

Barrier to Rotation about Sulfur-Sulfur Bonds in Homocyclic Sulfur Molecules [1]

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It is shown that the distances (d) of the 19 longest bonds in 9 homocyclic sulfur rings of type S_n ($n = 6-20$) depend on the torsional angles (τ) which vary between 0° and 140° . The function $d = f(\tau)$ is smallest for $\tau = 90-100^\circ$ and largest for $\tau = 0^\circ$; the corresponding bond distance variation amounts to 13 pm or 6%. The height of the torsional *cis*-barrier is estimated from the enthalpy of formation of gaseous S_7 as equal to or smaller than 24 kJ/mol.

The rotational barrier in H_2S_2 and its organic derivatives, R_2S_2 , is well established and has been studied by various experimental techniques as well as by molecular orbital calculations [2, 3]. Due to the lone pair – lone pair interaction of the two sulfur atoms a torsional angle (τ_{SS}) of approximately 90° is most favorable energetically while angles of both 0° and 180° correspond to energy maxima and, therefore, rotational barriers. Most authors agree that the *cis*-barrier ($\tau = 0^\circ$) is higher than the *trans*-barrier ($\tau = 180^\circ$) but there is no agreement on the barrier heights. MO calculations on H_2S_2 and $(CH_3)_2S_2$ have resulted in *cis*-barriers of between 3 and 192 kJ/mol and *trans*-barriers of between 6 and 61 kJ/mol [3]. For longer sulfur chains as in H_2S_n or R_2S_n ($n > 2$) no such calculations have been published.

The most reliable information about the actual barrier height comes from the NMR spectroscopic observation of the rotation about the SS bond in certain acyclic organic disulfides, $R-S-S-R'$. In the absence of steric effects the magnitude of the barrier was found to be 28 kJ/mol [4].

Deviations from the most favorable torsional angle of 90° result in weak SS bonds as can be seen from the dependence of both the bond distance [5] and the wavenumber of the SS stretching vibration [6] on τ_{SS} . Disulfides with τ_{SS} ranging from 0° to 180° are known, and the SS bond length varies accordingly between 200 and 211 pm [5, 7].

However, extensive studies on numerous compounds have shown that in addition to the torsional angle the inductive effect of certain substituents

as well as the overall conformation of the molecule influence the SS bond strength [4, 8]. In homocyclic sulfur molecules of type S_n no such problems are to be expected. So far 15 crystalline sulfur allotropes consisting of ring molecules have been studied by X-ray diffraction and torsional angles of between 0° and 140° have been observed (Table I). These data allow to correlate τ_{SS} with the corresponding bond distance, d_{SS} , as shown in Fig. 1. It can be seen that the most favorable τ values are those near 90° while both larger and smaller torsional angles result in longer and therefore weaker bonds.

In previous publications we have shown that a weak SS bond in a homoatomic chain or ring, caused

Table I. Smallest and largest torsional angles (τ_{SS}) and related bond distances (d_{SS}) in sulfur allotropes consisting of cyclic molecules.

Compound	τ_{SS} ($^\circ$)	d_{SS} (pm)	Ref.
δ - S_7	0.3	218.2	9a
γ - S_7	0.4	217.5	9a
δ - S_7	2.4	218.0	9a
S_{13}	29.5	211.3	9b
S_{20}	66.3	210.4	9c
β - S_{18}	66.5	209.7	9d
S_6	73.8	206.8	9e
S_{12}	86.0	205.2	9f
S_{12}	88.6	204.8	9f
S_{12}	89.4	205.7	9f
$S_{12} \cdot CS_2$	87.2	205.4	9f
S_8	98.5	205.1	9g
S_{13}	111.2	207.3	9b
S_{13}	113.1	207.3	9b
S_{13}	114.1	207.3	9b
S_{13}	116.3	206.9	9b
S_{10}	121.5	207.8	9h
S_{10}	123.7	207.1	9h
S_{11}	140	211.0	9i

by either torsional strain or the impact of substituents, results in a reinforcement of the two neighboring bonds whose bond distances therefore decrease resulting in the well known alternation of bond distances observed in many polysulfur compounds [2]. The length of a particular bond in a molecule S_n ($n \geq 6$) is therefore not only a function of the torsional angle but is influenced also by the strength of the neighboring bonds. To avoid difficulties from this effect only those bonds have been listed in Table I and are shown in Fig. 1 which exhibit the smallest or largest torsional angles in the particular ring and whose neighbors show normal torsional angles ($75\text{--}110^\circ$). These bonds will be either the longest or the shortest in the molecule.

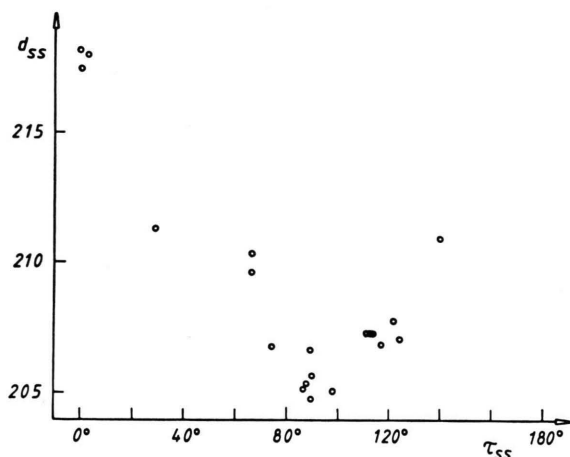
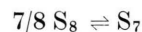


Fig. 1. Dependence of the sulfur-sulfur bond distance (d_{SS} in pm) in homocyclic sulfur molecules S_n on the torsional angle τ_{SS} .

The relationship between τ_{SS} and d_{SS} shown in Figure 1 is very similar to the corresponding relationship found for disulfides [5]. The three values with τ_{SS} near 0° were taken from the two allotropes of cyclo-heptasulfur (S_7) the molecules of which are of C_s symmetry and can be derived formally from S_8 by removal of one atom and connection of the chain ends by a particularly long bond. It is this bond which exhibits the unusual torsional angle of 0° , while the other six torsional angles are found in the region $75\text{--}109^\circ$. The average length of the six related bonds amounts to 205 pm, the value observed for S_8 and S_{12} with $\tau = 90\text{--}100^\circ$ (see Table I). The torsional strain of the S_7 molecule can therefore in a first approximation be regarded as re-

stricted to the unique bond, and under these circumstances the height of the torsional barrier can be estimated from the enthalpy of formation of the S_7 molecule from S_8 . In the vapor phase ΔH°_{300} of the reaction



amounts to 24 kJ/mol [10]. When six of the seven bonds of S_7 are on the average energetically almost equivalent to those of S_8 , then the observed ΔH° must be the enthalpy change for the transformation of one SS bond from $d_{SS} = 205$ pm and $\tau = 98^\circ$ in S_8 to 218 pm and $\tau = 0^\circ$ in S_7 . In other words, the height of the torsional *cis*-barrier in homocyclic S_n molecules must be equal to or lower than 24 kJ/mol. The actual barrier height might be even somewhat smaller since there is evidence for a certain amount of additional strain in the S_7 molecule as can be seen from the bond angles, two of which amount to 102° , while the most favorable value is in the region $105\text{--}108^\circ$ as in S_8 and S_{12} [2]. The actual barrier height therefore might be as low as 20 kJ/mol and the *trans*-barrier will be even lower. It follows that sulfur rings S_n ($n \geq 7$) cannot be regarded as rigid molecules at 25°C or higher temperatures but must be of considerable conformational flexibility both in solution and in the gaseous state. The torsional pseudorotation of S_7 in the vapor phase has already been deduced from its entropy [11]. The same low barrier can be assumed for compounds containing longer sulfur chains including polymeric sulfur which is an important equilibrium component of liquid sulfur especially at temperatures above 160°C .

The barrier height deduced above is lower than that observed for organic disulfides. This is a consequence of the bond-bond interaction effect: part of the energy needed to stretch the central bond in the structural unit --S--S--S-- from 205 pm (S_8) to 218 pm (S_7) is gained by the reinforcement of the two neighboring bonds which contract from 205 pm (S_8) to 200 pm (S_7). While in organic disulfides a torsional angle τ_{SS} of 0° results in a bond length d_{SS} of 211 pm [5, 7] (without any significant bond-bond interaction), it creates a considerably longer bond (218 pm) in S_7 . The larger bond distance results in a weaker lone pair-lone pair interaction with the consequence of a lower torsional barrier.

While the above discussion applies to S_7 and larger rings it should be noted that S_6 might be a much

more rigid molecule. Molecular models show that pseudorotation of S_6 also requires a considerable deformation of the bond angles and, therefore, the barrier height will be higher than in the case of S_7 .

According to a CNDO/2–MO calculation, the boat form of S_6 is less stable by 16 kJ/mol than the chair form with an interconversion barrier of 90 kJ/mol [12].

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