Partially Hydrogenated [2.2]Paracyclophanes as Precursors in Polycyclic Hydrocarbon Chemistry[‡]

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Dedicated to Robert L. Lichter on the occasion of his 60th birthday

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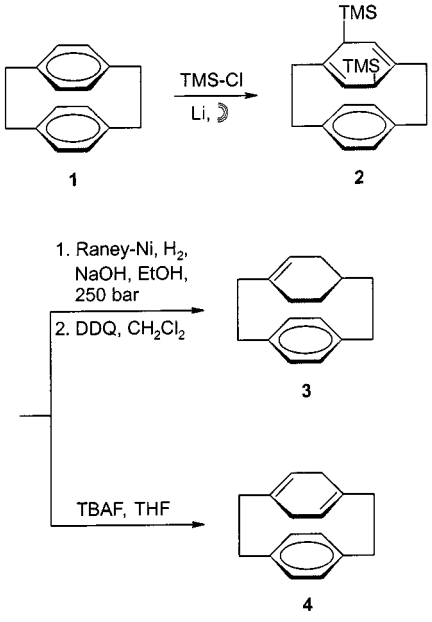
The chemical behavior of the tetrahydro- and dihydro[2.2]paracyclophanes, **3** and **4**, respectively, was investigated. In particular, **3** was subjected to carbene addition (methylenation with triethylaluminum/diiodomethane, dichloro- and dibromocarbene addition) and epoxidation with *m*-chloroperbenzoic acid. The resulting mono adducts **5a**, **5b**, and **5d** were characterized by spectroscopic methods and by chemical transformations to **6**, **7**, and **10**. Reaction of **3** with dehydrobenzene (**8**) furnished the ene-product **9**. Similarly, the bis adducts **14a–c** were formed, each in good to excellent yield, from the bis-olefin **4**. When **14c** was ring-opened by treatment with trifluoroacetic acid, the chiral diol **16** was produced, which was then oxidized to the diketone **18** and brominated to give the dibromide **19**. When the latter was treated with potassium *tert*-butoxide in tetrahydrofuran, it produced the bridged benzobarrelene **21**, the smallest and most highly strained representative of this class of hydrocarbons. On pyrolysis, **21** underwent a retro-Diels–Alder reaction to pyracene (**20**) and ethylene. The derivatives **14b** and **16**, which show polymorphism and crystallized in two macroscopically distinguishable crystal forms **16-I** and **16-II**, together with compounds **19** and **21** were amenable to X-ray crystal structure analysis. The structural properties of these compounds are discussed in detail.

Introduction

Cyclophanes have been studied for decades, largely because of their unusual electronic and steric properties.[2a−2d] Recently, a growing number of researchers have become interested in using chiral cyclophanes, in particular derivatives of [2.2]paracyclophane, as ligands in stereoselective synthesis.[3a−3m]

Another modern concept in cyclophane chemistry involves the use of these now readily available compounds as substrates for the preparation of novel polycyclic hydrocarbon systems.[4a,4b] Fully hydrogenated cyclophanes are particularly valuable in this respect since they are susceptible to Lewis acid-catalyzed rearrangements, comparable to the celebrated isomerization of tetrahydrodicyclopentadiene to adamantane.[2d,5a,5b] However, partially hydrogenated cyclophanes, possessing residual π-electron density, could also be useful for the preparation of various types of cage hydrocarbons. Two prototypes of these derivatives, 4,5,6,7-tetrahydro[2.2]paracyclophane (**3**) and 4,7-dihydro[2.2]paracyclophane (**4**) have recently been prepared in our laboratories in a straightforward manner from the parent hydrocarbon **1** via 4,7-bis(trimethylsilyl)-4,7-dihydro[2.2]paracyclophane (**2**, Scheme 1),[4] providing these *anti*-Bredt systems in sufficient quantities to investigate their chemical behavior.



Scheme 1. The preparation of the partially hydrogenated [2.2]paracyclophanes **3** and **4** from [2.2]paracyclophane (**1**, TBAF = tetrabutylammonium fluoride)

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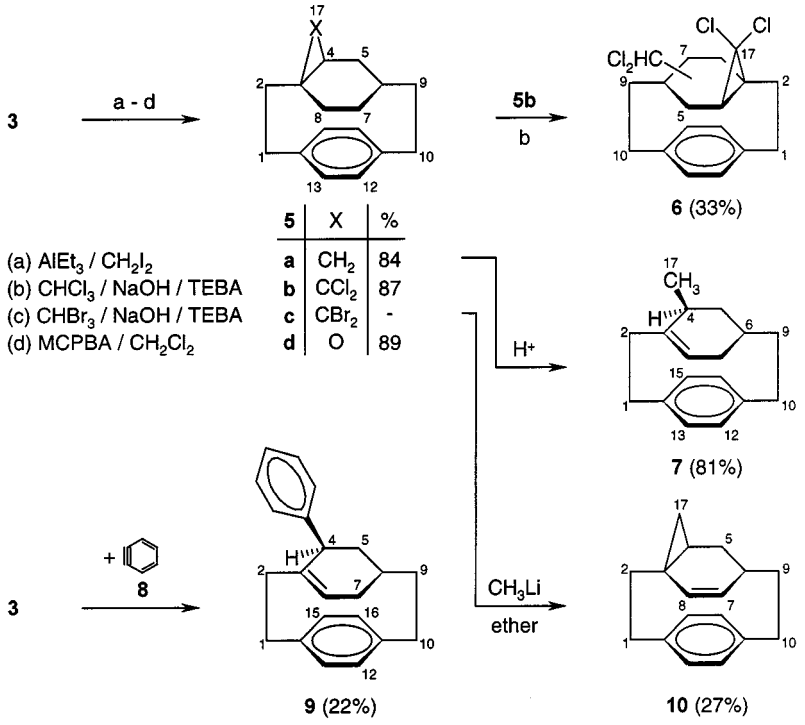


Scheme 2. Cycloaddition experiments with 4,5,6,7-tetrahydro[2.2]paracyclophane (**3**)

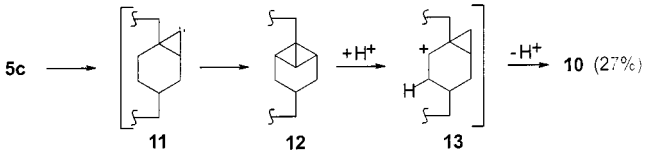
After describing some typical reactions of **3** and **4**, this paper presents the conversion of **4** − and, hence, implicitly of **1** − into a novel benzobarrelene derivative, thus providing a link between two areas of hydrocarbon chemistry, which at first sight, by simple comparison of substrate and product structures, might be thought to be totally unrelated.[6]

Results and Discussion

Reactivity of the Double Bond of the Mono-Alkene 3

In a first series of cycloaddition experiments hydrocarbon **3** was subjected to various cyclopropanation reagents (Scheme 2). Methylenation with triethylaluminum/diiodomethane according to the method of Yamamoto[7] at −5 °C afforded the expected cyclopropane **5a** after the very short reaction time of 15 min in good yield. The high reactivity of **3** is presumably caused by its high strain, "normal" alkenes such as 1-dodecene or cyclooctene require reaction times of several hours at room temperature.[7] Although **5a**, which was characterized by the usual spectroscopic methods (see Exp. Sect.), can be purified by column chromatography on silica gel at room temperature, it slowly decomposes as shown by gas chromatographic analysis of a sample that had been kept for several days in the refrigerator. Whereas addition of dichlorocarbene, generated from chloroform with sodium hydroxide under phase-transfer conditions at 0 °C, to **3** leads to the isolable dichloride **5b** in good yield again, the dibromide **5c** cannot be obtained by dibromocyclopropanation of the olefin with bromoform/sodium hydroxide. TLC of the crude reaction mixture showed that only one product was formed, but this could not be isolated because of its extreme instability.

All cyclopropanation products undergo secondary reactions readily. When **5a** was treated with concentrated hydrochloric acid in dichloromethane, the three-membered ring could be opened and the methyl derivative **7** was formed in 81% yield. Presumably one of the C−C bonds of the cyclopropane ring is opened by protonation and the resulting bridgehead carbocation stabilizes itself by proton loss and regeneration of the double bond. When the reaction time of the dichlorocarbene addition experiment was extended (from 3 h to 2 d) and the temperature increased (from 0 °C to room temperature) the tetrachloride **6** was isolated as well as **5b**. Clearly this is a secondary product from **5b** and was presumably formed by insertion. Insertion into bridgehead C−H bonds of polycyclic hydrocarbons is a known phenomenon and has been observed for example, when adamantane is treated with chloroform and base under phase transfer conditions.[8] Although **5c** could not be isolated (see above), treatment of the crude product mixture with methyllithium in diethyl ether furnished a characterizable compound, the vinylcyclopropane derivative **10**. For its formation we propose that the carbene generated from **5c** by debromination, the intermediate **11**, first undergoes in-



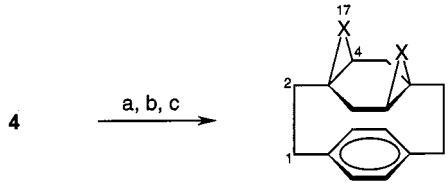
Scheme 3. Treatment of **5c** with methyllithium

sertion to a tricyclo[4.1.0.0^{4,7}]heptane derivative, **12**, as has been described for simpler dibromonorcarane derivatives (Scheme 3).[9]

These tricyclic hydrocarbons are extremely acid-sensitive and open to yield vinylcyclopropane derivatives on treatment with acid.[10] In the case of **12** this would lead to the carbocation **13**, from which **10** would be formed by loss of a proton. Hydrocarbon **10**, stable only at room temperature (in dichloromethane), is the first partially hydrogenated cyclophane with a double bond not involving a bridgehead carbon atom. When **3** was epoxidized with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at room temperature in the presence of potassium carbonate, the epoxide **5d** was obtained as the sole product in 89% yield. Interestingly, in both carbon and oxygen addition, no products were formed by attack of the benzene ring of **3**, indicating a much higher reactivity of the olefinic double bond of this hydrocarbon than of the aromatic subunit. Both cyclopropanation and epoxidation of [2.2]paracyclophanes are well-documented processes,[11] and examples are even known where the benzene rings are attacked preferentially over double bonds in methylenations of paracyclophanes.[12] In a final competition experiment with **3**, the addition of dehydrobenzene (**8**), the double bond was again the exclusive point of attack, yielding the phenyl-substituted hydrocarbon **9**, albeit in poor yield. The structure of **9**, formed most probably by an ene-reaction of **3**, was proved by extensive NMR studies, including NOE, C,H-correlation, and H,H-COSY experiments (see Exp. Sect.).

Reactivity of the Double Bonds of the Diene 4

The addition of divalent species to **4** led to the expected 2:1-products in all cases (Scheme 4), although reactivity differences were noted.



14	X	%
a	CH_2	87
b	CCl_2	75
c	O	89

(a) $AlEt_3$ / CH_2I_2
(b) $CHCl_3$ / NaOH / TEBA
(c) MCPBA / CH_2Cl_2

Scheme 4. Cycloaddition experiments with 4,7-dihydro[2.2]paracyclophane (**4**)

Thus, cyclopropanation of **4** required longer reaction times (2 h) and higher temperatures (8 °C) than in the case of **3**. Performing the reaction at even higher temperatures resulted in the rapid consumption of **14a**, presumably by further addition of methylene to the primary adduct. Surprisingly, the addition of dichlorocarbene to **4** also yielded a bis adduct, the tetrachloride **14b**, in good yield. Clearly, the steric congestion in the monoadduct formed en route to **14b** was not enough to prevent further dichloromethylen-

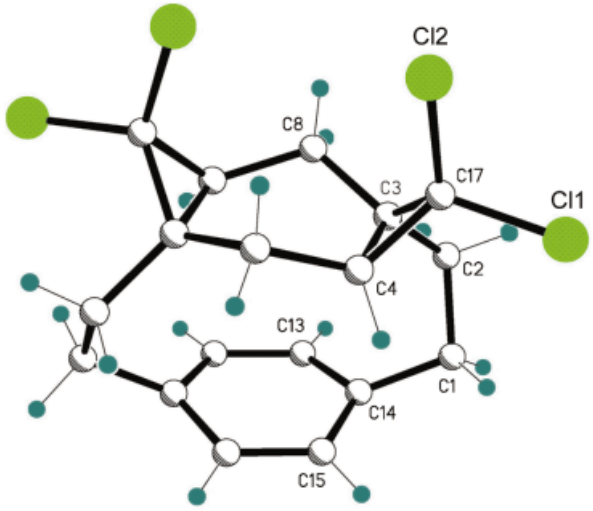


Figure 1. Structure of **14b** in the crystal; radii are arbitrary

ation. In this case no further adducts were produced on extending the reaction time (up to 3 d), demonstrating the lower reactivity of dichlorocarbene as compared to methylene. Single crystals suitable for X-ray crystal structure determination were obtained by fractional sublimation of **14b**. The crystal structure of the tetrachloride is shown in Figure 1.

Compound **14b** crystallized with imposed C_2 symmetry. The aromatic ring (C13−C14−C15−C13A−C14A−C15A) is puckered into a boat form typical of [2.2]paracyclophane derivatives. The angle of 12.9(1)° between the plane of the four coplanar atoms (C13/C15/C13A/C15A) and the displaced plane of C13−C14−C15 is similar to that in the unsubstituted parent compound [2.2]paracyclophane (12.5°).[13] The second characteristic angle in the unsaturated part of **14b** (C13−C14−C15 to C14−C1 15.5°) is markedly larger than in the parent compound (11.1°). The distortion of the carbon skeleton is also reflected by the torsion angle C14−C1−C2−C3 of 53.4(2)° compared to −0.1°, the corresponding angle in the unsubstituted cyclophane. In comparison to paracyclophane, the strain in **14b** is smaller, as indicated by the distinctly shortened Csp^3−Csp^3 bond length of the ethano bridges: C1−C2 153.9(2) pm (157.1 pm). The cyclohexane ring of **14b** also shows a boat form, with C8 bent out of the plane by 46.8(2) pm. The geometry of the cyclopropyl moiety in **14b** is asymmetric (cf. the data for 1,1-dichlorocyclopropane, which are given in parentheses). The distal bond C3−C4, opposite the substituent, is lengthened by the π-donor chloro substituents: 154.0(2) pm [153.5(9) pm]. The vicinal bonds are shortened asymmetrically. The bond C3−C17 involving the bridgehead C3 is slightly longer at 151.9(2) pm than C4−C17 149.4(2) pm [149.4(3) pm]. The Csp^3−Cl bonds correspond well to those of 1,1-dichlorocyclopropane [175.6(2) pm]: 176.4(2) pm (C17−Cl1) and 175.4(2) pm (C17−Cl2).

The crystal packing of **14b** shows Cl1···Cl2 contacts, 372.2(1) pm, slightly longer than the sum of the van-der-

Waals radii (362 pm). These weak interactions lead to zigzag chains parallel to the diagonal [101].

The epoxidation of **4** with MCPBA in a two-phase system (dichloromethane/15% aqueous potassium carbonate solution) furnished the bis(epoxide) **14c** in excellent yield. The structure of this thermally extremely stable addition product (m.p. 285 °C) was established by the usual spectroscopic methods (see Exp. Sect.).

From the Bis(epoxide) 14c to the Doubly-Bridged Barrelene 21

When **14c** was treated with trifluoroacetic acid (TFA) in dichloromethane for 2 h and the crude reaction mixture hydrolyzed with sodium hydroxide solution, the diol **16** could be isolated in 53% yield. It is obvious from the spectroscopic data of the hydrolysis product that a fundamental change of the carbon skeleton of the substrate had taken place during the epoxide ring opening reaction. Unambiguous structural proof, however, was only possible after fractional sublimation, which provided single crystals of **16** amenable to X-ray crystal structure analysis. The results of this analysis are shown in Figure 2, the packing diagrams in Figures 3 and 4.

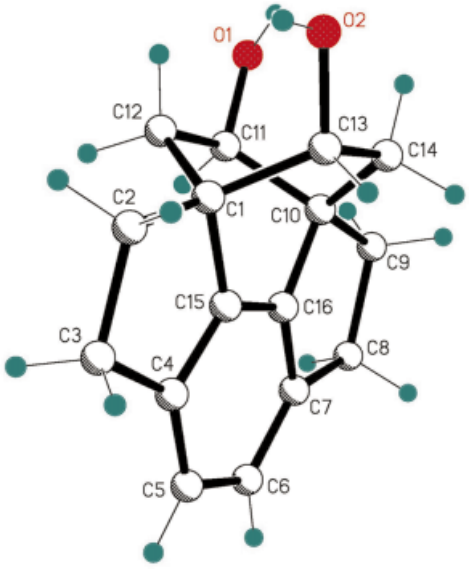


Figure 2. Structure of **16** in the crystal; radii are arbitrary; this is modification **16-I**, molecule on general position

Compound **16** shows polymorphism and crystallized in two macroscopically distinguishable crystal modifications. The first, **16-I**, formed colorless square tablets in the space group *P*2/*c*. The crystal structure **16-I** contains one and a half independent molecules in the asymmetric unit; the half molecule is completed by C_2 symmetry. The carbon skeleton C1 to C10, C15, and C16 can be considered as nearly planar with mean deviations from the plane of 5.0 pm (C1 to C16) and 1.9 pm (C1′ to C15′). The two ethano bridges are structure determining in **16-I**. In the benzobicyclo[2.2.2]octene moiety, the single bonds adjacent to the aromatic ring are slightly shorter than in the unsaturated compound **21** (see below): 147.7(4), 147.3(4), and 146.5(3) (C1−C15, C10−C16, and C1′−C15′, respectively). The saturated bonds C11−C12 and C13−C14 are associated with a small elongation of the bond C15−C16: 134.6(4) (C15−C16) and 134.8(5) (C15′−C15′A). The intramolecular distance between the bridgehead atoms amounts to 266.6(4) (C1···C10) and 266.7(5) pm (C1′···C1′A). The single bonds lying in the plane of the boat-shaped cyclohexane ring are markedly lengthened in comparison to those in unsubstituted cyclohexane (153.5 pm) to reduce the strain of the molecule: 156.7(4), 157.1(4), and 156.9(4) pm (C11−C12, C13−C14, and C11′−C12′, respectively). Around the bridgehead atoms, however, a strong distortion of the angles was observed: 99.9(2)−119.0(2)° (C1), 100.5(2)−119.3(2)° (C10), and 100.8(2)−119.2(2)° (C1′).

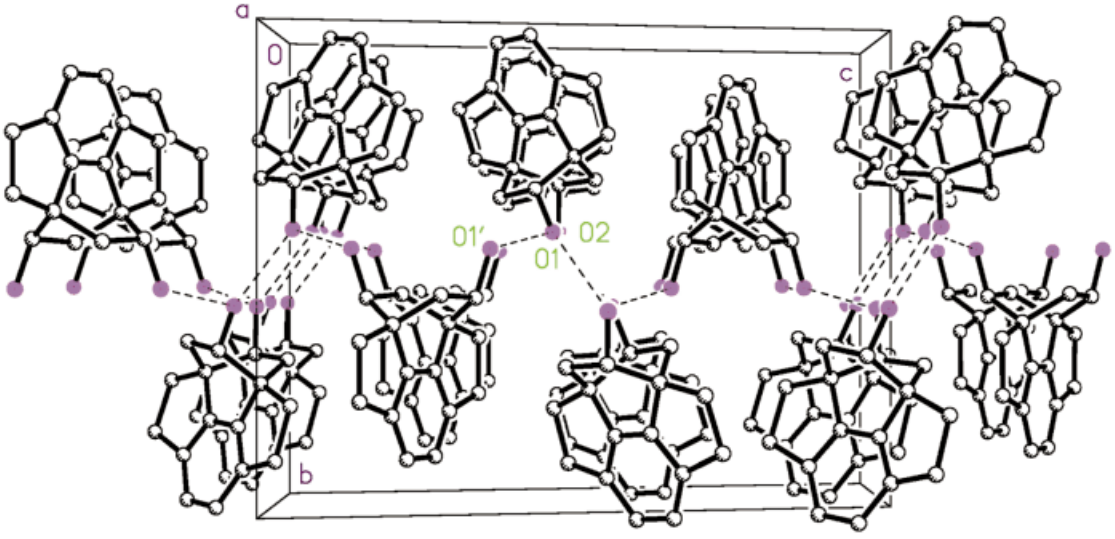


Figure 3. The packing diagram for **16-I** viewed parallel to the *x* axis; H atoms have been omitted for clarity; the oxygen atom O2 is obscured by O1

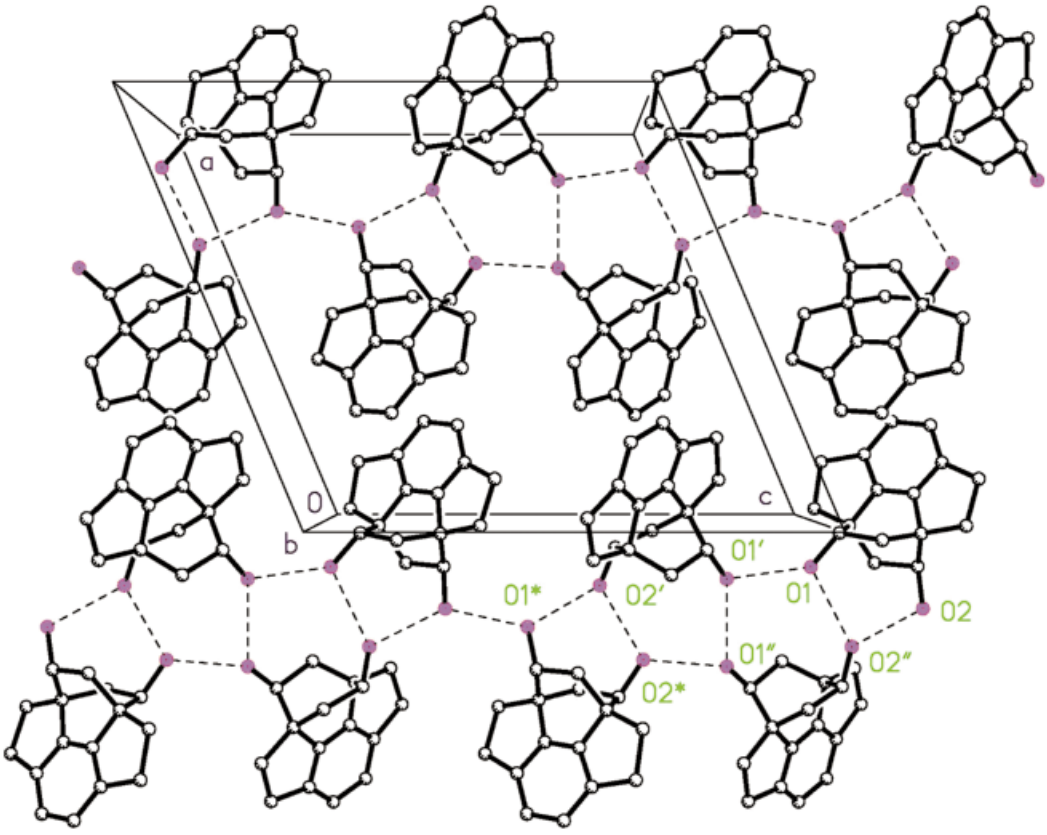


Figure 4. The packing diagram for **16-II** viewed parallel to the *y* axis. H atoms have been omitted for clarity

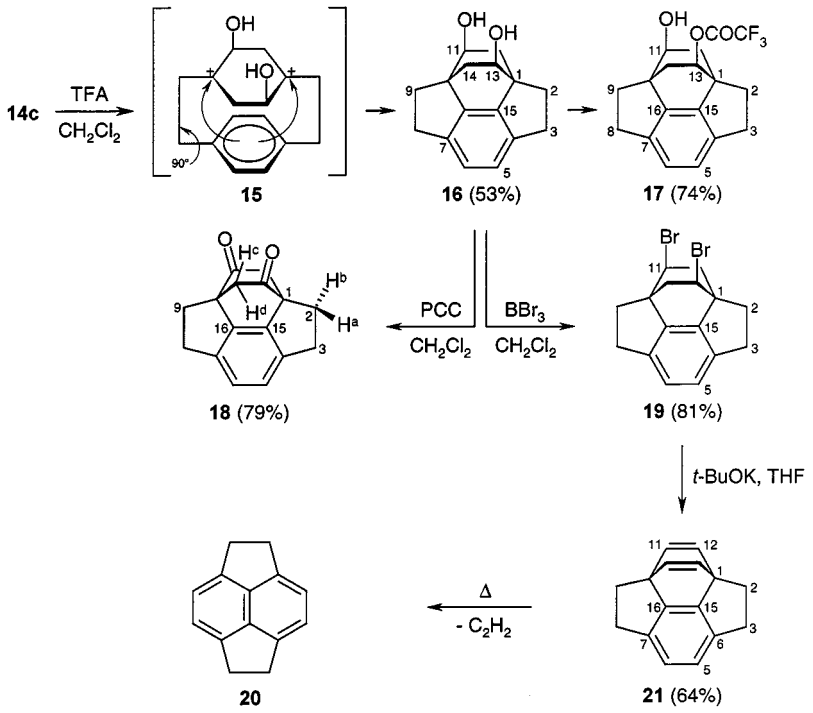
The determining factor in the crystal packing are the two hydroxyl groups of the diol **16-I**, which are involved in classical hydrogen bonding, the parameters of which are given in Table 1. The molecules are linked to form double layers parallel to the *xz* plane with the hydrophilic region in the centre, shown in Figure 3. The enantiomers of **16** crystallized separately from each other, in that the upper part of each layer consists of one pure enantiomer, the lower part of the other pure enantiomer.

The second crystal modification formed colorless pentagonal tablets in the non-centrosymmetric space group $P2_1$. The asymmetric unit of **16-II** contains four molecules, two in the *RR*- (O1 to C16 and O1′′ to C16′′) and two in the *SS*-configuration (O1′ to C16′ and O1* to C16*). The bond lengths and angles are, as expected, similar to those of **16-I**. The carbon skeletons are nearly planar with mean deviations form the plane varying from 2.6 (C1′ to C10′, C15′, and C16′) to 6.1 pm (C1 to C10, C15, and C16). The single bonds at the bridgeheads range in length between 146.7(6) (C10′′−C16′′) and 148.8(6) pm (C1−C15). The relatively short aromatic double bond C15−C16 shows distances between 133.7(6) (C15−C16) and 135.0(6) pm (C15*−C16*). The greatest deviation of the ideal sp^3 bridgehead angle exists at the carbon atom C10′ [100.1(3)−121.1(4)°]. The intramolecular bridgehead distances vary from 265.7(6) (C1*···C10*) to 267.53(6) pm (C1···C10). As in the crystal structure of **16-I**, the dominant feature of the packing are the hydrogen bonds formed by the hydroxyl groups. The molecules are arranged parallel to the *z* axis in double chains containing the two enantiomers in alternate sequences (see Figure 4). In contrast to the layers in **16-I**, the chains are not extended to layers in a second dimension.

Table 1. Hydrogen bonding parameters of **16-I** and **16-II**

	Bridge	H···O [pm]	O···O [pm]	O−H···O [°]
16-I	O2−H02···O1′	190(3)	277.3(3)	165(3)
	O1−H01···O2	207(3)	280.8(3)	139(3)
	O1′−H01′···O1	183(3)	268.5(3)	161(3)
16-II	O1−H01···O2′′	193(4)	283.4(4)	155(4)
	O2−H02···O1*	188(3)	273.7(3)	170(4)
	O1′−H01′···O1	197(4)	270.6(4)	164(5)
	O2′−H02′···O2*	182(4)	276.0(4)	158(3)
	O1′′−H01′′···O1′	204(4)	280.6(3)	148(4)
	O2′′−H02′′···O2	185(4)	275.6(4)	170(3)
	O1*−H01*···O2′	200(4)	276.5(4)	171(4)
	O2*−H02*···O1′′	182(4)	269.2(4)	158(4)

To account for the **14c** → **16** ring closure we propose a double intramolecular electrophilic substitution as symbolized by structure **15** in Scheme 5. By opening the oxirane rings, bridgehead carbocations are generated[14] that can be attacked by the juxtaposed benzene ring, which during this process has to undergo a 90° rotation (arrows in **15**). Intramolecular ring closures of this type have been recorded in [*n*]paracyclophane chemistry;[15] an example related to the above cyclization is the conversion of [8]paracyclophane-



Scheme 5. From the bis-epoxide **14c** to the doubly-bridged benzobarrelene **21**

3,6-ditosylate to tetrahydropyracene.[16] The hydrolysis product **16** is a novel C_2-symmetric diol and, indeed, when it was analyzed by gas chromatography on a chiral capillary column the two enantiomers were completely separated.[17] By omitting the saponification step during workup (see above) we were able to isolate the monoester **17**. In fact, since this derivative is much more soluble than its precursor **16**, it was advisable to increase the reaction time (to 6 h) and avoid isolation of **16** altogether. This resulted in a 74% yield of **17** from which **16** could subsequently be liberated by saponification. As expected, oxidation of **16** with pyridinium chlorochromate (PCC) furnished the diketone **18**, again in satisfactory yield (79%, Scheme 5).

Treatment of **16** with boron tribromide in dichloromethane yielded the dibromide **19** in good yield (81%). This readily soluble derivative could be recrystallized from petroleum ether to provide single crystals suitable for X-ray structural investigation. The results are shown in Figure 5.

Compound **19** crystallized with imposed C_2 symmetry. The carbon skeleton (C1−C5, C1A−C5A, C8, and C8A) is planar with a mean deviation from planarity of 0.8 pm. The typical deformations of the strained ethano bridged unit seen in the structures of **16** are also observable in the structure of **19**. The single bonds to the aromatic ring in the benzobicyclo[2.2.2]octene moiety are slightly shorter than in the benzobarrelene derivative **21** (see below): 147.7(3) pm (C1−C8). The aromatic bond length C8−C8A is equal within the standard deviations to the respective distances in both structures of **16**: 134.8(5) pm. The elongated saturated bond C11−C12 [156.9(3) pm] slightly reduces the strain in the carbon skeleton. The intramolecular distance between the bridgehead atoms also increases slightly to

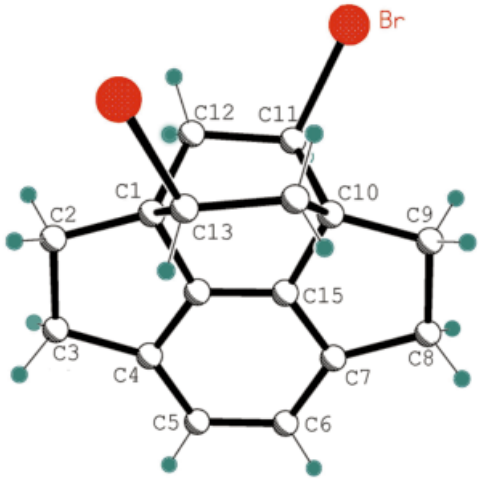


Figure 5. Structure of **19** in the crystal; radii are arbitrary

267.5(5) (C1···C1A). The C−Br bond is not affected and shows a normal length of 197.1(3) pm (standard value: 196.7 pm). The angles around the bridgehead atom show the characteristic distortion of this class of molecule: 100.7(2)−119.2(2)° (C1).

In the crystal packing of **19**, two types of intermolecular interactions are noticeable; a bromine−bromine interaction with a distance of 369.1(1) pm, distinctly shorter than the sum of the van-der-Waals radii (390 pm), and a weak non-classical hydrogen bond: H7B···Br 305 pm, C7···Br 403.5(3) pm, C7−H7B···Br 171°. These contacts build a three dimensional framework in the packing with T-shaped coordination at the bromine atoms.

Obviously the bromination of **16** has occurred with retention of configuration, and we assume that this process took place by two sequential S_Ni-substitution steps.

With the dibromide **19** in hand, elimination to give **21** could be attempted. Indeed, this hydrocarbon was produced in acceptable yields (64%) when **19** was treated with potassium *tert*-butoxide in refluxing tetrahydrofuran. Crystals of X-ray quality were obtained by sublimation and the molecular structure of this new barrelene derivative is reproduced in Figure 6.

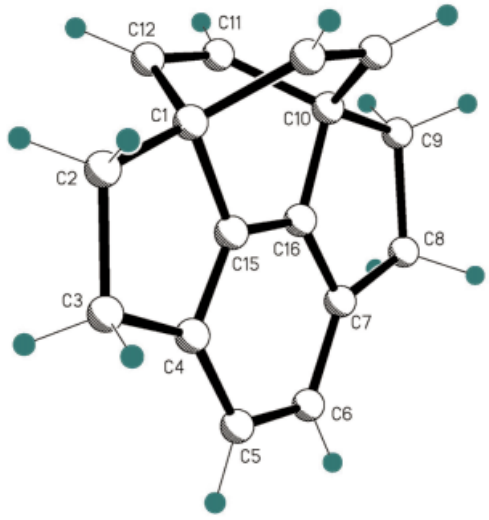
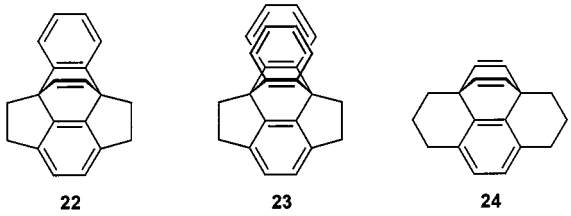


Figure 6. Structure of **21** in the crystal; radii are arbitrary

Compound **21** crystallized in the space group *C*2/*m*. The planar part of the molecule (C1 to C10, C15, and C16) lies exactly in the crystallographic mirror plane. The two ethano bridges C2−C3 and C8−C9 determine the geometry of the carbon skeleton. The bond lengths to the sp^3 bridgeheads C1 and C10 are markedly longer than in the strained unsubstituted [2.2]paracyclophane (151.0 pm, 157.1 pm): 154.6(4), 155.7(4) pm (C1−C2, C9−C10), 158.2(4), and 157.4(4) pm (C2−C3, C8−C9). Other bond lengths are also affected by the ethano bridges; the distances C4−C15, C15−C1, C7−C16, and C16−C10 [135.3(4), 149.5(4), 135.9(4), and 148.6(4), respectively] are significantly shorter than corresponding bond lengths in other regions of **21**. The aromatic double bond C15−C16 is slightly shorter than the corresponding bond in **16** and resembles, at 133.4(4) pm, an isolated double bond (C=C−C*ar*: 134.0 pm).[18] The double bonds in the benzobicyclo[2.2.2]octatriene moiety are only slightly shorter: 131.5(3) pm (C11−C12). The intramolecular distance between the bridgehead atoms C1 and C10 is reduced by the boat conformation to 263.9(5) pm, markedly shorter than in **16**. The strain in **21** is also reflected clearly in the unusual bond angles around these bridgeheads, whereby the values deviate significantly from the ideal sp^3 angle, as in the compounds **16** and **19**: 100.8(2)−122.3(2)° (C1) and 100.1(2)−122.3(2)° (C10).

Hydrocarbon **21** is, to the best of our knowledge, the smallest ethano-bridged barrelene prepared so far. Higher benzologs such as the dibenzobarrelene **22**[19] and the triptycene derivative **23**[20] have been described, as has the propano-bridged hydrocarbon **24** (Scheme 6). Indeed, the latter compound was obtained by Longone and Gladysz by the intramolecular addition of the dehydrobenzene generated from 5-bromo-[3.3]paracyclophane by base treatment to the opposing benzene ring.[21] Although the corresponding aryne from [2.2]paracyclophane (4,5-dehydro[2.2]paracyclophane) has also been generated,[22] it does not undergo intramolecular trapping, presumably because of excessive strain. Formally, hydrocarbon **21** is the product of such an intra-annular process.



Scheme 6. A selection of bridged benzobarrelenes

The temperature employed during the dehydrobromination of **19** had a pronounced influence on the outcome of the reaction: When the process was carried out under phase-transfer conditions with potassium *tert*-butoxide in boiling naphthabenzene (boiling point ca. 120 °C)[23] the barrelene **21** was produced, but the pyracene derivative **20** was the main elimination product; in diazabicycloundecene (DBU) at 160 °C **20** was the exclusive product. Clearly, **21** undergoes a retro-Diels−Alder reaction under these conditions by splitting off acetylene. This process has also been described for benzobarrelene itself,[24,25] but requires significantly harsher reaction conditions (690 °C, 3−5 s or 350−370 °C, 2 h). When **24** was heated at 180 °C, no hexahydropyrene, the product expected for a retro-Diels−Alder reaction, could be detected, as shown by comparison with an authentic sample.[21] It is evident that **21** is a highly strained hydrocarbon.

Experimental Section

General Remarks: The instrumentation used for structure determination was described previously, see ref.[1] Compounds **3** and **4** were prepared as described in ref.[4]

Cycloadditions with the Mono-Ene 3. − a) Cyclopropanation: To a cooled (−5 °C) solution of 220 mg (1.04 mmol) of **3** and 0.13 mL (1.6 mmol) of diiodomethane in 30 mL of anhydrous dichloromethane was added 1.3 mL of 1 M triethylaluminum in hexane. The mixture was stirred for 15 min and hydrolyzed at ice bath temperature by the addition of 20 mL of 10% aqueous sodium hydroxide. After phase separation, the organic phase was washed with 10% sodium hydroxide solution and water and dried with sodium sulfate. Thick layer chromatography on silica gel with petroleum ether provided 198 mg (84%) of **3,4-cyclopropa-5,6,7,8-tetrahydro[2.2]paracyclophane** (**5a**) as a colorless solid, m.p. 120 °C (decomp.). − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.00−0.02 (ps-t, 1 H, 17-H), 0.21 (dd, ^2J = 9.4, ^3J = 4.0 Hz, 1 H, 17-H), 0.38−0.43 (m, 1

H, 4-H), 0.74−0.83 (m, 1 H, 7- or 8-H), 0.97−1.12 (m, 4 H, 7-H, 8-H, 9-H), 1.19−1.26 (m, 1 H, 2-H), 1.37 (dd, 1 H, ^2J = 15.3, ^3J = 11.3 Hz, 5-H), 1.64−1.69 (m, 1 H, 6-H), 1.87−1.96 (m, 2 H, 2-H, 5-H), 1.98−2.07 (m, 1 H, 9-H), 2.49 (dt, 1 H, ^2J = 13.5, ^3J = 2.8 Hz, 10-H), 2.74−2.59 (m, 2 H, 1-H), 2.91 (dt, 1 H, ^2J = 13.7, ^3J = 3.9 Hz, 10-H), 7.09−7.11 (m, 1 H, arom. H), 7.23−7.26 (m, 2 H, arom. H), 7.29−7.31 (m, 1 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 16.8 (t, C-17), 17.2 (s, C-3), 18.8 (d, C-4), 20.3 (t, C-5), 22.9 (t, C-7 or C-8), 23.9 (d, C-6), 28.7 (t, C-7 or C-8), 31.5 (t, C-1), 32.3 (t, C-10), 38.6 (t, C-9), 39.5 (t, C-2), 129.4 (d), 130.0 (d), 130.7 (d), 131.2 (d), 138.5 (s), 141.5 (s, all arom. C). − IR (KBr): $\tilde{\nu}$ = 3055 (m) cm^{-1} (m), 3033 (m), 2993 (s), 2909 (vs), 2852 (vs), 1598 (m), 1502 (m), 1468 (m), 1449 (s), 1411 (m), 1103 (m), 1009 (m), 941 (m), 840 (m), 804 (s), 720 (s). − UV (acetonitrile): λ_{max} (log ε) = 208 nm (4.22), 242 (3.76). − MS (EI, 70 eV): *m/z* (%) = 226 [M^+] (28), 117 (16), 104 (100), 91 (16). − HRMS: *m/z* calcd. for $C_{17}H_{22}$ 226.172; found 226.172.

b) Dichlorocyclopropanation: To a solution of 400 mg (1.89 mmol) of **3** in 20 mL of anhydrous dichloromethane were added at 0 °C, 5 mL of chloroform, 30 mL of aqueous sodium hydroxide solution (20%), and 80 mg (0.36 mmol) of benzyltriethylammonium chloride. The mixture was stirred vigorously for 3 h and then poured into 100 mL of water. After twofold extraction with dichloromethane, the organic phases were combined, dried with sodium sulfate and passed over a short silica gel column. The oil obtained after solvent removal was purified by sublimation (100 °C, 10^{-3} mbar), resulting in 483 mg (87%) of **3,4-dichlorocyclopropa-5,6,7,8-tetrahydro[2.2]paracyclophane** (**5b**), colorless solid, m.p. 83 °C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.83−1.00 (m, 2 H, 7-H or 8-H), 1.13−1.20 (m, 1 H, 7-H or 8-H), 1.28−1.39 (m, 3 H, 4-H, 5-H, 7-H or 8-H), 1.51−1.69 (m, 3 H, 5-H, 6-H, 9-H), 1.81−1.92 (m, 2 H, 2-H, 9-H), 2.24 (dt, 1 H, ^2J = 14.9, ^3J = 5.5 Hz, 2-H), 2.55 (ddd, 1 H, ^2J = 14.1, ^3J = 10.0, ^3J = 5.5 Hz, 1-H), 2.57−2.83 (m, 1 H, 10-H), 2.89−2.96 (m, 2 H, 1-H, 10-H), 7.11 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H), 7.21 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H), 7.25 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H), 7.29 (dd, 1 H ^3J = 8.1, ^4J = 1.5 Hz, 12-H, 13-H, 15-H, 16-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 17.3 (t, C-5), 24.5 (d, C-6), 23.0, 27.3 (t, C-7, C-8), 28.2 (s, C-3), 31.2 (t, C-10), 31.7 (d, C-4), 32.5 (t, C-1), 34.1 (t, C-9), 36.8 (t, C-2), 73.8 (s, C-17), 129.5, 129.9, 131.9, 132.0 (d, C-12, C-13, C-15, C-16), 138.7, 193.3 (s, C-11, C-14). − IR (KBr): $\tilde{\nu}$ = 2917 (vs) cm^{-1}, 2874 (s), 2851 (s), 1502 (m), 1444 (s), 1040 (m), 979 (m), 948 (m), 909 (m), 827 (s), 778 (m), 715 (m). − UV (hexane): λ_{max} (log ε) = 210 nm (4.33), 242 (3.80), 286 (2.60). − MS (EI, 70 eV): *m/z* (%) = 294 [M^+] (80), 259 (100), 223 (80), 167 (48), 155 (50), 143 (76), 141 (70), 131 (60), 129 (74). − $C_{17}H_{20}Cl_2$ (295.3): calcd. C 69.16, H 6.83; found C 69.32, H 6.92.

c) Double Dichlorocarbene Addition: Using the same amounts of reagents as described above for the preparation of **5b** the reaction time was extended to 2d (room temp.) After thick layer chromatography on silica gel with petroleum ether 235 mg (33%) of **dichloromethyl-3,4-dichlorocyclopropa-5,6,7,8-tetrahydro[2.2]paracyclophane** (**6**) was isolated as a viscous oil. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.93−1.03 (m, 1 H, 7-H or 8-H), 1.44−1.52 (m, 1 H, 7-H or 8-H), 1.27−1.41 (m, 5 H, 2-H, 5-H, 6-H, 7-H, 8-H), 1.67−1.77 (m, 1 H, 9-H), 2.10 (dd, ^2J = 16.3, ^3J = 9.8 Hz, 1 H, 5-H), 2.28−2.43 (m, 3 H, 2-H, 9-H, 10-H), 2.67−2.75 (m, 1 H, 1-H), 2.99−3.05 (m, 1 H, 10-H), 3.10 (dt, 1 H, ^2J = 14.4, ^3J = 4.7 Hz, 1-H), 5.21 (s, 1 H, 18-H), 7.10 (d, 1 H, 15-H or 16-H), 7.22 (d, 1 H, 15-H or 16-H), 7.34 (s, 2 H, 12-H, 13-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = ^{13}C NMR (100.6 MHz, [D_8]toluene, 70 °C): δ = 23.9, 37.8 (t, C-2, C-5), 28.8 (s, C-3), 31.5 (d, C-6), 27.3, 31.6 (t, C-7, C-8), 32.7 (t, C-10), 33.0 (t, C-1), 36.6 (t, C-9), 40.5 (s, C-4), 72.9 (s, C-17), 87.1 (d, C-18), 129.8, 130.1 (d, C-12, C-13), 131.3 (d, C-15), 132.2 (d, C-16), 139.1 and 140.3 (s, C-11, C-14). − IR (KBr): $\tilde{\nu}$ = 2973 (m) cm^{-1}, 2929 (s), 2901 (s), 2860 (m), 1451 (s), 1432 (s), 836 (s), 815 (s), 778 (s), 754 (s), 730 (s). − UV (hexane): λ_{max} (log ε) = 206 nm (4.34), 242 (3.78), 284 (2.68). − MS (EI, 70 eV): *m/z* (%) = 376 [M^+] (3), 341 (8), 191 (6), 117 (24), 86 (64), 84 (100). − HRMS: *m/z* calcd. for $C_{18}H_{20}{}^{35}Cl_4$ 376.032; found 376.032.

d) Dibromocyclopropanation and Reaction with Methyllithium: To a cooled (0 °C) solution of 400 mg (1.89 mmol) of **3** in 20 mL of anhydrous dichloromethane were added 1 mL of bromoform, 30 mL of aqueous sodium hydroxide solution (20%), and 80 mg (0.36 mmol) of benzyltriethylammonium chloride. After stirring vigorously for 3 h the reaction mixture was poured into 100 mL of water. The product mixture was extracted twice with dichloromethane, the organic phases were combined and dried with sodium sulfate. Attempts to purify the addition product **5c** by chromatography on silica gel resulted in decomposition. Therefore, the volume of the dichloromethane solution was reduced to ca. 50 mL, and 20 mL of methyl lithium in diethyl ether (1.6 M) was slowly added at −30 °C. After decomposition with ice/water the product mixture was extracted with dichloromethane, the combined organic phases dried (sodium sulfate), and the oil remaining after solvent removal was purified by thick layer chromatography (silica gel, petroleum ether), providing 114 mg (27%) of **3,4-cyclopropa-5,6-dihydro[2.2]paracyclophane** (**10**) as an unstable viscous, colorless oil. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.28 (d, ^2J = 2.4 Hz, 1 H, 17-H), 0.37−0.42 (m, 2 H, 4-H, 17-H), 1.14 (dt, 1 H, ^2J = 14.4, ^3J = 9.2 Hz, 2-H), 1.62−1.77 (m, 2 H, 9-H, 5-H), 1.84−1.93 (m, 2 H, 5-H, 6-H), 1.96−2.06 (m, 1 H, 9-H), 2.25 (ddd, 1 H, ^2J = 14.3, ^3J = 8.9, ^3J = 1.8 Hz, 2-H), 2.61 (dt, 1 H, ^2J = 13.5, ^3J = 8.9, 1-H), 2.70 (dt, 1 H, ^2J = 13.9, ^3J = 8.7 Hz, 10-H), 2.91−3.01 (m, 2 H, 1-H, 10-H), 4.50 (dd, ^3J = 10.2, ^4J = 3.2 Hz, 1 H, 7-H), 5.27 (dd, ^3J = 10.2, ^4J = 2.7 Hz, 1 H, 8-H), 6.94 (d, 1 H, ^3J =7.5 Hz), 7.03 (d, 1 H, ^3J =7.9 Hz), 7.07 (dd, ^3J = 7.5, ^4J = 1.4 Hz, 1 H), 7.16 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 1 H, all arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 17.2 (s, C-3), 20.6 (t, C-5), 20.8 (d, C-4), 25.7 (t, C-17), 26.8 (d, C-6), 31.0 (t, C-10), 31.8 (t, C-1), 34.7 (t, C-9), 39.1 (t, C-2), 128.1 (d, C-7), 129.3 (d, C-8), 128.3, 130.6, 131.2, 133.0 (all d, all arom. C), 138.7 and 139.8 (s, arom. C). − IR (film): $\tilde{\nu}$ = 3008 (m) cm^{-1}, 2993 (m), 2926 (s), 2855 (s), 1712 (s), 1660 (m), 1641 (m), 1505 (m), 1450 (s), 1438 (s), 1034 (m), 1017 (m), 806 (s), 720 (m). − UV (acetonitrile): λ_{max} (log ε) = 196 nm (4.31), 222 (3.83, sh), 230 (3.74, sh), 236 (3.68), 260 (2.79). − MS (EI, 70 eV): *m/z* (%) = 224 [M^+] (34), 209 (6), 195 (10), 145 (14), 118 (24), 117 (58), 104 (100), 91 (30). − HRMS: *m/z* calcd. for $C_{17}H_{20}$ 224.157; found 224.157.

e) Epoxidation: In small portions, 1 g of *meta*-chloroperbenzoic acid (peracid content ca. 75%) was added under ice cooling to a mixture of 20 mL of dichloromethane and 50 mL of aqueous potassium carbonate (30%). After the evolution of gas had ceased, 400 mg (1.89 mmol) of **3** in 30 mL of dichloromethane was added, and the mixture stirred vigorously overnight. After the addition of 20 mL of water and thorough extraction with dichloromethane the organic phases were combined and dried with sodium sulfate. The solvent was removed in vacuo and the remainder purified by thick layer chromatography (silca gel, dichloromethane) to yield 385 mg (89%) of **3,4-epoxy-5,6,7,8-tetrahydro[2.2]paracyclophane** (**5d**), colorless solid, m.p. 173 °C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.71−0.77 (m, 1 H, 7-H), 0.98−1.07 (m, 1 H, 9-H), 1.09−1.17 (m, 1 H, 8-H), 1.21−1.26 (m, 1 H, 8-H), 1.38−1.46 (m, 1 H, 7-H),

1.45−1.53 (m, 1 H, 2-H), 1.58−1.68 (m, 1 H, 5-H), 1.71−1.79 (m, 1 H, 6-H), 1.91−1.97 (m, 1 H, 5-H), 1.98−2.02 (m, 1 H, 2-H), 2.04−2.12 (m, 1 H, 9-H), 2.43−2.51 (m, 1 H, 10-H), 2.52 (d, ^3J = 4.4 Hz, 1 H, 4-H), 2.76−2.82 (m, 2 H, 1-H), 2.91−2.97 (m, 1 H, 10-H), 7.09 (d, ^3J = 7.9 Hz, 1 H), 7.20 (d, ^3J = 7.9 Hz, 1 H), 7.25−7.30 (m, 2 H, all arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 21.7 (t, C-5), 23.3 (d, C-6), 25.2 (t, C-8), 27.3 (t, C-7), 30.3 (t, C-1), 32.0 (t, C-10), 37.4 (t, C-9), 37.8 (t, C-2), 58.8 (s, C-3), 60.3 (d, C-4), 129.4, 130.2, 130.3, 131.3 (all d, C-12, C-13, C-15, C-16), 138.2 and 141.8 (s, C-11, C-14). − IR (KBr): $\tilde{\nu}$ = 3008 (w) cm^{-1}, 2917 (s), 2851 (s), 1502 (m), 1445 (s), 1430 (m), 995 (s), 975 (m), 893 (m), 868 (s), 857 (m), 808 (m), 793 (m), 724 (s). − UV (hexane): λ_{max} (log ε) = 192 nm (4.15), 208 (4.35), 230 (3.67), 240 (3.83), 286 (2.60). − MS (EI, 70 eV): *m*/*z* (%) = 228 [M^+] (40), 210 (10), 170 (20), 157 (20), 143 (24), 117 (30), 104 (100), 91 (20). − $C_{16}H_{20}O$ (228.3): calcd. C 84.16, H 8.83; found C 84.16, H 8.73.

f) Reaction with Dehydrobenzene (8): Solutions of 1.0 g (7.29 mmol) anthranilic acid in 25 mL of dimethoxyethane and 1.5 mL (11.2 mmol) isopentylnitrite in 25 mL of dimethoxyethane were added whilst stirring during 4 h to a refluxing solution of 0.5 g (2.36 mmol) of **3** in 25 mL of dimethoxyethane. After heating under reflux for 1 h the cooled solution was treated with 300 mL of aqueous sodium hydroxide solution (10%), and the product mixture extracted carefully with diethyl ether. After solvent removal, the oily residue was purified by thick layer chromatography (silica gel, petroleum ether) to provide 115 mg (17%) of **4-phenyl-4,5,6,7-tetrahydro[2.2]paracyclophane** (**9**) as a colorless oil. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 1.28−1.50 (m, 3 H, 5-H, 9-H), 1.61−1.68 (m, 1 H, 2-H), 1.95−2.13 (m, 4 H, 2-H, 6-H, 7-H), 2.15−2.23 (m, 1 H, 9-H), 2.47−2.55 (m, 1 H, 10-H), 2.63−2.71 (m, 1 H, 1-H), 2.84−2.91 (m, 1 H, 1-H), 2.95−3.07 (m, 2 H, 4-H, 10-H), 4.70−4.97 (m, 1 H, 8-H), 6.91−6.93 (m, 1 H, arom. H), 6.97−7.00 (m, 2 H, phenyl H), 7.11−7.16 (m, 3 H, arom. H), 7.19−7.24 (m, 3 H, arom. H). When the signal at 4.80 (8-H) was irradiated in an NOE experiment, significant signal enhancements were observed at δ = 1.95−2.13 (7-H) and 6.91−6.93 (13-H), whereas the multiplet at 6.91−6.93 (13-H) was only weakly affected. − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 25.0 (t, C-7), 26.8 (d, C-6), 31.7 (t, C-10), 34.0 (t, C-1), 35.1 (t, C-2), 37.0 (t, C-9), 41.9 (t, C-5), 42.1 (d, C-4), 131.5 (d, C-8), 125.7, 128.15, 128.24, 129.5, 130.3, 130.8, 131.8 (all d, all arom. C), 133.6, 140.8, 141.4, 146.1 (all s, C-3, arom. C). − IR (film): $\tilde{\nu}$ = 3024 (w) cm^{-1}, 2922 (s), 2853 (s), 1598 (m), 1492 (m), 1449 (s), 807 (m), 758 (m), 719 (m), 702 (s). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.73), 220 (sh, 4.15), 248 (3.55), 254 (3.34), 260 (3.05). − MS (EI, 70 eV): *m*/*z* (%) = 288 [M^+] (22), 208 (24), 169 (20), 142 (8), 104 (100), 94 (14). − HRMS: *m*/*z* calcd. for $C_{22}H_{24}$ 288.188; found 288.188.

Acid-Catalyzed Ring Opening of 5a: A solution of 170 mg (0.75 mmol) of **5a** in 30 mL of dichloromethane was stirred vigorously with 2 mL of conc. HCl for 30 min. After phase separation, the organic layer was washed twice with water and dried with sodium sulfate. The solution was passed through a short silica gel column, the solvent removed, and the remaining oil purified by thick layer chromatography (silica gel, petroleum ether): 138 mg (81%) of **4-methyl-4,5,6,7-tetradehydro[2.2]paracyclophane** (**7**) as a colorless oil. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.76 (d, ^3J = 6.9 Hz, 3 H, 17-H), 1.00−1.07 (m, 1 H, 5-H), 1.26−1.35 (m, 1 H, 9-H), 1.30−1.37 (m, 1 H, 5-H), 1.79−1.88 (m, 1 H, 4-H), 1.89−1.99 (m, 2 H, 7-H), 2.02−2.11 (m, 1 H, 6-H), 2.12−2.28 (m, 3 H, 2-H, 9-H), 2.46−2.54 (m, 1 H, 10-H), 2.80−2.87 (m, 1 H, 1-H), 2.92−3.04 (m, 3 H, 1-H, 10-H), 4.53 (m, 1 H, 8-H), 6.94−6.96 (m, 1 H), 7.09−7.14 (m, 3 H, all arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 19.6 (q, C-17), 24.9 (t, C-7), 26.6 (d, C-6), 28.0 (d, C-4), 31.6 (t, C-10), 33.9 (t, C-2), 34.0 (t, C-1), 36.9 (t, C-9), 40.2 (t, C-5), 129.5 (d, C-8), 129.4, 130.3, 130.5, 131.7 (all d, C-12, C-13, C-15, C-16), 136.3, 140.3, 141.2 (all s, C-3, C-11, C-14). − IR (film): $\tilde{\nu}$ = 3033 (w) cm^{-1}, 2915 (vs), 2859 (s), 1500 (m), 1446 (s), 807 (s), 714 (m). − UV (hexane): λ_{max} (log ε) = 202 nm (4.33), 228 (3.82), 240 (3.74), 288 (2.48). − MS (EI, 70 eV): *m*/*z* (%) = 226 [M^+] (18), 156 (8), 130 (6), 118 (8), 117 (10), 104 (100), 91 (10). − HRMS: *m*/*z* calcd. for $C_{17}H_{22}$ 226.172; found 226.172.

Cycloadditions with the diene 4. − a) Cyclopropanation: To a solution of 350 mg (1.67 mmol) of **4** and 0.4 mL (4.97 mmol) of diiodomethane in 30 mL of anhydrous dichloromethane was added, at 0 °C, 4.5 mL of triethyl aluminum in hexane (1 M). The mixture was stirred for 2 h at 0−8 °C and the reaction was terminated by the addition of 1 g (23.8 mmol) of sodium fluoride. The solution was filtered, the solvents removed, and the remaining solid purified by thick layer chromatography (silica gel, petroleum ether), yielding 347 mg (87%) of **3,4:6,7-dicyclopropa-5,8-dihydro[2.2]paracyclophane** (**14a**), colorless solid, m.p. 73 °C (decomp.). − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = −0.86 (dd, ^2J = 4.0, ^3J = 6.4 Hz, 2 H, 17-H), 0.03 (dd, ^2J = 4.0, ^3J = 9.5 Hz, 2 H, 17-H), 0.25 (ddd, 2 H, ^3J = 9.4, ^3J = 9.4, ^3J = 6.4 Hz, 4-H), 0.77 (ps-dt, 1 H, ^2J = 14.7, ^3J = 9.8/9.4 Hz, 2-H), 1.21 (d, ^2J = 14.7 Hz, 2 H, 5-H), 1.91 (dd, ^2J = 14.7, ^3J = 9.3 Hz, 2 H, 5-H), 2.17 (dd, ^2J = 14.3, ^3J = 8.2 Hz, 2 H, 2-H), 2.63 (ddd, 2 H, ^2J = 13.8, ^3J = 10.3, ^3J = 8.3 Hz, 1-H), 3.03 (dd, ^2J = 13.8, ^3J = 9.1 Hz, 2 H, 1-H), 7.11−7.16 (m, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 13.6 (s, C-3), 19.8 (t, C-17), 22.47 (d, C-4), 22.53 (t, C-5), 31.7 (t, C-1), 39.7 (t, C-2), 129.3 and 130.7 (d, arom. C), 137.4 (s, arom. C). − IR (KBr): $\tilde{\nu}$ = 3043 (w) cm^{-1}, 2997 (m), 2983 (m), 2920 (vs), 2900 (vs), 2852 (vs), 1463 (m), 1451 (s), 1437 (s), 1032 (s), 806 (s). − UV (acetonitrile): λ_{max} (log ε) = 196 nm (4.27), 206 (4.25), 280 (2.70). − MS (EI, 70 eV): *m*/*z* (%) = 238 [M^+] (44), 104 (100), 91 (24). − HRMS: *m*/*z* calcd. for $C_{18}H_{22}$ 238.172; found 238.172.

b) Dichlorocyclopropanation: To a solution of 280 mg (1.33 mmol) of **4** in 20 mL of dichloromethane were added 5 mL of chloroform, 30 mL of aqueous sodium hydroxide solution (30%), and 80 mg (0.36 mmol) of benzyltriethylammonium chloride. After vigorous stirring for 16 h at room temp. the mixture was poured into 100 mL of water. The mixture was extracted twice with dichloromethane, and after drying the combined organic phases (sodium sulfate), they were passed over a short silica gel column. The solvent was removed in vacuo and the remaining solid purified by sublimation (130 °C, 10^{-3} mbar): 376 mg (75%) of **3,4:6,7-bis(dichlorocyclopropa)-5,8-dihydro[2.2]paracyclophane** (**14b**), colorless solid, m.p. 149 °C (decomp.) − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 1.02 (dd, ^2J = 16.3, ^3J = 6.1 Hz, 2 H, 5-H), 1.33 (dd, ^3J = 9.6, ^3J = 6.1 Hz, 2 H, 4-H), 1.97−2.07 (m, 4 H, 2-H, 5-H), 2.21−2.29 (m, 2 H, 1-H), 2.59−2.65 (m, 2 H, 2-H), 2.99−3.04 (m, 2 H, 1-H), 7.14 (d, ^3J = 8.0 Hz, 2 H, arom. H), 7.27 (br. d, 2 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 27.4 (s, C-3), 28.4 (t, C-5), 30.9 (d, C-4), 32.3 (t, C-1), 40.4 (t, C-2), 74.0 (s, C-17), 127.6, 131.9 (d, arom. C), 139.6 (s, arom. C). − IR (film): $\tilde{\nu}$ = 2962 (w) cm^{-1}, 2931 (s), 1451 (s), 1202 (m), 1025 (m), 921 (m), 852 (s), 830 (s), 722 (m). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (4.44), 202 (4.42), 236 (3.79), 280 (2.80) − MS (EI, 70 eV): *m*/*z* (%) = 382 (0.06), 380 (0.8), 378 (4), 376 (8), 374 (7) [M^+], 117 (100), 118 (20), 105 (20), 104 (88), 91 (22). − $C_{18}H_{18}Cl_4$ (376.2): calcd. C 57.48, H 4.82, Cl 37.70; found C 57.14, H 4.77, Cl 37.75.

c) Epoxidation: In small portions, 3 g of *meta*-chloroperbenzoic acid (peracid content ca. 75%) was added under ice cooling to a mixture of 20 mL of dichloromethane and 50 mL of aqueous potassium carbonate (30%). After the evolution of gas had ceased, a solution of 0.5 g (2.38 mmol) of **4** in 30 mL of dichloromethane was added, and the mixture stirred vigorously for 16 h. Workup was started by the addition of 200 mL of water, and after thorough extraction with dichloromethane the combined organic phases were dried with sodium sulfate. The solvent was removed in vacuo and the raw product purified by thick layer chromatography (silica gel, dichloromethane) to provide 0.51 g (89%) of **3,4:6,7-diepoxy-5,8-dihydro[2.2]paracyclophane** (**14c**), colorless solid, m.p. 285 ° C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 1.26 (dt, 2 H, ^2J = 13.8, ^3J = 9.8 Hz, 2-H), 1.73 (d, ^2J = 16.9 Hz, 2 H, 5-H), 1.92 (dd, ^2J = 16.9, ^3J = 6.0 Hz, 2 H, 5-H), 2.26 (dd, ^2J = 13.8, ^3J = 8.8 Hz, 2 H, 2-H), 2.49 (d, ^3J = 6.0 Hz, 2 H, 4-H), 2.60−2.68 (m, 2 H, 1-H), 3.19 (dd, ^2J = 14.0, ^3J = 9.8 Hz, 2 H, 1-H), 7.15−7.21 (m, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 26.1 (t, C-5), 30.2 (t, C-1), 35.9 (t, C-2), 56.0 (s, C-3), 60.9 (d, C-4), 129.7 and 130.8 (d, arom. C), 137.4 (s, arom. C) − IR (KBr): $\tilde{\nu}$ = 2988 (m) cm^{-1}, 2926 (s), 2903 (s), 2859 (s), 1506 (m), 1459 (m), 1441 (m), 1416 (s), 1330 (m), 1098 (m), 1018 (s), 913 (m), 809 (s). − UV (acetonitrile): λ_{max} (log ε) = 198 nm (4.31), 204 (4.39), 232 (3.80). − MS (EI, 70 eV): *m*/*z* (%) = 242 [M$^+$] (28), 198 (8), 146 (10), 118 (22) 104 (100). − $C_{16}H_{18}O_2$ (242.3): calcd. C 79.31, H 7.49; found C 79.05, H 7.35.

From 14c to the Bridged Benzobarrelene 21. − a) Acid-Catalyzed Ring Closure of 14c: To a solution of 300 mg (1.24 mmol) of **14c** in 30 mL of dichloromethane was added 1 mL of trifluoroacetic acid. After 2 h at room temp. the reaction mixture was washed thoroughly with water to remove the acid, and 10 mL of aqueous sodium hydroxide solution (10%) was added. After 1 h of vigorous stirring the mixture was diluted with 200 mL of water and extracted thoroughly with dichloromethane. The combined organic layers were dried with sodium sulfate and the solvent removed in vacuo. Sublimation (120 °C, 4·10^{-3} mbar) provided 160 mg (53%) of the diol **16** as a colorless solid, m.p. 166 °C − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 1.62−1.68 (m, 2 H, 12-H, 14-H), 2.08−2.18 (m, 4 H, 2-H, 9-H, 12-H, 14-H), 2.30−2.37 (m, 2 H, 2-H, 9-H), 3.10 (t, ^3J = 7.1 Hz, 4 H, 3-H, 8-H), 3.74 (dt, 2 H, ^3J = 9.1, ^3J = ^4J = 2.4 Hz, 11-H, 13-H), 7.00 (s, 2 H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 32.4 (t, C-2, C-9), 33.5 (t, C-3, C-8), 38.8 (t, C-12, C-14), 49.9 (s, C-1, C-10), 76.4 (d, C-11, C-13), 123.5 (d, C-5, C-6), 135.8 (s, C-4, C-7), 145.5 (s, C-15, C-16). − IR (KBr): $\tilde{\nu}$ = 3379 (vs) cm^{-1}, 3057 (w), 2955 (s), 2881 (m), 2849 (s), 1776 (m), 1706 (m), 1479 (m), 1344 (m), 1282 (m), 1269 (m), 1175 (m), 1098 (m), 1059 (s), 1037 (s), 1003 (m), 799 (m). − UV (acetonitrile): λ_{max} (log ε) = 206 nm (4.56), 218 (4.03), 222 (3.98), 266 (2.69). − MS (EI, 70 eV): *m*/*z* (%) = 242 [M$^+$] (14), 198 (100), 181 (36), 180 (30), 165 (28), 153 (24). − $C_{16}H_{18}O_2$ (242.3): calcd. C 79.31, H 7.49; found C 79.04, H 7.44.

When the base treatment in the last step of the above cyclization was omitted, the ester **17** could be isolated by thick layer chromatography followed by distillation (120 °C, 4·10^{-3} mbar), 310 mg (74%) as a colorless, highly viscous oil. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 1.77 (ddd, 1 H, ^3J = 2.5, ^3J = 9.4, ^2J = 13.4 Hz, 13-H), 1.85 (ddd, 1 H, ^3J = 2.2, ^3J = 9.5, ^2J = 13.7 Hz, 14-H), 2.12−2.19 (m, 3 H, 2-H, 9-H, 12-H), 2.29−2.40 (m, 3 H, 2-H, 9-H, 14-H), 3.14 (t, ^3J = 7.0 Hz, 4 H, 3-H, 8-H), 3.78 (br-dt, 1 H, ^3J = 2.4, ^3J = 9.2 Hz, 11-H), 4.82 (dt, 1 H, ^3J = 2.7, ^3J = 9.3 Hz, 13-H), 7.066, 7.070 (d, ^3J = 7.8 Hz, 2 H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 32.0, 32.2 (t, C-2, C-9), 33.5, 33.7 (t, C-3, C-8), 34.9 (t, C-14), 38.9 (t, C-12), 48.2, 49.5 (s, C-1, C-10), 75.8 (d, C-11), 82.9 (d, C-13), 114.6 (d, J_{C-F} = 286.1 Hz, C-18), 124.2, 124.5 (d, C-5, C-6), 136.1, 136.2 (s, C-4, C-7), 142.8, 145.0 (s, C-15, C-16), 157.7 (d, J_{C-F} = 42.0 Hz, C-17). − IR (film): $\tilde{\nu}$ = 3558 (m) cm^{-1}, 3544 (m), 3440 (s), 3423 (s), 2938 (s), 2893 (m), 2854 (m), 1779 (vs), 1481 (m), 1388 (m), 1346 (m), 1224 (s), 1161 (vs), 1017 (s), 852 (s). − UV (acetonitrile): λ_{max} (log ε) = 204 nm (4.62), 222 (3.98, sh), 232 (3.16), 266 (2.72), 272 (2.70). − MS (EI, 70 eV): *m*/*z* (%) = 338 [M$^+$] (10), 294 (40), 180 (100), 94 (20). − HRMS: *m*/*z* = calcd. for $C_{18}H_{17}O_3F_3$: 338.113; found 338.112.

b) Bromination of 16 to the Dibromide 19: A solution of 400 mg (1.65 mmol) of **16** in 30 mL of anhydrous dichloromethane was cooled to −5 °C, and 250 mg (1 mmol) of boron tribromide in 20 mL of dichloromethane was added whilst stirring. When TLC control had shown that conversion was complete, the reaction mixture was poured onto ice, and after careful extraction with dichloromethane the combined organic phases were dried with sodium sulfate. Thick layer chromatography on silica gel with petroleum ether provided 495 mg (81%) of the dibromo derivative **19** as a colorless solid, m.p. 130 °C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 2.03 (ddd, 2 H, ^2J = 13.9, ^3J = 10.0, ^4J = 3.1 Hz, 11-H, 12-H), 2.14−2.21 (m, 2 H, 2-H, 9-H), 2.30−2.37 (m, 2 H, 2-H, 9-H), 2.94 (dd, ^2J = 13.9, ^3J = 4.5 Hz, 2 H, 12-H, 14-H), 3.09 (pst, 4 H, ^3J = 7.1 Hz, 3-H, 8-H), 3.83 (ddd, 2 H, ^3J = 10.0, ^3J = 4.5, ^4J = 3.1 Hz, 11-H, 13-H), 7.07 (s, 2 H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 32.8, 33.9 (t, C-2, C-3, C-8, C-9), 41.8 (t, C-12, C-14), 50.4 (s, C-1, C-10), 58.5 (d, C-11, C-13), 124.8 (d, C-5, C-6), 136.1 (s, C-4, C-7), 143.2 (s, C-15, C-16). − IR (KBr): $\tilde{\nu}$ = 3053 (w) cm^{-1}, 2964 (s), 2940 (s), 2912 (s), 2872 (m), 2837 (m), 1477 (s), 1445 (s), 1428 (m), 1233 (s), 1208 (m), 1162 (s), 1124 (m), 940 (m), 859 (s), 805 (s), 639 (s). − UV (hexane): λ_{max} (log ε) = 192 nm (4.33), 208 (4.57), 228 (4.07), 268 (2.56). − MS (EI, 70 eV): *m*/*z* (%) = 368 [M$^+$] (1), 289 (56), 287 (54), 207 (16), 181 (100), 152 (14). − $C_{16}H_{16}Br_2$ (368.1): calcd. C 52.21, H 4.38; found C 52.12, H 4.30.

c) Elimination of 19 to the Bridged Benzobarrelene 21: To a solution of 360 mg (0.98 mmol) of **19** in 50 mL of anhydrous tetrahydrofuran was added 2 g of potassium *tert*-butoxide, and the mixture was heated under reflux for 16 h. Most of the solvent was removed in vacuo, dichloromethane (30 mL) was added and the suspension washed twice with water. The organic phase was dried (sodium sulfate), the solution passed through a short silica gel column, and after solvent removal the remainder was purified by thick layer chromatography on silica gel with petroleum ether. After sublimation (80 °C, 3·10^{-3} mbar) 134 mg (64%) of the doubly bridged **benzobarrelene 21** was obtained, colorless crystals, m.p. 137−138 °C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 2.96−2.97 (m, 4 H, 2-H), 3.32−3.35 (m, 4 H, 3-H), 6.77 (s, 4 H, 11-H), 6.82 (s, 2 H, 5-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 32.7 (t, C-2), 35.2 (t, C-3), 61.9 (s, C-1), 121.3 (d, C-5, 132.1 (s, C-6), 144.6 (d, C-11), 152.8 (s, C-15). − IR (KBr): $\tilde{\nu}$ = 3061 (w) cm^{-1}, 3039 (m), 3026 (s), 3012 (m), 2961 (m), 2936 (s), 2843 (m), 1460 (m), 1444 (s), 1315 (s), 1290 (m), 786 (vs), 704 (vs). − UV (hexane): λ_{max} (log ε) = 200 nm (4.13), 218 (4.38), 232 (3.52), 246 (3.13), 258 (2.85). − MS (EI, 70 eV): *m*/*z* (%) = 206 [M$^+$] (60), 205 (100), 191 (60), 190 (55), 189 (35), 178 (40), 165 (25). − $C_{16}H_{14}$ (206.3): calcd. C 93.16, H 6.84; found C 93.21, H 6.91.

Oxidation of 16 to the Diketone 18: To a solution of 180 mg (0.74 mmol) of **16** in 20 mL of dichloromethane was added 0.5 g (2.32 mmol) of pyridinium chlorochromate (PCC), and the solution was stirred vigorously for 16 h. For workup, 50 mL of water was

added and the mixture was thoroughly extracted with dichloromethane. After drying (sodium sulfate) the solution was passed through a short silica gel column, the solvent removed and the solid residue purified by thick layer chromatography on silica gel with petroleum ether. The diketone **18** was obtained (140 mg, 79%) as colorless crystals, m.p. 154 °C. − ^{1}H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 2.07−2.14 (m, 2 H, 2-H^b, 9-H^b), 2.23 (d, ^2J = 17.7 Hz, 2 H, 11-H^d, 13-H^d), 2.65 (d, ^2J = 17.7 Hz, 2 H, 11-H^c, 13-H^c), 2.97−3.04 (m, 2 H, 2-H^a, 9-H^a), 3.11−3.22 (m, 4 H, 3-H, 8-H), 7.08 (s, 2 H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$/TMS): δ = 26.6 (t, C-2, C-9), 33.4 (t, C-3, C-8), 42.7 (t, C-11, C-13), 59.3 (s, C-1, C-10), 125.4 (d, C-5, C-6), 136.6 (s, C-4, C-7, C-15, C-16), 206.6 (s, C-12, C-14). − IR (KBr): $\tilde{\nu}$ = 2940 (m) cm^{-1}, 2928 (m), 1720 (vs), 1621 (m), 1475 (s), 1398 (m), 1153 (m), 1081 (m), 1023 (s), 841 (s). − UV (hexane): λ_{max} (log ε) = 194 nm (4.48), 218 (4.17), 232 (4.04), 280 (3.08). − MS (EI, 70 eV): *m*/*z* (%) = 238 [M$^+$] (30), 196 (100), 182 (16), 168 (20), 167 (34), 165 (22), 153 (22). − HRMS: *m*/*z* calcd. for $C_{16}H_{14}O_2$ 238.099; found 238.099.

X-ray Crystallography

Structure Determination of 16-I, 16-II, 19, and 21: A cut tablet (**16-I**, **16-II**, and **21**) or cut prism (**19**) was mounted on a glass fiber in inert oil, and transferred to the cold gas stream of a Siemens P4 diffractometer fitted with an LT-2 low-temperature attachment. Data were collected with the ω-scan method using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). Absorption correction making use of a semiempirical method (ψ scans) was applied for **19**. All unique data were used for calculations (program SHELXL-97, G. M. Sheldrick, University of Göttingen). The structures were solved by direct methods and refined anisotropically by full-matrix least-squares on F^2. The hydrogen atoms were refined with a riding model except for freely refined hydroxyl hydrogen atoms. The high displacement parameters of the freely refined hydroxyl hydrogen atoms of **16-II** may indicate some disorder; for these hydrogens, therefore, the isotropic displacement parameters were constrained to 1.5 times the isotropic *U* values of the respective oxygen atoms. For **16-I**, **16-II**, and **21**, which diffracted more weakly, similarity restraints were applied to the *U* components of the C atoms, and for **16-I** and **16-II** also of the oxygen atoms. Additionally, the four independent molecules of **16-II** were restrained to have equal distances in equivalent positions.

Structure determination of 14b: A cut tablet was mounted in inert oil and measured by ω/θ scans by using Mo-K_α radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. All other details as above.

A summary of the crystal data, data collection and refinement parameters for the five crystal structures reported in this paper is given in Table 2.

Full details of the crystal determination (except structure factors) have been deposited under the numbers CCDC-172348 (**14b**), -172349 (**16-I**), -172350 (**16-II**), -172351 (**19**), and -172352 (**21**) at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Fax: Int. +44 (0)1123/336-033; E-mail: deposit@ccdc.cam.ac.uk)

Table 2. Crystal data, data collection and refinement parameters for the five crystal structures reported in this paper

Compound	**14b**	**16-I**	**16-II**	**19**	**21**
Empirical formula	$C_{18}H_{18}Cl_4$	$C_{16}H_{18}O_2$	$C_{16}H_{18}O_2$	$C_{16}H_{16}Br_2$	$C_{16}H_{14}$
M_r	376.12	242.30	242.30	242.30	206.27
Crystal habit	colourless tablet	colourless square tablet	colourless pentagonal tablet	colourless prism	colourless tablet
Crystal size [mm]	0.80×0.60×0.20	0.80×0.35×0.12	0.80×0.35×0.12	0.60×0.30×0.30	1.00×0.52×0.12
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2/*c*	*P*2$_1$	*C*2/*c*	*C*2/*m*
Cell constants					
a [pm]	1481.1(3)	786.2(2)	1384.6(2)	1037.77(16)	1514.6(2)
b [pm]	917.2(3)	1346.3(4)	1253.89(16)	1301.5(2)	745.24(18)
c [pm]	1224.5(3)	1793.2(6)	1534.0(2)	1056.4(2)	938.6(3)
α [°]	90	90	90	90	90
β [°]	99.30(2)	101.14(2)	112.945(10)	107.559(14)	92.32(3)
γ [°]	90	90	90	90	90
V [nm^3]	1.6416	1.8623	2.4526	1.3604	1.0586
Z	4	6	8	4	4
D_x [Mg·m^{-3}]	1.522	1.296	1.312	1.797	1.294
μ [mm^{-1}]	0.714	0.084	0.085	5.937	0.073
Transmissions				0.662−0.935	
F(000)	776	780	1040	728	440
T [°C]	−130	−100	−100	−100	−100
$2\theta_{max}$	55	50	50	55	50
No. of reflections					
measured	3580	3395	4699	3063	1101
unique	1885	3279	4508	1561	1002
R_{int}	0.024	0.020	0.020	0.030	0.036
Parameters	100	256	673	82	91
Restraints	0	269	1129	0	145
$wR(F^2$, all refl.)	0.081	0.145	0.081	0.062	0.184
$R(F, >4\sigma(F))$	0.030	0.055	0.039	0.026	0.063
S	1.07	1.03	0.86	0.97	1.08
max. Δρ [e·Å^{-3}]	0.46	0.23	0.14	0.48	0.59

Acknowledgments

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