

## Polythiene, a Novel Hypothetical Carbon–Sulfur Polymer

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**Abstract:** We propose a hypothetical carbon–sulfur polymer (CS), which conceptually derives from both the experimentally known trithiapentalene molecule (TTP) and the theoretically suggested “polyketone”. Using the extended Hückel method, we examine the electronic structure of this system first in a planar conformation. The polytrithiapentalene formulation, with electron-rich multicenter S–S bonding and six electrons in the  $\pi$  system of each  $C_2S_2$  repeat unit, fits best the electronic structure calculated. The  $\pi$  band filling suggests both that the carbon sublattice will undergo a Peierls distortion and that the intriguing multicenter sulfur bonding of TTP carries over into the polymer; however, half-filled sulfur lone pair bands imply that a pairing distortion is likely in the sulfur sublattice too. We contrast this with planar polyketone, where there is no electronic reason for pairing but rather a driving force to distort into a helix. Studying the likely pairing distortions of carbon and sulfur sublattices in polythiene, we conclude that pairing of the carbons is marginally energetically favorable, whereas pairing of the sulfurs is strongly favorable. Two possible combinations of carbon and sulfur pairing compete for being the lowest-energy conformation. We examine helical (i.e., nonplanar) conformations and find an energy minimum for a very slightly twisted conformation. Finally we discuss the role, we think small, of 3d basis functions on sulfur.

Conjugated organic polymers have long been of interest because they are potentially conducting, superconducting, or magnetic, and may combine with these electronic features some of the proven useful mechanical properties of their nonconjugated analogues.<sup>1–3</sup> Polyacetylene is the archetypical example, being a low-band-gap polymer which becomes highly conducting upon doping.<sup>4</sup> Polythiophene and polypyrrole, two other currently popular polymers,<sup>4</sup> show smaller increases in conductivity when doped; their advantage is that they provide endless possibilities in terms of side chains and fused conjugated rings through which their electrical and mechanical properties can be tailored. These latter two also exemplify the important role that heteroatoms, particularly nitrogen and sulfur, play in current research on conjugated polymers. Another example is  $[SN]_x$ , a stunningly simple conjugated polymer which is metallic at room temperature and displays superconductivity at low temperatures.<sup>5</sup>

In this paper we examine the electronic structure and likely distortions of an as yet unsynthesized conjugated organic polymer termed “polythiene”.

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(1) *Organic Conductors*; Farges, J.-P., Ed.; Marcel Dekker: New York, 1994. *Conjugated Polymers*; Brédas, J. L., Silbey, R., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1991. Whangbo, M.-H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982.

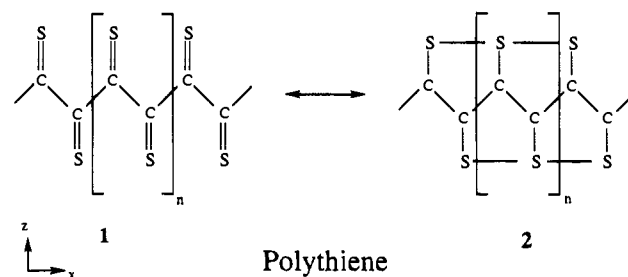
(2) Little, W. A. *Phys. Rev. A* **1964**, *134*, 1416–1424. Crayston, J. A.; Iraqi, A.; and Walton, J. C. *Chem. Soc. Rev.* **1994**, *23*, 147–153.

(3) (a) Korshak, Yu. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. N. *Nature* **1987**, *26*, 370–372. But see also: Miller, J. S. *Adv. Mater.* **1992**, *4*, 298–300. Miller, J. S. *Adv. Mater.* **1992**, *6*, 435–438. (b) For a theoretical study of ferromagnetism in polyaniline, see: Yoshizawa, K.; Takata, A.; Tanaka, K.; Yamabe, T. *Polym. J.* **1992**, *24*, 857–864. (c) For theoretical studies of ferromagnetism in poly(*m*-phenylenemethylene), see: Yoshizawa, K.; Hoffmann, R. *Chem.—A Eur. J.*, in press. Gregorius, H.; Baumgarten, M.; Reuter, R.; Tyutyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1653–1655. Hughbanks, T.; Kertesz, M. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 115–124. Yoshizawa, K.; Tanaka, K.; Yamabe, T. *J. Phys. Chem.* **1994**, *98*, 1851–1855.

(4) See for example: Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM '94), Seoul, Korea, 24–29 July 1994. *Synth. Met.* **1995**, *69*.

(5) Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6687–6693. Labes, M. M.; Love, P.; Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1. Greene, R. L.; Street, G. B.; Suter, L. J. *Phys. Rev. Lett.* **1975**, *34*, 577.

From one point of view, this polymer is simply the sulfur analogue of polyketone<sup>6–8</sup> and so is represented by **1**. But as we will show, there is another, quite different, perspective on the polymer, one peculiar to sulfur chemistry and iconically represented by **2**.<sup>9</sup> First we look at the electronic structure of



an idealized planar polythiene, comparing it to polyketone and model hypervalent sulfur systems; then we examine several likely distortions that retain planarity. Finally, we investigate possible helical structures. Consideration will be given to the role of d orbitals on sulfur.

## Idealized Polymer

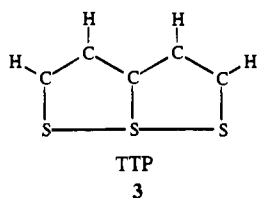
Polyketone is one parent structure of polythiene. But sulfur has its own chemistry, quite distinct from that of oxygen. The inspiration for polythiene derives from the intriguing orange-colored compound 1,6,6a $\lambda^4$ -trithiapentalene (“TTP”, **3**; no bonding implications in this drawing) with its unusual arrangement of linear, equidistant sulfur atoms (S–S = 2.36 Å) and

(6) Cui, C.-X.; Kertesz, M. *Chem. Phys. Lett.* **1990**, *169*, 445–449.

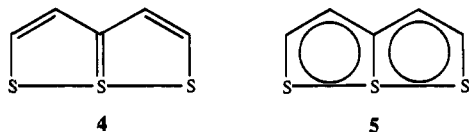
(7) Rubin, M. *Chem. Rev.* **1975**, *75*, 177–199

(8) Kroner, J.; Strack, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 220–221.

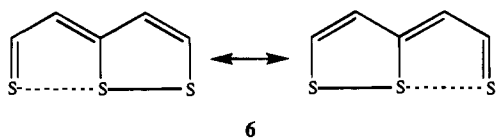
(9) An analogous chain made of boron and carbon (in place of carbon and sulfur, respectively) has recently been noted and analyzed as a component in rare earth metal boron carbides: Wiltkar, F.; Kahla, S.; Halet, J.-F.; Saillaird, J.-Y.; Bauer, J.; Rogl, P. *Inorg. Chem.* **1995**, *34*, 1248–1256. It is amusing to note the differences and similarities in the BC versus the CS polymer. Linear chains of main-group atoms have been seen elsewhere, too; see for example: Keszlér, D. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 118–124. The authors describe the electronic structure of NbPS, which contains Peierls-distorted linear chains of P atoms.



its naphthalene-like 10-electron  $\pi$  system.<sup>10,11</sup> Various resonance structures may be drawn for the molecule:<sup>12</sup> **4** has a hypervalent sulfur, while **5** emphasizes (in a very nonspecific

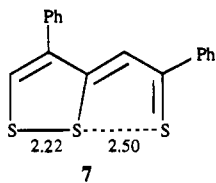


way) the 10-electron  $\pi$  system. Still another representation, **6**, indicates the "single-bond no-bond resonance"<sup>13</sup> in TTP; in molecular orbital language the critical S-S-S interaction would be termed an "electron-rich three-center bond".<sup>14</sup>



Early extended Hückel calculations by Gleiter and Hoffmann found that inclusion of 3d basis functions on sulfur was necessary to rationalize the symmetrical sulfur configuration in TTP.<sup>14</sup> Later HF-SCF studies found that 3d basis functions did not affect the bonding other than as polarization functions; however, these calculations still could not satisfactorily explain geometrical details of the structure.<sup>15</sup> High-level *ab initio* studies on TTP<sup>16</sup> and the related dioxo compound<sup>17</sup> indicate that only electron correlation can account for the stability of the symmetrical, nonclassical structure over the pairing of two sulfur atoms. Correlation may therefore play an important role in polythiene.

Trithiapentalene is not a curiosity, but instead a system with a rich chemistry.<sup>18</sup> Numerous substituted derivatives are known, all of which are nearly planar and have S-S distances in the range 2.1–2.6 Å, e.g., **7**.<sup>19</sup> Related tetra- and pentasulfur



compounds are also nearly planar and have S-S distances from about 2.0 to 3.0 Å, e.g., **8** and **9**.<sup>18,20</sup> Comparing these distances to the S-S single bond distance of 2.08 Å and the estimated van der Waals contact of 3.70 Å,<sup>21</sup> there can be no doubt that significant S-S interactions are present in all these substances.

(10) Hansen, L.; Hordvik, A. *Acta Chem. Scand.* **1973**, *27*, 411–420.

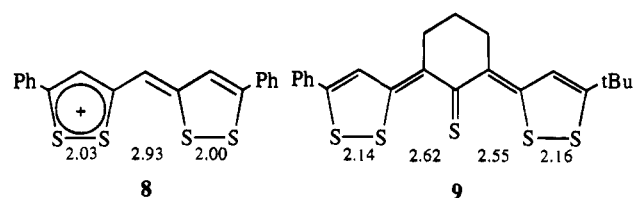
(11) Spanget-Larsen, J.; Erting, C.; Shim, I. *J. Am. Chem. Soc.* **1994**, *116*, 11433–11435.

(12) Gleiter, R.; Gygas, R. *Top. Curr. Chem.* **1976**, *63*, 49–87. This is an excellent review of trithiapentalene and related "no-bond" resonance structure compounds.

(13) Sletten, J. *Acta Chem. Scand.* **1971**, *25*, 3577–3592.

(14) Gleiter, R.; Hoffmann, R. *Tetrahedron* **1968**, *24*, 5899–5911.

(15) Palmer, M.; Findlay, R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1885–1893. See also Calzaferrri, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 559–566.



By examining the dependence of S-S bond lengths on the substituents on carbon, it was found that the S-S interaction is highly sensitive to minor changes in molecular structure.<sup>22</sup>

This family of compounds suggests an alternative valence structure to polymer **1**, namely, planar extended system **2**. We draw **2** for the moment as a resonance structure of **1**. The relationship of these two structures to each other is more complex and will be explored in detail below.

Consider geometrics first: in **2** we have a kinked carbon backbone, like that in polyacetylene, meshing perfectly with two offset, linear chains of sulfur. Assuming a planar geometry having C-C = 1.40 Å and a C-C-C angle of 122°, the S-S distance is thus fixed at 2.45 Å and our only structural degree of freedom is the C-S bond length. The range of observed C-S distances in TTP-related compounds is 1.68–1.78 Å, indicative of partial double-bond character (compare C-S = 1.71 Å in thiophene). We have chosen 1.70 Å for all C-S bonds.

The localized C-S double bonds in resonance structure **1** imply a butadiene-like unit cell in which there are four  $\pi$  orbitals per cell, two of which are filled. The number of filled  $\pi$  orbitals in delocalized resonance structure **2** is not obvious. However, we will show that **2** implies six electrons in the four  $\pi$  orbitals, i.e., three out of the four orbitals (bands) of a C<sub>2</sub>S<sub>2</sub> unit filled. We will see which of these bonding pictures best matches calculational results.

### Electronic Structure of Polythiene

We carried out extended Hückel band calculations (details in the Appendix) on polythiene in the geometry specified. Figure 1 (middle) shows the band structure of polythiene; four bands which we will not discuss lie above the energy window chosen. The Fermi level, at -8.19 eV, is in the middle of two bands and near the meeting point of two others: this structure would be conducting. Note how the bands pair up at X. This results from the 2<sub>1</sub>-screw axis of our polymer; all the bands are "folded back".<sup>23</sup> Using helical symmetry, these bands may actually be "unfolded", which will be shown below in the section on helical isomers of polythiene.

On the way to understanding the electronic structure of the polymer, it is instructive to examine its carbon and sulfur sublattices. (Note that the polymer chain extends along the *x* axis, as it will throughout this paper. The planar polymer lies in the *x-z* plane.) The sulfur sublattice consists of two very weakly interacting linear chains. Because its electronic structure is important in the subsequent polymer, we take some space

(16) Cimraglia, R.; Hofmann, H.-J. *J. Am. Chem. Soc.* **1991**, *113*, 6449–6451.

(17) Saebø, S.; Boggs, J. E.; Fan, K. *J. Phys. Chem.* **1992**, *96*, 9268–9272.

(18) Lozac'h, N. In *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Pergamon: New York, 1984; Vol. 6, pp 1049–1070.

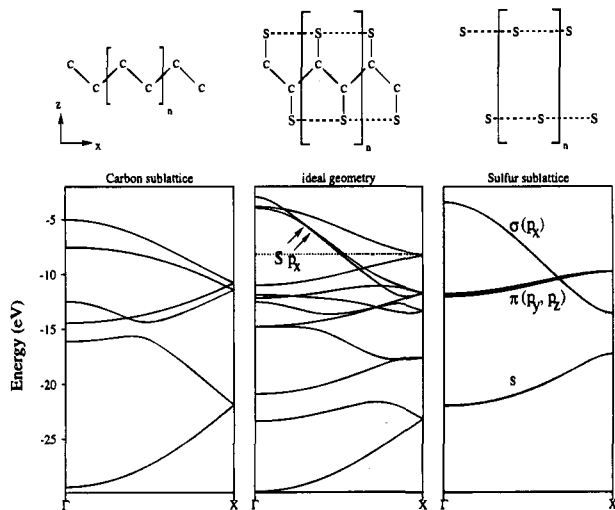
(19) Hordvik, A.; Sletten, E.; Sletten, J. *Acta Chem. Scand.* **1969**, *23*, 1852–1870.

(20) Sletten, J. *Acta Chem. Scand.* **1970**, *24*, 1464–1466.

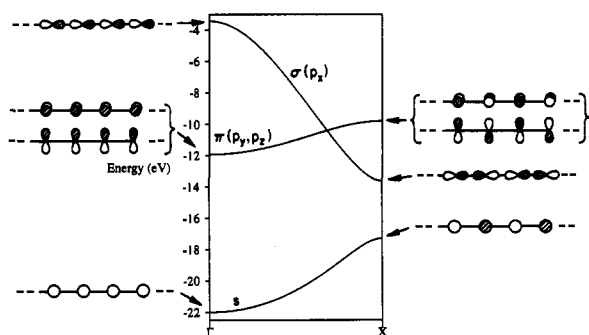
(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1989.

(22) Sletten, J. *Acta Chem. Scand. A* **1974**, *28*, 499–506.

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



**Figure 1.** Band structures of (left) the carbon sublattice of polythiophene, (middle) the whole polythiophene, and (right) the sulfur sublattice of polythiophene. A dotted line indicates the Fermi level. The arrows point to the polymer bands which are derived from sulfur  $3p_x$  orbitals.



**Figure 2.** Band structure of a single linear chain of equidistant sulfur atoms, 2.45 Å apart, showing the orbitals at  $\Gamma$  and X.

here to discuss it in detail. The sulfur sublattice is shown at the top right of Figure 1.

Consider first a single S chain. It has the characteristic band structure sketched in Figure 2. Note the  $s$  bands "running up" from  $\Gamma$ , the less dispersed  $\pi$  bands ( $p_y, p_z$ ) behaving similarly. The  $p_x$  band "runs down", crossing the  $\pi$  bands. The situation depicted in Figure 2 is for relatively large S-S separations (2.45 Å); at shorter distances the  $s$  and  $p_x$  bands would mix strongly, such that the resulting bands would be better described as  $\sigma$  and  $\sigma^*$ .<sup>24</sup>

The complete sulfur sublattice of polythiophene contains two such chains. In the temporary absence of the centering carbon atoms, these chains interact only very, very weakly. This is the origin of the right side of Figure 1; the bands are all doubled in number relative to Figure 2. The interchain interaction is so weak that the bands appear as single bands even if they are really doubled. Only in the  $p_z$  bands do we see the interaction at the resolution of this energy window.

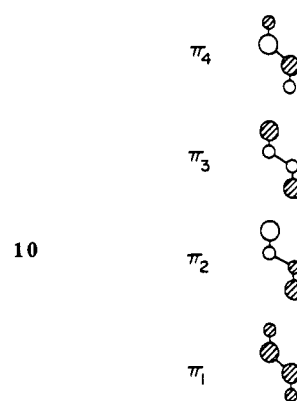
Notice the important  $p_x$  bands in the sulfur sublattice. Polythiophene also has a pair of nearly degenerate bands running down from  $\Gamma$  to X which cross the Fermi level, marked with arrows in Figure 1 (center). These bands are almost entirely sulfur  $p_x$ , with now a slight degeneracy-breaking admixture of carbon  $p_x$  and  $p_z$ . These bands can be seen at about the same energy as the  $p_x$  bands in the sulfur sublattice. We will return to these important bands later.

The bands of the kinked polyacetylene-like carbon sublattice

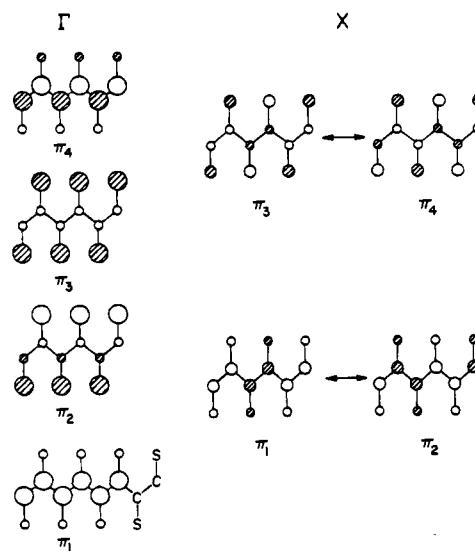
(24) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University: New York, 1995.

(Figure 1, left) have been explained elsewhere.<sup>25</sup> The lowest four bands of polythiophene derive from the two lowest bands of the carbon sublattice ( $\sigma$  bands: mostly  $s$  with some  $p_x$  and  $p_z$  near the top) and the two  $s$  bands of the sulfur sublattice, whose degeneracy is now lifted via interaction with carbon. The two carbon  $p_z$  bands interact with the two sulfur  $p_z$  bands to form two C-S  $\sigma$  bonding bands in the energy range  $-11$  to  $-15$  eV, and two C-S  $\sigma^*$  antibonding bands from 2 to 18 eV.

The  $\pi$  bands are best understood in reference to butadiene orbitals, perturbed by the special geometrical features of this polymer. Sulfur  $p$  orbitals in our calculations are assigned an  $H_{ii}$  of  $-11.0$  eV, which is very close to the  $-11.4$  eV used for carbon  $p$  orbitals. Therefore, an S=C-C=S system has very similar  $\pi$  orbital behavior to a C=C-C=C system. The  $\pi$  orbitals of butadiene are sketched in 10 in the geometry appropriate to the polymer. Figure 3 repeats the band structure of polythiophene, now in a magnified energy window from  $-15$  to  $-2$  eV.



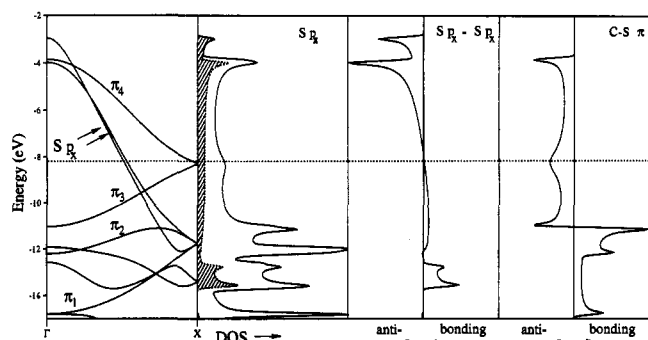
A strict  $\sigma$ - $\pi$  separation is maintained in the planar polymer; the  $\pi$  orbitals are specifically labeled. As in butadiene, the following orbital trends are present (compare 10 and 11; the



**11**  
 $\pi$  orbitals of polythiophene at  $\Gamma$  and at X

latter shows the approximate form of the crystal orbitals at  $\Gamma$  and X):  $\pi_1$  is bonding between all atoms and is concentrated on the center two carbons.  $\pi_2$ , concentrated on the outer two atoms, has one node (in addition to the node in the plane of the

(25) Hoffmann, R.; Janiak, C.; Kollmar, C. *Macromolecules* **1991**, *24*, 3725-3746.

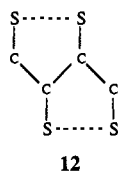


**Figure 3.** (Far left) Band structure of polythiene in the energy window  $-15$  to  $-2$  eV, with the  $\pi$  bands and the two bands derived from sulfur  $p_x$  orbitals labeled. (Second panel from left) Density of states of polythiene showing the sulfur  $p_x$  contribution (lined region). (Second panel from right)  $S p_x-S p_x$  COOP curve. The average overlap population is 0.11. (Far right) Carbon  $p_y$ -sulfur  $p_y$  (i.e., the C-S  $\pi$  interaction) COOP curve. The average C-S  $\pi$  overlap population is 0.05.

polymer), and is C-S bonding and C-C antibonding.  $\pi_3$ , also concentrated on the outer two atoms, contains two nodes and has C-S antibonding character and C-C bonding character.  $\pi_4$ , concentrated on the center two atoms, has three nodes, and is both C-S and C-C antibonding.

Another way to look at these bands is to think of them as just two bands, folded back at  $X$ : a C-S  $\pi$  band ( $\pi_1$  and  $\pi_2$ ) and a C-S  $\pi^*$  band ( $\pi_3$  and  $\pi_4$ ). In Figure 3, a crystal orbital overlap population (COOP) curve (which is an overlap population-weighted density of states<sup>23</sup>) for the  $C p_y-S p_y$  interaction confirms that the lowest two  $\pi$  bands are C-S bonding in character, while the upper two are C-S antibonding. Note that, at  $\Gamma$ , the polythiene orbitals are substantially more localized (on C or S) than the orbitals of the parent diene.

The analysis presented above assumes dominant C-C and C-S bonding. The detailed features of the  $\pi$  bands are determined by their butadiene parentage and by their linkage in the polymer, which is via both the carbons and the sulfurs (see the two interactions emphasized as dashed lines in **12**).



For instance, one might have thought that the band generated from  $\pi_2$  should run "down", if its slope were determined by C-C interactions alone. But in fact band  $\pi_2$  runs up because it is concentrated on the sulfurs across most of the zone. C-C interactions between cells at  $\Gamma$  of band  $\pi_2$  are antibonding, but the wave function has much larger coefficients on sulfur ( $\pi_2$  at  $\Gamma$  is 92% sulfur) so the dominant interaction is sulfur-sulfur bonding between cells. As  $k$  increases, the sulfur-sulfur interaction becomes antibonding, which would tend to make the band run up. However, the ratio of sulfur to carbon coefficients decreases with increasing  $k$  until at  $X$  the carbon atom accounts for 65% of this orbital and sulfur only 35%. This accounts for the downturn of the band near  $X$ .

Bands  $\pi_3$  and  $\pi_4$ , which are C-S antibonding throughout the zone, are important because the Fermi level lies almost exactly at their meeting point at  $k = \pi/a$ . As **11** shows, at  $X$  each carbon has one bonding and one antibonding  $\pi$  interaction to a neighbor carbon. This suggests that the carbon chain of polythiene may behave exactly like the carbon chain of polyacetylene and

undergo a Peierls or pairing distortion. More details about that will be discussed later. Note that, at the Fermi level, the S-S  $\pi$  interaction (between cells) is antibonding.

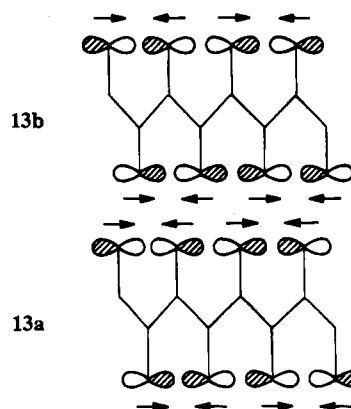
We see in Figure 3 an important result: *three of the four  $\pi$  bands are filled in polythiene*. Band  $\pi_3$  is C-S antibonding and filling it weakens the C-S bond, so the C-S double bond drawn for structure **1** is not an accurate picture of the bonding in the polymer. Certainly some degree of double-bond character exists, because the computed C-S overlap population (OP) of 0.81 is higher than a typical single-bond value (e.g., 0.65 in  $H_3C-SH$ ). Thus, the "nonclassical" (hypervalent) resonance structure **2**, with S-S bonding, is a more accurate representation of the polymer than a structure in which purely localized S-C double bonds exist.

There are two vital bands still to consider: the sulfur  $p_x$  bands running down from  $\Gamma$  to  $X$  which cross the Fermi level near  $k = \pi/2a$ . Figure 3 emphasizes the crucial bands (marked with arrows), and shows the contribution of the sulfur  $p_x$  orbitals to the density of states in a separate panel. Interaction with the carbon  $p_x$  bands splits the two sulfur  $p_x$  bands at  $\Gamma$ . As  $k$  increases, though, the S  $p_x$  bands mix to differing degrees with the carbon and sulfur  $p_z$  bands, which reverses the ordering and results in an avoided crossing near  $X$ .

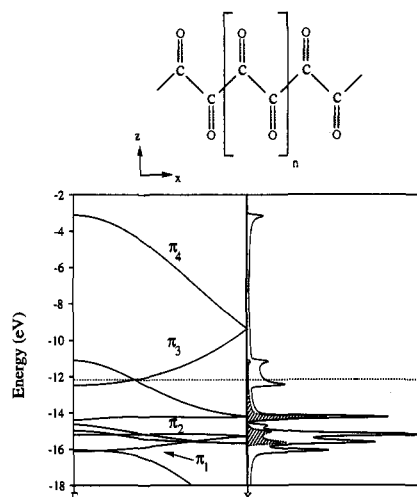
A COOP curve (second panel from the right in Figure 3) reveals that the bonding portion of the band is almost exactly filled, as reflected in the positive S  $p_x-S p_x$  overlap population of 0.11. This also supports the conclusion that resonance structure **2** is a better representation of polythiene bonding.

Because they are half-filled, the sulfur  $p_x$  bands are ripe for a Peierls distortion. Consider now just the symmetric (with respect to inversion)  $p_x$  band at  $k = \pi/2a$ . If we double the size of our unit cell from  $C_2S_2$  to  $C_4S_4$ , without perturbing the polymer, our Brillouin zone is halved and  $k = \pi/2a$  in the old zone becomes  $k = \pi/a$  (or  $X$ ) in the new zone. In order to conserve the number of orbitals, every  $k$  point in the halved zone now has twice as many orbitals. Doubling the unit cell and halving the Brillouin zone results in the bands being "folded". Note that we have not (yet) distorted the polymer, so the electronic structure has not changed; only our pictorial representation of it has changed.

Now, at the new  $X$ , there are two degenerate orbitals in the folded-back symmetric S  $p_x$  band. A pairing distortion leads to one combination being stabilized and one destabilized. If we pair the atoms as shown by the arrows in **13**, then **13a** would be lowered in energy because S-S bonding interactions are being made more bonding, while **13b** would be raised in energy



because antibonding interactions are being made more antibonding. Since only one of these two orbitals is filled, the net result is stabilization. There are in fact two  $p_x$  bands, one



**Figure 4.** Band structure (left) and density of states (right) of planar polyketone showing the contribution of oxygen  $p_x$  orbitals. The  $\pi$  bands are labeled, and the Fermi level is indicated by the dotted line.

symmetric and the other antisymmetric with respect to inversion. So the net stabilization from pairing will be twice as large.

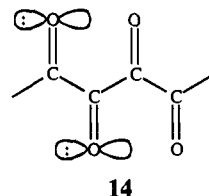
To summarize the results so far, (1) the polythiène polymer is predicted to be conducting, (2) 3/4 of the  $\pi$  bands are filled, implying that a delocalized  $\pi$  system (six electrons per  $C_2S_2$ ) as in resonance structure **2** is the best representation of the electronic structure of the polymer, (3) the Fermi level lies near the meeting of two  $\pi$  bands, implying that a Peierls distortion in the carbon backbone is likely, and (4) the Fermi level also intersects two sulfur  $p_x$  bands at roughly half-filling, implying that a Peierls distortion of the sulfur chains is likely. We will probe these qualitative conclusions in some detail below; the half-filling of several different types of bands is a harbinger of a complex set of distortions.

### Polyketone

Before proceeding with analysis of the possible deformations, though, let us compare polythiène with polyketone. Polyketone is predicted to distort to a helical conformation,<sup>6,8,26</sup> but we will look at the planar system for comparison. The band structure and density of states (DOS) for this oxygen analogue of polythiène are shown in Figure 4; we have chosen the C–C–C angle at  $122^\circ$  and the C–O distance at 1.24 Å. Cui and Kertesz<sup>6</sup> have previously calculated an EH band structure of planar polyketone which is qualitatively very similar to Figure 4; differences arise because they used an unspecified MNDO-AM1-optimized geometry which likely has a longer C–C bond length (we used 1.40 Å to facilitate comparison with polythiène) and possibly a different C–C–C angle.

While of necessity there are similarities in the band structures of polythiène and polyketone, it is the differences that are most striking. Note the four  $\pi$  bands, the bottom two low-lying and C–O bonding (as a COOP curve not shown here indicates) and the top two mostly unfilled and C–O antibonding. The two  $p_x$ -type bands are now best described as oxygen lone pairs (see **14**). These lie at much lower energy in polyketone than in polythiène; they are centered around the oxygen  $2p H_{ii}$  of  $-14.8$  eV and lie mostly below  $\pi_3$ . Hence, the oxygen lone pair bands are almost filled, while the C–O antibonding states are mostly empty. Planar polyketone, then, is best described by a valence structure such as **1**, which has localized C=O double bonds.

(26) Tetra- and pentaketones have been synthesized, and are indeed found to be helical. See: Gleiter, R.; Dobler, W. *Chem. Ber.* **1985**, *118*, 1917–1926. Gleiter, R.; Litterst, E.; Oeser, T.; Irngartinger, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1048–1050.

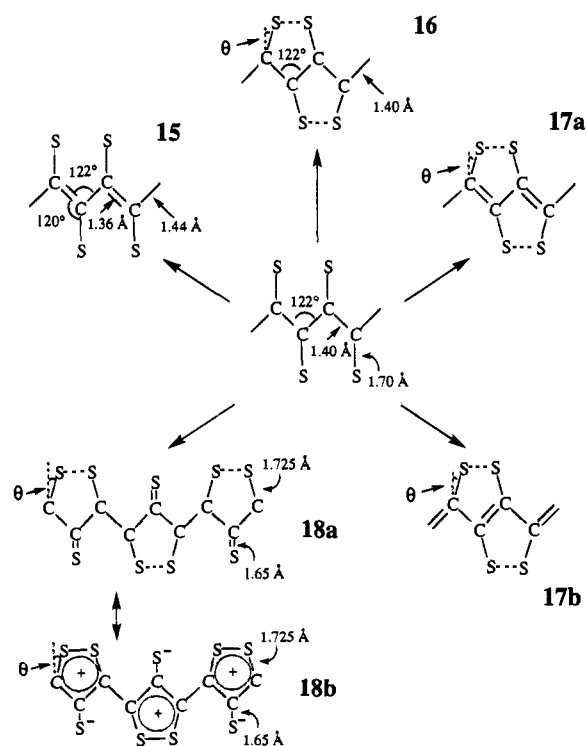


There is in polyketone some repulsive interaction between the oxygen lone pairs, leading to the higher of the two lone pair bands coming above  $\pi_3$  near  $\Gamma$ . This repulsion provides some impetus for distortion to a helical structure in which the oxygen atoms are much farther apart; such a distortion minimizes O–O repulsive electrostatic interactions, as well as repulsive electrostatic ones. But it is  $\sigma$ – $\pi$  mixing between  $\pi_3$  and the lone pair band, possible once planarity is removed, which contributes most to the stability of the helix.<sup>6</sup>

In polythiène the S  $p_x$ –S  $p_x$  interaction is net bonding, and thus there is no reason for helical distortion. From an orbital perspective, the S lone pairs are participating in electron-rich multicenter bonding, which is not destabilizing. As we will see,  $\sigma$ – $\pi$  mixing does not favor the helical conformation of polythiène, but the  $p_x$  bands still give reason to suspect a helically distorted isomer may be stable for polythiène as well.

### Planar Distortions of Polythiène

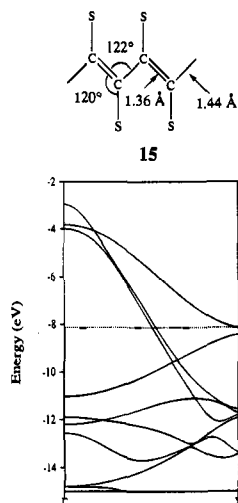
A great variety of distortions are available to polythiène. This is indicated by its electronic structure, which as we saw has several distinct half-filled bands. Structures **15**–**18** summarize some of the geometrical richness we looked at. Let us examine them in turn.



(1). **Distortion of the Carbon Sublattice.** Keeping the sulfur sublattice unaltered, we can distort the carbon backbone in a classical Peierls fashion, making alternate C–C bonds short (1.36 Å) and long (1.44 Å), as in **15**.<sup>27 28</sup>

Such a Peierls distortion removes the  $2_1$ -screw axis, splitting the degeneracy of all bands at X. Figure 5 shows the results.

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



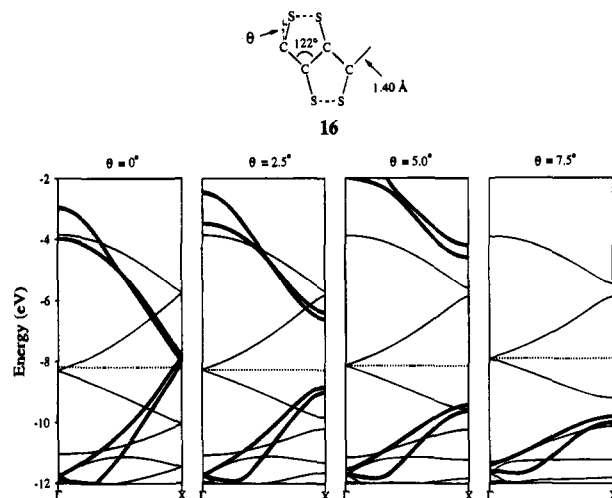
**Figure 5.** Band structure of polythiene distorted as shown in **15**. The dotted line indicates the Fermi level.

Bands  $\pi_3$  and  $\pi_4$ , which were degenerate at  $X$ , have now split apart analogously to the  $\pi$  bands of polyacetylene.<sup>27</sup> However, the two S  $p_x$  bands remain essentially unaltered, and they contribute some density of states at the Fermi level. Distortion of the carbon backbone in polythiene does not lead to a band gap opening up for the polymer as a whole, only for that substructure (the polyacetylene chain) where the deformation takes place. The calculated stabilization from this distortion is, in contrast to the case of polyacetylene, negligible.

(2). **Distortion of the sulfur sublattice.** As we reasoned above, a Peierls distortion of the sulfur chains should be, and indeed is, strongly favored. Keeping the carbons equidistant and fixed, we “rotate” the sulfurs as pictured in **16**. Essentially the same mechanism is at work here as for the carbon distortion: a half-filled band is split into a filled bonding band which moves down in energy and an unfilled antibonding band that moves up. However, in this case the unit cell is doubled (to  $C_4S_8$ ), the bands are folded back yet again (see left side of Figure 6), and the gap opens up where it has maximum effect—in the middle of the S  $p_x$  bands. Note that the “degeneracy” at the Fermi level is accidental (these bands are actually separated by 0.0006 eV at the computed minimum energy conformation).

Figure 6 shows the evolution of the electronic structure of **16** with  $\theta$ . Notice how the gap that develops between sulfur  $p_x$  bands is larger than it was for the  $\pi$  bands in the carbon-based Peierls distortion (Figure 6). The sulfurs of the undistorted chain are located slightly beyond single-bond range from each other, so when they are moved, the short S–S distance approaches a single bond. This is very favorable energetically. Also, the sulfur  $p_x$  bands are strongly affected because the  $p_x$  orbitals extend out toward each other and have a much longer reach than two p orbitals interacting in a  $\pi$  fashion. So it makes sense that the pairing effect is much stronger for these  $\sigma$  bonding  $p_x$  orbitals than for  $\pi$  bonding  $p_y$  orbitals of distortion **15**.

(28) Up to now, we have used the value of 122° for the C–C–C or “squeeze” angle. In our calculations, the computed optimum angle is 126.5°, and the energy stabilization is 0.056 eV relative to the conformation at 122°. Electronically, however, the difference has little consequence: the S–S contact between cells moves from 2.45 Å at 122° to 2.50 Å at 126.5°, so the only significant change in the electronic structure is the subsequent narrowing of the S  $p_x$  band width. These bands remain half-filled, and the Fermi level remains very near the meeting point of the highest two  $\pi$  bands. Because there are no significant qualitative differences in electronic structure and we have already thoroughly examined the polymer at a squeeze angle of 122°, we will fix this angle at 122° for all further distortions—except where the carbon sublattice distorts. In those cases, the angle is in the range  $\sim 118.1$ –122°.



**Figure 6.** Band structure of the distorted polymer **16** for values of the sulfur rotation angle (defined in **16**) of 0°, 2.5°, 5.0°, and 7.5° in the energy window from –12 to –2 eV. The sulfur  $p_x$  bands are indicated by bold lines; the Fermi level is indicated by a dotted line.

A minimum energy is reached for  $\theta = 6.94^\circ$ , at a stabilization of 0.31 eV relative to the undistorted polymer. This geometry corresponds to a short S–S distance of 2.04 Å—pretty much a normal S–S single bond.

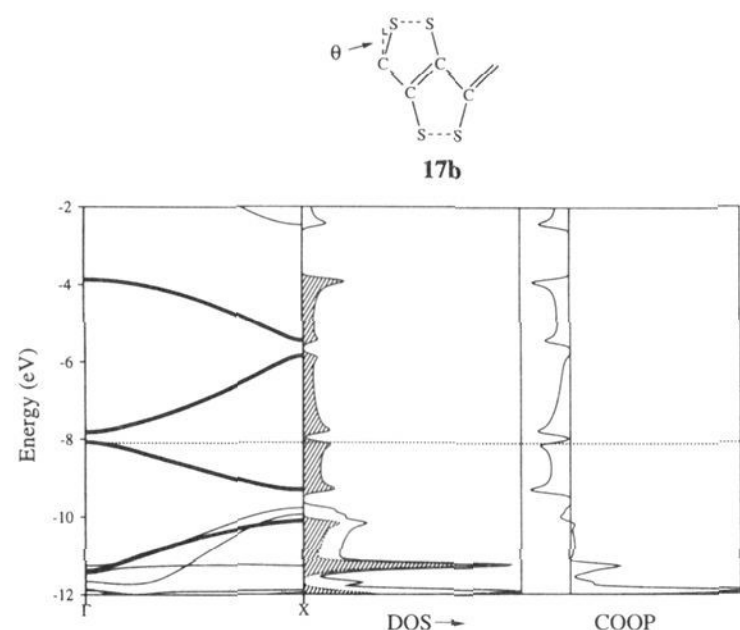
(3). **Distortion of Both Sulfur and Carbon Sublattices Together.** Now we will pair up the carbons, as in **15**, and simultaneously examine the energy as a function of the sulfur rotation angle  $\theta$ . Two alternative, isomeric pairing modes are possible: **17a** shows a pairing such that a single C–C bond exists at the common edge of two five-membered rings, while **17b** indicates the other possibility, a C–C double bond as a common edge of the two rings.

Both isomers reach their minimum energy around a sulfur rotation angle of 6.9°—about the same angle as for isomer **16**—with **17b** marginally more stable. This turns out to be the lowest energy distortion of all that we have considered, stabilized by 0.32 eV relative to the undistorted polymer **1**.

The stability of **17b** compared to **17a** results from a complicated trade-off in the stability of the  $\pi$  bands. That complicated behavior plus the small net energy difference suggests that our computational procedure may not be reliable in predicting the stability of **17b** over **17a**.

Figure 7 displays the band structure, DOS, and COOP for **17b** (all important features are the same in **17a**). As was the case for distortion **16** (Figure 6), the sulfur  $p_x$  bands no longer intersect the Fermi level. Due to the pairing distortion, half of the S  $p_x$  bands have moved down in energy to well below the Fermi level, while the other half have moved much higher in energy and lie above the energy window chosen in Figure 7. The states near the Fermi level are now  $\pi$  in character, as the projected DOS (Figure 7, middle) confirms. These  $\pi$  bands have split at  $\Gamma$ , opening up a gap of 0.27 eV in the density of states. The orbitals at the Fermi level derive from  $\pi_3$  of the undistorted polymer, which was S–C antibonding and S–S antibonding, and for which each carbon had one bonding and one antibonding interaction with nearest neighbor carbons. The right side of Figure 7 shows the S–C COOP, which displays the expected S–C  $\pi$  antibonding at the Fermi level, and confirms that the highest occupied crystal orbital contains both sulfur and carbon character.

(5). **Other Peierls Distortions.** Distortions **15**, **16**, **17a**, and **17b** are the simplest pairings, but there is an infinite variety of possible Peierls distortions. One interesting possibility is shown in **18**. This geometry is suggested by the structures of several



**Figure 7.** Band structure (left), density of states showing the contribution from all  $\pi$  ( $p_x$ ) orbitals (middle), and sulfur-carbon COOP curve (right) of the distorted polymer **17b** for a sulfur rotation angle of  $6.94^\circ$ . The  $\pi$  bands in the band structure are indicated by bold lines.

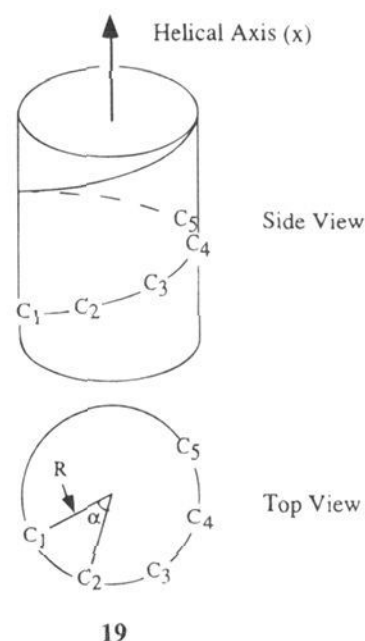
pentasulfur derivatives of TTP, e.g., **9**, which show a tendency for a five-sulfur chain to have a two-one-two pattern of sulfur pairing, where the paired sulfurs have relatively long S-C bonds (1.75 Å or so) and the lone sulfurs have shorter S-C bonds. Additionally, there is a resonance structure for this configuration in which the five-membered ring gives up one electron to the lone sulfur so that the ring becomes aromatic (with six  $\pi$  electrons in it), **18b**. This resonance structure may contribute to the stability of such a polymer.

We have studied this model in detail. The net stabilization we compute for **18** is small compared to the cases of distortions **15–17b** above, and it is probably overestimated due to unrealistically large charge shifts. This isomer is likely not the most stable one.

### Helical Distortion

Planar pairing deformations are not the only ones available to polythiophene.  $\sigma$ - $\pi$  mixing may favor a twisting of the polymer, leading to a helical conformation. Similar distortions have been studied for polyketone and polyisocyanides; they lead to the most stable isomers of these systems.<sup>6,30</sup> That stabilization depends strongly on the oxygen (or nitrogen)  $p_x$  bands, and similarly, the sulfur  $p_x$  bands will figure importantly for polythiophene too. The difference between polythiophene and those other two cases, however, is that (a) the sulfur lone pair interaction is favorable in a planar structure (average OP 0.11), due to the half-filled lone pair band. In contrast, lone pair interactions are unfavorable in both polyketone and polyisocyanide due to their lower-lying completely filled  $p_x$  or lone pair bands. Furthermore (b) the C-C  $\pi$  interaction in polythiophene is significantly stabilizing (average C-C  $\pi$  OP 0.19), in contrast to polyisocyanide, where there is only a small stabilizing effect of the carbon  $\pi$  system, or to planar polyketone, where the stabilization is also less (average C-C  $\pi$  OP 0.12). A helical distortion of polythiophene, if it is to be stabilizing, must entail very favorable  $\sigma$ - $\pi$  mixing to make up for the loss of the  $\pi$  and S  $p_x$  effects.

We consider only helices where the C-S bond points radially outward from the helix axis. Four parameters are necessary to uniquely fix the geometry of our helix: C-C and C-S bond lengths, the C-C-C angle, and the helical angle  $\alpha$ . The radius of the helix is fixed by these other parameters. The helical angle and radius are defined in **19**. Bond lengths will be assumed,



as above, 1.40 Å for the C-C and 1.70 Å for C-S, and we will consider only helices having a C-C-C angle of  $122^\circ$ . Our



calculations reveal a minimum at  $\alpha = 169^\circ$ , depicted in two views in **20**; otherwise, the energy profile is quite flat. The twist per “monomer” unit for  $\alpha = 169^\circ$  is small; it takes  $\sim 33$  units to complete a turn of the helix (though the translational unit cell is actually infinite).

In Figure 8 the band structures at two values of the helical angle are displayed. Note how the bands are “unfolded” with respect to the band structure of planar polythiophene (cf. Figure 1). We have taken advantage of the screw-axis symmetry in order to use a smaller unit cell.<sup>29–32</sup> Just a single C-S unit suffices, so that we have only eight orbitals in the unit cell and eight corresponding bands in the band structure. The sulfur  $p_x$  bands which were shown in Figure 1, running down from  $\Gamma$  to  $X$ , are here displayed as a single band running down from  $\Gamma$  to  $k = \pi/2a$  and up from  $k = \pi/2a$  to  $X$ . Essentially, “ $X$ ” of the former Brillouin zone lies at  $k = \pi/2a$  of the helical cell’s Brillouin zone. The former  $\pi_3$  and  $\pi_4$  are now one band running down from  $\Gamma$  to  $X$ , which crosses the  $p_x$  band. This can now be characterized clearly as a C-S  $\pi^*$  band, and the former  $\pi_1$  and  $\pi_2$  as the new C-S  $\pi$  bonding band.

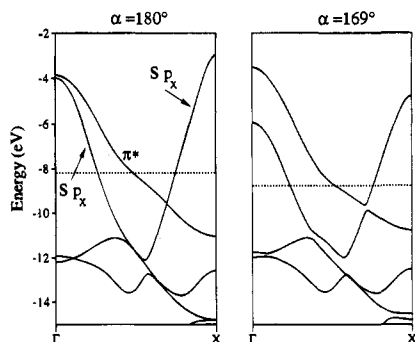
When the polymer twists, separation of  $\sigma$  from  $\pi$  orbitals is lost; note how the S  $p_x$  band has a slightly avoided crossing with the  $\pi^*$  band at  $169^\circ$ . The most significant change, however, is “flattening” of the sulfur  $p_x$  band with a decreasing

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(30) Hoffmann, R. *Vestn. Mosk. Univ., Ser. Fiz. Atr.* **1962**, *69*, 69–77 (in Russian).

(31) Hoffmann, R.; Minot, C.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2001–2005.

(32) Zheng, C.; Hoffmann, R.; Nelson, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3784–3791.



**Figure 8.** Band structure of the helical distortion for helical angles of 180° and 169°. The C–S  $\pi$  antibonding band is labeled, as well as the band derived from sulfur  $p_x$  orbitals.

helical angle, due to the increasing distance between nearest neighbor sulfur atoms. As the overlap (and hence the interaction) decreases, the S  $p_x$  antibonding states are lowered significantly in energy. These rapidly downward-moving antibonding  $p_x$  states depopulate the  $\pi^*$  band, resulting in a net lowering of energy. However, the bands below are at the same time being destabilized, which is also a result of flattening due to increased separation. This process contends with the energy gains from the flattening of the S  $p_x$  band, and eventually wins out.

The result is a small energy minimum for a helical conformation at 169°. This helical polymer has a nearest neighbor S–S distance of 2.57 Å, and an S–S average OP of 0.19 (only slightly lower than the 0.20 computed for planar polythiene). Note that this helical isomer is predicted to be conducting. However, the helical minimum is 0.08 eV higher in energy than the minimum for the most stable planar sulfur Peierls-distorted isomer (**17b**). In general, we would characterize the drive toward and the extent of helicity in polythiene as small, compared, for instance, to those of the polyisocyanides which have a 4-fold ( $\alpha = 90^\circ$ ) helical geometry.

### Role of 3d Orbitals

Although *ab initio* calculations have shown that 3d orbitals on sulfur serve only as polarization functions, Gleiter and Hoffmann found a significant qualitative difference in the geometry optimization of the molecule TTP upon using d orbitals in EH calculations.<sup>14</sup> We have investigated all the above distortions also with the inclusion of 3d orbitals on sulfur with the following parameters:  $H_{ii} = -4.0$ ,  $\zeta = 0.80$ . In almost all cases, net energies as well as Fermi levels were lowered due to these high-lying d orbitals mixing in with and pushing down the lower, occupied levels. For the idealized polymer as well as all the distorted polymer geometries, no significant qualitative differences were found, except that sulfur–sulfur distances optimized to slightly smaller values. The squeeze angle optimized at 121.5°, and distortions **15–17** all optimized the S–S distance at 1.96 Å. For distortion **18**, the minimum calculated with 3d orbitals on sulfur was actually higher in energy, but occurred at the same conformation. Similarly, the shape of the energy curve for the helical distortion was not significantly altered, except that the shallow minimum at 169° disappeared.

### Conclusions

Polythiene is a hypothetical sulfur analogue of polyketone. Its idealized structure is reminiscent of the family of thiothiophene molecules. In an idealized planar structure, the polymer has significant stabilizing S–S through-space interactions due

to a half-filled sulfur  $p_x$  band and is best described by resonance structure **2** with its extended multicenter electron-rich S–S bonding. This conformation is not the most stable one, however. The electronic properties of this conformation and the possible distorted isomers are determined in large part by the bands at the Fermi level: a folded-back sulfur  $p_x$  band and a folded-back  $\pi^*$  band. Since both of these bands are half-filled, pairing distortions in both the sulfur and carbon sublattices are favorable. Many different pairings are possible, and *all* of those investigated here were found to be more stable than the undistorted polymer.

The behavior of the sulfur-based  $p_x$  band is extremely sensitive to changes in polymer geometry, much as the S–S interactions in molecular TTP derivatives are sensitive to minor changes in molecular geometry. This sensitivity results in a band that changes drastically with each distortion and provides the interesting electronic behavior; however, such sensitivity also implies that calculations are overly dependent on the sulfur parameters used. As a counterpoint, addition of d orbitals to the sulfur parameters did not significantly affect the results. While we like our calculations and value their transparency, we are not so enamored of them as to overestimate their reliability; in the case at hand, we ultimately do not trust them to predict the distortion that actually will be found.

A helical distortion is also possible, as in the case of polyketone. Our calculations find a small minimum at a helical angle of 169°, which is caused when the flattening sulfur  $p_x$  band depopulates high-energy  $\pi^*$  states. The extent of helicity engendered by this distortion is relatively small, and S–S bonding is retained.

The most stable conformation of those investigated appears to be **17b**, which has undergone Peierls distortions in both sulfur and carbon sublattices and is predicted to be a low-band-gap semiconducting polymer. There are however several close competitors for lowest energy. Addition of high-lying 3d orbitals on sulfur does not qualitatively change these results. We feel that correlated *ab initio* studies are necessary in order to provide reliable predictions of this polymer's most stable conformation. Whatever it turns out to be, we think it will be quite different from polyketone, and will be an intriguing conducting system.

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### Appendix

Extended Hückel<sup>33</sup> computations were performed mainly using the YAeHMOP package<sup>34</sup>. A weighted  $H_{ij}$  was employed, as were the following atomic parameters ( $H_{ii}$  = orbital energy,  $\zeta$  = Slater exponent): C 2s, -21.4 eV, 1.625; 2p, -11.4 eV, 1.625; S 3s, -20.0 eV, 2.122; 3p, -11.0 eV, 1.827. 3d orbitals were not used on sulfur except where explicitly mentioned in the text: -4.0 eV, 0.8. A 100-*k*-point set was usually used for average property calculations.

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(33) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *37*, 2872; *36*, 2179.

(34) Landrum, G. *YAeHMOP - Yet Another Extended Hückel Molecular Orbital Package*, version 1.0; Cornell University: Ithaca, NY, 1995. This freeware package is available on the World Wide Web: <http://overlap.chem.cornell.edu:8080/yaehmop.html>.