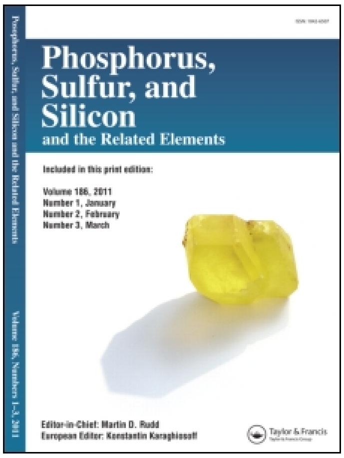

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The Lower Oxides of Sulfur and Related Organic Sulfoxides

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THE LOWER OXIDES OF SULFUR AND RELATED ORGANIC SULFOXIDES

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Abstract. The preparation, structures, spectra and other properties of organic sulfane oxides, R_2S_nO (n=3,4), and dioxides, $R_2S_nO_2$ (n=3,4), as well as of the homocyclic sulfur oxides S_nO (n=6...1o) and S_nO_2 (n=7,12) are discussed. All compounds are sulfoxides and contain two or more homonuclear S-S bonds.

INTRODUCTION

The element sulfur is unique in many respects. For instance, it is the element with the largest number of allotropes [1,2], with the largest number of molecular oxides [3,4] and also with the largest number of binary nitrides [5]: while 20 crystalline sulfur allotropes have been well characterized, 15 molecular oxides and 1O nitrides have been prepared. In all three cases the thermodynamic stability of the homonuclear sulfur-sulfur bond [6] is one of the reasons for these large numbers, since all of the allotropes and most of the oxides and nitrides contain one or more S-S bonds.

Most of the existing 15 sulfur oxides form small molecules but some are polymeric, e.g. $(SO_3)_x$ and $(SO_{3+n})_x$ with x being a very large number and $0 < n \ll 1$. The best known and most important oxides are, of course, SO_2 and SO_3 with oxidation numbers of sulfur of +4 and +6, respectively. Oxides with an average oxidation number of less than +4 are called "lower sulfur oxides" [7].

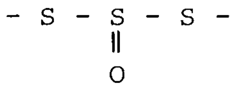
The number of known lower sulfur oxides has increased from 2 in the year 1960 to 10 in 1984 and most of the new species have been prepared in Berlin; the following compounds are presently known:

SO S_2O_2 S_2O S_5O S_6O S_7O S_7O_2 S_8O S_9O $S_{10}O$

The sulfur to oxygen ratio in these molecules varies between 10:1 and 1:1 and the thermal stability (or "life-time") of these thermodynamically unstable compounds is related to this ratio: while S_8O survives as a crystalline compound for several hours at 25°C, the short-lived sulfur momoxide SO can be detected for only some milliseconds after its preparation in the vapor phase [7,8].

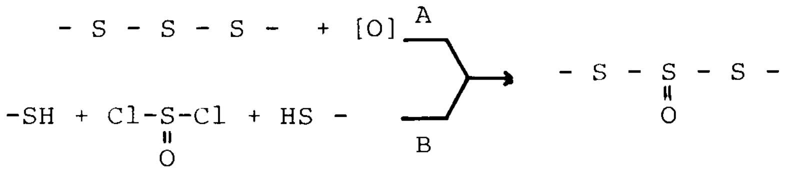
All lower sulfur oxides excepting SO contain one or more S-S bonds.

For reasons of space the following discussion will be restricted to the 7 homocyclic species S_nO (n=6...1o) and S_nO_2 (n=7 and 12). These compounds all contain the structural element



$$-S-\underset{\underset{O}{\|}}{S}-S-$$

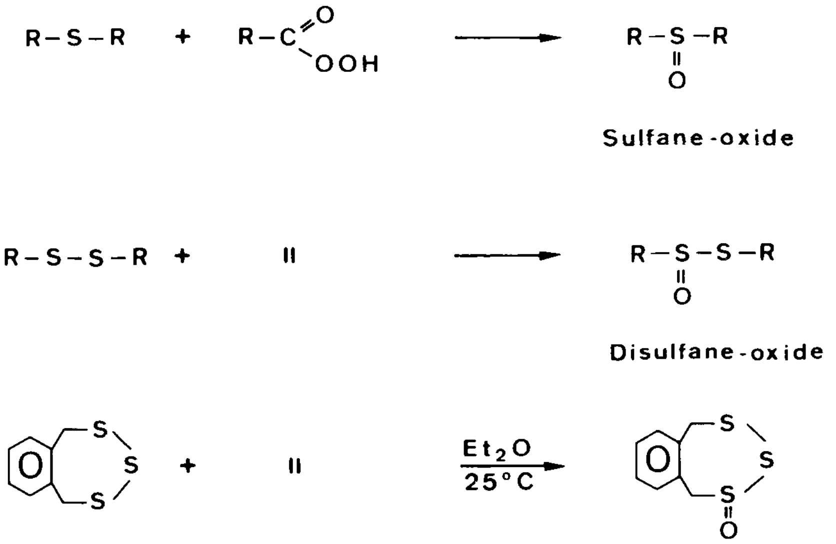
which can be synthesized by two principally different routes: route A starts from an existing homoatomic chain or ring of sulfur atoms which is oxidized by a suitable reagent, e.g. a peroxyacid, while according to route B a condensation reaction between thionylchloride and a thiol with elimination of hydrogen chloride provides the "oxidized sulfur chain":



Besides the lower S oxides mentioned the "oxidized sulfur chain" is also a constituent of certain organic sulfoxides which are formally derived from bis-organyl sulfanes, R_2S_n (n > 1), and which therefore have been termed sulfane oxides. These compounds will be dealt with in the following section.

ORGANIC SULFANE OXIDES

It has been known for some time that organic sulfanes (sulfides), R_2S, as well as disulfanes (disulfides), R_2S_2, can be oxidized by peroxyacids to give the corresponding sulfoxides which have also been termed as sulfane oxides since this nomenclature can easily be extended to sulfanes with more than two sulfur atoms in a row:



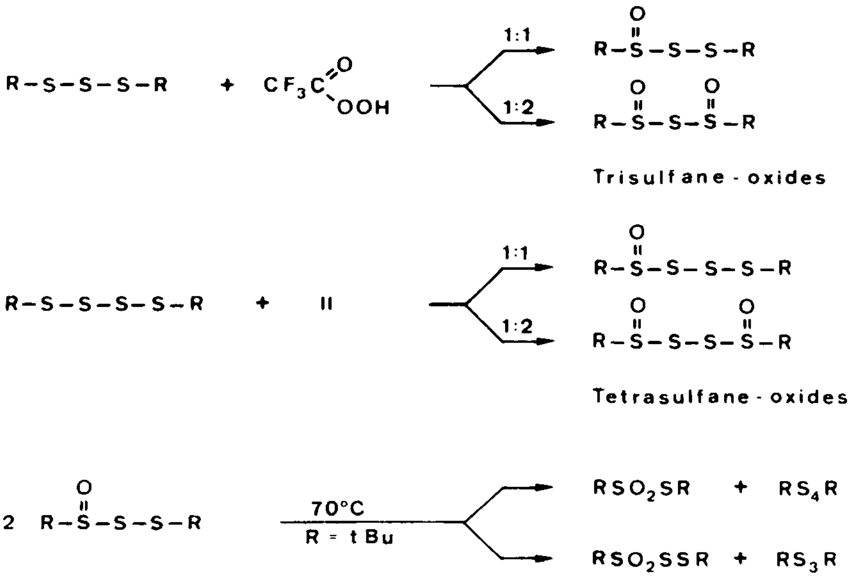
Sulfane-oxide

Disulfane-oxide

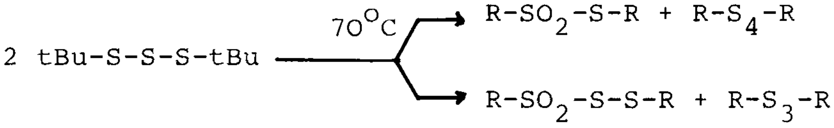
Trisulfane-1-oxide
m.p. 133°C

The first oxidation of a trisulfane by peroxyacid was reported in 1965 by Milligan and Swan [9] and it was shown that the α sulfur atom is the one which is oxidized in this reaction (sulfur atom nr. 1). The sulfoxide formed should therefore be termed as trisulfane-1-oxide. It is a yellow crystalline material.

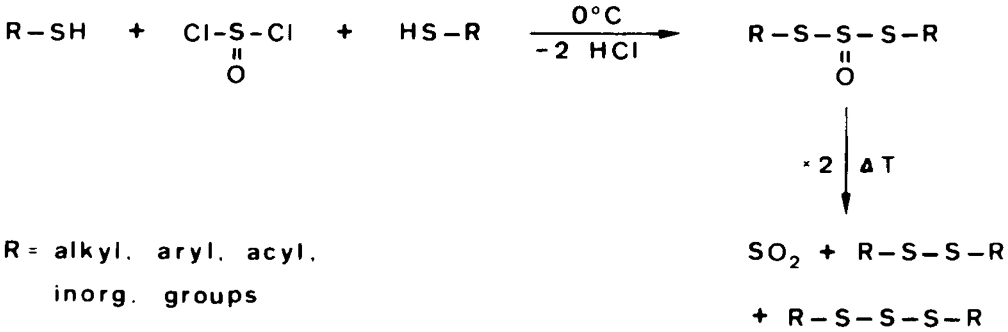
The oxidation of tri- and tetrasulfanes has been studied in some detail by the present author [10]. Using trifluoroperoxyacetic acid at -40°C and in different molar ratios several trisulfane monoxides and trisulfane-1,3-dioxides as well as a tetrasulfane monoxide and a tetrasulfane-1,4-dioxide have been prepared:



All compounds have been obtained as crystalline solids and have been characterized by infrared and mass spectra, elemental analysis and in some cases molecular weight determinations. These materials are unstable at 25°C and decompose to mixtures of sulfones, sulfoxides and sulfanes [10], e.g.:



From the above results it is obvious that only the terminal sulfur atoms can be oxidized by peroxyacids. Excess of peroxyacid yields sulfones rather than sulfoxides. To get an oxygen atom linked to the middle (or β) sulfur atom(s) of a tri- or tetrasulfane route B has to be followed. According to this route quite a number of trisulfane-2-oxides (dithiosulfites) have been prepared by various authors with R being an alkyl, aryl, acyl or inorganic group [11-17]:



The thermal stability of these compounds very much depends on the group R, and the products are always SO_2 and oxygen-free sulfanes rather than sulfones [11,12,15]. The question whether the oxygen atom is linked to one of the terminal sulfur atoms or to the (or one of the) central S atom(s) of a bis-organyl tri- or tetrasulfane can easily be answered on the basis of the infrared spectrum. The SO stretching vibration of acyclic sulfoxides X-SO-Y systematically depends on the electronegativity (x_E) of the substituents X and Y [18]. Three linear relationships $\nu_{SO} = a \cdot \Sigma x_E + b$ have been derived depending on the position of X and Y in the periodic table (see Fig. 1).

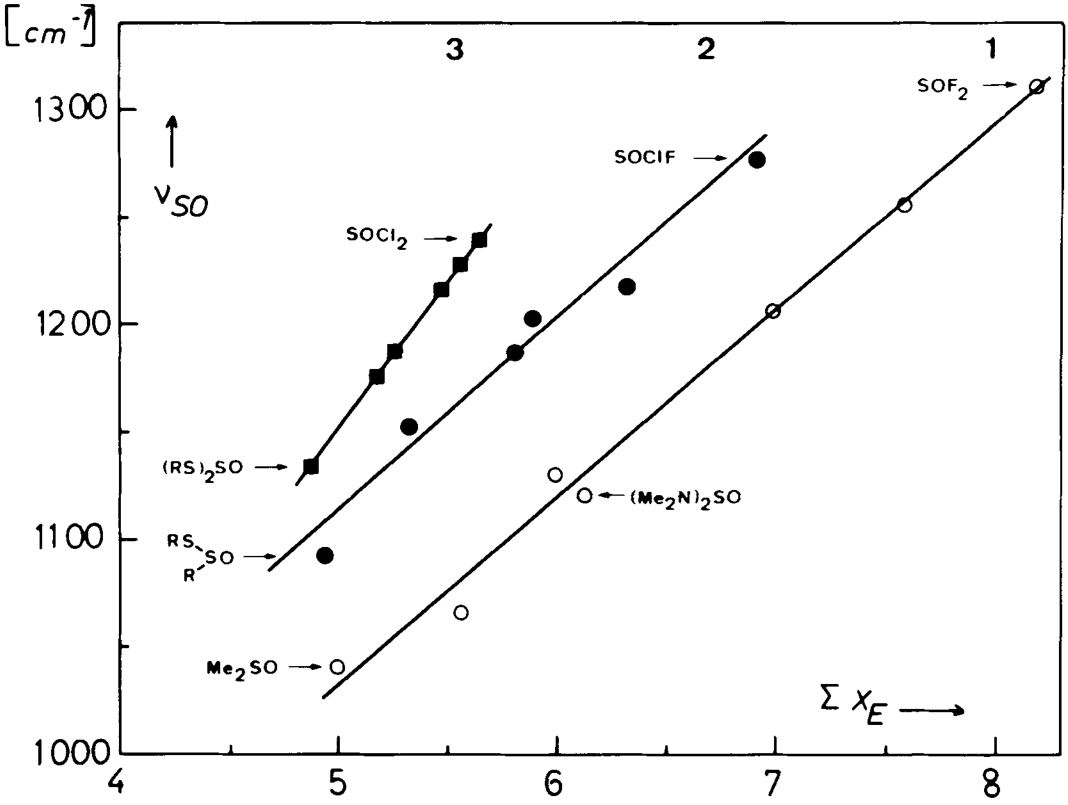
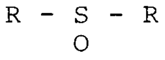
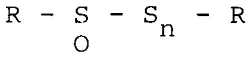
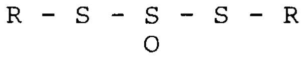


FIGURE 1 Dependence of the SO stretching wavenumber (ν_{SO}) on the sum of the electronegativities (x_E) of the substituents X and Y in sulfoxides X-SO-Y. Curve 1 holds for compounds with X and Y linked to the sulfoxide group via a first row element (F, O, N, C), curve 3 for second or third row elements (Cl, Br, S, Se, etc.) and curve 2 for cases with one first row and one second or third row element.

For X,Y = aryl or alkyl groups the electronegativity of carbon is used and the following wavenumbers have been observed for the three types of organic sulfoxides (ν_{SO} in CCl_4 or CS_2 solution); all values ± 10 cm^{-1})[9,18]:

	 $R-\underset{O}{S}-R$	 $R-\underset{O}{S}-S_n-R$	 $R-S-\underset{O}{S}-S-R$
ν_{SO}:	1060	1100	1130

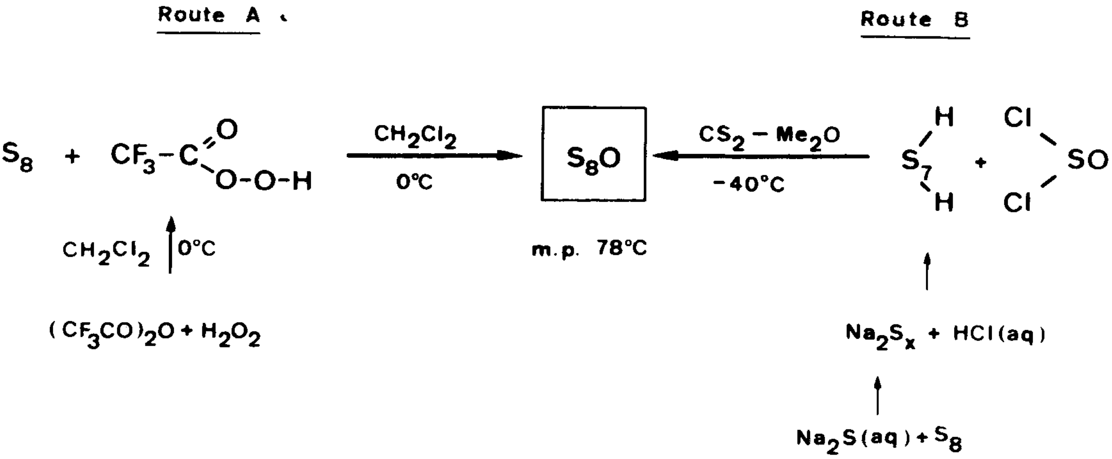
CYCLO OCTASULFUR OXIDE, S_8O

Those lower sulfur oxides which contain an oxidized sulfur ring can also be prepared by the two routes discussed above. The first compound of this type has been the cyclo-octasulfur monoxide, S_8O, which is a derivative of S_8 to which one exocyclic oxygen atom has been added:

S_8
(symmetry D_{4d})

S_8O
(symmetry C_s)

We have found that trifluoroperoxyacetic acid is the only peroxyacid which attacks elemental sulfur (S_8) at low temperatures. The reaction is carried out in CS_2 or CH_2Cl_2 solution at 0°C and S_8O can be isolated in 30% yield [19,20]:



The peroxyacid must be freshly prepared from concentrated H_2O_2 and trifluoroacetic acid anhydride.

According to route B the preparation of S_8O starts from sodium sulfide which is converted to polysulfide by reaction with sulfur in aqueous solution. The polysulfide solution is poured into ice-cold concentrated hydrochloric acid to give a sulfane mixture which inter alia contains heptasulfane, H_2S_7.This sulfane mixture reacts with thionyl chloride under the conditions of the dilution principle to give S_8O in gram quantities.[8,21].

S_8O forms yellow needle-like crystals slowly decomposing to SO_2 and sulfur at 25°C. The crystal structure is shown in Figure 2.

As can be seen from this figure the sulfoxide groups of neighboring molecules interact with each other to form an infinite planar zig-zag-chain. The dipole moment of the SO groups will certainly be responsible for this type of interaction[22,23].

The oxygen atoms are in axial rather than equatorial positions with respect to the S_8 ring. This ring exhibits

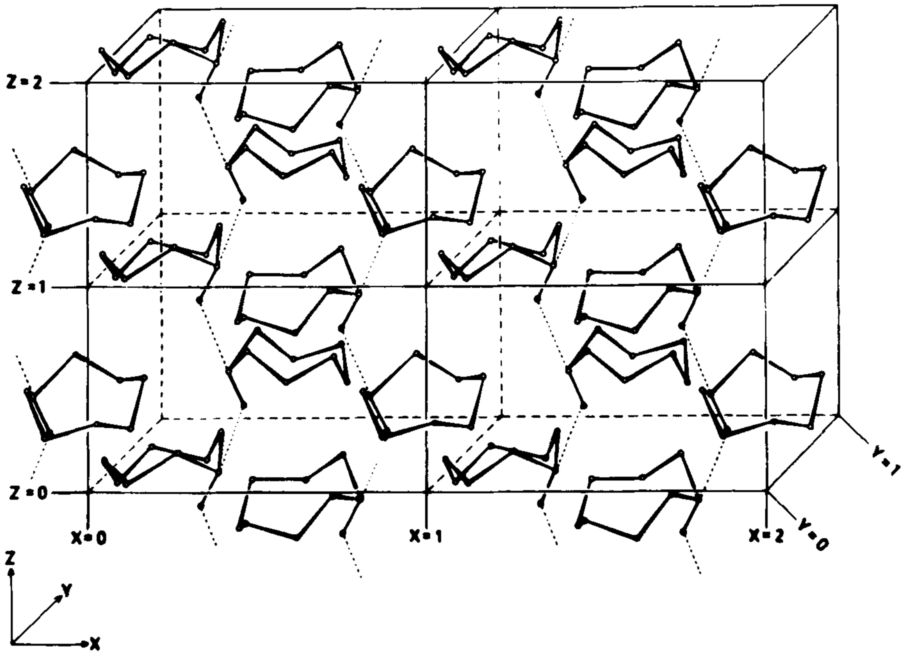
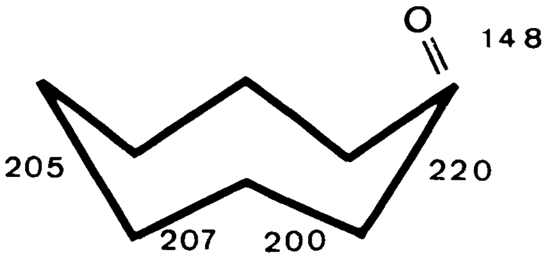


FIGURE 2 Crystal structure of cyclo-octasulfur monoxide, S_8O. The orthorhombic unit cell contains four molecules, the intermolecular interaction of the sulfoxide groups is indicated by dotted lines (SO....SO....).

the same crown conformation as in S_8 itself but as the following diagram shows the S-S bond distances (in pm) have changed dramatically:



ν_{SO} (cm^{-1})

1085 (solid)

1130 (CS_2)

ν_{SS} (cm^{-1})

300 - 520

The S-S bond lengths vary between 200 and 220 pm compared to the 205 pm observed for the S_8 molecule. The two S-S bonds neighboring to the sulfoxide group are the weakest (longest) and must be responsible for the thermal instability of the compound [8]. Going from right to left, the next two bonds are the strongest S-S bonds in the molecule, and then four bonds of almost normal length follow. This alternation of the bond lengths symmetrically to the mirror plane of the molecule is a characteristic feature of cumulated S-S bonds.

The vibrational spectra of S_8O clearly reflect its crystal and molecular structure. The SO stretching vibration shifts from 1130 cm^{-1} in CS_2 solution to 1085 cm^{-1} in the solid state due to the intermolecular SO...SO interaction. The SS stretching vibrations as observed in the Raman spectrum are distributed over the large region of 300-520 cm^{-1} due to the differing bond strengths of the four

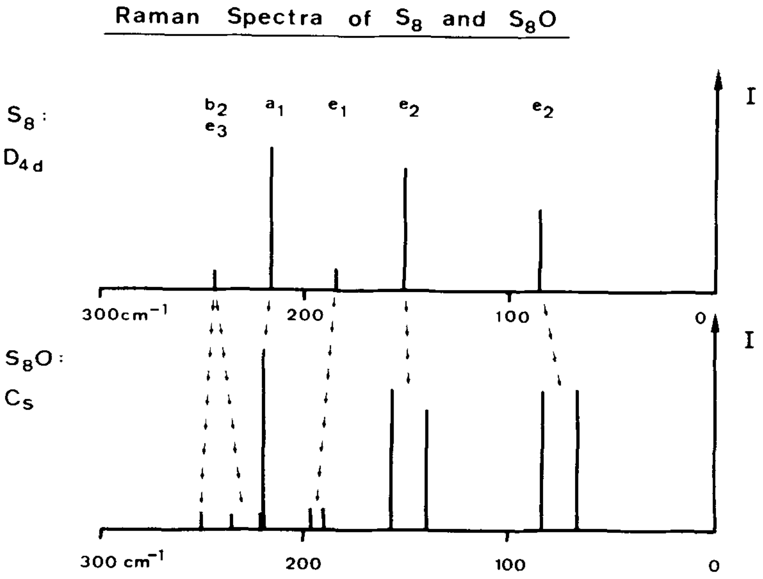
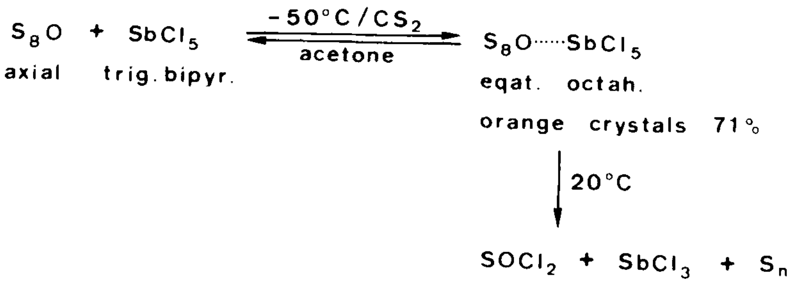


FIGURE 3 Correlation of the Raman spectra of S_8 (symmetry D_{4d}) and S_8O (C_s) in the ring bending region. Vibrations degenerate in S_8 split into their components in S_8O. The wavenumber of the totally symmetrical ring bending mode (a_1 in S_8, a'_2 in S_8O) is characteristic for the ring size [24].

pairs of equivalent bonds within the ring[24].
A comparison of the ring bending vibrations of the high-symmetry molecule S_8 (D_{4d}) with the low-symmetry species S_8O (C_s) is shown in Figure 3. This figure reveals the overall similarity of the two ring conformations. However, vibrations doubly degenerate in S_8 split into their components in S_8O. The most characteristic feature is the totally symmetrical ring bending mode which gives rise to the very strong Raman line at 218 cm^{-1} and whose wavenumber depends on the ring size. This wavenumber can therefore be used to determine the number of sulfur atoms in the ring in cases where no single crystals are available to carry out an X-ray structural analysis. The complete assignment of the infrared and Raman spectra of S_8O together with the calculation of force constants[25,26] provided the know-how necessary to understand the more complicated spectra of the other homocyclic sulfur oxides to be discussed below.

ADDUCTS OF S_8O WITH LEWIS ACIDS

Like other sulfoxides S_8O forms adducts with certain Lewis acids, for instance antimony pentachloride and tin tetrachloride. With $SbCl_5$ an interesting isomerization of the S_8O molecule takes place since the oxygen atom in the adduct is found in the equatorial position. The adduct is unstable at 20°C decomposing to $SOCl_2$, $SbCl_3$ and sulfur. Treatment with acetone results in the liberation of S_8O since the carbonyl oxygen is obviously a stronger donor than S_8O. The recovered S_8O is identical with the starting material containing the oxygen in the axial position[27]:



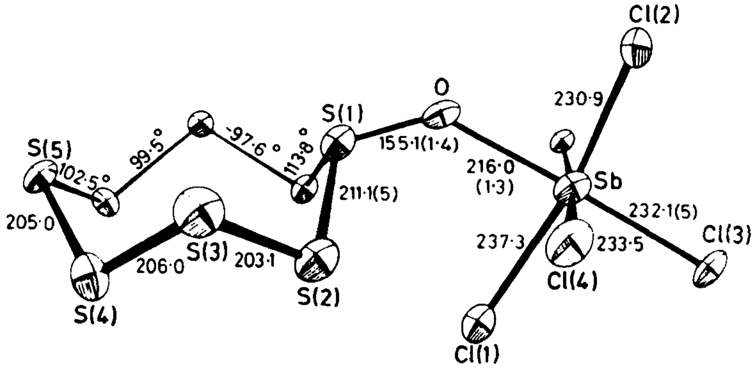


FIGURE 4 Molecular structure of the adduct $S_8O.SbCl_5$ (molecular symmetry C_s; given are the bond lengths in pm and the torsional angles of the sulfur ring). The oxygen atom is in an equatorial position with respect to the ring and links the S_8 unit to the nearly octahedrally coordinated antimony atom.

In Figure 4 the molecular structure of $S_8O.SbCl_5$ is shown; the coordination of the Sb atom is nearly octahedral [27]. The fact that the isomerization of S_8O takes place rapidly even at low temperatures indicates a low activation energy and thus excludes a pyramidal inversion at the three-coordinated sulfur atom. More likely is the stepwise ring inversion shown in Figure 5 which also transforms an axially bound exocyclic substituent into an equatorial position via a number of torsional motions [27]. This picture is of course an idealized description of the ring inversion since twisted conformations may also be involved. The torsional barrier to rotation about the S-S bonds in homocyclic S_n molecules is known to be quite low ($\lesssim$ 24 kJ/mol [28]) as will be discussed below.

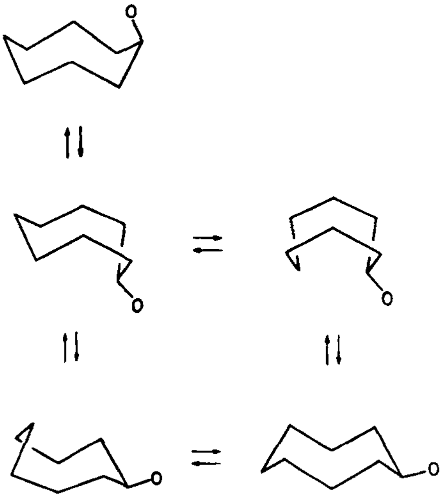


FIGURE 5 The most probable but idealized reaction pathway for the exchange of the oxygen atom of S_8O between the axial and equatorial positions by ring inversion.

Figure 6 shows the molecular structure of an adduct between S_8O and $SnCl_4$ containing the two sulfoxide ligands in cis positions to each other [3,29]. In this compound the oxygen atoms are in their usual axial positions with respect to the sulfur ring.

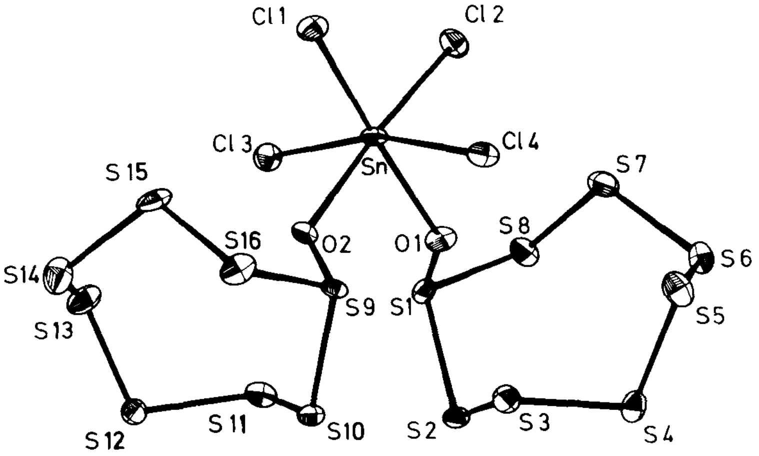


FIGURE 6 Molecular structure of the adduct $(S_8O)_2SnCl_4$. The S_8O ligands occupy cis positions at the tin atom.

OTHER HOMOCYCLIC SULFUR OXIDES

The eight-membered sulfur ring is the most stable one but many other ring sizes are known. Figure 7 shows the molecular structures of all those sulfur allotropes which so far have been investigated by X-ray crystallography. These results have been obtained in several laboratories; for recent reviews on elemental sulfur see [1,2,30]. The structures of sulfur rings S_n with $n \neq 8$ differ from the one of S_8 mainly by the varying bond distances which are a result of the differing torsional angles at these bonds. In S_8 all torsional angles are identical and therefore all bonds are equivalent leading to the high D_{4d} symmetry. The same holds for the S_6 (symmetry D_{3d}) and S_{12} molecules (symmetry also D_{3d}). All other rings show several differing torsional angles (τ) and τ values between 0° and 140° have been observed [28]. Figure 8 shows the relationship between the bond length d_{SS} and the

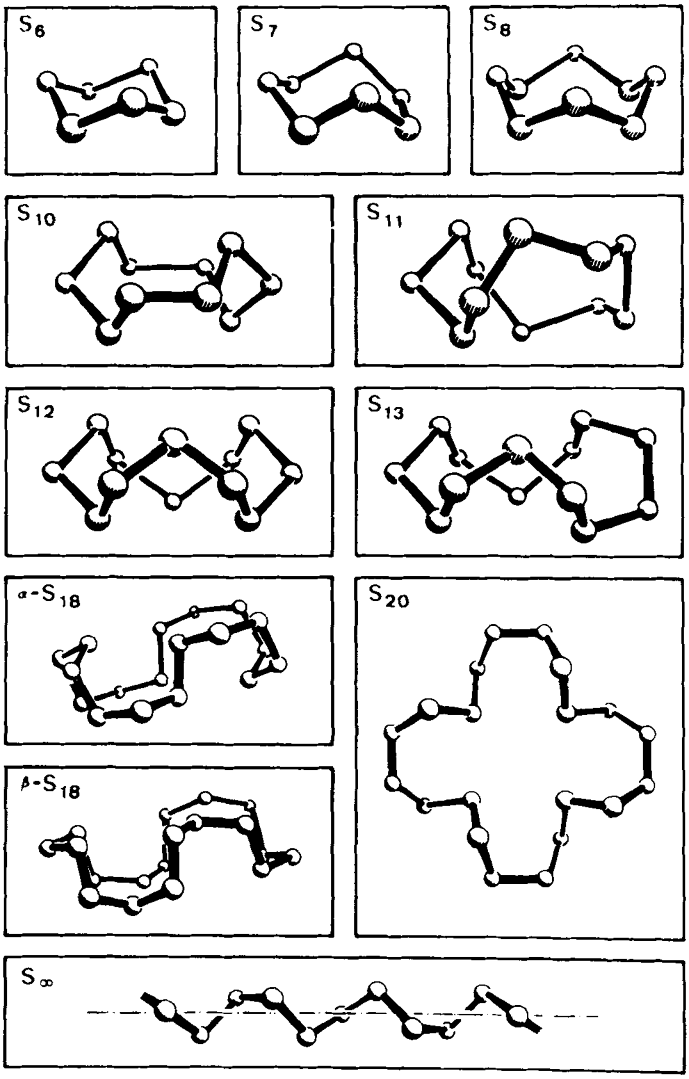


FIGURE 7 Molecular structures of the rings S_6, S_7, S_8, S_{10}, S_{11}, S_{12}, S_{13}, α-S_{18}, β-S_{18} and S_{20} as well as of polymeric sulfur S_∞ according to X-ray structural analyses.

torsional angle at this bond. The optimum value of τ resulting in the shortest S-S bond is obviously found near 90° (S_8, S_{12}) but neither the cis- nor the trans-barrier of the potential energy curve are very high. A cis-planar configuration has been observed for the S_7 molecule (one bond with $\tau = 0$) and from the heat of formation of S_7 from S_8 in the vapor phase the torsional barrier (cis-barrier) has been derived as $\lessapprox$ 24 kJ/mol[28].

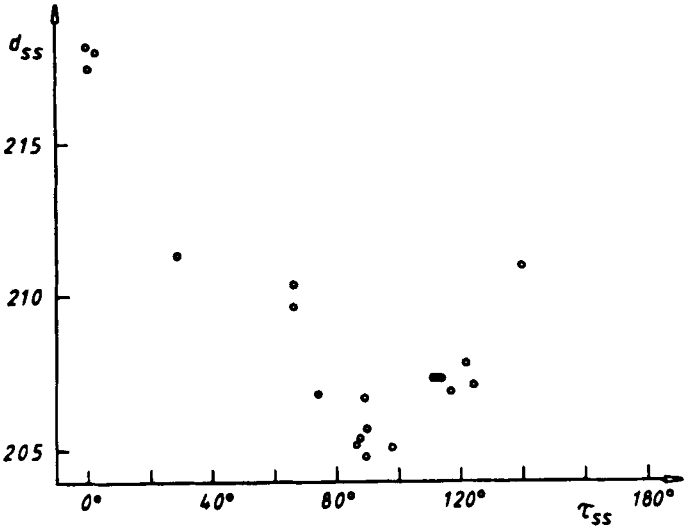
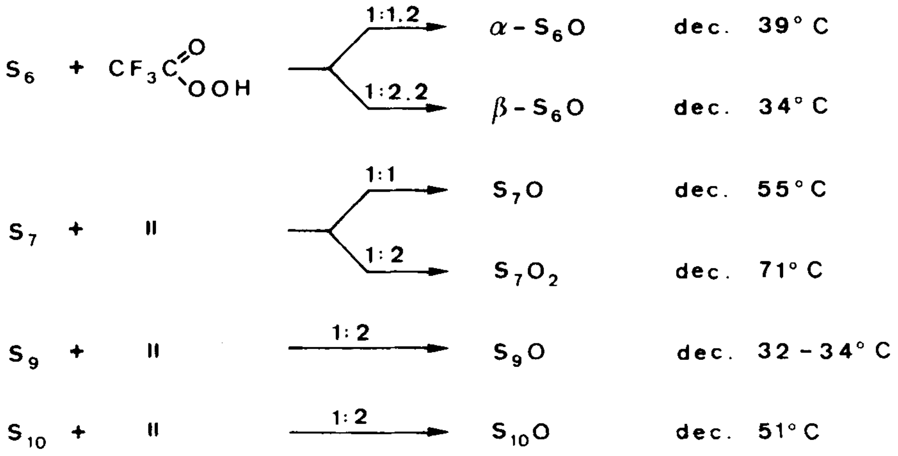


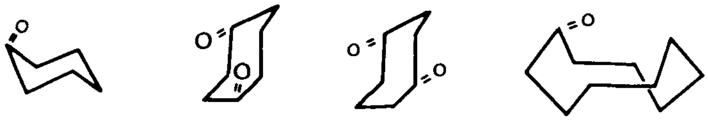
FIGURE 8 Dependence of the SS bond distance (d_{SS} in pm) in homocyclic S_n molecules on the torsional angle τ_{SSSS} of the corresponding bonds. Structures with values ranging from 0° to 140° have been observed.

Four of the sulfur rings shown in Figure 7 as well as S_9 have been used for the preparation of the corresponding homocyclic sulfur oxides resulting in the following new compounds:

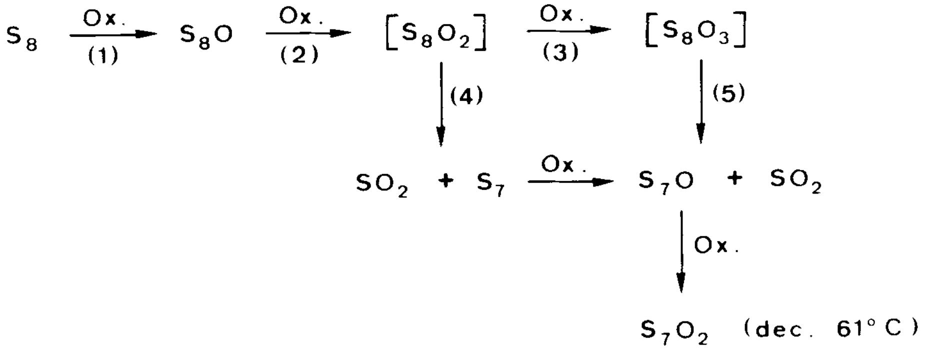


The oxidation reactions are carried out at low temperatures in methylene chloride solution. In the case of S_6 two oxides of identical composition have been obtained which may be either polymorphic modifications of one and the same compound or conformational isomers differing just in the axial or equatorial position of the oxygen atom [31]. All oxides shown form yellow or orange crystals which decompose at 25°C more or less rapidly (faster than S_8O). Spontaneous decomposition with liberation of SO_2 takes place at the temperatures indicated.

So far, S_7 is the only sulfur ring of which a monoxide[32] as well as a dioxide [33] have been prepared. The infrared spectra of both compounds show that they are sulfoxides; with other words the oxygen atom of S_7O is exocyclic [34] and the very unstable S_7O_2 is a disulfoxide rather than a sulfone. S_6O, S_9O and $S_{10}O$ according to their vibrational spectra are also sulfoxides derived from the corresponding rings [31,35]. The following molecular structures have been derived from the vibrational spectra (in the case of S_7O_2 two structures explain the spectra equally well):



The two most interesting homocyclic oxides of sulfur are S_7O and S_7O_2. The existence of the latter has prompted us to attempt the preparation of a dioxide of S_8 which should be more stable than S_7O_2 due to the higher stability of the eight-membered ring compared to the rather unstable S_7. However, the oxidation of S_8 dissolved in methylene chloride by excess of CF_3COOH did not give any di- or trioxide of S_8 but SO_2 and S_7O_2 were obtained instead [33]:



It is believed that an unstable octasulfur dioxide or even a trioxide are formed as intermediates which obviously eliminate SO_2 to yield S_7 or S_7O, respectively, which then are oxidized further to give S_7O_2. In fact, the Raman spectrum of the S_7O_2 prepared in this way always shows the presence of traces of S_7O. The above mechanism requires step (1) being fast, step (2) slow and steps (3), (4) and (5) very fast.

The exact molecular structure of S_7O_2 is not known yet but S_7O has been investigated by X-ray diffraction on single crystals [34].

Figure 9 shows the crystal structure. The molecules have the same ring conformation as S_7 [36,37] but the oxygen atoms lower the molecular symmetry to C_1. As has been observed for S_8O, the sulfoxide groups of S_7O interact to form chains SO···SO··· with S···O distances much smaller than the van der Waals distance.

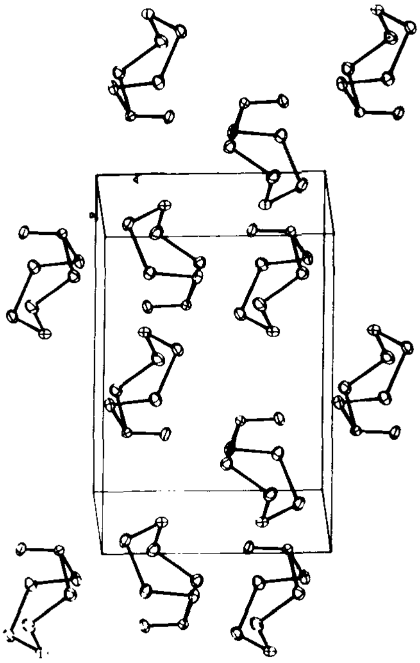


FIGURE 9 Crystal structure of cyclo-heptasulfur monoxide, S_7O. The monoclinic unit cell contains four molecules. The ring conformation is the same as in S_7 (see Fig. 7).

In Figure 10 the molecular structures of S_7O and S_7 (symmetry C_s) are compared. Due to the varying torsional angles the S_7 molecule exhibits S-S bonds ranging from 200 to 218 pm in length [36,37]. As can be seen from the Figure, the bond distances alternate symmetrically to the mirror plane.

In S_7O this alternation of bond lengths is enhanced by the effect of the oxygen atom which weakens the two neighboring bonds. As a result, the longest bond now becomes 227 pm long and its neighbor is only 196 pm long [34]. With other words, the bond order varies considerably. The observed bond lengths are to be compared with the single bond distance of 205 pm as in S_8 and the double bond distance of 189 pm as in the S_2 molecule whose electronic structure is analogous to that of O_2.

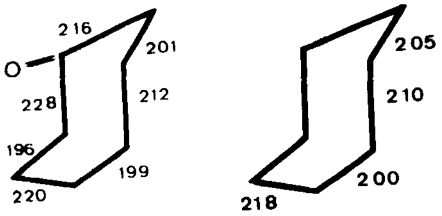


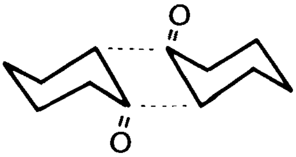
FIGURE 10 Sulfur-sulfur bond distances (in pm) in S_7O (left) and in S_7 (right). The alternating bond distance pattern can clearly be recognized.

From the Raman spectrum of S_7O_2 it has been concluded that the second sulfoxide group - provided the first one is in the same position as in S_7O - must be separated from the other one by two sulfur atoms. The most probable molecular structures are therefore those shown in the above diagram [3,33].

In all cases where single crystals of the homocyclic sulfur oxides could not be obtained, we have tried to prepare adducts with $SbCl_5$ or $SnCl_4$ hoping that these may be grown as well developed single crystals. In fact, all homocyclic sulfur oxides do form such adducts, but these not always crystallize very well. In the case of S_6O the reaction with $SbCl_5$ led to an unexpected new product the formation of which can be understood by a dimerization of S_6O yielding the species $S_{12}O_2$ linked to two $SbCl_5$ molecules[38] as shown in the following diagram:

$$2\ S_6O + 2\ SbCl_5 \xrightarrow[-78^\circ]{CS_2} S_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$$

orange crystals



The compound $S_{12}O_2(SbCl_5)_2$ forms unstable orange crystals which contain some CS_2 molecules in addition. The molecular structure of this adduct is shown in Figure 11[38]. The molecule is of C_i symmetry (a center of inversion as the only symmetry element) which supports the idea of a dipolar addition of two S_6O molecules as shown above. The S-S bond distances in the twelve-membered ring range from 199 to 219 pm and torsional angles of between 84° and 168° have been observed. The formation of $S_{12}O_2$ from S_6O is the first dimerization reaction of a sulfur ring yet observed.

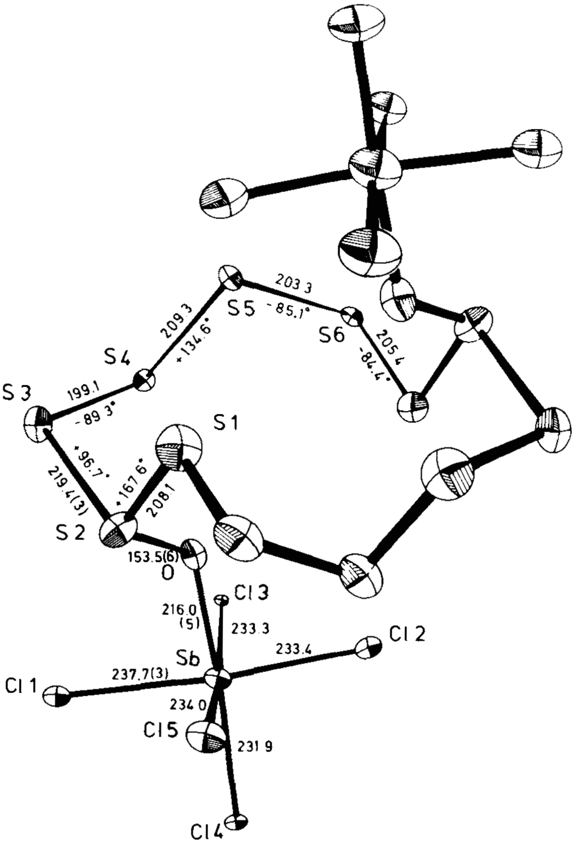


FIGURE 11 Molecular structure of the adduct $S_{12}O_2(SbCl_5)_2$ prepared from S_6O and $SbCl_5$ (molecular symmetry C_i; given are the bond distances in pm and the torsional angles of the ring).

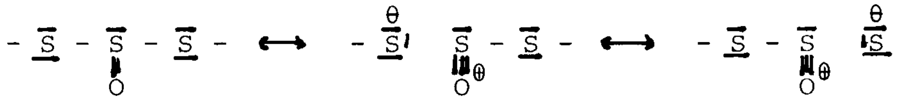
CORRELATION OF SULFUR-SULFUR BOND PROPERTIES

A covalent S-S bond can be characterized by its bond distance, the stretching force constant and wavenumber, the bond energy and the torsional angle. All these quantities are - as we have found - correlated to each other. In Figure 12 the correlation of the S-S bond length with both the stretching frequency (in cm^{-1}) and the stretching force constant is shown [1,3] (the two latter quantities are correlated to each other by the harmonic oscillator model).

These correlations can be used to estimate bond lengths from Raman spectra when crystal structure determinations are not possible due to the lacking single crystals, for instance in the case of S_6O, S_7O_2, S_9, S_9O and $S_{10}O$.

The data used in Figure 12 show already the extreme flexibility of covalent S-S bonds which can vary in length between 180 and 300 pm while force constants of between 1.5 and 6.2 N cm^{-1} have been calculated. Obviously, the S-S bond is not always a single bond as in S_8 and in organic polysulfanes, R_2S_n [1,6].

Another interesting and highly characteristic feature of S-S bonds is the unusually strong bond-bond interaction in systems with cumulated sulfur-sulfur bonds as in homoatomic chains and rings [6]. This phenomenon can best be explained using the molecular structure of S_8O. In this molecule the S-S bond lengths vary between 200 and 220 pm and they alternate symmetrically to the mirror plane of the molecule. Since the torsional angles τ_{SSSS} are all near 100^o as in S_8 itself the varying bond lengths can only be caused by the oxygen atom. We believe that one of the two lone pairs at oxygen - the one in the 2p orbital - is partly delocalized into the antibonding σ^* molecular orbital of the two neighboring SS bonds causing the length of these bonds to increase from 205 pm in S_8 to 220 pm in S_8O. The following resonance structures show this effect using valence bond theory models [23]:



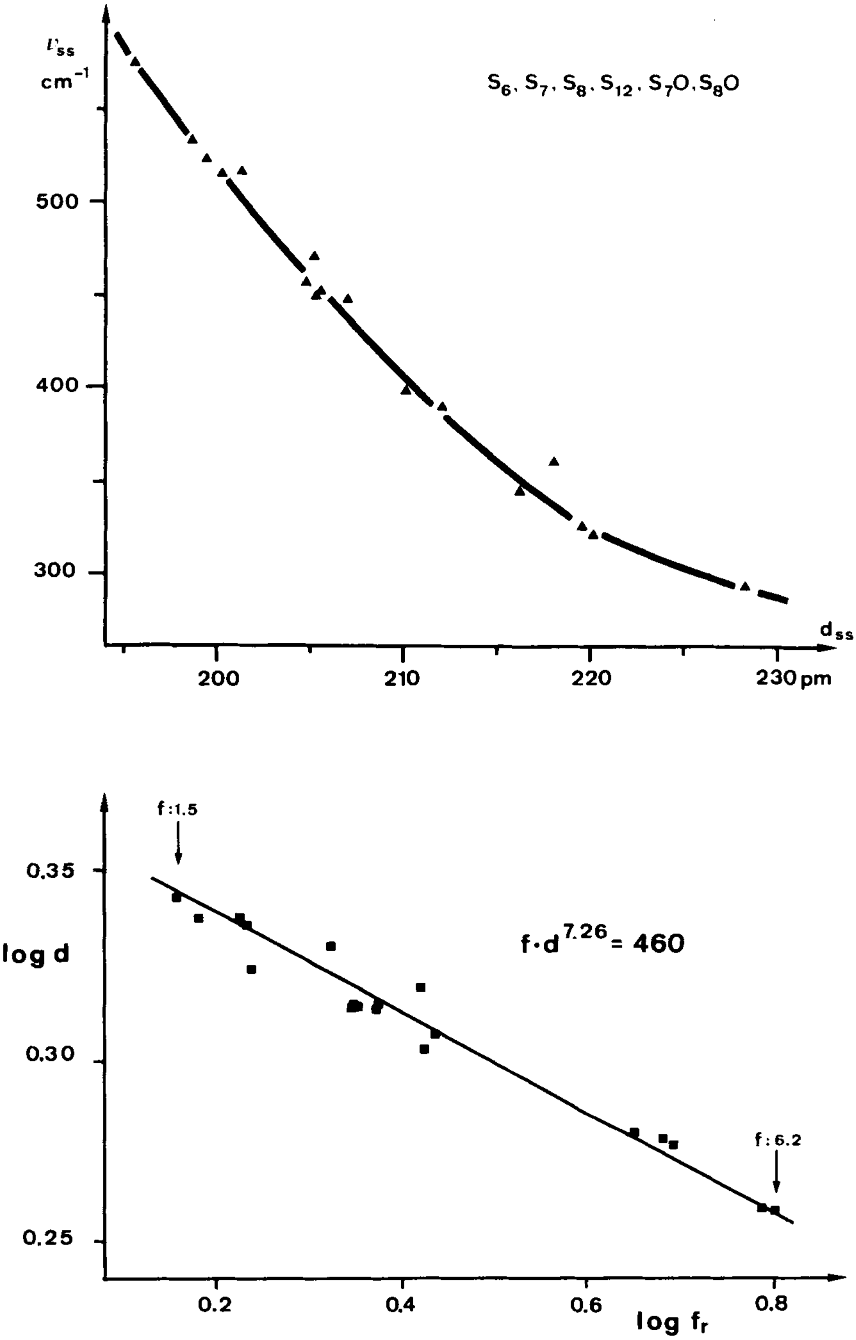
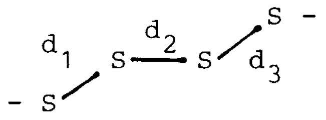


FIGURE 12 Correlation between the bond lengths d_{SS} of the bonds in S_6, S_7, S_8, S_{12}, S_7O and S_8O and the corresponding stretching wavenumber ν_{SS} (above), and between the logarithms of d_{SS} and the corresponding valence force constant f_r of cyclic and acyclic sulfur compounds (below). The diagrams demonstrate the wide range of values which the bond lengths, wavenumbers and force constants can have according to a considerable variation in bond orders.

The bond-bond interaction now results in a shrinking of the two S-S bonds next to the two long bonds and these short bonds in turn cause the next two bonds to increase somewhat in length. In this way the alternating bond distances are generated and this view is supported by an analysis of the corresponding molecular orbitals.

The correlation between the lengths of neighboring bonds can be seen from the mathematical relationship between d_2 and the arithmetic mean of d_1 and d_3 in the structural unit



This relationship is shown in Figure 13 which is based on the structural data of the cyclic species S_6, S_7, S_{10}, S_{12}, S_7O and S_8O [1,3,34]. The existence of this interaction shows that the electrons in cumulated sulfur-sulfur bonds must be regarded as considerably delocalized.

MOLECULAR STRUCTURES OF TRISULFANE-2-OXIDES

The molecular structures of S_8O and of the trisulfane-2-oxides discussed above obviously must be related to each other. We have therefore carried out an X-ray structural analysis of the compound $(ClC_6H_4S)_2SO$ [39]. In Figure 14 the crystal structure of this compound is shown. The most remarkable feature of the structure is the planar central backbone consisting of the five atoms C-S-S-S-C which are located in a plane. The sulfur-oxygen bond is approximately perpendicular to this plane. The torsional angles

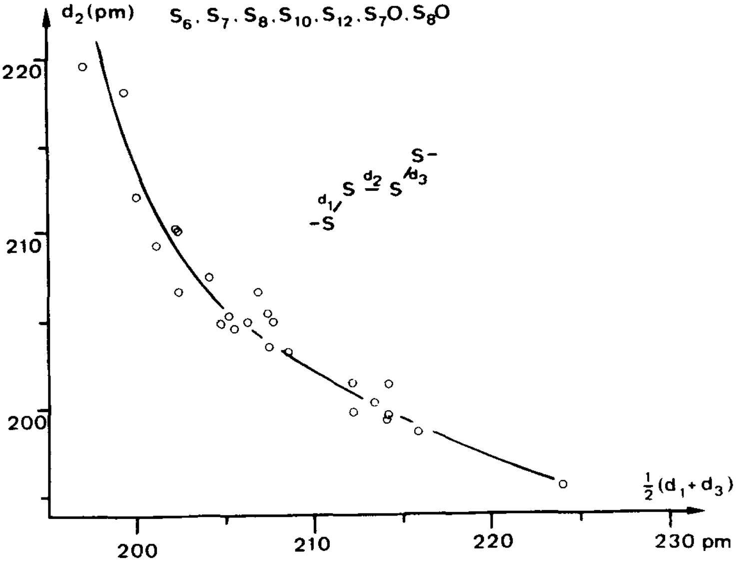
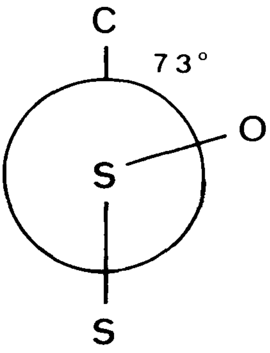


FIGURE 13 The strong bond-bond interaction in systems with cumulated sulfur-sulfur bonds is demonstrated by the unique correlation between the lengths of neighboring bonds originating from two-coordinated sulfur atoms. If d_2 is small then the arithmetic mean of d_1 and d_3 becomes large and vice versa. The data have been taken from the structures of the compounds indicated in the figure.

τ_{CSSS} amount to 177° and the two angles τ_{CSSO} amount to 73° leading to the following Newman projection:



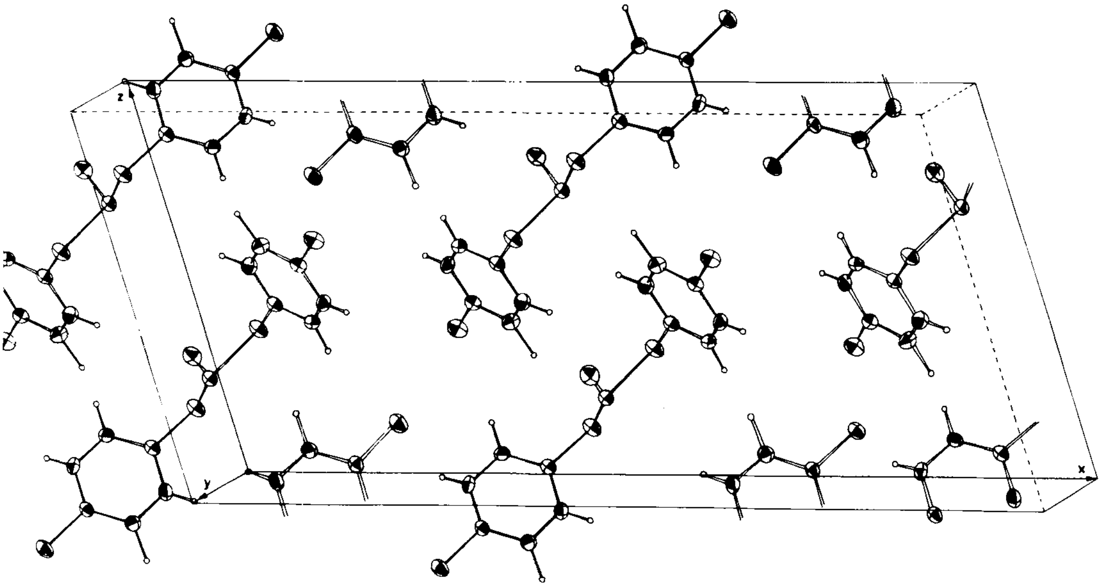


FIGURE 14 Crystal structure of the trisulfane-2-oxide $(ClC_6H_4S)_2SO$. The monoclinic unit cell contains four molecules the central part CSSSC of which is planar.

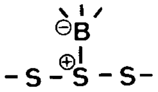
The bond distances in the central part of the molecule are: d_{SO} = 145, d_{SS} = 213 and d_{CS} = 178 pm, the molecular symmetry is C_s [39]. Very similar values have been observed for the analogous compound $(C_6H_5S)_2SO$ [40].

Only the S-S bond length is worth to be commented on. It is by 8 pm (or 4%) larger than the single bond value and this must again be caused by the oxygen atom. Therefore, all attempts to react compounds of this type in order to substitute the oxygen atom by some other group have failed so far since always the S-S bonds brake down [41]. The same holds for the homocyclic sulfur oxides. Consequently, very few reactions of the -S-SO-S- group have been studied so far. Besides the thermal decomposition yielding SO_2 and oxygen free sulfanes or sulfur [12,15] the reaction with chlorine and bromine may be mentioned which results in a stepwise fission of the two S-S- bonds leading finally to thionyl chloride [8,17].

CONCLUSION

Summarizing, it can be stated that homoatomic sulfur chains and rings can be oxidized by the (formal) addition of one or two oxygen atoms leading to branched structures which can be described by the two resonance structures <u>1a</u> and <u>1b</u> in the following diagram.

1a 1b



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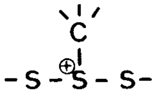

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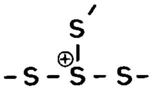

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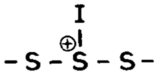

5

Other structural units of this type have been prepared with boron, carbon, sulfur and even iodine atoms linked to the homoatomic sulfur chain or ring, respectively. These units are present, for example, in the following compounds:

<u>2</u> in $[(CH_3)_2N]_2B(CH_3)B_2S_4Br_2$ [42]
<u>3</u> in $(CH_3S)_3SbCl_6$ [43]
<u>4</u> in $S_{19}(AsF_6)_2$ [44]
<u>5</u> in $(S_7I)(SbF_6)$ [45].

All these species have been prepared or properly characterized for the first time within the last 10 years and it therefore can be expected that more fascinating compounds of this type will be found in the near future.

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REFERENCES

[1] R. Steudel, Top. Curr. Chem. 1o2, 149 (1982).
[2] R. Steudel, in "Sulfur - Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology", edited by A. Müller and B. Krebs (Elsevier, Amsterdam, 1984), Chap. 1, pp. 1-37.
[3] R. Steudel, Comments Inorg. Chem. 1, 313 (1982).
[4] Gmelin Handbuch der Anorg. Chemie, Schwefel, Ergänzungsband 3, 8. Auflage, Springer, Berlin 1980.
[5] N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford 1984, pp. 854-863.
[6] R. Steudel, Angew. Chem. 87, 683 (1975), Angew. Chem. Int. Ed. Engl. 14, 655 (1975).
[7] P.W. Schenk and R. Steudel, Angew. Chem. 77, 437 (1965), Angew. Chem. Int. Ed. Engl. 4, 4o2 (1965).
[8] R. Steudel and M. Rebsch, Z. Anorg. Allg. Chem. 413, 252 (1975).

[9] B. Milligan and J.M. Swan, J. Chem. Soc. 29o1 (1965).

[1o] R. Steudel and J. Latte, Chem. Ber. 11o, 423 (1977).

[11] P.W. Schenk, R. Steudel and J. Bilal, Angew. Chem. 78, 717 (1966), Angew. Chem. Int. Ed. Engl. 5, 673 (1966).

[12] L. Field and W.B. Lacefield, J. Org. Chem. 31, 3555 (1966).

[13] S. Motoki and H. Satsumabayashi, J. Org. Chem. 38, 3654 (1973).

[14] E. Fluck, F. Ibanez and H. Binder, Z. Anorg. Allg. Chem. 397, 147 (1973).

[15] R. Steudel, P.W. Schenk and J. Bilal, Z. Anorg. Allg. Chem. 353, 250 (1967).

[16] K. Steinle and M. Schmidt, Z. Naturforsch. 27b, 83 (1972).

[17] R. Steudel and G. Scheller, Z. Naturforsch. 24b, 351 (1969).

[18] R. Steudel, Z. Naturforsch. 25b, 156 (1970).

[19] R. Steudel and J. Latte, Angew. Chem. 86, 648 (1974), Angew. Chem. Int. Ed. Engl. 13, 603 (1974).

[2o] R. Steudel and T. Sandow, Inorg. Syntheses 21, 172 (1982).

[21] R. Steudel and M. Rebsch, Angew. Chem. 84, 344 (1972), Angew. Chem. Int. Ed. Engl. 11, 302 (1972).

[22] R. Steudel, P. Luger, H. Bradaczek and M. Rebsch, Angew. Chem. 85, 452 (1973), Angew. Chem. Int. Ed. Engl. 12, 423 (1973).

[23] P. Luger, H. Bradaczek and R. Steudel, Chem. Ber. 109, 180 (1976).

[24] R. Steudel and M. Rebsch, J. Mol. Spectrosc. 51, 334 (1974).

[25] R. Steudel and D.F. Eggers, Spectrochim. Acta 31A, 871 (1975).

[26] R. Steudel, Spectrochim. Acta 31A, 1065 (1975).

[27] R. Steudel, T. Sandow and J. Steidel, J. Chem. Soc. Chem. Commun. 180 (1980).

[28] R. Steudel, Z. Naturforsch. 38b, 543 (1983).

[29] R. Steudel and J. Steidel, unpublished results.

[3o] R. Steudel, J. Steidel and R. Reinhardt, Z. Naturforsch. 38b, 1548 (1983).

[31] R.Steudel and J. Steidel, Angew. Chem. 9o, 134 (1978), Angew. Chem. Int. Ed. Engl. 17, 134 (1978).

[32] R. Steudel and T. Sandow, Angew. Chem. 88, 854 (1976), Angew. Chem. Int. Ed. Engl. 15, 772 (1976).

[33] R. Steudel and T. Sandow, Angew. Chem. 90, 644 (1978), Angew. Chem. Int. Ed. Engl. 17, 611 (1978).

[34] R. Steudel, T. Sandow and R. Reinhardt, Angew. Chem. 89, 757 (1977), Angew. Chem. Int. Ed. Engl. 16, 716 (1977).

[35] R. Steudel, J. Steidel and T. Sandow, Z. Naturforsch., in print.

[36] R. Steudel, J. Steidel, J. Pickardt, F. Schuster and R. Reinhardt, Z. Naturforsch. 35b, 1378 (1980).

[37] R. Steudel, R. Reinhardt and F. Schuster, Angew. Chem. 89, 756 (1977), Angew. Chem. Int. Ed. Engl. 16, 715 (1977).

[38] R. Steudel, J. Steidel and J. Pickardt, Angew. Chem. 92, 313 (1980), Angew. Chem. Int. Ed. Engl. 19, 325 (1980).

[39] R. Steudel, P. Luger and H. Bradaczek, Chem. Ber. 11o, 3553 (1977).

[4o] C. Th. Kiers and A. Vos, Rec. Trav. Chim. Pays-Bas 97, 166 (1978).

[41] R. Steudel, J. Latte and S. Paßlack-Stephan, unpublished results.

[42] H. Nöth and R. Staudigl, Chem. Ber. 115, 813 (1982).

[43] R. Weiss and C. Schlierf, Synthesis 323 (1976); G. Capozzi, V. Lucchini, G. Modena and F. Rivetti, J. Chem. Soc. Perkin Trans. II, 900 (1975).

[44] R.C. Burns, R.J. Gillespie and J.F. Sawyer, Inorg. Chem. 19, 1432 (1980).

[45] J. Passmore, G. Sutherland and P.S. White, J. Chem. Soc. Chem. Commun. 330 (1980); J. Passmore, P. Taylor, T. Whidden and P. White, J. Chem. Soc. Chem. Commun. 689 (1976).