Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Gray, G. W. , Lacey, D. , Stanton, J. E. and Toyne, K. J.(1986) 'The effect of lateral fluoro-substitution on the liquid crystal behaviour of some 4'-alkylphenylethyl- and trans-4'-alkylcyclohexylethyl-4,4'-disubstituted biphenyls', Liquid Crystals, 1: 5, 407 — 413

To link to this Article: DOI: 10.1080/02678298608086265

URL: http://dx.doi.org/10.1080/02678298608086265

LIQUID CRYSTALS, 1986, VOL. 1, NO. 5, 407–413

The effect of lateral fluoro-substitution on the liquid crystal behaviour of some 4″-alkylphenylethyl- and trans-4″-alkylcyclohexylethyl-4,4′-disubstituted biphenyls[†]

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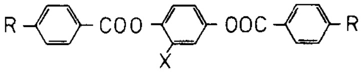
(*Received 29 May 1986; accepted 29 June 1986*)

The preparation of several 4″-alkylphenylethyl- and trans-4″-alkylcyclohexylethyl-4,4′-disubstituted biphenyls and their 2-fluoro derivatives is described and their transition temperatures are reported. The effect on the transition temperatures caused by the replacement of a cyclohexane ring by a benzene ring and the effect of fluoro-substitution on nematic, smectic A and smectic B thermal stabilities is discussed. In these systems, and in others, when the lateral fluoro-substituent points towards the longer terminal aliphatic unit (alkyl or alkylcyclohexylethyl) it causes a greater depression of smectic properties.

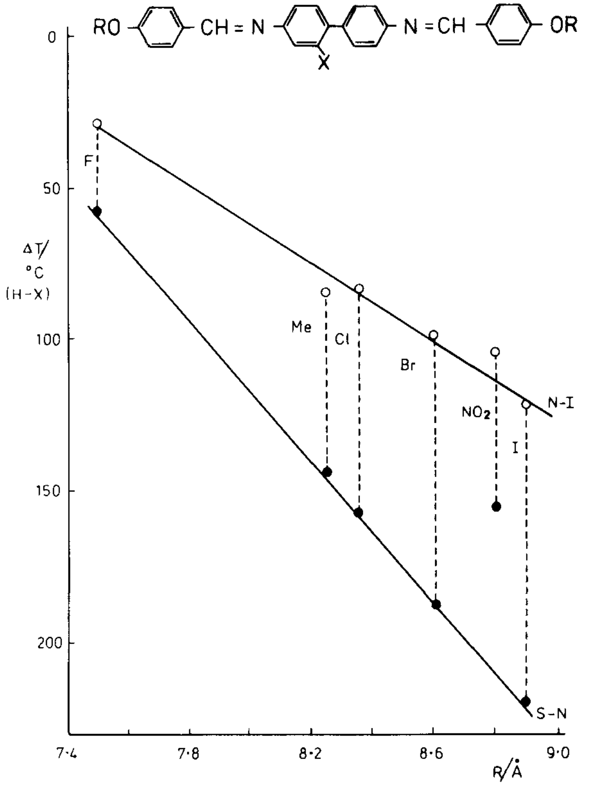
Fluoro-substitution of organic molecules has, in recent years, provided a wide range of useful, novel compounds [1]. For example, the properties of pharmaceuticals, pesticides and dyes can be changed fundamentally by fluoro- mono-substitution and, even more recently, it has been shown that such substitution leads to a significant improvement in some of the properties of liquid crystals used in electro-optic display devices [2–4]. In all of these examples fluorine shows its exceptional behaviour because it is both the smallest possible substituent (van der Waals radius for hydrogen is 1·2 Å and for fluorine is 1·35–1·47 Å) and the most electronegative element (the electronegativities of chlorine, oxygen and fluorine are 3·0, 3·5 and 4·0 respectively). In the context of the physical properties of liquid crystals, both of these features can be advantageous because the small size of the fluoro-substituent leads to the least possible disruption of the lath-like nature of a molecule with a lateral fluorine substituent, and the polarity of the C–F bond may lead to increased values of the dielectric anisotropy.

The effect of lateral substituents in many systems has been considered in the past few years, with regard to the effect on clearing temperatures and other physical properties (e.g. in systems of type I [5, 6]), and a general review of the effects of lateral substituents has appeared [7]. However the crucial advantage which arises from the presence of a lateral fluoro-substituent in systems of low polarity was demonstrated



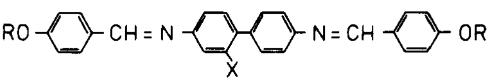
(I)

[†] Presented at the Annual Meeting of the British Liquid Crystal Society, University of Manchester, 24–26 March 1986.



Depressions in smectic A–nematic and nematic–isotropic transition temperatures plotted against the molecular breadth (defined as the diameter of the narrowest cylinder through which the molecule may pass, flexible alkyl chains being assumed not to interfere).

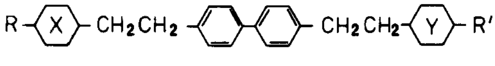
more than 20 years ago for lateral substituents in compounds II [8]. The summarized results from that work are given in the figure which shows how lateral substituents


(II)

depress the smectic A–nematic transition much more than the nematic–isotropic transition; the plot of T_{NI} exhibits a regular depression to which all the substituents conform (including dipolar substituents) whereas the T_{S_AN} for the dipolar nitro-substituent is higher than the general trend, probably because dipolar attractions are stabilizing the more condensed smectic phase [8]. In addition to a slight increase in molecular breadth caused by the fluoro-substituent, the biphenyl system (II), and the other biphenyl and terphenyl systems reported in this paper, have an increased molecular twist because of the steric interaction between the fluoro-substituent and the ortho-hydrogen atoms in the neighbouring ring. However, once again, the fluoro-substituent should have less effect than any other substituent in twisting the molecule and thereby reducing conjugation between the rings [9].

The other feature of fluoro-substitution is that the polar substituent can lead to increased values of positive dielectric anisotropy as has been shown in cyanobiphenyl systems [10, 11] and, most dramatically, in 4-cyano-3-fluorophenyl esters [12, 13]. In such terminal cyano compounds, the fluoro-substituent can have a pronounced effect on the extent of antiparallel correlation in the parent systems.

Because fluoro-substitution gives a greater depression in smectic thermal stability and, in many instances, causes the complete disappearance of enantiotropic smectic phases, it has not been possible previously to assess the real effect of fluoro-substitution on different types of smectic phase. However, we have found that fluoro-substitution in compounds of type III does allow a few comparisons to be



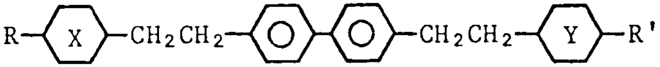
(III)

made of the effect of the presence of fluorine on nematic, smectic A and smectic B phases. The transition temperatures for the parent compounds with various combinations of substituted cyclohexyl and phenyl rings (X, Y = trans-cyclohexyl or phenyl) are shown in table 1. The compounds with X and/or Y equal to benzene further illustrate the now generally recognized detrimental effect on liquid crystal properties of separating flat, π systems from each other. Comparing compounds 1 and 4 shows that smectic A thermal stability has decreased by 14·4°C and the non-existent nematic phase has been suppressed by at least 27·1°C; comparison of the values for compounds 3 and 5 shows that the clearing point is decreased by 27·5°C.

The transition temperatures for the fluorinated compounds prepared are shown in table 2 and the values in parentheses give the reduction in the phase transitions caused by incorporation of fluorine. These results allow a comparison to be made of the effect of fluoro-substitution on nematic, smectic A, smectic B and, in some instances, smectic J thermal stability. In the examples where comparisons can be made, the depressions for the transitions increase in the order N–I < S_A–N < S_B–S_A (with the exception of compound 7, for which the depressions in $T_{S_BS_A}$ and T_{S_AN} are similar). These results would appear to extend the general observation referred to here (i.e. that fluorine depresses the thermal stability of a smectic phase more than that of a less condensed nematic phase), to include the effect on thermal stability of the even more condensed smectic B phase, for which the fluoro-substitution gives an even greater depression. Probably this superficial comparison of the density of packing in smectic B and A phases is acceptable because in both phases molecules are orthogonal to the layer plane, but comparison with a tilted phase, such as the smectic J phase present in some of these compounds, is not so reasonable because of the different nature of the molecular packing.

Another interesting result to emerge from the values in table 2 is for the compounds 6/7 and 8/9, which are isomeric pairs for which one can either regard the terminal alkyl chains as being interchanged or the fluoro-substituent as being moved from the position shown in the structure in the table to the ortho-position in the other ring of the biphenyl unit. In each of these pairs, the 2- or 2′-fluoro-substituent is almost centrally placed and should occupy almost the same position relative to each of the two rings of biphenyl. Indeed this close similarity between the structures of the isomeric pairs leads to an almost identical effect on the nematic–isotropic transition (20·9/19·8°C and 20·8/20·2°C). However, for each pair, the effect on the transition temperatures of the orthogonal smectic phases differs significantly—compounds 7 and 9 having lower smectic thermal stabilities than compounds 6 and 8 respectively, i.e. the *higher* smectic A and B thermal stabilities are shown for compounds in which the

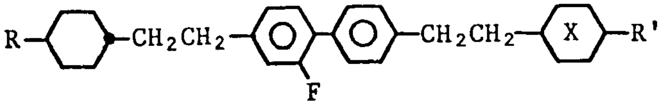
Table 1. Transition temperatures (°C) for compounds.



Compound	*R*		*R′*		C–C	C–S_J	S_J–S_B	S_B–S_A	S_A–N	S_B/S_A/N–I
1	C_5H_{11}		C_3H_7		—	65·8	146·8	190·8	214·2	226·9
2	C_7H_{15}		C_3H_7		—	30·0	142·0	195·6	213·1	218·3
3	C_5H_{11}		C_5H_{11}		68·0	81·6	156·8	202·2	—	224·5
4	C_3H_7		C_5H_{11}		—	—	120·0	195·5	—	199·8
5	C_5H_{11}		C_5H_{11}		—	—	93·0	—	—	197·0

Smectic phases were identified by optical microscopy and confirmed by X-ray analysis (by Dr. R. M. Richardson, University of Bristol).

Table 2. Transition temperatures (°C) for compounds.



Compound	*R*	*R′*		C–S_B	S_J–S_B	S_B–S_A	S_A–N	N–I
6	C_5H_{11}	C_3H_7		—	81·3 (65·5)	110·1 (80·7)	139·0 (75·2)	206·0 (20·9)
7	C_3H_7	C_5H_{11}		76·4	—	103·5 (87·3)	123·3 (90·9)	207·1 (19·8)
8	C_7H_{15}	C_3H_7		—	54·0 (88·0)	137·0 (58·6)	170·1 (43·0)	197·5 (20·8)
9	C_3H_7	C_7H_{15}		—	66·4 (75·6)	128·6 (67·0)	165·0 (48·1)	198·1 (20·2)
10	C_5H_{11}	C_5H_{11}		85·0	—	132·6 (69·6)	174·7	204·4 (20·1)†
11	C_3H_7	C_5H_{11}		—	60·0 (60·0)	111·4 (84·1)	130·7	174·7 (25·1)†

The values in parentheses are the depressions in the temperature of the phase transition caused by incorporation of the fluoro-substituent.

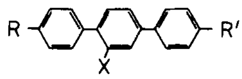
† Decrease = $T_{S_AI}-T_{NI}$.

Smectic phases were identified by optical microscopy (as yet unconfirmed by X-ray analysis).

C–F bond *points towards the shorter* terminal alkyl chain. To reach such a generalization would be unsound simply on the basis of the two comparisons in table 2, but two different systems, exemplified by compounds 12–14 and compounds 15–21, for which the fluoro-substituent is also in a biphenyl-like environment, show a similar effect.

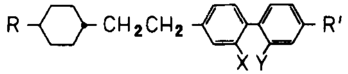
The transition temperatures for compounds 12–14 (see table 3) [14] once again illustrate how the strongly smectic character of the parent system (compound 12) is removed (compound 13) or reduced (compound 14) by fluoro-substitution. The T_{NI} for compounds 13 and 14 are closely similar and the greater smectic character of compound 14 (smectic A stability is at least 50°C higher) is again associated with the C–F bond pointing towards the shorter alkyl group.

Table 3. Transition temperatures (°C) for compounds.



Compound	*R*	*R'*	*X*	C–S_E/S_A/N	S_E–S_B	S_B–S_A	S_A–N	S_A–I	N–I
12	C_5H_{11}	C_3H_7	H	180·0	200·0	214·0	—	218·0	—
13	C_5H_{11}	C_3H_7	F	50·0	—	—	—	—	140·6
14	C_3H_7	C_5H_{11}	F	61·0	—	—	99·5	—	141·5

Table 4. Transition temperatures (°C) for compounds.



Compound	*R*	*R'*	*X*	*Y*	C–S	C–N	S–S	S–N	N–I
15	C_3H_7	C_3H_7	H	H	67	—	—	119	144
16	C_3H_7	C_3H_7	H	F	—	40	—	—	108
17	C_3H_7	C_3H_7	F	H	—	59	—	(34)	108
18	C_5H_{11}	C_2H_5	H	F	—	24	—	(14)	103
19	C_5H_{11}	C_2H_5	F	H	23	—	27	56	104
20	C_5H_{11}	C_5H_{11}	H	F	17	—	34	37	108
21	C_5H_{11}	C_5H_{11}	F	H	—	—	56	92	110

For compounds 15–21 (see table 4) [3, 15] the isomeric pairs of fluoro-compounds have very similar T_{NI} and in each of three cases quoted the greater smectic character in each pair is shown for the case when X = F, i.e. with the C–F bond pointing to the alkyl unit (R'), which is smaller than the trans-cyclohexylethyl unit.

Experimental

Compounds in table 1 were prepared by Friedel–Crafts acylations of biphenyl using a trans-4-*n*-alkylcyclohexylacetyl chloride or a 4-*n*-alkylphenylacetyl chloride followed by reduction of the ketone with triethylsilane in trifluoroacetic acid [16]. A second sequence of reactions gave the required compounds.

Compounds in table 2 were prepared by similar reactions on 1-(2-fluorobiphenyl-4-yl)-2-(trans-4-*n*-alkylcyclohexyl)ethane which was prepared by a cuprous chloride-catalysed reaction of 2-fluorobiphenyl-4-magnesium bromide with trans-4-*n*-alkylcyclohexylacetyl chloride followed by Huang–Minlon reduction of the ketone [15].

trans-4-*n*-Alkylcyclohexylacetyl chlorides and 4-bromo-2-fluorobiphenyl were supplied under M.O.D. Contract DCVD AT/2119/013, by BDH Chemicals Ltd (Poole, Dorset), to whom we express our thanks.

This work was carried out as part of a collaborative programme with the Ministry of Defence (U.K.) and the authors gratefully acknowledge the associated research grant. This paper is published by permission of the Controller, HMSO.

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