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

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X-ray structural analyses of two monoclinic allotropes of cycloheptasulfur carried out at -110°C revealed almost identical chair-like molecular structures of approximate C_s 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].

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 C_s symmetry with bond lengths

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

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

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structure of S_7 by investigating another of its allotropes (γ - S_7) by X-ray diffraction methods. The results are reported here together with the detailed information about the structural analysis of δ - S_7 .

Preparation of S_7 Allotropes

α - S_7 is obtained on rapid cooling of solutions of S_7 in CS_2 , CH_2Cl_2 or toluene almost saturated at 25 °C. This allotrope crystallizes as intense yellow, needle-like, 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 γ - S_7 is obtained.

β - S_7 is formed as a powder on decomposition of crystals of δ - S_7 either by careful mechanical impact (crushing with a glass rod) or simply by storage at 25 °C for 10 min. Sometimes β - S_7 crystallizes from solutions at -78 °C but is always obtained as a powder. γ - 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.

δ - S_7 crystallizes from CS_2 solutions at -78 °C on slow evaporation and forms block-shaped, tetragonal-bipyramidal and sarcophag-like crystals.

Structure Determination

γ - 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 γ and δ - S_7 at -110 °C (standard deviations in brackets).

	γ - S_7	δ - S_7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Lattice constants a (pm):	968.0(3)	1510.5(5)
b (pm):	764.1(2)	599.8(7)
c (pm):	940.9(2)	1509.6(5)
β :	102.08°	92.15(5)°
Volume of unit cell (nm ³)	0.6805(3)	1.366
Molecules in unit cell	4	8
Calculated density (g · cm ⁻³)	2.190	2.182
Linear absorption coefficient (cm ⁻¹) (MoK α radiation)	20.9	20.8
Reflections measured	1387	4826
Independent reflections ($I > 2\sigma$)	1205	2243

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

Intensity data were collected on an automated four-circle diffractometer (Syntex P2₁) with graphite-monochromated MoK α radiation ($\lambda = 71.069$ pm) using an ω -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, but no significant variation was observed. A total of 1252 independent reflections in the hkl and $h\bar{k}l$ octants with $\theta \leq 25^\circ$ 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 II. Molecular parameters of γ - and δ - S_7 as well as CH_2S_6 (standard deviations in brackets). For numbering of atoms see Fig. 1.

	γ -S ₇	δ -S ₇		CH ₂ S ₆ [31]
		Molecule 1	Molecule 2	
Bond lengths				
S(1)–S(2)	204.6(1)	204.8(3)	204.6(3)	
S(1)–S(3)	205.0(1)	205.3(3)	205.1(3)	—
S(2)–S(4)	209.7(1)	210.1(4)	210.6(4)	202.4(10)
S(3)–S(5)	210.1(1)	210.3(4)	209.8(4)	202.8(9)
S(4)–S(6)	199.8(1)	199.5(3)	199.7(3)	207.6(9)
S(5)–S(7)	199.7(1)	199.5(3)	199.8(3)	207.3(10)
S(6)–S(7)	217.5(1)	218.2(3)	218.0(3)	203.6(9)
Bond angles at atom				
S(1)	104.97(6)	106.3(1)	105.9(1)	—
S(2)	102.34(5)	101.5(1)	102.8(1)	107.3(8)
S(3)	101.90(6)	102.5(1)	102.1(1)	107.6(7)
S(4)	104.60(6)	105.6(1)	105.0(1)	102.9(5)
S(5)	106.07(5)	105.1(1)	105.4(1)	102.5(5)
S(6)	107.44(6)	106.9(1)	106.5(1)	104.6(4)
S(7)	107.41(6)	107.5(1)	107.5(1)	104.4(4)
Torsion angles at bond				
S(1)–S(2)	– 77.73(7)	– 75.2(1)	– 74.4(1)	47.4(CS)
S(1)–S(3)	75.60(6)	75.8(1)	75.4(1)	39.9(CS)
S(2)–S(4)	108.78(6)	107.6(1)	107.2(1)	101.4
S(3)–S(5)	– 106.78(6)	– 107.0(1)	– 108.0(1)	100.2
S(4)–S(6)	– 82.48(6)	– 84.3(1)	– 85.6(1)	85.8
S(5)–S(7)	83.97(6)	83.6(1)	82.5(1)	89.1
S(6)–S(7)	– 0.43(7)	– 0.3(1)	2.4(1)	70.8

Table III. Atomic positions and temperature factors (pm^2) of $\gamma\text{-S}_7$ (standard deviations in brackets).

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.61914(9)	0.18403(12)	0.45995(10)	190(5)	230(6)	252(6)	— 19(4)	75(5)	35(5)
S(2)	0.53478(9)	0.39128(12)	0.33346(10)	133(5)	229(6)	297(6)	— 2(4)	26(5)	12(5)
S(3)	0.77761(9)	0.09190(12)	0.36586(10)	192(5)	166(6)	275(6)	— 13(4)	41(5)	— 28(5)
S(4)	0.68352(9)	0.58937(12)	0.40265(10)	191(5)	186(6)	262(6)	7(4)	64(5)	— 47(5)
S(5)	0.93633(9)	0.28026(12)	0.43110(10)	155(5)	201(6)	180(5)	— 4(4)	— 6(4)	— 1(5)
S(6)	0.78008(9)	0.62254(12)	0.23659(10)	190(5)	204(6)	286(6)	22(4)	61(5)	56(5)
S(7)	0.94255(9)	0.42237(12)	0.25439(10)	173(5)	210(6)	234(6)	19(4)	68(4)	16(5)

Table IV. Atomic positions and temperature factors (pm^2) of $\delta\text{-S}_7$ (standard deviations in brackets).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S11	.7854(1)	.9477(4)	.4905(1)	297.(11)	247.(11)	208.(10)	— 10.(9)	— 4.(8)	— 28.(9)
S12	.8964(1)	.8451(4)	.4281(1)	243.(10)	283.(12)	257.(11)	— 23.(9)	6.(8)	— 23.(9)
S13	.6797(1)	.8726(4)	.4064(1)	265.(11)	270.(12)	259.(11)	36.(9)	— 15.(8)	4.(9)
S14	.8898(1)	.4977(4)	.4447(1)	253.(10)	273.(12)	203.(10)	0.(9)	— 50.(8)	— 15.(9)
S15	.6677(1)	.5258(4)	.4223(1)	250.(11)	286.(12)	244.(10)	— 22.(9)	22.(8)	17.(9)
S16	.8559(1)	.3748(4)	.3254(1)	242.(10)	278.(12)	216.(10)	1.(9)	— 13.(8)	— 43.(9)
S17	.7118(1)	.3945(4)	.3109(1)	240.(10)	329.(12)	236.(10)	— 12.(9)	— 56.(8)	— 27.(10)
S21	.4876(1)	.2985(4)	.2751(1)	240.(10)	285.(12)	256.(11)	— 36.(9)	— 19.(8)	— 23.(9)
S22	.4023(1)	.2065(4)	.1730(1)	267.(11)	270.(12)	229.(10)	— 9.(9)	— 40.(8)	— 14.(9)
S23	.4283(2)	.2027(4)	.3981(1)	324.(12)	278.(12)	216.(10)	— 6.(10)	— 21.(9)	— 26.(9)
S24	.4192(1)	— .1418(4)	.1683(1)	236.(10)	273.(12)	211.(10)	— 15.(9)	— 1.(8)	— 31.(9)
S25	.4485(1)	— .1434(4)	.3892(1)	271.(11)	302.(12)	240.(11)	39.(9)	— 59.(8)	16.(9)
S26	.3087(1)	— .2679(4)	.2168(1)	238.(10)	287.(12)	234.(10)	— 39.(9)	— 42.(8)	— 6.(9)
S27	.3295(1)	— .2760(4)	.3604(1)	275.(11)	309.(12)	230.(10)	— 11.(9)	4.(8)	10.(9)

sulfur atoms in the asymmetric unit produced a value of 0.028 for R ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). The results are given in Tables II and III; the crystal structure is shown in Fig. 2.

The structure determination of $\delta\text{-S}_7$ 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

Fig. 2. Projektion of the $\gamma\text{-S}_7$ crystal structure on the plane defined by axes b and c . The asymmetric unit is formed by molecule 1 while molecules 1' and 1'' are generated from 1 by glide reflection and screwing, respectively.

Fig. 3. Projection of the $\delta\text{-S}_7$ 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.

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 ≤ 360 pm of both $\gamma\text{-}$ and $\delta\text{-S}_7$ are given in Table V.

Table V. Intermolecular distances < 360 pm in γ - and δ -S₇.

γ -S ₇		δ -S ₇	
S(7)–S(3) ^I	340.3(2)	S(5)–S(3) ^I	349.3(3)
S(5)–S(7) ^{II}	340.3(2)	S(4)–S(4) ^{II}	349.7(3)
S(6)–S(7) ^I	351.7(2)	S(3)–S(3) ^{III}	357.5(4)
S(2)–S(3) ^{III}	355.5(2)		
S(7)–S(5) ^I	357.2(2)	S(4)–S(4) ^{IV}	350.8(4)
S(4)–S(2) ^{III}	357.2(2)	S(2)–S(2) ^{IV}	355.1(4)
S(2)–S(4) ^{IV}	358.5(2)		
symmetry operations:		symmetry operations:	
I: $2-x, 1/2+y, 1/2-z$		I: $x, \pm 1+y, z$	
II: $x, 1/2-y, 1/2+z$		II: $\pm 1/2+x, -1-y, \pm 1/2+z$	
III: $1-x, 1/2+y, 1/2-z$		III: $1-x, -y, 1-z$	
IV: $1-x, 1-y, 1-z$		IV: $3/2-x, \pm 1/2+y, 1/2-z$	

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 C₁ symmetry although the molecular symmetry is almost C_s. The same slightly twisted chair conformation has been found for the homocyclic derivatives S₇O [26], S₇I⁺ [27] and [(S₇I)₂I]³⁺ [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 ($5 \cdot 10^{-7}$ 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 σ molecular orbitals at bonds S(2)–S(4) and S(3)–S(5) thus increasing the lengths 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 hexathiepane (CH₂S₆) [31]. This molecule can be derived formally from S₇ by substituting atom S(1) by a methylene group. It exhibits C₂ symmetry (twist-chair conformation) with "normal" SS bond lengths ranging from 202 to 208 pm (see Table II). The main differences between S₇ and CH₂S₆ are the differing torsional angles at bonds S(6)–S(7) which amount to $1 \pm 2^\circ$ in γ - and δ -S₇ compared with 71° in CH₂S₆. 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 have been observed for S₆, S₈ and S₁₂ [32]. It nevertheless can be expected that the C₂ conformation of S₇ will be only slightly less stable than the C_s 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 C_s and C₂ structures but, on the other hand, completely failed to predict the experimental bond distance pattern for the C_s geometry [33]. This may be the reason why the C₂ 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 H_2S_2 and $(\text{CH}_3)_2\text{S}_2$ [32] since as the torsional angle approaches 0° or 180° the increase in energy due to lone pair repulsion is partly compensated by the energy gain from additional π bonds to neighboring atoms. For the same reason the mean bond energy in S_7 is only slightly smaller than in S_8 and almost identical to the one of S_6 [34] although the bond distances are dramatically different.

The different packing patterns of γ - and δ - 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° and inversion in an angle of 180° , 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° and the values in Table VI. For example, molecule 1

Table VI. Angles between equivalent bonds of neighboring molecules in γ - and δ - S_7 . Molecules 1 and 2 are transformed into 1' and 2', respectively, by glide reflection.

Molecules	Bond S(6)–S(7)		Bond S(4)–S(6)	
	γ - S_7	δ - S_7	γ - S_7	δ - S_7
1–1'	89°	6°	15°	43°
2–2'	—	3°	—	45°
1–2	—	102°	—	90°

of γ - 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° and in molecules 1 and 1'' to $180 - 89 = 91^\circ$. 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 δ - S_7 which are not related by symmetry operations.

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