Structure and Electronic Structure of Low-Band-Gap Ladder Polymers

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ABSTRACT: Unique new ladder polymers consisting of condensed succession of six- and five-membered conjugated carbon rings have been made recently by Scherf and Müllen. This paper compares the electronic structures of six topological isomers of these poly(indenoindenes). The results are analyzed in terms of topological band gaps and geometry relaxation. While all isomers have seven electrons in their chemical repeat units, only a few are expected to have a band gap smaller than 0.5 eV. The possibility of a ferrimagnetic ground state for some low-band-gap isomers is also discussed. Optical properties of the precursor planarized polyphenylenes are analyzed. Present calculations also predict that the transition to the highly conducting state should occur at significantly lower dopant concentrations compared to single-chain conducting polymers, such as polyacetylene or polythiophene.

1. Introduction: Scherf–Müllen Polymers

Scherf and Müllen have recently made a new ladder polymer,[1] which consists of fully condensed chains of alternating six- and five-membered rings, with all ring carbon atoms being in their sp^2 hybrid state and each contributing one π electron. These ladder polymers have been made via dehydrogenation from ladder precursors,[2–4] which are essentially rigid planarized polyphenylenes (PLPP). Other types of ladder polymers exhibiting novel conjugated backbones have been recently made by several groups.[5] Three of the abovementioned PLPP precursors have been already made by Scherf and Müllen. These isomers are shown in Figure 1 where unessential side groups have been omitted. The o, m, and p suffixes after their names indicate the relative ortho, meta, and para positions of the bridging methylene carbons adjacent to a given six-membered ring.

The dehydrogenation of PLPP(p,m) in Figure 1 yields the new conjugated rigid ladder polymer by turning the bridging methylene carbons into methine carbons with an additional π-electron available for delocalization. The aim of Scherf and Müllen has been to make new small-band-gap polymers. This goal is realistic, because the repeat units have an odd (7) number of electrons. We have adopted the name poly(indenoindene) (PInIn) for the whole class, a name which emphasizes the repeated condensation of six- and five-membered rings. Figure 2 shows the traditional bond-localized chemical structures of a few isomers of the dehydrogenated polymers. The nature of this electron localization and the related bond relaxation is a key issue in this paper. The bridging methine carbons provide the odd electrons and are more important in determining the properties of the PInIn's than the bonds completing the five-membered rings labeled *L* and producing the ladder topology. However, without these *L* bonds, planarity of the polymers would be lost. Of course, these *L* bonds provide the only path of conjugation in the parent PLPP's.

Low-band-gap polymers are being sought for several reasons: they are easy to dope with both donors and acceptors and mild reagents, they have unusual properties such as simultaneous high conductivity and transparency in the visible, and they are expected to have large nonlinear optical responses. The quest for new low-band-gap organic polymers[4–39] has proceeded in the last decade or so along two alternative routes. Chemical variations of *single main-chain* polymers have yielded materials with band gaps as low as 0.5 eV. The other route involved the building of ladder polymers, which in some sense represents a transition from one-dimensional to two-dimensional materials.[19] Polyacene (PAc) is a prototype of this category, being the first member in a series of hypothetical polymers bridging quasi-one-dimensional polyacetylene (PA) and quasi-

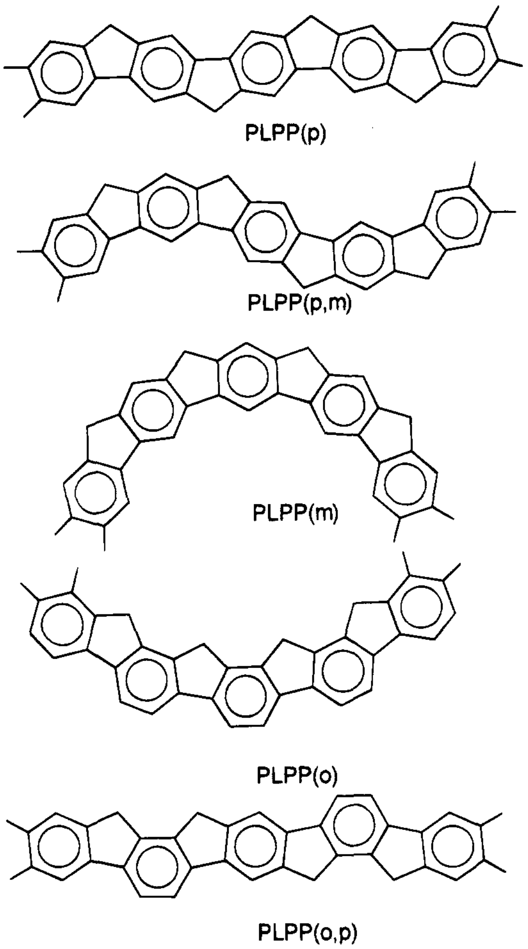

Figure 1. Planarized polyphenylene (PLPP) isomers.[2,3]

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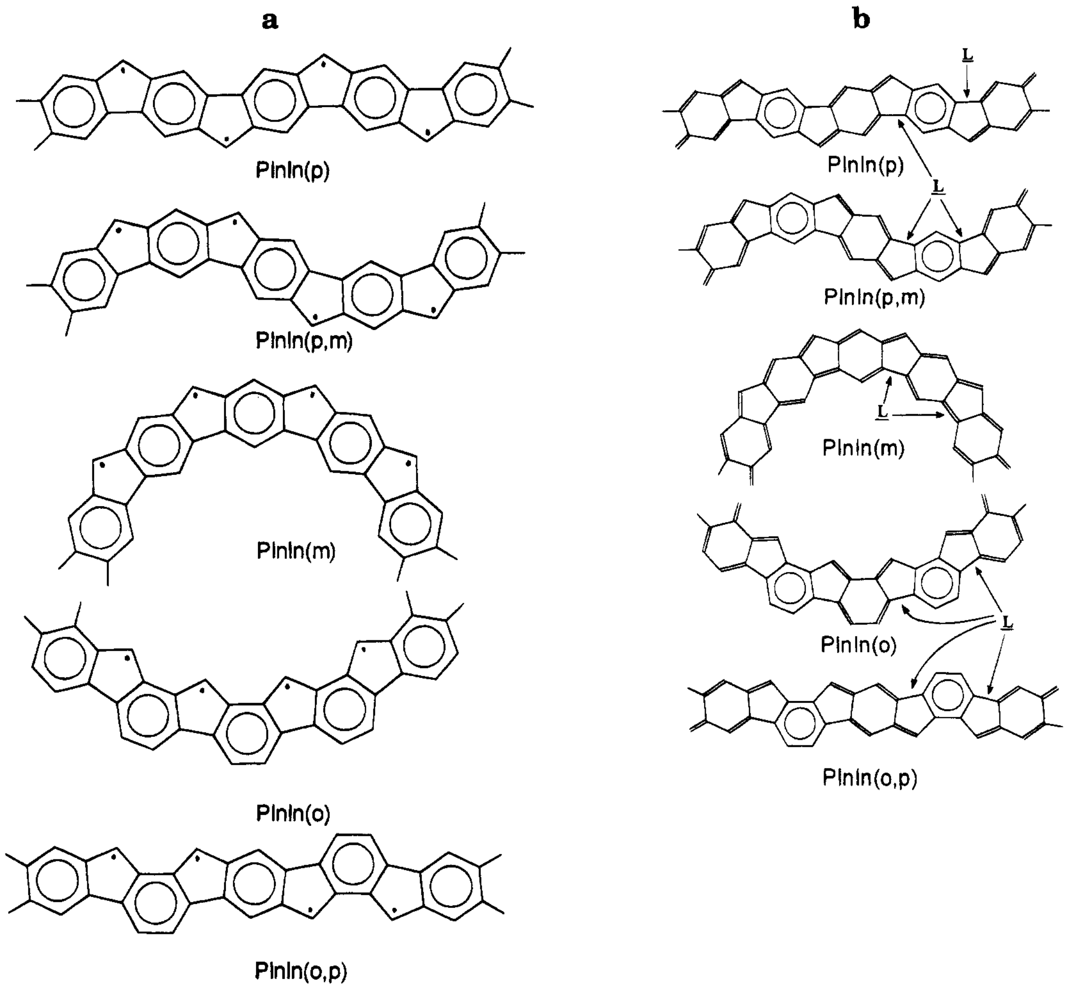
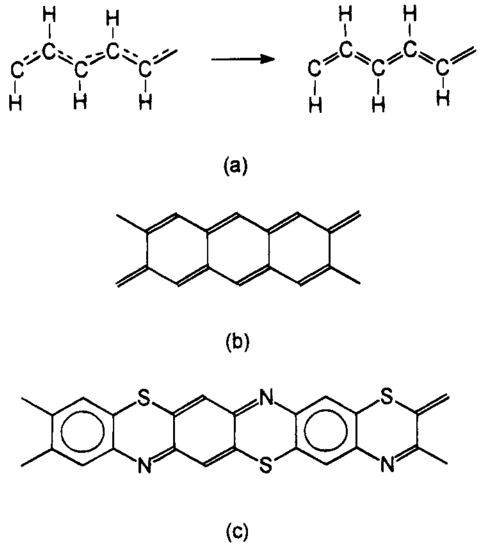


Figure 2. Poly(indenoindene) (PInIn) polymers. Suffixes indicate the relative position of edge carbons in the adjacent five-membered rings, relative to the adjoining six-membered rings showing the expected bond localization. For discussion concerning the ladder-forming *L* bonds, see text. (a) shows the odd electrons before localization; (b) shows the classical localization pattern.



(a)

(b)

(c)

Figure 3. Bond localization in (a) polyacetylene (PA), (b) polyacene (PAc), and (c) polyphenothiazene (PTL).

two-dimensional graphite. (See Figure 3a,b.) Even though polyacene has not been made yet, experimental data on oligomers, combined with calculations on infinite periodic models of PAc, indicate that it should have an intrinsic gap of ~0.4 eV.[40]

It has been shown recently[16] that heterocyclic ladder macromolecules of the polyphenothiazine (PTL; shown in Figure 3c), polyphenoxazine (POL), and polyphenoquinoxaline (PQL) types have intrinsic band gaps in the 0.3–0.4 eV range. These polymers consist of condensed six-membered rings only, arranged similarly to polyacene. However, due to the heteroatoms, each chemical repeat unit has an odd number of π-electrons (9), which makes them analogous to the PInIn's.

The purpose of this paper is to describe the fundamental electronic and structural properties of a few isomers of the PInIn polymers separating the effects of topology and geometry relaxation.

2. Topological and Peierls Gap

What happens to the unpaired π-electrons in the five-membered rings in any of the PInIn isomers? The tendency of unpaired electrons to form localized pairs in polyacetylene (PA) is strong, which leads to a structure of alternating single and double bonds with a sizable gap of 1.5 eV[41] (see Figure 3a for the bond-localized structure). In PA the band gap resulting from this Peierls distortion[10,42,43] is approximately proportional to the difference between the long and short bond distances, δr:

$$E_{\mathrm{g}}^{\mathrm{Peierls}} = k\delta r$$

By contrast, bond localization is weaker in the ladder polymer polyacene (PAc), which is estimated to have a gap of 0.4 eV.[40] The ladder topology is essential for achieving this small gap. Would any of the PInIn isomers shown in Figure 2 have a small gap? In

Table 1. Energy Gaps (eV) of Scherf/Müllen and Related Conjugated Polymers[a]

polymer (PInIn = poly(indenoindene))	hydrogenated precursor polymer	topological	PM3	LHS	expt
PInIn(p)	PLPP(p)	0.0	0.91	0.55	
PInIn(p,m)	PLPP(p,m)	0.59	1.19	0.98	0.7–0.9[b]
PInIn(m)	PLPP(m)	0		0.12	
PInIn(o)	NA	0		0.88	
PInIn(p,o)	NA	0		0.55	
PInIn(p,m,m)	NA	0		0.13	
PinIn(m′)	NA	0		0	
	Isoelectronic Polymers without Five-Membered Rings Closed—poly(arylenemethines) (PAM)				
PAM(p)		0	1.04	0.80[c]	
PAM(p,m)		1.02	1.93	1.67	
PAM(m)		0		no Peierls[d]	
PAM(o)		0		0.81	
PAM(p,o)		0		0.80	
PAM(p,m,m)		0		no Peierls[d]	
PAM(m′)		0		no Peierls[d]	

[a] NA = has not been made yet. [b] Reference 3. [c] Reference 7 (by LHS method). [d] But spin-Peierls is expected—possible magnetic polymer.

accordance with Peierls' general argument[43] as applied to this polymer, a lower symmetry structure with two inequivalent rings is expected at least for those isomers shown in Figure 2, which correspond to a half-filled band, i.e., zero band gap, case. Due to the complex topology of the ladder polymers being discussed in this paper, it is not trivial to determine, which isomer would undergo a Peierls distortion, because the topology of the material may be such that its band gap is intrinsically, so to speak, topologically not zero. For instance, the recently discovered fourth elemental allotrope of carbon, fullerene (C_{60}), has a sizable gap of 1.8 eV,[32] which is largely determined by the topology of fused five- and six-membered rings. Similarly, the band gap of polyphenylenes is largely determined by the topology and to a lesser degree by the geometry relaxation. For more about polyphenylenes, see section 5.

The concept of topological gap is useful: it is the energy gap of the system if bond localization is not taken into account, i.e., the energy gap calculated in a Hückel model with all resonance integrals assumed to be equal, or in systems with heteroatoms topological gap is the one corresponding to a higher symmetry structure. Polyacetylene, polyacene, graphite, and PTL have zero topological gaps, while poly(*p*-phenylene), C_{60}, and polythiophene do not.

If the translational repeat unit has an odd number of electrons, the topological gap is zero by symmetry and the system has a partially filled energy band. Polyacetylene in this model is, for instance, a half-filled band system, because there is one odd electron per repeat unit. Accordingly, a polymer of I_3^- ions whould have a $^2/_3$-filled band[44] if all I–I contacts were equivalent, etc. However, the topological gap may be nonzero if the chemical repeat unit has an odd number of electrons, but the translational repeat unit has an even number. This will turn out to be the case for one of the PInIn polymers, the (p,m) isomer.

In this context it is worthwhile to mention that, if present, the relevant symmetry is a screw axis of symmetry.[43,44] For example, both polyacetylene and PInIn(p) have therefore a half-filled band before the effects of the Peierls distortion are taken into account; they have one[44] and seven π-electrons in the unit, respectively, which is then repeated by the screw axis of symmetry. In contrast, in PInIn(p,m) the neighboring C_7 units are not related by translation or screw axis, and the truly unique repeat unit has 14 π-electrons.

We have performed calculations without and with complete geometry optimizations, assuming a closed-shell electron configuration. The calculations without geometry optimizations provide band-gap values, which can be considered purely topological, while the geometry-optimized gap values incorporate the combined effects of topology *and* relaxation due to bond localization. Symbolically:

$$E_g = E_g^{\text{topol}} + E_g^{\text{relax}} + E_g^{\text{correc}}$$

where E_g^{topol} is the gap calculated without geometry relaxation, E_g^{relax} is the corection due to geometry relaxation, and E_g^{correc} includes terms due to ring closure (see below) and other corrections. If $E_g^{\text{topol}} = 0$, then E_g may likely be dominated by the geometry relaxation, which may, in turn, be dominated by the Peierls distortion operative for systems with an odd number of electrons per repeat unit.

3. Poly(indenoindenes)

Table 1 lists the energy gap values obtained for seven topological isomers of PInIn. Results of the PM3[45] and Longuet-Higgins–Salem[20,34,46,47] (LHS) type calculations, where both are available, agree very well with each other. Geometry relaxation is important in most cases, and the general pattern of single and double bonds, obtained in the geometry optimization, usually agrees with the bond patterns shown in Figure 2b. One system has a sizable topological gap, which happens to be the isomer that has been made and studied by Scherf and Müllen. Two others, however, have an especially small predicted band gap, while the unique m' isomer is predicted to have a zero gap.

The optimized geometries obtained with the above two methods are compared in Figure 4. Both theoretical structures indicate the alternation of aromatic (A) and quinonoid (Q) type C_6 rings with maintaining an inversion center for each. The structure is degenerate in the same sense as that of polyacetylene: the bond alternation pattern can be reversed to obtain a structure that is equivalent to the original one. Such a degeneracy allows the persistence of local solitonic defects, which can be created upon doping or during synthesis and which are consequences of the Peierls distortion of the undoped structure.

4. Poly(arylenemethines) as Interpretative Tools for PInIn's

The electronic structure of PInIn isomers can be analyzed conveniently by severing the bonds indicated

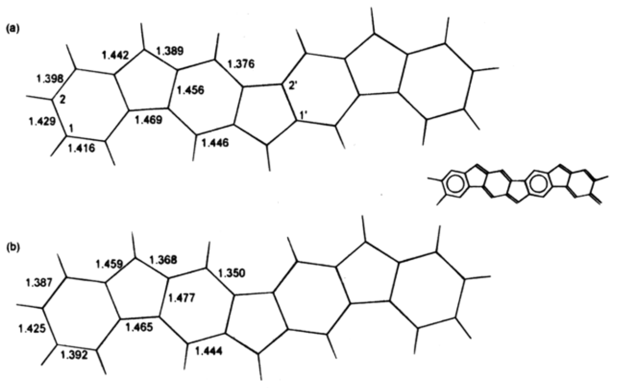


Figure 4. Geometry of PInIn(p), calculated by (a) LHS and (b) PM3. The bond distances indicate an alternating pattern of aromatic and quinonoid rings, as shown in the inset.

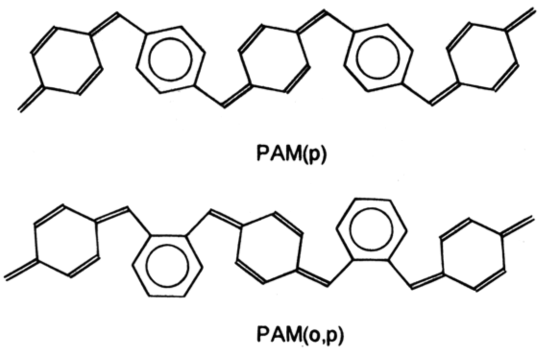


Figure 5. Two poly(acrylenemethines), used in the interpretation of the electronic structure of poly(indenoindenes).

by *L* in Figure 2b, leading to the corresponding isomers of poly(arylenemethine) (PAM), two of which are shown in Figure 5. Of course, in reality, PAM's would not be planar, but in order to trace the effects of the ladder-forming *L* bonds, planarity is assumed in the calculations.

The lower part of Table 1 shows the corresponding gap values. The large gap of the (p,m) conformer is due to the presence of a substantial topological gap which is further increased by bond localization and the corresponding geometry relaxation.

The (m) and (p,m,m) isomers of PAM have zero band gaps. By reconnecting the *L* bonds and allowing a subsequent geometry relaxation, the gap increases only slightly. This unusual situation arises, because both frontier orbitals of these PAM isomers are nonbonding with respect to the *L* bonds. The (m′) isomer of PInIn has an intrinsic zero band gap; this is a reflection of the fact that no consistent bond-localized structure can be written for it. Its band structure is the most complex of all isomers and contains two overlapping bands at the Fermi level. Such a band structure is least prone to Peierls distortions. In the analysis we can relate this system to a PAM. By cutting its *L* bonds we arrive at PAM(m′) which is identical to PAM(m), another super-degenerate[52] polymer.

The other isomers of PAM, (p), (o), and (p,o), undergo Peierls distortion as illustrated for the (p) isomer in Figure 6. ψ_a and ψ_b are the degenerate nonbonding frontier orbitals of the polymer before distortion, as can be determined from the Coulson–Rushbroke theorem.[47] These two orbitals can be combined into ψ_+ and ψ_- with the same energy. These new orbitals change their energies linearly with the distortion parameter δ, which is defined in such a way that it carries the structure from a uniform geometry to the distorted one with alternating A and Q rings, as shown in the inset in Figure 6.

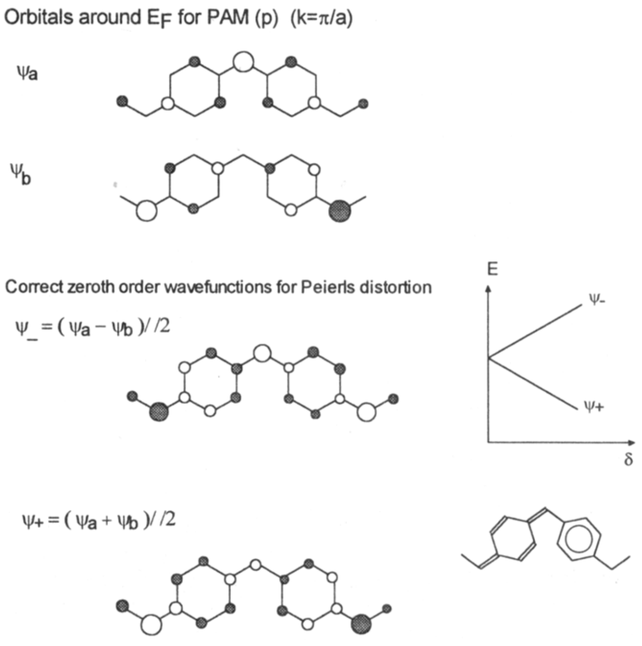


Figure 6. Peierls distortion of poly(arylenemethine)(p), PAM-(p).

After having established the electronic structures of the PAM models, the electronic structures of PInIn polymers can be derived by considering the effects of the *L* bonds as perturbations. In the (p), (p,m), and (p,o) isomers, the *L* bonds completing the five-membered rings substantially *reduce* the band gap, which is a direct consequence of the frontier orbital patterns. For the (o) isomer the change is minor, because the *L* bonds affect the highest occupied and lowest empty levels by almost the same amount.

The (m) and the (p,m,m) isomers ar peculiar: their orbitals at the Fermi level are completely localized at the connecting methine carbons and thus, within the present level of theory, no localization of the double bonds occurs. It has been argued that such systems would become (spin-Peierls) magnetic materials with a nonzero band gap.[48–62] The basic argument in suggesting a magnetically ordered ground state relies on the zero or very small value of the gap as calculated for a nonmagnetic Hückel-type calculation.[48,49] The applicability of this argument depends strongly on this gap, which is not zero for most of the PInIn isomers.

The *L* bonds cause gaps, as do geometry distortions. The distortions usually develop according to the patterns shown in Figure 2. However, in some cases the geometry distortion is not well represented by the traditional single–double bond patterns, as shown in Figure 2b. Such exceptions are isomers (m), (m′), and (p,m,m). These isomers deserve special attention, because their small band gaps and nontraditional bond localizations might be indicative of a low-energy magnetic ground state, as will be discussed in section 6.

5. Planarized Polyphenylenes

It is encouraging that the precursor polymers to the first three PInIn's in Table 1 have already been made by Scherf and Müllen. From a π-electron point of view these precursors are not ladders but rather CH_2-bridged planarized polyphenylenes. As can be seen from the calculations presented in Table 2, their energy gaps are dominated by the topological component of the gap. The corresponding optimized geometry for the (p) isomer is shown in Figure 7, which is consistent with the experimental data of fluorene. The inter-ring bond length is

Table 2. Calculated Energy Gaps vs Experiment (eV): Planarized Polyphenylenes (Methylene-Bridged Polyphenylenes)

		relaxed geometry[a]		
	topological gap	(PM3)	(LHS)	expt
PLPP(p)	2.28	2.52	2.44	2.8[b]
PLPP(p,m)	3.32		3.32	3.2[c]
PLPP(m)	3.96		3.38	3.4[d]

[a] Optimized LHS inter-ring C–C bonds are all 1.475 ± 0.002 Å. [b] Reference 4. [c] Reference 1. [d] Reference 4.

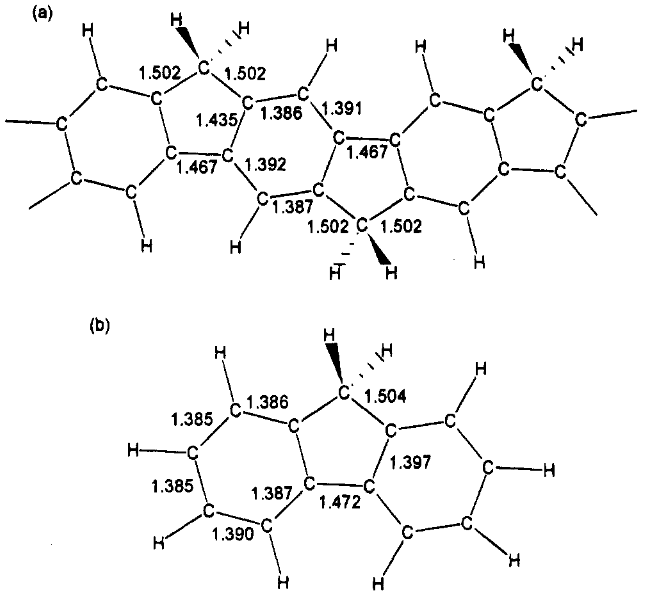


Figure 7. Optimized geometry of planarized poly(*p*-phenylene), PLPP(p) (a: optimized by the PM3 method using periodic boundary conditions), compared with (b) experimental data on fluorene (Gerkin et al.[70]).

somewhat shorter than that of undoped poly(*p*-phenylene),[63] which is in accordance with the fact that the forced planarity in PLPP's should lead to somewhat better conjugation along the polymer backbone.

6. Magnetic Ground States?

In order to check the possibility of a high-spin magnetic ground state,[48–62] we performed spin-unrestricted Hartree–Fock calculations on PInIn(m), using the crystal orbital version[52,62] of the Pariser–Parr–Pople model. The following states were considered:

PM: paramagnetic (every orbital doubly occupied, system has a half-filled band)

NM: nonmagnetic (every orbital doubly occupied, no partially filled band)

FM: ferromagnetic (can be considered ferrimagnetic at the atomic level but ferromagnetic in terms of complete unit cells: different orbitals are determined for different spins, but the two highest bands are assumed to have parallel spins)

AF: antiferromagnetic (different orbitals for different spins, but the number of up and down spin bands is the same).

The following relative total energy per repeat unit values were obtained for PInIn(m):

$$E(\mathrm{PM}) = 0 \qquad E(\mathrm{FM}) = -18\ \mathrm{kcal/mol} \qquad E(\mathrm{AF}) = -5\ \mathrm{kcal/mol}$$

The two latter (magnetic) states turn out to be more stable than the non(para)magnetic state. Surprisingly, the ferromagnetic state is much more stable than the other two, even though the antiferromagnetic wave function has twice as many free parameters (double unit cell has been used to accommodate the spacial symmetry breaking of orbitals inherent in the AF state), which often gives the AF wave function an "unfair" advantage and makes it the most stable wave function. This is not so in this case, however, clearly indicating that the ferromagnetic ordering is strongly favored for this isomer.

Table 3. Effect of Charge Transfer on Bond-Length Alternation Using Band Theory

polymer	critical charges (in |e|) at which alternation vanishes	geom optimized by
$(CH)_x$[a]	0.1/carbon	MNDO
	0.1/carbon	LHS
PTL(ladder)[b]	0.8/unit cell = 0.05/π-atom	MNDO
isoelectronic with PAM(p), no closed five-membered ring	0.25/unit cell = 0.017/carbon	LHS
PInIn(p)	0.18/unit cell = 0.012/carbon	LHS

[a] Reference 68. [b] Reference 16.

The next relevant issue is whether this stabilization energy will qualitatively change when the geometry distortion (Peierls) is taken into consideration. This calculation is aimed at comparing the stabilization effect of geometry relaxation versus magnetic ordering. The following total energies were obtained:

$$E(\mathrm{NM}) = 0 \qquad E(\mathrm{FM}) = -23\ \mathrm{kcal/mol} \qquad E(\mathrm{AF}) = -13\ \mathrm{kcal/mol}$$

The ferromagnetically coupled state offers so much stability that it again comes out as the most stable state. (In the latter calculations the unit cell has been doubled to account for the Peierls distorted geometry). This result indicates the ground state of the PInIn(m) isomer to be quite possibly ferromagnetic.

Gregorius et al.[65] and Yamabe et al.[21] have recently advocated the notion that *m*-phenyl units serve as conjugation barriers in conjugated polymers. From the present calculations it appears that, out of the three different isomers containing meta-linkages considered so far, PInIn(m) and PInIn(p,m,m) are the most likely high-spin materials, while PInIn(p,m) is the least. Obviously, a larger "database" is needed before a general pattern may emerge.

7. Effect of Doping

A measure of the strength of the geometry relaxation, albeit a somewhat crude one, is the critical amount of charge transfer at which the symmetry-breaking distortion disappears in the calculation.[66–69] Table 3 displays the calculated critical charge-transfer values for a few systems with degenerate ground states. It is well-known that at very low doping levels topological solitons can be generated by doping.[42] However, above a critical charge-transfer amount a new metallic state is stabilized, the nature of which is still being debated even in the best understood and most studied case of polyacetylene.[69] Nevertheless, it seems that the quite low critical doping value for PInIn(p) calculated in this oversimplified manner can be traced back to a similar behavior of the corresponding PAM(p) polymers. The fact that this critical concentration is very low makes PInIn's attractive, because they may be doped into the highly conductive regime at relatively low dopant concentrations. This result provides further motivation to synthesize more isomers of poly(indenoindenes).

8. Concluding Remarks

Theoretical calculations including geometry optimization indicate that certain isomers of the PInIn polymers have an intrinsically small band gap. Isomers which have a significant topological band gap are not expected to be low-band-gap polymers. The possibility of a high-spin magnetic ground state for some isomers cannot be ruled out. Unique behavior as a function of doping is predicted in PInIn(p) in that it is expected to become metallic at a very low dopant concentration.

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