# Theoretical Analysis of the Geometric and Electronic Structure of Small-Band-Gap Polythiophenes: Poly(5,5′-bithiophene methine) and Its Derivatives

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*Received March 9, 1993; Revised Manuscript Received June 24, 1993*®

ABSTRACT: Results of geometry optimizations and band-structure calculations are reported on poly(5,5′-bithiophene methine), a small-band-gap conjugated polymer made of alternating aromatic and quinoid thiophene rings. Derivative are also investigated in which two methyl groups are added to, or a benene ring fused on, positions 3 and 4 of either the aromatic or quinoid rings of the backbone. It is shown that the small band gap calculated for poly(5,5′-bithiophene methine), 1 eV, arises from a mixing of the highest occupied molecular orbital and lowest unoccupied molecular orbital wavefunctions of polythiophene chains possessing, on the one hand, totally aromatic and, on the other hand, totally quinoid geometric structures. In the substituted derivatives, the results indicate a weak influence of the methyl groups on the geometric and electronic structure of poly(5,5′-bithiophene methine); much more pronounced modifications are obtained for the benzene-substituted compounds, leading to a polymer with a calculated 0.5-eV band gap when benzene rings are fused along the 3–4 bonds of the poly(5,5′-bithiophene methine) quinoid rings.

## I. Introduction

Since the discovery that polyacetylene can be made highly electrically conducting by exposure to oxidizing or reducing agents (a reaction usually called "doping" by loose analogy to what takes place in inorganic semiconductors), a lot of work has focused on conjugated polymers.[1] These studies have led to the achievement of high conductivity in other conjugated polymers, such as poly(*p*-phenylene),[2] polypyrrole,[3] polythiophene,[4] or polyaniline.[5] Improved characterization of these compounds has been obtained as a consequence of their solubilization in common organic solvents[6–8] or even water.[9,10]. Also, novel polymerization techniques have given rise to well-oriented polymeric compounds, resulting in new forms of polyacetylene that exhibit an electrical conductivity after doping on the order of $10^5$ S/cm, i.e., a value about as high as that of copper.[11,12] In the meantime, the range of applications of conjugated polymers has considerably broadened; they can be used, for example, as storage elements in batteries,[13] components in integrated circuits,[14] electrochromic materials in display devices,[15] reference compounds to check the freshness of fruits and vaccines,[16] or electroluminescent diodes.[17]

Recently, a number of studies have been devoted to the search for polymers that would possess small intrinsic band gaps, i.e., that are intrinsically good electrical conductors or semiconductors without the need of any chemical or electrochemical doping reaction. The optical properties of small-band-gap polymers also make them interesting. Indeed, most of the conjugated organic polymers are colored as a consequence of their band gaps in the 2–3-eV range. However, if the band-gap energy is smaller, the lowest electronic transition could lie in the infrared region and the corresponding materials could be transparent in either the neutral or doped state. The possibility of dealing with processible, transparent conducting polymers would represent an important breakthrough for applications of conjugated polymeric materials.

Three routes are mainly explored in order to design and synthesize small-band-gap polymers. One of them consists of constructing fully fused-ring hydrocarbon structures in order to obtain systems corresponding more or less to a one-dimensional graphite. Examples are given by polyacene-like systems[18–21] or polyperinaphthalene,[22,23] the latter being of particular interest since well-defined oligomers have been recently solubilized in organic solvents.[24]

Small-band-gap polymers can also be obtained by modifying the geometric and/or electronic structure of known and well-characterized conjugated polymers that can be easily derivatized, especially polythiophene and polypyrrole. In this context, the relation outlined previously between the band-gap energy and the degree of bond-length alternation along the polymer backbone is a useful tool; it predicts that the band gap of aromatic polymers linearly decreases with the increase in quinoid contributions to the geometric or electronic structure.[25] From this theoretical relationship, it appears that what we are looking for is a compound in which the quinoid geometric form (possessing usually a smaller band gap but also a higher total energy than the aromatic geometric form) is favored or in which quinoid electronic contributions are stabilized in the ground state. This concept has first led to the synthesis of polyisothianaphthene (Figure 1), a polythiophene chain where benzene rings are fused along the 3,4 positions of the thiophene units; polyisothianaphthene exhibits a 1-eV band gap.[26–28] Following this synthesis, numerous compounds have been studied, such as poly(arene methines)[29–32] and copolymers of thiophene and isothianaphthene.[33–35]

A third route to small-gand-gap conjugated polymers has been recently initiated by Havinga and co-workers and proposes to build a conjugated backbone consisting of regularly alternating strong donor- and acceptor-like units. The main idea is to bring together, along a conjugated path, units with a low ionization potential and units with a large electron affinity so that the resulting conjugated polymer could exhibit a small-band-gap energy. This concept has already led to the synthesis of polysquaraines and polycroconaines (with compounds having a 0.5-eV band gap)[36] as well as that of polycyclopentadithiophene derivatives.[37]

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® Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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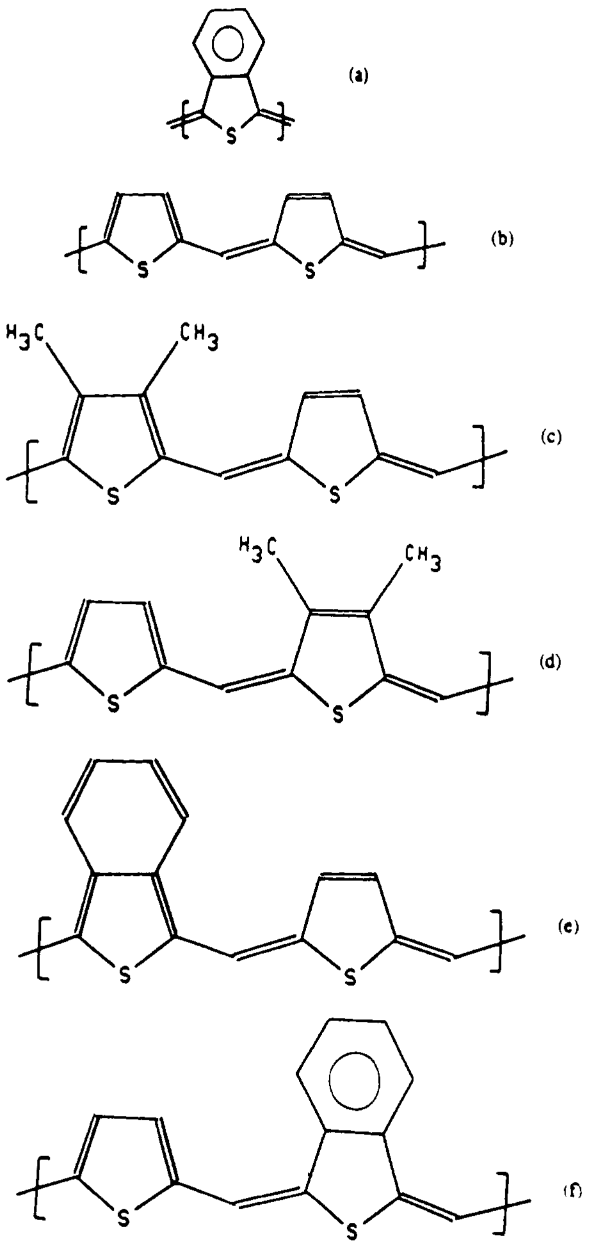


**Figure 1.** Sketch of the unit cells of polyisothianaphthene (a), poly(5,5′-bithiophene methine) (b), poly(3,4-dimethylthiophene) where the substitution takes place on the aromatic (c) or the quinoid rings (d), and poly(3,4-thiophene isothianaphthene methine) with the benzene rings fused on the aromatic (e) or the quinoid rings (f).

In this paper, we first study theoretically the geometric and electronic structure of poly(5,5′-bithiophene methine) (Figure 1), a compound that offers a simple way to introduce quinoid contributions to the ground-state geometry; the presence of one conjugated carbon atom between the rings indeed forces them to alternate between aromatic and quinoid geometries. We have recently presented a theoretical study of poly(5,5′-bipyrrole methine), the nitrogen analog of poly(5,5′-bithiophene methine); this compound exhibits a 1,1-eV band gap.[29] The present study is complementary and emphasizes the role played by the band gaps of the parent polymers on the electronic properties of the compounds in which quinoid rings are introduced within the polymer unit cell. Polythiophene in its ground state possesses a 2-eV band gap, i.e., a value about 1 eV smaller than the one of polypyrrole.

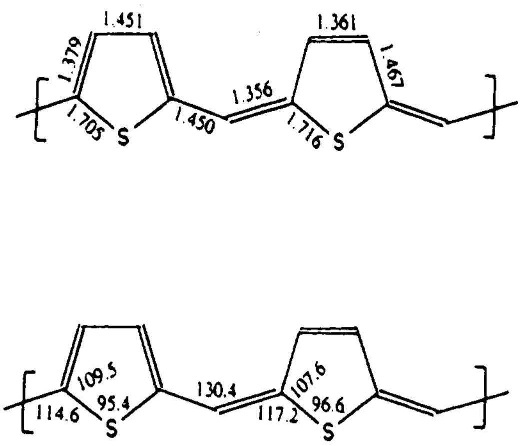


**Figure 2.** Geometric structure of the unit cell of poly(5,5′-bithiophene methine). Bond lengths are in angstroms and bond angles in degrees. The system is fully planar.

In a second part, we report theoretical results on the geometric and electronic structure of poly(3,4-dimethyl-5,5′-bithiophene methine) and poly(5,5′-thiophene isothianaphthene methine), polymers based on poly(5,5′-bithiophene methine) in which either the aromatic or quinoid rings are substituted on the 3,4 positions by two methyl groups or fused benzene rings (Figure 1). The substitution takes place on a single type of ring since it has been shown that substitution on both types of rings does equally affect the energy of the frontier orbitals and, as a result, induces no change in the band gap of the polymer.[27,30]

Due to the lack of available structural data, we follow the methodology that has been successfully used in previous instances.[29,38,39] First, the geometric structure of an oligomer representative of the whole polymeric chain (usually a pentamer unless otherwise indicated) is optimized by means of the MNDO (modified neglect of diatomic overlap) semiempirical technique. This method is known to afford good geometrical estimates for planar conjugated systems. For all the geometry optimizations, the systems were supposed to be planar since it is well-known that the MNDO method is unable to determine dihedral angles that are consistent with experimental data.[40] In a second step, the central part of the optimized oligomer is used as input for band-structure calculations with the VEH (valence effective Hamiltonian) technique.[41–43] This method is well-known to provide accurate determinations of essential electronic parameters in organic molecules and polymers, such as ionization potential, electron affinity, and band-gap values.[43,44] Note that the VEH ionization potentials and electron affinities that are calculated for isolated chains in the gas phase are scaled down to 2.3 eV to take into account the solid-state polarization energy.[45]

Results on the geometry optimizations and band-structure calculations of poly(5,5′-bithiophene methine) are presented in section II while the effects of methyl and benzene substitutions are given in section III for poly(3,4-dimethyl-5,5′-bithiophene methine) and in section IV for poly(5,5′-thiophene isothianaphthene methine). Conclusions of this work are given in the last section.

## II. Geometric and Electronic Structure of Poly(5,5′-bithiophene Methine)

The unit-cell geometric structure of poly(5,5′-bithiophene methine), as obtained after an MNDO geometry optimization on a five-ring oligomer, is presented in Figure 2. We observe that, due to the presence of an odd number of conjugated carbon atoms between the rings, these alternate between aromatic and quinoid geometries. Moreover, the geometry obtained for the aromatic ring of poly(5,5′-bithiophene methine) corresponds to the one optimized

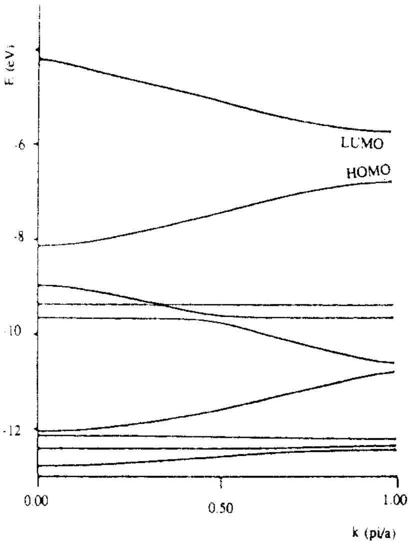


**Figure 3.** VEH band structure of poly(5,5′-bithiophene methine). Only the highest occupied and lowest unoccupied bands are represented.

**Table I. VEH Values of Ionization Potential (IP), Electron Affinity (EA), and Band Gap (Eg) for Poly(5,5′-bithiophene methine) (PBTM), "Aromatic" Polythiophene (the Stable Form of the Polymer), and "Quinoid" Polythiophene (the Unstable Form of the Polymer)**

| | IP (eV) | EA (eV) | Eg (eV) |
|---|---|---|---|
| PBTM | 4.46 | −3.41 | 1.05 |
| "aromatic" PTh | 4.94 | −3.10 | 1.84 |
| "quinoid" PTh | 3.99 | −3.80 | 0.19 |

for the stable form of the polymer, polythiophene in its ground state (i.e., with an aromatic geometry), while the geometry observed for the quinoid ring of poly(5,5′-bithiophene methine) is identical to the one obtained after optimization of a polythiophene chain that would possess a totally quinoid geometry.[46,47]

It should be pointed out that a three-ring oligomer of the sulfonated analog of poly(5,5′-bithiophene methine) has been recently synthesized.[32] The X-ray data obtained from a monocrystal confirm the planarity of the molecule as well as the presence of a ring with a quinoid geometry between two rings with aromatic geometries. Also, the molecular structure (bond lengths and angles) of this oligomer is very similar to the one we obtain after an MNDO geometry optimization on the oligomer without oxygen.

The VEH calculated values of ionization potential, electron affinity, and band gap for (i) poly(5,5′-bithiophene methine), (ii) a polythiophene chain with aromatic geometry ("aromatic" polythiophene), and (iii) a polythiophene chain adopting a totally quinoid geometry ("quinoid" polythiophene) are given in Table I. Note that the electronic parameters for "aromatic" ("quinoid") polythiophene are the ones calculated when the system adopts the geometry of the poly(5,5′-bithiophene methine) rings with aromatic (quinoid) geometry. The band structure of poly(5,5′-bithiophene) methine) is depicted in Figure 3. The electronic structure of poly(5,5′-bithiophene methine) has been previously determined at the Hückel level by Kertesz and Lee.[30]

The calculated band gap for poly(5,5′-bithiophene methine) is small, 1.05 eV, i.e., a value 0.8 eV smaller than the one calculated for polythiophene in its ground state. In order to rationalize the small band gap appearing in poly(5,5′-bithiophene methine), we have analyzed the bonding–antibonding electronic patterns appearing on top of the HOMO (highest occupied molecular orbital) and at the bottom of the LUMO (lowest unoccupied molecular orbital) of the polymers listed in Table I (see Figure 4).

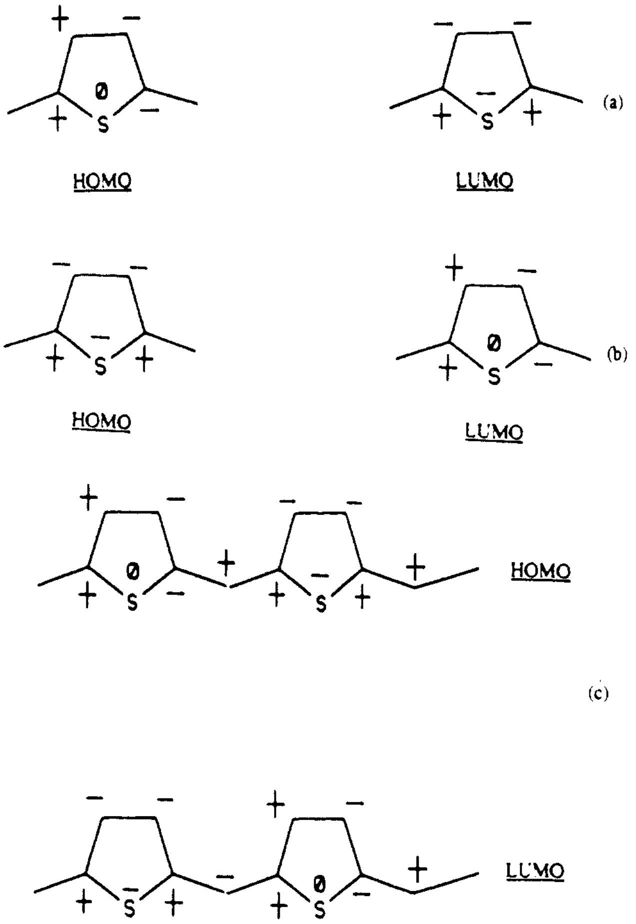


**Figure 4.** Bonding–antibonding electronic patterns of the HOMO and LUMO bands of (a) "aromatic" polythiophene, (b) "quinoid" polythiophene, and (c) poly(5,5′-bithiophene methione).

From Figure 4a, we observe that "aromatic" polythiophene possesses a so-called aromatic electronic structure. This is characterized on the HOMO by (i) the absence of contribution from the sulfur atom, (ii) bonding interactions between the $\alpha$ and $\beta$ carbon atoms, and (iii) antibonding interactions on the $\beta$–$\beta$ bonds and inter-ring bonds and on the LUMO by (i) antibonding interactions between $\alpha$ and $\beta$ carbons and (ii) bonding interactions on the $\beta$–$\beta$ bonds and inter-ring bonds. The electronic structure is thus said to be aromatic because the HOMO bonding–antibonding patterns are a reflection of an aromatic-like geometry. "Quinoid" polythiophene presents a quinoid electronic structure (Figure 4b); on the HOMO, there are antibonding interactions between $\alpha$ and $\beta$ carbons and bonding interactions on the $\beta$–$\beta$ bonds and inter-ring bonds; on the LUMO, there occur bonding interactions between $\alpha$ and $\beta$ carbons, antibonding interactions on the $\beta$–$\beta$ bonds and inter-ring bonds, and no contribution from the sulfur atoms. In other words, the electronic characters appearing on the HOMO (LUMO) of "quinoid" polythiophene are identical to those on the LUMO (HOMO) of "aromatic" polythiophene.

The bonding–antibonding electronic patterns of the HOMO and LUMO bands of poly(5,5′-bithiophene methine) are displayed in Figure 4c. The analysis of the electronic characters indicates that (i) on the HOMO the ring with an aromatic geometry possesses aromatic-like

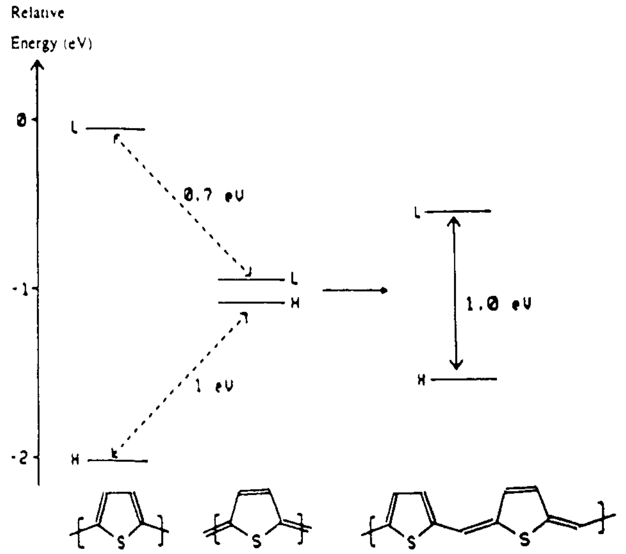


**Figure 5.** Schematic representation of the combination of the HOMO (H) and LUMO (L) levels of "aromatic" and "quinoid" polythiophenes to give the HOMO and LUMO levels of poly(5,5′-bithiophene methine).

electronic characters while the ring with a quinoid geometry carries quinoid-like electronic characters and (ii) on the LUMO there is an inversion of the bonding–antibonding patterns relative to the HOMO so that the ring adopting an aromatic geometry possesses quinoid-like electronic characters and the ring with a quinoid geometry has aromatic-like electronic characters.

As a result, when comparing to the HOMO and LUMO wavefunctions of "aromatic" and "quinoid" polythiophenes, it appears that the HOMO of poly(5,5′-bithiophene methine) arises from a combination of the HOMO's of "aromatic" and "quinoid" polythiophenes while the LUMO of poly(5,5′-bithiophene methine) is a combination of the LUMO's of those systems (see Figure 5). The relatively small energy difference (≈1 eV) between the levels that combine makes that the LCAO (linear combination of atomic orbitals) coefficients carried by the rings with an aromatic geometry and by the rings adopting a quinoid geometry have similar values on both the HOMO and LUMO levels of poly(5,5′-bithiophene methine). Thus, in poly(5,5′-bithiophene methine), the rings adopting aromatic and quinoid geometries possess exactly the same weight on the HOMO and LUMO levels; this feature is not encountered in the nitrogen analog.[29] As a consequence, the HOMO and LUMO levels of poly(5,5′-bithiophene methine) are located in between the levels of "aromatic" and "quinoid" polythiophenes (Figure 5): (a) the HOMO of poly(5,5′-bithiophene methine) (−4.46 eV) lies between the HOMO of "aromatic" polythiophene (−4.94 eV) and the HOMO of "quinoid" polythiophene (−3.39 eV); (b) the LUMO of poly(5,5′-bithiophene methine) (−3.41 eV) is located between the LUMO of "aromatic" polythiophene (−3.10 eV) and the LUMO of "quinoid" polythiophene (−3.80 eV).

The positions of the HOMO and LUMO levels of poly(5,5′-bithiophene methine) relative to the HOMO and LUMO levels of "aromatic" and "quinoid" polythiophene chains indicate that a smaller band gap could be obtained if the two rings constituting the poly(5,5′-bithiophene methine) unit cell had more similar geometries. In this case, the HOMO's of the "aromatic" and "quinoid" polythiophenes would be destabilized while the LUMO's of those systems would be stabilized, resulting in a decrease of the ionization potential and electron affinity values.

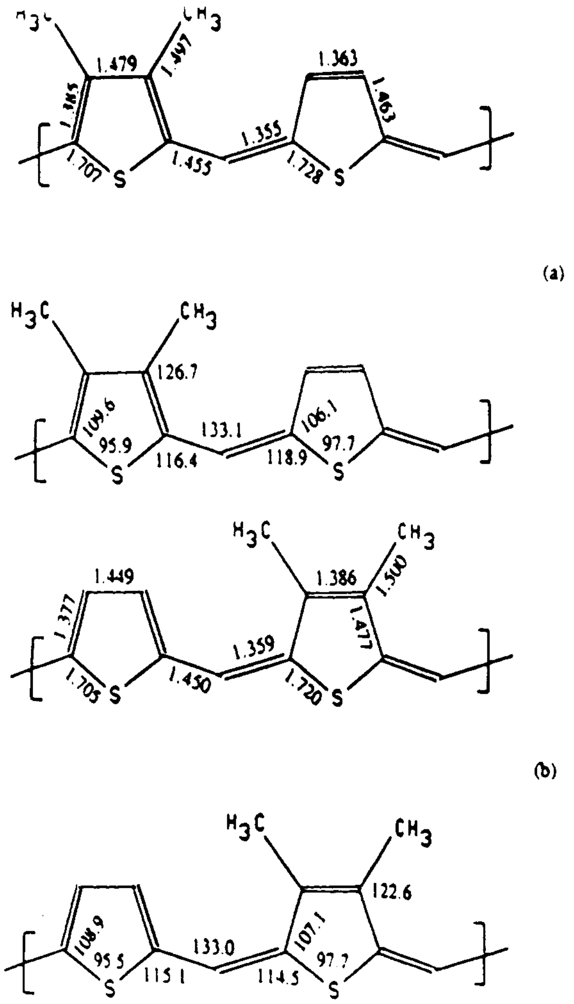


**Figure 6.** Geometric structures of (a) PDBTMa and (b) PDBTMq. Bond lengths are given in angstroms and bond angles in degrees. Except for the methyl hydrogen atoms, the chains are planar.

## III. Geometric and Electronic Structure of Dimethyl-Substituted Poly(5,5′-bithiophene Methine)

The unit-cell geometric structures of poly(3,4-dimethyl-5,5′-bithiophene methine) where the substitution takes place either on the ring with an aromatic geometry (PDBTMa) or on that with a quinoid geometry (PDBTMq) are given in Figure 6. We observe that the methyl groups induce very small geometrical changes relative to poly(5,5′-bithiophene methine). The ring that is not substituted presents a geometric structure identical to the one optimized for the equivalent ring in poly(5,5′-bithiophene methine); the substituted ring undergoes slight changes: if the substitution takes place on the ring with an aromatic geometry, the $\beta$–$\beta$ bond length increases from 1.451 Å in poly(5,5′-bithiophene methine) to 1.479 Å in PMBTMa and the $\alpha$–$\beta$ bond lengths increase from 1.379 to 1.385 Å; when the substitution occurs on the ring with a quinoid geometry, the $\beta$–$\beta$ and $\alpha$–$\beta$ bond lengths increase from 1.361 to 1.386 Å and from 1.467 to 1.477 Å, respectively.

Table II gives the principal electronic parameters calculated for PDBTMa, PDBTMq, "aromatic" poly(3,4-dimethylthiophene), "quinoid" polythiophene, "quinoid" poly(3,4-dimethylthiophene), "aromatic" polythiophene, and poly(5,5′-bithiophene methine). The electronic parameters given for "aromatic" ("quinoid") poly(3,4-dimethylthiophene) and "quinoid" ("aromatic") polythiophene are those obtained when the polymer adopts the geometric structures of the substituted and unsub-

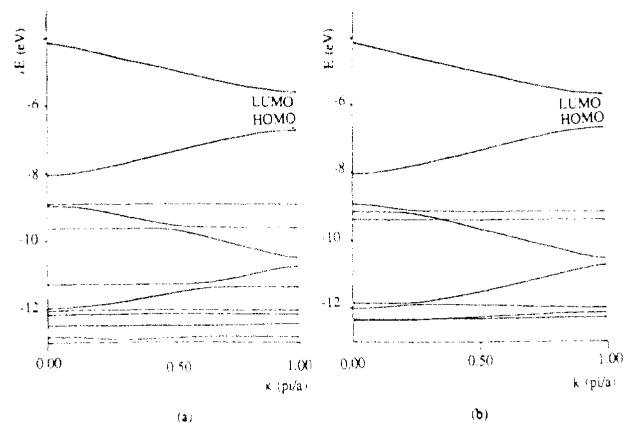


**Figure 7.** VEH band structures of (a) PDBTMa and (b) PDBTMq. Only the highest occupied and lowest unoccupied bands are represented.

**Table II. VEH Values of Ionization Potential (IP), Electron Affinity (EA), and Band Gap (Eg) Calculated for PDBTMa, PDBTMq, "Aromatic" Poly(3,4-dimethylthiophene), "quinoid" Polythiophene, "Aromatic" Polythiophene, "Quinoid" Poly(3,4-dimethylthiophene), and Poly(5,5′-bithiophene methine) (PBTM)**

| | IP (eV) | EA (eV) | Eg (eV) |
|---|---|---|---|
| PMBTMa | 4.44 | -3.31 | 1.13 |
| PMBTMq | 4.37 | -3.38 | 0.99 |
| "aromatic" PDTh | 4.76 | -2.86 | 1.90 |
| "quinoid" PTh | 4.06 | -3.84 | 0.22 |
| "aromatic" PTh | 4.95 | -3.15 | 1.80 |
| "quinoid" PDTh | 3.80 | -3.67 | 0.13 |
| PBTM | 4.46 | -3.41 | 1.05 |

stituted rings of PDBTMa and PDBTMq, respectively. The band structures of PDBTMa and PDBTMq are displayed in Figure 7.

We observe that the introduction of methyl groups on the thiophene rings of poly(5,5′-bithiophene methine) has different effects on the band-gap energy, depending on the nature of the ring where the substitution takes place. If the ring with an aromatic geometry is substituted, we observe an increase in band gap from 1.05 eV in poly(5,5′-bithiophene methine) to 1.13 eV in PDBTMa. This increase is mainly due to a LUMO destabilization after substitution. On the contrary, if the substitution takes place on the ring adopting a quinoid geometry, the band gap decreases from 1.05 eV in poly(5,5′-bithiophene methine) to 0.99 eV in PDBTMq, as a result of the HOMO destabilization occurring upon substitution.

In order to rationalize the band-gap evolutions upon substitution, we have analyzed the bonding–antibonding electronic patterns appearing on the HOMO and LUMO of PDBTMa and PDBTMq. The electronic characters of the HOMO and LUMO levels of PDBTMa are depicted in Figure 8. The bonding–antibonding electronic patterns of the frontier orbitals are identical to those observed on the HOMO and LUMO bands of poly(5,5′-bithiophene methine). Except for the carbon atoms on the methyl groups where the LCAO coefficients are very small (smaller than 0.05), we observe that the substituted and unsubstituted rings have exactly the same weight on both the HOMO and LUMO levels. In other words, the HOMO (LUMO) of PDBTMa is a combination of the HOMO (LUMO) of "aromatic" poly(3,4-dimethylthiophene) and of the HOMO (LUMO) of "quinoid" polythiophene. As a consequence, the HOMO level of PDBTMa (-4.44 eV) lies between the HOMO of "aromatic" poly(3,4-dimethylthiophene) (-4.76 eV) and the HOMO of "quinoid" polythiophene (-4.06 eV) while the LUMO of PMBTMa is located between the LUMO of "aromatic" poly(3,4-dimethylthiophene) (-2.86 eV) and the LUMO of "quinoid" polythiophene (-3.84 eV) (see Figure 9).

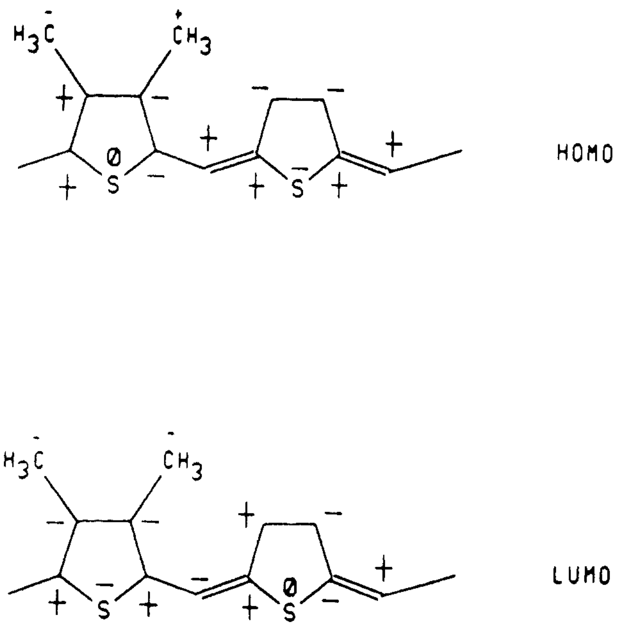


**Figure 8.** Bonding–antibonding electronic patterns appearing on the HOMO and LUMO bands of PDBTMa.

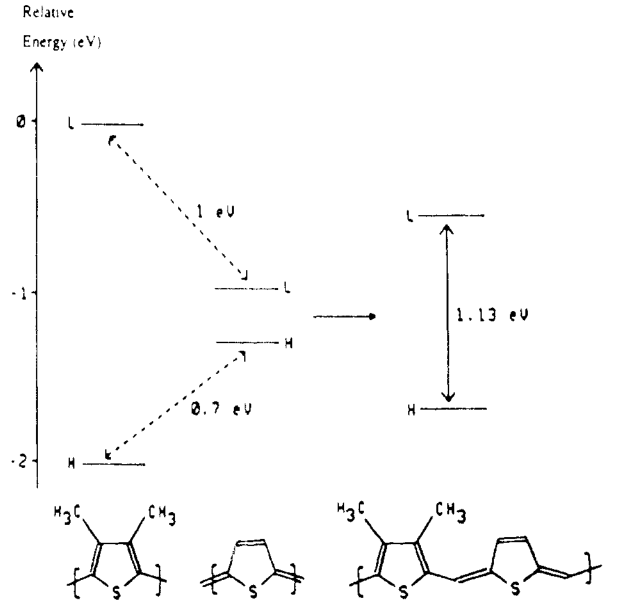


**Figure 9.** Schematic representation of the combination of the HOMO (H) and LUMO (L) levels of "aromatic" poly(3,4-dimethylthiophene) and "quinoid" polythiophene to give the HOMO and LUMO levels of PDBTMa.

The analysis of the electronic parameters indicates that the HOMO and LUMO levels of "aromatic" polythiophene are destabilized (by 0.19 and 0.29 eV, respectively) when methyl groups are introduced on the $\beta$ positions (compare the ionization potential and electron affinity values of "aromatic" polythiophene and "aromatic" poly(3,4-dimethylthiophene) in Table II). These HOMO and LUMO destabilizations allow one to understand why the HOMO and LUMO levels of PDBTMa are located at higher energies than those of poly(5,5′-bithiophene methine); the large destabilization of the LUMO level is responsible for the slight increase in band gap when going from poly(5,5′-bithiophene methine) to PDBTMa.

In PDBTMq, where the calculated band gap is 0.99 eV, the bonding–antibonding electronic patterns and the LCAO coefficient values appearing on the HOMO and

LUMO levels are identical to those obtained in PDBTMa. The HOMO level of PDBTMq (−4.37 eV) lies between the HOMO of "aromatic" polythiophene (−4.95 eV) and the HOMO of "quinoid" poly(3,4-dimethylthiophene) (−3.80 eV); the LUMO of PDBTMq (−3.38 eV) is located between the LUMO of "aromatic" polythiophene (−3.15 eV) and the LUMO of "quinoid" poly(3,4-dimethylthiophene) (−3.67 eV). The evolution of the HOMO and LUMO levels of poly(5,5′-bithiophene methine) upon substitution on the rings with quinoid geometry arises from the effect played by the methyl groups on the electronic structure of "quinoid" polythiophene (Table II): the HOMO (LUMO) of "quinoid" polythiophene is destabilized by 0.26 eV (0.17 eV) when methyl groups are introduced on the $\beta$ positions of "quinoid" polythiophenes; the larger destabilization of the HOMO level is responsible for the small band gap decrease in PDBTMq relative to poly(5,5′-bithiophene methine).

From the studies on poly(5,5′-bithiophene methine) in which one ring of the unit cell is substituted by methyl groups, it appears that the introduction of those electron-donating groups has only a weak effect on the geometric and electronic structure of the unsubstituted polymer. It should be pointed out that band-structure calculations on ethyl-substituted poly(5,5′-bithiophene methine) provide results identical to those observed in PDBTMa and PDBTMq (as a consequence of the small LCAO coefficients carried by the carbon atoms of the alkyl groups in the HOMO and LUMO levels).

## IV. Geometric and Electronic Structure of Poly(5,5′-bithiophene Methine) with Fused Benzene Rings

Studies on the geometric and electronic structure of polyisothianaphthene have shown that, whatever the geometric structure, the band-gap energy of the polymer is smaller by about 1 eV than that of polythiophene in its ground state.[27,28,48] It has been shown that the decrease in band gap after annelation is due to HOMO destabilization and LUMO stabilization.[27,28] Increasing evidence indicates that, in the ground state, polyisothianaphthene adopts a quinoid geometry.[27,49]

We have thus considered mixing thiophene and isothianaphthene units to form poly(5,5′-thiophene isothianaphthene methine), in order to examine the influence of the fusion of benzene rings on half the thiophene rings. Two possible situations have been studied: (i) a system in which thiophenes with aromatic geometries and isothianaphthenes with quinoid geometries are mixed (PTHaITNq) and (ii) a system in which thiophenes with quinoid geometries and isothianaphthenes with aromatic geometries alternate (PTHqITNa) (Figure 1).

**(a) Thiophenes with Aromatic Geometries and Isothianaphthenes with Quinoid Geometries.** The unit-cell geometry of the polymer made of thiophenes with aromatic geometries and isothianaphthenes with quinoid geometries, that are bridged by CH units (PTHaITNq), is given in Figure 10. The geometric structure, as obtained after an MNDO geometry optimization on a three-ring oligomer, agrees with the observations made on other alternating polymers: the rings with an aromatic (quinoid) geometry have geometric parameters corresponding to those optimized for polythiophene (polyisothianaphthene) in its ground state.[48] Since the system is forced to be planar, we note the opening of the inter-ring angle (136°) in order to minimize the steric repulsions between hydrogen atoms on neighboring thiophene and isothianaphthene rings. We mention that a three-ring oligomer (two thiophene and one isothianaphthene rings) of PTHaITNq has been recently synthesized.[32]

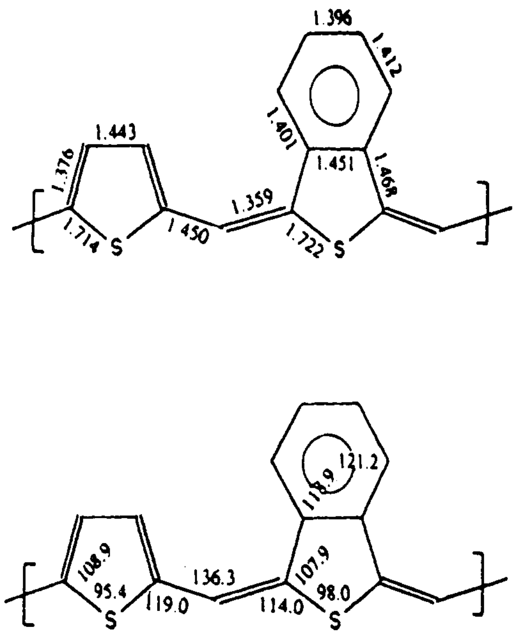


Figure 10. PTHaITNq unit-cell geometric structure. Bond lengths are given in angstroms and bond angles in degrees. The system is fully planar.

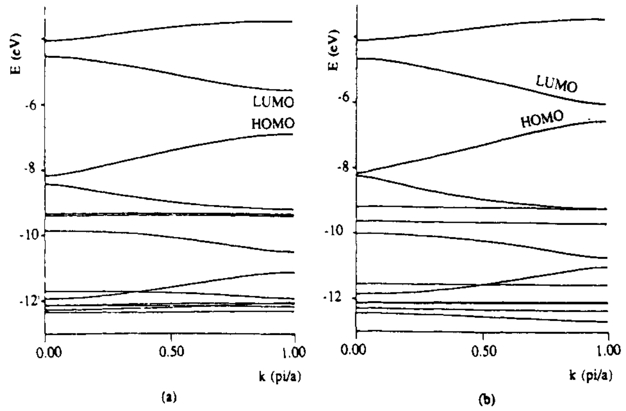


Figure 11. VEH band structures of (a) PTHaITNq and (b) PTHqITNa. Only the highest occupied and lowest unoccupied bands are shown.

Table III. VEH Values of Ionization Potential (IP), Electron Affinity (EA), and Band-Gap Energy (Eg) for PTHaITNq, "Aromatic" Polythiophene, and "Quinoid" Polyisothianaphthene and for PTHqITNa, "Quinoid" Polythiophene, and "Aromatic" Polyisothianaphthene

| | IV (eV) | EA (eV) | Eg (eV) |
|---|---|---|---|
| PTHaITNq | 4.58 | −3.25 | 1.33 |
| "aromatic" PTh | 4.89 | −3.17 | 1.72 |
| "quinoid" PITN | 4.36 | −3.26 | 1.10 |
| PTHqITNa | 4.19 | −3.67 | 0.52 |
| "quinoid" PTh | 4.03 | −3.86 | 0.17 |
| "aromatic" PITN | 4.13 | −3.68 | 0.45 |

The electronic parameters calculated for PTHaITNq are given in Table III together with those calculated for "aromatic" polythiophene and "quinoid" polyisothianaphthene when they adopt the geometric structure of the PTHaITNq rings. The VEH band structure of PTHaITNq is given in Figure 11a.

The band gap calculated for PTHaITNq is 1.33 eV, a value intermediate between those of "aromatic" polythiophene and "quinoid" polyisothianaphthene chains. The band gap in PTHaITNq is thus higher than that of

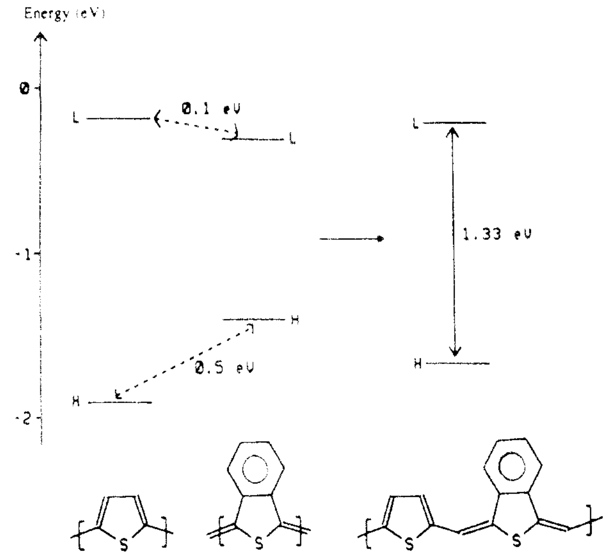


**Figure 12.** Schematic representation of the combination of the HOMO (H) and LUMO (L) levels of "aromatic" polythiophene and "quinoid" polyisothianaphthene to give the HOMO and LUMO levels of PTHaITNq.

poly(5,5′-bithiophene methine), the polymer in which only thiophene rings are mixed (Table I). In other words, the annelation of the ring with a quinoid geometry in poly(5,5′-bithiophene methine) induces an increase of the band-gap energy by 0.3 eV.

This increase in band gap can be explained by the fact that the HOMO (LUMO) level of "quinoid" polyisothianaphthene is stabilized by 0.30 eV (destabilized by 0.58 eV) and relative to the HOMO (LUMO) level of "quinoid" polythiophene. Indeed, the analysis of the electronic characters appearing on the highest occupied and lowest unoccupied bands of PTHaITNq indicates that the HOMO of PTHaITNq (−4.58 eV) lies between the HOMO of "aromatic" polythiophene (−4.89 eV) and the HOMO of "quinoid" polyisothianaphthene (−4.36 eV); the LUMO of PTHaITNq (−3.25 eV) is located between the LUMO of "aromatic" polythiophene (−3.17 eV) and the LUMO of "quinoid" polyisothianaphthene (−3.26 eV) (see Figure 12).

**(b) Isothianaphthenes with Aromatic Geometries and Thiophenes with Quinoid Geometries.** The situation where isothianaphthenes with aromatic geometries and thiophenes with quinoid geometries are separated by a conjugated carbon atom (PTHqITNa) is interesting since it presents two geometric structures that separately lead to small band-gap energies. Moreover, the major electronic parameters (ionization potential, electron affinity, and band-gap energy) of the two polymers based on those geometric structures have similar values.[48]

The unit-cell geometric structure of PTHqITNa, as obtained after a MNDO geometry optimization on a three-ring oligomer, is given in Figure 13. Once again, we observe geometries for the thiophene (isothianaphthene) rings that are similar to those optimized for a polythiophene chain with a quinoid geometry (polyisothianaphthene chain with an aromatic geometric structure). Note the opening of the inter-ring angle to minimize the steric repulsions between hydrogen atoms on neighboring rings.

The calculated electronic parameters for PTHqITNa, "aromatic" polyisothianaphthene, and "quinoid" polythiophene are given in Table III while the band structure of PTHqITNa is displayed in Figure 11b. We observe that the association of two small-band-gap polymers ("aromatic" polyisothianaphthene and "quinoid" polythiophene) gives rise to a polymer (PTHqITNa) with a small band-gap energy, 0.52 eV. However, the main feature of this electronic analysis is that, in opposition to what takes place in the other alternating polymers we have discussed so far, the calculated band gap for PTHqITNa (0.52 eV) is bigger than the one calculated for the homopolymers constituting its unit cell (0.17 eV for "quinoid" polythiophene and 0.45 eV for "aromatic" polyisothianaphthene).

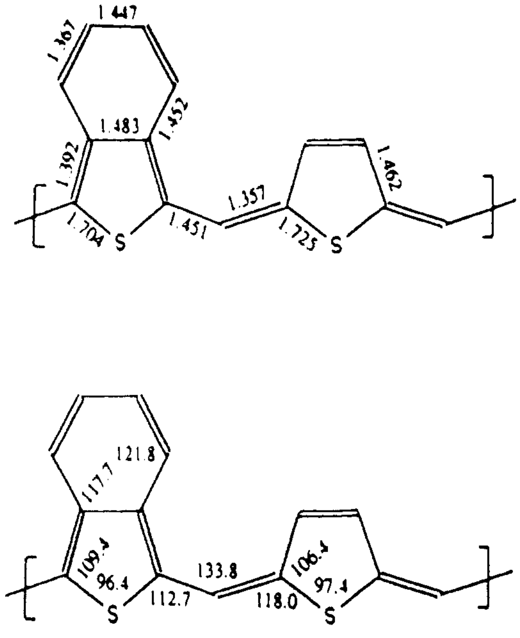


**Figure 13.** PTHqITNa unit-cell geometric structure. Bond lengths and bond angles are given in angstroms and degrees, respectively. The system is fully planar.

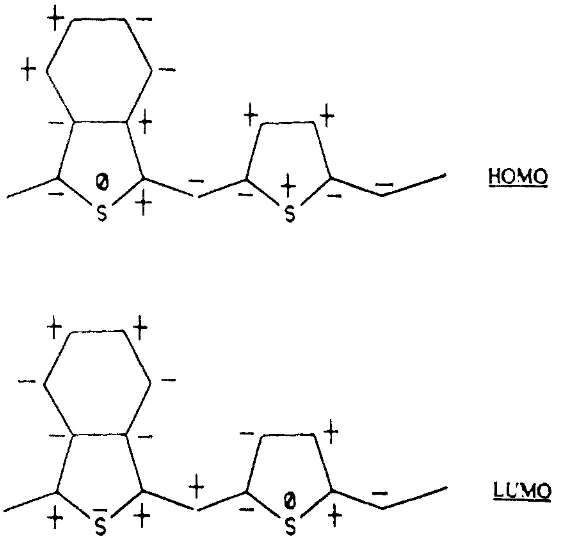
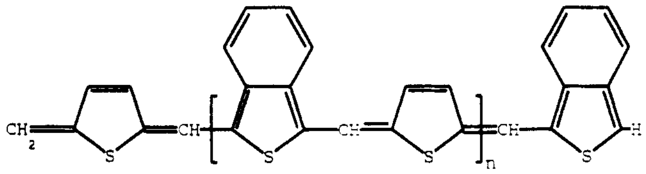


**Figure 14.** Bonding–antibonding electronic patterns appearing on the HOMO and LUMO levels of PTHqITNa.

The analysis of the bonding–antibonding electronic patterns of PTHqITNa, "aromatic" polyisothianaphthene, and "quinoid" polythiophene cannot explain this unusual behavior of the band-gap energy of the alternating polymer relative to those of its homopolymers. The analysis of the electronic characters of the HOMO and LUMO levels of PTHqITNa (Figure 14) indicates that the highest occupied level of PTHqITNa is a combination of the HOMO's of "aromatic" polyisothianaphthene and "quinoid" polythiophene while the lowest unoccupied level of PTHqITNa is a combination of the LUMO's of "aromatic" polyisothianaphthene and "quinoid" polythiophene. Nevertheless, the usual situation encountered in alternating polymers does not occur in PTHqITNa: the HOMO of PTHqITNa (−4.19 eV) does not lie between the HOMO's of "aromatic" polyisothianaphthene (−4.13 eV) and "quinoid" polythiophene (−4.03 eV); the LUMO of PTHqITNa (−3.67 eV) is not located between the LUMO of "aromatic" polyisothianaphthene (−3.68 eV) and the LUMO of "quinoid" polythiophene (−3.86 eV).

The respective positions of the electronic levels of "aromatic" polyisothianaphthene and "quinoid" polythiophene lead us to provide the following explanation for this phenomenon. The two HOMO's and the two LUMO's to be combined (to give the HOMO and LUMO levels of PTHqITNa, respectively) are very close in energy: −4.03 eV and −4.13 eV for the HOMO's and −3.86 eV and −3.68 eV for the LUMO's. Thus, it is likely that, as the energetic differences between the electronic levels of "aromatic" polyisothianaphthene and "quinoid" polythiophene are weak, the perturbation brought by the methine carbon atoms located between the rings plays a bigger role. In this context, we observe that the HOMO and LUMO electronic levels of PTHqITNa move toward those of *trans*-polyacetylene (where the HOMO and LUMO levels lie at −4.76 and −3.32 eV, respectively).

Even if the perturbation brought by the bridging carbon atoms causes a small increase of the PTHqITNa band gap by comparison to what we could expect from a simple combination of the HOMO and LUMO levels of the "aromatic" and "quinoid" homopolymers, it is clear that the association of two small-band-gap units with similar electronic parameter values gives rise to an alternating polymer with a small-band-gap energy. The major problem is of course related to the lack of stability of the polymer since both the thiophene and isothianaphthene rings are not in their ground-state configuration. Following a recent discussion on polyisothianaphthene itself,[27] it appears that it might be possible to stabilize a PTHqITNa-type structure in oligomers, by playing on the end groups. This would be achieved, for instance, by having the terminal α carbon of the external thiophene ring substituted by a $CH_2{=}$ unit and the terminal α carbon of the external isothianaphthene ring simply linked to a hydrogen, as sketched for the dimer:



Since PTHqITNa and PTHaITNq are valence bond isomers and since the thiophene and isothianaphthene rings are not in their ground-state configuration in PTHqITNa, one could think of a shift from this geometrical form (made of thiophene rings with a quinoid geometry and isothianaphthene rings with an aromatic geometry) to the one of PTHaITNq (i.e., where thiophene rings have an aromatic geometry and isothianaphthene rings a quinoid geometry) during the polymerization of oligomers of PTHqITNa. In this context, we have carried out AM1 calculations on the dimer of PTHqITNa, allowing for the possible appearance of a biradical structure. These were performed as ROHF triplets using the AM1 method as implemented in the GAMESS codes. This is a full ROHF calculation, allowing relaxation of all (valence) electrons. The results indicate that the initial dimer geometry evolves toward that of PTHaITNq and that the triplet dimer is ≈0.1 kcal/mol more stable than the closed shell structure. Though this energy difference is below the accuracy of the AM1 method, it suggests the structure would contain radicals at room temperature and have segments in both the PTHqITNa and PTHaITNq forms, thus allowing for the existence of polymeric chains with small band-gap energies.

## V. Conclusions

We have performed geometry optimizations and VEH band-structure calculations on poly(5,5′-bithiophene methine), a polymer made of thiophene rings alternating between aromatic and quinoid geometries, that are bridged by conjugated carbon atoms; we have also investigated its derivatives, poly(3,4-dimethyl-5,5′-bithiophene methine) and poly(5,5′-thiophene isothianaphthene methine). The analysis of the bonding–antibonding electronic patterns appearing on the HOMO and LUMO levels of poly(5,5′-bithiophene methine) allows for an understanding of the small band gap (1.05 eV) calculated for this compound: the HOMO (LUMO) arises from a combination of the HOMO's (LUMO's) of thiophene chains adopting a fully aromatic and a fully quinoid geometric structure. The band-gap value of the alternating system is determined more by the relative positions and electronic characteristics of the HOMO and LUMO levels of the constituting "aromatic" and "quinoid" chains than by the individual band gaps of those chains.

The analysis of the electronic patterns appearing on the highest occupied and lowest unoccupied bands of the methyl- and benzene-substituted polymers explains the evolution of the band gaps relative to poly(5,5′-bithiophene methine). We have shown the weak effect of the substitution by methyl groups and outlined the influence of the bridging conjugated carbon atoms on the band gap of the polymer made of alternating thiophene rings with quinoid geometries and isothianaphthene rings with aromatic geometies. The association of two small-band-gap polymers ("quinoid" polythiophene and "aromatic" polyisothianaphthene) in an alternating polymer gives rise to a small-band-gap polymer (Eg on the order of 0.5 eV). Stabilization of oligomers of this polymer could be achieved by a judicious choice of end groups.

**Acknowledgment.** We gratefully acknowledge support of this work by Wacker-Chemie GmbH Munich and the German Ministry of Research and Technology (BMFT). The authors thank Dr. D. Dudis, Dr. H. Bräunling, Dr. G. Blöchl, Dr. R. Becker, and Professor Hanack for stimulating and helpful discussions. This work is partly supported by the Belgian "Pôle d'Attraction Interuniversitaire: Chimie Supramoléculaire et Catalyse", the Belgian "Programme d'Impulsion en Technologie de l'Information", (Contract IT/SC/22), FNRS/FRFC, and an IBM Academic Joint Study.

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