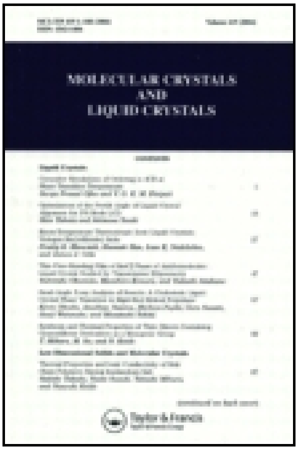

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Fluorination in Nematic Systems

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Fluorination in Nematic Systems†

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The effect of fluorine substitution into a mesogenic system depends critically on the manner in which it is introduced. The relative stabilities of smectic and nematic phases may be inverted by altering the site of substitution, and lateral fluorination is particularly interesting for the strong suppression of smectic phase stability which can result. This effect has been applied to hydrocarbon mesogens to obtain new series of wide range, room temperature nematics of low viscosity and moderately high birefringence. These properties are readily conferred on mixtures, and the technical utility of fluorinated LC's is illustrated by reference to wide nematic range, fast switching mixtures having high birefringence, and suitable for static or multiplex drive.

INTRODUCTION

Fluorinated nematic liquid crystalline materials have been known at least since 1925,[1] but it is only in the last several years that research activity in this field has become intense and provided sufficient examples of such nematogens as to allow proper evaluation of the effects of fluorine as a substituent. A very large number of fluorinated LC's are now known, and no attempt can be made to review fully the literature in the time available. Rather, some representative examples of different classes of fluorinated LC's will be chosen to demonstrate the changes of physical properties which can be obtained. Fluorine is well known as a substituent which is highly electronegative while having a Van der Waals radius only about 12.5% greater than that of hydrogen. The difference in covalent radii is greater and means that fluorine substitution may exert an appreciable steric effect, with-

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†Invited lecture presented at the Tenth International Liquid Crystal Conference, York, July 15-21, 1984.

out the substituent being so bulky as to disrupt completely the close packing necessary for a high mesophase stability.

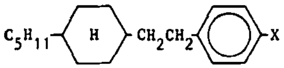
DISCUSSION

In principle, there exist three different sites of substitution onto a liquid crystal molecule. These arise when the substituent is introduced as a terminal group, as a substituent onto the end chain of a molecule, or laterally onto the rigid molecular core. It will be shown below that this third category may usefully be sub-divided into those cases where the substituent lies close to the center of the molecular core, and those where it points away from the end of the core. The effects of fluorine substitution into each of these sites will now be considered.

The first fluorinated nematogens synthesised carried their substituents as terminal groups.[1] Although enantiotropic phases were produced, the efficiency of fluorine in stabilising the liquid crystal was revealed to be less than that of other terminal groups including —Cl, —Br, —CH_3 and —NO_2. It is therefore not surprising that fluorine attracted no further attention as a LC building block for nearly 30 years. With greater understanding of the factors which contribute to mesophase stability, terminal fluorine atoms have been reappraised in more recent years. Comparison of the compounds in Tables I[2,3,4] and II[5,6] reveals that although the clearing points of fluorine derivatives are lower than those involving other terminal groups, useful clearing points can be obtained. The usefulness of such compounds arises not from their mesophase ranges but from the modest positive dielectric anisotropy which fluorine imparts, combined with a relatively low viscosity.

TABLE I

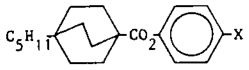
The nematic efficiency of some terminal substituents



X	K → N/I	N → I
—CN	28°	49°
—OC_2H_5	18°	47°
—C_3H_7	3° (K→S)	[3°]
—F	12°	(−6°)

TABLE II

The nematogenic efficiency (°C) of terminal substitutents



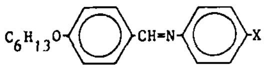
X	K → N	N → I
—CN	89	109
—OC_3H_7	41	95
—C_3H_7	59.5	66.5
—F	54	(41)

Table III presents data on compounds[7,8,9] carrying both terminal fluoro and trifluoromethyl groups, the latter being an example of the second substitution type referred to above. The effect of the trifluoromethyl group is striking and characteristic; the extrapolated N-I value is strongly depressed to a value even below that of the fluoro derivative, while a smectic phase (unclassified) is stabilised. A similar trend can be observed in phenyl benzoate esters,[10] where alkyl terminated derivatives lose all their mesogenic properties (Table IV), while only smectic phases are observed in the alkoxy compounds. Data are lacking for longer alkyl groups carrying progressive degrees of fluorine substitution, but perfluorination again results in smectic mesophases only (Table IV). Once again, the low nematogenic potential of these compounds does not preclude their use in cases where other physical parameters are important.

The history of laterally fluorinated nematic systems is an interesting

TABLE III

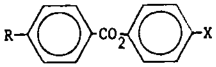
Relative mesogenic efficiencies (°C) of some terminal groups



X	K → S	K → N/I	S → N	S → I	N → I
H		48			[−52]
CH_3		61.5			73.7
F	55.5		62		63.5
CF_3	72			84.5	[27]

TABLE IV

Fluorinated phenyl benzoate esters

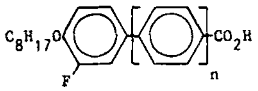


R	X	K → S	K → N	N → I	S → I
C_8H_{17}	CN		46°	55°	
C_8F_{17}	CN	118°			145°
C_8H_{17}	CF_3	58.5° (K→I)			

one. The first examples of such compounds[11,12] to be synthesised showed little effect of fluorination on the relative phase stability, the dominant effect being merely a modest reduction in clearing point ascribed to the broadening of the molecule—see Table V. Once again these results did little to excite further research, but when further examples were synthesised, it became clear that a depression of smectic phase stability may result from lateral fluorination.[13] Fortunately, many examples of these materials are now known,[14,15,16] and the consequences of structural modification can be examined. The compounds shown in Table VI are typical and it can at once be seen that whenever a lateral fluorine points towards the center of the molecular core, smectic phases are eliminated or strongly depressed. In contrast to this, substitution in lateral/terminal positions of the core leads to no significant reductions in smectic phase stability: indeed the smectic phase is sometimes enhanced. Furthermore, substitution in the lateral/central sites has a much smaller effect in depressing the nematic

TABLE V

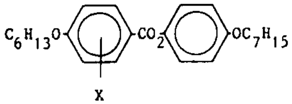
Lateral/terminal fluorine substitution in carboxylic acid derivatives



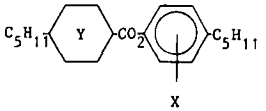
X	n	K → S	K → N	S → N	N → I
H	0	101°		108°	147°
F	0		117°		120.5°
H	1	183°		255°	264.5°
F	1	119.5°		254.5°	255.5°

TABLE VI

Thermal properties (°C) of laterally fluorinated mesogens



X	M.Pt.	S → N	N → I
H	55		87
2-F	44		70.9
3-F	63	(56.5)	71.5



X	Y	M.Pt.	S → N	N → I
H	CH	36.8	(28.3)	47.1
2-F	CH	17.5		36.5
3-F	CH	27.5	(18.7)	(26.3)
H	BCO	31		64.5
2-F	BCO	26		65
3-F	BCO	44.5		(38.5)

clearing point than lateral/terminal substitution. We may remark at this point that these effects do not seem to be confined to fluorine substitution, and that lateral/terminal substitution with higher halogens or nitrile groups[14] strongly favours smectic phases over nematic ones.

Finally, polyfluorination or perfluorination of the cyclic structures in a mesogenic molecule often leads to smectic phases or high-melting solids, with nematic behaviour being strongly depressed. To conclude therefore, the effect of substitution depends not only on the nature of the substituent, but very critically on the manner in which it is introduced into mesogenic species. The same substituent can strongly enhance or depress the stability of a phase according to its location, and only by studying numerous examples can the underlying rules be discerned.

The liquid crystal group in the UK has been working to exploit the

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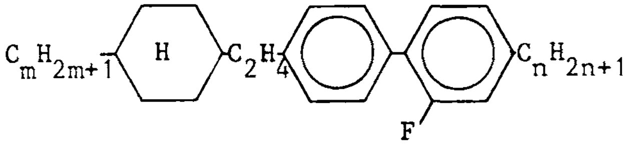


I'mn

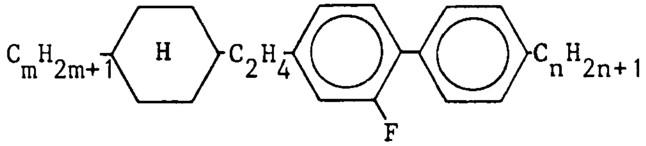


FIGURE 1 Structures of novel fluorinated nematogens.

factors described above, and several papers to be presented at this conference cover different aspects of the work. I would like to describe the application of lateral fluorination to hydrocarbon mesogens which are otherwise noted for their wide smectic mesophase ranges. The structures in question are shown in Figure 1. The syntheses outlined in the two schemes (Figures 2 and 3) are carried out using standard reactions and techniques, and the products are purified by column chromatography and recrystallisation.

Each homologous series of compounds carries a fluorine substituent in the lateral/central disposition and the resulting thermal properties are shown in the Tables VII and VIII. In each series wide nematic phase ranges are obtained, and in the case of I compounds, this extends in several cases from near room temperature to 100°C. Other

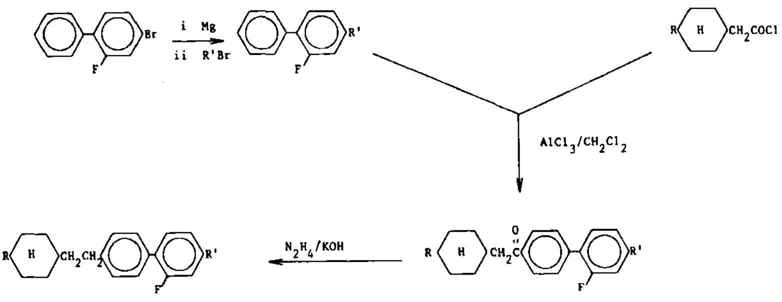


FIGURE 2 Synthesis of I series compounds.

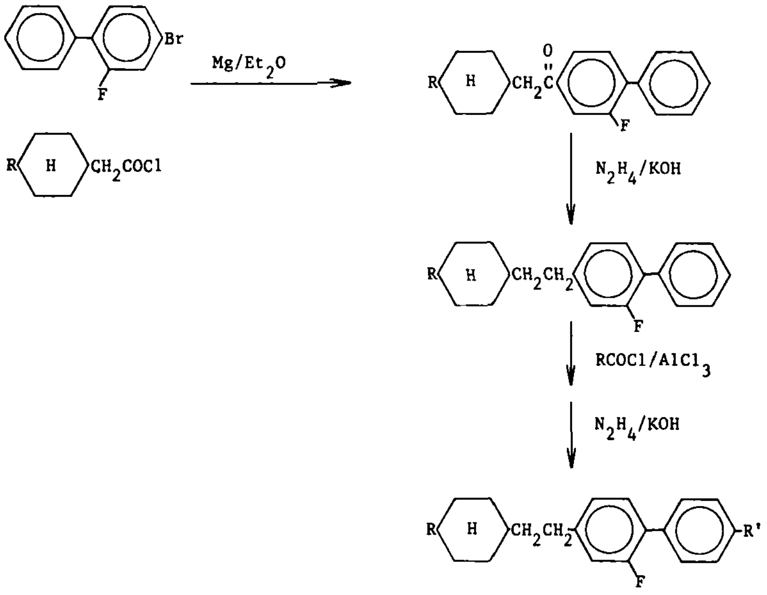


FIGURE 3 Synthetic route to I′ series compounds.

TABLE VII

Thermal properties (°C) of some I series homologues

M	N	K → S	K → N	S → S	S → N	N → I
2	4		−2			70
3	2		27			97
3	4		13			97
5	2		24		(14)	103
5	5	17		33	37	108

TABLE VIII

Thermal properties (°C) of some I′ series homologues

M	N	K → S	K → N	S → S	S → N	N → I
2	3		34			80
3	2		34		(15)	97
3	3		59		(34)	108
5	2	23		27	56	105
5	5			56	92	110

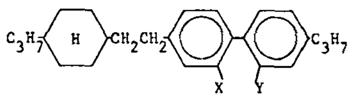
homologues present unusually wide nematic ranges from below room temperature, and the virtual absence of smectic phases is remarkable. The isomeric I′ series shows in general a higher smectic tendency combined with somewhat higher melting points and slightly higher clearing points. The predominant smectic phase in both series appears on the basis of its texture to be S_B, while in the longest homologues of the series a sequence $S_B - S_A - N$ is observed.

If like homologues of the fluorinated and non-fluorinated series are compared, the extent of destabilisation of the smectic phase can be appreciated, with an S-N of 119°C in the hydrocarbon being depressed by 85° in the I′ compound (Table IX). In the corresponding I compound no smectic phase is observable on supercooling. A further comparison may be made with the dialkyl BCH[17] compounds. The introduction of a fluorine atom into BCH52 again depresses the smectic phase strongly while the change in viscosity and clearing point is quite modest (Table X). The introduction of the ethyl link in I′52 gives a small decrease in melting point but introduces a smectic phase which is absent from its otherwise similar isomer. Finally, the difluoro BCH is included, and shows a rather large deleterious effect on both clearing point and viscosity of introducing a second substituent. The figures in the last column of the table show that the I compound is less viscous than the corresponding I′ homologue, and in this case at least the viscosity is less than that of the fluorinated BCH and only slightly higher than the extrapolated figure for the predominately smectic hydrocarbon.

It is clear that structures such as those I have been describing are capable of great variation, but two examples are shown to illustrate the possibilities. Extension of the rigid core of the molecules by addition of a fourth ring (see Figure 4) provides structures having

TABLE IX

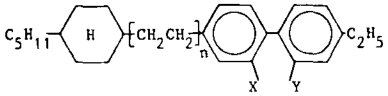
A comparison of a mesogenic hydrocarbon and its laterally fluorinated derivatives



X	Y	K → S	K → N	S → N	N → I
H	H	67°		119°	144°
F	H		59°	(34°)	108°
H	F		40°		108°

TABLE X

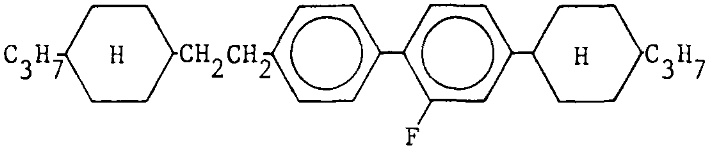
Comparative thermal properties (°C) of some 3-ring mesogens



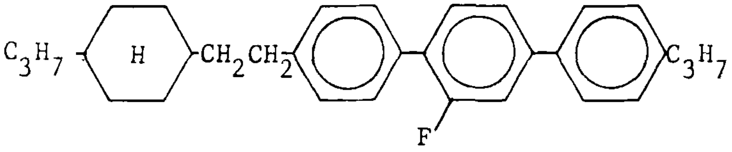
n	X	Y	K → S	K → N	S → N	N → I	η_{20}(cSt)
0	H	H	34		146	164	20
0	F	H		26		107	24
0	F	F		27		78	42
1	F	H	23		55.5	104.5	24
1	H	F		23.5	(14.5)	103	21.5

raised clearing points and retaining a low smectic tendency. Such compounds are useful for raising the N-I temperatures of practical mixtures.

By incorporating chiral groups in the structure (see Table XI), cholesteric phases are formed with wide ranges in the room temperature region. The pitch is such that selective reflection occurs in the



K → N	N → I
107	244

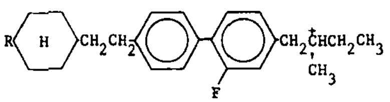


K → S	S → N	N → I
84	87	252

FIGURE 4 High clearing point fluorinated nematogens.

TABLE XI

Properties of some laterally fluorinated chiral nematic compounds



R	S → Ch	Ch → I
C_2H_5	−11°	45°
C_4H_9	6°	72° (P = 0.23 μ)
C_7H_{15}	55°	81°

UV, but dilution of these compounds with nematic materials gives bright selective reflection colours in the visible. Suitable mixtures showing a S_B − Ch transition change from a colourless state to a reflecting state of a single colour without passing through other spectral colours. This is in contrast to the behaviour of conventional thermochromic compositions based on S_A phases which always progress from the red end of the spectrum.

In order to illustrate the practical utility of fluorinated nematogens in display applications I would like to describe their use in mixtures for use over a wide temperature range. A basic performance target for such a mixture would require a clearing point of 85°C, combined with fast switching at −20°C. It is often desirable to operate the display from a 5V supply.

Compounds selected from the I series described above may readily be incorporated into eutectic systems (see Table XII). The enthalpies of solution are moderate and three component mixtures are available with nematic ranges of *ca* −10°C to +100°C. These form a basis for the formulation of practical mixtures for TN display use, but they must first be doped dielectrically positive. It is an experimental fact that the presence of lateral fluorination in the mesogenic structure depresses the stability, not only of neat smectic phases, but also of the injected smectic phases which often result from the doping of non-polar mesogens with terminal-cyano compounds. In the particular case of I series compounds, a further effect comes to our aid. Any injected smectic phase which does appear, peaks at a low concentration of positive additive, and mixtures doped to a dielectric anisotropy suitable for practical display use are free of observable smectic phases. These factors result in a considerable freedom of choice of positive dopant which may be chosen to optimise such properties as the birefringence or elastic constants in the final mixture.

In order to obtain a specified clearing point in the mixture, it is often desirable to incorporate a further component which may be a standard three or four ring high clearing point additive. Because of the high clearing point of the base eutectic, the quantities required are small, and the same considerations apply as are outlined above for positive dopants.

Such an approach to mixture formulation does not require the use of any volatile component to obtain wide nematic phase ranges and low viscosity in the final product. The resulting compositions (Table XIII) show a birefringence sufficiently high for use in 7μ cells even at elevated temperatures, and nematic ranges from +85°C or higher to −50°C without the appearance of any smectic phase. The mixtures switch well at 5V, and response time of approx. 500 mS at −20°C are obtained. Further properties are listed in the tables.

A further remarkable property of these nematogens which has not been mentioned, is the very low values of temperature dependance

TABLE XII

Properties of a low-melting eutectic of I compounds

I 33	26%	K → N	−10.5°
I 35	35%	N → I	103.5°
I 52	39%	Δn	0.150
		Δε	−0.02

TABLE XIII

Properties of wide range mixtures based on I series compounds

	E200	E203
S → N	< −50°	< −50°
N → I	88.5°	95.6°
η20	29.7 cSt	32.1 cSt
Δn	0.170	0.174
Δε	6.2	6.9
V_{TH}	2.35 V	2.23 V
M'_{20}	1.34	1.35
T_r (−20)	360 mS	740 mS
	(6V)	(5V)
T_d (−20)	496 mS	590 mS

TABLE XIV

Properties of multiplexable mixtures based on I series compounds

	E210	E220
S → N	< −50°	< −50°
N → I	85.9°	88.6°
η_{20}	24.7 cSt	25.5 cSt
Δn	0.1685	0.1607
$\Delta\epsilon$	8.6	6.8
V_{TH}	1.94V	2.30 V
M_{20}	1.79	1.77
M'_{20}	1.36	1.35
$-\frac{1}{V}\frac{dV}{dT}$	0.32% °C^{-1}	0.25% °C^{-1}
T_d (−20°)	650 mS	540 mS

of threshold voltage which can be obtained. This property is exploited in a further series of mixtures (Table XIV) which should be particularly suitable for multiplexing at moderate levels under outdoor conditions. Fast switching at −20°C, high birefringence and a clearing point in excess of 85°C are retained. A further application of these mixtures is as a host in pleochroic displays, and the materials act as good solvents for anthraquinone dyes.

Despite their unpromising beginnings, fluorinated liquid crystals are an area of intense current research activity. I hope to have illustrated some of the benefits and unique properties that can derive from this substitution, and look forward to a productive and interesting future for the field.

Acknowledgments

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