers. While enthalpy favors full conjugation, entropy favors twisting and eventually dominates. We were able to use some of the shorter untwisted wires to bridge a gap in a cut carbon nanotube.[2] This study used nanotubes as conducting electrodes, with a cut in the center achieved using an oxygen plasma to produce pairs of shorter nanotubes that could be covalently linked to molecular wires. Our molecules showed conductivity in this system, and so did many of the molecules made in the Colin Nuckolls group, who were the leaders in this particular study.

In later work we studied some molecular wires in which thiophenes and acetylene groups alternated to produce a molecular wire as long as 11 nm. By UV and fluorescence spectroscopy we again saw evidence that the wires were untwisted up to a certain length but when longer they were not fully conjugated because of twisting.[3] Using electrochemistry we were able to study the properties of these wires as we removed electrons from them. With the short wires we saw that the electrochemical oxidation potentials simply moved to the less positive direction and the molecules were easier to oxidize as the wires were longer, as expected, but with the longest wires a very interesting phenomenon was observed. The electrochemistry indicated that in the first oxidative wave two electrons were taken out of the long wires at once, making a dication, and then at higher positive potential a third electron could also be abstracted. This indicated that the originally twisted wires could be electrochemically oxidized, but when the monocation was produced the twisting straightened out and now the wires were fully conjugated. As a result the same potential that was needed to pull one electron out of a partially twisted wire was enough to pull a second electron out once the wire was straightened out and fully conjugated.

The conclusion from these studies was that long conjugated molecular wires are unlikely to be good useful electrical conductors when they get to significant lengths, but if they are simply electrochemically oxidized, quite an easy process with a long conjugated wire, the resulting charged wires are now fully conjugated and can be used as conductors in nanoscale molecular devices.

1.2. Aromaticity causes increased electrical resistance

In the meantime one of the members of the Columbia University Nanocenter, physicist Latha Venkataraman, had developed a way to connect molecular wires to electrodes and measure their conducting properties. She created what is called a gold break junction in a device with a gold surface and a gold tip that can be moved relative to the surface. As the tip was first pushed into the gold surface and then slowly withdrawn this generated a long gold thread that then broke, creating a gap across, which molecules could bridge (Fig. 1). The device formed and broke this junction many thousands of times in the device, giving highly reproducible data on the conductivity of molecules that could bridge the gap. By changing the concentrations of the molecules in solution where this gap was being created it was possible to show that one was measuring the conducting properties of a single molecular wire rather than of a group of wires bridging the gap.[4]

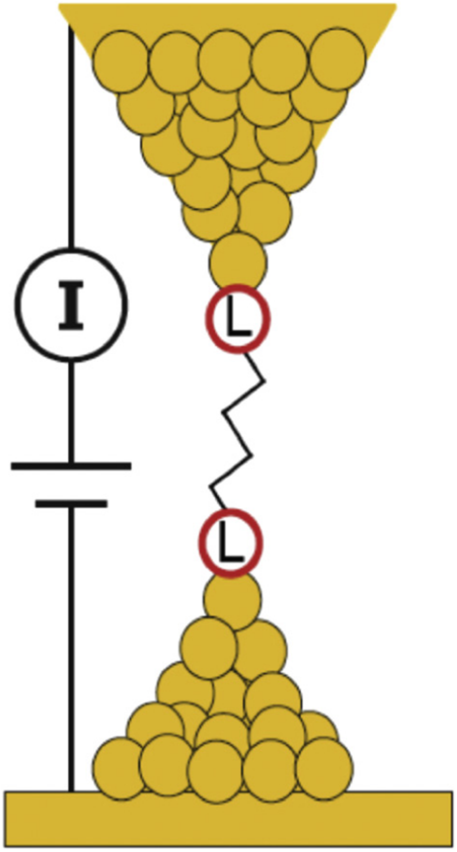


Fig. 1. A molecule binds in the gap created by a gold break junction, sometimes using special contacts symbolized as L.

We realized that this would give us an opportunity to investigate some very interesting questions about small molecular wires in order to relate their properties to the chemical structures of the molecules used in the experiment. Colin Nuckolls had already performed several studies using this break junction gap with a different group of molecules from the ones we were interested in.

In order to get contact with the gold electrodes that were formed by breaking this thin wire it was necessary at that time (see later) to have contacts—attached to the molecules of special interest—that would bind to the gold. In the first work done by the Venkataraman group the contacts used were simply amino groups, so she was able to measure the properties of molecules with amino groups at each end, such as 1,4-diaminobenzene. This gave us a chance to investigate the role of aromaticity in molecular conductance. Although molecular wires were generally constructed with aromatic units, such as thiophene rings, we thought it likely that the aromaticity of the rings causes a problem with respect to conductivity.

In the simplest case, if one used 1,4-diaminobenzene and it bridged gold electrodes and electricity went through the benzene ring, it seemed likely that the ring would achieve quinoid character as electricity passed through it (Fig. 2). With the gold linked to an amino group as electricity was passed through from the cathodes there should be extra π bonding character between the nitrogen and the ring, with partial double-bond character to that connection. At the other end of the ring there should also be double-bond character developed outside the ring as the electricity passed from the ring into the amino group and then into the gold anodes. To see whether this was true we decided to investigate structure–property relationships in this simple system of an aromatic ring with two amino groups as contacts for the gold electrodes.[4]

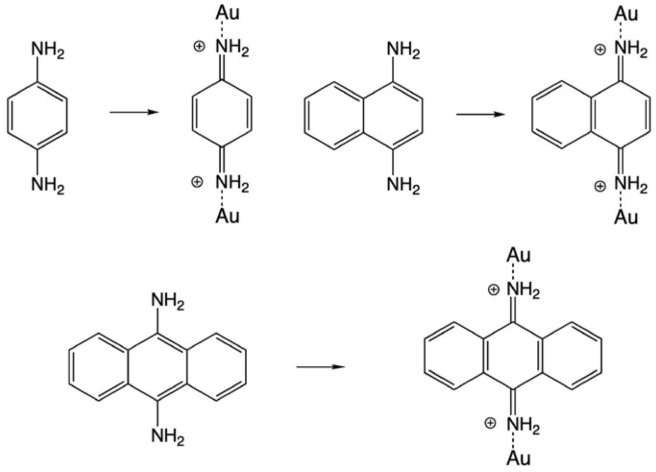


Fig. 2. Passage of electricity through benzene rings induces some loss of aromaticity as the rings become partially quinoid. As expected, this is less of a problem with 9,10-diaminoanthracene than with 1,4-diaminonaphthalene, and 1,4-diaminobenzene has the largest energy cost.

As Fig. 3 shows, we found that 1,4-diaminonaphthalene was a significantly better electrical conductor than was 1,4-diaminobenzene, and 9,10-diaminoanthracene was better still. This is directly related to the energies of the corresponding quinones, in which 9,10-anthraquinone is the most stable because with that structure two of the benzene rings are fully aromatic, while with the hydroquinone at least one of the rings does not have the three internal double bonds needed for greatest stability. By contrast, if with naphthalene and anthracene we simply put amino groups in the 2 and 6 positions, we saw much poorer conductivity relative to diaminobenzene since in these systems the quinoid structures we propose would in fact de-aromatize all the rings. We found that 2,7-diaminonaphthalene was not a conductor at all, related to the fact that there is no quinone with oxygens at the 2 and 7 positions. These findings supported our picture.

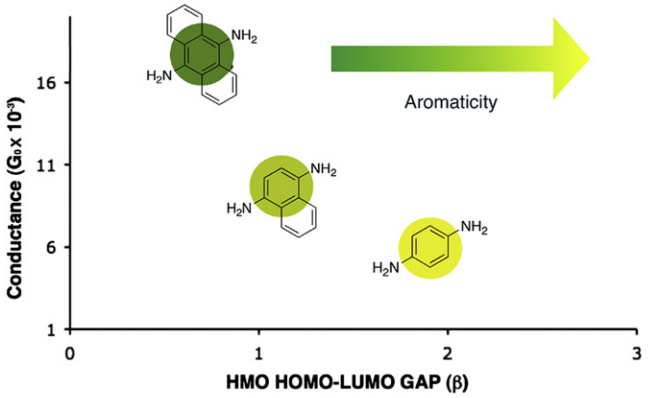


Fig. 3. Plot of the molecular conductance values versus the HOMO-LUMO gaps of the parent hydrocarbons (benzene, naphthalene, and anthracene) as determined with Hückel Molecular Orbital (HMO) theory. Increased aromatic stabilization leads to an increase in the HOMO–LUMO gap, which lowers the observed conductivities as expected if there is some quinoid character in the aminated rings during electrical conduction.

We also studied oxidation potentials in this series of aromatic compounds with two amino groups as contacts for the gold electrodes.[5] As an example, when 9,10-diaminoanthracene loses one electron by electrochemical oxidation the resulting cation radical has resonance forms in which there are two fully benzenoid rings, just as with the quinone, which can be thought of as a doubly oxidized ring. As Fig. 4 shows, we saw a direct correlation between ease of oxidation and conductivity through the hydrocarbon series. The 9,10-diaminoanthracene was at the same time the molecule with the highest electrical conductivity and also with the most negative oxidation potential, corresponding to easy removal of an electron.

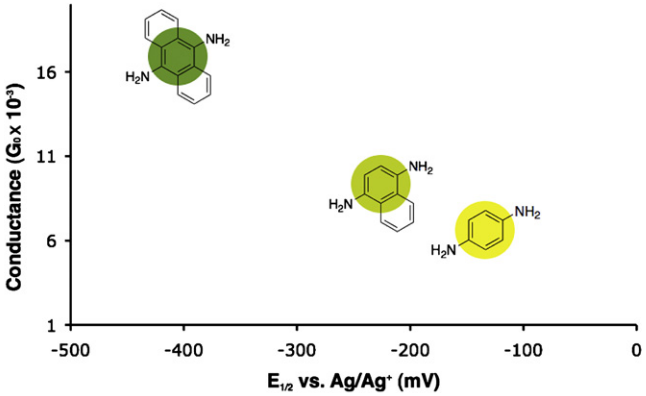


Fig. 4. Plot of molecular conductance values versus first oxidation potentials determined with cyclic voltammetry in acetonitrile.

However the correlation was not perfect. We found that 2,3,5,6-tetrafluoro-1,4-diaminobenzene was comparable in conductivity to the molecule without the fluorine atoms, but was much more difficult to oxidize.[5] This indicates a diminished amount of positive charge on the ring with the fluorines than in the unfluorinated compound when electricity is passed.

In one way to describe it, 1,4-diaminobenzene unsubstituted by fluorine atoms is more easily oxidized than reduced, so when it is between two electrodes it is likely that in the beginning of electrical conduction some positive charge goes into the ring as electrons flow to the anode a little before they can start feeding in from the cathode. Then the cathode can pass electrons into the electron-deficient ring. Thus with electron rich molecules we think it likely that they have a partial positive charge in their conducting state, related to some extent to our previous studies on the electrical conduction of positively charged wires described above. However, in 1,4-diaminobenzene with four fluorine atoms it is likely that there is no significant amount of positive charge being put onto the ring from the anode before electrons feed in from the cathode, and thus there is likely to be much less positive character in the conducting state of the ring with this tetrafluoro compound.

We saw something related in unsubstituted 4,4′-diaminobiphenyl compared with its fully substituted derivative with eight fluorine atoms, which is much harder to oxidize electrochemically.[5] Their conductivities are similar, with the fluorinated compound being only a slightly poorer conductor than the one without fluorines. In principal the wire may pick up either a little positive or a little negative charge depending on whether electron flow at the beginning of the process is easiest to the anode or from the cathode. In some compounds an equally balanced initial electron flow to the anode and from the cathode could maintain a more or less uncharged ring system. Thus in these fluorinated compounds the conductivities are not low even though they are hard to oxidize. (In later studies, which will be described further in this review, we also found a large difference in electrochemical oxidation potential relative to conductivity in an antiaromatic system.)

Our data on oxidation potentials versus conductivities were analyzed using a theoretical treatment.[5] The theory was consistent with the idea that the conduction through these systems occurs by a process called non-resonant tunneling, or superexchange. In that theory the tunneling rates decrease exponentially with increasing conductor length and with the barrier for tunneling. The distance is roughly the nitrogen–nitrogen separation, and the barrier height was related to the energy difference between the gold Fermi level and the molecular HOMO level.

1.3. Antiaromaticity in a molecular wire

We reviewed much of this in a solicited article in the *Journal of Physics*, in which we described to the physics community the meaning of aromaticity in chemistry, and how it is related to electrical conductivity.[6] We also pointed out what the phenomenon of antiaromaticity is, and made a prediction that we have more recently pursued. Since passing electrical current through an aromatic ring comes at the expense of partial loss of aromatic stabilization, causing some resistance, we predicted that passing electricity through an antiaromatic system might be made easier by disrupting the antiaromatic conjugation in such a system.

This was related to work we had done many years ago studying molecules in which electron donor *p*-anisyl groups were pushing electrons into a naphthoquinone, either directly or through a fused cyclobutadiene ring.[7] We found that the electron transfer between the directly linked anisyl groups and the quinone in compound **1** (Fig. 5) was three times less effective in modifying the reduction potential of the quinone ring than it was if the quinone and the anisyl groups were linked through the cyclobutadiene in compound **2**. Since such electron transfer through a connector is related to what is involved in electrical conductivity, we thought there was a good chance that a cyclobutadiene ring would constitute an exceptionally good component in a molecular wire.

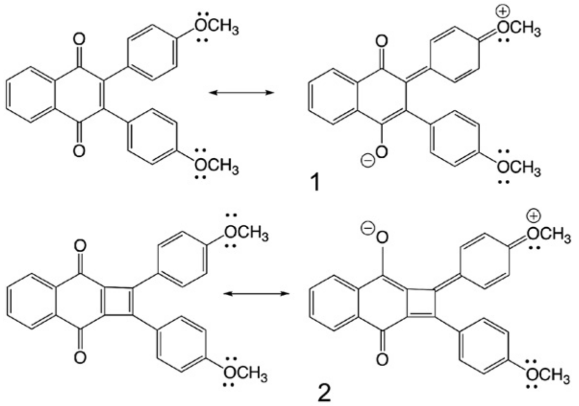
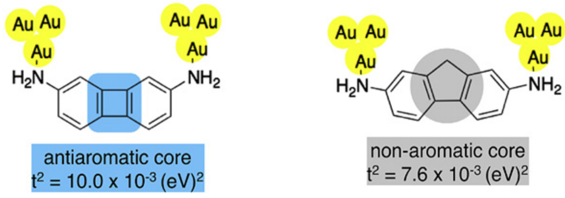


Fig. 5. The stabilization of the napthoquinone by the *p*-anisyl groups in compound **2** was threefold as great as that in compound **1**, since electron passage through the cyclobutadiene ring is promoted by antiaromaticity.[7]

Thus we took up the study of various biphenylenes, with at least some antiaromatic character because of the four-membered ring between the two benzenes.[8] We first studied 2,7-diaminobiphenylene (**3**) and its related 2,7-diaminofluorene (**4**) to see whether we could detect any special character in the antiaromatic biphenylene case. The fluorene is a reasonable comparison model. As Fig. 6 shows, it was predicted by computation that the conductance of **3** would be 32% higher than that of **4**.



3 4

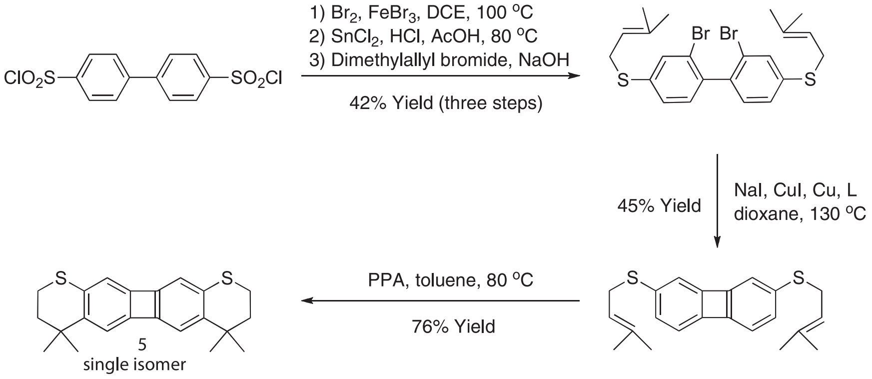
Fig. 6. DFT-Calculations predict that the biphenylene derivative **3** would be 32% more conductive than its fluorenyl analog **4**. t^2 represents the square of the calculated tunnel coupling, which is proportional to the conductance.[8]

We found that 2,7-diaminofluorene **4** was a perfectly well-behaved compound, and we were able to do a number of studies on it and measured its conductance in the gold break junction experiment. Its conductance and its one electron oxidation potential had both been described in the literature.[9] By contrast, 2,7-diaminobiphenylene **3** gave an undefined conductance and an irreversible oxidation wave in electrochemistry, apparently the result of the antiaromaticity of the central ring.[8] It was so easily oxidized that it could not be handled in the air, immediately turning into a colored irreversibly-degraded material. We used an inert atmosphere in order to examine its possible conductivity, but here too in the electrochemical apparatus there was an oxidative irreversible degradation of the molecule rather than a simple reversible conductivity measurement. Thus we had to go to a derivative of biphenylene that was less electron rich so we could measure its electrical and electrochemical behavior.

We synthesized compound **5** as shown in Scheme 1.[8] The striking result in the synthesis was that the ring closure onto the biphenylene unit occurred only on the β carbons of the benzene rings. This selectivity is a reflection of the antiaromaticity in the central cyclobutadiene ring. As the scheme in Fig. 7 shows, β attack onto a biphenylene produces three resonance forms in which the cation is delocalized (in this simple version we show the bottom benzene ring in one of its resonance forms, but in the expanded version we included both resonance forms of that ring.) In only one of these three delocalized structures is there an actual cyclobutadiene ring in the center, as compared with other structures without the cyclobutadiene character. By contrast (Fig. 7), in α attack—again keeping the bottom ring frozen—two of the three forms in which the positive charge is delocalized produce cyclobutadiene rings in the center and only one of them does not. A theoretical treatment of this situation has been described by Streitwieser.[10]

The preference in this case is in contrast with the well known preference for α substitution in naphthalene, in which it is possible to delocalize the positive charge in the ring being substituted without interfering with the aromatic benzene character of the ring to which it is fused. However, in the biphenylene case it is desirable to interfere with the antiaromaticity of the cyclobutadiene ring. When we made the same type of compound in the fluorene derivative by a cyclization, we found a mixture of products in which cyclization occurred on both the α and β carbons, and only by putting bulky ethyl groups on the fluorenyl carbon were we able to get a single isomer with substitution on the unhindered carbon in this cyclization. We obtained pure **6** by preparative HPLC.

We were able to do cyclic voltammetry (Fig. 8) on both compounds **5** and **6**, and found that the oxidation potential of compound **5** was 100 mV less positive than that for the fluorenyl analog **6**.[8] As with the diamines, in the biphenylene system oxidation is much easier than it is in the fluorene case, probably reflecting the advantage of removing one of the four offending π electrons in



Scheme 1. The synthesis of the biphenylene derivative **5**. L=*trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine.[8]

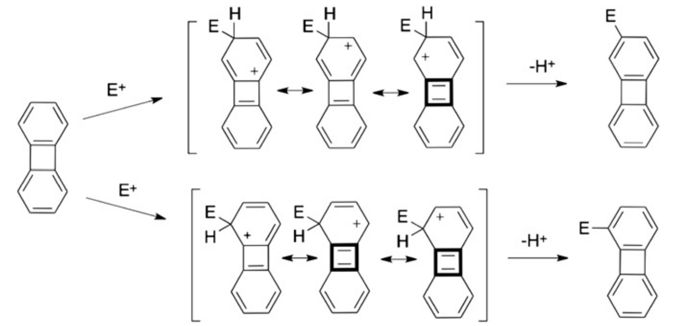


Fig. 7. The reason why biphenylenes prefer to substitute on the β positions, in contrast to naphthalenes, which preferentially substitute in the α positions.

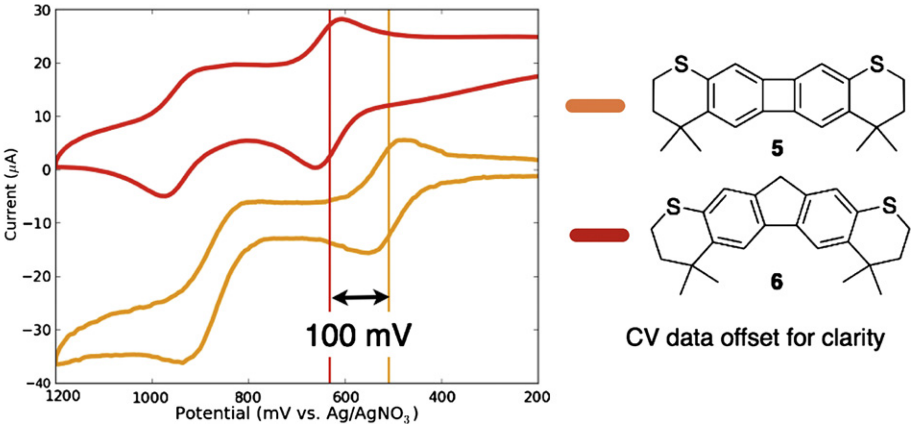


Fig. 8. CV traces of compounds **5** and **6** in Acetonitrile. The biphenylene derivative **5** is 100 mV more easily oxidized to the cation radical than is the fluorenyl compound **6**. For clarity the orange line was moved down from its starting point at zero current.

a cyclobutadiene. However, the conductance of the biphenylene **5**, measured with the break junction method, was within experimental error the same as the conductance of the fluorenyl compound **6**, so the cyclobutadiene compound is not a better molecular wire than the compound with the fluorene ring system.

We think we understand the reason for this result. In cyclobutadiene itself the elongated rectangular form is the stable one, in which the two double bonds can be as far apart as possible, and it turns out that this is also true in the biphenylene system. An X-ray crystal structure of biphenylene,[11a] (Fig. 9), indicates that the single bonds between the two benzene rings in biphenylene have a length of 1.514 Å, quite close to the bond distance for an ordinary single bond between sp^3 carbons, rather than the normal shorter bond between sp^2 carbons. Such a bond length should make the conductivity worse, since passing electrons from one benzene ring to the other requires crossing what is a rather long distance for π conjugation. As another striking result, the benzene rings in biphenylene (Fig. 9) are almost classical cyclohexatriene rings with alternating long and short bonds, in order to decrease the π electron density in the four-membered ring. In a sense the antiaromaticity in the cyclobutadiene ring has partially de-aromatized two benzene rings. Such situations have been remarked on previously.[12]

Thus we think the best summary of what this has told us is that the antiaromaticity in the central ring of biphenylene is indeed there, as demonstrated by the unusual aromatic substitution pattern, the distorted structure, and the easy oxidation of the system, but it does not show up in conductivity because there are two competing considerations. One is that the quinoid character of the system when it conducts electricity will diminish the cyclobutadiene character of the central ring; that was the effect we were expecting to lead to better conductivity. The other is that the conductivity should be worse because of the long bonds connecting the two benzene rings, and perhaps the bond length alternation in the benzene rings. The two effects apparently more or less compensate, but they would also be partly present in a simple cyclobutadiene derivative. Thus there seems to be little hope for high conductivity in cyclobutadiene-based molecular wires.

1.4. Tin and gold connectors between the electrodes and the molecules

In all of these systems—with the aromatic and the partially antiaromatic cases—we were able to measure conductivities only

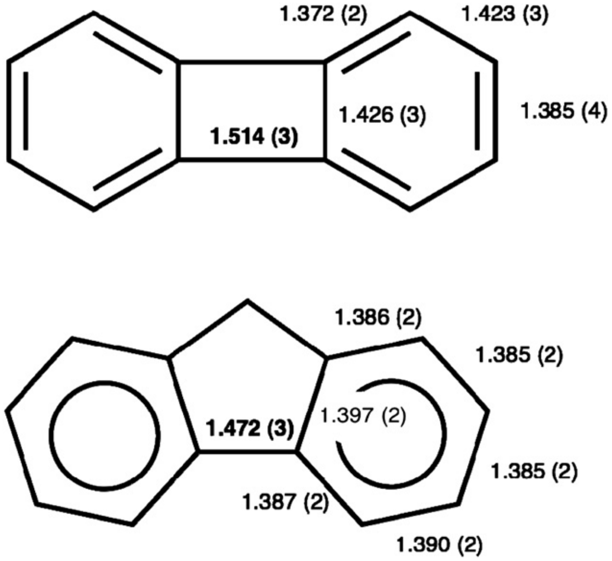


Fig. 9. The structures of biphenylene[11a] and fluorene[11b] determined by X-ray crystallography, indicating the very long bonds between the two benzenes in biphenylene and the cyclohexatriene-like character of those benzene rings, with alternating bond lengths.

by having the gold break junction electrodes contact an intervening atom of some sort that was attached to the conjugated system of interest. Some of our very recent work indicates how to avoid this extra requirement of an attached connector, which contributes its own resistance in the contact with the electrode.

We examined trimethyltin groups as potential attachments for conductivities, and saw a remarkable result.[13] With the benzene derivative **7** carrying two trimethyltin groups (Fig. 10) on the 1 and 4 positions we found something we had never seen before. The solutions in contact with the gold showed no conductivities when the break junction process was initiated until several hours had passed, but then the molecules showed conductivity of a very high order.

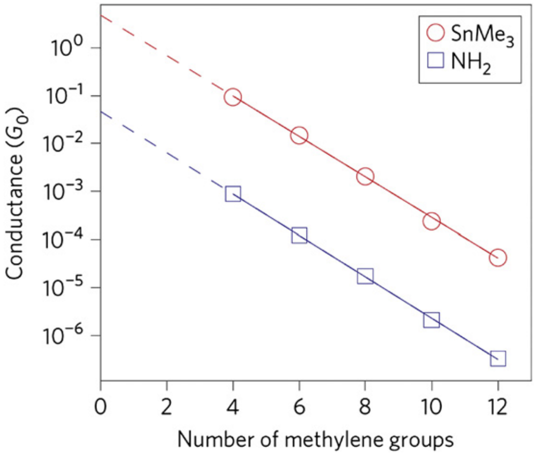


Fig. 11. In the polymethylene series, the trimethyltin derivatives (red) are much better electrical conductors than are those with amino groups (blue).

There is no basis on which to expect that tin groups would be remarkably good bridges between the gold and the molecules, so we suspected that something else was going on. Especially because of the need to wait in the benzene series, we thought it likely that there was insertion of the gold between the carbon and the tin that took several hours with the benzene case but occurred essentially instantly with the flexible polymethylenes. Ultimately the gold atoms were directly attached to the benzene system, and they were part of the electrodes so the gold electrodes were directly linked to the hydrocarbons. In the benzene case they were thus in the plane of the ring, not overlapping with the π electrons of benzene, but electron delocalization in benzene through sigma bonds instead of π bonds still leads to a significant conductivity.

To test this we were able to synthesize the benzene derivative **9** with gold atoms on carbons 1 and 4 as the triphenylphosphine complexes, and found that these instantly showed exactly the same conductivity as with the tin compounds except that no waiting was required. The gold atoms we attached to the benzene—directly or by waiting with the tin compounds—had incorporated themselves into the electrodes, probably losing the triphenylphosphine ligands, and were then indistinguishable from electrode gold atoms, showing no extra barrier between the electrode and the benzene ring. It seemed likely that this process was also occurring during the conductivity measurements in the saturated polymethylene chain series (**8**). This was easily verified when we were also able to synthesize the polymethylene chains carrying gold atoms with triphenylphosphine ligands (**10**) and saw that they showed the same behavior as the original tin compounds did in the flexible saturated series. Again this is through sigma bond delocalization of the electrons in the conductivity measurements.

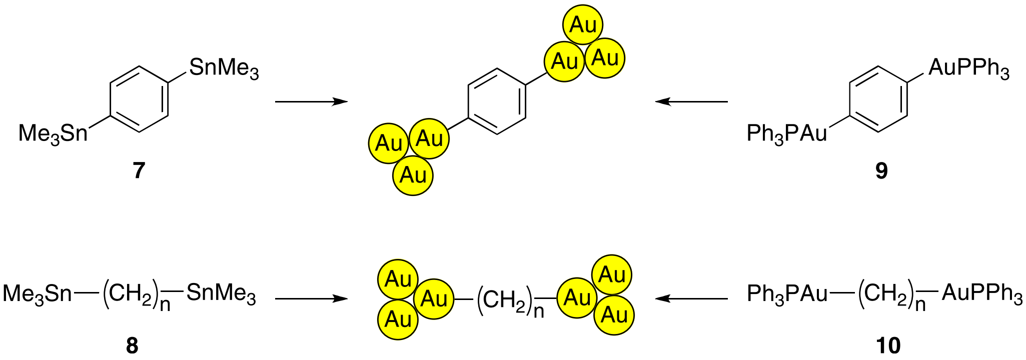


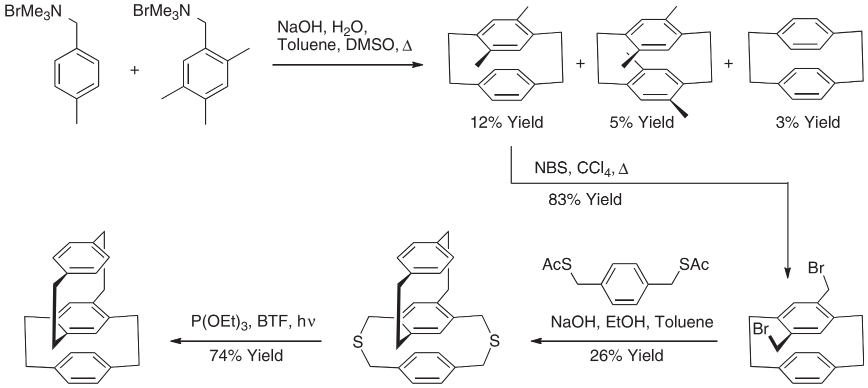
Fig. 10. The trimethyltin derivatives and the gold/phosphine derivatives become directly attached to the gold electrodes.

We also examined the conductivities of simple polymethylene chains with 4–12 methylenes (Fig. 10) terminated with two trimethyltin groups (**8**). Although chemists might not normally think of such chains as being electrical conductors, they are indeed conductors, if poor ones, by a simple tunneling mechanism, and the conductivities are a well-ordered function of the length of the chains. We found that when these molecules were examined in the break junction they immediately showed conductivity with no need for waiting, and furthermore the conductivity was ca. one hundred times greater than had been seen previously with amino groups on the ends of such chains. The data are shown in Fig. 11.

Another piece of evidence about what is going on in this series is that when we start with a trimethyltin-terminated flexible polymethylene chain of six carbons and have a reasonably high concentration of the material in solution we get conductivities for chains twice as long accompanying the conductivities of the original chain length. In the break junction technique it is possible to determine the average length of the wire through which electricity is being passed. Since the mechanism by which the tin compounds would react to insert gold, when those tin compounds are on the surface of the gold, could well involve the equivalent of carbon radicals skating on the gold surface, it is reasonable that there could be some coupling processes occurring if the concentrations are high, as we observed. Thus this process is not only a way to avoid the extra resistance from attached contact atoms on conducting wires, it also is a way to carry out coupling reactions to synthesize even larger species on the gold surface.

The very high conductivities seen here are extremely promising for this field, indicating that it is possible to replace an attachment atom with an atom of the electrode, either from the gold electrode itself or from an external attachment of gold that then incorporates into the electrode. The results are conductivities two orders of magnitude higher than those obtained by using other intervening attachment atoms.

We are now putting gold atoms into positions where they will overlap with π electrons in conjugated systems to see whether we can use them as the best way to connect into π conjugated molecular wires. In very recent still unpublished work we have examined the conductivity of *p*-xylene with a trimethylstannyl group substituted on each methyl. When this binds to gold electrodes the stannyl groups are replaced by gold electrode atoms, leading to a diradical covalently bound to the gold surface. The electrical conductivity of this molecule through the conjugated π system is 90% as high as that for gold metal itself, the highest known for a hydrocarbon conductor.



Scheme 2. The synthesis of the triple-stacked paracyclophane[14] represents a modified version of the synthesis developed originally by Mitsumi et al.[15] BTF is trifluoromethylbenzene.

1.5. Contact of electrodes with π orbitals of conducting molecules

In the work just described we have been able to delete the intervening atoms between the electrodes and the molecules because the intervening atoms were in fact atoms of the electrodes themselves, either supplied from the gold surfaces or placed there by synthesis. We have recently found another way in which it is possible to get direct contact of electrodes with a conducting molecule without using any intervening atoms, by having the gold electrodes bind to distorted benzene rings in paracyclophanes.[14]

In [2.2]-paracyclophane—with two stacked benzene rings that are somewhat distorted because of the short ethylene chains linking them—we saw conductivity with the gold break junction that involved direct binding of the gold electrodes to the π electron surfaces of the two benzene rings. Such molecules are also known with three and even four stacked benzene rings[15] (Fig. 12), so we also examined them. The synthesis of the triple stack is shown in Scheme 2. The magnitudes of the conductivities showed an exponential decay with increasing calculated top to bottom length of the paracyclophanes, indicating that the conductivities were directly through the stack. This was also confirmed from the length measurement intrinsic to the break junction measurements.

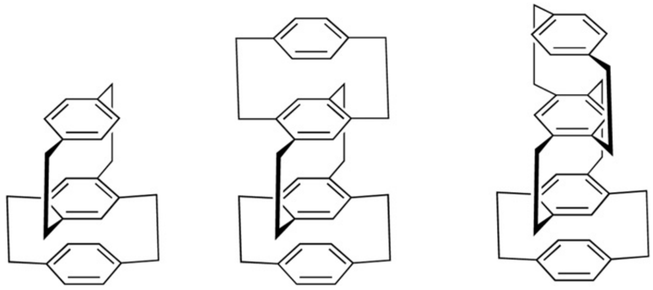


Fig. 12. Paracyclophanes with three and four stacks, linked by (saturated) ethylene chains.

From the magnitude of the conductivities observed, and from calculations on what would be the preferred pathway for electrical conduction through such a stack, we determined that the major part of it certainly involved direct passage through the π system of one benzene to the π system of another against, which it is pressed within the stack. A minor conductance pathway may also involve some current passing through the ethylene chains. We found that when slightly longer chains were used to hold two benzene rings together there was no conductivity, presumably reflecting the fact that there was no longer distortion and that binding to a flat benzene is not as favorable as binding to one that becomes distorted, and thus more reactive, because of the short distance between the neighboring components of the stack.

Conduction vertically through the stacks must pass through nodes at each carbon nucleus, but this is the same situation as when an electron in a p orbital is delocalized between the upper and lower lobes of the orbital. Our calculations indicate that the gold electrodes bind between two neighboring carbons of the terminal benzene rings.

In biology there is a lot of interest in the properties of stacked aromatic rings as electrical conductors. In particular, there is evidence that electricity can be conducted through stacks of aromatic side chains in DNA.[16] There is also interest in how electrons move through proteins, in which the stacking of aromatic rings on each other may furnish an attractive part of the lowest energy path.[17] Such stacks are also of interest in the field of photovoltaics. In this work we have furnished direct measurements of conduction through a structurally-defined stack.

The other interesting aspect of this work is that it indicates a second way to avoid having to use a connecting atom for passing electricity through conjugated systems, besides the use of electrode atoms as connectors. It seems likely that many other strained conjugated systems will also be able to bind directly to electrodes, so a conjugated molecular wire terminated by a somewhat strained conjugated system could well have good conductivity. We are currently examining such cases.

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