Crystal and Molecular Structure ofcyclo-Heptasulfur (delta-S7)

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Crystal and Molecular Structure of cyclo-Heptasulfur (δ-S₇)[1]

By *Ralf Steudel, Richard Reinhardt*, and *Fritz Schuster*[*]

Together with S_8, cyclo-heptasulfur is a principal component of molten[2] and gaseous[3] sulfur, and can be prepared by extraction of quenched sulfur melts[2] or by condensation of $(C_5H_5)_2TiS_5$ with S_2Cl_2[4]. An incomplete X-ray structure analysis (*xy* projection of the molecule) was interpreted in terms of a puckered seven-membered ring[5], and internuclear distances of 200—215 pm[6a] were deduced from the Raman spectrum. However, the precise molecular structure is not known.

We found by Raman spectroscopy that S_7 crystallizes in at least four modifications which differ significantly from one another primarily in their lattice vibrations, and also in the stretching and bending regions, with regard to the wave numbers and relative intensities of the lines. We have obtained single crystals of one of these modifications, which we call δ-S_7, by evaporation of a CS_2 solution at $-78\,°C$[7] and subjected them to X-ray analysis at $-110\,°C$. Since the modification is a low-temperature form, whose crystals rapidly disintegrate to a powder at $25\,°C$, the substance was handled at temperatures below $-50\,°C$.

de Jong-Bouman and precession diagrams revealed the monoclinic space group $P2_1/n$ with $Z=8$, $a=1510.5(5)$, $b=599.8(7)$, $c=1509.6(5)$ pm, $\beta=92.15(5)°$, $d_{calc.}=2.182\,g\,cm^{-3}$ ($-110\,°C$). Using an automatic Siemens single crystal diffractometer, 2263 symmetry-independent reflections up to $\theta=25°$ were recorded with $Mo_{K\alpha}$ radiation; 20 reflections were classified as unobserved ($I\leq2\sigma$). The phase problem was solved by direct methods and the structure refined to an R value of 7.0 % with anisotropic temperature factors (absorption correction, $\mu=20.8\,cm^{-1}$).
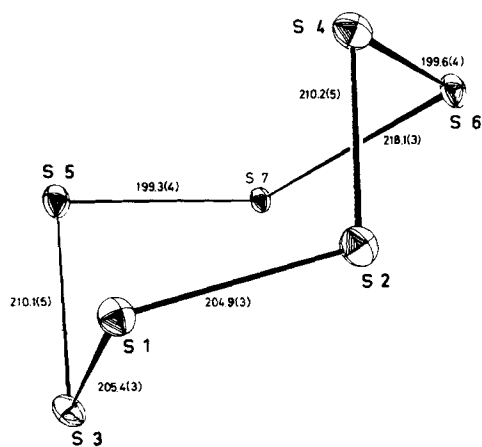

Fig. 1. Molecular shape, numbers of atoms, and internuclear distances [pm] of δ-S_7; standard deviations in parentheses (the values apply to molecule I).

One of the molecules in the asymmetric unit cell is depicted in Figure 1. Although the molecules occupy general sites, the molecular symmetry is approximately C_s. The internuclear distances are identical to within the simple standard deviation; among the angles, however, the differences are considerably greater (Table 1). The bond lengths deviate from the spectros-

copically predicted values by at most 3 pm[6a] and thus confirm the theory of bond interaction in sulfur chains, explaining the alternancy of the internuclear distances[6], upon which the prediction is based.

Table 1. Valence and torsional angles [°] in δ-S_7; standard deviations in parentheses.

Valence angle at atom no.		Torsional angle at bond between atoms no:	
Molecule I	Molecule II	Molecule I	Molecule II
1: 106.3(1)	105.9(1)	1—2: −75.2	−74.4
2: 101.5(1)	102.8(1)	1—3: 75.8	75.4
3: 102.5(1)	102.1(1)	2—4: 107.6	107.2
4: 105.6(1)	105.0(1)	3—5: −107.0	−108.0
5: 105.1(1)	105.4(1)	4—6: −84.3	−85.6
6: 106.9(1)	106.5(1)	5—7: 83.6	82.5
7: 107.5(1)	107.5(1)	6—7: −0.3	2.4

The shape of the δ-S_7 molecule resembles that of S_7I^{+}[8] and can be formally derived from that of S_8 by excision of one atom and connection of the resulting chain ends by an unusually long bond. The large internuclear distance of this bond is primarily due to the small S4-S6-S7-S5 torsional angle of *ca.* 1°, which normally corresponds to a maximum of the torsional potential[6b]. However, as a result of the bond weakening, the adjacent bonds are strengthened: they are the shortest ones in the molecule, the same effect having also been observed in other sulfur rings (S_8O, S_7I^+, S_7O). Simple MO considerations show that a four-center bond occurs between atoms 4 to 7, which is responsible for the almost coplanar arrangement of these atoms. This geometry, and hence C_s symmetry, are therefore also predicted for the free (gaseous) S_7 molecule. The average distance between atoms 4 and 5 is 335.5(3) pm.

As a consequence of the alternating bond lengths, the average SS distance of 206.8 pm is only slightly greater than that in S_6, S_8, and S_{12} (205 pm[6b]), so that the average bond energy can differ only slightly from that of the other rings. The average value of the bond angles (105.1°) lies exactly halfway between those of S_6 (102.2°) and S_8 (108.0°). The smallest intermolecular distances (339.7 pm) correspond to those found for other sulfur rings[9]. Particularly effective packing of the S_7 molecules in the lattice leads to a high density, which together with that of S_6 (2.18 g cm^{-3}[9]) surpasses that in all other forms of sulfur (1.94—2.09 g cm^{-3}).

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[7] This modification forms block-shaped, tetragonal-bipyramidal, and sarcophage-like crystals and differs from α-, β-, and γ-S_7 in that the most intense Raman line in the 20—600 cm^{-1} region lies at 400 cm^{-1} ($-100\,°C$, spectrometer Cary 82, spectral slit width 2 cm^{-1}, krypton laser 647.1 nm).

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