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Theoretical Investigation of the Structure and Electronic Properties of Poly(dithieno[3,4-*b*:3′,4′-*d*]thiophene), a Small-Band-Gap Conjugated Polymer

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ABSTRACT: We use a quantum chemical approach to investigate the chemical and electronic structure of poly(dithieno[3,4-*b*:3′,4′-*d*]thiophene) (pDTT′). In this compound, the monomer unit possesses four potential linking sites on α carbon positions. Semiempirical Austin Model 1 (AM1) calculations are performed on oligomer systems, considering different types of connection between the DTT′ units, in order to determine the most favorable chain conformation and the relative stabilities of the oligomer segments. The theoretical data indicate that, as a function of the connection mode, the pDTT′ sequences can either be totally planar and highly conjugated or strongly nonplanar, depending on the existence of steric interactions between sulfur and hydrogen atoms located on adjacent units. The electronic properties of the corresponding polymers are calculated with the valence effective Hamiltonian (VEH) method and compared to the results of optical spectroscopy measurements. Finally, we study the energetics of the pDTT′ chain on the basis of the energy per repeat unit (E_{pru}), and we compare the structure and electronic properties of this polymer to those of polyisothianaphthene.

1. Introduction

In the past decade, a major effort in the field of conjugated polymers has been the design of novel systems with a low-energy band gap. One successful approach to this goal is based on the substitution of the thiophene monomer unit in order to modify its electronic structure and, as a result, to modulate the electronic properties of the corresponding conjugated polymer. For instance, grafting a benzene ring upon the thiophene unit leads to a 1-eV reduction in the band gap of the so-obtained polyisothianaphthene relative to polythiophene.[1,2]

Along the same line, Taliani et al.[3,4] have synthesized poly(dithieno[3,4-*b*:3′,4′-*d*]thiophene) (pDTT′) from the monomer shown in Figure 1. This polymer shows a 1.1-eV band gap and has an electrical conducivity in the doped state of the same order of magnitude as that of polythiophene. The evidence for a small band gap in undoped pDTT′ comes from (i) the optical absorption spectrum (Figure 2, right), in which the onset of the absorption is located near 1.1 eV, and (ii) the luminescence spectrum (Figure 2, left), which shows a maximum at 1.24 eV. These data are to be compared with the values obtained with the same technique on polythiophene: 2.0 and 1.93 eV, respectively.[5,6] The DTT′ monomer possesses four quasi-equivalent α carbon sites, which in principle may lead to the creation of a quasi-two-dimensional network of conjugated chains upon polymerization. That network would in turn allow for supramolecular electron delocalization.

Because the electronic properties of a conjugated polymer are directly related to the geometric structure of the chain, it is of prime importance to determine the macromolecular structure of pDTT′, where the possibilities for connecting the monomer units are manifold. The investigations performed up to now on pDTT′ only give partial information on its structure:

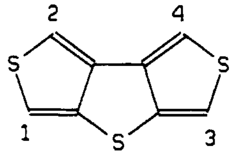

Figure 1. Structure of dithieno[3,4-*b*:3′,4′-*d*]thiophene (DTT′).

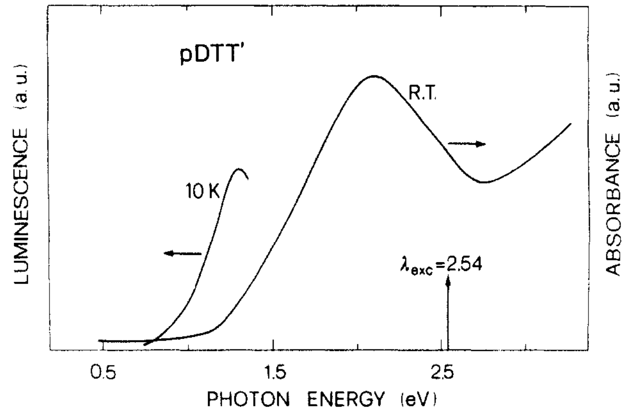

Figure 2. Optical absorption and luminescence spectra of pDTT′. The absorption spectrum was recorded at room temperature, while the luminescence spectrum was obtained at 10 K with 2.54-eV exciting light. No data are available above 1.3 eV because of the cutoff of the Ge/Cu detector used in those measurements.

(i) The molecular structure of the DTT′ monomer has been determined by X-ray diffraction on a single crystal. The same experiments performed on the polymer point to the existence of a graphitelike spacing between the polymer layers (d = 3.6 Å).[7]

(ii) The infrared absorption spectrum of the polymer reflects the presence of C–H bonds,[2] indicating that the polymerization does not proceed by removing all hydrogen atoms as would be expected if both external thiophene subunits were involved in the formation of pDTT′.

(iii) Resonance Raman experiments[8] show the presence of at least two electronic states: one may be related to the

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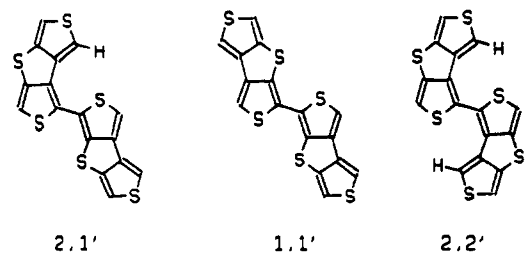

Figure 3. Structures of the DTT′ dimers. The numbering corresponds to the connection type (see text).

backbone conjugation path and conformation similar to those of polythiophene, while the other may correspond to the presence of some chain cross-links via the four reactive sites of the monomer, thereby creating a two-dimensional conjugation path.

(iv) Molecular modeling calculations suggesting that the connections, where the monomer units are linked through the two α carbon positions of the same thiophene subunit, are more favorable as far as planarity and conjugation of the chain are concerned.[9]

In this work, we have used quantum chemical calculations in order to gain information on the geometric structure of the polymer and to understand its electronic properties.

2. Methodology

The structure of the DTT′ polymer is obtained from full geometry optimizations on model oligomers linked in different ways via two of the four possible α carbons. These calculations are performed with the Hartree–Fock semiempirical Austin Model 1 method (AM1),[10] which is well-known to provide accurate geometries and heats of formation, particularly for organic systems. With respect to its parent MNDO technique,[11] the AM1 technique provides a much improved determination of torsion potentials.

In the first part of the work, we have considered all the different possibilities of connections for short oligomers up to the trimers; with this approach we aim at determining the basic geometric and electronic interactions taking place between the monomer units, depending on the connection mode. We also evaluate the relative stabilities of the different isomers from the AM1-calculated heats of formation. In order to facilitate the description of the oligomers connected in different modes, we have introduced the following nomenclature: the four α sites of the monomer are denoted 1–4 (Figure 1), and we describe the oligomers by the numbering of the carbons involved in the connections. This is illustrated in Figure 3 for the dimers.

On the basis of the optimized geometries, the electronic properties of pDTT′ polymers are calculated with the valence effective Hamiltonian (VEH) method, which was designed to provide reliable estimates of the major electronic parameters of conjugated and nonconjugated polymers: band gap (Eg), ionization potential (IP), width of the highest-occupied electronic band (BW).[12-16] We have considered the most stable systems (based on the AM1 calculations) and those which are likely to be the most conjugated, and we compare the theoretical results to the experimental data, mainly optical spectroscopy measurements.

In a recent paper, we have shown,[17] in agreement with the results of others,[18,19] that the quinoid form of polyisothianaphthene (PITN) is slightly more stable than its aromatic counterpart, the relative stability of the two forms being estimated on the basis of the energy per repeat unit (E_{pru}) for oligomers of increasing chain length. In this work, we determine the configuration of the ground state of pDTT′ using the same strategy and we compare these results to the case of PITN.

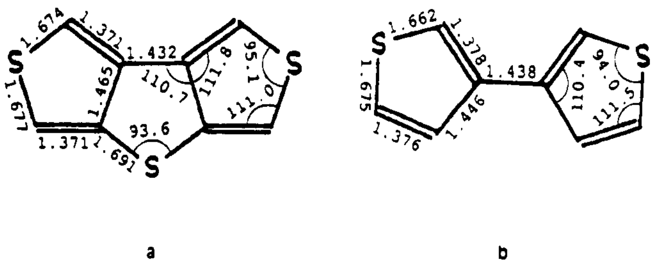

Figure 4. AM1-calculated geometry of DTT′ (left) and β,β'-bithiophene (right). Bond lengths are in angströms; bond angles are in degrees.

3. Results and Discussion

(A) Geometric Properties. Full geometry optimizations are performed at the AM1 level for DTT′ oligomers using the Mopac 6.0 package running on an IBM RISC/6000 workstation. As shown in Figure 4a, the geometric structure of the DTT′ monomer is aromatic, i.e., in the two external thiophene units, the α–β carbon–carbon bonds have a strong double-bond character (d = 1.371 Å) while β–β carbon–carbon bonds have a single-bond character (d = 1.465 Å); the central part of the monomer can be thought of as a link between the two external rings. Indeed, the geometry of the monomer is similar to that obtained for an aromatic β–β' bithiophene molecule (Figure 4b). In the later case, the inter-ring bond length is calculated to be 1.44 Å, while it is 1.43 Å in the DTT′ monomer.

As mentioned above, we describe the oligomers by the numbering of the carbons involved in the connection. Therefore, there are three different possibilities of linking the dimers (Figure 3). The first two isomers, (2,1′) and (1,1′), are totally planar, whereas the third structure, (2,2′), presents a dihedral angle between the planes of the two units of about 42° to prevent steric interactions. In this twisted system, the shortest distances between sulfur and hydrogen atoms located on different units are 2.6 Å. This distance would be on the order of 2.1 Å in a hypothetical planar conformation, which is destabilized by about 1.4 kcal/mol relative to the nonplanar conformation. Due to these contacts, the rings thus rotate around the inter-ring bond.

As is often the case in polyaromatic systems, there is a compromise between steric interactions (which tend to favor nonplanar conformations) and conjugation effects (which tend to favor planar conformations). Along this line, dimer (1,1′) represents the most favorable situation because no significant steric interaction appears in this molecule. Therefore, this system is planar and is more stable than dimers (2,1′) and (2,2′) by about 0.9 and 2.2 kcal/mol, respectively. For the (2,1′) dimer, there is one major steric interaction between sulfur and hydrogen atoms (the H atom involved appears in Figure 3); the geometry, however, can relax to allow the structure to be planar, the S–H distance being then calculated to be 2.35 Å. In contrast, the (2,2′) molecule is characterized by the existence of two S–H interactions. The only way for the system to reduce the steric hindrance is to twist around the interunit single bond, which decreases the π conjugation. It has to be noted that the AM1-calculated inter-ring bond length (1.42 Å) appears to be slightly too short when compared to X-ray diffraction data on thiophene oligomers;[20,21] this is a typical feature of the AM1 parametrization, as reported previously.[17]

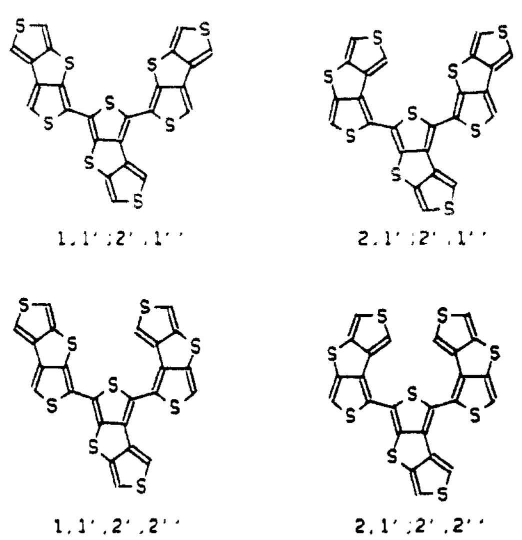

Figure 5. Structures of the "polythiophene-like-connected" DTT′ trimers. The numbering corresponds to the connection type (see text).

Figure 5 shows the isomers of the trimers which possess polythiophene-like connections; i.e., the connection of the central DTT′ unit takes place on the two α positions of the same thiophene subunit. There are only four possibilities to link the trimers in such a way. The first two systems, (1,1′:2′1″) and 2,1′:2′1″), are totally planar, while isomers (1,1′:2,2″) and (2,1′:2′2″) present a nonplanar conformation. This is consistent with the results obtained for the dimers. Indeed, the first two trimers are formed by the pairs (2,1′) and/or (1,1′) which possess a planar geometric structure, as shown above. On the contrary, the (1,1′:2′,2″) and (2,1′:2′,2″) trimers present a dihedral angle of about 45–50° between the two rings on the right-hand side of the oligomer since the units of the (2,2′) dimer tilt around the inter-ring bond.

The geometry of the rings does not change significantly with respect to the dimers; the differences are less than 0.01 Å for the bond lengths and 1.0° for the bond angles. The calculated heats of formation of the four trimers are consistent with the values found for the dimers. The most stable system is the (1,1′:2′,1″) trimer since it contains the (1,1′) pair which is the dimer possessing the smallest heat of formation. This molecule is more stable by about 0.7, 1.0, and 1.7 kcal/mol with respect to the (2,1′:2′1″), (1,1′:2′2″), and (2,1′:2′,2″) systems, respectively.

These results clearly indicate that the structural characteristics of an N-oligomer (where N is the number of units) can be determined by the pair sequence forming the oligomer. For instance, the (2,1′:2,′1″:2″,1‴) tetramer is completely planar because it only contains (2,1′) pairs, which have been calculated to be planar.

Figure 6 shows six trimers where the two connections of the central DTT′ unit take place on α positions situated on different thiophene subunits. In the first two systems, (2,2′:4′,2″) and (1,2′:4′,1″), strong steric interactions do appear between the sulfur atoms of the first and third DTT′ units. The dihedral angle between each external DTT′ unit and the central unit is calculated to be ≈80°. The S–S distance in the optimized geometry is 4.37 Å, while in a hypothetical planar conformation it would be on the order of 0.9 Å, hence the marked tilting away from planarity. Evidently, this is not the best way to obtain extended π-electron conjugation; consequently, the AM1 ionization potentials of these trimers (7.76 and 7.82 eV, respectively) are of the same order as the IP of the monomer (7.86 eV), while in the planar, conjugated trimers, it is around 7.4 eV. The heats of formation of the (2,2′:4′,2″) and (1,2′:4′,1″) molecules are found to be higher than that of the (1,1′:2′,1″) trimer by about 6.0 kcal/mol.

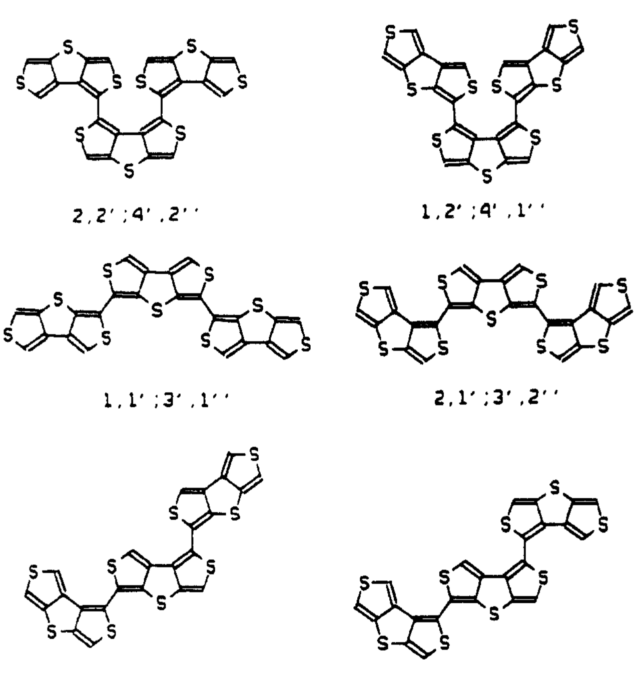

Figure 6. Structures of the "non-polythiophene-like-connected" DTT′ trimers. The numbering corresponds to the connection type (see text).

The (1,1′:3′,1″) and (2,1′:3′,2″) trimers shown on the central part of Figure 6, possess a planar conformation. There is no steric interaction between the sulfur atoms, in contrast to the two previous cases. The first structure is more stable than the (1,1′:2′1″) trimer by about 1.0 kcal/mol; this system is the most stable since it is formed by identical pairs, (1,1′) and (3′,1″), which have the smallest heat of formation. The (2,1′:3′,2″) oligomer is destabilized by about 1.9 kcal/mol with respect to the (1,1′:3′,1″) system, probably due to the fact that there are two weak steric interactions between sulfur and hydrogen atoms (S–H distance = 2.37 Å).

The last two trimers are connected in the (2,1′:4′,1″) and (2,1′:4′,2″) positions. The first system may adopt a planar or nonplanar conformation, the energy difference between these two forms being only 0.6 kcal/mol in favor of the planar molecule. The (2,1′:4′,2″) trimer is a twisted system, the difference in heat of formation between the twisted and planar conformations being on the order of 1.9 kcal/mol. This can be rationalized by the fact that there exist multiple contacts between sulfur and hydrogen atoms. These two trimers are less stable by about 1.8 and 2.6 kcal/mol, respectively, with respect to the (1,1′:3′,1″) oligomer. Accordingly, the ionization potentials of these trimers are intermediate (7.6 eV) between those of fully planar and 80°-tilted isomers. These results show that a given type of connection, which gives rise to nonplanar adjacent units, expectedly induces a decrease in the degree of π-electron conjugation along the chain.

Finally, we have optimized the (2,1′:2′,1″:2″,1‴) tetramer which is formed exclusively from (2,1′) pairs. The system is completely planar as expected by the results obtained on the dimers and trimers. The geometry does not undergo strong modifications compared to the smaller oligomers having the same type of connection, i.e., dimer (2,1′) and the trimer (2,1′:2′,1″). The geometric structure remains aromatic; the bond-length alternation between the single

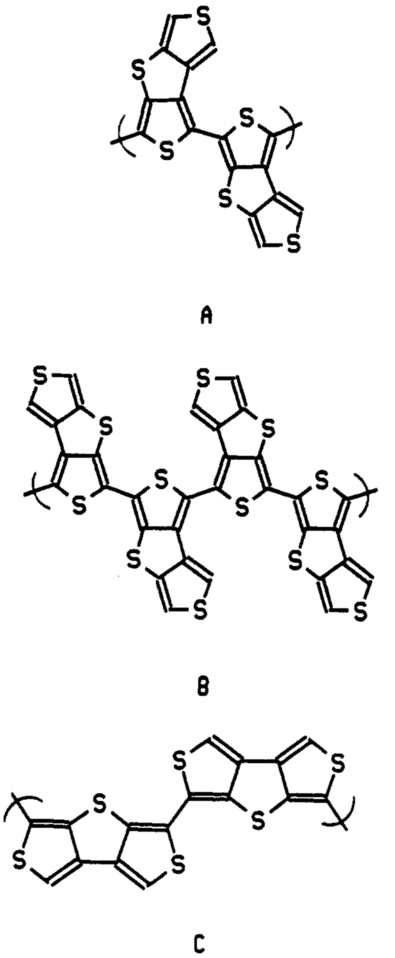

Figure 7. Structures of the pDTT′ polymers considered in the VEH calculations. Structures A and C are fully planar, while structure B shows a 42° dihedral angle between the second and third units.

and double bonds is almost identical to that found in the monomer, and there is no tendency toward a reversed bond-length alternation which would correspond to a quinoid geometric structure.

All these results show that, in order to predict the conformational structure of larger oligomer sequences, we can utilize the results obtained on DTT′ pairs, combined with the fact that short S–S contacts between nearest-neighbor DTT′ units always lead to strongly nonplanar geometries (this last point is illustrated by the (2,2′:4′,2″) and (1,2′:4′,1″) trimers). Finally, it has to be noted that we have discussed the structure of oligomers in terms of thermodynamic stability but the coupling reactions taking place during the polymerization are principally controlled by kinetic parameters. Therefore, the mode of connection leading to the most stable system is not necessarily the only one occurring in the actual polymer chain.

(B) Electronic Structure. We have performed band-structure calculations with the VEH method on the basis of the optimized-AM1 geometries of the trimers. Three types of pDTT′ polymers are considered: (i) a polythiophene-like system with all (2,1′) connections and possessing a planar geometric structure (Figure 7a); (ii) another polythiophene-like polymer where the links repeat in the following way: (1,1′:2′,2″:1″,1‴:2‴,2⁗) [the first DTT′ pair is planar and shows a 40° dihedral angle with the second pair, which is also planar (Figure 7b)]; (iii) a planar polymeric chain formed the most stable (1,1′:3′,1″) trimer (Figure 7c). Other model polymers, based on trimers such as 2,2′:4′2″, were not considered due to the fact that they are much less stable than the above-mentioned systems and basically nonconjugated (they are thus expected not to lead to small-gap configurations).

Table I
VEH-Calculated Band Gap (Eg) and Ionization Potential (IP) of pDTT′ Polymers (Structures Described in Figure 7)[a]

polymer structure	Eg	IP
A	1.27	4.41
B	1.77	4.67
C	2.39	4.94

[a] All values are in electronvolts.

As mentioned above, the inter-ring bond length estimated at the AM1 level appears to be on the short side (1.42 Å) compared to what is known in thiophene systems. Therefore, our calculations are performed with an interunit distance of 1.45 Å, which corresponds to the results of X-ray diffraction performed on thiophene oligomers.[20,21]

In Table I, we compare the band gap (Eg) and ionization potential (IP) of the different pDDT′ polymers. The first system (A) shows a small band gap (1.3 eV) compared to the value calculated for aromatic polythiophene (1.6–1.7 eV). The calculated band-gap reduction (0.3–0.4 eV) is lower than the shift observed experimentally in optical absorption when going from polythiophene[5] to pDTT′ (from 2 eV down to 1.1 eV). However, the situation evolves in the same direction as the experimental measurements. The band gap of the second polythiophene-like-connected system (B) is found to be larger (1.8 eV). The increase in the energy of the HOMO–LUMO transition is due to the appearance of a nonzero dihedral angle between certain adjacent units along the polymer. Hence, the conjugation is lower along the chain with respect to system A and the value of the band gap is larger by about 0.5 eV. The third system (C) is a pDTT′ formed by the connections corresponding to the most stable trimer (1,1′,3′,1″). Although this polymer possesses a planar conformation, the band gap is calculated at about 2.4 eV which is 1.1 eV higher with respect to the first system, indicating that the π conjugation is not strong for the polymer linked in this way. This is also supported by the values of the ionization potentials listed in Table I. The last system shows the highest IP (4.9 eV) versus 4.7 eV for the twisted system and 4.4 eV for the planar pDTT′. These values can be compared with that calculated for polythiophene (4.7–5.0 eV). (Note that the IP is scaled down by 2.3 eV in order to account for solid-state polarization effects.[12])

These results emphasize the fact that trimer sequences having almost the same stability can lead to polymers possessing very different electronic properties. Therefore, the quite broad absorption observed on the optical spectrum of pDTT′ (onset a 1.1 eV, peak at 2.1 eV) could result from a mixture of many sequences containing diverse geometric structures, with different electronic properties, which are expected to contribute to the absorption at different energies. These less regular structures should possess intermediate electronic properties relative to those of models A–C, as has been obtained in the case of phenylene–vinylene conjugated copolymers.[22]

It also appears that the absorption at the lowest energies would be principally due to the planar chain connected like in polythiophene (all 2,1′). The HOMO–LUMO transition of the polymer formed in this way is calculated at 1.3 eV, in good agreement with the onset of the absorption spectrum. The luminescence data are also consistent with the calculations, considering that emission, which occurs at 1.24 eV, originates from the lowest-lying electronic states, which can correspond here to the highly-conjugated, (2,1′)-connected, pDTT′ segments.

(C) Comparison to Polyisothianaphthene (PITN). It has been shown that the quinoid geometric structure of polyisothianaphthene (PITN) is more stable than its aromatic counterpart and that the band gap observed in that polymer can be understood in terms of the highly quinoid structure.[17-19] The relative stabilities of the two forms were estimated from the values of the energy per repeat unit (E_{pru}) for AM1-optimized oligomers of increasing chain length. The energy difference between the two conformations was calculated to be about 2.2 kcal/mol at the AM1 level.[17]

In this work, we use the same strategy for DTT′ oligomers connected in (2,1′). We induce a quinoid geometric structure in the pDTT′ chain by introducing one extra hydrogen atom on each of the two terminal α carbons of the chain and we calculate $E_{\text{pru}}(N) = E(N) - E(N\text{-}1)$, which is known to provide good estimates of E_{pru}[23,24] for the quinoid and the aromatic forms. The results indicate that the aromatic geometric structure is favored over its quinoid counterpart by about 7.7 kcal/mol. This value is close to that obtained for polythiophene (8.7 kcal/mol).[17] This indicates that the fusion of the thienothiophene unit on the thiophene ring (to give pDTT′) does not produce the same effect as the fusion of a benzene ring (to give PITN). In the latter case the substituents induce the compound to possess a quinoid conformation. Instead, the aromatic geometric structure of pDTT′ appears clearly predominant, like in the parent polymer, polythiophene.

Finally, we have also performed band-structure calculations on the quinoid pDTT′ polymer corresponding to model A in Figure 7. The band gap is very small (0.11 eV), in clear disagreement with the experimental value (1.1 eV). This is a further argument which confirms the aromatic character of pDTT′. In the case of PITN, the band gap for the quinoid structure is higher (1.19 eV) and closer to experiment[2] than that of the aromatic form (0.2–0.6 eV).

4. Synopsis

Full geometry optimizations were performed at the AM1 level for DTT′ oligomers in order to determine the structure and relative stability of oligomers connected via the four potential linking sites on α carbon positions. The results show that the most stable systems are fully planar and avoid S–H or S–S steric interactions. It also appears that the conformational structure and the stability of larger oligomers can be predicted on the basis of the sequences of DTT′ pairs along the chain.

The band gaps of the corresponding DTT′ polymers were calculated with the VEH method for structures based on different sequences. The results indicate that oligomers having almost the same stability can lead to polymers possessing very different electronic properties. This feature can rationalize the broad optical absorption spectrum of pDTT′ since the actual chain is likely to contain sequences with different geometric structures, hence different electronic properties, which could all contribute to the absorption. The onset of the optical spectrum at 1.1 eV is principally due to planar chains connected in the same way as in polythiophene, which is also consistent with the peak located at 1.24 eV in the luminescence spectrum.

From the values of the energy per repeat unit for AM1-optimized oligomers of increasing chain length, the geometry of the ground state is clearly found to be aromatic. This situation is close to what is found in the parent polythiophene polymer; it is fundamentally different from the geometric structure of polyisothianaphthene, the prototypical low-band-gap conjugated polymer.

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