

## NOTIZEN

**Redetermination of the  
Crystal and Molecular Structure of  
Cyclohexasulfur, S<sub>6</sub> [1]**

Jürgen Steidel, Joachim Pickardt,  
and Ralf Steudel

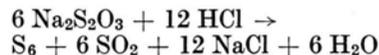
Institut für Anorganische und Analytische  
Chemie der Technischen Universität Berlin,  
Berlin-Charlottenburg

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Cyclohexasulfur, X-ray

A low temperature (−90 °C) X-ray structural analysis of S<sub>6</sub> single crystals yielded improved data for the bond distances (206.8 pm), bond angles (102.6°), and torsion angles (73.8°) of the D<sub>3d</sub> molecule which are in agreement with current theories of homonuclear sulfur bonds.

Light and temperature sensitive crystals of cyclohexasulfur can be easily obtained according to [2, 3]



and have been shown by X-ray structural analysis to consist of homocyclic molecules of D<sub>3d</sub> symmetry occupying sites of  $\bar{3}$ -S<sub>6</sub> symmetry [4]. The rhombohedral unit cell of space group R $\bar{3}$  contains six atoms [4]. However, due to the equipment available (Weißberg camera, intensities estimated visually) and because of the rapid decomposition of the S<sub>6</sub> crystals in the X-ray beam at 25 °C the standard deviations of the molecular parameters published in 1961 were rather high (see Table I). Since S<sub>6</sub> is an important constituent of gaseous [5] and liquid [6] sulfur we carried out a new X-ray structural analysis of S<sub>6</sub> single crystals at −90 °C at which temperature no decomposition occurred in the X-ray beam. S<sub>6</sub> was prepared from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>. According to the Raman spectrum the transparent crystals did not contain any impurities like other sulfur molecules.

Utilizing an automatic single-crystal diffractometer (Syntex P2<sub>1</sub>) operating with MoK $\alpha$  radiation 811 reflections were measured. As in ref. [4] we choose the hexagonal unit cell containing three molecules for all calculations. The lattice constants

Table I. Molecular parameters of cyclohexasulfur.

	Ref. [4]	This work
Bond distance	205.7(1.8)	206.8(2) pm
Bond angle	102.2(1.6)	102.61(6)°
Torsion angle	74.5(2.5)	73.8(1)°
Shortest and next	350.1	344.3(2) pm
shortest intermolecular	352.6	347.1(2) pm
distances	374.9	369.7(2) pm

were found from 15 Bragg angles by least-squares treatment as  $a = 1076.6(4)$  and  $c = 422.5(1)$  pm (standard deviations in brackets). The calculated density of 2,260 g · cm<sup>−3</sup> (−90 °C) is considerably higher than Engel's value [2] of 2.14 g · cm<sup>−3</sup> (20 °C) which we verified suggesting substantial lattice defects.

Using the programs MULTAN and X-RAY 76 [7] the structural parameters were derived from 286 independent reflections ( $3^\circ \leq \theta \leq 38^\circ$ ), 15 of which were classified as unobserved ( $I \leq 2\sigma$ ). After the usual corrections including absorption ( $\mu = 21.7 \text{ cm}^{-1}$ ) a final  $R$  value of 0.034 was obtained applying anisotropic temperature factors.

The positional parameters of the single atom in the asymmetric unit are as follows:  $x = 0.1905(1)$ ,  $y = 0.1475(1)$ ,  $z = 0.3940(3)$ , with the temperature factor parameters [in pm<sup>2</sup>]  $U_{11} = 106(4)$ ,  $U_{22} = 115(4)$ ,  $U_{33} = 313(6)$ ,  $U_{12} = 49(3)$ ,  $U_{13} = 22(3)$ ,  $U_{23} = 20(3)$ .

In Table I the molecular parameters are compared with the earlier work; as can be seen, the new data were found within the standard deviations of the older data.

It is well known that the bond distances ( $d$ ) of homonuclear sulfur bonds depend on the torsion angles ( $\tau$ ) [8], and from the structures of S<sub>8</sub> and chain-like molecules it follows that  $\tau$  values of  $90 \pm 10^\circ$  are most favorable [8], which can be rationalized in terms of a simple electron pair repulsion model [9]. Since in S<sub>6</sub>  $\tau = 74^\circ$  a substantially larger bond distance than in S<sub>8</sub> ( $d = 204.8$  pm,  $\tau = 98.5^\circ$  [10]) was to be expected. The bond length difference of 2 pm between S<sub>8</sub> and S<sub>6</sub> corresponds to a difference in mean bond energies [11] of 4.3 kJ/mol per bond. It is interesting to note that the average bond distances in S<sub>6</sub> and S<sub>7</sub> (206.8 pm [14]) are identical, and at the same time the mean bond energies of both molecules [11] differ by only 0.7 kJ/mol per bond. It may well be that a correlation between the average bond distances and the mean bond energies of sulfur rings exists, but a more detailed investigation must await more reliable bond energy data.

Requests for reprints should be sent to Prof. Dr. R. Steudel, Sekr. C2, Technische Universität Berlin, D-1000 Berlin 12.

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