Density functional and Monte Carlo studies of sulfur. I. Structure and bonding in S_n rings and chains ($n=2-18$)

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Density functional calculations have been performed for ring isomers of sulfur with up to 18 atoms, and for chains with up to ten atoms. There are many isomers of both types, and the calculations predict the existence of new forms. Larger rings and chains are very flexible, with numerous local energy minima. Apart from a small, but consistent overestimate in the bond lengths, the results reproduce experimental structures where known. Calculations are also performed on the energy surfaces of S_8 rings, on the interaction between a pair of such rings, and the reaction between one S_8 ring and the triplet diradical S_8 chain. The results for potential energies, vibrational frequencies, and reaction mechanisms in sulfur rings and chains provide essential ingredients for Monte Carlo simulations of the liquid–liquid phase transition. The results of these simulations will be presented in Part II. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1568081]

I. INTRODUCTION

Sulfur is the element with the largest number of solid allotropes.[1–3] In addition to those comprising cyclic molecules ($n=6-14$, 18, 20 and $S_6 \cdot S_{10}$), there are two polymeric forms, S_∞. Theoretical studies include those on neutral molecules up to $n=13$ by Hohl *et al.*[4] [using a combination of density functional (DF) calculations with molecular dynamics (MD)] and Raghavachari *et al.*[5] [using Hartree–Fock calculations with fourth-order Møller–Plesset (MP4) corrections]. Cations S_n^+ were detected up to $n=56$ some years ago,[6] and anions S_n^- have been studied many times. For example, anions up to $n=9$ were identified mass spectroscopically, and comparison of the measured vertical detachment energies with calculated (DF) values showed that both rings and chain isomers could be identified for $n=6$, 7.[7] The past 2 years have seen considerable attention devoted to theoretical studies of isolated neutral and charged sulfur molecules: S_n^- for $n=3-13$,[8] S_3-S_{11},[9] S_6-S_{16},[10] S_2-S_{12},[11] S_5-S_8,[12] S_8^+,[13] and S_8.[14]

The constitution of *liquid* sulfur has also been the subject of much experimental and theoretical investigation for many years. Above the melting point (113 °C) sulfur is believed to be comprised mainly of S_8 rings with small concentrations of homocyclic rings with up to 23 atoms.[15] At 159 °C, there are dramatic changes in viscosity, specific heat, and other properties, and this liquid–liquid phase transition is often interpreted as a ring-opening polymerization (ROP) of the S_8 rings. Its apparent simplicity has made it the subject of experimental measurement[16–18] and theoretical model calculations,[19–28] but debate continues about the nature of the transition and the molecules taking part. In particular, neutron scattering studies indicate that simple models involving S_8 rings and freely rotating chains could not describe the measurements above *and* below the temperature of the transition, the origin of which was described as percolation rather than polymerization.[18]

We showed recently that a Monte Carlo and molecular dynamics calculations for a simplified model could describe catalyst-induced ROP (or ''living polymerization'') in cyclic oligomers of bisphenol A polycarbonate (BPA-PC).[29] Extensions of the model to incorporate multiple active sites[30] and multifunctional sites[31] showed that polymerization can occur in all cases, and multifunctional sites can lead to branching and gel formation. Similarities between ''living polymers'' and the phase transition in sulfur have been noted previously.[32] In both cases, polymerization proceeds by replacing covalent bonds with others that are equivalent, so that there is very little change in enthalpy. There is also little change in vibrational entropy, and it is natural to ask whether our model for polymerization in polycarbonate can be extended to the liquid sulfur. In order to determine appropriate parameters for such a study and to understand better the energetics of ring formation in sulfur, we have carried out an extensive series of density functional (DF) calculations on isomers of S_n for $n=2-18$, as well as DF calculations with simulated annealing for S_8 rings and related structures. A forthcoming paper (Part II) will discuss Monte Carlo simulations of the ring-opening polymerization of sulfur rings.

In Sec. II we outline necessary details of the methods we use, in Sec. III we present the results for the structures and relative energies for isomers of different S_n rings and chains and discuss the trends observed. In Sec. IV A we present results for the energy surfaces of S_8 rings, and in Sec. IV B we discuss the energy changes occurring when two S_8 rings approach each other, as well as the changes when an S_8 ring

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interacts with a helical diradical (triplet) S_8 chain. We summarize and conclude in Sec. V.

II. METHODS OF CALCULATION

The structures and relative energies presented below were determined using all-electron DF calculations with an extended one-electron basis of contracted Gaussian-type orbitals.[33] The results described adopted a triple-zeta valence type basis with a *d*-type polarization function,[34] with the A1 auxiliary basis[33] to represent the density and exchange-correlation potential. Calculations were performed with the gradient-corrected approximation to the exchange-correlation energy of Perdew and Wang.[35] Many of the larger ring structures are extremely flexible and correspond to shallow minima in the energy surface with low-frequency vibration modes. In such cases the tolerance on the energy gradient has been reduced from 2.0×10^{-4} to 1.0×10^{-4} Hartree/Bohr.

For starting geometries we have used structures of S_n molecules found in earlier calculations[4] using a combination of DF calculations with simulated annealing (MD/DF).[36] The same method has been used to generate additional structures, particularly those found by modifying known forms by rotating and translating structural groups. The MD/DF calculations use periodic boundary conditions with a (simple cubic) unit cell with lattice constant 11.64 Å, a plane wave basis set with a single point $(k=0)$ in the Brillouin zone, and an energy cutoff of 30 Hartree. The electron–ion interaction is described by the nonlocal pseudopotential of Troullier and Martins,[37] and there is a very good correspondence between the structures and relative energies found using the two methods. All energies given below refer to all-electron calculations.

The most stable state of a sulfur ring is generally a singlet, but the incorporation of spin is often essential. Almost all chain structures are more stable as triplet states, with the unpaired electrons localized on the terminal atoms or groups. This is similar to the situation found previously in sulfur anions,[7] and we discuss the parallels below. Higher spin states were also calculated if required by symmetry or if the spin-free calculations led to a small gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. Relationships between the structures of singlet and triplet states will also be discussed.

III. SULFUR RINGS AND CHAINS (ALL-ELECTRON CALCULATIONS)

In this section we discuss the structures and binding trends in sulfur molecules with up to 18 atoms, as well as other results obtained using the all-electron, Gaussian basis calculations. Instead of proving tables of structural parameters for over 60 different isomers, we provide supplementary information[38] covering atomic coordinates and energies of all structures, and the vibration frequencies and infrared activities of most. Parameters of particular interest will be discussed below.

The calculated structures are shown in Figs. 1–7. ''Bonds'' are generally shown for atomic separations less than 2.40 Å, 15% longer than the standard single bond length and close to the minimum in the pair correlation function of liquid sulfur between the first peak for covalently bonded pairs and the second peak for nonbonded pairs.[23] For some smaller molecules we have adopted a cutoff distance of 2.8 Å, and we show some weak ''bonds,'' e.g., the longer bonds in the isomers **4a** of S_4 and **6c** of S_6. The isomer labels **nm** reflect the number of atoms *n* and the energy ordering **m**, which is alphabetic with **a** the most stable. Atom labels are cyclic unless shown otherwise. The numbers of both ring and chain isomers increase dramatically with increasing *n*. For $n\leqslant10$ we focus on rings and on the patterns of the chain structures. For $n>10$ we discuss ring structures alone.

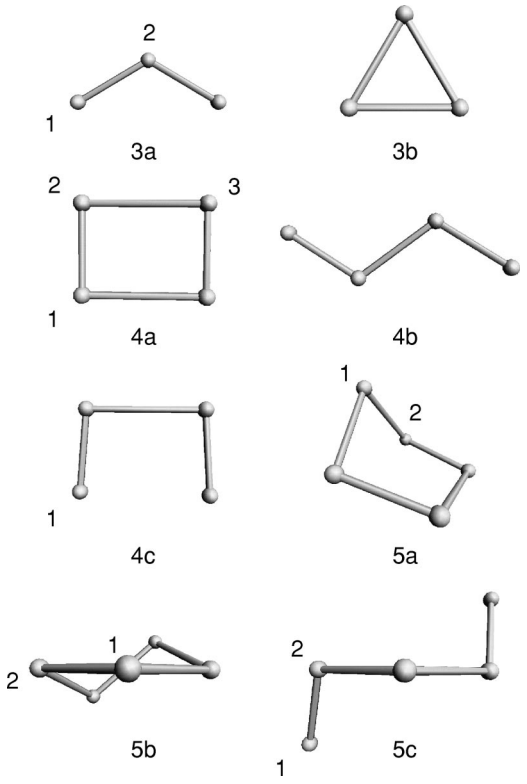

FIG. 1. Structures of isomers of S_3, S_4, and S_5.

A. Sulfur rings and chains: Structure and energies

1. S_2–S_5

The structures of the most stable isomers of these molecules are shown in Fig. 1, and bond lengths and angles are given in Table I. In the dimer S_2 the calculated values ($r_e=1.94$ Å, $\omega_e=665\ \mathrm{cm}^{-1}$) agree reasonably well with experimental values (1.89 Å, $726\ \mathrm{cm}^{-1}$).[39] Direct measurements of the structures of S_3, S_4, and S_5 have not yet been performed. The structure of the most stable isomer of S_3 (**3a**) is in good agreement with the results of Refs. 5 and 8. The calculated vibration frequencies (249, 548, $619\ \mathrm{cm}^{-1}$) are in reasonable agreement with the measured values (256, 575, $656\ \mathrm{cm}^{-1}$).[40] The equilateral triangular structure (**3b**) lies 10.4 kcal/mol higher in energy.

The most stable form of the tetramer (**4a**) is a $(S_2)_2$ ''dimer'' with D_{2h} symmetry. Several calculations[8,10,11,41] have predicted that a C_{2v} structure lies slightly lower, but

TABLE I. Bond lengths (Å) and angles (deg) for S_n, $n=2-5$.

Structure, symmetry	Parameters
2(a)	$r_{12}=1.94$
3(a) C_{2v} singlet	$r_{12}=1.97$, $\alpha_{123}=118.3$
3(b) D_{3h} singlet	$r_{12}=2.12$, $\alpha_{123}=60.0$
3(c) C_{2v} triplet	$r_{12}=2.04$, $\alpha_{123}=90.5$
4(a) D_{2h} singlet	$r_{12}=1.93$, $r_{23}=2.61$
4(b) C_{2h} singlet	$r_{12}=1.96$, $r_{23}=2.19$, $\alpha_{123}=111.4$
4(c) C_{2v} triplet	$r_{12}=1.94$, $r_{23}=2.70$, $\alpha_{123}=94.0$
4(d) C_{2h} triplet	$r_{12}=1.96$, $r_{23}=2.37$, $\alpha_{123}=107.1$
5(a) C_s singlet	$r_{12}=2.16$, $r_{23}=2.05$, $r_{34}=2.29$, $\alpha_{123}=101.3$, $\alpha_{234}=100.1$, $\alpha_{512}=88.4$
5(b) C_2 singlet	$r_{12}=2.17$, $r_{23}=2.06$, $r_{34}=2.21$, $\alpha_{123}=103.6$, $\alpha_{234}=93.6$, $\alpha_{512}=99.7$
5(c) C_2 triplet	$r_{12}=1.98$, $r_{23}=2.17$, $\alpha_{123}=113.3$, $\alpha_{123}=109.3$

this isomer reverts to the D_{2h} structure in the present work. A singlet C_{2h} isomer (**4b**) is 7.6 kcal/mol higher (the corresponding triplet is 5.2 kcal/mol above this), and the C_{2v} triplet (**4c**) is essentially degenerate with **4b**. A ''roof'' structure (D_{2d}, $r_{12}=2.17$ Å, $\alpha_{123}=84.8°$, dihedral angle $\gamma_{12}=33.4°$) lies 26.8 kcal/mol above **4a**. Infrared spectra of S_4 isolated in an argon matrix show peaks at 642.4 and 661.6 cm^{-1}, which were assigned to two different open-chain S_4 isomers.[42] The vibration frequencies calculated here for **4b** structures are significantly lower than the measured values, while the values for **4c** (triplet) agree better with experiment than those of **4a**.

Most previous calculations for S_5 indicate that the C_s (**5a**) and C_2 (**5b**) structures are almost degenerate, with the former lying slightly lower in energy. In fact, molecular dynamics (MD-DF) simulations[4] showed that the energy barrier between them was so low that interconversion between them could be observed. The present calculations and those of Ref. 8 find a small imaginary vibration frequency in **5b**, indicating that it is a transition state. The chain structure **5c** lies higher in energy, as found in previous calculations.[5,8]

The most detailed calculations on these molecules give a consistent picture of the structures and their relative energies, although there are differences that reflect the different methods and basis sets used. These are greatest in structures with low-frequency vibration modes, particularly those subject to pseudorotation. In isomer **5a**, for example, hybrid-DF (B3LYP) and second-order Møller–Plesset (MP2) calculations using the same basis (6-31G*) (Ref. 12) showed a scatter in bond lengths of up to 0.06 Å, and similar differences can be found in the hybrid-DF (B3PW91) calculations of Peter.[10] In most isomers, however, the differences in structural parameters are small, although the relative energies of near-degenerate states can differ. Our emphasis in this work is on more pronounced differences that are important for the interconversion and reaction of sulfur rings and chains.

Some general features of the results are already apparent in these small systems. First, singlet rings are more stable than triplet chains. Second, comparison of related singlet and triplet structures, such as **5b** and **5c**, shows that the latter are more open or ''chainlike.'' The occupied molecular orbitals with the highest energies are localized at the chain ends, which stabilizes the chain in the same way as found for sulfur anions.[7] Finally, the terminal S–S bonds in open chain structures are shorter and have higher vibration frequencies than other bonds. As a general rule, the vibration frequencies of S rings are below 500 cm^{-1}, while the stretching frequencies of terminal bonds are $\gtrsim 600$ cm^{-1}.

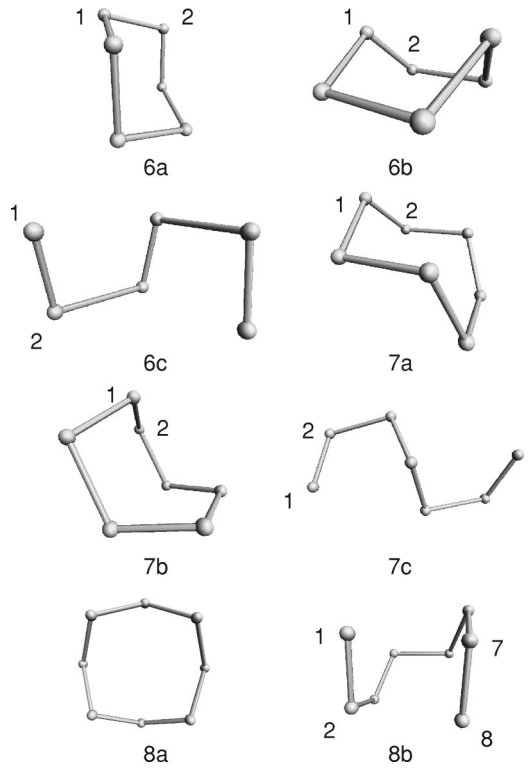

FIG. 2. Structures of isomers of S_6, S_7, and S_8.

2. S_6–S_8

Some low-lying isomers of S_6, S_7, and S_8 are shown in Fig. 2. The D_{3d} structure of S_6 (**6a**) occurs in the crystalline samples and is the most stable in all calculations. The present structure ($r_{12}=2.12$ Å, $\alpha_{123}=103.1°$, $\gamma_{12}=73.0°$) and the energy difference (11.3 kcal/mol) between **6a** and **6b** isomers are in excellent agreement with B3LYP calculations,[11,12] although the bond lengths in both are 2.5% longer than the measured value (2.068 Å).[43] A six-atom segment of a regular (all-*trans*) helical chain is unstable against formation of **6c** (C_2, triplet). As in the case of **4c**, r_{23} is long (2.53 Å), so that the structure may be viewed as a $(S_2)_3$ trimer.

The most stable form of S_7 (**7a**, C_s) is the chair structure found in the crystalline form. The structural parameters are very close to those found in B3LYP calculations,[11,12] and the bond lengths are again 1%–3% longer than those measured. The energy difference between **7a** and the boat isomer **7b** (2.1 kcal/mol) is close to the B3LYP value (3.0 kcal/mol). The C_2 chain isomer **7c** is a triplet, and it follows the pattern of almost planar terminal tetramers, with a long bond ($r_{23}=2.29$ Å).

The most stable isomer of S_8 is the ''crown'' (D_{4d}, **8a**). The structural parameters ($r_{12}=2.11$ Å, $\alpha_{123}=109.5°$, $\gamma_{12}=97°$) are again close to the B3LYP values,[11,12] again with bond lengths 2.5% longer than the measured value in monoclinic S_8.[44] Isomer **8b** (C_2, singlet) was reported by Jones

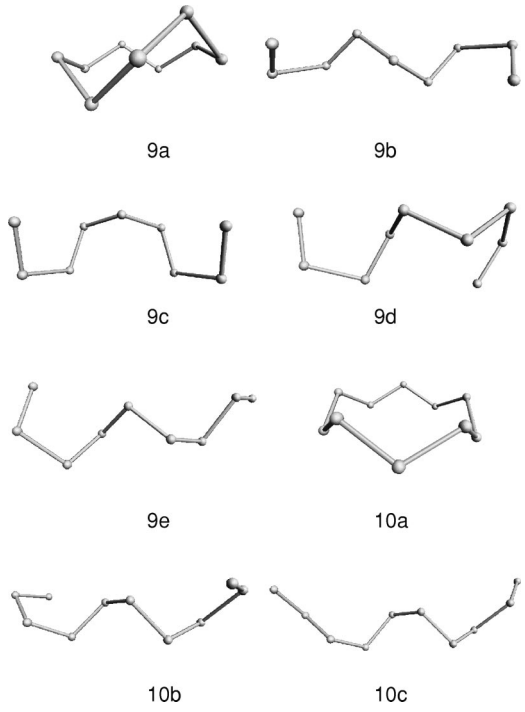

FIG. 3. Structures of isomers of S_9 and S_{10}.

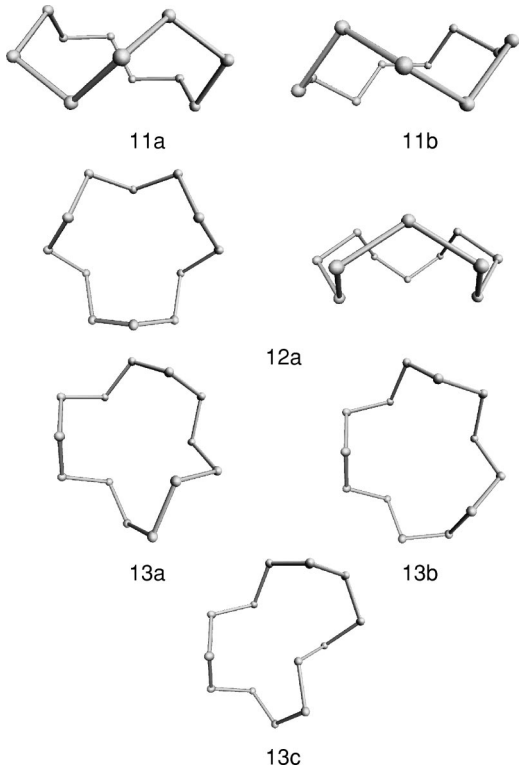

FIG. 4. Structures of isomers of S_{11}, S_{12}, and S_{13}.

and Hohl,[45] and it lies 11.6 kcal/mol higher in energy than **8a**. The atoms (1,2,7,8) form a rectangle of sides 1.95 Å and 2.86 Å, in good agreement with the B3LYP structures of Wong *et al.*,[14] who find the energy differences between **8a** and **8b** to be 7.8 kcal/mol. In the triplet structure corresponding to **8b**, r_{17} and r_{28} increase to 4.40 Å, and we have the familiar pattern of two planar tetramers, now separated by a bond of length 2.23 Å. We return to other isomers of S_8 below.

3. S_9–S_{10}

The most stable isomer of S_9 (**9a**, C_2) was predicted by Hohl *et al.*[4] and found experimentally when the structure of α-S_9 was determined by x-ray diffraction.[46] The present calculations overestimate the bond lengths by $\sim 2\%$, as in the systems mentioned above.

There are numerous open chain triplet structures in S_9 and all larger systems. We show four for S_9 in Fig. 3 (**9b**–**9e**), and analogous structures will occur in all longer chains. The first three are almost degenerate in energy (**9b** is 24.3 kcal/mol above **9a**) and show again the way that planar tetramer groups are favored. Isomer **9e**, with one planar C_{2v} and one C_{2h} terminal groups, is 1.5 kcal/mol higher in energy than **9d**.

A very similar situation can be found in the isomers of S_{10}. The ring structure (**10a**, D_{2d}) is more stable by 25.1 kcal/mol than the most stable chain (**10b**) with two C_{2v} terminal groups. This in turn is 4.6 kcal/mol more stable than the chain structure with two C_{2h} terminal groups (**10c**). There are other chain structures intermediate in energy.

4. S_{11}–S_{13}

The form of S_{11} found in single crystals[47] is shown in Fig. 4 (**11a**, C_2) and is the most stable form in these and earlier calculations.[10,11] The overall agreement between the calculations is very good, although the calculated bond lengths are 2%–3% longer than those measured. We have also found a second C_2 form (**11b**) lying 6.2 kcal/mol higher in energy. The main difference between these two structures is the "motif" of dihedral angles. There are many chain structures with higher energies.

The ring structure of S_{12} (**12a**, D_{3d}) is one of the most stable sulfur molecules. The calculated structural parameters ($r_{12}=2.11$ Å, $\alpha_{123}=109.2°$, $\gamma_{12}=86.9°$) show the familiar overestimate of bond lengths (measured values: $r_{12}=2.052$ Å, $\alpha_{123}=106.6°$, $\gamma_{12}=88.0°$).[48]

This feature is also found for S_{13}, where the crystalline form has a C_2 structure (**13a**) with a range of bond lengths 1.978–2.113 Å, bond angles from 104.6° to 112.0°, and dihedral angles 29.5° to 116.3°.[47] The corresponding calculated ranges are 2.06–2.17 Å, 104.6°–112.0°, and 34.0°–108.4°. We have found, however, two additional ring structures (**13b**, **13c**) with different dihedral motifs and similar energies. In our calculations, **13b** is essentially degenerate with **13a**, and **13c** is only 3.6 kcal/mol higher.

5. S_{14}–S_{15}

Low-lying isomers of these molecules are shown in Fig. 5. *Cyclo*-S_{14} has been prepared in crystalline form and its structural parameters determined by x-ray diffraction.[49] This structure (**14a**, C_s) is also the most stable in the present calculations. The bond lengths lie in narrow ranges in both

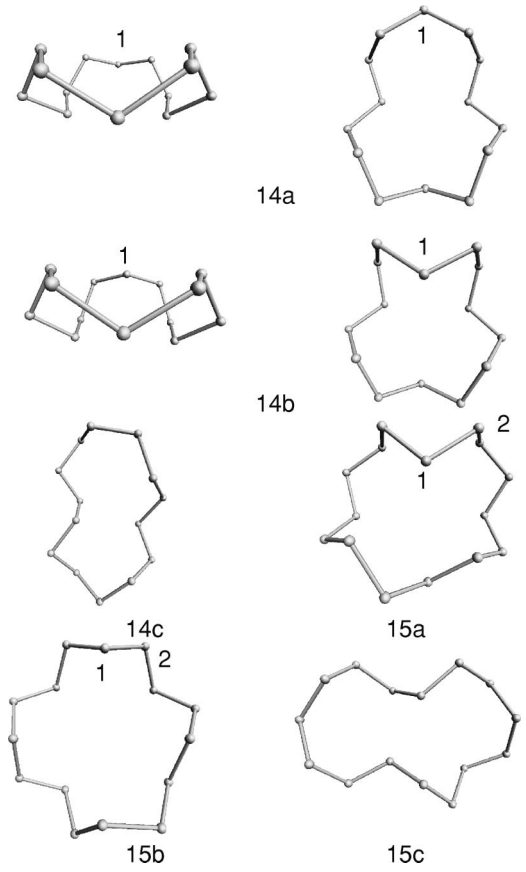

FIG. 5. Structures of isomers of S_{14} and S_{15}.

the measurements (2.047–2.061 Å, average 2.053 Å) and calculations (2.107–2.115 Å, average 2.110 Å), as do the bond angles (experiment, 104.0°–109.3°; calculated, 106.7°–111.1°). A second C_s structure (**14b**) is only 4.4 kcal/mol higher in energy, with a C_1 structure (**14c**) an additional 1.1 kcal/mol higher.

Isomers **14a** and **14b** differ only in the orientation of one triangular segment, and the most stable isomer found for S_{15} (**15a**) is related to the latter by replacing one atom by a dimer unit with dihedral angle $\gamma_{78}=180°$. Isomer **15b** is related to **14a** in the same way and lies only 0.2 kcal/mol above **15a**. It has one very small imaginary frequency, but extensive simulated annealing calculations on both **15a** and **15b** indicate that both are stable minima. A third isomer **15c** lies 2.7 kcal/mol above **15a**. There are certainly many other low-symmetry ring structures with different dihedral motifs and similar energies.

6. S_{16}–S_{18}

Two isomers of S_{16} (**16a**, **16b** in Fig. 6) have almost equal energies. The former (C_s) has an obvious relationship to **15a** and lies less than 0.3 kcal/mol below the more symmetric **16b** (D_{4d}), which is closely related to **12a** and has been calculated by Peter.[10] In our calculations all bond lengths are 2.11 Å, the bond angles centered on atoms in the central plane are 111.4°, those centered on other atoms 106.8°, while the magnitude of the dihedral angles lies in a narrow range between 97°–99°.

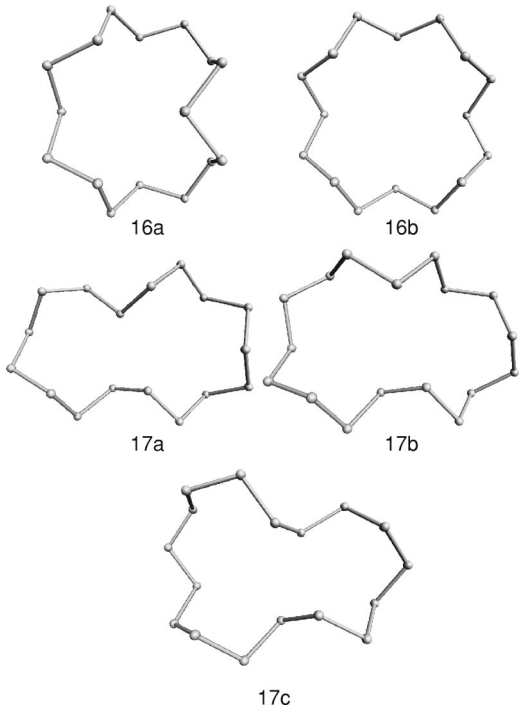

FIG. 6. Structures of isomers of S_{16} and S_{17}.

The three isomers of S_{17} shown in Fig. 6 differ in the pattern of dihedral angles. Isomer **17a** is the most stable of the three, **17b** is 3.1 kcal/mol higher in energy, and **17c** is a further 1.6 kcal/mol higher. These structures are very flexible with low frequency vibration modes, and there will be numerous other low-symmetry structures with similar energies.

Figure 7 shows five isomers of S_{18}, which is the only

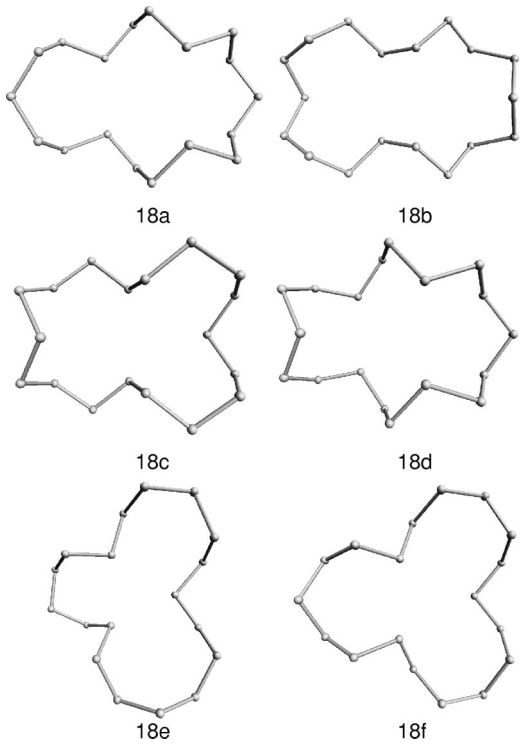

FIG. 7. Structures of isomers of S_{18}.

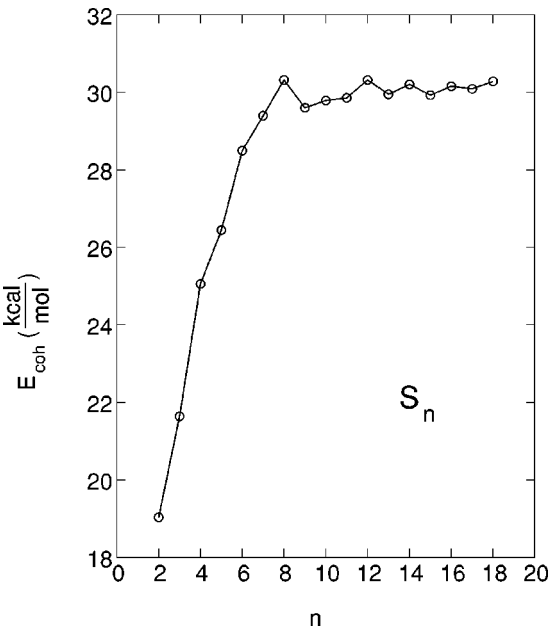

FIG. 8. Cohesive energy (binding energy per atom, kcal/mol) of the most stable isomer of S_n for $n=2,18$.

sulfur molecule with two distinct structures determined from x-ray diffraction.[3,50] The most stable isomer in the present calculations (**18a**, C_{2h}) is neither of these. It was obtained by relaxing a C_i structure found in crystalline β- or exo-S_{18}, and is 0.2 kcal/mol more stable than **18b** (C_{2h}). The latter may be viewed as two S_8 helices joined by a pair of symmetrically placed S atoms. Isomer **18c** (C_{2h}), which is found in α- or endo-S_{18}, is an additional 2.2 kcal/mol higher in energy, and **18d** is a further 4.5 kcal/mol higher in energy. **18e** and **18f** lie 6.4 and 8.0 kcal/mol, respectively, above **18a**. Their structures are closely related, and it is interesting that the *more* symmetric molecule (**18f**, C_s) is less stable. We have observed this in clusters of other elements, and it is a case where the constraints of a higher symmetry appear to be energetically unfavorable. The main difference between the structures **18a**, **18c**, and **18d** is the orientation of the extremal triangular units.

B. Cohesive energies

The binding energies per atom of the most stable isomer calculated for S_2-S_{18} are shown in Fig. 8. The variation with increasing n shows that even-numbered molecules are generally more stable than their odd-numbered, less symmetric neighbors, with S_8, S_{12}, S_{14}, S_{16}, and S_{18} being particularly stable. The calculations of Peter[10] showed similar trends in S_6 to S_{16}, and it is striking how little the cohesive energy varies for $n>12$. MP3 calculations of Raghavachari *et al.*[5] also found that the cohesive energies of S_8 and S_{12} were isoenergetic within the accuracy of the calculations. The special status of S_8 and S_{12} is also evident in the measured binding energies of rings found in liquid sulfur.[15]

While S_8 and S_{12} are energetically favored, the relative weakness of the bonds in S_{10} is no less striking. All bonds in S_8, S_{10}, and S_{12} have the same length (2.11 Å), and all bond angles are in a narrow range from 109° to 113°. The dihedral angles differ significantly, however, the magnitudes being 97° in S_8, 87° in S_{12}, and 112.5° in S_{10}. This is another indication of the particular stability of structures with $\gamma \sim 90°$, which minimizes the repulsion between lone pair electrons on adjacent atoms.

C. Binding trends

The structural trends found here for S_n rings with $n \leqslant 12$ are consistent with the those found in previous studies[4,5,10] and in experiment.[3] Where experimental data are available, we find bond lengths that are 2.5%–3% longer than the measured values. This is consistent with the results of other DF calculations, with the exception of the recent results of Peter,[10] which agree very well with measured bond lengths. The calculations of Peter[10] show that bond and dihedral angles are not too sensitive to the choice of basis set and functional form, but bond lengths are. The best results were obtained with the 6-311+G($3df$) basis, i.e., a triple-zeta basis with diffuse and polarization functions.

For larger molecules the number of stable ring isomers increases rapidly with increasing n, and the number of structures with similar energies means that those found in crystalline sulfur allotropes are not necessarily the most stable. For example, the form of S_{18} with the calculated lowest energy is not found in the crystalline forms α-S_{18} or β-S_{18}. In S_{15}, for which the structure is not known experimentally, we find two isomers containing a tetramer unit with dihedral angle near 180°. The most stable structures of S_{17} have low symmetry, are very flexible, and have low-lying vibrational modes. There are certain to be other structures with similar energies. Ring structures have a strong preference to be singlet states, and the HOMO–LUMO gaps are large and remarkably uniform ($\sim$50 kcal/mol).

The rapid increase in the number of chain isomers as n increases can be appreciated by examining the pattern of the signs of the dihedral angles ("motif") in different structures. Closed structures require distinct patterns [such as $+-+-+-+-$ in the "crown" (D_{4d}) isomer of S_8], while open structures can have many combinations of $+$, $-$, and 0, since the beginning and the end of the chain need not coincide. Chains are generally energetically less stable than rings, but their configurational freedom and large number mean that they can be observed in molecular beams of S_n^- if the time available is too short to allow annealing to ring structures.[7]

The patterns found in S_n^- structures are also clear in the present results. The regular (all-*trans*) helical structures are usually less stable than chains with a planar tetramer (with approximately C_{2v} symmetry) at one or both ends. The latter occur in S_4^-, in the neutral tetramer, and in sections of the longer chains. The calculations on the anions[7] indicated that hybrids of all-*trans* chains with the C_{2v} *cis*-planar unit are on average $\sim$0.1 eV more stable than their all-*trans* counterparts.

There are pronounced similarities between the trends in the anions and those found here in the neutral chains, which are triplet radicals in their most stable forms. The highest occupied molecular orbitals in both cases are localized on the

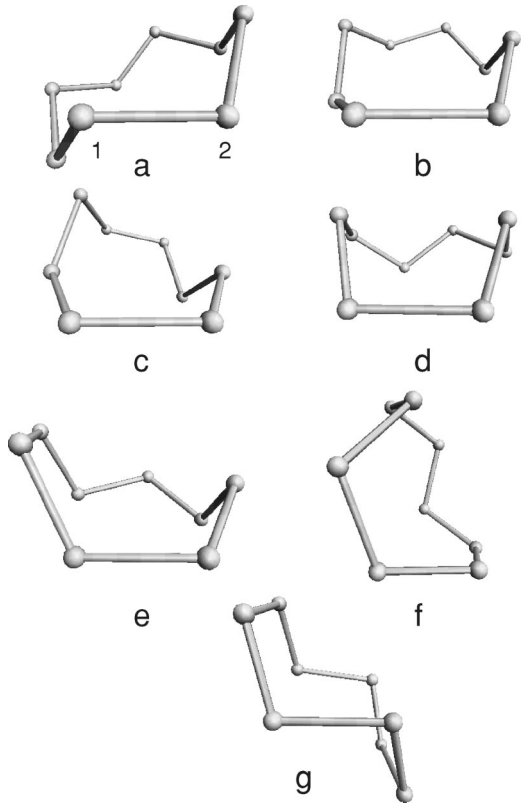

FIG. 9. Structures of S_8 homocycles for values of dihedral angle γ_{12}: (a) 97.3°, (b) 50°, (c) 0°, (d) −10°, (e) −60°, (f) −110°, (g) −160°.

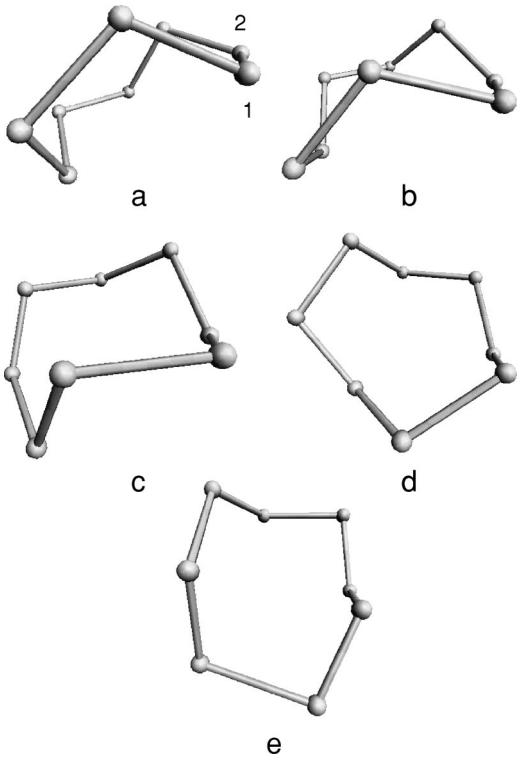

FIG. 10. Structures of S_8 homocycles for values of dihedral angle γ_{12}: (a) −10°, (b) 30°, (c) 70°, (d) 110°, (e) 150°.

extremities of the chain. This minimizes in the anion the electrostatic repulsion arising from the additional charge. The correlation between the lengths of bonds in sulfur chains and the dihedral angles[3,4] means that the almost planar units are characterized by unusually long bonds. We have noted that the isomer of S_8 with this structural unit at each end (**8b**) has been discussed recently by Wong *et al.*[14]

IV. ISOMERS OF S_8 AND THEIR REACTIONS

The octamer is the main component of liquid sulfur below 159 °C,[15] and it has received particular attention. The reaction limiting step is presumed to be the opening of the ring to a chain radical (''initiation''), followed by the reaction of this radical with other rings (''propagation''):

$$\text{cyclo-}S_8 \rightarrow \text{chain-}S_8^{\cdot\cdot}(+nS_8) \rightarrow S_{\text{poly}}^{\cdot\cdot}. \quad (1)$$

The reaction enthalpy for this process has been estimated by ESR measurements above 550° to be 36.4 kcal/mol,[51] and static magnetic susceptibility measurements up to 600° give a value of 34.9 kcal/mol.[52] The enthalpies of the initiation and propagation reactions have been estimated by Tobolsky and Eisenberg[20] to be 32.8 and 3.17 kcal/mol, respectively.

The interest in liquid sulfur, particularly the phase transition at 159 °C, has motivated extensive studies of the isomers of the octamer. These include a characterization of all isomers of S_8 and their interconversion,[12] as well as a study of nine isomers.[14] In this section we describe calculations involving structures related to the D_{4d} isomer as well as reactions between a pair of these isomers and between the D_{4d} isomer and an S_8 chain radical. The focus of these calculations differs from that of Ref. 12, which emphasized the energy barriers between different conformers of S_8. We seek more general information about the energy surface, including that far from extrema.

A. S_8 rings: Simulated annealing results

The interconversion of ring isomers of S_8 has been studied here by performing a series of calculations with a *single* constraint, the dihedral angle γ_{12} (97° in the D_{4d} isomer). The energy increases by 26.5 kcal/mol as γ_{12} is lowered to 0° [Fig. 9(c)] and passes through a maximum at 28.2 kcal/mol ($\gamma_{12}=-5°$), before dropping rapidly to 11.5 kcal/mol at −10° [Fig. 9(d)]. This structure is very flexible, and a further decrease of γ_{12} of 100° [Fig. 9(f)] causes very little energy change. Optimization of the structure without constraints leads to a minimum 9.8 kcal/mol (all-electron value) above the D_{4d} form ($\gamma_{12}=-29°$). The energy then rises slowly to Fig. 9(c), which has approximately C_{2h} symmetry.

The dihedral angle in structure 9(d) can also be *increased* with little change in energy, and we show a different perspective in Fig. 10. The energy of Fig. 10(d) is essentially the same as in Fig. 10(a), and it is only for $\gamma_{12}>120°$ that the energy changes significantly. This picture is similar to that found in recent work,[12] where the most stable D_{4d} structure is separated from other low-lying ring structures by a barrier of ~25 kcal/mol. Several of these structures are capable of pseudorotation.

B. Reaction of pairs of S_8 units

We have performed all-electron calculations of the energy change as two S_8 rings (D_{4d}, singlet) approach each

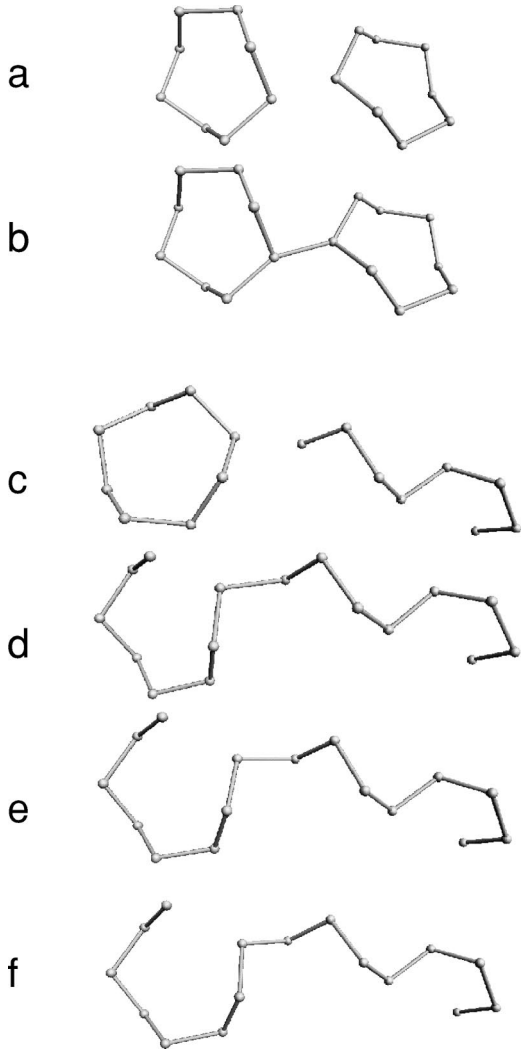

FIG. 11. Reactions of (a)–(b) two S_8 (D_{4d}) rings, (d)–(f) an S_8 chain (triplet) with an S_8 ring (D_{4d}). The shortest distances between the units are (a) 2.53 Å, (b) 2.32 Å, (c) 2.58 Å, (d) 2.38 Å, (e) 2.28 Å, (f) 2.13 Å.

other. The only constraint is the separation between one atom on each ring. The interaction is repulsive, as expected, and we show in Fig. 11 the structures for separations of (a) 2.53 Å and (b) 2.32 Å. The latter is 8.3 kcal/mol higher in energy, and the energy continues to increase as the separation is reduced.

The same calculations have been performed for the interaction between an S_8 triplet diradical chain and the D_{4d} isomer. There are numerous chains isomers analogous to those of S_9 in Fig. 3, and we have chosen a helix with the planar tetramer at one end. The spin configuration is constrained to be a triplet throughout. The reaction proceeds in a dramatic fashion, as shown in Figs. 11(c)–11(f). A bond in the ''crown'' increases in length as the diradical approaches, and a bond forms between the chain and an atom of the original ring. The result is an entity referred to by Stillinger *et al.*[23] as a ''tadpole.'' There is an energy barrier of 5.4 kcal/mol at a separation of $\sim$2.4 Å, after which the energy drops to a value 1.9 kcal/mol above that found for large separation of the reactants. Our estimate of the barrier is subject to two sources of uncertainty: (a) The computation of the lowest crossing point between two energy valleys yields an upper bound to the activation energy, (b) DF estimates of transition state energies are generally less reliable than those involving stable minima.

The cohesive energy of S_n rings varies only weakly for all but the smallest values of n. The spin density in both the S_8 chain and the reaction product 11(f) is located on the terminal atoms, and neither the total spin degeneracy nor the number of bonds changes during the reaction. The initial and final energies should then be very similar. These are all features of the model we adopted to study equilibrium polymerization in BPA-PC, indicating that the model is appropriate to study the phase change in liquid sulfur.

V. CONCLUDING REMARKS

We have performed a study of sulfur rings with up to 18 atoms and chains of up to 10 atoms, focusing on trends in the geometries and energy differences. The numbers of both ring and chain isomers increase rapidly with increasing n, and—with the exception of an almost uniform overestimate of bond lengths of 2%–3%—the geometries of the former agree well with x-ray diffraction studies of molecular crystals where available. Trends in the cohesive energies and structures have been discussed in Secs. III A 7 and III A 8, respectively. Studies of the energy surfaces of S_8 show that there are several large regions of configuration space where the energy changes very little. We have also studied the repulsive interaction between two S_8 (singlet) rings, as well as the energy changes occurring when an S_8 triplet diradical approaches an S_8 ring. The ring opens in the latter case, leading to a diradical chain of 16 atoms. This process is the same as that shown in Eq. (1), and the calculated energy barrier is at most 5.4 kcal/mol.

One aim of the present calculations was to provide information for a further study of the liquid–liquid phase transition in sulfur at 159 °C. The structural patterns found are remarkably consistent: Structural groups are readily transferable between molecules, there is a relatively narrow range of bond angles, and there is a well-known relationship between the length of a bond in a chain or ring and the corresponding dihedral angle. Triplet states of chains are more stable and more open than their single counterparts. The most stable chains are terminated by an almost planar tetramer, a feature found previously in sulfur anions.[7] We note that this planar structural unit with a dihedral angle of 180° is associated with unusually long and weak bonds. The observation of dimer elimination from sulfur chains[53] is consistent with this feature.

Trends in the vibration frequencies (provided as supplementary information)[38] are also quite consistent: The ring structures have maximum frequencies that are typically below 500 cm^{-1}, while terminal groups of chains have frequencies above 600 cm^{-1}. Integrated properties, such as the zero point energies per atom, are remarkably transferable.

Our previous model calculation designed to describe rings and chains in polycarbonate showed that polymerization can occur even if neither potential energy nor vibrational entropy increases significantly. The driving force for this phase transformation and for gelation, which can occur in the

presence of branching agents, is provided by the entropy of the bond distribution. There are clear parallels with situation in liquid sulfur, and Monte Carlo studies of this material are in progress. The results will be presented elsewhere (Part II).

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