New C_{3v}-symmetrical tribenzotriquinacenes bearing extended and oxy-functionalised alkyl groups at their benzhydrylic bridgeheads†

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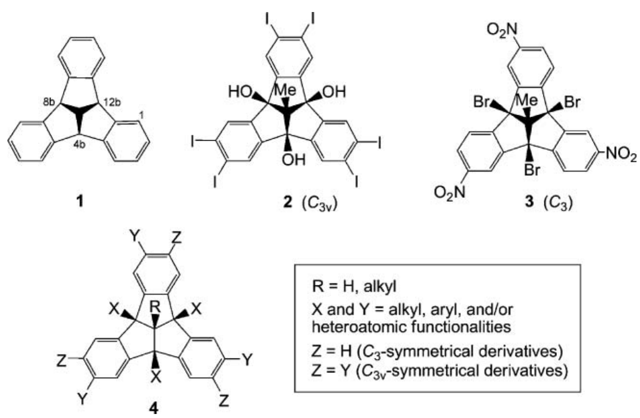
Received 28th June 2010, Accepted 18th August 2010
DOI: 10.1039/c0ob00337a

A series of tribenzotriquinacene derivatives bearing three oxy-functionalised alkyl groups at the benzhydrylic bridgeheads (C-4b, C-8b and C-12b) have been synthesised. The 4b,8b,12b-triallyl derivative was used to generate the corresponding TBTQ-tris-acetaldehyde and TBTQ-tris(acetic acid), in which the functional groups stretch out from the convex rigid molecular surface. The corresponding tribromo derivate was found to undergo smooth Lewis acid-catalyzed C–C coupling with appropriate silyl enol ethers to afford a series of threefold 4b,8b,12b-(2-oxoalkyl)-substituted tribenzotriquinacenes. Six-fold nitration at the arene periphery was performed with 4b,8b,12b-tripropyltribenzotriquinacene and with the TBTQ-tris(acetic acid) to check for the effect of the bridgehead groupings as solubilising auxiliaries.

Introduction

Tribenzotriquinacene **1** and its derivatives[1] represent polycyclic structures with unique geometrical features and a particularly high chemical versatility.[2] Owing to the rigid, convex–concave triquinacene core,[3,4] the tribenzotriquinacenes contain three indane wings stretching at right angles into space,[5] which has opened a facile access to extended conformationally rigid, convex–concave scaffolds with pronounced propensity to form non-covalent adducts with globular partners, such as C_{60}.[6,7] In recent years, the potential of multiple functionalisation and polycyclic extension of the arene periphery of the tribenzotriquinacene framework has been demonstrated in detail and the potential of tribenzotriquinacene-derived building blocks in supramolecular chemistry and other fields of application has become obvious.[2,5–10] Both C_{3v}-symmetrical (and thus achiral, *e.g.* **2**) and C_3-symmetrical (and thus chiral, *e.g.* **3**), derivatives have been synthesised, as generalised by structure **4** in Scheme 1. The unique geometrical properties of the tribenzotriquinacene motif has proven to materialize in self-organised supramolecular structures, such as in enantiopure cubic aggregates consisting of the hexafunctionalised derivative **3**.[11]

However, enlargement of highly regular polycyclic structures is often accompanied by restricted solubility. While introduction of long-chain solubilising residues at the aromatic periphery may rather prevent a desired intended supramolecular aggregation, attachment of such groupings at the three benzhydrylic bridgeheads (C-4b, C-8b and C-12b) of the tribenzotriquinacene skeleton represents a promising alternative. Thus, three (possibly functionalised) alkyl groups at these outer bridgehead positions are expected to increase the solubility of tribenzotriquinacene derivatives bearing multiple functional groups and/or polycyclic extensions at the aromatic periphery. In this article, we wish to report on our first progress in this respect.



Scheme 1 Tribenzotriquinacene **1**, two particular derivatives (**2**, **3**) and generalised derivatisation (**4**).

Results and discussion

As shown earlier for numerous cases, the 4b,8b,12b-tribromo derivative **5** of 12d-methyltribenzotriquinacene is the most easily accessible starting point for bridgehead substitution.[12,13] This compound can be converted by S_N1-type reactions into a large variety of heteroatom-coupled derivatives, including alkyl ethers and thioethers as well as some respective oligoethers.[5,14] However, coupling of **5** with metal–organic reagents, such as Grignard compounds or organolithium partners, proved to be difficult.[5a] This may be attributed to the inevitable S_N1-type reactivity at the bridgehead positions of the three-fold benzhydrylic bromide **5**. In turn, just because of that reactivity, various Lewis acid-catalyzed condensation reactions of this key compound, including the condensation with allyltrimethylsilane (see below), were found to be useful. In our attempts to introduce various larger aliphatic residues at the bridgehead positions, condensation of tribromide **5** with several trimethylsilyl enol ethers was studied. The silyl enol ethers **6a–6f** were synthesised according to Corey's method[15] and then reacted with tribromide **5** in the presence of either tin tetrachloride or titanium tetrachloride in

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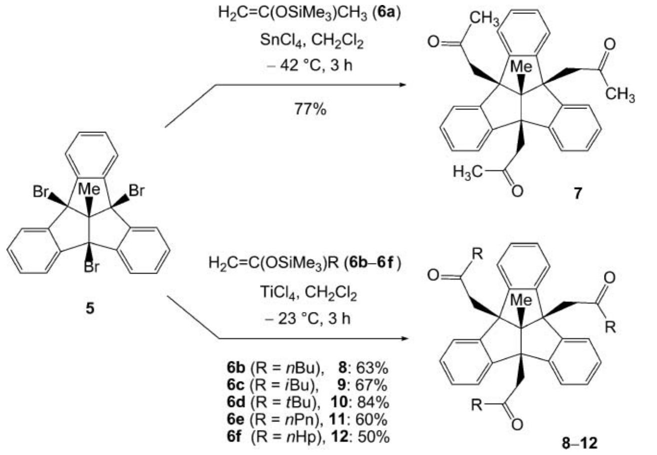
† Electronic supplementary information (ESI) available: ^1H NMR spectra. See DOI: 10.1039/c0ob00337a



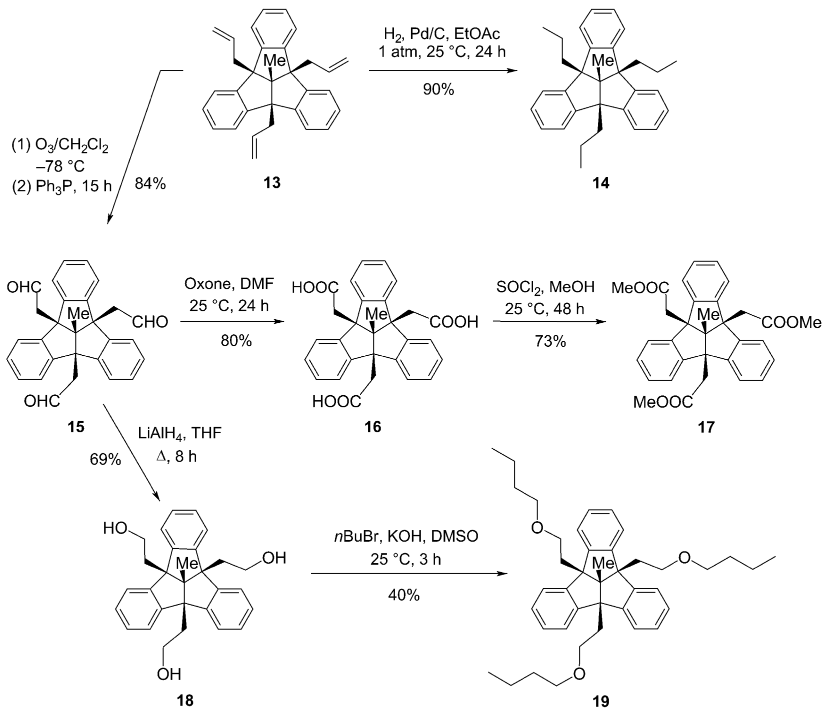
Scheme 2 Condensation of tribromotribenzotriquinacene **5** with the silyl enol ethers **6** giving the tris(2-oxoalkyl)tribenzotriquinacenes **7–12**.

dichloromethane (Scheme 2). Thus, 4b,8b,12b-tris(acetonyl)-12d-methyltribenzotriquinacene (**7**) was synthesised in good yield by use of $SnCl_4$ as the catalyst. Surprisingly, however, it did not form when $TiCl_4$ was employed. By contrast, all of the higher 2-oxoalkyl derivatives **8–12** were obtained in moderate to good yields by use of the latter catalyst. Most of these triketones (**7–10**) were found to crystallize readily and even the long-chain derivatives **11** and **12** formed waxy solids, in spite of the considerably elongated bridgehead substituents.

Triallyltribenzotriquinacene **13**, which is easily accessible from **5** as described previously,[5a] may also be used as a valuable key intermediate. Catalytic hydrogenation using Pd/C in ethyl acetate under normal pressure smoothly afforded the corresponding tripropyl congener **14** in good yield (Scheme 3).[16] Since, unfortunately, metathesis reactions of triallyltribenzotriquinacene **13** with 1-alkenes under various conditions proved to be unsuccessful,[17,18] we focused our efforts on the use of this hydrocarbon as a starting material for the synthesis of new bridgehead-oxyfunctionalised derivatives.

Ozonolysis of hydrocarbon **13** followed by reductive work-up using triphenylphosphine gave the tribenzotriquinacene-based tris-acetaldehyde **15** in good yield.[19] This work-up procedure turned out to be productive when run at ambient temperature for an extended period of time. However, it may be noted that the cleavage of the three olefinic bonds in compound **13** and/or of the ozonide intermediates is not at all trivial. In spite of the fact that consumption of three equivalents of ozone was observed as expected, several reductive work-up procedures failed, including the use of dimethyl sulfide (in the presence or absence of methanol),[20a] zinc and acetic acid,[20b] and aqueous acetone.[20c] None of these reagents gave the desired tris-aldehyde **15**. Similarly, oxidative work-up of the ozonide mixture by use of hydrogen peroxide and acetic acid[20d] under various conditions failed. The extent of conversion was checked by NMR spectroscopy and the ozonides were found to be partially persistent under the various conditions and with different reagents examined. Moreover, the direct attempts to oxidatively cleave the olefinic double bonds in compound **13** by using osmium tetroxide/oxone in dimethylformamide,[20e] aqueous potassium permanganate/Adogen 464 in dichloromethane[20f] or aqueous potassium permanganate/$NaIO_4$/SiO_2 in dichloromethane–acetonitrile[20g] led to failure.

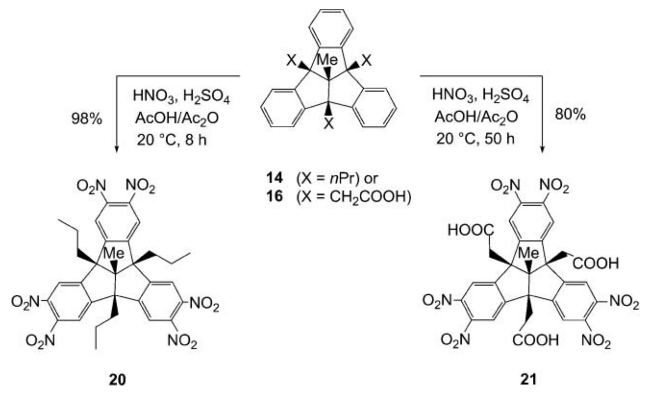
Notwithstanding these difficulties, tris-aldehyde **15** obtained after work-up with triphenylphosphine was found to be surprisingly stable under air and the subsequent oxidation with



Scheme 3 Triallyltribenzotriquinacene **13** as the key intermediate in the synthesis of some new tribenzotriquinacene derivatives, most of which bear three oxy-functionalised bridgehead groups.

oxone (2 $K_2SO_5 \cdot K_2SO_4 \cdot KHSO_4$) afforded the corresponding tribenzotriquinacene-tris(acetic acid) **16** in good yield. Esterification of this compound with methanol in the presence of thionyl chloride proceeded at ambient temperature to furnish the corresponding three-fold methyl acetate **17**. Reduction of the tris-aldehyde **15** by use of lithium aluminium hydride in tetrahydrofuran gave the corresponding tris-ethanol **18**, and subsequent etherification of the latter compound with *n*-butyl bromide in dimethyl sulfoxide led to the respective long-chain tris-ether **19**. Yields of these conversions were satisfactory in all cases. The compounds were obtained in pure form by chromatography or crystallisation and all of them were found to crystallise quite readily. In all cases, spectroscopic and other analytical results documented the absence of products of incomplete (*e.g.*, two-fold) conversions. The expected C_{3v} molecular symmetry of compounds **15–19** was confirmed by their ^{1}H and ^{13}C NMR spectra.

Finally, some of the new bridgehead-substituted tribenzotriquinacenes were subjected to electrophilic substitution at the six peripheral arene positions (Scheme 4). Six-fold nitration of the fully bridgehead-alkylated hydrocarbon **14** was attempted by use of a mixture of nitric acid (100%) and concentrated sulfuric acid, in analogy to the very efficient sixfold nitration of the tetramethyl congener.[8] Remarkably, this conversion was found to be considerably hampered due to a *reduced* solubility of **14** in the highly polar acid mixture, resulting in the visible aggregation of partially nitrated products. However, this problem was circumvented by use of a mixture of acetic anhydride and glacial acetic acid as a co-solvent. With this modification, the 2,3,6,7,10,11-hexanitrotribenzotriquinacene **20** was obtained in virtually quantitative yield. Under the same conditions, the corresponding hexanitrotribenzotriquinacene-tris(acetic acid) **21** was synthesised from tris-acid **16** in excellent yield albeit with increased reaction time to ensure the exhaustive nitration of the six peripheral positions.



Scheme 4 Six-fold nitration of the tribenzotriquinacenes **14** and **16** at their arene periphery.

Conclusion

In summary, we have developed a facile access to several new C_{3v}-symmetrical tribenzotriquinacenes bearing elongated and, in most cases, functionalised alkyl groups at their benzhydrylic bridgeheads. The bridgehead tribromide **5** and the triallyl congener **13** were used as the starting compounds. On the one hand, Lewis acid-assisted three-fold C–C coupling of **5** with various trimethylsilyl enol ethers afforded the introduction of three (2-oxo)-functionalised alkyl chains; on the other hand, ozonolytic cleavage of **13** followed by re-functionalisation led us to new tribenzotriquinacenes bearing three functionalised C_2 residues. Among these, the tris-aldehyde **15** promises to be another key intermediate for the synthesis of long-chain bridgehead TBTQ derivatives. In line with expectation, the presence of three larger (and possibly functionalised) bridgehead substituents were found to affect the solubility of the tribenzotriquinacenes, as observed in the case of six-fold nitration of the arene periphery. This first access to tribenzotriquinacenes bearing extended solubilising bridgehead substituents and multifunctionalised arene peripheries is encouraging in view of the vast potential of the tribenzotriquinacenes for the construction of novel three-dimensional, non-covalent aggregates but also for covalently bound, nanoscale molecular containers with, for example, nanocubic topology.[2,11,21]

Experimental section

General

Melting points (uncorrected): Electrothermal melting point apparatus. Infrared spectra were recorded on an FT-IR spectrometer, Model Nicolet-380. Most of the NMR spectra were measured on a Bruker DRX 500 instrument (^{1}H, 500 MHz, ^{13}C: 125.7 MHz); only in one case a Bruker Avance 600 instrument (^{1}H, 600 MHz, ^{13}C: 150.8 MHz) was employed. Mass spectra were recorded with a VG Autospec double focusing mass spectrometer. MALDI measurements were made with Voyager-DE MALDI-TOF. Accurate mass measurements were performed with a VG Autospec X sector-field instrument and a Bruker APEX III (7.0 T) FT ion cyclotron mass spectrometer. Combustion analyses were carried out with a Perkin-Elmer Model 240 instrument. Tetrahydrofuran was dried over potassium and dichloromethane was used as delivered (p.a). *n*-Pentane and ethyl acetate were distilled before use. Reactions requiring anhydrous conditions were performed in oven-dried glassware under argon.

General procedure for the preparation of silyl enol ethers 6a–6f

Into an oven-dried 25 mL flask under argon was placed lithium diisopropyl amide from a commercially available 2.0 M solution (0.60 mL, 1.2 mmol) in 1 mL of dry tetrahydrofuran at −78 °C. A solution of trimethylsilyl chloride (6.00 mmol) in 2.0 mL of THF was added and stirred, followed by dropwise addition of the substrate (1.00 mmol) in 1.0 mL of THF. After 1 min, 0.80 mL of anhydrous triethylamine was added and stirring was continued for 50 min at the same temperature. Then the mixture was allowed to warm to ambient temperature and then quenched by addition of saturated aqueous sodium bicarbonate. The product was extracted twice into *n*-pentane and the combined extracts were washed first with water, then with 0.05 M citric acid solution and again with water. Drying over Na_2SO_4 followed by evaporation of the solvent gave the crude silyl enol ethers, which were purified by Kugelrohr distillation.

12d-Methyl-4b,8b,12b-tris(2-oxopropyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (7)

A solution of tribromide **5** (531 mg, 1.00 mmol) in anhydrous dichloromethane (10 mL) was stirred under argon and cooled to −42 °C. Tin tetrachloride (0.38 mL, 3.3 mmol) was added under argon through a septum. After dropwise addition of 2-propenyl trimethylsilyl ether (**6a**) (0.60 mL, 3.6 mmol), stirring was continued at the same temperature for a further 2–3 h, while the reaction was monitored by TLC. After the complete consumption of compound **5**, the reaction mixture was quenched with water and then extracted several times with dichloromethane. The combined organic extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent furnished the crude product, which was recrystallised from ethanol to give the triketone **7** (yield 356 mg, 77%) as colorless crystals, mp 290–292 °C; IR (neat): $\tilde{\nu}$ = 3023, 2917, 2359, 1705, 1588, 1480, 1154, 746, 553 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 and 7.11 (*AA′BB′*, 2 × 6H, Ar–H), 3.59 (s, 6H, 3 × CH_2), 2.10 (s, 9H, 3 × $COCH_3$), 1.29 (s, 3H, 12d-Me); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.9 (CO), 147.6 (C), 127.9 (CH), 122.5 (CH), 71.1 (C), 65.9 (C), 51.3 (3 × CH_2), 31.3 (3 × CH_3), 15.7 (CH_3, 12d-Me); MS (EI, 70 eV): *m/z* (%), 462 (19, $[M]^{+\bullet}$), 405 (100), 347 (54), 305 (14), 289 (40); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{32}H_{30}O_3$ 462.2195; found 462.2192.

General procedure for the preparation of the tribenzotriquinacene-based triketones 8–12

A solution of tribromide **5** (1.00 mmol) in anhydrous dichloromethane (10 mL) was stirred under argon and cooled to −23 °C. Titanium tetrachloride (0.36 mL, 3.3 mmol) was added under argon through a septum followed by the dropwise addition of the appropriate silyl enol ether (**6b–6f**) (3.6 mmol). Stirring was continued at the same temperature for a further 2–3 h, while the reaction was monitored by TLC. After the complete consumption of compound **5**, the reaction mixture was allowed to warm to ambient temperature, then quenched with water and extracted several times with dichloromethane. The combined organic extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent furnished the crude product, which was recrystallised from ethanol to give the respective pure triketones **8–12**.

12d-Methyl-4b,8b,12b-tris(2-oxohexyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (8)

Yield 370 mg, 63%; colorless crystalline solid, mp 175–176 °C; IR (neat): $\tilde{\nu}$ = 3022, 2956, 2871, 1709, 1588, 1489, 1031, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 and 7.13 (*AA′BB′*, 2 × 6H, Ar–H), 3.61 (s, 6H, 3 × CH_2), 2.44 (t, J = 7.5 Hz, 6H, 3 × CH_2), 1.52-1.49 (m, 6H, 3 × CH_2), 1.30-1.25 (m, 9H, 3 × CH_2 and 12d-CH_3) 0.91 (t, ^3J = 7.5 Hz, 9H, 3 × Me); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 209.9 (CO), 147.3 (C), 127.4 (CH), 122.1 (CH), 70.1 (C), 65.5 (C), 50.2 (3 × CH_2), 43.3 (3 × CH_2), 26.0 (6 × CH_2), 22.3 (3 × CH_3) 13.9 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 588 (13, $[M]^{+\bullet}$), 489 (100), 389 (12), 305 (9), 289 (18); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{41}H_{48}O_3$ 588.3604; found 588.3604.

12d-Methyl-4b,8b,12b-tris(4-methyl-2-oxopentyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (9)

Yield 394 mg, 67%; colorless crystalline solid, mp 202–203 °C; IR (neat): $\tilde{\nu}$ = 3023, 2948, 2867, 1707, 1479, 747, 607, 580 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 and 7.12 (*AA′BB′*, 2 × 6H, Ar–H), 3.61 (s, 6H, 3 × CH_2), 2.30 (d, J = 6.9 Hz, 6H, 3 × CH_2), 2.10 (m, 3H, 3 × CH), 1.32 (s, 3H, 12d-CH_3), 0.88 (d, ^3J = 6.6 Hz, 18H, 3 × $C(CH_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 208.8 (CO), 146.7 (C), 126.7 (CH), 121.4 (CH), 69.9 (C), 64.8 (C), 51.8 (3 × CH_2), 50.2 (3 × CH_2), 23.9 (3 × CH), 21.8 (3 × $C(CH_3)_2$), 14.8 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 588 (11, $[M]^{+\bullet}$), 489 (100), 389 (12), 319 (10), 289 (17); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{41}H_{48}O_3$ 588.3604; found 588.3600.

12d-Methyl-4b,8b,12b-tris(3,3-dimethyl-2-oxobutyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (10)

Yield 494 mg, 84%; colorless crystalline solid, mp 259–261 °C; IR (neat): $\tilde{\nu}$ = 3024, 2965, 2359, 1708, 1478, 1054, 997, 972 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 and 7.12 (*AA′BB′*, 2 × 6H, Ar–H), 3.73 (s, 6H, 3 × CH_2), 1.21 (s, 3H, 12d-CH_3), 1.17 (s, 27H, 3 × $C(CH_3)_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 214.7 (CO), 147.6 (C), 127.3 (CH), 122.0 (CH), 70.5 (C), 65.2 (C), 44.6 (3 × CH_2), 44.3 (3 × $\mathit{C}(CH_3)_3$), 26.9 (3 × $C(\mathit{CH_3})_3$), 15.2 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 588 (4, $[M]^{+\bullet}$), 489 (100), 389 (9), 319 (12), 289 (16); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{41}H_{48}O_3$ 588.3604; found 588.3597.

12d-Methyl-4b,8b,12b-tris(2-oxoheptyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (11)

Yield 378 mg, 60%; colorless solid; mp 166–168 °C; FT-IR (neat): $\tilde{\nu}$ = 3023, 2955, 2871, 1710, 1479, 1368, 1065, 739, 508 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 and 7.13 (*AA′BB′*, 2 × 6H, Ar–H), 3.61 (s, 6H, 3 × CH_2), 2.43 (t, ^3J = 7.5 Hz, 6H, 3 × CH_2), 1.54–1.51 (m, 6H, 3 × CH_2), 1.30–1.22 (m, 15H, 6 × CH_2 and 12d-CH_3), 0.90 (t, ^3J = 7.0 Hz, 9H, 3 × CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 209.2 (CO), 146.7 (C), 126.7 (CH), 121.8 (CH), 69.9 (C), 64.8 (C), 49.6 (3 × CH_2), 42.9 (3 × CH_2), 30.7 (3 × CH_2), 22.9 (3 × CH_2), 21.8 (3 × CH_2), 14.9 (12d-CH_3), 13.2 (3 × CH_3); MS (EI, 70 eV): *m/z* (%), 630 (6, $[M]^{+\bullet}$), 517 (100), 405 (11), 403 (11), 305 (11), 289 (19); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{44}H_{54}O_3$ 630.4073; found 630.4058.

12d-Methyl-4b,8b,12b-tris(2-oxononyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (12)

Yield 357 mg, 50%; colorless solid, mp 157–159 °C; IR (neat): $\tilde{\nu}$ = 3023, 2955, 2921, 1708, 1480, 1368, 1127, 730, 615 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 and 7.13 (*AA′BB′*, 2 × 6H, Ar–H), 3.61 (s, 6H, 3 × CH_2), 2.43 (t, ^3J = 7.3 Hz, 6H, 3 × CH_2), 1.53–1.50 (m, 6H, 3 × CH_2), 1.30–1.26 (m, 27H, 12 × CH_2 and 12d-CH_3), 0.90 (t, ^3J = 7.0 Hz, 9H, 3 × CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 209.3 (CO), 146.7 (C), 126.7 (CH), 121.4 (CH), 69.9 (C), 64.8 (C), 49.6 (3 × CH_2), 42.9 (3 × CH_2), 31.0 (3 × CH_2), 28.5 (3 × CH_2), 28.4 (3 × CH_2), 23.2 (3 × CH_2), 21.9 (3 × CH_2), 14.8 (12d-CH_3), 13.4 (3 × CH_3); MS (EI, 70 eV): *m/z* (%), 714 (7, $[M]^{+\bullet}$), 573 (100), 433(7), 431 (9), 305 (11), 319(9), 289 (15); accurate mass (EI-MS) of $[M]^{+\bullet}$: calcd. for $C_{50}H_{66}O_3$ 714.5012; found 714.5013.

12d-Methyl-4b,8b,12b-tri-*n*-propyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [12d-methyl-4b,8b,12b-tri(*n*-propyl)tribenzotriquinacene, 14]

A solution of triallyltribenzotriquinacene **13** (414 mg, 1.00 mmol) in anhydrous EtOAc (30 mL) was mixed with palladium on charcoal (10%, Sigma-Aldrich) (40 mg) in a hydrogenation flask and the mixture was vigorously agitated in a hydrogenation shaker at ambient temperature and pressure for 24 h. Filtration through a pad of silica gel and evaporation of the solvent under reduced pressure gave a colorless solid which was recrystallised from ethanol furnishing hydrocarbon **14** (yield 378 mg, 90%) as fine, transparent needles, mp 240–241 °C; IR (neat): $\tilde{\nu}$ = 3063, 3021, 2953, 1477, 1452, 1026, 741, 655 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 and 7.14 (*AA′BB′*, 2 × 6H, Ar–H), 2.19 (t, ^3J = 8.1 Hz, 6H, 3 × CH_2), 1.63 (s, 3H, 12d-CH_3), 1.24-1.16 (m, 6H, 3 × CH_2), 0.95 (t, ^3J = 7.5 Hz, 9H, 3 × CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.1 (C), 127.1 (CH), 123.3 (CH), 71.7 (C), 67.2 (C), 40.8 (CH_2), 20.5 (CH_2), 15.1 (12d-CH_3 and 4b, 8b,12b-CH_3); MS (EI, 70 eV): *m/z* (%), 420 (3, [M]$^{+\bullet}$), 377 (100), 334 (3), 305 (8), 289 (10); Elemental analysis: Found C, 91.25; H, 8.62; Calc. for $C_{32}H_{36}$: C, 91.37; H, 8.63.

4b,8b,12b-Tris(formacylmethyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (12d-methyltribenzotriquinacene 4b,8b,12b-tris-acetaldehyde, 15)

A solution of triallyltribenzotriquinacene **13** (414 mg, 1.00 mmol) in anhydrous dichloromethane (6.0 mL) was placed in a two-necked round bottom flask and cooled to −78 °C. An ozone/oxygen mixture was bubbled through the solution until the blue color appeared. After a further 3 min, the excess of ozone was removed by flushing the solution with argon. Then triphenylphosphine (2.36 g, 9.00 mmol) was added to the solution. The mixture was allowed to warm to 20 °C and then stirred for 15 h. The solvent was removed under reduced pressure and the crude mixture was then purified by chromatography through silica gel (EtOAc/*c*-C_6H_{12} 1 : 3) to furnish the tris-aldehyde **15** (yield 353 mg, 84%) as colorless crystals, mp 260–262 °C; IR (neat): $\tilde{\nu}$ = 3420, 3069, 2967, 2740, 1715, 1480, 763, 510 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 9.48 (s, 3H, 3 × CHO), 7.62 and 7.21 (*AA′BB′*, 2 × 6H, Ar–H), 3.47 (s, 6H, 3 × CH_2), 1.21 (s, 3H, 12d-CH_3); ^{13}C NMR (125.7 MHz, DMSO-d$_6$): δ 202.8 (CHO), 146.4 (C), 127.9 (CH), 123.3 (CH), 70.2 (C), 64.8 (C), 50.7 (CH_2), 18.6 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 420 (15, [M]$^{+\bullet}$), 377 (100), 348 (42), 335 (28), 289 (46). Elemental analysis: Found C, 82.68; H 5.84; Calc. for $C_{29}H_{24}O_3$: C, 82.83; H, 5.75.

4b,8b,12b-Tris(carboxylmethyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [12d-methyltribenzotriquinacene 4b,8b,12b-tris(acetic acid), 16]

A solution of tris-aldehyde **15** (420 mg, 1.00 mmol) in dimethylformamide (25 mL) was stirred while oxone (9.8 g, 16.00 mmol) was added in one portion. Stirring was continued for 24 h and the reaction was monitored by TLC. Aqueous hydrochloric acid (1 N) was added to dissolve the salts and the organic products were extracted with ethyl acetate. The combined organic extracts were washed with HCl (1 N), brine and water and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product, which was then purified by diffusion crystallisation using chloroform and diethyl ether giving the tris-acid **16** (yield 374 mg, 80%) as colorless crystals (containing some incorporated diethyl ether), mp 281–283 °C; IR (neat): $\tilde{\nu}$ = 3234, 2905, 2525, 1736, 1692, 1479, 749, 514 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 11.88 (s, 3H, 3 × COOH), 7.49 and 7.08 (*AA′BB′*, 2 × 6H, Ar–H), 3.26 (s, 6H, 3 × CH_2), 1.56 (s, 3H, 12d-CH_3); ^{13}C NMR (125.7 MHz, acetone-d$_6$): δ 172.4 (COOH), 147.5 (C), 127.2 (CH), 122.7 (CH), 70.6 (C), 65.4 (C), 40.7 (CH_2), 14.7 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 468 (29, [M]$^{+\bullet}$), 409 (100), 349 (84), 303 (23), 289 (35); accurate mass (EI-MS) of [M]$^{+\bullet}$: calcd. for $C_{29}H_{24}O_6$ 468.1573; found 468.1590.

4b,8b,12b-Tris(methoxycarbonylmethyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (trimethyl 12d-methyltribenzotriquinacene 4b,8b,12b-tris-acetate, 17)

A solution of the triacid **16** (468 mg, 1.00 mmol) in anhydrous methanol (12.0 mL) was stirred and cooled to 0 °C. Thionyl chloride (0.89 mL, 12.0 mmol) was added dropwise under argon through a septum and then stirring was continued for 48 h at 25 °C. The solvent was removed under reduced pressure and the residual product was extracted with diethyl ether. The ethereal layer was washed first with saturated sodium bicarbonate solution and then with water, and then dried over Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product, which was recrystallised from ethanol to give triester **17** (yield 372 mg, 73%) as colorless crystals, mp 197–198 °C; IR (neat): $\tilde{\nu}$ = 3627, 2949, 2600, 1732, 1558, 1478, 1154, 750, 680 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 and 7.19 (*AA′BB′*, 2 × 6H, Ar–H), 3.55 (s, 9H, 3 × OCH_3), 3.41 (s, 6H, 3 × CH_2), 1.69 (s, 3H, 12d-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 171.2 (*C*OOCH_3), 145.7 (C), 126.7 (CH), 121.5 (CH), 69.8 (C), 64.3 (C), 50.3 (CH_3), 40.4 (CH_2), 14.4 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 510 (13, [M]$^{+\bullet}$), 437 (100), 363 (15), 303 (14), 289 (29); accurate mass (EI) of [M]$^{+\bullet}$: calcd. for $C_{32}H_{30}O_6$ 510.2042; found 510.2048.

4b,8b,12b-Tris(2-hydroxyethyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (12d-methyltribenzotriquinacene 4b,8b,12b-tris-ethanol, 18)

To a suspension of ground lithium aluminium hydride (74 mg, 2.0 mmol) in anhydrous tetrahydrofuran (30 mL) was added dropwise a solution of tris-acetaldehyde **15** (420 mg, 1.00 mmol) and then the mixture was refluxed for 8 h. After cooling with ice/water, the product mixture was carefully hydrolyzed with crushed ice and extracted several times with diethyl ether. The combined organic extracts were washed with water and dried over Na_2SO_4. The solvent was evaporated to give the trialcohol **18** (yield 294 mg, 69%) as a colorless, fluffy solid, mp 289–291 °C; IR (neat): $\tilde{\nu}$ = 3299, 2922, 2363, 1478, 1439, 1000, 752, 508 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 7.47 and 7.14 (*AA′BB′*, 2 × 6H, Ar–H), 4.46 (s, 3H, 3 × OH), 3.20 (m, 6H, 3 × CH_2), 2.40 (t, *J* = 7.5, 6H, 3 × CH_2), 1.56 (s, 3H, 12d-CH_3); ^{13}C NMR (125.7 MHz, DMSO-d$_6$): δ 146.9 (C), 127.0 (CH), 123.2 (CH), 70.0 (C), 65.5.3 (C), 58.8 (CH_2), 48.4 (CH_2), 15.9 (12d-CH_3); MS (EI, 70 eV): *m/z* (%), 426 (3, [M]$^{+\bullet}$), 381 (100), 335 (38), 319 (14), 289 (22); accurate mass (EI-MS) of [M]$^{+\bullet}$: calcd. for $C_{29}H_{30}O_3$ 426.2196; found 426.2176.

— Compound **18** was also obtained by the reduction of tris-acid **16** under similar conditions and in the same (69%) yield.

4b,8b,12b-Tris(2-butoxyethyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [12d-methyl-4b,8b,12b-tris(3-oxaheptyl)tribenzotriquinacene, 19]

A suspension of powdered potassium hydroxide (196 mg, 3.5 mmol) in dimethyl sulfoxide (5 mL) was vigorously stirred for 15 min. Stirring was continued while trialcohol **18** (106 mg, 0.25 mmol) and, immediately thereafter, *n*-butyl bromide (0.25 mL, 2.25 mmol) were added. After stirring for a further 3 h, the mixture was poured onto water and extracted repeatedly with diethyl ether. The combined organic extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent gave the crude product which was purified by chromatography through silica gel (EtOAc/*c*-C_6H_{12} 1 : 3) to give the triether **19** (yield 238 mg, 40%) as a light-yellow, viscous oil; IR (neat): $\tilde{\nu}$ = 2926, 2850, 2358, 2252, 1464, 1377, 1099, 903, 726, 649 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 and 7.17 (*AA′BB′*, 2 × 6H, Ar–H), 3.33–3.26 (m, 12H, 6 × OCH_2), 2.56 (t, J = 7.2 Hz, 6H, 3 × CH_2), 1.54 (t, J = 7.2 Hz, 6H, 3 × CH_2), 1.36–1.28 (m, 9H, 3 × CH_2 and 12d-CH_3), 0.94 (t, ^3J = 7.5 Hz, 9H, 3 × CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.9 (C), 127.6 (CH), 123.3 (CH), 71.0 (3 × OCH_2), 70.8 (3 × OCH_2) 68.8 (C), 66.1 (C), 38.2 (3 × CH_2), 31.7 (3 × CH_2), 29.7 (3 × CH_2), 19.3 (3 × CH_3), 14.1 (12d-CH_3); MS [(+)-ESI, $CHCl_3$–MeOH]: m/z 617 (95, $[M + Na]^+$), 612 (82, $[M + NH_4]^+$), 595 (100, $[M + H]^+$); accurate mass [(+)-ESI, $CHCl_3$–MeOH] of $[M + H]^+$: calcd. for $C_{41}H_{55}O_3$ 595.4145; found 595.4141.

12d-Methyl-2,3,6,7,10,11-hexanitro-4b,8b,12b-tri(*n*-propyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [12d-methyl-2,3,6,7,10,11-hexanitro-4b,8b,12b-tri(*n*-propyl)-tribenzotriquinacene, 20]

Nitric acid (100%, 5.0 mL) was placed into a 25-mL flask and then cooled to 0 °C with stirring. Sulfuric acid (98%, 7.0 mL) was admixed, followed by the dropwise addition of a 1 : 1 (v/v) mixture of acetic anhydride and glacial acetic acid (6.0 mL). The mixture was allowed to warm to 20 °C and then, under vigorous stirring, hydrocarbon **14** (220 mg, 0.50 mmol) was added in small portions. Stirring was continued for 7–8 h under TLC monitoring. After completion of the reaction, the mixture was poured onto crushed ice and neutralised with sodium hydroxide. The mixture was extracted thrice with ethyl acetate and the combined extracts were washed with saturated aqueous sodium bicarbonate and then with water and dried over Na_2SO_4. Removal of the solvent under reduced pressure furnished a yellowish crude product, which was recrystallised from chloroform to give hexanitrotribenzotriquinacene **20** (yield 338 mg, 98%) as a yellowish solid, mp 338 °C (decomp.); IR (neat): $\tilde{\nu}$ = 3104, 3043, 2961, 1476, 1343, 846, 748, 507, 457 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ 8.58 (s, 6H, Ar–H), 2.56 (t, J = 6.9 Hz, 6H, 3 × CH_2), 1.90 (s, 3H, 12d-CH_3), 1.30 (m, 6H, 3 × CH_2), 0.98 (t, J = 6.1 Hz, 9H, 3 × CH_3); ^{13}C NMR (125.7 MHz, acetone-d_6): δ 152.6 (C), 144.2 (C), 122.2 (CH), 78.9 (C), 69.0 (C), 39.6 (CH_2), 20.8 (CH_2), 15.1 (12d-CH_3), 14.5 (4b-, 8b-,12b-CH_3); MS [(–)-MALDI, DCTB matrix, acetone]: m/z 690 (100, $[M]^{-\bullet}$), 660 (32, $[M–NO]^-$); accurate mass [(–)-MALDI, DCTB matrix, acetone] of $[M]^{-\bullet}$ and $[M - NO]^-$: calcd. for $C_{32}H_{30}N_6O_{12}$ 690.1927; found 690.1936; calcd. for $C_{32}H_{30}N_5O_{11}$ 660.1947; found 660.1944. —Mass and ^1H NMR spectral analyses of compound **20** indicate that the crystals tend to incorporate minor amounts of chloroform (<25 mol%). Moreover, the combustion analyses repeatedly resulted in the same deficiencies for each C, H and N (35–38% in one series and 50–52% in another). The major reason for this finding is tentatively attributed to a too vigorous decomposition of this hexanitro compound upon heating.

4b,8b,12b-Tris(carboxymethyl)-12d-methyl-2,3,6,7,10,11-hexanitro-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [12d-methyl-2,3,6,7,10,11-hexanitrotribenzotriquinacene 4b,8b,12b-tris(acetic acid), 21]

Nitric acid (100%, 6.0 mL) was placed into a 25-mL flask and then cooled to 0 °C with stirring. Sulfuric acid (98%, 8.0 mL) was admixed, followed by the dropwise addition of a 1 : 1 (v/v) mixture of acetic anhydride and glacial acetic acid (6.0 mL). After allowing the mixture to warm to 20 °C, tris-acid **16** (234 mg, 0.50 mmol) was added in small portions with vigorous stirring. Stirring was continued under TLC monitoring of the reaction progress. After completion of the process (50–55 h), the mixture was poured onto crushed ice and carefully neutralised with sodium hydroxide to pH 5. The product was extracted thrice with ethyl acetate and the combined organic extracts were washed twice with water and dried over Na_2SO_4. Evaporation of the solvent under reduce pressure gave a yellowish crude product, which was recrystallised by applying the vapor diffusion method ($CHCl_3$–EtOAc) giving the hexanitro-triacid **21** (yield 295 mg, 80%) as yellowish crystals, mp 339–341 °C; IR (neat): $\tilde{\nu}$ = 3629, 3466, 3041, 2359, 1738, 1540, 1482, 1344, 864, 786, 615 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ 8.69 (s, 6H, Ar–H), 3.80 (s, 6H, 3 × CH_2), 1.84 (s, 3H, 12d-CH_3); ^{13}C NMR (125.7 MHz, acetone-d_6): δ 171.9 (COOH), 151.3 (C), 143.7 (C), 120.9 (CH), 70.3 (C), 66.2 (C), 39.8 (CH_2), 14.0 (12d-CH_3); MS [(–)-ESI, acetone/MeOH]: m/z 737 (100, $[M – H]^-$), 693 (4, $[M – CO_2]^-$), 605 (28, $[M –3\ CO_2]^-$); accurate mass [(–)-ESI, acetone–MeOH) of $[M – H]^-$: calcd. for $C_{29}H_{17}N_6O_{18}$ 737.0605; found 737.0613.

Acknowledgements

A generous stipend by the Heinrich–Hertz–Stiftung (Düsseldorf, Germany) is gratefully acknowledged. We are also thankful to Dieter Barth for his technical assistance in some of the experiments and to Dr Matthias Letzel for expert mass spectrometric measurements.

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