Solitons in a Box: The Organic Chemistry of Electrically Conducting Polyenes

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I. Introduction

Since Heeger and MacDiarmid discovered in 1975 that polyacetylene can be doped to metallic conductivity through simple oxidants or reductants, the synthesis of new materials with unusual conductive and electronic properties has been an area of intense activity and frequent reviews.[1] This interest has been accelerated by the recent development by Naarmann and co-workers at BASF of techniques for polyacetylene synthesis yielding material which, upon doping with reducing metals, reportedly exceeds copper in specific conductivity.[2] The advancement in understanding and design of new materials in this area has relied largely on the techniques and symbology of solid-state physics. The use of arcane language and descriptions has sometimes limited the impact of organic chemistry, yet charge transport in such conductive materials is at root a problem in mechanistic organic chemistry involving electron transport in organic molecules. Our purpose in this Account, therefore, is to provide a general exposition of the principles underlying electrical conductivity in organic polymers which, unlike previous more extensive treatments,[1] develops a connection between the bulk material properties and properties of discrete organic molecules. We want to demonstrate how application of theoretical, synthetic, and mechanistic organic techniques can provide paradigms for studies of partially ordered or semicrystalline materials and provide insights into basic issues of conductivity in such materials. While the solid-state physics approach is to begin with a regular infinite material and impose boundary conditions, our approach is to begin with discrete molecules and examine their properties as they expand toward the polymeric domain.

II. Polyacetylene and the SSH Soliton Theory

Polyacetylene itself is intractable and has poor environmental stability. Nevertheless, because of its structural simplicity, its ready conversion to metallic conductivity by a variety of doping methods, and the association of conductivity with the formation of resonance-stabilized carbocations and carbanions (a subject of considerable interest and expertise in our

laboratories[3]) our efforts have concentrated on this material. Studies on the transient formation of polarons in polyacetylene have led to analogous studies of radical cations in polyenes by the Bally group.[4]

Polyacetylene provides the limiting case of a polyene of infinite conjugation length. The Hückel energy levels for any polyene with n unsaturated carbon atoms and with equal bond lengths can be obtained by appeal to the Frost mnemonic for linear polyenes in which a polygon of order $2n + 2$ is inscribed in a circle of radius 2β (see Figure 1).[5] At the limit of infinite chain length, this relationship still holds, except the polygon is the circle itself. Projection of the semicircle containing the equal density of energy levels along the circumference produces an envelope of energy levels commonly referred to as a density of states.[6] Significantly, the HOMO–LUMO energy difference, or band gap, vanishes. Population of the conduction band requires no energy and thus the system should be metallic. This nonsensical result arises from the error in assumption of equal bond lengths and resonance integrals. In fact, half-occupation of the conduction bands leads to a Jahn–Teller distortion for quasi-one-dimensional systems called the Peierls distortion.[7] The result of this "dimerization" is two inequivalent ground states "R" and "L" with alternating bond lengths and a nonzero gap requiring activation for conversion of the two forms and thus forming an insulating material.

(1) A number of excellent monographs on the subject of conducting polymers are now available: (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1 and 2. (b) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Materials Science*; Academic Press: Orlando, 1984. (c) Skotheim, T. A. *Electroresponsive Molecular and Polymeric Systems*; Marcel Dekker: New York, 1991; Vols. 1 and 2. (d) Brédas, J. L.; Chance, R. R. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, NATO ASI Series E: Vol. 182; Kluwer Academic Publishers: Boston, 1990. (e) For an excellent "layman's guide", see: Kaner, R. B., MacDiarmid, A. G. *Sci. Am.* 1988, February, 106–111.
(2) (a) Munardi, A.; Theophilou, N.; Aznar, R.; Sledz, J.; Schué, F.; Naarmann, H. *Makromol. Chem.* 1987, *188*, 395. (b) Basescu, N.; Liu, Z.-X.; Moses, D.; Heeger, A. J.; Naarmann, H.; Theophilou, N. *Nature* 1987, *327*, 403. (c) Naarmann, H.; Theophilou, N. *Synth. Metals* 1987, *22*, 1. (d) Schimmel, T.; Denninger, G.; Riess, W.; Voit, J.; Schwoerer, M.; Schoepe, W.; Naarmann, H. *Synth. Metals* 1989, *28*, D11. (e) Naarman, H. *Synth. Metals* 1991, *41*, 1. For other recent syntheses of highly ordered polyacetylene, see: (f) Iqbal, Z.; Ivory, D. M.; Szobota, J. S.; Elsenbaumer, R. L.; Baughman, R. H. *Macromolecules* 1986, *19*, 2992. (g) Akagi, K.; Katayama, S.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. *Synth. Metals* 1987, *17*, 241.
(3) Tolbert, L. M. *Acc. Chem. Res.* 1986, *19*, 268.
(4) See: Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* 1992, *114*, 2440 and references therein.
(5) (a) Frost, A. A.; Musulin, B. *J. Chem. Phys.* 1953, *21*, 572. (b) For a discussion, see: Zimmerman, H. E. *Quantum Mechanics for Organic Chemists*, Academic Press, Inc.: New York, 1975; pp 24–39.
(6) For an excellent discussion, see: Hoffmann, R.; Janiak, C.; Kollmar, C. *Macromolecules* 1991, *24*, 3725.
(7) For an excellent discussion, see: André, J.-M.; Delhalle, J.; Brédas, J.-L. *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific Publishing: Singapore and Teaneck, NJ, 1991.

Laren Tolbert is a Southerner by birth and early education, although after a B.A. in mathematics and chemistry at Tulane University he completed his education in the North with a Ph.D. at the University of Wisconsin and postdoctoral fellowship at Harvard University. However, he gradually returned to his Southern roots with faculty positions at the University of Kentucky and, currently, Georgia Institute of Technology, where he is Professor of Chemistry. He was an Alfred P. Sloan Fellow, and his current interests include electroactive materials, acid–base properties of photoexcited molecules, radical ion chemistry, and mechanistic probes of organic reactions. Aside from chemistry, his interests lie in the fields of European history and American politics.
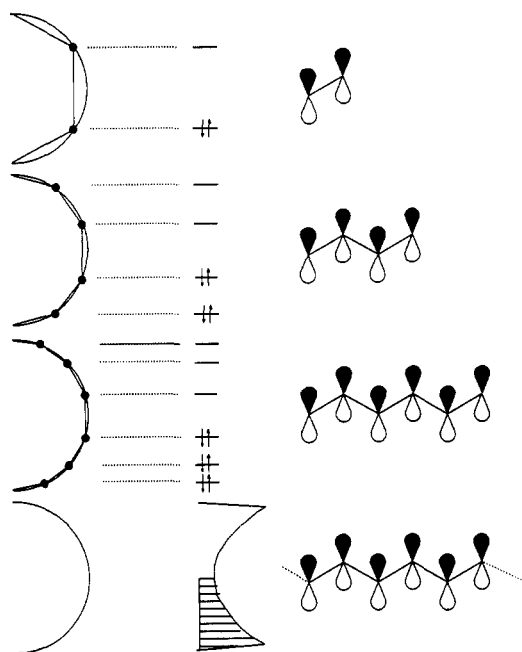
Figure 1. Frost mnemonic for polyene π-orbitals.

The Peierls distortion can be most easily understood in terms of symmetry arguments leading to a forbidden transition between the R and L forms. Examination of the highest occupied molecular orbitals (HOMOs) for a polyene of arbitrary length reveals that the HOMO in each case is characterized by bonding interactions between "doubly"-bonded carbon and antibonding interactions between "singly"-bonded carbon. The LUMOs are analogously obtained, except that antibonding interactions are found between "doubly"-bonded carbon and bonding between "singly"-bonded carbon. Examination of the corresponding symmetries reveals that, in fact, the symmetric HOMO of the R form corresponds to the LUMO of the L form and the antisymmetric HOMO of the L form corresponds to the LUMO of the R form. Thus what we call the Peierls distortion corresponds to a thermally forbidden energy level crossing problem in the Woodward–Hoffmann sense (see Figure 2).

Upon "doping" with strong oxidants or reductants, polyacetylene undergoes an insulator to metallic transition. Associated with this transition is the development of a new optical absorption at approximately one-half the band gap appropriately called the "mid-gap" state, without increase in the magnetic susceptibility.[8] On the basis of these observations, which require the formation of closed-shell charge carriers rather than the open-shell species which might be expected from the doping method, Su, Schrieffer, and Heeger (SSH) proposed that a new mode of conduction is involved. As a necessary consequence of the asymmetry of the polyacetylene ground state, two equivalent polyene chains R and L are interconverted through the intervention of a mobile charge carrier, a "soliton".[9] The soliton is described as a mobile charged or neutral defect, or "kink", in the polyacetylene chain that propagates down the chain and thus reduces the barrier for interconversion (see Figure 3).

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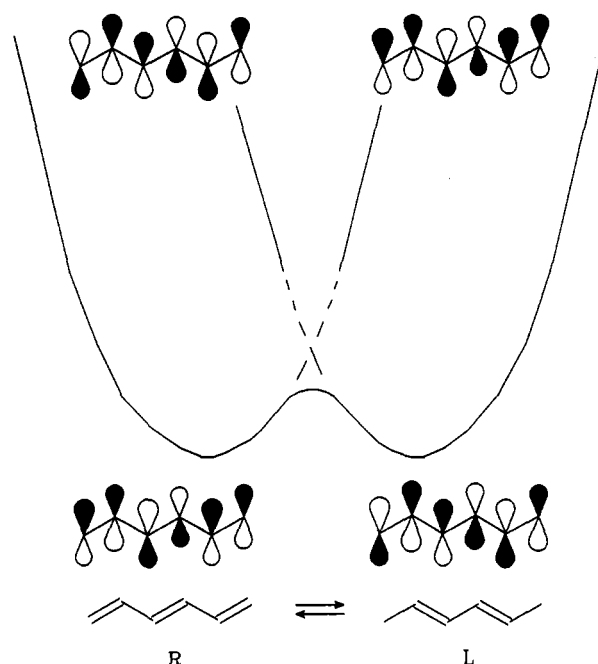(9) Su, W. P.; Schrieffer, J. R.; Heeger, A. *J. Phys. Rev. Lett.* **1979**, *42*, 1698.

Figure 2. Peierls distortion as Woodward–Hoffmann forbidden reaction.
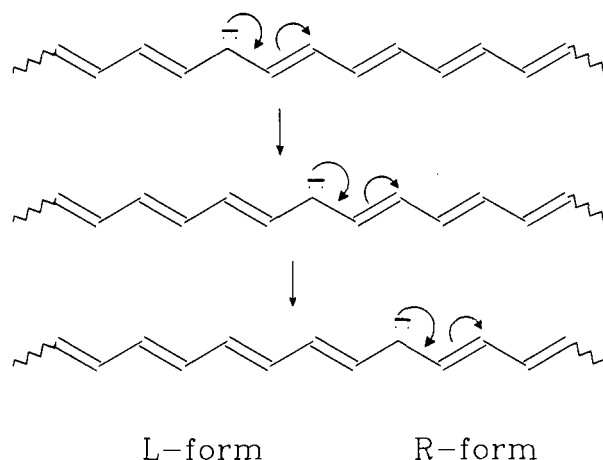

L–form   R–form

Figure 3. The soliton and polyacetylene conduction.

According to the soliton theory, the charge carrier in n-doped polyacetylene is a resonance-stabilized polyenyl anion of approximately 29–31 CH units in length, with highest amplitude at the center of the defect.[10] This result coincides with the simple resonance picture as well as with chemical shifts of the carbon atoms in the ^{13}C NMR spectrum of polyenyl anions, which indicate increased charge density at the center of such anions. Moreover, the mid-gap state can be understood in terms of the nonbonding molecular orbital (NBMO) characteristic of such odd-alternant hydrocarbon anions. Other features of the soliton model fit the general organic chemical description of odd-alternant anions and cations. For instance, more sophisticated calculations using MNDO techniques confirm the prediction that, for discrete polyenyl anions, the same localization of charge at the center is predicted as in the soliton case. However, these same calculations also indicate substantial positive charge density at the even-num-

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Solitons in a Box

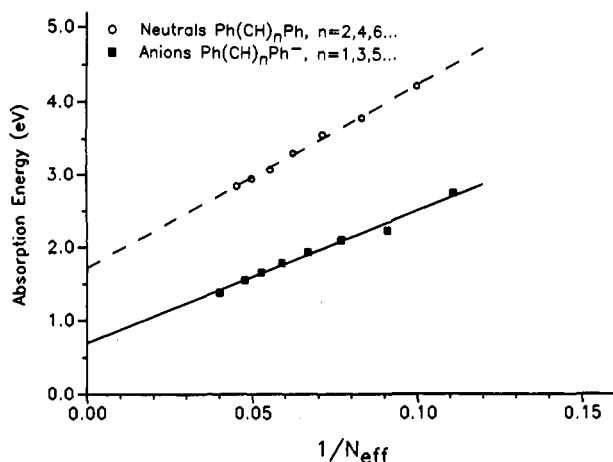*Acc. Chem. Res., Vol. 25, No. 12, 1992* **563**

Figure 4. Comparison of neutral and anionic diphenylpolyene band gaps.

bered atoms, a result more in line with the Pople–Pariser–Parr (PPP) model[11] than the SSH model.

In order to test these general predictions for n-doped polyacetylene, we developed an approach in which odd-alternant hydrocarbon anions of discrete lengths were generated and their spectroscopic properties as a function of chain length were examined. For ease of synthesis, α,ω-diphenylpolenyl anions of the general form $[Ph(CH)_nPh]^-$, $n = 1, 3, 5, 7, 9, 11, 13$ were used, which, for pedagogical purposes, may be viewed as "solitons in a box".

Theory predicts that, for linear polyenes, the absorption maximum should reach a limiting level. Brédas, Silbey, Boudreaux, and Chance (BSBC) have observed a linear correlation of energy gap with $1/n$ for neutral (even) polyenes of carbon length n.[12] The relationship between energy gap and $1/n$ has been observed for linear cyanines and is readily derived from the particle in a box model.[13] Such a relationship should also exist for the odd polyenyl anions. If we recognize that the resonance stabilization by a single phenyl group roughly correlates with that of two vinyl groups, we can also consider each phenyl group to add 4 CH units to the chain. Thus we plot energy gap vs $1/(n + 8)$. For neutral diphenylpolyenes, BSBC use $1/(n + 5.4)$. Our plot is nearly linear (see Figure 4), with approximately half the energy gap for diphenyl polyenes,[14] and the particle in a box model readily accommodates a soliton in a box.

Using O'Brien's application[15] of the Spiesecke–Schneider formalism,[16] we have determined the charge density on the individual carbon atoms.[17] This formalism adopts a first-order relationship between chemical shift and charge density (eq 1) in which α and δ_0

are adjustable parameters relating charge density ρ and observed ^{13}C chemical shift δ_c. The parameters α and δ_0 are determined by linear least-squares fitting techniques over a family of compounds, in our case, the diphenylpolyenyl anions DPN. A more rigorous approach has been developed by extension of the work of Edlund and co-workers.[18] That is, we consider only the increment in charge between an atom in a diphenylpolyenyl anion and the equivalent atom in diphenyloctatetraene, assigning δ_0 as chemical shift for the neutral. Thus eq 1 becomes eq 2 in which only a single parameter is involved. Since the sum over all charge densities $\Sigma\Delta\rho$ in a given anion is -1, the parameter α can be easily determined from eq 3, allowing us to use eq 2 to determine charge density in each case.[19] The result for $Ph(CH)_{13}Ph^-$ is shown in Figure 5. In addition to confirming the accumulation of charge at the center of the resonance-stabilized carbanion, Figure 5 clearly demonstrates the charge polarization characteristic of the higher order (PPP or MNDO) models. That the

$$\delta_c = \alpha\rho + \delta_0 \tag{1}$$

$$\Delta\delta_c = \alpha\Delta\rho \tag{2}$$

$$-\sum\Delta\delta_c = \alpha \tag{3}$$

soliton has a finite width is intrinsic to the mechanism of intrachain charge transport. When the polymer chain exceeds the soliton width, the soliton becomes mobile, since the soliton may localize at any arbitrary site on the polyene chain with no change in energy. This prediction is difficult to rationalize with conventional resonance theory, which tends to view the valence bond structures of Figure 3 as resonance structures describing a single entity. This view is fallacious, since it is based upon common experience with resonance-delocalized ions of rather small breadth. This is readily illustrated again by considering the ^{13}C NMR chemical shifts of the diphenylpolyenyl anions. In this case, a plot vs $1/N$ (where N is the total number of carbon atoms) of the chemical shift differences $\Delta\delta$ for alpha (α), ipso (i), ortho (o), meta (m), and para (p) carbon atoms shows a linear dependence of the aromatic and alpha chemical shifts for all anions of length greater than 5.[20] Moreover, these chemical shift differences vanish at $N = 43–45$, corresponding to a polyene length of ca 30 after substraction of the two benzyl "boundary" groups (see Figure 6). This provides direct verification of the soliton width and serves to illustrate that resonance delocalization represents a compromise between resonance energy and the bond localization represented by the Peierls distortion.

In addition to soliton generation by oxidative or reductive doping, soliton–antisoliton pairs may be produced by photoexcitation.[21] This observation also has its counterpart in discrete molecule photochemistry. For instance, tetraphenylethylene upon photoexcitation

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(20) For *ortho* and *para* carbon atoms, a second-order fit must be used.

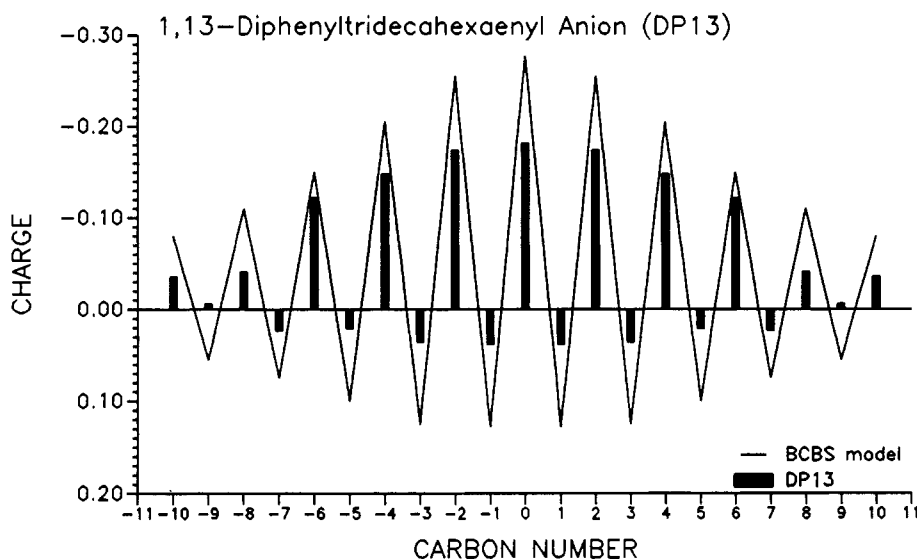(21) Wu, W.-K.; Kivelson, S. *Synth. Metals* **1987**, *17*, 51.

Figure 5. Comparison of predicted and observed soliton charge densities.
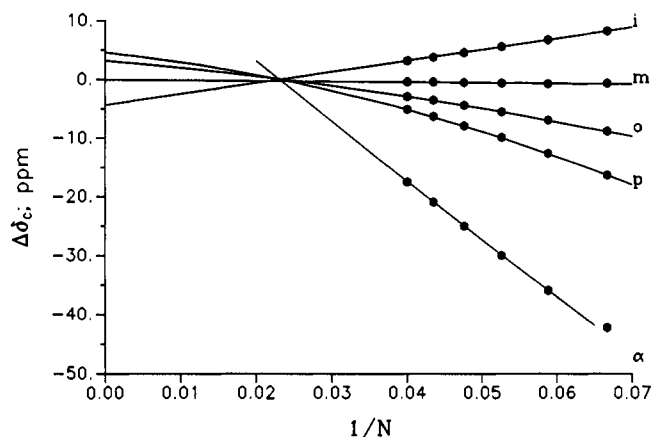

Figure 6. Comparison of neutral and anionic chemical shifts for α and phenyl carbon atoms.

produces a dipolar intermediate upon relaxation of the initially formed excited state.[22] This phenomenon is commonly known as "sudden polarization".[23] Curiously, if polyacetylene is stretch-oriented, polarized excitation along the chain axis produces soliton–antisoliton pairs, while polarized excitation perpendicular to the stretch axis apparently produces polarons, i.e. radical ion pairs.[4,24] Neutral soliton pairs may be formed thermally upon annealing of *cis*-polyacetylene to *trans*-polyacetylene,[25] a process which clearly requires twisting about the double bond and transient formation of a biradical-like state on the energy surface.

III. The Importance of Dianions and Ion Triplets

Although we have associated a static resonance-stabilized carbanion with a dynamic soliton model, much evidence exists that propagation along the chain axis is not the limiting event in charge transport for

polyacetylene. MacDiarmid[26] and Chien[27] have discovered that long conjugation lengths are unnecessary for significant conductivity,[28] a fact which might rule against intervention of charge propagation down the polymer chain. Most experimental data is consistent with a rate-limiting interchain change transport.[29] If short chains are involved, conduction in polyacetylene requires some mechanism for transfer of charge from one chain to another (e.g., "intersoliton hopping").[30] Since intersoliton hopping may be the limiting charge propagation process, a solution to this mechanistic problem is critical. Some schools even challenge the intervention of solitons in the major charge carrying process.[31,32] Current theories for interchain charge transfer center around the Kivelson "percolation" mechanism.[30] For *n*-type solitons (carbanions), this involves electron transfer from the anion to a neutral soliton (radical) in a neighboring chain to form a new radical and new anion in an isoenergetic process. The lattice distortion associated with "interpolaron hopping", i.e., between a radical anion and neutral polyene chain, is thought to present inaccessible energy barriers.[30]

Organic carbanion chemistry provides a ready solution to this dilemma. That is, charge transfer between carbanions often involves a disproportionation equilibrium between a neutral/dianion pair (ion triplet[33]) and a radical anion pair. For instance, tetraphenyl-ethylene radical anion undergoes a known disporpor-

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Solitons in a Box

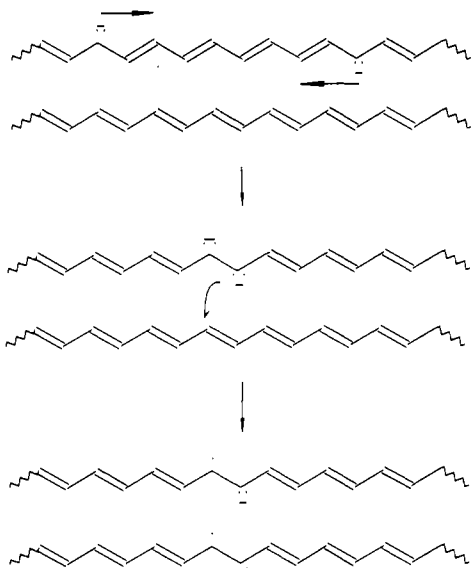*Acc. Chem. Res., Vol. 25, No. 12, 1992* **565**

Figure 7. Bipolaron hopping mechanism for charge transport.

tionation reaction to yield a neutral olefin and a dianion.[34] Other olefins known to undergo a disproportionation or related reaction are 1,1-diphenylethylene[35] and cyclooctatetraene.[36] Thus a modification of Chance's mechanism,[37] involving encounter of two solitons (a bipolaron in solid-state terms) followed by single-electron transfer to neutral polyene to produce two radical anions (polarons), provides a precedented mechanism which involves isoergic electron transfer (see Figure 7). This "bipolaron hopping" mechanism is now recognized to most closely match the charge transport energetics.

This radical anion disproportionation mechanism also provides a mechanism for the doping process itself, which involves taking a neutral polyene of necessarily even conjugation length to produce a soliton with an odd number of CH units. If we view the formation of solitons as arising from initial radical anion (polaron) formation followed by disproportionation to the dianion/neutral pair (bipolaron), then the formation of an odd-numbered soliton is exactly analogous to one of the two diphenylmethyl anions formed from tetraphenylethylene reduction.[20,34] The formation of dianions is not as energetically forbidding as it might seem even for relatively unstabilized π-systems, since ion pairing provides electrostatic stabilization of dianion formation. That is, formation of an ion triplet consisting of two alkali-metal ions and one polyacetylene dianion doubles the number of electrostatic interactions in two cation/monoanion pairs and stabilizes the dianionic form.[33b] For example, hexatriene is readily reduced to its dianion, and the crystal structure of its dilithium–TMEDA derivative has been determined.[38] This discrete dianion provides a good model for highly doped polyacetylene, since it consists of coupled allyl anions. We note with

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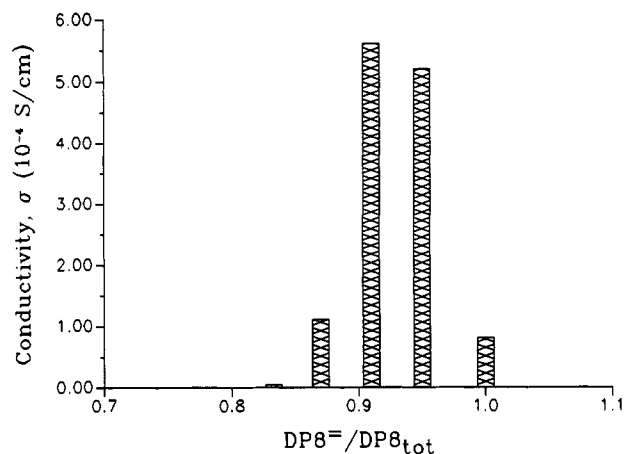(38) Arora, S. K.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 6271.

Figure 8. Conductivity of $DP8^{2-}$ vs dianion mole fraction.
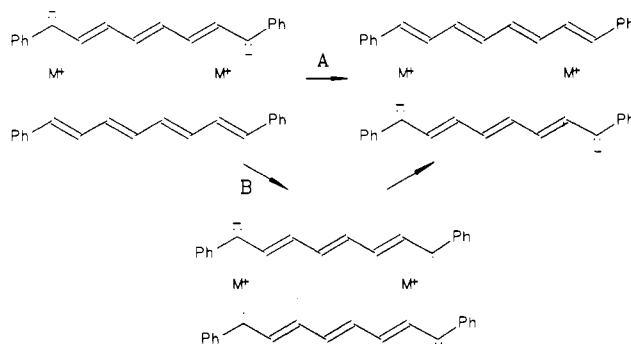

Figure 9. Mechanisms for electron transfer in $DP8^{2-}$.

some interest the observation[39] that the most conductive form of potassium-doped polyacetylene has the general formula C_6H_6K, which corresponds exactly to a hexatriene dianion and a neutral hexatriene in equilibrium with two hexatriene radical anions.

To bridge the gap between Szwarc's solution studies and solid-state polyacetylene, we employed studies of the solid-state alkali-metal reduction of the polyacetylene model compounds 1,4-diphenylbutadiene (DP4) and 1,8-diphenyloctatetraene (DP8).[40] The potassium salts of 1,4-diphenyl-1,3-butadienide (DP4[2-]) or 1,8-diphenyl-1,3,5,7-octatetraenide (DP8[2-]) were prepared by reducing the corresponding hydrocarbon with excess potassium. Pressed-powder pellets of the potassium-doped DP4 were weakly semiconducting (<10[-6] S/cm), while the potassium-doped DP8[2-] was semiconductive (0.001 S/cm). The conductivity increased upon addition of neutral DP8, reaching a maximum at a ratio of neutral to reduced material of ca. 10:90 (see Figure 8). Two mechanisms are possible for the conduction in these materials (see Figure 9). In the concerted mechanism (path A), a two-electron transfer from dianion to neutral may take place. This mechanism has analogy to the bipolaron hopping mechanism. In the stepwise mechanism (path B), single-electron transfer occurs from the dianion to neutral to form two radical anions. Subsequent electron transfer from a radical anion to a different radical anion serves ultimately to regenerate the dianion and maintain the electron-transfer chain. This mechanism has its analogy in polyacetylene through a bipolaron to two polaron interconversion

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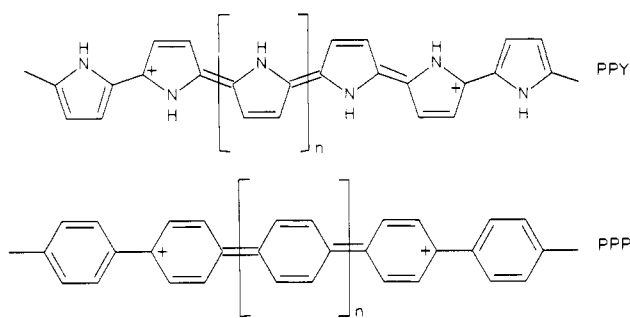(40) Tolbert, L. M.; Schomaker, J. A. *Synth. Metals* **1991**, *41*, 165.

Figure 10. Bipolarons in PPY and PPP.

process. Although our work alone cannot distinguish between these two mechanisms, the latter has ample precedent in solution chemistry, while the former has no precedent.

This mechanism of soliton formation and propagation also provides clues to the types of polymers which will support charge migration. Specifically, polymers which utilize soliton conduction mechanisms are characterized by 2-fold translational symmetry, since dianion formation will necessarily involve production of two charge sites at symmetry-equivalent centers. Polymers from unsymmetrical acetylenes such as poly(1,6-heptadiyne) or poly(phenylacetylene) exhibit poorer conductivity, generally involving radical anion (polaron) states.[41] Similarly, formation of isolated solitons in a C_{2v}-symmetric polymer such as polyphenylene is energetically unfavorable, since the solitonic center requires displacement of bond alternation in such a manner as to form higher energy quinoid structures. A second solitonic center restores aromaticity (see Figure 10). Thus in polymers other than polyacetylene the solitons are confined in pairs called bipolarons.

Despite the common representation of solitons as uncompensated ions, the dynamic SSH model suffers from one additional flaw by comparison with discrete organic anions. That is, in nonpolar solvents, resonance-stabilized carbanions invariably exist as ion pairs. The counterion forms a very tight electrostatic bond, which while stabilizing the ion pair (or ion triplet) creates a substantial barrier to charge migration. In the case of doping by the hard lithium counterion, ion triplets are very stable and both DP8^{2-} and polyacetylene are poorly conductive. By analogy to the solution phenomenon of ion pairing, this immobilization of charge and inhibition of charge transport is referred to by physicists as "ion pinning".[42] Even in the case of alkali-metal doping, AC-conductivity measurements have demonstrated that ion migration is not involved.[43] Rather, a form of soliton hopping must be involved both in the longitudinal (solitonic) and transverse (bipolaronic) mechanisms. As we see in Figure 9, hopping of negative charge without migration of cation is possible within the $(CH)_x$K lattice in which a soliton migrates to a lattice site adjacent to a countercation. Such a mechanism is

consistent both with known crystal structures and with the optimum doping level of ca. one potassium for 6–8 carbon atoms.[44]

When polyacetylene is stretch-oriented, the longitudinal conductivity *increases* by several orders of magnitude while the transverse conductivity *decreases*.[2b] This phenomenon can be readily understood when we realize that solitonic conductivity along the polymer chain will predominate along the stretch axis while interchain hopping (bipolaronic) conductivity must prevail across polymer chains. We note, for instance, that conductivity in DP8^{2-}-K$_2^+$, which can only occur via hopping processes, is several orders of magnitude lower than that for K-doped polyacetylene. However, as Enkelmann has pointed out, the temperature dependence of the conductivity still requires that hopping dominate conductivity even in the parallel direction.[45]

Finally, we note that, although our studies have been largely directed to carbanions, our field of expertise, the general principles outlined here apply to organic cations as well. Thus charge transport in *p*-doped polypyrrole (PPY) or poly(*p*-phenylene) (PPP) apparently involves a dication, or bipolaron on a carbon backbone[46] which looks suspiciously like a substituted polyacetylene (see Figure 10). The same principles that govern radical ion to dication disproportionation with ion pair involvement apply equally well to these p-doped systems.

IV. Interrupted Polyacetylene

The correspondence between *n*-type solitons and resonance-stabilized carbanions requires that *n*-doped polyacetylene be identical, within a matrix effect, to polyenyl anions synthesized by standard techniques for carbanion generation, i.e., by deprotonation. In order to test the feasibility of the approach, we investigated the polymer generated by methanol quench of *n*-doped polyacetylene, more popularly referred to as segmented polyacetylene (SPA).[47]
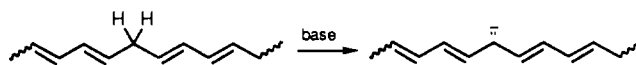
Treatment of the polymer SPA with the "super base" *n*-butyllithium/potassium *tert*-butoxide produced a color change from metallic golden slowly to metallic dark blue and a conductivity of 160 S/cm, decreasing to a final, constant value of 52 S/cm after 8 h. Thus formation of charge carriers either through one-electron reduction followed by polaron–polaron recombination into closed-shell anionic solitons (or bipolarons) or by deprotonation to yield the same closed-shell species indicates that the identity of the charge carriers is

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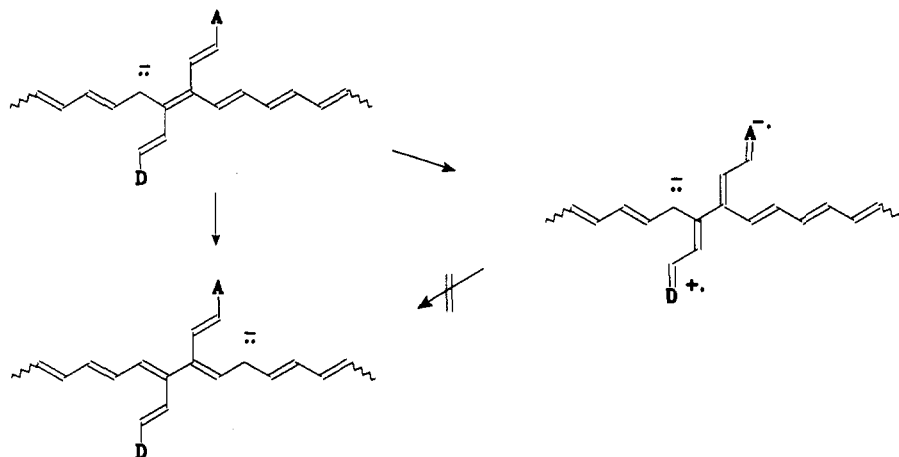
Figure 11. A molecular "gate" for soliton production.

independent of their method of generation. Apparently either redox or acid–base chemistry can take place in polyacetylene without disrupting the polymer morphology, allowing insulator to metallic transitions to take place reversibly upon deprotonation.

V. Molecular Switching and Molecular Wires

The reduction of electronic devices to the size of molecules, so-called "molecular electronics" has been a tantalizing dream since Carter's early proposals.[48] One approach to molecular "wires" involves solitons as charge carriers along polyene chains. A further proposal for solitons in molecular electronics is their use as molecular gates or "switches". That is, passage of a soliton switches the bond alternation pattern and blocks charge propagation in a transverse direction (see Figure 11).

Molecular electronics has been the subject of much controversy due to two fundamental limitations. The first limitation arises from the difficulty, if not impossibility, of addressing a discrete molecule.[49] A second and related limitation results from the nature of the conductivity measurement itself, which invariably involves not only parallel molecular ensembles but also interchain soliton hopping. That is, the chain length of discrete polyacetylene chains is not long enough to traverse conventional microelectrodes. Although the implementation of these radical, but increasingly tenable, proposals remains elusive, our results allow us to begin setting boundary conditions on the molecular dimensions required for observing such phenomena.

We begin by considering diphenylpolyenyl anions in which each para carbon is replaced by nitrogen, i.e., phenyl becomes 4-pyridinium. We would expect that the negative soliton localized in the center of such a moiety would migrate to one end or the other to annihilate the positive charge. In fact, each resulting structure corresponds to one of two equivalent resonance forms of a cyanine dye (see Figure 12). On the one hand, we would expect the energy gap to approach zero as N_{eff} approaches infinity and bond lengths remain comparable. On the other hand, at sufficient length the Peierls distortion will intervene and bond
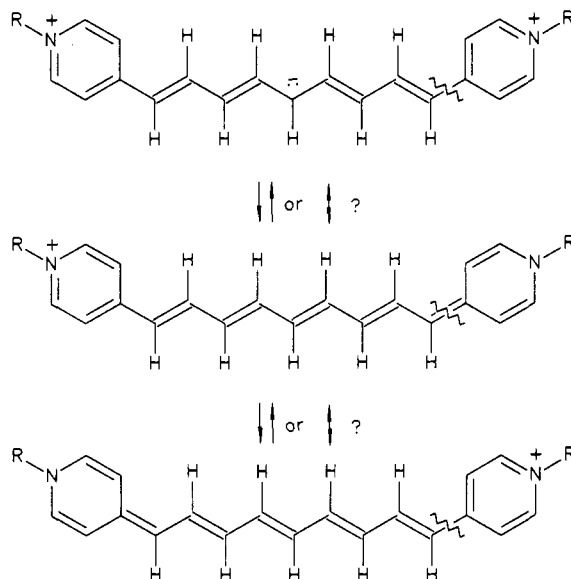

**Figure 12.** Charge migration in dipyridylpolyenyl anions.

alternation will take place. Indeed, a finite soliton width requires that the two forms become inequivalent. On the basis of a one-electron particle-in-a-box model,[50] Kuhn has a similar prediction for cyanines terminated with iminium groups. Thus the electron density localizes at one end or the other of the polyene, but the ends do not communicate except through solitonic motion.

Preliminary calculations at the AM1 level predict that formation of the asymmetric ground state occurs as early as 13 carbon centers. This phenomenon can be seen most readily by an examination of the bond alternation as a function of symmetry and substituent. The diphenyltridecahexaenyl anion (DP13) has a symmetric ground state, with bond alternation increasing with distance from the anionic center (see Figure 13a, in which the difference in adjacent bond lengths, Δr, is plotted versus the position of the atom). When the terminal para carbons are replaced with nitrogen to form the isoelectronic dipyridyltridecahexaenyl cation (DPy13, a cyanine dye), but C_{2v} symmetry is enforced, the bond alternation is greatly diminished

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(49) This is becoming less problematic. See: (a) Joachim, C. *New J. Chem.* **1991**, *15*, 223. (b) Joachim, C.; Launay, J. P. *J. Mol. Electronics* **1990**, *6*, 37.

(50) (a) Kuhn, C. *Synth. Metals* **1991**, *43*, 3681. See also: (b) Reimers, J. R.; Craw, J. S.; Hush, N. S. *Proceedings, U.S. Engineering Foundation Conference on Molecular Electronics: Science and Technology*, St. Thomas, U.S.V.I., 1991. (c) Craw, J. S.; Reimers, J. R.; Bacskay, G. B.; Wong, A. T.; Hush, N. S. *Chem. Phys.*, in press.
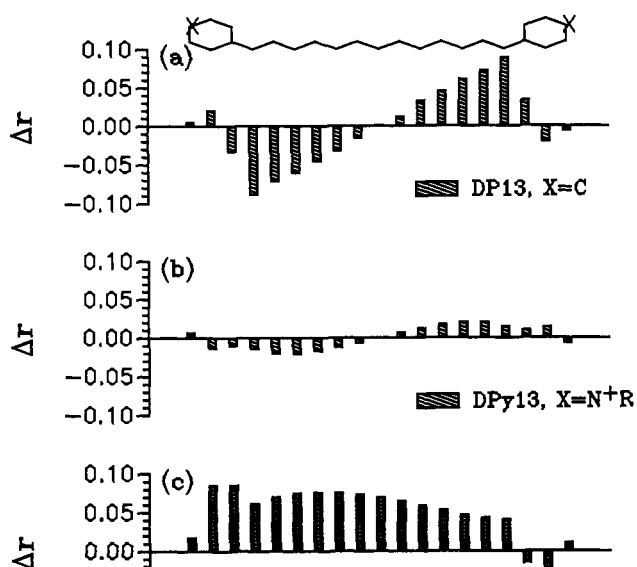
Figure 13. Bond alternation in DPy13 and DP13: (a) DP13, (b) DPy13 with enforced symmetry, (c) DPy13 fully relaxed.

(see Figure 13b). This situation is unstable relative to a Peierls distortion and undergoes a lifting of the symmetry to produce the unsymmetric ground state shown in Figure 13c. Thus DP13 clearly exhibits C_{2v} symmetry and the antisymmetric bond-alternation characteristic of a confined soliton,[51] while DPy13 does not.

Although the use of approximate molecular orbital theory to predict the onset of bond alternation must be treated with circumspection, known crystal structures of cyanines indicate uniform bond lengths.[52] These structures all involve chain lengths of seven or less. As

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such cyanines become larger, the equal bond lengths will either cause the energy gap to vanish or, more probably, will undergo Peierls distortion to an asymmetric ground state. Thus molecules of type DPy13 or higher constitute examples of molecular wires in which solitonic motion produces alternating reduction and oxidation of the pyridine moieties. Such an alternating donor/acceptor polyene, now actively under investigation in our laboratories, in principle allows construction of a molecular switch along lines originally proposed by Carter.[48]

VI. Concluding Remarks

In many areas of materials science, the properties of materials are now being addressed at the molecular level. At this level, questions of structure and function properly fall under the purview of mechanistic organic chemists. The particular area of electroactive materials is one of the most promising of these areas for organic chemists, since the issues involved—electron transfer, bond alternation, excitation energies—are all ones which have been subjected to intense scrutiny over the past decades. Although our work does not prove the mechanism of electrical conductivity in polyacetylene, in the sense that no mechanism can formally be proved, it provides powerful underpinnings for the one-dimensional soliton migration and hopping mechanisms. Given the phenomenal advances made during this same period in organic synthesis, coupled with extraordinary progress made in the fields of patterning (i.e., microlithography) and imaging (i.e., atomic force microscopy and scanning tunneling microscopy), the molecular engineering of solid-state devices based upon electroactive linear molecules appears to be a less daunting challenge. The field is ripe for further exploration once the language is learned.