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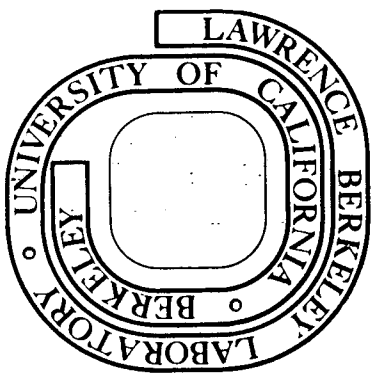

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THE STRUCTURES OF ELEMENTAL SULFUR

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I. Introduction

A. SUMMARY

Sulfur is mentioned in the old testament, and by Homer, and has been widely used for many thousands of years. The thermodynamically stable form of sulfur forms deep yellow, non-oderous orthorhombic crystals with a space group Fddd-D^{24}_{2h}, containing 16 molecules, i.e. 128 atoms in the unit cell. It has a density of 2.069 g/cm^3 and is well soluble in CS_2. Its molecular unit is S_8, cycloocta sulfur, a crown-shaped molecule with a symmetry of D_{4d}. The pale flowers of sulfur, prepared already by alchemists by distillation are insoluble in CS_2, and their structure is not yet fully understood. A third form, plastic sulfur, is obtained by melting sulfur to about 180°, where it forms as highly viscous syrup. Up to date, some 45 different forms of sulfur have been described (25,61,62), and for 12 of these detailed structural data is available. These forms differ in intramolecular and intermolecular structure.

Sulfur can form rings and chains of various shapes and sizes. In addition, the crown-shaped cyclo S_8, nine other types of rings can be prepared: The first of these, cyclohexa sulfur, also called Engel's or Aten's sulfur, or rhomboedral sulfur, S_ρ, was first described by Engel in 1891 (28). The other 8 types of rings were all discovered during the last ten years by Schmidt and his coworkers (87,88) notably Wilhelm (125).

Sulfur chains of uniform length cannot be made. All catena-allotropes are mixtures, containing molecules of varying lengths. There is still much question whether pure polymeric chains can exist at room temperature, or whether the terminal atoms of long chains are bound to

impurities, to sulfur rings, forming charge transfer complexes of catena sulfur with cyclo-sulfur, 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). Much data on preparation, stability and structure of rings can be found in a recent review paper by Schmidt (87,88). As will be seen below, our knowledge of sulfur allotropes is still very incomplete, because the chemistry of elemental sulfur with itself is far more complex than anyone suspected. During the last hundred 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 obey the basic characteristics of the S-S bond. It is noteworthy, at this place, 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 chapter heavy emphasis is given to recent work.

B. STRUCTURAL CONSIDERATIONS

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 101° in

Table I

S_8O (105) and 108° in monoclinic γ-sulfur (120). In cycloocta sulfur 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° in S_8. Normal bond values are shown in Fig. 1.

Figure 1

Experimental and theoretical ramifications of S-S bond properties observed of S_8, S_6 and polymeric sulfur have been reviewed by Pauling 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 by Skjerven (102) and others, that various experimental observations indicated the existence of large rings (62). The distrust of large rings was proven unfounded prejudice when Schmidt and Wilhelm 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 discovery of S_{12} Schmidt has prepared 7 other types of rings. Bond properties and characteristics of some of these have been reviewed (88). Properties and characteristics of 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).

Figure 2

In sulfur chains, subsequent sulfur atoms can take either cis or trans positions. Figure 1 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), while 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 semiempirical 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 (2) 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 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. Molecular Variety

A. SPECIES WITH LESS THAN 6 ATOMS

Due to the S-S bond geometry, rings with less than six 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 to quickly 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. S_2, with a bond distance of 1.89 Å in the ground state, is paramagnetic, like O_2, and has a ground state $^3\Sigma_g^-$. The electron configuration of over 18 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. S_3 is found together with S_4 in sulfur vapor at a temperature around 450°C and pressures around 1 torr. S_3 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).

S_4 occurs in a mixture with S_3 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 spectrum. A variety of structures are feasible, Fig. 3. The planar ring is also the structure proposed for

Figure 3

S_4^{2+} (41) which is considered to be aromatic in character. Calculations indicate that the branched structure, analogue to the SO_3 structure, should be most stable (65). The most likely structure for this very unstable molecule is the trans-chain. S_4, as well as S_3 and S_2 have been identified by mass spectroscopy (9).

S_5 also occurs in sulfur vapor (9,24). It is not clear whether the vapor contains cyclopenta sulfur or catenapenta sulfur, 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, S_6

Engel (28) prepared cyclo-hexasulfur in 1891, and Aten (2) identified, in 1914, the rhomboedral 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 (1950), Donnay (1955), and, especially, Donohue (14), presented a series of papers until all details of the structure were determined.

Figure 4 The molecule has chair form, Fig. 4, and

S-S bond length: 2.057 ± 0.018 Å

S-S-S bond angle: 102.2 ± 1.6°

S-S-S-S torsion angle: 74.5 ± 2.5°

the substance can be crystallized from toluene, or CS_2. It forms orange-red rhomboedral crystals with a density of 2.209 g/cm^3, the highest density of any known sulfur allotrope. Eighteen S_6 molecules occupy a unit cell

with the space group $R3\text{-}C^2_{3i}$. 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

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

In their quest for new methods for preparing new sulfur rings (94), Wilhelm and Schmidt (1966) 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 preparation of S_{12}, and other, before inaccessible, molecules. S_6 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 the sulfur vapor. Its mass spectrum and IR spectrum has been investigated by Berkowitz (8), and others (74). The packing of S_6, which is extremely efficient, as demonstrated by the density above, is beautifully visualized in the reference by Donohue (25).

C. CYCLOHEPTASULFUR, S_7

Schmidt (92) succeeded in 1968 to prepare 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 (53), as the result of work based on experiences gained with $(NH_4)_2PtS_{15}$, a compound which was first described (44) by Hoffmann in 1903. In these compounds, and in the corresponding MoS_4 (51), the sulfur atoms form rings in which one sulfur atom is replaced by the central metal ion, Figure 5. S_7 molecules have the structure (47) shown in Fig. 4. Four sulfur atoms lie on one plain. 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). S_7 forms light yellow needles with a density of d = 2.090 g/cm^3. The lattice constants of this unstable compound had to be determined at -80°C (47):

Figure 5

$$a = 21.77 \text{ Å}$$

$$b = 20.97 \text{ Å}$$

$$c = 6.09 \text{ Å}$$

$\alpha = \beta = \gamma = 90°$.

The space group is not yet known. Sixteen molecules, i.e.112 atoms, occupy the unit cell. The molecule decomposes at 39°. 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)

S-S bond length = 2.060 ± 0.003 Å

S-S-S bond angle = 108.0° ± 0.7

S-S-S-S torsion angle = 98.3° ± 2.1°

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. 1. In orthorhombic sulfur, the symmetry is $82m$-D_{4d} (109). The above-mentioned bond data is compared with that of other sulfur species in Table II. The S_8 data are carefully reviewed by Donohue (25).

Table II

Three of the polymorphs of cycloocta sulfur 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, either because of their instability, impurity, or because of both.

Figure 6

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 (72) and confirmed the earlier work. The most precise lattice constants are those of copper, computed for 24.8°C.

$$a = 10.4646 \text{ Å}$$

$$b = 12.8660 \text{ Å}$$

$$c = 24.4860 \text{ Å}$$

$$\alpha = \beta = \gamma = 90° \text{ Å}$$

The space group is Fddd-D^{24}_{2h}; the unit cell contains 16 molecules, i.e. 128 atoms, the density is 2.069 g/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), Figure 6a.

Since α-sulfur converts into monoclinic β-sulfur upon heating, one cannot grown 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 (61). However, for many purposes the method might provide ideal single crystals. In studying reports of IR and Raman spectra of α-sulfur (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 (104). 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 Forrestier(113). Burwell (13) and Sands (85) refined the structure:

$a = 10.778$ Å

$b = 10.844$ Å

$c = 10.924$ Å

$\beta = 95.80°$

The density of this form is 1.94 g/cm^3. Six S_8 molecules, i.e. 48 atoms, occupy the unit cell, the space group is $P2_1/a\text{-}C^5_{2h}$. The ideal melting point has been recently computed to be 133°C (91), 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 was a true allotrope. This is because it was 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 cyclo-octa sulfur 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) discussed 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 4X γ-sulfur, and found them to be very similar to those of orthorhombic α-sulfur. The lattice constants are

$$a = 8.442 \text{ Å}$$

$$b = 13.025 \text{ Å}$$

$$c = 9.356 \text{ Å}$$

$$\beta = 124°98'$$

Four S_8 molecules, i.e. 32 atoms occupy one unit cell; the space group is P2/c, the density is 2.19 g/cm^3, i.e. larger than that of either α or β sulfur. Thus, γ-sulfur contains more efficiently packed cycloocta sulfur 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 labelling. 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, Figure 6c.

Figure 7

E. CYCLOENNEA SULFUR, S_9

Schmidt and Wilhelm (1970) prepared cycloennea sulfur (96) by reaction of

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

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. CYCLODECA SULFUR, S_{10}

Wilhelm and Schmidt prepared lightly yellow-green solids, containing S_{10} rings by reaction of various matching combinations of sulfanes and

chlorosulfanes (94,125), for example;

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

The yellow S_{10} has since been prepared in far better yield (92) 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. CYCLOUNDECA SULFUR, S_{11}

Schmidt and Wilhelm prepared this compound by reaction of

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

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. CYCLODODECA SULFUR; 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. 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 seven 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.

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

$$H_2S_4 + S_2Cl_2 = S_6(50\%) + S_{12}(3\%) + 2HCl, \quad \text{or (93)}$$

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

S_{12} is amazingly stable. It apparently exists in liquid sulfur, because it can be found in quenched melts (90), and it is formed in solutions of S_6 in toluene, during decomposition under the influence of light (91). 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 lies between those of S_6 and S_{12}:

$$\text{S-S} = 2.053 \pm 0.007 \text{ Å}$$

$$\text{S-S-S} = 106.5 \pm 1.4°$$

$$\text{S-S-S-S} = 86.1 \pm 5.5°$$

The atoms are stacked in threeparallel planes, as shown in 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 cycloocta sulfur. 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):

$$a = 4.730 \text{ Å}$$

$$b = 9.104 \text{ Å}$$

$$c = 14.7574 \text{ Å}$$

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

S_{12} will make possible comparison of stability of different sulfur allotropes. The order of reactivity towards diphenyl-o-tolylphosphine is:

$$6 > 7 > 12 > 8$$

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

I. CYCLOOCTADECA SULFUR, S_{18}

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

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

As S_8H_2 and $S_{10}Cl_2$ are both not easily prepared in pure form, 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°. This molecule is unexpectedly stable. It melts at 128°, and if stored in the dark, displays unchanged X-ray diffraction patterns after five years. The bond parameters are (22,98):

$$S\text{-}S = 2.059\,\text{Å}$$

$$S\text{-}S\text{-}S = 106.3°$$

$$S\text{-}S\text{-}S\text{-}S = 84.4°$$

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

$$a = 21.152\,\text{Å}$$

$$b = 11.441\,\text{Å}$$

$$c = 7.581\,\text{Å}$$

Four molecules, i.e. 72 atoms, are contained in a unit cell. The density is 2.090 g/cm^3, the space group is $P_{2_1}2_12_1$.

The discovery of this large ring will undoubtedly lead to re-examination 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, S_{20}

Schmidt synthesizes S_{20} from sulfanes and chlorosulfanes (98) using carefully designed mixtures of compounds, and catalizing the reaction with HCl:

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

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

$$a = 18.580 \text{ Å}$$

$$b = 13.181 \text{ Å}$$

$$c = 8.600 \text{ Å}$$

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}, $S_{fibrous}$, and lie between the values for S_6 and S_8:

$$S\text{-}S = 2.047 \text{ Å}$$

$$S\text{-}S\text{-}S = 106.5°$$

$$S\text{-}S\text{-}S\text{-}S = 83.0°$$

K. POLYCATENA SULFUR, S_∞

Polycatenasulfur is also called fibrous sulfur, polymeric sulfur, plastic sulfur, or Sμ. 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, an on concentration of rings. Schmidt (87) has shown that 2% S_6 suffice to induce polymerization at 150°, i.e. 10 degrees 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 ten atoms for every three turns. The best presently available bond data is (25):

$$S\text{-}S = 2.066\ \text{Å}$$

$$S\text{-}S\text{-}S = 106°$$

$$S\text{-}S\text{-}S\text{-}S = 85.3°$$

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 in all these compounds are closely observed. The first structure determinations were authored by Trillat and Forrestier in 1931, and Meyer and Go in 1934. The present data was provided by Donohue (27), Tuinstra (114,115) and Geller (39,59). The structure is not as certain as that for the above-mentioned rings.

$a = 13.8$ Å

$b = 4x\ 8.10$ Å

$c = 9.25$ Å

$\gamma = 85.3°$

One hundred sixty atoms fill a unit cell which has the space group $Ccm2_1$-C^{12}_{2v}. The density is $d = 2.01\ g/cm^3$.

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

There is still much unsettled discussion about the arrangement of left and right turn helices and the over-all structure.

Fibrous sulfur is probablyrarely pure. Impurities can influence the structure in many ways. As long as only mixtures are available, there is no end of apparently contradictory reports on similar structures to be expected. We will discuss some of these forms in the section on mixtures and insufficiently characterized forms.

L. CYCLOCATENA SULFUR

Charge transfer complexes between cyclooctasulfur and other compounds have been proposed for some time. I_2-complexes were described by Jander (45) and Meyer (65a). Complexes with CHI_3 by Bjorvatten (6). 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). Fig. 3b shows a charge transfer complex of cyclosulfur with catena sulfur. 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° causes polymerization lasting twenty minutes, 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°), 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 are not yet known. Maybe photosulfur, prepared by illuminating solutions of cycloocta sulfur in benzene or toluene, consist of such a substance. Photosulfur is insoluble, and in the dark slowly converts to cycloocta sulfur (61,62).

M. MOLECULAR IONS

Negative ions of sulfur exist in aqueous polysulfide solutions (112b) and non-aqueous solutions (16). The structure of these ions are presumed to be similar to those of Feher's sulfanes (87), and their corresponding salts. Fig. 1 shows that in these compounds cis-cis or trans-trans configurations are possible. Some bond data is given in Fig. 2 and Table I. Typical values are (101)

$$S\text{-}S = 2.048\ \text{Å}$$

$$S\text{-}S\text{-}S = 107°55'$$

$$S\text{-}S\text{-}S\text{-}S = 90°$$

Positive ions of sulfur have been identified by Gillepsy (41,42) and others in concentrated acids, in minerals (99,100) and doped salts (40). Three ions, S_4^{2+}, S_8^{2+}, and S_{16}^{2+} (41) seem to exist. 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. 8. It is similar to cycloocta sulfur, 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 Gillespy (41).

Figure 8

N. RINGS CONTAINING OTHER ELEMENTS

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

1. S_8O

Using the synthetic method of Feher modified by Schmidt and Wilhelm, Steudel and Rentsch (106) prepared a sulfur ring S_8O, Fig. 7, by the reaction of

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

S_8O is stable if stored at low temperature. This molecule contains an oxygen attached to the normal cycloocta sulfur molecule. The branching of the sulfur ring is quite surprising. The presence of the oxygen influences the bonding, as expected: 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 = 2.04 Å
(2.20 Å, for the bonds 1,8 and 1,2)

S-S-S angle = 108°
(101° for bonds 1,8 and 1,2)

S-S-S-S = 101°.

The lattice constants (105) of the yellow crystals, with a space group Pca2 and a density of d = 2.13 g/cm^3 are

$$a = 13.197 \text{ Å}$$

$$b = 7.973 \text{ Å}$$

$$c = 8.096 \text{ Å}$$

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) 40 isomers are possible. S_7Se has been described (121); a lemon-yellow S_6Se_2 and an orange-red S_5Se_2 seven-ring (122). The synthesis proceeds via

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

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

$$a = 4.774 \text{ Å}$$

$$b = 9.193 \text{ Å}$$

$$c = 14.68 \text{ Å}$$

These values are similar to those of S_{12}. The space group is Pnmmm-D_{2h}^{12}. The S-S bond distance is 2.10, S-S-S bond angle 106° and the torsion angle is 106°.

3. Tellurium-Sulfur rings

Weiss (122) prepared S_7 Te Cl_2, using the reaction

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

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

4. Organic compounds

A variety of rings with $C_nH_mS_x$, containing S-S bonds can be prepared. Several seven, eight, nine, ten, eleven, and twelve membered rings containing three to eight sulfur atoms, as polysulfide, have been prepared (63) from:

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

Feher (33) used a similar technique to make pentathiepin, benzopentathiepin, and similar compounds.

Of further interest are eight membered rings, containing alernating S-C bonds. Frank and Degen (37) published the structure of 1,3,5,7-tetrathiocane $(CH_2S)_4$, which is shown in Fig. 8. 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 group is $P2_1/c$. The bond characteristics are;

$$S\text{-}C = 1.817 \text{ Å}$$

$$\text{C-S-C bond angle} = 103°$$

$$\text{S-C-S bond angle} = 119°$$

Torsion angles are about 80°, except for C(1)-S(2), and S(8)-C(1) = 109, and 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

A. INTRODUCTION

In section II, the structure of 14 well-defined allotropes has been described. About 40 other allotropes have been reported, but for these structural data is incomplete or contradictory. The reason for this varies: Some allotropes such as τ-sulfur, which form only in 2 out of 5000 experiments (31) are hard to prepare or are unstable. Others, such as ω-sulfur are easy to prepare and reasonably stable, but X-ray data is contradictory and has led to much confusion and controversy. 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 which 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 which were believed to be new allotropes are in reality merely new mixtures of well-established allotropes.

In the following sections a short summary of the better known of the incompletely characterized allotropes is given. The data is 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.

B. FROM SOLUTIONS OF CYCLOOCTA SULFUR

Below 90°C, solutions of sulfur in organic solvents contain normally cycloocta sulfur. Muthman (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 receipes 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 12 new allotropes. None is stable for more than 15 minutes. As structural data is lacking, we will not further dwell on them. The case of γ-sulfur, first prepared by Muthman in 1890, shows that some of these allotropes might later be confirmed, but likely only after better synthetic methods for preparing them will be 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 upmost caution is in order in dealing with these systems, as sulfur reacts with all solvents above 120°C quite smoothly.

B. FROM CHEMICAL REACTIONS IN SOLUTION

Section II shows 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 classical synthesis of Engel (65). A further problem arises if large species are produced in aqueous solution, because in that environment polythionates are stable, too, 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 the synthetic approach to the preparation for new sulfur allotropes has not yet been exhausted, and can be very reliable.

Das (21) and others have used reagents without solvents for synthesizing new materials. ω-sulfur is such an example. It shows that mixtures result which are very hard to analyze. For details on the controversy about ω-sulfur, we refer to reference 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 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 are very likely mixtures, from which component cannot be separated unharmed. Nevertheless, these compounds 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 work, led to reports of over 12 new phases by Vezzoli (116-117), Ward (119), Susse (110), 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 (7) reports that above 235°C equilibrium is not nearly reached after 3 days. Thus, properties of samples reflect their history.

D. FROM LIQUID SULFUR

Fibrous sulfur, described in section II, is prepared by quenching liquid sulfur. Atens' and Eräemetsäs' π-sulfur is obtainted from the melt, at 120°. Schmidt (90), showed that the melt contains rings other than S_8, for example S_{12}. Above 156° 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, much new data is becoming available quickly. Bröllos studied the thermal analysis of sulfur, at various pressures (11), and the optical absorption at various pressures (55), and its influence on the polymerization. Kuballa (55) and Klement (49) also studied thermal analysis, and determined kinetics of intramolecular conversion, which was found to be slow. Baur (5) reports that the 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. 7. Hot liquid sulfur looses 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. Wiesiorowski has proposed that charge transfer complexes (124) are present in liquid sulfur, and explains much of its behaviour, as has been explained in section II. Obviously, much remains to be learned about the complex chemical system called liquid sulfur.

E. SULFUR VAPOR

Sulfur vapor contains small molecules, of which on S_8, at low temperature, and S_2, at high temperature, can be separated in pure form. Both have been described in Section II. In an intermediate pressure and temperature range, mixtures of molecules with the formula S_n, with $2 < n < 12$ 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 the gas phase molecules are present as rings or chains.

Quenched sulfur vapor has been studied for a long time. Slowly quenched to room temperature it yields flowers of sulfur, which were already 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 (103), a widely used insoluble form of sulfur, also called supersublimation sulfur, is not fully established. As explained above, these and similar compounds are bound to be mixtures, and their structural data depends on the method of preparation, history of the reagents and product, and the age of the sample. Several of these allotropes are only stable 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, even though much progress has been made in purification (80,112a).

ACKNOWLEDGMENT

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

List of Tables

TABLE I

Structural Parameters of Molecules with S-S Bond

Molecule	S-S Bond Length (Å)	Reference
S_8	2.060	17
S_{12}	2.053	57
S_∞	2.066	105
H_2S_2	2.	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

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.)	Reference
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) 2.20(S_1,S_8,S_1,S_2) 2.04	101.8 108	101.4	105

Table III

Structural Data for Solid Sulfur Allotropes

Molecule	Color	Unit Cell (Å) a	b	c	β (deg.)	unit cell[a]	Space group	density gm/cm^3	decomp. or melting pt. (°C)	Ref.
S_6	orange-red	10.818	c/a=0.3956	4.280±0.001		18	$\bar{R}3$-C_{3i}^2	2.209	50-60	14
S_7	yellow	21.77±0.01	20.97	6.09	90°	16-112	?	2.090	39	47
$S_{8-\alpha}$	yellow	10.4646	12.8660	24.4860	90°	16-128	Fddd-D_{2h}^{24}	2.069	94(112)	17
$S_{8-\beta}$		10.778	10.844	10.924	95.80°	6-48	$P2_1/a$-C_{2h}^5	1.94	133	85
$S_{8-\gamma}$	light-yellow	8.442	13.025	9.356	124°98'	4-32	$P_{2/c}$	2.19	~20	120
S_{12}	pale yellow	4.730	9.104	14.574		2-24	P_{nnm}-D_{2h}^{12}	2.036	148°	57
S_{18}	lemon-yellow	21.152	11.441	7.581		4-72	$P_{2_12_12_1}$	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	4x8.10	9.25	85.3	160[b]	$Ccm2_1$-C_{2v}^{12}	2.01	104°	59
S_8O	yellow	13.197	7.973	8.096			Pca2	2.13	20-78°	105
S_7TeO_2		8.82	9.01	13.28			Pmnb-D_{2h}^{16}	2.65	---	122

(a) First number = number of atoms, second number = number of molecules in unit-cell.

(b) 10 atoms for 3 turns.

TABLE IV

Summary of Allotropes

Reagent	Product		
	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, §, 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 $3 < n < 10^5$	α, β, S_{12} $\psi(=\mu)$	π, ι, ν, ψ
Sulfur Vapor	$2 < n < 12$	α, S_∞	Crystex, ω, Red Green, Blue

Figure Captions

Fig. 1. (a) S-S bond parameters

(b) S-S bond configurations

Fig. 2. Different views of cycloocta sulfur and cyclododeca sulfur

Fig. 3. (a) Isomers and conformers of S_4 (65)

(b) Charge transfer complex S_8-S_2-S_8 (65)

Fig. 4. Six well established sulfur allotropes

Fig. 5. (a) $(C_5H_5)_2MoS_4$

(b) $(C_5H_5)_2TiS_5$

(c) $(NH_4)_2PtS_{15}$

Fig. 6. (a) Structure of S_α

(b) Structure of S_β

(c) Structure of S_γ

Fig. 7. Correlation between different unit cells of S_γ

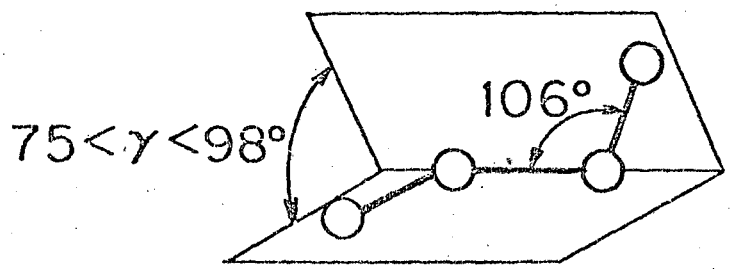
Fig. 8. Eight-membered sulfur rings

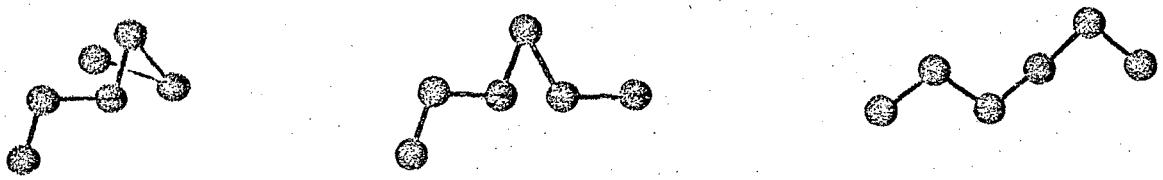
(a) S_8

(b) S_8O

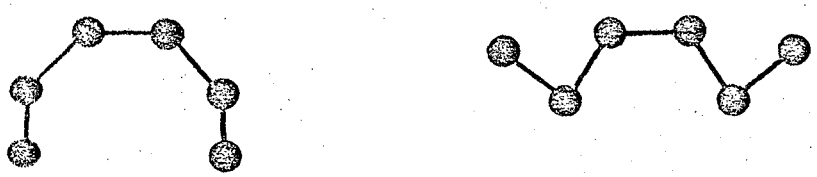
(c) S_8^{2+}

(d) $(CH_2S)_4$



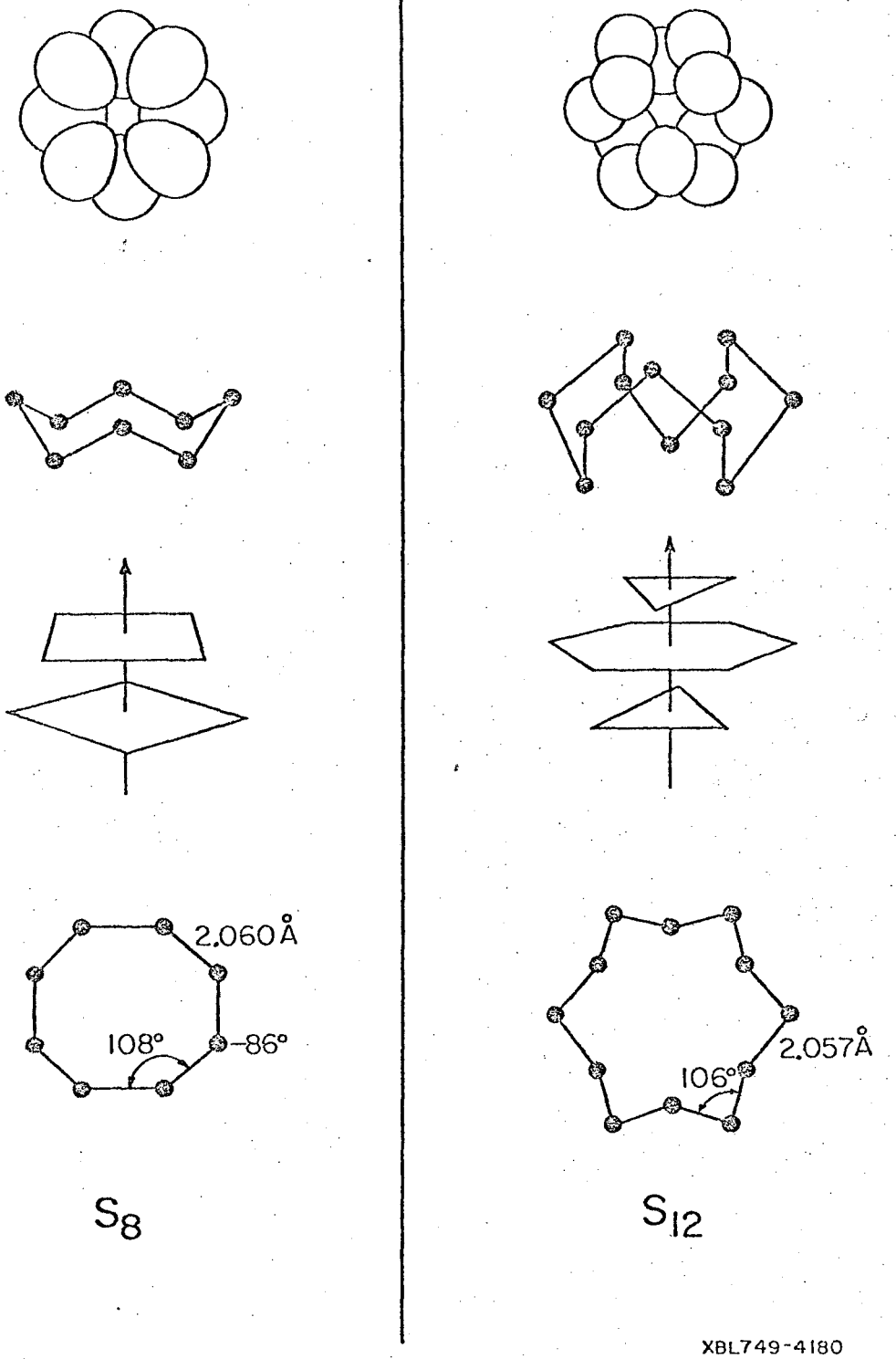


cis-cis cis-trans trans-trans



XBL749-4171

Figure 1



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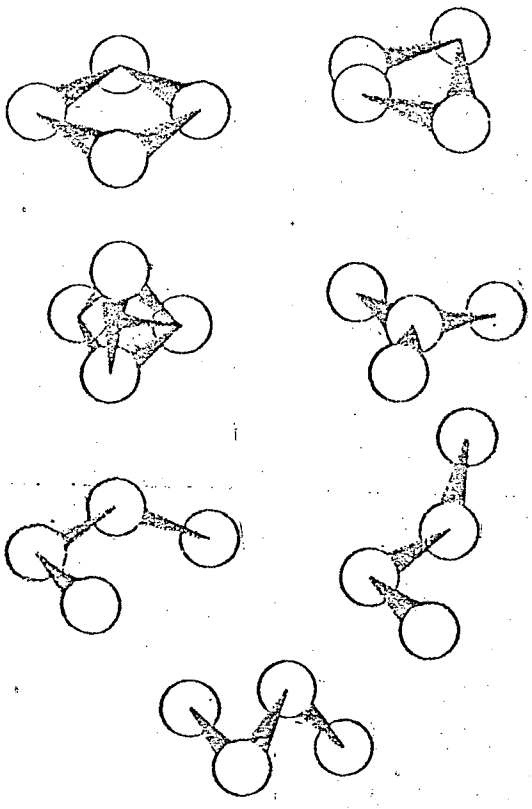

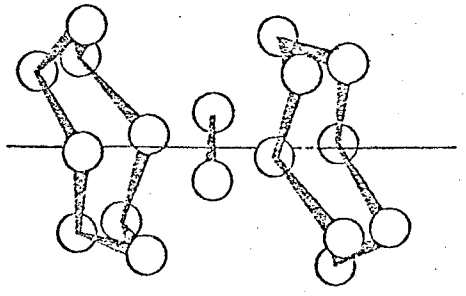

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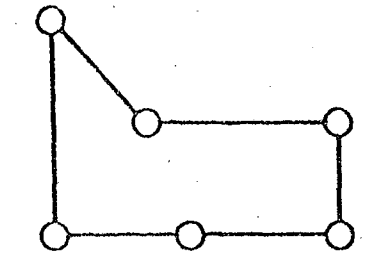
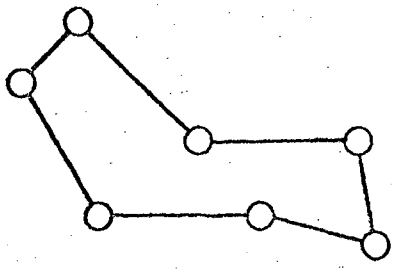


S_6



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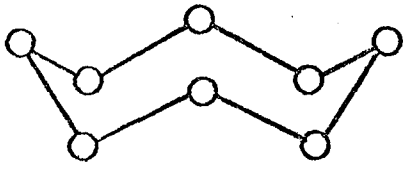
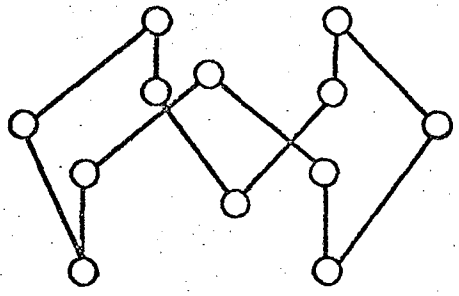
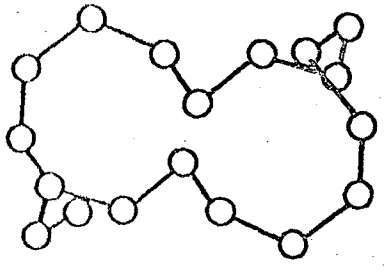


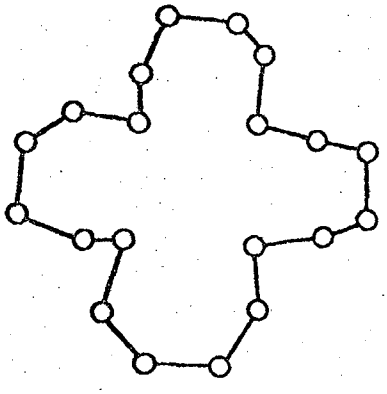
S_8



S_{12}



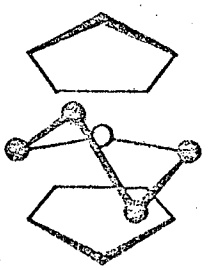
S_{18}



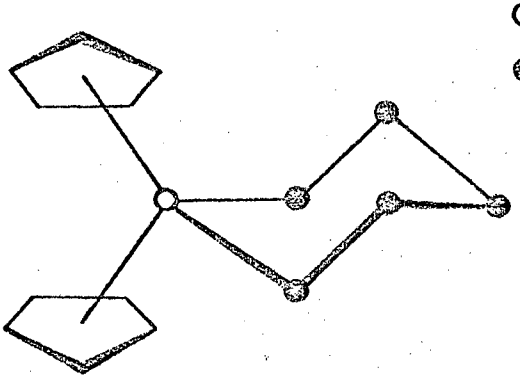
S_{20}

XBL749-4172

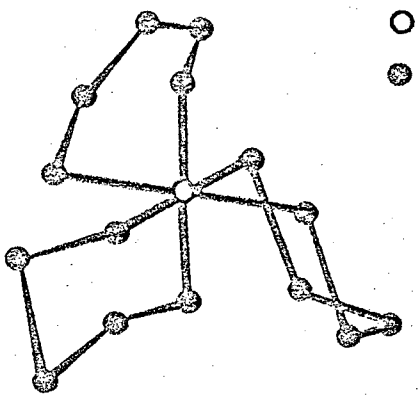
Figure 4



o Mo
● S



o Ti
● S



o Pt
● S

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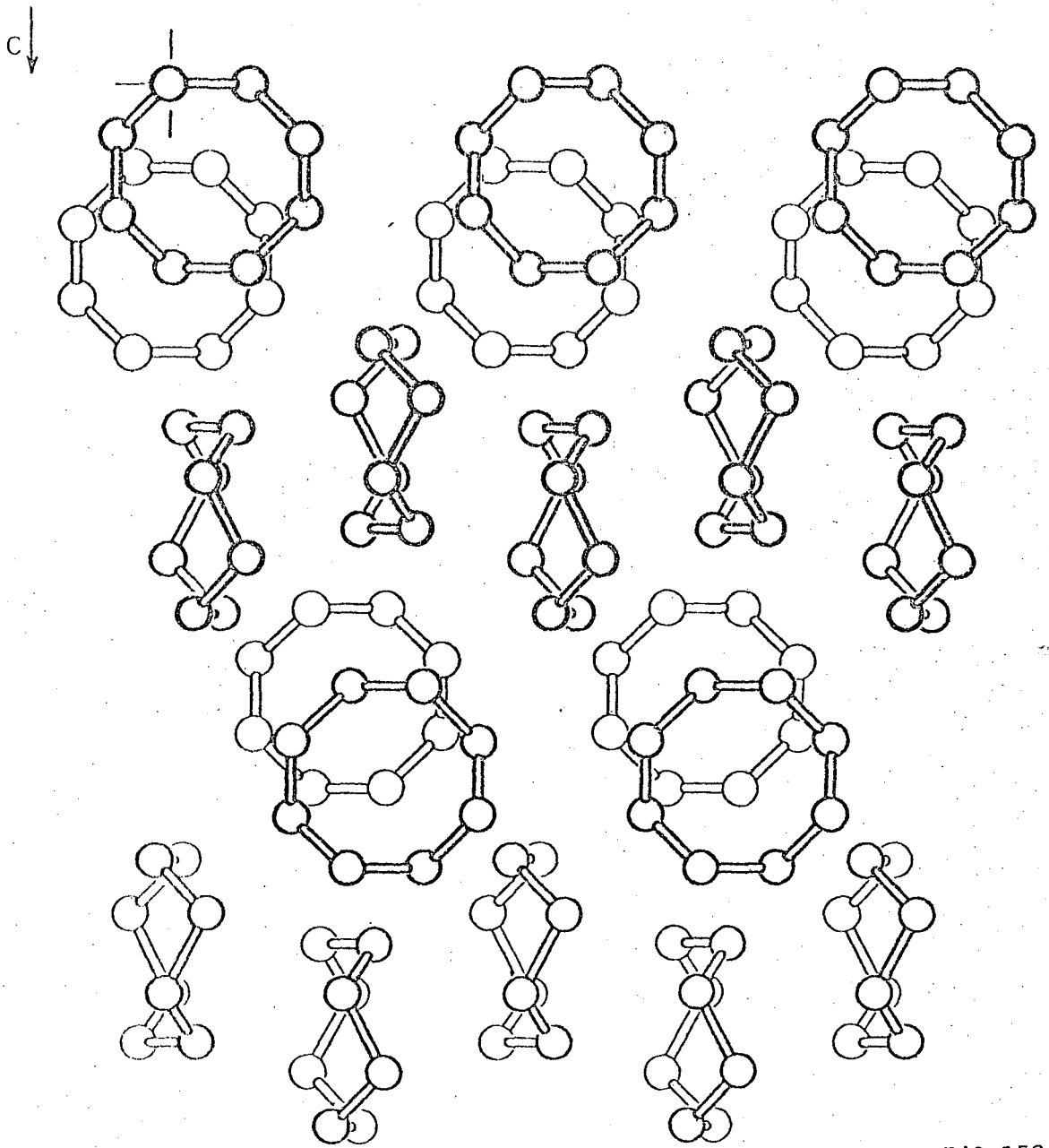
Figure 5



XBL 749-1524

Figure 6a

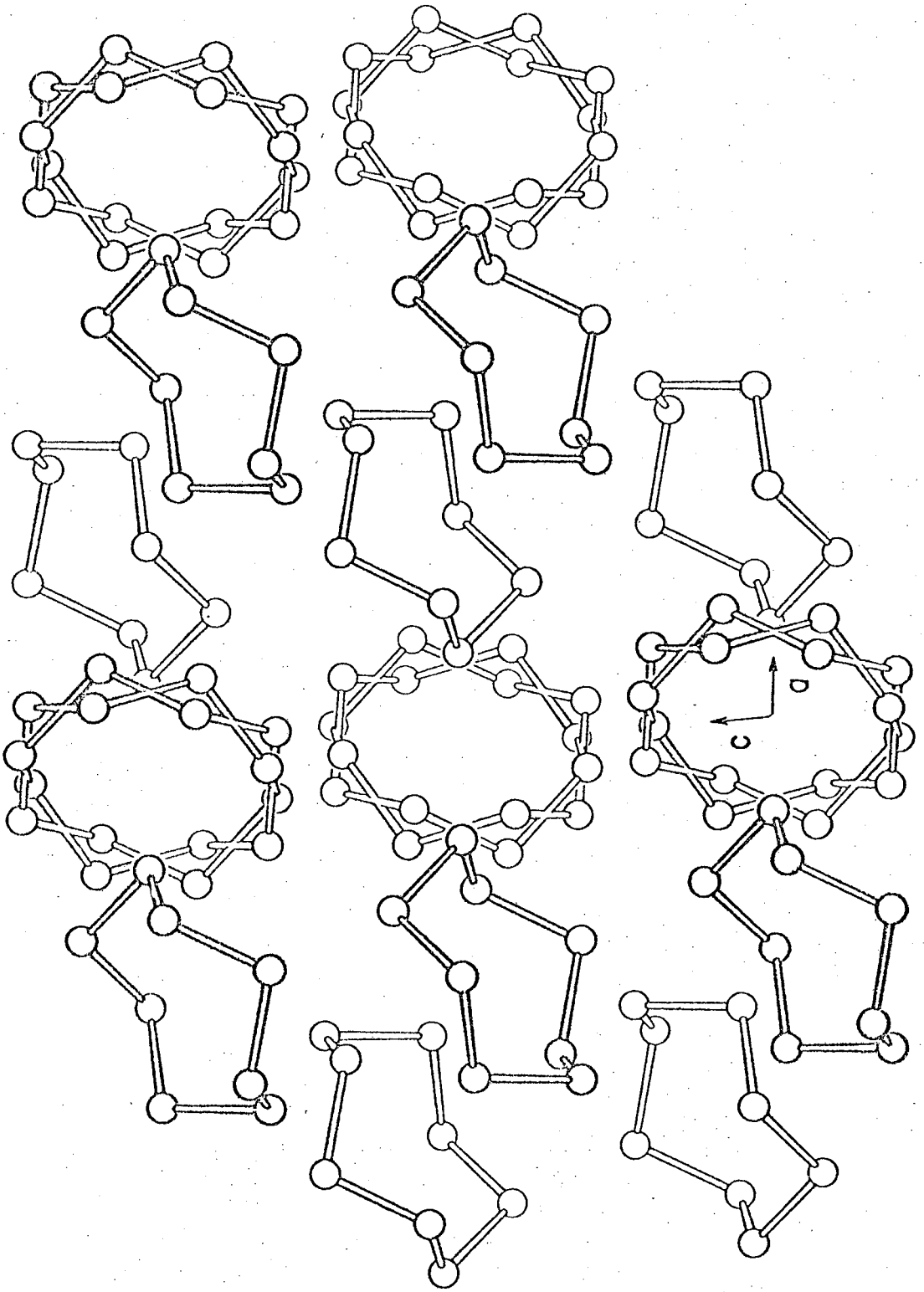


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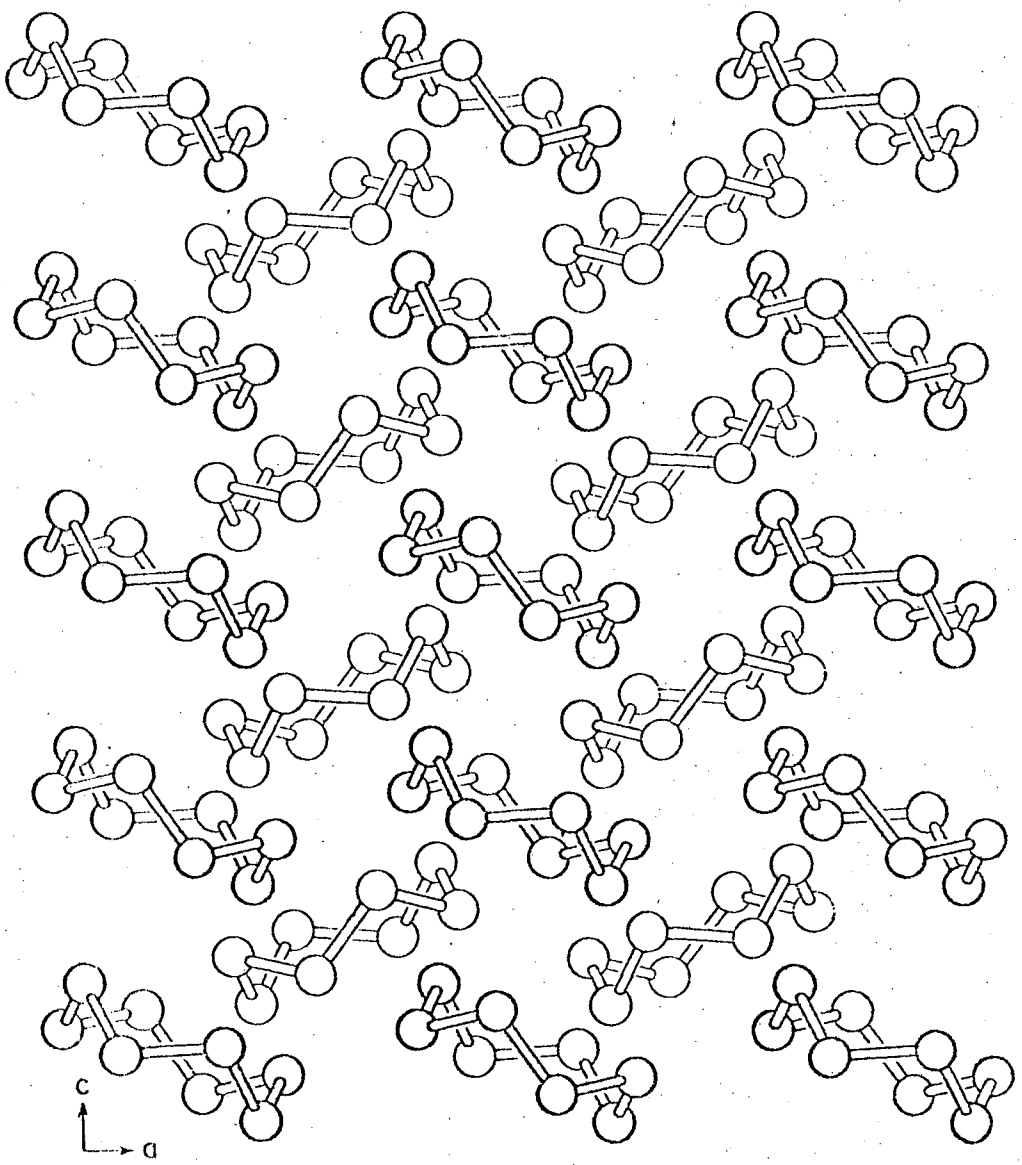
Figure 6b



XBL 749-7146

Figure 6c

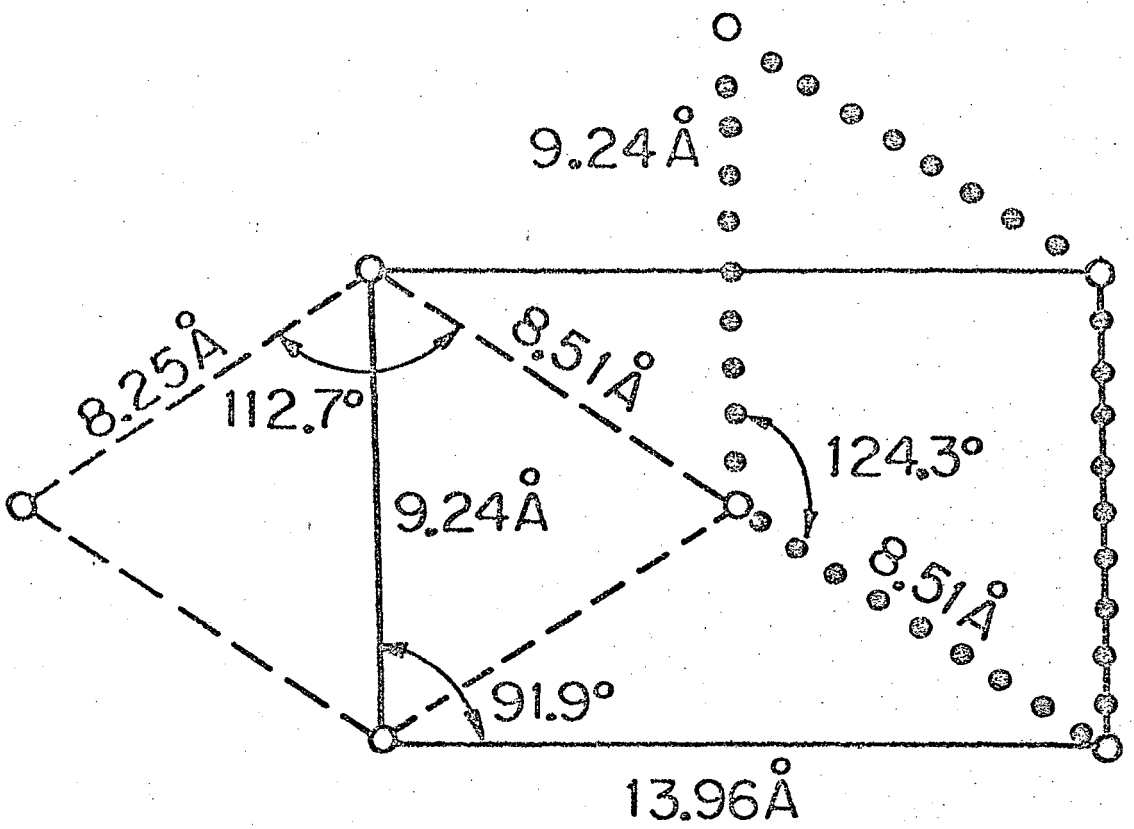


Figure 7

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