A New Allotrope of Elemental Sulfur: Convenient Preparation of *cyclo*-S_{14} from S_8[**]

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Sulfur forms far more allotropes than any other element. At present, at least 21 sulfur allotropes are known to exist at ambient pressure, 17 of which have been characterized by X-ray crystallography.[1] They all contain sulfur atoms with a coordination number (CN) of 2. The densities of these compounds range between 1.9 and 2.2 $g\,cm^{-3}$, and the internuclear distances between 200 and 218 pm.[2] All investigated low-pressure allotropes are excellent electrical insulators (band gap ca. 2.9 eV). At high pressures, at least four additional allotropes have been obtained, three of which have been studied by X-ray diffraction. At 33 GPa sulfur becomes a semiconductor (of unknown structure), and at 83 GPa a metallic conductor. This "sulfur metal" crystallizes in an orthorhombic layer structure with $CN = 4$, but at 162 GPa the structure transforms into that of β-polonium with $CN = 6$. At 206 GPa the density reaches 6.6 $g\,cm^{-3}$; however, the internuclear distances of 207.9 pm are "normal"[3] (α-S_8: 205 pm[4]). The two metallic sulfur modifications become superconductors below 10 and 17 K, respectively.[5]

Here we report on a new monotropic low-pressure allotrope of sulfur which can be prepared in three steps from the thermodynamically stable form α-S_8. The starting material is the hexasulfido complex **1**, which was prepared by Rauchfuss et al.[6] from zinc powder, orthorhombic α-S_8, and *N,N,N′,N′*-tetramethylethylenediamine (tmeda) at 90 °C in 75% yield [Eq. (1)].

$$Zn + 3/4\,S_8 + tmeda \rightarrow [(tmeda)ZnS_6] \quad \mathbf{1} \qquad (1)$$

Complex **1** forms yellow air-stable crystals, and its molecules contain a seven-membered metallacycle with the chelating ligand S_6^{2-}. Like $[(C_5H_5)_2TiS_5]$ the zinc complex acts as a sulfur-transfer reagent. For instance, treating a suspension of **1** in CS_2 with Se_2Cl_2 at −60 °C afforded the heterocycle 1,2-Se_2S_6.[7] We studied the reaction of a solution of **1** in CS_2 at 0 °C with dichlorooctasulfane S_8Cl_2 [Eq. (2)], which is accessible by careful chlorination of *cyclo*-S_8 with elemental chlorine.[8] The HPLC analysis[9] of the mixture indicated the formation of *cyclo*-tetradecasulfur in high concentration.

$$[(tmeda)ZnS_6] + S_8Cl_2 \rightarrow cyclo\text{-}S_{14} + [(tmeda)ZnCl_2] \quad \mathbf{2} \qquad (2)$$

However, on attempting to isolate S_{14} from the mixture, decomposition to S_8 occured regularly. This may be due to the presence of the strong nucleophile tmeda ($pK_a = 5.85/8.97$),[10] which is only partly removed by the insoluble zinc complex **2**. Strong nucleophiles are known to catalyze the decomposition of thermodynamically unstable sulfur homocycles.[11] After addition of P_4O_{10} to the reaction mixture to remove the remaining amine, pure S_{14} could be isolated in 11% yield (based on **1**). As side product S_{12} was isolated, which apparently originates from the reaction of **1** with the S_6Cl_2 that was present in S_8Cl_2 as another chlorination product.

S_{14} forms intense yellow rodlike crystals, which intergrow to form bundles and melt at 117 °C with decomposition. The primary decomposition products are S_7 and S_8, but not S_6; therefore, a reaction sequence $S_{14} \rightarrow 2\,S_7 \rightarrow\rightarrow S_8$ is likely. At 20 °C S_{14} is stable for days in the crystalline state and as a solution in CS_2. The solubility in CS_2 is greater than that in $CHCl_3$.The EI mass spectrum (70 eV) exhibits only peaks for the sulfur ions S_n^+ ($n = 1-9$). It contains no other elements, and the molecular ion was not observed. The Raman spectrum at −100 °C (Table 1)[12] differs from those of all other cyclic sulfur allotropes, but is consistent with expectations. Besides eight lines, two of which are shoulders, in the S–S stretching region (440–485 cm^{-1}), several bands for the deformation, torsion, and lattice vibrations are present in the region below 290 cm^{-1}. Signals due to S_8 and S_{12} are not detectable.

Table 1. Wavenumbers [cm^{-1}] of the Raman bands of crystalline S_{14} at −100 °C (krypton laser, 674 nm; relative intensities in parentheses).

Stretching modes	Bending modes	Torsional and lattice modes
483 (7)	270 (7)	122 (7)
474 (5)	252 (2)	90 (23)
468 (25)	243 (5)	79 (14)
462 sh	234 (23)	69 (59)
460 (59)	212 (2)	61 (41)
453 sh	198 (18)	57 (36)
447 (11)	189 (7)	47 (100)
444 (11)	177 (11)	34 (23)
	163 (25)	
	153 (16)	
	128 (48)	

The reversed-phase HPLC chromatogram of pure S_{14} shows only one large peak, the retention time of which lies between those of S_{13}[8] and S_{15}.[14] With this technique S_{14} was identified previously as a trace component in quenched sulfur melts and in synthetic sulfur mixtures.[9, 15]

The cyclic structure of S_{14} was confirmed by a single-crystal X-ray structure analysis.[16] At 20 °C the crystals decomposed rapidly in the X-ray beam. Therefore, the sample was cooled to −100 °C, and at this temperature the reflection intensities remained constant. The structure is triclinic with two molecules in the unit cell and a density of 2.045 $g\,cm^{-1}$ at −100 °C. The S_{14} molecules occupy general sites but have approximately C_S molecular symmetry (Figure 1). The noncrystallo-

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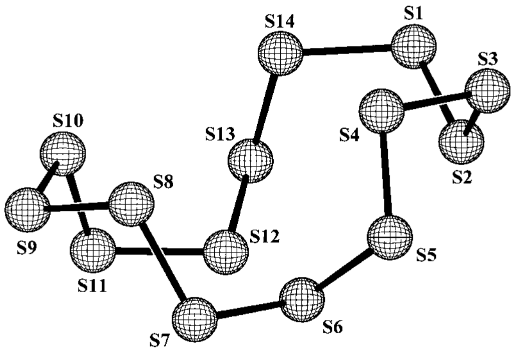

Figure 1. Structure of *cyclo*-S_{14} in the crystal. Bond lengths [pm], angles [°], and torsional angles [°]: S1–S2 205.5(4), S2–S3 205.1(3), S3–S4 205.4(3), S4–S5 206.1(4), S5–S6 205.0(4), S6–S7 204.7(4), S7–S8 205.6(4), S8–S9 204.7(3), S9–S10 204.9(3), S10–S11 206.0(3), S11–S12 205.5(4), S12–S13 205.2(4), S13–S14 205.9(3), S14–S1 205.1(4); S1-S2-S3 108.4(2), S2-S3-S4 107.8(2), S3-S4-S5 104.4(2), S4-S5-S6 104.0(2), S5-S6-S7 104.95(14), S6-S7-S8 108.3(2), S7-S8-S9 106.95(13), S8-S9-S10 109.32(14), S9-S10-S11 106.0(2), S10-S11-S12 107.1(2), S11-S12-S13 105.0(2), S12-S13-S14 104.5(2), S13-S14-S1 105.1(2); S1-S2-S3-S4 +96.0(2), S2-S3-S4-S5 +72.5(2), S3-S4-S5-S6 −100.8(2), S4-S5-S6-S7 −94.9(2), S5-S6-S7-S8 +82.7(2), S6-S7-S8-S9 +107.1(2), S7-S8-S9-S10 −100.7(2), S8-S9-S10-S11 +95.9(2), S9-S10-S11-S12 −100.7(2), S10-S11-S12-S13 −75.9(2), S11-S12-S13-S14 +101.7(2), S12-S13-S14-S1 +101.5(2), S13-S14-S1-S2 −77.9(2), S14-S1-S2-S3 −94.7(2).

graphic mirror plane contains S2 and S9. The internuclear distances vary from 204.7 to 206.1 pm; the arithmetic mean of 205.3 pm is only insignificantly larger than that of orthorhombic α-S_8.

The conformation of sulfur homocycles is best described by the "motif", which is the order of the signs of the torsional angles around the ring. The motif of S_{14} is $++--++--++--+-$. Since the first 12 signs are the same as those of the S_{12} molecule,[17] the structure of S_{14} can be generated from that of *cyclo*-S_{12} by opening any bond and inserting an S_2 fragment (S9 and S10). The absolute values of the torsional angles in S_{14} are in the range of 72.5–101.7°; the arithmetic mean of 93.1° is also close to the corresponding value of S_{12} (89°). The mean bond energy of S_{12} is only 1 kJ mol^{-1} smaller than that of S_8. Therefore, S_{12} is only second to S_8 in thermodynamic stability. The difference between the mean bond energy of S_{14} and that of S_8 is 2 kJ mol^{-1}.[18]

Experimental Section

cyclo-S_{14}: Solvents were dried over P_4O_{10} and distilled. Under an atmosphere of dry nitrogen, S_8Cl_2 (4.2 g, 12.8 mmol) in CS_2 (17.5 mL) was added dropwise over 1 h to **1** (4.8 g, 12.8 mmol) in CS_2 (70 mL) at 0 °C. The temperature was then allowed to rise to 20 °C over 1 h. The colorless precipitate of **2** was collected by filtration and washed with 50 mL of CS_2; the filtrate and wash solutions were combined. To remove dissolved tmeda P_4O_{10} (ca. 0.4 g) was added to the clear yellow solution (the hygroscopic P_4O_{10} contains strongly acidic POH groups which protonate the amine). $CHCl_3$ (10 mL) was added to precipitate sparingly soluble S_{12}. After cooling to −35 °C the mixture of S_{12} and P_4O_{10} was filtered off. Addition of a further 10 mL of $CHCl_3$ to the filtrate and cooling to −35 °C for several days afforded yellow bundles of S_{14} (yield 650 mg).

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[1] The following phases consist of cyclic molecules: S_6, S_7 ($\alpha-\delta$), S_8 ($\alpha-\gamma$), S_9 (α,β), S_{10}, S_{11}, S_{12}, S_{13}, S_{15}, S_{18} (α,β), S_{20}, $S_6 \cdot S_{10}$. In addition, two polymeric allotropes S_∞ are known (also termed S_μ or S_ω).

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[12] Investigating unstable sulfur allotropes by Raman spectroscopy requires the use of a laser beam with low-energy radiation (red or infrared); otherwise, photochemical conversion into S_8 may occur. For experimental details, see ref. [8].

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[16] Crystal structure analysis of S_{14}: 0.55 × 0.16 × 0.15 mm, triclinic, space group $P\bar{1}$ (no. 2), $Z=2$, $a=5.469(3)$, $b=9.662(5)$, $c=14.331(7)$ Å, $\alpha=95.97(4)$, $\beta=98.96(4)$, $\gamma=100.43(4)°$, $V=728.8(7)$ Å^3, $\mu=2.044$ mm^{-1}, Mo$_{K\alpha}$ radiation, $\lambda=0.71068$ Å. Of 4440 measured reflections ($2.16 \leq \theta \leq 30.00°$), 54 % with $I \leq 2\sigma(I)$, 4270 were independent; $R_{int}=0.051$. Due to the large width (1.7°, ω scan) and irregular form of the reflection profiles the ω scan mode was used, the background on both sides of the reflections was measured point by point. Initial coordinates of the sulfur atoms from direct methods with SIR92. Refinement on F^2 (SHELXL93), 127 refined parameters, $R1=0.084$, $R1=\Sigma_H||F_o|-|F_c||/\Sigma_H|F_o|$, $wR2=0.25$ with all independent reflections, $wR2=\{\Sigma_H[w(F_o^2-F_c^2)^2]/\Sigma_H wF_o^4\}^{1/2}$, $w=[\sigma^2(F_o^2)+(0.1542P)^2]^{-1}$ with $P=[\max(F_o^2,0)+2F_c^2]/3$; max./min. residual electron density 1.51/−1.13 e Å^{-3}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408504.

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