Synthesis and Reactions of Thioether–Thiolate Compounds of 1,3-Dithiole-2-thione-4,5-dithiolate (dmit)

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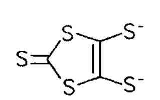
An efficient method for the preparation of the unsymmetrically substituted 1,3-dithiole-2-thione-4,5-dithiolate (dmit) is reported. Its application is demonstrated by obtainment of various 1,3-dithiole-2-thione-4-thiolate-5-thioesters and ethers. Starting from these compounds an expedient route to novel unsymmetrical crown compounds and tetrathiafulvalenes is shown.

The potential of the 1,3-dithiole-2-thione-4,5-dithiolate (dmit)[1,2] system (**1**) as a starting material in syntheses of molecular metals is well documented.[3–8] Whereas the unstable alkali metal salts of the dianionic dmit have been widely employed in synthesis, surprisingly, no procedure for generation of stable monosubstituted, monoanionic dmit compounds had been devised until now. Suitable monoanionic dmit derivatives might be advantageously employed as building blocks in the synthesis of, for example, crown compounds, tetrathiafulvalenes and bioinorganic model compounds.

These considerations led us to reinforce our studies in preparing these novel dmit derivatives.

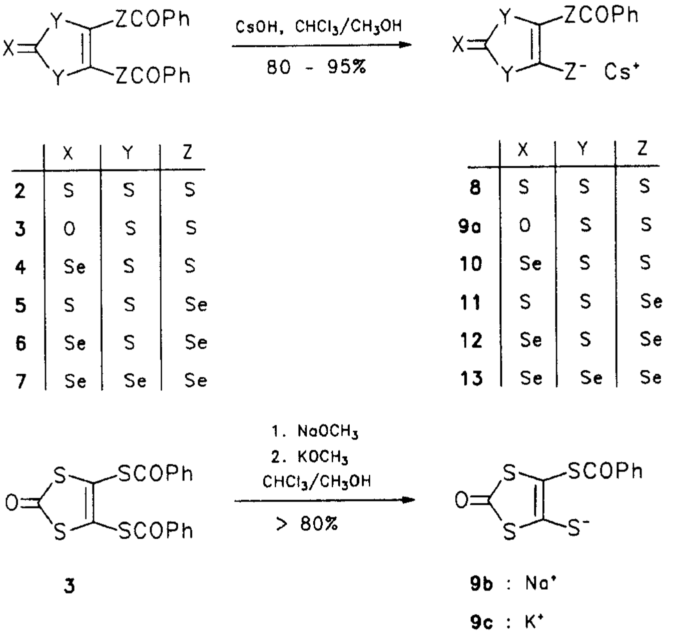


1 dmit

We report herein of an efficient method to prepare stable monoanionic alkali metal salts of dmit and its isologues dmid (1,3-dithiole-2-one-4,5-dithiolate), dmise (1,3-dithiole-2-selone-4,5-dithiolate), dsit (1,3-dithiole-2-thione-4,5-diselenolate), dsise (1,3-dithiole-2-selone-4,5-diselenolate) and dsis (1,3-diselenole-2-selone-4,5-diselenolate) via their bisbenzoyl derivatives **2**,[1,2] **3**,[9] **4**,[10] **5**,[11] **6**,[12] and **7**,[13] respectively.

Generation of the monoanionic derivatives **8–13** is achieved by ester cleavage of **2–7** in chloroform using half an equivalent of alkali metal hydroxide, preferably caesium hydroxide (Scheme 1). The resulting caesium salts are precipitated in almost quantitative yield. These monoalkali metal salts are notably more air- and moisture-stable, as shown with compound **9** (**a**: Cs^+, **b**: Na^+, **c**: K^+), than the corresponding disodium or dipotassium salts. Only a similar relative stability in the dicaesium salt of **1** has been noted previously.[14] It should also be noted that stability differences between the salts **8–13** are observable. This depends on the chalcogen atom X, and the air- and moisture-stability of the prepared salts (Schemes 1 and 3) which increases in the order O (**9a–9c**, **22**), Se (**10**, **12**, **13**), S (**8**, **21**).

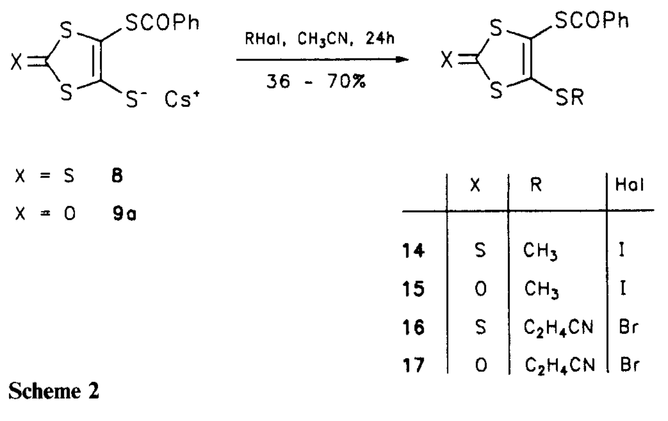
In order to study various applications of these novel salts we focused our efforts upon the thiolates **8** and **9a**. Reaction of **8** or **9** with alkylating reagents such as methyl iodide or 3-bromopropionitrile[15] affords the thioether compounds **14–17** (Scheme 2).



	X	Y	Z
2	S	S	S
3	O	S	S
4	Se	S	S
5	S	S	Se
6	Se	S	Se
7	Se	Se	Se

	X	Y	Z
8	S	S	S
9a	O	S	S
10	Se	S	S
11	S	S	Se
12	Se	S	Se
13	Se	Se	Se

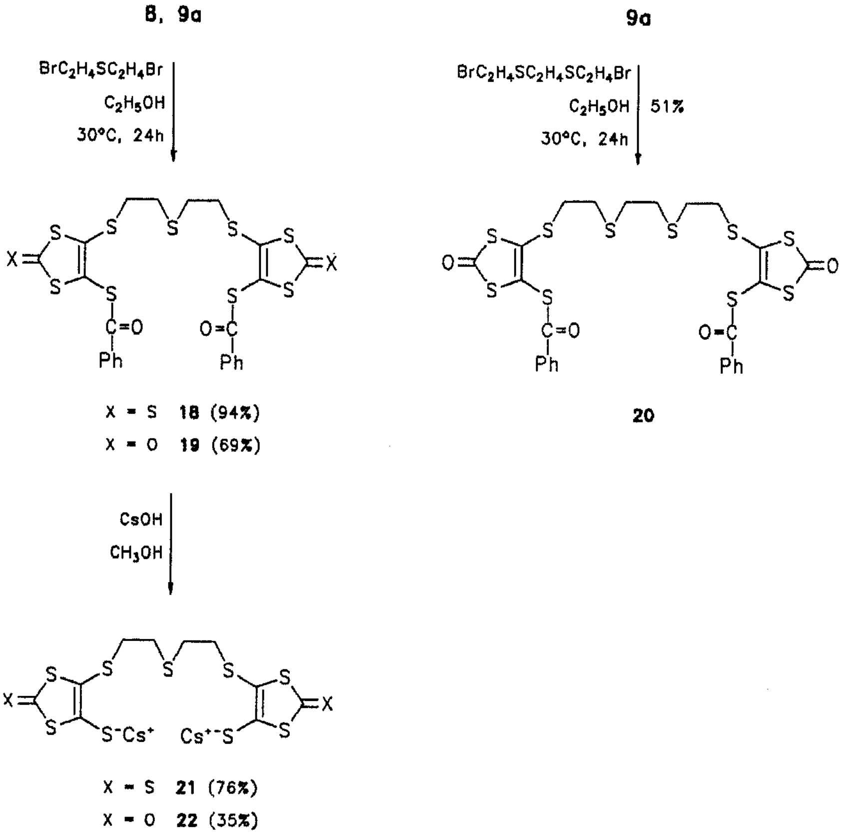
Scheme 1



	X	R	Hal
14	S	CH_3	I
15	O	CH_3	I
16	S	C_2H_4CN	Br
17	O	C_2H_4CN	Br

Scheme 2

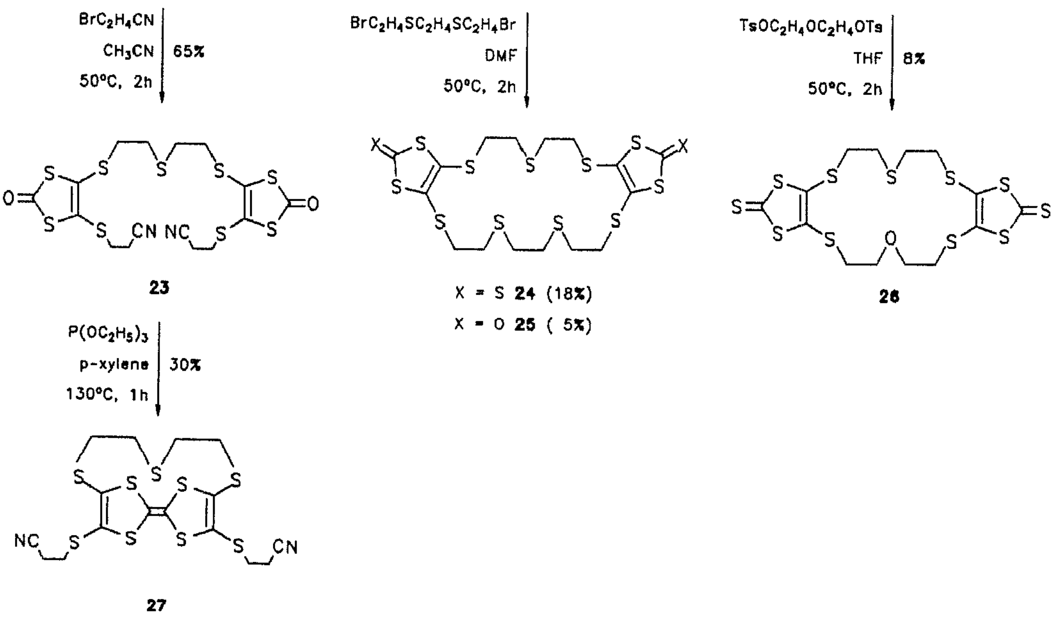
The reaction of ethylene dibromide with the thiolate **8** was expected to take place in a similar manner, the anticipated major product being two ethylene bridged dmit. However, the yellow product which was actually isolated in ca. 80% yield from this reaction, was a one-to-one mixture of the parent compound **2** and 4,5-ethylenedithio-1,3-dithiole-2-thione. Addition of alkyl dihalogenides such as 1,5-dibromo-3-thiapentane to an ethanolic solution of **8** or **9a** resulted in the formation of **18** and **19** (**20** from reaction of **9a** with 1,8-dibromo-3,5-dithiaoctane). Treatment of chloroformic solutions of **18** and **19** with caesium hydroxide in methanol smoothly furnished **21** and **22** respectively, in high yield (Scheme 3). Because of their solubilities in water, methanol, ethanol, and acetonitrile, and reactivities the caesium salts **21** and **22** are novel building blocks for the preparation of, for instance, crown ethers[7,8] and bioinorganic model compounds.[16]



Scheme 3

To demonstrate that the latter salts are convenient precursors for the synthesis of a great variety of unsymmetrical tetrasubstituted tetrathiafulvalenes, we have studied their reactions with mono- and dialkylating reagents. Scheme 4 shows the compounds obtained, **23**–**26**. Finally, the novel tetrathiafulvalene derivative **27** was prepared via standard triethylphosphite self coupling of **23** in refluxing *p*-xylene.

In conclusion, starting from the monoalkali metal salts (Scheme 1) an expedient route to new crown compounds and tetrathiafulvalenes (Scheme 4) has been developed. An application of tetrathiafulvalene **27** in the synthesis of oligomers of tetrathiafulvalenes appears promising by cleavage of the cyanoethyl substituent.[15]



Scheme 4

Microanalyses were performed at the Microanalytical Lab., University of Leipzig. IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, NMR spectra on a Varian GEMINI 300 spectrometer and mass spectra on a V6-12-250 GC-MS (Fa. V6 MASS-LAB) spectrometer. The synthetic procedures for the parent benzoyl compounds **2–7** were adopted from the literature.[1,2,9–13] All reactions were carried out under inert atmosphere (Ar).

Monocaesium Salts 8, 9a, 10–13; General Procedure:

To a stirred solution of the corresponding bisbenzoyl compound **2–7** (1 mmol) in $CHCl_3$ (10 mL) was added caesium hydroxide hydrate (0.17 g, 1 mmol) in MeOH (2 mL). After about 1 min the 4-benzoylchalcogeno-1,3-dichalcogenole-2-chalcogenone-5-chalcogenolate **8, 9a, 10–13** starts to separate. Et_2O (30 mL) was added to precipitate the product completely. The solid monocaesium salt was recovered by filtration, washed with Et_2O and air dried. Crystallization from MeOH/Et_2O (**12** and **13** from CH_3CN/Et_2O) gave pure samples.

Caesium 4-benzoylthio-1,3-dithiole-2-thione-5-thiolate (**8**): shiny golden solid; yield: 415 mg (96%).

$C_{10}H_5OS_5Cs$	calc.	C 27.69	H 1.15	S 36.86
(434.38)	found	27.45	1.38	36.06

^{1}H NMR (CD_3OD/TMS): $\delta = 7.99$ (d, 2H), 7.67 (t, 1H), 7.53 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 215.8$, 191.6, 169.4, 137.5, 135.3, 130.2, 128.5, 110.4.

IR (KBr): $\nu = 1660$ (C=O), 1445 (C=C), 1380 (C=C), 1060 (C=S), 1025 (C=S) cm^{-1}.

Caesium 4-benzoylthio-1,3-dithiole-2-one-5-thiolate (**9a**): shiny pale yellow solid; yield: 360 mg (86%).

$C_{10}H_5O_2S_4Cs$	calc.	C 28.71	H 1.20	S 30.66
(418.32)	found	28.41	1.52	30.65

^{1}H NMR (CD_3OD/TMS): $\delta = 7.97$ (d, 2H), 7.65 (t, 1H), 7.51 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 196.3$, 192.2, 157.1, 137.6, 135.3, 130.2, 128.5, 99.9.

IR (KBr): $\nu = 1640$ (C=O), 1575 (C=O), 1420 (C=C), 1410 (C=C) cm^{-1}.

Caesium 4-benzoylthio-1,3-dithiole-2-selone-5-thiolate (**10**): orange solid; yield: 420 mg (87%).

$C_{10}H_5OS_4SeCs$	calc.	C 24.96	H1.05	S 26.65
(481.28)	found	24.53	1.35	26.14

^{1}H NMR (CD_3OD/TMS): $\delta = 8.19$ (d, 2H), 7.86 (t, 1H), 7.72 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 205.8$, 191.1, 175.0, 137.8, 135.5, 130.3, 128.8, 114.8.

IR (KBr): $\nu = 1645$ (C=O), 1430 (C=C), 1360 (C=C), 925 (C=Se) cm^{-1}.

Caesium 4-benzoylseleno-1,3-dithiole-2-thione-5-selenolate (**11**): orange solid; yield: 430 mg (81%).

$C_{10}H_5OS_3Se_2Cs$	calc.	C 22.74	H 0.95	S 18.21
(528.17)	found	22.32	1.19	18.79

^{1}H NMR (CD_3OD/TMS): $\delta = 7.90$ (d, 2H), 7.69 (t, 1H), 7.54 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 221.7$, 194.7, 169.5, 139.2, 135.8, 130.6, 128.4, 123.9.

IR (KBr): $\nu = 1655$ (C=O), 1430 (C=C), 1400 (C=C), 1015 (C=S), 1035 (C=S) cm^{-1}.

Caesium 4-benzoylseleno-1,3-dithiole-2-selone-5-selenolate (**12**): red solid; yield: 460 mg (80%).

$C_{10}H_5OS_2Se_3Cs$	calc.	C 20.89	H 0.88	S 11.15
(575.07)	found	20.29	1.05	11.66

^{1}H NMR (DMSO-d_6/TMS): $\delta = 7.88$ (d, 2H), 7.42–7.29 (m, 3H).

^{13}C NMR (DMF-d_7/TMS): $\delta = 208.2$, 195.2, 171.4, 140.3, 136.6, 131.7, 129.1, 128.8.

IR (KBr): $\nu = 1650$ (C=O), 1425 (C=C), 1375 (C=C), 945 (C=Se); 925 (C=Se) cm^{-1}.

Caesium 4-benzoylseleno-1,3-diselenole-2-selone-5-selenolate (**13**): red/violet solid sparingly soluble in CH_3CN and DMF; yield: 600 mg (90%).

$C_{10}H_5OSe_5Cs$	calc.	C 17.96	H 0.75
(668.85)	found	17.02	0.88

^{1}H NMR (CD_3CN/TMS): $\delta = 8.01$ (d, 2H), 7.75 (t, 1H), 7.60 (t, 2H).

IR (KBr): $\nu = 1650$ (C=O), 1420 (C=C), 1375 (C=C), 950 (C=Se) cm^{-1}.

Sodium and Potassium 4-Benzoylthio-1,3-dithiole-2-one-5-thiolate (9b and c); General Procedure:

The procedure is as described above for the preparation of the caesium salts, but using sodium or potassium methanolate (1 mmol) in methanol (1 mL) instead of caesium hydroxide hydrate in methanol.

Sodium 4-benzoylthio-1,3-dithiole-2-one-5-thiolate (**9b**): pale yellow solid; yield: 255 mg (83%).

$C_{10}H_5O_2S_4Na$	calc.	C 38.95	H 1.63	S 41.59
(308.40)	found	38.56	1.85	41.02

^{1}H NMR (CD_3OD/TMS): $\delta = 7.95$ (d, 2H), 7.64 (t, 1H), 7.50 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 196.6$, 192.1, 156.8, 137.6, 135.2, 130.1, 128.5, 100.1.

IR (KBr): $\nu = 1650$ (C=O), 1530 (C=O), 1430 (C=C), 1410 (C=C) cm^{-1}.

Potassium 4-benzoylthio-1,3-dithiole-2-one-5-thiolate (**9c**): yellow solid; yield: 280 mg (86%).

$C_{10}H_5O_2S_4K$	calc.	C 37.01	H 1.55	S 39.53
(324.51)	found	36.73	1.71	39.26

^{1}H NMR (CD_3OD/TMS): $\delta = 7.96$ (d, 2H), 7.65 (t, 1H), 7.51 (t, 2H).

^{13}C NMR (CD_3OD/TMS): $\delta = 196.5$, 192.2, 156.8, 137.7, 135.2, 130.1, 128.5, 100.0.

IR (KBr): $\nu = 1660$ (C=O), 1590 (C=O), 1445 (C=C), 1425 (C=C) cm^{-1}.

Thioethers 14–17; General Procedure:

To a well stirred solution of the corresponding monocaesium salt (10 mmol; **8**: 4.34 g, **9a**: 4.18 g) in CH_3CN (50 mL) was added dropwise the alkylating reagent (10 mmol; methyl iodide: 1.42 g, 3-bromopropionitrile: 1.33 g). The resulting mixture was stirred at r.t. for 24 h (methyl iodide), or for 2 h at 60 °C (3-bromopropionitrile), and evaporated to about 20 mL under reduced pressure. After filtration the residue was redissolved in CH_2Cl_2. Insoluble CsI was filtered off and the filtrate was refluxed with charcoal. Filtration followed by evaporation yielded products **14–17** as solids.

4-Benzoylthio-5-methylthio-1,3-dithiole-2-thione (**14**): yellow crystals; yield: 1.15 g (36%); mp 61–65 °C (CH_3CN).

$C_{11}H_8OS_5$	calc.	C 41.75	H 2.55	S 50.65
(316.48)	found	42.02	2.60	50.87

^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.97$ (d, 2H), 7.67 (t, 1H), 7.52 (t, 2H), 2.52 (s, 3H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 211.2$, 185.9, 146.4, 135.0, 134.8, 129.1, 127.9, 122.5, 19.4.

MS (EI): m/z (%) = 316 (M^+, 1), 226 (20), 150 (3), 135 (14), 106 (100), 105 (61).

IR (KBr): $\nu = 1670$ (C=O), 1435 (C=C), 1415 (C=C), 1055 (C=S), 1030 (C=S) cm^{-1}.

4-Benzoylthio-5-methylthio-1,3-dithiole-2-one (**15**): yellow oil; yield: 0.85 g (56%).

$C_{11}H_8O_2S_4$	calc.	C 43.97	H 2.68	S 42.69
(300.45)	found	43.34	2.42	42.17

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.98$ (d, 2H), 7.66 (t, 1H), 7.52 (t, 2H), 2.49 (s, 3H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 189.7$, 186.3, 137.8, 135.2, 134.7, 129.2, 127.9, 114.5, 19.4.

MS (EI): m/z (%) = 300 (M$^+$, 1), 210 (8), 182 (10), 135 (4), 118 (9), 105 (100).

IR (KBr): $\nu = 1670$ (C=O), 1616 (C=O), 1448 (C=C), 1428 (C=C) cm^{-1}.

4-Benzoylthio-5-cyanoethylthio-1,3-dithiole-2-thione **(16)**: pale yellow needles; yield: 2.47 g (70 %); mp 112–116 °C [toluene/petroleum ether (bp 80–100 °C)].

$C_{13}H_9NOS_5$	calc.	C 43.92	H 2.55	N 3.94	S 45.09
(355.55)	found	43.66	2.63	4.00	44.83

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.98$ (d, 2H), 7.69 (t, 1H), 7.49 (t, 2H), 3.11 (t, 2H), 2.75 (t, 2H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 210.7$, 186.1, 140.3, 135.1, 134.7, 131.4, 129.2, 128.1, 117.1, 32.2, 18.7.

MS (EI): m/z (%) = 355 (M$^+$, 3), 304 (< 1), 270 (< 1), 251 (< 1), 198 (< 1), 174 (2), 105 (100), 104 (58).

IR (KBr): $\nu = 2250$ (CN), 1680 (C=O), 1447 (C=C), 1424 (C=C), 1414 (C=C), 1058 (C=S), 1028 (C=S) cm^{-1}.

4-Benzoylthio-5-cyanoethylthio-1,3-dithiole-2-one **(17)**: pale yellow needles; yield: 2.10 g (62 %); mp 80–82 °C [toluene/petroleum ether (bp 80–100 °C)].

$C_{13}H_9NO_2S_4$	calc.	C 45.99	H 2.67	N 4.13	S 37.78
(339.48)	found	45.62	2.72	4.52	37.90

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.97$ (d, 2H), 7.67 (t, 1H), 7.52 (t, 2H), 3.08 (t, 2H), 2.73 (t, 2H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 188.6$, 186.4, 135.0, 134.9, 132.5, 129.2, 128.0, 123.0, 117.1, 32.0, 18.7.

MS (EI): m/z (%) = 339 (M$^+$, 30), 226 (28), 104 (85).

IR (KBr): $\nu = 2230$ (CN), 1660 (C=O), 1600 (C=O), 1438 (C=C), 1415 (C=C), 1400 (C=C) cm^{-1}.

Sulfides 18–20; General Procedure:

To a stirred solution of caesium 4-benzoylthio-1,3-dithiole-2-chalcogenone-5-thiolate (20 mmol; **8**: 8.68 g, **9a**: 8.36 g) in EtOH (400 mL) was added solid 1,5-dibromo-3-thiapentane[17] (2.48 g, 10 mmol) or 1,8-dibromo-3,6-dithiaoctane[17] (3.08 g, 10 mmol). After stirring at 30 °C for 24 h the reaction mixture was concentrated to 150 mL on a rotary evaporator. The resultant yellow precipitate **(18–20)** was collected by filtration, washed with H$_2$O (150 mL), MeOH (100 mL), and air dried.

2,2'-Bis(4-benzoylthio-1,3-dithiole-2-thione-5-thio)diethylsulfide **(18)**: yellow powder; yield: 6.5 g (94 %); mp 115–119 °C (CHCl$_3$/MeOH).

$C_{24}H_{18}O_2S_{11}$	calc.	C 41.71	H 2.63	O 4.63	S 51.04
(691.13)	found	41.46	2.65	5.30	51.95

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.97$ (d, 4H), 7.67 (t, 2H), 7.52 (t, 4H), 3.05 (m, AA'XX', $J_{AX} = 9$ Hz, $J_{AX'} = 6$ Hz, 4H), 2.80 (m, AA'XX', 4H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 211.1$, 186.1, 142.7, 135.0, 134.9, 129.2, 128.2, 128.0, 36.7, 32.1.

MS (EI): m/z (%) = 512 (< 1), 494 (< 1), 375 (< 1), 316 (< 1), 270 (2), 224 (1), 106 (100).

IR (KBr): $\nu = 1640$ (C=O), 1440 (C=C), 1405 (C=C), 1065 (C=S), 1020 (C=S) cm^{-1}.

2,2'-Bis(4-benzoylthio-1,3-dithiol-2-one-5-thio)diethylsulfide **(19)**: colorless solid; yield: 4.5 g (69 %); mp 104–109 °C (CHCl$_3$/MeOH).

$C_{24}H_{18}O_4S_9$	calc.	C 43.74	H 2.75	O 9.71	S 43.79
(658.95)	found	43.97	2.89	9.95	43.15

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.97$ (d, 4H), 7.66 (t, 2H), 7.52 (t, 4H, 3.02 (m, AA'XX', $J_{AX} = 9$ Hz, $J_{AX'} = 6$ Hz, 4H), 2.77 (m, AA'XX', 4H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 189.4$, 186.4, 135.1, 134.8, 134.5, 129.2, 127.9, 119.9, 36.5, 32.0.

MS (EI): m/z (%) = 454 (< 1), 390 (< 1), 300 (< 1), 240 (1), 208 (1), 105 (100), 104 (90).

IR (KBr): $\nu = 1680$–1600 (C=O), 1440 (C=C), 1420 (C=C) cm^{-1}.

1,8-Bis(4-benzoylthio-1,3-dithiole-2-one-5-thio)-3,6-dithiaoctane **(20)**: pale yellow solid; yield: 3.7 g (51 %); mp 102–104 °C (CHCl$_3$/MeOH).

$C_{26}H_{22}O_4S_{10}$	calc.	C 43.43	H 3.08	S 44.59
(719.12)	found	43.70	3.14	44.75

^{1}H NMR (CDCl$_3$/TMS): $\delta = 7.97$ (d, 4H), 7.66 (t, 2H), 7.52 (t, 4H), 3.05 (m, AA'XX', $J_{AX} = 10$ Hz, $J_{AX'} = 6$ Hz, 4H), 2.79 (m, AA'XX', 4H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 189.4$, 186.4, 135.2, 134.8, 134.7, 129.2, 128.0, 119.7, 36.7, 32.4, 32.1.

IR (KBr): $\nu = 1645$ (C=O), 1595 (C=O), 1435 (C=C), 1405 (C=C) cm^{-1}.

Sulfides 21 and 22; General Procedure:

To a stirred solution of the benzoyl compound **18** (1.38 g, 2 mmol) or **19** (1.35 g, 2 mmol) in CHCl$_3$ (50 mL) was added caesium hydroxide hydrate (0.68 g, 4 mmol) in MeOH (10 mL). After about 1 min the corresponding caesium salt starts to separate. Et$_2$O (30 mL) was added to precipitate the product completely. The solid product was recovered by filtration, washed with Et$_2$O and air dried.

Caesium 2,2'-bis(1,3-dithiole-2-thione-4-thiolato-5-thio)diethylsulfide **(21)**: recrystallization from MeOH/Et$_2$O gave an orange solid; yield: 1.13 g (76 %).

$C_{10}H_8S_{11}Cs_2$	calc.	C 16.09	H 1.08	S 47.24
(746.71)	found	16.29	1.25	46.58

^{1}H NMR (CD$_3$OD/TMS): $\delta = 3.26$ (m, AA'XX', $J_{AX} = 9$ Hz, $J_{AX'} = 6$ Hz, 4H), 3.04 (m, AA'XX', 4H).

^{13}C NMR (CD$_3$OD/TMS): $\delta = 215.0$, 166.1, 118.7, 36.6, 32.8.

IR (KBr): $\nu = 1400$ (C=C), 1055 (C=S), 1025 (C=S) cm^{-1}.

Caesium 2,2'-bis(1,3-dithiole-2-one-4-thiolato-5-thio)diethylsulfide **(22)**: shiny yellow, air- and moisture-sensitive solid; yield: 0.5 g (35 %). The instability of the solid hindered its characterization by microanalysis.

^{1}H NMR (CD$_3$OD/TMS): $\delta = 3.04$ (m, AA'XX', 4H), 2.85 (m, AA'XX', 4H).

^{13}C NMR (CD$_3$OD/TMS): $\delta = 196.3$, 152.7, 107.6, 36.7, 32.8.

IR (KBr): $\nu = 1645$ (C=O), 1590 (C=O), 1425 (C=C) cm^{-1}.

Sulfide 23 and Crown Thioethers 24–26; General Procedure:

To a well stirred solution of **18** (1.38 g, 2 mmol) or **19** (1.35 g, 2 mmol) in an organic solvent (30 mL; for **23**: CH$_3$CN; **24** and **25**: DMF; **26**: THF) was added caesium hydroxide hydrate (0.68 g, 4 mmol) in MeOH (4 mL). After stirring at r. t. for 10 min a solution of the corresponding alkylating reagent [for **23**: 3-bromopropionitrile (0.53 g, 4 mmol); **24** and **25**: 1,8-dibromo-3,6-dithiaoctane[17] (0.62 g, 2 mmol); **26**: diethylene glycol ditosylate (0.83 g, 2 mmol] in the same organic solvent (10 mL) was added dropwise over a 10 min period. The mixture was heated to 50 °C for 2 h with stirring and then allowed to cool to r.t. The following workup procedures yielded the desired products **23–26**.

2,2'-Bis(4-cyanoethylthio-1,3-dithiole-2-one-5-thio)diethylsulfide **(23)**: The crude mixture was reduced to half its volume and triturated with MeOH (20 mL). The precipitated solid was filtered, washed with MeOH, air dried and recrystallized from CHCl$_3$/MeOH to yield colorless **23**; yield: 0.73 g (65 %); mp 95–98 °C.

$C_{16}H_{16}N_2O_2S_9$	calc.	C 34.51	H 2.90	N 5.03	S 51.82
(556.91)	found	34.24	2.97	5.14	51.09

^{1}H NMR (CDCl$_3$/TMS): $\delta = 3.11$ (m, 8H), 2.87 (m, 4H), 2.76 (t, 4H).

^{13}C NMR (CDCl$_3$/TMS): $\delta = 188.3$, 130.8, 123.9, 117.3, 36.5, 32.2, 31.8, 18.9.

IR (KBr): $\nu = 2220$ (CN), 1640 (C=O), 1595 (C=O), 1410 (C=C) cm^{-1}.

2,5,8,10,12,14,17,20,23,25,27-Undecathiatricyclo[22.3.0.0^{9,13}]heptacosa-1(24),9(13)diene-11,26-dithione (**24**): The DMF solution was diluted with $CHCl_3$ (40 mL) and water (100 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layers were dried ($MgSO_4$), and evaporated to dryness. The residue was redissolved in $CHCl_3$ (10 mL) and separated by preparative layer chromatography (Merck silica gel 60 PF_{254}) using $CHCl_3$ as eluent. The top yellow band was extracted, giving the product as a yellow solid; yield: 0.23 g (18%); mp 123–125°C.

$C_{16}H_{20}S_{13}$	calc.	C 30.54	H 3.20	S 66.25
(629.19)	found	30.71	3.32	65.44

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.19–3.12$ (m, 8 H), 2.95–2.89 (m, 8 H), 2.83 (s, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 210.2$, 136.0, 36.7, 36.5, 32.7, 32.4, 32.3.

IR (KBr): $\nu = 1050$ (C=S), 1400 (C=C) cm^{-1}.

2,5,8,10,12,14,17,20,23,25,27-Undecathiatricyclo[22.3.0.0^{9,13}]heptacosa-1(24),9(13)diene-11,26-dione (**25**): A workup procedure identical to that for **24** afforded the pale yellow dione **25**; yield: 60 mg (5%); mp 112–115°C.

$C_{16}H_{20}O_2S_{11}$	calc.	C 32.19	H 3.38	S 59.08
(597.06)	found	32.13	3.08	60.08

^{1}H NMR ($CDCl_3$/TMS): $\delta = 2.85–2.78$ (m, 8 H), 2.69 (s, 4 H), 2.62–2.56 (m, 8 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 188.7$, 127.2, 126.9, 36.4, 36.3, 32.4, 32.05, 32.0.

IR (KBr): $\nu = 1645$ (C=O), 1590 (C=O), 1400 (C=C) cm^{-1}.

5-Oxa-2,8,10,12,14,17,20,22,24-nonathiatricyclo[19.3.0.0^{9,13}]tetracosa-1(21),9(13)-diene-11,23-dithione (**26**): The crude mixture was evaporated and the residue was extracted into $CHCl_3$ (10 mL). The residue from the $CHCl_3$ extract was preparative layer chromatographed on silica (Merck silica gel 60 PF_{254}), using $CHCl_3$ as eluent. The top yellow band was extracted, giving the product as a yellow solid; yield: 90 mg (8%); mp 192–194°C.

$C_{14}H_{16}OS_{11}$	calc.	C 30.41	H 2.92	S 63.78
(553.01)	found	29.93	2.74	63.09

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.75$ (t, 4 H), 3.13 (t, 4 H), 3.12 (t, 4 H), 2.89 (t, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 210.4$, 137.6, 135.2, 69.9, 36.7, 36.5, 32.3.

IR (KBr): $\nu = 1400$ (C=C), 1065 (C=S), 1045 (C=S), 1015 (C=S) cm^{-1}.

4,4′-Bis(2-cyanoethylthio)-5,5′-(3-thiapentyl-1,5-dithio)-[7]-tetrathiafulvalenophane (27):

To 2,2′-bis(4-cyanoethylthio-1,3-dithiole-2-one-5-thio)diethylsulfide (**23**) (1.11 g, 2 mmol) in *p*-xylene (20 mL) was added freshly distilled $P(OEt)_3$ (10 mL). After heating at 130°C for 1 h, the mixture was cooled to 20°C and MeOH (50 mL) was added. The resulting yellow precipitate was collected, washed with MeOH, and dried. The product was redissolved in $CHCl_3$ (10 mL) and separated by preparative layer chromatography (Merck silica gel 60 PF_{254}) using $CHCl_3$ as eluent. The top yellow band was extracted, giving the product as a yellow solid; yield: 310 mg (30%); mp 172–176°C.

$C_{16}H_{16}N_2S_9$	calc.	C 36.61	H 3.07	N 5.34	S 54.98
(553.01)	found	36.91	3.28	5.22	54.71

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.43–3.27$ (m, 4 H), 3.09 (dt, 2 H), 2.95–2.68 (m, 8 H), 2.59 (dt, 2 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 131.1$, 128.5, 128.2, 118.2, 38.9, 34.3, 31.4, 19.9.

IR (KBr): $\nu = 2215$ (CN), 1400 (C=C) cm^{-1}.

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