Recent Liquid Crystal Material Development for VA-TFT

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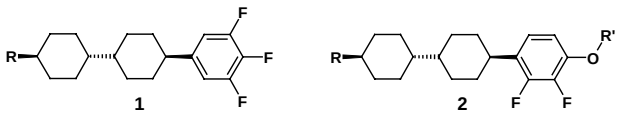
Abstract
A large size flat panel LCD-TV must fulfill different requirements than a desktop LCD-monitor: The contrast must be much larger, the viewing angle should be as wide as possible and the switching times must be shorter to allow moving pictures to be displayed naturally. The "Vertically Aligned" technology is most promising to realize such a product. LC-material development for this technology began at Merck about 10 years ago. New materials based on the 1,1,6,7-tetrafluoroindane skeleton were recently 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:

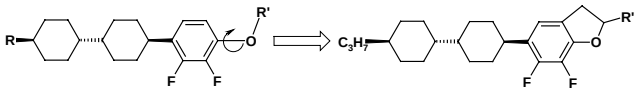


Compounds of type **2** (R=n-alkyl) have become popular in the mid 1990s when the so-called Multi-Domain Vertical Alignment technology (MVA)[2] was introduced, which is now widely employed in desktop computer monitors. In the MVA-mode, the molecules are oriented perpendicular to the glass plates in the 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 inch 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 fulfill a complicated interdependent set of properties.[1] First of all, there must be a broad nematic phase range from typically –30 ^{o}C to +80 ^{o}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 fulfill the LCD manufactures' request.

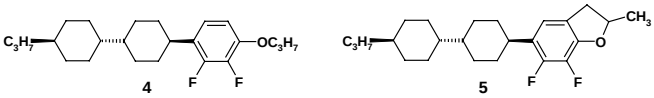
In the molecular design of new liquid crystals electrooptical properties can now be predicted quite precisely based on molecular modeling,[1,5] and there are some qualitative empirical structure property relationships regarding nematogenicity and viscosity. Nevertheless, full evaluation of a new structure's 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, caused by nearly free rotation around the carbon-oxygen bond the average dipole moment and hence the absolute dielectric anisotropy in **2** is reduced. A straightforward approach is to fix the side chain to the aromatic ring leading to benzofurans or related dihydrobenzofurans **3**.



2 3

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



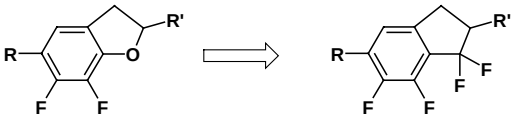
4 5

K 63 SmB 94 N 169.6 I
Δε = -5.4
Δn = 0.0837
γ_1 = 304
Clp = 169.7

K 112 (N 105.1) I
Δε = -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 gem-difluoro group led to new LCs based on the 1,1,6,7-tetrafluorindane skeleton **6**:



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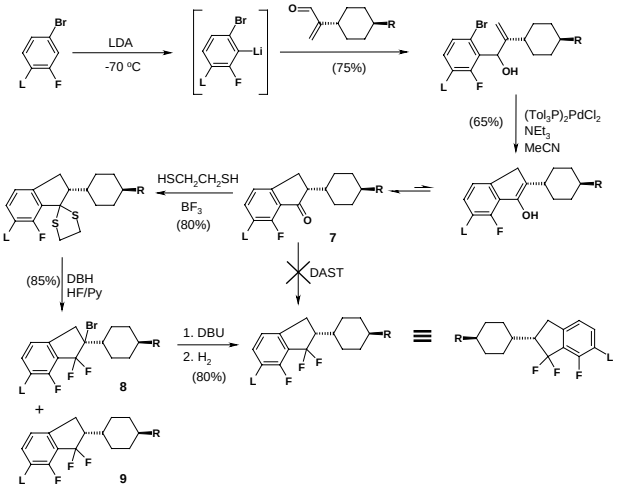
The synthesis of novel materials of this type is shown in Scheme 1. The key steps are a directed ortho-metallation[13] and functionalization with an appropriate α,β-unsaturated aldehyde followed by an intramolecular Heck cyclization.[14] This approach offers complete control with regard to regiochemistry. Unfortunately, it was not possible to convert the intermediate 2-indanones **7** directly to the target molecules by using diethylaminosulfurtrifluoride (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 used for the final synthetic steps, which involve elimination of hydrogen bromide and finally catalytic hydrogenation.



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

Trifluoroindanes (L=H) already offer interesting properties:

10 11

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 new material **10** does not exhibit any mesophase in the pure state but the "virtual" clearing point 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.

12 11

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

12 can easily be functionalized via ortho-metallation and was alkylated with methyl iodide. The resulting product **13** exhibits even higher polarity although the

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

concomitant increase in γ_1 now is too high to be useful.

The X-ray crystal structure of **13** 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.

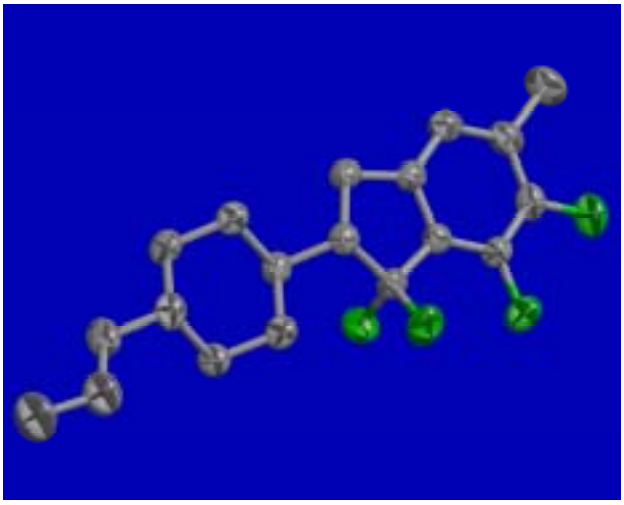


Figure 1. X-ray crystal structure of **13** (ORTEP)

Acknowledgements

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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 γ1 were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 (T_{NI} = 92.8°C, Δε = 5.3, Δn = 0.0964). The extrapolated values are corrected empirically for differences in the order parameter. Δε was extrapolated from ZLI-2857 (T_{NI} = 82.3°C, Δε = -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-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 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.