X-Ray Structural Analyses of Cyclodecasulfur (S_{10}) and of a Cyclohexasulfur-Cyclodecasulfur Molecular Addition Compound ($S_6 \cdot S_{10}$) [1]

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Dedicated to Professor Dr. Karl Winnacker on the occasion of his 80th birthday

Low temperature X-ray structural analyses of monoclinic single crystals of S_{10} and $S_6 \cdot S_{10}$ (prepared from the components) show that the cyclic S_{10} molecule exhibits the same D_2 conformation in both compounds with bond distances between 203.3 and 208.0 pm, bond angles (a) between 103 and 111°, and torsional angles (τ) between 73 and 124°. The S_6 molecule (site symmetry C_i) in $S_6 \cdot S_{10}$ is very similar to the one in pure S_6 ($d_{SS} = 206.2$ pm, $a = 103°$, $\tau = 74°$). All intermolecular interactions are of van-der-Waals type. The Raman spectrum of $S_6 \cdot S_{10}$ can be explained by a superposition of the S_6 and S_{10} spectra.

Introduction

The tremendous industrial importance of elemental sulfur and its surplus expected for the near future (and occasionally already experienced in the past) have stimulated considerable research activities with the result that 19 well characterized sulfur allotropes are presently known; most of these compounds have been investigated by X-ray diffraction on single crystals [2]. The majority of the sulfur allotropes consists of cyclic molecules S_n ($n \geqslant 6$) which have also been shown to be important constituents of liquid sulfur [3] and – some of them – of sulfur vapor [4–6]. The molecular structures of the cyclic species S_6 [7, 8], S_7 [9], S_8 [10, 11], S_{11} [12], S_{12} [13, 14], S_{13} [15], a-S_{18} [13, 16], β-S_{18} [17] and S_{20} [13] show that two principally different classes of rings exist:

A. Highly symmetrical species with equal (or almost equal) bond distances within the molecule (S_6, S_8, S_{12}, a-S_{18})

B. Less symmetrical species with unequal and usually alternating long and short bonds within the molecule (S_7, S_{11}, S_{13}, β-S_{18}, S_{20}).

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In all cases the reason for the differing bond distances is the variation of the torsional angles leading to a varying degree of lone-pair-lone-pair repulsion between neighboring atoms. In fact, the torsional angles τ in sulfur rings S_n vary between 0° and 140° resulting in a bond length variation of 19 pm or 9% [18]. In compounds of group A all torsional angles are found within a range of 10° in each molecule; the corresponding bond distance variation amounts to less than 2.8 pm. Species belonging to group B show bond length variations of between 5 and 19 pm and torsional angle differences of up to 108° within one molecule (*e.g.* S_7).

Cyclodecasulfur S_{10} has first been prepared by Schmidt *et al.* [19] according to the equation

$$2\,(C_5H_5)_2TiS_5 + 2\,SO_2Cl_2 \rightarrow \qquad (1)$$
$$2\,(C_5H_5)_2TiCl_2 + S_{10} + SO_2$$
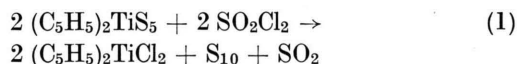
and obtained as yellow light-sensitive plate-like crystals which slowly decompose at 25 °C. Single crystals of S_{10} were first obtained in our laboratory from a solution containing S_6 and excess of trifluoroperoxoacetic acid [20]:
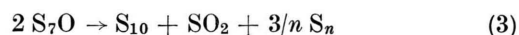
$$2\,S_6 + 4\,CF_3CO_3H \rightarrow \qquad (2)$$
$$S_{10} + 2\,SO_2 + 4\,CF_3CO_2H$$
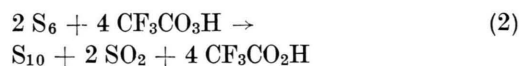
A still unidentified oxide of S_6 (presumably S_6O_2) formed as an intermediate decomposes to give S_{10},

SO$_2$ and some unsoluble sulfur. In a similar fashion S$_7$O decomposes in dichloromethane solution at 5 °C to give S$_{10}$ in low yield [21]:

$$2\,S_7O \rightarrow S_{10} + SO_2 + 3/n\,S_n \qquad (3)$$

On this occasion it was observed that S$_6$ and S$_{10}$ form a yellow crystalline addition compound of composition S$_6 \cdot$ S$_{10}$ and of melting point 92 °C. The infrared and Raman spectra of this compound indicated the presence of both molecules in the same conformations as in the pure compounds [21].

Before any structural work on S$_{10}$ had been published, several authors had suggested on theoretical grounds [22, 23] that the molecular symmetry of S$_{10}$ should be D$_{5d}$ (two sets of five atoms in two parallel planes) in analogy to S$_8$ (D$_{4d}$) and S$_6$ (D$_{3d}$). In this case S$_{10}$ would belong to the above group A. The following structure determinations of S$_{10}$ and of the S$_6 \cdot$ S$_{10}$ addition compound show that the S$_{10}$ molecule has a different and unexpected molecular structure.

Structure Determination

S$_{10}$: A single crystal of S$_{10}$ was obtained by reaction (2). The space group and approximate lattice constants were determined from deJong-Bouman and precession photographs at *ca.* —110 °C. The results showed the monoclinic space group C2/c with an unusually small angle of 37° for the normal setting, but with an angle of 110° after transformation into I2/n. Refinement of 24 Bragg angles according to the method of least squares afforded the cell constants given in Table I. 4721 reflections up to $\theta = 40°$ were measured at —110 °C on an automated Siemens four circle diffractometer and corrected in the usual way. A meaningful prediction of the structure was not achievable with direct methods and the interpretation of a Patterson syn-

Table I. Crystal data of S$_{10}$ and of S$_6 \cdot$ S$_{10}$ at —110 °C (standard deviations in brackets).

	S$_{10}$	S$_6 \cdot$ S$_{10}$
Crystal system	monoclinic	monoclinic
Space group	C2/c	I2/a
Lattice constants, *a* (pm)	1253.3(9)	1954.1(8)
b (pm)	1027.5(9)	943.1(3)
c (pm)	1277.6(9)	883.1(3)
β (°)	37.98(2)	105.11(3)
Volume of unit cell (nm³)	1.0125	
Molecules in unit cell (Z)	4	4
Calculated density (g/cm³)	2.103	2.17
Linear absorption coefficient (MoK$_\alpha$ radiation; in cm⁻¹)	20.07	20.2
Reflections measured	4721	1445
Independent reflections	2465	1269
	(all pos. imp.)	(I > 2σ)

thesis did not appear promising. However, on the basis of Raman spectroscopic measurements and symmetry considerations the possible arrangements of the atoms were so limited that the phase problem could be solved by trial and error methods and the structure refined with anisotropic temperature factors to $R = \sum_h ||F_{obs}(\vec{h})| - |F_c(\vec{h})||/\sum_h |F_{obs}(\vec{h})| = 0.039$ using the program systems X-Ray 76 and MULTAN. Corrections for absorption and extinction have been carried out.

The results are given in Tables II, III and IV and shown in Fig. 1 and 2.

The four S$_{10}$ molecules in the unit cell occupy sites of C$_2$ symmetry, but to a good approximation have the rare point group symmetry D$_2$ (three orthogonal twofold axes of rotation as the only symmetry elements). Six atoms (S1–S3–S5–S1′–S3′–S5′) are located in a plane (maximum deviation from the least squares plane 1.4 pm) while two sets of two atoms are found above or below the plane, respectively, by 123 pm.

Table II. Fractional atomic coordinates and anisotropic temperature factors (in pm²) of S$_{10}$. For numbering of atoms see Fig. 1.

Atom	x/a	y/b	z/c	U$_{11}$	U$_{22}$	U$_{33}$	U$_{12}$	U$_{13}$	U$_{23}$
S1	0.5959(1)	0.2878(1)	0.7308(1)	254(3)	194(3)	326(3)	— 7(2)	—236	36(2)
S2	0.7609(1)	0.4401(1)	0.5640(1)	218(3)	201(4)	289(3)	— 1(2)	—182	— 6(2)
S3	0.7657(1)	0.5517(1)	0.6931(1)	264(3)	253(3)	437(4)	34(3)	—297	—44(3)
S4	0.5457(1)	0.6627(1)	0.8726(1)	263(3)	314(3)	267(3)	46(3)	—216	—31(2)
S5	0.5947(1)	0.8144(1)	0.7321(1)	263(3)	209(3)	355(3)	—30(2)	—251	3(2)

Table III. Molecular parameters of S_{10}, $S_6 \cdot S_{10}$ and – for comparison – S_6 (standard deviations in brackets). For the numbering of atoms see Fig. 1.

		S_6 in $S_6 \cdot S_{10}$	S_6 [8]
Site symmetry:		C_i	D_{3d}
Bond distances (pm):	S 6–S 7	206.4(3)	
	S 7–S 8	206.2(3)	206.8(2)
	S 8–S 6^1	206.1(3)	
Bond angles:	S 8^1–S 6–S 7	102.6(1)°	
	S 6–S 7–S 8	102.1(1)°	102.61(6)°
	S 7–S 8–S 6^1	103.1(1)°	
Torsional angles:	S 8^1–S 6–S 7–S 8	− 73.5(1)°	
	S 6–S 7–S 8–S 6^1	+ 73.8(1)°	± 73.8(1)°
	S 7–S 8–S 6^1–S 7^1	− 74.2(1)°	
		S_{10} in $S_6 \cdot S_{10}$	S_{10}
Site symmetry:		C_2	C_2
Bond distances (pm):	S 1^2–S 1	204.2(3)	203.9(4)
	S 5–S 5^2	203.9(3)	203.3(4)
	S 1–S 2	208.0(3)	207.8(3)
	S 4–S 5	206.5(2)	207.1(3)
	S 2–S 3	204.7(2)	204.9(4)
	S 3–S 4	205.5(3)	204.8(3)
Bond angles (°):	S 1^2–S 1–S 2	104.9(1)	106.2(2)
	S 4–S 5–S 5^2	106.3(1)	108.0(2)
	S 1–S 2–S 3	105.2(1)	103.5(2)
	S 3–S 4–S 5	103.7(1)	103.4(2)
	S 2–S 3–S 4	111.4(1)	110.2(2)
Torsional angles (°):	S 2^2–S 1^2–S 1–S 2	− 77.8(1)	− 76.8(1)
	S 4–S 5–S 5^2–S 4^2	− 73.1(1)	− 75.4(1)
	S 1^2–S 1–S 2–S 3	123.2(1)	123.7(1)
	S 3–S 4–S 5–S 5^2	121.7(1)	121.5(1)
	S 1–S 2–S 3–S 4	− 77.6(1)	− 78.4(1)
	S 2–S 3–S 4–S 5	− 83.2(1)	− 78.7(1)

Table IV. Intermolecular distances < 350 pm in S_{10} crystals (in pm; standard deviation 0.4 pm) [24].

Contact	Distance	Symmetry Operation
S 3···S 5	323.1	
S 1···S 3	324.0	
S 1···S 2	329.1	$1—x, y, 3/2—z$
S 4···S 5	332.0	
S 2···S 4	336.0	
S 4···S 5	348.9	$x \pm 1/2,\ 3/2—y,\ z \mp 1/2$
S 1···S 2	349.7	$3/2—x,\ 1/2—y,\ 1—z$

Fig. 1. Conformation of the molecules in S_{10} (cyclodecasulfur) and $S_6 \cdot S_{10}$ (molecular addition compound) and numbering of atoms. In the case of the S_{10} molecules atom S 1^2 (S 2^2, ...) is generated from S 1 (S 2, ...) by rotation about the twofold axis bisecting the bonds S 1–S 1^2 and S 5–S 5^2. In the case of the S_6 molecule atom S 6^1 (S 7^1, S 8^1) is generated from S 6 (S 7, S 8), by inversion at the center of symmetry.
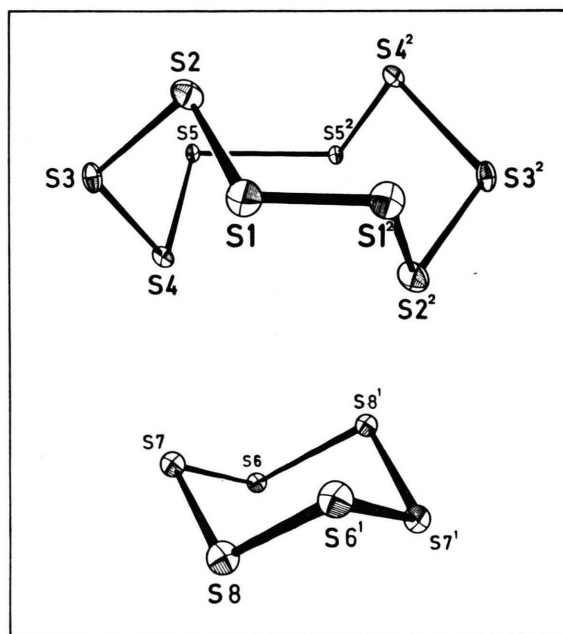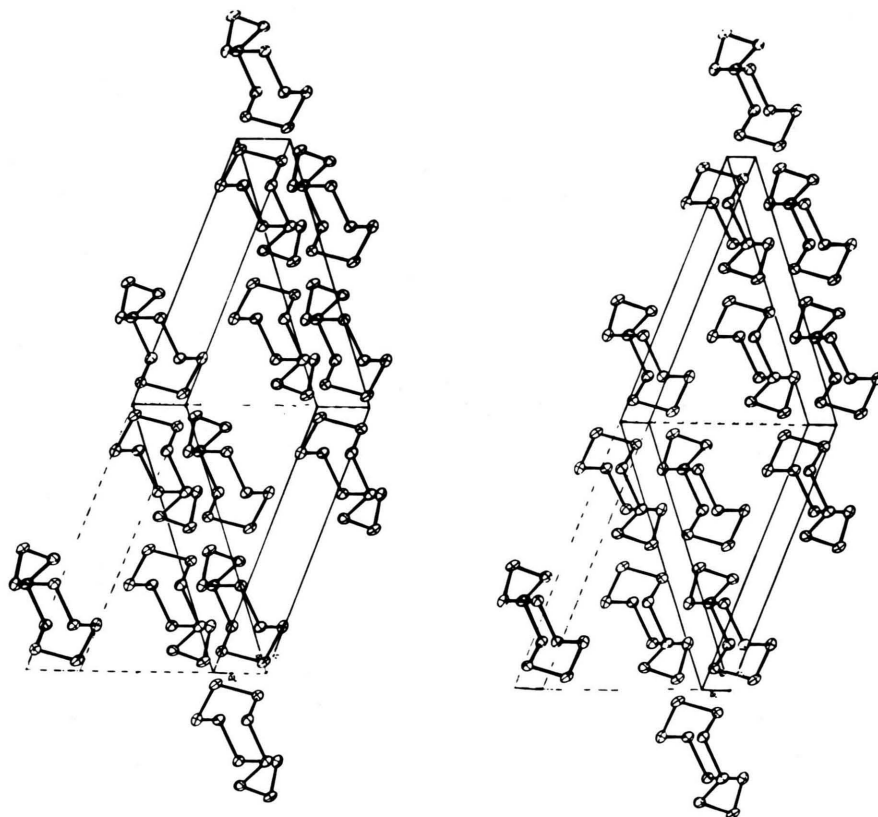
Fig. 2. Stereoscopic view of the crystal lattice of S_{10} (solid lines: unit cell in the space group $C\,2/c$; broken lines: unit cell in the space group $I\,2/n$).

$S_6 \cdot S_{10}$. A suitable single crystal of $S_6 \cdot S_{10}$ was grown from a CS_2 solution of the components at 10 °C (see Experimental) and was obtained as a monoclinic prism of dimensions $0.25 \times 0.20 \times 0.05$ mm. The lattice constants were determined from 15 reflections ($10^0 \leqslant 2\theta \leqslant 20^0$) at -110 °C and are given in Table I. The intensities of 1445 reflections were measured using a Syntex $P2_1$ automated four circle diffractometer at -110 °C. The lattice constants, the systematic extinctions and the distri-

bution of the normalized structure factors (E) led to the space group $I\,2/a$ (an alternative setting of $C\,2/n$). From the experimental density of 2.14 g/cm³ (20 °C) the unit cell content of four molecules $S_6 \cdot S_{10}$ was obtained. The structure was solved by direct methods using the programs SHELX 76 and MULTAN, the atomic coordinates were calculated by the X-RAY 76 program system. The final R value for 1269 independent reflections amounted to 0.048. No absorption correction was carried out.

Table V. Fractional atomic coordinates and anisotropic temperature factors (in pm²) of $S_6 \cdot S_{10}$ (space group $I\,2/a$; for numbering of atoms see Fig. 1).

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S 1	0.19995(9)	0.27051(18)	0.01505(22)	187(9)	114(9)	243(10)	—12(6)	+ 90(7)	—17(7)
S 2	0.19912(9)	0.43643(19)	0.16974(20)	253(9)	139(9)	152(8)	+37(7)	+ 67(6)	+12(7)
S 3	0.11820(9)	0.56635(19)	0.05509(20)	207(9)	143(9)	186(9)	+14(7)	+100(7)	+28(7)
S 4	0.14744(9)	0.68845(19)	—0.11040(20)	229(9)	156(9)	137(8)	—28(7)	+ 54(7)	+ 9(7)
S 5	0.20037(9)	0.85730(19)	0.01703(22)	206(9)	119(9)	236(10)	+ 3(6)	+ 63(7)	—41(7)
S 6	0.03845(9)	0.44632(20)	0.33035(21)	268(10)	155(9)	186(9)	—17(7)	+132(7)	— 6(7)
S 7	0.02108(9)	0.30167(19)	0.49180(21)	260(9)	100(8)	182(9)	— 3(7)	+ 83(7)	+ 1(7)
S 8	0.04652(9)	0.41784(19)	0.69666(21)	291(10)	129(9)	146(9)	+ 1(7)	+ 32(7)	+ 2(7)

The results are given in Tables III, V and VI and shown in Fig. 1 and 3.

Table VI. Intermolecular distances < 360 pm in S$_6$ · S$_{10}$ crystals (in pm; standard deviation 0.3 pm; symmetry operations in brackets) [24].

a) between S$_6$ and S$_{10}$ molecules

S4···S8	339.9	$(x, y, z-1)$
S3···S6	340.5	
S3···S8	341.1	$(x, y, z-1)$
S3···S7	345.2	$(-x, 1/2+y, 1/2-z)$
S1···S7	351.4	$(x, 1/2-y, z-1/2)$

b) between S$_6$ molecules

S7···S8	346.5	$(x, 1/2-y, z-1/2)$

c) between S$_{10}$ molecules

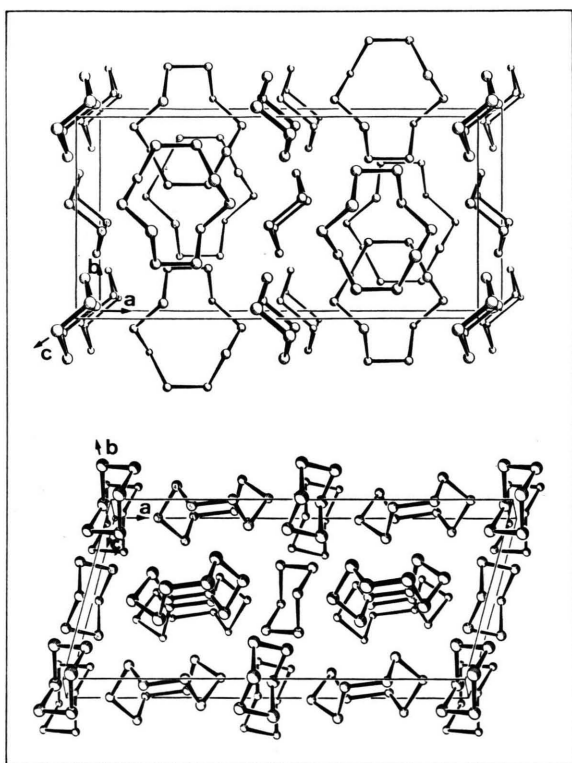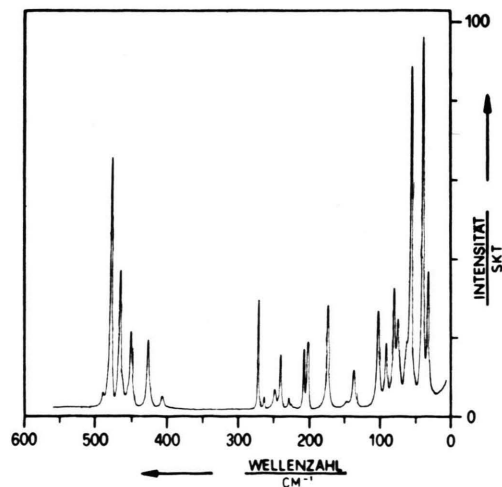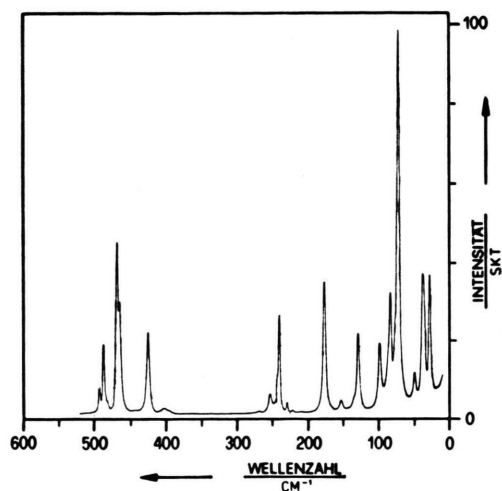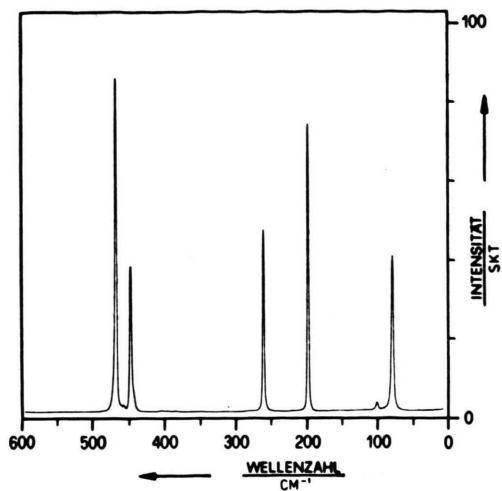|		
S2···S5	353.0	$(1/2-x, 3/2-y, 1/2-z)$
S1···S2	354.8	$(1/2-x, 1/2-y, 1/2-z)$

Fig. 3. Two views of the crystal lattice of S$_6$ · S$_{10}$ (top: projection on the plane a/b; bottom: projection onto the plane a/c).

Fig. 4. Raman spectra of solid S$_6$ (top), S$_{10}$ (middle) and S$_6$ · S$_{10}$ (bottom) at -80 to -100 °C (Cary 82 Raman spectrometer with triple monochromator; spectral slit width 1.3–1.5 cm^{-1}). For wavenumbers see Table VII.

The molecules S_6 and S_{10} in $S_6 \cdot S_{10}$ exhibit exactly the same molecular conformations as in pure S_6 (D_{3d}) and pure S_{10} (D_2). The site symmetry of the S_6 component is, however, only C_i compared to D_{3d} in pure S_6 [7]. The lattice of $S_6 \cdot S_{10}$ consists of alternating layers of S_6 and S_{10} molecules, respectively. The twofold screw axes and the center of symmetry of the space group $I2/a$ are found within the S_6 layers while the S_{10} layer contains the twofold rotation axes and further centers of symmetry. The glide planes are perpendicular to these layers. As in pure S_{10} both enantiomorphic molecules of S_{10} are present in equal amounts (generated by inversion).

The four shortest intermolecular distances (339.9–345.2 pm) are found between S_6 and S_{10} molecules (Table VI). The shortest contacts between S_6 molecules amount to 346.5 pm and between S_{10} molecules 353.0 pm. The calculated density of $S_6 \cdot S_{10}$ (2.17 g/cm³ at —110 °C) is halfway between the densities of pure S_6 (2.26 g/cm³ at —90 °C [8]) and of pure S_{10} (2.10 g/cm³ at —110 °C).

Vibrational Spectra

Fig. 4 shows the Raman spectra of solid S_6, S_{10} and $S_6 \cdot S_{10}$ at —90 °C using the red line of a krypton laser which does not initiate any photodecomposition of these light-sensitive compounds. The vibrational spectrum of S_6 has been thoroughly analyzed [25, 26] and the same holds for S_7 [27], S_8 [28, 29] and S_{12} [29, 30]. From these results it is known that the Raman lines of sulfur rings can be used to detect these species in mixtures [3]. In fact, the spectrum of $S_6 \cdot S_{10}$ shows the presence of S_6 and S_{10} and since the relative intensities of the S_6 and S_{10} lines, respectively, were always the same with different samples, the molecular composition must be constant and therefore $S_6 \cdot S_{10}$ is not a mixed crystal but a well defined stoichiometric compound. A closer inspection of the $S_6 \cdot S_{10}$ spectrum shows, however, that the S_6 line at 203 cm⁻¹ (originating from a doubly degenerate e_g vibration) is split into a doublet (201/207 cm⁻¹) as a result of the non-degenerate site symmetry C_i of the S_6 molecule in $S_6 \cdot S_{10}$ compared with D_{3d} in pure S_6. On the other hand, the rule of mutual exclusion of the normal modes as a consequence of the center of symmetry holds both for S_6 and for S_6 in $S_6 \cdot S_{10}$ (see Table VII). The S_{10} molecule is of C_2 symmetry

Table VII. Raman and infrared spectra of solid S_6, S_{10} and $S_6 \cdot S_{10}$ (wavenumbers in cm⁻¹; IR spectra as CsI discs at 25 °C; Perkin-Elmer IR spectrometer 325; Raman intensities in brackets; abbrev.: vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder).

Raman			IR		
S_6	S_{10}	$S_6 \cdot S_{10}$	S_6	S_{10}	$S_6 \cdot S_{10}$
	495(6)				
	487(16)	489(4)		482 w	483 w
	481 sh	479(69)			
471(100)	469(36)	466(38)	463 s	456 vw	461 vs
461(2)	466 sh	461 sh			
		455 sh			
451(44)		451(21)			
	425(18)	428(19)			
	403(2)	408(4)			
			390 vw		387 vw
			313 s		315 sh
					310 m
		272(31)			
266(55)	255(5)	265(3)			264 vw
	246 sh	249(6)			
	243(24)	240(15)		244 sh	242 vs
				239 vs	240 sh
	231(3)	228(3)		226 sh	231 sh
		225(1)		220 s	221 m
		207(17)			211 s
203(86)		201(19)		204 m–s	207 sh
					201 sh
	178(31)	172(29)	180 s		
	155(2)	145(3)			
	131(20)	136(10)			
106(3)	100(19)	103(26)			
		92(17)			
84(46)	85(33)	81(31)			
	73(100)	76(23)			
		64 sh			
	51(6)	58(92)			
	39(37)	42(100)			
	29(26)	34(34)			

both in pure S_{10} and in $S_6 \cdot S_{10}$ but the molecular parameters show that approximately the symmetry D_2 holds. In this case all 24 fundamental vibrations of S_{10} (7 a, 6 b_1, 5 b_2, 6 b_3) are allowed in the Raman spectrum and all excepting the 7 a vibrations are active in the infrared. The stretching vibrations of S_6, S_{10} and $S_6 \cdot S_{10}$ occur in the region 390–500 cm⁻¹, the bending modes as well as the single torsional vibration of S_6 are found in the region 110–320 cm⁻¹, while at lower wavenumbers the lattice modes and the torsional modes of the S_{10} molecule are to be expected.

Discussion

With the present structure determination, 14 sulfur allotropes consisting of cyclic molecules have now been characterized by complete X-ray structural analysis. The rings found in this way are shown in Fig. 5 together with the helical chain of stretched or high pressure induced polymeric sulfur [10]. As can be seen, S_{18} is the only ring existing in two different conformations: α-S_{18} ("*endo*-S_{18}") and β-S_{18} ("*exo*-S_{18}"). Although the rotational barrier in sulfur rings is low (15–20 kJ/mol [18]) conformational isomerization has never been observed and the structures of S_6, S_{10} and $S_6 \cdot S_{10}$ show once more that the two molecules S_6 and S_{10} exist in identical conformations in different lattices as has been observed in the case of S_8 [10] and S_7 [9]. Table VIII shows that even the mean bond distances of S_6 and S_{10} are almost identical in the two sets of compounds.

Table VIII. Mean bond parameters of the S_6 and S_{10} molecules in pure S_6, pure S_{10} and the compound $S_6 \cdot S_{10}$ (d_{SS} bond distance in pm, α bond angle, $|\tau|$ absolute value of the torsional angle).

Molecule	S_6		S_{10}	
Compound	S_6 [8]	$S_6 \cdot S_{10}$	S_{10}	$S_6 \cdot S_{10}$
d_{SS}	206.8	206.2	205.6	205.8
α	102.6°	102.6°	106.2°	106.3°
$|\tau|$	73.8°	73.8°	95.7°	96.2°

Since the mean bond distance of S_{10} is very close to that of S_8 (204.8 pm [11]) its mean bond energy should also be close to the S_8 value (264 kJ/mol). Therefore, the enthalpy of formation of gaseous S_{10} from gaseous S_8 must be quite small. In the case of S_6 ($\bar{d}_{SS} = 206.8$ pm [8]) and S_7 ($\bar{d}_{SS} = 206.8$ pm [9]) a difference of 2 pm in the mean bond distances $\bar{d}$ compared with the S_8 value corresponds to a difference in the mean bond energies of 4 kJ/mol per bond [8]. The smaller difference of 0.9 pm in the case of S_{10} ($\bar{d}_{SS} = 205.7$ pm, see Table VIII) indicates an even smaller bond energy difference (estimated as 2 kJ/mol per bond).

The conformation of the S_{10} molecule is similar to the one of S_{12} in so far as the atoms are located in *three* parallel planes (rather than *two* as in S_6 and S_8). In fact, S_{10} can formally be composed of two identical S_5 units cut from the S_{12} molecule (left and right halves of the molecule in Fig. 1). The mean bond distance of S_{12} (205.2 pm [14]) is only slightly smaller than the S_{10} value. The torsional angles of S_{10} are partly smaller (75°) and partly larger (124°) than the optimum value of 90–100° resulting in a distribution of the bond lengths between 203.3 and 207.8 pm. The molecule therefore belongs to the group B defined in the Introduction. The bond distances clearly alternate around the ring (symmetrically to the C_2 axis through atoms $S3$ and $S3^2$) and the longest bonds are those whose dihedral angles deviate most from the optimum value. The observation [2, 31] that the length d_2 of a particular bond in an S_n molecule is a function of the arithmetic mean $1/2\,(d_1 + d_3)$ of the distances

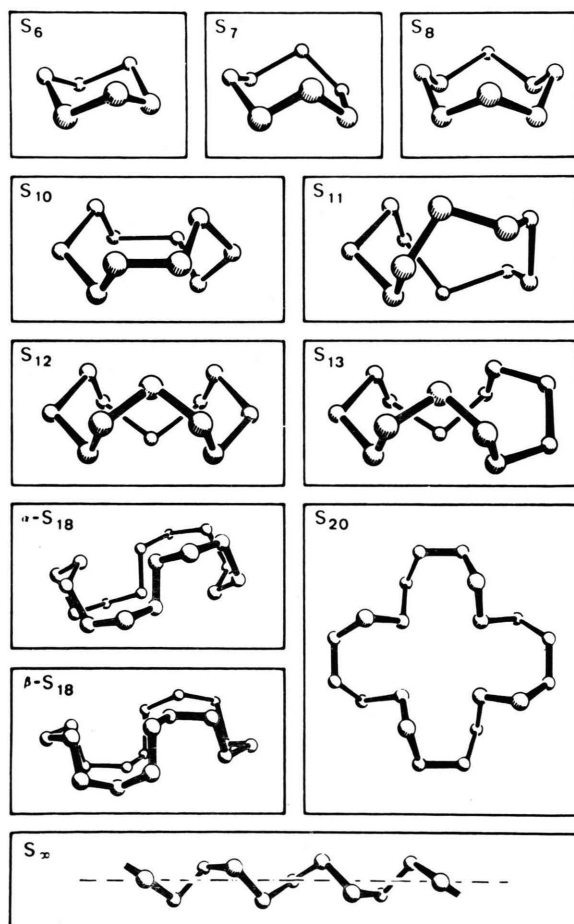

Fig. 5. Molecular structures of the homocyclic sulfur molecules S_n ($n = 6, 7, 8, 10, 11, 12, 13, 18, 20$) [7–17] and of polymeric sulfur S_∞ (helical chain [10]) according to X-ray structural analyses.

of the two neighboring bonds, d_1 and d_3, also holds for S_{10}.

The question why the S_{10} molecule does not exhibit the symmetrical structure of D_{5d} symmetry mentioned above can now be answered. For such symmetrical species the torsional angle is a function of the ring size and the bond angle a according to the following relationship [32] (n is the number of atoms per molecule):

$$\cos \tau = \frac{1 - \cos a - 2 \cos (2\,\pi/n)}{1 + \cos a}$$

A bond angle of 107° would lead to a torsional angle of $\pm$ 117° which in turn would result in (ten equal) bond distances of about 207 pm [18]. This value is larger and therefore less favorable energetically than the experimental mean bond length discussed above.

Experimental

Preparation of S_{10} from $(C_5H_5)_2TiS_5$ and SO_2Cl_2 (improved procedure): 67 g of titanocenepentasulfide [33] dissolved in 2.4 l CS_2 are cooled to 0 °C and a solution of 16 ml SO_2Cl_2 in 80 ml CS_2 is added dropwise within 20 min. The stirring is continued for another 30 min at 0 °C and after filtration the orange-red solution is evaporated in a vacuum to a volume of 1 l. Addition of 2 l CH_2Cl_2 results in a precipitation which is removed by filtration. Cooling of the filtrate to —78 °C initiates crystallization of 15 g crude S_{10} within 1–2 days. The crystals are isolated by filtration, washed with 50 ml n-pentane and recrystallized from 1 l CS_2 by addition of n-pentane till a little precipitation occurs and subsequent cooling to —78 °C for 1 day.

Yield: 12 g S_{10}. The purity was checked by Raman spectroscopy and no other rings S_n could be detected.

Preparation of S_{10} from S_6: 6.25 ml H_2O_2 (80%; density 1.36 g/cm³) are added to 152 ml CH_2Cl_2 (purified by filtration through a column filled with basic Al_2O_3), shaken to generate an emulsion and 40.9 ml $(CF_3CO)_2O$ (density 1.51 g/cm³) are added dropwise with vigorous stirring at 0 °C. After removal of the ice bath the stirring is continued till all H_2O_2 droplets have dissolved. Concentration of CF_3CO_3H: 1 mol/l; immediate use of the solution is recommended. – 10 g S_6 dissolved in 1.9 l CH_2Cl_2 are cooled to 0 °C and 100 ml of the above CF_3CO_3H solution are added dropwise within 20 min. The stirring is continued for further 1.5 h at 0 °C and the solution is then kept for 2 days at +5 °C followed by 2 days at —50 °C. The precipitate of S_{10} crystals and powder-like polymeric sulfur is vigorously shaken and rapidly filtered through a D2 glass frit. 0.91 g of crude S_{10} is collected on the frit, washed with 200 ml cold CH_2Cl_2 (5 °C) and recrystallized from as little as possible CH_2Cl_2 (ca. 1.8 l) by dissolution at 25 °C and cooling at —50 °C. Yield: 0.68 g S_{10}.

Preparation of $S_6 \cdot S_{10}$: 25 ml CS_2 and 1.00 g S_{10} are stirred magnetically at 20 °C for 15 min followed by decantation from the undissolved S_{10}. After addition of 4.50 g S_6 to the solution, stirring for 15 min at 20 °C and decantation from undissolved S_6 the solution is cooled to —20 °C resulting in the crystallization of intense orange hexagonal plate-like crystals which are isolated after 12 h, washed with n-pentane and dried in a vacuum. Yield: 1.28 g $S_6 \cdot S_{10}$. Properties: Melting point 92 °C (dec.); density 2.14 g/cm³ (by flotation at 20 °C); relative molecular mass in CS_2 at 20 °C (osmometrically): 258 (indicating complete dissociation to S_6 and S_{10}); the compound can be stored at 20 °C for several days, at —30 °C for several months without decomposition.

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