extension are increasingly suppressed at higher shear rates. The conclusion that shear decreases the number of configurations in which the polymer would feel the presence of the wall is consistent with our observation of shear-induced enhancement of the surface excess Γ.

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The Interplay between Geometric and Electronic Structures in Polyisothianaphthene, Polyisonaphthothiophene, Polythieno(3,4-*b*)pyrazine, and Polythieno(3,4-*b*)quinoxaline

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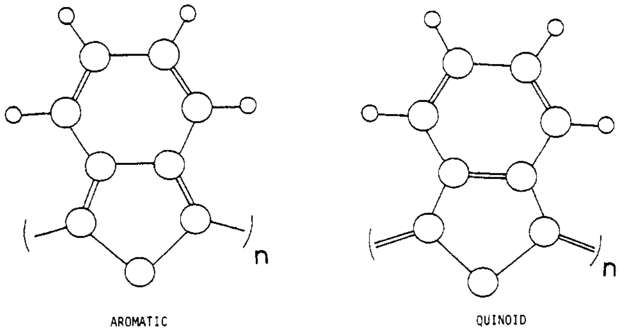
ABSTRACT: PRDDO and ab initio molecular orbital calculations are employed to show that polyisothianaphthene and polyisonaphthothiophene are nonplanar polymers in their aromatic forms, due to steric interactions between the sulfur and hydrogen atoms from adjacent monomeric units; however, the planar quinoid form of polyisothianaphthene is calculated to be ~2 kcal/mol more stable than the aromatic nonplanar form. A simple procedure is introduced for extrapolating the conformational energetics calculated from oligomers to the infinite polymeric system. Similar calculations show that polythieno(3,4-*b*)pyrazine and polythieno(3,4-*b*)quinoxaline are perfectly planar systems in both the aromatic and quinoid forms. The extended Hückel technique is used to evaluate the electronic properties of both the aromatic and quinoid forms of these polymers. The band gaps obtained for the quinoid structure of these polymers are in good agreement with the experimental and other theoretical findings. These results have important implications for the design of new conducting polymers.

Introduction

Among electrically conducting polymers, polythiophenes have emerged as versatile conducting materials upon redox doping.[1] Substitution on the carbons at the β-positions has led to new polymers that are solution processible and others in which optical properties can be enhanced.[2] The "nonclassical" polythiophenes, polyisothianaphthene (PITN), and polyisonaphthothiophene (polynaphtho[2,3-*c*]thiophene) (PINT), whose monomers were initially prepared by Cava et al.,[3,4] are of particular interest, since both experimental[5-10] and theoretical[11-13] work suggest that these systems have very small or even vanishing band gaps. From the theoretical perspective, a number of studies[11-17] have appeared leading to a controversy concerning the relative energies of the aromatic and quinoid forms of polythiophene and its derivatives.

Isothianaphthene (ITN) can be viewed as a thiophene ring on which a benzene ring has been fused along the C_β–C_β bond. Wudl et al.[5-10] have successfully synthesized PITN and have reported the reduction in the energy gap of PITN to about half that of the parent polythiophene (E_g(PT) − E_g(PITN) = 1 eV). These polymers may assume two distinctly different electronic structures, commonly referred to as the "aromatic" and "quinoid" forms, as shown below. Brédas et al.[11-13] have also reported theoretical calculations that suggest a very small



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band gap for PITN and a vanishingly small band gap for PINT; however, they assumed that PITN and PINT have planar aromatic geometries for their band structure calculations. Superficially, a planar structure appears unlikely because of adverse steric interactions between the hydrogen on the fused benzene ring and the sulfur on an adjacent monomeric unit. However, Lee and Kertesz,[15-17] using band structure calculations within the MNDO[18,19] approximations, have predicted the planar quinoid form of PITN to be the ground-state geometry. They estimated an energy difference of 10.6 kcal/mol per ring between the aromatic and quinoid forms of PITN. They postulated that the delocalization energy of π electrons over the neighboring rings and the six-membered side rings offsets the repulsion energy arising from the steric interactions between hydrogen and sulfur atoms on adjacent units. Moreover, they predicted an energy difference of 3.4 kcal/mol per ring between the coplanar and the nonplanar (ϕ = 95°) forms of the aromatic polymer, favoring the latter conformation. This indicates that the energy loss due to the relaxation from the quinoid to the planar aromatic form is much larger than the energy gained from the relaxation from a planar aromatic to a twisted aromatic structure. They also predicted that the planar aromatic form of polythiophene (PT) is 3.5 kcal/mol per ring more stable than its quinoid form. However, since *the semiempirical MNDO method is well-known to yield* relatively poor estimates for nonbonded repulsions and rotation angles about single bonds in conjugated molecules,[18,20,21] these results cannot be considered definitive. A number of other papers relevant to this general issue have appeared.[22-24] Lee and Kertesz's[15-17] results contrast significantly with those of Brédas et al.[25] who have carried out ab initio calculations with an STO-3G basis set and report a value of 16.6 kcal/mol per ring favoring the planar aromatic form over the planar quinoid form, quite different from the value of 3.5 kcal/mol per ring found by Lee and Kertesz.[15-17] This difference could be attributed to the overestimation of the stability of the quinoid form within the band structure/MNDO approach, an inadequacy in the basis set of the ab initio level, or an artifact of the assumption[25] that the geometry of the tetramer will properly mimic the infinite system. The latter assumption is particularly suspect, since the thiophene tetramer calculations assume chain termination by a single hydrogen. This is appropriate for the aromatic form, but not for the quinoid form, which is more properly terminated by H_2 or $=CH_2$ groups. Thus, the question of the relative stability of the aromatic and quinoid forms of PT and related systems remains open.

Since PITN, the first example of a transparent conducting polymer, exhibits the smallest band gap of any known conducting polymer (E_g = 1 eV) and also displays a high contrast electrochromic color change through reversible electrochemical doping (p-type only),[5-7] it is a logical candidate for a detailed study of the relationship between the chemical structure of the monomer and oligomer units and the electronic properties of the resulting polymer. In this paper, we use both quantum chemical methods and molecular design techniques to gain more insight into the molecular and electronic structures of PITN and PINT. We confirm that, because of steric interactions between the aromatic rings fused to the β-positions of the thiophene backbone and the sulfurs of adjacent thiophene units, PITN is a nonplanar polymer in the aromatic form but that the planar quinoid form of this polymer appears to be slightly more stable. A new method for estimating the relative energies of various geometric forms of these polymers is developed. This method is based upon a simple thermodynamic cycle to eliminate end-group effects in oligomer calculations, followed by an extrapolation to the infinite chain length limit. The energetics of the aromatic and quinoid forms of PT and PITN are analyzed in detail by using this approach. We also present here the structural analysis of polythieno(3,4-*b*)pyrazine (PTHP) and its next analogue polythieno(3,4-*b*)quinoxaline (PTHQ).[26-29] These systems are of interest because the adverse H···S steric interactions alluded to above are absent, and the planar forms should therefore be stabilized. Our results have important implications for the theoretical design of low band-gap polyheterocycles.

Table I
The Geometry of Thiophene (Refer to the Thiophene Unit of Figure 1) Obtained from Different Theoretical and Experimental Techniques[a]

	PRDDO	MNDO[b]	exp[c]
C1–S1	1.71	1.69	1.71
C3–C1	1.35	1.37	1.37
C4–C3	1.43	1.46	1.42
C1–S1–C2	92.5	92.7	92.2
C3–C1–S1	111.7	112.4	111.5
C4–C3–C1	112.0	111.2	112.5

[a] The bond lengths and bond angles are given in Å and deg, respectively. [b] Reference 11. [c] References 34 and 35.

Methodology

The method of partial retention of diatomic differential overlap (PRDDO)[30-32] was used to optimize the geometries of all the systems considered here. PRDDO is a minimum basis set method that reproduces the results of ab initio calculations with only a fraction of the computational expense. The theoretical details of the method can be found elsewhere.[30-32] The PRDDO approach is particularly useful for predicting the geometries of complex molecules.[32,33] As an example, we compare in Table I the structure of thiophene based upon various theoretical[1,11] and experimental[34,35] methods. PRDDO also appears to work well for determining dihedral angles in partially conjugated systems. For instance, the conformation of thianisole is predicted to be planar by both PRDDO and ab initio STO-3G calculations, with energy differences between the planar and perpendicular forms of 3.8 and 1.8 kcal/mol, respectively. In contrast, our calculations using the MOPAC program package within CHEMX[36] predicted that the perpendicular form is 2.6 kcal/mol more stable than the planar conformation. Experimental evidence[37,38] favors the quasi-planar conformation. The PRDDO approach clearly gives very reasonable results for thiophene and thianisole and is also expected to yield accurate results for thiophene derivatives. To obtain the geometries of the aromatic polymers, we first chain-optimized the monomers of all molecules at the PRDDO level. These optimizations were performed by using internal bond-stretch and angle-bend variations. In order to avoid problems with strongly coupled modes typical of ring systems, a redundant set of modes was chosen and extensive chain optimizations were performed. For ITN and thieno(3,4-*b*)pyrazine (THP), we completely reoptimized the structures of the dimers. Because the aromatic forms of the monomer and dimer of ITN and THP showed insignificant geometrical variations in the internal ring parameters (see below), the geometries of the dimers of the much larger isonaphthothiophene (INT) and thieno(3,4-*b*)quinoxaline (THQ)

Table II
Comparison of the Geometries of the Aromatic and Quinoid Forms of Isothianaphthene Obtained from PRDDO and MNDO[c]

	monomer[a]		dimer[a]		
	PRDDO	MNDO[c]	aromatic[b]	quinoid[b]	quinoid[c]
C1–S1	1.71	1.68	1.71	1.78	1.71
C3–C1	1.34	1.38	1.35	1.49	1.48
C4–C3	1.44	1.48	1.43	1.38	1.45
C5–C3	1.44	1.45	1.44	1.38	1.40
C7–C5	1.34	1.37	1.33	1.37	1.41
C8–C7	1.44	1.45	1.44	1.38	1.40
C2–H2	1.08	1.08	1.08	1.07	
C5–H5	1.08	1.09	1.07	1.07	1.09
C7–H7	1.08	1.09	1.07	1.07	1.09
C1–S1–C2	91.4	94.1	92.7	95.4	99.3
C3–C1–S1	112.3	112.0	111.1	107.4	107.2
C4–C3–C1	111.9	111.0	112.5	114.8	113.1
C5–C3–C4	119.3	118.8	118.5	119.5	119.1
C7–C5–C3	118.8	120.0	120.4	120.6	120.8
C8–C7–C5	121.9	121.3	121.0	119.9	120.0
H1–C1–S1	121.8	118.4			
H5–C5–C3	119.5	118.6	118.6	120.7	
H7–C7–C8	120.3	121.0	118.1	120.1	121.4
C1–C1′[d]			1.47	1.34	1.36
S1–C1–C1′[d]			121.8	123.3	132.2
C3′–C1′–C1–C3[d]			121.3	180.0	180.0

[a] Bond lengths in Å and bond angles in deg. [b] PRDDO. [c] MNDO calculation.[11–13,15–17] [d] Refers to the dimer of the isothianaphthene.

molecules were assumed to be the same as that of the monomers except for the inter-ring distances and the corresponding bond angles. Similar optimizations were performed on the quinoid forms of the dimers, which were modeled by employing CH_2 end groups rather than the CH end groups appropriate for the aromatic forms. These optimized geometries were then used for band structure calculations employing extended Hückel theory,[39–42] and comparisons were made with the existing theoretical and experimental results. Molecular mechanics calculations and structural plots were obtained with the program CHEMX.[36] In order to assess the nonbonded interactions in the dimer of ITN, we calculated the van der Waals energy from the molecular mechanics method within CHEMX with a potential energy function taken from the literature.[43] A torsional term derived from the rotational barrier of the thiophene dimer (~1.3 kcal/mol) obtained from ab initio (STO 4-31G basis set)[44] calculations was used.

Conformational Analysis

The PRDDO-optimized geometries of the aromatic forms of the monomer and the dimer of isothianaphthene are given in Table II, and the corresponding atom numbering system is given in Figure 1. There is insignificant variation between the geometries of the monomer and dimer of the ITN except of course for the inter-ring distance and the corresponding angles. By analogy to polythiophene, we assumed our initial geometry to be a coplanar structure with the sulfur atoms transoid. However, the strong steric interactions between S1 and H5′ and between S1′ and H5 force the inter-ring torsion angle (C3′–C1′–C1–C3) to assume a value of 121.3°, resulting in a nonplanar backbone. In the minimum energy conformation, the nonbonded distance between S1–H5′ (and S1′–H5) is found to be 2.93 Å, compared to 2.15 Å in the coplanar form. The energy difference (ΔE) between the coplanar and the nonplanar form of the dimer of ITN is of the order of 15.6 kcal/mol at the PRDDO level. To verify this result, ab initio STO-3G level calculations using PRDDO-optimized geometries were also performed, yielding a similar value of 9.4 kcal/mol. In order to assess the steric interactions present in the polymeric system, we have carried out molecular mechanics calculations on the dimer of ITN. The van der Waals energy (repulsive) is found to be 16.0 kcal/mol higher in the coplanar form compared to that of the nonplanar one. This strongly suggests that simple steric interactions are responsible for the nonplanar minimum energy conformation of the backbone. To confirm this, we have carried out ab initio STO 4-31G level calculations on the model nonbonded system thiophene + methane at internuclear S···H distances of 2.15 and 2.93 Å, and we find a ΔE of 9.1 kcal/mol favoring the longer distance (two such nonbonded interactions exist in the dimer of ITN). Finally, we note that the calculated equilibrium S_1–$H_5{}'$ distance of 2.93 Å is very close to the sum of the van der Waals radii of the two atoms, which is in the range 3.0–3.25 Å.[45] In order to obtain the geometry of the quinoid form, a full geometry optimization was carried out for the dimer of ITN terminating the C2's with H_2 groups. A completely converged equilibrium geometry was obtained in which the structure assumed a quinoid form with an inter-ring distance of 1.34 Å as compared to the value of 1.36 Å determined by Lee and Kertesz.[17] The geometrical parameters for both aromatic and quinoid structures of ITN are given in Table II.

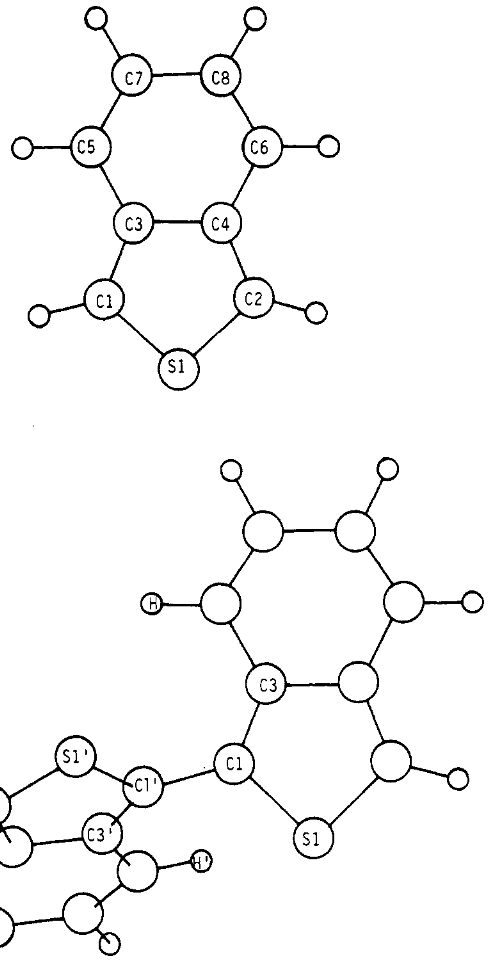

Figure 1. The structure of the monomer and dimer of isothianaphthene (ITN).

Similar optimization procedures at the PRDDO level were adopted for the aromatic form of the INT monomeric unit as shown in Figure 2 and Table III. The ini-

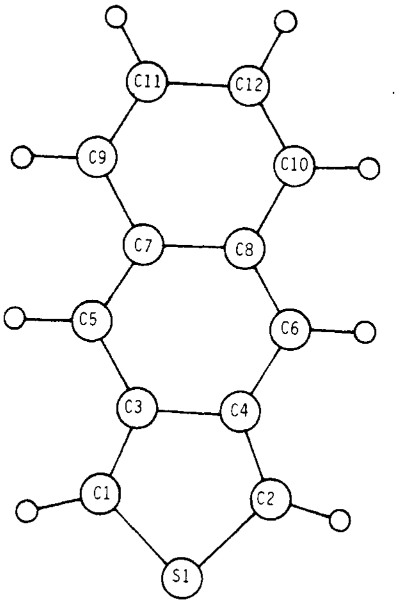

Figure 2. The structure of isonaphthothiophene (INT).

Table III
The Geometry of the Aromatic Isonaphthothiophene Monomeric Unit and the Geometrical Parameters for Coupling the Two Monomers of Isonaphthothiophene Obtained from PRDDO

S1-C1	1.70	C1-C3	1.35
C3-C4	1.44	C5-C3	1.43
C7-C5	1.34	C8-C7	1.47
C9-C7	1.45	C11-C9	1.32
C12-C11	1.44	C-H (all)	1.08
C1-S1-C2	92.3	C3-C1-S1	112.0
C4-C3-C1	111.9	C5-C3-C4	119.4
C7-C5-C3	119.9	C8-C7-C5	120.7
C9-C7-C8	118.4	C11-C9-C7	119.3
C12-C11-C9	122.3	H1-C1-S1	121.9
H5-C5-C3	119.2	H9-C9-C7	118.7
H11-C11-C9	120.6	C1-C1′[b]	1.50
S1-C1C1′[b]	121.2	C3′-C1′-C1-C3[b]	121.3

[a] Bond lengths in Å and bond angles in deg. [b] Refers to the dimer of isonaphthothiophene.

tial structure is a thiophene ring onto which a naphthalene ring is fused at C_β–C_β positions. The torsion angle about the inter-ring bond is found to be 121.3°, in excellent agreement with that of the dimer of ITN. The calculated barrier between the coplanar aromatic structure and the nonplanar aromatic one is found to be 12.5 kcal/mol at the PRDDO level.

The optimized geometries of the monomers and dimers of THP and THQ are presented in Figures 3 and 4 and Tables IV and V. The geometrical parameters are found to be in good agreement with the results of previous molecular orbital studies of thienopyrazines.[27] The minimum energy conformation of both dimers was determined to be coplanar, with the heteroatoms (S) trans to each other on adjacent rings. The rotation barriers for the dimers of the aromatic forms of THP and THQ are calculated to be 9.7 and 10.5 kcal/mol, respectively.

The above results clearly indicate that the aromatic forms of PITN and PINT cannot be planar, due to simple monomer–monomer steric interactions. In contrast, the aromatic forms of PTHP and PTHQ, in which the adverse steric interactions are absent, are clearly planar. Note that the S···N nonbonded (van der Waals) interactions introduced in PTHP and PTHQ are only slightly (~5 kcal/mol) more repulsive than the corresponding S···C interactions present in PINT and PITN, while the elimination of the adverse S···H interactions are energetically favored by ~16 kcal/mol.

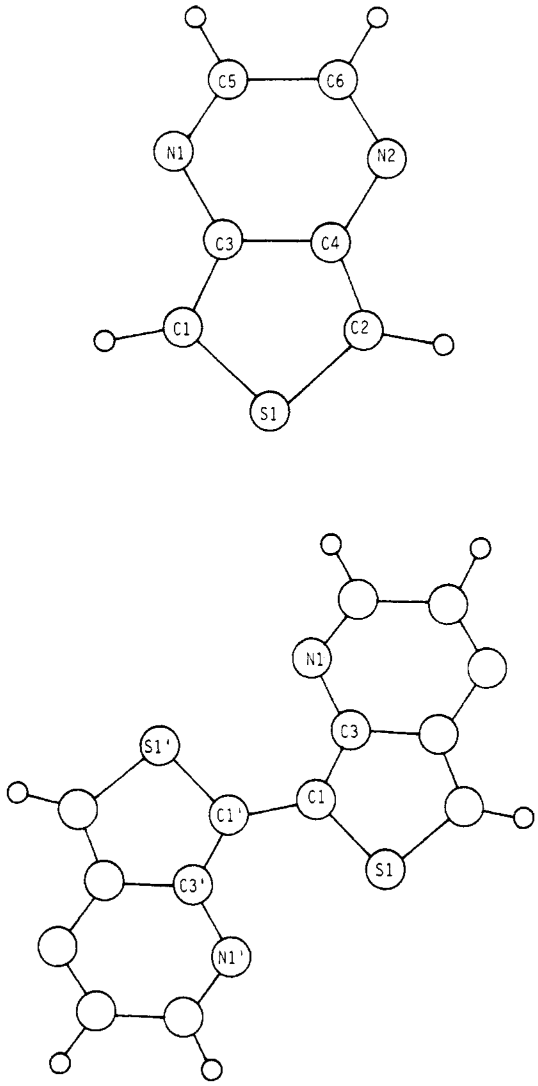

Figure 3. The structure of the monomer and dimer of thieno(3,4-*b*)pyrazine (THP).

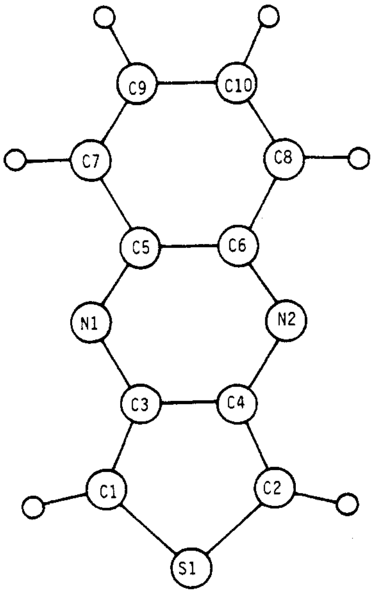

Figure 4. The structure of the monomer of thieno(3,4-*b*)quinoxaline (THQ).

However, these calculations have no direct bearing on the question of the relative stability of the quinoid vs

Table IV
The Geometrical Parameters of the Monomer and Dimer of Thieno(3,4-*b*)pyrazine (THP) Obtained from PRDDO[a]

	monomer		dimer	
	aromatic[b]	aromatic[c]	aromatic[b]	quinoid[b]
S1-C1	1.70	1.71	1.70	1.79
C1-C3	1.36	1.38	1.35	1.48
C3-N1	1.41	1.38	1.41	1.36
N1-C5	1.30	1.31	1.29	1.33
C3-C4	1.45	1.44	1.42	1.38
C5-C6	1.45	1.43	1.46	1.40
C5-H5	1.08		1.07	1.07
C1-S1-C2	92.8		93.3	93.6
C3-C1-S1	111.7		110.5	108.7
C4-C3-C1	111.9		112.9	114.5
N1-C3-C4	120.4		121.2	122.2
C5-N1-C3	116.3		115.2	115.1
C6-C5-N1	123.3		123.5	122.7
H5-C5-C6	118.8		118.1	119.7
C1-C1′			1.45	1.32
S1-C1C1′			123.1	126.4
C3-C1-C1′			126.4	124.9
S1-C1-C1′-S1′			180.0	180.0

[a] The bond lengths and bond angles are given in Å and deg, respectively. [b] PRDDO results. [c] Reference 27.

Table V
The Geometrical Parameters of the Aromatic Thieno(3,4-*b*)quinoxaline (THQ) Monomeric Unit Obtained from PRDDO[a]

S1-C1	1.69	C3-C1	1.36
N1-C3	1.38	C5-N1	1.30
C7-C5	1.45	C9-C7	1.32
C4-C3	1.43	C6-C5	1.45
C10-C9	1.45	C1-S1-C2	92.5
C3-C1-S1	111.8	C4-C3-C1	111.9
N1-C3-C4	120.6	C5-N1-C3	117.1
C6-C5-N1	122.2	C7-C5-C6	118.0
C9-C7-C5	121.0	C10-C9-C7	121.1
H7-C7-C5	117.1	H9-C9-C10	117.9
C1-C1′a	1.45	S1-C1-C1′a	122.4
C3-C1-C1′a	125.8	S1-C1-C1′-S1′a	180.0

[a] The inter-ring distance, corresponding bond angle and the torsion angle about the inter-ring bond are given for the dimer of THQ. The bond lengths and bond angles are given in Å and deg, respectively.

Table VI
Comparison of Energy Differences (kcal/mol) between the Quinoid and Aromatic Forms of Thiophene Oligomers Based upon Various Methods and Assuming Chain Termination with a Single Hydrogen

chain length	ab initio[a]	PRDDO	MNDO[b]
2	19.2	19.6	14.3
3	18.6	18.8	13.8
4	17.9	18.2	13.4
5	17.4	17.8	13.1

[a] STO-3G. [b] CHEMX version of the MNDO program.

aromatic forms, since the dimers are terminated with single hydrogen atoms, which mimics the situation expected for the aromatic forms (inter-ring bond order equal or close to 1.0) as opposed to the quinoid forms (inter-ring bond order equal or close to 2.0). This prejudice toward the aromatic structure could in principle be eliminated by increasing the chain length and calculating an energy difference (ΔE) between the two forms as a function of chain length. Such a series of calculations for polythiophene using ab initio, PRDDO, and MNDO methodology is shown in Table VI. Here we have employed literature values[15,24] for the aromatic and quinoid geometries. In the case of the quinoid geometry the C2's were terminated with H only. There are several points of interest in this table. First, all three methods predict PT to be aromatic, as expected. Second, the PRDDO and ab initio ΔE's agree extremely well, while the MNDO calculations appear to overestimate the stability of the quinoid form slightly. Finally, the calculated ΔE's vary extremely slowly with chain length, and it is not at all clear that convergence has been obtained. To avoid these problems, we have devised a simple procedure described below and have applied it to the polymers of interest.

Table VII
Energy Difference per Unit Chain Length ($\Delta E_{qa}/N$) between the Quinoid and Aromatic Structures of PT, PITN, PTHP, PINT, and PTHQ as a Function of Chain Lengths (N)[a]

chain length	thiophene[b]	thiophene[c]	ITN[b]	THP[b]	INT[b]	THQ[b]
1	37.4	49.3	11.9	13.5	3.8	9.6
2	24.2	28.5	3.8	3.5	−4.8	−5.2
3	19.8	21.5	1.6	0.6	−6.5	−7.1
4	17.4	18.0	0.5	−0.8		
5	16.1		−0.1	−1.3		
6	15.2		−0.6	−1.8		
∞	10.6	7.4	−2.4	−4.2		

[a] The geometrical parameters for both structures were obtained from PRDDO calculations. The $\Delta E_{qa}/N$ is given in kcal/mol per ring. [b] $\Delta E_{qa}/N$ from PRDDO. [c] $\Delta E_{qa}/N$ from ab initio calculations using an STO 4-31G basis set.

We first find the quinoid form of the geometry by terminating the end C2's with H_2 groups and completely reoptimizing the geometry (Tables II and IV). The inter-ring distances of 1.32–1.34 Å are typical for double bonds, as expected for quinoid structures. Now, we define a thermodynamic cycle to estimate the stability of the quinoid form relative to the aromatic form (ΔE_{qa}) *in the absence of end groups.* Let H–P_A–H be the aromatic form, H_2–P_Q–H_2 be the quinoid form, P_A be the aromatic form in the absence of terminating groups (with a similar definition of P_Q), E_{CH} be the (positive) bond dissociation energy of a CH bond, and E_H be the (negative) electronic energy of a free hydrogen atom. The calculated energies of H_2–P_Q–H_2 and H–P_A–H are $E(H_2\text{–}P_Q\text{–}H_2)$ and $E(\text{H–}P_A\text{–H})$, respectively. While ΔE_{qa} cannot be calculated directly, it can be defined by the following cycle:

$$\begin{tikzcd}
P_A + 4H \arrow[r, dashed, "\Delta E_{qa}"] \arrow[d, "\Delta E_1"] & P_Q + 4H \\
\text{H-}P_A\text{-H} + 2H \arrow[r, dashed, "\Delta E_2"] & H_2\text{–}P_Q\text{–}H_2 \arrow[u, "\Delta E_3"']
\end{tikzcd}$$

where

$$\Delta E_1 = -2E_{CH}$$

$$\Delta E_2 = E(H_2\text{–}P_Q\text{–}H_2) - E(\text{H–}P_A\text{–H}) - 2E_H$$

$$\Delta E_3 = 4E_{CH}$$

yielding

$$\Delta E_{qa} = E(H_2\text{–}P_Q\text{–}H_2) - E(\text{H–}P_A\text{–H}) - 2E_H + 2E_{CH}$$

E_H was calculated by using an atomic self-consistent field program[46] with an exponent of 1.24 for hydrogen (E_H = −0.4712 au), while E_{CH} was taken as the average value found[47] for CH_4 at the STO6-G basis set level (90.3 kcal/mol).

Calculations of $\Delta E_{qa}/N$ as a function of N (the chain length) are presented in Table VII for PT, PITN, PTHP, PINT, and PTHQ. For PT, both ab initio (4-31G) and PRDDO results are shown, and excellent agreement is seen between the two methods, particularly for longer chain lengths. The large size of the PITN, PTHP, PINT, and PTHQ systems precludes the calculation of ΔE's at the ab initio level. In marked contrast to the chain length dependence seen with termination of the chain by single hydrogens (Table VI), $\Delta E_{qa}/N$ falls off rapidly with N, suggesting that extrapolations to the infinite system may be possible. Indeed, remarkably accurate least-squares fits (average absolute deviation = 0.04 kcal/mol) of $\Delta E_{qa}/N$ vs N are obtained from the simple three-parameter function:

$$\Delta E_{qa}/N = a_0 + a_1/N + a_2/N^2$$

The infinite chain length limits of $\Delta E_{qa}/N$ are clearly equal to a_0 and were found to be +10.6, -2.4, and -4.2 kcal/mol/ring for PT, PITN, and PTHP, respectively, at the PRDDO level. For PT, the STO 4-31G calculations yield a limiting value of 7.4 kcal/mol per ring. This clearly indicated the thermodynamic stabilization of the quinoid structures of both PITN and PTHP over their aromatic counterparts, in marked contrast to that of PT. More recent experimental findings of Wallnöfer et al.[48] are consistent with our theoretical predictions, as are the calculations of Lee and Kertesz.[17] Finally, we should point out that the extrapolated values are actually independent of E_{CH} and E_H terms. Inclusion of these terms only serves the purpose of getting more realistic estimates of ΔE_{qa} for small chain lengths. Physically, this must be the case, since the end-group effects are overwhelmed by the energetics of the infinite polymer. Computationally, errors in the energetics of the end groups must vary as $2/N$ and are therefore accounted for in the second term of the above equation, which is zero in the infinite limit. Also, expanding the polynomial to include an a_3/N^3 term leaves a_0 unchanged to three significant figures. For the larger systems of PINT and PTHQ, we extended our calculations up to the trimers and found the $\Delta E_{qa}/N$ on the order of -6.5 and -7.1 kcal/mol per ring, respectively. These results strongly suggest that the higher fused derivatives of thiophene would prefer the quinoid forms to their aromatic ones.

Band Structure Analysis

Polyisothianaphthene (PITN) and Polyisonaphthothiophene (PINT). Because the aromatic and quinoid forms of these systems are apparently energetically competitive, it is necessary to examine the band structures of both forms. Since the previous band structure analyses of the aromatic forms of these systems[11-13] assumed coplanar geometries, it is extremely important to examine how relaxation of the geometry to the minimum energy nonplanar form affects the band structure, which should be very sensitive to the amount of conjugation in the polymer backbone. To gain a qualitative feel for this effect, we have employed extended Hückel theory within the tight binding approximation.[39,40] The extended Hückel parameters were taken from the literature.[39-42] The dimers of aromatic ITN and INT in the transoid form with a reverse twist of 30° about the inter-ring bond were chosen as the repeat units for both the nonplanar polymers. The geometrical parameters (bond lengths and bond angles) of the repeat units of ITN and INT were obtained from the PRDDO calculations described previously. Parts a and b of Figure 5 show the band structure of PITN within the first half of the first Brillouin zone for the planar and nonplanar geometries, respectively. It consists of the four highest occupied valence bands (HOVB) and the lowest unoccupied conduction band (LUCB). The band gap (E_g) is calculated to be 0.68 eV in the coplanar and 1.64 eV in the nonplanar form of PITN. The increase in band gaps with the evolution of nonplanarity in the polymeric systems is expected and is consistent with previous theoretical predictions.[49,50] The band structures of PINT within the first half of the first Brillouin zone for both the planar and nonplanar forms are displayed in parts c and d of

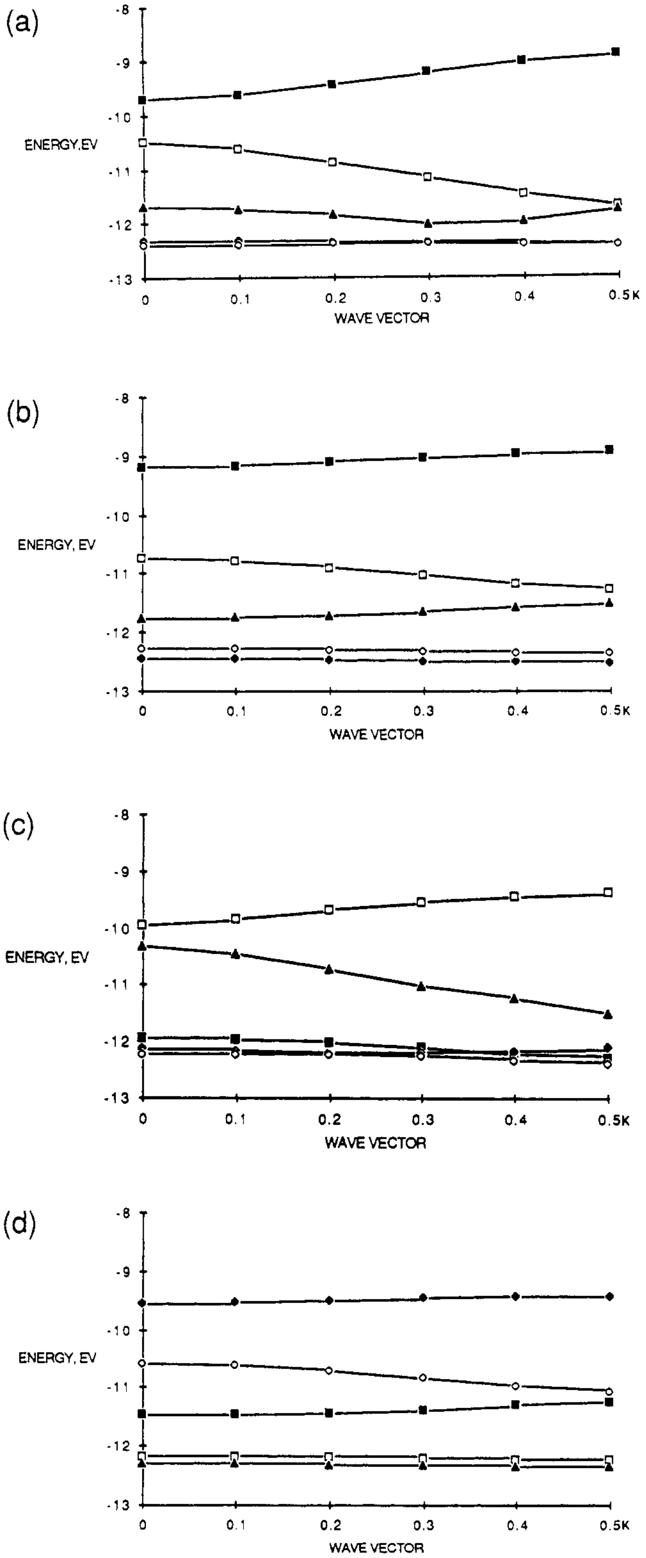

Figure 5. (a) The band structure of polyisothianaphthene in the planar form. The four highest occupied valence bands along with the lowest unoccupied conduction band are displayed. (b) The band structure of polyisothianaphthene in the nonplanar form. (c) The band structure of polyisonaphthothiophene in the planar form. (d) The band structure of polyisonaphthothiophene in the nonplanar form.

Table VIII
Band Gaps (E_g, eV) of PITN, PINT, PTHP, and PTHQ in Their Aromatic and Quinoid Forms

polymer[a]	extended Hückel	Hückel[b]	exp
PT(a,p)	1.76	1.83	2.0–2.2
PITN(a,p)	0.68	0.73	1.0
PITN(a,n)	1.64		1.0
PITN(q)	0.80	1.16	1.0
PINT(a,p)	0.37	0.28	1.4
PINT(a,n)	1.03		1.4
PINT(q)	1.10	1.50	1.4
PTHP(a,p)	0.12		
PTHP(q)	0.70		
PTHQ(a,p)	0.27		
PTHQ(q)	0.53		

[a] Abbreviations: a, aromatic; p, planar; n, nonplanar; q, quinoid. [b] Hückel molecular orbital.[15-17]

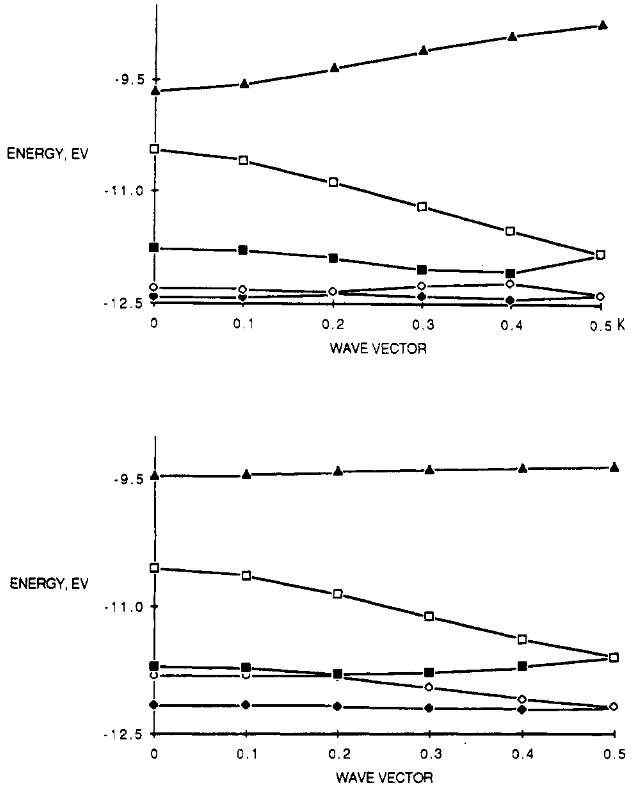

Figure 6. Top: the band structure of quinoid polyisothianaphthene. Bottom: the band structure of quinoid polyisonaphthothiophene.

Figure 5, respectively. The corresponding band gap is 0.37 eV in the coplanar and 1.03 eV in the nonplanar form of PINT. Our calculated band gaps for the planar aromatic system agree quite well with those derived from VEH calculations[11-13] (1.71, 0.54, and 0.01 eV for PT, PITN, and PINT, respectively). However, the band gaps in the nonplanar ground-state geometries of the aromatic forms are all significantly higher than those calculated for the planar configurations. Good agreement is also found between our extended Hückel and the Hückel[15-17] band structure calculations on the coplanar systems (Table VIII). The band gaps obtained for the planar aromatic structures are clearly too low when compared to the experimental values. We have calculated the band gaps of quinoid PITN and PINT by using the geometries obtained from our PRDDO dimer optimizations, and the band structures are shown in parts a and b of Figure 6, respectively. The band gaps are of the order of 0.8 and 1.1 eVs for the quinoid forms of PITN and PINT, respectively. In the quinoid forms, our calculated band gaps are found to be in good agreement with the experimental values of 1.0[5-9] and 1.4 eV.[51]

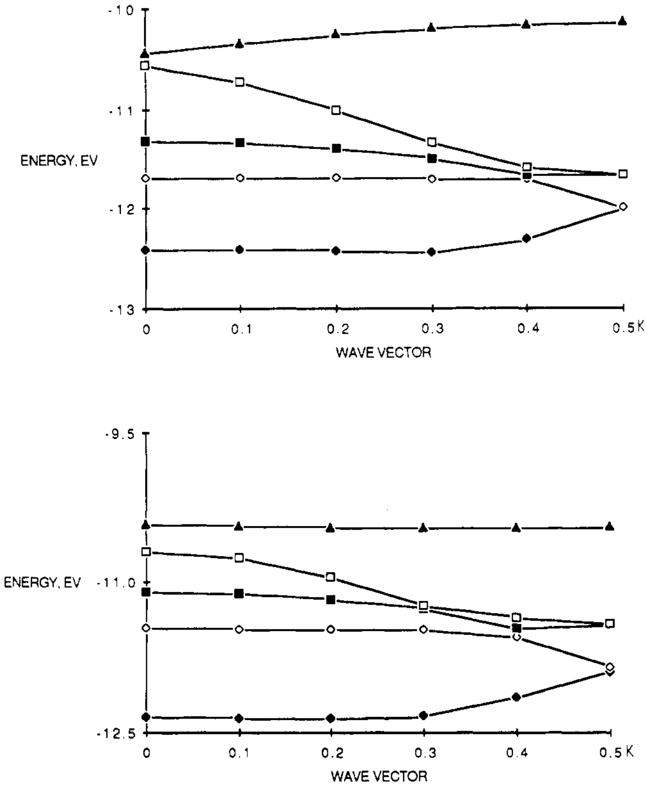

Figure 7. Top: the band structure of aromatic polythieno(3,4-*b*)pyrazine in the planar form. Bottom: the band structure of aromatic polythieno(3,4-*b*)quinoxaline in the planar form.

Polythieno(3,4-*b*)pyrazine (PTHP) and Polythieno(3,4-*b*)quinoxaline (PTHQ). Band structure calculations were carried out at the extended Hückel level for both the aromatic and quinoid structures of PTHP and PTHQ. The structures were assumed to be coplanar with sulfur atoms in the transoid configuration. The band structures within the first half of the first Brillouin zone for the aromatic and quinoid forms of PTHP and PTHQ are shown in Figures 7 and 8, respectively. The band gaps in the aromatic and quinoid forms for PTHP were determined to be 0.12 and 0.70 eV, while the corresponding values for PTHQ are calculated to be 0.27 and 0.53 eV. In contrast to the trend in the band gaps obtained for the quinoid forms of PITN and PINT, somewhat different trends are noticed in the case of PTHP and PTHQ. While there are no experimental results available to date to compare with the above theoretical predictions, these systems are quite interesting in that they are both predicted to possess lower band gaps than PITN.

Conclusions

We have shown that there is a subtle interplay between the geometric and electronic structures of polythiophenes and related systems. Steric effects may strongly favor nonplanar geometries, but electronic effects associated with increased conjugation along the backbone are also very significant and in some cases may be sufficient to force the polymer into a planar quinoid structure. A method has been developed for extrapolating the ab initio and/or PRDDO oligomer energetics to the infinite system. This approach allows for energetic assessment of the relative energies of the aromatic and quinoid forms at a relatively high theoretical level. Application of this method to PITN suggests that the ground state is quinoid, but the relative energies of the quinoid and aromatic forms are so close that both structures may exist

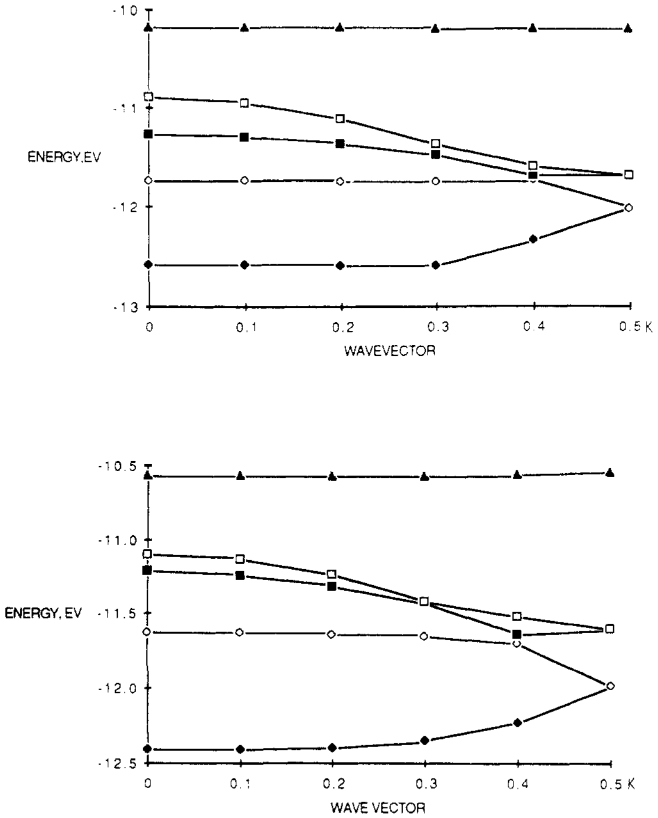

Figure 8. Top: the band structure of quinoid polythieno(3,4-*b*)pyrazine. Bottom: the band structure of quinoid polythieno-(3,4-*b*)quinoxaline.

as local minima in the real polymeric system. In addition, it is clear that the details of the polymer chain termination in these systems is extremely important. Termination in a quinoid fashion will result in a quinoid structure for very short (N = 3 or 4) chains, while termination in an aromatic fashion will likely force the aromatic structure for much longer chain lengths. This conclusion is consistent with very recent experimental work, in which a detailed vibrational study of PITN failed to distinguish between the two forms.[52] Finally, PTHP and PTHQ, which do not possess the adverse steric interactions found in PITN and PINT, are coplanar in both the aromatic and quinoid forms and appear to be promising candidates for new low band-gap polymers.

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Registry No. PITN, 91201-85-3; PINT, 107949-39-3; PTHP, 125541-34-6; PTHQ, 125541-35-7.

Physical Gels of Aqueous Poly(vinyl alcohol) Solutions: A Small-Angle Neutron-Scattering Study

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ABSTRACT: The melting behavior of aqueous poly(vinyl alcohol) gels was studied by using small-angle neutron scattering. Emphasis was placed on solutions with a polymer concentration around ϕ^*, the concentration threshold at which the polymer chains start to overlap. At this particular concentration, a maximum was observed in the polymer–polymer correlation length and the zero angle scattering intensity as the gel was melted. An attempt to interpret this observed maximum in terms of a simple two-phase model will be presented.

Introduction

Physical gelation in various polymer solutions has been a subject of interest to many researchers.[1-4] Poly(vinyl alcohol) (PVA) in water is one of the physical gel systems studied rather extensively;[5-7] after all, PVA fibers have been produced commercially from aqueous PVA solutions for many years. Compared to chemical gelation, the gelation process in physical gels has not been widely studied by scattering techniques. This does not imply that other transitions, e.g., liquid–liquid phase transitions in physical gels, have not been studied with scattering techniques. For instance, the spinodal transition in PVA–water has been determined via an elastic light-scattering technique.[6] For the sol–gel transition problem, the change in the cluster size or molecular weight distribution during gelation is an essential parameter to monitor. The sol–gel transition is defined as the point at which the average cluster size goes to infinity. To measure the molecular weight or the cluster size distribution with either chromatographic or scattering techniques, the material must be diluted. However, dilution will cause physical gels to be highly disturbed or even completely dissolved. Consequently, scattering and other techniques in which dilution is a prerequisite are applicable only in studying the sol–gel transition in chemical gels. However, as will be shown, it is possible to study certain aspects of physics gelation without resorting to a dilution scheme where even the cluster size is inaccessible to the measurements. In other words, it is not the intention of this work to detect the connectivity among the molecules within a cluster using a scattering technique.

The basic process of physical gelation in polymer solutions is the formation of thermally reversible junctions between the molecules. Regardless of the nature or the origin of the junction, the local polymer segment density around a junction point changes from that of a linear chain in solution. For example, in a good solvent the mass fractal dimension, D, is 5/3 and 2 for linear chains and branched ones, respectively.[8] The parameter D is defined as $N \propto r^D$ where N is the number of segments within a volume of r^3 in three-dimensional space considered herein. Accordingly, the local segment density is expected to increase upon interchain cross-linking. For a polymer solution with its concentration near ϕ^* and its temperature above the Θ temperature, the length scale of the density fluctuation is the size of an individual molecular coil. When the temperature is lowered toward its sol–gel transition, some interchain cross-links or junctions are formed among neighboring pairs, and the local segment density is enhanced around the junctions. Solvent-rich regions must be formed surrounding these cross-linked molecules. This is assuming that cross-linking does not perturb the position of any other adjacent molecules not connected directly to the cluster under consideration. According to this picture of cross-linking, the polymer–polymer correlation length must increase, and this change in correlation length should be observable in small-angle scattering (SAS) measurements. In this work, deuterated water was used as the solvent, and neutron scattering was used to determine the temperature dependence of the correlation length. No deuterated PVA was used in this work; therefore, the only correlation mea-

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