# Doubly Bridged Biscyclopropenones, a New Family of Phanes†

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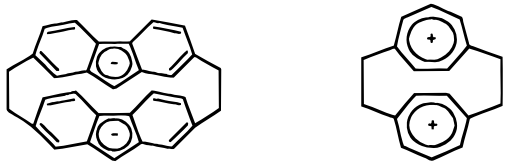
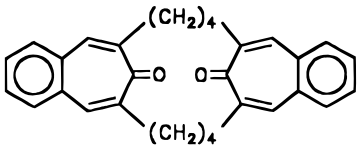
The first representatives, **10**−**12**, of the new species of double-decked cyclopropenonophanes were synthesized by cycloaddition reactions of dichlorocarbene to alkynylenecyclopropenonophanes **7**−**9** followed by hydrolysis as well as in an alternative route involving hydride abstraction from dichlorotricycloalkadienes **16** and **17** to dichlorocyclopropenyliophanes and in situ hydrolysis of the latter. The X-ray analysis of [3.3]cyclopropenonophane **10** reveals a considerable tetragonalization of the bridgehead carbon atoms, indicating a significant deformation of the cyclopropenone moieties in the phane corset. According to ab initio calculations, the $\pi$ orbitals of the cyclopropenones display transannular interactions of nearly the same scale as found in **7**.

## Introduction

Phanes containing nonbenzenoid annular Hückel systems are attractive targets both for synthetic and theoretical chemistry. Due to their generally smaller resonance energies, deformations of the ring (accompanied by partial dearomatization) can be achieved more easily than in benzenoid systems.[1,2] Paired or combined with other functional groups, nonbenzenoid aromatics can give rise to transannular $\pi-\pi$, charge−charge, and dipole−dipole interactions. Some nonbenzenoid phanes containing two 6$\pi$-Hückel systems are presently known, e.g., the dianionic dibenzocyclopentadienidophane **1**,[1,3] the dicationic tropyliophane **2**,[4] and the dipolar benzotroponophane **3**.[5]

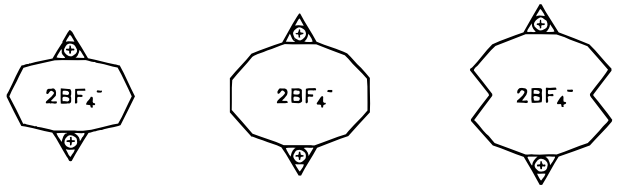


**1** **2**



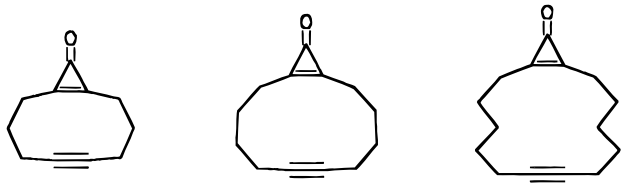

**3**

In 1992, we reported on the synthesis of the double-decked cyclopropenyliophanes **4**−**6**, thus introducing the first phane species of the 2$\pi$-system cyclopropenylium ion.[6] Compounds **4**−**6** exhibit, like their counterpart [2.2]-tropyliophane **2**, a considerably higher tendency to decompose than the corresponding monocations, apparently due to destabilizing intramolecular interactions of the functional groups, increasing from **6** to **4**.




**4** **5** **6**

Meanwhile, we have furthermore presented some phanes of the 2$\pi$-species cyclopropenone (**7**−**9**),[7,8] the bridges of which include alkyne functionalities.




**7** **8** **9**

According to their delocalization energies and their chemical properties, cyclopropenones fulfill the Hückel criteria of aromaticity much better than tropone[9] and, in spite of their ring strain of up to about 280 kJ/mol,[9,10] disubstituted cyclopropenones are normally fairly stable compounds.

In **7**, the X-ray structure reveals a slight deformation of the cyclopropenone by pyramidalization of both bridgehead carbon atoms. A considerable interaction between the cyclopropenone moiety and the triple bond, both having similar basis orbital energies, has been deduced.[8]

We reasoned that two 2$\pi$-functions of the same basis orbital energy, namely two cyclopropenone units, could display similar effects even if located at slightly larger distances from each other. Therefore, we extended our

† Dedicated to Professor Nicolai S. Zefirov on the occasion of his 60th birthday.

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(2) Vögtle, F. *Cyclophanchemie*; Teubner: Stuttgart, 1990; p 155.
(3) Haenel, M. W. *Tetrahedron Lett.* **1976**, 3121.
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(6) Gleiter, R.; Merger, M. *Tetrahedron Lett.* **1992**, *33*, 3473. Gleiter, R.; Merger, M.; Oeser, T.; Irngartinger, H. *Tetrahedron Lett.* **1995**, *36*, 6425.
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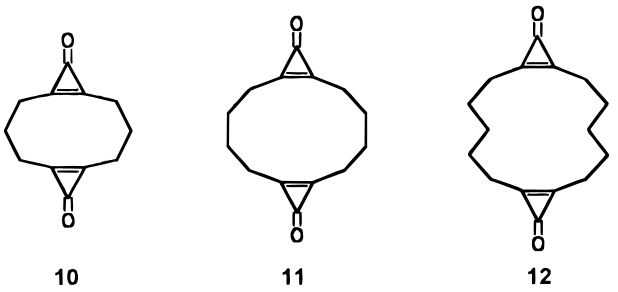
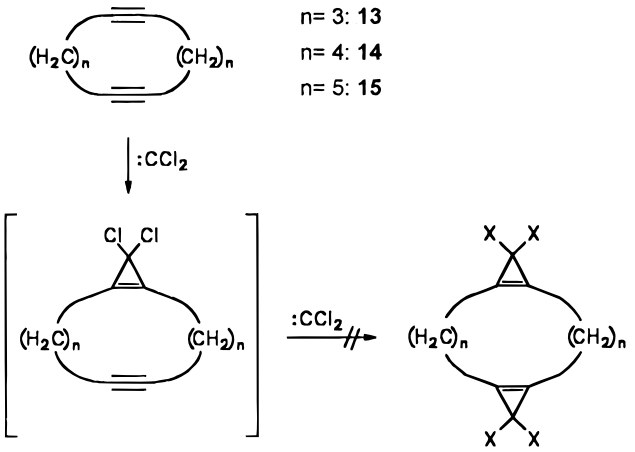
efforts to synthesize the double decked [*n.n*]cyclopropenonophanes **10**−**12** from cycloalkadiynes.




## Results and Discussion

In the syntheses of **7**−**9** along with cycloalkadiynones,[7] the generation of the dichlorobicycloenyne intermediates (monoaddition products, Scheme 1) has been performed

**Scheme 1. Dichlorocyclopropenation of Cycloalkadiynes**

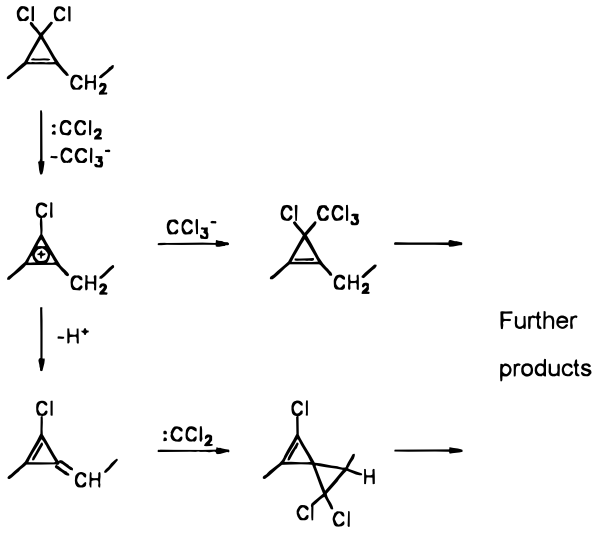



with unusual efficiency by using $LiCCl_3$ in THF as the source of dichlorocarbene. Though the method described may overcome problems in the syntheses of cyclopropenones from monoacetylenes in general, it turned out to be ineffective with respect to difunctional transformations of the cycloalkadiynes to bisdichlorocyclopropenes. No [*n.n*]cyclopropenonophanes could be detected after hydrolyzing the products obtained by reaction of the cycloalkadiynes with 1 equiv of $LiCCl_3$ in THF. Higher amounts of $LiCCl_3$ do not overcome this limitation but drastically reduce the yield of **7**−**9**. Apparently, the second triple bond cannot be dichlorocyclopropenated in the (intramolecular) presence of a dichlorocyclopropene unit.

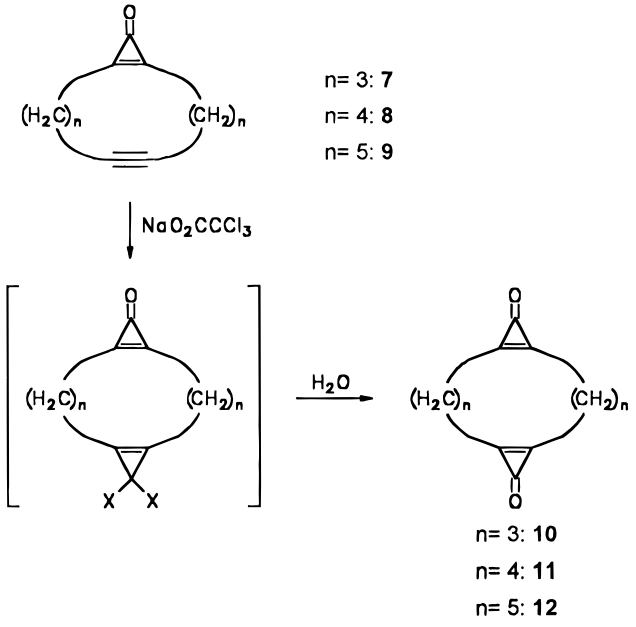
We suppose that the dichlorocyclopropene moiety (in equilibrium with the chlorocyclopropenylium ion) may function as a trapping agent, predominantly reacting with $CCl_2$ and/or its $CCl_3^-$ precursor[11,12] (Scheme 2), thus shielding the remaining triple bond nearby.

Consequently, the second dichlorocyclopropenation step must be separated from the first one. We fell back upon an observation of Breslow who pointed out that dipropylcyclopropenone is far less sensitive than its dipropyldichlorocyclopropene precursor to reaction with $NaO_2CCCl_3$ under similar conditions.[12]

**Scheme 2. Reactions of Dichlorocyclopropene Moieties with Dichlorocarbene and Trichloromethide**




**Scheme 3. [*n.n*]Cyclopropenonophanes from Alkinylenecyclopropenonophanes 7−9**




Hence, we employed the bicycloalkenynones **7**−**9** for the addition of dichlorocarbene. Indeed, we succeeded in preparing the [*n.n*]cyclopropenonophanes **10**−**12** from the reactions of **7**−**9** with 1 equiv of $NaO_2CCCl_3$ in 1,2-dimethoxyethane at 70−75 °C followed by subsequent hydrolysis at ambient temperature (Scheme 3). The compounds could be isolated by column chromatography in yields up to about 5% (based on conversion) which are of the same order of magnitude as those reported for the analoguous transformations of monoacetylenes.[12,13]

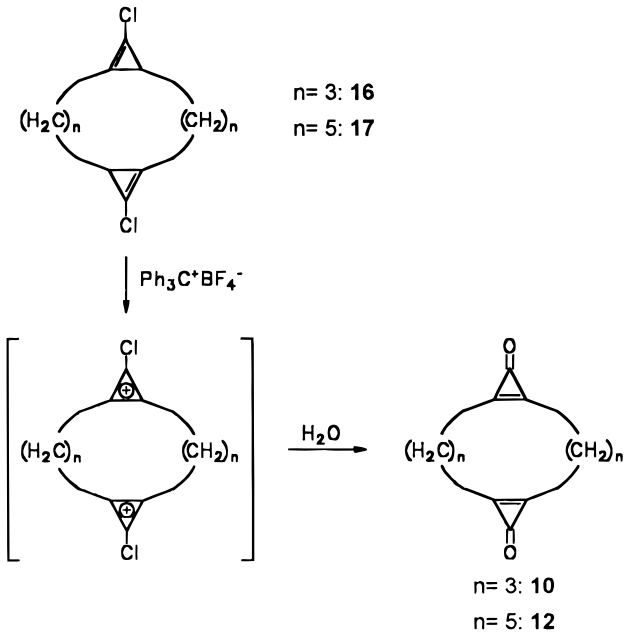
In order to exclude the specified side reactions (Scheme 2) entirely and to increase preparative productivity we developed an alternative approach which avoids any dichlorocyclopropenation of triple bonds. The key step consists of hydride abstraction from dichlorotricycloalkadienes using the method of Breslow and Dauben,[14]

(11) Dehmlow, E. V. *Chem. Ber.* **1967**, *100*, 3829. Dehmlow, E. V. *Tetrahedron Lett.* **1965**, 4003.

(12) Breslow, R.; Altman, L. J.; Krebs, A.; Mohacsi, E.; Murata, I.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1326.

(13) Breslow, R.; Peterson, R. *J. Am. Chem. Soc.* **1960**, *82*, 4426.

**Scheme 4. [*n.n*]Cyclopropenonophanes from Dichlorotricycloalkadienes 16 and 17**

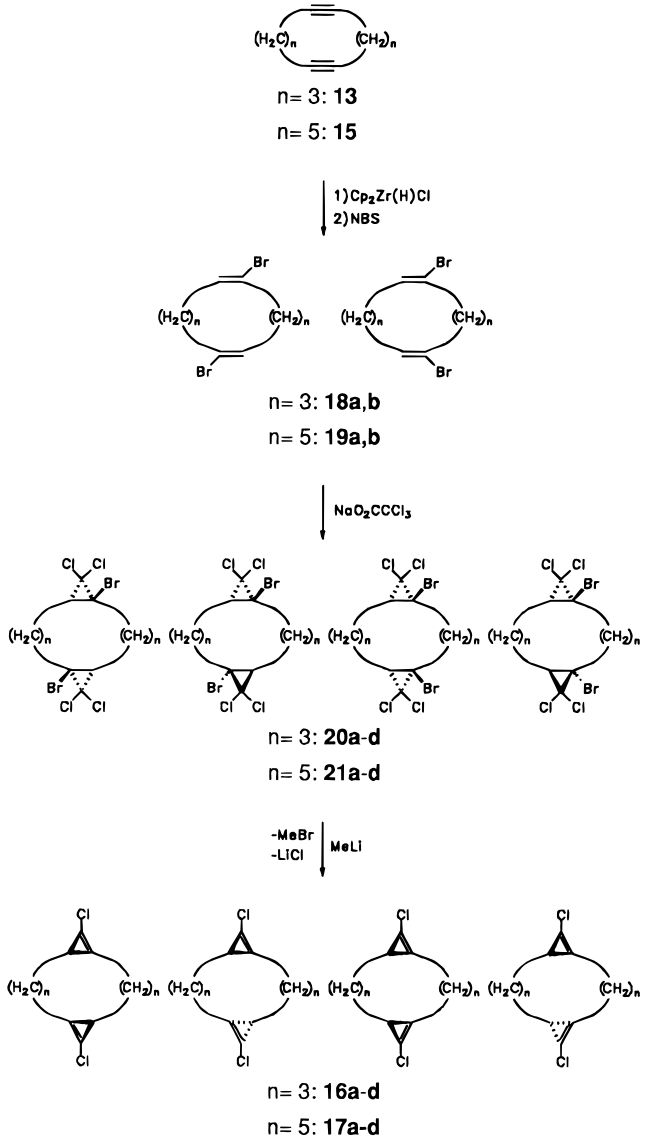



leading to dichloro[*n.n*]cyclopropenyliophanes that should be hydrolyzable to the [n.n]cyclopropenonophanes (Scheme 4).

Dichlorotricycloalkadienes had not been known to date, neither were any bis(1-halocyclopropenes). A number of monofunctional mono- and bicyclic 1-halocyclopropenes have been described.[15] These generally unstable compounds[16] strongly tend to undergo strain-diminishing addition reactions, isomerizations with ring retention, or transformations via ring opening to highly reactive vinyl carbenes. Nevertheless, they are considered as useful synthetic intermediates.[15] Concerning our concept, during the course of our work, White and Bromley[17] successfully converted 2,3-dialkyl-1-chlorocyclopropenes to cyclopropenones, thus confirming the principal feasibility of hydride abstraction in the case of chlorocyclopropenes. 9-Chlorobicyclo[6.1.0]non-1(9)-ene, described by Banwell and co-workers,[18] and approximately comparable with the target dichlorotricycloalkadiene molecules, is reported to be unstable but isolable. Thus, we concluded that the dichlorotricycloalkadienes also might have sufficient lifetimes, to be isolated and transformed into [*n.n*]-cyclopropenonophanes.

Though complicated by the formation of two constitutional isomers, and with further ramifications due to the possibility of configurational isomers, the syntheses of the first tricyclic bischlorocyclopropenes **16** and **17** could be achieved by three-step transformations of cycloalkadiynes **13** and **15** applying methods principally developed for monofunctional targets (Scheme 5): hydrobromination of the diynes **13** and **15** to dibromocycloalkadienes **18** and **19** ("masked diynes"), additions of dichlorocarbene to both double bonds, and eliminations of BrCl from the resulting dibromotetrachlorotricycloalkanes **20** and **21** to form **16** and **17**.

**Scheme 5. Synthesis of Dichlorotricycloalkadienes 16 and 17**




In the first step the bis-hydrobromination[19] of cyclodeca-1,6-diyne (**13**) by hydrozirconation with $Cp_2Zr(H)Cl$ (Schwartz's reagent) in toluene at ambient temperature and subsequent reaction with NBS[20] yielded a mixture of 1,6- and 1,7-dibromocyclodecadiene **18a**,**b** in a molar ratio of ≈1:1, which could be isolated in 76% yield and characterized, but not separated.

In the following cycloaddition reaction with dichlorocarbene we profited from the fact that olefin cyclopropanations are usually more efficient than alkyne cyclopropenations and are not limited to the attack of just one double bond in polyolefins as shown by the phase transfer-catalyzed (PTC) tetrakis-dichlorocyclopropanation of cyclooctatetraene with $HCCl_3$/KOH.[21] Taking into account the fact that halogens increase the ionization

(14) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168. Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

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(17) White, J. M.; Bromley, M. K. *Tetrahedron Lett.* **1993**, *34*, 4091.

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energies of olefins and hence diminish their nucleophilic reactivities, we chose to use the nonbasic $NaO_2CCCl_3$ instead of $HCCl_3$/KOH, to avoid dehydrohalogenation reactions during the relatively long reaction times.

A high surplus of $NaO_2CCCl_3$ is needed for the complete conversion of the dibromocyclodecadienes in 1,2-dimethoxyethane at 80 °C. Four isomeric dibromotetrachlorotricycloalkanes **20a**−**d** were formed, two of which exist in addition as pairs of enantiomers. They were separated from precipitates and eluted through alumina without difficulties. The isolated products proved barely soluble, and their recrystallization required large amounts of $CH_2Cl_2$. The yields of about 51% correspond well with the 70% per unit yields generally cited for monofunctional reference syntheses via the PTC method.[22]

Generation and isolation of the dichlorotricyclododecadienes **16a**−**d** from the dibromotetrachlorotricyclododecanes **20a**−**d** should ideally be carried out under the mildest conditions possible in view of their presumed instability. However, because of the extremely low solubility of **20**, the dehalogenation with methyllithium in ether could not be performed at temperatures as low as those applied by Baird[23] (−80 °C) and White[17] (−78 °C) in the transformations of simpler trihalocyclopropanes. Here, it must be carried out in the range of −5 to −10 °C to provide sufficient dissolution of **20**. Compound **16** was isolated within 1 h by quenching and washing with water, replacing the ether by cyclohexane, eluting through basic alumina, and finally removing the solvent. It was obtained as a pure (TLC) colorless oil in yields exceeding 90%, corresponding to an overall yield of up to 38% based on cyclodecadiyne **13**. It cannot be stored for a longer time even at −40 °C without decomposition (indicated by its turning yellow) but it is stable enough to be characterized spectroscopically. As a synthetic intermediate, therefore, **16** should be promptly utilized. The spectroscopic data are in good agreement with those reported for 9-chlorobicyclo[6.1.0]nonene.[18]

In parallel investigations we subjected cyclotetradecadiyne **15** to the same synthetic procedures (Scheme 5). A considerable difference was found only with respect to the ratio of the two isomers **19a**,**b** produced in the hydrobromination step, which led to 70% yield of a 3:1 mixture of 1,8- and 1,9-dibromocyclotetradecadienes. We succeeded in isolating the predominant 1,8-dibromocyclotetradecadiene **19a** by fractional crystallization from cyclohexane. Thus, we were able to continue the synthetic sequence with this single isomer. Dichlorocyclopropanation produced the *syn*- and *anti*-dibromotetrachlorotricyclohexadecanes **21a**,**b** (50%), and dehalogenation with methyllithium yielded the *syn*- and *anti*-dichlorotricyclohexadecadienes **17a**,**b** (87−95%). On the basis of the cyclotetradecadiyne **15** the overall yields varied from 30 to 33% in several runs.

Having prepared the dichlorotricycloalkadienes in fairly good yields, it remained to convert them to the [*n*.*n*]-cyclopropenonophanes **10**,**12** by hydride abstraction to the intermediate dichloro[*n*.*n*]cyclopropenyliophanes and subsequent hydrolysis (Scheme 4). For the application of the method which was used by Breslow and Dauben for the preparations of single cyclopropenyl cations from cyclopropenes,[14] the low stability of [*n*.*n*]cyclopropenyliophanes has to be considered, as well as the presumably higher activation energies required for their generation.

Hydride abstraction from **17a**,**b** in $CH_2Cl_2$ at 0 °C with triphenylcarbenium tetrafluoroborate over a period of 1 h led to dichloro[5.5]cyclopropenyliophane intermediates. After extraction of triphenylmethane by using a procedure outlined by White[17] for the preparation of dialkylated cyclopropenones, hydrolysis led to [5.5]cyclopropenonophane **12** in 30% yield.

In contrast, immediate hydrolysis without any separation steps proceeded with a much higher efficiency. The phane **12** could be isolated by column chromatography in a yield of 78%, corresponding to an overall yield of 25%, based on **15**, on a scale of 250 mg per run.

Unfortunately, the conditions for converting **16** to the [3.3]cyclopropenonophane **10** are much more limited than those for **17** to **12**. Hydride abstraction from **16** with triphenylcarbenium tetrafluoroborate proved remarkably slower, and hence decomposition reactions of the particularly unstable dichloro[3.3]cyclopropenyliophane intermediate may become much more competitive. In order to optimize hydride abstraction relative to decomposition, we carried out the reaction between −15 and 4 °C for 2 h. After hydrolysis, **10** was isolated in a yield of about 13%. Attempts to obtain a hydride abstraction reagent having a higher oxidation potential and to thereby rise the efficiency of this reaction are underway.

The [*n*.*n*]cyclopropenonophanes **10**−**12** are crystalline, fairly stable compounds. At temperatures above 190 °C, they tend to decompose, splitting off carbon monoxide. Their polarity, increasing in the sequence **12**, **11**, **10**, corresponds with their increasingly high melting points (**12**, 131 °C; **11**, 191−193 °C; **10**, 215 °C dec) and pronounced hydrophilic properties, particularly in the case of **10**.

From a solution in dichloromethane we succeeded in producing a single crystal of **10**, which was subjected to an X-ray analysis.

**X-ray Investigations on 10.** The structure of **10** found in the crystal is depicted in Figure 1, and geometrical data are collected in Table 1.

Similar to the cyclopropenylium units in [5.5]cyclopropenyliophane **6**,[6] the cyclopropenones in **10** are approaching face to face arrangement to an angle of 95.5(3)° between the cyclopropenone planes. The 10-membered ring of **10** adopts a boat conformation with carbon atoms C(5) and C(5)* on the same side. Thus, the molecule has $C_2$ symmetry in the crystal with the axis being perpendicular to the plane formed by C(2), C(2)*, C(3), and C(3)*. The cyclopropenone moieties are arranged on the side opposite to C(5) and C(5)*. This feature appears surprising since the analogous conformer of **7** in the solid state[8] had turned out to be less stable than the boat conformer, having C(5)/C(5)* and the cyclopropenone units on the same side.

The transannular distance between the double-bonded bridgehead carbon atoms amounts to 3.39 Å, being increased by 0.28 Å compared to **7** and by 0.4 Å compared to **13**.[25] Nevertheless, all bridgehead carbon atoms are pyramidalized by 8.0 and 8.9°, respectively, even more

(21) Dehmlow, E. V.; Stiehm, T. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 329. Dehmlow, E. V. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 170.

(22) Baird, M. S.; Nethercott, W.; Slowey, P. D. *J. Chem. Res., Synop.* **1985**, 370; *J. Chem. Res., Miniprint* **1985**, 3815. Baird, M. S.; Hussain, H. H.; Nethercott, N. *J. Chem. Soc. Perkin Trans. 1* **1986**, 1845.

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(25) Gleiter, R.; Karcher, M.; Jahn, R.; Irngartinger, H. *Chem. Ber.* **1988**, *121*, 735.

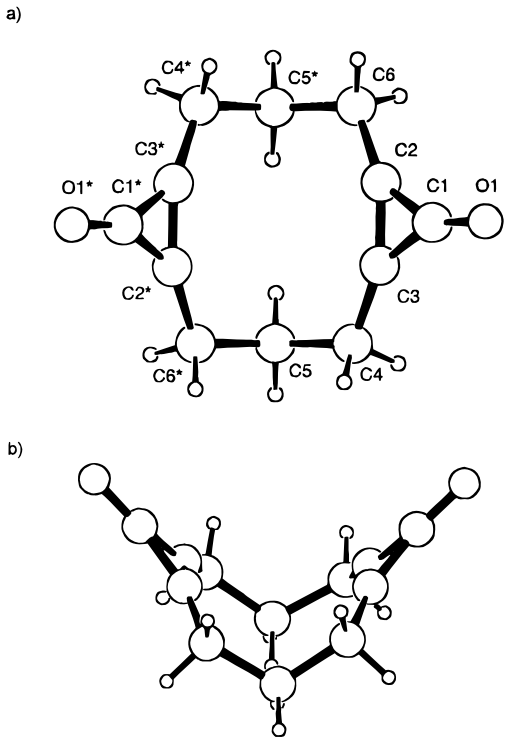


**Figure 1.** Perspective view of **10**: (a) top view, (b) side view.[24]

**Table 1. Comparison of Selected X-ray Structural Parameters of 10 with a 6-31G* Calculation Employing Full Geometry Optimization (Conformer 10a)**

| distances (Å) | X-ray | 6-31G* | distances (Å) | X-ray | 6-31G* |
|---|---|---|---|---|---|
| O(1)−C(1) | 1.226(2) | 1.197 | C(3)−C(4) | 1.483(2) | 1.492 |
| C(1)−C(2) | 1.409(2) | 1.408 | C(4)−C(5) | 1.526(2) | 1.533 |
| C(1)−C(3) | 1.411(2) | 1.408 | C(5)−C(6)* | 1.527(2) | 1.532 |
| C(2)−C(3) | 1.357(1) | 1.338 | C(2)···C(3)* | 3.394(1) | 3.433 |
| C(2)−C(6) | 1.483(2) | 1.493 | | | |
| **angles (deg)** | **X-ray** | **6-31G*** | **angles (deg)** | **X-ray** | **6-31G*** |
| O(1)−C(1)−C(2) | 151.3(1) | 151.62 | C(1)−C(3)−C(2) | 61.2(1) | 61.63 |
| O(1)−C(1)−C(3) | 151.2(1) | 151.65 | C(1)−C(3)−C(4) | 149.0(1) | 147.99 |
| C(2)−C(1)−C(3) | 57.5(1) | 56.71 | C(2)−C(3)−C(4) | 149.2(1) | 149.94 |
| C(1)−C(2)−C(3) | 61.3(1) | 61.65 | C(3)−C(4)−C(5) | 117.6(1) | 117.41 |
| C(1)−C(2)−C(6) | 149.3(1) | 147.94 | C(4)−C(5)−C(6)* | 114.6(1) | 114.95 |
| C(3)−C(2)−C(6) | 148.6(1) | 149.99 | C(2)−C(6)−C(5)* | 116.9(1) | 117.61 |

than in **7** (3 and 4.3°), indicating considerable strain in the 10-membered ring.

**Interactions of Cyclopropenones in [*n.n*]Cyclopropenonophanes.** According to arguments of perturbation theory,[26] a $\pi,\pi$ interaction between two functional groups depends on the difference of their basis orbital energies and on the resonance integral between them. Recently, we reported that in **7** the $\pi$ orbitals of the cyclopropenone unit and the in plane $\pi$ orbital of the triple bond display a considerable interaction, manifested by its PE spectrum.[8] This proved to be remarkably well reproduced by ab initio calculations using a 6-31G* basis set.

Whereas in **7** the basis orbital energies of the two $\pi$ fragments are similar but not equal, **10** provides optimal conditions for an interaction of the two $\pi$-functions with respect to their basis orbital energies. Conversely, the extended separation in **10** might be somewhat unfavorable, compared to **7**. Insufficient volatility and stability of the high melting **10** (mp 215 °C) had prevented PE spectroscopic measurements. The excellent accuracy of the calculations in the case of **7** supports the validity of using the same methods for the elucidation of possible transannular interactions in **10**. Thus, we investigated the conformer **10a** as well as three other conformers **10b**−**d** (Figure 2), which differ from each other by the orientations of the bridges and of the cyclopropenone moieties.

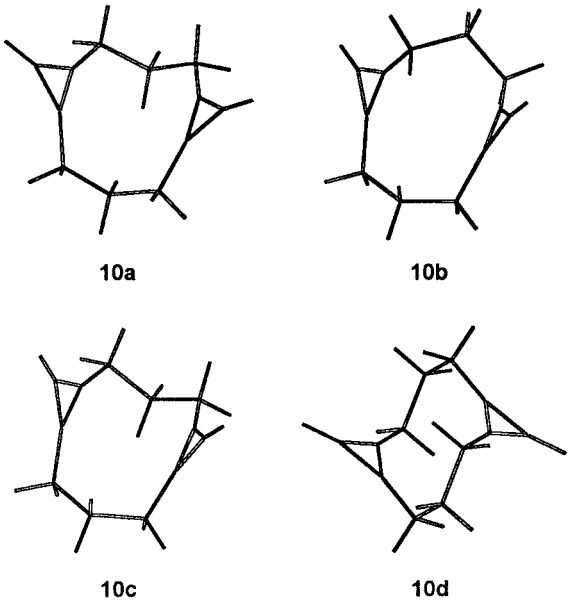


**Figure 2.** Conformers of [3.3]cyclopropenonophane (**10a** corresponds to the conformation found in the solid state).

The results of ab initio calculations[27] on the four confomers **10a**−**d** (6-31G*, geometry optimization in $C_2$ symmetry for **10a**, without symmetry restrictions for **10b**−**d**) are collected in Table 2.

The geometrical data calculated for the conformation **10a** correspond well with the experimental data (Table 1).

The four conformers differ only slightly in their SCF-energies. Here, we show that it is apparently not **10a**, the conformer of the molecule in the solid state, which is the most stable conformer in the gas phase, but **10b**, the analogue to the most stable conformer of **7**.

Obviously, in all conformers interactions occur: the two linear combinations of the cyclopropenone $\pi$-orbitals (HOMO-2 and HOMO-3) differ considerably in energies. However, the interactions in the conformers **10a**−**d** differ by up to almost 0.3 eV (**10a**, **10b**). In **10b**, the orbital overlap apparently is more effective, due to a smaller distance of the $\pi$-centers (3.23 Å) and a more favorable angle between the cyclopropenone units (≈46°). In Figure 3 we show the wave functions of the four highest occupied molecular orbitals of **10b**. They indicate through-bond as well as through-space interactions.[28]

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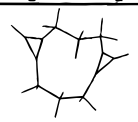
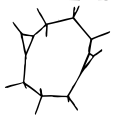
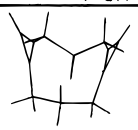
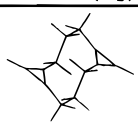
**Table 2. Calculated Energies of the Highest Occupied MOs of Conformers 10a–d (6-31G* Basis)**

| conformer (symmetry) | orbital | 6-31G* [eV] | split [eV] | E(HF) [a.u.] |
|---|---|---|---|---|
|  **10a** ($C_2$) | $n_o$–$n_o$<br>$n_o$+$n_o$<br>$\pi_\Delta$–$\pi_\Delta$<br>$\pi_\Delta$+$\pi_\Delta$ | -9.85<br>-9.99<br>-10.30<br>-10.83 | $n_o$: 0.14<br>$\pi$: 0.53 | -610.99338 |
|  **10b** ($C_{2v}$) | $n_o$–$n_o$<br>$n_o$+$n_o$<br>$\pi_\Delta$–$\pi_\Delta$<br>$\pi_\Delta$+$\pi_\Delta$ | -9.92<br>-9.97<br>-10.13<br>-10.96 | $n_o$: 0.05<br>$\pi$: 0.83 | -610.99422 |
|  **10c** ($C_s$) | $n_o$–$n_o$<br>$n_o$+$n_o$<br>$\pi_\Delta$–$\pi_\Delta$<br>$\pi_\Delta$+$\pi_\Delta$ | -9.90<br>-9.97<br>-10.17<br>-10.93 | $n_o$: 0.07<br>$\pi$: 0.76 | -610.99384 |
|  **10d** ($C_{2h}$) | $n_o$–$n_o$<br>$n_o$+$n_o$<br>$\pi_\Delta$–$\pi_\Delta$<br>$\pi_\Delta$+$\pi_\Delta$ | -10.08<br>-10.22<br>-10.40<br>-10.99 | $n_o$: 0.14<br>$\pi$: 0.59 | -610.99300 |

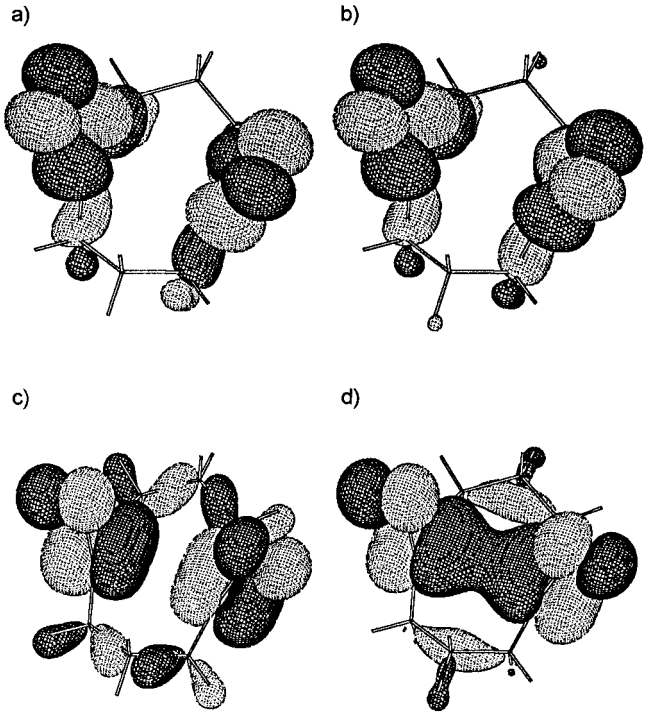



**Figure 3.** Highest occupied $\pi$-MOs of the most stable conformer **10b** (6-31G* basis): (a) HOMO ($n_o - n_o$), (b) HOMO-1 ($n_o + n_o$), (c) HOMO-2 ($\pi_\Delta - \pi_\Delta$), and (d) HOMO-3 ($\pi_\Delta + \pi_\Delta$). Value = 0.032.[29]

In order to differentiate the contributions of through-space and through-bond interactions, we performed NBO analyses[30] for the conformers **10a–d** analogously to the NBO analysis of **7**.[8] The results in the case of **10b** are presented in Figure 4.

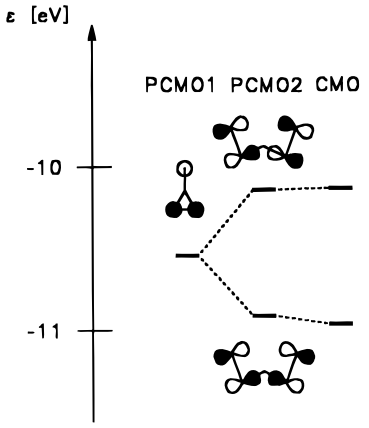



**Figure 4.** Precanonical and canonical $\pi$ MOs in the conformer **10b**, calculated with GAUSSIAN92 and G92NBO (6-31G* basis).

The precanonical molecular orbitals PCMO1 represent the $\pi$-systems ($\pi_= - \pi_{C=O} + \pi_{C=O}$*) of isolated cyclopropenone units. Through-space interaction leads to precanonical MOs PCMO2, while additional through-bond interactions lead to the canonical orbitals CMO. In all four conformers the differences of the $\pi$-orbital energies are mainly caused by through-space interactions; the contributions of through-bond interactions are minor. Interestingly, in [4.4]cyclopropenonophane (**11**) and [5.5]-cyclopropenonophane (**12**), preliminary MINDO/3 calculations[31] did not indicate significant $\pi$,$\pi$ interactions.

## Conclusions

Convenient methods have been developed to synthesize the [*n.n*]cyclopropenonophanes **10–12** ($n$ = 3–5) via dichlorocyclopropenation of alkynylenecyclopropenonophanes **7–9** or, alternatively, via hydride abstraction from dichlorotricycloalkadienes **16** and **17** and subsequent hydrolysis. As in the series of the starting

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compounds **13**−**15**,[32] as well as in the series of alkinylenecyclopropenonophanes **7**−**9**,[8] the smallest homologue **10** ($n = 3$) stands out, displaying considerable through-space interactions of its $\pi$ orbitals.

The much more distinct pyramidalizations of the C(2) and C(3) carbon atoms in the cyclopropenone moieties, compared to those of **7**, might partially result from additional dipole−dipole interactions. These might even be effective across the larger distances in **11** and **12**, but have not yet been quantified.

## Experimental Section

All reactions were carried out under an Ar atmosphere with magnetic stirring. Toluene, 1,2-dimethoxyethane, and diethyl ether were freshly distilled from Na−benzophenone, while dichloromethane was distilled from $P_4O_{10}$. Cycloalkadiynes **13**−**15**,[33] Schwartz's reagent,[34] and bicycloenynones **7**−**9**[7] were prepared according to the literature procedures. HRMS spectra were recorded on a VG-ZAB (experimental error ±5 mmass units).

**X-ray Structure Analysis of 10.** The compound was crystallized from dichloromethane at ambient temperature. The X-ray data (Table 1) were collected at 263 K on an automated diffractometer (Enraf-Nonius CAD4, graphite monochromator, Mo Kα radiation, $\omega - 2\Theta$ scan). Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MULTAN[35]). Refinements on $F^2$ were carried out by full-matrix least-squares procedures with anisotropic thermal parameters for the carbon and oxygen atoms. The MolEN program system[36] was used for crystallographic calculations.[37]

**Preparation of Dibromocycloalkadienes 18 and 19: (*E*,*E*)-1,6-Dibromocyclodeca-1,6-diene (18a) and (*E*,*E*)-1,7-Dibromocyclodeca-1,6-diene (18b).** To a mixture of 1.032 g (4 mmol) of Schwartz's reagent and 300 mL of toluene was added 0.263 g (1.99 mmol) of cyclodeca-1,6-diyne. After the mixture was stirred for 20 h at rt the diyne was completely converted. The resulting red suspension showed two close spots by TLC ($Al_2O_3$, cyclohexane). NBS (0.730 g, 4.1 mmol) was added to give a pale yellow mixture, which was stirred for 40 min and then filtered through neutral alumina (elution with cyclohexane). The solvent was removed, and the resulting residue was purified by column chromatography on silica with cyclohexane as eluent to yield 444 mg (76%) of a mixture of **18a** and **18b** in a ratio of about 1:1 (estimated from $^{13}$C NMR). The two isomers could not be separated by column chromatography or crystallization: mp 122−123 °C; $^1$H NMR-(300 MHz, $CDCl_3$) $\delta$ 5.84−5.78 (m, 2H), 2.84−2.74 (m, 2H), 2.27−1.94 (m, 8H), 1.55−1.43 (m, 2H); IR (KBr) 2949, 2940, 2914, 2903, 2854, 2829, 1643, 1441, 1192, 1025, 1011, 891, 839, 768, 631, 587 cm$^{-1}$; MS(EI) *m*/*z* 296 ($M^+$, 2), 294 ($M^+$, 3), 292 ($M^+$, 2), 215(3), 213 (3), 133 (67), 105 (32), 91 (100), 79 (33), 77 (31); $^{13}$C-NMR (75.47 MHz, $CDCl_3$) $\delta$ 133.1 and 132.8 (CH), 126.2 and 126.0 (C), 32.0, 31.3, 27.1, 26.3, 25.4, 24.2, 22.8 (7 $CH_2$). Anal. Calcd for $C_{14}H_{22}Br_2$: C, 40.85; H, 4.80; Br, 54.35. Found: C, 40.88; H, 4.83; Br, 54.19.

**(*E*,*E*)-1,8-Dibromocyclotetradeca-1,8-diene (19a) and (*E*,*E*)-1,9-Dibromocyclotetradeca-1,8-diene (19b).** The same procedure as above with 0.677 g (2.6 mmol) of Schwartz's reagent, 300 mL of toluene, 0.245 g of cyclotetradeca-1,8-diyne, and 0.47 g of NBS yielded 317 mg (70%) of a mixture of the two isomers **19a** and **19b** in a ratio of ≈3:1 (estimated from $^{13}$C-NMR): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.87−5.81 (m, 2H), 2.47−2.41 (m, 4H), 2.09−2.00 (m, 4H), 1.61−1.50 (m, 4H), 1.41−1.24 (m, 8H); IR (KBr) 2945, 2853, 1643, 1459, 1445, 1429, 1287, 1238, 1187, 965, 873, 862, 796, 724, 606 cm$^{-1}$; MS-(EI) *m*/*z* 352 ($M^+$, 2), 350 ($M^+$, 5), 348 ($M^+$, 3), 271 (1), 269 (1), 190 (5), 189 (32), 147 (11), 133 (10), 121 (37), 107 (42), 95 (57), 93 (46), 91 (30), 81 (54), 79 (71), 67 (88), 53 (52), 41 (100); $^{13}$C-NMR (75.47 MHz, $CDCl_3$) $\delta$ 132.8 and 132.7 (CH), 126.2 and 126.0 (C), 34.5, 33.9, 29.4, 28.9, 27.8, 27.4, 27.1, 26.8, 26.8, 26.5, 26.4 (11 $CH_2$). Anal. Calcd for $C_{14}H_{22}Br_2$: C, 48.03; H, 6.33; Br, 45.64. Found: C, 47.80; H, 6.15; Br, 45.36.

By fractional crystallization from cyclohexane, about 200 mg of **19a** was produced in pure form: mp 121 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.85 (t, $J = 8.37$ Hz, 2H), 2.44 (t, $J = 6.84$ Hz, 4H), 2.09−2.02 (m, 4H), 1.60−1.51 (m, 4H), 1.40−1.29 (m, 8H); $^{13}$C-NMR (75.47 MHz, $CDCl_3$) $\delta$ 132.7 (CH), 126.2 (C), 33.9, 29.4, 27.8, 26.8, 26.5 (5 $CH_2$).

**1,7-Dibromo-6,6,12,12-tetrachlorotricyclo[9.1.0.0$^{5,7}$]-dodecanes (20a,b) and 1,5-Dibromo-6,6,12,12-tetrachlorotricyclo[9.1.0.0$^{5,7}$]dodecanes (20c,d).** To a stirred solution of 2.17 g (7.38 mmol) of **18a,b** in 400 mL of 1,2-dimethoxyethane was added 300 g (1.618 mol) of the sodium salt of trichloroacetic acid over a period of about 20 h at 85 °C. According to TLC ($SiO_2$, cyclohexane; detection with ethanol/$H_2SO_4$, hot air), the starting material was completely converted to give mainly the bis-dichlorocarbene adduct. The resulting dark black mixture was filtered through alumina (elution with cyclohexane). After the solvent was removed the residue was treated with hexanes. An insoluble ochre colored powder was left, which proved to be mainly the desired product **20a**−**d**. The solution was chromatographed on silica with hexanes as eluent to yield further product. Both fractions were recrystallized from large amounts of dichloromethane yield 1.73 g (51%) of colorless crystals; mp 240 °C; $^1$H NMR(250 MHz, $CDCl_3$) $\delta$ 2.33−1.23 (m); IR (KBr) 3004, 2942, 2865, 1449, 881, 817, 777, 752 cm$^{-1}$; $^{13}$C NMR (62.90 MHz, $CDCl_3$) $\delta$ 66.7 and 66.6 (C), 47.5 and 47.4 (C), 44.4 and 43.5 (CH), 30.1, 29.1, 27.6, 26.9, 22.8, 21.9 (6 $CH_2$). Anal. Calcd for $C_{12}H_{14}Br_2Cl_4$: C, 31.34; H, 3.07; Br, 34.75; Cl, 30.84. Found: C, 31.33; H, 3.09; Br, 34.67; Cl, 30.75.

**1,9-Dibromo-8,8,16,16-tetrachlorotricyclo[13.1.0.0$^{7,9}$]-hexadecanes (21a,b).** As described above for **20a**−**d**, to a stirred solution of 600 mg (1.71 mmol) of **19a** in 30 mL of 1,2-dimethoxyethane was added 11 g of the sodium salt of trichloroacetic acid over a period of 15 h at 85 °C. After the workup and recrystallization from large amounts of dichloromethane, 440 mg (50%) **21a**,**b** were obtained: mp 216−217 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.06−1.25 (m); IR (KBr) 2952, 2926, 2916, 2857, 1461, 1451, 943, 867, 852, 785, 772, 602 cm$^{-1}$; $^{13}$C-NMR (50.32 MHz, $CDCl_3$) $\delta$ 67.5 (C), 48.5 (C), 43.5 (CH), 32.4, 27.8, 27.12, 27.10, 24.8 (5 $CH_2$). Anal. Calcd for $C_{16}H_{22}Br_2Cl_4$: C, 37.25; H, 4.30; Br, 30.97; Cl, 27.48. Found: C, 37.11; H, 4.28; Br, 31.11; Cl, 27.59.

**6,12-Dichlorotricyclo[9.1.0.0$^{5,7}$]dodeca-1(12),6-diene (16a,b) and 6,12-Dichlorotricyclo[9.1.0.0$^{5,7}$]dodeca-1(12),5-diene (16c,d).** To a suspension of 471 mg (1.02 mmol) of **20a**−**d** in 500 mL of diethyl ether was added 1.4 mL (2.24 mmol) of a 1.6 N solution of methyllithium in ether at −10 to −5 °C within 20 min. The reaction mixture was stirred at −5 °C until the solid had dissolved and TLC showed only one spot. Then, 10 mL of water was added. After the mixture was warmed to ambient temperature, the organic layer was washed several times with water until the aqueous phase was neutral. Evaporation of the solvent gave an unstable yellow oil, which was rapidly purified on basic alumina with cyclohexane as eluent to yield 199−233 mg (85−99%) of a colorless oil: $^1$H NMR(200 MHz, $CD_2Cl_2$) $\delta$ 2.69−2.42 (m, 4H), 2.11−2.00 (m, 2H), 1.95−1.67 (m, 4H), 1.59−1.43 (m, 2H), 1.16−0.97 (m, 2H); $^{13}$C NMR (50.32 MHz, $CD_2Cl_2$) $\delta$ 118.7 (C), 115.5 (C), 34.7 ($CH_2$), 32.6 ($CH_2$), 31.0 (CH), 30.7 (CH), 25.7, 25.6, 24.4, 23.7, 22.9 (5 $CH_2$). The compound was subjected directly to the hydride abstraction step.

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(34) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
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(36) MolEN: Structure Determination System, Enraf-Nonius, Delft Instruments X-Ray Diffraction B. V., Delft, Niederlande, 1990.
(37) The authors have deposited tables of crystallographic refinement parameters, atomic coordinates, and the thermal parameters of **10** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge, Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK.

**8,16-Dichlorotricyclo[13.1.0.0$^{7,9}$]hexadeca-1(16),8-dienes (17a,b).** As described for the synthesis of **16a**−**d**, to a suspension of 517 mg (1 mmol) of **21a**,**b** in 500 mL of diethyl ether was added 1.25 mL of a 1.6 N solution of methyllithium in ether at −10 °C within 20 min. The mixture was stirred at −10 °C for an additional 20 min, until the solid had dissolved and TLC showed only one spot. Workup as described above for **16a**−**d** gave an unstable yellow oil, which was rapidly purified on basic alumina with cyclohexane as eluent, yielding 249−271 mg of **17a**,**b** (87−95%) as a colorless oil: $^1$H NMR (200 MHz, $CD_2Cl_2$) $\delta$ 2.51−2.45 (m, 4H), 2.04 (dd, $J_1$ = 2 Hz, $J_2$ = 6.5 Hz, 2H), 1.88−1.76 (m, 2H), 1.66−1.10 (m, 14H); IR (KBr) 2928, 2856, 1832, 1695, 1458, 1441, 1078, 1028 cm$^{-1}$; $^{13}$C NMR (50.32 MHz, $CD_2Cl_2$) $\delta$ 119.1 (C), 113.2 (C), 34.2 ($CH_2$), 30.2 (CH), 28.4, 27.1, 26.8, 23.4 (4 $CH_2$); HRMS calcd for $C_{16}H_{22}{}^{37}Cl$ (M − Cl) 251.1381, found 251.1381. The compound was subjected directly to the hydride abstraction step.

**[3.3]Cyclopropenonophane 10. (a) From 16a−d.** To a solution of 251 mg (0.76 mmol) of triphenylmethyl tetrafluoroborate in 10 mL of dichloromethane was added a solution of 87 mg of **16a**−**d** in 20 mL of dichloromethane at −15 °C within 5 min. The color of the solution remained dark orange. After 2 h of stirring at −15 to +4 °C, 5 mL of a saturated aqueous solution of $NaHCO_3$ was added. No product could be detected in the yellow organic layer. The aqueous phase was extracted with 50 mL of chloroform 50 times. From the combined extracts the chloroform was removed, and the resulting solid was chromatographed on neutral alumina with chloroform/ethanol (100:1), which gave 9 mg (13%) of **10**: mp 215 °C dec; $^1$H NMR (200 MHz, $CDCl_3$) 2.85−2.79 (m, 8H), 2.28−2.16 (4H); IR (KBr) 2949, 2943, 2903, 1830, 1617, 1423, 1406, 1070 cm$^{-1}$; MS(EI) *m*/*z* 188 (M$^+$, 1), 160 (1), 132 (20), 131 (31), 117 (80), 115 (80), 104 (41), 91 (100); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 161.3 (C), 159.2 (C), 26.1 ($CH_2$), 21.9 ($CH_2$); HRMS calcd for $C_{12}H_{12}O_2$ 188.0837; found: 188.0809.

**(b) From 7.** A mixture of 0.592 g (3.7 mmol) of **7** and 0.7 g (3.8 mmol) of the sodium salt of trichloroacetic acid in 80 mL of 1,2-dimethoxyethane was stirred for 1.5 h at 70−75 °C. One hundred mL of ethyl acetate were added, and the cyclopropenonophane was extracted from the brown organic solution with water. From the organic solution, 305 mg (2.31 mmol) of **7** could be recovered (48.5% conversion) by column chromatography on neutral alumina with ethyl acetate as eluent. The aqueous phase was extracted with chloroform (50 times with 50 mL). Evaporation of the solvent and chromatography on neutral alumina with chloroform/ethanol (100:1) as eluent gave 13 mg of **10** (4% based on conversion).

**[4.4]Cyclopropenonophane 11.** A mixture of 360 mg (1.91 mmol) of **8** and 355 mg (1.91 mmol) of the sodium salt of trichloroacetic acid in 60 mL of 1,2-dimethoxyethane was stirred for 1.5 h at 70−75 °C. Workup as described above for b gave 176 mg (0.94 mmol) of recovered **8** (51% conversion) and 11 mg of **11** (5% based on conversion): mp 191−193 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 2.72 (m, 8H), 1.75−1.74 (m, 8H); IR (KBr) 2940, 2904, 2866, 1830, 1613, 1462, 1447, 1267, 1221, 1091 cm$^{-1}$; MS *m*/*z* 216 (M$^+$, 4), 188 (4), 160 (26), 131 (58), 117 (100), 104 (59), 91 (99.5), 79 (31); $^{13}$C NMR (50.32 MHz, $CDCl_3$) $\delta$ 161.6 (C), 160.2 (C), 26.2 ($CH_2$), 25.2 ($CH_2$); HRMS calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1128.

**[5.5]Cyclopropenonophane 12. (a) From 17a,b.** To a solution of 890 mg (2.7 mmol) of triphenylmethyl tetrafluoroborate in 40 mL of dichloromethane was added a solution of 365 mg (1.28 mmol) of **17a**,**b** in 10 mL of dichloromethane at 0 °C within 5 min. The initially dark orange colored solution brightened up noticeably. After 1 h of stirring, according to TLC **17a**,**b** had completely reacted, and 10 mL of a saturated aqueous solution of $NaHCO_3$ was added. The organic layer was washed with water, and the combined aqueous phases were extracted 20 times with 50 mL of chloroform. All organic solutions were combined. After removal of the solvents, the residue was separated on neutral alumina with chloroform/ethanol (100:1) as eluent, which gave 243 mg (78%) of **12**: mp 131 °C; $^1$H NMR(200 MHz, $CDCl_3$) $\delta$ 2.66−2.60 (m, 8H), 1.78−1.64 (m, 8H), 1.38−1.26 (m, 4H); IR (KBr) 3012, 2932, 2858, 1843, 1619, 1613, 1216 cm$^{-1}$; MS(EI) *m*/*z* 244 (M$^+$, 0.1), 216 (1), 188 (2), 187 (2), 173 (7), 159 (8), 145 (21), 131 (30), 117 (42), 105 (33), 91 (57), 79 (57), 41 (100); $^{13}$C NMR (50.32 MHz, $CDCl_3$) $\delta$ 161.4 (C), 160.2 (C), 28.9, 25.7, 25.5 (3 $CH_2$); HRMS calcd for $C_{16}H_{20}O_2$ 244.1463, found: 244.1449.

**(b) From 9.** A mixture of 1.040 g (4.78 mmol) of **9** and 0.89 g (4.8 mmol) of the sodium salt of trichloroacetic acid in 80 mL of 1,2-dimethoxyethane was stirred at 70−75 °C within 1.5 h. Then, 60 mL of brine, 60 mL of water, and 100 mL of ethyl acetate were added. After extraction of the aqueous layer with chloroform (20 times with 30 mL), all organic layers were combined and the solvents were evaporated. The resulting residue was chromatographed on neutral alumina with chloroform/ethanol (100:1) as eluent, which gave 625 mg of recovered **9** (39.6% conversion) and 15 mg (3% based on conversion) of **12**.

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**Supporting Information Available:** $^1$H NMR and $^{13}$C NMR spectra of **10**−**12** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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