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 \( \text{S}_n \) (\( n = 6–20 \)) depend on the torsional angles (\( \tau \)) which vary between 0° and 140°. The function \( d = f(\tau) \) is smallest for \( \tau = 90–100° \) and largest for \( \tau = 0° \), 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 \( \text{S}_2 \) as equal to or smaller than 24 kJ/mol.

The rotational barrier in \( \text{H}_2\text{S}_2 \) and its organic derivatives, \( \text{R}_2\text{S}_2 \), 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 (\( \tau_{\text{SS}} \)) 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 (\( \tau = 0° \)) is higher than the trans-barrier (\( \tau = 180° \)) but there is no agreement on the barrier heights. MO calculations on \( \text{H}_2\text{S}_2 \) and \( \text{CH}_3\text{S}_2 \) 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 \( \text{H}_n\text{S}_n \) or \( \text{R}_n\text{S}_n \)\( (n > 2) \) 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, \( \text{R}–\text{S}–\text{S}–\text{R}’ \). 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 \( \tau_{\text{SS}} \). Disulfides with \( \tau_{\text{SS}} \) 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 \( \text{S}_n \) 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 \( \tau_{\text{SS}} \) with the corresponding bond distance, \( d_{\text{SS}} \), as shown in Fig. 1. It can be seen that the most favorable \( \tau \) 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 homatomic chain or ring, caused

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau_{\text{SS}} ) (°)</th>
<th>( d_{\text{SS}} ) (pm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta\text{-S}_7 )</td>
<td>0.3</td>
<td>218.2</td>
<td>9a</td>
</tr>
<tr>
<td>( \gamma\text{-S}_7 )</td>
<td>0.4</td>
<td>217.5</td>
<td>9a</td>
</tr>
<tr>
<td>( \delta\text{-S}_8 )</td>
<td>2.4</td>
<td>218.0</td>
<td>9a</td>
</tr>
<tr>
<td>( \text{S}_9 )</td>
<td>29.5</td>
<td>211.3</td>
<td>9b</td>
</tr>
<tr>
<td>( \text{S}_{10} )</td>
<td>66.3</td>
<td>210.4</td>
<td>9c</td>
</tr>
<tr>
<td>( \beta\text{-S}_{11} )</td>
<td>66.5</td>
<td>209.7</td>
<td>9d</td>
</tr>
<tr>
<td>( \text{S}_{12} )</td>
<td>73.8</td>
<td>206.8</td>
<td>9e</td>
</tr>
<tr>
<td>( \text{S}_{13} )</td>
<td>86.0</td>
<td>205.2</td>
<td>9f</td>
</tr>
<tr>
<td>( \text{S}_{14} )</td>
<td>88.6</td>
<td>204.8</td>
<td>9f</td>
</tr>
<tr>
<td>( \text{S}_{15} )</td>
<td>89.4</td>
<td>205.7</td>
<td>9f</td>
</tr>
<tr>
<td>( \text{S}_{12} \cdot \text{CS}_2 )</td>
<td>87.2</td>
<td>203.4</td>
<td>9f</td>
</tr>
<tr>
<td>( \text{S}_{16} )</td>
<td>98.5</td>
<td>202.1</td>
<td>9g</td>
</tr>
<tr>
<td>( \text{S}_{17} )</td>
<td>111.2</td>
<td>207.3</td>
<td>9b</td>
</tr>
<tr>
<td>( \text{S}_{18} )</td>
<td>113.1</td>
<td>207.3</td>
<td>9b</td>
</tr>
<tr>
<td>( \text{S}_{19} )</td>
<td>114.1</td>
<td>207.3</td>
<td>9b</td>
</tr>
<tr>
<td>( \text{S}_{20} )</td>
<td>116.3</td>
<td>206.9</td>
<td>9b</td>
</tr>
<tr>
<td>( \text{S}_{21} )</td>
<td>121.5</td>
<td>207.8</td>
<td>9h</td>
</tr>
<tr>
<td>( \text{S}_{22} )</td>
<td>123.7</td>
<td>207.1</td>
<td>9h</td>
</tr>
<tr>
<td>( \text{S}_{23} )</td>
<td>140</td>
<td>211.0</td>
<td>9i</td>
</tr>
</tbody>
</table>
by either torsional strain or the impact of substitu-
ents, results in a reinforcement of the two neigh-
boring bonds whose bond distances therefore de-
crease resulting in the well known alternation of
bond distances observed in many polysulfur com-
ounds [2]. The length of a particular bond in a
molecule \( S_n \) \((n > 6)\) is therefore not only a function
of the torsional angle but is influenced also by the
strength of the neighboring bonds. To avoid diffi-
culties 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 nor-
mal torsional angles (75-110°). These bonds will be
either the longest or the shortest in the molecule.

The relationship between \( \tau_{SS} \) and \( d_{SS} \) shown in
Figure I is very similar to the corresponding rela-
tionship found for disulfides [5]. The three values
with \( \tau_{SS} \) near 0° were taken from the two allotropes
ey 75-110°. These bonds will be
either the longest or the shortes 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 \( \tau_{SS} \).]

The torsional strain of the \( S_7 \) molecule can there-
fore in a first approximation be regarded as re-
stricted to the unique bond, and under these cir-
cumstances 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 \( \Delta H^{250} \) of
the reaction

\[
\frac{7}{8} S_8 \rightarrow S_7
\]

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 \( \Delta H^0 \)
must be the enthalpy change for the transformation
of one \( SS \) bond from \( d_{SS} = 205 \) pm and \( \tau = 98° \) in
\( S_8 \) to 218 pm and \( \tau = 0° \) 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 105-108° 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 \( S_n \) \((n > 7)\) 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 tor-
sional 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 con-
sequence of the bond-bond interaction effect: part
of the energy needed to stretch the central bond in
the structural unit -S-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 \( \tau_{SS} \) 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 lar-
ger rings it should be noted that \( S_n \) 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].