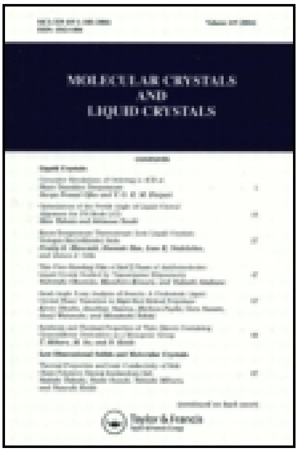

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Use of the Boulder Model to Predict Coupling between Dipoles in the Core and Chiral Tail of Fluorinated Ferroelectric Liquid Crystals

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Use of the Boulder Model to Predict Coupling between Dipoles in the Core and Chiral Tail of Fluorinated Ferroelectric Liquid Crystals

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Ferroelectric (chiral) smectic C* liquid crystals have been shown to exhibit high speed, multistate electro-optic, display device and opto-electronic computing applications, particularly when incorporated into the surface stabilized ferroelectric liquid crystal (SSFLC) light valve. High polarizations are necessary to achieve the speeds desired in opto-electronic computing, waveguide, and fiber-optic applications. By coupling the dipole(s) in the core of the FLC with dipole(s) associated with the chiral tail, a significant increase in polarization can be achieved.

Use of the Boulder Model allows us to examine the most probable conformations of an FLC molecule in a hypothetical smectic C "binding site" and thereby predict the sign and order of magnitude of the spontaneous polarization based on electronic and steric arguments for the particular chemical structure.

I. INTRODUCTION—THE NEED FOR FAST FLCs

Development of a flat panel display device capable of high quality color/gray scale output is an important technological goal of the 1990s. Once the problem is adequately addressed, the cathode ray tube (CRT) will likely be replaced in most devices, including TV screens. Clearly, the applications of such flat panel displays (and spin-off technologies such as very large area format projection displays) are numerous and important.

One highly promising approach to this long standing problem is the ferroelectric liquid crystal (FLC) display. In such a device, a thin layer of FLC material is placed between glass plates, and the optical properties of small regions (e.g. pixels) in the layer is controlled by application of electric fields with high spatial resolution. Thus, Ferroelectric Liquid Crystal (FLC) materials may provide an inexpensive way to fabricate large area flat panel displays when incorporated into the Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) geometry. In an SSFLC cell, due to the presence of a ferroelectric polarization **P**, the orientation of the molecules in the FLC phase is strongly coupled to externally applied fields, affording a fast light valve with high contrast, bistability, a sharp threshold, low power requirements, and high spatial resolution.

In addition, it seems clear that in the future many computing tasks will be handled using *optoelectronic* approaches. Optical computing is in its infancy, and increases in speed over todays electronic computers of a factor of 10^5 seem realizable. Also, parallelism and interconnections are in principle much more easily implemented using optical configurations. With their inherent speed and parallelism, optoelectronic computing systems could revolutionize the electronics, information processing, computing, robotics, artificial intelligence, process control, and communication industries. For example, in robot vision and manufacturing inspection systems, a major breakthrough is needed if robots and other artificial intelligence (AI) machines are going to "see" at video rates.

In opto-electronic computing applications speed, of course, is of the essence. It is certain that opto-electronic computing will put even greater demands upon FLC materials than flat panel displays. The lack of suitable *materials*, however, is certainly still a major issue, especially when high switching speeds at room temperature with good contrast (required for gray-scale video panels and optical computing modulators) are required. In striving for low-viscosity, high-polarization FLCs to meet these ends, we have explored the possibility of coupling dipoles associated with a fluorine on the core with a chiral fluorinated tail. The following sections describe our approach to obtaining an increase in spontaneous polarization of the FLC.

II. THE BOULDER MODEL—A PREDICTIVE MODEL FOR THE MOLECULAR ORIGINS OF P

The Boulder model states that the molecules in an FLC phase are ordered with respect to conformation and "rotational state", or rotational orientation relative to the smectic C tilt plane, by a "binding site" resulting from the time-average interaction with neighboring molecules which behaves analogously to a biological receptor site. Each conformation of the LC molecules is oriented in this binding site such that one rotational state is preferred, i.e. there is a well in the energy surface for rigid rotation of a conformation about the director. The plane congruent with the tilt plane when the conformation is at the bottom of the rotational well is the molecular tilt plane.

The polarization of the phase is given approximately by Equations 1 and 2, where

$$\vec{P} = \sum_{\text{over all i conformations}} D_i \cdot \vec{P}_i \qquad \text{equ 1}$$

$$\vec{P}_i = \vec{\mu}\perp_i \cdot \text{ROF}_i \qquad \text{equ 2}$$

D_i is the number density of the ith conformation and $\mathbf{P}_i$ is the contribution to the polarization for the ith conformation. The contribution to the polarization for the ith conformation is given by Equation 2, where $\tilde{\mu}(\text{perp})_i$ is the component of the molecular dipole moment normal to the molecular tilt plane and ROF_i is the rotational orientation factor (a number between zero and one which reflects how deep the rotational well is).

In order to predict the *sign* of the polarization for an FLC material, the *shape* of the binding site must be understood. For simple phenylbenzoates, we propose that the binding site has the shape of a *bent cylinder*, with the tails of the cylinder *less tilted* from the layer normal than the core of the cylinder.[8] This proposal is based upon examination of CPK molecular models, and also on the assumption that the tails are melted relative to the cores in smectic C liquid crystals, and therefore the tails behave as if they were larger than the cores, and the preferred packing arrangement puts the tails less tilted than the cores. High resolution X-ray scattering measurements with the smectic C phase of 4′-butoxyphenyl-4-decyloxybenzoate are interpreted in terms of the tails less tilted than the cores, and provide experimental verification of this concept.[1]

Numerous FLC examples have been designed and synthesized in the Boulder group including the lactate ethers,[2] epoxy ethers,[3] 1-fluoro-2,3-epoxy ethers,[4] and the 1-methyl-2,3-epoxy ethers.[5] All of these examples support the Boulder Model where the sign and order of magnitude of the polarization have been successfully predicted. We refer the reader to the referenced articles on the subject for a thorough discussion of the Boulder Model and the FLC compounds described above.

One of the more interesting examples, from the stand point of a potentially commercial low-viscosity, high-polarization tail, is the 2,3-difluoroalkoxy moiety, first developed at Displaytech. This system shows a relatively high **P** (-300 nC/cm^2 for the phenylpyrimidine analog extrapolated from a 10% mixture in **W82**) resulting from the coupling of the oxygen and fluorine dipoles in the tail. Indeed, this compound exhibits an extrapolated polarization nicely consistent with the model, and to our knowledge has the highest polarization known for an FLC material with no carbonyl groupings (unpublished results).

The 2-fluoroalkoxy and 2,3-difluoroalkoxy tails were chosen because of their potential to prefer a gauche bend (substituents on adjacent carbons at 30° to each other) at the C-1, C-2 carbon and thus allow the ring oxygen and ring fluorine to additively couple to **P**, similar in function to the well studied 1-methylalkoxy system. In addition, the electronic gauche effect (similar in nature to the anameric effect that stabilizes the axial methoxy conformation in sugars) stabilizes a gauche conformation between the oxygen and the fluorine(s). This preferentially biases the dipolar species in the same direction and can cause a further increase in **P**.

Use of the Phenylbenzoate Core as a Model for Core Coupling

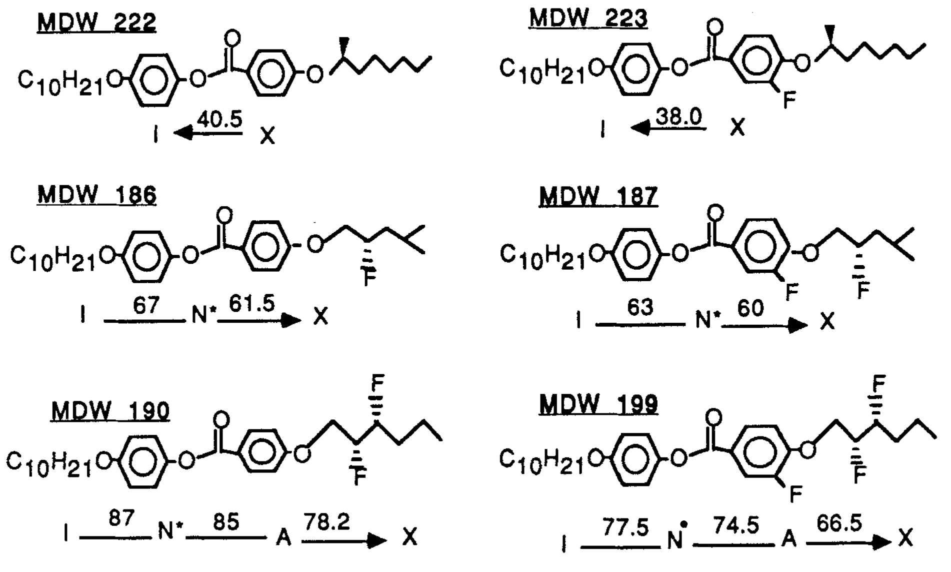
Although the phenylbenzoate core system is known for its relatively high orientational viscosity and therefore not the core of choice for the development of fast FLC mixtures, it is one of the most well understood structures from the stand point of ring orientation—a critical point in understanding the coupling of ring dipoles with dipoles on the chiral tail. Although the reversed phenyl benzoate system (chiral tail attached to the benzoate ring) is known to afford significantly lower values of **P** than the regular phenyl benzoate core (chiral tail attached to the hydroquinone ring), it was still chosen for this work due to its ease of synthesis. Although the value of **P** is typically lower in this reversed system, measurement of the relative value of **P** between the fluorinated and non-fluorinated homologs is still an accurate probe into the core—tail dipole coupling phenomena.

Synthesis of the Reported Compounds

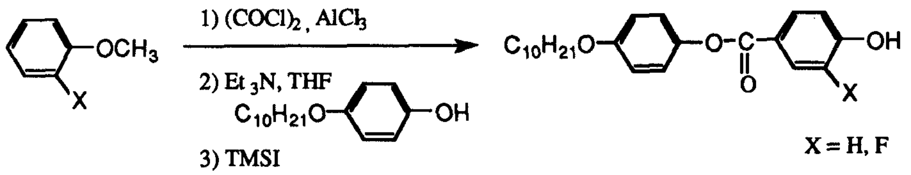
Chart 1 shows the structures and mesophoric properties of the six compounds synthesized.

The phenylbenzoate core phenol was synthesized starting from either the methoxy benzoyl chloride or 2-fluoro anisole as shown in Scheme 1. Scheme 2 shows the synthesis of the chiral alcohols. The 3-propyl-2S, 3S-epoxy alcohol was made by Sharpless epoxidation[6] of 2-hexenol. The 2-fluoro alcohol was derived from HF/pyridine treatment of the amino acid leucine, followed by lithium aluminum hydride reduction of the resulting α-fluoro acid. Shown in Scheme 3 is the conversion of the FLC epoxide to the difluoride. This was accomplished in two steps by ring-opening of the epoxide to the fluorohydrin followed by DAST (diethylaminosulfur

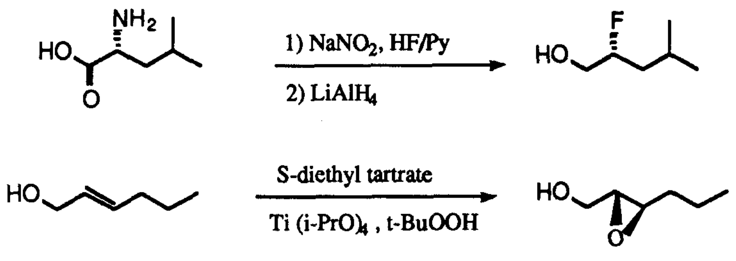
Chart 1. Stucture and phase sequence of compounds synthesized.



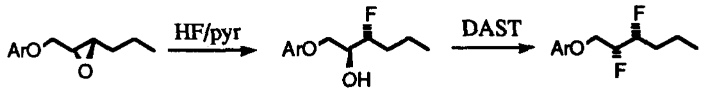
Scheme 1. Synthesis of the reversed phenylbenzoate phenol.



Scheme 2. Synthesis of the chiral tails.



Scheme 3: Synthesis of the Difluoroalkoxy tail.

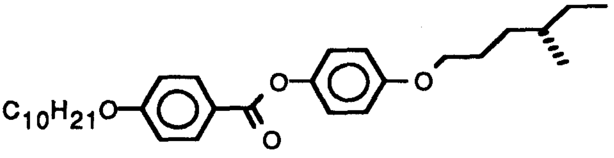


trifluoride)[7] dehydroxyfluorination. Attachment of the chiral tails was accomplished by Mitsinobu coupling[8] (diethylazodicarboxylate, triphenylphosphine) of the appropriate chiral alcohols.

Evaluation of FLC Materials in Mixtures

The phenylbenzoate compound **W82**, shown below,[9] was chosen as smectic C* host material. Thus, mixing experiments were performed using this host because of its broad smectic C* phase and low inherent polarization. Measurements made in this matrix allowed comparison of the variations in the spontaneous polarization predicted in the new compounds.

Although several of the compounds synthesized possessed liquid crystalline phases (Chiral nematic and smectic A), none exhibited the desired C* phase. Upon mixture in host **W82** at concentration of 10%, all mixtures showed a broad C* phase, typically 35–40° in width. Polarization and tilt angle measurements were performed



W82

$X \xrightarrow{35} C^* \xleftrightarrow{70.5} A \xleftrightarrow{72} N^* \xleftrightarrow{75} I$

$X \longleftarrow S_B \xleftarrow{30.5} C^*$

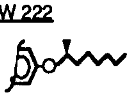
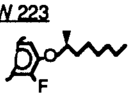
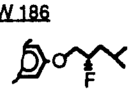
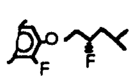
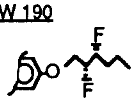
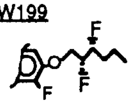
at 30°C below the A to C* transition. The polarization was then corrected for contributions arising from the C* host. Since **P** is a function of the tilt angle, this effect needs to be taken into account to allow for accurate comparison. A normalized polarization was afforded by dividing the extrapolated polarization by sin θ and allows for a reasonable comparison between the non-fluorinated fluorinated analogs with the same chiral tail. Table I shows the phase diagram, tilt angle and normalized extrapolated polarization of the six compounds synthesized.

Effect of the 1-Methylalkoxy Tail on P in the Phenylbenzoate System

It is well known that the 1-methylheptyloxy chiral tail imparts high polarization to FLCs (about 50 nC/cm^2).[10] Our interpretation of this result is that: 1) the alkoxy system prefers a conformation wherein the first carbon of the tail is in the plane of the aromatic ring; and 2) the methyl grouping at C1 prefers the anti conformation. This can be seen in Figure 1 (X = H), illustrating the FLC in a C* matrix.

TABLE I

Phase sequence, polarization and tilt angle data for C* mixtures using **W82** as host and containing 10% of the newly synthesized compounds

COMPONENT	Phase Sequence (°C)	Ps† (nC/cm^2)	Tilt angle† (Deg)	Ps (ext)*	Ps (ext)* / sin θ
MDW 222 	$\mathrm{I} \overset{65.0}{—} \mathrm{A} \overset{60.3}{—} \mathrm{C}^* \overset{28.5}{—} \mathrm{X}$	- 5.1	28.5	- 42	-88
MDW 223 	$\mathrm{I} \overset{65.6}{—} \mathrm{A} \overset{58.6}{—} \mathrm{C}^* \overset{25.5}{—} \mathrm{X}$	- 8.5	29.5	- 76	-154
MDW 186 	$\mathrm{I} \overset{73.3}{—} \mathrm{N}^* \overset{72.3}{—} \mathrm{A} \overset{68}{—} \mathrm{C}^* \overset{28}{—} \mathrm{X}$	-2.3	25	-14	-33
MDW 187 	$\mathrm{I} \overset{71.5}{—} \mathrm{N}^* \overset{70.5}{—} \mathrm{A} \overset{68.1}{—} \mathrm{C}^* \overset{26}{—} \mathrm{X}$	-5.1	28	-42	-89
MDW 190 	$\mathrm{I} \overset{71.4}{—} \mathrm{A} \overset{66.2}{—} \mathrm{C}^* \overset{33.5}{—} \mathrm{X}$	-3.8	26.5	-29	-65
MDW199 	$\mathrm{I} \overset{71.5}{—} \mathrm{A} \overset{67.5}{—} \mathrm{C}^* \overset{24.5}{—} \mathrm{X}$	-12.1	27.5	-112	-243

* Extrapolated to 100% concentration of chiral dopant.

† Measured at T_{A/C^*} = -30°C

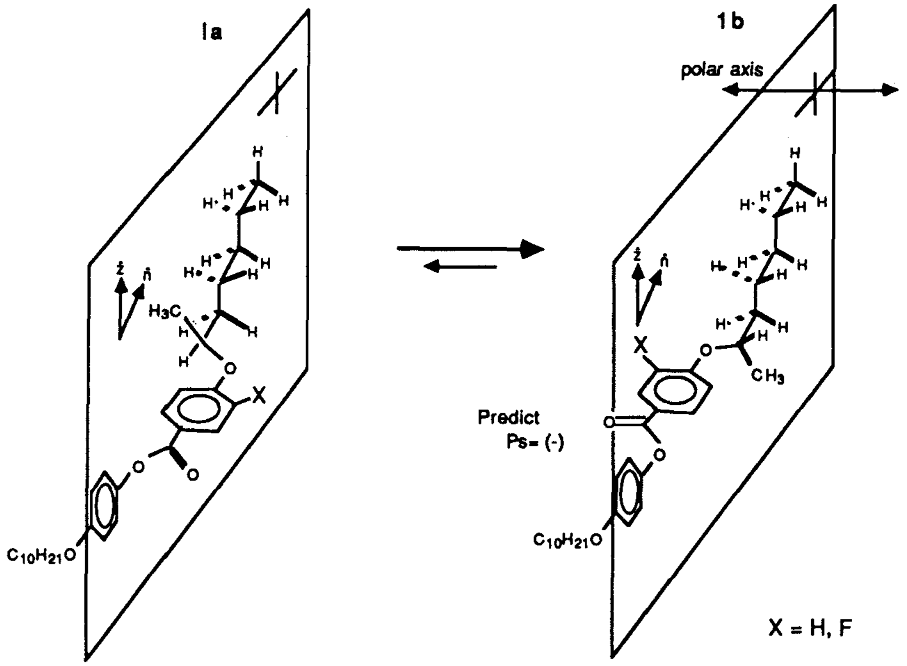


FIGURE 1 Orientation of 1-methylalkoxy ring system in the C* Binding site.

Conformation 1b is preferred due to the above arguments and implies that for the (S) configuration at the stereocenter, **P** should be negative, as is indeed observed.

Ortho-Fluoro 1-Methylheptyl FLC

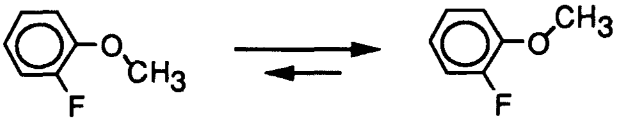
Although the dipolar orientation of many chiral tails have been analyzed using the Boulder Model as an interpretive tool, only recently has it been applied to FLCs with dipoles attached to the core. Polarization can be used as a probe as to the orientation of the aromatic ring by attachment of a dipole to the ortho position of the aromatic ring.

If a functionalized aromatic ring could be oriented relative to the tilt plane, then an increase in **P** would result. An approach for achieving this type of orientation by *steric coupling of the ring to stereocenters in the chiral tail*, is illustrated in Figure 1(X = F). This effect was originally demonstrated by workers at Chisso Corp. in the fluorinated and non-fluorinated 1-methylheptyloxy system. Using the traditional 1-methylheptyloxy tail, this work was repeated to check for core—tail coupling in our specific core system. The results for FLCs MDW222 and 223 are shown in Table I and show nearly a two-fold increase in **P**, from -88 to -154 nC/cm^2, upon addition of a ring fluorine. This corroborates the findings of the scientists at Chisso. We believe that the increase in **P** arises from the steric interaction of the C-1 methyne group with the ring fluorine causing the ring oxygen and ring fluorine to align in the same direction *and* oriented normal to the tilt plane. Although in the 1-methyl heptyloxy system a clear coupling is observed, it was not clear if this coupling effect could be extrapolated to the chiral mono and difluorinated tails lacking a methyl group at the C-1 carbon.

Effect of Ring Fluorine on 2-Fluoroalkoxy Tail

The steric coupling effect of the 2-fluoroalkoxy tail is not as intuitively obvious as in the case of the 1-methylalkoxy tail. It is not clear if the steric bulk of the C-1 methylene is great enough to cause repulsion of the ring fluorine and thus cause the C-2 fluorine to align on the same side as the ring fluorine. Molecular mechanics calculations in the Boulder Group on the simple fluorinated model system, 2-fluoro anisole, suggest that the conformational energy difference between the syn (F and methyl on the same side) and anti forms (F and methyl on opposite sides) in the two conformations will cause anti alignment as strong as that expected in the 1-methylalkyloxy case.

Polarization studies of MDW187 show that, indeed, the polarization was tripled to 89 nC/cm^2 by the simple addition of a fluorine to the ortho position of the ring indicating a good alignment of the dipoles *and* a significant conformer population with the fluorine-containing ring oriented normal to the tilt plane.



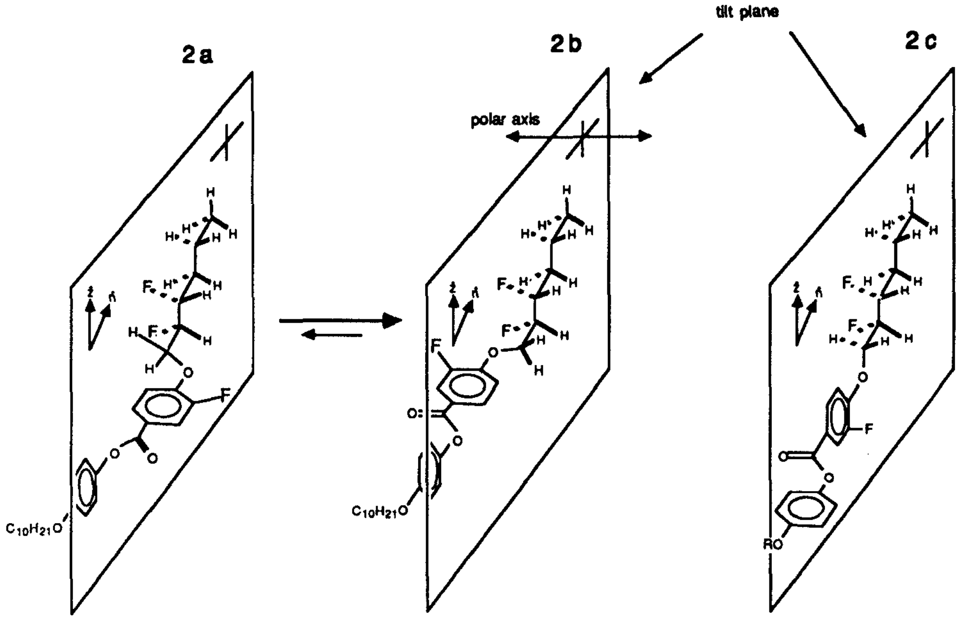


FIGURE 2 Three conformations of ring fluorinated 2,3-difluoroalkoxy FLC in the C* phase.

Effect of Ring Fluorine on 2R.3R-Difluoroalkoxy Tail

As described for the monofluoro case above, the conformations predicted by the "Boulder Model" in the 2R,3R-difluoroalkoxy tail allow for the ring to orient either *in* the tilt plane or *normal* to the tilt plane. Thus, ortho fluorination of the ring becomes an efficient tool in determining which conformation is preferred. Figure 2 shows three possible conformations of the ring-fluorinated 2,3-difluoro FLC in the FLC binding site. Figures 2b and 2c are low energy conformations and 2a is less favored. An important stabilizing effect seen in vicinal heteroatoms with lone pairs is the electronic gauche effect. The conformation shown in Figure 2a sacrifices part of this effect by having the ring oxygen and the fluorine on C-2 anti to each other. Both conformations in Figures 2b and 2c are aligned such that there is a stabilizing gauche interaction between the oxygen and both fluorines. Only in the former case (2b) will an increase in **P** be observed upon fluorination of the ring. Examination of the polarization of compound MDW199 shows a dramatic four-fold increase over its non-ring fluorinated counterpart, MDW190. This finding implies that a C-1, C-2 gauche bend exists with the ring spending a significant part of its time normal to the tilt plane and due to the electronic gauche coupling, causes an ordering of all four dipoles in the direction normal to the tilt plane.

III. CONCLUSIONS

Ortho ring fluorination is an effective technique for probing the orientation of the aromatic ring. A significant coupling effect is observed when applied to certain chiral tails and results in an increase in **P**. A two fold increase in **P** was noted with the 1-methylheptyloxy tail when attached to an ortho fluorinated reversed phenylbenzoate. A further increase in orientation was gained with use of the 2-fluoroalkoxy tail resulting in a measured **P** of three times the non-fluorinated case. Finally, the best orientation was obtained by the use of the 2,3-difluoroalkoxy tail, affording a four-fold increase in **P**. By applying the Boulder Model to other core and tail systems, we believe it is possible to gain a greater understanding into the molecular orientation of the FLC moelcule and thereby effectively design FLC materials that will meet the challenges presented by the next generation of high speed devices.

Acknowledgment

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