Synthesis and Structures of Three- and Hexa-armed Benzene Derivatives Featuring Lateral Benzoic Ester and Benzoic Acid Functions

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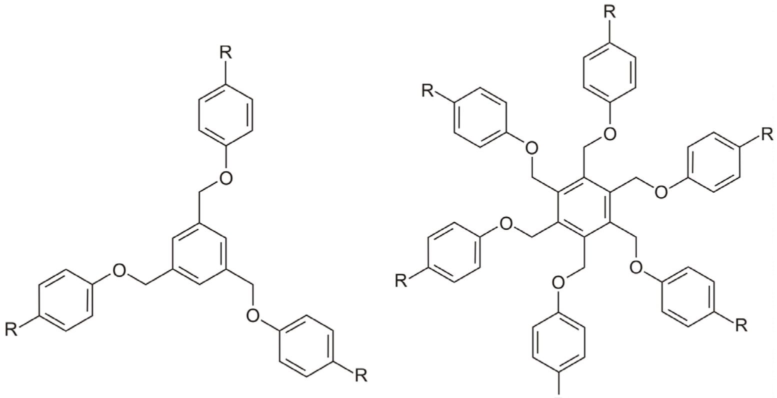
The new 1,3,5-tri-substituted and hexa-substituted benzoic methyl esters **1**, **3** and benzoic acids **2**, **4** have been synthesized. Single-crystal structure determinations of **1** – **3** are reported, which show specific molecular conformations and packings in the crystal. In all structures, the conformation of the molecules deviates considerably from threefold and sixfold symmetry, respectively. Columnar packings are observed in the crystal structures of the esters **1** and **3**, stabilized by weak C–H$\cdots$O and C–H$\cdots\pi$ interactions, while the packing of **2** features the formation of supramolecular strands involving the dimerization of the carboxylic acid group.

Key words: Tri- and Hexa-substituted Benzene Derivatives, Benzoic Acid, Benzoic Ester, X-Ray Diffraction Analysis

Introduction

Due to their structural behavior, symmetrically tri- and in particular hexa-substituted benzenes have arisen interest for a long time [1, 2]. With the development of supramolecular chemisty, they have become increasingly useful as construction elements for the design of tectons and other geometrically controlled framework structures including chelating metal complexants, molecular capsules and containers, dendritic compounds as well as crystalline hosts and spacer-type building blocks for the formation of hydrogen bonded, organic-inorganic hybrid or covalently linked aggregate structures [3 – 5]. Typical examples of these substance classes are, for instance, the octopus molecules [6], the hexahosts [7, 8] and piedfort hosts [8 – 11], the three-armed layer forming [12, 13] or MOF-type linker molecules [14, 15], and recently described glycodendrimers [16]. Though the tri- and hexa-substituted benzenes have mainly been applied in the realm of supramolecular host-guest chemistry [3, 4], currently corresponding compounds have



1 R = $COOCH_3$
2 R = COOH

3 R = $COOCH_3$
4 R = COOH

Fig. 1. Formulae of compounds studied.

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Table 1. Crystal data and parameters pertinent to data collection and structure refinement of compounds **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{33}H_{30}O_9$	$C_{30}H_{24}O_9$	$C_{60}H_{54}O_{18}$
Formula weight	570.57	528.49	1063.03
Crystal data			
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	12.7224(11)	6.3135(2)	8.2997(2)
b, Å	29.475(2)	10.6536(3)	10.8798(2)
c, Å	7.3457(7)	18.1229(6)	15.9153(3)
α, deg	90	86.380(1)	99.420(1)
β, deg	93.784(3)	88.673(1)	99.844(1)
γ, deg	90	79.350(1)	107.883(1)
V, Å^3	2748.6(4)	1195.50(6)	1311.27(5)
Z	4	2	1
$F(000)$	1200	552	558
D_{calcd}, Mg m^{-3}	1.38	1.47	1.33
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	0.1	0.1	0.1
Data collection			
Temperature, K	153(2)	100(2)	90(2)
θ range, deg	1.8–26.1	1.1–28.3	1.3–28.1
Index ranges $\pm h$, $\pm k$, $\pm l$	−15/14, −36/34, −9/8	−8/6, −14/14, −24/24	−9/10, −14/14, −21/21
No. of collected reflections	26793	21705	25242
No. of unique reflections / R_{int}	5449 / 0.0457	5909 / 0.0313	6262 / 0.0206
No. of F values with $I \geq 2\sigma(I)$	3498	4556	4893
Refinement			
No. of refined parameters	382	355	355
Final $R1$ (all data)[a]	0.0459	0.0423	0.0391
Final $wR2$ (all data)[b]	0.1429	0.1187	0.1305
Weighting scheme A / B [b]	0.0585 / 2.2978	0.0587 / 0.4414	0.0728 / 0.3373
S (Goodness of fit on F^2)[c]	1.000	1.028	1.071
Final $\Delta\rho_{\mathrm{max/min}}$, e Å^{-3}	0.53 / −0.31	0.45 / −0.25	0.37 / −0.29

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\mathrm{obs}} - n_{\mathrm{param}})]^{1/2}$.

also been used for the formation of discotic mesogens [17] and amphiphiles [18] or organic electronic and optoelectronic materials [19–22], showing the great diversity and applicational multipurpose derived from these basic kinds of molecular structures.

Being potentially connected with these fields of application, we report the synthesis of the new tri- and hexa-armed benzenes **1**–**4** (Fig. 1), representing specific constitutions with methyl benzoate and benzoic acid end groups. We also describe the crystal structures of the respective tri- and hexaesters (**1** and **3**) as well as of the tricarboxylic acid **2**.

Results and Discussion

Preparations

The tri- and hexaesters **1** and **3** were synthesized by the reaction of tris(bromomethyl)benzene [23] and hexakis(bromomethyl)benzene [24], respectively, with methyl 4-hydroxybenzoate in the presence of potassium carbonate, potassium iodide and a few drops of Aliquat 336 in acetone. The potassium iodide was added to start an initial Finkelstein exchange reaction [25] from the tribromo to the corresponding triiodo compounds having better leaving groups for the substitution, while the Aliquat 336 assisted the reaction as a solid-liquid phase-transfer catalyst [26]. Under these conditions, the compounds **1** and **3** were obtained in yields (83 and 88 %, respectively) similar to that of a related synthesis of an ethyl ester derivative of **1** [27]. The esters **1** and **3** were hydrolyzed with potassium hydroxide and subsequently acidified to yield the corresponding acids **2** (86 %) and **4** (50 %). Single crystals of **1**, **2** and **3** were obtained on slow evaporation of solutions in DMSO. However, we did not succeed in growing crystals suitable for X-ray diffraction analysis of the hexaacid **4**.

X-Ray diffraction studies

The crystal structures of **1**, **2** and **3** were determined in order to collect information about the molecular ge-

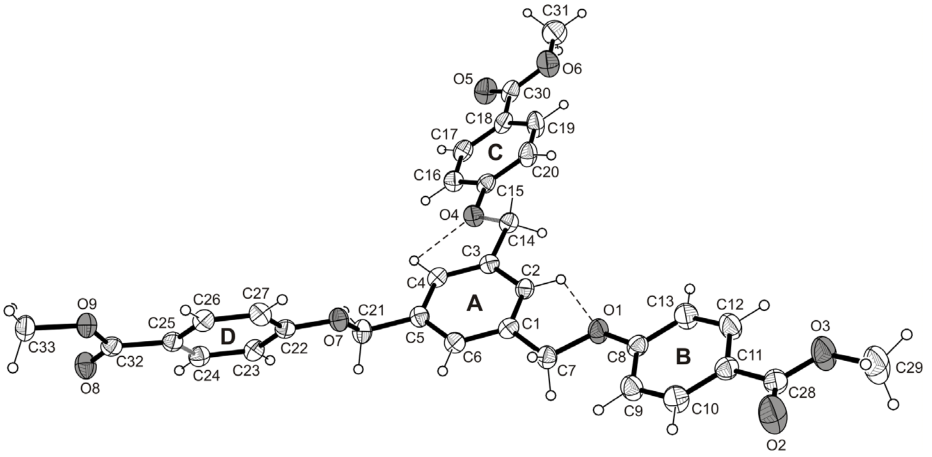

Fig. 2. Illustration of the molecular structure of **1** including the atom numbering and ring specification. Displacement ellipsoids are drawn at the 50 % probability level. Grey ellipsoids represent oxygen atoms.

ometry and packing behavior in the solid state. Crystallographic data, experimental parameters and selected details of the refinements are summarized in Table 1. The geometric features of the molecules can be expressed by a set of dihedral angles describing the inclination of the outer aromatic rings with respect to the central arene ring. These parameters together with relevant torsion angles are summarized in Table S1, while information regarding possible non-covalent interactions in the crystal structure are listed in Table S2 (see note at the end of the paper for availability of the Supplementary Information). Perspective views of the molecular structures including atom numbering and ring specification as well as illustrations of the packing structures are presented in Figs. 2 – 7.

Compound **1** crystallizes from DMSO as colorless plates in the monoclinic space group $P2_1/c$ with the asymmetric part of the unit cell containing one molecule. An ORTEP drawing of the molecular structure is depicted in Fig. 2. The conformation of the molecule deviates considerably from trigonal symmetry which is obvious from inclination angles of 16.3(1), 22.9(1) and 65.9(1)° formed between the benzoate rings B–D and the central aromatic ring A. The torsion angles along the $C_{(arene)}$–C–O–$C_{(arene)}$ fragments are 124.6(1) – 176.4(1)°. The tilt angles of the methoxycarbonyl groups with respect to the aromatic rings to which they are attached range from 4.6(1) to 8.9(1)°. The conformation is stabilized by two intramolecular C–H···O hydrogen bond type contacts [28] [C(2)–H(2)···O(1) 2.40 Å, 101°; C(4)–H(4)···O(4) 2.44 Å, 100°].

As displayed in Fig. 3, the molecules of **1** adopt a columnar structure extending along the crystallographic *c* axis which, however, lacks arene stacking. Within a given column, consecutive molecules are displaced such that the carboxylate residues of two of their arms are located in a distance of 3.7 Å between the arene rings of adjacent molecules indicating weak $\pi\cdots\pi$ interactions [29, 30]. Interstack association is established by a variety of weak C–H···O hydrogen bonding [28] [d(H···O) 2.51 – 2.69 Å] and C–H···π interactions [31, 32].

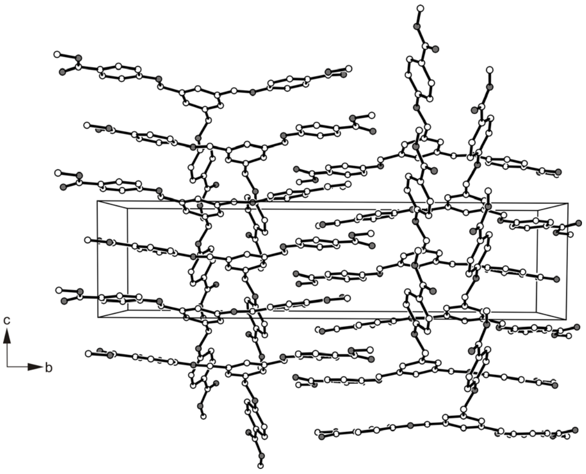

Fig. 3. Packing diagram of **1** as viewed down the crystallographic *a* axis. The oxygens atoms are displayed as grey circles. The hydrogen atoms are omitted for clarity.

The crystals of the tricarboxylic acid **2** are triclinic, space group $P\bar{1}$, with one molecule in the asymmetric part of the unit cell. The geometry of the molecule differs from that of **1**, as two of the molecular branches are arranged in a pincer-like fashion, the formation of which is induced by the mode of intermolecular

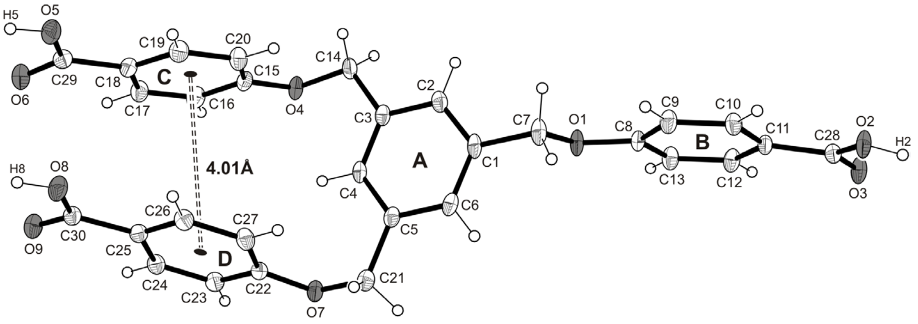

Fig. 4. Illustration of the molecular structure of **2**. Displacement ellipsoids are drawn at the 50 % probability level. The oxygens atoms are displayed as grey ellipsoids. Dotted double lines represent arene-arene interactions.

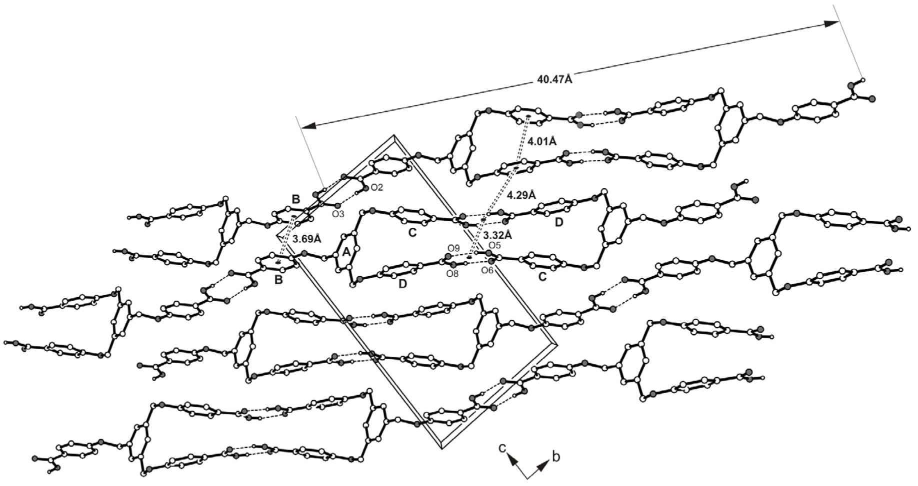

Fig. 5. Crystal structure illustration of **2** as viewed down the crystallographic *a* axis. The oxygen atoms are displayed as grey circles. Dotted lines represent hydrogen bond-type, dotted double lines $\pi\cdots\pi$ stacking interactions. With the exception of the carboxylic hydrogens all other hydrogen atoms are omitted for clarity.

association and furthermore appears to be stabilized by an intramolecular face-to-face interaction between the aromatic rings C and D (centroid···centroid distance 4.01 Å, Fig. 4). The third molecular 'arm' is oriented in the opposite direction with respect to the first two segments resulting in an elongated molecular conformation. Looking at the torsion angles along the phenoxymethylene fragments, one finds *gauche* conformations for the atomic sequences C(3)–C(14)–O(4)–C(15) [91.3(2)°] and C(5)–C(21)–O(7)–C(22) [−81.0(2)°], whereas the sequence C(1)–C(7)–O(1)–C(8) exists in an *anti* conformation [−171.2(1)°]. The interplanar angle between rings C and D is 18.2(1)°; the dihedral angles of these rings with reference to the central aromatic ring A are 89.8(1) and 73.4(1)°, respectively. The planes of the arene rings A and B are arranged approximately perpendicular to one another [86.8(1)°].

In the crystal structure of **2**, the molecules are linked *via* carboxylic acid dimerization [33] [O(5)–H(5)···O(9) 1.87 Å, 168°, O(8)–H(8)···O(6) 1.73 Å, 170°] to infinite chains. In this arrangement the benzoic acid fragments C and D of two molecules form a closed loop in which the centroid···centroid distance of the eight-membered rings is as short as 3.32 Å (Fig. 5) indicating strong $\pi\cdots\pi$ interactions [29, 30]. The second structure element of the molecular chain is defined by a pair of benzoic acid fragments B, the carboxyl groups of which form a ring through hydrogen bonding [O(2)–H(2)···O(3) 1.82 Å, 174°]. The distance between two repeating units along the supramolecular chain is 40.47 Å. The molecular strands interact by stacking of their π electron-rich molecular parts comprising offset face-to-face arene interactions (centroid···centroid 3.69 Å) and stacking interactions between arene and hydrogen bonded rings [34] (centroid···centroid 4.29 Å). Moreover, a close network of weak C–H···O hydrogen bonds [d(H···O) 2.65 – 2.68 Å] and C–H···π contacts have a stabilizing effect on the lattice structure.

Crystallization of the hexacarboxylate **3** from DMSO yields colorless plates. It crystallizes in the triclinic space group $P\bar{1}$ with the asymmetric part of the unit cell containing one half of the molecule. A per-

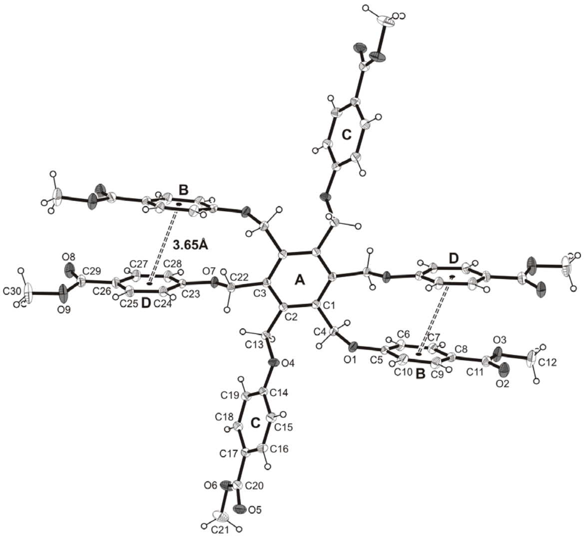

Fig. 6. Perspective view of the molecular structure of **3**. Displacement ellipsoids are drawn at the 50 % probability level. The oxygen atoms are displayed as grey ellipsoids. Dotted double lines represent arene-arene interactions.

spective view of the molecular structure is presented in Fig. 6. The aromatic rings B–D are inclined at angles of 76.4(1) – 78.9(1)° with respect to the central arene ring A. The molecular conformation strongly deviates from sixfold symmetry which is to be ascribed to packing forces rather than coordination effects. In a similar fashion as in the aforementioned case, pairs of methoxycarbonylphenoxy fragments point in the same direction with a nearly parallel arrangement of their aromatic rings [centroid(ring B)$\cdots$centroid(ring D) 3.65 Å].

A view of the crystal structure of **3** along the *a* axis reveals a columnar packing of molecules. As illustrated in Fig. 7, C–H$\cdots$O hydrogen bonds [28] with the oxygens O(2) and O(4) acting as acceptors [d(H$\cdots$O) 2.35, 2.54 Å] stabilize the crystal lattice along the stacking axis, while the oxygens O(3), O(5) and O(8) are involved in interstack association *via* C–H$\cdots$O bonding [d(H$\cdots$O) 2.38 – 2.56 Å].

Conclusions

The occurence of threefold molecular symmetry is realized in a wide range of tri-substituted benzene [11, 35] and triazine derivatives [36, 37] as well as in hexasubsutituted benzenes [38, 39], often giving rise to trigonal crystallographic symmetry. The molecular assembly in the crystal lattice is governed by the rigidity of the side arms. In the presence of flexible side arms, as is the case in compounds **1** – **3**, the molecular symmetry is reduced by conformational variations induced by coordination and packing effects. A clear tendency to a columnar packing of molecules is observed in the crystal structures of **1** and its hexa-substituted analog **3**. The molecular structure of the latter is characterized by intramolecular $\pi\cdots\pi$ interactions and a nearly parallel arrangement of pairs of molecular branches. A similar situation is found in the crystal structure of **2**, where the molecule adopts a so-called φ conformation [40] with two of the molecular branches oriented in one direction, while the third arm is pointing in the opposite direction. This leads to the formation of parallel O–H$\cdots$O-bonded supramolecular strands through carboxylic acid dimers. Two- or

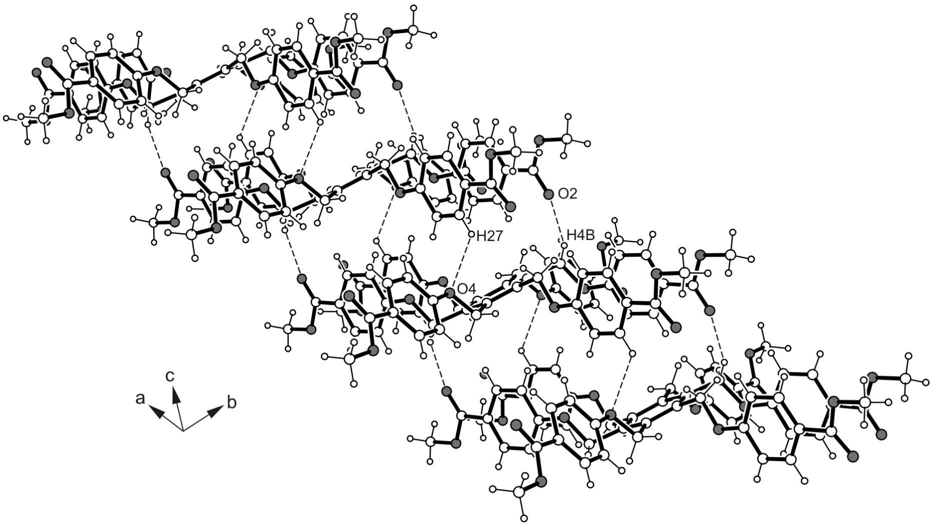

Fig. 7. Crystal structure of **3**. The oxygen atoms are displayed as grey circle. Dotted lines represent hydrogen bond-type interactions.

three-dimensional hydrogen-bonded frameworks, as in some known porous solids [41 – 44], are excluded owing to the flexibility of the side arms. A piedfort type of molecular association found in the structures of other three-armed compounds [8, 9] which are useful synthons in crystal engineering [10, 11, 45, 46], was also not observed in the present structures.

Experimental Section

General

Melting points: Kofler melting point microscope (uncorrected). IR: Nicolet FT-IR 510. ^{1}H and ^{13}C NMR (chemical shifts δ in ppm *vs.* TMS as internal standard): Bruker Avance DPX 400. MS (ESI): Bruker Daltonics ESQUIRE-LC. MS (MALDI-TOF): Bruker Daltonics BIFLEX III. Elemental analysis: Heraeus CHN rapid analyzer. TLC analysis: aluminum sheets precoated with silica gel 60 F_{254} (Merck).

1,3,5-Tris(bromomethyl)benzene [23] and 1,2,3,4,5,6-hexakis(bromomethyl)benzene [24] were synthesized following the described procedures. Mesitylene, hexamethylbenzene and methyl 4-hydroxybenzoate, as well as other common reagents were purchased from commercial sources.

*Preparation of the esters **1** and **3***

*Trimethyl 4,4′,4″-[benzene-1,3,5-triyl-tri(methyleneoxy)]tribenzoate (**1**)*

A stirred mixture of 1,3,5-tris(bromomethyl)benzene (1.78 g, 5.0 mmol), methyl 4-hydroxybenzoate (2.43 g, 16.0 mmol), potassium carbonate (2.21 g, 16.0 mmol), potassium iodide (0.83 g, 5.0 mmol), and a few drops of Aliquat 336 in acetone (100 mL) was heated to reflux for 50 h. After cooling to r. t., water (100 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated to yield 2.37 g (83 %) of a colorless solid; m. p. 115 – 117 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 9 H, CH_3), 5.15 (s, 6 H, CH_2), 6.99 (d, $^{3}J_{HH}$ = 8.8 Hz, 6 H, Ar-H), 7.48 (s, 3 H, Ar-H), 8.00 (d, $^{3}J_{HH}$ = 9.2 Hz, 6 H, Ar-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.9 (CH_3), 69.6 (CH_2), 114.4, 123.1, 126.0, 131.6, 137.5, 162.2 (Ar-C), 166.7 (carbonyl-C). – IR (KBr): ν = 3082, 3034, 2946, 1717, 1600, 1508, 1439, 1005, 872 cm^{-1}. – MS (ESI): m/z = 609.0 (calcd. 609.29 for $C_{33}H_{30}O_9$, $[M+K]^+$).

*Hexamethyl 4,4′,4″,4‴,4⁗,4′′′′′-[benzene-1,2,3,4,5,6-hexayl-hexa(methyleneoxy)]hexabenzoate (**3**)*

1,2,3,4,5,6-Hexakis(bromomethyl)benzene (3.18 g, 5.0 mmol), methyl 4-hydroxybenzoate (4.86 g, 32.0 mmol), potassium carbonate (4.42 g, 32.0 mmol), potassium iodide (0.83 g, 5.0 mmol), and a few drops of Aliquat 336 in acetone (100 mL) were reacted and worked up as desribed for **1** to yield 4.67 g (88 %) of a colorless solid; m. p. 259 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 18 H, CH_3), 5.24 (s, 12 H, CH_2), 6.87 (d, $^{3}J_{HH}$ = 8.8 Hz, 12 H, Ar-H), 7.92 (d, $^{3}J_{HH}$ = 8.8 Hz, 12 H, Ar-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.9 (CH_3), 63.7 (CH_2), 114.1, 123.7, 131.7, 137.7, 161.7 (Ar-C), 166.5 (carbonyl-C). – IR (KBr): ν = 3075, 2949, 1717, 1606, 1508, 1432, 1008 cm^{-1}. – MS (MALDI-TOF): m/z = 1085.7 (calcd. 1085.23 for $C_{60}H_{54}O_{18}$, $[M+Na]^+$).

*Preparation of the carboxylic acids **2** and **4***

*4,4′,4″-[Benzene-1,3,5-triyl-tri(methyleneoxy)]tribenzoic acid (**2**)*

Solutions of **1** (2.28 g, 4.0 mmol) in methanol (50 mL) and of potassium hydroxide (2.24 g, 4.0 mmol) in water (5 mL) were combined and the stirred mixture heated to reflux for 20 h. After cooling to r. t. and filtration, the solution was acidified to pH = 1 by the addition of conc. hydrochloric acid. The precipitate which formed was collected and washed with water until neutral pH of the washing. The gelatinous residue was dried to yield 1.82 g (86 %) of a colorless solid; m. p. 268 – 273 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.22 (s, 6 H, CH_2), 7.11 (d, $^{3}J_{HH}$ = 8.4 Hz, 6 H, Ar-H), 7.54 (s, 3 H, Ar-H), 7.90 (d, $^{3}J_{HH}$ = 8.4 Hz, 6 H, Ar-H), 12.65 (s, 3 H, COOH). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.3 (CH_2), 114.8, 123.4, 126.8, 131.5, 137.4, 162.0 (Ar-C), 167.1 (carbonyl-C). – IR (KBr): ν = 3422, 3074, 2665, 2532, 1681, 1603, 1576, 1426, 1162, 846 cm^{-1}. – MS (ESI): m/z = 529.0 (calcd. 529.15 for $C_{30}H_{24}O_9$, $[M+H]^+$).

*4,4′,4″,4‴,4⁗,4′′′′′-[Benzene-1,2,3,4,5,6-hexayl-hexa(methyleneoxy)]hexabenzoic acid (**4**)*

Solutions of **3** (4.25 g, 4.0 mmol) in DMF (150 mL) and of potassium hydroxide (4.49 g, 80.0 mmol) in water (10 mL) were combined and the stirred mixture heated at 90 °C for 20 h. Work-up of the reaction mixture as described for **2** gave a yield of 1.96 g (50 %) of a colorless solid; m. p. > 350 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (s, 12 H, CH_2), 6.99 (d, $^{3}J_{HH}$ = 8.8 Hz, 12 H, Ar-H), 7.78 (d, $^{3}J_{HH}$ = 8.8 Hz, 12 H, Ar-H), 12.61 (s, 6 H, COOH). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.0 (CH_2), 114.6, 123.5, 131.2, 137.6, 161.7 (Ar-C), 166.9 (carbonyl-C). – IR (KBr): ν = 3422, 3075, 2665, 2553, 1685, 1606, 1578, 1435, 1169 cm^{-1}. – MS (MALDI-TOF): m/z = 1001.4 (calcd. 1001.23 for $C_{54}H_{42}O_{18}$, $[M+Na]^+$).

X-Ray structure determinations

The intensity data of **1** – **3** were collected on a Kappa APEX II diffractometer (Bruker AXS) with MoK_α radiation (λ = 0.71073 Å). Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by application of Direct Methods [47] and were refined by full-matrix least-squares calculations based on F^2 for all reflections [47]. All hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms.

The crystal data and parameters pertinent to data collection and structure refinement of the compounds studied are summarized in Table 1.

Supplementary information

CCDC 833268, 833269 and 833270 contain the crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Further details on the crystal structures, including tables of conformational parameters (Table S1) and geometric parameters for non-covalent contacts (Table S2) are given as Supplementary Information available online (www.znaturforsch.com/ab/v66b/c66b.htm).

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Synthesis and Structures of Three- and Hexa-armed Benzene Derivatives Featuring Lateral Benzoic Ester and Benzoic Acid Functions

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Supplementary Information

Table S1.	Relevant conformational parameters of the compounds studied.
Table S2.	Geometric parameters for non-covalent contacts of the compounds studied.

Table S1. Relevant conformational parameters of the compounds studied.

Compound	**1**	**2**	**3**
Dihedral angles (deg)			
mpla(A)-mpla(B)[a]	16.3(1)	86.8(1)	76.4(1)
mpla(A)-mpla(C)	22.9(1)	89.8(1)	76.8(1)
mpla(A)-mpla(D)	65.9(1)	73.4(1)	78.9(1)
mpla(B)-mpla(D)			6.2(1)
mpla(C)-mpla(D)		18.2(1)	
mpla(B)-mpla(B')[b]	8.9(1)	7.8(1)	2.2(1)
mpla(C)-mpla(C')	4.6(1)	3.7(1)	11.4(1)
mpla(D)-mpla(D')	6.1(1)	4.1(1)	10.6(1)
Torsion angles (deg)			
C(1)-C(7)-O(1)-C(8)	168.7(2)	-171.2(1)	
C(3)-C(14)-O(4)-C(15)	-176.6(2)	91.3(2)	
C(5)-C(21)-O(7)-C(22)	177.6(2)	-81.0(2)	
C(2)-C(1)-C(7)-O(1)	8.2(3)	-88.4(2)	
C(4)-C(3)-C(14)-O(4)	-21.3(3)	-0.4(2)	
C(6)-C(5)-C(21)-O(7)	63.2(3)	-165.5(1)	
C(1)-C(4)-O(1)-C(5)			-124.6(1)
C(2)-C(13)-O(4)-C(14)			-173.7(1)
C(3)-C(22)-O(7)-C(23)			-176.4(1)
C(2)-C(1)-C(4)-O(1)			-105.8(1)
C(3)-C(2)-C(13)-O(4)			-107.8(1)
C(1)-C(3)-C(22)-O(7)			104.4(1)

[a] Means least-squares plane through the aromatic ring (ring specification in Figs. 2, 4 and 6). **1**, **2**: Ring A: C(1)…C(6), ring B: C(8)…C(13), ring C: C(15)…C(20), ring D: (22)…C(27); **3**: Ring A: C(1)…C(3), C(1A)…C(3A) ring B: C(5)…C(10), ring C: C(14)…C(19), ring D: C(23)…C(28).

[b] Means least-squares plane through the carboxylate fragment. **1**: B': C(11),C(28),O(2),O(3), C': C(18),C(30),O(5),C(6), D': C(25),C(32),O(8),O(9); **2**: C': C(18),C(29),O(5),C(6), D': C(25),C(30),O(8),O(9); **3**: B': C(8),C(11),O(2),O(3), C': C(17),C(20),O(5),C(6), D': C(26),C(29),O(8),O(9).

Table S2. Geometric parameter for non-covalent contacts of the compounds studied.

Atoms involved	Symmetry	Distance (Å)			Angle (deg)
D-H···A		D-H	D···A	H···A	D-H···A
1					
C(33)-H(33C)···O(1)	1+*x*, *y*, -1+*z*	0.98	3.635(3)	2.66	173
C(2)-H(2)···O(1)	*x*, *y*, *z*	0.95	2.744(3)	2.40	101
C(6)-H(6A)···O(2)	1-*x*, -*y*, 2-*z*	0.95	2.415(3)	2.51	160
C(4)-H(4)···O(4)	*x*, *y*, *z*	0.95	2.758(3)	2.44	100
C(17)-H(17)···O(5)	1-*x*, 1-*y*, 2-*z*	0.95	3.198(3)	2.65	118
C(29)-H(29B)···O(6)	-*x*, -0.5+*y*, 2.5-*z*	0.98	3.388(3)	2.55	144
C(29)-H(29A)···O(9)	1-*x*, -*y*, 1-*z*	0.98	3.435(3)	2.60	143
C(14)-H(14A)···O(8)	-1+*x*, 0.5-*y*, 0.5+*z*	0.99	3.635(3)	2.69	160
C(13)-H(13)···C(32)[a]	-1-*x*, -*y*, 1-*z*	0.95	3.803(3)	2.85	178
C(24)-H(24)···C(32)[a]	*x*, 0.5-*y*, 0.5+*z*	0.95	3.525(3)	2.88	126
2					
O(2)-H(2)···O(3)	-1-*x*, 3-*y*, -*z*	0.84	2.659(2)	1.82	174
O(5)-H(5)···O(9)	3-*x*, -*y*, 1-*z*	0.84	2.692(2)	1.87	168
O(8)-H(8)···O(6)	3-*x*, -*y*, 1-*z*	0.84	2.565(2)	1.73	170
C(13)-H(13)···O(1)	1-*x*, 2-*y*, -*z*	0.95	3.503(3)	2.65	149
C(7)-H(7B)···O(7)	-1+*x*, *y*, *z*	0.99	3.121(3)	2.68	107
C(2)-H(2A)···O(3)	-*x*, 2-*y*, -*z*	0.95	3.616(3)	2.67	171
C(19)-H(19)···O(9)	-1+*x*, *y*, *z*	0.95	3.505(3)	2.67	147
C(23)-H(23)···C(5)[a]	1+*x*, *y*, *z*	0.95	3.736(3)	2.78	178
3					
C(4)-H(4B)···O(2)	1+*x*, *y*, *z*	0.99	3.241(3)	2.35	150
C(19)-H(19)···O(3)	1-*x*, 1-*y*, -*z*	0.95	3.296(3)	2.51	141
C(27)-H(27)···O(4)	1+*x*, *y*, *z*	0.95	3.225(3)	2.54	129
C(16)-H(16)···O(5)	1-*x*, 1-*y*, 1-*z*	0.95	3.354(3)	2.56	133
C(21)-H(21B)···O(8)	3-*x*, 1-*y*, 1-*z*	0.98	3.240(3)	2.38	146
C(9)-H(9)···C(1)[a]	-1+*x*, *y*, *z*	0.95	3.550(3)	2.62	167

[a] To achieve reasonable hydrogen bond geometries, individual atoms instead of ring centroids were choosen as acceptors.