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Liquid Crystals with Pentafluorosulfuranyl as a Polar Terminal Group

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The pentafluorosulfuranyl group is one of the strongest electron-withdrawing groups which act purely by an inductive effect. The strong dipole moment of its derivatives and its chemical stability make it highly attractive as a terminal group for polar nematic liquid crystals which are used in active matrix displays. A method for the prediction of the electrooptic parameters of pentafluorosulfuranyl based liquid crystals is presented.

Keywords: liquid crystals; pentafluorosulfuranyl function; molecular modeling; active matrix display

1. INTRODUCTION

One possible way to achieve a reduced power consumption of active matrix liquid crystal displays (AM-LCD) is the use of a lower driving voltage. On the materials side this results in a demand for liquid crystals with very high dielectric anisotropy ($\Delta\varepsilon$) combined with an excellent voltage holding ratio. Conventional materials which derive their polarity e.g. from a terminal trifluoromethyl group often suffer from prohibitively low clearing temperatures. On the other hand, the cyano group which induces excellent mesogenic and dielectric properties cannot be used for AM-LCD because of the insufficient voltage holding

ratio of its derivatives. Therefore, the potential of some new liquid crystals based on the pentafluorosulfuranyl function was explored.[1]

2. SYNTHESIS AND PHYSICAL PROPERTIES

Because of the inconvenient and expensive synthesis of pentafluorosulfuranyl derivatives,[2] which is based on a two-step oxidation of aromatic disulfides with AgF_2, there have been only few examples so far for more complex organic molecules derived from this structure. Recently, a new synthesis based on direct fluorination was introduced, and subsequently some pentafluorosulfuranyl aryl derivatives became commercially available in bulk quantities.[3] Now it was possible to start a systematic survey and evaluation of liquid crystals based on this structure element. Starting from 4-nitro-1-pentafluorosulfuranyl benzene (**1**) a variety of liquid crystals with different mesogenic core structures was synthesized.[4]

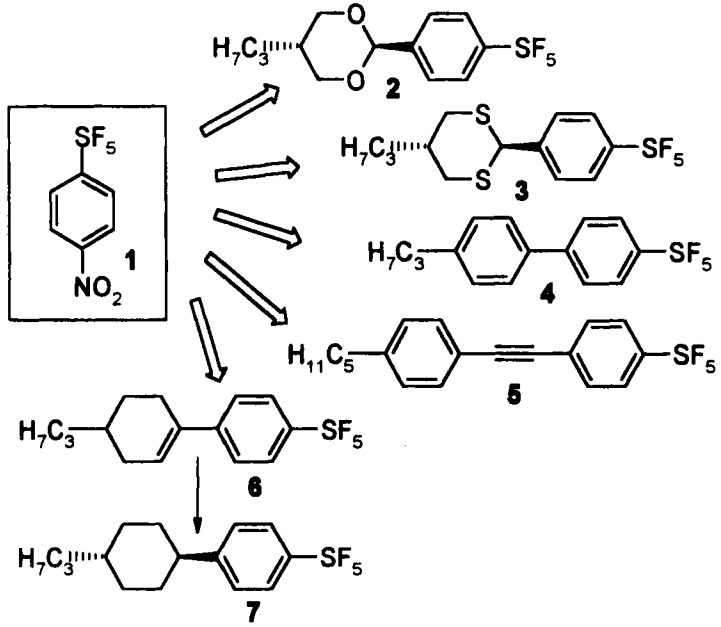


FIGURE 1 General synthetic pathway for the pentafluorosulfuranyl substituted liquid crystals **2-7**.

The comparison of „conventional" fluorinated liquid crystals with their pentafluorosulfuranyl substituted analogues shows some outstanding properties, such as a highly desirable combination of strong dielectric anisotropy ($\Delta\varepsilon$) with reasonably high extrapolated („virtual") clearing temperatures ($T_{NI,extr}$).

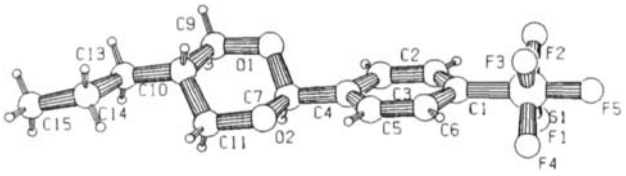
No.	(Meso)phases	$T_{NI,extr}$	$\Delta\varepsilon$	Δn
2	C 69 I	-79.9	20.3	0.091
3	C 93 I	-66.4	22.3	0.096
4	C 68 I	-84.5	15.8	0.161
5	C 68 I	-16.8	16.4	0.224
6	C 29 I	-84.9	14.2	0.124
7	C 11 I	-96.8	12.0	0.087

TABLE 1 Physical properties of pentafluorosulfuranyl based two-ring materials. Phase transitions and „virtual" clearing points ($T_{NI,extr}$) are cited in °C. $T_{NI,extr}$, $\Delta\varepsilon$ and Δn were extrapolated from a 10% w/w solution in the Merck mixture ZLI-4792.

3. PREDICTION OF THE ELECTROOPTIC PROPERTIES OF PENTAFLUOROSULFURANYL BASED LIQUID CRYSTALS

The strong dipole moment of pentafluorosulfuranyl substituted benzene, which is even exceeding the dipole of trifluoromethyl benzene is – superficially seen – a paradox, because the four local equatorial S-F dipoles are cancelling each other. Thus, the whole molecular dipole should be due mostly to only one axial S-F bond.

The X-ray structure analysis of one of the liquid crystals (**2**) as well as molecular modeling on different levels of theory helped to elucidate the reason for the unexpectedly large dipole moment of the hypervalent sulfur species: The dielectric anisotropy ($\Delta\varepsilon$) depends critically on the angle α between the aromatic carbon (C1), sulfur (S1) and the equatorial fluorine atoms (F1-F4). The strong dipole is therefore caused by the increased polarization of the axial sulfur-fluorine bond due to its hypervalent character, and by an additional dipole component in the direction of the molecular long axis by a slight „forward" tilt (*ca.* 2.5°) of the equatorial fluorine atoms out of the equatorial plain.



Parameter	Experimental	PM3//PM3	PM3//HF/6-31G*
C_{ar}-S [Å]	1.8066(18)	1.833	-
S-F_{eq} [Å]^a	1.5827(13)	1.590	-
S-F_{ax} [Å]	1.5791(12)	1.609	-
C_{ar}-S-F_{eq} [°]^a	92.31(7)	95.6	-
μ [Debye]	-	7.07	5.58
$\Delta\varepsilon$	20.3	35.9	21.3
Δn	0.091	0.091	0.088

TABLE 2 Experimental and calculated parameters for **2**. [a]Average over all four equatorial fluorine atoms.

A model study on pentafluorosulfuranyl benzene indicated that this deformation requires only a minimal amount of energy for moderate deformations (*ca.* 0.3 kcal·mol^{-1}·°$^{-1}$) while even a small deformation results in a large increase of the molecular dipole moment (*ca.* 0.4 D·°$^{-1}$).

Comparison between the experimental data (X-ray crystallography and extrapolated electrooptical properties) and calculated data show that the most reliable prediction[5,6] for liquid crystals based on hypervalent sulfur fluorides can be obtained by an *ab initio* (HF/6-31G*) structure optimization, followed by the calculation of the electrooptical data on a semiempirical (PM3) single point.

4. SUMMARY

Pentafluorosulfuranyl derivatives are so far the most polar class of liquid crystals which still can be used for active maxtrix displays. They are chemically inert, and they exhibit a favourable combination of high dielectric anisotropy and reasonably high extrapolated clearing points, compared to conventional fluorinated materials. A sequence of *ab initio* (HF/6-31G*) and semiempirical (PM3) methods allows a reliable

prediction of the electrooptical properties of liquid crystals based on hypervalent sulfur fluorides.

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