Benzoanellated Centropolyquinanes, 15[1]

Benzoanellated Fenestranes with [5.5.5], [5.5.5.6], and [5.5.5.5] Frameworks: The Route from 1,3-Indandione to Fenestrindan☆

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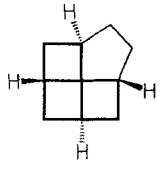
Received September 1, 1993

Key Words: Fenestranes / Polyquinanes / Centropolyindans / Polycyclic compounds

The synthesis and spectroscopic characterization of several benzoanellated [5.5.5]-, [5.5.5.6]-, and [5.5.5.5]fenestranes, including the parent *difuso*-centrotriindan **7**, the parent *tetrafuso*-centrotetraindan **8** ("fenestrindan") as well as the tribenzo[5.5.5.6]- and tribenzo[5.5.5.5]fenestranes **27** and **35**, are described and discussed in full experimental detail. The highly efficient twofold cyclodehydration of 2,2-dibenzyl-1,3-indandiol **15** and the related spiro-condensed 1,3-indandiols **23** and **29** is the keystep of the synthetic strategy. The new synthetic variant involving the one-pot cyclodehydration/deketalization of the dispiro-ketal diol **29** is particularly convenient. In the case of **7**, an alternative Lewis acid-catalyzed double cyclization has been developed. Stereochemical aspects of the 1,3-indandiols and the key tribenzo[5.5.5.6]fenestranes **24** and **25** are discussed in detail.

Fenestranes represent a particularly interesting family of polycyclic organic compounds. Several reviews[2–6] appeared during the recent years; nevertheless, the chemistry of fenestranes has remained rather exotic. This is certainly due, in part, to the synthetic challenge of bridging a central quaternary carbon atom by four rings in a straightforward way. Another reason for the peculiarity of fenestrane chemistry may be the special notice devoted to aspects of strain, geometry and other physical properties of the framework of fenestranes. Hence, great experimental efforts have been invested to construct an impressive series of small-ring fenestranes. Recent highlights in this context have been the synthesis of derivatives of [4.4.4.5]fenestrane (**1**) by Agosta et al.[7] and the syntheses of *cis,trans,cis,cis*-[4.5.5.5]fenestranes derived from **2** by Grieco et al.[8] and by Keese[9].



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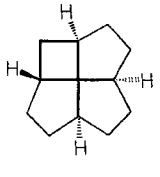

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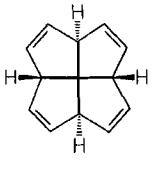

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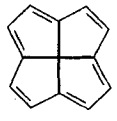

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With regard to strain effects, [5.5.5.5]fenestranes, such as **3**, represent the least critical system because of the favorable "steric fit" of five-membered rings at the central carbon atom. In fact, several syntheses of *all-cis*-[5.5.5.5]fenestranes have been developed during the past decade, including those of the parent hydrocarbons[10,11] and an impressively increasing number of functionalized systems[10–13]. However, along with the considerable theoretical interest in fenestrane chemistry[2–7,14–22] the preparative mastery of this field of polycyclics, including the [5.5.5.5]fenestrane congeners, is still a challenging objective, hiding a great potential to be explored and developed. For example, no purely alicyclic fenestrane bearing more than two bridgehead substituents or functional groups has been synthesized to date, although systematic computational studies have been performed, e.g. on fourfold bridgehead-substituted [5.5.5.5]fenestranes[19,20].

A strong impetus to investigate the chemistry of fenestranes stems from the idea[15] that the geometry of the central, tetracoordinated carbon in fenestranes could be planar or, at least, flattened to a considerable degree. In this context, *alicyclic* fenestranes with completely unsaturated periphery, e.g. **4**, have been envisaged and studied computationally[15–17] but not by experiment.

For these reasons, it appears curious that fenestranes bearing aromatic rings appended to the central neopentane core have been investigated rarely. Besides the vespirenes (**5**) studied by Prelog et al.[23], mostly from a chiroptical point of view, the only reported attempt to tackle "aromatic" fenestranes was published by Ten Hoeve and Wynberg[24], who followed several lines along "the long and winding road to planar carbon"[25]. One of the reasons for these authors to use arene precursors for their attempted construction of (strained) fenestranes was the hoped-for stability gained by

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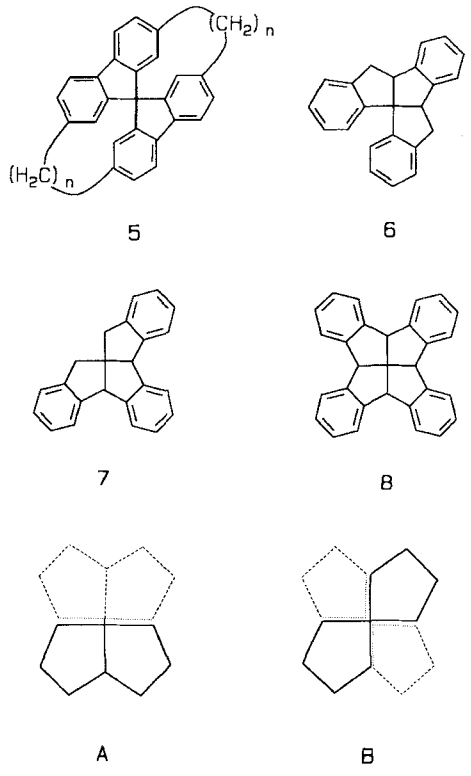


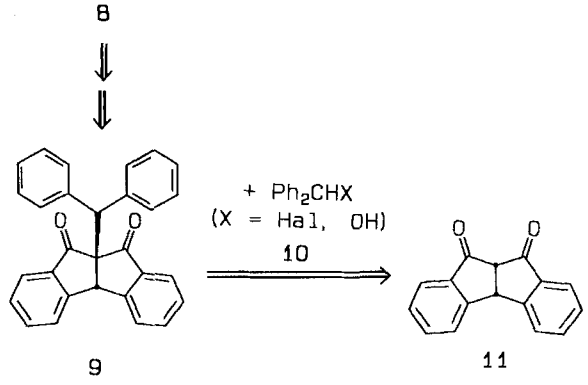
the arene rings. Ten Hoeve and Wynberg's strategy did not provide access to "regular", (i.e., centrotetracyclic) benzoanellated fenestranes, but rather "broken" (centrotricyclic) fenestranes such as **6**[24a]. Nevertheless, credit has to be given to these authors for having paved the way to the chemistry of aromatically anellated fenestranes with [5.5.5.6] and [5.5.5.5] skeletons first described by us in 1986[26]. The most remarkable [5.5.5.5] congener of our approach has been the tetrabenzo analogue of **3**, "fenestrindan" **8**, which represents a prototype hydrocarbon of the centropolyindan family[27]. A number of interesting bridgehead-substituted fenestrindans have been synthesized since[28], promising the chemistry of benzoanellated fenestranes to be broadened quickly.

In this paper, we present a full experimental account of the synthetic parcours to benzoanellated fenestranes with the [5.5.5.6] and [5.5.5.5] ring systems. Because of the close structural interrelation, the discussion will be started with the synthesis of the angular centrotriindan **7**[29]. It may be noted at this point that the successful synthesis of this broken fenestrane (a *difuso*-triindan), being closely related to Ten Hoeve and Wynberg's triindan **6**[24b], also marked the outset proper of our research into the chemistry of centropolyindans[29].

Synthetic Strategies

The fenestrane skeleton may be regarded as consisting of either two bicycloalkanes mutually fused at two geminal bridgehead C–C bonds, as shown in **A** for the [5.5.5.5] type, or as consisting of two spiranes mutually fused at the neopentane core of both, as shown in **B**. Retrosynthetically, the first aspect has been followed for the construction of the above-mentioned alicyclic [5.5.5.5]fenestranes reported from other laboratories. In our hands, this approach proved unsuccessful, as shown recently[30], although the known diindan diketone **11**[31] and an appropriately functionalized diphenylmethane derivative (**10**) appeared promising to start with (Scheme 1). Notwithstanding the prochirality of the benzhydryl group as an unfavorable factor in the envisaged (twofold) cyclization to **9**, the condensation of a benzhydrylic electrophile at the bridgehead 1,3-diketone **11** failed, in contrast to a related strategy using (enolized) 1,3-indandiones as the nucleophile[29,30,32–34].

Scheme 1. *fuso*-Diindan retrosynthesis (**A**) of fenestrindan

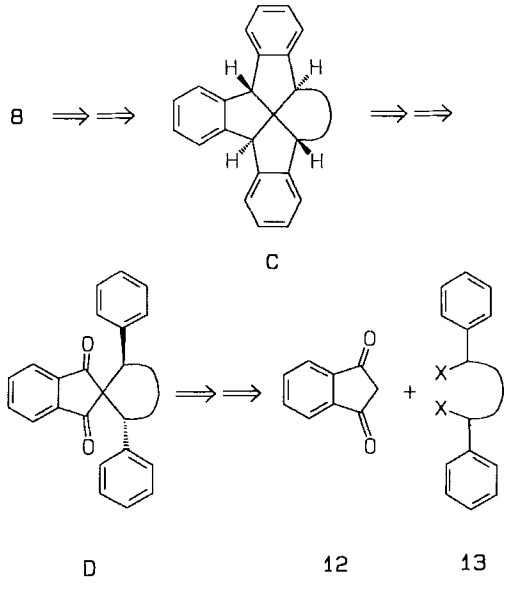


According to our present knowledge, the "spiro" approach (cf. **B**) represents the only practicable way to construct the skeleton of simple benzoanellated fenestranes[35]. The retrosynthetic approach is shown in Scheme 2. The framework of the ultimate target, fenestrindan **8** or precursor benzofenestranes **C**, is constructed from the spiro indandione **D**. Of course, *trans* orientation of the phenyl rings in **D** is a prerequisite to enable the energetically favorable *all-cis* fusion (i.e., α,β,α,β orientation of the bridgehead hydrogen atoms) in **C**. In principle, intermediates of type **D** may be obtained from 1,3-indandione **12** and an appropriate bidentate electrophile **13**.

Freimanis et al.[36] and Ten Hoeve and Wynberg[37] reported on the synthesis of several spiro[5.5]undecane and spiro[6.5]dodecane ketones, including spiro-1,3-indandiones of type **D**, by a twofold Michael addition of cyclic 1,3-diketones to diarylideneacetones. Both *cis* and *trans* isomers have been described, and, fortunately, the crucial *trans* stereochemistry is particularly easily achieved with indandiones[30,36a,37]. In contrast, a number of synthons of type **13** tested in our laboratory proved unsuitable[38].

The construction of the benzofenestrane framework requires, besides the accessibility of *trans*-diphenyl-spiro-1,3-indandiones of type **D**, the conversion of the diketone to the corresponding spiro-1,3-indandiol and the twofold cyclization to **C**. This two-step sequence was accomplished previously with related indandiols[29,33], and in fact turned out to be the synthetic key to the benzoanellated fenestranes reported here and to many other centropolyindans[27–30,32]. As will be shown in the following section, our synthesis of

Scheme 2. Spiro-type retrosynthesis (**B**) of fenestrindan



fenestranes and related polycycles has been based on the convenient preparation of the simpler centrotriindan **7**.

Synthesis of the *difuso*-Centrotriindan 7, a [5.5.5] ("Broken") Fenestrane

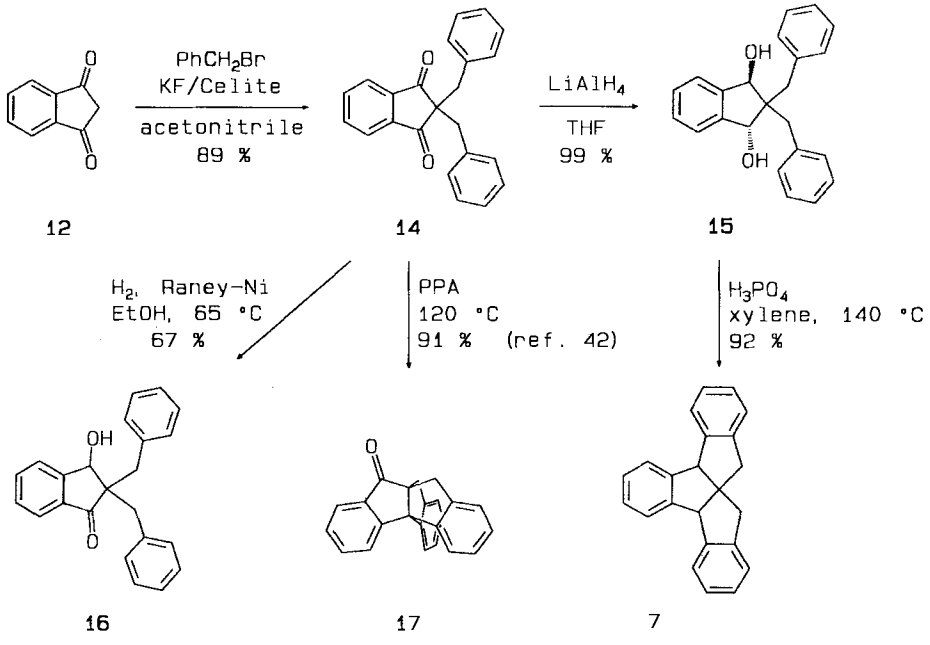
The triindan **7** is synthesized in three steps by starting from 1,3-indandione (**12**) (Scheme 3). Twofold benzylation to **14** is achieved in high yield by using an excess of potassium fluoride on Celite 545 ("KF/Celite") in acetonitrile. This method, first applied to 1,3-indandione by Bloch and Orvane[39], is far superior to other methods of benzylation of **12** and other 2-unsubstituted 1,3-indandiones. It has been known for a long time that highly acidic diketones such as **12** notoriously undergo base-catalyzed self-condensation[40], and the yield of **14** in conventional base-assisted benzylation reactions does not surpass 40%[41]. The KF-Celite method is very useful for large-scale reactions and, in general, does not give rise to significant amounts of by-products such as *C,O*-benzylation unless steric hindrance interferes[32]. On the basis of this efficient access to **14**, we have recently developed a particularly short, high-yield synthesis of 9-triptindanone **17** by twofold cyclization with concomitant *single* dehydration (Scheme 3)[42].

Reduction of **14** with $LiAlH_4$ in tetrahydrofuran gives the corresponding *trans*-diol **15** in near-quantitative yield. The stereochemistry of **15** follows unambiguously from the ^1H-NMR spectrum, which shows an AB spin system reflecting the diastereotopy of the two protons within each of the (magnetically equivalent) methylene groups in the chiral *trans* isomer. The hypothetical (achiral) *cis*-1,3-diol, by contrast, should exhibit two distinct singlet methylene resonances. In fact, with the corresponding 1,3-dibromoindan **18** (Scheme 5), which is obtained as a mixture of diastereomers **18a** and **18b**, both of these NMR features are verified. Attempts to prepare the *cis*-diol by catalytic hydrogenation of **14** (Raney nickel/ethanol, 65°C) resulted only in the formation of the ketol **16** in moderate yield.

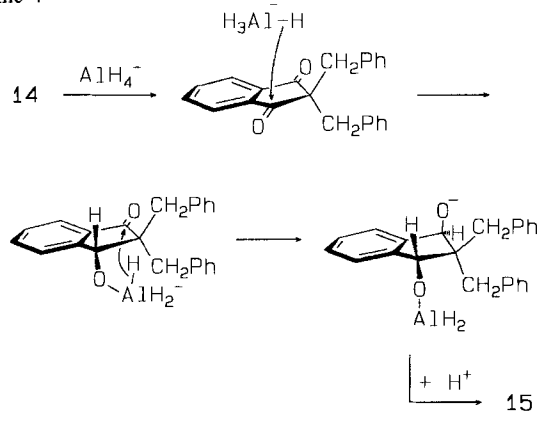
The formation of the *trans*-1,3-indandiol **15** as the single isomer is remarkable with respect to the mechanism of the reduction. As discussed in a previous paper[32], it reflects the high degree of steric control after the first nucleophilic attack, the intramolecular transfer of the second hydride being much faster than the reaction with a second reagent anion (Scheme 4).

Treatment of **15** with orthophosphoric acid in toluene or xylene at reflux temperatures gives rise to the twofold cyclodehydration to form the angular (*difuso*-) triindan **7** in 92% yield (Scheme 3). The same hydrocarbon has been synthesized via the dibromide **18**, which is obtained by treatment

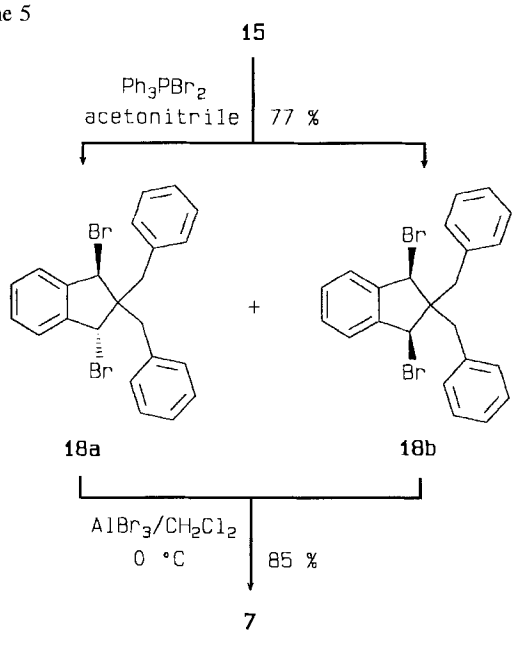
Scheme 3



Scheme 4



Scheme 5



of **15** with triphenylphosphine-bromine adduct[43] as a mixture of the *trans* and *cis* isomers (Scheme 5). The *trans* isomer **18a** has been isolated by crystallization and characterized. Lewis acid-catalyzed twofold cyclization of **18** with aluminium tribromide gives the *difuso*-triindan **7** in 85% isolated yield. This alternative route has been studied in order to improve the synthesis of related centrotriindans, however without success[44]; but even in the present case the direct route to **7** by dehydration of **15** (Scheme 3) is superior.

The identity of **7** is clearly documented by mass and NMR spectrometry. The mass spectrum is dominated by the molecular ion peak reflecting the high stability of the multiply fused polycyclic skeleton. The simple ^{1}H- and ^{13}C-NMR spectra reflect the C_2 molecular symmetry of **7**. Thus, the two methylene groups give rise to equivalent AB spin systems (δ = 3.15 and 3.34, ^2J = −16.4 Hz). The equivalent benzhydrylic protons are represented by the singlet at δ = 4.44. The ^{13}C-NMR spectrum shows only three lines for the aliphatic and only nine signals for the arene carbon nuclei, as expected for this centrotriindan. The UV/Vis spectrum of **7** exhibits the π,π^* transition at λ = 274.0 nm, in line with that of other centropolyindans with a conformationally non-rigid polycyclic framework (e.g. **8**, see below)[32].

The high efficiency of the twofold cyclodehydration is remarkable. Similar 1,3-indandiols bearing a benzhydryl group instead of two benzyl substituents at C-2 undergo a twofold cyclization as well to give tribenzotriquinacenes[29,32], but the yields are only moderate or low (11−33%), depending on the second substituent at C-2. In those cases, several unfavorable factors such as the electrofugacity and prochirality of the benzhydryl group may limit the yields of the triindan formed; in the case of 2,2-dibenzyl-1,3-indandiol **15** and related substrates[30], however, both of these factors vanish. Each of the benzyl groups may be assumed to be oriented favorably in the vicinity of one of the carbinol functions, as shown in Scheme 6.

Whereas the stability of the benzylic C(2)−C(α) bonds is not surprising, the cleavage of the 1,3-diol system of **15** appeared to be critical under the relatively harsh standard reaction conditions used (H_3PO_4/xylene at 135°C). Although the literature on 1,3-indandiols was remarkably limited prior to our studies, the fragility of this doubly benzylic 1,3-diol is evident[45,46]. In fact, Grob fragmentation of **15** takes place under modified acidic conditions (e.g. with *p*-toluenesulfonic acid as the catalyst), and may be used to prepare single-dehydration products in good yields, e.g. **19**[29,47]. Moreover, Grob fragmentation may lead to other products of twofold dehydration, viz. naphthalenes such as **20**[47]. With orthophosphoric acid, however, the triindan **7**, as a "three-dimensional" isomer of **20**, is formed exclusively.

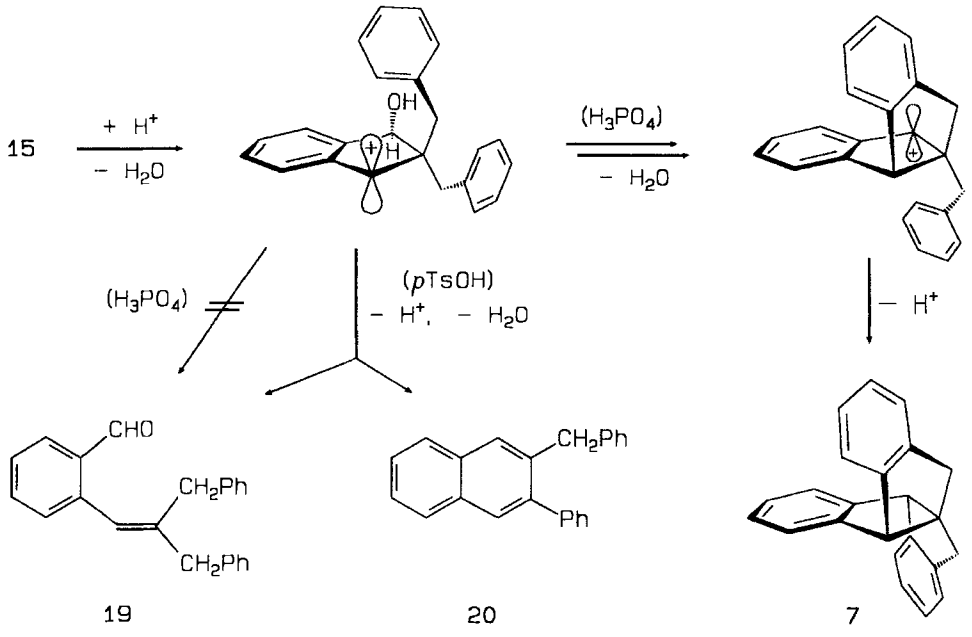
With these results in hand, the availability of spiro-1,3-indandiones of type **D** (Scheme 2) encouraged us to pursue the synthesis of centrotetracyclic congeners of **7** via related, *spirocyclic* 1,3-indandiols. In fact, the preorientation of the two benzyl units within a *trans*-diphenyl-substituted, rigidifying cyclohexane ring turned out to be ideal to perform an efficient twofold cyclization, thus producing a [5.5.5.6]-fenestrane nucleus.

Tribenzo[5.5.5.6]fenestranes by Twofold Cyclodehydration of Phenyl-Substituted Spiro[cyclohexane-1,2′-indan]-1′,3′-diols

The synthetic sequence from 1,3-indandione **12** to the [5.5.5.6]fenestranes is shown in Scheme 7. It is based on the twofold Michael addition of dibenzylideneacetone (**21**) to **12**, as reported by Freimanis et al.[36] and by Ten Hoeve and Wynberg[37]. In acetic acid, the product of the kinetically controlled reaction, *trans*-2,6-diphenylspirotrione **22**, is obtained in ca. 65% yield[36a,37]. Most importantly, prolongated heating or utilization of a base as a catalyst leads to the corresponding *cis* isomer as the thermodynamically more stable product[36a,37].

Reduction of **22** with an excess of $LiAlH_4$ in tetrahydrofuran gives the spirotriol **23** as a mixture of at least three of the four possible diastereoisomers. ^{1}H-NMR analysis of the crude product indicates the presence of two major triols

Scheme 6



and a minor one in a ratio of ca. 10:6:1. Whereas satisfying separation by chromatography failed so far, the minor isomer (**23a**, m.p. 286–288°C) and the most abundant one (**23b**, m.p. 192–194°C) could be isolated by repeated crystallization (see Experimental).

Stereochemical analysis of **23a** and **23b** was only partially successful, however. For both of the isomers, ^{1}H-NMR spectra measured in both [D_8]THF and in [D_5]pyridine reveal that the phenyl groups rotate freely in spite of the highly crowded environment at the spiro center. It is also evident that, as expected, the salient *trans* orientation of the two phenyl groups is retained during the reduction, as shown by the characteristically distinct twofold vicinal ^{1}H-^{1}H spin coupling of the benzylic protons 2-H and 6-H with the methylene protons at C-3 and C-5. ^{1}H-^{1}H COSY spectrometry confirms the assignments of the appropriate proton resonances for both isomers. However, in spite of intriguing differences in both the ^{1}H-^{1}H NOESY spectra and the 70-eV EI mass spectra of the triols (e.g. **23a**, $[M - H_2O]^{\cdot+}/[M]^{\cdot+}$ = 40:1, for **23b** $[M - H_2O]^{\cdot+}/[M]^{\cdot+}$ = 7:1), the relative orientation of the hydroxy groups at the 1,3-indandiol moiety could not be identified unequivocally. More detailed investigations including an X-ray structural analysis of the readily crystallizing isomer **23b** (see Experimental) appear promising.

As in previous cases, the stereochemical differences at the 1,3-indandiol moiety are cancelled during the cyclodehydration step. In contrast, the stereochemistry of the twofold phenyl-substituted cyclohexanol moiety *is* relevant, and chemical proof for the *trans* orientation of the two phenyl groups comes from the surprisingly efficient twofold cyclodehydration of **23** (used as the mixture of the triol stereoisomers) to give the [5.5.5.6]fenestranol **24** in 90% yield. Obviously, each of the two benzyl groupings "cramped" into the spiro framework of **23** is highly favorably oriented to one of the carbinol functions of the 1,3-indandiol system. Hence, in fact, the *trans*-2′,6′-diphenyl substitution of **23** translates directly into the sterically favorable *all-cis* (or 4bα,8bβ,12bα,15aβ) fusion of the [5.5.5.6]fenestrane nucleus.

Interestingly, the cyclohexanol ring does not suffer dehydration to a significant degree under the relatively harsh reaction conditions. After treatment with orthophosphoric acid in xylene at 140°C for 20 h, only 2–5% of the fenestrene **26** is formed (Scheme 8). This is attributed to the rigidity of the six-membered ring fused to two vicinal C–C bonds of the triindan moiety of **24**. Similar reluctance of the tribenzo[5.5.5.6]fenestrane system to the introduction of an endocyclic double bond has been encountered in related studies[48]. In contrast, fenestrene **26** is obtained in 53% yield by heating **23** in hexamethylphosphoric triamide (HMPA) at 240°C (Scheme 8).

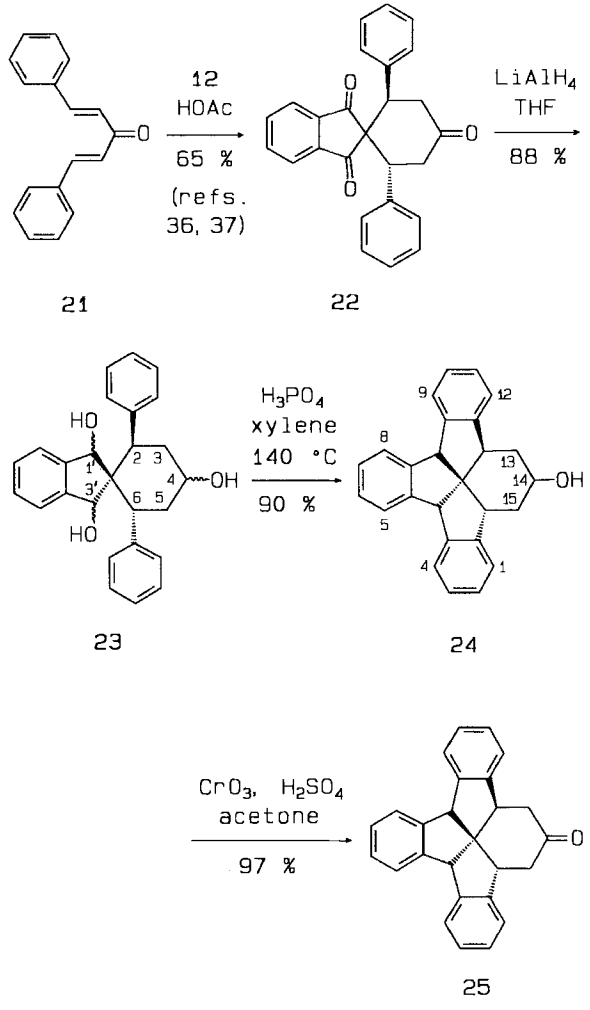
The persistence of the hydroxy group in **24** offers an elegant way to manipulate the functionality of the non-benzoanellated ring of the fenestrane core and, eventually, to transform it into a fourth indan entity, as will be shown below. As a first step, oxidation of **24** in acetone suspension with chromium(VI) oxide gives the corresponding ketone **25** in 95% yield (Scheme 7). Wolff-Kishner reduction of **25** leads to the parent tribenzo[5.5.5.6]fenestrane **27**, which is obtained alternatively by catalytic hydrogenation of the fenestrene **26** (Scheme 8).

To circumvent the process of reduction/reoxidation of the cyclohexanone moiety, the spirotrione **22** is ketalized to **28** (Scheme 9). In analogy to the reduction of **22** itself, treatment of **28** with $LiAlH_4$ in tetrahydrofuran leads to a mixture of stereoisomeric spiro-1,3-indandiols **29**, the major of which is obtained in pure form by recrystallization in 52% yield. Both the ^{1}H- and ^{13}C-NMR spectra indicate the formation of a conformationally flexible structure with apparent C_2 molecular symmetry, and hence the presence of the *trans*-1,3-indandiol moiety spiro-fused with the central

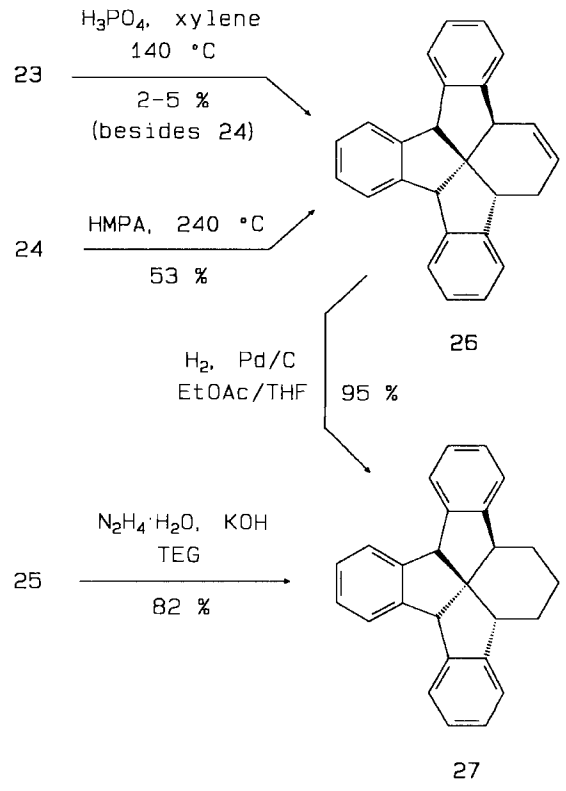
trans-1,3-diphenylcyclohexane unit (cf. **29a** and **29b**, Scheme 9). Unequivocal stereochemical identification has not been achieved, however. In fact, a critical conformational analysis of **29a** and **29b** reveals that the crosspeaks observed in the ^{1}H-^{1}H NOESY spectrum of the obtained diol (see Experimental) would allow for either diastereomer. On the basis of previous results on the reduction of 1,3-indandiones with $LiAlH_4$[30,32,49], however, it appears tempting to speculate that stereocontrolled hydride transfer may lead preferably to the *syn,syn* orientation of the hydroxyl groups (cf. **29a**) with respect to the adjacent phenyl substituents, rather than to the *anti,anti* form (**29b**).

Treatment of **29** under standard dehydration conditions (cf. **15** → **7**, **23** → **24**) gives rise to twofold cyclization with concomitant hydrolysis of the ketal group to give the fenestrane ketone **25** in 92% yield. The overall yield of the "ketal variant" (**22** → **25**) is lower (60%) than that of the reduction/reoxidation sequence (**22** → **25**, 77%); it may be noted, however, that both the reduction (**22** → **23**) and reoxidation (**24** → **25**) steps of the latter require particularly careful control to achieve complete conversion of the respective starting materials, whereas the ketal route is performed more conveniently.

Scheme 7



Scheme 8



In contrast to the asymmetrical fenestranol **24** (see below), the fenestranes **25** and **27** formally display C_2 molecular symmetry which is clearly reflected by their NMR spectra. The ^{1}H-NMR spectrum of **25**, for example, shows only one singlet for the equivalent benzhydrylic methine protons and an ABX spin pattern for the two equivalent $CHCH_2$ groups of the cyclohexanone ring. Accordingly, the ^{13}C-NMR spectrum of **25** exhibits only thirteen (of fourteen possible) lines for the 26 carbon atoms (see Experimental). This demonstrates the conformational flexibility preserved in the fenestrane skeleton.

Conformational Analysis of the Tribenzo[5.5.5.6]fenestranes 24 and 25

Whereas the twist form has been deduced as the most stable conformation of the cyclohexanone ring in **22**[37], the fenestrane ketone **25** rather exists in an equilibrium of two degenerate conformers comprising a flattened chair-type cyclohexanone moiety (Figure 1)[50]. This follows from the analysis of the ^{1}H-^{1}H spin coupling constants of **25**. Besides the geminal coupling (e.g. $^2J_{13\alpha,13\beta} = -13.6$ Hz), the two equivalent ABX systems of the cyclohexanone ring show closely similar vicinal coupling constants (e.g. $^3J_{12\alpha,13\alpha} \approx {}^3J_{12a\alpha,13\beta} = 7.2$ Hz), indicating average dihedral angles in the range of 20–45 and 115–140°. Both values fit well with the geometry of the CH–CH_2 groups in the two equilibrating chair conformers **25′** and **25″**, e.g. $|\sphericalangle(H_{12b\alpha}C-CH_{13\alpha})| \approx 30$ and 45°, respectively, and $|\sphericalangle(H_{12b\alpha}C-CH_{13\beta})| \approx 90$ and 175°, respectively. By contrast, a (flattened) boat form would imply dihedral angles

in the order of $|\sphericalangle(H_{12b\alpha}C-CH_{13\alpha})| \approx 10$ and 20° and $|\sphericalangle(H_{12b\alpha}C-CH_{13\beta})| \approx 105$ and 145° and thus clearly distinct vicinal coupling constants. In addition, a "W coupling" between the protons of the two methylene groups is observed ($^4J_{13\alpha,15\alpha} \equiv {}^4J_{13\beta,15\beta} = 1.6$ Hz). While this feature allows for both the chair (Figure 1) and the boat forms, it clearly rules out the presence of a stable twist conformation. Thus, in summary, the polycyclic skeleton of **25** avoids the C_2-symmetrical ground-state conformation in favor of a C_1-symmetrical *difuso*-triindan subunit, which in turn gives rise to a slightly distorted chair form of the cyclohexane part of the fenestrane framework[51].

The fenestrane alcohol **24** is asymmetrical (point group C_1) due to the presence of the carbinol group at C-14. This leads to distinct ^{1}H resonances for all of the alicyclic protons of the [5.5.5.6]fenestrane nucleus (Figure 2) and also accounts for the full set of 26 different lines in the ^{13}C-NMR spectrum. Analysis of the cyclohexanol part of the ^{1}H-NMR spectrum and ^{1}H-^{1}H- and ^{1}H-^{13}C-COSY spectrometry of **24** allow the individual proton and carbon resonances to be assigned as indicated in Figure 2. Again, the twist conformation can be ruled out by the observation of a "W coupling" between one proton of each of the methylene groups (see below), in line with force-field calculations[51]. The "anchor" resonance of the carbinol proton 14-H is identified by the triplet of triplets at $\delta = 3.78$, and the size

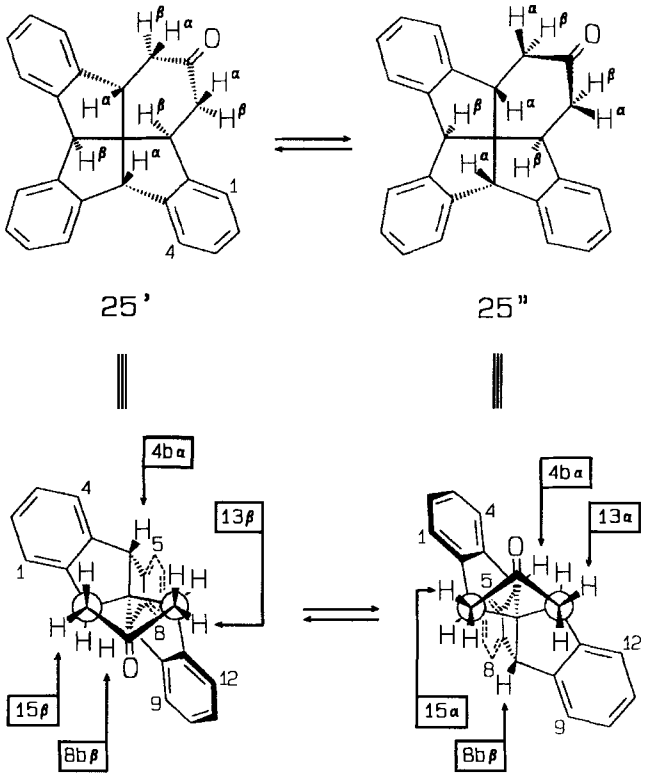
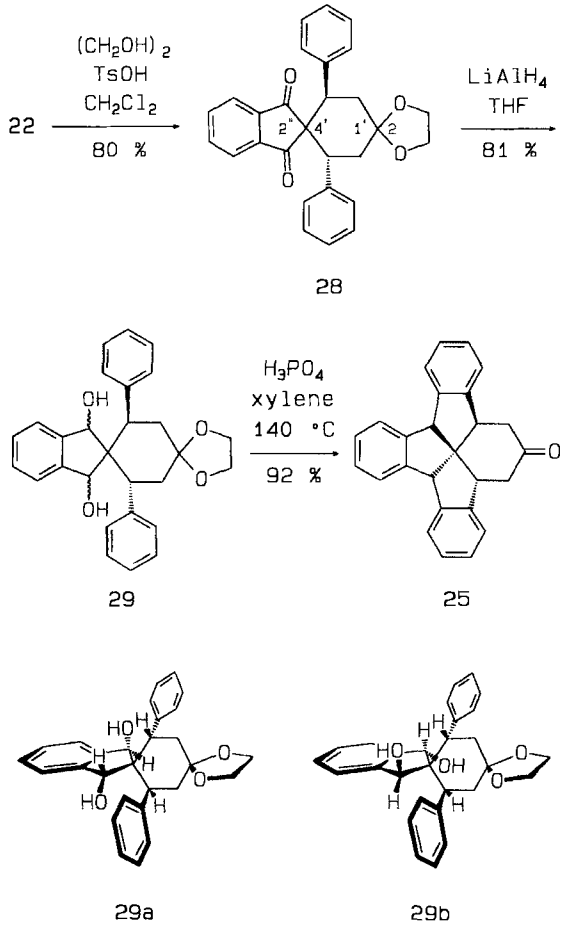


Figure 1. Degenerate equilibrium of the (quasi-chair) conformers of **25**

Scheme 9



of its vicinal coupling with the four adjacent methylene protons (viz. $^3J_{14\beta,13\alpha} \approx {}^3J_{14\beta,15\alpha} \approx 10.6$ and $^3J_{14\beta,13\beta} \approx {}^3J_{14\beta,15\beta} \approx 3.3$ Hz) clearly demonstrates the prevailing quasi-equatorial position of the hydroxyl group in either a chair or boat conformation. The long-range coupling is larger than that found for **25** ($^4J_{13\beta,15\beta} = 3.3$ Hz) and operates for the quasi-equatorial protons (13β-H and 15β-H) only. The resonances of the two benzylic protons 12bα-H and 15aβ-H exhibit distinct doublets ($^3J_{12b\alpha,13\alpha} = 6.1$, $^3J_{12b\alpha,13\beta} = 3.3$ and, respectively, $^3J_{15a\beta,15\alpha} = 11.3$, $^3J_{15a\beta,15\beta} = 6.0$ Hz).

The ensemble of these data unambigously reflects an equilibrium between a flattened chair and a flattened boat form of **24** as the dominating conformations. Flattening of the cyclohexane ring results, as in **25**, from the angular fusion with the *difuso*-triindan subunit of **24**, levelling to a certain degree the energy contents of the two conformers. In other words, limited rotation of the fenestrane skeleton of **24**, which has been found for other benzoanellated fenestranes as well[27,28a,30], enforces a "semi-flip" of the cyclohexanol at its fused end, leaving the conformation of the free, carbinol part of it essentially unaffected.

Ring Contraction to [5.5.5.6]Fenestranes and Synthesis of Fenestrindan

Ketone **25** represents the central intermediate product of the synthesis of the target centropolycycle, fenestrindan **8**. As will be shown, the conversion of **25** to **8** requires another five steps. The contraction of the six-membered ring is accomplished by twofold bromination and Favorskii re-

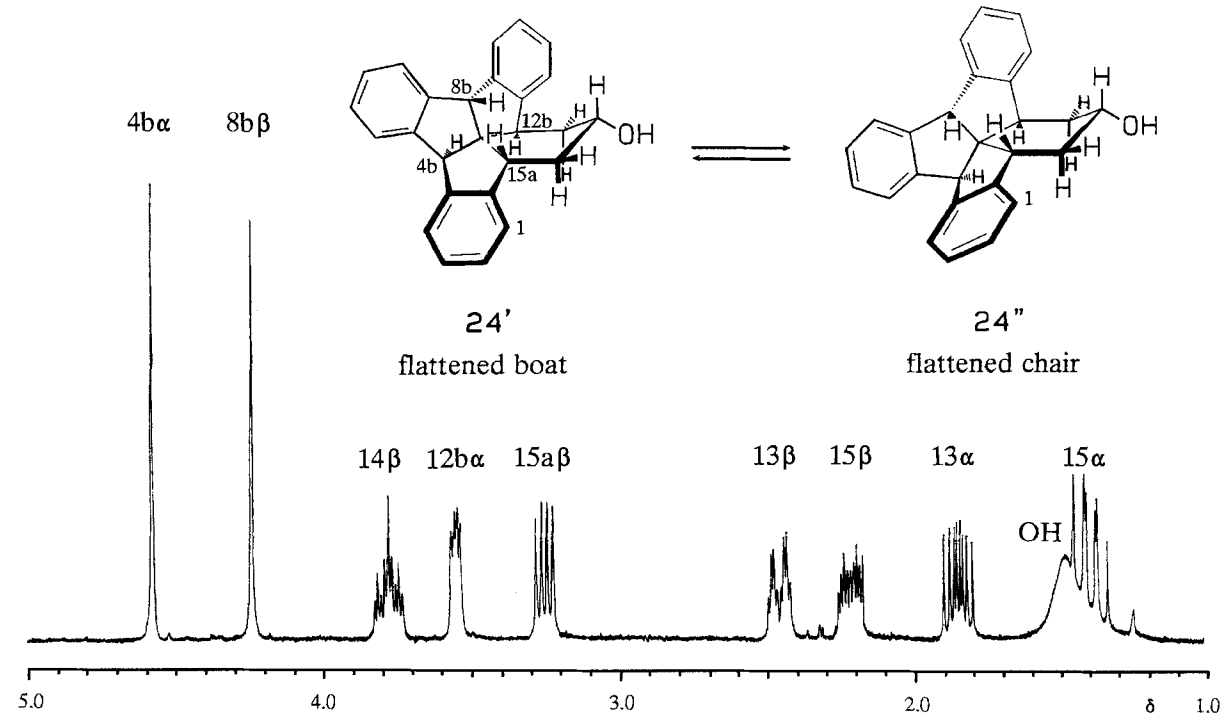
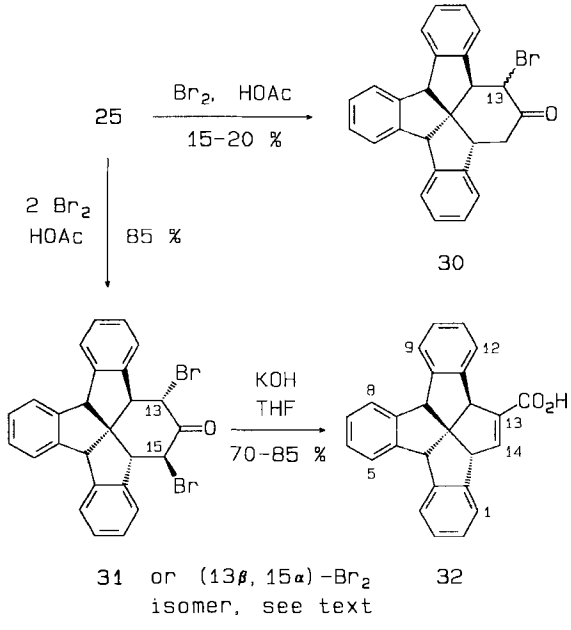


Figure 2. Partial ^{1}H-NMR spectrum of **24** (300 MHz, $CDCl_3$) and equilibrium between the quasi-boat and the quasi-chair conformers bearing equatorial OH groups

arrangement (Scheme 10). Whereas the introduction of chlorine substituents does not proceed in a sufficiently uniform way, bromination of **25** in acetic acid takes place with high selectivity. With two equivalents of the reagent, another C_2-symmetrical fenestrane, viz. the *trans*-1,3-dibromoketone **31** is obtained in high yield. Unequivocal assignment of the stereochemistry of this compound is difficult on the basis of ^{1}H-NMR spectrometry: the medium-sized vicinal ^{1}H-^{1}H coupling constant ($^3J_{12b\alpha,13a\beta} = {}^3J_{14a\beta,15\beta} = 6.7$ Hz), as an average value of equilibrating conformers, may account for both the 13α,15β- and the 13β,15α-dibromo substitution. However, the fenestrane ketone **31** is proposed to be the 13α,15β-dibromo diastereomer, as shown in Scheme 10. This stereoisomer should present the thermodynamically more stable form because of the bulkiness of the two large bromine substituents oriented away from the adjacent benzo rings. With only one equivalent of bromine and very slow addition of the reagent, the monobromo ketone **30** is obtained in low yield. In this compound, all of the three vicinal coupling constants of the cyclohexanone ring are in the range of $^3J = 7.0 \pm 0.3$ Hz, suggesting in fact 13α-rather than 13β-bromination as the first step on the way to **31**.

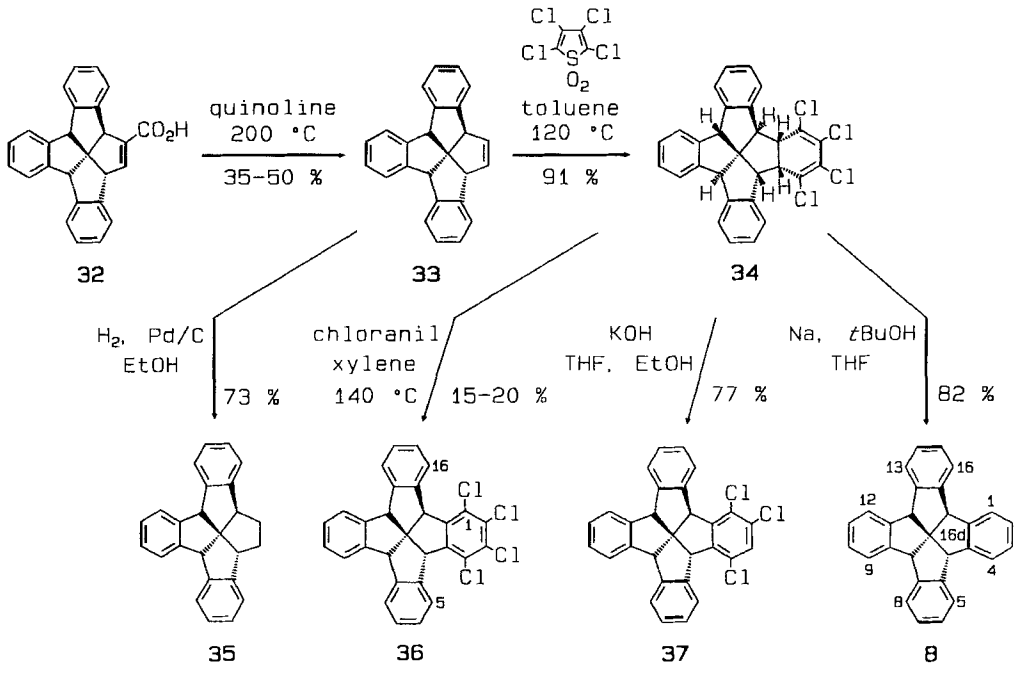
Scheme 10



In the following step, ring contraction to the [5.5.5.5]fenestrane skeleton is achieved by treatment of **31** with potassium hydroxide in tetrahydrofuran, giving the unsaturated fenestranecarboxylic acid **32** as a crude product in 70–85% yield. Purification of this material has been performed by flash chromatography but found to be wasteful.

Decarboxylation of the acrylic acid **32** requires rigorous conditions (Cu/quinoline at 200°C) (Scheme 11). This reaction is the most critical and tedious step of the overall synthetic sequence to fenestrindan **8**; it furnishes the tribenzofenestrene **33** in ca. 50% yield. Catalytic hydrogenation of **33** leads to the corresponding fenestrane **35**. The ^{1}H- and ^{13}C-NMR spectra of these two centrotriindans clearly demonstrate that the formal C_2 molecular symmetry is restored by the decarboxylation step. For example, the pairs of benzylic and the benzhydrylic protons of **33** both display singlet resonances observed at $\delta = 4.42$ and 4.82, respectively.

Scheme 11



Anellation of the fourth six-membered ring to the [5.5.5.5]fenestrane nucleus is easily accomplished in the two final steps (Scheme 11). Reaction of **33** with tetrathiophene *S,S*-dioxide[52] is performed by heating the reactants in highly concentrated toluene solution to 120°C for a total of 24 h. The cycloadduct **34** is obtained in high yield. The *cis* fusion of the tetrachlorodiene unit to the fenestrane core of **33** again breaks the C_2 symmetry of the latter, as reflected by the complex ^{1}H- and ^{13}C-NMR spectra of **34**. The *cis* fusion about the newly formed C–C junction is evident from the large vicinal coupling constant, $^3J_{4a\alpha,16c\alpha}$ = 10.3 Hz. Dehydrogenation of **34** with *p*-chloranil in refluxing xylene is very slow, leading, with low conversion, to the fully aromatic 1,2,3,4-tetrachlorofenestrindan **36** as a readily crystallizing material of m.p. 306–309°C. It is clearly identified by spectrometry, in particular by the relatively simple ^{1}H- and ^{13}C-NMR spectra. Thus, two singlets are observed for the two pairs of equivalent benzhydryl protons (δ = 4.81 and 5.12). Notably, the two equivalent *ortho* protons at C-5 and C-16 in **36** resonate at δ = 7.85, that is, the vicinity of the perchlorobenzo nucleus leads to an extra deshielding of ca. 0.35 ppm as compared to the other *ortho* protons. The twofold degeneracy of all the ^{13}C resonances of **36** except that of the central carbon atom also corroborates its structure.

Elimination of hydrochloric acid from **34** with potassium hydroxide in THF/ethanol solution occurs in a straightforward way to give the trichlorofenestrindan **37** in good yield. In line with previous results[52,53], one of the peripheral chlorine atoms is removed, as revealed by the ^{1}H-NMR spectrum of **37**. This clearly follows from the (apparent) equivalency of again two deshielded *ortho* protons (5-H and 16-H) at δ = 7.86, together with a distinct singlet at δ = 7.41 for 3-H.

Fenestrindan

Finally, reduction of **34** with sodium/*tert*-butyl alcohol in tetrahydrofuran[54] furnishes the target hydrocarbon, fenestrindan **8**, in improved yield[26] (82%) as a colorless, beautifully crystallizing solid of m.p. 325–330°C. As compared to the tetrachloro derivative **36**, introduction of the last of the four uniformally fused arene rings to the [5.5.5.5]fenestrane nucleus increases the formal molecular symmetry (from C_2 in **36** to D_{2d} in **8**) and evidently leads to a more closely packed crystal structure[26].

The identity of **8** is unequivocally revealed by spectrometry, X-ray structural analysis[26], and by the chemical reactivity of this centrotetraindan. According to its formal (apparent) D_{2d} symmetry, the ^{1}H-NMR spectrum of **8** exhibits only a single resonance for the four benzhydrylic bridgehead protons (δ = 4.89) and a fourfold degenerate AA'BB' pattern due to the arene protons. In line with the spectra of other centropolyindans[29,32,34,42,55], the *ortho* protons resonate at slightly lower field than those at the *meta* positions (Δδ = 0.26) due to the deshielding field of the adjacent arene ring. The ^{13}C-NMR spectrum of **8** is particularly simple: in accordance with the effective symmetry, it consists of only five lines representing a total of twenty-nine carbon atoms.

It appears clear that the conformational ground state of **8** is again distorted to a lower symmetry to avoid the all-eclipsed conformation of the central neopentane unit, similar to the conformational effects discussed above for **25**. In this case, the actual ground state has S_4 molecular symmetry, which is also found for the solid state by X-ray crystallography[26]. In solution, the dynamic equilibrium of two such degenerate S_4 conformers is fast at room temperature for the parent fenestrindan, **8**, leading to the higher, appar-

ent C_{2d} symmetry of the system. This equilibrium is suppressed or its dynamics is considerably hampered in fenestrindans bearing bulky bridgehead substituents as reported in refs.[28a,55]. The details of the distortion of the ground-state geometry of the fenestrindan system by bridgehead substitution are under investigation[56].

As has been found for other centropolyindans, the UV spectrum of **8** displays a π-π^* transition in the normal range of simple *ortho*-substituted benzene derivatives. The lowest-energy absorption (λ_{max} = 273.5 nm) is identical with those of other centropolyindans with a residual conformational flexibility (e.g. **7**)[32,57]. Beyond that, no hints are found for significant electronic interactions of the four arene rings across the benzhydrylic bridgeheads.

The standard 70-eV mass spectrum of fenestrindan is dominated by the molecular ion peak (*m/z* 368). Besides the minor losses of a hydrogen atom and/or one of the benzene rings, there is virtually no significant fragmentation of the singly charged molecular ion. It is remarkable, however, that a fragment ion peak at *m/z* 145 of considerable intensity (20–30%) is observed, suggesting the loss of C_6H_6 from the *doubly* charged molecular ions $\mathbf{8}^{2+}$. Since the peak corresponding to the latter ions (*m/z* 184) is very small (≤2%) it appears likely that the fragmentation channel leading to ions [$\mathbf{8}^{2+}$ – C_6H_6] (*m/z* 145) is highly thermochemically favorable and hence corresponds to the loss of benzene as the neutral fragment. The mechanistically intriguing possibility of specific bridgehead-hydrogen (or proton) transfer processes in this particular alkylbenzene ion[62] will be studied in a separate investigation.

In conclusion, the synthesis of a particularly interesting member of the centropolyindan family, fenestrindan **8**, has been described in full detail, including stereochemical aspects of key synthetic intermediates. This hydrocarbon is available now by routine work in our laboratory on a several-gram scale according to a nine-step protocol by starting from unsubstituted 1,3-indandione (**12**). Besides the special interest from the viewpoint of fenestrane chemistry and the geometrical aspects of the central carbon atoms of fenestranes, fenestrindan **8** may serve as a versatile basis for further benzoanellated derivatives such as centropenta- and centrohexacyclic arenes. A number of these have already been synthesized in our laboratory[28b,28c,55,58], including several isocyclic and heterocyclic compounds with a high degree of three-dimensional ring fusion.

I wish to thank Mr. *D. Barth* for his skilled technical assistance and Dipl.-Ing. *J. Kruckemeyer* for synthetic contributions at early stages of this work. I also thank Dr. *T. Wippermann* for performing some early 2D-NMR measurements. Financial support by the *Deutsche Forschungsgemeinschaft* (DFG, Ku 663/1–2) is gratefully acknowledged.

Experimental

Melting point (uncorrected): Büchi 512, and, for m.p. > 300°C, Electrothermal melting point apparatus. – IR: Perkin-Elmer models 377 and 841. – UV: Beckman model 25. – ^{1}H NMR: Bruker AM 300 and Bruker AC 250 P; $CDCl_3$/TMS. – ^{13}C NMR: Bruker AM 300 (*J*-modulated spin echo experiments); $CDCl_3$/TMS. ^{1}H-^{1}H COSY measurements: Bruker AM 300, and ^{1}H-^{1}H, ^{1}H-^{13}C COSY, and ^{1}H-^{1}H NOESY measurements: Bruker AC 250 P. – MS: Finnigan MAT 311 A and Finnigan MAT CH 5 DF; EI, 70 eV. – Combustion analyses: Perkin-Elmer 240 and LECO CHNS-932 Analysator. – Thin layer chromatography (TLC): Silica gel (Kieselgel 60) on Al foil (Merck, F 254).

2,2-Dibenzyl-2,3-dihydro-1H-indene-1,3-dione (**14**): Preparation of potassium fluoride/Celite 545[39,59]: A suspension of 58.1 g of celite 545 (Fluka) in 1.0 l of water is added to a solution of 58.1 g (1.00 mol) of potassium fluoride in 500 ml of water, and the mixture is allowed to stand for 1 h with occasional shaking. The major portion of the water is removed in a rotary evaporator at 20 mbar while heating in a water bath at 45–65°C to give a crusty residue. (Careful control of the niveau of the water bath is recommended to avoid complete drying of the material.) The KF/Celite is collected and suspended in 300 ml of acetonitrile, the solvent is removed in a suction funnel, and the residue is washed twice with another 150 ml of acetonitrile. The material is dried by further suction, then finely homogenized in a mortar, and kept in vacuo over phosphorus pentoxide for 3 d. The final yield is 117 g of KF/Celite containing 1.00 mol (ca. 50% w/w) of KF.

To a stirred solution of 14.6 g (100 mmol) of 1,3-indandione (**12**) in 150 ml of freshly distilled acetonitrile is added 51.3 g (300 mmol) of benzyl bromide and then 59.0 g of potassium fluoride/Celite 545 (ca. 0.50 mol of KF), while the color of the mixture turns immediately to deep-red. The suspension is vigorously stirred for 18 h at 75°C (bath temperature) with a magnetic stirrer. The yellow solution is filtered by suction through a sintered glass funnel, and the residue is washed with small amounts of acetonitrile until the yellow color has been removed. The solvent is evaporated to give a light-brown residue which is recrystallized from anhydrous methanol to give **14** as yellowish crystals (29.0 g, 89%); m.p. 157–158°C (158–158.5°C[41]). – IR (KBr): $\tilde{\nu}$ = 3405 cm^{-1} (w, $2\nu_{CO}$), 3065, 3045, 3020, 2940, 2915, 2840, 1740, 1695, 1590, 940, 755, 748, 697. – ^{1}H NMR (300 MHz): AA'BB' spin system δ_A = 7.53 (2H), δ_B = 7.42 (2H), 6.85–6.95 (m, 10H), 3.19 (s, 4H, CH_2). – ^{13}C NMR (300 MHz): δ = 203.4 (s, C=O), 142.7 (s), 135.32 (s), 135.07 (d), 129.9 (d), 128.0 (d), 126.7 (d), 122.3 (d), 62.2 (s, C-2), 41.4 (t). – MS, *m/z* (%): 326 (34) [M$^{\cdot+}$], 235 (100) [M$^{\cdot+}$ – C_7H_7], 207 (6), 178 (9), 91 (90), 77 (8), 76 (7), 65 (12).

trans-2,2-Dibenzyl-2,3-dihydro-1H-indene-1,3-diol (**15**): A suspension of 5.00 g (120 mmol) of $LiAlH_4$ in 250 ml of anhydrous tetrahydrofuran is stirred while a solution of 16.3 g (50 mmol) of **14** in 175 ml of the same solvent is slowly added through a dropping funnel. The mixture is heated to reflux for ca. 4 h, while the reaction is controlled by TLC (silica gel, petroleum ether/ethyl acetate, 3:1). Subsequently, ca. 300 ml of the solvent is distilled off, the reaction mixture is allowed to cool to room temp., then cooled in an ice/water bath, and hydrolyzed by careful addition of ice/water (ca. 20 ml). After addition of saturated aqueous sodium chloride, the suspension is extracted several times with diethyl ether. The combined extracts are dried with Na_2SO_4 and the solvents are carefully evaporated in vacuo (0.05 mbar) to give an oily residue which crystallizes spontaneously on standing. This material represents almost pure **15** (16.3 g, 99%) and may be used in the double cyclodehydration step. Recrystallization from ethanol furnishes **15** as colorless, waxy crystals; m.p. 104–105°C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (br), 3090, 3065, 3040, 2960, 2930, 2870, 1595, 1040, 990, 790, 755, 745, 695. – ^{1}H NMR (300 MHz): δ = 7.21–7.29 (m, 14H), 5.16 [s (80 MHz: d, ^3J = 5.1 Hz), 2H, C*H*OH], two AB spin systems δ_A = 2.86, δ_B = 2.99 (^2J = –13.9 Hz, 4H, CH_2), 1.39 [br s (80 MHz: d, ^3J = 5.0 Hz), 2H, OH]. – ^{13}C NMR (75 MHz): δ = 142.9 (s), 139.0 (s), 130.5 (d), 128.6 (d), 128.3 (d), 126.2 (d), 124.4

(d), 78.7 (d, CHOH), 55.6 (s, C-2), 36.5 (t). – MS, *m/z* (%): 330 (3) [$M^{\cdot+}$], 312 (30) [$M^{\cdot+} - H_2O$], 294 (5) [$M^{\cdot+} - 2\,H_2O$], 239 (37), 238 (58), 221 (83), 203 (12), 193 (13), 178 (12), 165 (8), 161 (11), 147 (92), 143 (24), 135 (18), 131 (13), 118 (15), 115 (28), 105 (12), 92 (26), 91 (100), 77 (19), 65 (17). – $C_{23}H_{22}O_2$ (330.4): calcd. C 83.60, H 6.71; found C 83.71, H 6.72.

2,2-Dibenzyl-2,3-dihydro-3-hydroxy-1H-inden-1-one (**16**): In a hydrogenation apparatus furnished with an all-glass heating mantle ca. 2.0 g of Raney nickel W2 (prepared from 5.0 g of 50% Al-Ni alloy) is added to a solution of 2.00 g (6.1 mmol) of **14** in 60 ml of anhydrous ethanol, and the mixture is shaken at 60–65°C until one equivalent of hydrogen (ca. 150 ml) has been absorbed (2–3 h). The catalyst is carefully removed by filtration, and the solvent is evaporated. The glassy residue is redissolved in toluene to give, upon cooling to –15°C, the ketol **16** (1.35 g, 67%) as colorless, waxy crystals, m.p. 155–156°C. [The reaction rate drops only slightly after absorption of the first equivalent of hydrogen, and prolonged shaking gives 2,2-dibenzylindan-1-one[60] as the major product, as shown by TLC and ^{1}H-NMR analysis.] – IR (KBr) of **16**: $\tilde{\nu}$ = 3440 cm^{-1} (br), 3080, 3040, 2930, 1690, 1605, 1495, 1260, 1070, 940, 755, 745, 700. – ^{1}H NMR (300 MHz): δ = 7.54 (d, ^3J = 7.6 Hz, 1H), 7.40–7.47 (m, 2H), 7.23 (t, $^3J \approx$ 7.4 Hz, 1H), 7.09–7.19 (m, 5H), 6.98–7.09 (m, 5H), 5.16 (s, 1H, C*H*OH), AB spin system δ_A = 2.92, δ_B = 3.22 (^2J = –13.7 Hz, 2H, CH_2), AB spin system δ_A = 2.89, δ_B = 3.08 (^2J = –13.5 Hz, 2H, CH_2), 1.85 (br s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 205.6 (s, C=O), 153.2 (s), 137.7 (s), 136.7 (s), 135.5 (s), 134.9 (d), 130.6 (d), 130.3 (d), 128.8 (d), 128.5 (d), 127.8 (d), 126.54 (d), 126.38 (d), 124.5 (d), 123.0 (d), 73.7 (d, C-3), 61.4 (s, C-2), 40.49 (t), 40.11 (t). – MS, *m/z* (%): 328 (4) [$M^{\cdot+}$], 310 (4) [$M^{\cdot+} - H_2O$]), 237 (100) [$M^{\cdot+} - C_7H_7$], 219 (31) [$M^{\cdot+} - (H_2O, C_7H_7)$], 191 (12), 178 (8), 165 (9), 159 (41), 133 (11), 115 (15), 105 (15), 92 (25), 91 (79), 77 (19), 65 (17). – $C_{23}H_{20}O_2$ (328.4): calcd. C 84.12, H 6.14; found C 84.18, H 6.34.

cis- and trans-2,2-Dibenzyl-1,3-dibromo-2,3-dihydro-1H-indene (**18**): A solution of 5.30 g (20 mmol) of triphenylphosphane in 100 ml of freshly distilled acetonitrile is cooled to 0°C in an ice/water bath and stirred while 3.10 g (20 mmol) of bromine is slowly added through a dropping funnel. The colorless solution should turn to pale yellow upon addition of the last drop of bromine. The cooling bath is removed, a solution of 3.30 g (10 mmol) of **15** in 50 ml of acetonitrile is slowly added, and the mixture is heated to reflux for 40 min. The solvent is evaporated under reduced pressure, and the brown residue is recrystallized from methanol to give **18** (3.5 g, 77%) as colorless crystals; m.p. 130–131°C (mixture of isomers).

trans Isomer **18a**: Several recrystallizations give the *trans*-dibromide **18a**, m.p. 150°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2920, 2855, 1600, 1495, 1455, 1435, 750, 740, 700. – ^{1}H NMR (300 MHz): δ = 7.18 (s, 4H), 7.12–7.16 (m, 6H), 7.03–7.10 (m, 4H), 5.46 (s, 2H, CHBr), AB spin system δ_A = 3.24, δ_B = 3.06 (^2J = –14.2 Hz, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 141.7 (s), 137.3 (s), 130.6 (d), 129.1 (d), 128.1 (d), 126.5 (d), 125.0 (d), 62.0 (d, C-1, C-3), 56.0 (s, C-2), 41.1 (t). – MS, *m/z* (%): 454/456/458 (0.1/0.2/0.1) [$M^{\cdot+}$], 375/377 (0.8/0.8) [$M^{\cdot+}$ – Br], 374/376 (1.0/1.0) [$M^{\cdot+}$ – HBr], 296 (35), 295 (87) [$M^{\cdot+}$ – (Br, HBr)], 294 (15), 206 (24), 205 (81), 204 (36), 203 (50), 202 (36), 178 (13), 128 (15), 91 (100), 80/82 (12/12). – $C_{23}H_{20}Br_2$ (456.3): calcd. C 60.55, H 4.42; found C 61.19, H 4.54.

cis Isomer **18b** (as evaluated from a ca. 1:1 the mixture of the isomers), ^{1}H NMR (300 MHz): δ = 7.55 (m, 2H), 7.00–7.45 (m, 10H), 7.80 (m, 2H), 5.40 (s, 2H, $CHAr_2$), 3.48 (s, 2H, CH_2), 2.70 (s, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 142.2 (s), 138.3 (s), 136.4 (s), 130.49 (d), 130.06 (d), 129.4 (d), 128.39 (d), 128.24 (d), 126.75 (d), 126.38 (d), 125.5 (d), 59.8 (d, C-1, C-3), 54.8 (s, C-2), 42.7 (t), 40.9 (t).

4b,8b,13,14-Tetrahydrodiindeno[1,2-a:2',1'-b]indene (*difuso*-Centrotriindan, **7**)

a) *By Cyclodehydration of* **15**: In a reaction apparatus equipped with a water separator is placed 3.30 g (10.0 mmol) of **15** in 120 ml of xylene (mixture of isomers), then 1.6 g of orthophosphoric acid (85%) is added. The mixture is stirred magnetically and heated to reflux overnight. After cooling to room temp., the mixture is washed with aqueous sodium carbonate and then with water and dried with $MgSO_4$. The solvent is removed in vacuo to give an oily residue which is redissolved in hot ethanol. On cooling **7** is obtained in several fractions as colorless needles (combined yield 2.70 g, 92%); m.p. 148°C. – IR[61] (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3035, 3020, 2935, 2900, 2840, 1475, 1455, 1430, 750, 715, 700. – ^{1}H NMR[61] (300 MHz): δ = 7.35–7.41 (m, 4H), 7.16–7.24 (m, 8H), 4.48 (s, 2H, H-4b, H-8b), two AB spin systems δ_A = 3.19, δ_B = 3.38 (^2J = –16.4 Hz, 4H, CH_2). – ^{13}C NMR (20 MHz): δ = 144.23 (s), 144.06 (s), 142.72 (s), 127.28 (d), 127.00 (d), 126.87 (d), 124.87 (d), 124.65 (d), 124.52 (d), 62.76 (s, 13a-C), 62.14 (d), 44.48 (t). – MS, *m/z* (%): 294 (100) [$M^{\cdot+}$], 293 (18), 291 (5), 289 (7), 279 (15), 278 (8), 277 (7), 276 (7), 217 (21), 216 (18), 215 (22), 203 (43), 202 (24), 178 (16), 115 (8), 91 (13). – UV (*n*-hexane, $c = 3.5 \cdot 10^{-4}$ mol l^{-1}): λ_{max} (nm) = 274.0 (ε = 4540), 267.5 (3840), 261.0 (2310). – $C_{23}H_{18}$ (294.4): calcd. C 93.84, H 6.16; found C 93.73, H 6.27.

b) *By Lewis Acid-Catalyzed Cyclization of* **18**: A suspension of 1.4 g (5.0 mmol) of aluminium tribromide in 70 ml of dry dichloromethane is stirred and cooled to 0°C in an ice/water bath, and a solution of 3.4 g (7.4 mmol) of **18** (mixture of isomers) in 35 ml of dichloromethane is added very slowly to maintain the temp. of the suspension at 0°C. The solution is stirred for 17 h at room temp. and then poured on ice. The two layers are separated, the aqueous layer is extracted with dichloromethane, and the combined organic layers are washed with water, aqueous sodium carbonate, and again with water, and then dried with $MgSO_4$. Evaporation of the solvent gives a yellow oil, which readily crystallizes on standing. Recrystallization from methanol furnishes **7** (1.90 g, 85%) as colorless needles; m.p. 146°C.

trans-1',3'-Dihydro-2,6-diphenylspiro[cyclohexane-1,2'-[2H]indene]-1',3',4-triol (**23**): To a stirred suspension of 8.4 g (220 mmol) of $LiAlH_4$ in 1000 ml of dry tetrahydrofuran is added a solution of 40.0 g (105 mmol) of **22** in 300 ml of the same solvent within 3 h. The mixture is heated to reflux temp. for 10 h with continuous stirring, then allowed to cool, and the major part of the solvent is distilled off and replaced by 300 ml of diethyl ether. The mixture is cooled with ice and water and stirred vigorously, while ice/water (ca. 150 ml) is cautiously added in small portions. The mixture is extracted several times with diethyl ether. The combined organic extracts are dried with Na_2SO_4, and the solvents are evaporated to give a yellowish, oily residue from which a colorless precipitate (34.5–38.5 g, 85–95%) forms upon addition of chloroform. This material may be used for cyclodehydration to **24** (see below). – ^{1}H-NMR analysis (300 MHz, [D_8]THF or [D_5]pyridine, see below) of this material reveals the presence of virtually all of the four possible diastereomeric triols, two of which (**23a** and **23b**) may be isolated as described below. The molar ratio of these triols in the precipitate mixture is [**23a**]/[**23b**] ≈ 1:10. Attempts to fully separate the diastereomers by chromatography on silica gel were unsuccessful. Recrystallization of the mixture from refluxing chloroform followed by two recrystallizations from chloroform/tetrahydrofuran (1:3) gives colorless crystals of a single isomer, m.p. 286–288°C, which represents a minor component (**23a**) of the precipitate de-

scribed above. The mother liquors are redissolved in refluxing ethyl acetate to give, upon cooling, a major isomer (**23b**) as large colorless crystals, m.p. 189–191°C. This material contains ethyl acetate, which may be removed by recrystallization in chloroform to give colorless crystals of m.p. 192–194°C.

23a (m.p. 286–288°C, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 3564 cm^{-1} (s), 3304 (s br), 3155 (br), 3029, 2958, 2909, 1599, 1493, 1451, 1407, 1180, 1120, 1067, 1045 (s), 1012, 791, 767 (s), 744, 700 (s). – ^1H NMR (300 MHz, ^1H-^1H COSY, [D_8]THF): δ = 7.59 (d, ^3J = 7.5 Hz, 2H, *o*-Ph), 7.25–7.30 (m, 4H, *m*-Ph and *o*-Ph′), 7.14 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 7.06 (d, ^3J = 7.4 Hz, 1H, *o*-C_6H_4), 6.90 (t, ^3J = 7.2 Hz, 1H, *m*-C_6H_4), 6.67–6.79 (m, 4H, *m,p*-Ph′ and *m*-C_6H_4), 6.59 (d, ^3J = 7.3 Hz, 1H, *o*-C_6H_4), AB spin system δ_A = 5.49, δ_B = 5.03 (^3J = 6.4 Hz, 2H, CH and OH, respectively, of a benzylic CHOH), AX spin system δ_A = 4.85, δ_B = 2.81 (^3J = 5.9 Hz, 2H, CH and OH, respectively, of a benzylic CHOH), 3.98 [m, $^3J \approx$ 6.5 Hz, 1H, C(4)*H*OH], 3.76 (dd, ^3J = 13.3, ^3J = 3.8 Hz, 1H, CHPh), 3.66 (dd, ^3J = 5.5, ^3J = 2.7 Hz, 1H, CHPh′), 3.43 [d, ^3J = 4.7 Hz, 1H, C(4)HO*H*], 2.90 (quasi-q, $|\,^2J\,| \approx {}^3J$ = 12 Hz, 1H, C*H*H), 2.53 [dt, $|\,^2J\,| \approx {}^3J$ = 12.3, ^3J = 5.5 Hz, 1H, (C*H*H)′], 2.01 [br d, $|\,^2J\,| \approx$ 12.4 Hz, 1H, (CH*H*)′], 1.86 (br m, 1H, C*H*H). – ^1H NMR (300 MHz, [D_5]pyridine): δ = 7.98 (d, ^3J = 7.4 Hz, 2H), 7.92 (d, ^3J = 6.4 Hz, 1H), 7.71 (d, ^3J = 7.0 Hz, 2H), 7.48 (two isochronous t, ^3J = 7.6 Hz, 3H), 7.32 (t, ^3J = 7.2 Hz, 1H), 7.12 (dd, ^3J = 7.2, ^4J = 1.3 Hz, 1H), 6.88–7.03 (m, 5H), 6.18 (d, ^3J = 6.0 Hz, 2H), 5.80 (d, ^3J = 5.9 Hz, 1H), 5.42 (br d, ^3J = 4.5 Hz, 1H), 4.64 [m, 1H, C*H*(4)OH], 4.32 (m_c, 1H, CHPh′), 4.27 (dd, ^3J = 13.5, ^3J = 3.8 Hz, 1H, CHPh), 3.87 (quasi-q, $|\,J\,| \approx$ 12 Hz, 1H, C*H*H), 3.45 [td, $|\,^2J\,| = {}^3J$ = 12.0 Hz, ^3J = 5.4 Hz, 1H, (C*H*H)′], 2.65 [br. d, $^3J \approx$ 12.5 Hz, 1H, (CH*H*′)], 2.50 [br m_c, 1H, CH*H*). – ^{13}C NMR (62.9 MHz, DEPT, [D_8]THF): δ = 147.72 (s), 147.16 (s), 144.50 (s), 144.30 (s), 131.26 (d, 2 C), 130.50 (d, 2 C), 128.68 (d, 2 C), 127.80 (d), 127.44 (d, 2 C), 127.39 (d), 125.98 (d), 125.75 (d), 124.22 (d), 123.28 (d), 85.99 (d, CHOH), 80.33 (d, CHOH), 66.52 [d, C(4)HOH], 58.73 (s, C-1), 51.03 (d, CHPh), 48.03 (d, CHPh), 41.22 (t), 40.78 (t). – MS ($T_{source} \approx$ 220°C), *m/z* (%): 386 (1.5) [$M^{\cdot+}$], 368 (58) [$M^{\cdot+}$ – H_2O], 350 (40) [$M^{\cdot+}$ – 2 H_2O], 332 (28) [$M^{\cdot+}$ – 3 H_2O], 246 (31), 245 (34), 237 (42), 234 (43), 233 (86), 221 (44), 220 (82), 219 (66), 191 (32), 178 (17), 147 (55), 133 (51), 131 (69), 129 (41), 118 (57), 117 (33), 115 (47), 105 (76), 91 (100), 77 (52). – $C_{26}H_{26}O_3$ (386.5): calcd. C 80.80, H 6.78; found C 80.46, H 6.68.

23b (m.p. 192–194°C, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 3580 cm^{-1} (s), 3410 (br. s) 3090, 3061, 3033, 2937 (s), 2852, 1599, 1494, 1451, 1394, 1208, 1180, 1117, 1072 (s), 1013 (s), 756 (s), 700 (s), 643. – ^1H NMR (300 MHz, ^1H-^1H COSY, [D_8]THF): δ = 7.64 (d, ^3J = 7.9 Hz, 2H, *o*-Ph), 7.29 (t, ^3J = 7.7 Hz, 2H, *m*-Ph), 7.17–7.22 (d and m overlapped, $^3J \approx$ 7.0 Hz, 3H, *p*-Ph and *o*-Ph′), 7.14 (m, 1H, *o*-C_6H_4), 6.68–6.77 (m, 5H, *m*-Ph′ and *o,m*-C_6H_4), 6.62 (t, ^3J = 7.1 Hz, 1H, *p*-Ph′), AX spin system δ_A = 5.29, δ_B = 4.11 (^3J = 7.1 Hz, 2H, CH and OH, respectively, of a benzylic CHOH), AX spin system δ_A = 5.03, δ_B = 2.89 (^3J = 5.7 Hz, 2H, CH and OH, respectively, of a benzylic CHOH), 4.29 [m, 1H, C(4)*H*OH], 3.95–4.04 (two overlapping m, 2H, CHPh and CHPh′), 3.61 [d, ^3J = 4.4 Hz, 1H, C(4)HO*H*], 2.24 (quasi-dt, $|\,^2J\,| = {}^3J \approx$ 12 Hz, 1H, C*H*H), 1.94–2.02 (m, 3H, CH*H* and CH_2'). – ^1H NMR (300 MHz, [D_5]Pyridine): δ = 7.82 (d, ^3J = 7.5 Hz, 2H), 7.61 (d, ^3J = 7.6 Hz, 2H), 7.27 (t, ^3J = 7.4 Hz, 2H), ca. 7.22 (m, 1H), 7.18 (t, ^3J = 7.2 Hz, 1H), 7.09 (quasi-t, $^3J \approx$ 4 Hz, 1H), 6.92–6.98 (two overlapping t, $^3J \approx$ 6.5 Hz, 4H), 6.83 (t, ^3J = 7.2 Hz, 1H), 6.1 (very br s, 1H, OH), 5.86 (br s, 1H, OH), 5.66 (d, ^3J = 6.2 Hz, 1H, C*H*OH), 5.41 (d, ^3J = 5.8 Hz, 1H, C*H*OH), 4.83 [mc, 2H, CH(4)OH and OH], 4.55 and 4.53, partially overlapping (mc, 1H, CHPh, and dd, $^3J \approx$ 13, ^3J = 3.2 Hz, 1H, CHPh′), 2.84 (quasi-q, $|\,J\,|$ = 11.2 Hz, 1H, C*H*H), 2.73 (dt, $|\,J\,|$ = 12, ^3J = 5.5 Hz, 1H, CH_2), 2.50 (br t, $|\,J\,|$ = 13.1 Hz, 2H, CH_2). – ^{13}C NMR (75.4 MHz, [D_8]THF): δ = 147.04 (s), 146.55 (s), 144.30 (s), 144.08 (s), 131.79 (d, 2 C), 131.09 (d, 2 C), 128.68 (d, 2 C), 127.95 (d), 127.23 (d, 3 C), 126.63 (d), 125.60 (d), 125.24 (d), 123.16 (d), 80.00 (d, CHOH), 75.68 (d, CHOH), 65.78 [d, C(4)HOH], 57.32 (s, C-1), 46.74 (d, CHPh), 41.17 (d, CHPh), 40.55 (t), 40.33 (t). – MS ($T_{source} \approx$ 220°C), *m/z* (%): 386 (11) [$M^{\cdot+}$], 368 (70) [$M^{\cdot+}$ – H_2O], 350 (56) [$M^{\cdot+}$ – 2 H_2O], 332 (40) [$M^{\cdot+}$ – 3 H_2O], 246 (33), 245 (37), 237 (59), 234 (41), 233 (68), 221 (45), 220 (78), 219 (76), 218 (50), 202 (47), 191 (39), 178 (23), 165 (28), 147 (60), 133 (55), 131 (40), 129 (41), 115 (51), 105 (90), 91 (100), 77 (59). – $C_{26}H_{26}O_3$ (386.5): calcd. C 80.80, H 6.78; found C 80.66, H 6.64.

(4ba,8bβ,12ba,15aβ)-8b,12b,13,14,15,15a-Hexahydro-4bH-dibenzo[2,3:4,5]pentaleno[1,6-jk]fluoren-14-ol (**24**): A suspension of 50.0 g (129 mmol) of **23** in 1200 ml of freshly distilled xylene and 10 ml of orthophosphoric acid (85%) are stirred vigorously and heated to reflux temp. in a reaction vessel equipped with a water separator. The reaction is monitored by TLC (CH_2Cl_2) and by the formation of water, which is complete within 2–3 h. The clear solution is allowed to cool while a major part of the product precipitates as a colorless, fine-crystalline material. The product suspension is decanted carefully from a brownish, viscous residue and filtered by suction, the precipitate is washed with petroleum ether and dried in vacuo. The crude product is recrystallized from tetrahydrofuran or from toluene/ethyl acetate to give **24** as a colorless powder (40.8 g, 90%); m.p. 242°C (dec., from THF) and 240–241°C (dec., from PhMe/EtOAc). – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (br), 3070, 3015, 3010, 2920, 2925, 2880, 2860, 1460, 1050, 765, 760, 755, 745. – ^1H NMR (300 MHz), ^1H-^1H COSY (300 MHz) and ^1H-^{13}C COSY as well as ^1H-^1H NOESY (250 MHz): δ = 7.50 (d, ^3J = 7.2 Hz, 1H), 7.44 (m, 1H), 7.10–7.35 (m, 10H), 4.58 (s, 1H, 4bα-H), 4.24 (s, 1H, 8bβ-H), 3.78 [tt, ^3J = 10.5, ^3J = 3.3 Hz, 1H, 14β-H], 3.55 (dd, ^3J = 3.3, ^3J = 5.9 Hz, 1H, 12bα-H), 3.25 (dd, ^3J = 11.4, ^3J = 6.0 Hz, 1H, 15aβ-H), 2.46 (dq, ^2J = −13.4, $^3J \approx {}^3J \approx {}^4J \approx$ 3.0 Hz, 1H, 13β-H), 2.22 (ddt, ^2J = −12.7, $^3J \approx$ 6.0, $^3J \approx {}^4J$ = 3.0 Hz, 1H, 15β-H), 1.85 (ddd, ^2J = −13.4, ^3J = 10.6, ^3J = 6.1 Hz, 1H, 13α-H), 1.50 (br s, 1H, OH), 1.40 (ddd, $^2J \approx$ −12.7, ^3J = 11.4, ^3J = 10.5 Hz, 1H, 15α-H). The ^1H-^1H NOESY spectrum shows distinct crosspeaks for 4bα-H and 12bα-H as well as for 8bβ-H and 15aβ-H. – ^{13}C NMR (75 MHz): δ = 147.0 (s), 145.8 (s), 144.4 (s), 143.1 (s), 142.6 (d), 142.3 (s), 127.3 (d) and 127.2 (d, overlapping of many lines), 125.4 (d), 125.1 (d), 124.8 (d), 124.5 (d), 124.2 (d), 122.8 (d), 66.7 (d, C-14), 66.3 (s, C-12c ≡ *centro*-C), 61.1 (d, C-8b), 57.2 (d, C-4b), 46.0 (d, C-15a), 43.9 (d, C-12b), 41.1 (t, C-13), 34.8 (t, C-15). The ^{13}C resonances were assigned by ^1H-^{13}C COSY spectrometry and in-resonance measurements. – MS, *m/z* (%): 350 (46) [$M^{\cdot+}$], 332 (100) [$M^{\cdot+}$ – H_2O], 304 (30), 303 (37), 291 (61), 290 (23), 289 (28), 215 (21). – $C_{26}H_{22}O$ (350.5): calcd. C 89.11, H 6.33; found C 88.92, H 6.53.

(4ba,8bβ,12ba,15aβ)-4b,8b,12b,13,15,15a-Hexahydro-14H-dibenzo[2,3:4,5]pentaleno[1,6-jk]fluoren-14-one (**25**)

a) *By Oxidation of* **24**: A suspension of **24** (40.0 g, 114 mmol) in 1000 ml of freshly distilled acetone is added slowly to a stirred solution of chromium trioxide (10.0 g, 100 mmol; 32% excess) in 500 ml of 2 N H_2SO_4. The mixture is stirred at room temp. for 4 h while the color of the liquid phase turns yellow-green. Additional reagent (20–30%) and a longer reaction time may be necessary in some cases, as indicated by TLC (petroleum ether/ethyl acetate, 3:1). The solid phase is filtered by suction, washed several times with water, and dried in vacuo to give crude **25** (38.6 g, 97%), m.p. 279–281°C. Recrystallization from tetrahydrofuran/ethanol gives a sample with m.p. 286°C. – IR[61] (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3040,

3025, 2960, 2900, 1720, 1715, 1600, 760, 740, 640. – ^{1}H NMR[61] (300 MHz): δ = 7.30–7.45 (m, 4H), 7.15–7.30 (m, 8H), 4.57 [s, 2H, 4bα(8bβ)-H], two ABM (A′B′M′) spin systems $\delta_{M(M')} \approx 3.80$, $\delta_{B(B')} = 2.81$, $\delta_{A(A')} = 2.69$ [$^2J_{AB(A'B')} = -13.6$, $^3J_{AM(A'M')} \approx {}^3J_{BM(B'M')} = 7.2$ Hz with additional, intersystem fine coupling $^4J_{AB'} = {}^4J_{A'B} = 1.6$ Hz, 6H, 13(15)-CH_2 and 12bα(15aβ)-CH]. – ^{13}C NMR (75 MHz): δ = 210.5 (s, C=O), 145.2 (s), 143.0 (s), 142.1 (s), 127.7 (d), 127.6 (d), 127.5 (d), 125.4 (d), 124.7 (d), 66.6 (s, C-12c ≡ *centro*-C), 58.8 [d, C-4b(8b)], 48.2 [d, C-12b(15a)], 43.3 [t, C-13(15)]. – MS, *m/z* (%): 348 (100) [M^{+}], 305 (30), 303 (20), 302 (17), 291 (65), 290 (45), 289 (30), 270 (11), 228 (16), 215 (15), 202 (21), 178 (13), 153 (10), 151 (12), 145 (15), 144.5 (15), 138 (11), 91 (8). – $C_{26}H_{20}O$ (348.5): calcd. C 89.62, H 5.79; found C 89.08, H 5.82. – Calcd. 348.1514; found C 384.1512 (MS).

b) *By Cyclodehydration-Hydrolysis of* **29**: To a suspension of 2.00 g (4.67 mmol) of **29** in 120 ml of xylene (mixture of isomers) is added 3.0 ml of orthophosphoric acid (85%), and the mixture is vigorously stirred and heated to reflux temp. for 8 h. (Utilization of a water separator or water trap is not necessary.) The reaction may be monitored by TLC (CH_2Cl_2); formation of the corresponding [5.5.5.6]fenestrane ketal[48] is not observed. Pure ketone **25** crystallizes in part from the reaction mixture upon cooling; therefore, the warm xylene layer is carefully decanted from the inorganic layer and concentrated to dryness under reduced pressure to give a white-yellow crude solid. The inorganic layer is diluted with water and extracted twice diethyl ether, the combined extracts are washed with aqueous hydrogen carbonate and water and dried with Na_2SO_4. The extracts are then added to the residue obtained from the xylene layer, and the solvent is evaporated. The residue obtained is recrystallized from tetrahydrofuran/ethanol (ca. 5:1) to give **25** (1.51 g, 93%); m.p. 285–286°C. – ^{1}H-NMR spectrometry further confirms the identity of the product.

(4bα,8bβ,12bα,15aβ)-4b,8b,12b,15a-Tetrahydro-13H-dibenzo-[2,3:4,5]pentaleno[1,6-jk]fluorene (Tribenzo[5.5.5.6]fenestr-5-ene, **26**)

a) *As a By-Product of the Cyclodehydration of* **23**: Fenestrene **26** is obtained in minor amounts as a by-product of the cyclodehydration of **23** (see above), if the reaction mixture is heated for ≥20 h. The mother liquors obtained after recrystallization of the major product (**24**) are allowed to concentrate slowly during several days to give the olefin **26** as a colorless solid, which is recrystallized from benzene to yield 2.20 g (2.0%, from 50.0 g of **23**); m.p. 196°C. – IR (KBr): $\tilde{\nu}$ = 3081 cm^{-1}, 3060, 3035, 2920, 2892, 2850, 1655, 1583, 1465, 1437, 1243, 1040, 780, 770, 750, 730, 675, 663, 627. – ^{1}H NMR (300 MHz), ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY (250 MHz): δ = 7.42 (d, ^3J = 6.7 Hz, 2H), 7.10–7.30 (m, 10H), 6.13 (br d, ^3J = 10.0 Hz, 1H, 15-H), 5.87 (m with fine coupling, 1H, 14-H), 4.52 (s, 1H, 8bβ-H), 4.37 (s, 1H, 4bα-H), 3.76 (br s, 1H, 15aβ-H), ABM spin system $\delta_M = 3.25$, $\delta_B = 2.53$, $\delta_A = 2.12$ [$^3J_{AM} \approx {}^3J_{BM} = 7.6$, $^2J_{AB} = -18.0$ Hz, 3H, 12bα-H and 13-CH_2, resp.]. The ^{1}H-^{1}H-NOESY spectrum shows distinct crosspeaks for 4bα-H/12bα-H and for 8bβ-H/15aβ-H. – ^{13}C NMR (75 MHz): δ = 148.0 (s), 146.2 (s), 143.82 (s), 143.74 (s), 142.58 (s), 142.51 (s), 127.60 (d), 127.18 (d), 127.13 (d), 126.93 (d), 126.88 (d), 125.47 (d), 124.73 (d), 124.65 (d), 124.24 (d), 124.11 (d), 123.41 (d), 65.6 (s, C-12c ≡ *centro*-C), 60.3 (d, $CHAr_2$), 59.2 (d, $CHAr_2$), 45.3 (d, CHAr), 42.0 (d, CHAr), 29.1 (t, C-13). – MS, *m/z* (%): 332 (100) [M^{+}], 331 (6), 317 (10), 303 (17), 291 (12), 290 (6), 289 (10), 255 (4), 254 (5), 253 (5), 166 (5), 151 (6), 150 (4). – $C_{26}H_{20}$ (332.5): calcd. C 93.94, H 6.06; found C 93.85, H 6.22.

b) *By Dehydration of* **24** *with HMPA:* A mixture of 1.10 g (3.14 mmol) of **24** and 30 ml of freshly distilled hexamethylphosphoric triamide (predried with molecular sieves; caution, HMPA is a cancerogenic agent) is heated to reflux in a liquid-metal bath for 18 h (ca. 240°C). The black reaction mixture is allowed to cool and then diluted with 120 ml of water to give a brown-grey precipitate. The mixture is extracted several times with *n*-hexane/diethyl ether (ca. 10:1), the combined extracts are washed with water and dried with Na_2SO_4. Evaporation of the solvent gives an oil which is redissolved in ethyl acetate/ethanol (ca. 1:1) and then crystallized from benzene to give light-yellow crystals; a further recrystallization yields **26** (0.55 g, 53%) as light-yellow crystals, m.p. 195–197°C. – ^{1}H-NMR spectrometry shows the identity of this material with the product described above.

(4bα,8bβ,12bα,15aβ)-8b,12b,13,14,15,15a-Hexahydro-4bH-dibenzo[2,3:4,5]pentaleno[1,6-jk]fluorene
(Tribenzo[5.5.5.6]fenestrane, **27**)

a) *By Catalytic Hydrogenation of* **26**: To a solution of 1.00 g (3.01 mmol) of **26** in 150 ml of ethyl acetate/tetrahydrofuran (3:2, THF freshly distilled from $LiAlH_4$) is added 200 mg of palladium on charcoal (10%, Merck), and the mixture is shaken with hydrogen (1 bar) at room temp. for ca. 2 d. Filtration of the catalyst and evaporation of the solvent from the filtrate give an oily residue, which is redissolved in ethanol/diethyl ether to yield **27** (0.96 g, 95%) as colorless crystals; m.p. 202°C. – IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1}, 3036, 3021, 2928, 2852, 1473, 1454, 1444, 1021, 772, 755, 694, 643, 621. – ^{1}H NMR (300 MHz): δ = 7.30–7.42 (m, 4H), 7.15–7.25 (m, 8H), 4.38 [s, 2H, 4bα(8bβ)-H], 3.19 [t, $^3J \approx 6.5$ Hz, 2H, 12bα(15aβ)-H], 1.88 (mc, $J \approx 6$ Hz, 2H), 1.74 (mc, $J = 6$ Hz, 2H), 1.46 (mc, $J \approx 6$ Hz, 2H). – ^{13}C NMR (75 MHz): δ = 147.0 (s), 143.7 (s), 143.0 (s), 127.11 (d), 126.92 (d), 126.78 (d), 125.04 (d), 124.60 (d), 123.57 (d), 66.8 (s, C-12c ≡ *centro*-C), 59.3 [d, C-4b(8b)], 45.0 [d, C-12b(15a)], 29.1 [t, C-13(15)], 20.6 (t, C-14). – MS, *m/z* (%): 334 (100) [M^{+}], 291 (18), 289 (12), 256 (14), 215 (16), 202 (13), 144.5 (11), 115 (9), 91 (20). – $C_{26}H_{22}$ (334.5): calcd. C 93.37, H 6.63; found C 93.00, H 6.97. – Calcd. 334.1722; found 334.1722 (MS).

b) *By Wolff-Kishner Reduction of* **25**: A mixture of 1.40 g (4.02 mmol) of **25**, 10 ml of triethylene glycol, 1.0 ml of hydrazine hydrate (100%, 26 mmol), and 1.0 g (18 mmol) of finely powdered potassium hydroxide is placed in a 100-ml flask and stirred and heated in a metal bath to 130°C for 3 h. The temperature is then slowly raised to 240°C, while the volatile components are distilled off, and the mixture is kept at this temp. for a further 3 h until the evolution of nitrogen has ceased. After cooling, the solid residue formed is dissolved with water, the solution acidified with hydrochloric acid (10%) and extracted several times with dichloromethane. The combined extracts are washed with water and dried with Na_2SO_4. The solvent is evaporated to give a white-yellow residue which is recrystallized from diethyl ether/tetrahydrofuran (ca. 4:1) to give **27** (1.10 g, 82%), m.p. 204–205°C. – ^{1}H-NMR spectrometry shows the identity of this material with the product described above.

trans-3′,5′-Diphenyldispiro[1,3-dioxolane-2,1′-cyclohexane-4′,2″-[2H]indene]-1″,3″-dione (**28**): In a reactor equipped with a water separator containing 30 g of freshly dried molecular sieves (4 Å), a solution of 27.0 g (70 mmol) of **22**, 4 ml (70 mmol) of ethylene glycol, and ca. 30 mg of *p*-toluenesulfonic acid in 450 ml of dichloromethane is heated under reflux for 30 h. The solvent is removed in vacuo to give a solid residue which is redissolved in dichloromethane. The solution is washed with aqueous sodium carbonate, then twice with water and dried with $MgSO_4$, and the solvent is evaporated to give **28** (23.5 g, 80%) as colorless powder; m.p. 256–257°C. – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 3037, 2986, 2889,

1736, 1703, 1592, 1494, 1350, 1336, 1249, 1119, 767, 758, 689. – ^{1}H NMR (300 MHz): δ = 7.41–7.48 (sym m [AA'BB'], 4H), 6.92–7.00 (m, 10H), 4.05–4.12 [m, 2H, 4(5)-H], 3.88–3.93 [m, 2H, 4(5)-H], two AMX spin systems δ_X = 3.84, δ_M = 3.11, δ_A = 2.08 [$^3J_{MX}$ = 14.4, $^3J_{AX}$ = 2.3, $^2J_{AM}$ = −14.1 Hz, 6H, C(2')H_2C(3')H and C(6')H_2C(5')H]. – ^{13}C NMR (75 MHz): δ = 203.8 (s, C=O), 142.4 (s), 138.7 (s), 134.9 (d), 128.4 (d), 127.9 (d), 126.8 (d), 122.1 (d), 110.4 (s, C-2), 64.1 [t, C-4(5)], 63.1 (s, C-4' ≡ *centro*-C), 43.3 [d, C-3'(5')], 36.3 [d, C-2'(6')]. – MS, *m/z* (%): 424 (3) [$M^{\cdot+}$], 320 (41) [$M^{\cdot+}$ − C_8H_8], 233 (11), 193 (13), 175 (63), 150 (16), 131 (9), 104 (11), 86 (100), 42 (19). – $C_{28}H_{24}O_4$ (424.5): calcd. C 79.23, H 5.70; found C 79.13, H 5.68.

trans-1'',3''-Dihydro-3',5'-diphenyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',2''-[2H]indene]-1'',3''-diol (**29**): To a suspension of 2.00 g (53 mmol) of $LiAlH_4$ in 100 ml of dry tetrahydrofuran is added a solution of 12.5 g (29.4 mmol) of **28** in 350 ml of the same solvent, and the mixture is heated to reflux for 5 h. It is then allowed to cool, the reaction flask is connected to a distillation apparatus and the major part of the solvent (ca. 350 ml) is distilled off. The residue is diluted with 200 ml of diethyl ether, cooled to room temp. and then carefully hydrolyzed with ice/water. The suspension is extracted with dichloromethane overnight, the extract is dried with $MgSO_4$, and the solvents are evaporated. The resulting yellow oil (ca. 11 g, 87%) readily crystallizes to give a colorless solid containing a mixture of isomers. Repeated recrystallization from chloroform/ethyl acetate (8:1) yields the *trans*-diol **29a** as a colorless solid (6.50 g, 52%); m.p. 176°C. Further crystal fractions obtained (3.70 g, 29%; total yield 81%) are mixtures of isomers which may be used in the cyclodehydration to **25** as well. – IR (KBr) of **29a**: ṽ = 3464 cm^{-1} (br), 3069, 3029, 2984, 2953, 2893, 1601, 1492, 1339, 1272, 1113, 1032, 1008, 939, 826, 760, 749, 700. – ^{1}H NMR (300 MHz); ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY (250 MHz): δ = 7.41 (d, ^3J = 7.6 Hz, 4H; *o*-H^{ph}), 7.01–7.11 (m, 6H, *m,p*-H^{ph}), 6.84–6.98 (AA'BB', 4H, H^{benzo}), 5.28 [d, ^3J = 5.7 Hz, 2H, 1''(3'')-H], 3.94 [br s, 4H, 4(5)-H], two ABX spin systems δ_X = 3.98, δ_B = 2.43, δ_A = 2.13 [$^3J_{BX}$ = 9.5, $^3J_{AX}$ = 4.9, $^2J_{AB}$ = −14.2 Hz, 6H, C(2')H_2C(3')H and C(6')H_2C(5')H], 1.39 (d, ^3J = 5.8 Hz, 2H, OH). The NOESY spectrum shows, inter alia, distinct cross-peaks for the *o*-H^{ph} and the carbinol protons [1''(3'')-H]. – ^{13}C NMR (75 MHz): δ = 142.9 (s), 142.7 (s), 130.4 (d, 2 C), 128.0 (d), 127.6 (d, 2 C), 126.1 (d), 123.4 (d), 109.0 (s, C-2), 77.6 [d, C-1''(3'')], 64.1 [t, C-4(5)], 57.2 (s, C-4' ≡ *centro*-C), 41.5 [d, C-3'(5')], 38.1 [t, C-2'(6')]. – MS, *m/z* (%): 428 (24) [$M^{\cdot+}$], 410 (28), 366 (21), 348 (30), 306 (17), 305 (13), 291 (7), 281 (10), 261 (12), 237 (100), 220 (55), 219 (42), 217 (16), 216 (8), 215 (15), 205 (15), 203 (19), 192 (41), 191 (63), 177 (41), 176 (26), 175 (47), 165 (13), 147 (31), 133 (25), 131 (37), 118 (14), 115 (27), 105 (44), 104 (52), 103 (29), 91 (52), 87 (65), 86 (34), 77 (28). – $C_{28}H_{28}O_4$ (428.5): calcd. C 78.48, H 6.59; found C 77.89, H 6.45.

(4bα,8bβ,12bα,13aβ,15aβ)-13-Bromo-4b,8b,12b,13,15,15a-hexahydro-14H-dibenzo[2,3:4,5]pentaleno[1,6-jk]fluoren-14-one (**30**): To a stirred suspension of 5.00 g (14.4 mmol) of **25** in 160 ml of glacial acetic acid is added a solution of 0.74 ml (14.4 mmol) of bromine in 20 ml of the same solvent. The rate of addition is kept extremely low (ca. 20 s per drop) by using a high-precision dropping funnel. After the addition is completed, stirring is continued overnight, and the mixture is worked up as described above for **31** to give a colorless solid, which is recrystallized from 150 ml of chloroform/ethyl acetate (1:2). The first crop of crystals (1.6 g) consists of mainly **30**, whereas the next two crops (2.4 g) contain predominantly the dibromoketone **31**, as shown by ^{1}H NMR and TLC [petroleum ether/ethyl acetate, 3:1; R_f(**30**) 0.80, R_f(**31**) 0.90]. The first crystal fraction is further purified by gravity column chromatography (silica gel, dichloromethane) to give pure **30** (1.00 g, 16%) as colorless crystals; m.p. 245°C (dec.). – IR (KBr): ṽ = 3447 cm^{-1}, 3071, 3025, 2960, 2882, 2854, 1735, 1470, 1457, 1432, 1159, 762, 753, 637, 629. – ^{1}H NMR (250 MHz): δ = 7.15–7.50 (m, 12H), 4.728 (s, 1H, $CHAr_2$), 4.62 (s, 1H, $CHAr_2$), AB spin system δ_B = 4.271 (partially overlapped and with additional fine coupling $^4J_{13\beta,15\beta}$ = 1.2 Hz) and δ_A = 4.02 (^3J = 7.0 Hz, 2H, 13β-H and 12bα-H), ABC spin system δ_C = 3.82, δ_B = 3.36, δ_A = 2.86 ($^2J_{AB}$ = −13.7, $^3J_{AC}$ = 7.2, $^3J_{BC}$ = 6.7 Hz; 3H, C(15)H_2C(15aβ)H, additional fine coupling $^4J_{15\beta,13\beta}$ = 1.2 Hz). – ^{13}C NMR (75 MHz): δ = 202.0 (s, C=O), 143.9 (s), 142.53 (s), 142.36 (s), 142.05 (s), 141.88 (s), 128.6 (d), 127.97 (d), 127.76 (d), 127.63 (d), 127.28 (d), 125.4 (d), 124.73 (d), 124.55 (d), 123.7 (d), 67.8 (s, C-12c ≡ *centro*-C), 59.8 (d), 58.5 (d), 56.6 (d), 55.4 (d), 47.8 (d, C-15a), 39.2 (t, C-15). – MS, *m/z* (%): 426/428 (51/51) [$M^{\cdot+}$], 348 (78, see remark below), 347 (100) [$M^{\cdot+}$ − Br], 346 (40) [$M^{\cdot+}$ − HBr], 305 (65), 304 (35), 303 (71), 302 (58), 291 (54), 290 (57), 389 (54), 228 (18), 215 (30), 178 (16), 152 (22), 151.5 (18), 151 (35), 150 (18), 145 (23), 144.5 (30), 143.5 (13). The peak at *m/z* 348 (among some others) seems to be due to reductive decomposition of **30** upon heating in the aluminium crucible utilized for sample introduction. – $C_{26}H_{19}BrO$ (427.3): calcd. C 73.08, H 4.48; found C 72.46, H 4.50. – Calcd. 426.0619; found 426.0629 (MS, ^{79}Br).

(4bα,8bβ,12bα,13aβ,15βa,15aβ)-13,15-Dibromo-4b,8b,12b,13,15,15a-hexahydro-14H-dibenzo[2,3:4,5]pentaleno[1,6-jk]fluoren-14-one (**31**): A suspension of **25** (30.0 g, 86.1 mmol) in 950 ml of glacial acetic acid is vigorously stirred at room temp. for 20 min. Then a solution of 9.10 ml (178 mmol) of bromine in 200 ml of the same solvent is added very slowly (5–7 s per drop) through a high-precision dropping funnel. While the solution remains almost colorless, it turns yellow after the addition is completed (ca. 7 h). Stirring is continued overnight (TLC control with petroleum ether/ethyl acetate, 3:1). The mixture is poured on 750 ml of ice/water, the solid component is separated by suction through a sintered glass filter and washed with cold water. Drying in vacuo with potassium hydroxide gives an almost colorless, finely powdered material (43.0 g, 98%), which is recrystallized from chloroform/ethyl acetate (1:2) to yield **31** (37.3 g, 85%) as colorless crystals; m.p. 228°C (dec.). – IR (KBr): ṽ = 3070 cm^{-1}, 3040, 3020, 2900, 1740, 1610, 770, 762, 752, 748, 685, 640, 600. – ^{1}H NMR (300 MHz): δ = 7.20–7.45 (m, 12H), 5.39 [d, ^3J = 6.7 Hz, 2H, 13β(15α)-H], 4.83 [s, 2H, 4bα(8bβ)-H], 4.03 [br d, ^3J = 6.7 Hz, 2H, 12bβ(15aα)-H]. – ^{13}C NMR (75 MHz): δ = 195.6 (s, C=O), 142.09 (s), 142.00 (s), 141.6 (s), 128.9 (d), 127.89 (d), 127.45 (d), 125.50 (d), 125.25 (d), 124.6 (d), 68.7 (s, C-12c ≡ *centro*-C), 59.8 (d), 56.0 (d), 51.4 (d). – MS, *m/z* (%): 504/506/508 (63/100/64) [$M^{\cdot+}$], 425/427 (66/67) [$M^{\cdot+}$ − Br], 346 (61), 345 (82), 318 (44), 317 (62), 316 (36), 315 (53), 313 (34), 305 (64), 304 (47), 303 (78), 302 (71), 289 (48), 178 (30), 158.5–156.5 (cluster, ≤26), 151.5 (20), 151 (36), 82 (13), 80 (13). – $C_{26}H_{18}Br_2O$ (506.2): calcd. C 61.69, H 3.58; found C 62.12, H 3.99. – Calcd. 503.9724; found 503.9726 (MS, $^{79}Br_2$).

(4bα,8bβ,12bα,14aβ)-4b,8b,12b,14a-Tetrahydrodibenzo[a,f]-benzo[2,3]pentaleno[1,6-cd]pentalene-13-carboxylic Acid (**32**): Finely powdered potassium hydroxide (19.0 g, 340 mmol) is suspended in 190 ml of freshly distilled, dry tetrahydrofuran under nitrogen. A solution of 35.0 g (69.1 mmol) of **31** in 650 ml of the same solvent is added within 2 h. Stirring is continued while the mixture is heated to reflux temp. for 15 h (TLC control with petroleum ether/ethyl acetate, 3:1). The mixture is allowed to cool and poured into 1200 ml of water, acidified with 2 N H_2SO_4 and then extracted four times with diethyl ether. The combined extracts are washed with water and dried with $MgSO_4$, and the solvent is evaporated to give a light-brown, powdery residue. Two recrystalliz-

ations from petroleum ether/ethyl acetate (dissolution in hot EtOAc followed by addition of the cosolvent until clouding) furnishes **32** as light-brown powder (17.5–21.3 g, 70–85%). Further purification of a sample by chromatography (silica gel, CH_2Cl_2/EtOAc, 2:1) followed by recrystallization from EtOAc furnishes a colorless crystalline powder, m.p. 295–298°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2600–3500 cm^{-1} (very br), 3080, 3030, 2880, 1725, 1715, 1690, 1685, 1680, 1620, 780, 765, 750, 700, 650. – ^1H NMR (300 MHz), COSY and NOESY (250 MHz): δ = 7.69 (d, ^3J = 7.3 Hz, 1H), 7.53 (m, 4H), 7.27 (m, 8H), 7.14 (t, $^3J_{14,14a}$ = 2.2 Hz, 1H, 14-H), 4.87 (s, 1H, 4b-H), 4.84 (s, 1H, 8b-H), 4.73 (br s, 1H, 12b-H), 4.57 (br s, 1H, 14a-H). The NOESY spectrum shows strong crosspeaks for both 8bβ-H and 14-H with 14aβ-H and a weaker one for 4bα-H and 12bα-H. – ^{13}C NMR (75 MHz): δ = 170.1 (s, CO_2H), 147.4 (d, C-14), 144.09 (s), 143.89 (s), 143.85 (s), 143.58 (s), 142.5 (s), 141.4 (s), 136.8 (s), 128.01 (d), 127.90 (d), 127.74 (d), 127.61 (d), 126.4 (d), 124.92 (d), 124.82 (d), 124.47 (d), 124.40 (d), 70.5 (s, C-12c ≡ *centro*-C), 63.9 (d), 62.82 (d), 62.40 (d), 62.29 (d). – MS, *m/z* (%): 362 (100) [$M^{\cdot+}$], 361 (4), 344 (7), 317 (81), 316 (25), 315 (33), 313 (17), 302 (18), 289 (14), 239 (14). – $C_{26}H_{18}O_2$ (362.4): calcd. C 86.17, H 5.01; found C 86.15, H 5.26. – Calcd. 362.1307; found 362.1306 (MS).

(4baα,8bβ,12baα,14aβ)-4b,8b,12b,14a-Tetrahydrodibenzo[a,f]benzo[2,3]pentaleno[1,6-cd]pentalene (Tribenzo[5.5.5.5]fenestr-11-ene, **33**): To a solution of 15.0 g (41.4 mmol) of **32** in 600 ml of freshly distilled quinoline is added 70 g of finely powdered copper (cuprum purum per electrolysi, Merck), and the mixture is stirred vigorously and heated to 200°C (inner temp.) under nitrogen. The reaction is controlled by TLC (sample workup with HCl/diethyl ether; eluent petroleum ether/ethyl acetate, 5:1) and is complete within 8–10 h. If necessary, further catalyst (e.g. 15 g) is added and heating is continued. After cooling, the solvent is removed as far as possible in a rotary evaporator under reduced pressure, the residue is diluted with water and aqueous hydrogen chloride and extracted with chloroform. The organic extract is washed with diluted aqueous hydrogen chloride and with water, then dried with Na_2SO_4. The solvent is evaporated to give a foamy residue (ca. 12 g, 90%). Careful kugelrohr distillation of this material yields a major fraction (250°C, 0.1 mbar) as an orange, glassy oil (7.2–8.7 g, 55–66%), which is redissolved in ethanol/acetone (1:1) to give **33** (6.3–7.0 g, 48–52%); m.p. 185–190°C. Further purification of the product is achieved by flash chromatography (kieselgel 60, petroleum ether/dichloromethane) yielding 4.4–5.0 g (33–38%) of pure **33**; m.p. 192°C (ethanol/acetone). – IR[61] (KBr): $\tilde{\nu}$ = 3075 cm^{-1}, 3050, 3025, 3005, 2880, 2875, 1585, 1480, 765, 760, 750, 730, 720, 645. – ^1H NMR[61] (300 MHz): δ = 7.53 (m, 4H), 7.25 (m, 8H), 6.00 [s, 2H, 13(14)-H], 4.82 [s, 2H, 4bα(8bβ)-H], 4.42 [s, 2H, 12bα(14aβ)-H]. – ^{13}C NMR (75 MHz): δ = 144.21 (s, 2 C), 144.04 (s, 4 C), 132.4 (d), 127.54 (d), 127.46 (d), 127.37 (d), 124.67 (d), 124.44 (d), 69.9 (s, C-12c ≡ *centro*-C), 64.9 (d), 62.8 (d). – MS, *m/z* (%): 318 (100) [$M^{\cdot+}$], 317 (33), 316 (9), 315 (21), 314 (6), 313 (15), 303 (54), 302 (28), 289 (19), 276 (6), 241 (13), 239 (16), 159 (9) [M^{2+}], 157.5 (9), 156.6 (13), 151 (28), 145 (13). – $C_{25}H_{18}$ (318.4): calcd. C 94.30, H 5.70; found C 94.23, H 5.96.

(4aα,4baα,8bβ,12baα,16bβ,16caα)-1,2,3,4-Tetrachloro-4a,4b,8b,12b,16b,16c-hexahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene (**34**): A mixture of 3.50 g (11.0 mmol) of pure **33** (m.p. 190–192°C), tetrachlorothiophene *S,S*-dioxide[52] (2.90 g, 11.4 mmol), and 5 ml of dry toluene is stirred and heated to 120°C (bath temp.) to give a clear solution. If the mixture solidifies after 1–2 h, a few ml of toluene is added to maintain a homogeneous medium. After heating for a total of 24 h (TLC control with petroleum ether/dichloromethane, 4:1), the solvent is evaporated, and the solid residue is recrystallized from ethyl acetate (ca. 40 ml) to give **34** (5.11 g, 91%) as a colorless, crystalline powder; m.p. 223–224°C. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3040, 3025, 2900, 2870, 1610, 820, 775, 765, 755. – ^1H NMR (300 MHz): δ = 7.45–7.60 (m, 4H), 7.15–7.40 (m, 7H), 7.06 (d, ^3J = 7.6 Hz, 1H), 4.80 (s, 1H, 12bα-H), 4.77 (s, 1H, 8bβ-H), 4.49 (s, 1H, 16bβ-H), 4.03 (d, $^3J_{4b\alpha,4a\alpha}$ = 9.1 Hz, 1H, 4bα-H), 3.71 (dd, $^3J_{16c\alpha,4a\alpha}$ = 10.3, $^3J_{16c\alpha,16b\beta}$ = 1.7 Hz, 1H, 16cα-H), 3.55 (dd, $^3J_{4a\alpha,16c\alpha}$ = 10.3, $^3J_{4a\alpha,4b\alpha}$ = 9.2 Hz, 1H, 4aα-H). The NOESY spectrum shows distinct crosspeaks for 4bα-H and 12bα-H as well as for 8bβ-H and 16bβ-H. – ^{13}C NMR (75 MHz): δ = 144.19 (s), 143.83 (s), 143.62 (s), 143.42 (s), 143.22 (s), 140.9 (s), 132.4 (s), 129.9 (s), 128.26 (d), 128.09 (d, 2 C), 127.78 (d), 127.70 (d), 127.32 (d), 125.01 (d), 124.66 (d, 2 C), 124.37 (d, >2 C), 70.5 (s, 16d-C), 63.9 (d), 62.6 (d), 62.0 (d, 2 C), 52.0 (d), 50.9 (d). – MS, *m/z* (%): 506/508/510/512 (6/8/4/1) [$M^{\cdot+}$], 471/473/475/477 (73/71/33/5) [$M^{\cdot+}$ – HCl], 470 and higher corresponding isotopomers (7), 435 (cluster, 3), 393 (cluster, 3), 363 (4), 292 (100) [$M^{\cdot+}$ – $C_6H_2Cl_4$], 291 (70), 290 (32), 289 (45), 276 (14), 215 (11), 146.0 (12) [M^{2+} – $C_6H_2Cl_4$]). – $C_{29}H_{18}Cl_4$ (508.3): calcd. C 68.53, H 3.57; found C 68.58, H 3.63.

(4baα,8bβ,12baα,14aβ)-4b,8b,12b,13,14,14a-Hexahydrodibenzo[a,f]benzo[2,3]pentaleno[1,6-cd]pentalene (Tribenzo[5.5.5.5]fenestrane, **35**): To a solution of 4.00 g (12.6 mmol) of **33** in 400 ml of ethyl acetate and dried ethanol (1:1) is added 500 mg of palladium/charcoal (10%, Merck), and the suspension is shaken with hydrogen in a Parr hydrogenation apparatus at 3.9 bar and room temp. for 60 h. The catalyst is removed by filtration and the solvent evaporated from the filtrate to give a colorless residue of crude **35** (TLC dichloromethane/*n*-hexane). Recrystallization from ethanol yields pure **35** (2.90 g, 73%) as colorless crystals; m.p. 173–175°C. – IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1}, 3023, 2963, 2934, 2884, 2853, 1476, 1453, 1443, 1022, 752, 728, 642, 614. – ^1H NMR (300 MHz): δ = 7.44 (m, 4H), 7.15–7.22 (m, 8H), 4.68 (s, 2H, $CHAr_2$), 3.68 (dd, $^3J \approx$ 8.0 Hz, 2H, CHAr), 2.44 (m, 2H), 1.63 (m, 2H). – ^{13}C NMR (75 MHz): δ = 146.8 (s), 144.6 (s), 144.1 (s), 127.26 (d), 127.17 (d), 127.09 (d), 124.47 (d), 124.34 (d), 73.4 (s, C-12c ≡ *centro*-C), 62.0 (d), 57.5 (d), 37.3 [t, C-13(14)]. – MS, *m/z* (%): 320 (100) [$M^{\cdot+}$], 319 (18), 292 (80), 291 (25), 290 (11), 289 (18), 279 (13), 276 (7), 229 (6), 228 (7), 215 (15), 202 (8), 144.6 (12), 145.0 (10). – $C_{25}H_{20}$ (320.4): calcd. C 93.71, H 6.29; found C 93.55, H 6.38.

(4baα,8bβ,12baα,16bβ)-1,2,3,4-Tetrachloro-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene (1,2,3,4-Tetrachlorofenestrindan, **36**): A mixture of 0.26 g (1.10 mmol) of 2,3,5,6-tetrachloro-*p*-benzoquinone, 0.41 g (8.1 μmol) of **34**, and 6 ml of xylene is heated to reflux temp. for 8 h. The darkened, homogeneous solution is allowed to cool, and the solvent is removed in vacuo. The residue is redissolved in dichloromethane and the solution washed with aqueous sodium hydroxide (10%) and water, then dried with Na_2SO_4. Evaporation of the solvent leaves a solid mixture which is recrystallized from acetone/ethanol. The first crystal fraction (60 mg, 15%) represents crude **36** as a light-brownish powder, whereas the remaining fractions contain mainly the starting material [various TLC runs show that R_f(**34**) ≈ R_f(**36**)]. The product fraction is recrystallized from dichloromethane/*n*-hexane (1:1) to give **36** as colorless, microcrystalline solid, m.p. 307–309°C. – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3039, 3020, 2928, 2888, 1600, 1470, 1458, 1370, 1287, 1231, 1225, 1146, 780, 760, 747, 738, 730, 663, 637. – ^1H NMR (300 MHz): δ = 7.85 (d, ^3J = 7.5 Hz, 2H), 7.50 (two d, overlapped, $^3J \approx$ 7 Hz, 4H), 7.22–7.33 (m, 6H), 5.12 (s, 2H, $CHAr_2$), 4.81 (s, 2H, $CHAr_2$). – ^{13}C NMR (250 MHz, DEPT, CD_2Cl_2): δ = 144.9 (s), 143.8 (s),

142.0 (s), 132.5 (s), 130.1 (s), 128.78 (d), 128.26 (d), 127.92 (d), 127.82 (d), 125.18 (d), 125.15 (d), 73.0 (s, C-16d ≡ *centro*-C), 61.8 [d, C-4b(16b)], 60.6 [d, C-8b(12b)]. – MS, *m/z* (%): 504/506/508/510/512 (77/100/51/12/1) [$M^{\cdot+}$], 469/471/473/475 (11/10/4/1) [$M^{\cdot+}$ – Cl], 426–236 (Cluster, 3–10), 391–401 (Cluster, 2–9), 357–364 (Cluster, 2–10), 252 (5), 198.6 (10), 182 (11), 181.5 (19), 181.1 (12), 180.6 (22), 180.0 (6), 179.6 (12). – $C_{29}H_{16}Cl_4$ (506.3): calcd. C 68.80, H 3.19; found C 68.02, H 3.40. – Calcd. 504.0006; found 503.9975 (MS, $^{35}Cl_4$).

(4bα,8bβ,12bα,16bβ)-1,2,4-Trichloro-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene (1,2,4-Trichlorofenestrindan, **37**). To a solution of 0.35 g (690 μmol) of **34** in 5.0 ml of dry tetrahydrofuran is added a solution of 0.63 g (11 mmol) of potassium hydroxide in anhydrous ethanol, and the homogeneous mixture is stirred and heated to reflux temp. A precipitate forms upon warming, and heating is continued for 2 h. The mixture is allowed to cool, and the solvent is evaporated in vacuo. After the addition of water to the residue and acidification with diluted hydrochloric acid, the mixture is extracted several times with dichloromethane, the combined extracts are washed with water and dried with Na_2SO_4. The solvent is removed leaving a white-yellow solid (0.32 g, 98%) which is recrystallized from xylene to give **37** (0.25 g, 77%) as colorless crystals; m.p. 294–295°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1}, 3035, 2878, 1474, 1454, 1420, 1179, 1140, 1118, 1026, 937, 867, 807, 766, 748, 732, 668, 659, 624, 614, 607. – ^1H NMR (250 MHz): δ = 7.86 [d, ^3J = 7.6 Hz, 2H, 5(16)-H], 7.46–7.53 [m, 4H, 8(9,12,13)-H], 7.41 (s, 1H, 3-H), 7.22–7.31 (m, 6H), 5.12 (s, 1H, CH_2Ar), 5.06 (s, 1H, CH_2Ar), 4.82 (s, 2H, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 145.8 (s), 144.3 (s, 2 C), 143.3 (s, 2 C), 142.3 (s), 141.95 (s), 141.81 (s), 132.6 (s), 130.1 (d), 129.9 (s), 128.5 (s), 128.27 (d), 128.21 (d), 127.81 (d, 2 C), 127.64 (d), 127.43 (d), 127.36 (d, 2 C), 124.79 (d, 2 C), 124.65 (d, 2 C), 72.8 (s, C-16d), 61.3 (d), 60.5 (d), 60.2 (d, 2 C). – MS, *m/z* (%): 470/472/474/476 (100/96/40/5) [$M^{\cdot+}$], 469 and corresponding higher isotopomers (15) [$M^{\cdot+}$ – H], 435/437/439 (13/8/1) [$M^{\cdot+}$ – Cl], 433 (6), 431 (3), 400/402 (10/3) [$M^{\cdot+}$ – 2 Cl], 399/401 (12/5) [$M^{\cdot+}$ – (Cl, HCl)], 397 (8), 395 (6), 393 (7), 365 (10), 364 (9), 363 (17), 361 (9), 359 (10), 357 (12), 323/325 (7/2), 289 (4), 287 (3), 234/235/236 (4/6/3) [M^{2+}], 182.5 (9), 182 (17), 181.5 (23), 181 (10), 180.5 (20), 179.5 (13), 178.5 (9), 145 (9) [$C_{23}H_{14}^{2+}$]. – $C_{29}H_{17}Cl_3$ (471.8): calcd. C 73.83, H 3.63; found C 73.67, H 3.63.

(4bα,8bβ,12bα,16bβ)-4b,8b,12b,16b-Tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene (Fenestrindan, **8**): A mixture of 215 ml of dry tetrahydrofuran and 31 ml of *tert*-butyl alcohol is heated to reflux under nitrogen. Sodium (8.6 g, 370 mmol) is added in small pieces to the vigorously stirred solution, followed by 4.00 g (7.90 mmol) of **34**. Heating is continued for 16 h under TLC control (petroleum ether/CH_2Cl_2). After cooling to room temp., the solution is decanted from excess sodium, diluted with water and acidified with 2 N H_2SO_4. After repeated extraction with diethyl ether/THF (ca. 2:1), the combined extracts are dried with Na_2SO_4, heated with some charcoal and filtered through a pad of silica gel. The product crystallizes from the hot solution upon concentration and is then recrystallized from toluene/ethanol to give **8** (2.38 g, 82%) as colorless crystals, m.p. 325–330°C (erroneous melting range given in ref.[26]). – IR[61] (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3035, 3018, 2925, 2895, 1602, 1583, 1478, 1475, 763, 760, 754, 730, 655, 615. – ^1H NMR[61] (300 MHz): AA'BB' spin system δ_A = 7.53, δ_B = 7.27 (16H), 4.89 [s, 4H, 4bα(8bβ,12bα,16bβ)-H]. – ^{13}C NMR (75 MHz): δ = 144.1 (s), 127.6 (d), 124.6 (d), 71.9 (s, C-16d ≡ *centro*-C), 62.2 [d, C-4b(8b,12b,16b)]. – MS, *m/z* (%): 368 (100) [$M^{\cdot+}$], 367 (46), 291 (33), 290 (25), 289 (36), 145 (31) [M^{2+} – C_6H_6]. – UV (*n*-heptane, $c = 2.5 \cdot 10^{-5}$ mol l^{-1}): λ_{max} (nm) = 273.5 (ε = 5000), 267.0 (4130), 261.5 (2380). – $C_{29}H_{20}$ (368.5): calcd. C 94.53, H 5.47; found C 94.53, H 5.52.

☆ Dedicated to Professor *Eckehard V. Dehmlow* on the occasion of his 60th birthday.

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