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Solid-State Enantiopure Organic Nanocubes Formed by Self Organization of a C_3-Symmetrical Tribenzotriquinacene

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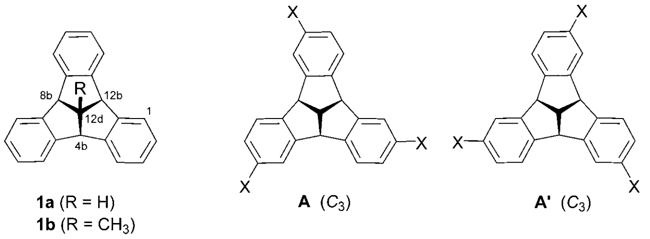
The development of large, spatially well-defined, covalent, supramolecular networks from conformationally rigid, geometrically highly regular molecular building blocks has become an inspiring and challenging topic in contemporary chemistry.[1–6] In particular, cubic aggregates[7–9] built from C_3-symmetrical subunits[10] have attracted considerable attention. As has been pointed out recently,[11] the rigid, convex–concave framework of tribenzotriquinacene (**1a**) and its derivatives (Scheme 1) is particularly promising as a building block for nanocubic arrangements because of the almost perfect orthogonal orientation of its three indane wings in space.[12,13] This unique motif has started to receive attention in various areas, including host–guest chemistry with fullerenes[14,15] and molecular structures bearing orthogonal chromophores.[16]



Scheme 1. C_{3v}- and C_3-symmetrical tribenzotriquinacenes.

Along with orthogonality, the three indane wings of the tribenzotriquinacenes give rise to a pronounced concavity and a highly negative electrostatic potential within the bowl-shaped molecular surface.[17] Therefore, the search for suitably functionalized tribenzotriquinacenes that can form large concave frameworks including even globular, covalently bound container molecules is challenging.[11,14,15,18,19] In this vein, C_3-symmetrically functionalized tribenzotriquinacenes of type **A** (or **A′**; Scheme 1) have been envisaged as promising starting materials since condensation of two or more such molecules of the same absolute configuration, for example, **A**, would be forced to take place in an all-concave manner (Figure 1).[11,20]

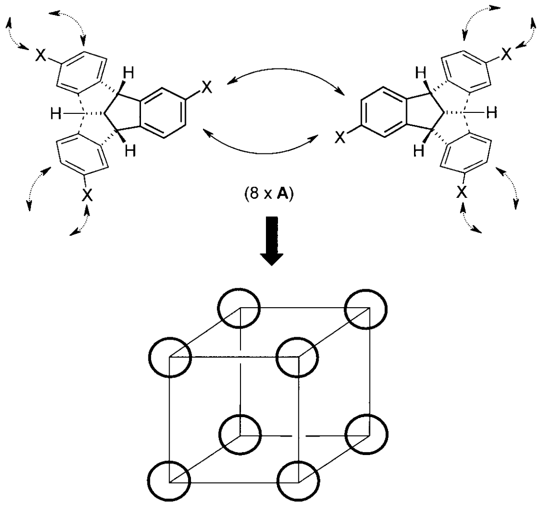


Figure 1. Hypothetical condensation of two (or more) homochiral C_3-symmetrically trifunctionalized tribenzotriquinacenes (TBTQ) of type **A** in an enforced concave–concave orientation. Twelve such condensation reactions are envisaged to give rise to a cubic molecule comprising eight covalently bound TBTQ units (circles).

Herein we report on the self-organized formation in the solid-state of a supramolecular nanocube in a manner closely corresponding to the strategy outlined above for covalently bound cubes. We found that, in the solid state, a particular derivative of methyltribenzotriquinacene (**1b**)[21] bearing both bridgehead and peripheral functionalities, namely the C_3-symmetrical tribromotrinitrotribenzotriquinacene **4**,

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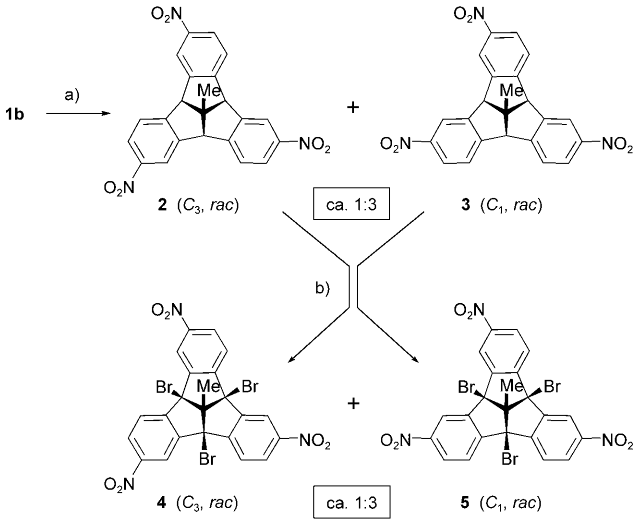
forms nanometer-sized cubes consisting of eight identical enantiomers. Thus, the previously envisaged principle of construction of covalently bound nanocubes has materialized in a novel, purely organic, supramolecular aggregation.

The synthesis of **4** was achieved by regioselective threefold nitration of **1b** using sodium nitrate in trifluoroacetic acid (Scheme 2). Single nitration was found to take place at one of the peripheral positions of each of the benzene nuclei of this hydrocarbon. The rate constants of the individual steps of electrophilic substitution are virtually independent of the presence or absence of nitro groups at the adjacent rings, giving rise to an apparently statistical ratio of the two possible trinitro derivatives, namely, the C_3-symmetrical isomer **2** (ca. 25 %) and the C_1-symmetrical isomer **3** (ca. 75 %), as shown by ^{1}H NMR spectroscopy. Separation of the constitutional isomers by preparative HPLC is feasible but cumbersome; therefore, in general, further conversions are carried out with mixtures of the two racemates, *rac*-**2** and *rac*-**3**.[16,22] Bromination of the three bridgehead positions leads to a mixture of the corresponding racemates, *rac*-**4** and *rac*-**5**, in excellent yield and virtually unchanged ratio (1:3) of the constitutional isomers. When the clear solution of this mixture in chloroform or acetone was allowed to cool to ambient temperature, single, colorless, cubic (or flattened-cubic) crystals of sizes in the range of 0.1–0.8 mm formed. The absolute overall yield of the single crystals obtained in this manner was low (≤5 %) and the crystals tend to de-solvate within a few hours under air. ^{1}H and ^{13}C NMR spectroscopy of the re-dissolved precipitate revealed the typical threefold degenerate resonances of the C_3-symmetrical tribenzotriquinacene core. Careful ^{1}H NMR measurements with [D$_6$]DMSO solutions of freshly sampled single crystals obtained after recrystallization from acetone showed the incorporation of 0.9–1.2 molecules of this solvent per molecule of **4**, as documented by integration of the respective resonances.



Scheme 2. Synthesis of the mixture of racemic C_1- and C_3-symmetrical hexafunctionalized tribenzotriquinacenes **4** and **5**. Reaction conditions and yields: a) $NaNO_3$, CF_3COOH, 20 °C, 48 h; quantitative; b) Br_2, CCl_4, *hν*, 50 °C, 20 min, then *Δ*, 1 h; 92 %.

In fact, the results of the X-ray structure analysis of single crystals of **4** were surprising.[23] As visualized in Figure 2 and Figure 3, the unit cell of the lattice is identical to one single nanocube, and each cube is composed of eight identical, homochiral enantiomers, that is, either (*P*)-**4** or (*M*)-**4** (however, see below for an alternative view). Accordingly, the nanocubes are chiral with *O*-symmetry and crystallize in the fitting chiral space group *P*432. The void inside each of the nanocubes, which has been determined by use of the PLATON program,[24] is 1948 Å, a volume large enough to incorporate several solvent molecules. The residual electron density inside the voids (the maximum being only 0.54 e Å^{-3}) does not provide any structurally meaningful information neither for acetone nor chloroform molecules.[25] However, based on the ^{1}H NMR measurements mentioned above, we assume that up to ten molecules of acetone can fill the interior of each cube, and the voids between the cubes, in a heavily disordered manner. The total potential solvent-containing volume is calculated to be 2480 Å^3 per unit cell, which is sufficiently large to accommodate this amount of the solvent.[26]

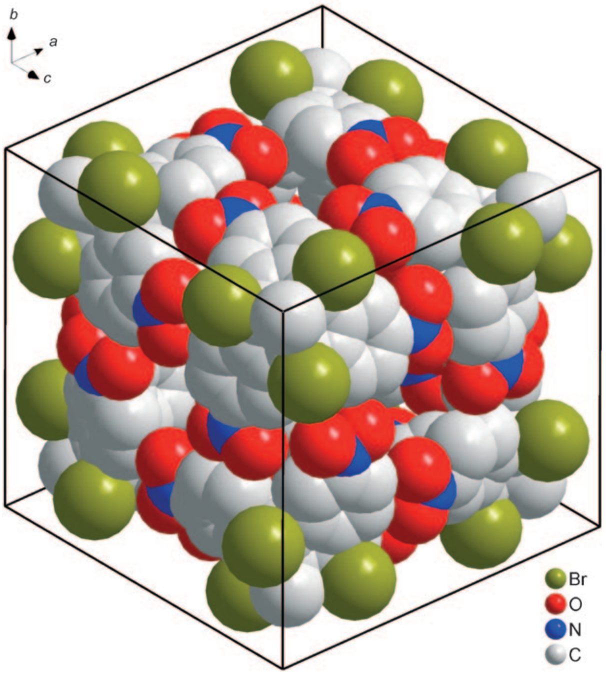


Figure 2. Cubic arrangement of eight molecules of (*M*)-**4**, representing the unit cell of the single crystals of **4**, as viewed approximately along a C_3 axis (111) onto one of the 1,4,7-tribromo-10-methyl-substituted tribenzotriquinacene cores. Hydrogen atoms have been omitted for clarity.

The single crystals are formed by packing octameric nanocubes in a cubic lattice (Figure 3), suggesting the possibility that enantiopure crystals may be generated in this way. Unfortunately, however, all of the individual crystals analyzed

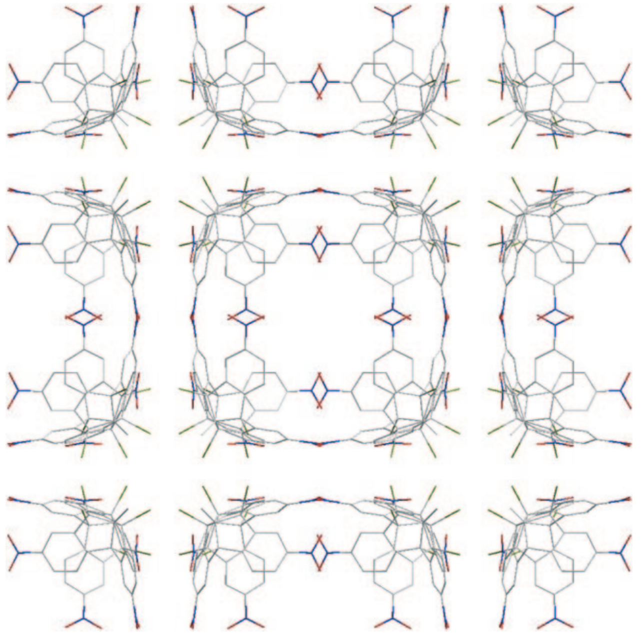


Figure 3. Crystal structure of **4** as depicted by a perpendicular view onto a plane of cubes consisting of the (*M*)-enantiomer. For the sake of simplicity, only one entire cube, corresponding to the unit cell shown in Figure 2, is shown together with sections of its neighboring cubes within the same plane. An animated GIF picture of the entire cube is provided electronically (see the Supporting Information).

turned out to be merohedrally twinned. Hence, separation of the enantiomers by manual selection of individual crystals to determine their chiroptical properties has not been possible so far and, in fact, CD spectroscopy of such single crystals was not successful.

The formation of solid-state cubes consisting of eight homochiral molecules of **4** suggests a particular driving force to result from such a unique all-concave aggregation. Moreover, the concept to synthesize covalently bound nanocubes by multiple condensation of tribenzotriquinacenes (Figure 1) renders this arrangement highly appealing. However, owing to the cubic packing of the nanocubes observed with compound **4**, there are four symmetrically independent ways to divide a single crystal into unit cells, one of which, besides that shown in Figure 2 and Figure 3, is of particular interest. When the origin is shifted to the center of the nanocube, a complementary mode of association becomes obvious, namely, the likewise cubic aggregation of eight molecules of **4** agglutinated by their electron-rich tribromotriquinacene surfaces in an all-convex manner. Four such arrangements can be located in Figure 3. In the following, we qualitatively address the potentially important intermolecular interactions that contribute to the stabilization of both sorts of cubic aggregations and, accordingly, to the whole crystal structure.

The mutual coordination of two adjacent molecules of (*P*)-**4** or (*M*)-**4** along the edges of the cubic octamers slightly deviates from the conceptual, strictly linear, twofold covalent bonding within each pair of homochiral tribenzotriquinacenes (cf. Figure 1). Actually, two molecules of (*M*)-**4**, for example, associate by interlocking *two pairs* of nitrobenzene units (Figure 2 and Figure 4). Every nitro group of a given molecule is oriented towards a non-substituted $(CH)_2$ edge of a nitrobenzene unit of an adjacent molecule, giving rise to a mutual, twofold off-axis fitting within each pair of molecules. Therefore, both spatial fitting and polar interactions between the nitrobenzene units located along each of the cube's edges appear to be favorable for the octameric assembly. This type of coordination causes a slight turn of the tribromotriquinacene cores about the C_3 axes of the cube (cf. Figure 2).

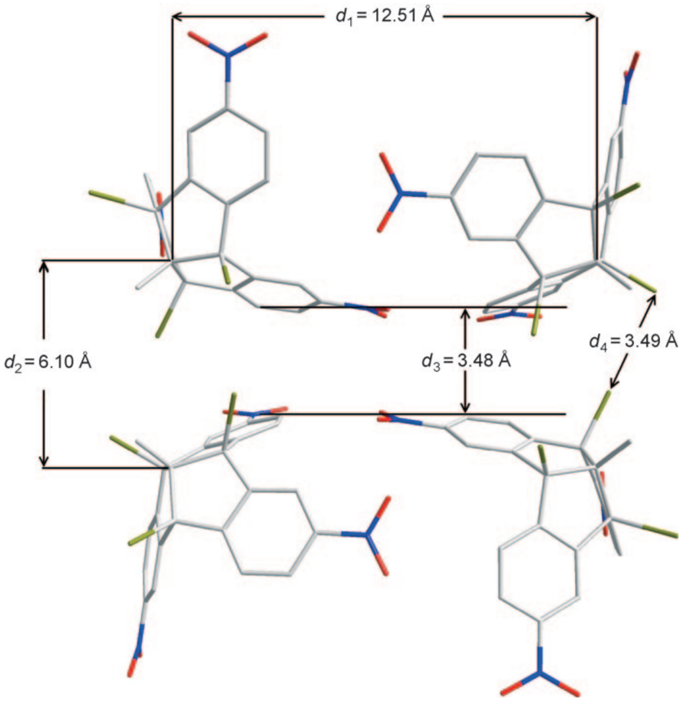


Figure 4. Intra- and inter-cube distances (d_1 and d_2–d_4, respectively) in two neighboring pairs of tribenzotriquinacenes (*M*)-**4**, both forming the adjacent edges of two adjacent cubes. Distance d_2 is the geometrical inter-cube rapport. The vicinity of two opposite nitro groups is characterized by d_3, which represents the distance between two parallel planes, each containing four nitrogen atoms. Distance d_4 corresponds to the edge of a square of four bromine atoms (cf. Figure 5 and text).

In addition to the favorable multiple fit within each of these cubes, the cubic crystal packing in the single crystals of **4** reflects also an *inter-cube* stabilization across the edges and the corners of the adjacent cubes. One major contribution to the intermolecular forces[27] operating between the cubes may originate from the attraction within pairs of adjacent nitrobenzene units; the closest contact between the nitrogen and oxygen atoms of counter-oriented nitro groups being only 3.49 Å (Figure 4).[28] However, the most important contribution to the intermolecular forces within the crystal structure may be the tight aggregation of eight 1,4,7-tribromo-10-methyltriquinacene units at the convex faces of **4** (Figure 5). These "cubes of tips" contain six squares of

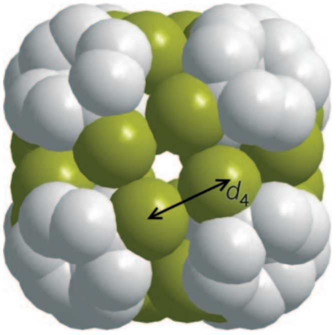


Figure 5. Cubic arrangement formed by the tips of eight cubes, presented as cuttings of the X-ray crystal structure by illustrating the 1,4,7-tribromo-10-methyltriquinacene cores of (*M*)-**4** only. This arrangement contains six squares of four bromine atoms with edge lengths of sub-Van-der-Waals distance (d_4, cf. Figure 4 and text).

four bromine atoms with edge lengths of 3.49 Å and, thus, 24 intermolecular Br···Br interactions at a distance well below the Van der Waals contact (3.90 Å).[29–33] Therefore, we are tempted to speculate that the stabilization exerted by that many attractive Br···Br interactions within the all-convex cubic aggregation (which fills an alternative unit cell of the crystal structure) may represent a by far stronger driving force than the interactions within the all-concave cubic association—in spite of its figurative attraction. If so, the unexpected formation of the supramolecular nanocubes reported here represents a fortunate outgrowth from the particularly efficacious agglomeration of eight bromine-rich convex C_3-symmetrical molecules. However, more detailed understanding of the interplay of geometrical fitting and thermodynamic stabilization of this wholly organic and enantiopure aggregation of C_3-symmetrical molecular entities forming nanometer-sized cubes, and the extension to similar cubic crystal architecture, represent inspiring goals.

Experimental Section

12d-Methyl-2,6,10-trinitro-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-*ab*]indene (2) and 12d-methyl-2,6,11-trinitro-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (3): Methyltribenzotriquinacene (**1**; 500 mg, 1.70 mmol) was suspended in trifluoroacetic acid (90 mL), and sodium nitrate (1.70 g, 20.0 mmol) was added slowly. The suspension was stirred at ambient temperature for 48 h, while the hydrocarbon dissolved slowly and the mixture turned into a homogenous yellow solution. After dilution with water (25 mL), sodium hydroxide was added (either as a 6 M aqueous solution or as pellets) until pH ≥ 10 was reached. After threefold extraction with chloroform (50 mL each), the combined extract solutions were dried over anhydrous sodium sulfate. The solvent was evaporated and the residue recrystallized from chloroform giving a mixture of the isomeric trinitrotribenzotriquinacenes **2** and **3** (730 mg, 100%) in a ratio of [**2**]:[**3**] = 0.25 (by ^{1}H NMR). Separation required HPLC through Nucleosil 100–7 C18 with $CHCl_3$. C_3 isomer (**2**): R_f (silica gel/$CHCl_3$) 0.31; m.p. >360 °C; C_1 isomer (**3**): R_f (silica gel/$CHCl_3$) 0.29; m.p. >360 °C. For spectroscopic details, see the Supporting Information.

4b,8b,12b-Tribromo-12d-methyl-2,6,10-trinitro-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (4) and 4b,8b,12b-tribromo-12d-methyl-2,6,11-trinitro-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-*ab*]indene (5): A suspension of the 1:3 mixture of the trinitrotribenzotriquinacenes **2** and **3** (500 mg, 1.17 mmol) in tetrachloromethane (100 mL) was stirred and irradiated with a photolamp (500 W) such that the temperature was maintained at 50 °C, while a solution (1.0 M) of bromine in tetrachloromethane (4.0 mL, 4.0 mmol) was added dropwise. Addition of bromine was completed within about 20 min, during which the mixture turned into a clear, dark brown solution. It was heated to reflux for an additional 60 min, then allowed to cool, and the solvent was evaporated. The yellow-brown residue was recrystallized from chloroform (or acetone, respectively) to give the mixture of the racemic tribromotrinitrotribenzotriquinacenes **4** and **5** (710 mg, 92%, no residual solvent incorporated). Separation of the C_3 and the C_1 isomers was achieved by repeated fractional recrystallization, yielding the pure C_3 isomer **4** (30–50 mg, 4–6%) first. R_f (silica gel/$CHCl_3$) 0.76; m.p. 316 °C (decomp). C_1 isomer (**5**): R_f (silica gel/$CHCl_3$) 0.70; m.p. 302 °C (decomp). For spectroscopic details, see the Supporting Information.

Keywords: convex–concave molecules · cubic structures · enantioselective aggregation · noncovalent interactions · supramolecular chemistry · tribenzotriquinacenes

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[23] Crystallographic analysis for **4** ($C_{23}H_{12}Br_3N_3O_6$): colorless cube, $0.18 \times 0.18 \times 0.17\ mm^3$, cubic space group $P432$, $a = 18.6080(2)$ Å, $V = 6443.16(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.373\ g\,cm^{-3}$, $3° < \theta < 25°$, $R_1 = 0.0294$ for 1803 reflections with $I = 2\sigma(I)$, $wR_2 = 0.0865$ for all 1900 reflections, 105 parameters. The max/min residual electron density is as low as $+0.54/-0.29\ e\,Å^{-3}$; therefore, despite the large void, the reflection data were not squeezed with the PLATON program (see ref. [24]). CCDC-703495 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[26] Co-crystallization of mixtures of **4** with C_{60}-fullerene from benzene solutions furnished crystals in which each molecule of C_{60} is embedded into a pair of (*P*)-**4**, or (*M*)-**4**, each pair being arranged similarly to that found in pure crystalline **4** (ref. [14b] and [22b]).

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[33] The closest C–C nonbonding distances between the eight methyl carbon atoms within the cube shown in Figure 5 are 4.47 Å.

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