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Liquid Crystals

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Lateral fluoro substituted 4-alkyl-4''-chloro-1,1':4',1''-terphenyls and derivatives. Useful high birefringence, high stability liquid crystals

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Lateral fluoro substituted 4-alkyl-4''-chloro-1,1':4',1''-terphenyls and derivatives

Useful high birefringence, high stability liquid crystals

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By modification of the basic 4-alkyl-4''-chloro-1,1':4',1''-terphenyl structure with lateral fluoro substituents and ethyl linking groups, a wide range of mesogens has been synthesized. Control over the phase behaviour, especially optimization of nematic properties, can be achieved by the degree and position of lateral fluoro substitution and/or the presence and position of an ethyl linking group. The effect of these changes on the physical properties such as dielectric anisotropy ($\Delta\epsilon$) and birefringence (Δn) has also been studied. Compounds of low melting point, wide nematic range and high birefringence (>0.2) have been made. These materials are suitable for active matrix display applications where high chemical and photostability are necessary.

1. Introduction

Nematogenic liquid crystals with terminal cyano groups have been used in liquid crystal devices such as the twisted nematic cell for many years. However, there are some display applications that cannot successfully use terminal cyano materials. For example, an active matrix addressed display can only contain a liquid crystal material which possesses a very high degree of chemical and photostability. The reason for this is that if a liquid crystal is degraded by heat or light, the resistivity and therefore the capacitive ability of a mixture in which it is contained is adversely affected. Yamagishi *et al.* [1] first demonstrated that terminal cyano compounds could be degraded by heat and light and Plach *et al.* [2] showed by means of a 'holding ratio' [3,4] test that terminal cyano compounds were not of sufficient stability to be used in active matrix displays. It has been shown previously [5] that a terminal chlorine in place of a terminal cyano group can produce nematogens of positive dielectric anisotropy ($\Delta\epsilon$) and moderate birefringence (Δn). Appropriate terminal chloro substituted materials possess excellent chemical and photostability [5,6] and are well-suited for use in active matrix display applications such as 2nd minimum TN/TFT and PDLC/TFT [7].

Additionally, the mesophase behaviour in terphenyl structures can be significantly altered by the position and degree of lateral fluoro substitution [8], to give in some cases, an enantiotropic nematic phase.

This background knowledge led to an investigation of materials of types 1, 2 and 3 (as shown in the figure) all being modifications of the 4-alkyl-4''-chloro-1,1':4',1''-terphenyl (alkyl chloroterphenyl) [9] structure. Modification of the basic alkyl chloroterphenyl structure was necessary, as it is very smectogenic in nature.

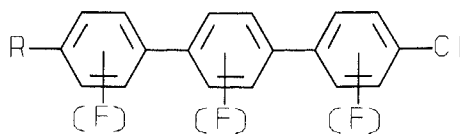
* Author for correspondence.

For example, 4-*n*-pentyl-4''-chloro-1,1':4',1''-terphenyl has a mesophase sequence of C 105°C S_B 245°C I. The alkyl chloroterphenyl structure was modified by lateral fluoro substitution and ethyl linking groups. The properties of 31 of these materials are now reported.

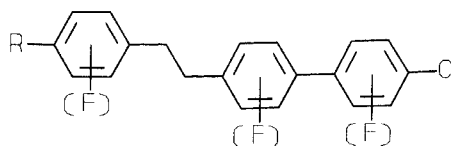
2. Experimental

The compounds reported in this paper were synthesized by standard synthetic organic procedures involving for example Friedel Crafts acylation, Huang Minlon reductions and boronic acid couplings [10]. The crude materials were purified by flash column chromatography on Merck 40–63 μm silica gel, using petroleum spirit (bp 40–60°C) as the eluant and then recrystallized to > 99.5 per cent purity from petroleum spirit (bp 80–100°C) or propan-1-ol. The materials were analysed by reverse phase high performance liquid chromatography using a Hewlett-Packard 1090 instrument with diode array detector.

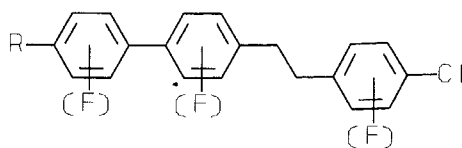
The structure of each of the compounds was confirmed by ¹H NMR spectroscopy using a Jeol PMX 60 SI and by GC mass spectrometry using a Nermag R1010S quadrupole instrument. Phase transition temperatures were measured using a Du Pont 1090 differential scanning calorimeter and by polarizing microscopy using a Mettler FP 52 hot stage to control the temperature of the sample. Physical measurements (dielectric anisotropy, birefringence, and extrapolated N-I values) were made using a 10 per cent w/w solution of each test compound in a chemically related medium dielectric anisotropy ($\Delta\epsilon$) mixture Merck ZLI 4792 ($\Delta\epsilon=5.1$) at 20°C. The birefringence (Δn) was measured using an Abbé refractometer and Na_D light (589.7 nm) at 20°C and the dielectric anisotropy was measured by an electrical capacitance method at 20°C and 1 kHz.



1.



2.



3.

The Δn and $\Delta \epsilon$ data were in all cases, obtained from solutions of the compounds in the host nematic liquid crystal mixture at 20°C. Therefore the data refer to the behaviour of the compound in a liquid crystal mixture rather than to that typical for the pure compound. Compounds with a high clearing point will for example give anomalously higher values than related materials of lower clearing point. For this applications-related work the values for mixtures were most appropriate to obtain, and it must be recognized that the values, as presented, cannot be interpreted as being those of the pure compounds.

Holding ratio measurements were performed on 15 per cent w/w solutions of the test compound in a chemically stable mixture (Merck ZLI 3086) in the following manner. The solution of test compound was filled into a glass cell. 100 mV was applied to the thin film of liquid crystal under test. 100 ms after the field had been removed, the charge remaining across the cell was remeasured. The final value is expressed as a percentage of the initial value (100 mV) to give the percentage holding ratio. The filled glass cells were then either UV irradiated for 2 h using a Heraeus 'Suntest' apparatus, or heated to 100°C for 2 h and the holding ratio measured again.

3. Results and discussion

The effect of ethyl linkage and/or lateral fluoro substitution on the basic 4-alkyl-4'-chloro-1,1':4',1''-terphenyl core will be discussed with respect to mesomorphic behaviour, birefringence and dielectric anisotropy.

The effect of inclusion of a *trans* cyclohexyl ring into the structure on the mesophase behaviour will also be discussed

3.1. Mesomorphic behaviour

3.1.1. Effect of an ethyl linking group

This effect is clearly shown by comparing compound **9** (pentyl chloro terphenyl), which has a melting point at 105°C and a smectic B phase to isotropic liquid transition at 245°C, with compounds **26** (or **27**), where one of the two inter-annular direct linkages has been replaced by an ethyl linkage; there is a considerable lowering of the mesophase temperature stability. In the case of compound **26**, the high melting point and ease of crystallization preclude an accurate determination of the clearing point; however, an extrapolated N-I of 106.5°C has been measured. In compound **27**, the clearing point has been reduced (by 122°C), relative to compound **9** with the nematic phase replacing the S_B phase. The same detrimental effect on the mesophase stability due to inclusion of an ethyl linkage between aromatic rings is also seen when there is lateral fluoro substitution of the molecule. If compound **13** is compared to its corresponding ethyl linked variant, compound **20**, it is again seen that the mesophase stability is greatly reduced (by 91°C); the smectic phase depression could not be measured directly. This difference in the clearing points is typical for mesogens whose structures vary by the presence of an ethyl link between aromatic rings. (Compare the N-I of compound **4** at 162°C with the extrapolated N-I of compound **22** at 71°C.) The lowering of transition temperatures by the incorporation of an ethyl linkage between aromatic centres is well-known and is accounted for in terms of greater molecular flexibility and reduced polarizability [11].

Table 1. Mesophase, birefringence and dielectric anisotropy data for the 4-alkyl-4'-chloro-1,1':4',1''-terphenyls (1) with varying lateral, reverse-pointing fluoro substitution patterns; temperatures in °C. Extrapolated [] values were measured using 10 per cent w/w of guest compound in Merck ZLI 4792. () values are for monotropic phases.

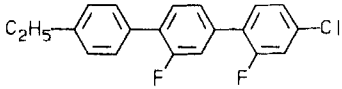
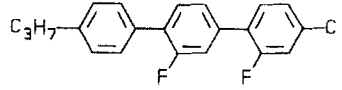
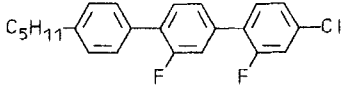
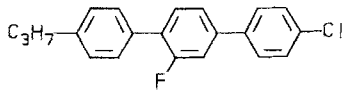
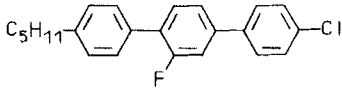
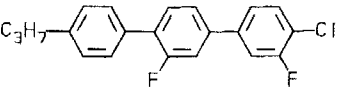
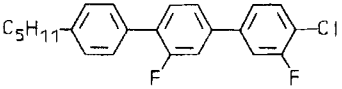
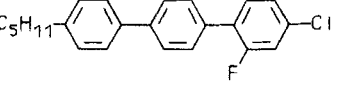
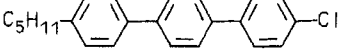
Compound	Phase behaviour/°C	Δn	$\Delta \epsilon$
1 	C 104 I [N 101.5 I]	0.25	+3
2 	C 75 N 105.2 I	0.26	+3
3 	C 68 N 105.5 I	0.24	+3
4 	C 126.5 S _A (125.7) N 162.5 I	0.28	—
5 	C 96.3 S _A 134.2 N 157.6 I	0.27	+5
6 	C 85.1 N 109.5 I	0.26	—
7 	C 54 S _A 101.7 N 112.9 I	0.25	+6
8 	C 64.8 S 94.0 S _A 151 N 158.8 I	0.27	+6
9 	C 105 S _B 245 I	—	—

Table 2. Mesophase, birefringence and dielectric anisotropy data for the 4-alkyl-4'-chloro-1,1':4',1''-terphenyls (**1**) with varying lateral forward-pointing fluoro substitution patterns; temperatures in °C. Extrapolated [] values N-I values were measured using 10 per cent w/w of guest compound in Merck ZLI 4792. () values are for monotropic phases.

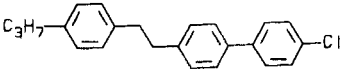
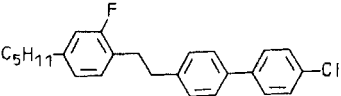
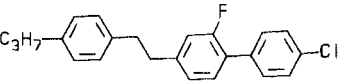
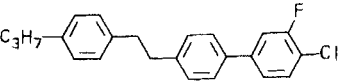
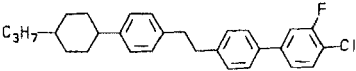
Compound	Phase behaviour/°C	Δn	$\Delta \epsilon$
10	C 91.6 N 112.7 I	0.26	—
11	C 60.3 N 111.7 I	0.25	+12
12	C 96.7 N 246.5 I	0.26	+12
13	C 124.9 S _A 132 N 169.2 I	0.29	+10
14	C 66 N 76.6 I	0.22	+14
15	C 112 I	0.22	—
16	C 96.7 I	0.24	—
17	C 121.8 I	0.26	+18
18	C 171 S _E 178 S _A 194 I	0.27	—

Table 3. Mesophase, birefringence and dielectric anisotropy data for the 4-(β -4-chlorophenylethyl)-4'-*n*-alkylbiphenyls (**3**) with varying lateral fluoro substitution patterns; temperatures in °C. Extrapolated [] N-I values were measured using 10 per cent w/w of guest compound in Merck ZLI 4792. () values are for monotropic phases.

Compound	Phase behaviour/°C	Δn	$\Delta \epsilon$
19	C 64 N 64.2 I	0.18	+5
20	C 80 N (78.1) I	0.21	+5
21	C 53 S _B (19) S _A (43) N 82 I	0.19	+4
22	C 94.2 I [N 71.4 I]	0.20	—
23	C 75 I [N 58.2 I]	0.19	—
24	C 116 N 230 I	0.22	—
25	C 102 N 208 I	0.20	—
26	C 128.8 I [N 106.5 I]	0.21	—

When the two series of ethyl linked structures are examined, it can also be seen that the N-I transitions are highest wherever a 4-chlorobiphenyl moiety is maintained. This is exemplified by comparing compound **28** with **21** and also compound **26** with **27**. This effect can be rationalized in terms of the higher polarizability of a chlorobiphenyl moiety compared to an alkylbiphenyl moiety.

Table 4. Mesophase, birefringence and dielectric anisotropy data for the 4-chloro-4'-(β -4-n-alkylphenylethyl) biphenyls (**2**) with varying lateral fluoro substitution patterns; temperatures in °C. Extrapolated [] N-I values were measured using 10 per cent w/w of guest compound in Merck ZLI4792. () values are for monotropic phases.

Compound	Phase behaviour/°C	Δn	$\Delta \epsilon$
27 	C 111 N 123 I	0.22	+7
28 	C 76.8 N 93.8 I	0.21	+9
29 	C 97.0 I [N 61.7 I]	0.20	+6
30 	C 64 N 68 I	0.21	+6
31 	C 100 N 208 I	0.22	—

3.1.2. Effect of lateral fluoro substitution

The effect of lateral fluoro substitution in liquid crystals is very well-reported [4] and summarized [12, 13]. The use of lateral fluoro substitution to modify phase behaviour in terphenyl systems has been reported by Chan *et al.* [14–16] who compared various monofluoro substituted alkyl and alkoxyterphenyls. The reason stated for the differences in mesomorphic behaviour between laterally fluoro substituted and non-laterally substituted materials was that a lateral fluoro substituent was capable of disrupting both the intermolecular crystalline packing and the preferred molecular conformation in space.

From a comparison of compound **9**, the unsubstituted alkyl chloroterphenyl, with compounds **3**, **5**, **7**, **8**, **11**, **14** and **18** it is clear that in alkyl chloroterphenyls, lateral fluoro substitution has a considerable effect on the mesomorphic behaviour. The extent to which the mesomorphic behaviour is affected relative to the parent structure **9** is determined by the position and degree of lateral fluoro substitution.

(i) *Lateral monofluoro substitution* Lateral monofluoro substitution has a large effect on the phase behaviour, but the compounds are predominantly smectic, for example, compound **18**. However, relative to compound **9** the phase types are

different, with the less ordered S_A phase replacing the S_B phase. It has also reduced mesophase stability due to the lateral fluorine substituent broadening the molecule and reducing intermolecular attractions. Nematic behaviour in monofluoro chloroterphenyls appears in compounds **4**, **5**, **8** and **13**, with the fluorine substituent either on the middle ring or directed towards the centre of the molecule, but in all cases an underlying smectic A phase is also present. These compounds also have fairly high melting points, indicating that the strong packing energies of the terphenyl core may have been only partially disrupted by the presence of one lateral fluorine substituent.

(ii) *Lateral difluoro substitution* Lateral difluoro substitution produces compounds that are predominantly nematic, for example, compounds **2**, **3** and **11**. Only in compound **7**, where there is a smectic phase-inducing fluoro substituent in the 3'' position in combination with the longer *n*-pentyl chain in the 4-position, does a smectic A phase appear. Relative to the corresponding monofluoroterphenyls, difluoroterphenyls have lower N-I transition temperatures. Comparing compounds **3** and **5**, **8** or **2** and **13**, the N-I is lowered by 50–75°C for the difluoro compounds. A comparison of compounds **2** and **6** or **3** and **7** shows that the clearing point is highest where there is a biphenyl moiety uninterrupted by 2- or 2'-substitution in the molecule. Toyne *et al.* [17] also show that the clearing points in isomeric difluoro substituted alkyl-alkoxy terphenyls were highest where an 'uninterrupted' biphenyl unit was present. The reason cited for this was that lateral fluoro substitution in an interannular (2- or 2'-) position produced an interannular twist which reduced the mesophase stability.

The lower melting points of lateral difluoro substituted alkyl chloroterphenyls do not extend to compounds which have a 'forked' difluoro substitution pattern. Compounds **15**–**17** which have 'forked' difluoro substitution in the middle ring have high melting points and do not exhibit enantiotropic mesophases. Comparing compounds **10** and **17**, the 'forked' difluoro substitution pattern also reduced the extrapolated clearing point relative to that with two lateral fluorines that can be written on the same side of the molecule. This can be readily rationalized by considering that, allowing for rotational effects, the 'average' molecular breadth of compound **10** will be less than that of compound **17**.

(iii) *Lateral multifluoro substitution* Lateral multifluoro substitution in alkyl chloroterphenyls reduces the clearing point still further relative to lateral monofluoro or difluoro substitution. Comparing compound **14** with compounds **5**, **9** and **11**, it can be seen that successive addition of lateral fluoro substituents lowers the clearing point from 245°C for compound **9** to 76°C for compound **14**. This can be explained in terms of the overall liquid crystalline order being decreased by the larger number of lateral fluoro substituents in the molecules, both broadening the molecule and disrupting the overall molecular polarisability by twisting the phenyl rings.

When lateral multifluoro substitution in alkyl chloroterphenyls includes 'forked' difluoro substitution, the compounds are again high melting and do not exhibit enantiotropic mesophases (**15** and **16**).

(iv) *Lateral fluoro substitution in ethyl linked materials* When the alkyl chloroterphenyl structure has been modified by an ethyl linkage between phenyl rings, the effect of lateral fluoro substitution on mesomorphic behaviour is similar. Comparing

compounds **21** and **26** or **27** and **30**, it can be seen that a lateral fluoro substituent lowers the melting point by 50–75°C. Increasing the degree of lateral fluoro substitution lowers the clearing point, for example, compounds **22** and **23**.

By comparing compounds **27**, **28**, **29** and **30**, it is shown that the position of the lateral fluoro substituent affects the clearing point, which can again be rationalized in terms of the work of Toyne *et al.* [17]. If the N-I values for compounds **28** and **30**, neither of which has fluoro substitution in an interannular position, are examined, the large increase in N-I which is seen in compound **28** is more than can be readily explained by an increase in alkyl chain length. It is possible, in compound **28** that the fluoro substituent is making a similar contribution to the overall molecular breadth, due to a shielding effect, similar to that observed in 6-*n*-alkoxy-5-substituted-2-naphthoic acids [18].

3.1.3. Effect of inclusion of a *trans* cyclohexyl ring

In compounds **12**, **24**, **25** and **31** the effect of inclusion of a *trans* cyclohexyl ring on the basic structure can be seen. In all cases, the clearing points have been significantly increased and the nematic ranges of the compounds are much widened (100–150°C) by the fourth ring compared with the corresponding fully aromatic three ring materials. Additionally, the inclusion of a *trans*-cyclohexyl ring into the structure has not made the compounds more smectogenic. No enantiotropic smectic phases are observed in compounds **12**, **24**, **25** and **31**.

To summarize, it is clear that ethyl linking groups and lateral fluoro substitution can considerably alter mesomorphic phase behaviour. Subtle changes in the patterns of lateral fluoro substitution in alkyl chloroterphenyl structures also have a large effect, which can be used for optimization of the mesophase behaviour. Also, the inclusion of a *trans* cyclohexane ring into the structure can greatly extend the nematic range of the material.

3.2. Birefringence

Birefringence data for the compounds are shown in tables 1–4: from these the effects of different structural variations can be identified.

3.2.1. Effect of alkyl chain length

Comparing the birefringence values for compounds **2** and **3**, **4** and **5**, **6** and **7**, **10** and **11** or **20** and **21** it is seen that increasing the length of the alkyl chain decreases the birefringence. This effect can largely be attributed to a diluting effect of the increasing size of the alkyl chain on the aromatic content of the system which principally determines the birefringence. However, the values of birefringence for the terminal ethyl chain containing compounds **1** and **19** are anomalously low when compared to their propyl homologues compounds **2** and **20**. This may be due to an 'odd – even' effect in a homologous series, and possibly to small order parameter effects.

3.2.2. Effect of ethyl linking groups

The birefringence of a compound is influenced in part by its optical polarizability. This is mainly due to delocalized electrons not participating in chemical bonds and to π electrons. It is well known [19] that compounds containing benzene rings show higher birefringence values than the corresponding cyclohexane compounds. Also, compounds which are highly conjugated, such as tolanes, have higher than

expected birefringence values compared to non-conjugated systems [19]. It would be expected, therefore, that the incorporation of an ethyl linkage would lower the birefringence value of a conjugated system, such as a terphenyl, due to disruption of the overall conjugation. By comparing compounds **4** and **22**, **6** and **23** or **13** and **20**, the terphenyl structures do exhibit a considerably higher birefringence than the ethyl linked materials. Note however, that these measurements were made using 10 per cent w/w solutions of the guest molecule in a common host at 20°C. Due to the higher N-I of the terphenyl compounds, there will be a small contribution to their higher measured birefringence values arising from the higher N-I values and order parameters of the guest/host mixture.

3.2.3. *Effect of lateral fluoro substitution*

Modification of the basic alkyl chloroterphenyl core with lateral fluoro substitution alters the birefringence value. For example, comparing compounds **2** and **4**, **3** and **5** and **5** and **7**, increasing the number of lateral fluorine atoms decreases the birefringence value. This is also apparent when a comparison of compounds **11**, **14** and **18** is made. In the series of ethyl linked compounds, **22**, **23** and **26** show the same trend. The effect of additional lateral fluorine atoms on birefringence is more pronounced in the alkyl chloroterphenyl structure than in the ethyl linked structures. Comparing compounds **2** and **4**, **11** and **14** or **11** and **18**, the birefringence in alkyl chloroterphenyl structures is decreased by 0.02–0.03 for each additional lateral fluorine atom. However, comparing compounds **22** and **23**, the birefringence in the ethyl linked structures is decreased by only approximately 0.01 for each additional lateral fluorine atom. Although the decrease in absolute birefringence values is greater for the terphenyl materials, the percentage decrease in birefringence caused by increased lateral fluoro substitution is the same for both types of materials.

It is also seen that when the fluoro substituents point towards the polar terminal group (compound **10**), the birefringence is slightly higher than when they point away from the polar terminal group (compound **3**). This may be due to the overall molecular polarizability having been slightly increased.

To summarize, the birefringence of alkyl chloroterphenyls may be influenced by alkyl chain length, presence of an ethyl link, and degree and position of lateral fluoro substitution.

3.3. *Dielectric anisotropy*

Dielectric anisotropy values for the compounds are shown in tables 1–4. From the data in the tables, the following observations can be made. If compounds **11** and **14** are compared, it can be seen that an increase in the degree of ‘forward-pointing’ lateral fluoro substitution causes an increase in the positive dielectric anisotropy. If a comparison of compounds **3** and **5** is made, it can be seen that an increase in the degree of ‘backward-pointing’ lateral fluoro substitution causes a decrease in the positive dielectric anisotropy. This can be rationalized in terms of the contribution of the individual fluorine dipole moments to the overall molecular dipole moment relative to the director.

3.4. *Holding ratio studies*

The test of holding ratio is an electrical capacitive test to determine the chemical and photostability of a liquid crystal. The initial holding ratio value is a measure of the resistivity of the sample and the final values after heat treatment or UV

irradiation demonstrate the stability of the compound. Only the most stable compounds have a holding ratio over 97 per cent after UV and heat treatment. For example, compounds containing a cyano group have holding ratios below 83 per cent after heat treatment. Holding ratio [2–4] data for selected compounds are shown in table 5. The holding ratio values are very high, which demonstrates the good temperature and photochemical stability of the reported mesogens with a terminal chloro substituent. This is in agreement with the work of Wu [6] who also demonstrated the good stability of such materials. They are suitable for use in active matrix display devices.

Table 5. Holding ratio data at (a) 25°C, (b) after 2 h UV irradiation in a Heraeus 'Suntest' apparatus and (c) after heat treatment at 100°C for 15 per cent w/w solutions in the neutral dielectric anisotropy mixture Merck ZLI 3086.

Compound No.	(a) % holding ratio – 25°C	(b) % holding ratio – UV	(c) % holding ratio – 100°C
2	98.6	98.3	98.6
3	98.6	98.6	97.9
6	97.7	98.5	98.4
11	98.4	98.4	98.3
19	98.5	98.0	97.5
20	98.2	98.0	97.5
21	98.2	98.2	97.5

4. Conclusions

By controlling specific molecular design features, it has been possible to synthesize nematogens of moderate melting point that are of potential use in liquid crystal mixtures. These compounds may exhibit very high birefringence values. They also exhibit excellent chemical and photostability. It has also been confirmed that mesophase stability is reduced when an ethyl linkage is present between aromatic rings in the molecule and that the mesomorphic behaviour can be altered by lateral fluoro substitution. In order to optimize the nematogenic character of the materials, lateral 'non-forked' difluoro substitution is required, although the direction of the lateral difluoro substitution is not critical.

The birefringence values can be modified by the presence of an ethyl linkage and the degree of lateral fluoro substitution. The position of lateral difluoro substitution in these materials has a minor effect on the birefringence. The dielectric anisotropy can be controlled by the position and degree of lateral fluoro substitution. However, the optimization of a material property for a given compound invariably has an effect on other properties of that compound. Usually the effect on the other properties is a detrimental one. For example, maximizing the birefringence value by removing the lateral fluoro substituents may remove the nematic phase altogether. The optimum materials must therefore be a compromise of various properties.

Finally, it has been shown that these materials have very good holding ratio characteristics and are suitable for active matrix display applications which require high birefringence materials, for example, 2nd minimum TN/TFT or PDLC/TFT.

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