

Synthesis and Stereochemistry of Bis(dithiacrown ether) and Dodecylthio Substituted (*E*)-Thiodesaurines

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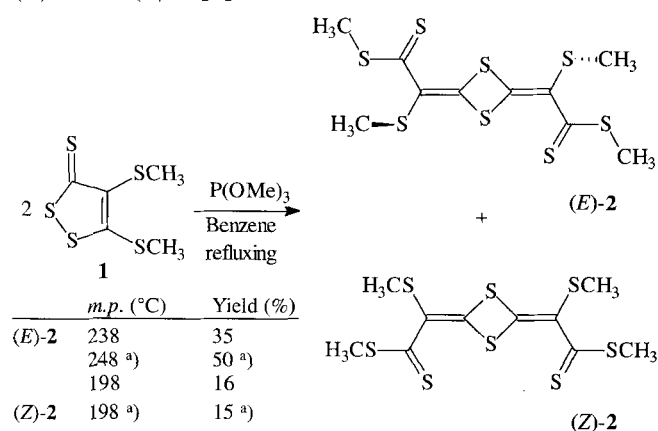
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Abstract. Reductive dimerization of dodecylthio substituted 1,2-dithiole-3-thiones **6a–b** and trithion-dithiacrown ethers **10a–c** with triethyl phosphite furnished bis- and tetrakis (dodecylthio), and bis(dithiacrown ether) substituted thiodes-

aurines (*E*)-**11a–b** and (*E*)-**12a–c**. The stereochemistry of bis(dithia[15]crown-5)-thiodesaurine (*E*)-**12b** has been determined by X-ray crystallographic analysis.

2,4-Bis-(2-oxo-ethylidene)-1,3-dithietane derivatives are well known as desaurines [1–3]. Thioxo-analogous desaurines which we would like to call thiodesaurines were unknown, until some years ago. Mollier *et al.* showed that 5-methylthio substituted 1,2-dithiole-3-thiones with trimethyl phosphite dimerize to yield 1,3-dithietane-2,4-diylidene-bis(methylthioacetate) derivatives [4]. Desulfurization of 4,5-bis(methylthio)-1,2-dithiole-3-thione (**1**) with trimethyl phosphite in refluxing benzene furnished the thiodesaurine 2,4-bis(3-thioxo-2,5-dithiahex-4-ylidene)-1,3-dithietane (**2**) (Scheme 1). Thiodesaurine **2** was produced, as a mixture of its geometrical isomers (*E*)-**2** and (*Z*)-**2** [4].

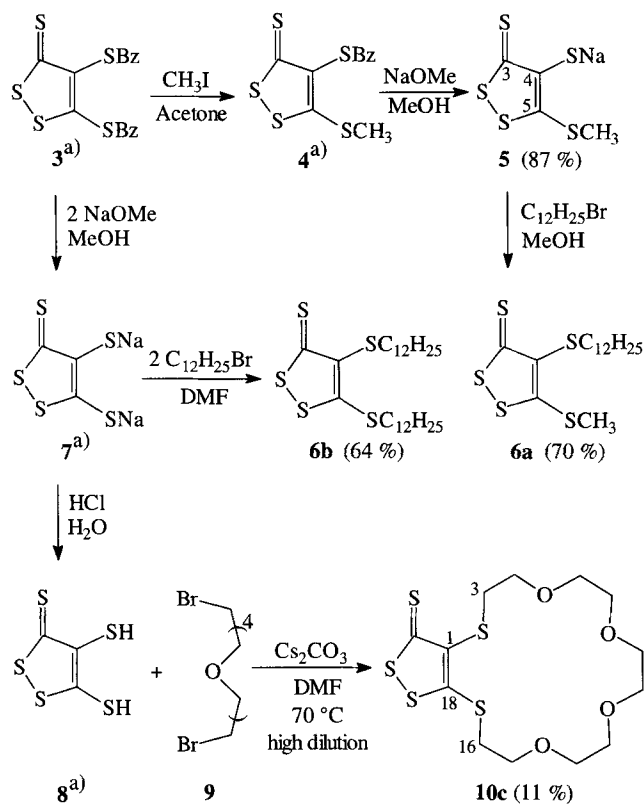


Scheme 1 Dimerization of 4,5-bis(methylthio)-1,2-dithiole-3-thione (**1**) [4]; ^{a)} Present work, reaction with P(OEt)₃ in *p*-xylene at 130 °C

Recently, we repeated the synthesis of **2** with triethyl phosphite in *p*-xylene, at 130 °C, and noticed comparable results (Scheme 1). The stereochemistry of (*E*)-**2** could be confirmed by X-ray crystallographic analysis [5]. (*E*)-**2** is an almost complete planar molecule. Only the methyl groups of the methylthio substituents at the C,C-double bonds are orientated approximately orthogonal to the molecule plane (compare stereo formula of (*E*)-**2** in Scheme 1). In an effort to use the plane (*E*)-thiodesaurine unit for new liquid crystalline compounds, we synthesized bis- and tetrakis(dodecylthio) substituted (*E*)-thiodesaurines. These molecules comprise a nearly flat sulphur-rich core connected with two and four long chain substituents. The tetrakis(dodecylthio) substituted (*E*)-thiodesaurine could be a new disc-shaped molecule [6]. In addition, we are interested in the complexing properties of thiodesaurines which could be useful as preorganized polydentate sulfur ligands. The tetrakis(methylthio) substituted thiodesaurines (*E*)-**2** and (*Z*)-**2** are not particularly useful for metal-complexation studies because they are only sparingly soluble in most solvents. Therefore, the chromatographical separation of (*E*)-**2** and (*Z*)-**2** is very time and material consuming. That's why we are looking for derivatives of 4,5-dithio-1,2-dithiole-3-thiones which permit the stereoselective synthesis of (*E*)- and (*Z*)-thiodesaurines and increase the solubility of thiodesaurines. Here, we wish to report the dimerization of dodecyl and of crowned 4,5-dithio-1,2-dithiole-3-thione derivatives by triethyl phosphite in *p*-xylene in high yields to well soluble (*E*)-thiodesaurines.

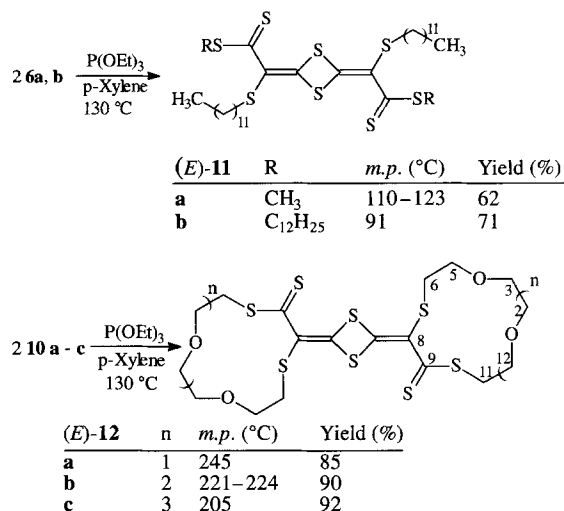
Results and Discussion

4-Dodecylthio-5-methylthio- and 4,5-bis(dodecylthio)-1,2-dithiole-3-thione (**6a**) and (**6b**), and trithion-dithia[18]crown-6 (**10c**) were prepared from 4,5-bis(benzoylthio)-1,2-dithiole-3-thione [7] (**3**), as shown in Scheme 2. For the synthesis of the unsymmetrically substituted 1,2-dithiole-3-thione **6a** 4-benzoylthio-5-methylthio-1,2-dithiole-3-thione (**4**) [7] was saponified to the thiolate **5** and then alkylated. The symmetrically substituted 1,2-dithiole-3-thione **6b** could be prepared by alkylation of dithiolate **7** [7]. **10c** was synthesized by the method we recently used for the preparation of trithion-dithia[12]crown-4 (**10a**) and trithion-dithia[15]crown-5 (**10b**) [8]. Cyclization of dimercaptane **8** [7] with dibromide **9**, in DMF, using caesium carbonate as base and high dilution, yielded **10c**.



Scheme 2 Synthesis of dodecylthio substituted 1,2-dithiole-3-thiones **6a–b** and trithion-dithiacrown ethers **10a–c**, a) Steimecke *et al.* [7]

Reaction of dodecylthio substituted 1,2-dithiole-3-thiones **6a–b** and trithion-dithiacrown ethers **10a–c** with five to six equiv. triethyl phosphite in *p*-xylene, at 130 °C, furnished, in any case, one dimerization product (Scheme 3). They were identified as thiodesaurines by the three characteristic ¹³C NMR signals of the thio-



Scheme 3 Dimerization of dodecylthio substituted 1,2-dithiole-3-thiones **6a–b** and trithion-dithiacrown ethers **10a–c**

Table 1 Characteristic ¹³C NMR data of the thiodesaurine unit in (*Z*)-**2**, (*E*)-**2**, (*E*)-**11a–b** and (*E*)-**12a–c**

Thiodesaurines	¹³ C NMR (CDCl ₃): δ (ppm)		
	CS ₂	C=CS ₂	C=S
(<i>Z</i>)- 2	165.1	132.5	211.8
(<i>E</i>)- 2	159.6	128.2	219.4
(<i>E</i>)- 11a	161.5	125.6	219.6
(<i>E</i>)- 11b	162.0	125.4	218.9
(<i>E</i>)- 12a	162.0	125.5	220.5
(<i>E</i>)- 12b	162.2	125.3	219.6
(<i>E</i>)- 12c	161.9	125.1	219.1

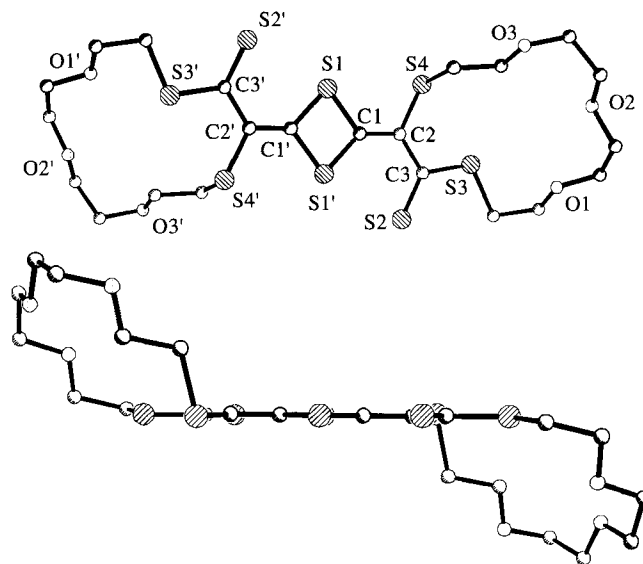


Fig. 1 Molecular structure of bis(dithia[15]crown-5)-thiodesaurine (*E*)-**12b** in the crystal is shown in two different views, above: vertical and below: parallel to the (*E*)-thio-desaurine unit

desaurine unit. Table 1 compares the corresponding ^{13}C NMR data of (*E*)-**2** and (*Z*)-**2** with those of bis- and tetrakis(dodecylthio) substituted thiodesaurines (*E*)-**11a–b** and bis(dithiacrown ether)thiodesaurines (*E*)-**12a–c**. (*E*)- and (*Z*)-**2** can be distinguished by their IR spectra [4]. The IR spectrum of the centrosymmetrical (*E*)-**2** shows fewer bands than that of its (*Z*)-isomer. Comparison of IR spectra of (*E*)-**11a–b** with that of (*E*)-**2** allows us to assume that dodecylthio substituted thiodesaurines exhibit (*E*)-stereochemistry. The stereochemistry of the bis(dithia[15]crown-5)-thiodesaurine (*E*)-**12b** has been determined by X-ray crystallographic analysis. As Figure 1 shows, both thioxo-dithiacrown ether rings are (*E*)-configured with respect to the 2,4-dimethylidene-1,3-dithietane unit. We conclude that the bis(dithiacrown ether)-thiodesaurines **12a** and **c** are (*E*)-configured, too, since their IR spectra are comparable with the spectrum of (*E*)-**12b**.

The bond lengths and angles of the (*E*)-thiodesaurine unit in (*E*)-**12b** are comparable with those in (*E*)-**2** [5]. As already observed for (*E*)-**2**, in (*E*)-**12b** the eight sulfur and the six central carbon atoms lie almost in a plane. In contrast, to the reductive dimerization of 4,5-bis(methylthio)-1,2-dithiole-3-thione (**1**) with triethyl phosphite which leads to an (*E*)/(*Z*)-thiodesaurine mixture, the dimerizations of dodecyl and crowned 4,5-dithio-1,2-dithiole-3-thiones derivatives, exclusively, yielded the (*E*)-isomers. These results could be explained by the greater sterical demand of the substituents in (*E*)-**11a–b** and (*E*)-**12a–c**, compared to those in **2** which should be better fulfilled in the (*E*)- than in the (*Z*)-thiodesaurines. For generalizing this assumption other 4,5-dithio-1,2-dithiole-3-thione derivatives than **1** which also have substituents with little steric demand as 9-thioxo-2,5,7,8-tetrathiabicyclo[4.3.0]non-1-en [9] and 10-thioxo-2,6,8,9-tetrathiabicyclo[5.3.0]-dec-1-en [9] with triethyl phosphite were reduced, however thiodesaurines were not formed. Instead mixtures of up to now unidentified products with smaller molecular masses than the expected thiodesaurines were isolated.

The thermal behaviour of bis(dodecylthio) and tetrakis(dodecylthio) thiodesaurine (*E*)-**11a–b** were investigated by polarising microscopy. Unfortunately, these compounds showed no liquid crystalline (mesogenic) properties.

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Experimental

All experiments were carried out under an atmosphere of dry, pure argon. Standard equipment was used throughout the experiments. Solvents were dried by conventional methods.

4,5-Bis(benzoylthio)-1,2-dithiole-3-thione (**3**) was synthesized according to Jakisch *et al.* [10]; disodium 1,2-dithiole-3-thione-4,5-dithiolate (**7**), 4,5-dimercapto-1,2-dithiole-3-thione (**8**) and 4-benzoylthio-5-methylthio-1,2-dithiole-3-thione (**4**) according to Steimecke *et al.* [7]. Trithion-dithia[12]crown-4 (**10a**) and trithion-dithia[15]crown-5 (**10b**) were prepared as recently reported [8].

Melting points: not corrected, hot-stage microscope. – IR: Nicolet 205 ET-IR. – UV/Vis: SPECORD M40 (Carl Zeiss Jena). – ^1H NMR and ^{13}C NMR: Bruker ARX 300. – MS: Finnigan MAT. – CC: Merck silica gel 60, 63–200 μm . – TLC: Merck silica gel 60. – The thermal behaviour of the thiodesaurines **11a–b** was investigated by polarising microscope (LEITZ, Laborlux 12 POL with Mettler heating stage FP 90) with rates of two K/min for heating and cooling.

Sodium 5-methylthio-1,2-dithiole-3-thione-4-thiolate (**5**)

To a suspension of 4-benzoylthio-5-methylthio-1,2-dithiole-3-thione (**4**) (0.4 g; 1.27 mmol) in methanol (4 ml), sodium (0.03 g; 1.3 mmol) in methanol (7 ml) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered into 80 ml of diethylether. The red sodium salt crystallized at 6 °C. Yield 0.26 g (87%) of red crystals. – IR (KBr): ν/cm^{-1} = 2970 (w), 2924 (w), 2902 (m), 1414 (w), 1363 (s), 1247 (s), 1230 (s), 1055 (w), 975 (w), 933 (m), 836 (m), 730 (w), 667 (w). – ^1H NMR (CH_3OD): δ/ppm = 2.76 (s, 3H, SCH_3). – ^{13}C NMR (CH_3OD): δ/ppm = 14.38 (SCH_3), 151.52 (C-4), 166.52 (C-5), 207.18 (C=S).

$\text{C}_4\text{H}_3\text{NaS}_5$ Calcd.: C 20.50 H 1.29 S 68.40
(234.35) Found: C 20.32 H 1.44 S 68.82.

4-Dodecylthio-5-methylthio-1,2-dithiole-3-thione (**6a**)

3.4 g (15 mmol) sodium 5-methylthio-1,2-dithiole-3-thione-4-thiolate (**5**) was dissolved in 50 ml of methanol and 3.74 g (15 mmol) 1-bromododecane added. The reaction mixture was refluxed for 1 h, filtered while warm and stored in a refrigerator at 6 °C for crystallization. Yield 4 g (70%) of yellow crystals; *m.p.* 63–65 °C (MeOH). – IR (KBr): ν/cm^{-1} = 2950 (m), 2918 (s), 2849 (s), 1471 (m), 1391 (s), 1263 (s), 1246 (s), 1060 (m), 971 (m), 934 (m), 833 (w), 824 (w), 725 (w), 718 (w), 520 (w). – ^1H NMR (CDCl_3): δ/ppm = 0.86 (t, *J* (H,H) = 7 Hz, 3H, CH_3), 1.12–1.61 (m, 20H, CH_2), 2.75 (s, 3H, SCH_3), 2.87 (t, *J* (H,H) = 7 Hz, 2H, SCH_2). – ^{13}C NMR (CDCl_3): δ/ppm = 14.09 (CH_3), 15.18 (SCH_3), 22.67 (CH_3CH_2), 28.18–31.90 (CH_2), 33.07 (SCH_2), 134.16 (C-4), 180.97 (C-5), 209.39 (C=S). – MS (70 eV): *m/z* (%): 380 (5) [M^+], 365 (3) [$\text{M}^+ - \text{CH}_3$], 347 (11) [$\text{M}^+ - \text{S}$], 333 (8) [$\text{M}^+ - \text{CH}_3\text{S}$], 212 (100) [$\text{M}^+ - \text{C}_{12}\text{H}_{25}$], 179 (28) [$\text{M}^+ - \text{C}_{12}\text{H}_{25}\text{S}$].

$\text{C}_{16}\text{H}_{28}\text{S}_5$ Calcd.: C 50.48 H 7.41 S 42.11
(380.69) Found: C 50.24 H 7.12 S 41.82.

4,5-Bis(dodecylthio)-1,2-dithiole-3-thione (**6b**)

To disodium 1,2-dithiole-3-thione-4,5-dithiolate (**7**) (2 g; 8.26 mmol) in 40 ml DMF, 1-bromo-dodecane (4.12 g; 16.52 mmol) was added. The reaction mixture was stirred at 70–80 °C for 4 h. The solvent was removed and the remaining residue diluted with 50 ml of *n*-hexane. The resulting suspension was refluxed for 30 min, the NaBr filtered off and the organic phase extracted three times with water (20 ml) and dried over

MgSO₄. The organic phase was reduced to 1/3 of its volume and stored at 6 °C. After some days the yellow compound crystallized. Yield 2.83 g (64%) of yellow crystals; *m.p.* 59–63 °C (MeOH). – IR (KBr): ν/cm^{-1} = 2957 (m), 2920 (s), 2850 (s), 1467 (w), 1388 (s), 1382 (s), 1264 (m), 1244 (s), 1054 (m), 949 (m), 832 (w), 821 (w), 720 (w). – ¹H NMR (CDCl₃): δ/ppm = 0.87 (t, *J* (H,H) = 7 Hz, 6H, CH₃), 1.13–1.61 (m, 38H, CH₂), 1.83 (quint, *J* (H,H) = 7 Hz, 2H, SCH₂CH₂), 2.88 (t, *J* (H,H) = 7 Hz, 2H, C(4)SCH₂), 3.21 (t, *J* (H,H) = 7 Hz, 2H, C(5)SCH₂). – ¹³C NMR (CDCl₃): δ/ppm = 14.07 (CH₃), 22.66 (CH₃CH₂), 28.37–31.90 (CH₂), 32.57(C(4)SCH₂), 33.12 (C(5)SCH₂), 134.27 (C-4), 180.35 (C-5), 209.27 (C=S). – MS (70 eV): *m/z* (%): 535 (18) [M⁺], 366 (79) [M⁺ – C₁₂H₂₅], 333 (62) [M⁺ – C₁₂H₂₅S], 198 (100) [M⁺ – C₂₄H₄₈].

C₂₇H₅₀S₅ Calcd.: C 60.62 H 9.42 S 29.96
(534.99) Found: C 60.82 H 9.28 S 29.54.

21-Thioxo-5,8,11,14-tetraoxa-2,17,19,20-tetrathiabicyclo [16.3.0]heneicos-1-en (10c)

A solution of 4,5-dimercapto-1,2-dithiole-3-thione (**8**) (2.38 g; 12 mmol) and 1,14-dibromo-3,6,9,12-tetraoxatetradecane (**9**) (4.37 g; 12 mmol) in DMF (90 ml) was added dropwise, at 65 °C, to a stirred suspension of Cs₂CO₃ (3.94 g; 12 mmol) in DMF (665 ml) within a period of 30 h. The reaction mixture was stirred at 65 °C for another 48 h. After cooling, the reaction mixture was reduced *in vacuo* to 1/3 of its volume, CsBr filtered off and DMF removed. The remaining brown oil was dissolved in 150 ml CH₂Cl₂. The organic phase was extracted three times with water (30 ml) and dried over MgSO₄. The solvent was removed *in vacuo* and the remaining residue purified by column chromatography (SiO₂, methanol/chloroform 1:10, *R_f* = 0.6). The crystallization of the remaining red oil was induced by addition of diethylether and storage at 6 °C. Yield 0.51 g (11%) of orange crystals; *m.p.* 121 °C (CHCl₃/hexane), [MeOH/CHCl₃ (1:10)]. – IR (KBr): ν/cm^{-1} = 2933 (m), 2909 (m), 2866 (s), 1457 (w), 1377 (s), 1354 (w), 1265 (m), 1247 (s), 1156 (w), 1123 (s), 1054 (m), 950 (s), 830 (w), 722 (w), 500 (w). – UV/Vis (CHCl₃): λ_{max} (lg ϵ) = 335 nm (4.02), 423 (4.05). – ¹H NMR (CDCl₃): δ/ppm = 3.12 (t, 2H, SC(16)H₂), 3.24–4.10 (m, 18H, OCH₂, SC(3)H₂). – ¹³C NMR (CDCl₃): δ/ppm = 32.6 (SC(16)H₂), 33.1 (SC(3)H₂), 68.4–71.0 (CH₂O), 133.4 (C-1), 181.3 (C-18), 209.1 (C=S). – MS (70 eV): *m/z* (%): 401 (100) [M⁺].

C₁₃H₂₀O₄S₅ Calcd.: C 38.98 H 5.03 S 40.02
(400.60) Found: C 38.78 H 4.88 S 40.57.

Dimerization of Dodecylthio Substituted 1,2-Dithiole-3-thiones and Trithion-dithiacrown Ethers to (*E*)-Thiodesaurines¹⁾

To the 1,2-dithiole-3-thione (0.32 mmol) in *p*-xylene (40 ml) was added triethyl phosphite (0.3 ml, 1.72 mmol). The reaction mixture was stirred at 130 °C for 30 min. Subsequently, the solvent was removed *in vacuo* and the remaining residue dissolved in CH₂Cl₂ (50 ml). The solution was filtered, diluted with *n*-hexane (20 ml). At 6 °C in a refrigerator, the thiodesaurines crystallized.

2,4-Bis(3-thioxo-2,5-dithiaheptadec-4-ylidene)-1,3-dithietane (*E*)-(11a)

Yield 69 mg (62%) of red crystals; *m.p.* 110–123 °C (CH₂Cl₂). – IR (KBr): ν/cm^{-1} = 2954 (w), 2922 (s), 2851 (m), 1481 (s), 1432(w), 1386(w), 1212(w) 1180 (s), 1022 (w), 649 (w). – UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 359 nm (4.62), 485 (5.02). – ¹H NMR (CDCl₃): δ/ppm = 0.86 (t, *J* (H,H) = 7 Hz, 6H, CH₃), 1.12–1.78 (m, 40H, CH₂), 2.56 (m, 6H, SCH₃), 2.79 (m, 4H, SCH₂). – ¹³C NMR (CDCl₃): δ/ppm = 14.42 (CH₃), 20.97 (CH₃CH₂), 29.14–29.99 (CH₂), 32.28 (SCH₃), 37.39 (SCH₂), 125.58 (C=CS₂), 161.48 (CS₂), 219.61 (C=S). – MS (70 eV): *m/z* (%): 696 (19) [M⁺], 527 (23) [M⁺ – C₁₂H₂₅].

C₃₂H₅₆S₈ Calcd.: C 55.12 H 8.10 S 36.78
(697.27) Found: C 55.32 H 8.27 S 36.94.

2,4-Bis(14-thioxo-13,16-dithiaoctaeicos-15-ylidene)-1,3-dithietane (*E*)-(11b)

Yield 114 mg (71%) of red crystals; *m.p.* 91 °C (CH₂Cl₂). – IR (KBr): ν/cm^{-1} = 2956 (w), 2921 (s), 2850 (s), 1470 (s), 1386 (w), 1301 (w), 1256 (w), 1182 (s), 1100 (w) 1012 (m), 956 (w), 720 (w), 677 (w), 635 (w). – UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 385 nm (4.67), 486 (5.61). – ¹H NMR (CDCl₃): δ/ppm = 0.86 (t, *J* (H,H) = 7 Hz, 12H, CH₃), 1.12–1.78 (m, 80H, CH₂), 2.80 (t, *J* (H,H) = 7 Hz, 4H, C=CSCH₂), 3.12 (t, *J* (H,H) = 7 Hz, 4H, S=CSCH₂). – ¹³C NMR (CDCl₃): δ/ppm = 14.08 (CH₃), 22.68 (CH₃CH₂), 27.22–31.92 (CH₂), 37.00 (C(4)SCH₂), 37.48 (C(5)SCH₂), 125.40 (C=CS₂), 161.99 (CS₂), 218.93 (C=S). – MS (70 eV): *m/z* (%): 1004 (5.5) [M⁺], 940 (3.1) [M⁺ – S₂], 835 (2.5) [M⁺ – C₁₂H₂₅], 501 (2.6) [M⁺ – C₂₇H₅₀S₄], 57 (100) [M⁺ – C₅₀H₉₁S₈].

C₅₄H₁₀₀S₈ Calcd.: C 64.48 H 10.02 S 25.50
(1005.86) Found: C 64.22 H 10.25 S 25.72.

2,4-Bis(9-thioxo-1,4-dioxa-7,10-dithiacyclododec-8-ylidene)-1,3-dithietane (*E*)-(12a)

Yield 76 mg (85%) of red crystals; *m.p.* 245 °C (CH₂Cl₂). – IR (KBr): ν/cm^{-1} = 2920 (m), 2854 (m), 1478 (s), 1383 (m), 1287 (w), 1178 (m), 1138 (m), 1108 (m), 1022 (m), 1000 (m), 690 (w), 646 (w). – UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 357 nm (3.53), 461 (3.97). – ¹H NMR (CDCl₃): δ/ppm = 3.00 (t, *J* (H,H) = 5 Hz, 4H, SC(6)¹H₂), 3.44–3.61 (m, 12H, SC(11)H₂, SCH₂CH₂O), 3.65 (t, *J* (H,H) = 5 Hz, 4H, OC(3)H₂CH₂O), 3.79 (t, *J* (H,H) = 5 Hz, 4H, OCH₂C(2)H₂O). – ¹³C NMR (CDCl₃): δ/ppm = 29.71 (SC(6)H₂), 37.32 (SC(11)H₂), 66.44 (SCH₂C(5)H₂O), 69.93 (SCH₂C(12)H₂O), 70.25 (OC(3)H₂CH₂O), 71.11 (OCH₂C(2)H₂O), 125.51 (C=CS₂), 162.04 (CS₂), 220.51 (C=S). – MS (70 eV): *m/z* (%): 560 (48) [M⁺], 528 (48) [M⁺ – S], 496 (82) [M⁺ – S₂], 82 (23) [M⁺ – C₆H₁₂O₂S₂], 350 (18) [M⁺ – C₆H₁₂O₂S₃], 312 (55) [M⁺ – C₉H₁₂O₄S₂], 198 (100) [M⁺ – C₁₂H₂₄O₄S₄].

C₁₈H₂₄O₄S₈ Calcd.: C 38.55 H 4.31 S 45.73
(560.87) Found: C 38.24 H 4.59 S 45.34.

2,4-Bis(12-thioxo-1,4,7-trioxa-10,13-dithiacyclopentadec-11-ylidene)-1,3-dithietane (*E*)-(12b)

Yield 94 mg (90%) of red crystals; *m.p.* 221–224 °C (CH₂Cl₂). – IR (KBr): ν/cm^{-1} = 2962 (m), 2923 (m), 2855 (m), 1479 (s), 1358 (w), 1262 (s), 1177 (m), 1101 (s), 1021 (s), 961 (w),

¹⁾ For the Numbers of the C-atoms of the macrocyclic ring, as in the systematic name, compare corresponding numbers for (*E*)-**12a** in Scheme 3.

803 (s), 695 (w), 650 (w). – UV/Vis (CH₂Cl₂): λ_{\max} (lg ϵ) = 385 nm (4.04), 465 (sh, 4.62), 479 (4.93). – ¹H NMR (CDCl₃): δ /ppm = 3.40 (t, *J* (H,H) = 7 Hz, 4H, SC(9) ¹ H₂), 3.82 (t, *J* (H,H) = 5 Hz, 4H, SC(14)H₂), 3.92–4.28 (m, 24H, OCH₂). – ¹³C NMR (CDCl₃): δ /ppm = 36.84 (SC(9)H₂), 38.20 (SC(14)H₂), 67.12 (SCH₂C(8)H₂O), 69.67 (SCH₂C(15)H₂O), 69.97 (C(6)H₂O), 70.44 (C(2)H₂O), 70.69 (C(5)H₂O), 71.84 (C(3)H₂O), 125.26 (C=CS₂), 162.21 (CS₂), 219.61 (C=S). – MS (70 eV): *m/z* (%): 648 (2.4) [M⁺], 616 (3.8) [M⁺ – S], 584 (6.5) [M⁺ – S₂], 323 (22) [M⁺ – C₁₁H₁₆O₃S₄], 198 (100) [M⁺ – C₁₆H₃₂O₆S₄].

C₂₂H₃₂O₆S₈ Calcd.: C 40.72 H 4.97 S 39.52
(648.97) Found: C 40.49 H 5.14 S 39.83.

2,4-Bis(15-thioxo-1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-ylidene)-1,3-dithietane (E)-(12c)

Yield 108 mg (92%) of red-brown crystals; *m.p.* 205 °C (CHCl₃). – IR (KBr): ν /cm⁻¹ = 2919 (m), 2854 (m), 1470 (s), 1350 (w), 1179 (s), 1117 (s), 1014 (s), 958 (m), 911 (w), 800 (w), 696 (w), 646 (w). – UV/Vis (CHCl₃): λ_{\max} (lg ϵ) = 383 nm (4.25). – ¹H NMR (CDCl₃): δ /ppm = 3.46 (t, *J* (H,H) = 6 Hz, 4H, SC(12) ¹ H₂), 3.79 (t, *J* (H,H) = 6 Hz, 4H, SC(17)H₂), 3.97–4.26 (m, 32H, OCH₂). – ¹³C NMR (CDCl₃): δ /ppm = 36.41 (SC(12)H₂), 38.20 (SC(17)H₂), 67.86 (SCH₂C(11)H₂O), 69.91 (SCH₂C(18)H₂O), 70.83 (OCH₂CH₂O), 125.06 (C=CS₂), 161.89 (CS₂), 219.12 (C=S). – MS (70 eV): *m/z* (%): 736 (0.3) [M⁺], 704 (0.3) [M⁺ – S], 672 (1.1) [M⁺ – S₂], 400 (25) [M⁺ – C₁₃H₂₀O₄S₃], 367 (35) [M⁺ – C₁₃H₂₀O₄S₄], 198 (100) [M⁺ – C₂₀H₄₀O₈S₄].

C₂₆H₄₀O₈S₈ Calcd.: C 42.37 H 5.47 S 34.80
(737.08) Found: C 42.52 H 5.64 S 35.04.

Crystal Structure Determination of Bis(dithia[15]crown-5)-thiodesaurine (E)-12b [12]

STOE-IPDS, MoK α -Radiation (λ = 71.073 pm), room temperature; The structure was solved by direct methods (XS program for crystal structure solution, version 4.2 für MS-DOS, Copyright Siemens Analytical Xray Inst. Inc.) and refined by full-matrix least-squares method of (SHELXL-93) [11]. All nonhydrogen atoms were refined anisotropically (except the disordered O21/O21'). The hydrogen atoms were placed into theoretical positions and refined by using the riding model. Crystal Structure Data: C₂₂H₃₂O₆S₈, *M* = 648.97 g mol⁻¹, Crystal size: 0.40 × 0.10 × 0.08 mm³, mono-clinic, Space group P2(1)/c, *Z* = 4, *a* = 1061.1 (2), *b* = 1487.2 (3), *c* = 1853.3 (4) pm, β = 97.81(3)°, *V* = 2.897 (1) nm³, *d_c* = 1.488 Mg/m³, *F*(000) = 1360, μ = 0.65 mm⁻¹, 5855 reflections

collected in the scan range of 3.52° ≤ 2 Θ ≤ 44.00°, 3398 independent reflections, 1811 observed reflections, R1 (2 σ (I)) = 0.0472, R1 (all data) = 0.0988, wR2 (all data) = 0.01445, GooF = 1.058 for 325 Parameter and 4 Restraints, Weighting scheme: $\omega = 1/[\sigma^2(\text{Fo}^2) + (0.0662\text{P})^2 + 0.0000\text{P}]$ with *P* = (Fo² + 2Fc²)/3. The asymmetric unit comprises two half-molecules, thus forming a unit cell with two slightly different molecules.

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- [12] Crystallographic data for the structure reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101005. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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