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

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1. Abstract

New non-symmetrical bent core mesogens with a variable flexible chain length have been synthesized. 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 one is saturated. The compounds represent novel non-symmetric molecules both in their core and tails. The main features of DSC, polarizing optical microscopy, electro-optical and polarization current measurements for all studied materials indicate a transition between single tilted synclinic ferroelectric and an antiferroelectric smectic phases. However details show important deviations from the simplest picture, which will be the subject of future X-ray studies.

Keywords: Bent-core liquid crystals, ferroelectric, antiferroelectric switching, non-symmetrical

2. Introduction

Initially the research in bent-core (BC) liquid crystals concentrated on the preparation and investigation of symmetrical BC molecules [1, 2, 3, 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 in the design of BC molecules one can prepare BC polymers, for example by acyclic diene methathesis polycondenzation (ADMET). Unsaturated BC monomers can also be copolymerized with calamitic monomers by alternating methathesis polycondenzation (ALTMET) method preserving liquid crystalline properties [7, 8].

In addition to the symmetrical BC molecules eventually many non-symmetrical BC mesogens have also been synthesized and investigated [9-39]. The non-symmetry can be introduced by different lengths and type of the terminal chain [9, 10,11, 12, 13, 14], by different functionalities in the central unit [9, 15, 16, 17, 18, 19, 20], different number and lateral substitution of the benzene units in the

arms [9, 10, 20, 21, 22, 23, 24, 25] and type, number and orientation of the linking groups [19, 26, 27, 28, 29, 30, 31, 32]. A special sub-type of non-symmetrical bent shaped liquid crystals are the hockey-stick shape molecules [33, 34, 35, 36] which represent the borderline between BC and rod-like mesogens. A simple way to escape the symmetrical molecular structure of BC materials utilized 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 bent-core mesogens the influence of all the possible orientation of the linking ester units was studied [19] and it was found that orientation of the ester group strongly affects the transition temperatures and type of the formed phases. In addition to low molecular weight non-symmetric molecules, non-symmetric main-chain BC polyesters (BPE-Cn) were synthesized, too [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-symmetric bent-core compounds as one wing connected to the central aromatic ring is based on biphenyl unit and the other one is formed by alkyl benzoyloxybenzoates. 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 bent-core molecules the terminal alkyl chains are mainly connected directly or by ether linkage[39,40,41]. We introduced two additional ester groups for connection of terminal chains and so contribute to enhance the polarity of the system. In planning the structure of 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.

In addition the synthesis of novel BC materials that have lack of symmetry both on the rigid bent-core and in their terminal chains, we also describe their electro-optical and polarization 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 due to single tilted synclinic ferroelectric (*Sm C$_s$P$_{FE}$*) and antiferroelectric (*Sm C$_s$P$_{AF}$*) phase , however details show important deviation from this simple picture, that requires future X-ray measurements.

3. 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 utilized for polymerization, 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 influences the viscosity and packing. The main steps of the synthesis of the intermediates and the asymmetric bent-core compounds **1a-1d** are summarized in **Figure 1.**

First the lengthening arm **5** was prepared (**Figure 1**) by a DCC mediated coupling of the 4-benzyloxybenzoic acid (**2**) [42] with alkyl 4-hydroxybenzoates (**3a-3d**) [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. Debenzylation 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

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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 derivatives **9** was acylated with acid chloride **6a** to give rise to the target materials **1a-1d**.
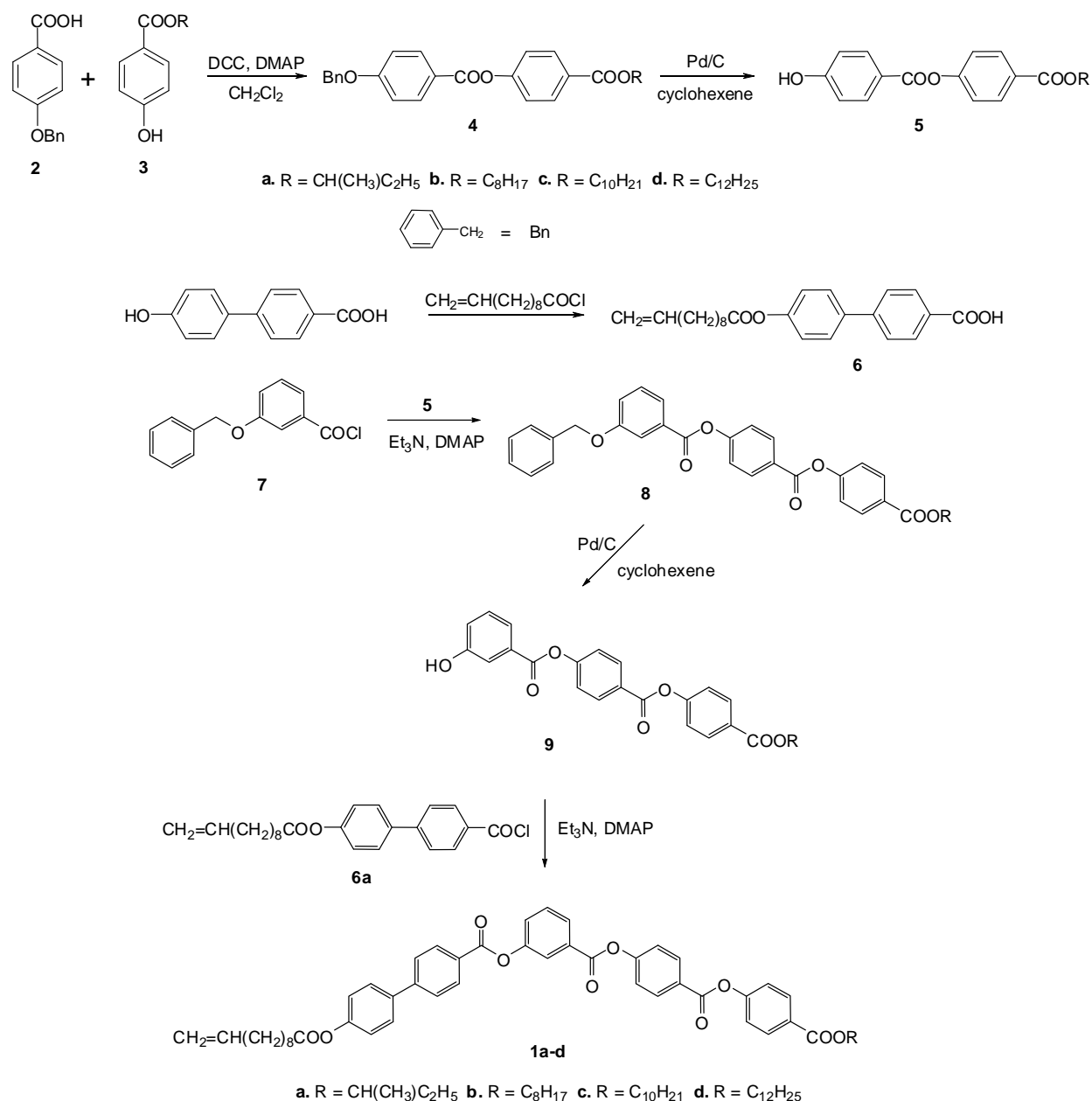

a. R = CH(CH₃)C₂H₅ **b.** R = C₈H₁₇ **c.** R = C₁₀H₂₁ **d.** R = C₁₂H₂₅

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.

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4. Chemical Characterization

Structures of intermediates and products were confirmed by 1H NMR, J values are given in Hz. For column chromatography Kieselgel 60 (Merck) (0.063-0.2mm) and for flash chromatography was used Kieselgel 60 (Merck) (0.063-0.020mm) support. The eluents are given at the individual compounds. The experimental part summarizes procedures for the synthesis of representative intermediates and target compounds.

The phase transition temperatures were determined by differential scanning calorimetry (DSC-Pyris Diamond Perkin-Elmer 7) on cooling/heating runs at rates of 5K 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 polarization current, transmission and textural measurements 5 µm thick, 0.25 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 polarizing microscope fitted with a custom made heating stage and photodiode with rubbing direction at 45 deg to the crossed analyzer and polariser. For the polarization current measurements the triangular voltage signal was applied by a HP33120A function generator and an FLC F20AD voltage amplifier and the time dependence of the current signal was measured by a HP 54600B oscilloscope.

(*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 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 crystallized from ethanol. It was obtained (4.95 g, 96 %) of ester **4a**, mp 99-101 °C. (Found 74.68 % C, 6.30 % H. $C_{26}H_{26}O_5$ requires 74.62 % C, 6.26 % H); δ(400 MHz; CDCl$_3$; Me$_4$Si) 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 102-104 °C, Iso 85 (SmA) 75 Cr), **4c** (R = $C_{10}H_{21}$, yield 84%, mp 102-103 °C, Iso 103 (SmA) 75 Cr) and **4d** (R = $C_{12}H_{25}$, yield 92%, mp 104-106 °C, Iso 91 (SmA) 72 Cr) were obtained.

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

To a hot solution of benzyl protected **4a** (4.7 g, 11.6 mmol) in cyclohexene (25 ml) 10% Pd/C (0.5 g) was added and the reaction mixture was heated and stirred 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 crystallized from a toluene/hexane mixture. (2.7 g, 74 %) of ester **5a** was obtained, mp 91.5-93 °C. (Found 69.58 % C, 6.49 H. $C_{19}H_{20}O_5$ requires 69.50 % C, 6.14 % H.); δ(400 MHz; CDCl$_3$; Me$_4$Si) 0.96 (3 H, t, CH$_3$), 1.02 (3 H, d, CH$_3$), 1.30, 1.53 (2 H, m, CH$_2$), 1.88 (1 H, m, CH), 4.15, 4.23 (2 H, dd, COOCH$_2$), 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 = C_8H_{17}, yield 80%, mp 96-98 °C), **5c** (R = $C_{10}H_{21}$, yield 73%, mp 96-99.5 °C) and **5d** (R = $C_{12}H_{25}$, yield 59%, mp 103-104 °C) were prepared.

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 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 CHCl$_3$ (100 ml). Layers were separated and the water layer was washed with CHCl$_3$ (2x30 ml). The combined organic solution was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed and the crude product was crystallized from toluene to afford (4.9 g, 55 %) of **6**, mp 159-164 °C. (Found 75.80 % C, 7.46 % H. C$_{24}$H$_{28}$O$_4$ requires 75.76 % C, 7.42 % H); δ(400 MHz; CDCl3; Me4Si)1.26-1.48 (10 H, m, CH$_2$), 1.77 (2 H, m, CH$_2$), 2.04 (2 H, m, CH$_2$), 2.58 (2 H, t, CH$_2$), 4.93, 4.99 (2 H , m, CH=<u>CH$_2$</u>), 5.81 (1 H, m, <u>CH</u>=CH$_2$), 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).

(*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 catalytic amount of DMAP (50 mg) in dry CH$_2$Cl$_2$ (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 CH$_2$Cl$_2$ (2x25 ml). The combined organic solution was washed with water (25 ml) and dried with anhydrous magnesium sulfate. The solvent was removed and the crude product was crystallized from ethanol. (1.95 g, 86 %) of **8a** was obtained, mp 81-82 °C. Found 73.72 % C, 5.68 H. C$_{33}$H$_{30}$O$_7$ requires 73.59 % C, 5.61 % H); δ(400 MHz; CDCl3; Me4Si) 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$_2$), 7.27 (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 = C$_8$H$_{17}$, yield 89%, mp 94-97 °C), **8c** (R = C$_{10}$H$_{21}$, yield 49%, mp 91-93 °C) and **8d** (R = C$_{12}$H$_{25}$, yield 91%, mp 93-100 °C) were obtained.

(*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). (0.41 g, 89 %) of **9a** was obtained, mp 152-155 °C. (Found 69.80 % C, 5.42 H. C$_{26}$H$_{24}$O$_7$ requires 69.63 % C, 5.39 % H); δ(400 MHz; CDCl3; Me4Si) 0.97 (3 H, t, CH$_3$), 1.03 (3 H, d, CH$_3$), 1.30, 1.54 (1 H, m, CH$_2$), 1.88 (1 H, m, CH), 4.16, 4.23 (2 H, dd, CH$_2$), 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 = C$_8$H$_{17}$, yield 81%, mp 157-158 °C), **9c** (R = C$_{10}$H$_{21}$, yield 91%, mp 149-151 °C) and **9d** (R = C$_{12}$H$_{25}$, yield 99%, mp 148-150 °C) were prepared.

(*S*)-(2-Methylbutyl) 4-((4-((3-([4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)-oxy)benzyol)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 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 CH$_2$Cl$_2$ (2x30 ml). The combined organic solution was washed with 5%

aq. HCl (20 ml), water (25 ml), and dried with anhydrous MgSO$_4$. 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. C$_{50}$H$_{50}$O$_{10}$ requires 74.06 % C, 6.21 % H); δ(400 MHz; CDCl3; Me4Si) 0.97 (3 H, t, CH$_3$), 1.02 (3 H, d, CH$_3$), 1.24-1.60 (12 H, m, CH$_2$), 1.78 (2 H, m, CH$_2$), 1.87 (1 H, m, CH), 2.05 (2 H, m, CH$_2$), 2.59 (2 H, t, CH$_2$), 4.15, 4.23 (2 H, dd, CH$_2$), 4.94, 5.00 (2 H, m, <u>CH$_2$</u>=CH), 5.82 (1 H, m, CH$_2$=<u>CH</u>), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ^3J = 8.2, $^4J_1$ = 2.3, $^4J_2$ = 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, $^4J_1$ = 1.9, $^4J_2$ = 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).

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. C$_{53}$H$_{56}$O$_{10}$ requires 74.63 % C, 6.62 % H); δ(400 MHz; CDCl3; Me4Si) 0.89 (3 H, t, CH$_3$), 1.24-1.49 (20 H, m, CH$_2$), 1.73-1.82 (4 H, m, CH$_2$), 2.05 (2 H, m, CH$_2$), 2.59 (2 H, t, CH$_2$), 4.33 (2 H, t, COOCH$_2$), 4.94, 5.00 (2 H, m, <u>CH$_2$</u>=CH), 5.82 (1 H, m, CH$_2$=<u>CH</u>), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ^3J = 8.2, $^4J_1$ = 2.3, $^4J_2$ = 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, $^4J_1$ = 1.9, $^4J_2$ = 1.7, 2-H), 8.14 (2 H, d), 8.15 (1 H, ddd, ^3J = 7.9, $^4J_1$ = 1.4, $^4J_2$ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

Decyl 4-((4-((3-([4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)benzoyl)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. C$_{55}$H$_{60}$O$_{10}$ requires 74.98 % C, 6.86 % H); δ(400 MHz; CDCl3; Me4Si) 0.89 (3 H, t, CH$_3$), 1.24-1.49 (24 H, m, CH$_2$), 1.73-1.82 (4 H, m, CH$_2$), 2.05 (2 H, m, CH$_2$), 2.59 (2 H, t, CH$_2$), 4.33 (2 H, t, COOCH$_2$),), 4.94, 5.00 (2 H, m, <u>CH$_2$</u>=CH), 5.82 (1 H, m, CH$_2$=<u>CH</u>), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ^3J = 8.2, $^4J_1$ = 2.3, $^4J_2$ = 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, $^4J_1$ = 1.4, $^4J_2$ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

Dodecyl 4-((4-((3-([4'-((undec-10-en-1-ylcarbonyl)oxy)biphenyl-4-carbonyl]oxy)-benzoyl)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 % H, 7.15 % H. C$_{57}$H$_{64}$O$_{10}$ requires 75.31 % C, 7.10 % H); δ(400 MHz; CDCl3; Me4Si) 0.89 (3 H, t, CH$_3$), 1.24-1.49 (28 H, m, CH$_2$), 1.73-1.82 (4 H, m, CH$_2$), 2.05 (2H, m, CH$_2$), 2.59 (2 H, t, CH$_2$), 4.33 (2 H, t, COOCH$_2$), 4.94, 5.00 (2 H, m, <u>CH$_2$</u>=CH), 5.82 (1 H, m, CH$_2$=<u>CH</u>), 7.21 (2 H, d), 7.31 (2 H, d), 7.41 (2 H, d), 7.56 (1 H, ddd, ^3J = 8.2, $^4J_1$ = 2.3, $^4J_2$ = 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, $^4J_1$ = 1.4, $^4J_2$ = 1.4 Hz), 8.28 (2 H, d), 8.30 (2 H, d).

5. Physical characterization

Phase structure characterization 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 differential

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scanning calorimetry (DSC), polarizing optical microscopy (POM), electro-optical and polarization current measurements, are shown in **Figure 2**.
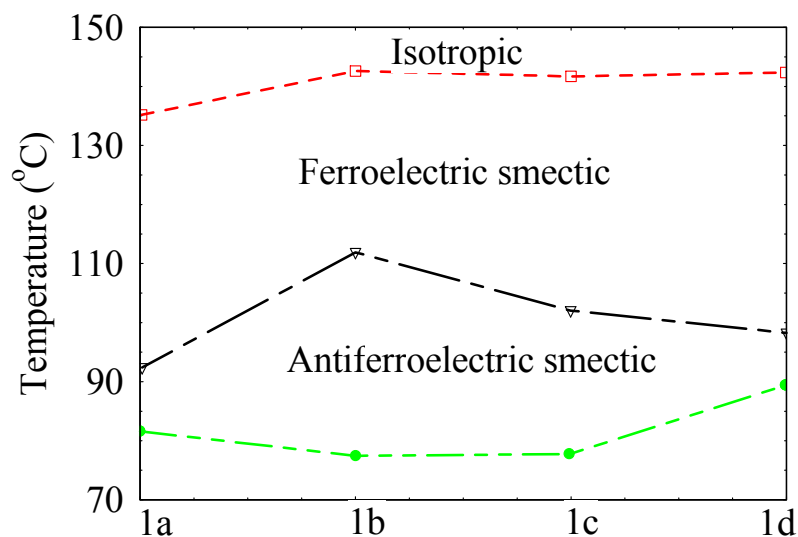
Comp.	chain R	m.p. [ΔH]	c.p. [ΔH]	Cr	T_c [ΔH]	AF	T_c [ΔH]	FE	T_c [ΔH]	Iso	Mol wt [g mol⁻¹]
1ᵃ	**2MeBu**	120.9 [+45.4]	135.8 [+18.0]	●	80.5 [-17.6]	●	92.3 [-0.5]	●	133.7 [-18.0]	●	823.0
1b	**C₈H₁₇**	105.5 [+35.6]	143.6 [+19.8]	●	77.4 [-14.1]	●	111.0 [-0.6]	●	142.4 [-19.5]	●	857.0
1c	**C₁₀H₂₁**	105.7 [+21.0]	143.0 [+19.0]	●	77.7 [-20.1]	●	101.8 [-0.3]	●	141.3 [-19.1]	●	885.1
1d	**C₁₂H₂₅**	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 polarizing microscopic and polarization current measurements.*
Lower part: Molecular weight, transition temperatures and enthalpies (in J/g) of 1a-d as determined by DSC measurements; Note: "●" the phase exists.

The DSC plots of the compounds investigated are depicted in **Figure 3**.
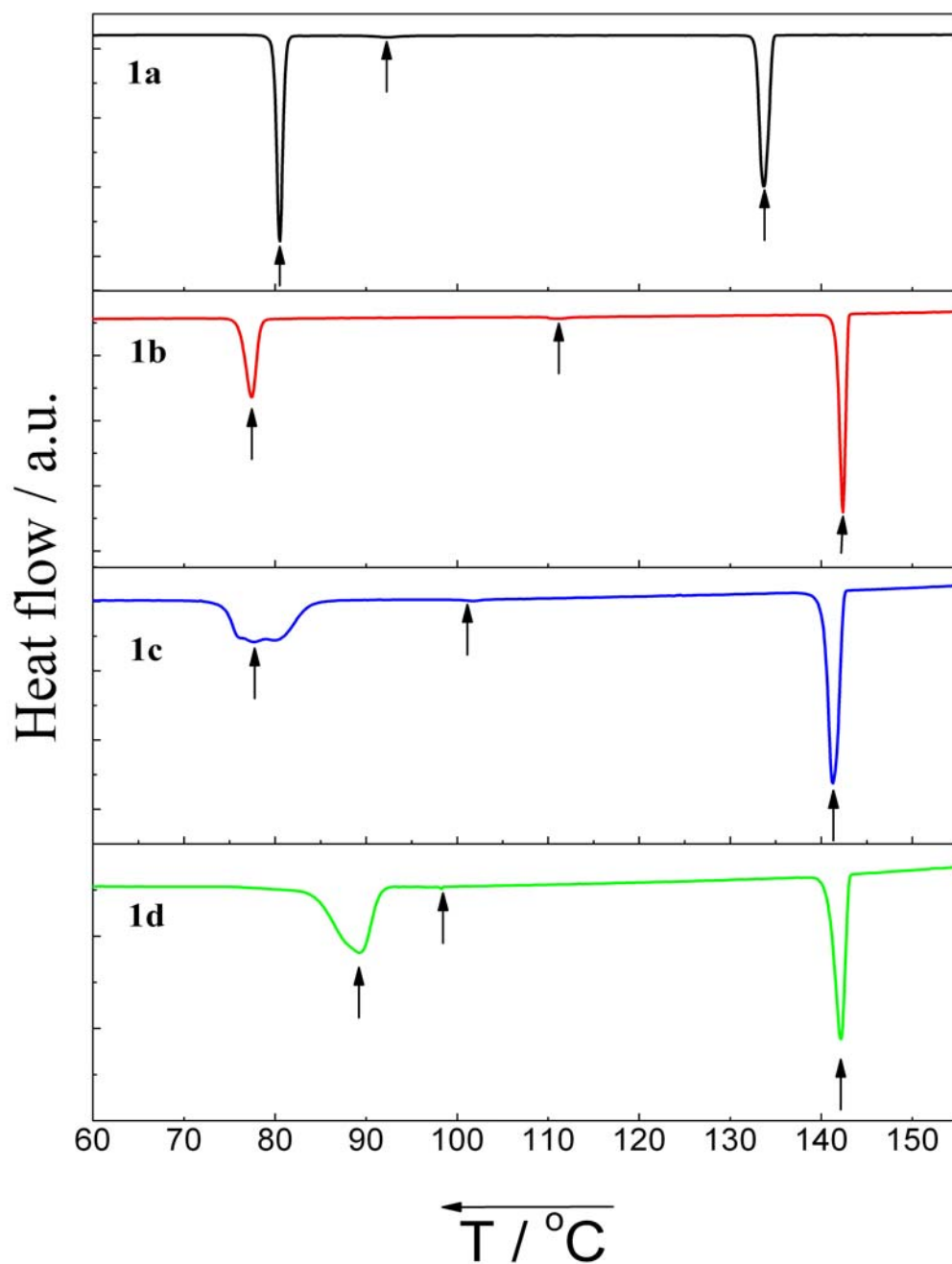

*Figure 3: DSC plots on cooling runs for compounds **1a-d**. Arrows indicate the phase transitions.*

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Textural and DSC measurements reveal two smectic mesophases below the clearing point that increases from 134 ^{o}C at (**1a**) to 142°C (**1b**), then basically stays constant as the chain length increases. The crystallization 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 observed (see top row of **Figure 4/a**). At this transition the enthalpies for all materials show strongly first order transitions with about 18-19J/g enthalpies. The transitions between the two smectic phases are of weakly first order with ΔH~0.2-0.6 J/g transition enthalpies. The phase range of the lower temperature smectic phase depends on the extent of molecular asymmetry: it has only 7-10°C range for **1a** and **1d**, and about 35°C, 25°C range in **1b** and **1c**, respectively. The transitions to the crystalline phases are of first order with transition enthalpies increasing with the length of R.
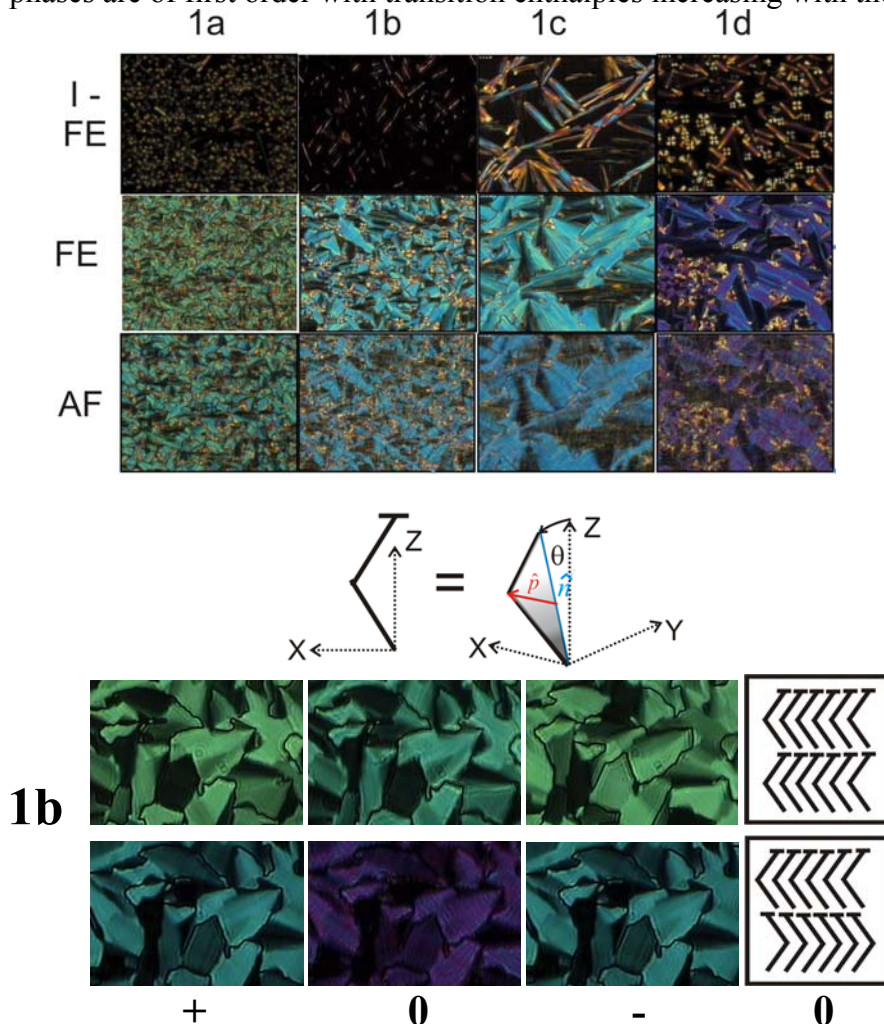
*Figure 4: Upper part: Typical textures observed in polarizing microscope of 5μm cells of **1a-d**. The size of the individual pictures is roughly 250 x 300 μm². 1st row: at the isotropic to ferroelectric smectic transition; 2nd row: ferroelectric (FE) phase; 3rd row: antiferroelectric smectic (AF) phase;*

*Lower part: Textures of 5μm **1b** sample at +20V/μm, 0V/μm and -20V/μm fields and their possible director structure at zero fields with the explanation of notation above the textures. Upper row: FE phase with possible SmC$_s$P$_{FE}$ structure, Lower row: AF phase with possible SmC$_s$P$_{AF}$ structure.*

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The upper temperature mesophase optically is characterized 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 polarizer or analyzer, 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 to synclinic 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 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^oC to a saturated value of about 40° at or below 130^oC. In contrary, 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. Polarization 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 **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 anticlinic ferroelectric states[3].

Up to this point all observations indicate that the smectic phases have simple synclinic structures where the layer polarizations are along the smectic layers, but in the higher temperature phase the polarization is in the same direction in subsequent layers (SmC_sP_{FE}), whereas in the lower temperature phase the polarization is alternating in subsequent layers (SmC_sP_{AF}) (see **Figure 4/b**). However further reveal that this simple picture may not correspond to the real case.

(i) For SmC_sP_{AF} the structure composed by oppositely tilted synclinic stripes, where each synclinic stripe should have larger birefringence than of the field induced anticlinic structure. This does not correspond to our situation shown in the bottom row of **Figure 4/b** where Δn decreased from 0.16 to 0.12 in each stripes formed at zero fields **.**

(ii) According to our measurements the temperature dependences of the magnitude of the spontaneous polarization shows a step-wise increase at the ferroelectric to antiferroelectric transition. (e.g. from $250nC/cm^2$ to $480 nC/cm^2$ for **1a,** and from $100nC/cm^2$ 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. 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 C_1 symmetry.[45,46] (W also e note that at the transition between the ferroelectric and antiferroelectric states there is a co-existence region of around 1 - 2 ^oC, although DSC indicated very week first order transitions for **1a** and **1d**.)
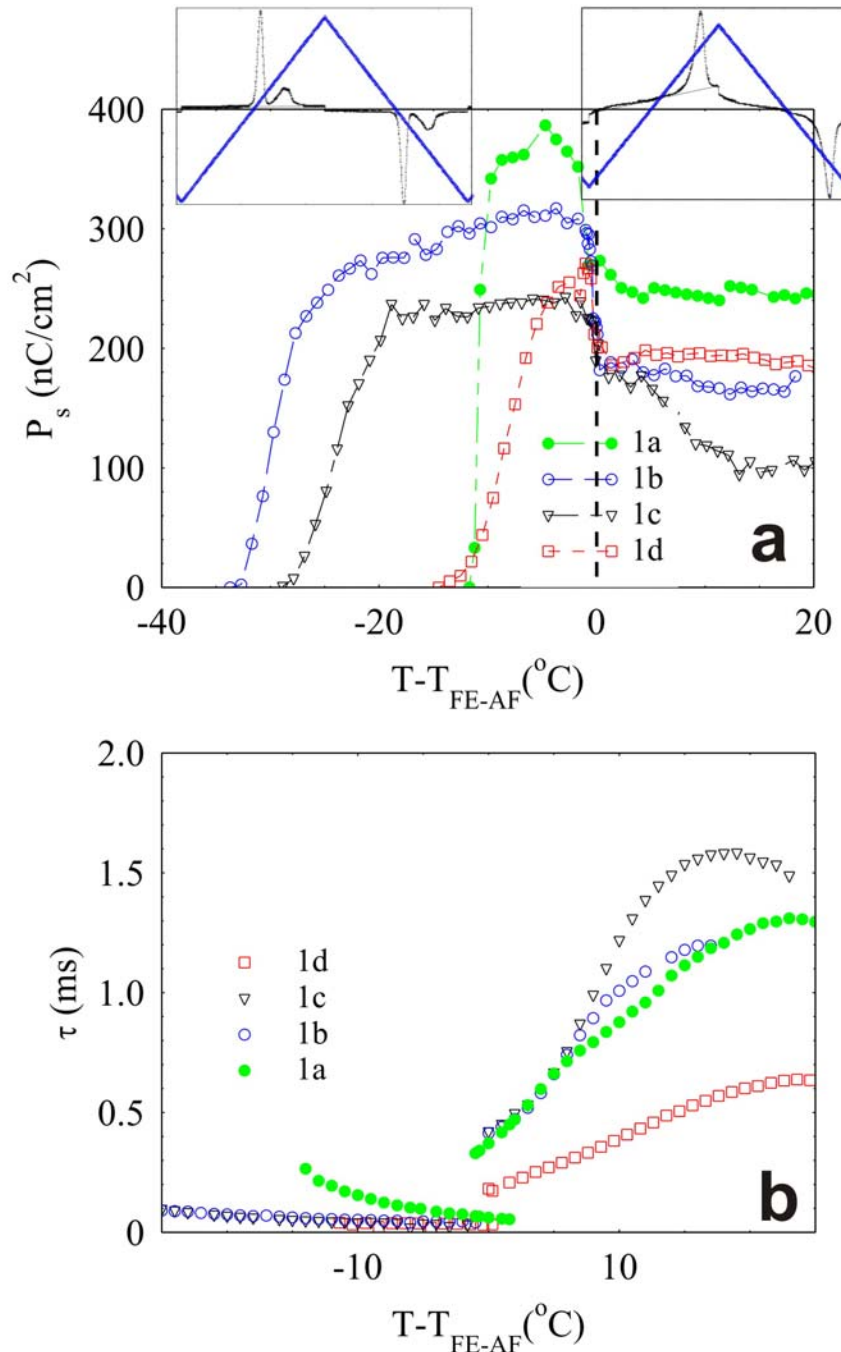
*Figure 5: The magnitude of the spontaneous polarization (a) and the switching time (b) at the function of reduced temperature (T-T$_{TFE-AF}$) of materials **1a-d**. Typical polarization current wave forms under triangular fields are shown at the top of (a). All measurements were performed at a constant cooling rate of 1 $^oC/min$ with an applied triangular (a) or rectangular (b) wave voltages with amplitude of 18 V/um 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 polarization.*

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6. Conclusions

We reported the synthesis of novel bent core 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 as 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. 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 behavior is caused by the combination of rigid biphenyl part in one side chain and 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 behavior. 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 preference is most probably caused by the certain rigidity of the system because of the presence of biphenyl part and by short length of the chiral terminal chain, where the chiral centre is close to the outer phenyl ring.

 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-symmetric materials, indicating that the ferroelectric state is resulted by the molecular asymmetry. Although the key features of the measurements point to synclinic ferroelectric (SmC_sP_{FE}) and antiferroelectric racemic (SmC_sP_A) structures, important details of the temperature dependence of the polarization, and switching time, and the decreased birefringence in the antiferroelectric state indicate more complicated director and layer structure. These results make these new materials worthwhile for further physical studies, such as small angle X-ray which are out of the scope of our present paper.

7. Acknowledgement

8. References

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