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Ferroelectric liquid crystals derived from isoleucine I. Synthesis and characterization

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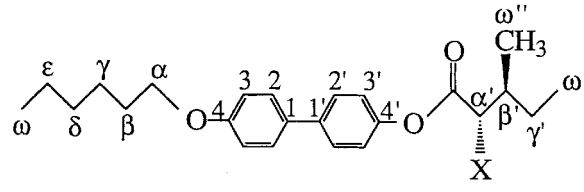
A series of ferroelectric liquid crystals (FLCs), 4′(3-methyl-2-halopentanoyloxy)-4-hexyloxybiphenyls (3M2**X**PHOB, **X** = **F** for fluorine, **C** for chlorine, **B** for bromine) and their racemates (3M2**X**PHOB-R), were synthesized and characterized. The FLCs contain a chiral tail comprised of α-halo acids which are derived from L-isoleucine (DL-isoleucine for the racemates). The mesogens were characterized by high-resolution ^{1}H and ^{13}C NMR and their phase behaviour was studied by optical microscopy and differential scanning calorimetry. The chloro and bromo derivatives show both chiral smectic C (SmC*) phases and smectic A (SmA) phases, while the fluoro derivatives exhibit only a SmA phase. The spontaneous polarization of 3M2**C**PHOB and 3M2**B**PHOB were measured in the respective SmC* phases; that of the fluoro derivative was inferred by extrapolating its concentration dependent polarization in an achiral SmC solvent, a racemic mixture of 3M2**B**PHOB.

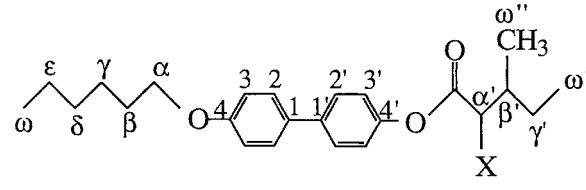
1. Introduction

Since the discovery of ferroelectricity in the chiral, tilted smectic C phase of *p*-decyloxybenzylidene-*p*′-amino-2-methylbutylcinnamate by Meyer *et al.* [1], considerable efforts have been devoted to the synthesis of new liquid crystalline materials. The focus is on structures that give rise to stable SmC* phases and large spontaneous polarizations. The relationship between molecular structure and ferroelectricity is still a subject of controversy. Chirality, for example, has always been believed to be a prerequisite for ferroelectricity, but recently researchers have speculated that achiral, kinked molecules can also lead to ferroelectricity [2–5].

Recently Photinos and Samulski described a model [6] that appears to be capable of predicting spontaneous polarization from the FLCs' molecular structure [7]. In order to make available more systematic data on ferroelectric liquid crystals (FLCs), to test such models, we synthesized a series of FLCs with different halogens in their chiral chains. In this series the spontaneous polarization will be influenced by only minimal variations in molecular structure—changing the halogen at the chiral centre. In a separate study, the segmental orientational order parameters exhibited by these liquid crystals were measured with NMR [8]. Herein we present the synthesis and characterization of a series of liquid crystals; 4′(3-methyl-2-halopentanoyloxy)-4-hexyloxybiphenyls (3M2**X**PHOB, where **X** = **F** represents fluorine, **C** chlorine, and **B** bromine) and their racemates (3M2**X**PHOB-R).



X = Fluorine (3M2**F**PHOB), Chlorine (3M2**C**PHOB), Bromine (3M2**B**PHOB)



X = Fluorine (3M2**F**PHOB-R), Chlorine (3M2**C**PHOB-R), Bromine (3M2**B**PHOB-R)

2. Synthesis

The series of FLCs were synthesized as outlined in the scheme. The α-haloacyl chlorides were prepared

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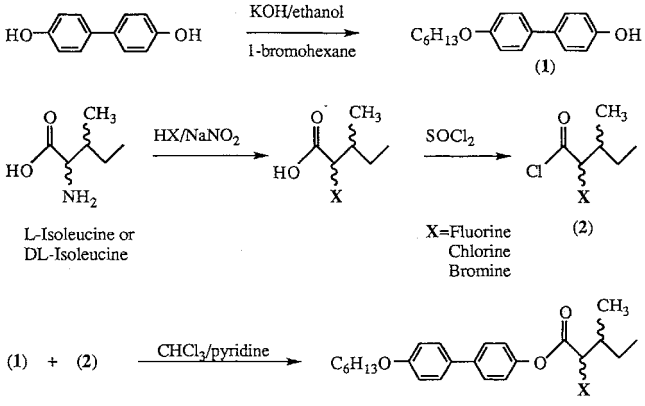

X = Fluorine (3M2**F**PHOB), Chlorine (3M2**C**PHOB), Bromine (3M2**B**PHOB)

Fluorine (3M2**F**PHOB-R), Chlorine (3M2**C**PHOB-R), Bromine (3M2**B**PHOB-R)

Scheme

using known literature procedures [9–11] and subsequently coupled with 4-hexyloxy-4′-hydroxybiphenyl to obtain the enantiomerically pure [12] α-halo ester compounds (3M2**F**PHOB, 3M2**C**PHOB and 3M2**B**PHOB) and their racemates (3M2**F**PHOB-R, 3M2**C**PHOB-R and 3M2**B**PHOB-R).

3. Results and discussion

The thermal properties of the 3M2**X**PHOB and 3M2**X**PHOB-R series are presented in the table (K and K′ refer to different crystalline polymorphs).

A SmA phase with a focal conic texture could be readily recognized for all three pure mesogens and the racemates. Upon cooling, only 3M2**C**PHOB, 3M2**B**PHOB and their racemates showed the broken focal-conic texture indicative of a SmC* phase (achiral SmC phases for the racemates). The mesogen 3M2**B**PHOB has been reported before but with a different phase behaviour [13]. We found for 3M2**B**PHOB a crystal to SmC* transition at 45·9°C, a SmC* to SmA transition at 47·3°C, and a SmA to isotropic transition at 55·1°C. Ozaki *et al.* [13] found a crystal to SmC* transition at 47°C and a SmC* to isotropic transition at 55°C. We believe that this latter phase identification could be simply an error in the data entry of their table, but they fail to report the lower temperature smectic (SmC*). For the record, however, we note that in their synthesis of 3M2**B**PHOB they use DCC as a coupling agent. Sierra *et al.* [12] found that the use of DCC as coupling agent may lead to racemization. The fluoro derivative, 3M2**F**PHOB, has not been reported before. Unfortunately, a SmC* phase could not be observed.

Table. Transition temperatures (°C) of the 4′(3-methyl-2-halopentanoyloxy)-4-hexyloxybiphenyls.

	K		K′		S_c^*, S_c		S_A		I
3M2**F**PHOB	69·4	•	79·4				•	81·9	•
3M2**C**PHOB			49·0	•	53·6	•		63·1	•
3M2**B**PHOB			45·9	•	47·3	•		55·1	•
3M2**F**PHOB-R	59·9	•	83·6				•	90·6	•
3M2**C**PHOB-R			44·8	•	50·9	•		63·5	•
3M2**B**PHOB-R			34·2	•	40·1	•		50·0	•

The thermodynamic behaviour of these compounds is summarized in figure 1. The racemates, 3M2**F**PHOB-R, 3M2**C**PHOB-R and 3M2**B**PHOB-R, showed broader liquid crystalline ranges relative to their enantiomerically pure counterparts.

The spontaneous polarization ($\mathbf{P}_s$) measurements of 3M2**C**PHOB and 3M2**B**PHOB as a function of temperature are shown in figure 2. The $\mathbf{P}_s$ values at the reduced temperature $T_{red}=0{\cdot}99$ are 296 nC cm^{-2} for 3M2**C**PHOB and 78 nC cm^{-2} for 3M2**B**PHOB. (As a

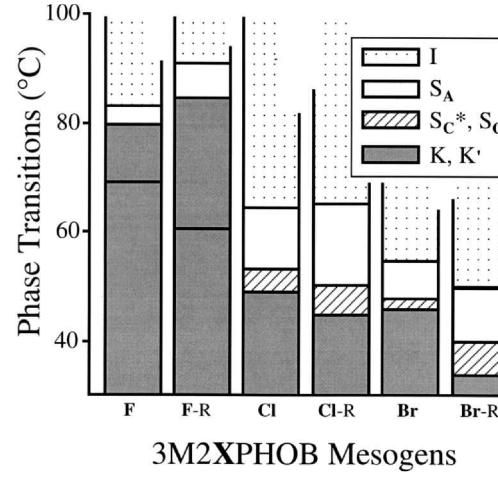

Figure 1. Mesophase ranges for pure 3M2**X**PHOB and their respective racemates.

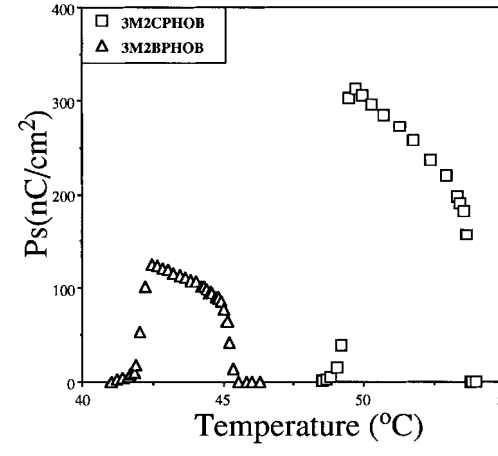

Figure 2. The spontaneous polarization of 3M2**C**PHOB and 3M2**B**PHOB as a function of temperature.

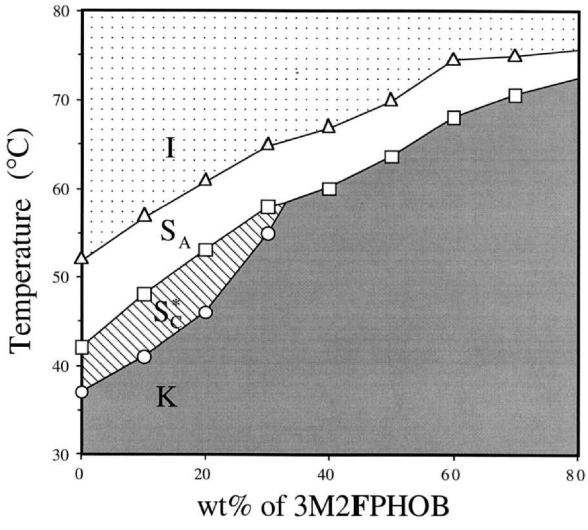

Figure 3. The phase behaviour of 3M2**F**PHOB in a zero-$\mathbf{P}_S$ solvent (65:35 mixture of 3M2**B**PHOB-R and 3M2**B**PHOB).

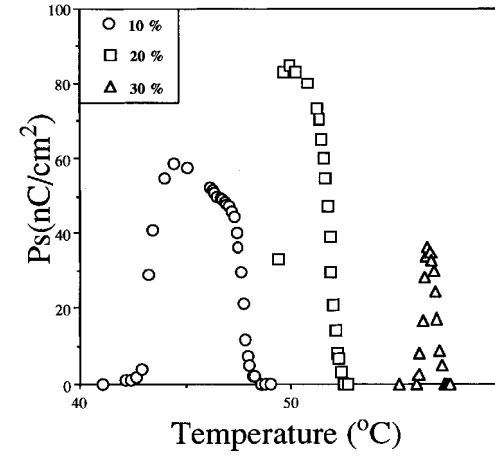

Figure 4. The spontaneous polarization of 3M2**F**PHOB measured at three different concentrations as a function of temperature.

working definition we define $T_{red} = T/T_{onset}$, and T_{onset} is the temperature at which $\mathbf{P}_s$ first becomes observable.)

Since 3M2**F**PHOB does not exhibit a SmC* phase, we measured its spontaneous polarization in an achiral solvent at different concentrations and extrapolated the concentration dependence of our findings to the pure mesogen. For this purpose we used a 65:35 mixture of 3M2**B**PHOB-R and 3M2**B**PHOB as the solvent. (We found that our preparations of neat 3M2**B**PHOB-R exhibited some spontaneous polarization undoubtedly because of a stoichiometric imbalance in stereo isomers of the mesogen precusors, e.g. DL-isoleucine.) The 65:35 mixture, i.e. the actual racemate of 3M2**B**PHOB-R, shows a relatively broad SmC phase but no measurable spontaneous polarization. The phase behaviour of 3M2**F**PHOB in the 3M2**B**PHOB-R, zero $\mathbf{P}_s$, solvent at different solute concentrations is shown in figure 3.

The spontaneous polarization of solutions of 3M2**F**PHOB was measured at three different concentrations (10, 20 and 30%) in the SmC phase of 3M2**B**PHOB-R. The findings are presented in figure 4 where we compare $\mathbf{P}_s$ values at $T_{red} = 0{\cdot}99$. The $\mathbf{P}_s$ values at 10% and 20% at $T_{red} = 0{\cdot}99$ (58 and 85 nC cm^{-2}, respectively) were extrapolated to 100% 3M2**F**PHOB to obtain a value of 430 nC cm^{-2} for the neat hypothetical SmC* phase. (The 30% concentration of 3M2**F**PHOB is too close to the phase boundary for a reliable estimate of $\mathbf{P}_s$ at any reduced temperature, so this data was omitted from our extrapolation procedure.) This three-point extrapolation is admittedly rather dubious and the reliability of $\mathbf{P}_s$ for 3M2**F**PHOB may be subject to significant uncertainty. Nevertheless, despite the coarseness of the extrapolation, we find a systematic increase in $\mathbf{P}_s$ (78, 296 and 430 nC cm^{-2}) as the halogen at the chiral centre of the optically active tails of 3M2**X**PHOB is varied (Br, Cl and F, respectively) in this series of FLCs. It may be desirable to extract a better value of $\mathbf{P}_s$ for 3M2**F**PHOB in a dilution experiment in a more robust SmC solvent before much significance can be attached to this trend with halogen substitution. Alternatively, it would be instructive to estimate the reliability of this $\mathbf{P}_s$ value for 3M2**F**PHOB with simulation methods recently reported [7].

4. Conclusions

We have synthesized and compared the physical properties of a series of enantiomerically pure 4′(3-methyl-2-halopentanoyloxy)-4-hexyloxybiphenyls and their racemates. The chloro and bromo derivatives both show stable SmA and SmC* phases, however the SmC* of the later mesogen is very narrow. The fluoro compound exhibits only a SmA phase and crystallizes before a stable SmC* phase can be formed. Observations indicate that the spontaneous polarization in this series of ferroelectric liquid crystals is a strong function of halogen present in the chiral tail. And, insofar as the extrapolated value for the $\mathbf{P}_s$ of the fluoro derivative is qualitatively correct, this series exhibits a trend in $\mathbf{P}_s$—F > Cl > Br—which conforms to the general observation that fluoro and chloro derivitization at the FLC's chiral centre leads to high $\mathbf{P}_s$ values [12].

5. Experimental

5.1. *Materials*

L-Isoleucine, DL-isoleucine, 1-bromohexane, 4,4′-biphenol, HF/pyridine (70/30), silica gel (Merck, grade

9385, 230–400 mesh, 60 Å) and precoated TLC plates (silica gel 60 F 254, layer thickness 0·2 mm, Riedel de Haen) were purchased from Aldrich and used as received. Chloroform and pyridine were dried over and distilled from CaH_2 before use.

5.2. *Measurements*

5.2.1. *Structure determinations*

The structures of intermediates and products were confirmed by ^{1}H NMR (Bruker WM250, 250 MHz) and ^{13}C NMR (Varian Gemini 2000-300, 75·46 MHz). All of the two-dimensional NMR experiments were carried out with a Bruker AMX300 NMR spectrometer. Reactions were monitored by thin layer chromatography using an eluant of hexane/ethyl acetate (9/1). Mass spectra (MS) were obtained using a Hewlett Packard 5972 spectrometer; M+ represents the molecular ion.

5.2.2. *Thermodynamic properties*

Transition temperatures were determined by using a Seiko DSC 120 differential scanning calorimeter, calibrated with indium (99·99%) (m.p., 156·5°C, ΔH= 28·315 J g^{-1}) and tin (99·99%) (m.p., 232·0°C, ΔH= 54·824 J g^{-1}). The second heating (5°C min^{-1}) as well as the cooling scans (2°C min^{-1}) were recorded. Mesophases were identified with a Nikon Microphot-FX polarizing microscope equipped with a linkam hot stage.

5.2.3. *Spontaneous polarization*

The spontaneous polarization was measured by a D-E hysteresis loop tracer using a conventional Sawyer–Tower bridge circuit. The samples were prepared in commercially available cells (polyimide coating, parallel rubbed, 15 μm cell gap, 16 mm^2 electrode area). A triangular wave was employed as the applied electric field for tracing the hysteresis loops. In order to avoid sample heating due to dielectric loss, only a few cycles of the field were applied (instead of a continuous wave train). The voltage across a capacitor which is in series to the sample cell was measured and stored on a digital oscilloscope used for tracing hysteresis loops and subsequently transferred to a computer for loop compensation [14, 15]. After the compensation, ideal hysteresis loops without distortion were obtained, enabling us to estimate the values of spontaneous polarization.

5.3. *Synthesis*

5.3.1. *4-Hexyloxy-4′-hydroxybiphenyl* (**1**)

A solution of potassium hydroxide (5·6 g, 0·1 mol) in 100 ml ethanol was added dropwise to a stirred solution of 4,4′-biphenol (27·9 g, 0·15 mol) in 200 ml ethanol. The mixture was then heated under reflux for 1 h. To the final mixture a solution of 1-bromohexane (16·5 g, 0·1 mol) in 50 ml ethanol was added dropwise; the resulting mixture was allowed to boil under reflux for 24 h. The mixture was then cooled, diluted with 100 ml water and acidified with aqueous HCl (3N). The crude product obtained by filtration was purified by chromatography over silica gel eluting with *n*-hexane and ethyl acetate (9:1). Pure compound **1** was obtained (11·1 g, 41%); ^{1}H NMR (DMSO-d$_6$) δ (ppm): 0·88 (t, J=6·9, ω-C$\underline{\text{H}}_3$), 1·35 (m, γ,δ,ε-C$\underline{\text{H}}_2$), 1·67 (m, β-C$\underline{\text{H}}_2$), 3·93 (t, J=6·6, α-C$\underline{\text{H}}_2$), 5·38 (b,=O$\underline{\text{H}}$), 6·57 (d, J=6·0, 2′-Ar$\underline{\text{H}}$), 6·88 (d, J=7·0, 2-Ar$\underline{\text{H}}$), 7·20 (d, J=7·0, 3′-Ar$\underline{\text{H}}$), 7·39 (d, J=7·0, 3-Ar$\underline{\text{H}}$); MS (*m/z*): 270 (M+), 186, 157, 128.

5.3.2. *Representative procedure for the synthesis of α-fluoroacyl chlorides; (2S,3S)-2-fluoro-3-methylpentanoyl chloride* (**2a**)

A polypropylene flask equipped with a magnetic stirring bar and argon inlet was charged with L-isoleucine (23·6 g, 0·18 mol) and 125 ml dry pyridine. This mixture was cooled to 0°C and 300 g of commercial HF/pyridine (70/30) was slowly added by cannula. Under vigorous stirring $NaNO_2$ (22 g, 0·32 mol) was added in three portions over 30 min; this reaction mixture was stirred at 0°C for 5 h. The crude product was extracted into diethyl ether (4 × 150 ml), and the solution was washed with brine and dried over $MgSO_4$. After removal of the solvent by distillation the crude product was distilled twice to obtain 3·75 g (16%) of (2*S*,3*S*)-2-fluoro-3-methylpentanoic acid; b.p. 45°C, 1 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·95 (t, J=7·3, ω′-C$\underline{\text{H}}_3$), 1·07 (d, J= 6·7, ω″-C$\underline{\text{H}}_3$), 1·45 (m, γ′-C$\underline{\text{H}}_2$), 2·09 (dm, $^3J_{FH}$=25, β′-C$\underline{\text{H}}$), 4·85 (dd, $^2J_{FH}$=49, J=5, α′-C$\underline{\text{H}}$), 11·83 (s, COO$\underline{\text{H}}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 11·3 (ω′-C$\underline{\text{H}}_3$), 14·7 (d, $^3J_{CF}$=4, ω″-C$\underline{\text{H}}_3$), 23·4 (d, $^3J_{CF}$=4, γ′-C$\underline{\text{H}}_2$), 37·4 (d, $^2J_{CF}$=19, β′-C$\underline{\text{H}}$), 92·2 (d, $^1J_{CF}$=188, α′-C$\underline{\text{H}}$), 176·1 (d, $^2J_{CF}$=30, C=O).

The 2*S*,3*S*-2-fluoro-3-methylpentanoic acid (3·75 g, 28 mmol) was treated with 13 ml $SOCl_2$ in 13 ml $CHCl_3$ at 0°C until the initial reaction subsided. The mixture was boiled under reflux until no more HCl was evolved. $CHCl_3$ and excess $SOCl_2$ were removed by distillation and the product purified by vacuum distillation to afford 2·9 g (68%) of the title compound; b.p. 20°C, 15 mmHg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·93 (t, J=7·9, ω′-C$\underline{\text{H}}_3$), 1·07 (d, J=6·7, ω″-C$\underline{\text{H}}_3$), 1·45 (m, γ′-C$\underline{\text{H}}_2$), 2·15 (dm, $^3J_{FH}$=25, β′-C$\underline{\text{H}}$), 4·85 (dd, $^2J_{FH}$=45, J=4, α′-C$\underline{\text{H}}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 11·2 (ω′-C$\underline{\text{H}}_3$), 14·7 (d, $^3J_{CF}$=3, ω″-C$\underline{\text{H}}_3$), 23·0 (d, $^3J_{CF}$=4, γ′-C$\underline{\text{H}}_2$), 37·0 (d, $^2J_{CF}$=20, β′-C$\underline{\text{H}}$), 97·1 (d, $^1J_{CF}$=198, α′-C$\underline{\text{H}}$), 173·0 (d, $^2J_{CF}$=30, C=O).

5.3.3. *Analytical data for 2-fluoro-3-methylpentanoyl chloride made from* DL-*isoleucine* (**3a**)

Vacuum distillation afforded 0·9 g (48%) of the title compound; b.p. 35°C, 30 mm Hg; ^{1}H NMR ($CDCl_3$) δ

(ppm): 0·91 (2t, ω′-C<u>H</u>$_3$), 0·99 (2d, ω″-C<u>H</u>$_3$), 1·43 (m, γ′-C<u>H</u>$_2$), 2·12 (dm, $^3J_{FH}$=27, β′-C<u>H</u>), 4·80 (dd, $^2J_{FH}$=33, J=5, α′-C<u>H</u>), 5·00 (dd, $^2J_{FH}$=34, J=4, α′-C<u>H</u>).

5.3.4. *Representative procedure for the synthesis of α-chloroacyl chlorides; (2S,3S)-2-chloro-3-methylpentanoyl chloride* (**2b**)

A flask equipped with a magnetic stirring bar was charged with L-isoleucine (6·6 g, 0·05 mol) and 63 ml of 6N aqueous HCl. The suspension was cooled to 0°C and under vigorous stirring $NaNO_2$ (5·5 g, 0·08 mol) was added in several portions over 1·5 h; this reaction mixture was stirred at 0°C for 4 h. The crude product was extracted into diethyl ether (4 × 150 ml) and the solution washed with brine and dried over anhydrous $MgSO_4$. After removal of the solvent by distillation the crude product was distilled twice to obtain 3·4 g (45%) of (2*S*,3*S*)-2-chloro-3-methylpentanoic acid; b.p. 110°C, 10 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·92 (t, J=7·9, ω′-C<u>H</u>$_3$), 1·05 (d, J=7·3, ω″-C<u>H</u>$_3$), 1·49 (dm, J=76·2, γ′-C<u>H</u>$_2$), 2·09 (m, β′-C<u>H</u>), 4·22 (d, J=7, α′-C<u>H</u>–Cl), 11·39 (s, COO<u>H</u>); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·82 (ω′-<u>C</u>H$_3$), 15·84 (ω″-<u>C</u>H$_3$), 24·76 (γ′-<u>C</u>H$_2$), 38·73 (β′-<u>C</u>H), 62·66 (α′-<u>C</u>H-Cl), 175·79 (<u>C</u>=O).

The (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (3·4 g, 23 mmol) was treated with 12 ml $SOCl_2$ in 12 ml $CHCl_3$ at 0°C until the initial reaction subsided. The mixture was heated under reflux until no more HCl was evolved. $CHCl_3$ and excess $SOCl_2$ were removed by distillation and the product was purified by vacuum distillation to afford 2·6 g (68%) of the title compound; b.p. 62°C, 15 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·96 (t, J=7·5, ω′-C<u>H</u>$_3$), 1·12 (d, J=8, ω″-C<u>H</u>$_3$), 1·49 (dm, J=62·5, γ′-C<u>H</u>$_2$), 2·28 (m, β′-C<u>H</u>), 4·44 (d, J=7·5, α′-C<u>H</u>–Cl); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·89 (ω′-<u>C</u>H$_3$), 16·12 (ω″-<u>C</u>H$_3$), 24·23 (γ′-<u>C</u>H$_2$), 38·49 (β′-<u>C</u>H), 70·80 (α′-<u>C</u>H–Cl), 170·56 (<u>C</u>=O).

5.3.5. *Analytical data for chloro-3-methylpentanoyl chloride made from* DL-*isoleucine* (**3b**)

Vacuum distillation afforded 3·9 g (51%) of the title compound; b.p. 32°C, 1 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·91–0·99 (2 t, ω′-C<u>H</u>$_3$, d, ω″-C<u>H</u>$_3$), 1·07 (d, ω″-C<u>H</u>$_3$), 1·44, 2·27 (m, β′-C<u>H</u> and γ′-C<u>H</u>$_2$), 4·41 (d, J=6·0, α′-C<u>H</u>–Cl), 4·61 (d, J=5·0, α′-C<u>H</u>–Cl); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·8, 11·28 (ω′-<u>C</u>H$_3$), 13·87, 16·02 (ω″-<u>C</u>H$_3$), 24·16, 26·7 (γ′-<u>C</u>H$_2$), 38·06, 38·4 (β′-<u>C</u>H), 70·12, 70·73 (α′-<u>C</u>H–Cl), 170·47, (<u>C</u>=O).

5.3.6. *Representative procedure for the synthesis of α-bromoacyl chlorides; (2S,3S)-2-bromo-3-methylpentanoyl chloride* (**2c**)

A flask equipped with a magnetic stirring bar was charged with L-isoleucine (7·9 g, 0·06 mol) and 75 ml of 6N HBr. The suspension was cooled to 0°C and under vigorous stirring $NaNO_2$ (6·2 g, 0·09 mol) was added in several portions over 1·5 h; this reaction mixture was stirred at 0°C for 4 h. The crude product was extracted into diethyl ether (4 × 150 ml) and the solution was washed with brine and dried over $MgSO_4$. After removal of the solvent by distillation the crude product was distilled twice to obtain 8·6 g (73%) of 2*S*,3*S*-2-bromo-3-methylpentanoic acid; b.p. 140°C, 20 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·89 (t, J=7·9, ω′-C<u>H</u>$_3$), 1·02 (d, J=6·7, ω″-C<u>H</u>$_3$), 1·32, 1·72 (m, γ′-C<u>H</u>$_2$), 2·05 (m, β′-C<u>H</u>), 4·09 (d, J=8, α′-C<u>H</u>-Br), 11·80 (s, COO<u>H</u>); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·52 (ω′-<u>C</u>H$_3$), 16·13 (ω″-<u>C</u>H$_3$), 26·09 (γ′-<u>C</u>H$_2$), 34·91 (β′-<u>C</u>H), 52·40 (α′-<u>C</u>H–Br), 175·89 (<u>C</u>=O).

The 2*S*,3*S*-2-bromo-3-methylpentanoic acid (8·6 g, 44 mmol) was treated with 25 ml $SOCl_2$ in 25 ml $CHCl_3$ at 0°C until the initial reaction subsided. The mixture was heated under reflux until no more HCl evolved. $CHCl_3$ and excess $SOCl_2$ were removed by distillation and the product was purified by vacuum distillation to afford 7·8 g (83%) of the title compound; b.p. 85°C, 15 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·92 (t, J=7·6, ω′-C<u>H</u>$_3$), 1·08 (d, J=6·9, ω″-C<u>H</u>$_3$), 1·34, 1·72 (m, γ′-C<u>H</u>$_2$), 2·13 (m, β′-C<u>H</u>), 4·39 (d, J=8, α′-C<u>H</u>–Br); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·52 (ω′-<u>C</u>H$_3$), 16·31 (ω″-<u>C</u>H$_3$), 25·68 (γ′-<u>C</u>H$_2$), 38·11 (β′-<u>C</u>H), 61·09 (α′-<u>C</u>H–Br), 169·55 (<u>C</u>=O).

5.3.7. *Analytical data for bromo-3-methylpentanoyl bromide made from* DL-*isoleucine* (**3c**)

Vacuum distillation afforded 6·0 g (77%) of the title compound; b.p. 32°C, 0·5 mm Hg; ^{1}H NMR ($CDCl_3$) δ (ppm): 0·92 (2 t, ω′-C<u>H</u>$_3$), 1·04 (2 d, ω″-C<u>H</u>$_3$), 1·55, 2·15 (m, β′-C<u>H</u> and γ′-C<u>H</u>$_2$), 4·37 (d, J=8·0, α′-C<u>H</u>–Br), 4·54 (d, J=7·0, α′-C<u>H</u>–Br); ^{13}C NMR ($CDCl_3$) δ (ppm): 10·55, 11·24 (ω′-<u>C</u>H$_3$), 15·58, 16·34 (ω″-<u>C</u>H$_3$), 25·69, 27·3 (γ′-<u>C</u>H$_2$), 37·92, 38·13 (β′-<u>C</u>H), 61·11, 61·68 (α′-<u>C</u>H–Br), 169·47, 169·55 (<u>C</u>=O).

5.3.8. *Representative procedure for the synthesis of 4′-[(2S,3S)-3-methyl-2-fluoropentanoyloxy]-4-hexyloxybiphenyl (3M2FPHOB)*

A flask equipped with a magnetic stirring bar, reflux condenser and argon inlet was charged with 4-hexyloxy-4′-hydroxybiphenyl (**1**) (1·22 g, 4·5 mmol), triethylamine, (0·53 g, 5·2 mmol) and 30 ml $CHCl_3$. This reaction mixture was cooled to 0°C and (2*S*,3*S*)-2-fluoro-3-methylpentanoyl chloride (**2a**) (0·8 g, 5·2 mmol) in 10 ml $CHCl_3$ was slowly added over 15 min; this mixture was stirred for 24 h at room temperature. The reaction mixture was then cooled to 0°C and treated with 50 ml of 2N HCl. The solids were filtered off and washed with water. The dried product was taken up in a minimum

amount of CH_2Cl_2 and purified by column chromatography (silica gel/*n*-hexane–ethyl acetate, 9:1); the product was recrystallized twice from ethanol/*n*-hexane. The purity of the product was checked by TLC, one spot (silica gel, t_r=0·31). Yield 1·6 g (80%); ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=6·9, ω-C$\underline{H}_3$), 1·03 (t, J=7·5, ω′-C$\underline{H}_3$), 1·17 (d, J=7·0, ω″-C$\underline{H}_3$), 1·38 (m, δ-C$\underline{H}_2$), 1·38 (m, ε-C$\underline{H}_2$), 1·50 (m, γ-C$\underline{H}_2$), 1·61 (m, γ′-C$\underline{H}_2$), 1·83 (m, β-C$\underline{H}_2$), 2·21 (md, $^3J_{FH}$=23·7, β′-C$\underline{H}$), 4·01 (t, J=6·5, α-C$\underline{H}_2$), 5·03 (dd, J=4·4, $^2J_{FH}$=48·5, α′-C$\underline{H}$–F), 6·99 (d, J=8·8, 3-Ar$\underline{H}$), 7·18 (d, J=8·7, 3′-Ar$\underline{H}$), 7·51 (d, J=8·7, 2-Ar$\underline{H}$), 7·58 (d, J=8·6, 2′-Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·68 (C1), 128·35 (C2), 115·06 (C3), 159·12 (C4), 139·45 (C1′), 128·04 (C2′), 121·70 (C3′), 149·06, (C4′), 68·33 (α-$\underline{C}H_2$), 29·49 (β-$\underline{C}H_2$), 25·98 (γ-$\underline{C}H_2$), 31·84 (δ-$\underline{C}H_2$), 22·87 (ε-$\underline{C}H_2$), 14·30 (ω-$\underline{C}H_3$), 92·84 (d, $^1J_{CF}$=187·2, α′-$\underline{C}$H–F), 38·11 (d, $^2J_{CF}$=19·9, β′-$\underline{C}$H), 24·10 (d, $^3J_{CF}$=5, γ′-$\underline{C}H_2$), 11·75 (ω′-$\underline{C}H_3$), 15·10 (d, $^3J_{CF}$=3·8, ω″-$\underline{C}H_3$), 168·43 ($\underline{C}$=O).

5.3.9. *Analytical data for 4′-(3-methyl-2-**fl**uoropentanoyloxy)-4-hexyloxybiphenyl (3M2**F**PHOB-R)*

Yield 2·3 g (68%); the purity of the product was checked by TLC, one spot (silica gel, t_r=0·37). ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=6·9, ω-C$\underline{H}_3$), 1·04, 1·07 (t, ω′-C$\underline{H}_3$), 1·17, 1·12 (d, ω″-C$\underline{H}_3$), 1·38 (m, δ-C$\underline{H}_2$), 1·38 (m, ε-C$\underline{H}_2$), 1·50 (m, γ-C$\underline{H}_2$), 1·70, 1·47 (m, *RR*,*SS*, γ′-C$\underline{H}_2$), 1·60, 1·50 (m, *RS*,*SR*, γ′-C$\underline{H}_2$), 1·83 (m, β-C$\underline{H}_2$), 2·21, 2·17 (md, β′-C$\underline{H}$), 4·01 (t, J=6·6, α-C$\underline{H}_2$), 5·03 (dd, J=4·5, $^2J_{FH}$=48·6, *RR*,*SS*, α′-C$\underline{H}$-F), 5·15 (dd, J=3·0, $^2J_{FH}$=48·9, *RS*,*SR*, α′-C$\underline{H}$–F), 6·99 (d, J=8·7, 3-Ar$\underline{H}$), 7·18 (d, J=8·7, 3′-Ar$\underline{H}$), 7·50 (d, J=8·7, 2-Ar$\underline{H}$), 7·58 (d, J=8·6, 2′-Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·66 (C1), 128·33 (C2), 115·04 (C3), 159·10 (C4), 139·42 (C1′), 128·02 (C2′), 121·69 (C3′), 149·05, (C4′), 68·32 (α-$\underline{C}H_2$), 29·48 (β-$\underline{C}H_2$), 25·97 (γ-$\underline{C}H_2$), 31·83 (δ-$\underline{C}H_2$), 22·86 (ε-$\underline{C}H_2$), 14·29 (ω-$\underline{C}H_3$), 92·82 (dd, $^1J_{CF}$=187·5, *RR*,*SS*, α′-$\underline{C}$H–F), 91·34 (dd, $^1J_{CF}$=188·7, *RS*,*SR*, α′-$\underline{C}$H–F), 38·10 (dd, $^2J_{CF}$=19·9, *RS*,*SS*, β′-$\underline{C}$H), 38·12 (dd, $^2J_{CF}$=20·1, *RS*,*SR*, β′-$\underline{C}$H), 24·10 (td, $^3J_{CF}$=5·0, *RR*,*SS*, γ′-$\underline{C}H_2$), 25·74 (td, $^3J_{CF}$=2·6, *RS*,*SR*, γ′-$\underline{C}H_2$), 11·73, 11·86 (q, ω′-$\underline{C}H_3$), 15·08 (qd, $^3J_{CF}$=3·7, *RR*,*SS*, ω″-$\underline{C}H_3$), 13·63 (qd, $^3J_{CF}$=4·9, *RS*,*SR*, ω″-$\underline{C}H_3$), 168·39 (sd, $^2J_{CF}$=25·4, *RR*,*SS*, $\underline{C}$=O), 168·74 (sd, $^2J_{CF}$=25·4, *RS*,*SR*, $\underline{C}$=O).

5.3.10 *Analytical data for 4′-[(2S,3S)-3-methyl-2-chloropentanoyloxy]-4-hexyloxybiphenyl (3M2**C**PHOB)*

Yield 1·6 g (67%); the purity of the product was checked by TLC, one spot (silica gel, t_r=0·49). ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=7 t, ω-C$\underline{H}_3$), 1·01 (t, J=7·5, ω′-C$\underline{H}_3$), 1·17 (d, J=6·8, ω″-C$\underline{H}_3$), 1·38 (m, δ-C$\underline{H}_2$), 1·38 (m, ε-C$\underline{H}_2$), 1·49 (m, γ-C$\underline{H}_2$), 1·80, 1·45 (m, γ′-C$\underline{H}_2$), 1·82 (m, β-C$\underline{H}_2$), 2·26 (m, β′-C$\underline{H}$), 4·01 (t, J=6·6, α-C$\underline{H}_2$), 4·42 (d, J=7·1, α′-C$\underline{H}$), 6·99 (d, J=8·8, 3-Ar$\underline{H}$), 7·18 (d, J=8·7, 3′-Ar$\underline{H}$), 7·50 (d, J=8·7, 2-Ar$\underline{H}$), 7·58 (d, J=8·6, 2′-Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·68 (C1), 128·34 (C2), 115·04 (C3), 159·10 (C4), 139·41 (C1′), 128·00 (C2′), 121·60 (C3′), 149·47 (C4′), 68·32 (α-$\underline{C}H_2$), 29·48 (β-$\underline{C}H_2$), 25·98 (γ-$\underline{C}H_2$), 31·84 (δ-$\underline{C}H_2$), 22·86 (ε-$\underline{C}H_2$), 14·30 (ω-$\underline{C}H_3$), 62·90 (α′-$\underline{C}$H–Cl), 39·30 (β′-$\underline{C}$H), 25·38 (γ′-$\underline{C}H_2$), 11·14 (ω′-$\underline{C}H_3$), 16·24 (ω″-$\underline{C}H_3$), 168·32 ($\underline{C}$=O).

5.3.11. *Analytical data for 4′-(3-methyl-2-chloropentanoyloxy)-4-hexyloxybiphenyl (3M2**C**PHOB-R)*

Yield 1·2 g (63%); the purity of the product was checked by TLC, one spot (silica gel, t_r=0·53). ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=6·9 t, ω-C$\underline{H}_3$), 1·02, 1·04 (t, ω′-C$\underline{H}_3$), 1·18, 1·15 (d, J=6·4, ω″-C$\underline{H}_3$), 1·38 (m, δ-C$\underline{H}_2$), 1·38 (m, ε-C$\underline{H}_2$), 1·50 (m, γ-C$\underline{H}_2$), 1·81, 1·45, 1·63, 1·45 (m, γ′-C$\underline{H}_2$), 1·82 (m, β-C$\underline{H}_2$), 2·27, 2·31 (m, β′-C$\underline{H}$), 4·01 (t, J=6·6, α-C$\underline{H}_2$), 4·42, 4·58 (d, J_1=7·0, J_2=5·4, α′-C$\underline{H}$), 6·98 (d, J=8·8, 3-Ar$\underline{H}$), 7·18 (d, J=8·7, 3′-Ar$\underline{H}$), 7·50 (d, J=8·8, 2-Ar$\underline{H}$), 7·57 (d, J=8·5, 2′-Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·74 (C1), 128·34 (C2), 115·11 (C3), 159·15 (C4), 139·42 (C1′), 128·00 (C2′), 121·60 (C3′), 149·54, 149·59 (C4′), 68·38 (α-$\underline{C}H_2$), 29·52 (β-$\underline{C}H_2$), 26·00 (γ-$\underline{C}H_2$), 31·85 (δ-$\underline{C}H_2$), 22·87 (ε-$\underline{C}H_2$), 14·28 (ω-$\underline{C}H_3$), 62·91, 62·99 (α′-$\underline{C}$H–Cl), 39·34, 39·15 (β′-$\underline{C}$H), 25·43, 26·98 (γ′-$\underline{C}H_2$), 11·14, 11·67 (ω′-$\underline{C}H_3$), 16·25, 15·07 (ω″-$\underline{C}H_3$), 168·27, 168·48 ($\underline{C}$=O).

5.3.12. *Analytical data for 4′-[(2S,3S)-3-methyl-2-bromopentanoyloxy]-4-hexyloxybiphenyl (3M2**B**PHOB)*

Yield 2·0 g (75%); the purity of the product was checked by TLC, one spot (silica gel, t_r=0·5). ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=7, ω-C$\underline{H}_3$), 1·00 (t, J=7·4, ω′-C$\underline{H}_3$), 1·17 (d, J=6·7, ω″-C$\underline{H}_3$), 1·37 (m, δ -C$\underline{H}_2$), 1·37 (m, ε-C$\underline{H}_2$), 1·50 (m, γ-C$\underline{H}_2$), 1·90, 1·42 (m, γ′-C$\underline{H}_2$), 1·83 (m, β-C$\underline{H}_2$), 2·23 (m, β′-C$\underline{H}$), 4·01 (t, J=6·7, α-C$\underline{H}_2$), 4·34 (d, J=8·5, α′-C$\underline{H}$), 6·99 (d, J=8·8, 3-Ar$\underline{H}$), 7·19 (d, J=8·7, 3′-Ar$\underline{H}$), 7·51 (d, J=8·7, 2-Ar$\underline{H}$), 7·58 (d, J=8·6, 2′-Ar$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·73 (C1), 128·34 (C2), 115·05 (C3), 159·09 (C4), 139·38 (C1′), 127·98 (C2′), 121·54 (C3′), 149·54 (C4′), 68·33 (α-$\underline{C}H_2$), 29·49 (β-$\underline{C}H_2$), 25·98 (γ-$\underline{C}H_2$), 31·84 (δ-$\underline{C}H_2$), 22·86 (ε-$\underline{C}H_2$), 14·30 (ω-$\underline{C}H_3$), 52·72 (α′-$\underline{C}$H–Cl), 38·55 (β′-$\underline{C}$H), 26·65 (γ′-$\underline{C}H_2$), 10·85 (ω′-$\underline{C}H_3$), 16·52 (ω″-$\underline{C}H_3$), 168·36 ($\underline{C}$=O).

5.3.13. *Analytical data for 4′-(3-methyl-2-bromopentanoyloxy)-4-hexyloxybiphenyl (3M2**B**PHOB-R)*

Yield 3·2 g (73%); the purity of the product was checked by TLC, one spot (silica gel, t_r=0·39). ^{1}H NMR ($CDCl_3$) δ (ppm): 0·94 (t, J=6·9, ω-C$\underline{H}_3$), 1·01, 1·03 (t,

ω′-C<u>H</u>$_3$), 1·18, 1·19 (d, J_1=6·7, J_2=6·5, ω″-C<u>H</u>$_3$), 1·38 (m, δ-C<u>H</u>$_2$), 1·38 (m, ε-C<u>H</u>$_2$), 1·50 (m, γ-C<u>H</u>$_2$), 1·88, 1·42, 1·63, 1·42 (m, γ′-C<u>H</u>$_2$), 1·83 (m, β-C<u>H</u>$_2$), 2·21, 2·17 (m, β′-C<u>H</u>), 4·01 (t, J=6·5, α-C<u>H</u>$_2$), 4·34, 4·47 (d, J_1=8·5, J_2=7·0, α′-C<u>H</u>), 6·99 (d, J=8·8, 3-Ar<u>H</u>), 7·18, 7·19 (d, J_1=8·7, J_2=8·7 3′-Ar<u>H</u>), 7·50 (d, J=8·8, 2-Ar<u>H</u>), 7·58 (d, J=8·5, 2′-Ar<u>H</u>); ^{13}C NMR ($CDCl_3$) δ (ppm): 132·72 (C1), 128·33 (C2), 115·04 (C3), 159·08 (C4), 139·36 (C1′), 127·97 (C2′), 121·55 (C3′), 149·53, 149·57 (C4′), 68·33 (α-<u>C</u>H$_2$), 29·49 (β-<u>C</u>H$_2$), 25·99 (γ-<u>C</u>H$_2$), 31·84 (δ-<u>C</u>H$_2$), 22·87 (ε-<u>C</u>H$_2$), 14·31 (ω-<u>C</u>H$_3$), 52·72, 53·76 (α′-<u>C</u>H–Cl), 38·55, 38·59 (β′-<u>C</u>H), 26·65, 27·49 (γ′-<u>C</u>H$_2$), 10·85, 11·66 (ω′-<u>C</u>H$_3$), 16·52, 16·70 (ω″-<u>C</u>H$_3$), 168·34, 168·39 (<u>C</u>=O).

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References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Physique (lett.)*, **36,** L-69.

[2] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 1231.

[3] Watanabe, J., Nakata, Y., and Shimizu, K., 1994, *J. Phys. II.*, **4,** 581.

[4] Tournilhac, F., Blinov, L. M., Simon, J., and Yablonsky, S. V., 1992, *Nature*, **359,** 621.

[5] Lee, J., and Lee, S.-D., 1994, *Mol. Cryst. liq. Cryst.*, **254,** 395.

[6] Photinos, D. J., and Samulski, E. T., 1995, *Science*, **270,** 783.

[7] Terzis, A. F., Samulski, E. T., and Photinos, D. J., *J. chem. Phys.* (in the press).

[8] Chen, A., Poon, C.-D., Dingemans, T. J., and Samulski, E. T., *Liq. Cryst.*, **24**(2), 255.

[9] Fu, S. C. J., Birnbaum, S. M., and Greenslein, I. P., 1954, *J. Am. chem. Soc.*, **76,** 6054.

[10] Olah, G. A., Surya Prakash, G. K., and Chao, Y. L., 1981, *Helv. Chim. Acta*, **64,** 2528.

[11] Barber, J., Keck, R., and Retey, J., 1982, *Tetrahedron Lett.*, **23,** 1549.

[12] Sierra, T., Serrano, J. L., Ros, M. B., Ezcurra, A., and Zubia, J., 1992, *J. Am. chem. Soc.*, **114,** 7645.

[13] Ozaki, M., Yoshino, K., Sakurai, T., Mikami, N., and Higuchi, R., 1987, *J. chem. Phys.*, **86,** 3648.

[14] Hatano, J., Takeuchi, H., Harazaki, M., and Watanabe, T., 1992, *Jpn. J. appl. Phys.*, **31,** 3235.

[15] Hatano, J., Watanabe, T., and le Bihan, R., 1992, *Ferroelectrics*, **126,** 311.