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# A Convenient Synthetic Route to Tetrahydropyran-Based Liquid Crystals

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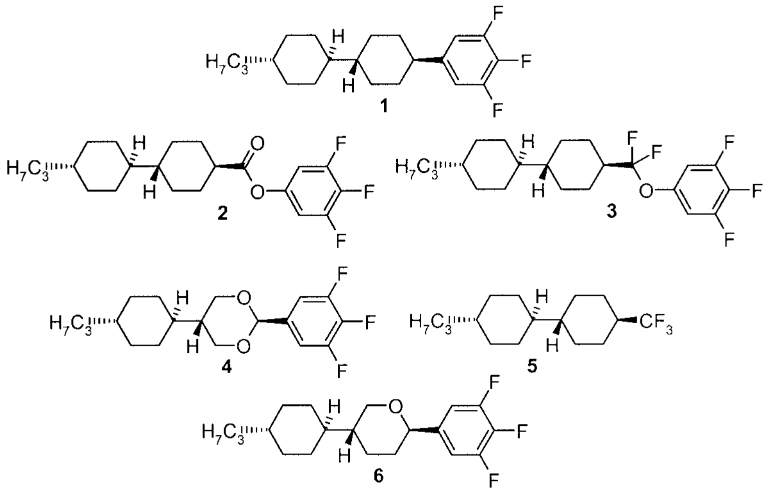
The tetrahydropyran moiety has been identified as a highly advantageous addition to the toolbox for the design of nematic liquid crystals for LCD applications. A new synthetic procedure based on the Lewis acid catalysed ring opening of oxetanes by lithium iminoenolates followed by reductive dehydroxylation of the resulting hemiketal provides a convenient preparative access to this class of materials.

## Introduction

The ubiquitous use of mobile electronic devices, such as cellular phones, personal digital assistants (PDAs) or video games, has created a strong demand for very robust active matrix liquid crystal displays (AM-LCDs) with long lifetimes even under extreme environmental conditions.[1] As a consequence, the nematic liquid crystals used in such LCD devices are required to show extreme endurance under photochemical, thermal and oxidative stress. The manufacturers of LCD panels can achieve significant reductions in device production cost and extensions of battery lifetimes by using liquid crystal mixtures with high dielectric anisotropies ($\Delta\varepsilon$). Reflective and transflective LCDs make no or only rather limited use of energy-consuming backlights. For these even more power-efficient applications, very low birefringence ($\Delta n$) of the material is required in addition.[2] Combining extremely high reliability with strong polarity and low birefringence is a very challenging task for the developer of liquid crystals.

The liquid crystals currently in use for active matrix LCDs are so-called superfluorinated materials (SFMs), mostly based on phenylbicyclohexyl mesogenic core structures with fluorine-containing polar terminal groups (**1**; Scheme 1).[2] The polarities of materials based on this basic structure can be enhanced by insertion of polar bridges, such as esters (**2**) or difluorooxymethylene groups (**3**),[3] into their mesogenic core structures. An alternative means to achieve higher dielectric anisotropy is the replacement of one cyclohexane moiety by a polar 1,3-dioxane unit (**4**).[4] If even lower



Scheme 1. Examples of liquid crystals used for mobile devices, combining polarity (i.e., high $\Delta\varepsilon$) with low birefringence ($\Delta n$) (**1**–**5**), together with an example of a new material based on a tetrahydropyran subunit (**6**).

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birefringence is required, (perfluoroalkyl)bicyclohexyl systems (**5**) without polarizable olefinic substructures are used.

With increasing polarity of the liquid crystal mixture it becomes more and more challenging to design materials that will also maintain high voltage holding ratios and specific resistivities after extended heat load or UV irradiation. In particular, some esters and dioxane derivatives show insufficient reliability under harsh conditions, probably due to the formation of oxidative or hydrolytic decomposition products.

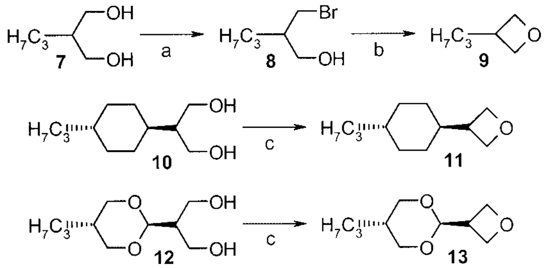
Against this background, we have recently been focusing our attention on liquid crystals containing tetrahydropyran (THP) moieties as polar rings within their mesogenic core structures (e.g., **6**). Somewhat counterintuitively, the local dipole moment of the THP moiety is quite effective for increasing the dielectric anisotropy in spite of its oblique orientation relative to the long molecular axis.

This report is mainly centered on the synthesis of the THP building block. A more general account of the chemistry, together with a detailed discussion of the unique physicochemical properties of THP-based liquid crystals, will be the subject of a forthcoming publication.

A major obstacle for the practical application of liquid-crystalline tetrahydropyran derivatives is their rather inconvenient synthetic accessibility. Most methods reported in the literature are based on the derivatization of carbohydrate precursors,[5] and these reactions usually give single enantiomers of the products, whereas we were interested primarily in racemic liquid crystals. Other major approaches include the use of lactone derivatives as intermediates,[6] ring-closing olefin metathesis[7] or application of the Ferrier reaction.[8] All these methods suffer either from low yields or from limited structural scope, too narrow for the synthesis of typical highly fluorinated liquid crystals.

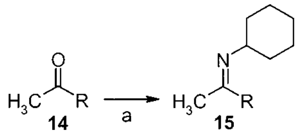
## Results and Discussion

In order to gain access to liquid-crystalline tetrahydropyran derivatives, we developed a new synthetic method based



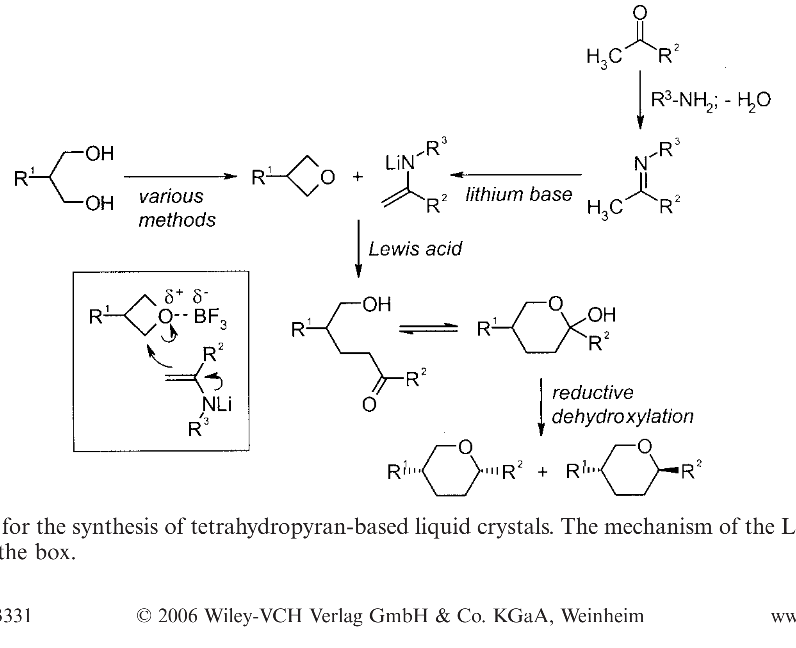
Scheme 3. Synthesis of the different 3-substituted oxetane precursors **9**, **11** and **13**: a) $Br_2$, $PPh_3$, pyridine, $CH_2Cl_2$, room temp., 18 h (65%). b) $Bu_3SnOMe$, 50 °C, 100 mbar, distillative removal of MeOH, then 200 °C, 90 mbar, distillative collection of **9** (86%). c) 1. *n*BuLi (1.0 equiv.), THF; 0 °C, 40 min, 2. TsCl, THF, room temp., 1 h, 3. *n*BuLi (1.0 equiv.), THF, addition at 0 °C, then 60 °C, 4 h (**11**: 65%, **13**: 75%).

Table 1. Preparation of the cyclohexylimines (**15a–j**) from the corresponding methyl ketones (**14a–j**): a) cyclohexylamine, cat. TsOH, toluene, reflux with azeotropic water removal.



| Ketone | R | Imine | Yield [%] |
|---|---|---|---|
| **14a** | $n$-$C_3H_7$ | **15a** | 80[a] |
| **14b** | $CF_3$ | **15b** | 39[a–c] |
| **14c** | $C_2F_5$ | **15c** | 44[a–c] |
| **14d** | $n$-$C_3F_7$ | **15d** | 32[a–c] |
| **14e** | Ph | **15e** | 82[a,b] |
| **14f** | $C_6H_4$-4-$CF_3$ | **15f** | 95 |
| **14g** | $C_6H_4$-4-$OCF_3$ | **15g** | 83 |
| **14h** | $C_6H_4$-4-Br | **15h** | 87[d] |
| **14i** | $C_6H_4$-4-$n$-$C_3H_7$ | **15i** | 91 |
| **14j** | $C_6H_3$-3,5-$F_2$ | **15j** | 84 |

[a] Benzene was used instead of toluene as solvent, due to the low boiling point of the ketone. [b] No *p*TsOH was used. [c] Reaction was performed in a Soxhlet apparatus charged with $MgSO_4$. The imines were purified by distillation under reduced pressure (**15b**: b.p. 60–62 °C, 14–15 mbar; **15c**: b.p. 76–78 °C, 30–33 mbar; **15d**: b.p. 73–75 °C, 22–24 mbar). [d] **15h** is a colourless solid that was purified by recrystallization from toluene.

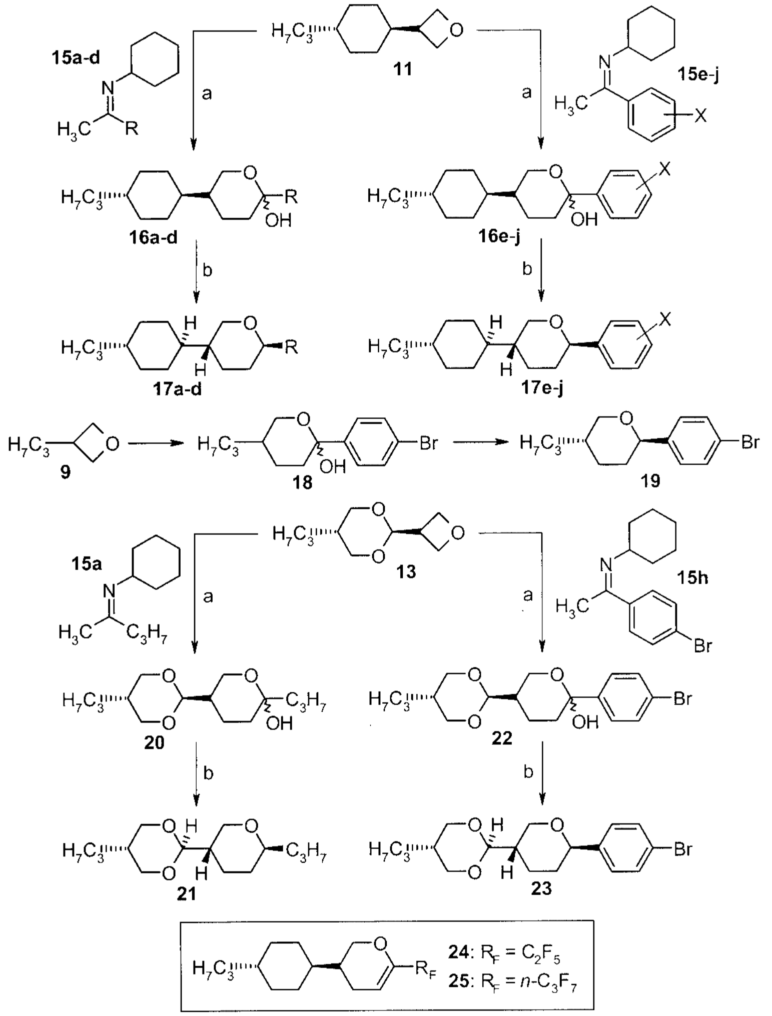


Scheme 2. General pathway for the synthesis of tetrahydropyran-based liquid crystals. The mechanism of the Lewis acid catalysed oxetane ring-opening is depicted in the box.

on the Lewis acid catalysed ring-opening of 3-substituted oxetanes with lithium iminoenolates (Scheme 2).[9] This step furnishes a hemiketal intermediate, which is reductively dehydroxylated to give the corresponding *trans*-2,5-disubstituted tetrahydropyran derivative.

The oxetane precursors are readily available from the corresponding 1,3-diols (Scheme 3). Compounds containing primary alkyl substituents (**9**) were synthesized by cyclization of the 3-bromo alcohols with tributyl(methoxy)tin.[10] Oxetanes with more bulky substituents (such as **11**)

Table 2. Synthesis of the tetrahydropyran-based liquid crystals **17a**–**j**, **19**, **21** and **23**: a) 1. TMP, *n*BuLi, THF, –78 °C, 20 min, 2. imine, THF, –70 to –60 °C, 40 min. 3. oxetane, $BF_3{\cdot}OEt_2$, THF, –60 °C, 1.5 h, then room temp., 10 h. b) $Et_3SiH$, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, –70 °C, 3 h, then –10 °C. The dihydropyrans **24** and **25** (box) were formed as byproducts during the reduction of **16c** and **16d**.



| Imine | R | Oxetane | X | Hemiketal: yield (%) | THP: yield (%), *trans* (%) |
|---|---|---|---|---|---|
| **15a** | $n$-$C_3H_7$ | **11** | – | **16a:** 59 | **17a:** 99, 91 |
| **15b** | $CF_3$ | **11** | – | **16b:** 24 | **17b:** 55[a], 80 |
| **15c** | $C_2F_5$ | **11** | – | **16c:** 10 | **17c:** 30[a,b], – |
| **15d** | $n$-$C_3F_7$ | **11** | – | **16d:** 15 | **17d:** 59[a,c], – |
| **15e** | Ph | **11** | H | **16e:** 69 | **17e:** 94, 93 |
| **15f** | $C_6H_4$-4-$CF_3$ | **11** | 4-$CF_3$ | **16f:** 81 | **17f:** 91, 91 |
| **15g** | $C_6H_4$-4-$OCF_3$ | **11** | 4-$OCF_3$ | **16g:** 84 | **17g:** 93, 94 |
| **15h** | $C_6H_4$-4-Br | **11** | 4-Br | **16h:** 60 | **17h:** 82, 92 |
| **15i** | $C_6H_4$-4-$n$-$C_3H_7$ | **11** | 4-$n$-$C_3H_7$ | **16i:** 51 | **17i:** 98, 60 |
| **15j** | $C_6H_3$-3,5-$F_2$ | **11** | 3,5-$F_2$ | **16j:** 7 | **17j:** 88, 95 |
| **15h** | $C_6H_4$-4-Br | **9** | 4-Br | **18:** 74 | **19:** 91, 92 |
| **15a** | $n$-$C_3H_7$ | **13** | – | **20:** 48 | **21:** 82, 88 |
| **15h** | $C_6H_4$-4-Br | **13** | 4-Br | **22:** 20 | **23:** 69, 71 |

[a] The reaction mixture was heated to 40 °C until completion of the reduction. [b] Crude reduction product, mixture of **17c** (29%) and **24** (71%). [c] Crude reduction product, mixture of **17d** (29%) and **25** (71%).

were prepared directly from the diols by a one-pot activation/cyclization procedure.[11] The same method was also applied for the synthesis of the 3-(*trans*-5-alkyl-1,3-dioxan-2-yl)oxetane **13** from the diol **12**.[4]

Necessary requirements for the iminoenolate building block are sufficient reactivity to accomplish the opening of the oxetane ring, convenient synthetic accessibility and ease of the hydrolytic workup after the addition reaction. As also reported by J.-F. Le Borgne[12] for similar ring-opening reactions of epoxides, lithium (cyclohexylimino)enolates were found to fit this property profile. They were readily prepared by acid-catalysed condensation of the corresponding methyl ketones with cyclohexylamine with azeotropic removal of water.[13] For the more reactive and volatile methyl perfluoroalkyl ketones the procedure had to be slightly modified, the acid catalysis not being necessary.[14] Except for **15b–d** and **15h**, the imines were isolated as yellow or brown liquids after simple concentration and filtration of the reaction mixtures and were used directly for the next step (Table 1).

The deprotonation of the imines to afford the corresponding lithium (cyclohexylimino)enolates was achieved by use of lithium 2,2,6,6-tetramethylpiperidine (LiTMP) (prepared in situ from *n*-butyllithium and 2,2,6,6-tetramethylpiperidine) as a powerful base with low nucleophilicity. A nonnucleophilic base is essential because the subsequent oxetane ring-opening is catalysed by the Lewis acid boron trifluoride–diethyl ether, which would otherwise be deactivated. These reactions were conducted between –78 and –60 °C, furnishing equilibrium mixtures of two hemiketal isomers and the corresponding δ-hydroxy ketone (see also Scheme 2). The subsequent reductive dehydroxylation of the hemiketal was achieved with a combination of triethylsilane and boron trifluoride–diethyl ether in dichloromethane.[15] For most of the substrates ($R^2$ = aryl or alkyl; see Scheme 2 and Table 2) the reaction proceeds at temperatures between –70 and –10 °C. For the less reactive perfluoroalkyl hemiketals **16b–d** the temperature had to be raised to 40 °C in order to drive the conversion to completion. Even under these more vigorous conditions, the THP derivatives **17c** and **17d** were accompanied by large quantities of their elimination products, the corresponding dihydropyrans **24** and **25**. The reason for this lack of reactivity is the destabilization of the transient α-perfluoroalkyl carbocations formed during the reduction by the negative inductive effects (*–I*) of the trifluoromethyl, pentafluoroethyl and perfluoro-*n*-propyl groups.[16] The *trans*/*cis* isomer ratios of the dehydroxylation products are typically in the range of 8:1 to 9:1.

The very low yield of **16j** is caused by *ortho*-lithiation between the two aromatic fluorine substituents, competing with the formation of the lithium iminoenolate by the very strong base LiTMP.

The liquid crystals containing tetrahydropyran subunits show some highly advantageous characteristics (Table 3):[17] as expected, they have high dielectric anisotropies (Δ$\varepsilon$) in combination with low birefringences (Δ$n$) and low rotational viscosities ($\gamma_1$). In contrast with many other highly polar fluorinated liquid crystals, their solubilities in all kinds of nematic host mixtures are excellent. This is also apparent in the order of the melting points, with **4** (74 °C) > **1** (66 °C) > **6** (57 °C). In the neat materials, slight tendencies towards the formation of smectic phases are observed, but these are less pronounced than in 1,3-dioxane derivatives with similar structures.[4] The virtual clearing temperatures are generally a little lower than those of their cyclohexane analogues (e.g., **1**: 74.3 °C → **6**: 62.3 °C).

Table 3. Physical properties of some selected pyran-based liquid crystals in comparison to conventional materials (**1**–**5**) with similar areas of application.[17]

| No. | Phase sequence | $\Delta\varepsilon_{\mathrm{virt}}$ | $\Delta n_{\mathrm{virt}}$ | $T_{\mathrm{NI,virt}}$ | $\gamma_{1,\mathrm{virt}}$ |
|---|---|---|---|---|---|
| **1** | C 66 N 94.1 I | 9.7 | 0.0750 | 74.3 | 160 |
| **2** | C 56 N 117.2 I | 11.1 | 0.0670 | 115.0 | 175 |
| **3** | C 44 N 105.3 I | 10.5 | 0.0668 | 91.5 | 145 |
| **4** | C 74 N (51.2) I | 17.0 | 0.0680 | 63.2 | 201 |
| **5** | C 19 $S_H$? (8) $S_B$? 41 I | 6.8 | 0.0594 | –44.4 | 63 |
| **6** | C 57 N (50.9) I | 12.7 | 0.0778 | 62.3 | 182 |
| **17a** | C 28 $S_B$ 62 I | –0.5 | 0.0482 | 36.1 | 56 |
| **17b** | C 59 I | 8.8 | 0.0606 | –57.6 | – |
| **17f** | C 73 $S_B$ 115.5 I | 13.2 | 0.0853 | 104.2 | 351 |
| **17g** | C 71 $S_B$ 86 N 136.6 I | 6.7 | 0.0831 | 134.2 | 179 |
| **17h** | C 98 N 176.8 I | – | – | – | – |
| **17j** | C 64 N (53.7) I | 4.7 | 0.0863 | 44.1 | 216 |
| **21** | C 64 $S_B$ (53) I | 3.6 | 0.0506 | –9.6 | 78 |

In addition to their favourable electrooptical and mesogenic properties, the tetrahydropyran-based materials show excellent reliability profiles.[2]

## Conclusions

A new, convenient synthetic procedure allows the synthesis of a variety of liquid crystals containing tetrahydropyran moieties in their mesogenic core structures. The materials have a highly advantageous combination of high dielectric anisotropy (Δ$\varepsilon$) and low birefringence (Δ$n$), together with excellent mesogenic properties and high chemical stability. The synthetic methodology is generally applicable not only for the preparation of materials but also for tetrahydropyran-based natural products, pharmaceuticals and agrochemicals.

## Experimental Section

**General:** The following synthetic procedures have been selected as examples for the preparation of the different classes of liquid crystals. The hemiketal intermediates (**16b**, **16f** and **20**) each exist in equilibrium between two cyclic hemiketal isomers and the open δ-hydroxy ketone. The compounds have not been fully characterized, but their purities and identities were verified by HPLC and GC-MS. All reactions were carried out in dry solvents and under nitrogen.

**Trifluoromethyl Hemiketal 16b:** A mixture of TMP (2,2,6,6-tetramethylpiperidine, 4.75 mL, 28.0 mmol) and THF (30 mL) was treated dropwise at –78 °C with *n*BuLi (15% solution in *n*-hexane) (17.50 mL, 27.90 mmol). The resulting mixture was stirred at the same temperature for 20 min, followed by dropwise addition of a solution of 1,1,1-trifluoroacetone *N*-cyclohexylimine (**15b**, 5.41 g, 28.0 mmol) in THF (30 mL). The resulting deep violet solution was stirred between –60 °C and –70 °C for 15 min, and a solution of 3-(*trans*-4-propylcyclohexyl)oxetane (**11**, 4.00 g, 21.9 mmol) in THF (20 mL) was added, followed by $BF_3$·$OEt_2$ (6.28 mL, 50.0 mmol). The solution was stirred at –60 °C for 2.5 h and was then allowed to warm to room temperature. After 10 h of stirring at room temperature, the reaction was quenched by addition of a saturated aqueous $NH_4Cl$ solution (80 mL). The aqueous phase was separated and extracted with *tert*-butyl methyl ether (2 × 50 mL). The combined organic phases were washed with brine (40 mL), dried with $Na_2SO_4$ and filtered, and the solvents were evaporated to dryness. The residue was purified by chromatography (silica gel; *n*-heptane/ethyl acetate, 7:1) to afford a yellow oil (2.66 g). In order to remove residual traces of the cyclohexylimine, the crude product was dissolved in a mixture of *tert*-butyl methyl ether (40 mL) and hydrochloric acid (10 %, 20 mL). The biphasic mixture was vigorously stirred for 15 min, the layers were separated, the organic phase was dried with $Na_2SO_4$ and filtered, and the solvents were evaporated. The hemiketal **16b** was obtained as colourless crystals (1.58 g, 24 %), which were used for the subsequent synthetic step without further characterization.

The pentafluoroethyl and perfluoro-*n*-propyl hemiketals **16c** and **16d** were prepared according to an analogous procedure.

**Liquid Crystal 17b:** A solution of the hemiketal **16b** (1.35 g, 4.57 mmol) in dichloromethane (50 mL) was treated dropwise at –70 °C with triethylsilane (1.21 mL, 7.50 mmol), followed by $BF_3$·$OEt_2$ (0.49 mL, 7.50 mmol). The reaction mixture was allowed to warm to room temperature over 1 h and was then heated to 40 °C and stirred until the complete disappearance of the starting material **16b** was confirmed by TLC after ca. 6 h. After cooling in an ice bath, the mixture was hydrolysed and neutralized by careful addition of a solution of aqueous sodium hydroxide (10 %). The aqueous phase was extracted twice with dichloromethane (30 mL), and the combined organic phases were washed with brine (30 mL), dried with $Na_2SO_4$ and concentrated in vacuo to afford a colourless oil (1.22 g). Purification by column chromatography (silica gel; *n*-heptane/ethyl acetate, 8:1) afforded **17b** (0.70 g, 55 %), containing 80 % (HPLC) *trans* isomer. Repeated recrystallization from *n*-heptane afforded pure (96.5 % by HPLC) *trans-trans*-**17b**. For melting point and electrooptical characteristics see Table 3. $^1$H NMR (500 MHz, $CDCl_3$, 303 K): $\delta$ = 4.13 (ddd, $J$ = 11.2 Hz, $J$ = 4.0 Hz, $J$ = 2.0 Hz, 1 H), 3.68–3.54 (m, 1 H), 3.19 (t, $J$ = 11.2 Hz, 1 H), 2.05–1.95 (m, 1 H), 1.88–1.37 (m, 7 H), 1.35–1.07 (m, 6 H), 1.05–0.91 (m, 3 H), 0.87 (t, $J$ = 7.3 Hz, 3 H), 0.84–0.76 (m, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 303 K): $\delta$ = 124.0 (q, $^1J_{CF}$ = 278.8 Hz, $CF_3$), 75.2 (q, $^2J_{CF}$ = 31.1 Hz, $CHCF_3$), 72.0, 40.3, 39.6, 39.5, 37.2, 33.0, 30.0, 29.7, 25.7, 24.3, 19.8, 14.2 ppm. $^{19}$F NMR (235 MHz, $CDCl_3$, 300 K): $\delta$ = –79.6 (d, $^3J_{HF}$ = 6.3 Hz, 3 F, $CF_3$). MS (EI, 70 eV): *m/z* (%) = 278 (18) [M]$^+$, 235 (24), 139 (16), 124 (58), 109 (19), 95 (25), 83 (78), 69 (100), 57 (15), 55 (61).

The liquid crystals **17c** and **17d** were prepared from the corresponding methyl perfluoroalkyl *N*-cyclohexylketimines according to an analogous procedure. Nevertheless, **17c** and **17d** could not be isolated cleanly because they were accompanied by the corresponding dihydropyranes **24** and **25**, respectively.

**Hemiketal 16f:** A solution of TMP (3.90 mL, 22.90 mmol) in tetrahydrofuran (30 mL) was treated dropwise at –78 °C with *n*BuLi (15 % solution in hexane, 14.37 mL, 22.90 mmol). The mixture was stirred at the same temperature for 20 min, and a solution of 4-(trifluoromethyl)acetophenone *N*-cyclohexylimine (**15f**, 6.19 g, 23.00 mmol) in THF (30 mL) was then added slowly. The resulting mixture was stirred between –60 and –70 °C for 40 min before addition of a solution of 3-(*trans*-4-propylcyclohexyl)oxetane (**11**, 3.0 g, 16.5 mmol) in THF (20 mL) and subsequent slow addition of $BF_3$·$OEt_2$ (5.10 mL, 40.60 mmol). The solution was stirred at –60 °C for an additional 90 min, and was then allowed to warm to room temperature. After the mixture had been stirred at room temperature for 10 h, saturated aqueous $NH_4Cl$ (70 mL) was added, and the aqueous phase was separated and extracted twice with *tert*-butyl methyl ether (30 mL). The combined organic phases were washed with brine (30 mL), dried with sodium sulfate, filtered and concentrated in vacuo. The residue was chromatographed (silica gel; *n*-heptane/ethyl acetate, 8:1) to afford **16f** (4.92 g, 81 %) as a colourless solid, which was used for the subsequent synthetic step without further characterization.

The hemiketals **16a**, **16e**, **16g**–**j**, **18**, **20** and **22** were prepared according to an analogous procedure.

**Liquid Crystal 17f:** A solution of the adduct **16f** (3.0 g, 8.10 mmol), dissolved in dichloromethane (100 mL), was treated dropwise at –70 °C with triethylsilane (2.10 mL, 13.0 mmol) and then with $BF_3$·$OEt_2$ (0.85 mL, 13.0 mmol). The mixture was stirred at the same temperature for 3 h and was then allowed to warm to –10 °C. The reaction was quenched and the mixture neutralized by careful addition of aqueous sodium hydroxide (10 %). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 × 40 mL). The combined organic layers were washed with brine (30 mL), dried with sodium sulfate and concentrated in vacuo to afford colourless crystals of **17f** (2.64 g, 91 %), containing 91 % (HPLC) of the desired *trans* isomer. Repeated recrystallization from *n*-heptane afforded *trans*,*trans*-**17f** with high purity (>99 % by HPLC). For mesophase sequence and electrooptical characteristics see Table 3. $^1$H NMR (500 MHz, $CDCl_3$, 303 K): $\delta$ = 7.58 (d, $J$ = 8.4 Hz, 2 H, ar-*H*), 7.44 (d, $J$ = 8.4 Hz, 2 H, ar-*H*), 4.29 (d, $J$ = 11.0 Hz, 1 H), 4.19 (dq, $J$ = 11.0 Hz, $J$ = 3.5 Hz, 1 H), 3.33 (t, $J$ = 11.0 Hz, 1 H), 2.03–1.86 (m, 2 H), 1.81–1.69 (m, 3 H), 1.60–1.23 (m, 6 H), 1.19–1.11 (m, 3 H), 1.07–0.98 (m, 3 H), 0.88 (t, $J$ = 7.3 Hz, 3 H, $CH_3$), 0.89–0.81 (m, 2 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 303 K): $\delta$ = 147.1, 129.3 (q, $^2J_{CF}$ = 32.3 Hz, ar-$C$-$CF_3$), 125.8, 125.0 (d, $^3J_{CF}$ = 3.5 Hz, ar-$C$), 124.1 (q, $^1J_{CF}$ = 272.3 Hz, $CF_3$), 79.1, 72.3, 40.8, 40.0, 39.6, 37.3, 34.2, 33.2, 30.2, 29.8, 27.7, 19.8, 14.2 ppm. $^{19}$F NMR (235 MHz, $CDCl_3$, 300 K): $\delta$ = –60.68 (s, 3 F, $CF_3$). MS (EI, 70 eV): *m/z* (%) = 354 (55) [M]$^+$, 335 (15), 323 (15), 210 (17), 198 (12), 185 (12), 172 (37), 164 (26), 159 (20), 123 (40), 109 (52), 95 (44), 83 (100), 79 (17), 69 (79), 55 (77).

The liquid crystals **17a**, **17e**, **17g**–**j**, **19**, **21** and **23** were prepared according to an analogous procedure.

**Hemiketal 20:** The dioxanyl hemiketal **20** was prepared analogously to **16f**. The crude product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate, 3:1) to furnish **20** as a yellowish solid in 48 % yield. The product was used without further characterization as starting material for **21**.

**Liquid Crystal 21:** The liquid crystal **21** was prepared from the dioxanyl hemiketal **20** analogously to the synthesis of **17e**. The crude product was purified by chromatography (silica gel; *n*-heptane/ethyl acetate, 5:1) to furnish **20** as a colourless solid (82 % yield) containing 88 % (HPLC) of the desired *trans* isomer. Two consecutive recrystallizations from ethanol afforded *trans*,*trans*-**21** with high purity (100 % purity by HPLC). For mesophase sequence and electrooptical characteristics see Table 3. $^1$H NMR (500 MHz, $CDCl_3$, 303 K): $\delta$ = 4.18 (d, $J$ = 5.3 Hz, 1 H), 4.08–3.99 (m, 3 H), 3.28–3.12 (m, 4 H), 2.03–1.76 (m, 3 H), 1.66–1.61 (m, 1 H), 1.52–1.15 (m, 8 H), 1.02–0.95 (m, 2 H), 0.90 (t, $J$ = 6.9 Hz, 3 H), 0.89 (t, $J$ = 7.3 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$, 303 K): $\delta$ =

102.9, 77.5, 72.2, 68.9, 40.6, 38.5, 34.1, 31.0, 30.4, 24.8, 19.5, 18.8, 14.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 256 (3) $[M]^+$, 213 (18), 129 (100), 83 (40), 55 (44).

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[17] The "virtual" parameters $T_{\mathrm{NI,virt}}$, $\Delta\varepsilon_{\mathrm{virt}}$, $\Delta n_{\mathrm{virt}}$ and $\gamma_{1,\mathrm{virt}}$ were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 ($T_{\mathrm{NI}}$ = 92.8 °C, $\Delta\varepsilon$ = 5.3, $\Delta n$ = 0.0964). The extrapolated values are corrected empirically for differences in the order parameter induced by the analyte. For the pure substances, the phase transition temperatures were measured by differential scanning calorimetry (DSC), whilst the phase type was assigned by optical polarization microscopy.

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