decrease in the corresponding selective catalytic sites concentration.

To elucidate the potential catalytic role of M_1, M_2, and D species, ESR and XPS studies of CuThO catalysts in the reduced state are in progress.[5]

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Registry No. Cu, 7440-50-8; ThO_2, 1314-20-1.

Importance of Energetics in the Design of Small Bandgap Conducting Polymers

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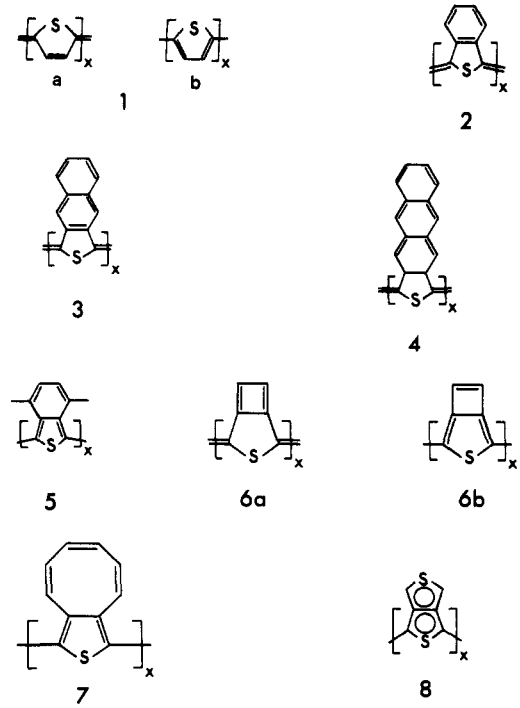
With a combination of semiempirical quantum chemical methods applicable for geometry optimization and energy band structure calculation, several heteroatomic conjugated polymers based on polythiophene have been studied with the goal to correlate the chemical composition and topology of the unit cells with energetics and bandgaps. In the theoretical design of small E_g polymers the relative stability of structural isomers of a given polymer plays a crucial role. We have found for the materials investigated in this work that the structure having the larger bandgap among structural isomorphs is the more stable one. The combination of MNDO and Hückel crystal orbital methods provide a firm theoretical basis to the synthesis of small-bandgap conducting polymeric materials.

Introduction

The synthesis of conjugated polymers exhibiting high electrical conductivity has drawn considerable interest in recent years.[2] Concomitant with the synthesis of conducting polymers, electronic structure calculations have been developed for understanding electrical and optical properties of these materials.[2-16] Many of the theoretical calculations on conducting polymers have dealt with the understanding of the electronic structure of small energy bandgap (E_g) polymers. Such calculations may help in designing new small E_g polymers. Recently Dougherty et al.[9,10] have also studied possible small E_g polymers.

Chart I



Several theoretical calculations concerning small E_g have put emphasis on calculating the E_g of polymers without taking energetics into consideration.[9-16] However, determining the relative stability between structural isomers or conformers of a given polymer becomes a crucial matter in those cases where alternative structures possess essen-

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tially different electronic structures. For example, the values of E_g differ greatly for the quinoid (Q, **1a**, Chart I) and aromatic (A, **1b**) structures of polymers such as polythiophene.[5] In this paper we extend the discussion concerning the importance of energetics of polymers in the design of small-E_g polymers based on the structure–property relationship that we have established earlier.[6] We have shown that there is an interplay of the effects of heteroatoms and bond length alternation along the polymer backbone on E_g and that small E_g does not necessarily arise for a quinoid structure. On the contrary, the quinoid structure may be more stable and may have a larger E_g depending on the interplay of the factors mentioned above.[8] For instance, this is the case for poly(isothianaphthene) (PITN, **2**) poly(isonaphthothiophene) (PINT, **3**), and poly(isoanthrothiophene) (PIAT, **4**).

Methods of Calculations

We employ a modified neglect of diatomic overlap[17] (MNDO) band theoretical method,[4,18] which is based on periodic boundary conditions, with the purpose of determining the total energy and thereby the fully optimized geometry of polymers. Planarity of polymer backbone has been assumed unless noted otherwise; geometry has not been fully optimized for two systems with the largest repeat units: **3** and **4**. MNDO band theory has been tested for polyacetylene and several other conjugated polymers as well as graphite, boron nitride, and diamond; the deviations of optimized bond distances from experiments are between 0.01 and 0.03 Å, as customary with MNDO molecular orbital theory for molecules.[6,18] It is well-known[3] that solid-state theoretical calculations that are based on the Hartree–Fock self-consistent field theory grossly overestimate the energy gap of insulators and semiconductors. Since MNDO is such a theory, it has to be combined with a more reliable band theoretic approach. In our work we have used specially parametrized Hückel calculations with bond-distance-dependent resonance integrals, as well as extended Hückel theory (EHT). Others have used similar methods[5,11,16] In this work we used our version of Hückel energy band theory[6] to determine E_g and the energy band structures of the polymers. The input for these calculations are the geometries that we obtained from the fully optimized MNDO solid-state total energy calculations. In this way the effect of bond length changes, heteroatoms, and fused rings on E_g are automatically accounted for in a balanced manner.

The present approach has the advantage[6] that the various ground states (e.g., quinoid vs aromatic) can be investigated without a bias. Cluster calculations can be used for such purposes also, but the clusters have to be enormous to produce reliable results for polymers with two possible (quinoid and aromatic) structures.[19,20]

Compounds that will be discussed are related to PITN (**2**), such as substituted PITN with bulky enough side groups to make its aromatic form more stable (**5**), and various rings fused to the thiophene rings of PT, such as 2,4-poly(3-thiabicyclo[3.2.0]-1,4,6-heptatriene) (PTBH, **6**), 9,11-poly(10-thiabicyclo[6.3.0]-2,4,6,8,11-undecapentaene) (PTBU, **7**), and poly(thieno[3,4-*c*]-thiophene) (PTT, **8**).

Transition from Quinoid Structures to Aromatic Structures by Substitution

Conjugated polymers possessing a very small bandgap may not require doping to produce high electrical conductivity. However the achievement of the goal to synthesize systems with small E_g has been hampered by the strong nuclear–electron coupling. This is apparent for systems such as polyacetylene (PA), where the Peierls distortion[21] creates a substantial E_g (1.5 eV)[22,23] at the Fermi level. For heteroconjugated ring polymers, the presence of the strong electron–nuclear coupling is signalled by the viability of alternative structures, such as **1a** and **1b** or **6a** and **6b** etc. The key point is that even though for PA the two-bond alternating structures are equivalent, this is not the case for these and similar heteroconjugated ring systems. Therefore, information on the relative stability of the two alternative forms (e.g., **1a** vs **1b**) is of fundamental importance in the process of interpreting or predicting the properties of such systems.

Table I. E_g of Polythiophene and Its Derivatives

		MNDO ΔH_f,[a] kcal/mol	E_g, eV Hückel	E_g, eV expt	ref
1b (PT)	A	*32.63*	*1.83*	2.1	27
1a	Q	36.15	0.47		
2 (PITN)	A	58.58	0.73		
	Q	*48.03*	*1.16*	1.0	24
3 (PINT)[b]	A		0.28		
	Q		*1.50*	1.4–1.5	26
4 (PIAT)[b]	A		0.08		
	Q		*1.66*		

[a] Heat of formation, from the elements, per ring or per formula unit. The italicized values denote the more stable of the two isomeric structures. [b] Geometry estimated; see ref 8.

Heterocyclic conjugated polymers have yielded good results in engineering new small E_g polymers (the presence of heteroatoms in the chain often increases the stability of polymers against oxidation). In an effort to make small E_g polymers, PITN (**2**) has been synthesized with a reported E_g of 1.0 eV,[24] half that of the (aromatic) polythiophene. We have successfully explained the origin of the narrower bandgap for PITN.[6,8] We had predicted the quinoidal ground structure of PITN (**2**) as opposed to the aromatic structure as suggested by Bredas et al.[11,12] Our theoretical prediction on the ground structure of PITN has been supported by a resonance Raman study of Wallnofer et al.[25] and recent calculations by Kurti and Surjan.[19] Further addition of a benzene ring to PITN resulted in increasing the bandgap (E_g = 1.4 to 1.5 eV), an experimental finding[26] that can be also understood by using our theoretical approach.[8]

The trend of E_g as well as the energetics of the aromatic vs quinoid structures with a different number of fused rings is summarized in Table I. Note that the carbon–carbon bond lengths between the monomeric units correspond to single bonds for the aromatic and double bonds for the quinoid structures. This table illustrates the trend that the structural isomer having the larger E_g is the more stable one. The calculated gaps and stabilities can be easily rationalized by considering the symmetry of the highest occupied (HOMO) and lowest empty (LUMO) polymer orbitals and how these mix with the butadienic fragment frontier orbitals, since one such fragment is added each

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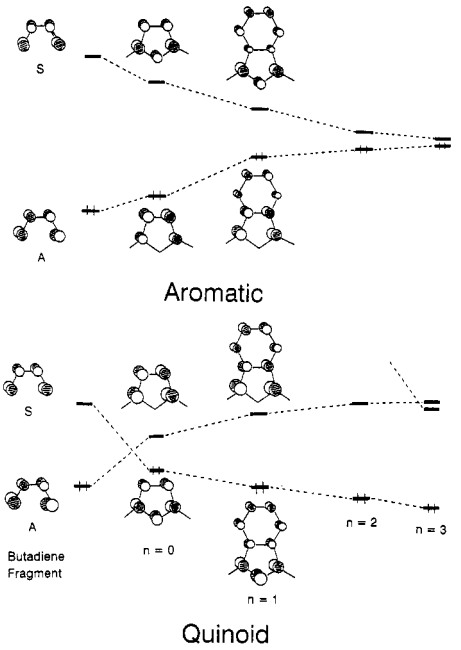

Figure 1. HOMO and LUMO levels of the aromatic and quinoid forms of PT (**1a**, **1b**, $n = 0$), PITN (**2**, $n = 1$), PINT (**3**, $n = 2$) and PIAT (**4**, $n = 3$). n corresponds to the number of benzene rings in the unit cell. S and A indicate the orbital symmetry with respect to the mirror plane perpendicular to the translational vector, which determines the mixing of the orbitals of the butadienic fragment with those of the polymer.

Table II. Energy Gap, E_g, as a Function of Inter-ring Dihedral Angle for Poly(4,7-dihydroxyisothianaphthene)

dihedral angle	E_g, eV	dihedral angle	E_g, eV
40	1.19	120	1.80
60	1.80	140	1.11
80	2.58	160	0.71
100	2.58	180	0.59

time another ring is added to the repeat unit. Figure 1 shows this trend in the orbital mixing. Note the crossover between the stability of the aromatic (PT) and the quinoid forms (PINT, PITN, PIAT), which occurs according to the calculations between $n = 0$ (no added ring to PT) and $n = 1$ (one ring per repeat unit, PITN).

From Table I, we can also infer that somehow stabilizing the aromatic structures of the later members of the series ($n > 0$, PITN, PINT, PIAT) would favor smaller bandgaps. The difficulty in this strategy has the inherent limitation that by pushing the system in the direction of the aromatic structure can only be achieved by substitutions. Then, however, nonplanarity will cause loss of conjugation and a gap increase. Still, overall a gap reduction may result. This objective may be achieved by substituting the 4,7 positions of PITN with some bulkier side groups (e.g., OH or CH_3). Table II shows how the gap is increased by the loss of planarity for the 4,7-dihydroxy substitution. The steric hindrance between hydroxy or methyl and sulfur in the neighboring unit will also elongate the inter-ring C–C bond, forcing the aromatic form to become more stable than the quinoid one. Dimer calculations for 4,7-dihydroxyisothianaphthene (**5**, $(DHITN)_2$) yielded the most stable form with a torsional angle of 80° between two rings. We may conclude that the strategy to push these systems to the aromatic form can be accomplished by the 4,7-substitution, but due to loss of planarity, no overall gap reduction is expected.

A less dramatic change in the conformation is expected at the 5,6-substitution, because of a larger distance between the 5,6-substituted groups and the sulfur in the neighboring unit. Indeed, Wallnofer et al.[25] measured an E_g of 1.5 eV for poly(benzo[*c*]thiophene-5-ylphenylmethanone) (PBPM, **9**, Chart II). The increase of the bandgap with respect to the quinoid PITN may be attributed to the nonplanarity of the polymer backbone.[28]

Chart II

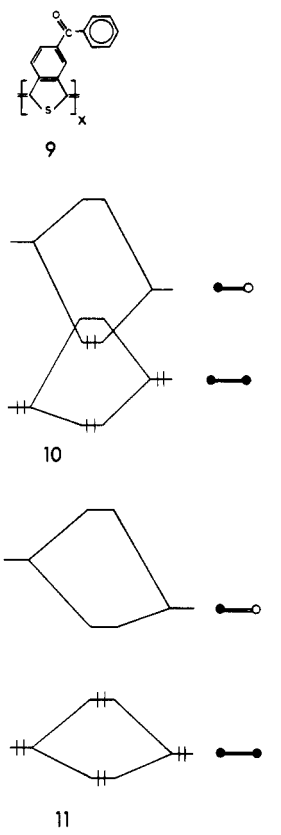

Table III. Energetics and Bandgaps of PTBH, 6

	MNDO ΔH_f, kcal/mol per ring	Hückel E_g, eV
A	(**6b**) 101.34	(**11**) 2.56
Q	(**6a**) 114.83	(**10**) 0.97

Addition of Rings to PT Backbone

Another way of reducing the E_g of sulfur-containing polymers is by attaching side groups to the PT (**1**) backbone such that one attempts to stabilize the small E_g form over the large E_g form.[29] As mentioned above, fused rings strongly influence the electronic structure of polythiophene. As a starting point, we show the energy band structures of the quinoid and aromatic forms of polythiophene in Figure 2.

The effect of fusing four- and eight-membered rings to polythiophene is expected to be quite different from that of six-membered rings. We have performed calculations by attaching four- (**6**) and eight- (**7**) membered rings to the PT backbone to compare the energetics and bandgaps of the aromatic and the quinoid forms. For the four-membered ring case, MNDO calculations show that the aromatic structure (**6b**) is energetically more stable than the quinoid one (**6a**) by 13.5 kcal/mol per ring: the corresponding calculated Hückel E_g values are 2.56 and 0.97 eV, respectively (see Table III).

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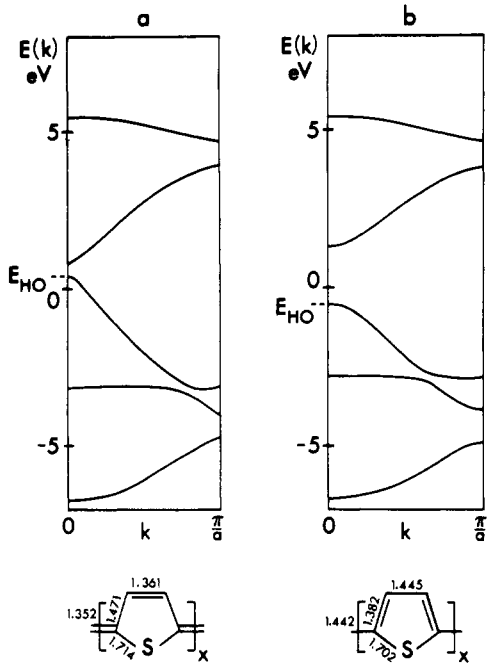

Figure 2. Energy band structure of the quinoid (**1a**) and aromatic (**1b**) PT as calculated by a Hückel model based on MNDO optimized geometries. E_{HO} indicates the highest occupied crystal orbital.

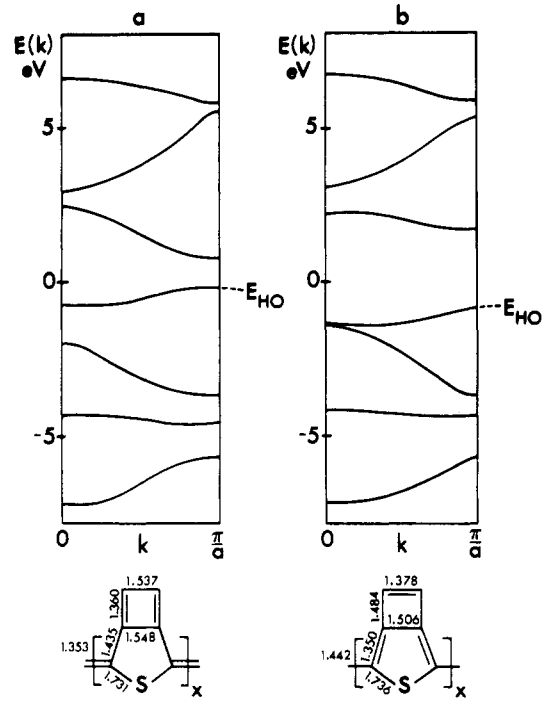

Figure 3. Energy band structure of the quinoid (**6a**) and aromatic (**6b**) forms of PTBH as calculated by a Hückel model based on MNDO optimized geometries. E_{HO} indicates the highest occupied crystal orbital.

The band structures for both forms are depicted in Figure 3. These bands are strongly perturbed relative to those of the unsubstituted PT or PITN. Still, the orbitals of the quinoid (**10**) and the aromatic (**11**) forms at the Fermi level ($k = \pi/a$) can be easily constructed from the π-orbitals of a repeat unit of polythiophene and the π-orbitals of an "ethylene-like" unit, using perturbation arguments.[3]

In both cases, the HOMO becomes destabilized after mixing of the "ethylene" orbitals with those of PT. Besides destabilization, a level crossing occurs for the quinoid PTBH (**6a**). The very strong bonding interaction between the LUMO of PT and the LUMO of "ethylene" causes the level crossing. In contrast to the six-membered ring case (PITN), the four-membered aromatic structure is energetically more stable than the quinoid one. The aromatic form of PT (**1b**) is more stable than the quinoid form of PT (**1a**) to begin with, and the addition of the four-membered ring destabilizes both forms. The destabilization of the occupied orbital is partially responsible for a large positive heat of formation for the polymer with the attached four-membered ring compared to the six-membered ring (114.83 kcal/mol per ring for quinoid PTBH (**6a**) as opposed to 48.03 kcal/mol per ring for quinoid PITN). These calculations suggest that for a four-membered ring case one has to stabilize the quinoid structure over the aromatic one to obtain a small E_g. On the basis of these calculations, we predict that the polymerization of the monomer (**6**)[30] would not yield very small E_g polymers.

MNDO polymer calculations were done by attaching eight-membered rings to the unit cell of PT, assuming a planar polymer backbone (PTBU, **7**). The optimized geometry of PTBU (**7**) turned out to be the aromatic one regardless of the starting geometries (quinoid or aromatic). This is in accordance with general orbital symmetry rules[3,8] since the symmetry of the HOMO and the LUMO of the corresponding six-π-electron system is the same as that of the ethylenic fragment in the case of PTBH (**6**) as discussed above. The inter-ring C–C bond distance has lost conjugation character due to the bulky substituent at the 3,4-positions, resulting in a flat valence band. The Hückel calculation for this structure gives an E_g of 1.89 eV; see Table IV. This should be considered as a lower bound estimate for the energy gap, due to the assumption of planarity.

Bredas has proposed another potentially small E_g polymer, PTT (**8**),[31] which contains two sulfurs per unit cell. However our MNDO calculations indicate that the quinoid structure of this polymer is more stable than the aromatic one (**8**) and that the calculated E_g of this polymer would be larger (2.00 eV) instead of the 1.02-eV value calculated by Bredas. This large difference is primarily due to the fact that Bredas' geometry was based on monomer calculations inherently preferring an aromatic geometry by the choice of the side groups.[31] This is another example illustrating the importance of energetics among structural isomers, which has a profound effect on the

Table IV. Energetics and Bandgaps of PTBU (A) and PTT (Q)

	MNDO ΔH_f, kcal/mol per ring	Hückel E_g, eV
7 (PTBU, A)	112.23	1.89
8 (PTT, Q)	54.33	2.00

Table V. E_g of the Stable Forms of PT and Its Derivatives[a]

	PT (1)	PTBH (6)	PITN (2)	PTT (8)	PTBU (7)	PINT (3)
no. of π-electrons per repeat unit	6	8	10	10	12	14
stable form	A	A	Q	Q	A	Q
Hückel E_g, eV	1.83	2.56	1.16	2.00	1.89	1.5

[a] A, aromatic; Q, quinoid.

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prediction of the bandgap and other properties of these materials with variable backbone structures.[19]

Summary

The stable forms of structural isomers of PT and PT derivatives along with their calculated E_g values are summarized in Table V. The trend of these stabilities can be rationalized in terms of orbital symmetry.[3,8] It seems that from the point of view of small E_g it will be hard to beat PITN (2). Another route toward a small E_g is offered by the group of ladder type polymers, and work along those lines is in progress.[32]

Acknowledgment. This work was supported by the National Science Foundation through a grant (DMR-8702148) and the Camille and Henry Dreyfus Foundation. This paper is based on parts of the Ph.D. thesis of Y.-S.L.

Registry No. 1 (homopolymer), 25233-34-5; 2 (homopolymer), 91201-85-3; 3 (homopolymer), 107949-39-3; 4 (homopolymer), 115980-30-8; 6 (homopolymer), 128495-73-8; 7 (homopolymer), 128495-74-9; 8 (homopolymer), 111740-85-3.

Sodium Insertion Reactions into V_6O_{13} Single Crystals

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The kinetics of the electrochemical insertion of sodium into V_6O_{13} single crystals from an organic solvent based electrolyte have been studied by using the coulometric titration and impedance analysis techniques. The studies have shown that V_6O_{13} is electrochemically active and highly reversible to sodium. A single-phase region was found in the range $0 \leq x \leq 0.16$ for $Na_xV_6O_{13}$ with no distinct discontinuity. The solid-state diffusion kinetics were found to be quite rapid with values for the chemical diffusion coefficient being about 1.1×10^{-8} cm^2 s^{-1} at 25 °C.

Introduction

A number of transition metal compounds based on either two-dimensional van der Waals bonded layer structures or three-dimensional framework tunnel structures are of interest as potential electroactive materials for high-energy-density secondary lithium batteries. There have been numerous studies made during the past two decades on the layered dichalcogenides,[1-4] layered chalcogenophosphates,[5,6] ternary sulfides,[7,8] oxyhalogenides,[9] and oxides of transition metals.[10,11] These materials undergo reversible topotactic insertion reactions with lithium. That is, the cathode materials, which are the oxidizing phases, are reduced by lithium during an insertion process and oxidized during a deinsertion process. Although the bulk of the attention has been given to the layered chalcogenides, transition-metal oxides such as those based on titanium,[12] molybdenum,[13] vanadium,[10,12,14-16] chromium,[17] manganese,[18], and tungsten[19] metal oxides have also been shown to undergo reversible lithium incorporation both chemically and electrochemicaly with rate capabilities of some to be comparable or even higher to those shown by the layered structures.[10,13,14,20] In recent years, attention has also been directed toward the amorphous transition-metal oxides.

The vanadium oxides provide classical examples of the framework structure oxides.[12,14-16] The most popular of these are V_2O_5, LiV_3O_8, and V_6O_{13}. In this laboratory, major efforts have been aimed at studying the V_6O_{13} cathode material. The material is highly promising because of its high theoretical energy density for Li insertion (890 W h/kg)[21,22] compared to the other vanadium oxides such as V_2O_5 (440 W h/kg),[22] and V_3O_8 (670 W h/kg)[23] or the dichalcogenides such as TiS_3 (480 W h/kg).[22] The structure of V_6O_{13} has been carefully elucidated by Wilhelmi et al.[24] Unlike the layered dichalcogenides, the oxide can be thought of as formed from a double shearing of the

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