Ester Type Banana-Shaped Liquid Crystalline Monomers: Synthesis and Physical Properties

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New ester-type banana (bent-shaped) monomers, 1,3-phenylene bis[4-(alken-1-yloxy)-biphenyl-4-carboxylate]s Ia–Vb, with different substituent(s) on the central phenyl ring (H, CH₃, Cl or NO₂) and alkanyl tails in the side arms (decenyl or undecenyl) were prepared. The analogues IIIa–IVb with 4-chloro- or 4,6-dichloro-substituents exhibited a nematic phase, while Va–Vb with 2-nitro-substituent showed a B₇ phase at relatively low temperature. All the compounds were stable, no degradation or polymerization was observed under applied electric fields or heat treatments. Electro-hydrodynamic instabilities were observed in the nematic phase of each sample. In the B₇ phase of Vb there was an electro-optical switching in the range 112–114.5 °C with a switching time of about 150 μs at 20 V μm⁻¹ field. At lower temperatures no electro-optical switching occurred, but a ferroelectric-type spontaneous polarization of 22 nC cm⁻² could be detected. The bend angle was calculated by the semiempirical CAChe/MOPAC/PM5 method.

Introduction

It has been known since 1996 that achiral banana-shaped (bent-core) molecules may form polar smectic layers with ferroelectric or antiferroelectric behavior. Soon after it became also clear that the layers with tilted director structure may become chiral and can self-assemble in a macroscopically chiral structure, when the layer chirality is the same in adjacent layers, or a racemic structure, when the layer chirality alternates in adjacent layers. This wealth of new phenomena of chirality and polarity has led to a new subfield of liquid crystal research. In the past several years a great number of banana-shaped compounds have been synthesized and characterized, and at least seven different phases (chronologically assigned as B₁–B₇) have been identified. More recently, banana-shaped liquid crystals have also been described that form smectic and/or nematic mesophases. Among the B phases, electro-optical switching has been observed in the smectic B₁, B₃ and B₇ phases. The most widely studied B₇ phase is identified as a tilted antiferroelectric polar smectic (SmCP₀) phase with either synclinic (SmCₜP₀) or anticlinic (SmCₘP₀) structures. The B₁ phase is very unique and interesting due to its beautiful and extraordinary textures and some of them are thought to have a double tilted director structure with C₁ symmetry. The B₁ phase has been designated as a columnar phase with rectangular lattice. The B₃ and B₇ phases are considered to be crystalline phases.

Among rod-shaped liquid crystals, it is well known that azomethine-type compounds (Schiff’s bases) tend to form smectic phases. The first smectic mesophases of banana-shaped molecules with five aromatic rings also had azomethine connecting groups. It is found that the mesophase behavior of azomethane banana molecules is very sensitive to the effects of substituents at various positions on the aromatic rings. The situation is more complicated if the azomethine linking groups are replaced by different groups, like ester, thioester or vinyl-carboxylate groups, so that the banana molecule contains ester-type linking groups only. In fact, a few purely ester-type banana liquid crystals have been published up to now.

So far little work has been devoted to polymers based on banana monomers. Bent-shaped diacrylate monomers were synthesized but showed mesomorphic properties only after polymerization in a mixture with an appropriate banana liquid crystal. In one other work 1,3-diene monomers presented various mesophases but were not stable and suffered degradation under heat or electric field treatment. In our previous work divinyl banana monomers, 1,3-phenylene bis(alkenyloxy)benzoyloxy)benzoates, were prepared with thermal and field stability. These compounds exhibited monotropic B₂ and enantiotropic nematic phases below 100 °C. The aim of this work was to investigate the effect of rigidity and/or flexibility of the arms of banana shaped monomers with five aromatic rings where the terminal chains have polymerizable double bonds at both ends of the molecule in a new class of banana monomers, 1,3-phenylene bis[4-(alkenyloxy)biphenyl-carboxylate]s Ia–Vb (Fig. 1). The effect of substitution and
phase behavior was also studied. In addition, due to the presence of the double bonds in the terminal chains these compounds could also serve as precursors of polymers built up from banana-shaped monomers as was shown in our earlier paper for acrylic diene metathesis polymerization.10

Experimental

Physical investigations

Confirmation of the structures of intermediates and products was obtained by infrared spectra (resolution 4 cm⁻¹) taken with a Nicolet Magna 750 FT-IR spectrophotometer on KBr pellets and ¹H NMR spectra recorded on a Varian XL-400 spectrometer, the chemical shifts referenced to the internal tetramethylsilane peak. ¹H assignments, when necessary, were performed with the aid of homonuclear spin decoupling experiments. Assignments of the proton signals were made according to Fig. 2. The purity of the samples was checked by high performance liquid chromatography (HPLC) with a Merck-Hitachi chromatograph equipped with a Merck RP18 column (Cat. No 16051).

Transition temperatures were measured with an Amplival POL-U polarizing microscope equipped with a Boeotius hot stage. These data were controlled by differential scanning calorimetry using a Perkin-Elmer DSC-7.

High resolution X-ray measurements were carried out in the Midwest Universities Collaborative Access Team (MUCAT) Powder Diffraction station of the Advanced Photon Source of Argonne National Laboratory (λ = 9.684 keV, λ = 1.2803 Å, resolution: 3450 × 3450 and detector is at 378.499 mm from the sample). In the X-ray measurements 20 μm thick samples were sandwiched between 0.1 mm thick microscopy cover slides.

For the polarizing microscopy, electro-optical and polarization current measurements the materials were placed in ready made 4 μm and 10 μm thick cells purchased from Displaytech and EHC, Co., respectively. The liquid crystal mixtures were placed in a computer controlled heat stage (STC200F from INSTEC) and the phase sequences were investigated by polarizing microscopy (BX60 from Olympus), electric current measurements and electro-optical studies. For these measurements a Digital Oscilloscope (HP 54600B), Digital Multimeter (HP 34401A) and Arbitrary Waveform Generator (HP 33120A) were used.

Synthesis

The starting materials, ethyl 4'-hydroxybiphenyl-4-carboxylate (3), resorcinol (7), 2-methyl-resorcinol (8), 4-chloro-resorcinol (9), 4,6-dichloro-resorcinol (10), 2-nitro-resorcinol (11), dec-1-en-1-ol (1a), and undecen-1-ol (1b), were purchased from Aldrich and used without further purification. Preparation and spectroscopic data of 4a, 4b, 5a, 5b, 6a, and 6b are collected in ESI.†

Ethyl 4'-(9-decen-1-yloxy)-1',1'-biphenyl-4-carboxylate (4a)22.

Cr 37.0 °C [5.51] Cr 66.2 °C [6.97] SmE 77.7 °C [0.47] SmA 87.7 °C [0.41] 100.7 °C Iso [2.03 kcal mol⁻¹].

Ethyl 4'-(10-undecen-1-yloxy)-1',1'-biphenyl-4-carboxylate (4b).

Cr 48.1 °C [2.96] Cr 54.2 °C [0.33] SmE 74.5 °C [0.44] SmA 85.2 °C [0.42] 98.8 °C Iso [2.02 kcal mol⁻¹].

4'-(9-Decen-1-yloxy)-1',1'-biphenyl-4-carboxylic acid (5a). Cr 167 °C SmC 251 °C N 252 °C Iso.

4'-(10-Undecen-1-yloxy)-1',1'-biphenyl-4-carboxylic acid (5b)23.

Cr 160 °C SmC 245 °C N 246 °C Iso.

4'-(9-Decen-1-yloxy)-1',1'-biphenyl-4-carbonyl chloride (6a). Mp. 82 °C.

4'-(10-Undecen-1-yloxy)-1',1'-biphenyl-4-carbonyl chloride (6b). Mp. 80 °C.

General procedure for the preparation of the monomers Ia–Vb

Resorcinol derivatives (10 mmol) and an excess of triethyl amine (30 mmol) were dissolved in dry 2-butanol (20 ml) and 4'-alken-1-yloxy)-1',1'-biphenyl-4-carbonyl chloride (22 mmol) was added dropwise. The reaction mixture was puried by flash chromatography on a Kieselgel 60 (0.063-0.20 mm) column with 1,2-dichloroethane elution. Phase transition temperatures and enthalpies are summarized in Table 1. The reaction conditions, quantities of the reagents and yields for the final compounds Ia–Vb are summarized in ESI.†

1,3-Phenylene bis[4-(9-decen-1-yloxy)-1',1'-biphenyl-4-carboxylate (Ia, 10PBBC).

IR νmax(KBr)/cm⁻¹: 3078 (νas =CH₂, vinyl), 2924 (νs =CH₂), 2853 (νCH₃), 1730 (νC=O, ester), 1641 (νC=O, vinyl), 1603, 1528 and 1497 (νCArC₅H₃), 831 (γC =CArH, p-disub.), 783 and 692 (γC =CArH and γC=CAr, m-disub.), 11 H NMR (CDCl₃); δ = 1.25-2.08 (m, 28H, aliphatics), 4.04 (t, 4 H, 6H, 2 × OCH₂), 4.93 (m, 2H, J = 10.3 Hz, =CH₂), 4.98 (m, 2H, Jtrans = 17.1 Hz, =CH₂), 7.62 (m, 2H, CH⁻), 6.98 (m, 4H, 2 × H3⁻ + 2 × H5⁻), 7.60 (m, 2H, CH⁻), 7.45 (m, 4H, 2 × H3⁻ + 2 × H5⁻), 8.21 (m, 4H, 2 × H2⁻ + 2 × H6⁻); elemental analysis calcd (% for C₂₉H₂₄O₉: 137.94% C, 80.17, H, 7.50, found C, 80.11, H, 7.48.

1,3-Phenylene bis[4-(10-undecen-1-yloxy)-1',1'-biphenyl-4-carboxylate (Ib, 11PBBC).

IR νmax(KBr)/cm⁻¹: 3079 (νas =CH₂, vinyl), 3043 (νC=CArH), 2923 (νs =CH₂), 2852 (νCH₃), 1730 (νC=O, ester), 1642 (νC=C, vinyl), 1603 (νC=CArH), 831 (γC =CArH, p-disub.), 783 and 693 (γC =CArH and γC=CAr, m-disub.). 1H NMR(CDCl₃); δ = 1.3-2.06 (m, 32H, 16H, CH₂), 4.03 (t, 4 H, J = 6.8 Hz, 20CH₂), 4.94 (m, 2H, Jcis = 10.1 Hz, CH⁻), 5.00 (m, 2H, Jtrans = 17.1 Hz, CH⁻), 5.82 (m, 2H, =CH⁻), 7.00 (m, 4H, 2(H3⁻ and H5⁻)), 7.19 (dd, 2H, J = 8.2 + 2.2 Hz, H₄ and
H6, 7.23 (t, 1H, J = 2.2 Hz, H2), 7.49 (t, 1H, J = 8.2 Hz, H5), 7.59 (m, 4 H, 2(H2’ and H6’)), 7.69 (m, 4 H, 2(H3’ and H5’)), 8.22 (m, 4 H, 2(H2’ and H6’)); elemental analysis calcld (%) for C24H26O8 (507.09): C, 80.36; H, 7.74; found C, 80.29, H, 7.72.

2-Methyl-1,3-phenylene bis[4-(decan-1-yloxy)-1,1’-biphenyl-4-carboxylate] (IIa, 10MePBBC). IR νmax(KBr)/cm⁻¹: 3078 ν(CH=CH2, vinyl), 2924 ν(CH3, CH2), 2854 ν(CH2), 1731 ν(C=O, ester), 1641 ν(C=C, vinyl), 1603 ν(C=C, p-disubst.), 767 and 693 ν(C=CH2, 1,2,3-trisubst.). "H NMR (CDCl₃): δ = 1.3–2.08 (m, 28H, 16CH2), 2.16 (s, 3H, 2-CH3), 4.05 (t, 4 H, J = 6.8 Hz, 20CH2), 4.90 (m, 2H, J = 10.2 Hz, CH=), 5.02 (m, 2H, Jtrans = 17.1 Hz, CH=), 5.83 (m, 2H, CH=), 7.00 (m, 4 H, 2(H3’ and H5’)), 7.18 (d, 2H, J = 8.3 Hz, H4 and H6), 7.32 (t, 1H, J = 8.3 Hz, H5), 7.59 (m, 4 H, 2(H2’ and H6’)), 7.72 (m, 4 H, 2(H3’ and H5’)), 8.275 (m, 4 H, 2(H2’ and H6’)); elemental analysis calcld (%) for C24H26O8 (507.09): C, 80.27, H, 7.63, found C, 80.22, H, 7.60.

2-Methyl-1,3-phenylene bis[4-(undecan-1-yloxy)-1,1’-biphenyl-4-carboxylate] (IIb, 11MePBBC). IR νmax(KBr)/cm⁻¹: 3078 ν(CH=CH2, vinyl), 3037 ν(CH3, CH2), 2923 ν(CH3, CH2), 2852 ν(CH2), 1741 and 1726 ν(C=O, ester), 1642 ν(C=C, vinyl), 1604 ν(C=C, p-disubst.), 833 ν(C=CH2, p-disubst.), 7.83 and 690 ν(C=C, 1,2,3-trisubst.). "H NMR (CDCl₃): δ = 1.3–2.08 (m, 32H, 16CH2), 2.18 (s, 3H, 2-CH3), 4.03 (t, 4 H, J = 6.8 Hz, 20CH2), 4.93 (m, 2H, J = 10.2 Hz, CH=), 5.00 (m, 2H, Jtrans = 17.1 Hz, CH=), 5.81 (m, 2H, CH=), 6.99 (m, 4 H, 2(H2’ and H5’)), 7.17 (d, 2H, J = 8.3 Hz, H4 and H6), 7.35 (t, 1H, J = 8.3 Hz, H5), 7.58 (m, 4 H, 2(H2’ and H6’)), 7.70 (m, 4 H, 2(H3’ and H5’)), 8.25 (m, 4 H, 2(H2’ and H6’)); elemental analysis calcld (%) for C24H26O8 (507.09): C, 81.12; C, 80.45, H, 7.86, found C, 80.39, H, 7.81.

4-Chloro-1,3-phenylene bis[4-(decan-1-yloxy)-1,1’-biphenyl-4-carboxylate] (IIa, 10ClPBBC). IR νmax(KBr)/cm⁻¹: 3076 ν(CH=CH2, vinyl), 3041 ν(CH3, CH2), 2926 ν(CH3, CH2), 2854 ν(CH2), 1743 ν(C=O, ester), 1641 ν(C=C, vinyl), 1604 ν(C=C, p-disubst.). "H NMR (CDCl₃): δ = 1.3–2.08 (m, 28H, 16CH2), 4.02 (t, 4 H, J = 6.8 Hz, 20CH2), 4.93 (m, 2H, J = 10.2 Hz, CH=), 4.98 (m, 2H, J = 17.2 Hz, CH=), 5.82 (m, 2H, CH=), 6.99 (m, 4 H, 2(H3’ and H5’)), 7.19 (dd, 1H, J = 8.8 and 2.7 Hz, H6), 7.33 (d, 1H, J = 2.7 Hz, H2), 7.54 (d, 1H, J = 8.8 Hz, H5), 7.59 (m, 4 H, 2(H2’ and H6’)), 7.59–7.74 (m, 4 H, 2(H3’ and H5’)); elemental analysis calcld (%) for C23H25ClO8 (513.84): C, 76.78, H, 7.06, Cl, 4.36, found C, 76.72, H, 6.99, Cl, 4.32.

4-Chloro-1,3-phenylene bis[4-(undecan-1-yloxy)-1,1’-biphenyl-4-carboxylate] (IIb, 11ClPBBC). IR νmax(KBr)/cm⁻¹: 3077 ν(CH=CH2, vinyl), 3041 ν(CH3, CH2), 2926 ν(CH3, CH2), 2853 ν(CH2), 1743 ν(C=O, ester), 1641 ν(C=C, vinyl), 1604 ν(C=C, p-disubst.). "H NMR (CDCl₃): δ = 1.25–2.06 (m, 32H, 16CH2), 3.98 (t, 4 H, J = 6.8 Hz, 20CH2), 4.90 (m, 2H, J = 10.2 Hz, CH=), 4.98 (m, 2H, Jtrans = 17.2 Hz, CH=), 5.82 (m, 2H, CH=), 6.99 (m, 4 H, 2(H3’ and H5’)), 7.19 (dd, 1H, J = 8.8 and 2.7 Hz, H6), 7.33 (d, 1H, J = 2.7 Hz, H2), 7.54 (d, 1H, J = 8.8 Hz, H5), 7.59 (m, 4 H, 2(H2’ and H6’)), 7.59–7.74 (m, 4 H, 2(H3’ and H5’)); elemental analysis calcld (%) for C23H25ClO8 (513.84): C, 76.78, H, 7.06, Cl, 4.36, found C, 76.72, H, 6.99, Cl, 4.32.

Table 1 Phase transitions (in °C) and enthalpies [in kcal mol⁻¹] of the 1,3-phenylene bis[4-(alken-1-yloxy)-1,1’-biphenylcarboxylates]

<table>
<thead>
<tr>
<th>Code</th>
<th>n</th>
<th>R²</th>
<th>R⁴</th>
<th>R⁵</th>
<th>C₁</th>
<th>C₂</th>
<th>N</th>
<th>B⁷</th>
<th>I</th>
</tr>
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<tr>
<td>Ia</td>
<td>8</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>143.6 [11.46]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ib</td>
<td>9</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>131.2 [1.69]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Ia'</td>
<td>8</td>
<td>CH₁</td>
<td>H</td>
<td>H</td>
<td>140.5 [13.05]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Ib'</td>
<td>9</td>
<td>CH₁</td>
<td>H</td>
<td>H</td>
<td>138.6 [10.57]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>IIIa</td>
<td>8</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>84.5 [4.02]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>IIIb</td>
<td>9</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>75.5 [2.11]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>IVa</td>
<td>8</td>
<td>H</td>
<td>Cl</td>
<td>Cl</td>
<td>85.9 [5.52]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>17.6 [0.19]</td>
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<tr>
<td>IVb</td>
<td>9</td>
<td>H</td>
<td>Cl</td>
<td>Cl</td>
<td>81.8 [0.18]</td>
<td>—</td>
<td>—</td>
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<tr>
<td>V</td>
<td>8</td>
<td>NO₂</td>
<td>H</td>
<td>H</td>
<td>74.9 [3.97]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>119.2 [10.84]</td>
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<tr>
<td>Vb</td>
<td>9</td>
<td>NO₂</td>
<td>H</td>
<td>H</td>
<td>79.8 [7.73]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>107.2 [0.22]</td>
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* Additional unidentified mesophase at 63.2 °C, ΔH = 6.78 [kcal mol⁻¹]. * Additional unidentified mesophase at 50.1 °C, ΔH = 7.15 [kcal mol⁻¹].
1,2,3-trisubst.). H NMR (CDCl₃): δ = 1.27–2.07 (m, 32H, 16CH₂), 4.02 (t, 4 H, J ~ 6.7 Hz, 20CH₂), 4.96 (m, 2H, Jcis ~ 10.2 Hz, CH₃), 5.00 (m, 2H, Jtrans ~ 17.1 Hz, CH₃), 7.00 (m, 4 H, 2(H₃ and H₅)), 7.42 (d, 2H, J ~ 7.4 Hz, H₄ and H₆), 7.58 (m, 4 H, 2(H₃ and H₅′)), 7.66 (t, 1H, J ~ 7.4 Hz, H₅), 7.70 (m, 4 H, 2(H₃′ and H₅′)), 8.14 (m, 4 H, 2(H₂′ and H₆′)). Elemental analysis calcd (%) for C₈₅H₆₁NO₈ (852.08): C, 76.12, H, 7.22, N, 1.64 found C, 76.08, H, 7.19 N, 1.61.

**Results and discussion**

**Synthesis**

For the synthesis of the key intermediates, 4'-alkenyloxy-biphenyl-4-carboxylic acids we carried out a Williamson-type ether formation on ethyl 4'-hydroxy-biphenyl-4-carboxylate with the appropriate alkenyl bromide (n ~ 8 and 9, respectively) (Scheme 1). Hydrolysis of the esters allowed the 4'-(alken-1-yloxy)-1,1'-biphenyl-4-carboxylic acids to be obtained with high purity and yield in a short reaction time. An alternative procedure based on the direct reaction of 4'-hydroxy-biphenyl-4-carboxylic acid with alkenylbromides in the presence of potassium hydroxide in ethanol/water solution led to low purity compounds in low reaction yields. Reaction with oxalyl chloride of the carboxylic acids then led to the corresponding acid chlorides which were finally reacted with the substituted resorcinol of choice.

The HPLC chemical purity of the monomers Ia–Vb was >99.8%.

**Phase properties**

Most banana liquid crystals contain five phenyl rings, the overall bent shape deriving from a central 1,3-phenylene core. Starting from this general formula, several options for variation of the chemical structure may be considered, including the introduction of different substituents on and interconnecting groups between the phenyl rings and the addition of terminal flexible tails.

We focused our attention on the nature of the substituents on the central phenyl ring of purely ester-type banana mesogens (Fig. 1). One special variation of the chemical structure was the use of alkenyl chains as terminal groups. The C=C double bonds of the vinyl groups in fact may be exploited to incorporate banana mesogens into new structures of polymers. The monomers Ia–Vb comprised a central 1,3-phenylene ring from resorcinol carrying substituent(s) of various nature (R², R⁴ = H, CH₃, Cl, NO₂) at different sites (2-, 4-, 6-positions). Either a decenyl or an undecenyl segment at both arm sides was used as the terminal tail.

The phase transition temperatures and sequences of the monomers greatly depended on their chemical structure (Table 1). No mesophase was formed by either the unsubstituted Ia, Ib or 2-methyl-substituted IIa, IIb derivatives. Each of the chloro-substituted analogues IIIa–IVb presented a nematic phase. The introduction of a large chlorine substituent at the 4-position widens the bend angle of the unsubstituted 1,3-phenylene ring (120°) to ~135°, rendering the molecules less prone to polar packing in layers. This ability is more depressed in 4,6-dichloro-substituted molecules, in which the bend angle is further enlarged resulting in an elongated, close to rod-like conformation as was previously reported for other azomethine banana compounds. Consistent with this interpretation, IVa and IVb formed an enantiotropic, high-clearing nematic phase relative to IIIa and IIIb, for which the nematic phase was monotropic. It is worth mentioning that IIIb was difficult to crystallize and the nematic mesophase could be frozen in the glassy state on cooling below the glass transition temperature at Tg ~ 74 °C. On the other hand, the 2-nitro-derivatives Va and Vb exhibited a B₇ phase that was.

![Scheme 1](image)
enantiotropic for the latter sample only. The finding of a B phase in the present monomers supports previous observations that the introduction of dipolar groups, like the NO$_2$ group, at the 2-position of the central phenyl ring favors the occurrence of such phases.\(^6\)

One should note that the compounds without substituents or having electron-donating groups on their central aromatic ring did not show any mesophase property. By contrast, banana nematic or B phases were present when electron-withdrawing substituents (like chloro or nitro) were connected to the central phenyl ring. Prevention of the onset of a richer variety of mesophases was most probably due to the presence of very rigid arms built up from biphenyl carboxylate structures.

**Physical properties**

We investigated the optical textures and electro-optical behavior of the monomers IIIa–Vb and present the results in separate sections.

*IIIa* (10ClPBBC). The monotropic nematic phase appeared on cooling to 72 °C with textures in which the optical axis was oriented along the rubbing direction. Just before freezing at 60 °C some area became completely dark (Fig. 3a and b). X-ray analysis confirmed the nematic structure but could not reveal the nature of the optically isotropic metastable state. IIIb (11ClPBBC). The X-ray patterns of IIIb only presented a diffuse diffraction at wide angles corresponding to a nematic phase. We note that no diffuse peak was observed in the small angles indicating the absence of layer fluctuations. Similar to IIIa, the textures of nematic IIIb also showed a uniform planar alignment (Fig. 3c) in rubbed polymer coated cells. At frequencies above the hydrodynamic instability region (> 100 Hz) no field-induced realignment was observed thus indicating a negative dielectric anisotropy. The only difference was that here the director fluctuation appeared to be even stronger than in the previous case, and the electro-hydrodynamic instabilities weaker. On cooling, an additional unidentified metastable X phase was formed at 62 °C with strong turbulence and dark fan shaped domains. A typical texture in the X phase is shown in Fig. 3d. Interestingly, the texture shows electro-optical switching under fields larger than 15 V μm$^{-1}$. Under these conditions the extinction brushes rotated by about ±10° with the frequency of the field. However, no simultaneous polarization current peak could be detected. We suggest that the X phase has a highly ordered smectic or columnar structure. Unfortunately X-ray studies of this phase are difficult due to its metastable nature and its precise structure remains to be fully characterized.

*IVa* (10DCIPBBC). This material also presented uniform alignment in the nematic phase. At high frequencies there was no realignment indicating a negative dielectric anisotropy. At high frequencies (above ~ 200 Hz) and above 3.5 V μm$^{-1}$ instabilities in the form of regular stripes appeared as shown in Fig. 4a. At low frequencies the stripes were decorated with "worm"-like defects as shown in Fig. 4b. IVb (11DCIPBBC). Similar to IVa, in its nematic phase the director aligned parallel to the rubbing direction quite well (see Fig. 4c). Under applied electric fields up to 100 V there was no obvious texture change in the frequency range f > 50–100 Hz. At low frequencies f < 10–50 Hz (depending on the field and temperature) a hydrodynamic instability occurred with wide stripes (~ 50 μm) perpendicular to the rubbing directions decorated with narrow (5 μm wide) stripes running about ±45° with respect to the main stripes (see Fig. 4d). In the subsequent wide stripes the direction of the narrow stripes interchanged. Such textures indicate electro-hydrodynamic instabilities of ionic origin.

On cooling from the isotropic phase, both Va (10NO2PBBC) and Vb (11NO2PBBC) formed filaments (ribbons) and other exotic chiral objects characteristic of B$_{T}$ textures (see Fig. 5a and c). Application of electric fields during the phase transition made the smectic front undergo a jerky motion with the frequency of the applied field. This is reminiscent of the behavior

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**Fig. 3** Textures of IIIa and IIIb. Pictures indicate 140 μm × 110 μm areas. Polarizers are vertical and horizontal. Upper row: 8 μm cell of 10ClPBBC. (a) Uniform texture in the nematic phase at 70 °C. Polarizers make ±45° angle with the rubbing direction. (b) Texture during crystallization at 60 °C. The coexistence of crystalline and optically isotropic domains (dark between crossed polarizers) can be seen. Lower row: 4 μm cell of 11ClPBBC. (c) Uniform texture in the nematic phase at 70 °C. Rubbing direction along the arrow. (d) Texture in the unidentified X phase at 60 °C.
of some \( B_7 \) materials, which were identified as smectics with triclinic symmetry.\(^{12}\) Both materials showed electro-optical switching in about 2–5 °C range below the isotropic transitions. In addition, ferroelectric type polarization peaks appeared under triangular waveform excitations (see Fig. 6), that disappeared in the isotropic phase and decreased slowly at lower temperatures (for \( V_b \) it could be detected down to 40 °C). The maximum of the polarization is about 55 nC cm\(^{-2} \) for \( V_a \) and 22 nC cm\(^{-2} \) for \( V_b \). These values are much smaller than those typically observed for other bent core smectics and should be related to their relatively small molecular dipoles. For example, the molecular dipole of \( V_b \) is 1.92 debye (see Table 2), which with molar masses of about 1000 g mol\(^{-1} \) and mass density of about 1 g cm\(^{-3} \), would add up to about 300 nC cm\(^{-2} \) for
CAChe/MOPAC/PM5 calculations on the monomers

Heat of formation/ kcal mol$^{-1}$ | Bend angle/ degree | $\mu$/D | $L$\,/Å
---|---|---|---
Ib | −117.6 | 133 | 1.82 | 50.1
IIb | −117.8 | 133 | 1.89 | 50.8
IIIb | −117.6 | 133 | 1.89 | 50.8
IVb | −118.2 | 122 | 3.20 | 47.9
Vb | −117.4 | 110 | 1.92 | 44.8

* Distance between the outermost carbon atoms in the two side arms.

Quantum-chemical calculations

The quantum-chemical calculations were carried out by the semi-empirical CAChe/MOPAC/PM5 method. The PM5 Hamiltonian is claimed to have an improvement in accuracy by a factor of 4, compared to AM1 or PM3. Table 2 contains the heat of formation of the most stable conformers, the dipole moments and the bend angles of the compounds in gas phase, and the distance between the most distant carbons of the two arms of the mesogens with undecenyl tails. We expect that no appreciable differences would be computed for the mesogens with just shorter decenyl tails. It must be emphasized, however, that the calculated data in Table 2 are valid for isolated molecules like those in the gas phase. In condensed phases like those of liquid crystals, due to intermolecular interaction the molecular shape can be substantially changed. One should note that the evaluated bend angle was lowest for the 2-nitro-derivative Vb. This value is close to the tetrahedral angle and may suggest a better suitability to form a B phase for this type of bent-shaped structure. The other derivatives investigated possessed much wider bend angles (>120°). However, the bend angle computed for Vb showed a large deviation (Table 2) from the empirical results obtained by $^1$H NMR spectroscopy, which gave a value of about 156°. The bend angles in the mesophase are under investigation by $^1$H NMR spectroscopy of appropriately deuterated analogues. On the other hand, the 4,6-dichloro-derivative presented the greatest dipole moment in the series (3.20 D). The optimized structures derived by CAChe/MOPAC/PM5 are illustrated in Fig. 8 for representative monomers.

Conclusion

The studied 1,3-phenylene bis[4′-(alken-1-yloxy)-1,1′-biphenyl-4-carboxylate]s present a complex phase dependence on the chemical structure, with nematic, smectic or B phases being formed in the different analogues. It is remarkable that the parent, unsubstituted banana monomers do not present liquid crystal behavior, not even monotropic in character. Nonetheless, the mesophase ranges appear at relatively low temperatures compared to other nematic bent core materials. Thus, fine details of the chemical structure can affect significantly the mesophase behavior in banana molecules. The structural requirements for this class of liquid crystal materials appear to be more stringent than for calamitic mesogens, for which more reliable guidelines are available for the design of materials.
with desired phases and physical properties. One special feature of these banana monomers may be associated with the electro-hydrodynamic instabilities in the nematic phase. They indicate unconventional behavior with possible involvement of flexoelectricity, and further investigations are in progress. The \( B_2 \) structure of the 2-nitro-derivatives also has one of the lowest temperature ranges in the literature, which should make easier future studies of the polarization and electro-optical switching properties in such materials.

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References