THE STRUCTURES OF ELEMENTAL SULFUR

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I. Introduction

Elemental sulfur is commonly known and widely used. Its properties are already described in the Old Testament and in Homer's Odyssey. It exists in several different forms.

Thermodynamically stable sulfur forms deep yellow, nonodorous orthorhombic crystals with a space group $Fddd\text{-}D_{2h}{}^{24}$, containing 16 molecules, i.e., 128 atoms in the unit cell. It has a density of 2.069 gm/cm^3 and is well soluble in CS_2. Its molecular unit is S_8, cyclooctasulfur, a crown-shaped molecule with a symmetry of D_{4d}. The pale "flowers of sulfur," prepared by alchemists by distillation, are insoluble in CS_2, and the structure is not yet fully understood. Another form, plastic sulfur, is obtained by melting sulfur to about 180°C, where it forms as highly viscous syrup. To date, some forty-five different forms of sulfur have been described (*25*, *61*, *62*), and for twelve of these detailed structural data are available. These forms differ in intramolecular and intermolecular structure.

Sulfur can form rings and chains of various shapes and sizes. In addition to the crown-shaped cyclo-S_8, nine other types of rings can be prepared: the first of these, cyclohexasulfur, also called Engel's or Aten's sulfur, or rhombohedral sulfur, S_ρ, was first described by Engel in 1891 (*28*). The other eight types of rings were all discovered during the last 10 years by Schmidt and his co-workers (*87*, *88*) notably Wilhelm (*125*).

Sulfur chains of uniform length cannot be made. All catenallotropes are mixtures, containing molecules of varying lengths. There is still much question whether pure polymeric chains can exist at room temperature and whether the terminal atoms of long chains are bound to impurities, to sulfur rings, forming charge-transfer complexes of catenasulfur with cyclosulfur or whether they curl up and form long chains (*50*).

Three polymorphs of S_8 are well established and recipes for preparing some twenty others have been published and much tried. The knowledge of sulfur allotropes up to 1965 has been reviewed in detail (*61*, *62*). Recently, a detailed summary of much of the crystallographic work on solids, showing the history of structure determination, has been published in an excellent book by Donohue (*25*). Many data on the preparation, stability and structure of rings can be found in recent review papers by Schmidt (*87*, *88*). As will be seen below, our knowledge of sulfur allotropes is still very incomplete, because the chemistry of elemental sulfur is far more complex than anyone suspected. During the last 100 years, as our knowledge and techniques of chemistry became more sophisticated, more and more riddles appeared, but it seems now that we might have reached a turning point, because we know now that many different types of sulfur rings can exist, but that they all show the basic characteristics of the S—S bond. It is noteworthy here that progress in this field was not caused by the availability of advanced technology, but based on ingenious use of chemical knowledge, thought, and intuition. In this review heavy emphasis is given to recent work.

STRUCTURAL CONSIDERATIONS

The S—S bond distances observed in various compounds range from 1.89 Å in S_2 (*5*) and S_2F_2 (*56*) to 2.20 Å in S_8O (*105*). The bond length depends on molecular geometry and substitution. Normally, the bond distance is close to 2.05 Å (Table I). The S—S—S bond angle lies between

TABLE I

STRUCTURAL PARAMETERS OF MOLECULES WITH S—S BOND

Molecule	S—S bond length (Å)	Ref.
S_8	2.060	*17*
S_{12}	2.053	*57*
S_∞	2.066	*105*
H_2S_2	2.0	*101*
S_2F_2	1.89	*56*
Me_2S_2	2.038	*101*
$S_3(CF_3)_2$	2.04	*101*
$S_3(Me)_2$	2.04	*101*
S_8O	2.04–2.20	*105*
Diphenyl disulfide	2.03	*82*
2,2′-Biphenyl disulfide	2.03	*82*
α-Cystine hydrochloride	2.05	*82*
α-Cystine	2.03	*82*

101° in S_8O (*105*) and 108° in monoclinic γ-sulfur (*120*). In cyclooctasulfur, it is 108°; in polymeric sulfur, it is 106°. The S—S—S—S dihedral angle can be as small as 66°, in S_{20} (*98*), or as large as 98° and S_8. Normal bond values are shown in Fig. 1a.

Experimental and theoretical ramifications of S—S bond properties observed in S_8, S_6, and polymeric sulfur have been reviewed by Pauling

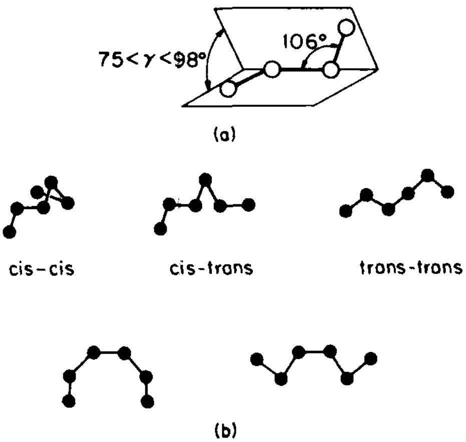


FIG. 1. (a) S—S bond parameters; (b) S—S bond configurations.

in 1949 in a paper (*79*) in which he elucidated much of what had been previously observed. He proposed that the S—S bond had natural, "free" values close to those found in cyclo-S_8, the thermodynamically stable form. He concluded that the stability of this molecule precluded rings of other than S_8, or a very similar size, such as S_6. Pauling's paper discounted, in advance, future claims of Skjerven (*102*) and others, that various experimental observations indicated the existence of large rings (*61*). The distrust of large rings was proven unfounded prejudice when Schmidt and Wilhelm, in 1966, demonstrated (*95*) simple and reliable ways for making S_{12}. The existence of S_{12}, which is amazingly stable, showed that molecules other than S_8 can fulfill the S—S bond requirements, but its structure confirmed that Pauling's assumption about bond characteristics is correct. The S_{12} structure (Fig. 2) is surprisingly simple. Since the time that S_{12} was discovered, Schmidt has prepared seven other types of rings. Bond properties and characteristics

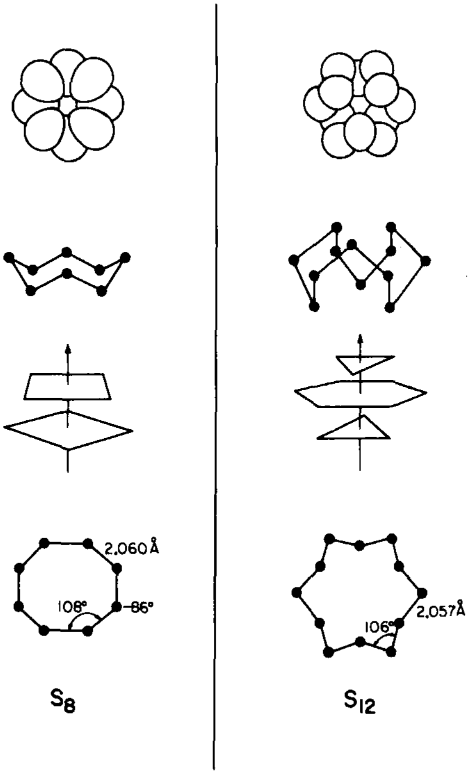


FIG. 2. Different views of cyclooctasulfur and cyclododecasulfur.

of some of these have been reviewed (*88*). Properties and characteristics of the S—S bond in other sulfur compounds have been discussed by Foss (*34–36*), and others. Reviews of structural considerations were written by Tuinstra (*115*) and Rahman (*82*).

In sulfur chains, subsequent sulfur atoms can take either cis or trans positions. Figure 1b shows three enantiomers: cis–cis, cis–trans, and trans–trans configurations. Cis–cis occurs in the S_{12} rings, cis–trans in cyclo-S_8, and trans–trans yields the helices of fibrous sulfur. Pauling discussed the structure of sulfur helices. Semlyen (*101*) updated and enlarged the models for the unperturbed dimensions of catenapoly sulfur. Potassium barium hexathionate crystallizes as cis–cis (*35*), whereas the hexathionate of *trans*-dichlorobis(ethylenediamine)cobalt(III) dihydrate (*36*) and cesium hexasulfide crystallize in trans–trans configurations (*82*). The electron configuration and electron density at various positions in rings and chains have been computed using various semi-empirical and *ab initio* models. Work by Cusachs and his group (*20*, *68–70*) and others (*65*) has given convincing evidence that ground-state properties of sulfur compounds are not influenced by d-orbital participation. However, properties connected with excited states of sulfur depend on d-orbital considerations. Miller (*70*), Wiewiorowski (*124*), and Cusachs (*20*) have used their model to develop an acid–base model for charge-transfer complexes between rings and chains. This model provides a very useful approach to explaining the ESR spectrum (*50*) and other properties of viscous liquid sulfur. These calculations will be mentioned in later sections. They helped explain the color of liquid sulfur (*65*). The nature of sulfur–sulfur bonds in compounds and minerals has been reviewed in recent papers based on the K_α or K_β X-ray spectrum of the sulfur atom (*73*, *123*). The thermodynamics of S—S bonds have been reviewed by Tobolski (*48*) and Jensen (*46*).

II. Well-Established Allotropes of Sulfur

A. MOLECULES WITH LESS THAN 6 ATOMS

Owing to the S—S bond geometry, rings with less than 6 atoms are highly strained and unstable. Pure S_4 and S_5 have not yet been produced, or at least not yet identified. Chains, neutral or charged, are structurally allowed, but they have unstable electron configurations at their terminal atoms. Thus, they have a tendency to rearrange and quickly to form equilibrium mixtures of molecules, all of which are unstable at room temperature and which convert to polymeric chains and then, eventually, to cyclo-S_8. Of the small species, only S_2 is well-known: S_2 exists at a temperature above 800°C and pressures below 1 torr in high purity.

With a bond distance of 1.89 Å in the ground state, S_2 is paramagnetic, like O_2, and has a ground state $^3\Sigma_g^-$. The electron configuration of over eighteen excited states has been established by Barrow and his group (*4, 127*), who studied a large number of electronic spectra using isotopes.

Thiozone (S_3) has a ground state of $^1\Sigma$, like ozone. It is found together with S_4 in sulfur vapor at a temperature around 450°C and pressures around 1 torr. Thiozone can be prepared in low-temperature glasses and rare gas matrices, by photolysis of S_3Cl_2 (*64, 75*). The electronic structure was investigated by Spitzer (*65*).

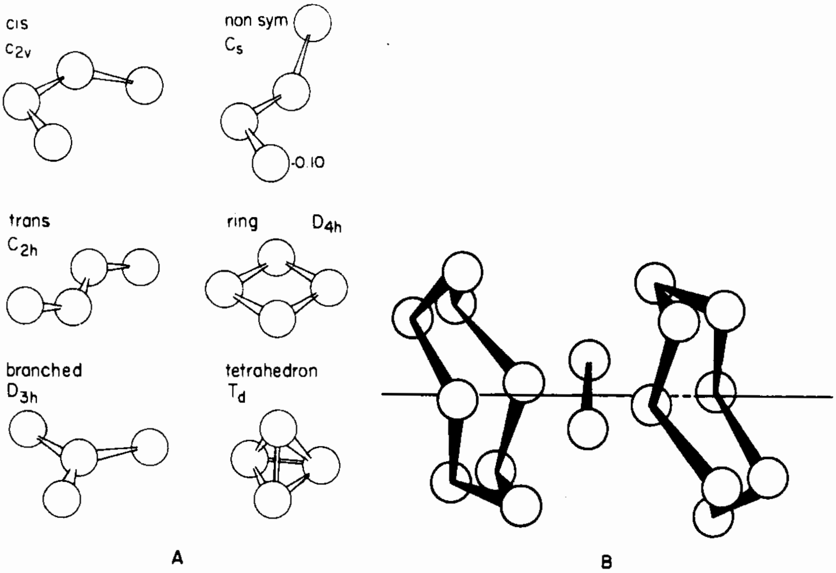


FIG. 3. (A) Isomers and conformers of S_4 (*65*); (B) Charge-transfer complex S_8–S_2–S_8 (*65*).

Species S_4 occurs in a mixture with S_8 in the gas phase, as indicated above. It can be synthesized in matrices by photolysis of S_4Cl_2 or S_2Cl_2 (*67*), or simply by recombination diffusion of S_2 (*66*). This molecule has been identified by its UV and IR spectra. A variety of structures are feasible (Fig. 3a). The planar ring is also the structure proposed for S_4^{2+} (*41*) which is considered to be aromatic in character. Calculations indicate that the branched structure, analogous to the SO_3 structure, should be most stable (*65*). The most likely structure for this very unstable molecule is the trans chain. Species S_4, as well as S_3 and S_2, have been identified by mass spectroscopy (*7*).

The S_5 also occurs in sulfur vapor (*7*, *24*). It is not clear whether the vapor contains cyclopentasulfur or catenapentasulfur, or both. Schmidt (*87*) proposes that S_5 can be prepared from bis-π-cyclopentadienylmolybdenum tetrasulfide by reaction with monosulfurdichloride:

$$(C_5H_5)_2MoS_4 + SCl_2 = S_5 + (C_5H_5)_2MoCl_2$$

The reaction product is a liquid at room temperature.

B. Cyclohexasulfur, Engel-Aten's Rhombohedral S_6

Engel (*28*) prepared cyclohexasulfur in 1891, and Aten (*2*) identified, in 1914, the rhombohedral crystals, but ingrained notions that S_8 should be the only possible molecule stifled acceptance of their work. The existence of S_6 was disbelieved or ignored by most chemists, until Frondel and Whitfield (*37a*), Donnay (*24a*), and, especially, Donohue (*14*), presented a series of papers and all details of the structure were determined. The molecule has a chair form (Fig. 4), and the following parameters:

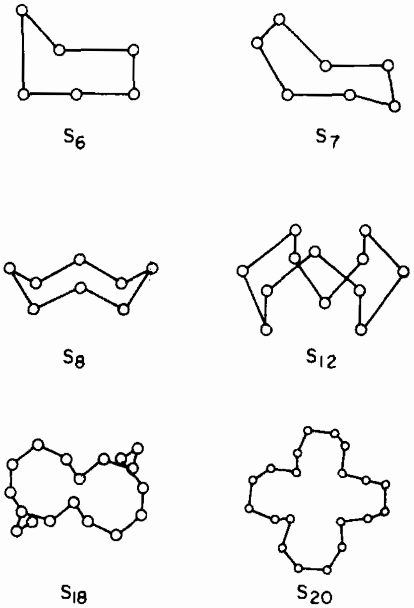


FIG. 4. Six well-established sulfur allotropes.

$$\text{S—S bond length} = 2.057 \pm 0.018\ \text{Å}$$
$$\text{S—S—S bond angle} = 102.2 \pm 1.6°$$
$$\text{S—S—S—S torsion angle} = 74.5 \pm 2.5°$$

The substance can be crystallized from toluene or CS_2. It forms orange-red rhombohedral crystals with a density of 2.209 gm/cm^3, the highest density of any known sulfur allotrope. Eighteen S_6 molecules occupy a unit cell with the space group $R3\text{-}C_{3i}{}^2$. The lattice constants are

$$a = 10.818\ \text{Å}$$
$$c = 4.280\ \text{Å}$$
$$c/a = 0.3956$$

The crystals decompose above 50°C. Engel and Aten prepared the substance by the reaction

$$NaHS_2O_3 + HCl(conc) = S_6 + S_8 + NaCl + H_2O$$

In their quest for new methods for preparing new sulfur rings (*94*), Wilhelm and Schmidt (*125*) studied the simultaneous addition of sulfane and chlorosulfane to cold dry ether,

$$S_2Cl_2 + H_2S_4 = S_6 + 2HCl$$

and succeeded in obtaining S_6 in 87% yield. This synthesis is the basis for the preparation of S_{12}, and other hitherto inaccessible, molecules. Cyclohexasulfur is sensitive to light (it decomposes, leaving S_8 and small amounts of S_{12}), and reacts about 10^4 times faster than S_8 with nucleophilic agents. This molecule exists also in sulfur vapor. Its mass spectrum and IR spectrum have been investigated by Berkowitz (*6*) and others (*74*). The packing of S_6, which is extremely efficient, as demonstrated by the density referred to above, is beautifully visualized in the reference by Donohue (*25*).

C. CYCLOHEPTASULFUR, SCHMIDT'S S_7

Schmidt (*90*) succeeded in 1968 in preparing S_7, the first sulfur ring with an odd number of atoms. The synthetic path employed for preparing S_6 and S_{12} does not provide high yields, thus a new method had to be found. The reaction

$$(C_5H_5)_2TiS_5 + S_2Cl_2 = S_7 + (C_5H_5)_2TiCl_2$$

was made possible after synthesis of the cyclopentadienyl titanium pentasulfide became available (*52*, *53*), as the result of work based on experiences gained with $(NH_4)_2PtS_{15}$, a compound which was first described by Hoffmann (*44*) in 1903. In these compounds, and in the corresponding MoS_4 derivative (*51*), the sulfur atoms form rings in which 1 sulfur atom is replaced by the central metal ion (Fig. 5). The S_7 molecules have the structure (*47*) shown in Fig. 4: 4 sulfur atoms lie on one plane; the IR spectrum indicates that the S—S bond is unequal in different positions (*38*). The existence of the compound was confirmed by mass spectroscopy (*128*). Cycloheptasulfur forms light yellow needles

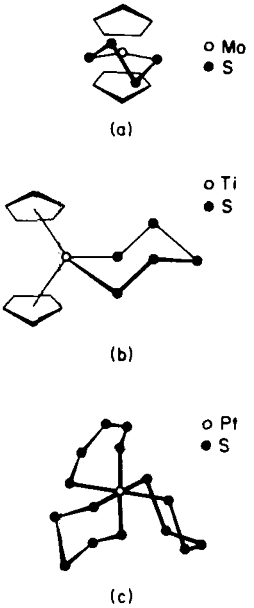


FIG. 5. Molecular structures of (a) $(C_5H_5)_2MoS_4$; (b) $(C_5H_5)_2TiS_5$; and (c) $(NH_4)_2Pt_{15}$.

with a density of $d = 2.090$ gm/cm^3. The lattice constants of this unstable compound had to be determined at −80°C (*47*):

$$a = 21.77\ \text{Å}$$
$$b = 20.97\ \text{Å}$$
$$c = 6.09\ \text{Å}$$
$$\alpha = \beta = \gamma = 90°$$

The space group is not yet known. Sixteen molecules, i.e., 112 atoms, occupy the unit cell. The molecule decomposes at 39°C. It must be stored in the dark and at a low temperature.

D. CYCLOOCTASULFUR

The crown-shaped cyclooctasulfur molecule has been thoroughly studied. The distances and angles within the molecule are (*25*)

$$\text{S—S bond length} = 2.060 \pm 0.003\ \text{Å}$$
$$\text{S—S—S bond angle} = 108.0^\circ \pm 0.7^\circ$$
$$\text{S—S—S—S torsion angle} = 98.3^\circ \pm 2.1^\circ$$

The molecule was first studied in orthorhombic solid sulfur by Bragg (*10*) in 1914. Its properties have been well-reviewed (*25*). It is remarkable that the light sensitivity of this molecule, which remains one of the riddles of elemental sulfur, has not been investigated. There is not one report on experimental work on the determination of the lowest triplet state, which very likely accounts for the dissociation of the ring in room light, a process which probably accounts for the formation of many of the poorly defined allotropes of sulfur. The symmetry of an isolated molecule is D_{4h} as shown in Fig. 2. In orthorhombic sulfur, the symmetry is $82m$–D_{4d} (*109*). The above-mentioned bond data are compared with that of other sulfur species in Table II. The S_8 data are carefully reviewed by Donohue (*25*).

TABLE II

STRUCTURAL PARAMETERS OF ELEMENTAL SULFUR MOLECULES

Molecule	S—S bond length (Å)	S—S—S bond angle (deg)	S—S—S—S torsion angle (deg)	Ref.
S_2	1.890			*4*
$S_{8\alpha}$	2.060 ± 0.003	108.0 ± 0.7	98.3 ± 2.1	*17*
S_{12}	2.053 ± 0.007	106.5 ± 1.4	86.1 ± 5.5	*57*
S_{18}	2.059	106.3	84.4	*22, 98*
S_{20}	2.047	106.5	83.0	*98*
S_∞	2.066	106.0	85.3	*39, 59*
$S_{8\text{-ion}}$	2.04	—	—	*41*
S_8O	(1.483: S—O)	—	—	*105*
	2.20 (bond 1,8 and 1,2)	101.8	101.4	—
	2.04	108	—	—

Three of the polymorphs of cyclooctasulfur are firmly established: orthorhombic α-sulfur, monoclinic β-sulfur, and monoclinic γ-sulfur. Their structure, along different axes, is shown in Fig. 6. Over a dozen of the other allotropes have been reported, but so far they all defy conclusive structure determination, because of their instability, impurity, or both.

1. *Orthorhombic α-Sulfur*

The first accurate structure was presented by Abrahams (*1*). It was refined by Caron and Donohue (*15*), Pawley and Rinaldi (*81*) restudied it and confirmed the earlier work (*72*). The most precise lattice constants are those of Cooper (*17*), computed for 24.8°C:

$$a = 10.4646\ \text{Å}$$
$$b = 12.8660\ \text{Å}$$
$$c = 24.4860\ \text{Å}$$
$$\alpha = \beta = \gamma = 90^\circ$$

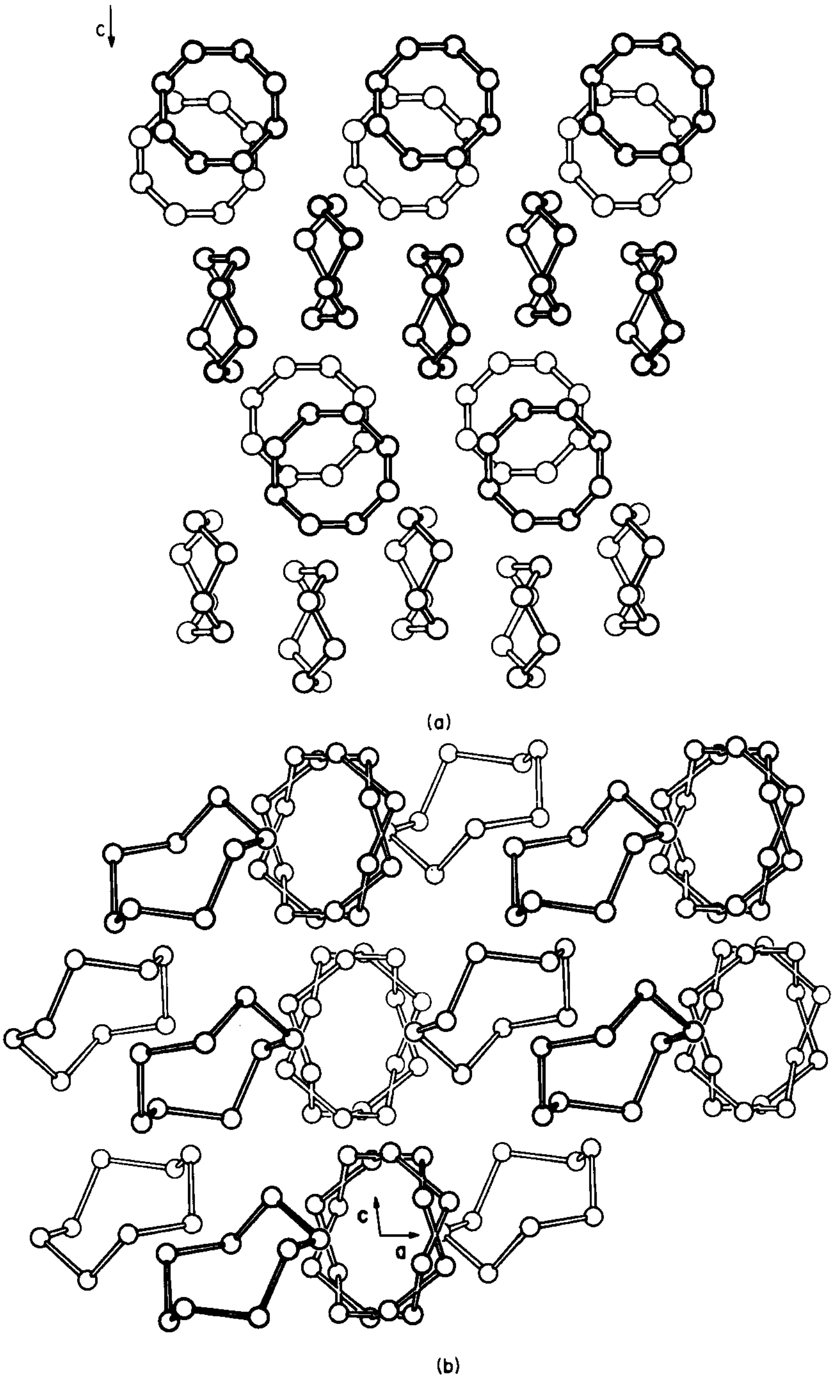
The space group is $Fddd\text{-}D_{2h}^{24}$; the unit cell contains 16 molecules, i.e. 128 atoms, and the density is 2.069 gm/cm^3. The stacking of molecules has been explained by Donohue (*15*). The molecules are not stacked along an axis, but follow a "crankshaft" arrangement. Thus, projections along the axes are quite involved (*26*) (see Fig. 6a).

Since α-sulfur converts into monoclinic β-sulfur upon heating, one cannot grow single crystals from the melt. Very recently a method was described for growing very perfect single crystals from CS_2 solution. It is claimed that they are "almost free" of solvent (*43*). This claim is in conflict with the observation that CS_2 forms a stable, well-defined inclusion in α-sulfur (*62*). However, for many purposes the method might provide ideal single crystals. In studying reports of the IR and Raman spectra of α-sulfur (*76*, *77*, *109*, *118*), it should be remembered that a strong band, believed to be a fundamental of S_8, was identified as belonging to CS_2 (*103*). Thermal analysis shows that single crystals of sulfur do not convert to S_β, even after an hour, but melt at 112°C (*19*).

2. *Monoclinic β-Sulfur*

The first structure determination of β-monoclinic sulfur, which forms from β-orthorhombic by phase transition at 94.2°C, was performed by Trillat and Forestier (*113*). Burwell (*13*) and Sands (*85*) refined the structure:

$$a = 10.778\ \text{Å}$$
$$b = 10.844\ \text{Å}$$
$$c = 10.924\ \text{Å}$$
$$\beta = 95.80^\circ$$


c
(a)
c
a
(b)

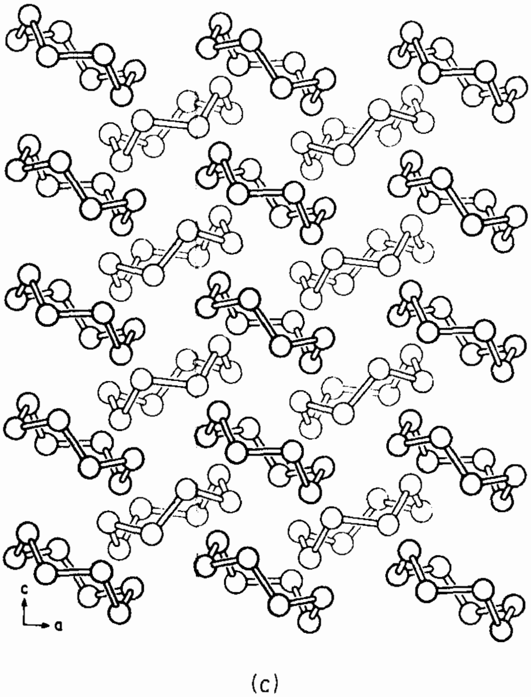


FIG. 6. Structures of (a) S_α; (b) S_β; and (c) S_γ.

The density of this form is 1.94 gm/cm^3. Six S_8 molecules, i.e., 48 atoms, occupy the unit cell; the space group is $P2_1/a\text{-}C_{2h}{}^5$. The ideal melting point has been recently computed to be 133°C (*92*), but the crystals melt around 128° because of decomposition of the S_8 ring, and subsequent melting point depression by solution of the resulting rings and chains.

There has been much controversy over the structure of β-sulfur, and the question of whether it is a true allotrope. It has been suggested that it constitutes merely a thermally distorted lattice expansion of orthorhombic sulfur. Furthermore, phase transition, at 101°C, has been described by various authors (*32*), but it has been shown that this effect was due to traces of water in the lattice (*65*). However, recently a true anomaly in the heat capacity has been found (*71*) at −75°C.

3. *Monoclinic* γ-*Sulfur*; *Muthmann's Sulfur* (*III*)

Until very recently, the existence of γ-sulfur as a pure allotrope of cyclooctasulfur remained in doubt. Despite the fact that it was first described by Muthmann (*72*) in 1890, it was very difficult to prepare until 1974, when Watanabe (*120*) reported a new method. It forms best not from cyclo-S_8 solutions, but from cuprous ethylxanthate which decomposes upon dissolving in pyridine, leaving a brownish solution from which the light yellow γ-sulfur needles crystallize. They decompose when dried. Watanabe (*120*) determined the molecular constants of S_8 in monoclinic γ-sulfur and found them to be very similar to those of orthorhombic α-sulfur. The lattice constants are:

$$\begin{aligned} a &= 8.442 \text{ Å} \\ b &= 13.025 \text{ Å} \\ c &= 9.356 \text{ Å} \\ \beta &= 124°98' \end{aligned}$$

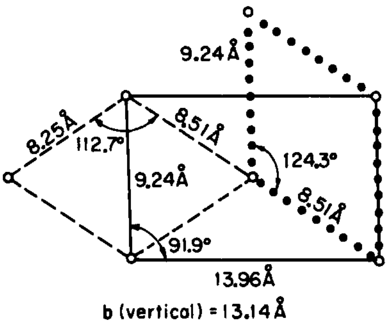


FIG. 7. Correlation between different unit cells of S_γ.

Four S_8 molecules, i.e., 32 atoms occupy one unit cell; the space group is $P2/c$, the density is 2.19 gm/cm^3, i.e., larger than that of either α- or β-sulfur. Thus, γ-sulfur contains more efficiently packed cyclooctasulfur than any other crystal. The crystals decompose upon standing.

The discussion of the structure of this formerly elusive sulfur form had been long hampered by three different choices of axes for labeling. Figure 7 shows the correlation between the three different unit cells. The molecular packing proved to be that proposed by deHaan (*23*). He called it a "sheared penny roll" structure, it is shown in Fig. 6c.

E. CYCLOENNEASULFUR, SCHMIDT'S S_9

Schmidt and Wilhelm in 1970 prepared cycloenneasulfur (*96*) by the reaction:

$$(C_5H_5)_2TiS_5 + S_4Cl_4 = (C_5H_5)_2TiCl_2 + S_9$$

The molecules are apparently of comparable stability with S_6, but the structure has not yet been published. The substance forms deep yellow needles.

F. Cyclodecasulfur, Schmidt's S_{10}

Wilhelm and Schmidt prepared lightly yellow–green solids, containing S_{10} rings by reactions of various matching combinations of sulfanes and chlorosulfanes (*94, 125*), e.g.,

$$H_2S_6 + S_4Cl_2 = S_{10} + 2HCl$$

The yellow S_{10} has since been prepared in far better yield (*90*) according to:

$$(C_5H_5)_2TiS_5 + 2SO_2Cl_2 = S_{10} + 2SO_2 + (C_5H_5)_2TiCl_2$$

At –78°C, 35% yield can be obtained. The compound must be stored at –40°C. The structure has not yet been published; the mass spectrum has been difficult to obtain (*128*).

G. Cycloundecasulfur, Schmidt's S_{11}

Schmidt and Wilhelm prepared this compound by the reaction

$$(C_5H_5)_2TiS_5 + S_6Cl_2 = (C_5H_5)_2TiCl_2 + S_{11}$$

Details of the properties and structure have not yet been released (*97*). The structure of the titanium–sulfur compound is shown in Fig. 5b.

H. Cyclododecasulfur, Schmidt-Wilhelm's S_{12}

Publications of Schmidt and Wilhelm's careful work (*125*) on new synthetic methods for preparing sulfur rings opened a new chapter in our knowledge of elemental sulfur in 1966. Cyclododecasulfur (S_{12}) was discovered 75 years after S_6. It is the third elemental sulfur ring discovered. Its preparation and identification was followed in the 7 subsequent years by the synthesis of another six new types of rings by the same group. The existence of S_{12} shows that large rings can exist and are far more stable than anyone would have thought.

The S_{12} is prepared by reaction of sulfanes with chlorosulfanes (*95*):

$$H_2S_4 + S_2Cl_2 = S_6(50\%) + S_{12}(3\%) + 2HCl$$

or (*93*)

$$H_2S_8 + S_4Cl_2 = S_{12}(18\%) + 2HCl$$

It is amazingly stable. Apparently, S_{12} exists in liquid sulfur, because it can be found in quenched melts (*91*), and it is formed in solutions of S_6 in toluene during decomposition under the influence of light (*92*). The vapor is, however, unstable; thus, mass spectroscopic identification proves to be difficult (*12*). The molecules have $2/m\text{–}C_{2h}$ symmetry in the crystal, but are close to $3m\text{–}D_{3d}$. Table II shows that the bond properties lie between those of S_6 and S_8:

$$\begin{aligned} \text{S—S bond length} &= 2.053 \pm 0.007\ \text{Å} \\ \text{S—S—S bond angle} &= 106.5 \pm 1.4^\circ \\ \text{S—S—S—S torsion angle} &= 86.1 \pm 5.5^\circ \end{aligned}$$

The atoms are stacked in three parallel planes (see Fig. 2) yielding a highly symmetric molecule which forms such a stable solid that the melting point is 148°C, i.e., almost 20° higher than that of orthorhombic cyclooctasulfur. Separation of S_{12} from S_8 is aided by the low solubility of the first: S_{12} is about 150 times less soluble (*93*). The lattice constants are (*57*):

$$\begin{aligned} a &= 4.730\ \text{Å} \\ b &= 9.104\ \text{Å} \\ c &= 14.7574\ \text{Å} \end{aligned}$$

The unit cell contains two molecules, i.e., 24 atoms. The density is 2.036 gm/cm^3. The space group is $Pnmm\text{–}D_{2h}{}^{12}$.

A comparison of the stability of different sulfur allotropes will be made possible with S_{12}. The order of reactivity toward diphenyl-*o*-tolylphosphine is

$$S_6 > S_7 > S_{12} > S_8$$

A recent report deals with the IR spectrum (*107*) of S_{12} and confirms that very pure crystals free of S_6 and S_8 can be prepared.

I. CYCLOOCTADECASULFUR, SCHMIDT'S S_{18}

Very recently, details of the preparation, properties, and structure of S_{18} have become available (*22, 98*). It is best prepared by the reaction:

$$H_2S_8 + S_{10}Cl_2 = S_{18} + 2HCl$$

As S_8H_2 and $S_{10}Cl_2$ are both not easily prepared in the pure state, the starting materials are specially designed mixtures containing impurities of the correct chain length. The lemon-yellow crystals are separated from S_{20} by recrystallization from CS_2. The solubility of S_{18} is 240 mg/

100 ml CS_2 at 20°C. This molecule is unexpectedly stable. It melts at 128°, and, if stored in the dark, displays an unchanged X-ray diffraction pattern after 5 years. The bond parameters are (*22, 98*):

S—S bond length = 2.059 Å
S—S—S bond angle = 106.3°
S—S—S—S torsion angle = 84.4°

The bond data are very similar to those of fibrous sulfur, and the values are intermediate between those of S_6 and S_8, and similar to those of S_{12}. The lattice constants are

$a = 21.152$ Å
$b = 11.441$ Å
$c = 7.581$ Å

Four molecules, i.e., 72 atoms, are contained in a unit cell. The density is 2.090 gm/cm^3, the space group is $P2_12_12_1$.

The discovery of this large ring will undoubtedly lead to reexamination of the properties of melts around the melting point: Krebs and many others proposed long ago that liquid sulfur contained a large ring, S_π, which was to be responsible for the melting point depression during melting.

J. CYCLOICOSASULFUR, SCHMIDT'S S_{20}

Schmidt synthesized S_{20} from sulfanes and chlorosulfanes (*98*) by using carefully designed mixtures of compounds and catalyzing the reaction with HCl.

$$H_2S_{10} + S_{10}Cl_2 = S_{20} + 2HCl$$

The S_{20} was described in a very recent paper. It melts at 124°C, but in solution, where it is more soluble than S_{18}, the molecule decomposes already at 35°C. In this molecule, 4 atoms are each in a plane (see Fig. 4). The density is the lowest of any known allotrope, $d = 2.016$ gm/cm^3. The pale yellow crystals have the following lattice parameters (*98*):

$a = 18.580$ Å
$b = 13.181$ Å
$c = 8.600$ Å

Four molecules, i.e., 80 atoms fill the unit cell. The space group is *Pbcn*. The bond characteristics are similar to those of S_{18}, S_{12}, and S_{fibrous}, and lie between the values for S_6 and S_8:

$$S{-}S \text{ bond length} = 2.047 \text{ Å}$$
$$S{-}S{-}S \text{ bond angle} = 106.5°$$
$$S{-}S{-}S{-}S \text{ torsion angle} = 83.0°$$

K. POLYCATENASULFUR, FIBROUS SULFUR, S_∞

Polycatenasulfur is also called fibrous sulfur, polymeric sulfur, plastic sulfur, or S_∞. It is formed by quenching a viscous sulfur melt. Liquid polymeric sulfur is a kinetic equilibrium mixture containing a very large number of molecules with an average chain length of up to 10^5. The chain length depends on temperature, and on the concentration of rings. Schmidt (*87*) has shown that 2% S_6 suffice to induce polymerization at 150°C, i.e., 10° below the normal temperature. He also demonstrated that stable sulfur-containing rings, added at 200°C, can reduce the average chain length drastically.

Crystalline samples are produced by stretching polymeric sulfur during or after chilling (*25*). Solid samples contain always other sulfur allotropes, among them rings. It is now believed that the long sulfur helices contain 10 atoms for every three turns. The best presently available bond data (*25*) are

$$S{-}S \text{ bond length} = 2.066 \text{ Å}$$
$$S{-}S{-}S \text{ bond angle} = 106°$$
$$S{-}S{-}S{-}S \text{ torsion angle} = 85.3°$$

These values are often taken as the "free" sulfur–sulfur bond characteristics (*101*). The recent preparation of rings with 12, 18, and 20 atoms has shown that the bond angle and torsion angle given above are closely observed in all these compounds. The first structure determinations were authored by Trillat and Forestier in 1931 (*113*), and Meyer and Go (*67a*) in 1934. The present data were provided by Donohue (*27*), Tuinstra (*114*, *115*), and Geller (*39*, *59*). The structure is not as certain as that for the above-mentioned rings. The lattice constants are

$$a = 13.8 \text{ Å}$$
$$b = 4 \times 8.10 \text{ Å}$$
$$c = 9.25 \text{ Å}$$
$$\gamma = 85.3°$$

One hundred sixty atoms fill a unit cell that has the space group $Ccm2_1$–$C_{2v}{}^{12}$. The density is $d = 2.01$ gm/cm^3.

As mentioned, freshly drawn fibrous sulfur is a mixture, containing S_8 and possibly other rings. Geller prepared a substance with an identical X-ray pattern by applying a pressure of 27 kbar (*57*).

The arrangement of left- and right-turn helices and the overall structure still remain to be elucidated.

Fibrous sulfur is probably rarely pure. Impurities can influence the structure in many ways. As long as only mixtures are available, further, apparently contradictory reports on similar structures are to be expected. We discuss some of these forms in Section III.

L. CYCLOCATENASULFUR: CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes between cyclooctasulfur and other compounds have been proposed for some time. Iodine complexes were described by Jander (*45*) and Meyer (*65*) and complexes with CHI_3 by Bjorvatten (*8*). Wiewiorowski proposed a complex of sulfur with itself, cyclo-S_8–catena-S_8–cyclo-S_8 (*124*), in order to explain the low ESR intensity of liquid sulfur (*50*). Figure 3b shows a charge-transfer complex of cyclosulfur with catenasulfur. Semiempirical Hückel calculations indicate that such complexes are stable (*65*). The recent work of Koningsberger (*50*) has lent support to this postulate. Schmidt (*87*) discovered that 2% S_6, added to sulfur at 150°C causes polymerization lasting 20 min, and that sulfur rings, e.g., 2% trithiane or trimeric thioacetaldehyde (which are not known to react, as they can be recovered unchanged even at 200°C), reduce the viscosity. This also supports the belief that rings and chains interact to form a charge-transfer complex, probably containing two rings and a chain. It is also possible for a chain to complex both sides of a ring. The stability of such complexes is not yet known. It may be that photosulfur, prepared by illuminating solutions of cyclooctasulfur in benzene or toluene, consists of such a substance. Photosulfur is insoluble and, in the dark, slowly converts to cyclooctasulfur (*61, 62*).

M. MOLECULAR IONS

Negative ions of sulfur exist in aqueous polysulfide solutions (*112a*) and nonaqueous solutions (*16*). The structure of these ions is presumed to be similar to that of Feher's sulfanes (*87*) and their corresponding salts. Figure 1 shows that in these compounds cis–cis or trans–trans configurations are possible. Some bond data are given in Table II. Typical values are (*101*)

$$\text{S—S bond length} = 2.048\ \text{Å}$$
$$\text{S—S—S bond angle} = 107°55'$$
$$\text{S—S—S—S torsion angle} = 90°$$

Positive ions of sulfur have been identified by Gillespie (*41*, *42*) and others in concentrated acids, in minerals (*99*, *100*), and in doped salts (*40*). Three ions, S_4^{2+}, S_8^{2+}, and S_{16}^{2+} (*41*) seem to exist. The S_4^{2+} is pale yellow, diamagnetic, and, as X-ray studies indicate, very likely planar, with aromatic character. Solutions containing S_8^{2+} are deep blue. The structure of the S_8^{2+} ring is shown in Fig. 8c. It is similar to cyclooctasulfur, but the crown-structure, exo-exo is changed to exo-endo. The nature of various singly charged ions S_n^+, with $4 < n < 8$ is not yet understood. An excellent review of recent work is given by Gillespie (*41*).

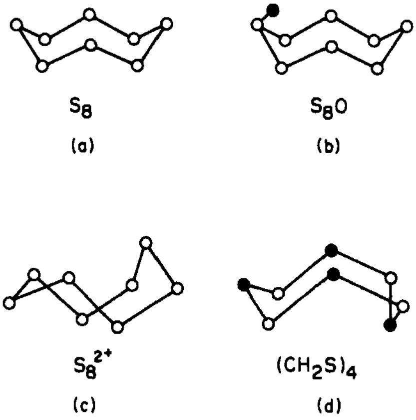


FIG. 8. Eight-membered sulfur rings: (a) S_8; (b) S_8O; (c) S_8^{2+}; and (d) $(CH_2S)_4$.

N. RINGS CONTAINING OTHER ELEMENTS

This is not the place for a review of sulfur-containing rings. We mention merely some selected species which have been described in the recent literature.

1. S_8O

By using the synthetic method of Feher modified by Schmidt and Wilhelm, Steudel and Rentsch (*106*) prepared a sulfur ring S_8O (Fig. 8b) by the reaction:

$$H_2S_n + SOCl_2 = S_8O + 2HCl$$

The S_8O is stable if stored at low temperature. This molecule contains an oxygen attached to the normal cyclooctasulfur molecule. The branching of the sulfur ring is quite surprising. The presence of the oxygen, as expected, influences the bonding: the S—S bond distance in neighboring S atoms increases to 2.20 Å ,the highest yet known value, indicating a greatly weakened bond. The average S—S bond distance is 2.04. The bond characteristics (*105*) are

S—S bond length = 2.04 Å (2.20 Å for bonds 1, 8 and 1, 2)
S—S—S bond angle = 108° (101° for bonds 1, 8 and 1, 2)
S—S—S—S torsion angle = 101°

The lattice constants (*105*) of the yellow crystals, with space group *Pca*2 and density $d = 2.13$ gm/cm^3 are

$a = 13.197$ Å
$b = 7.973$ Å
$c = 8.096$ A

The substance decomposes above room temperature, but the IR and Raman spectra have been reported (*108*).

2. *Selenium–Sulfur Rings*

Cooper (*18*) prepared mixed S_nSe_{8-n} rings, as did Schmidt and others (*65*); forty isomers are possible. Compound S_7Se has been described (*121*) together with a lemon-yellow S_6Se_2 and an orange-red S_5Se_2 seven-ring (*122*). Synthesis proceeds as follows:

$$H_2S_n + SeCl_4 = Se_nS_m + 4HCl$$

In this way, mixed crystals containing both S_{12} and Se_2S_{10} were prepared (*121*). Their lattice parameters are

$a = 4.774$ Å
$b = 9.193$ Å
$c = 14.68$ Å

These values are similar to those of S_{12}. The space group is *Pnmmm*-$D_{2h}{}^{12}$. Bond data are as follows:

S—S bond distance = 2.10 Å
S—S—S bond angle = 106°
S—S—S—S torsion angle = ~ 100°

3. *Tellurium–Sulfur Rings*

Weiss (*122*) prepared S_7TeCl_2, using the following reaction:

$$H_2S_n + TeCl_4 = S_7TeCl_2 + 2HCl$$

The orange crystals decompose at 95°C and melt at 110°C. The tellurium atom is coordinated as a distorted bipyramid, with Cl occupying the apices of the pyramid.

4. *Organic Compounds*

A variety of rings of formula $C_nH_mS_x$, containing S—S bonds, can be prepared. Several seven-, eight-, nine-, ten-, eleven-, and twelve-membered rings containing 3–8 sulfur atoms, as polysulfide, have been prepared (*63*) by the reaction:

$$(CH_2)_n - (SH)_2 + S_mCl_2 = (CH_2)_n - S_{m+2} \text{ ring}$$

Fehér (*33*) used a similar technique to make pentathiepin, benzopentathiepin, and similar compounds (*125*).

Of further interest are eight-membered rings containing alternating S—C bonds. Frank and Degen (*37*) published the structure of 1,3,5,7-tetrahiocane, $(CH_2S)_4$, which is shown in Fig. 8d. Its lattice constants are

$$a = 20.340 \text{ Å}$$
$$b = 8.747 \text{ Å}$$
$$c = 13.466 \text{ Å}$$

The unit cell contains 12 molecules in three crystallographically independent sites. The space group is $P2_1/c$. The bond characteristics are

S—C bond length = 1.817 Å
C—S—C bond angle = 103°
S—C—S bond angle = 119°

Torsion angles are about 80°, except for C(1)–S(2) and S(8)–C(1) = 109° and for C(3)–S(4) and S(6)–C(7) = 49°. Schmidt prepared thiaformaldehyde (*89*) and other cyclic compounds during his studies of sulfur polymers (*86*). The structures of all allotropes are compared in Table III.

III. Incompletely Characterized Allotropes and Mixtures

In Section II, the structures of fourteen well-defined allotropes have been described. About forty other allotropes have been reported, but for these structural data are incomplete or contradictory. The reason for this varies. Some allotropes, such as τ-sulfur that forms only in 2 out of 5000 experiments (*29*), are hard to prepare or are unstable. Others, such as ω-sulfur are easy to prepare and reasonably stable, but X-ray data are contradictory and have led to much confusion and controversy.

TABLE III

STRUCTURAL DATA FOR SOLID SULFUR ALLOTROPES

Molecule	Color	Unit cell (Å)			Angle β (deg)	Space cell[a]	Space group	Density (gm/cm^3)	Decomp. or melting pt. (°C)	Ref.
		a	*b*	*c*						
S_6	Orange-red	10.818	($c/a = 0.3956$)	4.280 ± 0.001	—	3; 18	$\bar{R}3\text{–}C_{3i}^2$	2.209	50–60	*14*
S_7	Yellow	21.77	20.97	6.09	—	16; 112	?	2.090	39	*47*
$S_{8-\alpha}$	Yellow	10.4646	12.8660	24.4860	—	16; 128	$Fddd\text{–}D_{2h}^{24}$	2.069	94(112)	*17*
$S_{8-\beta}$	Yellow	10.778	10.844	10.924	95.80	6; 48	$P2_1/a\text{–}C_{2h}^5$	1.94	133	*85*
$S_{8-\gamma}$	Light yellow	8.442	13.025	9.356	124.98	4; 32	$P_2/c\text{–}C_{2h}^4$	2.19	~20	*120*
S_{12}	Pale yellow	4.730	9.104	14.574	—	2; 24	$Pnnm\text{–}D_{2h}^{12}$	2.036	148	*57*
S_{18}	Lemon-yellow	21.152	11.441	7.581	—	4; 72	$P2_12_12_1\text{–}D_2^4$	2.090	128	*22, 98*
S_{20}	Pale yellow	18.580	13.181	8.600	—	4; 80	$Pbcn$	2.016	124–125	*98*
S_∞	Yellow	13.8	4 × 8.10	9.25	85.3	160[b]	$Ccm2_1\text{–}C_{2v}^{12}$	2.01	104	*59*
S_8O	Yellow	13.197	7.973	8.096	—	4; 32	$Pca2\text{–}C_{2v}^5$	2.13	20–78	*105*
S_7TeO_2	Orange	8.82	9.01	13.28	—	4; 28	$Pmnb\text{–}D_{2h}^{16}$	2.65	—	*122*

[a] First number = number of molecules; second number = number of atoms in unit cell.

[b] Ten atoms for three turns.

The reason for the lack of progress on this allotrope, which was first reported in 1939, and on which over a dozen publications have appeared, is often misunderstood. The difficulty is intrinsic. The existence of a great variety of intramolecular and intermolecular allotropes proves that many species must have comparable stability, i.e., that they can coexist. Thus, many contradictory allotropes are mixtures. We know now that the challenge of preparing and identifying a new allotrope does not end with its synthesis, but includes isolation of the metastable species from a mixture of equally metastable compounds, a process that can be very difficult. Separation is impossible if it leads to chemical reactions, as is the case with ω-sulfur, and others, which even decompose during low-temperature chromatography (*30*). Thus, not all new allotropes are pure; many allotropes are complex mixtures, and many materials that were believed to be new allotropes are in reality merely new mixtures of well-established allotropes.

TABLE IV

SUMMARY OF ALLOTROPES

	Product		
Reagent	Molecular species	Well-established	Inconclusive or mixture
Cyclo-S_8 solution	Cyclo-S_8	α, β, γ,	γ, δ, ξ, ψ, μ, ψ, η, o, χ, κ, ζ, θ, τ, ψ
Sulfur compounds in solution	Cyclo-(S_5), S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}, S_{20}, S_∞	S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}, S_{20}, S_∞	ϵ, ν, ω, red, orange
Solid sulfur	Cyclo-S_8 catena-S_∞	S_ψ	Laminar, ω, orange, metallic, cubic
Liquid sulfur	Cyclo-S_6, S_{12} Catena $C < n < 10^5$	α, β, S_{12} $\psi(= \mu)$	π, ι, ν, ψ
Sulfur vapor	$2 < n < 12$	α, S_∞	Crystex, ω, red, green, blue

In the following sections a short summary of the better known of the incompletely characterized allotropes is given. The data are summarized in Table IV; for details, we refer to reviews (*25*, *65*) or the original literature. The study of the latter is, however, often hard, as different authors use different conventions and nomenclature, and many researchers are not familiar with all earlier literature. We use the preparation method as a basis for this review, as it constitutes the most reliable identification.

A. FROM SOLUTIONS OF CYCLOOCTASULFUR

Below 90°C, solutions of sulfur in organic solvents contain normally cyclooctasulfur. Muthmann (*72*) in 1890, Korinth (*54*) in 1928, and Erämetsä (*29–31*) in 1953 are among the many who tried to produce new types of sulfur allotropes from solution. Korinth (*54*) used various solvents and additives, such as selenium, rubber, and nitrobenzene to induce formation of unusual crystal forms. He succeeded in finding recipes for four new allotropes which were reinvestigated by Erämetsä (*29–31*). The latter found that several of these could be separated into various fractions. In the process of doing so, Erämetsä identified twelve new allotropes. None is stable for more than 15 min. As structural data are lacking, we will not further dwell on them. The case of γ-sulfur, first prepared by Muthmann in 1890, shows that some of these allotropes may be confirmed in the future but probably only after better synthetic methods for preparing them have been found.

Some attempts have been made to prepare new allotropes from hot solutions. The phase equilibria of solutions of various organic solvents with liquid sulfur have been reported (*58*), but the upmost caution is in order in dealing with these systems, as sulfur reacts quite smoothly with with all solvents above 120°C.

B. FROM SOLUTIONS CONTAINING OTHER SULFUR COMPOUNDS

In Section II it is shown that many new allotropes can be very elegantly prepared if matched reagents are used to build up the molecular unit in dilute solution, before the metastable molecules come in contact with each other. Difficulty arises if the reagents are not selective. This is the case if sulfane mixtures, called "raw oil," are used, or if chains are built up by continued addition of a sulfur group, as is the case in the classic synthesis of Engel (*28*). A further problem arises if large species are produced in aqueous solution, because in that environment polythionates are also stable, and the resulting product might contain 99% sulfur, but the terminal group of chains might be another element. The work by Watanabe (*120*) and Schmidt (*88*, *125*) proves that this synthetic approach to the preparation for new sulfur allotropes has not yet been exhausted.

Das (*21*) and others have used reagents without solvents for synthesizing new materials. ω-Sulfur is such an example, showing that the resultant mixtures are very hard to analyze. Details on the controversy about ω-sulfur are given in Donohue (*25*).

C. From Solid Sulfur

Irradiation of sulfur by various means yields discoloration of elemental sulfur, but it is doubtful that these forms will ever lead to pure allotropes. Above 92°C, α-sulfur converts into monoclinic sulfur. The kinetics of the transformation depend on various factors. Thermal analysis of single crystals of α-sulfur shows that the conversion is so slow that α-sulfur can be heated to 112°C, where it melts, before β-sulfur is formed (*19*).

Exposure of solid sulfur to pressure has proven more fruitful (*60*) than was assumed when Bridgman reported that sulfur did not display any new properties at high pressure. The work of Bååk (*3*), who reported the preparation of cubic sulfur by application of pressure to α-sulfur, stimulated much interest and led Geller (*39*, *59*, *60*) and others to pay attention to this system. Geller made several new allotropes. One has the same X-ray pattern as fibrous sulfur (*39*). Another is similar to laminar sulfur, and new forms were reported by Das (*21*) and Tuinstra (*114*). Much structural elucidation (*60*, *84*) is still going on, but after careful study of the literature, it seems that all these allotropes probably are mixtures, from which a component cannot be separated unharmed. Nevertheless, these substances demand attention, because the structural patterns might yield new information on the nature of the sulfur–sulfur bond. Tuinstra's suggestion (*115*) of a "cross-grained plywood structure" for his ω-2-sulfur shows that not all steric considerations have been properly explored: If the pitch of sulfur helices is, indeed, equal to the distance between adjacent helix axes (*25*), chains and rings might convert into each other with ease. This might explain why polymeric sulfur, under dynamic stress, is far more stable than if it is not worked.

High-pressure investigations led to reports of over twelve new phases by Vezzoli (*116*, *117*), Ward (*119*), Susse (*111*), and Pankov (*78*). In evaluating this work it should be known that equilibria are established very slowly, especially at high temperatures where viscous species are produced. Block (*9*) reported that above 235°C equilibrium is not nearly reached after 3 days. Thus the properties of samples reflect their history.

D. From Liquid Sulfur

Fibrous sulfur, described in Section II, is prepared by quenching liquid sulfur. Aten and Erämetsä's π-sulfur is obtained from the melt at

120°C. Schmidt (*91*) showed that the melt contains rings other than S_8, for example S_{12}. Above 156°C, the well-known polymerization sets in, and species with up to 10^5 sulfur atoms are in equilibrium with various rings and chains. Allotropes prepared from such a complex mixture cannot be expected to be pure. Much more needs to be known about the liquid before systematic attempts can be made to exploit the species in the liquid for synthetic purposes. However, many new data are becoming available quickly. Bröllos studied the thermal analysis of sulfur at various pressures (*11*), the optical absorption at various pressures (*55*), and its influence on the polymerization. Kuballa (*55*) and Klement (*49*) also studied the thermal analysis, and determined the kinetics of intramolecular conversion, which was found to be slow. Baur (*5*) reports that molar polarization indicates the presence of a new species in liquid sulfur, below the polymerization temperature. He assigned it tentatively to the chair form of S_8, which would be similar to that observed for the S_8^{2+} ion (Fig. 8c). Hot liquid sulfur loses its viscosity and turns very dark, due to the formation of small species such as S_3 and S_4 (*75*). Freezing of such species leads to a red glass from which, with ingenuity, various species might conceivably be isolated. Wiewiorowski has proposed that charge-transfer complexes (*124*) are present in liquid sulfur and account for much of its behavior, as has been explained in Section II. Obviously, much remains to be learned about the complex chemical system called liquid sulfur.

E. From Sulfur Vapor

Sulfur vapor contains small molecules, of which only S_8, at low temperature, and S_2, at high temperature (*4*, *6*, *7*, *83*), can be separated in the pure state. Both have been described in Section II. In an intermediate pressure and temperature range, mixtures of molecules with the formula S_n $(2 < n < 12)$ have been identified with mass spectroscopy. The components of sulfur vapor at low temperature and very high pressure are not yet known. It is not even known whether gas-phase molecules are present as rings or as chains.

Quenched sulfur vapor has been studied for a long time. Slowly quenched to room temperature it yields flowers of sulfur, which were prepared by alchemists. The flowers can be separated into several phases by elution with CS_2. Thermal analysis (*19*) shows that α-sulfur, β-sulfur, and ω-sulfur are present. The latter melts at 104°C. The X-ray structure of ω-sulfur, prepared in this way, and that of Crystex (*104*), a widely used insoluble form of sulfur, also called supersublimation sulfur, are not fully established. As explained above, these and similar substances are probably mixtures, and their structural data depends on the method of preparation, history of the reagents and products, and the age of the sample. Several of these allotropes are stable only if traces of additives are present. In conclusion, we want to point out that many of the doubtful allotropes are not pure elemental sulfur. It is difficult to purify the element, although there has been much progress in this work (*80*, *112*).

ACKNOWLEDGMENTS

The work reported here was done under the auspices of the U.S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory.

The author wishes to thank Dr. L. Brewer for valuable suggestions and support.

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