Application of Dicyanohexasulfane for the Synthesis of *cyclo*-Nonasulfur. Crystal and Molecular Structures of $S_6(CN)_2$ and of α-S_9[1]

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A novel synthesis for dichlorotetrasulfane is reported. Careful chlorination of *cyclo*-hexasulfur yields S_4Cl_2 (besides S_2Cl_2), which is used to prepare $S_6(CN)_2$ by reaction with $Hg(SCN)_2$. An X-ray diffraction analysis of $S_6(CN)_2$ shows nonhelical chainlike molecules with the following molecular parameters: SS bond lengths 203.4−207.4 pm, SSS valence angles 104.95−105.96°, SS torsion angles 81.2−94.5° (motif: $++--+$). The chain-terminating SCN groups exhibit a parallel orientation within the molecules and are antiparallel in neighboring molecules. $S_6(CN)_2$ reacts with titanocene pentasulfide to give S_9 and titanocene diisothiocyanate. α-S_9 was obtained as single crystals, the structure of which was determined by X-ray diffraction. The two independent molecules occupy sites of C_1 symmetry, but the molecular symmetry is approximately C_2, in agreement with predictions by density functional and *ab-initio* MO calculations. Molecular parameters: bond lengths 203.2−206.9 pm, valence angles 103.7−109.7°, torsion angles 59.7−115.6° (motif: $++--++-+-$). The average SS bond lengths in $S_6(CN)_2$ and α-S_9 agree with the single-bond value of 205 pm as observed in H_2S_2 and in α-S_8.

Introduction

Sulfur is still the element with the largest number of solid allotropes, most of which consist of homocyclic molecules. The rings S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{13}, S_{15}, S_{18}, and S_{20} have been prepared as pure materials,[2] but the complexity of this element is even further increased by the fact that the homocycles S_7,[3] S_8,[4] S_9,[5] and S_{18}[6] crystallize as different crystalline phases (α, β, γ, ...) and even cocrystallization of S_6 with S_{10} in a well-ordered phase of composition $S_6{\cdot}S_{10}$ has been observed.[7] In addition, there are at least two crystalline polymeric allotropes of sulfur consisting of helical chains.[4]

The synthesis of sulfur homocycles has dramatically profited from the discovery that titanocene pentasulfide $(\eta^5\text{-}C_5H_5)_2TiS_5$ acts as a transfer reagent for the S_5 unit when treated with dichlorosulfanes[8] (eq 1).

$$Cp_2TiS_5 + S_nCl_2 \rightarrow S_{n+5} + Cp_2TiCl_2 \qquad (1)$$

Using S_4Cl_2, *cyclo*-nonasulfur (*c*-S_9) was prepared.[9] Single crystals of S_9 had so far not been obtained, but a detailed Raman spectroscopic study of microcrystalline samples indicated[5] that S_9 crystallizes as two allotropes, termed α- and β-S_9. From the spectra it was concluded that the molecules must be of either C_2 or C_1 symmetry and that the SS bond distances are in the range 203−209 pm.[5] Density functional calculations on S_9 molecules resulted in a number of conformations, the most stable of which is of C_2 symmetry with bond distances in the range 209−211 pm.[10] *Ab-initio* MO calculations at the HF/3-21G* level of theory also resulted in a ground state of C_2 symmetry for S_9 with bond lengths between 204 and 207 pm.[11]

c-S_9 is a component of liquid sulfur,[12] which is industrially produced on a very large scale; S_9 is also formed on UV irradiation of S_8 or S_7 in CS_2 solution at 25 °C,[13] on heating of S_8 in CS_2 solution to 130−155 °C,[14] and on thermal depolymerization of industrially produced polymeric sulfur ("μ-sulfur") in the presence of an organic solvent like cyclohexane or carbon disulfide.[15] Traces of S_9 have also been detected in certain commercial samples of elemental sulfur consisting mainly of S_8.[16] Furthermore, S_9 is a component of several synthetic sulfur mixtures as obtained by acid decomposition of thiosulfate[17] or by reaction of SCl_2 with aqueous potassium iodide.[18] On reaction with trifluoroperoxyacetic acid, S_9 is oxidized to the sulfoxide S_9O.[5] Therefore, the structure of the S_9 molecule is of general interest. Here we report a new synthesis of S_9 which allowed the growth of single crystals and subsequently a full characterization of this allotrope by X-ray crystallography.

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Results

The dichlorotetrasulfane needed for the synthesis of S_9 by reaction 1 is usually prepared by a condensation reaction of disulfane with sulfur dichloride[19] (eq 2). We have found that

$$\mathrm{Cl{-}S{-}Cl + H{-}S_2{-}H + Cl{-}S{-}Cl \rightarrow Cl{-}S_4{-}Cl + 2HCl} \qquad (2)$$

S_4Cl_2 can be prepared more conveniently from *cyclo*-hexasulfur[20] by careful chlorination at 25 °C (eqs 3 and 4). The

$$c\text{-}\mathrm{S_6 + Cl_2 \rightarrow Cl{-}S_6{-}Cl} \qquad (3)$$

$$\mathrm{S_6Cl_2 + Cl_2 \rightarrow S_4Cl_2 + S_2Cl_2} \qquad (4)$$

synthesis of S_6Cl_2 by reaction 3 has already been reported, and the product obtained was used to prepare S_{11} by reaction 1.[21] The further chlorination of S_6Cl_2 results in crude S_4Cl_2, which after evaporation of the byproduct S_2Cl_2, is sufficiently pure for preparative work, the impurities being other dichlorosulfanes S_nCl_2 with $n = 1-6$.

Dichlorosulfanes react with mercury(II) rhodanide to give the corresponding dicyanosulfanes[22] (eq 5). All members of this

$$\mathrm{S}_n\mathrm{Cl_2 + Hg(SCN)_2 \rightarrow S}_{n+2}\mathrm{(CN)_2 + HgCl_2} \qquad (5)$$

series with $n = 1-9$ have been prepared,[22,23] and the structures of $S_3(CN)_2$,[24] $S_4(CN)_2$,[25] and $S_9(CN)_2$[23] have been determined by X-ray crystallography. The dicyanosulfanes form chainlike molecules which interact via N···S contacts or by dipole−dipole interaction. These intermolecular interactions are probably responsible for the fact that $S_n(CN)_2$ molecules crystallize much easier than the corresponding S_nCl_2 species, which tend to form oils or glasses (on cooling). The crude S_4Cl_2 obtained by reaction 4 was used to prepare $S_6(CN)_2$ by treatment with $Hg(SCN)_2$. The dicyanohexasulfane (mp 35 °C) could be purified by crystallization (yield 27% based on S_6) and structurally characterized by single-crystal X-ray diffraction (see below). $S_6(CN)_2$ is unstable at 20 °C and spontaneously transforms to a red insoluble polymer. The time for which it can be handled without decomposition varies with the purity of the sample but can be estimated as ≤10 min. Beginning decomposition can be detected by a yellow coloration accompanied by a liquidlike appearance of the surface of the crystals.

During the course of this work, it was discovered that dicyanosulfanes $S_n(CN)_2$ react with titanocene pentasulfide analogously to dichlorosulfanes (eq 6). As can be seen from

$$\mathrm{Cp_2TiS_5 + S_6(CN)_2 \rightarrow S_9 + Cp_2Ti(NCS)_2} \qquad (6)$$

eq 6, the pseudohalogen SCN is transferred from the sulfur chain in $S_6(CN)_2$ to the titanium atom in a manner similar to the chlorine atom transfer in reaction 1. Thus, $S_6(CN)_2$ reacts as $S_4(SCN)_2$ and can substitute S_4Cl_2 in the preparation of S_9! The use of $S_6(CN)_2$ has the following advantages: (1) $S_6(CN)_2$ is a solid which is easier to handle (e.g. on weighing) than the oily S_4Cl_2; (2) $S_6(CN)_2$ can be obtained pure by crystallization while S_4Cl_2 can be neither crystallized nor distilled and therefore is never very pure; (3) $S_6(CN)_2$ is odorless while S_4Cl_2 shows the typical unpleasant smell of sulfur chlorides. The titanocene dirhodanide formed in reaction 6 is identical to the known N-bonded isomer $Cp_2Ti(NCS)_2$;[26] this follows from its orange color, its insolubility in *n*-hexane, and its IR absorption at 825 cm^{-1}, which is typical for −NCS.[26] The S-bonded isomers $Cp'_2Ti(SCN)_2$, known only with alkyl-substituted cyclopentadiene ligands (Cp′), are green, are soluble in *n*-hexane, and exhibit a characteristic IR absorption for −SCN between 690 and 720 cm^{-1}.[26]

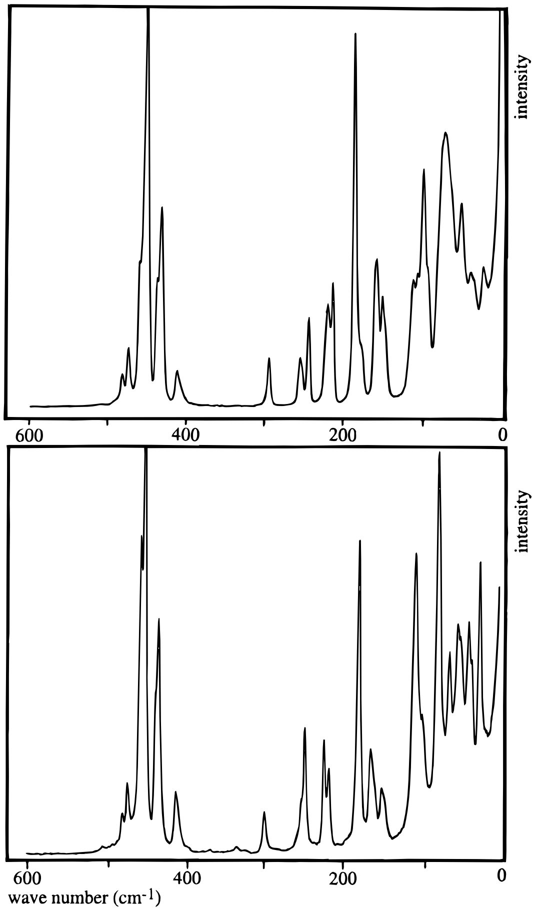

Figure 1. Raman spectra of α-S_9 (top) and *β*-S_9 (sample temperature −100 °C; krypton laser at 647.1 nm).

The *cyclo*-nonasulfur prepared by reaction 6 was obtained as deep yellow single crystals from a chloroform solution. Thus the crystal and molecular structure could be determined by X-ray diffraction. The Raman spectrum of the crystal used for the diffraction measurements matches the reported spectrum of α-S_9.[5] In Figure 1 the Raman spectra of α- and *β*-S_9 are shown for comparison. As expected for allotropes, the spectra differ mainly in the region of the lattice vibrations (<100 cm^{-1}).

On heating with a rate of 2−10 K min^{-1}, solid S_9 melts at 63 °C. HPLC analysis of the rapidly cooled melt (after heating to 70 °C) dissolved in CS_2 showed that S_9 was still the dominating species. In addition, some S_7 and S_8 were detected. The thermal decomposition of other metastable sulfur allotropes like S_6 and S_{10} also proceeds rapidly at higher temperatures only (≥90 °C).[15]

Structure of Dicyanohexasulfane. The conformation of sulfur chains is governed by the so-called motif, i.e. the signs

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Table 1. Bond Lengths [pm], Angles [deg], and Torsion Angles [deg] for Dicyanohexasulfane

N1−C1	114.4(5)	N1−C1−S1	178.2(4)	N1−C1−S1−S2	138(13)
C1−S1	171.1(4)	C1−S1−S2	98.7(2)	C1−S1−S2−S3	90.12(14)
S1−S2	207.1(2)	S1−S2−S3	105.81(6)	S1−S2−S3−S4	89.76(7)
S2−S3	203.4(2)	S2−S3−S4	105.96(6)	S2−S3−S4−S5	−82.81(8)
S3−S4	207.4(2)	S3−S4−S5	104.95(6)	S3−S4−S5−S6	−94.48(7)
S4−S5	203.9(2)	S4−S5−S6	105.87(6)	S4−S5−S6−C6	81.2(2)
S5−S6	207.0(2)	S5−S6−C6	98.35(13)	S5−S6−C6−N6	−134(9)
S6−C6	170.5(4)	S6−C6−N6	177.3(4)		
C6−N6	114.6(5)				

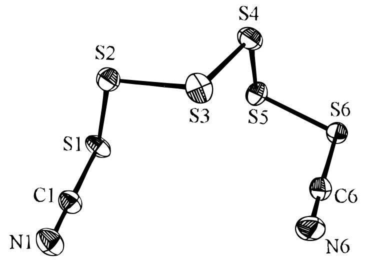
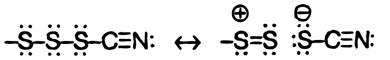


Figure 2. Structure of $S_6(CN)_2$ with atom labels (ORTEP plot with 50% probability).

of the torsional angles at the SS bonds. In the past, it had been assumed that the helix is the most stable conformation of a sulfur chain (motif + + + ... for the right-handed helix or − − − ... for the left-handed form). However, recent high-level *ab-initio* MO calculations on H_2S_4 have shown that the three conformations with motifs + + +, + + −, and + − + are practically of identical energy.[27] For a molecule with five SS bonds like $S_6(CN)_2$ there are theoretically $2^5 = 32$ possible rotamers, including enantiomers, and it can be expected that many of these exist in equilibrium in solution. However, the crystals of $S_6(CN)_2$ obtained from a *n*-hexane/carbon disulfide solution show only one conformation: a chain of motif + + − − + (Figure 2). The molecular symmetry is C_1; the geometrical parameters are given in Table 1.

The torsional angles at the SS bonds of $S_6(CN)_2$ are in the narrow range 81.2−94.5°. From the relationship between torsion angles and bond distances,[2] one would expect a narrow range of SS bond lengths also. However, the latter vary from 203.4 to 207.4 pm with a clear alternation: the terminal SS bonds are long, the neighboring ones are short, and the central bond is long again. As in the case of other dicyanosulfanes, this behavior may be rationalized by a resonance between the following structures:[23,25]



$$-\ddot{S}-\ddot{S}-\ddot{S}-C{\equiv}N: \leftrightarrow -\overset{\oplus}{S}{=}S\ \ :\overset{\ominus}{S}-C{\equiv}N:$$

The weakness of the terminal SS bonds explains why $S_6(CN)_2$ reacts as a tetrasulfane pseudohalide. The mean SS bond length (205.8 pm) of $S_6(CN)_2$ is practically identical to the single-bond value of 205 pm observed in H_2S_2 and in c-S_8.[28]

The two SCN groups of $S_6(CN)_2$ are almost linear and oriented approximately along the crystallographic *b* axis. The SCN groups of neighboring molecules are antiparallel (Figure 3). The shortest intermolecular contacts between such groups are S6−N6 = 298.0(5) pm and S1−N1 = 299.1(5) pm. These distances are about 30 pm smaller than the van der Waals distance of 330 pm.[29] It is obvious that the antiparallel direction of the CN dipoles results in attraction assisting the crystal growth process.

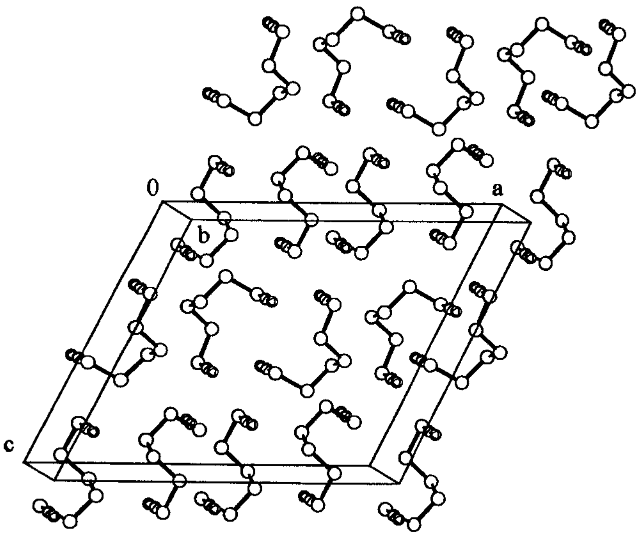


Figure 3. Molecular packing in solid $S_6(CN)_2$ showing the antiparallel orientation of neighboring SCN groups (SCHAKAL).

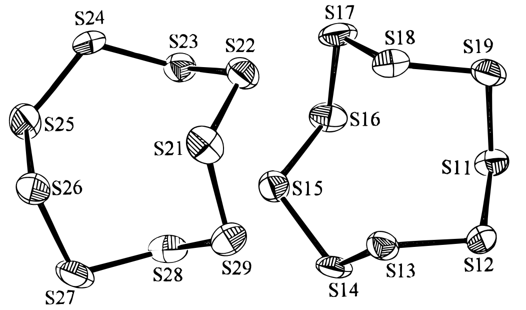


Figure 4. Structure of S_9 with atom labels (the first number of the label indicates the molecule; the second, the atom (ORTEP plot with 70% probability).

Structure of *cyclo*-Nonasulfur. α-S_9 crystallizes as a racemic mixture in the monoclinic space group $P2_1/n$. The two independent molecules in the unit cell of α-S_9 occupy sites of C_1 symmetry, but the molecular symmetry is approximately C_2 (Figure 4). The two molecules are rather similar. The motif is + + − − + + − + −, which is very different from that of S_8 (+ − + −...) but similar to that of S_{10} (+ + − + − + + − + −) and, in particular, to that of S_{12} (+ + − − + + − −...). In contrast to the highly symmetrical S_8 and S_{12} molecules in which all torsion angles have the same value (S_8 98.8°;[28] S_{12} 87.2° [30]), the absolute values of these angles in S_9 vary from 59.7 to 115.6° (Table 2). This pattern of torsion angles has been fairly well predicted by the density functional (DF)[10] and the *ab-initio* MO (HF) calculations.[11]

The internuclear distances of S_9 vary between 203.2(4) and 206.9(5) pm, with the average value of both molecules being 205.25 pm, which is practically identical to the single-bond length of 205 pm in H_2S_2.[28] As the comparison of the data in

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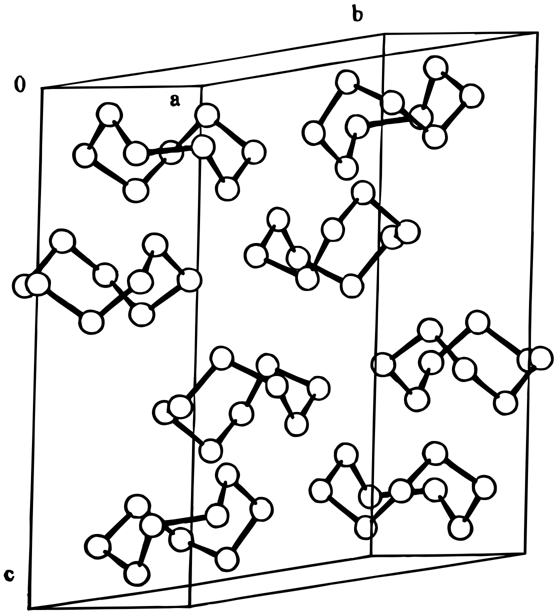

Figure 5. Unit cell of α-S_9 (SCHAKAL).

Table 2. Internuclear Distances [pm] and Bond and Torsion Angles [deg] for *cyclo*-Nonasulfur (Standard Deviations in Parentheses) As Obtained by X-ray Diffraction, by *ab-Initio* MO (HF), and by Density Functional (DF) Calculations

	molecule 1	molecule 2	HF[11]	DF[10]
S1−S2	203.9(4)	203.2(4)	204.4	209.0
S2−S3	206.5(4)	206.8(4)	207.0	211.1
S3−S4	204.8(4)	205.2(4)	205.8	210.1
S4−S5	205.2(4)	205.4(4)	205.8	210.6
S5−S6	204.8(4)	204.7(4)	205.8	210.1
S6−S7	206.8(4)	206.8(4)	207.0	211.1
S7−S8	204.5(4)	203.7(4)	204.4	209.0
S8−S9	205.0(4)	204.4(5)	205.7	210.6
S9−S1	205.9(4)	206.9(5)	205.7	210.6
S9−S1−S2	108.8(2)	109.3(2)	108.5	108
S1−S2−S3	107.4(2)	107.1(2)	107.2	108
S2−S3−S4	106.1(2)	105.4(2)	105.9	107
S3−S4−S5	107.7(2)	108.1(2)	106.8	107
S4−S5−S6	108.2(2)	108.6(2)	106.8	107
S5−S6−S7	105.8(2)	105.4(2)	105.9	107
S6−S7−S8	107.7(2)	107.2(2)	107.2	108
S7−S8−S9	109.6(2)	109.7(2)	108.5	108
S8−S9−S1	103.7(2)	103.7(2)	104.3	103
S9−S1−S2−S3	77.6(2)	77.6(2)	76.4	75
S1−S2−S3−S4	60.5(2)	59.7(2)	61.7	66
S2−S3−S4−S5	−115.6(2)	−115.4(2)	−115.4	−114
S3−S4−S5−S6	86.7(2)	86.8(2)	88.0	81
S4−S5−S6−S7	−112.9(2)	−113.0(2)	−115.4	−114
S5−S6−S7−S8	64.2(2)	64.9(2)	61.7	66
S6−S7−S8−S9	74.3(2)	73.4(2)	76.4	75
S7−S8−S9−S1	−77.3(2)	−78.6(2)	−75.3	−74
S8−S9−S1−S2	−72.9(2)	−72.7(2)	−75.3	−74

Table 2 shows, the *ab-initio* MO calculations reproduce the bond lengths particularly well while the DF method overestimates the internuclear distances by ca. 4 pm. The bond angles are equally well reproduced by both methods.

The near agreement of the average bond lengths in S_8 and S_9 explains why the mean bond energy of S_9 is only by ca. 3 kJ mol^{-1} smaller than that of S_8.[12] The formation of S_9 from S_8 by eq 7 is endothermic by only 28 ± 2 kJ mol^{-1} (116−159°C).[12]

$$^{9}/_{8}S_8 \rightarrow S_9 \tag{7}$$

Table 3. Crystal Data, Measurement of X-ray Reflections, and Structure Refinement for Dicyanohexasulfane and *cyclo*-Nonasulfur

	$S_6(CN)_2$	S_9
mol wt	244.40	288.54
a, pm	2002.4(8)	790.2(3)
b, pm	584.02(5)	1390.8(4)
c, pm	1656.8(6)	1694.8(6)
α, deg	90	90
β, deg	115.15(1)	103.26(3)
γ, deg	90	90
V, 10^6 pm^3	1753.8(10)	1812.9(11)
space group	*C*2/*c*	*P*2$_1$/*c*
Z	8	8
D(calc), g cm^{-3}	1.851	2.114
μ, mm^{-1}	1.484	2.113
F(000)	976	1152
crystal size, mm	0.4 × 0.15 × 0.05	0.6 × 0.4 × 0.03
diffractometer type	Siemens four-circle diffractometer with N_2 gas stream cooling device[35]	
radiation/wavelength, pm	Mo Kα, Nb filter/71.068	
temp, °C	−100(1)	−100(1)
scan method/steps, deg	$\omega-2\theta$/0.02−0.04	$\omega-2\theta$/0.02−0.04
scan width	$\Delta\omega = 1.42 + 0.52 \tan \omega$	$\Delta\omega = 1.90 + 0.52 \tan \omega$
$2\theta_{\min-\max}$, deg	4.50−50.10	5.3−52.0
no. of collected reflns	2477	5189
no. of unique reflns/R_{int}	1540/0.0284	3549/0.0396
no. of unique reflns with $F_o > 4\sigma(F_o)$	1088	2217
refinement	full-matrix least-squares on F^2 [36]	
no. of parameters	91	163
largest residual peak and hole in ΔF Fourier synthesis, e/10^6 pm^3	0.679 and −0.330	1.409 and −1.015
final R_{2w}[a] (all data)	0.0880	0.2211
final R[b] ($F_o > 4\sigma(F_o)$)	0.0339	0.0723

[a] $R_{2w} = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters [10^4 pm^2] for Dicyanohexasulfane

	x	*y*	*z*	*U*(eq)
N1	0.4313(2)	−0.3450(6)	0.8536(3)	0.036(1)
C1	0.4300(2)	−0.1494(7)	0.8563(3)	0.026(1)
S1	0.4303(1)	0.1435(2)	0.8595(1)	0.028(1)
S2	0.3175(1)	0.1986(2)	0.7969(1)	0.028(1)
S3	0.2827(1)	0.2043(2)	0.8957(1)	0.032(1)
S4	0.2904(1)	0.5428(2)	0.9365(1)	0.032(1)
S5	0.3981(1)	0.5856(2)	1.0241(1)	0.026(1)
S6	0.4021(1)	0.5298(2)	1.1495(1)	0.024(1)
C6	0.4040(2)	0.2380(7)	1.1492(2)	0.026(1)
N6	0.4033(2)	0.0418(6)	1.1502(2)	0.038(1)

The shortest intermolecular distances in α-S_9 amount to 338.3 (S24−S26) and 339.2 pm (S18−S25). These values are in line with the observations made with other sulfur allotropes. If for each atom of the two independent molecules the shortest distance to a neighboring molecule is considered, one finds values in the range 338.3−364.3 pm. The arithmetic mean of these 18 values is 349.3 pm, which may be used to define the van der Waals radius of sulfur in this allotrope as 174.6 pm.

Conclusion

The synthesis of S_9 reported here can be considered as a transformation of S_8 into S_9 via the following steps:

$$S_8 \rightarrow S_2Cl_2 \rightarrow S_6 \rightarrow S_4Cl_2 \rightarrow S_6(CN)_2 \rightarrow S_9$$

The thermodynamically stable allotrope of sulfur, α-S_8, is used on a large scale to produce S_2Cl_2 by treatment with chlorine. S_2Cl_2 can be transformed into S_6 (the high-pressure allotrope of sulfur) by reaction with potassium iodide (via the unstable S_2I_2).[20] Chlorination of S_6 yields S_4Cl_2, which either is used directly to make S_9 or is converted into $S_6(CN)_2$ by reaction with $Hg(SCN)_2$ and thus purified. The dicyanosulfane was

Table 5. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters [10^4 pm^2] for *cyclo*-Nonasulfur (α-S_9)

	x	*y*	*z*	*U*(eq)
S11	0.7058(4)	0.3491(2)	0.5692(2)	0.029(1)
S12	0.7788(4)	0.2412(2)	0.6514(2)	0.032(1)
S13	0.5960(4)	0.2341(2)	0.7209(2)	0.029(1)
S14	0.3639(4)	0.2045(2)	0.6420(2)	0.030(1)
S15	0.2029(4)	0.3202(2)	0.6423(2)	0.031(1)
S16	0.2484(4)	0.4180(2)	0.5593(2)	0.030(1)
S17	0.3584(4)	0.5362(2)	0.6257(2)	0.034(1)
S18	0.5922(4)	0.4943(2)	0.6968(2)	0.031(1)
S19	0.7703(4)	0.4789(2)	0.6267(2)	0.032(1)
S21	0.3948(4)	0.3811(2)	0.9448(2)	0.036(1)
S22	0.3900(3)	0.4837(2)	0.8589(2)	0.033(1)
S23	0.1365(3)	0.4933(2)	0.7919(2)	0.028(1)
S24	−0.0082(4)	0.5302(2)	0.8736(2)	0.034(1)
S25	−0.1750(4)	0.4187(2)	0.8799(2)	0.039(1)
S26	−0.0494(4)	0.3217(2)	0.9640(2)	0.035(1)
S27	−0.0202(4)	0.1995(2)	0.8990(2)	0.036(1)
S28	0.1410(4)	0.2340(2)	0.8251(2)	0.035(1)
S29	0.3903(4)	0.2467(2)	0.8922(2)	0.041(1)

found to react with Cp_2TiS_5 in a novel sulfur-transfer reaction to give S_9 and $Cp_2Ti(NCS)_2$. The latter reaction will only be the first example for the application of the many dicyanosulfanes $S_n(CN)_2$ ($n = 3-9$) for the synthesis of new sulfur compounds by reaction with titanocene polysulfide chelates.[31]

Experimental Section

Preparation of Dichlorotetrasulfane. To a solution of 500 mg (2.6 mmol) of *cyclo*-hexasulfur in 20 mL of carbon disulfide was added 7.8 mL of a chlorine solution (1.0 M) in tetrachloromethane (7.8 mmol of Cl_2). After 5 h of stirring at ambient temperature, the solvents were evaporated under vacuum and the residue was extracted with pentane (2×10 mL). The extract was evaporated to dryness at 40 °C in an oil-pump vacuum (10 min), yielding a malodorous orange-yellow oily residue (320 mg; 62%).

Preparation of Dicyanohexasulfane. To 320 mg (1.6 mmol) of crude dichlorotetrasulfane in 20 mL of carbon disulfide was added at 0 °C 637 mg (2.0 mmol) of mercury(II) rhodanide. After being stirred for 2 h, the mixture was filtered and the solvent volume reduced to 10 mL in a vacuum. To initiate crystallization, 10 mL of *n*-hexane was added and the mixture stored at −50 °C. (In the case that no crystals appear, more hexane is added. Should there be an oily liquid precipitate, small amounts of carbon disulfide are added.) The mother liquor was separated from the crystals at −50 °C using a pipet and excluding any moisture (N_2 atmosphere). The crystals were dried under vacuum allowing the temperature to rise to 20 °C. Yield: 169 mg (43%); to be stored at −50 °C. The elemental analysis agrees with expectations. Other data: ^{13}C NMR (69.68 MHz, $CDCl_3/CS_2$, 25 °C) 109.8 ppm; Raman [cm^{-1}] 2152 (40) ν_{CN}, 669 (10) ν_{CS}, 479 (100) ν_{SS}, 458 (22) ν_{SS}, 420 (43), 400 (9), 260 (23), 247 (23), 193 (35), 180 (74), 161 (20), 147 (29), 127 (10), 86 (56); IR (in KCl) [cm^{-1}] 2149 (s), 668 (m); MS (EI 70 eV, 90 °C) *m/z* 122 (B^+) S_2SCN^+, 244 (M^+). At 20 °C, solid dicyanohexasulfane starts decomposing to a polymer if handled for more than 10 min, but solutions in CS_2 are more stable (decomposition after 1 day).

Preparation of *cyclo*-Nonasulfur. To a solution of 138 mg (0.41 mmol) of titanocene pentasulfide in 10 mL of carbon disulfide was added 100 mg (0.41 mmol) of dicyanohexasulfane in 5 mL of carbon disulfide within 5 min with stirring. After 45 min of stirring, the solvent volume was reduced under vacuum to 5 mL and the mixture cooled to −22 °C. The precipitated titanocene dirhodanide (87.2 mg; 72%) was filtered off. To the filtrate was added 20 mL of toluene. Evaporation of the carbon disulfide in a vacuum followed by cooling to −22 °C for 1 day resulted in a precipitate of polymeric and unidentified sulfur, which was filtered off. Repeated cooling of the filtrate to −50 °C followed by reduction in volume afforded pure S_9: 22 mg (18%). fp 63 °C; MS (EI 70 eV, 90 °C) *m/z* 288 (13; M^+), 256 (38), 224 (55), 192 (24), 160 (60), 128 (32), 96 (35), 64 (100), 32 (14).

Structure Determination. During the single-crystal X-ray diffraction experiments, the crystals were kept at a constant temperature of −100 °C. For the dicyanohexasulfane crystal an automatic recentering of the 72 orientation reflections was used to redetermine lattice constants and cell orientation each time the intensity of one of the three check reflections dopped by more than 5%; this happened about once every 7 h. The reflection intensities were scaled according to the change in the check reflections and Lp corrected. The structure solution was obtained by direct methods.[32] The coefficients for anomalous atomic scattering[33,34] were included in the structure factor calculation for the least-squares refinement. Details regarding the crystals of the two compounds, the data collections, and the structure refinements are listed in Table 3. The atomic coordinates of $S_6(CN)_2$ and α-S_9 are given in Tables 4 and 5. For the graphic representation the programs ORTEP[37] and SCHAKAL[38] were used. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-404230 [$S_6(CN)_2$] and CSD-404231 [S_9].

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