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The synthesis and transition temperatures of some 4′-alkyl- and 4′-alkoxy-4-cyano-3-fluorobiphenyls

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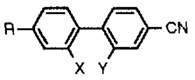
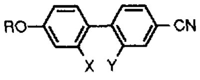
The preparation of 4′-alkyl- and 4′-alkoxy-4-cyano-3-fluorobiphenyls by four different procedures is described and discussed; the best method involves palladium(0)-catalysed coupling of arylboronic acids and 4-bromo-(or 4-iodo-)-2-fluorobenzonitrile. The effects on transition temperatures of fluoro substitution *ortho* to the terminal cyano group in biphenyls are compared with the effects in other terminal cyano compounds and in mesogens without a terminal cyano group. The effect of the *ortho* fluoro substituent in 4-cyanobiphenyls is particularly large and is probably due to the severe disruption of antiparallel correlations; the depressions of the smectic A and nematic phase stabilities are similar which suggests that, as for compounds with alkyl or alkoxy terminal groups, the fluoro substituent at the 3-position has a tendency to enhance smectic character, but this is offset by the molecular broadening it causes.

1. Introduction

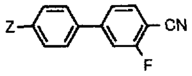
4′-Alkyl- and 4′-alkoxy-4-cyanobiphenyls (**1** and **2**, respectively) and the related terphenyl systems have, over many years, proved to be extremely useful materials for twisted nematic electro-optic display devices [1, 2] and for electrically-addressed smectic A storage devices [3]. The major requirements which are met by such compounds for use in twisted nematic and related devices is that they have acceptable nematic ranges for room temperature displays, high birefringence (Δn) and high positive dielectric anisotropy ($\Delta\varepsilon$) values. So long as other physical properties were not adversely affected, compounds of even higher positive $\Delta\varepsilon$ values would be most useful so that lower operating voltages could be used. One way of seeking such an improvement is by considering appropriate fluoro-substituted cyano systems in the hope that the small, polar fluoro-substituent will not depress the mesophase thermal stabilities too severely and that its dipole will increase the overall molecular dipole and possibly reduce the antiparallel correlations present in terminal cyano systems. We have previously reported our work on 4′-alkyl and 4′-alkoxy-4-cyanobiphenyls, and related systems, with a 2- or 2′-fluoro-substituent (compounds **3**, **5** and **4**, **6** respectively) [4] and the physical properties of some of these compounds in mixtures has been described [5]. When the dipole of the fluoro-substituent reinforces the dipole of the cyano group (compounds **5** and **6**) then higher values of $\Delta\varepsilon$ were obtained and the depression in T_{N-I} values caused by fluoro-substitution was 35–41°C. Conversely, when the dipoles of fluoro-substituents and cyano groups are partially opposed (compounds **3** and **4**), then decreased values of $\Delta\varepsilon$ were obtained, but the depression in T_{N-I} values arising from fluoro-substitution was only 13–20°C. In each of these cases one would expect the fluoro-substituent to cause an increased twist about the inter-annular biphenyl bond to about the same extent [6] but the effects on antiparallel correlation would probably be different.



1, X = Y = H
3, X = H, Y = F
5, X = F, Y = H



2, X = Y = H
4, X = H, Y = F
6, X = F, Y = H



7, Z = R
8, Z = RO

We now report the preparation of some 4′-alkyl- and 4′-alkoxy-3-fluoro-4-cyanobiphenyls (compounds **7** and **8**) and we compare the liquid crystalline behaviour of these compounds and compounds **1**, **3**, **5** and **2**, **4**, **6**. For compounds **7** and **8**, the twist about the inter-annular biphenyl bond should not be affected by fluoro-substitution and, on this basis, transition temperatures should be considerably higher than for compounds **3**, **5** and **4**, **6**. However, the fluoro-substituent is *ortho* to the cyano group and it should give an increased longitudinal dipole, and hence higher positive $\Delta\varepsilon$ values; moreover, such fluoro-substitution should have a more dramatic influence on antiparallel correlations and mesophase stabilities because of its proximity to the cyano group. A few short chain members and a longer chain compound in each case were chosen in order to reveal the trends in transition temperatures within the homologous series and to determine the effect of

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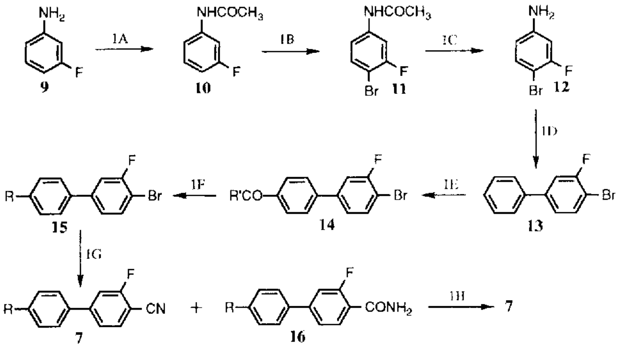
fluoro-substitution *ortho* to the cyano group on parent compounds which show nematic or smectic phases.

2. Discussion

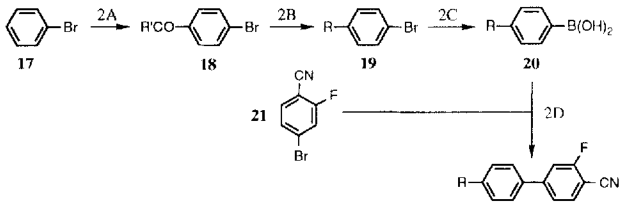
Several possible routes were tested for the synthesis of compounds **7** and **8**. The first, shown in scheme 1, is based on the preparation of compound **13** from which the alkyl series could be obtained by the sequence of Friedel-Crafts acylation, reduction and cyanation. The second route, shown in Scheme 2, uses palladium(0)-catalysed boronic acid couplings with compound **21** or **24** to give the alkyl series of compounds. This route could also have been used for the alkoxy series with 4-alkoxyphenylboronic acids, but rather than carry out separate couplings for each alkoxy compound, 4-methoxyphenylboronic acid (**26**) was used to obtain **8a** (see scheme 3; **a–e** correspond to the terminal groups in the table), which was demethylated and then alkylated to give specific alkoxy compounds. Some examples of both the alkyl and alkoxy series were also prepared by arylzinc chloride couplings with compound **24** as shown in scheme 4. All the methods presented here for the preparation of compounds **7** and **8** were satisfactory in most cases, but the following problems were noted in two instances. Cyanation of compound **15c** (*R* = pentyl) readily gave the amide **16c** as a byproduct if the workup procedure using iron(II) sulphate and 18 per cent hydrochloric acid was prolonged. The preparation of compound **7c** by the arylzinc chloride procedure shown in scheme 4 sometimes gave a small amount of an impurity which was extremely difficult to isolate from the low melting nitrile. Analysis of the crude product by GC/MS and by ^{1}H NMR spectroscopy with a chemical shift reagent indicated that 3-butyl-4-cyano-4′-pentylbiphenyl had been produced and this presumably arose by reaction of a slight excess of butyllithium with compound **7c** which had been produced by the organozinc coupling. For these specific reasons and for the general reasons given in [7], the best method of preparation of compounds **7** and **8** uses the coupling of arylboronic acids to aryl bromides/iodides.

Lateral fluoro substitution, because of the small size of the substituent and its high electronegativity, is widely used in the design of liquid crystal materials to achieve a variety of physical effects and (i) depression of melting point, (ii) suppression of smectic phase stability, (iii) creation of molecules with $-\Delta\varepsilon$ values, or (iv) with enhanced $+\Delta\varepsilon$ values, is possible. Successful achievement of points (i)–(iii) is seen, for example in [8–13] and point (iv) is demonstrated in [14, 15]. A cyano group ranks highly in the order of efficiency of terminal groups for generating mesophases, particularly because it is capable of causing antiparallel associations of molecules which enhance geometrical anisotropy. A fluoro-substituent placed *ortho* to a terminal cyano group with the intention of disrupting antiparallel associations and giving



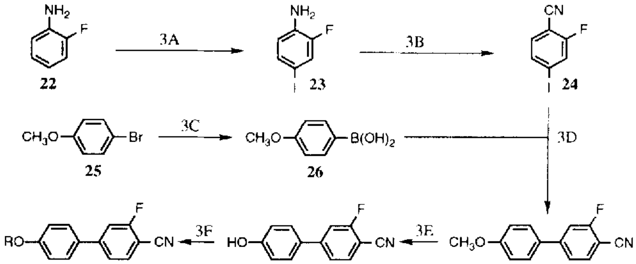
1A...CH_3CO_2H, $(CH_3CO)_2O$
1B...NBS, CCl_4
1C...conc. HCl, EtOH aq.
1D...$C_5H_{11}ONO$, C_6H_6
1E...R′COCl, $AlCl_3$, $Cl_2CHCHCl_2$
1F...Et_3SiH, CF_3CO_2H
1G...CuCN, *N*-methylpyrrolidin-2-one, 185 °C
1H...$SOCl_2$, DMF

Scheme 1



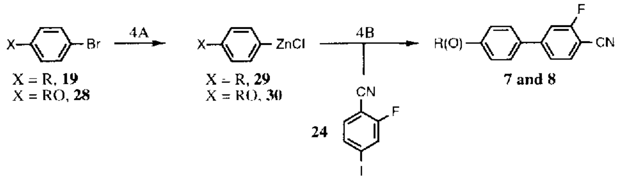
2A...R′COCl, $AlCl_3$
2B...$N_2H_4.H_2O$, KOH, diethylene glycol
2C...**Either** (i) Mg, THF (ii) $B(O^iPr)_3$, THF, -75 °C (iii) HCl aq.
Or (i) Mg, Et_2O (ii) $B(OMe)_3$, Et_2O, -65 °C (iii) HCl aq.
2D...$Pd(PPh_3)_4$, EtOH, C_6H_6, 2M-Na_2CO_3

Scheme 2



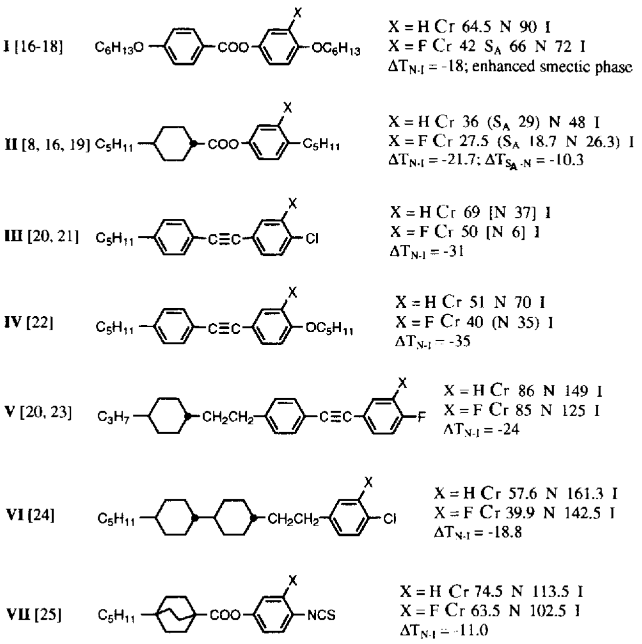
3A...I_2, $NaHCO_3$, H_2O
3B...(i) H_2SO_4 aq., CH_3CO_2H, 0-4 °C (ii) $NaNO_2$ aq.
(iii) $CuSO_4$ aq., KCN. $NaHCO_3$, C_6H_6 (iv) 50°C
3C...**Either** (i) Mg, THF (ii) $B(O^iPr)_3$, -75 °C (iii) HCl aq.
Or (i) Mg, Et_2O (ii) $B(OMe)_3$, Et_2O, -65 °C (iii) HCl aq.
3D...2M-Na_2CO_3 aq., C_6H_6, EtOH, $Pd(PPh_3)_4$
3E...BBr_3, CH_2Cl_2, -75 °C
3F...RBr or RI, K_2CO_3, butanone

Scheme 3



4A...(i) BuLi (ii) $ZnCl_2$
4B...$Pd(PPh_3)_2$ from $PdCl_2(PPh_3)_2$ and $(^iBu)_2AlH$

Scheme 4



I [16-18]
X = H Cr 64.5 N 90 I
X = F Cr 42 S_A 66 N 72 I
$\Delta T_{N\text{-}I}$ = -18; enhanced smectic phase

II [8, 16, 19]
X = H Cr 36 (S_A 29) N 48 I
X = F Cr 27.5 (S_A 18.7 N 26.3) I
$\Delta T_{N\text{-}I}$ = -21.7; $\Delta T_{S_A\text{-}N}$ = -10.3

III [20, 21]
X = H Cr 69 [N 37] I
X = F Cr 50 [N 6] I
$\Delta T_{N\text{-}I}$ = -31

IV [22]
X = H Cr 51 N 70 I
X = F Cr 40 (N 35) I
$\Delta T_{N\text{-}I}$ = -35

V [20, 23]
X = H Cr 86 N 149 I
X = F Cr 85 N 125 I
$\Delta T_{N\text{-}I}$ = -24

VI [24]
X = H Cr 57.6 N 161.3 I
X = F Cr 39.9 N 142.5 I
$\Delta T_{N\text{-}I}$ = -18.8

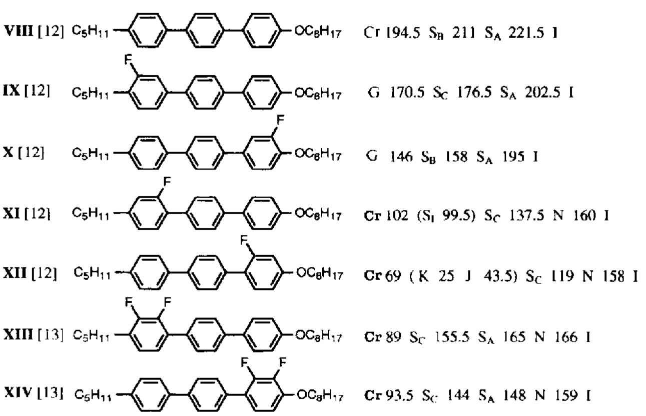
VII [25]
X = H Cr 74.5 N 113.5 I
X = F Cr 63.5 N 102.5 I
$\Delta T_{N\text{-}I}$ = -11.0

Figure 1. Transition temperatures (°C) for compounds with a fluoro-substituent *ortho* to a non-cyano terminal group and for the parent compounds.

enhanced + $\Delta\varepsilon$ values would also be expected to cause a severe depression of nematic phase stability. Initially, therefore, it is essential to establish the typical magnitude of the effect on nematic (and in a few cases, smectic) phase stability caused by a fluoro-substituent *ortho* to terminal groups other than cyano, before considering terminal cyano systems. Very many different non-cyano terminal groups could be considered but examples are given of alkyl, alkoxy, chloro, fluoro and isothiocyanato groups (see figure 1). In all these cases fluoro-substitution lowers the melting point and the $T_{N\text{-}I}$ depressions range from -11 to -35°C. It is notable that the tolane systems **III–V** give the greatest depression (-31, -35 and -24°C) and for **III** and **IV**, in which the core system is perfectly linear, the largest values of -31 and -35°C are obtained; the other bent core systems can shield the lateral fluoro-substituent to some extent and, additionally, with a partly cylindrical-shaped unit such as bicyclo[2.2.2]octane, this shielding is particularly effective. Two other effects are noticeable in these examples; when *ortho* to a terminal alkoxy group, the fluoro substituent actually enhances smectic character (see **I**), and when *ortho* to an alkyl terminal group, smectic character is affected less than nematic (see **II**).

Examples of fluoro-substitution *ortho* to a non-cyano terminal group in terphenyls are not included in figure 1 because the parent systems do not usually show a nematic phase (for example, see **VIII** and **IX** in figure 2). However, it is possible to gain an insight into the effect on nematic and smectic phases of fluoro-substitution *ortho* to a terminal group in terphenyls by comparing certain difluoro and monofluoro systems, although such comparisons are slightly different from those shown in figure 1, since the introduction of a second fluoro-substituent into an already fluoro-substituted molecule is being considered. Comparisons of transition temperatures for compounds **XIV** and **XII** and for **XIII** and **XI** show that the 3-fluoro-substituent barely affects nematic character (increases of 1 and 6°C, respectively) when the additional substituent is not increasing the breadth of the molecules. The same comparisons show that smectic A character is increased by at least 29°C (cf., compounds **XIV** and **XII**) and by at least 27·5°C (cf., compounds **XIII** and **XI**) by 3-fluoro-substitution. The conclusion to be drawn is that fluoro-substitution at such a position in these molecules is favourable for the promotion of smectic and, possibly, nematic stability but the effects is usually masked by the unfavourable molecular broadening resulting from fluoro-substitution in the parent molecule. However, with compounds **I** and **II** (see figure 1), the bent nature of ester-linked core systems shields the substituent and smectic character is enhanced or only slightly diminished. Comparison of compounds **VIII–X** shows that the $T_{S_A\text{-}I}$ values are only depressed by 19 (cf., **IX** and **VIII**) and 26·5°C (cf., **X** and **VIII**); these are very modest reductions in smectic stability in comparison with the reductions seen for inner-core fluoro-substitution (**XI** and **XII**) and represent the compromise of the dominant broadening effect over the enhancement of phase stability by fluoro-substitution at the 3-position.

Part of the purpose of this work was to investigate whether or not there is any evidence in compounds which are known to have pairwise association of molecules, for 3-fluoro-substitution to show relative influences on smectic and nematic character which are similar to



VIII [12] Cr 194.5 S_B 211 S_A 221.5 I
IX [12] G 170.5 S_C 176.5 S_A 202.5 I
X [12] G 146 S_B 158 S_A 195 I
XI [12] Cr 102 (S_I 99.5) S_C 137.5 N 160 I
XII [12] Cr 69 (K 25 J 43.5) S_C 119 N 158 I
XIII [13] Cr 89 S_C 155.5 S_A 165 N 166 I
XIV [13] Cr 93.5 S_C 144 S_A 148 N 159 I

Figure 2. Transition temperatures (°C) for some fluoro-substituted terphenyls.

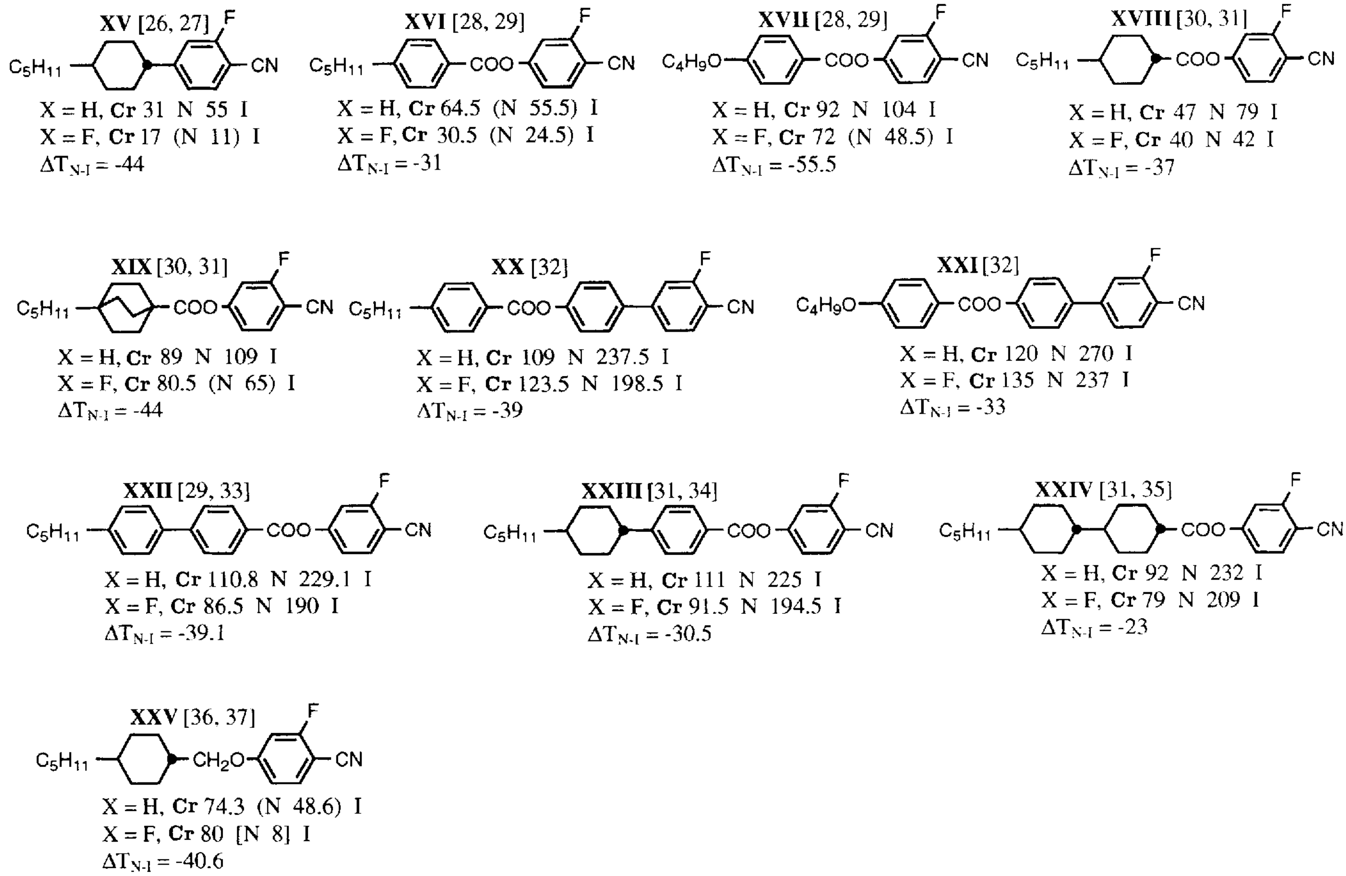


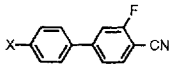
Figure 3. Transition temperatures (°C) for 1-substituted-3-fluoro-4-cyanophenyl compounds and for the parent compounds.

those identified in compounds **I**, **II** and the terphenyls in figure 2.

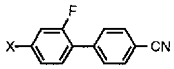
Many different core systems have been used with a terminal cyano group (for example, see figure 3) and structure **XV** is the one most closely related to the biphenyls reported here. The overall conclusion from the values given in figure 3 is that the depressions in $T_{\text{N-I}}$ values, which range from 31–55·5°C, are larger than those shown in figure 1. This is probably because terminal cyano compounds give antiparallel correlations and therefore fluoro-substitution *ortho* to a terminal cyano group leads to an additional significant depression of mesophase stability because of the disruption of the pairwise associations; melting points are frequently reduced, but not in all cases.

The transition temperatures for componds **7** and **8** are shown in the table and, for convenience in comparisons, the transition temperatures for the 2- and 2′-fluoro-substituted compounds and the parent cyanobiphenyls are also given. None of the 3-fluoro-4-cyano compounds reported here give enantiotropic phases and only the long terminal chain members in each series gave monotropic transitions; all the other members of the series were non-mesomorphic, and so virtual $T_{\text{N-I}}$ values were determined by extrapolation from mixtures in E7. The values for compounds **7** and **8**, in comparison with compounds **1** and **2**, respectively, show that fluoro-substitution has an irregular effect on melting points; for the methyl and methoxy containing compounds, the substituent causes an increase in melting point but then, with one exception, for every other member of these series, the melting point of the 3-fluoro compound is lower. The depressions of $T_{\text{N-I}}$ values are more difficult to assess with certainty because many of the values for compounds **7** and **8** are virtual transitions. As presented, the alkyl compounds **7a–d** have depressions of 8, 33, 50 and 55·5°C, respectively and the last value is accurate since it is based on observable transitions. For the alkoxy compounds **8a–d**, *ortho*-fluoro-substitution gives even larger depressions in $T_{\text{N-I}}$ values of 79, 55, 57 and 69°C based on virtual measurements, and these values are generally greater than the depressions for the terminal cyano compounds in figure 3. Two assessments can be made of the effect of *ortho*-fluoro-substitution on S_A phase stability; for compounds **7e** and **8e** the depressions in $T_{\text{S}_\text{A}\text{-N/I}}$ values are only 39·5°C in each case and this is similar to, or even smaller than, the

Table. Transition temperatures (°C) for compounds **1** to **8**.

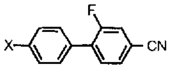


(**7** and **8**)

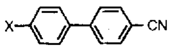


(**5** and **6**)

		7							**5**						
	X	Cr		S_A		N		I	Cr		S_A		N		I
a	CH_3	●	131	—	—	[●	37†]	●							
b	C_3H_7	●	41/64	—	—	[●	− 8‡]	●	●	90	—	—	[●	− 11]	●
c	C_5H_{11}	●	− 5	—	—	[●	− 15§]	●	●	59	—	—	[●	0]	●
d	C_7H_{15}	●	38	—	—	(●	− 12·5)	●	●	40/46	—	—	[●	4]	●
e	$C_{12}H_{25}$	●	43	(●	18·5	●	20)	●	●	63	—	—	(●	27)	●
		8							**6**						
a	CH_3O	●	153	—	—	[●	6¶]	●							
b	C_2H_5O	●	89	—	—	[●	35‖]	●	●	76	—	—	(●	49)	●
c	C_4H_9O	●	47	—	—	[●	18‡]	●	●	57	—	—	(●	35)	●
d	$C_6H_{13}O$	●	50	—	—	[●	6†]	●	●	55	—	—	(●	41)	●
e	$C_{11}H_{23}O$	●	48·5	(●	47·5	[●	32††])	●	●	56	(●	47	●	52)	●



(**3** and **4**)



(**1** and **2**)

		3							**1**						
	X	Cr		S_A		N		I	Cr		S_A		N		I
a	CH_3								●	109	—	—	(●	45)	●
b	C_3H_7	●	71	—	—	[●	7]	●	●	66	—	—	(●	25)	●
c	C_5H_{11}	●	51	—	—	(●	22)	●	●	22	—	—	●	35	●
d	C_7H_{15}	●	56	—	—	(●	29)	●	●	30	—	—	●	43	●
e	$C_{12}H_{25}$	●	67	(●	44	—	—)	●	●	48	●	58	—	—	●
		4							**2**						
a	CH_3O								●	105	—	—	(●	85)	●
b	C_2H_5O	●	81	—	—	(●	70)	●	●	102	—	—	(●	90)	●
c	C_4H_9O	●	68‡‡	—	—	(●	59)	●	●	78	—	—	(●	75)	●
d	$C_6H_{13}O$	●	56	—	—	●	60	●	●	57	—	—	●	75	●
e	$C_{11}H_{23}O$	●	73	(●	68	—	—)	●	●	71	●	87	—	—	●

( ) Denote a monotropic transition.

[ ] Denote the transition temperature from mixtures in E7, † 18 per cent, ‡ 40 per cent, § 35 per cent, ¶ 10 per cent, ‖ 20per cent, †† 17 per cent w/w.

‡‡ Another crystal form melts at 56°C.

general depression seen in the T_{N-I} values for compounds **7** and **8**. Certainly the *ortho*- fluoro-substituent does not lead to a dramatically greater depression in smectic relative to nematic stability such as that seen, for example, with non-terminally fluoro-substituted terphenyls [12]. This value for the depression of smectic A phase stability indicates that even in systems which show anti parallel correlations, an *ortho*- fluoro-substituent depresses smectic and nematic character to about the same extent.

The variations of nematic and smectic phase stability along a homologous series of alkyl or alkoxy compounds depends on the nature of the core system and the other terminal group; two related compounds which give contrasting variations are the alkyl- (and alkoxy)-cyanobiphenyls (**1** and **2**) [38] and the 4-(*trans*-4-alkylcyclohexyl)benzonitriles (PCHs) [27, 39–41]. The short-chain members of the PCH compounds have low T_{N-I} values which *rise* steeply along the series and then level off [42]. For both the odd and even series of compounds **1** and **2** however, the T_{N-I} values for the short chain members initially *fall* and then rise before the emergence of an increasingly stable smectic A phase overrides the nematic phase [42]. The transition temperatures for compounds **7a–d** show that the T_{N-I} values also fall along the homologous series for the *ortho*-fluoro compounds and then rise again. For the long chain dodecyl compound (**7e**, a member of the even series), nematic character has increased quite substantially compared to compound **7d** and the nematic phase has still not been eliminated by the smectic A phase; for this compound it is clear that smectic A character must have been depressed (by 39·5°C compared to compound **1e**) to a greater extent than nematic character.

3. Experimental

All final products were shown to be pure by TLC, GLC or HPLC analysis. Structural confirmation of final products and intermediates was obtained by ^{1}H NMR spectroscopy (JEOL JNM-PMX60 and JEOL JNM-GX270 FT spectrometers), infrared spectroscopy (Perkin–Elmer 457 grating spectrometer) and mass spectrometry (AEI MS902 and Finnigan-MAT 1020 GC/MS spectrometers). Transition temperatures were measured using a Mettler FP5 hot stage and control unit in conjunction with an Olympus BDSP 753 polarizing microscope. In several cases differential scanning calorimetry was used to confirm transition temperatures (Perkin–Elmer DSC-2C and DSC-7 with data station).

The preparation of the following compounds has been reported previously: compounds **10**, **11** and **12** in [43]; compounds of structure **18** and **19** in [13]; compounds of structure **20** in [12]; compounds **21**, **26**, **8a** and **27** in [32]; compound **23** in [44]; compound **28** as in [13]; compounds **9**, **17**, **22** and **25** were commercially available. Representative examples of the methods used for the preparation of the various classes of novel compounds are given below.

3.1. *Synthesis of 4-bromo-3-fluorobiphenyl* (**13**)

A solution of compound **12** (9·45 g, 0·05 mol) in dry benzene (60 ml) was slowly added over 1 h to a cooled (0°C) solution of pentyl nitrite (6·21 g, 0·053 mol) in dry benzene (45 ml). The reaction mixture was heated under reflux for 1·5 h and the cooled solution then diluted with diethyl ether (200 ml). The organic solution was washed with water (150 ml), saturated aqueous sodium bicarbonate (2 × 150 ml), aqueous hydrochloric acid (10 per cent, 2 × 150 ml), water (150 ml), dried ($MgSO_4$) and the solvent evaporated off *in vacuo* to afford a dark-brown solid. The crude product was chromatographed on silica gel (400 g) and eluted with light petroleum (b.p. 60–80°C) to afford a slightly impure brown oil which solidified on standing. Yield 6·20 g; m.p. 47–51°C; ^{1}H NMR δ 0·67–2·00 (impurities), 7·00–7·73 (m); IR $\nu_{max.}$ (KCl) 1565, 1470, 1405, 1200, 1030, 875 cm^{-1}; MS *m/z* 252/250 (M$^+$), 170.

3.2. *Synthesis of 4-alkanoyl-4′-bromo-3′-fluorobiphenyls* (**14**)

These compounds were prepared from compound **13** by the method used for compounds **18**.

Pentanoyl compound (**14c**); yield 47 per cent; m.p. 62·5–66°C; ^{1}H NMR δ 0·67–2·10 (7 H, m), 2·97 (2 H, t), 6·90–7·33 (3 H, m), 7·53 (2 H, d), 7·97 (2 H, d); IR $\nu_{max.}$ (KCl) 2960, 1680, 1480, 1390, 1215 cm^{-1}; MS *m/z* 336/334 (M$^+$), 294/292, 279/277, 170.

3.3. *Synthesis of 4-alkyl-4′-bromo-3′-fluorobiphenyls* (**15**)

These compounds were prepared from compounds **14** using triethylsilane in trifluoroacetic acid [45].

Pentyl compound (**15c**): yield 70 per cent; pale green oil; ^{1}H NMR δ 0·57–2·13 (9 H, m), 2·63 (2 H, t), 7·00–7·67 (7 H, m); IR $\nu_{max.}$ (film) 2930, 1475, 1395, 1195, 1055 cm^{-1}; MS *m/z* 322/320 (M$^+$), 265/263, 183.

3.4. *Synthesis of 4′-alkyl-4-cyano-3-fluorobiphenyls* (**7**)

Method A: Pentyl compound (**7c**): 2 M sodium carbonate (15 ml) was added to a solution of tetrakis(triphenylphosphine)palladium (0) (0·82 g, 0·71 mmol) and compound **21** (2·84 g, 14·2 mmol) in benzene (30 ml) under nitrogen. A solution of compound **20c** (3·00 g, 15·6 mmol) in ethanol (7·0 ml) was then added to the vigorously stirred reaction mixture which was then heated under reflux for 2 h. The cooled reaction mixture was treated with hydrogen peroxide (30 per cent, 1·0 ml) and stirred at room temperature for 1 h. The reaction mixture was then diluted with diethyl ether (100 ml), washed with water (2 × 75 ml), brine (100 ml), water (75 ml), dried ($MgSO_4$) and the solvent evaporated off *in vacuo* to give a brown oil. The crude product was chromatographed on silica gel (250 g) and eluted with light petroleum (b.p. 60–80°C)–chloroform (3:1) to give an oil which was distilled *in vacuo*: yield 69 per cent; b.p. 145–155°C/ 0·15 mmHg; m.p. −5°C by DSC; ^{1}H NMR δ 0·85 (3 H, t), 1·25–1·40 (4 H, m), 1·65 (2 H, m), 2·65 (2 H, t), 7·25–7·70 (7 H, m); IR $\nu_{max.}$ (film) 2930, 2240, 1620, 1555, 1490, 1400 cm^{-1}; MS *m/z* 267 (M$^+$), 210, 84.

Method B: Compounds **15** were cyanated using copper(I) cyanide in *N*-methylpyrrolidin-2-one [46].

The solid filtered off from the reaction mixture for the pentyl compound **7c** contained compound **16c**: yield 25 per cent; m.p. 177·2–177·6°C; ^{1}H NMR δ 0·92 (3 H, t), 1·13–1·87 (6 H, m), 2·67 (2 H, t), 6·07 (1 H, s), 6·77 (1 H, s), 7·17–7·70 (6 H, m), 8·17 (1 H, t); IR $\nu_{max.}$ (KCl) 3470, 3185, 2930, 1650, 1620, 1405 cm^{-1}: MS *m/z* 285 (M$^+$), 235, 192, 184, 157.

Method C: Compound **16c** was dehydrated using thionyl chloride in *N,N*-dimethylformamide to give compound **7c**.

Method D:The aryl bromides (**19** or **28**) were metallated with *n*-butyllithium, reacted with zinc chloride in THF to give compounds **29** or **30** which were then coupled *in situ* with compound **24** using bis(triphenylphosphine)palladium(0) catalyst as described in [47].

Pentyl compound (**7c**) and butoxy compound (**8c**): yields 70 and 75 per cent, respectively.

3.5. *Synthesis of 2-fluoro-4-iodobenzonitrile* (**24**)

Compound **24** was prepared from compound **23** using the method described for 4-bromo-2-fluorobenzonitrile [32]. Yield 60 per cent; m.p. 95–96°C; ^{1}H NMR δ 7·18–7·84 (m); IR $\nu_{\max.}$ (KCl) 2240, 1555, 1460, 1030, 855, 800 cm^{-1}; MS *m/z* 247 (M$^+$), 127, 120, 100, 93.

3.6. *Synthesis of 4'-alkoxy-4-cyano-3-fluorobiphenyls* (**8**)

Compound **27** was alkylated using the appropriate alkyl bromide or iodide with potassium carbonate in butanone as described in [13].

Butoxy compound (**8c**): yield 86 per cent; m.p. 47°C; ^{1}H NMR δ 0·72–2·16 (7 H, m), 4·04 (2 H, t), 7·04 (2 H, d), 7·28–7·96 (5 H, m); IR $\nu_{\max.}$ (KCl) 2230, 1605, 1395, 1250, 1175, 820 cm^{-1}; MS *m/z* 269 (M$^+$), 212, 195, 183, 157.

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References

[1] Gray, G. W., Harrison, K. J., and Nash, J. A., 1973, *Electron. Lett.*, **9**, 130.

[2] Ashford, A., Constant, J., Kirton, J., and Raynes, E. P., 1973, *Electron. Lett.*, **9**, 118.

[3] Coates, D., 1987, *Thermotropic Liquid Crystals*, edited by G. W. Gray (Wiley, Chichester), Vol. 22, p. 99.

[4] Fearon, J. E., Gray, G. W., Ifill, A. D., and Toyne, K. J., 1985, *Molec. Crystals liq. Crystals*, **124,** 89.

[5] McDonnell, D. G., Raynes, E. P., and Smith, R. A., 1985, *Molec. Crystals liq. Crystals*, **123,** 169.

[6] Field, L. D., and Sternhell, S., 1981, *J. Am. chem. Soc.*, **103,** 738.

[7] Hird, M., Gray, G. W., and Toyne, K. J., 1991, *Molec. Crystals liq. Crystals*, **206,** 187.

[8] Gray, G. W., Hogg, C., and Lacey, D., 1981, *Molec. Crystals liq. Crystals*, **67,** 1.

[9] Balkwill, P. H., Bishop, D. I., Pearson, A. D., and Sage, I. C., 1985, *Molec. Crystals liq. Crystals*, **123,** 1.

[10] Eidenschink, R., 1985, *Molec. Crystals liq. Crystals*, **123,** 57.

[11] Gray, G. W., Lacey, D., Stanton, J. E., and Toyne, K. J., 1986, *Liq. Crystals*, **1,** 407.

[12] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Molec. Crystals liq. Crystals*, **195,** 221.

[13] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1989, *J. chem. Soc., Perkin Trans. 2*, 2041.

[14] Schad, H., and Kelly, S. M., 1985, *J. Physique*, **46,** 1395.

[15] Schad, H., and Kelly, S. M., 1984, *J. chem. Phys.*, **81,** 1514.

[16] Osman, M. A., 1985, *Molec. Crystals liq. Crystals*, **128,** 45.

[17] Steinsträsser, R., 1972, *Z. Naturf.* (*b*), **27,** 774.

[18] Gunjima, T., Nakagawa, Y., and Masuda, Y., 1982, *Rep. Res. Lab. Asahi Glass Co.*, **32,** 87.

[19] Deutscher, H.-J., Laaser, B., Dölling, W., and Schubert, H., 1978, *J. prakt. Chem.*, **320,** 191.

[20] Greenfield, S., Coates, D., Brown, E., and Hittich, R., 1993, *Liq. Crystals*, **13,** 301.

[21] Coates, D., Greenfield, S., and Goulding, M., 1990, GB Patent 2240544.

[22] Takatsu, H., Takeuchi, K., Tanaka, Y., and Sasaki, M., 1986, *Molec. Crystals liq. Crystals*, **141,** 279.

[23] Goto, Y., and Ogawa, T., 1988, Patent EP 0276067.

[24] Wu, S.-T., Coates, D., and Bartmann, E., 1991, *Liq. Crystals*, **10,** 635.

[25] Dabrowski, R., Dziaduszek, J., Drzewinski, W., Czuprynski, K., and Stolarz, Z., 1990, *Molec. Crystals liq. Crystals*, **191,**171.

[26] Osman, M. A., and Huynh-ba, T., 1983, *Molec. Crystals liq. Crystals Lett.*, **82,** 331.

[27] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew. Chem., Int. Ed. Engl.*, **16,** 100.

[28] Boller, A., and Scherrer, H., 1974, Patent DE-OS 2,415,929.

[29] Kelly, S. M., 1984, *Helv. Chim. Acta.*, **67,** 1572.

[30] Kelly, S. M., 1983, *J. chem. Soc., chem. Commun.*, 366.

[31] Kelly, S. M., and Schad, H., 1984, *Helv. Chim. Acta*, **67,** 1580.

[32] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1989, *Molec. Crystals liq. Crystals*, **172,** 165.

[33] Coates, D., and Gray, G. W., 1976, *Molec. Crystals liq. Crystals*, **37,** 249.

[34] Eidenschink, R., 1979 (1), *Kontakte* (*Darmstadt*), 15.

[35] Krause, J., Eidenschink, R., and Pohl, L., Patent USP 4 229 315.

[36] Gray, G. W., and McDonnell, D. G., 1979, *Molec. Crystals liq. Crystals*, **53,** 147.

[37] Kelly, S. M., and Schad, H., 1985, *Helv. Chim. Acta*, **68,** 1444.

[38] Gray, G. W., 1978, *Advances in Liquid Crystal Materials for Applications*, BDH Special Publication, BDH Chemicals Ltd, Poole, England and BDH Chemicals Ltd Product Information on Liquid Crystal Materials.

[39] Pohl, L., Eidenschink, R., Krause, J., and Erdmann, D., 1977, *Phys. Lett.* A, **60,** 421.

[40] Eidenschink, R., Krause, J., and Pohl, L., Ger. Patent 2,636,684; 1978, *Chem. Abs.*, **88,** 169762c..

[41] Szczucinski, T., and Dabrowski, R., 1981, *Biul. Wojsk. Acad. Tech.*, **30,** 109.

[42] Toyne, K. J., 1987, *Thermotropic Liquid Crystals*, edited by G. W. Gray (Wiley, Chichester), Vol. 22, P. 28.

[43] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Molec. Crystals liq. Crystals*, **204.** 43.

[44] Callaghan, P. D., and Gibson, M. S., 1970, *J. chem. Soc.* (*C*), 2106.

[45] West, C. T., Donnelly, S. J., Kooistra, D. A., and Doyle, M. P., 1973, *J. org. Chem.*, **38,** 2675.

[46] Ellis, G. P., and Romney-Alexander, T. M., 1987, *Chem. Rev.*, **87,** 779.

[47] Negishi, E., King, A. O., and Okukado, N., 1977, *J. org. Chem.*, **42,** 1821.