

Synthesis and Solid-state Structure of a Star-shaped Oligobenzoate

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A star-shaped oligobenzoate with short peripheral propyloxy chains (**1**) forms single crystals $1 \cdot (\text{Me}_2\text{CO})_{0.5}$ with a triclinic unit cell from acetone. The oligobenzoate arms are fully extended, possessing only carboxy groups with *s-trans* conformation. Aliphatic chains and oligobenzoate scaffold do not nano-segregate as proposed for other derivatives which assemble in liquid crystalline phases, but instead, the polar arms occupy the voids between arms of neighboring stars. Although a model based on this scenario may rationalize the small column diameter in the LC phase of long-chain derivatives, the low density of the resulting material points rather to the recently established representation with folded conformers self-assembling in columns by nano-segregation.

Key words: Star-shaped Molecules, Single Crystal, Supramolecular Chemistry, Mesogens, Liquid Crystals, Nano-segregation

Introduction

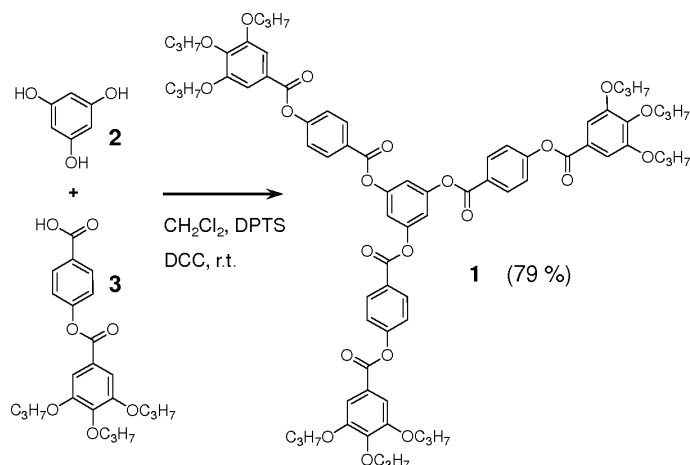
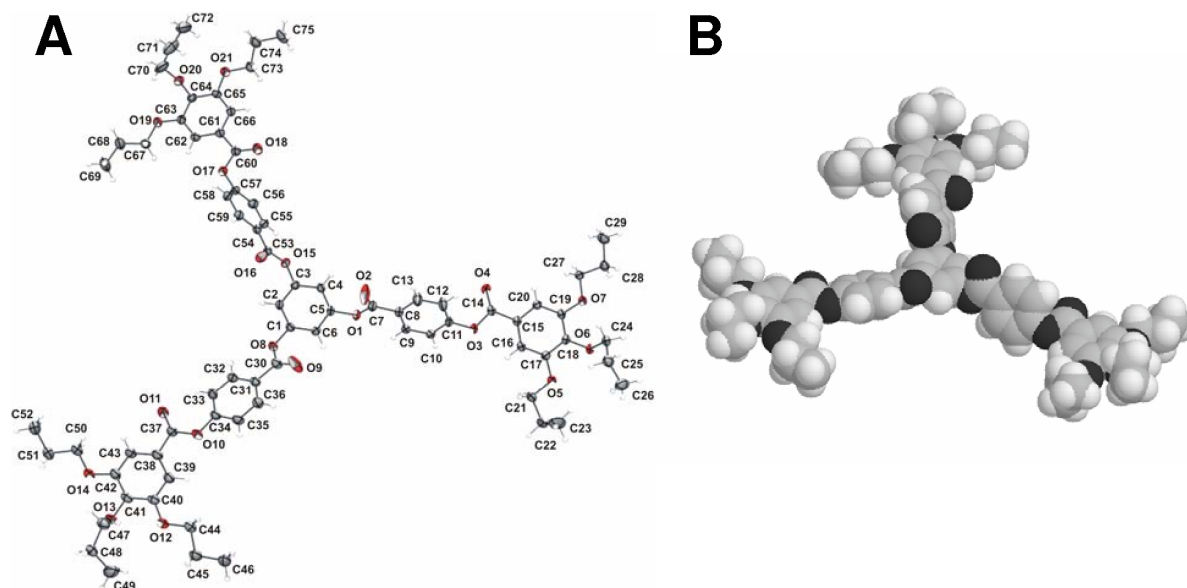
Molecules forming columnar liquid crystals have attracted great interest during the last decade due to their potential applications in plastic electronics [1]. Nano-segregation is discussed as the main driving force of self-organization in columnar structures [2]. This has been shown recently also for three-armed, non-conventional mesogens [3]. However, a series of symmetric star-shaped oligobenzoates with nine peripheral dodecyloxy chains forming hexagonal and rectangular columnar liquid crystal phases (Col_h and Col_r) [4] possess column diameters in the Col_h phase which are much smaller than expected from molecular models, even if flexible alkyl chains are assumed. Therefore, a model was discussed, where conformers other than the most extended star-shaped oligobenzoates form the columns by nano-segregation of polar aromatic cores and non-polar flexible aliphatic chains [3c, 4, 5]. The smallest derivative rearranges to a not yet fully characterized crystalline columnar superstructure templated by the hexagonal liquid crystal when annealed at room temperature (r.t.) for one day [6]. However, these mesogens with long alkoxy chains evade attempted crystallization in the form of single crystals and there-

fore no detailed information about conformers which assemble in these mesostructures has been obtained. Consequently, we synthesized a derivative with short propyloxy chains, because they are known to assist single crystal formation of different star-shaped molecules [7].

Results and Discussion

The target molecule **1**, shown in Fig. 1, was prepared by a threefold esterification of the phloroglucinol core **2** with the oligobenzoate units **3**, in analogy to the procedure reported recently [4]. The oligobenzoate arms **3** were synthesized starting with 3,4,5-tripropyloxybenzoic acid [8].

Single crystal preparation was intended from acetone and hexane solution. The first solvent is believed to interact well with the polar benzoate core, whereas in the second one solvation of the peripheral chains should be favored. Therefore, crystallization from hexane was expected to furnish a core packing similar to the folded molecules proposed in the mesophases for derivatives with long dodecyloxy chains. However, single crystals suitable for single crystal analyses were obtained exclusively from acetone solution as colorless needles as the $1 \cdot (\text{Me}_2\text{CO})_{0.5}$ solvate.

Fig. 1. Synthesis of star-shaped molecule **1**.Fig. 2. A: ORTEP plot (displacement ellipsoids at the 50 % probability level) of the molecular structure of **1** with the atom numbering scheme. The acetone solvate molecule as well as disordered atoms have been omitted for clarity. B: Molecular structure of **1** (CPK space filling plot).

The molecular structure of **1** is shown in Fig. 2. Selected torsion angles are presented in Table 1.

The molecule shown in Fig. 2 exhibits various interesting features. In agreement with the energetically minimized structures reported earlier [5] the star-shaped compound is almost planar with the benzoate units in an all-*s-trans* conformation (Table 1, Fig. 2) [9]. Only the inner benzoate repeating units (*i*-COO) are rotated out of the molecular plane by up to 79° , thus creating local dipoles orthogonal to the central benzene plane. These dipoles are oriented anti-parallel in consecutive layers along the *a* axis,

thus stabilizing the crystal structure (Fig. 3A). In the mesophases of the long-chain derivatives similar local conformations of carboxy groups with dipoles along the columns are thought to play a key role for mesophase stabilization. When viewed along the *a* axis (Fig. 3B) the crystalline order is found to be similar to a columnar assembly, where molecules pack with their molecular planes on top of each other. The molecules are tilted by 22.8° versus the *a* axis, as was also confirmed by optical investigations of the crystal needles between crossed polarizers. Extinction of light is observed at approximately 23° from the position where

Dihedral angles			
all- <i>s-trans</i> conformation		peripheral benzoates (<i>ob</i>)	
C1–O8–C30–C31	178.18(13)	O4–C14–C15–C20	0.2(2)
C3–O15–C53–C54	–172.94(12)	C43–C38–C37–O11	–7.8(3)
C5–O1–C7–C8	179.56(13)	O18–C60–C61–C62	179.70(19)
C34–O10–C37–C38	–178.10(14)	inner benzoates (<i>ib</i>)	
C11–O3–C14–C15	169.66(13)	C13–C8–C7–O2	–12.8(3)
C57–O17–C60–C61	–178.28(14)	C36–C31–C30–O9	–10.0(3)
inner carboxyl groups (<i>i</i> -COO)		C59–C54–C53–O16	0.9(2)
C30–O8–C1–C6	42.0(2)	outer carboxyl groups (<i>o</i> -COO)	
C7–O1–C5–C4	79.11(18)	C37–O10–C34–C35	163.18(16); {192.35} ^a
C53–O15–C3–C2	53.0(2)	C14–O3–C11–C12	–52.4(2); {16.74} ^a
		C60–O17–C57–C58	117.07(17); {170.77} ^a

Table 1. Selected dihedral angles (deg) for **1** with estimated standard deviations in parentheses.

^a Values in curly brackets are calculated dihedral angles between the plane of the central benzene ring and the peripheral benzoyl group.

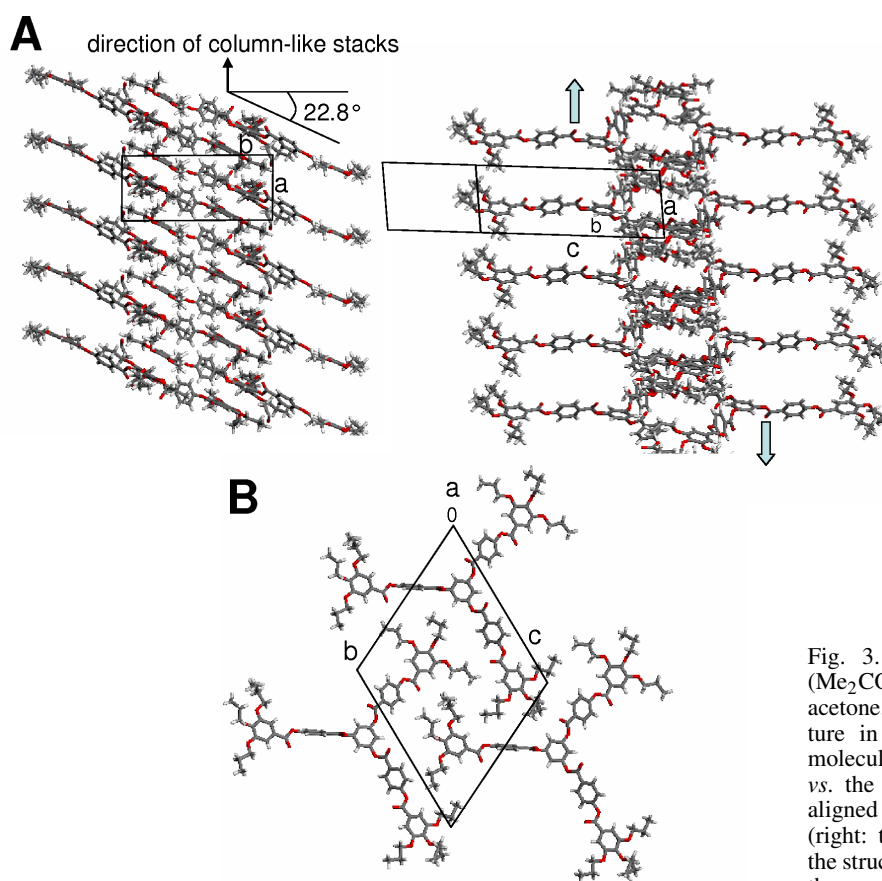


Fig. 3. Crystal structure of **1** · (Me₂CO)_{0.5} as crystallized from acetone. A: Column-like structure in direction of the *a* axis; molecules are inclined by 22.8° vs. the *a* axis. Local dipoles are aligned in anti-parallel fashion (right: thick arrows). B: View of the structure onto the *bc* plane. The three molecules are positioned in the Miller plane (110).

the needle's long axis is parallel to the polarizer or analyzer, indicating that the crystals grow more rapidly in column-like stacks along the *a* axis (Fig. 4). However, unlike columnar liquid crystals, where different molecular segments such as polar benzoate units

and non-polar aliphatic chains tend to nano-segregate, in the crystal of **1** the propyl chains are too short to let nano-segregation play a major role in molecular stacking. In contrast, arms of molecules in the same layer [Miller plane (110)] fill the space between

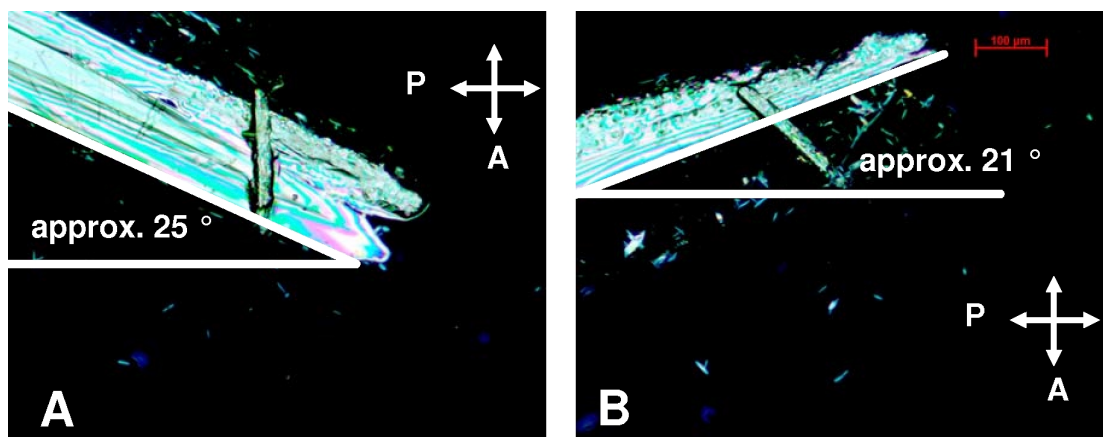


Fig. 4. Crystal needle observed between crossed polarizers. The needle consists of a crystal twin. A: the upper part of the crystal became dark. B: the lower part of the crystal became dark. In average the crystal must be inclined by approximately 23° relative to the polarizer (P) in order to observe extinction of light. At this angle one director of the crystal coincides with the direction of the polarizer (P) or the analyzer (A). This is attributed to the inclination of star-shaped molecules by 22.8° vs. the *a* axis of the crystal.

arms of their star-shaped neighbors, together with solvate molecules [10]. Thereby, the aliphatic chains are not segregated from the benzoate scaffold. The intermolecular core–core distance in the Miller plane ($1\bar{1}0$) amounts to 23.0 \AA and is comparable with the diameter $d = 24.0 \text{ \AA}$ of the benzoate core as calculated for the hexagonal columnar mesophases of the same parent molecule with peripheral dodecyloxy chains for perfect nano-segregated molecular segments [4, 11]. In the ($1\bar{1}0$) plane of the crystal the molecular arrangement resembles a hexagonal packing (Fig. 5A). Thus, in principle, this arrangement could serve as a model for the previously found hexagonal liquid crystal phases of star-shaped molecules. The alkyl chains penetrating the polar scaffold might be one possible scenario, different from the one previously presented based on nano-segregation and folded mesogens [4, 11] which may explain their small columnar diameters [12].

On the basis of the crystal data a model which might rationalize the self-assembly in the liquid crystal phase of the dodecyloxy derivative can be envisioned. Fig. 5B shows the hexagonal liquid crystal cell with the reported parameter $a = 42.5 \text{ \AA}$. The height $h = 3.8 \text{ \AA}$ is the distance measured between the almost planar star-shaped cores orthogonal to the ($1\bar{1}0$) planes in the crystal [13]. The circular cross section with $r = 15.3 \text{ \AA}$ is the region where the star-shaped benzoate core with interdigitating aliphatic chains is to be positioned. As shown, only a single benzoate core fits into the unit cell, if a similar packing as in the crys-

tal of **1** is assumed (*cp.* Fig. 3B). The residual volume (gray and white space in Fig. 5B) has to be filled with aliphatic chains. Comparison of $V_{\text{cell}} - V_{\text{core}} = 3124.7 \text{ \AA}^3$ (gray space) and the volume of the aliphatic chains of one molecule, as calculated from dilatometry data [14] amounting to 2954 \AA^3 [15], shows clearly that the non-polar chains of one molecule cannot even completely fill the space between the cores (gray). Even with the relatively dense packing along the columns (3.8 \AA separation of aromatic segments), the unit cell must contain more than one molecule to optimize space filling. The calculated density in this model with one molecule per unit cell attains only $d_{\text{calcd}} = 0.69 \text{ g cm}^{-3}$. Thus, a self-assembly as envisioned by the crystal structure is improbable for the liquid crystal. These results substantiate that folded benzoates are building blocks for the self-organization in the columnar mesophase of mesogens **1** with dodecyloxy chains as proposed previously [4].

Conclusion

In conclusion, the star-shaped molecule **1** shows the most extended all-*s-trans* conformation of carboxy groups, which was recently proposed as the minimized structure in theoretical studies of isolated molecules [5]. Local dipole moments which orient anti-parallel along the *a* axis stabilize a column-like structure. In the title compound, the propyl chains are too short to nano-segregate, but are small enough to fill the voids between arms of neighboring molecules

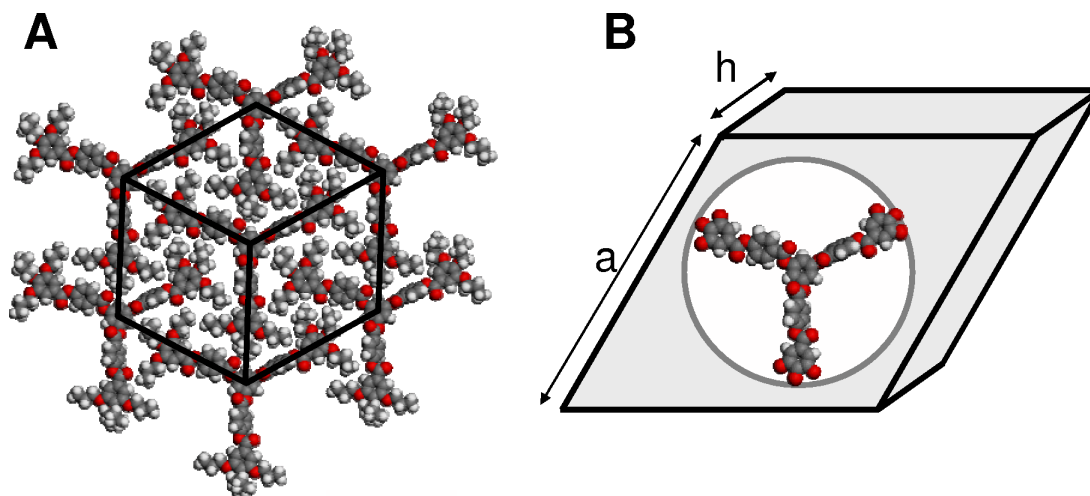


Fig. 5. A: Distorted hexagonal packing of star-shaped molecules **1** in the $(1\bar{1}0)$ plane of the crystal. B: Model of the hexagonal columnar liquid crystal phase of a derivative with nine dodecyloxy chains ($M = 2457.6 \text{ g mol}^{-1}$) assuming the unit cell of the mesophase at 35°C with $a = 42.5 \text{ \AA}$, the height $h = 3.8 \text{ \AA}$, as taken from the crystal structure [13], and a self-assembly similar to the packing in the crystal. The gray and the white volume should then be filled by aliphatic chains.

in the $(1\bar{1}0)$ plane of the crystal. The arrangement could explain also the diameters of LC phases of previously published mesogens [4] if not nano-segregation but space-filling plays the major role in the self-organization process. However, the low density of the presented model supports the recently proposed folded benzoate conformers as building blocks in the columnar liquid crystal phase.

Experimental Section

General methods

Chemicals were obtained from Acros and Sigma-Aldrich and used as received. Column chromatography was carried out on silica 60 (Merck, mesh 70–230). PFT ^1H and ^{13}C NMR spectra were recorded in CDCl_3 with a Varian Oxford 400 MHz spectrometer with the residual solvent signal at 7.26 ppm as a reference. Mass spectra were obtained on a Finnigan MAT95 (FD MS). Elemental analysis was carried out in the Microanalytical Laboratory of the University of Mainz.

Synthesis of 4-(3,4,5-tripropoxybenzoyloxy)benzoic acid (**3**)

3,4,5-tripropoxybenzoic acid [8] (2.77 g, 9.35 mmol), 4-hydroxybenzoic acid benzyl ester (2.24 g, 9.81 mmol), dicyclohexylcarbodiimide (DCC; 4.05 g, 19.63 mmol), and 1.44 g (4.89 mmol) of dimethylaminopyridinium *p*-toluenesulfonate (DPTS) were dissolved in 90 mL of dry dichloromethane and stirred over night at r.t. The solvent was re-

moved and the residue was extracted with hot hexane and filtered. The crude product, which was obtained by evaporation of the solvent, was purified by column chromatography (silica, hexane/ethyl acetate = 4 : 1) to afford a colorless solid (4.40 g, 93 %). For the cleavage of the benzyl protecting group, the product was dissolved in diethyl ether (100 mL) and 20 mg of Pd/C (10 %) was added. The mixture was stirred at r.t. over night under a hydrogen atmosphere. The reaction mixture was filtered over Celite 512, and the solvent was removed. Crystallization from hexane afforded a colorless solid product. Yield: 2.95 g (82 %); m. p. = 141°C . ^1H NMR (400 MHz, CDCl_3): $\delta = 1.06, 1.07$ (2 \times t, $^3J_{\text{HH}} = 7.4 \text{ Hz}$, 9 H, CH_3), 1.75–1.92 (m, 6 H, CH_2), 4.03, 4.06 (2 \times t, $^3J_{\text{HH}} = 6.4 \text{ Hz}$, 18H, OCH_2), 7.33 (AA'BB', 2 H, arom. H), 7.42 (s, 2 H, arom. H), 8.21 (AA'BB', 2 H, arom. H).

Synthesis of 1,3,5-tris-[4-(3,4,5-tripropoxybenzoyloxy)benzoyloxy]benzene (**1**)

Acid **3** (1.30 g, 3.12 mmol), phloroglucinol (0.13 g, 1.00 mmol), DCC (1.48 g, 6.39 mmol), and 0.45 g (1.55 mmol) of DPTS were added to 30 mL of dry dichloromethane and the mixture was stirred over night at r.t. The solvent was removed and the residue was dissolved in 50 mL of hexane. The suspension was filtered. After evaporation of the solvent, the crude product was purified by column chromatography (silica, hexane/ethyl acetate = 3 : 1). After recrystallization from hexane the product was obtained in the form of colorless crystals. Yield 1.03 g (79 %), m. p. = 98°C . ^1H NMR (400 MHz, CDCl_3): $\delta = 1.06,$

Table 2. Crystallographic data for **1** · (Me₂CO)_{0.5}.

Formula	C _{76.5} H ₈₇ O _{21.5}
<i>M_r</i> , g mol ^{−1}	1350.46
Habit	colorless needle
Cryst. size, mm ³	0.4 × 0.1 × 0.1
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	8.2436(14)
<i>b</i> , Å	21.235(3)
<i>c</i> , Å	22.711(4)
α , deg	64.407(16)
β , deg	83.531(14)
γ , deg	88.074(13)
<i>V</i> , Å ³	3562.2(10)
<i>Z</i>	2
<i>d</i> _{calcd.} , g cm ^{−3}	1.26
Radiation, wavelength	CuK α , λ = 1.541838 Å
μ , mm ^{−1}	0.8
<i>F</i> (000), e	1436
θ_{\max} (deg)	60.36
Refl. measured	27608
Refl. independent	10481
Refl. observed [<i>F</i> _o ≥ 2.0σ(<i>F</i> _o)]	9013
<i>R</i> _{int}	0.013
Param. refined	912
w <i>R</i> (<i>F</i> ²), all refl.	0.111
<i>R</i> [<i>F</i> ² ≥ 2σ(<i>F</i> ²)]	0.0392
<i>S</i>	1.079
$\Delta\rho$ max/min, e Å ^{−3}	0.67/−0.54

1.08 (2 × t, ³*J*_{HH} = 7.4 Hz, 27 H, CH₃), 1.75–1.92 (m, 18 H, CH₂), 4.03, 4.06 (2 × t, ³*J*_{HH} = 6.4 Hz, 18 H, OCH₂), 7.20 (s, 3 H, arom. H), 7.37 (AA'/BB', 6 H, arom. H), 7.43 (s, 6 H, arom. H), 8.29 (AA'/BB', 6H, arom. H). – ¹³C NMR (100 MHz, CDCl₃): δ = 10.5, 10.6 (CH₃), 22.6, 23.5 (CH₂), 70.8, 75.2 (OCH₂), 108.7, 113.3, 122.2 (aromat.

CH), 123.2, 126.2 (C_q), 131.9 (aromat. CH), 143.3, 151.5, 153.0, 155.5 (C_q), 163.7, 164.4 (C_q, C=O). – C₁₈₄H₂₆₂O₂₉, calcd. C 68.17, H 6.41; found C 68.30, H 6.37. – MS (FD): *m/z* (%) = 1320.8 (100).

X-Ray structure determination

Crystal data and details of the data collection and data processing are listed in Table 2. The following computer software was used: Data collection: CRYSTALIS CCD Software [16], data reduction and absorption correction: CRYSTALIS RED Software [17, 18]. The structure was solved with Direct Methods using SIR-92 [19] and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed at calculated positions and refined as riding model together with the atoms to which they are attached. The acetone molecule within the crystal structure of **1** was refined assuming statistical disorder around a crystallographic center of symmetry. Thus, the atoms O22 and C76 were given occupation factors of 0.5, whereas C77 exhibits an occupation factor of 1.00. The atoms C23 and C71, respectively, were refined on two disordered positions (C23/C23A and C71/C71A, respectively) with occupation factors of C23/C23A = 0.64/0.36 and C71/C71A 0.73/0.63.

CCDC 626761 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.

Acknowledgement

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- [9] Nomenclature has been used as discussed in A. G. Pinkus, E. Y. Lin, *J. Mol. Struct.* **1975**, 24, 9. Thus, aryl

- groups attached to the carboxyl units are in *s-trans* position relative to each other.
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- [12] X-Ray and dilatometry data for derivative **1** with dodecyloxy chains (refs. [4] and [11]) in its columnar hexagonal phase at 35 °C have shown that the core diameter amounts to 24 Å if benzoate core and alkyl chains are fully nano-segregated. However, if a structure like in the crystal of **1** (*cp.* Fig. 3B) is assumed as starting point for a model, then the aliphatic chain length has to be simply increased to dodecyloxy chains and the distance between two cores has to be determined. The extended chains possess a length of 15.8 Å. If a propyl chain, *i. e.* 25 % of a dodecyl chain, penetrates the star-shaped core of 15.2 Å radius, then the distance between two phloroglucinol centers can be approximated by $2 \times 15.3 \text{ Å} + 15.8 \text{ Å} - 0.25 \times 15.8 \text{ Å} = 42.5 \text{ Å}$. This estimated value is in perfect agreement with the experimental value of 42.5 Å.
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