Synthesis and mesomorphic properties of unsymmetrical banana-shaped 1,3-dihydroxybenzene esters

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Synthesis and mesomorphic properties of unsymmetrical banana-shaped 1,3-dihydroxybenzene esters

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The novel asymmetrical banana-shaped compounds – esters of 1,3-dihydroxybenzene and 4-substituted benzoic acids – have been synthesised. Dependent on the length of the molecular branches either B_2 or B_1 phase has been observed. The introduction of the polar substituent at one of the lateral fragments destabilises the mesomorphic properties.

Keywords: synthesis; 1,3-dihydroxybenzene esters; unsymmetrical banana-shaped mesogenes

1. Introduction

One of the main goals in liquid crystal (LC) chemistry is to find the connection between a chemical structure and the mesophase type. The main molecular factors determining the mesomorphism are the shape of the mesogenic core [1], the anisotropy of the core [2] and the flexibility of the molecular structure [3].

The larger the molecular structure, the greater the possibility for its modification. Unfortunately, however, large molecules often have high clearing temperatures, which makes their processing difficult. It is general knowledge that phase transition temperatures can be lowered by introducing some asymmetry into the molecular structure. This method was successfully applied to obtain low melting 'bent-core' materials [4] – a new class of liquid crystal materials able to form polar phases [5]. In previous work [6] we have synthesised the derivatives of 2,7-dihydroxynaphtalene bent-core molecules containing the bromine atom in the lateral fragments. It was shown that the homologues with terminal substituents containing up to 10 carbon atoms give the nematic phase; the elongation of the alkyl chain then leads to the disappearance of this nematic phase and the appearance of the smectic mesophase typical for bent-core materials.

Here we present studies of the asymmetrically substituted banana-shaped 1,3-hydroxybenzene esters. Synthesised bent-shaped molecules have mesomorphic properties similar to that observed for 3-aminophenol and 3-hydroxybenzaldehyde derivatives, as described previously [7, 8].

The mesogenic derivatives of 3-hydroxybenzoic acid are well known to be thermally and chemically stable; thus they are widely studied [9–11] although their synthesis is many-stage and time consuming. Previously obtained asymmetric banana-shaped 1,3-hydroxybenzene esters, which differ by the number of carbon atoms in the terminal alkoxy groups [12], with the presence in one molecular arm of a lateral substitute – a fluorine atom F – and a double bond as the linking group, have already been described [13]. We decided to study the influence of some other structural changes: (a) the introduction of a polar substituent at different fragments of the mesogenic core; (b) the replacement of the terminal alkoxy group in one of the fragments by an alkyl group; (c) the introduction of a different number of aromatic cycles into a 'molecular branch'. The influence of these modifications is now described.

2. Experimental

2.1 Physical investigations

The chemical structure of 5–10% solutions of all compounds was confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy using a Varian VXR-300 spectroscope with working frequency 300 MHz with the internal standard being tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Specord IR-75 spectrophotometer in $CHCl_3$ solution. The purity of the compound was controlled by thin-layer chromatography (TLC), commercial brand plate (PTSC-AF-V-UF 'Sorbfil'), with the following developing in UV light. All the compounds were purified by column chromatography (Al_2O_3 L 5/40, eluent: chloroform–methanol, 5:1). The phase transition temperature was studied by polarised light microscopy (POLAM R-312 microscope) and a calorimetric method (Perkin Elmer DSC7 calorimeter). The X-ray diffraction was performed in reflection mode for one surface free sample using the Bruker GAADS system. Dielectric response

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was measured using a Solartron impedance analyser for the 5 μm thick cells with gold electrodes.

2.2 Synthesis

The synthesis of resorcinol esters containing bromine atoms in the aromatic cycles of the lateral branch (compounds **9a,b**) was carried out under Scheme 1. The synthesis of the asymmetrical banana-shaped resorcinol esters with an aromatic cycle in one of the lateral fragments (compounds **17a**) or the alkyl terminal group (compound **17c**), and also the symmetric compound **17b** containing a tree aromatic ring in each of the lateral branches, is illustrated in Scheme 2.

For synthesis of novel asymmetrical bent-shaped compounds, the 3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenol **8** procedure described by Murthy and Sadashiva [11] was applied. The preparation procedure of 3-bromo-4-hydroxybenzoic acid **2** and 4-(4-dodecyloxybenzoyloxy)-3-bromobenzoic acid **7** are described by Maksimenko *et al.* [14].

The 3-bromo-4-hexadecyloxybenzoic acid **3a** was obtained by alkylation of the hydroxyl group of 3-bromo-4-hydroxybenzoic acid by 1-hexadecylbromine [15]. Then 3-bromo-4-hexadecyloxybenzoyl chloride **4a** was prepared by interaction of acid **3a** with thionyl chloride according to the procedure described by Weygand and Hilgetag [16] and this compound was used in the following reactions

a) X = Br, Y = H; n = 12
б) X = H, Y = Br; n = 16
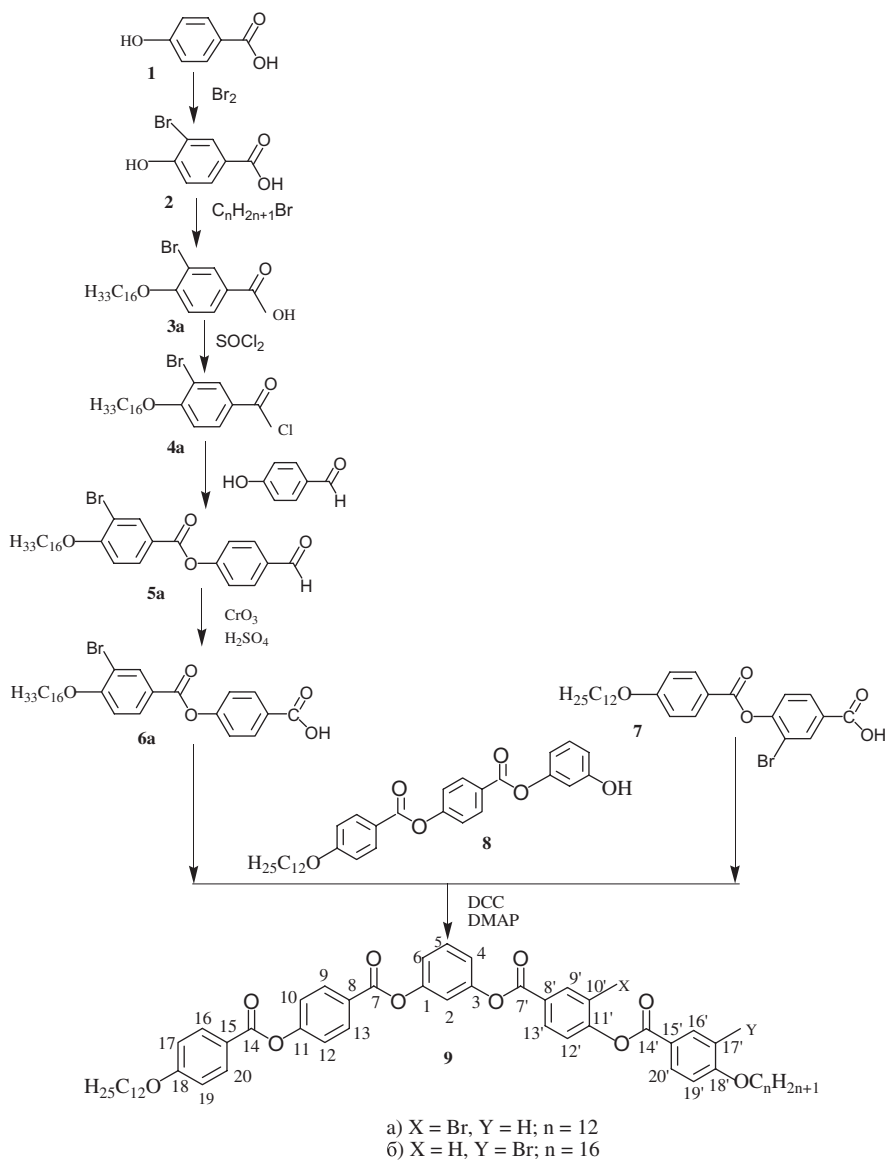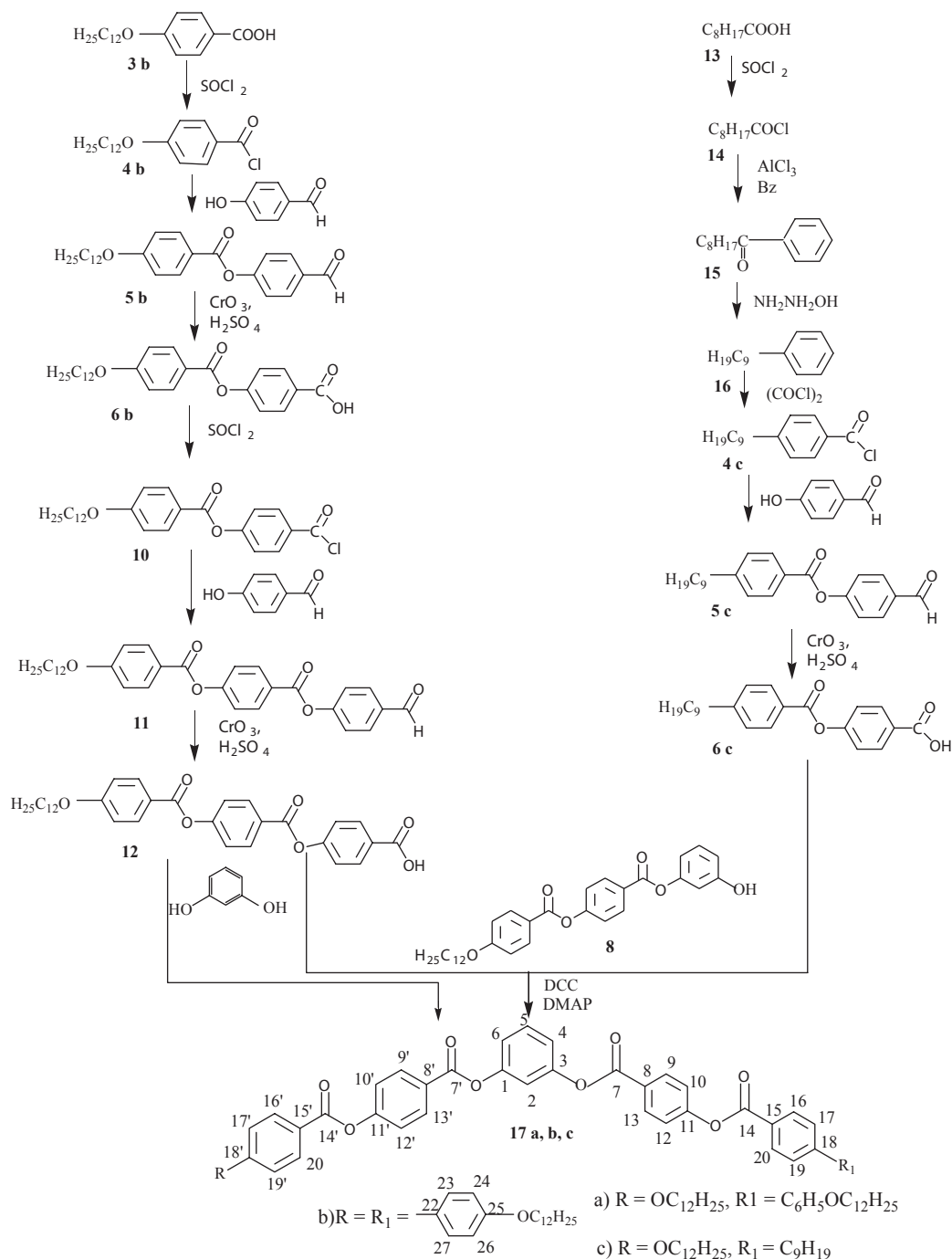
Scheme 1.

Scheme 2.

without additional purification. The acylation of 4-hydroxybenzaldehyde by chloride **4a** in dry pyridine at 0°C leads to 4-(3-bromo-4-hexadecyloxybenzoyloxy)benzaldehyde **5a** (Scheme 1) [17].

The corresponding chloride (14) **4b** was obtained by interaction of *n*-dodecyloxybenzoic acids **3b** with thionyl chloride [16]. This chloride was then used in the reaction of the acylation of 4-hydroxybenzaldehyde in conditions

analogous to the synthesis of aldehyde **5a**, for preparation of 4-*n*-dodecyloxybenzoylbenzaldehyde **5b**. The procedure for the synthesis of nonylbenzoylchloride **4c** (see Scheme 2) is given by Galatina and Novikova [18]. The synthesis of 4-(4-*n*-nonylbenzoyloxy)benzaldehyde **5c** is given in Scheme 2; it forms the nematic phase at a temperature range 34.6–40.7°C. 4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]benzaldehyde **11**

was synthesised according to procedure described by Kondrat'eva and Novikova [19].

The oxidation of the aldehydes **5a–c** and **11** to the corresponding acids **6a–c** and **12** that followed was carried out by the Jones reagent in acetone [20] (Scheme 2).

The structure of **6a,c** and **12** compounds was confirmed by element analysis and proved by ^{1}H NMR spectroscopy. Note that, in the ^{1}H NMR spectra of 4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzoic acids **12**, all three protons signals at the o-position of the aromatic cycles according to the carbonyl group are observed as doublets in the range 7.92–8.35 ppm. The unsymmetrical 1,3-dihydroxybenzene esters **9a,b** (Scheme 1) and **17a,c** (Scheme 2) were obtained by interaction of synthesised acids **6a,c,7,12** with 3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenol **8** with *N,N'*-dicyclohexylcarbodiimide. For comparison with the unsymmetrical analogue **17a** the symmetrical ester **17b** which contains three benzoic rings in the lateral branches (Scheme 2) was obtained by interaction of 4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-benzoic acids **12** with 1.3-dihydroxybenzene after a carbodiimide procedure. Their structures were confirmed by ^{1}H NMR spectroscopy. The appearance of the triplet signals of the methylene group protons connected with the aromatic cycle at 2.71 ppm is a peculiarity of the ^{1}H NMR spectra of compound **17c**.

4-Substituted benzaldehydes (5a,b, 11) – the general procedure. A solution of the chloride of the acid **4a,b,10** (9 mmol) in dry benzene (10 ml) was added dropwise to a solution of 4-hydroxybenzaldehyde (10 mmol) in dry pyridine (10 ml) with cooling with an ice bath. The cooling was then stopped and the reaction mixture was stirred for 20 h at room temperature. 100 g of ice was then added. The remaining white residue was filtered and washed out many times with water with following recrystallisation from ethanol.

4-(4-Nonylbenzoyloxy)benzaldehyde (5c). Yield 52%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (3H, CH$_3$, $J = 6.81$), 1.25–1.44 m (10H, CH$_2$), 1.55–1.72 m (4H, CH$_2$CH$_2$Ar), 2,71 t (2H, CH$_2$Ar, $J = 6.54$), 6.98 d (2H, Ar, $J = 8.74$), 7.34 d (2H, ArCOH, $J = 7.74$), 7.98 d (2H, ArCOH, $J = 8.40$), 8.12 d (2H, Ar, $J = 9.02$),10.03 s (1H, COH). Elemental analysis: C$_{23}$H$_{28}$O$_3$ requires C 71.37, H 8.01; found: C 71.45, H 7.98%. Cr 34.6°C N 40.7°C Iso.

4-Substituted benzoic acids (6a,c, 12) – the general procedure. To a solution of aldehyde **5a,c,11** (7.9 mmol) in 100ml of dry acetone at cooling a Jones reagent (20 ml) [20] was added. The reaction mixture was stirred at room temperature for 4 h. Then the mixture was added to water with ice. The precipitate was filtered off and washed with water to pH 7, dried and then recrystallised from ethanol.

4-(3-Bromo-4-*n*-hexadecyloxybenzoyloxy)benzoic acid (6a). Yield 61%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (3H, CH$_3$, $J = 6.23$), 1.24–1.6 m (26H, CH$_2$), 1.82–1.96 m (2H, CH$_2$CH$_2$O), 4,13 t (2H, CH$_2$O, $J = 6.54$), 6.97 d (1H, ArBr, $J = 9.03$), 7.34 d (2H, Ar, $J = 8.71$), 8.13, 8.10 dd (1H, ArBr, $^3J = 8.72$, $^4J = 2.18$), 8.20 d (2H, Ar, $J = 8.72$), 8.39 d (1H, ArBr, $J = 2.17$). Elemental analysis: C$_{30}$H$_{41}$BrO$_5$ requires C 64.17, H 7.36, Br 14.23; found: C 64.16, H 7.30, Br 14.50%.

4-(4-Nonylbenzoyloxy)benzoic acid (6c). Yield 52%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (3H, CH$_3$, $J = 6.81$), 1.75–1.90 m (2H, CH$_2$CH$_2$Ar), 1.20–1.55 m (12H, CH$_2$), 2,71 t (2H, CH$_2$Ar, $J = 6.54$), 6.98 d (1H, Ar, $J = 8.73$), 7.34 d (2H, ArCOOH, $J = 7.75$), 8.1–8.3 m (2H, Ar + 2H, ArCOOH). Elemental analysis: C$_{24}$H$_{28}$O$_5$ requires C 72.70, H 7.12; found: C 72.88, H 7.41%.

4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy] benzoic acid (12). Yield 77%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (3H, CH$_3$, $J = 7.16$), 1.20–1.53 m (24H, CH$_2$), 1.76–1.90 m (2H, CH$_2$CH$_2$O), 4,06 t (2H, CH$_2$O, $J = 6.53$), 7.00 d (2H, ArAlkO, $J = 9.03$), 7.34–7.47 m (2H, Ar, 2H, ArCOOH), 8.00 d (2H, ArAlkO, $J = 8.40$), 8.15 d (2H, Ar, $J = 8.71$), 8.28 d (2H, ArCOOH, $J = 8.71$). Elemental analysis: C$_{34}$H$_{38}$O$_7$ requires C 73.10, H 6.86; found: C 73.30, H 6.87%.

Unsymmetrical banana-shaped 1,3-dihydroxybenzene esters (9a,b, 17a,c) - the general procedure. To a solution of the corresponding acids **6a,d**, **7**, **12a,b** (1,8 mmol) and 3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy] phenol (2.0 mmol) in 20 ml of dry chloroform was added 4-dimethylaminopyridine (DMAP) (0.18 mmol) with stirring. The mixture was stirred for 10 min. To this *N,N'*-dicyclohexylcarbodiimide (DCC) (1.8 mmol) was added and the reaction mixture was stirred at room temperature for 10 h. The precipitate was filtered off and washed with chloroform. The solvent was removed under reduced pressure. The obtained product was crystallised twice from a mixture of ethanol and benzene (10:1) and then purified by column chromatography.

4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-dodecyloxybenzoyloxy)-3-bromobenzoyl-oxy] benzene (9a). Yield 61%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.88 t (6H, CH$_3$, $J = 6.85$), 1.2–1.5 m (36H, CH$_2$), 1.77–1.91 m (4H, CH$_2$CH$_2$O), 4,05 t (4H, CH$_2$O, $J = 6.85$), 6.96–7.05 m (4H, H-17,19,17',19v), 7.16–7.24 m (3H, H-2,4,6), 7.38 d (2H, H-10,12, $J = 8.71$), 7.43–7.46 m (2H, H-5, 12'), 8.13–8.24 m (5H, H-13', 16, 20, 16', 20'), 8.28 d (2H, H-9,13, $J = 8.71$), 8.50 d (1H, H-9', $J = 2.18$). Elemental analysis: C$_{58}$H$_{69}$BrO$_{10}$ requires C 69.24, H 6.91, Br 7.94; found: C 69.07, H 7.18, Br 7.96%.

1-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-hexadecyloxy-3-bromobenzoyl-oxy)benzoyloxy]benzene (9b). Yield 44%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):

0.88 t (6H, CH$_3$, $J = 6.85$), 1.19–1.53 m (44H, CH$_2$), 1.77–1.95 m (4H, CH$_2$CH$_2$O), 4,06 t (2H, CH$_2$OAr, $J = 6.85$), 4,13 t (2H, CH$_2$OArBr, $J = 6.54$), 6.96–7.05 m (3H, H-17,19,19′), 7.16–7.24 m (3H, H-2,4,6), 7.38 d (4H, H-10,12, 10′,12′, $J = 8.71$), 7.50 t (1H, H-5, $J = 6.85$), 8.12–8.20 m (3H, H-, 16, 20, 16′, 20′), 8.25–8.34 m (4H, H-9,13, 9′, 13′), 8.50 d (1H, H-16′, $J = 2.18$). Elemental analysis: C$_{62}$H$_{77}$BrO$_{10}$ requires C 70.11, H 7.31, Br 7.5; found: C 70.36, H 7.26, Br 7.69%.

1-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-3-{4-[4-(4-dodecyloxybenzoyloxy)-benzoyloxy] benzoyloxy}benzene (17a). Yield 56%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (6H, CH$_3$, $J = 6.85$), 1.20–1.53 m (36H, CH$_2$), 1.77–1.92 m (4H, CH$_2$CH$_2$O), 4,06 t (4H, CH$_2$O, $J = 6.54$), 6.95–7.04 m (4H, H-17,19,24,26), 7.16–7.24 m (3H, H-2,4,6), 7.35–7.44 m (6H, H-10,12, 10′,12′, 17′,19′), 7.50 t (1H, H-5, $J = 6.85$), 8.16 d (4H, H-, 16′, 20′, 23,27, $J = 8.40$), 8.26–8.35 m (6H, H-9,13, 9′, 13′, 16,20). Elemental analysis: C$_{65}$H$_{74}$O$_{12}$ requires C 74.54, H 7.12; found: C 74.69, H 7.32%.

1,3-bis{4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]benzoyloxy} benzene (17 b). The mixture of 4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy] benzoic acid (**12**), (0.92 mmol), 1.3-dihydroxybenzene (0. 46 mmol), 4-dimethylaminopyridine (0.092 mmol), in 10 cm^3 dry chloroform was stirred for 10 min. To this reaction mixture N,N'-dicyclohexylcarbodiimide (0.92 mmol) was added and the reaction mixture was stirred at room temperature for 10 h. The precipitate was filtered off and washed with chloroform (10 cm^3). The solvent was removed under reduced pressure. The obtained residue was crystallised from a mixture of ethanol and benzene (3:1) and then purified by column chromatography.

Yield 50%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (6H, CH$_3$, $J = 7.16$), 1.23–1.50 m (36H, CH$_2$), 1.77–1.88 m (4H, CH$_2$CH$_2$O), 4,06 t (4H, CH$_2$O, $J = 6.54$), 6.99 d (2H, H-24, 26, $J = 9.03$), 7.18–7.27 m (3H, H-2,4,6), 7.38–7.44 m (8H, H-10,12,17,19), 7.50 t (1H, H-5, $J = 6.85$), 8.16 d (4H, H-23,27, $J = 9.03$), 8.28–8.35 m (8H, H-9,13, 16,20). Elemental analysis: C$_{80}$H$_{94}$O$_{14}$ requires C 75.33, H 7.11: found: C 75.40, H 6.99%.

1-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-nonylbenzoyloxy)benzoyloxy]benzene (17c). Yield 40%. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 0.89 t (6H, CH$_3$, $J = 6.22$), 1.20–1.55 m (24H, CH$_2$), 1.77–1.90 m (4H, CH$_2$CH$_2$O), 4,05 t (4H, CH$_2$O, $J = 6.85$), 6.99 d (4H, H-17,19, 17′,19′, $J = 9.02$), 7.16–7.23 m (3H, H-2,4,6), 7.34–7.42 m (4H, H-10,12, 10′,12′), 7.50 t (1H, H-5, $J = 6.85$), 8.15 d (4H, H-, 16,20, 16′, 20′, $J = 8.71$), 8.26–8.35 m (4H, H-9,13, 9′, 13′). Elemental analysis: C$_{55}$H$_{64}$O$_9$ requires C 76.01, H 7.42; found: C 75.90, H 7.55%.

2.3 Results

The synthesised acid intermediates with two (**6b**, **6c**) and three (**12**) phenyl rings in the mesogenic core show a smectic phase. For an acid derivative with the dodecyloxy end group (**6b**) an additional nematic mesophase is observed above the smectic A phase (Table 1). High clearing temperatures for these compounds, ~200°C, signified strong intermolecular interactions due to the hydrogen bonding between acid groups. However, X-ray studies show that the layer spacing ($d \sim 36$ Å for **12**) is close to that of the monolayer smectic phase; it corresponds to the length of a single molecule ($L \sim 35$ Å for **12**). Thus, although intermolecular hydrogen bonds are strong in the studied material, they do not cause breaking of the up–down distribution of the molecules in the smectic layer, apparently the hydrogen bonded 'heads' do not form a distinguishable sublayer. Also bromine substituted acid **6a** forms a monolayer smectic C phase with ~20 degree lower clearing point than the non-substituted analogue compounds **6c** and **6b**. Slightly modified bromine substituted 4(4-hexadecyloxybenzoyloxy)3-bromobenzoic acid **7** [6], in which the bromine atom is moved to the phenyl ring closer to the acid group, exhibits a nematic phase with clearing temperature a few degrees lower than for compound **6a**. The compounds that do not form hydrogen bonds between end molecular groups are either not mesogenic (**5a**) or mesogenic with much low clearing points (**5b**).

The final product (see Table 2), bent-core compound **17c**, in which slight asymmetry of the molecular structure was introduced by differentiating the length of end alkyl chains, forms a mesophase of modification SmC$_S$P$_A$ with antiferroelectric properties. A synclinic tilt structure in the neighbouring layers is consistent with the stripe texture observed for the planar sample while the antiferroelectric properties are confirmed by low dielectric response with high relaxation frequency mode, which is typical for the phase with compensated spontaneous polarisation (Figure 1).

Table 1. Phase transition temperatures (in °C) of four substituted benzoyloxybenzoic acids – materials **5b**, **6a–c**, **12** and **7**.

Compound	Cr		SmA		SmC		N		Iso
5a	•	105	–		–		–		•
5b	•	55.8	•	95.4	–		•	114.4	•
6a	•	135.3	–		•	181.7	–		•
6b	•	130.0	•	202.0	–		•	218.0	•
6c	•	155.7	–		•	199.2	–		•
7[6]	•	129.3	–		–		•	176.4	•
12	•	169.8	–		•	>250	–		•

Cr – solid crystal; SmA – smectic A mesophase; SmC – smectic C mesophase; N – nematic mesophase; Iso – isotropic liquid; '–' – absence of a mesophase; '•' – presence of a mesophase.

Table 2. Phase transition temperatures (in °C) and enthalpies (in J g^{-1}) in parentheses of the unsymmetrical banana-shaped 1,3-dihydroxybenzene esters, materials **9a,b**, **17a,c**, and the symmetrical ester **17b**.

Compound	Cr		B$_1$	B$_2$		Iso
9a	●	110.6 (58.3)	–	–	–	●
9b	●	116.0 (20.3)	–	–	–	●
17a	●	121.0 (0.5)	–	●	153.0 (18.9)	●
17b	●	104.1 (30.03)	●	–	208.1 (17.4)	●
17c	●	69.0 (9.7)	–	●	110.0 (17.4)	●

Cr – state for solid crystal; B$_1$ – columnar broke layer type mesophase; B$_2$ – SmCP$_A$ mesophase; Iso – isotropic liquid; '–' – absence of a mesophase; '●' – presence of a mesophase.
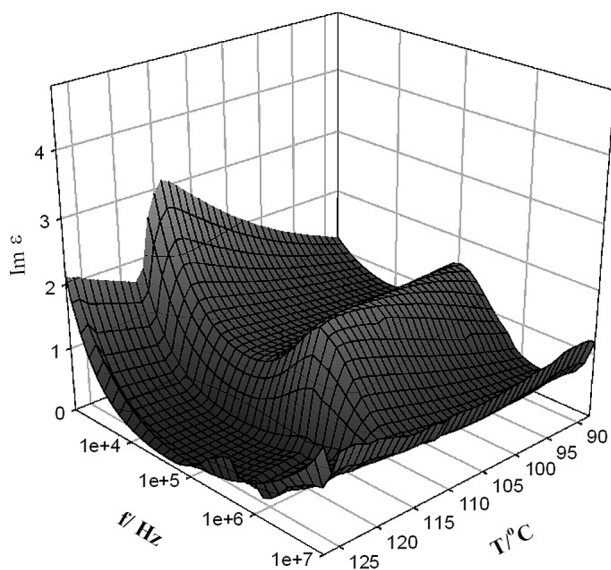

Figure 1. Temperature– frequency plot of the imaginary part of the dielectric constant for compound **17c**.
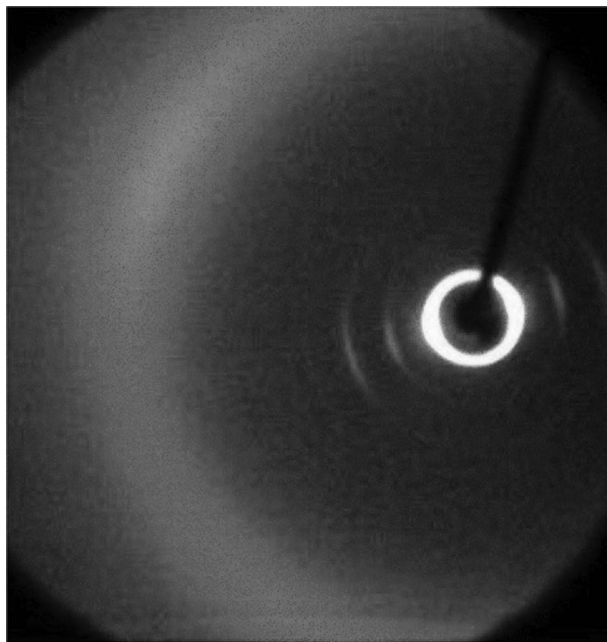

Figure 2. The X-ray diffraction pattern obtained for compound **17a** at 150°C in the B$_2$ phase. The position of the high angle diffused signal (corresponding to 4.5 Å) is inclined by about 45 degrees from the laser normal defined by the position of the low angle signals.

For compound **17c** the calculated tilt, obtained by comparing the layer spacing and molecular length, is about 40 degrees. The high tilt is consistent with the X-ray pattern obtained for the aligned sample of material **17c**, in which the maximum intensity for the high angle signal, reflecting the order of the molecules inside the layer, is inclined by about 45 degrees with respect to the layer normal defined by the position of the low angle signals (Figure 2).

The bent-core material **17a** with larger asymmetry obtained by differentiating the number of phenyl rings in the banana branches, in which the molecule has two and three phenyl rings in the arms, also shows the SmC$_S$P$_A$ phase but has considerably higher clearing

temperature. For comparison, the long branched symmetric molecule **17b**, with three phenyl rings in each molecular arm and dodecyloxy terminal chains, forms a columnar B$_1$-type phase. This phase is made from smectic layer fragments arranged into a body-centred rectangular lattice.

The columnar lattice parameters (a = 45.9 Å and b = 56 Å) are nearly temperature independent. In the X-ray pattern of the aligned sample (Figure 3) the position of the maximum intensity for the diffused high angle signal along the (10) direction suggests that molecules in the blocks are not tilted and oriented with their long axes along the crystallographic cell side b. The signal indexed as (02) corresponds to half of the molecular length. The size of the block cross section (related to half of the crystallographic unit side a) is small and the column cross section contains approximately five molecules arranged side by side. The texture of this phase (Figure 4), observed on cooling the isotropic phase, is characteristic of a columnar rather than a smectic-like structure, and such texture seems typical for the B$_1$ phase with a small size of the blocks [21]. The clearing point for compound **17b** is above 200°C, as expected for such a large symmetric molecule.

The bent-core compounds **9a** and **9b**, asymmetrically substituted with the bromine atom, independently of the bromine atom position, at the outer or inner phenyl rings in the arm, do not form mesophases. The
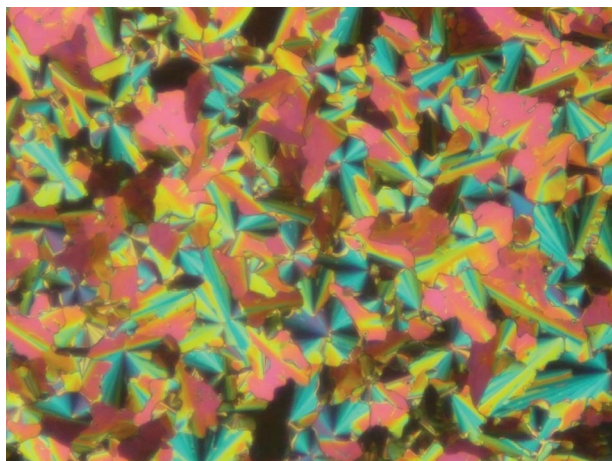
Figure 3. The X-ray diffraction pattern for the partially oriented sample of compound **17b** at 200°C in the B_1 columnar phase. The indexing of low angle signals (assuming a two-dimensional rectangular centred crystallographic unit cell) are given. Signals which do not match the indicated reciprocal lattice come from a different, slightly rotated domain. The diffused signal at large angle reflects the liquid-like order of the molecules inside the columns. The inset shows a schematic drawing of the crystallographic unit cell filled with layer fragments made of bent-core molecules.
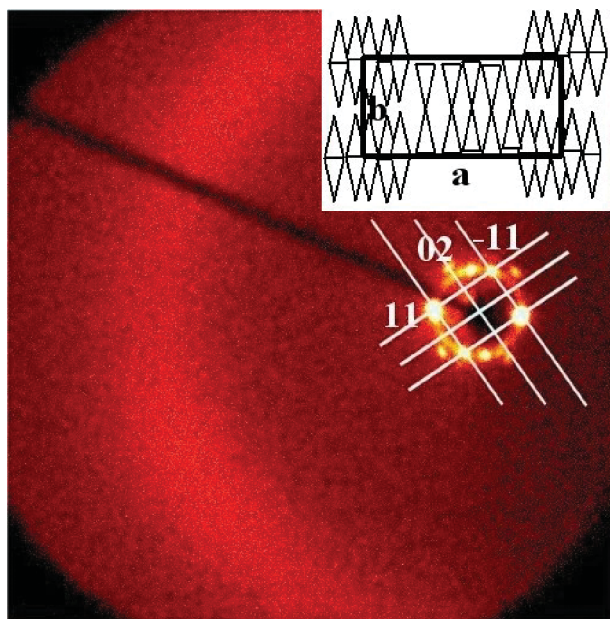

Figure 4. The optical texture of material **17b** in the B_1 columnar phase.

crystalline phase is clearly distinguished by its X-ray diffraction pattern with a large number of sharp signals also at high angles. Despite the crystal structure the phase texture reminds us of the B_4 phase; it has low birefringence sometimes with optically active domains that are spontaneously formed on cooling from the iso-tropic phase.

4. Conclusion

We have studied the mesomorphic behaviour of the banana-shaped 1,3-dihydroxybenzene ester derivatives and their acid precursors. The bent-core molecules with 'short arms' exhibit a lamellar structure, while the 'long arm' molecules have a tendency to break layers and form a columnar B_1 broken-layer type structure. Introduction of a large lateral substituent (the bromine atom) into one of the banana branches disturbs the formation of the liquid crystal and the material exhibits a direct crystal–isotropic phase transition. Interestingly, similarly to the B_4 phase, the crystal phase exhibits optically active domains.

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