

Liquid crystals with partially fluorinated side chains: Highly polar materials with very low birefringence

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Abstract

Highly polar liquid crystals with very low birefringence were synthesized by a reaction sequence starting with the radical addition of a secondary alcohol to pentafluoropropene and perfluoropropene, respectively. The mesophases and electrooptical properties of the new materials were interpreted using a detailed computational analysis of the conformational equilibrium.

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1. Introduction

Our daily lives have come to rely more and more on the ubiquitous presence of portable electronic devices, such as cellular phones, personal digital assistants (PDA) or video games. The function of these devices depends critically on a liquid crystal display (LCD) as the central user interface. In order to reduce energy consumption and to extend battery lifetime, the majority of these LCDs are either of a reflective or transmissive type with active matrix addressing [1]. Reflective LCDs do not need a backlight, thus requiring 70–90% less energy than conventional LCDs.

The liquid crystals used for these applications are so-called super-fluorinated materials (SFM) [1] having a combination of high dielectric anisotropy ($\Delta\epsilon$), very low birefringence (Δn) and a high clearing temperature (T_{NI}) [2]. Low rotational viscosity (γ_1) is a necessary prerequisite to achieve video-compatible switching times of the LCD.

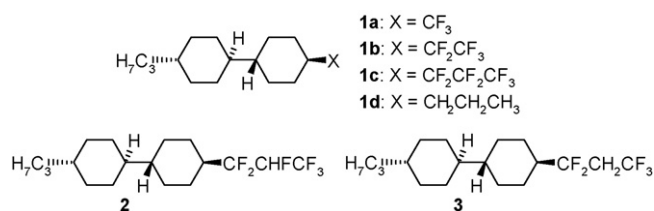
A standard approach to achieve low birefringence (which is related to the molecular polarizability $\Delta\alpha$) [2] is to use an alkyl bicyclohexyl moiety as the mesogenic core structure. High-dielectric anisotropy can be obtained by introducing a terminal, polar perfluoroalkyl group. Materials with a terminal trifluoromethyl group (**1a**, Scheme 1) have been used in active matrix LCDs for several years [1], but a higher clearing point and even lower birefringence at similar or higher polarity would be a valuable improvement.

The clearing temperature T_{NI} can be raised by up to 80 K by replacing the trifluoromethyl group with the longer pentafluoroethyl (**1b**) and perfluoro-*n*-propyl chain (**1c**), but at the price of a concomitant increase of the birefringence (Δn_{virt}) from 0.0594 (for **1a**) to 0.0622 (for **1c**) (Table 1). The increase of Δn seems to be related to the degree of fluorination.

Using a quick and simple, “virtual” screening approach based on a semiempirical method (AM1) [3], the two structures **2** and **3** were identified as interesting target structures. Both compounds are partially defluorinated analogues of **1c**, and they were expected to show similar or higher dielectric anisotropy ($\Delta\epsilon$) at significantly lower birefringence ($\Delta\epsilon$). The calculations used for the virtual screening did not include a

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Scheme 1. Fluorinated liquid crystals **1a–c** combining strong dielectric anisotropy ($\Delta\epsilon$) with low birefringence (Δn). The target compounds **2** and **3** were identified by a quick, “virtual” screening based on semiempirical (AM1) calculations [3].

Table 1
Application relevant properties of the liquid crystals **1a–1d**, **2** and **3**

Number	Phase sequence	$T_{\text{NI, virt}}$	$\Delta\epsilon_{\text{virt}}$	Δn_{virt}
1a	C 19 S ₇ (8) S _B 41 I	−44.4	6.8	0.0594
1b	C 10 S ₇ (1) N (1.7) I	−24.1	5.8	0.0504
1c	C 22 S _B 77 I	39.5	6.8	0.0622
1d	C 65 S _B 83 I	69.1	−0.3	0.0430
2	C 42 S ₇ (36) S _B 59 I	20.2	7.7	0.0592
3	C 76 I	−9.9	6.6	0.0529

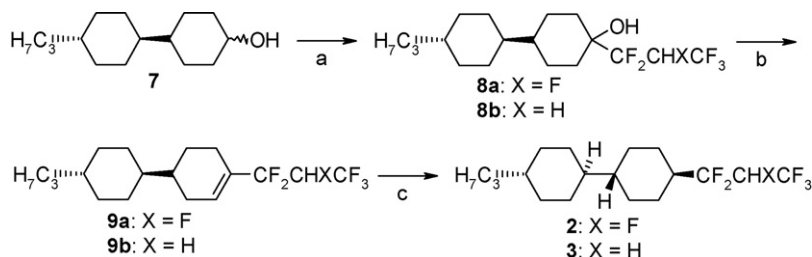
The phase transition temperatures and the virtual clearing points ($T_{\text{NI, virt}}$) are cited in °C. Numbers in parentheses denote monotropic phase transitions (C = crystalline, S_B = smectic B, S₇ = unknown smectic phase, N = nematic, I = isotropic) [7].

systematic conformer search, and they took only one linear conformation of the side chain into account.

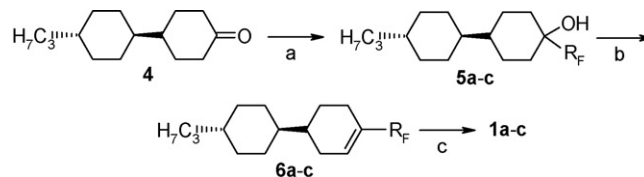
2. Results and discussion

The perfluoroalkyl compounds **1a–c** were synthesized by fluoride-induced addition of the corresponding Ruppert–Prakash silane reagents Me₃SiR_F (R_F = CF₃, C₂F₅, *n*-C₃F₇) to the ketone **4** [4], followed by desilylation with potassium fluoride in methanol (Scheme 2). Alternatively, the alcohol **5a–c** is also available by reaction of the ketone **4** with C₃F₇I and MeLi·LiBr at low temperature [5]. Elimination of the tertiary alcohols **5a–c** was achieved with thionyl chloride furnishing the olefins **6a–c**, which were subsequently hydrogenated. The resulting mixtures of *cis* and *trans* isomers were separated by crystallization from *n*-heptane, yielding the pure *trans–trans* isomers.

For the introduction of the partially defluorinated side chains for **2** and **3**, no corresponding silane reagents Me₃SiR_F are



Scheme 3. Synthesis of the liquid crystals **2** and **3** with partially fluorinated polar side chains: (a) CF₃CX = CF₂ (1.4 equiv.), bis(*tert*-butyl) peroxide (0.13 equiv.); 140 °C, 24 h (**8a**: 11.6%, **8b**: 2.9%; not optimized). (b) SOCl₂, pyridine; r.t. (**9a**: 90%; **9b**: 82%). (c) 10 bar H₂, 5% Pd-C, THF; r.t.; 2, crystallization from *n*-heptane, preparative HPLC (**2**: 27.8%, **3**: 44.4%).



Scheme 2. Synthesis of the perfluoroalkyl substituted liquid crystals **1a–c**: (a) 1, Me₃SiR_F, cat. Bu₄NF, THF; −78 °C to r.t.; 2, KF, MeOH; reflux (**5a**: R_F = CF₃, 90%; **5b**: R_F = C₂F₅, 82%; **5c**: R_F = *n*-C₃F₇, 67%), for **5c** alternatively: *n*-C₃F₇I, MeLi·LiBr, Et₂O; −78 °C (67%). (b) SOCl₂, pyridine; r.t. (**6a**: 84%; **6b**: 69%; **6c**: 76%). (c) 1. 5 bar H₂, 5% Pd-C, THF; r.t.; 2, crystallization from *n*-heptane at −30 °C (**1a**: 63%; **1b**: 18%; **1c**: 27%).

commercially available. Therefore, the synthetic approach depicted in Scheme 3 chosen [6]: the tertiary alcohols **8a** and **8b** were obtained by the “inverse” radical addition of the cyclohexanol derivative **7** to 1,1,1,3,3-pentafluoropropene and perfluoropropene, respectively. The radical reaction was initiated thermally by bis(*tert*-butyl) peroxide, under strict exclusion of oxygen which acts as a radical quencher. The resulting alcohols **8a** and **8b** were subsequently converted into the liquid crystals **2** and **3** by the same method as described for compounds **1a–c**.

The physical characterization [7] of the compounds **2** and **3** (Table 1) shows that the birefringence Δn is indeed decreasing with the degree of fluorination. The data also show that the fluorination pattern of the side chain has a dramatic influence on the mesophase sequence: the “virtual” clearing points ($T_{\text{NI, virt}}$) [7] are dropping with decreasing degree of fluorination, and also the tendency to form thermodynamically stable mesophases is reduced. On the other hand, for compound **2** a significant increase of $\Delta\epsilon$ occurs compared to **1a** or **1c**, together with a decrease of Δn . This results in a considerably more attractive electrooptical property profile of **2** compared to conventional, perfluoroalkyl substituted materials, such as **1a**. Material **3** shows a similar $\Delta\epsilon$ as **1c**, but its birefringence (Δn) is significantly lower.

Whereas in aromatic liquid crystals an increase of aromatic fluorination results in a drop of the clearing point by 30–40 K for each additional fluorine substituent [1], for the fluoroaliphatic systems **1c**, **2** and **3** the opposite is observed: the loss of each aliphatic fluorine is accompanied by a decrease of the virtual clearing point by 20–30 K. This can be explained by the unique steric characteristics of highly fluorinated alkyl chains [8].

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