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NEW CHIRAL DOPANTS BASED ON THE 2-FLUORO-2-METHYLALKOXY TAIL FOR USE IN FERROELECTRIC LIQUID CRYSTAL MIXTURES

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Abstract A new class of FLC materials based on the 2-fluoro-2-methylalkoxy tail is reported. This new class of materials consistently shows an N* helical pitch opposite in sign to that of the polarization. These materials are compared to their 2-fluoroalkoxy analogs to explore the methyl group's effect on the N* pitch and polarization.

I. Introduction

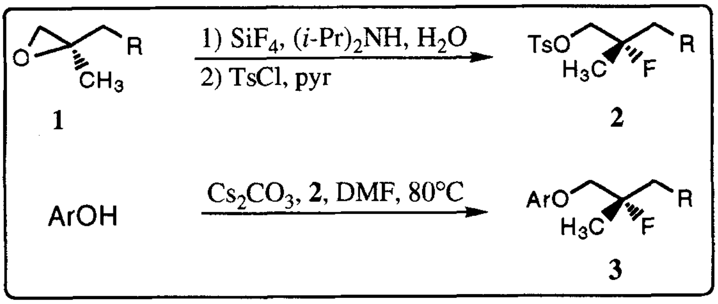
Ferroelectric smectic C* liquid crystals (FLCs) have been shown to exhibit high speed electrooptic response when used in surface stabilized FLC light valves. Formulating easily alignable FLC mixtures plays an important part in optimizing the operation of these devices. For optimal alignability, the FLC mixtures should have an I—N*—A—C* phase sequence with a long nematic helical pitch. In a process known as pitch compensation, a material with a negative N* pitch can counteract a material with a positive N* pitch, resulting in a mixture with almost infinitely long pitch. Since typical materials show the same sign of N* pitch and spontaneous polarization (P_S), pitch compensation generally reduces a mixture's polarization, thus reducing its switching speed. Materials that possess oppositely signed N* pitch and P_S, and that are thus able to pitch compensate while also increasing P_S, are both unusual and useful.

The new class of LCs reported in this paper possess this desirable property of oppositely signed pitch and polarization. They also have low viscosity and high polarization, necessary for dopants to be used in mixtures for FLC displays.

II. Results and discussion

a. Synthesis of 2-fluoro-2-methylalkoxy LCs

Synthesis of the fluoromethyl tosylate **2**, shown in scheme 1, is accomplished in a straightforward manner starting from the commercially available[1] 2-(S)-methyl-1,2-epoxyalkane **1**. The epoxide is opened with silicon tetrafluoride in aqueous diisopropylamine[2], resulting in fluorination at the more substituted carbon. Tosylation of the resulting alcohol affords methylfluoro tosylate **2**. This fairly hindered tosylate is coupled to various phenols using cesium carbonate in heated dimethylformamide, affording the product **3**, typically in 50-60% yield. All compounds were purified by flash chromatography followed by sequential recrystallizations from hexane and acetonitrile.



Scheme 1. Synthesis of 2-(S)-fluoro-2-methylalkoxy liquid crystals.

b. Examples of three-ring 2-(S)-fluoro-2-methylalkoxy dopants.

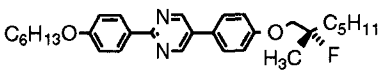
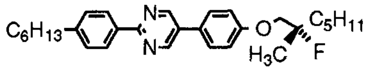
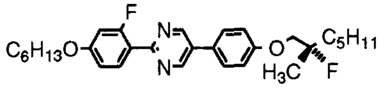
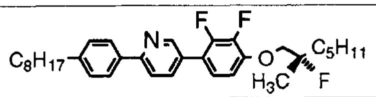
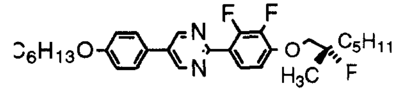
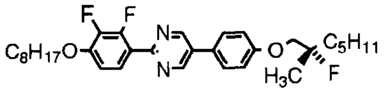
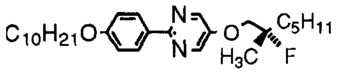
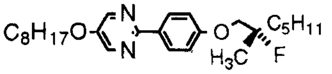
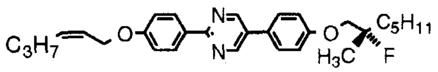
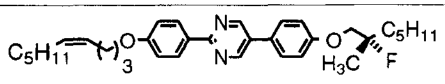
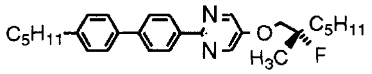
ID#	Structure	Mesomorphic properties
MDW607		$I \xrightarrow{144} C^* \xrightarrow{112} S_X \xrightleftharpoons[81]{67} X$
MDW624		$I \xrightarrow{128} C^* \xrightarrow{120} S_X \xrightleftharpoons[102]{75} X$
MDW628		$I \underset{\xleftarrow[107]{\qquad\qquad\qquad}}{\xrightarrow{99} C^* \xrightarrow{98}} X$
MDW652		$I \xleftrightarrow{79} A \xrightleftharpoons[68]{34} X$
MDW662		$I \xleftrightarrow{152} C^* \xleftrightarrow{102} S_X \xrightleftharpoons[94]{52} X$
MDW686		$I \underset{\xleftarrow[117]{\qquad\qquad\qquad}}{\xrightarrow{116} C^* \xrightarrow{106}} X$
MDW746		$I \xrightleftharpoons[93]{71} X$
MDW747		$I \xleftrightarrow{130} A \xleftrightarrow{126} C^* \xrightarrow{89} S_X \xrightarrow{87} X$
MDW756		$I \xleftrightarrow{158} A \xleftrightarrow{149} C^* \xrightarrow{80} X$
MDW759		$I \xleftrightarrow{107} A \xrightleftharpoons[78]{62} X$
MDW760		$I \underset{\xleftarrow[115]{\qquad\qquad\qquad}}{\xrightarrow{97} C^* \xrightarrow{95}} X$

Figure 1. 2-Fluoro-2-methylalkoxy liquid crystals.

Nearly all three-ring analogs showed broad C* phases and good miscibility with standard phenylpyrimidine hosts. Several of these compounds had an unidentified higher-order smectic phase underlying the C* phase. This underlying phase was optically indistinguishable from the C* phase, but could be observed in a DSC scan and by other physical properties. Fluorination of the core suppressed this higher ordered smectic phase. Replacing the achiral alkyl chain with an alkenyl chain also gave this desired result.

The two-ring 2-fluoro-2-methyl ethers gave surprising results. When doped into achiral hosts (or, if a C* phase was present, when examined in their pure form), they showed little or no polarization, whereas the three-ring materials with the same chiral tail showed polarizations of up to 300 nC/cm^2. In contrast, the 2-fluoroalkoxy tail, presented next, consistently showed moderate polarization when linked to both two and three-ring cores.

c. Examples of 2-(S)-fluoroalkoxy liquid crystals.

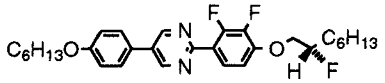
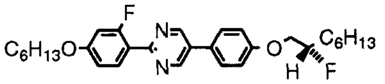
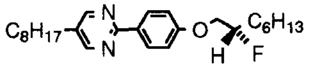
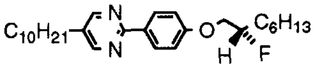
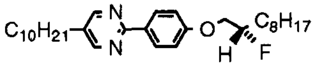
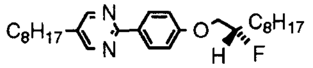
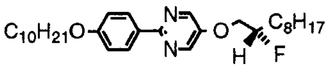
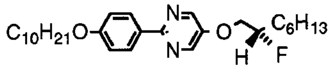
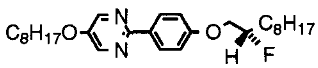
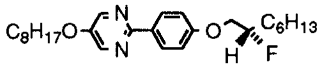
ID#	Structure	Mesomorphic properties
MDW786		$I \xrightarrow{182} A \xrightarrow{136} C^* \underset{94}{\overset{82}{\rightleftarrows}} S_X \underset{76}{\overset{57}{\rightleftarrows}} X$
MDW787		$I \xrightarrow{171} N^* \xrightarrow{162} C^* \overset{\xrightarrow{66} S_X \xrightarrow{61}}{\xleftarrow[85]{\qquad\qquad}} X$
MDW788		$I \underset{68}{\overset{57}{\rightleftarrows}} X$
MDW789		$I \xrightarrow{68} A \overset{\xrightarrow{54} C^* \xrightarrow{44}}{\xleftarrow[55]{\qquad\qquad}} X$
MDW792		$I \xrightarrow{70} A \xrightarrow{66} C^* \underset{64}{\overset{56}{\rightleftarrows}} X$
MDW793		$I \underset{74}{\overset{61}{\rightleftarrows}} X$
MDW794		$I \xrightarrow{99} C^* \underset{75}{\overset{57}{\rightleftarrows}} X$
MDW795		$I \xrightarrow{97} A \xrightarrow{88} C^* \underset{60}{\overset{48}{\rightleftarrows}} X$
MDW801		$I \xrightarrow{95} A \xrightarrow{78} C^* \underset{73}{\overset{54}{\rightleftarrows}} X$
MDW802		$I \xrightarrow{93} A \xrightarrow{74} C^* \underset{69}{\overset{48}{\rightleftarrows}} X$

Figure 2. 2-Fluoroalkoxy liquid crystals

To examine the effect that removing the 2-methyl group has FLC properties, a series of ten new 2-fluoroalkoxy analogs were synthesized. Most showed C* phases in the pure form and were miscible in the phenylpyrimidine host, making comparison with the 2-fluoro-2-methylalkoxy materials a straightforward task. Interestingly, core fluorination in this series does not suppress the higher-ordered phases, and none of the two-ring analogs showed higher order phases.

d. Pitch and polarization properties of 2-(S)-fluoro-2-methylalkoxy FLC dopants.

All dopants show a temperature-increasing effect on the A-C transition of the host (57°C) with the greatest improvement, 14°C, coming from MDW686, a core-difluorinated FLC. This material also shows the highest polarization of the 2-fluoro-2-methylalkoxy dopants.

All of the dopants show a negative polarization and a positive N* pitch. Even the two-ring derivatives, which do not show a measurable polarization, still show a positive N* pitch. Nearly all compounds (except MDW652) show a negative C* pitch.

Dopant	Phase Diagram	Ps	N* pitch	C* pitch
MDW607	I 80 N 75 A 67 C*	-6	**+13**	-8
MDW624	I 82 N 79 A 64 C*	-8	**+6**	-5
MDW628	I 82 N 75 A 68 C*	-6	**+8**	-5
MDW652	I 78 N 73 A 65 C*	-3	**+3**	+2
MDW662	I 79 N 66 A 53 C*	<0.5	**>+30**	-4
MDW686	I 80 N 75 A 71 C*	-9	**>+30**	-7
MDW746	I 74 N 64 A 32 C*	<0.5	**>+30**	—
MDW747	I 72 N 52 A <21 C*	<0.5	**>+30**	—
MDW756	I 79 N 74 A 62 C*	-6	**+23**	-9
MDW759	I 77 N 72 A 60 C*	-5	**+9**	-9
MDW760	I 77 N 68 A 62 C*	-6	**+4**	-2

Measurements on 10% mixture in a phenylpyrimidine host. N* pitch measured at $T_{N\text{-}A}$ = +1°C. C* pitch and P_s measured at 25°C.

Figure 3. N* and C* pitch of 2-fluoro-2-methylalkoxy LCs

MDW652 is the only compound that shows reversal of the C* pitch. This occurs when two fluorines are attached to the phenyl ring adjacent to the chiral tail, indicating that interaction between the core and the tail causes the pitch inversion. This interaction is quite complicated, as can be seen by comparing the pyridine (MDW652) with its pyrimidine analog (MDW662). The pyrimidine's C* pitch is not reversed, indicating that intra-ring geometry plays a significant role in the pitch's magnitude and sign. We have previously seen similar unusual pitch behavior in FLCs with fluorinated tails and varying degrees of core-fluorination[3].

The previously reported[4] 2-(S)-fluoro-2-methyl esters are analogs of the 2-methyl-2-fluoro ethers. Two such esters were investigated in this study. Interestingly, we found that the esters did not show the pitch inversion seen in the ethers. They instead showed moderate negative N* pitch (-8 to -11 μm in a 10% mixture) and moderate negative C* pitch (-7 to -13 μm pitch in a 10% mixture). These results were corroborated by studies done on commercial JEC[1] mixtures which contained fluoromethyl esters, and which also showed moderate negative N* and C* pitch. The esters have previously been shown to have moderate to high negative polarization.

e. Pitch and polarization properties of 2-(S)-fluoroalkoxy FLC dopants.

While the 2-fluoroalkoxy dopants have the same sign of polarization and C* pitch as their methylated cousins, their N* pitch is reversed making it the same sign as the P_S and the C* pitch. This behavior is more typical of liquid crystals. Thus, mixtures of fluoromethylalkoxy and fluoroalkoxy dopants can be self-pitch-compensated, giving the long N* helices needed for good alignment while retaining high polarization. The 2-fluoroalkoxy FLC dopants consistently showed moderate polarization regardless of the size and substitution of the core.

Dopant	Phase Diagram	Ps	N* pitch	C* pitch
MDW786	I 83 N 77 A 63 C*	-3	**>-30**	-8
MDW787	I 83 N 76 A 67 C*	-10	**-3**	-3
MDW788	I 72 N 68 A 50 C*	-9	**-7**	-5
MDW789	I 73 N 70 A 53 C*	-7	**-13**	-5
MDW792	I 73 N 70 A 52 C*	-8	**-7**	-2
MDW793	I 71 N 65 A 50 C*	-9	**-6**	-4
MDW794	I 75 N 72 A 60 C*	-5	**-3**	-6
MDW795	I 75 N 70 A 60 C*	-6	**-3**	-4
MDW801	I 76 N 72 A 57 C*	-5	**-8**	-7
MDW802	I 76 N 72 A 56 C*	-5	**-6**	-5

Measurements on 10% mixture in a phenylpyrimidine host. N* pitch measured at $T_{N\text{-}A}$ = +1°C. C* pitch and P_s measured at 25°C.

Figure 4. N* and C* pitch of 2-fluoroalkoxy LCs.

f. Polarization vs. Temperature of typical 2-fluoro-2-methylalkoxy LC

The following plot of polarization vs. temperature shows that the methylfluoro alkoxy dopants possess a moderately high P_S approaching 300 nC/cm^2. When cooled into the underlying more-ordered tilted smectic phase, the dopants exhibited a discontinuity in the P_S vs. temperature graph, leading to even higher P_S.

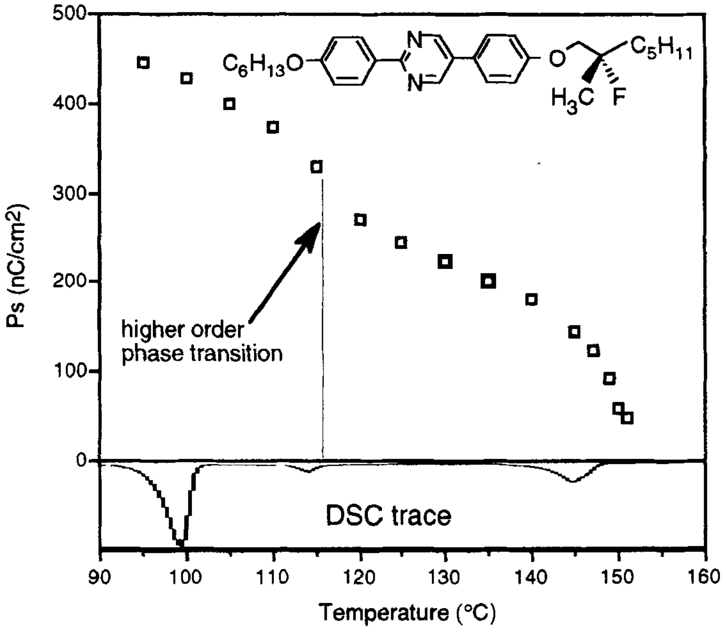


Figure 5. T vs. P_S and DSC of the 2-fluoro-2-methylalkoxy FLC MDW607.

III. Comparison of the 2-(S)-fluoro-2-methylalkoxy and 2-(S)-fluoroalkoxy dopants

1. All dopants with a 2-(S)-fluoro-2-methyl tail show negative P_S and **positive** nematic pitch. Most show a negative C* pitch.

2. All dopants with a 2-(S)-fluoroalkoxy tail (no methyl group at the 2-position) show **negative** N* pitch, negative C* pitch, and negative P_S.

3. Two-ring dopants with the 2-(S)-fluoro-2-methylalkoxy tail show no measurable polarization whereas the three-ring analogs show moderately high Ps in mixtures, and in the pure form show P_S values of nearly 300 nC/cm^2 in the C* phase.

4. Both the two and three-ring analogs in the 2-fluoroalkoxy system show moderately high Ps values.

5. Core fluorination adjacent to the 2-fluoro-2-methylalkoxy tail results in reversal of the C* pitch in the diphenylpyridine case (MDW652), but not in the diphenylpyrimidine case (MDW662). Also, in MDW662, P_S is almost completely suppressed by the core fluorination, indicating that opposing dipoles cancel the polarization.

IV. Conclusions

Methyl group substitution plays an important role in controlling the properties of the 2-fluoroalkoxy tail. When a methyl is added to the chiral center of this tail to form the 2-fluoro-2-methyl tail, it has minimal effect on the P_S. However, methylation can have a profound effect on the pitch properties of LCs. The pitch properties of mixtures are often manipulated to give long N* pitch (for better alignment) while retaining high polarization.

The N* pitch of the unmethylated material is opposite in sign from that of the methylated material. The two types of materials generally have the same sign of C* pitch. This strongly suggests that N* pitch and C* pitch are caused by different mechanisms. For instance, the N* pitch may be caused by molecular migration perpendicular to the molecule's long axis, thus making the molecule's side profile very important. The C* pitch, on the other hand, is an inter-layer phenomena, and is probably caused by molecular migration between the layers. Molecules would migrate almost perpendicular to the long molecular axis, thus making the molecule's end profile more significant.

In specific instances, core fluorination can reverse the C* pitch's sign as well. The mechanism for this reversal is not currently understood.

---

[1] Japan Energy Corporation, 3-17-35, Niizo-Minami Toda-shi, Saitama, 335

[2] Shimizu, M.; Yoshioka, K. *Tetrahedron Lett.* **29**, 4101-4104 (1988).

[3] Thurmes, W. N.; Wand, M. D.; Vohra, R. T.; More, K. M.; Walba, D. M. *Liquid Cryst.* **14**, 1061-1068 (1993).

[4] a) Shiratori, N.; Nishiyama, I.; Yoshizawa, A.; Hirai, T. *Jpn. J. Appl. Phys.* **29**, L2086 (1990). b) Shiratori, N.; Yoshizawa, A.; Nishiyama, I.; Fukumasa, M.; Yokoyama, A.; Hirai, T.; Yamane, M. *Mol. Cryst. Liq. Cryst.* **199**, 129 (1991). Hirai, T., Yoshizawa, A., Shiratori, N., Yokoyama, A., Sherman, C., Pagano-Stauffer, L., Vohra, R. and Wand, M. *Proc. SPIE* **1665**, 134-145 (1992).