Sulfur Compounds, 212[‡]

Preparation of Organic Polysulfanes R_2S_n ($n = 5, 7, 8, 9$) from Sulfenyl Chlorides, RSCl, and Transition Metal Polysulfido Complexes

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The preparation of seven novel organic polysulfanes is reported. Bis(*n*-octyl)heptasulfane R_2S_7 **1** is formed upon reaction of RSCl with $[Cp_2TiS_5]$, while the corresponding nonasulfane R_2S_9 **2** is obtained by reaction of RSSCl with $[Cp_2TiS_5]$. The bis(*n*-octyl)pentasulfane R_2S_5 **3** is obtained from RSCl and $[(Cp'_2TiCl)_2S_3]$ by transfer of the S_3 ligand at 20 °C. The new alkyl polysulfanes **1**–**3** have been obtained in quantitative yields. They are liquids at 20 °C, having freezing points below –50 °C, but do not form mesogenic phases. Reactions of $[Cp_2TiS_5]$ with 2-naphthyl- and 4-chlorophenyl sulfenyl chloride furnish the corresponding heptasulfanes **4** and **5**, respectively, which are solids at 20 °C. 1,2-Benzodisulfenyl chloride $C_6H_4(SCl)_2$ reacts with $[(Cp'_2TiCl)_2S_3]$ to give the known 1,2,3,4,5-benzopentathiepin $C_6H_4S_5$ **6**, with $[Cp_2TiS_5]$ to give the novel 1,2,3,4,5,6,7-benzoheptathionin $C_6H_4S_7$ **7**, and with $[(TMEDA)ZnS_6]$ to give the novel 1,2,3,4,5,6,7,8-benzooctathiecin $C_6H_4S_8$ **8**. The cyclic polysulfanes **6**–**8** are solids at 20 °C and have been recovered in yields of 60–83%. The orthorhombic structure of 1,2-$C_6H_4S_7$ has been investigated by single-crystal X-ray diffraction analysis. The molecules are found to be located at sites of C_s symmetry and the motif of the C_2S_7 heterocycle is +–+–+–+–, with the torsion angle of zero at the carbon–carbon bond. The three internuclear SS distances measure 205.0(1), 203.7(1), and 205.7(1) pm.

Introduction

Sulfur-rich organic polysulfanes R_2S_n ($n > 2$) may be synthesized by a variety of methods starting from either thiols, sulfenyl chlorides, elemental sulfur, sulfanes (H_2S_n), chlorosulfanes (S_nCl_2), ionic polysulfides (e.g. Na_2S_n), or other sulfur compounds.[1] In most cases, mixtures of polysulfanes of varying chain length *n* are obtained, which have to be separated by repeated crystallization or by chromatography. Such separations have to be conducted under mild conditions owing to the thermal and thermodynamic instability of the longer-chain polysulfanes, which tend to equilibrate with species of other chain lengths or to split off S_8, S_7, or S_6 (Equation 1 and 2):[2]

$$2\,R_2S_n \rightarrow R_2S_{n+x} + R_2S_{n-x} \tag{1}$$
$$R_2S_n \rightarrow R_2S_{n-8} + S_8\ (n > 8) \tag{2}$$

In recent years, the enormous potential of titanocene polysulfide complexes for the synthesis of novel homocyclic and heterocyclic organic and inorganic sulfur compounds has been demonstrated.[3,4,5,6] Using these reagents, a large number of interesting sulfur-rich species have been prepared, for which no synthetic route had hitherto been available. When organic sulfenyl chlorides or related SCl compounds are allowed to react with titanocene pentasulfide, chain-like polysulfanes with up to nine sulfur atoms may be generated (Equation 3 and 4; Cp = η^5-C_5H_5):[7,8]

$$2\,CCl_3SCl + [Cp_2TiS_5] \rightarrow (CCl_3)_2S_7 + [Cp_2TiCl_2] \tag{3}$$
$$2\,iPrOSSCl + [Cp_2TiS_5] \rightarrow (iPrO)_2S_9 + [Cp_2TiCl_2] \tag{4}$$

In a similar fashion, bifunctional organic sulfenyl chlorides and chlorodisulfanes have been treated with titanocene pentasulfide or similar complexes, thereby generating cyclic sulfur-rich polysulfanes with up to 11 sulfur atoms (Equation 5 and 6):[9,10,11]

$$1,2\text{-}C_2H_4(SCl)_2 + [Cp_2TiS_5] \rightarrow C_2H_4S_7 + [Cp_2TiCl_2] \tag{5}$$
$$1,2\text{-}C_7H_{10}(SCl)(SSCl) + [Cp_2TiS_5] \rightarrow C_7H_{10}S_8 + [Cp_2TiCl_2] \tag{6}$$

A relatively new titanocene polysulfide complex is $[Cp'_2Ti(Cl)–S_3–(Cl)TiCp'_2]$,[12] which reacts with sulfenyl chlorides as an S_3 group transfer reagent (Equation 7 and 8; Cp′ = $CH_3C_5H_4$):[13]

$$C_{10}H_{12}(SCl)_2 + [(Cp'_2TiCl)_2S_3] \rightarrow C_{10}H_{12}S_5 + 2\,[Cp'_2TiCl_2] \tag{7}$$
$$C_{10}H_{12}(SCl)(SSCl) + [(Cp'_2TiCl)_2S_3] \rightarrow C_{10}H_{12}S_6 + 2\,[Cp'_2TiCl_2] \tag{8}$$

In this work, we report the synthesis of five chain-like and three cyclic organic polysulfanes with between 5 and 9 sulfur atoms. In the case of the chain-like species, we used alkyl as well as aryl substituents. The *n*-octyl substituent was employed in the hope that the rather long chains of (*n*-

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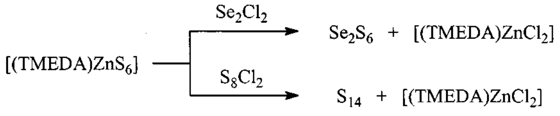
octyl)$_2$S$_n$ would result in a high degree of anisotropy and consequently in mesogenic properties. The aryl groups 4-chlorophenyl and 2-naphthyl were used in the expectation that readily crystallizable products suitable for X-ray crystallographic analysis would be obtained. In the case of the cyclic species, 1,2-substituted benzene was used for the same reason. A further aim of this work was to study the utility of the zinc polysulfide chelate complex [(TMEDA)ZnS$_6$] in the preparation of sulfur-rich organic heterocycles. This compound has previously been used to prepare inorganic rings such as 1,2-Se$_2$S$_6$ [14] and S$_{14}$ (Equation 9).[15]



$$[(TMEDA)ZnS_6] \xrightarrow{Se_2Cl_2} Se_2S_6 + [(TMEDA)ZnCl_2]$$
$$[(TMEDA)ZnS_6] \xrightarrow{S_8Cl_2} S_{14} + [(TMEDA)ZnCl_2] \quad (9)$$

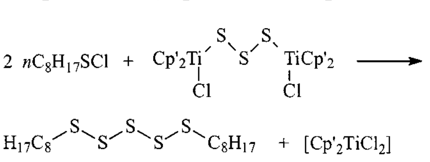
Results and Discussion

Aliphatic Polysulfanes[16]

Octylsulfenyl chloride was prepared by chlorination of *n*-octanethiol. Titanocene pentasulfide was found to react with this sulfenyl chloride at temperatures below 0 °C in carbon disulfide to quantitatively afford bis(*n*-octyl)heptasulfane **1** (Equation 10; $x = 1$). This compound is a viscous red liquid at ambient temperature and has a freezing point of –60 °C.

$$2\ nC_8H_{17}S_xCl + [Cp_2TiS_5] \rightarrow (nC_8H_{17})_2S_{5+2x} + [Cp_2TiCl_2] \quad (10)$$

Reaction of *n*-octanethiol with dichlorosulfane gives *n*-octylchlorodisulfane, which reacts with titanocene pentasulfide under the same experimental conditions as above to yield the orange bis(*n*-octyl)nonasulfane **2** (Equation 10; $x = 2$). This product freezes to a glass at –52 °C. Bis(*n*-octyl)pentasulfane **3**, a yellow liquid with freezing point –67 °C, was prepared by the reaction of *n*-octylsulfenyl chloride with bis[bis(methylcyclopentadienyl)chlorotitanium]trisulfide [(Cp′$_2$TiCl)$_2$S$_3$] in carbon disulfide at low temperatures (Equation 11; Cp′ = CH$_3$C$_5$H$_4$).



(11)

Analyses by ^{1}H-NMR and HPLC showed that the unusual red color of the heptasulfane 1 is not due to traces of titanocene pentasulfide or titanocene dichloride as might be suspected. Bis(*n*-octyl)nonasulfane **2** is the most sulfur-rich of all selectively available diorganylpolysulfanes that is *liquid* at ambient temperature.

The lengths of the sulfur chains in these novel compounds have been assessed not only by microanalysis, but also by reversed-phase HPLC. A linear relationship exists between the number of sulfur atoms in the chain (n_S) and the natural logarithm of the capacity factor (ln k'), which is calculated from the retention time. This has previously been demonstrated for other polysulfanes bearing alkyl and aryl substituents.[10,11,13,17] On heating of the nonasulfane **2** at 80 °C for 30 min., decomposition occurred resulting in a mixture of polysulfanes with up to 15 sulfur atoms. A plot of ln k' versus the number of sulfur atoms n_S for the bis(*n*-octyl)polysulfanes formed in this reaction is shown in Figure 1.

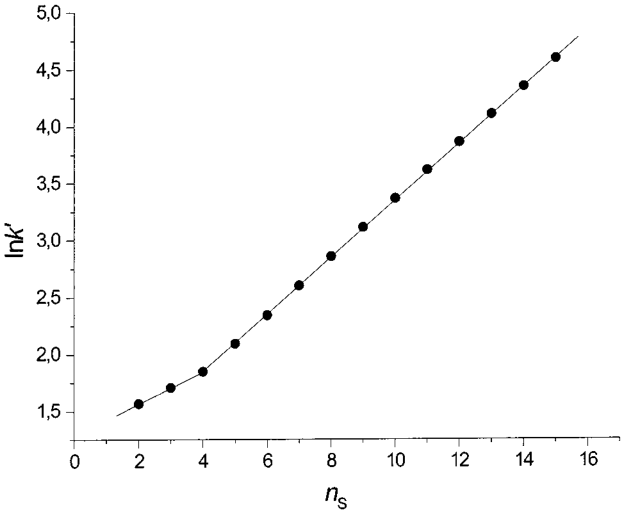


Figure 1. Dependence of the chromatographic retention times of the bis(*n*-octyl)polysulfanes (C$_8$H$_{17}$)$_2$S$_n$ (n = 2–15) on the number of sulfur atoms n_S; here, ln k' is plotted against n_S [$k' = (t_r - t_0)/t_0$; t_0 = dead time, t_r = retention time]

Table 1. Retention data (retention times t_R, capacity factors k', and retention index values *RS*) of the homologous series (C$_8$H$_{17}$)$_2$S$_n$ (n = 2–15)

n_S	t_R [min]	ln k'	*RS*	n_S	t_R [min]	ln k'	*RS*
2	8.10	1.565	941	9	32.83	3.111	1384
3	9.11	1.706	982	10	41.92	3.365	1457
4	10.28	1.847	1022	11	53.41	3.615	1529
5	12.47	2.092	1092	12	67.93	3.861	1599
6	15.96	2.342	1164	13	86.19	4.104	1669
7	20.23	2.600	1238	14	109.89	4.350	1740
8	25.69	2.854	1311	15	139.91	4.595	1810

The chromatographic data and the retention indices *RS* [18] derived therefrom are given in Table 1. The retention indices are independent of the chromatographic system used and can therefore be used for the identification of these species in a similar manner as spectroscopic data.

The chromatograms of the pure products **1**–**3** showed neither traces of other polysulfanes nor of sulfur homocycles, the other products of the disproportionation of polysulfanes according to Equations 1 and 2. The three liquid bis(*n*-octyl)polysulfanes can be stored at –25 °C for several months without decomposition. After storage at ambient temperatures for three days, HPLC analysis showed that about 10% of the products had undergone disproportionation. The ^{1}H- and ^{13}C-NMR spectra of **1**–**3** did not reveal any unusual features. The proton signals exhibit a very slight downfield shift with increasing number of sulfur atoms, reflecting the increase in acidity of the sulfanes H_2S_n with increasing chain length n.[19]

The infrared spectra of **1**–**3**, recorded at ambient temperatures, are almost identical. They show mainly the absorptions of the *n*-octyl substituents, i.e. strong signals due to the CH stretching modes in the range 2850–2960 cm^{-1} and the CH_2 bending modes between 1200 and 1470 cm^{-1}. More interesting are the SS stretching modes, which can best be detected by Raman spectroscopy. The low-temperature (–135 °C) Raman spectra exhibit, besides weak to strong lines in the ranges 2700–3000 cm^{-1} and 1300–1500 cm^{-1} attributable to the *n*-octyl substituents, several lines between 420 and 510 cm^{-1}, which are characteristic of catenated sulfur. In this region, the spectrum of $(nC_8H_{17})_2S_5$ is characterized by three peaks at 435, 459, and 493 cm^{-1}, and a shoulder at 505 cm^{-1}. The heptasulfane spectrum features four lines at 429, 445, 470, and 495 cm^{-1}, and a shoulder at 463 cm^{-1}. The Raman spectrum of $(nC_8H_{17})_2S_9$ features medium to strong lines at 423, 437, 463, and 494 cm^{-1}, with shoulders at 452 and 472 cm^{-1}. All these lines must stem from SS stretching modes as the Raman spectrum of *n*-octanethiol does not feature any lines in this region (see Figure 2). The number of lines in the region 400–510 cm^{-1} is smaller than the expected number of SS stretching modes of **1**–**3**, indicating that there must be some coincidental degeneracies.

In view of the low freezing points of these liquid polysulfanes, no mesogenic properties were to be expected near room temperature. All three compounds solidify as glasses on rapid cooling to –70 °C.

Aromatic Polysulfanes

Chain-Like Heptasulfanes[20]

The 2-naphthyl and 4-chlorophenyl groups have previously been used in the preparation of relatively stable sulfur-rich derivatives, from which it can be concluded that these residues stabilize either sterically or electronically the thermodynamically unstable sulfur compounds. Since the corresponding sulfenyl chlorides are readily available,[21] we have prepared bis(2-naphthyl)heptasulfane **4** and bis(4-chlorophenyl)heptasulfane **5** by reaction with titanocene pentasulfide (Equation 12).

$$2\ RSCl + [Cp_2TiS_5] \rightarrow R_2S_7 + [Cp_2TiCl_2] \qquad (12)$$

These reactions were carried out at 20 °C in carbon disulfide solution; **4** was obtained as a pale-yellow powder in 51% yield, while **5** formed lemon-yellow microcrystals (44% yield). Despite the bulky substituents, these compounds are characterized by relatively low melting points of 55 °C (4) and 40 °C (**5**). Reversed-phase HPLC analyses of the rapidly quenched melts did not reveal the presence of any decomposition products. However, when the heptasulfanes were heated to twice the melting temperatures (110 °C and 80 °C, respectively) for 5 min., the naphthyl derivative decomposed to give a mixture of polysulfanes R_2S_n with up to 11 sulfur atoms, while the chlorophenyl derivative produced a similar series of homologous sulfanes with 3–12 sulfur atoms. As mentioned above, such homologous series can be analysed by the systematic increase of the retention

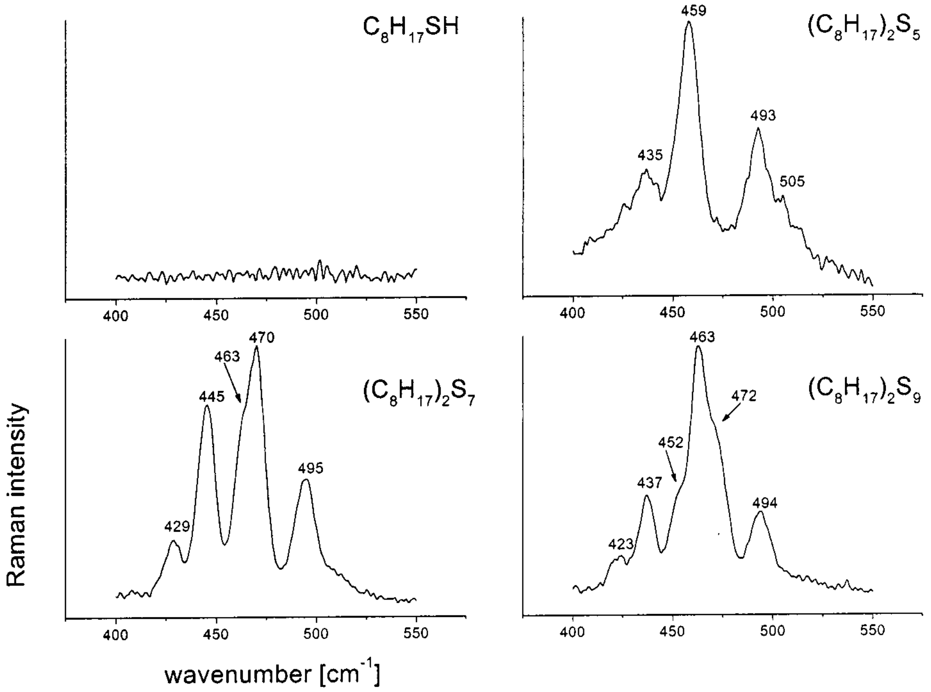


Figure 2. Raman spectra of *n*-octanethiol and of the bis(*n*-octyl)polysulfanes $(nC_8H_{17})_2S_n$ (n = 5, 7, 9) in the range 400–550 cm^{-1}

time with increasing number n_S of sulfur atoms. The retention index *RS* is a linear function of n_S and the following data were determined using methanol as an eluent:

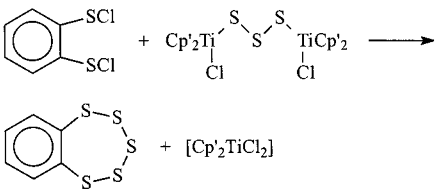
$RS = a + bn_S$
4: $n_S = 2–11$, $a = 517$, $b = 69$
5: $n_S = 2–12$, $a = 382$, $b = 67$

The linear correlation coefficients were better than 0.999.

Both heptasulfanes were found to be well-soluble in carbon disulfide and in chlorinated aliphatic hydrocarbons. They may be stored for long periods at 4 °C without decomposition, but slow decomposition occurs at 20 °C. HPLC analysis, mass spectrometry, as well as infrared, Raman, ^{1}H- and ^{13}C-NMR spectroscopic data confirmed the identities and purities of **4** and **5**. Their low melting points can be explained as follows. The torsion angle at SS bonds is usually about 90°, but may be positive or negative (enantiomeric forms). A chain with six SS bonds can therefore theoretically exist as $2^6 = 64$ conformational isomers. It has previously been shown that many of these conformers will be of almost identical energy.[22] However, in crystals of polysulfanes usually only one conformer is found.[1] It therefore seems reasonable to assume that only a single conformation of the CSSSSSSSC chain is present in solid **4** and **5**, while several conformations will be present in their melts, thus resulting in a strong increase in entropy. The melting temperature T_m and the melting entropy ΔS_m are inversely related to each other, with the melting enthalpy as an additional factor: $T_m = \Delta H_m/\Delta S_m$. Therefore, long chain-like polysulfanes are either liquid at 20 °C or have melting points only slightly above ambient temperature.

Cyclic Polysulfanes

The titanocene complex $[(Cp'_2TiCl)_2S_3]$ reacts with 1,2-benzenebis(sulfenyl chloride), prepared by chlorination of 1,2-benzenedithiol, at low temperatures in carbon disulfide solution to yield the known yellow 1,2,3,4,5-benzopentathiepin **6** (Equation 13).



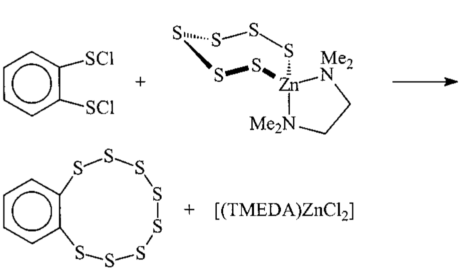
(13)

Compound **6** was first synthesized by Fehér and Langer[23] by condensation of 1,2-benzenedithiol $C_6H_4(SH)_2$ with dichlorotrisulfane S_3Cl_2. It was obtained in a yield of just 50% and was seemingly not very pure since the reported melting point of 65–66 °C differs substantially from our measurements. Our product was analytically, chromatographically, and spectroscopically pure and was found to melt at 58 °C. It was recovered in 73% yield. In 1979, Fehér and Engelen determined the molecular and crystal structure of **6**,[24] and in 1984 Chenard and Miller reported a new synthesis of **6** from 1,2-benzothiadiazole and elemental sulfur in the presence of DABCO at 160–185 °C (yield 54%).[25] The melting point of **6** measured by these authors was 58–60 °C, which agrees well with our findings.

Under similar conditions as those used to generate **6**, 1,2-benzenebis(sulfenyl chloride) was found to react with titanocene pentasulfide to yield the novel 1,2,3,4,5,6,7-benzoheptathionin **7**, which was obtained in 83% yield as a yellow solid with m.p. 107 °C (Equation 14).

$$1{,}2\text{-}C_6H_4(SCl)_2 + [Cp_2TiS_5] \rightarrow 1{,}2\text{-}C_6H_4S_7 + [Cp_2TiCl_2] \qquad (14)$$

The new octasulfane 1,2,3,4,5,6,7,8-benzooctathiecin **8**, a yellow solid with m.p. 73 °C, was obtained in 60% yield following reaction of the zinc hexasulfido chelate complex $[(TMEDA)ZnS_6]$ [26] with 1,2-benzenebis(sulfenyl chloride) in carbon disulfide at ambient temperature (Equation 15; TMEDA = tetramethylethylenediamine).



(15)

The number of sulfur atoms in these cyclic polysulfides can again be assessed by reversed-phase HPLC, since there is a linear relationship between the number of sulfur atoms in the ring and the logarithm of the capacity factor (not shown). The ^{1}H-NMR spectra of **6**–**8** each feature an AA′BB′ system, which is centered at δ = 7.61 for the C_2S_5 ring, at δ = 7.63 for the C_2S_7 ring, and at δ = 7.59 for the C_2S_8 ring. The ^{13}C-NMR spectra feature only three signals in the expected region. The infrared spectra are all very similar, in line with expectation. They are dominated by a very strong absorption near 750 cm^{-1}, which is typical for 1,2-substituted benzene rings. More interesting are the Raman spectra, which show the SS stretching modes between 400 and 520 cm^{-1} (see Figure 3). The three heterocycles each exhibit a distinct pattern of SS stretching modes. In the relevant region, the spectrum of the benzopentathiepin features four lines at 418, 429, 467, and 490 cm^{-1}, that of the benzoheptathionine features five lines at 436, 451, 471, 495, and 518 cm^{-1} and a shoulder at 480 cm^{-1}, while that of the benzooctathiocene is characterized by six lines at 416, 428, 438, 460, 467, and 512 cm^{-1} with shoulders at 476 and 515 cm^{-1}.

The crystal structure of $C_6H_4S_7$ was determined by single-crystal X-ray diffraction analysis. The crystals were found to be orthorhombic with four molecules in the unit cell and a density of 1.765 g cm^{-3} at 20 °C. The molecules have C_s symmetry (Figure 4). The crystallographic mirror plane passes through the center of the C3–C3′ bond and contains S4.

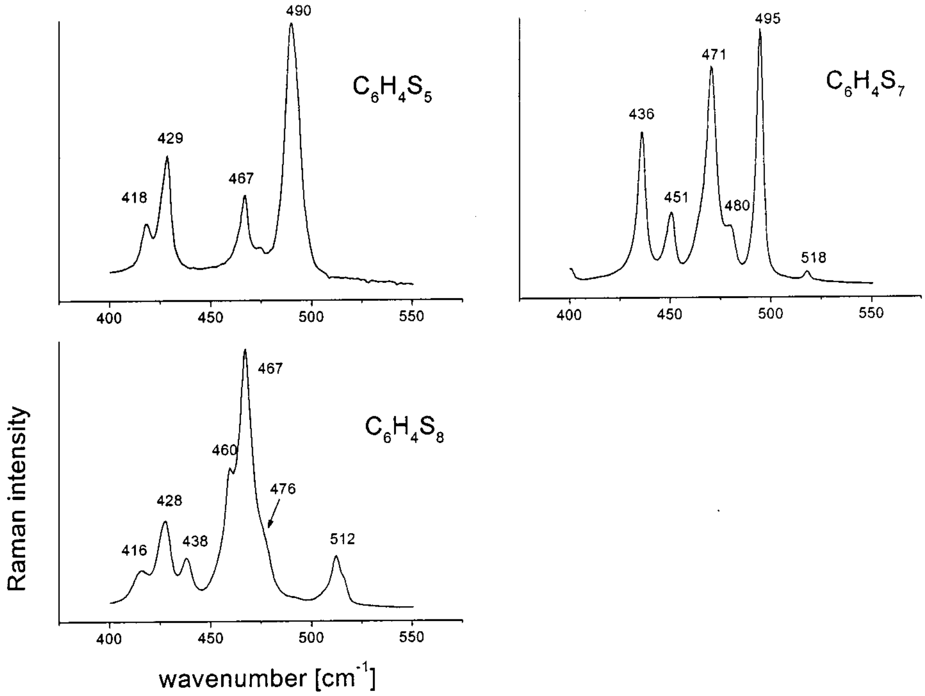


Figure 3. Raman spectra of the solid 1,2-benzenepolysulfanes $C_6H_4S_n$ (n = 5, 7, and 8) at 20 °C in the range 400–550 cm^{-1}

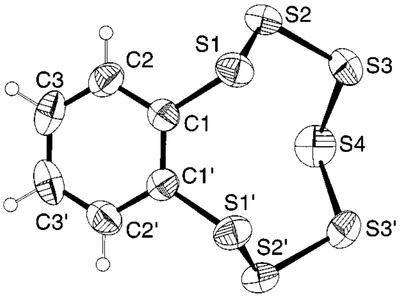


Figure 4. Structure of the 1,2-$C_6H_4S_7$ molecule in the crystal (PLATON plot)

Table 2. Selected bond lengths [pm], valence angles [°], and torsion angles [°] for $C_6H_4S_7$ (symmetry transformations used to generate equivalent atoms: ′ = x, $-y + 1/2$, z)

S(1)−S(2)	205.02(14)	S(1)–S(2)–S(3)	108.20(6)
S(2)−S(3)	203.73(13)	S(2)–S(3)–S(4)	109.66(6)
S(3)−S(4)	205.73(13)	S(3)–S(4)–S(3′)	103.76(8)
		C(1)–S(1)–S(2)	101.04(11)
S(1)−C(1)	177.0(3)	C(1′)–C(1)–S(1)	121.67(10)
C(1)−C(1′)	138.3(6)	C(1′)–C(1)–C(2)	119.4(2)
C(1)−C(2)	139.2(5)	C(2)–C(1)–S(1)	118.9(2)
C(2)−C(3)	136.9(5)	C(1)–C(2)–C(3)	120.6(3)
C(3)−C(3′)	138.2(8)	C(2)–C(3)–C(3′)	120.0(2)
C(1)–S(1)–S(2)–S(3)	103.60(12)	S(2)–S(1)–C(1)–C(2)	66.5(3)
S(1)–S(2)–S(3)–S(4)	–84.73(7)	C(1′)–C(1)–C(2)–C(3)	2.0(4)
S(2)–S(3)–S(4)–S(3′)	110.18(7)	S(1)–C(1)–C(2)–C(3)	180.0(3)
S(2)–S(1)–C(1)–C(1′)	–115.57(7)	C(1)–C(2)–C(3)–C(3′)	–2.0(4)

Selected internuclear distances, bond angles, and torsion angles are listed in Table 2.

The geometrical parameters show the expected values with an arithmetic mean of 138.1 pm for the CC bonds and an average of 204.8 pm for the SS bonds. The latter value is identical to the average bond length in S_8. There is a slight alternation in the SS bond lengths in **7**: d(S1−S2) = 205.0(1), d(S2−S3) = 203.7(1), and d(S3−S4) = 205.7(1) pm. The conformations of sulfur homocycles and sulfur-rich heterocycles can best be characterized by the *motif*, which describes the order of the signs of the torsion angles around the ring. The motif for the C_2S_7 heterocycle is +-+-0+-+-, with a value of zero at the carbon–carbon bond. Such a motif has not previously been observed for any nine-membered heterocycle of the type C_xS_y. The absolute values of the torsion angles at the SS bonds lie between 85° and 110° (see Table 2).

Conclusions

We have shown that sulfur-rich organic polysulfanes can be prepared in good yield not only from titanocene polysulfido complexes, but also from the relatively new zinc hexasulfido complex, despite the presence of the amine TMEDA. Normally, amines catalyze the decomposition of thermodynamically unstable polysulfur compounds. The novel bis(n-octyl)polysulfanes described here, which consist of chains of more than 20 non-hydrogen atoms, do not form mesogenic phases at ambient temperature since their freezing temperatures are quite low. These chains most probably have a random coil conformation rather than a straight chain structure in the liquid phase and therefore the materials solidify as glasses. The chain-like polysulfanes bearing aromatic substituents are solids at 20 °C, even when the sulfur chain is quite long. Most probably, they exist as *a single* conformer in the solid state, but as many rotational isomers in the liquid state, leading to a high melting entropy and hence to a depression of the melting temperature. Once again, we have observed that the homologous members of the series R_2S_n with $n = 2–12$ exhibit a systematic increase in their reversed-phase HPLC retention times with increasing number of sulfur atoms.

Experimental Section

General: The reactions were carried out under exclusion of moisture using carefully dried solvents. The chromatographic system used has been described previously.[11] Octadecylsilane (C18) was used as a stationary phase throughout. The following spectrometers were used: Nicolet Magna 750 FT-IR spectrometer (using KBr or CsCl sample discs); Bruker RFS 100 FT Raman spectrometer, equipped with an Nd-YAG laser (1064 nm); Bruker ARX 200 and ARX 400 NMR spectrometers.

Synthesis of Bis(*n*-octyl)pentasulfane (1): *n*-Octylsulfenyl chloride was first prepared by chlorination of the corresponding thiol with one equivalent of sulfuryl chloride in dichloromethane at 0 °C according to standard procedures. At –70 °C, a solution of the sulfenyl chloride (0.181 g, 1 mmol) in CS_2 (25 mL) was added dropwise over a period of 1 h to a solution of $[(Cp'_2TiCl)_2S_3]$ (0.290 g, 0.5 mmol) in CS_2 (25 mL), which resulted in a color change from dark-green to light-red. The reaction mixture was allowed to warm to 20 °C, the volume was reduced to one-half of the original, and then the concentrated solution was cooled to –50 °C for several hours. The precipitated $[Cp'_2TiCl_2]$ was filtered off. This procedure (partial evaporation of the solvent and subsequent cooling) was repeated until no more titanocene dichloride was precipitated. The remaining solvent was then completely removed under reduced pressure yielding the liquid product. Yield: 0.193 g (quantitative); freezing temp. –66 to –68 °C. – $C_{16}H_{34}S_5$ (386.8): calcd. C 49.7, H 8.9, S 41.5; found C 50.8, H 8.2, S 40.4. – UV/Vis (methanol): λ_{max} (%) = 216 nm (100), 292 (sh). – MS (120 °C): *m*/*z* (%) = 386 (23) $[M^+]$, 322 (100). – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.99 (t, 4 H), 1.78 (tt, 4 H), 1.45–1.29 (br. s, 20 H), 0.89 (t, 6 H). – $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 39.9, 31.8, 29.1, 29.1, 28.8, 28.4, 22.6, 14.1. – Raman (80 mW, 20 °C): $\tilde{\nu}$ = 505 cm^{-1} (SS), 493 (SS), 459 (SS), 435 (SS).

Synthesis of Bis(*n*-octyl)heptasulfane (2) and -nonasulfane (3): To a stirred solution of $[Cp_2TiS_5]$ (0.846 g, 2.5 mmol) in CS_2 (30 mL) at –20 °C (**2**) or at –70 °C (**3**), a solution of *n*-octylsulfenyl chloride (0.904 g, 5 mmol) or *n*-octylchlorodisulfane (1.064 g, 5 mmol) in CS_2 (40 mL) was added dropwise. [The chlorodisulfane, a yellow viscous liquid, had been prepared from the thiol (10 mmol) and SCl_2 (12 mmol) in CH_3OtBu at –70 to +20 °C]. The color turned from dark-red to light-red. The precipitated $[Cp_2TiCl_2]$ was removed by filtration at 20 °C in the case of **2** and at –20 °C in the case of **3** and the filtrate was concentrated to one-half of its original volume. After cooling to –50 °C for several hours, the precipitated $[Cp_2TiCl_2]$ was filtered off. On complete removal of the solvent under reduced pressure, the liquid polysulfane was obtained. Yield: 1.127 g of the heptasulfane or 1.290 g of the nonasulfane (both quantitative). – **2:** freezing temp. –61 °C. – $C_{16}H_{34}S_7$ (450.9): calcd. C 42.6, H 7.6, S 49.8; found C 43.3, H 7.8, S 48.0. – UV/Vis (methanol): λ_{max} (%) = 226 nm (100), 300 (sh). – MS (160 °C): *m*/*z* (%) = 450 (1) $[M^+]$, 418 (7) $[M^+ – S]$, 386 (10) $[M^+ – 2S]$, 322 (100) $[M^+ – 4S]$. – ^1H NMR (200 MHz, $CDCl_3$): δ = 3.00 (t, 4 H), 179 (tt, 4 H), 1.46–1.29 (br. s, 20 H), 0.90 (t, 6 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.8, 31.8, 29.1, 29.1, 28.9, 28.4, 22.6, 14.1. – Raman (40 mW, –135 °C): $\tilde{\nu}$ = 429 cm^{-1} (SS), 445 (SS), 463 (SS), 470 (SS), 495 (SS). – **3:** freezing temp. –53 °C. – $C_{16}H_{34}S_9$ (515.1): calcd. C 37.3, H 6.7, S 56.0; found C 37.7, H 6.4, S 56.3. – UV/Vis (methanol): λ_{max} (%) = 228 nm (100), 284 (sh). – MS (160 °C): *m*/*z* (%) = 450 (0.2) $[M^+ – 2S]$, 418 (2) $[M^+ – 3S]$, 386 (4) $[M^+ – 4S]$, 145 (100) $[C_8H_{17}S]$. – ^1H NMR (200 MHz, $CDCl_3$): δ = 3.01 (t, 4 H), 1.79 (tt, 4 H), 1.47–1.29 (br. s, 20 H), 0.90 (t, 6 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.8, 31.8, 29.1, 28.9, 28.4, 22.6, 14.1. – Raman (40 mW, –135 °C): $\tilde{\nu}$ = 423 cm^{-1} (SS), 437 (SS), 452 (SS), 463 (SS), 472 (SS), 494 (SS).

Synthesis of Bis(2-naphthyl)heptasulfane (4): To a stirred solution of $C_{10}H_7SCl$ (0.29 g, 1.49 mmol) in CS_2 (40 mL), $[Cp_2TiS_5]$ (0.25 g, 0.74 mmol) was added at 20 °C under an N_2 atmosphere. After the color had changed to orange-red, the precipitated $[Cp_2TiCl_2]$ was filtered off and the filtrate was stirred with a few mg of silica gel to bind residual titanocene dichloride. After filtration, the solvent was evaporated to leave a yellow oil, which was dissolved in a small volume of CH_2Cl_2. A little *n*-hexane was added and the mixture was concentrated until some turbidity appeared. It was then cooled to –50 °C, which led to the deposition of crystals of **4**. The collected crystals were washed with *n*-hexane and dried to give **4** as a yellow powder, m.p. 55–58 °C; yield 0.18 g (51%). – $C_{20}H_{14}S_7$ (478.8): calcd. C 50.2, H 3.0, S 46.9; found C 50.1, H 3.1, S 45.3. – UV/Vis (methanol): λ_{max} (%) = 222 nm (92), 233 (97), 236 (100), 240 (98), 281 (34), 334 (14). – MS (210 °C): *m*/*z* (%) = 446 (0.3) $[M^+ – S]$, 115 (100) $[C_9H_7]$. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 8.09 (d), 7.83 (m), 7.68 (dd), 7.53 (m). – ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 127.0, 127.5, 127.8, 127.8, 129.3, 129.9, 133.0, 133.1, 133.4. – Raman (40 mW; 20 °C): $\tilde{\nu}$ = 394 cm^{-1} (m), 417 (sh), 430 (vs), 441 (s), 473 (vs), 505 (sh), 511 (s), 521 (m).

Synthesis of Bis(4-chlorophenyl)heptasulfane (5): To a stirred solution of $[Cp_2TiS_5]$ (1.00 g, 2.96 mmol) in CS_2 (70 mL), ClC_6H_4SCl (1.06 g, 5.91 mmol) was added at 20 °C. After 5 min., the color had changed to orange and the precipitated $[Cp_2TiCl_2]$ was filtered off. A few mg of silica gel was added to the filtrate to bind residual titanocene dichloride. After stirring for a few min., the solution was filtered, the filtrate was concentrated to a volume of 5 mL, and then *n*-pentane (10 mL), MTB ether (15 mL), and ethanol (15 mL) were added. The solvents were then evaporated until the solution became turbid. Cooling of the solution to –78 °C led to the deposition of crystals of **5** (m.p. 40 °C), which were filtered off, washed with *n*-pentane, and dried in air; yield 0.58 g (44%). – $C_{12}H_8Cl_2S_7$ (447.6): calcd. C 32.2, H 1.8, S 50.2; found C 32.3, H 1.7, S 50.2. – UV/Vis (methanol): λ_{max} (%) = 211 nm (93), 240 (100), 292 (30), 327 (23). – MS (160 °C): *m*/*z* (%) = 418 (0.2), 414 (0.4) $[M^+ – S]$, 382 (2) $[M^+ – 2S]$, 175 (100) $[C_6H_4ClS_2]$. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.57 (dm, 4 H), 7.36 (dm, 4 H). – ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 129.5, 132.0, 134.4, 135.0. – Raman (40 mW; 20 °C): $\tilde{\nu}$ = 376 cm^{-1} (m), 419 (w), 435 (vs), 456 (vw), 473 (vs), 509 (m), 541 (m).

Synthesis of 1,2,3,4,5-Benzopentathiepin (6): To a stirred solution of $[(Cp'_2TiCl)_2S_3]$ (0.150 g, 0.259 mmol) in CS_2 (40 mL) at –78 °C, a solution of 1,2-benzenebis(sulfenyl chloride) (0.055 g, 0.259 mmol) in CS_2 (40 mL) was added dropwise over a period of 20 min. [The bis(sulfenyl chloride) had been prepared by chlorination of the corresponding dithiol using elemental chlorine in CCl_4 at 0 °C]. On warming the reaction mixture to ambient temperature, the color changed from dark-green to light-red. After filtering off the precipitated $[Cp'_2TiCl_2]$, the filtrate was concentrated to one-quarter of its original volume and the mixture was cooled to –55 °C for several hours. After another filtration, the solvent was completely removed under reduced pressure. The yellow crude product was recrystallized from a mixture of CS_2 and CH_3OtBu (1:1). Yield: 0.045 g (73%); m.p. 58 °C. – $C_6H_4S_5$ (236.4): calcd. C

30.4, H 1.7, S 67.7; found C 30.3, H 1.4, S 66.1. – UV/Vis (methanol): λ_{max} (%) = 223 nm (100), 272 (sh), 314 (sh). – MS (88 °C): *m/z* (%) = 236 (16) [M^+], 172 (100) [$M^+ - S_2$]. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.85 (m, 2 H), 7.36 (m, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.8, 135.8, 129.6. – Raman (150 mW, 20 °C): $\tilde{\nu}$ = 418 cm^{-1} (SS), 428 (SS), 467 (SS), 490 (SS).

Synthesis of 1,2,3,4,5,6,7-Benzoheptathionin (7): The synthesis was carried out in analogy to the preparation of **4** starting from [Cp_2TiS_5] (0.8 g, 2.37 mmol) in CS_2 (150 mL) and 1,2-benzenebis(sulfenyl chloride) (0.5 g, 2.37 mmol) in CS_2 (50 mL). Yield: 0.59 g (83%); m.p. 107 °C. – $C_6H_4S_7$ (300.6): calcd. C 24.0, H 1.3; found C 24.2, H 1.1. – UV/Vis (methanol): λ_{max} (%) = 218 nm (100), 295 (sh). – MS (149 °C): *m/z* (%) = 300 (2) [M^+], 172 (100) [$C_6H_4S_3$]. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.77 (m, 2 H), 7.48 (m, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.9, 135.2, 131.3. – Raman (150 mW, 20 °C): $\tilde{\nu}$ = 436 cm^{-1} (SS), 451 (SS), 471 (SS), 495 (SS), 518 (SS).

Synthesis of 1,2,3,4,5,6,7,8-Benzooctathiecin (8): To a stirred solution of [(TMEDA)ZnS_6] (0.326 g, 0.94 mmol) in CS_2 (30 mL), a solution of 1,2-benzenebis(sulfenyl chloride) (0.2 g, 0.94 mmol) in CS_2 (20 mL) was added dropwise over a period of 30 min. After stirring for 1 h, the precipitated [(TMEDA)$ZnCl_2$] was filtered off and the solvent was removed completely from the filtrate. The crude yellow oil was crystallized from a mixture of CS_2 and MTB ether (1:1). Yield: 0.19 g (60%); m.p. 73 °C. – $C_6H_4S_8$ (332.6): calcd. C 21.7, H 1.2; found C 21.2, H 0.9. – UV/Vis (methanol): λ_{max} (%) = 213 nm (100), 235 (sh), 318 (sh). – MS (120 °C): *m/z* (%) = 332 (1) [M^+], 172 (100) [$C_6H_4S_3$]. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.74 (m, 2 H), 7.43 (m, 2 H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.4, 133.9, 129.8. – Raman (150 mW, 20°C): $\tilde{\nu}$ = 416 cm^{-1} (SS), 428 (SS), 438 (SS), 460 (SS), 467 (SS), 512 (SS).

Table 3. Crystal data and structure refinement for $C_6H_4S_7$

Empirical formula	$C_6H_4S_7$
Formula weight	300.51
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	orthorhombic
Space group	*Pnma*
Z	4
a [Å]	17.7990(7)
b [Å]	13.2422(6)
c [Å]	4.7990(2)
V [Å^3]	1131.11(8)
D (calcd.) [g cm^{-3}]	1.765
μ [mm^{-1}]	1.342
Crystal size [mm]	0.3 × 0.08 × 0.08
2θ range [°]	4.58–55.00
Index ranges	$h \pm 22$, $k + 17$, $l \pm 6$
Collected reflections	7947
Independent reflections	1358 (R_{int} = 0.0625)
Obsd. with $I > 2\sigma(I)$	916
Data/restraints/parameters	1358/0/61
Goodness-of-fit on F^2	1.119
R_1 [$I > 2\sigma(I)$]	0.0507
R_1 (all data)	0.0889
Largest diff. peak/hole [eÅ^{-3}]	0.425/–0.229

Crystallography: Crystals were obtained by dissolving **7** in carbon disulfide and adding *n*-hexane until the mixture became turbid. On cooling this mixture to 4 °C, crystals separated. Diffraction measurements were made at room temperature using a Siemens SMART CCD diffractometer (Mo-K_α radiation, 10 s per frame, 0.3° ω-scan increments, specimen–detector distance 3 cm). Preliminary lattice constants were obtained from 45 orientation frames and final unit cell dimensions by refinement of the reflections obtained from all frames. The compound crystallizes in the space group *Pnma* (no. 62). An empirical absorption correction (SADABS[27]) was performed. Structure solution and refinement were performed using SHELXTL.[28] H atom positions were calculated assuming trigonal-planar coordination of C atoms with C–H distances of 93 pm and were refined as riding on the C atoms with isotropic temperature factors $1.2U_{equiv.}$ of the corresponding C atoms. A summary of data collection and refinement is given in Table 3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136074. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax.: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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