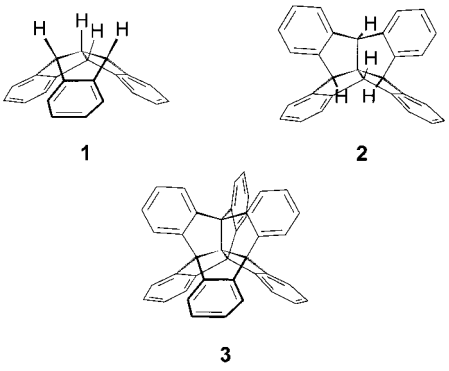
Tribenzotriquinacenes with Sixfold Peripheral Functionalization—Potential Building Blocks for Novel Organic Networks**

Jörg Tellenbröker and Dietmar Kuck*

Dedicated to Professor Kurt Heyns on the occasion of his 90th birthday

Imaginative further development of polycyclic parent compounds and consequent application of synthetic methodology of organic chemistry has opened up new perspectives on the construction of three-dimensional cage compounds and networks in recent years.[1] Impressive examples have been established not only in the chemistry of fullerenes[2] and of fullerene segments such as corannulene and the semifullerenes,[3] but also with spheriphanes,[4] cyclophanes,[5] cyclacenes,[6] and propellanes.[7] Likewise, considerable progress has been achieved in the chemistry of two-dimensional networks (graphite cuttings).[8] In this context polycyclic ring systems with bent, that is, convex–concave or saddle-like molecular surfaces, for example, the [*n*]circulenes ($n=5$: corannulene,[9] $n=7$: pleiadannulene[10]), are of particular interest.

Tribenzotriquinacene **1**[11] and fenestrindane **2**[12] represent alicyclic variants of this structural principle and they constitute, on their own, cuttings of the three-dimensional "molecular lattice" of centrohexaindane **3**.[13, 14] Structural



expansion of the hatlike **1** and the saddle-like **2** by condensed arene networks can be envisioned to eventually result in novel graphite segments, in which the alicyclic "perturbations" would give rise to directed deformations of the otherwise planar surfaces. This is demonstrated by a hypothetical example for the case of **1** shown in Figure 1.

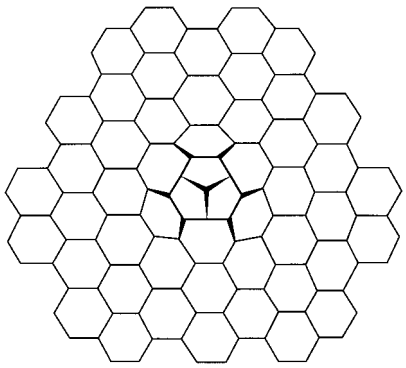
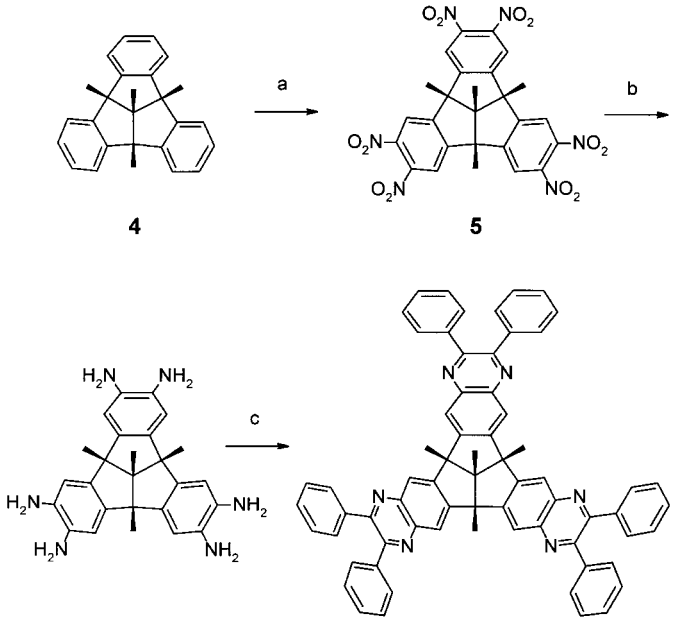


Figure 1. A hypothetical triquinacene bearing a completely closed arene periphery (schematic).

In this work we present the first results of our current investigation on the systematic functionalization of the six peripheral arene positions of tribenzotriquinacene, which may also be of interest for other fields of modern organic chemistry.[15] For these studies we mainly employed 1,4,7,10-tetramethyltribenzotriquinacene **4**[16] since this model substrate is chemically inert not only at the central but also at the three benzhydrylic bridgehead positions, which are very reactive in the parent hydrocarbon **1**. We expected the six *ortho* positions at the benzene nuclei to also be unreactive for steric reasons. In fact, we found that nitration of **4** in 100% HNO_3 and 98% H_2SO_4 (5/7) gives the 2,3,6,7,10,11-hexanitro derivative **5** in 90% yield (Scheme 1, Table 1). This clearly



Scheme 1. a) HNO_3 (100%), H_2SO_4 (98%) (5/7), 0→20°C, 6 h, yield 90%; b) H_2, Pd/C, EtOH, 4 bar, 20°C, 24 h; c) $(PhCO)_2$, EtOH/AcOH/H_2O (10/4/1), 120°C, 4 h, yield 43%.

corroborates the high efficiency of steric shielding at the *ortho* positions of the centropolyindanes against electrophilic attack.[17]

Reduction of the hexanitro compound **5** is carried out most favorably by catalytic hydrogenolysis over palladium on charcoal in ethanol.[18] Notably, the threefold *ortho*-phenyl-

[*] Priv.-Doz. Dr. D. Kuck,[+] Dipl.-Chem. J. Tellenbröker
Fakultät für Chemie der Universität
Universitätsstrasse 25, D-33501 Bielefeld (Germany)
Fax: (+49) 521-106-6417
E-mail: kuck@chema.uni-bielefeld.de

[+] Additional address:
Fachbereich Chemie und Chemietechnik
der Universität-Gesamthochschule
Warburger Strasse 100, D-33098 Paderborn (Germany)

[**] We are grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.

Table 1. Analytical and spectroscopic data of selected compounds.[28]

5 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexanitro-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous colorless solid (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (70 eV): *m/z* (%): 606 (7) [M^+], 591 (100), 546 (16), 499 (5), 407 (4), 315 (5); ^1H NMR (500 MHz, [D_6]DMSO): $\delta = 8.76$ (s, 6H), 1.80 (s, 9H), 1.38 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]DMSO): $\delta = 152.6$ (s), 143.0 (s), 121.4 (d), 71.2 (s), 63.5 (s), 23.9 (q), 15.0 (q); IR (KBr): $\tilde{\nu} = 3049$, 2974, 1593, 1545, 1478, 1453, 1440, 1398, 1365, 1143, 916, 862, 853, 756, 742 cm^{-1}.

7 (5b,11b,17b,18b-Tetramethyl-2,3,8,9,14,15-hexaphenyl-5b,11b,17b,18b-tetrahydropyrazino[2″,3″:5′,6′]indeno[1′,2′,3′:3,4]quinoxalino[6′,7′:5,6]pentaleno[1,2-*g*]quinoxaline): long, colorless needles (from $CHCl_3$), m.p. $>360\,^{\circ}C$; LSI-MS (3-nitrobenzyl alcohol (NBA)): *m/z* (%): 949 (100) [M^+], 933 (31); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.37$ (s, 6H), 7.46 (d, $^3J = 7.9$ Hz, 12H), 7.29 (m, 18H), 2.02 (s, 9H), 1.59 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 152.8$ (s), 152.5 (s), 141.3 (s), 138.9 (s), 129.8 (d), 128.7 (d), 128.2 (d), 123.0 (d), 70.8 (s), 62.8 (s), 27.2 (q), 16.5 (q); IR (KBr):$\tilde{\nu} = 3061$, 2970, 1551, 1466, 1438, 1403, 1392, 1342, 1261, 1188, 1076, 1056, 1023, 971, 893, 766 cm^{-1}; UV/Vis (CH_2Cl_2, $c = 5.43 \times 10^{-6}$ mol L^{-1}): λ_{max} ($\lg \varepsilon$) = 257 (5.13), 368 (4.79) nm.

8 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexabromo-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous colorless solid (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (70 eV): *m/z* (%): 810 (41) [M^+], 795 (100), 730 (6), 715 (18), 635 (7); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.49$ (s, 6H), 1.55 (s, 9H), 1.28 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 148.6$ (s), 128.0 (d), 124.3 (s), 71.2 (s), 62.0 (s), 25.5 (q), 16.0 (q); IR (KBr): $\tilde{\nu} =$ 3060, 3001, 2978, 2962, 2955, 2927, 2899, 2870, 1477, 1469, 1461, 1446, 1391, 1377, 1365, 1349, 1272, 1248, 1204, 1179, 1121, 1104, 1083, 1034, 887, 874, 772, 763, 684, 640 cm^{-1}.

9 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexa(*n*-butylthio)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6- *ab*]indene): glassy colorless oil (from $CHCl_3$); MS (70 eV): *m/z* (%): 864 (100) [M^+], 849 (23), 810 (16), 776 (59), 761 (17); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.21$ (s, 6H), 2.86 (oct., $^3J = 7.3$ Hz, 12H), 1.63 (sext., $^3J = 7.6$ Hz, 12H), 1.60 (s, 9H), 1.46 (sext., $^3J = 7.5$ Hz, 12H), 1.30 (s, 3H), 0.92 (t, $^3J = 7.3$ Hz, 18H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 146.8$ (s), 136.8 (s), 123.6 (d), 70.7 (s), 62.2 (s), 33.4 (t), 30.9 (t), 25.6 (q), 22.1 (t), 16.0 (q), 13.7 (q); IR (KBr): $\tilde{\nu} = 3015$, 2996, 2982, 2966, 2948, 2932, 2919, 2894, 2867, 2854, 2840, 2816, 1587, 1474, 1468, 1460, 1452, 1433, 1402, 1387, 1373, 1355, 1259, 1217, 1187, 1121, 1103, 1084, 1040, 905, 889, 865, 846, 778, 733 cm^{-1}.

10 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexa(phenylethynyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous brownish solid (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (DEI, 70 eV): *m/z* (%): 936 (100) [M^+], 921 (94) [$M^+ - CH_3$], 468 (10) [M^{2+}], 461 (20) [$M^{2+} - CH_3$], 178 (45); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.58$ (m, 18H), 7.31 (m,18H), 1.68 (s, 9H), 1.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 148.4$ (s), 131.7 (d), 128.3 (d), 126.4 (d), 125.7 (s), 123.3 (s), 93.3 (s), 88.6 (s), 70.5 (s), 62.6 (s), 25.7 (q), 16.0 (q); IR (KBr): $\tilde{\nu} = 3058$, 2966, 2925, 1596, 1492, 1473, 1452, 1442, 1405, 1392, 1081, 1068, 1025, 903, 749, 687 cm^{-1}; UV/Vis (CH_2Cl_2, $c = 4.38 \times 10^{-6}$ mol L^{-1}): λ_{max} ($\lg \varepsilon$) = 288 (5.22) nm.

11 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexaiodo-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous colorless solid (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (DEI,70 eV): *m/z* (%): 1092 (76) [M^+], 1077 (100), 966 (5), 965 (4), 951 (8), 950 (4), 823 (22), 696 (2), 681 (4); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.72$ (s, 6H), 1.51 (s, 9H), 1.24 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 149.5$ (s), 133.6 (d), 107.1 (s), 70.7 (s), 61.5 (s), 25.1 (q), 15.7 (q); IR (KBr): $\tilde{\mu} = 2967$, 2926, 1474, 1453, 1440, 1392, 1375, 1335, 1267, 1251, 1090, 1030, 891, 860 cm^{-1}.

12 (4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexaphenyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): colorless needles (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (70 eV): *m/z* (%): 792 (69) [M^+], 777 (100), 716 (16), 701 (27), 389 (18); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.47$ (s, 6H), 7.18 (m, 18H), 7.08 (d, $^3J = 7.6$ Hz, 12H), 1.86 (s, 9H), 1.54 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 148.2$ (s), 141.8 (s), 140.6 (s), 130.0 (d), 127.7 (d), 126.3 (d), 125.0 (d), 71.3 (s), 62.7 (s), 26.1 (q), 16.3 (q); IR (KBr): $\tilde{\nu} =$ 3063, 3029, 2968, 1600, 1493, 1477, 1446, 1393, 1229, 1073, 1023, 897, 887, 781, 765, 697, 621 cm^{-1}; UV/Vis (CH_2Cl_2, $c = 5.23 \times 10^{-6}$ mol L^{-1}): λ_{max} ($\lg \varepsilon$) = 248 (4.94) nm.

13 (5b,15b,25b,30c-Tetramethyl-5b,15b,25b,30c-tetrahydro-benzo[*l*]benzo-[9′,10′]phenanthro[2′,3′:5,6]phenanthro-[9″,10″:5′,6′]indeno[1′,2′,3′:3,4]-pentaleno[1,2-*b*]phenanthrene): amorphous colorless solid (from $CHCl_3$), m.p. $>360\,^{\circ}C$; MS (70 eV): *m/z* (%): 786 (5) [M^+], 771 (5); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.84$ (s, 6H), 8.78 (d, $^3J = 8.2$ Hz, 6H), 8.55 (d, $^3J =$ 8.1 Hz, 6H), 7.69(t, $^3J = 7.6$ Hz, 6H), 7.59 (t, $^3J = 7.4$ Hz, 6H), 2.07 (s, 9H), 1.61 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 148.9$ (s), 129.8 (s), 129.4 (s), 129.2 (s), 127.2 (d), 127.0 (d), 123.2 (d), 122.9 (d), 117.2 (d), 71.4 (s), 62.8 (s), 26.8 (q), 16.3 (q); IR (KBr): $\tilde{\nu} = 3077$, 2966, 2922, 2854, 1493, 1447, 1434, 1261, 1092, 1049, 1030, 885, 753, 720, 710 cm^{-1}; UV/Vis (CH_2Cl_2, $c = 4.07 \times 10^{-6}$ mol L^{-1}): λ_{max} ($\lg \varepsilon$) = 262 (5.33), 312 (4.43), 332 (3.99), 348 (3.89) nm.

15 (12d-Methyl-4b,8b,12b-trihydroxy-2,3,6,7,10,11-hexaiodo-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous colorless solid (from $CHCl_3$), m.p. 314 °C (decomp); MS (DEI, 70 eV): *m/z* (%): 1098 (19) [M^+], 1081 (3), 1049 (3), 972 (4), 128 (100); ^1H NMR (500 MHz, [D_6]DMSO): $\delta = 8.18$ (s, 6H), 6.07 (s, 3H), 1.08 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]DMSO): $\delta = 146.6$ (s), 134.7 (d), 109.4 (s), 88.1 (s), 77.2 (s), 12.1 (q); IR (KBr): $\tilde{\nu} = 3533$, 3422, 3375, 3365, 2987, 2977, 2934, 1790, 1618, 1577, 1442, 1335, 1237, 1183, 1078, 1034, 970, 927, 886, 755, 726, 681, 618 cm^{-1}.

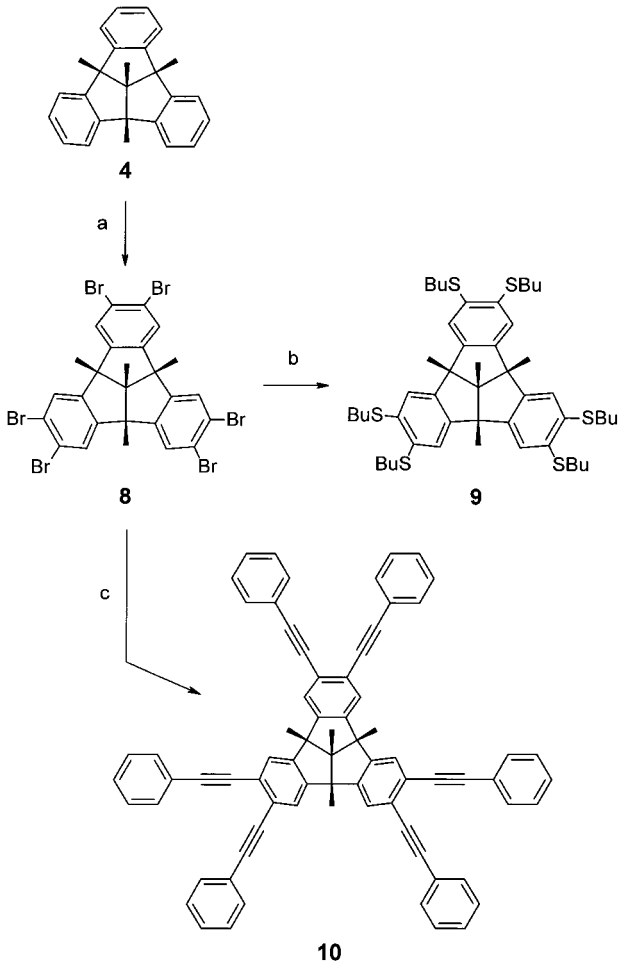
16 (12d-Methyl-4b,8b,12b-tribromo-2,3,6,7,10,11-hexaiodo-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene): amorphous colorless solid (from $CHCl_3$), m.p. 254 °C (decomp); MS (APCI (chemical ionization at atmospheric pressure)): *m/z* (%): 1206 (100) [$M^+ - Br$], 1158 (23), 1128 (22), 1047 (12); ^1H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 8.08$ (s, 6H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 143.7$ (s), 136.0 (d), 111.4 (s), 79.5 (s), 75.6 (s), 36.5 (q); IR (KBr): $\tilde{\nu} = 3070$, 2990, 2958, 2947, 2941, 2929, 1573, 1562, 1453, 1441, 1433, 1425, 1420, 1378, 1347, 1341, 1267, 1240, 1214, 1208, 1083, 1061, 921, 867, 856, 846, 838, 823, 815, 755, 699, 674 cm^{-1}.

enediamine **6** formed in this way is extremely sensitive towards oxidation; therefore, it has to be subjected to subsequent conversions in solution after separation of the inorganic components from the reaction mixture. In contrast to other 1,2-diketones, hexaaminotribenzotriquinacene **6** easily reacts with benzil to give the threefold quinoxaline **7**,[19] which, in view of the sensitivity of the hexaamine, is isolated in relatively good yield.

Bromination of the six peripheral positions of **4** is also performed under suitable conditions (Scheme 2, Table 1).[20] Best results are obtained by working with a slight excess (10%) of bromine in the presence of catalytic amounts of iron and iodine. Hexabromotribenzotriquinacene **8** is isolated in 93% yield and affords a valuable basis for the synthesis of a number of other sixfold functionalized congeners or C–C coupled derivatives. For example, the sixfold thioether **9** and the threefold *ortho*-ditolane **10** are accessible from **8** in very good yields.[21, 22] The pronounced vaulting of the convex–concave molecular structure of **10**, which is strongly enlarged by the six appending phenylethynyl units, is illustrated in Figure 2.

Iodination of **4** with potassium iodide/periodic acid[23] gives the hexaiodo derivative **11** (Scheme 3, Table 1), in analogy to bromination. This sixfold functionalized tribenzotriquinacene is considered an important key compound for the construction of more highly condensed benzenoid arenes, the ring systems of which are fixed at the central triquinacene unit in an almost perfectly orthogonal orientation to each other. Thus, for example, C–C coupling with phenylboronic acid under Suzuki

  1433-7851/99/3807-0920 $ 17.50+.50/0



Scheme 2. a) Br_2, Fe (cat.), I_2 (cat.), CCl_4, 60 °C, 24 h, yield 93 %; b) CuS*n*Bu, pyridine, quinoline, 170 °C, 24 h, yield 94 %; c) phenylacetylene, NEt_3, $[(Ph_3P)_2PdCl_2]$, CuI, Ph_3P, 120 °C, 48 h, yield 87 %.

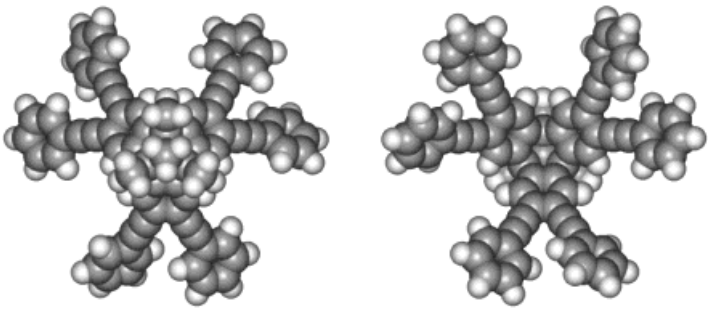
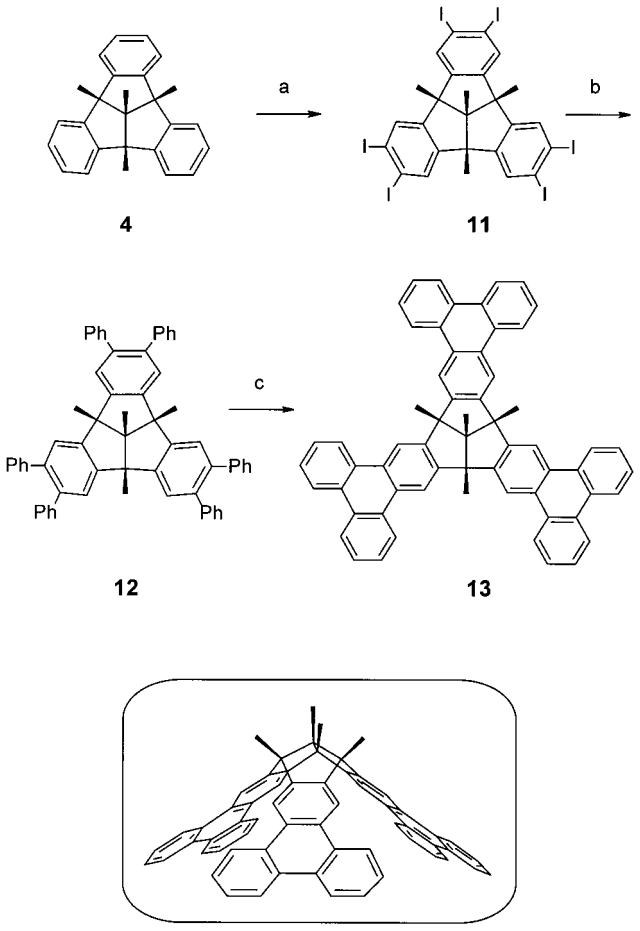


Figure 2. Molecular shape of hexatolane **10** (from MM + calculations); viewed onto the convex (left) and the concave surface (right).

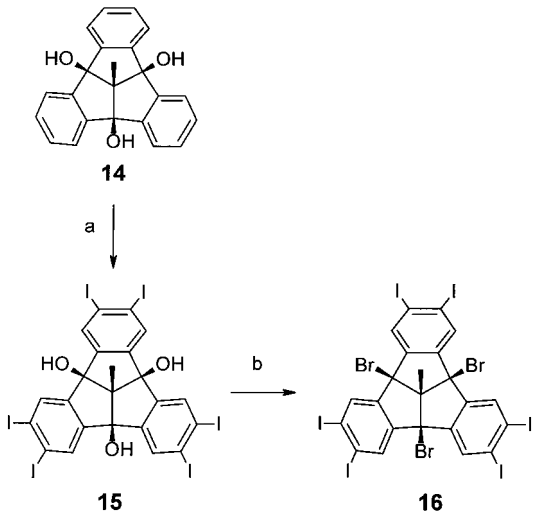
conditions[24] gives the hexaphenyltribenzotriquinacene **12** in excellent yield (Scheme 3), and subsequent photocyclodehydrogenation under Mallory conditions[25] yields the tris(triphenylene) **13**.

These examples demonstrate that, besides their versatile conversions at the bridgehead positions,[11a, 14, 16, 26] tribenzotriquinacenes may also be used as building blocks for various synthetic reactions that lead to complex ring systems. We are currently investigating the synthetic access to higher analogues of **12** and **13**. Moreover, the combined functionalization at both the bridgehead and the peripheral positions is



Scheme 3. a) KI, H_5IO_6, conc. H_2SO_4, 0 → 20 °C, 12 h, yield 76 %; b) $PhB(OH)_2$, $[Pd(dba)_2]$, KOH, PPh_3, $PhNO_2/H_2O$, 100 °C, 24 h, yield 90 %; c) I_2, PhH, *hν*, 20 °C, 18 h, yield 47 %. A spatial representation of **13** is given in the box. dba = dibenzylideneacetone.

possible in particular cases. For example, the tetramethyl compound **4** can be replaced by the easily accessible trihydroxytribenzotriquinacene **14**,[16a, 27] which is converted sequentially into the corresponding trihydroxyhexaiodotribenzotriquinacene **15** and the tribromohexaiodo derivative **16** (Scheme 4, Table 1). These compounds represent the first



Scheme 4. a) KI, H_5IO_6, conc. H_2SO_4, 0 → 20 °C, 12 h, yield 63 %; b) THF, PBr_3, 0 → 20 °C, 12 h, yield 55 %.

  1433-7851/99/3807-0921 $ 17.50+.50/0

ninefold functionalized tribenzotriquinacenes and offer interesting possibilities for further synthetic reactions.

On the basis of these results a large variety of novel convex–concave polycyclic hydrocarbon frameworks will become available. In addition, the peripheral functionalization also offers a synthetic access to complex ligands bearing three, possibly cooperative, ligand spheres, such as threefold crown ethers and cryptands, as well as to dendrimers based on the tribenzotriquinacene core.[15] Moreover, the strategy of synthesis presented here may be successfully transferred to fenestrindane **2** and, at least in part, to centrohexaindane **3**, to incorporate benzoannelated fenestranes as unusual bulding blocks into extended carbocyclic frameworks or into the core of the polyfunctionalized host molecules.

Received: October 19, 1998 [Z12536IE]
German version: *Angew. Chem.* **1999**, *111*, 1000–1004

Keywords: carbocycles · polycycles · triquinacene

[1] a) Z. Wu, J. S. Moore, *Angew. Chem.* **1996**, 108, 320–322; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 297–299; b) Y. Rubin, T. C. Parker, S. J. Pastor, S. Jalisatgi, C. Boulle, C. L. Wilkins, *Angew. Chem.* **1998**, *110*, 1353–1356; *Angew. Chem. Int. Ed.* **1998**, 37, 1226–1229; c) M. M. Haley, S. C. Brand, J. J. Pak, *Angew. Chem.* **1997**, *109*, 864–866; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 836–838; d) C. Eickmeier, H. Junga, A. J. Matzger, F. Scherhag, M. Shim, K. P. C. Vollhardt, *Angew. Chem.* **1997**, *109*, 2194- 2199; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2103–2108.

[2] a) F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M. M. Kappes, D. Fuchs, M. Bürk, K. Kobayashi, S. Nagase, *Angew. Chem.* **1996**, *108*, 1839–1841; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1732–1734; b) R. F. Curl, *Angew. Chem.* **1997**, *109*, 1636–1647; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1566–1576; c) H. W. Kroto, *Angew. Chem.* **1997**, *109*, 1648–1664; *Angew. Chem. Int. Ed. Engl.* **1997**, *39*, 1578–1593; d) R. E. Smalley, *Angew. Chem.* **1997**, *109*, 1666–1673; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1594–1601.

[3] S. Hagen, M. S. Bratcher, M. S. Erickson, G. Zimmermann, L. T. Scott, *Angew. Chem.* **1997**, *109*, 407–409; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 406–407.

[4] J. Gross, G. Harder, F. Vögtle, H. Stephan, K. Gloe, *Angew. Chem.* **1995**, *107*, 523–526; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 481–484.

[5] a) H. Meier, K. Müller, *Angew. Chem.* **1995**, *107*, 1598–1600; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1437–1439; b) Y. Sakamoto, N. Miyoshi, T. Shinmyozu, *Angew. Chem.* **1996**, *108*, 585–586; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 549–550; c) G. J. Bodwell, *Angew. Chem.* **1996**, *108*, 2221–2224; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2085–2088; d) S. Kammermeier, P. G. Jones, R. Herges, *Angew. Chem.* **1997**, *109*, 2317–2319; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2200–2202; e) H. Kawai, T. Suzuki, M. Ohkita, T. Tsuji, *Angew. Chem.* **1998**, *110*, 827–829; *Angew. Chem. Int. Ed.* **1998**, *37*, 817–819.

[6] a) F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1987**, *99*, 941–943; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 892–894; b) P. R. Ashton, N. S. Isaacs, F. H. Kohnke, A. M. Z. Slawin, C. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem* **1988**, *100*, 981–983; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 966–969; c) A. Schröder, H.-B. Mekelburger, F. Vögtle, *Top. Curr. Chem.* **1994**, *172*, 179–201; d) R. M. Cory, C. L. McPhail, A. J. Dikmans, J. J. Vittal, *Tetrahedron Lett.* **1996**, *37*, 1983–1986; e) R. M. Cory, C. L. McPhail, *Tetrahedron Lett.* **1996**, *37*, 1987–1990.

[7] "Propellanes": Y. Tobe in *Carbocyclic Cage Compounds: Chemistry and Applications* (Eds.: E. Osawa, O. Yonemitsu), VCH, New York, **1992**; pp. 125–153.

[8] a) M. Müller, H. Mauermann-Düll, M. Wagner, V. Enkelmann, K. Müllen, *Angew. Chem.* **1995**, *107*, 1751–1754; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1583–1586; b) A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768–1770; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609–1611; c) M. Müller, J. Petersen, R. Strohmaier, C. Günther, N. Karl, K. Müllen, *Angew. Chem.* **1996**, *108*, 947–950; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 886–888; d) F. Morgenroth, E. Reuther, K. Müllen, *Angew. Chem.* **1997**, *109*, 647–649; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 631–634; e) V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra, K. Müllen, *Angew. Chem.* **1997**, *109*, 1676–1679; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1604–1607; f) M. Müller, V. S. Iyer, C. Kübel, V. Enkelmann, K. Müllen, *Angew. Chem.* **1997**, *109*, 1679–1682; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1607–1610.

[9] a) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380–381; b) R. G. Lawton, W. E. Barth, *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745; c) J. C. Hanson, C. E. Nordman, *Acta Crystallogr. Sect. B* **1976**, *32*, 1147–1153; d) L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084.

[10] a) K. Yamamoto, T. Harada, Y. Okamoto, H. Chikamatsu, M. Nakazaki, Y. Kai, T. Takano, M. Tanaka, S. Harada, N. Kasai, *J. Am. Chem. Soc.* **1988**, *110*, 3578–3584; b) K. Yamamoto, Y. Saitoh, D. Iwaki, T. Ooka, *Angew. Chem.* **1991**, *103*, 1202–1203; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1173–1174; c) K. Yamamoto, *Pure Appl. Chem.* **1993**, *65*, 157–163; d) K. Yamamoto, H. Sonobe, H. Matsubara, M. Sato, S. Okamoto, K. Kitaura, *Angew. Chem.* **1996**, *108*, 69–70; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 69–70; e) J. S. Siegel, T. J. Seiders, *Chem. Br.* **1995**, 313–316.

[11] a) A. Schuster, D. Kuck, *Angew. Chem.* **1991**, *103*, 1717–1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1699–1702; b) D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449–1460; c) D. Kuck, E. Neumann, A. Schuster, *Chem. Ber.* **1994**, *127*, 151–164.

[12] a) D. Kuck, *Chem. Ber.* **1994**, *127*, 409–425; b) D. Kuck, H. Bögge, *J. Am. Chem. Soc.* **1986**, *108*, 8107–8109; c) D. Kuck, R. A. Krause, D. Gestmann, F. Posteher, A. Schuster, *Tetrahedron* **1998**, *54*, 5247–5258; d) D. Kuck, A. Schuster, R. A. Krause, *J. Org. Chem.* **1991**, *56*, 3472–3475.

[13] a) D. Kuck, B. Paisdor, D. Gestmann, *Angew. Chem.* **1994**, *106*, 1326–1328; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1251–1253; b) D. Kuck, A. Schuster, B. Paisdor, D. Gestmann, *J. Chem. Soc. Perkin Trans. 1* **1995**, *1*, 721–732; c) D. Kuck, A. Schuster, D. Gestmann, *J. Chem. Soc. Chem. Commun.* **1994**, 609–610; d) D. Kuck, A. Schuster, *Angew. Chem.* **1988**, *100*, 1222–1224; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1192–1194.

[14] For recent reviews on centropolyindanes, see a) "Carbon Rich Organic Compounds I": D. Kuck, *Top. Curr. Chem.* **1998**, *196*, 167–220; b) D. Kuck in *Advances in Theoretically Interesting Molecules*, *Vol. 4* (Ed.: R. P. Thummel), JAI Press, Greenwich, London, **1998**, pp. 81–155; c) D. Kuck, *Liebigs Ann.* **1997**, 1043–1057; d) D. Kuck, *Synlett* **1996**, 949–965.

[15] Derivatives of tribenzotriquinacene are also conceivable as building blocks for supramolecular aggregates.

[16] a) A. Schuster, Dissertation, Universität Bielefeld **1991**; b) 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.

[17] J. Tellenbröker, Diplomarbeit, Universität Bielefeld **1995**.

[18] a) B. Kohne, K. Praefcke, T. Derz, T. Gondro, F. Frolow, *Angew. Chem.* **1986**, *98*, 627–628; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 650–651; b) B. Kohne, K. Praefcke, *Liebigs Ann. Chem.* **1987**, 265.

[19] B. Kohne, K. Praefcke, *Liebigs Ann. Chem.* **1985**, 522–528.

[20] E. Klingsberg, *Synthesis* **1972**, 29–30.

[21] R. Adams, W. Reifschneider, A. Ferretti, *Org. Synth.* **1962**, *42*, 22–25.

[22] K. Praefcke, B. Kohne, D. Singer, *Angew. Chem.* **1990**, *102*, 200–202; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 177–179.

[23] D. L. Mattern, *J. Org. Chem.* **1983**, *48*, 4772–4773.

[24] M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578–4593.

[25] a) F. B. Mallory, C. W. Mallory, *Org. React.* (*NY*) **1984**, *30*, 1–456; b) T. Sato, Y. Goto, K. Hata, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1994–1995.

[26] D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626–628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595–597.

[27] D. Kuck, A. Schuster, C. Fusco, M. Fiorentino, R. Curci, *J. Am. Chem. Soc.* **1994**, *116*, 2375–2381.

[28] The new compounds **5**, **8**, **9**, and **11** gave correct elemental analytical data and/or exact mass measurements. Compound **16** exhibits a tendency to include solvents.

  1433-7851/99/3807-0922 $ 17.50+.50/0