LETTER

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1,1,6,7-Tetrafluoroindanes: improved liquid crystals for LCD-TV application†

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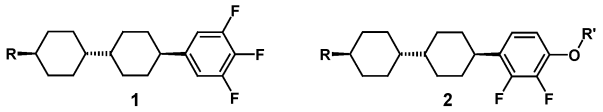
Received (in Durham, UK) 17th September 2004, Accepted 12th November 2004
First published as an Advance Article on the web 8th December 2004

New materials based on the 1,1,6,7-tetrafluoroindane skeleton were synthesized *via ortho*-metallation and intramolecular Heck cyclization followed by an oxidative fluorination procedure. The materials offer improved properties over liquid crystals currently employed in flat panel LCD-TVs.

A fast-growing flat panel display industry constantly requires improved materials for the manufacture of high resolution Active Matrix Liquid Crystal Displays (AM-LCDs), especially for flat panel large size TV applications. Research in the "device chemicals" area focuses in particular on fluorinated liquid crystals, which combine the necessary polarity with chemical stability and low polarizability.[1]

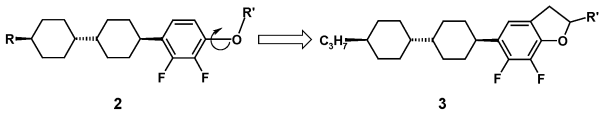
The presence of a permanent dipole moment is a prerequisite for the nematic liquid crystal being moved (switched) in an electric field. There are two basic types of LCs, which either have the dipole moment oriented parallel or perpendicular to the long molecular axis, examples being **1** and **2**, respectively:



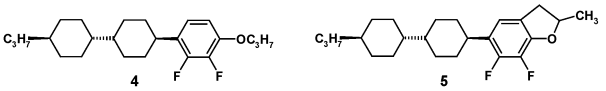
Compounds of type **2** (R = *n*-alkyl) have become popular in the mid 1990s when the so-called Multi-Domain Vertical Alignment technology (MVA)[2] was introduced, which is now widely employed in desktop computer monitors. In the MVA mode, the molecules are oriented perpendicular to the glass plates in the off-state (dark) and are switched to a parallel orientation when the electric field is applied (bright). This mode offers intrinsically better contrast and faster switching than the conventional TN mode (where compounds of type **1** are used), and therefore is the technology of choice for television. LCD-TV sets with sizes of 37 inches and larger (screen diagonal) are now commercially available. For the two major technologies, "Advanced Super View" (ASV)[3] and "Patterned Vertical Alignment" (PVA)[4] liquid crystals of type **2** are required as well. Liquid crystals for display applications have to fulfil a complicated interdependent set of properties.[1] First of all, there must be a broad nematic phase range from typically −30 °C to +80 °C. The absolute value for the dielectric anisotropy $\Delta\varepsilon$ should be large to decrease the operating voltage towards lower power consumption. The rotational viscosity γ_1 should be as low as possible to allow fast switching, and the birefringence Δn has to be adjusted to fit the precise display configuration, in particular the cell gap. In addition, the elastic constants of the liquid crystal also influence the operating voltage. A suitable set of properties cannot be achieved with a single material, instead a mixture of up to 30 compounds has to be optimized to fulfil the LCD manufacturers' request.

In the molecular design of new liquid crystals electrooptical properties can now be predicted quite precisely based on molecular modelling,[1,5] and there are some qualitative empirical structure–property relationships regarding nematogenicity and viscosity. Nevertheless, full evaluation of a new structure's value is still only possible after synthesis, especially because this evaluation has to be carried out in application-relevant LC mixtures.

In the past years many attempts have been made to improve the properties of nematic liquid crystals based on the 2,3-difluorophenyl moiety present in **2**.[6–10] In addition to the fluorine atoms, polarity is provided by the alkoxy group. However, because of nearly free rotation around the carbon–oxygen bond, the average dipole moment and hence the absolute dielectric anisotropy in **2** are reduced. A straightforward approach is to fix the side chain to the aromatic ring leading to benzofurans or related dihydrobenzofurans **3**.



After materials of structure **3** were synthesized,[11,12] the expected increase in polarity was observed but other properties deteriorated:



K 63 SmB 94 N 169.6 I
$\Delta\varepsilon$ = -5.4
Δn = 0.0837
γ_1 = 304
Clp = 169.7

K 112 (N 105.1) I
$\Delta\varepsilon$ = -6.7
Δn = 0.0739
γ_1 = 1254
Clp = 91.5

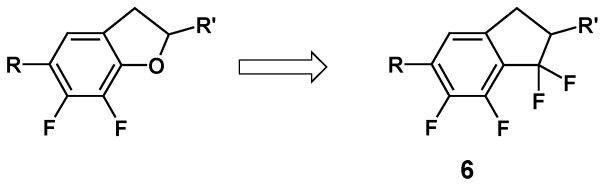
Not only is the rotational viscosity γ_1 increased dramatically, the phase behavior is also poorer: **4** exhibits a broad nematic phase and a smaller smectic phase, **5** is only monotropically nematic with a temperature range of merely 7 K, and the extrapolated clearing point (Clp) is even 80 K lower.

Keeping the idea of fixing the most polar conformation but replacing the oxygen by a difluoromethylene group led to new

† Electronic supplementary information (ESI) available: experimental details for the synthesis of fluorinated indanes. See http://www.rsc.org/suppdata/nj/b4/b414312d/

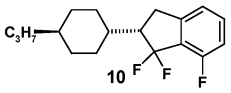
DOI: 10.1039/b414312d

LCs based on the 1,1,6,7-tetrafluorindane skeleton **6**:

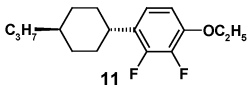


The synthesis of novel materials of this type is shown in Scheme 1. The key steps are a directed *ortho*-metallation[13] and functionalization with an appropriate α,β-unsaturated aldehyde followed by an intramolecular Heck cyclization.[14] This approach offers complete control with regard to regiochemistry. Unfortunately, it was not possible to convert the intermediate 2-indanones **7** directly to the target molecules by using diethylaminosulfur trifluoride (DAST) or related reagents,[15] although fluorination with sulfur tetrafluoride remains to be tested. Furthermore, the indirect approach[16] was complicated by partial bromination in the oxidative fluorination procedure. The mixture of **8** and **9** was directly used for the final synthetic steps, which involve elimination of hydrogen bromide and finally catalytic hydrogenation.

Trifluoroindanes (L = H) already offer interesting properties:



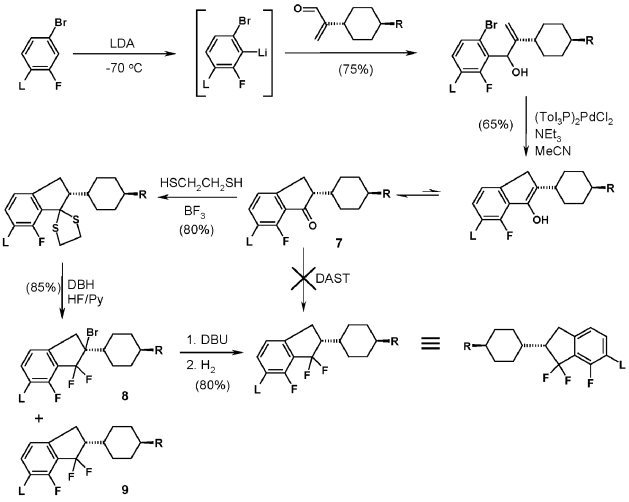
K 99 I
Δε = -7.1
Δn = 0.0860
γ_1 = 136
Clp = 18.1



K 60 I
Δε = -5.4
Δn = 0.1060
γ_1 = 112
Clp = -15.1

The material does not exhibit any mesophase in the pure state but the "virtual" clearing point of **10** measured in an application relevant LC mixture[12] is more than 30 K higher than that of the reference compound **11**. Although indane **10** does not contain any additional polar oxygen containing substituent, the dielectric anisotropy Δε is increased compared to **11**.

The introduction of a fourth fluorine atom leads to even further improvement: not only is the polarity in **12** increased again but also the virtual clearing point. The small increase in γ_1 is tolerable.



Scheme 1 Synthetic route to tri- and tetrafluoroindanes (L = H, F). LDA = lithium diisopropylamide; R = *n*-alkyl; DBH = 1,3-dibromo-5,5-dimethylhydantoin; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DAST = diethylaminosulfur trifluoride.

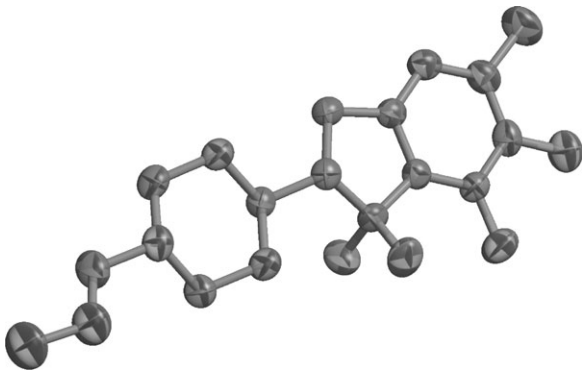
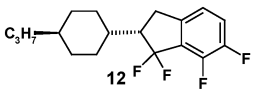
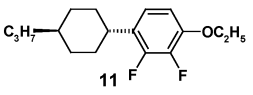


Fig. 1 X-Ray crystal structure of **13** (ORTEP).



K 85 I
Δε = -8.6
Δn = 0.0852
γ_1 = 142
Clp = 49.4



K 60 I
Δε = -5.4
Δn = 0.1060
γ_1 = 112
Clp = -15.1

Compound **12** can easily be functionalized *via ortho*-metallation and was alkylated with methyl iodide. The resulting product **13** exhibits even higher polarity although the concomitant increase in γ_1 now is too high to be useful.

K 90 I
Δε = -9.9
Δn = 0.0840
γ_1 = 221
Clp = 48.7

The X-ray crystal structure of **13** (Fig. 1) shows no unusual features.[17] A B3LYP/6-31G(d)//B3LYP/6-31G(d) calculation yields a very similar geometry but predicts a value of only −6.2 for Δε. The reason for this discrepancy is not yet clear and further work is necessary.

In summary, we have described the synthesis and physical properties of a new class of materials for nematic liquid crystal mixtures which offer high absolute values for the dielectric anisotropies, high clearing temperatures and low rotational viscosities.

Acknowledgements

This work was supported by the Bundesministerium für Bildung und Forschung (FKZ 01 BM 904). We thank Dr Melanie Klasen-Memmer and Volker Reiffenrath for experimental support and discussions, and Ingrid Svoboda (Materials Science, Technical University of Darmstadt) for the X-ray crystal structure determination.

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12 The phase transition temperatures are given in °C, the γ_1 values in mPa s. K = crystalline, Sx = smectic X, N = nematic, I = isotropic. Clp, 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, $\Delta\varepsilon$ = 5.3, Δn = 0.0964). The extrapolated values are corrected empirically for differences in the order parameter. $\Delta\varepsilon$ was extrapolated from ZLI-2857 (T_{NI} = 82.3 °C, $\Delta\varepsilon$ = −1.4, Δn = 0.0776). 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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17 Crystal data for **13**: $P\bar{1}$, a = 8.961(1) Å, b = 9.253(1) Å, c = 11.405(2) Å, α = 109.38(1)°, β = 103.19(1)°, γ = 96.75(1)°, V = 849.1(2) Å^3, Z = 2, T = 299(2) K. 7986 reflections were measured ($2\theta_{max}$ = 52.74°). 3434 unique reflections (R_{int} = 0.0306). Full matrix least squares refinement with 282 parameters converged to $R1$ = 0.0550 and $wR2$ = 0.1181. CCDC 229584. See http://www.rsc.org/suppdata/nj/b4/b414312d/ for crystallographic data in .cif or other electronic format.