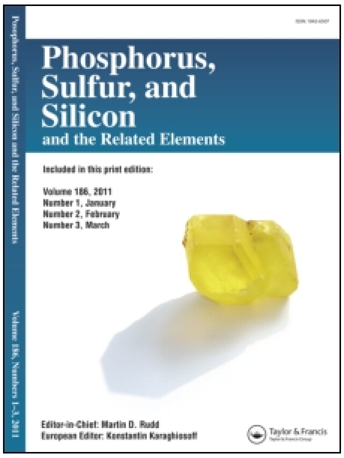

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PREPARATION AND CHARACTERIZATION OF LONG-CHAIN DI-*n*-ALKYL DISULFIDES

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The preparation of long-chain symmetric di-*n*-alkyl disulfides based on the reaction of BUNTE SALTS (RS_2O_3Na) with iodine is reported.

^{1}H-NMR, FT-IR, and FT-RAMAN spectra of the solid and liquid/molten aliphatic title disulfides were recorded. An assignment of the vibrational frequencies is proposed especially in regard to the S-S and C-S vibrations. Distinct spectral differences are determined between the solid and liquid state, as well as between disulfides with even and those with odd numbered alkyl substituents, respectively. The observed phenomena are ascribed to different species in the solids and liquids/melts and their respective VAN DER WAALS interactions.

In addition, mass spectra, GC-MS studies, as well as the thermal behaviour of the disulfides, based on investigations by DSC and TGA, are reported.

Keywords: Di-*n*-Alkyl Disulfides; RSSR ($R = C_nH_{2n+1}$ with n = 7–12,15,16,18); ^{1}H-NMR; IR; RAMAN, and Mass Spectra; GC-MS; DSC; TGA

INTRODUCTION

In the past, extensive interest has been drawn on the chemistry and, moreover, the biochemistry of organic disulfides not only due to the fact that this class of compounds is almost ubiquitous in nature, [1,2] but also due to their ability to give protection against ionizing radiation.[3] Our specific interest on the chemistry of these compounds derives from their ability to

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mobilize and transport elemental mercury, one of the most hazardous inorganic species which has a tremendeous impact on both our natural environment and human health.[4–9] The photochemical induced redox reaction of disulfides with elemental mercury is well-documented.[10–13] Recently, we[14–16] have investigated the thermal induced redox reaction of dimethyl disulfide, as well as of diphenyl disulfide with mercury. These results prompted us to specifically investigate the behaviour of long-chain symmetric di-*n*-alkyl disulfides towards mercury and inorganic, as well as organic mercury compounds. [17] On that behalf we prepared nine symmetrical long-chain di-*n*-alkyl disulfides. The results of these investigations include considerable work on ^{1}H-NMR, IR, and RAMAN spectroscopy, as well as mass spectrometry and GC-MS coupling. The thermal behaviour of these compounds, investigated by DSC and TGA, is also presented (Tab. VI).

RESULTS AND DISCUSSION

Preparation

The title compounds were prepared from the corresponding alkyl bromides and sodium thiosulfate in aqueous ethanol as solvent:

$$RBr + Na_2S_2O_3 \longrightarrow RS_2O_3Na + NaBr \qquad (1)$$

The resulting corresponding BUNTE SALT (RS_2O_3Na) was treated with iodine to form the respective di-*n*-alkyl disulfide:

$$2RS_2O_3Na + I_2 + 2H_2O \rightarrow RSSR + 2NaHSO_4 + 2HI \qquad (2)$$
$$R = C_7H_{15}\text{-}C_{12}H_{25},\ C_{15}H_{31},\ C_{16}H_{33},\ \text{and}\ C_{18}H_{37}$$

The used method of WESTLAKE and DOUGHERTY[19] was modified when deemed appropriate and conveniently afforded products in satisfactory yields. The purity of the disulfides was checked by GC and GC-MS methods. The results are given in Tab. I. As could be elucidated from the FPD signals of the gas chromatogrammes and the mass spectra the compounds mostly contain by-products (corresponding di-*n*-alkyl sulfides and di-*n*-alkyl trisulfides). The amounts of the by-products were not quantified.

TABLE I Retention times, R_t [min] and molecular ions, M^+ of the di-*n*-alkyl disulfides and of their by-products (mono and trisulfides) observed by GC(FPD) and GC-MS

	Monosulfide, RSR		*Disulfide, RSSR*		*Trisulfide, RSSSR*	
R	*M^+*	*R_t [min]*	*M^+*	*R_t [min]*	*M^+*	*R_t [min]*
C_7H_{15}	230	36.6	262	41.7	294	46.0
C_8H_{17}	258	-	290	45.9	322	50.0
C_9H_{19}	286	45.0	318	49.4	350	53.6
$C_{10}H_{21}$	314	48.9	346	53.1	378	57.0
$C_{11}H_{23}$	342	52.4	374	56.1	406	59.9
$C_{12}H_{25}$	370	55.7	402	59.1	434	63.0
$C_{15}H_{31}^*$	454	-	486	75.0	518	-
$C_{16}H_{33}^*$	-	69.5	514	74.9	-	-
$C_{18}H_{37}^*$	-	76.9	570	80.5	-	-

* Altered temperature programme; prolonged halt.

Nuclear Magnetic Resonance Spectra

The results of the ^{1}H-NMR spectra are listed in Tab. II. The spectra show the expected four signal groups in the regions of $\delta = 2.7$ ppm ($S\text{-}CH_2\text{-}CH_2$, triplett structure), $\delta = 2.0 - 1.6$ ppm ($S\text{-}CH_2\text{-}CH_2$, "t of t" structure), $\delta = 1.4 - 1.2$ ppm (all other CH_2 groups), and $\delta = 0.9$ ppm (CH_3, triplett structure). The absence of further resonances indicates high symmetry in solution as expected for symmetrical disulfides. Signals deriving from the by-products (di-*n*-alkyl sulfides, di-*n*-alkyl trisulfides) cannot be distinguished.

Vibrational Spectra (IR, RAMAN)

In the past, several disulfides, R-S-S-R, with a broad palette of organyl substituents have been investigated in detail by Infra-red and RAMAN spectroscopy.[20–24] Especially, the S-S vibrational frequencies in such compounds have been of interest because S-S groupings are present in rubber materials, cutting oil, and proteins. Connected to mobilization processes of environmentally relevant metals (e.g. mercury) a comprehensive investigation of a series of diorganyl disulfides was undertaken. While the disulfides with short alkyl chains are well characterized we direct our attention to di-n-alkyl disulfides with long-chain organyl groups, $(C_7H_{15}S)_2$ to $(C_{18}H_{37}S)_2$.

TABLE II ^{1}H-NMR data of the title di-*n*-alkyl disulfides; δ [ppm]; solvent: $CDCl_3$ internal standard: TMS

$(C_7H_{15}S)_2$ (1)	δ = 2.72 t, J = 8.0 Hz (SCH_2); 2.25 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.3 “s” (all other CH_2 protons); 0.92 t, J = 5.1 Hz (CH_3)
$(C_8H_{17}S)_2$ (2)	δ = 2.72 t, J = 7.0 Hz (SCH_2); 1.70 “t”, J = 6.6 Hz ($SCH_2C\underline{H}_2$) ; 1.4 “s” (all other CH_2 protons); 0.92 t, J = 5.4 Hz (CH_3)
$(C_9H_{19}S)_2$ (3)	δ = 2.78 t, J = 6.6 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.35 “s” (all other CH_2 protons); 0.95 t, J = 4.4 Hz (CH_3)
$(C_{10}H_{21}S)_2$ (4)	δ = 2.75 t, J = 7.2 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.35 “s” (all other CH_2 protons); 0.95 t, J = 3.0 Hz (CH_3)
$(C_{11}H_{23}S)_2$ (5)	δ = 2.75 t, J = 7,4 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.38 “s” (all other CH_2 protons); 0.92 t, J = 4.4 Hz (CH_3)
$(C_{12}H_{25}S)_2$ (6)	δ = 2.75 t, J = 7.2 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.35 “s” (all other CH_2 protons); 0.92 t, J = 4.4 Hz (CH_3)
$(C_{15}H_{31}S)_2$ (7)	δ = 2.70 t, J = 7.2 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.31 “s” (all other CH_2 protons); 0.90 t, J = 4.8 Hz (CH_3)
$(C_{16}H_{33}S)_2$ (8)	δ = 2.69 t, J = 7.3 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.26 “s” (all other CH_2 protons); 0.88 t, J = 5.1 Hz (CH_3)
$(C_{18}H_{37}S)_2$ (9)	δ = 2.70 t, J = 7.4 Hz (SCH_2); 2.0 – 1.6 “t” ($SCH_2C\underline{H}_2$) ; 1.27 “s” (all other CH_2 protons); 0.90 t, J = 4.5 Hz (CH_3)

In general, spectroscopic data of long-chain di-*n*-alkyl disulfides are scarce and incomplete or even missing for some compounds, e.g. for C_{11}, C_{15}, C_{16} representatives. Furthermore, it is often unclear whether the data belong to the liquid or to the solid state, and older polarisation data are questionable, too.[20–23]

In Tabs. VII, VIII and III and Figs. 1–4 the vibrational frequencies and spectra of the series of the investigated liquid/molten and solid disulfides are presented along with their estimated intensities, polarisation data, and proposed assignment.

The spectral feature of the whole series shows expected similarities, and the most frequencies are caused by the long-chain alkyl substituents.

Therefore, considering the disulfide spectra in comparison to those of higher paraffins and their appropriate derivatives all their spectroscopic phenomena and characteristics are recovered.[20–30] Therein included are also distinct differences of the vibrational spectra of the liquid/molten and the solid state, respectively. The liquid/melt is considered as molecular melt with several coiled conformers (with folded/tangled alkyl chains) and VAN DER WAALS interactions (alkyl-alkyl, alkyl-sulfur) between the disulfide molecules. A more or less imperfect crystallinity of the investigated solids is indicated by many coincidences of IR and RAMAN bands with interchanging intensities, and by splittings [c.f Ref. [25,28]] Moreover, efforts on X-ray crystallographic determinations of di-*n*-dodecyl disulfide failed until now. The reason could be discussed with a highly disordered structure of the disulfides in the solid state.[31]

Consequently, the vibrational spectra of the liquids/melts and the solids differ occasionally, and especially for the S-S vibrations (see discussion below).

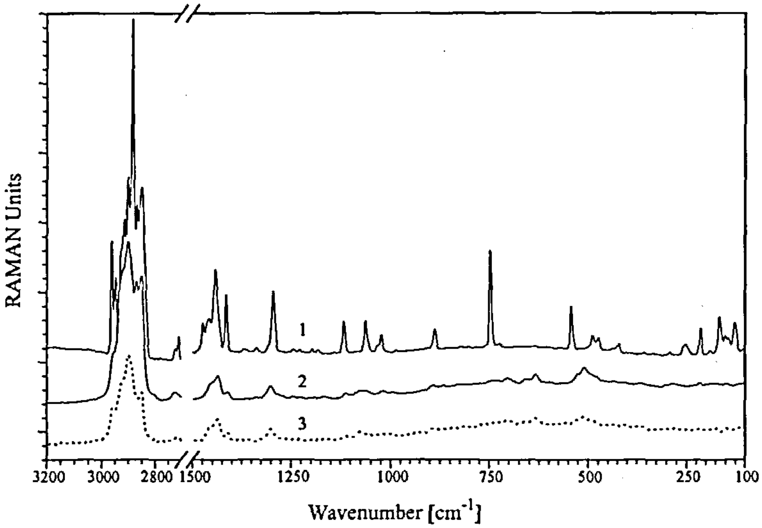
The relevant frequency regions are discussed in the following (c.f Tabs. VII, VIII and III including the proposed assignments):

The $>CH_2$ and $-CH_3$ stretchings are localized between 2700–3000 cm^{-1}. Their respective positions are generally agreed,[25–30] and the according assignments are made (Tab. VII, Figs. 1 and 2).

Below 1500 cm^{-1}, following a large frequency gap, the different $>CH_2$ and $-CH_3$ bendings, as well as the non-pronounced chain vibrations arise sometimes overlapping. Their sequence for paraffins and their derivatives is agreed, too[25-30], as $>CH_2$ scissoring at $\approx$ 1470 cm^{-1}, δ_{as} $(-CH_3)$ at $\approx$ 1460 – 1470 cm^{-1} and δ_s $(-CH_3)$ at $\approx$1380 cm^{-1}, respectively. The $>CH_2$ wagging and twisting vibrations are close together around 1300 cm^{-1}, respectively.

A series of equidistant bands is (often) seen in the region of 1180 – 1350 cm^{-1} ("progression bands" [28]) caused by twisting and rocking of trans-orientated $>CH_2$ groups. Their number is dependent upon the chain length (Tab. VIII, Figs. 1 and 2).

The strong IR absorption at 720 – 730 cm^{-1} ($>CH_2$ rocking) is both significant and useful for identification. Its appearance as a doublett is characteristic of the crystallinity and it allows the determination of the crystalline fraction of paraffins.[25,28]



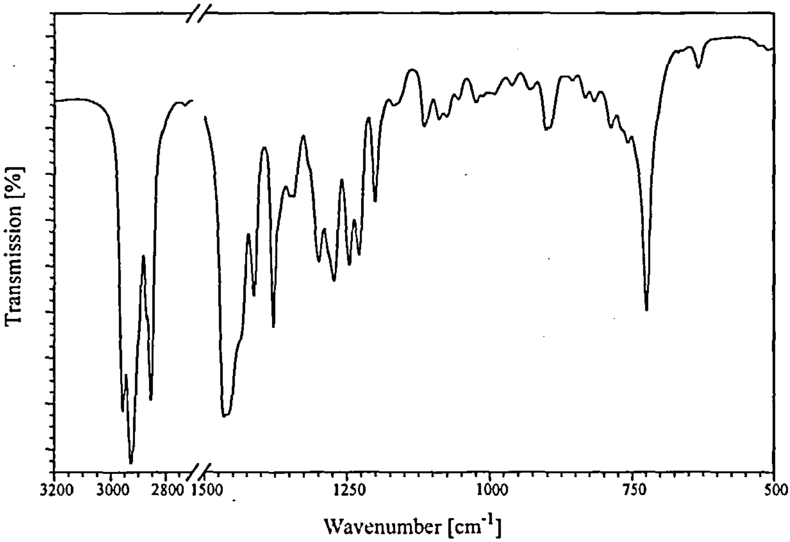
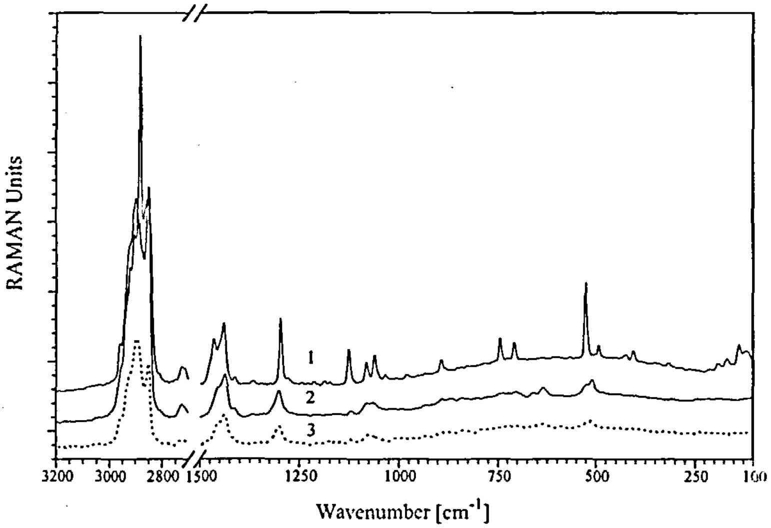


FIGURE 1 FT-RAMAN and FT-IR spectra of solid and liquid di-n-heptyl disulfide. Empty sections 4000- 3200 cm^{-1} and 2700–1500 cm^{-1} are cut off.

a: RAMAN, *solid: –100 °C (1)* RAMAN, *liquid: RT (2), and* RAMAN, *polarization of spectrum at* RT (3);

b: IR, film on KBr pellet: RT



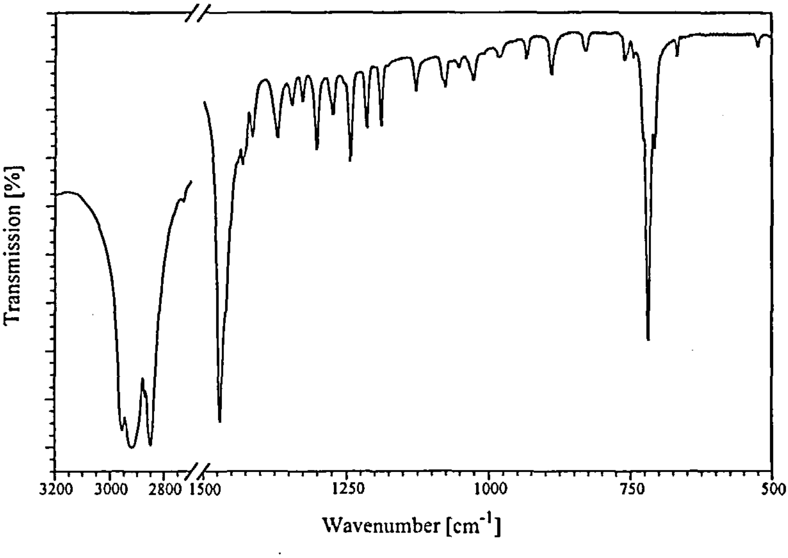


FIGURE 2 FT-RAMAN and FT-IR spectra of solid and molten di-n-dodecyl disulfide. Empty sections 4000–3200 cm^{-1} and 2700–1500 cm^{-1} are cut off.
a: RAMAN, solid: RT (1), RAMAN, liquid: +50 °C (2), and RAMAN, polarization of spectrum at +50 °C (3);
b: IR, KBr/PE pellet: RT

TABLE III Summarization of the S-S and C-S vibrational frequencies (480–780 cm^{-1}) of the investigated di-*n*-alkyl disulfides with estimated intensities, polarization data and proposed assignment. Abbreviations as in Tab. VII

$(C_7H_{15}S)_2$ (1)			$(C_8H_{17}S)_2$ (2)		$(C_9H_{19}S)_2$ (3)			$(C_{10}H_{21}S)_2$ (4)			
RE_s	RE_l	*IR*	RE_l	*IR*	RE_s	RE_l	*IR*	RE_s	RE_l	*IR*	*Proposed assignment*
-100 °C	*RT*	*RT*	*RT*	*RT*	*- 50 °C*	*RT*	*RT*	*- 30 °C*	*RT*	*RT*	
759 vvw				757 vvw						762 vvw	δ (C-C)
744 s	746 vvw	747 vvw			743 s			742 m			ν_{as}(C-S), δ (C-C)$^{1)}$
				730 vvw							($>CH_2$) rocking
725 vvw		723 vs		722 vs	725 vvw		721 vs	722 vvw		721 vs	($>CH_2$) rocking
	702 vvw					702 vw-w		706 w	704 w		ν_{as} (C-S)
	658 vvw, dp		658 vvw, dp			650 vvw, dp			658 vvw, dp		ν_{as} (C-S)
	634 w-m, p	632 w	634 w, p	632 w		634 w-m, p	633 w		634 w-m, p	632 vw	ν_s (C-S)
543 m					543 m						ν (S-S)$^{2)}$
	526 vvw, dp		520 vvw, dp	522 vvw		523 vvw		524 s	525 vvw, dp	523 vvw	ν (S-S)$^{3)}$
	511 m, p	510 vvw	509 m,p	508 vvw		507 m,p			509 m,p	510 vvw	ν(S-S)$^{4)}$
489 vw								490 vw			

$(C_{11}H_{23}S)_2$ (5)			$(C_{12}H_{25}S)_2$ (6)			$(C_{15}H_{31}S)_2$ (7)		$(C_{16}H_{33}S)_2$ (8)		$(C_{18}H_{37}S)_2$ (9)		
RE_s	RE_l	*IR*	RE_s	RE_l	*IR*	RE_s	*RI*	RE_s	*IR*	RE_s	*IR*	*Proposed assignment*
< 20 °C	50 °C	*RT*	< 25 °C	50 °C	*RT*	*RT*	*RT*	*RT*	*RT*	*RT*	*RT*	
		768 w-m					773 vw		765 vvw			δ (C-C)
744 vs	740 vvw	743 vvw	744 w-m	734 vvw	744 vvw	744 m		743 w-m		744 w		ν_{as}(C-S), δ (C-C)[1]
		729 vs					730 vs				730 vvw	($>CH_2$) rocking
		719 vs			719 vs		720 vs		718 vvs		719 vs	($>CH_2$) rocking
	703 vw		707 w-m	703 w, dp	707 vvw			707 w	708 vvw	707 w	707 vvw	ν_{as} (C-S)
	658 vvw			658 vw, dp								ν_{as} (C-S)
	634 w			635 w, p	630 vvw							ν_s (C-S)
541 m-s		541 vvw				541 w-m	540 vvw					ν (S-S)[2]
	525 vvw		525 s	521 vw, dp	525 vw			525 m-s	525 vw	525 s	525 vvw	ν (S-S)[3]
	510 m			*508 m, p*	*510 vvw*	*505 vvw*		506 vvw		510 vw		ν (S-S)[4]
487 vw			492 vw		492 vvw	489 vvw		487 vvw	490 vw			

[1] c. f. discussions; [2] Bound to solid disulfides with odd numbered alkyl substituents; [3] Characteristic for solid disulfides with even numbered alkyl substituents and similar species in the liquid/molten state; [4] Dominant in liquid/molten disulfides.

Chain bendings and >CH_2 torsions are indicated in the region of about 250 – 400 cm^{-1}. Socalled lattice vibrations of molecular crystals are detected below 200 cm^{-1} (20 – 200 cm^{-1}).[28,30] Both types are not indicative and not pronounced here.

The S-S vibrational behaviour is the most interesting here. $\nu_{(s\text{-}s)}$ is described as medium-strong RAMAN band and a very weak IR absorption in the region of 430 to 550 cm^{-1}, and, therefore, without significance.[20–23,28–30] Between 490 and 550 cm^{-1} there are only a few bands, and in each case only one with a sufficient RAMAN intensity (Tab. III, Figs. 3 and 4).

A remarkable difference for $\nu_{(ss)}$ is obvious for the liquid/molten and solid compounds. For the solids an intense RAMAN band is seen around 525 and 540 cm^{-1}, respectively. The band at 525 cm^{-1} belongs to disulfides with an even numbered alkyl substituent, whereas the band at 540 cm^{-1} belongs to those with an odd numbered alkyl substituent verified here for the C_7, C_9, C_{11} and C_{15} compounds. This can be understood by the different packing of even and odd numbered alkyl groups, as suggested for higher corresponding paraffins, too.[32] The mentioned strong $\nu_{(s\text{-}s)}$ RAMAN band of the solids is often associated with a very weak IR absorption around 525 $cm^{-1}$and a (very) weak RAMAN band around 490 cm^{-1}. The RAMAN spectra of the liquid/molten compounds are dominated in this relevant region by a medium-strong and polarized RAMAN absorption around 510 cm^{-1}, which is accompanied by a very weak and depolarized RAMAN band and a very weak IR band, both located around 525 cm^{-1}. As discussed before, coiled disulfide molecules with folded alkyl substituents and intramolecular alkyl-alkyl, as well as alkyl-sulfur interactions of VAN DER WAALS type are very likely in the liquid state. The polarized 510 cm^{-1} RAMAN band obviously arises from such species. The bands around 525 cm^{-1} are then ascribed to species similar to those of the solid state. Because this RAMAN band is depolarized its attribution to a cis-trans isomer as discussed by ALLUM et al.[22] is debatable.

The $\nu_{(c\text{-}s)}$ vibrations are established in the regions of 570 to 730 cm^{-1} for R-CH_2-S-CH_2-R type compounds [22,28–30] and at 630 to 790 cm^{-1} for aliphatic sulfides,[21] respectively. For the liquid/molten disulfides only one weak to medium and polarized RAMAN frequency around 634 cm^{-1} (with a very weak IR counterpart) and two (very) weak and depolarized RAMAN bands around 658 and 705 cm^{-1} are found. Therefore, the symmetric $\nu_{(c\text{-}s)}$ vibration is attributed to the 634 cm^{-1} band, the other two are proposed as asymmetric C-S vibrations of different coiled disulfide molecules (c.f Tab. III and Figs. III and IV).

TABLE IV Observed molecular and fragment ions in the mass spectra of di-*n*-alkyl disulfides (Base peak: m/e = 57)

$(C_7H_{15}S)_2$ (1): m/z: 262 ($M^{+\cdot}$); 164 ($C_7H_{15}SSH^{+\cdot}$); 131 ($C_7H_{15}S^+$)	71; 69;57; 55; 43; 41
$(C_8H_{17}S)_2$ (2): m/z: 290 ($M^{+\cdot}$); 178 ($C_8H_{17}SSH^{+\cdot}$); 145 ($C_8H_{17}S^+$)	85; 83; 71; 69; 57; 55; 43; 41
$(C_9H_{19}S)_2$ (3): m/z: 318 ($M^{+\cdot}$); 192 ($C_9H_{19}SSH^{+\cdot}$); 159 ($C_9H_{19}S^+$)	85; 83; 71; 69; 57; 55; 43; 41
$(C_{10}H_{21}S)_2$ (4): m/z: 346 ($M^{+\cdot}$); 206 ($C_{10}H_{21}SSH^{+\cdot}$); 173 ($C_{10}H_{21}S^+$)	99; 97; 85; 83; 71; 69; 57; 55; 43; 41
$(C_{11}H_{23}S)_2$ (5): m/z: 374 ($M^{+\cdot}$); 220 ($C_{11}H_{23}SSH^{+\cdot}$); 187 ($C_{11}H_{23}S^+$)	99; 97, 85; 83; 71; 69; 57; 55; 43; 41
$(C_{12}H_{25}S)_2$ (6): m/z: 402 ($M^{+\cdot}$); 234 ($C_{12}H_{25}SSH^{+\cdot}$); 201 ($C_{12}H_{25}S^+$)	113; 111; 99; 97; 85; 83; 71; 69; 57; 55; 43; 41
$(C_{15}H_{31}S)_2$ (7): m/z: 486 ($M^{+\cdot}$); 276 ($C_{15}H_{31}SSH^{+\cdot}$); 243 ($C_{15}H_{31}S^+$)	127; 125; 113; 111; 99; 97; 85; 83; 71; 69; 57; 55; 43; 41
$(C_{16}H_{33}S)_2$ (8): m/z: 514 ($M^{+\cdot}$); 290 ($C_{16}H_{33}SSH^{+\cdot}$); 257 ($C_{16}H_{33}S^+$)	141; 139; 127; 125; 113; 111; 99; 97; 85; 83; 71; 69; 57; 55; 43; 41
$(C_{18}H_{37}S)_2$ (9) : m/z: 570 ($M^{+\cdot}$); 318 ($C_{18}H_{37}SSH^{+\cdot}$); 285 ($C_{18}H_{37}S^+$)	155; 153; 141; 139; 127; 125; 113; 111; 99; 97; 85; 83; 71; 69; 57; 55; 43; 41

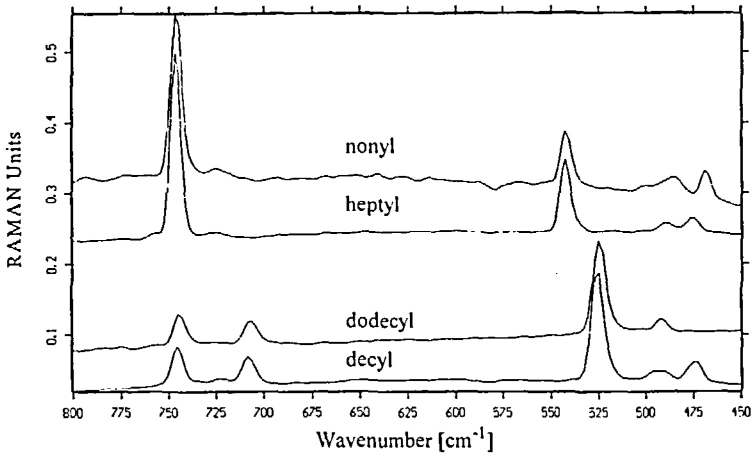


FIGURE 3 Comparison of the RAMAN spectra (relevant S-S- and C-S vibrational frequency region) of selected solid di-*n*-alkyl disulfides (*n*-alkyl = heptyl, nonyl, decyl, and dodecyl) with even and odd numbered alkyl substituents

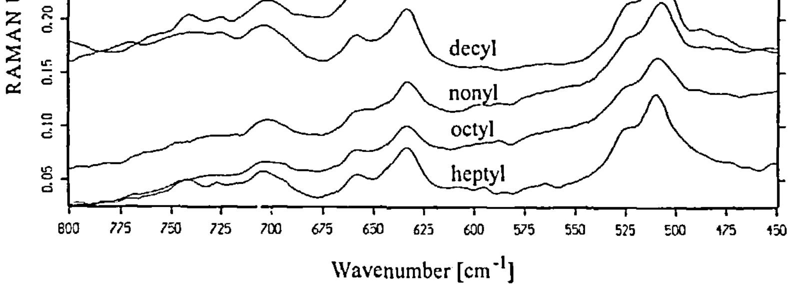


FIGURE 4 Comparison of the RAMAN spectra (relevant S-S and C-S vibrational frequency region) of the liquid/molten n-alkyl disulfides R-S-S-R with R: $C_n H_{2n+1}$ and n = 7 – 12

In the solid compounds a medium-strong RAMAN band appears around 743 cm^{-1}. This absorption might be assigned to the symmetric $\nu_{(C-S)}$ vibration for the species in the crystalline state or to C-C-C bendings, respectively.

Mass Spectra

The mass spectra (main fragmentation patterns) of the di-*n*-alkyl disulfides are summarized in Tab. IV.

Molecular ion peaks M^+ are observed with intensities of about 20% of the base peak which appears at m/e=57 ($C_4H_9^+$) or m/e = 43 ($C_3H_7^+$), respectively. Alkyl fragments typical for long-chain alkyl groups dominate peaks at lower masses. The largest alkyl fragment is observed at $C_{n-3}H_m^+$, indicating that C-S, α-, β-, and γ-C bond cleavages do not occur in di-n-alkyl disulfides. Characteristic fragment ions $RSSH^+$, RS^+ , and $C_nH_{2n}^+$ are abundant in the spectra of all compounds investigated (Tab. V). In Fig. 5 the mass spectrum of di-*n*-pentadecyl disulfide is given as an example.

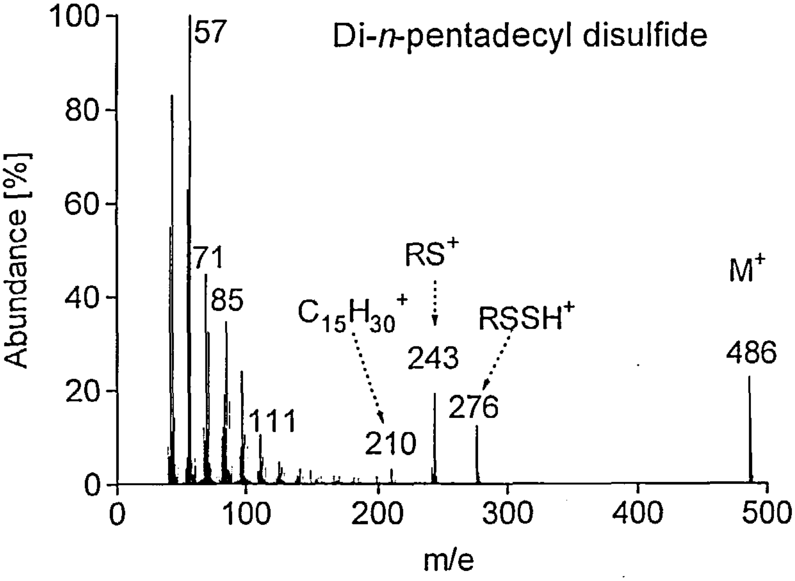


FIGURE 5 Mass spectrum of di-*n*-pentadecyl disulfide

The abundance of an intense molecular ion peak and of the $RSSH^+$ fragment ion has been reported for smaller di-*n*-alkyl disulfides up to di-*n*-octyl disulfide.[33–40] According to GUPTA[36] the $RSSH^+$ fragment ion is formed by a 1,3-hydrogen shift to the sulfur followed by elimination of an alkene. The further decomposition of the $RSSH^+$ fragment ions differs for di-*n*-alkyl sulfides with long-chain ($>C_7$) and short-chain alkyl substituents. Instead of $HSSH^+$ formed by another alkene elimination in short-chain di-n-alkyl disulfides for the longer-chain derivatives S-S-bond cleavage occurs. The intensity of the resulting RS^+ fragment relative to the $RSSH^+$fragment increases with increasing alkyl-chain length. Other characteristic peaks are odd electron ions $C_nH_{2n}{}^+$, conserving one entire alkyl group. These fragments are most likely formed from a cyclic rearrangement of the $RSSR^+$ fragment or the $RSSH^+$ fragment, respectively, with the charge being located on the carbon rather then the sulfur.[40] These species have not been reported, yet. Further information on the precursor and the structure cannot be derived from the current experiments.

TABLE V Characteristic ions in the mass spectra of di-*n*-alkyl disulfides

n	M^+	$RSSH^+$	RS^+	C_nH_{2n}	*Metastable Ions**	
($R= C_nH_{2n+1}$)	*m/e (% of base peak)*				$M^+ - RSSH^+$	$RSSH^+ - RS^+$
7	262 (13)	164 (14)	131 (8)	98 (2)	- (102.7)	- (104.6)
8	290 (23)	178 (22)	145 (14)	112(1)	109.2 (109.3)	118.3 (118.1)
9	318 (23)	192 (13)	159 (10)	126 (1)	116.0 (115.9)	131.8 (131.9)
10	346 (24)	206 (13)	173 (12)	140 (3)	122.8 (122.6)	145.4 (145.9)
11	374 (18)	220 (12)	187 (13)	154 (3)	129.3 (129.4)	159.1(159.0)
12	402 (21)	234 (9)	201 (11)	168 (4)	136.2 (136.3)	172.9 (172.7)
15	486 (23)	276 (12)	243 (19)	210 (3)	156.9 (156.7)	214.3 (213.9)
16	514 (22)	290 (7)	257 (16)	224 (6)	- (163.6)	- (227.8)
18	570 (32)	318 (8)	285 (14)	252 (2)	- (177.4)	- (255.4)

* Observed (calculated) mass.

The tentative mechanisms of the formation of the characteristic fragments in the mass spectra of di-*n*-alkyl disulfides are summarized in Fig. 6. This consecutive fragmentation is corroborated by the abundance of metastable peaks for the transitions $M^+ \rightarrow RSSH^+$, $RSSH^+ \rightarrow RS^+$ (cf. Tab. V) and $RSSH^+ \rightarrow HSSH^+$ (BOWIE et al.[39]). A metastable peak for the transition $M^+ \rightarrow RS^+$ observed in the spectrum of di-*n*-hexadecyl disulfide at m/e = 128.5 indicates that in longer-chain disulfides the direct formation of RS^+ from the molecular ion is also possible.

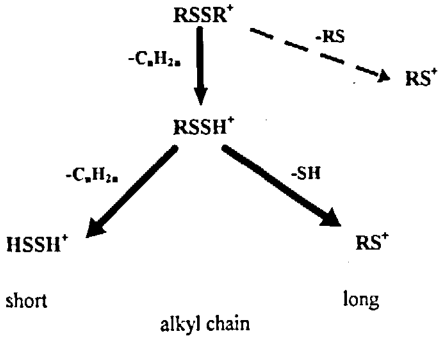


FIGURE 6 Fragmentation pattern of di-*n*-alkyl disulfides

CONCLUSION

A series of long-chain di-*n*-alkyl disulfides has been prepared and investigated by ^{1}H-NMR, IR, RAMAN, GC, and GC-MS, as well as DSC and DTG methods.

Distinct structural differences between the solid and liquid/molten state, as well as between disulfides with even and odd numbered alkyl subsituents are indicated by the IR and RAMAN spectra. Due to their non-rigidity long-chain substituted disulfide molecules occupy a disordered structure in the solid state. Moreover, strong dynamic effects of the disulfides in the liquid/molten state complicate the respective structural arrangement in the measured temperature range.

Intense molecular ion peaks and three characteristic fragment ions with one alkyl group conserved facilitate the identification of di-*n*-alkyl disulfides by mass spectrometry. The spectra show characteristic fragmentation patterns with differences between long-chain and short-chain alkyl substituents which, to our knowledge, have not been previously reported.

Acknowledgements

We thank N. Florescu for recording vibrational spectra, T. Reid for language corrections, and Dr. B. Essiger for thermoanalytical investigations.

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EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Bruker AC 80 FT-NMR spectrometer at 80.131 MHz using $CDCl_3$ as solvent and TMS as internal standard. Chemical Shifts are stated in ppm relative to TMS.

The RAMAN spectra of the title compounds were recorded with a RAMAN module FRA 106 (Nd: YAG laser: 1064 nm, < 200 mW) attached to a Bruker IFS 66v interferometer. RAMAN spectra at different temperatures were obtained with a heating/cooling unit.[18] Corresponding IR spectra were received from KBr-, CsI-, and PE-disulfide pellets, nujol grindings and films, respectively, with the forementioned FT-IR interferometer and a Perkin Elmer Paragon 1000 FT-IR spectrometer.

Mass spectra were run on a Kratos MS 50 TC mass spectrometer equipped with an electron impact ion source (70 eV) at a resolution of m/Δm = 1000, using GC-MS coupling (C_7-C_{12}) or a direct probe inlet system (C_{15}, C_{16}, C_{18}). For GC-MS 0.3 µl of pure liquid samples were injected into a split injector (split ratio 1: 100) of a Carlo Erba gas chromatograph equipped with a nonpolar fused silica capillary column (length: 25m, i.d. : 0.25 mm, film thickness: 0.25µm; temperature programme: 5 min at 50° C, 5 °C/min to 300°C, 10 min at 300 °C). Following this procedure small amounts of by-products (mono- and trisulfides) could be separated from the di-*n*-alkyl disulfides. For the direct probe measurements 1 mg of the sample was transferred into the mass spectrometer and heated at a rate of 10 °C/min, until a sufficient vapour pressure was established. Data were recorded and processed with Kratos software on a Data General Nova Eclipse computer.

Gas chromatographical investigations were performed using a Hewlett Packard Model 5890 Series II instrument, equipped with a 30 m DB 5 capillary column (i.d. : 0.25 mm) and a Hewlett Packard Flame Photometric Detector (FPD). The run conditions were initial temperature 35 °C and ramping to 320 °C at 5 °/min. The injector temperature and the detector temperature were set to 280 °C, respectively, and the helium carrier-gas flow was 1 ml/min.

TABLE VI Analytical data and yields of the title di-*n*-alkyl disulfides

Species (Numbering)	*Formula (Molecular Weight)*		*C [%]*	*H [%]*	*S [%]*	*Yield [g]*	*Yield ([%])*	*Mp [°C]*	*Decomposition [°C]*
Di-*n*-heptyl disulfide (1)	$[CH_3(CH_2)_6S]_2$ (262.5)	calc. found	64.1 63.2	11.5 11.8	24.4 22.7	5.94	(45.3)	- 4.0	204.5
Di-*n*-octyl disulfide (2)	$[CH_3(CH_2)_7S]_2$ (290.6)	calc. found	66.1 65.1	11.8 11.6	22.1 21.4	6.46	(44.4)	3.9	232.8
Di-*n*-nonyl disulfide (3)	$[CH_3(CH_2)_8S]_2$ (318.6)	calc. found	67.9 67.5	12.0 12.1	20.1 19.4	11.46	(71.8)	17.9	238.9
Di-*n*-decyl disulfide (4)	$[CH_3(CH_2)_9S]_2$ (346.7)	calc. found	69.4 69.5	12.1 12.4	18.5 17.6	7.41	(42.6)	22.2	240.0
Di-*n*-undecyl disulfide (5)	$[CH_3(CH_2)_{10}S]_2$ (374.72)	calc. found	70.5 69.6	12.3 12.6	17.1 16.2	7.24	(38.5)	36.0	266.4
Di-*n*-dodecyl disulfide (6)	$[CH_3(CH_2)_{11}S]_2$ (402.78)	calc. found	71.6 70.6	12.4 12.5	15.9 16.0	7.80	(38.5)	39.4	262.8
Di-*n*-pentadecyl disulfide (7)	$[CH_3(CH_2)_{14}S]_2$ (486.9)	calc. found	74.0 73.8	12.8 12.7	13.2 12.9	20.04	(82.3)	56.8	296.3
Di-*n*-hexadecyl disulfide (8)	$[CH_3(CH_2)_{15}S]_2$ (515.0)	calc. found	75.1 74.7	12.9 12.7	12.5 13.3	22.51	(87.4)	57.0	301.9
Di-*n*-octadecyl disulfide (9)	$[CH_3(CH_2)_{17}S]_2$ (571.1)	calc. found	75.7 74.9	13.1 12.9	11.2 11.9	21.81	(76.4)	62.8	314.2

Elemental analyses (C, H, S) were performed with a Heraeus Elemental Analyser. DSC and TGA measurements were obtained using a 910 Differential Scanning Calorimeter, a 951 Thermogravimetric Analyser, and a Thermal Analyst 2100 for data analyses. The procedure used to prepare the disulfides was that of WESTLAKE and DOUGHERTY[19] using BUNTE SALTS (RS_2O_3Na). Some modifications were necessary due to the liquid or solid state of the different products at RT. Yields and analytical data (elemental analyses, melting point and decomposition temperature) of the disulfides are given in Tab. VI.

Di-*n*-Heptyl Disulfide $(C_7H_{15}S)_2$ (1)

17.9 g (100 mmol) of *n*-heptyl bromide and 15.8 g (100 mmol) of $Na_2S_2O_3$ were dissolved in a mixture of 75 ml ethanol and of 75 ml water. The resulting reaction mixture was refluxed until a homogeneous solution resulted. Then iodine was added in small portions until the colour of iodine remained (approximately 12.6 g (100 mmol)). The water phase was separated and the residual oil washed twice with an aqueous solution of sodium hydrogensulfite to quantitatively remove iodine. After drying with sodium sulfate, filtration, and removal of the solvent the remaining oil was distilled at 1×10^{-3} mbar and 120 °C to yield 5.94 g (45.3 %) of **1**. IR and RAMAN data are given in Tabs. VII and VIII.

Di-*n*-Octyl Disulfide. $(C_8H_{17}S)_2$ (2)

Prepared as **1** from 0.1 mol portions of starting materials. The resulting oil was distilled at 1×10^{-3} mbar and 150 °C to yield 6.46 g (44.4 %) of 2.

IR (KBr) (cm^{-1}): 2954 vw, 2920 vvs, 2852 vs, 1465 vvs, 1455 sh, 1412 m, 1377 vs, 1348 vvw, 1293 vvw, 1289 w, 1267 vvw, 1260 w, 1236 w-m, 1221 vw, 1197 w-m, 1114 w, 1030 w, 913 vvw, 847 vvw, 805 vw, 757 vvw, 730 vvw, 722 vs, 632 w, 522 vvw, 508 vvw, 478 vw.

RAMAN (20 °C, liquid) (cm^{-1}) : 2957 vvw, dp, 2920 vvw, 2900 vs, p, 2872 vvw, p, 2851 s, p, 2808 vvw, 2724 w, p, 2710 vvw, 1452 vvw, dp, 1438 s, p, 1414 vvw, dp, 1301 m, 1269 vvw, 1112 vvw, 1076 vvw, 1062 vw, 1031 vw, 892 vvw, 871 vvw, 841 vw, 658 vvw, dp, 634 w, p, 520 vvw, dp, 509 m, p, 288 vvw.

Di-*n*-Nonyl Disulfide $(C_9H_{19}S)_2$ (3)

Prepared as **1** from 0.1 mol portions of starting materials. After washing twice with an aqueous solution of sodium hydrogensulfite the resulting mixture was cooled to 6 °C. The precipitated product was filtered and recrystallized from hot ethanol to yield 11.46 g (71.8 %) colourless crystalline solid **3**.

IR (KBr) (cm^{-1}): 2953 vw, 2924 vvs, 2852 vs, 1464 vs, 1456 sh, 1412 m-s, 1377 s, 1349 vvw, 1299 vw, 1280 w, 1252 m, 1228 m, 1214 vvw, 1195 vw, 1116 w, 1076 vw, 1040 vw, 954 w, 889 w, 816 w, 721 vs, 633 w, 479 m.

RAMAN (-50 °C) (cm^{-1}) : Measured region: 800- 450 cm^{-1} : 743 s, 725 vvw, 543 m, 485 vw.

RAMAN (20 °C, liquid) (cm^{-1}) : 2958 vw, dp, 2920 vvw, 2899 vs, p, 2872 vvw, p, 2851 s, p, 2808 vvw, 2727 w, p, 2710 vvw, 1454 vvw, dp, 1437 s, p, 1413 vw, dp, 1301 m-s, 1285 vvw, 1229 vvw, 1115 vw, 1065 w, br, 1033 vvw, 868 vvw, br, 702 vw-w, 650 vvw, dp, 634 w-m, p, 523 vvw, 507 m, p, 483 vvw, dp.

Di-*n*-Decyl Disulfide $(C_{10}H_{21}S)_2$ (4)

Prepared as described for **3** from 0.1 mol portions of starting materials. The product was filtered and recrystallized from hot ethanol to yield 7.41 g (42.6 %) colourless crystalline solid **4**.

IR (KBr) (cm^{-1}) : 2955 vw, 2921 vvs, 2870 vvw, 2851 vs, 1465 vs, 1459 sh, 1412 m, 1377 s, 1299 w, 1273 w-m, 1253 w, 1223 w, 1118 w, 1073 vw, br, 960 vw, br, 891 w-m, 803 vw, 721 vs, 632 vw, 523 vvw, 510 vvw.

RAMAN (-50 °C, solid) (cm^{-1}): 2958 vvw, 2920 vw, 2912 w, 2881 vs, 2851 m, 2720 w, 1470 m, 1438 s, 1412 vw, 1292 s, 1260 vvw, 1224 vvw, 1189 vvw, 1125 s, 1067 m, 1058 m, 1050 vvw, 1035 vvw, 886 w, 742 m, 722 vvw, 706 w, 524 s, 490 vw, 409 vw, 354 vvw, 155 vw, 131 vw, 93 w.

RAMAN (20 °C, liquid) (cm^{-1}) : 2957 vw, dp, 2921 vvw, 2899 vs, p, 2895 s, dp, 2872 vvw, p, 2850 s, p, 2807 vvw, 2727 w, p, 2712 vvw, 1453 vvw, dp, 1437 s, p, 1412 vvw, dp, 1376 vvw, 1300 m-s, 1150 vvw, 1117 vvw, 1073 vvw, 1063 w, br, 891 vw, 704 w, 658 vvw, dp, 634 w-m, p, 525 vvw, dp, 509 m, p.

Di-*n*-Undecyl-Disulfide $(C_{11}H_{23}S)_2$ (5)

Prepared as **1** from 0.1 mol portions of starting materials. The mixture was allowed to cool at RT. The solid product separated from the solution was filtered and dissolved in hot ethanol. Iodine was removed with a warm aqueous solution of sodium hydrogensulfite. The product precipitated again at RT and was filtered, dissolved in CH_2Cl_2 and dried with sodium sulfate. After filtration the solvent was evaporated. **5** remained as a colourless crystalline solid (7.24 g; 38.5 %).

IR (KBr) (cm^{-1}) : 2953 vw, 2919 vvs, 2870 vvw, 2850 vvs, 1472 s, 1462 vvs, 1448 vvw, 1434 w, 1368 w, 1353 vvw, 1336 vvw, 1308 w, 1278 vw, 1248 w-m, 1217 w-m, 1188 w, 1125 vw, 1062 vvw, 1026 vw, 1013 vw, 975 vvw, 891 vvw, 862 w, 768 w-m, 743 vvw, 729 vs, 719 vs, 541 vvw.

Raman (<20 °C, solid) (cm^{-1}) : 2964 vw, 2949 vvw, 2932 vvw, 2917 vw, 2897 vvw, 2882 vs, 2848 s, 2722 w, 2705 vvw, 1489 vvw, 1466 w, 1440 vs, 1417 s, 1368 vw, 1338 vvw, 1294 vs, 1261 vvw, 1216 vvw, 1188 vvw, 1175 vw, 1124 s, 1074 m, 1061 m-s, 1026 vvw, 1012 vw, 889 m, 744 vs, 541 m-s, 487 vw, 414 w, 394 w, 306 w, br, 162 w, 140 m, 111 m.

Raman (> 20 °C, liquid) (cm^{-1}): 2959 vvw, 2919 vvw, 2898 vs, 2850 s, 2725 w, 2712 vvw, 1454 vvw, 1438 s, 1416 vvw, 1300 m-s, 1121 vvw, 1076 vvw, 1063 w, 884 vvw, br, 740 vvw, 703 w, 658 vvw, 634 w, 525 vvw, 510 m.

Di-*n*-Docedyl Disulfide $(C_{12}H_{25}S)_2$ (6)

Prepared as described for **5** from 0.1 mol portions of starting materials. **6** remained as a colourless crystalline solid (7.80 g; 38.5 %). IR and RAMAN data are given in Tabs. VII and VIII.

Di-*n*-Pentadecyl Disulfide $(C_{15}H_{31}S)_2$ (7)

Prepared as described for **5** from 0.1 mol portions of starting materials. **7** remained as a colourless crystalline solid (20.0 g; 82.3 %).

IR (KBr) (cm^{-1}) : 2953 w, 2919 vvs, 2870 vvw, 2850 vvs, 1472 vvs, 1462 vvs, 1433 vvw, 1406 vvw, 1370 vw, 1351 vvw, 1336 vvw, 1316 vvw, 1294 vvw, 1272 vvw, 1249 vw, 1226 w, 1205 w, 1184 vvw, 1128 vw, 1061 vvw, 1006 vvw, 975 vw, br, 925 vvw, 891 vw, 842 vw, 773 vw, 730 vs, 720 vs, 540 vvw.

Raman (20 °C, solid) (cm^{-1}): 2964 vw, 2949 vvw, 2928 vvw, 2916 vw, 2905 vvw, 2882 vs, 2847 s, 2716 w, 2695 vvw, 1463 w, 1440 s, 1416 w-m, 1368 vvw, 1295 vs, 1172 vvw, 1127 m, 1093 w, 1062 m, 1045 vvw, 1022 vvw, 1005 vvw, 890 w, 744 m, 541 w-m, 505 vvw, 489 vvw, 126 vw, 104 vw.

TABLE VII Observed vibrational frequencies [cm^{-1}] (region above 2700 cm^{-1}; -CH3 and >CH_2 vibrations) of solid and molten di-*n*-heptyl and di-*n*-dodecyl disulfide with estimated intensities, polarization data and proposed assignment as exemplary specification. Practically identical alkyl chain related data were determined for the other investigated disulfides, RSSR with $R = C_nH_{2n+1}$ and n = 7 – 11, 15, 16, and 18

Di-n-heptyl disulfide			*Di-n-dodecyl disulfide*				*Proposed assignment*
RE_s (-100°C)	*RE_l (RT)*	*IR (RT)*	*RE_s (RT/ -25 °C)*	*RE_l (50°C)*	*RE_l [22]*	*IR_s (RT)*	
2962 m	2955 vvw	2953 vvw	2959 vw	2958 vw, dp		2953 vw	ν_{as} (-CH_3)
2944 w							Combination ?
2912 vvw	2917 vvw	2922 vvs	2920 vvw	2925 vw, dp	2931 m	2919 vvs	(>CH_2) Stretching
2899 w	2901 vs, p		2906 vvw	2902 vs, p	2898s		(>CH_2) Stretching
2881 vs			2881 vs	2894 s, dp			(>CH_2) Stretching
2865 vvw	2872 vw, p	2870 vvw				2870 vvw	ν_s (-CH_3)
		2854 vs	2856 vvw			2850 vvs	(>CH_2) Stretching
2849 m	2852 s, p		2848 s	2852 s, p	2853 m		(>CH_2) Stretching
	2809 vvw						Combination bands
2721 vvw	2728 w, p	2730 w	2725 w	2725 w, p			Combination bands
2712 w	2717 vvw		2708 vvw	2719 vvw			Combination bands

RE_s: RAMAN, solid; RE_l: RAMAN, liquid; IR_s: Infrared, solid.
s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, p = polarized, dp = depolarized.

TABLE VIII Observed vibrational frequencies [cm^{-1}] of solid and liquid/molten di-*n*-heptyl and di-*n*-dodecyl disulfide with estimated intensities, polarization data and proposed assignment (region below 1500 cm^{-1}, c.f Tab. VII and Tab. III) as exemplary specification. Practically identical alkyl chain related data were determined for the other title disulfides.

The sometimes weak sulfur RAMAN bands (S_8: 152, 218 and 472 cm^{-1}), occuring from the thermal decomposition during distillative purifications, were omitted. Abbreviations as in Tab. VII

Di-n-heptyl disulfide			*Di-n-dodecyl disulfide*			
RE_s (-100 °C)	*RE_l (RT)*	*IR (RT)*	*RE_s (RT/ -25 °C)*	*RE_l (50°C)*	*IR_s (RT)*	*Proposed assignment*
1474 vw		1465 vs			1470 vvs	$\delta_{as}(-CH_3) + \delta(>CH_2)$
1465 vvw	1454 vvw, dp	1457 sh	1464 w	1460 vvw	1462 sh	Scissoring
1442 s	1437 s, p		1439 s	1439 s (dp ?)		(C-C-C)
1413 s	1413 vvw, dp	1412 s	1415 vvw	1415 vvw, dp	1414 vvw	
1365 vvw		1377 vs	1367 vvw		1370 w-m	$\delta_S(-CH_3)$
1336 vvw		1342 vvw			1344 vvw	
					1325 vvw	
1290 s	1301 m (p ?)	1299 m	1296 s	1298 s, dp	1301 w-m	$\omega(>CH_2)$ and $\tau(>CH_2)$[a)]
		1272 m-s	1282 vvw		1272 vw	$\omega(>CH_2)$ and $\tau(>CH_2)$[a)]
1240 vvw	1246 vvw	1245 m-s			1243 m	$\omega(>CH_2)$ and $\tau(>CH_2)$[a)]
1224 vvw	1225 ww	1228 m-s	1223 vvw		1215 w-m	$\omega(>CH_2)$ and $\tau(>CH_2)$[a)]
1197 vvw		1200 s			1188 w-m	$\omega(>CH_2)$ and $\tau(>CH_2)$[a)]
	1166 vvw	1168 vvw				
1114 m	1113 vvw	1114 w-m	1126 m-s	1115 vvw	1127w	(C-C-C ?)
	1074 vw, br	1088 vvw	1081 w	1072 w-m, dp	1075 vw	(C-C-C ?)
1061 m	1062 vvw, br		1060 w-m		1051 vvw	
1021 w	1020 vw	1024 vvw	1035 ww		1025 vw	$\rho(-CH_3)$
			1008 vvw			

Di-n-heptyl disulfide			*Di-n-dodecyl disulfide*			
RE_s (-100 °C)	*RE_l (RT)*	*IR (RT)*	*RE_s (RT/ -25 °C)*	*RE_l (50°C)*	*IR_s (RT)*	*Proposed assignment*
		960 vvw	978 vvw		979 vvw	
		913 vvw			933 vw	
905 vvw		900 w-m, br				
883 w-m	890 vw, dp	830 vvw	891 w-m	885 vw	889 w	
		816 vvw				
		786 vvw				
759 vvw						δ(C-C-C)
744 s	746 vvw	747 vvw	744 w-m	734 vvw	744 vvw	c.f Tab. III
725 vvw		723 vs			719 vs	$\rho(>CH_2)$
	702 vw		707 w-m	703 w, dp	707 vvw	ν_{as} (C-S)
	658 vvw, dp			658 vw, dp		ν_{as} (C-S)
	634 w-m, p	632 w		635 w, p	630 vvw, br	ν_s (C-S)
543 m	526 vvw, dp		525 s	521 vw, dp	525 vw	ν_s (S-S)
	511 m,p	510 vvw		508 m,p	510 vvw	ν_s (S-S)
489 vw			492 vw		492 vvw	
			405 vw			$\tau(>CH_2)$; $\tau(-CH_3)$ and/or δ_s(C-C-C)
	286 vw, br					$\tau(>CH_2)$; $\tau(-CH_3)$ and/or δ_s(C-C-C)
252 w						
213 w-m						
186 vvw	182 vvw, br					$\tau(>CH_2)$; $\tau(-CH_3)$ and/or δ_s(C-C-C)
165 w-m			170 vvw			Lattice vibrations
149 vvw			136 vw			Lattice vibrations
125 w			110 vvw			Lattice vibrations

[a] See also discussions.

Di-*n*-Hexadecyl Disulfide $(C_{16}H_{33}S)_2$ (8)

Prepared as described for **5** from 0.1 mol portions of starting materials. **8** remained as a colourless crystalline solid (22.5 g; 87.4 %).

IR (KBr) (cm^{-1}): 2954 vw, 2918 vvs, 2870 vvw, 2849 vvs, 1471 vvs, 1466 sh, 1414 vvw, 1376 vs, 1343 vvw, 1311vw, 1292 vvw, 1271w, 1247 vw, 1225 w-m, 1203 w, 1184 w, 1130 vw, 1097 vvw, 1075 vw, 1016 vvw, 975 w, 889 w, 765 vvw, 718 vvs, 708 vvw, 525 vw, 490 vvw.

RAMAN (20 °C, solid) (cm^{-1}) : 2959 vvw, 2932 vvw, 2904 vvw, 2881 vs, 2853 vvw, 2848 s, 2810 vvw, 2723 w, 2708 vvw, 1465 w, 1440 s, 1412 vvw, 1368 vvw, 1296 s, 1129 m, 1097 w, 1061 m, 1007 vvw, 888 vw, 743 w-m, 707 w, 525 m-s, 506 vvw, 487 vvw, 131 vw, 106 vvw.

Di-*n*-Octacedyl Disulfide $(C_{18}H_{37}S)_2$ (9)

Prepared as described for **5** from 0.1 mol portions of starting materials. **9** remained as a colourless crystalline solid (21.8 g; 76.4 %).

IR (KBr) (cm^{-1}) : 2954 vw, 2918 vvs, 2870 vvw, 2850 vvs, 1471 vvs, 1467 sh, 1413 vvw, 1376 vs, 1297 w, 1279 vvw, 1259 vw, 1238 vvw, 1218 w-m, 1200 vvw, 1183 vw, 1130 vvw, 1075 w, 1051 vvw, 889 w, 849 vvw, 730 vvw, 719 vs, 707 vvw, 525 vvw.

RAMAN (20 °C, solid) (cm^{-1}): 2958 vvw, 2932 vvw, 2918 vvw, 2905 vvw, 2881 vs, 2853 vvw, 2848 s, 2725 w, 2706 vvw, 1465 w, 1440 s, 1414 vvw, 1370 vvw, 1295 vs, 1129 m, 1103 w, 1060 m, 1026 vvw, 891 vw, 744 vw, 707 w, 525 s, 510 vw, 329 vvw, II 0 w, br.

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