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New class of soliton-supporting polymers: Theoretical predictions

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Theoretical predictions for a new class of organic polymers, polyarenemethides, are presented and discussed. These polymers are designed to possess degenerate ground-state bonding patterns as in trans-polyacetylene, thus allowing for the existence of isolated soliton defects. The generic backbone is given by the repeat unit [-phenyl-CH=quinoid=CH-]. Variations on this backbone have been conceived by the inclusion of bridging atoms between the phenyl and quinoid groups to yield planar ladder structures. The geometries and electronic structures of the polymers and their oligomeric counterparts have been calculated. Ionization potentials and band gaps are significantly less than those of polyacetylene. Calculations are also reported for the geometries, charge distributions, and energetics of soliton- and polaron-type defects.

Over the last few years numerous polymeric materials have been synthesized which on ionization yield complexes with conductivities in the semiconductor-to-metal range. Ionization of these conjugated-backbone polymers is achieved by addition of electron donor or acceptors to polymer precursors, examples of which include polyacetylene (PA),[1] polyparaphenylene (PPP),[2] polypyrrole (PPY),[3] poly(paraphenylene sulfide) (PPS),[4] and polythiophene (PT).[5] Because these doped materials exhibit similar electronic properties, a search has ensued for an underlying model of electronic structure to correlate their electronic properties. The concept of conduction by spinless charged defects has been introduced by Su, Schrieffer, and Heeger (SSH)[6] in a theoretical description of solitons in PA. The SSH model has been refined and extended to apply to PPP,[7] PPY,[8] and PT;[8] in addition, various approaches have been used to explore the mathematical consequences of the SSH Hamiltonian.[9] It is now generally recognized[10] that *trans*-PA is fundamentally different from other conjugated polymers in that its ground-state bonding geometry has two energetically degenerate forms:

$$\ldots =C-C=C-C=C- \ldots$$

and

$$\ldots -C=C-C=C-C= \ldots .$$

One consequence of this degeneracy is that in doped PA the possibility exists for intrachain transport by isolated charged solitons, e.g.,

$$\ldots =C-C=C-\overset{+}{C}-C=C-C= \ldots .$$

The lack of a similar set of degenerate ground-state geometries in the other doped polymers constrains the description of mobile defects to coupled pairs of solitonlike defects, referred to as polarons or bipolarons.[7,11,12]

In this paper, we describe a new class of polymers, polyarenemethides (as yet unsynthesized[13]), whose atomic connectivities also yield degenerate ground-state bonding patterns (equal energy resonance structures).[14] An example of the polyarenemethide (PAM) is shown in Fig. 1 along with PA for comparison of their bonding patterns. A family of such polymers can be derived on addition of bridging units between adjacent rings, opposite the existing CH bridges (e.g., see Table I).[15] To explore the consequences of soliton defects in such polymers we report a series of calculations predicting geometric and electronic properties. The ground-state geometries are determined by a semiempirical quantum chemical method designed primarily for geometry predictions.[16] The electronic structure of the polymers is then computed and used to predict band gaps, bandwidths, ionization potentials, and electrochemical redox potentials. Finally, a very simple theoretical method (basi-

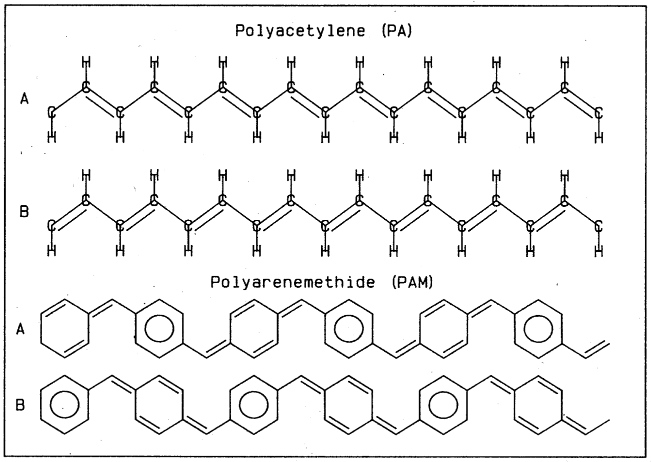
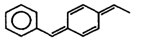
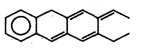
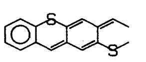
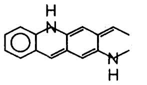
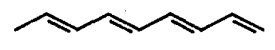


FIG. 1. Ground-state degenerate bonding patterns in polyacetylene and in polyarenemethide. Soliton defects can link phases A to B.

TABLE I. Schematic repeat units for the generic PAM structure (top) and members of its family. A section of a polyacetylene chain (bottom) is shown for comparison. Calculated values characterizing the electronic properties of these polymers are given and compared to calculated and experimentally determined values for PA

Unit Cell	Energy Gap	Band Width	Ionization Potential	Electron Affinity	Oxidation Potential	Reduction Potential
	eV	eV	eV	eV	V vs SCE	V vs SCE
	1.17	0.44	4.2	3.03	−0.20	−1.37
	0.97	1.35	4.3	3.3	−0.14	−1.10
	1.02	0.89	4.1	3.0	−0.35	−1.37
	0.60	1.60	3.4	2.8	−1.00	−1.61
	1.4	6.5	4.7	3.3	+0.4	−1.1
Exp:	1.5		4.7	3.2	0.2	−1.2

cally identical to the SSH approach[6]) is used to estimate the energetics of defect formation and the associated geometric distortions and charge distributions. Soliton defects in PAM polymers are shown to be qualitatively similar to those in *trans*-PA.

To theoretically explore the electronic structure of the proposed polymer systems, an accurate description of the atomic geometry is required. For hydrocarbons a reliable computational technique best known by its acronym MNDO has been developed by Dewar and Thiel.[16] (MNDO stands for modified neglect of differential overlap and refers to the specific approximations made in constructing the Hamiltonian.) In applying the MNDO technique, we construct for each polymer a corresponding oligomer (short-chain analog) containing at least five repeat units; the oligomers are terminated with hydrogens. The geometry of each oligomer is optimized using the MNDO method. To eliminate any effects due to end groups, the atomic geometry of the central repeat unit of the oligomer is transferred to constitute the periodic description of the polymer. The band structure of this periodic system is then determined with the valence effective Hamiltonian (VEH) technique,[17] a non-self-consistent pseudopotential calculation which has been highly reliable for other polymeric systems.[17]

The predicted geometry of the generic PAM backbone is not planar (as depicted in Fig. 1) but helical, the twist angle between adjacent rings being 30°. Otherwise, there are no unusual features of the bonding pattern; all of the single bonds indicated in the figure are of length 1.47 Å and all double bonds are of length 1.37 Å, much the same as in PA. In this and other PAM derivatives considered here, there is no significant difference between internal (endocyclic) and external (exocyclic) single or double bonds. The resonant bonds within the benzene rings are of length 1.41 Å. The other three members of the PAM family indicated in Table I are CH_2-, NH-, and S-bridged polymers. All three have planar structures; i.e., the dominant effect of the bridging unit is to eliminate the helical twist. There is no change in single, double, or aromatic bond lengths on going from the generic PAM backbone to the CH_2- and S-bridged versions; the single bonds to CH_2 and S are 1.51 and 1.71 Å, respectively. In the NH-bridged polymer the "single" bonds to N are 1.40 Å and, interestingly, the bond-length alternation of the backbone is significantly reduced, the single and double bond lengths being 1.45 and 1.38 Å. Thus, the nitrogen bridges induce notable geometric change in the backbone, and in the predictions of electronic properties (discussed below).

A summary of results from VEH band-structure calculations for the PAM polymers is shown in Table I along with the calculated and measured values on PA for comparison. All of the PAM polymers have band gaps less than that of PA (which has the smallest band gap of the known precursors to conducting polymer systems). The ionization potentials, which measure the relative ease of removing an electron, are also significantly smaller than for PA. Therefore, acceptor species (oxidants) which are not powerful enough to ionize PA may be sufficiently electronegative to ionize PAM to *p*-type conductivity. The ionization properties are also given as electrochemical potentials (relative to a saturated calomel electrode, SCE) since the doping procedure is frequently performed electrochemically and ionization data on conducting polymers can be derived in this manner. Though the most obvious role of the bridging units (CH_2, S, or NH) is to force the system to a planar geometry, it is clear from the table that they also play an important role in influencing the accessible energy levels near the band edges. Results for the NH bridged polymer are significantly different from those for the other PAM polymers. The same trend can be found when S and NH are used as bridging groups in *cis*-PA to yield polythiophene and polypyrrole, respectively. For example, the VEH result for the oxidation potential of polypyrrole is $-0.6\,V$ ($-0.4\,V$, experiment) compared to $0.7\,V$ ($0.6\,V$, experiment) for polythiophene.[17] Variations for the PAM polymers displayed in Table I are similar.

The VEH predictions for π-electron bandwidths (valence bandwidth) are smaller in the PAM polymers than PA, as could be expected for the larger repeat unit in PAM. This implies lower charge carrier (hole) mobilities in the PAM system; soliton mobilities should also be lower than in PA.

The calculations have been extended to describe defect formation in PAM. A less sophisticated computational procedure is applied in which the physics of the defects is embodied in the interactions of the π electrons (interacting out-of-plane p orbitals) on a σ-bonded atomic framework. The total energy, π electron plus σ framework, is a function of the bond lengths. Although this situation can be modeled by the SSH Hamiltonian, it has been dealt with here in a more direct (but equivalent) manner by application of Hückel theory including σ-bond compressibility. The Hückel Hamiltonian considers only interactions between adjacent carbon atoms. The strength of the π-electron interaction is modeled by a bond-length dependent factor $\beta(r)$. The contribution to the total energy from each σ bond, $f(r)$, is added:

$$\beta(r) = A\exp(-r/B)$$

and

$$f(r) = C\beta(r)(r - r_0 + B) \ .$$

Values for the parameters *A*, *B*, and *C* are taken from previous work on PPP,[7] where they were chosen to model the band gap, bandwidth, and geometry of PPP. Here, we apply the same model to a 20 ring (140 carbon) cyclic model of PAM (adjacent rings being bridged only with CH in a planar approximation).

Results for the defect-free PAM polymer are considered first, as they provide the basis for the calculations of defect structures to follow. The geometry is chosen in accordance with the results described above (CH_2- or S-bridged polymers), but we find that in the Hückel approximation, the energy can be lowered slightly if the double bonds are shortened from 1.37 to 1.36 Å and the benzene bonds from 1.41 to 1.40 Å. Under these conditions, the calculated band gap is 1.05 eV, in very good agreement with the 1.17-eV VEH value for the polymer chain twisted at 30° (and with the 0.97-eV value for the planar CH_2-bridged polymer, which is probably a more appropriate comparison). It is also fairly easy to optimize a completely "undimerized" model system in which the backbone bonds connecting the rings are forced to be equal. (This is analogous to "undimerized" *trans*-PA in which all bond lengths are equal.) In this model, all rings in PAM adopt a complete quinoid geometry (1.47- and 1.36-Å bonds) and all bonds connecting adjacent rings are 1.40 Å long. In this approximation, the increase in energy with respect to the lowest-energy ("dimerized") structure is only 0.094 eV per repeat unit (14 carbons/unit). This can be compared to the dimerization stabilization energy in PA, as calculated by SSH[6] of 0.015 eV per CH unit. The predictions of this simplified model for the undoped polymer are in general agreement with more detailed calculations that we have carried out within the MNDO scheme.

The same procedure has been used to model the PAM polymer containing various soliton and polaron defects. A neutral soliton (radical) defect is simulated by constraining the bonds on both sides of one bridging CH unit to be of equal length. This forces a phase shift in the bonding pattern of the polymer backbone as shown in Fig. 2(a). Geometrically this corresponds to introducing a radical at the bridging site. The geometry of rings in the vicinity of the defect is then subjected to an optimization procedure, the results of which are shown in Fig. 2(b). Quinoidlike structures develop on the rings near the soliton site and are stabilized by the resonance energies of allyl-like fragments on the bridges. The distortions to the geometry due to the presence of a soliton are almost completely localized within four rings. The electronic structure associated with the defect has a single half-filled level at midgap, exactly as in PA. The spin density in this state is more extended than the geometric distortions; the total spin density within six rings is $0.9\times\frac{1}{2}\hbar$. Interestingly, it is exactly zero on the defect site (bridging carbon). The extension of spin or charge density beyond the region of geometric distortion is similar to that observed in calculations for PA.[18] The energy required to create the soliton in PAM is 0.33 eV; this can be considered as the energy of vertical excitation by half the band gap, 0.53 eV, followed by a geometric relaxation around the defect site which returns 0.2 eV. The energies are smaller than in PA due to the smaller gaps in PAM, but the physics of defect formation is the same.

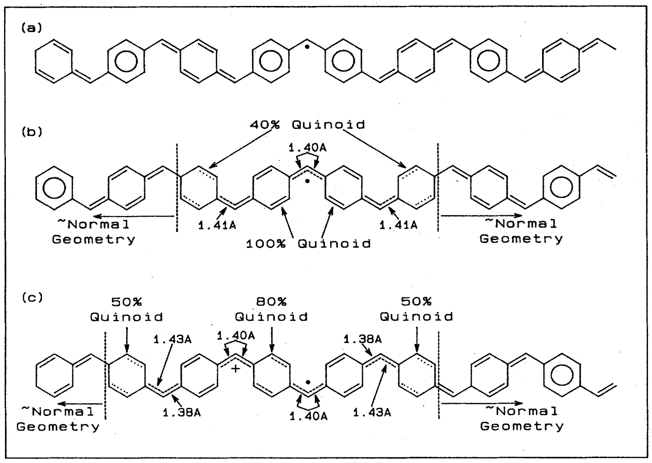


FIG. 2. (a) Schematic introduction of a soliton defect in a chain of PAM; (b) the relaxed geometry of the equilibrium configuration surrounding the soliton defect; (c) the equilibrium geometry of a positive polaron (radical cation) on a PAM chain. The notations of percent quinoid are determined from a linear interpolation of the relaxed bond lengths between pure quinoid and pure benzenoid.

A polaron corresponds to a radical-ion associated with a local lattice distortion and can be viewed as a coupled pair of soliton defects, one charged and the other uncharged [Fig. 2(c)]. For initial studies on the PAM system, the modified Hückel theory is applied to the PAM polymer with a polaron (radical cation) introduced by removing one electron from the system. Optimization of the geometry yields the results presented in Fig. 2(c). Geometrically the polaron extends over about five rings; however, its spin density is calculated to extend beyond the range of geometric distortion, the total density within seven rings being $0.79\times\frac{1}{2}\hbar$. The PAM system shows an interesting feature that we have not seen before: the maximum spin density occurs on the bridging carbon site one ring away from the central site of the polaron.

The calculations indicate that the polaron has a binding energy of 0.02 eV, compared to 0.05 eV in PA and 0.03 eV in PPP. The interaction between the charged and neutral soliton defects (each of which, if separated, would cause the existence of a midgap energy level) splits the electronic levels in the gap by 0.74 eV; thus, the half-filled level of the positive polaron is 0.15 eV above the valence band edge. The splitting is 70% of the total gap as compared to 57% in PA.[7] We have not yet studied the interactions between two neutral solitons ($\cdot\,\cdot$ pair) or two charged solitons ($+\,+$ pair), although it is to be expected that the $\cdot\,\cdot$ pair would simply recombine to form the neutral polymer backbone and the $+\,+$ pair would separate into isolated positively charged solitons as in PA.[7]

In summary, we have presented theoretical predictions for the electronic structure of a new class of conjugated polymers, polyarenemethides. These polymers are predicted to have lower band gaps and lower ionization potentials than polyacetylene. Their backbones support isolated soliton defects whose physics should be similar to solitons in *trans*-PA. We expect that analogous results would be obtained for similarly constructed materials involving pyrrole or thiophene rings bridged by CH groups.

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