Syntheses and Structural Properties of Cyclic Tetrathiadiynes

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Dedicated to Professor Franz Effenberger on the occasion of his 70th birthday

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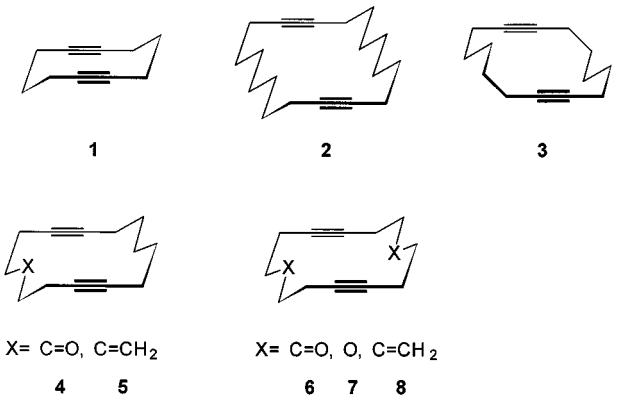
The four-component cyclization of dilithium acetylide with dithiocyanatoalkanes yielded the hitherto unknown tetrathiacyclodiynes **34**, **38**, **41**, and **43** in moderate yields. The use of the trimethylsilyl protecting group allowed a more efficient and flexible stepwise approach with good yields. The resulting tetrathiacyclodiynes **25**–**44** were investigated by X-ray analysis. For ring systems with a twist-chair conformation the torsion angle between the CH_2–S σ-bonds of the CH_2–S–C≡C–S–CH_2 moiety adopts values between 75° and 110°. These values are due to electronic effects, as shown by HF/6-31G* calculations.

Introduction

In his seminal paper on the conformations of medium-sized rings J. Dale discussed,[1] among other systems, the conformations of minimal energy of cyclic diynes with diametrically placed triple bonds. He concluded that in the rings with 14, 18, and 22 carbon atoms a strain-free conformation is possible while in the rings with 12, 16, and 20 carbon atoms this is not the case. This difference shows up in the corresponding melting points.[1] Those rings with an odd (3, 5, 7, 9) number of CH_2 groups between the triple bonds melt at higher temperatures than those with an even number (4, 6, 8, 10) of CH_2 groups. The predictions of Dale have been confirmed for cyclodeca-1,6-diyne[2] (**1**) and cyclooctadeca-1,10-diyne[3] (**2**) by X-ray diffraction studies on single crystals.



For cyclotetradeca-1,8-diyne (**3**) a conformation with two *gauche* interactions is present in the solid state.[4,5] This conformation was also found in 5,12-dimethylidenecyclotetradeca-1,8-diyne[5] (**8**), while in cyclotetradeca-4,11-diynone[5] (**4**), cyclotetradeca-4,11-diyne-1,8-dione[5] (**6**) and 1,8-dioxacyclotetradeca-4,11-diyne[5] (**7**) a zigzag arrangement of the chains is adopted in the solid state.[6]

These few examples show that heteroatoms in the chains contribute considerably to the conformations. We therefore thought it of interest to probe the conformational preference in cyclic diynes with heteroatoms, which provide lone pairs, in the positions α to the triple bonds. This situation allows competition between steric and electronic effects and, furthermore, provides electron-rich cyclic alkynes. In the following we will report on the synthesis and structural properties of cyclic diynes with sulfur atoms in the position α to the triple bonds.

Syntheses

The usual approach for synthesizing dithiaalkynes is to treat dichloroacetylene with alkyl- or arylthiols in the presence of potassium hydride[7] or LiHMDS.[8] The main disadvantages of this method are that the dichloroacetylene is explosive and carcinogenic. Furthermore, the thiols are very malodorous and toxic substances. We therefore used a route[9] in which the lithium salt of an acetylene was treated with a dithiocyanatoalkane as shown in Schemes 1 and 2. This route also provides higher yields and less side products than the route using dichloroacetylene.

We used two routes; a four-component condensation in which dilithium acetylide was treated with a dithiocyanatoalkane (Scheme 1), and a stepwise approach (Scheme 2). We will discuss the latter route in more detail because it proved to be more efficient and flexible than the four-component condensation.

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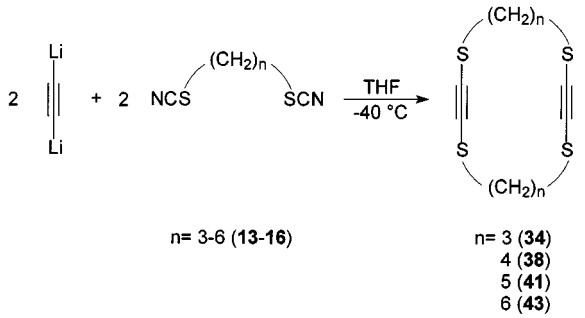
Our synthesis is summarized in Scheme 2. It starts from trimethylsilylacetylene (TMSA) (**9**). Compound **10**, the lithium salt of **9**, was treated with various α,ω-dithiocyanatoalkanes **11**−**17**, the preparation of which has been described in the literature.[10−14] This reaction could be carried out to give yields in excess of 80%. The resulting α,ω-bis(trimethylsilylalkynethio)alkanes **18a**−**24a** were transformed into the corresponding α,ω-bis(alkynethio)alkanes **18**−**24** by treatment with 0.1 N NaOH in methanol. The yields of this step varied between 36 and 80% with the exception of **18**, where a yield of only 11% was obtained. In the ring-closing step we treated the dilithium salts of **18**−**24** with the α,ω-dithiocyanatoalkanes **11**−**17** under high-dilution conditions in THF. The yields obtained by this protocol depend on the ring size and are shown in Table 1.

For systems containing the S−CH_2−S building block (**25**−**28**) and other smaller ring systems (**29**) the yields obtained varied between 14 and 25%, whereas larger systems (**30**−**33**, **35**−**37**, **39**, **40**, **42**, **44**) produced yields between 36 and 57%. These yields are considerably higher than those obtained in the four-component condensation, which varied between 5 and 9% for **34**, **38**, **41**, and **43**. The resulting substances proved to be slightly light-sensitive, colorless solids that could be recrystallized from toluene or hexane/dichloromethane mixtures.

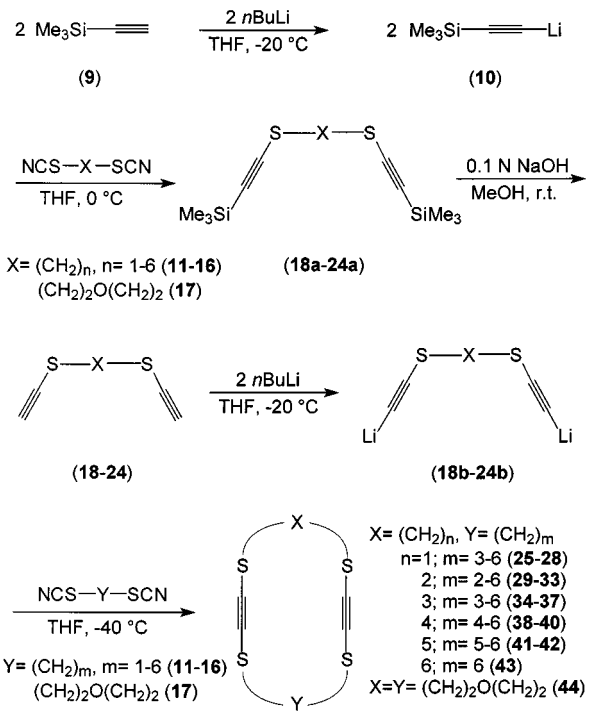
Table 1. Yields and melting points of the tetrathiacyclodiynes

Compound	Yield [%]	mp. [°C]	Compound	Yield [%]	mp. [°C]
25	15[a]	30	**35**	36[a]	166
26	23[a]	87[b]	**36**	38[a]	89
27	20[a]	94[b]	**37**	25[a]	59
28	21[a]	72	**38**	7.5[c]	83
29	14[a]	123[b]	**39**	39[a]	75
30	54[a]	119	**40**	43[a]	47
31	49[a]	95	**41**	5.8[c]	149[b]
32	57[a]	84	**42**	46[a]	132
33	48[a]	91	**43**	6.4[c]	70
34	8.3[c]	188[b]	**44**	55[a]	138

[a] Stepwise approach according to Scheme 2. − [b] Decomposition. − [c] Four-component condensation according to Scheme 1.



Scheme 1



Scheme 2

Structural Investigations and Discussion

We were able to grow single crystals of **26**−**34** and **36**−**44** that could be investigated by X-ray diffraction. As examples we show in Figure 1 the molecular structures of **27**, **29**, **31**, and **34**.

In Table 2 we list the most relevant distances and angles found in the solid state. Not listed are the lengths of the triple bonds and the distances between C(sp) and sulfur atoms that remain essentially constant and show the same values as obtained for cyclic mono- and diynes.[15] As seen in Table 2, larger variations were found in the transannular distances t_1 and t_2 of the sp-carbon atoms (Figure 2). These distances vary from 350 pm in the 13-membered ring **26** to 826 pm in the 19-membered ring **42**. This was anticipated

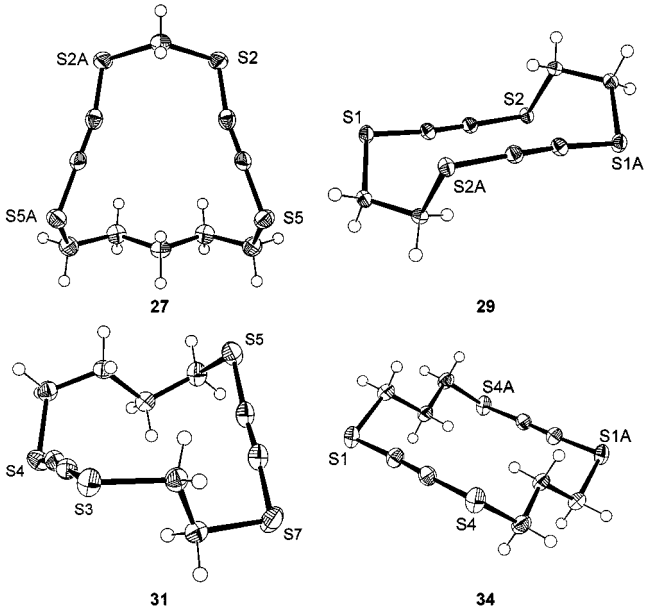


Figure 1. ORTEP plots (50% ellipsoid probability) of the molecular structures of **27**, **29**, **31** and **34**

Table 2. Most relevant distances and angles of the tetrathiacyclodiynes; for the definition of the distances and angles see Figure 2

Cpd.	n m	t_1 [pm] t_2 [pm]	α_1 [°] α_2 [°]	α_3 [°] α_4 [°]	β [°]	γ_1 [°] γ_2 [°]
26	1 4	350.1 410.0	173.6 177.4	169.3 170.0	3.6	96.4 102.9
27	1 5	356.9 440.1	166.8 175.3	166.8 175.3	0.0	111.5 111.5
28	1 6	367.8 498.3	166.2 177.1	174.5 178.6	59.1	100.5 103.2
29	2 2	356.2 356.2	177.1 174.9	174.9 177.1	0.0	99.3 99.3
30[a]	2 3	383.0 424.9	176.3 175.2	173.7 178.2	18.4	80.1 83.4
30[a]	2 3	384.8 425.7	179.1 173.0	167.0 177.2	13.9	82.5 87.1
31[a]	2 4	444.5 459.7	174.3 171.8	177.2 174.2	54.0	81.1 81.8
31[a]	2 4	448.5 463.3	177.7 171.2	175.1 172.7	48.7	76.5 79.2
32	2 5	466.7 495.0	178.4 177.1	179.4 174.0	24.7	78.0 89.2
33	2 6	498.4 582.6	175.8 174.3	178.3 174.3	57.6	81.9 83.9
34	3 3	544.8 544.8	177.0 176.3	176.3 177.0	0.0	63.5 63.5
36[b]	3 5	552.3 569.5	175.0 173.9	175.0 173.9	0.0	106.2 106.2
37[a]	3 6	570.5 606.2	172.3 176.3	174.0 171.0	12.7	96.6 104.9
37[a]	3 6	574.2 616.7	172.2 173.0	174.2 173.2	6.5	93.1 109.1
38	4 4	535.7 540.8	178.8 179.1	174.2 176.9	58.7	75.2 77.8
39[b]	4 5	649.2 709.8	170.9 170.0	166.6 166.1	27.2	61.9 96.1
40	4 6	654.9 705.1	176.2 175.0	178.6 173.9	26.4	93.2 105.7
41	5 5	802.8 802.8	176.5 177.7	177.7 176.5	0.0	62.9 62.9
42[b]	5 6	817.9 825.9	177.7 173.1	178.2 177.9	6.2	66.0 99.1
43	6 6	767.9 767.9	178.6 176.3	176.3 178.6	82.2	82.4 82.4
44	5 5	676.1 679.2	175.9 176.6	174.9 177.5	26.3	91.5 92.0

[a] Two independent molecules exist in the unit cell. – [b] Molecule is disordered.

in so far as larger chains imply larger separations. Remarkably, the S–CH_2–S building block turns out to be very rigid and the transannular distance t_1 between the two sp centers directly connected to this unit only increases from 350.1 pm (**26**) to 367.8 pm (**28**) if the other alkane bridge is enlarged. In line with these results are the angles α at the sp centers. The smallest angles were found in the cases of rings with one methylene group and were close to 179° in larger rings. The dihedral angle β between the triple bonds was found to be 0° in the cases of **27**, **34**, **36**, and **41** where both alkane chains have an odd number of methylene groups and therefore chair conformations are adopted. Unexpectedly, **29** also showed a dihedral angle of 0° and a distorted chair conformation was observed in the solid state. Small deviations from 0° are encountered in **26** and **42**. On considering the results reported for cyclic diynes (see Introduction) it can be seen that the small dihedral angles in the cases of **27**, **34**, **36**, and **41** were expected whereas for **26**, **29**, and **42** they were not anticipated.

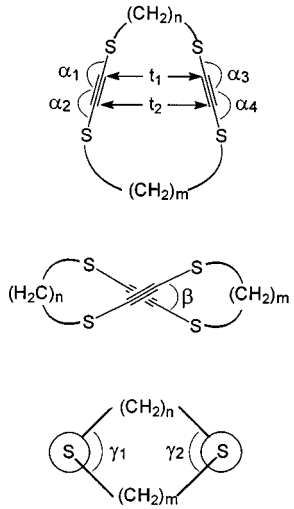


Figure 2. Definition of transannular distances t_1 and t_2, angle α and torsion angles β and γ in **26**–**34** and **36**–**44**

The comparison of the dihedral angles γ between the CH_2–S σ-bonds of the CH_2–S–C≡C–S–CH_2 unit with these findings, shows that the molecular geometry of the compounds is determined by both steric and electronic factors. If both alkane chains have the same odd number of carbon atoms (**34**, **41**) γ varies between 62.9 and 63.5° as expected for a chair conformation and observed for many of the corresponding carbon compounds. In all other cases the values of γ are considerably larger and usually range between 75° and 110° (Figure 3).

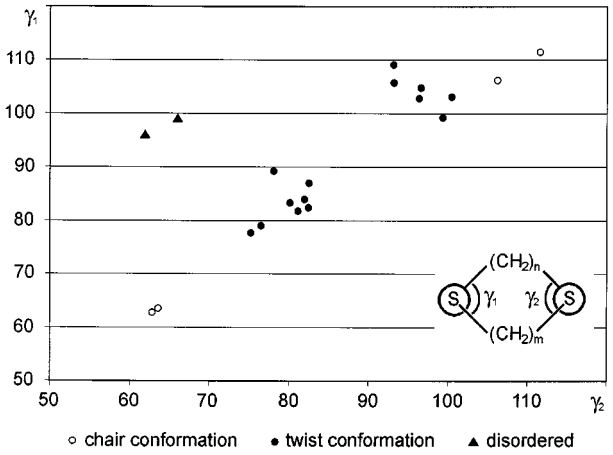


Figure 3. Correlation between torsion angles γ_1 and γ_2 [°] of the CH_2S σ-bonds in the CH_2–S–C≡C–S–CH_2 moieties

We ascribe this behavior to the sulfur atoms, whose lone pairs interact through the π-system of the triple bond and finally lead to the observed values for γ of nearly 90°.

In order to substantiate this proposal we considered the results of HF/6-31G* calculations[16] on 3-hexyne (**45**) and

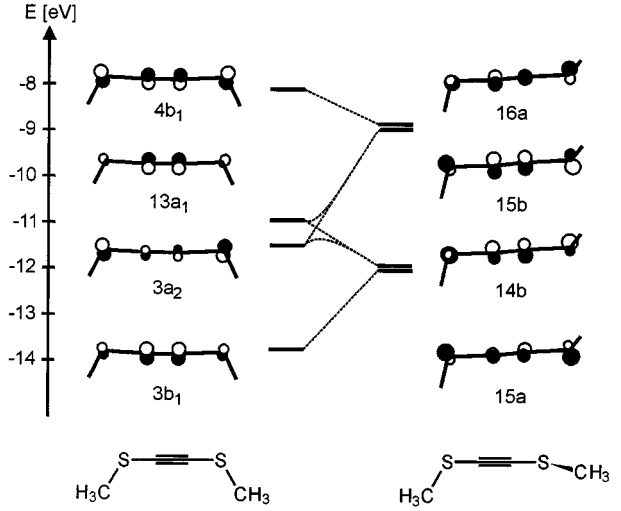
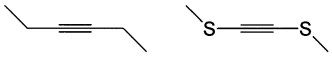


Figure 4. Correlation diagram for the highest occupied MOs of **46** with *syn*-periplanar ($\gamma = 0°$) and orthogonal ($\gamma = 90°$) methyl groups

2,5-dithia-3-hexyne (**46**). In the case of **45** the *gauche* conformation was predicted to be a local minimum. For **45** the conformation of minimum energy has a torsion angle of 180° at the sp centers while for **46** a dihedral angle of 91.4° was found in a B3LYP/6-31G* optimization.



45 **46**

To understand why **46** prefers a conformation with a torsion angle of about 90° we must consider the highest occupied molecular orbitals (MOs) of this species (Figure 4) in a *syn*-periplanar (C_{2v}) and a perpendicular (C_2) conformation.

In the planar conformation (Figure 4, left) the four highest occupied molecular orbitals belong to the irreducible representations A_1, A_2, B_1, and B_2. The MOs $3b_1$ and $4b_1$ can be described as the bonding and antibonding linear combination of the out-of-plane π-MO of the alkyne unit with the through-space bonding combination of the sulfur 3p orbitals. MO $3a_2$ mainly consists of the through-space antibonding linear combination of sulfur 3p orbitals, in bonding combination with the out-of-plane π* MO of the alkyne unit. MO $13a_1$ results from an antibonding interaction of the in-plane π-MO of the alkyne unit with the symmetrical linear combination of the sp^n-type lone pairs of the two sulfur atoms. By bending one methyl group by 90° out of the molecular plane (Figure 4, right side) the former $4b_1$ MO is stabilized and the former $3b_1$ MO is destabilized because one of the π-3p interactions is removed. The former $4b_1$ MO correlates with 16a and the former $3b_1$ with 15a. The same holds for $13a_1$ and $3a_2$, the former being stabilized and the latter destabilized. However, in point group C_2 both MOs belong to the same irreducible representation (B) and so an avoided crossing occurs by mixing.

As a result of the geometrical change ($C_{2v} \rightarrow C_2$) a net stabilization of 4.68 kcal/mol is found because the antibonding interactions in C_2 are somewhat smaller than in the C_{2v} conformation. As occurs in H_2S_2, the terminal *S*-alkyl groups adopt a conformation that is nearly perpendicular. This situation minimizes the repulsive interaction between the occupied 3p orbitals and the π-MOs of the triple bond. In **46** the triple bond acts as a relay for the interaction of the lone pairs of the terminal SCH_3 groups. As in H_2S_2 this destabilizing interaction will be smallest for a perpendicular conformation. In the minimum conformation of **46** the C(sp)−S bonds and the C−C triple bond are shortened (1.70 and 1.19 Å, respectively) with respect to the *syn*-periplanar conformation.

In the medium-sized rings of **28**−**44** the alkane chains between the S−C≡C−S units try to adopt a strain-free conformation, i.e. a zigzag arrangement with a staggered conformation between neighboring CH_2 groups. To achieve this, the dihedral angles γ of the cycles are distorted from orthogonality by up to 16° in both directions. Variation of γ between 60° and 90° "cost" only 1.23 kcal/mol for **46** (B3LYP/6-31G*). This value increases up to 18 kcal/mol on varying γ of only one S−C≡C−S unit in the cycles because of the ring strain. The dihedral angle γ also affects the orientation of the zigzag chain and the dihedral angle β between the alkyne groups. We also checked the influence on the total energy of the dihedral angle β between the alkyne group. Freezing β to 0° costs up to 8.38 kcal/mol for **32** while creating strained dihedral angles γ (43.2° for **39**). In the case of C_2-symmetric **29**, the alkyne groups are already oriented planar to each other in the global minimum conformation.

Similarly to **46**, this distortion causes a mixing of sp- and p-type sulfur lone pairs and the in-plane and out-of-plane π-orbitals in the highest occupied molecular orbitals, as can be seen in Figure 4.

Structural investigations on 2,5-dithia-3-hexyne (**46**) were reported by Connor[17] and Bock.[18] The structure of **46** was determined by means of electron diffraction in the gas phase[17] and gave a torsion angle of 86±5°. Photoelectron spectra supported by MNDO calculations[18] also showed that a dihedral angle of 86° is favored in **46**.

Conclusions

By changing the polarity ("umpolung") of the usual reagents for the synthesis of dithiaalkynes (chloroalkynes and alkylthiols) we were successful in obtaining a number of cyclic tetrathiadiynes. Our approach uses the readily available α,ω-dithiocyanatoalkanes as the electrophilic component and the easily prepared lithium salts of terminal alkynes as nucleophiles. In those cases where the twist conformation is adopted by the ring systems we find the dihedral angles between the CH_2−S σ-bonds of the CH_2−S−C≡C−S−CH_2 moiety to be between 80 and 110°. This relatively large dihedral angle, as compared to the hydrocarbons (60°), is due to the electronic effects and minimizes the repulsion between the lone pairs at the sulfur centers and the π-bonds of the alkyne groups.

Experimental Section

General Methods: Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon. THF was dried with sodium/benzophenone and distilled under argon before use; hexane, toluene, petroleum ether, diethyl ether, and methanol were distilled before use. − Melting points are uncorrected. − Materials used for column chromatography: Silica gel 60 (Machery−Nagel). − ^{1}H NMR and ^{13}C NMR: Bruker Avance 300 (^{1}H at 300 MHz and ^{13}C at 75.47 MHz), Bruker Avance 500 (^{1}H NMR at 500 MHz and ^{13}C at 125.77 MHz) using the solvent as internal standard. − IR: Bruker Vector 22 FT-IR. − MS: Low resolution: ZAB-2F; high resolution: JEOL JMS-700. − Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. − Trimethylsilylacetylene (**9**)[19] and the dithiocyanatoalkanes **12**,[10] **13**,[11] **14**,[12] **15**,[13] **16**,[14] **17**[14] were prepared according to literature methods. Dithiocyanatomethane (**11**) was purchased from Acros and recrystallized from ethanol before use.

General Procedure for the Preparation of the Dithiaalkadiynes 18−24. − Step 1: To a solution of trimethylsilylacetylene (TMSA) in 250 mL of anhydrous THF was added *n*-butyllithium (1.6 M solution in *n*-hexane) dropwise at −10 °C over a period of 15 min. The solution was stirred for 1 h at −10 °C. A solution of the dithiocyanate in 100 mL of anhydrous THF was added dropwise over a period of 30 min while keeping the temperature between −10 and −5 °C. In the case of **24** the temperature should not exceed −20 °C. After completing the addition, the reaction mixture was stirred for 3 h at −10 °C. 100 mL of saturated NH_4Cl solution and 200 mL of petroleum ether (diethyl ether in the case of **24**) were added, the layers were separated and the aqueous layer was extracted several times with petroleum ether (diethyl ether in the case of **24**). The combined organic layers were washed with saturated NaCl solution and dried with Na_2SO_4. After evaporation of the solvent, crude bis(trimethylsilyl)dithiaalkadiyne was obtained by flash filtration (SiO_2, petroleum ether/diethyl ether, 10:1) and was used for the next step without further purification. − **Step 2:** To a solution of the bis(trimethylsilyl)dithiaalkadiyne in 200 mL of methanol was added 0.1 N aqueous NaOH dropwise over a period of 15 min. The reaction mixture was stirred for 1 h at room temperature. The mixture was poured into 400 mL of ice/water and 300 mL of diethyl ether was added. The layers were separated and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were washed with saturated NaCl solution, dried with Na_2SO_4 and the solvents removed by rotary evaporation. The crude dithiaalkadiyne was purified by kugelrohr distillation under reduced pressure.

3,5-Dithiahepta-1,6-diyne (18): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 3.38 g (26.0 mmol) of dithiocyanatomethane (**11**). Step 2: 3.94 g (14.5 mmol) of crude **18a** and 14.5 mL (1.45 mmol) of 0.1 N NaOH. Yield: 200 mg (11%) of **18** as a yellow oil, b.p. 30 °C/0.08 mbar. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99 (s, 2 H, ≡C−H), 4.05 (s, 2 H, CH_2). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 42.6 (CH_2), 72.7 (S−C≡), 86.1 (≡C−H). − IR (film): $\tilde{\nu}$ = 3286 cm^{-1}, 2044, 1204, 843, 721, 690, 559. − MS; (EI, 70 eV): 127 [M − H$^+$], 84, 71, 57. − HRMS; (EI, 70 eV): [M$^+$] $C_5H_4S_2$: calcd. 127.9754; found 127.9739.

3,6-Dithiaocta-1,7-diyne (19): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 3.70 g (26.0 mmol) of 1,2-dithiocyanatoethane (**12**). Step 2: 3.30 g (11.5 mmol) of crude **19a** and 11.5 mL (1.15 mmol) of 0.1 N NaOH. Yield: 575 mg (36%) of **19** as a white solid, m.p. 56 °C. − ^{1}H NMR (300 MHz, C_6D_6): δ = 2.31 (s, 2 H, ≡C−H), 2.50 (s, 4 H, CH_2). − ^{13}C NMR (75.47 MHz, C_6D_6): δ = 34.6 (CH_2), 73.8 (S−C≡), 84.2 (≡C−H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3303 cm^{-1}, 2938, 2044, 1423, 1280, 1260, 1205, 1125, 560, 533. − MS; (EI, 70 eV): 142 [M$^+$], 114, 85, 69, 57. − HRMS; (EI, 70 eV): [M$^+$] $C_6H_6S_2$: calcd. 141.9911; found 141.9922.

3,7-Dithianona-1,8-diyne (20): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 4.11 g (26.0 mmol) of 1,3-dithiocyanatopropane (**13**). Step 2: 3.55 g (12.0 mmol) of crude **20a** and 12.0 mL (1.20 mmol) of 0.1 N NaOH. Yield: 1.50 g (80%) of **20** as a colorless oil, b.p. 50 °C/0.13 mbar. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.81 (quint, ^3J = 6.9 Hz, 2 H, CH_2CH$_2$S), 2.23 (t, ^3J = 6.9 Hz, 4 H, CH$_2$S), 2.35 (s, 2 H, ≡C−H). − ^{13}C NMR (125.77 MHz, C_6D_6): δ = 29.1 (*C*H$_2$CH$_2$S), 33.3 (CH$_2$S), 74.6 (S−C≡), 83.5 (≡C−H). − IR (film): $\tilde{\nu}$ = 3286 cm^{-1}, 2923, 2855, 2041, 680, 550. − MS; (EI, 70 eV): 156 [M$^+$], 128, 114, 84, 71, 57.

3,8-Dithiadeca-1,9-diyne (21): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 4.50 g (26.0 mmol) of 1,4-dithiocyanatobutane (**14**). Step 2: 3.55 g (11.3 mmol) of crude **21a** and 11.3 mL (1.13 mmol) of 0.1 N NaOH. Yield: 1.06 g (55%) of **21** as a pale yellow oil, b.p. 90 °C/0.04 mbar. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.40 (m, 4 H, CH_2CH$_2$S), 2.10 (m, 4 H, CH$_2$S), 2.40 (s, 2 H, ≡C−H). − ^{13}C NMR (125.77 MHz, C_6D_6): δ = 28.3 (*C*H$_2$CH$_2$S), 34.8 (CH$_2$S), 75.1 (S−C≡), 83.3 (≡C−H). − IR (film): $\tilde{\nu}$ = 3286 cm^{-1}, 2935, 2856, 2040, 678, 548. − MS; (EI, 70 eV): 170 [M$^+$], 142, 128, 114, 97, 71, 57.

3,9-Dithiaundeca-1,10-diyne (22): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 4.84 g (26.0 mmol) of 1,5-dithiocyanatopentane (**15**). Step 2: 4.23 g (13.0 mmol) of crude **22a** and 13.0 mL (1.30 mmol) of 0.1 N NaOH. Yield: 1.31 g (55%) of **22** as a pale yellow oil, b.p. 120 °C/0.03 mbar. − ^{1}H NMR (500 MHz, C_6D_6): δ = 0.98 (quint, ^3J = 8.0 Hz, 2 H, CH_2CH$_2$CH$_2$S), 1.32 (m, 4 H, CH_2CH$_2$S), 2.17 (t, ^3J = 6.8 Hz, 4 H, CH$_2$S), 2.41 (s, 2 H, ≡C−H). − ^{13}C NMR (125.77 MHz, C_6D_6): δ = 27.4 (*C*H$_2$CH$_2$CH$_2$S), 29.3 (*C*H$_2$CH$_2$S), 35.3 (CH$_2$S), 75.3 (S−C≡), 83.1 (≡C−H). − IR (film): $\tilde{\nu}$ = 3286 cm^{-1}, 2934, 2857, 2039, 677, 547. − MS; (EI, 70 eV): 184 [M$^+$]. − HRMS; (EI, 70 eV): [M$^+$] $C_9H_{12}S_2$: calcd. 184.0380; found 184.0342.

3,10-Dithiadodeca-1,11-diyne (23): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 5.21 g (26.0 mmol) of 1,6-dithiocyanatohexane (**16**). Step 2: 6.65 g (19.4 mmol) of crude **23a** and 19.4 mL (1.94 mmol) of 0.1 N NaOH. Yield: 2.39 g (62%) of **23** as a pale yellow oil, b.p. 130 °C/0.02 mbar. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (m, 4 H, CH_2CH$_2$CH$_2$S), 1.77 (m, 4 H, CH_2CH$_2$S), 2.74 (t, ^3J = 7.2 Hz, 4 H, CH$_2$S), 2.76 (s, 2 H, ≡C−H). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.3 (*C*H$_2$CH$_2$CH$_2$S), 29.6 (*C*H$_2$CH$_2$S), 35.6 (CH$_2$S), 75.2 (S−C≡), 82.6 (≡C−H). − IR (film): $\tilde{\nu}$ = 3287 cm^{-1}, 2933, 2855, 2041, 1460, 676, 546. − MS; (EI, 70 eV): 197 [M − H$^+$]. − HRMS; (EI, 70 eV): [M$^+$] $C_{10}H_{14}S_2$: calcd. 198.0537; found 198.0520.

6-Oxa-3,9-dithiaundeca-1,10-diyne (24): Starting materials: Step 1: 5.11 g (52.0 mmol) of TMSA (**9**), 32.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 4.90 g (26.0 mmol) of bis(2-thiocyanatoethyl) ether (**17**). Step 2: 4.80 g (14.5 mmol) of crude **24a** and 14.5 mL (1.45 mmol) of 0.1 N NaOH. Yield: 2.07 g (77%) of **24** as a pale yellow oil, b.p. 95 °C/0.02 mbar. − ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 2.76 (s, 2 H, ≡C−H), 2.91 (t, ^3J = 6.5 Hz, 4 H, CH_2S), 3.80 (t, ^3J = 6.5 Hz, 4 H, CH_2O). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 35.0 (CH_2S), 69.6 (CH_2O), 74.5 (S−C≡), 82.8 (≡C−H). − IR (film): $\tilde{\nu}$ = 3284 cm^{-1}, 2933, 2864, 2040, 1360, 1294, 1113, 684, 554. − MS; (EI, 70 eV): 186 [M^+]. − HRMS; (EI, 70 eV): [$M^+ - C_2H_4$] $C_6H_6S_2O$: calcd. 157.9860; found 157.9857.

General Procedure for the Preparation of the Symmetrical Tetrathiacycloalkadiynes 34, 38, 41, 43 from Dilithium Acetylide and Dithiocyanatoalkane: A suspension of dilithium acetylide in THF was prepared from *n*-butyllithium and acetylene in the usual manner.[20] To 1000 mL of anhydrous THF, a suspension of dilithium acetylide in THF and a solution of dithiocyanatoalkane in THF were added dropwise simultaneously at −40 °C over a period of 8 h. After complete addition, the reaction mixture was allowed to warm up to room temperature overnight. The solvents were removed by rotary evaporation and polymers and salts were removed by flash filtration {SiO_2 [3% NEt_3 (v/v)], toluene}. The solvent was removed by rotary evaporation and the product was isolated by column chromatography {SiO_2 [3% NEt_3 (v/v)], *n*-hexane/toluene, 3:1}.

1,4,8,11-Tetrathiacyclotetradeca-2,9-diyne (34): Starting materials: Dilithium acetylide, prepared from acetylene and 60 mmol of *n*BuLi in 250 mL of THF and 4.51 g (28.5 mmol) of 1,3-dithiocyanatopropane (**13**) in 250 mL of THF. Yield: 308 mg (8.3%) of **34** as a colorless solid, m.p. 188 °C (decomposition). − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.36 (quint, ^3J = 7.3 Hz, 4 H, SCH_2CH_2), 2.73 (t, ^3J = 7.3 Hz, 8 H, SCH_2). − ^{13}C NMR (75.47 MHz, C_6D_6): δ = 30.3 (SCH_2CH_2), 34.9 (SCH_2), 86.9 (≡C). − IR (KBr): $\tilde{\nu}$ = 2966 cm^{-1}, 2924, 1446, 1413, 1253, 1107, 1025, 1004, 729. − MS; (CI+): 261 [M + H^+], 260 [M^+], 219, 187. − $C_{10}H_{12}S_4$ (260.5): calcd. C 46.11, H 4.64, S 49.25; found C 46.12, H 4.65, S 49.15.

1,4,9,12-Tetrathiacyclohexadeca-2,10-diyne (38): Starting materials: Dilithium acetylide, prepared from acetylene and 60 mmol of *n*BuLi in 250 mL of THF and 5.00 g (29.0 mmol) of 1,4-dithiocyanatobutane (**14**) in 250 mL of THF. Yield: 313 mg (7.5%) of **38** as a colorless solid, m.p. 83 °C. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.97 (m, 8 H, CH_2CH_2S), 2.67 (m, 8 H, CH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.0 (CH_2CH_2S), 36.1 (CH_2S), 86.7 (≡C). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2932, 2912, 2859, 1449, 1417, 1299, 1283, 1232, 736. − MS; (EI, 70 eV): 288 [M^+], 260 [$M^+ - C_2H_4$], 255 [M^+ − SH], 200, 185, 172, 112, 88, 55. − HRMS; (EI, 70 eV): [M^+] calcd. 288.0135; found 288.0133. − $C_{12}H_{16}S_4$ (288.5): calcd. C 49.95, H 5.59; found C 49.96, H 5.65.

1,4,10,13-Tetrathiacyclooctadeca-2,11-diyne (41): Starting materials: Dilithium acetylide, prepared from acetylene and 50 mmol of *n*BuLi in 250 mL of THF and 4.47 g (24.0 mmol) of 1,5-dithiocyanatopentane (**15**) in 250 mL of THF. Yield: 222 mg (5.8%) of **41** as a colorless solid, m.p. 149 °C (decomposition). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56 (m, 4 H, $CH_2CH_2CH_2S$), 1.84 (m, 8 H, CH_2CH_2S), 2.62 (t, ^3J = 7.2 Hz, 8 H, CH_2S). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.8 ($CH_2CH_2CH_2S$), 30.2 (CH_2CH_2S), 36.6 (CH_2S), 86.4 (≡C). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1}, 2852, 1452, 1224, 723. − MS; (EI, 70 eV): 316 [M^+], 283 [M^+ − SH], 214, 160, 101, 88. − HRMS; (EI, 70 eV): [M^+] calcd. 316.0448; found 316.0444. − $C_{14}H_{20}S_4$ (316.6): calcd. C 53.11, H 6.37, S 40.52; found C 53.03, H 6.34, S 40.24.

1,4,11,14-Tetrathiacycloeicosa-2,12-diyne (43): Starting materials: Dilithium acetylide, prepared from acetylene and 40 mmol of *n*BuLi in 250 mL of THF and 3.81 g (19.0 mmol) of 1,6-dithiocyanatohexane (**16**) in 250 mL of THF. Yield: 211 mg (6.4%) of **43** as a colorless solid, m.p. 70 °C. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (m, 8 H, $CH_2CH_2CH_2S$), 1.81 (m, 8 H, CH_2CH_2S), 2.65 (t, ^3J = 6.9 Hz, 8 H, CH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.5 ($CH_2CH_2CH_2S$), 29.6 (CH_2CH_2S), 36.6 (CH_2S), 86.5 (≡C). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1}, 2851, 1458, 1423, 1303, 1262, 1212, 1046, 836, 806, 726, 700. − MS; (EI, 70 eV): 344 [M^+], 311 [M^+ − SH], 228, 172, 115, 88. − HRMS; (EI, 70 eV): [M^+] calcd. 344.0761; found 344.0756.

General Procedure for the Preparation of the Tetrathiacycloalkadiynes 25−33, 35−37, 39, 40, 42, 44 from Dithiaalkadiynes and Dithiocyanatoalkanes: To a solution of the dithiaalkadiyne in anhydrous THF was added *n*-butyllithium at −25 °C over a period of 15 min. The solution was stirred for 1 h at −25 °C and then allowed to warm up to room temperature. To 1000 mL of anhydrous THF were added solutions of the dilithiated dithiaalkadiyne in THF and the dithiocyanatoalkane in THF dropwise at −40 °C over a period of 8 h. Further workup was carried out as described above for the reaction with dilithium acetylide with dithiocyanatoalkane.

1,4,6,9-Tetrathiacyclododeca-2,7-diyne (25): Starting materials: 1.56 g (10.0 mmol) of 3,7-dithianona-1,8-diyne (**20**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.30 g (10.0 mmol) of dithiocyanatomethane (**11**) in 250 mL of THF. Yield: 349 mg (15%) of **25** as a colorless solid, m.p. 30 °C. − ^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (quint, ^3J = 6.8 Hz, 2 H, SCH_2CH_2), 2.78 (t, ^3J = 6.8 Hz, 4 H, SCH_2CH_2), 3.98 (s, 2 H, SCH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.6 (SCH_2CH_2), 34.3 (SCH_2CH_2), 44.4 (SCH_2S), 85.4 [≡C(s)], 90.4 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1}, 2851, 2061, 1445, 1415, 1356, 1282, 1190, 823, 769, 701. − MS; (EI, 70 eV): 231 [M − H^+], 204 [$M^+ - C_2H_4$], 199 [M^+ − SH], 186, 171, 112, 88, 58. − HRMS; (EI, 70 eV): [M + H^+] calcd. 232.9587; found 232.9566. − $C_8H_8S_4$ (232.4): calcd. C 41.34, H 3.47, S 55.19; found C 41.41, H 3.69, S 55.24.

1,4,6,9-Tetrathiacyclotrideca-2,7-diyne (26): Starting materials: 1.70 g (10.0 mmol) of 3,8-dithiadeca-1,9-diyne (**21**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.30 g (10.0 mmol) of dithiocyanatomethane (**11**) in 250 mL of THF. Yield: 562 mg (23%) of **26** as a colorless solid, m.p. 87 °C (decomposition). − ^1H NMR (500 MHz, $CDCl_3$): δ = 2.06 (m, 4 H, SCH_2CH_2), 2.74 (m, 4 H, SCH_2CH_2), 3.94 (s, 2 H, SCH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 29.0 (SCH_2CH_2), 36.5 (SCH_2CH_2), 45.3 (SCH_2S), 85.0 [≡C(s)], 91.2 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2929, 2061, 1445, 1415, 1355, 1281, 1190, 823, 700. − MS; (EI, 70 eV): 245 [M − H^+], 213 [M^+ − SH], 112, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 245.9665; found 245.9682. − $C_9H_{10}S_4$ (246.5): calcd. C 43.86, H 4.09, S 52.05; found C 44.04, H 4.22, S 52.08.

1,4,6,9-Tetrathiacyclotetradeca-2,7-diyne (27): Starting materials: 1.85 g (10.0 mmol) of 3,9-dithiaundeca-1,10-diyne (**22**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.30 g (10.0 mmol) of dithiocyanatomethane (**11**) in 250 mL of THF. Yield: 510 mg (20%) of **27** as a colorless solid, m.p. 94 °C (decomposition). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (quint, ^3J = 7.0 Hz, 2 H, $SCH_2CH_2CH_2$), 1.88 [tt, $^3J(SCH_2CH_2CH_2)$ = 7.0 Hz, $^3J(SCH_2)$ = 7.0 Hz, 4 H, SCH_2CH_2], 2.74 (t, ^3J = 7.0 Hz, 4 H, SCH_2CH_2), 3.86 (s, 2 H, SCH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 25.3 ($SCH_2CH_2CH_2$), 27.9 (SCH_2CH_2), 35.6 (SCH_2CH_2), 43.2 (SCH_2S), 83.7 [≡C(s)], 91.3 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1}, 2068, 1455, 1420, 1354, 1302, 1272, 1251, 811. − MS; (EI, 70 eV): 259 [M − H^+], 192, 172, 112, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 259.9822; found 259.9817. − $C_{10}H_{12}S_4$ (260.5): calcd. C 46.11, H 4.64, S 49.25; found C 46.27, H 4.69, S 48.99.

1,4,6,9-Tetrathiacyclopentadeca-2,7-diyne (28): Starting materials: 1.98 g (10.0 mmol) of 3,10-dithiadodeca-1,11-diyne (**23**) in 200 mL of THF, 12.5 mL *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.30 g (10.0 mmol) of dithiocyanatomethane (**11**) in 250 mL of THF. Yield: 576 mg (21%) of **28** as a colorless solid, m.p. 72 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 (m, 4 H, $SCH_2CH_2CH_2$), 1.88 (m, 4 H, SCH_2CH_2), 2.64 [t, $^3J(SCH_2CH_2)$ = 7.3 Hz, 4 H, SCH_2CH_2], 3.86 (s, 2 H, SCH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 26.6 ($SCH_2CH_2CH_2$), 28.1 (SCH_2CH_2), 36.1 (SCH_2CH_2), 44.5 (SCH_2S), 84.5 [≡C(s)], 91.7 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 1458, 1415, 1300, 1263, 1199, 722. − MS; (EI, 70 eV): 274 [M^+], 241 [M^+ − SH]. − HRMS; (EI, 70 eV): [M^+] calcd. 273.9978; found 273.9971.

1,4,7,10-Tetrathiacyclododeca-2,8-diyne (29): Starting materials: 1.42 g (10.0 mmol) of 3,6-dithiaocta-1,7-diyne (**19**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.44 g (10.0 mmol) of 1,2-dithiocyanatoethane (**12**) in 250 mL of THF. Yield: 331 mg (14%) of **29** as a colorless solid, m.p. 123 °C (decomposition). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.17 (s, 8 H, CH_2). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 37.1 (CH_2), 86.5 (≡C). − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 1401, 1275, 1122, 1021, 907, 828. − MS; (EI, 70 eV): 232 [M^+], 204 [$M^+ - C_2H_4$], 160, 100, 88. − HRMS; (EI, 70 eV): [$M^+ - C_2H_4$] calcd. 203.9196; found 203.9193. − $C_8H_8S_4$ (232.4): calcd. C 41.34, H 3.47, S 55.19; found C 41.54, H 3.66, S 55.00.

1,4,7,10-Tetrathiacyclotrideca-2,8-diyne (30): Starting materials: 1.50 g (9.6 mmol) of 3,7-dithianona-1,8-diyne (**20**) in 200 mL of THF, 12.0 mL *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.39 g (9.6 mmol) of 1,2-dithiocyanatoethane (**12**) in 250 mL of THF. Yield: 1.27 g (54%) of **30** as a colorless solid, m.p. 119 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (quint, ^3J = 7.5 Hz, 2 H, $SCH_2CH_2CH_2$), 2.76 (t, ^3J = 7.5 Hz, 4 H, $SCH_2CH_2CH_2$), 3.10 (s, 4 H, SCH_2CH_2S). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.7 ($SCH_2CH_2CH_2$), 33.9 ($SCH_2CH_2CH_2$), 37.1 (SCH_2CH_2S), 86.4 [≡C(l)], 87.2 [≡C(s)]. − IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1}, 2065, 1407, 1246, 903, 825, 746. − MS; (EI, 70 eV): 246 [M^+], 218 [$M^+ - C_2H_4$], 190, 174, 118, 112, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 245.9665; found 245.9662. − $C_9H_{10}S_4$ (246.5): calcd. C 43.86, H 4.09, S 52.05; found C 44.05, H 4.10, S 51.79.

1,4,7,10-Tetrathiacyclotetradeca-2,8-diyne (31): Starting materials: 1.70 g (10.0 mmol) of 3,8-dithiadeca-1,9-diyne (**21**) in 200 mL of THF, 12.5 mL *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.44 g (10.0 mmol) of 1,2-dithiocyanatoethane (**12**) in 250 mL of THF. Yield: 1.28 g (49%) of **31** as a colorless solid, m.p. 95 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.00 (m, 4 H, $SCH_2CH_2CH_2$), 2.69 (m, 4 H, $SCH_2CH_2CH_2$), 3.04 (s, 4 H, SCH_2CH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 27.8 ($SCH_2CH_2CH_2$), 35.1 (SCH_2CH_2S), 36.2 ($SCH_2CH_2CH_2$), 85.3 [≡C(s)], 87.7 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1}, 2075, 1439, 1416, 1281, 1199, 755. − MS; (EI, 70 eV): 260 [M^+], 232 [$M^+ - C_2H_4$], 204, 199, 172, 144, 132, 100, 88, 55. − HRMS; (EI, 70 eV): [M^+] calcd. 259.9822; found 259.9831. − $C_{10}H_{12}S_4$ (260.5): calcd. C 46.12, H 4.64, S 49.24; found C 46.25, H 4.63, S 49.07.

1,4,7,10-Tetrathiacyclopentadeca-2,8-diyne (32): Starting materials: 1.85 g (10.0 mmol) of 3,9-dithiaundeca-1,10-diyne (**22**) in 200 mL of THF, 12.5 mL *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.44 g (10.0 mmol) of 1,2-dithiocyanatoethane (**12**) in 250 mL of THF. Yield: 1.57 g (57%) of **32** as a colorless solid, m.p. 84 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.71 (m, 2 H, $SCH_2CH_2CH_2$), 1.84 (m, 4 H, $SCH_2CH_2CH_2$), 2.70 (t, ^3J = 5.9 Hz, 4 H, $SCH_2CH_2CH_2$), 3.00 (s, 4 H, SCH_2CH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 24.9 ($SCH_2CH_2CH_2$), 28.0 ($SCH_2CH_2CH_2$), 36.2 ($SCH_2CH_2CH_2$), 38.1 (SCH_2CH_2S), 86.4 [≡C(s)], 86.9 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1}, 1415, 1298, 1271, 1197. − MS; (EI, 70 eV): 274 [M^+], 246 [$M^+ - C_2H_4$], 241 [M^+ − SH], 218, 190, 172, 144, 100, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 273.9978; found 273.9948. − $C_{11}H_{14}S_4$ (274.5): calcd. C 48.14, H 5.14, S 46.72; found C 48.26, H 5.13, S 46.88.

1,4,7,10-Tetrathiacyclohexadeca-2,8-diyne (33): Starting materials: 1.98 g (10.0 mmol) of 3,10-dithiadodeca-1,11-diyne (**23**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.44 g (10.0 mmol) of 1,2-dithiocyanatoethane (**12**) in 250 mL of THF. Yield: 1.39 g (48%) of **33** as a colorless solid, m.p. 91 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (m, 4 H, $SCH_2CH_2CH_2$), 1.83 (m, 4 H, $SCH_2CH_2CH_2$), 2.62 (t, ^3J = 6.6 Hz, 4 H, $SCH_2CH_2CH_2$), 3.00 (s, 4 H, SCH_2CH_2S). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.0 ($SCH_2CH_2CH_2$), 28.9 ($SCH_2CH_2CH_2$), 35.7 (SCH_2CH_2S), 36.1 ($SCH_2CH_2CH_2$), 85.0 [≡C(s)], 87.7 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1}, 2852, 2068, 1450, 1213. − MS; (EI, 70 eV): 288 [M^+], 260 [$M^+ - C_2H_4$], 255 [M^+ − SH], 218, 204, 190, 174, 100, 88, 55. − HRMS; (EI, 70 eV): [M^+] calcd. 288.0135; found 288.0138. − $C_{12}H_{16}S_4$ (288.5): calcd. C 49.96, H 5.59, S 44.45; found C 49.97, H 5.65, S 44.36.

1,4,8,11-Tetrathiacyclopentadeca-2,9-diyne (35): Starting materials: 1.50 g (9.6 mmol) of 3,7-dithianona-1,8-diyne (**20**) in 200 mL of THF, 12.0 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.65 g (9.6 mmol) of 1,4-dithiocyanatobutane (**14**) in 250 mL of THF. Yield: 950 mg (36%) of **35** as a colorless solid, m.p. 166 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (m, 4 H, $SCH_2CH_2CH_2CH_2$), 2.30 (quint., ^3J = 7.8 Hz, 2 H, $SCH_2CH_2CH_2S$), 2.70 (m, 8 H, SCH_2). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 29.4 ($SCH_2CH_2CH_2CH_2$), 30.5 ($SCH_2CH_2CH_2S$), 34.7 ($SCH_2CH_2CH_2S$), 36.9 ($SCH_2CH_2CH_2CH_2$), 85.7 [≡C(s)], 87.8 [≡C(l)]. − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2070, 1449, 1414, 1326, 1294, 733. − MS; (EI, 70 eV): 273 [M − H^+], 241 [M^+ − SH], 227, 213, 186, 153, 112, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 273.9978; found 273.9959. − $C_{11}H_{14}S_4$ (274.5): calcd. C 48.14, H 5.14, S 46.72; found C 48.17, H 5.08, S 46.58.

1,4,8,11-Tetrathiacyclohexadeca-2,9-diyne (36): Starting materials: 1.45 g (9.3 mmol) of 3,7-dithianona-1,8-diyne (**20**) in 200 mL of THF, 11.6 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.64 g (8.8 mmol) of 1,5-dithiocyanatopentane (**15**) in 250 mL of THF. Yield: 964 mg (38%) of **36** as a colorless solid, m.p. 89 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.64 (m, 2 H, $SCH_2CH_2CH_2CH_2$), 1.88 (m, 4 H, $SCH_2CH_2CH_2CH_2$), 2.28 (m, 2 H, $SCH_2CH_2CH_2S$), 2.67 (m, 8 H, SCH_2). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 26.4 ($SCH_2CH_2CH_2CH_2$), 28.6 ($SCH_2CH_2CH_2CH_2$), 30.8 ($SCH_2CH_2CH_2S$), 35.2 ($SCH_2CH_2CH_2S$), 36.2 ($SCH_2CH_2CH_2CH_2$), 85.9/86.9 (≡C). − IR (KBr): $\tilde{\nu}$ = 2931 cm^{-1}, 2075, 1418, 1304, 1264, 1246, 1036, 737. − MS; (EI, 70 eV): 288 [M^+], 255 [M^+ − SH], 219, 186, 153, 130, 112, 88, 58. − HRMS; (EI, 70 eV): [M^+] calcd. 288.0135; found 288.0132. − $C_{12}H_{16}S_4$ (288.5): calcd. C 49.95, H 5.59, S 44.46; found C 50.03, H 5.52, S 44.36.

1,4,8,11-Tetrathiacycloheptadeca-2,9-diyne (37): Starting materials: 1.50 g (9.6 mmol) of 3,7-dithianona-1,8-diyne (**20**) in 200 mL of THF, 12.0 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.92 g (9.6 mmol) of 1,6-dithiocyanatohexane (**16**) in 250 mL of THF. Yield: 734 mg (25%) of **37** as a colorless solid, m.p. 59 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (m, 4 H, $SCH_2CH_2CH_2CH_2$), 1.83 (m, 4 H, $SCH_2CH_2CH_2CH_2$), 2.23 (m, 2 H, $SCH_2CH_2CH_2S$), 2.62 (t, ^3J = 7.1 Hz, 4 H,

$SCH_2CH_2CH_2CH_2$), 2.69 (t, ^3J = 7.5 Hz, 4 H, $SCH_2CH_2CH_2S$). – ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.2 ($SCH_2CH_2CH_2CH_2$), 29.4 ($SCH_2CH_2CH_2CH_2$), 31.1 ($SCH_2CH_2CH_2S$), 35.3 ($SCH_2CH_2CH_2S$), 36.5 ($SCH_2CH_2CH_2CH_2$), 85.9 [≡C(s)], 87.7 [≡C(l)]. – IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1}, 2852, 2073, 1448, 1416, 1263, 726. – MS; (EI, 70 eV): 302 [M^+], 269 [M^+ – SH], 241, 218, 186, 118, 102, 88, 55. – HRMS; (EI, 70 eV): [M^+] calcd. 302.0291; found 302.0277. – $C_{13}H_{18}S_4$ (302.6): calcd. C 51.61, H 6.00, S 42.39; found C 51.69, H 6.01, S 42.55.

1,4,9,12-Tetrathiacycloheptadeca-2,10-diyne (39): Starting materials: 1.40 g (8.22 mmol) of 3,8-dithiadeca-1,9-diyne (**21**) in 200 mL of THF, 10.3 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.53 g (8.21 mmol) of 1,5-dithiocyanatopentane (**15**) in 250 mL of THF. Yield: 960 mg (39%) of **39** as a colorless solid, m.p. 75 °C. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.62 (quint., ^3J = 7.1 Hz, 2 H, $SCH_2CH_2CH_2CH_2CH_2$), 1.86 (m, 4 H, $SCH_2CH_2CH_2CH_2CH_2$), 1.96 (m, 4 H, $SCH_2CH_2CH_2CH_2S$), 2.64 (t, ^3J = 7.0 Hz, 4 H, $SCH_2CH_2CH_2CH_2CH_2$), 2.70 (m, 4 H, $SCH_2CH_2CH_2CH_2S$). – ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 26.7 ($SCH_2CH_2CH_2CH_2CH_2$), 28.1 ($SCH_2CH_2CH_2CH_2S$), 29.5 ($SCH_2CH_2CH_2CH_2CH_2$), 36.1 ($SCH_2CH_2CH_2CH_2CH_2$), 36.8 ($SCH_2CH_2CH_2CH_2S$), 86.7/86.8 (≡C). – IR (KBr): $\tilde{\nu}$ = 2931 cm^{-1}, 2854, 2074, 1454, 1416, 1282, 1226, 732, 700. – MS; (EI, 70 eV): 302 [M^+], 269 [M^+ – SH], 233, 214, 200, 172, 146, 101, 88. – HRMS; (EI, 70 eV): [M^+] calcd. 302.0291; found 302.0292. – $C_{13}H_{18}S_4$ (302.6): calcd. C 51.61, H 6.00, S 42.39; found C 51.79, H 6.00, S 42.17.

1,4,9,12-Tetrathiacyclooctadeca-2,10-diyne (40): Starting materials: 1.40 g (8.22 mmol) of 3,8-dithiadeca-1,9-diyne (**21**) in 200 mL of THF, 10.3 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 1.65 g (8.24 mmol) of 1,6-dithiocyanatohexane (**16**) in 250 mL of THF. Yield: 1.13 g (43%) of **40** as a colorless solid, m.p. 47 °C. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.54 (m, 4 H, $SCH_2CH_2CH_2CH_2CH_2CH_2$), 1.82 (m, 4 H, $SCH_2CH_2CH_2CH_2CH_2$), 1.97 (m, 4 H, $SCH_2CH_2CH_2CH_2S$), 2.64 (t, ^3J = 6.8 Hz, 4 H, $SCH_2CH_2CH_2CH_2CH_2$), 2.67 (m, 4 H, $SCH_2CH_2CH_2CH_2S$). – ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 27.7 ($SCH_2CH_2CH_2CH_2S$), 28.5 ($SCH_2CH_2CH_2CH_2CH_2$), 29.7 ($SCH_2CH_2CH_2CH_2CH_2$), 36.1 ($SCH_2CH_2CH_2CH_2S$), 36.6 ($SCH_2CH_2CH_2CH_2CH_2$), 86.3 [≡C(s)], 87.0 [≡C(l)]. – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2852, 1419, 1271, 907, 777, 730. – MS; (EI, 70 eV): 316 [M^+], 283 [M^+ – SH], 255, 228, 200, 159, 146, 112, 88, 55. – HRMS; (EI, 70 eV): [M^+] calcd. 316.0448; found 316.0448. – $C_{14}H_{20}S_4$ (316.6): calcd. C 53.11, H 6.37, S 40.52; found C 53.18, H 6.35, S 40.24.

1,4,10,13-Tetrathiacyclononadeca-2,11-diyne (42): Starting materials: 1.85 g (10.0 mmol) of 3,9-dithiaundeca-1,10-diyne (**22**) in 200 mL of THF, 12.5 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 2.00 g (10.0 mmol) of 1,6-dithiocyanatohexane (**16**) in 250 mL of THF. Yield: 1.51 g (46%) of **42** as a colorless solid, m.p. 132 °C. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.53 (m, 6 H, $SCH_2CH_2CH_2CH_2CH_2S$ and $SCH_2CH_2CH_2CH_2CH_2CH_2$), 1.82 (m, 8 H, m, 6 H, $SCH_2CH_2CH_2CH_2CH_2S$ and $SCH_2CH_2CH_2CH_2CH_2CH_2$), 2.63 (m, 8 H, SCH_2). – ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.0 ($SCH_2CH_2CH_2CH_2CH_2S$), 28.9 ($SCH_2CH_2CH_2CH_2CH_2CH_2$), 30.0 ($SCH_2CH_2CH_2CH_2CH_2S$), 30.3 ($SCH_2CH_2CH_2CH_2CH_2CH_2$), 36.2 ($SCH_2CH_2CH_2CH_2CH_2S$), 37.0 ($SCH_2CH_2CH_2CH_2CH_2CH_2$), 86.2 [≡C(s)], 87.1 [≡C(l)]. – IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1}, 2854, 1458, 1414, 1231. – MS; (EI, 70 eV): 330 [M^+], 297 [M^+ – SH], 228, 214, 160, 146, 101, 88, 55. – HRMS; (EI, 70 eV): [M^+] calcd. 330.0604; found 330.0618. – $C_{15}H_{22}S_4$ (330.6): calcd. C 54.50, H 6.71, S 38.79; found C 54.50, H 6.59, S 38.55.

Table 3. Crystallographic data of **26**–**31**

Compound	**26**	**27**	**28**	**29**	**30**	**31**
Empirical formula	$C_9H_{10}S_4$	$C_{10}H_{12}S_4$	$C_{11}H_{14}S_4$	$C_8H_8S_4$	$C_9H_{10}S_4$	$C_{10}H_{12}S_4$
Molecular mass [g/mol]	246.5	260.5	274.5	232.4	246.5	260.5
Crystal size [mm]	0.46×0.26×0.16	0.28×0.28×0.04	0.30×0.25×0.10	0.46×0.42×0.32	0.46×0.22×0.11	0.37×0.24×0.21
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Crystal shape	polyhedron	plate	polyhedron	polyhedron	polyhedron	polyhedron
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$Cmc2_1$	$P\bar{1}$	$P2_1/n$	$P2_1$	$P2_1/n$
a [Å]	8.1588(3)	15.4588(4)	5.0718(5)	6.2778(5)	5.2233(3)	12.7402(3)
b [Å]	15.2742(6)	9.9164(2)	7.8019(8)	8.9738(7)	11.5419(7)	10.8240(3)
c [Å]	9.2466(4)	7.8405(2)	8.9096(9)	8.9577(7)	18.498(1)	17.9252(4)
α [°]	90	90	102.586(1)	90	90	90
β [°]	107.135(1)	90	103.326(1)	104.350(1)	91.266(1)	93.405(1)
γ [°]	90	90	91.482(1)	90	90	90
V [Å^3]	1101.16(8)	1201.91(5)	333.74(6)	488.89(7)	1114.9(1)	2467.5(1)
$D_{calcd.}$ [Mg/m^3]	1.486	1.439	1.366	1.579	1.468	1.402
Z	4	4	1	2	4	8
F(000)	512	544	144	240	512	1088
Temperature [K]	200(2)	200(2)	200(2)	173(2)	200(2)	173(2)
h_{min}/h_{max}	−9/9	−18/18	−6/6	−8/8	−6/6	−16/16
k_{min}/k_{max}	−18/17	−11/11	−9/8	0/11	−13/13	0/14
l_{min}/l_{max}	−10/10	−9/8	−10/10	0/11	−21/21	0/23
μ [mm^{-1}]	0.813	0.749	0.678	0.910	0.803	0.730
Refl. collected	8029	4325	2534	3242	8329	21481
Refl. unique	1905	1075	1968	1165	3722	5966
Refl. observed	1784	1028	1920	1136	3632	4972
Variables	158	95	192	71	235	349
$R(F)$	0.029	0.022	0.020	0.026	0.020	0.027
$R_w(F^2)$	0.069	0.054	0.053	0.074	0.051	0.069
S (Gof) on F^2	1.10	1.05	1.09	1.11	1.13	1.01
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.36	0.43	0.19	0.60	0.16	0.28
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.34	−0.15	−0.14	−0.25	−0.25	−0.24

Table 4. Crystallographic data of **32**−**34** and **36**−**38**

Compound	**32**	**33**	**34**	**36**	**37**	**38**
Empirical formula	$C_{11}H_{14}S_4$	$C_{12}H_{16}S_4$	$C_{10}H_{12}S_4$	$C_{12}H_{16}S_4$	$C_{13}H_{18}S_4$	$C_{12}H_{16}S_4$
Molecular mass [g/mol]	274.5	288.5	260.5	288.5	302.6	288.5
Crystal size [mm]	0.32×0.28×0.24	0.38×0.26×0.10	0.25×0.25×0.10	0.26×0.38×0.42	0.48×0.30×0.20	0.38×0.34×0.34
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Crystal shape	plate	polyhedron	polyhedron	polyhedron	prism	polyhedron
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1$	$P2_1/c$	*Pnma*	$Pca2_1$	$P2_1/c$
a [Å]	9.311(3)	5.6479(1)	4.5519(2)	8.9355(5)	15.990(4)	12.1514(1)
b [Å]	10.215(3)	15.1633(3)	13.2144(5)	16.9866(9)	10.450(2)	13.19.58(1)
c [Å]	28.69(1)	8.569(1)	9.9309(3)	9.2762(5)	18.850(5)	9.7243(1)
α [°]	90	90	90	90	90	90
β [°]	90	96.960(1)	96.852(1)	90	90	107.67(1)
γ [°]	90	90	90	90	90	90
V [Å^3]	2729(1)	728.5(1)	593.08(4)	1408.0(1)	3150(1)	1485.73(2)
$D_{calcd.}$ [Mg/m^3]	1.34	1.315	1.458	1.361	1.28	1.290
Z	8	2	2	4	8	4
F(000)	1152	304	272	608	1280	608
Temperature [K]	253(2)	200(2)	200(2)	173(2)	293(2)	200(2)
h_{min}/h_{max}	0/12	−6/6	−5/5	0/11	0/21	−14/14
k_{min}/k_{max}	0/13	−17/18	−15/15	0/22	0/13	−15/15
l_{min}/l_{max}	0/37	−9/9	−11/11	0/12	−24/0	−11/11
μ [mm^{-1}]	0.66	0.625	0.759	0.647	0.58	0.613
Refl. collected	3280	5405	4277	9419	3899	10880
Refl. unique	3280	2276	1033	1775	3899	2569
Refl. observed	1970	2199	929	1651	2470	2185
Variables	192	209	88	116	307	209
R(*F*)	0.033	0.020	0.023	0.032	0.038	0.031
$R_w(F^2)$	0.081	0.049	0.062	0.086	0.090	0.076
S (Gof) on F^2	0.99	1.06	1.08	1.04	1.02	1.05
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.24	0.16	0.25	0.61	0.25	0.32
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.27	−0.12	−0.23	−0.29	−0.23	−0.44

Table 5. Crystallographic data of **39**−**44**

Compound	**39**	**40**	**41**	**42**	**43**	**44**
Empirical formula	$C_{13}H_{18}S_4$	$C_{14}H_{20}S_4$	$C_{14}H_{20}S_4$	$C_{15}H_{22}S_4$	$C_{16}H_{24}S_4$	$C_{12}H_{16}O_2S_4$
Molecular mass [g/mol]	302.6	316.6	316.6	330.6	344.8	320.5
Crystal size [mm]	0.38×0.29×0.07	0.28×0.16×0.05	1.00×0.10×0.04	0.34×0.23×0.16	0.50×0.34×0.27	0.28×0.26×0.24
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Crystal shape	polyhedron	polyhedron	needle	polyhedron	polyhedron	polyhedron
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Fdd*2	$P2_1/c$
a [Å]	4.8369(1)	11.6300(8)	4.6068(3)	9.511(1)	20.3154(4)	10.4706(1)
b [Å]	14.5765(3)	12.3704(9)	17.056(1)	10.7159(1)	34.0337(6)	10.1634(1)
c [Å]	10.7460(3)	11.1893(8)	10.0169(6)	17.0341(2)	5.2874(1)	14.7718(1)
α [°]	90	90	90	90	90	90
β [°]	96.702(1)	99.462(1)	92.982(1)	95.084(1)	90	104.24(1)
γ [°]	90	90	90	90	90	90
V [Å^3]	752.47(3)	1587.9(2)	786.02(8)	1729.23(3)	3655.7(1)	1523.64(2)
$D_{calcd.}$ [Mg/m^3]	1.335	1.324	1.337	1.270	1.252	1.397
Z	2	4	2	4	8	4
F(000)	320	672	336	704	1472	672
Temperature [K]	173(2)	200(2)	200(2)	200(2)	173(2)	200(2)
h_{min}/h_{max}	−6/6	−13/14	−5/5	−11/11	0/26	−13/13
k_{min}/k_{max}	0/19	−14/14	−19/19	−12/12	0/44	−13/13
l_{min}/l_{max}	0/14	−13/13	−11/11	−20/20	−7/7	−19/19
μ [mm^{-1}]	0.608	0.580	0.586	0.535	0.509	0.615
Refl. collected	6967	11548	5680	12740	12111	15312
Refl. unique	3581	2758	1356	3026	2237	3497
Refl. observed	3203	2077	1126	2450	2194	3077
Variables	229	243	122	200	139	227
R(*F*)	0.030	0.031	0.039	0.049	0.022	0.028
$R_w(F^2)$	0.073	0.064	0.095	0.145	0.057	0.071
S (Gof) on F^2	1.04	1.02	1.04	1.06	1.06	1.06
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.49	0.26	0.38	0.52	0.27	0.26
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.24	−0.22	−0.31	−0.36	−0.15	−0.29

7,16-Dioxa-1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (44): Starting materials: 466 mg (2.5 mmol) of 6-oxa-3,9-dithiaundeca-1,10-diyne (**24**) in 200 mL of THF, 3.3 mL of *n*-butyllithium (1.6 M solution in *n*-hexane) and 470 mg (2.5 mmol) of bis(2-thiocyanatoethyl) ether (**17**) in 250 mL of THF. After flash filtration with toluene the pure compound was obtained. Yield: 439 mg (55%) of **44** as a colorless solid, m.p. 138 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.82 (t, ^3J = 6.7 Hz, 8 H, CH_2S), 3.84 (t, ^3J = 6.7 Hz, 8 H,CH_2O). − ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 35.6 (CH_2S), 70.1 (CH_2O), 86.2 (≡C). − IR (KBr): $\tilde{\nu}$ = 2882 cm^{-1}, 2858, 1355, 1292, 1107, 1035, 1009. − MS; (EI, 70 eV): 320 [M^+], 287 [M^+ − SH], 216, 188, 146, 112, 88. − HRMS; (EI, 70 eV): [M^+] calcd. 320.0033; found 320.0024. − $C_{12}H_{16}O_2S_4$ (320.5): calcd. C 44.97, H 5.03, O 9.98, S 40.02; found C 44.93, H 5.03, S 39.92.

X-ray Diffraction Analyses: The reflections were collected with a Nonius-CAD4 diffractometer (**32**, **37**) and a Siemens CCD diffractometer (**26**−**31**, **33**−**36**, **38**−**44**) (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods (**34**: SHELXS-86;[21] **26**−**33**, **36**−**44**: SHELXS-97[22]). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were either refined isotropically (**26**−**29**, **31**−**36**, **38**, **40**, **43**, **44**) or calculated according to stereochemical aspects (**30**, **37**, **39**, **41**, **42**). The carbon atom C-7 in compound **36** was refined at two positions (88 and 12% multiplicity). In **39** the butano moiety and the adjacent sulfur and sp carbon atoms are disordered with approximately 50% multiplicity. In **42** the pentano and hexano moieties are disordered with 86 and 14% multiplicity. Refinement was carried out with SHELXL-93[23] (**34**) and SHELXL-97[24] (**26**−**33**, **36**−**44**). Table 3, Table 4, and Table 5 contain the crystallographic data and details of the refinement procedure. ORTEP drawings were obtained using the ORTEP-3 for Windows program[25] by L. Farrugia. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk], on quoting the deposition number CCDC-138421 (**26**), -138422 (**27**), -138423 (**28**), -138424 (**29**), -138425 (**30**), -138426 (**31**), -138427 (**32**), -138428 (**33**), -138429 (**34**), -138430 (**36**), -138431 (**37**), -138432 (**38**), -138433 (**39**), -138434 (**40**), -138435 (**41**), -138436 (**42**), -138437 (**43**), -138438 (**44**).

Computational Details: The geometries of **28**−**48** were fully optimized with GAUSSIAN98[16] at the density functional (B3LYP) or Hartree−Fock (HF) level of theory using the split-valence 6-31G* basis set. The electronic structures were analyzed by means of a natural bond orbital (NBO) analysis.[26]

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