Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A new series of nematic and smectic liquid crystals with negative dielectric anisotropy: the effect of terminal chain substitution on thermal and electro-optical properties

Aleksandra Jankowiak[a]; Adam Januszko[a]; Bryan Ringstrand[a]; Piotr Kaszynski[a]
[a] Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville TN 37235, USA

To cite this Article Jankowiak, Aleksandra , Januszko, Adam , Ringstrand, Bryan and Kaszynski, Piotr(2008) 'A new series of nematic and smectic liquid crystals with negative dielectric anisotropy: the effect of terminal chain substitution on thermal and electro-optical properties', Liquid Crystals, 35: 1, 65 — 77

To link to this Article: DOI: 10.1080/02678290701744561
URL: http://dx.doi.org/10.1080/02678290701744561

Liquid Crystals, Vol. 35, No. 1, January 2008, 65–77

A new series of nematic and smectic liquid crystals with negative dielectric anisotropy: the effect of terminal chain substitution on thermal and electro-optical properties

ALEKSANDRA JANKOWIAK, ADAM JANUSZKO, BRYAN RINGSTRAND and PIOTR KASZYNSKI*
Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville TN 37235, USA

(*Received 24 August 2007; accepted 12 October 2007*)

Two alkyl (**1b** and **1c**) and four fluoroalkyl derivatives (**1d**–**1f**) of 4-arylbutyric acid (**1c**, **1d** and **1e**) and 4-arylbutanol (**1b**, **1f** and **1g**) [aryl=2′,3′-difluoro-4′-(2-(*E*-4-pentylcyclohexyl)ethyl)-biphenyl-1-yl] were prepared and investigated in the pure form as nematic materials (**1b** and **1c**) and as additives to a ferroelectric liquid crystal (FLC) host (**1d**–**1f**). A comparison of **1b** and **1c** with the decyl analogue **1a** demonstrates the effect of terminal chain modification on thermal and electro-optical properties. The substitution of the –CH_2O– (**1b**) or –COO– (**1c**) for –CH_2CH_2– in **1a** destabilized the N and SmA phases or completely eliminated the smectic behaviour (**1c**). Dielectric analysis revealed that the chain modification increased the negative $\Delta\varepsilon$, reduced elastic constant K_{11} and moderately decreased rotational viscosity γ_1. The temperature dependence of the key electro-optical parameters was analysed for ester **2**, the methyl analogue of **1c**, which exhibits a 45 K wide N phase. All four fluoroalkyl derivatives **1d**–**1f** showed enantiotropic SmA phases and **1e** also exhibited a monotropic SmC phase. Solutions of **1d**–**1f** in a FLC host (0.2 mmol g^{-1}) increased the tilt angle Θ (up to 45° for **1g**), reduced rotational viscosity γ_1 and the risetime τ. The most dramatic changes were observed for **1g**, which contains 15 fluorine atoms.

1. Introduction

There is continuous interest in new nematic and tilted smectic liquid crystals with negative dielectric anisotropy for applications in flat panel display technology (liquid crystal display (LCD)) [1–7]. A particularly valuable class of such materials is based on laterally fluorinated biphenyls and terphenyls [8–13]. Their relatively low rotational viscosity and high resistivity combined with the often-found SmC–SmA–N sequence make these derivatives well suited to ferroelectric liquid crystal (FLC) applications [8, 9, 11, 14–16], although they have also been used as components of nematic materials [1–4]. It was also discovered [17] that partial fluorination of the terminal alkyl chain could help to overcome important challenges in FLC technology. Thus, many such SmC materials have high tilt angle θ (see [18]), essentially temperature-independent smectic layer spacing and low Δn (see [19, 20]). Further impetus to the study of partially fluorinated smectic materials was provided by the discovery [21–23] of orthoconic antiferroelectric liquid crystals (OAFLCs) and their technological promise [24].

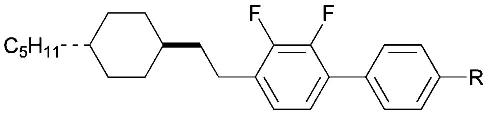
Among the fluorinated biphenyls are their 4-(2-cylcohexylethyl) derivatives of the general structure **1**. Several of these compounds containing an alkoxy (R=OAlkyl), an alkyl (R=C_5H_{11}) or an ester group (R=$COOCHMeC_6H_{13}$) were investigated as smectogenic materials [10] and also described in the patent literature as components of ferroelectric and nematic mixtures [25–28]. We are interested in expanding this class of compounds and the investigation of other substituents R, which would improve the properties of the material. Therefore, we have focused on alkyl derivatives of **1** and terminal chain modifications as a means to optimize their thermal and electro-optical properties for both nematic and SmC applications (see figure 1).

Here we describe nematic and smectic properties of derivatives **1a**–**1g**. We selected the n-$C_{10}H_{21}$ chain as R (**1a**) and modified it by replacing one CH_2 group with an oxygen atom (**1b**) or a CH_2CH_2 group with a carboxy group (**1c**). Subsequently, the pentyl substituent on the oxygen atom in **1b** and **1c** was replaced with a partially fluorinated group in derivatives **1d**–**1g**. We studied the effect of this terminal chain modification on

---

*Corresponding author. Email: piotr.kaszynski@vanderbilt.edu

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2008 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701744561



1 **a**: R = $(CH_2)_3$–CH_2CH_2–$(CH_2)_4CH_3$
b: R = $(CH_2)_3$–CH_2O–$(CH_2)_4CH_3$
c: R = $(CH_2)_3$–COO–$(CH_2)_4CH_3$
d: R = $(CH_2)_3$–COO–$CH_2C_2F_5$
e: R = $(CH_2)_3$–COO–$CH_2CH_2C_4F_9$
f: R = $(CH_2)_3$–CH_2O–COC_2F_5
g: R = $(CH_2)_3$–CH_2O–$CH_2C_7F_{15}$

Figure 1. Compound **1**.

dielectric permittivity and rotational viscosity of the nematogens **1a**–**1c** and methyl ester **2**, a shorter homologue of **1c**. Smectogenic derivatives **1d**–**1g** were investigated as additives to a FLC host with the emphasis on the additive's impact on spontaneous polarization, the tilt angle and rotational viscosity of the host.

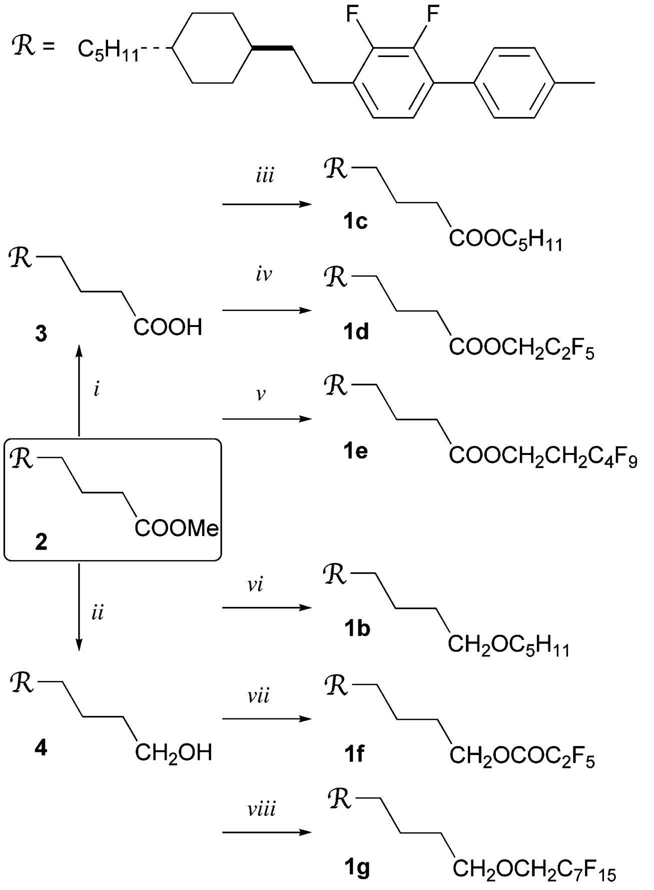
2. Results and discussion

2.1. *Synthesis*

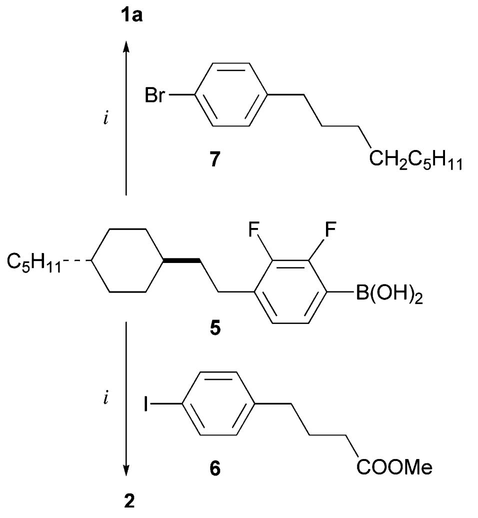
The series of compounds **1b**–**1g** was prepared from methyl ester **2** as shown in scheme 1. Thus, the ester was hydrolysed to the carboxylic acid **3**, which was esterified with appropriate alcohol in the presence of DCC/DMAP to yield **1c**–**1e**. Reduction of ester **2** gave alcohol **4**, which was alkylated with 1-bromopentane in DMSO to give the ether **1b**. Ester **1f** was prepared from alcohol **4** and perfluoropropionic anhydride. The preparation of ether **1g** was accomplished using Mitsunobu conditions from the literature optimized for reactions with moderately acidic alcohols [29]. All compounds were purified by chromatography followed by recrystallization.

Ester **2**, the common intermediate for series **1**, was prepared by Suzuki coupling of the known boronic acid **5** [10] and iodide **6** [30] (see scheme 2)[1]. Also, the decyl derivative **1a** was prepared by Suzuki coupling of boronic acid **5** with 4-bromo-1-decylbenzene (**7**) [31] according to a general procedure from the literature [10].

The preparation of the boronic acid **5** [10] followed a modified general procedure from the literature for similar compounds [16]. It was accomplished in eight steps and 20% overall yield starting from *E*-4-pentylcyclohexylcarboxylic acid (**8**) as shown in scheme 3. Thus, reduction of acid **8** with $LiAlH_4$ gave alcohol **9**, which was converted to tosylate **10**. A subsequent reaction of



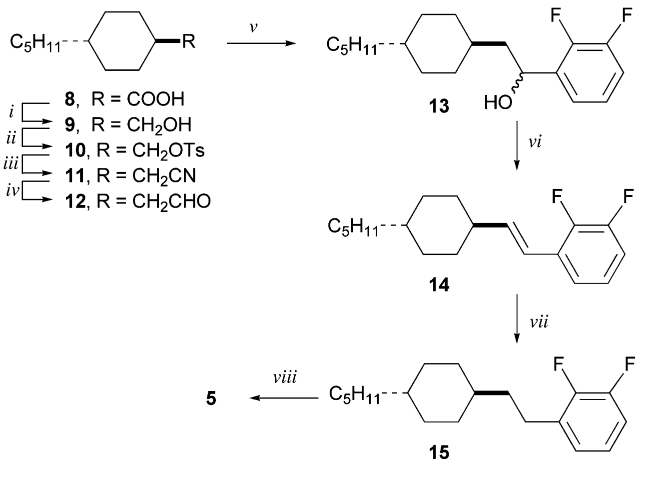
Scheme 1. *i*: 1. NaOH, EtOH, 2. aqueous HCl, 79%. *ii*: $LiAlH_4$, Et_2O, reflux, 98%. *iii*: *n*-$C_5H_{11}OH$, DCC, DMAP, CH_2Cl_2, 76%. *iv*: $C_2F_5CH_2OH$, DCC, DMAP, CH_2Cl_2 78%. *v*: $C_4F_9CH_2CH_2OH$, DCC, DMAP, CH_2Cl_2 71%. *vi*: *n*-$C_5H_{11}Br$, KOH, DMSO, 75%. *vii*: $(C_2F_5CO)_2O$, pyridine, 84%. *viii*: $C_7F_{15}CH_2OH$, ADDP, Bu_3P, benzene, 69%.



Scheme 2. *i*: $(PPh_3)_2PdCl_2$, 2M Na_2CO_3, benzene, EtOH, reflux.

---

[1] A by-product, 2,3-difluoro-4-(2-(*E*-4-pentylcyclohexyl)ethyl)-biphenyl, was isolated in 5% yield as a nematic oil with the clearing temperature of 39°C.



Scheme 3. *i*: $LiAlH_4$, Et_2O, 94%; *ii*: TsCl, pyridine, 83%; *iii*: NaCN, Bu_4NBr, MeCN, 89%; *iv*: DIBAL, toluene, 68%; *v*: 1,2-$C_6H_4F_2$, BuLi, THF −78°C, 82%; *vi*: P_2O_5, cyclohexane, 77%; H_2/Pd, cyclohexane, 89%; *vii*: 1. BuLi, THF, 2. $(MeO)_3B$, 3. aqueous HCl, 73%.

the crude tosylate with NaCN yielded nitrile **11**. Overall, the nitrile was obtained in three steps and 60% yield from acid **8**.

The nitrile **11** was reduced using DIBAL [32] to afford 2-(*E*-4-pentylcyclohexyl)acetaldehyde (**12**). The preparation of boronic acid **5** from the aldehyde represents an adaptation of a general method for other 4-alkylphenylboronic acids [16]. Thus, the treatment of aldehyde **12** with lithium derivative of 1,2-difluorobenzene afforded alcohol **13**, which without rigorous purification was dehydrated to alkene **14** and subsequently reduced to 1,2-difluoro-3-(2-(*E*-4-pentylcyclohexyl)ethyl)-benzene (**15**). The overall yield of **15** was 58% for four steps starting from the nitrile **11**. Finally, lithiation of **15** with *n*-BuLi followed by a reaction with $B(OMe)_3$ gave boronic acid **5**.

Methyl 4-(4-iodophenyl)butanoate **6** was obtained in two steps from 4-phenylbutanoic acid according to a procedure from the literature [30].

2.2. *Thermal analysis*

Phase transition temperatures and enthalpies for series **1** and also intermediates **2**–**4** are shown in table 1. Phase structures were assigned by comparison of microscopic textures observed using a birefractive setup with those published for reference compounds [33, 34].

All compounds exhibit enantiotropic nematic (**1c** and **2**), nematic and smectic (**1a**, **1b**, **4**) or exclusively smectic (**1d**–**1g**, **3**) phases with clearing temperatures in the range between 54°C (**1b**) and 127°C (**4**). Monotropic SmC phases were found in the decyl derivative **1a**, fluorinated ester **1e** and intermediates **3** and **4**.

Inspection of the first three members of series **1** allows for an analysis of the structural effects on mesogenic properties. Among the three compounds **1a**–**1c**, the most stable nematic phase is displayed by **1a**. Replacement of the $C(5)H_2$ group in **1a** with an oxygen atom in **1b** has the most destabilizing effect (~40 K) on the nematic phase, while the introduction of the carboxyl group in **1c** has a 5 K smaller effect on the phase stability. Thus, the effectiveness of the group X in stabilization of the nematic phase in series **1** follows the order $CH_2CH_2 > COO > CH_2O$.

The SmA phase in series **1a**–**1c** is destabilized by the CH_2O group by 43 K relative to **1a**. A markedly stronger destabilization of the SmA phase was found for the carboxy group in **1c** in which no smectic behaviour was observed even in samples supercooled to ambient temperature.

The presence of the oxygen atom in **1b** lowers the melting point by approximately 15 K relative to hydrocarbon **1a**. In contrast, the melting point of ester **1c** is considerably higher by nearly 25 K than that of **1a**. Results indicate that the carboxyl group is the most effective substituent in the terminal chain to enhance nematic behaviour; it only moderately lowers the T_{NI} and suppresses the smectic phases by at least 50 K.

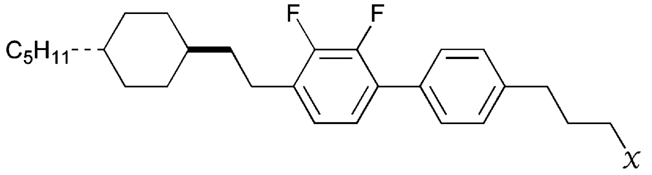
Results obtained for series **1a**–**1c** are consistent with findings reported in the literature for other nematic and smectic materials with functionalized terminal chains. Thus, it was found that the introduction of an oxygen atom into the terminal alkyl group typically decreases the clearing temperature by about 20–30 K (see [35, 36]), while the substitution of an ester group in the terminal alkyl group usually increases melting points and destabilize the mesophase [37–40].

A comparison of the hydrocarbon **1a** with its decyloxy [10] analogue **16** (figure 2) shows that the nematic, SmA and crystal phases are less stable by about 28 K, while the SmC phase is destabilized by over 50 K relative to **16**.

In contrast to **1a**–**1c**, all four tail-fluorinated compounds form SmA phases with relatively high clearing temperatures between 83°C (**1f**) and 117°C (**1g**). The widest SmA phase is observed for the ether **1g** which also has the lowest melting point. Microscopic observations of the supercooled materials showed a monotropic SmC phase only for **1e**.

A comparison of transition temperatures for two isomeric esters **1d** and **1f** shows that both have similar melting points but the former has a higher SmA–I transition temperature by 9 K. Extension of the fluorinated alkyl chain in **1d** by two CF_2 units in **1e** increases the clearing temperature by nearly 10 K and also induced a monotropic SmC phase 10 K below

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1} in parentheses) determined for **1**–**4** in the heating mode. Cr, crystal; Sm, smectic; N, nematic, I, isotropic.

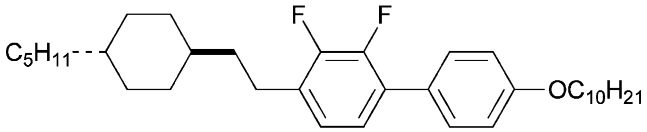


	X	Phase transition
1a	–CH_2CH_2–C_5H_{11}	Cr~22^{a} (SmC 5)^{b,c} SmA 78 N 93 I (0.6) (2.3)
1b	–CH_2O–C_5H_{11}	Cr~8^{c} SmA 35 N 54 I (0.4) (0.9)
1c	–COO–C_5H_{11}	Cr 49 N 59 I (33.8) (0.9)
1d	–COO–$CH_2C_2F_5$	Cr 47 SmA 92 I (30.1) (6.8)
1e	–COO–$CH_2CH_2C_4F_9$	Cr 51 (SmC 41)^{b,c} SmA 103 I 30.0 0.0 (8.3)
1f	–CH_2O–COC_2F_5	Cr 48 SmA 83 I (21.3) (6.1)
1g	–CH_2O–$CH_2C_7F_{15}$	Cr 35 SmA 117 I (20.6) (8.6)
2	–COOMe	Cr 38 N 83 I (23.0) (1.3)
3	–COOH	Cr 86 (SmC 80)^{b,c} SmA 124 I (29.9) (6.0)
4	–CH_2OH	Cr 48 (SmC 40)^{b,c} SmA 124 N 127 I (19.6) (4.1) (1.8)

[a]Estimated temperature. [b]Monotropic transition. [c]Microscopic observation.

melting. Differential scanning calorimetry (DSC) analysis showed practically no enthalpy change at the SmA–SmC transition suggesting a second-order process.

The highly smectogenic effect of the partially fluorinating alkyl chain is clearly seen in esters derived from acid **3**. While the Me and pentyl esters, **1c** and **2**, exhibit only nematic phases with the clearing temperatures of 83°C and 59°C, respectively, the introduction of even five F atoms in ester **1d** completely eliminates the nematic behaviour and increases the clearing temperatures by the estimated 40 K for **1e**.



16

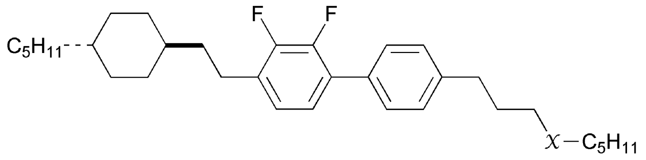
Figure 2. Compound **16**.

Ester **2** showed no SmA phase even upon supercooling to ambient temperature. It is interesting to note that extending the alkyl chain from Me in **2** to pentyl in **1c** considerably narrows the range of the nematic phase by simultaneous increasing the melting point and lowering the T_{NI}.

2.3. *Electro-optical measurements*

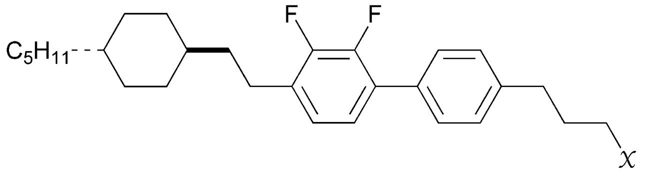
Electro-optical properties were measured for compounds in series **1** and for ester **2**. The results of nematic properties measurements for **1a**–**1c** and **2** were obtained using the single-cell method [41] at the same shifted temperature $\Delta T = T - T_{NI} = -6$ K and are shown in table 2. The effects of fluoroalkyl derivatives **1d**–**1g** on thermal and electro-optical parameters of a chiral FLC host mixture of phenylpyrimidines (MX 6146) are presented in table 3.

Table 2. Phase parameters measured by electro-optical methods at the shifted temperature $T–T_{NI}=-6$ K. Average values of three measurements for three cells are given. Standard deviation for dielectric permittivities $\varepsilon_{\perp}$, $\varepsilon_{\parallel}$ and $\Delta\varepsilon$ is calculated at less than ± 0.07, for the elastic constant K_{11} it is less than ± 0.4 pN and for the viscosity γ_1 it is less than ± 10 mPs.



	X	T (°C)	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	K_{11}(pN)	γ_1(mP s)
1a	$–CH_2CH_2–$	87	2.7	3.35	−0.65	6.3	41
1b	$–CH_2O–$	48	3.3	4.1	−0.80	4.0	64
1c	–COO–	53	3.8	4.55	−0.75	5.0	55
2		77	3.75	4.8	−1.05	8.2	43

Table 3. Thermal and electro-optical data for 0.20 mmol g^{-1} solutions of **1d**–**1g** in a ferroelectric host MX 6146 at ambient temperature. Change of clearing temperatures (ΔT_{NI}), N–SmA transition (ΔT_{NA}), SmA–SmC transition (ΔT_{AC}), electric risetime ($\Delta\tau$), rotational viscosity ($\Delta\gamma_1$), normalized spontaneous polarization ($\Delta P_s{}^{o}$) and tilt angle ($\Delta\Theta$) upon addition of the dopant to the pure host are given.



	X	ΔT_{NI}[a] (K)	ΔT_{NA}[a] (K)	ΔT_{AC}[a] (K)	$\Delta\tau$ (μs)	$\Delta\gamma_1$ (P s)	$\Delta P_s{}^{o}$ (nC cm^{-2})	$\Delta\Theta$
1d	$–COO–CH_2C_2F_5$	−2	0	−3	−25	−0.70	−11.4	+7°
1e	$–COO–CH_2CH_2C_4F_9$	−1	0	−5[b]	+45	−0.84	−8.1	+11°
1f	$–CH_2O–COC_2F_5$	−1	+4	−3	—[c]	—[c]	—[c]	—[c]
1g	$–CH_2O–CH_2C_7F_{15}$	—	+7[d]	−20[d]	−90	−1.24	−15.0	+23°
1g	$–CH_2O–CH_2C_7F_{15}$[f]	0	+3	−9[b]	−45	−0.44	−7.0	+8°
Host[e]		73[f]	67[f]	54[f]	170 ± 10[f]	1.35 ± 0.2[f]	18.4 ± 2[f]	22 ± 1[f]

[a] Difference in the peak of the transition. [b] The SmA–SmC transition obtained from $P_s(T)$ measurements. [c] Not measured, see the text. [d] The difference between SmA–N of the host and SmA–I transition of the mixture. [e] Concentration of **1g** in the host is 0.10 mmol g^{-1}. [f] Absolute value in degrees centigrade.

Electro-optical analysis for solutions of ester **1f** was not performed owing to the low resistivity of the mixture.

2.3.1. Nematic materials.

Results show that all three compounds **1a**–**1c** are weakly polar with small negative dielectric anisotropy $\Delta\varepsilon$ in a range of −0.65 (**1a**) to −0.8 (**1b**) at $\Delta T=-6$ K (table 2). Modification of the alkyl chain in **1a** increases both dielectric components $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ by up to 1.2, and also moderately the dielectric anisotropy $\Delta\varepsilon$. This is expected, because the polar group in the terminal chain is disordered and its dipole moment only weakly contributes to the material's dielectric anisotropy. Results for ester **2**, which has a much wider range of the nematic phase (figure 3), show

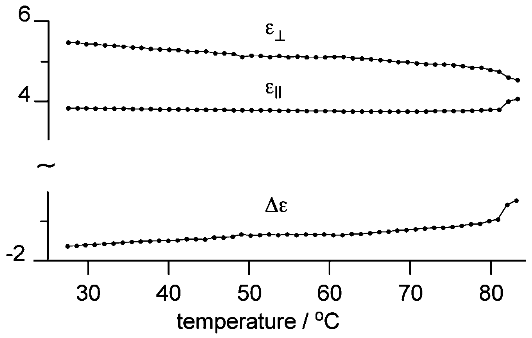


Figure 3. Dielectric permittivity of **2** as a function of temperature.

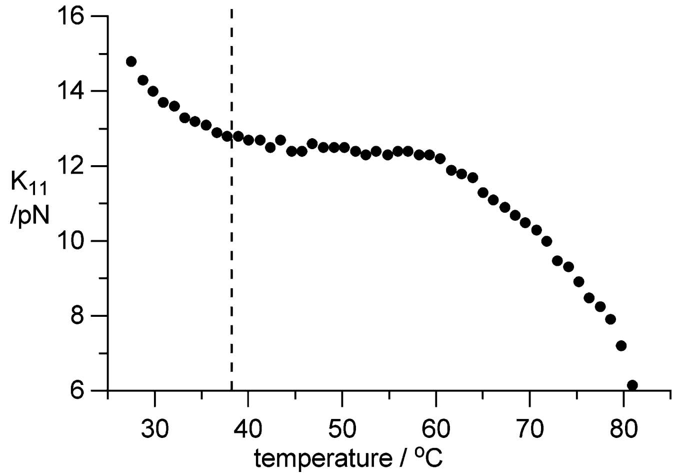


Figure 4. Splay elastic constant K_{11} of **2** as a function of temperature. The line marks the melting temperature of **2**.

that $\Delta\varepsilon$ is larger by about 60% at $\Delta T = -50$ K relative to the value at $\Delta T = -6$ K. This change is mainly due to the increase of the transverse component of the dielectric permittivity $\varepsilon_\perp$, while the $\varepsilon_\parallel$ remains practically constant in this temperature range. Consequently, $\Delta\varepsilon$ extrapolated to ambient temperature for compounds in series **1a**–**1c** can be expected to be about 1.5.

Values of splay elastic constant K_{11} measured for compounds in series **1a**–**1c** (table 2) are in the range of 4.0–6.3 pN, which is typical for nematics [42]. The highest K_{11} was measured for **1a** and the modification of the decyl chain in **1a** lowers the K_{11} value by up to 35%. A temperature dependence of the K_{11} value is shown for **2** in figure 4. As the temperature decreases, the K_{11} value reaches a plateau of about 12 pN at the shifted temperature of -25 K. The elastic constant value starts to increase again at the temperatures below the melting point of **2**, when the material is in its supercooled state. On the basis of the temperature dependence for **2**, a 50% increase of K_{11} can be estimated for compounds **1a**–**1c** further away from the clearing point.

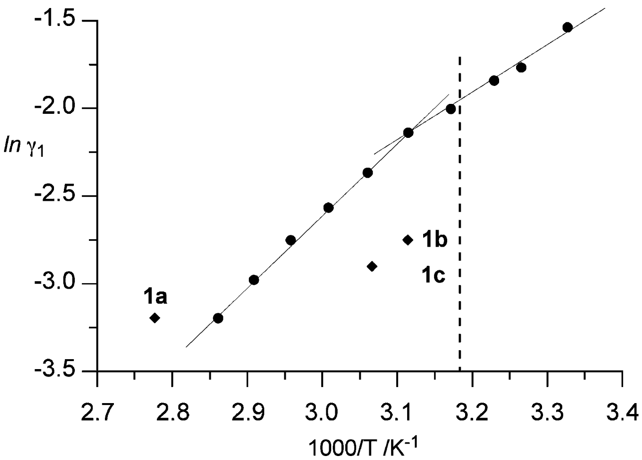


Figure 5. Arrhenius plot of rotational viscosity γ_1 for **2** (circles). Diamonds show single datapoints for **1a**–**1c**. The vertical line marks the melting temperature of **2**.

Rotational viscosity γ_1 (see [43]) was measured for **1a**–**1c** at $\Delta T = -6$ K and for ester **2** as a function of temperature. Analysis of the Arrhenius plot for **2** presented in figure 5 shows two linear regions with the change of the slope at about 10 K above the melting point of the ester. Similar change of phase behaviour was also observed for the $K_{11}(T)$ just above the melting point (figure 4). Fitting the high-temperature datapoints to the following equation gave 8.2 ± 0.1 kcal mol^{-1} as the rotational viscosity activation energy E_a for the nematic phase of **2**:

$$\ln\gamma_1 = \ln\gamma^* + \frac{E_a}{R}\frac{1}{T} \tag{1}$$

A quantitative comparison of rotational viscosity γ_1 within series **1a**–**1c** is difficult since all values were obtained at different absolute temperatures. Assuming, however, that the activation energies E_a for **1a**–**1c** are similar to that for **2** (figure 5), it can be speculated that the trend in viscosity follows **1a**>**2**>**1b**~**1c**.

2.3.2. Effect on ferroelectric properties.

The addition of 0.20 mmol g^{-1} (about 15% w/w) of the tail-fluorinated derivatives **1d**–**1g** had relatively little effect on the clearing temperature of the FLC host, and the largest change of -2 K was observed for **1d** (table 3). The SmA–N transition temperature, T_{AN}, remains practically unchanged for solutions of esters **1d** and **1e**, while it is higher for solutions of **1f** (by +4 K) and **1g** at the expense of the nematic phase, which is completely absent for the latter. This, combined with the depression of the

SmA–SmC transition temperature, leads to the expansion of the SmA phase by up to 27 K observed for **1g**. A less-concentrated solution of **1g** in the host showed a significantly smaller expansion of the SmA phase and a narrow range nematic phase. Stabilization of smectic phases by partial fluorination of the terminal chain is a well-known phenomenon [44–48], which has been ascribed to the rigidity of the fluorinated alkyl chain and interactions of the polar flourous fragments [49]. Similar enhancement of smectic phases was observed in mixtures of tail-fluorinated and non-fluorinated mesogens [48, 50].

Optical investigation of the solutions in the FLC host demonstrated that all additives **1d**–**1g** increased the tilt angle Θ (table 3). The increase appears to be greater for the additives with a higher degree of tail-fluorination. Remarkably, 0.2 $\mathrm{mmol\,g^{-1}}$ of **1g** induced a 45° tilt angle in the host. These results are consistent with other observations of generally higher tilt angle Θ in compounds with fluorinated tails [47, 51]. It has also been found that tail-fluorinated additives increase the value of Θ significantly more than that the non-fluorinated analogues [50]. This tendency to the formation of high-tilt phases has been attributed to conformational properties of the partially fluorinated alkyl chains [52] and increased free volume created by these groups.

For the purpose of comparison of the electro-optical data for the additives, polarization and the rotational viscosity were normalized to remove their dependence on the tilt angle Θ and the calculated P_s^o and γ_1 are shown in table 3. The tilt-independent cone rotational viscosity γ_1 was calculated from the measured viscosity γ_s assuming the negligibly small contribution from the on-axis rotational viscosity γ_2 (equation (2)). The normalization of the polarization P_s (equation (3)) also largely removed its dependence on temperature:

$$\gamma_s = \gamma_1 \sin^2(\Theta) + \gamma_1 \sin^2(\Theta) \approx \gamma_1 \sin^2(\Theta) \qquad (2)$$

$$P_s^o = P_s / \sin(\Theta) \qquad (3)$$

Data in table 3 revealed that all three additives decrease the polarization of the host. This is expected to some degree, because the additives dilute the chiral content. The smallest decrease of about 44% of the normalized spontaneous polarization P_s^o is observed for ester **1e**. The most dramatic decrease in P_s^o by about 80% was measured for **1g** at the concentration of 0.2 $\mathrm{mmol\,g^{-1}}$. This, however, is due in large part to the depression of the host's phase transition temperature by 20 K and, consequently, to the proximity to the SmC–SmA transition. This additive also shows a significant decrease of rotational viscosity γ_1 by about 60% relative to that for the pure host, which again is partially due to the depression of the host's SmC–SmA transition. Further away from the transition point (T–T_{AC} = −19 K), **1g** at a concentration of 0.1 $\mathrm{mmol\,g^{-1}}$ exhibits the expected moderate lowering of the viscosity. Electro-optical analysis of the solutions also shows that the electric rise time τ is lowered for two additives **1d** and **1g**, and is moderately increased for ester **1e**. The observed lowering of the rise time by the fluorinated additives can be attributed to the increased free volume in the material by the sterically demanding R_f groups. Such an effect has been observed for tail-fluorinated [50], carborane-containing [48] and non-mesogenic cyclodextrine additives [53].

3. Summary and conclusions

Investigation of series **1** demonstrated that tuning of thermal and electro-optical properties is possible by judicious choice of the functional group and the F-content in the terminal chain. For instance, the introduction of the ester functionality (**1c**) destabilizes the smectic phases, decreases the splay elastic constant and only moderately increases the rotational viscosity relative to the decyl derivative **1a**. On the other hand, derivatives with partially fluorinated alkyl substituents (**1d**–**1g**) exhibit enhanced smectic stability and induced high tilt angles in ferroelectric materials. Both classes of materials are promising candidates for applications and the results warrant further studies.

The stability of the smectic phase appears to increase with the increasing number of F atoms in the series of tail-fluorinated derivatives **1d**–**1g**. Results show that esters **1d** and **1e** give the desired improvement of electro-optical properties of the FLC host. Ether **1g** with 15 F atoms is a powerful dopant, which significantly alters all parameters. The addition of **1g** to a FLC hosts leads to significant expansion of the SmA phase, destabilization of the SmC* phase, but also to an increase of the tilt angle of up to 45° for concentrations of 0.2 $\mathrm{mmol\,g^{-1}}$.

The availability of the common intermediates, acid **3** and the corresponding alcohol **4**, has opened convenient access to a number of other derivatives of the general structure **1**. This, in turn, enables further and more precise adjustment of properties of nematic and smectic materials by varying the length, the structure and the F-content of the substituent on the oxygen atom.

The synthetic methodology described here provides a general synthetic path for the introduction of an oxygen atom and an ester group to the terminal alkyl chain, and lends itself to the expansion to other chain-functionalized derivatives. Thus, the use of other phenylalkanecarboxylic acids instead of 4-phenylbutyric acid opens the possibility to prepare analogues of **1** with a variable length of the alkyl spacer between the core and the functional group and also permits the introduction of a chiral centre.

4. Experimental details

4.1. *General*

All ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$. Chemical shifts were referenced to the solvent. IR spectra were recorded for neat samples (liquid or microcrystalline) on NaCl plates using an ATI Mattson Genesis Series FTIR. Mass spectrometry was acquired using a HP 5890 Series II GC with attached 5971 Series MS in EI mode. Elemental analysis was provided by Atlantic Microlabs. Fast atom bombardment mass spectrometry (FAB/MS) and exact mass spectrometry was performed at University of Notre Dame, IN. For DSC and microscopic analyses, each compound was rigorously purified by dissolving in CH_2Cl_2, filtering to remove particles, condensing and recrystallization from an appropriate solvent until constant transition temperatures were obtained. The resulting crystals were dried in vacuum at ambient temperature.

Optical microscopy and phase identification was performed using a PZO 'Biolar' polarized microscope equipped with a HCS250 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 differential scanning calorimeter. Transition temperatures (onset) and enthalpies were obtained using small samples (1–2 mg) and a heating rate of 5 K min^{-1} under a flow of nitrogen gas.

4.2. *Measurements*

4.2.1. Nematic dielectric measurements. Properties of compounds **1a**–**1c** and ester **2** were measured using Liquid Crystal Analytical System (LCAS; Series II, LC Analytical Inc.) using GLCAS software version 0.929 and implemented algorithms.

The compounds were loaded into ITO electro-optical cells by capillary action at the isotropic state. The cells (about 5 μm thick, electrode area of 0.28 cm^2 covered with a surfactant to impose a homeotropic alignment) were obtained from LCA Inc. and their precise thickness was measured by LCAS using the capacitance method. The filled cells were conditioned for an hour at the appropriate temperature before measurement.

Dielectric constants were measured using the single-cell method [41] and the following default parameters: triangular-shaped voltage ranging from 15–0.5 V at 1 kHz frequency. The threshold voltage V_{th} was measured as 5% of the change. Each compound was measured in three cells and for each cell the measurement was repeated three times (3×3). The resulting parameters were averaged and are presented in table 2. The temperature reading in LCAS and DSC was made consistent by a comparison of the isotropic transitions observed in the two instruments.

4.2.2. FLC electro-optical measurements. All solution studies of series **1d**–**1g** were performed in a FLC host MX 6146 (Displaytech) using LCAS II with the software version 0.929 in standard 4 μm cells using a bias of 6 V μm^{-1} and a frequency of 100 Hz triangular waveform at 26°C. Both, electric risetime [54] and rotational viscosity [55] were measured using methods implemented in the literature. The risetime was measured as the time from the onset of the driving square wave to the maximum polarization reversal peak.

Solutions of **1d**–**1g** in the host with a concentration of 0.2 mmol g^{-1} (and also 0.1 mmol g^{-1} for **1g**) were prepared and conditioned for 12 h at 50°C. The mixtures were loaded into ITO electro-optical cells by capillary action at about 90°C. The cells (about 4 μm thick, electrode area of 0.56 cm^2 and antiparallel rubbed polyimide layer 2–3° pre-tilt) were obtained from LCA Inc. and their precise thickness (±0.05 μm) was measured using dielectric methods. The samples were aligned by heating the cells to the isotropic phase followed by slow cooling to the SmC* phase at a cooling rate of 2°C min^{-1} under a permanently applied square-form electric field of 1.5 V μm^{-1} and a frequency of 100 Hz.

Each solution was studied in at least two different cells and the measurements were repeated 10 times for each cell. The results were averaged and are presented in table 3.

Solution of **1d**, **1e** and **1g** had a specific resistivity of more than 20 MΩ cm. In contrast, conditioned solutions of **1f** had low resistivity, which prevented electro-optical measurements.

The tilt angle Θ was measured using a published method [56] as one-half of the rotation of the fully extinguished state between crossed polarizers in an electric square wave field of 4.0 V μm^{-1} and a frequency of 100 Hz.

The MX 6146 hosts had the following parameters: Cr<20 SmC* 54 SmA 67 N 73 I (peak transitions); $\tau=170\pm10$ μs, $\gamma_s=0.19\pm0.02$ P s, $P_s=6.9\pm0.4$ nC cm^{-2}, $\Theta=22°\pm1°$. The error bars for the host represent the typical accuracy of the measurement.

4.3. *Synthesis*

4.3.1. 1′-Decyl-2,3-difluoro-4-(2-(E-4-pentylcyclohexyl)-ethyl)-biphenyl (1a). Compound **1a** was prepared in a Suzuki coupling reaction of boronic acid **5** and 1-bromo-4-decylbenzene (**7**) [31] according to a general procedure [10]. The crude product was passed through a silica gel plug, which was washed with hexanes. The eluent was evaporated leaving 22 mg (49% yield) of the crude product as a glassy solid. The analytical sample was obtained by recrystallization from EtOH/AcOEt followed by MeCN/toluene at −10°C: ^{1}H NMR δ 0.88 (t, J=6.6 Hz, 6H), 0.80–1.11 (m, 3H), 1.11–1.38 (m, 23H), 1.45–1.55 (m, 2H), 1.57–1.63 (m, 2H), 1.65–1.85 (m, 4H), 2.64 (t, J=7.9 Hz, 2H), 2.69 (t, J=7.3 Hz, 2H), 6.97 (td, J_1=7.4 Hz, J_2=1.2 Hz, 1H), 7.08 (td, J_1=7.5 Hz, J_2=1.5 Hz, 1H), 7.25 (d, J=8.2 Hz, 2H), 7.45 (dd, J_1=8.0 Hz, J_2=1.3 Hz, 2H). HRMS, calculated for $C_{35}H_{52}F_2$: *m*/*z* 510.4037; found: *m*/*z* 510.4027.

4.3.2. 1′-(4-Pentyloxybutyl)-2,3-difluoro-4-(2-(E-4-pentylcyclohexyl)ethyl)biphenyl (1b). Alcohol **4** (36 mg, 0.08 mmol) was added to the suspension of powdered KOH (18 mg, 0.32 mmol) in anhydrous DMSO (4 ml) at room temperature. After stirring for 30 min, 1-bromopentane was added (24 mg, 0.16 mmol) and the reaction mixture was stirred for 72 h. H_2O (3 ml) was added and the organic products were extracted with EtOAc (3 × 10 ml), extracts were dried (Na_2SO_4) and the solvent was evaporated to give 30 mg (75% yield) of ether **1b** as a transparent oil. The crude product was purified by column chromatography (SiO_2, hexanes). The analytical sample was obtained by recrystallization from *i*-PrOH (2 ×) followed by MeCN/AcOEt at −15°C: ^{1}H NMR δ 0.88 (t, J=7.1 Hz, 3H), 0.90 (t, J=6.7 Hz, 3H), 0.80–1.13 (m, 3H), 1.12–1.38 (m, 10H), 1.47–1.88 (m, 6H), 2.64–2.72 (m, 4H), 3.39 (t, J=6.8 Hz, 2H), 3.43 (t, J=6.4 Hz, 2H), 6.96 (t, J=7.4 Hz, 1H), 7.08 (td, J_1=7.5 Hz, J_2=1.5 Hz, 1H), 7.26 (d, J=8.1 Hz, 2H), 7.45 (dd, J_1=8.0 Hz, J_2=1.2 Hz, 2H). HRMS, calculated for $C_{34}H_{44}F_2O$: *m*/*z* 512.3830; found: *m*/*z* 512.3854.

4.3.3. Pentyl 4-(2′,3′-difluoro-4′-(2-(E-4-pentylcyclohexyl)-ethyl)biphenyl-1-yl)butanoate (1c). 1-Pentanol (0.12 ml, 0.11 mmol) was added to the solution of carboxylic acid **3** (50 mg, 0.11 mmol), DCC (27 mg, 0.11 mmol) and 4-(dimethylamino)pyridine (DMAP, 3 mg, 0.02 mmol) in anhydrous CH_2Cl_2 (2 ml). The reaction mixture was stirred at room temperature for 1 h, concentrated and the product was isolated by flash chromatography (SiO_2, hexane/CH_2Cl_2, 1:1) affording 44 mg (76% yield) of the pentyl ester **1c** as a white crystalline solid. The analytical sample was obtained by crystallization from *i*-octane (3 ×): ^{1}H NMR δ 0.88 (t, J=7.1 Hz, 3H), 0.91 (t, J=7.0 Hz, 3H), 0.80–1.05 (m, 3H), 1.15–1.41 (m, 13H), 1.47–1.70 (m, 4H), 1.70–1.88 (m, 4H), 2.02 (quint, J=7.5 Hz, 2H), 2.36 (t, J=7.5 Hz, 2H), 2.70 (br t, J=7.5 Hz, 4H), 4.07 (t, J=6.6 Hz, 2H), 6.97 (td, J_1=7.4 Hz, J_2=1.2 Hz, 1H), 7.08 (td, J_1=7.4 Hz, J_2=1.5 Hz, 1H), 7.26 (d, J=8.1 Hz, 2H), 7.45 (dd, J_1=8.1 Hz, J_2=1.5 Hz, 2H). Anal. calculated for $C_{34}H_{48}F_2O_2$: C, 77.53; H, 9.19. Found: C, 77.27; H, 9.23.

4.3.4. 3,3,3,2,2-Pentafluoropropyl 4-(2′,3′-difluoro-4′-(2-(E-4-pentylcyclohexyl)ethyl)biphenyl-1-yl)butanoate (1d). Alcohol $C_2F_5CH_2OH$ (0.11 mmol) was added to the solution of carboxylic acid **3** (50 mg, 0.11 mmol), DCC (27 mg, 0.11 mmol), DMP (3.0 mg, 0.02 mmol) in dry CH_2Cl_2 (2 ml). The reaction mixture was stirred at room temperature for 1 h, concentrated and separated by flash chromatography (SiO_2, hexane/CH_2Cl_2, 1:1) to give 50 mg (78% yield) of ester **1d** as a colourless solid. The analytical sample was obtained by two recrystallizations from *i*-octane followed by one recrystallization from MeCN: ^{1}H NMR δ 0.88 (t, J=6.7 Hz, 3H) 0.80–1.03 (m, 4H), 1.10–1.35 (m, 10H), 1.47–1.57 (m, 2H), 1.71–1.87 (m, 4H), 2.03 (quint, J=7.4 Hz, 2H), 2.47 (t, J=7.3 Hz, 2H), 2.63–2.77 (m, 4H), 4.54 (t, J=13.0 Hz, 2H), 6.97 (t, J=7.2 Hz, 1H), 7.08 (t, J=7.5 Hz, 1H), 7.25 (d, J=7.2 Hz, 2H), 7.46 (d, J=7.2 Hz, 2H). Anal. calculated for $C_{32}H_{39}F_7O_2$: C, 65.29; H, 6.68. Found: C, 65.50; H, 6.61.

4.3.5. 6,6,6,5,5,4,4,3,3-Nonafluorohexyl 4-(2′,3′-difluoro-4′-(2-(E-4-pentylcyclohexyl)ethyl)biphenyl-1-yl)butanoate (1e). The ester was prepared in 71% yield according to the procedure described for **1d**. The analytical sample was obtained by two recrystallizations from *i*-octane: ^{1}H NMR δ 0.88 (t, J=6.8 Hz, 3H), 0.90–1.0 (m, 4H), 1.11–1.37 (m, 9H), 1.47–1.59 (m, 4H), 1.71–1.87 (m, 4H), 2.00 (quint, J=7.4 Hz, 2H), 2.38 (t, J=7.4 Hz, 2H), 2.47 (tt, J_1=18.3 Hz, J_2=6.4 Hz, 1H), 2.70 (br t, J=7.3 Hz, 4H), 4.38 (t, J=6.5 Hz, 2H), 6.97 (t, J=7.7 Hz, 1H), 7.08 (td, J_1=7.5 Hz, J_2=1.5 Hz, 1H), 7.24 (d, J=7.1 Hz, 2H), 7.45 (d, J=6.9 Hz, 2H). Anal. calculated for $C_{35}H_{41}F_{11}O_2$: C, 59.82; H, 5.88. Found: C, 59.92; H, 5.87.

4.3.6. 4-(2′,3′-Difluoro-4′-(2-(E-4-pentylcyclohexyl)ethyl)-biphenyl-1-yl)butyl pentafluoropropionate (1f). A pyridine solution (2 ml) of perfluoropropionyl anhydride (56 mg, 0.18 mmol) was added to the solution of alcohol **4** (40 mg, 0.09 mmol) in dry pyridine (2 ml) at 0°C. The reaction mixture was stirred at room temperature overnight, then it was poured into 5% HCl (5 ml), extracted with CH_2Cl_2 (5 ml, 3 ×) and the extracts were washed with saturated $NaHCO_3$. The crude product was purified by flash chromatography (SiO_2, hexane/CH_2Cl_2, 2:1) to give

45 mg (84% yield) of pure ester **1f**. The analytical sample was obtained by recrystallization first from MeCN, then from *i*-octane and finally from *i*-PrOH: ^{1}H NMR δ 0.88 (t, J=6.9 Hz, 3H), 0.84–1.02 (m, 4H), 1.13–1.33 (m, 10H), 1.49–1.57 (m, 2H), 1.73–1.85 (m, 8H), 2.69 (t, J=7.2 Hz, 2H), 2.71 (t, J=7.1 Hz, 2H), 4.41 (t, J=6.1 Hz, 2H), 6.97 (t, J=7.3 Hz, 1H), 7.08 (t, J=7.4 Hz, 1H), 7.25 (d, J=7.0 Hz, 2H), 7.46 (d, J=7.2 Hz, 2H). Anal. calculated for $C_{32}H_{39}F_7O_2$: C, 65.29; H, 6.68. Found: C, 65.22; H, 6.78.

4.3.7. 8-(4-(2′,3′-Difluoro-4′-(2-(E-4-pentylcyclohexyl)-ethyl)-biphenyl-1-yl)butyloxy)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentadecafluoroctane (1g). Following the general procedure [29], a solution of ADDP (50 mg, 0.2 mmol) in dry benzene (3 ml) and tributylphosphine (40 mg, 0.2 mmol) were added to the solution of alcohol **4** (46 mg, 0.1 mmol) and $C_7F_{15}CH_2OH$ (320 mg, 0.8 mmol) and the reaction mixture was stirred for 20 h at 60°C. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 5:1) to give 56 mg (69% yield) of pure ether **1g**. The analytical sample was obtained by recrystallization first from *i*-octane and then from MeCN/AcOEt: ^{1}H NMR (500 MHz) δ 0.88 (t, J=7.0 Hz, 3H), 0.80–1.04 (m, 4H), 1.13–1.33 (m, 10H), 1.49–1.55 (m, 2H), 1.65–1.85 (m, 8H), 2.66–2.71 (m, 4H), 3.63 (t, J=6.1 Hz, 2H), 3.92 (t, J=13.9 Hz, 2H), 6.96 (t, J=7.1 Hz, 1H), 7.08 (t, J=7.5 Hz, 1H), 7.25 (d, J=7.3 Hz, 2H), 7.44 (d, J=7.1 Hz, 2H). Anal. calculated for $C_{37}H_{41}F_{17}O$: C, 54.02; H, 4.78. Found: C, 54.48; H, 5.02.

4.3.8. Methyl 4-(2′,3′-difluoro-4′-(2-(E-4-pentylcyclohexyl)-ethyl)biphenyl-1-yl)butanoate (2). A solution of iodo ester **6** (1.31 g, 4.3 mmol) and boronic acid **5** (1.58 g, 4.73 mmol) in benzene (35 ml), 2M Na_2CO_3 (5 ml) and EtOH (5 ml) was degassed with Ar for 45 min. $(PPh_3)_2PdCl_2$ (0.15 g, 0.215 mmol) was the added and the resulting reaction mixture was vigorously stirred and gently refluxed. The reaction progress was monitored with ^{1}H NMR and, if necessary, more catalyst was added. When the starting iodide **6** was no longer detected (about 24 h), the reaction mixture was diluted with water, the pH was adjusted with aqueous HCl (10%) and the organic products were extracted with Et_2O. The organic layers were combined, washed with brine, dried ($MgSO_4$) and the solvents were evaporated to yield a reddish oil. The crude product was passed through a silica gel plug using hexane first to remove a fast moving by-product and then (CH_2Cl_2/hexane, 1:1) to elute the product. The product was purified further by column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) to give 1.45 g (73% yield) of methyl ester **2** as a colourless oil that solidified upon standing. An analytical sample was obtained by recrystallization first from MeCN and then from hexane: ^{1}H NMR δ 0.88 (t, J=6.6 Hz, 3H), 0.80–1.05 (m, 3H), 1.15–1.38 (m, 11H), 1.48–1.58 (m, 2H), 1.73–1.85 (m, 4H), 2.00 (quint, J=7.5 Hz, 2H), 2.37 (t, J=7.4 Hz, 2H), 2.70 (br t, J=7.6 Hz, 4H), 3.68 (s, 3H), 6.97 (t, J=7.3 Hz, 1H), 7.08 (t, J=7.4 Hz, 1H), 7.28 (d, J=7.8 Hz, 2H), 7.45 (d, J=8.0 Hz, 2H). Anal. calculated for $C_{30}H_{40}F_2O_2$: C, 76.56; H, 8.57. Found: C, 76.15; H, 8.57.

2,3-Difluoro-4-(2-(*E*-4-pentylcyclohexyl)ethyl)biphenyl was isolated in 5% yield as a by-product in the preparation of ester **2** as a fast-moving component in the chromatographic separation: ^{1}H NMR δ 0.90 (t, J=7.1 Hz, 3H), 0.80–1.05 (m, 3H), 1.15–1.38 (m, 11H), 1.48–1.58 (m, 2H), 1.73–1.86 (m, 4H), 2.72 (br t, J=8.0 Hz, 4H), 6.99 (t, J=7.3 Hz, 1H), 7.09 (t, J=7.1 Hz, 1H), 7.37 (t, J=7.1 Hz, 1H), 7.45 (t, J=7.3 Hz, 2H), 7.54 (d, J=7.8 Hz, 2H). HRMS, calculated for $C_{25}H_{32}F_2$: *m*/*z* 370.2472; found: *m*/*z* 370.2483.

4.3.9. 4-(2′,3′-Difluoro-4′-(2-(E-4-pentylcyclohexyl)ethyl)-biphenyl-1-yl)butanoic acid (3). Methyl ester **2** (300 mg, 0.64 mmol) was added to the solution of NaOH (53 mg, 1.3 mmol) in EtOH (10 ml). The reaction mixture was refluxed (30 min) and H_2O (10 ml) followed by concentrated HCl (2 ml) were added. After stirring for 15 min, the organic products were extracted (CH_2Cl_2, 10 ml, 3 ×), extracts were dried (Na_2SO_4) and the solvents were evaporated. The resulting solid residue was recrystallized (*i*-octane) affording 230 mg (79% yield) of acid **3** as a white crystalline solid. Analytical sample was obtained by three recrystallizations from MeCN: ^{1}H NMR δ 0.88 (t, J=6.6 Hz, 3H), 0.80–1.05 (m, 3H), 1.09–1.36 (m, 11H), 1.45–1.56 (m, 3H), 1.69–1.86 (m, 4H), 2.01 (quint, J=7.5 Hz, 2H), 2.37 (t, J=7.4 Hz, 2H), 2.70 (t, J=7.5 Hz, 2H), 2.72 (t, J=8.0 Hz, 2H), 6.97 (t, J=7.3 Hz, 1H), 7.08 (td, J_1=7.5 Hz, J_2=1.5 Hz, 1H), 7.26 (d, J=7.8 Hz, 2H), 7.46 (d, J=7.8 Hz, 2H). Anal. calculated for $C_{29}H_{38}F_2O_2$: C, 76.28; H, 8.39. Found: C, 76.14; H, 8.47.

4.3.10. 4-(2′,3′-Difluoro-4′-(2-(E-4-pentylcyclohexyl)ethyl)-biphenyl-1-yl)butanol (4). A solution of methyl ester **2** (1.11 g, 2.37 mmol) in dry Et_2O (35 ml) was slowly added to a suspension of $LiAlH_4$ (0.18 g, 4.74 mmol) in dry Et_2O (35 ml). The reaction mixture was refluxed overnight and quenched with aqueous Et_2O (10 ml), followed by H_2O (0.5 ml), 15% NaOH (0.5 ml) and finally H_2O (1.6 ml). The resulting white precipitate was filtered through Celite, the filtrate was dried (Na_2SO_4) and the solvent was evaporated to give a pale white solid. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) followed by recrystallization (*i*-octane) to give 1.02 g (98% yield) of alcohol **4** as a white crystalline solid. The analytical sample was obtained by two recrystallizations from MeCN/AcOEt: ^1H NMR δ 0.89 (t, J=6.6 Hz, 3H), 0.83–1.04 (m, 3H), 1.08–1.36 (m, 11H), 1.48–1.57 (m, 2H), 1.60–1.87 (m, 6H), 2.70 (br t, J=7.5 Hz, 4H), 3.69 (pseudo q, J=6.0 Hz, 2H), 6.97 (t, J=7.3 Hz, 1H), 7.08 (t, J=7.4 Hz, 1H), 7.27 (d, J=7.8 Hz, 2H), 7.45 (d, J=7.8 Hz, 2H). Anal. calculated for $C_{29}H_{40}F_2O$: C, 78.69; H, 9.11. Found: C, 78.72; H, 9.23.

4.3.11. 2,3-Difluoro-4-(2-(E-4-pentylcyclohexyl)ethyl)-phenylboronic acid [10] (5). A 2.5 M hexane solution of *n*-BuLi (1.7 ml, 4.3 mmol) was added dropwise to a solution of compound **15** (1.23 g, 4.2 mmol) in THF (20 ml) at −78°C under Ar atmosphere. The mixture was stirred for 2.5 h after which $(CH_3O)_3B$ (0.87 g, 8.4 mmol) was added. The mixture was stirred at room temperature overnight, acidified with aqueous HCl (10%) and stirred for 1 h. The mixture was extracted (Et_2O), extracts were dried ($MgSO_4$), the was solvent evaporated and the solid residue was purified by recrystallization (*iso*-octane/toluene) to give 1.04 g (73% yield) of boronic acid **5** as a white crystalline solid: melting point 104°C; ^1H NMR δ 0.88 (t, J=7.1 Hz, 3H), 0.82–1.05 (m, 3H), 1.15–1.38 (m, 11H), 1.49–1.54 (m, 2H), 1.71–1.83 (m, 4H), 2.69 (t, J=8.0, 2H), 4.95 (br, 2H), 6.99 (brt, J=6.7 Hz, 1H), 7.45 (t, J=6.2 Hz, 1H). Anal. calculated for $C_{19}H_{29}BF_2O_2$: C, 67.47; H, 8.64. Found: C, 66.82; H, 8.55.

More product **5** was recovered from the mother liquor by passing it through a silica gel plug and using hexane to elute **15** and subsequently CH_2Cl_2 for eluting the boronic acid **5**.

4.3.12. Methyl 4-(4-Iodophenyl)butanoate (6) [30]. 4-Phenylbutanoic acid (20.0 g, 121.8 mmol), elemental I_2 (12.37 g, 48.7 mmol) and periodic acid (5.55 g, 24.4 mmol) were slowly added to a mixture of concentrated H_2SO_4 (5 ml), acetic acid (165 ml) and H_2O (35 ml). The solution was stirred at 75°C for 18 h and cooled. H_2O (200 ml) was added and the precipitate was filtered and dissolved in CH_2Cl_2. The organic solution was washed with H_2O and saturated Na_2SO_3, dried ($MgSO_4$) and the solvent was evaporated to give 31.1 g of a white solid. Three recrystallizations (*iso*-octane/toluene, 5:1) gave 16.00 g (45% yield) of 4-(4-iodophenyl)butanoic acid as a white crystalline solid: melting point 90°C (the literature [57] gives the melting point as 89–90.5°C). ^1H NMR was identical to the reported data [30].

Oxalyl chloride (2 M solution in CH_2Cl_2, 3 ml, 6 mmol) was slowly added to 4-(4-iodophenyl)butanoic acid (1.5 g, 5.15 mmol). After 30 min volatiles were removed and CH_3OH (50 ml) was added. The resulting mixture was stirred and gently refluxed for 1 h. Excess methanol was evaporated and the resulting crude product was purified by short-path distillation (Kugel-Rohr; 130°C/0.15 mm Hg) to give 1.44 g (92% yield) of methyl ester **6** as a colourless liquid. ^1H NMR was identical to the reported data [30].

4.3.13. 2-(E-4-Pentylcyclohexyl)acetonitrile (11). A diethyl ether solution (350 ml) of *E*-4-pentylcyclohexylcarboxylic acid (**8**, 48.3 g, 0.24 mol) was added dropwise to a suspension of $LiAlH_4$ (14.0 g, 0.36 mol) in dry diethyl ether (350 ml) and the mixture was stirred (mechanical stirrer) and refluxed overnight. Et_2O saturated with H_2O (300 ml) was added followed by H_2O (15 ml), 15% NaOH (15 ml) and finally H_2O (40 ml). After stirring for 30 min, the white precipitation was filtered, the filtrate was dried ($NaHCO_3$) and the solvent was evaporated leaving 44.5 g (99% yield) of crude alcohol **9** as a colourless oil.

A solution of crude alcohol **9** (44.5 g, 0.24 mol) in pyridine (200 ml) was added slowly to a suspension of toluenesulfonyl chloride (57.0 g, 0.30 mol) in dry pyridine (100 ml) at 0°C. The reaction mixture was stirred for 3 h after which it was stored in a refrigerator overnight. The solution was washed with aqueous HCl (10%) followed by Na_2HSO(sat), extracted (CH_2Cl_2), dried ($MgSO_4$) and the solvent was evaporated. The crude of 1-(*E*-4-pentylcyclohexyl)methyl *p*-toluenesulfonate (**10**, 78.0 g, 96% yield) was obtained as a pale yellow oil, which was used in the subsequent reaction without further purification.

A suspension of NaCN (32.5 g, 0.66 mol), crude tosylate **10** (78.0 g, 0.23 mol) and tetrabutylammonium bromide (3.7 g, 0.011 mol) in dry acetonitrile (300 ml) was refluxed overnight. The precipitation was filtered, the solvent was evaporated and the residue was passed through a silica gel plug (hexane). Further purification by short-path distillation (Kugel-Rohr, 120°C/0.3 mmHg) gave 27.8 g (62% yield) of 2-(*E*-4-pentylcyclohexyl)acetonitrile (**11**) as a colourless liquid: ^1H NMR δ 0.88 (t, J=6.9 Hz, 3H), 0.92–1.33 (m, 13H), 1.54–1.66 (m, 1H), 1.82 (br t, J=11 Hz, 4H), 2.24 (d, J=6.6 Hz, 2H); IR 2246 (CN) cm^{-1}; MS, *m*/*z* 192 (M-1, 2), 164 (100), 81 (94). Anal. calculated for $C_{13}H_{23}N$: C, 80.76; H, 11.99. Found: C, 80.71; H, 11.84.

4.3.14. 2-(E-4-Pentylcyclohexyl)acetaldehyde [10, 58] (12). DIBAL (1 M solution in hexane, 150 ml, 0.15 mol) was added slowly to a solution of nitrile **11** (27.8 g, 0.14 mol) in dry toluene (800 ml) at −10°C and the reaction mixture was stirred for 45 min. A 5% aqueous solution of HCl (50 ml) was added, the mixture was stirred for 15 min at 0°C, filtered through Celite. The organic layer was separated, dried (Na_2SO_4) and the solution was passed through a silica gel plug. The solvent was evaporated to give 27.45 g (quantitative yield) of an oily residue, which was used in the next step without further purification. The analytical sample was additionally purified by short-path distillation (Kugel-Rohr, 130°C/0.15 mmHg; the literature gives: boiling point 135°C (bath)/0.5 mmHg in [58]; or boiling point 92–94°C/0.5 mmHg in [10]) to give aldehyde **12** as a colourless oil. ^{1}H NMR δ 0.88 (t, J=6.9 Hz, 3H), 0.92–1.33 (m, 13H), 1.74 (br d, J=10 Hz, 4H), 1.75–1.85 (m, 1H), 2.28 (dd, J_1=6.7 Hz, J_2=2.3 Hz, 2H), 9.75 (t, J=2.4 Hz, 1H); MS, *m/z* 196 (M, 1), 152 (53), 96 (81), 81 (100).

4.3.15. 1,2-Difluoro-3-(2-(E-4-pentylcyclohexyl)ethyl)-benzene [10] (15). A 2.4 M hexane solution of *n*-BuLi (3.0 ml, 7.34 mmol) was slowly added to a cooled solution (−78°C) of 1,2-difluorobenzene (0.83 g, 7.34 mmol) in dry THF (15 ml) under an Ar atmosphere. The mixture was stirred for 2.5 h and a solution of aldehyde **12** (1.20 g, 6.1 mmol) in THF (5 ml) was added dropwise. The reaction mixture was stirred for 1.5 h, quenched with saturated NH_4Cl, extracted (CH_2Cl_2), extracts were dried ($MgSO_4$) and the solvent was evaporated. The oily residue was passed through a silica gel plug (hexane, then CH_2Cl_2/EtOAc, 10:1) to give 1.88 g (82% yield) of 1-(2,3-difluorophenyl)-2-(*E*-4-pentylcyclohexyl)ethanol (**13**) as a colourless oil (melting point given as 42–43°C in [10]). ^{1}H NMR δ characteristic signal: 5.15 (dd, J_1=8.7 Hz, J_2=4.8 Hz, 1H).

Without further purification, crude alcohol **13** (1.88 g. 6.1 mmol) was dissolved in cyclohexane (15 ml) and P_2O_5 (2.60 g, 18.3 mmol) was added. The suspension was stirred at room temperature overnight. The reaction mixture was passed through a silica gel plug (petroleum ether) and the solvents were evaporated to give 1.37 g (77% yield) of 1,2-difluoro-3-(2-(*E*-4-pentylcyclohexyl)-*E*-ethenyl)benzene (**14**) as a colourless oil: ^{1}H NMR δ 0.88 (t, J=6.8 Hz, 3H), 0.92–1.05 (m, 2H), 1.10–1.35 (m, 11H), 1.75–1.86 (m, 4H), 2.03–2.17 (m, 1H), 6.28 (dd, J_1=16.2 Hz, J_2=6.9 Hz, 1H), 6.50 (d, J=16.2 Hz, 1H), 6.95–7.01 (m, 2H), 7.16–7.21 (m, 1H); MS, *m/z* 292 (M, 35), 165 (61), 140 (89), 127 (95) 81 (100). The oil was used in the subsequent step without further purification.

A solution of olefin **14** (1.37 g, 4.7 mmol) in cyclohexane was slowly added to a suspension of Pd/charcoal (10%, 131 mg) in cyclohexane (20 ml) under a H_2 atmosphere. The reaction mixture was stirred at room temperature for 5 h, passed through a silica gel plug (hexane), the solvent was evaporated and the residue was short-path distilled (Kugel-Rohr, boiling point 140°C/0.05 mmHg) to give 1.23 g (58% overall yield based on **12**) of 1,2-difluoro-3-(2-(*E*-4-pentylcyclohexyl)ethyl)benzene (**15**) as a colourless oil: ^{1}H NMR δ 0.89 (t, J=6.7 Hz, 3H), 0.80–1.05 (m, 3H), 1.15–1.38 (m, 11H), 1.47–1.53 (m, 2H), 1.71–1.85 (m, 4H), 2.68 (t, J=8.1 Hz, 2H), 6.90–7.02 (m, 3H); MS, *m/z* 294 (M, 4), 128 (100). Anal. calculated for $C_{19}H_{28}F_2$: C, 77.51; H, 9.59. Found: C, 78.12; H, 10.15.

Acknowledgements

Partial financial support for this work was received from the National Science Foundation (DMR-0606317). We thank Dr Bill Thurmes of Displaytech for his generous gift of the MX 6146 host. We also thank Dr Wiktor Piecek for helpful discussions.

References

[1] P. Kirsch, V. Reiffenrath, M. Bremer. *Synlett*, 389–396 (1999).

[2] P. Kirsch, M. Bremer. *Angew. Chem. Int. Ed. Engl.*, **39**, 4216–4235 (2000).

[3] D. Pauluth, K. Tarumi. *J. Mater. Chem.*, **14**, 1219–1227 (2004).

[4] M. Bremer, L. Lietzau. *New J. Chem.*, **29**, 72–74 (2005).

[5] S.T. Lagerwall. *Handbook of Liquid Crystals*, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Vol. 2B, pp. 515–664, Wiley-VCH, New York (1998).

[6] S.T. Lagerwall. *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley-VCH, New York (1999).

[7] J. Dijon. *Liquid Crystals, Applications and Uses*, B. Bahadur (Ed.), Vol. 1, pp. 305–360, World Scientific, Singapore (1990).

[8] G.W. Gray, M. Hird, K.J. Toyne. *Mol. Cryst. Liq. Cryst.*, **195**, 221–237 (1991).

[9] G.W. Gray, M. Hird, K.J. Toyne. *Mol. Cryst. Liq. Cryst.*, **204**, 43–64 (1991).

[10] M. Hird, G.W. Gray, K.J. Toyne. *Liq. Cryst.*, **11**, 531–546 (1992).

[11] M. Hird, K.J. Toyne, A.J. Slaney, J.W. Goodby. *J. Mater. Chem.*, **5**, 423–430 (1995).

[12] C.C. Dong, P. Styring, J.W. Goodby, L.K.M. Chan. *J. Mater. Chem.*, **9**, 1669–1677 (1999).

[13] G.-X. Sun, B. Chen, H. Tang, S.-Y. Xu. *J. Mater. Chem.*, **13**, 742–748 (2003).

[14] M.E. Glendenning, J.W. Goodby, M. Hird, K.J. Toyne. *J. Chem. Soc. Perkin Trans.*, **2**, 27–34 (2000).

[15] M.E. Glendenning, J.W. Goodby, M. Hird, K.J. Toyne. *J. Chem. Soc. Perkin Trans.*, **2**, 481–491 (1999).

[16] G.W. Gray, M. Hird, D. Lacey, K.J. Toyne. *J. Chem. Soc. Perkin Trans.*, **2**, 2041–2053 (1989).

[17] E.P. Janulis, J.C. Novack, G.A. Papapolymerou, M. Tristani-Kendra, W.A. Huffman. *Ferroelectrics*, **85**, 763–772 (1988).

[18] W. Piecek, Z. Raszewski, P. Perkowski, J. Kedzierski, J. Rutkowska, J. Zielinski, E. Nowinowski-Kruszelnicki, R. Dabrowski, M. Tykarska, J. Przedmojski. *Mol. Cryst. Liq. Cryst.*, **436**, 149–165 (2005).

[19] M.J. O'Callaghan, M. Wand, C. Walker, W. Thurmes, K. More. *Ferroelectrics*, **343**, 201–207 (2006).

[20] S.J. Cowling, A.W. Hall, J.W. Goodby, Y. Wang, H.F. Gleeson. *J. Mater. Chem.*, **16**, 2181–2191 (2006).

[21] R. Dabrowski. *Ferroelectrics*, **243**, 1–18 (2000).

[22] K. D'havè, A. Dahlgren, P. Rudquist, J.P.F. Lagerwall, G. Andersson, M. Matuszczyk, S.T. Lagerwall, R. Dabrowski, W. Drzewinski. *Ferroelectrics*, **244**, 115–128 (2000).

[23] R. Dabrowski, J. Gasowska, J. Otón, W. Piecek, J. Przedmojski, M. Tykarska. *Displays*, **25**, 9–19 (2004).

[24] S. Lagerwall, A. Dahlgren, P. Jägemalm, P. Rudquist, K. D'havè, H. Pauwels, R. Dabrowski, W. Drzewinski. *Adv. Funct. Mater.*, **11**, 87–94 (2001).

[25] J.W. Goodby, K.J. Toyne, M. Hird, R.A. Lewis. PCT International Application WO 9601246 (1996).

[26] I.C. Sage, D.G. Mcdonnell, J.C. Jones, A. Slaney. PCT International Application WO 9516760 (1995).

[27] V. Reiffenrath, J. Krause, G. Weber, U. Finkenzeller, A. Waechtler, T. Geelhaar, D. Coates, I.C. Sage, S. Greenfield. Ger. Offen. DE 3906019 (1989).

[28] V. Reiffenrath, J. Krause, A. Waechtler, G. Weber, U. Finkenzeller, D. Coates, I.C. Sage, S. Greenfield, G.W. Gray. Ger. Offen. DE 3807861 (1989).

[29] J.R. Falck, J. Yu, H.-S. Cho. *Tetrahedron Lett.*, **35**, 5997–6000 (1994).

[30] S.E. Gibson, J.O. Jones, S.B. Kalindjian, J.D. Knight, N. Mainolfi, M. Rudd, J.W. Steed, M.J. Tozer, P.T. Wright. *Tetrahedron*, **60**, 6945–6958 (2004).

[31] M.J. Pugia, B.E. Knudsen, C.V. Cason, R.A. Bartsch. *J. Org. Chem.*, **52**, 541–547 (1987).

[32] J.A. Marshall, N.H. Andersen, J.W. Schlicher. *J. Org. Chem.*, **35**, 858–861 (1970).

[33] D. Demus, L. Richter. *Textures of Liquid Crystals,* 2nd edn, VEB, Leipzig (1980).

[34] I. Dierking. *Textures of Liquid Crystals*, Wiley-VCH, Weinheim (2003).

[35] S.M. Kelly. *Liq. Cryst.*, **17**, 211–225 (1994).

[36] S.M. Kelly, A. Germann, M. Schadt. *Liq. Cryst.*, **16**, 491–507 (1994).

[37] H. Schubert, H. Dehne. *Z. Chem.*, **12**, 241–250 (1972).

[38] M.E. Neubert, K. Leung, M.R. Jirousek, M.C. Ezenyilimba, S. Sabol-Keast, B. Ziemnicka-Merchant, R.B. Sharma. *Mol. Cryst. Liq. Cryst.*, **197**, 21–41 (1991).

[39] R. Lunkwitz, C. Tschierske, S. Diele. *J. Mater. Chem.*, **7**, 2001–2011 (1997).

[40] H. Fadel, T. Ishida, G. Wegner, D. Guillon, A. Skoulios. *Mol. Cryst. Liq. Cryst.*, **241**, 195–204 (1994).

[41] S.-T. Wu, D. Coates, E. Bartmann. *Liq. Cryst.*, **10**, 635–646 (1991).

[42] D.A. Dunmur. *Physical Properties of Liquid Crystals: Nematics*, D.A. Dunmur, A. Fukuda, G.R. Luckhurst (Eds.), pp. 216–229, IEE, London (2001).

[43] V.V. Belyaev. *Physical Properties of Liquid Crystals: Nematics*, D. Dunmur, A. Fukuda, G. Luckhurst (Eds.), pp. 414–428, IEE, London (2001).

[44] F. Guittard, E.T. deGivenchy, S. Geribaldi, A. Cambon. *J. Fluorine Chem.*, **100**, 85–96 (1999).

[45] W.J. Cumming, R.A. Gaudiana. *Liq. Cryst.*, **20**, 283–286 (1996).

[46] S.V. Arehart, C. Pugh. *J. Am. Chem. Soc.*, **119**, 3027–3037 (1997).

[47] J. Gasowska, R. Dabrowski, W. Drzewinski, M. Filipowicz, J. Przedmojski, K. Kenig. *Ferroelectrics*, **309**, 83–93 (2004).

[48] W. Piecek, K.L. Glab, A. Januszko, P. Kaszynski, in preparation.

[49] M. Hird, K.J. Toyne. *Mol. Cryst. Liq. Cryst.*, **323**, 1–67 (1998).

[50] R. Dabrowski, J.M. Otón, V. Urruchi, J.L. Gayo, K. Czuprynski, S. Gauza. *Polish J. Chem.*, **76**, 331–344 (2002).

[51] E.P. Janulis, D.W. Osten, M.D. Radcliffe, J.C. Novack, M. Tristani-Kendra, K.A. Epstein, M. Keyes, G.C. Johnson, P.M. Savu, T.D. Spawn. *Proc. SPIE*, **1665**, 146–153 (1992).

[52] Y.H. Chiang, A.E. Ames, R.A. Gaudiana, T.G. Adams. *Mol. Cryst. Liq. Cryst.*, **208**, 85–98 (1991).

[53] A. Yasuda, E. Matsul. Patent EP0808887, Sony Corporation (1997).

[54] I. Dahl, S.T. Lagerwall, K. Skarp. *Phys. Rev. A.*, **36**, 4380–4389 (1987).

[55] C. Escher, T. Geelhaar, E. Bohm. *Liq. Cryst.*, **3**, 469–484 (1988).

[56] S. Bezner, M. Krueger, V. Hamplová, M. Glogarová, F. Giesselmann. *J. Chem. Phys.*, **126**, 054902 (2007).

[57] J.T. Plati, W.H. Strain, S.L. Warren. *J. Am. Chem. Soc.*, **65**, 1273–1276 (1943).

[58] W. Sucrow, G. Rädecker. *Chem. Ber.*, **121**, 219–224 (1988).