Charge transport in nanoscale aromatic and antiaromatic systems

Charge transport in nanoscale aromatic and antiaromatic systems

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Abstract
Molecules such as benzene, that have six pi electrons cyclically delocalized, have the special stability that chemists call aromaticity. When electricity passes through a molecular wire containing a benzene ring a quinone-like structure is induced, and there is some loss of aromaticity. The conductance of such systems correlates with the magnitude of this effect. A molecule such as cyclobutadiene with only four cyclically delocalized pi electrons has special instability, called antiaromaticity. Evidence that such antiaromatic systems could convey high conductance in appropriate systems is derived from electrochemical studies, which also detect geometric changes in some thiophene-derived nanolength wires.

1. Introduction

The 'bottom up' approach to molecular electronics involves constructing wires comprising electronically conjugated units, and studying their electronic properties including their electrical conductivities. The ultimate goal is to incorporate such wires in field effect transistors where the source, drain and gate will all be connected by such wires. Nanoscale molecular wires are usually constructed from linked conjugated units from the class called aromatic systems. Examples of aromatic compounds include benzene (1) and thiophene (2), molecules with six conjugated pi electrons in a single ring. Such systems have exceptional stability, because the pi electrons comprise a filled molecular shell; filled shells are also exceptionally stable in atoms (the rare gases) and in nuclei (nuclear shell theory). Recent advances have made it possible to measure the electronic effect of linking aromatic units into molecular wires, exploring both their conductivity and their electrochemical oxidation potentials. As we will describe below, the two properties are related.
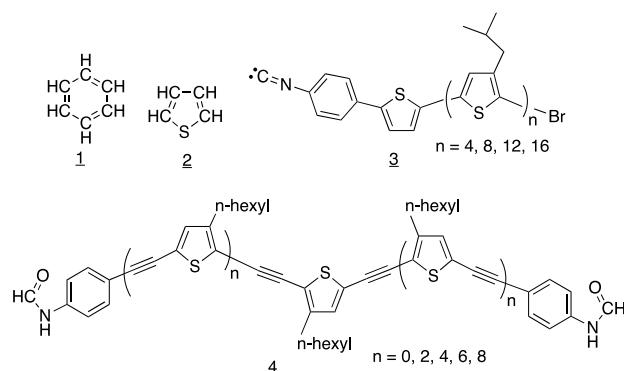
Much of the effort at the Columbia University nanocenter, of which one of us (RB) is a co-director, is aimed at understanding the relationship between chemical structure and physical properties of such wires, and using this information to guide the construction of even more effective new systems. In this short article we will describe the progress achieved in such efforts. We will focus on our work and on the substantial results obtained by the research groups of Professor Colin Nuckolls, of Professor Latha Venkataraman, and of Dr Mark Hybertsen, all of our nanocenter, but will also refer to relevant work elsewhere. We will not repeat all the citations that appear in our references, however. Latha Venkataraman and Mark Hybertsen are authors of another paper in this issue of the journal [1].

Wires comprised of linked thiophene units have been extensively studied [2–5]. We undertook the challenge of producing such wires with substantial length, and with contacts to metal electrodes using hard platinum rather than soft gold, and isocyanide groups as the contacts. In our first work we described the synthesis of such wires (3), with linked thiophene rings and lengths of 2.6, 4.0, 5.5, and 7.0 nm [6, 7]. Infrared and x-ray photoelectron spectroscopy results indicated that they bound to platinum surfaces. The ultraviolet (electronic) spectra indicated that the conjugated electronic system increased in length up to a point, but did not increase in the longest wire. This suggested that with the longest wire there was twisting around one or more single bonds that link the thiophenes, which would break the conjugation. Such twisting of the conformational structure is disfavored by enthalpy considerations, but favored by entropy.

This interpretation was supported in a second study of related polythiophene wires, using cyclic voltammetry to

determine their in-solution oxidation potentials [8]. We prepared wires of alternating thiophene and ethynyl units (4) with lengths of 2.1, 4.4, 6.6, 8.8, and 11 nm. We saw the normal behavior with the shorter wires (2.1–8.8 nm), with a first and then a second oxidation potential at increasing positive voltages. Both of them occurred at decreasing positive potentials (easier oxidation) as the wires became longer, indicating that conjugation stabilized the cation radical for the first oxidation or the dication for the second oxidation more than it stabilized the neutral ground state. It is well precedented that electron delocalization in neutral molecular species is less stabilizing than is the delocalization in species whose charges can be distributed by conjugation.

With the longest wire (11 nm) the first oxidation wave came at a more positive potential than in the shorter one. This otherwise unusual result supported the idea that twisting decreased the effective conjugated length in the longest wire. Also, the succeeding oxidation wave in the longest wire now appeared where the third oxidation was expected, to a trication, so the first wave actually involved removing two electrons. The result is what is called in electrochemistry an ECE (electrochemistry, chemistry, electrochemistry) process, in which the first oxidation then induces chemistry that makes the system more easily oxidized. The process must be an oxidation of the twisted wire that then causes the system to untwist and become fully conjugated, so the second oxidation is even easier than the first one.

Taken together, these results indicate that when the molecular wires consisting of aromatic units linked by single bonds or by ethynyl groups get long enough, the neutral wires may not be fully conjugated because of twisting, but the cationic (p-doped) wires will be untwisted and fully conjugated. We will return to additional evidence for this conclusion in later work to be discussed.

A major problem in measuring the conductivities of molecular wires is linking their two ends to a source and a drain. In our nanocenter an exciting approach to this was invented by Philip Kim, in which a conducting single-walled carbon nanotube was cut with an oxygen plasma, and molecular wires were chemically linked across the gap [9]. The cut edges of the nanotube have oxidized carbons, including carboxylic acid groups, and these can be chemically coupled to amino groups on the ends of the wires. When this was done, it was possible to measure conductivities of our polythiophenes (the needed amino groups were already there on the synthetic path to the isocyanides discussed above) and of a group of diamino compounds from the Nickolls group. This is still an area of active research, particularly aimed at producing a third nanotube contact for the gate in a field effect transistor.

A second approach was developed by Latha Venkataraman [10], extending work by three other groups [11–13], and it has opened up a convenient method to determine the conductivities in many different compounds. In brief (this is described by her elsewhere in this issue [1]), she created a gold break junction in a solution of molecules with several terminal possible bonding groups. She examined the method with 1,4-benzenedithiol, 1,4-benzenediisonitrile, and
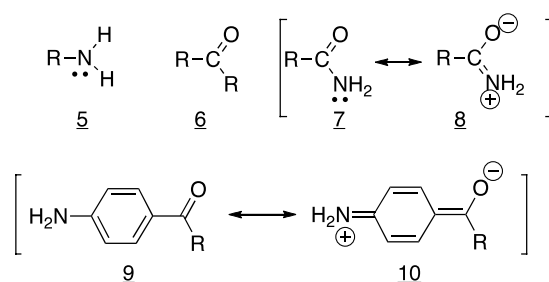
Figure 1. Electron flow from an amino group into a carbonyl group, either directly or through a benzene ring. The double-headed arrows and the brackets indicate that the true structure is a hybrid, an average weighted by the calculated energy of the two resonance forms shown. In these cases there is partial positive charge on nitrogen, partial negative charge on oxygen, and many of the bonds have partial bond orders, intermediate between double and single. As can be seen, electron passage through the benzene ring causes it to lose some aromatic stabilization.

1,4-benzenediamine. The diamine was the best contact, leading to excellent reproducibility in the conductivity. Apparently the thiol and isonitrile contacts to gold are too strong; they cause the rupture of gold–gold links when the contact is broken, while this does not happen with the amine links. Then she examined a series of alkanes carrying terminal amino groups, and measured conductivities for linear saturated hydrocarbon chains comprising from 2 to 8 methylene units. Theoretical DFT calculations by Hybertsen were consistent with the findings.

Thus when diamine molecules spontaneously attach to the two new gold electrodes their conductivities can be determined. The variations with different molecules reflect their conductivities through electronic systems, since they have the same gold/amine junctions. Our group and Colin Nuckolls' group have taken great advantage of this breakthrough in our nanocenter.

2. A chemical model for electrical conduction through conjugated systems

Some chemical groups are electron donors and some are electron acceptors. When they are linked the resulting structure will have some displacement of charge from the donor to the acceptor, and simple measurements can reveal the extent of this displacement (figure 1). For example, an amino group 5 is a donor, and if it is directly linked to a carbonyl group 6, which is an electron acceptor, the resulting structure, an amide group 7, is a resonance hybrid of the simple linked structure 7 and the structure 8 in which the electron pair of the amino group has been donated into the pi system of the carbonyl group. The true structure of compound 7 is a weighted average of 7 and 8 with some positive charge on the nitrogen and some negative charge on the oxygen. This leads to a measurable increase in the dipole moment compared with that expected for structure 7.

When a conducting group is inserted between the donor and acceptor (analogs of the source and the drain in conductivity) the donation can continue, but to a diminished extent. For example, in compound 9 the amino group can
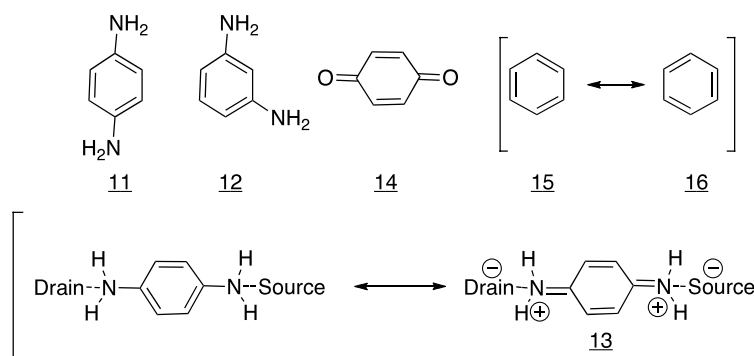
Figure 2. In its conducting state, 1,4-diaminobenzene linked to the source and drain has some double-bond character in the carbon–nitrogen bonds, reflecting a contribution to its average structure from a quinoid structure 13 related to the quinone 14. In both cases, the aromatic stabilization of a benzene ring is partially lost.

still donate electron into the carbonyl group, but in the hybrid structure between the simple one 9 and the electron donated one 10 there is less weighting of the donated structure 10 in the average real structure—with partial charges on the nitrogen and the oxygen—because structure 9 has an aromatic benzene ring that has special stabilization, while in structure 10 that ring has lost its three conjugated double bonds that would make it particularly stable. In the next section of this chapter we will see that such changes in the structure of aromatic rings such as a benzene ring will also affect electrical conductivity. In a further section we will see that there are also compounds that possess antiaromaticity, for which opposite effects are predicted and to some extent already observed.

3. Change in aromatic stabilization during electrical conduction

In our first paper using gold break junctions, we studied the conductivities of a series of relatively simple molecules having two amino groups attached at important positions [14]. We saw that 1,4-diaminobenzene 11 was a good conductor but that the 1,3 isomer 12 was not. The path is shorter in the 1,3 isomer, normally leading to better conductivity, but there is a problem in delocalizing the pi electrons. As figure 2 shows, when electrons pass from the source through the amino group and into the ring, and when they pass from the ring to the drain via the second amino group, there is some double-bond character between the amino groups and the ring carbons. The structure 13 shown is related to the structure of benzoquinone (14), a stable known compound. However, no such structure can be drawn for the 1,3-diaminobenzene, and no dicarbonyl compound related to benzoquinone can exist with oxygens on the 1 and 3 positions.

Putting it another way, the six-fold symmetrical benzene ring is often described as a resonance hybrid of two more classical structures, 15 and 16, and in each of them the 1 and 4 amino groups would be at the two ends of two conjugated double bonds, not possible with the 1,3 isomer. The resulting conclusions were: (1) that electrical conduction through a benzene ring demands that a quinone-like structure be possible, and (2) that electrical conduction through a benzene ring must occur with the sacrifice of some of the 'aromatic stabilization'
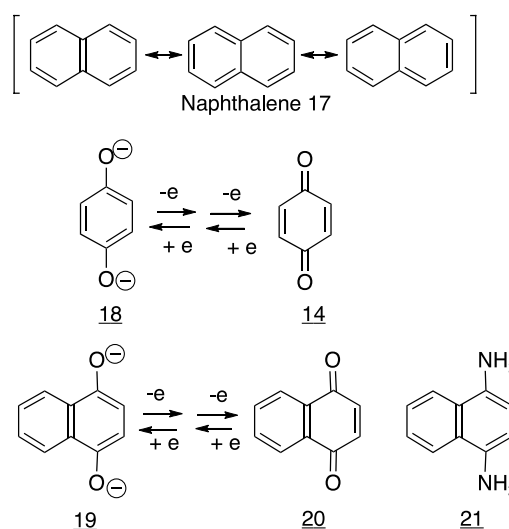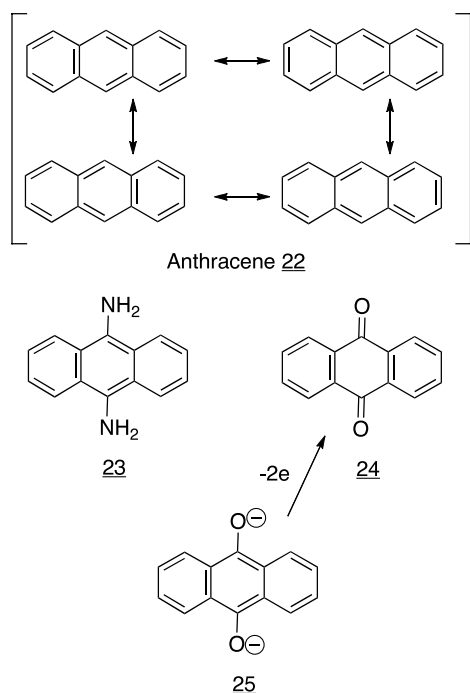

Figure 3. In only one of the resonance forms of naphthalene are there two true benzene structures, so the oxidation of the dianion 19 is thermodynamically more favorable than that for dianion 18. This correlates with the fact that 1,4-diaminonaphthalene is a better electrical conductor than is 1,4-diaminobenzene.

that results from the cyclic delocalization of six pi electrons around the ring. We decided to explore this further [14].

Naphthalene (17) is an aromatic compound with two fused benzene rings, but it is not as stabilized by electron delocalization as two separate benzenes would be. In two of the three resonance forms of naphthalene (figure 3) one ring has the three double bonds of benzene but the other does not. While the aromatic stabilization of benzene is 36 kcal mol^{-1}, as determined by heats of combustion, that of naphthalene is only 61 kcal mol^{-1}, 12 kcal less than for two isolated benzene rings [15]. The result is that it is energetically easier to disrupt one of the rings of naphthalene than the ring of benzene, and this shows up in some oxidation potentials.

The oxidation of hydroquinone dianion 18 to benzo-quinone (14) has reversible potentials of −1210 and −522 mV for the first and second one-electron oxidation, while for the naphthalene analog (19) going to 20 the potentials are −1343 and −706 mV [16]. Making a quinone from one ring of
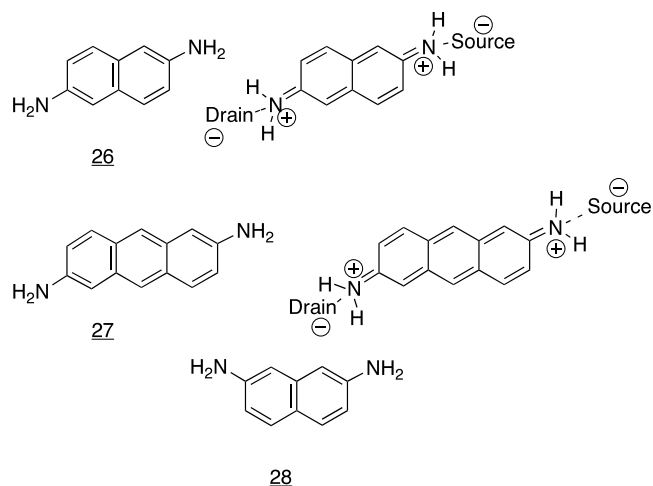
Figure 4. In none of the resonance forms for anthracene 22 are all three rings benzene-like, so conversion of the dianion 25 to the quinone 24 is particularly easy thermodynamically. This correlates with the high conductivity of 9,10-diaminoanthracene 25.


Figure 5. In 2,6-diaminonaphthalene 26 and 2,6-diaminoanthracene 27 conversion to a quinoid form during electrical conduction erases the aromaticity of all the rings, correlating with their relatively poor conductivities. 2,7-diaminonaphthalene 28 is not a conductor, since it cannot have a quinoid form.

naphthalene is easier energetically, so we expected that 1,4-diaminonaphthalene (21) would be a better electrical conductor than p-diaminobenzene. As expected, the conductance G_0 for 1,4-diaminonaphthalene was 9000 Ω^{-1}, while that for 1,4-diaminobenzene (11) was only 6400 [14]. This supports the idea that aromatic rings suffer some decrease in aromatic stabilization during electrical conduction, with the cost being less in the naphthalene case.

Anthracene (22) has three linearly fused benzene rings and, as figure 4 shows, no resonance form has all three rings with the formal three double bonds of benzene. Thus anthracene, with an aromatic stabilization judged from heats of combustion of 84 kcal mol^{-1}, is even less well stabilized by pi electron conjugation than are three benzenes, which would have a total of 108 kcal mol^{-1} of aromatic stabilization [15]. We examined the conductivity of 9,10-diaminoanthracene (23) with the gold break-junction method [14]. The conductivity, 17 000 Ω^{-1}, was even greater than that for 1,4-diaminonaphthalene (21), as expected from the change in aromatic stabilization. In the corresponding quinone (24) there are now two real benzene rings, so dearomatizing the central ring costs only 12 kcal mol^{-1} in terms of benzene-like aromaticity. As expected, the oxidation potentials for converting the dianion 25 to the quinone 24 are only −1498 and −952 mV, taking even less energy than for the naphthalene case [16].

We also examined the conductance G_0 of 2,6-diamino naphthalene 26 (2600 Ω^{-1}) and of 2,6-diaminoanthracene 27 (1600 Ω^{-1}). As figure 5 shows, making the quinoid structures involved in passing electricity through these systems

led to the loss of all the aromatic ring structures, so the conductances become less, not more as in the 1,4 and 9,10-diaminated cases. Of course the conductivities will decrease with increasing distance, but the distance dependence from the Simmons model is not enough to account for these changes. Losses of aromatic stabilization are also involved. As expected, 2,7-diaminonaphthalene 28 is a very poor conductor, since it cannot form a quinoid structure with C–N double bonds. Our DFT calculations predict this low conductivity for 1,3-diaminobenzene and 2,7-diaminonaphthalene, related to the quinoid model for conductivity in these compounds.

4. Relationship of conductivities to electrochemical oxidation potentials

As the discussion of quinone reversible reduction potentials (interconverting the quinone and benzene dioxyanions) indicated, we expected that the conductivities of aromatic diamines would correlate with their one-electron or two-electron oxidation potentials. The removal of one electron from 9,10-diaminoanthracene (23) forms a cation radical that is the hybrid of two resonance forms 29 and 30, while the second electron abstraction forms the dication 31.
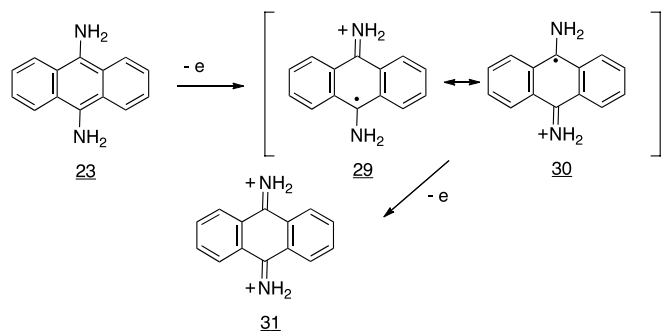

In both cases the results have two regular benzene rings, as we have invoked for the molecule during electrical conduction.

Thus we determined the first and second oxidation potentials of a group of aromatic diamines, using cyclic voltammetry, and plotted them (all potentials versus the ferrocene/ferrocenium reference) against their observed conductivities from the gold break-junction measurements [17]. They correlated over ca three orders of magnitude.

Using these electrochemical potentials, we plotted the observed conductances (the log of G_0) versus $\Delta E \times L$ [17] and saw an excellent linear relationship, as expected for non-resonant tunneling [10, 18–21]. As another aspect, we saw that the simple slope of $\log G_0$ versus the first oxidation potential $E_{1/2}$ became steeper when 1,4-diaminobenzene was substituted on the ring by two or four methyl groups (making the ring more electron rich) but shallower when the substituents were instead fluorine atoms (making the ring less electron rich). We believe that these effects reflect the timing of electron transport through the rings. When a molecular wire is attached to a source and a drain, electron removal at the drain can initially precede electron donation at the source, producing a wire with some partial positive charge. Of course from then on electron donation and removal are synchronous. This will occur with electron-rich aromatic rings, but less so if at all with electron-poor aromatic rings, accounting for the slopes we observed. In another study, Nuckolls *et al* have reported related substituent effects indicating some positive character in the conducting wires [19].

5. Antiaromaticity
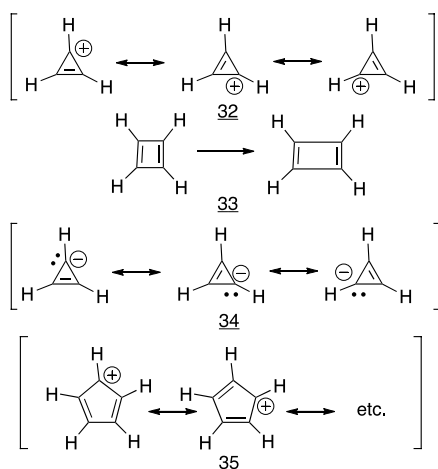
Compounds with six conjugated pi electrons in a ring, like benzene, have special stability that chemists call aromaticity. In line with molecular quantum mechanical predictions, six is only one of a series of magic numbers, the series of 2, 6, 10, etc pi electrons in a ring corresponding to filled electronic shells. The simplest member of the series—cyclopropenyl cation 32 with two pi electrons and a vacant p orbital—was first prepared in our laboratory and shows clearly aromatic properties [22]. It is the cation with mass 39 seen in many gas-phase spectra.

Four pi electron cyclic conjugated systems are conspicuously missing from that list. A simple example would be cyclobutadiene (33), which on first sight might seem to be another ideal case for pi electron delocalization. However, in contrast to benzene, which is made rather unreactive by its aromatic stabilization, cyclobutadiene is enormously reactive and

can be isolated only in a frozen matrix at low temperature, or trapped inside a molecular cage [23]. Furthermore, in contrast with benzene with its regular hexagonal structure, cyclobutadiene is a rectangle, not a square. The pi electrons in the two double bonds repel each other, and the square geometry with four equal pi bonds of order 1.5 is a higher energy intermediate point in the vibration between the two possible rectangular structures.

We have studied the energetics of the four-pi-electron monocyclic systems cyclobutadiene, cyclopropenyl anion (34), and cyclopentadienyl cation (35), and have clear evidence that the pi electron conjugation in these compounds is destabilizing [23]. High-level quantum mechanical calculations account for this effect, which RB has named 'antiaromaticity'. Just as perturbing the electronic structure in aromatic rings is resisted, leading to lower conductivities, it is expected that perturbing the electronic structure in an antiaromatic cyclobutadiene ring will be assisted and should lead to higher conductivities. A clear example of this effect was seen in our laboratory some years ago.

In the PhD work of graduate student Robert Grubbs (Nobel Laureate in chemistry in 2006 for his later independent and unrelated work) and other co-workers we observed by electrochemical measurements of oxidation/reduction potentials that electron donation from electron-rich oxygens into electron-poor carbonyl groups was amplified if the donation passed through a cyclobutadiene ring in structure 36 [24].
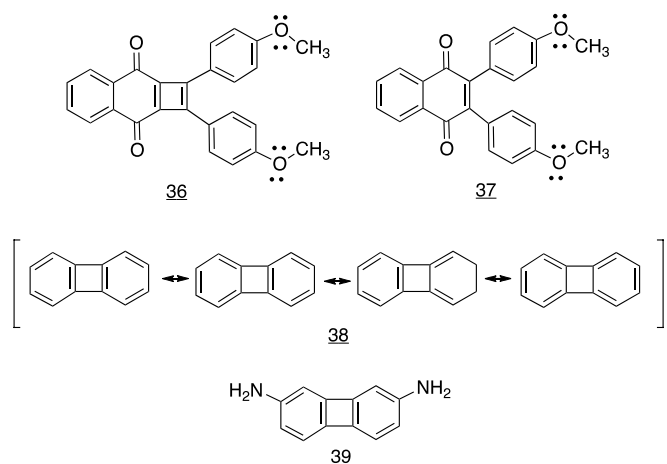
That is, the donation was three-fold more energetically favored through the cyclobutadiene ring than in a related molecule 37 where the electron donor and electron acceptor were directly connected. As mentioned above, such electronic effects in molecules are similar to electrical conduction, although there was no source and drain to make it a true continuous conduction process. Based on this result, and the theory that underlies it, we have set out to incorporate a cyclobutadiene ring into a molecular wire, to determine whether it will show significantly higher electrical conductivity.

Simple cyclobutadienes are too unstable to be practical for such a study. The compound biphenylene 38 has a central cyclobutadiene ring in one of its resonance structures, but not in the three others shown. Thus the antiaromaticity of cyclobutadiene is not fully expressed in the resonance hybrid

of 38, so biphenylene and various of its derivatives can be synthesized and handled under normal conditions. We have synthesized 2,7-diaminobiphenylene 39 and attempted to determine its conductivity by the gold break-junction method. To date these attempts have been defeated by the extraordinarily high reactivity of 39; it immediately oxidizes on exposure to air, in contrast with the other diamines we have examined. Studies are now proceeding with more oxidatively stable biphenylene derivatives.

6. Related work by Colin Nuckolls

Professor Colin Nuckolls is a highly inventive and productive member of the Columbia University Nanocenter. We will briefly describe his work related to our studies of conductivity that was not cited above. He has used both the cut nanotube contacts and the gold break junction to determine conductivities of some interesting species.

The first report of the use of the cut nanotube in the Columbia Nanocenter was his paper [25] with a large group of coauthors, including James Yardley, Michael Steigerwald, and Philip Kim, principal scientists in the Columbia Nanocenter. A self-assembled stack of derivatives of hexabenzocoronene was contacted by the electrodes of a cut nanotube, and showed electrical conductivity that could be modulated by a gate consisting of a doped silicon layer. Then the paper previously described above [9] used the cut nanotubes to covalently attach single molecules, both our polythiophenes and a number of other conjugated species prepared by Nuckolls. In one case, a short polyaniline, the conductivity measured could be modulated by chemical oxidation or reduction, or by pH.

In a subsequent paper [26], the gap in the cut nanotube was bridged by a molecule that carried a biotin unit, and it was shown that the conductivity of the resulting system could be modulated when streptavidin was introduced. Streptavidin is a protein with a high affinity for biotin, and the experiment indicated the applicability of such nanoscale devices for the detection of biologically relevant binding interactions. Then a molecule was used to bridge the gap in the cut nanotube that had the interesting feature that it was an insulator but isomerized to form a conducting species when irradiated with ultraviolet light, and did not reverse [27]. A related molecule was then used that also changed to the conducting structure with light, but then reverted to the insulating structure thermally on standing. Work by Feringa [28] used bridging of a different molecule across a gold break junction, and did not have the same properties as the Nuckolls system.

In a paper coauthored with Jacqueline Barton, Nuckolls showed that DNA molecules could be covalently attached across the nanotube cut, and showed some conductivity that was greatly decreased if mismatches were introduced into the DNA duplex [29]. This demonstrated that the base stacking in perfect double-stranded DNA does in fact lead to detectable electrical conduction by the stacked pi electrons in the bases of DNA.

In a paper with Venkataraman, Hybertsen, and Steigerwald, Nuckolls used the gold break-junction method to determine the conductivities of a series of diaminobiphenyl molecules with varying decrees of twist around the single bond between the two phenyl groups [18]. As theory predicted, the conductivity varied as the cosine squared of the twist angle, with a twist angle of zero for fluorene (39) leading to the highest conductance. With the same principal scientists as coauthors, Nuckolls also described studies of substituent effects on the conductivities of some substituted 1,4-diaminobenzenes, and concluded that the molecules had some positive charge during electrical conduction [19], a conclusion we had also reached as described above [17].

Recently Nuckolls, Venkataraman, Hybertsen, Steigerwald and co-workers have described the relative effectiveness of amino groups, of thiomethylgroups, and of dimethylphosphine groups at the two ends of saturated alkane chains as linkers to the gold break junctions [30]. The thioether groups and even more so the dimethylphosphine groups gave smaller contact resistances with the gold electrodes than did the amino groups.

We are examining these new contacts with our series of aromatic compounds, to see if the trends we have seen with the amines are observed with thioether or phosphine groups. We are also using them with our proposed antiaromatic molecular wires.

Acknowledgments

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