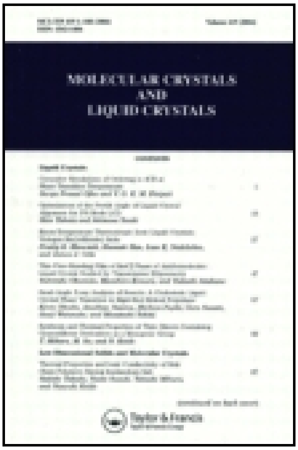


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Physical Properties of Fluorine Derivatives of 4-Cyanobiphenyls

D. G. Mcdonnell [a] , E. P. Raynes [a] & R. A. Smith [a]
[a] Royal Signals and Radar Establishment, Malvern, Worcs, WR14 3PS, United Kingdom

To cite this article: D. G. Mcdonnell , E. P. Raynes & R. A. Smith (1985): The Physical Properties of Fluorine Derivatives of 4-Cyanobiphenyls, Molecular Crystals and Liquid Crystals, 123:1, 169-177

To link to this article: http://dx.doi.org/10.1080/00268948508074775

Mol. Cryst. Liq. Cryst., 1985, Vol. 123, pp. 169–177
0026-8941/85/1234–0169/$15.00/0

Printed in the United States of America

The Physical Properties of Fluorine Derivatives of 4-Cyanobiphenyls†

D. G. McDONNELL, E. P. RAYNES and R. A. SMITH

Royal Signals and Radar Establishment, Malvern, Worcs, WR14 3PS, United Kingdom.

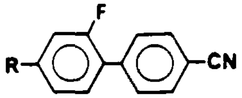
(*Received September 10, 1984*)

The physical properties of two new series of liquid crystalline materials, the 2- and 2′-fluoro-substituted derivatives of the 4-n-alkyl-4′-cyanobiphenyls, have been examined and compared to their unfluorinated analogues. The presence of the lateral fluorine substituent is found to suppress both the injected smectic phases found in the hybrid mixtures with esters, which are designed for use in multiplexed displays, and the strong anti-parallel correlations normally present in cyanobiphenyls.

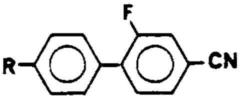
INTRODUCTION

The use of lateral fluorine substitution in benzoate and cyclohexane carboxylate esters has been shown[1] to depress the smectic phase thermal stability in these materials compared to their unfluorinated analogues. This property is particularly advantageous since in the formulation of hybrid mixtures of esters and strongly polar nematogens, suitable for use in multiplexed twisted nematic displays,[2,3] injected smectic phases can be troublesome. Ifill has recently reported the synthesis of the 2- and 2′-fluoro derivatives of the 4-n-alkyl-4′-cyanobiphenyls, see ref 4.

4-n-alkyl-4′-cyano-2-fluoro-biphenyl



4-n-alkyl-4′-cyano-2′-fluoro-biphenyl



---

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

In this paper we examine the physical properties of these new materials and assess their use as positive dielectric anisotropy dopants in mixtures designed for use in high level multiplexed twisted nematic displays.

EXPERIMENTAL METHODS

Transition temperatures were measured using a polarising microscope fitted with a Mettler FP52 heating stage and FP5 control unit. Bulk viscosities were measured to an accuracy of 3% using a Brookfield rotating cone viscometer whose temperature was controlled over the range −15°C to +85°C by a circulating thermostated fluid. The dielectric permittivities were determined to an absolute accuracy of 1% from the capacitance of a parallel plate capacitor surrounded by a 'guard' electrode and measured both empty and full of liquid crystal. The temperature was controlled to within 0.1°C over the range 0°C to 100°C using thermostated dry nitrogen gas. $\epsilon_\perp$ was determined directly from low voltage data using electrodes coated with SiO_x, and $\epsilon_\parallel$ by extrapolating the high voltage data.[5] Splay and bend elastic constants (K_{11} and K_{33}) were calculated by fitting the detailed capacitance-voltage data from the permittivity determination to the continuum theory, using a three parameter non-linear least-squares fitting program.[2] The estimated accuracy of this determination is 2% for K_{11} and 5% for K_{33}. The molecular dipole moments (μ) were obtained from the dielectric permittivities and refractive indices measured for dilute solutions.[6] Refractive indices were measured to an accuracy of 0.01% at 589.6 nm (D_1 sodium line) using an Abbé refractometer with prisms coated with lecithin to induce homeotropic alignment of the liquid crystal. The electro-optic properties were determined in 8 μm, low tilt, twisted nematic devices using standard methods and nomenclature.[7]

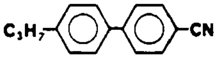
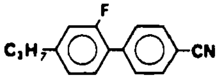
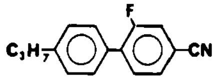
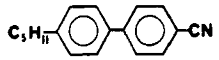
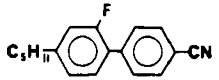
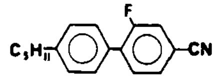
PHYSICAL PROPERTIES OF THE COMPOUNDS

The transition temperature of the fluorinated and unfluorinated biphenyls studied are given in Table I together with their acronyms.

The relative tendencies of the materials to form injected smectic phases were studied by examining binary mixtures of the pentyl de-

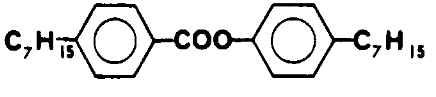
TABLE I

4-n-alky-4'-cyanobiphenyls and 2- and 2'-fluoro-derivatives

Structure	Acronym	mpt (°C)	N–I (°C)	Ref
	3CB	66	(25.5)	8
	2F3CB	89.6	[−11]	4
	2'F3CB	71.3	[7]	4
	5CB	22.5	35.0	8
	2F5CB	59.0	[0]	4
	2'F5CB	51.0	[21.6]	4

[ ] denotes a virtual transition
( ) denotes a monotropic transition

rivatives with the long alkyl chain benzoate ester ME 77 (BDH Chemicals Ltd).

ME 77  Nematic Range 26–33°C

The results in Figure 1 show the S_A–N transition temperatues as a function of composition. The presence of the fluorine in either the 2- or 2'- positions of the cyanobiphenyl causes a large reduction in the temperature of the injected smectic phase and also shifts the peak slightly towards the ester end of the phase diagram.

Measurements of viscosities of the pentyl derivatives were made using dilute solutions in the PCH mixture ZLI 1132 (E Merck) followed by extrapolation to 100% cyanobiphenyl using the Arrhenius equation for the viscosity of mixtures.[9] The resulting extrapolated viscosities are reported in Table II and show a small increase for the fluorinated compounds. The solubilities of the propyl derivatives were too low for meaningful measurements to be made.

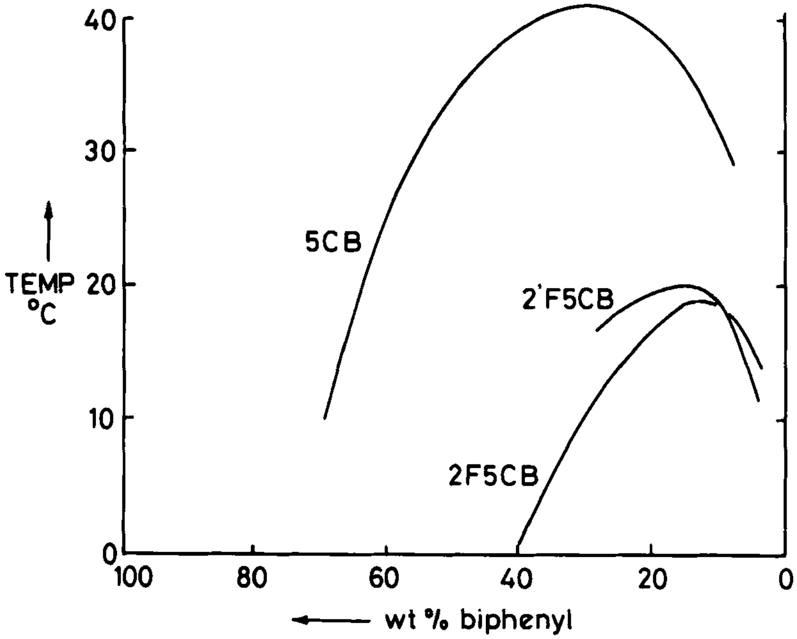


FIGURE 1 Variation in T_{S-N} of mixtures of pentyl cyanobiphenyl derivatives with ME 77.

The isotropic permittivities for the pentyl derivatives are shown in Figure 2. The differences in the magnitude and slopes of the three curves reflect the variation in the dipole moments (μ) of the compounds as well as the extent to which each material shows anti-parallel ordering. The extent of the latter effect is given by the Kirkwood correlation factor (g), which relates the actual dipole (μ), measured from dilute solution, with the effective dipole (μ eff) calculated from the isotropic permittivity.[12]

$$\mu^2 = \mu^2 \text{ eff} \cdot g$$

TABLE II

Extrapolated viscosities

Material	η 0°C (cps)	η 20°C (cps)
5CB	138	34
2F5CB	168	39
2'F5CB	207	41

TABLE III

Dipole moments and Kirkwood factors

	μ (D)	*g* (65°C)
5CB	4.8	0.53
2F5CB	5.2	0.67
2'F5CB	4.2	0.62

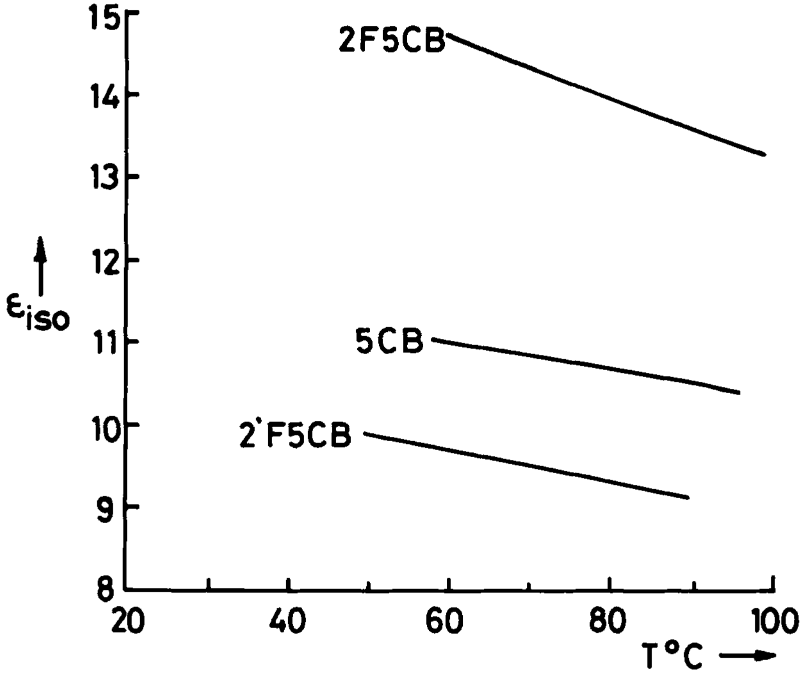
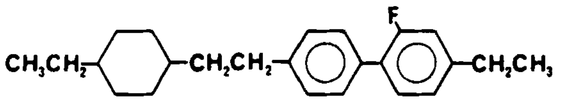


FIGURE 2 Isotropic permittivities of the pentyl cyanobiphenyl derivatives.

The dipole moments and Kirkwood correlation factors given in Table III indicate that the fluorinated materials have less anti-parallel ordering at 65°C than 5 CB. The dipole moment values also clearly reflect the position in the molecules of the fluorine substitution.

Since the neat fluorinated materials do not exhibit an enantiotropic nematic phase, the dielectric anisotropies as a function of reduced temperature (T/T_{N-I}) were determined in solutions of I 22[10] containing 10% by weight (Figure 3). This gives a direct measure of the usefulness of the compounds as positive dielectric anisotropy dopants.

I 22



Nematic Range
14–66°C

I 22 was chosen for its wide nematic range and low polarity, $\epsilon_{\parallel} = 3.0$ and $\epsilon_{\perp} = 3.0$. It is interesting to note that the dielectric anisotropies in dilute solution shown in Figure 3 are not significantly affected by any anti-parallel ordering and are therefore approximately proportional to the square of the molecular dipole moments reported in Table III, as predicted by the Maier-Meier theory.[13]

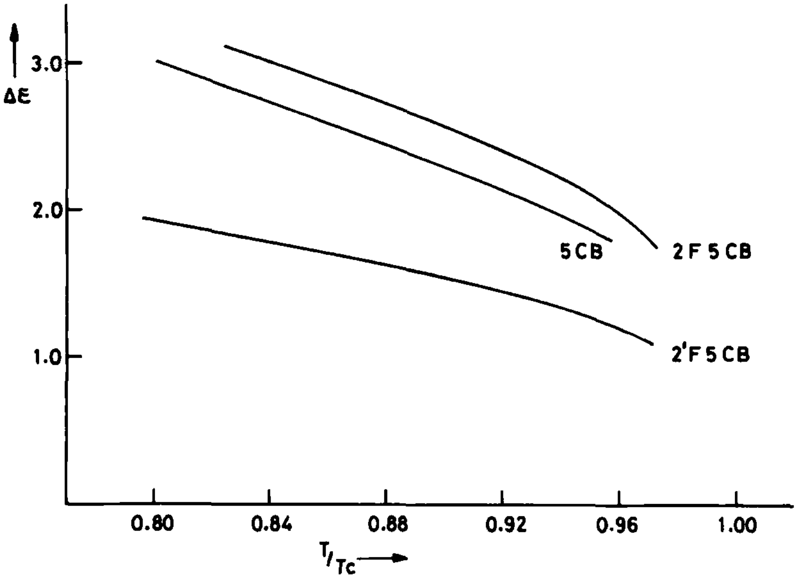


FIGURE 3 Dielectric anisotropies of mixtures of the pentyl cyanobiphenyl derivatives with I 22.

MIXTURES FOR HIGH LEVEL MULTIPLEXING

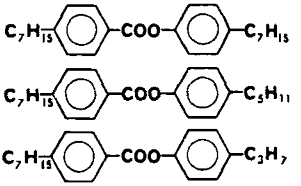
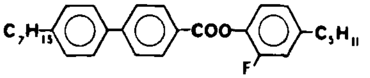
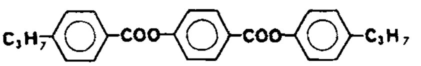
The large dielectric anisotropies of the fluorinated cyanobiphenyls, coupled with their low tendency to form injected smectic phases makes them useful materials as positive dielectric anisotropy dopants in mixtures for high level multiplexed twisted nematic displays. We use as a basis for our assessment the hybrid mixtures described by Sturgeon[11] which were derived from the weakly polar ester mixture 1 (Table IV) doped with 4-n-alkyl-4′-cyanobiphenyls.

We investigated the effect of the fluorinated cyanobiphenyls on the thermal stability of the injected smectic phase with Mixture 1. The results in Table V show a very useful depression of about 20°C in the smectic-nematic transition temperatures compared to the unfluorinated materials.

These mixtures demonstrate that the fluorinated cyanobiphenyls considerably depress the injected smectic phase while the physical and electro-optic properties (Table VI) maintain their excellent characteristics for application to high level multiplexed twisted nematic displays. A further point to note is that since the constraint of the

TABLE IV

Weakly polar ester mixture 1

		Weight %	Nematic range
	Ternary Eutectic	72	-10 – 58°C
		18	
		10	

smectic phase has been reduced, additional reformulation of the mixture to a new optimum may be considered. Such work is outside the scope of this paper.

CONCLUSION

The 4-n-alkyl-2- and 2'-fluoro-4'-cyanobiphenyls do not exhibit enantiotropic nematic phases so their physical properties have been studied in the isotropic phase and in dilute solutions with nematic solvents. These show that the strong anti-parallel ordering normally present in cyanobiphenyls has been reduced by the introduction of

TABLE V

S–N transition temperatures for mixture 1 with 5 wt % of positive $\Delta\epsilon$ component

Positive $\Delta\epsilon$ component	S-N (°C)
3CB	$+2$
2F3CB	< -20
2'F3CB	< -20
5CB	$+11$
2F5CB	-6
2'F5CB	-11

TABLE VI

Physical properties of mixture 1 with 5 wt % positive $\Delta\epsilon$ component

Property		Positive $\Delta\epsilon$ Component		
		2CB	2F3CB	2'F3CB
N-I	(°C)	59	55	58
S-N	(°C)	-7.4	<-20	<-20
Δn at 589.6 nm	(20°C)	0.14	0.14	0.14
V_{90} (0°) at 20°C		3.72	3.53	4.44
M_{20}		1.55	1.55	1.57
M'_{20}		1.22	1.22	1.23
$1/V_{Th}\,\dfrac{dV_{Th}}{dT(0°C\rightarrow30°C)}$		0.93	0.74	0.85
$\Delta\epsilon$	(20°C)	1.86	1.94	1.27
$K_{11}\times10^{-12}$ N	(20°C)	15.6	14.3	15.3
K_{33}/K_{11}	(20°C)	0.78	0.83	0.81
$\Delta\epsilon/\epsilon_{\perp}$	(20°C)	0.44	0.45	0.30

$$M_{20} = \frac{V_{10}\,(0°)}{V_{90}\,(45°)} \text{ at } 20°\mathrm{C}$$

$$M'_{20} = \frac{V_{50}\,(10°)}{V_{90}\,(45°)} \text{ at } 20°\mathrm{C}$$

the lateral fluorine substituents. In hybrid mixtures with esters the fluorinated cyanobiphenyls show a much reduced tendency to form injected smectic phases than the unfluorinated cyanobiphenyls, whilst preserving the excellent multiplexing properties. The fluorinated cyanobiphenyls therefore are attractive for use as positive dielectric anisotropy dopants in hybrid mixtures for use in high level multiplexed twisted nematic displays.

Acknowledgments

We gratefully acknowledge our colleagues at Hull University, BDH Chemicals Ltd. and E. Merck for supplying the liquid crystal materials and Miss J Allmann and Dr. M. J. Bradshaw for advice on the molecular dipole moment measurements.

References

1. G. W. Gray, D. Lacey, and C. Hogg, *Mol. Cryst. Liq. Cryst.*, **67**, 1 (1981).
2. M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **91**, 145 (1983).
3. M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **99**, 107 (1983).

4. J. E. Fearon, G. W. Gray, A. D. Ifill and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, in press.
5. M. G. Clark, E. P. Raynes, R. A. Smith, and R. J. A. Tough, *J. Phys. D : Appl. Phys.*, **13**, 2151 (1980).
6. N. F. Hill, W. E. Vaughan, A. H. Price and M. Davies, "*Dielectric Properties and Molecular Behaviour*," Van Nostrand Reinhold, London, 1969.
7. E. P. Raynes, *IEEE Trans. Electron. Devices*, **ED-26**, 1116 (1979).
8. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, "*Liquid Crystals and Ordered Fluids*," (eds. J. F. Johnson and R. S. Porter) Plenum Press, New York, 1974.
9. J. Constant and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **62**, 115 (1980).
10. I. Sage, P. Balkwill, D. Bishop, and A. Pearson, *Mol. Cryst. Liq. Cryst.*, in press.
11. B. Sturgeon, *Phil. Trans. Roy. Soc. Lond.*, **A309**, 231 (1983).
12. J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).
13. W. Maier and G. Meier, *Z. Naturforsch.*, **16a**, 262 (1961).