Liquid Crystals Based on Axially Fluorinated 1,3-Dioxanes: Synthesis, **Properties and Computational Study**

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lar modelling.

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A new class of liquid crystals with strongly negative dielectric anisotropy has been prepared by the exploitation of the somewhat "ambivalent" characteristics of the 1,3-dioxane structure with respect to its polarity and by the axial fluorination of this structure, which gives these compounds attractive mesogenic and electrooptic properties. The increased chemi-

Introduction

Recently, liquid crystal displays (LCD) have become an integral part of our daily lives.^[1,2] The transition from cathode ray tube (CRT) based displays to LCD technology was initiated by notebook PCs and gained additional impetus from the replacement of desktop PC monitors by flat panel displays. Currently, the market for LCD TV sets continues to grow rapidly. Technologically, LCD TV is dominated by the so-called vertical alignment (VA) technology, which requires nematic liquid crystals with negative dielectric anisotropy $(\Delta \varepsilon)$.^[3] The advantages of this technology are fast switching times, high brightness and an excellent contrast ratio.

With very few exceptions,^[4] most liquid crystals that are in practical use for VA LCDs are based on a 2,3-difluorobenzene subunit as their polar group (such as 1, Scheme 1).^[3d] This functionality conveys a dipole moment perpendicular to the molecular long axis and thus gives a negative value to $\Delta \varepsilon$. Nevertheless, there is a need for other dielectrically negative materials with low rotational viscosity and with lower birefringence (Δn). One class of materials fulfilling these requirements are axially fluorinated cyclohexane derivatives.^[5] Besides their low rotational viscosity (γ_1) , these compounds also have low birefringence because their substructures show low polarizability.

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cal stability of these materials compared with their carbocy-

clic analogues has been analyzed and explained by molecu-

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Scheme 1. Examples of liquid crystals with negative dielectric anisotropy ($\Delta \varepsilon$).

Unfortunately, axially fluorinated cyclohexane derivatives (such as 2) never found their way into industrial application because of their propensity to unpredictably and autocatalytically eliminate hydrofluoric acid.

Because of the attractive mesogenic and electrooptic property profile of this substance class, we sought to improve the stability problem. In addition, it was our aim to obtain structurally related materials with low birefringence and an even more strongly negative dielectric anisotropy.

In liquid crystals with *positive* $\Delta \varepsilon$, one method to increase the dielectric anisotropy is to include trans-1,3-dioxane-2,5divl building blocks into the mesogenic core structure (Scheme 2).^[2] This works because the dioxane carbon-oxygen bonds add their dipole moments to that of the polar terminal group into the direction of the long molecular axis. Thus, the dielectric anisotropy of 4 ($\Delta \varepsilon = 9.7$) can be increased by 7 units by the replacement of one cyclohexane unit by 1,3-dioxane (5, $\Delta \varepsilon = 17.0$). However, the 1,3-dioxane unit has a somewhat ambivalent character as a polar ring element (Scheme 2); the orientation of its local group dipole moment is oblique relative to the long molecular axis of the resulting liquid crystal. Therefore, it can be used to enhance the perpendicular dipole moment of a lateral polar group in dielectrically *negative* liquid crystals (3)^[6] as well.

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Scheme 2. Schematic representation of the underlying concept for the design of ax-5-fluoro-1,3-dioxane derived liquid crystals.

Therefore, liquid crystals based on an axially fluorinated 1,3-dioxane substructure were chosen as candidates for materials with low birefringence and enhanced negative dielectric anisotropy. The influence of the orientation of the fluorodioxane moiety within the mesogenic core structure on mesogenic and electrooptic properties was another topic of our interest.

Results and Discussion

The synthesis of our target compounds (Scheme 3) was centered around malonic ester precursors **6** and **11**, which were deprotonated and fluorinated with the electrophilic fluorination reagent F-TEDA [Selectfluor; 1-(chloro-methyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetra-fluoroborate)] to furnish fluoromalonates **8** and **12**.^[7] Alternatively, the two alkylfluoromalonates can be obtained by the alkylation of diethyl fluoromalonate (**7**).^[8] Although the

yields of the alkylation procedure are very low in the case of **12**, the purification of the product is easier than that of the electrophilic fluorination route. Alkylfluoromalonic esters **8** and **12** were carefully reduced to corresponding diols **9** and **13**,^[8] which were subsequently converted into bis(trimethylsilyl) ethers **10** and **14**. With the use of trimethylsilyl triflate as a catalyst,^[9,10] the ethers were condensed under very mild conditions with *trans*-4-propylcyclohexyl carbaldehyde and butyric aldehyde, respectively. Pure *transtrans* target compounds **3**, **15**, and **16** were isolated by their repeated crystallization from *n*-heptane.

In contrast to the previously described axially fluorinated cyclohexane derivatives (e.g., 2),^[5] all newly synthesized fluorodioxane-based liquid crystals, as well as their precursors, are chemically stable even at elevated temperatures without any precautions such as the addition of acid scavengers. In no case was the elimination of hydrofluoric acid observed.

Unfortunately, from the application point of view, the new liquid crystals **3**, **15**, and **16** have high melting points. Their solubility in organic solvents and in the nematic screening mixtures^[11] is very poor (Table 1), which impeded experimental determination of their electrooptic properties. Compounds **15** and **16** show only smectic B phases – in the case of **15** only a monotropic one – at relatively high temperatures. Only our primary target, compound **3**, was sufficiently soluble in the nematic screening host to be able to obtain the full set of its "virtual"^[11] properties, such as its clearing temperature ($T_{\text{NI,virt}}$), dielectric anisotropy ($\Delta \varepsilon$ -virt), and birefringence (Δn_{virt}). The birefringence is – as expected – in the same range as that for carbocyclic analogue **2**. The dielectric anisotropy of **3** ($\Delta \varepsilon = -4.8$) shows a pronounced increase compared with that of **2** ($\Delta \varepsilon = -2.2$),



Scheme 3. Synthesis of axially fluorinated 1,3-dioxane derivatives **3**, **15**, and **16**. a) 1. NaH, THF; 2. Selectfluor (**8**: 66%, **12**: 77%). b) 1. NaH, THF, 2 h, 0–45 °C; 2. 1-Bromopropane; 18 h, room temp. (68%). c) LiAlH₄, THF, toluene, 2 h, –30–30 °C (**9**: 51%, **13**: 50%). d) Me₃SiCl, NEt₃, DMF, 2 h, room temp. (**10**: 69%, **14**: 90%). e) *trans*-4-Propylcyclohexyl carbaldehyde, cat. Me₃SiOTf, CH₂Cl₂, –78 °C (**3**: 24%, **16**: 38%). f) 1. NaH, *cis*-4-propyl-bromocyclohexane, 15 h, 0 °C to reflux (6%). g) Butyric aldehyde, cat. Me₃SiOTf, CH₂Cl₂, –78 °C (**15**: 48%).

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which was intended by the design of the materials. Another remarkable feature, particularly of material **15**, is the extremely large discrepancy between its "real" (monotropic) crystalline-smectic B phase transition temperature (97 °C) and the "virtual" crystalline-nematic phase transition (6.3 °C). Also for compound **3**, which shows no real mesophase, the virtual clearing point is unusually low ($T_{\rm NI,virt} = 14.8$ °C) compared for example with carbocyclic analogue **2** ($T_{\rm NI,virt} = 87.3$ °C).

Table 1. Comparison of the physical properties of liquid crystals 2–5 and 15–17. The virtual electrooptical parameters (Δn_{virt}) and clearing points ($T_{NI,virt}$) were extrapolated from Merck mixture ZLI-4792. The dielectric anisotropies $\Delta \varepsilon_{virt}$ of 1, 2, 3, and 17 were extrapolated from ZLI-2857 and those of 4 and 5 from ZLI-4792.^[11] (C = crystalline, S_B = smectic B, I = isotropic. The phase transition temperatures are given in °C, the number in parentheses denotes a monotropic phase transition).

Compound	Phase sequence	$T_{\rm NI,virt}$	$\Delta \varepsilon_{ m virt}$	$\Delta n_{\rm virt}$
1	C 67 N 145.3 I	137.1	-2.8	0.095
2	C 75 S _B 94 I	87.3	-2.2	0.054
3	C 112 I	14.8	-4.7	0.055
4	C 66 N 94.1 I	74.3	9.7	0.075
5	C 74 N (51.2) I	63.2	17.0	0.068
15	C 97 S _B (97) I	6.3	_	_
16	C 109 $S_B > 200$, dec.	_	_	_
17	C 100 S _B 153 I ^[a]	105.7	-2.5	0.035

[a] Decomposition.

The crystal structure of $3^{[12]}$ provides some insight into the reason for the high melting point and poor solubility of the compound. The crystal packing is dominated by an eclipsed stacking of the single molecules with a nearly perfect alignment of the axial C–F bonds (with a nonbonded C…F distance of 3.413 Å) and of the local dipole moments from the dioxane substructure (Figure 1). Thus, a strong electrostatic component increases the lattice energy. A very similar effect has been observed for the crystal structure of liquid crystal 17,^[5a] which has two *ax*-fluorocyclohexane units. In liquid crystal 17, a ladder-like stacked arrangement is stabilized by aligned C–F bonds (with a C···F distance of 3.575 Å), which stabilizes the packing by their dipole-dipole interactions. In the case of solid 17 the *anti*-parallel arrangement of the two C–F bonds is stabilized by the crystal packing; in solution, the liquid crystalline host is composed of two cyclohexane subunits that are twisted around the central axis by ca. 75°, which breaks the symmetry of the molecule and provides the compound with a negative dielectric anisotropy ($\Delta n_{virt} = -2.5$).

The increased stability of ax-5-fluoro-1,3-dioxanes compared with their carbocyclic analogues can be rationalized and explained by DFT calculations^[13] based on their structure and the supposed decomposition mechanism. Remarkably, the isodesmic equation [B3LYP/6-311+G(2d,p)// B3LYP/6-31G(d)+ZPE level of theory] in Scheme 4 shows that a switch of the fluorine atom from fluorocyclohexane 18 to fluorodioxane 21 actually *increases* the energy of the system by 3.5 kcal mol⁻¹. At the same time, the bond length decreases from 1.421 Å in 18 to 1.404 Å in 21, which indicates a strengthening of the C–F bond. This apparent paradoxical result can be explained by the repulsive interaction between the axial lone electron pairs of the two oxygen atoms and the lone pairs of electrons on the axial fluorine. The resulting increase in the transannular strain explains the higher energy of the system in spite of the stronger C-F bond.

The decomposition reaction of axially fluorinated cyclohexane derivatives is autocatalytically promoted by hydrofluoric acid, and it is assumed to proceed via tertiary cationic intermediate **22** (Scheme 5), which is stabilized by inductive effects and by hyperconjugation. The abstraction of



Figure 1. The packing of axially fluorinated dioxane (3) (*top* and *bottom left*) and cyclohexane-based molecules (17) (*middle* and *bottom right*) is dominated by a strong correlation of the local C-F dipole moments.

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Scheme 4. DFT calculations [B3LYP/6-311+G(2d,p)]/B3LYP/6-31G(d)+ZPE level of theory]^[13] show that the axial C–F bond is shorter (i.e. more stable) in the dioxane system **21** compared with that of the cyclohexane analogue **18**. The overall energy increase of 3.5 kcal mol⁻¹ in the isodesmic equation is caused by the additional transannular strain that is induced by the repulsion of the axial electron pairs of the oxygen atoms and the fluorine substituent.



Scheme 5. Proposed mechanism for the autocatalytic elimination of HF from tertiary axially fluorinated cyclohexanes and 1,3-dioxanes (*top*). The thermodynamic stabilization of the axial carbon–fluorine bond in **21**, or in other words, the destabilization of the carbocationic intermediate **23** by the presence of ring oxygen atoms, is estimated to be $10.2 \text{ kcalmol}^{-1}$ [*bottom*: isodesmic equation at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) + ZPE level of theory].^[13]

the fluoride ion as well as the subsequent deprotonation is facilitated by the HF catalyst. The isodesmic equation depicted in Scheme 5 indicates that carbocationic dioxane intermediate **23**, afforded from the elimination reaction, is destabilized by 10.2 kcalmol⁻¹ compared with **22**. This is predominantly due to the combined negative inductive effects (-I) of the two ring oxygen atoms. In other words, the C–F bond in **21** is stabilized (compared with that of **18**) by this amount of energy with regard to its heterolytic dissociation.^[14] A secondary contribution is the release of transannular strain by "shifting" the fluorine substituent from **21** to **18**.

Summary and Conclusion

ax-5-Fluoro-1,3-dioxane has been identified as a highly effective structural building block that imparts a strongly negative dielectric anisotropy in liquid crystals that are suitable for LCD applications. Compared with the analogous materials that are based on axially fluorinated cyclohexane, the dioxane substructure does not only increase the dipole moment perpendicular to the long molecular axis, but it also significantly improves the chemical stability of the compound. The observed stabilization of the tertiary alkyl fluoride – compared with its carbocyclic analogue – can be attributed to the inductive destabilization of the corresponding carbocation by the ring oxygen atoms.

Experimental Section

General: All reactions – in particular those with NaH and LiAlH_4 – were carried out in carefully dried solvents and under a nitrogen atmosphere. The reagents *trans*-4-propylcyclohexyl carbaldehyde and diethyl *trans*-4-propylcyclohexylmalonate were obtained from Merck KGaA. The mesophase sequence and electrooptical parameters for compound **3**, **15**, and **16** are gathered in Table 1.

8: A suspension of NaH (80% in paraffin, washed before use with dry THF, 1.2 g, 40 mmol) in THF (70 mL) was cooled to 0 °C. A solution of diethyl n-propylmalonate (6, 6.7 g, 33 mmol) in THF (30 mL) was added dropwise while the cold bath was maintained. The reaction was stirred for 2 h at 0 °C. The temperature was then raised to room temperature over the course of 1 h and raised again to 45 °C over a one hour period. The mixture was then stirred for 18 h at room temperature. After the reaction was cooled to 0 °C, a suspension of Selectfluor (17.0 g, 44 mmol) in acetonitrile (100 mL) was added dropwise. The mixture was stirred for 2 h at 0 °C and for 2 h at room temperature.CH2Cl2 (300 mL) was then added followed by HCl (1 N, 100 mL). The organic layer was separated and washed with saturated aqueous NaHCO3 solution and then with water. The solution was dried with Na₂SO₄, the solvent removed in vacuo, and the crude product purified by Kugelrohr distillation (100 °C, 0.3 mbar) to yield product 8 (4.8 g, 66%) as a colorless oil (88% purity by GC, contains ca. 10% of unreacted 6). ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 4.29 (q, J = 7.3 Hz, 4 H), 2.23–2.06 (m, 2 H), 1.51-1.37 (m, 2 H), 1.22 (t, J = 6.8 Hz, 6 H), 0.97 (t, J= 7.5 Hz, 3 H) ppm. MS (EI = 70 eV): m/z (%) = 221 (0.5) [M + $11^+, 178$ (27), 160 (10), 150 (11), 148 (24), 122 (13), 119 (40), 102 (23), 99 (19), 91 (77), 73 (22), 55 (16), 43 (12), 29 (100).

9: A suspension of LiAlH₄ (4.0 g, 105 mmol) in a mixture of toluene (25 mL) and THF (90 mL) was cooled to -30 °C. At this temperature, a solution of 8 (purity 90.5% by GC, 15.5 g, 64 mmol) in THF (20 mL) was added dropwise. The mixture was warmed to 30 °C (under careful temperature control; the reaction was occasionally cooled with a water bath). This temperature was maintained for 20 min and then stirred for 90 min at room temperature under temperature control. The reaction mixture was ice-cooled and quenched by the careful addition of a solution of Na₂CO₃ (29 g) in water (12 mL). The precipitate was filtered, the filtrate dried with Na₂SO₄, and the solvents evaporated to dryness. The crude product was purified by chromatography (silica gel, n-hexane/ethyl acetate 3:2), to yield two fractions. The first fraction (1.5 g) was discarded. The second fraction afforded 9 (5.5 g, 51%) as a colorless oil (80% purity by GC, contains ca. 10% of the nonfluorinated diol analogue). ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 3.83-3.66 (m, 4 H), 2.90 (br. s, 2 H), 1.71-1.56 (m, 2 H), 1.471.35 (m, 2 H), 0.95 (t, J = 7.1 Hz, 3 H) ppm. ¹⁹F NMR (280 MHz, CDCl₃, 303 K): $\delta = -172.52$ (mc, 1F) ppm. MS (EI = 70 eV): m/z (%) = 137 (2) [M + 1]⁺, 131 (5), 103 (7), 98 (8), 88 (100), 75 (16), 67 (13), 60 (75), 41 (32), 29 (30).

10: A solution of 9 (80% by GC, 5.0 g, 29 mmol) in DMF (50 mL) and triethylamine (22.2 mL, 160 mmol) was treated dropwise with Me₃SiCl (10.1 mL, 80 mmol) while a maximum temperature of 30 °C was maintained. The reaction was stirred for 2 h at room temperature and n-pentane (100 mL) was added. The organic phase was separated, washed twice with ice-cold saturated aqueous NaHCO3, once with ice-cold HCl (3%), again with aqueous NaHCO₃, and finally with brine. The collected aqueous layers were extracted with n-pentane. All organic phases were combined, dried with Na₂SO₄, and the solvents evaporated to dryness. The crude product (8.8 g) was subjected to Kugelrohr distillation. Three fractions were obtained. Fraction 1 (1.0 g, b.p. 63-65 °C/0.4 mbar, 71 % purity by GC), fraction 2 (6.0 g, b.p. 65-68 °C/0.4 mbar, 84% purity) and fraction 3 (0.7 g, 68–69 $^{\circ}\text{C}/0.4$ mbar, 88% purity). Fractions 2 and 3 were combined to yield 10 (6.7 g, 69%) as a colorless oil. ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 3.65–3.43 (m, 4 H), 1.59-1.43 (m, 2 H), 1.38-1.23 (m, 2 H), 0.85 (t, J = 7.7 Hz, 3 H), 0.03 (s, 18 H) ppm. MS (EI = 70 eV): m/z (%) = 280 (0.5) [M]⁺, 265 (20), 260 (29), 217 (75), 191 (10), 173 (12), 170 (12), 159 (23), 147 (38), 107 (21), 103 (71), 77 (32), 75 (25), 73 (100), 45 (13).

3: A mixture of 10 (85% purity, 6.5 g, 20 mmol), CH₂Cl₂ (80 mL) and Me₃SiOTf (0.6 mL, 3 mmol) was cooled to -70 °C.A solution of trans-4-propylcyclohexyl carbaldehyde (86% purity, 3.9 g, 25 mmol) in CH₂Cl₂ (20 mL) was then added dropwise at the same temperature. After stirring for 2 h at -70 °C, the reaction was quenched by the addition of pyridine (2.4 mL), and the mixture was warmed to room temperature. Saturated aqueous NaHCO3 (100 mL) was added. The reaction was stirred for 15 min, the organic layer separated, and the aqueous layer extracted with CH₂Cl₂. The organic phases were combined, washed with water, dried with Na₂SO₄, and the solvents evaporated to dryness. The crude product (8.7 g) was purified by chromatography (silica gel, n-hexane/methyl tert-butyl ether 4:1) and subsequently crystallized from *n*-hexane at -20 °C to furnish product 3 (1.3 g, 24%) as colorless crystals. M.p. 112 °C (n-hexane). ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 4.18 (d, J = 5.3 Hz, 1 H), 4.13 (t, J = 13.2 Hz, 2 H), 3.60 (dd, J = 35.3 Hz, J = 13.2 Hz, 2 H), 1.92–1.72 (m, 4 H), 1.63– 0.97 (m, 14 H), 0.93 (t, J = 6.6 Hz, 3 H), 0.86 (t, J = 6.8 Hz, 3 H)ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): δ = 105.4, 89.6 (d, $J_{C,F}$ = 178.7 Hz), 72.4 (d, $J_{C,F}$ = 21.9 Hz), 42.6, 40.1, 37.7, 36.9 (d, $J_{C,F}$ = 21.4 Hz), 32.8, 27.7, 20.4, 15.7 (d, $J_{C,F}$ = 3.5 Hz), 14.8 ppm. ¹⁹F NMR (235 MHz, CDCl₃, 300 K): $\delta = -169.60$ (mc, 1F) ppm. MS $(EI = 70 \text{ eV}): m/z \ (\%) = 272 \ (0.6) \ [M]^+, \ 271 \ (2.5), \ 147 \ (100), \ 81$ (15), 55 (10), 41 (10). C₁₆H₂₉FO₂: calcd. C 70.5, H 10.7; found C 70.7, H 10.6.

12: A suspension of NaH (60% in paraffin, washed before use with dry THF, 6.4 g, 160 mmol) in THF (200 mL) was cooled to 2 °C. A solution of diethyl *trans*-4-propylcyclohexylmalonate (11, purity 96.6%, 31.3 g, 106 mmol) in THF (25 mL) was added dropwise while the reaction was cooled. The reaction was stirred for 2 h at 2 °C. The temperature was then raised to room temperature over the course of 1 h and raised again to 40 °C over a three hour period. The mixture was cooled to 5 °C, and a suspension of Selectfluor (50.0 g, 130 mmol) in acetonitrile (200 mL) was added in small portions. The mixture was stirred for 3 d at room temperature.CH₂Cl₂ (500 mL) was then added followed by water (300 mL). The organic layer was separated and washed with HCl (1 N³, saturated aqueous NaHCO₃ and then with water. The combined aque-

ous phases were extracted once with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄, the solvent was removed in vacuo, and the crude product was purified by chromatography (silica gel, *n*-heptane/methyl *tert*-butyl ether 4:1) to yield product **12** (19 g, 77%) as a colorless oil (86% purity by GC). ¹H NMR (250 MHz, CDCl₃, 303 K): $\delta = 4.30$ (q, J = 7.1 Hz, 4 H), 2.44–2.22 (m, 1 H), 1.85–1.76 (m, 2 H), 1.65–1.55 (m, 2 H), 1.40–1.10 (m, 13 H), 1.05–0.84 (m, 5 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): $\delta = 166.1$ (d, $J_{C,F} = 25.8$ Hz), 97.3 (d, $J_{C,F} = 203.0$ Hz), 62.4, 42.7 (d, $J_{C,F} = 20.6$ Hz), 39.4, 36.7, 32.4, 25.9, 19.9, 14.3, 14.1 ppm. ¹⁹F NMR (235 MHz, CDCl₃, 300 K): $\delta = -178.39$ (d, J = 27.5 Hz, 1F) ppm. MS (EI = 70 eV): *m/z* (%) = 303 (1) [M]⁺, 178 (100), 150 (21), 122 (19), 83 (5), 81 (8), 67 (7), 55 (11).

13: A suspension of LiAlH₄ (5.7 g, 150 mmol) in a mixture of toluene (18 mL) and THF (140 mL) was cooled to -30 °C. At this temperature, a solution of 12 (purity 85% by GC, 29.0 g, 82 mmol) in THF (20 mL) was added dropwise. The reaction was stirred for 30 min, and the mixture was warmed to room temperature (under careful temperature control and a water bath if necessary to cool the reaction). The reaction was then stirred for an additional 3 h. The reaction mixture was ice-cooled and quenched by the careful addition of a solution of Na₂CO₃ (41 g) in water (18 mL). After 30 min, the precipitate was filtered off and washed with methyl tertbutyl ether. The filtrate was dried with Na₂SO₄ and the solvents evaporated to dryness. The crude product (24 g) was crystallized from acetonitrile (ca. 75 mL) at -20 °C to afford 13 (10.0 g, 50%) as a colorless solid (86% purity by GC). ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 3.89 (d, J = 6.3 Hz, 2 H), 3.81 (dd, J = 8.5 Hz, J = 3.4 Hz, 2 H), 2.50 (br. t, J = 6.3 Hz, 2 H), 1.86–1.70 (m, 5 H), 1.38-1.26 (m, 2 H), 1.20-1.05 (m, 5 H), 0.99-0.84 (m, 5 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): δ = 99.1 (d, $J_{C,F}$ = 172.6 Hz), 63.6 (d, $J_{C,F}$ = 25.8 Hz), 41.0 (d, $J_{C,F}$ = 20.0 Hz), 39.3, 37.0, 32.8, 26.3 (d, $J_{C,F} = 5.3$ Hz), 19.8, 14.2 ppm. ¹⁹F NMR (235 MHz, CDCl₃, 300 K): $\delta = -176.20$ (mc, 1F) ppm. MS (EI = 70 eV): m/z(%) = 218 (1) [M]⁺, 198 (10), 180 (14), 170 (100), 149 (21), 141 (13), 128 (22), 123 (67), 121 (34), 109 (25), 107 (27), 95 (37), 93 (28), 81 (94), 69 (90), 67 (70), 57 (23), 55 (84), 43 (32), 41 (84).

14: A solution of 13 (89% by GC, 10.0 g, 41 mmol) in DMF (65 mL) and triethylamine (30.5 mL, 220 mmol) was treated dropwise with Me₃SiCl (13.9 mL, 110 mmol) while a temperature of 30 °C was maintained. The reaction was stirred for 2 h at room temperature and *n*-pentane (150 mL) was added. The organic phase was separated, washed twice with ice-cold saturated aqueous NaHCO₃, once with ice-cold HCl (3%), again with aqueous NaHCO₃, and finally with brine. The collected aqueous layers were extracted with n-pentane. All organic phases were combined, dried with Na₂SO₄, and the solvents evaporated to dryness. Crude product 14 (16.0 g, 90%, 83% purity by GC) was used for the next reaction step without further purification. ¹H NMR (250 MHz, CDCl₃, 303 K): δ = 3.83–3.63 (m 4 H), 1.85–1.70 (m, 6 H), 1.40– 1.00 (m, 8 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.12 (s, 18 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): δ = 99.6 (d, J_{CF} = 175.8 Hz), 62.6 (d, $J_{C,F}$ = 27.6 Hz), 40.6 (d, $J_{C,F}$ = 20.8 Hz), 40.2, 37.8, 33.7, 27.0, 26.9, 20.4, 14.9 ppm. ¹⁹F NMR (280 MHz, CDCl₃, 300 K): δ = -173.90 (mc, 1F) ppm. MS (EI = 70 eV): $m/z \text{ (\%)} = 362 \text{ (1)} \text{ [M]}^+$, 347 (10), 342 (25), 252 (17), 241 (11), 217 (100), 191 (9), 163 (19), 147 (20), 129 (12), 121 (12), 103 (36), 73 (60), 55 (14), 41 (12).

15: A mixture of **14** (8.0 g, 22 mmol), CH_2Cl_2 (50 mL), and Me₃Si-OTf (0.5 g, 2 mmol) was cooled to -70 °C. A solution of butyric aldehyde (2.3 mL, 25 mmol) in CH_2Cl_2 (10 mL) was then added dropwise at the same temperature. The reaction was stirred for 2 h at -70 °C. The reaction was quenched by the addition of pyridine

(2.3 mL), and the mixture was warmed to room temperature. Saturated aqueous NaHCO₃ (50 mL) was added. The reaction was stirred for 15 min, the organic layer separated, and the aqueous layer extracted with CH₂Cl₂. The organic phases were combined, washed with water, dried with Na₂SO₄, and the solvents evaporated to dryness. The crude product (10 g) was purified by chromatography (silica gel, n-heptane/methyl tert-butyl ether 4:1) and subsequently crystallized from *n*-heptane/methyl tert-butyl ether (4:1) at -20 °C to furnish product 15 (2.9 g, 48%) as colorless crystals (99.5% purity by HPLC). M.p. 97 °C (n-heptane/methyl tert-butyl ether 4:1). ¹H NMR (250 MHz, CDCl₃, 303 K): $\delta = 4.48$ (t, J =5.5 Hz, 1 H), 4.04 (t, J = 12.8 Hz, 2 H), 3.62 (dd, J = 36.2 Hz, J = 13.0 Hz, 2 H), 1.75–1.68 (m, 2 H), 1.65–1.52 (m, 4 H), 1.45–1.05 (m, 12 H), 0.84 (t, J = 7.1 Hz, 3 H), 0.74 (t, J = 7.1 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): δ = 102.5, 91.3 (d, J_{C,F} = 182.9 Hz), 71.8 (d, $J_{\rm C,F}$ = 22.8 Hz), 42.5 (d, $J_{\rm C,F}$ = 20.5 Hz), 40.4, 37.8, 37.6, 33.6, 26.5 (d, $J_{C,F}$ = 3.6 Hz), 20.8, 18.3, 15.3, 14.9 ppm. ¹⁹F NMR (235 MHz, CDCl₃, 300 K): $\delta = -175.60$ (mc, 1F) ppm. MS (EI = 70 eV): m/z (%) = 271 (10) [M – H]⁺, 229 (100), 170 (7), 163 (15), 123 (8), 121 (9), 107 (11), 81 (15), 69 (16), 67 (14), 55 (18), 43 (14), 41 (18).

16: By the same method with *trans*-4-propylcyclohexyl carbaldehyde as the aldehyde component, **16** (38%) was obtained as colorless crystals (99.6% purity by HPLC). M.p. 109 °C (*n*-heptane/ methyl *tert*-butyl ether 4:1). ¹H NMR (250 MHz, CDCl₃, 303 K): $\delta = 4.06-3.97$ (m, 3 H), 3.58 (dd, J = 35.3 Hz, J = 13.2 Hz, 2 H), 1.83-1.55 (m, 8 H), 1.44-0.88 (m, 20 H), 0.80 (mc, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 303 K): $\delta = 104.0$, 89.6 (d, $J_{C,F} =$ 180.7 Hz), 70.1 (d, $J_{C,F} = 22.7$ Hz), 41.4, 40.7 (d, $J_{C,F} = 20.4$ Hz), 38.9, 38.7, 36.5, 36.0, 31.9, 31.7, 26.5, 24.8, 24.7, 19.2, 19.1, 13.5 ppm. ¹⁹F NMR (235 MHz, CDCl₃, 300 K): $\delta = -175.65$ (mc, 1F) ppm. MS (EI = 70 eV): *m/z* (%) = 353 (3) [M – H]⁺, 229 (100), 163 (10), 107 (5), 81 (9), 69 (14), 55 (12), 41 (9).

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proximated by the long molecular axis. The correlation between $\Delta \varepsilon$, the dipole moment μ , and the angle β between the molecular dipole and the director is the following: $\Delta \varepsilon \approx \Delta a -$ F ($\mu^2/2kT$) (1–3cos^{2 β}) *S*; Δa is the anisotropy of the polarizability, *S* the order parameter: a) W. Maier, G. Meier, *Z. Naturforschg.* **1961**, *16a*, 262–267; b) D. Demus, G. Pelzl, *Z. Chem.* **1981**, *21*, 1–9.

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- [12] a) Crystal structure data for 3 (C₁₆H₂₉FO₂), by crystallization from *n*-hexane: monoclinic, P21/*n*, a = 4.841(1) Å, b =9.731(1) Å, c = 35.171(1) Å, $a = \gamma = 90^{\circ}$, $\beta = 92.47(1)^{\circ}$, V =1655.3(4) Å³, Z = 4, $\rho_{calcd.} = 1.093$ g·cm⁻¹, R(F) = 6.5% for 2709 observed independent reflections (2.17° $\leq \vartheta \leq 25.00^{\circ}$). The data were collected at 198 K. b) Crystal structure data for 17 (C₂₂H₄₀F₂), by crystallization from *n*-heptane: monoclinic, P21/*n*, a = 19.016(4) Å, b = 5.0060(10) Å, c = 22.038(4) Å, a = $\gamma = 90^{\circ}$, $\beta = 100.79(3)^{\circ}$, V = 2060.8(7) Å³, Z = 4, $\rho_{calcd.} =$ 1.104 g·cm⁻¹, R(F) = 5.7% for 4209 observed independent reflections (2.82° $\leq \vartheta \leq 74.39^{\circ}$). The data were collected at 223 K. CCDC-607632 (3) and CCDC-607631 (17) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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