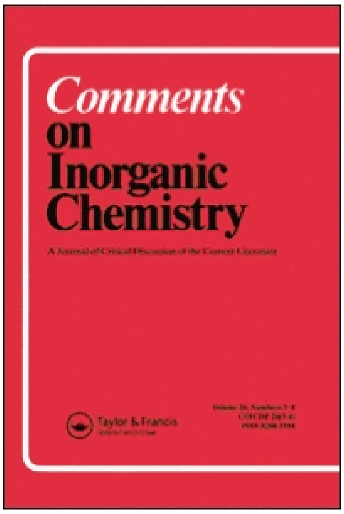

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Homocyclic Sulfur Oxides

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INTRODUCTION

Within the last decade the number of simple, nonpolymeric sulfur oxides has tripled, and sulfur is now the element with the largest number of oxides. Excluding polymeric compounds, five binary sulfur–oxygen compounds were known in 1970: the short-lived, diatomic sulfur monoxide (SO), the well known sulfur dioxide (SO_2), two molecular forms of sulfur trioxide (monomeric SO_3 and the heterocyclic S_3O_9), and the long disputed disulfur monoxide (S_2O). Several reviews covering the chemistry of these important compounds have been published.[1-4]

Since 1970 the preparation of a number of homocyclic sulfur oxides has been reported. These compounds are of types S_nO (n = 5–10) and S_nO_2 (n = 7, 12), respectively, and can formally be derived from the corresponding homocyclic sulfur molecules S_n by replacing one or two sulfur atoms by sulfoxide groups, $>S{=}O$. For example, the S_8 molecule can be oxidized to S_8O, the structure of which is closely related to the well known crown conformation of S_8:

S_8 (symmetry D_{4d})

S_8O (symmetry C_s)

Diagram 1

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Below we discuss the preparation, properties, structures, and spectra of these homocyclic sulfur oxides, the investigation of which has revealed surprising facts about the behavior of sulfur–sulfur bonds.

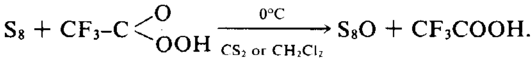
PREPARATION AND PROPERTIES

Monoxides

The first homocyclic sulfur oxide prepared as a pure substance was S_8O, which was first obtained in a laborious synthesis from thionyl chloride ($SOCl_2$) and a sulfane mixture (H_2S_n, $n = 3, 4, \ldots$) by condensation according to the equation

$$SOCl_2 + H_2S_7 \xrightarrow[Me_2O/CS_2]{-40^\circ C} S_8O + 2\ HCl.$$

The sulfane mixture used was so-called "crude sulfane" containing not only the chainlike heptasulfane (H_2S_7) but other members of the homologous sulfane series as well, resulting in a complex reaction mixture. Ring formation was enforced by the dilution principle and S_8O was isolated as the most stable species by CS_2 extraction and repeated recrystallization of the reaction product.[5] Later it was discovered that S_8O can be prepared much more conveniently from commercially available reagents by simple oxidation of S_8 with trifluoroperoxyacetic acid[6]:



$$S_8 + CF_3\text{-}C\begin{smallmatrix}\nearrow O\\ \searrow OOH\end{smallmatrix} \xrightarrow[CS_2\ \text{or}\ CH_2Cl_2]{0^\circ C} S_8O + CF_3COOH.$$

The peroxy acid is prepared immediately prior to use from concentrated aqueous H_2O_2 (80%) and trifluoroacetic anhydride in dichloromethane at 0°C:

$$H_2O_2 + (CF_3CO)_2O \rightarrow CF_3CO_3H + CF_3CO_2H.$$

S_8O is obtained as orange-yellow, needle-shaped crystals of mp 78°C which decompose at 20°C within a few hours to SO_2 and polymeric sulfur (S_μ); however, these can be stored for longer periods of time without decomposition at −20°C in a dry atmosphere. At the melting point all oxygen is given off as SO_2. Although S_8O is readily soluble in CS_2, it is much less so than S_8.[5]

Like other sulfoxides, S_8O reacts with Lewis acids yielding well crystallized adducts, e.g., $S_8O \cdot SbCl_5$[7] and $(S_8O)_2 \cdot SnCl_4$[8] in which the oxygen is linked to the metal atom, resulting in octahedral coordination; the structures of these compounds will be discussed below.

The advantage of the peroxy acid oxidation of sulfur is that it can be applied to different sulfur rings. This way the following compounds have been prepared:

S_6O mp 39° (α), 34°C (β); dark orange crystals[9];
S_7O mp 55°C; orange crystals[10];
S_9O mp 33°C; dark yellow[8];
$S_{10}O$ mp 51°C; orange-yellow.[8]

The thermal stability of these oxides is lower than that of the corresponding sulfur molecules. In the preparations special reaction conditions have to be applied since the reactivities and solubilities of the various sulfur allotropes S_n ($n = 6$–10) are quite different. The extremely low solubilities of S_{12}, S_{18} and S_{20} have so far prevented the preparation of pure oxide derivatives by direct oxidation. S_5O is the only oxide which obviously cannot be obtained by peroxy acid oxidation since S_5 is unknown. Diluted solutions of S_5O have been prepared according to the equation

$$3\, S_2O \rightarrow S_5O + SO_2$$

by bubbling a gaseous S_2O/SO_2 mixture (obtained by low pressure combustion of sulfur in pure oxygen) into $CHCl_3$ at −60°C and removing the dissolved SO_2 in a vacuum. The compound left in the yellow solution was analyzed and found to be S_5O (S:O ratio, molecular weight, IR spectrum), but all attempts to remove the solvent resulted in decomposition to sulfur and SO_2.[11]

Dioxides

Treatment of sulfur rings with excess peroxy acid should result in the formation of dioxides, trioxides, etc. However, since the thermal stability of disulfoxides decreases with decreasing distance between the SO groups,[12] increasing numbers of oxygen atoms will lead to very unstable compounds. Therefore, it is not surprising that so far only one dioxide has been prepared in a pure state. Oxidation of both S_7 or S_7O with excess CF_3CO_3H resulted in formation of S_7O_2 which surprisingly can also and more conveniently be obtained from S_8 (or S_8O):

$$S_7 + 2\ CF_3CO_3H \rightarrow S_7O_2 + 2\ CF_3CO_2H,$$

$$S_8 + 4\ CF_3CO_3H \rightarrow S_7O_2 + SO_2 + 4\ CF_3CO_2H.$$

The latter reaction presumably proceeds via S_8O, S_8O_2 and finally S_8O_3, which then spontaneously eliminates SO_2, yielding S_7O which may further be oxidized.[13] Alternatively, S_8O_2 could eliminate SO_2 resulting in ring contraction to S_7 followed by further oxidation to S_7O_2.

S_7O_2 forms dark-orange crystals which are less stable than S_7O and spontaneously decompose at 60–62°C with vigorous evolution of SO_2. Infrared spectra show that S_7O_2 is a disulfoxide rather than a sulfone.[13]

When S_6O dissolved in CS_2 is treated with $SbCl_5$ a compound of composition $S_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$ crystallizes out whose x-ray structural analysis showed the presence of a new dioxide, $S_{12}O_2$, linked to two $SbCl_5$ units via the exocyclic oxygen atoms. Since the $S_{12}O_2$ unit possesses a center of symmetry (Figure 1) it is assumed that it is formed from S_6O by dipolar addition:

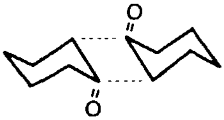


Diagram 2

This reaction would then be the first dimerization of a sulfur homocyclic molecule.[14]

STRUCTURES AND BONDING

The crystal and molecular structures of S_8O [15] and S_7O [16] have been investigated by x-ray structural analysis. In case of S_6O, $S_{10}O$ and S_7O_2 structural information is available from the vibrational spectra only, while the structures of S_5O and S_9O are still unknown. At first glance, the structure of S_8O (Figure 2) resembles that of S_8 with an additional oxygen atom in an axial position. The SO bond length (148 pm) equals that in sulfur monoxide and is slightly larger than the one in SO_2 (142 pm). However, the four nonequiv-

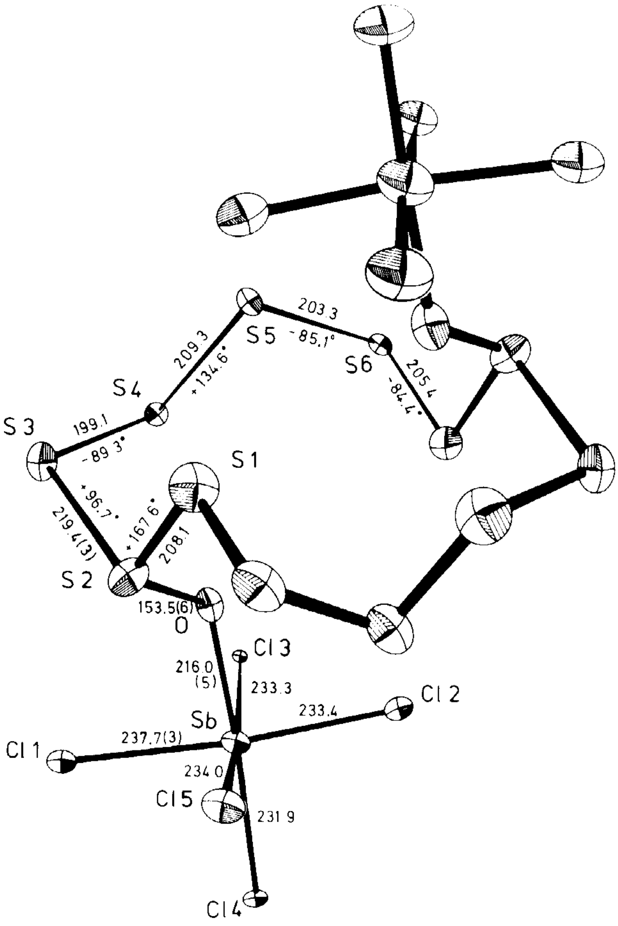


FIGURE 1 Molecular structure of the adduct $S_{12}O_2 \cdot 2SbCl_5$ prepared from S_6O and $SbCl_5$ (symmetry C_i; given are the bond distances in pm and the torsional angles).

alent SS bond distances are dramatically different from each other and partly larger and partly smaller than the 205 pm found in S_8, which under the point group symmetry D_{4d} has equivalent bonds only. As an explanation it is assumed that the oxygen lone pair in a p-type orbital is partly delocalized into antibonding σ orbitals of the two neighboring SS bonds, resulting in an increase of their length from 205 to 220 pm.[15] This in turn causes the two neighbor-

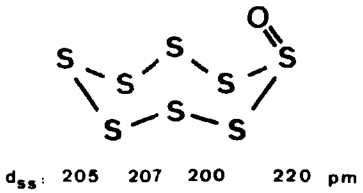


FIGURE 2 Molecular structure of S_8O (symmetry C_s; the bond distances of the four pairs of equivalent bonds are indicated).

ing bonds to decrease in length due to the strong bond–bond interaction effective in homoatomic sulfur rings and chains.[17] Consequently, only the two bonds furthest from the oxygen atom show normal bond distances.

Support for the above hypothesis comes from the structures of the adducts $S_8O \cdot SbCl_5$[7] and $(S_8O)_2 \cdot SnCl_4$.[8] In these compounds the electron density on oxygen is diminished due to the electron withdrawing effect of the Lewis acids $SbCl_5$ and $SnCl_4$, respectively. In Table I it is shown how the distances of the SS bonds neighboring the oxygen atom decrease on adduct formation while the SO bond length increases. This effect is more pronounced in the $SbCl_5$ adduct since in $(S_8O)_2 \cdot SnCl_4$ the Lewis acidity of $SnCl_4$ must be shared by two sulfoxide groups which are in cis positions (Figure 3).

The above discussion shows that the sulfur–sulfur bonds in S_8 and S_8O cannot be simple two-center bonds; extensive electron delocalization must be assumed. Therefore, any perturbation at a particular sulfur atom (e.g., by oxidation) influences the bonds in the whole ring system. This can even be better seen in the structure of S_7O (Figure 4). The chairlike S_7 molecule is of C_s symmetry and exhibits an alternating bond distance pattern as a result of the un-

TABLE I

Bond distances of S_8O and two of its adducts (M = metal; the SS bonds are those neighboring the sulfoxide group; values in pm)

	S_8O	$(S_8O)_2 \cdot SnCl_4$	$S_8O \cdot SbCl_5$
d(SO)	148.3	152.8	155.1
d(SS)	220.0	218.0	211.1
d(OM)	···	220	216
Ref.	15	8	7

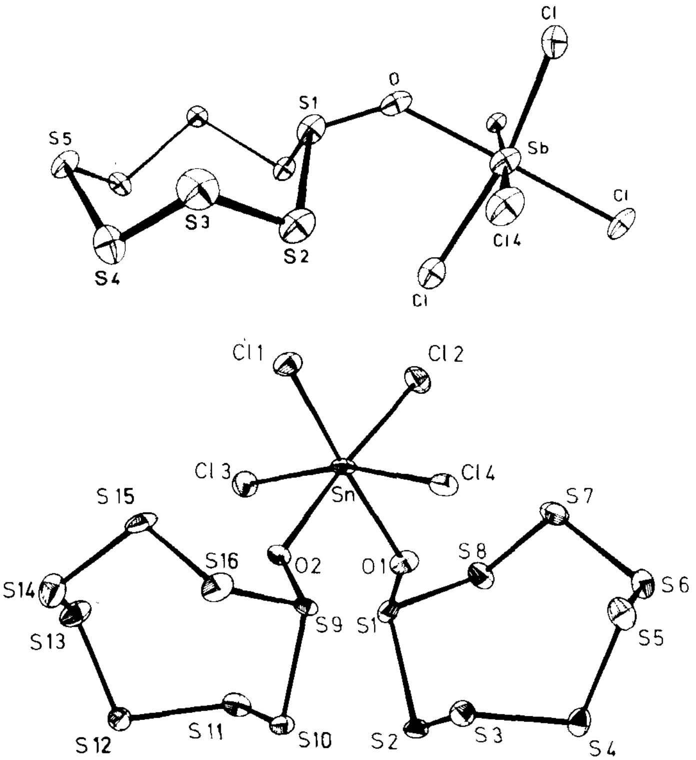


FIGURE 3 Molecular structures of $S_8O \cdot SbCl_5$ (top) and $(S_8O)_2 \cdot SnCl_4$ (bottom). While for the $SnCl_4$ adduct the oxygen atom occupies an axial position with regard to the sulfur ring, in the $SbCl_5$ adduct it has moved to the alternative equatorial position. On treatment of $S_8O \cdot SbCl_5$ with acetone, S_8O in its normal conformation with axially bonded oxygen can be recovered, indicating a reversible isomerization.[7]

favorable torsional angle of 0° at one bond (perpendicular to the molecular mirror plane), making this bond the longest in the molecule. Due to the bond-bond interaction, the two neighboring bonds decrease in length, the next-neighboring ones increase, and only the two bonds furthest from the perturbation are of normal distance.[18] In S_7O the effect of the oxygen atom on the neighboring SS bonds as observed in S_8O is now superimposed on the bond distance pattern of S_7 resulting in extremely different distances of neighboring bonds. Compared with S_7, the two bonds next to the oxygen atom are longer, the following two are shorter and so on.

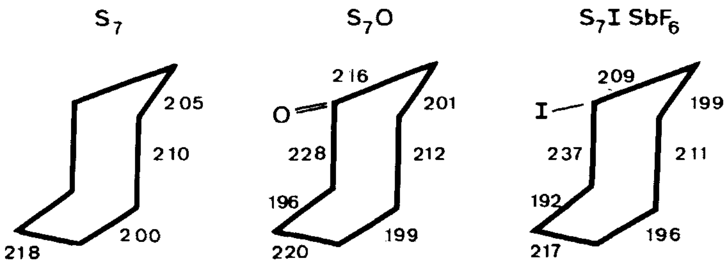


FIGURE 4 Bond distances in S_7, S_7O and S_7I^+ (values in pm; symmetry of S_7: C_s).

As can be seen from Figure 4 the oxygen atom occupies the one (out of four) position in which its impact on the SS bonds enforces the alternation of bond lengths existing already in S_7.

It is interesting to note that the S_7I^+ cation prepared and structurally characterized by Passmore *et al.*[19] exhibits a structure very similar to the isoelectronic S_7O (Figure 4).

The strong bond-bond interaction characteristic of systems of cumulated sulfur-sulfur bonds can best be seen from Figure 5. Let d_2 be the length of a bond between two-coordinated atoms in a homonuclear sulfur ring or chain and d_1 and d_3 the lengths of the neighboring SS bonds. Then a nonlinear relationship exists between d_2 and the arithmetic mean of d_1 and d_3. This relationship holds for S_6, S_7, S_8, S_{10}, S_{12}, S_7O, S_8O, $S_8O \cdot SbCl_5$, $(S_8O)_2 \cdot SnCl_4$, $S_{12}O_2 \cdot 2SbCl_5$, S_{18}, S_{20} and several polythionate anions but not for species with positive ionic charges (e.g., S_4^{2+}, S_8^{2+}, S_7I^+).[17]

Extrapolation of the curve in Figure 5 for values of d_2 larger than the van der Waals distance of two sulfur atoms (360 pm) shows that homolytic bond scission in, for example, S_8 must result in a diradical with terminal bonds of about 195 pm in length. Thus, part of the energy needed to dissociate one bond (d_2) is gained by the strengthening of the neighboring bonds (d_1, d_3), and therefore the dissociation energy of about 150 kJ mol^{-1} [17,20] is much lower than the mean bond energy of cumulated SS bonds of 265 kJ mol^{-1}.[17] Dissociation of the long bonds in S_7, S_7O and S_8O will require even less energy, making these compounds thermally unstable even at room temperature. The homolytic mechanism of this decomposition, however, has not yet been proven.

Increase of bonds d_1 and d_3 in a sulfur molecule to the van der

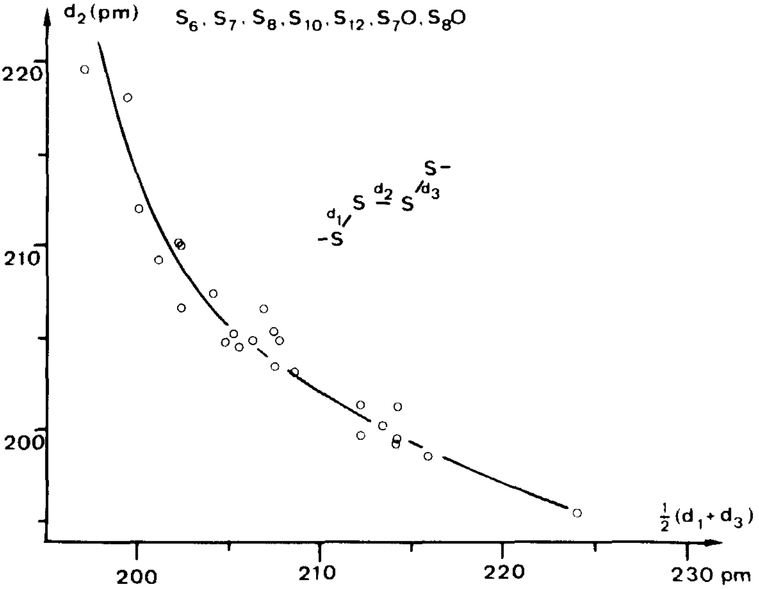


FIGURE 5 Relationship between the bond lengths of neighboring bonds in sulfur rings indicating strong bond–bond interaction. The distance d_2 of a certain bond between two-coordinated atoms is a function of the arithmetic mean of the distances of the two neighboring bonds, d_1 and d_3.

Waals distance generates the molecule S_2 where the bond length of 189 pm terminates the curve in Figure 5 on the right side.

VIBRATIONAL SPECTRA

Vibrational spectroscopy is the most powerful method to identify homocyclic sulfur oxides as well as their adducts and to check their purity. Infrared spectra provide information on the SO stretching and SSO bending frequencies mainly, while Raman spectra show the ring stretching, bending and torsional vibrations usually with high intensity. Due to the thermal and photochemical instability of most of the oxides the spectra must be recorded at low temperatures.

The wave number of the SO stretching mode of sulfoxides

X–SO–Y strongly depends on the substituents X and Y as well as on the state of aggregation.[21] Compounds with X,Y = S (e.g., sulfane oxides R–S–SO–S–R) show ν(SO) near 1130 cm^{-1} (in CS_2). All oxides of type S_nO also exhibit one strong IR band near 1130 cm^{-1} (in CS_2), which shifts to slightly lower wave numbers in $CHCl_3$ solution, due to hydrogen bonding. In the solid state the SO stretching mode usually gives rise to several neighboring and weak signals in the Raman spectrum due to vibrational coupling between different molecules of the unit cell.[8–10]

S_7O_2 in CS_2 solution exhibits two IR bands at 1127 and 1138 cm^{-1}, showing that it must be a disulfoxide rather than a sulfone and that there must be at least one sulfur atom between the SO groups since otherwise strong vibrational coupling would lead to a larger separation between the two SO stretching modes.[13] Comparable sulfones exhibit two strong bands (ν_{as} and ν_s of the group SO_2) in the IR separated by at least 200 cm^{-1} (e.g., SO_2Cl_2: 1182 and 1419 cm^{-1}).

The Raman spectra of homocyclic sulfur oxides provide information both on the bond distances as well as on the ring size. For example, the spectra of both S_8 and S_8O show a very strong line near 220 cm^{-1} which represents the totally symmetrical ring bending vibration (all angles SSS decrease or increase simultaneously and in phase; Figure 6) and whose wave number is a characteristic function of the ring size as the following examples show (in cm^{-1})[22–26]:

S_6: 266, S_7: 238, S_8: 219, S_9: 188, S_{10}: 178, S_{12}: 127.

Since the corresponding Raman line is usually the strongest in the region of the bending modes it can easily be identified. In this way it was possible to show that the oxidation products S_6O and $S_{10}O$ must contain rings of the same size as the starting materials S_6 and S_{10}, respectively.

Detailed analyses of the vibrational spectra of S_7,[23] S_7O,[8] S_8O [26,27] and other compounds have shown that there exists a relationship between the SS bond lengths and SS stretching wave numbers of cumulated sulfur–sulfur bonds (Figure 7).[17] This relationship enables one to estimate the region of bond distances from the vibrational spectra for those compounds whose exact structures are not known. This way the most probable conformations of S_6O,[9] S_7O_2 [13]

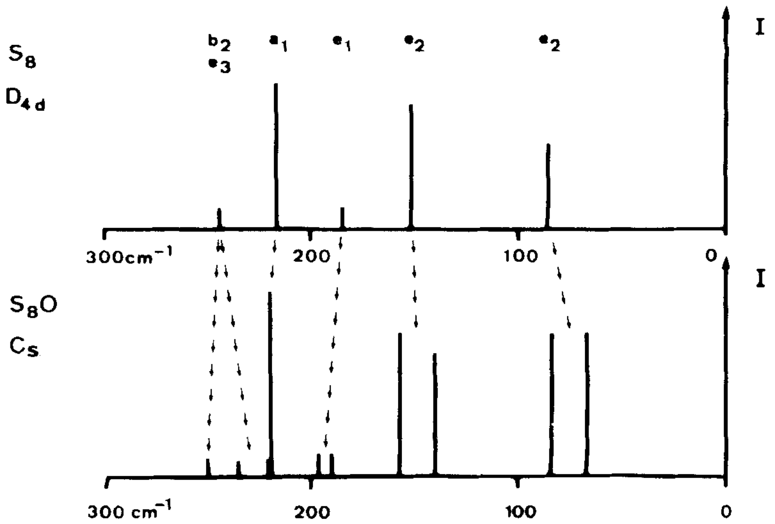


FIGURE 6 Schematic representation of the Raman spectra of S_8 and S_8O in the region of bending and torsional vibrations (only the fundamental vibrations are given). The relative Raman intensities are indicated by the heights of the bars. Vibrations degenerate in S_8 split into doublets in S_8O due to the lower symmetry. The totally symmetrical ring bending vibration (a_1 in S_8) occurs at a wave number characteristic for the particular ring size (see text).

and $S_{10}O$[8] were derived as follows:

Diagram 3

These suggestions need, of course, confirmation by x-ray diffraction analysis.

CONCLUSIONS AND OUTLOOK

The preparation of homocyclic sulfur oxides has shown that sulfur atoms that are part of homocyclic rings can take part in much stronger bonding arrangements than most chemists may have considered. The unique structures of these compounds have already greatly enlarged our knowledge of the behavior of sulfur–sulfur

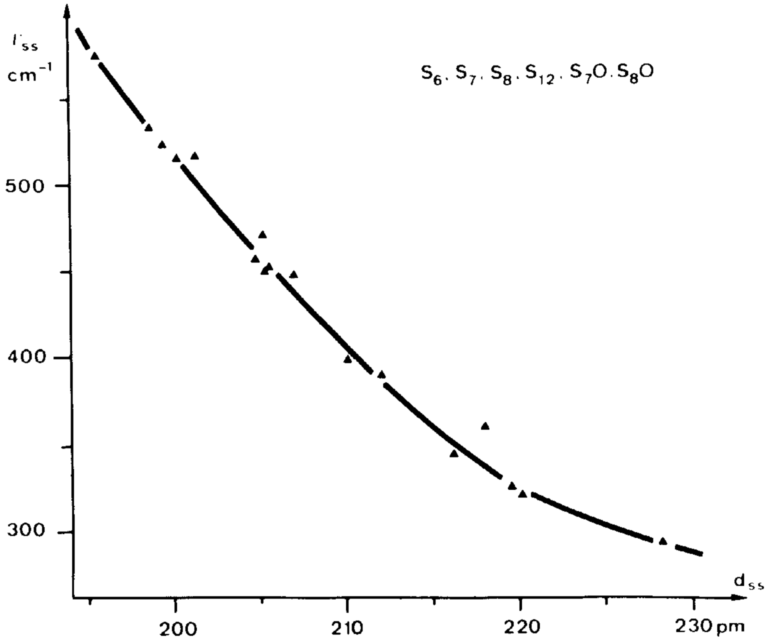


FIGURE 7 Relationship between the sulfur–sulfur stretching vibration ν(SS) of a certain bond in homocyclic sulfur rings and the corresponding bond length *d*(SS). For equivalent bonds within a molecule [equal *d*(SS) values] the ν(SS) values were averaged to eliminate the splitting by vibrational coupling. The data were taken from the compounds indicated in the figure.

bonds under various conditions. This homonuclear bond has turned out to be one of the most flexible structural units known[17]: its length can vary between 181 and 300 pm, bond angles SSS between 90 and 180° and torsional angles at SS bonds between 0° and 180°. Detailed molecular orbital treatments of S_7, S_7O and S_8O as examples for molecules with alternating bond distances may provide further insight into the bonding between heavier nonmetal atoms. Such calculations may also be able to explain, for example, the bond–bond interaction mechanism discussed above and the stability of the homocyclic S_7O versus an alternative heterocyclic eight-membered ring structure which would resemble the well known isoelectronic S_7NH:

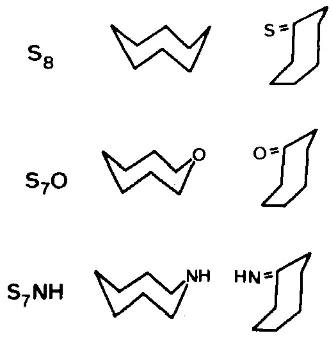
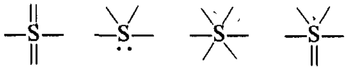
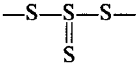


Diagram 4

The synthesis of "oxidized sulfur rings" raises the question whether other structural units like

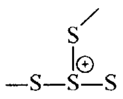


which are well known from sulfuranes and persulfuranes may be realized as part of a sulfur ring. Furthermore, substituents other than oxygen may be suitable for linkage to a sulfur ring, e.g., nitrogen (group =N–R) or carbon (=CR_2). However, it seems unlikely that the oxygen in homocyclic sulfur oxides can be replaced by sulfur, leading to structures isomeric with homocyclic rings (e.g., S_7S versus S_8; see the above diagram). Branched sulfur chains of type

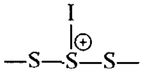


$$\text{—S—}\underset{\underset{\text{S}}{\|}}{\text{S}}\text{—S—}$$

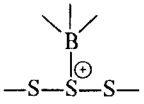
are known to be very unstable, if they exist at all,[28] but the following structures have already been synthesized:



e.g., S_8^{2+}, S_{19}^{2+}
Refs. 29,30



S_7I^+, $S_{14}I_3^{3+}$
Ref. 19



$[(CH_3)_2N]_2B(CH_3)B_2S_4Br_2$
Ref. 31

These examples show that there might be quite a number of new homocyclic sulfur compounds waiting for discovery.

But even the number of homocyclic sulfur oxides may increase after the preparation of $S_{12}O_2 \cdot 2SbCl_5$ has shown that rings larger than S_{10} can be obtained as oxides, too. On the other hand, with increasing numbers of sulfur and oxygen atoms the number of possible conformational and structural isomers increases rapidly, perhaps resulting in serious difficulties with the preparation, purification, and characterization of such substances.

Another field of interest is the so far almost unexplored reactivity of homocyclic sulfur oxides. A few observations like the decomposition of S_7O in solution yielding S_{10}[24] and the reversible isomerization of S_8O on reaction with $SbCl_5$[7] show that future investigations using the successful combination of low temperature synthetic procedures with Raman spectroscopy and x-ray crystallography will probably produce further interesting results in this fascinating area of main group chemistry.

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