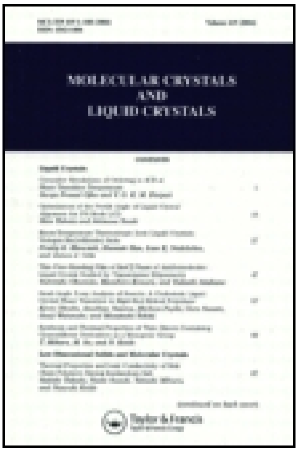

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Synthesis and Characterization of a Series of High Polarization Difluorinated Ferroelectric Liquid Crystal Dopants

W. N. Thurmes [a], M. D. Wand [a], R. T. Vohra [a] & D. M. Walba [b]
[a] Displaytech, Inc., 2200 Central Avenue, Boulder, Colorado, 80301
[b] Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0215

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Synthesis and Characterization of a Series of High Polarization Difluorinated Ferroelectric Liquid Crystal Dopants

W. N. THURMES,* M. D. WAND and R. T. VOHRA
Displaytech, Inc., 2200 Central Avenue, Boulder, Colorado 80301

and

D. M. WALBA
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0215

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Two series of difluorinated ferroelectric liquid crystal dopants were synthesized by our researchers. The first series, dubbed the difluoroalkoxy series, had spontaneous polarizations of up to 300 nC/cm^2. The second series, dubbed the difluorodialkoxy series, was more versatile and contained compounds with polarizations of over 400 nC/cm^2. The proton, fluorine, and carbon NMRs of these compounds were interpreted to determine the regio- and stereochemistry.

Keywords: F.L.C., difluorinated F.L.C., polarization, high polarization F.L.C.

Liquid crystal displays are nearly ubiquitous in our society. They are found in everything from wristwatches to automobiles. Virtually all of these displays are made using nematic liquid crystals (NLCs). Although NLC displays are well-established and extremely versatile, they have one major shortcoming: they are slow. The fastest NLC displays switch in approximately one millisecond. While switching them from the off to the on state can be accomplished much more quickly (about a microsecond), switching back to the off state necessarily involves molecular relaxation, which cannot be accelerated. They are therefore useless for any applications requiring rapid cycling of the on/off states. In such cases an alternative must be found, and one such alternative is the ferroelectric liquid crystal (FLC) display.

Ferroelectric liquid crystal displays are generally based on the surface stabilized FLC (SSFLC) light valve. When used in the SSFLC configuration, FLC cells can be actively switched in both the on/off and the off/on directions, leading to theoretical switching times of less than a microsecond and currently practical switching speeds of about 5 microseconds. When FLCs rather than NLCs are used in a display, the driving force behind the substitution is usually the increased speed with which FLCs switch. Most applications for FLCs rely on this increased switching speed and would benefit from even greater speed. Therefore, our goal is to develop materials with even faster switching speeds.

The switching speed of an SSFLC light valve is characterized by the electro-optic rise time τ_r, the time required for the valve to go from 10% to 90% of the optical response. This time is given by the equation

$$\tau_r \approx \frac{1.8\eta}{P^*E}, \tag{1}$$

where E is the applied voltage, η is the orientational viscosity, and P is the ferroelectric polarization density. As can be seen from the equation, τ_r is proportional to the spontaneous polarization and inversely proportional to the viscosity. Thus, to increase the switching speed, it is best to increase the polarization while concomitantly decreasing the orientational viscosity. Unfortunately, these two properties are related to one another—in many cases, an increase in polarization will lead to a comparable increase in viscosity, resulting in a stalemate. However, this is not always the case, or switching speeds would never change.

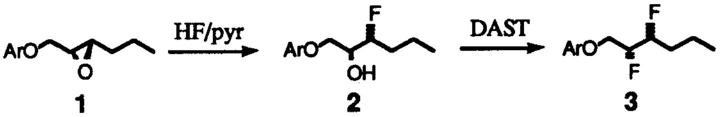
One method of decreasing the viscosity of a system is to use structural features which impart lower viscosities when incorporated into an FLC molecule. One such feature is the phenylpyrimidine core, which appears to be a relatively low-viscosity core. We believed that another such feature would be a polyfluorinated chiral tail. By combining these two, we anticipated a net result of liquid crystals with markedly reduced viscosity.

It was also necessary to increase the polarization of the material. Increasing polarization in a ferroelectric liquid crystal is generally accomplished by including heteroatoms such as fluorine, chlorine, or oxygen into at least one of the tails. The tail must contain one or more chiral centers, and the heteroatom-carbon dipole moments must in some way be linked to the chiral center(s). Although a carbon-fluorine bond has a smaller dipole moment than a carbon-chlorine bond, vicinal difluorides tend to prefer a gauche conformation,[1] in which case their dipoles are additive. Chlorine atoms are much larger than fluorine atoms, so a chlorine-chlorine gauche conformation is sterically disfavored, thereby increasing the energy of the gauche conformation. Accordingly, we decided to synthesize chiral tails containing optically active vicinal difluorides. Based upon simple conformational analysis arguments, in combination with our model[2] for the origin of P in FLCs, the syn difluorides of type **3** were chosen as the targets of this work.

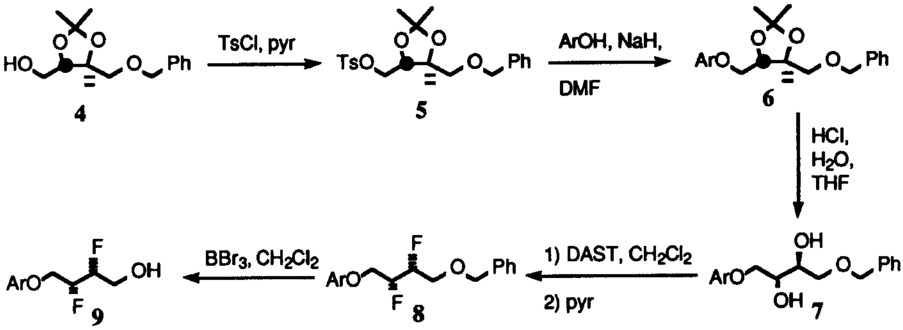
SYNTHESIS OF THE FLC DOPANTS

The chiral difluorides were also chosen due to their ease of synthesis. The Sharpless epoxidation method[3] gives chiral epoxides, which can be elaborated into a difluoride in the manner shown in Scheme I.

The first step in this transformation is treatment of an epoxide **1**[4] with pyridinium polyhydrofluoride, affording the fluorohydrin **2**. This acidolysis is known to proceed with complete stereospecificity and good regioselectivity. The regiochemistry of



SCHEME I Synthesis of the difluoroalkoxy systems.



SCHEME II Synthesis of the difluorodialkoxy system.

this compound was demonstrated using ^{13}C NMR, revealing the hydroxy and fluorine to be in the two and three positions, respectively. This regiochemistry is surprisingly specific, with >90% of the mixture having the fluorine in the three position.

Our method of determining the regiochemistry was rather interesting. In ^{13}C NMR, one generally broad-band decouples the entire proton spectrum, suppressing all proton-carbon coupling. Therefore, each carbon in the spectrum appears as a singlet. Fluorine, however, has a spin of $\frac{1}{2}$, and is not decoupled in the experiment. It can therefore couple with the carbons near it, leading to doublets for each of these signals. As it happens, the coupling constant magnitude in the doublet is proportional to that carbon's distance from the fluorine. By combining the observed splitting with the chemical shift expected for each carbon in the compound, the ^{13}C spectra of the compound can be easily analyzed to determine the regiochemistry.

The fluorohydrin is then converted into the difluoride by use of diethylaminosulfur trifluoride (DAST).[1,5] This fluorinating reagent gives predominantly inversion at the reactive stereocenter, leading to the syn difluoride **3**. We will refer to this tail as the difluoroalkoxy tail. It gives high polarization compounds, indicating syn stereochemistry, but the relative stereochemistry has not yet been proven. Efforts to unambiguously determine the stereochemistry are currently in progress.

The encouragingly high polarization of the difluoroalkoxy system led us to attempt the synthesis of another chiral tail which would simultaneously be more versatile and have higher polarization. Synthesis of this difluorodialkoxy tail, outlined in Scheme II, is more complicated than that of the difluoroalkoxy tail, but in the last step produces a much wider variety of derivatives.

The starting material, alcohol **4**, was prepared in a manner described by Kibayashi.[6] This compound then treated with toluenesulfonyl chloride in pyridine to give the tosylate **5**. The tosylate was in turn treated with a phenol in a dimethylformamide/sodium hydride suspension, giving the aryl ether **6**. Removal of the acetonide group with acid gave the vicinal diol **7** in good yield. Treatment of this diol with an excess of DAST at −70°C followed by treatment with pyridine at −30°C resulted in simultaneous difluorination, giving the vicinal difluoride **8**. The benzyl group is finally removed from the vicinal difluoride using boron tribromide, affording a good yield of difluoroalkoxyalcohol **9**. We shall refer to derivatives of this compound as difluorodialkoxy derivatives.

While most of the chemistry outlined above is relatively straightforward, the DAST reaction requires closer attention. This instance is the only time, to our knowledge, that DAST has been used to simultaneously difluorinate a vicinal diol. We found that an excess of DAST is imperative, for if too little is used the major product of the reaction is an alkenyl diether. This reaction typically proceeds in about 50% yield, which is respectable for so powerful a reaction.

This difluoroalkoxy alcohol could be elaborated into liquid crystal in a variety of ways, which are outlined in Table I. First, it can be treated with methyl formate and titanium triisopropoxide,[7] affording the formyl ester. An ester may also be formed by treating the alcohol with an acid chloride in the presence of triethylamine and DMAP. Finally, treatment with sodium hydride and an alkyl halide in dimethylformadide solution converts the compound into an ether.

POLARIZATION AND OTHER PROPERTIES OF THE DIFLUOROALKOXY AND DIFLUORODIALKOXY SYSTEMS

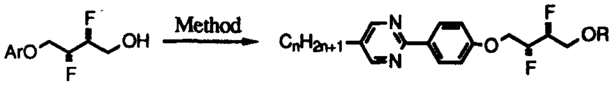
As expected, compounds containing difluoroalkoxy and difluorodialkoxy tails tended to have high spontaneous polarizations, some over 430 nC/cm^2. The results of our tests on the difluoroalkoxy and difluorodialkoxy compounds are shown in Table I. Note that the tail length on the pyrimidine side of the materials varied somewhat, making correlations between the structure and polarization of the compound ambiguous. However, two general trends can be noted: 1) esters generally give higher polarizations than ethers, although the formyl ester has a markedly lower polarization than other esters, and 2) difluoroalkoxy compounds have extrapolated polarizations higher than those of the corresponding difluorodialkoxy ethers.

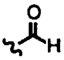
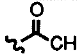
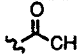
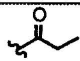
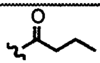
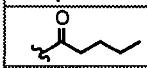
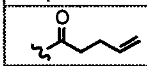
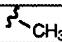
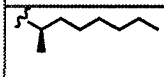
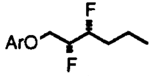
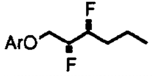
NMR STUDIES

Schlosser[1] studied a vicinally difluorinated system by NMR and found that when the fluorines were syn, they tended to fall into a gauche configuration. This resulted in a vicinal hydrogen-fluoride coupling ($^3J_{HF}$) of about 22 Hz. On the other hand, when the fluorines were in an anti configuration there was no strongly preferred configuration, and the resulting free rotation led to a $^3J_{HF}$ of about 14 Hz. Our initial attempts to apply an NMR coupling analysis to our difluoroalkoxy system met in failure, due in part to the presence of an ab-quartet in the proton NMR region containing the α-to-F hydrogens. While the fluorine spectra of a difluoride

TABLE I

Conversion of difluoroalcohol IX into various derivatives[a]



R	Cpd #	n	Method	P_{ext} (b)	θ (deg)	$T-T_c$	Mesomorphic Properties	Phase Diagram of Mixture (10%)
	10	6	A	230			$$\begin{tikzcd} & S \arrow[dr, "67^\circ"] & \\ X \arrow[ur, "54^\circ"] & & I \arrow[dl, "40^\circ"] \\ & A \arrow[ul, "36^\circ"] & \end{tikzcd}$$	
	11	6	B	302	22	19	$X \xrightarrow{80^\circ} I$	
	12	7	B	410	27	37		$X \xleftarrow{26^\circ} C \xleftarrow{63^\circ} A \xleftarrow{68.5^\circ} I$
	13	6	B	339	22	19	$X \xrightarrow{83^\circ} I$ $X \xleftarrow{74^\circ} I$	
	14	6	B	356	22.5	19	$X \xrightarrow{80^\circ} I$ $X \xleftarrow{74^\circ} I$	
	15	7	B	374	28	33	$X \xrightarrow{74^\circ} I$ $X \xleftarrow{72^\circ} I$	$X \xleftarrow{27^\circ} C \xleftarrow{60^\circ} A \xleftarrow{68^\circ} I$
	16	6	B	437	28			
	17	7	C	190	26.5		$X \xrightarrow{70^\circ} I$	
	18	7	C	220	28		$X \xrightarrow{53^\circ} I$	$X \xleftarrow{23^\circ} C \xleftarrow{57.2^\circ} A \xleftarrow{67.2^\circ} I$
	19	6	C	22	21		liq. at 20°	$X \xleftarrow{23^\circ} C \xleftarrow{46^\circ} A \xleftarrow{60^\circ} I$
Difluoroalkoxy compounds								
	20	6	X	300	25	24		$X \xleftarrow{<RT} C \xleftarrow{48^\circ} A \xleftarrow{63^\circ} I$
	21	7	X	279	22	26		$X \xleftarrow{<RT} C \xleftarrow{50^\circ} A \xleftarrow{63^\circ} I$

Methods: A, ROH + large excess methyl formate + $Ti(OiPr)_4$ (cat); B, ROH + R'COCl + pyr + DMAP (cat); C, ROH + R'X (X = Br, I, or Ts) + NaH + DMF.

[a] P_{ext} and phase diagram of mixture are taken with a 10% mixture of the compound in a C* host, 4-(4-(S)-methylhexyloxy)phenyl 4' decyloxybenzoate.

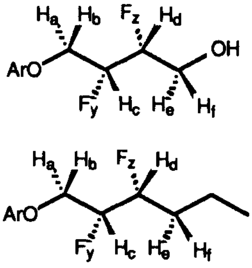
[b] P extrapolated is determined by measuring the polarization of the mixture, subtracting the polarization of the host, and multiplying by 10.

is less complicated than the proton spectra, even the fluorine spectra has too many couplings to determine which are attributable to F-F couplings and which derive from H-F couplings.

The recent synthesis of the difluoroalkoxyalcohol **9** greatly simplified matters. This difluoride, rather than having an alkyl chain terminating the chain, instead has a terminal hydroxyl group. This alcohol's proton NMR was fortuitously simple, leading to complete interpretation of the coupling constants in the α-to-F protons. The coupling constants that assist in structural analysis are shown in Figure 1. We determined the $^3J_{HF}$ of the difluoride to be approximately 22 Hz, roughly equivalent to the coupling in Schlosser's syn compounds. Furthermore, examination of the compound's fluorine NMR revealed the F-F coupling to be 11.7 Hz.

Using this F-F coupling constant as a starting point, we went back and re-analyzed the fluorine and proton NMRs of the difluoroalkoxy system. We found that the major product had a $^3J_{HF}$ of 18.2 Hz, therefore falling halfway between the expected value for the syn and the anti compounds. This leaves the relative stereochemistry of the two fluorines ambiguous, thus requiring another method of stereochemical proof. We are currently investigating other means of unambiguously determining the stereochemistry of this system.

The carbon, proton, and fluorine NMR spectra of several compounds are listed in Table II. Of particular interest in this table are the carbon spectra of the fluorohydrin **22**, in which the coupling of the fluorine to the carbons is readily apparent,



Coupling constants

$J_{cz} = 21.7$ Hz
$J_{dy} = 21.9$ Hz

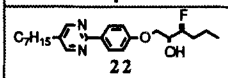
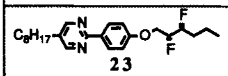
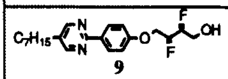
Coupling constants

$J_{cz} = 18.2$ Hz

FIGURE 1

TABLE II

NMR data of some fluorinated compounds[a]

Compound	^{1}H NMR	^{13}C NMR	^{19}F NMR
 **22**	0.88 (t, 3H, J = 7), 0.98 (t, 3H, J = 7), 1.2 - 1.8 (m, 14H), 2.60 (t, 2H, J = 7), 4.13 (m, 3H), 4.62 (dm, 1H, J = 49), 7.02 (d, 2H, J = 8), 8.37 (d, 2H, J = 9), 8.58 (s, 2H)	13.7, 13.9, 18.1(d, J = 3.3), 22.4, 28.8, 29.9, 30.5, 31.6, 33.1 (d, J = 20.6), 68.5 (d, J = 5.5), 71.1 (d, J = 24.2), 93.2 (d, j = 170.8), 114.4, 129.5, 130.7, 132.2, 156.9, 160.4, 162.2	-193.5 (dtd, J = 10.9, 23.3, 47.5)
 **23**	0.88 (t, 3H, J = 6.8), 1.00 (t, 3H, J = 7), 1.2 - 2.0 (m, 16H), 2.60 (t, 2H, J = 7.8), 4.28 (t, 2H, J = 5), 4.35 (m, 2H), 4.78 (m, 2H), 7.02 (d, 2H, J = 8), 8.38 (d, 2H, J = 9), 8.58 (s, 2H)	13.7, 14.0, 18.2 (d, J = 4.9), 22.6, 29.0, 29.1, 29.3, 30.0, 30.8, 31.8, 32.1 (dd, J = 4.9, 20.9), 66.4 (dd, J = 7.1, 26.9), 91.0 (dd, J = 19.8, 180.2), 91.2 (dd, J = 20.3, 175.8), 114.5, 129.5, 131.2, 132.4, 157.0, 160.1, 162.3	-199.75 (m, 1F), -204.73 (ddtd, 1F, J = 9.6, 18.2, 22.4, 45.9)
 **9**	0.88 (t, 3H, J = 7), 1.3 (m, 8H), 1.62 (m, 2H), 2.03 (t, 1H, J = 3), 2.60 (t, 2H, J = 7.8), 3.99 (ddd, 2H, J = 3, 4.4, 22.2), 4.36 (dd, 2H, J = 4.9, 20.0), 4.89 (qdd, 1H, J = 4.4, 21.9, 47.1), 5.05 (qdd, 1H, J = 4.9, 21.7, 47.6), 7.02 (d, 2H, J = 8), 8.38 (d, 2H, J = 9), 8.58 (s, 2H)		-205.18 (dqd, 1F, J = 11.7, 20.7, 47.0), -207.05 (dqd, 1F, J = 11.7, 22.3, 47.6)

[a] All coupling constants listed in Hz.

^{13}C and ^{1}H data shifts relative to TMS, ^{19}F data shifts relative to $CFCl_3$.

and the fluorine spectra of the difluoroalkoxyalcohol **9**, in which the coupling pattern has been completely analyzed.

CONCLUSION

Two series of difluorinated ferroelectric liquid crystal dopants were synthesized by our researchers. The first series, dubbed the difluoroalkoxy series, had spontaneous polarizations of up to 300 nC/cm^2. The second series, dubbed the difluorodialkoxy series, was more versatile and contained compounds with polarizations of over 400 nC/cm^2. The proton, fluorine, and carbon NMRs of these compounds were interpreted to determine the regio- and stereochemistry. We determined that the difluorodialkoxy compounds had a syn difluoride configuration, but have not yet unambiguously determined the stereochemistry of the difluoroalkoxy system.

Acknowledgment

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