X-ray Structural Analyses of Two Allotropes of Cycloheptasulfur
(γ and δ-S7) [1]

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Z. Naturforsch. 35b, 1378-1383 (1980); received July 9, 1980

Elemental Sulfur, Sulfur Rings, Structure

X-ray structural analyses of two monoclinic allotropes of cycloheptasulfur carried out at —110 °C revealed almost identical chair-like molecular structures of approximate Cs symmetry with bond distances between 199.5 and 218.2 pm, bond angles between 101.5° and 107.5°, and torsional angles between 0° and 109°.

Introduction

Besides the well known S8, cycloheptasulfur is the most interesting allotrope of elemental sulfur. S7 was first prepared from titanocene pentasulfide and dichlorodisulfane and was obtained as intense yellow crystals of m.p. 39 °C which rapidly decompose at room temperature [2]. The EI mass spectrum of pure S7 exhibits the molecular ion with high intensity [3] and several authors observed the S7+ ion in saturated and unsaturated sulfur vapors of different origins [5–10]. A detailed analysis of extensive pressure measurements of saturated sulfur vapor showed S7 to be one of the major components of this complex mixture with S7 concentrations ranging from 12 mol-% at 200 °C to 26% at 400 °C [6, 11]. Later it was discovered by IR and Raman spectroscopy that liquid sulfur after equilibration, besides S8, contains the cyclic molecules S6, S7, and S12 [12] as well as larger rings [13], and pure S7 could be obtained from the quenched melt by CS2 and toluene extraction [14]. Recent investigations have further shown that S7 is one of those ubiquitous molecules produced in many reactions but discovered only recently by means of molecular spectroscopy. Such reactions are, for example, the irradiation of S6, S8, and S10 in CS2, CH2Cl2 or toluene solutions [15], the acid decomposition of aqueous sodium thiosulfate [16], and the thermal decomposition of sulfur diiodide at 25 °C [17].

Fig. 1. Molecular structure of cycloheptasulfur and numbering of atoms.

A first X-ray structural analysis of S7 was attempted by Kawada and Hellner [18] who derived a two-dimensional projection of the molecule from Weissenberg exposures but failed to obtain any molecular parameters [19].

Extensive IR and Raman spectroscopic studies on solid and dissolved S7 have shown that S7 crystallizes as four different allotropes (α, β, γ, δ-S7) whose thermodynamic stability relationships are unknown [21]. In a preliminary communication we reported the crystal and molecular structure of δ-S7 showing that the molecules form chair-like rings of approximately Cs symmetry with bond lengths ranging from 200 to 218 pm (Fig. 1) [20]. Similar values had been derived earlier from the vibrational spectra using a relationship between bond length and wavenumber of the stretching vibration of sulfur-sulfur bonds [22]. Nevertheless, the very much differing bond lengths found for S7, which are unique for a homocyclic molecule lacking substituents are in sharp contrast to the structures of S6 and S8 which both contain bonds of very similar lengths (S6: 206 pm [23], S8: 205 pm [24]). We, therefore, felt it necessary to confirm the molecular
structure of $S_7$ by investigating another of its allotropes ($\gamma$-$S_7$) by X-ray diffraction methods. The results are reported here together with the detailed information about the structural analysis of $\delta$-$S_7$.

Preparation of $S_7$ Allotropes

$\alpha$-$S_7$ is obtained on rapid cooling of solutions of $S_7$ in $\text{CS}_2$, $\text{CH}_2\text{Cl}_2$ or toluene almost saturated at 25 °C. This allotrope crystallizes as intense yellow, needlelike, lancet-shaped crystals of melting point 38.5 to 39 °C. These crystals are, however, disordered. They are also obtained on crystallization of molten $S_7$. However, under the same conditions sometimes $\gamma$-$S_7$ is obtained.

$\beta$-$S_7$ is formed as a powder on decomposition of crystals of $\delta$-$S_7$ either by careful mechanical impact (crushing with a glass rod) or simply by storage at 25 °C for 10 min. Sometimes $\beta$-$S_7$ crystallizes from solutions at $-78$ °C but is always obtained as a powder. $\gamma$-$S_7$ is usually obtained as needle-shaped disordered crystals of m.p. 38.5–39 °C by rapid cooling of $S_7$ solutions saturated at 25 °C to $-78$ °C. The well developed single crystals used in this work crystallized from an $S_7$ solution in dichloromethane containing small amounts of tetracyanoethylene at $-25$ °C during several days.

$\delta$-$S_7$ crystallizes from $\text{CS}_2$ solutions at $-78$ °C on slow evaporation and forms block-shaped, tetragonal-bipyramidal and sarcophag-like crystals.

Structure Determination

$\gamma$-$S_7$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with the lattice dimensions obtained from a least-squares refinement of 15 reflections.

Table I. Crystal data of $\gamma$ and $\delta$-$S_7$ at $-110$ °C (standard deviations in brackets).

<table>
<thead>
<tr>
<th>$\gamma$-$S_7$</th>
<th>$\delta$-$S_7$</th>
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<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>Lattice constants $a$ (pm)</td>
<td>968.0(3)</td>
</tr>
<tr>
<td></td>
<td>$b$ (pm)</td>
</tr>
<tr>
<td></td>
<td>$c$ (pm)</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
</tr>
<tr>
<td>Volume of unit cell (nm$^3$)</td>
<td>0.6805(3)</td>
</tr>
<tr>
<td>Molecules in unit cell</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (g · cm$^{-3}$)</td>
<td>2.190</td>
</tr>
<tr>
<td>Linear absorption coefficient (cm$^{-1}$)</td>
<td>20.9</td>
</tr>
<tr>
<td>(MoK$_x$ radiation)</td>
<td></td>
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<tr>
<td>Reflections measured</td>
<td>1387</td>
</tr>
<tr>
<td>Independent reflections (I &gt; 2$\sigma$)</td>
<td>1205</td>
</tr>
</tbody>
</table>

(4.3 < $\theta$ < 14.9°) measured at a temperature of $-110$ °C given in Table I.

Intensity data were collected on an automated four-circle diffractometer (Syntex P2$_1$) with graphite-monochromated MoK$_x$ radiation ($\lambda = 71.069$ pm) using an $\omega$-scan with a varying scan rate. Weaker reflections were therefore examined more slowly and counting errors minimized. Background counts with a time equal 2/3 the scan time for each reflections, were made at the end of the scan range. Two standard reflections were regularly checked to monitor the stability of the instrument, the crystal, and its alignment, and no significant variation was observed. A total of 1252 independent reflections in the $hkl$ and $hkl$ octants with $\theta < 25°$ were measured. 1205 reflections which had intensities greater than two times their standard error were considered observed and used in the refinement.

After Lorentz and polarization corrections (but without absorption correction) the data were normalized and the structure solved by direct methods. A full-matrix least-squares refinement of 63 positional and anisotropic thermal parameters for seven

<table>
<thead>
<tr>
<th>Bond lengths</th>
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<tbody>
<tr>
<td>S(1)–S(2)</td>
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<tr>
<td>S(1)–S(3)</td>
</tr>
<tr>
<td>S(2)–S(4)</td>
</tr>
<tr>
<td>S(3)–S(5)</td>
</tr>
<tr>
<td>S(4)–S(6)</td>
</tr>
<tr>
<td>S(5)–S(7)</td>
</tr>
<tr>
<td>S(6)–S(7)</td>
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</tbody>
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<thead>
<tr>
<th>Bond angles at atom</th>
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</thead>
<tbody>
<tr>
<td>S(1)</td>
</tr>
<tr>
<td>S(2)</td>
</tr>
<tr>
<td>S(3)</td>
</tr>
<tr>
<td>S(4)</td>
</tr>
<tr>
<td>S(5)</td>
</tr>
<tr>
<td>S(6)</td>
</tr>
<tr>
<td>S(7)</td>
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</tbody>
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<tr>
<th>Torsion angles at bond</th>
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<tbody>
<tr>
<td>S(1)–S(2)–S(3)</td>
</tr>
<tr>
<td>S(1)–S(3)</td>
</tr>
<tr>
<td>S(2)–S(4)</td>
</tr>
<tr>
<td>S(3)–S(5)</td>
</tr>
<tr>
<td>S(4)–S(6)</td>
</tr>
<tr>
<td>S(5)–S(7)</td>
</tr>
<tr>
<td>S(6)–S(7)</td>
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Table II. Molecular parameters of $\gamma$- and $\delta$-$S_7$ as well as CH$_3$S$_6$ (standard deviations in brackets). For numbering of atoms see Fig. 1.
The structure determination of $\delta$-S$_7$ has briefly been described earlier [20] (for further experimental details see ref. [25]). For comparison the crystal data are included in Table I and the complete molecular parameters as well as the atomic positions and temperature factors are given for the first time in Tables II and IV; the crystal structure is shown in Fig. 3.

The intermolecular distances $\leq 360$ pm of both $\gamma$- and $\delta$-S$_7$ are given in Table V.

![Fig. 3. Projection of the $\delta$-S$_7$ structure on the plane defined by axes a and b. The asymmetric unit is formed by molecules 1 and 2 while 1' and 2' are generated by glide reflection and 1" and 2" by screwing.](image)

![Fig. 2. Projektion der $\gamma$-S$_7$ Kristallstruktur auf die Ebene definiert durch die Achsen b und c. Der asymmetrische Einheit ist durch Molekül 1 gebildet, während 1' und 1" durch Gleitspiegelung und 2' und 2" durch Wendeschraubung erzeugt werden.](image)
The structural analyses were carried out using the programs MULTAN and XRAY 76.

### Results and Discussion

γ-S₇ like δ-S₇ consists of chair-like molecules of C₄ symmetry although the molecular symmetry is almost C₄. The same slightly twisted chair conformation has been found for the homocyclic derivatives S₂O [26], S₂I⁺ [27] and [S₂I₃]⁺ [28].

The molecular parameters of γ-S₇ show smaller standard deviations than those of δ-S₇ (Table II) presumably as a result of the smaller unit cell. Five of the seven equivalent bond lengths of both allotropes are identical within the single standard deviation; only the two largest bond lengths S(2)-S(3) and S(6)-S(7) differ by as much as 0.6 pm (twice the standard deviation). Equivalent bond angles and torsional angles differ by less than 3.3° in both allotropes. These results clearly show that the unusual molecular structure of S₇ is not a result of intermolecular forces. This view is supported by the intermolecular nuclear separations (Table V) which are of the same order as found for other sulfur allotropes [29]. The exceptional high solubility of S₇ in organic solvents, which by far exceeds those of S₆ and S₈, as well as the low melting point (39°C) and the relatively high vapor pressure (5·10⁻⁶ bar at 25°C [30]) also indicate weak intermolecular interactions despite effective packing in the molecular lattice which can be seen from the high densities (Table I).

The repulsion of lone pairs in p-type orbitals at atoms S(6) and S(7) is the main reason for the differing bond distances within the S₇ ring as has already been discussed elsewhere [21]. As a consequence of their destabilization these lone pairs are partly delocalized into antibonding π molecular orbitals at bonds S(2)-S(4) and S(3)-S(5) thus increasing the length of these bonds and decreasing the lengths of bonds S(4)-S(6) and S(5)-S(7) due to π bonding. It is interesting to compare the structures of γ- and δ-S₇ with the recently published molecular structure of hexathiane (CH₃S₆) [31]. This molecule can be derived formally from S₇ by substituting atom S(1) by a methylene group. It exhibits C₃ symmetry (twist-chair conformation) with "normal" SS bond lengths ranging from 202 to 208 pm (see Table II). The main differences between S₇ and CH₃S₆ are the differing torsional angles at bonds S(6)-S(7) which amount to 1±2° in γ- and δ-S₇ compared with 71° in CH₃S₆. The latter value results in torsional angles of 40-47° at the two carbon-sulfur bonds which is perfectly acceptable since carbon lacks lone pairs. For S₇, however, two torsional angles near 45° are obviously less favorable than just one torsional angle of 0° which allows all other torsional angles to assume normal values near 90° as has been observed for S₆, S₈ and S₁₂ [32]. It nevertheless can be expected that the C₄ conformation of S₇ will be only slightly less stable than the C₃ conformation and that pseudorotation will occur at moderate temperatures in mobile phases as has in fact been concluded from the entropy of gaseous S₇ [21]. The crystal structures of γ- and δ-S₇, however, do not show any indication of pseudorotation (no unusual U₁₁ values) but the disorder of some S₇ phases may be related to this phenomenon.

Force field calculations of the molecular geometry of S₇ resulted in a very small energy difference (1.3 kJ/mol) between the C₄ and C₃ structures but, on the other hand, completely failed to predict the experimental bond distance pattern for the C₄ geometry [33]. This may be the reason why the C₃ conformation was found to be more stable and why the enthalpy of formation of gaseous S₇ derived from these calculations (131 kJ/mol) does not agree with the best experimental values (109-114 kJ/mol [6, 11]) although the authors believed that their "calculated values are probably more reliable than the experimental ones" [33]. The corresponding force field calculations for other sulfur molecules should, therefore, be taken with caution.

The structure of S₇ indicates that the torsional barrier of longer sulfur chains and of homocyclic
sulfur molecules may be much lower than for \( \text{H}_2\text{S}_2 \) and \((\text{CH}_3)\text{S}_2\) [32] since as the torsional angle approaches \(0^\circ\) or \(180^\circ\) the increase in energy due to lone pair repulsion is partly compensated by the energy gain from additional \(\pi\) bonds to neighboring atoms. For the same reason the mean bond energy in \(\text{S}_7\) is only slightly smaller than in \(\text{S}_8\) and almost identical to the one of \(\text{S}_8\) [34] although the bond distances are dramatically different.

The different packing patterns of \(\gamma\)- and \(\delta\)-\(\text{S}_7\) can best be illustrated by the different orientations of neighboring molecules related to each other by the crystallographic symmetry elements. These orientations can be described in terms of the angles between equivalent bonds of neighboring molecules. While translation results in an angle of \(0^\circ\) and inversion in an angle of \(180^\circ\), the effects of the two-fold screw-axis and the glide plane are more complicated. The angles resulting in the latter case are listed in Table VI and the ones resulting from screwing are obtained as differences between \(180^\circ\) and the values in Table VI. For example, molecule 1 of \(\gamma\)-\(\text{S}_7\) is transformed into molecule 1' by glide reflection and into 1'' by screwing; the angles between bonds S(6)-S(7) in molecules 1 and 1' amount to \(89^\circ\) and in molecules 1 and 1'' to \(180^\circ - 89^\circ = 91^\circ\).

As can be seen from Table VI, bonds S(6)-S(7) in both allotropes are either almost parallel or nearly perpendicular to each other. This holds also for molecules 1 and 2 of \(\delta\)-\(\text{S}_7\) which are not related by symmetry operations.

Financial support by the Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie is gratefully acknowledged.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Bond S(6)-S(7) (\gamma)-S&lt;sub&gt;7&lt;/sub&gt;</th>
<th>Bond S(4)-S(6) (\gamma)-S&lt;sub&gt;7&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1'</td>
<td>89°</td>
<td>6°</td>
</tr>
<tr>
<td>2-2'</td>
<td>—</td>
<td>3°</td>
</tr>
<tr>
<td>1-2</td>
<td>—</td>
<td>102°</td>
</tr>
</tbody>
</table>

Table VI. Angles between equivalent bonds of neighboring molecules in \(\gamma\)- and \(\delta\)-\(\text{S}_7\). Molecules 1 and 2 are transformed into 1' and 2', respectively, by glide reflection.