Nematogenic laterally fluorinated biphenyls with polar terminal groups

S. Greenfield[a]; D. Coates[a]; M. Goulding[a]; R. Clemitson[a]

[a] Merck Ltd., Poole, England

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by S. GREENFIELD*, D. COATES, M. GOULDING and R. CLEMITSON

Merck Ltd., West Quay Road, Poole, BH15 1HX, England

The physical properties are reported for a series of positive dielectric anisotropy ($\Delta\varepsilon$) alkylbiphenyls possessing a halogen-containing terminal group and incorporating varying degrees of lateral fluorination. The nematic range and dielectric and optical anisotropies can be varied by the appropriate choice of terminal group and extent of lateral substitution. These materials possess greater stability than the corresponding cyano compounds and are suitable for use in applications that require high stability.

1. Introduction

Liquid crystal materials with a terminal cyano group have for many years proved to be essential positive dielectric anisotropy ($\Delta\varepsilon$) components of mixtures for simple liquid crystal displays. In recent years however, there has been a growing interest in complex displays capable of greater information content, of which the super-twisted nematic (STN) and the active matrix (AM) are commercially the most important. These have much more stringent materials requirements than simple twisted nematic (TN) displays, demanding, for example, low viscosity (STN) and very high stability and high resistivity (AM), while retaining a sufficiently high $\Delta\varepsilon$ to achieve low operational voltages. Such parameters cannot be met solely with cyano-based compounds which tend to have a relatively high viscosity, high affinity for ionic impurities (leading to low resistivity) and inadequate chemical and photochemical stability [1].

To address this problem, new polar materials with terminal groups other than cyano have recently been developed. Fluorine [2,3] and fluorinated groups [4–9] have been widely studied since the high electronegativity of the fluorine atom gives rise to a strong dipole along the molecular axis, a factor which contributes to a moderately positive $\Delta\varepsilon$ in these compounds. In addition the stability of these groups has been shown to be adequate for AM applications [2,8,10]. We have previously demonstrated that a terminal chloro substituent attached to a number of mesogenic cores also produces materials with a positive $\Delta\varepsilon$, but with higher nematic phase stability and birefringence than fluorinated terminal groups provide [11]. Such compounds are also potentially useful for display applications [12].

We now report the results of a comparative study on the effect of various halogen-based polar end groups on the physical properties of trans-4-n-alkylcyclohexylethylbiphenyls. We have also investigated the effect of lateral fluorination in the same system, and by combining the two features sought to optimise the properties of these materials.

2. Experimental

The compounds were prepared by the standard synthetic techniques outlined in the scheme and purified by column chromatography on silica gel, eluting with petroleum spirit (b.p. 40–60°). The products were then recrystallized to > 99·5 per cent purity as determined by reverse phase HPLC using a Hewlett–Packard 1090 instrument with diode array detector.

Phase transition temperatures were measured using a Du Pont 1090 differential scanning calorimeter and by polarising optical microscopy using a Mettler FP52 hot stage to control the temperature of the sample. Physical measurements (dielectric anisotropy and birefringence) were made on a 10% w/w solution of the test compound in a chemically related mixture of medium dielectric anisotropy ($\Delta\varepsilon$) at 20°C, and values for the pure materials obtained by extrapolation. 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 capacitative method at 20°C and 1 kHz.

Holding ratio measurements were performed on 15% w/w solutions of the test compound in a chemically stable mixture (Merck ZLI 3086). 100 mV was applied to the thin film of the liquid crystal solution under test in a glass cell. 100 ms after the field had been removed, the charge remaining across the cell was remeasured, and the

*Author for correspondence.
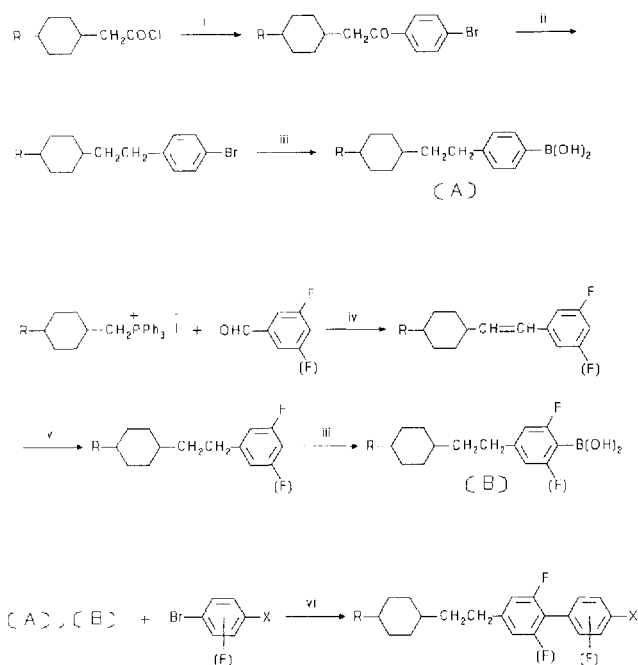
Scheme. The general synthetic route to the *trans*-4-alkyl-cyclohexylethylbiphenyls **1–36**. Reagents: (i) AlCl₃, CH₂Cl₂, C₆H₅Br; (ii) N₂H₄.H₂O, KOH, HOCH₂CH₂OH; (iii) *n*-BuLi, THF (− 70°)/B(OCH₃)₃/H⁺; (iv) *n*-BuLi, THF; (v) Pd-charcoal, H₂; (vi) Toluene, ethanol, 2 M Na₂CO₃, Pd(PPh₃)₄.

final value 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.

Molecular energy versus interannular torsion angle calculations were performed using NEMESIS V1·1, PC based version (available from Oxford Molecular Ltd). Molecular models were constructed and then iteratively calculated to a minimum molecular energy using the COSMIC [13] optimized energy calculation. The molecular energy versus interannular torsion angle calculations were started with the benzene rings of the biphenyl system in a co-planar conformation and energy values were calculated for 1° incremental rotations.

3. Results and discussion

A total of 36 compounds has been prepared with either cyano, chloro, fluoro, trifluoromethoxy or trifluoromethyl terminal groups, and varying degrees of lateral fluorination. The transition temperatures and physical properties of these materials are given in tables 1–6 and the effects of both terminal group and lateral fluorination are discussed below.

Table 1. Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-propylcyclohexylethyl-biphenyls with a terminal fluoro group. ( ) relates to a monotropic transition. In this and subsequent tables: C = crystal; N = nematic; I = isotropic liquid.
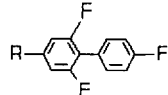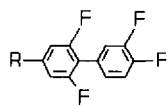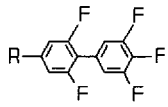
Compound	C–N/I	N–I	Δ*n*	Δε
R = C₃H₇—⬡—C₂H₄				
1	76·7	126·7	0·132	3·6
2	61·1	92·6	0·130	6·3
3	62·0	93·5	0·132	3·0
4	47·0	88·7	0·137	5·1
5	38·7	61·9	0·130	8·6
6	91·8	(57·0)	0·112	3·7
7	102·0	(67·0)	0·102	4·7
8	37·4	(34·0)	0·115	12·9
9	83·0	(36·1)	0·091	3·9

3.1. *Nematic phase range*

3.1.1. *Effect of terminal group*

In figure 1 the clearing points of compounds **1–36** are plotted against the total number of lateral fluorine substituents and according to type of polar terminal group. The relative ability of the cyano, chloro and fluoro terminal groups to stabilizing the nematic phase thermally is seen to follow the usual order (CN > Cl > F) [14]. The

Table 2. Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-pentylcyclohexylethyl-biphenyls with a terminal fluoro group. ( ) relates to a monotropic transition.

Compound	C–N/I	N–I	Δn	$\Delta\varepsilon$
R = C₅H₁₁—⬡—C₂H₄				
10	91·0	(67·6)	0·113	6·1
11	40·0	46·6	0·095	8·6
12	65·5	(28·8)	0·080	14·9
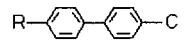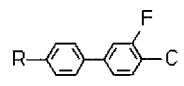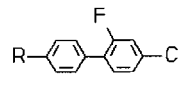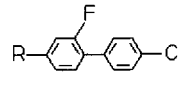
trifluoromethoxy group behaves very similarly to a terminal fluorine, while the trifluoromethyl group is the least nematogenic.

3.1.2. *Effect of lateral fluorination*

For a given terminal group, the clearing point shows an approximately linear decrease with increasing lateral fluorination. Each additional fluorine depresses the clearing point by between 20°C and 35°C and the effect is cumulative, although it tends to level off at high levels of substitution. Osman has shown that in the case of lateral mono-substitution, the clearing point decreases as the van der Waals volume of the substituent increases, the points falling on a smoothly diverging curve. [15]. In the present case, the total van der Waals volume of the substituents increases linearly with each successive replacement of a hydrogen atom by the larger fluorine and the clearing points are found to decrease in a similar fashion. The tendency for the decrease to level off at high levels of substitution is to be expected, since the later fluorines to be added can be partially accommodated within the existing cylinder of rotation of the molecule and do not therefore cause as large a perturbation. An additive effe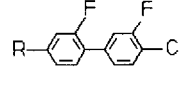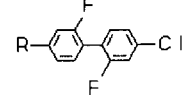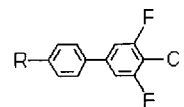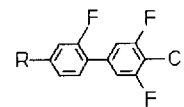ct of lateral substitution on the stability of the nematic phase has also previously been demonstrated in a series of 4,4′-di-(*p*-alkoxybenzylideneamino)biphenyls [16].

It is noticeable that the effect of the position of lateral fluorination on the clearing point is small compared to the degree of lateral fluorination. For example, in the two series of laterally mono-fluorinated compounds **2**, **3**, **4**
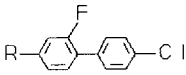
Table 3. Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-propylcyclohexylethyl-biphenyls with a terminal chloro group.

Compound	C–N	N–I	Δn	$\Delta\varepsilon$
R = C₃H₇—⬡—C₂H₄				
13	101·2	158·2	0·169	3·5
14	64·7	120·6	0·170	5·6
15	46·7	116·0	0·178	4·3
16	72·1	120·0	0·170	5·3
17	55·0	96·6	0·168	9·0
18	38·3	79·7	0·150	4·3
19	61·2	87·3	0·166	12·2
20	47·2	72·0	0·151	13·4

(with a terminal fluorine) and **14**, **15**, **16** (with a terminal chlorine), the clearing point varies by less than 5°C. In the corresponding difluorinated compounds, the spread of clearing points is higher, mainly due to the particularly low values for compounds **6** and **18**. This is clearly seen by comparing **6**, **7** and **10**, all of which have two lateral fluorine substituents between the biphenyl rings, but in **7** and **10** the substituents are located on the same ring (a 'forked' 2,6-disubstitution pattern); however, in **6** they are on different rings (2,2′-disubstitution). This latter arrangement results in a clearing point some 10°C lower than **7** and **10** (which have nearly identical clearing points).

As well as causing an increase in molecular breadth,

Table 4.   Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-pentylcyclohexylethyl-biphenyls with a terminal chloro group. ( ) relates to a monotropic transition.

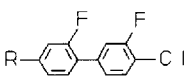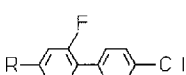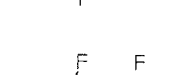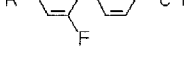| Compound	C–N/I	N–I	Δn	$\Delta \varepsilon$
R $= C_5H_{11}$—◯—C_2H_4				
21 R—⬡F—⬡—C l	65·0	122·8	0·169	6·8
22 R—⬡F—⬡F—C l	50·5	98·7	0·155	10·3
23 R—⬡F—⬡F—C l	54·0	91·0	0·145	7·6
24 R—⬡FF—⬡F—C l	47·2	74·5	0·128	8·8
25 R—⬡FF—⬡FF—C l	66·0	(60·8)	0·105	14·3

lateral substitution in biphenyls can also increase the interannular torsion angle leading to a reduction in the conjugation between the two rings and a lower molecular polarizability [17]. This reduces the attractive intermolecular forces and results in a lowering of the clearing point. This rationale has been used to explain the effect of fluorine substitution on the transition temperatures of terphenyls [18]. The influence of lateral fluorine substitution on the interannular torsion angle is illustrated in figure 2 for the terminal chloro compounds **13**, **16**, **18** and **23**. These plots were generated using NEMESIS molecular modelling software and were obtained by first calculating the overall minimum energy conformation for each structure and then plotting the energy as a function of increasing torsion angle. Although figure 2 relates only to isolated molecules, and so must be treated with caution, a number of interesting observations can be made.

For all four compounds, the minimum energy is calculated to occur at a torsion angle of 43 ± 1° and in each case the energy is similar. For compound **18**, there are two distinct minima, one for the *transoid* conformation in which the fluorines are located on opposite sides of the molecular and one for the *cisoid*, where they are on the same side. The *transoid* minimum has a slightly lower

energy than the *cisoid* and occurs at a smaller torsion angle, 44° compared to 49°. Previous calculations based on the van der Waals radii of the substituents have suggested torsion angles of 54° for 2,2′-difluorinated biphenyls and 41° for 2-monofluorinated biphenyls [19], whereas NMR studies on 2,6-difluorinated biphenyls have indicated an angle of 51°C [20]

While generally the plots are all very similar, they diverge as the planar conformations (torsion angle = 0° and 180°) are approached and the steric interactions between the substituents become more pronounced. The energy of the planar conformations increases with the increasing degree of substitution in the order **13** < **16** < **23** ≈ **18** *trans* ≪ **18** *cis*. The very close similarity of the curves for compound **23** and compound **18** in the *transoid* conformation would lead us to anticipate near identical clearing points for the two materials. (Compound **23** might even be expected to have the lower clearing point due to the greater average molecular breadth resulting from the two fluorine substituents being fixed 180° apart). In fact **18** has a clearing point some 11° lower than **23** which can be accounted for if it is the *cisoid* conformation

Table 5.   Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-alkylcyclohexylethyl biphenyls with a terminal trifluoromethyl/trifluoromethoxy group. ( ) relates to a monotropic transition.
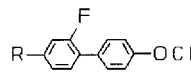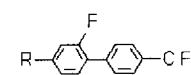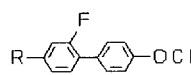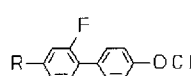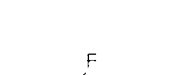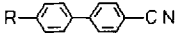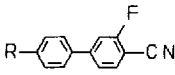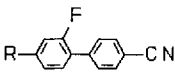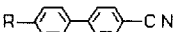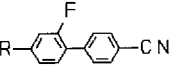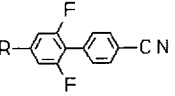
Compound	C–N/I	N–I	δn	$\Delta \varepsilon$
R $= C_3H_7$—◯—C_2H_4				
26 R—⬡F—⬡—O C F$_3$	36·0	89·1	0·130	6·6
27 R—⬡F—⬡—C F$_3$	80·4	(68·4)	0·138	12·3
R $= C_5H_{11}$—◯—C_2H_4				
28 R—⬡F—⬡—O C F$_3$	35·9	93·0	0·127	9·5
29 R—⬡FF—⬡—O C F$_3$	49·0	65·8	0·086	9·1
30 R—⬡FF—⬡—C F$_3$	93·0	(48·0)	0·112	11·4

Table 6. Transition temperatures (°C) and physical properties for laterally fluorinated *trans*-4-alkylcyclohexylethyl-biphenyls with a terminal cyano group. S_A = smectic A.

Compound	C–N	N–I	Δn	$\Delta \varepsilon$
R = C₃H₇—◯—C₂H₄				
31 † R—◯—◯—CN	74·0	188·0	—	—
32 R—◯—◯(F)—CN	74·6	153·0	0·21	16·6
33 † R—◯(F)—◯—CN	63·1	159·7	0·21	20·0
R = C₅H₁₁—◯—C₂H₄				
34 † R—◯—◯—CN	C 79 S_A 87 N	184·0	0·23	24·0
35 † R—◯(F)—◯—CN	71·0	158·0	0·18	19·3
36 R—◯(F,F)—◯—CN	123·0	131·0	0·17	22·4

† Compounds previously reported in [25].

which is actually adopted in the nematic phase, in line with the findings of a previous study of 2,2′-disubstituted biphenyls [16]. In the *cisoid* conformation the energy minimum occurs at a larger torsion angle, reducing the conjugation between the aromatic rings and hence the molecular polarizability, so leading to the lower observed clearing point.

Moreover, in the nematic phase, intermolecular forces may result in the biphenyl ring system being forced towards a more planar conformation, the torsion angle being as small as 20° in the absence of lateral substituents [19]. Free rotation about the interannular bond probably does not occur and the interannular angle adopted is a balance between the repulsive forces between the substituents and the residual forces from the crystalline state tending to make the system coplanar [19, 21]. For compound 18, the very steeply rising energy as the *cis*-planar conformation is approached means that any reduction of the torsion angle in the nematic phase will be less than is the case for 23, so accentuating the difference.

Changing the terminal alkyl group from propyl to pentyl
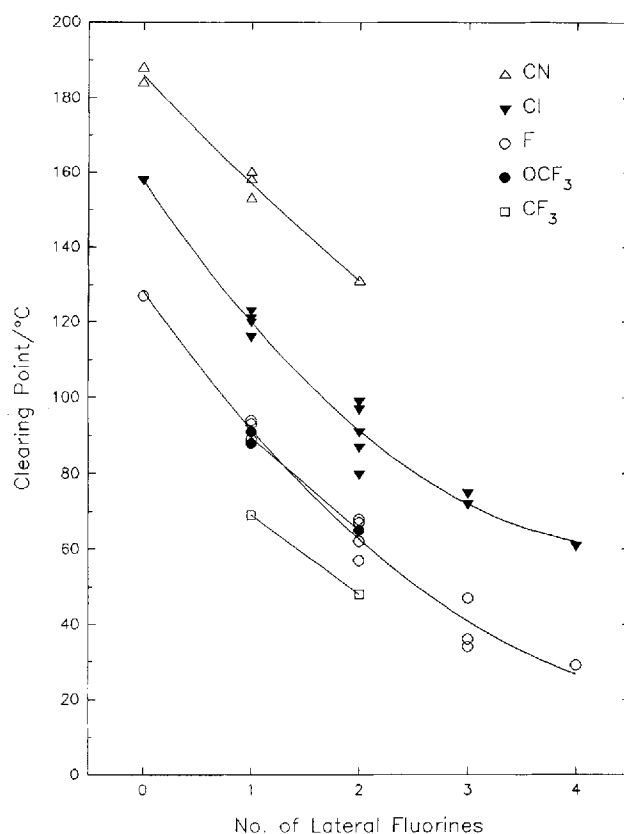
Figure 1. The dependence of the clearing point on the number of lateral fluorine substituents for the *trans*-4-alkylcyclo-hexylethylbiphenyls 1–36.

increases the clearing point by only 2–3°C (for example, 16 and 21, 17 and 22). Accordingly, for a given terminal group, the clearing point is determined firstly by the
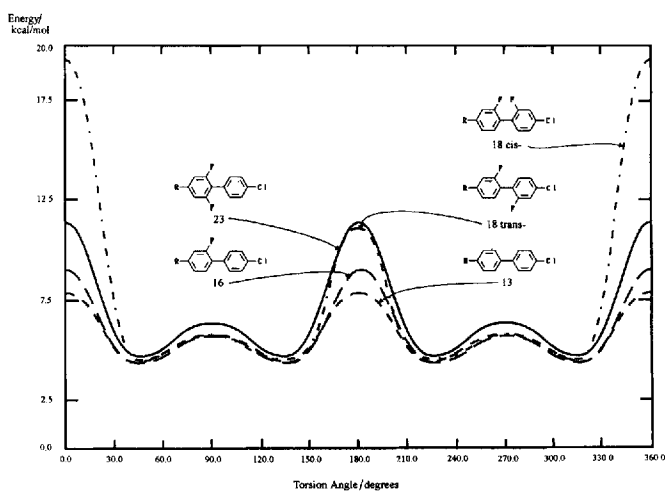
Figure 2. The calculated molecular energy (kcal mol⁻¹) as a function of the interannular torsion angle for components 13, 16, 18 and 23.

number of lateral fluorine substituents and secondly by their position, the terminal alkyl chain length being of minor importance.

Melting points generally decrease with increasing fluorination, although some compounds (**10, 12, 25, 30, 36**) exhibit anomalously high values. These are all materials with a symmetrical pattern of substitution which can be presumed to aid efficient packing within the crystal lattice. As far as terminal groups are concerned, the fluoro and OCF_3 compounds have the lowest melting points, and the cyano and CF_3 the highest.

3.2. Birefringence (Δn)

3.2.1. Effect of terminal group

As expected, the cyano group promotes the highest birefringence due to the high polarizability of the carbon–nitrogen triple bond, while the three fluorinated groups give rise to very similar low values. Chlorine is intermediate between the two extremes and provides materials of moderately high Δn.

3.2.2. Effect of lateral fluorination

Generally birefringence falls with increasing fluorination, which may be attributed to a decrease in density resulting from the increased molecular breadth. However, there is a significant effect associated with difluoro substitution between the rings of the biphenyl, leading to a substantial decrease in Δn. Compare, for example, the difluorinated chlorobiphenyls **17, 18, 19** and **23**, where compounds **18** and **23** which have interannular substitution have a considerably lower Δn than compounds **17** and **19**. Similarly in the series of laterally difluorinated fluorobiphenyls, **6, 7** and **10** exhibit a lower Δn than compound **5**, where only one of the substituents is between the rings.

The presence of the interannular difluoro substitution also magnifies the effect of adding additional fluorines into the end ring. Compare the large fall in Δn for the 'forked' difluoro series **23, 24, 25** with the much smaller decrease for the equivalent monofluoro series **16, 17, 20** and the negligible change in **13, 14, 19** where there are no fluorines between the biphenyl rings. This pattern is also seen in the series of compounds with a terminal fluoro group.

Interestingly, in a related study of lateral fluorination in chloroterphenyls, this interannular disubstitution effect is not seen [22]. This may be because in the larger, more highly polarizable terphenyl system, the effect of the substituents on only one of the two interannular bonds has a proportionately smaller effect. It should be noted that this observed effect does not merely arise from the birefringence being measured at a constant absolute temperature, rather than at the same reduced temperature. Thus, for example, compounds **20** and **24** have very similar clearing

points, yet the influence of the interannular fluorines on the birefringence is clearly seen. It must be stressed however, that the birefringence values discussed above were obtained by extrapolation of results from measurements made on mixtures in a nematic host and therefore minor discrepancies may result from such factors as variation in clearing point or non-linearity of mixing. Such measurements are useful however for comparing the relative effect of each compound in a mixture, but should not be taken as absolute values which can be precisely related to the molecular structure. A similar caveat also applies to the dielectric measurements discussed below.

3.3. Dielectric anisotropy $\Delta\varepsilon$

3.3.1. Effect of terminal group

The influence of the terminal group on dielectric anisotropy can be seen in the series of monofluorinated compounds **4, 16, 26, 27** and **33**. As expected the cyano group gives rise to the largest dielectric anisotropy $(\Delta\varepsilon \approx 20)$, followed by CF_3 $(\Delta\varepsilon \approx 12)$ and then OCF_3 $(\Delta\varepsilon \approx 6)$. Significantly, chlorine as a terminal group has much the same effect as fluorine $(\Delta\varepsilon \approx 5)$, despite the greater electronegativity of the latter, but in line with the similar bond dipole moments [6].

3.3.2. Effect of lateral fluorination

Generally, increasing the number of lateral fluorine substituents pointing in the same direction as the polar terminal group increases the dielectric anisotropy, although the position of substitution is important. Thus, introducing the fluorine *ortho* to the polar group is the most efficient way of increasing $\Delta\varepsilon$, and again the interannular 'forked' 2,6-difluoro substitution is found to be not very beneficial.

For example, considering the chloro and fluoro biphenyls, the introduction of the first fluorine (for example, compounds **2, 4, 14, 16**) increases $\Delta\varepsilon$ by approximately 2–3 compared to the unsubstituted compounds, while the additional effect of a second fluorine in the other ring (i.e., compounds **5, 17**) shows a slightly larger increase, suggesting some cooperative interactions between the dipoles. If however the second fluorine is placed in the same ring as the first, then the picture is very different. Forked difluoro substitution between the rings (compounds **10** and **23**) leads to a much lower $\Delta\varepsilon$ than forked difluoro substitution in the terminal ring (compound **19**). In the latter case, where fluorine substituents occupy both sites *ortho* to the terminal group, a particularly high value of $\Delta\varepsilon$ can be obtained. Comparing, for example, **19** and **23**, in both compounds the symmetrical disposition of the fluorines with respect to the long axis of the molecule minimises their contribution to $\varepsilon_\perp$. The large observed difference in $\Delta\varepsilon$ can then be attributed to a

synergistic interaction between the terminal group and the fluorines which is maximised in the case of **19**, but hindered in **23**, possibly because of an increase in the interannular torsion angle reducing the effect through bond interactions, or because of the greater spatial distance between fluorines and terminal group. Previous studies on the effect of lateral fluorination on $\Delta\varepsilon$ in cyanobiphenyls have also shown that the highest dipole moment is obtained when a fluoro substituent is *ortho* to the cyano group [23].

As would be expected, the introduction of a lateral fluorine substituent pointing away from the terminal group tends to reduce $\Delta\varepsilon$ (compare **1**, **3**, **4**), although the effect is rather small. Thus, compound **7** with two 'backward' pointing substituents has a dielectric anisotropy only slightly less than compound **10** which has both substituents 'forward' pointing. However, a combination of substituents pointing in both directions, as in **6**, leads to a lower $\Delta\varepsilon$, again possibly due to excessive disruption of the biphenyl coplanarity.

Progressing to tri- and tetra-fluoro substitution, the same factors can be seen to operate; increasing the extent of 'forward' pointing substitution increases $\Delta\varepsilon$, with the largest effects being observed *ortho* to the terminal group. This can lead to multisubstituted compounds with high dielectric anisotropies for example, **12** and **25**.

3.4. *Stability*

An essential requirement of liquid crystal materials destined for use in active matrix addressed devices is a high resistivity, since a pixel must be capable of retaining the applied voltage from one addressing cycle to the next. Therefore the liquid crystal must initially be free of ionic impurities and also not undergo any degradation due to the action of heat or UV light during the lifetime of the display. The ability of a particular material to meet these criteria is conveniently measured as the voltage holding ratio, which is defined as the ratio between the voltage remaining on a pixel after 100 ms and the initial applied voltage [10].

It has been shown that materials containing cyano groups, such as cyanobiphenyls, do not possess sufficient stability for AM applications. The difficulty in removing ionic impurities from such polar compounds leads to a low initial holding ratio value which further degrades over time under the influence of heat or UV light [1, 10]. On the other hand, materials containing fluorinated terminal groups (–F, –CF$_3$, –OCF$_3$) exhibit much higher stabilities and have been used as components of mixtures for AM use [1, 8, 24]. However, the stability of chlorine containing materials has not been widely studied.

In table 7 the holding ratio measurements are given for a number of biphenyls with a terminal chloro or fluoro group. It can be seen that the chloro materials show a stability comparable with that of the terminal fluoro

Table 7. Temperature dependence and UV stability of the holding ratio for *trans*-4-alkylcyclohexylethylbiphenyls with a terminal chloro or fluoro group.

Compound	Terminal group	At room temperature	At 100°	After 2 h UV
		Holding ratio/per cent		
5	F	98·5	98·5	95·5
16	Cl	98·0	97·3	97·6
17	Cl	98·0	95·5	—
19	Cl	98·5	—	96·5

compound, and that they are stable to the action of heat and light. Terminal chloro compounds are therefore ideally suited for applications which require a higher birefringence than can be obtained with fluorine containing groups and where a high degree of stability is important.

4. Conclusions

Cyclohexylethylbiphenyls with halogen-containing terminal groups show a number of advantages over the corresponding cyano compounds, particularly increased stability and lower viscosity, and while the nematic range and dielectric anisotropy are not as great, they are still sufficient for use in many modern applications. By combining lateral fluorination with an appropriate choice of terminal group, it is possible to fine tune the physical properties in order to achieve the values required for a particular application. The compounds described here exhibit clearing points in the range 28–158°, birefringences between 0·08 and 0·17, and dielectric anisotropies from 3 to 14. However, it is necessary to strike the correct balance, as using lateral fluorination to improve one physical property may have a detrimental effect on another. For example, multiple fluorination allows high dielectric anisotropies to be realised, but at the expense of a greatly reduced clearing point.

In many cases, optimum properties are achieved with 'forward-pointing' mono- or di-fluorination, as in for example the chlorobiphenyls **14**, **16** and **17** which offer a useful nematic range with a moderate dielectric anisotropy and high birefringence. These are useful components of liquid crystal mixtures for applications which require a combination of high birefringence and high stability, for example, TFT/PDLC displays [26]. On the other hand, a terminal fluoro or trifluoromethoxy group can provide low melting point, positive dielectric anisotropy materials with low viscosities that are potentially suited for use in STN displays (for example, compounds **5** and **26**).

Generally, the interannular 'forked' 2,6-difluorination was found to be not particularly advantageous in these

materials. The symmetrical substitution pattern tends to give high melting points and values of dielectric anisotropy that are lower than can be obtained with the fluorines in other positions. While a single 'backward-pointing' interannular fluorine can be useful (for example, compound 15), the combination of two opposed interannular fluorines excessively restricts free rotation about the interannular bond, so reducing the polarizability of the molecule and leading to particularly low values for the clearing point and the optical and dielectric anisotropies.

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References

[1] RIEGER, B., BÖHM, E., and WEBER, G., 1989, *18. Freiburger Arbeitstagung Flüssigkristalle*, Conference Proceedings.

[2] GOTO, Y., OGAWA, T., SAWADA, S., and SUGIMORI, S., 1991, *Molec. Crystals liq. Crystals*, **209**, 1.

[3] TAKATSU, H., TAKEUCHI, K., SASAKI, M., OHNISHI, H., and SCHADT, M., 1990, paper presented at the *13th International Liquid Crystal Conference*, Vancouver, Canada, 22–27 July.

[4] FINKENZELLER, U., KURMEIER, H. A., and POETSCH, E., 1989, *18. Freiburger Arbeitstagung Flüssigkristalle*, Conference Proceedings.

[5] COATES, D., and GRAY, G. W., 1976, *J. chem. Soc. Perkin Trans. 2*, 300.

[6] BARTMANN, E., DORSCH, D., FINKENZELLER, U., KURMEIER, H. A., and POETSCH, E., 1990, *19. Freiburger Arbeitstagung Flüssigkristalle*, Conference Proceedings.

[7] BARTMANN, E., FINKENZELLER, U., KURMEIER, H. A., POETSCH, E., REIFFENRATH, V., and SCHEUBLE, B. S., 1990. paper presented at the *13th International Liquid Crystal Conference*, Vancouver, Canada, 22–27 July.

[8] PLACH, H. J., RIEGER, B., POETSCH, E., and REIFFENRATH, V., 1990, *Eurodisplay '90*, Amsterdam, p. 136.

[9] LIANG, J. C., and KUMAR, S., 1987, *Molec. Crystals liq. Crystals*, **142**, 77.

[10] RIEGER, B, POETSCH, E., and REIFFENRATH, V., 1990, *19. Freiburger Arbeitstagung Flüssigkristalle*, Conference Proceedings.

[11] COATES, D., GREENFIELD, S., SAGE, I., and SMITH, G., 1990, paper presented at the *13th International Liquid Conference*, Vancouver, Canada, 22–27 July.

[12] WU, S., COATES, D., and BARTMANN, E., 1991, *Liq. Crystals*, **10**, 635.

[13] (a) VINTER, J. G., DAVIS, A., and SAUNDERS, M. R., 1987, *J. comput. aided molec. Design*, **1**, 31. (b) ABRAHAM, R. J., and SMITH, P. E., 1989, *J. comput. aided molec. Design*, **3**, 175.

[14] GRAY, G. W., and WINSOR, P. A., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 1 (Ellis Horwood, Chichester, England).

[15] OSMAN, M. A., 1985, *Molec. Crystals liq. Crystals*, **128**, 45.

[16] BYRON, D. J., GRAY, G. W., and WORRALL, B. M., 1965, *J. chem. Soc.*, p. 3706.

[17] AVERYANOV, E. M., 1987, *Liq. Crystals*, **2**, 491.

[18] GRAY, G. W., HIRD, M., and TOYNE, K. J., 1991, *Molec. Crystals liq. Crystals*, **204**, 43.

[19] BRANCH, S. J., BYRON, D. J., GRAY, G. W., IBBOTSON, A., and WORRALL, B. M., 1964, *J. chem. Soc.*, p. 3279.

[20] FIELD, D., and STERNHELL, S., 1981, *J. Am. chem. Soc.*, **103**, 738.

[21] BYRON, D. J., GRAY, G. W., IBBOTSON, A., and WORRALL, B. M., 1963, *J. chem. Soc.*, p. 2246.

[22] GOULDING, M, J., GREENFIELD, S., COATES, D., and CLEMITSON, R., 1993, *Liq. Crystals*, **14**, 1397.

[23] McDONNELL, D. G., RAYNES, E. P., and SMITH, R. A., 1989, *Liq. Crystals*, **6**, 515.

[24] PLACH, H. J., WEBER, G., and RIEGER, B., 1990, presented at the *SID International Symposium and Exhibition '90*, Las Vegas, *SID 90 Digest*, p. 91.

[25] FEARON, J. E., GRAY, G. W., IFILL, A. D., and TOYNE, K. J., 1985, *Molec. Crystals liq. Crystals*, **124**, 89.

[26] COATES, D., GREENFIELD, S., GOULDING, M. J., BROWN, E., and NOLAN, P., 1993, *IS&T/SPIE Symposium on Electric Imaging Science and Technology*, San Jose, U.S.A., 31 January–4 February, paper 1911-01.