

Isomers among the carbon sulfides C_4S_6 —synthesis and crystal structures of α,α - C_4S_6 , α,β - C_4S_6 , and of a second polymorph of the diiodine adduct α,β - $C_4S_6 \cdot I_2$

Johannes Beck,* Jörg Daniels, Albrecht Roloff and Norbert Wagner

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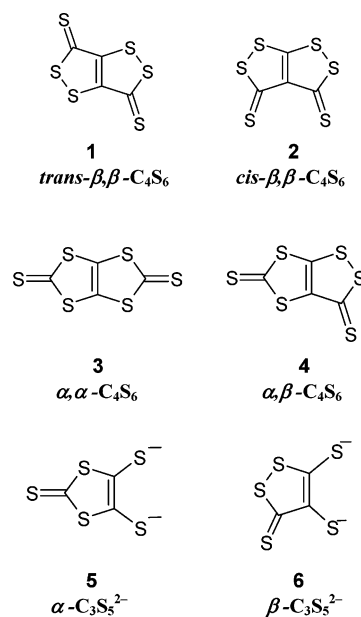
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The reaction of the α and β forms of $C_3S_5^{2-}$ with thiophosgene yields two isomeric carbon sulfides α,α - C_4S_6 and α,β - C_4S_6 , respectively. The crystal structures of both compounds could be determined for the first time. Both structures are made up of almost planar molecules. The α,α -isomer (1,3-dithiolo-(4,5-*d*)-1,3-dithiol-2,5-dithione) is D_{2h} -symmetric, while the α,β -isomer is approximately C_s -symmetric. In the molecules of both isomers the two different C_3S_5 units are retained without significant alterations of structural parameters. α,α - C_4S_6 is unstable with respect to α,β - C_4S_6 . The molecular rearrangement can be induced by a short thermal treatment at 150 °C. Significant differences are found in the mass spectra fragmentation patterns. Only α,β - C_4S_6 shows an intense signal for $C_3S_5^+$ and is therefore a potential source for the synthesis of carbon subsulfide *via* flash vacuum pyrolysis. Only α,β - C_4S_6 forms a stable adduct with I_2 . α,β - $C_4S_6 \cdot I_2$ was already known (F. L. Lu, K. M. Keshavarz-K, G. Srdanov, R. H. Jacobson and F. Wudl, *J. Org. Chem.*, 1989, **54**, 2165, ref. 19), but a second polymorph is formed on crystallisation from a different solvent. The two polymorphic forms do not show differences in the structures of the individual molecules but show a different packing pattern. α,β - $C_4S_6 \cdot I_2$ is remarkably thermally stable. Thermal analysis shows that I_2 cleavage occurs in that temperature region above 200 °C when C–S bonds are broken and CS_2 and I_2 are simultaneously liberated. Performed at 270 °C thermolysis of α,β - $C_4S_6 \cdot I_2$ yields under cleavage of I_2 and CS_2 a black polymeric carbon sulfide $(CS)_x$ which is probably a mixture of graphitic carbon and unidentified amorphous polymeric carbon sulfides.

Introduction

Carbon sulfides are a class of binary compounds with remarkable features. Among the neutral species the composition ranges from the most sulfur-rich representative, carbon disulfide CS_2 , to the most carbon-rich compound, carbon subsulfide C_3S_2 , both forming linearly shaped molecules. Between these two compositions a large number of carbon sulfides exist. Most of them are deeply colored and of planar molecular shape, indicating expanded π electron systems. Essential progress has been achieved in the last decade by the work of Rauchfuss *et al.*^{1–5} Besides the molecular compounds, polymeric carbon sulfides, commonly with compositions like $(C_3S_5)_n$,¹ $(C_3S_2)_n$ ^{6,7} or $(CS_2)_n$ ^{8,9} are known. Polymeric $(\alpha-C_3S_5)_n$ has found a role as a synthon in organic syntheses.¹⁰ These polymers are generally poorly characterized, mainly due to their lack of crystallinity.

Based on a bicyclic molecular tetrathiapentalene system consisting of two condensed five-membered rings, four isomers are possible for a carbon sulfide of the formula C_4S_6 and are shown in Scheme 1. Two of these isomers are well known. 1,2-Dithiolo-(4,3-*c*)-1,2-dithiol-3,6-dithione (**1**) was first prepared by sulfuration of thiofumaric esters with P_4S_{10} .¹¹ Later an improved synthesis from hexachlorobutadiene, sulfur and sodium sulfide



Scheme 1

was published.¹² The crystal structure determination showed the planarity of the molecule.¹³ Compound **2**, the *cis* isomer of **1**, is still unknown, but its monooxo derivative C_4S_5O has been synthesized and structurally characterized.¹⁴ The centrosymmetric

Institute for Inorganic Chemistry, University of Bonn, Gerhard-Domagk-Str. 1, D-53121, Bonn, Germany. E-mail: j.beck@uni-bonn.de; Fax: + 49 228 73 5660

1,3-dithiolo-(4,5-*d*)-1,3-dithiol-2,5-dithione (**3**) has been obtained in different ways. With thiophosgene α -C₃S₅²⁻ (**5**)[†], obtained by electrochemical reduction of CS₂, gives **3** as an orange solid of mp 240.5–242 °C.¹⁵ With thiophosgene the complex [Zn(α -C₃S₅)₂]²⁻ yields **3** as a compound of mp 254–256 °C.¹⁶ **3** can also be obtained from the respective tetrathiapentalene dione C₃S₄O₂ by sulfuration with neat B₂S₃ at 100 °C as a yellow solid of mp 207–210 °C.¹⁷ The significant discrepancies in the reported melting points have not been explained to this day. Compound **4** is the isomer of lowest symmetry. Its synthesis from β -C₃S₅²⁻ (**6**) with thiophosgene has been described¹⁸ and it has been prepared by flash vacuum pyrolysis of the fulvalene derivate C₆H₄S₆.¹⁹ The difficulties in obtaining single crystals of **4** are described, and only the structure of the diiodine adduct **4**·I₂ could be determined.¹⁹

We report here on the synthesis, properties and structure determinations of α , α -C₄S₆ (**3**), of α , β -C₄S₆ (**4**), and of a second crystalline polymorph for the diiodine adduct of **4**.

Experimental

Infrared spectra were recorded with a Bruker IFS113 spectrometer, ¹³C NMR spectra were obtained using a Bruker DPX 300 instrument. Powder diffractograms were recorded with a Stoe STADIP diffractometer equipped with Cu K α radiation and a position sensitive detector in thin layer transmission technique. Thermoanalytical measurements were performed with a Netzsch STA429 instrument under a continuous flow of argon. Raman spectra were recorded with a Bruker RFS100 instrument. The laser used was a Nd:YAG laser operated at 1064 nm and an output power of 100 mW. UV/VIS spectra were recorded in toluene solution using a Gröbel diode array spectrometer. Na₂(α -C₃S₅) was prepared according to literature methods and transformed to Na₂(β -C₃S₅) by heating the crude reaction mixture to 140 °C.²⁰ Thiophosgene was used as obtained (ALDRICH).

α , α -C₄S₆ (**3**)

Na₂(α -C₃S₅) (1 g, 4.1 mmol) was suspended in 70 ml of dry THF and 0.5 g thiophosgene (4.3 mmol), dissolved in 50 ml THF was added dropwise. The temperature of the reaction mixture was kept below 10 °C using an ice bath. The reaction mixture turned dark during this process. The mixture was stirred for 16 h at ambient temperature, the precipitate was separated by filtration and thoroughly washed with water, ethanol, THF and ether. After drying *in vacuo* there remained 0.6 g of a yellow, crystalline powder (yield 60%). Melting point > 280 °C (decomp.). IR (KBr): ν = 1506 cm⁻¹ (w), 1188 (m), 1060 (vs), 952 (vs), 890 (w), 765 (s), 488 (w). MS (70 eV): m/z (%) = 240(10)[M⁺], 164(3) [M⁺ – CS₂], 88(5)[C₂S₂⁺], 76(100) [CS₂⁺], 64(5)[S₂⁺]. ¹³C NMR [DMF]: δ = 198, 120. Elemental analysis: Found C, 21.0; S, 79.7; H, 0.2, C₄S₆ (M_r = 240.40) requires C, 20.0, S, 80.0, H 0.0%.

[†] It was Rauchfuss who introduced the designators α and β for the two forms **5** and **6** of C₃S₅²⁻ (Scheme 1 and ref. 2). These designators can be applied to assign related molecules. If the characteristic five-membered heterocycle 1,3-dithiol-2-thione is present this part of the molecule is assigned to be of the α type, if 1,2-dithiol-3-thione is present the designator β is used.

α , β -C₄S₆ (**4**)

Na₂(β -C₃S₅) was converted with thiophosgene to α , β -C₄S₆ (**4**) as described above for α , α -C₄S₆ (**3**). Instead of filtering the reaction mixture was evaporated to dryness and the dark residue was extracted several times with hot toluene. **4** crystallizes in form of shiny dark-brown to dark-red needles in an overall yield of 70%. Melting point after recrystallization from toluene 199–200 °C. IR and mass spectra are identical to those in ref. 19. IR(KBr): ν = 1432cm⁻¹ (s), 1291 (s), 1062/1055 (vs), 963 (s), 876 (m), 828 (w), 729 (w), 607 (vw), 486 (m). MS (70 eV): m/z (%) = 240(100)[M⁺], 164(20) [M⁺ – CS₂], 132(5) [M⁺ – CS₃], 100(45) [C₃S₂⁺], 88(18) [C₂S₂⁺], 76(10) [CS₂⁺], 64(5) [S₂⁺]. ¹³C NMR [DMF]: δ = 215, 198, 162, 147; [DMSO]: 217, 199, 163, 147. Elemental analysis: Found C, 20.7; S, 79.2; H, 0.2, C₄S₆I₂ (M_r = 494.21) requires C, 20.0, S, 80.0, H 0.0%.

α , β -C₄S₆·I₂ (**4**·I₂)

To a saturated solution of **4** in CS₂ a solution of I₂ in the same solvent was added. Immediately a crystalline precipitation occurred and cooling to 0 °C afforded black, lustrous crystals of **4**·I₂ in almost quantitative yield in the form of flat needles which are dark red in transmitted light. Melting point 227 °C. IR (KBr): ν = 1496 cm⁻¹ (vw), 1394 (s), 1308 (m), 1072/1063 (s), 980 (s), 882 (w), 799 (w), 721 (w), 493/484 (m). Elemental analysis: Found C, 9.8; S, 39.2; H, 0.3, C₄S₆ (M_r = 240.40) requires C, 9.7, S, 38.9, H 0.0%; I, 51.4.

Crystal structure determinations

Data sets were recorded with a Nonius kappa-CCD diffractometer using Mo K α radiation for **3** and **4**, and with a Nonius CAD4 diffractometer using Cu K α radiation for **4**·I₂. Crystal systems and space groups were unequivocally derived from the data sets and reciprocal space images. Analytical absorption corrections were applied to all data sets. The crystal structures were solved by direct methods²¹ and refined based on full matrix least squares with anisotropic displacement factors for all atoms.²² Table 1 contains the crystallographic data and details of data collections and refinements, Table 2 selected bond lengths and angles. CCDC reference numbers 281527 (α , β -C₄S₆·I₂-II), 281528 (α , α -C₄S₆) and 281529 (α , β -C₄S₆). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511746a

Results and discussion

The two isomeric carbon sulfides α , α -C₄S₆ (**3**) and α , β -C₄S₆ (**4**) can be obtained by the reaction of the α and β form of C₃S₅²⁻, respectively, with thiophosgene in good yields.

We obtained α , α -C₄S₆ (**3**) by the reaction of α -C₃S₅²⁻ with thiophosgene as a yellow powder of low crystallinity as indicated by broad and weak reflections in the powder X-ray diffractogram. Single crystals of **3** are difficult to obtain. The solubility in all organic solvents is very low but just sufficient for NMR spectroscopy and crystal growth. According to the D_{2h} point symmetry of the molecule only two ¹³C resonances at 120 and 198 (C=S) ppm are expected. The grade of crystallinity of **3** can be enhanced by prolonged exposition to carbon disulfide at room temperature. If the crude material is extracted in a Soxhlet

Table 1 Crystal data and details of data collection and refinement of α,α -C₄S₆ (**3**), α,β -C₄S₆ (**4**), and α,β -C₄S₆·I₂-II (**4**·I₂)

Formula	α,α -C ₄ S ₆	α,β -C ₄ S ₆	α,β -C ₄ S ₆ ·I ₂ -II
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Unit cell dimensions (pm, °)	$a = 580.5(1)$ $b = 636.8(1)$ $c = 1043.1(1)$ $\beta = 102.55(1)$	$a = 764.4(1)$ $b = 1045.9(1)$ $c = 990.1(1)$ $\beta = 105.92(3)$	$a = 1544.3(4)$ $b = 992.2(2)$ $c = 1637.5(5)$ $\beta = 116.79(2)^\circ$
$10^{-6} \times$ Unit cell volume/pm ³	392.3	761.21	2239.7
Number of formula units	$Z = 2$	$Z = 4$	$Z = 8$
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	2.035	2.098	2.931
Absorption coefficient μ/cm^{-1}	16.5 (Mo-K α)	17.0 (Mo-K α)	541.4 (Cu-K α)
Range of data collection	$2\theta < 55.0^\circ$	$2\theta < 48.8^\circ$	$2\theta < 108.0^\circ$
Measured reflections	10994	18274	6072
Independent reflections, R_{int}	899, 0.038	1224, 0.096	1359, 0.046
Reflections in least squares	895	1224	1359
Refinement parameters	46	92	109
$wR(F^2)$	0.068	0.1020	0.119
$R(F)$ for [number] of reflections with $I > 4\sigma(F)$	0.025 [807]	0.060 [1116]	0.046 [1132]
$10^{-6} \times$ Residual electron density/ $e \text{ pm}^{-3}$	+0.41/−0.27	+0.44/−0.42	+2.02/−1.80

Table 2 Selected distances and angles in the structures of α,α -C₄S₆ (**3**), α,β -C₄S₆ (**4**), and α,β -C₄S₆·I₂-II (**4**·I₂)

α,α -C ₄ S ₆ distances/pm			
C1–C1'	135.3(4)	C2–S1	173.9(2)
C1–S1	173.3(2)	C2–S2	173.2(2)
C1–S2'	173.3(2)	C2–S3	164.5(2)
Angles/°			
S1–C1–S2'	126.2(1)	S1–C2–S2	114.6(1)
S1–C1–C1'	117.0(2)	S1–C2–S3	122.9(1)
S2'–C1–C1'	116.8(2)	S2–C2–S3	122.5(1)
C1–S1–C2	95.7(1)		
α,β -C ₄ S ₆ distances/pm			
C1–C3	135.5(8)	C3–S2	1.727(6)
C1–S1	172.6(6)	C4–S4	1.646(6)
C1–S6	173.1(6)	C4–S5	1.744(6)
C2–S1	175.6(6)	S5–S6	2.073(2)
C2–S2	173.0(6)	C2–S3	1.627(6)
C3–C4	141.9(8)		
Angles/°			
S1–C1–S6	125.6(3)	C3–C4–S4	126.2(5)
S1–C1–C3	116.7(5)	S4–C4–S5	122.5(4)
S6–C1–C3	117.7(5)	C3–C4–S5	111.2(4)
C1–C3–C4	120.1(6)	C4–S5–S6	98.0(2)
C1–C3–S2	117.4(5)	C1–S6–S5	92.9(2)
C4–C3–S2	122.5(5)	S1–C2–S2	114.1(4)
S2–C2–S3	121.9(4)	S1–C2–S3	124.0(4)
C1–S1–C2	95.8(3)	C3–S2–C2	96.0(3)
C1–S6–S5	92.9(2)	C1–C3–C4	120.1(6)
α,β -C ₄ S ₆ ·I ₂ -II distances/pm			
C1–C3	138(1)	C3–S2	173(1)
C1–S1	173(1)	C4–S4	170(1)
C1–S6	172(1)	C4–S5	172(1)
C2–S1	176(1)	S5–S6	207.8(4)
C2–S2	173(1)	S4–I1	269.8(3)
C2–S3	162(1)	I1–I2	286.6(1)
C3–C4	140(1)		
Angles/°			
S1–C1–S6	125.1(7)	C3–C4–S4	122.6(6)
S1–C1–C3	116.9(9)	S4–C4–S5	122.8(6)
S6–C1–C3	118.0(9)	C3–C4–S5	114.5(9)
C1–C3–C4	117(1)	C4–S5–S6	96.7(4)
C1–C3–S2	116.9(9)	C1–S6–S5	93.3(4)
C4–C3–S2	125.6(9)	C4–S4–I1	100.2(3)
S1–C2–S2	115.1(6)	S4–I1–I2	178.02(7)
S2–C2–S3	122.6(8)		
S1–C2–S3	122.3(7)		

apparatus for one week, only a small amount of the yellow powder is dissolved. The extracted material is partially converted to intergrown brown crystal aggregates. Crystals suitable for X-ray structure determination were obtained by slow evaporation of a saturated solution in CS₂. The brown crystals had an inevitable tendency to form agglomerates and a single crystal could only be obtained by cutting a multiple intergrown aggregate with a razor blade.

The crystal structure is built of essentially planar molecules (Fig. 1). With 4 pm S3 and S3' show the largest distance from the least-squares plane through all ten atoms of the molecule. A centre of inversion is present in the middle of the central C–C bond giving the molecule crystallographic C_i symmetry. The molecule, however, nearly fulfils the higher symmetry D_{2h} . With a length of 135 pm the central C1–C1' bond represents a localized double bond. The terminal C=S bonds with lengths of 165 pm are in the expected range for thioketones. The molecular structure is thus in a close relationship to the respective oxygen bearing analogue 1,3,4,6-tetrathiapentalene-2,5-dione.²³

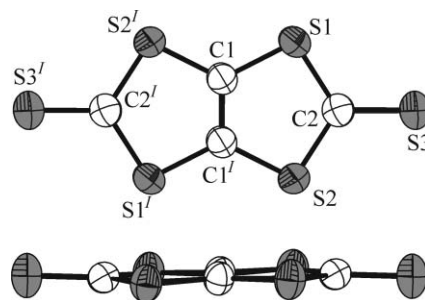


Fig. 1 The molecular structure of α,α -C₄S₆ (**3**) from two different points of view. Top: the view perpendicular to the plane of the molecule, bottom: a view along the C1–C1' axis which shows that the molecule is essentially planar. Displacement ellipsoids are drawn to enclose a 70% probability density. Symmetry operation I: $1 - x, -y, -z$.

In the crystal the molecules are arranged in the motif of a body centered packing with a pronounced tetragonal distortion (Fig. 2). Each molecule exhibits six S...S contacts below 350 pm

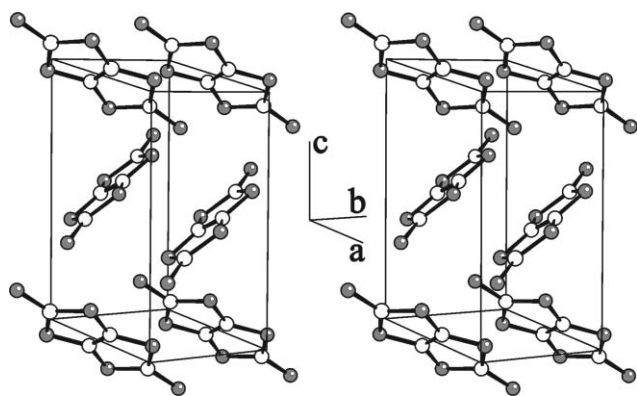


Fig. 2 The unit cell of $\alpha,\alpha\text{-C}_4\text{S}_6$ (**3**) in a stereoscopic view.

to S atoms of neighbouring molecules (the shortest of which are $\text{S2} \cdots \text{S3}'$ 341 pm, $\text{S1} \cdots \text{S1}'$ 342 pm) which are significantly shorter than the sum of the van der Waals radii of sulfur atoms (360 pm). All molecules are arranged in two interpenetrating sets of parallel planes. The angles between the two sets of planes are 67.8° , the distances between the parallel planes are 370 pm. With respect to the perpendicular of the planes the molecules are shifted largely away from each other. So π orbital overlap is not possible and intermolecular π stacking effects are not present in this structure.

In comparison to the α,α -isomer **3**, $\alpha,\beta\text{-C}_4\text{S}_6$ (**4**) exhibits with its central $\text{C1}=\text{C3}-\text{C4}=\text{S4}$ group a larger moiety capable of electron delocalization and accordingly has a deeper, brown color. It has a higher solubility as **3** and shows volatility at temperatures above 100°C . Crystals of **4** can be obtained either by crystallization from a saturated solution in boiling toluene on cooling to 0°C or by sublimation. From toluene solution dark-brown transparent crystals are obtained. In contrast, by sublimation in a closed evacuated glass ampoule in a temperature gradient $190^\circ\text{C} \rightarrow 100^\circ\text{C}$ dark-red crystals are obtained. Examination of crystals obtained by both methods revealed their chemical and crystallographical identity, so the formation of polymorphic forms can be ruled out. An explanation for the different colorations has not been found so far.

The crystal structure of **4** consists of almost planar molecules (Fig. 3). The *exo* sulfur atom S3 shows, with only 10 pm, the largest deviation from the least squares plane through all 10 atoms of the

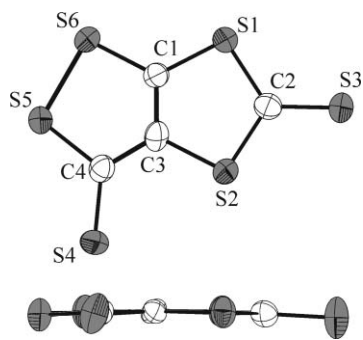


Fig. 3 The molecular structure of $\alpha,\beta\text{-C}_4\text{S}_6$ (**4**) from two different points of view. Top: the view perpendicular to the plane of the molecule, bottom: a view along the $\text{C1}-\text{C3}$ axis which shows that the molecule is almost plane. Displacement ellipsoids are drawn to enclose a 70% probability density.

molecule. Assuming planarity the molecule has C_s point symmetry but actually no crystallographic symmetry is present. Within the C_3 moiety $\text{C1}-\text{C3}-\text{C4}$, two different $\text{C}-\text{C}$ bond lengths are present. At 136 pm the $\text{C1}-\text{C3}$ bond represents a double bond while $\text{C3}-\text{C4}$ at 142 pm is between a single and a double bond. The two thione $\text{C}=\text{S}$ bonds (163 and 165 pm) and the $\text{S5}-\text{S6}$ single bond (207 pm) show no unexpected features.

The molecular packing in the crystal of **4** shows some relationship to the packing in the structure of **3**. Again, the motif of a body centered structure is realized and all molecules are arranged with their molecular planes in two sets of interpenetrating, parallel planes (Fig. 4). The angle between the two sets of planes is 39.4° and the distance between parallel planes is 348 pm and thus much shorter than in the structure of **3**. Additionally, neighbouring molecules are only slightly shifted towards each other and exhibit a large overlap. This gives rise to an alternative interpretation of the crystal structure: the individual molecules form stacks in a direction slightly inclined to the *a*-axis. Two kinds of stacks are present with different orientations of the molecules. There are eight $\text{S} \cdots \text{S}$ contacts below 350 pm to S atoms of neighbouring molecules (the shortest of which are $\text{S3} \cdots \text{S6}'$ 329 pm, $\text{S4} \cdots \text{S6}'$ 332 pm). The intermolecular interactions in the structure of **4** are generally stronger than those in the structure of **3** what finds its expression in a 3% higher density of **4** with respect to **3**.

A profound difference between the C_4S_6 isomers **3** and **4** is observed in the mass spectra fragmentation patterns. In both spectra the M^+ signal at $m/z = 240$ is observed. Whereas the spectrum of **3** shows a weak M^+ signal and is dominated by the strongest signal of CS_2^+ at $m/z = 76$, the spectrum of **4** shows strong signals for M^+ and for C_3S_2^+ at $m/z = 100$. This observation is in line with the reported ability of the $\beta,\beta\text{-C}_4\text{S}_6$ isomer **1** to act as a source for carbon subsulfide C_3S_2 under flash vacuum pyrolysis conditions.²⁴ Both **1** and **4** contain in the molecule a SCCCS moiety whereas this moiety is not present in the structure of **3** and accordingly no fragmentation to C_3S_2 is observed in its mass spectrum. Compound **4** can thus also be expected to be a source for the synthesis of carbon subsulfide C_3S_2 under flash vacuum pyrolysis conditions.

Compound **3** is thermally unstable with respect to **4** and is converted to **4** either in the solid state or in solution. If the solution of **3** in DMF or DMSO is heated for just a few seconds to temperatures above 150°C its two ^{13}C NMR signals disappear. Instead the four resonances typical for **4** are observed. This thermal rearrangement is also observed in the mass spectrum. The typical fragmentation pattern for **3** is only observed when the sample chamber is left at ambient temperature. When heated to 180°C the mass spectrum shows the fragments typical for **4** including the characteristic C_3S_2^+ signal. Since we succeeded in solving the single crystal structure of **3** we could check the purity of our samples of **3** via powder X-ray diffractometry. The yellow powder showed no additional reflections compared with a simulated spectrum based on the single crystal data. This sample gave no sharp melting point; only darkening and decomposition above 280°C was observed. The wide spread of melting points reported so far for **3** can be understood with the knowledge of this rearrangement reaction. Any thermal treatment will cause at least partial conversion to **4** which melts lower than **3**. Probably in the former investigations melting points of mixtures of isomers were determined.

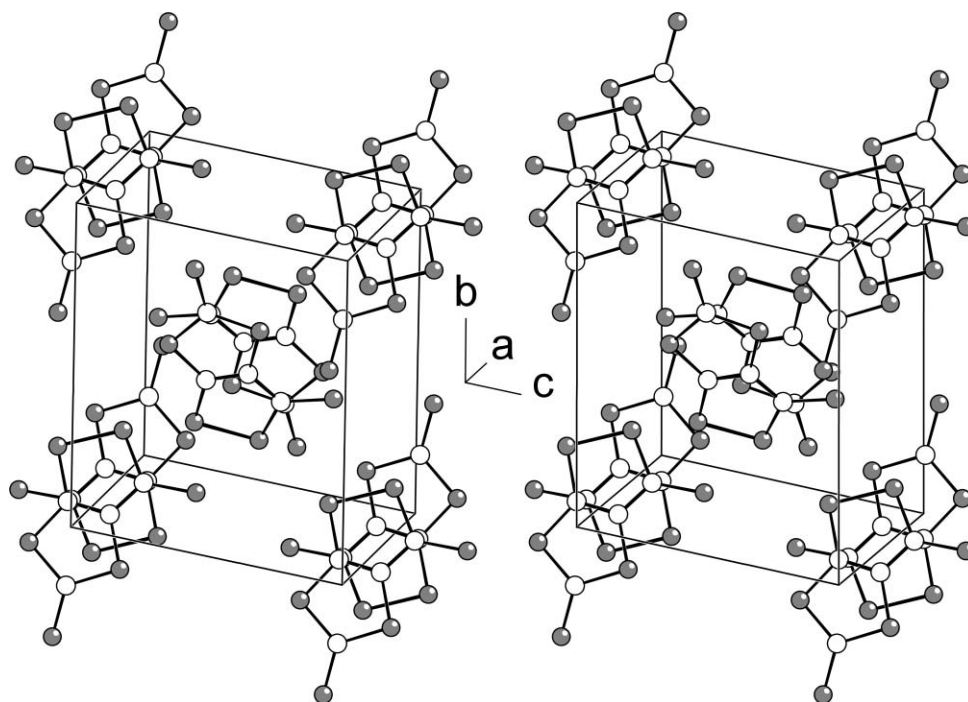


Fig. 4 The unit cell of $\alpha,\beta\text{-C}_4\text{S}_6$ (**4**) in a stereoscopic view.

Compound **4** is reported to form an adduct with I_2 ¹⁹ as do other thiocarbonyl compounds, *e.g.* thioamides, thiazolidinethiones²⁵ or the dimethyl derivative of **5**.²⁶ On crystals obtained from acetonitrile the structure of the compound **4**· I_2 was determined (referred to from now on as $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2\text{-I}$). On repeating this reaction in CS_2 as solvent we observed reproducibly formation of a second polymorph, from now on labeled as $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2\text{-II}$. The formation of such an adduct was not observed for **3**.

Fig. 5 shows the structure of the molecule $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2$ as it occurs in the new, second polymorph. The molecule **4** offers, as a unique feature among all hitherto known thiocarbonyl donors, two different thiocarbonyl groups for the formation of the I_2 adduct. However, up to now no isomers of I_2 adducts of **4** were observed and the (C)(S)C=S thiocarbonyl group is preferred for I_2 coordination over the (S)(S)C=S group. C4 is part of a C_3 moiety with delocalized electronic character what apparently enhances the donor strength of the thione sulfur atom S4. Though the

molecule has no crystallographic symmetry it is essentially planar. The biggest deviation from the least-squares plane through all carbon and sulfur atoms is observed at S1 with 3 pm. The I_2 molecule deviates slightly from the molecular plane. The linear group S4–I1–I2 forms an angle with the molecular plane of 3.3° , I1 deviates from the least squares plane of C and S atoms by 11 pm and I2 by 32 pm. The S5–S6 bond has a length of 208 pm and represents a S–S single bond. The I_2 molecule is attached to S4 with a S–I distance of 270 pm. As a consequence the C4–S4 bond length is slightly enlarged (170 pm) with respect to the uncoordinated thione group C2–S3 (162 pm) or the respective group in $\alpha,\alpha\text{-C}_4\text{S}_6$ (**3**) (165 pm). The I–I bond (287 pm) is also enlarged with respect to an uncoordinated I_2 molecule (268 pm²⁷). The geometrical parameters of the molecular unit are in close relationship to those found in the structure of $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2\text{-I}$.¹⁹

Fig. 6 shows the arrangement of the molecules in the unit cell. All molecules are arranged with their molecular planes spread out parallel to the *b*–*c* plane. Several short $\text{S}\cdots\text{S}$ and $\text{S}\cdots\text{I}$ contacts

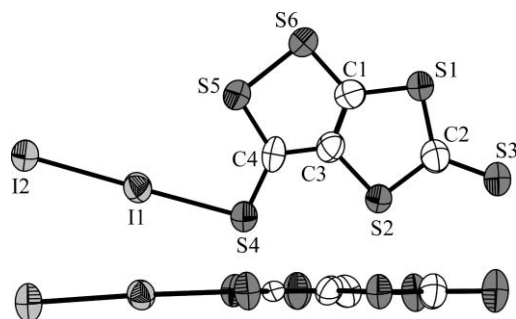


Fig. 5 The molecular structure of $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2\text{-II}$ from two different points of view. Top: the view perpendicular to the plane of the molecule, bottom: a view along the C3–C1 axis in the plane of the molecule. Displacement ellipsoids are drawn to enclose a 70% probability density.

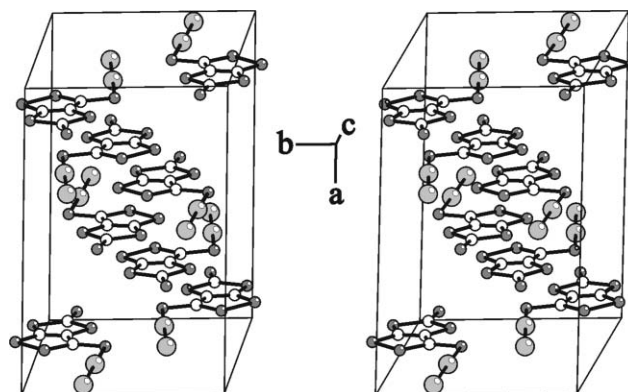


Fig. 6 The unit cell of $\alpha,\beta\text{-C}_4\text{S}_6\cdot\text{I}_2\text{-II}$ in a stereoscopic view.

below 350 pm are present between the molecules ($S3 \cdots S6' = 335$ pm, $I2 \cdots S6' = 340$ pm).

The two crystalline forms of $4 \cdot I_2$ consist of molecules with essentially identical geometric parameters but have different packing modes and different orientation of the molecules. Fig. 7 shows the two unit cells in a view along the planes of the molecules. In the structure of $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2\text{-I}$,¹⁹ the molecules are arranged in two sets of planes whereas in the structure of $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2\text{-II}$ all molecules are oriented in an almost parallel alignment.

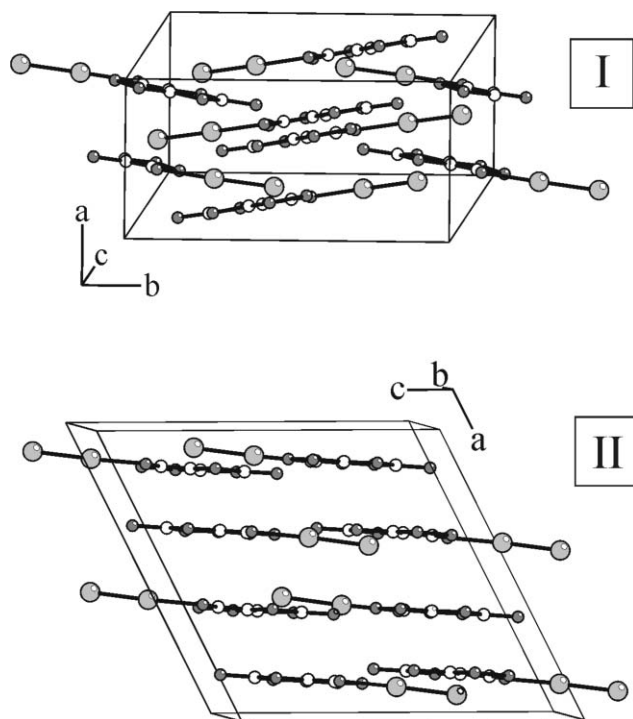


Fig. 7 The unit cells of $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2\text{-I}$,¹⁹ and $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2\text{-II}$ [this work]. For comparison both structures are depicted in a view perpendicular to the stacking direction of the molecules.

Over a dozen I_2 adducts of thiocarbonyls have been structurally characterized so far.²⁸ All show the same main characteristic features: an almost linear S–I–I group and an angle at the contact S atom of around 100° . Deplano has suggested a classification of S-donor- I_2 adducts into three types, depending on the strength of the bond between the donor atom (D) and the contact I atom: $D \cdots I-I$ (A), $D-I-I$ (B), $D-I^+ \cdots I^-$ (C).²⁸ The frequency of the I–I stretching vibration in the Raman spectra turned out to be the most distinctive method for classification. $4 \cdot I_2$ has a Raman peak at 154 cm^{-1} attributable to the I–I stretching mode which is lower than for I_2 in CHCl_3 solution (209 cm^{-1}).²⁹ Thus $4 \cdot I_2$ belongs to the class A of donor adducts.

In solution optical absorption spectroscopy can help to estimate the strength of the $S \cdots I$ bond. Fig. 8 shows the absorption spectra of dissolved I_2 , $\alpha, \beta\text{-C}_4\text{S}_6$ (**4**), and $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2$ ($4 \cdot I_2$), in the range from 280 to 650 nm. The spectra of **4** and $4 \cdot I_2$ are nearly identical. This indicates that the electronic system of $\alpha, \beta\text{-C}_4\text{S}_6$ is not significantly altered by the diiodine adduct formation. The only deviations in the spectra are observed in those regions where I_2 has its two strong absorption bands at about 330 and 500 nm. Here, the transmissions for $4 \cdot I_2$ are somewhat lower than

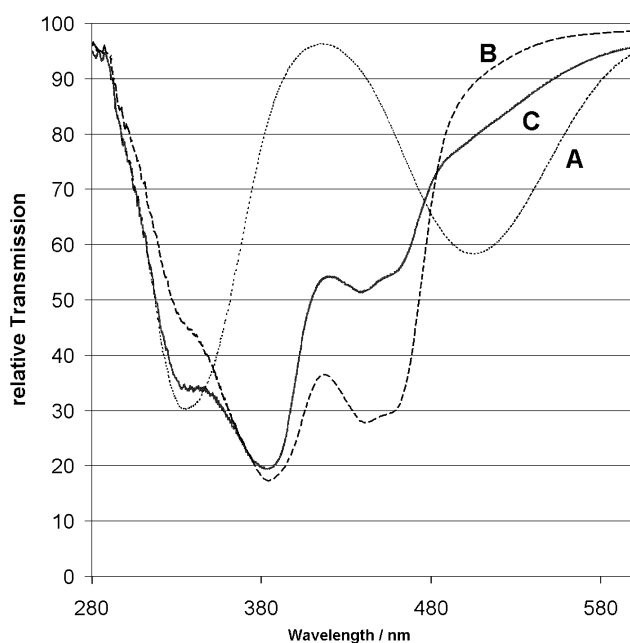


Fig. 8 UV/VIS spectra of I_2 (A), $\alpha, \beta\text{-C}_4\text{S}_6$ (B) and $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2$ (C). All spectra were recorded in toluene solution and are baseline corrected with the spectrum of the pure solvent.

for neat **4**, indicating that only small quantities of I_2 are liberated in solution. Since the absorption bands of free iodine are very strong the spectra give evidence that in solution $\alpha, \beta\text{-C}_4\text{S}_6 \cdot I_2$ is dissociated only to a small extent. This observation is in line with the pronounced thermal stability of this diiodine adduct.

A thermoanalytical investigation (DTA/TG) of $4 \cdot I_2$ shows that a detectable weight loss occurs starting at 200°C accompanied by a weak endothermic process around 216°C . This is in line with the visual melting point of 227°C . The overall weight loss between 200 and 270°C is 82%. If only I_2 left the sample a weight loss of 51% would be expected. The observed much higher weight loss can be explained by the simultaneous loss of I_2 and two equivalents of CS_2 from one equivalent of $\text{C}_4\text{S}_6 \cdot I_2$ what corresponds to 82% weight loss. The thermal behaviour indicates that in the solid state a relatively strong bond is present between the diiodine unit and thione group of the C_4S_6 molecule since the I_2 cleavage occurs in a temperature range where decomposition of the C_4S_6 moiety takes place. The residue of the thermal decomposition at 270°C is a black powder of tentative formula $(\text{CS})_x$ as revealed by the elemental analysis (Found C, 26.5; S, 73.3. $(\text{CS})_x$ requires C, 27.3; S, 72.7%) It is insoluble in all solvents. Conductivity measurements on pressed pellets showed it to be a high-resistance semiconductor with a resistivity in the range of $10^{11}\ \Omega\text{ cm}$. In the temperature range 30–300 K the resistivity decreases slightly by half an order of magnitude. The X-ray powder diffractogram with a very strong reflection at $2\theta = 25.6^\circ$ and three weak reflections at $2\theta = 42.0^\circ, 44.1^\circ, 51.2^\circ$ is almost identical to the diffractogram of 2H graphite.³⁰ In the IR spectrum the positions of the broad absorption bands are not in line with those of **4**, except a weak band at 1060 cm^{-1} which coincides with the strongest absorption of **4** at $1061/1055\text{ cm}^{-1}$. As a conclusion these findings lead to the hypothesis that the residue of the thermal treatment is not homogeneous but rather a mixture of some graphitic carbon and unidentified carbon sulfur compounds.

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