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Synthesis and liquid crystal properties of 4-alkoxybenzylidene-4'-aminocinnamic acid 1-trifluoromethylalkyl esters The ABACT series

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**Synthesis and liquid crystal properties of
4-alkoxybenzylidene-4'-aminocinnamic acid
1-trifluoromethylalkyl esters**

The ABACT series

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The synthesis of homologues of 4-alkoxybenzylidene-4'-aminocinnamic acid 1-trifluoromethylalkyl esters is reported. Only three of the compounds exhibit smectic phases. Phases were identified using optical and electro-optic techniques together with X-ray diffraction studies. Some of the compounds, while not exhibiting liquid crystal phases, show crystalline polymorphism.

1. Introduction

Here we report the synthesis and characterization of a new homologous series of liquid crystals. The structure was chosen to be a variant of the well known DOBAMBC [1], AOBA-1-MPC and AOBA-1-MBC [2] systems (see table 1) to see if the smectic C phase is preserved when a structural modification is made around the chiral centre. The underlying reason for our interest is the eventual preparation of chiral smectic C materials and the exploration of their switching properties. Our strategy has been to synthesize the racemic modifications with a view to the future preparation of the chiral isomers of the most promising compounds. The chosen compounds incorporate a trifluoromethyl group in the asymmetric centre so that the effect on the spontaneous polarization (P_s) could be measured should suitable smectic phases be found. The materials have been given the acronym ABACT M N (see table 1) which is derived from 4-alkoxybenzylidene-4-aminocinnamic acid 1 trifluoromethylalkyl ester; M and N are integers indicating the number of carbon atoms in the alkoxy and ester chains, respectively.

2. Synthesis

The chosen route to the ABACT series is given in figure 1. The required products were obtained by condensation of 4-alkoxybenzaldehyde (6) and 1-trifluoromethylalkyl 4-aminocinnamate (5). The alkoxybenzaldehydes (6) were prepared by alkylation of 4-hydroxybenzaldehyde with the appropriate alkylbromide under standard conditions [3]. 1-Trifluoromethylalkyl 4-aminocinnamate (5) was synthesised from 4-nitrocinnamic acid (1). Conversion of the acid (1) to the corresponding acid chloride

Table 1. Molecular structures of DOBAMBC, AOBA 1 MPC, and AOBA 1 MBC.

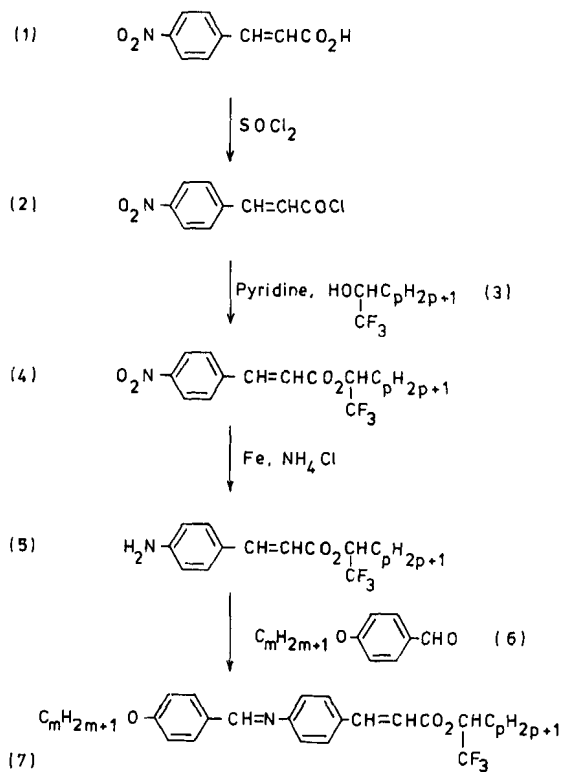
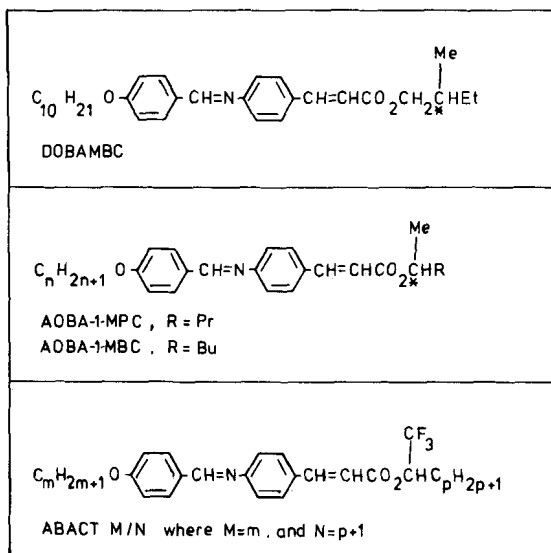


Figure 1. Synthesis of 4-alkoxybenzylidene-4-aminocinnamic acid 1-trifluoromethylalkyl esters.

(2) and esterification with 1,1,1-trifluoroalkan-2-ol (3) furnished, after chromatography, 1-trifluoromethylalkyl 4-nitrocinnamate (4) (60–70 per cent).

The nitro compound (4) was smoothly and efficiently reduced (80–90 per cent) under neutral conditions using a mixture of reduced iron powder and ammonium chloride in refluxing ethanol to give 1-trifluoromethylalkyl 4-aminocinnamate (5). The trifluoroalkan-2-ols (3) were synthesised (see figure 2) by reaction of ethyl (or butyl) trifluoroacetate (9) and the appropriate alkylmagnesiumbromide (8) under Grignard conditions [4]. Satisfactory I.R. and ^1H N.M.R. (60 MHz) spectra were obtained for intermediates and products. In addition, all members of the ABACT series gave satisfactory combustion analyses.

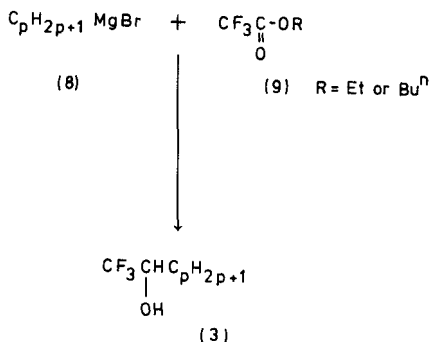


Figure 2. Synthesis of 111-trifluoroalkan-2-ols.

3. Phase identification

3.1. Thermal phase sequences

The thermal phase sequences were investigated by two methods: (i) an optical method and (ii) an electrical method.

- (i) In the optical method the samples were observed through crossed polarizers using a transmission microscope equipped with a hot stage. The samples were heated and cooled slowly ($\sim 0.5^\circ\text{C}/\text{min}$) and the observed phase transitions noted.
- (ii) The electrical method is based on the change in dielectric constant with temperature. Briefly, the sample is placed in a cell $12\ \mu\text{m}$ thick having transparent conducting walls (usually indium-tin oxide) enabling the capacitance of the cell to be measured. From a knowledge of the cell dimensions the dielectric constant can be determined. The dielectric constant depends on the polarizability of the material between the electrodes which in turn depends on the orientation of the molecules. If reorientation of the liquid crystal molecules occurs, such as at a phase transition, the polarizability changes and hence the dielectric constant. Differentiation of the dielectric constant with respect to temperature generates a peak for each phase transition. This technique, which in our experience has been more reliable for determining phase transitions than the optical methods, is discussed in more detail in [5].

Optically the materials can be classified into three groups depending on the texture observed on cooling the sample from the isotropic state. Type I shows focal conic-like textures obviously smectic in nature (see plate 1). Type II exhibits a smooth

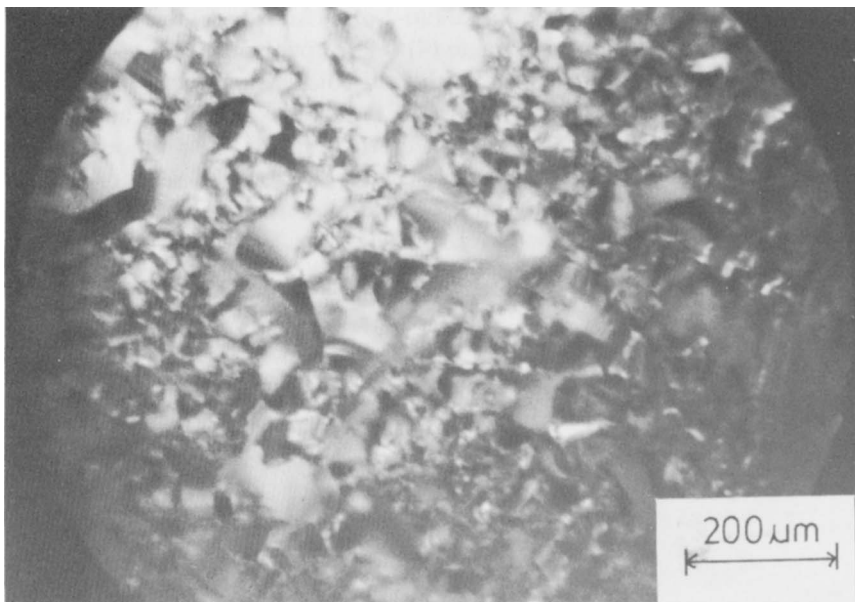


Plate 1. Type I texture.

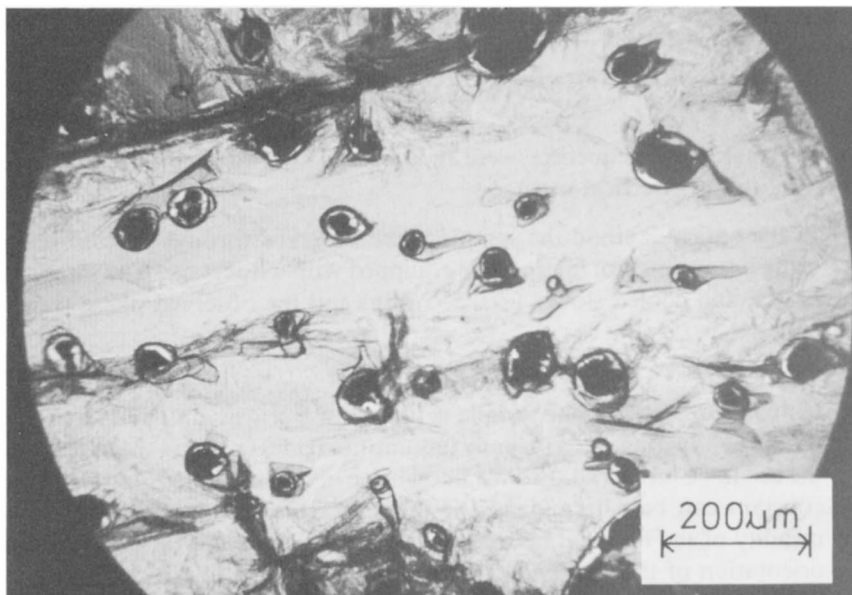


Plate 2. Type II texture.

uniform texture (see plate 2) which on cooling to room temperature breaks up to an obviously crystalline structure (this shattered texture can take several hours to develop). Type III (see plate 3) shows only a crystalline phase. For ABACT M/N a plot of M versus N produces a map showing the extent of each type of texture (shown in figure 3).

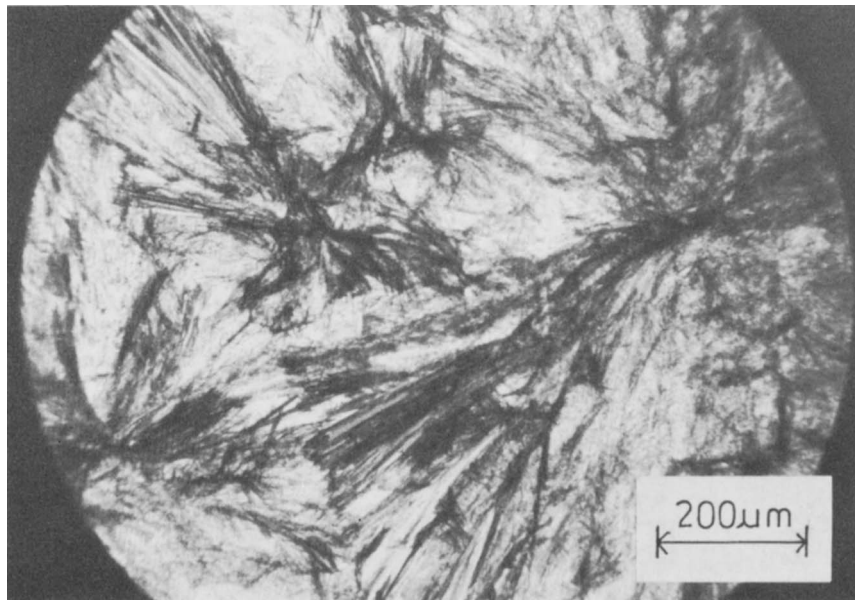


Plate 3. Type III texture.

<i>N</i>							
7	III	I	I	II	III	III	III
6	III	I	II	III	II	III	III
5	III	III	II	II	III	III	III
4	III	III	II	III	III	III	III
	5	6	7	8	9	10	12 <i>M</i>

Figure 3. Plot of *M* versus *N* showing the extent of each texture type.

The transition temperatures for types I, II and III are shown in tables 2, 3 and 4, respectively. An interesting point to note that ABACT 6/7 under optical observation shows only one phase (type I) but when examined by the capacitance method two phases are apparent. The presence of two phases was confirmed by X-ray diffraction, see § 3.2.

3.2. X-ray diffraction studies

X-ray diffraction patterns from ABACT 6/7 and 8/7 were obtained using nickel filtered copper *K_α* radiation and a flat plate camera. The samples were contained in

Table 2. Phase transition temperatures (in °C) for type I materials.

<i>N/M</i>	Melting Point	Isotropic → Smectic 1	→ Smectic 2	→ Crystal
6/6	74.1	64.7		49.5
6/7	74.6	55.7	46.3	< 25
7/7	58.3	46.1		40.9

Table 3. Phase transition temperatures (in °C) for type II materials.

<i>N/M</i>	Melting point	Isotropic → Type II Phase
8/7	67.8	54.4
9/6	76.6	58.6
7/6	76.2	63.6
8/5	96.1	88.7
7/5	91.8	85.5
7/4	90.1	88.5

Table 4. Phase transition temperatures (in °C) for type III materials.

<i>N/M</i>	Melting point	Isotropic → Type III Phase
5/7	79.8	61.7
9/7	59.6	43.7
10/7	57.0	43.1
12/7	61.6	49.1
5/6	85.7	69.7
8/6	79.5	70.1
10/6	67.9	50.1
12/6	62.8	54.9
5/5	83.5	81.5
6/5	86.9	74.7
9/5	78.9	69.6
10/5	69.7	61.3
12/5	77.0	67.1
5/4	103.8	97.5
6/4	92.6	88.7
8/4	99.9	95.5
9/4	83.3	79.3
12/4	74.8	71.1

1 mm Lindemann tubes and their temperature were controlled to within one degree using a Eurotherm temperature controller. Partially aligned samples were prepared by cooling the sample from the isotropic phase into the smectic phase over a period of about 30 min in a 1 T magnetic field. Unfortunately the alignment was not sufficiently good to greatly facilitate the identification of the phases. ABACT 8/7 tended to crystallise rapidly and so no useful diffraction patterns were obtained from it. ABACT 6/7 remained liquid-crystalline for many hours once cooled into a smectic phase. Figure 4 shows X-ray photographs of the two mesophases exhibited by unaligned samples of ABACT 6/7, and the *d* spacings corresponding to the Bragg reflexions are given in table 5. The upper mesophase (see figure 4(a)) is clearly identified as a smectic, giving intense sharp layer reflexions but with only short range order within the layers, giving diffuse outer ring scattering. On alignment the diffuse ring condensed towards the equatorial plane while the sharp rings condensed towards the meridian. The 002 layer reflection appears to be absent in both phases but since the 004 is clearly observed in the lower temperature phase it appears that this is just due to some fortuitous minimum in the molecular form factor and does not have any implications regarding the symmetry of the mesophase. The *d* spacing calculated from the layer reflexions is 29.8 ± 0.5 Å which is 13 per cent less than the molecular length

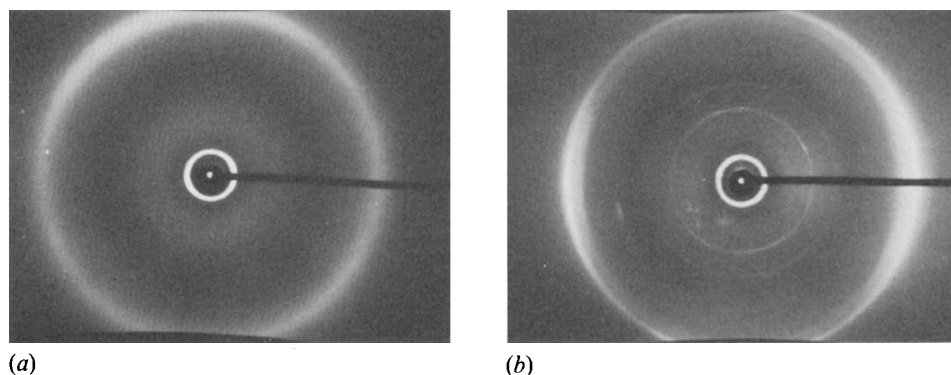


Figure 4. X-ray photographs of mesophases exhibited by unaligned samples of ABACT 6/7. (a) smectic C phase. (b) smectic J phase.

Table 5. d -spacings corresponding to the Bragg reflections in ABACT 6/7.

		d observed/Å	d Calculated/Å	hkl
S_C		29.8	29.8	001
		9.91	9.92	003
		4.1		Diffuse
		Mean layer spacing = 29.8 Å		
S_J	Strong	30.1 ± 1.0	30.0	001
		9.94	10.0	003
		7.40	7.51	004
		4.46	4.46	111
	Strong	4.42 ± 0.1	4.22	110 + 020
	Not seen		4.18	021 + 021
	Not seen		3.94	111
	Not seen		3.19	120
	Mean layer spacing = 29.8 Å			

(l) of 34.4 ± 0.5 Å (estimated using CPK space filling molecular models). This is strongly suggestive of a smectic C rather than a smectic A and this was confirmed by the optoelectronic switching experiment described in §4.3. The tilt angle, θ , of the molecules in this smectic C phase was estimated to be $\sim 30 \pm 3^\circ$ using the expression

$$\theta = \cos^{-1}(d/l).$$

Partially aligned samples of the lower temperature phase showed two equatorial arcs which are actually easier to see in the diffraction pattern from the unaligned sample shown in figure 4(b). These rings are not any broader than expected from the resolution of the X-ray camera which implies that this phase is a smectic with long range translational order within the layers (not one of the hexatic phases). We considered three possibilities for the identity of this phase. They can all produce a split equatorial reflection and they are discussed later with reference to figure 5. The smectic E phase has a unit cell in which C is perpendicular to the ab plane but which is distorted from hexagonal symmetry (i.e. $a \neq \sqrt{3b}$) and which has no C face centring on the lattice [6] (i.e. the molecule at the centre of the C face is not equivalent to those at the corners). It gives a split equatorial Bragg reflection (i.e. the 200 and

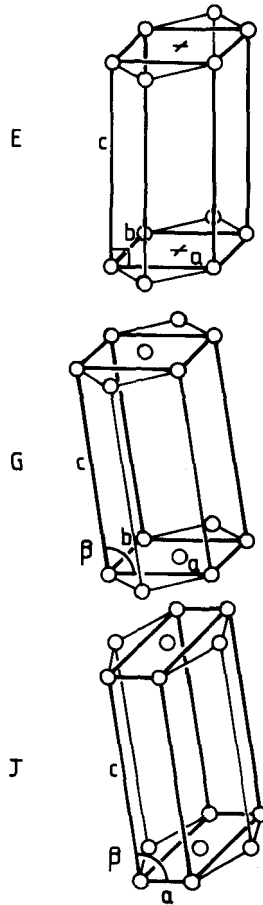


Figure 5. The unit cells for the smectic E, G, and J phases discussed in the text. The circles represent lattice points. An equivalent molecule would be centred on each lattice point and, in the smectic E, a non-equivalent molecule would be centred at the two crosses.

110) which should have an intensity ratio 1 : 2. In the original photographs the inner equatorial reflection appears considerably weaker (~ 5 times) than the outer one which is inconsistent with the ratio expected from a smectic E. Furthermore, very long exposures have not revealed a 210 reflection which would be expected from a non C centred cell. It is therefore very unlikely to be a smectic E phase. The smectic G and J phases both have tilted pseudo-hexagonal unit cells that are C centred so no 210 (S_G) or 120 (S_J) is expected. The smectic J unit cell is tilted towards the apex of the hexagon while the G is tilted towards an edge so their diffraction patterns are different. Both have monoclinic unit cells which have a roughly $\sqrt{3}$ relationship between a and b and their diffraction has been discussed by Gane *et al.* [7, 8] (where smectic J was referred to as smectic G')

$$S_J: \quad b \approx \sqrt{(3a)} \sin \beta \text{ if pseudo hexagonal,}$$

$$S_G: \quad b \approx \frac{a}{\sqrt{3}} \sin \beta \text{ if pseudo hexagonal.}$$

We now discuss the positions of the Bragg reflections in terms of the scattering vector Q , where

$$Q = \frac{4\pi \sin(\phi/2)}{\lambda}; \quad (1)$$

here ϕ is the scattering angle and λ is the X-ray wavelength. The positions of the Bragg reflections are given by the usual crystallographic formula for a monoclinic cell,

$$Q_{hkl} = (h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hkla^*c^* \cos \beta^*)^{1/2}, \quad (2)$$

where

$$a^* = \frac{2\pi}{a \sin \beta}; \quad b^* = \frac{2\pi}{b}; \quad c^* = \frac{2\pi}{c \sin \beta}; \quad \beta^* = 180 - \beta.$$

The d spacing corresponding to a Bragg reflection is related to its Q value by

$$d_{hkl} = \frac{2\pi}{Q_{hkl}}. \quad (3)$$

We have attempted to index the powder diffraction pattern assuming either smectic G or J types of structure.

(i) Assuming a smectic G ($b \sim \frac{a}{\sqrt{3}}$)

If the strong equatorial reflection is a superposition of the 110 and 200 reflections then calculations using equations (1) to (3) show that there should be two reflections (a $11\bar{1}$ and a $20\bar{1}$) at lower scattering vector (higher d spacing) than the 110/200. Inspection of the diffraction pattern shows that there is only one subsidiary reflection at a lower scattering angle than the strong 110/200 so we do not believe the phase to be smectic G.

(ii) Assuming a smectic J ($b \sim \sqrt{3}a$).

In this case we assume the strong reflection to be a combination of the 110 and 020 reflections. Calculations using equations (1) to (3) show that the 021 and $02\bar{1}$ would also occur at a very similar Q value and so would not be seen as separate rings in the diffraction pattern. The $11\bar{1}$ would occur at a lower Q and this is identified as the ring corresponding to a d spacing of 4.46 Å. Using this assignment for the indices of the rings we have calculated (using a least squares program, FITMON) the unit cell dimensions that give the best agreement with all the observed d spacings. The observed and calculated d spacings are compared in table 5 and the best fit unit cell is

$$\begin{aligned} a &= 5.7 \pm 0.2 \text{ \AA}, \\ b &= 8.4 \pm 0.1 \text{ \AA}, \\ c &= 35.0 \pm 1.0 \text{ \AA}, \\ \beta &= 121 \pm 2^\circ. \end{aligned}$$

The uncertainties in a , c and β are determined by the precision with which the splitting of the equatorial reflections is determined. The c dimension is in a very good agreement with the model molecular length (34.4 Å) and the tilt angle θ ($\theta = \beta - 90 = 31 \pm 2^\circ$) is very similar to that inferred from a comparison of molecular length and the layer

spacing in this phase (i.e. $30 \pm 2^\circ$). This appears to be the same as found in the smectic C phase. The observation of the $11\bar{1}$ reflection further confirms that it is not a hexatic phase (where the $l \neq 0$ reflections are absent except for $h = k = 0$ because of the very weak interlayer correlation). There is no hint of a 111 reflection which should be observable at a higher Q than the $110/020$. This can be rationalized easily since the disorder in the structure and the molecular form factor tend to reduce the intensity (drastically) as Q increases. We therefore conclude that the lower temperature phase of ABACT 6/7 is a smectic J. Since this phase has a three dimensional long range translation order it is better called a crystal smectic J in order to distinguish it from the smectics without such complete translational order.

3.3. Optoelectronic switching

The X-ray diffraction experiments indicated that the two phases in ABACT 6/7 were smectic C and J. In order to confirm the presence of a smectic C phase, ABACT 6/7 was doped (5–10 per cent by weight) with the chiral compound, 1-carvone. Doping with a chiral compound forces a degree of chirality on the liquid crystal. Provided the mesophase is a tilted smectic then the material will be ferroelectric. Thus the domains of a doped sample, viewed through crossed polarisers, will be seen to switch on application or removal of an electric field. Domain switching was observed for the higher temperature phase of ABACT 6/7 thus confirming that it was smectic C. The second phase did not switch. This was not unexpected since although the smectic J phase is tilted it is also more ordered [9] than the C phase and hence is more viscous. To obtain switching, fields higher than those which we could apply (30 V on a $12 \mu\text{m}$ cell) would be required. Doped samples of ABACT 6/6 and ABACT 7/7 both showed switching but only close to the smectic to isotropic phase transition. Switching was not observed in doped samples of ABACTs which exhibited type II and type III textures.

4. Discussion

Twentyseven members of the ABACT series were synthesized covering a range of length of both alkyl and ester chains. However, obvious smectic phases were observed in only three candidates: ABACT 6/6, 6/7 and 7/7. All three compounds showed a smectic C phase and one compound, ABACT 6,7 exhibited a smectic J phase. Smectic phases are injected when the alkoxy and ester chains exceed six carbons and are of approximately equal length.

It could be, therefore, that smectic phases would be found for ABACTs where the ester chain length is eight or more. The absence of smectic phases in ABACT M/4 and M/5 was somewhat surprising in view of the occurrence of mesophases in the analogues DOBAMBC, AOB-1-MBC, and AOBA-1-MPC. Chain branching at the first carbon of a terminal chain is known [10] to have a greater effect on liquid crystal thermal stability than chain branching further from the core. The effect, usually less marked in smectics than nematics, is to lower the crystal to liquid crystal transition temperature and to reduce the mesophase range. These effects together with a strong lateral dipole are probably responsible for the absence of mesophase in many of the ABACT compounds. The stability of the crystalline phase must be quite large since all the smectic phases were monotropic. It is of interest to note that mesophases were absent in ABACTs exhibiting type II and type III textures despite a long hysteresis in the cooling process (e.g. ABACT 5/7, $C \xrightarrow{79.8} I \xrightarrow{61.7} C$). Type II textures do

not appear to be liquid-crystalline. The texture is not disturbed when the cell walls are squeezed together (cf. a smectic C where the fluidity of the phase becomes apparent on squeezing the cell walls). However, type II textures do change slowly to an obviously crystalline texture. It is likely, therefore, that type II and type III textures are crystalline but in the case of type II materials more than one crystal structure exists. Crystalline polymorphism has been observed in liquid-crystalline structures by other workers [11]. Difficulty was experienced in identifying the mesophase in ABACT 6/6, 7/7 and the first mesophase in 6/7 using optical methods (study of textures). Although for ABACT 6/7 X-ray diffraction indicated that the higher temperature smectic phase was smectic C some doubt remained. The doping technique confirmed the presence of the smectic C phase in ABACT 6/7 and also in ABACT 6/6 and 7/7. The doping method was useful to us and may well have general applicability for identifying or confirming smectic C phases.

5. Conclusions

A synthetic route to liquid-crystalline structures having a trifluoromethyl group in the side chain has been established. The effect of a trifluoromethyl group at a chain branch close to the conjugated core is to decrease, strongly, the liquid crystal thermal stability, shown by comparing ABACT M/5 (no mesophases) with AOB-1-MBC (have short ranges of smectic A and C). Liquid-crystalline phases were found for ABACT 6/6, 6/7 and 7/7. All three had a smectic C phase and ABACT 6/7 showed a more order (S_j) phase. The usefulness of the doping technique for identification of the smectic C phase has been demonstrated.

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