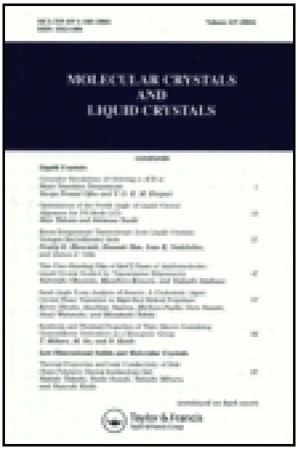

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The Effect of Lateral Fluorosubstitution on the Liquid Crystalline Properties of some 4-n-Alkyl-, 4-n-Alkoxy- and Related 4-Substituted-4′ -cyanobiphenyls

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The Effect of Lateral Fluoro-substitution on the Liquid Crystalline Properties of some 4-n-Alkyl-, 4-n-Alkoxy- and Related 4-Substituted-4′-cyanobiphenyls†

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(*Received October 15, 1984*)

The syntheses of several 4-n-alkyl-, 4-[2-(*trans*-4-n-alkylcyclohexyl)ethyl]-, 4-[2-(4-n-alkylphenyl)ethyl]- and 4-n-alkoxy-4′-cyano-2′-fluorobiphenyls and -4′-cyano-2-fluorobiphenyls are presented and the transition temperatures for these compounds are reported and discussed. In the alkylcyanobiphenyls, a 2-fluoro-substituent causes a greater depression of T_{N-I} (35-39°C) than a 2′-fluoro-substituent (13-18°C) and a similar situation arises for the cyclohexylethyl compounds. The fluoro-substituted alkoxy-compounds also give two series with depressions of T_{N-I} of 34-41°C for the 2-fluoro- and 15-20°C for the 2′-fluoro-compounds. In non-cyano systems, 2- and 2′-fluoro-substituents in biphenyl derivatives give similar depressions in T_{N-I}, which are larger than those found in cyano systems, and the different depressions for the fluoro-substituted cyano compounds are thought to arise because of the effect of the fluorine on the anti-parallel correlations of the parent systems. The effects on smectic and nematic thermal stabilities are qualitatively similar, but are usually greater for smectic transitions.

A comparison is made between 4-*trans*-cyclohexylethyl and 4-phenylethyl units in the 4′-cyano- and 4′-bromo-2′-fluorobiphenyls.

INTRODUCTION

The 4-n-alkyl- and 4-n-alkoxy-4′-cyanobiphenyls ((1) and (2) respectively) have been recognised for more than ten years as extremely

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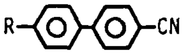
†Presented at the Tenth International Liquid Crystal Conference, York, June 15–21, 1984.

useful materials for twisted-nematic electro-optic display devices, principally because of the suitability of their nematic ranges for room temperature displays (see Tables I and III) and because of their high Δn and $\Delta\epsilon$ values, e.g., $\Delta\epsilon$ is approximately +11 for K compounds.[1,2] Subsequently, the *trans*-4-n-alkyl-1-(4-cyanophenyl)cyclohexanes (3)[3] were prepared; these have the advantage of higher T_{N-I} values (by approximately 20°C) and lower viscosity, but the disadvantage of slightly lower dielectric anisotropies. A further modification to the structure of the K compounds has provided the 1-(*trans*-4-n-alkylcyclohexyl)-2-(4′-cyanobiphenyl-4-yl)ethanes (4) which have very much higher T_{N-I} values[4] but have higher viscosities and lower $\Delta\epsilon$ values.

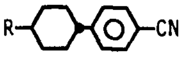


K

(1)

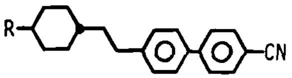
M

(2)



PCH

(3)



BECH

(4)

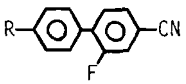
Improvements to each of these systems would be desirable and would involve producing compounds of even higher $+\Delta\epsilon$ values and of acceptably low viscosity so that such compounds could be used either as the major component in mixtures or as additives to increase the positive dielectric properties of systems with other favourable characteristics such as low viscosity, greater nematic range etc.

The most obvious way of increasing the positive dielectric anisotropies of compounds (1)–(4) is by appropriate further substitution with strongly electron-attracting groups such as cyano. However, the resulting compounds would have a much higher viscosity because of the lateral, diatomic substituent projecting across the axis of the molecule. An alternative approach to achieving these aims may be by substitution of fluorine in the biphenyl system of (1), (2) and (4) (the possibilities for substitution by fluorine in the PCH compounds are more limited but some results have been reported[5]). Fluorine has the highest electronegativity of all the elements and has a van der Waal's radius not too dissimilar from that of hydrogen (F = 1.35, H = 1.1 Å); indeed it has been claimed that the steric requirements of the two atoms are so similar that formal replacement of H by F can be regarded as an ‘isogeometric transformation’.[6] Such a small substituent may therefore be acceptable in a ‘lateral’ position without significantly increasing the viscosities and the effect on the T_{N-I} values will depend, in part, on whether the increased molecular polarisability or broadening of the molecule is dominant.[7] Usually the latter effect dominates and the thermal stabilities of nematic and smectic phases are reduced with the smectic phase being more severely affected. A fluorine substituent in the 2 (or 3′) position of the biphenyl system gives a C—F bond which makes an angle of 60° with the molecular axis and would be expected to contribute mainly to $\epsilon_{\perp}$ (making $\Delta\epsilon$ *less* positive[8]), but conjugative effects or a π-electron steric effect[9] may operate along the molecular axis (affecting $\epsilon_{\parallel}$). In addition, a fluorine substituent on the 2 or 2′ position may induce twisting about the inter-annular bond and, because cyanobiphenyls in the nematic phase have an anti-parallel correlation of molecules[10] which to some extent diminishes the $+\Delta\epsilon$ value and increases T_{N-I}, a lateral fluorine substituent may disrupt this antiparallel arrangement and give an increased $+\Delta\epsilon$ value and a decreased T_{N-I} value. Because of this complexity of possible or probable effects on viscosities, T_{N-I} values and dielectric properties, it was decided to prepare examples of the K, M, and BECH series with a 2- or 2′-fluoro substituent. In this paper we outline the synthetic methods and we report and discuss the transition temperatures for the fluorinated compounds and their precursors. Other physical properties of some of these compounds will be reported in another paper.

DISCUSSION

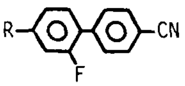
Alkyl-, Alkylcyclohexylethyl- and Alkylphenylethyl-cyanofluorobiphenyls ((5), (6), (7), (8), and (9))

The transition temperatures are shown in Table I for the 4-X-4′-cyano-2′-fluorobiphenyls (R–F,CN series), where X = alkyl- (5), 2-(*trans*-4-alkylcyclohexyl)ethyl- (7), and 2-(4-alkylphenyl)ethyl- (9), and for the 4-X-4′-cyano-2-fluorobiphenyls (R,F–CN series), where X = alkyl- (6) and 2-*trans*-4-alkylcyclohexyl)ethyl- (8).



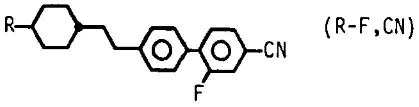
(R-F,CN)

(5)

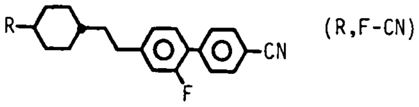


(R,F-CN)

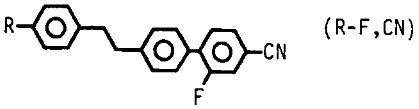
(6)



(7)



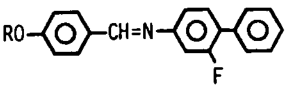
(8)



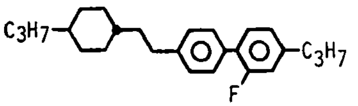
(9)

(a) Compounds (5) and (6)

The melting points of all these fluoro-substituted compounds are higher than the melting points of the parent systems and the T_{N-I} values are always lower and for the selected R, increase with chain length. For the R–F,CN series the T_{N-I} values are lower by 13–18°C and for the R,F–CN series the depression is 35–39°C. The effects in the two series are significantly different and can be compared with an average depression in T_{N-I} of 48.7°C for compounds (10)[11] ($R = C_7H_{15} - C_{10}H_{21}$) and of 36°C for compound (11).[12] Note too, that in both compounds (10) and (11), 2- and 2′-fluoro substituents have an almost identical effect.



(10)

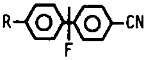
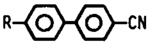


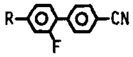
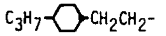
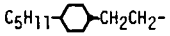
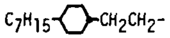
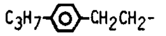
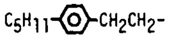
(11)

Figures 1 and 2 (drawn with the same extent of overlap as in the K compounds[10]) show why one might suggest that the T_{N-I} values in the R–F,CN series (Figure 1) are not depressed as much as for the R,F–CN series (Figure 2). In the latter series, the cyano group is positioned over the fluoro-substituted phenyl ring and possibly because of either the decreased electron density of this ring or repulsion

TABLE I

Transition temperatures (°C) for


and


	R-F,CN Series			R,F-CN Series				
								
		(5)		(6)			(1)	
R	C-I	S_A-I	N-I	C-I	N-I	C-S_A/N/I	S_A-I	N-I
C_3H_7-	71		[7]	90	[-11]	66		(25)
C_5H_{11}-	51		(22)	59	[0]	22		35
C_7H_{15}-	56		(29)	46 40	[4]	30		43
$C_{12}H_{25}$-	67	(44)		63	(27)[a]	48	58	
		(7)		(8)			(11)	
	C-S_A/N	S_A-N	N-I	C-N	N-I	C-S_A/N	S_A-N	N-I
	89		168	65	161	77		194
	76[b]		166	71[c]	157	79	86	184
	74[e]	108	157	72[d]	150	73	153	175
		(9)					(12)	
	C-N		N-I			C-N		N-I
	92		122			82		143
	82		116			60		136

a ... supercools to 24°C as a nematic
b ... supercools to 59°C as a nematic
c ... supercools to 47°C as a nematic
d ... supercools to 40°C as a nematic
e ... unclassified monotropic transition at 67°C
[ ] virtual transition ( ) monotropic transition

between the δ+ of the cyano group and the δ′+ of the carbon bonded to fluorine, the stability of this correlation may be diminished. The lateral fluorines also point towards and possibly interfere with a hydrogen atom *ortho-* to the cyano group. These appear to be the distinctive features of anti-parallel correlation in the R,F–CN series; in both these series and in compounds (10) and (11), the inter-annular twisting of the two phenyl rings will be affected by the fluoro-substituent, although one would expect the extent of this twisting to be

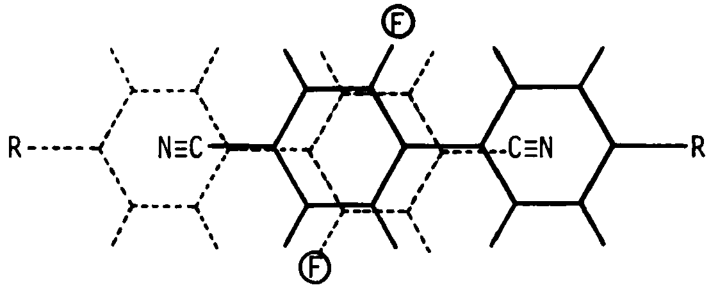


FIGURE 1 Possible arrangement of molecules in the anti-parallel pairwise association for the R–F,CN series.

similar in all the series. The specific antiparallel correlation of the biphenyl regions, as shown in Figure 1, may therefore cushion any disrupting effect the fluorine substituent may have on the thermal stability of the nematic phase, whereas the R,F–CN series, and compounds (10) and (11) (for which antiparallel correlation is not a factor), are more seriously influenced by fluorine.

The dodecyl derivatives were prepared to provide an example in these types of compound of the influence of fluorine on smectic stability. The parent compound's S_A–I transition is depressed by 14°C in the R–F,CN series (in close agreement with the effect on T_{N-I}) and a monotropic N–I transition is seen for the R,F–CN compound so that the smectic phase's thermal stability is decreased by at least 34°C. The monotropic I–S_A transition at 44°C for compound (5) (R = $C_{12}H_{25}$) was difficult to identify as smectic or nematic and it was finally characterised by observing the transitions for mixtures of compound (5) (R = $C_{12}H_{25}$) with K15 (compound (1), R = C_5H_{11}), particularly for the sample with 80.7% and 19.3% by weight of these

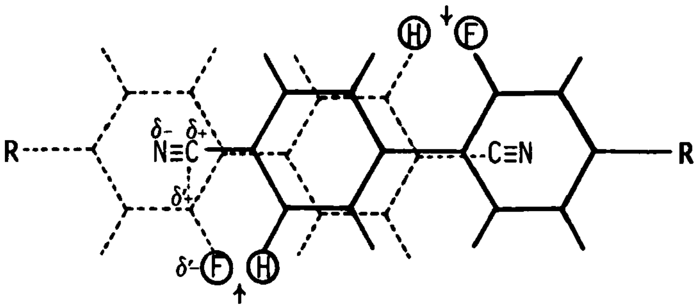


FIGURE 2 Possible arrangement of molecules in the anti-parallel pairwise association for the R,F–CN series.

compounds respectively (see Figure 3). A mixture of this composition gave monotropic I–N and N–S_A transitions before crystallising. Figure 3 also shows how rapidly the smectic properties of the dodecyl compound fall away when mixed with K15 and it also provides a clear example of a case in which the T_{N-I} line across the diagram of state is not straight, reinforcing the results of Schad and Osman[13] who

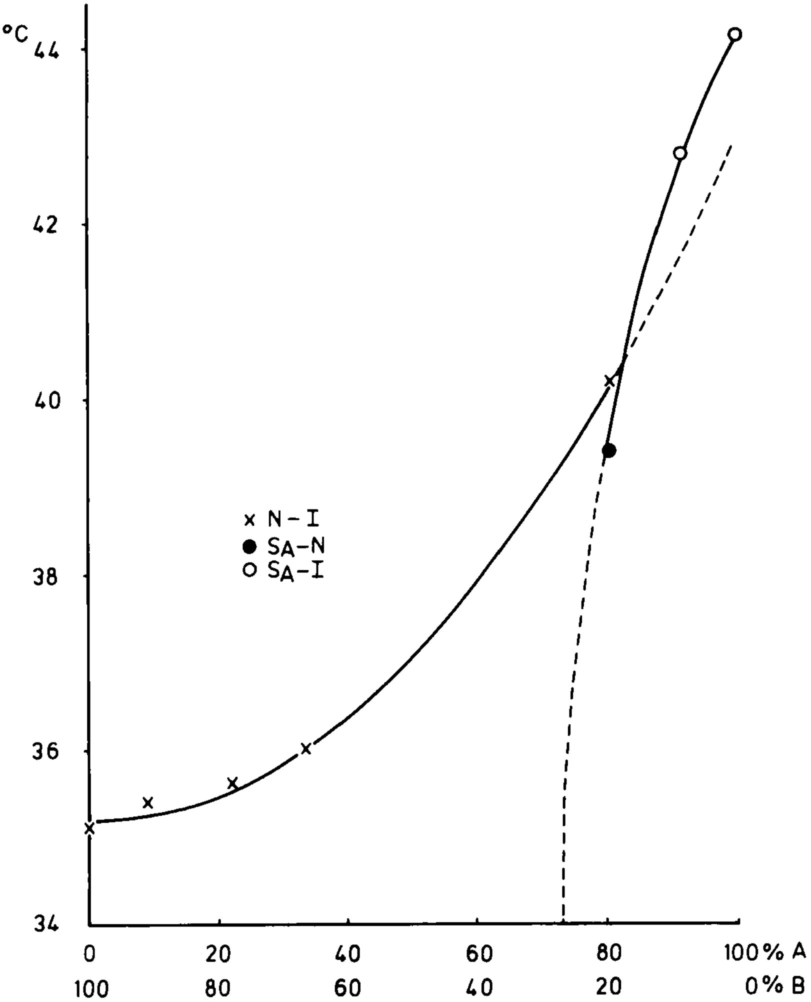


FIGURE 3 Transition temperature—composition diagram for binary mixtures of 4-dodecyl-4'-cyano-2'-fluorobiphenyl (*5*, R = $C_{12}H_{25}$)(A) and 4-pentyl-4'-cyanobiphenyl (*1*, R = C_5H_{11})(B).

reported deviations from linear relations between T_{N-I} and composition of binary mixtures.

Mixtures of compounds (5) (R = $C_{12}H_{25}$) in K36 (compound (1), R = $C_{12}H_{25}$) (up to 67% by weight of the former compound) gave a good straight line plot for the S_A–I transition which confirmed that the transition at 44°C is S_A–I.

(b) Compounds (7) and (8)

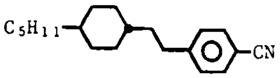
The melting points of these compounds are similar to those for the parent systems and the T_{N-I} values for each series decrease with increasing alkyl chain length as for the parent compounds (contrast with the K and fluoro-K series). The depressions in T_{N-I} values (18–26°C in the R–F,CN series and 25–33°C in the R,F–CN series) caused by fluorine substitution are also similar to those found for the simple alkyl derivatives.

Both the pentylcyclohexyl and heptylcyclohexyl parent compounds show smectic properties, but fluoro-substitution in the pentyl system suppresses the smectic phase so that only a nematic phase can be seen, and this represents depressions in T_{S_A-N} of at least 27°C and 39°C in the R–F,CN and R,F–CN series respectively. For the heptyl derivative of the R–F,CN series, a S_A–N transition which has been depressed by 45°C is seen, but the R,F–CN compound does not show a smectic phase and the S_A–N transition has therefore been depressed by at least 113°C. The effect of the fluorine substituent is therefore much greater on the S_A–N than on the N–I transition and each effect is more pronounced in the R,F–CN series.

(c) Compounds (9)

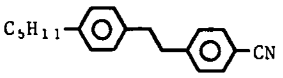
These compounds were prepared to allow a comparison between the cyclohexyl- and phenyl-ethyl derivatives of cyanofluorobiphenyls. The melting points are similar for each class of compound, but the T_{N-I} values for the aromatic compounds are 46°C and 50°C lower than for the cyclohexyl derivatives. These differences are very similar to the differences in the T_{N-I} values for the parent systems (4) and (12), i.e., 51° and 48°C. The comparison of the T_{N-I} values for compounds (9) and (12) also shows that the effect of the lateral fluorine substituent in the phenylethyl systems (depressing T_{N-I} by 21° and 20°C) is similar to that seen for the alkyl- and cyclohexylethyl- compounds.

For compounds (13) and (14) the difference in T_{N-I} is 75°C and the effect of the change of ring system is therefore less marked in the bigger molecules, but it is still large and can be attributed to the separation of polarisable regions in the fully aromatic systems, whereas the cyclohexyl compounds have only one π-electron region.[14]



(13)

T_{N-I} 51°C



(14)

T_{N-I} [-24°C]

Alkylcyclohexylethyl- and Alkylphenylethyl-bromofluorobiphenyls ((15) and (16))

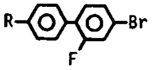
The transition temperatures are shown in Table II for the 2-(*trans*-4-alkylcyclohexyl)ethyl- (15), and 2-(4-alkylphenyl)ethyl-4′-bromo-2′-fluorobiphenyls (16).

The comparison of the cyclohexyl and phenyl substituents (see section (c) above) is also possible for derivatives of 4-bromo-2-fluorobiphenyl. Once again the melting points for the cyclohexyl and phenyl substituents are similar but the phenyl compounds have T_{N-I} values 51°C and 45°C lower than the cyclohexyl systems.

The introduction of the fluoro-substituent into the 4-bromobi-

TABLE II

Transition temperatures (°C) for



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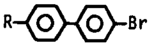
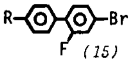
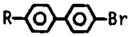
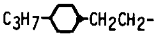
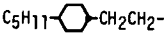
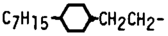
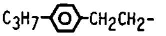
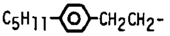


	 *(15)*				
R	C-N	N-I	C-S_A/N	S_A-N	N-I
	61	115	128		162
	57	114	106	107	160
	54	113			
	C-N/I	N-I			
	75	(64)	structure *(16)*		
	55	69			

( ) monotropic transition

phenyls causes a pronounced *reduction* in melting point (67°C and 49°C) (in marked contrast to the alkyl- and cyclohexyl-cyano- compounds (see Table I) and greater than for the alkoxy-cyano- compounds (see Table III)). The effect on T_{N-I} values is also quite different and reductions of approximately 47°C occur in the bromo-compounds on introduction of fluorine, whereas the depression is 13 to 18°C for the cyano-compounds. The value of 47°C is much more similar to the average value for the difference in T_{N-I} values of 48.7°C found for the introduction of fluorine into the parent compound to give (10) (see p. 92). The T_{N-I} values of the 4-bromobiphenyl systems are therefore influenced by fluorine substitution in a closely similar way to that revealed by compound (10) and in each of these cases the pairwise correlation of molecules does not arise. However, with the cyanobiphenyls, in which antiparallel correlation does arise, fluorine substitution is less influential and two distinct effects are seen for 2- or 2′-fluro substitution (see section (a), p. 92).

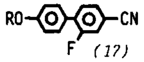
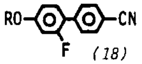
Alkoxycyanofluorobiphenyls ((17) and (18))

The transition temperatures are shown in Table III for the 4-alkoxy-4′-cyano-2′-fluorobiphenyls (RO–F,CN series) and the 4-alkoxy-4′-

TABLE III

Transition temperatures (°C) for

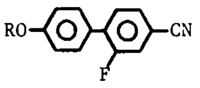
and

	RO-F,CN Series			RO,F-CN Series						
	 (17)			 (18)			 (2)			
RO	C-N/I	S_A-I	N-I	C-N/I	S_A-N	N-I	C-S_A/N/I	S_A-N	S_A-I	N-I
C_2H_5O	81		(70)	76		(49)	102			(90)
C_4H_9O	68 (C_1-I) 56 (C_2-N)		59	57		(35)	78			(75)
$C_6H_{13}O$	56		60	55		(41)	57			75
$C_8H_{17}O$	59[a]		63	45[b]		46	54	67		80
$C_{11}H_{23}O$	73	(68)		56	(47)	(52)	71		87	

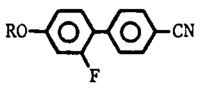
a .. supercools to 30°C as a nematic b .. supercools to 25°C as a nematic

( ) monotropic transition

cyano-2-fluorobiphenyls (RO,F–CN series). The melting points of the fluoro compounds are generally *lower* or very similar to those for the parent systems, in contrast to the situation for the alkyl analogues ((5) and (6)). However the depressions of T_{N-I} values for the alkoxyfluoro compounds are 15–20°C for the RO–F,CN series and 34–41°C for the RO,F–CN series, and these values are similar to those found for the alkyl and the alkylcyclohexylethyl compounds. Once again the fluoro derivatives and the parent system follow the same type of curve for T_{N-I} value plotted against length of the alkoxy group which, in this case, falls initially and then rises.


(RO-F,CN)

(17)


(RO,F-CN)

(18)

The octyloxy parent compound has a T_{S_A-N} value at 67°C which has been lost for each of the fluoro compounds and the extent of supercooling shows that the transition has been depressed by at least 37°C and 42°C for the two series. However, the undecyloxy compounds allow a better assessment of the effect of fluorine on smectic thermal stability, because here the monotropic formation of the S_A phase can be observed. The S_A–I transition of the parent compound is depressed by 19°C in the RO–F,CN series and for the RO,F–CN series a nematic phase is revealed and the thermal stability of the S_A phase is decreased by 40°C. The greater reduction in mesophase thermal stability is therefore seen once again in the RO,F–CN series, but the effects on smectic thermal stability are not as great as those seen for the heptyl derivative of compounds (7) and (8) (see Table I).

EXPERIMENTAL

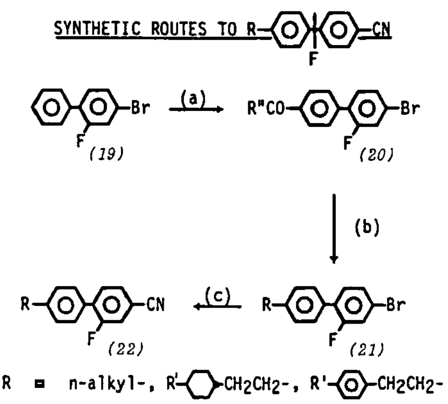
Materials

All materials prepared were checked for purity by the usual methods (t.l.c., g.l.c., h.p.l.c.) and the structures of all final products (and where necessary those of the synthetic intermediates) were confirmed by mass spectrometry, and n.m.r. and infra-red spectroscopy.

The routes for the syntheses of the cyano-compounds discussed in this paper are summarized below with brief comments on some of the reaction conditions. The route to the R–F,CN compounds is shown in Scheme 1. 4-Bromo-2-fluorobiphenyl (19) (supplied by B.D.H. Chemicals Limited) undergoes Friedel-Crafts acylation in the 4′-position in good yield (>70%) and without any complications from isomeric substitution products. Reduction of the keto group by using Huang-Minlon type conditions was unsatisfactory and even under mild conditions (i.e., below 130°C) the 2-fluoro atom was partially replaced in nucleophilic attack by hydroxide and alkoxide ions. The ketone (20) was successfully reduced by triethylsilane in trifluoroacetic acid[15] or, alternatively, the ketone was reduced to the alcohol with sodium borohydride, and the alcohol produced was dehydrated to the alkene which was then catalytically reduced (10% Pt/C) to give (21). Attempts to reduce the ketone with $LiAlH_4/AlCl_3$/ether/$CHCl_3$[16] always gave some alkene impurity in the major product (21); this mixture could also be catalytically reduced to give pure (21). A standard cyanation procedure (copper(I) cyanide in 1-methylpyrrolidin-2-one) gave compound (22).

The route to the isomeric alkylcyanofluoro-compounds (R,F-CN) also starts with compound (19) (see Scheme 2) and involves a catalysed coupling reaction of 2-fluorobiphenyl-4-yl magnesium bromide with the appropriate alkyl bromide to give 4-alkyl-2-fluorobiphenyl. Carboxylation at the 4′-position was achieved with oxalyl chloride/aluminium chloride[17] or *via* acetylation and oxidation. The acid was required for other work but it is also feasible to ammoniate the product from the oxalyl chloride reaction and so obtain the amide

Scheme 1

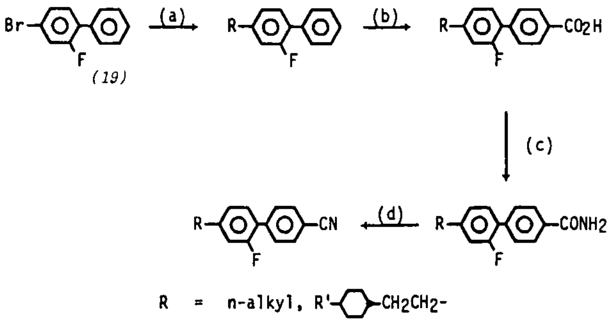


(a) ... R"COCl, $AlCl_3$, $Cl_2CHCHCl_2$

(b) ... Et_3SiH, CF_3CO_2H

(c) ... CuCN, N-methylpyrollidin-2-one

Scheme 2



(a) ... (i) Mg, THF; (ii) CuCl, RBr, THF

(b) ... (i) $(COCl)_2$, $AlCl_3$, CH_2Cl_2; (ii) KOH, H_2O, EtOH; (iii) H^+

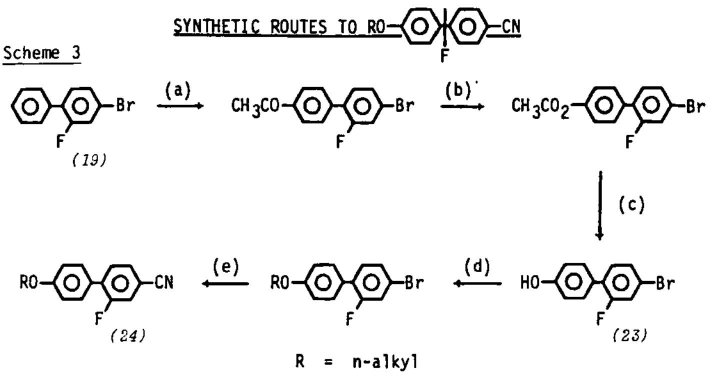
(c) ... (i) $SOCl_2$; (ii) conc NH_3/H_2O

(d) ... $SOCl_2$, DMF

directly. Dehydration of the amide was achieved by using thionyl chloride in DMF.

The preparation of the alkoxy compounds of type RO–F,CN again uses the ubiquitous compound (19) (see Scheme 3); acetylation followed by Baeyer-Villiger oxidation with *m*-chloroperbenzoic acid in dichloromethane gave the biphenyl acetate without contamination by the biphenylcarboxylate. Hydrolysis of the ester, followed by alkyl-

Scheme 3



(a) ... CH_3COCl, $AlCl_3$, $Cl_2CHCHCl_2$

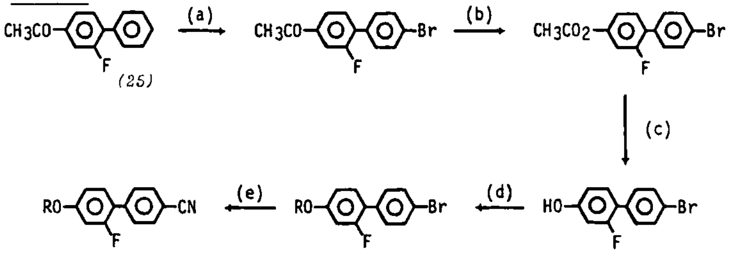
(b) ... m-$ClC_6H_4CO_3H$, CH_2Cl_2

(c) ... NaOH, H_2O

(d) ... RHal, K_2CO_3, butanone

(e) ... CuCN, N-methylpyrollidin-2-one

Scheme 4



R = n-alkyl

(a) ... Br_2, $AlCl_3$, CH_2Cl_2
(b) ... $\underline{m}$-$ClC_6H_4CO_3H$, CH_2Cl_2
(c) ... NaOH, H_2O
(d) ... RHal, K_2CO_3, butanone
(e) ... CuCN, N-methylpyrollidin-2-one

ation and cyanation in standard procedures gave compound (24); cyanation of (23) and alkylation of the cyanophenol was also successful.

The fourth group of compounds was prepared from 4-acetyl-2-fluorobiphenyl (25) (supplied by B.D.H. Chemicals Limited) (see Scheme 4). Bromination at the 4′-position was achieved with $Br_2/AlCl_3$ in dichloromethane by a method based on the technique described in ref. 18. The subsequent steps were closely similar to those shown in Scheme 3.

Many of the organic reactants used were commerically available, apart from the compounds whose preparations are described below. The 4-alkylphenylacetic acids were prepared from 4-alkylacetophenones by using a Willgerodt reaction.[19] The preparation of the *trans*-4-alkylcyclohexylacetic acids (carried out by B.D.H. Chemicals Limited) starts with the 4-alkylbenzoic acids which were hydrogenated and isomerised to the *trans*-4-alkylcyclohexanecarboxylic acids; reduction of the acid chloride to the alcohol, followed by tosylation, reaction with cyanide ion, and hydrolysis, gave the required substituted acetic acids.

Physical Measurements

Transition temperatures were obtained by optical microscopy using a Nikon LKe polarising microscope equipped with a Mettler hot stage and control unit.

Acknowledgments

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