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Naphtho-anellated [5.6.5]- and [6.5.5.5]Fenestranes†

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Abstract: The synthesis of several naphtho-anellated fenestrane derivatives **16** and **20-26** is described for the first time. Among these, a "broken" dibenzo,(naphtho-*d,e*)[5.6.5]fenestrane, **9**, and two isomeric benzo,di(naphtho-*a*)[6.5.5.5]fenestrane ketones, **23** and **24**, were obtained in good yields by using the two-fold cyclodehydration route via the corresponding (spiro-) 1,3-indandiols. Attempts to prepare fenestranes that contain more than one six-membered ring failed.

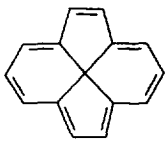
Introduction

The synthetic access to fenestrane chemistry[1-4] has gained a new dimension by using benzoanellated synthons as starting materials. As shown in several recent papers from one of these laboratories,[5-7] [6.5.5.5]- and [5.5.5.5]fenestranes bearing three or four benzo nuclei fused at the [m.n.o.p]fenestrane core are easily synthesized by using the two-fold cyclodehydration of 1,3-indanediols as a key step.[8] Ring fusion in [5.5.5.5]fenestranes is particularly favourable because of the almost perfect steric fit of four pairwise all-*cis* anellated cyclopentane or cyclopentene rings; in contrast, the presence of six-membered rings in the fenestrane skeleton appears less straightforward and increases the strain of the polycyclic framework. Several reports[9-11] point to considerable difficulties in synthesizing fenestrane cores which bear more than one six-membered ring.

On the other hand, [6.6.5.5]- and [6.5.6.5]fenestranes (e.g. **1** and **2**) have been suggested as model compounds for testing the hypothesis of planar tetracoordinate carbon raised by R. Hoffmann et al. in 1970.[12] Therefore, it appeared interesting to explore an access to the field of areno-anellated [m.n.o.p]-fenestranes containing more than one six-membered ring. To give only one challenging example, we have envisaged a hypothetical derivative of **1**, the highly interesting, strained target **3**, bearing a closed periphery of two annulene π electron systems around a central tetracoordinate carbon atom.[13]

This paper reports on our first steps in this field, which have been obtained on the basis of our experience in the construction of benzoanellated centropolyquinanes. It demonstrates that, in fact, severe limitations are encountered on way to arene-anellated fenestrane cores with more than one six-membered ring. In the same time, it represents an expansion of the synthesis of fenestranes containing fused arene nuclei. Thus, by applying our two-fold cyclodehydration strategy,[8] several naphtho-anellated [5.6.5]- and [6.5.5.5]fenestranes have been prepared for the first time.

†Dedicated to Professor Hans Brockmann on the occasion of his 60th birthday.



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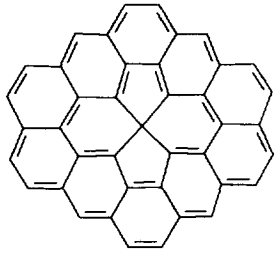

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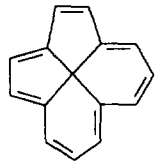

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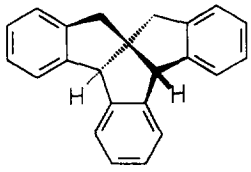

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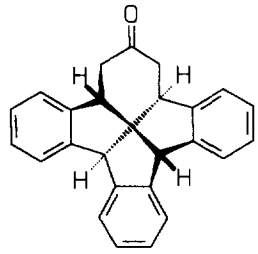

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RESULTS AND DISCUSSION

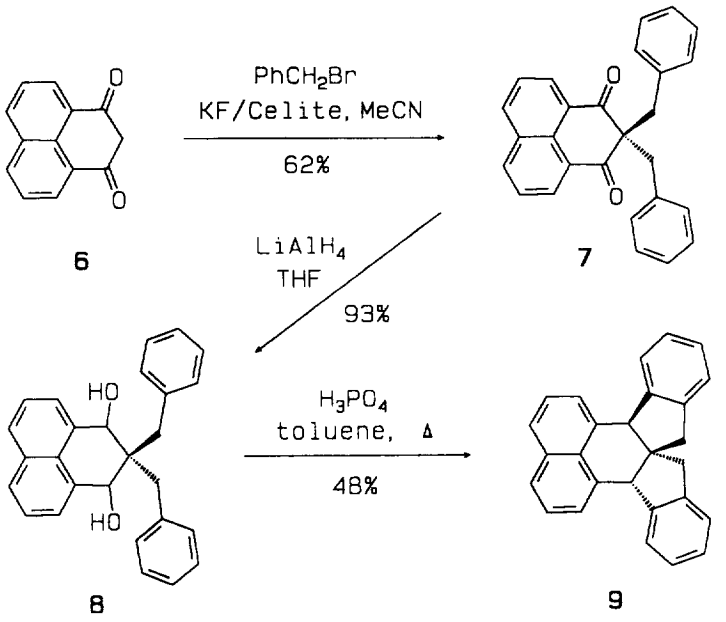
A Naphthoanellated [5.6.5]Fenestrane

1,3-Indanedione and 2-substituted derivatives have been used as starting materials in the syntheses of centrotriindanes such as **4** and **5**. In analogy, we subjected 2,3-dihydrophenalene-1,3-dione (**6**) to two-fold alkylation at C-2 by reacting it with benzyl bromide (Scheme 1) and with dibenzylideneacetone (Scheme 2). Only the first approach worked successfully. Two-fold benzylation of **6** using potassium fluoride on Celite furnished the dihydrophenalenedione **7** in good yield. Subsequent reduction with lithium aluminium hydride gave diol **8**, which was subjected to two-fold cyclodehydration with ortho-phosphoric acid in toluene at reflux temperature. In this way, 1,1'-(1,8-naphthylene)-2,2'-spirobiindane **9** was obtained in moderate yield. The efficiency of this cyclodehydration is significantly lower than that of the cyclodehydration of 2,2-dibenzyl-1,3-indandiol[5a,8b] which may be traced to the less favourable fusion of two indane units to the strained naphtho-anellated cyclohexane ring in **9** as compared to the central benzoanellated cyclopentane ring in **4** and **5**.[14]

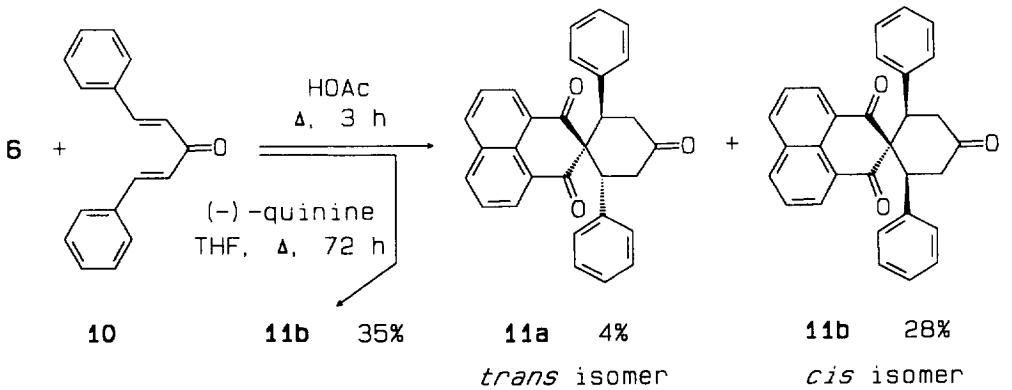
The structural identity of the broken [5.6.5]fenestrane **9** followed unequivocally from mass spectrometry and ^{1}H- and ^{13}C-NMR spectrometry. Of particular significance is the two-fold degeneracy of all ^{1}H resonances and most of the ^{13}C lines owing to the (apparent) C_2 molecular symmetry of **9** in solution, again in analogy to **4**.

Encouraged by these results, we tried to construct the corresponding (complete) [6.5.6.5]fenestrane framework (as suggested by **1** and **3**), again referring to previous results leading to the [6.5.5.5] analog **5**.[5,6] In this case, however, the first step of the synthetic sequence turned out to be blocked. In contrast 1,3-indandione (**12**), the two-fold Michael addition of 2,3-dihydrophenalenedione (**6**) to dibenzylideneacetone (**10**) led to exclusive or by far dominant formation of the *cis*-diphenyl stereoisomer **11b** instead of the desired *trans*-diphenyl compound **11a**. Use of tetrahydrofuran as the solvent and (−)-quinine as the catalyst[15] gave a very sluggish and incomplete reaction of the starting materials and,

eventually, pure *cis*-diphenylspirotriketone **11b** was isolated in 35 % yield by column chromatography. Running the reaction in acetic acid (i.e. under kinetic control leading to the corresponding *trans* isomer in the 1,3-indandione series[15]), a mixture of **11a** and **11b** was isolated in 32 % combined yield ([**11a**] : [**11b**] = 1 : 8, 48 % yield based on converted **6**).[16]



Scheme 1.



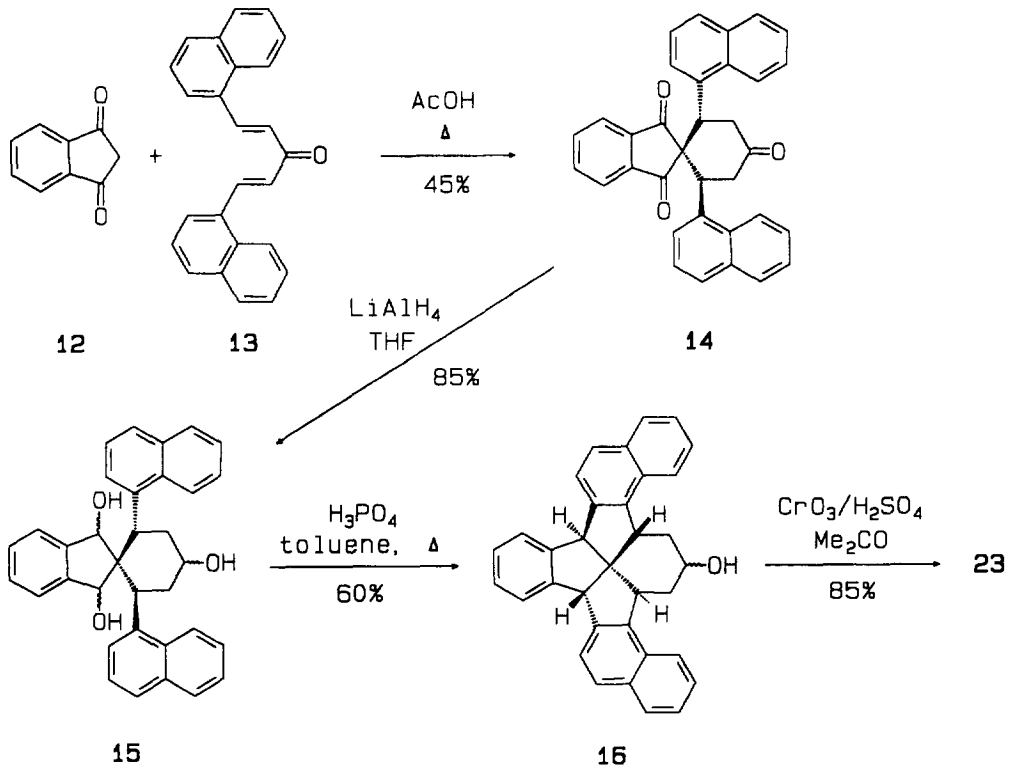
Scheme 2.

These results point to the fact the *trans* orientation of the two phenyl groups at [5.5]spiroundecane skeleton is much less favourable than in the [4.5]spirodecane series (cf. **5**). Since the *trans* orientation of the phenyl groups appears to be an important prerequisite for the formation of the [6.5.5.5]fenestrane framework, at least in the present case,[17] the construction of areno-anellated [6.5.6.5]fenestranes using the two-fold cyclodehydration strategy turned out to be disfavoured so far.

Dinaphtho-anellated [6.5.5.5]Fenestranes

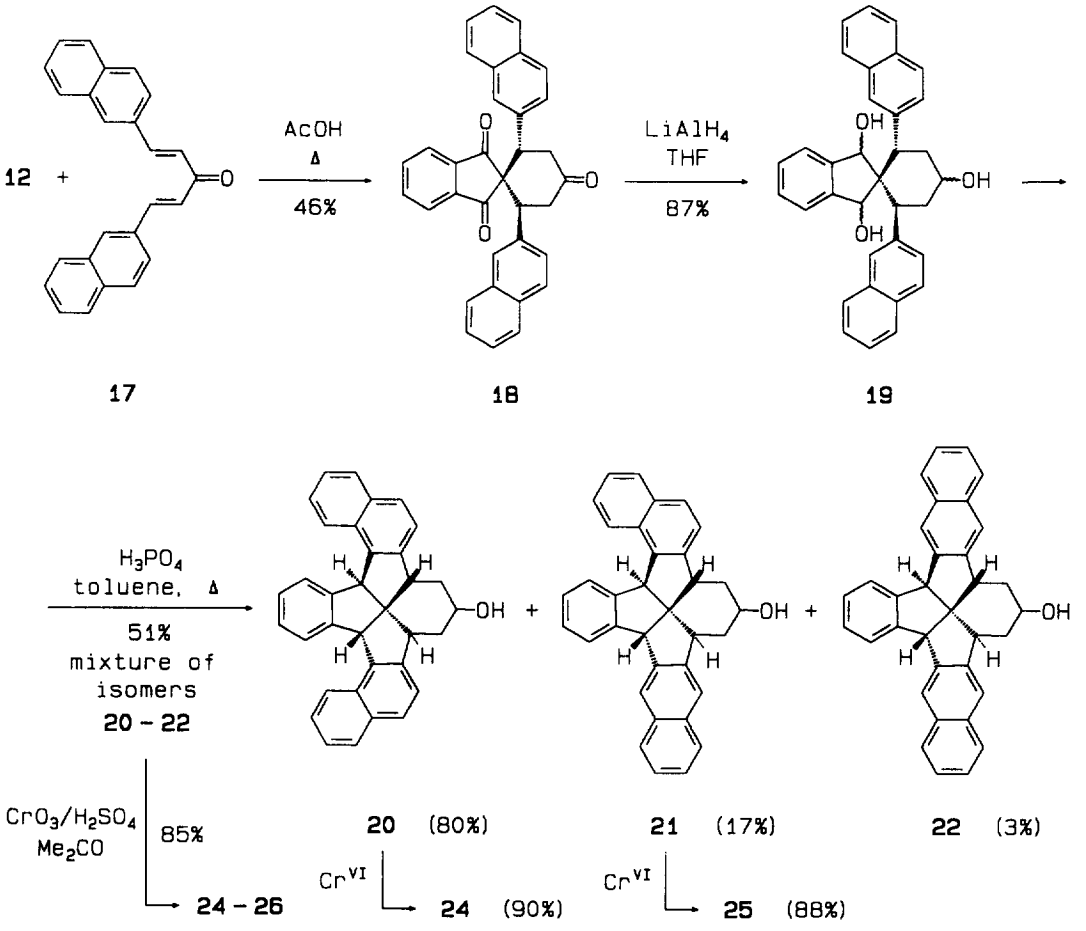
In a related series of experiments, we studied the synthesis of bis(naphtho)-anellated [6.5.5.5]-fenestrane ketones. Instead of dibenzylideneacetone, we started from di(α- and β-naphthylvinyl)ketones (**13** and **17**, respectively), which were subjected to two-fold Michael addition with 1,3-indandione (**12**) in this case. It appeared doubtful, of course, whether an α-naphthyl group would undergo cyclodehydration at the *peri* (C-8) position, thus giving rise to the formation of another six-membered ring. However, we deemed this series worth trying to screen the field more broadly and to check the accessibility of some other interesting naphtho-anellated [6.5.5.5]fenestranes, in addition to that of the (broken) [5.6.5]fenestrane **9**.

In contrast to dihydrophenalenedione (**6**), 1,3-indandione (**12**) readily underwent the two-fold Michael addition to give the *trans*-dinaphthylspirotriketones **14** and **18**, respectively (Schemes 3 and 4). Using the reaction under standard conditions (i.e. in acetic acid), yields were moderate (ca. 45 % in both cases) and fell short slightly of those obtained with dibenzylideneacetone (ca. 65 %).[15] Thus, steric repulsion between the bulky groups in the vicinity of the spiro center appears to be negligible here. The *trans*-stereochemistry (and hence C_2 molecular symmetry) of **14** and **18** is clearly reflected from their NMR spectra and confirmed by their further conversion. Reduction of the triones with lithium aluminiumhydride in tetrahydrofuran led to the corresponding *trans*-di(α-naphthyl)- and di(β-naphthyl)-spiro[4.5]decanetriols **15** and **19**, which were isolated in good yields (ca. 85 % in both cases) as mixtures of stereoisomeric triols, as shown by ^{1}H NMR spectrometry.



Scheme 3.

Finally, the spirotriols were subjected to cyclodehydration, again under standard conditions (H_3PO_4/toluene at reflux temperature). As expected, the di(α-naphthyl) triol **15** gave rise to only one product, viz. the all-*cis*-benzodi(naphtho-*a*)-[6.5.5.5]fenestrane alcohol **16** in good yield (60 %) after recrystallization. The identity of **16** was fully supported by spectrometry. The NMR spectra, in particular, exhibit the lack of molecular symmetry of these fenestranes due to the presence of the hydroxy function at C-4 (see Experimental). Oxidation of **16** with chromium(VI) oxide in acetic acid/acetone gave the corresponding [6.5.5.5]fenestrane ketone **23** which was isolated in 85 % yield. Owing to oxidation, the molecular C_2 symmetry was re-established in **23** and clearly reflected from the ^{1}H- and ^{13}C-NMR spectra. In the ^{1}H-NMR spectrum, for example, two equivalent ABC spin systems and a two-proton singlet were attributed to the cyclohexanone ring and the benzhydrylic methine bridgeheads of **23**, respectively. Thus, the all-*cis* fusion of the four rings in the [6.5.5.5]-fenestrane core of **23** was clearly confirmed.

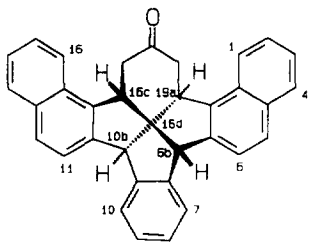


Scheme 4.

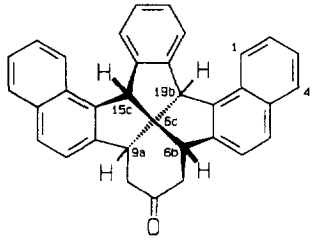
Two-fold cyclodehydration of the di(β-naphthyl)spiro[4.5]decanetriols **19** produced a mixture of the three possible benzodinaphtho[6.5.5.5]fenestranols **20**, **21** and **22**, which was obtained in (combined)

51 % yield after recrystallization. The isomers were separated by medium pressure liquid chromatography (MPLC) and characterized by mass and NMR spectrometry; their structural identity was established indirectly, i.e. after oxidation to the corresponding ketones **24**–**26** (vide infra). MPLC furnished the di(naphtho-*a*) isomer **20** as the major component (80 %), the "mixed" (naphtho-*a*)-(naphtho-*b*) isomer **21** as a minor one (17 %) and the remaining, di(naphtho-*b*) isomer **22** as the by far inferior product (3 %). The data correspond to a regioselectivity $[k_\alpha : k_\gamma] \approx 9 : 1$ in favour of the electrophilic attack at the α position of the β-naphthyl groups of **19** (assuming identical rates k_α for every attack at C^α and, likeweise, identical rates k_γ for every attack at C^γ. No products of *peri* attack were found.

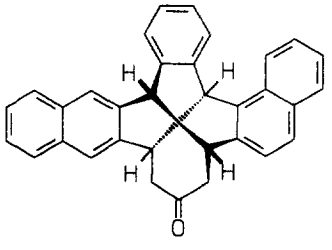
Oxidation of the three [6.5.5.5]fenestranols **20**–**22** with chromium(IV) oxide in acetic acid/acetone furnished the corresponding [6.5.5.5]fenestranones **24**–**26**. The two major alcohols, **20** and **21**, were oxidized separately to give the ketones **24** and **25** in 90 and 88 % yield, respectively, whereas alcohol **22** was oxidized in the mixture of **20**–**22**; the corresponding fenestranone **26** was identified by ^{1}H-NMR spectrometry of the ketone mixture by substracting the signals of the major isomers.



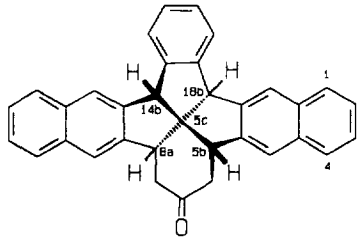
23 (C_2)



24 (C_2)



25 (C_1)



26 (C_2)

NMR Spectroscopy of the Dinaphtho-anellated [6.5.5.5]Fenestranones

Comparison of the ^{1}H NMR spectra of the four isomeric benzodinaphtho[6.5.5.5]fenestrane ketones **23**–**26** is noteworthy since it shows the magnetic deshielding effect of the extended naphtho-*a* nucleus in a systematic way (Table 1). For example, as compared to the tribenzo[6.5.5.5]fenestrane ketone **5**,[5] the benzhydryl protons are strongly deshielded if the pending benzo ring of each of the naphtho-*a* units point towards the benzhydryl bridgehead positions (cf. **24**, $\Delta\delta$ = 0.65 ppm). With the opposite orientation of the naphtho-*a* units, the deshielding is only moderate (cf. **23**, $\Delta\delta$ = 0.35 ppm). Correspondingly, the benzyl protons of these two C_2-symmetrical isomers are strongly deshielded in **23** ($\Delta\delta$ = 0.70 ppm) but only slightly in **24** ($\Delta\delta$ = 0.18 ppm). Thus, most of the doubly (naphtho-*a*) anellated isomers are magnetically shielded in a way that reflects the orientation of the peripheral arene

ring of the naphtho group (**23**: $\delta_{benzhydryl}$ = 4.92 and δ_{benzyl} = 4.50, respectively, **24**: $\delta_{benzhydryl}$ = 5.22 and δ_{benzyl} = 3.98, respectively). Also, the resonances of the two pairs of equivalent methylene protons in **23** are strongly affected by the adjacent naphtho group whereas in the case of the isomer **24** all of the methylene resonances are very close to those of the "parent" fenestranone **5**. In further accord with the above observations, the "mixed" anellation of the naphtho-*a*,naphtho-*b* isomer **25** is nicely reflected by the deshielding effect for only a half of the alicyclic protons. And finally, the doubly (naphtho-*b*)-anellated isomer **26** exhibits only a moderate deshielding on the benzhydryl and benzyl protons, as compared to **5**, in line with remote anellation of the additional benzo nuclei.

Table 1. Chemical shifts of the alicyclic protons of benzodinaphtho-[6.5.5.5]fenestranones **23**–**26** as compared to the tribenzo[6.5.5.5]-fenestrane **5**.[a]

Comp'd	$\delta_{benzhydryl}$	δ_{benzyl}	$\delta_{methylene}$	
5 [5]	4.57	3.80	2.81	2.69
23	4.92	4.50	3.22	2.58
24	5.22	3.98	2.88	2.74
25	4.84	4.19	3.08	3.04
	5.07	3.83	2.72	2.60
26	4.74	3.94	n.d.[b]	n.d.[b]

[a] The methylene proton resonances have not been assigned stereochemically (cf. ref. 5).
[b] Resonances could not been detected in the spectrum of the mixture (see text).

CONCLUSION

The results show that naphtho-anellated [5.6.5]- and [6.5.5.5]fenestranes are easily synthesized by two-fold cyclodehydration of appropriate dihydrophenalenediols and *trans*-dinaphthyl-substituted indane-[spiro]cyclohexanetriols, respectively. Yields are similar to those obtained previously with tribenzo-[6.5.5.5]fenestranes. As expected, cyclodehydration of the spirotriol bearing two α-naphthyl groups (**15**) occurs exclusively by electrophilic attack at the β positions, no *peri* attack giving rise to the formation of additional six-membered rings in the fenestrane skeleton was observed. Since the route to [6.5.6.5]-fenestranes via dihydrophenalene[spiro]cyclohexanetriols (to be derived from **11a**) appears to be also blocked, further efforts are required to explore a synthetic access to this rare class of fenestranes. In contrast, as demonstrated in this paper, the chemistry of areno-anellated [5.6.5]- (broken) and [6.5.5.5]-fenestranes may be easily broadened further.

EXPERIMENTAL SECTION

General Methods

Melting points (uncorrected): Electrothermal melting point apparatus. – IR: Perkin-Elmer models 377 and 841. – ^{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. ^1H-^1H COSY measurements: Bruker AM 300. – MS: Finnigan MAT CH5, EI, 70 eV; samples were introduced by the solids inlet probe. – Combustion analyses: Perkin-Elmer 240 and LECO CHNS-932 Analysator. – Thin layer chromatography (TLC): Silica gel (Kieselgel 60) on Al foil (Merck, F 254).

Synthesis of the Dibenzonaphtho[5.6.5]Fenestrane

2,2-Dibenzyl-2,3-dihydrophenalene-1,3-dione (7). To a solution of dihydrophenalenedione (**6**) (2.60 g, 13.3 mmol) in acetonitrile (200 ml) was added 4.00 g (34.5 mmol) of potassium fluoride on celite 545 (Fluka)[5,18,19]. Benzyl bromide (6.84 g, 40.0 mmol) was added in one single portion and the suspension was stirred and heated to 80 °C for 5 h. The mixture was allowed to cool and the solid components were removed by filtration and washed with dry tetrahydrofuran or with acetonitrile. After evaporation of the solvents, the residue obtained was recrystallized from ethanol to give diketone **7** (3.10 g, 62 %) as amber-coloured needles, m.p. 176 °C, R_f (CH_2Cl_2) 0.89. IR (KBr): $\tilde{\nu}$ = 3031 cm^{-1}, 2928, 1681, 1656, 1592, 1576, 1496, 1438, 1432, 1352, 1291, 1231, 1181, 842, 752, 700. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.53 (s, 4 H, CH_2), 6.88–7.02 (m, 10 H, C_6H_5), 7.58 (dd, J = 7.39 Hz, J = 8.19 Hz, 2 H, 5/8-H), 8.38 (dd, J = 7.26 Hz, J = 1.14 Hz, 2 H, 4/9-H), 8.37 (dd, J = 8.29 Hz, J = 1.06 Hz, 2 H, 6/7-H). MS (EI, 70 eV): m/z = 376 (4 %, [M^+·]), 285 (100), 155 (17), 127 (10), 91 (45), 65 (14). $C_{27}H_{20}O_2$ (376.5); calcd C 86.15, H 5.36; found C 86.33, H 5.31.

2,2-Dibenzyl-2,3-dihydrophenalene-1,3-diol (8). A suspension of lithium aluminium hydride (1.50 g, 39.5 mmol) in dry tetrahydrofuran (70 ml) was stirred while a solution of diketone **7** (2.50 g, 6.65 mmol) in dry tetrahydrofuran (70 ml) was added slowly. The mixture was heated to reflux for 4 h, then allowed to cool and hydrolyzed by careful addition of ice/water and dilute sulphuric acid. The layers were separated and the aqueous one was extracted with dichloromethane; the combined layers were dried with sodium sulphate and the solvent removed under reduced pressure. A foamy residue was obtained *in vacuo* (2.32 g, 93 %) and could be used without further purification in the next step. Diol **8** appeared at R_f(CH_2Cl_2) 0.41; IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (br, OH), 3059, 3028, 2924, 1678, 1672, 1493, 1453, 1389, 1369,, 1263, 1115, 1052, 777, 753, 700. MS (EI, 70 eV): m/z = 380 (2 %, [M^+·]), 362 (3), 271 (40), 253 (12), 197 (36), 181 (11), 91 (100). (MS found m/z 380.1770; $C_{27}H_{24}O_2$ requires 380.1776.)

(3bα,13bβ)-3b,8,9,13b-Tetrahydrodiindeno[1,2-a:2,1-b]phenalene (9). A mixture of diol **8** (1.00 g, 5.26 mmol) and toluene (70 ml) was heated to reflux in a flask carrying a Soxhlet extractor filled with dried mole sieves 4 Å (ca. 20 g). Orthophosphoric acid (85 %, 0.5 g) was added and heating was continued for 6 h. The mixture was allowed to cool, washed with aqueous sodium carbonate and water and dried with sodium sulphate. After removal of the solvent in vacuo, a red residue was obtained which was recrystallized from methanol to give **9** (430 mg, 48 %) as slightly red crystals, m.p. 231–232 °C. IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1}, 2934, 2892, 1592, 1581, 1472, 1454, 1387, 802, 770, 756, 750, 737. ^1H NMR (300 MHz, $CDCl_3$): AB spectrum δ_A = 3.12, δ_B = 2.99 (J = 15.4 Hz, 4 H, CH_2), 4.40 (s, 2 H), 7.14–7.31 (m, 6 H), 7.28–7.32 (m, 2 H), 7.41–7.51 (m, 4 H), 7.70 (d, J = 7.8 Hz, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 43.38 (s), 50.68 (t), 55.65 (q), 125.07, 125.35, 126.33, 126.38, 126.46, 126.85 (t), 128.60, 133.80, 133.90, 142.28, 146.25 (q). MS (EI, 70 eV): m/z = 344 (100 %, [M^+·]), 343 (32), 253 (67), 252 (37), 216 (10), 215 (9), 163 (11), 91 (10). $C_{27}H_{20}$ (344.5); calcd C 94.15, H 5.85; found C 92.40, H 5.94.

Michael Addition of Phenalene-1,3-dione to Dibenzylideneacetone

cis-2,6-Diphenylspiro[cyclohexane-1,2'-(2,3-dihydrophenalene)]-1',3',4-trione (11b). A solution of diketone **6** (1.96 g, 10.0 mmol), dibenzylideneacetone (**10**) (2.34 g, 10.0 mmol) and (−)-quinine (130 mg) in 40 ml of tetrahydrofuran was heated to reflux for 72 h. TLC monitoring of the reaction showed that complete conversion of the reactants was not achieved even with prolongated heating. The solvent was removed by distillation, the residue was redissolved in chloroform, and the solution was washed several times with aqueous hydrochloric acid (10 %) and water and then dried with sodium sulphate. The solvent was evaporated and the residue recrystallized from $CHCl_3$/EtOH. Repeated recrystallization gave the *cis*-diphenyl isomer **11b** (1.50 g, 35 %) as yellowish crystals, m.p. 218 °C, $R_f(CH_2Cl_2)$ 0.51. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2920, 1711, 1681, 1657, 1576, 1292, 765, 754, 701. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.68 (dd, *J* = 15.1 Hz, *J* = 4.4 Hz, 2 H, 8/10-H^e), 3.88 (quasi-t, *J* = 14.7 Hz, 2 H, 8/10-H^a), 4.20 (dd, *J* = 14.4 Hz, *J* = 4.4 Hz, 2 H, 7/11-H), 6.75–7.05 (m, 10 H), 7.57 (quasi-t, *J* = 7.7 Hz, 1 H), 7.64 (quasi-t, *J* = 7.6 Hz, 1 H), 7.88 (quasi-d, *J* = 8.1 Hz, 1 H), 7.93 (quasi-d, *J* = 8.1 Hz, 1 H), 8.24 (quasi-d, *J* = 7.9 Hz, 1 H), 8.42 (quasi-d, *J* = 7.4 Hz, 1 H). $C_{30}H_{22}O_3$ (430.5); calcd C 83.70, H 5.15; found C 83.44, H 5.08.

cis- and trans-2,6-Diphenylspiro[cyclohexane-1,2'-(2,3-dihydrophenalene)]-1',3',4-trione (11a and 11b). A solution of diketone **6** (3.92 g, 20.0 mmol) and dibenzylideneacetone (**10**) (4.68 g, 20.0 mmol) in 150 ml of glacial acetic acid was heated to reflux for 3 h. The mixture was allowed to cool while unreacted diketone **6** (1.32 g, 34 %) precipitates, which was removed by filtration. The sovent was distilled off and the dark-brown residue was passed through a short column (20 × 3.5 cm) of silica gel (petroleum ether/EtOAc 3:1). The first fraction consisted of a 4*H*-pyran **12**[16], the second one of the spirotriketones **11a** and **11b**. The latter two compounds were recrystallized as a mixture from chloroform/ethanol to give **11a**/**11b** (2.75 g, 32 %; 48 % based on the converted **6**) as yellow crystals. ^1H-NMR analysis shows the ratio [**11a**] : [**11b**] to be 1 : 8. All attempts to separate the isomers failed (R_f 0.49 in petroleum ether/EtOAc 3:1). ^1H NMR of **11a** (300 MHz, $CDCl_3$), as determined as a difference spectrum: δ = 2.76 (dd, *J* = 15.8 Hz, *J* = 4.1 Hz, 2 H, 8/10-H^e), 3.83–3.93 (overlapped, 2 H, 8/10-H^a), 4.48 (dd, *J* = 14.1 Hz, *J* = 4.2 Hz, 2 H, 7/11-H), 6.78–7.02 (m, 10 H), 7.44–7.59 (overlapped, 2 H), 7.98 (d, *J* = 8.6 Hz, 2 H), 8.17 (d, *J* = 8.3 Hz, 2 H).

Syntheses of Benzodinaphtho[6.5.5.5]fenestranes

1,5-Di(α-naphthyl)penta-1,4-diene-3-one (13). This compound was prepared according to the general aldol condensation procedure, as described in the literature.[20] Yellow crystals, m.p. 128 °C (EtOAc). ^1H NMR (80 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 15.6 Hz, 2 H, 2/4-H), 7.43–7.70 (m, 6 H), 7.86–7.98 (m, 6 H), 8.20–8.35 (m, 2 H), 8.65 (d, *J* = 15.7 Hz, 2 H, 1/5-H). MS (EI, 70 eV): *m/z* = 334 (100, $[M]^{+\cdot}$), 305 (10), 206 (20), 181 (48), 178 (23), 165 (15), 152 (79), 141 (30).

1,5-Di(β-naphthyl)penta-1,4-diene-3-one (17). This compound was prepared in the same way.[21] Yellow crystals, m.p. 243–244 °C (EtOAc). ^1H NMR (80 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 16.1 Hz, 2 H, 2/4-H), 7.47–7.65 (m, 5 H), 7.77–8.07 (m, 9 H), 7.96 (d, overlapped, *J* = 15.9 Hz, 2 H, 1/5-H). MS (EI, 70 eV): *m/z* = 334 (100, $[M]^{+\cdot}$), 305 (18), 206 (18), 181 (33), 178 (31), 165 (15), 152 (85), 141 (71).

trans-Spirotriketones 14 and 18 (General Procedure). 1,3-Indanedione (**12**) (1.05 equiv) and the appropriate di(naphthylvinyl)ketone **13** or **17** (1.00 equiv) were suspended in glacial acetic acid (5 ml/mmol of the dienone) and the mixture was heated to reflux for 2–5 h. After this period, the solution was concentrated to a small volume and ethanol was added to precipitate a yellow solid, which was filtered off and recrystallized from ethanol/chloroform. Further purification was achieved by three-fold recrystallization from the same solvent mixture or from chloroform.

trans-2,6-Di(α-naphthyl)spiro[cyclohexane-1,2'-indane]-1',3',4-trione (14). Starting from 7.30 g (50.0 mmol) of **12** and 16.0 g (47.9 mmol) of **13**, spirotriketone **14** (10.3 g, 45 %) was obtained as yellowish crystals, m.p. 252–254 °C (EtOH/$CHCl_3$), R_f(CH_2Cl_2) 0.55. IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1}, 2922, 1732, 1723, 1697, 1256, 1237, 802, 778, 720. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.04 (dd, *J* = 16.6 Hz, *J* = 4.3 Hz, 2 H, 3/5-H^e), 3.76 (dd, *J* = 16.6 Hz, *J* = 11.3 Hz, 2 H, 3/5-H^a), 4.97 (dd, *J* = 11.3 Hz, *J* = 4.3 Hz, 2 H, 2/6-H), 7.29–7.36 (m, 6 H), 7.39 (s, 4 H), 7.50 (d, *J* = 7.3 Hz, 2 H), 7.58–7.67 (m, 4 H), 7.78 (m, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 37.70 (t, C-2/6), 43.93 (s, C-3/5), 60.55 (q, C-1), 122.65, 123.21, 124.99, 125.45, 126.09, 126.94, 128.21, 128.75 (all t), 131.41, 133.67, 134.66 (all q), 135.26 (t), 141.71 (q), 202.08 (q, CO), 210.43 (q, CO). MS (EI, 70 eV): *m/z* = 480 (19 %, $[M^+\cdot]$), 326 (11), 284 (11), 181 (10), 154 (100), 153 (30). $C_{34}H_{24}O_3$ (480.6); calcd C 84.98, H 5.03; found C 85.03, H 4.98.

trans-2,6-Di(β-naphthyl)spiro[cyclohexane-1,2'-indane]-1',3',4-trione (18). The reaction of 6.00 g (41.1 mmol) of **12** and 13.1 g (39.2 mmol) of **17** gave spirotriketone **18** (8.53 g, 46 %) as yellowish crystals, m.p. 232 °C ($CHCl_3$), R_f(CH_2Cl_2) 0.52. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2908, 1731, 1697, 1244, 1230, 724. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.91 (dd, *J* = 16.7 Hz, *J* = 3.4 Hz, 2 H, 3/5-H^e), 3.78 (dd, *J* = 16.7 Hz, *J* = 13.3 Hz, 2 H, 3/5-H^a), 4.20 (dd, *J* = 13.4 Hz, *J* = 3.3 Hz, 2 H, 2/6-H), 7.08 (dd, *J* = 8.0 Hz, *J* = 1.8 Hz, 2 H), 7.35–7.68 (m, 16 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 42.02 (s, C-3/5), 43.86 (t, C-2/6), 61.74 (q, C-1), 122.56, 125.00, 126.10, 126.30, 127.39, 127.67, 127.88, 127.94 (all t), 132.40 (q), 132.91 (q), 134.96 (q), 135.44 (t), 141.98 (q), 202.84 (q, CO), 209.97 (q, CO). MS (EI, 70 eV): *m/z* = 480 (19 %, $[M^+\cdot]$), 326 (19), 298 (18), 283 (22), 154 (100), 153 (17). $C_{34}H_{24}O_3$ (480.6); calcd C 84.98, H 5.03; found C 84.81, H 5.12.

trans-Spirotriols 15 and 19 (General Procedure). A solution of the appropriate spirotriketone (**14** or **18**) in dry tetrahydrofuran (10–20 ml/mmol of the trione) was added to a stirred suspension of lithium aluminium hydride (6.00 mmol/mmol of the trione) in the same solvent (20–30 ml/mmol of the trione) under argon and the mixture was heated to reflux for 2–4 h. After being cooled in an ice/water bath, the mixture was hydrolyzed by careful addition of ice/water and then diluted sulphuric acid. The organic layer was separated and the aqueous one was extracted several times with dichloromethane. The combined organic extracts were dried with sodium sulphate and the solvent was removed under reduced pressure to give a light-brown, foamy residue, which was used without further purification in the cyclodehydration step (see below). Recrystallization from tetrahydrofuran/chloroform furnished pure products which were characterized as follows hereafter.

trans-2,6-Di(α-naphthyl)spiro[cyclohexane-1,2'-indane]-1',3',4-triol (15) (mixture of stereoisomers). The reaction of 4.80 g (10.0 mmol) of spirotriketone **14** gave 4.13 g (85 %) of spirotriol **15** as a colourless powder, m.p. 296 °C (at 290 ° decomp.), R_f(EtOAc) 0.77. IR (KBr): $\tilde{\nu}$ = 3589 cm^{-1}, 3368 (br, OH),

3039, 2919, 1597, 1508, 1394, 1199, 1070, 1005, 783, 773, 758. MS (EI, 70 eV): m/z = 486 (8, $[M]^{+\cdot}$), 468 (15, $[M - H_2O]^{+\cdot}$), 450 (16, $[M - 2\,H_2O]^{+\cdot}$), 283 (20), 270 (27), 269 (36), 253 (28), 239 (14), 181 (27), 179 (29), 155 (49), 153 (61), 141 (100), 128 (43), 115 (28), 77 (12). (MS found m/z 486.2190; $C_{34}H_{30}O_3$ requires 486.2195.)

trans-2,6-Di(β-naphthyl)spiro[cyclohexane-1,2'-indane]-1',3',4-triol (19) (mixture of stereoisomers). Reaction of 4.25 g (8.72 mmol) of spirotriketone **18** gave 3.70 g (87 %) of spirotriol **19** as a colourless powder, m.p. 303–305 °C, R_f(EtOAc) 0.75. IR (KBr): $\tilde{\nu}$ = 3590 cm^{-1}, 3364 (br, OH), 3039, 2921, 1597, 1508, 1199, 1070, 1020, 783, 773, 758. MS (EI, 70 eV): m/z = 486 (17, $[M]^{+\cdot}$), 468 (46, $[M - H_2O]^{+\cdot}$), 450 (41, $[M - 2\,H_2O]^{+\cdot}$), 309 (22), 295 (30), 287 (38), 269 (85), 167 (62), 155 (84), 147 (42), 141 (100), 128 (33), 115 (19). $C_{34}H_{30}O_3$ (486.6); calcd C 83.92, H 6.21; found C 83.81, H 6.03.

all-cis-[6.5.5.5]Fenestranols 16 and 20–22 (General Procedure). A suspension of the respective spirotriol **15** or **19** (as mixtures of stereoisomers) (5.00 mmol) in 85 ml of toluene was placed in a flask equipped with a Thiele-Pape extractor containing mole sieves 4 Å (ca. 15 g). Orthophosphoric acid (0.85 g, 85 %) was added and the mixture was stirred vigorously and heated to reflux for 8–12 h. The mixture was allowed to cool, washed with aqueous sodium carbonate and water and dried with sodium sulphate. The solvent was removed in vacuo to give a residue which was either directly recrystallized or filtered through a pad of silica gel before recrystallization.

(6bα,10bβ,16cα,19aβ)-6b,10b,16c,17,19,19a-Hexahydro-18H-benzo[c]benzo[4,5]naphtho[1',2':2,3]pentaleno[1,6-jk]fluoren-18-ol (Fenestrane alcohol 16). Spirotriol **15** (2.00 g, 4.12 mmol) gave fenestranol **16** (1.10 g, 58 %) as a colourless, fluffy solid, m.p. 252 °C ($CHCl_3$/EtOH), R_f(CH_2Cl_2) 0.54. IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (OH), 3051, 3021, 2927, 2862, 1624, 1591, 1370, 1065, 817, 758, 740. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (br s, 1 H, OH), 1.60 (dt, J ≈ 12.7 Hz, 1 H), 2.12–2.21 (m, 1 H), 2.64 (m, 1 H), 3.13 (br d, J = 13.2 Hz, 1 H), 3.86 (tt, J = 11.0 Hz, J = 2.6 Hz, 1 H), 3.97 (dd, J = 6.0 Hz, J = 11.2 Hz, 1 H), 4.24–4.27 (m, 1 H), 4.46 (s, 1 H), 4.83 (s, 1 H), 7.07–7.14 (m, 2 H), 7.18–7.28 (m, 1 H), 7.41–7.60 (m, 7 H), 7.72–7.91 (m, 5 H), 8.17 (d, J = 7.88 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 36.57 (s), 40.04 (s), 45.55 (t), 45.89 (t), 59.01 (t), 62.36 (t), 65.27 (q, C-14), 66.95 (t, C-3), 123.33, 123.35, 123.61, 124.14, 124.44, 124.73, 125.11, 126.00, 127.28, 127.30, 128.00, 128.41, 128.87, 129.20 (all t), 130.23, 130.87, 133.38, 133.94, 139.31, 139.56, 141.01, 141.80, 143.05, 144.27 (all q). MS (EI, 70 eV): m/z = 450 (100, $[M]^{+\cdot}$), 432 (35, $[M - H_2O]^{+\cdot}$), 391 (25), 254 (12), 252 (13), 179 (14). $C_{34}H_{26}O$ (450.6); calcd 450.1984, found 450.1954 (exact mass by MS).

Cyclodehydration of spirotriol **19** (4.00 g, 8.23 mmol) gave a mixture of the fenestranols **20–22** as a colourless solid which was obtained in several crystal fractions in a combined yield of 1.88 g (51 %). A sample (300 mg) of this mixture was separated by MPLC (CH_2Cl_2/EtOH 99 : 1) giving **21**, **22** and **23** as three fractions in the ratio of 24 : 5 : 1.

(6bα,9aβ,15cα,19bβ)-6b,7,9,9a,15c,19b-Hexahydro-8H-benzo[a]benzo[4,5]naphtho[2',1':2,3]pentaleno[1,6-jk]fluoren-8-ol (Fenestrane alcohol 20). Colourless, fluffy solid, m.p. 318 °C (decomp. ≥ 310 °C), R_f(CH_2Cl_2/EtOH, 99 : 1) 0.39. IR (KBr): $\tilde{\nu}$ = 3419 cm^{-1} (OH), 3052, 2894, 1590, 1513, 1473, 1056, 1039, 1025, 811, 775, 744. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31–1.43 (m, 1 H), 1.44–1.57 (br s, overlapped, 1 H, OH), 1.88–1.98 (m, 1 H), 2.21–2.27 (m, 1 H), 2.53–2.61 (m, 1 H), 3.42 (dd, J =

5.8 Hz, J = 11.2 Hz, 1 H), 3.72–3.82 (m, 2 H), 7.03 (t, J = 7.1 Hz, 1 H), 7.19–7.28 (m, 2 H), 7.37–7.58 (m, 7 H), 7.76–7.93 (m, 6 H), 8.09 (d, J = 8.3 Hz, 1 H), 8.4 (d, J = 8.4 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 34.81, 40.92 (s, CH_2), 44.14, 46.02, 57.13, 59.73,66.91 (CH), 68.09 (C-14), 122.9–128.9 (a total of 16 C), 131.08, 133.51, 133.47 (q), 133.37, 136.78, 139.09, 142.93, 143.21, 143.89, 144.88 (q). MS (EI, 70 eV): m/z = 450 (100, $[M]^{+\cdot}$), 432 (57, $[M - H_2O]^{+\cdot}$), 403 (20), 391 (46), 389 (16), 266 (15), 254 (25), 252 (21). $C_{34}H_{26}O$ (450.6); calcd C 90.63, H 5.82; found C 90.36, H 6.11.

(6bα,9aβ,15bα,19bβ)-6b,7,9,9a,15b,19b-Hexahydro-8H-benzo[a]benzo[4,5]naphtho[2',3':2,3]pentaleno[1,6-jk]fluoren-8-ol (Fenestrane alcohol 21). Colourless powder, m.p. 306 °C (decomp. ≥ 301 °C), R_f(CH_2Cl_2/EtOH, 99 : 1) 0.58. IR (KBr): $\tilde{\nu}$ = 3418 cm^{-1} (OH), 3050, 2891, 1590, 1512, 1470, 1052, 1040, 1025, 813, 777, 745. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48–1.59 (br s, overlapped, 1 H, OH), 1.89–1.98 (m, 1 H), 2.12–2.22 (m, 3 H), 3.59 (t, J = 6.0 Hz, 1 H), 3.65 (dd, J = 5.9 Hz, ^{3}J = 8.9 Hz, 1 H), 4.09–4.16 (m, 1 H), 4.72 (s, 1 H), 4.94 (s, 1 H), 7.12 (t, J = 6.9 Hz, 1 H), 7.22 (t, J = 7.3 Hz, 1 H), 7.38–7.57 (m, 7 H), 7.68 (s, 1 H), 7.78–7.82 (m, 4 H), 7.88 (d, J = 8.4 Hz, 1 H), 8.18 (d, J = 8.3 Hz, 1 H). MS (EI, 70 eV): m/z = 450 (100, $[M]^{+\cdot}$), 432 (21, $[M - H_2O]^{+\cdot}$), 391 (82), 253 (18), 252 (22), 194 (26). $C_{34}H_{26}O$ (450.6); calcd C 90.63, H 5.82; found C 90.41, H 6.18.

(5bα,8aβ,14bα,18bβ)-5b,6,8,8a,14b,18b-Hexahydro-7H-benzo[b]benzo[4,5]naphtho[2',3':2,3]pentaleno[1,6-jk]fluoren-7-ol (Fenestrane alcohol 22). Colourless powder, m.p. 297 °C (decomp. ≥ 286 °C), R_f(CH_2Cl_2/EtOH, 99:1) 0.45. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.57 (m, 1 H), 1.51–1.58 (br s, overlapped, 1 H, OH), 2.24–2.33 (m, 1 H), 2.59–2.67 (m, 1 H), 3.38 (dd, J = 5.9 Hz, J = 11.4 Hz, 1 H), 3.73 (br s, 1 H), 3.82–3.93 [m, quasi-tt, 1 H), 4.37 (s, 1 H), 4.77 (s, 1 H), 7.14–7.31 (m, 2 H), 7.38–7.47 (m, 5 H), 7.36–7.88 (m, 9 H). MS (EI, 70 eV): m/z = 450 (100, $[M]^{+\cdot}$), 432 (97, $[M - H_2O]^{+\cdot}$), 404 (32), 391 (66), 253 (24), 252 (21), 195 (25), 194 (29). (MS found m/z 450.1979; $C_{34}H_{26}O$ requires 450.1984.)

all-cis-[6.5.5.5]Fenestranones 23 and 24–26 (General Procedure). To a stirred solution of chromium(VI) oxide [0.20 g (2.0 mmol) per mmol of the fenestrane alcohol] in sulphuric acid (20 %, 20 ml per gram CrO_3) was dropped a suspension of the respective fenestranol (**16**, **20**, **21** or a mixture of **20**–**22**). The reaction mixture was heated at reflux temperature for 4 h and then stirred at room temperature overnight. The crude fenestranones were isolated by filtration, washed several times with water and then recrystallized.

(6bα,10bβ,16cα,19aβ)-6b,10b,16c,17,19,19a-Hexahydro-18H-benzo[c]benzo[4,5]naphtho[1',2':2,3]pentaleno[1,6-jk]fluoren-18-one (Fenestrane ketone 23). Oxidation of fenestranol **16** (100 mg, 0.22 mmol) gave fenestranone **23** (85 mg, 85 %) as a slightly beige solid, m.p. 252 °C (EtOH/$CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2881, 2870, 1711, 1591, 1513, 1243, 1163, 791, 773, 746. ^{1}H NMR (300 MHz, $CDCl_3$): ABX spectrum δ_A = 2.58 (2 H), δ_B = 3.22 (2 H), δ_X = 4.50 (2 H) (J_{AB} = 16.4 Hz, J_{AX} = 10.8 Hz, J_{BX} = 5.9 Hz), 4.92 (s, 2 H), 7.09–7.12 (m, 2 H, AA' part of AA'BB' spectrum), 7.34–7.37 (m, 2 H), 7.43–7.53 (m, 4 H), 7.50 (d, J = 8.3 Hz, 2 H), 7.74 (d, J = 8.4 Hz, 2 H), 7.82–7.86 (m, 4 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 45.72 (s), 47.42 (t), 62.94 (t), 63.60 (q, C-15d), 122.89, 123.81, 124.04, 125.30, 126.50, 127.30, 128.67, 128.88 (all t), 129.47, 133.34, 140.11, 140.53, 144.30 (all q), 210.89 (q, CO). MS

(EI, 70 eV): m/z = 448 (100, $[M]^{+\cdot}$), 405 (12), 391 (26), 389 (17), 253 (12). $C_{34}H_{24}O$ (448.6); calcd 448.1827, found 448.1842 (exact mass by MS).

(6b α,9a β,15c α,19b β)-6b,7,9,9a,15c,19b-Hexahydro-8H-benzo[a]benzo[4,5]naphtho[2',1':2,3]pentaleno[1,6-jk]fluoren-8-one (Fenestrane ketone 24). Oxidation of fenestranol **20** (300 mg, 0.67 mmol) gave fenestranone **24** (265 mg, 90 %) as a colourless powder, m.p. 284 °C ($EtOH/CHCl_3$), $R_f(CH_2Cl_2)$ 0.70. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1}, 2920, 2853, 1721, 814, 765, 742. ^1H NMR (300 MHz, $CDCl_3$): ABX spectrum δ_A = 2.74 (2 H), δ_B = 2.88 (2 H), δ_X = 3.98 (2 H) (J_{AB} = 13.5 Hz, $J_{AX} \approx$ 7.1 Hz, $J_{BX} \approx$ 7.1 Hz), 5.22 (s, 2 H), 7.15–7.18 (m, 2 H, AA' part of AA'BB' spectrum), 7.39 (d, J = 8.3 Hz, 2 H), 7.48 (t, J = 7.0 Hz, 2 H), 7.54–7.59 (m, 4 H, t and overlapping BB' part of AA'BB' spectrum), 7.81 (d, J = 8.3 Hz, 2 H), 7.90 (d, J = 8.1 Hz, 2 H), 8.28 (d, J = 8.2 Hz, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 43.34 (s), 48.43 (t), 58.24 (t), 68.31 (q, C-15d), 122.06, 124.55, 125.34, 126.31, 126.44, 127.41, 128.71, 128.91 (all t), 131.17, 133.75, 137.54, 142.80, 143.07 (all q), 210.51 (q, CO). MS (EI, 70 eV): m/z = 448 (100, $[M]^{+\cdot}$), 405 (12), 391 (22), 389 (17), 194 (13). $C_{34}H_{24}O$ (448.6); calcd C 91.04, H 5.39; found C 90.85, H 5.50.

(6b α,9a β,15b α,19b β)-6b,7,9,9a,15b,19b-Hexahydro-8H-benzo[a]benzo[4,5]naphtho[2',3':2,3]pentaleno[1,6-jk]fluoren-8-one (Fenestrane ketone 25). Oxidation of fenestranol **21** (120 mg, 0.27 mmol) gave fenestranone **25** (105 mg, 88 %) as a slightly beige powder, m.p. 324 °C ($EtOH/CHCl_3$), $R_f(CH_2Cl_2)$ 0.69. ^1H NMR (300 MHz, $CDCl_3$): ABX spectrum δ_A = 2.60 (1 H), δ_B = 2.72 (1 H), δ_X = 3.83 (1 H) ($J_{AB} \approx$ 12.5 Hz, $J_{AX} \approx$ 11.9 Hz, $J_{BX} \approx$ 6.4 Hz), ABX spectrum $\delta_A \approx$ 3.04 (1 H), δ_B = 3.08 (1 H), δ_X = 4.19 (1 H) ($J_{AB} \approx$ 15 Hz, $J_{AX} \approx$ 3.3 Hz, $J_{BX} \approx$ 7.1 Hz), 4.84 (s, 1 H), 5.07 (s, 1 H), 7.11 (t, J = 7.0 Hz, 1 H), 7.22–7.33 (m, 2 H), 7.41–7.57 (m, 5 H), 7.65 (s, 1 H), 7.71 (d, J = 7.5 Hz, 1 H), 7.67–7.83 (m, 4 H), 7.91 (d, J = 8.0 Hz, 1 H), 8.03 (d, J = 8.1 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 40.03, 46.75 (s), 47.82, 48.49, 55.76, 59.24 (t), 68.18 (q, C-15d), 121.43, 122.80, 124.74, 125.43, 125.67, 126.61, 127.79, 128.44, 128.79 (all t), 130.80, 133.21, 133.61, 138.27, 140.82, 141.45, 141.74, 144.72, 145.04 (all q), 210.29 (q, CO). MS (EI, 70 eV): m/z = 448 (100, $[M]^{+\cdot}$), 405 (14), 391 (27), 389 (25), 265 (30), 252 (61), 152 (18). $C_{34}H_{24}O$ (448.6); calcd C 91.04, H 5.39; found C 91.15, H 5.55.

(5b α,8a β,14b α,18b β)-5b,6,8,8a,14b,18b-Hexahydro-7H-benzo[b]benzo[4,5]naphtho[2',3':2,3]pentaleno[1,6-jk]fluoren-7-one (Fenestrane ketone 26). This fenestrane was formed in a mixture with the isomers **24** and **25** by oxidation of the mixture of the fenestrane alcohols **20**–**22** described above. Some significant ^1H-NMR resonances of **26** were determined as from a difference spectrum: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.70–2.91 (4 H, overlapped), 3.94 (t, $J \approx$ 7.5 Hz, overlapped), 4.74 (s, 2 H, benzhydryl-H), 7.11–7.84 (m, 16 H, overlapped).

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16. In addition, a by-product was isolated in 20 % yield by chromatography and identified as the 4*H*-pyran **27**, i.e. as a product of single Michael addition (see ref. 9d).
17. (a) Although recent observations (refs 8a, 17b) indicate the usefulness of *cis*-diphenylspirotriols within this strategy, considerable efforts seem necessary to incorporate two or more six-membered ring in centropolyquinane framework. Attempts to convert **11a** and **11b** to the target [6.5.6.5]fenestrane alcohol by $LiAlH_4$ reduction and subsequent cyclodehydration did not give any fenestrane-type dehydration products. (b) Kuck, D., to be published.
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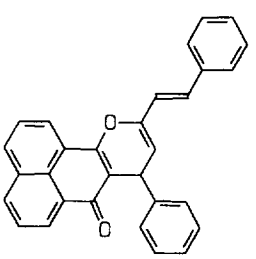

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