2,3,6,7,10,11-Hexamethoxytribenzotriquinacene: Synthesis, Solid-State Structure, and Functionalization of a Rigid Analogue of Cyclotriveratrylene

Marco Harig,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] and Dietmar Kuck*[a]

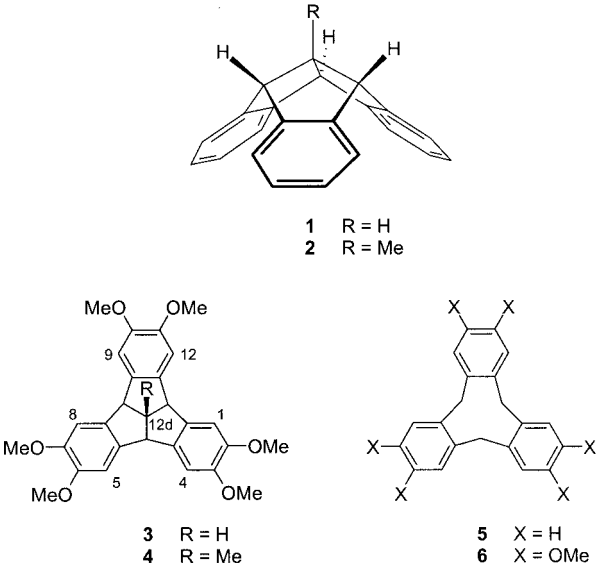
Dedicated to Professor Karsten Krohn (Universität Paderborn) on the occasion of his 60th birthday

Keywords: Convex/concave molecules / Cyclotriveratrylenes / Indane derivatives / Cyclization / Aromatic substitution

The syntheses of several tribenzotriquinacenes bearing six methoxy groups at the outer peripheral positions of the aromatic rings are reported. The *centro*-methyl derivative is accessible in surprisingly good yield through two-fold cyclodehydration in the final step of a synthesis route which requires special care in the preparation of some electron-rich key intermediates, such as 5,6-dimethoxy-2-methylindane-1,3-dione and bis(3,4-dimethoxyphenyl)methanol. X-ray single-crystal structure analysis of the *centro*-methyl derivative confirms its C_{3v}-symmetrical molecular structure but, at variance from the parent *centro*-methyltribenzotriquinacene and the similarly shaped cyclotriveratrylene, the hexamethoxytribenzotriquinacene analog does not form columnar stacks in the solid state. Functionalization of the three benzhydrylic bridgehead positions leads to the tetramethyl analog and the bridgehead triol in good yields. In contrast, attempts to functionalize the *ortho* positions by nitration or bromination mainly give rise to ring cleavage through electrophilic *ipso* attack, which parallels the behavior of cyclotribenzylenes and cyclotriveratrylenes.

Introduction

Prominent areas of supramolecular chemistry deal with C_3-and C_{3v}-symmetrical building blocks.[1−3] Among these, derivatives of catechol ethers, such as 2,3,6,7,10,11-hexamethoxytriphenylene[4] and 2,3,7,8,12,13-hexamethoxytruxene,[5] have been investigated in detail, mostly because of their propensity to form columnar aggregates in liquid crystals. Other variants of this type bear a bent, convex/concave molecular shape.[6] However, most of the investigations are centered on motifs derived from the cyclotriveratrylene **6**.[7−9] Cyclotriveratrylenes are best suited for the construction of cryptophanes, speleands, cavitands and tentacular molecules.[7a,10] Notwithstanding its considerable advances, the chemical variability of the cyclotriveratrylenes as molecular building blocks is limited mostly to the derivatization of the peripheral positions of their aromatic nuclei; the first syntheses of several monofunctionalized (and thus chiral) cyclotribenzylenes have recently been reported by Schmuck and Wienand.[11]



Scheme 1. Tribenzotriquinacene (**1**) and its *centro*-methyl derivative **2** (perspective views), the respective hexamethoxy derivatives **3** and **4**, and cyclotribenzylene (**5**) and cyclotriveratrylene **6**

In contrast, tribenzotriquinacenes, such as the parent hydrocarbon **1** [12] and the *centro*-methyl derivative **2**,[12a,13−15] which may be regarded as rigidified variants of cyclotribenzylene (**5**),[16] have been explored mainly with respect to the

[a] Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany
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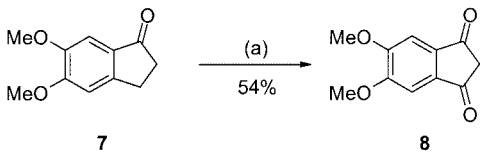
vast potential of their bridgehead substitution and functionalization.[12b,17−20] However, we recently demonstrated that the complete substitution of the six outer peripheral arene positions can be achieved to yield 2,3,6,7,10,11-hexahalo- and 2,3,6,7,10,11-hexanitrotribenzotriquinacenes as key intermediates to access a variety of interesting derivatives bearing extended, convex/concave molecular frameworks.[20,21] Unfortunately, subsequent introduction of six methoxy or hydroxy substituents at the peripheral positions of tribenzotriquinacene proved to be unsuccessful.[22] Therefore, we undertook an extended study to synthesize two 2,3,6,7,10,11-hexamethoxytribenzotriquinacenes, the "nor" compound **3** and the *centro*-methyl analog **4**, by pursuing essentially the routes developed for the syntheses of the parent hydrocarbons.[12−15] However, due to the drastically different electronic properties of the veratrol nuclei present in the various starting materials and intermediates of the synthesis, numerous difficulties had to be overcome. The X-ray structure analysis and some functionalization reactions of **4** have also been carried out.

Results and Discussion

Synthesis of 2,3,6,7,10,11-Hexamethoxytribenzotriquinacene (3)

With respect to the two independent syntheses of the parent hydrocarbon **1**,[12−15] we investigated the potential of these strategies to prepare the hexamethoxy congener **3**.[23] Only one of these, which is called here the "(benzhydryl)indanedione route", turned out to be viable with reasonable efficiency,[24] though being associated with a low overall yield similar to the parent compound **1**.[12a] However, the same strategy was found to be surprisingly efficient when applied to the *centro*-methyl derivative **4**, as described later in this paper. The synthesis of **3** will be reported first.

The first key intermediate in the chemistry of veratrole-type centropolyindanes, which have been studied recently in a broader context,[23] is 5,6-dimethoxyindane-1,3-dione (**8**). Three different methods have been described in the literature to synthesize this compound.[25] They suffer in part from incomplete characterization, poor availability of the starting materials or difficulties to produce larger amounts of **8** even on the laboratory scale. As the result of extended efforts,[26] we found that the indane-1,3-dione **8** is obtained most efficiently by oxidation of the corresponding indan-1-one **7**[27] with CrO_3 in acetic acid in up to 54% yield (Scheme 2). The oxidation of benzylic methylene groups with chromium(IV) oxide is well known, in particular for *para*-alkylanisoles;[28−30] however, the feasibility of this reaction varies strongly in individual cases. For example, we found that 6-methoxyindan-1-one, as a less electron-rich analog of **7**, does not give the corresponding diketone, 5-methoxyindane-1,3-dione, under the same conditions. Besides the starting ketone, only decomposition products were formed.



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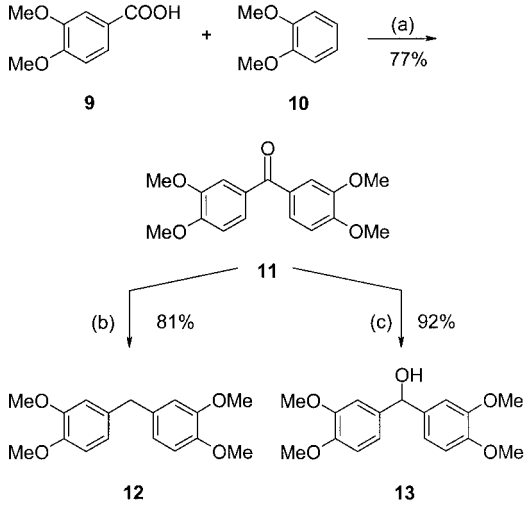
Scheme 2. (a) CrO_3, AcOH, H_2O, 20 °C, 3 d

The second key intermediate is the 2-(benzhydryl)indane-1,3-dione **14**, bearing six methoxy substituents in appropriate positions. In contrast to the experience with the parent system,[31,32] attempts to prepare this compound by 1,4-addition of 4-(bromomagnesio)veratrole, obtained from 4-bromoveratrole,[33] to the corresponding hexamethoxy-substituted 2-benzylideneindane-1,3-dione[25] were not successful.[23] Fortunately, proton-catalyzed C−C coupling of bis(3,4-dimethoxyphenyl)methanol (**13**) with 5,6-dimethoxyindane-1,3-dione (**8**) proved to be more efficient. However, the synthesis of **13** first required optimization for our purposes.

The known 3,3′,4,4′-tetramethoxybenzophenone (**11**)[34] was obtained according to the procedure published by Kulkarni et al.[34c] from 3,4-dimethoxybenzoic acid (**9**) and veratrole (**10**) in polyphosphoric acid (PPA) in 77% yield (Scheme 3). Surprisingly, subsequent reduction of **11**, according to various known procedures, was unsuccessful. These included reduction of **11** with zinc in alkaline ethanol solutions[35a] and Meerwein−Ponndorf−Verley reduction,[35b] giving rise to ether formation and over-reduction to the corresponding diphenylmethane **12**. Reduction with lithium aluminum hydride and sodium borohydride also yielded ethers as the main products, as detected by ^{1}H NMR spectroscopy and mass spectrometry of the crude product mixtures.

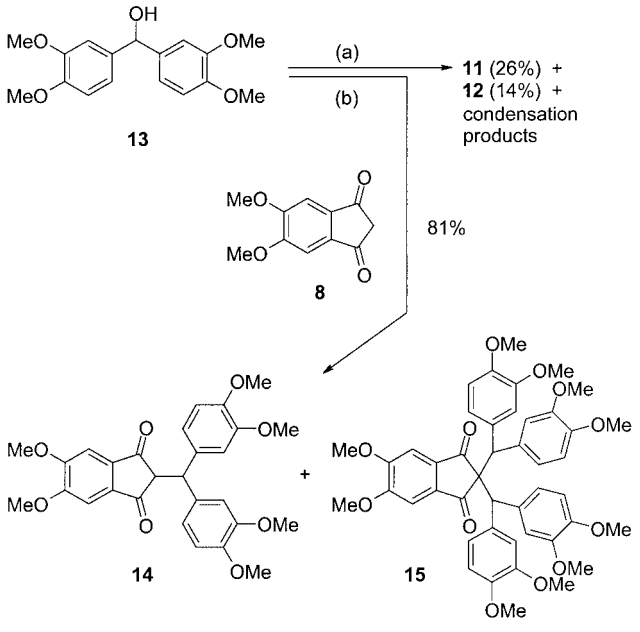


Scheme 3. (a) PPA, 80 °C, 30 min; (b) H_2, Pd/C, AcOH, 6.0 bar, 20 °C, 3 d; (c) H_2, Pd/C, pyridine, MeOH, 6.0 bar, 20 °C, 7 d

Compound **13** was eventually obtained by Pd/C-catalyzed hydrogenation under strictly acid-free conditions. For

this purpose, the methanol used as a solvent was deacidified with basic alumina. Furthermore, pyridine was added to neutralize traces of acids still present in the benzophenone **11** after two-fold recrystallization and to attenuate the activity of the heterogeneous catalyst. Under these conditions, **13** was formed quantitatively and isolated in 92% yield. According to elemental analysis, the compound forms as a monohydrate. Hirota et al.[36] have reported the use of a similar catalyst for the reduction of aromatic ketones. In contrast, Pd/C-catalyzed reduction of **11** in glacial acetic acid gave quantitative hydrogenolysis to diveratrylmethane (**12**), which was obtained in 81% yield after recrystallization, in analogy to a procedure published by Horning and Parker.[37]

Again in contrast to the parent system, alkylation of 5,6-dimethoxyindane-1,3-dione **8** with 3,3′,4,4′-tetramethoxybenzhydrol (**13**) (benzhydrol = diphenylmethanol), under conditions described first by de Winter and Nauta[32] and later used by ourselves[12a] gives rise to complex product mixtures. Due to the electron-rich arene rings, the simultaneous presence of compound **13** and the acidic catalyst gives rise to disproportionation of the former, yielding **11** and **12**. In addition, the product of dialkylation, 2,2-bis(benzhydryl)indane-1,3-dione **15**, was also formed in significant amounts (see below). Disproportionation of benzhydrols in acidic media is well known[38] and has been studied in the case of **13** in particular.[39,40] In fact, heating of **13** in benzene solution containing catalytic amounts of *para*-toluenesulfonic acid, but in the absence of **8**, yields benzophenone **11** and diveratrylmethane (**12**) in significant amounts (Scheme 4), along with condensation products.[23]



Scheme 4. (a) *p*TsOH, toluene, Δ*T*, 2 h; (b) *p*TsOH, benzene, 1,2-dichloroethane, Δ*T*, 2 h

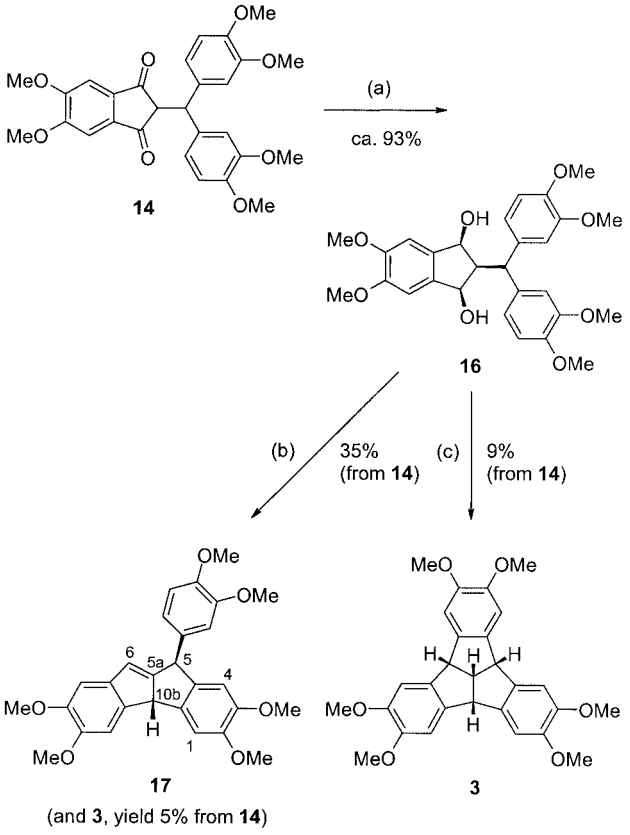
These undesired reactions can largely be suppressed when a solution of benzhydrol **13** in 1,2-dichloroethane is added slowly to 5,6-dimethoxyindane-1,3-dione **8** suspended in a solution of *para*-toluenesulfonic acid in benzene. The low stationary concentration of the benzhydrol is indicated by the fast disappearance of the purple color caused by the intermediate 3,3′,4,4′-tetramethoxybenzhydryl cation. This procedure affords the desired indanedione **14** in 81% yield. However, gravity column chromatography is necessary to remove the dialkylation product **15** (Scheme 4). Both diketones were fully characterized by NMR spectroscopy and mass spectrometry (see Exp. Sect.).

^{1}H NMR spectroscopic and semiempirical studies by de Winter and Nauta[41] have revealed that 2-(benzhydryl)indane-1,3-diones favorably adopt the *gauche* or *anti* conformation. Based on the coupling constant measured for the two aliphatic methyne protons, the *gauche* conformation was attributed to 2-(benzhydryl)indane-1,3-diones bearing no *ortho* substituents within the benzhydryl grouping (^3J = 1.5−3.5 Hz). In contrast, the *anti* conformation is the most stable state for derivatives with highly *ortho*-substituted benzhydryl groupings (^3J = 5.0−11.0 Hz). The electronic nature of the substituents was found to play only a minor role. In the present case, the ^{1}H NMR spectrum of the indanedione **14** displays a coupling constant of ^3J = 2.0 Hz, suggesting that the *gauche* conformation is preferred here, in line with the absence of *ortho* substituents.[42]

Again in contrast to the synthesis of the parent system **1**, reduction of indanedione **14** by catalytic hydrogenation using Urushibara nickel failed, and the use of palladium on charcoal in deacidified methanol in the presence of pyridine, in analogy to the reduction of **11** to **13**, left the starting material mainly unchanged. It is obvious that the sensitivity of the electron-rich diketone toward acids at elevated temperatures, combined with its intrinsic acidity as an easily enolizable 1,3-diketone and the especially facile loss of water from the alcohols derived from **14** is more critical than in the absence of the methoxy substituents.

Hellwinkel and Bohnet[43] have reported the successful reduction of dibenzoylmethane to the corresponding diastereomeric diols using diisobutylaluminum hydride (DIBAL-H), and use of this reagent followed by careful workup allowed us to prepare 5,6-dimethoxy-2-(3,3′,4,4′-tetramethoxybenzhydryl)indane-1,3-diol (**16**) in very good yield (Scheme 5). According to ^{1}H NMR spectroscopy, the all-*cis* isomer is formed exclusively. Thus, the usefulness of DIBAL-H to convert highly C−H-acidic 1,3-diketones into the corresponding 1,3-diols is nicely confirmed. The formation of the all-*cis* isomer parallels the stereochemical outcome of the catalytic reduction achieved previously in the parent system by use of Urushibara nickel.[12a] Obviously, and similar to catalytic hydrogenation, the hydride transfer occurring in the adducts formed from the indane-1,3-dione and the aluminum hydride reagent takes place preferentially at the sterically less hindered side of the five-membered ring.

The stereochemical identity of **16** is unequivocal. Both of the benzylic protons (1-H and 3-H) are magnetically equivalent and give rise to a relatively small vicinal coupling (^3J = 4.5 Hz) with 2-H. The vicinal coupling between the



Scheme 5. (a) DIBAL-H, CH_2Cl_2, 20 °C, 48 h; (b) H_3PO_4/Celite 545, chlorobenzene, ΔT, 2 h; (c) H_3PO_4 (85%), chlorobenzene, ΔT, 2 h

latter proton and the benzhydrylic methyne proton is characteristically large (^3J = 12.2 Hz). Comparison with the respective coupling constant observed for the corresponding indane-1,3-dione **14** (^3J = 2.0 Hz) suggests that the all-*trans* diol **16** preferably exists in the *anti* conformation. The ^{13}C NMR spectrum confirms the molecular C_s symmetry of the compound. Attempts to purify the indanediol **16** by recrystallization failed. However, it turned out that the crude product can be used in the subsequent two-fold cyclization without problems.

In the final step of this synthesis, cyclodehydration of the indanediol **16** in refluxing chlorobenzene in the presence of orthophosphoric acid generates a very complex mixture of products. As discussed previously for the parent system, a number of dehydration processes, among which 1,2-elimination of water may be dominant, compete with the desired two-fold cyclodehydration reaction to produce **3**. Nevertheless, 2,3,6,7,10,11-hexamethoxytribenzotriquinacene (**3**) was isolated by repeated gravity column chromatography and recrystallization from methanol as a colorless solid in 9% yield based on the indanedione **14** (Scheme 5). This is remarkably close to the yield (viz. 11%) obtained for the parent hydrocarbon **1** under similar cyclodehydration conditions. However, whereas **1** exhibits an extremely low solubility, which facilitates its complete isolation by recrystallization, the hexamethoxy derivative **3** is readily soluble in the usual organic solvents.

Owing to its C_{3v} symmetry, the ^{1}H NMR spectrum of the tribenzotriquinacene **3** displays only four resonances. Two singlets correspond to the 18 methoxy and the six *ortho* protons, respectively, and the remaining quadruplet (δ = 4.50 ppm) and doublet (δ = 4.75 ppm) reflect the protons of the triquinacene core. Accordingly, the ^{13}C NMR spectrum displays only six lines. The EI mass spectrum of **3** shows the molecular ion signal (*m*/*z* = 460) as the base peak, as expected for a polycyclic aromatic radical cation.

Attempts to increase the yield of **3** led us to the idea of using a solid support for the acid catalyst. However, when the orthophosphoric acid was impregnated onto Celite 545, the efficiency of the two-fold cyclodehydration was decreased to an absolute yield of 5%. Nevertheless, this method allowed us to isolate the product of single cyclization, viz. the diindene **17**, in 35% yield. It is assumed that this compound is also formed as an intermediate in the absence of the solid support but that subsequent conversion in the reaction mixture prevents its detection.

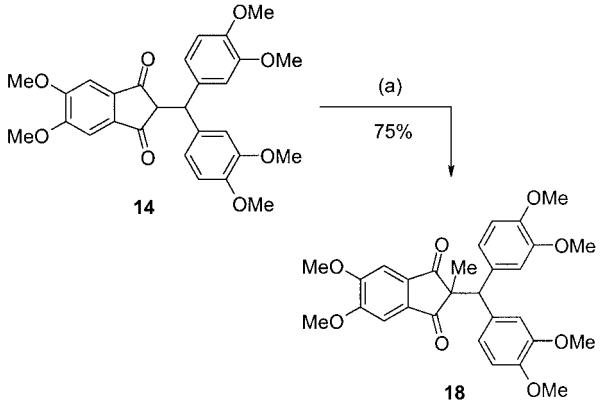
The formation of diindene **17** is remarkable since it essentially parallels the single cyclization of all-*cis*-2-(benzhydryl)-indane-1,3-diol in the case of the parent system.[12a] In that case, however, the C−C double bond is located in the diquinane ring junction (C-5a−C-10b),[12c] whereas in the present case diindene **17** contains the double bond between C-5a and C-6 (Scheme 5). The olefinic proton at C-6 resonates at δ = 7.06 ppm, with a four-bond coupling of 1.1 Hz to a methyne proton whose signal appears at δ = 4.98 ppm. The finding that no coupling is observed with the other methyne proton resonating at δ = 4.93 ppm suggests that the latter is oriented at the *endo* side of the diindene framework. Therefore, the doublet resonance at δ = 4.98 ppm is assigned to 10b-H and the singlet resonance at δ = 4.93 ppm to 5-H. The number of resonances of tertiary and quaternary C atoms in the ^{13}C NMR spectrum is in agreement with the structure postulated for **17**. Again, the EI mass spectrum of **17** displays the molecular ion peak (*m*/*z* = 460) as the largest signal. In contrast to the fully cyclized isomer **3**, however, loss of a methoxy group generating ions (*m*/*z* = 429) is much more pronounced for **17**, which indicates an increased tendency of the radical cation $\mathbf{17}^{\cdot+}$ to undergo skeletal isomerization, as compared to ions $\mathbf{3}^{\cdot+}$.

Synthesis of 2,3,6,7,10,11-Hexamethoxy-12d-methyltribenzotriquinacene (4)

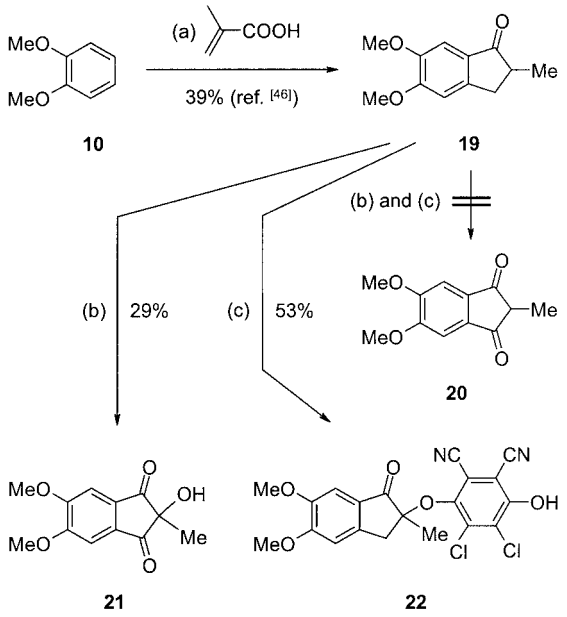
As shown in the previous section, the synthesis of hexamethoxytribenzotriquinacene **3** is associated with a low efficiency, similar to that of the parent hydrocarbon **1**. Therefore, the synthesis of the *centro*-methyl derivative **4** was explored, in view of the much more efficient access to the methyl-substituted parent compound **2**.[12a,13]

A direct step towards **4** is made by methylation of the indanedione **14** at C-2, using methyl iodide and potassium fluoride on Celite 545 in acetonitrile (Scheme 6),[44,45] giving 5,6-dimethoxy-2-methyl-2-(3,3′,4,4′-tetramethoxybenzhydryl)indane-1,3-dione (**18**) in 75% yield. However, prep-

aration of large amounts of this compound is inefficient because chromatographic purification of indanedione **14** cannot be avoided. Therefore, we developed an independent synthesis of **18** focussing on the hitherto unknown 2-methylindane-1,3-dione **20** (Schemes 7 and 8).



Scheme 6. (a) CH_3I, KF/Celite 545, MeCN, ΔT, 3 h

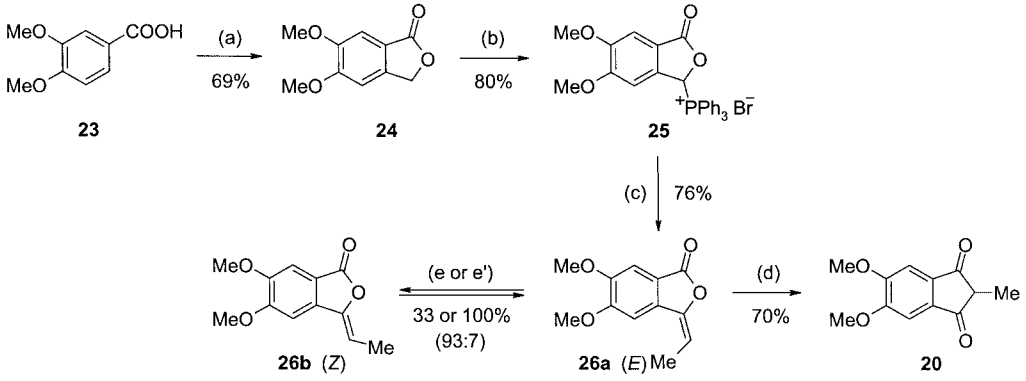


Scheme 7. (a) PPA, 80 °C, 40 min; (b) CrO_3, AcOH, H_2O, 20 °C, 3 d; (c) DDQ, AcOH, 70 °C, 16 h

According to the procedure reported by Marquardt,[46] condensation of veratrol (**10**) and methacrylic acid yields 5,6-dimethoxy-2-methylindan-1-one (**19**) on large scale (see Exp. Sect.). At variance with the lower homologue **7**, the C-2 position of the 2-methylindan-1-one **19** was found not to be inert under the oxidation conditions used to prepare **8** (see Scheme 2). Instead of the expected diketone **20**, the 2-hydroxyindane-1,3-dione **21** was isolated in moderate yield (Scheme 7). IR and ^1H NMR spectroscopy and EI mass spectrometry confirm the identity of this previously unknown compound. Remarkably, the most prominent fragmentation of the molecular ion $\mathbf{21}^{\cdot+}$ (m/z = 236) corresponds to the formal loss of $CH_3CO^{\cdot}$ (or $CH_3^{\cdot}$ and CO) to generate ions with m/z = 193, at variance to other simple ionized indane-1,3-diones.[47]

Attempts to oxidize the benzylic methylene group of **19** by treatment with 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ) in glacial acetic acid[48] also failed. Instead, C-2 was oxidized again to generate the 1,6-addition product **22** (Scheme 7), which readily precipitates from the reaction mixture. The identity of this compound was confirmed by IR, ^1H and ^{13}C NMR spectroscopy and EI mass spectrometry.

Due to the failure of this approach, we focussed on an independent but direct access to 2-methylindane-1,3-diones.[49] To this end, we developed a synthesis of 5,6-dimethoxy-2-methylindane-1,3-dione (**20**) by adapting, in part, steps of known methods, starting from 5,6-dimethoxyphthalide (*meta*-meconine, **24**) (Scheme 8).[50] This compound was subjected to benzylic bromination with *N*-bromosuccinimide,[51] and subsequent conversion into the corresponding triphenyl(phthalid-3-yl)phosphonium bromide **25**,[52] which was obtained in 80% yield. This compound was characterized by ^1H and ^{13}C NMR spectroscopy and MALDI mass spectrometry, which indicate the integrity of the phosphonium ion. Wittig reaction of **25** with



Scheme 8. (a) Aqueous CH_2O (37%), HCl, 60−70 °C, 7 h; (b) (1) NBS, dibenzoyl peroxide, benzene, ΔT, 3.5 h; (2) PPh_3, benzene, ΔT, 24 h; (c) MeCHO, NEt_3, CH_2Cl_2, 20 °C, 2 h; (d) (1) NaOMe, THF, ΔT, 2 h; (2) HCl (2 N), H_2O; (e) I_2, nitrobenzene, ΔT, 1 h or (e′) I_2, hν, EtOH, ΔT, 30 min

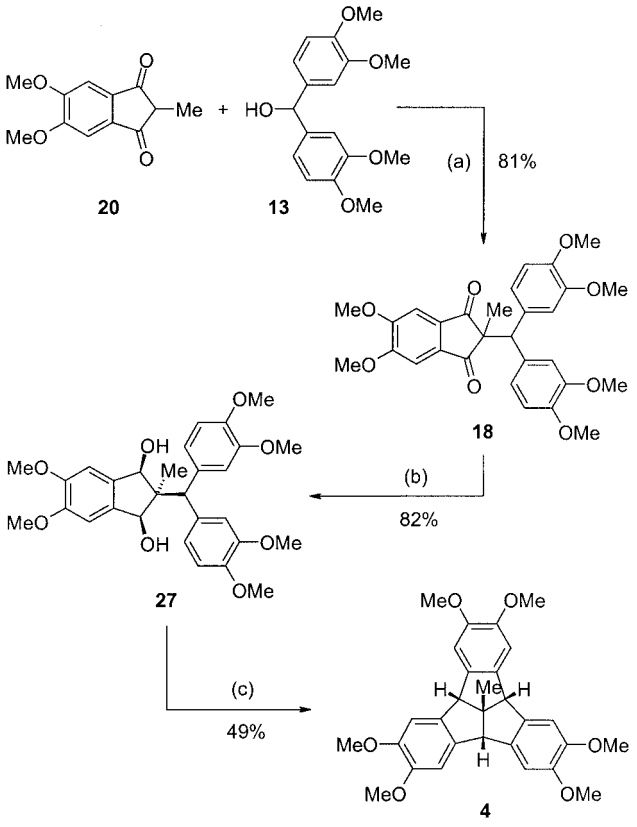
acetaldehyde furnishes (*E*)-5,6-dimethoxy-3-ethylidenephthalide (**26a**). According to the ^{1}H NMR spectrum of the crude product, the stereoisomer **26b** is also formed but can be completely removed by recrystallization. The (*E*)/(*Z*) ratio was found to depend strongly on the reaction conditions, in accordance with previous reports.[53] Control experiments showed that the (*E*) isomer is the product of kinetic control, and can be converted into the equilibrium mixture [(*Z*)/(*E*) = 93:7] by heating with iodine in nitrobenzene or by irradiation in the presence of iodine (see Exp. Sect.).[53,54] Although the photochemical isomerization led to quantitative formation of the equilibrium mixture of **26a** and **26b**, the (*Z*) isomer **26b** could not be isolated in pure form, in contrast to the (*E*) isomer **26a**. The stereochemical assignment is based on the increased steric interaction of the ethylidene group and the downfield chemical shift of its methyl resonance in the (*E*) isomer **26a**.

The base-catalyzed rearrangement of 3-alkylidenephthalide **26a** to the 2-alkylindane-1,3-dione **20**[55] takes place efficiently if the method of Nathanson[49a] is adapted and tetrahydrofuran is used as a solvent, from which the sodium salt of **20** precipitates (in contrast to the by-products). Further workup gives the neutral compound **20** in good yield. Thus, the four-step synthesis of **20** easily affords the product in multigram amounts with an overall yield of 29%.

Alkylation of the indane-1,3-dione **20** with the benzhydrol **13** gives the desired 5,6-dimethoxy-2-methyl-2-(3,3′,4,4′-tetramethoxybenzhydryl)indane-1,3-dione (**18**) in 81% yield after recrystallization (Scheme 9). In contrast to the lower homologue **14**, chromatographic purification is not necessary in this case. NMR spectroscopy and mass spectrometry confirm the identity of this non-enolizable 1,3-diketone.

Reduction of the indane-1,3-dione **18** with DIBAL-H leads to the all-*cis*-2-benzhydrylindane-1,3-diol **27** in high yield. Only one single diastereomer is observed, similarly to the lower homologue **16**. The mutual *cis* orientation of the hydroxy groups was determined by ^{1}H and ^{13}C NMR spectroscopy, which reflect the molecular C_s symmetry of **27**. The ^{1}H resonances of the six methoxy substituents are almost isochronous. The EI mass spectrum of the indane-1,3-diol **27** is remarkable because it exhibits the loss of two hydroxy radicals, generating fragment ions $[M - 2\ OH]^{\cdot+}$ with m/z = 476. Such a process is highly unusual. (Alternative origins for the occurrence of the m/z = 476 peak, such as loss of water from the $[M^{\cdot+}]$ ions of a potential impurity, a respective indane-1-ol, can be strictly excluded.) Elimination of two molecules of water (m/z = 474) occurs with a similar rate, possibly leading to the molecular ion of the tribenzotriquinacene **4**, which exhibits similar fragmentations (see below).

In the final step, the indane-1,3-diol **27** was subjected to two-fold cyclodehydration with orthophosphoric acid in refluxing chlorobenzene (Scheme 9). The desired polycycle, 2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene (**4**), was obtained after recrystallization in a surprisingly high yield (49%), which significantly exceeds that of the parent hydrocarbon **2** upon cyclodehydration of the corresponding parent indane-1,3-diol (33%).[12a] One reason for this finding may be the increased reactivity of the indane-1,3-diol **27** owing to its electron-releasing methoxy substitution, which may lead to relatively short reaction times. However, it may be speculated that the two-fold *syn* conformation of the benzhydryl group of **27**, required for two-fold cyclization to **4**, is adopted preferentially by locking it through complexation with orthophosphoric acid or its higher condensates.



Scheme 9. (a) *p*TsOH, benzene, $ClCH_2CH_2Cl$, Δ*T*, 2 h; (b) DIBAL-H, toluene, 20 °C, 24 h; (c) H_3PO_4 (85%), chlorobenzene, Δ*T*, 2 h

The C_{3v} symmetry of compound **4** is nicely reflected by the simple ^{1}H and ^{13}C NMR spectra. For example, the ^{1}H NMR spectrum of **4** exhibits only four singlet resonances. The stability of the molecular ion $\mathbf{4}^{\cdot+}$ (m/z = 474, 100%) and the appearance of relatively abundant doubly charged molecular ion $\mathbf{4}^{2+}$ (m/z = 237, 12%) under EI conditions is remarkable. The losses of $CH_3^{\cdot}$ (m/z = 459) and of $CH_3O^{\cdot}$ (m/z = 443) represent further characteristic fragmentation channels of ions $\mathbf{4}^{\cdot+}$.

Molecular and Crystal Structure of 2,3,6,7,10,11-Hexamethoxy-12d-methyltribenzotriquinacene (4)

A sample of 2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene (**4**) was obtained in the form of single crystals by recrystallization from methanol, and one of these crystals was subjected to structure analysis by X-ray diffraction.[56] The compound was found to form monoclinic crystals (space group $P2_1/n$). In contrast to the parent

hydrocarbon **2**, which aggregates in columnar stacks of strictly C_{3v}-symmetrical molecules bearing three planar indane units,[20] the molecular structure of **4** has a shape that markedly deviates from C_{3v} or C_3 symmetry. The three indane units adopt out-of-plane distortions to different extents. Clearly, these findings have to be attributed to packing effects.

The crystal structure of the hexamethoxytribenzotriquinacene **4** is illustrated in Figure 1. The compound crystallizes differently from both the parent hydrocarbon **2** (trigonal, *R*3*m*)[20] and also the closely related cyclotriveratrylene **6** (monoclinic, *C*2/*c*)[57b] and its derivatives.[7,57] Obviously, the presence of the methoxy groups at the molecular periphery prevents the stacking of the convex/concave molecules found in the case of **2**. Similar to the non-methylated analog **1**, the "nor" compound **3** did not yield crystals suitable for X-ray structure analysis.

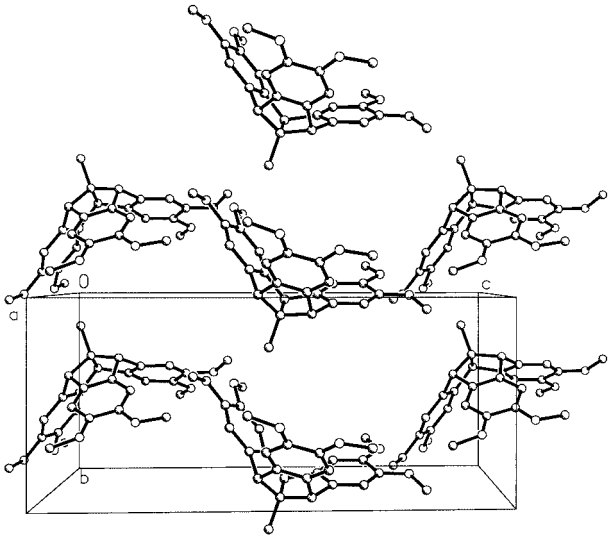
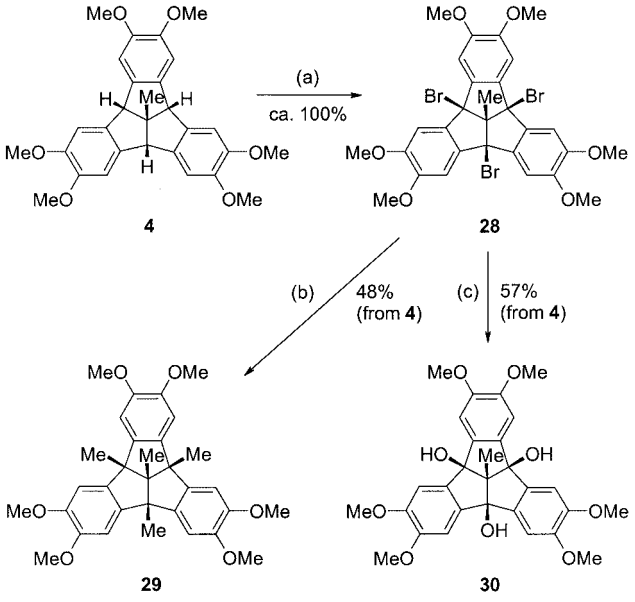


Figure 1. Crystal structure of tribenzotriquinacene **4**, as determined by X-ray analysis and viewed along the *a* axis; hydrogen atoms are omitted for clarity

Bridgehead and Limited Peripheral Substitution of 2,3,6,7,10,11-Hexamethoxy-12d-methyltribenzotriquinacene (4)

The close structural relationship between 2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene (**4**) and the cyclotriveratrylene **6** offers an interesting opportunity to compare the reactivities of these compounds. The latter has mostly been studied with respect of the transformations of the functional groups at the peripheral positions of the aromatic rings, whereas tribenzotriquinacenes, in general, have been subjected also to bridgehead functionalization.[19–21] In the following section, some examples are presented which open a first access to three-fold bridgehead derivatives of **4** and indicate some limitations concerning electrophilic attack at the arene units. Partial cleavage of the methoxy groups, which would lead to chiral phenolic derivatives of **2**, in analogy to chiral derivatives or analogs of **6**,[7–9,58] has not been successful so far.[23] In addition, independent studies of **4** and related multiply methoxy-substituted centropolyindanes were focussed on the directed degradation of the veratrole nuclei by ozonolysis.[23,59]

Three-fold bridgehead bromination of **4** can be achieved in virtually quantitative yield by a photoinduced radical chain-reaction employing *N*-bromosuccinimide in tetrachloromethane or benzene (Scheme 10). As expected, the tribromo derivative **28** is considerably more reactive than its analog derived from the parent tribenzotriquinacene **2**. Thus, the sensitivity of tribromide **28** to hydrolysis impedes its monitoring by thin layer chromatography. However, ^{1}H NMR spectroscopy of the crude product reflected its sufficient purity for further use without recrystallization.



Scheme 10. (a) NBS, AIBN, benzene, hν, 45 min; (b) $AlMe_3$, benzene, 50 °C, 1 h; (c) H_2SO_4 (20%), THF Δ*T*, 3 h (see text)

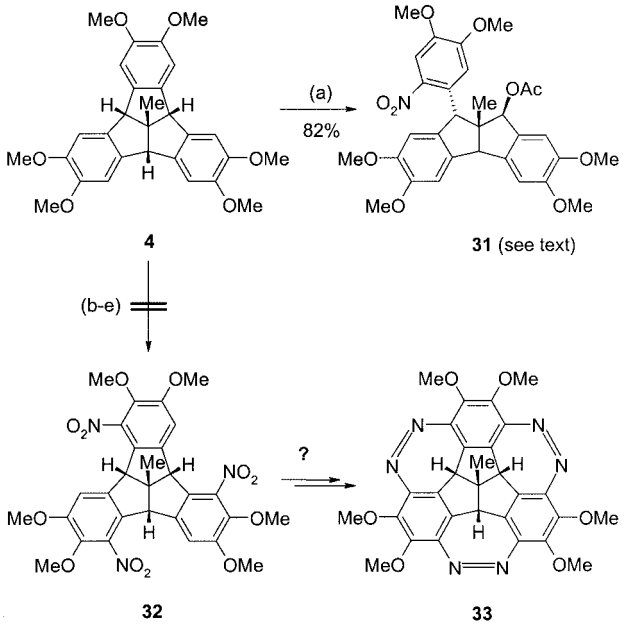
Treatment of the tribromide **28**, after careful removal of residual bromine originating from its preparation and dissolution in benzene, with trimethylaluminum, in analogy to the corresponding reaction in the parent system,[20] affords the hexamethoxy-tetramethyltribenzotriquinacene **29** in good yield. The ^{1}H and ^{13}C nuclei of the central methyl group of **29** exhibit a strong upfield chemical shift due to the presence of three strictly ecliptic methyl groups. Compound **29** nicely adds to the series of tribenzotriquinacenes that have all of their three benzhydrylic positions blocked by methyl groups, thus allowing them to be subjected to reactions which would otherwise oxidize the C–H bonds of the benzhydrylic bridgeheads (e.g. nitration and bromination).[21,22]

Instead of blocking the outer bridgehead positions, directed functionalization by hydroxy, alkoxy or acyloxy groups could also be interesting. In fact, the tribromide **28** can be easily converted into the corresponding triol, 4b,8b,12b-trihydroxy-2,3,6,7,10,11-hexamethoxy-12d-meth-

yltribenzotriquinacene (**30**), by hydrolysis with aqueous sulfuric acid in tetrahydrofuran. Notably, the product obtained by hydrolysis in the presence of silver(I) nitrate[60] was found to be much more contaminated. Due to its poor solubility in chloroform, the NMR spectra of **30** were determined from [D_4]methanol or, even better, from [D_3]acetonitrile. Again, these spectra reflect the high molecular symmetry of triol **30**. Unfortunately, acetylation of this compound by 4-(dimethylamino)pyridine and acetanhydride[61] according to the protocol recommended by Karimi and Seradj[62] for tertiary alcohols, in particular, was unsuccessful. Although thin layer chromatography indicated complete conversion of **30**, column chromatography of the crude product gave only the starting material. It is obvious that, similar to the tribromide **28**, the triacetate of triol **30** is much more sensitive to hydrolysis than the previously described triacetates of the parent system.[18b] Attempts to prepare the triacetate of **30** directly from tribenzotriquinacene **4**, for example with lead(IV) acetate, also failed; oxidation of **4** with 1 equiv. of lead(IV) acetate yielded only the corresponding monoalcohol, 4b-hydroxy-2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene, which was isolated by gravity column chromatography in 29% yield (see Electronic Supporting Information, compound **D**; for Supporting Information see also the footnote on the first page of this article). Since the corresponding monoacetate must have been generated under the conditions used, heterolysis of the bridgehead C−O bond at the electron-rich tribenzotriquinacene core during workup and/or chromatography is particularly fast.

Another facet to be illuminated in the functionalization of tribenzotriquinacenes concerns the substitution at the *ortho* positions, as the introduction of groups at these sterically considerably hindered regions of the molecular periphery of tribenzotriquinacenes and higher centropolyindanes containing this framework has been achieved only in a very few cases.[63,64] For example, nitration of **1** occurs readily at the outer positions but very scarcely *ortho* to the triquinacene core.[64] Introduction of appropriate *ortho* substituents could offer a possibility to enlarge the polycyclic framework by bridging the three "bays" of the tribenzotriquinacene skeleton by −C=C− and *ortho*-phenylene units. Special goals in this respect are three-fold azo-bridged tribenzotriquinacenes as intereresting convex/concave dye units. For example, compound **33** could be accessible via an appropriate trinitro derivative of **4**, such as **32**, as depicted in Scheme 11.

However, despite various attempts, nitration of the tribenzotriquinacene **4** did not occur without cleavage of the triquinacene core. Treatment with 1 equiv. of copper(II) nitrate in acetanhydride gave the product of single C−C cleavage, the *difuso*-diindane **31**, in good yield (Scheme 11), whereas the use of an excess of this reagent and several other reagent systems, including AcCl/$AgNO_3$, $Cu(NO_3)_2$/TFA and $NaNO_3$/TFA (and also $NaNO_2$/TFA), generated highly complex product mixtures. The constitution of **31**, formed as a single stereoisomer, was unequivocally determined by NMR spectroscopy and mass spectrometry al-



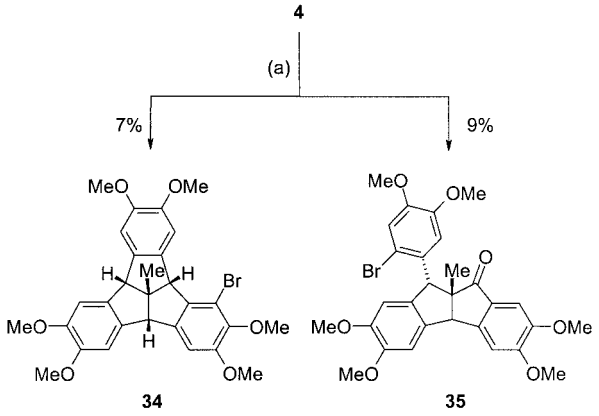
Scheme 11. (a) $Cu(NO_3)_2 \cdot 3H_2O$, Ac_2O, 20 °C, 40 min; (b)−(e) see text

though the stereoorientation of the acetoxy groups was not proven rigorously. However, due to the strong steric shielding of the concave face of the diindane by the pendant aryl group, it can be safely assumed that the acetoxy substituent has been attached from the convex (β) side.

Clearly, and different from the parent tribenzotriquinacenes, the particularly electron-rich derivative **4** suffers *ipso* attack by the nitronium cation, giving rise to heterolytic ring opening of the indane unit. Similar cleavage processes occur with cyclotriveratrylene (**6**) under comparable conditions, as reported by Sato et al.,[16] and indane itself has been found to undergo *ipso* substitution under various conditions.[65] It is interesting to note that, to the best of our knowledge, no substitution of the free aromatic positions of **6** has been reported previously other than the Claisen rearrangement of the corresponding triallyl ethers;[66] cyclotribenzylene (**5**) undergoes mononitration without ring opening.[16b] Thus, the tempting possibility to construct azo-bridged tribenzotriquinacenes remains elusive, all the more so because other efforts, such as azo coupling, were also unsuccessful.[23]

Finally, bromination of tribenzotriquinacene **4** was examined in preliminary experiments. Treatment of **4** with bromine in glacial acetic acid gives a complex mixture of products. By contrast, use of *N*-bromosuccinimide in moist 2-butanone, a standard method used in calixarene chemistry,[67] under argon and with exclusion of light, furnished two products, which could be isolated by chromatography in low yields (Scheme 12). Interestingly, one of them was identified as 1-bromo-2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene (**34**), that is, a product of single *ortho* substitution which has eluded ring opening. The second product, however, turned out to be a cleavage product, which obviously was formed by *ipso* attack followed by ring

opening and subsequent oxidation. This parallels results by Arnett and Klingensmith,[68] who observed that electron-rich benzhydrols are cleaved by treatment with bromine to give the corresponding bromobenzene and a carbonyl compound as fragments. Due to the low amount of products, their characterization remains incomplete although the spectroscopic data unequivocally confirm their identity. The stereochemistry of **35** is deduced from the preorientation of the aromatic rings in the starting material and the reaction conditions which suggest retention of configuration. Interestingly, the generation of **34** and **35** was not reproducible when anhydrous 2-butanone was used instead of the standard solvent.



Scheme 12. (a) NBS, 2-butanone (moist), 0 → 20 °C in the dark, 16 h (conversion 72%)

In contrast to the successful functionalization of the bridgehead positions of tribenzotriquinacene **4**, our attempts to functionalize its *ortho* positions have remained rather limited so far. Further efforts appear possible to introduce functional groups into the three unusual 3D-bent bays of this particular, electron-rich and conformationally rigid, polycyclic molecule.[69]

Experimental Section

General: Melting points (uncorrected): Electrothermal Melting Point Apparatus. Infrared (IR) spectra: Perkin−Elmer 841; KBr pellets or NaCl plates. NMR spectroscopy: Bruker DRX 500; data given as ppm; spectra referenced to the residual solvent peak. ^{1}H NMR spectra: 500.1 MHz; ^{13}C NMR spectra: 125.8 MHz, broad band decoupled, DEPT and APT method used generally. 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 with a direct inlet rod. Acceleration voltages 8 kV (EI) and 6 kV (CI). Data given as intensities relative to the base peak. Otherionization methods are detailed individually. Perfluorokerosine (PFK) was used as a reference to determine the accurate masses. MALDI-TOF mass spectra: Voyager™ DE (PE Biosystems GmbH, Weiterstadt, Germany) equipped with an LSI-N_2 laser (λ = 337 nm, pulse duration 3 ns, repetition rate 3 Hz). Combustion analysis: Perkin−Elmer model 240. Hydrogenation reactions: Parr apparatus type HyP series 77 (Gerhardt, Bonn, Germany). Kugelrohr distillation: Büchi model GKR-5. Photolamp used for photobromination: Philips PF 318E/44, 500 W. Thin layer chromatography: Silica gel (Kieselgel 60 F_{254}) on Al foil (Merck). Gravity column chromatography: Silica gel (Kieselgel 60, ∅ = 0.063−0.200 mm, J. T. Baker, Macherey−Nagel, or Merck). Flash chromatography: Silica gel (Kieselgel 60, ∅ ≤ 0.063 mm) for column chromatography (Merck). Alkylation by use of "KF/Celite": Celite (Kieselgur) 545 (Fluka). Cyclodehydration reactions: Polyphosphoric acid (Merck-Schuchardt). Hydrogenation reactions: Palladium on charcoal (10% Pd) (Aldrich). All solvents were purified by distillation before use and dried according standard procedures where necessary.[70]

2,3-Dihydro-5,6-dimethoxy-1*H*-indene-1,3-dione (8): A solution of 5,6-dimethoxyindan-1-one (**7**) [27] (38.4 g, 200 mmol) in 500 mL of acetic acid and 100 mL of water was stirred and cooled in an ice bath while chromium(VI) oxide (140 g, 1.40 mol) was added in portions over a period of about 2 h. The temperature of the reaction mixture was kept below 15 °C due to the exothermicity of the reaction. Stirring was continued at ambient temperature for 3 d. After addition of 2-propanol (100 mL) and stirring for a further 1 h, the solution was concentrated to dryness under reduced pressure at a bath temperature of ≤ 50 °C. The residue was dissolved in 800 mL of water and the solution extracted with dichloromethane (1 × 800 mL and 5 × 400 mL). The extracts were washed with 400 mL of water, dried with sodium sulfate and concentrated to a volume of ca. 80 mL. The crude product was precipitated by addition of *n*-hexane (200 mL), separated by suction filtration and dried in vacuo to give pure **8** (yield 22.3 g, 54%) as a pale-yellow solid, m.p. 267 °C (267 °C[25b,25c]), R_f (*n*-hexane/EtOAc, 1:1) = 0.55. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.19 (s, 2 H), 4.03 (s, 6 H), 7.33 (s, 2 H) ppm. ^{1}H NMR (500.1 MHz, [D_6]DMSO) δ = 3.24 (s, 2 H), 3.95 (s, 6 H), 7.33 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 44.7 (CH_2), 56.7 (CH_3), 103.2 (CH), 138.4 (C), 155.8 (C), 196.6 (C) ppm. ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = 44.5 (CH_2), 56.3 (CH_3), 103.2 (CH), 137.6 (C), 155.2 (C), 196.6 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2989 cm^{-1}, 2957, 2843, 1724, 1690, 1589, 1499, 1474, 1462, 1306, 1245, 1233, 1219, 1117, 1093, 1012, 865, 849, 731. MS (EI, 70 eV): *m*/*z* (%) = 206 (100) [M$^{\cdot+}$], 191 (26), 164 (14), 150 (25), 136 (38), 135 (34), 121 (13), 119 (17), 107 (10), 93 (17), 78 (10), 75 (10), 50 (20). $C_{11}H_{10}O_4$ (206.20): calcd. C 64.07, H 4.89; found C 63.97, H 4.70.

Bis(3,4-dimethoxyphenyl)methanone (11): Polyphosphoric acid (400 g) was heated to 80 °C in a three-necked flask (500 mL) equipped with a mechanical glass stirrer. 1,2-Dimethoxybenzene (**10**) (34.6 g, 250 mmol) and then 3,4-dimethoxybenzoic acid (**9**) (45.5 g, 250 mmol) were added, the mixture was stirred at 80 °C for 30 min and then, before cooling, carefully poured onto 2.0 L of ice/water. The brownish precipitate was filtered by suction, dried and recrystallized twice from ethanol to give **11** (58.4 g, 77%) as a light-brown solid, m.p. 147 °C (144−146 °C[34b]), R_f (*n*-hexane/EtOAc, 3:1) = 0.15. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.92 (s, 6 H), 3.94 (s, 6 H), 6.87 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.36 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.9 Hz, 2 H), 7.40 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.00 (CH_3), 56.03 (CH_3), 109.6 (CH), 112.2 (CH), 124.7 (CH), 130.7 (C), 148.8 (C), 152.5 (C), 194.4 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3081 cm^{-1}, 3005, 2975, 2938, 1754, 1632, 1574, 1511, 1465, 1451, 1416, 1295, 1240, 1220, 1170, 1151, 1141, 1122, 1022, 892, 880, 818, 795, 771, 750, 724, 619. MS (EI, 70 eV): *m*/*z* (%) = 302 (100) [M$^{\cdot+}$], 271 (41), 165 (99), 137 (16), 79

(14), 77 (14). $C_{17}H_{18}O_5$ (302.33): calcd. C 67.54, H 6.00; found C 67.45, H 5.99.

Bis(3,4-dimethoxyphenyl)methane (12): Palladium on charcoal (1.00 g, 10% Pd, oxidic form) was added to a solution of benzophenone **11** (12.1 g, 40.0 mmol) in 400 mL of glacial acetic acid. The suspension was shaken in a Parr apparatus under hydrogen (6.0 bar, 20 °C) for 3 d. The solution was then filtered through silica gel (Kieselgel 60, ∅ ≤ 0.063 mm, Merck) and the filter washed with dichloromethane. The combined solutions were concentrated to dryness and the residue obtained was recrystallized from methanol to give **12** as a colorless solid (9.39 g, 81%), m.p. 68−69 °C (69−71 °C[34b]), R_f (*n*-hexane/EtOAc, 1:1) = 0.64. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.83 (s, 6 H), 3.86 (s, 6 H), 3.88 (s, 2 H), 6.70 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.72 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 2.1 Hz, 2 H), 6.80 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 41.0 (CH_2), 55.8 (CH_3), 55.9 (CH_3), 111.1 (CH), 112.1 (CH), 120.7 (CH), 133.9 (C), 147.3 (C), 148.9 (C) ppm. IR (KBr): ṽ = 2968 cm^{-1}, 2942, 2897, 2845, 1608, 1589, 1513, 1466, 1449, 1417, 1334, 1295, 1242, 1201, 1188, 1154, 1135, 1027, 852, 816, 800, 770, 640. MS (EI, 70 eV): *m*/*z* (%) = 288 (100) [M$^{\cdot+}$], 287 (8), 273 (6), 257 (47), 242 (6), 241 (11), 213 (5), 199 (6), 166 (5), 151 (19), 144 (6), 128 (9), 115 (10), 107 (5).

Bis(3,4-dimethoxyphenyl)methanol Monohydrate (13·H_2O): The benzophenone **11** (24.2 g, 80.0 mmol) was suspended in methanol (400 mL), which had been deacidified by passing it through basic alumina. Pyridine (0.50 mL) and palladium on charcoal (1.40 g, 10% Pd, oxidic form) were then added and the mixture was shaken under hydrogen in a Parr apparatus (6.0 bar, 20 °C) for 7 d. The suspension was then filtered through silica gel (Kieselgel 60, ∅ ≤ 0.063 mm, Merck) and the filter washed with deacidified methanol (see above). Removal of the solvent under reduced pressure gave a residue which was recrystallized from toluene (technical grade) to furnish the monohydrate of **13** (23.6 g, 92%) as a colorless solid, m.p. 84−85 °C (95 °C[35a]), R_f (*n*-hexane/EtOAc, 1:1) = 0.34. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.94 (br. s, ca. 2 H, OH), 3.85 (s, 6 H), 3.87 (s, 6 H), 5.75 (s, 1 H), 6.82 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 6.88 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.8 Hz, 2 H), 6.92 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 55.85 (CH_3), 55.91 (CH_3), 75.7 (CH), 109.7 (CH), 110.9 (CH), 118.9 (CH), 136.6 (C), 148.4 (C), 149.0 (C) ppm. IR (KBr): ṽ = 3560 cm^{-1}, 3356, 3010, 2973, 2948, 2843, 1643, 1606, 1593, 1515, 1466, 1442, 1418, 1305, 1254, 1232, 1132, 1068, 1020, 870, 862, 813, 776, 767, 757, 645. MS (EI, 70 eV): *m*/*z* (%) = 304 (93) [M$^{\cdot+}$], 302 (12), 288 (87), 287 (32), 273 (10), 263 (12), 257 (39), 241 (11), 167 (11), 165 (100), 151 (30), 139 (91), 138 (39), 135 (17), 128 (10), 121 (10), 115 (11), 107 (10). Accurate mass by EI-MS ($C_{17}H_{20}O_5$): calcd. 304.1311; found 304.1329. $C_{17}H_{20}O_5$ (304.35): calcd. C 67.09, H 6.62; $C_{17}H_{20}O_5·H_2O$ (322.36): calcd. C 63.34, H 6.88; found C 63.36, H 7.08.

Disproportionation of Bis(3,4-dimethoxyphenyl)methanol (13): A solution of 3,3′,4,4′-tetramethoxybenzhydrol monohydrate, **13**·H_2O, (645 mg, 2.00 mmol) and *para*-toluenesulfonic acid monohydrate (38.0 mg, 200 μmol) in 50 mL of toluene (p.a.) was heated to reflux for 2 h. The water was removed by use of a Thiele−Pape extractor filled with molecular sieves (4 Å). The reaction mixture was allowed to cool to ambient temperature and then washed twice with 25 mL of aqueous sodium hydroxide (2 N) and once with 25 mL of water, then dried with sodium sulfate and concentrated to dryness. The residue was subjected to gravity column chromatography (hexanes/EtOAc, 1:1). Besides diveratrylmethane (**12**) (82.0 mg, 14%) and 3,3′,4,4′-tetramethoxybenzophenone (**11**) (160 mg, 26%), a third fraction [96.0 mg, R_f (*n*-hexane/EtOAc, 1:1) = 0.11] was obtained containing several condensation products, as indicated by mass spectrometry.[23]

2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-1*H*-indene-1,3(2*H*)-dione (14): A solution of the indane-1,3-dione **8** (3.61 g, 17.5 mmol) and *para*-toluenesulfonic acid monohydrate (380 mg, 2.00 mmol) in 100 mL of benzene (p.a.) was heated to reflux in a flask equipped with a Thiele−Pape extractor containing molecular sieves (4 Å). A solution of **13**·H_2O (6.45 g, 20.0 mmol) in 80 mL of 1,2-dichloroethane, formed by gentle warming, was added slowly. At the beginning of the reaction, purple streaks formed in the yellow reaction solution but vanished immediately due to the stirring. Towards the end of the addition, the reaction mixture turned red brown. Heating was continued for 1 h and the mixture was then allowed to cool. It was washed with water, dried with sodium sulfate and concentrated to dryness. The residue obtained was purified by column chromatography (EtOAc) and the product collected was recrystallized from methanol to furnish **14** (6.94 g, 81%) as a light yellow solid, m.p. 107−108 °C, R_f (EtOAc) = 0.81, R_f (*n*-hexane/EtOAc, 1:1) = 0.27. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.75 (m, 7 H), 3.77 (s, 6 H), 3.94 (s, 6 H), 4.94 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H), 6.68 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 6.85 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.9 Hz, 2 H), 6.91 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H), 7.17 (s, 2 H) ppm. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 3.03 (s, 6 H), 3.31 (s, 6 H), 3.49 (s, 6 H), 3.73 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H), 5.45 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H), 6.57 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.01 (s, 2 H), 7.26 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H), 7.29 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.0 Hz, 2 H) ppm. ^{1}H NMR (500.1 MHz, [D_6]DMSO): δ = 3.61 (s, 6 H), 3.66 (s, 6 H), 3.91 (s, 6 H), 4.12 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H), 4.79 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H), 6.75 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.8 Hz, 2 H), 6.78 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 6.90 (d, $^4J_{H,H}$ = 1.7 Hz, 2 H), 7.30 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 49.3 (CH), 55.7 (4 CH_3), 56.6 (2 CH_3), 58.0 (CH), 103.0 (CH), 110.6 (CH), 112.2 (CH), 121.0 (CH), 134.0 (C), 137.7 (C), 147.4 (C), 148.3 (C), 155.8 (C), 198.8 (C) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = 50.0 (CH), 55.4 (4 CH_3), 55.5 (2 CH_3), 58.4 (CH), 103.3 (CH), 112.0 (CH), 114.0 (CH), 121.7 (CH), 135.1 (C), 138.1 (C), 148.9 (C), 149.9 (C), 156.1 (C), 198.7 (C) ppm. IR (KBr): ṽ = 3094 cm^{-1}, 3002, 2952, 2911, 2837, 1728, 1690, 1582, 1518, 1463, 1445, 1416, 1318, 1263, 1238, 1227, 1202, 1177, 1141, 1114, 1039, 1026, 990, 858, 845, 767, 636. MS (EI, 70 eV): *m*/*z* (%) = 492 (16) [M$^{\cdot+}$], 287 (100), 257 (8), 241 (5), 206 (5), 181 (12), 165 (6), 151 (7), 149 (12), 136 (7). $C_{28}H_{28}O_8$ (492.53): calcd. C 68.28, H 5.73; found C 68.01, H 5.86.

2,2-Bis[bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-1*H*-indene-1,3(2*H*)-dione (15): Besides single alkylation, the reaction of the indanedione **8** and the benzhydrol **13** gave rise to dialkylation to produce varying amounts of the bis(benzhydryl)indanedione **15**. This compound was obtained by gravity column chromatography. It was isolated as a yellow solid after recrystallization from methanol, m.p. 128−129 °C, R_f (EtOAc) = 0.63. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.71 (s, 12 H), 3.75 (s, 12 H), 3.85 (s, 6 H), 4.63 (s, 2 H), 6.54 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 6.84 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.9 Hz, 4 H, 6.89 (d, $^4J_{H,H}$ = 1.8 Hz, 4 H), 6.91 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 55.57 (4 CH_3), 55.61 (4 CH_3), 55.7 (CH), 56.4 (CH_3), 67.3 (C), 102.0 (CH), 110.5 (4 CH), 113.0 (4 CH), 122.1 (4 CH), 132.5 (4 C), 138.1 (C), 147.2 (4 C), 148.0 (4 C), 155.6 (C), 203.4 (C) ppm. IR (KBr): ṽ = 2941 cm^{-1}, 2838, 1728, 1688, 1578, 1514, 1459, 1314, 1264, 1144, 1114, 1028, 810, 768, 646. MS (EI, 70 eV): *m*/*z* (%) = 778 (1) [M$^{\cdot+}$], 492 (3), 491 (2), 490 (2), 287 (100), 257 (14), 241 (4), 151 (4). $C_{45}H_{46}O_{12}$ (778.86): calcd. C 69.40, H 5.95; found C 69.33, H 6.14.

all-*cis*-2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxyindane-1,3-diol (16): A solution of the indane-1,3-dione **14** (4.93 g,

10.0 mmol) in 100 mL of dichloromethane (p.a.) was stirred under argon and cooled in an ice bath while a solution of diisobutylaluminum hydride (25.0 mL, 25.0 mmol; 1.0 M in dichloromethane) was added dropwise. The mixture was stirred at ambient temperature for 48 h. After careful addition of water (100 mL), the inorganic precipitate was filtered off by suction and washed repeatedly with dichloromethane. The combined organic solutions were washed with water, dried with sodium sulfate and concentrated to dryness to give the crude product **16** (4.63 g, ca. 93%) as a colorless oil, which can be used directly for cyclodehydration. R_f (EtOAc) = 0.47. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.98 (br. s, 2 H), 2.91 (dt, $^3J_{H,H}$ = 12.2, $^3J_{H,H}$ = 4.5 Hz, 1 H), 3.83 (s, 6 H), 3.84 (s, 6 H), 3.85 (s, 6 H), 4.42 (d, $^3J_{H,H}$ = 12.2 Hz, 1 H), 4.75 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H), 6.82 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 6.90 (s, 2 H), 6.99 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H), 7.01 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.1 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 46.3 (CH), 55.2 (CH), 55.85 (CH_3), 55.87 (CH_3), 56.0 (CH_3), 75.4 (CH), 107.6 (CH), 111.4 (CH), 111.6 (CH), 120.5 (CH), 135.8 (C), 137.3 (C), 147.6 (C), 149.0 (C), 150.2 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3502 cm^{-1}, 2938, 2839, 1606, 1590, 1513, 1463, 1416, 1263, 1142, 1106, 1026, 857, 813. MS (EI, 70 eV): *m*/*z* (%) = 496 (6) [M$^{\cdot+}$], 478 (8), 476 (5), 462 (8), 461 (10), 460 (27), 445 (7), 429 (20), 327 (6), 311 (9), 287 (100), 257 (9), 191 (25), 178 (14), 165 (6), 151 (12), 150 (7), 40 (5). Accurate mass by EI-MS ($C_{28}H_{32}O_8$): calcd. 496.2097; found 496.2118.

2,3,6,7,10,11-Hexamethoxy-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-*ab*]indene (2,3,6,7,10,11-Hexamethoxytribenzotriquinacene, 3): Chlorobenzene (100 mL) and orthophosphoric acid (85%; 1.00 mL) were heated to reflux in a two-necked flask equipped with a dropping funnel and a Thiele−Pape extractor filled with molecular sieves (4 Å). A solution of indane-1,3-diol **16** (4.63 g, ca. 9.0 mmol of the crude product described above), formed by gentle warming in 50 mL of chlorobenzene, was added dropwise. After the addition was complete, the mixture was heated to reflux for 1 h and then allowed to cool. The mixture was washed twice with 2 N aqueous sodium hydroxide (50.0 mL) and once with water (50.0 mL), then dried with sodium sulfate and concentrated to dryness. The residue obtained was purified by repeated gravity column chromatography (hexanes/EtOAc, 1:2 and 1:1, and then $CHCl_3$/EtOAc, 10:1). Recrystallization of the product thus obtained from methanol yielded tribenzotriquinacene **3** (425 mg, 9% from **14**) as a colorless solid, m.p. 228−229 °C, R_f (*n*-hexane/EtOAc, 1:2) 0.49, R_f (*n*-hexane/EtOAc, 1:1) = 0.17, R_f ($CHCl_3$/EtOAc, 10:1) = 0.61. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.85 (s, 18 H), 4.50 (q, $^3J_{H,H}$ = 9.4 Hz, 1 H), 4.75 (d, $^3J_{H,H}$ = 9.4 Hz, 3 H), 6.89 (s, 6 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 53.6 (CH), 55.5 (3 CH), 56.2 (CH_3), 107.2 (CH), 137.7 (C), 149.0 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1}, 2832, 1607, 1500, 1465, 1293, 1242, 1218, 1189, 1151, 1079, 1020, 979, 843, 781, 761. MS (EI, 70 eV): *m*/*z* (%) = 460 (100) [M$^{\cdot+}$], 445 (12), 429 (18), 354 (9), 230 (11), 181 (14), 166 (12), 165 (9), 151 (8), 149 (19). Accurate mass by EI-MS ($C_{28}H_{28}O_6$): calcd. 460.1886; found 460.1879. $C_{28}H_{28}O_6$ (460.53): calcd. C 73.03, H 6.13; found C 71.68, H 5.94.

Cyclodehydration of all-*cis*-2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxyindane-1,3-diol (16) by Use of Orthophosphoric Acid on Celite: Celite 545 (20.0 g) was suspended in a solution of 10 mL of orthophosphoric acid (85%) in 100 mL of water. After removal of the water under reduced pressure, the residue was dried in vacuo over phosphorus pentoxide. Chlorobenzene (50.0 mL) and orthophosphoric acid/Celite 545 (0.50 g) were heated to reflux in a two-necked flask equipped with a dropping funnel and a Thiele−Pape extractor filled with molecular sieves (4 Å). A solution of indane-1,3-diol **16** (1.14 g, ca. 2.2 mmol of the crude product described above), formed by gentle warming in 20 mL of chlorobenzene, was added dropwise. After the addition was complete, the mixture was heated to reflux for 1 h and then allowed to cool. It was washed twice with 2 N aqueous sodium hydroxide (20.0 mL) and then once with water (20.0 mL), dried with sodium sulfate and concentrated to dryness. The residue was subjected to gravity column chromatography (*n*-hexane/EtOAc, 1:2), giving diindene **17** as the major product and tribenzotriquinace **3** as the minor one.

5-(3,4-Dimethoxyphenyl)-2,3,8,9-tetramethoxy-5,10b-dihydroindeno-[1,2-*a*]indene (17): The major product obtained by chromatography (see above) was recrystallized from methanol, giving **17** as a light-brown solid (401 mg, 35% from **14**), m.p. 174−175 °C, R_f (*n*-hexane/EtOAc, 1:2) 0.76. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.818 (s, 3 H), 3.822 (s, 3 H), 3.826 (s, 3 H), 3.87 (s, 3 H), 3.92 (s, 3 H), 3.96 (s, 3 H), 4.93 (s, 1 H), 4.98 (d, $^4J_{H,H}$ = 1.2 Hz, 1 H), 6.61 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H), 6.80−6.79 (m, 3 H), 6.84−6.83 (m, 1 H), 6.89 (s, 1 H), 7.06 (d, $^4J_{H,H}$ = 1.1 Hz, 1 H), 7.28 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 48.7 (CH), 55.76 (CH_3), 55.83 (CH_3), 55.99 (CH_3), 56.04 (CH_3), 56.1 (CH_3), 56.6 (CH_3), 57.8 (CH), 105.2 (CH), 107.0 (CH), 108.5 (CH), 108.6 (CH), 110.6 (CH), 111.2 (CH), 119.0 (CH), 123.3 (CH), 130.8 (C), 135.2 (C), 136.7 (C), 139.4 (C), 141.0 (C), 146.9 (C), 147.6 (C), 148.6 (C), 148.81 (C), 148.84 (C), 148.9 (C), 158.1 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3009 cm^{-1}, 2997, 2927, 2856, 2837, 1606, 1515, 1487, 1468, 1442, 1332, 1316, 1297, 1280, 1265, 1235, 1217, 1183, 1173, 1140, 1100, 1073, 1024, 986, 866, 856, 783. MS (EI, 70 eV): *m*/*z* (%) = 460 (100) [M$^{\cdot+}$], 445 (10), 429 (77), 323 (6), 311 (15), 230 (10), 215 (8), 151 (9). Accurate mass by EI-MS ($C_{28}H_{28}O_6$): calcd. 460.1886; found 460.1886. The minor product, tribenzotriquinacene (**3**, 58.0 mg, 5% from **14**), was found to have the same analytical data as the compound synthesized in 9% yield by use of orthophosphoric acid in chlorobenzene (see above).

5,6-Dimethoxy-2-methylindan-1-one (19):[46] Polyphosphoric acid (350 g) was heated to 80 °C and stirred by means of a mechanical stirrer, while 1,2-dimethoxybenzene (**10**, 69.1 g, 500 mmol) and methacrylic acid (44.0 g, 500 mmol) were added. After stirring for 40 min at 80 °C, the mixture was carefully poured onto ca. 1000 mL of ice/water. The mixture was extracted with toluene (6 H 200 mL). The combined extracts were washed with 2 N aqueous sodium hydroxide and then with water, dried with sodium sulfate and concentrated to dryness. The residue was recrystallized twice from 2-propanol (2 × 500 mL) to give **19** (40.5 g, 39%) as a light-brown solid, m.p. 133 °C (133.5−134 °C [46a]), R_f (*n*-hexane/EtOAc, 1:1) = 0.60. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.30 (d, $^3J_{H,H}$ = 7.4 Hz, 3 H), 2.64 (dd, $^2J_{H,H}$ = 16.8, $^3J_{H,H}$ = 3.5 Hz, 1 H), 2.70 (m, 1 H), 3.31 (dd, $^2J_{H,H}$ = 16.8, $^3J_{H,H}$ = 7.4 Hz, 1 H), 3.91 (s, 3 H), 3.97 (s, 3 H), 6.87 (s, 1 H), 7.18 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 16.7 (CH_3), 34.8 (CH_2), 42.2 (CH), 56.1 (CH_3), 56.2 (CH_3), 104.4 (CH), 107.4 (CH), 129.0 (C), 148.7 (C), 149.4 (C), 155.5 (C), 208.3 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2969 cm^{-1}, 2938, 2874, 2844, 1686, 1591, 1500, 1466, 1445, 1434, 1424, 1365, 1323, 1294, 1261, 1240, 1215, 1181, 1125, 1085, 1046, 1001, 870, 836, 797, 766. MS (EI, 70 eV): *m*/*z* (%) = 206 (100) [M$^{\cdot+}$], 205 (19), 191 (92), 178 (12), 163 (27), 135 (18), 107 (15), 105 (11), 103 (13), 91 (25), 89 (13), 77 (15), 63 (11), 39 (11). $C_{12}H_{14}O_3$ (206.24): calcd. C 69.89, H 6.84; found C 69.79, H 6.80.

2-Hydroxy-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (21): A solution of the indan-1-one **19** (20.6 g, 100 mmol) in 250 mL of glacial acetic acid and 50 mL of water was cooled in an ice bath whilst being stirred by a mechanical stirrer, and chromium(VI) oxide (70.0 g, 700 mmol) was added in small portions over a period of ≥ 2 h. During the addition the temperature of the mixture was kept

below 15 °C due to the exothermicity of the reaction. Stirring was continued at ambient temperature for 3 d. After addition of 2-propanol (100 mL) and continued stirring for 1 h, the mixture was concentrated to dryness under reduced pressure at a bath temperature of ≤ 50 °C and the residue was redissolved in 400 mL of water. This solution was extracted once with 400 mL, and then five times with 200 mL, of dichloromethane. The combined extracts were washed with water, dried with sodium sulfate and then concentrated to a volume of ca. 40 mL. Addition of *n*-hexane (ca. 100 mL) formed a precipitate, which was collected by suction filtration and dried in vacuo to furnish **21** (6.80 g, 29%) as a colorless solid, m.p. 201 °C, R_f (*n*-hexane/EtOAc, 1:1) = 0.34. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.48 (s, 3 H), 2.96 (br. s, 1 H, OH), 4.01 (s, 6 H), 7.31 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.8 (CH_3), 56.8 (CH_3), 74.5 (C), 103.9 (CH), 134.7 (C), 156.7 (C), 198.8 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3492 cm^{-1}, 3086, 2990, 2945, 2841, 1741, 1703, 1579, 1503, 1466, 1320, 1242, 1223, 1166, 1103, 999, 773, 756. MS (EI, 70 eV): *m*/*z* (%) = 236 (80) [M$^{\cdot+}$], 193 (100), 165 (26), 164 (7), 150 (6), 137 (7), 136 (9), 122 (6), 93 (7), 79 (8), 77 (9), 51 (6), 50 (9), 43 (29). $C_{12}H_{12}O_5$ (236.23): calcd. C 61.02, H 5.12; found C 60.73, H 5.16.

4,5-Dichloro-3-[(5,6-dimethoxy-2-methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)oxy]-6-hydroxyphthalonitrile (22): A solution of the 1-indanone **19** (2.06 g, 10.0 mmol) in 100 mL of glacial acetic acid was stirred while a solution of 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (2.38 g, 10.5 mmol) in 100 mL of the same solvent was slowly added dropwise. After the addition was complete, the mixture was heated to 70 °C for 16 h and then cooled. The precipitate formed was collected by suction filtration, washed with a small amount of glacial acetic acid and dried in vacuo to yield **22** as a colorless solid (2.31 g, 53%), m.p. 218−219 °C, R_f (EtOAc) = 0.18. ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.63 (s, 3 H), 3.79 (s, 3 H), AB spin system (δ_A = 3.49, δ_B = 3.32, $^2J_{H,H}$ = 17.5 Hz, 2 H), 3.87 (s, 3 H), 7.10 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 24.0 (CH_3), 55.7 (CH_3), 56.1 (CH_3), 90.1 (C), 102.0 (C), 104.8 (CH), 108.2 (CH), 110.3 (C), 113.6 (C), 113.8 (C), 125.2 (C), 128.7 (C), 135.8 (C), 145.8 (C), 147.6 (C), 149.7 (C), 154.9 (C), 156.5 (C), 198.7 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3437 cm^{-1}, 2928, 2237, 1677, 1607, 1591, 1503, 1458, 1438, 1420, 1336, 1279, 1229, 1114, 1058, 1012, 901, 787, 678. MS (EI, 70 eV): *m*/*z* (%) = 436 (1) [{^{37}Cl$_2$}M$^{\cdot+}$], 434 (2) [{^{35}Cl^{37}Cl}M$^{\cdot+}$], 432 (2) [{^{35}Cl$_2$}M$^{\cdot+}$], 402 (1), 400 (2), 398 (5), 396 (1), 232 (6), 230 (36), 228 (56), 205 (85), 204 (100), 202 (17), 200 (27), 189 (21), 177 (10), 176 (19), 161 (16), 146 (13), 133 (18), 118 (12), 115 (13), 110 (12). $C_{20}H_{14}Cl_2N_2O_5$ (433.25): calcd. C 55.45, H 3.26, N 6.47; found C 55.39, H 3.42, N 6.40.

5,6-Dimethoxy-2-benzofuran-1(3*H*)-one (*meta*-Meconin, 24): Hydrogen chloride gas was bubbled through 700 mL of aqueous formaldehyde (37%) with initial cooling in an ice bath for ca. 1.5 h to reach saturation at ambient temperature. After addition of 3,4-dimethoxybenzoic acid (**23**) (91.1 g, 500 mmol), the mixture was heated to 60−70 °C for 7 h, while hydrogen chloride gas was continuously bubbled through the solution. The mixture was allowed to cool and left at ambient temperature overnight. The solvent was removed under reduced pressure, water (300 mL) was added to the residue and the mixture was neutralized by addition of aqueous ammonia (10%). The solid precipitate was collected by suction filtration, washed with water several times and then recrystallized from methanol to yield **24** as fine, colorless crystals (67.0 g, 69%), m.p. 154−155 °C (154−155 °C [50]), R_f (*n*-hexane/EtOAc, 1:1) = 0.32. Other analytical data were also found to be in accordance with the literature.[50] Especially careful work-up is recommended to achieve a sufficiently pure product, as otherwise the subsequent conversion (**24** → **25**) will not be successful.

(5,6-Dimethoxy-3-oxo-1,3-dihydro-2-benzofuran-1-yl)triphenylphosphonium Bromide (25): A mixture of the phthalide **24** (38.8 g, 0.20 mol), *N*-bromosuccinimide (33.8 g, 0.19 mol) and dibenzoyl peroxide (100 mg) in 800 mL of benzene (p.a.) was heated to reflux under argon for 3.5 h. The reaction mixture was allowed to cool and kept at ca. 5 °C overnight. The succinimide precipitated was removed by filtration to yield 1-bromo-1,3-dihydro-5,6-dimethoxybenzo[*c*]furan-3-one [R_f (*n*-hexane/EtOAc, 1:1) = 0.74] in benzene. Triphenylphosphane (65.6 g, 0.25 mol) was added to this solution and the resulting mixture was heated to reflux for 24 h. It was then allowed to cool; the solid precipitate was collected by suction filtration, washed with a small amount of benzene and dried to furnish **25** as a light-yellow solid (86.2 g, 80%), m.p. 229−230 °C (dec.). It should be noted that precipitation of **25** is a prerequisite for the successful synthesis of compound **26**. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.54 (s, 3 H), 3.85 (s, 3 H), 6.42 (s, 1 H), 7.06 (s, 1 H), 7.66−7.62 (m, 6 H), 7.82−7.76 (m, 9 H), 9.43 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.41 (CH_3), 56.44 (CH_3), 74.4 (CH, $^1J_{C,P}$ = 59.2 Hz), 105.9 (CH, $^3J_{C,P}$ = 2.8 Hz), 106.0 (CH), 114.6 (C, $^1J_{C,P}$ = 83.9 Hz), 118.4 (C, $^2J_{C,P}$ = 3.7 Hz), 130.4 (CH, $^2J_{C,P}$ = 13.6 Hz), 134.8 (CH, $^3J_{C,P}$ = 9.9 Hz), 135.3 (C, $^3J_{C,P}$ = 3.2 Hz), 135.8 (CH, $^4J_{C,P}$ = 3.1 Hz), 151.9 (C, $^5J_{C,P}$ = 2.5 Hz), 155.1 (C, $^4J_{C,P}$ = 2.9 Hz), 167.5 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3014 cm^{-1}, 2974, 2838, 1781, 1599, 1503, 1468, 1438, 1313, 1282, 1226, 1112, 1030, 1019, 1000, 837, 751, 730, 690. MS (MALDI, 2,5-dihydroxybenzoic acid): *m*/*z* = 455.29 [$C_{28}H_{24}O_4P$]$^+$. $C_{28}H_{24}BrO_4P$ (535.38): calcd. C 62.82, H 4.52; found C 62.93, H 4.52.

3-[(*E*)-Ethylidene]-5,6-dimethoxy-2-benzofuran-1(3*H*)-one (26a): A solution of triphenyl(phthalid-3-yl)phosphonium bromide (**25**, 53.5 g, 100 mmol) and acetaldehyde (4.84 g, 110 mmol) in 400 mL of anhydrous dichloromethane was stirred and cooled in an ice bath while anhydrous triethylamine (10.1 g, 100 mmol) was slowly added dropwise. Stirring was continued at ambient temperature for 2 h. The solvent was removed and the residue recrystallized from methanol (300 mL) to yield the (*E*) isomer **26a** (16.7 g, 76%) as a light-brown solid, m.p. 170−171 °C, R_f (EtOAc/*n*-hexane, 1:1) = 0.62. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.05 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H), 3.90 (s, 3 H), 3.95 (s, 3 H), 5.73 (q, $^3J_{H,H}$ = 7.9 Hz, 1 H), 7.12 (s, 1 H), 7.23 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 11.5 (CH_3), 56.32 (CH_3), 56.34 (CH_3), 104.1 (CH), 105.7 (CH), 106.1 (CH), 118.8 (C), 132.8 (C), 146.2 (C), 151.0 (C), 154.7 (C), 167.2 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3018 cm^{-1}, 2923, 2847, 1759, 1676, 1610, 1588, 1497, 1476, 1458, 1426, 1357, 1283, 1253, 1226, 1185, 1114, 1037, 862, 851, 816, 775, 677. MS (EI, 70 eV): *m*/*z* (%) = 220 (100) [M$^{\cdot+}$], 205 (10), 191 (8), 177 (7), 165 (27), 164 (36), 149 (11), 136 (23), 121 (10), 96 (11), 93 (9), 77 (8), 55 (9), 44 (11), 40 (23). $C_{12}H_{12}O_4$ (220.23): calcd. C 65.45, H 5.49; found C 65.19, H 5.69.

Equilibration of 3-[(*E*)-Ethylidene]- and 3-[(*Z*)-Ethylidene]phthalides 26a and 26b. A) By Thermolysis: A solution of the (*E*)-ethylidenephthalide **26a** (2.97 g, 13.5 mmol) and iodine (50.8 mg, 200 μmol) in 40 mL of freshly distilled nitrobenzene was heated to reflux under argon for 1 h. After the mixture had been allowed to cool, dichloromethane (20 mL) was added. The solution was washed with aqueous sodium thiosulfate (10%), dried with sodium sulfate and concentrated to dryness. The residue obtained was purified by gravity column chromatography (*n*-hexane/EtOAc, 2:3) followed by recrystallization from methanol to yield the (*Z*) isomer **26b** (993 mg, 33%) as a light-brown solid containing 7% of the (*E*) isomer **26a**, as detected by ^{1}H NMR spectroscopy. **B) By Photochemical Conversion:** A solution of the (*E*)-ethylidenephthalide **26a**

(22.0 mg, 100 μmol) in 10 mL of ethanol (p.a.), containing a trace of iodine, was heated to reflux under argon and irradiated 30 min. The solvent was removed under reduced pressure and the residue (21.9 mg, 100%) analyzed. ^{1}H NMR spectroscopy revealed that, here again, a 93:7 mixture of the (*Z*)- and (*E*)-ethylidenephthalides **26b** and **26a** had formed.

3-[(*Z*)-Ethylidene]-5,6-dimethoxy-2-benzofuran-1(3*H*)-one (26b) as a 93:7 Mixture with Its (*E*) Isomer (Procedure A): R_f (*n*-hexane/EtOAc, 2:3) = 0.40. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.96 (d, $^3J_{H,H}$ = 7.4 Hz, 3 H), 3.91 (s, 3 H), 3.96 (s, 3 H), 5.49 (q, $^3J_{H,H}$ = 7.5 Hz, 1 H), 6.95 (s, 1 H), 7.20 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 11.2 (CH_3), 56.3 (CH_3), 56.4 (CH_3), 100.5 (CH), 102.6 (CH), 105.2 (CH), 116.9 (C), 134.2 (C), 146.2 (C), 151.1 (C), 155.0 (C), 167.3 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2980, 2945, 2842, 1751, 1694, 1609, 1499, 1482, 1463, 1323, 1322, 1118, 1063, 1009, 820, 772. MS (EI, 70 eV): *m*/*z* (%) = 220 (100) [M$^{\cdot+}$], 205 (10), 191 (8), 177 (7), 165 (26), 164 (43), 149 (14), 136 (31), 121 (14), 103 (8), 96 (7), 93 (14), 91 (7).

5,6-Dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (20): A solution of the (*E*)-ethylidenephthalide **26a** (16.5 g, 75.0 mmol) and freshly prepared sodium methoxide (13.5 g, 250 mmol) in 300 mL of anhydrous tetrahydrofuran was heated to reflux for 2 h. The mixture was allowed to cool and the red precipitate was collected by suction filtration, washed with tetrahydrofuran and redissolved in 400 mL of water. Careful addition of 2 N hydrochloric acid precipitated a light-yellow solid, which was filtered by suction and recrystallized from methanol to yield indanedione **20** (11.6 g, 70%) as light-yellow crystals, m.p. 227−228 °C, R_f (*n*-hexane/EtOAc, 1:1) = 0.65. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.35 (d, $^3J_{H,H}$ = 7.9 Hz, 3 H), 2.96 (q, $^3J_{H,H}$ = 7.8 Hz, 1 H), 3.99 (s, 6 H), 7.29 (s, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 10.9 (CH_3), 48.2 (CH), 56.7 (CH_3), 103.3 (CH), 136.9 (C), 155.9 (C), 200.3 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2981 cm^{-1}, 2945, 2883, 2841, 1731, 1689, 1581, 1502, 1458, 1374, 1322, 1233, 1214, 1125, 1070, 1001, 947, 881, 856, 800, 753. MS (EI, 70 eV): *m*/*z* (%) = 220 (100) [M$^{\cdot+}$], 205 (10), 191 (6), 177 (7), 165 (26), 164 (37), 149 (10), 136 (22), 121 (9), 96 (9), 93 (9), 78 (7), 77 (7), 55 (6), 50 (9). $C_{12}H_{12}O_4$ (220.23): calcd. C 65.45, H 5.49; found C 65.18, H 5.34.

2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (18). A) By Condensation of 2-Methylindane-1,3-dione 20 with Benzhydrol 13: A mixture of the indane-1,3-dione **20** (11.0 g, 50.0 mmol) and *para*-toluenesulfonic acid monohydrate (951 mg, 5.00 mmol) in 300 mL of benzene (p.a.) was heated to reflux in a two-necked flask equipped with a dropping funnel and a Thiele−Pape extractor containing molecular sieves (4 Å). A solution of 3,3′,4,4′-tetramethoxybenzhydrol monohydrate **13**·H_2O (17.7 g, 55.0 mmol) in 200 mL of 1,2-dichloroethane, formed by gentle warming, was added. Upon initial addition, purple streaks formed in the yellow solution but immediately vanished due to the stirring. Towards the end of the addition the mixture turned violet. Heating to reflux was continued for 1 h and the mixture was then allowed to cool. It was washed twice with 2 N aqueous sodium hydroxide (200 mL) and once with water (200 mL), dried with sodium sulfate and concentrated to dryness. Recrystallization of the residue from methanol furnished the indanedione **18** (20.6 g, 81%) as colorless crystals, m.p. 162−163 °C, R_f (*n*-hexane/EtOAc, 1:1) = 0.33. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.25 (s, 3 H), 3.75 (s, 6 H), 3.83 (s, 6 H), 3.94 (s, 6 H), 4.45 (s, 1 H), 6.64 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 6.92 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.6 Hz, 2 H), 7.15 (s, 2 H), 7.16 (d, $^4J_{H,H}$ = 1.6 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 203.5 (C), 155.9 (C), 148.3 (C), 147.5 (C), 136.4 (C), 132.9 (C), 121.8 (CH), 112.7 (CH), 110.7 (CH), 102.3 (CH), 58.2 (C), 56.60 (CH), 56.58 (CH_3), 55.69 (CH_3), 55.65 (CH_3), 20.2 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1}, 2840, 1729, 1691, 1581, 1518, 1503, 1462, 1318, 1259, 1225, 1145, 1106, 1027, 1001, 859, 760, 648. MS (EI, 70 eV): *m*/*z* (%) = 506 (2) [M$^{\cdot+}$], 414 (8), 354 (6), 327 (23), 287 (100), 257 (6), 228 (6), 204 (12), 151 (7). Accurate mass by EI-MS ($C_{29}H_{30}O_8$): calcd. 506.1941; found 506.1941. $C_{29}H_{30}O_8$ (506.56): calcd. C 68.76, H 5.97; found C 68.91, H 5.94. **B) By Methylation of the Indane-1,3-dione 14:** A solution of the indane-1,3-dione **14** (4.93 g, 10.0 mmol) in 150 mL of acetonitrile (p.a.) was stirred while iodomethane (2.13 g, 15.0 mmol) and potassium fluoride on Celite 545[44,45] (12.5 g) were added. The suspension was heated to reflux for 3 h. It was then allowed to cool and filtered through a glass filter. The solid residue was washed carefully with several small portions of acetonitrile until its color had faded. The combined organic solutions were concentrated to dryness and the residue was recrystallized from methanol to yield the indane-1,3-dione **18** (3.79 g, 75%). The analytical data are identical with those of the product obtained from the procedure described above.

all-*cis*-2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-2-methyl-1,3-indanediol (27): A solution of indane-1,3-dione **18** (20.3 g, 40.0 mmol) in 150 mL of toluene (p.a.) was stirred under cooling in an ice bath while a 1.5 M solution of diisobutylaluminum hydride in toluene (66.7 mL, 100 mmol) was added dropwise. The mixture was stirred at ambient temperature for 24 h. After careful addition of saturated aqueous ammonium chloride (100 mL), the precipitated solid was collected by suction filtration and washed repeatedly with dichloromethane. The organic layer was separated and the aqueous one extracted with dichloromethane. The combined organic solutions were washed with water, dried with sodium sulfate and concentrated to dryness. The solid residue was recrystallized from benzene or benzene/cyclohexane (1:1) to yield the indanediol **27** (16.8 g, 82%) as a colorless solid, m.p. 148−149 °C, R_f (*n*-hexane/EtOAc, 1:2) = 0.28. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.83 (s, 3 H), 2.21 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H), 3.861 (s, 6 H), 3.864 (s, 6 H), 3.87 (s, 6 H), 4.49 (d, $^3J_{H,H}$ = 5.7 Hz, 2 H), 5.06 (s, 1 H), 6.83 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H), 6.95 (s, 2 H), 7.05 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.9 Hz, 2 H), 7.12 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.8 (CH_3), 48.0 (CH), 54.4 (C), 55.8 (CH_3), 55.86 (CH_3), 55.94 (CH_3), 82.3 (CH), 108.4 (CH), 111.0 (CH), 113.2 (CH), 121.5 (CH), 134.4 (C), 136.7 (C), 147.5 (C), 148.8 (C), 150.0 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3530 cm^{-1}, 3439, 3002, 2958, 2837, 1609, 1505, 1463, 1412, 1302, 1259, 1233, 1143, 1124, 1101, 1023, 836, 681. MS (EI, 70 eV): *m*/*z* (%) = 510 (1) [M$^{\cdot+}$], 476 (23), 474 (29), 459 (11), 443 (7), 325 (12), 287 (85), 257 (11), 241 (5), 205 (100), 191 (7), 178 (8), 165 (12), 151 (11). $C_{29}H_{34}O_8$ (510.59): calcd. C 68.22, H 6.71; found C 68.28, H 6.70.

2,3,6,7,10,11-Hexamethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (2,3,6,7,10,11-Hexamethoxy-12d-methyltribenzotriquinacene, 4): Chlorobenzene (250 mL) and orthophosphoric acid (85%; 5.00 mL) were heated to reflux for 30 min in a two-necked flask equipped with a dropping funnel and a Thiele−Pape extractor containing molecular sieves (4 Å). A solution of the indane-1,3-diol **27** (15.3 g, 30.0 mmol) in 150 mL of chlorobenzene, formed by gentle warming, was then added slowly dropwise. After the addition was complete, heating to reflux was continued for 1 h. The mixture was allowed to cool and washed twice with 2 N aqueous sodium hydroxide (100 mL) and once with water (100 mL), dried with sodium sulfate and concentrated to dryness. (Dichloromethane may be added to improve separation of the organic and aqueous layers.) The residue was recrystallized from ethanol to yield the tribenzotriquinacene **4** (7.02 g, 49%), as colorless crystals, m.p. 240−241 °C, R_f (*n*-hexane/EtOAc, 1:1) = 0.37,

R_f (*n*-hexane/EtOAc, 1:2) = 0.56. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 3.85 (s, 18 H), 4.27 (s, 3 H), 6.88 (s, 6 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 27.4 (CH_3), 56.2 (CH_3), 63.2 (CH), 63.3 (C), 107.3 (CH), 137.2 (C), 149.1 (C). IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2955, 2833, 1607, 1503, 1466, 1336, 1301, 1278, 1246, 1221, 1186, 1141, 1085, 993, 762. MS (EI, 70 eV): *m*/*z* (%) = 474 (100) [M$^{\cdot+}$], 459 (16), 443 (10), 298 (6), 237 (12). $C_{29}H_{30}O_6$ (474.56): calcd. C 73.40, H 6.37; found C 73.17, H 6.46.

4b,8b,12b-Tribromo-2,3,6,7,10,11-hexamethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (28): A mixture of the tribenzotriquinacene **4** (475 mg, 1.00 mmol), *N*-bromosuccinimide (712 mg, 4.00 mmol) and a small amount of 2,2′-azobis(isobutyronitrile) in 50 mL of tetrachloromethane (p.a.) was heated to reflux under argon and irradiated with an UV photolamp for 45 min. The mixture was allowed to cool, the precipitate was removed by suction filtration and washed with tetrachloromethane (p.a.). The solvent was removed under reduced pressure and the crude residue was directly used for further conversion into the triol **30**, but not to the tetramethyltribenzotriquinacene **29** (see below). The tribromo compound **28** was obtained in virtually quantitative yield and easily decomposes in the presence of moisture, for example on TLC foils. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.87 (s, 3 H), 3.35 (s, 18 H), 7.06 (s, 6 H) ppm.

2,3,6,7,10,11-Hexamethoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (29): *N*-Bromosuccinimide (712 mg, 4.00 mmol) and a small amount of 2,2′-azobis(isobutyronitrile) were added to a solution of tribenzotriquinacene **4** (475 mg, 1.00 mmol) in 50 mL of anhydrous benzene and the mixture was heated to reflux and irradiated with a UV photolamp for 45 min. The precipitate formed overnight was removed by suction filtration. The solution was concentrated to dryness and the residue redissolved in 50 mL of anhydrous benzene. The solution was stirred while a solution of trimethylaluminum (4.00 mL, 8.00 mmol) in toluene (2 M) was added dropwise. Stirring was continued whilst heating at 50 °C for 1 h. The mixture was cooled in an ice/water bath and then hydrolyzed by careful addition of 50 mL of water. The organic layer was separated and the aqueous one extracted with dichloromethane (3 × 25 mL). The combined organic solutions were washed with water, dried with sodium sulfate and concentrated to dryness. The residue was recrystallizaed from methanol to give tribenzotriquinacene **29** (249 mg, 48% from **4**) as colorless crystals, m.p. 231−232 °C, R_f ($CHCl_3$/EtOAc, 10:1) 0.60. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.33 (s, 3 H), 1.60 (s, 9 H), 3.84 (s, 18 H), 6.79 (s, 6 H) ppm. ^{13}C NMR (125.8 MHz): δ = 16.3 (CH_3), 25.6 (3 CH_3), 56.2 (CH_3), 62.1 (C, 3 C), 70.6 (C), 105.7 (CH), 140.4 (C), 149.2 (C). IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2834, 1606, 1498, 1463, 1401, 1314, 1285, 1233, 1193, 1155, 1117, 1065, 1035, 956, 873, 768, 754. MS (EI, 70 eV): *m*/*z* (%) = 516 (60) [M$^{\cdot+}$], 501 (100), 487 (19), 250 (7), 243 (8). Accurate mass by EI-MS ($C_{32}H_{36}O_6$): calcd. 516.2512, found 516.2514.

2,3,6,7,10,11-Hexamethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene-4b,8b,12b(12d*H*)-triol (30): A solution of the tribromotribenzotriquinacene **28**, prepared from 500 μmol of the tribenzotriquinacene **4** as described above, in 15 mL of tetrahydrofuran and 5 mL of sulfuric acid (20%) was heated to reflux for 3 h. After removal of the solvent under reduced pressure, water (100 mL) was added and the mixture was extracted with ethyl acetate (3 × 50.0 mL). The combined organic solutions were dried with sodium sulfate and then concentrated to dryness. The crude product obtained was recrystallized from dichloromethane/*n*-hexane to yield triol **30** (148 mg, 57% from **4**) as a colorless solid, m.p. 297−298 °C, R_f (EtOAc) = 0.19. ^{1}H NMR (500.1 MHz, CD_3CN): δ = 1.20 (s, 3 H), 3.64 (br. s, 3 H), 3.81 (s, 18 H), 7.11 (s, 6 H) ppm. ^{1}H NMR (500.1 MHz, CD_3OD): δ = 1.29 (s, 3 H), 2.00 (s, OH), 3.86 (s, 18 H), 7.18 (s, 6 H) ppm. ^{13}C NMR (125.8 MHz, CD_3CN): δ = 13.3 (CH_3), 56.6 (CH_3), 77.6 (C), 90.6 (3 C), 106.8 (CH), 137.7 (C), 151.7 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3509 cm^{-1}, 2942, 2840, 1607, 1502, 1465, 1360, 1275, 1223, 1148, 1086, 1003, 787, 766. MS (EI, 70 eV): *m*/*z* (%) = 522 (80) [M$^{\cdot+}$], 506 (58), 505 (100), 504 (48), 502 (14), 490 (38), 489 (35), 488 (13), 475 (13), 474 (27), 473 (21), 461 (12), 445 (28), 165 (15), 44 (13), 40 (17). Accurate mass by EI-MS ($C_{29}H_{30}O_9$): calcd. 522.1890, found 522.1890.

Nitration of the Hexamethoxytribenzotriquinacene 4. 6-(4,5-Dimethoxy-2-nitrophenyl)-2,3,8,9-tetramethoxy-5a-methyl-5,5a,6,10b-tetrahydroindeno[1,2-*a*]inden-5-yl Acetate (31): A solution of the tribenzotriquinacene **4** (1.19 g, 2.50 mmol) in 80 mL of acetanhydride was stirred under argon while copper(II) nitrate trihydrate (676 mg, 2.80 mmol) was added. The mixture was stirred at ambient temperature for 40 min and then poured into 400 mL of water. It was then extracted with dichloromethane (3 × 200 mL). The combined organic solutions were washed with 2 N aqueous sodium hydroxide (2 × 100 mL) and then with 100 mL of water, dried with sodium sulfate and concentrated to dryness. The residue obtained was subjected to gravity column chromatography ($CHCl_3$/EtOAc, 15:1) to yield the singly nitrated product **31** as a yellowish foam (1.18 g, 82%), which could not be crystallized despite considerable efforts; m.p. 114−116 °C, R_f ($CHCl_3$/EtOAc, 15:1) 0.64. R_f ($CHCl_3$) = 0.27. ^{1}H NMR (500.1 MHz): δ = 1.57 (s, 3 H), 1.99 (s, 3 H), 2.96 (s, 3 H), 3.63 (s, 3 H), 3.69 (s, 3 H), 3.82 (s, 3 H), 3.89 (s, 3 H), 3.98 (s, 3 H), 4.37 (s, 1 H), 4.79 (s, 1 H), 5.11 (s, 1 H), 5.54 (s, 1 H), 6.35 (s, 1 H), 6.43 (s, 1 H), 6.75 (s, 1 H), 7.05 (s, 1 H), 7.47 (s, 1 H) ppm. ^{13}C NMR (125.8 MHz): δ = 21.1 (CH_3), 21.9 (CH_3), 55.2 (CH), 55.97 (CH_3), 56.09 (2 CH_3), 56.15 (CH_3), 56.16 (CH_3), 56.23 (CH_3), 59.9 (C), 62.1 (CH), 79.7 (CH), 106.1 (CH), 107.0 (CH), 107.1 (CH), 108.6 (CH), 108.7 (CH), 113.1 (CH), 131.6 (C), 133.5 (C), 135.6 (C), 135.8 (C), 138.5 (C), 142.5 (C), 147.2 (C), 148.9 (C), 149.4 (C), 149.5 (C), 150.7 (C), 151.6 (C), 170.6 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1}, 2837, 1730, 1608, 1518, 1465, 1337, 1298, 1274, 1213, 1187, 1113, 1088, 1061, 1019, 995, 868, 795, 765. MS (EI, 70 eV): *m*/*z* (%) = 579 (10) [M$^{\cdot+}$], 562 (7), 520 (26), 519 (42), 518 (32), 505 (19), 504 (43), 503 (31), 502 (65), 490 (18), 489 (21), 488 (40), 487 (18), 476 (21), 475 (40), 474 (100), 473 (19), 472 (29), 471 (31), 460 (29), 459 (22), 331 (92), 330 (28), 316 (25), 315 (23), 314 (19), 313 (39), 205 (45), 189 (41), 180 (31), 166 (16), 165 (15), 43 (64). Accurate mass by EI-MS ($C_{31}H_{33}NO_{10}$): calcd. 579.2104, found 579.2115.

Electrophilic Bromination of Hexamethoxytribenzotriquinacene 4: A solution of the tribenzotriquinacene **4** (47.5 mg, 100 μmol) in 2 mL of 2-butanone was stirred under argon at 0 °C while *N*-bromosuccinimide (19.6 mg, 110 μmol) was added. Stirring was continued for 16 h in the dark, while the ice bath was allowed to melt slowly. Some aqueous sodium thiosulfate was added, the organic solvent was removed under reduced pressure and dichloromethane (100 mL) was added to the residue. The organic solution was washed with water, dried with sodium sulfate and concentrated to dryness. Gravity column chromatography of the residue (*n*-hexane/EtOAc, 1:1) yielded two singly brominated products, **34** (4.1 mg, 7%) and **35** (4.9 mg, 9%) as colorless films (see below). Some starting material **4** (13.2 mg, 28%), R_f (*n*-hexane/EtOAc, 1:1) 0.28, was also recovered.

1-Bromo-2,3,6,7,10,11-hexamethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (34): R_f (*n*-hexane/EtOAc, 1:1) = 0.43. ^{1}H NMR (500.1 MHz): δ = 1.64 (s, 3 H),

3.79 (s, 3 H), 3.81 (s, 3 H), 3.85 (s, 3 H), 3.86 (s, 6 H), 3.87 (s, 3 H), 4.25 (s, 1 H), 4.26 (s, 1 H), 4.54 (s, 1 H), 6.83 (s, 1 H), 6.87 (s, 1 H), 6.89 (s, 1 H), 6.90 (s, 1 H), 7.78 (s, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2943 cm^{-1}, 2863, 1606, 1503, 1466, 1318, 1276, 1249, 1222, 1086, 1032, 786, 759. MS (EI, 70 eV): *m/z* (%) = 554 (100) [$M^{\cdot+}$], 552 (99) [$M^{\cdot+}$], 539 (10), 537 (10), 523 (6), 521 (5), 277 (7), 276 (7). Accurate mass by EI-MS ($C_{29}H_{29}{}^{79}BrO_6$): calcd. 552.1148, found 552.1152.

6-(2-Bromo-4,5-dimethoxyphenyl)-2,3,8,9-tetramethoxy-5a-methyl-6,10b-dihydroindeno[1,2-*a*]inden-5(5a*H*)-one (35): R_f (*n*-hexane/EtOAc, 1:1) = 0.19. ^1H NMR (500.1 MHz): δ = 1.69 (s, 3 H), 3.70 (s, 3 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 3.84 (s, 3 H), 3.97 (s, 3 H), 3.98 (s, 3 H), 4.30 (s, 1 H)*, 4.81 (s, 1 H)*, 5.25 (s, 1 H)*, 6.35 (s, 1 H), 6.81 (s, 1 H), 6.86 (s, 1 H), 6.98 (s, 1 H), 7.01 (s, 1 H), 7.07 (s, 1 H) ppm. One of the marked (*) resonances is due to an unidentified impurity. IR (KBr): $\tilde{\nu}$ = 3158 cm^{-1}, 3079, 2958, 1771, 1693, 1605, 1502, 1466, 1352, 1292, 1243, 1223, 1190, 1091, 849, 820. MS (EI, 70 eV): *m/z* (%) = 570 (9) [$M^{\cdot+}$], 568 (8) [$M^{\cdot+}$], 489 (100), 474 (17), 459 (4), 313 (10), 245 (3), 237 (4). Accurate mass by EI-MS ($C_{29}H_{29}BrO_7$): calcd. 568.1097, found 568.1093.

Acknowledgments

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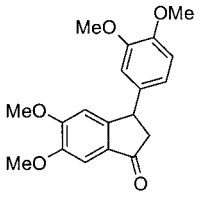
[1] C. Moberg, *Angew. Chem.* **1998**, *110*, 260−281; *Angew. Chem. Int. Ed.* **1998**, *37*, 248−268.
[2] L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080−1096; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018−1033.
[3] [3a] M. Mikulás, K. Rück-Braun, in *Organic Synthesis Highlights IV* (Ed.: H. G. Schmalz), Wiley-VCH, Weinheim, **2000**, pp. 187−193. [3b]K. Rück-Braun, *Nachr. Chem. Techn. Lab.* **1998**, *45*, 646−650.
[4] [4a] D. M. Collard, C. P. Lillya, *J. Org. Chem.* **1991**, *56*, 6064−6066, and references cited therein. [4b] H. Naarmann, M. Hanak, R. Mattner, *Synthesis* **1994**, 477−478, and references cited therein. [4c] S. Kumar, M. Manickam, *Chem. Commun.* **1997**, 1615−1616. [4d] J. Kopitzke, J. H. Wendorff, *Chem. Unserer Zeit* **2000**, *34*, 4−16. [4e] G. Cooke, A. Radhi, N. Boden, R. J. Bushby, Z. Lu, S. Brown, S. L. Heath, *Tetrahedron* **2000**, *56*, 3385−3390. [4f] H. Krempl, R. Mattmer, M. Hanack, *Synthesis* **2000**, 1705−1708. [4g] D. Hirst, S. Diele, S. Laschat, M. Nimtz, *Helv. Chim. Acta* **2001**, *84*, 1190−1196. [4h] S. R. Waldvogel, R. Fröhlich, C. A. Schalley, *Angew. Chem.* **2000**, *112*, 2580−2583; *Angew. Chem. Int. Ed.* **2000**, *39*, 2472−2475.
[5] [5a] C. Destrade, H. Gasparoux, A. Babeau, N. H. Tinh, J. Malthete, *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 37−48. [5b] N. H. Tinh, P. Foucher, C. Destrade, A. M. Levelut, J. Malthete, *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 277−292. [5c] J. Lejay, M. Pesquer, *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 293−310. [5d] P. Foucher, C. Destrade, N. H. Tinh, J. Malthete, A. M. Levelut, *Mol. Cryst. Liq. Cryst.* **1984**, *108*, 219−229.
[6] [6a] C. Zonta, S. Cossu, O. De Lucchi, *Eur. J. Org. Chem.* **2000**, 1965−1971. [6b] S. Cossu, C. Cimenti, P. Peluso, A. Paulson, O. De Lucchi, *Angew. Chem.* **2001**, *113*, 4210−4213; *Angew. Chem. Int. Ed.* **2001**, *40*, 4086−4089.
[7] [7a] A. Collet, *Tetrahedron* **1987**, *43*, 5725−5759. [7b] A. Collet, J.-P. Dutasta, B. Lozach, J. Canceill, *Top. Curr. Chem.* **1993**, *165*, 103−129.
[8] F. Vögtle, *Supramolekulare Chemie*, Teubner, Stuttgart **1992**.
[9] D. J. Cram, J. M. Cram, in *Monographs in Supramolecular Chemistry: Container Molecules and Their Guests* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge **1994**.
[10] [10a] D. J. Cram, J. Weiss, R. C. Helgeson, C. B. Knobler, A. E. Dorigo, K. N. Houk, *J. Chem. Soc., Chem. Commun.* **1988**, 407−409. [10b] J. A. Wytko, J. Weiss, *Tetrahedron Lett.* **1991**, *32*, 7261−7264.
[11] C. Schmuck, W. Wienand, *Synthesis* **2002**, 655−663.
[12] [12a] D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449−1460. [12b] D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626−628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595. [12c] D. Kuck, E. Neumann, A. Schuster, *Chem. Ber.* **1994**, *127*, 151−164.
[13] D. Kuck, *Angew. Chem.* **1984**, *96*, 515−516; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 508.
[14] For review concerning cyclodehydration, see: D. Kuck, *Synlett* **1996**, 949−965.
[15] For a review concerning the tribenzotriquinacenes as a particular sub-family of centropolyindanes, see: D. Kuck, *Top. Curr. Chem.* **1998**, *196*, 167−220.
[16] [16a] T. Sato, T. Akima, S. Akabori, H. Ochi, K. Hata, *Tetrahedron Lett.* **1969**, 1767−1770. [16b] T. Sato, T. Akima, K. Uno, *J. Chem. Soc., Perkin Trans. 1* **1973**, 891−895.
[17] [17a] R. Haag, B. Ohlhorst, M. Noltemeyer, A. Schuster, D. Kuck, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1993**, 1727−1729. [17b] R. Haag, D. Kuck, X.-Y. Fu, J. M. Cook, A. de Meijere, *Synlett* **1994**, 340−342. [17c] R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stahlke, A. Schuster, D. Kuck, A. de Meijere, *J. Am. Chem. Soc.* **1995**, *117*, 10474−10485.
[18] [18a] A. Schuster, D. Kuck, *Angew. Chem.* **1991**, *103*, 1717−1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1699−1702. [18b] D. Kuck, A. Schuster, C. Fusco, M. Fiorentino, R. Curci, *J. Am. Chem. Soc.* **1994**, *116*, 2375−2381.
[19] D. Kuck, A. Schuster, B. Paisdor, D. Gestmann, *J. Chem. Soc., Perkin Trans. 1* **1995**, 721−732.
[20] D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron* **2001**, *57*, 3587−3613.
[21] J. Tellenbröker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000−1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919−922.
[22] J. Tellenbröker, Doctoral thesis, University of Bielefeld, **1999**.
[23] M. Harig, Doctoral thesis, University of Bielefeld, **2002**.
[24] [24a] The alternative approach was focused on the stepwise construction of the tribenzotriquinacene framework, involving compounds **A** (m.p. 125−126 °C), **B** (m.p. 144−145 °C) and **C** (m.p. 200−201 °C, see electronic Supporting Information; for Supporting Information see also the footnote on the first page of this article). The synthesis of **A** has been improved compared to published procedures: [24b]E. N. Alesso, D. G. Tombari, G. Y. Moltrasio Iglesias, J. M. Aguirre, *Can. J. Chem.* **1987**, *65*, 2568−2574. [24c] J. F. Feeman, E. D. Amstutz, *J. Am. Chem. Soc.* **1950**, *72*, 1526−1531.



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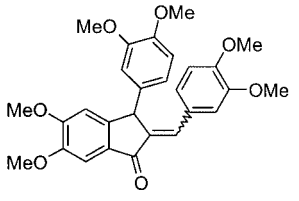

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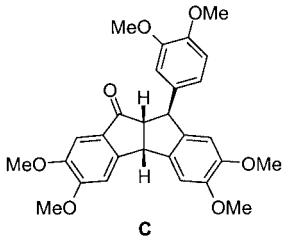

C

[25] [25a] V. Oshkaya, *Latv. PSR Zinat. Akad. Vestis, Khim. Ser.* **1971**, 730−734; *Chem. Abstr.* **1972**, *76*, 112940g. [25b] Y. Nagao, W.-S. Lee, K. Kim, *Chem. Lett.* **1994**, 389−392. [25c] P. Dallmagne, J. C. Pilo, S. Rault, M. Robba, *Bull. Soc. Chim. Fr.* **1993**, *130*, 121−124.
[26] M. Harig, Diploma thesis, University of Bielefeld **1998**.
[27] [27a] W. S. Johnson, H. J. Glenn, *J. Am. Chem. Soc.* **1949**, *71*, 1092−1096. [27b] E. C. Horning, J. Koo, G. N. Walker, *J. Am. Chem. Soc.* **1951**, *73*, 5826−5828. [27c] J. Koo, *J. Am. Chem. Soc.* **1953**, *75*, 1891−1894. [27d] S. O. de Silva, I. Ahmad, V. Snieckus, *Can. J. Chem.* **1979**, *57*, 1598−1605.
[28] W. Baker, H. L. Williams, *J. Chem. Soc.* **1959**, 1295−1299.
[29] [29a] J. D. Riedel, Akt.-Ges., D. R. P. 397150; *Chem. Zentralbl.* **1924**, *95 II*, 1404−1405. [29b] W. S. Johnson, J. M. Anderson, W. E. Shelberg, *J. Am. Chem. Soc.* **1944**, *66*, 218−222. [29c] J. W. Burnham, W. P. Duncan, E. J. Eisenbraun, G. W. Keen, M. C. Hamming, *J. Org. Chem.* **1974**, *39*, 1416−1420. [29d] R. Rangarajan, E. J. Eisenbraun, *J. Org. Chem.* **1985**, *50*, 2435−2438.
[30] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, Heidelberg, New York, Tokyo, **1984**, pp. 23−41.
[31] W. Baker, J. F. W. McOmie, S. D. Parfitt, D. A. M. Watkins, *J. Chem. Soc.* **1957**, 4026−4037.
[32] M. L. de Winter, W. T. Nauta, *Eur. J. Med. Chem.* **1977**, *12*, 125−130.
[33] [33a] G. E. Keck, R. R. Webb II, *J. Org. Chem.* **1982**, *47*, 1302−1309. [33b] E. Matarasso-Tchiroukhine, *Ann. Chim.* **1958**, 405−459.
[34] [34a] S. von Kostanecki, J. Tambor, *Ber. Dt. Chem. Ges.* **1906**, *39*, 4022−4027. [34b] E. C. Horning, J. A. Parker, *J. Am. Chem. Soc.* **1952**, *74*, 3870−3872. [34c] A. B. Diwadkar, H. D. Shroff, A. B. Kulkarni, *Curr. Sci. (India)* **1962**, *31*, 149−150; *Chem. Abstr.* **1962**, *57*, 12371c. [34d] B. D. Hosangadi, A. B. Kasbekar, M. J. Nabar, R. C. Desai, *Indian J. Chem.* **1973**, *11*, 711−713; *Chem. Abstr.* **1973**, *79*, 146114t.
[35] [35a] B. König, S. von Kostanecki, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 4027−4031. [35b] T. Garofano, A. Oliverio, *Ann. Chim. (Rome)* **1957**, *47*, 260−284; *Chem. Abstr.* **1957**, *51*, 12869 h.
[36] H. Sajiki, K. Hattori, K. Hirota, *J. Chem. Soc., Perkin Trans. 1* **1998**, 4043−4044.
[37] E. C. Horning, J. A. Parker, *J. Am. Chem. Soc.* **1952**, *74*, 3870−3872.
[38] [38a] P. D. Bartlett, J. D. McCollum, *J. Am. Chem. Soc.* **1956**, *78*, 1441−1450. [38b] M. J. Climent, A. Corma, H. Garcia, S. Iborra, J. Primo, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 275−278. [38c] Z. Zhu, J. H. Espenson, *J. Org. Chem.* **1996**, *61*, 324−328, and references cited therein. [38d] P. Gautret, S. El-Ghammarti, A. Legrand, D. Couturier, B. Rigo, *Synth. Commun.* **1996**, *26*, 707−713; and references cited therein.
[39] P. Dreyfuss, *Atti Accad. Gioenia Sci. Nat. Catania* **1939**, (6) 3, Mem. XV; *Chem. Zentralbl.* **1940**, *II*, 1712; *Chem. Abstr.* **1942**, *36*, 5471.
[40] C. Henneuse, T. Boxus, L. Tesolin, G. Pantano, J. Marchand-Brynaert, *Synthesis* **1996**, 495−501, and references cited therein.
[41] [41a] M. L. de Winter, W. T. Nauta, *Eur. J. Med. Chem. Chim. Thér.* **1977**, *12*, 131−136. [41b] M. L. de Winter, T. Bultsma, W. T. Nauta, *Eur. J. Med. Chem.* **1977**, *12*, 137−141.
[42] Indanedione **14** exhibits extremely strong aromatic solvent-induced shift (ASIS) effects, comparing, for example, the methoxy resonances in $CDCl_3$ and [D_6]benzene (see ref.[23]). In the latter solvent, the benzhydrylic proton signal is shifted by $\Delta\delta = +0.5$ ppm to lower field. Use of [D_6]DMSO gives similarly strong ASIS effects.
[43] D. Hellwinkel, S. Bohnet, *Chem. Ber.* **1987**, *120*, 1151−1173.
[44] R. Bloch, P. Orvane, *Synth. Commun.* **1981**, *11*, 913−915.
[45] D. Kuck, *Chem. Ber.* **1994**, *127*, 409−425.
[46] [46a] F.-H. Marquardt, *Helv. Chim. Acta* **1965**, *48*, 1476−1485. [46b] See also: A. K. Tashmukhamedova, G. M. Sarieva, M. G. Levkovich, F. G. Kamaev, *Chem. Nat. Compd.* **1983**, *19*, 489−492; *Khim. Prir. Soedin.* **1983**, *19*, 519−522.
[47] D. Kuck, *Org. Mass Spectrom.* **1994**, *29*, 113−125.
[48] [48a] M. Bouquet, A. Guy, M. Lemaire, J. P. Guette, *Synth. Commun.* **1985**, *15*, 1153−1157, and references cited therein. [48b] H. Lee, R. G. Harvey, *J. Org. Chem.* **1988**, *53*, 4587−4589. [48c] M. R. Paleo, D. Dominguez, L. Castedo, *Tetrahedron* **1994**, *50*, 3627−3638. [48d] T. Watanabe, Y. Oku, H. Ishii, T. Ishikawa, *Synlett* **1997**, 161−162.
[49] [49a] F. Nathanson, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 2576−2582. [49b] W. A. Mosher, R. W. Soeder, *J. Org. Chem.* **1971**, *36*, 1561−1563. [49c] K.-M. E. Ng, T. C. McMorris, *Can. J. Chem.* **1984**, *62*, 1945−1953. [49d] C.-J. Li, D.-L. Chen, Y.-Q. Lu, J. X. Habermann, J. T. Mague, *Tetrahedron* **1998**, *54*, 2347−2364.
[50] D. Bhattacharjee, F. D. Popp, *J. Pharm. Sci.* **1980**, *69*, 120−121.
[51] [51a] J. J. Brown, G. T. Newbold, *J. Chem. Soc.* **1952**, 4397−4403. [51b] J. Blair, W. R. Logan, G. T. Newbold, *J. Chem. Soc.* **1956**, 2443−2446. [51c] C. E. Slemon, L. C. Hellwig, J.-P. Ruder, E. W. Hoskins, D. B. MacLean, *Can. J. Chem.* **1981**, *59*, 3055−3060.
[52] P. Marshall, B. Mooney, R. Prager, A. D. Ward, *Synthesis* **1981**, 197−199.
[53] [53a] F. Sakamoto, S. Ikeda, G. Tsukamoto, *Chem. Pharm. Bull.* **1983**, *31*, 2698−2707. [53b] R. K. Howe, *J. Org. Chem.* **1973**, *38*, 4164−4167, and references cited therein.
[54] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley & Sons, Inc., New York, Chicester, Brisbane, Toronto, Singapore, **1994**.
[55] K. Bowden, M. Chehel-Amiran, *J. Chem. Soc., Perkin Trans. 2* **1986**, 2031−2034, and references cited therein.
[56] The unit cell parameters and the X-ray diffraction intensities were recorded with a Nonius KappaCCD area detector. The structure was solved by direct methods (SHELXS) and refined using a full-matrix least-squares method on F^2. Crystal data for $C_{29}H_{30}O_6$ (**4**): $M = 474.53$ g·mol^{-1}, monoclinic $P2_1/n$, $a = 16.1610(2)$, $b = 8.03800(10)$, $c = 18.4700(2)$ Å, $\beta = 93.9480(4)$, $V = 2393.60(5)$ Å^3, $T = 100(2)$ K, $Z = 4$, $\rho = 1.317$ Mg/m^3, λ(Mo-K_α) = 0.71073 Å, $F(000) = 1008$, absorption correction: multi-scan, index ranges $-22 \le h \le 22$, $-11 \le k \le 11$, $-25 \le l \le 25$, scan range $3.00° \le \theta \le 30.00°$, 61769 reflections collected, 6979 unique reflections, $R_{int} = 0.041$, 5457 reflections with $I > 2\sigma(I)$, 324 parameters, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0416$, $wR_2 = 0.1052$, R indices (all data) $R_1 = 0.0578$, $wR_2 = 0.1137$, goodness-of-fit on F^2 1.036, largest difference peak and hole 0.902/−0.217 e·Å^{-3}. CCDC-222768 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].
[57] [57a] J. Malthête, A. Collet, *Nouv. J. Chim.* **1985**, *9*, 151−153. [57b] G. I. Birnbaum, D. D. Klug, J. A. Ripmeester, J. S. Tse, *Can. J. Chem.* **1985**, *63*, 3258−3263. [57c] R. Poupko, Z. Luz, N. Spielberg, H. Zimmermann, *J. Am. Chem. Soc.* **1989**, *111*, 6094−6105, and references cited therein. [57d] H. Zhang, J. L. Atwood, *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 465−470.
[58] [58a] M. Farina, C. Morandi, *Tetrahedron* **1974**, *30*, 1819−1831. [58b] J. Constante, C. Garcia, A. Collet, *Chirality* **1997**, *9*, 446−453. [58c] C. G. Claessens, T. Torres, *Tetrahedron Lett.* **2000**, *41*, 6361−6365.
[59] M. Harig, D. Kuck, to be published.
[60] H. Stetter, M. Schwarz, A. Hirschhorn, *Chem. Ber.* **1959**, *92*, 1629−1635.
[61] [61a] A. Hassner, L. R. Krepski, V. Alexanian, *Tetrahedron* **1978**, *34*, 2069−2076. [61b] G. Höfle, W. Steglich, H. Vorbrüggen, *Angew. Chem.* **1978**, *90*, 602−615; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569.

[62] B. Karimi, H. Seradj, *Synlett* **2001**, 519−520.
[63] C. A. Dullaghan, G. B. Carpenter, D. A. Sweigart, D. Kuck, C. Fusco, R. Curci, *Organometallics* **2000**, *19*, 2233−2236.
[64] T. Hackfort, J. Tellenbröker, D. Barth, J. Strübe, D. Kuck, unpublished results.
[65] [65a] M. W. Galley, R. C. Hahn, *J. Am. Chem. Soc.* **1974**, *96*, 4337−4339, and literature quoted therein. [65b] A. Fischer, C. C. Greig, A. L. Wilkinson, D. R. A. Leonard, *Can. J. Chem.* **1972**, *50*, 2211−2216.
[66] J. Canceill, J. Gabard, A. Collet, *J. Chem. Soc., Chem. Commun.* **1983**, 122−123.
[67] [67a] D. J. Cram, S. Karbach, H.-E. Kim, C. B. Knobler, E. F. Maverick, J. L. Ericson, R. C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229−2237. [67b] J. C. Sherman, D. J. Cram, *J. Am. Chem. Soc.* **1989**, *111*, 4527−4528.
[68] [68a] E. M. Arnett, G. B. Klingensmith, *J. Am. Chem. Soc.* **1965**, *87*, 1023−1031. [68b] E. M. Arnett, G. B. Klingensmith, *J. Am. Chem. Soc.* **1965**, *87*, 1032−1037. [68c] E. M. Arnett, G. B. Klingensmith, *J. Am. Chem. Soc.* **1965**, *87*, 1038−1045.
[69] Studies aimed at the *ortho*-lithiation of **4** revealed that up to four-fold deprotonation can be achieved by use of an excess of phenyllithium and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in benzene at 20 °C, involving mostly the aromatic positions (see ref.[23]).
[70] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford, **1980**.
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