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The effect of lateral substitution on smectic C formation

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Two related ester systems having fluoro, chloro, bromo, methyl or cyano lateral substituents have been synthesised. The effect of lateral substitution on the thermal stability of the liquid crystal phases, and particularly the smectic C phase, was examined. In some instances, a small polar group was shown to increase the stability of the smectic C phase relative to the unsubstituted analogue. The position of the lateral substituent is important. Some of the compounds exhibit a very wide smectic C phase.

1. Introduction

There is an increasing interest in displays based on the ferroelectric chiral smectic C phase. These displays offer both very fast response time (μs rather than ms) and, due to the inherent bistability in certain types of display [1], high levels of multiplexing performance are possible. Indeed a 64 × 64 matrix display which can be addressed at video frame rates has recently been demonstrated [2]. One of the basic, vital requirements for such a display is materials which have a low melting point and a wide temperature range smectic C phase; such materials could be used to form wide temperature range smectic C mixtures. These mixtures can then be made ferroelectric by the use of chiral dopants. This work aims to determine how increased smectic C thermal stability can be achieved by the use of lateral substituents.

It has recently been shown [3] that the branching of a terminal alkyl chain can significantly increase the smectic C thermal stability of a compound relative to its *n*-alkyl analogue. The literature cites some instances [4] in which laterally substituted compounds exhibit a wide temperature range smectic C phase. However, the thermal stability is often lower than that of the unsubstituted analogue. To investigate this feature further, two diester systems which inherently exhibit a wide smectic C phase were laterally substituted with a range of small substituents. Large substituents were not examined as they were expected to depress seriously the thermal stability of all the liquid crystal phases.

2. Results

2.1. *Substituted 4-(4-(2-methylbutyloxycarbonyl)biphenylyl)4′-alkoxybenzoates (I)*

In this structure, *X* or *Y* were substituted with fluoro, chloro, bromo, methyl or cyano groups; the transition temperatures, obtained by hot stage optical microscopy and differential scanning calorimetry, are listed in table 1. Results on a few of the laterally substituted compounds have very recently been disclosed [5] and are in agreement with the values given here. For comparison, the unsubstituted analogues

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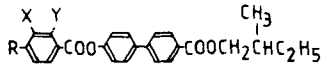
Table 1. Transition temperatures (in °C) for the substituted 4-(4-(2-methylbutyloxycarbonyl)-biphenylyl) 4′-alkoxybenzoates (I).



R	*X*	*Y*	C–S	S_C–S_A	S_A–N or I	N–I
$C_7H_{15}O$	H	H	69·0	119·5	163·3	172·6
$C_8H_{17}O$	H	H	84·0	123·0	166·0	171·8
$C_9H_{19}O$	H	H	83·5	126·7	165·1	168·0
C_8H_{17}	H	H	60·1	87·5	135·1	140·0
$C_8H_{17}O$	Cl	H	88·3	108·0	131·5	138·6
$C_9H_{19}O$	Cl	H	107·6	107·8	131·4	135·8
$C_{10}H_{21}O$	Cl	H	102·8	105·0	131·9	134·4
$C_8H_{17}O$	Br	H	77·3	96·9	119·6	130·1
$C_9H_{19}O$	Br	H	98·5	(97·0)	120·1	127·1
$C_{10}H_{21}O$	Br	H	99·1	(95·2)	123·1	128·0
$C_9H_{19}O$	CN	H	86·8	121·2	152·9	—
$C_{10}H_{21}O$	CN	H	75·5	118·5	152·9	—
$C_8H_{17}O$	CH_3	H	106·0	(79·9)	107·0	129·1
$C_9H_{19}O$	CH_3	H	91·4	(79·7)	109·2	125·3
$C_8H_{17}O$	H	CH_3	75·6	40†	79·1	105·3
$C_9H_{19}O$	H	CH_3	54·3	20†	83·4	102·5
$C_{10}H_{21}O$	H	CH_3	60·5	30†	87·1	102·6
$C_8H_{17}O$	H	Cl	85·6	20†	74·8	113·6
$C_9H_{19}O$	H	Cl	58·0	20†	83·7	111·2
$C_8H_{17}O$	F	H	101·0	121·1	155·7	157·8
$C_9H_{19}O$	F	H	102·8	121·9	154·0	154·6

† Temperature to which the compound was cooled. A smectic C phase was not found.

were also prepared and their properties are also given; these are consistent with the values previously reported [6].

As expected, the nematic to isotropic transition temperature of all the substituted analogues is lower than that of the unsubstituted compounds, the order of nematic phase thermal stability being

$$H < 3F < 3Cl < 3Br < 3Me < 2Cl < 2Me.$$

The 3CN substituent (X = CN) is unusual in giving a smectic A to isotropic transition with the smectic A phase having quite a high thermal stability.

The smectic A thermal stability is also decreased by lateral substitution. In this case the order of smectic phase thermal stability is

$$H < 3F < 3CN < 3Cl < 3Br < 3Me < 2Cl = 2Me.$$

Changes in smectic C thermal stability are more dramatic but the order of smectic C thermal stability is still the same

$$H < 3F < 3CN < 3Cl < 3Br < 3Me < 2Cl \text{ and } 2Me.$$

In all the cases examined, a 2-substituent (Y) lowers the thermal stability of the liquid crystal phase more than the same substituent in the 3-position; this effect is most marked in the smectic C phase. It is clear that smectic A and C phases are

stabilized by polar groups such as cyano, but the steric effect pushing the molecules apart counters this attraction with the net result that a less polar, but smaller substituent is more effective at stabilizing the smectic phase. However, even here the steric effect of fluorine causes a lowering of both smectic A and C phase stability, but only by a few degrees centrigrade for the smectic C to smectic A transition. It might be envisaged that in some systems one, or perhaps two, fluorine groups would increase the stability of the smectic C phase relative to the unsubstituted compound.

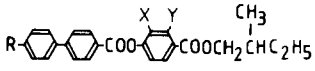
It was hoped that the usual lowering in melting point would occur and that even for materials in which the smectic C stability is lowered this would be countered by a lowering of the melting point. However, this is not the case; only the 2-substituted compounds have lower melting points and these compounds do not exhibit a smectic phase.

2.2. *Substituted 4-(4-(2-methylbutyloxycarbonyl)phenyl)4'-alkoxybiphenyl-4-carboxylates (II)*

Table 2 lists the results when X or Y in the structure is fluoro, chloro, bromo, methyl or cyano together with the unsubstituted compounds. Only the compounds with X = chloro exhibit nematic phases. One major effect of lateral substitution in this case is that the smectic I phase, exhibited by the parent compounds, is absent in the substituted analogues. On supercooling to -15°C there was no evidence, given by differential scanning calorimetry, of a higher ordered smectic phase being exhibited in any of the substituted compounds. This lack of a higher ordered phase could be very useful in smectic C mixture formulation.

A marked distinction between 2- and 3-substituted compounds is evident: the 3-substituted compound (X = chloro), although having a desirable nematic phase, has a much lower smectic C and smectic A thermal stability. The compounds having

Table 2. Transition temperatures (in °C) for the substituted 4-(4-(2-methylbutyloxycarbonyl)-phenylyl) 4'-alkoxybiphenyl-4-carboxylates (II).



R	X	Y	C–S	S_I–S_C	S_C–S_A	S_A–N or I	N–I
$C_8H_{17}O$	H	H	67·0	(61·5)	139·0	187·0	
$C_9H_{19}O$	H	H	52·5	57·0	143·5	184·5	
$C_8H_{17}O$	Cl	H	46·5	—	57·5	128·5	133·7
$C_9H_{19}O$	Cl	H	64·2	—	69·9	126·8	129·3
$C_8H_{17}O$	H	Cl	46·8	—	118·8	158·8	
$C_9H_{19}O$	H	Cl	39·3	—	121·1	155·8	
$C_{10}H_{21}O$	H	Cl	33·2	—	120·9	154·9	
C_8H_{17}	H	Cl	42·5	—	76·4	120·8	
$C_8H_{17}O$	H	CH_3	57·9	—	104·0	149·2	
$C_9H_{19}O$	H	CH_3	56·1	—	108·6	146·0	
$C_{10}H_{21}O$	H	CH_3	55·4	—	109·8	144·3	
$C_8H_{17}O$	H	F	59·5	—	145·0	186·0	
$C_9H_{19}O$	H	F	59·6	—	146·1	182·3	
$C_{10}H_{21}O$	H	F	56·8	—	145·2	180·1	

Y = chloro have lower melting points and exhibit a wide temperature range smectic C phase, for example 33·2°C to 120·9°C for the *n*-decyl homologue.

The 2-fluoro compounds have smectic C to smectic A transition temperatures higher than the unsubstituted analogues, and thus the fluoro group has stabilized the smectic C phase while the smectic A phase in each compound is of similar thermal stability. Therefore the order in which the groups stabilize the smectic C phase for this series of compounds is

$$2Fl > H > 2Cl > 2Me > 3Me.$$

3. Conclusion

The results from both series of laterally substituted esters demonstrate the following:

(i) Small polar groups favour smectic C phases, and can sometimes be preferable to hydrogen.
(ii) A lateral substituent is most efficient at producing a smectic C phase when it is pointing away from the centre of the molecule.
(iii) Lateral substitution in these systems has reduced the occurrence of higher ordered phases.
(iv) In most cases, but not all, the melting point of the unsubstituted analogue is not significantly reduced compared to the unsubstituted compounds. The exceptions to this have provided materials with a low melting point and wide temperature range smectic C phase.

4. Experimental

(1) *2- and 3-chloro-4-hydroxybenzoic acids.* These are commercially available.

(2) *3-Bromo-4-alkoxybenzoic acids.* 4-Alkoxybenzoic acids were prepared [8] by heating under reflux and stirring a mixture of 4-hydroxybenzoic acid (40 g, 0·29 m), alkyl bromide (0·43 m), potassium hydroxide (16·5 g), ethanol (900 ml) and water (100 ml) for 18 hours. To the cooled mixture was added a solution of 10 per cent potassium hydroxide (250 ml) and the mixture heated under reflux for 2 hours. With the longer alkyl chain homologues, the reaction mixture was carefully steam distilled to remove alkanol before being cooled and acidified. The solid was crystallized from ethanol; yield 75–80 per cent.

A finely ground suspension of 4-octyloxybenzoic acid (7 g) was stirred and heated at 55–60°C with water (35 ml); bromine (5 g) was slowly added over 7 hours and the mixture stirred and heated at 55°C for a further 16 hours. The solid was filtered off and crystallized from ethanol to give the required [7] 3-bromo-4-octyloxybenzoic acid in 88 per cent yield; melting point 111–112°C.

(3) *2- and 3-Fluoro-4-hydroxybenzoic acids.* These were prepared [9] from 2- and 3-fluoroanisole. 3-Fluoroanisole (50 g) was dissolved in dry chloroform (100 ml) at 20°C. Bromine was added dropwise over 2 hours and the solution warmed for 1 hour. After cooling, the solution was washed successively with brine (3 × 200 ml), 10 per cent sodium hydroxide solution (3 × 200 ml) and brine (2 × 200 ml); it was then dried and distilled (boiling point 130°C at 40 mm Hg); yield 69 g, 84 per cent.

The bromo compound was then cyanated by stirring and heating a mixture of 4-bromo-3-fluoroanisole (34 g), cuprous cyanide (19·1 g) and dry dimethylformamide (35 ml) at 185°C for 3 hours. On cooling the mixture was poured into a solution of water (300 ml), ferric chloride (30 g) and hydrochloric acid (2 ml) at 60°C and stirred for 30 min. After cooling the mixture was extracted with ether (4 × 200 ml), the ether extract washed with brine and dried. Two crystallizations from methanol gave 4-cyano-3-fluoroanisole in 57 per cent yield; melting point 59–60°C. 4-cyano-2-fluoroanisole was prepared in 66 per cent yield and had a melting point of 99–100°C.

The 4-cyano-2- and -3-fluorophenols were generated by demethylation of the anisole using crushed aluminium chloride and sodium chloride [9]. The isolated phenol (0·01 m) was alkylated by stirring and heating under reflux with the appropriate alkyl bromide (0·012 m) and potassium carbonate (0·04 m) in cyclohexanone (30 ml). The product was isolated in 80 per cent yield by vacuum distillation.

The required carboxylic acids were produced by heating under reflux, the appropriate nitrile (1·2 g), acetic acid (12 ml), sulphuric acid (6 g) and water (6 g) for 16 hours. The solution was poured into water, filtered and crystallized from methanol to yield 1 g of 4-alkoxy-2- or -3-fluorobenzoic acid.

(4) *3-Methyl-4-hydroxybenzoic acid.* This was prepared [10] by standard methods from 2-methylanisole.

(5) *Substituted 4-hydroxybenzoic acids.* Except for the fluoro analogues, these were alkylated [8] as described for 4-alkoxybenzoic acid.

(6) *4′-Alkoxybiphenyl-4-carboxylic acids.* These were prepared by acid hydrolysis of the corresponding 4-alkoxy-4′-cyanobiphenyl (supplied by BDH Chemicals Ltd) as described for the 4-alkoxy-2- and -3-fluorobenzoic acids, except that the product was crystallized from acetic acid.

(7) *2-Methylbutyl 4-hydroxy-2- and 3-substituted benzoates and 2-methylbutyl 4′-hydroxybiphenyl-4-carboxylates.* These were prepared by overnight heating, under reflux using a Dean and Stark apparatus, the relevant 4-hydroxy carboxylic acid (4 g), racemic 2-methylbutanol (50 ml) and sulphuric acid (0·3 g). The crude product, after washing, was purified by short path vacuum distillation or, in the case of the biphenylcarboxylic acids, by crystallization from methanol.

(8) *Esterification.* The 4′-alkoxybiphenyl-4-carboxylates or 4-alkoxy-2- or -3-substituted benzoic acids (0·01 m) were warmed with the appropriate phenol (from (7)) (0·01 m) and trifluoroacetic anhydride (0·025 m) in dry dichloromethane for 4 hours. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane as eluent. The product was then crystallized from ethanol until it was greater than 99·5 per cent pure (at 280 nm) by reverse phase HPLC.

(9) *3-Cyano-esters.* These were prepared [7, 11] by heating, at 150°C, a stirred mixture of bromo-ester (3·8 g), cuprous cyanide (1·9 g) and dry dimethylformamide (20 ml) for 4 hours under a nitrogen atmosphere. After cooling, the reaction mixture

was poured into a warm solution of water (100 ml), ferric chloride (2 g) and hydrochloric acid (1 drop) and stirred for 10 min. When cold, the mixture was extracted with dichloromethane, washed with water, dried and chromatographed on silica gel; crystallization from ethanol gave 80–85 per cent yield of the 3-cyano-ester.

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References

[1] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 889.
[2] Bone, M. F., Coates, D., Crossland, W. A., Gunn, P., and Ross, P., 1987, *Displays* (to be published).
[3] Coates, D., 1987, *Liq. Crystals*, **2**, 63.
[4] Le Pesant, J. P., Perbert, J. N., Mourey, B., Hareng, M., Decobert, G., and Dubois, J. C., 1985, *Molec. Crystals liq. Crystals*, **129**, 61.
[5] Dainippon Ink and Chemicals Inc., 1986, EP 0188,222.
[6] Hitachi Ltd., 1984, EP 0110,299.
[7] Thompson-CSF., 1978, US 4,173,545.
[8] Gray, G. W., and Jones, B., 1954, *J. chem. Soc.*, p. 2556; *Ibid.*, 1953, p. 4179.
[9] Kelly, S. M., 1984, *Helv. chim. Acta*, **67**, 1572.
[10] This compound was kindly supplied by Professor G. W. Gray's group at Hull University.
[11] Dubois, J. C., and Bêguin, A., 1978, *Molec. Crystals liq. Crystals*, **47**, 193.