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The goal of this project was to make liquid crystal materials suitable for use in a deformable helix ferroelectric liquid crystal (DHFLC) device for analog light transmission. Towards this goal, 141 new compounds were synthesized with potential in DHF mixtures, including compounds with novel chiral tails and cores. One class of achiral dopants was found to amplify the C* pitch induction abilities of chiral dopants. A subset of this family also helped decrease the crystallization point of mixtures. Other compounds, showed tight C* pitch and high polarization. Still other compounds had C* pitch and N* pitch of opposite signs, making them useful for N* pitch compensation. Several compounds, which increase the birefringence of mixtures while increasing solubility, are also reported. The newly synthesized compounds were extensively evaluated for relevant properties. Formulation efforts with these new materials resulted in new DHFLC mixtures with tight C* pitch (0.13 µm), long N* pitch, and very wide (<-30°C to 73°C) C* phases. These could potentially be used in fast-switching analog display devices. The mixtures were evaluated in FLC cells. Further research is required to optimize the LC cells and driving electronics to take full advantage of the newly formulated DHF mixtures.

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Design and Synthesis of Tight Pitch FLCs for Analog Voltage - Limited Electro-optic Modulators

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Final Report

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Introduction

The goal of this project was to make liquid crystal materials for use in deformable helix ferro-electric liquid crystal (DHFLC) devices. The following properties were needed in the FLC materials: a tight C* pitch (necessary to see the DHFLC response), a long N* pitch (necessary for good alignment of the liquid crystal), and high birefringence (to give stronger modulation depth between the fully on and fully off states). These requirements are specific to the DHFLC project. In addition, the materials needed a broad C* phase (the broader the phase, the greater the temperature range at which the device will operate), an N phase at least three degrees in width (to simplify FLC alignment), moderately high polarization (to increase the switching speed), and complete miscibility of all components of the liquid crystal mixture (separation of the components results in poor display characteristics).

The only type of FLC materials which could possibly meet the criteria set forth in the previous paragraph are mixtures. It is unlikely that any single component could have the combination of properties necessary for any practical application. In fact, most commercially available liquid crystalline materials are mixtures containing approximately ten components, each of which helps the mixture reach one to four of the goals outlined in the previous paragraph. Clearly, many different types of compounds are needed to make a homogenous mixtures with all the desired attributes. Our work focused on mixing materials using previously developed compounds, developing new dopants (both chiral and non-chiral) which provide tight C* pitch materials, and investigating alignment techniques which allowed these new DHF materials to be used in devices.

<u>Materials</u>

There are two main types of FLC configurations which are used for manipulation of light. The first is the surface-stabilized mode (SSFLC), in which the C* helix is unwound by alignment layers on the substrates holding the FLC material. The second type of FLC configuration is the deformable helix mode (DHF), in which the C* helix is too tight for the alignment layers to unwind. Below is a comparison of these two FLC modes, which give large changes in refractive index while being relatively temperature insensitive.

Table 1. SSFLC vs. DHFLC Cells

Type of Cell	SSFLC	DHFLC
Light Modulation Mode	Digital (Bistable)	Analog (linear)
Typical Operation Voltage	10.0 V/μ	1.0 V/μ
Delay time	Two to three times the switching speed	None
Typical Change in Refractive Index	0.10 to 0.26	0.06 to 0.13
Cell Thickness	1.8 μm	2.0-4.0 μm
C* pitch	> 4.0 μm	< 0.35 μm
N* pitch	> 10 μm	> 10 μm <u>or</u> no N* phase
Optimal Tilt Angle	22.5° (for 1/2 wave plate)	22.5° to 45°
Typical Demonstrated Optical Response	$\Upsilon_{10-90\%}$=20 μs	10 μs for 15% change in Δn or 200 μs for 100% change in Δn

Table 1 shows the two modes to be quite complementary. The SSFLC mode affords quick, bistable operation with memory while the DHFLC allows continuous adjustment of Δn with no delay time or threshold voltage and no memory. If memory is not needed, the DHFLC mode

becomes the more attractive vehicle for device fabrication, especially considering its low operating voltage.

The goal of this project was to make liquid crystal materials suitable for use in DHF devices for analog light transmission. These FLC materials required the following properties: a tight C* pitch, a long N* pitch, high birefringence, a broad C* phase, an N phase at least three degrees in width, moderately high polarization, and complete miscibility of all components of the liquid crystal mixture.

An FLC material with these specifications must necessarily be a mixture of many components. These components generally fall into two types of categories: non-chiral host materials, and chiral dopants. The general attributes of each category is described below.

Host Materials

Host materials are the bulk of the liquid crystal material, often making up 80 - 95% of the material. They are, for the most part, responsible for the phases exhibited by the material. For instance, in this project we tried to make two different types of DHF mixtures. The first had an N phase about three to five degrees in width, and a C phase from about 60 °C down to about -20 °C. This was useful in displays and similar applications. The second type of material was a high tilt material without an A phase. This was to be used for phase shifting applications, where a 45° tilt will allow a 180° phase shift. Each of these sets of properties is fine-tuned by altering the composition of the host material. The host materials, since they are the majority of the mixture, are also responsible for the birefringence and clarity of the mixture.

Although the host material *en masse* makes up about 80% of the mixture, each individual component comprises only 5-15% of the mixture, so an individual component will not heavily influence the properties of the final material. It is therefore difficult to determine one additional component's effect on a mixture. Mixing host materials is almost an art form, requiring years of experience to acquire the intuition necessary for regular success in FLC mixture formulation.

Chiral Dopants

Chiral dopants have a chiral center which in some manner affects the properties of the entire mixture. For instance, some chiral dopants give the bulk smectic C material a net dipole moment, imparting the moderately high polarization needed for fast switching. This requires that the chiral center somehow direct a molecular dipole. The particular configuration required for high polarization compounds is reasonably well understood[1].

Chiral dopants are also responsible for N* and C* pitch in the material. The molecular origins of these properties are less well understood. For instance, one Phase I discovery was that the N* and C* pitch of a material depended heavily on the host material used for the measurement. With one host material, a chiral component might have a moderate C* and moderate N* pitch, with another it might have a moderate C* and a tight N* pitch, and with still another it might have a tight C* and moderate N* pitch. In Phase II we found a class of non-chiral dopants containing a cyclohexyl group which could significantly tighten the C* helix of a material. Thus, both the host and the dopants play vital roles in determining a material's pitch.

Synthesis of New Materials

Throughout Phase II, we synthesized a variety of compounds with assorted combinations of different functional groups. Our objectives included finding new materials with tight C* pitch and/or high birefringence and/or high solubility to give more stable mixtures.

New Aromatic cores

Ferroelectric liquid crystals almost invariably possess a flat, rigid aromatic core with aliphatic tails on either end. In contrast to the rigidity of the rings, the aliphatic tails are composed of strings of atoms that, like a lion's tail, are anchored on one end and can move relatively freely on the other end. In practice, the tails gravitate towards a preferred conformation where the atoms form a zig-zag pattern. The tails of chiral dopants are responsible for chiral manifestations such as polarization and pitch. To a large extent, cores and tails can be mixed and matched. Thus, a high polarization tail and a highly birefringent core can be coupled, often producing a material with high polarization and high birefringence. The interplay of tails and core leads to most FLC properties, and seemingly minor changes in a core/tail combination can afford surprising results. To adequately assess tails and cores, a variety of core/tail combinations must be synthesized.

The long axis of the tails and the long axis of the core form an angle of about 35°. This angle is thought to be responsible for the tilt of the smectic C phase. In fact, it appears that tilted smectic phases are more likely in materials which have three rather than two rings, giving the overall molecule a larger tilt. Also, longer cores tend to have higher birefringence, which is particularly important for DHF materials. One disadvantage of longer cores is that they have higher viscosity, leading to slower switching times.
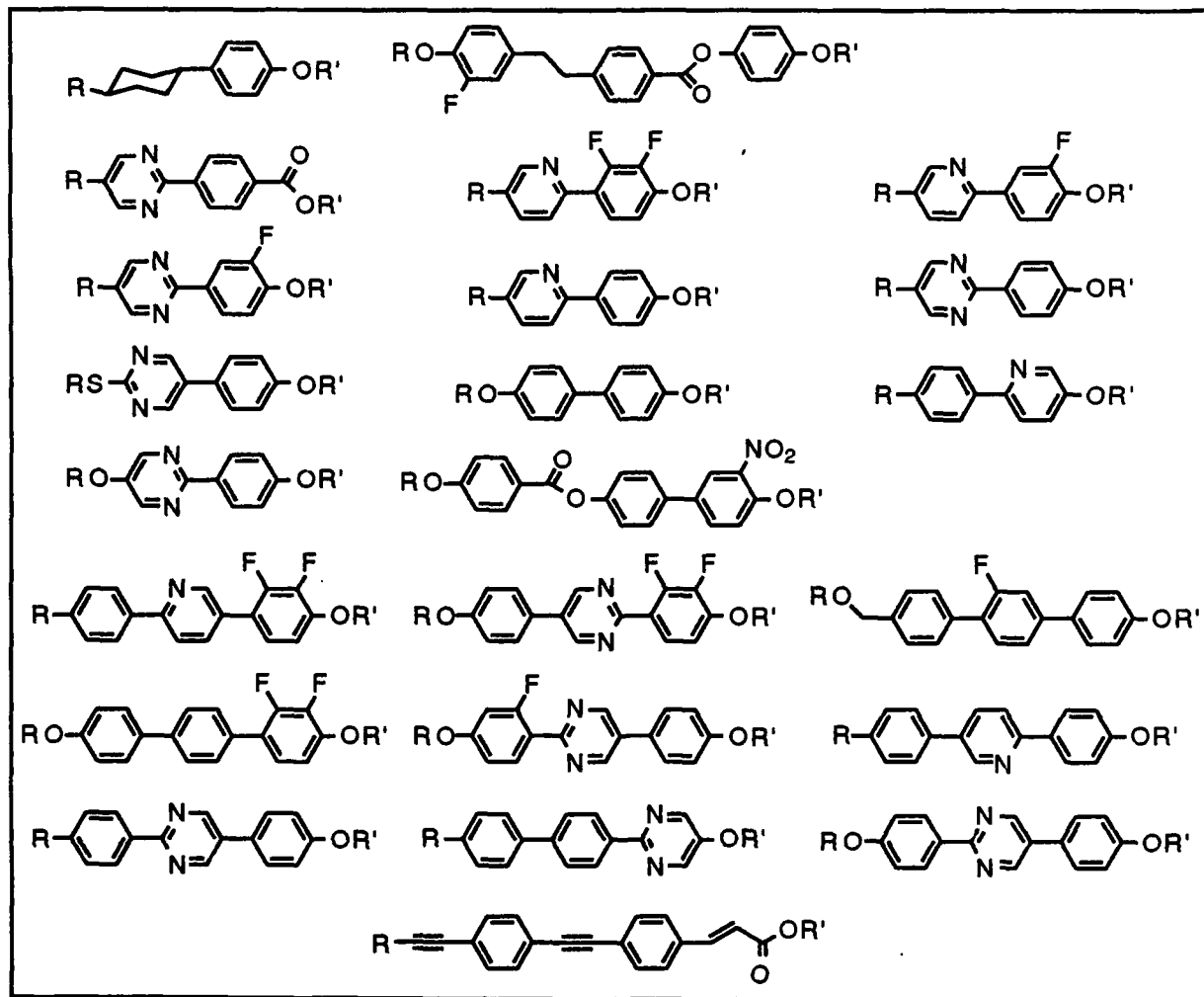

Figure 1. The cores used in Phase II, arranged in order of birefringence.
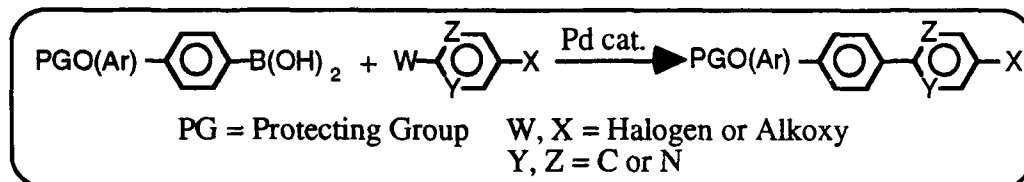
Figure 1 shows the cores used for new materials in this project. The **Figure** is roughly arranged in order of birefringence, with the higher birefringence cores nearer to the bottom. Thus, cores with only one aromatic ring or two uncoupled aromatic rings have a lower birefringence than cores with two coupled aromatic rings. Cores with three coupled rings have even higher birefringence. The highest birefringence core, invented by Displaytech, is shown at the bottom of the Figure. It has two alkynyl groups and an alkene carboxylate, making it a very long delocalized chain. Other cores of somewhat smaller birefringence have been reported in literature, but this core has the added advantage of being stable to ultraviolet light.

Fluorination leads to slightly lower birefringence cores, but has profound effects on the pitch-inducing capabilities of the resultant liquid crystals. For example, one particular unfluorinated-core difluoroalkoxy compound was found to have tight negative C* and moderate negative N* pitch, while its mono-fluorinated-core counterpart had a tight C* pitch and a long N* pitch, and their difluorinated-core counterpart had a tight negative C* pitch and a moderate *positive* N* pitch. Thus, the difluorinated compound could pitch-compensate for the unfluorinated compound, and their only difference was fluorination of the aromatic ring.

The selection of a core for a liquid crystal will affect not only its mesogenic properties and its birefringence, but also its interaction with the rest of the mixture. Sometimes a fluorine or a methyl group is added to the inner rings of a three-ring core, just to decrease the symmetry and thus increase the solubility of the material. A large core selection is needed to get a diversity of liquid crystal materials.

Synthesis Methods for Aromatic Compounds

One versatile method for the reproducible synthesis of aromatic rings is the palladium-catalyzed boronic acid coupling. This procedure couples an aromatic boronic acid to an aromatic halide[2], as shown in **Scheme 1**. By using functionalized aromatic rings or coupling again on the other end, a wide variety of cores can be synthesized. This is the preferred method for making about 40% of the cores shown in **Figure 1**.

$$\text{PGO(Ar)} - \bigcirc - B(OH)_2 \ + \ W - \bigcirc^Z_Y - X \ \xrightarrow{\text{Pd cat.}} \ \text{PGO(Ar)} - \bigcirc - \bigcirc^Z_Y - X$$

PG = Protecting Group   W, X = Halogen or Alkoxy
Y, Z = C or N

Scheme 1. The boronic acid coupling.

Of the cores which were not made using the boronic acid coupling, most are pyrimidine-containing compounds. These can be made by boronic acid coupling, but are easier to make by coupling a benzamidine with a methacrolein or some similar material. Two reactions of this sort, forming two and three ring cores, are shown in **Scheme 2**. Of course, derivatization of the core, by attaching fluorines, methyls, or other functional groups, is always possible. Phenylpyrimidines are particularly useful due to their high birefringence and low viscosity.
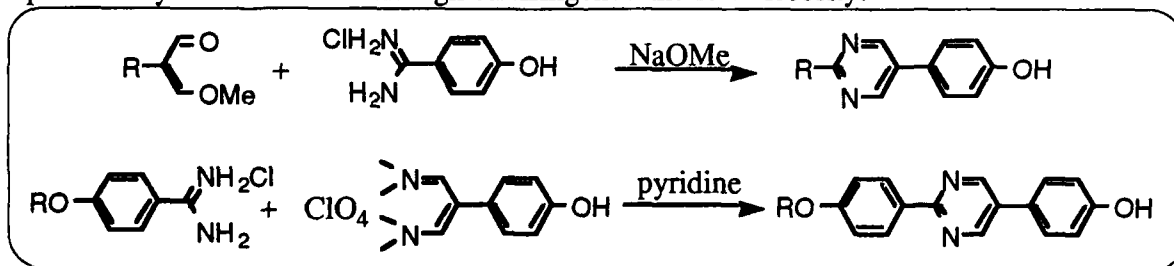
Scheme 2. A general coupling method for pyrimidine cores.

The coupling method shown in **Scheme 2** is quite versatile, although it does preclude the use of some groups during the reaction sequence. This is primarily due to the strongly acidic conditions needed to make the starting materials and the strongly basic conditions needed for the coupling. If these drawbacks can be circumvented, the coupling reaction can be used to make a wide variety of aromatic cores.

The highly birefringent alkynyl tolane cinnamate was made by a series of couplings of acetylenes with aromatic rings, as is shown in **Scheme 3**. The primary alkyne **1** and bromoiodobenzene **2** are coupled in the presence of a platinum catalyst to give the arylalkyne **3**. The trimethylsilylacetylene **4** and bromocinnamate **5** are also coupled using the catalyst, and the trimethylsilyl group is removed using tetrabutylammonium fluoride to give arylacetylene **6**. Finally, compounds **3** and **6** are coupled to give the end product **7**.
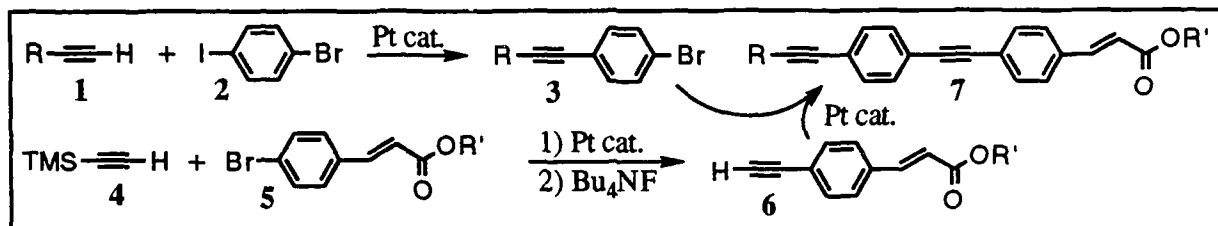
Scheme 3. The synthesis of alkynyl tolane cinnamates.

Tails for Liquid Crystals

Overview of Types of Tails

As was mentioned above, the interplay of core and tails in liquid crystals determines the LC's properties. Certain types of tails are particularly effective at promoting high polarization, others at promoting tight pitch, and still others at promoting smectic C phases. Some types of tails add slightly to the birefringence of the material, while others widen the liquid crystalline phases of mixtures. Since there are so many possible types of tails, and so many different desired properties for the final liquid crystal mixture, a wide variety of tails were used in this project. **Figure 2** shows some of the tails used in Phase II.

The tails in **Figure 2** fall into two main categories, achiral and chiral. Chiral tails are needed to impart pitch and polarization to a material. However, the bulk of a mixture is generally made up of achiral compounds, so achiral tails are also needed. Many of the achiral tails shown above are alkenes, used to slightly increase the birefringence of the compound. However, the tails on the right of the achiral section are more specialized tails, used to give the compounds a smectic C phase or to increase the width of the Sc range in the resultant mixture. In particular, the linoleyl tail has been shown to be give compounds with an Sc phase.

Several low-polarization chiral tails are also shown in **Figure 2**. These tails were used to synthesize tight-pitch materials. The top two are citronellol ethers, both as the alkene and the reduced compound. Another tail is a citronellol derivative, while the last comes from a chiral secondary alcohol.

The high polarization tails are used to give materials with high polarization and tight pitch. A wide variety of epoxide materials were made in Phase I and Phase II of this project. Epoxides are chemically stable, yet have high polarization and reasonably low viscosity, making them good candidates for use in Sc* materials. The dioxolanes have even higher polarization, but also have higher viscosity, resulting in slower-switching materials. They were explored primarily for their potential to produce tight-pitch materials.

The most significant discovery from Phase I was that compounds containing difluoroalkoxy tails had C* pitch significantly tighter than their N* pitch. This discovery was important because

DHF materials require a long N* but a short C* pitch. In addition to their singular pitch properties, the difluoroalkoxy compounds also have very high polarization and quite low viscosity, making them ideal Sc* mixture components. The difluoroalkoxy ether system was extended to include several different fluoro compounds, as well as a chloro and a cyano compound.
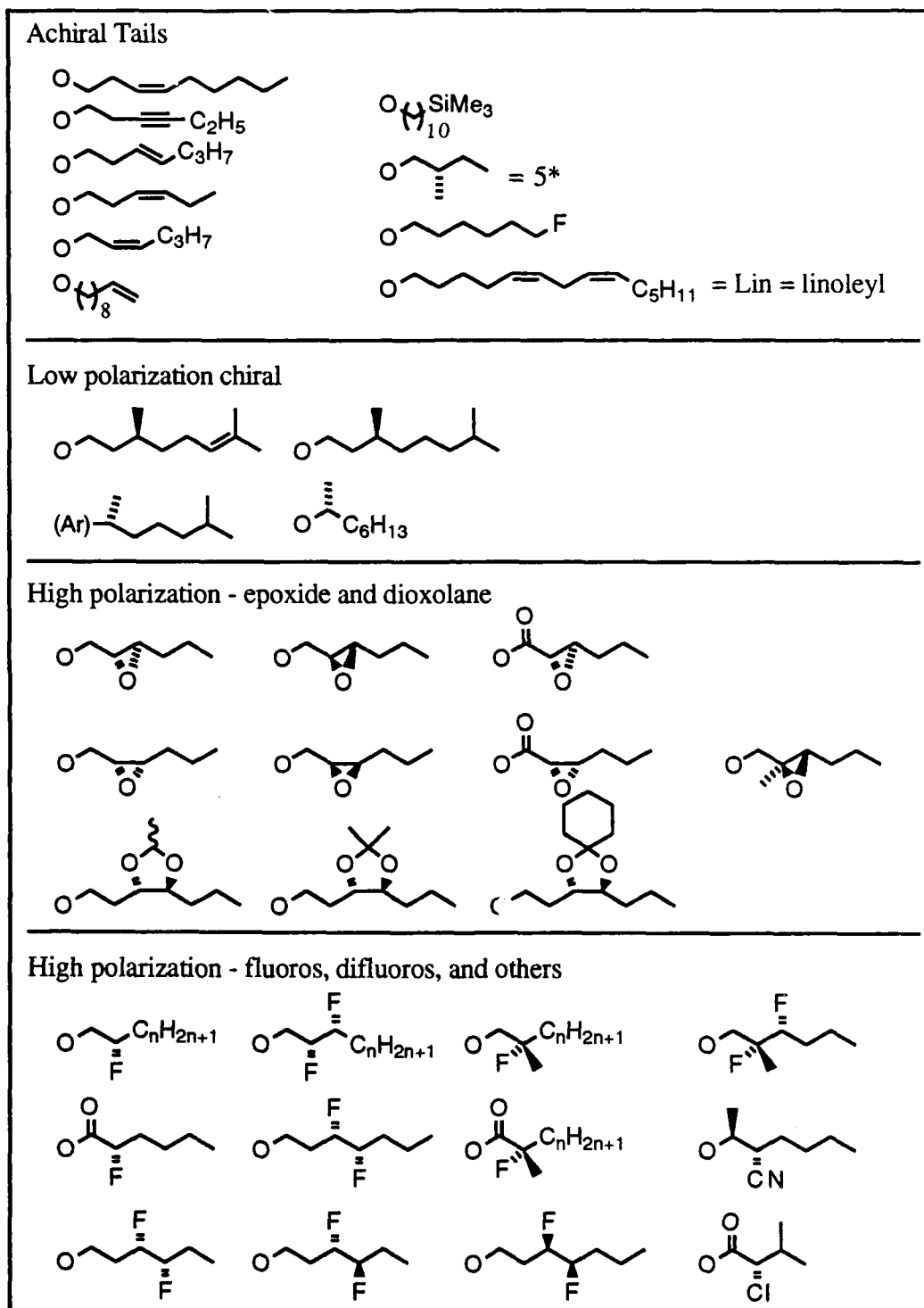

Figure 2. Tails used for new liquid crystals.

Difluoroalkoxy Tail

Our flagship chiral tail for this project was the difluoroalkoxy tail. When attached to a phenylpyrimidine ring, it gives a material with a C* pitch about 5-10 times tighter than the N* pitch. This unusual pitch disparity is very important, since a tight C* pitch is needed to make the deformable helix necessary for DHFLC devices, but a long N* pitch is needed so that the materials can be properly align d in the device. Most compounds - including pitch compensators - have N* and C* pitches of comparable magnitude and sign, so pitch-compensation is difficult if a mixture's N* pitch is as tight or tighter than the C* pitch. La Roche circumvented this problem by making a material without an N* phase, so the N* pitch of the material was never an issue. Unfortunately, this solution created a new problem, since materials align much more easily in the N phase than in the A phase. Our difluoroalkoxy tail, with its very tight C* pitch but only moderate N* pitch, is thus ideal for the creation of DHF materials.

We had myriad FLCs targeted for synthesis in this project, and generally synthesis of complicated compounds can be simplified by synthesizing parts, then coupling the parts together. This is definitely true of the difluoroalkoxy compounds, where our standard way to synthesize a compound was to attach an epoxide to the core, then go through two steps (with an overall yield of about 50%) to get the final difluoride. A more efficient way to do this synthesis was to make a difluoroalkoxy tosylate, which could be .oupled directly to the core to get the final product. Since the cores were often available only in limited quantities, our amounts of final product available for testing thus increased.

We tried several different methods for making the difluorotosylate before finally determining the optimal method, which is shown in **Scheme 4**. The epoxytosylate **8** was treated at low temperature with hydrogen fluoride/pyridine, giving the fluorohydrin **9**. Diethylaminosulfurtrifluoride (DAST) could transform this fluorohydrin into the difluorotosylate **10**, which could be recrystallized to enhance the optical purity. Finally, the difluorotosylate was coupled to a phenol giving the desired difluoroalkoxy aryl ether **11**.

Scheme 4. The synthesis of difluoroalkoxy aryl ethers.

In this project we invented a new difluoroalkoxy tail, in which the fluoride atoms are in the 3,4 positions. The precursor epoxide for this tail was not available, so it was instead made from the ɔ,4-diol **15**, as shown in **Scheme 5**. The alkene tosylate **13** was coupled with a phenol such as pyrimidyl phenol **12**, giving an alkenyl ether **14**. This compound was subjected to the recently discovered Sharpless diol reaction[3] conditions, giving the optically active diol **15**. The compound was insoluble under DAST fluorination conditions, but the solubility could be enhanced by treating the material with chlorotrimethylsilane to give the trimethylsilyl di-ether. Treatment with DAST removed the ether *in situ* giving the difluoride and a fluorohydrin, the latter of which could be converted to difluoride **16** with a second DAST treatment. Depending on the choice of Sharpless diol catalysts, either enantiomer of the diol, and thus either enantiomer of the difluoride, could be formed. This difluoride was similar in properties to the 2,3-difluoride, but had longer pitch and lower polarization. However, the 3,4-difluoride showed remarkably enhanced solubility, making it a valuable addition to our suite of high-polarization compounds.
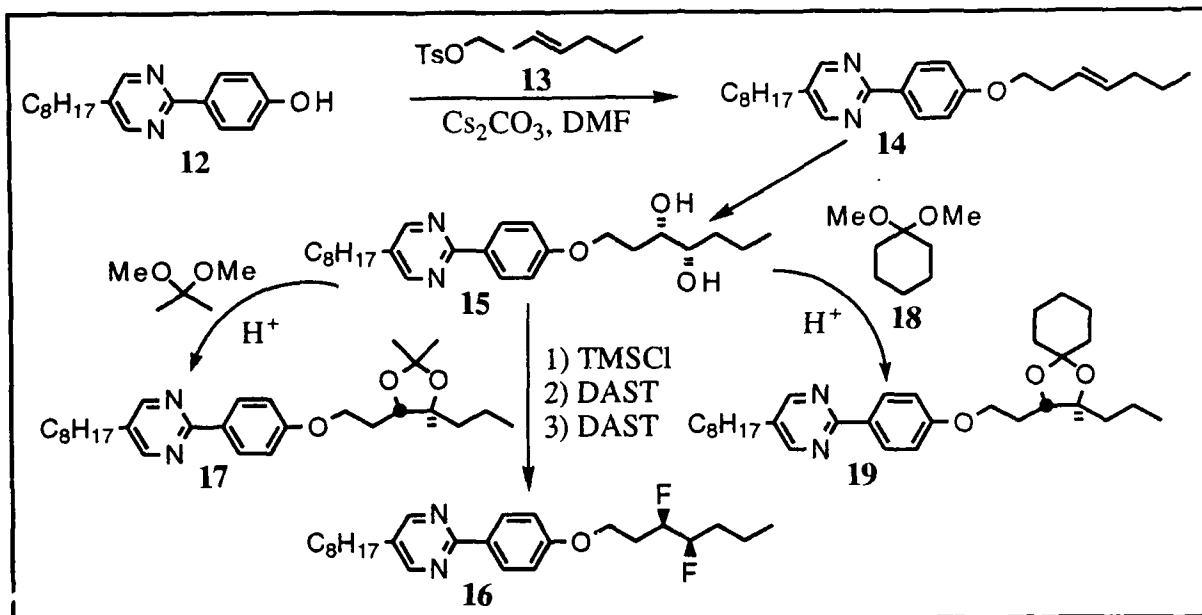
Scheme 5. Liquid crystals from the Sharpless diol.

Cyclohexenyl Oxirane Tail

Our observations led us to believe that chiral compounds with a large "chiral" profile from the *side* would tend to have tight N* pitch, whereas compounds with a large "chiral" profile from the *end* would have a tight C* pitch. The initial dimethyloxirane **21** shown in **Scheme 6** had an N* pitch which was much tighter than its C* pitch, and was thus a good pitch compensating agent. We believed that replacing the dimethyl group with a cyclohexane would give the compound a larger side profile, making it an even more effective pitch compensating agent. The dimethyloxirane **21** was made using the commercially available dimethyloxirane tosylate **20**. Hydrolysis of oxirane **21** gave the diol **22**, which was treated with dimethoxycyclohexane **18** to give the oxolane **23**.

The Sharpless diol product shown in **Scheme 5** could also be used to make tight-pitch dioxolanes. Thus, treatment of the diol **15** with dimethoxypropane resulted in dimethyloxolane **17**, whereas treatment with dimethoxycyclohexane **18** resulted in the cyclohexyloxolane **19**.
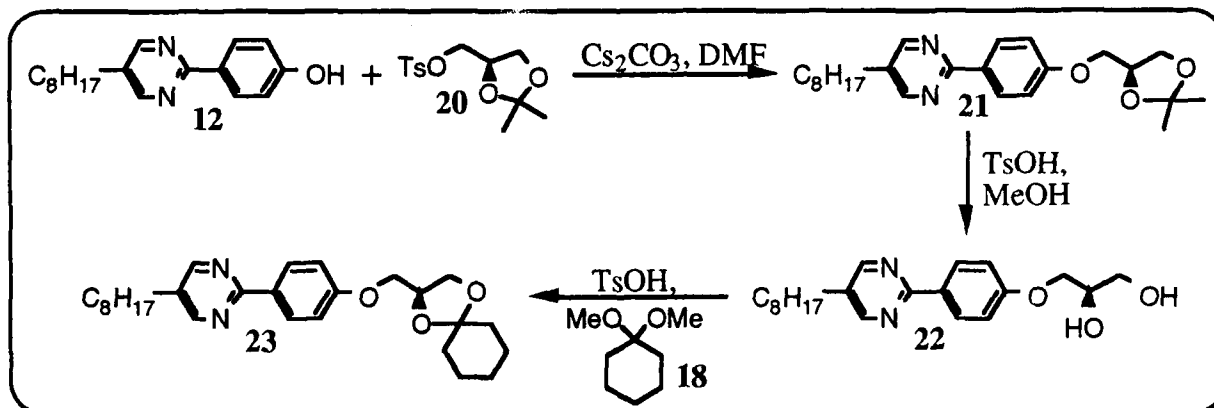
Scheme 6. The synthesis of cyclohexyl oxiranes.

1-Fluoroalkyl Tail

The Phase I proposal postulated that, since moving a chiral center closer to the core increases the pitch induction of a molecule, placing the chiral center right next to the core should result in a very tight-pitch molecule. This theory was neither confirmed nor disproved in Phase I, so further work of this type was carried out in Phase II. In Phase I, a methyl group was placed α to the core, but an α-fluoro group seemed equally likely to have the desired pitch induction. In addition, previous investigations in this laboratory had demonstrated the superior stability of the α-fluoro aromatic compounds. Thus, two different types of compounds with fluorinated chiral centers α to the aromatic ring were made. These two types of compounds are shown in **Schemes 7** and **8**.
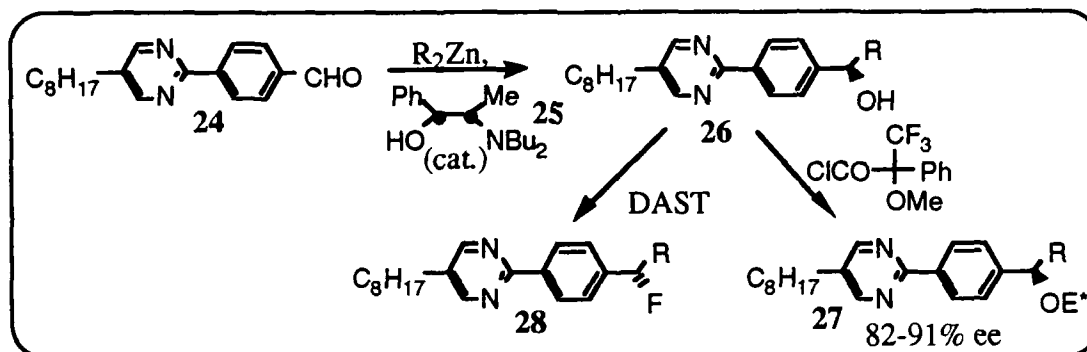
Scheme 7. The synthesis of the 1-fluoroalkyl tail.

A recent report[4] detailing the stereoselective addition of dialkylzinc reagents to aldehydes, yielding alcohols with high enantiomeric excess, showed us a simple entry into the α-fluoroalkyl system. The dialkylzinc reaction with aldehyde **24** is mediated by a chiral catalyst **25**, shown in **Scheme 7**. The optical enrichment of the resulting alcohol **26** could be assessed by coupling with Moser's acid and viewing the fluorine NMR of the resultant ester **27**. We found that if the alkyl group used was hexyl, the enantiomeric excess (ee) was 91%, whereas if the bulkier isopropyl group were used, the ee was 82%. Finally, the chiral alcohol could be treated with DAST to give the α-fluoro compound **28**, where R = hexyl.

1-Fluoro-2,3-Epoxy Tail
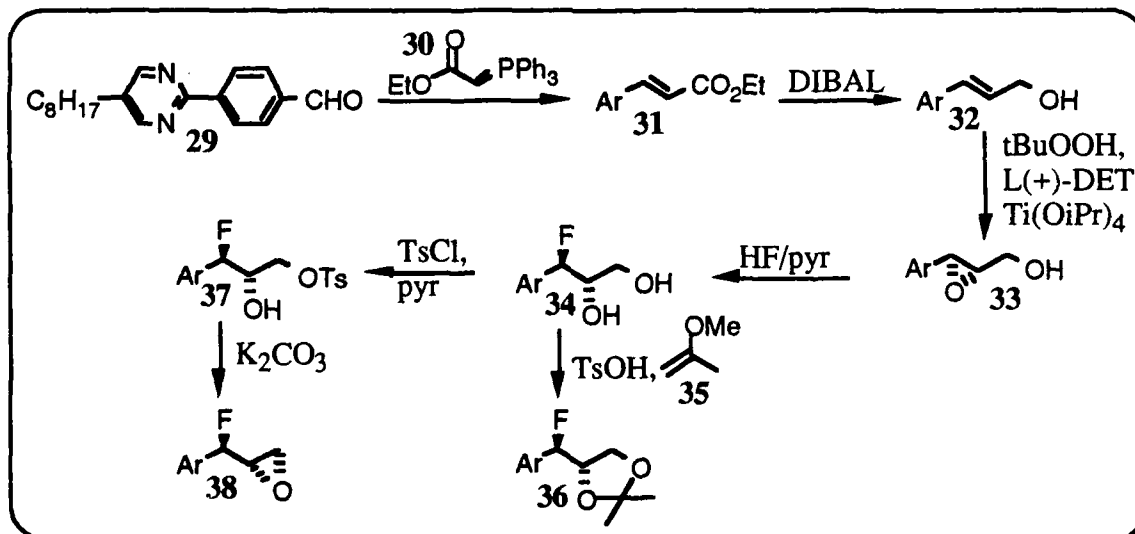
Scheme 8. Synthesis of the 1-fluoro-2,3-epoxy tail.

The other α-fluoro compound was made via a Wittig reaction followed by a Sharpless epoxidation. The aldehyde **29** was treated with the stabilized Wittig reagent **30**, giving exclusively the *trans*-alkene **31**. When reduced with diisobutylaluminum hydride, this compound gave the allyl alcohol **32**. Sharpless epoxidation conditions[5], using L-diethyltartrate, further transformed the molecule into the (S,R)-epoxyphenylpropanol **33**. Although α-arylepoxides are reputed to be unstable, this compound could be easily isolated. The epoxide was then opened using hydrogen fluoride in pyridine, resulting in the fluorodiol **34**. The diol was treated with 2-methoxypropene **35** and catalytic tosic acid to give dimethyloxirane **36**. It was also treated with tosyl chloride and pyridine to give the primary tosylate **37**, which could be separated from side products and treated with potassium carbonate to give the epoxide **38**. The last reaction gave insufficient product for further reactions.

2-Methyl-2-fluoro Tail

The 2-methyl-2-fluoro tail is rapidly becoming one of Displaytech's primary tails, due to its high polarization, chemical stability, and moderate pitch induction. This tail induces N* and C* pitches of opposite sign, making it useful for pitch compensation. In addition, this tail works particularly well with three-ring cores, which have high birefringence.

The 2-methyl-2-fluoro tail is made as shown in **Scheme 9**. The commercially available epoxide **39** reacts with silicon tetrafluoride[6] to give the fluorohydrin, which is then tosylated to **40** using toluenesulfonyl chloride. This tosylate couples with a phenol when mixed with cesium carbonate at high temperature, giving the ether **41**. If the intermediate fluorohydrin is instead oxidized to the acid, coupling to a phenol results in an ester.
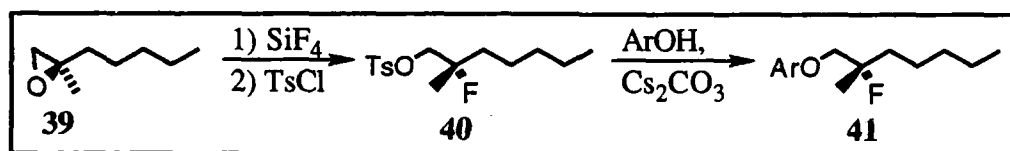
Scheme 9. Synthesis of 2-methyl-2-fluoro ethers.

2-Methyl-2,3-difluoro Tail

Since the 2-methyl-2-fluoro tail has been so useful for Displaytech, we decided to test its difluorinated analog, the 2-methyl-2,3-difluoro tail. This synthesis, shown in **Scheme 10**, starts with 2-hexyne **39**. Reduction with diisobutylaluminum hydride gives the aluminate, which can be lithiated with methyllithium. Subsequent treatment with paraformaldehyde gives the allylic alcohol **40**. Sharpless epoxidation using L-diisopropyl tartrate gives the S,S epoxide **44**. The tosylate can be made using tosyl chloride, and the tosylate is then coupled to a phenol to give the aryl ether **46**, which is interesting in its own right. The epoxide can be opened with hydrogen fluoride in pyridine, with the resultant fluorohydrin then being fluorinated with DAST to give the difluoride **47**.
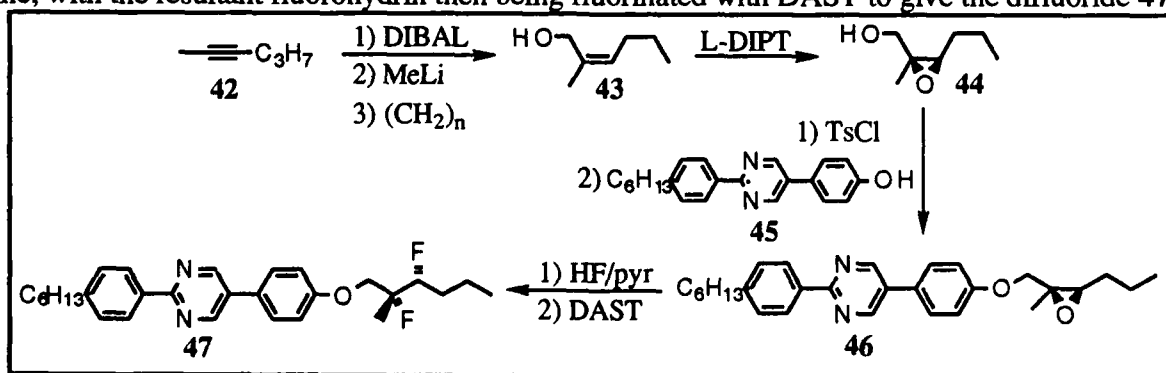
Scheme 10. Synthesis of the 2-methyl-2,3-difluoro tail

1-Methyl-2-cyano tail

Another potentially high polarization, tight pitch tail which we explored was the (R,R)-1-methyl-2-cyanopentoxy tail. This was made using Evan's[7] chiral auxiliary chemistry. The starting material was the pentanoic imide **48** of phenylmethyloxazolidinone (Xc), easily made from the chiral auxiliary and the acid chloride. Treatment with dibutylboron triflate converted this into the enolate, which stereospecifically reacted with acetaldehyde to give the alcohol **49**. This alcohol could be coupled with the phenol **12** using Mitsunobu conditions[8] to give the aryl ether **50**. The carbonyl group was then elucidated into the nitrile **51** using the following steps: hydrolysis to the acid using potassium hydroxide, conversion to the acid chloride using oxalyl chloride, conversion to the nitrile using ammonia in methanol, and finally dehydration to the nitrile **51** using phosphorus pentoxide.
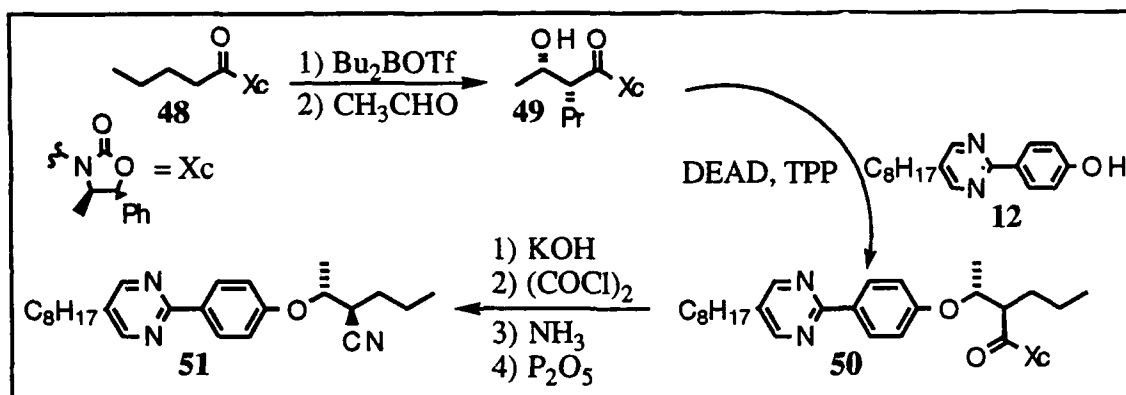
Scheme 11. Synthesis of the 1-methyl-2-cyano tail.

New Cyclohexyl-containing Tails

We have found that liquid crystals containing cyclohexyl and cyclohexenyl groups can amplify the pitch induction capabilities of chiral FLC dopants. Adding a moderate amount of cyclohexyl compound results in a tighter pitch mixture, or allows the same pitch while requiring less of the valuable chiral dopant. Thus, limited dopant solubility becomes less of a problem. The latter is particularly true for the cyclohexenyl compounds, which are significantly more soluble than cyclohexyl compounds when placed in low-temperature FLC mixtures. The synthesis of the cyclohexenyl compounds is outlined in **Scheme 12**.
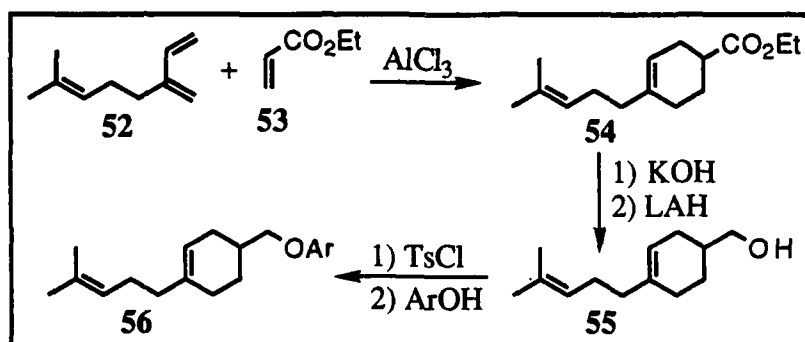
Scheme 12. Synthesis of cyclohexenyl ethers.

The starting material for the cyclohexenyl compounds is myrcene **52**. When combined with ethacrylate **53** in the presence of catalytic aluminum trichloride, Diels-Alder product **54** results. The cyclohexene is hydrolyzed to the acid and recrystallized, then reduced using lithium aluminum hydride to give alcohol **55**. The alcohol is then tosylated and coupled with a phenol to give the aryl

ether **56**. Alternatively, the acid resulting from the hydrolysis of ester **54** can be coupled to a phenol to give an aryl ester. A similar reaction scheme may also be done using isoprene as the starting material, in which case the Diels-Alder product has a methyl tail. Surprisingly, compounds with only a methyl group have been found to have properties quite similar to those with the much longer isopentyl group.
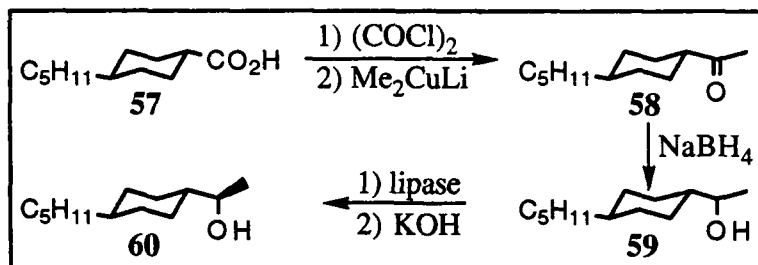
Scheme 13. Optically active cyclohexyl compounds.

The synthesis of one particularly interesting cyclohexyl tail is shown in **Scheme 13**. This tail is optically active, and gives materials with moderate polarization, tight N* pitch, and moderate C* pitch of the opposite sign. Thus, the material makes an excellent pitch compensating agent. The commercially available cyclohexyl acid **57** is used as the starting material. It is transformed into the acid chloride using oxalyl chloride, then turned into ketone **58** using methyl cuprate. Reduction with sodium borohydride gives the racemic alcohol **59**. Lipase-mediated esterification[9] can resolve the two enantiomers, giving either the ester or the leftover alcohol in very good enantiomeric excess, depending on the reaction conditions. Hydrolysis of the ester provides the optically active alcohol **60**.

Evaluation

Compounds Made in Phase II

Approximately 141 new compounds of various types were made in Phase II. They are shown in **Figures 3** through 15, grouped by general type of compound. Where known, the phase diagram and other figures of merit for each compound are given in the Table next to each Figure.

Achiral Host Materials

Figure 3 shows 19 new achiral host materials. Most of these new materials are specifically designed for high birefringence. **Table 2** shows the percent increase in birefringence of a mixture when 10% of the dopant was added. The starting birefringence of the mixture was in all cases about 0.150. We found that placing an alkenyl or alkynyl tail on an LC would slightly increase its birefringence, while often also increasing its mesogenicity. The top 14 compounds in **Figure 3** were synthesized with increased birefringence in mind. In particular, the linoleic tail used in **MDW705** and **MDW706** can increase both the birefringence and the width of the Sc phase. Some of the alkenyl compounds, such as **MDW605** and **MDW714**, were also intended to decrease the tilt angle of the mixture, for instances where a moderate tilt material is desired. Compounds with terminal trimethylsilyl groups, such as **MDW538**, are known to increase the width of the Sc phase. Indeed, **MDW538** was made from **MDW536**, and has an monotropic Sc phase over 25°C wider than its predecessor. This compound, along with the three compounds (**MDW536**, **MDW546**, and **MDW566**) with terminal alkene groups, also help promote S_A phases, which are useful for alignment purposes. The terminal fluorine in **MDW819** was intended to decrease the viscosity of the mixture. Other previously discovered compounds, not mentioned here, are also used in DHF host materials.
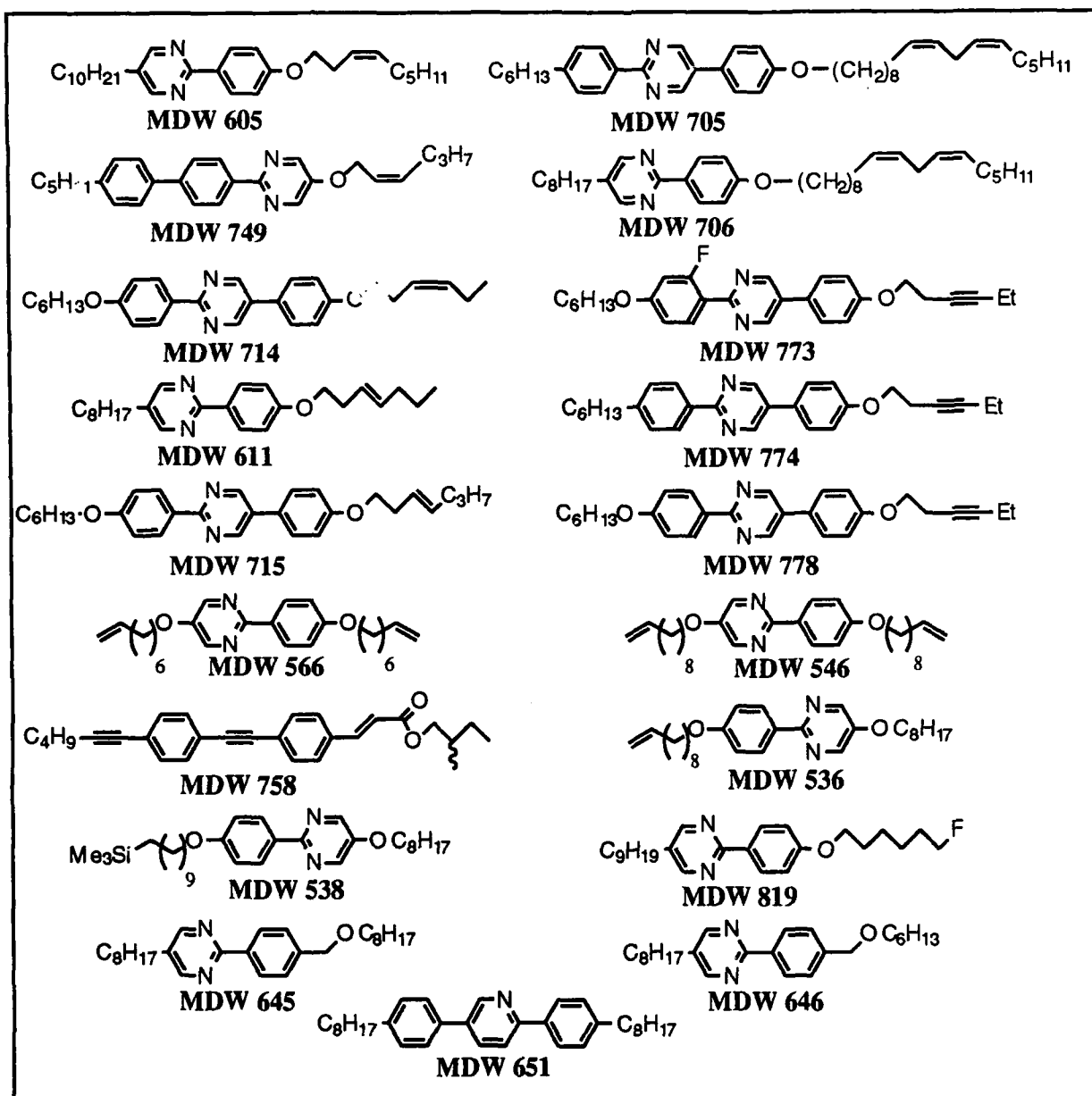
Figure 3. Difluoroalkoxy phenylpyrimidines and phenylpyridines.

Table 2. Phase sequence and change in birefringence of materials in Figure 3.

MDW #	Phase Sequence	$\Delta\Delta n$
536	I — 96 → A — 74 → C — 39 → X	
538	I — 95 → A — 83 → C — <RT → X X — 40 → C	
546	I — 94 → A — 80 → C — 34 → X X — 45 → C	1.3%
566	I — 86 → A — 57 → C — 35 → X X — 44 → C	
605	I — 49 → C — 6.3 → X X — 16.3 → C	
611	I — 36 → A ← 33 → X	

645	I — 30 → I X — 34 → I	
646	I — 20 → X X — 30 → I	
651	I — 75 → X X — 83 → I	
705	I — 146 → A — 143 → C — 85 → S? — 66 → X X — 112 → C	2.7%
706	I — 37 → A — 24 → C —	
714	I — 206 → A — 189 → C — 112 → X X — 122 → C — 189 → A — 206 → I	3.3%
715	I — 177 → N — 168 → C — 101 → X X — 120 → C — 168 → N — 177 → I	6.7%
749	I — 182 → N — 122 → C — 75 → X X — 118 → C — 122 → N — 182 → I	4.0%
758	I — 110 → X X — 119 → I	18.7%
773	I — 112 → N — 102 → X X — 130 → I	7.3%
774	I — 136 → A — 117 → C — 85 → X X — 108 → C	7.3%
819	I — 67 → N — 65.5 → A —	2.0%

Cyclohexyl and Cyclohexenyl Compounds

The dependence of a material's pitch on the choice of hosts, as reported in the Phase I final report, intrigued us and led to further exploration of the phenomena. We found that a particular non-chiral class of dopant, the cyclohexyl and cyclohexenyl ether and ester family shown below could significantly tighten the C* pitch of a material. This class of compounds had originally been used to broaden the N and C* phases of a material, so our discovery that they also tightened the C* pitch was fortuitous. The cyclohexyl group has been used by other researchers, but the cyclohexenyl groups are used solely by Displaytech. One advantage of the cyclohexenyl system is that it helps increase the miscibility of the mixture's other components.
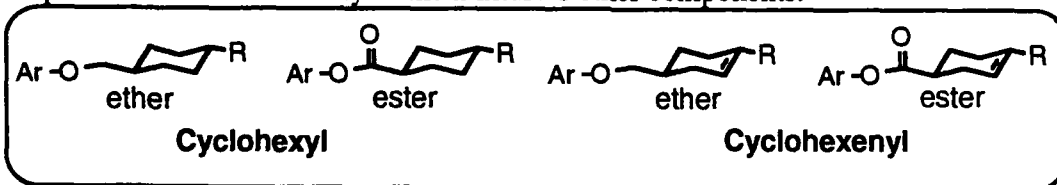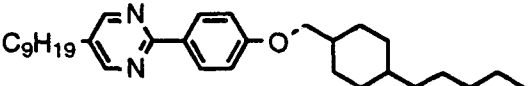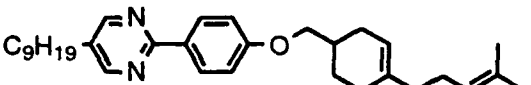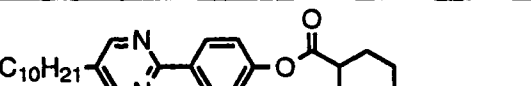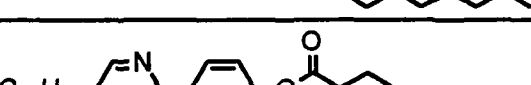
The effect of each of these ethers and esters on the C* pitch of a material was investigated. To do this, 20% of each compound was mixed into portions of a host material which contained a chiral dopant. The wavelength of light reflected by the C* helix of each mixture at 20° C was then measured. The results are summarized in **Table 3**.

We found that using the esters gave C* pitches about 16% tighter than the ethers, and the cyclohexyl compounds gave C* pitches about 18% tighter than the cyclohexenyl compounds. Thus, the cyclohexyl ester gave the tightest C* pitch, while the cyclohexenyl ether gave the longest C* pitch.

We also found that the cyclohexenyl compounds promote lower tilt mixtures, near an optimal 22.5°, and have a faster switching speed. This not only increases their functionality for DHFLC mixtures, but also makes them more useful for SSFLC mixtures.

Table 3. The pitch induction, speed, and tilt of the cyclohexyl series.

Name	Structure	C* pitch[a]	$\tau_{10\text{-}90}$, μsec[b]	θ°[b]
MDW 342	C₉H₁₉	0.37 μm	145	27.5
MDW 343	C₉H₁₉	0.44 μm	125	22.5
MDW 337	C₁₀H₂₁	0.30 μm	155	27
MDW 336	C₁₀H₂₁	0.38 μm	128	22.5

a. Results from mixtures of 20% compound in MX 6007 at 20 °C. MX 6007 is based on phenylpyrimidine dialkoxy compounds, and contains 25% phenylpyrimidine difluoroalkoxy dopants.

b. These measurements were taken with mixtures of 20% cyclohex(en)yl compound, 10% phenylpyrimidine difluoroalkoxy, and 70% MX 5343, a alkylalkoxyphenylpyrimidine mixture.

These materials also helped reduce crystallization at low temperatures. We compared mixtures containing the cyclohexyl or cyclohexenyl ethers and found that, at low temperature, the mixtures containing the cyclohexenyl ether were markedly more soluble. Thus, mixtures containing this dopant have a larger temperature range due to greater stability at low temperatures. Of course, even cyclohexyl compounds lower a mixture's freezing point — by using the compound **MDW502**, which has two cyclohexyls attached to a phenyl ring, we were able to make a mixture with a *freezing point of about -30°C.*

A further experiment was run to determine the cyclohexyl ester **MDW337**'s effect as a tight-pitch inducing agent. In this experiment, shown in **Figure 4** below, MDW337 was added at different concentrations into a host mixture. To that mixture was added 25% of a difluoroalkoxy mixture, to bring the final percent of **MDW337** to between 15% and 37.5%. The selective reflection of the mixtures was then measured at various temperatures, and the resulting wavelengths were converted to pitch data. The increasing concentration of **MDW337** clearly tightens the pitch, such that a mixture of 75% **MDW337** and 25% difluoroalkoxy has an extrapolated pitch of 0.23 μm at 35°, and a pitch of 0.14 μm at 20°C.
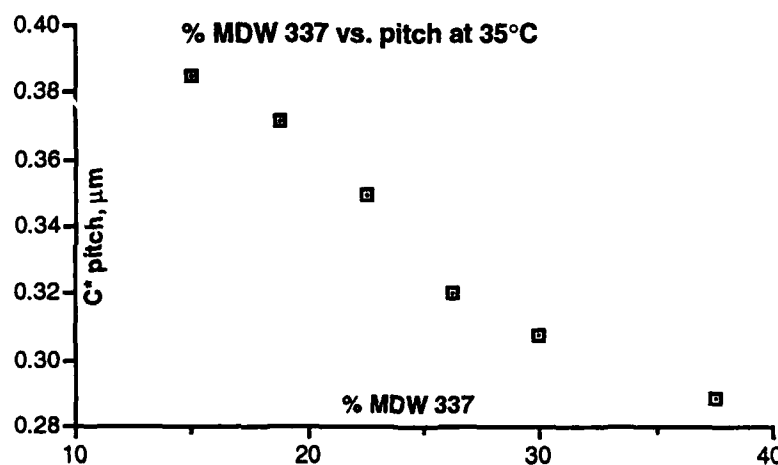
Figure 4. The effect of cyclohexyl ester concentration on a mixture's pitch.

Although only a chiral compound can induce a C* pitch in an FLC material, the data presented above clearly demonstrate that compounds containing a cyclohexyl or cyclohexenyl ring can have a synergistic effect, tightening the C* pitch far beyond what the difluoroalkoxy chiral dopant alone can do. Thus, a new set of non-chiral dopants opened a path towards tighter pitch, wider temperature range ferroelectric liquid crystal materials. They made a moderate pitch, extremely tight C* pitch material feasible.

Figure 5 shows ten new achiral compounds containing cyclohexyl rings. These compounds are mostly based on the phenylpyrimidine core, to which is attached either a cyclohexyl ether or a cyclohexyl ester. There are two special cases, **MDW514** and **MDW502**, in which two cyclohexyl esters are attached to a benzene ring. **MDW502** has been found to be particularly important, as it dramatically decreases the crystallization point of a mixture to less than -30°C. In addition, there are compounds in which a nitrile is attached directly to the cyclohexyl ring (**MDW513**) and which have a racemic 1-methyl group on the cyclohexyl ether (**MDW544** and **MDW545**). Attaching the nitrile gave a compound which was unusable due to high crystallinity and correspondingly low solubility in liquid crystals. However, groups containing the α-methyl group were deemed quite useful. Finally, there are three compound which contain cyclohexyl diethers (**MDW535, MDW541,** and **MDW542**). While these compounds were interesting, the synthetic route used to make them is not efficient enough for commercial use.
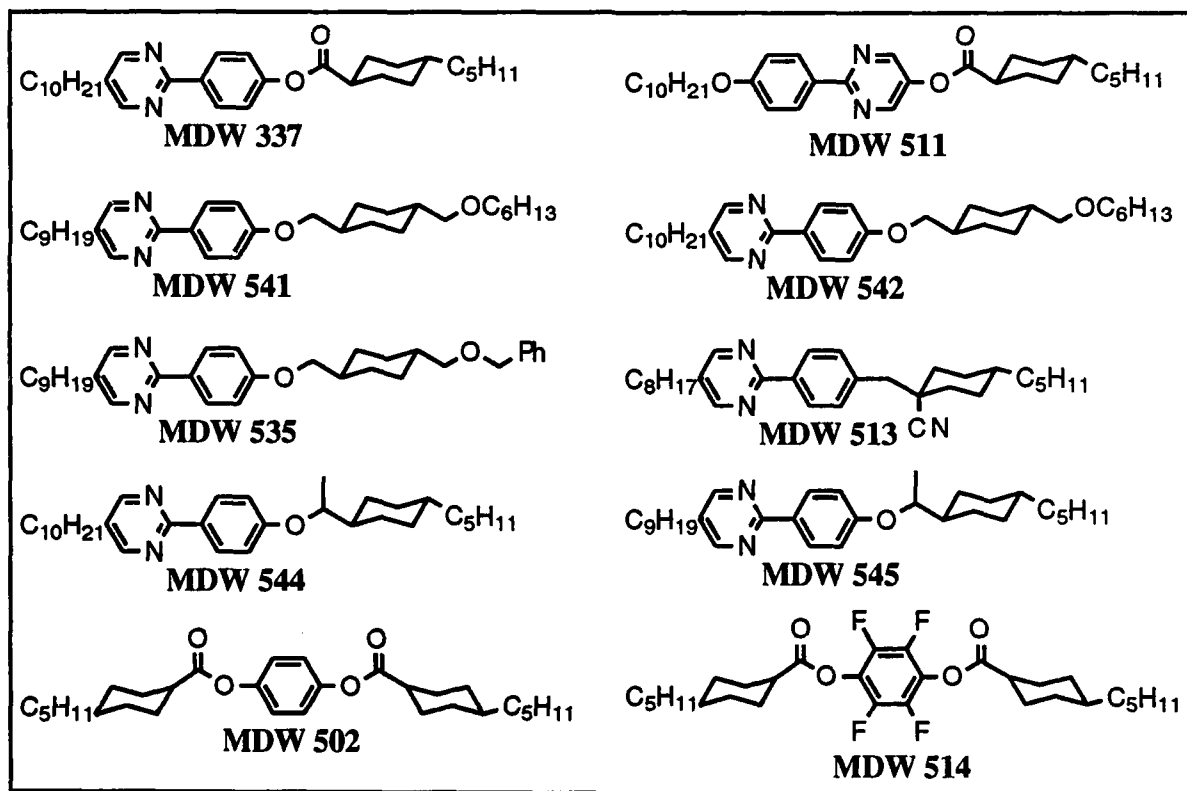
Figure 5. Achiral cyclohexyl compounds.

Table 4. Data from achiral cyclohexyl compounds.

MDW #	Phase sequence
337	I — 169 → N — 105 → C — 100 → X
502	I — 207 → N — 131 → SB — 40 → X
511	I — 197 → N — 185 → A — 57 → X
513	I —125 → X
	X — 112 → I

514	
535	
541	I — 105 → N — 93 → C — 83 → X
542	
544	I — 144 → N — 117 → C — 79 → X
545	I — 95 → N

Figure 6 shows the cyclohexenyl compounds made in Phase II. We found that cyclohexenyls are similar in pitch amplification to the cyclohexyls, but have increased solubility. Most of these cyclohexenyls are based mostly on the phenylpyrimidine core, although the phenylpyridine core was also used for one compound (**MDW555**). The octylcyclohexylphenyl core was also used (**MDW569** and **MDW571**), but was found to induce an unwanted smectic B phase. While most of the cyclohexenyl compounds had a 4-methyl-3-pentenyl tail (from synthesizing the cyclohexene using myrcene), the one compound made with just a methyl tail (**MDW576**, from synthesizing the cyclohexene using isoprene) had surprisingly similar FLC dopant properties.
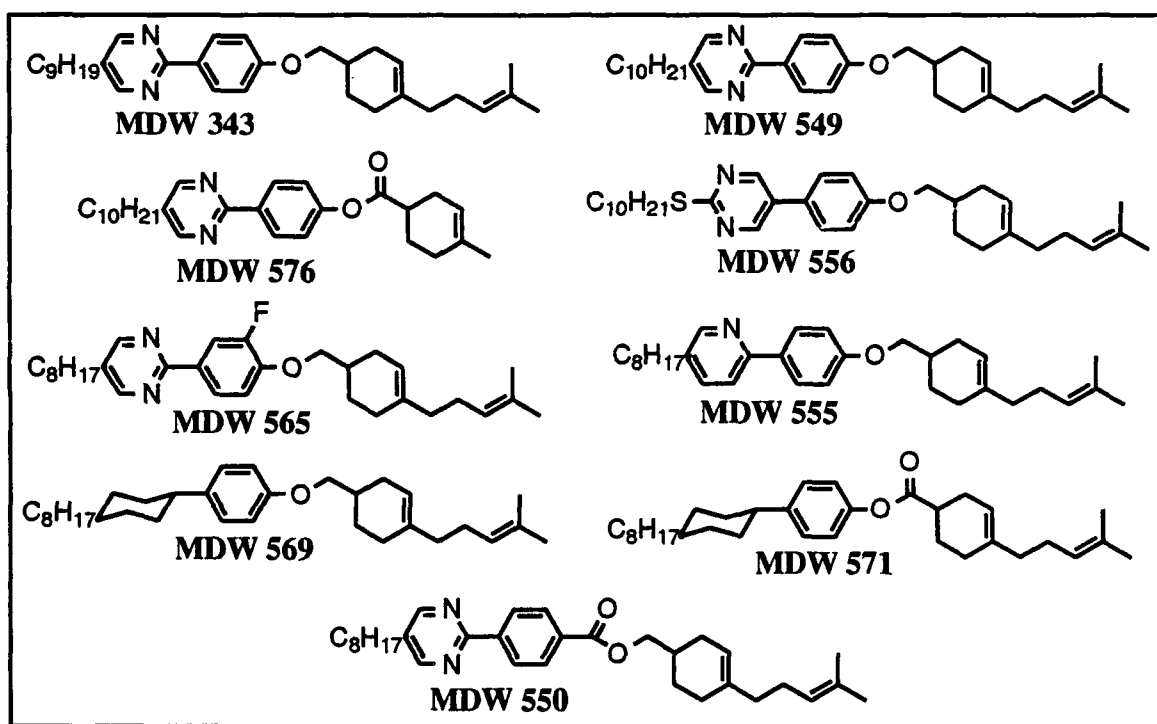
Figure 6. Achiral cyclohexenyl compounds.

Table 5. Phase diagrams for achiral cyclohexenyl compounds.

MDW #	FLC data, phase sequence
343	I — 100 → N — 89 → C — 32 → X X — 58 → C
549	I — 100 → N — 94 → C — 42 → X X — 51 → C
550	
555	I — 110 → C — 95 → X X — 97 → C
556	I — 89 → A — 74 → C — 68 → X X — 68 → C

565	I — 76 → N — 52 → C — 52 → X X — 72 → N
569	I — 98 → SB — <RT → X
571	I — 123 → SB — <RT → X
576	I — 107 → N — 68 → C — 45 → S? — 35 → X X — 50 → S? — 54 → C

If a chiral tail is necessary for a compound to induce pitch, and a cyclohexyl tail on a compound amplifies pitch induction, a compound made with a combination of the two systems (i.e., containing both a cyclohexyl tail and a chiral tail) should be a very good pitch-inducing agent. We have synthesized several members of this class of compounds, which are shown in **Figure 8**. Of these, one of the most interesting is **MDW533**, which has an epoxy tail on one end and a cyclohexyl ester on the other. This compound has a very tight negative C* pitch, but a tight positive N* pitch. The pitch behavior is shown in **Figure 7**. Thus, MDW533 can act as an internal pitch compensating agent, canceling out the rather tight negative N* pitch of the difluoroalkoxy phenylpyrimidines which we use as C* pitch inducing agents. Several other compounds, notably **MDW563, MDW826**, and **MDW836**, have similar behavior.
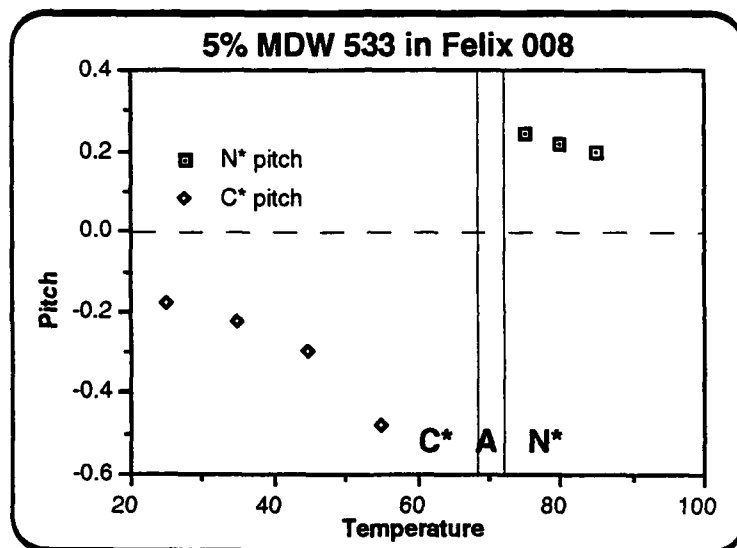
Figure 7. The N* and C* pitch of a mixture containing **MDW533**.

The 22 compounds shown in **Figure 8** possess a cyclohexyl or cyclohexenyl tail and also have a chiral tail. All compound in this **Figure** use the phenylpyrimidine core, with the exception of **MDW826**, which has a diphenylpyrimidine core. The chiral tails include citronellol tails (**MDWs 647, 698, 643**, and **700**), 1-methylheptyl tails (**MDW563** and **MDW562**), and 2-methylbutyl tails (**MDW743** and **MDW744**), all of which tend to give tight pitch but low polarization. There are four compounds (**MDWs 826, 827, 836**, and **837**) in which the cyclohexyl tail *is* the chiral tail. These were found to have C* pitch and N* pitch of opposite sign, making them good pitch compensating agents. Next, there are several compounds (**MDWs 533, 630, 636**, and **767**) with epoxide tails. Epoxides were shown in Phase I to be effective pitch tightening agents, although they had comparable N* and C* pitches. The two cis-epoxides (**MDW533** and **MDW767**) proved to have C* and N* pitch of opposite sign, making them useful pitch compensators. The most effective DHF tail in Phase I was the difluoroalkoxy tail, due to its low viscosity, tight C* pitch, and moderate N* pitch. Four new compounds were made combining the difluoroalkoxy tail with a cyclohexyl or cyclohexenyl group. These compounds, **MDWs 497, 564, 527**, and **648**, showed the expected tight C* pitch, and also showed S_B and S_A phases. In fact, the latter two were quite effective S_A phase inducers, which limited their usefulness as DHF dopants.

Lastly, two compounds (**MDW575** and **MDW661**) were made which had methylfluoro tails. The methylfluoro tail induced C* and N* pitches of opposite signs, and the pitches were particularly tight when combined with a cyclohexyl ring on the same compound. The latter compound strongly induced S_A phases in mixtures.
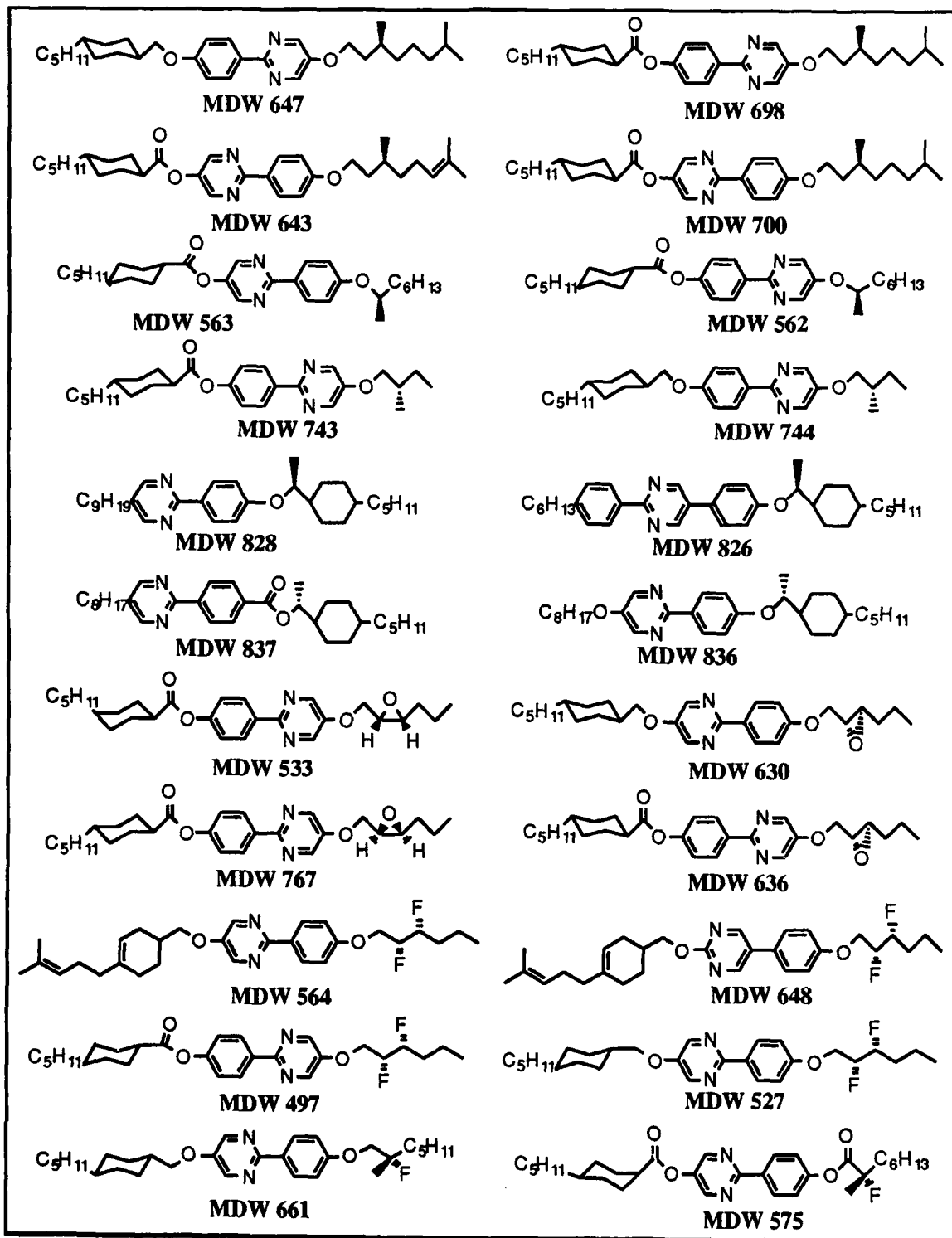
Figure 8. Chiral cyclohexyl compounds.

Table 6. Data from chiral cyclohexyl/cyclohexenyl compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
497	I — 203 → N — 129 → SB — 110 → X X — 115 → SB — 129 → N — 203 → I	-74	-0.3	
527	I — 173 → A — 120 → X X — 138 → A			
533	I — 146 → N — 82 → X X — 89 → N	-160	-0.48	+0.28
562	I — 107 → N — 55 → X X — 64 → N — 107 → I			+0.37
563	I — 132 → A — 25 → X X — 44 → A — 132 → I		-0.48	+0.37
564	I — 109 → A — 108 → SB — 100 → X X — 105 → SB — 120 → X			
575	I — 183 → A — 115 → C — 50 → X X — 95 → C — 115 → A* — 183 → I			
630	I — 190 → N — 187 → A — 87 → X X — 128 → A — 187 → N* — 190 → I			
636	I — 205 → N — 125 → SB — 120 → X X — 132 → N — 205 → I			
643	I — 181 → N — 158 → A — 60 → SB — 57 → X X — 68 → A — 158 → N* — 181 → I		+, long	+0.24
647	I — 153 → A — 65 → X X — 87 → A — 153 → I		+1.9	+0.30
648	I — 102 → A — 65 → X X — 95 → A — 102 → I			
661	I — 138 → A — 85 → X X — 107 → A — 138 → I			
698	I — 148 → N — 82 → SB — 70 → X X — 81 → SB — 83 → N — 148 → I		+0.3	+0.2
700	I — 203 → N — 185 → A — 62 → X X — 82 → A — 185 → N — 203 → I			
743	I — 175 → N — 115 → X X — 126 → N — 175 → I		-1.84	
744	I — 139 → N — 115 → X X — 124 → N — 139 → I		-2.2	
767			+1.26	negative
826	I — 161 → A — 74 → X X — 76 → A	-12	-0.2	+0.08
828	I — 35 → N — 23 → X X — 40 → I	-10		
836	I — 58 → N — 26 → X X — 48 → N	+17	+0.15	-0.07
837	I — 81 → A* — 81 → X X — 88 → I			

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

Other Chiral Compounds

Epoxide tails were used extensively in Phase I of this project to make DHF materials. Several materials with new configurations of epoxides are shown in **Figure 9**. Among them are cis-epoxides such as **MDW766**, which had C* and N* pitches of opposite signs, making them good

pitch compensators. The trans-epoxy esters such as **MDW777** had much tighter N* than C* pitch, making them undesirable for use in DHF materials. One of the compounds, **MDW784**, was reported[10] to have extremely high polarization. Our findings were that the compound had at best moderate polarization. In fact, the epoxides in general had only moderate polarizations.
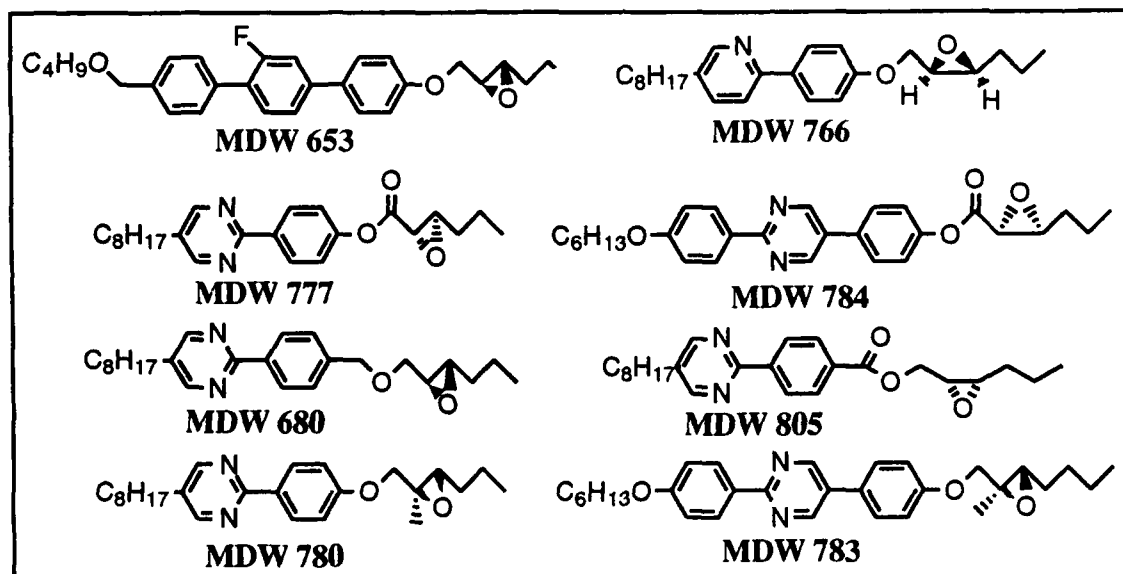
Figure 9. Epoxides made in this project.

Table 7. Data from epoxide compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
653	I — 163 → A — 140 → C	46.4*		
680	I — 21 → X X — 40 → I			
766	I — -3.7 → X X — 36.9 → I	+30	+0.3	-0.2
777	I — 45 → X X — 68 → I	-160.2	-0.2	-0.09
780	I — 7.2 → X X — 40.5 → I	+54.3		
783	I — 166 → A — 155 → C — 105 → X X — 115 → C	+30.6	-V. long	-1.0
784	I — 150 → A — 110 → X X — 133 → N/A — 152 → I	-76.2		-0.5
805	I — 48.5 → A — 47 → X X — 65 → I	-160.8	-0.3	

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

Table 8 presents eight new 2-fluoroalkoxy compounds. These materials contain phenylpyrimidine cores with either alkyl or alkoxy tails attached to the pyrimidine ring, and (S)-2-fluoroalkoxy tails of varying lengths on the phenyl ring. The (S,S)-2,3-difluoroalkoxy tails had proven to be excellent compounds for use in DHF materials, so the monofluorinated analogs appeared to be natural alternative targets for synthesis. In fact, the monofluorinated compounds were much less useful, since the alkylalkoxy materials had N* pitch only about twice as long as the C* pitch, and the dialkoxy materials had an N* pitch which was tighter than the C* pitch.
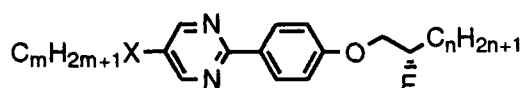
Table 8. Data from a series of fluoroalkoxy compounds

MDW	m	n	X	Phase sequence	Ps	C* pitch	N* pitch
788	8	6	-		-93	-0.47	-0.74
789	10	6	-	I — 68 → A — 54 → C — 44 → X X — 55 → A	-68.5	-0.51	-1.265
802	8	6	O	I — 93 → A —74 → C* — 48 → X X — 69 → C*	-60	-0.8	-0.65
795	10	6	O	I — 97 → A —88 → C — 48 → X X —60 → C	-58	-0.4	-0.26
793	8	8	-	I —61 → X X — 74 → I	-89	-0.4	-0.62
792	10	8	-	I — 70 → A — 66 → C — 56 → X X — 64 → C	-76	-0.17	-0.7
801	8	8	O	I —95 → A — 78 → C* — 54 → X X —73 → S? —76 → C*	-64	-0.5	-0.6
794	10	8	O	I — 99 → C — 57 → X X —75 → C	-47	-0.6	-0.25

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

Four other fluoroalkoxy compounds are presented in **Figure 10**. These materials also had moderate polarization, and also had long C* pitch, making them unsuitable for use as the primary DHF dopant. Where most of the materials presented in **Figures 7** and **8** have C* pitch comparable to the N* pitch, it is interesting to note that the N* pitch of **MDW786** is far longer than C* pitch of the material. This is due to the two fluorines on the ring closest to the chiral tail. These materials all had an unidentified smectic phase.
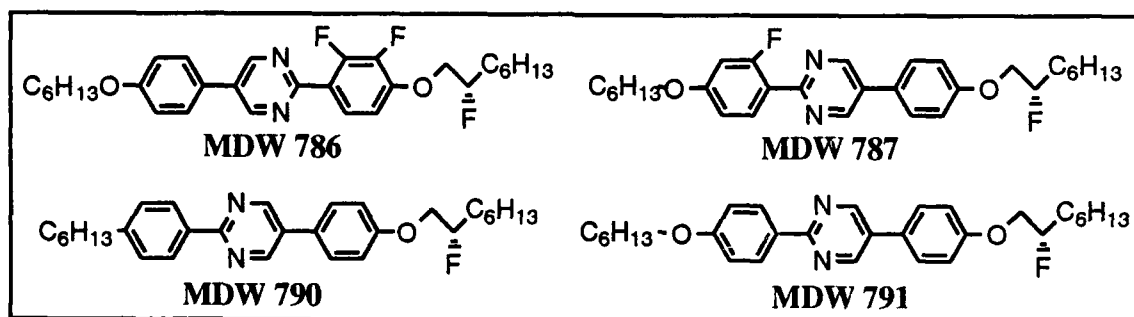
Figure 10. Other fluoroalkoxy compounds

Table 9. Data from other fluoroalkoxy compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
786	I — 182 → A —136 → C — 82 → S? — 57 → X X —76 → S? — 94 → C	-30.3	-0.82	-V. long
787	I —171 → N — 162 → C —66.4 → S? — 60.9 → X X — 85 → C	-101.8	-0.3	-0.3
790	I — 196 → A — 163 → C —123.8 → S? — 64.8 → S? — 44 → X X — 86.5 → S? —124 → C	-66.3	-1.8	

| 791 | I — 200.8 → A —190 → C — 120.7 → S? — 81.5 → S? — 80.4 → X X — 102.8 → S? — 105.8 → S? — 112.7 → C | -82 | -0.36 | |

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

The difluoroalkoxy compounds are the primary chiral dopant for many of Displaytech's mixtures, due to their high polarization, chemical stability, and interesting pitch characteristics. One of the most interesting findings from Phase I was that the difluoro compounds' C* pitch was about three times as tight as their N* pitch. One can see from the data in **Table 10** that this finding holds true in several different series of difluorides. Another interesting finding was that the N* and C* pitch depended heavily on the particular host material used. This accounts for the differences in the pitch magnitude of the first five and the last seven entries in the **Table**.
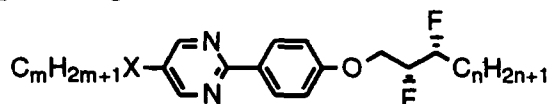
$$C_mH_{2m+1}X \diagdown\diagup N \diagup\diagdown N \diagdown\diagup O \diagdown\diagup \overset{F}{\underset{F}{|}} C_nH_{2n+1}$$

Table 10. Data from a series of difluoroalkoxy compounds

MDW	m	n	X	Phase sequence	Ps	C* pitch	N* pitch
198	6	3	-	X — 89 → I	-256		
206	7	3	-	X — 85 → I	-240	-.21	
232	8	3	-	X ← 84 → I	-230	-.23	-.7
116	9	3	-		-170	-.095	-.45
128	10	3	-		-144	-.21	
798	6	5	-	X ← 92 → S? ← 100 → I	-204	-0.12	-0.196
800	7	5	-	I —95 → X X — 104 → I	-204	-0.12	-0.4
797	8	5	-	X ←102 → I	-207	-0.15	-0.4
799	9	5	-	I — 92 → X X — 100 → I	-169	-0.17	-0.5
796	10	5	-	I — 88 → X X — 96 → I	-160	-0.17	-0.4
428	8	3	O	I — 84 → X X — 93 → I	-159	-0.15	-0.36
803	8	5	O	I — 99 → SB ← 85 → X	-124	-0.14	-0.4

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

Thirteen other two-ring difluoroalkoxy compounds were made during the course of this project, and are presented in **Figure 11**. We discovered in Phase I that, when the FLC core was fluorinated ortho to the difluoroalkoxy tail, the C* pitch was not dramatically altered, but the N* pitch greatly increased in length. Adding a second fluorine in the meta position further altered the N* pitch, changing it from a long negative pitch to a moderate positive pitch. Thus, two compounds with difluoroalkoxy tails, one with an unfluorinated core, one with a difluorinated core, could give a mixture with very tight C* pitch but infinitely long N* pitch. This N* pitch progression can be seen in the pitches of compounds **MDW510, MDW584,** and **MDW585**.

Most of the difluoroalkoxides were ultimately made from epoxides made using Sharpless' procedure[11]. However, four of these compounds were instead made using a enantioselective diolization procedure also discovered by Sharpless[12]. The first two of these materials, **MDW650** and **MDW776** are enantiomers. As expected, they have identical properties, except that the polarization and pitch have opposite signs. In these materials, the tail fluorines are one more carbon removed from the core, being in the 3,4 positions rather than the 2,3 positions. This leads to compounds with about half the polarization, tighter N* than C* pitch, but much higher solubility. The higher solubility means that more of these compounds can be included in the final mixture, certainly an appealing proposition. The other two 3,4-difluorides (**MDW768** and **MDW769**) have

one less carbon in the tail. These materials are diastereomers, made to demonstrate that compounds with a *syn*-difluoro tail have high polarization than compounds with an *anti*-difluoro tail. This indeed turned out to be the case.

The only two-ring difluorides with Sc phases are also included in this **Figure**. These materials, the terminal alkene **MDW548** and its trimethylsilyl daughter compound **MDW554**, have moderately wide Sc phases, particularly the alkene with its enantiotropic Sc phase.
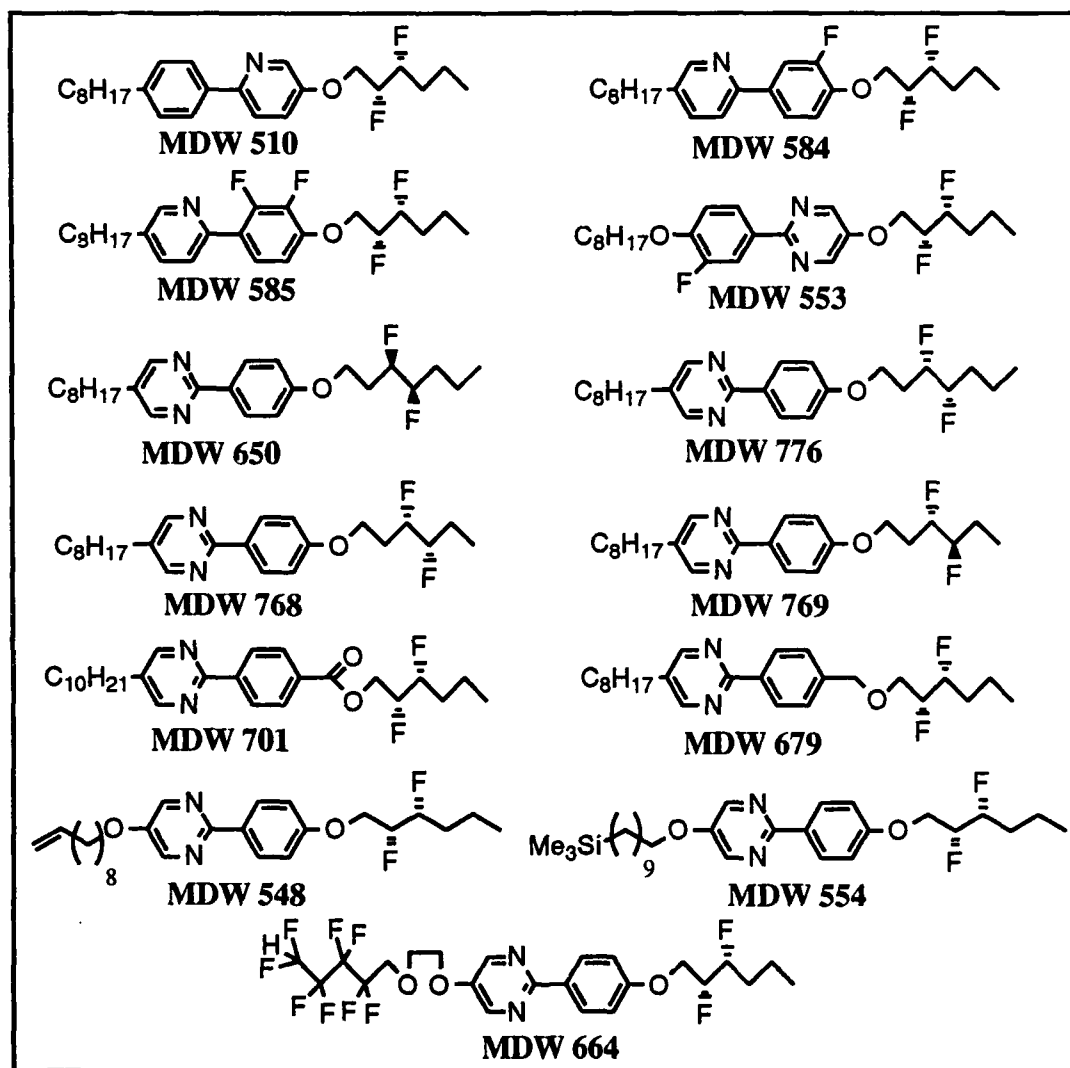
Figure 11. Other two-ring difluoroalkoxy compounds.

Table 11. Data from other two-ring difluoroalkoxy compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
510	I — 85 → X X — 86 → I	-279	-0.125	-0.6
548	I — 89 → A — 74 → C — 58 → SB — 54 → X X — 62 → SB — 78 → C* — 80 → A — 89 → I	-155*		
553		-188		
554	I — 90 → C* — 60 → X X — 96 → I	-224*		

584	I — 37 → A — 34 → X X — 43 → I	-179	-0.12	-4.25
585	I — 20.0 → X X — 53 → I	-142	-0.21	+1.2
650	I — 48 → A — 38 → X X — 58 → I	+124	+0.26	+0.133
664	I — 73 → X X — 88 → I	-57		
679	X — 48 → I I — 20.0 → X	-37		
701	I — 74 → X X — 79 → I	-80		+0.2
768	I — 50.1 → N — 48.7 → A — 10 → X X —51.6 → I	-90	-0.25	-0.15
769	I — 51 → N —47 → A — < -10 → X X — 44.5 → A	No Ps		
776	I — 48 → A — 38 → X X — 58 → I	-124	-0.26	-0.133

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

There were also ten new three-ring difluoroalkoxides made during Phase II. These new compounds are shown in **Figure 12**. Virtually all of them have Sc phases, some as wide as 118° including supercooling (**MDW597**). They also have increased birefringence ($\Delta n = 0.161$ for **MDW606**, while $\Delta n = 0.155$ for **MDW664**, a two-ring compound from **Figure 11**). The N* pitch trend seen in the difluorinated-core two ring compounds does not hold as strongly in the three-ring compounds, it seems: although the C* pitch of **MDW655** and **MDW649** is -2, the N* pitch of **MDW655** is very long negative rather than positive, and the N* pitch of **MDW649** is actually moderate negative.

Table 12. Data from three-ring phenylpyrimidine compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
596				
597	I — 200 → C — 82 → X X — 135 → C			
606	I — 201 → A — 164 → C — 126 → X X — 142 → C — 164 → A* — 201 → I	-122		
622	I — 200 → A — 191 → C — 135 → X X — 160 → C — 191 → A* — 200 → I			
623	I — 183 → N — 160 → C — 94 → X X — 126 → C — 160 → N* — 183 → I	-126	-0.26	
649	I — 144 → A — 122 → C — 92 → S? — 82 → X X — 96 → C — 122 → A* — 144 → I	-175*	-0.2	-1.02
654	I — 122 → A — 100 → X X — 120 → A — 122 → I			
655	I — 182 → A — 136 → C — 94 → S? — 90 → X X — 117 → C — 136 → A — 182 → I	-82	-0.2	-7.6
687	I — 185 → A — 154 → C — 116 → X X — 123 → S? — 128 → C → 154 → A — 185 → I			
775	I — 187 → A — 145 → C — 110 → X X — 127 → C	-100.3*	-V. long	

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.
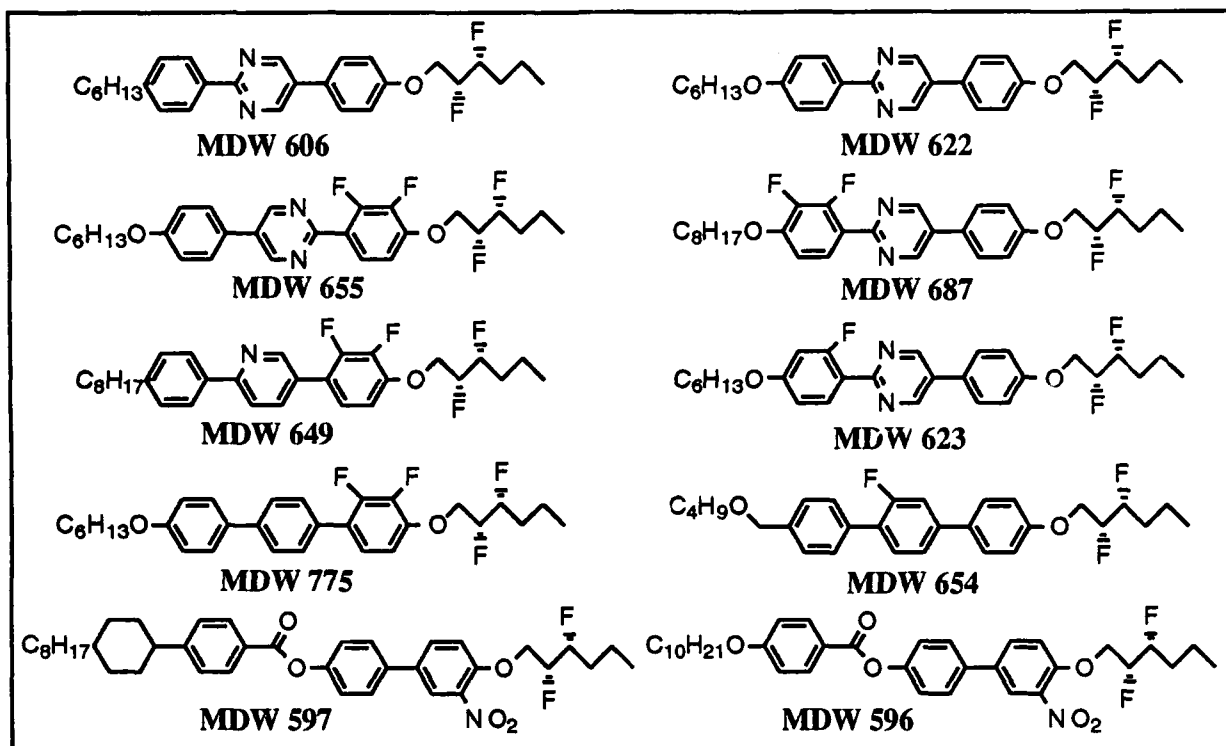
Figure 12. Three-ring difluoroalkoxy compounds.

The 2-methyl-2-fluoro tail is quickly becoming one of Displaytech's preferred tails for use in liquid crystal materials. Thirteen new materials possessing this tail are presented in **Figure** 13. Almost all of these materials have a Sc phase, even the two-ring compound **MDW746**. This tail affords compounds with high polarization, excellent chemical stability, moderate to tight negative C* pitch, and positive N* pitch. Thus, the methylfluoro compounds can be used as pitch compensators for the difluoro compounds. Whereas in the difluoroalkoxides, difluorinating the core gave a reversal of the N* pitch's sign, in the methylfluoroalkoxides the C* pitch's sign is reversed. Thus, other methylfluorides have negative C* pitch, but **MDW652** and **MDW771** have positive C* pitch. The sign of the N* pitch can be reversed by making the ester, such as in **MDW703** and **MDW704**, which both have negative N* pitch.

Table 13. Data from methylfluoroalkoxy compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
601	I — 126 → C — 85 → S? — 65 → X X — 74 → S? — 94 → C — 126 → I	-151		
607	I — 152 → C — 85 → X X — 102 → C — 152 → I	-445	-0.8	+1.25
624	I — 128 → C — 120 → X X — 120 → C — 128 → I	-196	-0.4	+0.56
628	I — 99 → C — 98 → X X — 107 → I	-64	-0.5	+0.8
652	I — 79 → C — 34 → X X — 68 → C	-34	+0.2	+0.25
657	I — 143 → C — 95 → S? — 50 → X X — 103 → C — 143 → I	-118		
662	I — 152 → A — 102 → C — 52 → X X — 94 → C — 102 → A — 152 → I		-0.36	

686	I — 116 → C — 106 → X X — 126 → I			
702	I — 116 → A — 85 → C — 51 → X X — 74 → C — 85 → A — 116 → I	-35		+ long
703	I — 92 → N — 70 → X X — 85 → N — 92 → I	-116	-1.1	-1.3
704	I — 105 → N — 108 → S? — 64 → X X — 78.5 → S? — 108 → N — 105 → I	-115	-0.85	-0.73
746	I — 130.5 → A — 126 → C — 89 → S? — 87 → X X — 125 → C — 126 → A — 130 → I			
771	I — 124.5 → C — 55.5 → S? — 54.5 → X X — 86.9 → C	-33.4	+0.2	+2.4

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.
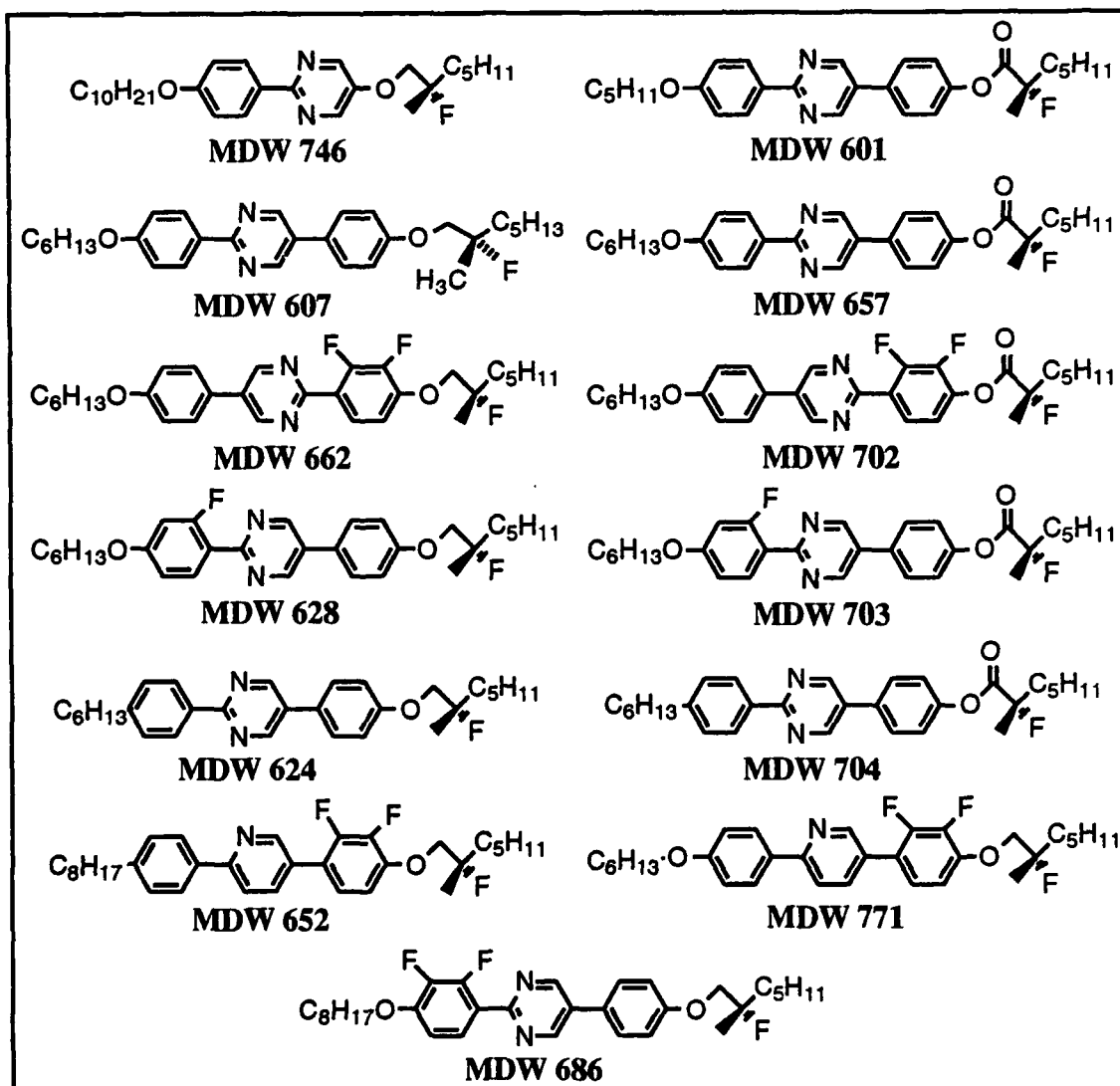

Figure 13. Methylfluoroalkoxy compounds

We found in Phase I that tight pitch compounds can be made by attaching two chiral tails to a core. The compounds **MDW814** and **MDW829** were found to be only sparingly soluble in other liquid crystals, and so could be only partially tested. However, they both had tight N* pitches,

indicating that they would not be optimal DHF dopants. The compounds **MDW781** and **MDW782** had tighter N* pitch than C* pitch, making them undesirable as DHF dopants. The compounds **MDW685** and **MDW692**, both citronellol derivatives, so greatly suppressed the Sc phase that they were not extensively tested. **MDW557** had a wide S_A phase, and could be used to induce that phase in mixtures. Aside from **MDW557**, none of the double-tailed compounds was found to be particularly usable in DHF mixtures.
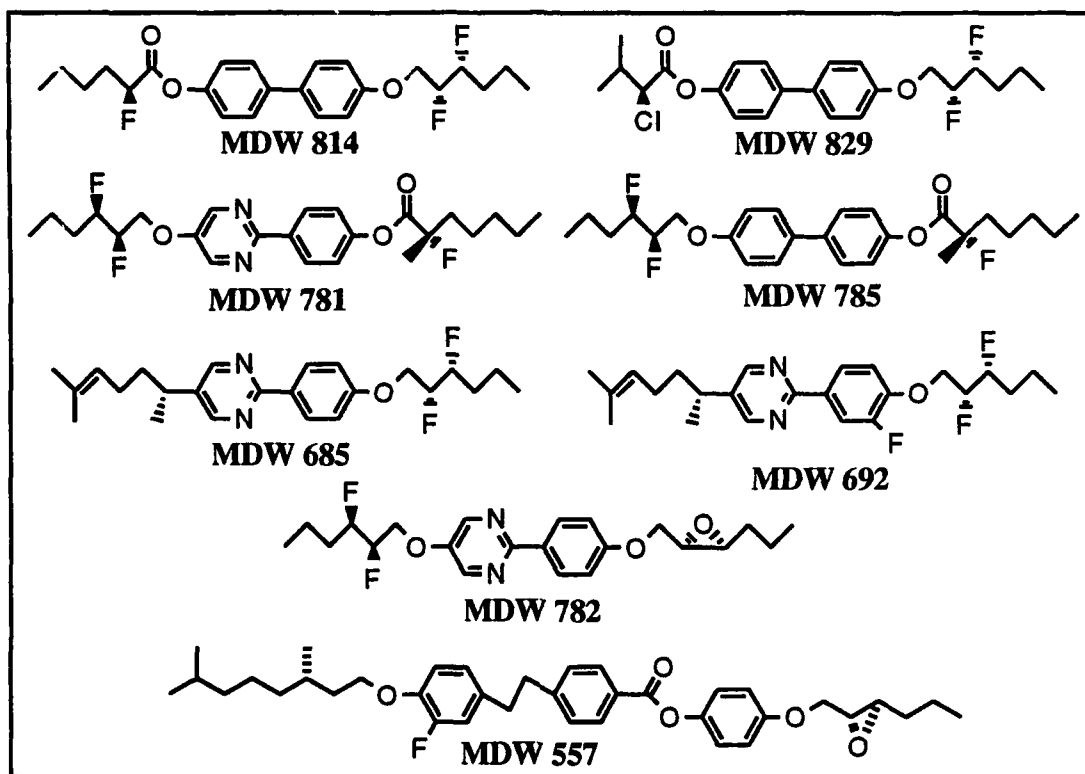
Figure 14. Compounds with two chiral tails.

Table 14. Data from compounds with two chiral tails.

MDW	Phase sequence	Ps	C* pitch	N* pitch
557	I — 133 → A — 77 → C — 55 → X X — 85 → A			
685		-138		
692	I — -20 → X			
781	I — 76 → X X — 87 → I	-24.2	-1.6	-0.1
782	I — 65 → X X — 79 → I	-56	-0.4	-0.12
785	I — 67 → X X — 98 → I	-98.6		-0.6
814	I — 126 → X X — 132 → X	-200		-0.12
829	I — 85 → S? — 75 → X X — 75 → S? — 90 → I	-264		-0.25

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

There were several compounds which did not fall into any previously defined category, which are presented in **Figure 15**. These miscellaneous compounds include three made from the Sharpless diol mentioned in the introduction to **Figure 11**. These three compounds, **MDWs 688, 689**, and **707**, are dioxolane ethers.
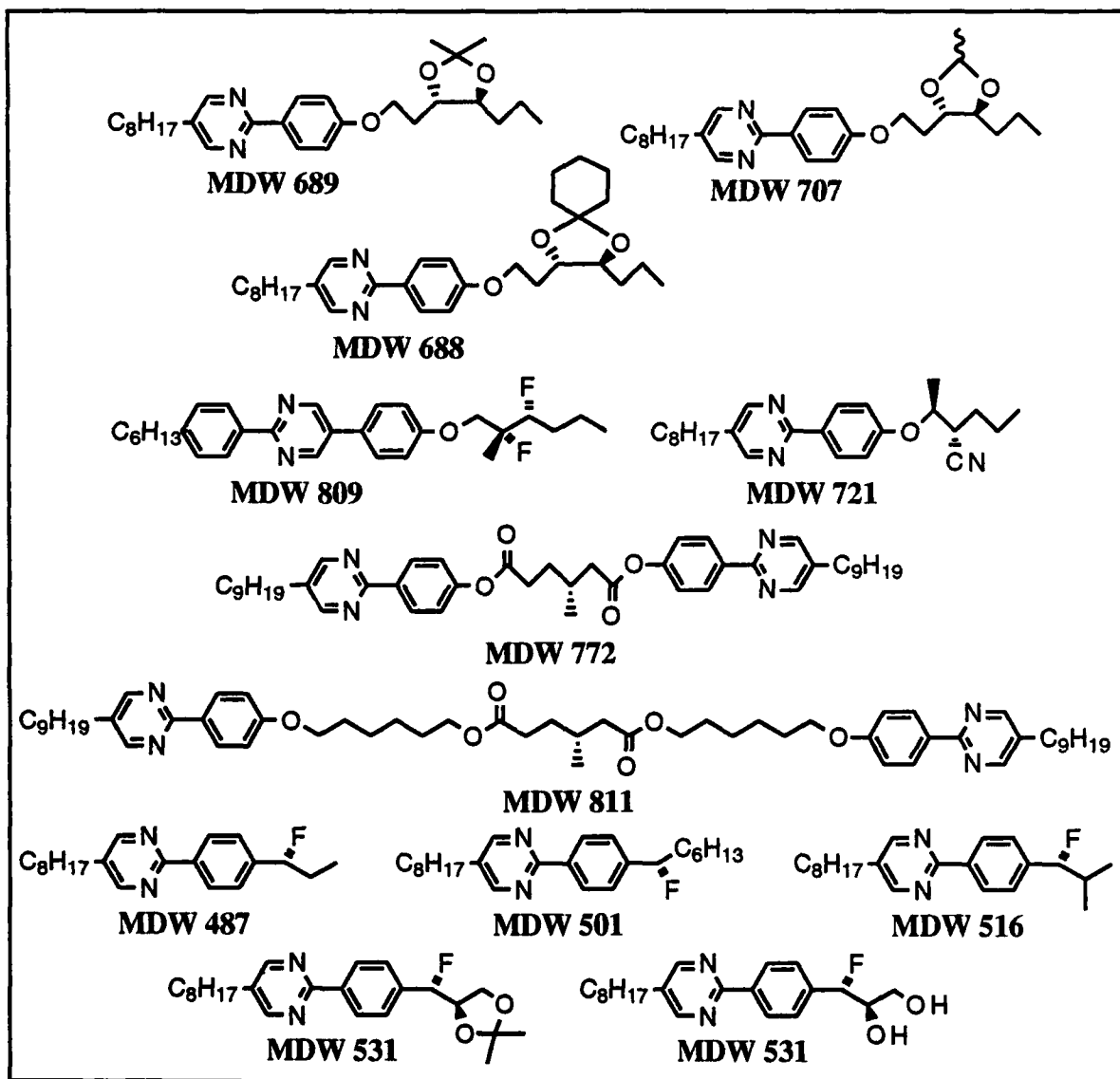
Figure 15. Miscellaneous compounds.

One very unusual compound containing two cores and one chiral tail was made. This compound[13], **MDW772**, appeared to straddle FLC layer boundaries, having cores in two different layers at one time. It had a tight C* pitch. Since we believe that a material's C* pitch is a result of molecules migrating from one layer to the next, having a chiral center near the layer boundary seemed to be an ideal pitch-inducing strategy. However, as this particular compound tended to suppress the Sc phase of a mixture, a compound with longer spacers between the core and the chiral group was designed. This new compound, **MDW811**, proved to have low polarization, long C* pitch, and long N* pitch. Thus it appears that the chiral center should be more rigid than is possible in a compound such as **MDW811**, with its long "floppy" spacers. The compound **MDW721** has an unusual structure, which apparently prevented it from adequately dissolving in

other liquid crystals, making measurements difficult. The five fluoroalkyl compounds, **MDWs 487, 501, 516, 531,** and **534,** had no spontaneous polarization, and so were not further tested.

Table 15. Data from miscellaneous compounds.

MDW	Phase sequence	Ps	C* pitch	N* pitch
487	I — 53 → A — 52 → S? — 51 → X			
501	I — 37 → A — ? → X			
516	I — <RT → X X — 40 → I			
531				
534				
688			- v long	- v long
689			- v long	- v long
707	I — 54 → X X — 55 → S? — 64 → I		+0.4	+0.95
721		-13		
772	I — 111.5 → S? — 54.5 → X X — 83.7 → S?		-0.1	
809	I — 96 → C* — 59 → X X — 66 → C*	-46	-1.8	+3.5
811	I — 36 → C* — -9 → X X — -8 → C* (X — 47 → I)	v. low	V. long	V. long

Ps (polarization) is extrapolated unless marked by *, where the neat material was used.

New mixtures

There were two general types of new mixtures made for this project: moderate tilt and high tilt. The moderate tilt materials had tilts of about 20-30°, and generally had an I-A-N-C phase sequence. The high tilt materials had tilts of about 45°, and generally had an I-N-C phase sequence. Several mixtures of each type were prepared. Some of the best representatives of each class are listed in **Table 16.** Also included in this Table is the Roche material **H 5679,** the only commercial DHF mixture. Note that all of the Displaytech mixtures have C* pitches which are significantly tighter than that of the Roche material.

Table 16. New DHF mixtures.

MX #	Tilt	Phase diagram	N* pitch	C* pitch	rise time	Ps
Roche		I — 62 → A — 60 → C — 5 → X	NA	-0.35		
6286		I — 104 → N — 73 → A — 71 → C — -4 → S_X	∞	-0.15		
6232	29	I — 99 → N — 78 → A — 73 → C — <RT → X	-30	-0.23	300	72
6442		I — 99 → N — 78 → A — 75 → C — <RT → X	-30	-0.15		-112
6447	32	I — 99 → N — 72 → A — 69 → C — <RT → X	-80	-0.13		-97
6307		I — 92 → N — 68 → C — <RT → X		-0.27		
6340	44	I — 90 → N — 66 → C — <RT → X		-0.16		
6440	44	I — 92 → N — 65 → C — <RT → X		-0.19	320	-120

The mixture **MX 6286** is made up of 35.4% cyclohexyl/cyclohexenyl compounds and 25.8% difluoroalkoxy compounds. (There is some overlap due to some of the multifunctional compounds used in the mixture.) It has a C* pitch twice as tight as the only commercial mixture, or half again as tight as the Phase I mixture. Its N phase, not present in the La Roche material, allows alignment. It has a C phase almost 20°C wider than the La Roche material. A cell made with **MX 6232** showed a contrast ratio of over 260:1.

Of the four N-A-C materials shown, two have C* pitch shorter than 0.15 μm at room temperature. Likewise, two of the three N-C materials also have C* pitch shorter than 0.2 μm at room temperature. It should be noted that the pitch of a material is measured by dividing the wavelength of light selectively reflected from it by its mean birefringence. Since the lowest wavelength of reflected light our detector can measure is 450 nm, which corresponds to a C* pitch of 0.29 μm, the actual pitch at room temperature must be extrapolated from pitches measured at higher temperature.

Material evaluation in DHF cells

Several DHF cells were made and extensively evaluated. They include cells using the new mixture **MX 6440**, which is a high tilt material that has a C* pitch of -0.1 at room temperature. The voltage versus tilt angle for the material is shown in **Figure 16**. It can be seen that the voltage and tilt angle are linearly related, with a higher applied voltage translating to a higher tilt angle. If a higher frequency is used, a higher voltage is required to attain the same tilt angle. The maximum attainable tilt angle is approximately 40°.
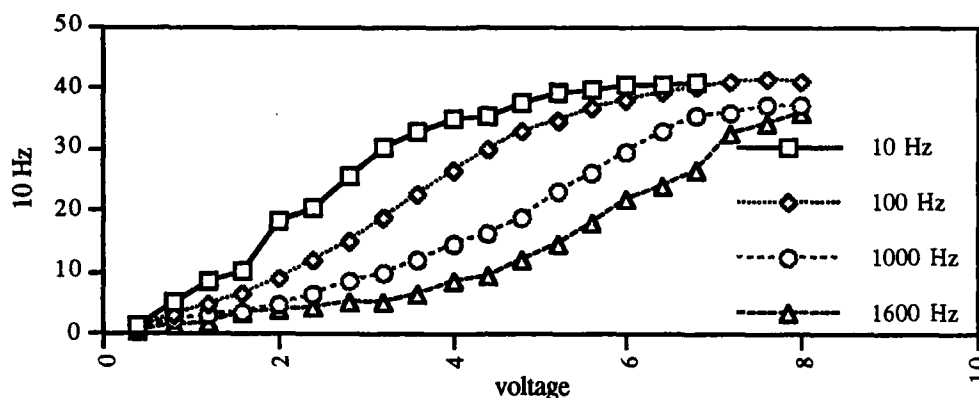

Figure 16. Tilt vs. voltage for an MX 6440 cell.

Figure 17 shows a slightly different voltage vs. tilt angle comparison, using **MX 6442** (labeled DTI) and Hoffman La Roche's experimental material **H 6300** (labeled HLR). These materials were ramped up in voltage to 6 volts, using a 100 Hz square wave, then ramped down to 0 volts again. Thus, the experiment measures not only the response at various voltages, but the reversibility of the system. The Displaytech mixtures appears to be more voltage-responsive, and gives a higher tilt angle at the highest voltage. However, the Roche material appears to be more symmetric, and hence more reversible.
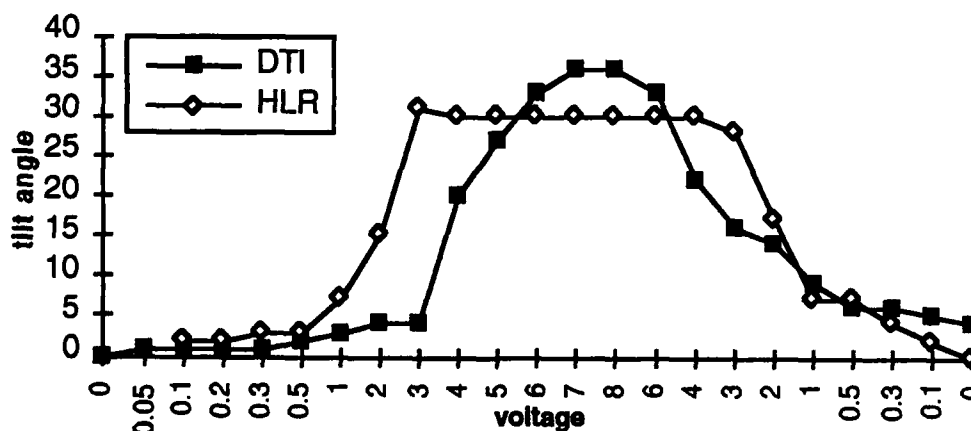

Figure 17. Comparison of tilt/voltage for **MX 6442** and **H 6300**.

Mixture **MX 6442** had relatively slow response to an applied field. When a sine wave was applied to a cell containing this mixture, the optical response mirrored the electrical signal quite well at 10 Hz, mirrored it well but more weakly at 100 Hz, tracked it well but was somewhat delayed at 1 KHz, tracked it weakly with a delay at 10 KHz, and couldn't track the electrical signal at all at 100 KHz.

The optical response of **MX 6540** was also measured in a different way. A cell containing this mixture was subjected to a pulse pattern that included a +5 V pulse of varying length, a 2 ms hold of 0 V, a 210 μsec pulse of -5 V to reset the cell, and a hold voltage of 0V for 5 msec. The response in terms of tilt angle vs. pulse width is shown in **Figure 18**. The response looks almost linear with respect to log t, until the cell reached a plateau at about 600 μsec.
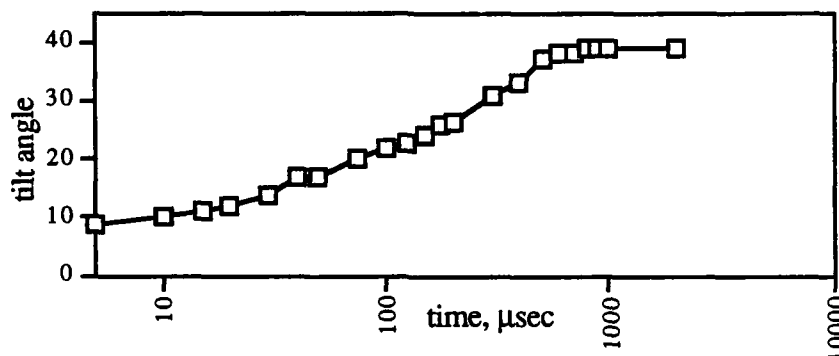

Figure 18. Pulse width vs. tilt angle for **MX 6440**.

We also tested a series of cells containing **MX 6232** to determine an optimal alignment layer combination and configuration. The variables included three different alignment layer materials [nylon, polyvinylalcohol (PVA), and polyimide (PI)] and two types of configurations (parallel, where the alignment layers of the two substrates were brushed in the same direction, and antiparallel, where they were brushed in opposite directions). The results are summarized in **Table 17**.

1st layer	2nd layer	Orientation	Visual strux[a]	Dynamic range[b]	Contrast ratio[c]
nylon	none	NA	4	44 ± 20	54:1
nylon	nylon	par	5	30 ± 9	68:1
nylon	nylon	antipar	4	26 ± 6	33:1
nylon	PVA	par	3	44 ± 7	136:1
nylon	PVA	antipar	2	33 ± 6	21:1
nylon	PI	par	3	26 ± 17	19:1
nylon	PI	antipar	3	21 ± 4	44:1
PVA	PVA	par	4	37 ± 17	24:1
PVA	PVA	antipar	3	29 ± 10	70:1
PI	PI	par	1	17 ± 8	247:1
PI	PI	antipar	1	18 ± 9	34:1

a   Visual structure is a subjective view of the degree of structure in virgin cells: 1 indicates very clean cells with little structure, 5 indicates cells with many lines, zig-zags, and intrusions.

b   Dynamic range indicates the difference in contrast of virgin cells between maximum transmittance and minimum transmittance. It is determined by rotating the cell between crossed polarizers. The standard deviation is determined from all cells of this type measured; generally 3 cells.

c   Contrast ratio is from only one cell, and is the ratio of maximum transmittance under positive field to minimum transmittance under negative field. The highest ratio, which generally occurred about 2.5 V, is given.

Although cells with a parallel alignment in general had more structure than antiparallel cells, they had about the same dynamic range. A large standard deviation in the dynamic range means that some cells were very good and some very bad, so the nylon/nothing cells, the nylon/PI parallel, and the PVA/PVA parallel cells were particularly variable. The contrast ratio was measured on only one cell, and is thus not necessarily indicative of what each type of cell's performance would be. However, the PI/PI parallel and nylon/PVA parallel cells showed that high contrast ratios are certainly possible with **MX 6232**. From the perspectives of both the amount of visual structure and the contrast ratio, the PI/PI system appears to be a clear forerunner.

One of the low tilt materials, **MX 6447**, was also extensively tested. The neat material's C* pitch was estimated by extrapolation to be -0.13 μm. It was diluted by the host material to 67% concentration, giving a material with a -0.33 C* pitch, and was further diluted to 50% concentration for a -0.47 μm C* pitch material. A -3.2 C* pitch material was also made by diluting it to 10% concentration. These materials were put into cells and tested for birefringence, by half-wave retardance, and DHF properties.

The tight pitch materials were expected to have lower birefringence than a corresponding SSFLC cell, due to the averaging effect of the DHF helix. Surprisingly, the material with a -0.47 μm pitch had the lowest birefringence, with the undiluted material having a birefringence comparable to an SSFLC cell. Another interesting result was that a 60 μm cell made with the -3.2 μm material showed diffraction, indicating a helix, whereas a 20 μm cell of the same material did not. Since the thickness of both cell was much more than the length of pitch, both cells were expected to exhibit diffraction.

Virtually all of the DHF cells we tested had lines, running roughly parallel to the alignment layer's rubbing direction, that were spaced about 1.7 - 2.4 μm apart. While much finer dechiralization lines were expected, they should appear perpendicular to the rubbing direction. This defect is still unidentified.

The DHF time constant is a measure of how fast the DHF responds to an applied field. The time constant for **MX 6447** was found to be small, only 22.8 μsec. However, a longer time constant on the order of 10 msec was also found. This appears to be due to ionic charge. Fortunately, a driving scheme which eliminates the problem of ions is available[14] for DHF materials.

Summary

The goal of this project was to make liquid crystal materials suitable for use in a deformable helix ferroelectric liquid crystal (DHFLC) device for analog light transmission. These materials were required to have a tight C* pitch but a long N* pitch, and a smectic C phase from less than 0°C to greater than 60°C. The material included both individual compounds and mixtures.

This report documents the synthesis of 141 new compounds with potential in DHF mixtures, including compounds with novel chiral tails and cores. One class of achiral dopants, the cyclohexyl family, was found to amplify the C* pitch induction abilities of chiral dopants. The cyclohexenyl compounds, a subset of this family, also helped decrease the crystallization point of mixtures. Other compounds, such as difluorides, had tight C* pitch and high polarization. Still other compounds, such as members of the methyl fluoro ether family, had C* pitch and N* pitch of opposite signs, making them useful for N* pitch compensation. Several three-ring alkenyl compounds, which increase the birefringence of mixtures while increasing solubility, are also reported. The newly synthesized compounds were extensively evaluated for relevant properties.

Some of the outstanding new compounds include: **MDW510**, a difluoro compound with high polarization and solubility-enhancing properties; **MDW 687**, a three-ring difluoro compound with high polarization, high birefringence, and improved solubility; **MDW497**, a cyclohexyl difluoride with high polarization and tight C* pitch which significantly decreases the crystallization point; **MDW533**, a cyclohexyl epoxide with high polarization and tight N* and C* pitches of opposite

sign; **MDW652**, a methylfluoro ether which has the extremely rare property of having negative polarization, but N* and C* pitch which are both positive; **MDW836**, a methylcyclohexyl compound with C* and N* pitches of opposite sign, both tight; and **MDW783**, a methyl epoxide compound with moderate polarization and tight N* pitch, useful for N* pitch compensation.

Several new DHFLC mixtures, with tight C* pitch, long N* pitch, and very wide (<-30°C to 73 °C) C* phases were also made. These could potentially be used in fast-switching analog display devices. The mixtures were evaluated in FLC cells. Further research is required to optimize the LC cells and driving electronics to take full advantage of the newly formulated DHF mixtures.

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Appendix A: Published paper
SPIE Proceeedings *1992*, **1665**, 176-183.

An Easily Aligned Deformable Helix Ferroelectric Liquid Crystal Mixture and its Use in Devices

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ABSTRACT

Ferroelectric smectic C* liquid crystals have been shown to exhibit high speed, multistate electro-optic and display device applications, particularly when incorporated into the surface stabilized ferroelectric liquid crystal (SSFLC) light valve. The SSFLC geometry results in two distinct stable states. Unfortunately, the lack of intermediate electrically addressed states precludes a natural gray-scale effect. The recently discovered Deformed Helix Ferroelectric liquid crystal (DHFLC) effect opens the door to linear gray scale or linear phase modulation in a ferroelectric liquid crystal device on a microsecond time-scale.

One drawback of currently available DHFLC materials is that their alignment quality is limited due to the lack of a nematic phase above their smectic A phase. While alignment can be improved by the use of shear techniques, this represents an undesirable option for a manufacturing process. We will show that DHFLC mixtures can possess a nematic phase with a long N* pitch and tight C* pitch in the C* phase. These new easily aligned DHFLC mixtures will be discussed as well as their use in beam-steering devices that can benefit from analog optical response.

II.   Introduction

a. Background

Research on ferroelectric liquid crystal based devices, driven by the potential market for flat panel displays, has focused primarily on FLCs in the surface-stabilized configuration[1]. In this configuration, surface interactions ensure a parallel alignment of all molecules and a suppression of the helix that would otherwise develop. This geometry results in two distinct stable states. Unfortunately, the lack of intermediate electrically addressed states precludes gray-scale without resort to indirect methods such as variable duty cycle switching or partial domain switching[2].

With the arrival of a new effect, Deformed Helix Ferroelectric liquid crystal mode[3], the possibility of linear gray scale FLC devices has arrived. In comparison to the ON/OFF SSFLC mode, the DHFLC mode affords linear intensity-voltage dependence (gray-scale). Devices operate at comparable operational speeds using lower voltages. The DHFLC effect allows continuous adjustment of the optic axis by electrical means at high speeds (10 µs demonstrated)[4] and low driving voltages (typical range 0.5 — 1.0 V/µm). This mode suggests many new and exciting applications made possible by this technology.

b. Commercial uses of linear electro-optic effect in DHFLCs

High speed analog intensity modulators based on the DHFLC effect can be applied to gray-scale active-matrix flat panel display technology. Other DHFLC products include analog beam deflectors, optical processing devices using the gray scale effect in coherent light (neural networks) and continuously tunable birefringence filters useful in imaging spectrometers. In addition, in the area of optically addressed spatial light modulators[5] (OASLMs) and integrated circuit ferroelectric liquid crystal[6] (ICFLC) devices, the introduction of gray scale significantly expands the usefulness of these device classes.

III. The DHFLC Effect

a. Method of Operation

In order to understand the linear electro-optic effect observed in a DHFLC cell, a brief description follows. In the surface-stabilized FLC cell, the C* pitch of the FLC mixture is typically greater than the thickness of the cell and results in an unwinding of the natural C* helix from surface interactions with the cell walls. In contrast to this, a DHFLC mixture possesses a much tighter C* pitch, on the order of tenfold tighter than the thickness of the cell. This allows the C* helix to be retained within the cell boundaries.

A DHFLC cell and an SSFLC cell are constructed in a similar fashion. The cells are composed of ITO coated glass with a brushed polymer alignment layer. Initial alignment of the DHFLC mixture occurs in either the smectic A phase (which does not possess a helix because of the orthogonal orientation of the director to the smectic layers), or in a nematic phase possessing a long N* pitch. Upon cooling from the isotropic liquid, alignment occurs in the initially formed phase, parallel to the rubbing direction. Empirically, the nematic phase affords better alignment and is therefor preferred. This is also true in a standard SSFLC mixture.

In a DHFLC mixture, at the A to C* transition, a helix forms parallel to the cell face and perpendicular to the smectic layers. A characteristic striped pattern, formed as a result of this C* helical winding, in effect, forms a diffraction grating. If the magnitude of the helix remains smaller than 0.35 μm, then visible light diffraction is minimized. The apparent refractive index of the liquid crystal is then the average over the many director orientations of the helix and can be operated as wave plate with a movable optic axis. This can be seen in **Figure 1** and whose operation is described in the next section.
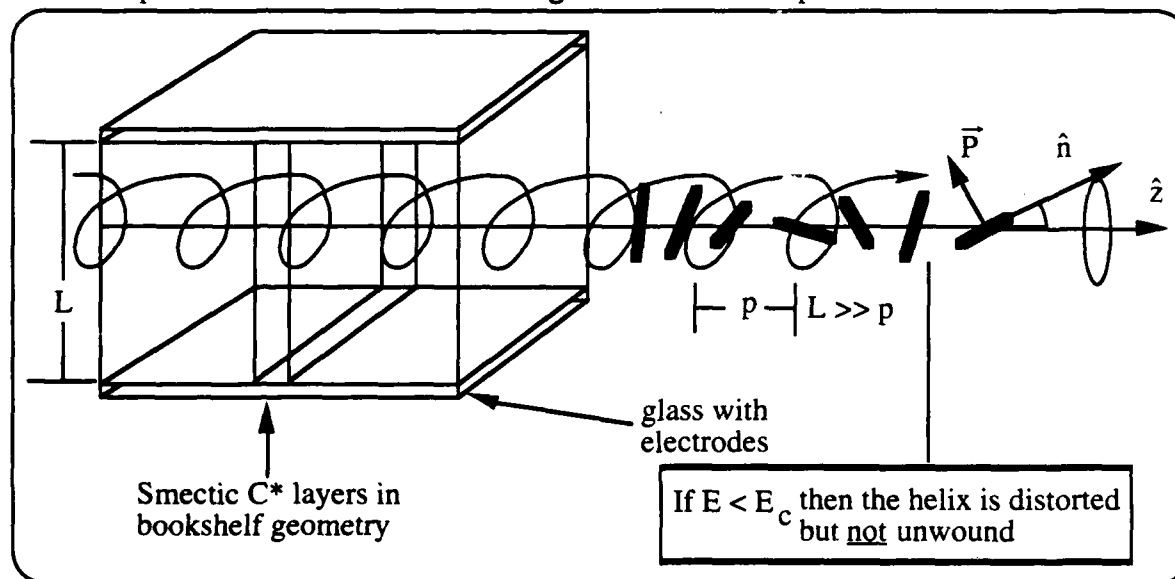

Figure 1. Deformable Helix Cell. The C* helical pitch is represented by p. The helical direction is $\hat{z}$ and L is the thickness of the cell. The long axis of the FLC is defined by $\hat{n}$ and the spontaneous polarization vector of the FLC is represented by **P**.

At zero field, the optical axis of the helical structure coincides with the helical axis. If the voltage is above a certain critical voltage E_c, the helix is completely unwound forming two distinct optical states identical to those in the SSFLC cell. This sacrifices the analog effect associated with the DHFLC mode. If the voltage is kept below this critical value, the helix is only deformed and not unwound. This allows adjustment of the optic axis orientation in a continuous fashion in response to the applied electric field.

Operation in the DHF mode also results in a small change in the apparent birefringence of the half wave plate on the order of 10%. This effect is small enough to have minimal impact on most applications requiring analog operation but should be taken into account when designing devices using these materials.

b. Advantage of a DHFLC mixture possessing a Long Pitch Nematic phase

Since DHFLC materials previously described in the literature[7] lack a nematic phase, they tend to be difficult to align by traditional manufacturing processes. Good alignment in these materials requires a technique known as "shearing." This technique involves placing the DHFLC material between two plates and gently sliding them back and forth. This technique is adequate for experimental demonstration of principal but does not lend itself to conventional manufacturing processes.

Traditional surface-induced alignment techniques standard in nematic and SSFLC devices are based on a rubbed polymer alignment layer and result in spontaneous alignment without the use of physical movement. This surface alignment technique is greatly improved when a nematic phase with a long N* helical pitch is present in the DHFLC mixture.

We have discovered that certain high polarization dopants afford a tight C* pitch. More important, when incorporated into mixtures with a broad nematic phase, they afford an N* pitch which is much longer than the C* pitch. The results are shown below for a series homologs of this class of dopants.

IV. DHFLC Mixtures

Dopants were screened for pitch induction properties at a concentration high enough to afford selective reflection at the visible wavelengths ($<0.5\mu$m) in the homeotropic orientation. The effect of tail length on N* and C* pitch induction and phase diagram was then examined.

a. Effect of Dopant tail length on C* pitch in a phenylpyrimidine host

Table 1. Dopants at 30% concentration in smectic C host[1]
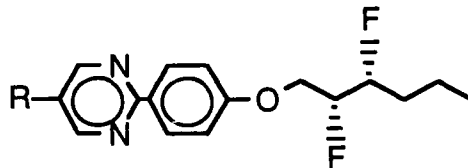
Dopant	R =	C* pitch	N* pitch [4]	phase diagram of mixture
MDW128	$C_{10}H_{21}$	0.36 μm [2]	1.5 μm	I--79--N*--66--A--56--C*
MDW116	C_9H_{19}	0.24 μm [3]	1.4 μm	I--80--N*--65--A--61--C*
MDW232	C_8H_{17}	0.22 μm [2]	1.3 μm	I--79--N*--57--C*
MDW198	C_6H_{13}	<0.15 μm [3]	1.0 μm	I--80--N*--50--C*

[1] Phase diagram I--82--N--72--A--66--C
[2] Measured at 20°C by selective reflection from a homeotropic sample.
[3] Extrapolated to 20°C by selective reflection from a homeotropic sample.
[4] Measured at 2°C above N* phase transition.

Four dopants with the structure shown in **Table 1**, varying only in alkyl chain length on the pyrimidine ring, were examined for N* and C* pitch in a smectic C host. Three trends are worth noting. First is the high ratio of N* to C* pitch. The difluoroalkoxy compounds show a long N* pitch (4-6 fold greater) relative to the C* pitch. This allows the N* pitch to be compensated to afford good alignment while still maintaining the tight C* pitch necessary for the DHF effect. Second, as the alkyl chain length is shortened, the C* and N* pitch increase in tightness. Third, the shorter chain lengths suppress the A phase. These last two properties can be effectively used to design a mixture with the desired phase sequence, I-N*-A-C*.

<u>b. DHFLC Mixture Formulated from the difluoroalkoxy Dopants</u>

A room-temperature DHFLC mixture was formulated from the difluoroalkoxy dopants described above. Several of these dopants were incorporated to a total of 25% concentration into a phenylpyrimidine smectic C host, and the N* pitch was lengthened with a compensating agent with minimal effect on the C* pitch. This afforded a mixture with the following properties:

MX5565; Phase Diagram: I↔80°↔N*↔65°↔A↔62°↔C*— <10°—X
N* pitch (66° C): >100 μm; C* pitch (20° C): 0.24 μm; P_S = -85 nC/cm^2 (20° C)
Δn = 0.09 (E = 0 V/μm); 0.13 (E = 3 V/μm, the unwound state)

Formulation efforts resulted in a mixture with the desired phase sequence, I-N*-A-C*. While the A phase is only 3° C wide, it provides adequate width for good bookshelf geometry -- generally necessary for good alignment in the C* phase. The N* and C* helical pitch versus temperature can be seen in **Figure 2**. It is interesting to note that while the C* pitch is mildly convergent, the N* pitch is strongly divergent — essentially infinite at the N* to A transition. This clearly shows that the N* and C* pitches are decoupled and most likely arise from different physical effects.
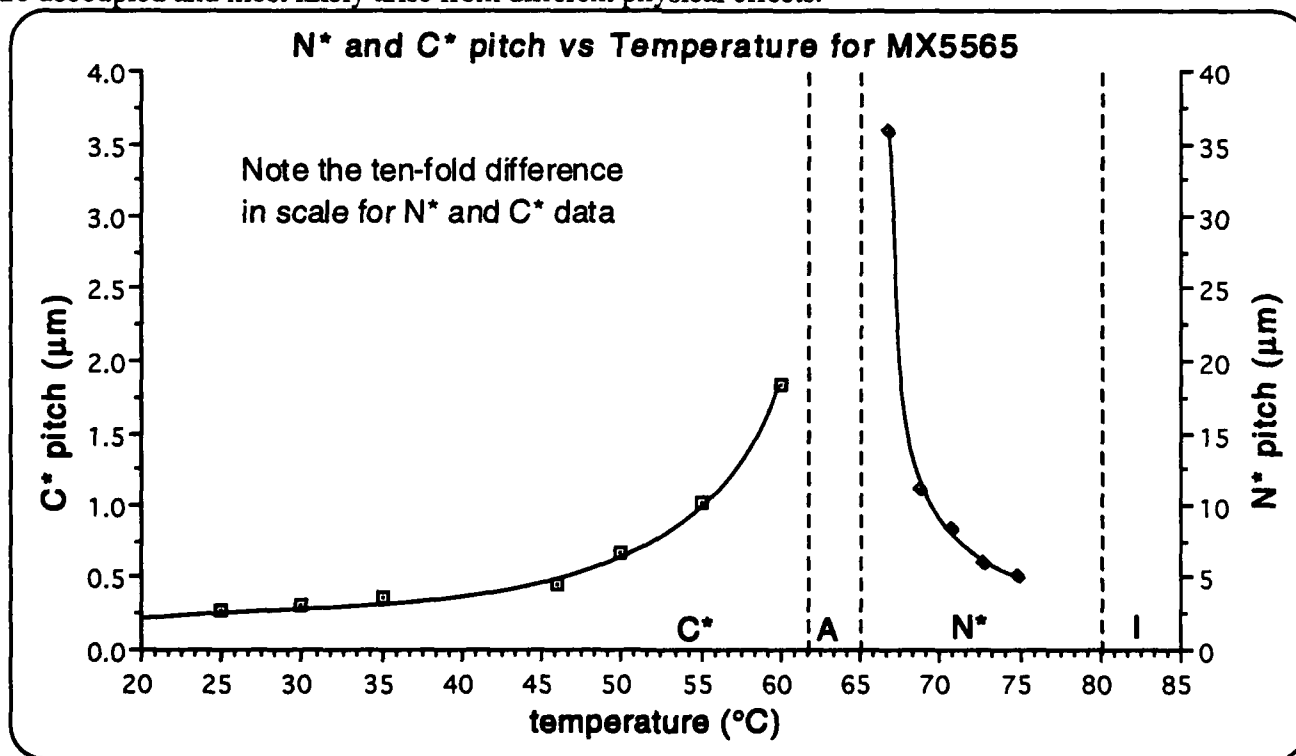

Figure 2. Phase diagram and helical pitch of the DHFLC mixture MX5565

c. Texture and Contrast of I-N*-A-C* vs. I-A-C* DHFLC mixtures

The alignment of nematic containing DHFLC mixture is demonstrated in the photomicrographs in **Figure 3**. Cells of similar thickness were filled with MX5565, described above, and mixture A, a DHFLC not possessing a nematic phase. Photomicrographs of the texture of the two cells show a much smoother texture in the N*-containing DHF mixture. This is further evidenced by a contrast measurement of 270:1 in MX5565 while the I-A-C* mixture shows a contrast of only 25:1 with cells constructed in an identical fashion. The measurement was performed by illumination from a 633 nm laser light source through crossed polarizers.
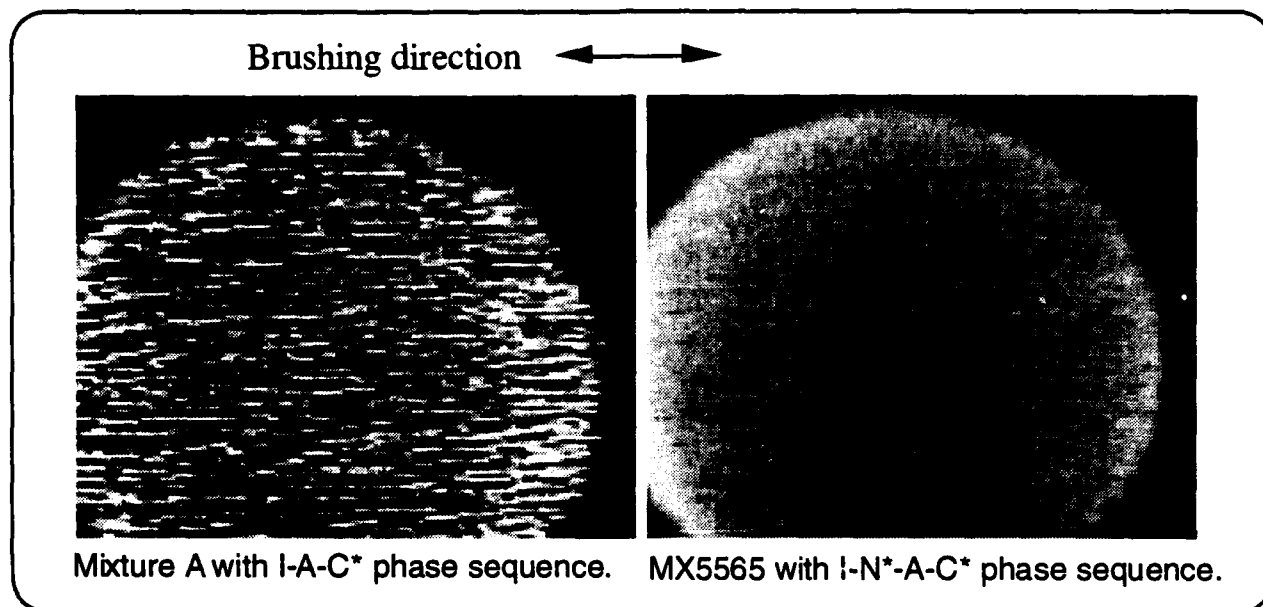

Brushing direction ◄──►

Mixture A with I-A-C* phase sequence.   MX5565 with I-N*-A-C* phase sequence.

Figure 3. Photomicrograph (50X magnification) of two DHFLC mixtures. Mixture A, without a nematic phase, and MX5565, containing a long pitch nematic phase, in cells spaced at 2.2 μm and 2.5 μm respectively.

V. DHFLC Analog Devices

a. Gray-scale Demonstration of DHFLC Mixture MX5565

Preliminary characterization of the DHFLC mixture in a single element device was carried out in order to optimize a driving scheme for use in the beam-steering device described in section IVb.

Figure 4 shows the optical response of the DHFLC cell when driven with a set of varying width pulses (changing the length of time that a constant voltage is applied) in order to obtain different gray levels. The critical unwinding voltage (E_c) for this DHFLC mixture is about one volt at pulse widths greater than the mixture's rise time of 120 μsec. Higher voltages can be used when the pulse width is significantly shorter than the rise time. The optical output in **figure 4** is representative of such a driving scheme and is derived from the work of Funfschilling and Schadt.[4]

The cell was driven with a variable width, +7V pulse followed by an open circuit for 2 ms. Then a -7V, 4 μs pulse was applied followed by a 2 ms, -1 V hold voltage. The variable widths, from 8 μs to 64 μs, of the positive pulse afforded the various gray levels. The desired gray-level electro-optic effect was demonstrated with a minimum of hysterisus as shown by the five different gray levels generated in **Figure 4**.
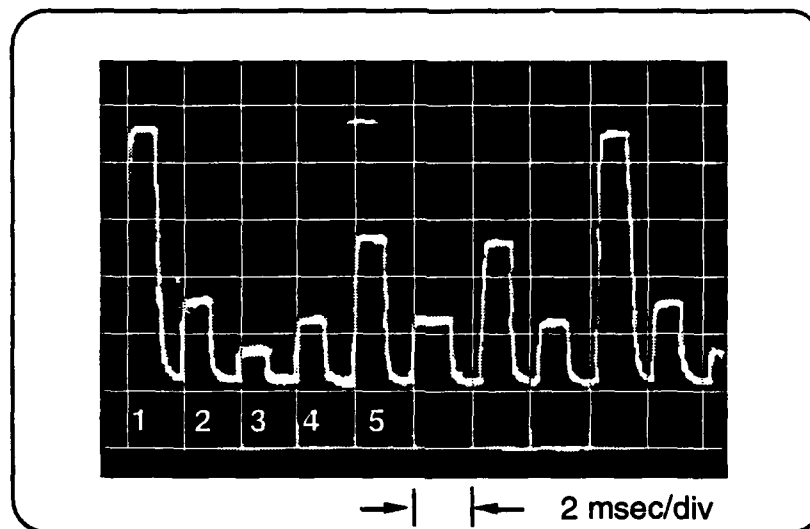
Figure 4. Gray-level demonstration of optical response by driving an MX5565 cell with a variable pulse width voltage. The numbers 1 through 5 represent different gray-levels.

b. FLC Beam-steering Devices

Spatial light modulators (SLMs, typically in the form of arrays of electro-optic modulators) are used to control the phase, polarization, or amplitude profile of light beams. A great deal of research has been focused on the development of high speed, high resolution, SLMs for use as displays, as key components for optical information processing, and for applications such as beam steering and image correction. The most common SLMs use nematic liquid crystals (NLCs) to modulate light. A significant limitation of the nematic liquid crystal SLMs is their slow switching speed. FLC based SLMs on the other hand have a large speed advantage over NLCs but have been limited to applications in which binary (ON/OFF) switching is sufficient. Despite this limitation, binary FLC SLMs have been constructed which can be used as polarization independent diffractive shutters[8] and as a means for projecting computer generated holograms[9],[10]. Due to their limited capabilities, however, binary FLC SLMs could not be used effectively for applications such as beam steering.

With the recent development of DHFLCs capable of analog modulation, applications such as high speed beam steering have become a real possibility. Displaytech has developed a prototype DHFLC array which has been used successfully for experiments in steering a laser beam and in steering the field of view of an optical system[11]. The basic idea is illustrated in **Figure 5**. The phase modulation induced by the array elements is used to produce an overall tilt (using a step-wise approximation) in the phase front of the outgoing beam. This tilt controls the direction of the beam. The beam can be steered to any direction within its field of view by imparting an appropriate tilt to the outgoing beam's phase front.
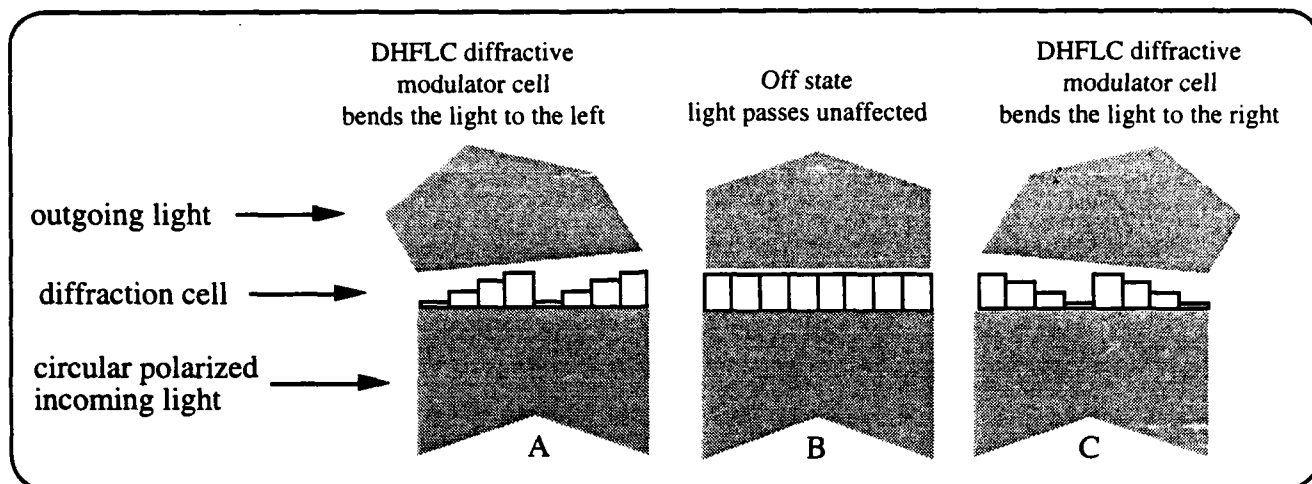
Figure 5. The Diffractive DHFLC Modulator.

The beam steering principle described above can also be used to steer the field of view of an optical system. In **Figure 6** we show the result of a field of view steering experiment performed using a 32 pixel linear DHFLC array. In this example, the field of view of the optical system is steered across a portion of an Air Force resolution chart.
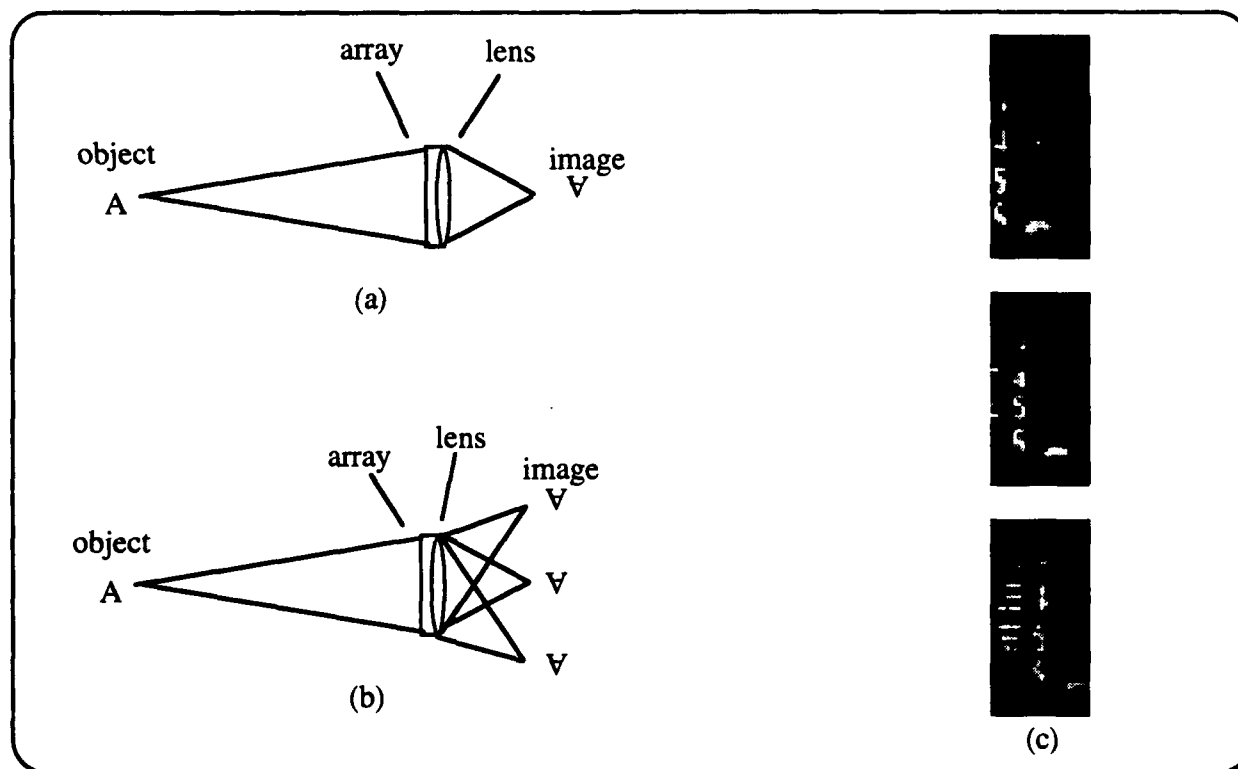

Figure 6. In a simplified illustration of the optical system: (a) All the pixels of the array produce the same phase shift (light is undeflected). In (b) the phases of the pixels have been set so as to steer the beam across a field of view. The series of three photos shown in (c) (from top to bottom) demonstrate the illustration in (b). A resolution chart is being electro-optically steered from left to right through the field of view of the camera.

VI. Summary

A new type of deformable-helix ferroelectric liquid crystal mixture containing a long helical pitch chiral nematic phase was developed. We have shown that the inclusion of this N* phase results in a smoother alignment in a DHFLC cell. This results in a significant improvement in contrast, making these materials more useful for a wide variety of applications.

The new DHFLC mixture was demonstrated in a beam-steering device based on the diffractive modulator principle. It showed analog phase shifting, and successfully steered the image of a resolution chart.

VII. Acknowledgments

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