Benzoanellated Centropolyquinanes, 12[1]

trifuso-Centrotetraindan – Two Syntheses of a New Centropolyindan☆

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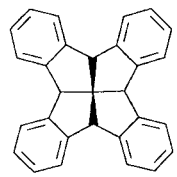
Two independent syntheses of the new centrotetraindan **2**, a "*trifuso*", C_s-symmetrical isomer of fenestrindan **1**, are described. The first approach is based on the "*endo*"-phenyldiindanone **7**, which is converted into **2** by benzylation to ketone **8** and subsequent cyclodehydration with polyphoshoric acid. The second, more efficient approach is based on the diindandione **17**, which is converted into ketol **19** in two steps, which, in turn, is subjected to a three-step cyclodehydration-reduction-cyclodehydration sequence via **26** and **27** to give **2** in 8% overall yield. Some limits of the cyclodehydration of diindan alcohols and ketones are demonstrated with regard to effects of steric crowding and fragmentation of the carbon skeleton. The steric hindrance of "*endo*"-phenyl-substituted diindans is demonstrated in the case of ketone **26**.

Among the centropolyindans, the D_{2h}-symmetrical congener, fenestrindan (**1**)[2], has gained particular interest because of its well-known [5.5.5.5]fenestrane framework. A closely related, isomeric centrotetraindan with C_s molecular symmetry, *trifuso*-centrotetraindan (**2**), may appear less attractive from an aesthetic point of view, but in fact it represents another polycyclic hydrocarbon with a particularly interesting carbon skeleton.



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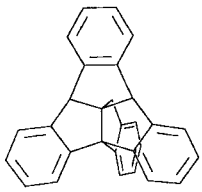
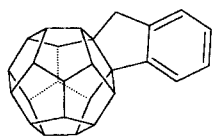


2

trifuso-Centrotetraindan (**2**) bears four indan units mutually fused at *three* of the four central C–C bonds. It comprises four different types of polyquinanes: One spiro[5.5]undecane and six bicyclo[3.3.0]octane systems, as for the diquinane subunits, and a [3.3.3]propellane as well as a triquinacene moiety, as for the triquinane subunits. Hence, the *trifuso* anellation of **2** gives rise to a variety of "molecular microsurfaces", in contrast to **1**. Moreover, the implementation of a triquinacene moiety should afford a completely rigid molecular skeleton, again in contrast to **1**, which is conformationally flexible[3].

trifuso-Centrotetracyclic polyquinanes are extremely rare, as have been *centro*-alkylated triquinacenes for a long time[4,5]. However, apart from the closely related centropolyindans[1,2,6,7], a number of triquinanes bearing an additional, *centro*-fused alicyclic unit have been synthesized recently. Two of them, indanodocecahedrane (**3**)[8] and cyclohexanotriquinacene (**4**)[5], are closely related to **2**. Two cyclopropatribenzotriquinacenes, **5a** and **5b**[9], have been synthesized recently as well as a number of related small-ring-anellated dodecahedranes[10,11].



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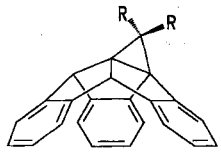


5 a R = H
5 b R = Me

In the present paper, we report on two independent syntheses and some properties of the new centropolyindan, *trifuso*-centrotetraindan (**2**). A significant part of the first approach has already been communicated with our first synthesis of tribenzotriquinacene[12,13].

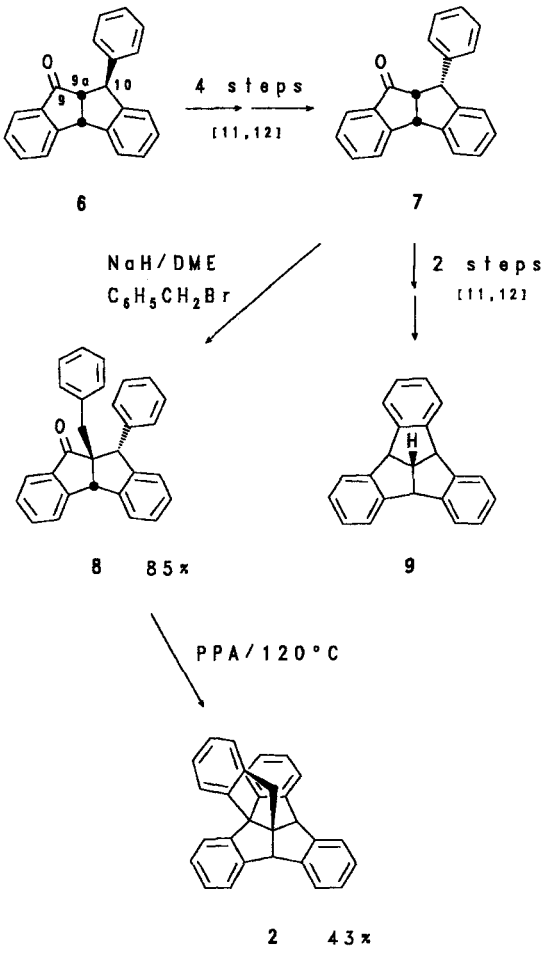
The First Synthesis of *trifuso*-Centrotetraindan

The first synthesis of **2** (Scheme 1) is based on the diindanone **6**, which has been described by Baker et al.[14] and identified by us as the "*exo*"-phenyl stereoisomer[13,15]. (In this paper, the terms *exo* and *endo* refer to the orientation of substituents at C-9 and C-10 of the bent diindan framework. According to the IUPAC nomenclature, *exo* groups

  0009–2940/92/0606–1461 $ 3.50+.25/0

in this system are oriented to the α, *endo* groups to the β "surface".) In a four-step dehydrogenation-rehydrogenation sequence **6** is epimerized at C-10 to give the "*endo*"-phenyl isomer **7** in 18% overall yield. The stereochemistry of **7** is then used, after reduction to a corresponding "*endo*"-phenyl alcohol, to achieve the first synthesis of tribenzotriquinacene **9**[12,13], a highly interesting cup-shaped triarene with four reactive bridgehead positions[9,16].

Scheme 1



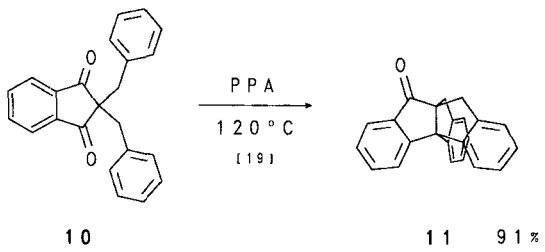
The benzylation of **7** with sodium hydride/benzyl bromide in DME gives the 9-benzyl-10-"*endo*"-phenyl ketone **8** in good yields and essentially without epimerization at C-10. The particular stereochemistry of this highly substituted "*endo*"-phenyldiindanone is reflected by the observation of considerable broadening of at least two resonance lines in the 300-MHz ^{1}H-NMR spectrum of **8**. One of the broadened signals exhibits a distinct high-field shift to δ = 6.55. Obviously, the "*endo*"-phenyl group is locked in the diindan cavity, and its rotation is sterically hindered, as indicated by the signals of its two *ortho* protons. A similar effect is found for the related "*endo*"-phenyl-substituted triindan **28** and is demonstrated in some detail in the next section (Figure 1).

In fact, the two pending arene groups of **8** display a rather different intramolecular mobility. Whereas the benzyl group is free to rotate above the convex side of the diindan framework, the "*endo*"-phenyl group should interact sterically with the carbonyl function, both pointing to the concave side of the molecule. We hoped, therefore, that acid-catalyzed cyclization of **8** to the title compound **2** would occur favorably by attack of the protonated carbonyl group at the "*endo*"-phenyl ring, and then proceed by attack of the tertiary carbenium ion at the benzyl group. Indeed, treatment of **8** with polyphosphoric acid (PPA) at 150°C for 20 h furnished the desired polycycle **2**, which was isolated in 43% yield as colorless, crystalline material. The identity and some further properties of **2** are discussed in the last section of this paper.

Thus, the target tetraindan **2** may be prepared by the dehydrogenation-rehydrogenation route[12,13] in six steps with a 6.5% overall yield from the diindanone **6**.

The cyclodehydration **8**→**2** does not take place by using less powerful catalysts such as *p*-toluenesulfonic acid. Thus, here again, PPA acts as a very powerful catalyst for the twofold cyclization of an electronically nonactivated α,α-dibenzyl ketone. While several cases of this type of cyclization have been described in the literature[17,18] the corresponding ring closure with nonactivated substrates is rare. We recently found a further example, namely the cyclodehydration of 2,2-dibenzyl-1,3-indandione (**10**) to 9-triptindanone (**11**; Scheme 2)[19].

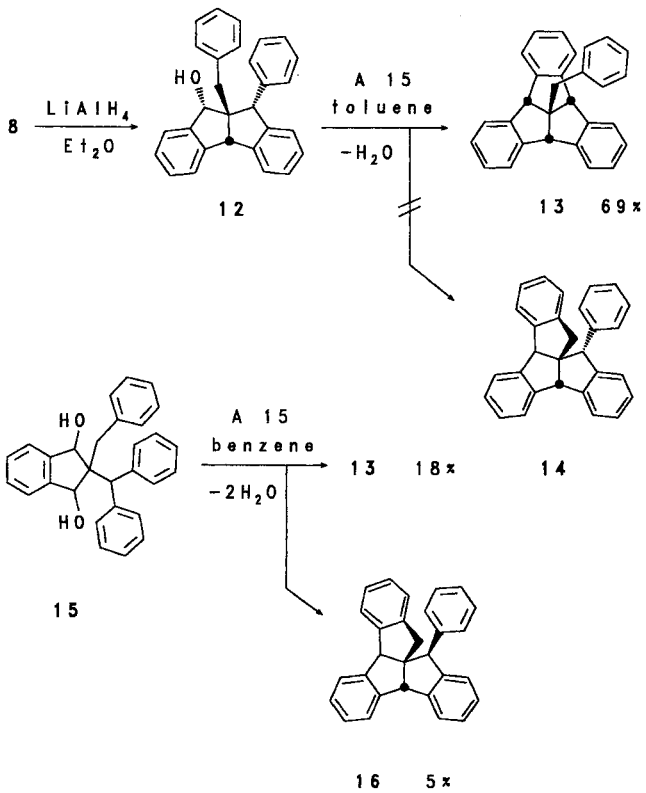
Scheme 2



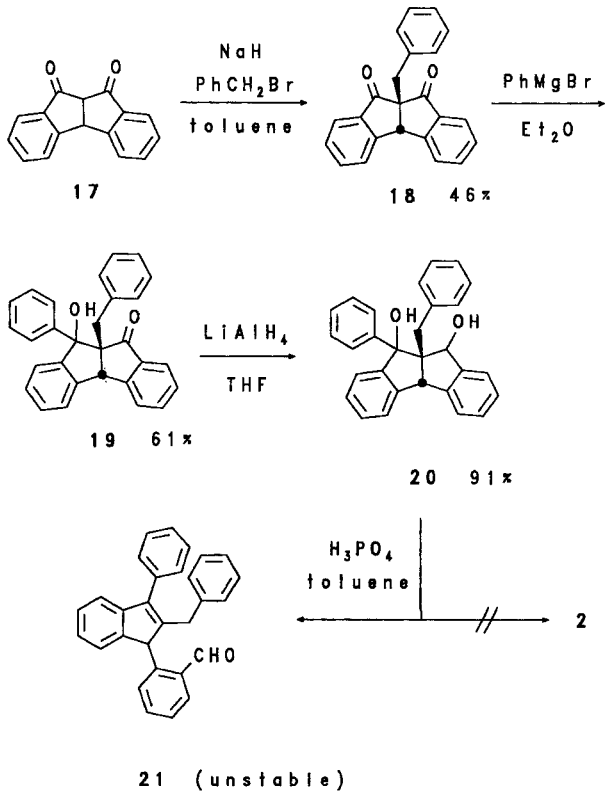
Whereas in the case of **10** the additional oxo group increases the electrophilicity of the intermediate carbenium ion at one of the benzyl groups, the highly entropically and sterically favorable orientation of the "*endo*"-phenyl group in **8** may be responsible for the efficient twofold ring closure there.

The particular readiness of the "*endo*"-phenyl group to undergo the first electrophilic attack by the carbenium center at C-9 is corroborated by the highly selective cyclization of alcohol **12** to **13** upon acid catalysis (Scheme 3). This alcohol is obtained from **8** by reduction with lithium aluminum hydride and gives, upon heating with Amberlyst 15 (A15) in toluene, 10-benzyltribenzotriquinacene (**13**) in 69% isolated yield, one of the *centro*-substituted derivatives of **9** obtained previously by double cyclodehydration of the appropriately substituted 1,3-indandiol **15**[1,6]. The alternative cyclodehydration product, i.e. *difuso*-centrotriindan **14**, has not been observed in the crude reaction mixture whereas **16**, the *exo*-phenyl isomer of **14**, is formed together with **13** upon cyclodehydration of **15**[1].

Scheme 3



Scheme 4

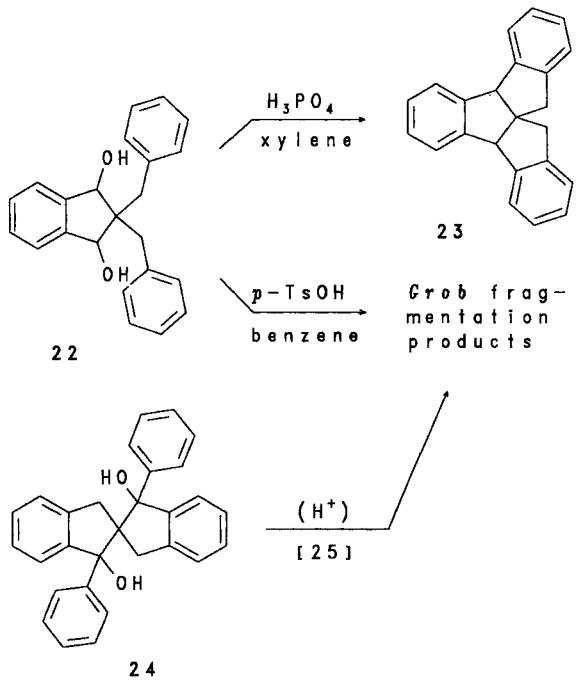


The Second Synthesis of *trifuso*-Centrotetraindan

In a search[20] for another, shorter synthesis of fenestrindan (**1**), we used the diindandione **17**, which had also been described previously[14,21], as the starting material. Whereas the introduction of a benzhydryl group at C-9a in **17** failed[20], we found that – not unexpectedly – the benzyl derivative **18** is easily obtained by alkylation with sodium hydride/benzyl chloride in toluene as the solvent (Scheme 4). When the inverse addition of the components (addition of **18** to one equivalent of phenylmagnesium bromide in diethyl ether) is used, the ketol **19** is formed and can be obtained in 61% yield after purification by flash chromatography. Small amounts of a bis-addition product and unreacted **18** are isolated as well. Subsequent reduction of **19** with lithium aluminum hydride in tetrahydrofuran furnishes the corresponding diol **20** without fragmentation of the 1,3-difunctionalized diquinane framework[22]. The stereochemistry of **19** and **20** has not been elucidated in detail.

Unfortunately, the last step of this reaction sequence proved to be unsuccessful under various conditions. Instead of the twofold cyclodehydration to the target centrotetraindan **2**, the diol **20** undergoes C–C bond cleavage to give an aldehyde, most probably **21**, as inferred from the IR, NMR, and MS analysis. Unequivocal identification of the product was not carried out because of its ready decomposition (see Experimental). Similar Grob-type fragmentation of 1,3-diols, in particular 1,3-indandiols (e.g., **22**)[6,23,24] and 2,2′-spirobiindan-1,1′-diols (e.g. **24**)[25], has been observed previously (Scheme 5). To our knowledge, however, this reaction has not been reported for *monofuso*-diquinane or -diindan, i.e. bicyclo[3.3.0]octane-type, 1,3-diols bearing the two alcohol functions in two different rings[22]. It is also interesting to note that a related *monofuso*-triindantriol[26] does undergo a *threefold* cyclodehydration under similar

Scheme 5

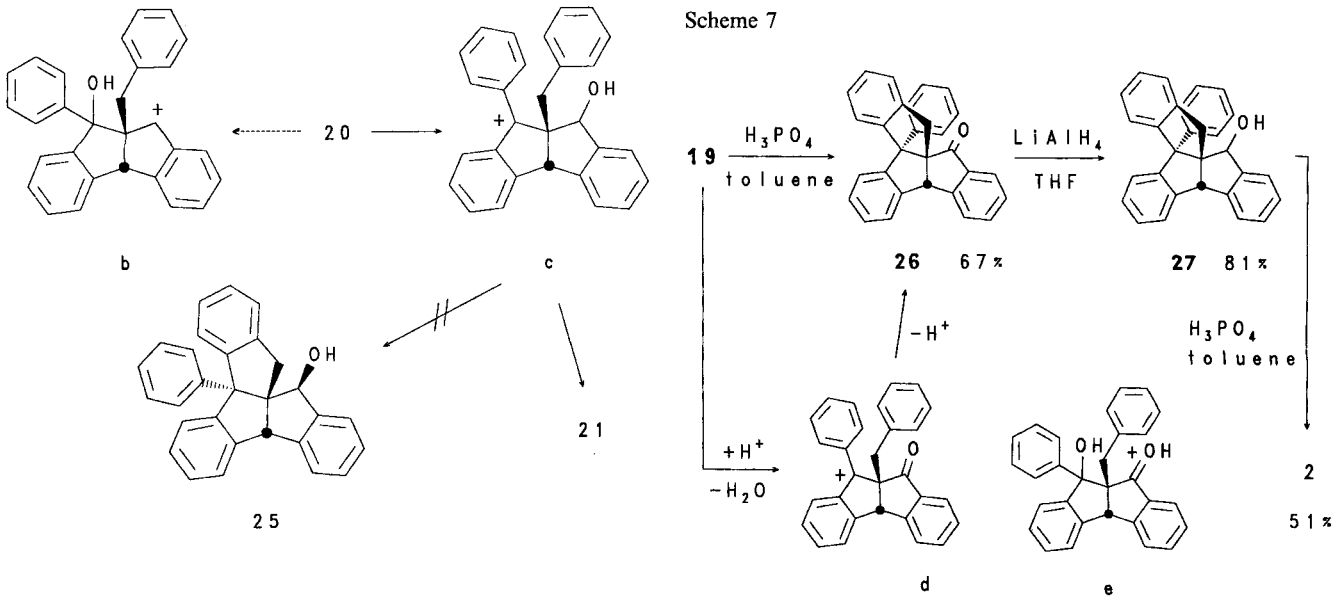


conditions without cleavage. It appears reasonable to assume that ionization of the benzhydrylic alcohol function (**20**→**c**; Scheme 6) is fast as compared to that of the benzylic one (**20**→**b**)[27] but that the subsequent electrophilic attack at the benzyl group (**c**→**25**) cannot compete with the cleavage reaction because of its free rotation above the convex side of the molecule.

Scheme 6

Fortunately, however, under the same conditions (H_3PO_4/toluene, 110°C) used for the diol **20**, the precursor ketol **19** undergoes a clean cyclodehydration to the *trifuso*-triindanone **26** (Scheme 7). In this case, the cleavage pathways (e.g., retro-aldol reaction via **d**), are suppressed. Obviously, similar to **20**, the ionization at the benzhydrylic alcohol function in **19** governs the course of the cyclodehydration by forming the intermediate ion **e** rather than **d**. The cyclodehydration of a 1,3-ketol (i.e. aldol) is, to the best of our knowledge, unprecedented.

Scheme 7



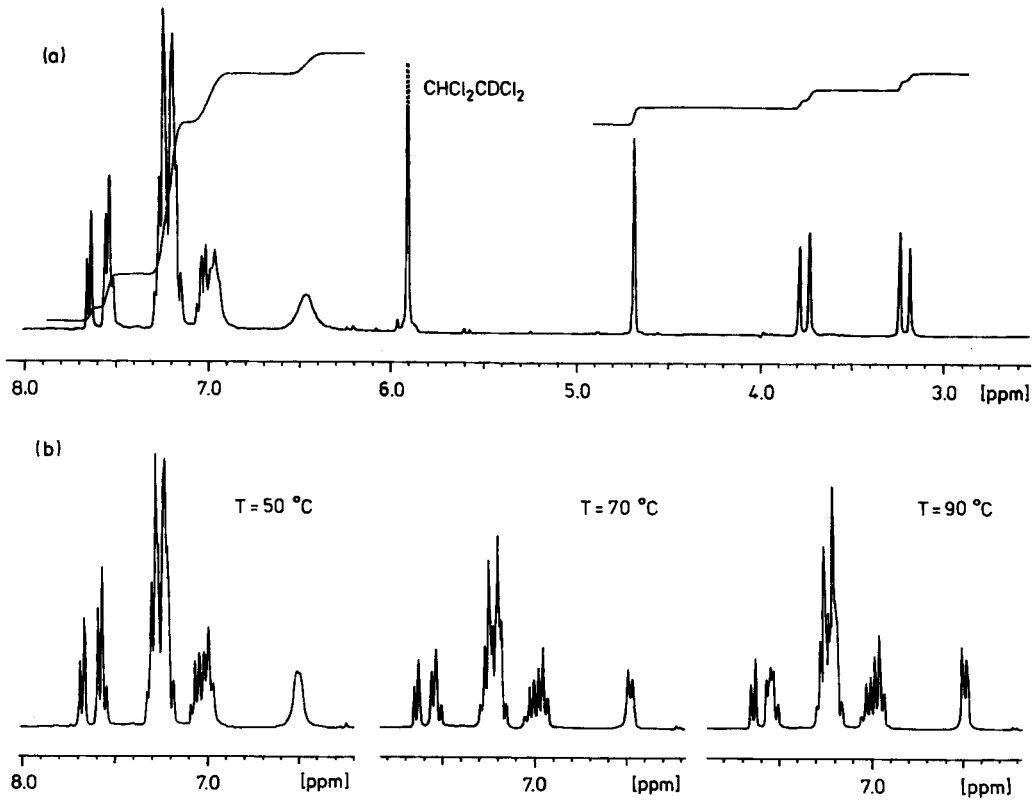
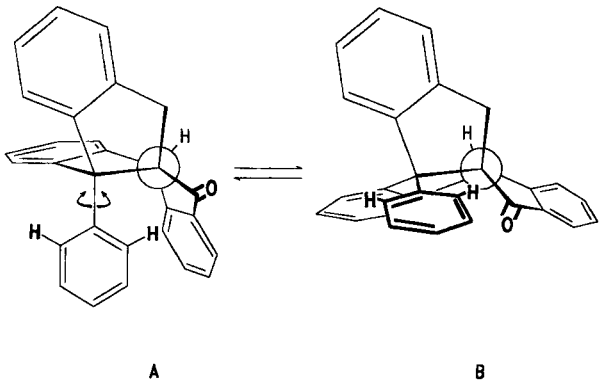


Figure 1. Temperature-dependent ^{1}H-NMR spectra (300 MHz, $CDCl_2CDCl_2$) of triindanone **26**; (a) complete spectrum at T = 30°C, (b) arene resonance region at T = 50, 70, and 90°C

Ketone **26** is reduced with lithium aluminum hydride to the corresponding alcohol **27**, which is obtained as a single diastereomer, presumably bearing the hydroxy group *syn* to the phenyl one. Finally, this alcohol is cyclodehydrated with H_3PO_4/toluene to give the target *trifuso*-centrotetraindan (**2**) in 41% yield. Thus, based on the diindandione **17**, the tetracycle **2** may be prepared in ca. 8% yield in five steps. Although being shorter by only one step than the first approach based on the ketone **6**, this second synthesis is considerably more efficient and convenient.

Again, the cyclization step (**27**→**2**) may be facilitated by the favorable orientation of the phenyl group to the concave side of the diindan framework. Thus, the incipient carbenium ion center formed after protonation of **27** is extremely close to the π system to be attacked. Some further insight into the stereochemistry of 10-"*endo*"-phenyldiindans has been obtained from the dynamic behavior of the precursor ketone **26**. At ambient temperatures, the 300-MHz ^{1}H-NMR spectrum of **26** (Figure 1a) exhibits remarkably broadened signals at δ = 6.50 and 6.95, which are assigned to the *ortho* and *meta* protons, respectively, of the phenyl group. Narrow signals are observed only at temperatures >70°C (Figure 1b). Since all other resonance lines remain essentially unaffected by the increase of the temperature, the dynamic behavior of **26** is governed by the hindered rotation of the phenyl substituent squeezed into the cavity of the diindan framework. Of the two conformational ground states of **26**, only one (**A**; Figure 2) allows for a slippage of the two *ortho*-hydrogen atoms below the opposite carbonyl group. In the other (**B**), the rotation of the phenyl group should be completely blocked. As mentioned above, a similar dynamic behavior has been found for the diindanone **8**. The latter ketone appears to be somewhat more flexible due to the lower number of anellated indan units.



A B

Figure 2. Two conformers of ketone **26** (projections along one of the central C–C bonds); rotation of the phenyl group is possible in conformer **A** but not in conformer **B**

Properties of *trifuso*-Centrotetraindan

The identity of **2** is unequivocally documented by its spectroscopic features. The 70-eV mass spectrum exhibits the molecular ion signal as the base peak, with the losses of $C_6H_5^{\bullet}$, C_6H_6, and ($C_6H_5^{\bullet}$ + H_2) being next frequent (12–17%). The doubly charged $(M - C_6H_6)^{2+}$ fragment ion (m/z = 145) of **2** is significantly less abundant (8%) than the corresponding ion observed in the mass spectrum of the isomeric fenestrindan (**1**; 31%)[2]. Obviously, the fact that **2**, in contrast to **1**, bears one indan unit attached to only one other (i.e., the *monofuso* anellation) is *not* reflected in a

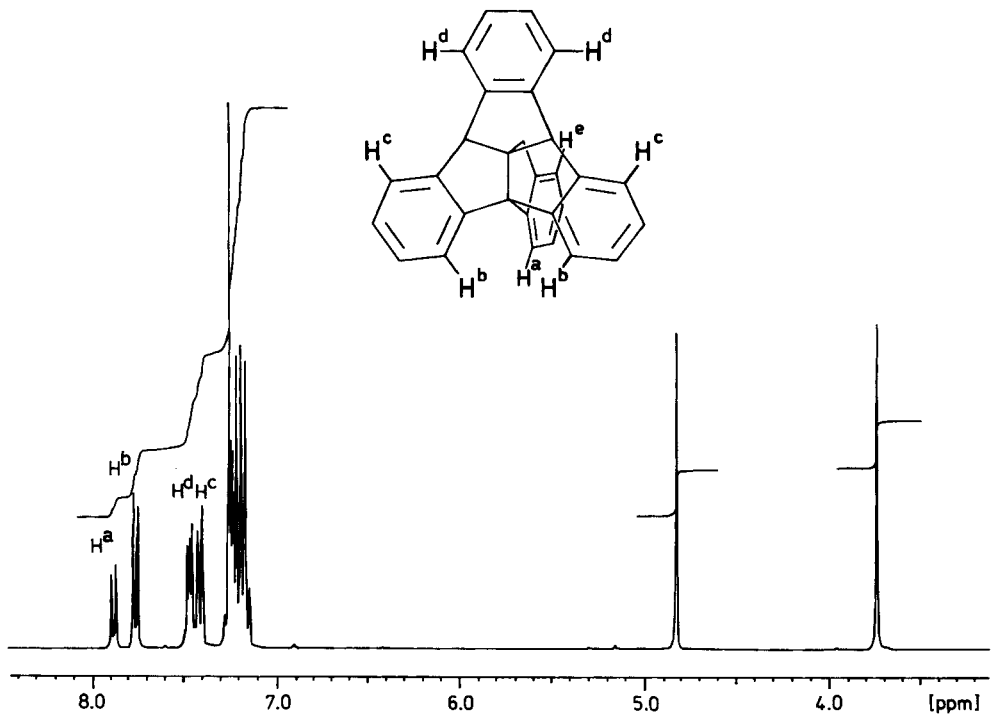


Figure 3. ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of *trifuso*-centrotetraindan (**2**); the singlets at δ = 3.74 and 4.82 correspond to the benzyl and benzhydryl protons, respectively

straightforward manner by the mass-spectrometric fragmentation. Thus, extensive isomerization seems to occur in the radical cations ($M^{\cdot+}$) of the centropolyindans.

The ^{1}H- and ^{13}C-NMR spectra of **2** clearly reflect the C_s molecular symmetry of this centrotetraindan. In the ^{1}H-NMR spectrum (Figure 3), two singlets at δ = 3.74 (2H) and 4.82 (2H) correspond to the equivalent methylene and benzhydrylic methine protons, respectively. Five signals for the eight *ortho* protons are observed as a typical feature of the three types of di- and triindan subunits. For symmetry reasons, the doublet at lowest field [δ = 7.88 (1H)] is assigned to the "*endo*" proton H^a of the triptindan subunit, whereas the adjacent doublet [δ = 7.76 (2H)] is due to the other two triptindan "*endo*" protons (H^b), which are also part of the tribenzotriquinacene subunit. The remaining *ortho* protons of this moiety (H^c and H^d) are shown by the doublet at δ = 7.41 and by the low-field part of an AA'BB' system at δ = 7.47, respectively. Only the signal of the single *ortho* proton H^e without adjacent "*endo*"-oriented arene groups overlaps with the resonance lines of the residual arene protons.

The ^{13}C-NMR spectrum of **2** shows fifteen different resonance lines for the twenty-four arene carbon atoms, as required for the twofold degeneracy of the tribenzotriquinacene subunit, as well as four lines for the five aliphatic carbon atoms. The chemical shift of the central carbon atom (δ = 70.90) is very close to that of the central carbon atom of fenestrindan (**1**; δ = 71.00)[2], reflecting the identical number of benzene rings that bridge the central neopentane cores of **2** and **1** in two different arrangements.

The UV spectrum of **2** exhibits the bands that are expected for a centropolyindan with four electronically separated arene units. The α bands appear at λ_{max} = 276.0 nm, exactly the same value as that found for the other centropolyindans containing a conformationally rigid tribenzotriquiancene subunit[1,6,7,12,28]. Once again, this represents a small but significant deviation from those congeners in the structures of which a limited conformational flexibility is preserved, e.g., in **1** and *difuso*-triindan derivatives such as **26**[2,7].

The authors would like to thank Dr. *Andreas Schuster* and Mr. *Dieter Barth* for experimental contributions and assistance in finishing this work. Financial support by the *Deutsche Forschungsgemeinschaft* (Ku 663-1) is also acknowledged. Special appreciation is due to Professor Dr. *H.-F. Grützmacher*, celebrating his jubilee, for his continuous support of our scientific efforts.

Experimental

Melting points (uncorrected): Büchi 512. – IR: Perkin-Elmer 377. – UV: Beckman model 25. – ^{1}H NMR: Bruker AM 300, Bruker WP 80; $CDCl_3$/TMS, if not stated otherwise. – ^{13}C NMR Bruker AM 300 (*J*-modulated spin-echo experiments); $CDCl_3$/TMS, if not stated otherwise. – MS: Finnigan MAT CH 5 DF; EI, 70 eV. – Combustion analyses: Perkin-Elmer 240, LECO CHNS-932 Analysator. – MPLC: Kieselgel LiChroprep Si 60, 25–60 µm (Merck), with Besta E 100 and Besta UV 1. – TLC: Kieselgel 60 on Al foil (Merck, F 254).

(4bα,9aα,10β)-9α-Benzyl-10-phenyl-4b,9,9a,10-tetrahydroindeno[1,2-a]inden-9-one (**8**): To a stirred suspension of 85 mg (3.5 mmol) of sodium hydride in 10 ml of anhydrous 1,2-dimethoxyethane (DME) is added under N_2 within 15 min a solution of 1.0 g (3.4 mmol) of "*endo*"-phenyl ketone **7** in 20 ml of DME. The mixture is heated to 80°C for 30 min, while its color turns deep green, and then cooled to room temp. A solution of 0.58 g (0.40 ml, 3.4 mmol) of benzyl bromide in 10 ml of DME is added dropwise while the color turns yellow-orange, and the mixture is heated under reflux for 19 h. After being cooled to 0°C, the reaction mixture is added dropwise to a vigorously stirred two-phase mixture of ice, excess 5 N H_2SO_4, and diethyl ether, in order to prevent epimerization. Control by TLC ($CHCl_3$) shows that no epimerization to the corresponding "*exo*"-phenyl ketone[13a] (R_f = 0.75) has occurred. After twofold extraction with ether, the combined organic solutions are washed with water, dried with Na_2SO_4, and the solvents are removed under reduced pressure to furnish the crude product as a yellow oil (1.1 g, 85%) which may be used in the cyclization step (see below). Flash chromatography (silica gel; CH_2Cl_2) followed by recrystallization from methanol gives a yellow powder, which is further purified by MPLC (CH_2Cl_2) and recrystallization from *n*-hexane to give (1.1 g (85%) of **8**; m.p. 120–122°C. – IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 3029, 2912, 1713, 1604, 1493, 1462, 1453, 1211, 1031, 938, 760, 747, 699. – ^{1}H-NMR (300 MHz): δ = 7.64 (d, ^3J = 7.6 Hz, 1H), 7.55 (d, ^3J = 7.5 Hz, 1H), 7.46 (td, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H), 7.36 (t, ^3J = 7.5 Hz, 1H), 7.00–7.28 (m, including broadened components, 12H), 6.97 (d, ^3J = 7.5 Hz, 1H), 6.3–6.8 (very br. s, 1H), 4.72 (s, 1H, $CHAr_2$), 4.52 (s, 1H, $CHAr_2$), AB spin system [δ_A = 3.85; δ_B = 3.04 (^2J = –13.5 Hz, 2H, CH_2)]. – ^{13}C NMR (75 MHz): δ = 206.1 (q, C=O), 154.7 (q), 144.7 (q), 142.8 (q), 141.3 (q), 137.3 (q), 134.6 (t), 130.3 (t), 129.5 (t, broadened), 128.2 (t), 127.9 (t), 127.6 (t), 126.7 (t), 126.5 (t), 125.0 (t), 124.4 (t), 123.6 (t), 66.7 (q, C-9a), 61.8 (t, $CHAr_2$), 54.0 (t, $CHAr_2$), 42.5 (s, CH_2). – MS: *m/z* (%) = 386 (7) [$M^{\cdot+}$], 295 (100) [$M^{\cdot+}$ – C_7H_7], 265 (13), 252 (6), 217 (17), 189 (6), 165 (7), 91 (20).

$C_{29}H_{22}O$ (386.5) Calcd. C 90.12 H 5.74
Found C 90.02 H 6.12

(4bα,9β,9aα,10β)-9α-Benzyl-10-phenyl-4b,9,9a,10-tetrahydroindeno[1,2-a]indene-9-ol (**12**): A solution of 780 mg (2.0 mmol) of **8** in 20 ml of anhydrous diethyl ether is added slowly to a suspension of 100 mg (2.5 mmol) of $LiAlH_4$ in 10 ml of diethyl ether stirred under N_2. The mixture is stirred and heated under reflux for 2 h, cooled in an ice bath, and hydrolyzed by careful addition of ice/water and then of 10% H_2SO_4. The mixture is extracted twice with diethyl ether, the combined organic solutions are washed with water and dried with Na_2SO_4, and the solvent is removed. A light-yellow oil (ca. 800 mg, quant.) results, which, according to ^{1}H-NMR spectroscopy, consists essentially of the two isomeric alcohols with R_f = 0.80 and 0.71 (CH_2Cl_2). MPLC (CH_2Cl_2) of the mixture furnishes 280 mg (36%) of the fast-eluting isomer as colorless crystals; m.p. 61–62°C (from CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3563 cm^{-1}, 3066, 3029, 2910, 1493, 1473, 1453, 1265, 1061, 1030, 747, 701. – ^{1}H NMR (300 MHz): δ = 7.59 (d, ^3J = 7.4 Hz, 1H), 7.15–7.37 (m, 14H), 6.82 (d, ^3J = 7.4 Hz, 1H), 6.45 (d, ^3J = 7.2 Hz, 2H, *o*-H, Ph), 5.24 (br. s, 1H, C*H*OH; 80 MHz: d, ^2J = 11.8 Hz), 4.46 (s, 1H, $CHAr_2$), 4.40 (s, 1H, $CHAr_2$), AB spin system [δ_A = 3.36; δ_B = 3.06 (^2J = –13.5 Hz, 2H, CH_2)], 1.50 (br. s, 1H, OH; 80 MHz; d, ^2J = 11.9 Hz). – ^{13}C NMR (75 MHz): δ = 146.8 (q), 145.3 (q), 143.9 (q), 141.6 (q), 141.2 (q), 138.0 (q), 131.2 (t), 130.4 (t), 128.2 (t), 128.0 (t), 127.8 (t), 127.7 (t), 127.5 (t), 127.2 (t), 126.7 (t), 126.4 (t), 126.0 (t), 124.5 (t), 124.1 (t), 122.7 (t), 79.0 (t, CHOH), 65.3 (q, C-9a), 60.6 (t, $CHAr_2$), 55.7 (t, $CHAr_2$), 43.6 (s, CH_2). – MS: *m/z* (%) = 388 (20) [$M^{\cdot+}$], 370 (3), [$M^{\cdot+}$ – H_2O], 310 (16) [$M^{\cdot+}$ – C_6H_6], 297 (42),

296 (55), 279 (45), 265 (11), 219 (40), 203 (12), 202 (14), 193 (12), 191 (21), 189 (16), 165 (23), 91 (100).

$C_{29}H_{24}O$ (388.5) Calcd. C 89.66 H 6.23
Found C 90.94 H 6.79

(4bα,8bα,12bα,12dα)-12d-Benzyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene ["10-Benzyltribenzotriquinacene" (**13**)][1,6] *by Cyclodehydration of* **12**: A solution of 400 mg (1.0 mmol) of **12** in 50 ml of anhydrous toluene is heated with 200 mg of predried ion exchange resin A-15 in a Soxhlet extractor containing 10 g of activated molecular sieves (4 Å). The reaction is monitored by TLC [petroleum ether/ethyl acetate (1:1)] to show complete conversion of the starting material after 4 h. The mixture is cooled to room temp. and filtered, the catalysts is washed with some toluene, and the combined solutions are concentrated to dryness in vacuo to give a yellow, crystalline residue (320 mg, 85%). ^{1}H-NMR spectroscopy (300 MHz) reveals the presence of **13** as the only cyclization product which is obtained pure by careful recrystallization from ethanol/diethyl ether (260 mg, 69%). The physical and spectroscopic data show this product to be identical with those described previously[1,6]. The tribenzotriquinacene **13** is also formed, together with its isomer **16**[13a], by heating a solution of diol **15** in benzene with 5% (w/w) of Amberlyst 15. According to ^{1}H-NMR analysis, the ratio in the crude product mixture is **13**:**16** = 18:5.

(4bα,9aα)-9a-Benzyl-4b,9,9a,10-tetrahydroindeno[1,2-a]indene-9,10-dione (**18**): A solution of 8.25 g (35.3 mmol) of **17**[14,21] in 75 ml of anhydrous toluene is stirred under N_2, while 1.00 g (41.7 mmol) of sodium hydride is added. The brownish solution turns yellow-green. A solution of 6.50 g (38.0 mmol) of benzyl bromide in 125 ml of toluene is added slowly through a dropping funnel, and the mixture is then heated under reflux for 5 h. The cooled, orange-red reaction mixture is hydrolyzed with 10% aqueous HCl, the organic layer is separated, the aqueous layer is extracted several times with diethyl ether, and the combined organic solutions are dried with Na_2SO_4. The solvents are removed in vacuo, and the brown residue is recrystallized from ethanol to give **18** (5.26 g, 46%) as light-brown crystals; m.p. 164–166°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 1720, 1690, 1600, 1445, 1250, 1045, 745, 690. – ^{1}H NMR (300 MHz): δ = 7.69 (d, ^3J = 7.7 Hz, 4H), 7.59 (t, ^3J = 7.5 Hz, 2H), 7.37 (t, ^3J = 7.5 Hz, 2H), 7.01–7.18 (m, 5H), 4.86 (s, 1H, $CHAr_2$), 3.51 (s, 2H, CH_2). – MS: *m/z* (%) = 324 (100) [$M^{\bullet+}$], 323 (12), 307 (19), 295 (16), 247 (15), 233 (27), 165 (19), 91 (30).

$C_{23}H_{16}O_2$ (324.4) Calcd. C 85.16 H 4.97
Found C 85.20 H 4.73

(4bα,9aβ,9aα)-9a-Benzyl-9-hydroxy-9-phenyl-4b,9,9a,10-tetrahydroindeno[1,2-a]inden-10-one (**19**): A suspension of 1.95 g (6.00 mmol) of **18** in 200 ml of diethyl ether is stirred under N_2 while a solution of phenylmagnesium bromide, prepared from 0.15 g (6.25 mmol) of magnesium turnings and 980 mg (6.25 mmol) of bromobenzene in 15 ml of diethyl ether, is added through a dropping funnel. The mixture is heated under reflux for 2 h, allowed to cool, and then carefully hydrolyzed with small portions of water and saturated aqueous NH_4Cl. The mixture is extracted repeatedly with diethyl ether, the combined extracts are dried with Na_2SO_4, and the solvent is removed to give a yellowish oil, which is purified by flash chromatography [petroleum ether/ethyl acetate (3:1)] to give, besides some starting material and the bis-Grignard adduct, ketol **19** (1.13 g, 61%, based on reacted **18**) as colorless crystals; m.p. 174°C. – IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1} (br), 3069, 3019, 2913, 1677, 1599, 1493, 1447, 1223, 1065, 756, 737, 701. – ^{1}H NMR (300 MHz): 7.15–7.55 (m, 13H), 6.85–7.00 (m, 5H), 4.71 (s, 1H, $CHAr_2$), 4.03 (s, 1H, OH), AB spin system [δ_A = 2.91; δ_B = 2.26 (^2J = –13.4 Hz, 2H, CH_2Ph)]. – MS: *m/z* (%) = 402 (23) [$M^{\bullet+}$], 284 (21) [$M^{\bullet+}$ – H_2O], 311 (100) [$M^{\bullet+}$ – C_7H_7], 293 (39), 105 (46), 91 (30), 77 (29).

$C_{29}H_{22}O_2$ (402.5) Calcd. C 86.54 H 5.51
Found C 85.80 H 5.61

(4bα,9aβ,9aα,10aβ)-9a-Benzyl-9-phenyl-4b,9,9a,10-tetrahydroindeno[1,2-a]indene-9,10-diol (**20**): A solution of 700 mg (1.74 mmol) of **19** in 30 ml of anhydrous THF is added dropwise slowly to a suspension of 150 mg (3.9 mmol) of $LiAlH_4$ in 15 ml of THF stirred under N_2, and the mixture is heated under reflux for 4 h. After being cooled, the mixture is carefully hydrolyzed with water and acidified by adding 10% aqueous H_2SO_4 to pH = 3 to dissolve the hydroxides. The layers are separated, and the aqueous phase is saturated with NaCl and extracted several times with diethyl ether. The combined organic solutions are dried with Na_2SO_4, the solvents are evaporated, and the residue is redissolved in hot ethyl acetate. Careful addition of petroleum ether leads to precipitation of **20** (640 mg, 91%) as colorless crystals; m.p. 189–191. – IR (neat): $\tilde{\nu}$ = 3549 cm^{-1} (br.), 3438 (br.), 3027, 2920, 1492, 1474, 1461, 1453, 1445, 1056, 700. – ^{1}H NMR (300 MHz): δ = 7.20–7.35 (m, 6H), 7.00–7.20 (m, 7H), 6.78–6.80 (m, 3H), 6.52 (dd, ^3J = 7.2 Hz, ^4J = 2.3 Hz, 2H), 5.62 (d, ^3J = 5.0 Hz, 1H, 10-H), 4.36 (s, 1H, $CHAr_2$), 3.15 (s, 1H, 9-OH), 2.74 (d, ^3J = 5.0 Hz, 1H, 10-OH), AB spin system [δ_A = 3.16; δ_B = 2.30 (^2J = –14.0 Hz, 2H, CH_2)]. – MS: *m/z* (%) = 404 (1) [$M^{\bullet+}$], 386 (8) [$M^{\bullet+}$ – H_2O], 313 (5) [$M^{\bullet+}$ – C_7H_7], 295 (100) [$M^{\bullet+}$ – (H_2O, C_7H_7)], 265 (8), 252 (5), 217 (12), 165 (7), 91 (34), 77 (17).

$C_{29}H_{24}O_2$ (404.5) Calcd. C 86.11 H 5.98
Found C 85.84 H 6.11

Attempted Cyclodehydration of Diol **20**. – *Formation of 2-(2-Benzyl-3-phenyl-1H-inden-1-yl)benzaldehyde* (**21**): To a solution of 300 mg (740 μmol) of **20** in 50 ml of toluene (or chlorobenzene) is added 0.15 ml of H_3PO_4, and the mixture is heated under reflux. The reaction of the diol is completed within 2 h. After being cooled, the mixture is washed with aqueous Na_2CO_3 and water, dried with Na_2SO_4, and the solvent is evaporated. The oily residue is recrystallized from petroleum ether/ethyl acetate to give an almost colorless solid which, upon standing, reacts to several unidentified products. The solid has been identified as aldehyde **21**. – IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 3030, 2929, 2858, 1693, 1598, 1492, 1453, 757, 700. – ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 10.06 (s, 1H), 6.82–7.89 (m, 18H), 5.64 (s, 1H), AB spin system [δ_A = 4.02; δ_B = 3.42 (^2J = –15.3 Hz, 2H, CH_2)]. – MS: *m/z* (%) = 404 (1) [$M^{\bullet+}$], 386 (17) [$M^{\bullet+}$ – H_2O], 368 (16) [$M^{\bullet+}$ – $2H_2O$], 295 (100) [$M^{\bullet+}$ – (H_2O, C_7H_7)], 265 (29), 252 (14), 217 (16), 202 (14), 189 (13), 165 (18), 91 (36).

(4bα,8bβ)-4b-Phenyl-4b,8b,13,14-tetrahydrodiindeno[1,2-a:2',1'-b]inden-13-one (**26**): To a solution of 250 mg (620 μmol) of **19** in 50 ml of toluene is added 0.5 ml of 85% H_3PO_4, and the mixture is stirred vigorously and heated under reflux for 2 h in a Soxhlet extractor which contains 7 g of molecular sieves (4 Å). After being cooled, the reaction mixture is washed with aqueous Na_2CO_3 and water, the organic layer is separated, dried with Na_2SO_4, and the solvent is evaporated. The product is purified by column chromatography (Si 60; CH_2Cl_2) to give 160 mg (67%) of **26** as colorless crystals; m.p. 227–229°C (from EtOH; R_f(CH_2Cl_2) = 0.45. – IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1}, 3027, 1704, 1601, 1282, 768, 747, 698. – ^{1}H NMR (300 MHz, $CDCl_2CDCl_2$, 90°C): δ = 7.64 (d, ^3J = 7.7 Hz, 1H), 7.55 and 7.53 (overlapping d and t, ^3J = 7.5 Hz each, 1 and 1H), 7.17–7.30 (m, 9H), 6.94–7.1 (m, ^3J = 7 Hz, 3H), 6.49 (d, ^3J = 7.5 Hz, 2H, *o*-H, Ph), 4.69 (s, 1H, 9b-H), AB spin system [δ_A = 3.82; δ_B = 3.22 (^2J = –16.6 Hz, 2H, CH_2)]. – ^{13}C NMR (75 MHz, $CDCl_2CDCl_2$): δ = 206.2 (q, C=O), 154.4 (q), 148.1 (q),

146.9 (q), 143.4 (q), 143.0 (q), 142.1 (q), 136.6 (q), 134.9 (t), 129.4 (t), 128.4 (t), 127.9 (t), 127.6 (t), 127.4 (t), 127.3 (t), 126.6 (t), 125.4 (t), 125.3 (t), 125.1 (t), 124.7 (t), 124.2 (t), 123.9 (t), 75.0 (q), 71.7 (q), 59.4 (t, C-8b), 42.1 (s, C-14). – MS: *m/z* (%) = 384 (100) [$M^{\bullet+}$], 307 (28) [$M^{\bullet+} - C_6H_5$], 293 (12), 278 (12), 276 (11).

$C_{29}H_{20}O$ (384.5) Calcd. C 90.59 H 5.24
Found C 90.75 H 5.42

(4bα,8bβ,13aβ)-4b-Phenyl-4b,8b,13,14-tetrahydrodiindeno[1,2-a:2',1'-b]inden-13-ol (**27**): A solution of 150 mg (0.39 mmol) of **26** in 15 ml of anhydrous THF is added slowly to a stirred suspension of 150 mg (39 mmol) of $LiAlH_4$ in 20 ml of the same solvent. The mixture is heated under reflux for 2 h and then stirred at room temp. for 20 h. The mixture is cooled with ice/water, hydrolyzed by dropwise addition of cold water, and then acidified to pH = 3 by the addition of 10% H_2SO_4. The organic layer is separated, the aqueous layer is extracted repeatedly with CH_2Cl_2, the combined organic solutions are washed with aqueous Na_2CO_3 and then with water. Evaporation of the solvents furnishes a foamy, yellowish residue, which crystallizes upon addition of ethyl acetate to give 123 mg (81%) of **27** as a fine, colorless precipitate, which may be used in the next step without further purification; m.p. 185–188°C. – IR (KBr): $\tilde{\nu}$ = 3557 cm^{-1}, 3064, 3024, 2925, 1598, 1474, 1457, 1444, 1067, 744, 722, 703. – ^1H NMR (300 MHz): δ = 7.46–7.50 (m, 1H), 7.43 (d, ^3J = 7.4 Hz, 1H), 7.05–7.35 (m, 12H), 7.01 (d, ^3J = 7.4 Hz, 1H), 6.93 (d, with fine coupling, 2H), 5.10 (s, 1H, C*H*OH), 4.38 (s, 1H, 9b-H), AB spin system [δ_A = 3.56; δ_B = 3.24 (^2J = –13.4 Hz, 2H, CH_2)], 1.67 (br. s, 1H, OH). – MS: *m/z* (%) = 386 (100) [$M^{\bullet+}$], 368 (63) [$M^{\bullet+} - H_2O$], 295 (31), 291 (27), 265 (25), 105 (39), 91 (30).

$C_{29}H_{22}O$ (386.5) Calcd. C 90.12 H 5.74
Found C 90.18 H 5.68

8bH,12bH-(4b,12d-[1,2]Benzenomethano)dibenzo-[2,3:4,5]pentaleno[1,6-ab]indene ["*trifuso*-Centrotetraindan" (**2**)]. – a) *By Cyclodehydration of* **8**: A suspension of 1.3 g (3.4 mmol) of **8** (purified by flash chromatography as described above) in 50 g of polyphosphoric acid (Merck) is prepared by thoroughly mixing the components at 80°C. The mixture is magnetically stirred and heated at 150°C for 20–24 h. The reaction may be monitored by TLC [petroleum ether/ethyl acetate (5:1)]; its completion depends critically on the control of the reaction temp. The cooled reaction mixture is diluted with water, the resulting mixture is extracted several times with diethyl ether, and the combined extracts are washed with aqueous Na_2CO_3 and water and then dried with Na_2SO_4. Removal of the solvent furnishes a foamy, brown residue, which is dissolved in $CHCl_3$/*n*-hexane and purified by MPLC [chloroform/*n*-hexane (1:1)] to give **2** (530 mg, 43%) as a fine yellowish powder after recrystallization from *n*-hexane.

b) *By cyclodehydration of* **27**: To a solution of 100 mg (260 μmol) of **27** in 30 ml of toluene is added 50 mg of 85% aqueous H_3PO_4. The mixture is heated under reflux for 13 h in a Soxhlet extractor filled with activated molecular sieves (4 Å). After cooling, the reaction mixture is washed with aqueous Na_2CO_3 and then with water, the organic solution is dried and the solvent evaporated. The residue is purified by filtration through a pad of silica gel [chloroform/petroleum ether (2:1)] and then recrystallized from ethanol/dichloromethane to give 48.0 mg (51%) of **2** as colorless crystals; m.p. 204–206°C. – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3024, 2903, 1595, 1471, 1456, 1432, 760, 737, 728, 712. – ^1H NMR (300 MHz): δ = 7.88 (d, ^3J = 7.3 Hz, 1H), 7.76 (d, ^3J = 7.9 Hz, 2H), AA'BB' spin system [δ_A = 7.47 (2H); δ_B = 7.24 (2H, partially overlapped)], 7.41 (d, ^3J = 7.2 Hz, 2H), 7.14–7.28 (m, 7H), 4.82 (s, 2H, $CHAr_2$), 3.74 (s, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 147.61 (q), 147.10 (q), 145.33 (q), 145.23 (q), 141.79 (q), 127.86 (t), 127.73 (t), 127.64 (t), 127.43 (t), 127.34 (t), 124.93 (t), 124.93 (t), 124.05 (t), 123.15 (t), 123.07 (t), 79.12 (q, CAr_3), 70.90 (q, C-*centro*), 65.16 (t, $CHAr_2$), 49.02 (s). – MS: *m/z* (%) = 368 (100) [$M^{\bullet+}$], 367 (18), 291 (16), 290 (12), 289 (17), 145 (8) [$M^{2+} - C_6H_6$].

$C_{29}H_{20}$ (368.5) Calcd. C 94.53 H 5.47
Found C 94.13 H 5.48

☆ Dedicated to Professor *Hans-Friedrich Grützmacher* on the occasion of his 60th birthday.

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