This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Ferroelectric properties of a series of core-fluorinated dopants containing the 2,3-difluoroalkoxy tail

William N. Thurmes[a]; Michael D. Wand[a]; Rohini T. Vohra[a]; Kundalika M. More[a]; David M. Walba[b]
[a] Displaytech, Inc., Boulder, Colorado, U.S.A. [b] Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, U.S.A.

To cite this Article Thurmes, William N. , Wand, Michael D. , Vohra, Rohini T. , More, Kundalika M. and Walba, David M.(1993) 'Ferroelectric properties of a series of core-fluorinated dopants containing the 2,3-difluoroalkoxy tail', Liquid Crystals, 14: 4, 1061 — 1068

To link to this Article: DOI: 10.1080/02678299308027814

URL: http://dx.doi.org/10.1080/02678299308027814

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 1061–1068

Ferroelectric properties of a series of core-fluorinated dopants containing the 2,3-difluoroalkoxy tail

by WILLIAM N. THURMES*, MICHAEL D. WAND, ROHINI T. VOHRA, KUNDALIKA M. MORE and DAVID M. WALBA†
Displaytech, Inc., 2200 Central Avenue, Boulder, Colorado 80301, U.S.A.
† Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0125, U.S.A.

Previous reports from these laboratories [1] have discussed the synthesis and properties of core-fluorinated phenylpyridines with an attached difluoroalkoxy tail. This paper discusses core-fluorinated phenylpyridine difluoroalkoxides and compares their properties to those of the corresponding phenylpyrimidines. The pyridine and pyrimidine series are found to be remarkably similar in properties. They have similar high polarizations and fast rise times, attractive in surface-stabilized ferroelectric liquid crystal (SSFLC) applications, and in high concentration have pitch properties compatible with deformable helix FLC applications.

1. Introduction

Many ferroelectric liquid crystal (FLC) applications depend on a rapid switching speed. The switching speed can be increased by doping FLCs with high polarization, low viscosity materials. We are developing a family of high-polarization, low viscosity dopants based on the enantiomerically enriched 2,3-difluoroalkoxy group. This difluoroalkoxy group has been attached to a number of types of aromatic cores, including a series of core-fluorinated phenylpyrimidines. The resultant FLC dopants were found to have high polarization, low viscosity, and tight C* pitch. This class of compounds is illustrated in figure 1, where Z is a nitrogen and R is either an alkyl or an alkoxy group. The series consists of compounds with no core fluorination ($X = Y = \mathrm{H}$), a single fluorine on the core ($Y = \mathrm{F}$, $X = \mathrm{H}$), or difluorination of the core ($Y = X = \mathrm{F}$). The properties of several members of the phenylpyrimidine series were discussed in a previous paper, but the synthesis and evaluation of an additional member of the series prompts us to complete the discussion in this paper.

This paper also presents another set of difluoroalkoxy compounds, wherein the aromatic cores are phenylpyridines with varying degrees of core-fluorination. This series is also represented by figure 1, where Z is a carbon atom and R is an alkyl group. One further compound, a phenylpyridine in which the core orientation has been reversed, is also presented. This compound, MDW510, and the other FLC dopants compared in this paper are shown in figure 2 along with their phase diagrams.

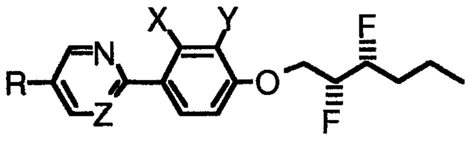
2. Results and discussion

The mesomorphic properties of the series of difluoroalkoxides were examined as neat materials, and also by doping them at 10 wt% concentration into an achiral phenylpyrimidine host and evaluating the mixtures for ferroelectric properties. Figure 2 shows the structures of the compounds discussed in this paper, along with the phase diagrams of the neat materials, while tables 1 and 2 address their respective ferroelectric

---

* Author for correspondence.

0267-8292/93 $10·00 © 1993 Taylor & Francis Ltd.



Z = C, N; X, Y = H, F

Figure 1. Difluoroalkoxyphenylpyridines and difluoroalkoxyphenylpyrimidines.

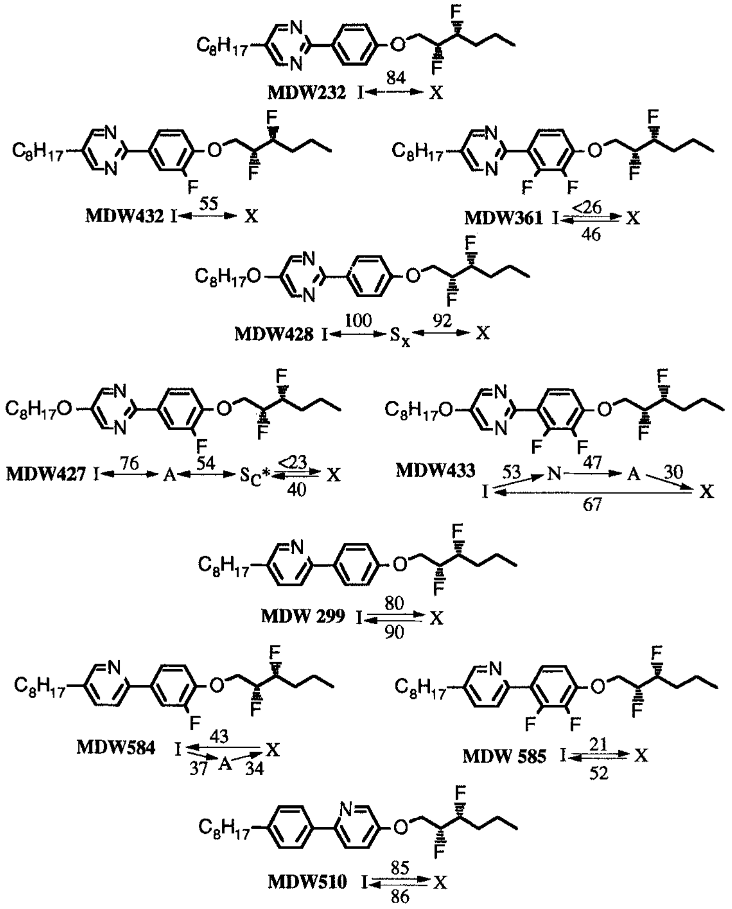


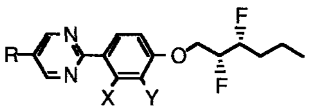
Figure 2. The structures and phase sequences of the difluoroalkoxy phenylpyridines and phenylpyrimidines. Temperatures are in °C.

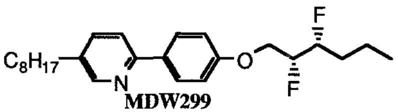
properties (phase diagrams P_s, τ, θ, pitch) in a phenylpyrimidine host. Table 1 shows data for the phenylpyrimidine series, including both the alkylalkoxy and the dialkoxy variants, while table 2 shows data for the phenylpyridine series. Note that two different phenylpyrimidine hosts were used for these evaluations, and that two compounds (MDW232 and MDW299) were evaluated in both hosts to provide standards for comparison.

2.1. *Phase diagrams*

It is interesting to note that, of the entire series, only the dialkoxyphenylpyrimidine MDW427 has a chiral smectic C phase, and the majority of the compounds have no liquid-crystalline phases whatsoever. In fact, with the exception of the monofluorinated

Table 1. Difluoroalkoxy dopants at 10 per cent concentration in phenylpyrimidine host MX6033†.





MDW299

ID number	*R*	*X*, *Y*	S_C		S_A		Ch		I	P_s/nC cm^{-2}	θ/°	P_0‡	γ_{10-90}/μs§	N* pitch/μm‖	S_C^* pitch/μm¶
MDW232	C_8H_{17}–	H, H	●	61	●	72	●	81	●	−23·5	27·5	−510	59	−7	−2
MDW299	Above	H, H	●	64	●	74	●	85	●	−24·9	27	−550	93	−3·3	−1·6
MDW432	C_8H_{17}–	H, F	●	54	●	74	●	81	●	−15·0	21·5	−410	120	+16	−6
MDW434	C_8H_{17}–	F, F	●	61	●	70	●	80	●	−18·3	26·5	−410	60	+3	−3
MDW428	$C_8H_{17}O$–	H, H	●	61	●	73	●	86	●	−13·7	25·0	−320	72	−4	−3
MDW427	$C_8H_{17}O$–	H, F	●	54	●	79	●	85	●	−8·9	22·5	−230	105	−4	−6
MDW433	$C_8H_{17}O$–	F, F		—		—		—		−12·7	26	−290	84	+7·1	−3

† MX6033 host phase sequence, S_C–63→S_A–77→N–85→I. The host contains 65 per cent dialkoxyphenylpyrimidines and 35 per cent alkylalkoxyphenylpyrimidines.

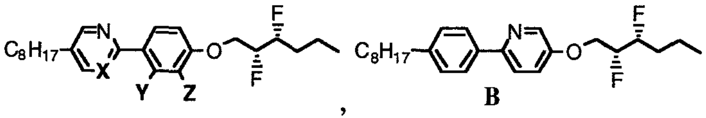
‡ P_0 was obtained by multiplying P_s by 10 to give P_{ext} and dividing by $\sin\theta$.

§ Rise time measurements performed using a 1·7 μm cell at 5 V μm^{-1}, at $T = 22$°C.

‖ N* pitch taken at 2° above $T_{S_A-S_C}$.

¶ S_C^* pitch taken at 22°C.

Table 2. Difluoroalkoxy dopants at 10 per cent concentration in phenylpyrimidine host MX6396†.



ID number	Type	X, Y, Z	X		S_C		S_A		Ch		I	P_s/nC cm^{-2}‖	θ/°	P_0‡	γ_{10-90}/μ^s§‖	N*pitch/μm (°C)¶	S_C^*/μm¶
MDW232	A	N, H, H	●	−1·1	●	65	●	78	●	86	●	−25·3	24	−620	55	−3 (80)	−1
MDW299	A	C, H, H	●	−0·4	●	68	●	78	●	86	●	−24·4	25	−580	62	−2 (79)	−1·2
MDW584	A	C, H, F	●	−2·5	●	58	●	74	●	83	●	−20·0	23	−510	59	−43 (76)	−1·2
MDW585	A	C, F, F	●	−2·1	●	54	●	68	●	81	●	−15·8	23	−400	77	+12 (69)	−2
MDW510	B	—	●	−1·1	●	66	●	77	●	86	●	−21·8	24	−540	61	−6 (78)	−1·25

† MX6396 host phase sequence, X–0·8→S_C–67·5→S_A–81→N–89→I. The host contains 50 per cent alkylalkoxyphenylpyrimidines, 40 per cent dialkoxyphenylpyrimidines, and 10 per cent alkylcarbonyloxyphenylpyrimidines.

‡ P_0 was obtained by multiplying P_s by 10 to give P_{ext} and dividing by sin θ.

§ Rise time measurements performed using a 1·7 μm cell at 5 V um^{-1}.

‖ Measurements performed at 22°C.

¶ N* *pitches all diverge;* S_C^* *pitches all converge.*

phenylpyridine (which has a 3° monotropic A phase), only those compounds with an alkoxy achiral tail have mesomorphic phases. However, the lack of mesomorphism in these compounds does not inhibit their usefulness as FLC dopants. In fact, when placed into a host mixture they do not greatly alter the mixture's phase diagrams, as can be seen from the data presented in tables 1 and 2.

Thus, many of the difluoroalkoxy compounds only moderately (0–5°C) suppress the I–N, N–S_A, and S_A–S_C phase transition temperatures. However, certain of the compounds strongly suppressed one or more of the phase transitions. It was found that the compounds with one fluorine on the core suppressed the S_A–S_C transition by approximately 9°C, and the compounds with two fluorines on the core suppressed the N–S_A transition by 7°C or more. The monofluorinated and difluorinated phenylpyridines strongly suppressed all three phase transitions.

2.2. *Polarization*

The sign of the polarization predicted by the Boulder model [2] is negative for the difluoroalkoxy tail in which both fluorines are in the *R*-configuration. This value is consistent with the values measured for all dopants. The magnitude for the nomalized polarizations ranged from -230 to $-620\,\mathrm{nC\,cm^{-2}}$. Fluorination of the core in all cases reduced the polarization. Replacing the phenylpryimidine's achiral alkyl tail with an alkoxy tail reduced the polarization, but changing from a pyrimidine to a pyridine had minimal effect on the polarization.

It is interesting to note that previous research [3] by Displaytech using the 2,3-difluoroalkoxy tail with the phenyl benzoate core showed a significant increase in polarization upon fluorination of the core, indicating orientation of the ring normal to the chiral smectic C layer tilt plane and consequent contribution of the ring fluorine dipole to P_s. Ring orientation in the phenylpyrimidine system is less well understood, but ring fluorination helps probe the ring orientation. Since fluorination of the ring does not increase P_s, the fluorinated ring probably resides in the tilt plane, therefore not contributing to P_s. Indeed, the rings are not sterically driven to be orthogonal [4], so it may be that the rings are coplanar, i.e. both in the tilt plane. Experimental error could account for the differences in P_s between the phenylpyrimidine and phenylpyridine series, so the two systems apparently have similar ring orientations. Inverting the aromatic core does not significantly affect the polarization, as can be seen from the virturally identical polarizations of phenylpryidine MDW299 and reversed-core phenylpyridine MDW510. We have no easy explanation for the 20 per cent decrease in P_s in both the mono- and di-fluorinated alkyl-pyridine and -pyrimidine cases or the further P_s decrease in the alkoxypyrimidine cases. It may be that the electron-withdrawing capabilities of the additional electronegative atoms reduces the C–O dipole moment of the chiral tail, or increases the likelihood of ring coplanarity.

2.3. *Rise time and viscosity*

The rise times of these materials vary from 55 to $120\,\mu$s at $5\,\mathrm{V\,\mu m^{-1}}$. While some variation in rise time can be attributed to the differences in polarization and tilt angle, this does not fully account for the rise time variability, so there must also be differences in orientational viscosity. Preliminary assessment of the rise time data indicates that, at least in these systems, monofluorination results in higher viscosity than the unfluorinated system, whereas difluorination results in lower viscosity than the unfluorinated system. The phenylpyridine system appears to be approximately as viscous as the phenylpyrimidine system.

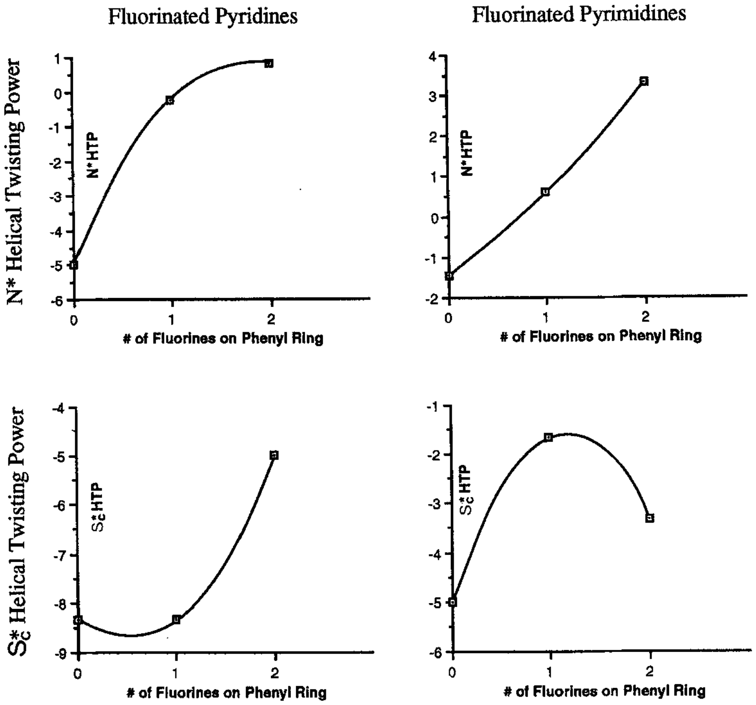


Figure 3. A comparison of the helical twisting power (HTP) of fluorinated phenylpyridines and phenylpyrimidines.

2.4. *N** and S_C^* *pitch*

The N* and S_C^* pitch are both manifestations of the chirality of the liquid crystal material. Although helices are formed by both liquid crystal phases, the helices propagate in different directions and bring different complications to a FLC light modulator. The N* helix, in a surface-stabilized FLC with planar geometry, runs perpendicular to the substrates, whereas in the same FLC, the S_C^* helix runs parallel to the substrate. The N* helical repeat length or pitch, measured at the $N^* \rightarrow S_A$ or $N^* \rightarrow S_C^*$ transition, should be more than four times the width of the cell to give proper alignment of the FLC [5]. Since good alignment is a prerequisite for SSFLC devices, a long N* pitch is invariably desired.

The S_C^* pitch tends to interfere with light as it passes through a celd, and can also interfere with alignment. A S_C^* pitch of the same or greater magnitude as the wavelength of modulated light passing can give undesired diffraction patterns and discontinuity lines in the cell. Thus, in bistable FLC cells, a long S_C^* pitch is generally [6] desired. However, a very tight S_C^* pitch, much less than the wavelength of light, can be used for analog switching via the deformable helix FLC (DHF) effect [7]. By applying a sub-critical field to the DHF material, the S_C^* helix can be deformed rather than unwound, resulting in a linear change in the apparent optic axial orientation, thus allowing analogue light modulation. In materials to be used in a DHF cell, a tight S_C^* pitch is desired.

Perhaps the simplest way to assess the N* and S_C^* pitch induction capability of materials is by determining the helical twisting power (HTP), defined as the inverse of the induced pitch extrapolated to 100 per cent concentration of the pitch inducer. The

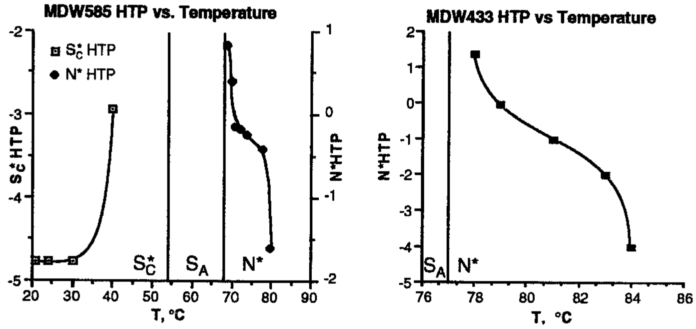


Figure 4. Anomalous N* pitch behaviour. An HTP of 0 designates an infinite pitch. Note that in MDW585, the S_C^* and N* HTP are on different scales.

HTP of the compounds discussed in this paper are shown graphically in figure 3. The top of figure 3 shows the N* HTP, while the bottom shows the S_C^* HTP; the left shows the phenylpyridine system, while the right shows the phenylpyrimidine system. Note that the phenylpryidines and phenylpyrimidines were tested in different host materials, with only the unfluorinated compounds being tested in both hosts. From the data in table 1, it appears that the host material MX6396, used with the phenylpyridines, induces a tighter N* pitch and a slightly tighter S_C^* pitch.

It can be seen from figure 3 that the number of fluorines on the aromatic core can profoundly affect both the S_C^* and the N* HTP of a material. For most compounds, the N* HTP is significantly smaller than the S_C^* HTP. In the S_C^* phase, the unfluorinated compounds have the largest magnitude HTP. For the pyridines, the monofluorinated compound has a stronger S_C^* HTP than the difluorinated compound, while the reverse is true for the phenylpyrimidines. Note that, in both the phenylpyridines and the phenylpyrimidines, the N* HTP is very small (i.e., the N* pitch is very long) for the monofluorinated compound, and the sign reverses for the difluorinated compound. This makes both the mono- and di-fluorinated compounds ideal for DHF applications, presenting the possibility of mixtures of difluoroalkoxy compounds which are self pitch-compensated in the N* phase.

The core-difluorinated phenylpyridine and phenylpyrimidine both showed anomalous N* HTP behaviour, as is shown in figure 4. At higher temperatures, they had strong negative N* HTP, but when the temperature decreased the N* pitch was unwound to infinity. Then, as the temperature continued to decrease, the N* helix rewound in the positive direction, giving a relatively strong positive N* HTP as the material reached the N→S_A transition temperature.

3. Conclusion

This paper discusses core-fluorinated phenylpyridine difluoroalkoxides and compares their properties to those of the corresponding phenylpyrimidines. The comparison shows the pyridine and pyrimidine series to be remarkably similar in properties. Only one of the neat compounds shows a S_C^* phase. When mixed into a smectic C host, they give a similar high polarization and fast rise time. The non-fluorinated and difluorinated materials have S_C^* and N* pitches opposite in sign, while the N* pitches of the monofluorinated compounds are somewhere in between. Thus, these materials have pitch properties ideal for deformable helix FLC applications.

This project is sponsored by the National Science Foundation (Grant No. 9000040) and the U.S. Army Research Office (Grant No. DAAL03-91-C-0051). The content of the information does not necessarily reflect the position or policy of the government and no official endorsement should be inferred.

References

[1] Wand, M. D., Thurmes, W. N., Vohra, R. T., More, K., and Walba, D. M., 1991, *Ferroelectrics*, **121,** 219 and references therein.

[2] Walba, D. M., Slater, S. C., Thurmes, W. N., Clark, N. A., Handschy, M. A., and Supon, F., 1986, *J. Am. Chem. Soc.*, **108,** 5210.

[3] Wand, M. D., Vohra, R. T., Walba, D. M., Clark, N. A., and Shao, R., 1991, *Molec. Crystals liq. Crystals*, **202,** 183.

[4] From a calculation by Alchemy II, from Tripos Associates.

[5] Uchida, T., Hirano, M., and Saksi, H., 1989, *Liq. Crystals*, **5,** 1127.

[6] Escher, C., Hemmerling, W., Ilian, G., Harada, T., and Murakami, M., European Pat. EP 04 040 81A2.

[7] Beresnev, L. A., Blinov, L. M., and Dergachev, D. I., 1988, *Ferroelectrics*, **85,** 173.