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Nematic Liquid Crystals with a Tetrafluoroethylene Bridge in the Mesogenic Core Structure

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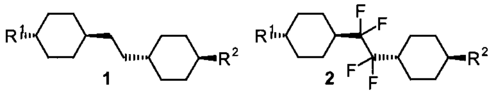
Abstract: A dramatic increase of the clearing temperatures of liquid crystals based on bis(cyclohexyl)ethane **1** by 50 to 70 K can be achieved by the perfluorination of the central ethylene link. Conformational analysis indicates that this effect is due to the increased rigidity of the mesogenic core structure and to the suppression of conformers with a bent shape. Materials based on bis(cylohexyl)tetrafluoroethane **2** might play a crucial role as materials for the next generation of active matrix LCDs with reduced power consumption.

During the past few years active matrix liquid crystal displays[1,2] (AM-LCD, or thin film transistor LCD, TFT-LCD) have rapidly developed toward the technological standard for flat panel displays. The widespread use of AM-LCDs in portable devices, such as notebook computers, PDAs (personal digital assistants), or video games, makes it desirable to reduce the power consumption of the display as far as possible, to extend the battery lifetime. The largest contributor to the power consumption of a typical AM-LCD is the backlight. Use of reflective displays without backlight can therefore cut the power consumption by more than 70%.[3] An additional reduction can be obtained by decreasing the operating voltage of the display driving circuitry to 3.3 or 2.5 V from currently 5 or 4 V. The latter option also allows a more compact device design and results in a significant reduction of production costs.

On the side of the liquid crystal materials, a reduction of the driving voltage requires a decrease of the threshold voltage of the electrooptical response, which can be most conveniently achieved by using a more polar material, i.e., by increasing the dielectric anisotropy ($\Delta\epsilon$) of the liquid crystal.[4] An additional requirement for displays based on a reflective twisted nematic (r-TN) mode is very low birefringence (Δn).[3]

Generally, polar liquid crystals become more sensitive toward ionic trace contaminations with increasing dielectric anisotropy ($\Delta\epsilon$).[5] This results in a reduced voltage holding ratio (VHR), which is manifesting itself as visible flicker and contrast loss of the display.[6] The extremely low birefringence ($\Delta n = 0.05-0.065$) required for reflective displays is creating an additional technological challenge: a common characteristic of nearly all currently known liquid crystals in this birefringence range is that they show no tendency to form the desired nematic mesophase but mostly smectic B (S_B) phases.[1]

Scheme 1. 1,2-Bis(cyclohexyl)ethane Derived Liquid Crystals (**1**) and Their 1,2-Bis(cyclohexyl)tetrafluoroethane Analogues (**2**)



Our approach to improve this situation was the systematic modification of liquid crystals based on 1,2-bis(cyclohexyl)ethane (**1**)[7] as a mesogenic core structure. Due to the lack of any multiple bonds contributing to the molecular polarizability,[8] this type of basic structure seemed a promising candidate for obtaining low birefringent materials with a significantly improved mesophase behavior. Assuming that one of the major structural determinants of the mesoscopic properties of **1** is the relatively flexible ethylene link between the two cyclohexane rings, we tried to increase the conformational rigidity of this bridge by perfluorination.[9] The resulting material **2** was expected to have at least a significantly higher clearing point than its

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(4) The dielectric anisotropy is defined as $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp}$, the birefringence as $\Delta n = n_{\|} - n_{\perp}$, where the suffix $\|$ stands for parallel and $\perp$ perpendicular to the nematic phase director, which can be approximated by the long molecular axis of a liquid crystal molecule. The correlation between $\Delta\epsilon$, the dipole moment μ, and the angle β between the molecular dipole and the director is the following: $\Delta\epsilon \sim \Delta\alpha - F(\mu^2/2kT)(1 - 3\cos^2\beta)S$; $\Delta\alpha$ is the anisotropy of the polarizability, S the order parameter: (a) Maier, W.; Meier, G. *Z. Naturforsch.* **1961**, *16a*, 262−267. (b) Demus, D.; Pelzl, G. *Z. Chem.* **1981**, *21*, 1−9. (c) Hirschmann, H.; Reiffenrath, V. Applications: TN, STN Displays. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2A, pp 199−229.

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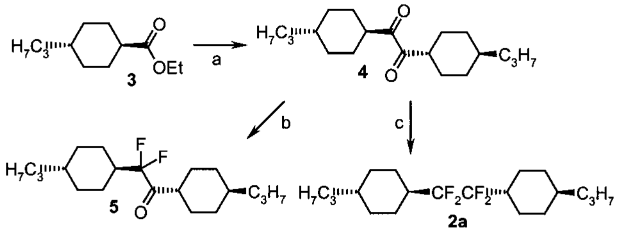
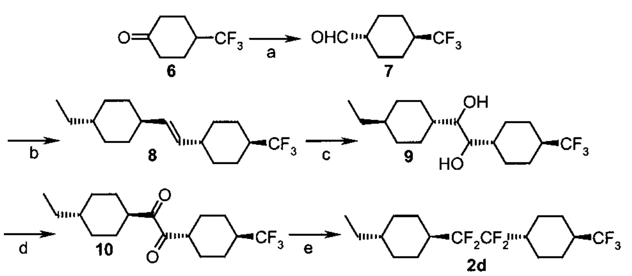
Scheme 2. Synthesis of Symmetrically Substituted Bis(cyclohexyl)tetrafluoroethane Derivatives[a]



[a] Conditions: (a) 1. Na suspension, Me_3SiCl, toluene; 40 °C; 2. NH_4NO_3, catalyst $Cu(OAc)_2$, HOAc; reflux, 5 h (37%). (b) DAST neat, catalyst ZnI_2; 60 °C (13%). (c) SF_4, catalyst HF, CH_2Cl_2; $-196 \rightarrow 70$ °C, 2 d (16%).

Scheme 3. Model Synthesis of Unsymmetrically Substituted Bis(cyclohexyl)tetrafluoroethane Derivatives[a]



[a] Conditions: (a) 1. $MeOCH_2PPh_3^+ Cl^-$, KO*t*Bu, THF; -10 °C → room temperature; 2. 98% HCOOH, toluene; room temperature, 18 h; 3. catalyst NaOH, MeOH; room temperature, 1 h (53%). (b) 1. (4-Propylcyclohexylmethyl)triphenylphosphonium bromide, LDA, THF; -10 °C → room temperature (54% crude product); 2. $MePhSO_2Na$, HCl, toluene; reflux, 16 h (88%). (c) *N*-Methylmorpholine-*N*-oxide, catalyst OsO_4, H_2O, dioxane; reflux, 18 h (65%). (d) 10 equiv of DMSO, 3 equiv of $(CF_3CO)_2O$, THF, CH_2Cl_2, NEt_3; $-60 \rightarrow 5$ °C, 18 h (75%). (e) SF_4, catalyst HF, CH_2Cl_2; -196 ° → 120 °C, 48 h (17%).

analogue **1**. In addition, the higher lipophilicity induced by the fluorination should reduce the ability of these materials to solvate ionic impurities.[5] The synthesis of the structurally simple, symmetrically substituted derivatives of **1** started with an acyloin condensation of the corresponding ethyl 4-alkylcyclohexylcarboxylates, followed by oxidation of the acyloin to the α-diketone.[10] Since it was not possible to fully convert the α-diketone to the tetrafluoroethylene group by use of diethylaminosulfurtrifluoride (DAST), the more reactive fluorination reagent sulfurtetrafluoride had to be used. Since the acyloin condensation only yields symmetric derivatives of **2**, a more generally applicable method was developed (Scheme 3): The *E*-vinylene linked bicyclohexane derivatives were subjected to a Sharpless dihydroxylation[11] and subsequently oxidized under Swern conditions,[12] furnishing the α-diketone intermediate. Unexpectedly, it was found that the dihydroxylation only proceeds from the *E*-olefin while the *Z*-olefin is completely unreactive under the same conditions. The fluorinated compounds were obtained by reaction of the α-diketone with SF_4[13] in reasonable yields.

For a comparative full evaluation of this novel class of materials, aliphatic three-ring materials (**11**) and some examples of aryl-substituted liquid crystals with positive (**13**, **15**, **17**) and with negative dielectric anisotropy (**18**) were synthesized by similar methods as depicted in Scheme 3. The newly synthesized materials were fully characterized by ^1H and ^{19}F NMR, and by mass spectrometry. The purity was confirmed to be higher than 99.8% by GC and HPLC. The physical properties of the liquid crystals in comparison with some of their nonfluorinated analogues[1,14] are summarized in Table 1. For better comparability in the application oriented development of liquid crystal mixtures, the "virtual" clearing points ($T_{NI,extr}$), obtained by extrapolation from the standard host mixture ZLI-4792, are also listed in Table 1.[15]

Compared with their conventional ethylene-linked analogues, the most striking difference of the new materials is the dramatically increased real and "virtual"[15] clearing temperatures, and for the purely aliphatic systems their improved tendency to form nematic mesophases (e.g. **1a** → **2a**). The increase of the virtual clearing temperatures compared to that of the ethylene-linked analogues ranges from 50 to 70 K. Remarkably, in contrast to our earlier attempts to increase the clearing point of highly fluorinated liquid crystals by axial fluorination of the cyclohexane moiety,[16] the fluorination of the central ethylene link leads only to an insignificant increase of the rotational viscosity (γ_1). Less favorably, the fluorination also induces a tendency to form smectic phases for the aryl-substituted liquid crystals **13**, **15**, **17**, and **18**. With the single exception of the pair **12** → **13** the birefringence (Δn) of the materials is slightly decreased. The dielectric anisotropy ($\Delta\epsilon$) is essentially not affected.

Especially the purely aliphatic, very low birefringent substance classes **2** and **11** are interesting for application in reflective TFT displays, due to their favorable combination of nematogenic mesophase behavior (with the exception of **2d**), high clearing points, and low rotational viscosity (γ_1). Materials such as **13**, **15**, **17**, or **18** might be useful in dielectrically positive (**13**, **15**, **17**) or negative (**18**) liquid crystal mixtures leading to reduced threshold voltage and strongly improved clearing point, without sacrificing switching time.

A comparative systematic conformational analysis on the model systems 1,2-bis(*trans*-4-methylcyclohexyl)tetrafluoroethane (**19**) and 1,2-bis(*trans*-4-methylcyclohexyl)ethane (**20**) indicates that the unexpected extent of improvement of the application relevant parameters can be attributed to the increased rigidity of mesogenic core. Using the SPARTAN program[17] and the MMFF94 force field,[18] 9 conformers of **19** and 14 conformers of **20** were found within 5 kcal·mol^{-1}. The enthalpies were then recomputed by single point calculations using density functional theory with the functional B3LYP[19]

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(15) The phase transition temperatures are given in °C, the γ_1 values in mPa·s. C = crystalline, S_X = smectic X, N = nematic, I = isotropic. Usually, the "virtual" parameters $T_{NI,extr}$, $\Delta\epsilon$, 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, $\Delta\epsilon = 5.3$, $\Delta n = 0.0964$). The extrapolated values are corrected empirically for differences in the order parameter. In some marked cases the following mixtures were used for extrapolation: ZLI-2857 ($T_{NI} = 82.3$ °C, $\Delta\epsilon = -1.4$, $\Delta n = 0.0776$) and ZLI-1132 ($T_{NI} = 71.0$ °C, $\Delta\epsilon = 12.8$, $\Delta n = 0.1406$). For the pure substances the mesophases were identified by optical microscopy, and the phase transition temperatures by differential scanning calorimetry (DSC).

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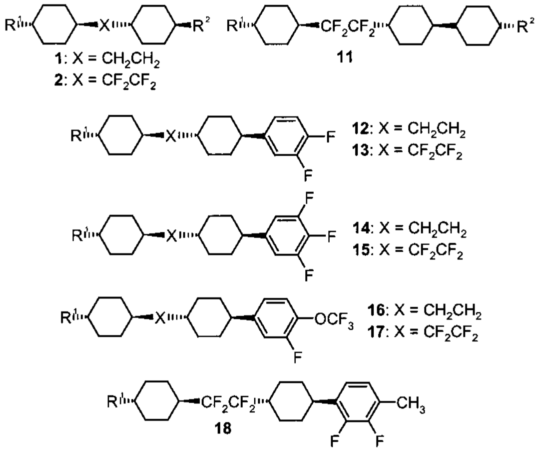
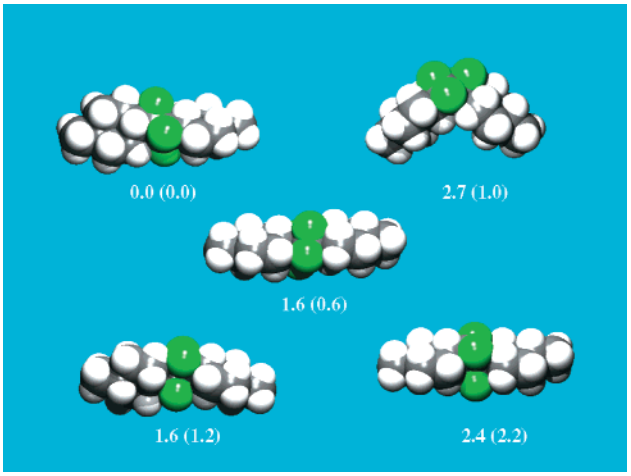
Table 1. Overview of the Physical Properties[15] of the Newly Synthesized 1,2-Bis(cyclohexyl)tetrafluorethane Derivatives in Comparison to Some of Their Nonfluorinated Analogues or, as for the Pair **1c**/**2d**, Homologues[a]



no.	R^1	R^2	mesophases	$T_{NI,extr}$	$\Delta\epsilon$	Δn	γ_1
1a	C_3H_7	C_3H_7	C 36 $S_?$ 26 S_B 73 I	55[a]			
1b	C_5H_{11}	C_5H_{11}	C 44 S_B 108 I	78.8	0.5	0.048	134
1c	C_3H_7	CF_3	C ? S_B 41 I	−39.1	6.1	0.058	
2a	C_3H_7	C_3H_7	C 28 S_B 93 N 126.5 I	122.3		0.044	68
2b	C_5H_{11}	C_5H_{11}	C 33 S_B 138 N 139.8 I	140.7	0.1	0.041	138
2c	C_5H_{11}	C_3H_7	C 43 S_B 115 N 136.1 I	134.2	0.8	0.055	
2d	C_2H_5	CF_3	C 52 S_B 116 I	3.9	6.2	0.054	110
11a	C_5H_{11}	C_3H_7	C 29 S_B 270 I	273.5	0.7	0.052	
11b	C_5H_{11}	C_5H_{11}	C −5 S_B 283 I	277.4	0.4	0.044	
12	C_3H_7		C 39 N 104.3 I	105.7	5.5	0.067	247
13	C_3H_7		C 95 S_B 121 N 178.1 I	150.0	5.4	0.079	267
14	C_3H_7		C 45 N 81.7 I	67.7	9.4	0.076	
15	C_3H_7		C 70 S_G 95 S_B 102 N 168 I	118.1	9.0	0.060	
16	C_3H_7		? $S_?$ 38 N 107.0 I	93.8	7.7	0.084	
17	C_3H_7		C 35 S_B 154 N 189.1 I	145.2	7.7	0.074	
18	C_3H_7		C 107 S_B 123 N 193.5 I	175.4	−2.9[b]	0.086	418

[a] Extrapolated from the Merck mixture ZLI-1132. [b] Extrapolated from ZLI-2857.

Scheme 4. The Five Lowest Energy Conformers of 1,2-Bis(*trans*-4-methylcyclohexyl)tetrafluoroethane (**19**)[a]



[a] The relative energies for the corresponding conformers of 1,2-bis(*trans*-4-methylcyclohexyl)ethane (**20**) are in parentheses [kcal·mol^{-1} at B3LYP/6-31G*//MMFF94].

and the 6-31G* basis set as implemented in the GAUSSIAN98 program.[20] The five lowest conformers for **19** are shown in Scheme 4. The lowest conformer of **20** with a bent shape is only 1.0 kcal·mol^{-1} higher than the global minimum whereas for **19** the corresponding conformer is at 2.7 kcal·mol^{-1}, and should therefore be only marginally represented in the conformer equilibrium. Preliminary calculations of the pair **14**/**15** (R = CH_3) indicate similar behavior. Therefore, use of the model systems **19** and **20** seems to be appropriate to give a representative description of the substance class as a whole. All deviations from an elongated, rodlike shape of the mesogenic core structure can be expected to degrade the phase behavior of its liquid crystalline derivatives.

The 1,2-bis(cyclohexyl)tetrafluoroethane derived liquid crystals are a new class of liquid crystals, which exhibit clearly superior properties with regard to application in AM-LCD. Compared to ethylene-linked analogues, the new materials show a dramatic increase of the clearing temperatures by 50−70 K without any significant concomitant increase of the rotational viscosity (γ_1). In purely cycloaliphatic systems an improved tendency to form a nematic mesophase was found. Conformational analysis indicates that these surprisingly pronounced effects are due to the increased rigidity of the fluorinated ethylene link and to the suppression of unfavorably bent conformers. The combination of these properties and their very low birefringence might place this type of liquid crystal at a focal point in the development of the next generation of full-

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color energy saving AM-LCDs for battery-powered devices, such as mobile phones with video-capability, sub-notebook PCs, and video games.

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Supporting Information Available: Exemplaric synthetic procedures and analytical data for **9**, **10**, and **2d** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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