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The First Centrohexaindane Bearing Twelve Functional Groups at Its Outer Molecular Periphery and Related Lower Veratrole-Derived Centropolyindanes

Marco Harig[a] and Dietmar Kuck*[a]

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The first T_d-symmetrical derivative of centrohexaindane bearing twelve functional groups has been synthesized. Six pairs of methoxy groups, each of which belong to six veratrole units fused to the topologically nonplanar (K_5) core, point outwards from the molecular center into the six directions of the Cartesian space. The synthesis of this first dodeca-substituted centrohexaindane was achieved along the "propellane route" established previously for the parent centrohexaindane, but the electron-rich character of some of the intermediates was found to require considerably modified methodology. Two hexamethoxy-substituted centrotriindanes, representing lower congeners of the title compound and bearing three veratrole units, were also synthesized.

Introduction

Centrohexaindane (**1**, Scheme 1), the largest of the parent centropolyindane hydrocarbons, is a highly unusual hydrocarbon because of the topologic non-planarity of its K_5-graph molecular framework[1–4] and the rigidity and strictly orthogonal orientation of the six centrosymmetrically indane units mutually fused therein.[5,6] Centrohexaindane may be considered a "Cartesian hexabenzene" owing to the fact that the aromatic rings are sticking out from the center of the molecule into the six directions of the three-dimensional space.[6] In view of the lively interest in building blocks with rigid, well-defined 3D-geometry of the framework and the pendant functionalities,[7–18] access to derivatives of **1** that bear functional groups at the twelve arene positions of the outer periphery of this $C_{41}H_{24}$ hydrocarbon is a promising goal. In this report, we disclose the synthesis of the first twelve-fold functionalized derivative of **1**, namely 2,3,6,7,10,11,14,15,20,21,26,27-dodecamethoxycentrohexaindane (**2**), bearing this particular, still T_d-symmetrical pattern of peripheral substituents. In this context, the syntheses of two lower congeners of **2**, which also belong to the centropolyindane family,[19] viz. the hexamethoxycentrotriindanes **3** and **4**, are reported as well. Together with the corresponding veratrole-derived tribenzotriquinacenes, such as isomer **5**, published recently[20] and being part of the skeleton of **2** as well, compounds **3** and **4** complement the group of three possible regular centrotriindanes[19,21] bearing three veratrole nuclei in a symmetrical orientation.

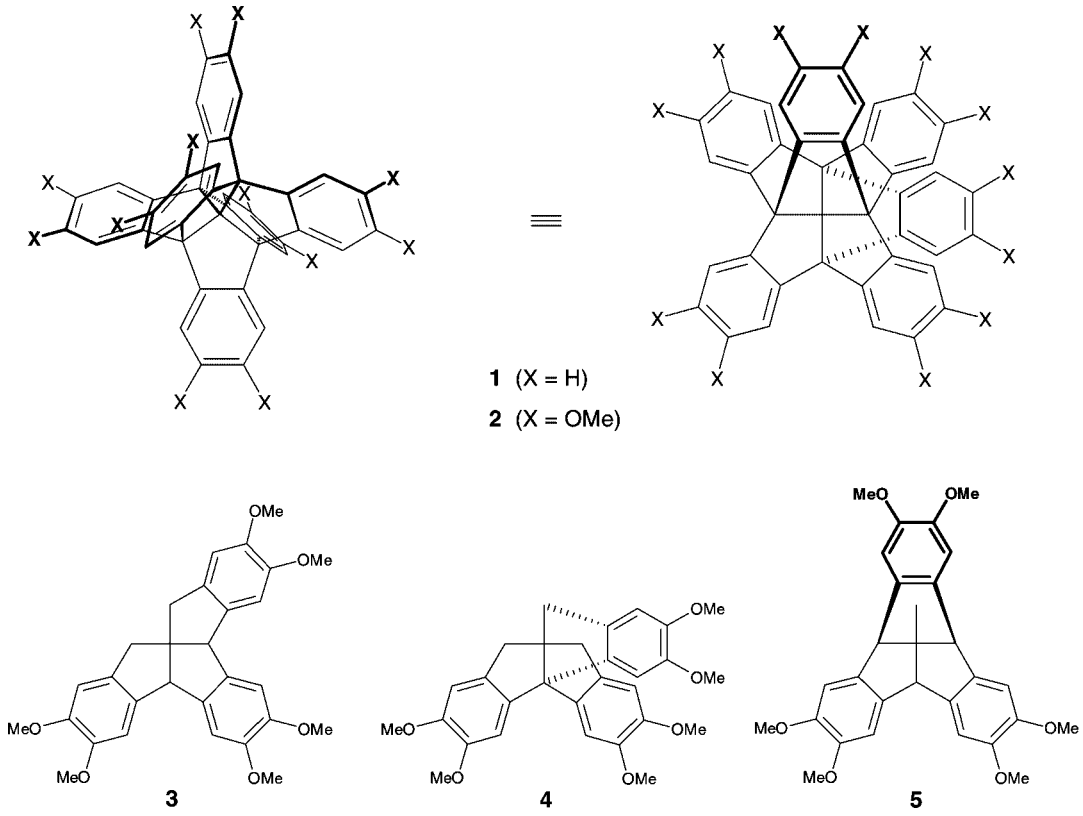
[a] Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany

Results and Discussion

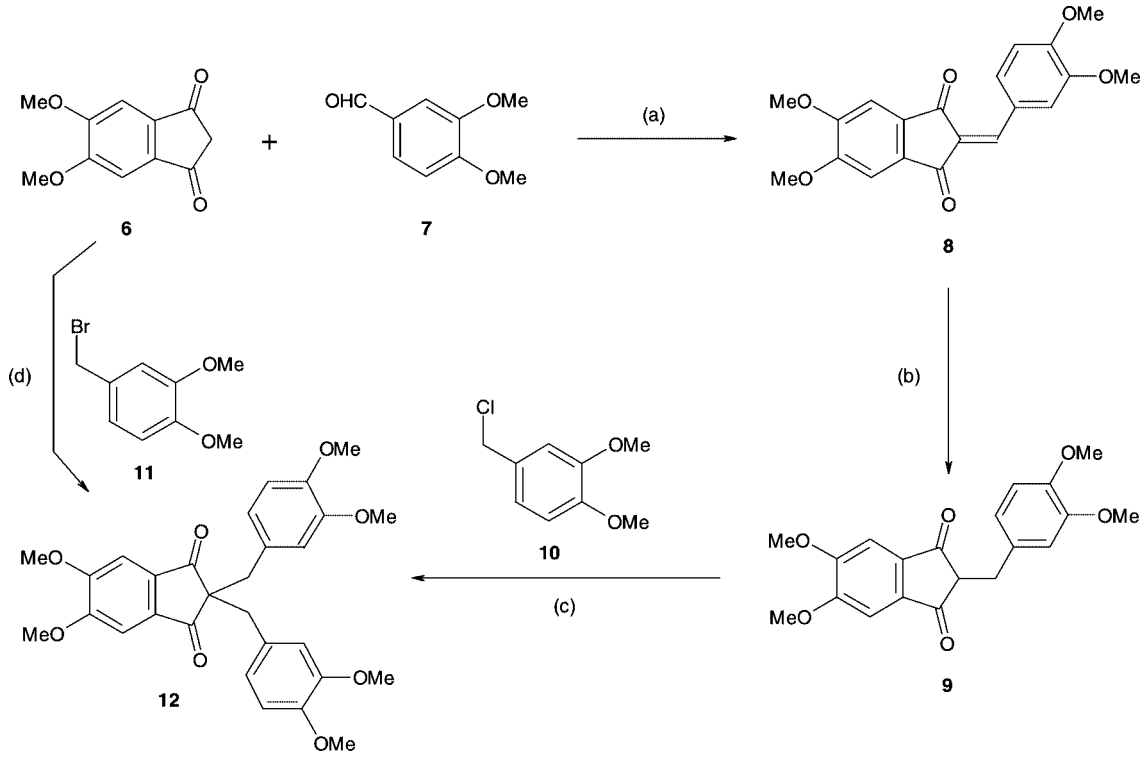
Different from the recently described synthesis of several tetramethoxy-substituted congeners of **1**[22] which was achieved following the "fenestrane route" to the centrohexacyclic framework,[5,19] the title compound **2** was obtained by following the complementary "propellane route",[5,19,23] making use of appropriate synthons derived from veratrole (Scheme 2). Starting from 5,6-dimethoxyindane-1,3-dione (**6**), the preparation of which was improved recently,[20] the conventional sequence, that is, condensation of **6** with 3,4-dimethoxybenzaldehyde (**7**), reduction of the product, chalcone **8**, with sodium borohydride and subsequent benzylation of the dihydrochalcone **9** with dimethoxybenzyl chloride (**10**), furnished the 1,3-indanedione **12** in good overall yield (58% from **6**). The alternative, twofold benzylation of **6** with 3,4-dimethoxybenzyl bromide (**11**) gave the diketone **12** in moderate (38%) yield only.[24]

The diketone **12** represents the key intermediate for the synthesis of two lower congeners of the title centropolyindane **2**, namely the isomeric "angular" ("*difuso*-"[25]) centrotriindane **3** and the propellane-type "triptindane"[26] **4** (Scheme 3). Reduction of **12** with lithium aluminum hydride gave the 1,3-indanediol **13** in good yield and exclusively as the *trans*-isomer, in analogy to previous results with the parent system.[19,27] Subsequent twofold cyclodehydration ("bicyclization")[19b] of the diol **13** by use of orthophosphoric acid in chlorobenzene led to the C_2-symmetrical centrotriindane **3**, the identity of which was unambiguously confirmed by mass spectrometry and NMR spectroscopy.

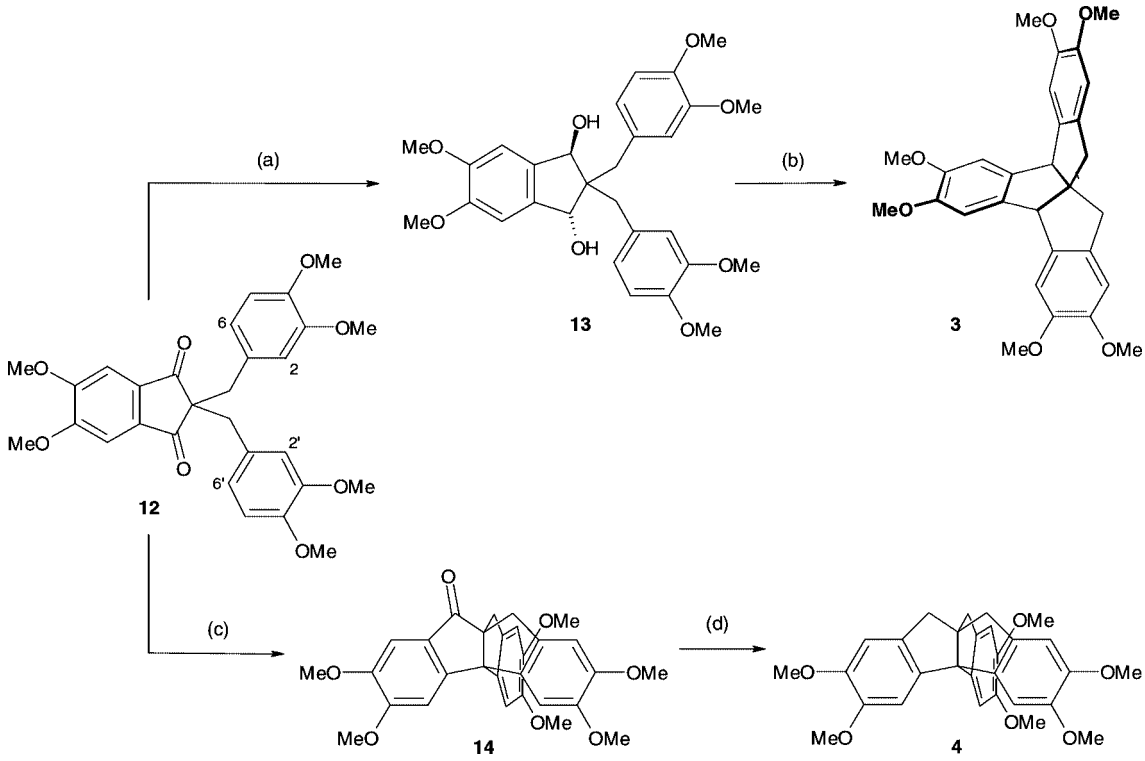
Direct bicyclization of the indanedione **12** by use of orthophosphoric acid in refluxing toluene gave the hexamethoxy-substituted triptindanone **14**, again in good yield. No-



Scheme 1. Centrohexaindanes **1** and **2** and the veratrole-type centrotriindanes **3**–**5**. The latter three formulae are presented strictly as cuttings of the right-hand formula of **2**.



Scheme 2. (a) AcOH, Δ, 2 h, 88%; (b) $NaBH_4$, pyridine, 60 °C, 20 min, 84%; (c) KF/celite 545, acetonitrile, 75 °C, 3 h, 79%; (d) KF/celite 545, acetonitrile, 75 °C, 4 h, 38%.

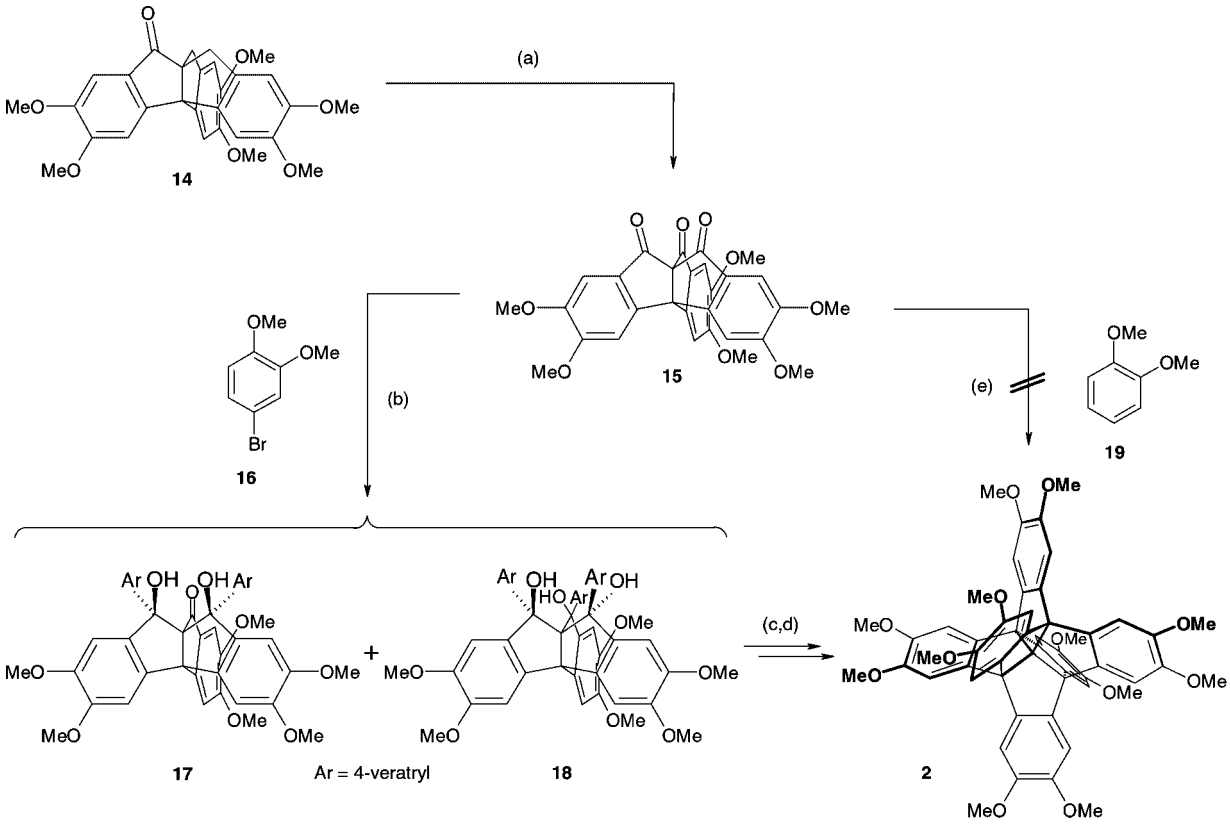


Scheme 3. (a) $LiAlH_4$, THF, Δ, 4 h, 73%; (b) H_3PO_4 (85%), chlorobenzene, Δ, 1 h, 66%; (c) H_3PO_4 (85%), toluene, Δ, 7 h, 73%; (d) $NaBH_4$, CF_3COOH/CH_2Cl_2, 20 °C, 48 h, 68%.

tably, the optimum reaction conditions for this cyclodehydration step were found to be different from those recommended for the analogous synthesis of the parent propellane ketone, which required use of polyphosphoric acid.[19,28] However, this is not surprising in view of the increased electron density of the aromatic species involved in the course of this two-step cyclodehydration. Also remarkable is the finding that, besides the C_s-symmetrical propellane **14**, no other regioisomers were observed in the crude product mixture of the bicyclization. In general, the twofold, sequential electrophilic attack leading to the triptindane skeleton normally involves either of the two *ortho* positions of the substituted benzyl groups, in spite of steric hindrance. This can be used to direct even up to three substituents into the cavity of the triptindane skeleton.[29] In the present case, it is conceivable that, owing to the increased electron density of the aromatic units, attack at the 2-positions of the 3,4-dimethoxybenzyl groups is reversible, whereas attack at the 6-position is not. Finally, reduction of the triptindanone **14** to the hexamethoxycentrotriindane **4** was achieved (Scheme 3). Once again, however, the standard method applied for the parent triptindane,[29] viz. hydrogenolysis of the remaining carbonyl functionality, did not work with the electron-rich ketone **14**. Instead, ionic hydrogenation by use of sodium borohydride in trifluoroacetic acid was found to occur smoothly in this case, giving the hexamethoxytriptindane **4** in good yield (68%). Mass spectrometry and NMR spectroscopy, in particular, confirmed the identity of this polycyclus and its molecular C_{3v} symmetry.[30]

Subsequently, construction of the centrohexacyclic framework of the title compound **2** (Scheme 4) required the conversion of the monoketone **14** into the corresponding triketone, viz. 9,10,11-triptindanetrione **15**. Instead of the two-step bromination/Kornblum oxidation sequence, which had enabled the synthesis of the parent triptindanetrione,[28] direct oxidation of **14** to **15** by use of chromium(VI) oxide was successful. The yields were found to be only moderate (27–52%) but were not optimized.[24b]

The C_{3v}-symmetrical hexamethoxytriptindanetrione **15** is a particular, non-enolizable 1,3,3′-triketone. It bears three rigidly fused indanone units, the carbonyl groups of each being in close mutual vicinity at the C_{3v}-symmetrical [3.3.3]-propellane skeleton. The poor solubility of compound **15** in the usual organic solvents and the high-field shift of its carbonyl carbon atoms (δ = 183.9 ppm, [D_6]DMSO) are remarkable. Due to the presence of the peripheral methoxy groups, the electrophilicity of the triketone should be markedly reduced as compared to the parent triptindanetrione, which was found to undergo threefold addition of nucleophiles, such as phenyllithium and methyl- and benzylmagnesium bromide.[5,23,28,31] In the present case, the addition of three veratryl residues to the triketone **15** was carried out by use of 4-veratrylmagnesium bromide, prepared from 4-bromoveratrole (**16**) in benzene solution at 20 °C. A mixture containing the diolone **17** and the triol **18** was obtained, as



Scheme 4. (a) CrO_3, AcOH/H_2O, 20 °C, 24 h, 27%; (b) 1. Mg, THF, **16**, Δ, 4 h; 2. benzene, 20 °C, 16 h; (c) 1. H_3PO_4 (85%), chlorobenzene, Δ, 2 h; 2. NaH, CH_3I, THF, Δ, 18 h, 6%; (e) see Exp. Sect..

determined in particular by the facile water loss from the highly fragile molecular ions $\mathbf{17}^{\cdot+}$ and $\mathbf{18}^{\cdot+}$ under EI mass spectrometry ($[M - H_2O]^{\cdot+}$ at m/z = 774 and m/z = 912, respectively). Similarly rapid, and highly stereospecific, loss of water is known for other preoriented bridgehead-hydroxylated centropolyindanes and simpler cyclic alcohols.[32–34] Attempts to isolate the triol **18** by chromatography failed; nevertheless, partial separation of the mixture by flash chromatography prior to the next synthesis step proved to be favorable.

Similar to previous cases, threefold cyclodehydration of the triol **18** contained in the mixture with **17** was found to be successful when orthophosphoric acid (85%) was used in chlorobenzene. The product mixture obtained turned out to be very complex, and flash chromatography and recrystallization did not furnish the desired compound in pure form. Rather, the presence of considerable amounts of mostly undefined by-products was indicated by spectroscopy and, moreover, mass spectrometry pointed to the presence of phenolic components in the mixture. In fact, methylation of the crude product mixture by use of a large excess of sodium hydride and iodomethane led to a modified mixture from which, after another careful gravity column chromatographic separation, the title compound, 2,3,6,7,10,11,14,15,20,21,26,27-dodecamethoxycentrohexaindane (**2**) was isolated in pure state, albeit in very low yield (6%), as a colorless solid with a m.p. above 360 °C.

The ^{1}H NMR spectrum of compound **2** is particularly simple and confirms the expected T_d molecular symmetry. It exhibits only two sharp singlets for the 12 *ortho*- and the 36 methoxy protons at δ = 7.14 and δ = 3.89 ppm, respectively, in the ratio of 1:3. Notable is also the extreme deshielding of the central carbon nucleus in the ^{13}C NMR spectrum (δ = 100.0 ppm). The $C_{53}H_{48}O_{12}^{\cdot+}$ molecular ion (m/z 876) is hardly visible under standard EI mass spectrometry conditions due to the low volatility of **2**; however, use of the electrospray (ESI) technique yields sodium adduct ions, $[C_{53}H_{48}O_{12} + Na]^+$ (m/z 899) of high relative abundance.

As the efficiency of the propellane route to **2** turned out to be low, an alternative approach was also studied according to some literature reports on the acylation of veratrole with aromatic ketones.[35–37] Thus, it appeared conceivable that dodecamethoxycentrohexaindane **2** could be accessible by a direct multiple condensation of the propellanetrione **15** with veratrole (**19**), as depicted in Scheme 4. However, in spite of several efforts using different reaction conditions, this strategy proved to be non-productive. For example, treatment of the triketone **15** with a considerable excess of **19** in hexafluorophosphoric acid for several days at ambient temperature gave a mixture of products, a major component of which was found to be 2,3,6,7,10,11-hexamethoxytriphenylene. Use of thiols as catalysts, as suggested by Tadao et al.,[38] did not improve the results either.

Conclusions

Based on strategies that had enabled the access to several parent centropolyindanes, such as centrohexaindane and the centrotriindanes, the syntheses of the corresponding multiply methoxy-functionalized analogues bearing several veratrole nuclei have been studied. The C_2-symmetrical hexamethoxytriindane **3** and the C_{3v}-symmetrical hexamethoxytriptindane **4** were prepared in good overall yields. In this way, and in particular by following the well-established propellane route, the synthesis of the first twelve-fold functionalized centrohexaindane, viz. the T_d-symmetrical dodecamethoxycentrohexaindane **2**, was achieved, albeit in low yields. It has become obvious from these studies that the strongly altered electronic properties of the intermediates involved in the synthesis of highly methoxy-substituted centropolyindanes, as compared to that of the respective parent hydrocarbons, requires application of varied methodology and may also set narrower limits to the efficiency of the synthesis approach. Centrohexaindane **2**, containing six electron-rich veratrole nuclei that are mutually orientated at 90 ° and 180 ° along the three axes of the Cartesian space, represents another topologically non-planar organic compound. Once the efficiency of the synthesis access is improved, the corresponding sixfold catechol analogue could be studied as a new challenge to construct metal ion complexes forming novel orthogonally fused three-dimensional networks.

Experimental Section

General: Melting points (uncorrected): Electrothermal Melting Point Apparatus. Infrared (IR) spectra: Perkin–Elmer 841; KBr pellets or NaCl plates. Nuclear magnetic resonance (NMR) spectroscopy: Bruker DRX 500; spectra referenced to the solvent used. ^{1}H NMR spectra: 500.1 MHz. ^{13}C NMR spectra: 125.8 MHz, broad band decoupled, DEPT and APT method used generally; the notation p, s, t and q refer to the degree of substitution of the C atoms. In some cases, special NMR techniques were used (^{1}H,^{1}H COSY, HMBC, HSQC). EI and/or CI mass spectra and accurate mass measurements: Autospec X sector-field instrument with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a combined EI and CI source. Samples were introduced in aluminum crucibles by a direct inlet rod. Acceleration voltages 8 kV (EI) and 6 kV (CI). Data given as relative intensities as compared to the base peak. Other ionization methods are detailled individually. Perfluorokerosine (PFK) was used as a reference to determine the accurate masses. Combustion analysis: Perkin–Elmer model 240. Thin-layer chromatography: silica gel (Kieselgel 60 F_{254}) on Al foil (Merck). Gravity column chromatography: silica gel (Kieselgel 60, Ø = 0.063–0.200 mm, from J. T. Baker, Macherey–Nagel, or Merck). Flash chromatography: silica gel (Kieselgel 60, Ø < 0.063 mm) for column chromatography (Merck). Alkylation by use of "KF/celite": celite (Kieselgur) 545 (Fluka). All solvents were purified by distillation before use and dried according standard procedures were necessary.[39]

2-(3,4-Dimethoxybenzylidene)-2,3-dihydro-5,6-dimethoxy-1*H*-indene-1,3-dione (8): 5,6-Dimethoxyindane-1,3-dione (**6**) (5.16 g, 25.0 mmol) and 3,4-dimethoxybenzaldehyde (**7**) (4.57 g, 27.5 mmol) were suspended in glacial acetic acid (30 mL) and heated for 2 h under reflux. After cooling to ambient temperature, the precipitate was filtered by suction, washed with glacial acetic acid and recrystallized from the same solvent, to give compound **8** as a yellow solid (7.82 g, 88%), m.p. 238–239 °C (223–224 °C[40]), R_f(hexane/EtOAc, 1:1) 0.59. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.94 (s, 3 H), 4.00 (s, 3 H), 4.01 (s, 3 H), 4.04 (s, 3 H), 6.90 [d, $^3J_{H,H}$ = 8.4 Hz, 1 H], 7.33 (s, 1 H), 7.34 (s, 1 H), 7.59 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.63 (s, 1 H), 8.81 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.0 (p), 56.7 (p), 103.6 (t), 103.7 (t), 110.5 (t), 115.2 (t), 126.88 (q), 126.94 (q), 130.6 (t), 134.9 (q), 137.7 (q), 144.3 (t), 148.7 (q), 153.2 (q), 155.3 (q), 155.4 (q), 189.2 (q), 190.0 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1}, 2842, 1712, 1664, 1578, 1502, 1303, 1271, 1217, 1161, 1143, 1072, 1024, 994, 786. MS (EI, 70 eV): *m/z* (%) = 354 (100) [M$^{\cdot+}$], 328 (55), 269 (18), 255 (33), 254 (28), 253 (20), 223 (24), 215 (20), 206 (18), 204 (20), 203 (41), 202 (31), 184 (17), 168 (37), 151 (75), 141 (40), 139 (24), 128 (21), 115 (38). Accurate mass by EI-MS ($C_{20}H_{18}O_6$): calcd. 354.1103; found 354.1117.

2-(3,4-Dimethoxybenzyl)-2,3-dihydro-5,6-dimethoxy-1*H*-indene-1,3-dione (9): A suspension of 5,6-dimethoxy-2-(3,4-dimethoxybenzylidene)indane-1,3-dione (**8**) (7.09 g, 20.0 mmol) in anhydrous pyridine (20 mL) was stirred while powdered sodium borohydride (0.83 g, 22.0 mmol) was added in small portions. The yellow suspension is converted into a deep-red solution while the temperature of the mixture increases to ca. 60 °C. Stirring was contined for 20 min at 60 °C; then the mixture was cooled to 0 °C. Addition of hydrochloric acid (2 N, 80 mL) precipitated a yellow solid, which was filtered off by suction and then suspended in ethanol (50 mL) under reflux. Finally, the product was filtered by suction and dried to give compound **9** as a light-yellow solid (5.97 g, 84%), m.p. 177–178 °C, R_f(hexane/EtOAc, 1:1) = 0.43. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.25–3.22 (m, 3 H), 3.73 (s, 3 H), 3.76 (s, 3 H), 3.95 (s, 6 H), 6.65–6.59 (m, 3 H), 7.19 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 32.0 (s), 54.7 (t), 55.62 (p), 55.67 (p), 56.6 (p, 2C), 103.0 (t, 2C), 110.7 (t), 112.7 (t), 121.7 (t), 129.5 (q), 137.8 (q, 2C), 147.5 (q), 148.3 (q), 155.7 (q, 2C), 199.3 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2961, 2911, 2841, 1729, 1697, 1584, 1497, 1338, 1301, 1271, 1243, 1027, 867, 844, 808. MS (EI, 70 eV): *m/z* (%) = 356 (100) [M$^{\cdot+}$], 328 (14), 325 (11), 287 (8), 176 (5), 164 (6), 151 (93), 136 (5), 107 (5). Accurate mass by EI-MS ($C_{20}H_{20}O_6$): calcd. 356.1260; found 356.1267. $C_{20}H_{20}O_6$ (356.38): calcd. C 67.41, H 5.66; found C 68.29, H 5.40.

5,6-Dimethoxy-2,2-bis(3,4-dimethoxybenzyl)-2,3-dihydro-1*H*-indene-1,3-dione 12. A. By Single Benzylation of 9: A solution of 5,6-dimethoxy-2-(3,4-dimethoxybenzyl)indane-1,3-dione (**9**) (10.7 g, 30.0 mmol) in acetonitrile (p.a. quality, 100 mL) was stirred while 3,4-dimethoxybenzyl chloride (**10**)[41] (14.0 g, 75.0 mmol) and potassium fluoride/celite 545 (20.0 g)[42] were added. The suspension was stirred and heated to 75 °C (bath temperature) for 3 h. The mixture was cooled to ambient temperature and then filtered through a sintered glass filter, and the residue was washed with small portions of acetonitrile until decolorization. The solvent was removed under reduced pressure and the residue was recrystallized from methanol/glacial acetic acid (9:1). Satisfying purification requires recrystallization at ambient temperature for several days. Yield of compound **12**: 12.0 g (79%); m.p. 136–137 °C, R_f(hexane/EtOAc, 1:1) 0.25. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.17 (s, 4 H), 3.71 (s, 6 H), 3.74 (s, 6 H), 3.88 (s, 6 H), 6.54–6.53 (m, 6 H), 6.97 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 41.0 (s), 55.6 (p), 55.7 (p), 56.5 (p), 62.1 (q), 102.3 (t), 110.5 (t), 112.9 (t), 122.0 (t), 128.2 (q), 138.2 (q), 147.5 (q), 148.0 (q), 155.5 (q), 202.7 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2948, 2840, 1735, 1696, 1581, 1517,

1466, 1443, 1421, 1363, 1305, 1261, 1240, 1222, 1163, 1138, 1119, 1039, 1026, 1003, 877, 863, 850, 807, 623. MS (EI, 70 eV): *m/z* (%) = 506 (20) [M$^{\cdot+}$], 355 (16), 287 (7), 151 (100), 107 (10), 106 (7). $C_{29}H_{30}O_8$ (506.56): calcd. C 68.76, H 5.97; found C 68.76, H 5.76.

B. By Twofold Benzylation of 6: To a solution of 5,6-dimethoxyindane-1,3-dione (**6**) (1.03 g, 5.00 mmol) in acetonitrile (p.a. quality, 20 mL) were added 3,4-dimethoxybenzyl bromide (**11**) (2.80 g, 15.0 mmol) and 8.0 g of potassium fluoride on celite 545.[42] This suspension was stirred and heated to 75 °C (bath temperature) for 4 h. The mixture was cooled to ambient temperature and then filtered through a sintered glass filter, the residue was washed with small portions of acetonitrile until it was decolorized. After removal of the solvent under reduced pressure, the residue was recrystallized from methanol/chloroform (9:1). Slow recrystallization of the product over several days gave compound **12** as yellow crystals (968 mg, 38%). The properties and analytical data of the product were found to be identical with those of the product described above.

C. 5,6-Dimethoxy-2-(3,4-dimethoxybenzyl)-2-[3,4-dimethoxy-6-(3,4-dimethoxybenzyl)benzyl]-2,3-dihydro-1*H*-indene-1,3-dione (A, see ref.[24]): During the two syntheses described above, varying amounts of a by-product were formed as a compound that was difficult to separate but which could be isolated by column chromatography using hexane/ethyl acetate (1:1) as the eluent. Use of 3,4-dimethoxybenzyl bromide (**11**) as the alkylation reagent produced markedly more amounts of **A** than use of 3,4-dimethoxybenzyl chloride (**10**). Compound **A** was obtained as a yellow, noncrystallizing oil, R_f(hexane/EtOAc, 1:1) = 0.16. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.16 (s, 2 H), 3.19 (s, 2 H), 3.66 (s, 3 H), 3.67 (s, 3 H), 3.71 (s, 3 H), 3.73 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H), 3.89 (s, 6 H), 3.98 (s, 2 H), 6.41 (s, 1 H), 6.54–6.52 (m, 5 H), 6.65 (s, 1 H), 6.76 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.00 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 37.0 (s), 37.6 (s), 41.2 (s), 55.53 (p), 55.57 (p), 55.63 (p), 55.8 (p), 55.9 (p), 56.5 (p, 2 C), 62.0 (q), 102.3 (t, 2 C), 110.5 (t), 111.0 (t), 111.9 (t), 112.9 (t), 113.4 (t, 2 C), 120.3 (t), 122.1 (t), 126.4 (q), 128.1 (q), 131.3 (q), 133.9 (q), 138.3 (q, 2 C), 146.5 (q), 147.1 (q), 147.3 (q), 147.5 (q), 148.0 (q), 148.8 (q), 155.6 (q, 2 C), 202.9 (q, 2 C) ppm. The resonances of two methoxy-carbon nuclei were found to be isochronous. IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1}, 2941, 2839, 1728, 1693, 1578, 1513, 1464, 1358, 1304, 1263, 1141, 1115, 1098, 1028, 1000, 869, 733. MS (CI, isobutane): *m/z* (%) = 657 (37) [M + H]$^+$, 519 (42), 367 (7), 355 (7), 341 (6), 301 (19), 300 (10), 287 (37), 269 (10), 151 (100), 137 (18). Accurate mass by EI-MS ($C_{38}H_{40}O_{10}$): calcd. 656.2621; found 656.2617.

***trans*-5,6-Dimethoxy-2,2-bis(3,4-dimethoxybenzyl)-2,3-dihydro-1*H*-indene-1,3-diol (13):** A suspension of lithium aluminum hydride (607 mg, 16.0 mmol) in anhydrous tetrahydrofuran (40 mL) was stirred while a solution of 5,6-dimethoxy-2,2-bis(3,4-dimethoxybenzyl)indane-1,3-dione (**12**) (2.03 g, 4.00 mmol) in 40 mL of the same solvent was added slowly. The mixture was heated under reflux for 4 h. Subsequently, the major part of the solvent was removed under reduced pressure and replaced by diethyl ether (100 mL). This mixture was stirred and cooled in an ice/water bath while a saturated aqueous solution of sodium chloride (50 mL) was added cautiously. The organic layer was separated and the aqueous layer was extracted thrice with diethyl ether (50 mL each). The combined organic solutions were washed with brine, dried with sodium sulfate and concentrated to dryness. The residue was recrystallized from toluene to give compound **13** as a colorless solid (1.49 g, 73%), m.p. 120 °C, R_f(hexane/EtOAc, 1:1) = 0.10. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.37 (br., 2 H), *AB* (δ_A = 2.95, δ_B = 2.87, J_{AB} = –14.1 Hz, 4 H), 3.83 (s, 6 H), 3.85 (s, 6 H), 3.86 (s, 6 H), 5.11 (s, 2 H), 6.76 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H), 6.790 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 6.791 (s, 2 H), 6.82 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.9 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 36.9 (s), 55.79 (p), 55.88 (q), 55.92 (p), 56.1 (p), 79.3 (t), 107.1 (t), 111.1 (t), 113.9 (t), 122.3 (t), 131.5 (q), 135.1 (q), 147.5 (q), 148.6 (q), 149.8 (q) ppm. IR (KBr): $\tilde{\nu}$ = 3403 cm^{-1}, 2994, 2929, 2835, 1606, 1588, 1513, 1449, 1418, 1345, 1264, 1186, 1156, 1141, 1114, 1071, 1027, 980, 872, 856, 821, 813, 769. MS (EI, 70 eV): *m/z* (%) = 510 (1) [M$^{\cdot+}$], 474 (37), 341 (9), 323 (8), 151 (22), 92 (70), 91 (93), 86 (60), 84 (100), 65 (16), 63 (11), 51 (57). $C_{29}H_{34}O_8$ (510.59): calcd. C 68.22, H 6.71; found C 68.19, H 6.70.

2,3,6,7,10,11-Hexamethoxy-4b,8b,13,14-tetrahydrodiindeno[1,2-*a*:2′,1′-*b*]indene (3): In a reaction apparatus equipped with a Thiele–Pape extractor containing molecular sieves (4 Å), a mixture of orthophosphoric acid (85%, 0.50 mL) and chlorobenzene (50 mL) was heated under reflux while a solution of *trans*-5,6-dimethoxy-2,2-bis(3,4-dimethoxybenzyl)indane-1,3-diol (**13**) (2.04 g, 4.00 mmol) in chlorobenzene (50 mL) was added slowly. After addition was completed, heating was continued for 1 h. Later the mixture was cooled, aqueous sodium hydroxide (2 N, 100 mL) was added. The organic layer was separated and the aqueous layer was extracted thrice with dichloromethane (100 mL each). The combined organic layers were washed with water and dried with sodium sulfate and the solvent was evaporated. The residue was recrystallized from methanol to give compound **3** as a colorless solid (1.26 g, 66%), m.p. 202–203 °C, R_f(hexane/EtOAc, 1:1) = 0.25. ^{1}H NMR (500.1 MHz, $CDCl_3$): AB (δ_A = 3.28, δ_B = 3.09, J_{AB} = –16.0 Hz, 4 H), δ = 3.83 (s, 6 H), 3.84 (s, 6 H), 3.87 (s, 6 H), 4.32 (s, 2 H), 6.72 (s, 2 H), 6.83 (s, 2 H), 6.85 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 44.5 (s), 56.0 (p), 56.17 (p), 56.21 (p), 62.1 (t), 64.7 (q), 107.6 (t, 4 C), 108.0 (t), 134.3 (q), 135.7 (q), 136.0 (q), 148.4 (q), 148.7 (q), 148.9 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1}, 2835, 1607, 1502, 1464, 1334, 1275, 1253, 1223, 1191, 1099, 1091, 1072, 1030, 986, 845. MS (EI, 70 eV): *m/z* (%) = 474 (100) [M$^{\cdot+}$], 459 (8), 443 (7), 336 (7), 323 (14), 151 (8). $C_{29}H_{30}O_6$ (474.56): calcd. C 73.40, H 6.37; found C 73.33, H 6.40.

2,3,6,7,13,14-Hexamethoxy-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]inden-9-one (2,3,6,7,13,14-Hexamethoxytriptindan-9-one, 14): A solution of 5,6-dimethoxy-2,2-bis(3,4-dimethoxybenzyl) indane-1,3-dione (**12**) (5.07 g, 10.0 mmol) in toluene (p.a. quality, 100 mL) was stirred in a reaction apparatus equipped with a Thiele–Pape extractor containing molecular sieves (4 Å). Orthophosphoric acid (85%, 2.00 mL) was added and the mixture was heated under reflux for 7 h. The mixture was cooled, the organic layer was separated and the residue was diluted with water (100 mL). The aqueous solution was extracted thrice with dichloromethane; the combined organic solutions were washed with water, dried with sodium sulfate, and the solvent was evaporated. The residue was recrystallized from cyclohexane to give compound **14** as a light-yellow solid (3.54 g, 73%), m.p. 127–128 °C, R_f(hexane/EtOAc, 1:1) = 0.18. ^{1}H NMR (500.1 MHz, $CDCl_3$): *AB* (δ_A = 3.45, δ_B = 3.17, J_{AB} = –16.8 Hz, 4 H), δ = 3.78 (s, 6 H), 3.84 (s, 3 H), 3.91 (s, 6 H), 4.02 (s, 3 H), 6.65 (s, 2 H), 7.12 (m, 3 H), 7.17 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 40.7 (s), 56.0 (p, 2 C), 56.1 (p), 56.3 (p), 56.8 (p, 2 C), 69.5 (q), 72.9 (q), 105.0 (t), 105.3 (t), 107.1 (t, 2 C), 108.4 (t, 2 C), 127.5 (q), 133.8 (q, 2 C), 136.2 (q, 2 C), 148.9 (q, 2 C), 149.86 (q, 2 C), 149.95 (q), 152.9 (q), 156.0 (q), 207.3 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1}, 2853, 1697, 1604, 1500, 1465, 1420, 1407, 1300, 1269, 1221, 1121, 1097, 1073, 1029, 1008, 877, 776. MS (EI, 70 eV): *m/z* (%) = 488 (100) [M$^{\cdot+}$], 487 (55), 473 (5), 337 (12), 336 (6), 288 (27), 287 (50), 257 (11), 244 (6), 238 (14), 223 (8), 185 (7), 165 (18), 161 (6), 151 (32), 149 (12). $C_{29}H_{28}O_7$ (488.54): C 71.30, H 5.78; found C 71.41, H 6.06.

2,3,6,7,13,14-Hexamethoxy-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]indene (2,3,6,7,13,14-Hexamethoxytriptindane, 4): A solution of 2,3,6,7,13,14-hexamethoxytriptindan-9-one (**14**) (2.44 g, 5.00 mmol) in trifluoroacetic acid (15.0 mL) and dichloromethane (15.0 mL) was stirred under argon while sodium borohydride (1.13 g, 30.0 mmol) was added in small pieces, such that the hydrogen evolution was kept well under control. The mixture was stirred for 24 h at ambient temperature. Further sodium borohydride (1.13 g, 30.0 mmol) was added in small pieces. After stirring was continued for additional 24 h, ice/water was added and the solution was brought to pH > 7 by adding solid sodium hydroxide. The solution was extracted five times with dichloromethane (50 mL each). The combined organic solutions were washed twice with saturated aqueous sodium chloride (50 mL each), dried with sodium sulfate, and the solvent was evaporated. The residue was recrystallized from cyclohexane or methanol to give compound **4** as a light-brown, crystalline solid (1.62 g, 68%), m.p. 224–225 °C, R_f(hexane/EtOAc, 1:1) = 0.36. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.03 (s, 6 H), 3.81 (s, 9 H), 3.90 (s, 9 H), 6.71 (s, 3 H), 7.00 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 43.2 (s), 56.0 (p), 56.5 (p), 65.4 (q), 76.6 (q), 107.2 (t), 108.4 (t), 134.7 (q), 137.4 (q), 148.7 (q), 148.9 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2997 cm^{-1}, 2936, 2839, 1607, 1503, 1463, 1317, 1279, 1220, 1192, 1113, 1078, 1025, 778. MS (EI, 70 eV): *m*/*z* (%) = 474 (100) [M$^{\cdot+}$], 460 (17), 355 (4), 323 (72), 309 (9), 293 (5), 265 (4), 237 (5), 151 (33). $C_{29}H_{30}O_6$ (474.56): calcd. C 73.40, H 6.37; found C 73.30, H 6.35.

2,3,6,7,13,14-Hexamethoxy-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]indene-9,10,11-trione (2,3,6,7,13,14-Hexamethoxytriptindane-9,10,11-trione, 15): A solution of 2,3,6,7,13,14-hexamethoxytriptindan-9-one (**14**) (2.44 g, 5.00 mmol) in glacial acetic acid (90 mL) was stirred while a solution of chromium(VI) oxide (3.00 g, 30.0 mmol) in water (10 mL) was added slowly. Stirring at ambient temperature was continued for 24 h. Then the mixture was concentrated to dryness in vacuo, water (50 mL) was added to give a precipitate which was filtered off by suction. The filtrate was extracted thrice with dichloromethane (50 mL), the combined organic solutions were washed with water (20 mL), dried with sodium sulfate, added to the product that had precipitated, and the solvent was removed under reduced pressure. The solid residue was recrystallized from ethyl acetate to give compound **15** as a colorless solid (707 mg, 27%), m.p. > 360 °C, R_f(EtOAc) = 0.21. ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 3.75 (s, 9 H) 4.10 (s, 9 H), 7.02 (s, 3 H), 8.03 (s, 3 H) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 55.9 (p), 57.4 (p), 60.6 (q), 86.9 (q), 105.2 (t), 107.7 (t), 125.4 (q), 148.4 (q), 150.8 (q), 156.8 (q), 183.9 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1}, 2839, 1742, 1591, 1500, 1464, 1413, 1299, 1235, 1092, 1013, 871, 783. MS (EI, 70 eV): *m*/*z* (%) = 516 (100) [M$^{\cdot+}$], 488 (12), 485 (9), 473 (7), 457 (5), 258 (5), 149 (6), 44 (6), 40 (7). $C_{29}H_{24}O_9$ (516.51): calcd. C 67.44, H 4.68; found C 67.14, H 4.95.

2,3,6,7,10,11,14,15,20,21,26,27-Dodecamethoxy-4b,12b-[1′,2′]:8b,16b[1″,2″]dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno-[1,6-*cd*]pentalene (2,3,6,7,10,11,14,15,20,21,26,27-Dodecamethoxycentrohexaindane, 2): 4-Bromoveratrole (**16**) (43.4 g, 200 mmol) was heated under argon with magnesium turnings (4.86 g, 200 mmol) and a few crystals of iodine in anhydrous tetrahydrofuran (600 mL) to reflux for 4 h. The solvent was removed under reduced pressure and the residue was partially redissolved in anhydrous benzene (500 mL). This mixture was stirred while 2,3,6,7,13,14-hexamethoxytriptindane-9,10,11-trione (**15**) (1.03 g, 2.00 mmol) was added. Stirring under argon was continued for 16 h at ambient temperature by use of a gas-tight mechanical stirrer. Then saturated aqueous ammonium chloride (300 mL) was added cautiously. The organic layer was separated and the aqueous layer was extracted thrice with dichloromethane (200 mL). The combined organic solutions were washed with water, dried with sodium sulfate, and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography with chloroform as the eluent to remove veratrol (**19**), bromoveratrole (**16**) and 3,3′,4,4′-tetramethoxybiphenyl. The fraction containing the addition products (**17** and **18**) was eluted by use of ethyl acetate and used without isolation of the triol **18** in the next conversion.

A mixture of orthophosphoric acid (85%, 4.00 mL) and chlorobenzene (200 mL) was heated to reflux for 30 min in an apparatus that was equipped with a Thiele–Pape extractor filled with molecular sieves (4 Å). The mixture was stirred and continuously heated to reflux while a solution of the product mixture containing the triptindane derivatives **17** and **18** (see above) in chlorobenzene (50 mL) was added dropwise. After the addition was completed, heating was continued for another 1.5 h. The mixture was cooled, the solvent was removed under reduced pressure and the residue was diluted with dichloromethane (300 mL). The organic layer was washed twice with aqueous sodium hydroxide (2 n, 100 mL) and then with water (100 mL), dried with sodium sulfate, and concentrated to dryness. The residue was subjected to flash chromatography with hexane/ethyl acetate (1:2) as the eluent. The fraction containing the centrohexaindane products, including **2**, was eluted by use of ethyl acetate and the crude product was recrystallized from ethanol.

The solid obtained in this way was redissolved in anhydrous tetrahydrofuran (100 mL) and this solution was added to sodium hydride (60% in paraffin, 300 mg, 12.5 mmol). The mixture was heated under reflux for 2.5 h and then cooled to ambient temperature. Then iodomethane (3.55 g, 25.0 mmol) was added and the mixture was heated under reflux for an additional 16 h. After cooling in an ice/water bath, the excess of sodium hydride was destroyed first by cautious addition of water and then of aqueous hydrochloric acid (2 N). The solvent was removed under reduced pressure and the residue was diluted with dichloromethane (100 mL). This solution was washed with aqueous sodium thiosulfate (10%) and then with water, dried with sodium sulfate, and concentrated to dryness in vacuo. The residue was subjected to column chromatography with chloroform/ethyl acetate (3:1) to give compound **2** as a colorless solid (98.0 mg, 6%), m.p. > 360 °C, R_f(hexane/EtOAc, 1:2) = 0.19, R_f($CHCl_3$/EtOAc, 3:1) = 0.25. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.89 (s, 36 H), 7.14 (s, 12 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.7 (p), 100.0 (*centro*-C), 71.7 (q), 107.6 (t), 140.2 (q), 150.2 (q) ppm. IR (KBr): $\tilde{\nu}$ = 2937 cm^{-1}, 2855, 1610, 1494, 1461, 1312, 1287, 1235, 1141, 1079, 1029, 994. MS (EI, 70 eV): *m*/*z* (%) = 876 [M$^{\cdot+}$] (very low ion current). MS (ESI): *m*/*z* = 899 [M + Na]$^+$. $C_{53}H_{48}O_{12}$ (876.97): calcd. C 72.59, H 5.52; found C 70.88, H 6.28. Accurate mass by ESI-MS ($C_{53}H_{48}O_{12}$ + Na$^+$) calcd. 899.3043; found 899.3020.

Attempts to Synthesize Centrohexaindane 2 from Triptindanetrione 15 and Veratrole: The following experiments were carried out: (A) Triptindanetrione **15** was treated with an excess of veratrole (**19**) in a dichloromethane solution in the presence of anhydrous aluminum trichloride at 20 °C for 24 h. (B) Use of orthophosphoric acid (85%), Amberlyst 15, or concentrated sulfuric acid, all in chlorobenzene as the solvent. (C) Use of pure **19** as the solvent and concentrated sulfuric acid, or aluminum tribromide, or trifluoroacetic acid, or hexafluorophosphoric acid as the catalyst, all experiments being run at 20 °C for 16 h. (D) Use of pure **19** as the solvent and concentrated sulfuric acid, thiophenol at 65 °C for 5 h. Unfortunately, centrohexaindane **2** could not be detected (by mass spectrometry and ^{1}H NMR spectrometry) in, or isolated from, any of the product mixtures obtained from these experiments.

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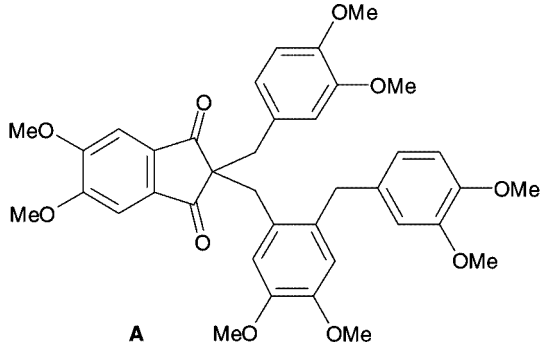
[24] a) In both of these synthesis routes, formation of an unexpected product of threefold benzylation was observed in varying amounts, to which the structure of 5,6-dimethoxy-2-(3,4-dimethoxybenzyl)-2-[3,4-dimethoxy-6-(dimethoxybenzyl)benzyl]-indane-1,3-dione **A** was assigned; see Exp. Sect. and ref.[24b]; b) M. Harig, Doctoral Thesis, University of Bielefeld, **2002**.



A

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