Centropentaindan, a Fenestrane Bearing Five Mutually Fused Indan Units: Syntheses, Molecular Structure, and Bridgehead Substitution**

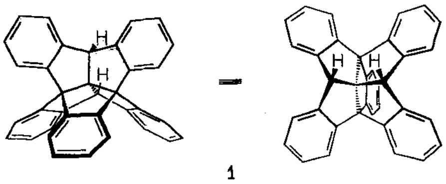
Dietmar Kuck,* Andreas Schuster, Detlef Gestmann, Frank Posteher, and Hans Pritzkow

Abstract: Syntheses, properties, and some reactions of a novel centropolycyclic hydrocarbon, centropentaindan (**1**), are described. The molecular structure of **1** consists of a tetrabenzo[5.5.5.5]fenestrane bearing a fifth centrically fused indan unit. Independent syntheses have been developed employing i) twofold cyclodehydrogenation of tribenzotriquinacene (**7**) with Pd/C at 500 °C, which gives **1** in 50% yield, and ii) a two-step procedure by tetrabromination of di-*fuso*-centrotriindan (**8**) followed by condensation with two molecules of benzene, which provides **1** in 88% yield. Some bridgehead-substituted centropentaindans are described, including the highly labile dibromo derivative **19**, and the centrohexacyclic, topologically nonplanar *endo*-peroxide **26** and *endo*-disulfide **28**. The notably rigid ring fusion in the molecular framework of **1** is shown both by X-ray structural analysis and by particular steric interactions of the two mutually compressed bridgehead substituents.

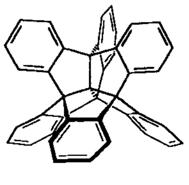
Keywords
centropolyindans · cyclodehydrogenation · fenestranes · polycycles · triquinacenes

Introduction

In 1981, Gund and Gund showed that centropolycyclic organic structures built up from cyclopentane rings should be particularly stable.[1] At the same time, we designed synthetic routes to a new family of centropolycyclic hydrocarbons that consist of multiply fused indan units,[2] and, with regard to Gund and Gund's terminology, we named this family the "centropolyindans".[3,4] During the last decade, all members of this novel class of polycyclic arenes as well as many derivatives have been synthesized[3-8] including the highest one, centrohexaindan (**2**).[4d,7,8] In this paper, we present the results of our investigation of the second highest congener, centropentaindan (**1**).[8a]



1
(C_{2v})



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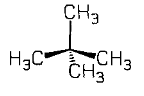
Two independent synthetic routes leading to **1** will be described in detail, and some spectral properties and the crystal structure of this parent centropolyindan **1** will be presented. In addition, we will discuss functionalization of one and both of the two benzhydrylic bridgehead positions of **1**, and we will show that twofold bridgehead-substituted centropentaindans are accessible, in spite of the considerable steric interaction between the two bridgehead substituents. This functionalization permits condensation reactions that convert the centropentacyclic, topologically planar skeleton of **1** into centrohexacylic, topologically nonplanar frameworks.

Results and Discussion

Structural and Synthetic Concepts: Conceptually, centropentaindan (**1**) may be envisaged as a derivative of neopentane (**3**), in which five pairs of nongeminal C–H bonds are substituted by *ortho*-phenylene groups. Thus, five of the six edges of a tetrahedron defined by the four α-carbon atoms of **3** are bridged by benzene rings to give the structure of **1**. The remaining nonbridged edge forms two benzhydrylic bridgehead positions, which are 1,3-oriented to each other on a particularly rigid pentacyclic backbone. Alternatively, **1** may be formally derived from centrohexaindan (**2**) by removal of any one of its six phenylene bridges.[1]



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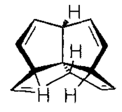

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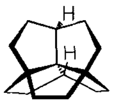

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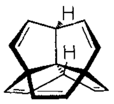

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[**] Benzoannelated Centropolyquinanes, Part 20; for Part 19, see ref. [8a], for Part 21, see ref. [7].

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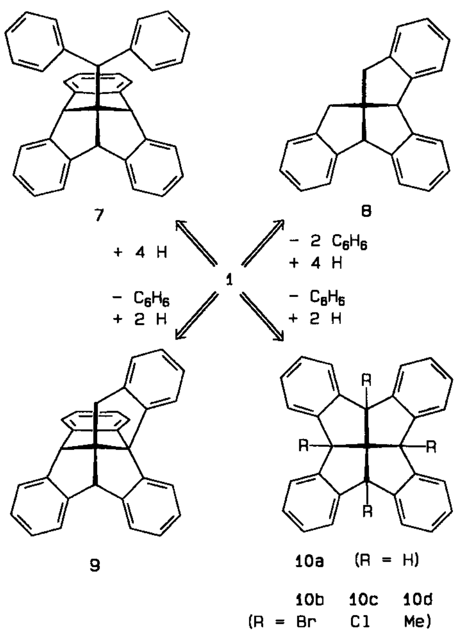
From a geometrical point of view, the steric fit of the five-membered rings at the common center is almost perfect, since the bond angle at C2 of indan is very close to the ideal tetrahedral angle (109°28′). Therefore, any increase in strain with an increasing degree of *centro*-annulation should be rather small. Force-field calculations for the corresponding alicyclic analogues, the centropoly*quinanes*, corroborate the inherently low strain of "centropolycyclanes", which comprise exclusively five-membered rings.[1]

Centropentaquinane (**5**) and the corresponding olefin, centropentaquinacene (**6**), are not yet known by experiment. A report by Paquette et al.[9a] summarized attempts to prepare the corresponding centro*hexa*cyclic hydrocarbons;[9, 10] however, the most highly fused centropolyquinane yet obtained is a derivative of **5**.[9a, 11] It is obvious that the construction of *alicyclic* compounds of so many rings fused around a common atom as in **5** and **6** must be obstructed by the steric congestion in the synthetic intermediates and by their tendency to escape from the desired cyclization path by rearrangement or fragmentation. The synthesis of centropolyquinacenes such as **6** represents an even greater challenge, since it requires a particularly high degree of functionalization to eventually introduce the olefinic double bonds: hence these "centropolycyclenes" have remained elusive as well. The highest non-benzoannelated centropolyquinacene known to date by experiment is all-*cis*-[5.5.5.5]fenestratetraene ("staurane-tetraene") (**4**), synthesized by Cook, Weiss and co-workers.[12]

In the case of benzoannelated centropolyquinanes, several of these drawbacks are considerably reduced. First of all, the inherent stability of aromatic substrates and use of the wealth of arene chemistry promised to be of great advantage. Hence the applicability of intramolecular electrophilic aromatic substitution in construction of centrically fused bi-, tri-, and tetraindan systems has been documented in a number of cases. An efficient cyclodehydration strategy starting from 1,3-indandiones and 1,3-indandiols allowed us to generate, in a single synthetic step, two new indan units fused to the original one. On that basis, several lower centropolyindans, for example **7**,[2, 4h] **8**,[2, 4k] **9**,[4i] and **10a**,[4a, k] became accessible on a relatively large preparative scale. Di-*fuso*-centrotriindan (**8**), in particular, was easily obtained on a half-mole scale in three steps from indan-1,3-dione. The two centrotetraindans **9** and **10a** appeared promising, in that only one further *ortho*-phenylene unit had to be incorporated into their highly fused polycyclic backbone. In fact, *twofold* bridging of **10a** with *ortho*-phenylene units by reaction of the tetrabromo derivative **10b** with benzene furnished **2** in high yield.[4d, 7] The synthesis of centropentaindan **1** from **9** or **10a** suffers, however, from the difficulties encountered with the partial (single or double) bridgehead functionalization of these centropolyindans.[13] Therefore, the route to **1** via **9** or **10** was not pursued experimentally.

A more suitable basis for the preparation of **1** was found to be the *centro*-substituted tribenzotriquinacene **7**.[4h] While, as a tri-*fuso*-centrotriindan, this substrate has a lower degree of annulation and a relatively labile, exocyclic benzhydrylic C–C bond, it already provides all of the five arene rings required for the construction of the pentaindan ring system of **1**. Here again, partial bridgehead functionalization (bromination) proved to be unsuccessful. Therefore, we sought to apply cyclodehydrogenation techniques to close the two new five-membered rings in one synthetic step (Scheme 1).



Scheme 1. Potential retrosyntheses of centropentaindan, **1**.

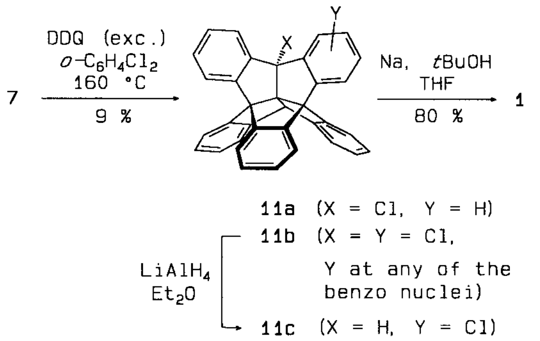
Our first attempt concentrated on the use of quinones as dehydrogenating agents. In fact, we succeeded in synthesizing **1** from **7** in a two-step, low-yield sequence (ca. 7%). To improve the conversion **7** → **1**, we then tried to apply direct cyclodehydrogenation techniques, encouraged by recent examples of successful ring closure reactions by dehydrogenation in the dodecahedrane series.[14, 15] In fact, utilization of the standard palladium/charcoal catalyst turned out to be surprisingly efficient.

In addition, an independent and very efficient synthesis of **1** has been accomplished in analogy to the particularly facile twofold condensation of tetrabromofenestrindan (**10b**) with benzene to give centrohexaindan (**2**).[4d, 7] Thus, by *decreasing* the number of *ortho*-phenylene units in the starting material using the readily available di-*fuso*-centrotriindan (**8**) (a "broken fenestrindan"), we synthesized the title centropolyindan **1** by the two-step bromination/condensation sequence in excellent yield.

Centropentaindan by Cyclodehydrogenation with DDQ: 2,3-Dichloro-4,5-dicyano-*para*-benzoquinone (DDQ) has been used successfully as a particularly strong and versatile dehydrogenation agent.[16] *Cyclo*dehydrogenation of hydrocarbons has remained relatively rare, however, and is limited to substrates bearing pairs of activated or particularly close C–H bonds. In most cases the reported yields hardly exceed 20%.

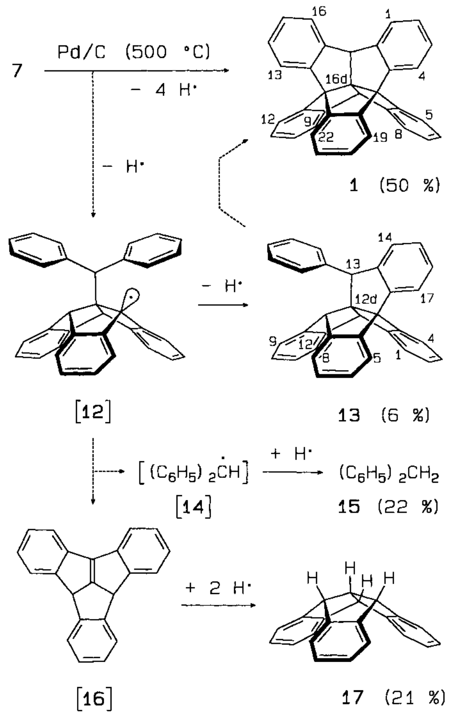
The twofold cyclodehydrogenation of **7** required particularly harsh conditions. Best results were obtained by using an approximately sevenfold molar excess of DDQ in high-boiling chlorobenzenes, for example, *ortho*-dichlorobenzene. The side reactions which also occurred were a drawback; in particular, chlorination of the remaining benzhydrylic bridgehead positions as well as at the aromatic rings was observed (Scheme 2). Prolonged heating for several hours led to a mixture of products which, according to ^{1}H NMR and mass spectrometric analysis, consisted mainly of the 8b-chlorocentropentaindan **11a** and several 8b,*aryl*-dichlorocentropentaindans **11b**.

Isolation of the centropentaindans by extraction of the complex reaction mixture followed by medium-pressure liquid chromatography (MPLC) gave a mixture containing the chlorinated centropentaindans in up to 9% yield. While the benzhydrylic C–Cl bonds were reduced very readily with lithium aluminum hydride, as shown by mass spectrometry, the removal of the *aryl* chloro substituents required treatment with sodium/*tert*-butanol in boiling THF.[17] Under these conditions, the mixture of



Scheme 2. Centropentaindan (1) by cyclodehydrogenation of 7 with DDQ.

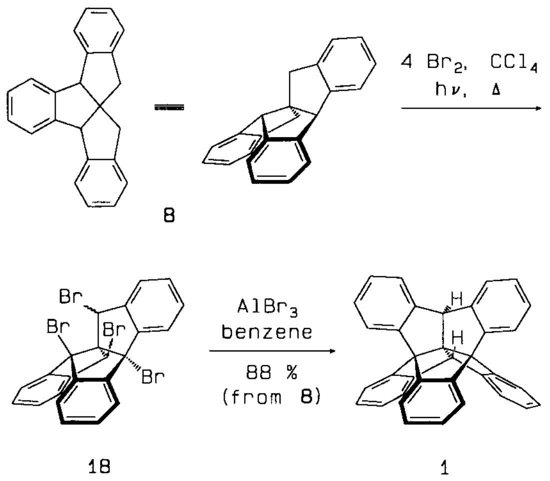
chlorocentropentaindans was completely reduced to 1 in >7% overall yield from 7.



Scheme 3. Centropentaindan (1) by cyclodehydrogenation of 7 with Pd/C.

Centropentaindan by Cyclodehydrogenation with Pd/C: In order to avoid the introduction of chlorine into the polycyclic framework of 1, alternative methods of cyclodehydrogenation were considered. Surprisingly, standard palladium/charcoal (Pd/C) catalyst[18] proved to be highly efficient for the direct conversion of 7 →1 (Scheme 3). Heating of a finely powdered mixture of 7 and Pd/C to 500 °C in a steel tube for 1 h resulted in the formation of a mixture of hydrocarbons containing 1 as the major product besides minor amounts of the corresponding product of single cyclization, 13-phenylcentrotetraindan (13), and two fragmentation products, tribenzotriquinacene (17) and diphenylmethane (15). MPLC was used to isolate 1 in 50% yield. The two fragmentation products 15 and 17 were obtained in similar yields (ca. 22%). Interestingly, some starting material 7 was isolated as well; this, together with the formation of 13, shows that the two cyclodehydrogenation steps occurred at comparable rates. Hydrogen atom abstraction from one of the bridgehead positions of 7 leads to the benzhydrylic radical 12 which may either undergo cyclization and hydrogen abstraction to give 13 and, in a similar sequence, the title compound 1, or eliminate the diphenylmethyl radical (14) to give dihydrotribenzoacepentalene (16). The latter, highly reactive intermediate has been generated recently from various tribenzotriquinacenes and found to dimerize by [2 + 2] cycloaddition across the central double bond.[19] Under the reaction conditions used here, dimerization of 16 was suppressed by hydrogenation to give 17.[4e,h] The homolytic C–C bond cleavage in 7 parallels the base-induced fragmentation[19b] of the same system but obviously requires much harsher conditions.

Centropentaindan by Condensation: The third synthesis of 1 is even more efficient than the cyclodehydrogenation route described above. It is based on readily available di-*fuso*-centrotriindan, 8[4k] (Scheme 4). Whereas, in general, partial bromination of the benzylic and benzhydrylic positions is difficult with 8 and various other centropolyindans,[13,20] we found that 8 was converted to the tetrabromo derivative 18 as a mixture of stereoisomers bearing one bromine atom at each of the benzylic and benzhydrylic positions. Tri- and pentabrominated triindans appeared to be formed as minor products only; but we were unable to separate or identify the stereoisomers because of the facile hydrolysis of the bromides. Inspection of molecular models reveals that complete (i.e. sixfold) bromination of the central neopentane core of 8 would imply highly unfavorable 1,3-interactions within three pairs of bromine substituents and that the fourfold brominated triindans 18 in fact exhibit at least one such interaction. On the other hand, the 1,3-interaction is attenuated by enhanced torsion of the conformationally flexible di-*fuso*-centrotriindan framework of 8, as observed for several other centropolyindans as well (cf. 10b, Scheme 5).[4a–c,f;5b,c;21]



Scheme 4. Centropentaindan (1) by condensation.

In the second step, crude tetrabromide 18 was treated with aluminum tribromide in benzene solution to achieve the condensation with two solvent molecules. As in our first synthesis of 2 from 10a via 10b,[4d] the multiple Friedel–Crafts reaction of benzene with 18 took place with high efficiency, producing 1 in a strikingly high two-step yield (88%) if the reaction was allowed to take place at ambient temperature over a period of several days. Thus, the bromination/condensation route is clearly superior to the two approaches described above, furnishing 1 in 71% overall yield in five steps starting from 1,3-indandione.

Spectroscopic Properties of Centropentaindan: The electron-impact mass spectrum of **1** is dominated by the molecular-ion signal at an m/z of 442. As might be expected from its multiply fused carbon framework, no significant fragmentation of the molecular skeleton is observable; the most intense fragment ion peak (24%) corresponds to the loss of a hydrogen atom. It is noteworthy that the doubly charged molecular ion ($m/z = 221$) is formed with considerable relative abundance (ca. 13%). The ^{1}H NMR spectrum reflects the C_{2v} molecular symmetry of the title compound by several degenerate resonances, for example that of the two bridgehead protons (8bH and 16bH) at $\delta = 5.08$. From symmetry considerations and comparison with the spectra of related higher centropolyindans,[4, 7] the arene resonances are easily assigned to the various *ortho* and *meta* protons. As expected, the ^{13}C NMR spectrum of **1** exhibits only three resonances for the five quaternary carbon atoms of the central neopentane unit; the central carbon nucleus was identified at $\delta = 83.2$.[22] Two groups of doubly and quadruply degenerate resonances are found for the arene carbon nuclei, again in line with the C_{2v} symmetrical structure of **1**. The UV spectrum of **1** is closely similar to those of the other centropolyindans. The low-energy (α) band is found at $\lambda_{max} = 276.0$ nm; this indicates a centropolyindan with conformationally rigid molecular framework owing to the presence of at least one tribenzotriquinacene unit.[23]

Table 1. Crystallographic data and structure refinement for centropentaindan (**1**).

empirical formula	$C_{36}H_{24}Cl_2$ [$C_{35}H_{22} \cdot CH_2Cl_2$]
formula weight	527.45
crystal system	orthorhombic
space group	$P2_12_12_1$
a (Å)	10.732(1)
b (Å)	14.637(2)
c (Å)	16.906(3)
V (Å^3)	2655.7(6)
Z	4
D (calcd) (g cm^{-3})	1.319
absorp. coef (mm^{-1})	0.269
F(000)	1096
crystal size (mm)	0.4 × 0.3 × 0.3
λ (Å)	0.71070
T (K)	293(2)
θ range (°)	1.84–26.99
index ranges	$0 \leq h \leq 13$, $0 \leq k \leq 18$, $0 \leq l \leq 21$
no. refl. collected	3210
no. indep. refls.	3210
absorption correction	ψ scan
max. and min. transmission	0.922 and 0.901
refinement method	full-matrix least-squares on F^2
parameters	367
GOF on F^2	1.029
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.046$, $wR2 = 0.107$
(all data)	$R_1 = 0.059$, $wR2 = 0.121$
absolute structure parameter	−0.03(12)
extinction coefficient	0.0068(9)
largest diff. peak and hole, eÅ^{-3}	0.150 and −0.166

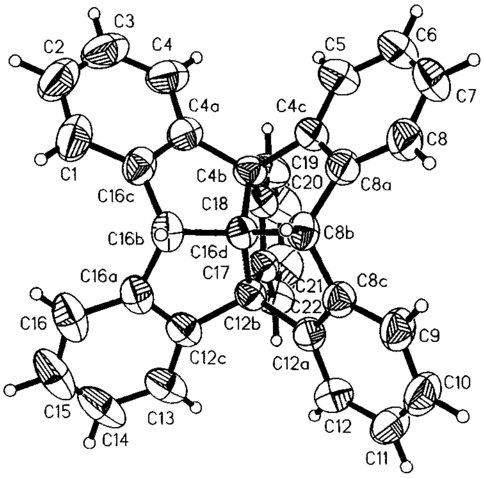


Fig. 1. Thermal ellipsoid diagram of centropentaindan (**1**).

Table 2. Selected bond lengths, bond angles, and torsion angles for centropentaindan, **1**.

Bond lengths (Å)			
C(16d)–C(4b)	1.563(4)	C(8b)–C(8a)	1.511(4)
C(16d)–C(8b)	1.552(4)	C(8b)–C(8c)	1.509(4)
C(16d)–C(12b)	1.557(4)	C(12b)–C(12a)	1.526(4)
C(16d)–C(16b)	1.549(4)	C(12b)–C(12c)	1.523(4)
C(4b)–C(4a)	1.523(4)	C(12b)–C(17)	1.525(4)
C(4b)–C(4c)	1.523(4)	C(16b)–C(16a)	1.508(4)
C(4b)–C(18)	1.526(4)	C(16b)–C(16c)	1.512(4)
Bond angles (°)			
C(4b)-C(16d)-C(8b)	107.7(2)	C(16b)-C(16d)-C(4b)	107.4(2)
C(8b)-C(16d)-C(12b)	107.5(2)	C(4b)-C(16d)-C(12b)	107.7(2)
C(12b)-C(16d)-C(16b)	108.2(2)	C(8b)-C(16d)-C(16b)	118.0(2)
Torsion angles (°)			
C(4a)C(4b)C(16d)C(16b)	4.9(3)	C(12a)C(12b)C(16d)C(8b)	6.1(3)
C(4c)C(4b)C(16d)C(8b)	−1.5(3)	C(12c)C(12b)C(16d)C(16b)	−0.8(3)
C(18)C(4b)C(16d)C(12b)	0.8(3)	C(17)C(12b)C(16d)C(4b)	0.8(3)
C(8a)C(8b)C(16d)C(4b)	0.5(3)	C(16a)C(16b)C(16d)C(12b)	0.3(3)
C(8c)C(8b)C(16d)C(12b)	−6.1(3)	C(16c)C(16b)C(16d)C(4b)	−5.6(3)
H(8b)C(8b)C(16d)C(16b)	−0.9(19)	H(16b)C(16b)C(16d)C(8b)	−4.5(20)

X-ray Molecular Structure of Centropentaindan: The molecular structure of **1** was confirmed by a single-crystal X-ray diffraction study (see Table 1 and Experimental Procedure). An ORTEP diagram of the molecule of **1** is shown in Figure 1 and some selected bond lengths and angles are given in Table 2. The framework of **1** adopts a nearly C_{2v} symmetrical conformation. Within this approximation, the fenestrane subunit is almost D_{2d} symmetrical, bearing the additional 4b,12b-phenylene bridge within a plane of symmetry, and both the two possible triptindan (propellane) subunits and the two possible (tribenzo)triquinacene subunits are nearly C_{3v} symmetrical (Fig. 2). Most remarkably, the unbridged angle at the central carbon atom ∢C(8b)-C(16d)-C(16b) is widened to 118.0°, whereas the (phenylene-bridged) counterangle ∢C(4b)-C(16d)-C(12b) and the remaining four C-C-C angles (107.4–108.2°) are close to the value of an ideal tetrahedrally coordinated center (Table 2). Within the set of the four central C–C bonds and within the sets of those C–C bonds connecting the bridgehead carbon atoms to the arene rings only slight but systematic differences are found: bonds involving the triphenylmethyl carbon atoms, C(4b) and C(12b), are slightly longer than those involving the benzhydryl carbon atoms, C(8b) and C(16b).

Closer inspection reveals a slight distortion of the centropentaquinacene framework, that is, a deviation in the molecular symmetry. This is evident from Fig. 2, top, which shows a slight non-C_3 type distortion of the propellane subunit, and even more so from Fig. 2, bottom. As listed in Table 2, some torsional angles at the central C–C bonds are found to deviate systematically from the 0° value expected for the perfectly eclipsed situation. As a further consequence of the tendency of **1** to avoid the all-eclipsed conformation, some of the interplanar angles be-

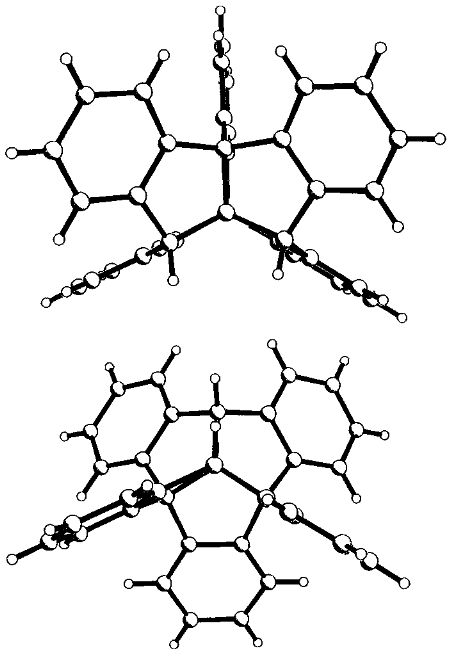
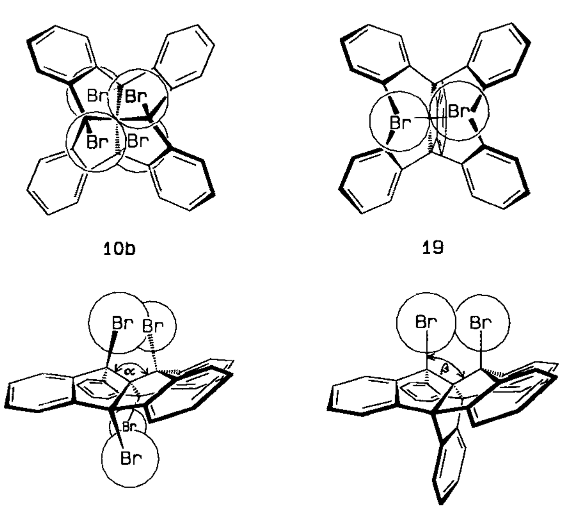


Fig. 2. Crystal structure of centropentaindan (**1**). Top: as viewed along the propellane axis C(12b)–C(16d) of a triptindan subunit; bottom: along the C(8b)–(C(16d) bond of a 10-methyltribenzotriquinacene unit.

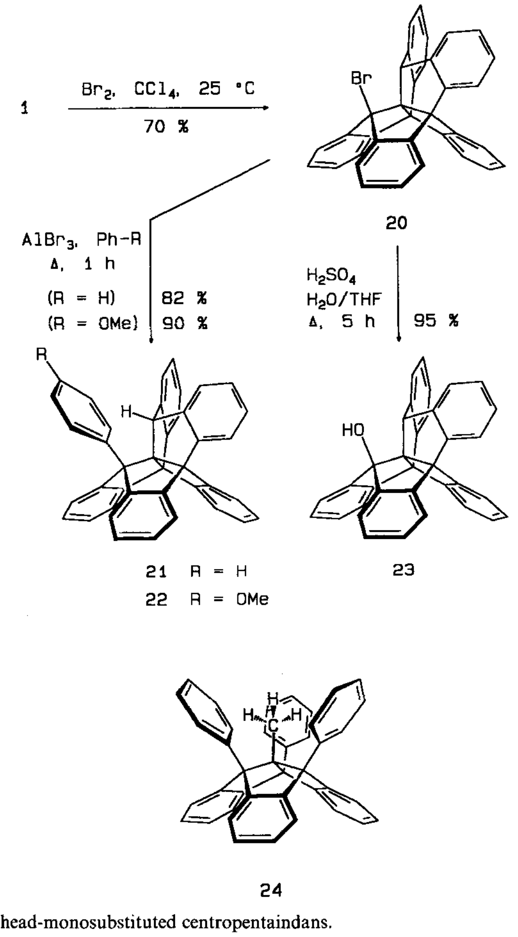
tween the five-membered rings deviate by approximately 4–5° from the ideal values (60° for the *fuso*-diindan subunits and 90° for the *spiro*-diindan subunits). This distortion leads to a slight out-of-plane orientation of the bridgehead C–H bonds at the "open" edge of the neopentane core (Fig. 1, Table 2).

Bridgehead Functionalization of Centropentaindan: The introduction of four pairwise *syn*-oriented substituents at the bridgehead positions of fenestrindan **10a** has been shown to induce a considerable distortion of the central neopentane skeleton,[4d, f, 24] in line with recent computational work on the corresponding [5.5.5.5]fenestranes.[20, 25] For example, the conformational flexibility of the fenestrindan framework in **10b** and **10c** is strongly reduced or even removed by 1,3-halogenation (Scheme 5). Replacing one pair of these substituents by another *ortho* phenylene bridge should considerably increase the unfavorable interaction of the two remaining bridgehead substituents.



Scheme 5. Torsion of bridgehead-brominated fenestrindan **10b** (left) and bridgehead-brominated centropentaindan **19** (right). For the sake of clarity, angles α and β have been labeled only once.

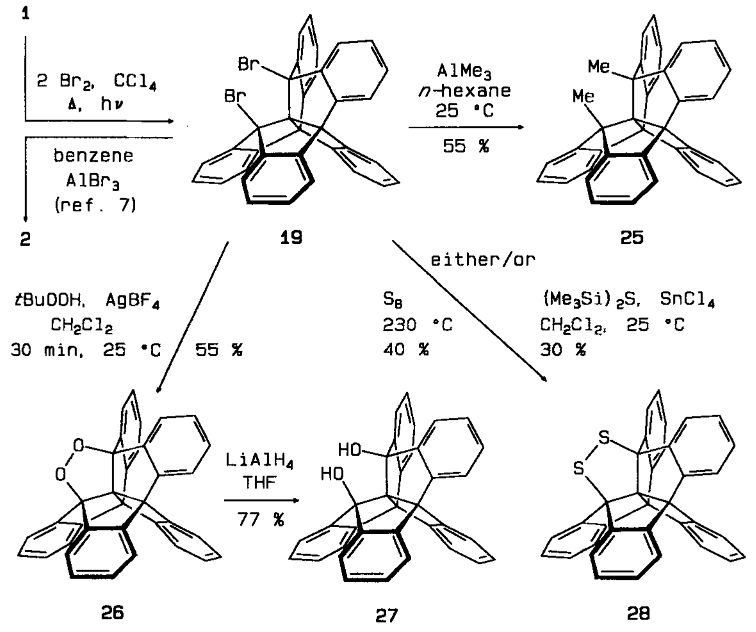
As corroborated by the X-ray structure analysis, introduction of the additional phenylene unit into the [5.5.5.5]fenestrane skeleton of **10a** to form **1** renders the molecular framework of the latter particularly rigid and its conformational ground state(s) nearly C_{2v} symmetrical.[26] This peculiarity of **1** is clearly attributable to the presence in the fused structure of a tribenzotriquinacene subunit that, on its own, would adopt a rigid, perfectly C_{3v} symmetrical ground-state conformation.[28] Therefore, we expected the introduction of substituents at both of the bridgehead positions of **1** to be critical. Much to our surprise, however, twofold substitution of **1** was possible; but some limitations due to the steric interaction of the two bridgehead substituents became evident as well.



Scheme 6. Bridgehead-monosubstituted centropentaindans.

Substitution of **1** with one equivalent of bromine occurred smoothly at ambient temperature without additional irradiation (Scheme 6). 8b-Bromocentropentaindan (**20**) was obtained in 70% yield as a stable, crystalline material, which only decomposed after standing for weeks. The corresponding monoalcohol **23** was easily prepared in near-quantitative yield from **20** by hydrolysis with dilute sulfuric acid in THF. The ^{1}H and ^{13}C NMR spectra of **20** and **23** reflect the reduced molecular symmetry ($C_{2v} \rightarrow C_s$) of these derivatives as compared with the parent hydrocarbon. It is noteworthy that the ^{1}H NMR AA'BB' spectrum of the non-fenestrane *ortho*-phenylene bridge is hardly affected by the substitution. The mass spectra of the compounds are dominated by the loss of a bromine radical (m/z = 441) and the highly entropically favored 1,3-*syn* elimination of water ($m/z = 440$).

In view of the potential use of **1** as a synthetic precursor of centrohexaindan (**2**), arylation of **20** was studied by analogy with the successful introduction of three aryl groups at the bridgehead positions of tribenzotriquinacenes (e.g., **24**, Scheme 6).[7,20] In fact phenyl- and *p*-anisylcentropentaindan, **21** and **22**, were obtained in good yields by treatment of **20** with aluminum tribromide in benzene and anisole, respectively. The hydrocarbon **21** may be regarded as a *seco* derivative of **2**, since a single C–C bond formation remains to be closed to generate the sixth indan unit. The catalytic dehydrocyclization technique described above (cf. **7** → **2**) was not applied in this case, since such a multistep approach to centrohexaindan appears inferior to direct access (see Scheme 7).[7]



Scheme 7. Bridgehead-disubstituted centropentaindans.

As a characteristic feature of the aryl-substituted centropentaindans **21** and **22**, the ^{1}H NMR spectra display a distinct highfield shift of the signal of the remaining bridgehead proton ($\Delta\delta = -1.0$ ppm compared with **1**). Similar and even more pronounced highfield shifts were found for phenylcentrotetraindan (**13**) and for (triaryl)methyltribenzotriquinacenes[7,20] such as **24**.

The EI mass spectrum of **21** has an intense peak for a fragment at an m/z of 440, which corresponds to the readily occurring elimination of benzene. Presumably this fragmentation is induced by the sterically favorable 1,3-H transfer, similar to the process that induces water loss from ionized **23**. 1,3-Eliminations of arenes from the radical cations of alkylbenzenes are frequent in energetically and sterically (i.e. entropically) favored cases.[29]

Treatment of **1** with a slight excess of bromine under forcing conditions (i.e., additional irradiation at elevated temperatures) gave 8b,16b-dibromocentropentaindan (**19**) (Scheme 7) in fairly good yields. This compound was found to be very sensitive to air and light; in contrast to the monobromide **20**, it decomposed readily during the standard workup procedure or upon standing in tetrachloromethane solution. However, careful workup under argon with the exclusion of light and heat furnished **19** as a crystalline material, which could be stored under argon for several days without decomposition. Mass spectrometry, ^{1}H NMR spectroscopy, and subsequent chemical transformations unequivocally confirmed the identity of this dibromide, though the product tended to contain minor amounts of the monobromide **20**. As expected, the mass spectrum of **19** shows the $[M-\text{Br}]^+$ and $[M-2\,\text{Br}]^{\cdot+}$ peaks (m/z 519/521 (Σ 21%), m/z 440 (100%), respectively) as well as a remarkably large peak corresponding to the doubly charged $[M-2\,\text{Br}]^{2+}$ fragment ions (m/z 220, 24%). As a characteristic feature, dibromide **19** exhibits *two* ^{1}H NMR resonances at low field ($\delta = 7.96$ and 7.81), which reflects the two sets of four equivalent *ortho* protons of the fenestrindan unit of this centropentaindan. Correspondingly, the spectrum of monobromide **20** displays only two resonances further downfield ($\Delta\delta = 0.3$ ppm) for *ortho* protons of the fenestrindan unit. In fact, the deshielding effect on *ortho* protons by a bridgehead benzhydrylic bromine atom is a recurring feature of these centropolyindan derivatives.[4d,20]

Force-field calculations (MM +)[27c] for dibromocentropentaindan **19** suggest a remarkable increase of the unbridged C-C-C bond angle ($\alpha = 124.5°$) and of the torsional angles Br-C(8b)-C(16d)-C(16b) and Br-C(16b)-C(16d)-C(8b) ($\beta = 22.5°$) compared with the parent hydrocarbon **1**.[30] Comparison with the corresponding angles calculated for **10b** ($\alpha = 118.2°$, $\beta = 36.4°$)[24b,30] again demonstrates the greatly reduced conformational flexibility of the centropentaindan framework. Nevertheless, the calculations indicate that the conformational ground state of 1,3-disubstituted centropentaindans such as **19** may significantly deviate from the ideal C_{2v} symmetrical, single-minimum structure, in favor of two equivalent conformers of C_2 symmetry.

The identity of the dibromide **19** is further corroborated by several synthetic conversions (Scheme 7). Treatment of a suspension of freshly prepared **19** with trimethylaluminum in *n*-hexane at room temperature gave the corresponding dimethylcentropentaindan (**25**) in 55% isolated yield. The spectroscopic data unambiguously support its structure. The arene proton region of the ^{1}H NMR spectrum is very similar to that of the parent centropentaindan (**1**). The ^{13}C NMR spectrum of **25** is also in accord with effective C_{2v} molecular symmetry; the resonance of the central carbon atom is shifted downfield ($\Delta\delta = 8.2$ ppm) compared with **1**.

The ready formation of **25** is surprising, since force-field calculations predict high steric strain for this molecule. In this case, two methyl groups in **25** strongly interact and cannot easily turn each other aside. Again, the central, unbridged C-C-C bond angle in **25** is calculated to be enlarged to 123.4° (MM +, 122° MM2, cf. 117° for **10d**[24b]).

Since hydrolysis of dibromide **19** did not take place cleanly, the corresponding diol **27** was obtained in a stepwise manner. The incorporation of an *endo*-peroxy bridge into the pentacyclic framework of **1** was achieved by means of Ag$^{\text{I}}$ ion assisted condensation of **19** with *tert*-butylhydroperoxide in methylene chloride.[31] The reaction proceeded smoothly and was completed within 30 min at ambient temperature, giving the centrohexacyclic *endo*-peroxide **26** in good yield, in analogy to the related fenestrindan bis-*endo*-peroxide synthesized from **10b** (cf. Scheme 1).[4f] Also analogously to the derivatization of fenestrindan,[4f] dibromide **19** was converted to the corresponding *endo*-disulfide **28** by treatment with hexamethyldisilthiane under Lewis acid catalysis with tin(IV) chloride or, alternatively, by heating with elemental sulfur at 230 °C. The ^{1}H NMR spectra of both centrohexacyclanes **26** and **28** show that the apparent molecular symmetry (C_{2v}) of the parent hydrocarbon **1** has been retained, in line with the symmetrical bridging in both cases. Besides the AA′BB′ spectra of the *ortho*-phenylene bridge opposite to the heteroatomic grouping (partially overlapped in the case of **26**), the pattern of the fourfold degenerate ABCD spin systems is clearly observed, reflecting the four equivalent arene rings of the fenestrindan moieties. In accordance with the high symmetry, the ^{13}C NMR spectrum of *endo*-peroxide **26** shows only nine arene and three alicyclic resonances and that of *endo*-disulfide **28** displays eight arene and, again, three alicyclic lines. The peroxy and dithio bridges give rise to large downfield shifts of the C8b and C16b bridgehead resonances ($\Delta\delta = 41.8$ and 27.3 ppm, respectively, relative to **1**) and of those of the central carbon nuclei ($\Delta\delta = 23.5$ and 22.5 ppm, respectively). The EI mass spectra of both **26** and **28** are remarkable because the dominant expulsion of O_2 and S_2 from the molecular ions (besides minor losses of atomic O and S) gives rise to base peaks at an m/z of 440. Elimination of molecular oxygen is particularly unusual in mass spectrometry but in full accord with the energetically favorable cleavage of the bridgehead C–O bonds in ionized **26**. Furthermore, and similar to the mass spectrum of phenylcentropentaindan **21** (vide supra), intense peaks are observed for the doubly charged ions $[\mathbf{26}-O_2]^{2+}$ and $[\mathbf{28}-S_2]^{2+}$ at an m/z of 220. The IR spectrum of **26** exhibits a very strong absorption band at $\tilde{\nu} = 759$ cm^{-1}, attributed to the O–O stretching vibration of bis-*tert*-alkyl peroxides.[32] Finally, *endo*-peroxide **26** was reduced with lithium aluminum hydride to give the bridgehead diol **27** in good yield. The ^{1}H NMR spectrum of this compound is of course similar to that of *endo*-peroxide **26**, but even more so to that of **25**. The mass spectrum of **27** reflects the relatively high stability of the molecular ions under electron-impact conditions ($[\mathbf{27}^{\cdot+}]/[\mathbf{27}^{\cdot+}-H_2O] = 0.50$). This is in line with the lack of a weak adjacent C–H bond in $\mathbf{27}^{\cdot+}$ (cf. $[\mathbf{23}^{\cdot+}]/[\mathbf{23}^{\cdot+}-H_2O] < 0.1$).

As has been found very recently,[7, 8a] the relatively facile accessibility of centropentaindan (**1**) and its dibromo derivative **19** opens up a new and efficient synthetic route to the highest congener of the centropolyindan family, centrohexaindan (**2**) (the "broken fenestrane" route, cf. Scheme 7). Details of this condensation reaction have been presented in detail in another paper[7] together with two other syntheses of **2**.

Conclusion

Centropentaindan (**1**), the second-highest congener among the regular centropolyindans,[33] has been prepared by two independent syntheses. The cyclodehydrogenation route starts from the tribenzotriquinacene **7** and furnishes **1** in 50% yield in one single step by utilizing palladium/charcoal as the catalyst. Use of DDQ as a dehydrogenation reagent has been successful, too, but is by far inferior to the catalytic technique. Alternatively, **1** is obtained by a two-step bromination/condensation sequence starting from di-*fuso*-centrotriindan, **8**. The latter synthesis gives **1** in 88% yield (i.e., 71% based on indan-1,3-dione as the starting material) and enables the preparation of **1** on a scale of several grams.

X-ray structure analysis confirms the rigidifying effect of the tribenzotriquinacene structures on the singly bridged fenestrane framework of **1**. Owing to the additional indan unit (conceptually part of either of the possible tribenzotriquinacene moieties but not of the fenestrindan unit), the remaining unbridged fenestrane C-C-C bond angle is widened to 118.0°. The solid-state molecular structure of **1** is close to the ideal (namely C_{2v}) symmetry, but a slight residual distortion is found by which the all-eclipsed conformation of the molecular framework is avoided.

Centropentaindan (**1**) is the highest of the parent centropolyindans containing bridgehead C–H bonds. Notwithstanding its highly rigidified pentaquinacene backbone, it may be easily functionalized at these positions; the doubly brominated derivative **19** displays both steric peculiarities and interesting potential for the synthesis of centropentaindans bearing various bridgehead substituents and linking groups. Thus, the steric repulsion and/or electronic interactions of two strictly *syn*-1,3 oriented substituents may be studied in more detail. Also, a variety of novel centrohexacyclic derivatives may be synthesized by further bridging the "alicyclic edge" of **1** across the C(8b)–C(16d)–C(16b) grouping to generate further interesting topologically nonplanar organic compounds.[34] As examples, the hexacyclic *endo*-peroxide **26** and *endo*-disulfide **28** were prepared via **19**. Finally, the results presented here may be viewed as a distinct step into the chemistry of fenestranes[35] bearing *more* than four rings at the central carbon atom.

Experimental Procedure

General: Melting points (uncorrected): Büchi 512 and Electrothermal melting point apparatus. IR: Perkin–Elmer 841. UV: Beckman model 25. ^{1}H NMR: Bruker AM 300; CDCl$_3$/TMS, if not stated otherwise. ^{13}C NMR: Bruker AM 300 (*J* modulated spin echo experiments); CDCl$_3$/TMS, if not stated otherwise. MS: Finnigan MAT 311 A and Finnigan CH5DF; EI, 70 eV. Combustion analyses: Perkin–Elmer 240 and LECO CHNS-932 Analysator. MPLC: Besta E100 and Besta UV1; column dimensions 25 × 250 mm and 25 × 500 mm; 6 mL min^{-1}; Kieselgel LiChroprep Si60, 40–60 µm (Merck), Matrex LC60, 20–45 µm and 35–70 µm (Grace). Thin layer chromatography (TLC): Kieselgel 60 F$_{254}$ on Al foil (Merck).

X-ray structure analysis: A colorless crystal of **1** grown by diffusion of *n*-hexane into a solution of **1** in dichloromethane with the approximate dimensions 0.4 × 0.3 × 0.3 mm was used for data collection on a Syntex R3 diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation at room temperature. The cell parameters were refined from 48 centered reflections ($6 < 2\theta < 25°$). Reflections in the 2θ range 2–54° were measured in the ω-scan mode. Three reflections measured every 97 reflections showed no decay of the intensity. An empirical absorption correction was applied ($0.901 < T < 0.922$). Of the 3210 unique reflections measured, 2568 were considered observed [$I \leq 2\sigma(I)$]. The structure was solved by direct methods by means of the SHELXS86 program. Carbon and chlorine atoms were refined with anisotropic thermal parameters. The hydrogen atoms could be located in difference Fourier syntheses, but were inserted in calculated positions. Only the two bridgehead hydrogen atoms, H(8b) and H(16b), were refined freely in the located positions. For the other hydrogen atoms a common isotropic temperature factor was refined. The dichloromethane is disordered and was refined by two CCl$_2$ groups (occupancy factors 0.81 and 0.19). The molecule with lower occupancy was refined isotropically with geometrical restraints. The structure was refined with 367 parameters and all 3210 unique reflections based on F^2 to $R = 0.046$ (for observed reflections only), $R = 0.059$ (for all reflections), and $wR2 = 0.122$ ($wR2 = [(\sum w(F_o^2 - F_c^2)^2)^2/\sum wF_o^2]^{-1/2}$) where $1/w = \sigma^2 F_o^2$) by means of the SHELXL93 program. Listings of final positional and thermal parameters have been deposited [36].

8b*H*,16b*H*-4b,12b[1′,2′]Benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (centropentaindan, 1) and 14-phenyl-14*H*-4b,13[1′,2′]-benzenodiindeno[1,2-*a*:2′,1′-*b*]indene (14-phenyl-tri-*fuso*-centrotetraindan, 13):

A. Cyclodehydrogenation of 7 with DDQ: 10-benzhydryltribenzotriquinacene [12d-(diphenylmethyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene] (**7**) [4h] (3.00 g, 6.70 mmol) and 2,3-dichloro-4,5-dicyano-*p*-benzoquinone (DDQ; 10.0 g, 44.1 mmol) were dissolved in *ortho*-dichlorobenzene (175 mL) which had been dried twice with phosphorous pentoxide. The red solution was stirred under nitrogen and heated to 180 °C for 4 h. After cooling, the solvent was evaporated in vacuo, and the brown residue was redissolved in chloroform and mixed with silica gel. The mixture was dried and extracted in a Thiele–Pape extractor with petroleum ether (45–65 °C) for 12 h. The muddy extract was filtered and the filtrate concentrated, redissolved in some chloroform and subjected to MPLC (chloroform/*n*-hexane azeotrope). Two fractions were obtained containing mixtures of isomeric mono- and dichlorocentropentaindans **11a** and **11b** (total yield 280 mg, ca. 9%), as shown by mass spectrometry and ^{1}H NMR specctroscopy.

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B. Reduction of the chlorocentropentaindans: A mixture of dry THF (50 mL), *tert*-butanol (10 mL), and finely cut sodium metal (2.30 g, 100 mmole) was stirred under nitrogen while a solution of the chlorocentropentaindans **11a** and **11b** (150 mg, ca. 300 μmole) in dry THF (5 mL) was added through a dropping funnel. The mixture was heated under reflux for 24 h, the excess sodium metal was removed and the residual reaction mixture was diluted with water and acidified with 2 N aqueous sulfuric acid. Workup by extraction with dichloromethane, drying with sodium sulfate and evaporation of the solvent yielded a crude product (120 mg) which was purified by MPLC (chloroform/*n*-hexane 1:2) to give centropentaindan, **1** (106 mg, 80%), as colorless crystals. M.p. 326 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.86$ (d, $^{3}J(\mathrm{H,H}) = 7.1$ Hz, 4H), AA'BB' spectrum $\delta_A = 7.66$ (2H) $\delta_B = 7.16$ (2H), 7.50 (d, $^{3}J(\mathrm{H,H}) = 6.7$ Hz, 4H), 7.31–7.21 (m, 8H), 5.08 (s, 2H, H8b, H16b); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.3$ (s), 147.5 (s), 145.0 (s), 128.1 (d), 124.6 (d), 123.5 (d), 123.4 (d), 83.2 (s, C16d), 76.3 (s, C4b, C12b), 61.8 (d, C8b, C16b); IR (KBr): $\tilde{\nu} = 3065$, 3023, 2904, 1471, 1455, 1262, 758, 731 cm^{-1}; UV (*n*-heptane, $c = 5.2 \times 10^{-5}$ M): $\lambda_{max}(\varepsilon) = 276.5$ (4500), 269 (4880), 263 (3580), 257 nm (s); MS (70 eV, EI): *m/z* (%): 442 (100) [M^+], 441 (24), 365 (5), 221 (13); $C_{35}H_{22}$ (442.6): calcd C 94.98, H 5.01; found C 94.56, H 4.91. The crystals tend to incorporate $CHCl_3$ or CH_2Cl_2. Crystals for X-ray analysis were grown from solutions of dichloromethane and *n*-hexane.

C. Centropentaindan (1) and 14-Phenyl-tri-*fuso*-centrotetraindan (13) by catalytic cyclodehydrogenation of 7: Finely powdered **7** (1.34 g, 3.00 mmole) and palladium/charcoal (2.0 g, 10%, Merck) were intimately mixed and placed in a steel tube (160 × 16 mm, inner volume 8 mL). The tube was hermetically closed and then heated to 500 °C in a cylindrical oven and kept at this temperature for 1 h. After cooling to room temperature, the tube was carefully opened while gas (H_2) was liberated. The partially sintered product mixture was collected as completely as possible and extracted with chloroform in a Soxhlet extractor. Evaporation of the solvent yielded a crude, partially crystallizing material (1.20 g, 90% mass recovery) which was purified by filtration through silica gel and then separated into five components by MPLC (*n*-hexane/dichloromethane 4:1). The component that eluted first was diphenylmethane, **15** (110 mg, 22% yield), as identified by mass spectrometry, the second was tribenzotriquinacene, **17** (180 mg, 21% yield). The properties of **17** proved to be identical with those described recently [4e,h,j]. The third fraction consisted of pure centropentaindan, **1** (660 mg, 50% yield, see above for physical data). The final fraction was a mixture of the starting material (**7**) and the singly cyclized hydrocarbon **13** (180 mg). Separation of **13** and **7** was difficult; careful fractional crystallization from dichloromethane gave **13** as a colorless solid (100 mg, 7.5% yield, ca. 85% purity). The spectroscopic data obtained by measurements of this material unequivocally showed the identity of **13**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.94$ (d, $^{3}J(\mathrm{H,H}) = 7.6$ Hz, 1H), 7.79 (t, $^{3}J(\mathrm{H,H}) = 7.3$ Hz, 2H), 7.47–6.96 (m, 18H), 5.11 (s, 1H), 5.07 (s, 1H), 4.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.1$ (s), 147.6 (s), 147.2 (s), 145.5 (s), 145.4 (s), 145.2 (s), 144.5 (s), 143.1 (s), 129.4 (d), 128.5 (d), 128.2 (d), 127.9 (d), 127.7 (d), 127.6 (d), 127.5 (d), 127.4 (d), 127.3 (d), 126.8 (d), 126.1 (d), 124.5 (d), 124.2 (d), 124.0 (d), 123.6 (d), 123.3 (d), 122.9 (d), 78.7 (s), 66.7 (s), 66.6 (d), 63.4 (d), 58.0 (d); IR (KBr): $\tilde{\nu} = 3065$, 3024, 2879, 1493, 1473, 1453, 1215, 1025, 907, 760, 702, 628 cm^{-1}; MS (70 eV, EI): *m/z* (%): 444 (100) [M^+], 366 (78), 365 (36), 183 (29) [$M^{2+} - C_6H_6$]; $C_{35}H_{24}$ (444.6) calcd 444.1878, found 444.1873 by high-resolution mass spectrometry (HRMS).

D. Centropentaindan (1) from centrotriindan (8) by bromination and condensation with benzene: A stirred solution of **8** (1.18 g, 4.00 mmole), in tetrachloromethane (150 mL) was irradiated with a photolamp (500 W) while a solution of bromine (0.40 M, 40 mL, 16.0 mmole) in the same solvent was added over 90 min. Irradiation was continued for another 30 min and the solvent was completely evaporated. TLC analysis (CH_2Cl_2) of the bright yellow, foamy residue suggested the presence of at least three components in the mixture (note that at least partial hydrolysis of the tetrabromides **18** during TLC is probable). Crude **18** was redissolved in dry benzene (150 mL), the solution was heated to 50 °C and a solution of aluminum tribromide (0.13 M, 40 mL, 5.20 mmole) in benzene was added over 30 min, during which the solution turned dark red. After being stirred for 7 d at room temperature the mixture was hydrolysed with water and extracted with dichloromethane. The extracted solution was dried with sodium sulfate and the solvents evaporated to give a crude product which was purified by filtration through silica gel and crystallized (chloroform/*n*-hexane) to give **1** (1.57 g, 88%) as an almost colorless, crystalline product. The physical properties of this product were identical to those obtained by the methods described above.

8b-Bromo-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene (8b-bromocentropentaindan, 20): A solution of **1** (442 mg, 1.00 mmole) in dry tetrachloromethane (25 mL) was stirred while a solution of bromine (100 mM, 10 mL, 1.00 mmole) in the same solvent was added through a dropping funnel over 10 min. The solution decolorized immediately on addition of the reagent; irradiation was not necessary. After the addition was complete, the volatile components were removed in vacuo and the solid, yellowish residue was recrystallized from dichloromethane/*n*-heptane. The product may be further purified by rapid filtration through silica gel (dichloromethane/*n*-heptane 1:1) without decomposition. Recrystallization from toluene furnished **20** (365 mg, 70%) as light yellow crystals, m.p. 364 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.88-7.80$ (m, 6H), 7.62 and 7.16 (AA'BB' spectrum, 4H), 7.58–7.54 (m, 2H), 7.35–7.26 (m, 8H), 5.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.2$ (s), 146.7 (s), 146.2 (s), 144.8 (s), 144.7 (s), 129.9 (d), 128.8 (d), 128.4 (d), 128.2 (d), 126.1 (d), 124.7 (d), 123.5 (d), 123.0 (d), 88.3 (s), 81.8 (s), 75.3 (s), 63.3 (d); IR (KBr): $\tilde{\nu} = 3067$, 3024, 2926, 1470, 1456, 1163 cm^{-1}; MS (70 eV, EI): *m/z* (%): 441 (100) [$M - Br$]$^+$, 221 (10); $C_{35}H_{21}Br$ (521.5): calcd C 80.62, H 4.06; found C 80.06, H 4.17.

8b-Phenyl-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene (8b-phenylcentropentaindan, 21): 8b-Bromocentropentaindan, **20** (255 mg, 500 μmole), was dissolved in dry benzene (20 mL), and a solution of aluminum tribromide (100 μM, 1.00 mL) in benzene was added. The mixture turned red-brown upon addition of the reagent and was heated under reflux for 1 h, then cooled and hydrolysed with water. The aqueous layer was extracted with dichloromethane; the combined organic solutions were dried with sodium sulfate and the solvents were removed in vacuo. The solid residue was recrystallized from chloroform/methanol to give **21** (212 mg, 82%) as colorless needles, m.p. 361 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.94$ (d, $^{3}J(\mathrm{H,H}) = 7.6$ Hz, 2H), 7.86 (d, $^{3}J(\mathrm{H,H}) = 7.6$ Hz, 2H), 7.74 (d, $^{3}J(\mathrm{H,H}) = 7.7$ Hz, 2H), 7.66 (AA' part of AA'BB' spectrum, 2H), 7.37–7.11 (BB' part of AA'BB' spectrum, 2H, partially overlapping with m, 16H), 4.06 (s, 1H, H16b); ^{13}C NMR (75 MHz, $CDCl_3$, 25°, TMS): $\delta = 148.6$ (s), 148.4 (s), 147.79 (s), 147.5 (s) 147.4 (s), 144.8 (s), 129.1 (d), 128.3 (d), 128.1 (d), 127.9 (d), 126.5 (d), 126.0 (d), 124.5 (d), 123.4 (d), 123.1 (d), 89.5 (s, C16d), 76.2 (s, C4b, C12b), 71.8 (s, C8b), 57.7 (d, C16b); IR (KBr): $\tilde{\nu} = 3066$, 3024, 1493, 1455, 1162, 1025 cm^{-1}; MS (70 eV, EI): *m/z* (%): 518 (39) [M^+], 440 (100), 363 (7), 259 (3), 220 (34); $C_{41}H_{26}$ (518.7): calcd 518.2035, found 518.2032 (by HRMS).

8b-(4-Methoxyphenyl)-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo-[2,3:4,5]pentaleno[1,6-*cd*]pentalene (8b-*p*-anisylcentropentaindan, 22): 8b-Bromocentropentaindan, **20** (255 mg, 500 μmole) was dissolved in dry anisole (20 mL) and a solution of aluminum tribromide (100 μM, 1.00 mL) in anisole was added. The mixture turned red-brown upon addition of the reagent and was heated under reflux for 1 h, cooled, and hydrolysed with water. Workup and recrystallization as described above gave **22** (246 mg, 90%) as pale yellow crystals, m.p. 360 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.91$ (d, $^{3}J(\mathrm{H,H}) = 7.0$ Hz, 2H), 7.84 (d, $^{3}J(\mathrm{H,H}) = 7.2$ Hz, 2H), 7.64 and 7.13 (AA'BB' spectrum, 4H), 7.36–7.13 (m, 12H), 6.64 (s, 4H), 4.10 (s, 1H, H16b), 3.73 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.2$ (s), 148.9 (s), 148.5 (s), 147.7 (s), 145.0 (s), 139.7 (s), 130.3 (d), 128.3 (d), 128.1 (d), 127.9 (d), 126.1 (d), 124.6 (d), 123.5 (d), 123.2 (d), 123.1 (d), 113.4 (d), 89.5 (s, C16d), 76.2 (s, C4b, C12b), 71.4 (s, C8b), 57.8 (d, C16b), 55.2 (q, OCH_3); IR (KBr): $\tilde{\nu} = 3066$, 3022, 2933, 2903, 2837, 1507, 1473, 1456, 1254, 1178 cm^{-1}; MS (70 eV, EI): *m/z* (%): 548 (22) [M^+], 441 (41), 440 (100), 363 (6), 274 (1), 220 (26); $C_{42}H_{28}O$ (548.7): calcd 548.2140; found 548.2139 (by HRMS).

8b*H*,16b*H*-4b,12b[1',2']Benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene-8b-ol (8b-hydroxycentropentaindan, 23): To a solution of **20** (256 mg, 500 μmole) in THF (10 mL) was added aqueous sulfuric acid (6 N, 3 mL) and the mixture was heated under reflux for 5 h. After cooling to room temperature, the mixture was neutralized with aqueous sodium carbonate and extracted with dichloromethane. The extracts were dried with sodium sulfate and the solvents were removed in vacuo to yield a crystalline residue which was recrystallized from methanol to give **23** (217 mg, 95%) as colorless needles, m.p. 366 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.88-7.82$ (m, 4H), 7.73 (d, $^{3}J(\mathrm{H,H}) = 7.1$ Hz, 2H), 7.66 and 7.18 (AA'BB' spectrum, 4H), 7.54 (d, $^{3}J(\mathrm{H,H}) = 6.7$ Hz, 2H), 7.39–7.23 (m, 8H), 5.57 (s, 1H, H16b), 2.62 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.7$ (s), 147.4 (s), 147.0 (s), 146.2 (s), 145.4 (s), 129.9 (d), 128.6 (d), 128.3 (d), 128.1 (d), 128.0 (d), 124.9 (d), 124.3 (d), 123.6 (d), 123.2 (d), 91.1 (s, 16d), 87.2 (s, 8b), 74.8 (s, 4b, 12b), 53.7 (d, 16b); IR (KBr): $\tilde{\nu} = 3639$, 3550, 3438, 3065, 3023, 1471, 1456, 756 cm^{-1}; MS (70 eV, EI): *m/z* (%): 440 (100) [$M^+ - H_2O$], 220 (15) [$M^{2+} - H_2O$]; $C_{35}H_{22}O$ (458.6): calcd C 91.67, H 4.83; found C 91.78, H 4.56.

8b,16b-Dibromo-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (8b,16b-dibromocentropentaindan, 19): A solution of **1** (663 mg, 1.50 mmole) in dry tetrachloromethane (p.a., 40 mL) was stirred and refluxed under argon while a solution of bromine (4.00 mmole) in tetrachloromethane (20 mL, 0.2 M) was added over 20 min under irradiation with a photolamp (500 W). Heating and irradiation was continued for 3 h, while after ca. 1 h the product started to precipitate as a fine crystalline material. The mixture was allowed to cool, the solvent was removed in vacuo, and the light beige, crystalline residue was kept under argon to prevent decomposition. Recrystallization from toluene gave fine, colorless crystals, m.p. 360–365° (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.96$ (dd, $^{3}J(\mathrm{H,H}) = 7$ Hz, 4H), 7.81 (dd, $^{3}J(\mathrm{H,H}) = 7$ Hz, 4H), 7.46 and 7.08 (AA'BB' spectrum, 4H), 7.36 (mc, 8H); MS (70 eV, EI): *m/z* (%): 519/521 (10/11) [$M^+ - Br$], 440 (100) [$M^+ - 2Br$], 363 (10), 220 (24) [$M^{2+} - 2Br$]. A peak appears at *m/z* 457 (20) which is attributed to 8b-bromo-16b-hydroxycentropentaindan formed from **19** by single hydrolysis (cf. MS of diol **27**).

8b,16b-Dimethyl-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (8b,16b-dimethylcentropentaindan, 25): According to the procedure given above, crude dibromocentropentaindan (**19**) was prepared from **1** (100 mg, 220 µmole) and the solvent was removed in vacuo. The material was suspended in dry *n*-hexane (10 mL) under nitrogen and a solution of trimethylaluminum (2.00 M, 1 mL, 2.00 mmole) in hexane (Aldrich) was added. The solution turned orange upon addition of the reagent but decolorized after ca. 15 min. After a total of 1 h, the reaction mixture was hydrolysed by careful addition of small pieces of ice and the precipitated aluminum salts were dissolved with hydrochloric acid. The aqueous layer was extracted with dichloromethane, the combined organic solutions were washed with aqueous sodium carbonate and water, and then dried with sodium sulfate. Evaporation of the solvents yielded a pale yellow, crystalline product, which was purified by MPLC (*n*-heptane/dichloromethane 4:1) to give **25** (58 mg, 55% with respect to **1**). The purity of **25** was found to depend on that of the dibromide **19**; attemps to obtain analytically pure **25** by repeated subjection to MPLC and recrystallization failed and the final product was contaminated with up to 3% of the corresponding monomethyl compound. The m.p. of **25** thus obtained was 396–400 °C (subl.); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.89–7.86 (m, 4H), 7.52 and 7.06 (AA'BB' spectrum, 4H), 7.54–7.51 (m, 4H), 7.29–7.25 (m, 8H), 2.07 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 150.3 (s, 4C), 148.4 (s, 2C), 145.7 (s, 4C), 128.05 (d, 4C), 127.98 (d, 4C), 127.8 (d, 2C), 123.22 (d, 4C), 123.04 (d, 2C), 123.0 (d), 122.62 (d, 4C), 91.4 (s, C16d), 76.0 (s, C4b(12b)), 64.0 (s, C8b(16b)), 31.0 (q, CH$_3$); IR (KBr): $\tilde{\nu}$ = 3069, 3023, 2970 (w), 2918 (w), 1596 (w), 1584 (w), 1474, 1454, 762, 737, 613 cm^{-1}; MS (70 eV, EI): m/z (%): 470 (42) [M^+], 471 (20), 455 (100), 440 (67), 376 (13), 375 (14), 235 (11), 220 (30); C$_{37}$H$_{26}$ (470.6): calcd 470.2035; found 470.2028 (by HRMS).

8b,16b-*endo*-Peroxy-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo-[2,3:4,5]pentaleno[1,6-*cd*]pentalene (centropentaindan 8b,16b-*endo*-peroxide, 26): Dibromide **19**, obtained from **1** (1.50 mmole) as described above, was suspended in dichloromethane (40 mL, p.a.) under argon. Anhydrous *tert*-butylhydroperoxide (2.8 mL) and silver tetrafluoroborate (545 mg, 2.8 mmole) were added and the suspension was stirred for 30 min at room temperature. The organic product was separated from the silver salts by filtration through silica gel with ethyl acetate as the eluent. The solvents were removed in vacuo and the light yellow residue was recrystallized from THF/isooctane to give **26** (390 mg, 55%) as a colorless, crystalline powder, m.p. >405 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.83 and 7.30 (AA'BB' spectrum, 4H, in part overlapped), 7.80 (d, ^3J(H,H) = 7.6 Hz, 4H), 7.62 (d, ^3J(H,H) = 7.5 Hz, 4H), 7.40 (t, ^3J(H,H) = 7.5 Hz, 4H), 7.31 (t, 4H, overlapped); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 148.9 (s, 4C), 145.8 (s, 2C), 141.1 (s, 4C), 130.7 (d, 4C), 129.1 (d, 2C), 128.8 (d, 4C), 125.6 (d, 4C), 125.3 (d, 2C), 124.8 (d, 4C), 106.8 (s, C16d), 103.6 (s, C8b(16b)), 69.1 (s, C4b(12b)); IR (KBr): $\tilde{\nu}$ = 3065, 3020, 2925, 1466, 1305, 1279, 1161, 759 cm^{-1}; MS (70 eV, EI): m/z (%): 472 (41) [M^+], 456 (8) [M^+-O], 440 (100) [M^+-O$_2$], 220 (45) [$M^{2+}-$O$_2$]; C$_{35}$H$_{20}$O$_2$ (472.5): calcd C 88.96, H 4.27; found C 88.94, H 4.66.

8b*H*,16b*H*-4b,12b[1',2']Benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene-8b,16b-diol (8b,16b-dihydroxycentropentaindan, 27): A suspension of lithium aluminum hydride (150 mg, 4.0 mmole) in dry THF (2 mL) was stirred under nitrogen while a solution of **26** (80 mg, 170 µmole) was added. The mixture was heated under reflux for 3 h with continual stirring, then allowed to cool and hydrolysed by addition of ice/water and 2 N sulfuric acid. The mixture was extracted with diethyl ether, the extract was dried with sodium sulfate and the solvent was evaporated to give a colorless solid. TLC (CH$_2$Cl$_2$) and MS analysis show the presence of **27** as the major component (R_f 0.12) along with minor amounts of **23** (R_f 0.47) and **1**. Recrystallization from ethyl acetate/cyclohexane (1:1) gave pure **27** (62 mg, 77%) as colorless crystals, m.p. 370–376 °C (decomp.); ^{1}H NMR (300 MHz, (CD$_3$)$_2$CO; 25 °C, C*H*D$_2$COCD$_3$): δ = 8.15 (d, ^3J(H,H) = 7.2 Hz, 4H), 7.85 and 7.16 (AA'BB' spectrum, 4H), 7.76 (d, ^3J(H,H) = 7.5 Hz, 4H), 7.31–7.42 (m (two quasi t) ^3J(H,H) ≈ 7.4 Hz, 8H), 2.90 (br s, $\nu_{1/2} \approx 3$ Hz, 2H, OH); ^{13}C NMR (75 MHz, (CD$_3$)$_2$CO, 25°): δ = 148.61 (s, 4C), 148.13 (s, 2C), 146.8 (s, 4C), 130.2 (d, 4C), 129.17 (d, 4C), 129.07 (d, 2C), 125.07 (d, 4C), 124.63 (d, 2C), 124.06 (d, 4C), 95.0 (s, C8b(16b)), 85.3 (s, C16d), 75.3 (s, C4b(12b)); IR (KBr): $\tilde{\nu}$ = 3574 (w), 3310–3425 (br), 3070, 3029, 1598 (w), 1474, 1456, 1206, 1063, 770, 753, 628, 618 cm^{-1}; MS (70 eV, EI): m/z 474 (50) [M^+], 473 (5), 457 (56) in part [M^+-OH], 456 (100) [M^+-H$_2$O], 455 (24), 442 (32), 441 (3), 440 (45), 429 (23), 428 (47), 427 (33), 426 (33), 425 (18), 424 (21), 352 (8), 350 (11), 228 (26) [$M^{2+}-$H$_2$O], 220 (13) [C$_{35}$H$_{20}$$^{2+}$], 213 (16), 212 (20), 206.5 (12), 205.5 (15); C$_{35}$H$_{22}$O$_2$ (474.6): calcd C 88.58, H 4.67; found C 88.64, H 4.89.

8b,16b-Dithio-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]-pentaleno[1,6-*cd*]pentalene (centropentaindan 8b,16b-*endo*-disulfide, 28):

A. From dibromide 19 with hexamethyldisilthiane: A solution of dibromide **19**, prepared from **1** (221 mg, 500 µmole) as described above, was stirred in anhydrous dichloromethane (25 mL, p.a.) under nitrogen while tin(IV) chloride (120 µL, 1.0 mmole) was added. The solution turned deep red, and hexamethyldisilthiane (Fluka) (350 µL, 1.7 mmole) was added from a syringe over 30 min. After 2 h of stirring, further catalyst (20 µL, 160 µmole) was added and stirring was continued overnight. After hydrolysis, the organic layer and extracts (CH$_2$Cl$_2$) were combined, washed with diluted aqueous hydrochloric acid and water and dried with sodium sulfate. The solvent was removed in vacuo, and the residue filtered through a pad of silica gel. MPLC (chloroform) and subsequent recrystallization from dichloromethane furnished **28** (170 mg, 30%) as light yellow crystals, m.p. > 400 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 7.76 (d, ^3J(H,H) = 7.8 Hz, 4H), 7.65 and 7.20 (AA'BB' spectrum, 4H), 7.57 (d, ^3J(H,H) = 6.7 Hz, 4H), 7.38–7.27 (m, 8H); ^{13}C NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 147.5 (s, 2C), 147.0 (s, 4C), 144.6 (s, 4C), 129.8 (d, 4C), 128.9 (d, 4C), 124.5 (d, 4C), 124.2 (d, 2C), 123.9 (d, 4C), 105.6 (s, C16d), 89.1 (s, C8b(16b)), 72.3 (s, C4b(12b)); IR (KBr): $\tilde{\nu}$ = 3067, 3021, 1467, 1162, 1023, 765, 744, 614 cm^{-1}; MS (70 eV, EI): m/z (%): 504 (82) [M^+], 472 (15) [M^+-S], 440 (100) [M^+-S$_2$], 363 (15), 220 (44) [$M^{2+}-$S$_2$]; C$_{35}$H$_{20}$S$_2$ (504.7): calcd C 83.30, H 3.99; found C 83.64, H 3.62.

B. From dibromide 19 with elemental sulfur: Dibromide **19** was prepared from **1** (442 mg,1.00 mmole) as described above and, prior to the removal of the last part of the solvent, elemental sulfur (500 mmol) was added. The residual solvent was then removed in vacuo; the flask was flushed with dry nitrogen, evacuated to 0.1 mbar, and heated to 230 °C for 24 h. The black-brown reaction mixture was allowed to cool, and separated by liquid chromatography (silica gel, carbon disulfide) to give, besides excess sulfur, the crude product, which was recrystallized from dichloromethane to yield pure **28** (200 mg, 40%). Spectroscopic properties of this product were found to be identical to those given above.

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[36] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD 401770.