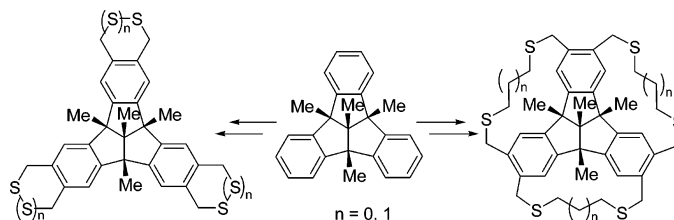# C_{3v}-Symmetrical Tribenzotriquinacenes Extended by Six C_1-Functional Groups and the First Triquinacene-Based Tris(dithiametacyclophanes)

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The first examples of novel bowl-shaped tribenzotriquinacenes (TBTQs) bearing three dithiametacyclophane units within their arene peripheries are reported. The synthesis is based on a C_{3v}-symmetrical hexakis(chloromethyl)tribenzotriquinacene as the key intermediate and yields the inter-ring metacyclophane-type macrocyclization instead of the intra-ring orthocyclophane-type cyclocondensation. Multiple nucleophilic substitution of the same key intermediate leads to a number of other new 6-fold functionalized tribenzotriquinacenes, some of which may be of interest as readily accessible building blocks for the construction of novel bowl-shaped organic networks. The molecular structures of the novel tris-(dithiametacyclophanes) and of the hexakis(chloromethyl)- and hexakis(hydroxymethyl)tribenzotriquinacenes have been determined by X-ray analysis and interesting host/guest aggregation and torsional effects in the solid state are discussed.

Introduction

Tribenzotriquinacenes (TBTQ's), such as the parent hydrocarbon **1** (Figure 1) and the bridgehead-methylated derivatives **2** and **3**,[1,2] represent fully benzoannelated congeners of triquinacene[3] and prototypical aromatic hydrocarbons of the centropolyindane family.[4−6] The molecular framework of the TBTQ's forms a conformationally rigid, C_{3v}-symmetrical, bowl-shaped structure consisting of three mutually fused indane units. Unidirectionally and strictly parallel columnar stacking has been found for the single crystals of both **1** and **2**.[2c,4] Owing to their

particular, mutually orthogonal orientation along the three axes of the Cartesian space, the three arene nuclei of **1**−**3** represent interesting anchor units for the simultaneous extension of the TBTQ framework.[2c,d,4,7,8] Various novel building blocks based

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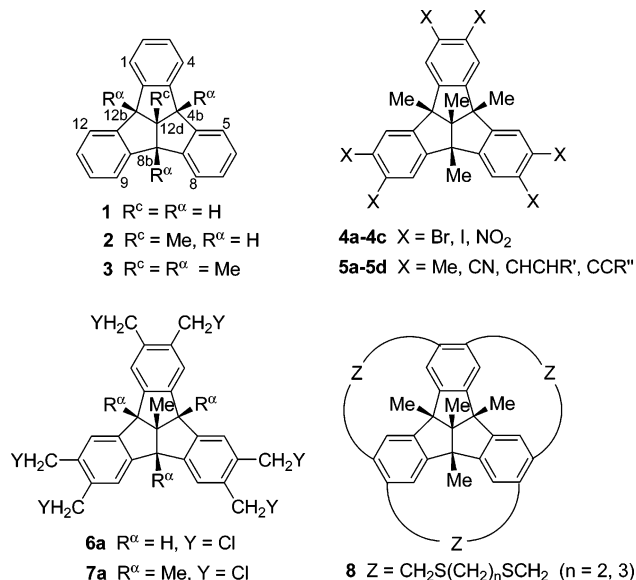
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FIGURE 1. Structures of C_{3v}-symmetrical tribenzotriquinacenes.

on the TBTQ core can be envisioned that may be of interest for the design and future development of complex organometallic compounds,[2d,8b–d,f] molecular containers,[4a,9] dendritic architectures,[10] supramolecular compounds,[11] and various other nanoscale molecular constructions.[4]

Multiple functionalization of **1** and **2** at their highly reactive benzhydrylic bridgehead positions was studied during recent years[2c,4] and enabled the access to a large variety of novel bowl-shaped structures. Hydrocarbon **3**, in particular, having all its bridgeheads blocked by methyl groups, allowed us to perform various multiple functionalization of the outer peripheral arene positions, e.g., by 6-fold bromination, iodination and nitration,[7a] and the corresponding products **4a**−**c** were shown to be highly versatile building blocks for the C_3-symmetrical extension of the bowl-shaped triquinacene core.[4] Among other groups, six methyl-, nitrile-, vinyl-, and ethynyl-based residues were introduced with high efficiency (cf. **5a**−**d**),[7] and TBTQs bearing polycondensed-arene units instead of the simple benzene nuclei have been described.[4,7a] The electrostatic properties of the tribenzotriquinacene core have been calculated and the concave face of the TBTQ framework found to be particularly attractive for electron-poor guests.[12]

In the present report we wish to present the results of further 6-fold functionalization at the peripheral positions of the TBTQ framework, as achieved by introduction of six C_1-functional groups via the hitherto unknown hexakis(chloromethyl) derivatives, such as **7a**, in particular. These efforts have been part of an ongoing project aiming at the mutual face-to-face condensation of two TBTQ bowls to develop a novel family of TBTQ-based cyclophanes of potential interest as novel host compounds. The design and synthesis of novel cyclophanes with unusual shapes and geometries continues to be a topic of current interest.[13−15] In the course of this work, we discovered a surprisingly facile access to macrocyclic thioether derivatives of **3**, that is, tribenzotriquinacenes **8** consisting of three metacyclophane units fused about a common triquinacene core.

Results and Discussion

As mentioned above, 6-fold electrophilic aromatic substitution of tribenzotriquinacenes proved to be successful in several cases.[2c,7a] In our most recent experiments, chloromethylation[16] of the aromatic nuclei of both **2** and **3** turned out to be successful as well. When these two analogous hydrocarbons were treated with a large excess of a mixture of chloromethyl methyl ether and stannic chloride (90 equiv of MOMCl and 30 equiv of SnCl$_4$) in refluxing carbon disulfide, the corresponding hexakis-(chloromethyl)-TBTQs **6a** and **7a** were obtained in good yields (Scheme 1). This clearly corroborates, once again, the recurring high efficiency of steric shielding at the ortho positions of the centropolyindanes against electrophilic substitution and is particularly noteworthy in view of the large excess of the reagents. In fact, use of a smaller excess (30 equiv of MOMCl and 10 equiv of SnCl$_4$) for the chloromethylation of **3** furnished a mixture of **7a** and the pentakis(chlormethyl) analogue **9** in an ca. 1:1 ratio. Separation of these products was achieved by careful chromatography but compound **9** could also be converted to **7a** by use of a higher excess of the reagents. In contrast to the complex peak multiplicity in the case of **9**, the ^{1}H NMR spectra of **6a** and **7a** exhibit only two singlet resonances for the aromatic and methylene protons, nicely reflecting the molecular C_{3v} symmetry. Moreover, whereas 13 lines were observed for arene carbons in the ^{13}C NMR spectrum (100 MHz) of **9**, the spectra of **6a** and **7a** showed only three signals, again in accordance with molecular symmetry. The structure of compound **7a** was further determined by X-ray single-crystal analysis (see the Supporting Information). Treatment of **6a** as well as of **7a** with sodium acetate in glacial acetic acid afforded the corresponding hexakis(acetoxymethyl) derivatives **6b** and

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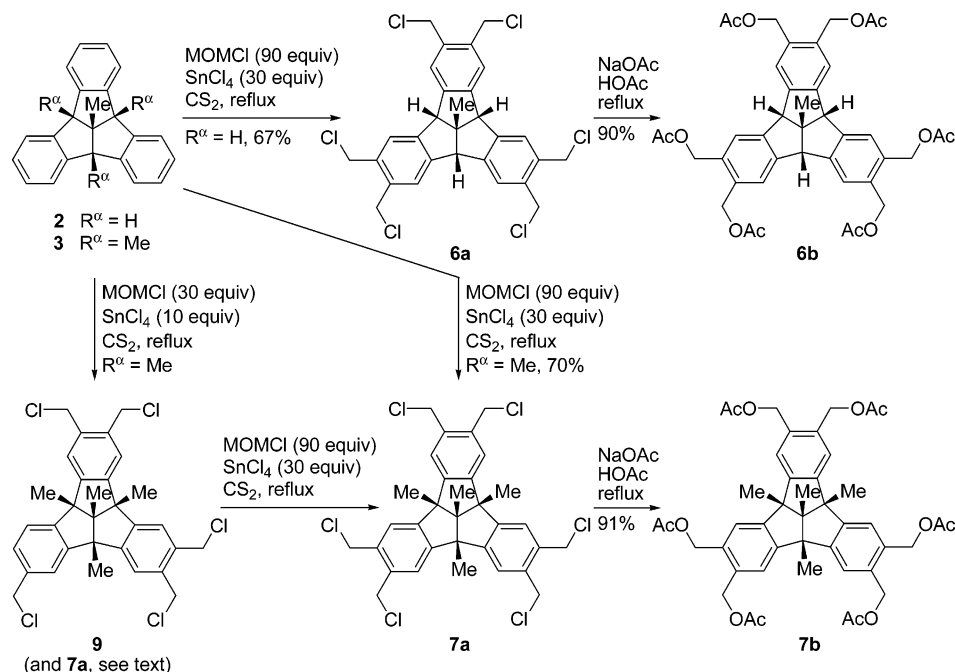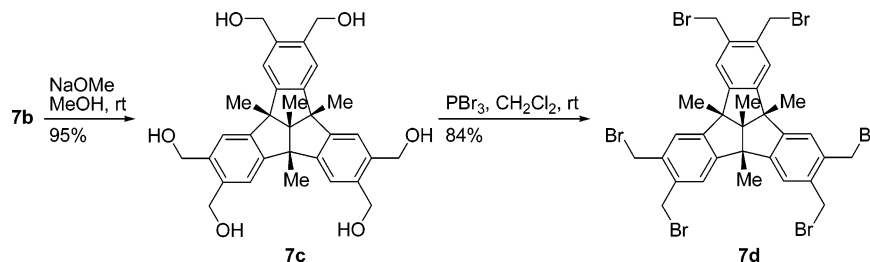
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SCHEME 1. Synthesis of the Hexakis(chloromethyl)tribenzotriquinacenes 6a and 7a and the Hexakis(acetoxymethyl)tribenzotriquinacenes 6b and 7b

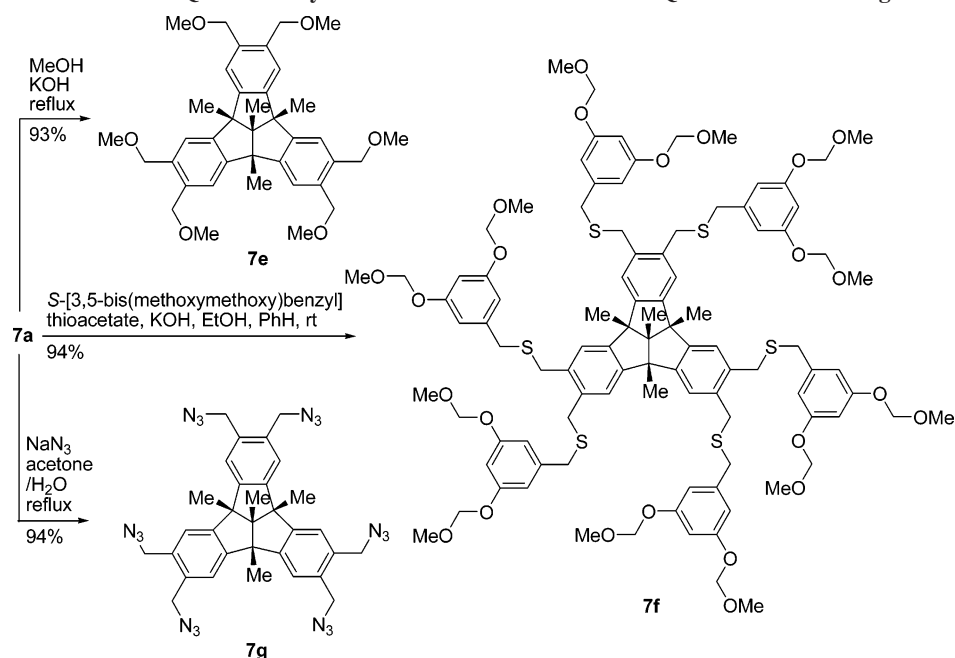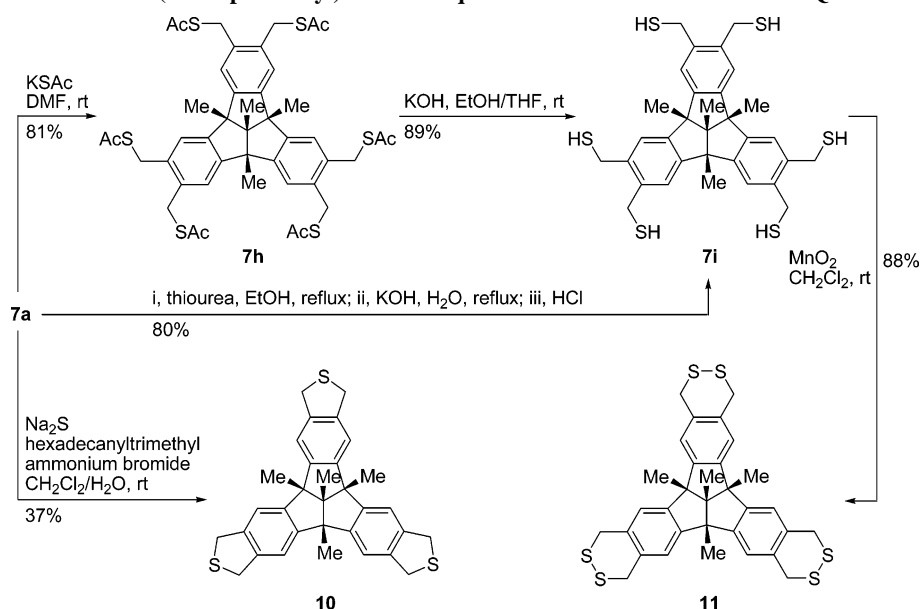**SCHEME 2. Synthesis of the Hexakis(bromomethyl)tribenzotriquinacene 7d**

7b in high yields. These first results show that, in fact, chloromethylation of the tribenzotriquinacene framework represents an efficient method to access 6-fold C_{3v}-symmetrically C_1-functionalized derivatives and may be also applicable for the multiple functionalization of higher centropolyindanes.[4]

Unfortunately, various attempts to synthesize the hexabromo analogues of **7a** by 6-fold bromination of **5a**[2c] by use of common methods failed. In every case, complex mixtures of various multiply and incompletely functionalized tribenzotriquinacenes were formed. However, an indirect access to the hexakis-(bromomethyl) derivative **7d** was established by saponification of the hexaester **7b** with use of sodium methoxide, giving the hexakis(hydroxymethyl) compound **7c**, followed by conversion of the latter to the bromomethyl analogue **7d** by use of phosphorus tribromide in dichloromethane (Scheme 2). Besides its spectroscopic identification, the 6-fold benzylic alcohol **7c** was also characterized by X-ray single crystal analysis (see below). The hexakis(bromomethyl)tribenzotriquinacene **7d** was obtained in very good overall yield.

With the readily accessible hexakis(chloromethyl)-substituted tribenzotriquinacenes in hand, we performed a number of nucleophilic substitution reactions to synthesize novel building blocks for potential application in supramolecular assemblies. In particular, compound **7a** was studied in this respect (Schemes 3−5). Simple solvolysis of this key product in methanol and potassium hydroxide furnished the hexakis(methoxymethyl)

derivative **7e** and treatment with sodium azide in aqueous acetone afforded the corresponding hexakis(azidomethyl) analogue **7g** (Scheme 3). Both compounds were obtained in excellent yields. In a particular attempt to generate a strongly branched TBTQ-based dendritic unit, the hexakis(bromomethyl) derivative **7a** was reacted with thioacetic acid S-[3,5-bis-(methoxymethoxy)benzyl] ester and potassium hydroxide in ethanol. Conversion to the 6-fold thioether **7f** was achieved again in excellent isolated yield (94%); this compound was obtained pure as a colorless oil and fully characterized by NMR spectroscopy and ESI mass spectrometry. The ^{1}H and ^{13}C NMR spectra both unequivocally confirmed the effective molecular C_{3v}-symmetry of this large $C_{98}H_{136}O_{24}$ derivative of triquinacene.

Conversion of the hexakis(chloromethyl) compound **7a** to the corresponding 6-fold mercaptane **7i** was achieved either directly by reaction with thiourea, followed by decomposition of the intermediary isothiuronium salts, or by synthesis of the respective 6-fold thioacetate **7h** as an intermediate and subsequent saponification (Scheme 4). In both cases, the hexakis(mercaptomethyl) derivate was obtained in high yields (80% and 72%, respectively) as a stable compound when stored under argon. Directed dehydrogenation of **7i** by use of activated manganese dioxide gave the corresponding 3-fold cyclodisulfide **11** in excellent yield. Treatment of **7a** with sodium sulfide by means of phase-transfer catalysis (PTC) afforded the corresponding tris-(dihydroisobenzothiophene) **10**, albeit only in moderate yield.

SCHEME 3.   Synthesis of the TBTQ-Based Polyethers 7e and 7f and of the TBTQ-based Hexaazide 7g

SCHEME 4.   Synthesis of Hexakis(mercaptomethyl)tribenzotriquinacene 7i and the Related TBTQ-Based Thioethers 10 and 11
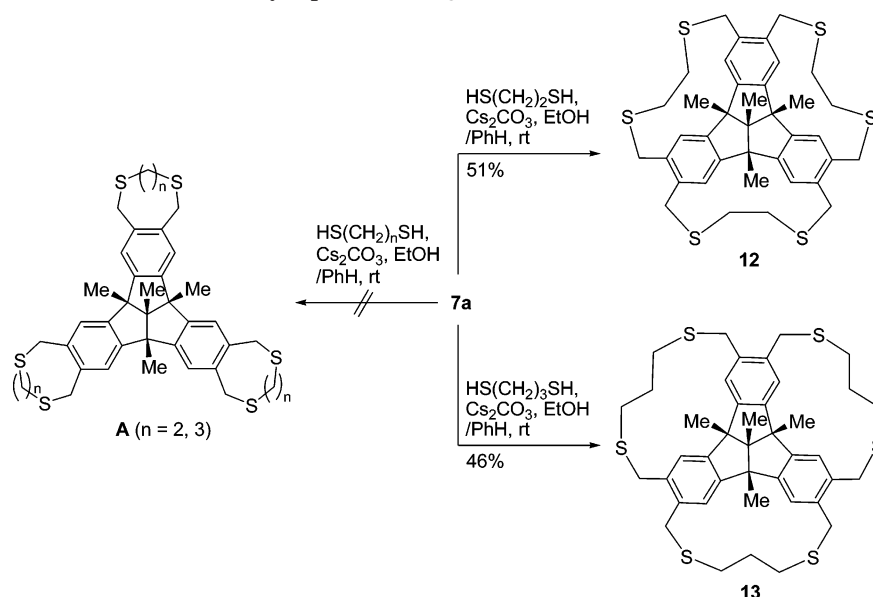

The 6-fold mercaptan **7i** and related thioethers including **11** may offer fascinating new possibilities to form self-assembled monolayers.[17]

Finally, we attempted to prepare TBTQ-based thioethers by starting from the 6-fold benzyl chloride **7a** and some α,ω-dimercaptoalkanes (Scheme 5). In contrast to expectation, the reaction of **7a** with both 1,2-ethanedithiol and 1,3-propanedithiol in ethanol/benzene solution in the presence of cesium carbonate did not furnish any products containing simple benzoannelated dithiacycloalkane units, such as the C_3-symmetrical structures **A**, in particular. Instead, the macrocyclic, formally C_{3v}-symmetrical tris(dithiametacyclophanes) **12** and **13** were isolated in surprisingly good yields (51% and 46%, respectively). The presence of higher condensation products containing more than

one TBTQ unit per molecule was ruled out by mass spectrometry, and ¹H and ¹³C NMR spectroscopy of compounds **12** and **13** confirmed the C_{3v}-symmetrical incorporation of three 1,2-ethano and 1,3-propano bridges, respectively, and the purity of these novel polycyclic thioethers. However, unequivocal distinction between the "orthocyclophanes" of type **A** containing medium-sized heterocyclic units and the macrocyclic metacyclophanes **12** and **13** by NMR spectroscopy was not possible. Identification of their structures was eventually achieved by single-crystal X-ray structure analysis (see below).

The facile formation of the MTBT-based tris(metacyclophanes) **12** and **13** is an intriguing result. It may be speculated on the role of template effects of the Cs⁺ ion and on favorable cation−π interaction between pendant cesium mercaptide groups and the formally remote aromatic ring, which would trigger the

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SCHEME 5.   Synthesis of the Tris(dithiametacyclophane)-TBTQs 12 and 13

macrocyclization path. Since the cyclization steps have to be considered irreversible, an estimation of the relative thermochemical stabilities of **12** and **13** with those of their respective orthocyclophane isomers of type **A** can provide a rather coarse approach only. Nevertheless, we performed calculations at the B3LYP/6-31G*//HF/6-31G* level. The results suggest that the most favorable (C_3-symmetrical) conformation of the lower macrocyclic homologue, **12**, is more stable than its orthocyclophane isomer **A** ($n = 2$) by $\Delta E = -1.1$ kcal mol^{-1}. In the case of the higher homologue, this difference is much more pronounced, the most favorable (again C_3-symmetrical) conformation of the macrocyclic isomer **13** being more stable than **A** ($n = 3$) by even $\Delta E = -14.9$ kcal mol^{-1}. This sheds some light on the favorable formation of the metacyclophane-type tribenzotriquinacenes **12** and **13**, although the energetics of reactive intermediates and the kinetics of their conversion remain obscure. (For details of the calculations, see the Supporting Information.)

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent from the solutions of compound **12** in dichloromethane, and of compound **13** in trichloromethane at 4 °C. The presence of three 13-membered rings in the case of **12** and three 14-membered rings in the case of **13** is clearly evident from the X-ray data. As compared to the parent hydrocarbons **1** and **2**,[2c,4] both of these TBTQ-based tris(cyclophanes) adopt reduced molecular symmetry in the solid

state: A C_s-symmetrical conformation was found in the case of the lower homologue, **12** (Figure 2), and a nonsymmetrical one (C_1) in the case of the higher homologue, **13** (Figure 4). Closer inspection of the molecular structures of **12** and **13** revealed that formation of the macrocyclic rings did not induce marked distortion of the tribenzotriquinacene core. Thus, the three benzene rings retain their planarity and even the three indane units do not exhibit significant distortion, in line with the facile formation of these tris(dithiametacyclophanes). In the crystals of the lower homologue, **12**, one dichloromethane molecule was found to be coordinated at the rim of the concave side of the molecule, with its two chlorine atoms placed in the common plane of symmetry (Figure 2b).

The crystal structure of **12** reveals the presence of parallel and unidirectionally oriented molecular stacks, in each of which the convex side of one molecule fits perfectly into the concave side of the next one (Figure 3a). This is reminiscent of the hithertho unique supramolecular arrangement of the parent compounds **1** and **2**, and as with those, the molecular C_{3v} axis containing the central C-12d−Me^c bonds of the stacked molecules is identical with the crystallographic axis.[2c,4] Morever, the molecules pack not only without any mutual tilting but also without any mutual turning (Figure 3b,c).

Different from the lower homologue, the solid-state molecular structure of the TBTQ-tris(cyclophane) **13** has C_1-symmetry (Figure 4a) and incorporates a solvent molecule (trichloromethane in this case) *within* the extended cavity formed at the concave side of the TBTQ framework (Figure 4b). As compared to the case of **12** and the associated CH$_2$Cl$_2$, the larger guest molecule, CHCl$_3$, is allowed to vanish almost completely into the void of the somewhat enlarged cavity of the higher homologue **13** (Figure 4b−d).[18] Nevertheless, the crystal structure of the latter compound is much less regular than that of **12**. Columnar aggregation is dominant here as well, but the stacks were found to be counter-oriented and the axes of the
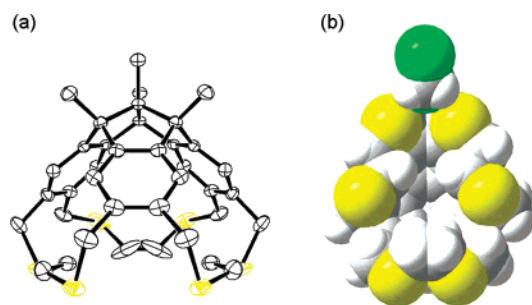

FIGURE 2. (a) Molecular structure of **12** (30% thermal ellipsoids) and (b) space-filling representation depicting the position of the CH$_2$-Cl$_2$ molecule in the plane of symmetry.

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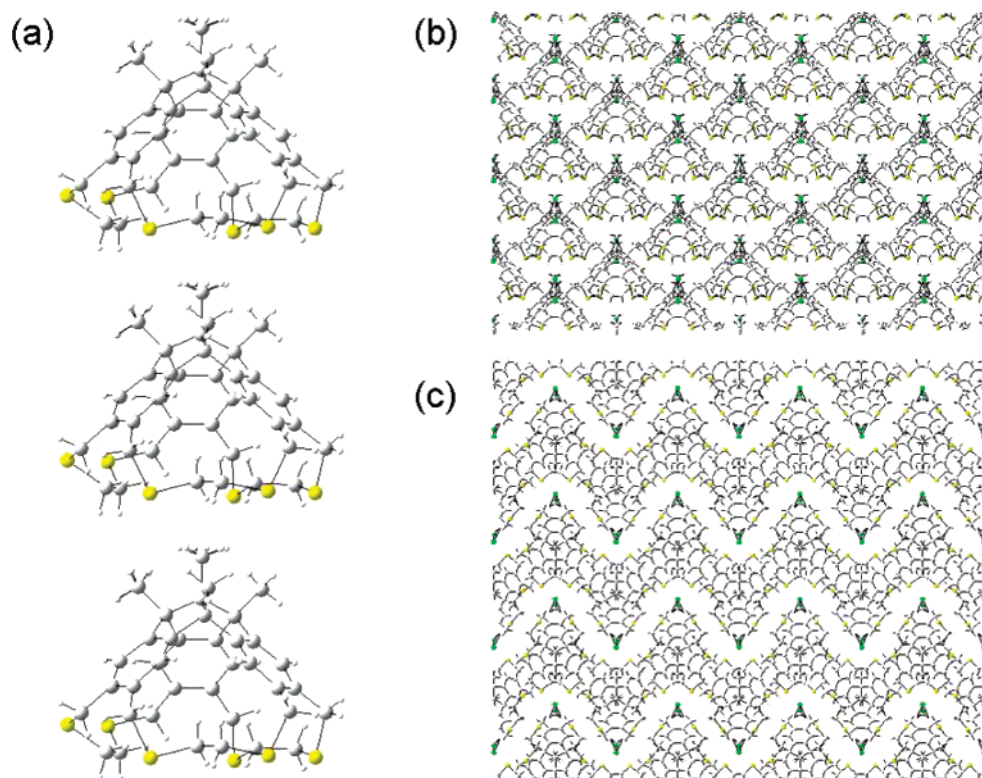
FIGURE 3. Crystal structure of **12** from X-ray structure analysis: (a) three adjacent molecules of **12**, as oriented within each molecular stack (CH$_2$Cl$_2$ not shown), (b) side view, and (c) top view on the molecular packing (including CH$_2$Cl$_2$).
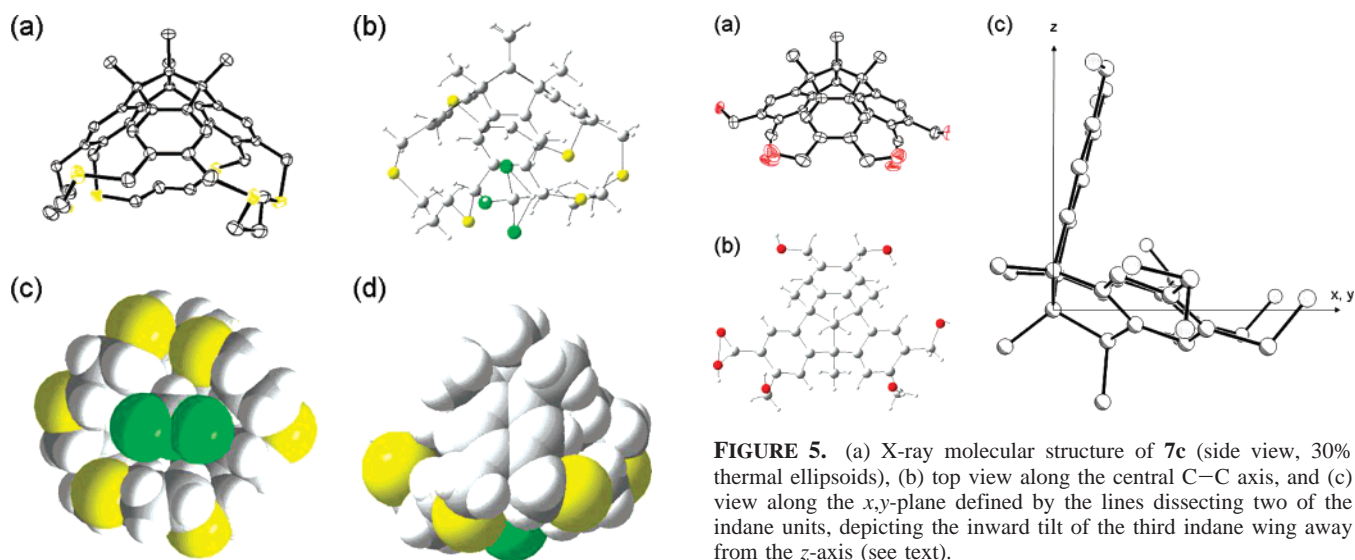

FIGURE 4. (a) Molecular structure of **13** (30% thermal ellipsoids), (b and d) side view of ball-and-stick and space-filling representations, and (c) bottom view depicting the position of the CHCl$_3$ molecule in the molecular cavity.

FIGURE 5. (a) X-ray molecular structure of **7c** (side view, 30% thermal ellipsoids), (b) top view along the central C−C axis, and (c) view along the *x,y*-plane defined by the lines dissecting two of the indane units, depicting the inward tilt of the third indane wing away from the *z*-axis (see text).

central C-12d−Me bond were found to be tilted with respect to the crystallographic axis (see the Supporting Information).

It is obvious from this and previous papers that the highly regular molecular geometry of the tribenzotriquinacenes may give rise to interesting and highly regular supramolecular structures in the solid state. In this context, the molecular and crystal structure of an apparently simple 6-fold C$_1$-functionalized derivative, namely, the hexakis(hydroxymethyl) derivative **7c**,

is also presented here because it exhibits unexpected and interesting solid-state interactions and unprecedented distortion of the TBTQ skeleton. This compound forms a colorless powder that is well soluble in methanol but only scarcely soluble in water. Strikingly, when a suspension of **7c** in a 3:1 mixture of water and methanol was allowed to stand for three weeks, it turned clear while single crystals precipitated. Obviously, self-assembling had occurred over this period of time. X-ray structure analysis of the crystals revealed that, in the solid state, the molecular skeleton of **7c** (Figure 5a) is heavily distorted by supramolecular hydrogen bonding. Instead of the usual C$_{3v}$-symmetrical tribenzotriquinacene core bearing three almost

perfectly orthogonally oriented indane wings—a characteristic feature found for all of the previously studied TBTQ derivatives—one of the indane wings is strongly bent inward, i.e., toward the molecular cavity. This may be evident from the view along the central C-12d—Me bond (Figure 5b), which demonstrates that one of the indane wings is clearly bent downward. The view depicted in Figure 5c is even more marked. The mean central axes of two of the three indane wings of **7c** can be taken (almost perfectly) as the *x*- and *y*-axes of the Cartesian coordinate system, but the third indane wing is clearly oriented toward the +*x*/+*y*/+*z* octant. Actually, the angle between the central axes of two indane wings ("*x*" and "*y*") is calculated to be 93.0 °, whereas the angles involving the remaining central axes ("*z*") are markedly smaller than 90 °, viz., $\angle(x,z) = 80.2°$ and $\angle(y,z) = 83.1°$. The origin of this unusual distortion is attributed to the multiple intermolecular hydrogen bonding and possibly also to the multiple C—H---π stacking interactions within the supramolecular arrangement in the solid state (see the Supporting Information). Therefore, it appears promising to study other tribenzotriquinacenes bearing polar and possibly acidic functional groups by which the multiple intermolecular aggregation of this regularly bent system can be promoted.

Conclusion

We have developed an efficient extension of the tribenzo-triquinacene framework by introducing six peripheral C_1-functional groups in a highly symmetrical orientation. The C_{3v}-symmetrical hexa(chloromethyl) derivative **7a** turned out to be the key intermediate. Novel triquinacene-based tris(dithiacyclophanes) have become accessible bearing significantly extended molecular cavities at the concave face of the TBTQ framework, thus being suitable as host sites for small guest molecules. Some of the new TBTQ derivatives may become useful as building blocks for novel dendrimers and ligands.[19] Furthermore, a large variety of novel supermolecular organic networks may become available on the basis of these results. The joint research on the functionalization and extension of the tribenzotriquinacene framework in our laboratories is continuing.

Experimental Section

General Procedure for Chloromethylation of TBTQs. A solution of hydrocarbons **2** or **3** (2.0 mmol) and methoxymethyl chloride (MOMCl) (13.6 mL, 180 mmol) in carbon disulfide (10 mL) was stirred under argon while tin(IV) chloride (7.0 mL, 60 mmol) was added dropwise. The mixture was refluxed for 8 h, cooled, and quenched with water (30 mL). After vigorous stirring for 2 h, the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH$_2$Cl$_2$, 5:1) afforded the hexakis(chloromethyl)-TBTQ derivatives **6a** and **7a** as colorless, amorphous solids.

2,3,6,7,10,11-Hexakis(chloromethyl)-12d-methyl-4b,8b,12b,-12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (6a): colorless solid, 784 mg, 67%; mp 300−302 °C dec; IR (neat) 2879, 1489, 1445, 1260, 817, 691 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.66 (s, 3H), 4.45 (s, 3H), 4.70 (s, 12H), 7.45 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 27.2, 43.2, 62.0, 62.8, 126.7, 136.1, 145.9;

accurate mass (ESI-MS) m/z [M + NH$_4$]$^+$ calcd for C$_{29}$H$_{28}$Cl$_6$N 600.0347, found 600.0351.

2,3,6,7,10,11-Hexakis(chloromethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (7a): colorless solid, 878 mg, 70%; mp 276−278 °C dec; IR (neat) 2964, 2923, 1489, 1449, 1260, 692 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.32 (s, 3H), 1.64 (s, 9H), 4.61 (s, 12H), 7.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 15.9, 25.5, 43.3, 62.5, 70.8, 125.2, 136.1, 149.3; accurate mass (ESI-MS) m/z [M + NH$_4$]$^+$ calcd for C$_{32}$H$_{34}$Cl$_6$N 642.0817, found 642.0827.

4b,9b,14b,15b-Tetramethyl-4b,6,8,9b,11,13,14b,15b-octahydro-1H,3H-[2]benzothieno[5′,6′:5,6]thieno[3″,4″:5′,6′]indeno-[1′,2′,3′:3,4]pentaleno[1,2-f][2]benzothiophene (10). A solution of the 6-fold benzyl chloride **7a** (63 mg, 0.1 mmol) and hexade-canyltrimethylammonium bromide (11 mg, 0.03 mmol) in dichloromethane (5 mL) was stirred under argon while a solution of sodium sulfide nonahydrate (87 mg, 0.36 mmol) in water (5 mL) was added dropwise.[20] The mixture was stirred in the dark at ambient temperature for 12 h. The organic layer was separated and the aqueous layer was extracted with dichlormethane (3 × 5 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH$_2$Cl$_2$, 2:1) afforded the product **10** (19 mg, 37%) as a colorless solid; mp >360 °C; IR (neat) 2958, 2920, 1740, 1688, 1479, 1226, 1175, 1050, 910 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.34 (s, 3H), 1.62 (s, 9H), 4.16 and 4.20 (AB, J = 12.3 Hz, 12H), 7.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.2, 26.2, 37.5, 61.5, 71.7, 118.7, 140.4, 148.0; accurate mass (ESI-MS) m/z [M + H]$^+$ calcd for C$_{32}$H$_{31}$S$_3$ 511.1582, found 511.1581.

5b,11b,17b,18b-Tetramethyl-5b,7,10,11b,13,16,17b,18b-oc-tahydro-1H,4H-[2,3]benzodithiino[6′,7′:5,6] [1,2]dithiino[4″,5″:5′,6′]indeno[1′,2′,3′:3,4]pentaleno[1,2-g][2,3]benzodithiine (11). A suspension of freshly prepared manganese dioxide[21] (52 mg, 0.6 mmol) and the 6-fold benzyl mercaptan **7i** (31 mg, 0.05 mmol) in dichloromethane was stirred at ambient temperature for 6 h. The mixture was filtered, the residue was washed with dichlormethane, and the combined solutions were concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH$_2$Cl$_2$, 1:1) afforded the product **11** (27 mg, 88%) as a colorless solid; mp >360 °C; IR (neat) 2960, 2239, 1685, 1489, 1402, 1236, 904, 729 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.30 (s, 3H), 1.59 (s, 9H), 4.00 and 4.08 (AB, J = 16.2 Hz, 12H), 7.01 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 16.0, 25.8, 35.0, 62.1, 70.6, 124.2, 132.4, 147.3; accurate mass (ESI-MS) m/z [M + Na]$^+$ calcd for C$_{32}$H$_{30}$NaS$_6$ 629.0564, found 629.0561.

General Procedure for the Syntheses of Tris(dithiocyclophanes) 12 and 13. A solution of Cs$_2$CO$_3$ (244 mg, 0.75 mmol) in ethanol (80 mL) was stirred under argon while a solution of **7a** (0.10 mmol) and the dithiol (0.30 mmol) in dry benzene (80 mL) was added dropwise within 8 h. Stirring was continued for another 10 h, then the solvent was removed under reduced pressure. The residue was diluted with water (15 mL) and extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/CH$_2$Cl$_2$, 2:1) afforded the cyclophanes **12** or **13**, respectively, as amorphous, colorless solids.

4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydro-2,11:3,6:7,10-tris(methanothioethanothiomethano)dibenzo[2,3:4,5]-pentaleno[1,6-ab]indene (12): colorless solid, 35 mg, 51%; mp >360 °C; IR (neat) 2958, 2919, 1483, 1414, 1190, 1033, 734 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.51 (s, 3H), 1.77 (s, 9H), 2.16−2.26 (m, 6H), 2.27−2.37 (m, 6H), 3.60 and 3.86 (AB, J = 15.0

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Hz, 12H), 7.45 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 15.9, 23.8, 32.3, 34.4, 63.1, 68.7, 124.4, 135.5, 147.4; accurate mass (EI-MS) m/z [M]$^+$ calcd for C$_{38}$H$_{42}$S$_6$ 690.1611, found 690.1611.

4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydro-2,11: 3,6:7,10-tris(methanothiopropanothiomethano)dibenzo[2,3:4,5]-pentaleno[1,6-*ab*]indene (13): colorless solid, 34 mg, 46%; mp >360 °C; IR (neat) 2956, 2918, 1483, 1412, 1188, 755 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.41 (s, 3H), 1.55−1.77 (m, 6H), 1.71 (s, 9H), 1.60−1.75 (m, 6H), 2.25−2.35 (m, 6H), 3.62 and 3.99 (AB, J = 15.0 Hz, 12H), 7.52 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 16.0, 25.0, 29.9, 30.6, 33.1, 62.5, 70.1, 124.4, 135.4, 147.6; accurate mass (ESI-MS) m/z [M + NH$_4$]$^+$ calcd for C$_{41}$H$_{52}$NS$_6$ 750.2419, found 750.2418.

Supporting Information Available: Experimental procedures and characterization data for compounds **6b**, **7b−i**, and **9**, ^{1}H NMR, ^{13}C NMR, and DEPT 135 spectra of compounds **6a** and **6b**, **7a−i**, and **9−13**, crystal data and packing of **7a**, **7c**, **12**, and **13**, structures and optimized Cartesian coordinates of **12**, **13**, and **A** obtained at the B3LYP/6-31G*//HF/6-31G* level, and X-ray crystallographic files (CIF) for **7a**, **7c**, **12**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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