

The Structure of Amorphous Sulfur

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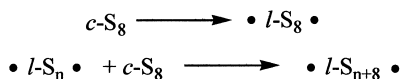
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SUMMARY: The λ -transition of elemental sulfur occurring at about 159°C has long been associated with the conversion of cyclic S₈ rings (*c*-S₈) to amorphous polymer (*a*-S) *via* a ring opening polymerization. Here we demonstrate, with the use of both density functional and Hartree-Fock quantum mechanical calculations, the existence of an energetically accessible, locally stable, hypervalent state of S that can form branch sites in the polymer. The significance of this finding is that the λ -transition is best described as a gelation transition. The geometry of the tetravalent S atom is trigonal bipyramidal, with a lone pair occupying one of the three equatorial sites; it lies in a local energy minimum about 31 kcal/mol above the normal divalent state, and so is accessible both thermally and photochemically. Because the branched structure is formed endothermically, Le Chatelier's principle confirms that a percolation network can form on heating the element. The reactions that form branched structures are reversible, implying that the gel is fluxional. It decomposes at higher temperatures as chain scission competes with branching. The hypervalent structure provides an essential insight into the chemistry of elemental sulfur.

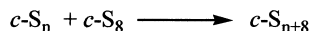
Introduction

Elemental sulfur is an important cross-linking agent for the production of rubber goods of all kinds, but is especially important in the manufacture of vehicular tires. Amorphous sulfur is used for vulcanization as it is more soluble in both natural and synthetic rubber than are any of the crystalline polymorphs of the element, and in this form it provides sufficient sulfur to accomplish the requisite degree of cure and prevents bloom. The structure of amorphous sulfur has long been assumed to consist of linear chains that are formed by the ring opening polymerization of the native *c*-S₈ rings. The mechanism proposed for this reaction by Tobolsky and Eisenberg,¹⁾ as based on the earlier work of Gee,²⁾ is very simple, consisting of the initiation and propagation steps



leading to a Flory distribution¹⁾ of molecular weights.

Semlyen³⁾ especially has pointed out that in a polymerization such as this there must be a ring-chain equilibrium, for any diradical $\bullet I-S_n \bullet$ can cyclize. The theory for the transition with cyclization included has been thoroughly worked out by Petschek, Pfeuty, and Wheeler,⁴⁾ and they conclude that their treatment accounts well for the properties of elemental sulfur. On the other hand, the inorganic chemist Steudel⁵⁾ has amassed a wealth of experimental data that suggests that a ring expansion process



is more likely the correct mechanism for the polymerization. This argument is based on a variety of evidence, most notably the absence of any detectable radicals^{6,7)} below the transition temperature and the fact that carefully isolated $c-S_7$ polymerizes⁸⁾ at about 45°C, well below the temperature at which radicals are believed to form.

Our research was undertaken in an effort to understand the reactions of elemental sulfur for commercial applications. For this work, we have applied high quality quantum mechanical density functional theory (DFT) calculations to a wide range of sulfur structures and putative transition states and reaction intermediates. In particular, we have carefully explored the several mechanisms for the polymerization of elemental sulfur that have been proposed by Steudel.⁵⁾ We believe that the DFT results shed new light on this old problem, which leads to a proposal for the mechanism of the λ -transition that resolves the major discrepancies between the polymerization theory and experimental observations. The important finding is that a hypervalent (4-coordinate) state of sulfur is found to be at a local energy minimum, and this state provides a branch point in the polymer. The consequence is that the λ -transition is not simply the floor temperature for the polymerization – it is instead a gel point. Furthermore, it is proposed that this hypervalent state is an intermediate in the polymerization-depolymerization mechanism.

Methods

The DMol³ program⁹⁾ from MSI was used for all calculations. This DFT program uses a numerical basis set – we used a double-numeric basis set with d-polarization functions (dnd), roughly comparable to a 6-31G** basis set in Hartree-Fock programs, for the calculations reported here. The geometries of all structures were obtained by minimization of the energies in the local density approximation (LDA) using the Vosko-Wilk-Nusair (VWN) exchange-correlation terms.¹⁰⁾ Subsequent to locating the optimal local geometries, single point evaluations of the energy were performed with the Becke-Perdew (BP) functional,¹¹⁾ which

supplies non-local corrections for exchange and correlation effects. This procedure is a recognized standard method in DFT calculations: Local Hamiltonians tend to overbind but give good geometries, whereas the non-local corrections give improved energies but at the cost of relaxing the structures. The hybrid method gives good (VWN) structures and reliable (BP) energies. For completeness, we report the energies obtained from both.

Results

Benchmark Studies

The relative merits of the results to be discussed will be more easily judged after a quick comparison is made between the quantum calculations and experimental data on sulfur compounds. Tables 1A and 1B show the geometries obtained from the *ab initio* calculations

Table 1A: Comparison of Experimental and Calculated *c*-S₈ Geometry.

	Experiment [†]	VWN
Bond length	2.059 ± 0.002 Å	2.066 Å
Bond angle	107.9 ± 0.6°	108.8°
Dihedral angle	98.9 ± 0.7°	±97.8°

Table 1B: Comparison of Experimental and Calculated *l*-S_ψ Geometry.

	Experiment [†]	VWN*
Bond length	2.069 ± 0.014 Å	2.068
Bond angle	106.0 ± 1.7°	108.0°
Dihedral angle	84.2 ± 1.0°	80.8 ± 0.4°

* VWN average geometrical measures on the four central bonds in H₂S₁₄.

with those determined by X-ray diffraction.¹²⁾ The general agreement is seen to be remarkably good for both the native *c*-S₈ (Table 1A) as well as for the linear chain, *l*-S_ψ (Table 1B). [The older literature labeled the CS₂-soluble portion of liquid sulfur S_γ, and the CS₂-insoluble

portion S_{ψ} . The latter component is understood to be synonymous with the polymer, *i.e.*, $l-S_{\psi} = l-S_n$.] Bond lengths are well within 0.01\AA of the experimental structures, bond angles within a degree or so, and torsions are within about 4° . Torsions are especially susceptible to packing effects, so this level of agreement must be judged to be quite adequate for the aims of this paper.

Molecular Binding Energies

The opening of the $c-S_8$ ring to form the diradical doubtless occurs, as there is a clear ESR signal⁶⁾ from molten sulfur at high temperatures. Any effort to understand the polymerization of the element must address this important part of the chemistry of S-S bonds. Prior work on sulfanes and dimethyl polysulfides was reported by Chaka, *et al.*¹³⁾ They found that the bond energy of the central S-S bond in $H-S_n-H$ converges to about 29 kcal/mol as n increases from 2 up to 6. They used a variety of quantum methods in that study, and suggested that the BLYP functional in DMol³ (yielding the number quoted) gives the best agreement with experiment for the energy of the S-S bonds in H_2S_2 and H_2S_3 . This functional is very similar to the BP functional used for our calculations, as will be seen. We repeated many of the calculations done by Chaka, *et al.*,¹³⁾ so as to compare functionals and validate the methods.

Table 2 contains the bulk of the molecular binding energies that will be used to study the various reactions of interest here. The energies of the low cyclics are included to enable one to extrapolate to get an estimate for the energy of the average S atom in a very large ring. Following this are: (i) two entries for the linear S_8 diradical, (ii) two different spiranes, (iii) six sulfanes, (iv) five thiyl radicals, and (v) five hypervalent sulfanes.

Reaction Energies

The strength of the S-S bond in a series of sulfanes and in the native $c-S_8$ ring can be deduced from the results in Table 2, as is shown in Table 3. The energies for homolytic bond scission in the H_2S_n series converge to about 32.5 kcal/mol, in reasonably good agreement with the results from Chaka, *et al.*¹³⁾ (Differences of 10-15% between energies calculated with different functionals or different approximations to the many-electron problem, *e.g.*, Hartree-Fock theory, are certainly within tolerable limits. We are not claiming absolute accuracy of energies calculated at the level of theory used here. Much more costly calculations would be required to make such claims. However, we believe that the results are good approximations to the true energies, and more importantly, relative differences of energies between different

Table 2: Binding Energies of Molecules and Radicals.

Molecule	Binding Energy	
	VWN/(kcal/mol)	BP/(kcal/mol)
<i>c</i> -S ₆ (boat)	-475.268	-385.701
<i>c</i> -S ₆ (chair)	-487.125	-397.612
<i>c</i> -S ₇	-574.663	-468.372
<i>c</i> -S ₈	-664.117	-543.217
<i>c</i> -S ₉	-739.505	-602.570
<i>c</i> -S ₁₀	-822.938	-670.082
<i>c</i> -S ₁₆	-1322.269	-1078.724
\cdot -S ₈ [§] [random]	-623.745	-509.399
\cdot -S ₈ [§] [helical]	-622.108	-506.224
<i>s</i> -S ₁₆ [7.8] [†]	-1305.509	-1039.150
<i>s</i> -S ₁₆ [6.9] [†]	-1301.654	-1032.411
H ₂ S ₂	-280.194	-243.712
H ₂ S ₃	-363.795	-312.041
H ₂ S ₄	-447.634	-380.296
H ₂ S ₅	-530.060	-447.302
H ₂ S ₆	-613.014	-514.964
H ₂ S ₁₄ [‡]	-1276.457	-1056.282
HS \cdot	-97.284	-87.191
HS ₂ \cdot	-196.145	-171.555
HS ₃ \cdot	-282.049	-241.214
HS ₄ \cdot	-365.059	-309.109
HS ₅ \cdot	-448.105	-376.849
H ₄ S ₅	-633.324	-527.050
H ₄ S ₇	-798.255	-660.394
H ₄ S ₉	-971.166	-796.807
H ₄ S ₁₁ [conf. 1]*	-1137.431	-929.141
H ₄ S ₁₁ [conf. 2]*	-1138.716	-933.265

[§] Two different conformers of the linear S₈ diradical, the first having a relatively arbitrary set of rotational states, and the [helical] conformer having all torsions at approximately the preferred helical state for fibrous sulfur (see H₂S₁₄ below). Both structures are at local energy minima, so that all torsion angles are fully relaxed.

[†] The *s*-S₁₆ spiranes, both [7.8] and [6.9], are optimized without constraints at local minima. Both are highly strained: the torsion angles of spiro[7.8]hexadecasulfur are (reading around the 9-ring from the tetravalent atom) -176.7°, 81.3°, 55.6°, -102.1°, 103.6°, -114.8°, 114.0°, -94.2°, 91.3°; and around the 8-ring they are -137.2°, 90.8°, 34.9°, 106.1°, 44.2°, 84.3°, -116.2°, 83.2°. The torsions in the helical configuration should be compared with these.

[‡] The five innermost torsion angles of the helical form of H₂S₁₄ have an average torsion angle of 81.0° (range: 80.4°-81.6°). The bond lengths are all 2.068 ± 0.001 Å, and the bond angles are 108.0° ± 0.1°.

* Two different conformers of H₄S₁₁ that differ only in torsion angles. The lower energy conformer is stabilized by non-bond interactions between atoms in relatively favorable van der Waals contact.

Table 3: Bond Strengths and Heats of Polymerization.

Reactants	Products	Energy of Reaction	
		VWN/(kcal/mol)	BP/(kcal/mol)
H ₂ S ₂	HS· + HS·	85.6	69.3
H ₂ S ₃	HS· + HS ₂ ·	70.4	53.3
H ₂ S ₄	HS· + HS ₃ ·	68.3	51.9
H ₂ S ₅	HS· + HS ₄ ·	67.7	51.0
H ₂ S ₆	HS· + HS ₅ ·	67.6	50.9
H ₂ S ₄	HS ₂ · + HS ₂ ·	55.3	37.2
H ₂ S ₅	HS ₂ · + HS ₃ ·	51.9	34.5
H ₂ S ₆	HS ₂ · + HS ₄ ·	51.8	34.3
H ₂ S ₆	HS ₃ · + HS ₃ ·	48.9	32.5
<i>c</i> -S ₈	· <i>l</i> -S ₈ · [random]	40.4	33.8
<i>c</i> -S ₈	· <i>l</i> -S ₈ · [helical]	42.0	37.0
<i>c</i> -S ₈ + H ₂ S ₆	H ₂ S ₁₄	0.7	1.9
<i>c</i> -S ₈ + H ₂ S ₆	<i>c</i> -S ₈ ·H ₂ S ₆	-6.9	5.7

molecules and reactions studied at the same level of theory are sufficiently reliable to make claims about the chemistry of the element.) The energy for breaking a bond in *c*-S₈ to form the random conformation of ·*l*-S₈· is slightly larger, perhaps owing to the stability of the native S₈ ring relative to the model sulfanes. The energy of the helical conformation of ·*l*-S₈· is somewhat larger than that for the “random” conformer, since the latter is stabilized by favorable van der Waals contacts between non-bonded atoms. Note that the bond energy of the disulfide is considerably larger than that for polysulfides. The reason for this is that the unpaired electron is delocalized in a polysulfide radical, which stabilizes it relative to the HS· radical.

The last two rows of Table 3 show that the energy of incorporation of a *c*-S₈ ring into a sulfane, as representative of the propagation step in the polymerization, is very weakly endothermic. For comparison, a representative van der Waals contact between the two molecules is formed with comparable energy. (The reason that the BP energy for the contact pair is endothermic is that the energies are not computed for geometries appropriate for the BP functional. The VWN geometry places the molecules closer together than the BP functional would have done had it been used for the geometry optimization. The consequence is that the BP functional senses a repulsion between the molecules. For this particular

example, it is more meaningful to look at just the VWN energies.) An endothermic heat of polymerization coupled with a positive entropy of polymerization constitute the necessary and sufficient conditions for the polymerization to have a floor temperature.¹⁴⁾ Which brings us to an analysis of the chain statistics to gain some insights into the entropy of polymerization.

Rotational Potentials and Chain Dimensions

It is claimed that the entropy of polymerization of *c*-S₈ is positive because polycatenasulfur is a flexible chain.¹⁴⁾ In addressing this point, it should first be noted that a positive enthalpy and entropy of polymerization are not uncommon for ring opening polymerizations. A number of lactones are reported to polymerize endothermically, as do oxepane and octamethyl cyclotetrasiloxane, to name a few.¹⁵⁾ Many of these examples also have a positive entropy of polymerization. However, as far as is known to the authors, none of these other endothermically polymerizing monomers exhibits the same type of transition as that of sulfur. Semlyen¹⁶⁾ made a thorough analysis of the rotational states of polycatenasulfur, and concluded that the chain has only two low energy torsional states at approximately $\pm 90^\circ$, and that the characteristic ratio for the polymer is very close to one. The compact size of the chain is a result of its geometry. Both the bond angle and most probable torsion angles are near 90° , which render the chain configurations nearly those of a random walk on a cubic lattice. The characteristic ratio for such a walk has to be close to one. This in itself is not indicative of chain flexibility. In fact, the chain has fewer states than polyethylene, and the barriers to rotation are larger, as inspection of Table 4 will reveal. The barriers that separate the states near $\pm 90^\circ$ in the central S-S bond of the H₂S₆ molecule are located very near 0° and 180° , and are between 3 and 6 kcal/mol higher in energy than the minima at -88.6° (VWN) or $+86.0^\circ$ (BP). (Again, the discrepancy between these two states with the two different functionals is probably a result of the VWN geometry not being optimal for the BP functional.) These barriers are somewhat smaller than those estimated by Semlyen.¹⁶⁾

So, there are two comments to be made about the positive entropy of polymerization. The first is that polycatenasulfur is not a typical flexible chain. It would be best to characterize it as a compact stiff chain. It is, therefore, difficult to see how the modest gain in rotational freedom that accompanies the opening of the *c*-S₈ ring is sufficient to overcome the very large loss of translational freedom that results from the polymerization. The second comment, already addressed above, is that sulfur is not unique amongst monomers in having a positive enthalpy and entropy of polymerization, but it seems to be unique in having a λ -transition. Perhaps there is more to this transition than just ring opening.

Table 4: Sulfur Torsion Potentials.

Dihedral	Value	Relative Energy of Conformation	
		VWN/(kcal/mol)	BP/(kcal/mol)
HS—SH	0°	8.80	8.35
	±90°	0.00	0.00
	180°	6.56	6.24
HSSS—SSSH [‡]	0.3°	2.84	5.26
	-88.6°	0.00	1.34
	-179.4°	5.73	4.50
	+86.0°	1.11	0.00
HSSS—S—SSSH [‡] (+ +)	78.0° 77.0°	1.38	0.00
	(- -) -94.6° -94.6°	1.47	0.68
	(- +) -88.5° 83.0°	0.02	1.58
	(+ -) 83.3° -89.0°	0.00	1.57

[‡] Geometries optimized at minima. The tails of the chains were set in helical conformations, but were allowed to relax during the optimization. For H₂S₆ at the maxima, the torsion angle was constrained at the nominal values 0° and 180°. The actual angles are given.

The Hypervalent State of Sulfur

As stated in the Introduction, our purpose in this work was to assess the relative merits of the several mechanisms for the polymerization that have been proposed by Steudel.⁵⁾ We systematically studied the energies and transition states for the six mechanisms that he proposed, and found that only the mechanism proceeding through a four-coordinate intermediate was sufficiently low in energy to compete with ring opening. The thermodynamics for insertion of a sulfur atom of one sulfane into the S-S bond of another is found in Table 5. The energy of the tetravalent state is approximately 31 kcal/mol higher than the divalent state, which is very comparable to the energy of the diradical. The structure of the H₄S₇ molecule is shown in Fig. 1.

The upshot of this finding is that the tetravalent intermediate provides a transient crosslink for the system that is at least as probable as the open chain diradical. This implies that the λ -transition is a gel point, which overcomes some of the difficulties that one encounters in attempting to reconcile a rather ordinary ring opening polymerization mechanism with a thermodynamic phase transition. Furthermore, the tetravalent intermediate provides a vivid

insight into the mechanism of the polymerization and rearrangement chemistry that is exhibited by elemental sulfur and by polysulfides in general.¹⁷⁾

Table 5: Energies of Formation of Hypervalent Sulfanes and Sulfur Spiranes.

Reactants	Products	Energy of Reaction	
		VWN/(kcal/mol)	BP/(kcal/mol)
H ₂ S ₂ + H ₂ S ₃	H ₄ S ₅	10.7	28.7
H ₂ S ₃ + H ₂ S ₄	H ₄ S ₇	13.2	31.9
H ₂ S ₄ + H ₂ S ₅	H ₄ S ₉	6.5	30.8
H ₂ S ₅ + H ₂ S ₆	H ₄ S ₁₁ [ave.] [†]	5.0	31.1
<i>c</i> -S ₈ + <i>c</i> -S ₈	<i>s</i> -S ₁₆ [7.8] [‡]	22.7	47.3
<i>s</i> -S ₁₆ [7.8]	<i>s</i> -S ₁₆ [6.9]*	3.9	6.7
<i>c</i> -S ₈ + <i>c</i> -S ₉	<i>c</i> -S ₇ + <i>c</i> -S ₁₀ *	6.0	7.3

[†] The energy of the product is the unweighted average of the energies of the two different conformers listed in Table 1. If the statistically weighted average were to be used the energy of reaction would be about 2 kcal/mol lower.

[‡] The spirane has considerable strain from high energy torsion angles that are required in order to satisfy the pseudo-trigonal bipyramidal structure at the hypervalent atom, as described in Table 2. Nonetheless, the spirane is at a local energy minimum.

* The energy change for rearrangement of the spirane from the [7.8] to [6.9] configuration is largely due to ring strain, as is seen in the close agreement between the energies for the last two rows. In the last row, the energy is for the gas phase reaction (as are nearly all of the other reactions considered here), and not for molecules in van der Waals contact.

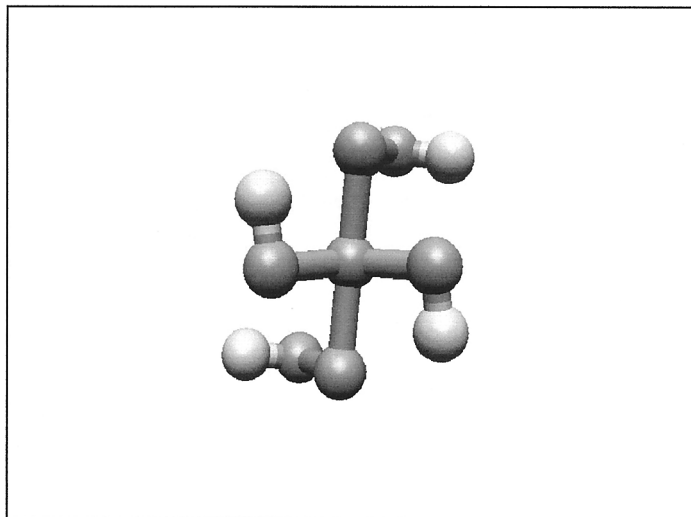


Fig. 1: A representative molecule, H₄S₇, containing a hypervalent sulfur atom. The geometry of the molecule is pseudo-trigonal bipyramid, with a lone pair occupying one of the three equatorial sites.

We have found that the spirane formed by the insertion of a sulfur atom from one $c\text{-S}_8$ ring into the S-S bond of another ring is at a local energy minimum (see Table 5), provided the torsion angles of the two rings adjust themselves to accommodate the geometry of the tetravalent spiro atom shown in Fig. 1. If one assumes that the spirane is subject to vibrationally induced rearrangement, then it is not difficult to see that the reversion to strictly divalent species can proceed by the three different channels shown in Fig. 2. Thus, if all combinations of bonding pairs are possible on reversing spirane formation, the $4!/2!2! = 6$ combinations lead to the proportions – polymerization : reversion : disproportionation as 4:1:1 – of reversion products.

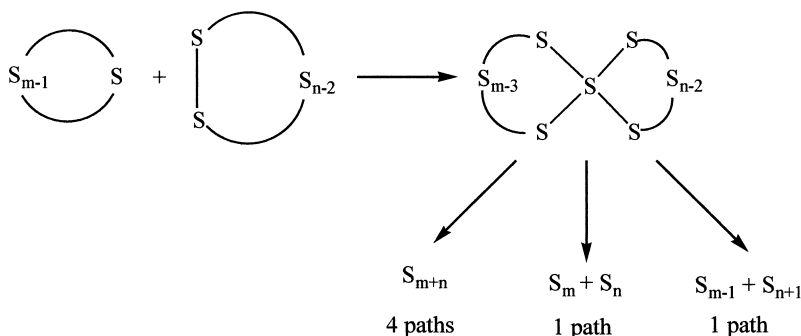


Fig. 2: The mechanism for ring expansion polymerization. The spirane on the right can potentially revert to strictly divalent cyclics by any of six routes, four of which lead to equivalent ring expanded polymer, one reverts to starting material, and the last leads to disproportionation.

This is sufficient to account for all of the cyclic products that are seen in both hot and quenched samples of amorphous sulfur.¹⁸⁾ The relative amounts of each at equilibrium are then determined by standard polymer statistical treatments of torsional states and ring closure via Jacobson-Stockmayer theory.^{16,19)}

Conclusions

We have shown with the use of high quality quantum calculations that there exists a relatively low energy tetravalent intermediate in polymeric sulfur. This trigonal bipyramidal atomic center provides a step on the pathway for polymerization of the element by a ring expansion polymerization, bypassing the ring opening mechanism with concomitant diradical formation. (Some interesting aspects of the molecular weight distribution for a ring expansion polymerization have been described.²⁰⁾ There is no doubt that chain scission competes with

polymerization at higher temperatures. On heating rubbery sulfur beyond the λ -transition the viscosity decreases and the color deepens.²¹⁾ Both phenomena are fully compatible with the increasing concentration of radicals as the temperature is raised. However, at lower temperatures the mechanism of polymerization described here must be, at the very least, competitive with the ring opening polymerization. This suggests that the theory for the polymerization be investigated anew, to determine whether better agreement with experiment might be obtained with inclusion of the tetravalent state. The interpretation of the λ -transition of sulfur as a gelation transition is not a new idea.²²⁾

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