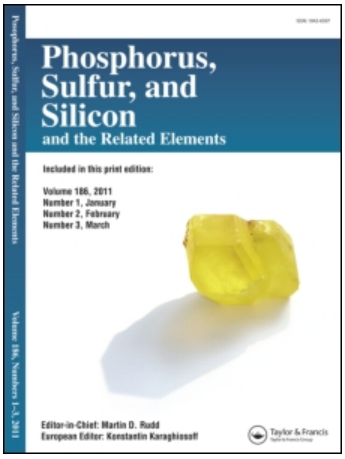

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Preparation of New *O*-Alkyl Naphthalenecarbothioates and Alkyl Naphthalenecarbodithioates, and EPR-Spectroscopic Study of Their Radical Anions[1,2]

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PREPARATION OF NEW *O*-ALKYL NAPHTHALENECARBOTHIOATES AND ALKYL NAPHTHALENECARBODITHIOATES, AND EPR-SPECTROSCOPIC STUDY OF THEIR RADICAL ANIONS[1,2]

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***O*-Alkyl naphthalenecarbothioates and bis-carbothioates are prepared by the reaction of the corresponding esters by use of Lawesson's reagent. The related naphthalenecarbodithioates are obtained (a) from methylnaphthalenes via bromination with NBS, subsequent methoxide-promoted reaction with sulfur, and finally alkylation of the carbodithioate salts with alkyl halides or (b) lithiation of bromonaphthalenes, reaction with carbon disulfide, and alkylation. The thiono- and dithioesters were transformed into persistent radical anions by in situ electroreduction. Spin density distributions were determined by EPR spectroscopy and MO calculations.**

Keywords O-Alkyl naphthalenecarbothioates; in situ electroreduction; MO calculations; naphthalenecarbodithioates; radical anions; spin densities

INTRODUCTION

We published EPR spectroscopic studies on the radical anions of naphthalene-[3] and anthracenecarboxylic esters[4] several years ago. Furthermore, we have investigated the spin density distributions in the radical anions of various types of thiocarbonyl compounds ("thioketyls") for decades.[5–9] The aim of our experiments and of the corresponding theoretical calculations was to explore the characteristic changes of the spin densities which are brought about through the replacement of oxygen by the significantly larger and thus easier to polarize sulfur atoms in a compound. As a result of these investigations, we have found that the thiono derivatives of carboxylic esters and amides were transformed into the radical anions at much lower one-electron reduction potentials as compared with the oxo analogs.[7] Thiocarbonyl and, even more pronounced, dithiocarboxylate substituents turned also out to

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.
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exhibit significantly stronger electron-withdrawing effects. Due to this effect, the spin density in the benzene moiety of benzoate derived radical anions considerably decreases in the order ester > thionester > dithioester[7] and also amide > thioamide.[9] The spin-attracting power of the dithiocarboxylate group is even surpassed by the α-oxo-dithiocarboxylate substituent in 2-phenyl-2-oxo-ethanedithioate esters[10–13] and the corresponding amides and thioamides.[12] Alternatively, we have found that ester substituents withdraw significantly less spin density from the extended delocalized π-electron systems of naphthalene-[3] and anthracenecarboxylate radical anions[4] as compared with the corresponding benzoates.

Since we were interested in the balance between these two competing effects, we have investigated the radical anions of thiono- and dithionaphthoate esters, which exhibit both an extended π-electron system and an effective spin-withdrawing substituent in one molecule. For comparison, we have also included derivatives with two of these functional groups.

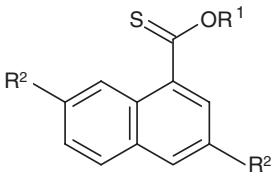
RESULTS AND DISCUSSION

Preparations

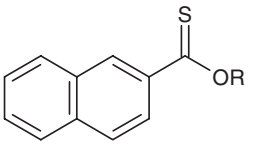
O-Ethyl naphthalene-1-carbothioate (**1b**)[14–16] and *O*-ethyl naphthalene-2-carbothioate (**2b**)[15,17] are described in the literature. We needed, however, further thionesters for our study and have also prepared **1a**, **1c**, **1e**, **2a**, **2c**, and **3–8** (Scheme 1) by thionation of the corresponding esters with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 1,3-disulfide (Lawesson's reagent, **LR**).[15,18]

The yields were low in several cases, but most of the desired thionesters could be obtained in sufficient amounts. The ^{1}H and ^{13}C NMR data (Table VI and VII) are in agreement with the structures. For the sake of completeness and comparison, the data of **1b** and **2b** are also included. The assignment of the signals was achieved by DEPT-135 or ^{1}H-^{1}H- and ^{1}H-^{13}C-COSY experiments. It was corroborated by comparison of the observed chemical shifts with theoretical values, which were calculated by use of increments for naphthalene and the respective substituents.[19] The ^{13}C shift increments for the CS substituent ($\Delta\delta_{ipso} = 16.6$, $\Delta\delta_{ortho} = -1.7$, $\Delta\delta_{meta} = -0.1$, $\Delta\delta_{para} = 3.9$ ppm) were derived from the spectra of related reference compounds.[20–22] When we prepared **1b** and **1c**, we found small amounts of their isomers **2b** and **2c** as byproducts. This was due to a contamination of the commercial α-naphthoic acid, which we had used as starting material. We found a content of 10% β-naphthoic acid by a careful ^{1}H NMR spectroscopic analysis of the methyl esters. Fortunately, the pairs of isomers could be separated by chromatography to yield in one batch both the thionesters as pure compounds. The thionester **1e** was prepared from 2,6-di-*tert*-butyl naphthalene via bromination, lithiation, carboxylation, esterification, and finally thionation of the ester **1d** with **LR** according to Scheme 2.[3,23]

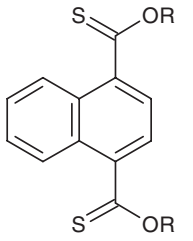
Thionation of diisopropyl naphthalene-1,5-dicarboxylate led to a separable mixture of the mono- (**4a**) and the bisthionester (**4b**), although we applied a 50% stoichiometric excess of **LR**, which is known to transfer, in general, two sulfur atoms per molecule to the carbonyl compound. The product ratio was 30:1 in favor of the mono-thionester **4a**, and the total yield was only 23%. Possibly this is due to steric hindrance, which impedes the attack of the bulky **LR** molecule at the isopropyl α-naphthoate moiety. Also the mono- and bis-thionesters **7a** and **7b** as well as **8a** and **8b** were obtained as separable mixtures when the corresponding esters were treated with **LR**.[18] In these cases, the total yields were high and more bis-thionester was formed, even though only a 10–20% excess of **LR** was used.



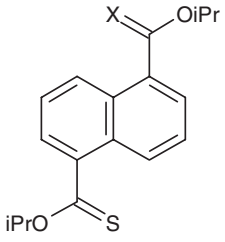
1a: R^1 = Me, R^2 = H
1b: R^1 = Et, R^2 = H
1c: R^1 = iPr, R^2 = H
1e: R^1 = Ph, R^2 = tBu



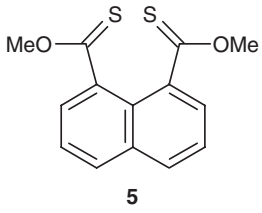
2a: R = Me
2b: R = Et
2c: R = iPr



3a: R = Me
3b: R = Ph



4a: X = O
4b: X = S



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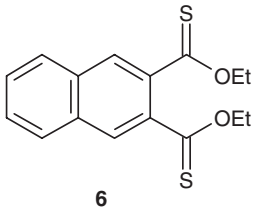

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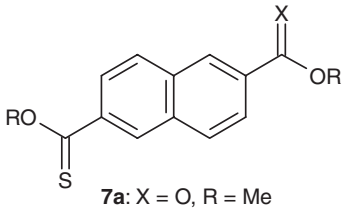
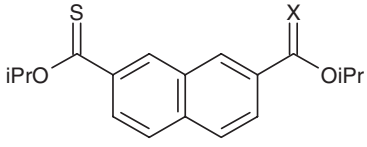


7a: X = O, R = Me
7b: X = S, R = Me
7c: X = S, R = iPr

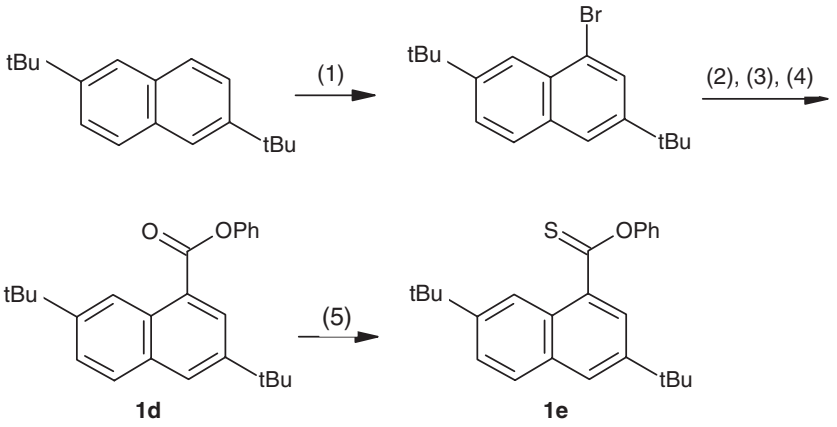


8a: X = O
8b: X = S

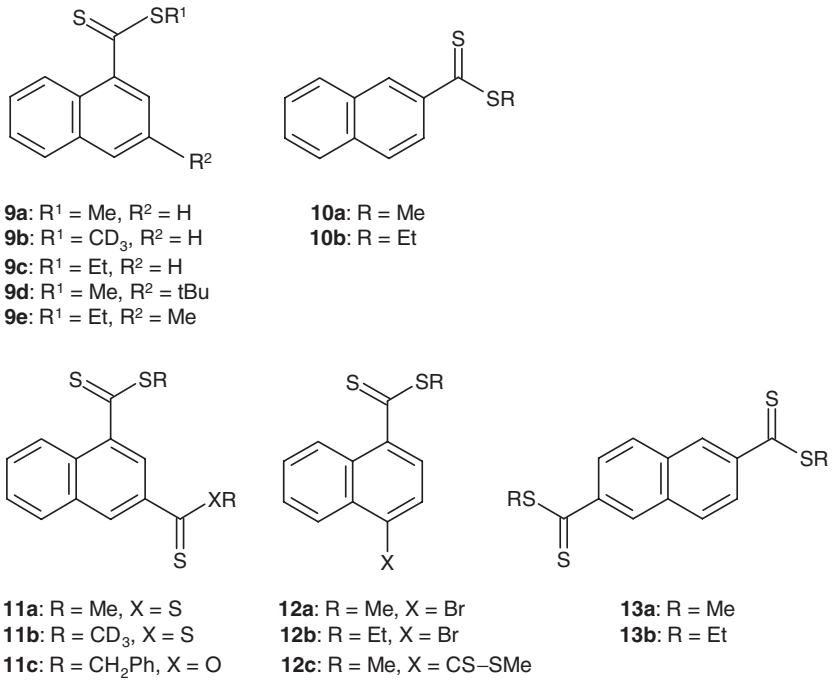
Scheme 1 *O*-Alkyl naphthalenecarbothioate esters **1**–**8**.

The dithionaphthoates **9a**,[24–26] **9c**,[24,26,27] **10a**,[28–30] **10b**,[26,31] and **13a**[32] are known compounds. Besides these five dithioesters, we have synthesized the naphthalenecarbodithioates **9b**, **9d**, **9e**, **12a**, and **12b** as well as the naphthalene-bis-carbodithioates **11a**, **11b**, **11c**, **12c**, and **13b** (Scheme 3).

Most of these dithioesters were prepared by reaction of the corresponding (bromomethyl)naphthalenes with sulfur and sodium methoxide, and subsequent alkylation.[33,34]



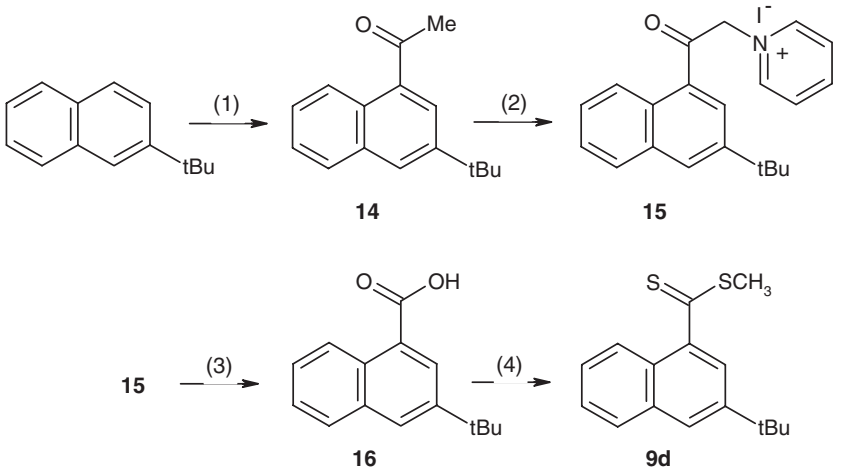
Scheme 2 (1): $Br_2/(MeO)_3PO$; (2): nBuLi/Et_2O; (3) CO_2; (4): PCl_5; (5): PhOH/pyridine/DMAP; (6): **LR**/C_6H_5Cl.



Scheme 3 Naphthalenecarbodithioate esters **9**–**13**.

In the case of the 1,3-dibenzyl derivative, only one bromomethyl group reacted as expected, whereas the second one was transformed into a thionoester group according to the analytical and spectroscopic data of the product (see the Experimental section and Tables IX–XI). We tentatively assigned the structure **11c** to the trithioester. The 4-bromo derivatives **12a** and **12b** were obtained by unintentional mono-lithiation of 1,4-dibromonaphthalene, subsequent reaction with carbon disulfide, and alkylation of the dithiocarboxylate with iodomethane

or iodoethane. The Grignard reaction did not work in this case. Neither were we able to achieve a di-metallation of 1,4-dibromonaphthalene. The desired **12c** could, however, be prepared from 1,4-bis(bromomethyl)naphthalene by the above-mentioned alternate method. The dithioester **9d** was synthesized from 2-*tert*-butyl-naphthalene via the ketone **14**, the pyridinium salt **15**, and the reaction of the carboxylic acid **16** with 2,4-bis(methylsulfanyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide ("Davy's reagent," **DR**[35]) according to Scheme 4.



Scheme 4 (1): $AcCl/AlCl_3$; (2): I_2/pyridine; (3): a) NaOH, b) HCl; (4): **DR**.

The ^1H and ^{13}C NMR data of the naphthodithioates (Tables IX and X) are in agreement with the structures. The signals were assigned as described for the thionesters.[19–21] The structure of **9d** and accordingly of its precursors was, furthermore, corroborated by an X-ray structure analysis (Figure 1).

Electroanalytical Results

Radical anions of thionesters and dithioesters in the benzene and other series exhibit considerable stabilities.[7] Their persistency is significantly enhanced compared with the radical anions of the corresponding esters or thiolesters.[36] We have now determined the half-wave reduction potentials $E_{1/2}$ of the single-electron transfer (SET) steps for selected thion- and dithioesters in the naphthalene series by differential pulse polarography (DPP). They represent a measure of the thermodynamic stability of the corresponding radical anions, whereas the ratios of the aniodic and cathodic cyclovoltammetric (CV) peak currents, i_{ap}/i_{cp}, which were determined by the approximate method of Nicholson,[37] correspond with their kinetic stabilization ("persistency"). The results are compiled in Table I.

Inspection of Table I shows that, in general, *O*-alkyl naphthothioates exhibit a reversible SET step at a low potential, which only slightly depends on the nature of the *O*-alkyl group (cf. **1a** vs. **1b** and **2a** vs. **2b**). The reduction potentials $E_{1/2}$ of the thionesters are shifted significantly to less negative values as compared with the corresponding esters (**1a**: $E_{1/2} = -0.95$ V; methyl α-naphthoate: $E_{1/2} = -1.40$ V[3]). This effect is due to the pronounced polarizability of the thiocarbonyl group, although one could think of the

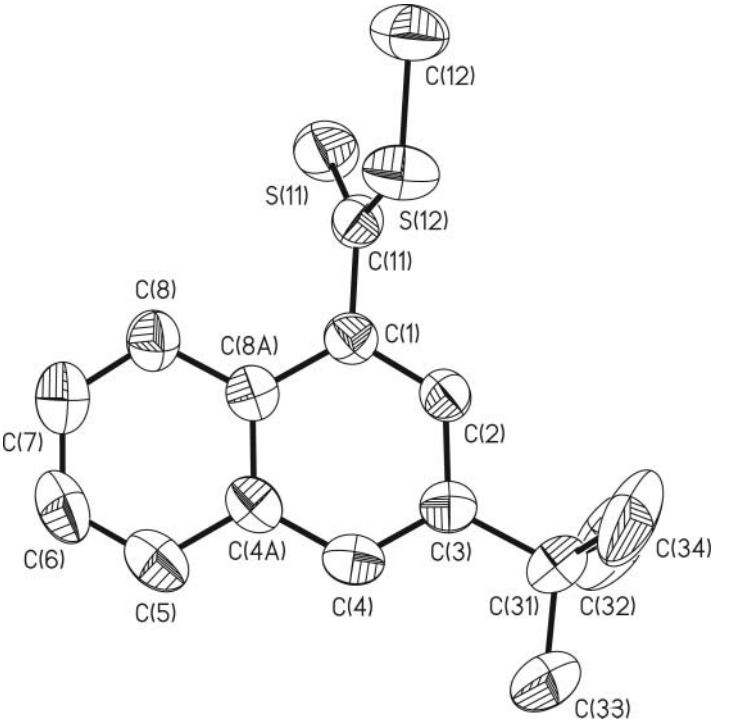
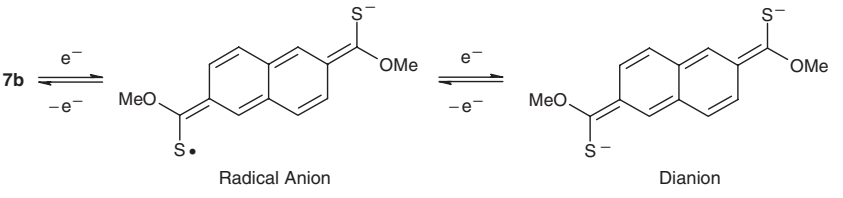


Figure 1 ORTEP view of the X-ray diffraction structure of **9d** (one of the two independent molecules in the cell is shown) with atom numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown. Relevant bond lengths of both the molecules (pm): C-1−C11: 147.8/148.6, C-11−S-11: 162.9/161.9, C-11−S-12: 171.9/172.6, C-12−S-12: 178.2/179.2; bond angles (°): S-11−C-11−S-12: 125.9/125.9, C-11−S-12−C-12: 104.7/105.6, and torsion angle (°): C-2−C-1−C-11−S-11: 109.0/110.8.

reverse effect on account of the higher electronegativity of oxygen compared with sulfur. The naphthalene derivative **1a** is also reduced at a less negative potential than *O*-methyl benzothioate ($E_{1/2} = -1.09$ V[7]), which should be due to the more extended naphthalene π-electron system of **1a**. The 2,6-bis-thionester **7b** is even easier to reduce. Its potential is shifted in the anodic direction by 0.35 V as compared with **2a**. Furthermore, **7b** exhibits a second reversible SET step at −0.88 V, which is due to the formation of a persistent diamagnetic dianion (Scheme 5). The same is true for the mono-thionester **7a**. Second reduction steps at $E_{1/2} \leq -1.30$ V are also observed for the mono-thionesters **1a**, **1b**, **2a**, **2b**, and **2c** and the 2,7-bis-thionester **8a**. These are, however, irreversible due to rapid follow-up reactions of the dianions.



Scheme 5 Dianion of *O,O*-dimethyl naphthalene-2,6-bis(carbothioate) **7b**.

Table I Polarographic half-wave potentials $E_{1/2}$ [V][a] and cyclovoltammetric peak ratios i_{ap}/i_{cp} of selected naphthothioates and naphthodithioates

Compound	$E_{1/2}(1)$	$i_{ap}/i_{cp}(1)$	$E_{1/2}(2, 3, 4)$	$i_{ap}/i_{cp}(2)$
1a	−0.95	0.60	−1.38	Irreversible
1b	−0.82	0.95	−1.32	Irreversible
2a	−0.91		−1.30	Irreversible
2b	−0.87	0.69	−1.52	Irreversible
2c	−0.95		−1.50	Irreversible
7a	−0.68	0.95	−1.13	0.95
7b	−0.56	0.85	−0.88	0.44
8a	−0.80		−1.38	Irreversible
9e	−0.78	0.76	−1.34	Irreversible
11a	−0.52	0.95	−0.70, −0.89	Irreversible
11b	−0.49	0.90	−0.70, −0.89	Irreversible
11c	−0.60	Irreversible	−1.35	Irreversible
12a	−0.65	Irreversible	−0.75, −1.30	Irreversible
12b	−0.63	Irreversible	−0.75, −1.31	Irreversible
12c	−0.64	0.86	−1.32	Irreversible
13a	−0.35	0.87	−0.52, −1.06, −1.43	Irreversible
13b	−0.32	0.83	−0.59, −1.13, −1.34	Irreversible

[a]Measured by use of an internal $Ag/Ag^+/AgBr/Br-$ reference electrode in DMF, the potential of which is shifted by −0.55 V *vs*. the aqu. SCE.

The peak current ratios i_{pa}/i_{pc} are ≥ 0.6.[37] As a rule of thumb, radical anions are stable enough for successful EPR measurements if i_{pa}/i_{pc} is ≥ 0.4. Thus, we expected good EPR results after in situ electroreduction of the naphthothioates at room temperature.

The first SET steps of the dithionaphthoates occur at even less negative potentials than those of the corresponding thionesters (cf. **1b/9e** and **7b/13a** in Table I), whereas only a marginal difference between **9e** ($E_{1/2} = -0.78$ V) and methyl dithiobenzoate ($E_{1/2} = -0.80$ V[7]) exists. The peak current ratios of $i_{pa}/i_{pc} \geq 0.76$ are indicative of a considerable persistency of the radical anions. We have observed the lowest reduction potential for the SET of diethyl 2,6-bis-dithionaphthoate **13b** ($E_{1/2} = -0.32$ V). The 1,3-dibenzyl derivative **11c** and the 4-bromonaphthodithioates **12a** and **12b** do not exhibit reversible reduction steps. Even the first SET steps at $E_{1/2} = -0.60$ V (**11c**) and $E_{1/2} = -0.63/-0.60$ V (**12a/12b**) are irreversible. This is not unexpected, since radical anions of benzyl esters exhibit a tendency to eliminate resonance-stabilized benzyl radicals[38] unless they are stabilized by particular effects, e.g., conjugation with carbonyl groups as in benzyl 2-oxo-2-phenylethanedithioate.[11] Bromoarene radical anions are also known to be a rather elusive species. *O*-Phenyl 2-bromobenzothioate and 4-bromobenzothioate thus show only quasireversible SET steps. Due to the high spin and negative charge densities in the *ortho*- and the *para*-positions and the resulting weak carbon–bromine bonds, bromide anions are easily eliminated. The radical anions of *O*-phenyl 3-bromobenzothioate can, however, be detected, as no destabilization of the C-Br bond occurs in the *meta*-position.[39,40] These aspects are further discussed in the EPR section (see below). In addition, all dithionaphthoates studied exhibit further irreversible reduction steps at more negative potentials (see Table I).

EPR Spectroscopy and MO Calculations

Thionester radical anions. In contrast to the naphthoate esters,[3] the corresponding thionesters gave less persistent radical anions. We were, for instance, not able to record EPR spectra of the naphthalene-1,4-bis(carbothioate) radical anions **3a**$^{-\bullet}$ and **3b**$^{-\bullet}$, or of the 2,3-isomer **6**$^{-\bullet}$. In other cases, the lability of the radical anions led to decomposition products and, as a consequence, to asymmetric spectra, which could not easily be analyzed and interpreted. Furthermore, the heavy-atom effect of the sulfur caused line-broadening. Thus several spectra were not well resolved. Figure 2 shows the EPR spectrum of **1e**$^{-\bullet}$ as an example.

The spectrum of **4a**$^{-\bullet}$, on the other hand, exhibits sharp lines. Obviously the additional doublet splittings observed in the low-field wings of the three pronounced multiplets result from an unknown impurity (see Figure 3).

The *g*-factors of the *O*-alkyl naphthothioate radical anions **1c**$^{-\bullet}$ (2.0060), **4a**$^{-\bullet}$ (2.0051), **7c**$^{-\bullet}$ (2.0054) and, in particular, of the bis-naphthothioate **8a**$^{-\bullet}$ (2.0068) are enhanced compared with the *g*-factors ($\approx$ 2.0032–2.0037) in the naphthoate series.[3] This increase is caused by the spin-orbit coupling (heavy-atom effect) of the thiocarbonyl sulfur atom ($\zeta_S = -382$ cm^{-1}). The calculation of π-spin densities ρ_μ^π from *g*-factors is not straightforward, although a quantitative relationship between ρ_μ^π, *g*, the spin-orbit coupling constant ζ, and the electronic excitation energy $\Delta E(\mathrm{n} \rightarrow \pi^*)$ exists.[41,42] However,

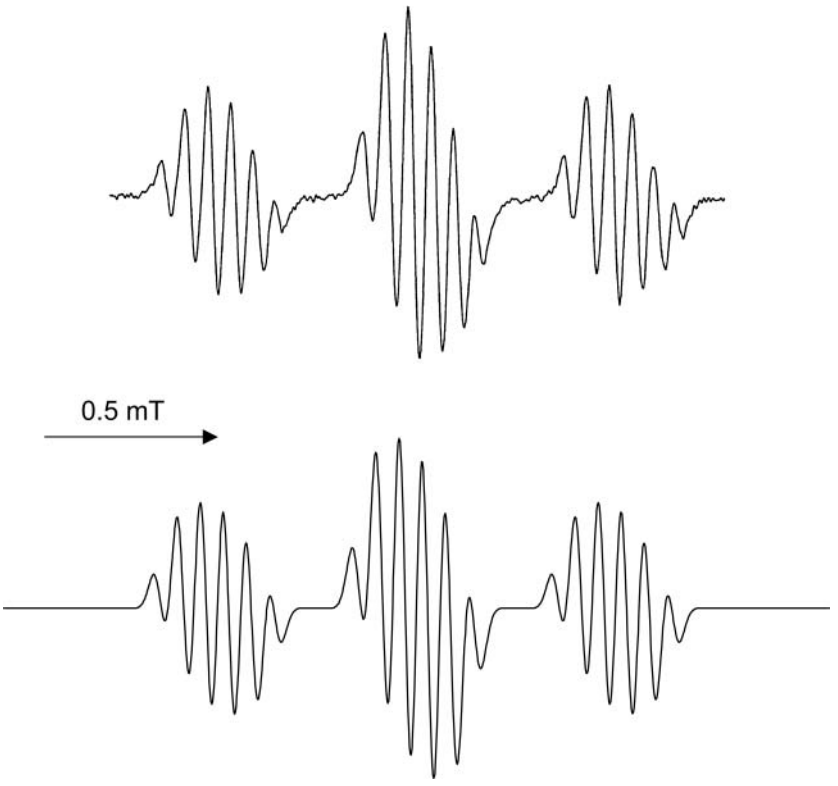


Figure 2 Experimental (top) and simulated (bottom) EPR spectrum of the *O*-phenyl 3,7-di-*tert*-butylnaphthalene-1-carbothioate radical anion **1e**$^{-\bullet}$.

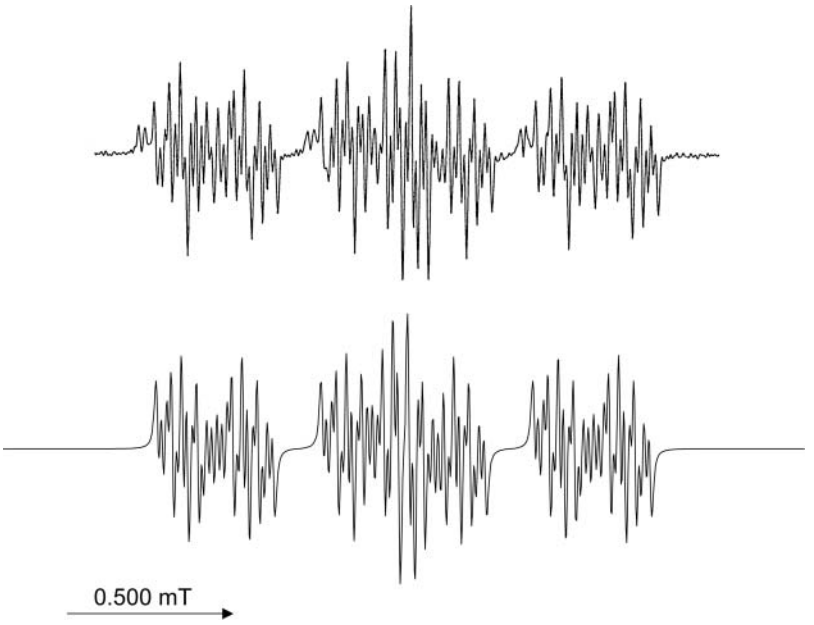


Figure 3 Experimental (top) and simulated (bottom) EPR spectrum of the *O,S*-diisopropyl naphthalene-1,5-bis-carbo-monothioate radical anion **4a**$^{-\bullet}$.

$\Delta E(\mathrm{n} \rightarrow \pi^*)$ of radical anions is not easy to determine, and, furthermore, the correct symmetry of the *g*-tensor must be known and taken into account. But in a semiquantitative sense, the increase of the *g*-factor is indicative of a considerable π-spin density in the thiocarbonyl group. The same increase of *g*-factors has been observed and discussed for benzoate esters and benzamides, and the corresponding sulfur and selenium analogs.[7,9,36,43]

The proton hfs coupling constants a_μ^{H} of the thionester radical anions are compiled in Table II. The assignment of the observed coupling constants a_μ^{H} to distinct positions μ

Table II EPR spectroscopic proton HFS coupling constants a_μ^{H} (mT) in the thionester radical anions $[C_{10}H_7\text{-CS-OR}^1]^{\bullet-}$ and $[R^1\text{O-CS-}C_{10}H_6\text{-CX-OR}^2]^{\bullet-}$, and the radical **17**

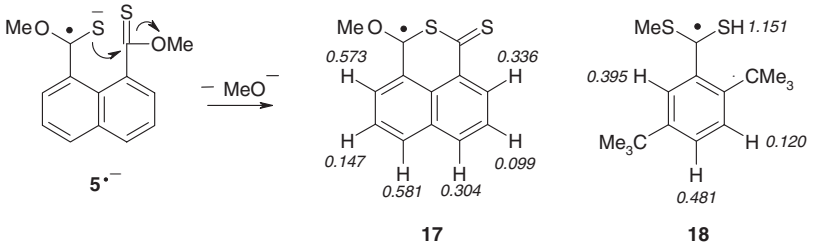
Compound	*a*(1-H)	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)	*a*(6-H)	*a*(7-H)	*a*(8-H)	*a*(R^1)	*a*(R^2)
1a	—	0.592	[a]	0.663	0.183	0.042	0.250	0.063	0.167	—
1b	—	0.595	0.017	0.663	0.183	0.046	0.246	0.063	0.129	—
1e	—	0.595	—	0.610	0.136	0.069	—	0.069	0.069[b]	—
2a	0.736	—	0.045	0.090	0.090	0.310	0.045	0.383	0.122	—
2c	0.736	—	0.045	0.090	0.090	0.327	0.045	0.365	0.045	—
4a	—	0.032	0.079	0.046	—	0.515	0.187	0.661	0.015[a]	[a]
7a	0.21	—	[a]	0.09	0.21	—	[a]	0.09	0.09	[a]
7b	0.22	—	0.030	0.11	0.22	—	0.03	0.11	0.11	0.11
7c	0.236	—	0.039	0.118	0.236	—	0.039	0.118	0.039	0.039
8a	0.478	—	[a]	0.196	0.196	[a]	—	0.478	[a]	[a]
17	—	0.336	0.099	0.304	0.581	0.147	0.573	—	—	—

[a]No resolved splitting observed.
[b]*a*(4′-H).

was not at all straightforward on account of the low symmetry of at least the mono-esters. Specific substitution of protons by *tert*-butyl groups[44] as in **1e**, and variation of the *O*-alkyl substituents, in particular the exchange of CH_3 by CD_3, was helpful. The absence of the large 0.25 mT and the very small 0.017 mT splitting in the 3,7-di-*tert*-butyl derivative $\mathbf{1e}^{-\bullet}$ as compared with $\mathbf{1a}^{-\bullet}$ and $\mathbf{1b}^{-\bullet}$ allows, for instance, an assignment of these two coupling constants to the 3- or the 7-position. Interestingly, the EPR spectrum of $\mathbf{1e}^{-\bullet}$ can only be simulated under the presumption of three nearly equal coupling constants of ca. 0.07 mT. Two of these belong to the naphthalene protons 6-H and 8-H. We assign the third one to the 4′-position of the *O*-phenyl substituent. In addition, the McConnell relationship between a_μ^H and the π-spin density ρ was used. This finally led to a(3-H) = 0.017 mT and a(7-H) = 0.25 mT for the radical anions $\mathbf{1}^{-\bullet}$.

The number and the relative intensities of the lines in the EPR spectrum observed for **5** are not in agreement with the highly symmetric structure of this compound. Instead of the three triplets expected for the radical anion $\mathbf{5}^{-\bullet}$, 42 clearly resolved sharp lines corresponding to six non-equivalent protons are observed in addition to a number of low intensity lines that cannot be assigned to the main radical species (see Figure 4).

We tentatively assign this spectrum to the asymmetric tricyclic benzyl-type radical **17**, which might be formed from the primary radical anion $\mathbf{5}^{-\bullet}$ by intramolecular nucleophilic displacement of a methoxide ion (Scheme 6). We have described the EPR spectroscopic detection of similar α,α-di-hetero-substituted benzyl radicals such as **18**, which are formed from the radical anions of the corresponding sterically hindered alkyl dithiobenzoates. These exhibit comparable proton hfs coupling constants (Scheme 6).[22]



Scheme 6 Formation of **17** and proton hfs coupling constants a (mT) of **17** and **18**.

Dithioester radical anions. As expected, according to the heavy-atom effect of the sulfur atoms, the naphthodithioate radical anions exhibit even higher g-factors as compared with the thionesters ($\mathbf{9a}^{-\bullet}$: 2.00697; $\mathbf{9b}^{-\bullet}$: 2.00712; $\mathbf{9c}^{-\bullet}$: 2.00694; $\mathbf{9d}^{-\bullet}$: 2.00664; $\mathbf{10a}^{-\bullet}$: 2.00675).

Their EPR spectra are not well resolved. Figure 5 shows the spectrum of $\mathbf{11a}^{-\bullet}$ as an example. Several of the coupling constants compiled in Table III are therefore given with only two decimal digits. Furthermore, very small splittings, which should, e.g., result from deuterium in the SCD_3 groups, are not observable. The corresponding coupling constants were however included in the simulations to improve the agreement with the experimental spectra.

The assignment of the observed coupling constants a_μ^H to distinct positions μ was achieved in the same way as in the thionester series, i.e., by comparison of suitably substituted derivatives and by applying the McConnell relationship.

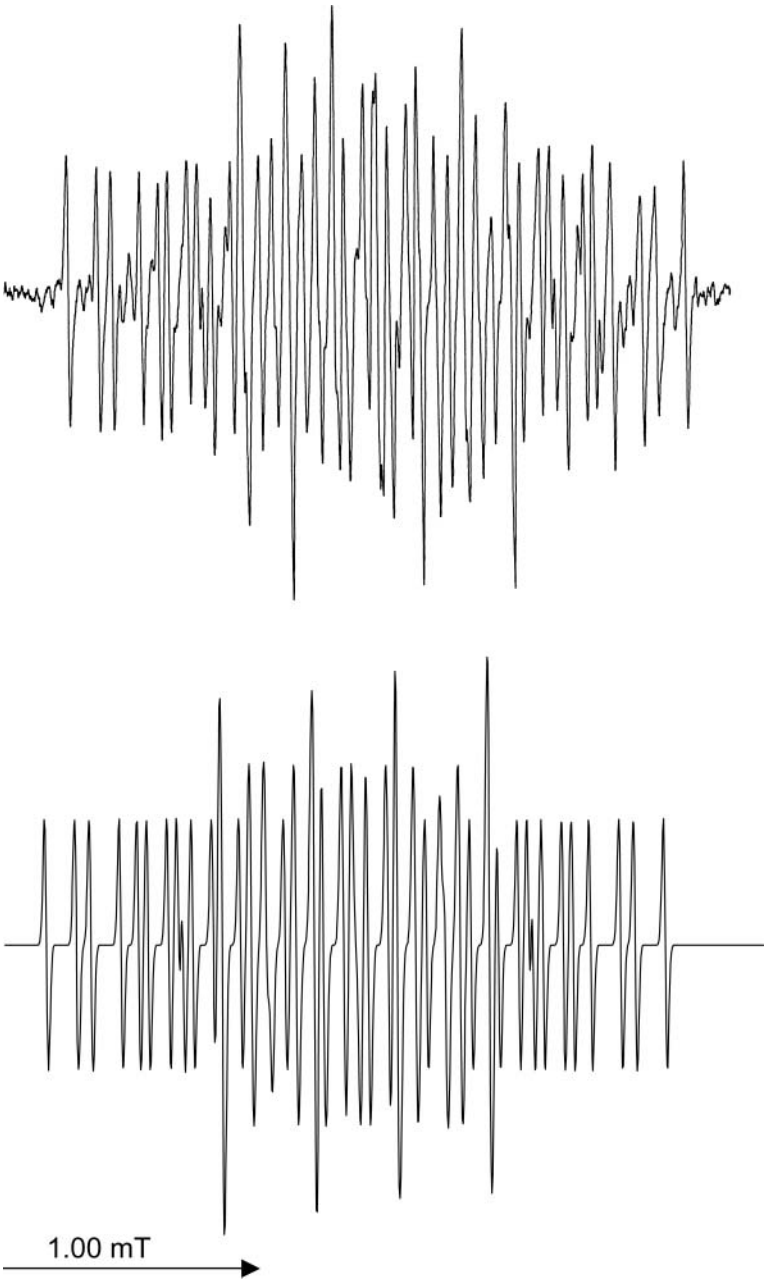


Figure 4 Experimental (top) and simulated (bottom) EPR spectrum of **17**.

We have also studied the radical anions of alkyl azulenecarboxylates and -carbothioates, which are the fascinating isomers and counterparts of the corresponding naphthalene derivatives. They exhibit a non-alternating aromatic π-electron system and consequently a particular spin density distribution.[45] These results will be published elsewhere.

Table III EPR spectroscopic proton HFS coupling constants a_{μ}^{H} [mT] in the dithioester radical anions **9**$^{\bullet-}$–**13**$^{\bullet-}$

Compound	a(1-H)	a(2-H)	a(3-H)	a(4-H)	a(5-H)	a(6-H)	a(7-H)	a(8-H)	a(R^1)	a(R^2)
9a	—	0.490	0.092	0.530	0.147	0.059	0.130	0.059	0.093	—
9b	—	0.49	0.13	0.53	0.13	0.05	0.13	0.05	0.01[a]	—
9c	—	0.494	0.100	0.527	0.147	0.049	0.130	0.049	0.029	—
9d	—	0.488	—	0.537	0.098	0.049	0.098	0.049	0.098	—
9e	—	0.49	0.12[b]	0.53	0.10	0.05	0.10	0.06	0.03	—
10a	0.602	—	0.006	0.205	0.175	0.205	0.006	0.253	0.088	—
11a	—	0.09	—	0.66	0.27	0.08	0.18	0.09	0.09	0.09
11b	—	0.09	—	0.63	0.29	0.09	0.20	0.09	0.01[a]	0.01[a]
12c	—	0.08	0.08	—	[c]	[c]	[c]	[c]	0.12	0.12
13a	0.20	—	0.01	0.04	0.20	—	0.01	0.04	0.09	0.09
13b	0.20	—	0.01	0.04	0.20	—	0.01	0.04	0.06	0.06

[a] a^{D}_{CD3}.
[b] a^{H}_{CH3}.
[c] No resolved splittings observed.

The radical anion of *O*-methyl anthracene-9-carbothioate was not persistent. Instead, only the EPR spectrum of the anthraquinone radical anions could be detected after in situ electroreduction of this thionester.[4]

Spin density distributions. We have determined the spin density distribution in the radical anions by use of HMO and semi-empirical (AM1 type) quantum chemical

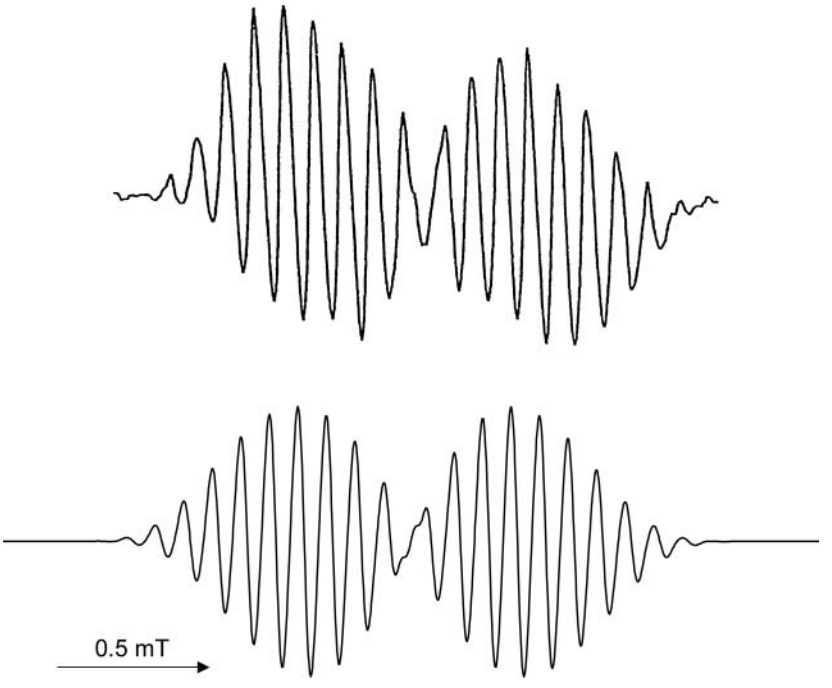


Figure 5 Experimental (top) and simulated (bottom) EPR spectrum of the dimethyl naphthalene-1,3-bis(carbodithioate) radical anion **11a**$^{-\bullet}$.

Table IV Spin densities ρ_μ^π in the *O*-alkyl naphthothioate radical anions **1**$^{-\bullet}$–**4**$^{-\bullet}$, **7**$^{-\bullet}$, **8**$^{-\bullet}$, and the benzyl type radical **17**

		Position μ							
Compound	$\rho_\mu^{\pi\,a}$	1	2	3	4	5	6	7	8
1b	Exp.		0.220	0.006	0.246	0.068	0.017	0.091	0.023
	HMO		0.144	0.017	0.185	0.073	0.012	0.048	0.040
	AM1		0.144	0.021	0.180	0.050	0.010	0.045	0.027
2	Exp.	0.273		0.017	0.033	0.033	0.121	0.017	0.135
	HMO	0.212		0.012	0.040	0.029	0.073	0.005	0.084
	AM1	0.165		0.027	0.020	0.016	0.072	0.001	0.049
4a	Exp.		0.012	0.029	0.017		0.191	0.067	0.245
	HMO		0.010	0.054	0.023		0.119	0.082	0.167
	AM1		0.025	0.058	0.067		0.094	0.039	0.152
7a	Exp.	0.074		0.000	0.074	0.109		0.020	0.035
	HMO	0.113		0.007	0.054	0.116		0.007	0.053
7c	Exp.	0.090		0.014	0.045	0.090		0.014	0.045
	HMO	0.109		0.006	0.048	0.109	0.109	0.006	0.048
	AM1	0.089		0.060	0.084	0.089		0.060	0.084
8a	Exp.	0.177		0.000	0.073	0.073	0.000		0.177
	HMO	0.210		0.013	0.046	0.048	0.003		0.235
17	Exp.		0.124	0.037	0.113	0.215	0.054	0.212	
	HMO		0.104	0.003	0.109	0.176	0.003	0.169	

[a]Exp. values as calculated from proton hfs coupling constants a_μ^H by use of the McConnell equation: $\rho_\mu^\pi = a_\mu^H/-2.7$.

calculations. They are compared with experimental values calculated as mentioned above from McConnell's relationship $a_\mu^H = Q\cdot\rho^\pi{}_\mu$ (Q = −2.7 mT) in Tables IV and V. The agreement between the experimental and the calculated spin densities is only moderate in certain cases, in particular for the bifunctional thioesters. In general, it is even better for the simple HMO type calculations as compared with the results of the more sophisticated semi-empirical methods. We attribute these deviations to the low symmetry of the mono-substituted naphthalene derivates and to the high number of sulfur centers in the bis-thioesters, since the parameters especially for thiocarbonyl sulfur atoms are not always appropriate. Nevertheless, interesting and valid conclusions can be drawn from the results.

Expectedly, the unpaired electron is mainly located in the thioester part of the naphthalene-1-carbothioate (**1**) and -carbodithioate (**9**) systems. The distribution is similar to the thiono- and dithiobenzoate series,[7] i.e., the *quasi-para* (4-) and the *quasi-ortho* (2-) positions exhibit the highest spin densities with $\rho_4^\pi > \rho_2^\pi$. We have observed the same effect in the naphthoate ester series.[3] It is more pronounced in **1**$^{-\bullet}$ compared with **9**$^{-\bullet}$. For instance, ρ_4^π (naphthoate ester[3]) = 0.281 > ρ_4^π (**1**$^{-\bullet}$) = 0.246 > ρ_4^π (**9**$^{-\bullet}$) = 0.196. The spin density in the unsubstituted part of the radical anions, on the other hand, is not negligible: $\rho_7^\pi = 0.091$ and $\rho_5^\pi = 0.068$ in the thionester radical anion **1b**$^{-\bullet}$. The highest spin densities in the naphthalene-2-carbothioate (**2**$^{-\bullet}$) and -carbodithioate (**10**$^{-\bullet}$) radical anions are observed in the 1- (*quasi-ortho*) positions: ρ_1^π (**2**) = 0.273; ρ_1^π (**10**$^{-\bullet}$) = 0.223. Somewhat surprisingly, but similar to the naphthoate ester series,[3] the 8- and the 6-positions exhibit however rather high spin densities as well: ρ_8^π (**2**$^{-\bullet}$) = 0.135; ρ_8^π (**10**$^{-\bullet}$) = 0.094;

Table V Spin densities ρ_μ^π in alkyl naphthodithioate radical anions

Compound		Position							
		1	2	3	4	5	6	7	8
9a	Exp.[a]		0.181	0.034	0.196	0.054	0.022	0.048	0.022
	HMO		0.140	0.021	0.186	0.077	0.016	0.052	0.046
	AM1		0.142	0.015	0.173	0.044	0.007	0.046	0.020
10a	Exp.[a]	0.223		0.002	0.076	0.065	0.076	0.002	0.094
	HMO	0.212		0.012	0.040	0.029	0.073	0.005	0.084
	AM1	0.161		0.020	0.020	0.026	0.017	0.068	0.051
11a	Exp.[a]		0.033		0.244	0.100	0.030	0.066	0.033
	HMO		0.052		0.247	0.115	0.020	0.077	0.069
	AM1		0.030		0.218	0.059	0.002	0.069	0.015
12c	Exp.[a]		0.030	0.030		0.000	0.000	0.000	0.000
	HMO		0.078	0.078		0.062	0.040	0.040	0.062
	AM1		0.068	0.068		0.028	0.019	0.019	0.028
13a	Exp.[a]	0.074		0.004	0.015	0.074		0.004	0.015
	HMO	0.146		0.000	0.095	0.146		0.000	0.095
	MNDO	0.076		0.013	0.033	0.076		0.013	0.033

[a]Calculated from the McConnell equation: $\rho_\mu^\pi = a_\mu^H/-2.7$.

ρ_6^π ($\mathbf{2}^{-\bullet}$) = 0.121; ρ_6^π ($\mathbf{10}^{-\bullet}$) = 0.076, whereas very low spin densities are observed in the second *quasi-ortho* (3-) positions of $\mathbf{2}^{-\bullet}$ and $\mathbf{10}^{-\bullet}$.

The situation is more complicated in the disubstituted radical anions. Obviously, the spin density distribution in the 1,3-derivatives **11** is predominantly determined by the dithioester substituent in the 1-position, whereas that in the 3-position plays only a minor role. Similar to **1**, high spin densities are found in the 4- (*quasi-para*) ($\rho_4^\pi = 0.244$), 5- ($\rho_5^\pi = 0.100$) and 7-position ($\rho_7^\pi = 0.066$) of $\mathbf{11}^{-\bullet}$. The spin density in the 2-position is however quite low (ρ_2^π ($\mathbf{11}^{-\bullet}$) = 0.033) just as in the corresponding ester radical anion ($\rho_2^\pi = 0.012$[3]), although it represents the *quasi-ortho* position with respect to two thionester groups. The spin density distribution in the symmetric 2,6-disubstituted thion- and diester radical anions $\mathbf{7}^{-\bullet}$ and $\mathbf{13}^{-\bullet}$ can best be compared with $\mathbf{2}^{-\bullet}$ and $\mathbf{10}^{-\bullet}$. But the total spin density in the naphthalene moiety is also low, as one easily recognizes from the low total widths of the corresponding EPR spectra. This can be explained by the assumption that a large part of the spin density is localized in the functional groups, i.e., the resonance formulae of type $\mathbf{7b}^{-\bullet}$ shown in Scheme 5 should exhibit particularly high statistic weights. This effect is even more pronounced in $\mathbf{12c}^{-\bullet}$ with two dithioester groups in the *quasi-para* positions of one ring. In this case, no spin densities (resolved proton hfs couplings) whatsoever are found experimentally in the unsubstituted ring. The corresponding calculated values, on the other hand, are low but not zero. The MO theory obviously underestimates the distinct resonance effect of two conjugated thionester groups. In so far, $\mathbf{12c}^{-\bullet}$ strikingly resembles the monocyclic dimethyl benzene-1,4-bis(carbodithioate) radical anion with $a_{2,3,5,6}^H = a_{Me}^H = 0.108$ mT.[43] The asymmetric radical anion $\mathbf{4a}^{-\bullet}$ exhibits spin density mainly in the thionester-substituted part of the naphthalene system, as one would expect. In the asymmetric 2,6- and 2,7-disubstituted counterparts $\mathbf{7a}^{-\bullet}$ and $\mathbf{8a}^{-\bullet}$, the spin density is more evenly delocalized over both rings.

Conclusions

A series of novel *O*-alkyl naphthalene-mono- and -bis-thionesters and alkyl naphthalene-mono- and -bis-dithioesters has been prepared. The corresponding radical anions could be generated by in situ electroreduction and studied by EPR spectroscopy. The spin density distributions in these radical anions as determined from the experimentally measured proton hfs couplings and from quantum chemical calculations are discussed. The distributions decidedly depend on the position of the thioester substituents and their relative orientation in case of the bis-thioester radical anions.

EXPERIMENTAL

Corrected melting points (m p) were determined on an Electrothermal apparatus. Boiling points (bp) were determined during distillation. Thin layer chromatography (TLC) was performed on Al foils coated with SiO_2 F_{254} (Merck, Darmstadt). The spots were detected by the extinction of the fluorescence or by spraying with the iodine/sodium azide reagent.[46] Column chromatography (CC) was performed on Kieselgel 60 (Merck, Darmstadt), 0.063–0.200 mm (70–230 mesh). Eluents [CCl_4, EtOAc, petroleum ether (PE)] were distilled prior to use. Solvents were purified and dried by standard laboratory procedures.[47]

IR spectra were measured as KBr pellets on a Perkin-Elmer FT-IR 1720 X spectrometer. NMR spectra were measured in $CDCl_3$ on Bruker WM 250, WM 400, or AMX 400 spectrometers. Chemical shifts δ are related to $SiMe_4$ ($\delta = 0.00$ ppm) as internal standard. Coupling constants J are given in Hz. Mass spectra were measured on Varian MAT CH 7 or CH 311 spectrometers at 70 eV. Electroanalytical measurements [differential pulse polarograpy (DPP) and cyclovoltammetry (CV)] were performed on a Metrohm polarograpy setup EA 354 with a Hewlett-Packard plotter HP 7040 A. Half-wave potentials $E_{1/2}$ (DPP) and peak potentials (CV) were measured in dry DMF[47] containing tetrapropylammonium bromide (2–5 mg/10 mL) by use of an internal Ag/AgBr reference electrode, the potential of which is shifted by -0.55 V vs. the aqu. SCE. In situ electrogeneration of the radical anions was achieved with a Bank Electronic (Wenking type) potentiostat MP 31. EPR spectra were measured in quartz flat cells on Bruker ER 420 S and ESP 300 E spectrometers at 25°C in dry and purified[47] DMF. The EPR spectra were simulated by use of the Symfonia program (Bruker).

Quantum chemical calculations of the spin densities were performed by use of the Hückel 88 or the SHMO[48] program (HMO and McLachlan calculations) and the QCPE software MOPAC 6.0 and MOPAC 93 (MNDO and AM1 calculations).

X-Ray Structure Analysis

The crystal data of **9d** and a summary of experimental details are given in Table VI. Data collection was performed with a CAD 4 SDP (Enraf Nonius) diffractometer with graphite-monochromated Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54184$ Å) in the $\theta/2\theta$ scan mode at 298 K. The structure was solved by the direct method MULTAN[49] and differential Fourier synthesis. Refinement was performed by least squares methods. Due to a disorder of the *tert*-butyl group, the H-atoms could not be localized. Crystallographic data of **9d** have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-710517. Copies of the data can be obtained free of charge on

Table VI Crystal data and structure refinement for **9d**

Empirical formula	$C_{16}H_{18}S_2$
Formula weight	274.46
Crystal system	Triclinic
Space group	Pī
a [pm]	976.8 (1)
b [pm]	1030.0 (1)
c [pm]	1546.1 (1)
α [°]	95.78 (1)
β [°]	98.25 (1)
γ [°]	90.32 (1)
V [pm^3]	$1531 \bullet 10^6$
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.19
μ [cm^{-1}]	29.29
F(000)	584
θ limits [°]	2/65
h/*k*/*l* limits	0, +11/−12, +12/−18, +18
Reflections collected ($I > 3\sigma_I$)	4069
Number of parameters	398
R index	0.071
R_w index ($w = {\sigma_I}^{-2}$)	0.080

application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (international) + 44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

Thionesters

The respective ester (1.00 mol. equiv.) and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 1,3-disulfide (**LR**)[15,18] ($\approx$ 0.60 mol. equiv.) were heated to reflux for 6 h in about the 20-fold amount of chlorobenzene or (if stated) toluene. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed by vacuum distillation in a rotary evaporator. The residue was purified by chromatography with a suitable eluent and/or recrystallization. NMR spectroscopic, MS, and analytical data of the thionesters are compiled in Tables VII–IX.

O-Ethyl naphthalene-1-carbothioate (**1b**)[14–16] and *O*-ethyl naphthalene-2-carbothioate (**2b**)[15,17] are described in the literature.

O-Methyl Naphthalene-1-carbothioate (1a)

Methyl α-naphthoate[3] (2.00 g, 10.50 mmol) was thionated with **LR** (2.50 g, 6.30 mmol). CC (CCl_4) gave **1a** (0.38 g, 18%) as an orange oil. IR: ν(C=S) 1235 cm^{-1}.

O-Isopropyl Naphthalene-1-carbothioate (1c) *and* *O*-Isopropyl Naphthalene-2-carbothioate (2c)

Isopropyl α-naphthoate[3] (1.25 g, 5.80 mmol, containing isopropyl β-naphthoate as a contamination) was thionated with **LR** (1.21 g, 2.99 mmol). CC (CCl_4) gave **1c** (F1,

Table VII Chemical shifts δ [ppm] and coupling constants J [Hz] in the ^{1}H NMR spectra[a] of the thionesters

Compound	Proton chemical shifts δ and proton–proton coupling constants J
1a	4.43 (s, 3 H, CH_3), 7.45–7.60 (m, 3 H, 3/6/7-H), 7.85–7.95 (m, 3 H, 2/4/5-H), 8.25 (d, $^3J_{H7,H8}$ = 8.6, 1 H, 8-H)
1b	1.51 (t, ^3J = 7.8, 3 H, CH_3), 4.78 (q, ^3J = 7.8, 2 H, CH_2), 7.35–7.55 (m, 3 H, 3/6/7-H), 7.78–7.87 (m, 3 H, 2/4/5-H), 8.19 (d, $^3J_{H7,H8}$ = 7.5, 1 H, 8-H)
1c	1.55 (d, ^3J = 6.1, 6 H, CH_3), 6.00 (sep, ^3J = 6.1, 1 H, C*H*Me$_2$), 7.40–7.55 (m, 3 H, 3/6/7-H), 7.80–7.90 (m, 2 H, 4/5-H), 7.90 (d, $^3J_{H2,H3}$ = 7.0, 1 H, 2-H), 8.19 (d, $^3J_{H7,H8}$ = 8.1, 1 H, 8-H)
1e	1.39 (s, 9 H, CH_3), 1.43 (s, 9 H, CH_3), 7.29 (d, $^3J_{H2',H3'}$ = 7.6, 2 H, 2′/6′-H), 7.36 (t, $^3J_{H3',H4'}$ = 7.2, 1 H, 4′-H), 7.53 (t, $^3J_{H2',H3'} \approx {}^3J_{H3',H4'}$ = 7.4, 2 H, 3′/5′-H), 7.60 (dd, $^3J_{H5,H6}$ = 8.4, $^4J_{H6,H8}$ = 1.8, 1 H, 6-H), 7.81 (d, $^3J_{H5,H6}$ = 8.4, 1 H, 5-H), 7.90 (d, $^4J_{H2,H4}$ = 1.6, 1 H, 4-H), 8.20 (d, $^4J_{H6,H8}$ = 1.8, 1 H, 8-H), 8.54 (d, $^4J_{H2,H4}$ = 1.6, 1 H, 2-H)
2a	4.35 (s, 3 H, CH_3), 7.50–7.65 (m, 2 H, 6/7-H), 7.82 (d, $^3J_{H5,H6}$ = 8.0, 1H, 5-H), 7.87 (d, $^3J_{H7,H8}$ = 8.5, 1 H, 8-H), 7.96 (d, $^3J_{H3,H4}$ = 8.3, 1 H, 4-H), 8.28 (dd, $^3J_{H3,H4}$ = 8.3, $^4J_{H1,H3}$ = 1.0, 1 H, 3-H), 8.71 (bs, 1 H, 1-H)
2b	1.58 (t, ^3J = 7.0, 3 H, CH_3), 4.79 (q, ^3J = 7.0, 2 H, CH_2), 7.45–7.62 (m, 2 H, 6/7-H), 7.80 (d, $^3J_{H5,H6}$ = 8.0, 1H, 5-H), 7.87 (d, $^3J_{H7,H8}$ = 8.5, 1 H, 8-H), 7.95 (d, $^3J_{H3,H4}$ = 7.2, 1 H, 4-H), 8.28 (d, $^3J_{H3,H4}$ = 7.2, 1 H, 3-H), 8.70 (s, 1 H, 1-H)
2c	1.45 (d, ^3J = 6.1, 6 H, CH_3), 5.85 (sep, ^3J = 6.1, 1 H, C*H*Me$_2$), 7.40–7.50 (m, 2 H, 6/7-H), 7.70 (d, $^3J_{H5,H6}$ = 8.0, 1 H, 5-H), 7.85 (d, $^3J_{H7,H8}$ = 8.5, 1 H, 8-H), 7.88 (d, $^3J_{H3,H4}$ = 7.5, 1 H, 4-H), 8.18 (d, $^3J_{H3,H4}$ = 7.5, 1 H, 3-H), 8.59 (bs, 1 H, 1-H)
3a	4.32 (s, 3 H, CH_3), 7.48 (m, 2 H, 6/7-H), 7.70 (s, 2 H, 2/3-H), 8.08 (m, 2 H, 5/8-H)
3b	7.26–7.32 (m, 4 H, 3′/5′-H), 7.36–7.41 (m, 4 H, 2′/6′), 7.52–7.58 (m, 2 H, 4′-H), 7.63–7.68 (m, 2 H, 6/7-H), 8.05 (s, 2 H, 2/3-H), 8.54–8.59 (m, 2 H, 5/8-H)
4a	1.44 [d, ^3J = 6.2, 6 H, 1-CH(CH_3)$_2$], 1.54 [d, ^3J = 6.6, 6 H, 5-CH(CH_3)$_2$], 5.36 (sep, ^3J = 6.1, 1 H, 1-C*H*Me$_2$), 5.94 (sep, ^3J = 6.3, 1 H, 5-C*H*Me$_2$), 7.53 (dd, $^3J_{H2,H3}$ = 7.2, $^3J_{H3,H4}$ = 8.6, 1 H, 3-H), 7.56 (dd, $^3J_{H6,H7}$ = 7.2, $^3J_{H7,H8}$ = 8.6, 1 H, 7-H), 7.80 (dd, $^3J_{H2,H3}$ = 7.2, $^4J_{H5,H7}$ = 1.0, 1 H, 2-H), 8.12 (dd, $^3J_{H2,H3}$ = 7.2, $^4J_{H6,H8}$ = 1.0, 1 H, 6-H), 8.38 (d, $^3J_{H7,H8}$ = 8.6, 1 H, 8-H), 8.98 (d, $^3J_{H3,H4}$ = 8.6, 1 H, 4-H)
4b[b]	1.55 (d, ^3J = 6.1, 12 H, CH_3), 5.94 (sep, ^3J = 6.1, 2 H, C*H*Me$_2$), 7.48 (dd, $^3J_{H2,H3}$ = 7.2, $^3J_{H3,H4}$ = 8.6, 2 H, 3/7-H), 7.77 (dd, $^3J_{H2,H3}$ = 7.2, $^4J_{H2,H4}$ = 1.0, 2 H, 2/6-H), 8.25 (d, $^3J_{H3,H4}$ = 8.6, 2 H, 4/8-H)
5[b]	4.10 (s, 6 H, CH_3), 7.50 (vt, $^3J_{H2,H3} \approx {}^3J_{H3,H4} \approx$ 8.6, 2 H, 3/6-H), 7.96 (d, $^3J_{H3,H4}$ = 8.6, 2 H, 4/5-H), 8.19 (d, $^3J_{H2,H3}$ = 7.6, 2 H, 2/7-H)
6	1.40 (t, ^3J = 7.0, 6 H, CH_3), 4.41 (q, ^3J = 7.0, 4 H, CH_2), 7.61 (m, 2 H, 6/7-H), 7.92 (m, 2 H, 5/8-H), 8.23 (s, 2 H, 1/4-H)
7a	3.98 (s, 3 H, $COOCH_3$), 4.39 (s, 3 H, $CSOCH_3$), 7.93 (d, $^3J_{H7,H8}$ = 8.6, 1 H, 8-H), 7.99 (d, $^3J_{H3,H4}$ = 8.4, 1 H, 4-H), 8.09 (dd, $^3J_{H3,H4}$ = 8.8, $^4J_{H1,H3}$ = 1.5, 1 H, 3-H), 8.31 (dd, $^3J_{H7,H8}$ = 8.6, $^4J_{H5,H7}$ = 1.6, 1 H, 7-H), 8.59 (bs, 1 H, 1-H), 8.72 (bs, 1 H, 5-H)
7b	4.39 (s, 6 H, CH_3), 7.95 (d, $^3J_{H3,H4}$ = 8.6, 2 H, 4/8-H), 8.35 (dd, $^3J_{H3,H4}$ = 8.6, $^4J_{H1,H3}$ = 1.7, 2 H, 3/7-H), 8.75 (d, $^4J_{H1,H3}$ = 1.7, 2 H, 1/5-H)
7c	1.54 (d, ^3J = 12.0, 6 H, CH_3), 5.93 (sep, ^3J = 6.0, 2 H, C*H*Me$_2$), 7.93 (d, $^3J_{H3,H4}$ = 8.4, 2 H, 4/8-H), 8.28 (dd, $^3J_{H3,H4}$ = 8.4, $^4J_{H1,H3}$ = 1.7, 2 H, 3/7-H), 8.65 (d, $^4J_{H1,H3}$ = 1.7, 2 H, 1/5-H)
8a	1.43 [d, ^3J = 6.0, 6 H, 6-CH(CH_3)$_2$], 1.55 [d, ^3J = 6.0, 6 H, 2-CH(CH_3)$_2$], 5.32 (sep, ^3J = 6.0, 1 H, 6-C*H*Me$_2$), 5.93 (sep, ^3J = 6.0, 1 H, 2-C*H*Me$_2$), 7.82–7.88 (m, 2 H, 4/5-H), 8.14 (dd, $^3J_{H3,H4}$ = 8.6, $^4J_{H1,H3}$ = 1.6, 1 H, 3-H), 8.36 (dd, $^3J_{H6,H7}$ = 8.6, $^4J_{H6,H8}$ = 1.6, 1 H, 6-H), 8.70 (s, 1 H, 1-H), 8.76 (s, 1 H, 8-H)
8b	1.54 (d, ^3J = 6.0, 12 H, CH_3), 5.94 (sep, ^3J = 6.0, 2 H, C*H*Me$_2$), 7.81 (d, $^3J_{H3,H4}$ = 9.2, 2 H, 4/5-H), 8.34 (dd, $^3J_{H3,H4}$ = 9.2, $^4J_{H1,H3}$ = 1.6, 2 H, 3/6-H), 8.78 (d, $^4J_{H1,H3}$ = 1.6, 2 H, 1/8-H)

[a]Compounds **1b**, **2**, **3a**, **6**, **7a**, **7b** were measured at 250 MHz, all other thionoesters at 400 MHz.
[b]Assignments were corroborated by COSY measurements.

Table VIII Chemical shifts δ [ppm] in the ^{13}C NMR spectra[a] of the thionesters

	C-1	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	α-CS	β-CS	OCH_n[b]	$OCCH_3$
1a	139.6	124.8	125.4	131.4	133.7	127.2	126.2	124.8	128.6	129.2	216.5		59.5	
1c	139.9	124.3	124.7	130.5	133.2	127.5	126.5	125.6	127.9	128.6	214.8		76.0	20.8
1e	132.1	120.2	138.6	129.0	126.5	128.2	122.5	146.9	125.1	127.5	207.0		[c]	
2a	128.2	135.0	125.0	129.0	135.0	129.1	127.2	126.2	129.4	132.0		211.6	58.9	
2b	129.0	136.8	125.6	129.*o*	134.2	129.6	128.6	125.7	130.1	134.0		211.0	59.1	13.9
2c	127.5	136.0	125.3	128.0	135.2	129.3	126.4	127.4	129.6	132.2		210.3	61.1	21.2
3a	141.7	125.5	125.5	141.7	129.3	127.0	126.4	126.4	127.0	129.3	215.6		59.5	
3b	141.2	125.3	125.3	141.2	129.4	127.1	126.8	126.8	127.1	129.4	213.5		[d]	
4a	130.9	127.1	124.9	127.9	129.0	140.5	129.3	125.9	129.7	128.1	214.5		76.1	21.6
											166.6[e]		68.3	20.8
4b	140.9	127.6	125.6	127.7	129.1	140.9	127.6	125.6	127.7	129.1	214.9		76.5	21.2
5	139.0	132.8	125.2	132.1	125.2	132.1	125.2	132.8	139.0	134.2	216.3		58.9	
6	128.6	133.4	133.4	128.6	128.8	130.0	128.5	128.5	130.0	128.8		208.8	61.7	14.2
7a	128.9	129.5	129.1	130.6	134.5	126.2	137.2	126.1	130.0	134.4		211.4	52.1	
												166.9[e]		
7b	128.8	137.1	126.2	129.1	134.3	128.8	137.1	126.2	129.1	134.3		211.4	59.5	
7c	128.8	137.7	126.2	129.4	134.3	128.8	137.7	126.2	129.4	134.3		209.0	76.0	21.3
8a	131.6	129.0	127.8	130.3	136.7	127.9	127.4	137.2	127.6	132.6		209.8	75.9	22.0
												165.8[e]	68.7	21.3
8b	130.0	137.1	127.3	130.9	136.8	130.9	127.3	137.1	130.0	131.4		209.1	75.9	21.4

[a]Compounds **1**, **3a**, **6**, and **8** were measured at 63 MHz, all other dithioesters at 100 MHz.

[b]n = 3 for **1a**, **2a**, **3a**, **5**, **7a**, **7b**; n = 2 for **1b**, **2b**, **6**; n = 1 for **1c**, **2c**, **4a**, **4b**, **7c**, **8a**, **8b**.

[c]31.26 [C(*C*H$_3$)$_3$], 31.29 [C(*C*H$_3$)$_3$], 34.8 [*C*(CH$_3$)$_3$], 35.3 [*C*(CH$_3$)$_3$], 122.1 (C-2′/6′), 127.1 (C-4′), 129.8 (C-3′/5′), 149.4 (C-1′).

[d]121.5 (C-2′/6′), 126.4 (C-4′), 129.5 (C-3′/5′), 154.0 (C-1′).

[e]C=O.

0.470 g, 35%); IR: ν(C=S) 1231 cm^{-1}, and **2c** (F2, 0.140 g, 11%); IR: ν(C=S) 1241 cm^{-1}, as orange oils.

Phenyl 3,7-Di-*tert*-butylnaphthalene-1-carboxylate (1d)[3,23]

Commercially available 2,6-di-*tert*-butylnaphthalene, containing substantial amounts of the isomer 3,7-di-*tert*-butylnaphthalene according to its ^1H NMR spectrum, was purified via its thiourea adduct.[50] The colorless crystals (3.00 g, 12.50 mmol), mp 148–149°C (lit.[50] 146–147°C), were dissolved in trimethyl phosphate (30 mL). Bromine (0.77 mL, 15.0 mmol) in trimethyl phosphate (10 mL) was added dropwise. After stirring at 70°C for 6 h and cooling to 20°C, the solution was extracted five times with PE. The extract was washed with $NaHSO_4$ solution and H_2O, and dried over $MgSO_4$. Removal of the PE and CC (PE) gave 1-bromo-3,7-di-*tert*-butylnaphthalene (3.87 g, 97%) as white crystals, mp 50°C (lit.[51]: 53–54°C). ^1H NMR (400 MHz): δ 1.38 (s, 9 H, CH_3), 1.42 (s, 9 H, CH_3), 7.58 (dd, 1 H, 6-H), 7.67 (d, 1 H, 2-H), 7.71 (d, 1 H, 5-H), 7.81 (d, 1 H, 4-H), 8.02 (d, 1 H, 8-H); $^4J_{H2,H4} = 1.5$, $^3J_{H5,H6} = 8.6$, $^4J_{H6,H8} = 2.0$. ^{13}C NMR (100 MHz): δ 30.8 (CH_3), 30.9 (CH_3), 34.7 (*C*Me$_3$), 35.0 (*C*Me$_3$), 121.4 (C-6), 122.2 (C-4), 122.5 (C-1), 125.1 (C-8), 127.6 (C-2), 128.4 (C-5), 128.7 (C-4a), 133.0 (C-8a), 148.6 (C-7), 149.5 (C-3). MS (70 eV): *m/z* (%) = 320/318 (13/15) [M$^+$], 305/303 (59/57) [M$^+$ − CH_3], 209 (9), 194 (7), 167 (9), 152 (6), 57 (100) [CMe_3^+]. The bromide (2.51 g, 7.80 mmol) was dissolved in

Table IX Chemical shifts δ [ppm] and coupling constants J [Hz] in the ^{1}H NMR spectra[a] of the dithioesters

Compound	Proton chemical shifts δ and proton–proton coupling constants J
9d	1.43 (s, 9 H, CH_3), 2.85 (s, 3 H, SCH_3), 7.45 (m, 2 H, 6/7-H), 7.58 (d, $^4J_{H2,H4} = 2.0$, 1 H, 2-H), 7.80 (m, 2 H, 4/5-H), 8.11 (d, $^3J_{H7,H8} = 8.0$, 1 H, 8-H)
9d[b]	7.46 (ddd, $^3J_{H5,H6} = 8.0$, $^3J_{H6,H7} = 6.8$, $^4J_{H6,H8} = 1.8$, 1 H, 6-H), 7.52 (ddd, $^3J_{H7,H8} = 8.0$, $^3J_{H6,H7} = 6.8$, $^4J_{H5,H7} = 1.4$, 1 H, 7-H), 7.63 (d, $^4J_{H2,H4} = 2.0$, 1 H, 2-H), 7.93 (ddd, $^3J_{H5,H6} = 8.0$, $^4J_{H5,H7} = 1.4$, $^4J_{H4,H5} = 0.8$, 1 H, 5-H), 7.96 (dd, $^4J_{H2,H4} = 2.0$, $^5J_{H4,H8} = 0.7$, 1 H, 4-H) 8.06 (dddd, $^3J_{H7,H8} = 8.0$, $^4J_{H6,H8} = 1.8$, $^4J_{H4,H5} = 0.8$, $^5J_{H4,H8} = 0.8$, 1 H, 8-H)
9e	1.45 (t, $^3J = 7.5$, 3 H, CH_2CH_3), 2.50 (s, 3 H, CH_3), 3.42 (q, $^3J = 7.5$, 2 H, CH_2CH_3), 7.32 (s, 1 H, 2-H), 7.38–7.48 (m, 2 H, 6/7-H), 7.62 (s, 1 H, 4-H), 7.75 (d, $^3J_{H5,H6} = 8.0$, 1 H, 5-H), 8.09 (d, $^3J_{H7,H8} = 8.0$, 1 H, 8-H)
10b	1.48 (t, $^3J = 7.5$, 3 H, CH_3), 3.43 (q, $^3J = 7.5$, 2 H, CH_2), 7.40–7.50 (m, 4 H, 4/5/6/7-H), 7.80–7.90 (m, 2 H, 3/8-H), 8.10–8.20 (m, 1 H, 1-H)
11a	2.82 (s, 3 H, 3-CS_2CH_3), 2.85 (s, 3 H, 1-CS_2CH_3), 7.50–7.63 (m, 2 H, 6/7-H), 8.00 (d, $^3J_{H5,H6} = 8.0$, 1 H, 5-H), 8.12 (d, $^3J_{H7,H8} = 8.0$, 1 H, 8-H), 8.16 (s, 1 H, 4-H), 8.52 (s, 1 H, 2-H)
11b	7.50–7.63 (m, 2 H, 6/7-H), 7.99 (d, $^3J_{H5,H6} = 8.0$, 1 H, 5-H), 8.12 (d, $^3J_{H7,H8} = 8.0$ 1 H, 8-H), 8.16 (s, 1 H, 4-H), 8.53 (s, 1 H, 2-H)
11c	4.38 (s, 2 H, SCH_2Ph), 4.67 (s, 2 H, OCH_2Ph), 7.31–7.46 (m, 10 H, H_{Ar}), 7.53–7.63 (m, 2 H, 6/7-H), 7.99 (d, $^3J_{H5,H6} = 8.0$, 1 H, 5-H), 8.12 (d, $^3J_{H7,H8} = 8.0$, 1 H, 8-H), 8.16 (s, 1 H, 4-H), 8.52 (s, 1 H, 2-H)
12a	2.78 (s, 3 H, CH_3), 7.31 (d, $^3J_{H2,H3} = 9.0$, 1 H, 3-H), 7.49–7.64 (m, 2 H, 6/7-H), 7.79 (d, $^3J_{H5,H6} = 9.0$, 1 H, 5-H), 8.12 (d, $^3J_{H2,H3} = 9.0$, 1 H, 2-H), 8.29 (d, $^3J_{H7,H8} = 9.0$, 1 H, 8-H)
12b	1.47 (t, $^3J = 7.5$, 3 H, SCH_2CH_3,), 3.44 (q, $^3J = 7.5$, 2 H, SCH_2CH_3), 7.28 (d, $^3J_{H2,H3} = 9.0$, 1 H, 3-H), 7.50–7.63 (m, 2 H, 6/7-H), 7.77 (d, $^3J_{H5,H6} = 9.0$, 1 H, 5-H), 8.12 (d, $^3J_{H2,H3} = 9.0$, 1 H, 2-H), 8.29 (d, $^3J_{H7,H8} = 9.0$, 1 H, 8-H)
12c	2.82 (s, 6 H, CH_3), 7.43 (s, 2 H, 2/3-H), 7.48–7.53 (m, 2 H, 6/7-H), 8.08–8.14 (m, 2 H, 5/8-H)
13a	2.82 (s, 6 H, CH_3), 7.95 (d, $^3J_{H3,H4} = 8.6$, 2 H, 4/8-H), 8.35 (dd, $^3J_{H3,H4} = 8.6$, $^4J_{H1,H3} = 1.7$, 2 H, 3/7-H), 8.75 (d, $^4J_{H1,H3} = 1.7$, 2 H, 1/5-H)
13b	1.48 (t, $^3J = 7.3$, 6 H, CH_3), 3.45 (q, $^3J = 7.3$, 4 H, CH_2), 7.93 (d, $^3J_{H3,H4} = 8.6$, 2 H, 4/8-H), 8.13 (dd, $^3J_{H3,H4} = 8.6$, $^4J_{H1,H3} = 1.3$, 2H, 3/7-H), 8.50 (d, $^4J_{H1,H3} = 1.3$, 2 H, 1/5-H)

[a]Measured at 250 MHz.
[b]Aromatic protons, measured in acetone-d_6 at 400 MHz.

dry diethyl ether (50 mL) under N_2. A solution of nBuLi in hexane (5.2 mL, 15%) was injected with a syringe through a septum, and the solution was stirred at 20°C for 2 h. Dry CO_2 was bubbled through the solution for 30 min. The clear yellow reaction mixture was cautiously hydrolyzed by stirring with ice/water (5 mL) and 4% aqu. HCl (8 mL) for 10 h. The solution was extracted four times with diethyl ether. The extract was dried over $MgSO_4$. Removal of the solvent gave 3,7-di-*tert*-butylnaphthalene-1-carboxylic acid (2.04 g, 90%) as white crystals, mp 186°C. IR: ν(OH) 3442, ν(C=O) 1688 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.48 (s, 9 H, CH_3), 1.51 (s, 9 H, CH_3), 7.79 (dd, 1 H, 6-H), 8.05 (d, 1 H, 5-H), 8.14 (d, 1 H, 4-H), 8.31 (d, 1 H, 2-H), 8.90 (d, 1 H, 8-H); $^4J_{H2,H4} = 2.0$, $^3J_{H5,H6} = 8.6$, $^4J_{H6,H8} = 2.0$. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 30.9 (CH_3), 31.0 (CH_3), 34.4 (CMe_3), 34.8 (CMe_3), 119.9 (C-6), 124.8 (C-2), 127.4 (C-8), 127.5 (C-1), 128.2 (C-5), 128.3 (C-4), 128.8 (C-8a), 131.8 (C-4a), 144.0 (C-3), 146.2 (C-7), 168.0 (C=O). The acid (0.55 g, 1.90 mmol) was mixed with PCl_5 (0.52 g, 2.48 mmol) and heated to 140°C for 3 h. $POCl_3$ was removed to yield 3,7-di-*tert*-butyl-1-naphthoyl chloride (1.00 g, 98%) as a deep green oil. IR: ν(C=O) 1757 cm^{-1}. ^{1}H NMR (400 MHz): δ 1.42 (s, 9 H, CH_3), 1.45 (s, 9 H, CH_3), 7.65 (dd, 1 H, 6-H), 7.83 (d, 1 H, 5-H), 8.02 (d, 1 H, 4-H), 8.64 (s, 1 H, 2-H), 8.68 (d,

1 H, 8-H); $^4J_{H2,H4} = 2.0$, $^3J_{H5,H6} = 8.6$, $^4J_{H6,H8} = 2.0$. The raw chloride was dissolved in dry pyridine (4 mL), and phenol (0.23 g, 2.40 mmol) and DMAP (100 mg) were added. The mixture was stirred at 0°C for 5 h, then hydrolyzed with ice/water (5 mL) and conc. aqu. HCl (5.3 mL), and extracted four times with diethyl ether. After drying over $MgSO_4$ and removal of the solvent, the residue was recrystallized from PE to give **1d** (0.30 g, 49%), light yellow crystals, mp 160–161°C. IR: ν (C=O) 1730 cm^{-1}.[3,23]

O-Phenyl 3,7-Di-*tert*-butylnaphthalene-1-carbothioate (1e)

The ester **1d** (200 mg, 0.54 mmol) was thionated with **LR** (138 mg, 0.34 mmol) to give 240 mg of a raw product. An aliquot of 100 mg was purified by preparative TLC (PE/EtOAc 20:1) to yield **1e** (7.3 mg, 8%) as a yellow solid besides the recovered **1d** (54 mg, 57%).

O-Methyl Naphthalene-2-carbothioate (2a)

Methyl β-naphthoate[52] (1.53 g, 8.04 mmol) was thionated with **LR** (1.80 g, 4.46 mmol) in toluene (3 mL). Yield: 0.69 g (43%) after CC (CCl_4), orange crystals, mp 41–42°C. IR: ν(C=S) 1234 cm^{-1}.

O,O-Dimethyl Naphthalene-1,4-dicarbothioate (3a)

Dimethyl naphthalene-1,4-dicarboxylate[3] (0.300 g, 1.23 mmol) was thionated with **LR** (0.550 g, 1.36 mmol). Yield: 18 mg (6%) after CC (CCl_4), orange needles. IR: ν(C=S) 1229 cm^{-1}.

O,O-Diphenyl Naphthalene-1,4-dicarbothioate (3b)

Diphenyl naphthalene-1,4-dicarboxylate[3] (0.720 g, 2.17 mmol) was thionated with **LR** (1.36 g, 3.36 mmol). Yield: 0.104 g (14%) after CC (PE:EtOAc 30:1) and recrystallization from toluene, yellow needles, mp 191–192°C. IR: ν(C=S) 1254 cm^{-1}.

Isopropyl 5-Isopropoxythiocarbonylnaphthalene-1-carboxylate (4a) *and* *O,O*-Diisopropyl Naphthalene-1,5-dicarbothioate (4b)

Diisopropyl naphthalene-1,5-dicarboxylate[3] (0.720 g, 2.40 mmol) was thionated with **LR** (1.36 g, 3.36 mmol) in toluene (3 mL). CC (PE/EtOAc 30:1) gave two fractions. F1: 5 mg (0.6%) **4b**, yellow powder, mp 178–180°C; IR: ν(C=S) 1263 cm^{-1}; F2: 240 mg (32%) **4a**, yellow powder, mp 68–69°C. IR: ν(C=O) 1712, ν(C=S) 1252 cm^{-1}.

O,O-Diisopropyl Naphthalene-1,8-dicarbothioate (5)

Diisopropyl naphthalene-1,8-dicarboxylate[3] (395 mg, 1.60mmol) was thionated with **LR** (398 mg, 0.984 mmol) in toluene (2 mL) under N_2. Yield: 67 mg (16%) after preparative TLC (PE:EtOAc 20:1), yellow crystals, mp 195°C; IR: ν(C=S) 1239 cm^{-1}.

O,O-Diethyl Naphthalene-2,3-dicarbothioate (6)

Diethyl naphthalene-2,3-dicarboxylate[53] (150 mg, 0.551 mmol) was thionated with **LR** (212 mg, 0.523 mmol) in toluene (0.6 mL) under N_2. Yield: 78 mg (46%) after preparative TLC (PE:EtOAc 10:1), orange-brown solid. IR: ν(C=S) 1260 cm^{-1}.

Methyl 6-Methoxythiocarbonylnaphthalene-2-carboxylate (7a) *and O,O*-Dimethyl Naphthalene-2,6-dicarbothioate (7b)

Dimethyl naphthalene-2,6-dicarboxylate[3] (2.44 g, 10.0 mmol) was thionated with **LR** (4.49 g, 11.1 mmol). CC (CCl_4) gave two fractions. F1: 1.80 g (65%) **7b**, orange crystals, mp 193–194°C (EtOAc); IR: ν(C=S) 1238 cm^{-1}; F2: 0.18 g (7%) **7a**, citrine crystals, mp 122–123°C. IR: ν(C=O) 1724, ν(C=S) 1265 cm^{-1}.

O,O-Diisopropyl Naphthalene-2,6-dicarbothioate (7c)

Diisopropyl naphthalene-2,6-dicarboxylate[3] (0.500 g, 1.66 mmol) was thionated with **LR** (807 mg, 2.00 mmol). Yield: 0.155 g (28%) after CC (CCl_4/$CHCl_3$ 3:1), orange crystals, mp 90–91°C. IR: ν(C=S) 1238 cm^{-1}.

Isopropyl 7-Isopropoxythiocarbonylnaphthalene-2-carboxylate (8a) *and O,O*-Diisopropyl Naphthalene-2,7-dicarbothioate (8b)

Diisopropyl naphthalene-2,7-dicarboxylate[3] (0.500 g, 1.66 mmol) was thionated with **LR** (807 mg, 2.00 mmol). CC (CCl_4/$CHCl_3$ 3:1) gave two fractions. F1: 0.210 g (40%) **8b**, orange oil; IR: ν(C=S) 1235 cm^{-1}. F2: 0.238 g (43%) **8a**, orange crystals, mp 74–75°C. IR: ν(C=O) 1713, ν(C=S) 1219 cm^{-1}.

Dithioesters

Methyl naphthalene-1-carbodithioate (**9a**),[24–26] ethyl naphthalene-1-carbodithioate (**9c**),[24,26,27] methyl naphthalene-2-carbodithioate (**10a**),[28–30] ethyl naphthalene-2-carbodithioate (**10b**),[26,31] and dimethyl naphthalene-2,6-bis-carbodithioate (**13a**)[32] are described in the literature. NMR spectroscopic, MS, and analytical data of the dithioesters are compiled in Tables IX–XI.

Trideuteromethyl Naphthalene-1-carbodithioate (9b)

The dithioester **9b** was obtained via the Grignard route described in the literature[25] for the preparation of **9a** by use of CD_3I instead of Me_2SO_4 as the alkylating agent. The physical and spectroscopic data of **9b** and **9a** were identical.

Methyl 3-*tert*-Butylnaphthalene-1-carbodithioate (9d)

Acetyl chloride (14.1 g, 0.183 mol) was dropped into a stirred solution of $AlCl_3$ (28.2 g, 0.210 mol) in 1,2-dichloroethane (74 mL) at 0°C under exclusion of moisture. 2-*tert*-Butylnaphthalene[54] (32.1 g, 0.174 mol) was slowly added at <20°C. After 12 h at 20°C and subsequent heating to 50°C for 1 h, the reaction mixture was poured on ice, acidified to

Table X Chemical shifts δ [ppm] in the ^{13}C NMR spectra (100 MHz) of the dithioesters ArCS-SR

	R	C-1	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	α-CS	β-CS
9c	Et[a]	145.4	123.9	124.7	130.0	133.8	126.9	125.0	126.4	128.2	129.4	231.7	
9e	Et[b]	144.6	124.2	133.7	128.3	133.4	125.8	125.4	125.4	126.9	127.1	231.2	
11a	Me[c]	145.2	122.5	140.8	130.0	131.3	129.0	125.1	127.4	128.0	133.0	230.0	227.2
11b	CD_3[d]	145.2	122.5	140.8	130.0	131.3	128.9	125.1	127.6	128.0	133.0	230.6	227.2
11c	CH_2Ph[e]	145.2	121.2	137.3	129.9	131.8	129.0	125.2	127.4	127.9	133.0	229.3	225.0
12a	Me[f]	145.1	127.4	128.9	124.8	132.2	127.8	125.6	124.5	127.6	130.6	230.8	
12b	Et[g]	145.1	127.4	128.9	124.7	132.1	127.7	125.6	123.9	127.6	130.5	230.2	
12c	Me[h]	146.6	122.8	122.8	146.6	129.8	127.2	125.3	125.3	127.2	129.8	231.4	
13a	Me[i]	126.1	143.6	125.6	127.2	130.4	126.1	143.6	125.6	127.2	130.4		229.4

[a] 12.2 (SCH_2CH_3), 31.9 (SCH_2CH_3).
[b] 11.6 (SCH_2CH_3), 20.9 (3-CH_3), 31.2 (SCH_2CH_3).
[c] 20.7 (3-SCH_3), 21.0 (1-SCH_3).
[d] 20.7 (sep, $^1J_{CD} = 22.5$, 3-SCD_3), 21.0 (sep, $^1J_{CD} = 22.5$, 1-SCD_3).
[e] 33.6 (CS-SCH_2Ph), 42.6 (CO-SCH_2Ph), C_{Ph}: 127.5, 128.7 (2 C), 128.9, 129.3, 129.6, 130.2, 133.0.
[f] 21.1 (CH_3).
[g] 12.1 (SCH_2CH_3), 31.9 (SCH_2CH_3).
[h] 21.0 (SCH_3).
[i] 20.8 (SCH_3).

pH 1 with conc. HCl, and extracted with 1,2-dichloroethane. The organic phase was washed subsequently with H_2O, aqu. NaOH (2×) and H_2O (→ pH 7), and dried over K_2CO_3. Removal of the solvent and fractionating distillation gave 1-acetyl-3-*tert*-butylnaphthalene (**14**), 19.9 g, 51%) as a colorless liquid, bp 126–133°C. IR: ν(C=O) 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.44 [s, 9 H, $C(CH_3)_3$], 2.75 (s, 3 H, SCH_3), 7.47 (ddd, 1 H, 6-H), 7.53 (ddd, 1 H, 7-H), 7.82 (dd, 1 H, 5-H), 7.90 (d, 1 H, 4-H), 7.99 (d, 1 H, 2-H), 8.61 (dd, 1 H, 8-H). $^4J_{H2,H4} = 1.7$, $^3J_{H5,H6} = 7.8$, $^4J_{H5,H7} = 1.7$, $^3J_{H6,H7} = 7.8$, $^3J_{H7,H8} = 8.6$, $^4J_{H6,H8} = 1.7$. $C_8H_{18}O$ (226.32), calcd. C 84.91, H 8.02; found C 85.02, H 7.80. This ketone (9.06 g, 40.0 mmol) and I_2 (5.10 g, 20.1 mmol) were heated to 100°C for 30 min in dry pyridine (20 mL) and then left at 20°C for 12 h. The mixture was filtered with suction, and the solid was washed with cooled (−28°C) MeOH and recrystallized from EtOH to yield N-[2-(3-*tert*-butyl-1-naphthyl)-2-oxoethyl]pyridinium iodide (**15**, 6.93 g, 40%), mp 249–250°C. IR: ν(C=O) 1747 cm^{-1}. ^1H NMR (DMSO-d_6, 60 Mz): δ 1.57 [s, 9 H, $C(CH_3)_3$], 2.27 (d, 1 H, CH_2), 2.52 (d, 1 H, CH_2), 6.90 (s, 1 H, 4-H), 7.65–7.85 (m, 2 H, 6/7-H), 8.1–8.9 (m, 7 H, 2/5-H, PyH), 9.38 (d, 1 H, 8-H). $^2J_{CH2} = 13$, $^3J_{H7,H8} = 6$. $C_{21}H_{22}ION$ (431.31), calcd. C 58.48, H 5.14, I 29.42, N 3.25; found C 58.35, H 5.19, I 29.91, N 2.93. **15** (5.00 g, 11.6 mmol) was heated to reflux for 1 h in a solution of NaOH (3.00 g, 50 mL EtOH, 50 mL H_2O). The solution was acidified to pH 1 with dil. HCl. Filtration gave 3-*tert*-butyl-1-naphthoic acid (**16**, 2.40 g, 26%), mp 161–162°C (EtOH). IR: ν(C=O) 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.47 [s, 9 H $C(CH_3)_3$], 7.50–7.85 (m, 3 H, 5/6/7-H), 8.04 (d, 1 H, 4-H), 8.64 (d, 1 H, 2-H), 9.15 (d, 1 H, 8-H), 13.0 (bs, 1 H, OH). $^4J_{H2,H4} = 2.0$, $^3J_{H7,H8} = 8.6$. $C_{15}H_{16}O_2$ (228.29), calcd. C 78.92, H 7.06; found C 79.10, H 7.04. **16** (1.60 g, 7.01 mmol) was heated to 80°C in chlorobenzene (7 mL). 2,4-Bis(methylsulfanyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide ("Davy's reagent" (**DR**),[35] 1.10 g, 3.90 mmol) was added. The solution was refluxed for 10 min and then heated to 80°C for 90 min. The solvent was removed. CC of the residue (1. PE, 2. hexane) and recrystallization from EtOH gave **9d** (0.88 g, 49%) as red crystals, mp 58–59°C. IR: ν(C=S) 1247 cm^{-1}.

Table XI Elemental analyses and mass spectra of thionesters and dithioesters

Compound	Elemental formulae Calcd.: C, H, S Found: C, H, S	Mass spectra *m/z* (% relative intensity) [assignment]
1a	$C_{12}H_{10}OS$ (202.3) 71.25, 4.98, 15.85 70.89, 5.05, 16.09	202 (95) [M^+], 187 (54) [$M^+ - CH_3$], 171 (68) [$M^+ - OCH_3$], 159 (100) [$C_{10}H_7S^+$], 155 (25) [$C_{10}H_7CO^+$], 127 (62) [$C_{10}H_7^+$], 115 (48) [$C_9H_7^+$]
1b	$C_{13}H_{12}OS$ (216.3) 72.19, 5.59, 14.82 72.60, 5.52, 13.74	216 (55) [M^+], 187 (54) [$M^+ - C_2H_5$], 172 (19) [$M^+ - OC_2H_4$], 171 (100) [$M^+ - OC_2H_5$], 159 (43) [$C_{10}H_7S^+$], 155 (46) [$C_{10}H_7CO^+$], 127 (83), [$C_{10}H_7^+$], 115 (28) [$C_9H_7^+$]
1c	$C_{14}H_{14}OS$ (230.3) 73.01, 6.13, 13.92 72.76, 6.24, 13.95	230 (51) [M^+], 188 (53) [$M^+ - C_3H_6$], 187 (73) [$M^+ - C_3H_7$], 171 (56) [$M^+ - OC_3H_7$], 159 (10) [$C_{10}H_7S^+$], 155 (100) [$C_{10}H_7CO^+$], 127 (88) [$C_{10}H_7^+$], 115 (22) [$C_9H_7^+$], 101 (7) [$C_8H_5^+$], 77 (15) [$C_6H_5^+$]
2a	$C_{12}H_{10}OS$ (202.3) 71.25, 4.98, 15.85 70.99, 4.88, 16.06	202 (67) [M^+], 171 (100) [$M^+ - OCH_3$], 155 (10) [$C_{10}H_7CO^+$], 141 (23), 127 (62) [$C_{10}H_7^+$], 115 (13) [$C_9H_7^+$]
2b	$C_{13}H_{12}OS$ (216.3) 72.19, 5.59, 14.82 71.62, 5.52, 15.04	216 (52) [M^+], 200 (10), 188 (6) [$M^+ - C_2H_4$], 172 (39) [$M^+ - OC_2H_4$], 171 (100) [$M^+ - OC_2H_5$], 155 (89) [$C_{10}H_7CO^+$], 127 (84) [$C_{10}H_7^+$], 115 (11) [$C_9H_7^+$]
2c	$C_{14}H_{14}OS$ (230.3) 73.01, 6.13, 13.92 72.64, 6.53, 13.80	230 (33) [M^+], 197 (10), 188 (16) [$M^+ - C_3H_6$], 187 (12) [$M^+ - C_3H_7$], 172 (32) [$M^+ - OC_3H_6$], 171 (36) [$M^+ - OC_3H_7$], 155 (100) [$C_{10}H_7CO^+$], 127 (88) [$C_{10}H_7^+$], 115 (10) [$C_9H_7^+$], 101 (5) [$C_8H_5^+$], 77 (8) [$C_6H_5^+$]
3b	$C_{24}H_{26}O_2S_2$ (400.5) 71.97, 4.03, 16.01 71.35, 4.01, 16.66	307 (39) [$M^+ - OC_6H_5$], 291 (30) [$M^+ - SC_6H_5$], 214 (100) [$M^+ - 2\ OC_6H_5$], 198 (8), 170 (86) [$C_{10}H_6CS^+$], 169 (20), 126 (20) [$C_{10}H_6^+$][a]
4a	$C_{18}H_{20}O_3S$ (316.4) 68.33, 6.37, 10.13 68.55, 6.51, 10.16	316 (11) [M^+], 257 (10) [$M^+ - OC_3H_7$], 241 (22) [$M^+ - C_3H_6S$], 231 (20), 215 (26) [$C_{12}H_7O_2S^+$], 199 (38) [$C_{12}H_7OS^+$], 187 (100) [$C_{11}H_7OS^+$], 171 (21) [$C_{11}H_7S^+$], 154 (18) [$C_{11}H_6O^+$], 126 (23) [$C_{10}H_6^+$], 115 (31) [$C_9H_7^+$]
5	$C_{14}H_{12}O_2S_2$ (276.4) 60.84, 4.38, 23.20 59.00[b], 4.41, 22.66	276 (1) [M^+], 245 (1) [$M^+ - OCH_3$], 212 (4) [$M^+ - S_2$], 201 (100) [$M^+ - CSOCH_3$], 186 (46) [$C_{11}H_{10}OS^+$], 158 (14) [$C_{10}H_6S^+$], 154 (10) [$C_{11}H_6O^+$], 126 (14) [$M^+ - 2\ CSOCH_3$]
7a	$C_{14}H_{12}O_3S$ (260.3) 64.60, 4.65, 12.32 64.66, 4.47, 12.34	260 (88) [M^+], 228 (100) [$M^+ - CH_3OH$], 199 (29) [$C_{12}H_7OS^+$], 168 (29), 138 (14), 126 (22) [$M^+ - CO_2CH_3 - CSOCH_3$]
7b	$C_{14}H_{12}O_2S$ (276.4) 60.84, 4.38, 23.20 60.47, 4.32, 23.14	276 (100) [M^+], 245 (60) [$M^+ - OCH_3$], 215 (30) [$C_{12}H_7S_2^+$], 171 (14) [$C_{11}H_7S^+$], 170 (56) [$C_{11}H_6S^+$], 169 (12), 158 (8) [$C_{10}H_6S^+$], 154 (6) [$C_{11}H_6O^+$], 126 (17) [$M^+ - 2\ CSOCH_3$], 107 (18)
7c	$C_{18}H_{20}O_2S_2$ (332.5) 65.02, 6.06, 19.29 64.80, 6.16, 18.76	MS not recorded
8a	$C_{18}H_{20}O_3S$ (316.4) 68.33, 6.37, 10.13 68.10, 6.85, 10.01	MS not recorded
8b	$C_{18}H_{20}O_2S_2$ (332.5) 65.02, 6.06, 19.29 65.22, 6.46, 18.45	MS not recorded
9c	$C_{13}H_{12}S_2$ (232.4) no analysis	232 (30) [M^+], 203 (15) [$M^+ - C_2H_5$], 171 (100) [$M^+ - SC_2H_5$], 127 (27) [$M^+ - CS_2C_2H_5$]
9d	$C_{16}H_{18}S_2$ (274.5) 70.02, 6.61, 23.37 70.24, 6.59, 23.24	MS not recorded

Table XI Elemental analyses and mass spectra of thionesters and dithioesters *(Continued)*

Compound	Elemental Formulae Calcd.: C, H, S Found: C, H, S	Mass spectra *m/z* (% relative intensity) [assignment]
9e	$C_{14}H_{14}S_2$ (246.4) 68.24, 5.73, 26.03 68.35, 5.84, 25.81	246 (28) [M^+], 217 (17) [$M^+ - C_2H_5$], 185 (100) [$M^+ - SC_2H_5$], 139 (12)
11a	$C_{14}H_{12}S_4$ (308.5) 54.50, 3.92, 41.57 54.67, 4.01, 40.53	308 (55) [M^+], 261 (100) [$M^+ - SMe$], 214 (21) [$M^+ - 2\ SMe$], 170 (34) [$M^+ - SMe - CS_2Me$], 126 (21), [$M^+ - 2\ CS_2Me$]
11b	$C_{14}H_6D_6S_4$ (314.6) 53.46, 1.92[c], 40.65 53.37, 1.81, 40.82	314 (56) [M^+], 264 (100) [$M^+ - SCD_3$], 245 (14) [$M^+ - CD_3 - SCD_3$], 214 (21) [M+ − 2 SCD_3], 170 (34) [$M^+ - SCD_3 - CS_2CD_3$], 126 (21), [$M^+ - 2\ CS_2CD_3$]
11c	$C_{26}H_{20}OS_3$ (444.64) 70.23, 4.53, 21.64 69.12, 4.53, 21.86	321 (45) [$M^+ - SCH_2C_6H_5$], 305 (5), 170 (23) [$C_{10}H_6CS$], 154 ($C_{10}H_6CO$), 126 (18) [$C_{10}H_6$], 91 (100), [$C_7H_7{}^+$]
12a	$C_{12}H_9BrS_2$ (297.2) 48.49, 3.05, 21.58[d]48.65, 2.90, 21.57	298/296 (39/37) [M^+], 251/249 (100) [$M^+ - SCH_3$], 170 (53) [$M^+ - SCH_3 - Br$], 126 (71) [$M^+ - CS_2CH_3 - Br$]
12b	$C_{13}H_{11}BrS_2$ (311.3) 50.16, 3.56, 20.60[e] 50.15, 3.47, 20.67	312/310 (35/33) [M^+], 283/281 (12/11) [$M^+ - C_2H_5$], 251/249 (100/95) [$M^+ - SC_2H_5$], 170 (51), [$M^+ - SC_2H_5 - Br$], 126 (56) [$M^+ - CS_2C_2H_5 - Br$]
12c	$C_{14}H_{12}S_4$ (308.5) 54.50, 3.92, 41.57 54.04, 3.85, 41.78	308 (38) [M^+], 261 (32) [$M^+ - SMe$], 245 (26), 214 (100) [$M^+ - 2\ SMe$], 170 (77) [$M^+ - SMe - CS_2Me$], 126 (34) [$M^+ - 2\ CS_2Me$]
13a	$C_{14}H_{12}S_4$ (308.5) 54.50, 3.92, 41.57 54.40, 4.02, 41.50	MS not recorded
13b	$C_{16}H_{16}S_4$ (336.5) 57.10; 4.79; 38.11 56.92; 5.13; 34.43[b]	MS not recorded

[a]CI-MS: 401 (100) [$M^+ + 1$], 307 (10) [$M^+ - OC_6H_5$], 291 (9) [$M^+ - SC_6H_5$], 214 (8) [$M^+ - 2\ OC_6H_5$].
[b]The deviating analyses are due to impurities that could not be completely removed.
[c]D: Calcd. 3.83, found 3.61.
[d]Br: Calcd. 26.88, found 26.67.
[e]Br: Calcd. 25.67, found 25.62.

Ethyl 3-Methylnaphthalene-1-carbodithioate (9e)

Compound **9e** was obtained as described for **11a** (see below) from the 1-bromomethyl-3-methylnaphthalene (0.091 g, 0.39 mmol), which was present as impurity (^{1}H NMR spectrum) in 1,3-bis(bromomethyl)naphthalene (4.00 g, 12.7 mmol) and EtI (12.0 g, 76.0 mmol). Yield: 0.065 g (68%), orange crystals, mp 56–57°C. IR: ν(C═S) 1237 cm^{-1}.

Dimethyl Naphthalene-1,3-bis-carbodithioate (11a)

1,3-Bis(bromomethyl)naphthalene[55] (2.00 g, 6.37 mmol) and S_8 (1.28 g, 40.0 mmol) were added to a NaOMe solution (1.00 g Na in 20 mL dry MeOH). The reaction mixture was heated to reflux for 4 h. The red-brown solution was cooled and mixed with ice (30 g). MeI (4.30 g, 30.3 mmol) was added slowly with a pipette. After stirring at 20°C for 1 h,

H_2O was added, and the solution was extracted with diethyl ether. The extract was dried over Na_2SO_4, the solvent was removed, and the residue was purified by CC (PE:EtOAc 9:1) and recrystallization (PE) to yield **11a** (0.175 g, 9%) as a light red powder, mp 81–82°C. IR: ν(C=S) 1232 cm^{-1}.

Bis-trideuteromethyl Naphthalene-1,3-bis-carbodithioate (11b)

Compound **11b** was prepared and purified as described for **11a** except by using CD_3I instead of MeI. Yield: 0.20 g (10%), mp 79–80°C. IR: ν(C=S) 1232 cm^{-1}.

O-Benzyl 1-Benzylthio-thiocarbonyl-naphthalene-3-carbothioate (11c)

Compound **11c** was prepared and purified as described for **11a** by use of $PhCH_2Br$ instead of MeI. Yield: 0.10 g (3%), orange needles, mp 110–111°C. IR: ν(C=S) 1237, ν(C=O) 1657 cm^{-1}.

Methyl 4-Bromonaphthalene-1-carbodithioate (12a)

An etheral solution of nBuLi (18.3 mL, 29.0 mmol) was dropped into a solution of 1,4-dibromonaphthalene[56] (3.50 g, 12.2 mmol) in diethyl ether at −10°C. A yellow precipitate formed, and the suspension was stirred at 20°C for 1 h. After cooling to −15°C, CS_2 (4.0 g, 53 mmol) was dropped in. The brown colored reaction mixture was warmed up to 20°C within 3 h. Ice (35 g) and then MeI (5.0 g, 35 mmol) were added, and the solution was rapidly stirred for 1 h. It was then diluted with H_2O and extracted with diethyl ether. The extract was dried over Na_2SO_4, and the solvent was removed. Purification by CC (PE:EtOAc 9:1) and recrystallization from PE gave **12a** (0.83 g, 22%), orange crystals, mp 72°C. IR: ν(C=S) 1202 cm^{-1}.

Ethyl 4-Bromonaphthalene-1-carbodithioate (12b)

Compound **12b** was prepared as described for **12a** from 1,4-dibromonaphthalene[56] (2.0 g, 7.0 mmol) by use of EtI (5.0 g, 28 mmol) instead of MeI. CC (PE:EtOAc 40:1) and recrystallization from PE gave **12b** (0.125 g, 6%), orange crystals, mp 42°C. IR: ν(C=S) 1200 cm^{-1}.

Dimethyl Naphthalene-1,4-bis-carbodithioate (12c)

Compound **12c** was prepared and purified as described for **11a** from 1,4-bis(bromomethyl)naphthalene[57] (1.10 g, 3.50 mmol), S_8 (0.47 g, 15.0 mmol), NaOMe (0.40 g, 17.0 mmol Na in 10 mL MeOH), and MeI (2.00 g, 14.1 mmol). Yield: 0.075 g (7%), light red powder, mp 95°C. IR: ν(C=S) 1245 cm^{-1}.

Dimethyl Naphthalene-2,6-bis-carbodithioate (13a)

Compound **13a** was prepared and purified as described for **11a** from 2,6-bis(bromomethyl)naphthalene[58] (1.10 g, 3.50 mmol), S_8 (0.47 g, 15.0 mmol), NaOMe (0.40 g, 17.0 mmol Na in 10 mL MeOH), and MeI (2.00 g, 14.1 mmol). Yield: 0.375 g (35%), red crystals, mp 188°C (toluene). IR: ν(C=S) 1238 cm^{-1}.

Diethyl Naphthalene-2,6-bis-carbodithioate (13b)

Compound **13b** was prepared and purified as described for **11a** from 2,6-bis(bromomethyl)naphthalene[58] (3.14 g, 10.0 mmol), S_8 (1.28 g, 40.0 mmol), NaOEt (1.80 g, 78.0 mmol Na in 35 mL EtOH), and EtI (20.1 g, 128 mmol) instead of MeI. Yield: 0.80 g (24%), red crystals, mp 120–121°C (toluene). IR: ν(C=S) 1238 cm^{-1}.

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