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The Synthesis and Properties of Some Novel Ferroelectric Materials—Hosts and Dopants

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(*Received September 15, 1989*)

The first indication that terphenyl derivatives might provide suitable host S_C systems which could be doped with chiral materials and used in ferroelectric smectic C devices arose with 4,4″-dialkyl- and 4,4″-alkoxyalkyl-*p*-terphenyls carrying a single lateral fluoro-substituent. Subsequently, 4,4″-dialkyl- and 4,4″-alkoxyalkyl-*p*-terphenyls with 2,3- or 2′,3′-difluoro-substituents (and related biphenyls) have been found to be superior, when doped with appropriate chiral cyanohydrin esters. The synthesis of these difluoro-oligophenyls will be discussed, with particular reference to the use of tetrakis(triphenylphosphine)palladium(0)-catalysed coupling of arylboronic acids with aryl halides.

The liquid crystal properties of the various materials will be discussed together with some results relating to the excellent ferroelectric behaviour of the doped systems. These mixtures provide wide range S_C^* phases, large Ps values, good aligning properties on rubbed polymers, switching times that are fast, and a multiplexing capability consistent with video line address times at room temperature.

INTRODUCTION

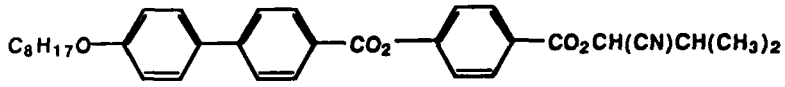
Over the last 3–4 years, as part of a Ministry of Defence funded contract, in conjunction with a JOERS/Alvey Research Programme,† we have been seeking superior ferroelectric liquid crystal (FLC) materials for fast switching displays and devices. With our colleagues at BDH Ltd., we have synthesised and examined the properties of a range of new materials either giving chiral S_C phases in their own right or for use as non-chiral S_C hosts with added chiral dopant(s), e.g., MBF esters,[1] lactates,[2] di-lactates, mandelates,[3] thiazoles,[4] thiadiazoles,[4] cyclic amides, biphenylcarboxylic esters, biphenylpropanoic esters,[5] terpenoid esters[6] etc.

In common with the experience of others, we have found that the many demanding physical requirements for FLC's are more readily met by a host S_C + dopant combination than by an intrinsically chiral S_C system.

†Funded by the Department of Trade and Industry and the Science and Engineering Research Council. Collaborators: University of Hull, BDH Ltd., Royal Signals and Radar Establishment, STC Technology Ltd. and Thorn EMI.

In the dopant area, the most successful materials have been the cyanohydrin ester dopants[7] developed in the Hull LC Group. These materials need not be and often are not liquid crystalline, as long as they are compatible with the S_C host, do not too adversely affect its transition temperatures and LC phase behaviour, and give a reasonable Ps and a long pitch.

An example of a mesomorphic cyanohydrin ester dopant is (I).

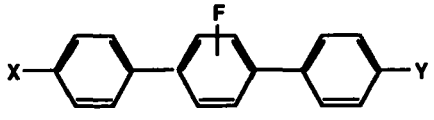


(I)

K 102° S_C 145° S_A 155° I

With their strong dipole attached directly to the chiral centre, these materials, which can be synthesised from available chiral amino-acids (*R* or *S* enantiomer), allow S_C^* mixtures with long pitches and appropriate Ps values to be produced from suitable S_C hosts.

The most successful S_C hosts developed in the Hull LC Group have been difluorinated terphenyls. Stemming from work on monofluoro-*p*-terphenyls[8,9,10] as high T_{N-I} materials—see structure (II)



(II)

where $X = R',R'O$; $Y = R,RO$

and as non-terminally polar systems giving mixtures exhibiting re-entrant nematic properties,[9] S_C properties were found in the systems where both *X* and *Y* are alkyl and more markedly where X = alkyl and Y = alkoxy for both 2′- and 3′-fluoro-substitution. Also instances of injected S_C properties were observed for binary mixtures of compounds (II) where neither pure component exhibited S_C properties. Although S_C properties were found for some of the dialkoxy compounds (II), the m.p.s. of these materials were rather high.

By comparison with the non-fluoro-substituted analogues of (II), the fluoro-substituent reduced m.p.s., considerably suppressed ordered smectic phase formation, and introduced a tendency to form tilted smectic phases, S_C, as well as S_F and S_I. With added chiral dopant of type (I), wide range mixtures of the compounds (II) were produced for ferroelectric studies. Their disadvantages as S_C hosts lay in their weakly positive $\Delta\varepsilon$ and the occurrence of ordered smectic phases (enantiotropic or monotropic), but the desirable phase sequence S_C^*, S_A, N^*, *I* could be obtained, and the ferroelectric response times obtained were fast (indicating a low viscosity).

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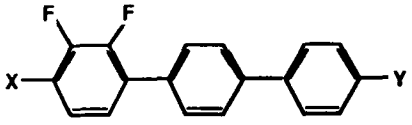
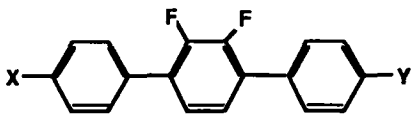
To achieve T_R values < 20 μs, structural improvements to the host were needed, and it was thought that beneficial effects would stem from difluoro-*p*-terphenyls (DFT) of structures (III) and (IV), where again $X = R',R'O$; $Y = R,RO$.



(III)



(IV)

The molecules would be no broader than those of the compounds (II) by using this positioning of the two fluorines; no very adverse effect on viscosity would therefore arise, and the second fluorine should both make $\Delta\varepsilon$ negative and supplement the ordered smectic phase-depressing effect of a single fluorine. As will be seen, beneficial effects on the physical properties of the materials have arisen from these structural changes, and they make excellent S_C hosts.

Full experimental details and data on the systems (III) and (IV) are to be published,[11] but this presentation serves to extract and present the salient features of their preparation and value as ferroelectric hosts.

Synthetic Routes

The availability of 4-bromo-2-fluorobiphenyl and the use of standard reactions make the monofluoro-*p*-terphenyls (II) quite readily accessible. Bromo-difluorobiphenyls are not however available as starting materials. The precursor had to be 1,2-difluorobenzene, and a critical factor in the synthesis has been the ability to monolithiate *ortho*- to one of the aryl fluorines. Methods were then optimised for preparation of the boronic acid from the lithio-compound and for coupling[12] with aryl bromides/iodides in the presence of tetrakis(triphenylphosphine)palladium(0) as catalyst[13] to yield difluorobiphenyls which could then be *ortho*-lithiated next to the second fluorine and converted to the boronic acid. Palladium catalysed coupling, again using appropriate aryl bromides/iodides, made all the DFT's (IV) available. The use of the *o*-boronic acid prepared from 1,2-difluorobenzene to prepare 1-alkoxy-2,3-difluorobenzenes (*via* the phenol[14]) and 1-alkyl-2,3-difluorobenzenes then made available all the DFT's (III) and also any of the analogous difluorobiphenyls—see the following scheme.

This elegant combination of procedures makes available any 2,3-difluorobiphenyl, 2,3-difluoro-*p*-terphenyl or 2′,3′-difluoro-*p*-terphenyl with any combination of alkyl and/or alkoxy groups in the terminal 4,4′- or 4,4″-positions. The overall yields are very good (37–90%; normally 70–80%). These valuable materials, which it is interesting to note would have been accessible ten years ago only by tedious and low yield procedures, are therefore now readily available and are viable systems for practical applications.

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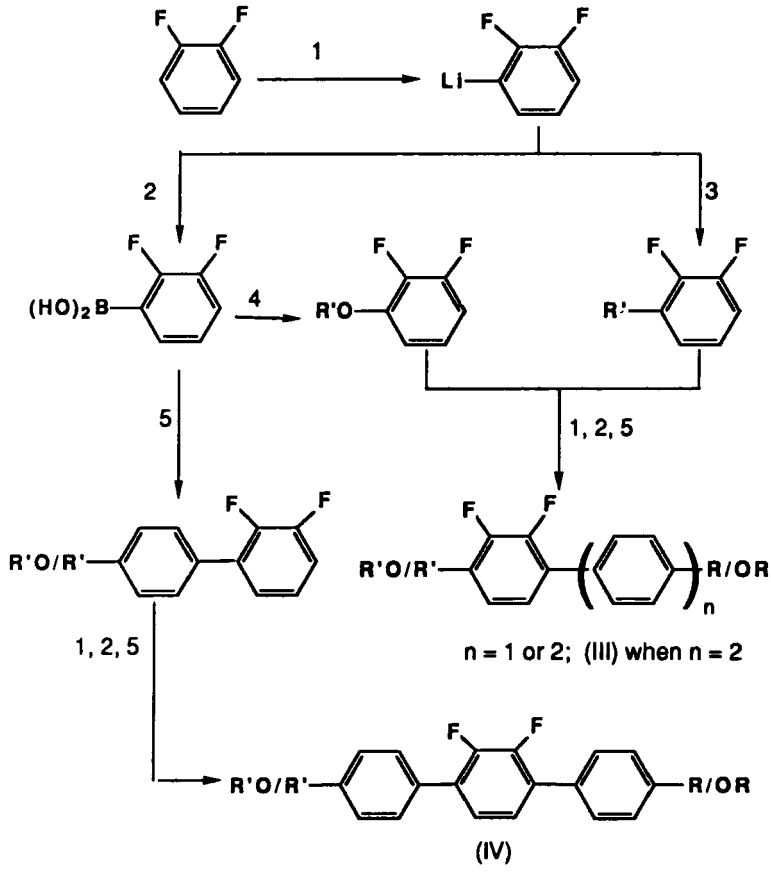

1. ^{n}BuLi, THF
2. $(^{i}PrO)_3B$, THF, −78°; 10% HCl, RT
3. R″CH_2CHO, THF, −78°; P_2O_5, pentane; 5% Pd/C
4. 10% H_2O_2, Et_2O; R′Br, acetone, K_2CO_3
5. ArBr, EtOH, benzene, 2M Na_2CO_3, $Pd(PPh_3)_4$, 95°;

where: Ar = 4-alkoxy- or 4-alkyl-phenyl or -biphenylyl

Many homologues of the difluoroterphenyls of structures (III) and (IV) have been prepared and examined, but the essential features of their phase behaviour are illustrated by the transition temperatures for the six materials given in Table I.

The difluoro-compound (IV) with $X = Y = C_5H_{11}$ is a pure nematogen (K 60° N 120° I), and to promote S_C properties materials with chains shorter than C_5H_{11} or $C_6H_{13}O$ have not been made for series (III) or (IV). Direct comparisons with the monofluoroterphenyls (II)[8,9] can therefore be made in only one or two cases because of the homologues studied in that work.[8,9] However, the smectic-depressing properties of the single fluoro-substituent seem to be further enhanced by the additional fluorine, as no smectic phases more ordered than S_I have been found

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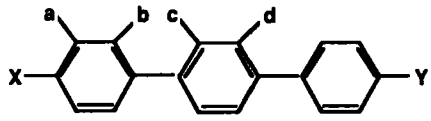
Table I Transition Temperatures (°C) for Difluoroterphenyls (III and IV)



X	Y	a	b	c	d	K	S_C	S_A	N	I
C_7H_{15}	C_5H_{11}	H	H	F	F	* 36.5	(* 24)	.....	* 111.5	*
C_5H_{11}	C_7H_{15}	F	F	H	H	* 65.5†	* 118.5	* 135	* 137	*
C_7H_{15}	C_5H_{11}	F	F	H	H	* 56 *	* 105.5	* 131	* 136	*
$C_6H_{13}O$	C_5H_{11}	H	H	F	F	* 54	* 67	.....	* 149	*
$C_6H_{13}O$	C_5H_{11}	F	F	H	H	* 97.5	* 145.5	.....	* 166	*
C_5H_{11}	$C_6H_{13}O$	F	F	H	H	* 101.5	* 156.5	* 167	* 171.5	*

†Also S_I-S_C at 74.5°

in the systems (III) and (IV). At the same time, the S_C properties of the difluoro-compounds are pronounced, five of the six compounds in Table 1 showing enantiotropic S_C phases that in four cases are of wide range. It is also clear that difluorination in an end ring is more favourable to S_C properties than in the middle ring, but generally speaking, m.p.s. are lower for the compounds with fluorines in the middle ring. The highest S_C thermal stabilities occur for the alkoxy/alkyl compounds with difluorination in an end ring, but the most favourable phase sequence (S_C, S_A, N, I) for FLC applications is not produced until longer chain lengths when the difluorinated ring carries the alkoxy group (X = $C_8H_{17}O$; Y = C_5H_{11}:K 93.5° S_C 144° S_A 148° N 159° I). These and other comparative features are illustrated in the bar diagram (Figure 1).

The fairly low m.p.s. of the DFT's, their broad S_C ranges and the fact that in many cases they exhibit the correct phase sequence for good alignment are attractive features, and our colleagues at RSRE, Malvern have shown[15] that interesting low m.p. mixtures can be produced from the compounds e.g.,

K 21° S_C 90.4° S_A 109.6° N 132.8° I (Mixture A)

and

K 15.5° S_C 91.5° S_A 97.2° N 127° I (Mixture B)

No more ordered smectic phases are observed for such mixtures prior to crystal-

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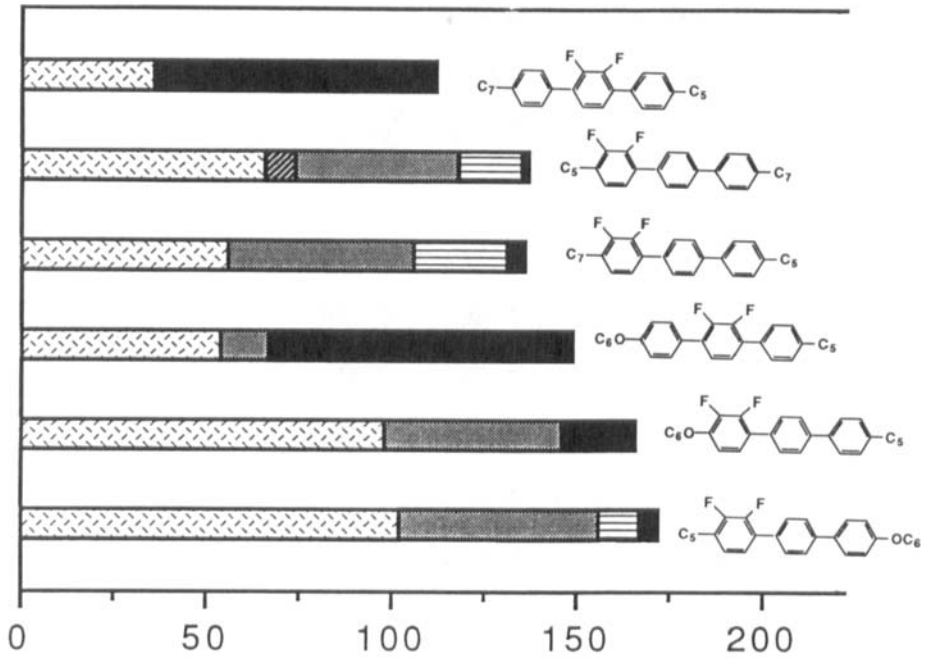

FIGURE 1 Phase behaviour of the difluoroterphenyls (III) and (IV).

lisation. In addition, analogous difluorobiphenyls (see reaction scheme where n = 1) are available (Table II) for further mixture modification.

The mixture B has $\Delta\varepsilon = -1.9$ and $\Delta n = 0.19$, but the dielectric anisotropies of the terphenyls with an alkoxy-difluoro-end group are much more negative (-4.2) than those with alkoxy/alkyl end groups and the fluorines in the middle ring or those with two terminal alkyl groups.[15] Useful mixtures consisting of only alkoxy/alkyl terphenyls can therefore be more strongly negative (e.g. $\Delta\varepsilon = -2.7$) and even when such a mixture exhibits only a S_C, N, I sequence, addition of a chiral dopant of the cyanohydrin ester type, e.g., compound (I) can induce S_A properties in the mixture, giving the correct sequence.[15] The cyanohydrin ester dopants mix well with the DFT's giving Ps values of up to about 40 nCcm^{-2}, dependent upon dopant concentration, and long pitch lengths, as measured for the N^* phase.

Such mixtures give[15] fast response times, confirming the relatively low viscosities of the DFT's (35–80 cS for the dialkyl systems and 60–130 cS for the alkoxy/alkyl systems, the lower values in each case being for difluorination in the central ring). S_C tilt angles are close to ideal (22.5°). Response times for ferroelectric cells depend of course upon dopant concentration and Ps of the mixture, but values of 3 μs for T_R (10 v/μm) have been recorded (Ps between 30 and 40 nCcm^{-2}) and a value of 1 μs has been obtained at a temperature of 30°C.

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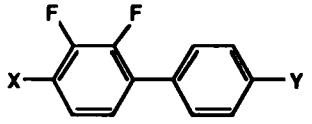
Table II Transition Temperatures (°C) for Difluorobiphenyls



X	Y	K	SC	SA	N	I
C_9H_{19}	$C_8H_{17}O$	• 25	(• 11.5)	• 33	• 34	•
$C_8H_{17}O$	C_7H_{15}	• 24	(• 6	• 13	• 23)	•

$X = C_7H_{15}$; $Y = C_5H_{11}$: K 0.5° I

These difluorinated oligophenyls, in combination with cyanohydrin ester dopants, therefore provide very good FLC materials for fast switching devices. The aligning properties on rubbed polymers are good and they have a multiplexing capability consistent with video line address times at room temperature. Mixtures incorporating DFT's are already available from BDH Ltd, Poole, Dorset, UK.

EXPERIMENTAL

(a) *Materials:* As noted earlier, full experimental details for the synthesis of these materials and evidence for their purities (> 99.9%) and structures are to be published elsewhere.
(b) *Transition temperatures* were obtained by optical microscopy (Mettler FP5 hot stage and control unit and an Olympus polarising microscope) and confirmed by DSC (Perkin-Elmer DSC-2C and data station).

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References

1. D. Bishop, J. A. Jenner and I. C. Sage, *Proc. 11th Int. Liq. Cryst. Conf.*, Berkeley, U.S.A. (1986).
2. M. F. Bone, M. J. Bradshaw, L. K. M. Chan, D. Coates, J. Constant, P. A. Gemmell, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **164**, 117 (1988).
3. G. W. Gray, A. Jackson, D. Lacey, R. M. Scrowston and K. J. Toyne, *Proc. 12th Int. Liq. Cryst. Conf.*, Freiburg, FRG (1988).

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4. G. W. Gray, R. M. Scrowston, K. J. Toyne, D. Lacey, A. Jackson, J. Krause, E. Poetsch, G. Weber and A. Wachtler, German Pat. DE 37 12995 A1 (1988).
5. G. W. Gray, D. Holmes, X. J. Hong, D. Lacey, R. M. Scrowston and K. J. Toyne, *Proc. 12th Int. Liq. Cryst. Conf.*, Freiburg, FRG (1988).
6. M. F. Bone, D. Coates, G. W. Gray, K. J. Toyne and D. J. Young, *Mol. Cryst. Liq. Cryst. Lett.*, **3**, 189 (1987).
7. G. W. Gray, *Rank Prize Funds Symposium*, Ledbury, UK (1987); M. J. Bradshaw, V. Brimmell, J. Constant, J. R. Hughes, E. P. Raynes, A. K. Samra, L. K. M. Chan, G. W. Gray, D. Lacey, R. M. Scrowston, I. G. Shenouda and K. J. Toyne, *Proc. S.I.D.*, **29**, 245 (1988); L. K. M. Chan, G. W. Gray, D. Lacey, R. M. Scrowston, I. G. Shenouda and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **172**, 125 (1989).
8. L. K. M. Chan, G. W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **123**, 185 (1985).
9. L. K. M. Chan, G. W. Gray, D. Lacey, T. Srithanratana and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **150b**, 335 (1987).
10. L. K. M. Chan, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **158B**, 209 (1988).
11. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc. Perkin 2*, to be published.
12. N. Miyaura, T. Yanagi and A. Susuki, *Synth. Commun.*, **11**, 513 (1981); R. B. Miller and S. Dugar, *Organometallics*, **3**, 1261 (1984).
13. D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
14. M. F. Hawthorne, *J. Org. Chem.*, **22**, 1001 (1957); R. L. Kidwell, M. Murphy and S. D. Darling, *Org. Synth.*, **49**, 90 (1969).
15. J. Constant, E. P. Raynes and A. K. Samra, presented at the British Liquid Crystal Society Meeting, Sheffield, April 1989.

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