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Properties of non-symmetric bent-core liquid crystals with variable flexible chain length

Michal Kohout^a, Martin Chambers^b, Aniko Vajda^c, Giancarlo Galli^d, Attila Domjan^e, Jiří Svoboda^a, Alexej Bubnov^f, Antal Jakli^b and Katalin Fodor-Csorba^{c*}

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New non-symmetrical bent-core mesogens with a variable flexible chain length have been synthesised. The compounds were derived from 3-hydroxybenzoic acid, which is the central unit of the molecules. The tails on both ends were connected by ester functionality, one tail contains a terminal double bond and the other is saturated. The compounds represent novel non-symmetric molecules both in their core and tails. The main features of differential scanning calorimetry, polarising optical microscopy, electro-optical and polarisation current measurements for all studied materials indicate a transition between a single tilted synclitic ferroelectric and an antiferroelectric smectic phase.

Keywords: bent-core liquid crystals; ferroelectric; antiferroelectric switching; non-symmetrical

1. Introduction

Initially the research into bent-core (BC) liquid crystals concentrated on the preparation and investigation of symmetrical BC molecules [1–4]. The mesomorphic properties of symmetrical BC materials can be greatly varied by lateral substitution of the central core, by varying the number and the type of lateral substitutions of the benzene units in the core, and by the type and length of the terminal groups. Such variations lead to the appearance or disappearance of mesophases [5], or to new phases specific to BC systems [6]. Also, by incorporating unsaturated terminal groups into the design of BC molecules one can prepare BC polymers, for example by acyclic diene metathesis (ADMET) polycondensation. Unsaturated BC monomers can also be copolymerised with calamitic monomers using an alternating metathesis (ALTMET) polycondensation method preserving the liquid crystalline properties [7, 8].

In addition to the symmetrical BC molecules, eventually many non-symmetrical BC mesogens have also been synthesised and investigated [9–39]. The non-symmetry can be introduced by varying the lengths and types of the terminal chain [9–14], by different functionalities in the central unit [9, 15–20], through different numbers and lateral substitution of the benzene units in the arms [9, 10, 20–25] and by varying the type, number and orientation of the linking groups [19, 26–32]. A special sub-type of non-symmetrical bent-shaped liquid crystals are the hockey-stick shape molecules [33–36] which represent the borderline

between BC and rod-like mesogens. A simple way to escape the symmetrical molecular structure of BC materials utilised two different functionalities bound to the central core, such as amino and carboxylic groups [9] and hydroxylic and carboxylic groups [9, 17–19]. In a series of five ring BC mesogens the influence of all of the possible orientations of the linking ester units was studied [19] and it was found that the orientation of the ester group has a major effect on the transition temperatures and type of phases formed. In addition to low-molecular-weight non-symmetrical molecules, non-symmetrical main-chain BC polyesters (BPE-*C_n*) were also synthesised [37]. An excellent review on the results on BC materials was published recently [38].

The materials reported in this paper represent a brand new type of non-symmetrical BC compound as one wing connected to the central aromatic ring is based on a biphenyl unit and the other is formed by alkyl benzyloxybenzoates. The polarity of the molecules is further enhanced by the orientation of the ester linking groups, e.g. the carboxylic groups are pointing in the same direction. In the known BC molecules the terminal alkyl chains are mainly connected directly or by ether linkage [39–41]. We introduced two additional ester groups for connection of terminal chains and so contribute to enhance the polarity of the system. In designing the structure of the molecule we assumed that these linkages combined with five rings in the system will secure lower transition temperatures than in systems with ether linkages or more aromatic rings.

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In addition the synthesis of novel BC materials that have lack of symmetry both on the rigid BC and in their terminal chains, we also describe their electro-optical and polarisation current properties. Our results reveal the presence of two distinct smectic phases: a ferroelectric at higher temperature ranges and an antiferroelectric at lower temperatures. The main features of the results can be interpreted as being due to a single tilted synclitic ferroelectric ($\text{SmC}_s\text{P}_{\text{FE}}$) and antiferroelectric ($\text{SmC}_s\text{P}_{\text{AF}}$) phase.

2. Synthesis

The new liquid crystalline mesogens based on 3-hydroxybenzoic acid were prepared by a stepwise acylation of the central 3-hydroxybenzoic acid. To introduce a terminal double bond which can be utilised for polymerisation, a 4'-(undec-10-enoyloxy)biphenyl-4-carboxylic group was connected to the central ring. Here in this study the length of the hydrocarbon chain is varied on one side of the BC mesogen with three linkages, thereby further pronouncing the non-symmetry of the molecular structure of the BC mesogen. The length of the tails also has an influence on the viscosity and packing. The main steps of the synthesis of the intermediates and the asymmetric bent-core compounds **1a–1d** are summarised in Figure 1.

First the lengthening arm **5** was prepared (Figure 1) by a DCC-mediated coupling of the 4-benzyloxybenzoic acid (**2**) (see [42]) with alkyl 4-hydroxybenzoates (**3a–3d**) (see [43]), (**a** *S*-2-methylbutyl, **b** octyl, **c** decyl, **d** dodecyl). It is remarkable that with the exception of the 2-methylbutyl ester **4a**, the linear alkyl esters **4b–4d** were mesogenic and exhibited a monotropic SmA phase. Debonylation of **4a–4d** was achieved by transfer hydrogenation with Pd/C and cyclohexene leading to the series of hydroxy esters **5**. The second arm **6** was prepared starting with 4'-hydroxybiphenyl-4-carboxylic acid which was acylated with undec-10-enoyl chloride. In the synthesis of the target materials **1a–1d**, first the hydroxylic group of 3-hydroxybenzoic acid was protected by benzylation and transformed to the acid chloride **7**. In the next step ester **5** was acylated with acid chloride **7** to afford the intermediate **8a–8d** (Figure 1). The benzylic group of **8a–8d** was removed by transfer hydrogenation as for compounds **4a–4d** and the released hydroxylic group in the derivative **9** was acylated with acid chloride **6a** to give rise to the target materials **1a–1d**.

3. Chemical characterisation

Structures of intermediates and products were confirmed by proton nuclear magnetic resonance (^1H NMR), *J* values are given in Hertz. For column chromatography we used a Kieselgel 60 (Merck)

(0.063–0.2mm) and for flash chromatography we used a Kieselgel 60 (Merck) (0.063–0.020mm). The eluents are given at the individual compounds.

The phase transition temperatures were determined by differential scanning calorimetry (DSC; Pyris Diamond Perkin-Elmer 7) on cooling/heating runs at rates of 5 K min^{-1} for the studied bent-shaped materials. The samples of 3–5 mg hermetically sealed in aluminum pans were placed in a nitrogen atmosphere. The temperature was calibrated on extrapolated onsets of melting points of water, indium and zinc. The enthalpy change was calibrated on enthalpies of melting of water, indium and zinc.

For polarisation current, transmission and textural measurements $5\ \mu\text{m}$ thick, $0.25\ \text{mm}^2$ electrode area cells with rubbed polyimide coated surfaces (supplied by E.H.C. Co. Ltd., Japan) were used. Optical transmission measurements were performed on all materials in an Olympus BX60 polarising microscope fitted with a custom made heating stage and photodiode with rubbing direction at 45° to the crossed analyser and polariser. For the polarisation current measurements, the triangular voltage signal was applied by an HP33120A function generator and an FLC F20AD voltage amplifier and the time dependence of the current signal was measured by an HP 54600B oscilloscope.

3.1 (*S*)-2-Methylbutyl 4-[(4-(benzyloxy)benzoyl)oxy] benzoate (**4a**)

A solution of hydroxy ester **3a** (2.9 g, 15.0 mmol), 4-benzyloxybenzoic acid (**2**) (3.4 g, 15.0 mmol), DCC (3.4 g, 16.5 mmol) and a catalytic amount of DMAP (50 mg) in dry CH_2Cl_2 (60 ml) was stirred at room temperature for 75 min. The mixture was decomposed with water (0.5 ml), the precipitate was filtered, the filtrate evaporated and the crude product was crystallised from ethanol. Ester **4a**, melting point (mp) $99\text{--}101^\circ\text{C}$, was obtained (4.95 g, 96%). (Found 74.68% C, 6.30% H. $\text{C}_{26}\text{H}_{26}\text{O}_5$ requires 74.62% C, 6.26% H.) δ (400 MHz; CDCl_3 ; Me_4Si) 0.97 (3 H, t, CH_3), 1.02 (3 H, d, CH_3), 1.30, 1.53 (2 H, m, CH_2), 1.87 (1 H, m, CH), 4.14, 4.22 (2 H, dd, COOCH_2), 5.16 (2 H, s, CH_2), 7.06 (2 H, d), 7.28 (2 H, d), 7.32–7.46 (5 H, m, Ph), 8.11 (2 H, d), 8.15 (2 H, d).

In the same way derivatives **4b** (R = C_8H_{17} , yield 83%, mp $102\text{--}104^\circ\text{C}$, Iso 85 (SmA) 75 Cr), **4c** (R = $\text{C}_{10}\text{H}_{21}$, yield 84%, mp $102\text{--}103^\circ\text{C}$, Iso 103 (SmA) 75 Cr) and **4d** (R = $\text{C}_{12}\text{H}_{25}$, yield 92%, mp $104\text{--}106^\circ\text{C}$, Iso 91 (SmA) 72 Cr) were obtained.

3.2 (*S*)-2-Methylbutyl 4-[(4-hydroxybenzoyl)oxy] benzoate (**5a**)

The benzyl protected **4a** (4.7 g, 11.6 mmol) in cyclohexene solution (25 ml) was heated at 60°C and 10% Pd/C

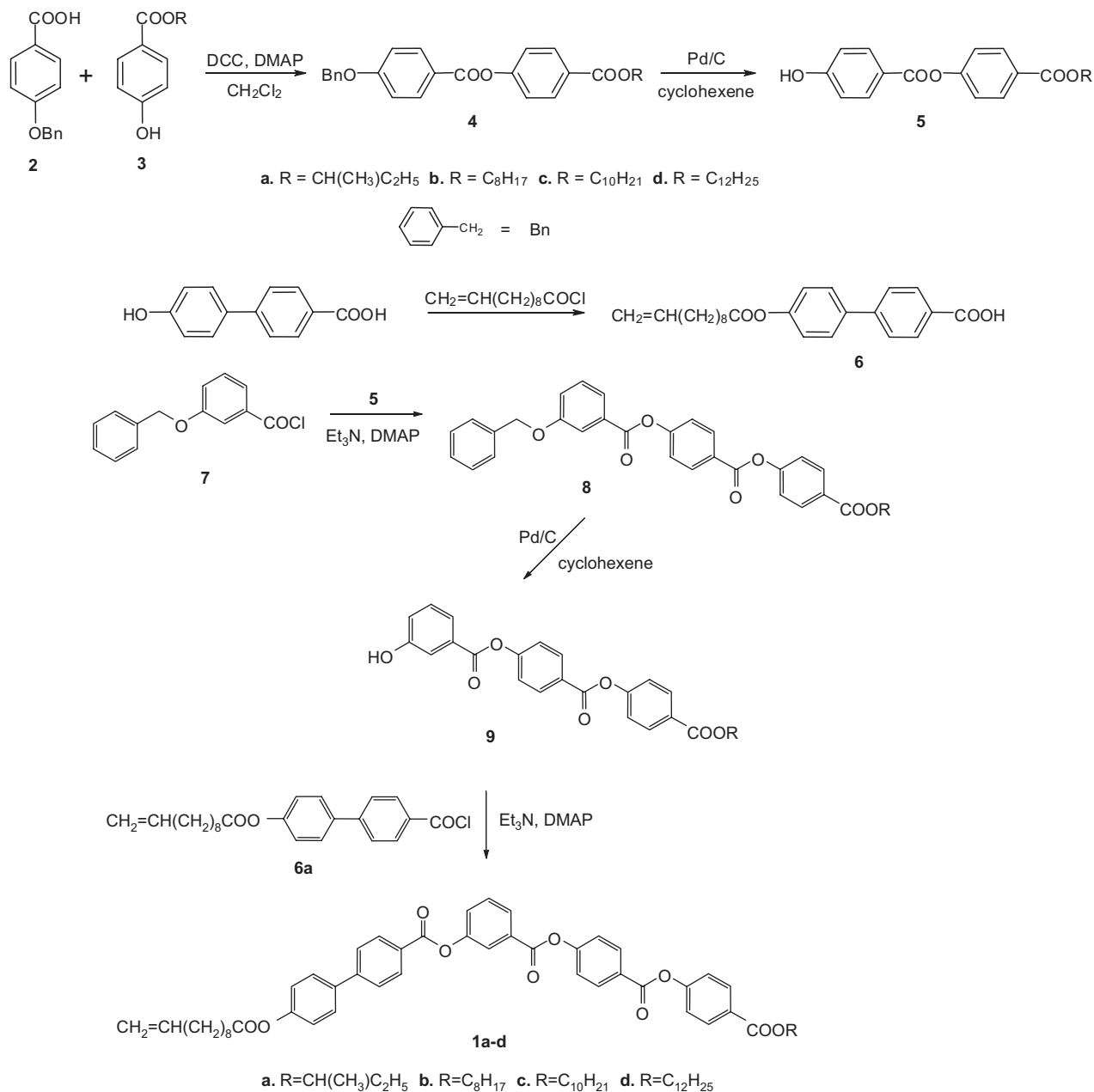


Figure 1. Schematics of the synthesis of the intermediates and the non-symmetrical bent-core molecule based on 3-hydroxybenzoic acid: (a) R = 2-methylbutyl; (b) R = octyl; (c) R = decyl; (d) R = dodecyl.

(0.5 g) was added. Then the reaction mixture was refluxed with stirring for 3 h. The suspension was filtered while hot, the filtrate evaporated and the crude product purified by column chromatography (Kieselgel, eluent toluene/tetrahydrofuran 20/1) and then crystallised from a toluene/hexane mixture. A yield of 2.7 g (74%) of ester **5a** was obtained, mp 91.5–93°C. (Found 69.58% C, 6.49 H. C₁₉H₂₀O₅ requires 69.50% C, 6.14% H.) δ (400 MHz; CDCl₃; Me₄Si) 0.96 (3 H, t, CH₃), 1.02 (3 H, d, CH₃), 1.30, 1.53 (2 H, m, CH₂), 1.88 (1 H, m, CH), 4.15, 4.23 (2 H, dd, COOCH₂), 6.09 (1 H, s, OH), 6.93 (2 H, d), 7.29 (2 H, d), 8.11 (2 H, d), 8.15 (2 H, d).

By the same procedure compounds **5b** (R = C₈H₁₇, yield 80%, mp 96–98 °C), **5c** (R = C₁₀H₂₁, yield 73%, mp 96–99.5°C) and **5d** (R = C₁₂H₂₅, yield 59%, mp 103–104°C) were prepared.

3.3 4'-[(Undec-10-enoyl)oxy]biphenyl-4-carboxylic acid (**6**)

To a solution of 4'-hydroxybiphenyl-4-carboxylic acid (5.0 g, 23.3 mmol), triethylamine (3.6 ml, 25.8 mmol) and a catalytic amount of DMAP (100 mg) in ethyl methyl ketone (100 ml), (undec-10-enoyl) chloride

(5.5 ml, 25.5 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 2 h and then decomposed with cold 1 M HCl, and diluted with CHCl₃ (100 ml). Layers were separated and the water layer was washed with CHCl₃ (2 × 30 ml). The combined organic solution was washed with water and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was crystallised from toluene to afford (4.9 g, 55%) of **6**, mp 159–164°C. (Found 75.80% C, 7.46% H. C₂₄H₂₈O₄ requires 75.76% C, 7.42% H.) δ(400 MHz; CDCl₃; Me₄Si) 1.26–1.48 (10 H, m, CH₂), 1.77 (2 H, m, CH₂), 2.04 (2 H, m, CH₂), 2.58 (2 H, t, CH₂), 4.93, 4.99 (2 H, m, CH=CH₂), 5.81 (1 H, m, CH=CH₂), 7.19 (2 H, d), 7.63 (2 H, d), 7.66 (2 H, d), 8.17 (2 H, d), 11.60 (1 H, br s, COOH).

3.4 (S)-(2-Methylbutyl) 4-((4-[3-benzyloxybenzoyl]oxy)benzoyl)oxy)benzoate (**8a**)

To a mixture of **5a** (1.35 g, 4.3 mmol), triethylamine (0.6 ml, 4.4 mmol) and a catalytic amount of DMAP (50 mg) in dry CH₂Cl₂ (60 ml), chloride **6a** (1.08 g, 4.4 mmol) in dry dichloromethane (15 ml) was added. The solution was stirred for 1 h at room temperature and diluted with water (50 ml). Layers were separated and the water layer was washed with CH₂Cl₂ (2 × 25 ml). The combined organic solution was washed with water (25 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was crystallised from ethanol. A yield of 1.95 g (86%) of **8a** was obtained, mp 81–82°C. Found 73.72% C, 5.68 H. C₃₃H₃₀O₇ requires 73.59% C, 5.61% H. δ(400 MHz; CDCl₃; Me₄Si) 0.97 (3 H, t, CH₃), 1.02 (3 H, d, CH₃), 1.30, 1.53 (2 H, m, CH₂), 1.87 (1 H, m, CH), 4.14, 4.22 (2 H, dd, COOCH₂), 5.16 (2 H, s, CH₂), 7.27 (1 H, ddd, ³J = 8.3, ⁴J = 2.6, 6-H), 7.31 (2 H, d), 7.32–7.48 (6 H, m, Ph, 5-H), 7.39 (2 H, d), 7.82 (1 H, s, 2-H), 7.83 (2 H, d), 8.14 (2 H, d), 8.29 (2 H, d).

Analogously, esters **8b** (R = C₈H₁₇, yield 89%, mp 94–97°C), **8c** (R = C₁₀H₂₁, yield 49%, mp 91–93°C) and **8d** (R = C₁₂H₂₅, yield 91%, mp 93–100°C) were obtained.

3.5 (S)-(2-Methylbutyl) 4-((4-[3-hydroxybenzoyl]oxy)benzoyl)oxy)benzoate (**9a**)

To a hot solution of **8a** (0.6 g, 1.14 mmol) in cyclohexene (25 ml), 10% Pd/C (60 mg) was added. The reaction mixture was stirred and heated to boiling for 3 h. The catalyst was filtered off and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, eluent toluene/tetrahydrofuran 20/1). A yield of 0.41 g (89%) of **9a** was obtained, mp 152–155°C. (Found 69.80% C, 5.42%

H. C₂₆H₂₄O₇ requires 69.63% C, 5.39% H.) δ(400 MHz; CDCl₃; Me₄Si) 0.97 (3 H, t, CH₃), 1.03 (3 H, d, CH₃), 1.30, 1.54 (1 H, m, CH₂), 1.88 (1 H, m, CH), 4.16, 4.23 (2 H, dd, CH₂), 5.89 (1 H, s, OH), 7.14 (1 H, dd, ³J = 7.8, ⁴J = 1.8 Hz, 4-H), 7.29 (2 H, d), 7.37 (2 H, d), 7.40 (1 H, t, J = 7.8 Hz, 5-H), 7.69 (1 H, t, ⁴J = 1.8 Hz, 2-H), 7.78 (1 H, dd, ³J = 7.8, ⁴J = 1.8 Hz, 6-H), 8.14 (2 H, d), 8.28 (2 H, d).

By the same procedure, compounds **9b** (R = C₈H₁₇, yield 81%, mp 157–158°C), **9c** (R = C₁₀H₂₁, yield 91%, mp 149–151°C) and **9d** (R = C₁₂H₂₅, yield 99%, mp 148–150°C) were prepared.

3.6 (S)-(2-Methylbutyl) 4-((4-((3-((4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)oxy)benzoyl)oxy)benzoate (**1a**)

A mixture of acid **6** (0.40 g, 1.05 mmol) and dimethylformamide (0.05 ml) in oxalyl chloride (25 ml) was stirred and heated to boiling for 1 h. The unreacted oxalyl chloride was evaporated. The crude acid chloride **6a** was dissolved in dry dichloromethane (10 ml) and added to a mixture of hydroxy ester **9a** (0.4 g, 0.90 mmol), triethylamine (0.15 ml, 1.07 mmol) and a catalytic amount of 4-dimethylaminopyridine (50 mg) in dry dichloromethane (50 ml). The reaction mixture was stirred for 30 min and decomposed with water (50 ml). Layers were separated and the water layer was washed with CH₂Cl₂ (2 × 30 ml). The combined organic solution was washed with 5% aq. HCl (20 ml), water (25 ml), and dried with anhydrous MgSO₄. The solvent was evaporated and the crude product was purified by column chromatography (dichloromethane); 0.54 g (75%) of **1a** was obtained. (Found 74.12% C, 6.28% H. C₅₀H₅₀O₁₀ requires 74.06% C, 6.21% H.) δ(400 MHz; CDCl₃; Me₄Si) 0.97 (3 H, t, CH₃), 1.02 (3 H, d, CH₃), 1.24–1.60 (12 H, m, CH₂), 1.78 (2 H, m, CH₂), 1.87 (1 H, m, CH), 2.05 (2 H, m, CH₂), 2.59 (2 H, t, CH₂), 4.15, 4.23 (2 H, dd, CH₂), 4.94, 5.00 (2 H, m, CH₂=CH), 5.82 (1 H, m, CH₂=CH), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ³J = 8.2, ⁴J₁ = 2.3, ⁴J₂ = 1.3, 4-H), 7.63 (1 H, dd, J = 8.2, J = 7.9 Hz, 5-H), 7.66 (2 H, d), 7.73 (2 H, d), 8.10 (1 H, dd, ⁴J₁ = 1.9, ⁴J₂ = 1.7, 2-H), 8.14 (2 H, d), 8.15 (1 H, ddd, ³J = 7.9, ⁴J = 1.4, 6-H), 8.28 (2 H, d), 8.30 (2 H, d).

3.7 Octyl 4-((4-((3-((4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)oxy)-benzoyl)oxy)-benzoate (**1b**)

From hydroxy ester **9b** (0.45 g, 0.92 mmol) and acid chloride **6a** (0.4 g, 1.00 mmol), 0.55 g (71%) of ester **1b** was obtained. (Found 74.69% C, 6.66% H. C₅₃H₅₆O₁₀

requires 74.63% C, 6.62% H.) δ (400 MHz; CDCl₃; Me₄Si) 0.89 (3 H, t, CH₃), 1.24–1.49 (20 H, m, CH₂), 1.73–1.82 (4 H, m, CH₂), 2.05 (2 H, m, CH₂), 2.59 (2 H, t, CH₂), 4.33 (2 H, t, COOCH₂), 4.94, 5.00 (2 H, m, CH₂=CH), 5.82 (1 H, m, CH₂=CH), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ³J = 8.2, ⁴J₁ = 2.3, ⁴J₂ = 1.3 Hz, 4-H), 7.63 (1 H, dd, J = 8.2, J = 7.9 Hz, 5-H), 7.66 (2 H, d), 7.73 (2 H, d), 8.10 (1 H, dd, ⁴J₁ = 1.9, ⁴J₂ = 1.7, 2-H), 8.14 (2 H, d), 8.15 (1 H, ddd, ³J = 7.9, ⁴J₁ = 1.4, ⁴J₂ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

3.8 Decyl 4-((4-((3-([4'-(undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)oxy)-benzoate (1c)

From hydroxy ester **9c** (0.58 g, 1.12 mmol) and acid chloride **6a** (0.45 g, 1.13 mmol), 0.65 g (66%) of ester **1c** was prepared. (Found 75.05% C, 6.91% H. C₅₅H₆₀O₁₀ requires 74.98% C, 6.86% H.) δ (400 MHz; CDCl₃; Me₄Si) 0.89 (3 H, t, CH₃), 1.24–1.49 (24 H, m, CH₂), 1.73–1.82 (4 H, m, CH₂), 2.05 (2 H, m, CH₂), 2.59 (2 H, t, CH₂), 4.33 (2 H, t, COOCH₂), 4.94, 5.00 (2 H, m, CH₂=CH), 5.82 (1 H, m, CH₂=CH), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ³J = 8.2, ⁴J₁ = 2.3, ⁴J₂ = 1.3 Hz, 4-H), 7.63 (1 H, dd, J = 8.2, J = 7.9 Hz, 5-H), 7.66 (2 H, d), 7.73 (2 H, d), 8.10 (1 H, dd, ⁴J = 1.9, ⁴J = 1.7, 2-H), 8.14 (2 H, d), 8.15 (1 H, ddd, ³J = 7.9, ⁴J₁ = 1.4, ⁴J₂ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

3.9 Dodecyl 4-((4-((3-([4'-(undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)oxy)benzoate (1d)

From hydroxy ester **9d** (0.60 g, 1.10 mmol) and acid chloride **6a** (0.44 g, 1.10 mmol), 0.71 g (71%) of ester **1d** was obtained. (Found 75.39% C, 7.15% H. C₅₇H₆₄O₁₀ requires 75.31% C, 7.10% H.) δ (400 MHz; CDCl₃; Me₄Si) 0.89 (3 H, t, CH₃), 1.24–1.49 (28 H, m, CH₂), 1.73–1.82 (4 H, m, CH₂), 2.05 (2 H, m, CH₂), 2.59 (2 H, t, CH₂), 4.33 (2 H, t, COOCH₂), 4.94, 5.00 (2 H, m, CH₂=CH), 5.82 (1 H, m, CH₂=CH), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ³J = 8.2, ⁴J₁ = 2.3, ⁴J₂ = 1.3 Hz, 4-H), 7.63 (1 H, dd, J = 8.2, J = 7.9 Hz, 5-H), 7.66 (2 H, d), 7.73 (2 H, d), 8.10 (1 H, dd, ⁴J = 1.9, ⁴J = 1.7, 2-H), 8.14 (2 H, d), 8.15 (1 H, ddd, ³J = 7.9, ⁴J₁ = 1.4, ⁴J₂ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

4. Physical characterisation

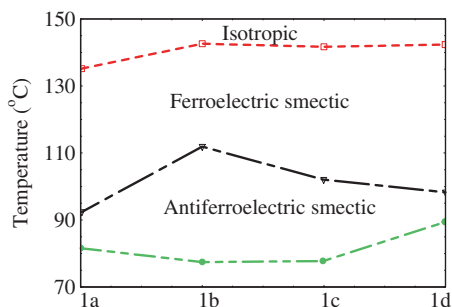
Phase structure characterisation measurements were carried out on compounds **1a–d** with molecular structures shown in Figure 1, where the length of the hydrocarbon chain is varied on one side of the BC mesogen

as follows: R = (S)-2-methylbutyl- (**1a**), octyl- (**1b**), decyl- (**1c**) and dodecyl- (**1d**) chains. The phase sequences deduced from the combinations of DSC, polarising optical microscopy (POM), electro-optical and polarisation current measurements are shown in Figure 2. The DSC plots of the compounds investigated are depicted in Figure 3.

Textural and DSC measurements reveal two smectic mesophases below the clearing point that increases from 134°C (**1a**) to 142°C (**1b**), then basically stays constant as the chain length increases. The crystallisation temperatures are in the 80°C range for **1a**, **1b** and **1c**, and around 90°C for **1d**. At the isotropic to upper range smectic transition long stick-like structures are observed (see the top row of Figure 4(a)). At this transition the enthalpies for all materials show strong first-order transitions with about 18–19 J g⁻¹ enthalpies. The transitions between the two smectic phases are of weak first order with $\Delta H \sim 0.2\text{--}0.6$ J g⁻¹ transition enthalpies. The phase range of the lower temperature smectic phase shrinks from 34°C as the chain length increases from C₈H₁₇ (**1b**) to 24°C and 10°C when the length is C₁₀H₂₁ (**1c**) and C₁₂H₂₅ (**1d**), respectively. The transitions to the crystalline phases are of first order with the magnitude of the transition enthalpies increasing with the length of R.

The upper temperature mesophase optically is characterised by smooth fan-shape domains with sizes increasing with the length of R, and where the optical extinction directions that appear on cooling without electric field applied, are roughly parallel to the polariser or analyser, indicating either orthogonal SmA or anticlinic tilted SmC type phase, or a structure where the smectic layers are tilted with respect to the substrates normal [44]. The lower temperature smectic phase shows fine stripe textures that resemble synclinc racemic antiferroelectric (SmC_sP_A) structures [3].

The characteristic textures under large electric fields applied are shown in Figure 4(b). In the ferroelectric phase it is clear that the optic axis is rotating as the electric field is changing sign, indicating a chiral tilted smectic phase [3]. When the field is switched off (either with short circuiting or breaking the circuit) the optic axis stays as it was in the previously applied field, except that the birefringence slightly decreases. For example, in the textures of the top row of Figure 4(b), Δn is decreasing from about 0.18 to 0.17. The angle of rotation increases on cooling from 0° at 142°C to a saturated value of about 40° at or below 130°C. In contrast, in the antiferroelectric phase (lower row in Figure 4(b)) the optic axis is basically parallel to the layer normal both under high or zero electric fields. Polarisation current measurements show one peak in the high-temperature smectic and two peaks in the low-temperature phase in one half period of the triangular waveforms (see



Comp.	chain R	m.p. [ΔH]	c.p. [ΔH]	Cr	T _c [ΔH]	AF	T _c [ΔH]	FE	T _c [ΔH]	Iso	Mol wt [g mol ⁻¹]
1a	2MeBu	120.9 [+45.4]	135.8 [+18.0]	•	80.5 [-17.6]	•	92.3 [-0.5]	•	133.7 [-18.0]	•	823.0
1b	C ₈ H ₁₇	105.5 [+35.6]	143.6 [+19.8]	•	77.4 [-14.1]	•	111.0 [-0.6]	•	142.4 [-19.5]	•	857.0
1c	C ₁₀ H ₂₁	105.7 [+21.0]	143.0 [+19.0]	•	77.7 [-20.1]	•	101.8 [-0.3]	•	141.3 [-19.1]	•	885.1
1d	C ₁₂ H ₂₅	109.5 [+27.5]	143.6 [+18.1]	•	89.3 [-25.0]	•	98.3 [-0.2]	•	142.2 [-18.5]	•	913.1

Figure 2. Phase behaviour of the non-symmetric bent-core materials alkyl 4-((4-((3-((4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]-oxy)benzoyl)oxy)benzoyl)oxy)benzoate (**1a–d**). Upper part: phase diagram as determined by polarising microscopic and polarisation current measurements. Lower part: molecular weight, transition temperatures and enthalpies (in J g⁻¹) of **1a–d** as determined by differential scanning calorimetry measurements. Note: '•' denotes that the phase exists; 'm.p.' denotes the melting point; 'c.p.' denotes the clearing point (the temperature where the isotropic phase appears) in heating.

Figure 5(a)) indicating ferroelectric and antiferroelectric phases, respectively. The absence of the rotation of the optic axis in high square wave fields of the antiferroelectric material indicates antclinic ferroelectric states [3].

Up to this point all observations indicate that the smectic phases have simple synclinc structures where the layer polarisations are along the smectic layers, but in the higher-temperature phase the polarisation is in the same direction in subsequent layers (SmC_sP_{FE}), whereas in the lower temperature phase the polarisation is alternating in subsequent layers (SmC_sP_{AF}) (see Figure 4(b)).

- (i) For SmC_sP_{AF} the structure is composed by oppositely tilted synclinc stripes, where each synclinc stripe should have larger birefringence than the field-induced antclinic structure. This does not correspond to our situation shown in the bottom row of Figure 4(b) where Δ*n* decreased from 0.16 to 0.12 in each stripe formed at zero fields.
- (ii) According to our measurements the temperature dependences of the magnitude of the spontaneous polarisation shows a stepwise increase at the

ferroelectric to antiferroelectric transition e.g. from 250 to 380 nC cm⁻² for **1a**, and from 100 to 240 nC cm⁻² for **1c** (see Figure 5(a)).

- (iii) Figure 5(b) shows that in the ferroelectric state the switching time is much larger than in the antiferroelectric state. In addition, in the ferroelectric state the switching time is decreasing on cooling, whereas in the antiferroelectric state it is increasing. Similar results were observed earlier in molecules with asymmetry and steric bumps in their cores, and attributed to the double tilted SmC_G phase with C₁ symmetry [45, 46]. (We also note that at the transition between the ferroelectric and antiferroelectric states there is a coexistence region of around 1–2°C, although DSC indicated very weak first-order transitions for **1a–1d**).

5. Conclusions

We have reported the synthesis of novel BC compounds with asymmetry both in the core and in the terminal chains. The materials have been prepared by stepwise synthesis, based on 3-hydroxybenzoic acid

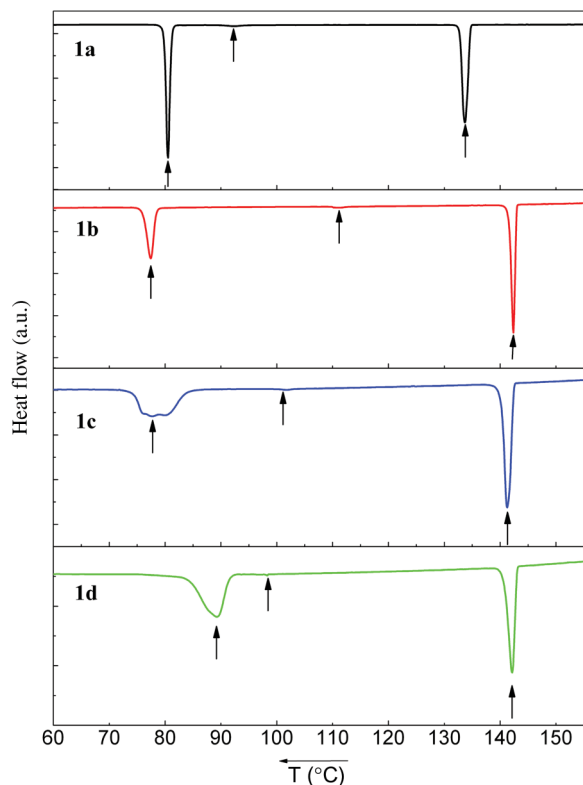


Figure 3. Differential scanning calorimetry plots on cooling runs for compounds **1a–d**. Arrows indicate the phase transitions.

as a central aromatic ring. The terminal chains were attached to the core by ester function. These additional ester groups raised the polarity of the compounds leading to the appearance of polar banana mesophases. The introduction of 3-hydroxybenzoic acid as the central core and further pronounced non-symmetry of the BC mesogens are very promising features. It should be pointed out that interesting properties of our new materials were obtained without a lateral substitution. We assume that this behaviour is caused by the combination of a rigid biphenyl part in one side chain and a much more flexible triester part in the other. Another interesting property of the new mesogens is that introduction of a chiral terminal chain does not influence the mesomorphic behaviour. We suppose that due to restricted rotation along the long axis of the BC molecule, the packing-induced dipoles are dominant and the chirality-induced dipole is therefore suppressed [25]. Such a preference is most probably caused by the certain rigidity of the system because of the presence of the biphenyl part and by the short length of the chiral terminal chain, where the chiral centre is close to the outer phenyl ring.

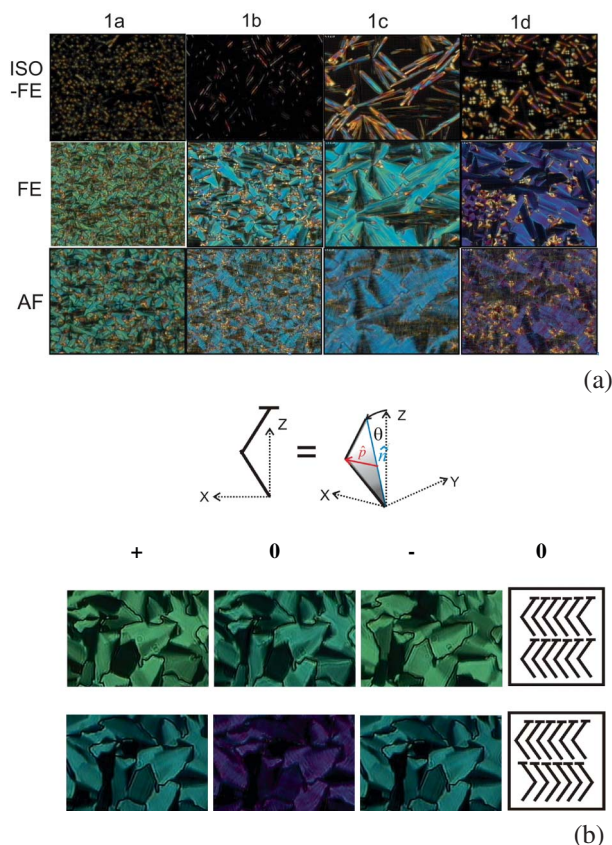


Figure 4. (a) Typical textures observed with a polarising microscope of 5- μm cells of **1a–d**. The size of the individual pictures is roughly $250 \times 300 \mu\text{m}^2$. 1st row: at the isotropic to ferroelectric smectic transition; 2nd row: ferroelectric (FE) phase; 3rd row: antiferroelectric smectic (AF) phase. (b) Textures of 5 μm **1b** sample at +20, 0 and $-20 \text{ V } \mu\text{m}^{-1}$ field and their possible director structure at zero field with the explanation of notation above the textures. Upper row: FE phase with possible $\text{SmC}_s\text{P}_{\text{FE}}$ structure. Lower row: AF phase with possible $\text{SmC}_s\text{P}_{\text{AF}}$ structure.

The series of BC mesogens **1a–1d** show isotropic fluid–ferroelectric smectic–antiferroelectric smectic–crystal series of transitions. The ferroelectric phase range is widest for **1a** and **1d**, which are the most non-symmetrical materials, indicating that the ferroelectric state should possibly result from the molecular asymmetry. Although the key features of the measurements point to synclinc ferroelectric ($\text{SmC}_s\text{P}_{\text{FE}}$) and antiferroelectric racemic ($\text{SmC}_s\text{P}_{\text{AF}}$) structures, important details of the temperature dependence of the polarisation, and switching time, and the decreased birefringence in the antiferroelectric state indicate a more complicated director and layer structure. These results make these new materials worthy of further physical studies, such as small-angle X-ray scattering, which are out of the scope of our present paper.

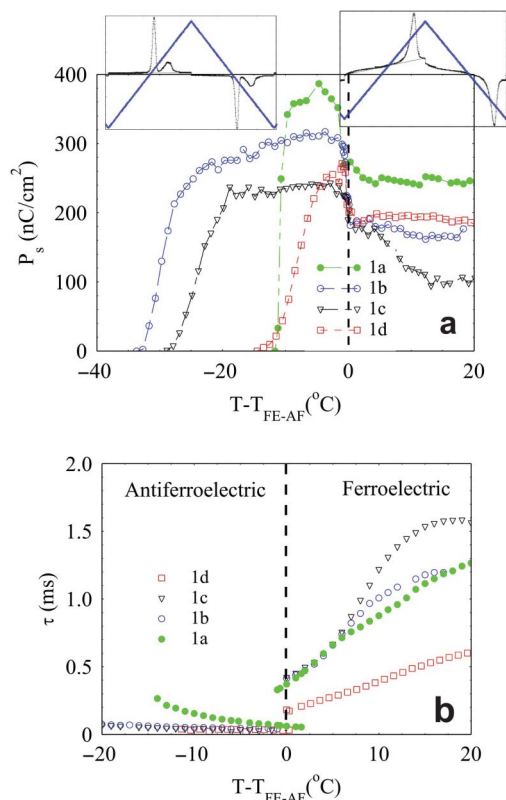


Figure 5. The magnitude of the spontaneous polarisation (a) and the switching time (b) as the function of reduced temperature ($T - T_{\text{FE-AF}}$) of materials **1a–d**. Typical polarisation current waveforms under triangular fields are shown at the top of (a). All measurements were performed at a constant cooling rate of $1^{\circ}\text{C}/\text{min}$ with an applied triangular (a) or rectangular (b) wave voltage with an amplitude of $18 \text{ V } \mu\text{m}^{-1}$ at a frequency of 23 Hz. In this latter case the switching time τ is the time interval between the maximum electric current response and the sign inversion of the applied voltage. This gives the time needed to switch the majority of the polarisation.

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