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Sulfur Multicenter Bonding and Distortions in a Hypothetical Polydithioquinone

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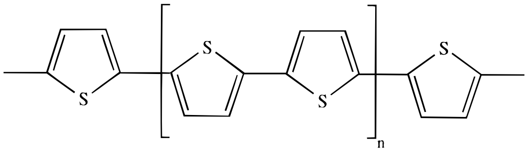
The electronic properties of polydithioquinone, a hypothetical C_4S_2 carbon−sulfur polymer related to both tetrathiotetracene and thiothiophthene, are examined using approximate molecular orbital calculations. We focus on a curious pattern of sulfur−sulfur bonding interactions suggested by the band structure calculations, a pattern observed in thiothiophthenes and other molecular analogues of our polymer. The π system of each C_4S_2 repeat unit contains eight electrons, consistent with a thiothiophthene-like rather than localized polydithioquinone valence structure. A pairing distortion in the carbon sublattice is implied; furthermore, the half-filled sulfur σ bands suggest that the sulfur sublattice is also likely to undergo distortions. Restricting our consideration to those distortions that retain planarity of the polymer, we find deformations of the carbon backbone considerably less favorable energetically than those of the sulfur sublattice. Four nicely bond-localized isomers result from the distortions of both carbon and sulfur sublattices; these all are found to be low bandgap semiconductors. We also examine helical distortions and find a stable isomer with an approximately 10-fold helical axis.

Introduction

Sulfur-containing molecules figure prominently in contemporary studies of polymeric and molecular conducting systems. For example, polythiophenes[1−3] (exemplified below by **1**), low-bandgap semiconductors when pure, increase their conductivity many-fold on doping.[4,5] Tetrathiofulvalene, **2**, and its derivatives also form a wide variety of conducting charge-transfer complexes with acceptor molecules, such as I_2 or AsF_5.[6,7] Tetrathiotetracene (TTT, **3**) and its homologues, molecules relevant to the polymer we will explore in this paper, have found use as donors as well.[8−10]



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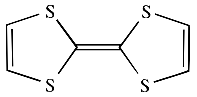

TTF
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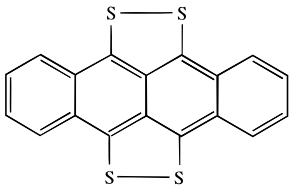

TTT
3

A number of compounds related to tetrathiotetracene, such as pentacene hexasulfide and tetrathionaphthalene, have been synthesized and characterized.[11,12] The structure of the TTT molecule itself was determined by X-ray crystallography[13] and has two dithiole units with single S−S bonds. Many charge-transfer complexes of TTT are remarkable conductors; their crystal structures and electronic properties have been studied both experimentally[14,15] and theoretically.[16,17]

Recently, two of us speculated about a novel, possibly conducting polymer of stoichiometry CS, **4**, which we dubbed "polythiene".[18] This polymer was inspired by the fascinating molecule of thiothiophthene, or trithiapentalene,[19,20] **5**, whose geometry makes extension to an infinite one-dimensional ribbon imaginable.

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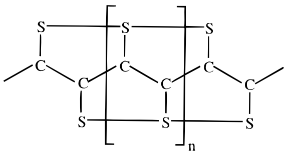
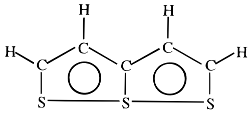


Polythiene

4

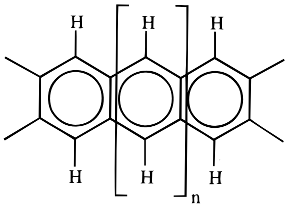


Trithiapentalene

5

We found that polythiene was in fact best described not as a thio analogue of polyketone but as a trithiapentalene analogue with strong S−S bonding. Theoretically, the polymer is also subject to a variety of Peierls distortions and could curl into a gentle helix.

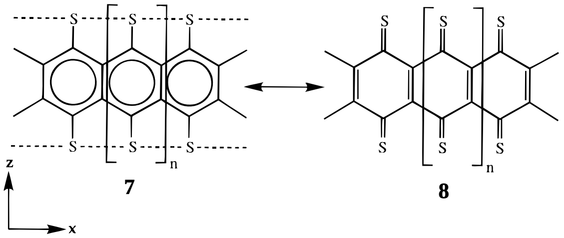
We consider an interesting extrapolation of polythiene in this paper, and one related to TTT, mentioned above. The idea is fairly simple. Polyacene, **6**, has been the subject of many calculations, even if it has escaped clean synthesis.[21,22]



Polyacene

6

What if we "insert" the carbon skeleton of polyacene between two linear sulfur chains (much as we constructed polythiene by "inserting" the polyacetylene skeleton between sulfur chains)? In this way we come to **7**. As one may anticipate, there is another resonance structure to consider, one with no S−S bonding (**8**). The latter has a clear-cut name, polydithioquinone, and without prejudice as to which valence structure, **7** or **8**, best describes the bonding, we will henceforth call this system "polydithioquinone".



7 **8**

We begin by carrying out extended Hückel calculations on the idealized polymer, so as to determine which of these resonance structures best represents the polymer. We then analyze several Peierls distortions that retain planarity of our polymer. Finally, we consider a possible helical isomer.

The Idealized Polydithioquinone

The following geometry is assumed for idealized polydithioquinone: a planar carbon backbone of fused perfect hexagons (CCC angle = 120°), C−C bond length set to 1.40 Å, and the sulfur sublattice set up as two parallel linear chains extending along the carbon backbone (CCS angle = 120°). These assumptions fix the S−S contact at 2.42 Å. The only geometric parameter still undefined is the C−S distance—we assign it the value of 1.70 Å, which reflects its partial double-bond character and is close to the C−S bond length observed in tetrathiotetracene.[13] Figure 1 (left) shows the band structure calculated for the idealized polydithioquinone. (The polymer is aligned so that it extends along the *x*-axis and lies in the *xz*-plane; thus it will remain throughout the paper.)

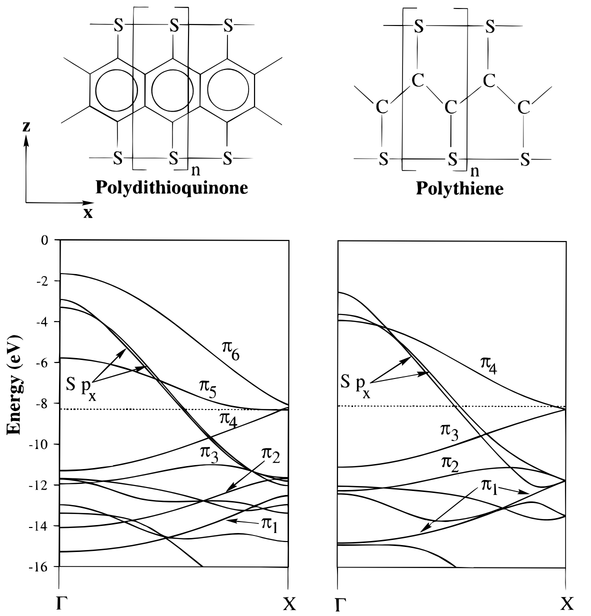


Figure 1. Band structures of polydithioquinone (left) and polythiene (right). Fermi levels are indicated with dotted lines. Sulfur p$_x$ and π bands are specifically labeled.

The computed Fermi level, at −8.29 eV, intersects two bands near the middle of the Brillouin zone ($k = \pi/2a$) and lies just below the (near) meeting point of two other bands at X; it is clear that this structure would be conducting.

One way to understand the band structure of polydithioquinone is by comparison with that of its principal sublattices. There are several well-understood polymer systems, such as a linear sulfur chain, polyacene, or polythiene, which could serve in this respect. We will limit ourselves to a comparison with polythiene; the bands of that polymer are shown in Figure 1 (right).[23] The energy window has been chosen to emphasize the π bands; some high- and low-energy σ bands, unimportant to this discussion, have been omitted.

There is obviously great similarity in the electronic structures of the two polymers—note the two broad S p$_x$ bands running down and the π bands converging at X. The sulfur p$_x$ orbitals' contribution to all but two bands of polydithioquinone is no greater than 15%. Those two very important bands, containing most of the S p$_x$ orbital contribution, are marked specifically in Figure 1. They run down from −3 eV at Γ to −11 eV at X, crossing the Fermi level on their way. These bands are crucial to the conductivity of the polymer and its behavior toward geometrical distortions; we will discuss

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(21) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London A*, **1979**, *366*, 23−46.

(22) Kertesz, M.; Hoffmann, R. *Solid State Commun.* **1983**, *47*, 97−102.

(23) We assume the following geometry for idealized polythiene: C−C bond length is 1.40 Å, CCC angle = 120°, C−S bond length is 1.70 Å, CCS angle = 120°.

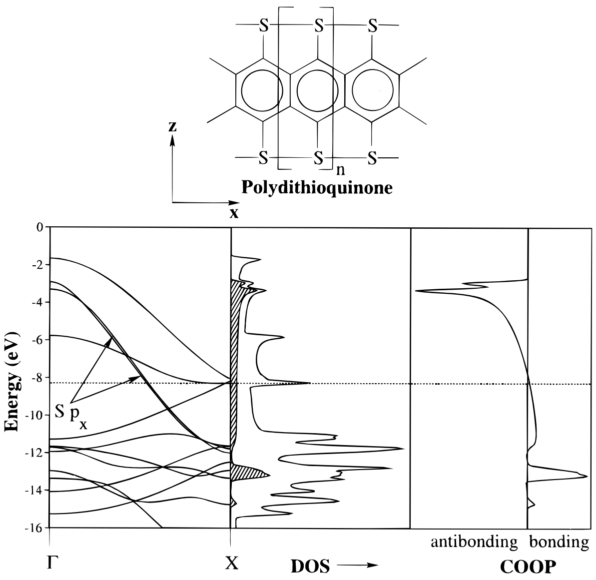


Figure 2. Band structure (left), density of states (DOS) with contribution of sulfur p_x orbitals lined (middle), and intercell S p_x−S p_x crystal orbital overlap population (COOP) curve (right). The average overlap population at the Fermi level is 0.11. The Fermi level is shown by dashed lines, and S p_x bands are indicated with arrows.

them in more detail later. Two very similar bands may be found, at the same energy, in polythiene; as discussed in our earlier paper,[18] these are also almost entirely S p_x in character.

The π bands of polydithioquinone may be related to the orbitals of some well-understood molecular model; one possibility is *s-cis*-hexatriene, and this analysis is carried through in Appendix 1.

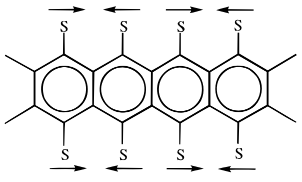
The most important feature of the π-electronic structure of this polymer is that *four out of six π bands are filled in polydithioquinone.* The highest filled π band (π_4 in Figure 1; see also Appendix 1) has three nodal planes in addition to that in the plane of the polymer and is C−S antibonding. This weakens the C−S double bonds which are fully formed when only three π levels are filled (as they would be in a hexatriene or dithiahexatriene model). Therefore, localized resonance structure **8**, which implies three filled π bands, is not an adequate representation for polydithioquinone. We retain the name, however, for there is no point yet in inventing a new name for this hypothetical polymer.

Consider now the three π bands nearest to the Fermi level (π_4, π_5, and π_6 in Figure 1; see also Appendix 2). Near X, these bands are quite close in energy; two of these bands, π_4 and π_5, also cross each other in that region of Brillouin zone, with the Fermi level lying just below their intersection. A pairing distortion in the carbon sublattice will remove the transverse symmetry planes and probably push these bands apart.

Two other essential bands still remain to consider—the sulfur p_x bands running down from Γ to X. These bands are closely related to the p_x bands of two sulfur chains, their initial degeneracy now lifted via a slight interaction with carbon p_x and p_z orbitals, as discussed previously for the similar bands in polythiene.[18] From the perspective of perturbation theory, if we view the carbon sublattice of planar polydithioquinone as a perturbation upon the sulfur sublattice, then we can say that these two bands are derived from the p_x bands of two isolated sulfur chains. Figure 2 shows the crucial segment of the polydithioquinone band structure, along with the contribution of sulfur p_x orbitals to the total density of states (DOS) and the sulfur−sulfur crystal orbital overlap population (COOP)[24] curve.

The bonding part of these bands is almost exactly filled, as the COOP curve shows; the average intercell overlap population between S p_x orbitals is positive and equals 0.11 (for comparison, the corresponding overlap population in trithiapentalene, **5**, which has a shorter S−S bond of 2.36 Å, is 0.25). This indicates considerable sulfur−sulfur bonding and thus also supports (as the analysis of π bands does) the preferred representation of polydithioquinone as **7**.

These half-filled S p_x bands create ideal conditions for a Peierls distortion,[25] specifically now in the sulfur sublattice. The most obvious of these, a pairing distortion, is illustrated in **9**. (Arrows denote the direction of atomic motion.)



9

We will discuss this and other possibilities for distortion of the sulfur sublattice below.

So far our results are as follows: (a) the idealized symmetric polydithioquinone should be conducting; (b) the π system of this polymer contains eight electrons, suggesting that resonance structure **7** is a better representation of the bonding in the polymer; (c) three π bands lie near the Fermi level, two of them intersecting each other; thus distortions of the carbon backbone are likely; (d) two sulfur p_x bands intersect the Fermi level and are roughly half-filled; therefore pairing distortions of the sulfur sublattice should also be favored. These qualitative predictions will now be examined in greater detail.

Peierls Distortions

Several half-filled bands in the electronic structure of polydithioquinone point to a wide variety of distortion possibilities. In this section, we consider only those distortions that retain planarity of the polymer; our choices are indicated in **10**−**17** (Chart 1). Two of these (**10** and **11**) result from distortions of the carbon backbone only, two more are the product of sulfur pairing (**12** and **13**) alone, and the remaining four (**14**−**17**) are combinations of both sulfur and carbon pairing. Distortions **12**−**17** are represented by structures with fully formed bonds. We will discuss each of these types of distortions in turn.

Distortions of the Carbon Sublattice. We implement these distortions as follows: keeping the sulfur sublattice unaltered, we contract some C−C bonds and simultaneously stretch others, creating a backbone of alternating short (1.36 Å) and long (1.44 Å) C−C bonds.

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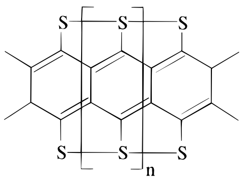
(24) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University: New York, 1995.

(25) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988.



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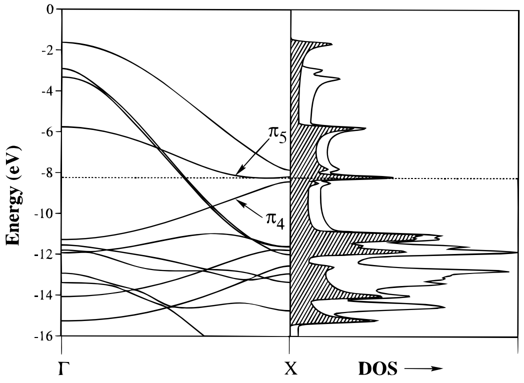
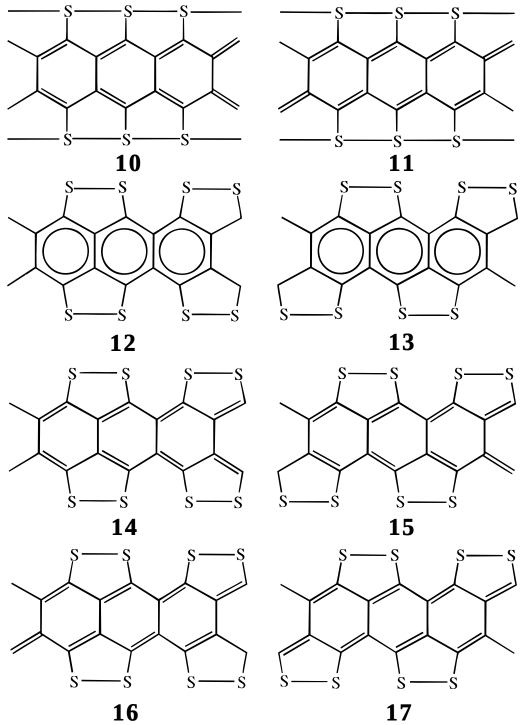


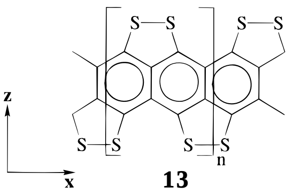
Figure 3. Band structure (left) and density of states showing π (p_y) orbital contribution (right) of *trans*-polydithioquinone (**11**). The highest occupied and lowest unoccupied π bands are shown with arrows. The Fermi level is indicated by dotted lines.

Chart 1



The bond lengths chosen match those in polyacetylene.[26] The resulting band structure and the contribution of the π orbitals to the DOS for **11** are shown in Figure 3; the electronic structure of **10** is nearly identical.

Not much happens to the electronic structure of our polymer, even though the symmetry of both **10** and **11** is reduced, compared to the idealized polymer. There is greater splitting of the bands near the Fermi level (π_4, π_5, and π_6), but the increased splitting is still relatively small. The sulfur p_x bands still cross the Fermi level, since the distortion really does not affect the sulfur sublattice.



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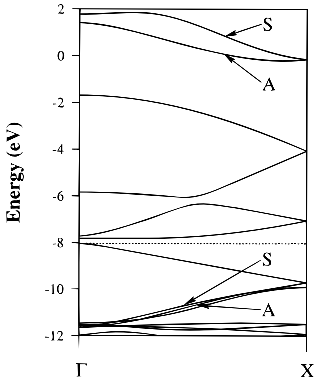

Figure 4. Band structure of the *anti* isomer (**13**) of polydithioquinone. The Fermi level is denoted by the dotted line. S p_x bands are labeled by symmetry (see discussion below).

It has been shown for a similar distortion of polyacene[22] that the net stabilization involved is typically small. In the case of polydithioquinone, we found both isomers (**10** and **11**) to be stabilized by approximately 0.011 eV per repeat unit compared to the idealized polymer. Our calculations also show that the total energy values for **10** and **11** differ by approximately 0.003 eV per repeat unit; given the limitations of the extended Hückel method, we just cannot judge which of the two isomers would actually be the more stable one.

Distortions of the Sulfur Sublattice. The way we choose to approach distortions **12** and **13** is to leave the carbon sublattice unchanged in its idealized geometry and “rotate” the sulfur atoms around the y-axis toward each other. In doing so, we bring sulfur p_x orbitals closer together, which facilitates their interaction. Sulfur—sulfur π interactions between cells are also affected.

As the sulfurs move to pair up, the repeat unit is doubled and the Brillouin zone halved. The bands of the idealized polymer will be “folded back”[25]—thus, two half-filled S p_x bands form four: two which are now filled and two which are empty. The interaction splits these bands near the new X, so that the filled ones are stabilized and the unfilled are destabilized. A gap opens up between these bands where the distortion has the most effect—at the new X, the midpoint of the former Brillouin zone.[27]

Two different isomers can be created by distortion of the sulfur sublattice; we term these “*syn*” (**12**) and “*anti*” (**13**). The band structure for the *anti* isomer is shown in Figure 4; the S p_x bands are labeled according to their symmetry properties (S for symmetric, A for antisymmetric) with respect to rotation around the 2_1 screw axis. (The conventional definition of a Fermi level is of the energy halfway between the top of the valence band and the bottom of the conduction band. We use a somewhat unconventional definition (of course, identical with the

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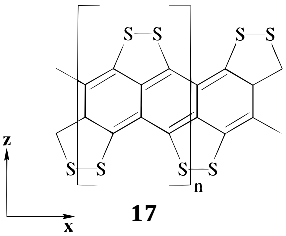
(26) Yannoni, C. S.; Clarke, T. C. *Phys.Rev. Lett.* **1983**, *51*, 1191.

(27) It is relative to the bands of the *old* unit cell (C_4S_2) that a gap opens up at X. There are still symmetry-enforced degeneracies at X in the Brillouin zone of the new, distorted polymer, due to the 2-fold screw axis remaining in the C_8S_4 polymer (**13**).



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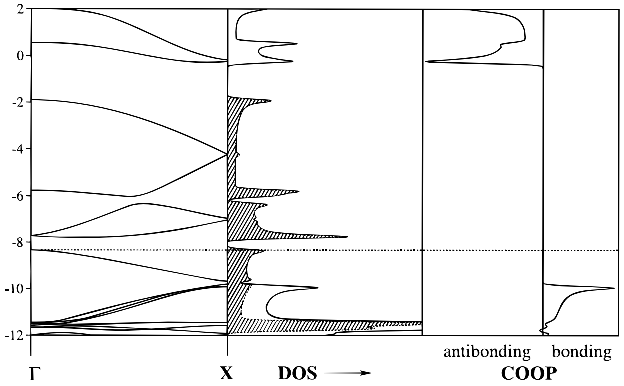

Figure 5. Band structure (left), density of states with a projection of all the π orbitals (middle), and intercell S p_x−S p_x COOP curve (right) of polydithioquinone distorted as in **17**. The average overlap population at the Fermi level is 0.44. The Fermi level is shown with dashed lines, S p_x bands are indicated with arrows. Note that the finite density of states in the DOS curve at the Fermi level is an artifact of curve-fitting; the actual value of the density of states at that energy is zero, as seen in the band structure.

usual one for the case of a metal) of the highest occupied crystal orbital; for an insulator or semiconductor as seen in Figure 4, this would be the top of the valence band.) Only the *anti* isomer's band structure is shown, because the electronic structures, and total energies, of both isomers are very similar.

Although several π bands carry considerable contributions from the sulfur atoms, they are not as strongly perturbed by the distortion; the changes in the π bands account only for some 10% of the net change in the total energy of the polymer.

Both isomers reach an energy minimum at a sulfur rotation angle $\Theta = 8.0°$, which places the nearest sulfurs only 1.95 Å apart—significantly shorter than a standard S−S single-bond length (2.04 Å). The net stabilization calculated is quite large, roughly 0.78 eV per C_4S_2 unit relative to the idealized polymer. The *anti* isomer has the lower total energy; it is 0.03 eV per repeat unit below the *syn* isomer. Again, we cannot trust our calculations for such small energy differences.

Distortions of Both Carbon and Sulfur Sublattices. Now we consider polymers **14**−**17**. All four isomers are calculated to be at their most stable for $\Theta = 8.0°$ (S−S bond distance equal to 1.95 Å), with their total energies approximately 0.79 eV per C_4S_2 unit below that of the idealized polymer. Recall that distortion of only the sulfur sublattice (**12** and **13**) results in stabilization by ~0.78 eV.

Figure 5 shows the band structure (left) and DOS contribution of all the π orbitals (middle) for one of the isomers (**17**). Our calculations indicate that it is the most stable structure of all considered, if only by a little. As one can see, none of the bands intersects the Fermi level; a complicated set of distortions in the carbon and sulfur sublattices has resulted in a modest bandgap.

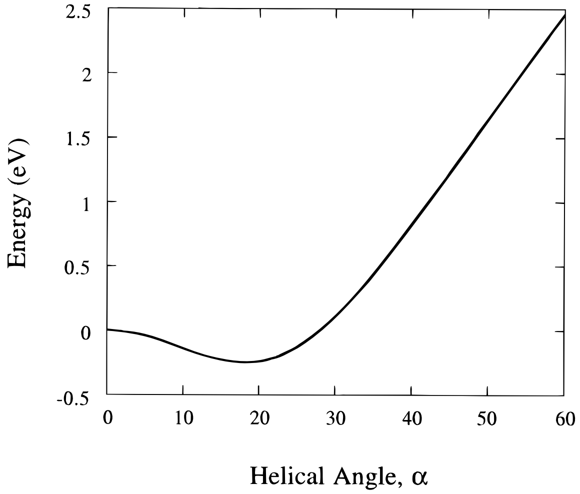

Figure 6. Total energy per C_4S_2 unit for the helically distorted polydithioquinone as a function of the helical angle α. Energies are given relative to the undistorted polymer. The curve has been fit to 23 data points.

Because of the pairing distortion, the S p_x bands are split and moved well above and below the Fermi level; the frontier bands now are π in character, as the projected DOS confirms. These π bands are also pushed apart, opening a bandgap of 0.44 eV at the Fermi level. The S p_x−S p_x intercell COOP curve (Figure 5, right) shows how far apart the S p_x bands have split. There are now two filled bonding and two empty antibonding sulfur p_x bands, corresponding to quite localized S−S bonds.

Helical Distortion

Planar distortions are not the only ones available to polydithioquinone. Breaking planar symmetry to form, for example, a helical isomer will lead to strong σ−π mixing, and that may be stabilizing. Such distortions have been extensively studied for polyketone and polyisocyanides,[28,29] as well as for polythiene.[18] In all these systems, distortion into a helix indeed causes energetically favorable mixing of σ and π bands; for polyketone and polyisocyanides, it leads to the most stable conformations. For polythiene, however, sulfur p_x and C−C π interactions (which are stabilizing for the planar conformation) compete with the σ−π mixing; as a result, the net energy of the stable helical isomer is only slightly lower than that of undistorted polythiene.

Idealized planar polydithioquinone, like polythiene, features significant bonding interactions between the valence p_x orbitals of its linear sulfur chains; its carbon π system also plays a role in stabilizing the planar conformation. Here too, it would require energetically very favorable σ−π mixing in a helical distortion to compensate for the loss of π and S p_x stabilization.

We consider only helixes where C−S bonds are perpendicular to and pointing radially away from the helical axis. The axis runs through the middle of the hexagonal units of the polymer and is parallel to the direction in which the polymer extends. The parameters of the helix (helical angle and radius) are defined in the earlier work on polythiene.[18] We assume, as for

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(28) Cui C.-X.; Kertesz, M. *Chem. Phys. Lett.* **1990**, *169*, 445−449.
(29) Kollmar, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230−8238.

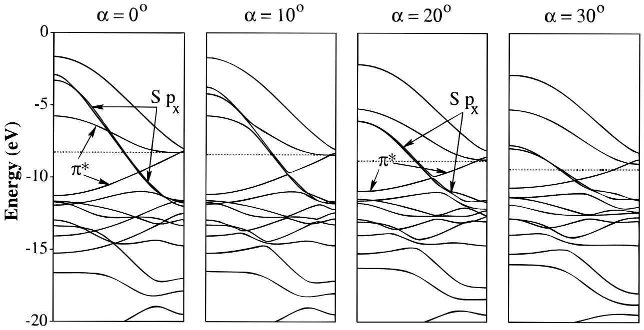
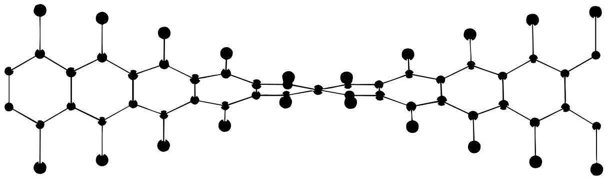


Figure 7. Band structures of helically distorted polydithioquinone at several values of the helical angle α. The Fermi levels are indicated by dashed lines. The π and S p_x bands are specifically labeled.

the idealized polymer, that all C−C distances are equal, and both C−C−C and C−C−S angles are equal to 120°. A helix then can be uniquely specified by three structural parameters: C−C and C−S bond lengths, and the helical angle. We assume bond lengths as in idealized polydithioquinone, 1.40 and 1.70 Å, respectively, and leave the angle freely varying between 0° and 180°. Figure 6 shows the total energy of the polymer as a function of the helical angle.

We find in our calculations a single minimum centered at about $\alpha = 18°$, with the total energy 0.25 eV below that of the planar idealized isomer. This structure is shown in **18**. If the twist per C_4S_2 unit is exactly 18°, the helix completes a full turn after 10 such units, i.e., the polymer has ten−fold helical symmetry.



18

In Figure 7 the band structures for different helicities are shown. The Brillouin zone is the same size as for the idealized polymer, because we employ the screw-axis symmetry in defining our unit cell.[30] A single C_4S_2 unit suffices; hence there are only 24 bands in the band structure.

At $\alpha = 0°$, the band structure is identical with that one shown earlier in Figure 1. As the helical angle increases, the planar symmetry of the polymer is destroyed, and its σ and π bands may mix; indeed, the S p_x bands have a number of avoided crossings with the π bands at nonzero values of α.

The effect of increasing helicity on the bands is similar to that described earlier for polythiene. The most significant feature is the "flattening" of S p_x and π bands. In the planar configuration, sulfur p_x orbitals "point" directly at each other, resulting in wide S p_x bands. As the helical angle increases, the p_x orbitals move apart and rotate so that they no longer point at each other; their overlap, and the corresponding bandwidth, decreases. Similarly, the π orbitals are moved out of their perfect parallel alignment in the helical isomer, also resulting in narrower bands. As the bands flatten, S p_x antibonding states are lowered considerably in energy, while the bonding ones are raised slightly.

The lowering of antibonding S p_x states causes depopulation of the π^* bands, which results in net stabilization. This can be seen in the C−S overlap population, which increases with the helical angle: at 10°, it equals 0.86; at 20°, 0.87; and at 30°, 0.88. However, the "flattening" of the bands lower in energy raises the total energy of the polymer at higher helical angles (a phenomenon observed also in helical distortions of polythiene[18]). This process opposes stabilization and eventually prevails over it for $\alpha > 18°$.

The net result of the distortion is a minimum energy conformation for helical polydithioquinone near $\alpha = 18°$. This stable helical isomer has a longish nearest-neighbor S−S distance of 2.55 Å, and an S−S average OP of 0.19, which is only slightly lower than the value of 0.22 calculated for the planar polymer. Note that a bandgap does not open at the Fermi level. Thus helical polydithioquinone should be conducting. However, the total energy of this isomer is still 0.54 eV higher than that of the most stable planar distorted isomer (**17**). We can characterize the drive toward helical distortion in polydithioquinone, and the extent of helicity in the most stable helical isomer, as relatively moderate, much as we found earlier for polythiene. We have not yet examined whether any of the localized-bond structures of the type **14**−**17** are likely to undergo helical distortions. We believe these distortions are likely to occur to a moderate extent in such structures too and may further stabilize them.

Conclusions

Polydithioquinone is a hypothetical carbon−sulfur ladder polymer related to both thiothiophthene and tetrathiotetracene. In the idealized planar structure, the polymer exhibits considerable S−S bonding and is best represented by resonance structure **7**, with multicenter electron-rich S−S bonding extending along the sulfur sublattice. A number of bands, namely two sulfur p_x and two C−S π^* antibonding, are half-filled; these drive the idealized polymer toward pairing distortions in both carbon and sulfur sublattices. The geometry of polydithioquinone also allows for a great variety of distortions; every one of those we have examined is found to be more stable than the idealized polymer. Helical distortions are also available as a means of stabilizing the polymer; we find a beautiful 10−fold helical isomer minimum for the idealized polydithioquinone.

While the driving force for distortions is clear, their actual extent in the polymer is difficult to predict, given the approximate nature of extended Hückel calculations. Clearly, sulfur pairing is much more productive in this respect than the carbon sublattice distortions. We think it is very likely that the polymer will in reality assume a structure of the type illustrated by **14**−**17**, and will be a low bandgap semiconductor if undoped. In our calculations, we find **17** to be the most stable of such structures by a small energy margin.

Appendix 1

To understand the π bands of polydithioquinone, we have chosen to compare the polymer with *s-cis-*

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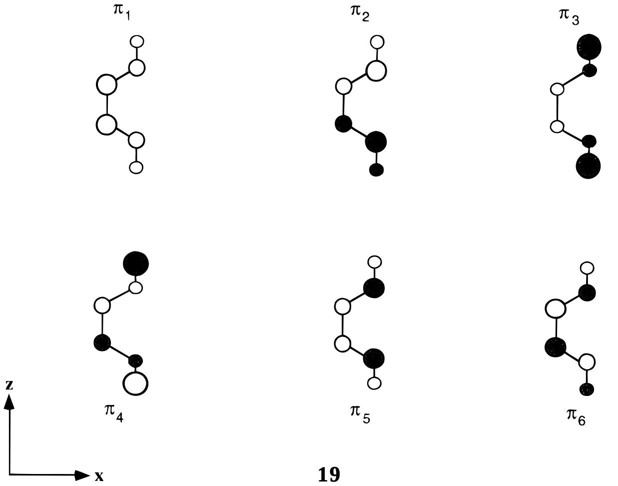
(30) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397−1412.

hexatriene, C_6H_8. The hexatriene π system should be similar to that of the polydithioquinone C_4S_2 repeat unit, since the energetic parameters of carbon 2p and sulfur 3p orbitals employed are quite close ($H_{ii} = -11.4$ and -11.0 eV, respectively). The π orbitals of hexatriene are shown in **19**.



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The molecule is aligned so that it lies in *xz*-plane; the view is from above the molecular plane, along the *y*-axis. The relative sizes of the wave function coefficients are shown approximately by the radii of the circles. The π orbitals of polydithioquinone are drawn explicitly at Γ and at X (Chart 2).

The similarity of polydithioquinone and hexatriene π orbitals is apparent at Γ. The slope of the π bands with wave vector *k* is determined by the nodal properties of these orbitals,[25] but the long-range sulfur–sulfur interactions also play an important role, as was discussed for polythiene in our earlier paper. Note that at X the π orbitals on the sulfurs (and on the carbons directly bonded to them) are decoupled from those on the interior carbons, due to the additional transverse planes of symmetry (shown in Chart 2 by dashed lines) which appear at that *k*-point. This effect is known for many ladder polymers of this type and has been discussed in detail earlier for polyacene.[22] Also notice that π_2 and π_3, as well as π_5 and π_6, are very nearly degenerate at X—it is only distant 1,4-interactions that distinguish these orbitals. However, EHT is an approximate method; we are sure that π_4, π_5, and π_6 lie close in energy at X, but we cannot be absolutely certain of their relative energy ordering.

Chart 2

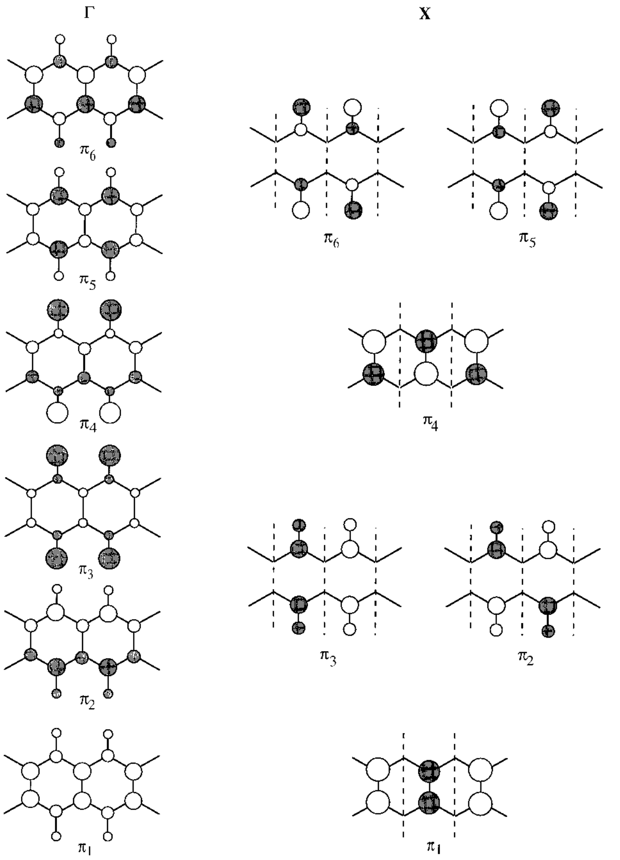

Table 1. Parameters Used in Extended Hückel Calculations[a]

atom	orbital	H_{ii} (eV)	ζ
C	2s	−21.4	1.625
	2p	−11.4	1.625
S	3s	−20.0	2.122
	3p	−11.0	1.827

[a] A 100 *k*-point set was used to calculate the average properties.

Appendix 2

Most of the extended Hückel[30,31] calculations for this work were carried out using the YAeHMOP software package,[32] freely available on the World Wide Web at http://overlap.chem.cornell.edu:8080/yaehmop.html.

The atomic parameters for our calculations were taken from the earlier work on polythiene;[18] they are listed in Table 1 (H_{ii}, orbital energy; ζ, Slater exponent).

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(31) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2872.

(32) Landrum, G. *YAeHMOP—Yet Another extended Hückel Molecular Orbital Package (V. 1.1)*, Ithaca, New York, 1995.