STRUCTURES OF COMPOUNDS CONTAINING CHAINS OF SULFUR ATOMS

Olav Foss

Chemical Institute, University of Bergen, Bergen, Norway

I. Introduction

The ability of sulfur to form chains is displayed in the allotropes of the element, and in a variety of compounds built up of sulfur chains terminated by other atoms or groups. The maximum number of sulfur atoms in the chain of compounds so far isolated and characterized, varies with the nature of the end groups; in some it is four or six, and in others reaches eight.

The major structural problem with regard to sulfur chain compounds originates in their tendency to give off sulfur when acted upon by bases or by sulfur acceptors like sulfite or cyanide. Are the sulfur atoms all divalent and part of unbranched chains, or are the labile ones attached in a different way, through coordinate sulfur-sulfur bonds? Closely connected are problems concerning reactivity, and the mechanisms by which desulfurations and shortenings of chains take place. There is at present convincing evidence, chemical as well as physical, that in compounds containing chains of sulfur atoms the chains are unbranched. Indeed, branching has not been found in any instance. This review is concerned with the physical evidence, particularly from structure determinations by X-ray methods; the chemical side is mentioned but only leading references are given.

II. Elemental Sulfur

The element in its various allotropes presents the prototype structures of the chains in compounds. An eight-membered ring occurs in orthorhombic, γ-monoclinic, and probably also β-monoclinic sulfur; a six-membered ring in the rhombohedral form; and long helical chains in fibrous and probably also in viscous sulfur.

The structure of orthorhombic or α-sulfur was redetermined a few years ago by Abrahams (*2*). The S_8 ring has a puckered "crown" form, with a sulfur-sulfur bond length of 2.04 Å, a sulfur valency angle of 107.5°, and a dihedral angle of 99° between successive planes through three and three sulfur atoms. De Haan (*45*) has recently reported a crystal structure analysis of γ-sulfur, the monotropic monoclinic allotrope discovered by Gernez in 1883 and by him called nacreous sulfur; the S_8 rings also occur there. No structure analysis appears to have been made of ordinary monoclinic sulfur, β-sulfur; Das (*42*) was not able to obtain X-ray photographs of it owing to too rapid transformation into α-sulfur. The preliminary results of a crystal structure analysis of rhombohedral or ρ-sulfur have been reported by Donohue *et al.* (*47*); the primitive rhombohedral cell contains six sulfur atoms in a puckered ring of sixfold molecular symmetry.

Liquid sulfur is almost entirely S_8 up to 160°; at higher temperatures equilibrium mixtures of S_8 and polymeric forms predominate. Work by Gee (*128*) and paramagnetic resonance measurements by Gardner and Fraenkel (*127*) show that the polymers are probably diradical chains with a maximum average length of about 10^6 atoms at approximately 170°. Schenk (*195*) has recently reviewed the evidence for long chain molecules in liquid sulfur; the alternative theory propounded by Krebs (*154*) is that large rings occur instead of open chains.

When viscous sulfur is chilled in water and strongly extended, so-called fibrous sulfur results. It gives an X-ray diagram and its structure has recently been elucidated by Prins *et al.* (*190*). The fibers contain two constituents, one consisting of very long, roughly close-packed helixes, and the other of small crystals of γ-sulfur (S_8 rings) located in needle-shaped holes of the helix structure. Each helix has periods of 10 atoms in three turns on a cylinder of 0.92 Å radius, the length of a period being 13.7 Å. This gives a S—S bond length of 2.04 Å and a sulfur valency angle of 107°, as in the S_8 ring, and a dihedral angle of 87° against 99° in the ring.

The same helixes occur, according to Prins, Schenk and Wachters, in the so-called ω-sulfur, which is the insoluble residue remaining when chilled viscous sulfur or flowers of sulfur are extracted with carbon disulfide, and which can be produced also in other ways, for instance by hydrolysis of disulfur dichloride. This form is hexagonal, as was discovered in 1938 by Das, who has recently (*42*) reviewed his X-ray powder studies on allotropes of sulfur.

The structure of the S_8 molecule in the gas phase has been determined by Lu and Donohue (*168*) by electron diffraction; the same puckered ring occurs as in the solid state. Assignment of infrared and Raman frequencies has been made by Guthrie *et al.* (*139*), who also discussed the relative stabilities of possible forms of the ring in the gas phase.

The different conformations of molecular sulfur in the eight- and six-membered rings and in the extended helixes are examples of rotational isomerism, encountered also in derivatives. The all-*cis* configuration of S_6 and S_8 transforms into the all-*trans* of the helixes on breaking of a bond and rotation of approximately 180° about the symmetrically located bond.

An eight-membered ring of seven sulfur atoms and an imide group, heptasulfur imide S_7NH, may be briefly mentioned here. According to Goehring *et al.* (*134*) the crystals are orthorhombic, with four molecules per unit cell, and space group probably D_{2h}^{16}–$Pnma$. If this is so, the molecule must have mirror plane symmetry in the crystals, and since it is certainly nonplanar, it lies across the mirror plane with the imide group and one sulfur atom in the plane. On this basis, a structure quoted by Goehring (*132*) can hardly be correct.

The largest molecule of oxygen is triatomic ozone, but selenium and tellurium form longer chains in the elemental state, like sulfur. The crystal structures of the two red, monoclinic (α and β) modifications of selenium have been determined by Burbank (*38*) and Marsh *et al.* (*170*). In these, the molecules are Se_8 rings of the same "crown" form as S_8 sulfur, while in hexagonal selenium and tellurium infinite helixes occur. The hexagonal space group being enantiomorphous, each single, untwinned crystal contains only right-handed or only left-handed helixes.

III. The Polysulfide Ions

The highest alkali polysulfides are hexasulfides, while in salts with organic bases, up to nonasulfides appear to exist. From the systematic studies by Fehér and co-workers of the systems sodium-sulfur (*61*), potassium-sulfur (*62*), and rubidium- and cesium-sulfur (*71*), the only polysulfides in the di- through hexasulfide series which do not exist as individuals in the solid state, are sodium trisulfide and hexasulfide, rubidium tetrasulfide and hexasulfide, and cesium tetrasulfide. The others, among them the whole series of potassium salts from di- through hexasulfide, were isolated in a pure state and gave characteristic X-ray powder patterns. The salts were in most cases prepared from the elements in liquid ammonia; some of them such as sodium tetrasulfide and potassium tri- and pentasulfide crystallize well from ethanol and were obtained from sulfur and the monosulfide in this solvent.

The color of the alkali polysulfides changes with increasing sulfur content from the light yellow of disulfides through orange to red or red-brown. Hexasulfides liberate sulfur when dissolved in water, which is understandable from the measurements of Arntson *et al.* (*8*) of the solubility of orthorhombic sulfur in aqueous sodium monosulfide. The equilibrium value of n in S_n^{--} was found to be approximately 4.8 at 25°, and varied at 50° from approximately 4.6 in dilute solutions to approximately 5.4 at higher concentrations.

Salts of hydrogen polysulfides with organic bases have been known for a long time; a strychnine hexasulfide was prepared by Hoffmann in 1868. Recently Krebs (*156*) obtained cyclohexylammonium hexasulfide, several heptasulfides, and triethyl- and di-*n*-propylammonium nonasulfide, from the amine, hydrogen sulfide, and sulfur in benzene. In the same way but using aqueous media, Krebs and Müller (*155*) prepared ethylenediammonium trisulfide, triethylenediammonium penta-, hexa-, and heptasulfides, and tetramethylenediammonium hexasulfide, and determined unit cells and space groups from single-crystal X-ray photographs. Three of the salts crystallize in the enantiomorphous space group D_2^3–$P2_12_12$ with four formula units per unit cell. The salts are relatively unstable.

The di- and trisulfide ions offer no structural problem apart from bond lengths, and the bond angle in the trisulfide. For the tetrasulfide and higher polysulfides branched structures can be imagined, such as a "tetrathiosulfate" structure for the pentasulfide. The recent crystal structure determinations by Abrahams and Grison (*5*) of cesium hexasulfide, and by Abrahams (*1*) of barium tetrasulfide monohydrate, provide proof of unbranched sulfur chain structures in these salts and, by inference, in other polysulfides.

The crystals of barium tetrasulfide monohydrate, $BaS_4 \cdot H_2O$, are orthorhombic, with four formula units in a cell of dimensions $a = 9.67$ Å, $b = 7.99$ Å, $c = 7.81$ Å. The space group is $D_2^3\text{–}P2_12_12$. The unbranched, nonplanar tetrasulfide ions lie on twofold axes of symmetry, with only right-handed or only left-handed forms in each unit cell.

Cesium hexasulfide, Cs_2S_6, crystallizes in the triclinic space group $C_i^1\text{–}P\bar{1}$ with $a = 11.53$ Å, $b = 9.18$ Å, $c = 4.67$ Å, $\alpha = 89.2°$, $\beta = 95.2°$, $\gamma = 95.1°$, and two formula units per unit cell. The hexasulfide ions are unbranched and nonplanar and have the shapes of extended helixes.

No crystal structure analysis of a pentasulfide has been reported. As for di- and trisulfides, Miller and King (*174*) worked out a structure for barium trisulfide on the basis of X-ray powder data, but, as pointed out by Wyckoff (*231*), the structure cannot be considered as well established. Sodium disulfide (*61*) occurs in a low-temperature (α) and a high-temperature (β) form which, according to Föppl (*81*), are isomorphous with sodium peroxide and lithium peroxide, respectively. Föppl obtained single crystals of β-Na_2S_2 and has tentatively reported (*81*) a length of 2.25 Å for the disulfide bond in this salt; the value appears unreasonably large in view of the lengths 2.02–2.11 Å found for bonds between divalent sulfur atoms in other compounds. For instance, in hydrogen disulfide (*211*) the S—S bond is 2.05 Å. The O—O distance in the peroxide ion, 1.49 Å, which is known accurately from Föppl's work (*80*) on alkali peroxides, is the same as in covalent peroxy compounds.

IV. The Sulfur Hydrides and Halides

The crude yellow oil resulting from the interaction of sodium polysulfide solutions with an excess of hydrochloric acid was discussed by Scheele in 1777, but one and a half centuries later the only hydrogen polysulfide isolated in a pure state was the trisulfide, obtained by Bloch and Höhn (*29*) in 1908 by fractional distillation of the crude oil under reduced pressure. Mills and Robinson (*175*) in 1928 prepared hydrogen pentasulfide from ammonium pentasulfide and formic acid, but according to later work (*64*) the product may not have been quite pure. Only during the last 15 years have Fehér and co-workers isolated and characterized the complete hydrogen polysulfide series up to and including the octasulfide.

The preparation and properties of hydrogen trisulfide (*58*), tetrasulfide (*59*), and penta- and hexasulfide (*60*) were described by Fehér and Baudler in 1947–1949. The tetra-, penta-, and hexasulfides were obtained by fractional distillation in high vacuum of crude hydrogen polysulfide oil, the hexasulfide only with difficulty. The crude oil normally does not contain any hydrogen tri- and disulfide, but yields these on cracking. Fehér, Laue, and Winkhaus (*68*) have later improved the procedure and the purity of the products. Fehér and Winkhaus (*78*) in 1956 reported the preparation of hydrogen penta- and hexasulfides, and also hepta- and octasulfides, by a new method consisting in the condensation of two moles of hydrogen disulfide with one mole of mono-, di-, tri-, or tetrasulfur dichloride. An excess of hydrogen disulfide must be used, but this compound is more volatile than the products and hence easily removed afterwards. The hepta- and octasulfide could not be distilled but were practically pure. By varying the sulfur content and the relative amounts of the starting hydride and chloride, the method can be used to prepare mixtures of hydrogen polysulfides with average chain lengths of from 6 to 30 sulfur atoms.

The hydrogen polysulfides are yellow liquids, which from the tetrasulfide upwards have no definite freezing points. They are labile with respect to change into sulfur and hydrogen sulfide, and decompose on contact with powdered quartz and glass, wood, or paper, or traces of basic substances; the same applies to hydrogen disulfide.

The situation with regard to polysulfur dichlorides and dibromides resembles that for the hydrogen polysulfides. Although the presence of trisulfur dichloride in heated mixtures of disulfur dichloride and sulfur had been assumed by Spong (*209*) and others, it was not until a few years ago that Fehér, Naused, and Weber (*72*) prepared polysulfur dichlorides S_nCl_2 with $n = 3$ through 6. The compounds were made by an adaption of the method used for the preparation of hydrogen polysulfides, by now condensing hydrogen mono-, di-, tri-, and tetrasulfides with an excess of monosulfur dichloride. By the use of disulfur dichloride instead of monosulfur dichloride, Fehér and Ristić (*73*) similarly prepared penta-, hexa-, hepta-, and octasulfur dichlorides.

The polysulfur dichlorides are orange-red, oily liquids, of deepening color with increasing chain length. S_3Cl_2 can be distilled in high vacuum, S_4Cl_2 only under partial decomposition. At $-20°$ they can be kept for some weeks without appreciable change; at room temperature half of a sample of S_3Cl_2 decomposed in about three weeks.

Hydrogen bromide reacts with di- and polysulfur dichlorides with elimination of hydrogen chloride, without rearrangement of the sulfur chain, to give di- and polysulfur dibromides. In this way, Fehér and Ristić (*74*) prepared practically pure di- through octasulfur dibromides. These are brown-red liquids, the color becoming less intense with increasing sulfur content.

Fehér has in two recent reviews (*55*, *56*) discussed preparative methods and properties of sulfur chain compounds studied by his group. The success of the work appears to be due to, beside a remarkable preparative skill, the use of Raman spectra for the identification and characterization of the different members of the series.

The Raman spectra are consistent with unbranched structures of the sulfur chains; they display characteristic S—S stretching and S—S—S bending frequencies but no frequencies corresponding to coordinate sulfur-sulfur bonds.

Further support for unbranched structures in hydrogen polysulfides and polysulfur dichlorides comes from molar volumes, refractions, and viscosities; these are discussed in Section V on organic disulfides and polysulfides.

In the case of hydrogen disulfide, the S—S bond length as determined by Stevenson and Beach (*211*) from electron diffraction indicates that branching does not occur. Electron diffraction studies by Palmer (*184*) and Guthrie (*138*) on disulfur dichloride show an unbranched, nonplanar structure. Smyth (*206*) has discussed the dipole moments of hydrogen disulfide, disulfur dichloride, and diselenium dichloride on the same basis; and Hooge and Ketelaar (*145*), the vibrational spectra of hydrogen disulfide and disulfur difluoride, dichloride, and dibromide.

V. Organic Disulfides and Polysulfides

These make up the largest class and display a wide variety of terminal groups, from simple and substituted alkyls and aryls to acyls and amino acid residues. Disulfides are usually quite stable; polysulfides are less stable but can, like the disulfides, be obtained in a variety of ways. Schöberl and Wagner (*198*) have recently reviewed preparative methods for tri-, tetra-, and pentasulfides. Only a few hexasulfides are known; for example, dimethyl, diethyl, and dibenzyl hexasulfides which were prepared by Böhme and Zinner (*34*) from the alkyl hydrogen trisulfides by oxidation with iodine; they are yellow oils at room temperature. The bis(thiocarbamyl)-hexasulfides studied by Levi (*164*) and Blake (*28*) are crystalline and apparently stable.

Cyanogen polysulfides, although organic in the sense that the bonding atom of the terminal group is carbon, constitute a unique series and are considered separately, in Section VI. Another, not strictly organic, series which may be briefly mentioned here, is the sulfur amides, $R_2N—S_n—NR_2$ with $n = 1$ through 4. The tri- and tetrasulfur derivatives are formed (*147*, *163*) when a secondary amine, like piperidine or dimethylamine, reacts with sulfur in benzene in the presence of lead oxide or mercury oxide as a sulfide acceptor. Goehring (*130*) has studied the Raman spectrum of disulfur bis(dimethylamide), and Jenne and Becke-Goehring (*147*) reported that the infrared spectra of di-, tri-, and tetrasulfur diamides in the range 700–5000 cm^{-1} are practically identical. Two oxygen disulfur analogs are known, namely, the alkoxides $S_2(OCH_3)_2$ and $S_2(OC_2H_5)_2$, but no higher members of this series. The structure of the alkoxides has been discussed by Goehring (*130*) on the basis of Raman spectra and measurements by other authors of dipole moments and diamagnetic susceptibilities.

The sulfur-sulfur bond in di- and polysulfides is easily cleaved, particularly by nucleophilic reagents. The reactions lead to interconversions and desulfurations and have often been taken to indicate branching of the sulfur chains, but are actually consistent with unbranched structures (*87, 97*).

A. VARIOUS PHYSICOCHEMICAL EVIDENCE

The literature on structure of organic di- and polysulfides is quite extensive. In the last decade convincing evidence has accumulated in favor of unbranched sulfur chain structures, as contrasted with branched, coordinated ones.

1. *Molar Volume and Refraction, Viscosity*

Accurate measurements have been carried out by Fehér and co-workers on dimethyl di- through tetrasulfides and diethyl di- through pentasulfides (*65*), hydrogen di- through octasulfide (*67, 69*), and monosulfur through hexasulfur dichlorides (*72*). Within a homologous series S_nX_2, the molar volume and Lorentz-Lorenz refraction and the logarithm of the dynamic viscosity are linear functions of chain length. The relation (*69*):

$$\left.\begin{array}{l}\text{Molar volume}\\ \text{Molar refraction}\end{array}\right\} = 2a + (n - 2)b$$

is followed within experimental error, a being the contribution of the end groups SX and b the increment for each inner sulfur atom. For molar refractions, R_D^{20}, $b = 8.6$, 8.9, 8.8, and 8.9 cm^3 in the hydrogen polysulfide, polysulfur dichloride, and dimethyl and diethyl polysulfide series, respectively, while for molar volumes, V_{20}, $b = 16.4$, 16.2, 16.3, and 16.3 cm^3.

As pointed out by Fehér (*56*) the constancy of the increments b supports the contention that the sulfur atoms are similarly linked together to form unbranched chains. It should be noted, though, that the regular increments are consistent with but do not prove unbranched structures; a homologous series having both hetero atoms or groups attached at the same end of the sulfur chain might well display similar properties.

Measurements by Minoura (*178*) of molar refraction of dibenzyl and di-*p*-tolyl di-, tri-, and tetrasulfide give increments between 9.1 and 12 cm^3 per sulfur atom; in the di-*n*-hexadecyl di- to tetrasulfide series (*230*) the increments are 8.2 and 11 cm^3.

2. Dipole Moments

Dipole moments in benzene of di-*n*-hexadecyl mono-, di-, tri-, and tetrasulfide have been reported by Woodrow, Carmack, and Miller (*230*), of dimethyl and diethyl di- and trisulfide and di-*n*-propyl disulfide by Smyth and co-workers (*160*, *225*), of the three isomeric dibutyl disulfides by Rogers and Campbell (*193*), and of diphenyl disulfide and *p*-substituted diphenyl disulfides by Gur'yanova (*137*).

In dialkyl di- and polysulfides, sulfur is the negative end of the dipole. The moment of a di-*n*-alkyl disulfide is approximately 2.00 D and of a trisulfide approximately 1.65 D, irrespective of the length of the carbon chain. In a tetrasulfide the moment is again higher; thus, the alternating values 1.47, 2.00, 1.63, and 2.16 D, respectively, were obtained by Woodrow *et al.* (*230*) for the di-*n*-hexadecyl mono- through tetrasulfide series.

In di-*t*-butyl disulfide (*193*), the moment 1.86 D is lower than in normal disulfides owing to steric effects. In diphenyl disulfides (*137*) the moments vary with the nature of the substituent, and in di-*p*-nitrophenyl disulfide (4.31 D in dioxane at 20°) sulfur is the positive end of the dipole.

The dipole moments support an unbranched chain structure for di- and polysulfides, and as referred to later, provide information about the stereochemistry of sulfur chains.

3. Diamagnetic Susceptibility

Fava and Iliceto (*54*) measured the susceptibilities of *n*-octane, di-*n*-butyl mono-, di-, tri-, and tetrasulfide and impure penta- and hexasulfide, and concluded on the basis of the found sulfur increments that the sulfur chains are unbranched. The fact that the increments decrease slightly with increasing chain length was interpreted as indicating partial double-bond character of the sulfur-sulfur bonds.

4. Ultraviolet Spectra

Measurements have been made by Koch (*152*, *153*) on disulfides and diethyl, diphenyl, and di-2-benzthiazyl tetrasulfide and dicyclohexyl hexasulfide, and by the following authors on complete series R_2S_n with $n = 1$ through 4: Baer and Carmack (*12*) for R = *n*-hexadecyl, Minoura for R = benzyl (*176*) and *p*-tolyl (*177*), and Haszeldine and Kidd (*142*) for *R* = trifluoromethyl. Harris (*140*) has recorded the spectra of the di-*o*-nitrophenyl mono- through pentasulfide series, Gorin and Dougherty (*135*) those of the di-*n*-alkyl disulfides from methyl through butyl, and dimethyl trisulfide, and Schotte (*199–203*) has recently carried out extensive spectrochemical studies of noncyclic and cyclic disulfides as well as of some polysulfides.

The ultraviolet spectra of polysulfides are difficult to interpret in terms of structure. However, as first pointed out by Koch (*152*), the fact that the various polysulfides all display characteristic absorption of the same spectral type, resembling the dialkyl disulfide spectrum displaced towards greater wave lengths and intensities, provides (in view of the known structure of disulfides) strong evidence in favor of unbranched structures also in polysulfides.

Noncyclic disulfides normally absorb in the near ultraviolet with a peak at about 2500 Å and more strongly in the vacuum ultraviolet with maximum at about 2000 Å. Studies of shifts in the position of the first peak have led to interesting results, to be discussed later, concerning the barrier to rotation about sulfur-sulfur bonds.

5. *Infrared and Raman Spectra*

The S—S stretching frequency gives rise to only rather weak absorption in the infrared, probably because the symmetrical vibration of the bond involves little change of dipole moment. It is strong and easily detected in the Raman spectrum, and usually occurs between 440 and 510 cm^{-1}. The S—S—S bending frequency normally lies at about 150–250 cm^{-1}, and the S—S torsional frequency at about 100–120 cm^{-1}. Recent careful assignments of vibrational frequencies have been made by Scott and co-workers for dimethyl disulfide (*204*), diethyl disulfide (*205*), and sulfur S_8 (*139*), and by Hooge and Ketelaar (*145*) for hydrogen disulfide, dimethyl disulfide, and the disulfur dihalides.

The vibrational frequencies are consistent with unbranched, nonplanar structures. The fact that the S—S stretching frequency, although weak, occurs in the infrared, excludes a planar, centrosymmetric *trans* form for disulfides. In the Raman spectra of di- and polysulfides, no lines are found which can be assigned to a coordinate sulfur-sulfur bond; such a bond should be characterized by a rather strong line and its absence implies that branching does not occur.

Recent studies of infrared spectra include those by Brandt, Emeléus, and Haszeldine (*36*) on bis(trifluoromethyl) disulfide and by Haszeldine and Kidd (*142*) on the tri- and tetrasulfides; the former authors have summarized available infrared and Raman data on disulfides. The infrared and Raman spectra of the corresponding trichloromethyl series have been recorded by Fehér and Berthold (*63*). Schotte measured and exhaustively discussed the infrared spectra of various types of disulfides (*199, 200, 201,* *203*) as well as of diethyl tri- and tetrasulfide, tetrathiodiglycolic acid, and three 1,2,3-trithianes (*202*). Fehér and Winkhaus (*79*) recently reported the Raman spectra of a mono- through tetrasulfide series derived from chloral. The work of Fehér, Krause, and Vogelbruch (*65*) on dimethyl and diethyl polysulfides, in which, beside viscosity and molar volume and refraction, the Raman spectra also were studied, provides particularly convincing evidence for unbranched structures in these compounds.

B. STRUCTURE DETERMINATIONS BY ELECTRON AND X-RAY DIFFRACTION METHODS

1. *Disulfides*

The structures of dimethyl disulfide and bis(trifluoromethyl) disulfide have been determined by electron diffraction, by Stevenson and Beach (*211*) and by Bowen (*35*), respectively. Crystal structure determinations of the following disulfides have been carried out: di-*p*-bromophenyl disulfide by Toussaint (*216*); *N*,*N'*-diglycyl-L-cystine dihydrate by Yakel and Hughes (*232*); hexagonal L-cystine by Oughton and Harrison (*183*); L-cystine hydrochloride by Steinrauf *et al.* (*210*); and formamidinium disulfide diiodide and dibromide monohydrates (*104*).

Nonplanar, unbranched disulfide groups occur in all these compounds. The values reported for the length of the S—S bond are, with the exception of the rather inaccurate value of 2.14 ± 0.08 Å in di-*p*-bromophenyl disulfide, remarkably invariant, namely 2.042 Å with an average deviation of 0.005 Å. The sulfur valency angle lies in the range 99–107°, and the dihedral angle between the planes of the valencies of the two sulfur atoms, between 79° and 105°.

The crystal structures of some cyclic disulfides have also been determined and are commented on in Section XI.

2. *Trisulfides*

Donohue and Schomaker (*48*) have determined the structure of dimethyl trisulfide by electron diffraction, and Bowen (*35*) the structure of bis(trifluoromethyl) trisulfide. The crystal structure of one representative, di-2-iodoethyl trisulfide, was first reported by Dawson and Robertson (*44*) and the carbon positions later revised by Donohue (*46*).

The trisulfide groups are unbranched and nonplanar, with reported S—S bond lengths of 2.04 ± 0.02 Å, 2.065 ± 0.016 Å, and 2.05 ± 0.04 Å, and S—S—S angles of 104 ± 5°, 103.8 ± 3°, and 113 ± 2°, respectively. The last angle, in di-2-iodoethyl trisulfide, is exceptionally large.

C. DI- AND TRISELENIDES, DITELLURIDES

The largest number of selenium atoms in covalent selenium chain compounds isolated so far appears to be three, and even so, the representative compounds known are relatively few in number. In the case of tellurium, the maximum number is two. Rheinboldt (*191*) has recently reviewed preparative methods for di- and triselenides, ditellurides, and compounds containing mixed sulfur-selenium and sulfur-tellurium chains.

The unbranched structure of diselenides, triselenides, and ditellurides is firmly established, although less structural work has been done on them than on disulfides and polysulfides. Rogers and Campbell (*192*) have studied the dipole moments of diphenyl, di-*p*-tolyl, di-*p*-bromophenyl, and dibenzyl diselenide, and later (*193*) those of diethyl and di-*t*-butyl diselenide. The moments of diselenides are normally a little lower (by about 0.1 D) than of the corresponding disulfides. Bergson (*25*) recently discussed ultraviolet and infrared spectra of noncyclic and cyclic diselenides; the diselenides were found to be more suitable than the disulfides for a study in the ultraviolet region, whereas in the infrared region the reverse is true. The same author (*23*) has given a preliminary report on the ultraviolet spectra of two aliphatic ditellurides, and Farrar (*51*) one on the spectrum of diphenyl ditelluride. Farrar supposed that ditellurides readily dissociate into free radicals; however, according to magnetic measurements on diaryl ditellurides at temperatures up to 80° this is not the case (*53*).

A crystal structure analysis of diphenyl diselenide has been carried out by Marsh (*169*) and of the isomorphous di-*p*-chlorophenyl diselenide and ditelluride by Kruse, Marsh, and McCullough (*157*). Bowen (*35*) in his electron diffraction work on trifluoromethyl derivatives also studied the diselenide. The results show nonplanar, unbranched diselenide and ditelluride groups.

The crystal structures of two triselenides, namely cyanogen triselenide and di-*p*-toluenesulfonyl triselenide, are known; these are referred to in other sections.

VI. Sulfur Chains Terminated by Cyano Groups

The first member of the series, cyanogen sulfide $S(CN)_2$, was prepared by Lassaigne in 1828; the second, thiocyanogen $(SCN)_2$, is known from the classic work of Söderbäck published in 1919. The next two homologs, cyanogen tri- and tetrasulfide, were described in 1922 by Lecher and Wittwer (*162*) and Lecher and Goebel (*161*), respectively; and Fehér and Weber (*77*) in 1958 prepared the penta-, hexa-, hepta-, and octasulfide and thus brought the series into line with the hydrogen polysulfide and polysulfur dichloride and dibromide series.

The method for the preparation of cyanogen tri- through octasulfides is to react mono- through hexasulfur dichlorides with an excess of mercury thiocyanate suspended in chloroform or carbon disulfide. The compounds are colorless or faintly yellow crystals, or greenish yellow liquids. The trisulfide melts and decomposes at 92–94°, the tetrasulfide melts at $-3°$, and the pentasulfide also below 0°, the hexasulfide at 38–39°, while the hepta- and octasulfide form glasses at low temperatures. The trisulfide is sparingly soluble in most solvents at room temperature; the others are more soluble. At temperatures below 0° they can be kept unchanged for weeks, but at higher temperatures a fairly rapid change to yellow, polymeric products takes place.

The thiocyanate group has pseudohalogen properties, and the cyanogen polysulfides may alternatively be termed sulfur thiocyanates. The behavior of the tri- and tetrasulfides towards nucleophilic reagents (*82*) is consistent with the thiocyanate nomenclature.

TABLE I

AXIAL LENGTHS (Å) OF CYANOGEN TRISULFIDE AND ISOMORPHOUS SELENIUM ANALOGS

Compound	*a*	*b*	*c*	Reference
$S(SCN)_2$	10.12	12.83	4.34	*94*
$Se(SCN)_2$	9.87	13.03	4.44	*181*
$Se(SeCN)_2$	10.07	13.35	4.48	*6*

The three lowest members of the corresponding selenium series are known. Cyanogen triselenide, or selenium diselenocyanate $Se(SeCN)_2$, was prepared by Verneuil (*219*) in 1886, by treatment of potassium selenocyanate with oxidizing agents; the yellow crystals melt at 132° and are quite stable in the dark. Three analogs containing mixed sulfur-selenium chains have been described, namely diselenium dithiocyanate $Se_2(SCN)_2$ and the compound $SeS(SCN)_2$ by Baroni (*16*) in 1936, and selenium dithiocyanate $Se(SCN)_2$ by Ohlberg and vander Meulen (*180*) in 1953.

The presence of unbranched sulfur chains in the cyanogen polysulfides is evident from the Raman spectra recorded by Fehér and Weber (*77*). The characteristic S—S stretching and S—S—S bending frequencies occur, and the C≡N frequency varies with increasing chain length in a way analogous to unbranched methylene α,ω-dinitriles.

The crystal structures of selenium dithiocyanate (*181*) and selenium diselenocyanate (*6*) have been determined by X-ray diffraction. The crystals of these compounds and of sulfur dithiocyanate (*94*) are isomorphous, and the three structures are accordingly analogous. The space group is D_{2h}^{16}–*Pnma* with four molecules per unit cell, of dimensions as listed in Table I. A mirror plane of molecular symmetry is crystallographically required; the molecules are unbranched and nonplanar and lie across the mirror plane with only the middle sulfur or selenium atom in the plane.

The dipole moment of selenium diselenocyanate in benzene at 25° has been measured by Rogers and Gross (*194*). The observed value, 3.98 D, can be accounted for (*194*) by assuming free rotation about the Se—Se bonds, or by postulating a mixture of rotational isomers.

VII. Sulfur Chains Terminated by Sulfonyl Groups

These compounds, disulfonyl mono-, di-, and polysulfides, are intermediates between organic mono-, di-, and polysulfides and the polythionates, in the sense that they are formally derived from the polythionic acids by substitution of alkyl or aryl groups for the hydroxyl groups of the acids. The monosulfides, like the trithionate ion, contain three sulfur atoms in a chain, but only the middle one is divalent. There is thus no real structural problem with regard to branching or nonbranching in disulfonyl monosulfides and trithionates.

A. Types of Compounds

The first representative, di-*p*-toluenesulfonyl trisulfide, was discovered by Blomstrand (*31*) in 1870. On treatment of sodium *p*-toluenethiosulfonate with iodine in ethanol, he obtained the trisulfide instead of the expected disulfide. Otto and Troeger (*182*) in 1891 showed that the disulfide is initially formed but rearranges easily into mono- and trisulfide. By the action of iodine or chlorine on potassium benzene- and *p*-toluenethiosulfonate they prepared the complete series of mono-, di-, and trisulfides. Troeger and Hornung (*217*) extended the benzene- and *p*-toluenesulfonyl series to include the tetrasulfides; all members were obtained from mono- or disulfur dichloride by reaction with an excess of the appropriate sodium or potassium sulfinate or thiosulfonate in an inert solvent.

The compounds are solids at room temperature, the melting points being 133°, 76–77°, 103°, and 84–85° for dibenzenesulfonyl mono-, di-, tri-, and tetrasulfides, respectively, and 138°, 114°, 183°, and 90° for the *p*-toluene compounds. Christiansen (*39*) observed an unstable form, mp 160°, of di-*p*-toluenesulfonyl trisulfide.

The only aliphatic derivatives reported are dimethanesulfonyl disulfide (*86*) and trisulfide (*88*), and diethanesulfonyl tri- and tetrasulfides (*82*). The first two are solids with mp 61° and 70°, respectively, the last two were obtained as oils.

Disulfonyl disulfides possess pseudohalogen properties (*86*), and the tri- and tetrasulfides in reactions with nucleophilic reagents behave as sulfur thiosulfonates (*82*). The thiosulfonate nomenclature is particularly suitable for some trisulfide analogs, namely selenium and tellurium thiosulfonates, $Se(S_2O_2R)_2$ and $Te(S_2O_2R)_2$. Of these, the methane (*88*) and benzene and *p*-toluene (*90*) derivatives have been prepared; with one exception the crystals are isomorphous with those of the corresponding trisulfides.

The selenium analogs, dibenzenesulfonyl and di-*p*-toluenesulfonyl mono-, di-, and triselenide, are obtainable (*89*) from diselenium dichloride and the sodium sulfinates.

Blomstrand (*31*) in 1870 formulated di-*p*-toluenesulfonyl trisulfide with an unbranched sulfur chain structure, in analogy with the polythionates. The dipole moments of di-*p*-toluenesulfonyl mono-, di-, tri-, and tetrasulfide were reported by Christiansen (*39*) in 1928, but the observed values, 0.75, 1.24, 1.22, and 1.25 D, respectively, gave little information about the structure. Decisive evidence of unbranched chains in the compounds has come from X-ray crystallographic work.

B. X-RAY STUDIES

Unit cells and space groups of disulfonyl mono- and disulfides are given in Table II, and of trisulfides in Table III, together with those of selenium and tellurium analogs. Data for only one tetrasulfide, the dibenzenesulfonyl compound (*95*), are available. This has a large unit cell not favorable for structure analysis.

1. *Monosulfides and Monoselenides*

The four derivatives listed (Table II) are isomorphous. A complete structure analysis of dibenzenesulfonyl monosulfide has been carried out by Mathieson and Robertson (*172*) and of the monoselenide by Furberg and Öyum (*126*). The molecules possess twofold symmetry in the crystals, a twofold axis passing through the divalent sulfur or selenium atom. The bond angles at these atoms are 106.5° and 105°, respectively, and the S—S and S—Se bond lengths, 2.07 and 2.20 Å.

2. *Disulfides and Diselenides*

The structure of the only aliphatic representative, dimethanesulfonyl disulfide, was reported by Sörum (*207*) in 1953. The sulfur chain has an unbranched, nonplanar structure, with S—S bond lengths of 2.10, 2.06, and 2.10 Å (±0.03 Å) and S—S—S bond angles of 104°. The SSS/SSS dihedral angle was found to be approximately 90°.

No structure analysis of any aromatic derivative has been made, but the unbranched structure can hardly be in doubt. The crystals of di-*p*-toluene-

TABLE II

UNIT CELLS AND SPACE GROUPS OF DISULFONYL MONO- AND DISULFIDES AND SELENIUM ANALOGS*

Compound	Axial lengths (Å)			β	Space group	Z	Molecular symmetry	Reference
	a	b	c					
SBs_2	15.90	5.53	15.90	113°	$A2/a$	4	Twofold axis	*43*
$SeBs_2$	16.16	5.61	15.86	112°				*89*
STs_2	16.52	5.86	18.90	120°				*43*
$SeTs_2$	16.83	5.77	19.09	119°				*89*
S_2Ms_2	5.52	15.78	10.05	97.6°	$P2_1/c$	4	None	*207*
S_2Bs_2	12.32	6.10	20.75	109°	$P2_1/c$	4	None	*93*
Se_2Bs_2	5.55	14.27	23.22	108°	$P2_1/c$	4	None	*93*
S_2Ts_2	9.98	15.09	11.26	95°	$P2_1/c$	4	None	*89*
Se_2Ts_2	10.17	15.50	11.28	94°				

* Ms = methanesulfonyl, Bs = benzenesulfonyl, Ts = *p*-toluenesulfonyl.

sulfonyl disulfide and diselenide are isomorphous and the structures are therefore analogous.

No molecular symmetry is crystallographically required in any of the disulfonyl disulfides or diselenides. The only possible symmetry element for a nonplanar disulfide or diselenide group is a twofold axis; a center would lead to a planar *trans* structure.

3. Trisulfides and Triselenides, and Compounds with Mixed Three-Membered Sulfur-Selenium and Sulfur-Tellurium Chains

These are pentathionic compounds, and have been the subject of more extensive studies.

The three methanesulfonyl derivatives, sulfur, selenium, and tellurium dimethanethiosulfonates, are isomorphous. Structure analyses have been carried out, starting with tellurium dimethanethiosulfonate and using tellurium as a heavy atom in the first stages. So far, the structure of the tellurium compound has been published in detail (*123*), and an electron density projection along the short crystal axis of the trisulfide (*98*) has shown the unbranched sulfur chain structure.

Of the eight aromatic representatives, six crystallize in the same tetragonal trapezohedral space group and are isomorphous. These include all four *p*-toluenesulfonyl compounds, namely, the trisulfide, triselenide, and the two with mixed chains. The only ones which do not belong to the isomorphous series are dibenzenesulfonyl triselenide, which is triclinic, and tellurium dibenzenethiosulfonate which has one orthorhombic and one

TABLE III

UNIT CELLS AND SPACE GROUPS OF DISULFONYL TRISULFIDES AND SELENIUM AND TELLURIUM ANALOGS*

Compound	Axial lengths (Å)			β	Space group	Z	Molecular symmetry	Reference
	a	b	c					
S(SMs)$_2$	11.35	5.22	16.17	91°	$P2_1/n$	4	None	*88*
Se(SMs)$_2$	11.40	5.24	16.26	91°				
Te(SMs)$_2$	11.45	5.30	16.35	91°				
S(SBs)$_2$	7.81	—	26.32	—	$P4_12_12$	4	Twofold axis	*43*
Se(SBs)$_2$	7.81	—	26.58	—				*90*
Te(SBs)$_2$†	14.48	11.20	10.50	—	*Pbcn*	4	Twofold axis	*90*
Te(SBs)$_2$‡	13.93	7.71	15.72	96°	$P2_1/c$	4	None	*95*
Se$_3$Bs$_2$	8.25	8.55	12.82	§	Triclinic	2	None	*90*
S(STs)$_2$	7.71	—	29.54	—	$P4_12_12$	4	Twofold axis	*43*
Se(STs)$_2$	7.71	—	29.65	—				*90*
Te(STs)$_2$	7.74	—	29.93	—				*90*
Se$_3$Ts$_2$	7.80	—	29.80	—				*90*

* Ms = methanesulfonyl, Bs = benzenesulfonyl, Ts = *p*-toluenesulfonyl.

† Orthorhombic.

‡ Monoclinic dimorph.

§ $\alpha = 105°$, $\beta = 95°$, $\gamma = 101°$.

monoclinic dimorph. A twofold axis of molecular symmetry is required by the tetragonal space group and twofold symmetry also by the orthorhombic one.

The crystal structure of orthorhombic tellurium dibenzenethiosulfonate was solved (*179*) by fairly straightforward use of the heavy atom technique. The molecular symmetry element is a twofold axis; the other possibility permitted by the space group, a center, would have led to a tellurium valency angle of 180°. The structure, although orthorhombic, is related to the tetragonal one and was of substantial aid in a subsequent structure analysis of tetragonal tellurium di-*p*-toluenethiosulfonate (*109*). The divalent S—Te—S chains are unbranched, with the sulfonyl groups in *trans* positions as demanded by the twofold axis.

An electron density projection (*110*) of another representative of the tetragonal series, di-*p*-toluenesulfonyl triselenide, shows the triselenide in the *trans* form, as contrasted with the *cis* form in cyanogen triselenide. On the basis of the isomorphism, the same unbranched, *trans* structures can be inferred for di-*p*-toluenesulfonyl trisulfide and selenium di-*p*-toluenethiosulfonate, as well as for the two tetragonal benzenesulfonyl compounds.

VIII. Sulfur Chains Terminated by Sulfonate Groups: The Polythionates

A. INTRODUCTORY REMARKS

The history of the polythionates is a long one and fraught with problems as to structure and reactivity. Dalton in 1808 in his "A New System of Chemical Philosophy" commented on the chemical nature of the constituents of the liquid which later came to bear the name of Wackenroder. The three lowest acids were discovered in 1840 to 1846, and Debus in 1888 from Wackenroder's liquid isolated a salt that analyzed for potassium hexathionate, but the existence of hexathionic acid was later doubted, and was not definitely established until the work of Weitz and Achterberg (*220*) in 1928. The literature on polythionates up to 1927 has been reviewed by Kurtenacker (*158*); a later review is by Goehring (*131*) in 1952.

The polythionates have no selenium counterparts, containing selenium and oxygen only, in the ions. However, compounds with divalent selenium chains and terminal sulfonate groups exist, although in accord with the lower chain-forming capacity of selenium relative to sulfur, the stability decreases rapidly with increasing number of selenium atoms in the chain. Selenotrithionic acid was discovered and isolated as the potassium salt, $K_2Se(SO_3)_2$, by Rathke in 1865. Not until quite recently did Yanitskiĭ and Zelionkaite (*236–238*) isolate the first salt of diselenotetrathionic acid, the monohydrate $K_2Se_2(SO_3)_2 \cdot H_2O$, and of triselenopentathionic acid, the nitron (Nt) salt $Nt_2 \cdot H_2Se_3(SO_3)_2$. The series has thus so far three members, like the disulfonyl mono-, di-, and triselenide series. The disulfonyl derivatives appear to be more stable.

Two acids with mixed three-membered chains are known, namely selenopentathionic and telluropentathionic acid. They are derived from pentathionic acid by substitution of selenium or tellurium for the middle sulfur atom of the latter, and behave in reactions with nucleophilic reagents as thiosulfates of divalent selenium and tellurium. The first salts of selenopentathionic (*84*) and telluropentathionic (*85*) acid were isolated in 1949, although the formation reactions in aqueous solutions had been known earlier. Wood (*229*) has by paper electrophoresis shown that the preparative methods lead to pure products.

The polythionic acids are strong, diprotic acids. The ions decompose in alkaline solutions and also, more or less readily, in strongly acid solutions, and free, unsolvated acids had not been prepared until quite recently: Fehér, Schotten, and Thomas (*75*) in 1958 announced the solvent-free synthesis of polythionic acids. Nothing was said about their stability at normal temperatures.

Blomstrand (*30*) in 1869 and one year later Mendelejeff (*173*) were the first to formulate the polythionates with unbranched sulfur chains terminated by sulfonate groups. As remarked in 1927 by Bassett and Durrant (*19*), these formulas were "more or less accepted ever since, although it has been recognized that the evidence in support of them was slender." Bassett and Durant themselves preferred formulas with branched sulfur chains, and so, indeed, did many workers, mostly on the ground that the sulfur atoms of tetra-, penta-, and hexathionate which are so readily given off by the action of basic reagents like hydroxide, sulfite, and cyanide ions, must be bonded differently from the others and therefore cannot be part of unbranched chains.

Hertlein (*143*) in 1896 measured refraction, viscosity, and electrical conductivity of aqueous potassium tri-, tetra-, and pentathionates and decided in favor of unbranched structures, and so did Martin and Metz (*171*) in 1924 on the basis of thermochemical measurements. Spacŭ and Popper (*208*) in 1939 reported the refraction of sodium tetrathionate; Grinberg (*136*) has later commented on the ionic refraction of tetrathionate as indicating negative charge on the divalent sulfur atoms. However, from Hertlein's measurements the increments per sulfur atom, from tri- to tetrathionate and tetra- to pentathionate, are about 9 cm^3. This is the same as in other series, for example, in the polysulfur dichlorides (*72*) where the sulfur atoms are hardly negative.

The ultraviolet absorption spectra of the tri-, tetra-, and pentathionate ions were measured by Lorenz and Samuel (*167*) in 1931 and their results have been confirmed (*9*, *150*). Andersen and Asmussen (*7*) studied the Faraday effect of aqueous potassium tri-, tetra-, and pentathionates, and concluded that the polythionates behave as a homologous series. Particularly indicative of unbranched structures are the measurements of the Raman spectra of potassium tri-, tetra-, and pentathionate by Eucken and Wagner (*49*) in 1948, of the $K\alpha$ X-ray fluorescence of sulfur in potassium tri- through hexathionates by Faessler and Goehring (*50*) in 1952, and of the diamagnetic susceptibility of the same salts by Croatto *et al.* (*41*) in 1952; a study of the Raman spectrum of aqueous sodium tetrathionate in 1950, however, did not enable Gerding and Eriks (*129*) "to draw any safe conclusion with reference to the real configuration of the tetrathionate ion." Palmer (*185*) in 1954 in reviewing Pauling's "General Chemistry" (*187*) remarked that "In presenting structures for the tetra- and hexathionic ions on p. 368 the author gives no hint that they are controversial, and that inorganic chemists still eagerly await a settlement by diffraction methods."

Pauling's structures, the Blomstrand-Mendelejeff unbranched ones, are at present substantiated through X-ray work. Also, the chemistry of the polythionates is fairly well understood (*37*, *40*, *52*, *82*, *87*, *96*) on the basis of unbranched sulfur chain structures.

B. STRUCTURE DETERMINATIONS BY X-RAY METHODS

Until 1950 the only X-ray crystallographic work on polythionates was Zachariasen's structure determination of potassium trithionate (*239*) published in 1934, a partial structure analysis of thallium trithionate by Ketelaar and Sanders (*151*) in 1936, and unit cell and space group determinations of rubidium trithionate (*151*) and potassium tetrathionate (*218*). Since then, surveys of unit cells and space groups of tetra-, penta-, and hexathionates and selenotrithionates, selenopentathionates, and telluropentathionates have been made, and structure determinations of two tetrathionates, three pentathionates, one selenopentathionate, two telluropentathionates, and two hexathionates have been carried out.

The sulfur chains, or in the case of seleno- and telluropentathionates the S—S—Se—S—S and S—S—Te—S—S chains, are in all salts unbranched and nonplanar. The tetra-, penta-, and hexathionate ions contain two, three, and four divalent sulfur atoms, respectively, in a chain between sulfonate groups; the latter, together with the nearest divalent sulfur atom, constitute thiosulfate groups which have the shapes of distorted tetrahedrons. The tetrathionate ion can alternatively be regarded as built up of two thiosulfate groups, linked together through the divalent sulfur atoms, and the penta- and hexathionate ions of one and two divalent sulfur atoms, respectively, to which are attached two thiosulfate groups.

1. *Trithionates and Selenotrithionates*

Potassium trithionate is orthorhombic bipyramidal, space group D_{2h}^{16}–*Pnma* with four formula units per unit cell. From Zachariasen's (*239*) structure analysis, carried out in the early thirties by trial and error methods, the trithionate ion has mirror plane symmetry in the crystals, lying with all three sulfur atoms and two of the oxygen atoms in the mirror plane. The rubidium salt (*151*) is isomorphous with the potassium salt. The third trithionate for which data are available, the thallium salt, is monoclinic prismatic, space group C_{2h}^{6}–*C*2/*c* with four formula units per unit cell (*151*). Here, the trithionate ion has a twofold axis as symmetry element.

X-ray crystallographic data on potassium, rubidium, cesium, and ammonium selenotrithionates (*108*) reveal no isomorphism between any of these and the above trithionates, although the structures of the tri- and selenotrithionate ions are undoubtedly analogous. Barium selenotrithionate dihydrate is orthorhombic, space group probably D_{2h}^{17}–*Cmcm* with eight formula units per unit cell (*108*). According to Patterson and preliminary Fourier projections the selenium atoms appear to lie in the intersection line of two mirror planes, with the sulfur atoms in one of the planes.

The selenotrithionate ion would thus have the symmetry C_{2v}–*mm* in this salt, but the structural data are incomplete.

2. *Tetrathionates*

The first structure determination of a tetrathionate, the barium salt, was published in 1954, 20 years after that of potassium trithionate.

Barium tetrathionate dihydrate is monoclinic prismatic, space group C_{2h}^{5}–$P2_1/c$, with four formula units in a cell of dimensions $a = 5.18$ Å, $b = 9.47$ Å, $c = 19.09$ Å, $\beta = 96°$. The structure analysis (*99*) led to an unbranched, nonplanar structure for the sulfur chain of the tetrathionate ion, and the following bond lengths and angles (± 0.03 Å and $\pm 2°$): S_1-S_2 = 2.10 Å, S_2-S_3 = 2.02 Å, S_3-S_4 = 2.13 Å, $\angle S_1$-S_2-S_3 = 104°, $\angle S_2$-S_3-S_4 = 102°. A value of 90° was derived for the $S_1S_2S_3/S_2S_3S_4$ dihedral angle.

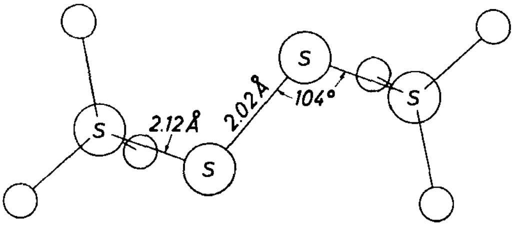


FIG. 1. The tetrathionate ion as seen along its twofold axis in the sodium salt (*101*).

These results have later been confirmed through a more accurate structure analysis of sodium tetrathionate dihydrate. This salt is monoclinic sphenoidal, with $a = 14.50$ Å, $b = 6.37$ Å, $c = 5.47$ Å, $\beta = 105.6°$, and two formula units per unit cell. The space group is C_2^3–$C2$, which requires that the tetrathionate ion lies on a twofold axis of symmetry. The *b*- and *c*-axis projections were solved through Patterson and Fourier syntheses and refined through difference syntheses. The atomic coordinates (*101*) give a length of 2.019 Å for the middle S—S bond across the twofold axis, and 2.116 Å for the end S—S bonds, with estimated standard deviations of 0.01 Å (see Fig. 1). There is, thus, no doubt that the middle bond, between the two divalent sulfur atoms of the tetrathionate ion, is shorter than the two other S—S bonds. The S—S—S bond angles are $103.8 \pm 0.5°$ and the SSS/SSS dihedral angle is $90.4 \pm 1°$.

The sulfonate groups have trigonal symmetry within the accuracy of the analysis. The axis of the trigonal pyramid does not quite coincide with the direction of the O_3S—S bond, the O—S—S angles being 108°, 108°, and 99°.

The crystals of sodium tetrathionate dihydrate, although monoclinic, are submicroscopically twinned (*91*, *93*) and appear orthorhombic; they have, indeed, earlier been described as orthorhombic. The space group, C_2^3–$C2$, is enantiomorphous, and a unit cell contains only one of the enantiomorphous forms of the tetrathionate ion. The twins thus appear to consist of alternating submicroscopic lamellae of right- and left-handed forms.

The isomorphous potassium (*218*) and rubidium (*91*) salts have large cells with two tetrathionate ions in the asymmetric unit.

3. Pentathionates, Selenopentathionates, and Telluropentathionates

Unit cells and space groups of alkali salts and barium salts are listed in Tables IV and V.

Among the alkali salts, seven hemitrihydrates, namely, three pentathionates, two selenopentathionates, and two telluropentathionates, are isomorphous. The unit cells are large, and the crystal structure is not known, but the isomorphism shows that the structures of the three anions are analogous. The only salt in Table IV for which a structure analysis has been carried out is ammonium telluropentathionate (*106*). The telluropentathionate ion has a *trans* form in this salt, the sulfonate groups being located on opposite sides of the S—Te—S plane (Fig. 5).

TABLE IV

UNIT CELLS AND SPACE GROUPS OF ALKALI SALTS OF PENTATHIONIC, SELENOPENTATHIONIC, AND TELLUROPENTATHIONIC ACID

Salt	Axial lengths (Å)			β	Space group	Z	Reference
	a	b	c				
$Na_2S(S_2O_3)_2 \cdot 2H_2O$	8.94	22.86	5.53	—	*Pnc2*	4	*111*
$K_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.12	9.18	12.32	—	*Pbcn*	8	*103*
$Rb_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.84	9.27	12.52	—			*103*
$(NH_4)_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.59	9.33	12.61	—			*111*
$Rb_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.87	9.24	12.50	—			*103*
$(NH_4)_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.61	9.25	12.59	—			*103*
$Rb_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	21.17	9.36	12.48	—			*103*
$Cs_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	21.79	9.56	12.93	—			*103*
$K_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	20.21	9.22	12.26	—	Orthorhombic	8	*103*
$Cs_2S(S_2O_3)_2$	9.69	18.03	6.31	—	Orthorhombic	4	*91*
$Cs_2Se(S_2O_3)_2$	9.76	18.19	6.41	—			*103*
$K_2Te(S_2O_3)_2$	11.22	5.55	16.67	91°	*P2₁/n*	4	*103*
$(NH_4)_2Te(S_2O_3)_2$	5.03	18.90	11.61	100°	*P2₁/c*	4	*106*

The crystal chemistry of the barium salts is interesting. There are five dihydrates, which crystallize in three different space groups, a triclinic, an orthorhombic, and a monoclinic one. Two dimorphs of barium pentathionate dihydrate exist, one triclinic and one orthorhombic, and two of barium telluropentathionate dihydrate, one triclinic and one monoclinic. The acetone and tetrahydrofuran solvates represent a fourth, closely related structure type. Structure determinations of five salts have been made; namely, of triclinic (*115*) and orthorhombic (*124*) barium pentathionate dihydrate, barium pentathionate hydrate acetonate (*119*), orthorhombic barium selenopentathionate dihydrate (*114*), and monoclinic barium telluropentathionate dihydrate (*120*). These include two representatives of the orthorhombic structure type and one of each of the three others.

TABLE V

UNIT CELLS AND SPACE GROUPS OF BARIUM SALTS OF PENTATHIONIC, SELENOPENTATHIONIC, AND TELLUROPENTATHIONIC ACID*

Salt	Axial lengths (Å) *a*	*b*	*c*	β	Space group	Z	Molecular symmetry	Reference
$BaS(S_2O_3)_2 \cdot 2H_2O$	5.01	10.37	11.54	†	$P\bar{1}$	2	None	*115*
$BaTe(S_2O_3)_2 \cdot 2H_2O$	4.99	10.57	12.38	‡				*116*
$BaS(S_2O_3)_2 \cdot 2H_2O$	5.01	10.31	21.81	—	$Pnma$	4	Mirror plane	*124*
$BaSe(S_2O_3)_2 \cdot 2H_2O$	4.99	10.37	22.23	—				*114*
$BaS(S_2O_3)_2 \cdot H_2O \cdot A$	5.04	10.47	13.61	104°	$P2_1/m$	2	Mirror plane	*118*
$BaSe(S_2O_3)_2 \cdot H_2O \cdot A$	5.02	10.56	13.78	105°				
$BaS(S_2O_3)_2 \cdot H_2O \cdot T$	5.03	10.56	13.81	104°				
$BaSe(S_2O_3)_2 \cdot H_2O \cdot T$	5.03	10.69	13.97	105°				
$BaTe(S_2O_3)_2 \cdot H_2O \cdot T$	5.00	10.82	14.21	106°				
$BaTe(S_2O_3)_2 \cdot 2H_2O$	4.99	10.59	23.61	98°	$A2/m$	4	Mirror plane	*116*
$BaSe(S_2O_3)_2 \cdot H_2O \cdot \frac{1}{2}D$	5.02	10.59	22.72	102°				*120*
$BaS(S_2O_3)_2 \cdot H_2O \cdot E$	9.18	13.27	21.25	—	$Pcab$	8	None	*117*
$BaSe(S_2O_3)_2 \cdot H_2O \cdot E$	9.19	13.30	21.37	—				
$BaTe(S_2O_3)_2 \cdot 3H_2O$	11.16	5.24	21.30	107°	$P2_1/c$	4	None	*116*

* In solvates: A = acetone, T = tetrahydrofuran, D = dioxane, E = ethanol.

† $\alpha = 109°$, $\beta = 97°$, $\gamma = 90°$.

‡ $\alpha = 106°$, $\beta = 101°$, $\gamma = 90°$.

The penta-, selenopenta-, and telluropentathionate ions have mirror plane symmetry in the crystals. This is crystallographically required in all four structure types except the triclinic one, but is realized even there. The ions thus have a *cis* form in these salts, with the terminal sulfonate groups on the same side of the plane through the three middle atoms. The occurrence of the *cis* form in the barium salts is perhaps due to the oxygen-coordinating power of the barium ion, and favorable lattice conditions for the mirror-plane *cis* arrangement.

The dimensions of the pentathionate ion are within the experimental error the same in the three studied salts (see Fig. 2). The average value for the length of the terminal S—S bonds is 2.12 Å and of the middle S—S bonds 2.04 Å, with estimated standard deviations of 0.02 Å. The sulfur valency angles are 105° and 106°. In the seleno- and telluropentathionate ions (Figs. 3–5) the observed values for the terminal S—S bonds range from 2.10 to 2.13 Å, with the same average as in the pentathionate ion, 2.12 Å.

The crystals of barium penta-, selenopenta-, and telluropentathionate dihydrates and acetone and tetrahydrofuran solvates are built up of layers parallel to the *c* crystal plane, and show a corresponding perfect cleavage along this plane. The thickness of the layers is approximately 11 Å in the dihydrates and approximately 13 Å in the solvates, and is equal to the *c* spacing when there are two formula units per unit cell, and half the *c* spacing when there are four. The atomic arrangement within a layer is the same in all four structure types, and the structures differ only in the way of packing of the layers. In the triclinic dihydrates, the oblique *β*- and *α*-angles lead to relative displacements of successive layers in the directions of the *a*- and *b*-axes, while in the acetone and tetrahydrofuran solvates, displacements occur in the *a*-axis direction only. In the orthorhombic dihydrates, adjacent layers are related through glide planes in the interface, and in the monoclinic dihydrate, through twofold rotation axes in the interface.

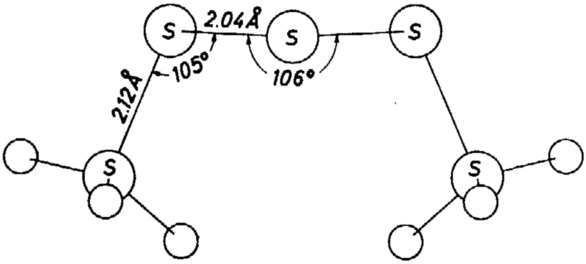


FIG. 2. The pentathionate ion as it occurs in the barium salts (*115*, *119*, *124*). A mirror plane of symmetry, normal to the plane of the paper, passes through the middle sulfur atom, and through the selenium and tellurium atom of Figs. 3 and 4 respectively.

In the dihydrate structures, one of the water molecules is firmly held in the lattice, being coordinated to two barium ions and forming hydrogen bonds to two sulfonate oxygen atoms. The other water molecule is loosely bound, to one barium ion only, and has a relatively spacious environment; it is this water molecule which in the solvates is replaced by acetone or tetrahydrofuran. The oxygen atom of the organic molecule is coordinated to a barium ion, like the oxygen atom of the replaced water molecule, and is located between the barium ion and the nearest layer interface, with the rest of the molecule directed towards the interface. In the dioxane solvate

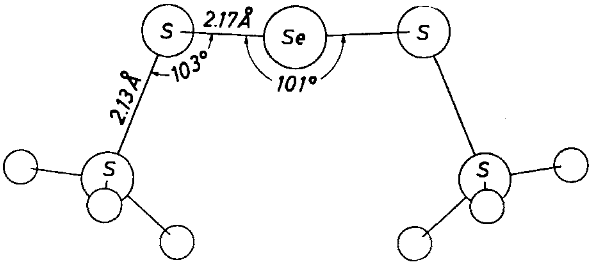


FIG. 3. The selenopentathionate ion in orthorhombic barium selenopentathionate dihydrate (*114*).

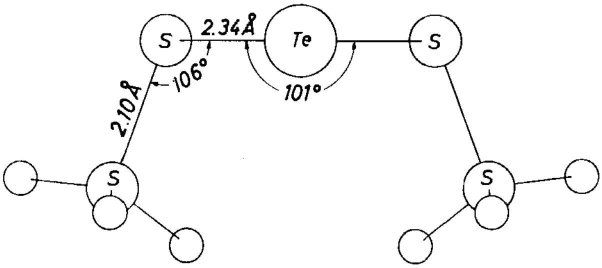


FIG. 4. The *cis* form of the telluropentathionate ion as it occurs in monoclinic barium telluropentathionate dihydrate (*120*).

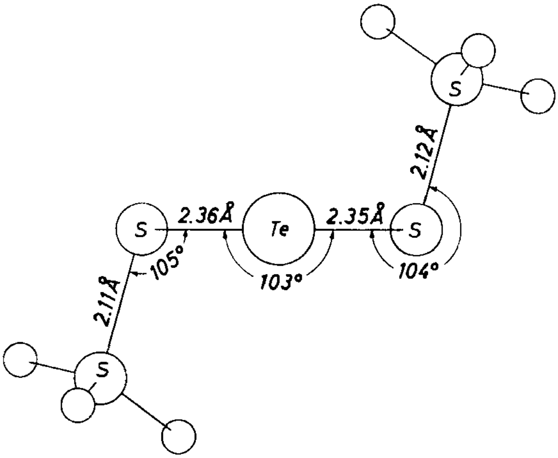


FIG. 5. The *trans* form of the telluropentathionate ion as found in the ammonium salt (*106*).

of Table V, isomorphous with monoclinic barium telluropentathionate dihydrate, the dioxane molecule presumably extends across the layer interface and replaces two water molecules, one in each of two adjacent layers. The layers are thereby held more firmly together, and the characteristic cleavage is lacking.

Two ethanol solvates and a trihydrate, conclude Table V. Strontium selenopentathionate gives a dihydrate (*95*) isomorphous with the two orthorhombic barium dihydrates.

4. Hexathionates

A preparative and X-ray crystallographic survey (*111*) of salts of hexathionic acid led to unit cell and space group data for two salts, the crystals of which are, in view of the rather unstable nature and poor crystallization power of hexathionates, surprisingly well developed and stable. One is a potassium barium double salt, and the other a cobalt complex salt.

The crystals of potassium barium hexathionate, $K_2Ba(S_6O_6)_2$, are monoclinic prismatic, with a = 11.58 Å, b = 10.81 Å, c = 9.14 Å, β = 112°, and two formula units per unit cell. The space group is C_{2h}^4–$P2/c$, which requires that the barium ions lie in special, twofold positions. The structure was solved (*102*) through projections along the b- and c-axes, by direct Fourier synthesis based on the strongest reflections with positive signs. The projections have later been refined (*105*) through difference syntheses.

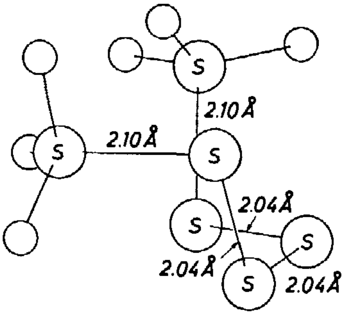


FIG. 6. The *cis-cis* form of the hexathionate ion as seen along the c crystal axis of the potassium barium salt (*102*, *105*).

The sulfur chain of the hexathionate ion is unbranched and nonplanar, and has in this salt the *cis-cis* configuration of the S_8 ring. The terminal S—S bonds are 2.10 Å and the three middle S—S bonds 2.04 Å, with estimated standard deviations of 0.02 Å (see Fig. 6). The bond angles at the divalent sulfur atoms are 101°, 113°, 109°, and 100°, and the SSS/SSS dihedral angles, 108°, 91°, and 105°, from one end of the chain to the other.

The differences between values for corresponding angles in the two halves of the ion are within the experimental errors.

The second salt, *trans*-dichloro-dien-cobalt(III) hexathionate monohydrate, is orthorhombic pyramidal, with two formula units in a cell of dimensions a = 12.12 Å, b = 19.13 Å, c = 6.43 Å. The space group C_{2v}^{8}–$Pba2$ requires that the hexathionate ions lie on twofold axes of symmetry.

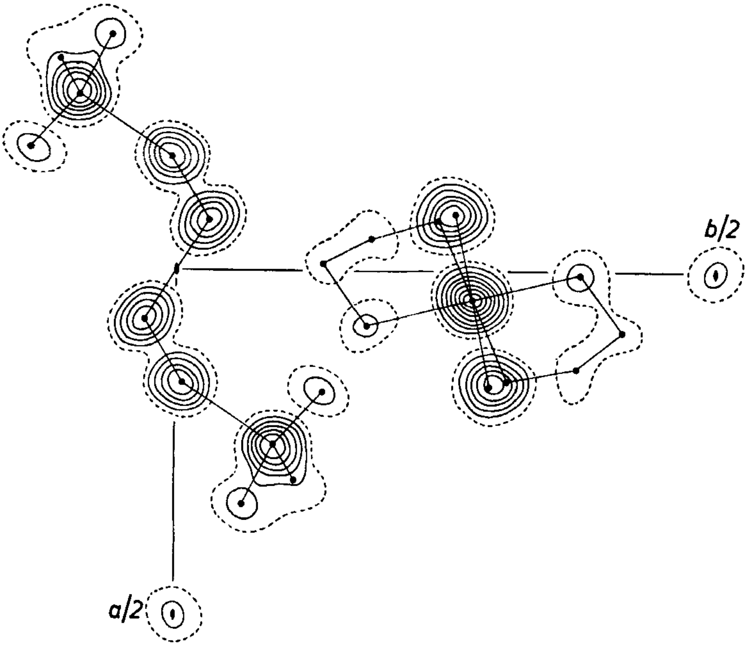


FIG. 7. Electron density projection along the twofold axis of *trans*-dichloro-dien-cobalt(III) hexathionate monohydrate, showing the *trans-trans* form of the hexathionate ion. Reproduced, with permission, from *Acta Chem. Scand.* **13,** 201 (1959).

An electron density projection (Fig. 7) along the c-axis (*107*) shows an unbranched structure for the sulfur chain of the hexathionate ion also in this salt, but here, the chain has the extended *trans-trans* form of the helixes of fibrous sulfur.

C. BOND LENGTHS IN THE SULFUR CHAINS

Two types of sulfur-sulfur bonds occur in the polythionates, namely, between divalent sulfur atoms in the middle of the chains and between one divalent and one sulfonate sulfur atom at the ends. The weighted average of the observed values for the length of the terminal bonds, in nine different salts including one selenopentathionate and two telluropentathionates, is 2.11 Å with an average deviation of 0.01 Å. The middle bonds have within the errors the same length as the S—S bonds in orthorhombic sulfur, 2.04 Å, which is also the value found for S—S bonds in organic di- and trisulfides.

The difference in length between the two types of bonds indicates, apart from a possible effect of different hybridization of σ-bond orbitals at divalent and sulfonate sulfur, that bonds between divalent sulfur atoms possess some *pd* π-bond character, or, what is less probable, that the terminal bonds are longer than single bonds.

D. Limit of the Polythionate Series

Weitz and Achterberg (*220*) in 1928 remarked that the mother liquor from the preparation of potassium pentathionate from acidified thiosulfate with arsenite as a catalyst—the Raschig method—contains appreciable amounts of polythionates with sulfur content higher than that of hexathionate. Kurtenacker and Matejka (*159*) in 1936 confirmed that higher polythionic acids are formed in thiosulfate-arsenite solutions at high concentrations of hydrochloric acid. The highest acid detected was decathionic acid; a product $K_2S_xO_6$ with x about 10 was characterized by X-ray powder lines.

The extensive studies of Weitz and co-workers on higher polythionates were published in full in 1956. Weitz and Spohn (*224*) found that in the Raschig method for pentathionate, from 30 to 40% of the total yield may be obtained as higher potassium polythionates $K_2S_xO_6$ with x from 6 to 12. They used fractional crystallization of benzidinium, tolidinium, or *trans*-dichloro-dien-cobalt(III) salts for analysis of crude products, but did not succeed in isolating pure salts higher than hexathionate; products with higher sulfur content were all mixtures. Comparing different methods for the preparation of potassium hexathionate, Weitz, Becker, and Gieles (*221*) stated that only the nitrite-thiosulfate method of Weitz and Achterberg give a pure product and not a mixture of higher and lower homologs. Thus, from a product prepared according to Goehring and Feldmann (*133*) from disulfur dichloride and thiosulfate, fractions with values of x from 4 to 15 were obtained. Fehér (*70*) has later remarked, though, that the Weitz-Achterberg and Goehring-Feldmann methods for hexathionate give identical products.

In 1953–1954 Yanitskiĭ and Valanchunas (*233*, *234*) reported the isolation of benzidinium octathionate from the reaction between sodium thiosulfate, sodium hydrogen sulfide, sodium hydrogen sulfite, and hydrochloric acid. This method yields, depending on the relative amounts of the reaction partners, still higher polythionates; thus, Yanitskiĭ and co-workers

(*235*) recently reproduced microphotographs of crystalline nitron (Nt) salts $Nt_2 \cdot H_2S_xO_6$ with $x = 13$ and 18 and dimethylphenylbenzylammonium salts $(C_{15}H_{18}N)_2S_xO_6$ with $x = 6, 9, 12,$ and 13. In view of the experience of Weitz and co-workers with regard to fractional crystallization of higher polythionates, one cannot feel sure that the products represent pure individuals and not mixtures of homologs. The ordinary analytical methods give the average sulfur content only, and the only safe way to ascertain the purity of a higher polythionate appears to be through chromatography or electrophoresis. Pollard *et al.* (*189*) and Bighi and Trabanelli (*27*) have worked out methods for paper chromatography, and Wood (*228*) a technique for paper electrophoresis.

Schmidt (*197*) in 1956 reported the preparation of an ether solvate of heptathionic acid from hydrogen pentasulfide and sulfur trioxide, and of solutions and potassium salts of octa-, deca-, and dodecathionic acids. Fehér *et al.* (*75*) in a preliminary report have described the use of condensation reactions between chlorosulfonic acid and higher hydrogen polysulfides, and between thiosulfuric acid and polysulfur dichlorides. They report the synthesis of free octa-, nona-, deca-, undeca-, and dodecathionic acids, and reproduce paper chromatograms of, among other samples, one of pure potassium octathionate.

The results of Weitz and co-workers (*222*, *223*) indicate that the polythionate series extends up to and including the hydrophilic Odén's sulfur sols. These appear to be sodium polythionates $Na_2S_xO_6$ with x from 50 to 100. The stability of the polythionates, with respect to liberation of sulfur, decreases monotonously up to x about 20 and then increases as the properties approach those of the sulfur sols.

IX. Unsymmetrical Compounds

In the compounds considered so far the sulfur chains are terminated by the same kind of atom or group at both ends. However, "mixed" organic disulfides and also other types of unsymmetrical di- and polysulfides exist.

Organic disulfur chlorides, R—S—S—Cl with R = *o*-nitrophenyl and 9-anthryl, were described as early as 1922. Harris (*140*) has recently studied properties and reactions of the *o*-nitrophenyl compound, and Himel and Edmonds (*144*) in patents described reactions of the *t*-butyl analog; other aliphatic disulfur chlorides were reported by Böhme and van Ham (*33*) and Fehér and Kruse (*66*) in 1958. With thiols, thioacetate, xanthates, and dithiocarbamates these compounds give unsymmetrical trisulfides. Böhme and Clement (*32*) in 1952 prepared acyl-disulfur and acyl-polysulfur chlorides, and derivatives such as an unsymmetrical pentasulfide.

Alkyl-hydrogen di- and trisulfides $R—S_n—H$ were reported in 1954 by

Böhme and Zinner (*34*), who prepared the methyl, ethyl, and benzyl derivatives. With iodine, the trisulfides give symmetrical hexasulfides. Fehér and Kruse (*66*) prepared phenyl-hydrogen tri- and tetrasulfide and *n*-butyl-hydrogen tetrasulfide and studied their Raman spectra. The compounds are sensitive to bases, and salts are apparently unstable, although White (*226*) in 1918 reported a stable sodium salt of 2-naphthyl-hydrogen disulfide.

Further examples include some in which the sulfur chains carry an alkyl or aryl group, or a hydrogen atom, at one end and a sulfonate group at the other. Sulfenyl thiosulfates $R\text{—}S\text{—}S\text{—}SO_3^-$ have been studied in solutions (*83*), and a trisulfide $R\text{—}S\text{—}S\text{—}S\text{—}SO_3^-$ was recently identified by Szczepkowski (*212*) as a minor product from the reaction of tetrathionate with cysteine. The trisulfide is evidently formed through a nucleophilic displacement of a sulfite group of tetrathionate, a less predominant reaction path (*96*). So-called sulfane-monosulfonic acids, $H\text{—}S_n\text{—}SO_3H$, were first prepared by Schmidt (*196*) from hydrogen di- and polysulfides and sulfur trioxide, and later by Fehér and co-workers (*75*) by use of chlorosulfonic acid instead of sulfur trioxide. The ionized species, $^-S_n\text{—}SO_3^-$ with $n = 8$ through 2, have been postulated (*87*) as intermediates in the reaction of sulfur S_8 with sulfite ion to give thiosulfate, and analogous unsymmetrical intermediates, $^-S_n\text{—}CN$ and $^-S_n\text{—}\overset{+}{P}(C_6H_5)_3$, occur in the reactions of sulfur S_8 with cyanide ion (*17*, *87*) and with triphenylphosphine (*18*).

X. Comments on Structural Evidence

Structure determinations by X-ray and electron diffraction methods have demonstrated the presence of unbranched chains of up to six divalent sulfur atoms in inorganic polysulfides, four divalent ones in salts of polythionic acids, and three in disulfonyl, dialkyl, and cyanogen derivatives. The synthetic and Raman-spectroscopic work of Fehér has established the presence of unbranched structures with up to five sulfur atoms in organic polysulfides, and eight in the cyanogen polysulfide, polysulfur dichloride, and hydrogen polysulfide series. The results are supported by extensive physicochemical evidence of less conclusive nature.

There exist in the literature claims concerning the occurrence of branching in particular compounds; the more definite of these have been refuted in recent years. Backer and co-workers (*10*, *11*) formulated some cyclic di- and trisulfides with branched sulfur groupings; from a comparison of their ultraviolet and infrared spectra with those of other di- and polysulfides, Schotte (*202*) concluded that branching does not occur. Baroni (*15*), on the basis of parachor measurements, assigned isomeric branched structures to two diethyl pentasulfides; this claim has been refuted by Fehér *et al.* (*65*), who were able to prepare only one diethyl pentasulfide the Raman spectrum of which agreed with an unbranched structure. The supposed low-melting isomer of di-2-naphthyl diselenide, to which a coordinated structure was ascribed by Loevenich *et al.* (*166*) was, according to Bergson (*22*), probably a mixture of monoselenide and normal, unbranched diselenide.

In fact, no substantiated example of branching is known. Fehér (p. 313 in ref. *56*) states that "We have tried for many years to prepare branched-chain polysulfides, but without success."

The only instances in which sulfur forms only one bond to sulfur and none to another atom, are apparently in the polysulfide ions as terminal atoms, and in the thiosulfate and thiosulfonate ions, $S—SO_3^{--}$ and $S—SO_2R^-$, in which the S—S bond appears to be partly double. Thus, crystal structure determinations of sodium thiosulfate pentahydrate (*213*) and sodium methanethiosulfonate monohydrate (*100*) have shown the S—S bond to be 1.97–1.98 Å, as compared with 2.04 Å in orthorhombic sulfur. The reason (*87*) why coordinated structures are unstable relative to unbranched ones may be that a sulfur atom as an electroneutral, nonpolar acceptor can add only to donors which are less electronegative, or to donors which can expand the valency shell for π-bonding.

XI. Stereochemistry

Fairly accurate values for bond lengths and angles in sulfur chains are known from X-ray and electron diffraction work; some have been commented on in earlier sections. A recent review is by Abrahams (*3*) in 1956.

A. NONPLANARITY OF SULFUR CHAINS

In the noncyclic compounds for which structural data are available, a dihedral angle of about 90° occurs between the planes of the valencies of adjacent sulfur atoms. Reported values lie between 74° in cesium hexasulfide (*3*) and 108° in barium pentathionates (*119*). In six- and particularly in five-membered cyclic disulfides, the angle is smaller, and may for steric reasons also become larger, but planar, *trans* groups with 180° dihedral angle have not been observed.

1. *Origin and Magnitude of the Barrier to Internal Rotation*

The barrier to rotation about a bond between two divalent sulfur atoms is thought to arise principally from the mutual interaction of the unshared pairs of $3p\pi$-electrons on the sulfur atoms. This explanation was first put forward by Penney and Sutherland (*188*) in 1934 to account for the nonplanarity of hydrogen peroxide and hydrazine, and was discussed with reference to elemental sulfur and sulfur compounds by Pauling (*186*) in 1949. The σ-bonding orbitals of sulfur are here assumed to be nearly pure p in character, and the second lone pair on each sulfur atom to occupy mainly the $3s$-orbital. The interaction between the two unshared pairs of $3p\pi$-electrons on adjacent sulfur atoms has a maximum when the orbitals are parallel (dihedral angle $\varphi = 0°$ or $180°$) and a minimum when they are orthogonal ($\varphi = 90°$). This leads to a simple twofold rotation barrier.

Important information concerning the $3p\pi$-interaction in disulfides has recently come from studies of ultraviolet spectra. As pointed out by Barltrop *et al.* (*14*) and Schotte (*201, 203*) the absorption peak near 2500 Å displayed by normal noncyclic disulfides is in five-membered cyclic disulfides shifted towards longer wave lengths, to about 3300 Å. According to molecular orbital calculations by Bergson (*24*), the red shift is due to a decrease in excitation energy of $3p\pi$-electrons with decreasing dihedral angle. The $3p\pi$-interaction satisfactorily accounts for a dihedral angle of 90° as the most stable conformation of a disulfide in the ground state, but is not a simple Coulombic repulsion between charge clouds; in order to calculate the torsion energy from the red shift it is necessary to know both the overlap integral of the $3p\pi$-electrons and the dihedral angle. For the barrier height, that is, the torsion energy when $\varphi = 0°$, in a five-membered cyclic disulfide, 1,2-dithiolane-4-carboxylic acid, Bergson (*25*) arrived at a value of 14 kcal/mole.

Two other approaches beside Bergson's have been used to derive torsion barriers for S—S bonds; namely, from the torsional frequency of the bond as observed in Raman spectra, and from measured thermodynamic data as compared with statistically calculated ones. According to Scott and coworkers the torsional frequencies in dimethyl disulfide (*204*), diethyl disulfide (*205*), and disulfur dichloride (*139*) correspond to barrier heights of 9.5, 13.2, and 14.2 kcal/mole, respectively. On the other hand, agreement between calculated and observed entropy and heat capacity of dimethyl disulfide was obtained (*146*) by use of 6.8 kcal/mole for the effective barrier height. From observed and calculated heat capacities, Fehér and Schulze-Rettmer (*76*) arrived at a value of 2.7 kcal/mole for the barrier height in hydrogen disulfide.

2. Rotational Isomerism

The nonplanarity of sulfur chains gives rise to rotational isomerism, namely, to two enantiomorphs of a disulfide, two forms of a trisulfide of which one is a pair of enantiomorphs, and to three pairs of enantiomorphs of a tetrasulfide. In gases and solutions, equilibrium mixtures probably occur, whereas in crystals, with fixed atomic positions, only one of the forms will normally be present. Depending on the symmetry of the crystal and the number of molecules per unit cell, the cell contains both or only one of a pair of enantiomorphs.

a. Disulfides, tetrathionates. The nonplanarity of the valencies of two bonded sulfur atoms was first suggested by Fehér and Baudler (*57*) for hydrogen disulfide from analogy with hydrogen peroxide. The exact value of the dihedral angle in hydrogen disulfide is uncertain (*227*). It is 101° in *N*,*N'*-diglycyl-L-cystine dihydrate (*232*), 79° in L-cystine hydrochloride (*210*), 105° in formamidinium disulfide diiodide monohydrate and 89° in the corresponding dibromide (*104*), and 76° in barium tetrasulfide monohydrate (*1*). The average of these values is exactly 90°, and this is the angle found in barium tetrathionate dihydrate (*99*) and sodium tetrathionate dihydrate (*101*).

Rogers and Campbell (*193*) have concluded from dipole moment measurements that the dihedral angle in di-*t*-butyl disulfide is larger than normal owing to spatial interference of the bulky *t*-butyl groups. This was first discussed by Koch (*152*) on the basis of ultraviolet absorption; the characteristic peak of normal disulfides at 2500 Å is for di-*t*-butyl disulfide shifted towards so low a wave length that it is overlapped by the strong absorption at about 2000 Å. However, as pointed out by Bergson (*21*, *25*), the blue shift is not a simple steric effect but principally an electronic (hyperconjugative and inductive) effect. Schotte (*199*) has demonstrated the same spectral effect for disulfides with carboxylic group substituents in α-positions to the disulfide bond.

The enantiomorphs of a nonplanar disulfide sometimes become separated in crystals. Thus, diphenyl disulfide (*43*) and probably also di-*p*-tolyl disulfide (*43*) crystallize in enantiomorphous space groups with only one enantiomorph per unit cell, and so do barium tetrasulfide monohydrate (*1*) and sodium tetrathionate dihydrate (*101*). The same applies, of course, to L-cystine and other optically active disulfides.

b. Trisulfides, pentathionates. Two rotational-isomeric forms of trisulfides X—S—S—S—X occur. The atoms or groups X are rotated about 90° out of the plane of the three sulfur atoms, either to the same side of the plane—*cis*—or to opposite sides—*trans*. There are two enantiomorphous *trans* forms. This holds also if X is sulfur; the *cis* form of the then five-membered sulfur chain is a segment of the S_8 ring of orthorhombic sulfur, while the *trans* forms are present in the helixes of fibrous sulfur. A *cis* form possesses a mirror plane of symmetry, and a *trans* form a twofold axis, provided that the two atoms or groups X are like, and that bond lengths and angles are the same in both halves of the molecule.

In the crystals of di-2-iodoethyl trisulfide (*46*) the configuration about the trisulfide group is *trans*, a twofold axis of molecular symmetry being crystallographically required. The *trans* form occurs also in the crystals of dibenzenesulfonyl and di-*p*-toluenesulfonyl trisulfide; here also the molecules are required to lie on twofold axes (*43*). These three trisulfides crystallize in the enantiomorphous space group, D_4^4–$P4_12_12$ (or the enantiomorph) with four molecules per unit cell. A unit cell, and whole single crystals provided twinning does not occur, thus contains only one of the *trans* enantiomorphs. The configuration of dimethanesulfonyl trisulfide is also *trans* (*98*); here, the space group is centrosymmetric and both enantiomorphs are present in each unit cell.

The *cis* form occurs in cyanogen trisulfide, where the molecules lie across mirror planes of symmetry (*94*). The trisulfide group of the pentathionate ion occurs in the *cis* form in the three barium salts (*115*, *119*, *124*) for which structure determinations have been carried out, a mirror plane of symmetry being demanded by the space group in two of the salts. In the six- and seven-membered rings of 1,2,3-trithianes (*202*) and the one known 1,2,3,5,6-pentathiepane (*125*) the configuration of the trisulfide group is necessarily *cis*.

The existence of the two forms, *cis* and *trans*, of a trisulfide was apparently first considered by Baudler (*20*) with reference to the Raman spectrum of hydrogen trisulfide, and later by Kushner *et al.* (*160*) and Woodrow *et al.* (*230*) on the basis of dipole moments of dialkyl trisulfides in solutions. The author (*92*) has discussed the occurrence of the forms in crystals.

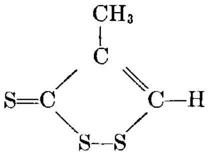
c. Tetrasulfides, hexathionates. In compounds X—S—S—S—S—X, three different rotational-isomeric forms, each consisting of a pair of enantiomorphs, are possible, as was pointed out by Woodrow *et al.* (*230*) in a discussion of the dipole moment of di-*n*-hexadecyl tetrasulfide. In the six-membered chain of the four sulfur atoms and their terminal bond partners, the fifth atom may be located *cis* or *trans* relative to the first, and the sixth similarly relative to the second. The three forms which thus arise are, one *cis-cis* in which the fifth and sixth atom are in *cis* positions relative to the first and second, respectively; one *cis-trans*, and one *trans-trans*. All three forms may be right- or left-handed; a *cis-trans* form is the mirror image of a *trans-cis*. A *cis-cis* form passes into a *trans-trans*, and vice versa, through a rotation of approximately 180° about the middle sulfur-sulfur bond. The *cis-cis* form is present in the S_8 ring, and the *trans-trans* in the helixes of fibrous sulfur; these two forms possess a twofold axis of symmetry provided that bond lengths and angles are equal in the two halves.

The *trans-trans* forms occur in the crystals of cesium hexasulfide (*5*) and of *trans*-dichloro-dien-cobalt(III) hexathionate monohydrate (*107*), and the *cis-cis* forms in the crystals of potassium barium hexathionate (*102*), these being the only compounds containing tetrasulfide groups for which structural data are available.

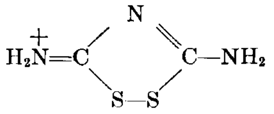
B. Cyclic Disulfides

When a disulfide group is part of a ring of small size, the group cannot, owing to the geometrical requirements of the ring, maintain the normal dihedral angle of about 90°. Thus, according to crystal structure determinations, the dihedral angle is 60° in the six-membered ring of *racem*-1,2-dithiane-3,6-dicarboxylic acid (*112*), and 27° in the five-membered ring of 1,2-dithiolane-4-carboxylic acid (*122*). With a simple cosine-type barrier to rotation about the S—S bond, the latter angle corresponds to a S—S torsion energy equal to 80% of the barrier height. Beside torsion, there is also stretching and bending strain in the rings; Bergson and Schotte (*26*) have, on the basis of structural data, carried out a conformational analysis of the rings of *racem*-1,2-dithiane-3,6-dicarboxylic acid and 1,2-dithiolane-4-carboxylic acid and concluded that the total strain is at least 5 kcal/mole in the 1,2-dithiane ring and 16 kcal/mole in the dithiolane ring. The large strain in the latter is in accordance with the highly unstable nature (*14*) of 1,2-dithiolane itself; in derivatives, the substituents stabilize the ring to some extent.

There exist some unsaturated five-membered cyclic disulfides which are remarkably stable, among them the 1,2-dithia-4-cyclopentene-3-thiones and 3,5-diimino-1,2,4-dithiazolidines, the so-called trithiones and thiurets, respectively. Here, the S—S $3p\pi$-interaction is either absent, or compensated by conjugative stabilization of the rings. Kehl and Jeffrey (*149*) have made a crystal structure analysis of 4-methyl-trithione, (I); the molecule was found to be planar within the experimental accuracy. In the crystals of thiuret hydroiodide, the cation of which (II) is a diamino and not a diimino derivative, the disulfide group lies across a mirror plane and is thus exactly planar (*121*); the cation as a whole is planar or nearly so.



(I)



(II)

C. Selenium and Tellurium Analogs

The same barrier to rotation about selenium-selenium and tellurium-tellurium bonds exists as in the case of sulfur. Bergson (*25*) has recently extended his discussion of $p\pi$-interaction in disulfides (*24*) to diselenides.

There have not been so many determinations of dihedral angles in selenium and tellurium compounds, but the available data show angles of about 90°. Thus, the reported value for the dihedral angle in diphenyl diselenide (*169*) is 82°, in di-*p*-chlorophenyl diselenide and ditelluride (*157*) 74° and 72°, respectively, and in cyanogen triselenide (*6*) 94°. In α-monoclinic (*38*) and β-monoclinic (*170*) selenium the angles are 102° and in hexagonal selenium and tellurium (*3*), 101°. Dihedral angles dependent on rotation about sulfur-selenium and sulfur-tellurium bonds have been reported for selenium dithiocyanate (*181*) and barium selenopentathionate dihydrate (*114*) and for several telluropentathionic compounds. In the first two the angles are 79° and 109°, respectively, and in the latter (*106*, *109*, *120*, *123*, *179*) the values range from 79° to 103°.

Planar *trans* diselenide or ditelluride groups, with 180° dihedral angles, have not been encountered. The smallest Se—Se dihedral angle determined is 56° in the six-membered ring of *racem*-1,2-diselenane-3,6-dicarboxylic acid (*105*, *113*). In saturated five-membered cyclic diselenides the dihedral angle is, for geometrical reasons, necessarily smaller, and in unsaturated ones probably zero, but no structure determinations have been carried out.

Triselenides, and compounds with mixed three-membered chains like seleno- and telluropentathionates, display the same rotational isomerism as trisulfides. Examples already referred to include the *cis* triselenide group of cyanogen triselenide and the *trans* one of di-*p*-toluenesulfonyl triselenide, and likewise, the *cis* telluropentathionate ion in the barium salts as contrasted with the *trans* form occurring in the ammonium salt.

D. PEROXY COMPOUNDS

These are, with one notable exception, nonplanar like disulfides, diselenides, and ditellurides; indeed, the nonplanarity of hydrogen peroxide was the first example discussed, by Penney and Sutherland (*188*) in 1934. Incidentally, here *pd* π-bonding can make no contribution to the nonplanarity, as has been suggested by Krebs (*154*) for sulfur and sulfur compounds.

Bain and Giguère (*13*) have recently discussed dihedral angle and barrier height in hydrogen peroxide on the basis of infrared and other data. From the crystal structure analysis of hydrogen peroxide by Abrahams *et al.* (*4*), the dihedral angle is 94 ± 1.5° at $-20°$. Harvey and Bauer (*141*) in an electron-diffraction study of bis(pentafluorosulfur) dioxide found a dihedral angle of 107 ± 5°. Dialkyl and diacyl peroxides are also nonplanar, according to dipole moment measurements by Lobunez, Rittenhouse, and Miller (*165*). The dipole moment of di-*t*-butyl peroxide indicates a larger than normal dihedral angle, namely about 125°, owing to the spatial requirements of the *t*-butyl groups, as earlier deduced on the same basis by Rogers and Campbell (*193*).

It is remarkable, then, that in the peroxydisulfate ion the peroxy group is planar *trans*. The crystal structures of ammonium and cesium peroxydisulfate were determined as early as 1934 by Zachariasen and Mooney (*240*) and that of the potassium salt one year later by Keen (*148*). The latter is triclinic, while the ammonium and cesium salts are monoclinic and isomorphous; in both space groups a center of symmetry is required for the peroxydisulfate ion. As stated earlier, no such structure has been found for disulfide, diselenide, or ditelluride groups.

A planar *trans* structure has recently been reported for a hydrazine derivative. Whereas hydrazine itself is nonplanar owing to interaction between $p\pi$-electron pairs as in compounds of sixth-group elements, Tomiie, Koo, and Nitta (*215*) found that diformylhydrazine is centrosymmetric in the crystalline state and its hydrazine group thus planar. Tomiie (*214*) has subsequently performed a molecular orbital calculation of the electronic structure of diformylhydrazine, and concluded that Coulombic repulsion between charged atoms in different halves of the molecule is the primary cause of the planar structure. A similar explanation may apply in the case of the peroxydisulfate ion. Also, different hydridization at the peroxy oxygen atoms, or π-bonding between these and sulfur, may lower the $p\pi$-interaction and contribute to the planarity.

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