Tethered Dithiacyclopropenones. Syntheses and Structural Properties of Tetrathiacyclopropenonophanes

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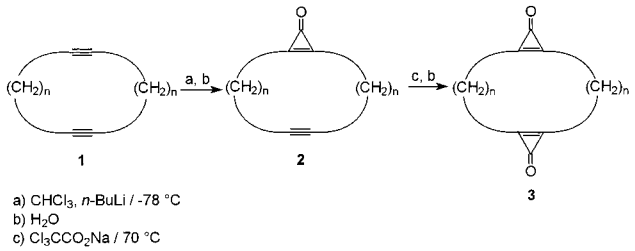
Received December 11, 2000

The reaction of the cyclic tetrathiadiynes **4(m.n)** (where **m** and **n** indicate the number of methylene groups between the dithiaacetylene units) with sodium trichloroacetate and subsequent hydrolysis of the *gem*-dichlorocyclopropenes afforded the mono- and biscyclopropenone derivatives **5(m.n)** and **6(m.n)** in moderate yields. Investigation of the X-ray crystal structures revealed small torsion angles between the CH_2−S bond and the C−C double bond, indicating conjugation between the sulfur 3p lone pair and the cyclopropenone ring. The maintenance of the conjugation determines the secondary structure of both (**5**, **6**) ring systems.

Introduction

Since the first synthesis of [2.2]paracyclophane,[1] the cyclophane chemistry has grown into several branches: the benzene rings have been replaced by other aromatic systems,[2−4] and the bridges have been increased to generate organic receptors[3,4] and container molecules,[5] to name only a few examples. In the most of these cases the aromatic building blocks were either the well-known five-membered 6π-heterocycles,[2] benzene and larger benzenoid and nonbenzenoid aromatic systems.[2−4] Cyclophanes with rings smaller than five have been investigated relatively late.[6] Cyclophanes with cyclopropenone rings as building blocks have become available from cyclic diynes and carbenes (see Scheme 1).[7] However, the yields, especially of double-decked [*n.n*]cyclopropenonophanes were low due to a number of side reactions[7] which are partly due to the kinetic instability of the cyclopropenone ring[8] and partly to the activation of the reactivity of the methylene groups next to the cyclopropenone ring.[7a] The kinetic stability of the cyclopropenone ring system can be increased by substitution with electron-donating or bulky groups. The first cyclopropenone derivative to be reported in the literature was diphenylcyclopropenone.[9]

Scheme 1



In addition to the synthesis of further aryl- and alkyl-substituted derivatives,[10] cyclopropenones bearing electron-donating substituents such as alkoxy, dialkylamino, and alkylthio groups have been reported.[11,12]

We recently reported a series of compounds in which two cyclopropenone rings were tethered by alkyl chains (**3**). These cyclophanes were available via a two-step sequence.[7b] In the first step one triple bond of the diyne **1** was reacted with chloroform/*n*-butyllithium in THF at −78 °C followed by hydrolysis to yield **2**. The second cyclopropenone unit was introduced by heating **2** with the sodium salt of trichloroacetic acid and subsequent hydrolysis. The resulting [*n.n*]cyclopropenonophanes **3** (Scheme 1) are crystalline, fairly stable species.

The recent availability of cyclic tetrathiadiynes[13] opens the possibility of extending the family of cyclopropenonophanes by synthesis of species containing dithioalkyl tethers. In this paper we report our experimental studies on tetrathiacyclopropenonophanes.

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Published on Web 04/14/2001

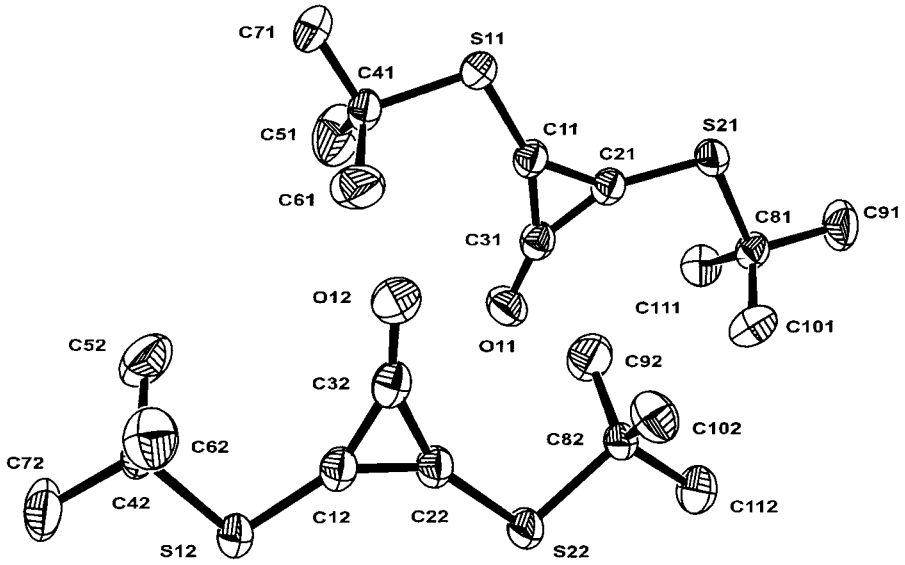
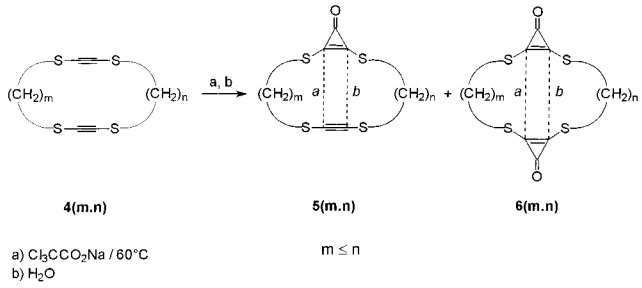


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **7**.

Scheme 2



Results

Syntheses. The starting point of our syntheses were the recently synthesized tetrathiacyclodiynes **4(m.n)** (Scheme 2).[13] The reaction of **4(m.n)** with dichlorocarbene, generated in situ from $CHCl_3$/*n*-butyllithium at −78 °C in THF,[7,14] gave only trace amounts of the monocyclopropenone derivative **5(m.n)**. Our efforts were more successful when we heated **4** with an excess of the sodium salt of trichloroacetic acid at 60 °C in DME. After hydrolysis of the *gem*-dichlorocyclopropenes, the products **5** and **6** were obtained in yields between 5% and 10%. Utilizing this method we prepared **5(3.4)**, **5(4.5)**, and **5(6.6)** as well as **6(3.5)**, **6(4.6)**, **6(5.5)**, **6(5.6)**, and **6(6.6)**. The structures of all eight compounds were assigned unequivocally by NMR studies. Furthermore, the new compounds show absorptions in the IR spectrum (1849−1860 cm^{-1} and 1499−1518 cm^{-1}) which are characteristic for substituted cyclopropenones.[12,15]

X-ray Investigations. Before presenting the X-ray crystal structures of **5(m.n)** and **6(m.n)**, we discuss the structure of a simple model compound bis(*tert*-butylthio)-cyclopropenone (**7**).[12] X-ray investigations on single crystals of **7** reveal two independent molecules in the unit cell. The molecular structure of both is shown in Figure 1; relevant geometrical parameters are given in Table 1. It is noteworthy that the torsional angle C−S−C=C varies only between 1° and 6°. This can be rationalized by assuming a conjugation between the 3p lone pair at the sulfur center and the cyclopropenone ring. To substantiate this explanation, we have carried out quantum chemical calculations on bis(methylthio)cyclopropenone (**8**) by using the DFT (B3LYP) method[16] applying a 6-311

Table 1. Comparison between Selected Experimental Determined Distances (Å) and Torsion Angles (deg) of 7 with Calculated Values for 8a

	7	8a
	Distances (Å)	
C−O	1.216(3)	1.204
	1.213(3)	
C=C	1.366(3)	1.363
	1.363(3)	
S−C (sp^2)	1.710(2)	1.725
	1.712(2)	
	1.708(2)	
	1.709(2)	
	Torsion Angles (deg)	
C−S−C−C	1.1(3)	0
	2.0(3)	
	3.9(3)	
	6.3(3)	

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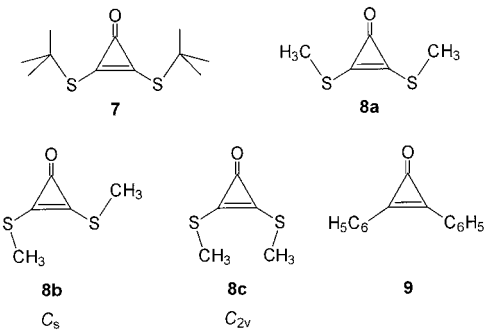
G* basis set.[17] The computations were carried out with the Gaussian 98 program[18] by optimizing all geometrical



parameters of **8**. Frequency calculations were carried out to characterize the nature of the stationary points. It was found that **8a** represents the global minimum of the potential surface. Local minima were **8b** and **8c** which were 3.6 kJ/mol (**8b**) and 15.0 kJ/mol (**8c**) higher in energy. The activation energy for transforming **8a** to **8b** and **8b** to **8c** was calculated to be 27.1 and 30.0 kJ/mol, respectively. The preference for planar conformations **8a**−**c** is due to conjugation between the 3p orbitals on the sulfur substituents and the cyclopropenone moiety, which is optimal for **8a**. Due to the conjugation between the sulfur atom and the adjacent sp^2 carbon atom, the bond index[19] of the S−C(sp^2) bond amounts to 1.14. It decreases to 1.02 when the methyl group adopts a conformation perpendicular to the molecular plane of the cyclopropenone ring. The geometrical parameters calculated for **8a** compare very well with those obtained for **7** (Table 1).

There are only three reports in the literature dealing with X-ray investigations on cyclopropenone derivatives without complexation or hydrogen bonds: diphenylcyclopropenone (**9**),[20] **2** ($n = 3$),[7b] and **3** ($n = 3$).[7c] With the exception of deltic acid[21] (which shows intermolecular hydrogen bonding between the OH groups and the CO group), no X-ray results are reported for heterosubstituted cyclopropenone derivatives. A comparison between the X-ray data of **7** and those reported in the literature for **2** ($n = 3$),[7b] **3** ($n = 3$),[7c] and **9**[20] reveals only small differences. The bond lengths of the various double bonds in the three-membered rings were found to be slightly shorter (1.349(1) Å in **9**, 1.351(2) Å in **2** ($n = 3$), and 1.357(1) Å in **3** ($n = 3$)) than in **7**, whereas the lengths of the CO bonds were slightly longer (1.225(1) Å in **9**,[20] 1.221(2) Å in **2** ($n = 3$),[3b] and 1.226(2) Å in **3** ($n = 3$)).[7c]

In the cases of **5(3.4)**, **5(4.5)**, **5(6.6)**, as well as **6(3.5)**, **6(4.6)**, and **6(5.5)** we were able to grow single crystals which were suitable for X-ray investigations. In Figure 2 the molecular structure of the monocyclopropenone **5(3.4)** is shown. In Table 2 we compare the most relevant distances and angles of the monocyclopropenone derivatives **5**. The most salient features are the large torsion angles between the CH_2−S···S−CH_2 bonds tied to the triple bond which vary between 73° and 85°. Similar values have been observed in **4**.[13] These values are due to the repulsion between the 3p lone pairs of the sulfurs and the π-MOs of the triple bond.[13] Also important for the conformations of **5** are small torsion angles (0° to 18°) between the H_2C−S bonds adjacent to the three-membered ring and the C−C double bond. These values are due to conjungation effects between the sulfur centers and the cyclopropenone unit as discussed for **8**. Together with the cyclopropenone ring, the two S−CH_2−R groups may adopt either a local C_{2v} (**5(4.5)**, **5(6.6)**) or a C_s (**5(3.4)**) symmetry. The flexible alkyl tethers adopt mainly a *zigzag* conformation, and the triple bonds slightly deviate from 180° by 2° to 7°, in accord with the properties of **3** and other alkynes of medium and large ring size.[22] As a result of the factors discussed above, it is anticipated that the transannular distances *a* and *b* (see Scheme 2) increase with increasing ring size.

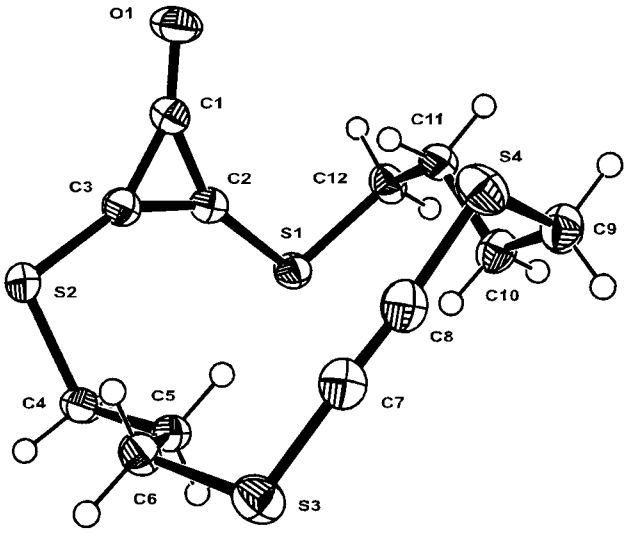


Figure 2. ORTEP plot (50% ellipsoid probability) of the molecular structure of **5(3.4)**.

Table 2. Most Relevant Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of 5(3.4), 5(4.5), and 5(6.6)[a]

	5(3.4)	5(4.5)	5(6.6)
	Distances (Å)		
a	4.899(3)	5.251(2)	7.408(4)
b	4.746(3)	5.332(2)	7.505(4)
C=O	1.220(3)	1.222 (2)	1.213(3)
C=C	1.358(3)	1.373(2)	1.366(3)
S−C (sp^2)	1.717(2)	1.710(2)	1.699(2)
	1.714(3)	1.709(2)	1.708(2)
S−C (sp)	1.686(3)	1.681(2)	1.677(3)
	1.680(3)	1.693(2)	1.672(3)
	Bond Angles (deg)		
C≡C−S	177.9(4)	173.7(2)	176.1(3)
	173.0(4)	176.3(1)	178.2(3)
	Torsion Angles (deg)		
C−S−C=C	10.1(4)	1.9(2)	4.3(3)
	17.6(4)	0.1(2)	8.0(4)
C_{sp^2}−C_{sp^2}···C_{sp}−C_{sp}	49.9(2)	27.3(1)	55.9(2)
C_{sp^3}−S···S−C_{sp^3}	84.6(1)	72.6(1)	75.8(1)

[a] The intramolecular distances *a* and *b* are defined in Scheme 2.

An example of a biscyclopropenone derivative is shown in Figure 3 as determined for **6(4.6)**, where two modifications **a** and **b** could be detected and isolated. Table 3 lists the most relevant bond distances and angles of **6**. The most salient feature of these compounds are the small torsion angles between the H_2C−S bonds and the neighboring C−C double bond, as already encountered in the monocyclopropenones **5** and **7**. The torsion angles be-

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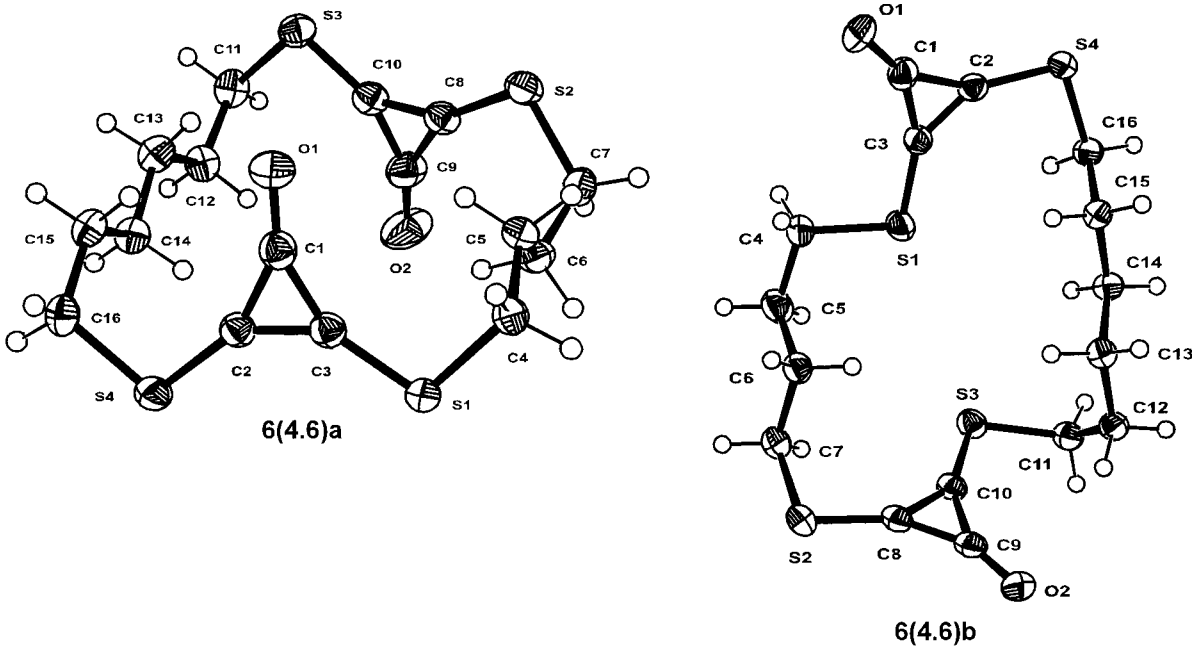

Figure 3. ORTEP plots (50% ellipsoid probability) of the molecular structures of **6(4.6)a** and **6(4.6)b**.

Table 3. Most Relevant Distances (Å) and Torsion Angles (deg) of 6(3.5), 6(4.6)a 6(4.6)b and 6(5.5)[a]

	6(3.5)	6(4.6)a	6(4.6)b	6(5.5)
	Distances (Å)			
a	5.264(2)	5.337(2)	6.845(4)	5.454(2)
b	4.738(2)	5.864(2)	7.294(4)	6.524(2)
C=O	1.218(2)	1.219(2)	1.221(3)	1.217(2)
	1.218(2)	1.220(2)	1.220(3)	1.216(2)
C=C	1.368(2)	1.361(2)	1.361(4)	1.369(2)
	1.366(2)	1.361(2)	1.367(4)	1.366(2)
S−C (sp^2)	1.707(2)	1.709(2)	1.720(3)	1.711(2)
	1.712(2)	1.710(2)	1.711(3)	1.712(2)
	1.703(2)	1.710(2)	1.712(3)	1.705(2)
	1.701(2)	1.712(2)	1.713(3)	1.702(2)
	Torsion Angles (deg)			
C−S−C=C	4.8(2)	0.6(2)	1.3(4)	4.0(2)
	5.0(3)	5.7(2)	4.6(4)	5.6(3)
	15.5(2)	7.0(3)	6.4(4)	6.3(2)
	14.2(2)	10.4(3)	9.9(4)	7.5(3)
$C_{sp^2}-C_{sp^2}\cdots C_{sp^2}-C_{sp^2}$	71.7(1)	1.9(2)	48.9(3)	74.6(2)

[a] The intramolecular distances *a* and *b* are defined in Scheme 2.

tween the C−C double bonds of the two cyclopropenone rings vary considerably. In the resulting structures the methylene chains mainly adopt a *zigzag* conformation. In view of the calculations, it is interesting to note that in the solid state the thioalkyl substituents adopt a local C_{2v} symmetry only in **6(4.6)a**, whereas in all other structures **6(3.5)**, **6(5.5)**, and **6(4.6)b** the local symmetry adopted by the substituted cyclopropenone ring is C_s as shown in **8b**. The bond distances within the cyclopropenone rings in **5(3.4)**, **5(4.5)**, and **5(6.6)** (Table 2) as well as **6(3.5)**, **6(4.6)**, and **6(5.5)** (Table 3) are close to those found for **7**.

Conclusions

Reaction of dichlorocarbene in a nonbasic medium with cyclic tetrathiadiynes followed by hydrolysis yields mono- and biscyclopropenones in which the cyclopropenone ring is substituted with two thiaalkyl groups. The coplanarity of the thiaalkyl groups with the cyclopropenone ring strongly influences the conformation of the ring systems of **5** and **6**. The conformations reported for **5** and **6** might change in solution as a consequence of the easy bond rotation of the C−C and C−S bonds.

Experimental Section

General Methods. All reactions were conducted in oven-dried glassware under an argon atmosphere with magnetic stirring. DME was dried with sodium/benzophenone and distilled under argon before use. Melting points are uncorrected. Materials used for column chromatography: neutral alumina (Merck). ^{1}H NMR and ^{13}C NMR were recorded either at 300 and 500 MHz (^{1}H NMR) or 75.5 and 125.8 MHz (^{13}C NMR), respectively, using the solvent as internal standard. The IR spectra were recorded with a FT-IR instrument. The high-resolution mass spectra (HRMS) were recorded in the positive-ion FAB mode in *m*-nitrobenzyl alcohol. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Cyclic tetrathiadiynes **4(m.n)** were prepared according to literature methods.[13]

General Procedure for the Preparation of Tetrathiacyclopropenonophanes 5(m.n) and 6(m.n). To a solution of cyclic tetrathiadiyne **4(m.n)** in 80−120 mL of anhydrous DME was added sodium trichloroacetate portionwise at 60 °C over a period of 2−3 h, yielding a dark black solution. The reaction mixture was then allowed to cool to room temperature, 180 mL of ethyl acetate was added, and the mixture was cooled to 0 °C. The reaction mixture was hydrolyzed by adding 25 mL of water. The layers were separated, and the aqueous layer was extracted five times with dichloromethane. The combined organic extracts were evaporated by rotary evaporation, and the resulting residue was filtered through neutral alumina with dichloromethane/ethyl acetate 10:1 as eluent. After rotary evaporation the product was isolated by column chromatography on neutral alumina, eluting with mixtures of hexanes/ethyl acetate or dichloromethane/ethyl acetate.

2,6,9,14-Tetrathiabicyclo[13.1.0]hexadec-1(15)-en-7-yn-16-one (5(3.4)). Starting materials: 452 mg (1.65 mmol) of 1,4,8,11-tetrathiacyclopentadeca-2,9-diyne (**4(3.4)**) and 6.1 g (32.9 mmol) of sodium trichloroacetate in 120 mL of DME. Column chromatography with hexanes/ethyl acetate (10:1 to 1:1) as eluent afforded 47 mg (9.4%) of **5(3.4)** as a colorless solid: mp 105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (m, 4H, $SCH_2CH_2CH_2CH_2S$), 2.31 (m, 2H, $SCH_2CH_2CH_2S$), 2.58 (m,

Table 4. Crystal Data and Structure Refinement for Compounds 5(3.4), 5(4.5), 5(6.6), and 7

	5(3.4)	5(4.5)	5(6.6)	7
		Crystal Data		
empirical formula	$C_{12}H_{14}OS_4$	$C_{14}H_{18}OS_4$	$C_{17}H_{24}OS_4$	$C_{11}H_{18}OS_2$
formula weight	302.51	330.56	372.64	230.40
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$C2/c$	$P2_1/c$	$P2_1/c$
unit cell dimensions	$a = 7.8492(2)$ Å	$a = 22.8091(1)$ Å	$a = 10.9650(2)$ Å	$a = 6.2306(1)$ Å
	$b = 8.2295(2)$ Å	$b = 14.1291(2)$ Å	$b = 21.2986(4)$ Å	$b = 38.6217(1)$ Å
	$c = 21.9416(4)$ Å	$c = 9.9537(1)$ Å	$c = 8.9659(1)$ Å	$c = 10.9766(1)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 96.57(1)°$	$\beta = 111.987(1)°$	$\beta = 92.306(1)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
volume	1417.32(6) Å^3	3186.73(6) Å^3	1941.60(6) Å^3	2639.23(5) Å^3
Z	4	8	4	8
density (calculated)	1.418 g/cm^3	1.378 g/cm^3	1.275 g/cm^3	1.160 g/cm^3
absorption coefficient	0.651	0.586	0.488	0.374
T_{min}	0.98	0.89	0.97	0.93
T_{max}	0. 78	0.76	0.82	0.69
F(000)	632	1392	792	992
crystal size (mm)	0.44 × 0.05 × 0.03	0.34 × 0.32 × 0.26	0.44 × 0.33 × 0.08	0.44 × 0.22 × 0.10
		Data Collection		
θ range	2.64° to 27.49°	1.80° to 27.43°	2.00° to 27.47°	1.93° to 27.50°
index ranges	$-10 \le h \le 10$	$-29 \le h \le 29$	$-14 \le h \le 14$	$-8 \le h \le 8$
	$-10 \le k \le 10$	$-18 \le k \le 18$	$-27 \le k \le 27$	$-50 \le k \le 50$
	$-28 \le / \le 28$	$-12 \le / \le 12$	$-11 \le / \le 11$	$-14 \le / \le 14$
reflections collected	14594	16004	19758	26840
independent	3252 with	3643 with	4451 with	6038 with
reflections	R(int) = 0.0600	R(int) = 0.0230	R(int) = 0.0339	R(int) = 0.0737
reflections observed	2683	3140	3090	4352
		Refinement		
data/parameters	3252/210	3643/172	4451/227	6038/265
goodness-of-fit on F^2	1.04	1.08	1.03	1.06
final R indices	R1 = 0.035	R1 = 0.026	R1 = 0.043	R1 = 0.047
[$I > 2\sigma(I)$]	wR2 = 0.061	wR2 = 0.070	wR2 = 0.107	wR2 = 0.095
R indices (all data)	R1 = 0.054	R1 = 0.034	R1 = 0.071	R1 = 0.077
	wR2 = 0.067	wR2 = 0.075	wR2 = 0.107	wR2 = 0.106
largest diff. peak and hole	0.24 and −0.23 eÅ^{-3}	0.31 and −0.23 eÅ^{-3}	0.56 and −0.30 eÅ^{-3}	0.27 and −0.28 eÅ^{-3}

2H, $SCH_2CH_2CH_2CH_2SC{\equiv}$), 2.69 (m, 2H, $SCH_2CH_2CH_2SC{\equiv}$), 3.01 (t, J = 7.0 Hz, 2H, $SCH_2CH_2CH_2SC{\equiv}$), 3.24 (t, 2H, $SCH_2CH_2CH_2CH_2S$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 24.88 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 27.78 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 31.45 ($SCH_2CH_2CH_2SC{\equiv}$), 32.10 ($SCH_2CH_2CH_2SC{\equiv}$), 33.16 ($SCH_2CH_2CH_2SC{\equiv}$), 34.30 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 34.89 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 85.18 [≡C(s)], 86.45 [≡C(l)], 144.78 [=C(s)], 146.97 [=C(l)], 152.52 (C=O); IR (KBr) 2934 (s), 1860 (vs), 1759 (vs), 1516 (vs), 1068 (vs), 713 (m) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 266 nm (5700); FAB HRMS Calcd for MH$^+$ ($C_{12}H_{15}OS_4$) 303.0006; found, 303.0009.

2,7,10,16-Tetrathiabicyclo[15.1.0]octadec-1(17)-en-8-yn-18-one (5(4.5)). Starting materials: 348 mg (1.15 mmol) of 1,4,9,12-tetrathiacycloheptadeca-2,10-diyne (**4(4.5)**) and 6.40 g (34.5 mmol) of sodium trichloroacetate in 130 mL of DME. Column chromatography with hexanes/ethyl acetate (10:1 to 2:1) as eluent afforded 34 mg (8.9%) of **5(4.5)** as a colorless solid: mp 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (m, 2H, $SCH_2CH_2CH_2CH_2CH_2S$), 1.79−1.89 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2S$), 1.94 (m, 4H, $SCH_2CH_2CH_2CH_2SC{\equiv}$), 2.58 (t, J = 6.9 Hz, 2H, $SCH_2CH_2CH_2CH_2SC{\equiv}$), 2.64 (t, J = 6.7 Hz, 2H, $SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 2.99 (t, J = 7.4 Hz, 2H, $SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 3.24 (t, J = 5.8 Hz, 2H, $SCH_2CH_2CH_2CH_2SC{\equiv}$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 26.08 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 26.88 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 28.15 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 28.46 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 31.25 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 33.27 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 33.75 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 34.90 ($SCH_2CH_2CH_2CH_2SC{\equiv}$), 35.68 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 85.28 [≡C(s)], 86.03 [≡C(l)], 145.17/145.36 (C=C), 152.39 (C=O); IR (KBr) 2925 (s), 1852 (vs), 1753 (vs), 1499 (vs), 1061 (vs), 722 (s) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 264 nm (8300); FAB HRMS Calcd for MH$^+$ ($C_{14}H_{19}OS_4$) 331.0319; found, 331.0344. Anal. Calcd for $C_{14}H_{18}OS_4$: C, 50.87; H, 5.49; S, 38.80. Found: C, 50.81; H, 5.62; S, 38.77.

2,9,12,19-Tetrathiabicyclo[18.1.0]hencos-1(20)-en-10-yn-21-one (5(6.6)). Starting materials: 500 mg (1.45 mmol) of 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (**4(6.6)**) and 270 mg (1.45 mmol) of sodium trichloroacetate in 100 mL of DME. Column chromatography with hexanes/ethyl acetate (10:1 to 1:1) as eluent afforded 23 mg (4.3%) of **5(6.6)** as a colorless solid: mp 74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45−1.47 (m, 8H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 1.71−1.85 (m, 8H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 2.59 (t, J = 7.0 Hz, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 3.08 (t, J = 6.6 Hz, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 27.19 ($SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 27.79 ($SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 29.14 ($SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 30.47 ($SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 34.04 ($SCH_2CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 36.00 ($SCH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 85.84 (≡C), 145.27 (=C), 152.60 (C=O); IR (KBr) 2924 (s), 1850 (vs), 1737 (m), 1515 (s), 1046 (s), 710 (m) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 264 nm (139000); FAB HRMS Calcd for MH$^+$ ($C_{17}H_{25}OS_4$) 373.0788; found, 373.0789. Anal. Calcd for $C_{17}H_{24}OS_4$: C, 54.79; H, 6.49; S, 34.42. Found: C, 54.66; H, 6.39; S, 34.26.

1,1′,5,7′-Tetrathia[5,7]cyclopropenonophane (6(3.5)). Starting materials: 261 mg (0.76 mmol) of 1,4,8,11-tetrathiacyclohexadeca-2,9-diyne (**4(3.5)**) and 4.21 g (22.73 mmol) of sodium trichloroacetate in 80 mL of DME. Column chromatography with dichloromethane/ethyl acetate (8:1) as eluent afforded 14 mg (4.5%) of **6(3.5)** as a colorless solid: mp 128 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (quint, 2H, $SCH_2CH_2CH_2CH_2CH_2S$), 1.87 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 2.27 (quint, J = 6.6 Hz, 2H, $SCH_2CH_2CH_2S$), 3.14 (m, 8H, SCH_2); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 22.33 ($SCH_2CH_2CH_2CH_2CH_2S$), 27.16 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 31.99 ($SCH_2CH_2CH_2S$), 32.65 ($SCH_2CH_2CH_2S$), 33.40 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 144.10 [=C(s)], 146.24 [=C(l)], 152.63 (C=O); IR (KBr) 2937 (m), 1860 (vs), 1758 (m), 1518 (vs), 1066 (m) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 260 nm (9300); FAB HRMS Calcd for MH$^+$ ($C_{14}H_{17}O_2S_4$) 345.0111; found, 345.0119.

1,1′,6,8′-Tetrathia[6,8]cyclopropenonophane (6(4.6)). Starting materials: 500 mg (1.58 mmol) of 1,4,9,12-tetrathiacyclooctadeca-2,10-diyne (**4(4.6)**) and 8.78 g (47.36 mmol) of

Table 5. Crystal Data and Structure Refinement for Compounds 6(3.5), 6(4.6)a, 6(4.6)b, and 6(5.5)

	6(3.5)	6(4.6)a	6(4.6)b	6(5.5)
		Crystal Data		
empirical formula	$C_{14}H_{16}O_2S_4$	$C_{18}H_{20}O_2S_4$	$C_{16}H_{20}O_2S_4$	$C_{16}H_{20}O_2S_4$
formula weight	344.54	372.60	372.60	372.60
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*P*bca	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit cell dimensions	$a = 9.0297(1)$ Å	$a = 9.2787(3)$ Å	$a = 16.9255(5)$ Å	$a = 10.0628(1)$ Å
	$b = 15.7598(2)$ Å	$b = 16.1092(5)$ Å	$b = 11.0753(3)$ Å	$b = 20.1422(3)$ Å
	$c = 22.6250(2)$ Å	$c = 12.3008(3)$ Å	$c = 9.5271(3)$ Å	$c = 10.0814(1)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 102.454(1)°$	$\beta = 91.608(1)°$	$\beta = 119.717(1)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
volume	3219.68(6) Å^3	1795.37(9) Å^3	1785.20(9) Å^3	1774.63(3) Å^3
Z	8	4	4	4
density (calculated)	1.421 g/cm^3	1.378 g/cm^3	1.386 g/cm^3	1.394 g/cm^3
absorption coefficient	0.587	0.532	0.535	0.539
T_{min}	0.93	0.94	0.98	0.94
T_{max}	0.77	0.77	0.82	0.85
$F(000)$	1440	784	784	784
crystal size (mm)	0.45 × 0.40 × 0.14	0.39 × 0.17 × 0.14	0.54 × 0.20 × 0.04	0.27 × 0.16 × 0.14
		Data Collection		
θ range	2.58° to 27.49°	2.11° to 27.47°	2.20 to 27.49°	2.02 to 27.48°
index ranges	$-11 \le h \le 11$	$-12 \le h \le 11$	$-21 \le h \le 21$	$-13 \le h \le 13$
	$-20 \le k \le 20$	$-20 \le k \le 20$	$-14 \le k \le 14$	$-26 \le k \le 26$
	$-29 \le / \le 29$	$-15 \le / \le 15$	$-12 \le / \le 12$	$-12 \le / \le 13$
reflections collected	31042	18179	17850	18113
independent	3697 with	4102 with	4093 with	4067 with
reflections	$R(\text{int}) = 0.0301$	$R(\text{int}) = 0.0345$	$R(\text{int}) = 0.0470$	$R(\text{int}) = 0.0498$
reflections observed	3146	3249	3085	3125
		Refinement		
data/parameters	3697/181	4102/199	4093/199	4067/199
goodness-of-fit on F^2	1.03	1.03	1.08	1.03
final R indices	R1 = 0.027	R1 = 0.031	R1 = 0.044	R1 = 0.032
$[I > 2\sigma(I)]$	wR2 = 0.071	wR2 = 0.074	wR2 = 0.098	wR2 = 0.074
R indices (all data)	R1 = 0.035	R1 = 0.046	R1 = 0.067	R1 = 0.051
	wR2 = 0.077	wR2 = 0.081	wR2 = 0.108	wR2 = 0.082
largest diff. peak and hole	0.37 and −0.31 eÅ^{-3}	0.27 and −0.24 eÅ^{-3}	0.40 and −0.26 eÅ^{-3}	0.26 and −0.24 eÅ^{-3}

sodium trichloroacetate in 100 mL of DME. Column chromatography with dichloromethane/ethyl acetate (15:1) as eluent afforded 64 mg (10.9%) of **6(4.6)** as a colorless solid: mp 118 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 1.83 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 1.95 (m, 4H, $SCH_2CH_2CH_2CH_2S$), 3.05 (t, J = 6.6 Hz, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 3.11 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 26.24 ($SCH_2CH_2CH_2CH_2CH_2S$), 28.78 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 29.77 ($SCH_2CH_2CH_2CH_2S$), 33.34 ($SCH_2CH_2CH_2CH_2S$), 33.36 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 144.40 [=C(s)], 145.13 [=C(l)], 152.52 (C=O); IR (KBr) 2929 (s), 1859 (vs), 1746 (vs), 1517 (vs), 1057 (vs), 716 (s) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 262 nm (161000); FAB HRMS Calcd for MH^+ ($C_{16}H_{21}O_2S_4$) 373.0424; found, 373.0451. Anal. Calcd for $C_{16}H_{20}O_2S_4$: C, 51.58; H, 5.41; S, 34.42. Found: C, 51.54; H, 5.48; S, 34.69.

1,1′,7,7′-Tetrathia[7,7]cyclopropenonophane (6(5.5)). Starting materials: 511 mg (1.61 mmol) of 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**4(5.5)**) and 8.98 g (47.40 mmol) of sodium trichloroacetate in 120 mL of DME. Column chromatography with dichloromethane/ethyl acetate (15:1) as eluent afforded 46 mg (7.6%) of **6(5.5)** as a colorless solid: mp 130 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (m, 4H, $SCH_2CH_2CH_2$), 1.86 (m, 8H, SCH_2CH_2), 3.08 (t, J = 6.7 Hz, 8H, SCH_2); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 24.81 ($SCH_2CH_2CH_2$), 29.69 (SCH_2CH_2), 33.34 (SCH_2), 144.93 (=C), 152.45 (C=O); IR (KBr) 2934 (s), 1852 (vs), 1734 (s), 1517 (vs), 1040 (s), 719 (m) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 262 nm (19000); FAB HRMS Calcd for MH^+ ($C_{16}H_{21}O_2S_4$) 373.0424; found, 373.0432. Anal. Calcd for $C_{16}H_{20}O_2S_4$: C, 51.58; H, 5.41; S, 34.42. Found: C, 51.41; H, 5.48; S, 34.19.

1,1′,7,8′-Tetrathia[7,8]cyclopropenonophane (6(5.6)). Starting materials: 496 mg (1.50 mmol) of 1,4,10,13-tetrathiacyclononadeca-2,11-diyne (**4(5.6)**) and 8.34 g (45.00 mmol) of sodium trichloroacetate in 120 mL of DME. Column chromatography with dichloromethane/ethyl acetate (8:1) as eluent afforded 37 mg (6.4%) of **6(5.6)** as a colorless solid: mp 142 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 1.59 (m, 2H, $SCH_2CH_2CH_2CH_2CH_2S$), 1.81 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 1.86 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 3.01 (t, J = 6.7 Hz, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$), 3.11 (t, J = 6.0 Hz, 4H, $SCH_2CH_2CH_2CH_2CH_2CH_2S$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 24.58 ($SCH_2CH_2CH_2CH_2CH_2S$), 26.93 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 29.23 ($SCH_2CH_2CH_2CH_2CH_2S$), 30.33 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 33.50 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 33.66 ($SCH_2CH_2CH_2CH_2CH_2CH_2S$), 144.73 [=C(l)], 144.93 [=C(s)], 152.56 (C=O); IR (KBr) 2935 (s), 1849 (vs), 1739 (s), 1511 (vs), 1051 (s), 717 (m) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 264 nm (20000); FAB HRMS Calcd for MH^+ ($C_{17}H_{23}O_2S_4$) 387.0581; found, 387.0599.

1,1′,8,8′-Tetrathia[8,8]cyclopropenonophane (6(6.6)). Starting materials: 500 mg (1.45 mmol) of 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (**4(6.6)**) and 8.07 g (43.50 mmol) of sodium trichloroacetate in 120 mL of DME. Column chromatography with dichloromethane/ethyl acetate (20:1 to 10:1) as eluent afforded 48 mg (8.3%) of **6(6.6)** as a colorless solid: mp 155 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (m, 8H, $SCH_2CH_2CH_2$), 1.82 (m, 8H, SCH_2CH_2), 3.04 (t, J = 7.0 Hz, 8H, SCH_2); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 26.95 ($SCH_2CH_2CH_2$), 30.41 (SCH_2CH_2), 33.53 (SCH_2), 145.05 (=C), 152.66 (C=O); IR (KBr) 2927 (s), 1854 (vs), 1747 (s), 1512 (vs), 1054 (s), 719 (s) cm^{-1}; UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 264 nm (16000); FAB HRMS Calcd for MH^+ ($C_{18}H_{25}O_2S_4$) 401.0738; found, 401.0742. Anal. Calcd for $C_{18}H_{24}O_2S_4$: C, 53.96; H, 6.04; S, 32.01. Found: C, 53.72; H, 6.06; S, 32.12.

X-ray Diffraction Analyses. The reflections were collected with a Bruker Smart CCD diffractometer (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[23] based on the Laue symmetry of

the reciprocal space. The structures were solved by direct methods. 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 (**5(3.4)**) or calculated according to stereochemical aspects (**5(4.5)**, **5(6.6)**, **6(3.5)**, **6(4.6)a**, **6(4.6)b**, **6(5.5)**, **7**). In **5(6.6)** three carbon atoms of one hexano moiety are disordered with 66% and 34% occupancy. Structure solution and refinement were carried out with SHELXTL (5.10) software package.[23] Table 4 and Table 5 contain the crystallographic data and details of the data collection and the refinement procedure. ORTEP drawings were obtained using the ORTEP-3 for Windows program by L. Farrugia.[24]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and BASF Aktiengesellschaft, Ludwigshafen, for financial support. D.B.W. thanks C. Benisch and T. H. Stäb for useful discussions and the Studienstiftung des deutschen Volkes for a scholarship.

Supporting Information Available: Tables of crystallographic data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters are available for structures **5(3.4)**, **5(4.5)**, **5(6.6)**, **6(3.5)**, **6(4.6)a**, **6(4.6)b**, **6(5.5)**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001721J

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