Energy Surfaces of Polymeric Sulfur: Structure and Electronic Properties

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The energy surfaces of polymeric sulfur have been calculated with use of a parameter-free density-functional method. We study a wide range of geometries with interesting results. The calculated ground-state geometry is in good agreement with experiment, and the flat energy surfaces near this energy minimum are consistent with the extreme flexibility of the molecule. There are other geometries with energies only slightly above the ground-state energy, and stretching of the molecule results in *metallic* behavior.

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Interest in both the electronic structure and statistical mechanics of polymers (and other chain molecules) has developed rapidly in the past decade. The development of computing facilities has resulted in *ab initio* electronic structure calculations of numerous simple polymers,[1] although the large number of coordinates usually restricts energy-surface calculations to regions near the experimental geometries. In the present work, we calculate the energy surfaces of fibrous sulfur, $(\text{—S})_x$, using an efficient, parameter-free method which allows us to study a wide range of geometries. Little is known about the electronic structure of this polymer, which is composed of parallel helical chains of atoms.[2] It is one of the most flexible of all polymers and is important in several areas.

Polymer statistics and the relationship to critical phenomena have been studied for many years, and the sulfur helix has provided instructive tests of theories of the spatial configurations of chain molecules.[3] The polymerization process in liquid sulfur leading to the helical structure is described very well by the $n \rightarrow 0$ vector model of ferromagnetism,[4] which is related in turn to the transition in a one-dimensional Ising ferromagnet and the helix-coil transition in proteins. Helical chains also occur in the liquid, amorphous, and crystalline phases of other group-VI*A* elements, and trends in the crystal structures, such as the relative separation of atoms in and between chains, can be correlated with the increased tendency to metallic behavior Se → Te → Po.[5] Interchain interactions also contribute to the properties of $(\text{SN})_x$, the first metallic and superconducting polymer to be found.[6] There is lively interest in finding intrinsically conducting polymers, with particular attention being paid to polymers containing sulfur.[7]

We describe here self-consistent calculations of the energy surfaces of an infinite sulfur helix. The simplicity of the molecule and the efficiency of the method allow us to study a range of geometries well beyond those of earlier parameter-free methods. We pay particular attention to structures which give rise to *conducting* behavior. We use the density-functional formalism with the local–spin-density (LSD) approximation for the exchange-correlation energy. This is the most widely used parameter-free method for electronic structure calculations in bulk systems, and is finding growing application to small clusters and molecules.[8] In the present context, it is interesting that density-functional calculations on thiozone, S_3,[9] predict two almost degenerate minima with widely differing bond angles ($\alpha_{\text{SSS}} = 60°$ and $114°$, respectively). This suggests that a molecule such as $(\text{—S—})_x$ may have more than one structure with comparable energies.

The method of solution of the single-particle density-functional equations has been described in detail elsewhere.[10] Inside nonoverlapping spheres centered on the nuclei, the potential, density and linearized muffin-tin-orbital basis functions are determined numerically. The basis functions are matched smoothly on the sphere boundaries to spherical Hankel functions, and there are two each for $l = 0, 1, 2$. Nearly linearly dependent functions are excluded, and the parameters defining the Hankel-function tails and the radii of the atomic spheres are fixed throughout. The basis set combines compactness with an accurate description close to the nucleus and has nearly double-zeta quality. We find that the total energy per atom in a chain with widely separated atoms is within 0.2 eV of the atomic value. The energy surfaces have been calculated by use of 21 points in the range $0 \leqslant k \leqslant \pi/v$.

We have performed a detailed search of a three-dimensional coordinate space for geometries ranging from linear to planar zigzag (torsion angle γ_{SSSS}

$=180°$) to a spiral with $\alpha_{SSS}=80°$. In order to allow comparison with the results for S_3, we show the resultant surfaces (Fig. 1) as a function of α_{SSS}. The minimum energy is found for an internuclear separation $r_{SS}=4.22$ a.u., $\alpha_{SSS}=109°$, and $\gamma_{SSSS}=86.5°$, and the energy surface is remarkably flat nearby. For the optimum choice of the bond and torsion angles, for example, the total energy changes by less than 3 mRy when the bond length changes from 4.07 to 4.34 a.u. The agreement with experiment[2] is then very good. The second minimum in Fig. 1 corresponds to the geometry $r_{SS}=4.37$ a.u., $\alpha_{SSS}=83.5°$, $\gamma_{SSSS}=91°$. This may be reached from the ground-state geometry by an increase in the angle of rotation v from 107° and 124°, although the optimum energy path may be rather different. The increased compression along the axis is accompanied by an increase in the radius and a small change in the torsion angle ($\sim 4.5°$). The relative compactness of the structure at the second minimum can be appreciated by noting that the second- and third-nearest-neighbor distances are 5.81 and 7.05 a.u., respectively, compared with 6.88 and 8.87 a.u. in the ground state. The calculated torsion angles for both minima are similar to the value predicted by Pauling[11] to be "normal" for the S—S bond (100°). We find no minima for bond angles less than 80°.

The geometrical structures, the projections along the helical axis, and the calculated energy bands for both minima are shown in Fig. 2. The energy gap is ~ 2 eV in each case. Since the LSD approximation used here usually leads to modest underestimates of band gaps, a single sulfur helix in the ground state should be insulating. LSD calculations often lead to overestimates in dissociation energies in small molecules,[12] and S_3 is a good example.[9] The calculated dissociation energy per bond in the sulfur helix (~ 2.3 eV) is also greater than the experimental estimates (~ 1.5 eV).[13] There were fewer linearly independent functions for geometries near the second minimum, and so the calculated excitation energy from the ground state (0.19 eV) probably overestimates the true LSD value.

The planar zigzag and linear structures are also energetically favorable, and have strikingly different electronic structures. The band structures are shown for the optimum geometries in Fig. 3, and the unfilled bands found in both cases means that one may expect *metallic* behavior. In the zigzag structure, we find a minimum energy for $r_{SS}=4.27$ a.u. and $\alpha=109.5°$. The bond angle and energy are very similar to those in the ground state. The energy is ~ 0.05 eV above the minimum, similar to the prediction[14] that this energy difference should be ~ 0.1 eV in the group-VI*A* elements. The energy surface is extremely flat in the neighborhood of the zigzag minimum, the optimum energy for a torsion angle of 140° being only about

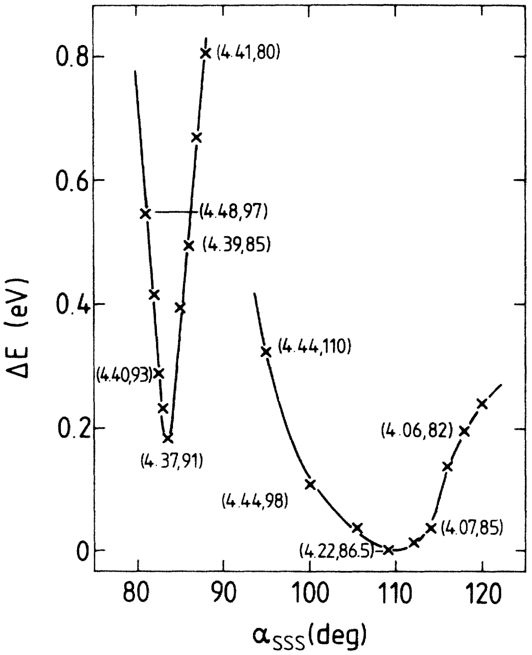

FIG. 1. Total energy surfaces (relative to ground-state minimum) of sulfur helix as a function of bond angle, α_{SSS}. Values of (r_{SS}, γ_{SSSS}) are also shown.

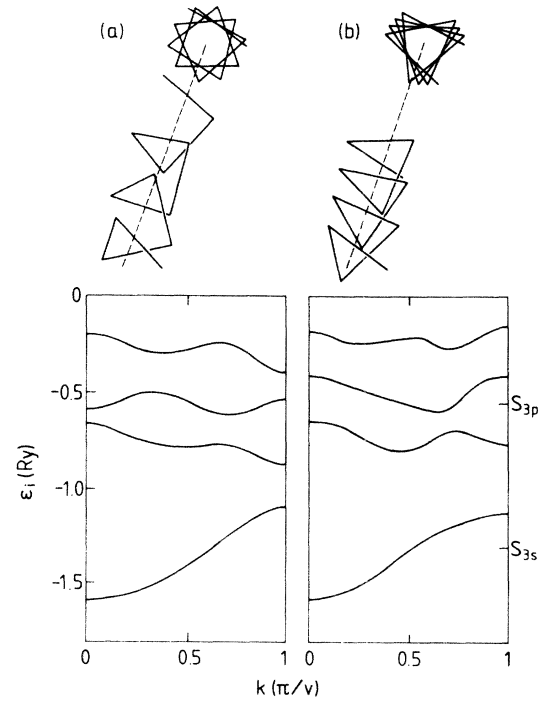

FIG. 2. Geometries (eleven bonds) and band structures of $(\text{—S—})_x$: (a) Calculated ground-state geometry, (b) geometry at second minimum in Fig. 1. The projections along the helical axis and the atomic eigenvalues are also shown.

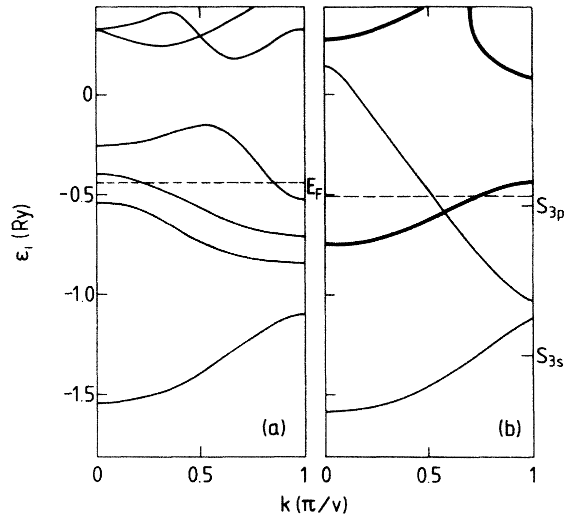

FIG. 3. Band structures corresponding to minimum energies for (a) planar zigzag ($v=\pi$) and (b) linear ($v=2\pi$) geometries. The atomic eigenvalues and the respective Fermi energies, E_F, are also shown. Thicker lines denote doubly degenerate bands.

0.01 eV above that for the planar structure ($\gamma_{SSSS}=180°$). The optimum linear geometry ($r_{SS}=4.15$ a.u.) corresponds to an energy ~ 0.2 eV above the ground state. Calculations for a range of torsion angles show that the linear structure corresponds to a flat energy maximum.

The importance of *d*-basis functions in describing bonds containing sulfur is well known. It is also evident in LSD calculations in both S_3 and the sulfur helix, where the coefficients of the normalized basis functions inside the spheres indicate the relative importance of *s*, *p*, and *d* contributions. In the plots of the single-particle eigenvalues, we show the 3*s* and 3*p* eigenvalues of atomic sulfur, and it is not surprising that the dominant contributions to the lowest three bands are *s*, *p*, and *p*, respectively. However, for all geometries there is a substantial *d* contribution to the lowest band and the uppermost occupied band. This is particularly evident for the structures with partially unoccupied bands and shows that *d* functions must be included in any realistic model of sulfur chains.

The energy surfaces in Fig. 1 show similarities with the corresponding results for S_3. There is a common tendency for bond lengths to increase as the bond angle is reduced, and the energy curves near the minima for open structures are flatter than the others. There are, however, differences between the two molecules. Small changes in bond angle in $(\text{—S—})_x$ can mean larger changes in geometry, since the torsion angle also changes, increasing with decreasing bond angle. Furthermore, symmetry does not require an energy minimum for a bond angle of 60° in the helix, where a larger bond angle (83.5°) is favored because of the repulsion between next nearest-neighbor nuclei. The calculated bond lengths are longer than in S_3. Together with the structural simplicity, this contributes to the polymer's flexibility.

The results obtained here are important on several grounds. They reproduce the measured geometry of a particularly flexible polymer very well, and they confirm expectations based on calculations for S_3 that there is a second energy minimum at a smaller bond angle. They also predict other structures where the energy has a local minimum. The band structures of two of these, the planar zigzag and the linear geometries, indicate metallic conduction. This is different from $(SN)_x$, where single chains are semimetallic and show a small Peierls instability. The unfilled bands arise on *stretching* of the molecule, i.e., the reverse of the common situation of metallization under high pressure. Fibrous sulfur is prepared by stretching, and its extreme flexibility means that the linear and zigzag structures are of practical interest. These structures may also be accessible by chemical means, and our findings should aid the search for stable, conducting polymers.

Of particular significance is the fact that the density-functional formalism makes such detailed energy-surface and band-structure calculations possible. Although the LSD approximation used here generally leads to overestimates of dissociation energies and underestimates of the band gaps in bulk systems, recent work has led to improved understanding of the origins and magnitudes of these errors. We know of no materials which are insulating and have such large band overlaps. Reliable Hartree-Fock calculations are difficult to perform for large molecules containing second-row atoms, and energy calculations for infinite chains using accurate correlated wave functions are presently out of the question. Our results show that polymer systems, which provide a bridge between the cluster and bulk applications of the method, are ideally suited to density-functional calculations. Other systems, including the selenium helix, are currently under study.

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sion (dihedral) angle is $\gamma_{SSSS} = 85.3°$. The geometry may also be described by the helix radius, r (here 1.80 a.u.), the translation along the axis, h (2.61 a.u.), and the rotation between successive atoms, ν (108.0°).

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