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Sterically Stabilized Cyclopropenonophanes and an Electronically Stabilized Cyclopropenethionophane: Syntheses, Structural Properties, and Reactivity

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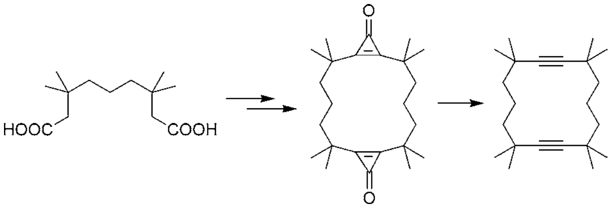
ABSTRACT



The syntheses of sterically stabilized cyclopropenonophanes as well as an electronically stabilized cyclopropenethionophane are reported, and their molecular structures in the solid state are elucidated. The sulfur of the CS moiety in cyclopropenethiones was shown to react as a nucleophile. Temperatures of more than 240 °C favor the extrusion of CO in the cyclopropenonophane to afford an α,α′-tetramethyl-substituted cyclodiyne.

One major goal of recent cyclophane chemistry[1] is the incorporation of less common π systems or unusual tethers between them. The tethers can inplement rigid π systems such as alkyne moieties (**1**)[2] or even benzene rings (**2**)[3] and various kinds of heteroatoms that can influence the electronic properties of adjacent conjugated systems or serve as donor atoms for host−guest interactions (**3**).[4] But the stability and reactivity of such systems is not only effected by heteroatoms, bulky groups are also able to induce a similar effect.[1]

Among the various π systems implemented in cyclophanes, the three-membered ring has attracted much less attention[5] than its larger counterparts such as metal-stabilized cyclobutadienes (**4**),[6] the five-membered 6π-heterocycles,[1c,d] and benzene and larger benzenoid and nonbenzenoid aromatic systems.[1] One reason for the rare appearance of cyclophanes with cyclopropenylium or cyclopropenone rings may be their intrinsic instability due to the high strain energy, which opens many possibilities to side reactions and degradation reactions.[7] However, the cyclopropenone acetals are remarkably stable and used for synthesis.[8]

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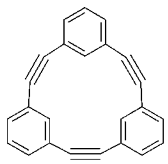

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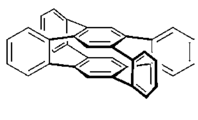

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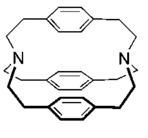

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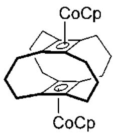

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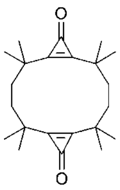
Herein, we report synthetic strategies for the assembly of sterically stabilized cyclopropenonophanes **5** and **6** as well as the electronically stabilized cyclopropenethionophane **7**. The latter compound bears a cyclopropenethione unit that is the C═S analogue of cyclopropenone.



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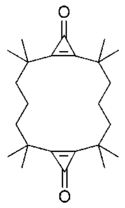

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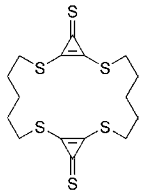
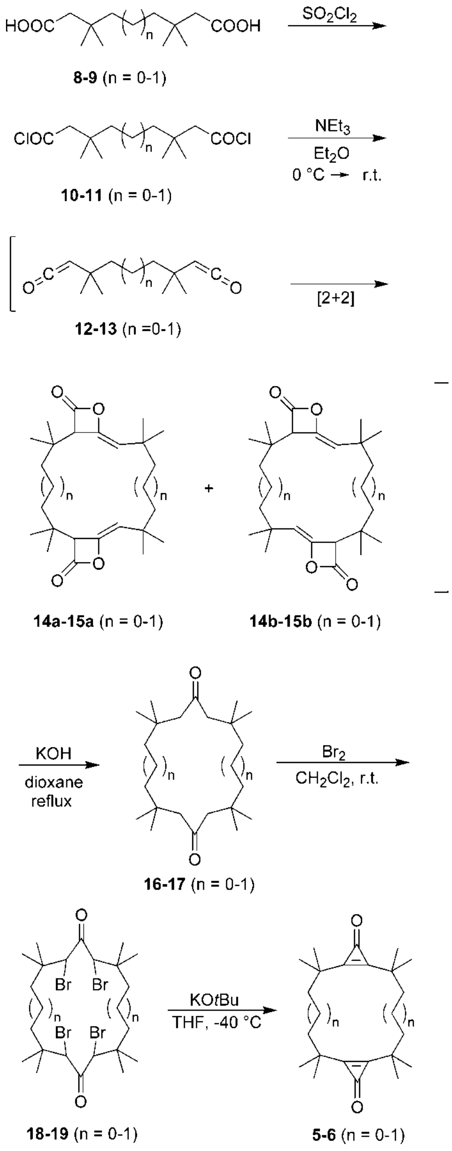


7

The starting points of the syntheses of **5** and **6** are the well-known tetramethyl-substituted dicarboxylic acids[9,10] **8** and **9**, respectively, which can be converted using standard methods into the corresponding diacyl chlorides **10** and **11** (Scheme 1).[11] The yields obtained in this reaction were in the range between 85 and 95%. The following in situ-generation of the bis-ketenes **12** and **13**, respectively, and their subsequent two-component ring-closure yielding isomeric mixtures of ketene dimerization products proved to be the crucial steps of the whole synthesis. Without further purification, **14** and **15**, respectively, were subjected to a base-induced decarbonylation that was carried out for several days with KOH in dioxane under reflux. The yields obtained in this three-step sequence were only about 5%. For the synthesis of the final products, first, a tetrabromination of **16** and **17**, respectively, was conducted to yield compounds **18** and **19**. Hereby, it proved to be essential that the reaction was carried out at room temperature under an air atmosphere. It is noteworthy that in the case of **19**, only one of five possible stereoisomers was formed, as NMR studies have shown. An X-ray analysis revealed the structure of **19** showing an anti orientation of the keto groups with four equatorial bromine atoms. For the final step, KO*t*Bu, a voluminous base and a hindered nucleophile, was used in a Favorskii-type reaction to induce the formation of the three-membered rings. Similar reactions have been used before in acyclic systems.[12] The best results, with yields of 27% (**5**) and 51% (**6**), were obtained in THF at −40 °C. Both compounds proved to be extremely stable when heated.

Scheme 1



The starting point of the cyclopropenethionophane synthesis was the recently synthesized cyclopropenonophane **20**,[13] a stable compound that can be stored for months (Scheme 2). The reaction of **20** with a large excess of oxalyl chloride in DME at 40 °C yielded the intermediate **21** bearing two dichlorocyclopropene moieties. The driving force to afford this highly energetic compound lacking any aromatic stabilization is the formation and release of CO_2 out of the reaction mixture. The thiocarbonyl groups were generated afterward by the addition of thioacetic acid affording the tetrathiacyclopropenethionophane **7** in 31% yield (Scheme 2). This synthesis starting from tetrathiacyclopropenonophane[13] proved to be superior over the direct synthesis starting from tetrathiacyclodiyne,[14] which results in many side products that are difficult to separate.

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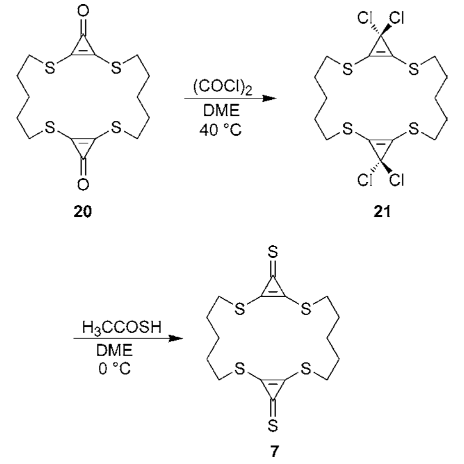
Scheme 2



In contrast to the cyclopropenonophanes **5**, **6**, and **20**, the cyclopropenethionophane **7** is much less stable and decomposes at about 110 °C. The cyclopropenethione unit is strongly UV-active, much more than the cyclopropenone unit. Compared to the latter, the absorption is shifted into the range of visible light, which gives the compound **7** a yellow color.

For the compounds **6** and **7**, we were able to grow single crystals[15] to elucidate their molecular structures. For both compounds, two different modifications (α and β) were found. In the case of **6**, the two modifications do not differ significantly. Both reveal a *syn* orientation of the cyclopropenone units, which are almost parallel to each other (Figure 1). Relevant geometrical data are given in Table 1. It is interesting to note that in [3.3]cyclopropenonophane[5c] and in [5.5]biscyclopropenyliumphane,[5b] the two π systems also face each other.

In contrast to **6**, the molecular stucture of **7** (modification α) shows an *anti* orientation (Figure 2) of the three-membered rings. Comparing the transannular distances t_1 and t_2 between the two π systems demonstrates that they are very similar, although the latter (**7**α) is tethered by seven atoms, whereas **6** is connected only by five atoms. As Table 1 shows, the torsional angles γ (C−X−C=C, X = CMe$_2$ (**6**), X = S (**7**)) vary strongly: in **7**α, the 3p orbitals of the sulfur atoms adjacent to the electron-poor cyclopropenethione moiety overlap with the π system. This overlap is optimal for a planar conformation, resulting in angles γ of about 0 and 180°. In contrast, **6** does not show such favoring structure-determining electronic effects. Also in the β modification of **7**, the planar feature of the cyclopropenethione moiety with the adjacent SCH$_2$ groups is maintained. Similar effects have been observed in cyclopropenones substituted with other electron-donating moieties.[13,16]

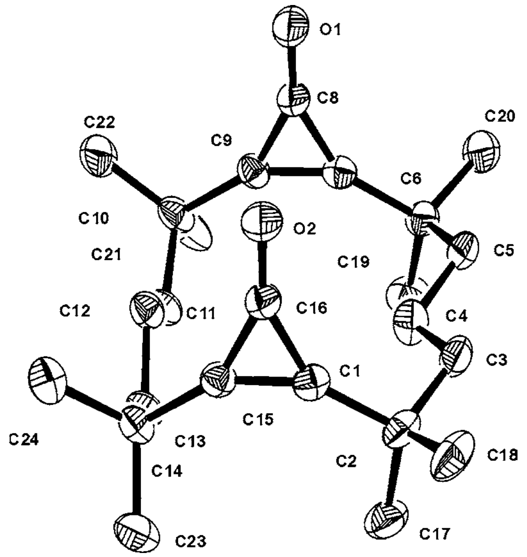


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **6** (modification α). Hydrogen atoms are omitted for the sake of clarity.

In Table 1, we show for comparison also data of the dithia-substituted cyclopropenethione **22**.[16e] This model compound was reacted with an excess of methyl iodide in dichloromethane to yield the trithia-substituted cyclopropenylium cation. This cationic species was prepared before by substitution of fully chlorinated cyclopropenes[16b] but not structurally characterized. The triiodide **24** was formed out of a solution of the iodide **23** that was left for several days in contact with air. Presumably, oxygen from the air converted the iodide into triiodide.

The molecular structures of **23** (two modifications α and β) and **24** do not show a C_3 axis as anticipated. Two methyl

Table 1. Comparison between Most Relevant Structural Data Determined by X-ray Analyses of **6**, **7**, and **22**

	t_1 [pm][a] t_2 [pm][a]	C=X (X = O, S) [pm]	C=C [pm]	C(sp^2)−S [pm]	γ [deg][b]
6α[c]	520.5(4)	121.8(3)	135.8(3)		66(4)[d] 116(3)[d]
6β[c]	520.7(4)	121.5(3)	135.8(4)		65(4)[d] 116(3)[d]
22		165.2(2)	136.0(3)	169.8(2)	180.0 0.0
7α	510.8(4)	165.0(2)	135.8(3)	169.4(2)	172(1)[d]
7β	e	164.6(2)	136.0(3)	169.9(2)	6(5)[d] 176(2)[d]

[a] Transannular distances between corresponding carbon atoms of the C=C bond. [b] Dihedral angle of C−X−C=C (X = CMe$_2$, X = S). [c] Two crystallographically independent molecules, the given numbers are mean values. [d] Mean values of equivalent units. [e] π systems do not face each other.

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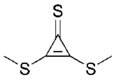
(15) (a) **Crystal Structure Determination of 6α:** $C_{24}H_{36}O_2$; MW = 356.53; colorless; polyhedron; 0.44 × 0.42 × 0.30 mm^3; orthorhombic; space group $Pna2_1$; a = 15.0286(3) Å; b = 7.4850(2) Å, c = 39.3182(8) Å; V = 4422.87(17) Å^3; Z = 8; T = 200(2) K; d_{calcd} = 1.071 g/cm^3; F(000) = 1568; μ = 0.066 mm^{-1}; 23 546 reflections collected; 7583 independent reflections; 6695 reflections observed; $R(F)$ = 0.034; $R_w(F^2)$ = 0.083; S (GOF) on F^2 = 1.04. $(\Delta\rho)_{max}$ = 0.14 e/Å^3; $(\Delta\rho)_{min}$ = −0.18 e/Å^3. (b) **Crystal Structure Determination of 7**α: $C_{16}H_{20}S_6$; MW = 404.72; yellow; polyhedron; 0.37 × 0.30 × 0.05 mm^3; monoclinic; space group $P2_1/n$; a = 9.0844(3) Å; b = 11.8406(3) Å, c = 9.8502(3) Å; β = 113.063(1)°; V = 974.85(5) Å^3; Z = 2; T = 200(2) K; d_{calcd} = 1.379 g/cm^3; F(000) = 424; μ = 0.695 mm^{-1}; 4668 reflections collected; 2093 independent reflections; 1654 reflections observed; $R(F)$ = 0.031; $R_w(F^2)$ = 0.074; S (GOF) on F^2 = 1.07; $(\Delta\rho)_{max}$ = 0.27 e/Å^3; $(\Delta\rho)_{min}$ = −0.24 e/Å^3.



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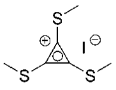

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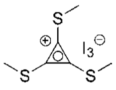


24

groups face each other. As an example, we show the molecular stucture of **24** in Figure 3.[17] An analysis of the bond lengths within the three-membered rings reveals values of 135.8 to 138.5 pm; these distances are about 3−4 pm longer than for non-donor-substituted cyclopropenylium cations.[5b] This result indicates a significant overlap of antibonding π* orbitals of the three-membered ring with the lone pairs of the sulfur atoms. This view is supported by the C(sp^2)−S bond lengths, which are 1−3 pm shorter than in the cyclopropenethiones **22**, **7**α, and **7**β.

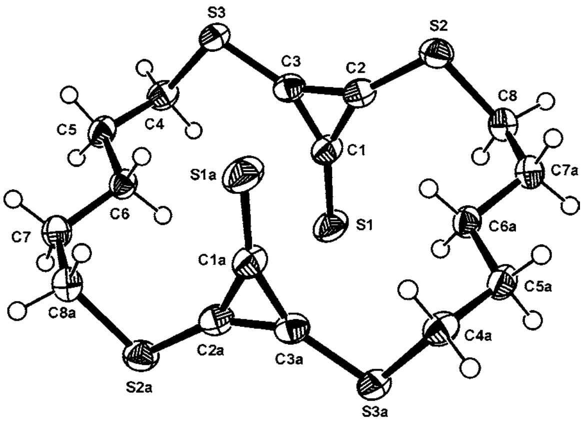


Figure 2. ORTEP plot (50% ellipsoid probability) of the molecular structure of **7** (modification α).

The sterically hindered cyclopropenonophane **6** was pyrolyzed to afford, via a [1 + 2]-cycloreversion, a cyclodiyne with methyl substituents in the α,α′-positions next to the triple bonds. Hitherto, all other methods such as four-component cyclizations involving either lithium acetylide or propargylic halides to afford such a compound failed.[18] Therefore, **6** was heated without solvent to 240 °C for 30 min (Scheme 3). Much soot was formed; still unreacted starting material could be recovered, and the desired product **25** could be separated by column chromatography and was obtained in a yield of 13%. The structure of **25** could be assigned unequivocally by NMR studies.

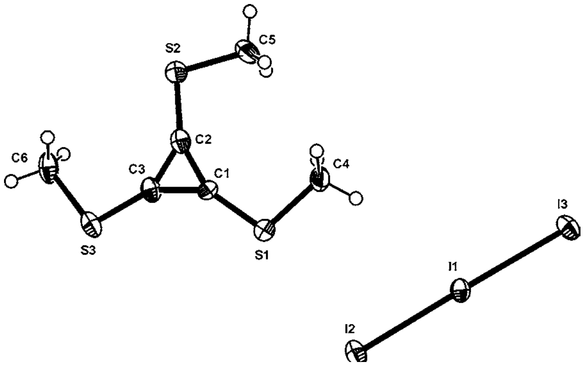
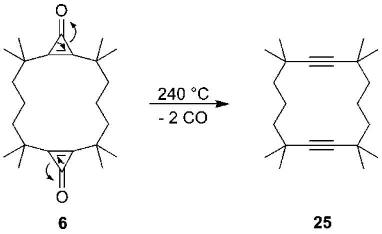


Figure 3. ORTEP plot (50% ellipsoid probability) of the molecular structure of **24**.

In summary, we report the syntheses of sterically stabilized cyclopropenonophanes bearing methyl substituents in the α,α′-position. The key steps are ketene dimerizations to build up the large cycles, base-induced decarbonylations, and a Favorskii-type reaction of tetrabromides that closes the three-membered rings. An electronically stabilized cyclopropenethionophane bearing sulfur atoms in the α,α′-position was synthesized from the corresponding CO analogue. Structural investigations by means of X-ray crystallography have shown that cyclopropenone moieties in **6** are situated *syn* to each other, whereas the cyclopropenethione units in **7** adopt an *anti* position. The CH$_2$−S−C═C unit in **7** proved to be nearly planar, indicating conjugation between the 3p lone pair of the sulfur and the electron-poor cyclopropenethione moiety. The thiocarbonyl group in cyclopropenethiones is readily attacked by electrophiles such as MeI, yielding the trithia-substituted cyclopropenylium cation.

Scheme 3



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Supporting Information Available: Experimental procedures and analytical data, as well as crystallographic data (CCDC-260677 to CCDC-260685) for compounds **6**α, **6**β, **7**α, **7**β, **19**, **22**, **23**α, **23**β**,** and **24** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) **Crystal Structure Determination of 24:** $C_6H_9S_3I_3$; MW = 558.01; dark red; polyhedron; 0.40 × 0.18 × 0.15 mm^3; monoclinic; space group $P2_1/n$; a = 9.6693(5) Å; b = 14.1562(3) Å, c = 10.6917(5) Å; β = 104.057-(2)°; V = 1419.66(10) Å^3; Z = 4; T = 200(2) K; d_{calcd} = 2.611 g/cm^3; F(000) = 1008; μ = 7.005 mm^{-1}; 4332 reflections collected; 2868 independent reflections; 2105 reflections observed; $R(F)$ = 0.033; $R_w(F^2)$ = 0.081; S (GOF) on F^2 = 1.13; $(\Delta\rho)_{\max}$ = 1.35 e/Å^3; $(\Delta\rho)_{\min}$ = −1.01 e/Å^3.

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