Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Theoretical Investigation of a New Class of Soliton-Supporting Conjugated Polymers: Polyarenemethides

J. L. Bredas [a] , D. S. Boudreaux [b] , R. R. Chance [b] & R. Silbey [c]

[a] Lab. Chimie Théorique Appliquée, Fac. Universitaires Notre-Dame de la Paix, B-5000, Namur, (Belgium)

[b] Allied Corporation, Corporate Research Center, Morristown, New Jersey, 07960

[c] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139

Version of record first published: 17 Oct 2011.

To cite this article: J. L. Bredas , D. S. Boudreaux , R. R. Chance & R. Silbey (1985): Theoretical Investigation of a New Class of Soliton-Supporting Conjugated Polymers: Polyarenemethides, Molecular Crystals and Liquid Crystals, 118:1, 323-326

To link to this article: http://dx.doi.org/10.1080/00268948508076233

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 323-326
0026-8941/85/1184-0323/$10.00/0

THEORETICAL INVESTIGATION OF A NEW CLASS OF SOLITON-SUPPORTING CONJUGATED POLYMERS: POLYARENEMETHIDES

J.L. BREDAS,[a,*] D.S. BOUDREAUX,[+] R.R. CHANCE,[+] and R. SILBEY[**]

[*] Lab. Chimie Théorique Appliquée, Fac. Universitaires Notre-Dame de la Paix, B-5000 Namur (Belgium)

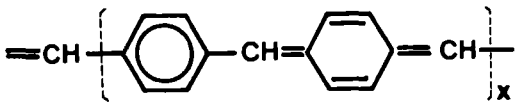
[+] Allied Corporation, Corporate Research Center, Morristown, New Jersey 07960

[**] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Abstract Theoretical predictions for the electronic properties of a new class of organic polymers, polyarenemethides, are discussed. These polymers are designed to possess a degenerate ground state analogous to that in trans-polyacetylene. The parent polymer backbone is given by the unit cell: (-phenyl-CH=quinoid=CH-). Calculations are presented for the geometric and electronic structures of the "undimerized" and "dimerized" chains, as well as those corresponding to soliton and polaron excitations in the "dimerized" chain. Significant differences with respect to polyacetylene are found.

To date, trans-polyacetylene (PA), is unique among conducting polymer systems in possessing a degenerate ground state, i.e. two geometric structures having exactly the same total energy. This degeneracy is a consequence of a Peierls distortion and leads to possible nonlinear soliton excitations.[1,2] Many peculiar phenomena that occur in trans-PA can be explained by the presence of soliton defects on the chains. One of the most exciting examples is the observation, for doping levels between ~0.2 and 7 mol% in AsF_5- and Na-doped PA, of high conductivity without significant Pauli susceptibility,[3,4] suggesting that spinless charged solitons may play an important role in the transport properties.

In this paper, we describe a new polymer system, polyarenemethide, which is as yet unsynthesized. Polyarenemethide (PAM) is interesting in that it also possesses a degenerate ground-state structure where the quinoid ring - phenyl ring alternation is the equivalent of the double bond - single bond alternation in trans-PA:

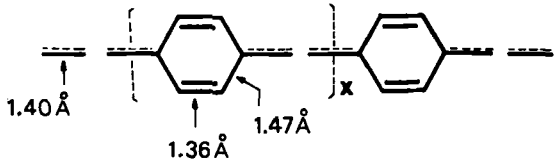


To explore the consequences of ground-state degeneracy in PAM, we have performed a series of calculations aimed at determining the energetics of defect formation and the atomic and charge distortions associated with them. We report here mainly on results obtained at the level of simple Hückel theory with σ bond compressibility, i.e. the quantum-chemical equivalent of the Su-Schrieffer-Heeger Hamiltonian.[1] This allows an easy comparison with the results previously obtained for trans-PA in the same theoretical framework.[1,5] The Hückel parameters we use are the same as those we optimized in the case of polyparaphenylene.[5] MNDO semiempirical Hartree-Fock geometry optimizations and Valence Effective Hamiltonian (VEH) band structure calculations have also been completed; results of these calculations can be found elsewhere.[6]

We first investigate the geometric and electronic structures of PAM without defects in the undimerized (metallic) and dimerized (Peierls distorted) states. We then describe calculations on polarons and solitons.

CHAINS WITHOUT DEFECTS

The Hückel geometry optimization of the "undimerized" PAM chain (all ring-connecting bonds of equal length) is shown below and is in very good agreement with the MNDO optimized geometry:



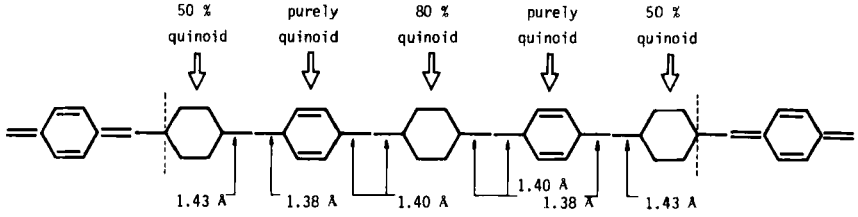
It is important to note that all rings adopt a quinoid structure and are linked by allyl-like fragments. This can be understood by the fact that if the rings had aromatic character, the two bonds between them would turn out quite long, thereby inhibiting electron delocalization along the chains.

This geometric structure is unstable with respect to a Peierls distortion to a "dimerized" state which leads to a doubling of the unit-cell size and a quinoid - benzenoid alternation as shown in the first graph above. The stabilization energy of the dimerized structure is 0.05 eV per C_7 unit. This can be compared with the 0.015 eV stabilization in trans-PA.[1] The Peierls distortion opens up a 1.052 eV gap at the Fermi level, which is 0.35 eV smaller than in PA. The width of the highest occupied band is 1.25 eV. VEH

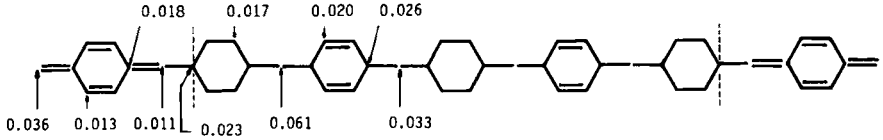
calculations yield similar results and indicate that the solid-state ionization potential is about 4.2 eV,[6] i.e. ~0.5 eV smaller than in PA.

POLARONS AND SOLITONS

Upon removal (or addition) of an electron, the geometry optimization calculations lead to the formation a polaron, i.e. a radical-ion associated with a local lattice distortion:



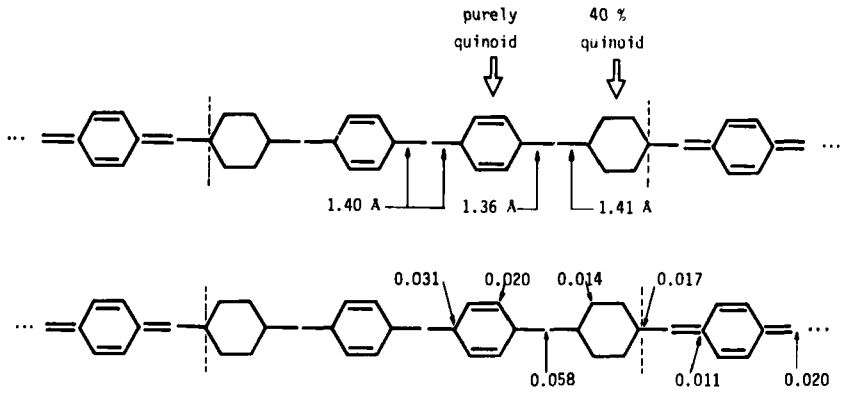
The polaron defect extends mainly over 5 rings (within the dashed lines in the figure) in which the quinoid rings remain unaffected and the benzenoid rings acquire a strong quinoid character. The charge (spin) density within the polaron is shown below:



Only the atomic charges (spin densities) larger than 0.01 e are given. Note that the largest charges (spin densities) are found one ring away from the center of the polaron. The total charge (spin density) for the seven rings drawn above is 0.79 e.

The presence of a polaron leads to the appearance of two localized electronic levels in the gap, 0.154 eV away from the band edges, i.e. 0.372 eV on either side of the Fermi level (center of the gap). This is in complete agreement with the value that would be predicted within the continuum field-theory limit as derived for trans-PA.[7] The polaron binding energy is about 0.02 eV, which is to be compared with ~0.03 eV in polyparaphenylene[5] and ~0.05 eV in trans-PA.[5,7]

When a second electron is removed from (or added to) the chain, our calculations indicate that two polarons are unstable by 0.35 eV with respect to the formation of two isolated charged solitons. The soliton creation energy is 0.329 eV; the continuum limit value (equal to the gap over π [1,7])would be 0.335 eV. The geometric structure and charge density (in e) of the soliton are illustrated below:



The soliton extends over ~4 rings and the charge density on the middle site is zero, in marked contrast with the PA case. The total charge for the six rings drawn above is 0.90 e. In the neutral soliton, the same characteristics apply for the spin density.

In summary, (i) polyarenemethide should be easily both p-doped (ionization potential around 4 eV) and n-doped (electron affinity around 3 eV); (ii) on doping, first polarons should be formed and then recombine to form charged solitons, since the creation energy of two solitons is lower by 0.35 eV than that of two polarons; (iii) due to the smaller bandwidths (HOMO bandwidth is ~1.25 eV), the maximum conductivities should be lower than in polyacetylene (where the HOMO bandwidth is ~5 eV).

REFERENCES

a. Chercheur qualifié of the Belgian National Fund for Scientific Research (FNRS).

1. W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. B 22,2209 (1980).
2. M.J. Rice, Phys. Lett. A 71, 152 (1979).
3. D. Moses, A. Denenstein, J. Chen, A.J. Heeger, P. McAndrew, T. Woerner, A.G. McDiarmid, and Y.W. Park, Phys. Rev. B 25, 7652 (1982).
4. T.C. Chung, F. Moraes, J.D. Flood, and A.J. Heeger, Phys. Rev. B 29, 2341 (1984).
5. J.L. Brédas, R.R. Chance, and R. Silbey, Mol. Cryst. Liq. Cryst. 77, 319 (1981); Phys. Rev. B 26, 5643 (1982).
6. D.S. Boudreaux, R.R. Chance, R.L. Elsenbaumer, J.E. Frommer, J.L. Brédas, and R. Silbey, Phys. Rev. B, submitted for publication; Bull. Am. Phys. Soc. 29, 316 (1984).
7. A.R. Bishop, D.K. Campbell, and K. Fesser, Mol. Cryst. Liq. Cryst. 77, 253 (1981).