Liquid crystals with multiple fluorinated bridges in the mesogenic core structure

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Abstract

A rational, building block oriented design approach gives rise to a new class of ''super fluorinated'' liquid crystals suitable for the newest generation of active matrix LCDs. These materials contain combinations of different fluorinated linking groups in their mesogenic core structure, resulting in a highly advantageous property profile including a broad nematic phase range, low rotational viscosity and high dielectric anisotropy. The large-scale synthesis of such complex materials became feasible only by some recent advances in the synthesis of α,α-difluoroether linkages. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The most prominent objectives in the search for new, superior liquid crystalline materials [1–4] for application in active matrix liquid crystal displays (AM-LCDs or thin-film transistor, TFT-LCDs) [5] are the reduction of the rotational viscosity (γ_1), the extension of the nematic phase range and the reduction of the driving voltage (often by increasing the dielectric anisotropy ($\Delta\varepsilon$) [6–8]).[1] Another important development target is the improvement of the ''reliability'' [1,2] which among others includes the chemical and photochemical stability of the liquid crystal, its specific resistivity and its voltage holding ratio. Development objectives on the side of the LCD manufacturers are video-compatible switching times (that is, less than 16.7 ms) for multimedia applications, low energy consumption for portable devices and the reduction of production costs.

In our previous communications [9,10] we presented two classes of nematic liquid crystals containing CF_2O and CF_2CF_2 bridges within their mesogenic core structures which can be considered a significant progress in this line of research. The new materials demonstrate which beneficial effects on the application relevant physico-chemical properties of nematic liquid crystals [1–4] can be achieved by the insertion of highly fluorinated linking groups into typical mesogenic core structures, such as the phenylbicyclohexyl **1**.

On the one hand, insertion of a tetrafluoroethylene bridge between two cyclohexane subunits (**2**) results in a dramatic increase of the clearing temperature compared to the directly linked analogues (**1**) by 50–70 K [10]. An undesirable side-effect is a concomitant increase of the melting point and a reduced solubility in liquid crystalline host mixtures. On the other hand, the insertion of a difluorooxymethylene link between a cyclohexane and a phenyl substructure (**3**) broadens the nematic phase range substantially, increases the dielectric anisotropy ($\Delta\varepsilon$) and reduces at the same time the rotational viscosity (γ_1) which is the parameter predominantly determining the switching time of LCDs [9] (Scheme 1).

A targeted, rational materials design is often impeded by negative trade-off relations between the physico-chemical parameters: in most cases an increase of the clearing temperature (e.g. by the elongation of the mesogenic core structure) has to be ''paid'' for by a concomitant increase of the rotational viscosity (γ_1). A most notable exception of this empirical ''rule of thumb'' are the materials containing a difluorooxymethylene bridge, such as **3**, where the opposite tendency is observed. Based on this surprising finding, we wanted to make use of the difluorooxymethylene bridge for the compensation of the less desirable side-effects of the clearing point increasing tetrafluoroethylene link. A material

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[1] The anisotropy is defined as $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, the birefringence as $\Delta n = n_{\parallel} - n_{\perp}$, where $\parallel$ stands for parallel and $\perp$ perpendicular to the nematic phase director, which can be approximated by the molecular orientation axis or by the long molecular axis, respectively.
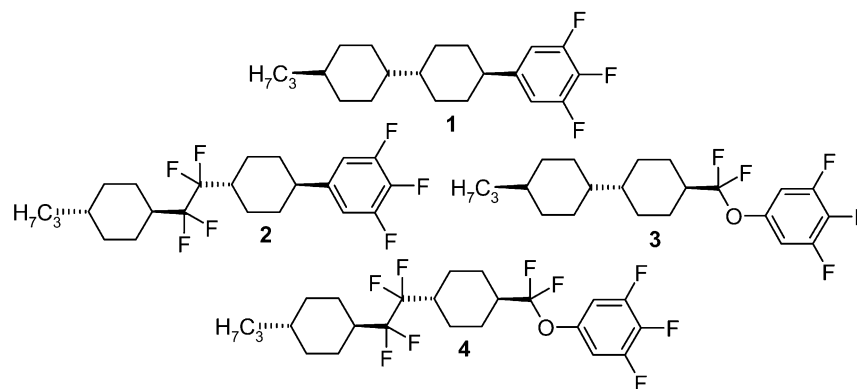
Scheme 1. The liquid crystalline basic structure **1**. Its bridged analogues are extended by a tetrafluoroethylene (**2**) [10] and a difluorooxymethylene link (**3**) [9]. The combined analogue **4** contains both bridging groups.

containing both bridges (such as **4**) was expected to possess a highly attractive combination of a high clearing point, broad mesophase range, good solubility, high dielectric anisotropy and reasonable rotational viscosity.

2. Results and discussion

The target compound **4** promises not only an interesting combination of the physico-chemical influences of the two bridges. It is also very challenging from the synthetic point of view containing two different fluorinated linking groups either of which had proved difficult to synthesize in the past. Retrosynthetic considerations (Scheme 2) based on our previous experience [9] suggested the following synthetic route: the difluorooxymethylene linked aryl moiety is introduced as the last step. This should be achievable via an intermediate dithioorthoester from the dithianylium salt **5** which again is available from the ketone **6**. As a central intermediate for all kinds of liquid crystals based on a di(cyclohexyl)tetrafluoroethane substructure, the monoketal **7** was proposed. This again was expected to be accessible from the commercially available 1,2-bis(4-hydroxyphenyl)-tetrafluoroethane **8**.[2]

The first step towards the building block **7** is the catalytic hydrogenation of **8**, followed by the oxidation of the resulting diol **9** to the diketone **10**. The selective monoketalization to compound **7** was accomplished by refluxing a mixture of **10** and 2,2-dimethylpropane-1,3-diol in a two-phase system of diluted sulfuric acid and cyclohexane (Scheme 3).

The synthesis of the liquid crystal **4** from the building block **7** is shown in Scheme 4. The side chain is introduced by a Wittig reaction (→**11**), followed by a catalytic hydrogenation and the selective cystallization of *trans*-**12** from *n*-heptane. The ketal **12** is deprotected (→**13**) and homologized via the enol ether **14** to the corresponding *trans–trans* aldehyde **15**. Oxidation of the aldehyde furnishes the carboxylic acid **16** which is condensed with 1,3-propanedithiol

to the dithianylium salt $17^+ \cdot CF_3SO_3^-$ [9]. The conversion to the target compound **4**[3] is accomplished by oxidative fluorodesulfuration [9,11–16] in the presence of 3,4,5-trifluorophenol.

A comparative overview of the physical data of the target compound **4** and its differently bridged analogues **1–3** is given in Table 1.

The data in Table 1 suggest, that at least for liquid crystals based on the phenylbicyclohexyl "backbone" (**1**) the mesogenic and viscoelastic properties can be modified by the quite independent choice of suitable bridge elements. Roughly speaking, for compound **4** the high clearing point (real as well as "virtual" T_{NI}) can be attributed to the tetrafluoroethylene bridge [10], and especially the low rotational viscosity (γ_1) but also the broad nematic phase to the difluorooxymethylene bridge [9].

In addition to the general improvement of the mesogenic and viscoelastic properties, the substance class **4** shows a significant improvement of the so-called "reliability" parameters, such as specific resistivity and voltage holding ratio [1,2]. This favorable combination of most of the application relevant properties of **4**, such as high clearing point, broad nematic phase, low rotational viscosity, high dielectric anisotropy and good reliability, shows that at least some of the above-mentioned negative trade-off relations can be overcome by a rational design of liquid crystalline materials.

These properties possibly make **4** and its structural analogues a potentially essential component for liquid crystal mixtures for the next generation of fast switching flat-panel displays for TV screens and portable devices capable of displaying moving pictures, such as cellular phones, video games, subnotebook computers and PDAs (personal digital assistants). On the synthetic side, the preparation of complex "super fluorinated materials" (SFMs) such as **4** became feasible only by a new synthetic route [9] allowing the easy formation of a difluorooxymethylene linkage between a

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[2] The product **8** was supplied by Bayer AG, Leverkusen, Germany.

[3] The starting material **4** confirmed by GLC and HPLC to be > 99.8%.
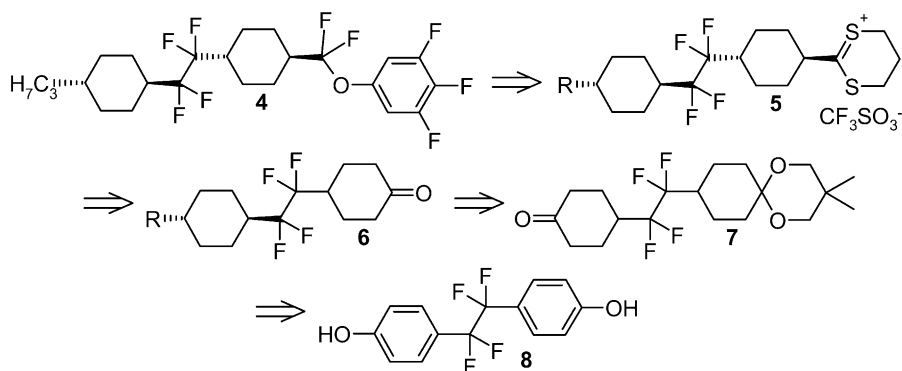
Scheme 2. Retrosynthetic considerations for the synthesis of **4**.
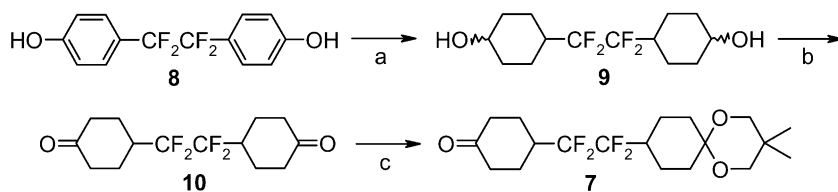
Scheme 3. Synthesis of the central building block **7**: (a) H$_2$, 5% Rh-C, 2-propanol; 5 bar, 60°C (76%). (b) Pyridinium chlorochromate (PCC), CH$_2$Cl$_2$; room temperature, 18 h (79%). (c) 2,2-Dimethylpropane-1,3-diol, cyclohexane, 0.01N H$_2$SO$_4$; reflux, 10 h (83%).
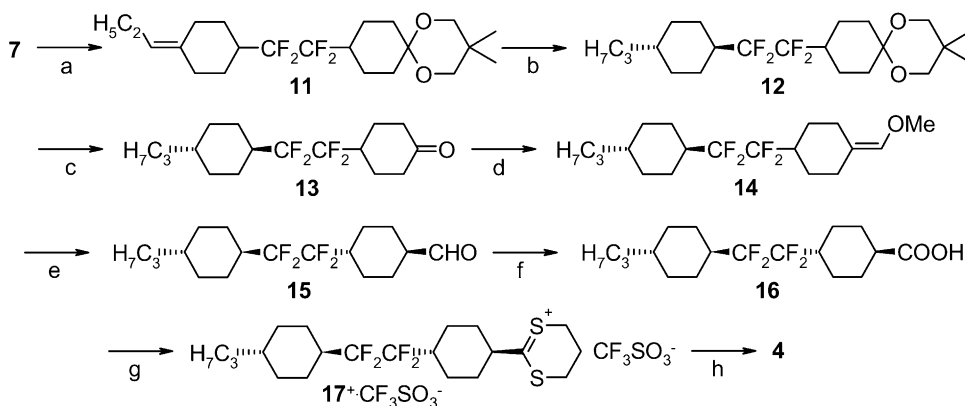
Scheme 4. Synthesis of **4**: (a) H$_7$C$_3$PPh$_3$$^+Br^-$, KO*t*Bu, THF; −10°C: room temperature, 18 h (95%). (b) 1: H$_2$, 5% Pd–C, THF; 1 bar, room temperature; 2: crystallization from *n*-heptane (64%). (c) 98% HCOOH, toluene; room temperature, 18 h (76%). (d) MeOCH$_2$PPh$_3$$^+Br^-$ KO*t*Bu, THF; −10°C: room temperature, 18 h (88%). (e) 1:98% HCOOH, toluene; room temperature, 18 h; 2: MeOH, kat. NaOH; −20°C: room temperature, 2 h (93%). (f) CrO$_3$/H$_2$SO$_4$ (Jones' reagent), acetone; 0°C: room temperature, 18 h (68%). (g) HS(CH$_2$)$_3$SH, CF$_3$SO$_3$H, toluene/isooctane 1:1; reflux, azeotropic removal of water (84%). (h) 1: 3,4,5-Trifluorophenol, NEt$_3$, CH$_2$Cl$_2$; −70°C, 30 min; 2: NEt$_3$·3HF; −70°C, 5 min; 3: Br$_2$, CH$_2$Cl$_2$; −70°C (1 h) −20°C; 4: 0.5N NaOH (33%).

Table 1
Physical properties of some examples for the different liquid crystals **1–4**[a]

Crystal	Mesophases	T_{NI}	$\Delta\varepsilon$	Δn	γ_1
1	C 66 N 94.1 I	74.7	9.7	0.075	171
2	C 70 S$_G$ 95 S$_B$ 102 N 168.6 I	122.0	9.0	0.060	269
3	C 44 N 105.3 I	91.5	10.5	0.067	145
4	C 49 S$_B$ 114 N 164.4 I	128.0	9.4	0.074	250

[a] "Virtual" clearing points (T_{NI}), dielectric anisotropies ($\Delta\varepsilon$), birefringences (Δn) and rotational viscosities (γ_1) are extrapolated from the Merck liquid crystal mixture ZLI-4792. The temperatures are given in degree Celsius, the γ_1 values in milli Pascal seconds. C: crystalline, S$_x$: smectic X, N: nematic, I: isotropic. The application oriented evaluation of liquid crystals for use in LCDs is centered around "virtual" clearing temperatures, electrooptic parameters and viscosities. These data are obtained by extrapolation from a standardized nematic host mixture: $T_{NI,extr}$, $\Delta\varepsilon$, Δn and γ_1 were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 (T_{NI} = 92.8°C, $\Delta\varepsilon$ = 5.27, Δn = 0.0964). The values thus obtained are empirically corrected for changes in the order parameter. For the pure substances the mesophases were identified by optical microscopy, and the phase transition temperatures by differential scanning calorimetry (DSC).

cyclohexane substructure and an aromatic ring with high yield and under very mild conditions.

3. Experimental

3.1. Preparation of the dithianylium salt $17^+ \cdot CF_3SO_3^-$

A suspension of 17.4 g (43 mmol) of the carboxylic acid **16** in toluene/isooctane (4:6) was treated at room temperature with 6.0 g (55 mmol) of 1,3-propanedithiol. The mixture was heated slowly to 60°C, and after dropwise addition of 8.0 g (53 mmol) of trifluoromethanesulfonic acid over a time span of 5 min, refluxed for 3 h under azeotropic removal of water. After cooling down to 85°C, 100 ml of dibutyl ether were added dropwise. Cooling down to 0°C under stirring precipitated the product which was filtrated-off, washed twice with 20 ml of ice-cold methyl *tert*-butyl ether and dried in vacuo. Yield: 20.8 g (84%) of $17^+ \cdot CF_3SO_3^-$ as yellowish crystals, which were used for the following reaction step without further purification.

3.2. Preparation of the liquid crystal 4

A suspension of 7.0 g (12 mmol) of $17^+ \cdot CF_3SO_3^-$ in 80 ml of CH_2Cl_2 was cooled to −70°C. Then, a mixture of 3 ml (22 mmol) of triethylamine and 2.22 g (15 mmol) of 3,4,5-trifluorophenol was added dropwise, followed after 1 h by 20 ml (124 mmol) of $NEt_3 \cdot 3HF$ and, after another 10 min, by 10.0 g (63 mmol) of bromine in 30 ml of CH_2Cl_2 over a time span of 30 min. After stirring for 90 min at −70°C, the mixture was allowed to warm up to −20°C and poured into a stirred ice-cold mixture of 350 ml 1N NaOH and 35 ml of saturated aqueous $NaHSO_3$. The organic phase was separated, and the aqueous phase was extracted twice with 80 ml of *n*-pentane. The combined organic phases were dried over Na_2SO_4 and evaporated to dryness. The semi-solid residue was dissolved in *n*-hexane and filtrated over a short silica gel column. A further purification was achieved by flash-chromatography (*n*-hexane; silica gel), followed by two recrystallizations from *n*-pentane. Yield: 2.0 g (33%) of **4** as colorless crystals. For phase transitions see Table 1; ^{1}H NMR (250 MHz, $CDCl_3$, 303 K): $\delta = 6.82$ (mc, 2H, ar-2,6-*H*), 2.15−1.77 (m, 12H), 1.48−1.12 (m, 12H), 0.90 (t, $J = 6.6$ Hz, 3H); ^{19}F NMR (235 MHz, $CDCl_3$, 303 K): $\delta = -164.8$ (mc, 1F, ar-4-*F*), −133.4 (mc, 2F, ar-3,5-*F*),

−117.1 (mc, 4F, C*F*$_2$CF$_2$), −79.3 (d, $J = 8.3$ Hz, 2F, C*F*$_2$O); MS (EI): m/z (%) = 504 [M^+] (55), 356 [$M^+ - F_3$PhOH] (100), 148 (72), 131 (18), 81 (21); HRMS (EI) for $C_{18}H_{29}F_9O$: calcd. 504.207470, exp. 504.208200.

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