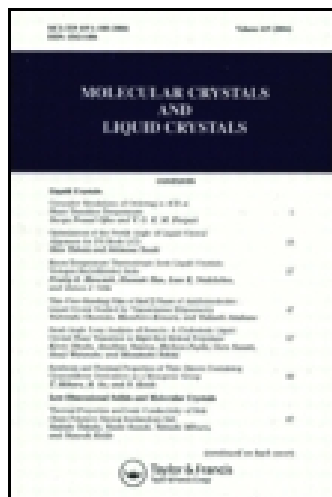




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New Star-shaped Mesogens with Three Different Arms on a 1,3,5-Benzene Core

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NEW STAR-SHAPED MESOGENS WITH THREE DIFFERENT ARMS ON A 1,3,5-BENZENE CORE

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The convergent synthesis of new symmetrical and non-symmetrical star-shaped mesogens based on a phloroglucinol core is presented. Molecules with three different arms were derived via esterification of various 4-benzoylbenzoic acid derivatives, substituted with polar groups and n alkoxy chains ($n = 1-3$), by using a combination of protecting group techniques and stoichiometric reactions. The thermotropic properties were investigated by differential scanning calorimetry, polarised optical microscopy and synchrotron X-ray diffraction. It is found that molecules with more than seven lateral chains form mesophases. The presence of strong polar groups ($-\text{NO}_2$) enlarges the temperature range of the liquid crystal phase. For all studied materials the diffractograms can be indexed according to a two-dimensional hexagonal lattice. The lattice parameters indicate that the flexible chains are interdigitated.

Keywords: columnar liquid crystal; dipolar interaction; non-symmetric mesogen; star-shaped molecule

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INTRODUCTION

The classical columnar phases are formed by planar aromatic mesogens, e.g. triphenylene, hexabenzocoronene, segregating from flexible chains, which are uniformly surrounding the rigid core. Such a supramolecular organisation can be also obtained by non-conventional multi-arm systems [1–3]. They may be built by linking three or more calamitic or non-mesogenic units to a central building block. Up to sixty-four mesogenic or promesogenic arms are attached in the case of starburst dendrimers, where the flexibility of the central dendritic scaffolds lead to self-assembly in lamellar, columnar or cubic phases, depending on the number of peripheral alkyl chains [4]. The simplest multi-arm mesogen is a structure containing three branches. Recently, thermotropic liquid crystal properties have been observed for various star-shaped, three-armed molecules with a 1,3,5-benzene core [2,6–14]. The supramolecular columnar arrangement was tuned by introduction of polar groups [10,11] and hydrogen bonds [12,13]. These molecules are non conventional discotic mesogens, where the single core can display cavities [6b]. In the condensed phase, molecules should assemble in uniformly space filling way. Consequently, the arms of the mesogens should deviate from coplanar stacking. In principle, space filling and specific interactions of star-shaped molecules, with attached polar groups at three different arms could lead to appearance of intra- or inter-columnar superstructures, e.g. staggered arrangement for anti-parallel dipoles, or helical displacement along the column. Theoretically, the equilibrium organisation of N polar molecules cannot be reliably predicted [15]. However, recent theoretical calculations envisage for discotic mesogens with transverse dipole moments potential application as biaxial switches [16].

In this contribution the synthesis of new star-shaped mesogens **1** (Chart 1) based on the phloroglucinol core is presented. Earlier publications reveal that direct attachment of alkyloxy substituted benzoic acid derivatives lead only to monotropic phase behaviour [14]. Elongation of

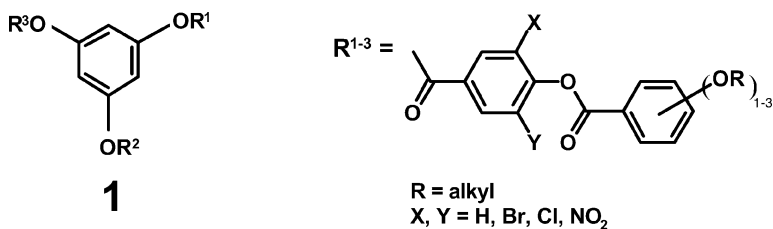


CHART 1 General structure of the star-shaped mesogens **1**.

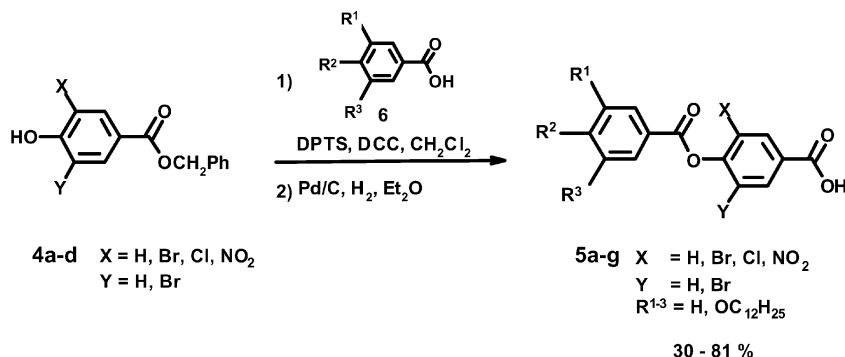
the arms could stabilise the supramolecular liquid crystal organisation. Derivatives of 4-benzoylbenzoic acid seem to be appropriate for this purpose, because peripheral alkoxy chains and internal polar substituents can be easily attached.

RESULTS AND DISCUSSION

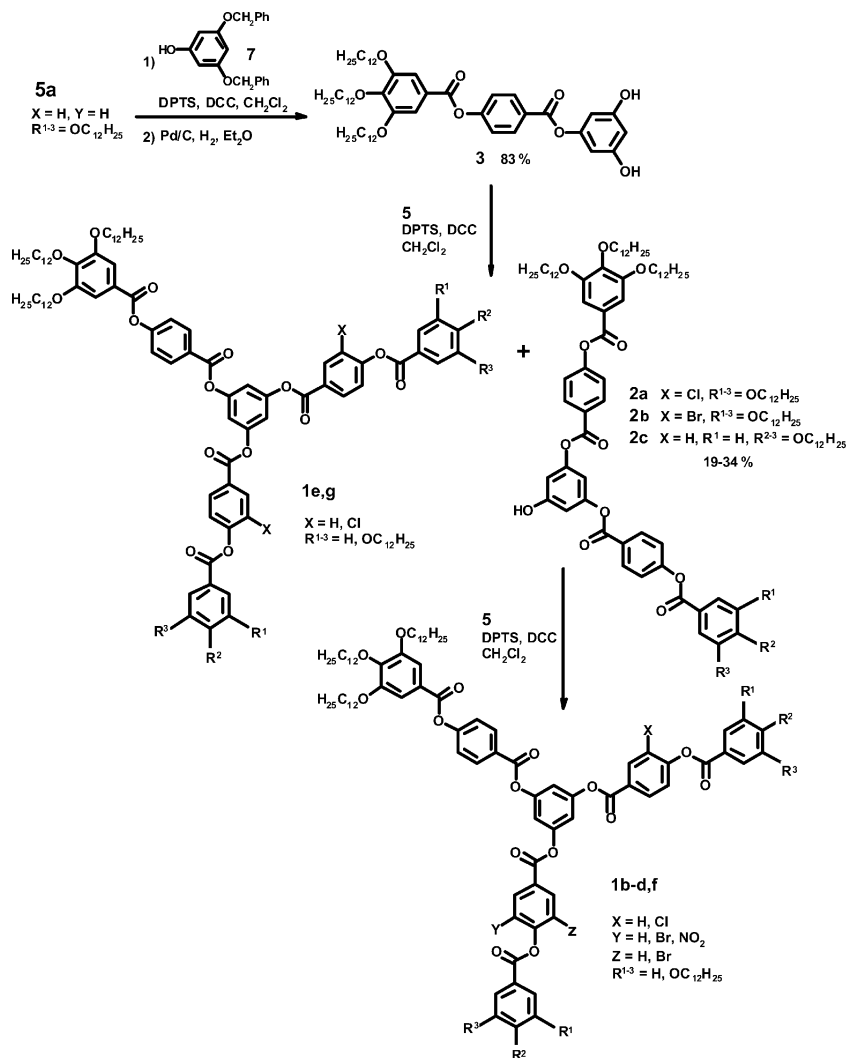
Synthesis

The synthesis was carried out following a convergent strategy outlined in Schemes 1 and 2. According to literature procedures, [17] the polycatenar arms **5a-g** were prepared by esterification of 4-hydroxy-(benzylbenzoate) derivatives **4a-g** [18] with benzoic acid building blocks bearing 1–3 peripheral dodecyloxy chains **6** and subsequent reductive cleavage of the protecting group (Scheme 1). The symmetrical star-shaped mesogen **1a** (Table I) were directly obtained by threefold coupling of arm **5a** (X, Y = H, R^{1–3} = C₁₂H₂₅) to the phloroglucinol core.

For the synthesis of non-symmetrical mesogens with three different arms, a combination of protecting group technique and stoichiometric reaction was chosen. In the first step, coupling of the arm **5a** (X, Y = H; R^{1–3} = OC₁₂H₂₅) to the twofold benzylether protected phloroglucinol **7** [19] and selective reductive cleavage gave the dihydroxy derivative **3**. Stoichiometric esterification of arms **5** with **3** resulted in up to 34% of **2** after exhaustive purification. As a side product, mesogens **1e,g** with twofold symmetry were isolated. In a final reaction a third different arm **5** were attached to form the target molecules **1b-d, f**. Yields of exhaustively purified materials **1** are given in Table I. The compounds **1** were characterised by ¹H and ¹³C NMR and elemental analysis [20].



SCHEME 1 Synthesis of various arms **5** with lateral dodecyloxy chains.



SCHEME 2 Synthesis of non-symmetrical star-shaped molecules **1**.

Thermotropic Properties

The thermotropic behaviour of the star-shaped molecules **1** was studied by means of differential scanning calorimetry (DSC), polarised optical microscopy (POM) and synchrotron X-ray diffraction (XRD). The DSC and POM results are collected in Table II. It is found that molecules with less than eight lateral dodecyloxy chains (**1b,g**) crystallise from the

TABLE I Yields of the Different Target Molecules **1** for the Final Reaction Step

Compound	n(R1)*	n(R2)*	n(R3)*	X	Y	Z	Yield [%]
1a	2	2	2	H	H	H	79
1b	1	2	0	H	H	H	46
1c	2	2	2	Br	Cl	H	84
1d	2	2	2	Cl	NO ₂	H	28
1e [#]	2	2	2	Cl	Cl	H	11
1f [§]	2	2	1	H	Br	Br	52
1g [#]	2	2	0	H	H	H	13

*n(R) = number of dodecyloxy chains (n = 0 i.e. R = H).

[§]Three chains at the dibromo substituted arm.[#]Side product obtained by the synthesis of **2**.

isotropic liquid and are not forming mesophases. All other molecules with eight and nine lateral chains organise in enantiotropic liquid crystal phases **M**. Most of them, i.e. **1c-f**, solidify into the glassy state close to room temperature. At lower temperatures an additional broad peak is observed, which can be probably attributed to partial crystallisation of the alkyl chains. The LC phase of the mesogen with the largest expected dipole moment owing to the nitro group, **1d**, is considerably more stable than the symmetrical non-substituted molecule **1a**. Halogen substituents do not seem to have a significant influence on the mesophase stability.

POM of **1a** and **1d** (Figs. 1 and 2) reveal a pseudo-focal-conic texture with homeotropic domains. These textures are frequently found for hexagonal columnar structures [21]. Homeotropic aligned domains are evidence for a uniaxial phase.

TABLE II Phase Transitions Determined by DSC and POM

Compound	DSC results of the second heating, rate 10°C/min (Onset [°C]/ΔH [kJ/mol])
1a	Cr – 25.9/21.5 M 50.7/3.3 I
1b	Cr 43.7/16.7 I
1c	g ₁ – 26.6/20.2 g ₂ 23.4 (T _g) M 50.3/3.6 I
1d	g ₁ – 35.6/32.6 g ₂ 29.4 (T _g) M 77.8/3.6 I
1e	g ₁ – 27.0/19.4 g ₂ 20.0 (T _g) M 41.2/3.7 I
1f	g 29.7 (T _g) M 44.6/3.6 I
1g	Cr 53.7/28.6 I

Cr crystal, **g** glassy phase, **M** mesophase, **I** isotropic liquid.

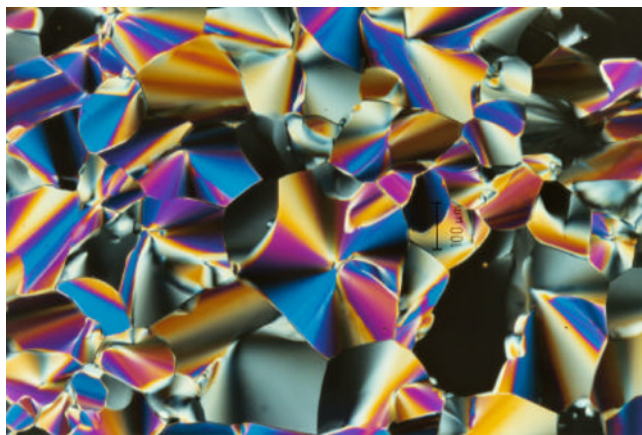


FIGURE 1 Pseudo-focal-conic texture of **1a** upon cooling between crossed polarisers at 47°C with homeotropic domains. (See COLOR PLATE XII)

Star-shaped molecules **1** are not typical discotic mesogens, since the three arms cannot fill the space belonging to the core region. They should rather be regarded as link between discotic and phasimidic compounds. Previous studies on mesogens with a phloroglucinol core, revealed only columnar and nematic mesomorphism [14]. In principle, smectic phases could also be formed as shown in Figure. 3. Alternately directing two or one arms to one side of the layer, molecules can form a smectic-like

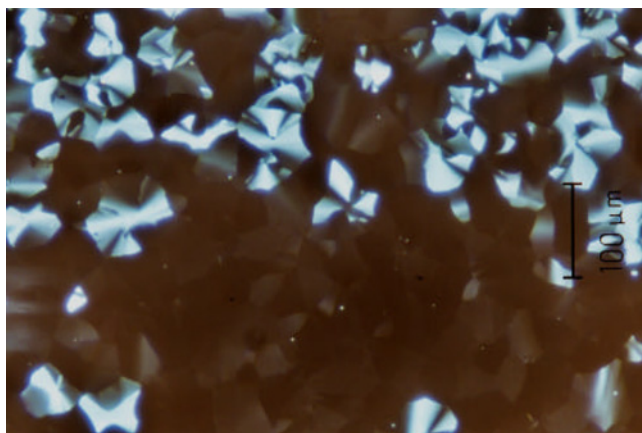


FIGURE 2 Pseudo-focal-conic texture of **1d** upon cooling between crossed polarisers at ambient temperature with homeotropic domains. (See COLOR PLATE XIII)

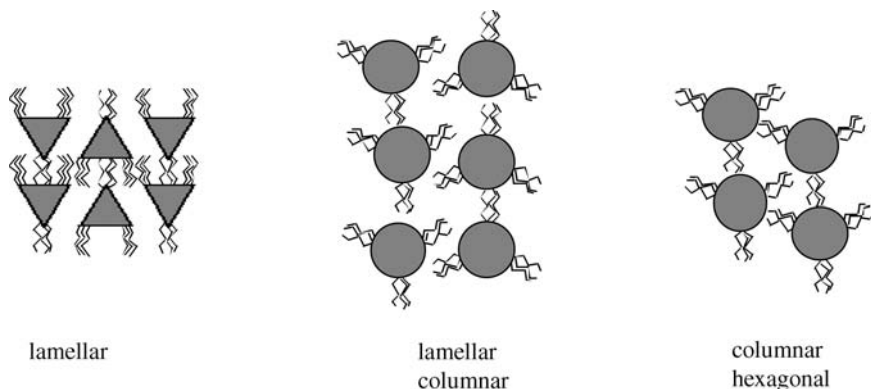


FIGURE 3 Model of possible mesophases: lamellar, lamellar columnar and hexagonal columnar phases.

arrangement, but no homeotropic alignment would be expected in this case. Homeotropic alignment can be achieved if the molecules assemble in columns which may then arrange in a lamellar or hexagonal superstructure.

The mesophase structures of compounds **1a,c,d,e** were studied by X-ray diffraction. The measurements were performed on the X33 camera of the European Molecular Biology Laboratory at the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY), Hamburg using two linear position sensitive detectors connected in series [22,23]. The X-ray diffraction pattern of the star-shaped mesogen **1d** (Fig. 4) shows a set of three reflections in the small angle region with reciprocal spacings in the ratio $1 : \sqrt{3} : 2$. These peaks are assigned to the (10), (11), (20) reflections of a hexagonal columnar mesophase. In the wide-angle region (Inlet, Fig. 4), X-ray diffraction data displays an amorphous halo reflecting the mean distance between the aliphatic side chains (0.43 nm). Superimposed on the small-angle region an additional halo is observed and could originate from a superstructure along the column. This has to be proven by recording two-dimensional X-ray scattering patterns from oriented samples. All other molecules **1a,c,e** yield analogous diffraction patterns.

Calculated cell parameters a for the Col_{hd} phases ($a = d_{10} \neq \sin 60^\circ$) vary from 4.16 nm (**1e**), 4.23 nm (**1b**), 4.25 nm (**1a**) up to 4.32 nm for **1d**. All cell parameters are significantly smaller than the molecular diameter, derived from a model with all *trans* configuration of the peripheral chains. The radius of the semi-flexible core were estimated to $r_{\text{core}} = 1.52$ nm, which is the distance between the centre of the molecule and the peripheral oxygen in *para* position, connecting an aliphatic side chain. The length of the alkyl chain in all *trans* configuration is calculated by

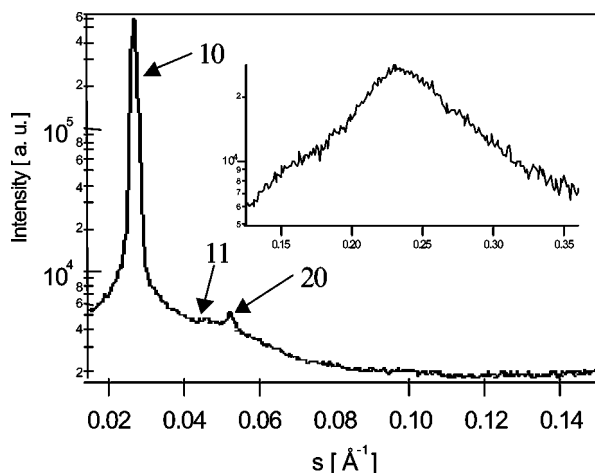


FIGURE 4 SAXS and WAXS X-ray diffractograms of **1d** recorded simultaneously with two position sensitive detectors connected in series, $\lambda = 0.154$ nm.

the formula $r_{\text{chain}} = (0.189 + 0.1265 \times n)$ nm given in reference [24], where n is the number of carbon atoms and thus, $r_{\text{chain}} (\text{C}_{12}\text{H}_{25}) = 1.707$ nm. The diameter of the molecule is consequently $d_{\text{molecule}} = 2(r_{\text{core}} + r_{\text{chain}})$ 6.45 nm. If the flexibility of the lateral chains is taken into account the diameter diminishes to $d_{\text{flex}} = 5.54$ nm. This value is still larger than the experimental measured columnar distances. Consequently, a model with interdigitated chains is proposed. On the basis of fully interdigitated flexible chains, a minimum value $d_{\text{column}} = 4.28$ nm for columns can be estimated, which is closer to experimental values (4.16–4.32 nm). Note that the distances vary within the series of different mesogens. The largest intercolumnar distance is found for the molecule with the largest estimated dipole, thus suggesting repulsive dipolar interactions between neighbouring columns. On the other hand, molecule **1d** shows the highest mesophase stability, thus attractive intracolumnar dipole interactions should be present. This can be explained by the semi-flexibility of the benzoylester core. Various conformations can be adapted by rotation about the C-O single bonds. Thus molecules can possess not only a transversal but also an axial dipole moment.

CONCLUSIONS

New star-shaped molecules **1** were synthesised with up to three different arms, bearing various polar groups on the central benzoyl ring and one

to three dodecyloxy chains on the peripheral benzoyl unit. Mesogens with more than seven flexible chains form mesophases. The columnar hexagonal LC phases are stabilised by dipolar interactions and interdigitation of the lateral chains. The largest unit cell parameter is found for the molecule with the largest dipole indicating the existence of repulsive dipolar interaction between neighbouring columns. Moreover, a diffuse halo observed in the small-angle region could be related to superstructure along the columns.

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- 1a** and **1c**. Analytical data for **1a**: ^1H NMR (300 MHz, CDCl_3) δ = 0.92 (m, 27H, CH_3), 1.26–1.55 (m, 162H, CH_2), 1.81 (m, 18H, CH_2), 4.06, 4.08 (2t, 18H, OCH_2), 7.20 (s, 3H, ArH), 7.42 (s, 6H, ArH), 7.37, 8.35 (AA'BB', 12H, ArH). ^{13}C NMR (75 MHz, CDCl_3) δ = 14.0, 22.6, 26.0, 26.8, 29.2, 29.3, 29.5, 29.6, 30.3, 31.8, 69.2, 73.5 (CH_3 , CH_2 , OCH_2), 108.6, 113.5, 122.2, 123.2, 126.4, 132.8, 143.3, 151.4, 152.9, 155.5, 163.6, 164.3 (C_{aromat} , C=O). EA ($\text{C}_{156}\text{H}_{246}\text{O}_{21}$) calculated %C 76.24, %H 10.09, found %C 76.12, %H 10.03.
- Analytical data for **1c**: ^1H NMR (300 MHz, CDCl_3) δ = 0.92 (m, 27H, CH_3), 1.26–1.55 (m, 162H, CH_2), 1.81 (m, 18H, CH_2), 4.06, 4.08 (2t, 18H, OCH_2), 7.21 (3H, ArH), 7.36–7.48 (10H, ArH), 8.18 (dd, ^3J = 8.6 Hz, ^4J = 2 Hz, 1H, ArH), 8.22 (dd, ^3J = 8.6 Hz, ^4J = 2 Hz, 1H, ArH), 8.29 (AA'BB', 2H, ArH), 8.35, 8.51 (2d, ^4J = 2 Hz, 2H, ArH). ^{13}C NMR (75 MHz, CDCl_3) δ = 14.1, 22.7, 26.1, 26.8, 29.3, 29.4, 29.5, 29.6, 30.4, 31.9, 69.3, 73.6 (CH_3 , CH_2 , OCH_2), 108.7, 108.8, 113.0, 113.5, 122.3, 124.2, 124.3, 129.9, 130.6, 131.9, 132.4, 135.4 ($\text{tert-C}_{\text{aromat}}$), 116.9, 122.5, 122.6, 123.2, 126.4, 127.8, 128.0, 130.9, 143.4, 143.6, 151.3, 151.6, 153.1, 155.6, 162.6, 163.5, 164.4 ($\text{quat-C}_{\text{aromat}}$, C=O). EA ($\text{C}_{156}\text{H}_{244}\text{BrClO}_{21}$) calculated %C 72.88, %H 9.57, found %C 73.17, %H 9.34.
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