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Preparation and Characterization of Bis(thioacyl) Tri- and Tetrasulfides

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Bis(thioacyl) tri- **1** and tetrasulfides **2** have been prepared by the reaction of dithiocarboxylic acids with sulfur- or disulfur dichloride. The crystalline aromatic bis(thioacyl) sulfides (**1**, **2**, R = aromatic) are stable towards heat and moisture. The $n \rightarrow \pi^*$ transitions (λ_{max}) of the thiocarbonyl groups of bis(thioacyl) sulfides [$RC(S)-S_x-(S)CR$, $x = 1-4$] are influenced by the number x of sulfur atoms. In addition, the remarkable difference in the $n \rightarrow \pi^*$ transitions (λ_{max}) between monosulfides [RC(S)S(S)CR] and polysulfides [$RC(S)-S_x-(S)CR$, $x = 2-4$] shows no contradiction with the results of the *ab initio* molecular-orbital calculation by employing bis(thioformyl) sulfides [$HC(S)-S_x-(S)CH$, $x = 1-3$] as model compounds. The results of the calculation of the charge distribution and the frontier-electron densities show that nucleophiles or electron-donating reagents attack the sulfide sulfur in a charge-controlled reaction and the thiocarbonyl sulfur in a frontier-orbital-controlled reaction.

Darstellung und Charakterisierung von Bis(thioacyl)tri- und -tetrasulfiden

Durch Umsetzung von Dithiocarbonsäuren mit Schwefeldichlorid oder Dischwefeldichlorid werden einige Bis(thioacyl)tri- **1** und -tetrasulfide **2** dargestellt. Die aromatischen Bis(thioacyl)-sulfide (**1**, **2**, R = Arylrest) sind thermisch stabile und nicht feuchtigkeitsempfindliche Kristalle. Die $n \rightarrow \pi^*$-Übergänge der Thiocarbonylgruppen in Bis(thioacyl)sulfiden [$RC(S)-S_x-(S)CR$, $x = 1-4$] sind von der Anzahl x der Schwefelatome abhängig. Ferner stimmt der merkliche Unterschied zwischen den $n \rightarrow \pi^*$-Übergängen (λ_{max}) der Monosulfide vom Typ RC(S)S(S)CR und denen der Sulfide $RC(S)-S_x-(S)CR$ ($x = 2-4$) mit dem Ergebnis von ab-initio-Molekül-Orbital-Berechnungen an Bis(thioformyl)sulfiden [$HC(S)-S_x-(S)CH$, $x = 1-3$] überein. Die Rechnungen zur Bestimmung der Ladungsverteilung und Grenzorbital-Elektronendichte sagen einen ladungskontrollierten Angriff von Nucleophilen oder Elektronen-Donoren auf den Sulfid-Schwefel voraus, während die Reaktion mit dem Thiocarbonyl-Schwefel der Grenzorbital-Kontrolle unterliegt.

Recently several acyclic and cyclic tri- and tetrasulfides have been found in naturally occurring compounds. For example, dimethyl trisulfide is found as a defensive secretion of the ant species *Paltothyreus tarsatus*[1]. Symmetrical alkyl trisulfides are found in the flavor components of garlic extract[2] and onion oil[3,4]. Mushrooms contain simple cyclic trisulfides[5]. Hawaiian algae also yield tri- and tetrasulfides[6]. Conformation analyses[7] and spectroscopical investigations[8-9] of simple acyclic polysulfides have been carried out[10]. Bis(acyl) polysulfides [$RC(O)-S_x-(O)CR$, $x = 3-5$] were prepared and characterized by *Böhme* and *Clement* in 1952[11]. In contrast,

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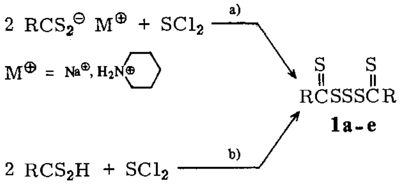
bis(thioacyl) polysulfides [RC(S) – S_x – (S)CR, $x \geqslant 3$] have not yet been investigated[12]. Previously, we reported a convenient preparation of bis(thioacyl) disulfides[13]. Recently, aromatic bis(thioacyl) sulfides were isolated as crystals in our laboratory[14].

These results stimulated us to prepare bis(thioacyl) polysulfides. In this paper we report the first isolation and characterization of bis(thioacyl) tri- **1** and tetrasulfides **2** and the comparison with their spectral data.

Results and Discussion

For the preparation of bis(thioacyl) trisulfides, two routes have been investigated: reaction of a) piperidinium or sodium dithiocarboxylates with sulfur dichloride and b) dithiocarboxylic acids with sulfur dichloride. Route a), however, proved to be unpractical due to problems with the purification of the products. Route b) was found to be successful.



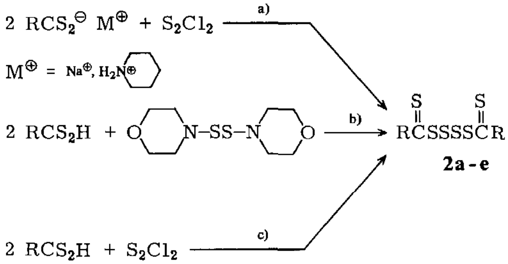
	R
1a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	4-ClC_6H_4
e	2,4,6-$(CH_3)_3C_6H_2$

For example, when a solution of sulfur dichloride in carbon tetrachloride was added to equivalents of 4-(methyl)dithiobenzoic acid in the same solvent at 0°C, a light purple solid precipitated. Filtration of this solid, followed by recrystallization gave the expected bis[4-(methyl)thiobenzoyl] trisulfide (**1b**) as light purple crystals in 57% yield.

The structure of **1b** was confirmed by IR, UV/Vis, and ^1H NMR spectra and elemental analyses. The IR spectrum of **1b** exhibits a medium absorption band near 1227 cm^{-1} due to the thiocarbonyl stretching vibration. In the electron spectrum, a characteristic weak absorption band at 530 nm (lg ε = 2.40) is observed in the visible region, apparently due to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. The ^1H NMR spectrum shows a methyl singlet at δ = 2.53 and a multiplet in the region of δ = 7.12 – 8.16 due to aromatic ring protons.

Similarly, the reactions of other dithiocarboxylic acids with sulfur dichloride gave the corresponding trisulfides **1a**, **1c – e** in moderate isolated yields (Table 5).

For the preparation of bis(thioacyl) tetrasulfides **2**, the following three routes have been investigated: a) reaction of disulfur dichloride with piperidinium or sodium



	R
2a	C_6H_5
b	4-$CH_3C_6H_4$
c	3-$CH_3OC_6H_4$
d	4-ClC_6H_4
e	2,4,6-$(CH_3)_3C_6H_2$

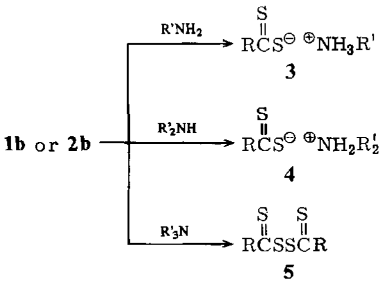
dithiocarboxylates, b) reaction of dithiobis(morpholine) with dithiocarboxylic acid, and c) reaction of disulfur dichloride with dithiocarboxylic acid. The most practical route was route c).

For example, when a solution of disulfur dichloride in carbon tetrachloride was added to two equivalents of 4-(methyl)dithiobenzoic acid in the same solvent at 0°C a violet solid precipitated which gave by recrystallization the expected bis[4-(methyl)thiobenzoyl] tetrasulfide (**2b**) as light purple crystals in 61% yield.

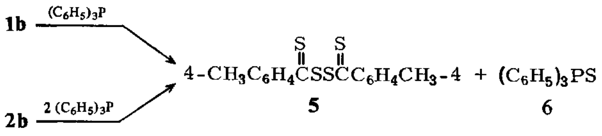
The structure of **2b** was established by IR, UV/Vis, and ^1H NMR spectra and elemental analyses. The IR spectrum of **2b** exhibits an absorption near 1234 cm^{-1} due to the thiocarbonyl stretching vibration. In the electron spectrum, a characteristic weak absorption band at 527 nm ($\lg \varepsilon = 2.49$) is observed in the visible region, apparently due to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. The ^1H NMR spectrum shows only a methyl singlet at $\delta = 2.34$ and a multiplet in the region of $\delta = 6.86 - 7.86$ due to aromatic ring protons.

By similar treatment of other dithiocarboxylic acids with disulfur dichloride, the corresponding tetrasulfides **2a**, **2c – e** were obtained in moderate isolated yields (Table 5).

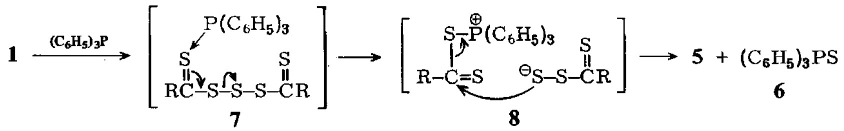
The aromatic bis(thioacyl) tri- and tetrasulfides obtained are red to purple crystals and very stable towards heat and moisture. On silica gel, however, they decompose. They are readily dissolved in dichloromethane, chloroform, benzene, and ether, but their solubilities are low in *n*-hexane, carbon tetrachloride, and ethanol. If **1b** is treated with primary and secondary amines such as cyclohexylamine and piperidine at 0°C, the corresponding ammonium 4-(methyl)dithiobenzoates **3a**, **4a** are obtained as main products, which gradually decompose at room temperature (ca. 30°C) to give the corresponding thioamides.



The same products are also obtained from the tetrasulfide **2b**. The similar reaction of **1b** with tertiary amines such as triethylamine gives the disulfide **5** in 70% yield. In addition, reaction of **1b** with the equivalent amount of triphenylphosphane affords **5** in 65% yield.



It is known that desulfurization of trisulfides (RSSSR, R = alkyl, aryl) with tertiary phosphorus compounds such as triphenylphosphane occurs on both the central and the terminal sulfur atoms[15]. In the case of bis(thioacyl) trisulfides, however, it is considered that desulfurization involving the thiocarbonyl sulfur removal by triphenylphosphane preferentially proceeds *via* the phosphonium-like intermediate 7, followed by an attack of the perdithiocarboxylate anion on the thiocarbonyl carbon.



The preferential attack of triphenylphosphane on the thiocarbonyl sulfur in bis(thioacyl) trisulfides is supported by the results of *ab initio* molecular-orbital calculations using bis(thioformyl) trisulfide as a model as mentioned later.

Structure

It is difficult to obtain single-crystals of **1** and **2** for X-ray crystal analysis. In order to obtain structural and spectral information, an *ab initio* molecular-orbital study was carried out by employing bis(thioformyl) sulfides [HC(S) – S_x – (S)CH, **I**: x = 1, **II**: x = 2, and **III**: x = 3] as model compounds.

SHC–S_x–CHS		**I**	**II**	**III**
I-III	x	1	2	3

The molecular geometries of **I** – **III** were optimized by *ab initio* MO calculations at STO-3G level with the energy gradient method. The results are shown in Table 1.

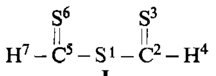
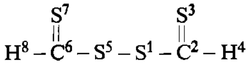
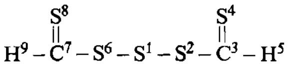
The C – S bond lengths (171.1 – 177.0 pm) of **I** – **III** are normal, but the C = S bond lengths (158.0 – 158.5 pm) are relatively short in comparison with those (160.0 – 166.0 pm) in common dithioesters[16–19]. In addition, the S – S bond lengths (207.2 and 207.0 pm) and C – S – S bond angles (101.5° and 102.6°) of the di- **II** and trisulfide **III** are close to the values generally accepted as S – S bond length and C – S – S bond angle[20]. The S – C = S bond angles (125.4°) of the disulfide **II** are close to those (129.4° and 130.4°) of the mono- **I** and trisulfide **III**.

IR Spectra

Bellamy[21] suggested that the thiocarbonyl stretching vibration band of dithioesters lies between 1190 and 1125 cm^{-1}. Previously, we reported that bis(thioacyl) mono-[14c] and disulfide[13] show a characteristic strong band due to $\nu C = S$ near 1240 and 1250 cm^{-1}, respectively. The $\nu_{as}C = S$ band of **1** and **2** ought to appear in the similar region because of their structural similarity. In fact, in the IR spectra of **1** and **2** a characteristic medium absorption band due to $\nu C = S$ can be observed within the range 1220 – 1250 cm^{-1} (Table 5a). In addition, we have found another characteristic absorption band in the region of 400 – 500 cm^{-1}, in which the S – S stretching mode normally appears[22].

Although it is premature to assign these bands to the S – S stretching vibration, bis(thioacyl) mono-, di-, tri-, and tetrasulfides can be determined conveniently by observing these bands.

Table 1. Bond lengths, bond angles, and dihedral angles of bis(thioformyl) sulfides **I** – **III**

	Bond lengths[a]	[pm]	Bond angles[a]	[°]	Dihedral angles[a]	[°]
 $H^7-\overset{\overset{S^6}{\|}}{C^5}-S^1-\overset{\overset{S^3}{\|}}{C^2}-H^4$ **I**	S(1) – C(2)	177.0	S(1) – C(2) – S(3)	129.4	S(3) – C(2) – C(5) – S(6)	48.4
	C(2) – S(3)	158.5	S(1) – C(2) – H(4)	107.3	S(6) – C(2) – C(5) – H(4)	121.3
	C(2) – H(4)	110.3	S(3) – C(2) – H(4)	122.7	S(6) – C(2) – C(5) – H(7)	34.5
			C(2) – S(1) – C(5)	107.4		
 $H^8-\overset{\overset{S^7}{\|}}{C^6}-S^5-S^1-\overset{\overset{S^3}{\|}}{C^2}-H^4$ **II**	S(1) – C(2)	171.1	S(1) – C(2) – S(3)	125.4	C(2) – S(1) – C(5) – C(6)	89.1
	C(2) – S(3)	158.0	S(1) – C(2) – H(4)	111.9		
	S(1) – S(5)	207.2	S(3) – C(2) – H(4)	122.7		
			C(2) – S(1) – S(5)	101.5		
 $H^9-\overset{\overset{S^8}{\|}}{C^7}-S^6-S^1-S^2-\overset{\overset{S^4}{\|}}{C^3}-H^5$ **III**	S(1) – S(2)	207.0	S(2) – C(3) – S(4)	130.4	C(3) – S(2) – S(6) – C(7)	163.2
	S(2) – C(3)	176.6	S(2) – C(3) – H(5)	102.7	C(3) – S(2) – S(6) – S(1)	98.4
	C(3) – S(4)	158.0	S(4) – C(3) – H(5)	122.2		
	C(3) – H(5)	109.3	C(3) – S(2) – S(1)	102.6		

[a] The standard values of reliability of MO calculations at STO-3G level are + 50 pm for bond distance and ± 10° for bond angle: *S. Iwata,* Quantum Chemistry Literature Data Base (edit. *K. Ohno* and *K. Morokuma*), p. 427, Elsevier, New York 1982.

Electron Spectra

Electron spectra of the trisulfides **1** and tetrasulfides **2** show two characteristic absorption maxima in the region of 270 – 360 and 510 – 530 nm which can be ascribed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thiocarbonyl group, respectively, on the basis of the magnitude of the molar extinction coefficient. The $n \rightarrow \pi^*$ transitions (λ_{max}) of the monosulfides were observed in region of long ones. The λ_{max} values increase and then decrease with the number of sulfide sulfurs, though the increment and the decrement are relatively small. This is the first example for the influence of the number of sulfide sulfur atoms on the $n \rightarrow \pi^*$ transition of a thiocarbonyl group.

In order to examine the remarkable difference in the $n \rightarrow \pi^*$ transitions between the monosulfide $[4\text{-}CH_3C_6H_4C(S)]_2S$ and polysulfides (**1**, **2**, **5**), HOMO (n-type of C=S) and LUMO (π^*-type of C=S) energy levels of bis(thioformyl) mono- (**I**), di- (**II**), and trisulfide (**III**) were calculated. The monosulfide has its HOMO at a higher level and the LUMO at a lower level. The calculated HOMO-LUMO energy gap (11.4 eV) of the monosulfide **I** is small enough to be distinguished from those (12.2 and 12.3 eV) of **II** and **III**. This is consistent with the observation.

The results allow us to examine, at the orbital level, the outstanding difference in the $n \rightarrow \pi^*$ transition energy. The difference between the monosulfide and the other is greater in the LUMO energy (0.506 and 0.161 eV) than in the HOMO ones (0.275 and 0.293 eV). The LUMO energy is primarily responsible for the transition energy difference. The LUMO is expected to result from the interaction of the thiocarbonyl π^* orbital with a lone-pair electron orbital of the adjacent sulfide sulfur. This is a charge-transfer interaction involving an electron flow from the sulfide sulfur to the thiocarbonyl bond. The charge transfer occurs in the monosulfide from a single sulfide sulfur to two thiocarbonyl groups. In the other sulfides, however, the charge transfer occurs from one sulfide sulfur to only one thiocarbonyl bond. Thus, the charge-transfer interaction is expected to be weaker in the monosulfide. The weak interaction results in a small orbital energy splitting. The LUMO energy remains at a low energy level.

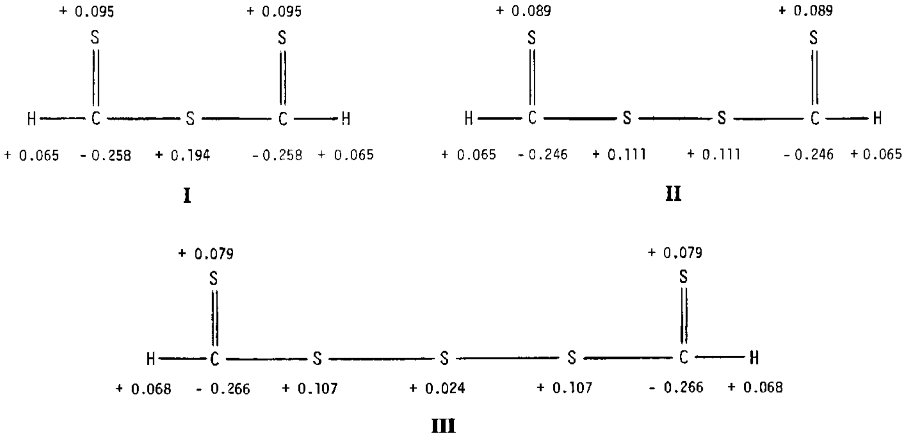


Figure 1. Charge distribution of bis(thioformyl) sulfides **I** – **III**

Reactivity

The charge distributions and the frontier-orbital electron densities are shown in Figures 1 and 2, respectively.

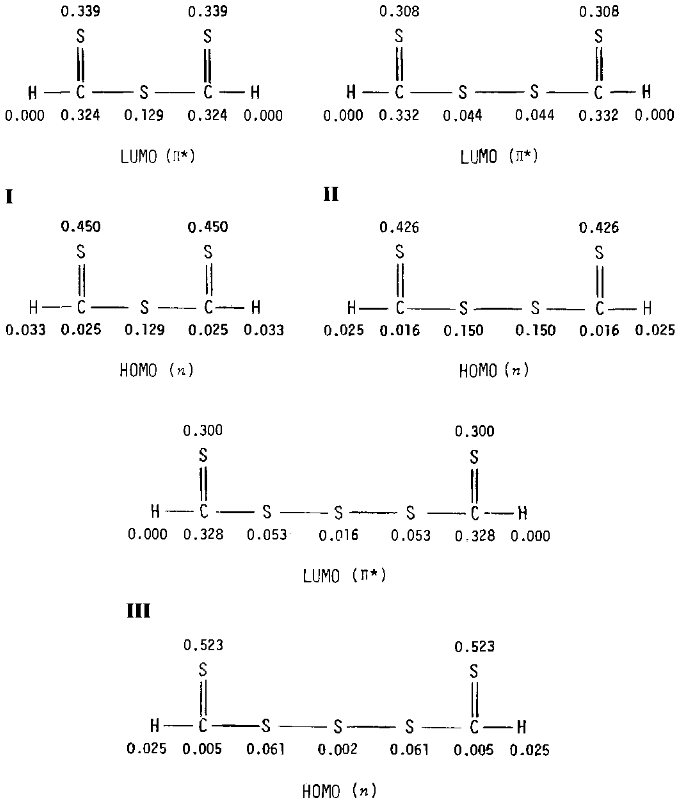


Figure 2. Frontier-orbital electron densities of bis(thioformyl) sulfides **I** – **III**

The HOMO of the bis(thioformyl) sulfides **I** – **III** is the nonbonding orbital of the thiocarbonyl sulfurs. The LUMO is the antibonding orbital of thiocarbonyl double bonds as expected. It is noteworthy that there appear positive charges on the thiocarbonyl sulfurs. The C = S bonds are polarized in the direction opposite to those of carbonyl bonds.

The sulfide sulfur is most positively charged, the LUMO is localized on the thiocarbonyl double bonds. These results show that nucleophiles or electron-donating reagents attack the sulfide sulfur in charge-controlled reactions (in case of "hard" bases) and the thiocarbonyl sulfur in frontier-orbital-controlled reactions (in case of "soft" bases)[23].

The thiocarbonyl carbon is most negatively charged. The HOMO is localized on the thiocarbonyl sulfur. "Soft" and "hard" electrophiles are predicted to react at the thiocarbonyl sulfur and carbon, respectively[23].

Table 2. Cartesian coordinates of bis(thioformyl) sulfide (**I**) optimized by *ab initio* molecular-orbital calculations at STO-3G level

Atom	x	y	z
S_1	0.0	0.0	0.0
C_2	1.426	0.0	−1.048
S_3	1.629	0.630	−2.451
H_4	2.259	−0.406	−0.457
C_5	−1.426	0.0	−1.048
S_6	−1.629	−0.630	−2.451
H_7	−2.259	0.406	−0.457

Table 3. Cartesian coordinates of bis(thioformyl) disulfide (**II**) optimized by *ab initio* molecular-orbital calculations at STO-3G level

Atom	x	y	z
S_1	1.035	−0.047	−0.0123
C_2	1.445	1.185	1.191
S_3	2.909	1.608	1.607
H_4	0.5521	1.638	1.630
S_5	−1.035	0.047	−0.012
C_6	−1.445	−1.185	1.191
S_7	−2.909	−1.608	1.607
H_8	−0.5521	−1.638	1.630

Table 4. Cartesian coordinates of bis(thioformyl) trisulfide (**III**) optimized by *ab initio* molecular-orbital calculations at STO-3G level

Atom	x	y	z
S_1	0.0	0.0	0.0
S_2	1.614	0.005	−1.294
C_3	1.900	1.729	−1.549
S_4	1.129	2.982	−0.975
H_5	2.761	1.831	−2.213
S_6	−1.614	−0.005	−1.294
C_7	−1.900	1.729	−1.549
S_8	−1.129	2.982	−0.975
H_9	−2.761	1.831	−2.213

The authors thank the *Computer Center, Institute for Molecular Science,* for making the HITAC M-200H computer and IMSPACK Program available.

Experimental Part

IR spectra: JASCO grating IR spectrophotometer IR-G. – UV and visible spectra: Hitachi 124 spectrophotometer. – ^{1}H NMR spectra (TMS as internal standard): Hitachi R-24 (60 MHz). – Mass spectra: Hitachi RMU-6M high-resolution mass spectrometer. – Elemental analyses: Elemental Analyses Center of Osaka University and Wako Junyaku Co. – Melting points (uncorrected): Yanagimoto micro melting point apparatus.

Materials: Sulfur dichloride (b.p. 60 – 62 °C, lit.[24a] b.p. 55 – 62 °C) and disulfur dichloride (b.p. 135 – 137 °C, lit.[24b] 138 °C) were carefully distilled before use. 4,4′-Dithiodi(morpholine) and triphenylphosphane were of commercial grade and used without further purification. The solvents (*n*-hexane, ether, dichloromethane, chloroform, ethyl acetate, and carbon tetrachloride) were dried by means of sodium metal (in the case of *n*-hexane and ether) or calcium chloride, respectively. Preparative thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with Wako gel B-5F. Column chromatography was performed on Fuji Davison silica gel BF-820 MH.

Preparation of aromatic dithiocarboxylic acids: To piperidinium dithiocarboxylates[25] (3 mmol) suspended in *n*-hexane (15 ml) in a separatory funnel, ice-cold water (ca. 10 ml) and then concentrated hydrochloric acid (ca. 8 ml) were added and the mixture was vigorously shaken until the water became colorless. After washing several times with cold water and drying with anhydrous sodium sulfate, the solvent was evaporated below 15 °C in reduced pressure. The resulting oily residue was redissolved in carbon tetrachloride (10 ml). This solution contained ca. 2.3 mmol of the aromatic dithiocarboxylic acid.

In the following general procedures for the preparation of the bis(thioacyl) tri- **1** and tetrasulfides **2** are given. Yields, physical properties, and microanalytical data are summarized in Tables 5a and 5b.

Table 5a. Yields and physical properties of bis(thioacyl) trisulfides **1** and tetrasulfides **2**

	Bis(thioacyl) tri- and tetrasulfides	% Yield[a] (m.p. [°C])[b]	IR [cm^{-1}][c] $\nu_{as}C=S$	UV/Vis [nm][d] λ_{max} (lg ε)	^1H NMR[e] δ values
1a	Bis(thiobenzoyl) trisulfide	42 (85 – 87)	1221	306 (4.39) 527 (2.36)	7.0 – 7.9 (m, 10H, Ar)
b	Bis[4-(methyl)thiobenzoyl] trisulfide	57 (129 – 130)	1227 492[f]	325 (4.60) 530 (2.40)	2.53 (s, 6H, CH_3), 7.1 – 8.2 (m, 8H, Ar)
c	Bis[4-(methoxy)thiobenzoyl] trisulfide	44 (141.5 – 143)	1245	357 (4.66) 520 (2.64)	3.80 (s, 6H, CH_3O), 6.6 – 8.1 (m, 8H, Ar)
d	Bis[4-(chloro)thiobenzoyl] trisulfide	38 (115 – 117)	1220 sh	322 (4.21) 535 (2.37)	7.1 – 8.1 (m, 8H, Ar)
e	Bis(2,4,6-trimethylthiobenzoyl) trisulfide	85 (130 – 133)	1236	298 (4.32) 513 (2.39)	
2a	Bis(thiobenzoyl) tetrasulfide	54 (56 – 57)	1240	310 (4.45) 524 (2.36)	7.16 – 8.12 (m, 10H, Ar)
b	Bis[4-(methyl)thiobenzoyl] tetrasulfide	61 (115 – 117)	1234 510[f]	327 (4.71) 527 (2.49)	2.34 (s, 6H, CH_3), 6.8 – 7.9 (m, 8H, Ar)
c	Bis[4-(methoxy)thiobenzoyl] tetrasulfide	26 (109 – 111)	1246	360 (4.63) 529 (2.64)	3.83 (s, 6H, CH_3O), 6.7 – 8.2 (m, 8H, Ar)
d	Bis[4-(chloro)thiobenzoyl] tetrasulfide	63 (108 – 109)	1228 sh	326 (4.78) 530 (2.46)	7.0 – 7.9 (m, 8H, Ar)
e	Bis(2,4,6-trimethylthiobenzoyl) tetrasulfide	95 (110 – 112)	1252	272 (4.38) 510 (2.15)	

[a] Isolated yields. – [b] Recrystallized from: $CHCl_3$/EtOH (2:1), except for **1d** [CH_2Cl_2/AcOEt (3:2)]. – [c] KBr. – [d] CH_2Cl_2. – [e] $CDCl_3$. – [f] $\nu_{as}S-S$.

Table 5b. Elemental analyses of bis(thioacyl) tri- **1** and tetrasulfides **2**

	Summation formula (Mol. mass)		Analysis C	Analysis H		Summation formula (Mol. mass)		Analysis C	Analysis H
1a	$C_{14}H_{10}S_5$[a)]	Calc.	49.67	2.98	**2a**	$C_{14}H_{10}S_6$[c)]	Calc.	45.37	2.72
	(338.5)	Found	49.37	3.00		(370.6)	Found	45.53	2.78
1b	$C_{16}H_{14}S_5$[b)]	Calc.	52.42	3.85	**2b**	$C_{16}H_{14}S_6$	Calc.	48.21	3.54
	(366.6)	Found	52.05	3.80		(398.7)	Found	47.95	3.41
1c	$C_{16}H_{14}O_2S_5$	Calc.	48.21	3.54	**2c**	$C_{16}H_{14}O_2S_6$[d)]	Calc.	44.62	3.28
	(398.6)	Found	48.05	3.39		(430.7)	Found	44.36	3.23
1d	$C_{14}H_8Cl_2S_5$	Calc.	41.27	1.98	**2d**	$C_{14}H_8Cl_2S_6$	Calc.	38.26	1.83
	(407.4)	Found	41.67	1.94		(439.5)	Found	37.94	1.98
1e	$C_{20}H_{22}S_5$	Calc.	56.84	5.25	**2e**	$C_{20}H_{22}S_6$	Calc.	52.82	4.88
	(422.7)	Found	56.54	5.01		(454.8)	Found	52.81	4.67

[a)] Calc. S 47.35 Found S 47.73. – [b)] Calc. S 43.73 Found S 43.71. – [c)] Calc. S 51.91 Found S 52.05. – [d)] Calc. S 44.67 Found S. 44.87.

Bis(thioacyl) trisulfides **1**: A solution of sulfur dichloride (103 mg, 1.0 mmol) in carbon tetrachloride (10 ml) was added dropwise at 0°C with stirring to a solution of the freshly prepared dithiocarboxylic acid (ca. 2.3 mmol) in the same solvent (10 ml) and the reaction mixture was stirred for 1 h. Filtration, washing several times with *n*-hexane, and recrystallization from chloroform/ethanol (2:1, ca. 15 ml) yielded chemically pure **1** as reddish orange to reddish purple crystals.

Bis(thioacyl) tetrasulfides **2**: A solution of disulfur dichloride (1.35 mg, 1.0 mmol) in carbon tetrachloride (10 ml) was added dropwise at 0°C with stirring to a solution of the freshly prepared dithiocarboxylic acid (ca. 2.3 mmol) in the same solvent (10 ml) and the reaction mixture was stirred for 1 h. The resulting precipitate was filtered and washed with *n*-hexane (4 x 5 ml), followed by recrystallization from chloroform/ethanol (2:1, ca. 45 ml), to yield chemically pure **2** as reddish orange to light purple crystals.

For the reaction of **1** and **2** with amines, three typical examples are described below. The products were confirmed by comparison of the m.p. and IR spectra with those of authentic samples.

Reaction of **1b** *with cyclohexylamine:* A solution of cyclohexylamine (198 mg, 2.0 mmol) in ether (10 ml) was added dropwise to a suspension of **1b** (367 mg, 1.0 mmol) in the same solvent (20 ml) and the reaction mixture was stirred for 30 min at 0°C. Filtration and washing of the precipitate with *n*-hexane (2 x 10 ml) followed by recrystallization from dichloromethane/*n*-hexane (2:1) gave 338 mg (52%) of cyclohexylammonium 4-(methyl)dithiobenzoate (**3a**) as orange crystals with m.p. 78–80°C. – IR (KBr): 1015 cm^{-1} (νCS_2). – Evaporation of the filtrate under reduced pressure, followed by preparative TLC using *n*-hexane/dichloromethane (1:1) gave 42 mg (10%) of *N*-cyclohexyl-4-(methyl)thiobenzamide as pale yellow crystals with m.p. 80–82°C. – IR (KBr): 1530 cm^{-1} (thioamide B)[14c)].

Reaction of **2b** *with piperidine:* A solution of piperidine (170 mg, 2.0 mmol) in ether (10 ml) was added dropwise to a suspension of **2b** (399 mg, 1.0 mmol) in the same solvent (20 ml) and the reaction mixture was stirred at 0°C for 15 min. Filtration of the resulting precipitate and washing with *n*-hexane (3 x 5 ml) gave 277 mg (71%) of piperidinium 4-(methyl)dithiobenzoate (**4a**) as red crystals[25)].

Reaction of **2b** *with triethylamine:* Triethylamine (202 mg, 2.0 mmol) and **2b** (399 mg, 2.0 mmol) were stirred in ether (30 ml) at 0 °C for 1 h. The color of the reaction mixture changed from red to pink. Filtration of the precipitate and washing with *n*-hexane (3 × 5 ml) yielded 228 mg (68%) of bis[4-(methyl)thiobenzoyl] disulfide (**5**) with m.p. 136 – 137 °C. – IR (KBr): 1240 cm^{-1} (νC=S)[13].

Table 6. Reactions of the tri- **1** and tetrasulfides **2** with amines
Molar ratio **1** or **2**: amine = 1:2

$[RC(S)]_2S_x$ **1** or **2**	Amine	Solvent	Temp. [°C]	Time [min]	Products (%) Dithio salts **3**, **4** or disulfide **5**
1b	cyclohexylamine	CCl_4/Et_2O	15	15	72 (**3a**)
	piperidine	CCl_4/Et_2O	18	15	78 (**4a**)
	diethylamine	CCl_4/Et_2O	15	15	93 (**4b**)
2b	cyclohexylamine	CCl_4/Et_2O	16	15	68 (**3a**)
	piperidine	Et_2O	15	15	70 (**4a**)
	triethylamine	Et_2O	20	24 h	63 (**5**)

Reaction of **1b** *with triphenylphosphane:* A solution of triphenylphosphane (103 mg, 0.5 mmol) and **1b** (183 mg, 0.5 mmol) in benzene (20 ml) was stirred at ca. 20 °C for 2 h. After evaporation of the solvent under reduced pressure, chromatography of the residue on silica gel (column; CH_3OH) yielded firstly 108 mg (65%) of bis[4-(methyl)thiobenzoyl] disulfide (**5**) as pink crystals and then 117 mg (79%) of triphenylphosphane sulfide (**6**) (m.p. 160 – 161 °C, lit.[26] 158 – 162 °C). The IR spectra and melting points of **5** and **6** were consistent with those of authentic samples.

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