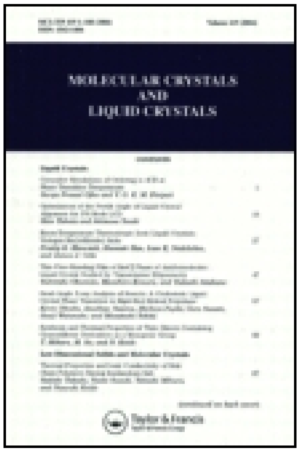

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Fluoro Substitution in Thermotropic Liquid Crystals

Michael Hird [a] & Kenneth J. Toyne [a]

[a] Department of Chemistry, University of Hull, Hull, HU6 7RX, UK

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Invited Article

Fluoro Substitution in Thermotropic Liquid Crystals

MICHAEL HIRD[a] and KENNETH J. TOYNE[b]

Department of Chemistry, University of Hull, Hull, HU6 7RX, UK

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Fluoro substitution in thermotropic liquid crystals provides a general way of modifying the properties of a parent system. Melting point, transition temperatures, mesophase types and other physical properties are affected by fluoro substitution so that frequently the behaviour of the parent compound can be manipulated and improved in a predictable manner. This review discusses the effects of fluoro substitution at different positions in a variety of core systems and briefly considers the problems arising in the synthesis of fluoro-substituted liquid crystals.

Keywords: Fluoro substitution; liquid crystals; lateral substitution; structure-property relationships; review

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[a] e-mail: m.hird@chem.hull.ac.uk
[b] e-mail: k.j.toyne@chem.hull.ac.uk

Fluoro substitution in liquid crystals has a considerable influence on properties such as melting point, phase transition temperatures, mesophase morphology, dipole moment, dielectric anisotropy, optical anisotropy, elastic constants and viscosity; for this reason it permits the design of mesogens with improved physical properties for electro-optic applications. Substitution may occur at many different positions within the core, the terminal chains or the linking groups, and the different points of substitution produce materials with widely different physical properties. This review considers the massive impact that fluoro substitution has had on the design of liquid crystal compounds, it discusses the steric and electronic effects arising from fluoro substitution, how they influence the physical properties of liquid crystals and it attempts to rationalise the substituent effects on mesophase behaviour. In addition, the review considers some of the important general issues confronted in the synthesis of fluoro-substituted materials.

Transition temperatures for mesogenic compounds have been comprehensively tabulated in books [1,2] and on a computer database [3] and several books have sections dealing with fluoro substitution [4–7].

1. INTRODUCTION AND GENERAL ISSUES

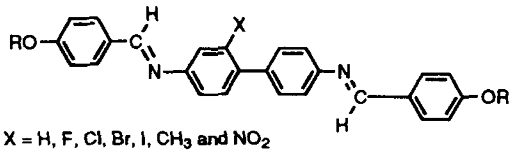
Liquid crystal mesophases depend for their existence on an adequate degree of intermolecular association to give a measure of order to the systems;

increasing disruption of molecular associations will reduce the tendency for a liquid crystalline mesophase to exist and will tend to favour the disorder of an isotropic liquid. One obvious and generally applicable way of overcoming the strength of the pre-existing molecular associations is by increasing the temperature of the system so that different mesophases may arise before the isotropic phase is reached. Another way of modifying intermolecular associations in a given molecular structure is by including a substituent which increases the separation of the molecules (for steric reasons) and diminishes the strength of the intermolecular forces or which may in some instances increase molecular associations, *e.g.*, by increasing dipolar attractions.

The range of acceptable substituents that can be considered for use in this way is very limited because all simple, common substituents based on the First Row elements carbon, nitrogen, oxygen are multi-atomic and often quite polar (*e.g.*, CH_3, CN, NO_2, NH_2, OH are the simplest, and the last two have dominating hydrogen-bonding possibilities) and only the halogens are mono-atomic. There is no possible way of designing a substituent or range of substituents with defined size and one has to acknowledge that very few substituents can be used in a general way to modify the structure of molecules and retain mesogenicity.

The influence of the size of a substituent on reactivity or physical properties is difficult to quantify because both steric effects (which imply a directional quality) and bulk effects (*i.e.*, related to volume) are involved and these effects are not directly related to each other except for 'symmetrical' or 'spherical' substituents such as CH_3 or F. Because of the directional nature of steric effects, more than one parameter is often needed to describe the effect of a substituent adequately, and several ways of expressing this are used in correlation analysis in chemistry and biology [8]. The same or even greater complexity will almost certainly apply to the way in which the size of a substituent affects intermolecular associations and the stability of a mesophase.

The quantitative correlation of structure with reactivity is widely and successfully used for organic and biological reactions [9–13] and it is tempting to consider the use of structure-property parameters to quantify the effect of substitution on mesophase transition temperatures, although it would be unreasonable to expect reaction-based parameters to be generally applicable. The major problem faced in rationalising substitution effects on mesogenicity is that there is no specific 'reaction site' to consider on which the steric or polar effects of the substituent can act. Attempts have been made (*e.g.*, Refs. [14–16]) to relate transition temperatures to molecular breadth (*i.e.*, the diameter of the narrowest cylinder through which the molecule may pass [14]), substituent volume [15] and van der Waals volume [16]. Branch *et al.* [14] reported the transition temperatures for compounds **1** and showed that the effects of all the substituents on $T_{N\text{-}I}$ values were correlated with increasing molecular breadth, as was the case for the $T_{S_A\text{-}N}$ values, except that the nitro substituent gave higher than expected smectic stability which was attributed to the dipolar character of the group.



1

X = H, F, Cl, Br, I, CH_3 and NO_2
R = C_7H_{15}, C_8H_{17}, C_9H_{19} and $C_{10}H_{21}$ (series with N-I transitions)
R = C_9H_{19} and $C_{10}H_{21}$ (series with S_A-N transitions)

The $T_{N\text{-}I}$ values for the heptyloxy to decyloxy series of compounds are also correlated quite well with steric substituent parameters, $-E'_s$, which are based on a revised Taft scale of steric parameters [17] (see Fig. 1) derived from kinetic data; this represents an alternative approach to that used by Branch [14], Demus [15] and Osman [16] and confirms that the effect of a substituent on $T_{N\text{-}I}$ values is largely determined by steric and bulk factors.

The effect of substituents on depressing the stability of the smectic A mesophase is however dependent on factors other than size. Data for the same set of compounds used in Figure 1 allows the $T_{S_A\text{-}N}$ values for the full range of substituents for the nonyloxy and decyloxy series to be plotted against $-E'_s$ values. The results shown in Figure 2 indicate that although steric factors are still important and predominant, the nitro group, presumably by dipolar attractive interactions, leads to a less severe depression of the stability of the smectic phase.

Without question, the fluoro substituent is the most acceptable substituent that can be tolerated in terminal chains, linking groups or cores; it is mono-atomic and is the next smallest unit after the hydrogen it replaces (claims that 'the steric requirements of the two atoms are so similar that formal replacement of H by F can be regarded as an isogeometric transformation' [18] are however disputed and fluorine and oxygen are more closely similar in size so that fluorine and the hydroxy group are essentially 'chemical isosteres' [19, 20]; the van der Waals radii for some common small atoms are give in Table I [21].

Fluoro substitution is important in biological systems and much work has been carried out on fluoro-substituted pharmaceutical materials [20]. In such systems it has been shown that the steric impact of the fluoro substituent is

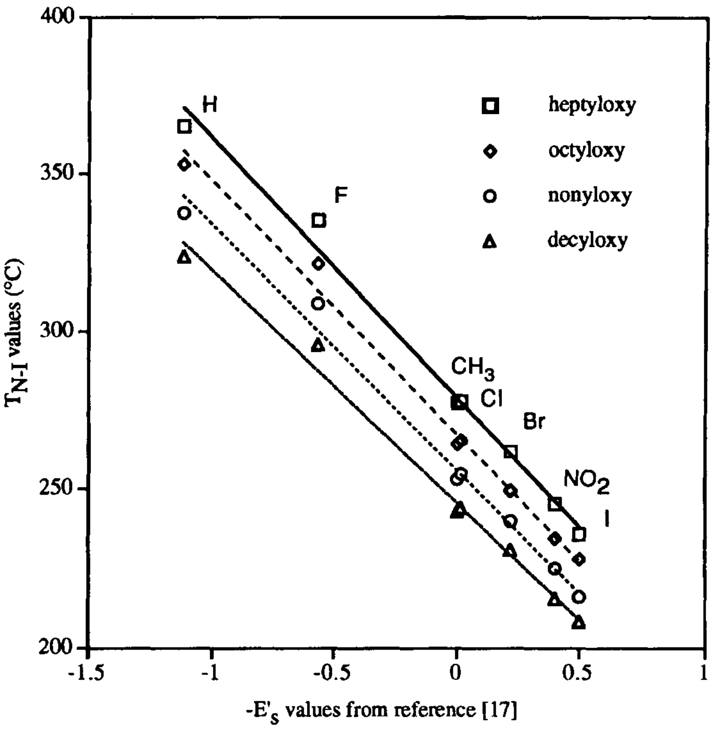
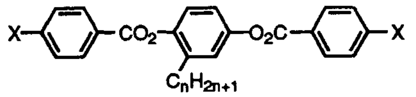


FIGURE 1 A plot of $T_{N\text{-}I}$ values for compounds **1** against $-E'_s$ values from Ref. [17].

not significant, and it emerges as a true hydrogen mimic. However, the true steric effect observed for a fluoro substituent must depend on the environment of the substitution, and in liquid crystals many locations have been investigated. The range of the magnitude of the steric effects arising from various types of fluoro substitutions will be seen in the later discussions.

Weissflog and Demus [22, 23] have considered more than one hundred 1,4-di-(4-substituted-benzoyloxy)-2-alkylbenzenes (**2**) to show the effect of increasing the length of a lateral alkyl group in systems with various terminal groups.

2



X = R, RO, RCOO, ROCOO
n = 0-16

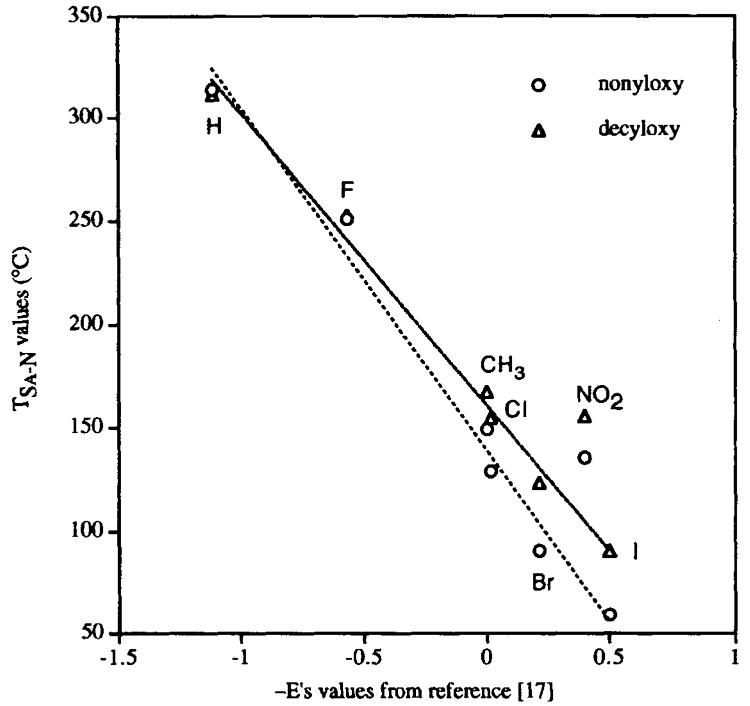
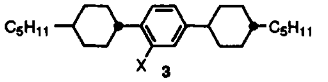


FIGURE 2 A plot of $T_{S_A\text{-}N}$ values for compounds **1** ($R = C_9H_{19}, C_{10}H_{21}$) against $-E'_s$ values from Ref. [17].

TABLE I The mean van der Waals radii for some common atoms [21]

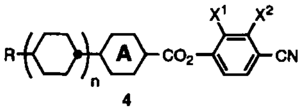
Substituent	*Size* (*Å*)
H	1.20
F	1.47
O	1.52
N	1.55
C	1.70
Cl	1.75
Br	1.85
I	1.98

It is clear from this work that substitution at a central position in the core separates the molecules to such an extent that the attractions responsible for smectic properties are decreased dramatically. Another study [16] of lateral substituent effects uses inflexible substituents with accurately definable volumes in parent systems based on terminally non-polar (compounds **3**) and terminally polar (compounds **4**) mesogens.



3

X = H, F, Cl, CH$_3$, Br, CN, NO$_2$, NH$_2$

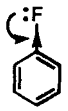


4

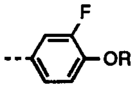
n = 0, A = phenyl or cyclohexyl
n = 1, A = phenyl
X^1 = H, F; X^2 = H, F, Cl, CN

Once again, the conclusion is that lateral substituents sterically force the molecules apart, hinder smectic packing and relatively favour the nematic phase. The nematic clearing point depends mainly on intermolecular separation and dipole attractive forces play a minor role compared to dispersive forces.

The overall effect of fluoro substitution depends not only on the small size of the substituent but also on the polarity of the substituent. Since fluorine is the most electronegative of all the elements, its polarity is a valuable feature in molecular design and the influence it has depends on the nature of the region of the molecule in which the substitution occurs. If the parent region is aliphatic or alicyclic then a strong dipole will be introduced by the



I



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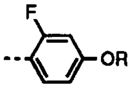
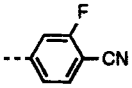
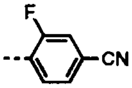


III



IV



V

C($\delta+$)—F($\delta-$) bond because of the inductive effect arising from the high electronegativity of F. If the fluoro substituent is in an aromatic system then the movement of electrons is more complicated. Not only is there an inductive effect towards the fluoro substituent (probably somewhat less than for the alkane situation because of the change from sp^3 hybridisation of the carbon in alkanes to sp^2 hybridisation in aromatic systems), but a resonance or mesomeric effect can operate in which a lone pair of electrons on fluorine is partially delocalised with the π-electrons of the aromatic ring and so opposes the inductive withdrawal (**I**). The extent to which this operates is

FIGURE 3 A typical structural template for a calamitic liquid crystal.

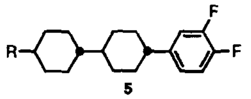
not easy to quantify but it will obviously depend on the nature of the aromatic ring and also upon whether the ring is 'electron-rich' (**II** or **III**) or 'electron-poor' (**IV** or **V**) or whether it is placed at a position of greater electron-richness (**II** or **V** rather than **III** or **IV** respectively). Even in apparently straight-forward issues such as the effect of substitution on acid or base strengths, it is not possible to separate polar and steric effects and it is still more difficult to quantify the origin of the influence of a substituent on mesomorphic behaviour.

There are many different positions within a molecular structure at which a fluoro substituent can be located and substitution at each of these positions produces its own distinct and characteristic effect on the properties of the parent system. A typical template for a liquid crystal molecule is shown in Figure 3, and this illustrates the various positions available for fluoro substitution; R and R' are the terminal substituents, X, Y and Z represent linking groups (which are often absent), M and N are lateral substituents (also often absent), and A and B are core units. Fluoro substitution in liquid crystals is therefore employed for many different reasons, but the overall aim is to modify material properties in order to optimise performance in applications.

2. GENERAL EXAMPLES OF FLUORO SUBSTITUTION

An outline of some of the wide variety of possible types of fluoro substitution will illustrate the potential for structural modification and will provide a framework for the more detailed subsequent discussion.

(a) Fluoro substitution at a terminal position (*e.g.*, Structure **5**) serves to provide nematic compounds with positive dielectric anisotropy, as normally provided by the terminal cyano substituent. However, the fluoro substituted compounds have the advantage of possessing a high resistivity and so they can be used in state-of-the-art active matrix (thin-film transistor, TFT) displays.



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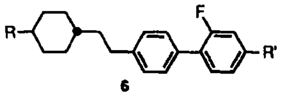

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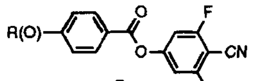

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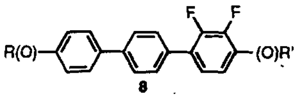

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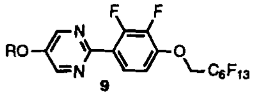

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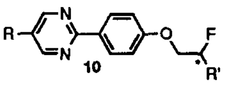


10

(b) Probably the most widely investigated type of fluoro substitution is that at lateral positions (*e.g.*, Structures **5**–**9**) and it has been employed for a variety of reasons. At first sight, it may be thought that anything that protrudes from the side of a molecule will obviously disrupt molecular packing and therefore reduce melting point and liquid crystal phase stability, but the real situation with lateral fluoro substitution is much more subtle. Generally, melting points are reduced, but this is not always the case, and usually smectic phase stability is reduced much more than nematic phase stability, and both of these general observations are invaluable in the generation of materials for nematic mixtures. However, lateral fluoro substitution in certain cores, and at specific core positions (notably at the 'outer edge' where space is filled) can uphold smectic phase stability and this provides some scope for the design of mesogens with smectic phases still present (*e.g.*, Structure **8**). Additionally, a lateral fluoro substituent (*e.g.*, Structure **8**) tends to increase the lateral dipole within a molecule which can generate molecular tilting and so produce phases such as the smectic C phase which are required for ferroelectric and antiferroelectric displays. There are three main effects which lateral substitution can achieve: (i) a lateral substituent which is shielded by the rest of the molecular structure may lead to a small decrease or even to an increase in mesophase stability, (ii) a lateral substituent may diminish the close broad-side association of molecules by steric or polar effects or by causing conformational changes in the molecule and these may lead to a reduction in melting point and in mesophase thermal stability (usually affecting smectic phases more than nematic phases), (iii) a dipolar lateral substituent (or substituents) may be used to generate systems with negative dielectric anisotropy values ($-\Delta\varepsilon$) or to enhance positive dielectric anisotropy values ($+\Delta\varepsilon$).

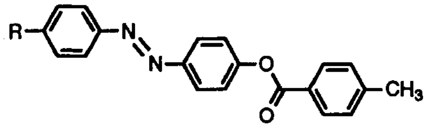
(c) More recently, fluoro substituents have been employed in the terminal chains of liquid crystal molecules in a wide variety of systems (*e.g.*, Structures **9** and **10**). The use of perfluoro-substituted terminal chains tends to create more elongated chains of increased rigidity [24], which serves to enhance liquid crystal phase stability, especially that of smectic mesophases. Compounds have also been prepared with partially fluorinated terminal chains consisting of segments of fluorocarbon and segments of hydrocarbon in an attempt to control the molecular self-assembly. One particularly important aspect of fluoro substitution in a terminal chain is where the fluoro substituent, or often a trifluoromethyl group, is positioned at a chiral centre to give an enantiomerically pure liquid crystal compound (*e.g.*, Structure **10**). Such optically pure chiral fluoro-substituted materials have been used in ferroelectric mixtures for very fast-switching displays.

In addition to tailoring the properties of molecules for practical applications, the synthesis and evaluation of fluoro-substituted liquid crystals has provided important information on structure-property relationships. This review will now consider some of the significant results that have been obtained in both of these areas.

3. TERMINAL FLUORO SUBSTITUTION

Many years ago liquid crystals with different terminal groups were prepared, in order to establish structure-property relationships and to determine the mesogenic order for each substituent, and it was found that a terminal fluoro substituent was poor at generating mesophases [1]. Although long hydrocarbon terminal chains have low polarisability, they increase considerably the length-to-breadth ratio of molecules, and so are good promoters of liquid crystal phases. On the other hand, a terminal cyano substituent does not increase the molecular length significantly, but it does have a high polarisability, facilitates antiparallel correlations, and is a good promoter of liquid crystal phases. A terminal fluoro substituent, however, has both the disadvantages of the previous examples, namely small size and low polarisability. Some enhancement of mesogenicity is achieved with bromo- and chloro-substituents because of their higher polarisability and greater size. Table II highlights the general trend in nematic phase stability for various terminal substituents in one particular structure and the general terminal group efficiency order given below shows that fluoro is the least effective terminal substituent [25].

TABLE II The effect of different terminal units on liquid crystal phase stability [1]

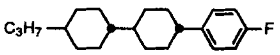


Compound		*Transition temperatures (°C)*				
Number	*R*	*C*		*N*		*I*
11	F	•	156.0	•	222.0	•
12	CH_3	•	160.0	•	243.5	•
13	I	•	187.0	•	243.5	•
14	Br	•	178.0	•	251.0	•
15	Cl	•	167.0	•	252.0	•
16	NO_2	•	179.5	•	289.0	•
17	CN	•	169.0	•	312.0	•

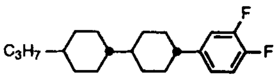
$$\mathrm{Ph} > \mathrm{NHCOCH_3} > \mathrm{CN} > \mathrm{OCH_3} > \mathrm{NO_2} > \mathrm{Cl} > \mathrm{Br} > \mathrm{N(CH_3)_2} > \mathrm{CH_3} > \mathrm{F} > \mathrm{H}$$

On this evidence it might be reasonable to assume that molecules with a terminal fluoro substituent are of little use as liquid crystals and this view persisted for many years. However, several years ago liquid crystal displays were developed that employ an active matrix addressing system through the use of thin film transistor (TFT) technology. Such technology requires a liquid crystal material of very high resistivity, but the existing positive dielectric anisotropy nematic materials contained a terminal cyano substitutent, which gives a very low resistivity, and so they are unsuitable for active matrix displays. Terminally fluoro-substituted materials were suitable because of their high chemical and photo-chemical stability, their low viscosity (because of the small fluoro substituent) and the positive dielectric anisotropy generated by the high polarity of the C—F bond. Additional desirable properties could be incorporated into the molecules through the choice of ring system used; for example, cyclohexane is chosen for low birefringence and benzene for higher birefringence systems and lateral fluoro substituents were also used to modify the dielectric anisotropy and elastic constants of the parent systems.

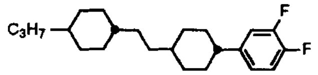
With these guidelines, a wide range of materials that contain a terminal fluoro substituent were synthesised (*e.g.*, **18**–**24**). A single fluoro as a terminal substituent in an aromatic system has a much lower dipolar effect than a trifluoromethyl group (typical dipole moments of fluorobenzene and trifluoromethylbenzene are 1.50 and 2.54 respectively; see Section 4.10.1) but, because it is smaller and less destructive of nematic character, a fluoro substituent *ortho* to a terminal fluoro may be used to increase the dipole without losing mesogenicity. Careful structural choice produced materials with high nematic phase stabilities (*e.g.*, compound **18**), but with melting points which are rather high. However, the introduction of a lateral fluoro substituent tends to prevent efficient intermolecular packing and provides materials with very low melting points (*e.g.*, compound **21** and compare compounds **18** and **19**). The nematic phase stability is reduced through the steric effect of the lateral fluoro substituent, but it still remains high in some compounds (*e.g.*, **19**, **23** and **24**).



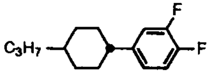
18
C 90.0 N 158.0 I



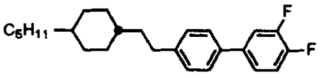
19
C 44.2 N 118.0 I



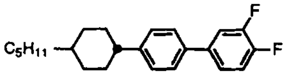
20
C 36.1 N 105.2 I



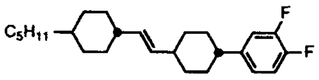
21
C -22.3 I



22
C 74.8 N 95.9 I



23
C 55.1 N 108.2 I

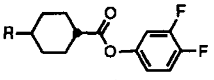


24
C 31.0 N 136.2 I

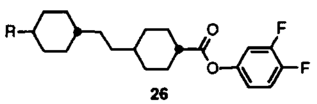
Many examples have appeared of this use of a 3,4-difluorophenyl unit attached to an extended core unit to achieve an adequate value of dielectric anisotropy from the two substituents. Eight different types of core unit were considered in one investigation [26] and in many cases quite useful nematic ranges were achieved, as shown by the examples **19**, **20**, **22**–**24**. The physical assessment of these compounds shows that their mixtures have reasonably high values of dielectric anisotropy ($\Delta\varepsilon = +4.1$ to $+6.6$), high stability, low viscosity (bulk viscosity is ~ 20 to 26 cP at 20°C) and a high resistivity ($\sim 3 \times 10^{13}$ to 2×10^{14} ohm cm) which makes them useful for TFT (thin-film-transistor) and MIM (metal-insulator-metal) active matrix displays.

Compounds in which other polar regions act cooperatively with 3,4-difluoro substituted phenyl rings have also been used (see Structures **25**–**27**

[27], **28** [28], **29** and **30** [29], and **31** and **32** [30]) and these also are low viscosity, low polarity nematogens; the dielectric anisotropy value of 20.8 for compound **32** is extremely large for halogeno nematics and the value is comparable to those of cyanopyrimidines and laterally fluorinated cyano esters. Their effect on a range of other device properties has been discussed and some of these compounds are useful for high-level multiplexed TN-LCDs (Twisted Nematic – Liquid Crystal Displays) and TFT-addressed TN-LCDs. All these 3,4-difluoro systems have the advantage that, unlike strongly polar cyano compounds, they have less tendency to dissolve residual ions trapped in the polyimide aligning layers of TN-LCDs and larger specific resistivities can be obtained. As a consequence, large holding ratios for charge storage are possible in TFT-TN-LCDs and this prevents the LCD picture element from discharging during the video frame time.



25



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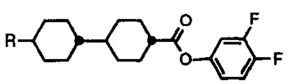
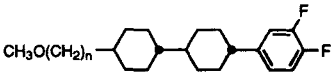


27



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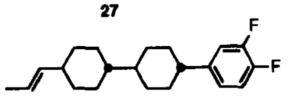

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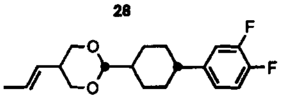

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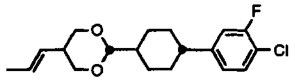
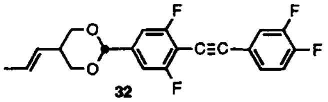


31

$\Delta\varepsilon\ (T_c\text{–}10\ °C) = 10.0$



32

$\Delta\varepsilon\ (T_c\text{–}10\ °C) = 20.8$

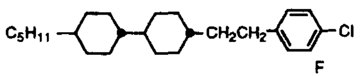
It is really quite remarkable that the above-mentioned structure-property relationships (Tab. II) were discovered, along with the first fluoro-substituted liquid crystals in the 1920s, and yet it was not until the 1990s that the true value of a terminal fluoro substituent was realised for designing molecules for use in applications.

4. FLUORO SUBSTITUTION AT LATERAL POSITIONS

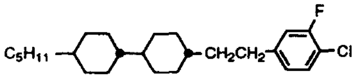
Examples of lateral fluoro substitution *ortho* to a terminal fluoro were given in Section 3 as one possible type of lateral substitution. Fluoro substitution at other lateral positions in a core unit offers further scope for structural variation because of the number and variety of different sites available; clearly, fluoro substitution in terminal chains is also possible at numerous and varied sites. As the number and nature of the rings used in a liquid crystal structure increases, the number of possible sites for lateral substitution increases and, as will be illustrated later, each site can have a completely different effect on the physical properties of the resultant compounds.

4.1. Terminal Chloro Substitution

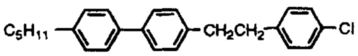
A terminal chloro substituent has also been considered for positive dielectric anisotropy materials; because of the longer C-halogen bond, chloro compounds have a greater dipole moment than fluoro compounds, and because chloro is larger than fluoro it tolerates an *ortho* fluoro substituent more readily. Terminally chloro-substituted compounds such as **33** [31] and **35**, **37** [32] have been prepared with fluoro substitution to assist the dipoles of the terminal chloro. The dielectric, optical and electro-optical properties of these compounds and of mixtures have been measured and are encouraging for the use of such materials in active matrix display applications.

33


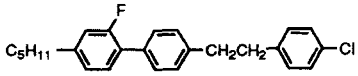
C 57.6 N 161.3 I

34


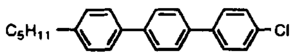
C 39.9 N 142.5 I

35


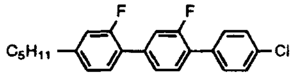
C 128.8 [N 106.5] I

36


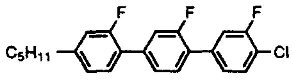
C 53.0 (S_B 19.0 S_A 43.0) N 82.0 I

37


C 105.0 S_B 245.0 I

38


C 60.3 N 111.7 I
{Δn 0.25; Δε +12}

39


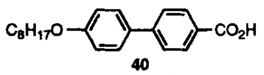
C 66 N 76.6 I
{Δn 0.22; Δε +14}

Some of the effects of fluoro substitution which are discussed more fully in later sections, are apparent from the set of terminal chloro compounds

33–**39**, *i.e.*, fluoro substitution leads to a lower melting point, outer-edge fluoro substitution (*ortho* to the terminal chloro substituent, compounds **33** and **34**) does not decrease the nematic stability too severely, mid-core fluoro substitution suppresses smectic character (compounds **37**, **38** and **39**).

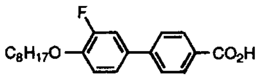
4.2. Carboxylic Acids

Fluoro substitution at a lateral position was first investigated many years ago (1950s) in benzoic acids [33] and biphenylcarboxylic acids (*e.g.*, compounds **40** and **41**) [34, 35] and the synthesis of such materials represents important investigations into structure-property relationships that have proved significant in later work on lateral fluoro-substituted compounds. Compound **40** has a high melting point, and high smectic and nematic phase stabilities, superficially unusual for two-ring compounds, but intermolecular hydrogen bonding of the carboxylic acid groups effectively generates a five-ring unit; the result is a 'dimeric' structure and the effect of introducing two fluoro substituents into the 'dimer' of the parent system is in reality being assessed. Fluoro substitution at the outer-edge position (compound **41**) considerably reduces the melting point, but has relatively little effect on the liquid crystal stability. In fact the outer-edge fluoro substituent has reduced the nematic phase stability by more than the smectic and, as will be seen later, this is a rather unusual situation. The fact that the fluoro substituent is small and occupies free-space at an outer-edge position explains why the overall effect on liquid crystal phase stability is minimal, and the additional fact that the fluoro substituent is polar upholds the smectic phase stability because of the enhanced lateral attractions off-setting the small steric effect disrupting the lamellar packing. On the other hand (*e.g.*, see Sections 4.8 and 4.9), the location of a fluoro substituent at an inner-core position can cause a considerable twisting of two aromatic rings, which reduces the longitudinal polarisability and so the liquid crystal phase stability is considerably affected.



40

C 183.0 S_X 255.0 N 264.5 I



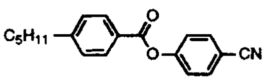
41

C 119.5 S_C 254.5 N 255.5 I

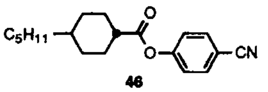
The suggestion has been made above than an outer-edge fluoro substituent helps to fill a structural void where the terminal group joins the core. An alternative way of expressing this is to regard the position *ortho* to a terminal group as being somewhat shielded by the group. The more impressive example of how a substituent can fill a shielded space effectively comes from 6-alkoxy-5-substituted-naphthalene-2-carboxylic acids [36].

4.3. Cyano Compounds

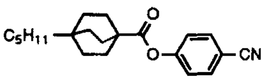
Fluoro substitution at a lateral position next to a terminal cyano group has been investigated intensively, for example in compounds with ester, dimethylene and methyleneoxy links and in biphenyl and terphenyl systems. Parent (*i.e.*, non-fluoro-substituted) terminal cyano liquid crystals (*e.g.*, compound **42**) [37] have a reasonably high positive dielectric anisotropy which is beneficial for low-voltage switching in TN-LCDs. However, because terminal cyano compounds give antiparallel correlation of their molecules, their dielectric anisotropy is not as high as might be expected. Fluoro substitution next to the terminal cyano group disrupts these antiparallel correlations and gives a larger positive dielectric anisotropy and in some cases the antiparallel correlations appear to be completely destroyed (see below), but the other consequence of reducing the antiparallel correlations is that the mesophase stability is reduced significantly (see compounds **42**–**45**) [37–38]. However, the advantages offered by such compounds are not as great as at first sight because in liquid crystal mixtures the antiparallel correlations would probably be disrupted by other components present in the mixture.



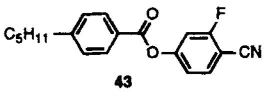
42
C 64.4 (N 55.4) I Δε = 40.1



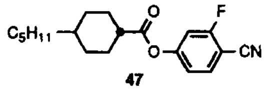
46
C 47 N 79 I



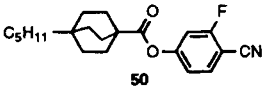
49
C 89 N 109 I



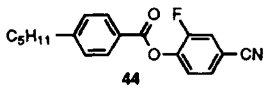
43
C 30.5 (N 24.5) I Δε = 41.0



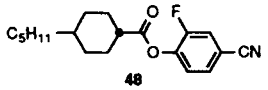
47
C 40 N 42 I



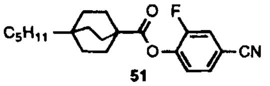
50
C 80.5 (N 65) I



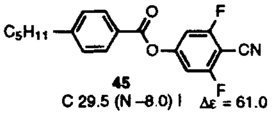
44
C 53.5 N 65 I



48
C 75.5 N 93.5 I



51
C 84 N 133 I



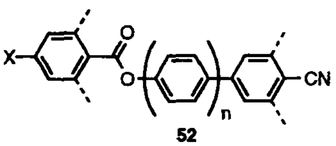
45
C 29.5 (N –8.0) I Δε = 61.0

Other examples of the use of lateral fluoro-substitution to increase $+\Delta\varepsilon$ values are provided by compounds **47**, **48**, **50** and **51** [16, 38–40] (see also [41]) where none of the esters gives smectic phases on supercooling to room temperature, and the clearing temperatures for the cyclohexyl and bicyclo[2.2.2]octyl 4-cyano-2-fluorophenyl systems are higher than for the parent compounds, partly because the substituent is shielded. Simple shielding of the fluoro substituent would result in its inability to depress transition temperatures, whereas in these examples there is a positive advantage for mesophase stability in having the 2-fluoro substituent present. The enhancing effect is not seen for non-cyano esters (*cf.*, compounds **72**, **75** and **78**) and would seem to indicate that the fluoro substituent in the cyano esters, in addition to being shielded, is assisting the antiparallel correlation for electronic reasons. A possibly related situation emerges for fluoro substitution in terminal cyanobiphenyls where the 4-cyano-2-fluorobiphenyls have higher nematic stability than the 4′-cyano-2-fluorobiphenyls, *i.e.*, the former compounds appear to be less destructive of antiparallel correlations [42–44].

Fluoro substitution *ortho* to the cyano group in the esters depresses the clearing point more severely as antiparallel associations are diminished but, for the same reason, compounds of higher $+\Delta\varepsilon$ value are obtained. The physical properties of 4-cyano-2-fluorophenyl (**44**, **48** and **51**) and 4-cyano-3-fluorophenyl esters (**43**, **47** and **50**) have been reported in great detail [45] in comparison with the unfluorinated esters. An exceptionally high value of $\Delta\varepsilon$ ($+48.9$ at $T/T_{N\text{-}I} = 0.95$) was obtained for 4-cyano-3-fluorophenyl 4-heptylbenzoate, which appears to exhibit no association whatsoever (Kirkwood–Fröhlich *g* factor = 1) [45, 46].

A lateral fluoro substituent next to the terminal cyano group (*e.g.*, compound **43**; dipole moment 6.6 D, $\varepsilon_{//} = 51.3$, $\varepsilon_{\perp} = 10.3$, $\Delta\varepsilon = 41.0$) contributes to both the parallel and perpendicular permittivities and leaves the overall anisotropy similar to that of the parent system (dipole moment 5.9 D, $\varepsilon_{//} = 49.9$, $\varepsilon_{\perp} = 9.8$, $\Delta\varepsilon = 40.1$). However, when a second fluoro substituent is located next to the terminal cyano group (*e.g.*, compound **45**, dipole moment 7.2 D, $\varepsilon_{//} = 70.7$, $\varepsilon_{\perp} = 9.7$, $\Delta\varepsilon = 61.0$), the perpendicular permittivity is reduced, but the parallel permittivity is further increased, and yields an extremely high positive dielectric anisotropy. The effect on melting point and liquid crystal phase stability of such lateral fluoro substitution in cyano esters is also very interesting. Introduction of the first fluoro substituent causes a 34°C reduction in melting point and a comparable 31°C reduction in nematic phase stability, but the second fluoro substituent leaves the melting point almost unchanged and the nematic phase stability is reduced by a further 32.5°C. Such reductions in melting point on monofluoro substitution are general and useful and often much greater depressions can arise (*e.g.*, see compounds **134**–**141**), however, exceptions do occur and these illustrate the difficulty in rationalising molecular structure and melting point behaviour. Reductions in nematic phase stability almost always arise from fluoro substitution and these depressions are usually not desirable; again exceptions to this general statement exist (*e.g.*, see compounds **46** and **48** *etc.*) but they occur less commonly than for the melting point exceptions. Disubstitution, as seen here, usually gives a further significant reduction in clearing point if the second substituent is not shielded, but melting points are depressed to a smaller extent or may frequently increase again. Although compound **45** is inferior to compounds **42** or **43** on the basis of clearing points, it may be possible to use it in small quantity in a nematic mixture to give a significant increase in dielectric anisotropy without too detrimental an effect on the overall nematic phase stability.

All possible combinations of monofluoro to tetrafluoro substitution at the positions *ortho* to the carboxylate and cyano groups in Structure **52** have been made in order to determine those features responsible for giving large positive values of dielectric anisotropy [37]; the physical property results for



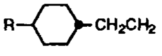
52

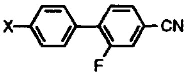
$X = C_5H_{11}$ or C_4H_9O
$n = 0$ or 1

these compounds are given in Ref. [47]. The $T_{N\text{-}I}$ values for all the series of esters corresponding to Structure **52** decrease steadily as one or two fluoro substituents are added to the phenol part or to the acid part, but the fluoro substituents near the cyano group have the greatest effect. In general, the phenyl benzoate esters gave monotropic or virtual $T_{N\text{-}I}$ values, but all the biphenyl benzoate esters have enantiotropic phases.

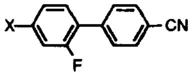
Lateral fluoro substitution in terminal cyano systems **53** and **54** are further examples of attempts to modify antiparallel associations, so influencing viscosity and elastic constants, in addition to the $+\Delta\varepsilon$ values. The results for fluoro substitution at 2- and 2′-positions in Structures **53** and **54** show that substitution as in **54** gives a greater depression (35–39°C) than

X = R, RO,



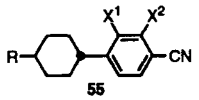


53



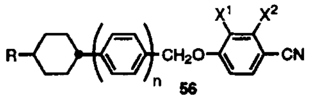
54

for Structures **53** (depression of 13 – 18°C) [42 – 44]. The depression of 13 – 18°C is a remarkably small effect for a lateral substituent which also increases the interannular dihedral angle of the biphenyl rings, but the fluoro substituent is in these cases opposing the dipole of the cyano group and gives a smaller $\Delta\varepsilon$ value [48]; similar relative effects on transition temperatures are seen for fluoro substitution in 4-(*trans*-4-alkylcyclohexyl)benzonitriles (**55**) (PCH systems) [49] and in methyleneoxy linked systems **56** [50].



55

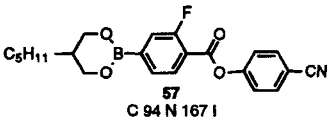
X^1, X^2 = H or F



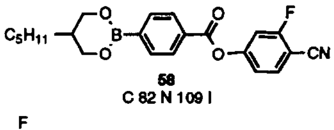
56

X^1, X^2 = H or F
n = 0 or 1

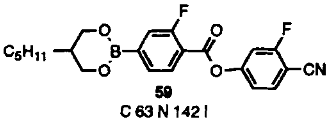
Terminal cyano 1,3,2-dioxaborinanes have higher values of $\Delta\varepsilon$ than the corresponding 1,3-dioxanes and attempts have been made to increase these values even further by halogen substitution at positions designed to augment the contribution to dielectric anisotropy from the 1,3,2-dioxaborinane ring and the cyano group [51]. For example, cyano compounds of type **57** – **59** were prepared and a dielectric anisotropy value of + 80 is reported for the C_3H_7 analogue of compound **59**.



57
C 94 N 167 I



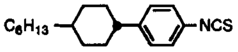
58
C 82 N 109 I



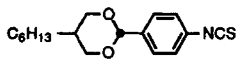
59
C 63 N 142 I
$\Delta\varepsilon$ = +46

4.4. Isothiocyanates

Compounds with isothiocyanato terminal groups give very different types of mesophase depending upon the nature of the core; sometimes a nematic phase of quite high thermal stability is obtained (*e.g.*, compound **60**) whereas the dioxane analogues (**61**) give only the smectic A phase [52]. In contrast

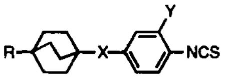


60
C 12.5 N 43.0 I

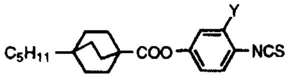


61
C 35 S_A 79 I

to cyano compounds, isothiocyanato systems exist in the mesophase as single, unpaired molecules and in the smectic phase the layer spacing is almost equal to the length of a single molecule. Several types of bicyclo[2.2.2]octanes with isothiocyanato terminal groups (**62**) have been



62 X = single bond, CH_2CH_2, COO, OOC, CH_2O
Y = H, F

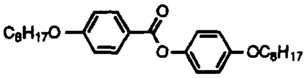


63, Y = H, C 74.5 N 113.5 I
64, Y = F, C 63.5 N 102.5 I

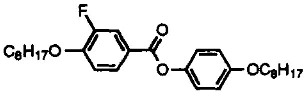
prepared and those with an *ortho* fluoro substituent [53] show that the clearing point is lowered by only about 10–11°C (see **63** and **64**). This reduction is a much smaller effect than with a terminal cyano group present (see compounds **49** and **50** which show a 44°C reduction) and it is compatible with the absence of antiparallel correlation.

4.5. Esters

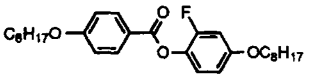
Lateral fluoro substitution in non-cyano esters has been studied extensively in the search for both nematic and smectic C materials. Phenyl benzoates and phenyl cyclohexanecarboxylates [54] are mesogens with simple structures and with two terminal alkoxy chains present (*e.g.*, compound **65**) they have quite high clearing points for two-ring systems; the combination of two outer polar units with the central polar ester function gives the tilted smectic C phase. There are four different positions for fluoro substitution in phenyl benzoates, two at 'inner-core' positions near the linking group and two at 'outer-edge' positions, and the transition temperatures for some dialkoxy compounds (**65**–**68**), alkylalkoxy compounds (**69**–**73**) and dialkyl compounds (**74**–**79**) demonstrate some significant variations in the effects on nematic, smectic A and smectic C phase stabilities arising from substitution at different positions. As noted above, outer-edge fluoro substitution (*e.g.*, at positions **a** and **d** in Structure **80**; see Tab. III) causes molecular broadening, which disrupts molecular packing, but at the same time space between the core and the terminal group is more efficiently filled with a polar unit which enhances lateral interactions and promotes smectic character. The balance of these two factors dictates the influence of such fluoro substitution on mesomorphic behaviour. A fluoro substituent at an inner-core position (*e.g.*, **b** and **c** in Structure **80**) may cause the ring in which it is substituted to twist with respect to the linking group (or in other cases, with respect to an interannular bond) and is more destructive of the smectic phase than the nematic. These observations on the effects of 'inner-core' and 'outer-edge' fluoro substitution apply to compounds with different mesogenic cores and are further illustrated in other sections of this review (particularly in Section 4.9).



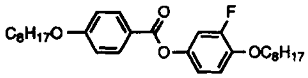
65
C 63.0 S_C 74.0 N 91.0 I



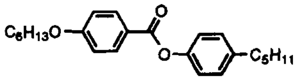
66
C 63.5 S_C 70.0 N 75.5 I



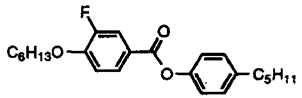
67
C 48.0 (S_C 19.0) N 65.0 I



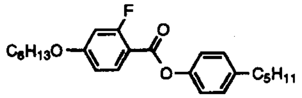
68
C 56.5 (S_C 55.0) S_A 78.0 I



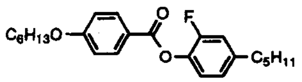
69
C 49.5 N 62.0 I



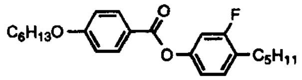
70
C 66.0 I



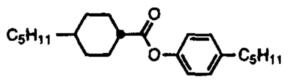
71
C 22.0 N 43.7 I



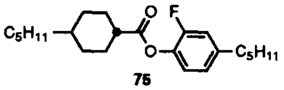
72
C 28.0 N 37.0 I



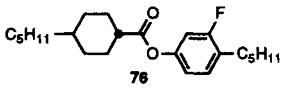
73
C 39.5 S_A 48.6 I



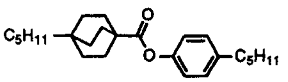
74
C 36.0 (S_A 29.0) N 48.0 I



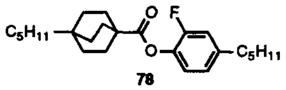
75
C 17.5 N 36.5 I



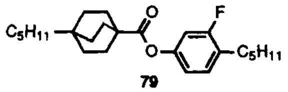
76
C 27.5 (S_A 18.7 N 26.3) I



77
C 31.0 N 64.5 I



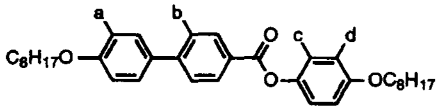
78
C 26.0 N 65.0 I



79
C 44.5 (N 38.5) I

TABLE III The effect of lateral fluoro substitution on some three-ring esters [56]

80



Compound					*Transition temperatures (°C)*										
No.	*a*	*b*	*c*	*d*	*C*		S_B		S_C		S_A		*N*		*I*
81	H	H	H	H	•	110.0	•	116.0	•	165.0	•	200.0	–	–	•
82	F	H	H	H	•	93.0	–	–	•	167.5	•	182.5	–	–	•
83	H	F	H	H	•	87.0	–	–	•	140.5	–	–	•	164.0	•
84	H	H	F	H	•	68.0	–	–	•	137.0	–	–	•	172.0	•
85	H	H	H	F	•	85.0	–	–	•	149.5	•	192.5	–	–	•

In some cases (*e.g.*, compounds **66** and **68**) the melting points and the smectic phase stability is affected only slightly, and the stability of the nematic phase, which depends less on polarity, is reduced more. In compound **66** the additional outboard polarity of the fluoro substituent combines suitably with other polar groups to maintain the tilted smectic C character, but the molecular broadening reduces the nematic phase stability to a greater extent. In compound **68** the polar fluoro substituent also fills space but enhances the smectic phase stability to such an extent that the nematic phase is removed; the smectic C phase stability is depressed more than for compound **66**. The influence of the outer-edge fluoro substitution contrasts remarkably with the inner-core effects. The inner-core fluoro substituent may affect the planarity of the molecule which arises from the conjugation of the phenyl rings through the ester link, although with esters the effect is less severe than in biphenyls and terphenyls (see Sections 4.8 and 4.9). Thus compound **67** shows a greater effect of fluoro substitution with a much reduced melting point and a greatly reduced smectic phase stability when compared with the parent compound (**65**). The nematic phase stability of compound **67** is only reduced slightly more than for compounds **66** and **68** and this, combined with a low melting point and very low smectic phase stability, leaves a wider nematic range. The effect revealed by compound **67** is clearly not simply attributable to molecular broadening (which would be similar to that in compound **68**), but shows how a twisting effect can diminish molecular polarisability (see Section 4.9 for a more detailed discussion).

With a bulkier core unit, the lateral substituents can be hidden more effectively, as shown for bicyclo[2.2.2]octane compounds **77**–**79** [55]. The average effect of a 2-fluoro substituent on the clearing point of several bicyclo[2.2.2]octanecarboxylates is remarkably small (decrease of 3°C) and in several cases the $T_{N\text{-}I}$ values are increased. The effects of analogous substitutions were decreases of ~ 10°C in dialkyl cyclohexanecarboxylates (**74** and **75**) and of ~25°C in alkyl/alkoxy benzoate esters (**69** and **72**). The reason for the small effect of 2-fluoro substitution is attributed to the shielding provided by the cylindrical bicyclo[2.2.2]octane unit and no matter how the 2-fluorophenyl ring is held in relation to the plane of the ester group it is still more shielded by bicyclo[2.2.2]octane than it is by the flatter phenyl group; the *trans*-1,4-cyclohexane has an intermediate effect. The shielding at the 2-position is sufficiently effective to allow larger substituents such as chloro and bromo to be present without loss of mesogenicity but a fluoro substituent at the 3-position is not shielded by the structure of the acid part of the molecule and a significant steric effect is revealed. Further examples of how the structure of a parent system can shield monofluoro substitution (Section 4.3) and of how a second fluoro substituent is shielded by the first (Section 4.9) appear in other sections of the review.

The scope for lateral fluoro substitution widens even more when phenyl biphenylcarboxylate esters are considered, and now fluoro substitution at interannular (2- and 2′-) positions of the biphenyl unit are possible [56]. These larger molecules have higher melting points and much higher liquid crystal phase stability, which generates wider liquid crystal phase temperature ranges than their rwo-ring analogues and gives opportunities for more extensive substitutions without loss of mesogenicity.

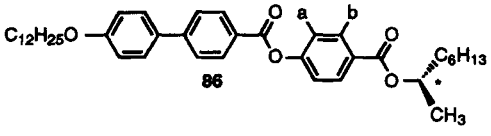
The parent system (compound **81**) has a high melting point and exhibits the ordered smectic B phase and other smectic phases without giving a nematic phase. The effect of fluoro substitution within the biphenyl esters depends significantly on its location, but in all cases the melting points are reduced and the smectic B phase is eliminated. The outer-edge fluoro substituent of compound **82** provides a lateral dipole close to the terminal group that complements the effect of other dipolar units to generate a higher smectic C phase stability than in the parent system. However, the smectic A phase stability has been reduced because of the steric effect of the lateral unit, but not sufficiently to allow the revelation of a nematic phase. Fluoro substitution at the other outer-edge position (compound **85**) causes a different effect to that seen for compound **82**, and the tilted smectic C phase stability is significantly reduced but the overall smectic phase stability of compound **85** is only slightly less than that of the parent system and is higher than for compound **82**; again the nematic phase is not exhibited. This example of different effects in the two outer-edge fluoro-substituted compounds parallels that seen for the two ring compounds discussed earlier (*e.g.*, see compounds **66** and **68**). The example of fluoro substitution leading to a higher smectic C phase stability but lower smectic A phase stability arises in many other systems and some of these are dicussed later (*e.g.*, see also compounds **189** and **190**).

As was noted for the phenyl benzoates, fluoro substitution towards the middle of the core causes much more disruption to molecular packing, and compound **84** shows the lowest melting point and a much reduced smectic phase stability so that the only smectic character now seen is for the tilted smectic C phase which has a reasonably wide temperature range. The reduced smectic A character allows a nematic phase to be exhibited over a moderate temperature range. Compounds such as **84** (known as MBF esters) were for several years considered to be excellent host materials for ferroelectric mixtures due to their reasonably wide smectic C phase range with no underlying ordered smectic phases; additionally their viscosity is moderately low, and the location of the fluoro substituent next to an oxygen function gave compounds with quite a high negative dielectric anisotropy. However (see Section 4.9.2), other fluoro-substituted materials have been developed with improved attributes for ferroelectric host mixtures. Compound **83** has fluoro substitution at an inner-core position that will cause an interannular twisting of the biphenyl rings. Such a twist reduces the longitudinal polarisability and so reduces the liquid crystal phase stability. There is no filling of free space by the fluoro substituent and so the lateral steric effect serves to reduce smectic phase stability more than nematic phase stability. In this particular core unit the smectic C phase is favoured by the presence of a lateral dipole on the biphenyl side of the core (compare compound **82** with compound **85**), and so the smectic C phase stability of compound **83** is still reasonably high.

A wide range of chiral esters have been prepared based on a core unit similar to that presented in Table III. Initially the objective was to achieve ferroelectric phases, but more recently attention has turned to analogous materials that exhibit the antiferroelectric phase. It has been shown that lateral fluoro substitution of the core can improve significantly the temperature range of the antiferroelectric phase due to a drastic reduction in melting point. However, some positions of lateral fluoro substitution depress the antiferroelectric phase stability too much to be beneficial.

The parent non-fluorinated compound **87** [57] (see Tab. IV) has a moderately high melting point but exhibits an interesting range of tilted chiral smectic phases (antiferroelectric, ferrielectric and ferroelectric) below a smectic A phase; in addition it exhibits a highly frustrated phase commonly called the chiral smectic C alpha phase. An outer-edge fluoro substituent

TABLE IV The effect of lateral fluoro substitution on some chiral esters



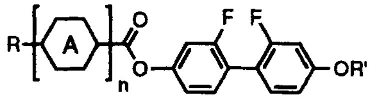
86

Compound			Transition temperatures (°C)												
No.	*a*	*b*	*C*		$S_{C^*_{anti}}$		$S_{C^*_{ferri}}$		$S_{C^*_{ferro}}$		$S_{C^*_{alpha}}$		S_{A^*}		*I*
87	H	H	●	72.9	●	99.9	●	103.5	●	117.0	●	122.2	●	132.7	●
88	H	F	●	39.6	●	108.4	–	–	●	118.6	–	–	●	126.7	●
89	F	H	●	53.3	●	78.3	●	82.0	●	90.7	–	–	●	105.7	●
90	F	F	●	52.8	●	94.0	●	95.2	●	99.5	–	–	●	110.8	●

close to the carboxylate group carrying the chiral centre (compound **88**) [58] dramatically reduces the melting point and yet enhances the thermal stabilities of the antiferroelectric and ferroelectric phases with that of the smectic A phase being slightly reduced. It is believed that subtle and specific interactions between the terminal chains of neighbouring molecules at the interlayer region cause the alternating tilt of the antiferroelectric phase, and the nature of the molecular structure close to the chiral centre is critical. The evidence provided by compound **88** is that a fluoro substituent in the crucial outer-edge position close to the chiral centre favours the generation of the antiferroelectric phase, probably through subtle polar and steric effects that cause alternate tilting at the molecular termini. The location of a fluoro substituent towards the centre of the molecular core (compound **89**) [59, 60] has a more usual effect on melting point and liquid crystal phase stabilities; all are reduced by around 20 to 25°C: with the point of substitution away from the terminal chiral centre, there is no enhancement of the antiferroelectric phase. The influence of a second fluoro substituent at the more favourable outer-edge position (compound **90**) [58] is most interesting and confirms the trends seen for monofluoro sbustitution to give compound **88**. Compared with compound **89**, the melting point of compound **90** is little changed but all the mesophase stabilities are enhanced; the antiferroelectric, ferrielectric, ferroelectric and smectic A phase stabilities are increased by 16, 13, 9 and 5°C respectively. Such comparisons again illustrate the value of the outer-edge fluoro substituent in the generation of the alternating tilt antiferroelectric phase.

Esters of type **91** have been reported and when $n = 1$ and A is phenyl, cyclohexyl or bicyclo[2.2.2]octyl, the compounds have wide nematic ranges [61]. The issue of 2,2′-difluoro substitution is discussed more fully in Section 4.9.2 where evidence is given which indicates that the fluoro substituents tend to lie on one side of the molecule. The compounds **91** have a negative dielectric anisotropy (– 2.7), in support of this view, and a large value of k_{33}/k_{11} (1.7 at 20°C) and a high optical anistropy (0.16–0.19).

91

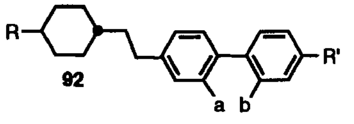


Three-ring esters are strongly smectogenic and the smectic phase stability is very much dependent on the polarity of the ester unit which enhances lateral attractions to give the lamellar structure. A lateral fluoro substituent increases the polarity and so in ester systems its effect, although dependent upon location, is generally not too destructive of smectic phase stability and in fact smectic phase stability can be enhanced in some cases. In less polar or non-polar compounds, the smectic phase character is determined by the efficiency of packing of the molecules (shape rather than polarity being the major factor). In these types of molecule the effect of lateral fluoro substitution will be much more destructive of smectic phases than for esters, but the nematic phase stability, which is not so polarity-driven, will be affected to a similar extent. However, the filling of space at an outer-edge position by a fluoro substituent in non-polar systems may uphold smectic character, but not to the same extent as for esters.

4.6. Dimethylene-linked Systems

With less polar, hydrocarbon systems, lateral fluoro substitution at an inner-core position was used to remarkable effect in the so-called I and I′ compounds (with the fluoro substituent at position **b** and **a** respectively in Structure **92**; Tab. V) [62]. These series are based on a parent biphenyl system (*e.g.*, compound **97**) that has a reasonably high liquid crystal phase stability, and gives smectic phases over a wide temperature range. Fluoro substitution at the inner-core interannular position of the biphenyl unit reduces melting points and overall liquid crystal phase stability, but has a far greater effect on smectic phases so that it leaves a wide temperature range nematic phase. Even though the inner-core fluoro substitution is very similar for compounds **98** and **99** (and also for **93**/**94**, **95**/**96** and **100**/**101**) in that the substituent at the 2- or 2′-position should have the same interannular twisting effect and be positioned at almost the same point in space, the effect on transition temperatures is subtly different. When the fluoro substituent is

TABLE V Transition temperatures (°C) for laterally fluorinated cyclohexylethylbiphenyls



92

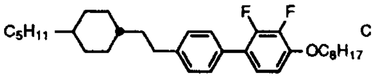
Compound					*Transition temperatures (°C)*								
No.	*R*	*R'*	*a*	*b*	*C*		S_B		S_A		*N*		*I*
93	C_2H_5	C_3H_7	H	F	•	21.3	–	–	–	–	•	78	•
94	C_2H_5	C_3H_7	F	H	•	34	–	–	–	–	•	80	•
95	C_3H_7	C_2H_5	H	F	•	27.5	–	–	–	–	•	97	•
96	C_3H_7	C_2H_5	F	H	•	34	–	–	(•	15)	•	97	•
97	C_3H_7	C_3H_7	H	H	•	67	–	–	•	119	•	144	•
98	C_3H_7	C_3H_7	H	F	•	40	–	–	–	–	•	108	•
99	C_3H_7	C_3H_7	F	H	•	59	–	–	(•	34)	•	109	•
100	C_5H_{11}	C_2H_5	H	F	•	23.5	–	–	(•	14)	•	103	•
101	C_5H_{11}	C_2H_5	F	H	•	23	•	27	•	55.5	•	104.5	•

S_A and S_B – defined since publication.

pointing towards the cyclohexyl unit (I compounds), the compounds have low melting points and the smectic phase is much reduced or completely eliminated [62, 63]. When the fluoro substituent is pointing towards the short alkyl chain (I′ compounds), the smectic phase is often still present, but its stability is again reduced compared with the parent system. On the other hand, the nematic phase stability is identical for both types of fluoro-substituted compounds and represents a relatively small reduction when compared to the parent systems. Quite why such similar fluoro substitution patterns should have a markedly different effect on the smectic phase stability, yet generate identical nematic phase stabilities is not fully understood, but it is not an isolated example. Other examples arise for monofluoroterphenyls [64] (*e.g.*, see Tab. VII in Section 4.9.1) and 4,4′-di(*trans*-4-alkylcyclohexylethyl)biphenyls with a 2- or 2′-fluoro substituent [65], and demonstrate that smectic phase stability is influenced much more by polarity that is nematic phase stability. One explanation for the differences between the I and I′ compounds may be that the 'better' mesogenic component (*i.e.*, the cyclohexylethylphenyl unit) can tolerate the fluoro substituent more easily and hence give higher smectic phase stability. A similar explanation can be used to account for the effects of fluoro substitution in terphenyls by considering the substitution as being in the biphenyl or phenyl region of the compound (see Section 4.9). The use of other homologues of the I compounds enables nematic mixtures to be formulated that have extremely low melting points. The effect of the fluoro substituent on the viscosity of compounds **98** and **99** is remarkably small, causing only approximately a 10% increase on the 20 cP (at 20°C) value of the parent system (**97**). Accordingly, the I compounds found application in nematic mixtures for display devices and mixtures with nematic ranges from − 50 to 110°C have been formulated.

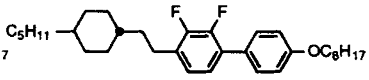
With the preparation of the I series of compounds, it was suggested [66] the PCH5 (**55**, $R = C_5H_{11}$, X^1, $X^2 = H$) and I52 (**100**) would be the most suitable polar and non-polar compounds respectively for reference of physical properties. These compounds are stable, have good nematic ranges and a whole range of macroscopic physical properties has been reported for them.

The success of the I compounds in low viscosity nematic mixtures prompted the investigation of similar materials with the aim of obtaining ferroelectric host materials [67]. The alkylbiphenyl unit was replaced with an alkoxylbiphenyl moiety to provide higher liquid crystal phase stability and increased lateral polarity, and a second fluoro substituent was located *ortho* to the original one so as to fix the relationship of the two fluoro substituents on one side of the molecule. Such an arrangement had already proved successful in terphenyl systems where a smectic C phase over a wide temperature range has been obtained (see Section 4.9.2.) [68]. The *ortho* difluoro substituents minimise the molecular breadth, thus minimising viscosity, and provide an enhanced lateral dipole, which aids the generation of the smectic C phase and gives a negative dielectric anistropy.



102

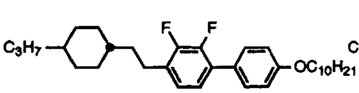
C 59.0 S_A 113.5 N 124.0 I



103

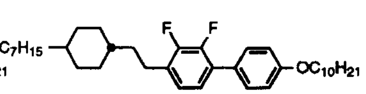
C 32.5 S_C 55.0 S_A 83.0 N 122.0 I

Compounds **102** and **103** again illustrate some of the remarkable results achieved with fluorosubstituted liquid crystals [67]. The fluoro substitution pattern used here provides one unit at an inner-core position and one unit at the outer-edge position. The outer-edge fluoro substituent is helpful in promoting smectic character and the inner-core fluoro is disrupting longitudinal polarisability, reducing melting point, smectic and nematic phase stabilities. This subtle and complex combination of effects allows the generation of both the smectic and nematic phases, and the smectic C phase exists over a reasonably wide temperature range. With the difluoro unit in the outer ring (compound **102**) the melting point is higher and the smectic phase stability is 30°C higher than when the fluoro substituents are located in the centre of the molecule (compound **103**); the smectic C phase is not seen in compound **102** and yet the nematic phase stability is little changed. Both compounds benefit from the space filling effect of a fluoro substituent at an outer-edge position of the biphenyl unit, but the space-filling effect is much more effective at the true outer-edge position of the molecule (compound **102**) and it leads to a much enhanced smectic character. The smectic C phase requires the appropriate arrangement of polar groups to provide molecular tilting (in addition to other structural features conducive towards the generation of smectic phases), and the separation of the polar units as in compound **103** provide easier molecular tilting than when the polar groups are adjacent (compound **102**).



104

C 38.5 S_C 68.5 S_A 88.0 N 119.0 I



105

C 36.5 S_C 55.0 S_A 116.0 N 121.0 I

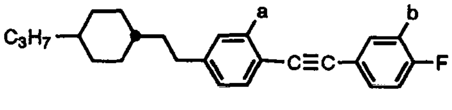
Homologues of compound **103** with a central location of the difluoro substituents (*e.g.*, compounds **104** and **105**) [67] show low melting points and reasonably wide temperature ranges of the smectic C phase and they illustrate the critical importance of terminal chain length in the fine-tuning of mesomorphic behaviour. A shorter terminal chain in the cyclohexyl ring gives a high smectic C phase stability (compound **104**), whereas a longer chain in the cyclohexyl ring promotes smectic A phase stability (compound **105**), but in all the homologues the nematic phase stability is similar.

4.7. Tolanes

The cylindrical π-electron region of a triple-bond allows conjugation to be extended on either side and molecules can be devised which have relatively high polarisability and low viscosity, as required for TN displays (see Refs. [69, 70] and references therein). Lateral fluoro substitution and a flexible molecular region have been used in an attempt to obtain lower melting tolanes of high birefringence and high $+\Delta\varepsilon$ values and some results are given in Table VI. Fluoro substitution at position **a** (compound **108**) is unusual in that it is at an inner-core position but because of the cylindrical nature of the π-region of the linking group, it does not exert a twisting effect; the result is a reduction in melting point and only an 18°C depression of clearing point.

TABLE VI Transition temperatures (°C), optical anisotropies and viscosities of tolane-linked compounds

106

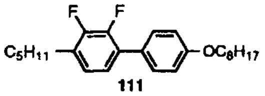


Compd. no.	*a*	*b*	*C*		*N*		*I*	Δn	η/cP
107	H	H	•	86	•	149	•	0.23	20
108	F	H	•	51	•	131	•	0.23	20
109	F	F	•	46	•	105	•	0.21	19
110	H	F	•	85	•	125	•	–	–

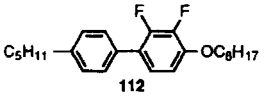
Compound **108** is useful, having a relatively low melting point, high birefringence, low viscosity and a dielectric anisotropy of + 9, and compound **109**, also with an inner fluoro substituent, has a similarly low melting point, whereas compound **110** with an outer-edge fluoro substituent has a high melting point.

4.8. Biphenyl and Related Systems

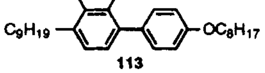
The cyclohexylethylbiphenyls considered here (compounds **93**–**105**) show more pronounced mesogenicity than simple alkyl or alkoxy substituted biphenyls which do not have the cyclohexyl ring present. None the less, although the transition temperatures are much lower, it is interesting to examine the mesomorphic behaviour of biphenyls with simple alkyl and alkoxy terminal chains (*e.g.*, compounds **111**–**114**) [68]. It is remarkable that such simple core systems with two lateral fluoro substituents still generate smectic phases. Once again the outer-edge fluoro substituent is important in filling space and providing polarity to facilitate the formation of smectic phases through enhanced lamellar packing.



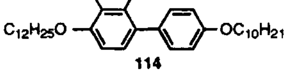
111
C 9.2 S_A 25.3 N 28.2 I



112
C 17.5 (S_C 1.0) N 23.0 I



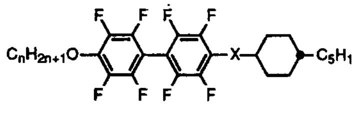
113
C 25.0 (S_C 11.5) S_A 33.0 N 34.0 I



114
C 70.5 (S_C 68.0 S_A 68.5) I

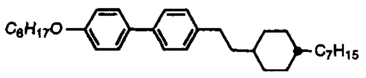
Compounds **111** and **112** illustrate the significant difference in mesomorphic behaviour that different patterns of fluoro substitution can generate in isomeric structures. One pattern of difluoro substitution (compound **111**) generates a material of high smectic character, which is attributable to the presence of the unsubstituted alkoxyphenyl section in the structure which has inherently more smectic character than comparable alkyl-substituted systems. Compound **112** is more polar and has a greater dielectric anisotropy than **111** because of the two fluoro substituents close to the ether oxygen ($\Delta\varepsilon = -4.7$ and -2.6 respectively). Accordingly, it may be expected that compound **112** would have the stronger lamellar attractions and higher smectic phase stability, but only the melting point has increased. An increase in the lengths of the terminal chains enhances the smectic phase stability and enables compound **113** to exhibit a smectic C phase, but the melting point is also increased. The increased longitudinal polarisability has increased the overall liquid crystal phase stability in the dialkoxy compound **114**, and because of increased polarity the melting point is high and only smectic phases are generated. In fact the polarity at each end of the molecule aids molecular tilting and the smectic C phase is almost as dominant as the smectic A phase of compound **114**.

A series of papers has examined in detail the effects of polyfluoro substitution in structures such as **115**, *e.g.*, for **115a** [71], **115b** [72], and **115c** [72], low to moderately low melting point nematogens are obtained and the strongly smectic character of the parent systems (see **115c** and the closely similar parent **116** [73]) is removed. Compounds with four, six or eight fluoro substituents in the biphenyl unit were also considered [74] and comparisons for the pentyloxy systems **117a–e** and **118a–e** show that the smectic A phase is gradually eliminated with higher degrees of fluoro substitution and the nematic clearing points are gradually reduced. The absence of interannular fluoro substitution at the 2,2′- or 6,6′-positions is more crucial to maintaining the mesophase stability of the alkene-linked compounds **117** than for the dimethylene-linked compounds **118** (see **117c–e** and particularly **117d**), presumably because a more extensive region of polarisability is present with the conjugated alkene when additional interannular twisting is absent, as in **117d**.

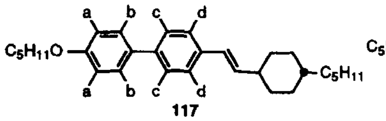


115a, n = 8, C 54 N 99 I
115b, n = 8, C 71 N 115 I
115c, n = 8, C 41.5 N 52 I

115
a = OOC, **b** = CH=CH, **c** = CH_2CH_2

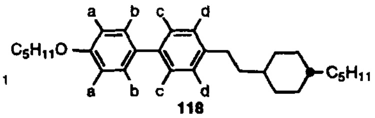


116
C 55 S_B 157 S_A 163 I



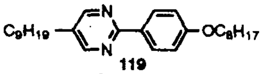
117

117a, a, b, c, d = F C 65 N 125 I
117b, a, b, d = F, c = H C 85 N 136 I
117c, a, c, d = F, b = H C 54 S_A 112 N 142 I
117d, a, d = F, b, c = H C 31 S_A 132 N 168 I
117e, a, c = F, b, d = H C 78 S_A 112 N 138 I



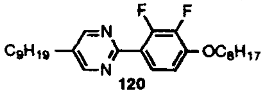
118

118a, a, b, c, d = F C 59 (N 54) I
118b, a, b, d = F, c = H C 69 (N 65) I
118c, a, c, d = F, b = H C 64.5 N 69 I
118d, a, d = F, b, c = H S_A 38 N 73 I
118e, a, c = F, b, d = H C 31 S_A 65 N 81 I



119

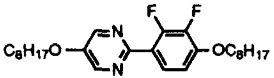
C 35.0 S_C 60.0 S_A 75.0 I



120

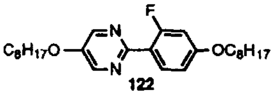
C 43.0 S_C 54.0 I

The major reason for the low transition temperatures of the biphenyls **111**–**114** is the interannular twisting caused by the inner-core fluoro substituent. The analogous phenylpyrimidines (*e.g.*, **119** and **120**) suffer less interannular twisting because the heterocyclic nitrogens have replaced CH units at the bay region, and because the rings are closer to coplanarity, the longitudinal polarisability and the resultant mesogenicity is higher [75–77]. Accordingly, the difluorophenylpyrimidines benefit from the outer-edge fluoro substituent in terms of smectic phase tendencies, and materials with low melting points and reasonably high smectic C phase stability have been produced. The parent phenylpyrimidine compound **119** has a low melting point and moderate smectic C phase stability along with a smectic A phase. The introduction of two fluoro substituents in compound **120** broadens the core and hence depresses liquid crystal phase stability by 20°C, but the lateral dipole is so strong that the smectic C phase stability is reduced by only 6°C, and the nematic phase (which often results from lateral fluoro substitution) is not exhibited.



121

C 48.0 S_C 76.0 N 77.0 I

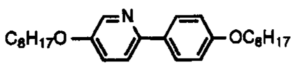


122

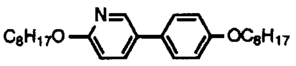
C 42.0 S_C 52.0 N 77.0 I

The use of two alkoxy chains (*e.g.*, compound **121**) [77] increases the liquid crystal phase stability still further, and the lateral dipole from the additional ether oxygen favours the smectic C phase, which is now 22°C higher than for compound **120**; the melting point of compound **121** is only slightly higher and a very short temperature range nematic phase is now revealed. The true significance of outer-edge fluoro substitution is again seen by comparison of the transition temperatures for compounds **121** and **122** [77]; the compounds have similar melting points but the smectic phase stability for **121** has increased by 24°C, yet the nematic phase stability is unchanged. The large increase in smectic C phase stability is due to the filling of space at the edge of the core which increases the lateral intermolecular attractions, and the increase in the lateral dipole which increases the tendency of the molecules to tilt. This comparison is another good example of how the generation of smectic phases is much more dependent upon polarity than for nematic phases, which are almost independent of polarity requirements.

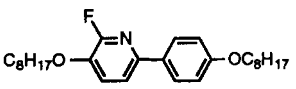
Fluoro-substituted phenylpyridines have also been prepared and some interesting effects are revealed in these compounds [78]. The parent systems have reasonably low melting points and exhibit ordered and disordered smectic phases. The compound with the heterocyclic nitrogen at the inner-core position (**123**) has reduced interannular twisting, greater longitudinal polarisability and a higher liquid crystal phase stability than the compound with the nitrogen at the outer-edge position (**124**). The mesophase morphology is also different and depends on the location of the heterocyclic nitrogen; in compound **123** the polarity of the inner-core nitrogen breaks the symmetry of the dipoles of the ether oxygens and generates molecular tilting whereas this is not achieved when the outer-edge nitrogen and ether oxygen are close together as in compound **124**.



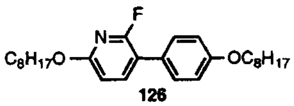
123
C 76.0 (S_X 75.0) S_C 110.0 I



124
C 50.0 S_B 69.0 S_A 80.0 I



125
C 81.0 S_C 89.0 I



126
C 48.0 (S_A 40.0) I

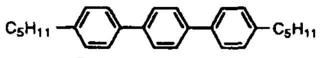
The fluoro substituent in compound **125**, despite filling space at the outer-edge position and not causing interannular twisting, broadens the molecule considerably because it protrudes further in relation to the neighbouring nitrogen region than when CH is present, and consequently the smectic phase stability is reduced by 21°C. In compound **126**, the fluoro substituent broadens the molecules, reduces longitudinal polarisability by interannular twisting, and so the smectic phase stability is reduced by 40°C. Undoubtedly, the preference for molecular tilting will have increased for both compounds **125** and **126**, but the liquid crystal phase stability of **126** is so low that a smectic C phase is not seen before crystallisation occurs.

4.9. Terphenyls

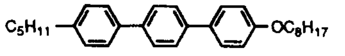
4.9.1. Monofluoro Systems

Liquid crystalline terphenyls have three benzene rings linked in a coaxial manner to give a structure with considerable scope for examining the effect of fluoro substitution because of the many different positions for substitution and the high mesogenicity of the parent system; mesogenicity is still retained even after multi-fluoro substitution in the lateral positions. As will be illustrated, fluoro substitution at the various positions generates compounds of widely different mesomorphic character and other physical properties which allow the requirements for specific applications to be achieved.

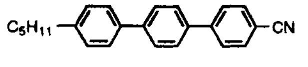
Terphenyls with alkyl or alkoxy substituents at the terminal 4- and 4″-positions give materials (*e.g.*, **127** and **128**) [79] with extremely high liquid crystal phase stability due to the highly anisotropic architecture. However, these structures also have strong intermolecular forces of attraction which give very high melting points and so the temperature ranges of the liquid crystal phases seen in the parent systems are short. The temperature and energy required to break down the side-to-side intermolecular attractions is so high that the nematic phase is not produced and hence the phase morphology is solely smectic. However, a terminal cyano substituent facilitates antiparallel correlations and the molecular pairs are less conducive to lamellar packing and a nematic phase of high stability is generated (*e.g.*, compound **129**) [80].



127
C 192.0 S_A 213.0 I



128
C 194.5 B 211.0 S_A 221.5 I

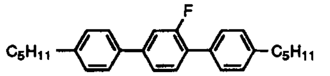


129
C 130.0 N 239.0 I

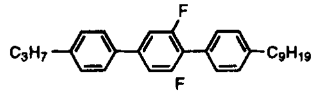
When a fluoro substituent is located at a lateral position on the terphenyl core the effect on melting points, transition temperatures, mesophase morphology and other physical properties is remarkable [79, 81–83]. As for all the classes of molecule considered previously, the precise influence of the fluoro substituent depends strongly on its the location in the core, and the nature and length of the terminal chains are also influential. Generally, the steric effect of the lateral fluoro substituent causes a severe disruption in the side-to-side molecular packing which leads to a massive reduction in melting point and a severe depression of smectic phase stability which allows a nematic phase to be generated at the upper temperature limit of the mesomorphic sequence. In addition to the steric effect, the lateral dipole of the fluoro substituent aids molecular tilting, and in most cases results in the generation of tilted smectic phases, particularly the smectic C phase, over a wide temperature range. In some cases, the tendency for molecular tilting is so strong that the smectic C phase extends to the limit of smectic phase stability and the smectic A phase is not present; this phenomenon is made possible by the steric effect reducing the lateral intermolecular attractions so that the full tilting effect of the lateral dipole is able to operate.

The alkyl- and alkoxy-substituted parent terphenyl systems are essentially non-polar and so the introduction of a lateral polar fluoro substituent causes many changes to other physical properties. The longitudinal polarisability of the aromatic rings generates a positive dielectric anisotropy which is reduced to almost zero by the lateral fluoro substituent; the lateral fluoro substituent also causes a small dilution in optical anisotropy from about 0.24 to 0.21. The steric and polar effects of the lateral fluoro substituent increase viscosity, but because fluoro is the smallest substituent possible, the increases are minimal when compared to the effects of larger lateral substituents [79]. A fluoro substituent at an inner-core position also causes a greater degree of interannular twisting than for the parent system [84], this reduces the longitudinal polarisability and is a significant contributory factor in reducing melting point and liquid crystal phase stability.

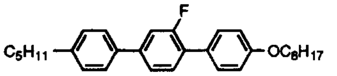
A fluoro substituent in the centre ring (*e.g.*, compounds **130**–**141**) causes the most severe reduction in melting points (around 150°C) and the terminal chains can greatly influence the effect of a lateral fluoro substituent, as illustrated by the isomeric compounds **132** and **133** [79, 81–83].



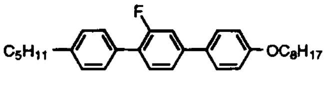
130
C 51.5 B 62.0 S_A 109.5 N 136.5 I



131
C 46.0 (B 35.0) S_C 52.0 S_A 89.0 N 126.5 I



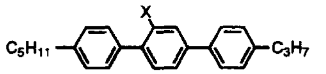
132
C 47.0 (J 40.0) S_I 53.5 S_C 116.5 S_A 130.0 N 155.0 I



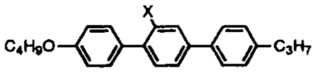
133
C 69.0 G 83.0 B 100.5 S_C 124.0 S_A 158.0 N 161.0 I

Compound **133** has a higher melting point and a higher level of smectic phase stability than compound **132** because the fluoro substituent in **133** is part of an untwisted biphenyl section with an alkoxy terminal chain (higher polarisability), and the extra breadth (which is similar for both compounds) is more easily tolerated than in compound **132** where the terminal chain on the normal biphenyl region is alkyl, and so the unit has a lower polarisability. Note that the nematic phase stability is less affected by such a change in terminal chains (compare compounds **156** and **157** for another example of this effect).

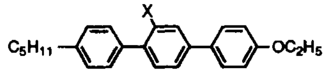
The examples given for compounds **134**–**141** show the transition temperatures for compounds in which a dialkyl system is systematically changed into a dialkoxy system of almost constant molecular length [64]. These comparisons show the very large reduction in melting point arising from fluoro substitution (130.0 to 147.0°C) but the smaller depressions in clearing point (54.0 to 77.4°C). All these examples are for compounds with relatively short alkyl and alkoxy chains, and the fluoro-substituted products are solely nematogenic; in comparison with the values for compounds **130**–**133**, for example, they show how sensitive is the occurrence of smectic C and A phases on the length of the terminal chains.



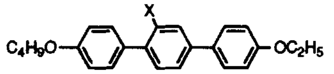
134, X = H C 180.0 E 200.0 S_B 214.0 S_A 218.0 I
135, X = F C 50.0 N 140.6 I



136, X = H C 239.0 E 241.0 S_A 249.5 I
137, X = F C 92.0 N 180.0 I



138, X = H C 234.0 E 237.0 S_A 242.0 N 248.0 I
139, X = F C 98.0 N 191.5 I

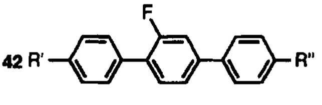


140, X = H C 270.0 (S_A 268.5) N 280.0 I
141, X = F C 136.0 N 226.0 I

One puzzling, but significant, additional effect is seen for fluoro substitution in dialkylterphenyls with different terminal chain lengths where the compound with a fluoro substituent pointing towards the longer alkyl chain has lower smectic phase stability. For example, the values in Table VII show that solely nematogenic compounds are obtained with the fluoro pointing towards the pentyl chain (compounds **143** and **145**) but with the terminal groups interchanged, smectic A phases are promoted by more than 49.5 and 45.5°C for the two examples **144** and **146**, but clearing temperatures are only slightly affected. The differences are quite surprising given the similarity of the chain lengths and the effect is reminiscent of that seen for the fluoro-substituted cyclohexylethylbiphenyls (see I compounds in Section 4.6, and Ref. [65]) and it illustrates the subtle effects of minor changes in molecular structure.

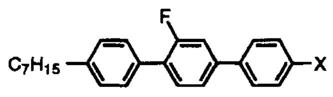
TABLE VII Transition temperatures (°C) for 4,4″-dialkyl-2′-fluoroterphenyls

142

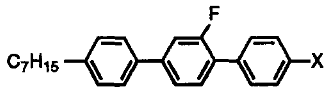


Compd. no.	*R′*	*R″*	*Transition temperatures (°C)*
143	C_5H_{11}	C_3H_7	C 50.0 N 140.6 I
144	C_3H_7	C_5H_{11}	C 61.0 S_A 99.5 N 141.5 I
145	C_5H_{11}	C_2H_5	C 54.5 N 127.5 I
146	C_2H_5	C_5H_{11}	C 64.0 S_A 90.0 N 128.7 I

The 4,4″-dialkyl-2′-fluoroterphenyls have extrapolated viscosities of about 40 and 115 cP at 20°C and 0°C respectively, birefringence values (Δn) of about 0.21 and very small dielectric anisotropies. Variations to these structures by placing an oxygen atom at different positions in one alkyl chain (4-alkyl-4′-alkoxyalkylterphenyls) gives, for example, compounds **148**–**150** and **152**–**154** (parent compounds **147** and **151** respectively) which have low smectic C character but they show interesting variations in viscosity and are suitable for use in ferroelectric smectic C mixtures [85].



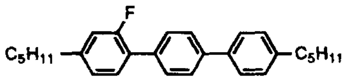
147, X = C_5H_{11} C 64.5 S_A 113.0 N 128.5 I
148, X = $CH_2OC_3H_7$ C 22.0 S_C 54.0 N 100.0 I
149, X = $(CH_2)_2OCH_2CH_3$ C 23.4 S_B 50.1 S_A 90.5 N 105.1 I
150, X = $(CH_2)_3OCH_3$ C 43.7 S_B 44.3 S_C 71.6 S_A 77.2 N 124.0 I



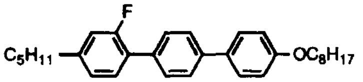
151, X = C_5H_{11} C <−20 S_B 87.5 S_A 123.5 N 129.4 I
152, X = $CH_2OC_3H_7$ C 40.2 S_B 60.1 S_A 110.8 N 104.8 I
153, X = $(CH_2)_2OCH_2CH_3$ C <−20 S_B 72.9 S_A 104.6 N 105.3 I
154, X = $(CH_2)_3OCH_3$ C <−20 S_B 71.2 S_A 99.3 N 118.9 I

The location of the fluoro substituent in compounds **155**–**157** at an interannular position in an outer ring means that it is no longer part of an untwisted biphenyl unit and the extra breadth created is not so well-tolerated in a single ring sub-unit [79]. This structural situation causes a general lower smectic phase stability when compared with the corresponding compounds **130**, **132** and **133**, and combined with the enhanced tendency of the molecules to tilt because the polar fluoro substituent is further away from the centre of the molecule it means that the smectic C phase persists to higher temperatures and for the full extent of the smectic phase stability. The smectic A phase is not seen for compounds **155**–**157**, but the different structural situation for substitution in the central or end ring does not affect the clearing points.

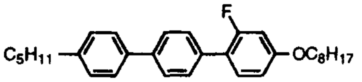
Those compounds (**132**, **133** and **156**, **157**) with a terminal alkoxy chain have a strong tendency to exhibit tilted smectic phases because of the combination of outboard lateral dipoles from the ether oxygen and the fluoro substituent [86]. The steric effect of the fluoro susbstituent reduces the efficiency of the molecular packing and so the least ordered tilted smectic phase (S_C) is particularly favoured.



155
C 72.5 S_C 80.0 N 136.0 I



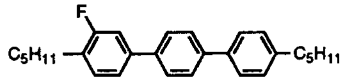
156
C 102.0 (S_I 99.5) S_C 137.5 N 160.0 I



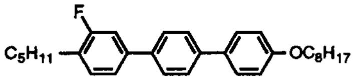
157
C 69.0 (K 25.0 J 43.5) S_C 119.0 N 158.0 I

When the fluoro substituent is located in the centre of the molecule and is the only polar unit (compounds **130** and **131**) the tilting power is low; with identical terminal chains (compound **130**) tilted smectic phases are not exhibited. However, with different terminal chains (compound **131**) molecular tilting is induced and the smectic C phase is present, but only to 52°C. In compound **155** the fluoro substituent is located in an end ring and even though the terminal chains are identical, the polarity is off-centre and a smectic C phase exists to quite a high temperature (*cf.*, compounds **130** and **131**). For reasons described above, the overall smectic phase stability of compound **155** is lower than for compound **130**.

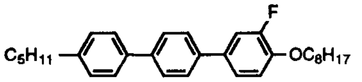
A fluoro substituent on the outer edge of the terphenyl core produces very different effects in terms of melting points, mesophase morphology and transition temperatures than a fluoro substituent within the core [79]. The difference is partially due to the fact that the fluoro substituent is now part of a terphenyl system in which no additional interannular twisting has been created. The basic core unit is retained and so the extra breadth is tolerated more successfully than for systems described above where the fluoro substituent is within the core unit. The terphenyl units in compounds **158**–**160** are similar to those of the parent systems and so they have a greater polarisability than for analogous systems with the fluoro substituent within the core. In addition, a fluoro substituent at an outer-edge position fills space, and thus provides greater lateral intermolecular forces of attraction. A combination of these factors probably explains why compounds with a fluoro substituent at an outer-edge position tend to be more crystalline, have a greater tendency to generate smectic liquid crystal phases, do not exhibit the nematic phase, and have higher clearing points when compared with analogous meterials with the fluoro substituent within the core.



158
G 156.5 S_A 185.5 I



159
G 170.5 S_C 176.5 S_A 202.5 I

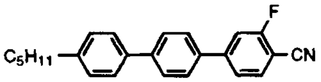


160
G 146.0 B 158.0 S_A 195.0 I

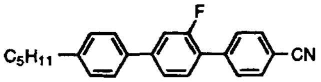
The phase morphology of compounds **158**–**160** is a delicate balance between the desire for molecular tilting generated by the lateral dipole of the fluoro substituent and the strong lateral intermolecular forces of attraction afforded by the terphenyl core which tends to promote orthogonal smectic mesophases. In each case, compounds **158**–**160** exhibit an ordered tilted mesophase (G) at low temperatures and the orthogonal smectic A phase at high temperatures. At intermediate temperatures, compound **159** exhibits the smectic C phase because the dipolar groups at each end of the molecule generate tilt, but the temperature range is very short because the lateral intermolecular attractive forces persist to higher temperatures than those over which the dipole can generate the tilt. Compound **160** has both dipolar groups at one end of the molecule, which in some instances is sufficient to generate a smectic C phase, but once again the lateral intermolecular attractions are too strong and a crystal B phase persists to such a high temperature that it excludes the generation of the tilted smectic C phase.

As described in Section 4.3, fluoro substitution next to the terminal cyano group enhances the terminal dipole and gives a greater dielectric anisotropy which may lead to shorter switching times and/or lower power consumption in nematic displays. Since the parent system is nematogenic (see compound **129**), fluoro substitution does not alter the mesophase morphology, but does have a remarkable effect in reducing melting points and clearing points [87].

Compound **161** has the fluoro substituent at an outer-edge position, which often does not depress the liquid crystal phase stability too severely (*e.g.*, compare the values for compounds **127** and **158** where the clearing



161
C 85.0 N 182.0 I



162
C 82.0 N 143.0 I

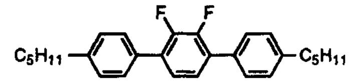
point depression is 27.5°C). However, the nematic phase stability of compound **161** is nearly 60°C lower than that of the parent system (compound **129**) and this larger reduction emphasises just how different are the forces controlling the formation of smectic and nematic phases. Antiparallel molecular correlations exist for terminal cyano compounds, and so the lateral fluoro substituent in compound **161** will also depress the stability of the nematic phase by reducing these interactions. Compound **162** has a fluoro substituent at an inner-core position and hence the longitudinal polarisability is disrupted by the interannular twisting resulting in an even lower clearing temperature than for compound **161**.

4.9.2. Difluoro Systems

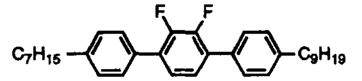
The very high mesophase stability of materials with a terphenyl core allows scope for the introduction of a second fluoro substituent to enable further tailoring of the physical properties of the materials for applications [68, 88–90]. For terphenyls with two different terminal chains, there are six different positions on the terphenyl core where a fluoro substituent can be located but with two fluoro substituents the number of possibilities has increased and 24 difluoroterphenyl combinations are possible. As found with monofluoroterphenyls, the melting points, transition temperatures and phase morphology of the difluoroterphenyls depends enormously on the relative positions, and can range from low melting nematic materials to high melting compounds with a very strong tendency to produce smectic phases. The most notable effect of the second fluoro substituent is that it leads to the complete elimination of all ordered smectic mesophases. On the contrary, in some systems the addition of a second fluoro substituent has disastrous consequences in terms of producing high melting points and large reductions in liquid crystal phase stability.

The *ortho* difluoroterphenyls (*e.g.*, **163–168**) [68, 88] are perhaps the most interesting class of difluoroterphenyl. The two fluoro substituents are inherently fixed on one side of the molecule, an arrangement, that provides a combination of useful physical properties. In comparison with the monofluoroterphenyls, the molecular breadth is not increased because the second fluoro substituent lies within the limits set by the first fluoro, but the molecular shape is smoothed, so that the viscosity of the difluoro compounds (35 to 100 cP) is in some cases actually lower than for the monofluoroterphenyls. With the exception of compounds such as pyridazines, most nematogenic cores intrinsically give a positive dielectric anisotropy, but the two fluoro substituents in *ortho* difluoroterphenyls reinforce each other's effect and give a high negative dielectric anisotropy (– 2.5 to – 5.0) and aid the generation of the smectic C phase.

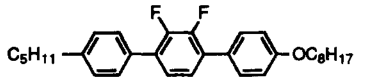
In the case of compounds **163**–**165**, the second fluoro substituent has not increased the maximum breadth of the molecule, but an additional interannular twisting has been introduced and hence liquid crystal phase stability has been reduced. The smectic phase stability is affected most, and all ordered smectic phases have been eliminated, but the smectic C phase is not significantly affected because the increased lateral dipole enhances the tendency of the molecules to tilt. Compound **163** does not generate smectic phases because the molecule is symmetrical and the two alkyl chains are too short, but when the terminal chains are longer (compound **164**), smectic phases are enhanced, and the smectic C phase now appears because the terminal chains have different lengths; a similar situation was shown for monofluoroterphenyls **130** and **131**. Compound **165** has the additional benefit of the polarity from the ether oxygen to aid molecular tilting and all of the smectic character is now exhibited as the smectic C phase.



163
C 60.0 N 120.0 I

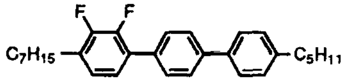


164
C 49.0 S_C 77.0 S_A 93.0 N 108.5 I

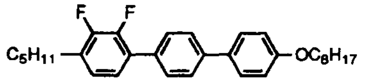


165
C 48.5 S_C 95.0 N 141.5 I

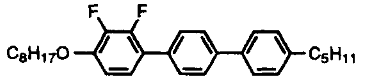
When the two fluoro substituents are in an end ring of the terphenyl system, compounds are produced (*e.g.*, **166**–**168**) that have very large smectic C temperature ranges. Several structural features, including the unsubstituted biphenyl section, only one interannular twisting, and the space-filling effect of the outer-edge fluoro substituent all combine to give high liquid crystal phase stability, especially smectic, which gives only narrow nematic ranges. The large lateral dipole from the two lateral fluoro substituents is at the end of the molecule which provides a large driving force for molecular tilting and ensures that most of the smectic phase character is exhibited as the smectic C phase.



166
C 56.0 S_C 105.5 S_A 131.0 N 136.0 I



167
C 89.0 S_C 155.5 S_A 165.0 N 166.0 I

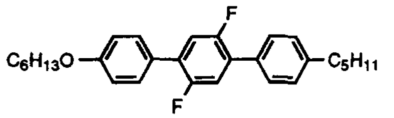


168
C 93.5 S_C 144.0 S_A 148.0 N 159.0 I

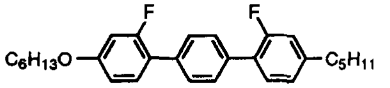
For compound **166**, where both terminal chains are non-polar, the melting point remains quite low and the smectic C phase stability is high. With the presence of an alkoxy terminal chain at the other end of the molecule from the difluorophenyl unit (compound **167**), molecular tilting is particularly favoured and the smectic C phase stability is extremely high, giving a wide phase range, despite a rather high melting point. The 4-alkoxy-3-fluoro-substitution pattern in compound **168** provides for a very high negative dielectric anisotropy ($\Delta\varepsilon = -4.2$). The explanation for this large value is either that, by resonance, the ether oxygen in compound **168** can increase the electron density on the 3-carbon atom to which the electron-attracting *ortho* fluoro is bonded, leading to a greater polarity or that the alkoxy group adopts a conformation so that the oxygen lone pairs of electrons enhance the polarity of the two fluoro substituents. However, such a high polarity leads to a high melting point and since the unsubstituted biphenyl section only has a terminal alkyl chain, the transition temperatures are lower than for compound **167**.

Other combinations of difluorination in a terphenyl core raise further interesting issues. Except where one of the fluoro substituents is at an outer-edge position, difluoroterphenyls other than the *ortho* types described above are generally nematogenic. The elimination of all smectic phases in such systems results from the large increase in molecular breadth due to the additional fluoro substituent which is either fixed on the opposite side of the core (compound **169**) or can be on the other side of the core through rotation (compound **170**). The low clearing point of compound **169** is attributed to the extra molecular breadth and both the examples **169** and **170** are situations where two interannular twistings occur [89].

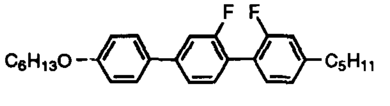
Compound **171** has a 2,2′-difluoro substitution pattern where one might expect that the two fluoro substituents would be positioned as far away from each other as possible. However, it has been shown by dielectric anisotropy measurements that the 2- and 2′-fluoro substituents appear to attract each



169
C 51.0 N 117.0 I



170
C 45.0 N 131.0 I

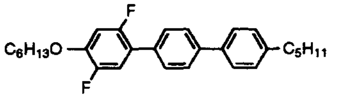


171
C 52.0 (S_C 41.5) N 122.0 I

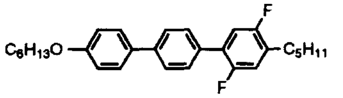
other (see Section 4.5; Ref. [61]). This is similar to the situation reported for 2,2′-dihalogenobiphenyls for which dipole moment measurements indicate that the two halogeno substituents preferentially lie on one side of the molecule [91, 92]. The presence of a monotropic smectic C phase supports the view that the two fluoro substituents preferentially lie together and so provide the necessary dipole for molecular tilting, but the clearing point of compound **171** is lower than that of compound **170**, possibly because the interannular twisting caused by the 2,2′-difluoro substituents is more deleterious than the two interannular twists in compound **170**, and so affects the nematic phase more than smectic phases [90].

Compounds **172** and **173** have a fluoro substituent fixed at each side of the molecule, but they are not solely nematogenic because only one interannular twist is created and the outer-edge fluoro substituent fills space and enhances intermolecular forces of attraction which favours smectic phases and causes higher melting points. The high polarity generated by having the outer-edge fluoro substituent next to the ether oxygen ensures that compound **172** has a higher melting point than the isomer **173**. Compound **173** has higher smectic and nematic phase stability than compound **172** because an alkoxy-, and not an alkyl-substituted, biphenyl unit is present which provides a greater longitudinal polarisability. However, the combination of dipoles in compound **172** ensures a slightly higher smectic C phase stability than in compound **173**. For compounds **174** and **175**, the fluoro substituents, as in **172** and **173**, are fixed on both sides of the molecule in one ring but there is no outer-edge fluoro substituent [89] and the compounds are simply nematogenic.

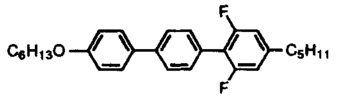
Compounds **176** and **177** have one fluoro substituent at an outer-edge position and another at an inner-core position, and they show quite different mesomorphic behaviour. Both **176** and **177** have an outer-edge fluoro substituent *ortho* to an ether oxygen, which by itself would give a high polarity and confer a high melting point and high smectic phase stability. This expectation is, however, considerably altered by the different influence



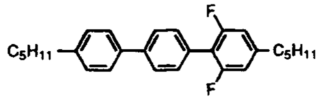
172
C 89.5 S_C 92.0 N 130.5 I



173
C 77.0 S_C 87.5 S_A 136.0 N 142.0 I

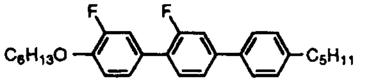


174
C 61.0 N 122.5 I

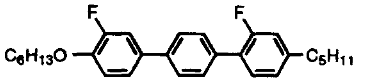


175
C 50.0 N 82.0 I

of the second fluoro substituent. The proximity of the inner-core fluoro substituent of compound **176** to that at the outer-edge position seems to reduce the intermolecular packing compared to that seen for compound **177**. The dipole separation in compound **177** ensures a higher phase stability for the smectic C phase, yet compound **176** exhibits smectic phase stability beyond the tilting influence of the lateral dipole with a very high smectic A phase stability. Possibly the space created by the separation of the two fluoro substituents in compound **177** limits the smectic phase stability in comparison with compound **176**. The nematic phase which is little affected by such space-filling influences is essentially the same for both compounds (**176** and **177**) [90].

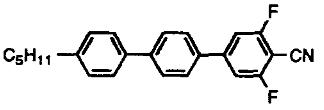


176
C 41.0 S_C 72.0 S_A 131.0 N 140.0 I



177
C 90.0 S_C 105.5 N 139.0 I

The use of two *ortho* fluoro substituents next to a polar terminal cyano group generates a compound with a melting point which, although lower than that of the parent system (compound **129**), is higher than for the monofluoro-substituted analogue (compound **161**). The molecular breath of compound **178** is also maximised which minimises the clearing point. Both of these points leave compound **178** with disappointing properties from a mesomorphic point of view, but the enhanced positive dielectric anisotropy may make the compound useful in nematic mixtures for displays [87].



178
C 103.0 N 120.0 I

The examples given in this section do not exhaust the possibilities for different classes of fluoro substitution in terphenyls. Many of the other possible fluoro-substituted terphenyls may well provide compounds with physical properties necessary for successful displays; for example, the high positive dielectric biaxiality which is required for ferroelectric displays that operate in the τVminimum mode [93–95]. With increasing fluoro substitution and increased polarity, the expectation is that eventually melting points will increase and any benefits of mesophase types will be lost, but the examples given in Section 4.8 of polyfluoro substitution in biphenyls shows that this is not always the case.

4.10. Fluoro Substitution in Terminal Chains

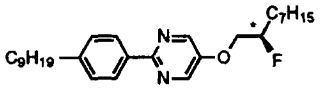
The terminal units of liquid crystal compounds usually consist of quite long alkyl and alkoxy chains, but alkenyl chains are also fairly widespread. Accordingly, there is great scope for fluoro substitution at various positions in a terminal chain, but only a few aspects of fluoro substitution within terminal chains have been investigated. Most reports on fluoro substitution in terminal chains have involved specific reasons for such substitution rather than being part of a general, fundamental and systematic study of the effects. As is the case for fluoro substitution in cycloalkyl units (see Section 4.11) [96, 97], the synthesis is much more difficult than for compounds with fluoro substitution in core aromatic positions.

The principal classes of fluoro substitution in terminal chains that have been investigated include compounds with (i) a fluoro substituent at a chiral centre for ferroelectric applications, (ii) a small perfluoro unit (*e.g.*, trifluoromethyl or pentafluoroethyl) at a chiral centre for ferroelectric and antiferroelectric applications, (iii) a perfluoro, superfluoro or semifluoro terminal chain for enhanced smectic phase stability in ferroelectric host materials, and (iv) the use of short fluorocarbon units (*e.g.*, trifluoromethyl, difluoromethyl and fluoromethyl) to provide a positive dielectric anisotropy in nematic mixtures for active matrix displays.

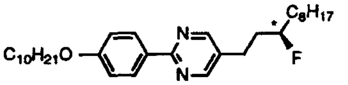
4.10.1. Fluoro Substitution at a Chiral Centre

One of the most widespread uses of fluoro susbstitution in a terminal chain is that of fluoro substitution at a chiral centre [98–103]. It is important in the formulation of ferroelectric mixtures to use a chiral component which gives a reasonably high spontaneous polarisation to ensure fast-switching devices. To achieve a high spontaneous polarisation, there should be high polarity at the chiral centre, and yet the chiral material must also have a low viscosity and not seriously depress or modify the mesomorphic behaviour of the achiral host mixture. Accordingly, a fluoro substituent at a chiral centre is often the ideal choice, because it is polar and small, and so it gives a fairly high spontaneous polarisation, yet the viscosity and the effect on mesomorphic behaviour on the host is minimised; as has been indicated previously, the characteristics of polarity and small size are also the key reasons for the value of fluoro substitution in core units.

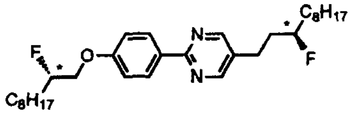
The greater ease of synthesis dictates that, in most cases, the fluoro substituent at a chiral centre forms part of an ether- or an ester-linked terminal chain, but in some cases the chain is directly linked to the core. The position of the fluoro substituent within the terminal chain is often determined by the synthetic routes available, and the position chosen is not necessarily optimised for mesomorphic behaviour and physical properties; once again, systematic studies of fluoro substitution in terminal chains are limited by synthetic problems. Achiral phenylpyrimidines (*e.g.*, compounds **119**–**122**) are commonly used as ferroelectric host materials, but their smectic C phase temperature limits are really quite low and any chiral dopant used must preserve, or if possible enhance, the upper temperature of the smectic C phase as a main priority. Accordingly, it is advantageous to use a chiral dopant with a phenylpyrimidine core (*i.e.*, a matched dopant) and a fluoro substituent at the chiral centre, *e.g.*, compounds **179**–**181** [99] and **183** [104]. The polarity of the fluoro substituent in a terminal chain tends to enhance smectic phase stability through enhanced lamellar attractions and by stiffening the chain. Such a situation can lead to high melting points, but careful selection of the detailed structural units enables low melting points and reasonably high smectic C phase stability to be obtained. The spontaneous polarisation of compounds such as **179**, with the chiral centre bearing the fluoro substituent in an alkyl chain, is only moderately high (around $20\,\mathrm{nC\,cm^{-2}}$), but phenylpyrimidine host mixtures doped with these compounds give short switching times. In fact compound **179**, and some other homologues, shows an inversion in the sign of spontaneous polarisation as the temperature of the smectic C phase is lowered; such a feature may prove useful in tailoring the temperature dependence of the spontaneous polarisation for improved device performance [103]. On the other hand, compounds based on Structure **183**, where the chiral fluoro centre is α- to the carbonyl group as part of an extended core system, have high values of spontaneous polarisation up to $400\,\mathrm{nC\,cm^{-2}}$. Compound **182** is closely analogous to the parent for compound **180** and comparison of their transition temperatures shows that fluoro substitution in the terminal chain gives enhanced smectic C and A character but a higher melting point.



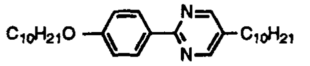
179
C 53.0 S_C* 67.0 S_A* 82.0 I



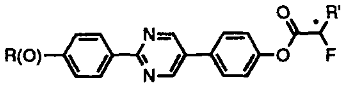
180
C 85.0 (S_C* 84.0) S_A* 86.0 I



181
S_X 64.0 S_C* 74.0 S_A* 79.0 I



182
C 36.0 S_C 73.0 S_A 77.0 I

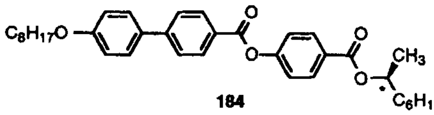


183
R' = $CH(CH_3)_2$, $CH_2CH(CH_3)_2$, $CH(CH_3)C_2H_5$, C_3H_7

4.10.2. Small Perfluoro Units at a Chiral Centre

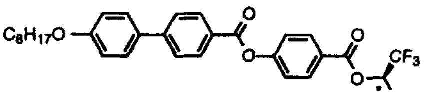
A trifluoromethyl group at a chiral centre is often used to generate chiral liquid crystals, or chiral dopants, of high spontaneous polarization for ferroelectric mixtures [105–107]. Additionally, a small perfluoro unit (*e.g.*, CF_3 or C_2F_5) is commonly employed at a chiral centre within a terminal chain to generate the antiferroelectric phase [108–111], which has a structure analogous to that of the ferroelectric (chiral smectic C) phase except that the tilt direction alternates from layer to layer. It is thought that 'bulky' branching causes the alternating tilt direction by specific interactions of the terminal chains at the interlayer region, and so the combination of steric bulk and high polarity of the small perfluoro units is particularly advantageous in generating the antiferroelectric phase and providing a reasonably high spontaneous polarisation.

Compound **185** is the trifluoromethyl-substituted analogue [109] of the common MHPOBC (**184**) [108] and, despite not being optimised for physical properties, such compounds and their homologues are used in Japan in mixtures for commerically available antiferroelectric displays. The effect of trifluorination in the methyl group at the chiral centre of compound **184** has been to depress the smectic A phase stability more severely (26.7°C) than for the smectic C^*_{ferro} and smectic C^*_{anti} phases (depressed by 12.6 and 10.8°C respectively). Although, at first sight, the three fluoro substituents in



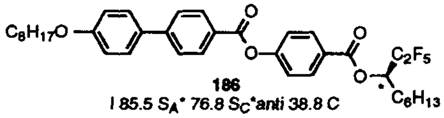
184

C 73.5 ($S_I{}^*{}_{anti}$ 62.2) $S_C{}^*{}_{anti}$ 118.8 $S_C{}^*{}_{ferri}$ 119.8 $S_C{}^*{}_{ferro}$ 121.6 $S_C{}^*{}_{alpha}$ 122.6 $S_A{}^*$ 147.7 I



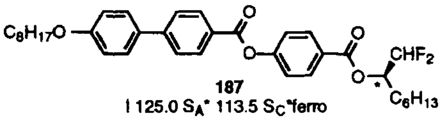
185

C 84.5 $S_C{}^*{}_{anti}$ 108.0 $S_C{}^*{}_{ferro}$ 109.0 $S_A{}^*$ 121.0 I



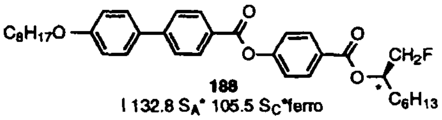
186

I 85.5 $S_A{}^*$ 76.8 $S_C{}^*anti$ 38.8 C



187

I 125.0 $S_A{}^*$ 113.5 $S_C{}^*ferro$

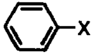
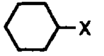


188

I 132.8 $S_A{}^*$ 105.5 $S_C{}^*ferro$

the trifluoromethyl group might be expected to give an extremely polar unit, it should be noted that the three substituents on the tetrahedral atom are not pointing in the same direction and the resultant of the dipole of the three fluoro bonds is only slightly greater than for a CF bond. In tetrafluoromethane, the CF dipole is equal to the CF_3 dipole, but at centres with bond angles which are not perfectly tetrahedral, the two dipoles will differ slightly; the FCF bond angles will be somewhat compressed and so give a higher resultant dipole [20]. It should be noted that the difference between the polarity of C—F and C—CF_3 is less in aliphatic than in aromatic systems (see Tab. VIII) because in aromatic systems the fluoro substituent interacts

TABLE VIII Dipole moments (D) of fluoro-substituted compounds

X			*CH_3X*
F	1.50 [112]	1.94 [113]	1.85 [114]
CF_3	2.54 [115]	2.40 [116]	2.32 [117]

mesomerically with the π-system of the ring and so diminishes the polarity arising from the electronegativity differences of carbon and fluorine (see Section 3).

As expected, the larger size of the pentafluoroethyl branch in compound **186** depresses the overall liquid crystal phase stability when compared to the analogous material (**185**) with a trifluoromethyl unit. However, the alternating tilt structure of the $S_{C^*_{anti}}$ phase is favoured over the conventional $S_{C^*_{ferro}}$ phase which has been eliminated. A smectic A phase is exhibited, but the phase stability has been reduced by 35.5°C compared to a 31.2°C depression for the $S_{C^*_{anti}}$ phase.

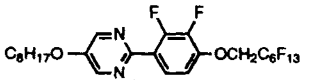
The favouring of the alternating tilt $S_{C^*_{anti}}$ phase by the longer fluorinated branch is in keeping with the widely held view that the alternating tilt phase is generated by the influence of the branched unit at the terminal chain with a terminal chain of the molecule in an adjacent layer. The larger, and/or the more fluorinated, the branch then the greater the influence on the alternating tilt effect, but of the course the overall phase stability is reduced by the steric effect of the larger unit.

When the branch point is composed of dichotomous units (*e.g.*, fluoro/hydrocarbon, compounds **187** and **188**) then the interaction with a terminal chain of a molecule in the adjacent layer is not favourable (as expected) and an alternating tilt structure is not possible. Although there is little difference in mesomorphic behaviour between compounds **187** and **188** it is worth noting that compound **187** with the more polar branch has the higher tilted smectic phase stability ($S_{C^*_{ferro}}$), yet the lower overall smectic phase stability (as seen through the S_{A^*} phase stability). This is yet another example of a common situation where a higher tilted smectic C phase stability is accompanied by a lower overall smectic phase stability (see Section 4.10.3); some other examples in this review of pairs of isomeric compounds showing this behaviour are **82/85**, **172/173**, **177/176**, **190/189** (compound with higher smectic C stability is given first).

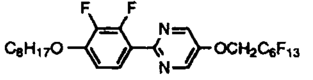
4.10.3. Multifluoro- and Perfluoro-substituted Chains

The more extensive fluorination of a terminal chain (*e.g.*, compounds **189** and **190**) tends to cause a stiffening [24] which facilitates a lamellar packing and thus enhances the smectic phase stability. The smectic phase stability is further enhanced by the polarity of the fluoro substituents increasing the lateral intermolecular forces of attraction. A comparison of compounds **189** and **190** with compound **121** provides a good example of the massive increase in smectic phase stability.

The major goal in using extensive fluorination of terminal chains is to provide wider smectic C phase temperature ranges for ferroelectric host materials. However, the strong tendency for lamellar packing often means that the orthogonal smectic A phase is favoured above the tilted smectic C phase. In order to generate the preferred tilted phase the overall molecular structure needs to be carefully designed to give the necessary polarity and steric effects in the correct molecular regions. Some very subtle structural changes can give a smectic C phase rather than a smectic A phase, such as by interchanging the ends of the fluorinated chain, as in compound **189** to give **190** which shows a 63°C increase in smectic C stability but has lost the smectic A phase [118]. Compounds **189** and **190** illustrate a situation which occurs quite frequently in that one isomer gives a smectic A phase to high temperature and (possibly) a smectic C phase to a low temperature, whereas the other isomer gives a lower overall smectic phase stability but the stability of the smectic C phase is higher than in the former case (see Section 4.10.2). It seems that if the dipoles are distributed to favour molecular tilting, and so encourage a high smectic C phase, then this will weaken the lamellar interactions and consequently give a lower smectic A phase stability.



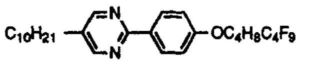
189
C 65.0 (S_C 64.0) S_A 138.0 I



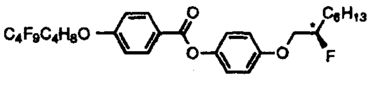
190
C 77.0 S_C 127.0 I

Compounds have also been prepared with equal extents of hydrocarbon and fluorocarbon within a terminal chain [100, 119, 120]. Such a terminal chain is intermediate in stiffness and polarity between a hydrocarbon chain and a perfluorocarbon chain, and this is reflected in the smectic phase stability. Compound **191** [119] is based on a phenylpyrimidine core and shows much higher smectic phase stability then compound **119**. Unfortunately, the reasons for enhanced smectic phase stability in these compounds with fluorocarbon units within a terminal chain are also responsible for higher melting points. A similar situation arises for the two-ring esters such as **194** which show a large increase in melting point, smectic C and A stability [121].

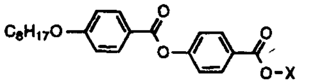
Compounds such as **192** with a semifluorocarbon terminal chain and a chiral terminal chain with a fluoro substituent at a chiral centre have been prepared. Such materials serve as chiral components in analogous achiral host mixtures to provide compatibility and give ferroelectric properties [100, 120].



191
C 58.0 S_C 80.0 S_A 106.0 I

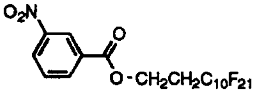


192
C 93.8 S_C^* 107.0 S_A^* 119.4 I

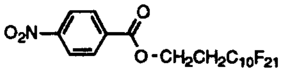


193
X = $C_{10}H_{21}$ C 54 S_A 76 I
194
X = $(CH_2)_2C_8F_{17}$ C 101 S_C 131 S_A 145 I

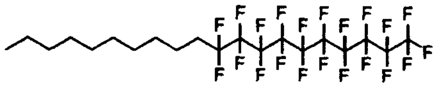
Even simple benzoate esters **195** and **196** reveal mesogenicity in single-ring compounds when a partially fluorinated alkyl chain is present. A polar substituent in the 3-position, as in compound **195**, was originally thought to be essential for mesogenicity [122] but subsequently the linear mesogenic compound **196** was prepared [123].



195
C 62 S_X 92 I



196
C 105 (S_X 85 S_A 92) I

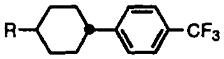


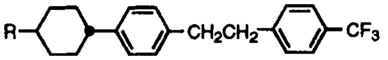
197
C 46.9 G or J 63.3 I

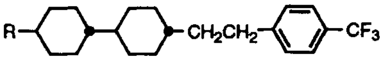
A rather unusual example involving fluorocarbon chains is seen in compound **197** which simply consists of a ten carbon hydrocarbon unit joined to a ten carbon fluorocarbon unit [124]. The fluorocarbon and hydrocarbon units are significantly different in terms of flexibility and polarity and this facilitates a self-assembled lamellar phase structure. Compound **197** has been shown to exhibit a tilted crystal smectic phase of the G or J type. Further compounds analogous to **197** have been prepared as non-ionic surfactants which exhibit lyotropic liquid crystal phases [125, 126].

4.10.4. Fluoro Substitution in Short Chains

The efficiency of a terminal trifluoromethyl group in generating liquid crystals has been tested in various systems. Compounds **198** [127] are non-mesogenic, **199** [128] are not mesogenic or give a highly ordered smectic phase and although **200** (R = C_3H_7 or C_5H_{11}) give nematic phases, smectic phases are very pronounced [129]. 4-Substituted-4′-trifluoromethylbiphenyls have also been prepared [130]; once again liquid crystals were produced but

198 

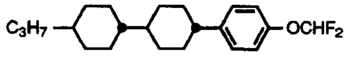
199 

200 

the smectic A phase and other orthogonal smectic phases predominate possibly because of the tendency for fluorocarbon and hydrocarbon molecular components to segregate, leading to layered structures [131].

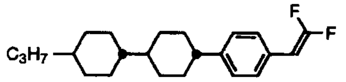
Other small perfluoro and partially fluorinated terminal chains have been employed to give liquid crystals of high resistivity for inclusion in nematic mixtures for active matrix displays (*e.g.*, compounds **201**–**204**, and many other terminal units and core systems) [132]. The small fluoro-containing chain provides a positive dielectric anisotropy in an alternative way to that in which a terminal fluoro substituent has been employed (see Section 3). As shown above, fluorinated chains tend to generate smectic phases, and in many cases this is true even of small trifluoromethyl terminal units, however, with some cores the nematic phase can be exhibited over a wide temperature range. Compounds **201** and **202** show a smectic phase at lower temperatures but give very high nematic phase stability. The larger sulfur unit in compound **203** disrupts the lateral intermolecular forces of attraction and produces a nematogen, but it has a lower clearing point than for compound **201**. Compound **204** has the terminal chain as an alkene unit that is in conjugation with the core and this extended longitudinal polarisability is responsible for the extremely high nematic phase stability.

201
C 38.0 S_X 69.0 N 154.0 I



202
C 52.0 S_B 69.0 N 174.0 I

203
C 51.0 N 109.5 I

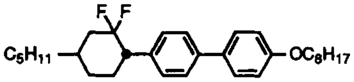


204
C 51.0 S_X 88.6 N 233.0 I

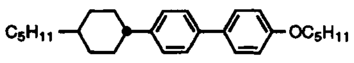
In all of the examples **201**–**204** it is remarkable that the phenylbicyclohexyl core and the terminal fluoro unit, which independently would be expected to give predominantly smectic systems, give strongly nematic materials.

4.11. Fluoro Substitution in Cyclohexanes

Compounds containing cyclohexane rings do not generally provide a good basis for the design of liquid crystals intended to give the smectic C phase, although this has been achieved in some cyclohexylethyl systems (*e.g.*, **103**–**105**) [67, 96, 133]. Compounds have been prepared with two fluoro substituents in the cyclohexane ring (*e.g.*, compound **205**) [133] in order to assess the possibility of generating smectic C phases of relatively low birefringence for ferroelectric host materials. Despite providing a lateral dipole, the few difluorocyclohexane materials prepared showed no tendency to exhibit a smectic C phase. The two fluoro substituents simply conferred a high melting point, reduced the crystal B phase stability and introduced a nematic phase (*e.g.*, compare the related compounds **205** and **206**). These results for fluoro substitution in saturated alicyclic units are a tremendous contrast to the effect of fluoro substituents in aryl rings. Given that the synthesis of such fluoro alkane systems is much more difficult than for fluoro-aryl compounds, the results do not encourage further work in this area.



205
C 95.0 B 99.0 N 147.0 I



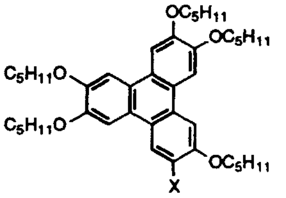
206
C 42.0 B 183.0 I

5. MISCELLANEOUS SYSTEMS

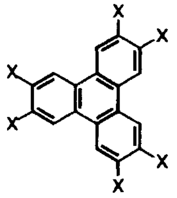
The majority of the examples given so far are of compounds designed for use in applications. In this section, examples are given showing the effects of fluoro substitution in more unusual systems.

5.1. Fluoro Substitution in Discotic Systems

Fluorosubstitution in one or all peripheral arms of a discotic molecule have been reported [134]. The mesophase type is essentially unchanged, but the temperature range of the mesophase is strongly affected by a fluorinated side-chain; one partially fluorinated chain (**208** compared to **207**) gives a decrease in clearing temperature but for symmetrically substituted systems (**210** compared to **209**) a broad mesophase range was observed which is attributed to the dichotomous region of the molecule giving a stabilized columnar structure.



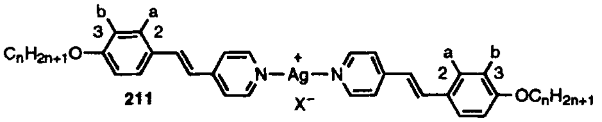
207, X = OC_5H_{11} C 69 D_h 122 I
208, X = $OOC(CH_2)_4(CF_2)_3CF_3$ C 38 D_h 98 I



209, X = $OCH_2COOC_2H_5$ C 122 D_h 172 I
210, X = $OCH_2COO(CH_2)_2C_6F_{13}$ C 30 D_h 210 decomp

5.2. Fluoro Substitution in Metal-containing Systems

Systematic studies of fluoro substitution in metal-containing systems are quite rare [135] but one thorough investigation deals with the mesomorphic properties of silver complexes of 4-alkoxy-4′-stilbazoles (**211**) [136–140]. These systems have a similar shape to non-metal-containing calamitic compounds but monofluoro substitution of the ligand inevitably leads to a symmetrical difluoro substitution effect in the complex; the general effects produced are similar to those seen in non-metal-containing compounds [139]. For 3-fluoro substitution in the triflates, the smectic C phase of the parent complexes is depressed by 40–50°C and smectic A values are increased by ~10°C so that the smectic A phase range is increased significantly. On the other hand, 2-fluoro substitution affects the phase behaviour in a completely different way and the smectic A phase stability is reduced and more nematic character is revealed (see the examples **211a–f**).



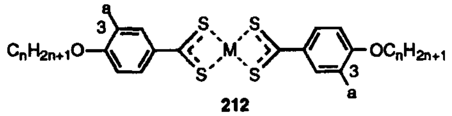
211

X = trifluoromethanesulfonate (OTf) or
dodecylsulfate (DOS)
n = 1-12

211a, X = OTf; n = 6; a, b = H C 178 (G 149 S_C 169) S_A 235 I
211b, X = OTf; n = 6; a = F, b = H C 156 S_A 184 N 194 I
211c, X = OTf; n = 6; a = H, b = F C 74 C′ 138 C″ 140 (S_C 116) S_A 256 I

211d, X = OTf; n = 8; a, b = H C 158 G 165 S_C 181 S_A 250 I
211e, X = OTf; n = 8; a = F, b = H C 110 C′ 119 S_C 149 S_A 198 I
211f, X = OTf; n = 8; a = H, b = F C 34 C′ 79 C″ 130 (S_C 126) S_A 257 I

Nickel(II), palladium(II) and zinc(II) complexes of laterally fluorinated alkoxydithiobenzoates are also calamitic-like systems and for the nickel and palladium complexes, 3-fluoro substitution promotes the smectic C phase at the expense of the nematic phase (see the example for the palladium complex **212**) [141, 142].

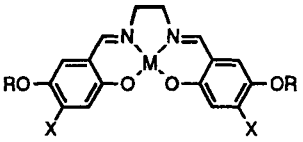


212

212a, M = Pd(II); n = 8; a = H C 232 S_C 307 N 318 I
212b, M = Pd(II); n = 8; a = F C 108 C' 129 C'' 209 S_C 315 I

In other situations (*e.g.*, for complexes **123**) [143], fluoro substitution can give large increases in melting points and mesogenicity is eliminated or drastically reduced. The values given for **213a–d** indicate that the fluoro susbstituent is not simply causing a steric effect, but dipolar effects are predominating.

213



M = Cu, Ni, VO; R = C_8H_{17}, $C_{11}H_{23}$; X = H or F

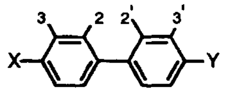
213a, M = Ni, R = C_8H_{17}, X = F C 250 (S_A 246) I
213b, M = Ni, R = C_8H_{17}, X = H C 61 S_I 186 S_A 300 I

213c, M = Ni, R = $C_{11}H_{23}$, X = F C 226 S_A 227 I
213d, M = Ni, R = $C_{11}H_{23}$, X = H C ~175 S_A ~300 I

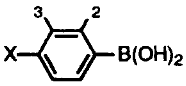
The effect of fluoro substitution on the mesophase type and stability of β-diketone derivatives and their copper(II) complexes [144–145] and of *bis* (*N*-aryl-4-decyloxybenzoyloxysalicylaldimine) copper(II) complexes [146] has also been briefly examined.

6. SYNTHESIS OF FLUORO-SUBSTITUTED LIQUID CRYSTALS

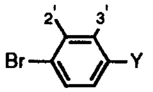
Although it is clear from the examples given above that fluoro substitution can be used in several different ways to achieve advantageous molecular properties, a significant issue to consider is the ease of synthesis of the target molecules. The first examples of fluorosubstitution in liquid crystals date back at least to 1925 [62] but it was only in the 1980s that the value of low-level substitutions (*i.e.*, a maximum of three or four fluoro substituents) was recognised. Until that time, the synthesis of fluoro-substituted compounds was quite difficult and only a limited range of suitable reactions was available. The standard method for introducing a fluoro substituent into an aromatic system is by the Balz–Schiemann reaction [147, 148] which involves the thermal decomposition of a diazonium tetrafluoroborate obtained by diazotization of an amine, which had itself usually been prepared from a nitro compound. The limitations imposed by a lack of more general methods of synthesis is best illustrated by a simple example. Consider the conventional approach to a biphenyl system with a fluoro substituent at any of the 2-, 2′-, 3- or 3′-positions (see **VI**). Starting from the readily obtainable 4,4′-disubstituted biphenyl, it would be unrealistic to efficiently introduce any 2- or 2′-substituent because of the severe steric hindrance at these positions in a biphenyl and it may also be impossible to obtain the 3- or 3′-substituent either because of the steric hindrance of the *X*- and *Y*-groups or their inappropriate directing effects; the problems involved in the synthesis of multifluoro-substituted systems is even greater. The alternative is a synthesis based on single benzene units which are then connected together to give the required biphenyl. Until recently the usual route to connecting aryl units together was by an Ullmann reaction [149] (the coupling of aryl halides, preferably iodides, with copper) or by a Gomberg reaction [150, 151] (the coupling of a diazonium salt with another aromatic ring); both of these approaches have serious limitations, as did some alternative methods of synthesis [152], and are unsuitable for the controlled design of multiaryl systems.



VI



VII



VIII

Fluoro substitution at the 2-, 2'-, 3- or 3'- position

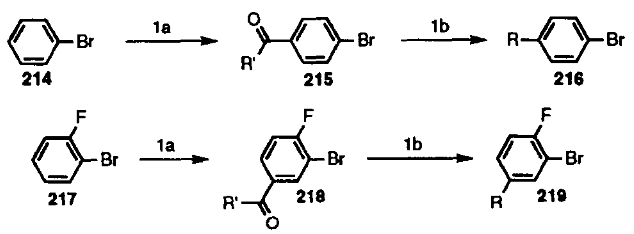
Fluorination methods have steadily improved over the years [19, 153, 154] but it was not until the early 1980s that most of the problems in this type of aryl synthesis were overcome by the development of efficient metal-catalysed aryl–aryl cross-coupling reactions; now liquid crystal core units based on aromatic systems (*i.e.*, systems composed of sp^2-hybridised carbon atoms) can be constructed efficiently. The synthetic approach for the example **VI** given above would probably now involve the coupling of compounds **VII** and **VIII**, for which synthetic methods are more likely to be available. The methods which are most applicable for the synthesis of liquid crystals are the palladium-catalysed cross-coupling reactions of arylboronic acids (or esters) and aryl bromides, iodides or triflates which were originally reported by Suzuki [155–158] and have been extended by many workers since then (see Refs. [159–166]) and applied in a variety of liquid crystal syntheses [68, 167–171]. Organozinc [162, 172] and organotin [173, 174] couplings are also now extremely useful in the preparation of multi-aryl systems.

Metal-catalysed coupling procedures have revolutionised the synthesis of liquid crystal cores in that each ring unit of the core system can often be constructed individually and then linked to another part of the core. Molecules can be constructed with substituents present at hindered positions, substituents can be included at positions to which normal substitution reactions on the core would not be directed, unusual combinations of different types of aromatic ring can be obtained, and terminal and linking groups (primarily with *sp* or sp^2 carbon attachments) can be included. With these new and powerful synthetic capabilities, it has become possible to prepare fluoro-substituted systems that were previously unattainable and many of the compounds discussed in this review were prepared by these methods.

6.1. Typical Syntheses of Some Fluoro-substituted Liquid Crystals

The use of aromatic rings (usually phenyl) in liquid crystals is extremely widespread because, through appropriate, 1,4-disubstitution, long, lath-like structures of high longitudinal polarisability can be produced which generate high mesogenicity. The desired 1,4-disubstitution pattern can be obtained relatively easily through normal electrophilic substitution, although many suitable precursors are commerically available.

For example (Scheme 1), simple Friedel-Crafts acylation on bromobenzene (**214**) followed by reduction of the aryl ketone (**215**) provides an excellent route to 1-alkyl-4-bromobenzenes (**216**) [68], because the bromo substituent is *para* directing. However, when a lateral fluoro substituent is required in that particular ring such Friedel-Crafts acylation reactions are then dominated by the more powerful *para* directing effect of the fluoro substituent, and so the undesired 1-alkyl-3-bromo-4-fluorobenzene (**219**) would be generated! Accordingly, another route to fluoro-substituted 1-alkyl-4-bromobenzenes is required. Conventional electrophilic substitution reactions can, in fact, be employed, but they need to be followed by

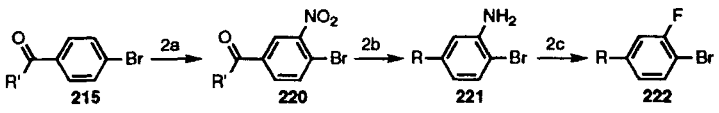


1a ... R'COCl, $AlCl_3$.
1b ... Hydrazine hydrate, KOH

SCHEME 1

functional group interconversions to generate the desired fluoro-substituted products. For example (Scheme 2) compound **215** could be nitrated in the desired position due to the reinforcing directing effects of the acyl and bromo substituents. The reduction of the two functional groups in compound **220** can fortunately be achieved in one step and the final step of this synthesis involves the introduction of the all-important fluoro substituent into the desired product (**222**) by a Balz–Schiemann reaction.

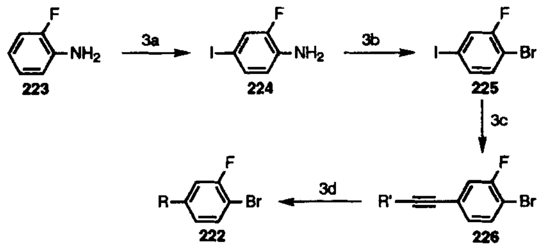
If possible, it is always more efficient to begin any such syntheses with a commercially available fluoro-substituted starting material and an alternative route to compound **222** is shown in Scheme 3.



2a ... HNO_3, H_2SO_4.
2b ... Reduction (see text).
2c ... (i) $NaNO_2$, H_2SO_4; (ii) HBF_4 or HF.

SCHEME 2

In Step 3c of this sequence, a recently developed carbon—carbon bond-forming metal-catalysed cross-coupling reaction is used. If an appropriately substituted system, such as 1-bromo-2-fluoro-4-iodobenzene (compound **225**), is available through conventional aromatic reactions and subsequent functional group interconversions, then a coupling reaction at the more labile iodo site will give the alkyl chain in the desired position. One problem still exists, namely that *sp*^{3} carbon centres do not undergo coupling in very high yields and the product may be difficult to separate from the starting material. Hence, a better coupling reaction is one that involves an acetylenic (*sp*) carbon, and this gives high yields and the purification is relatively



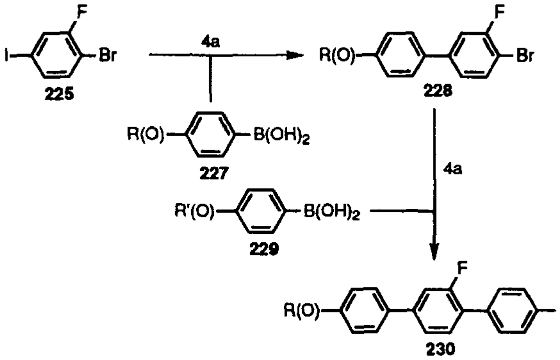
3a ... I_2, $NaHCO_3$.
3b ... (i) $NaNO_2$, HBr; (ii) CuBr.
3c ... R'-C≡C-ZnCl, $Pd(PPh_3)_4$, THF.
3d ... PtO_2, EtOH.

SCHEME 3

easy (compound **226**). Subsequent hydrogenation of the alkenic function introduces an alkyl chain by an indirect, but more efficient route (compound **222**) [89, 168].

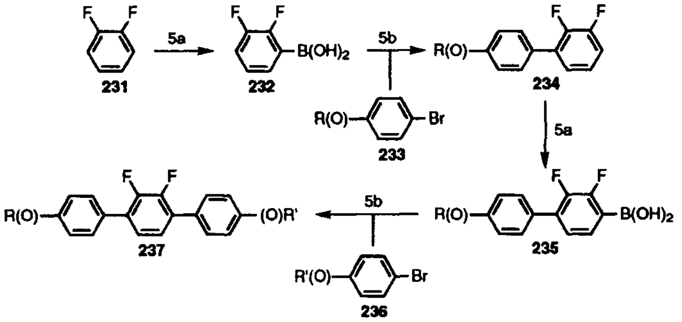
Most liquid crystals consist of more complex multi-aryl systems, which are not too synthetically challenging unless lateral fluoro or other substituents are required as part of the molecular architecture. In such cases, the introduction of a lateral fluoro substituent into the multi-aryl parent system is extremely difficult because of a number of considerations discussed above. Accordingly, lateral fluoro substituents need to be introduced at the required position in the appropriate ring initially, and then subsequent coupling of the sub-units can provide the multi-aryl liquid crystal. Coupling of the sub-units can be efficiently achieved using palladium-catalysed cross-coupling reactions which have been widely developed over the last twenty years. Such coupling reactions (Scheme 4) involve an organometallic unit and a compound that contains a leaving group (*e.g.*, iodo, bromo, trifluoromethane sulfonyl or, in some cases, chloro); probably the best organometallic unit for aryl–aryl coupling is the boronic acid (*e.g.*, **227** and **229**) or the ester analogues. Selectivity is possible such that one coupling can take place at an iodo site to give a biaryl intermediate (*e.g.*, **228**) and a second, different coupling, can proceed at the less reactive bromo site to provide a liquid crystal product (*e.g.*, **230**, Scheme 4) [168].

Another, extremely important aspect of fluoro-substituted aromatic systems is that the protons adjacent to a fluoro substituent are relatively acidic and can be removed by butyllithium or lithium diisopropylamide. For example, in 1,2-difluorobenzene, the positions *ortho* to the fluoro substituents can be exploited to generate liquid crystals (Scheme 5) [68]. Any electrophilic substitution in compound **231** would not produce the



4a ... Pd(PPh$_3$)$_4$, DME, Na$_2$CO$_3$, H$_2$O.

SCHEME 4



5a ... (i) nBuLi, THF; (ii) (MeO)$_3$B, THF; (iii) 10% HCl.
5b ... Pd(PPh$_3$)$_4$, DME, Na$_2$CO$_3$, H$_2$O.

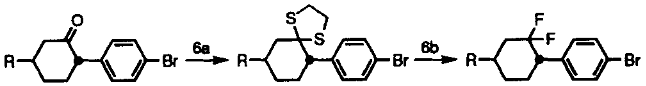
SCHEME 5

desired result, and any incoming electrophile would be directed *para* to a fluoro position. Fortunately, the acidity of the protons next to the fluoro substituents enables the introduction of a wide range of common functional groups (*e.g.*, aryl, hydroxyl, carboxyl, alkyl and alkoxy) which are valuable for producing liquid crystals. Both fluoro substituents in 1,2-difluorobenzene (Scheme 5) are equivalent and this allows the exploitation of one acidic proton to generate an arylboronic acid (**232**), which can then be involved in a palladium-catalysed cross-coupling reaction with an aryl bromide (**223**) to give the biaryl, **234**. The acidic proton of compound **234** can then be exploited in the same manner to generate a boronic acid (**235**) which can be coupled to a different aryl bromide (**236**) to give an unsymmetrical *p*-terphenyl liquid crystal (**237**).

Fluoro substituents have also been included at aliphatic and alicyclic sites in liquid crystals. Here, with the exception of some perfluorinated and partial fluorocarbon units, there are not any suitable fluoro-substituted precursors available commercially. Accordingly, fluoro substituents must be introduced through functional group interconversions, usually from aldehydes, ketones, alcohols and halides but many fluorinating reagents are non-selective and can affect other functional groups, so the choice of reagent is important. Scheme 6 shows the synthesis of the difluorocyclohexane system (**240**) from a ketone (**238**) *via* a dithiolane intermediate (**239**) which allows the use of a relatively mild fluorination reaction [96, 175]. A single fluoro substituent can be introduced into a saturated environment from an alcohol by using a variety of reagents, with diethylaminosulphur trifluoride (DAST) a popular choice (Scheme 7) [99, 176].

Where a halogeno substituent, *e.g.*, bromo, is α- to an electron-withdrawing group (**243**), then potassium fluoride can be used in a displacement reaction to generate the desired fluoro-substituted unit (**244**) [177].

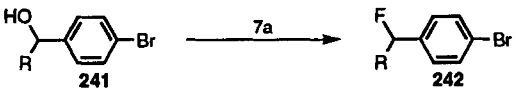
Furthermore, the fluoro substituent in Structure **244** is at a chiral centre, and when resolved into enantiomers, such chiral materials are very useful in ferroelectric mixtures. Scheme 8 shows the enzyme-based kinetic resolution of Structure **244** which leaves the (*S*)-isomer unhydrolysed (**244a**). The isolated **224a** can be converted easily into the acid (**245a**) or the alcohol (**246a**) without loss of configuration and both materials can be further modified to provide chiral esters or chiral ethers for liquid crystal applications [102].



238 **239** **240**

6a ... $HSCH_2CH_2SH$, $BF_3{\bullet}2HOAc$.
6b ... HF-pyridine, CH_2Cl_2.

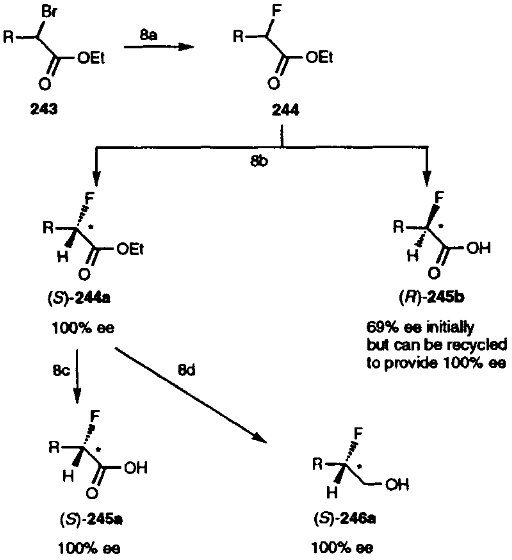
SCHEME 6



241 **242**

7a ... DAST.

SCHEME 7



8a ... KF.
8b ... lipase P-30 Amano (pseudomonas), pH 7.0.
8c ... HCl, H_2O.
8d ... $LiAlH_4$.

SCHEME 8

7. SUMMARY

In summary, fluoro substitution is now an extremely common way of modifying the behaviour and properties of liquid crystals. In this survey, the main characteristics which have been illustrated are given below. Many of the substituent effects appear consistently in different systems but some unusual and inexplicable effects occur here and there to emphasise how subtle are the effects which determine mesogenicity!

(a) Fluorine is the smallest substituent that can be used to replace hydrogen:

- (i) it can in some situations be shielded within the general shape of the molecule leading to maintained or enhanced mesogenicity;
- (ii) it can cause steric separation of molecules and/or an intramolecular conformational change (*e.g.*, interannular twisting in biaryls) which often leads to reduced mesogenicity, particularly of ordered phases, often lowers the melting point and still preserves liquid crystallinity;
- (iii) at the outer edge of a core unit its overall effect is a compromise between its broadening effect and its ability to fill space.

(b) Fluorine has the greatest electronegativity of all the elements and this can lead to

  (i) compounds with enhanced positive dielectric anisotropy values;
  (ii) compounds with negative dielectric anisotropy values;
  (iii) compounds with a dipolar substituent at a chiral centre to enhance spontaneous polarization values;
  (iv) substitution in saturated systems to give a greater polarity than for substitution in aromatic systems.

(c) Fluorine is usually a stable substituent in both aliphatic and aromatic environments.

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