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NON-CHIRAL COMPOUNDS EXHIBITING ALTERNATING TILT SMECTIC PHASES

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Abstract

In this article we present an investigation of the liquid crystal properties of nonchiral and racemic branched alkyl chain (swallow-tailed) molecules and some chiral analogues based on a cinnamic acid core group. It was found in these systems that increasing the extent of the branching of the terminal alkyl chain increased the incidence of alternating tilt smectic phases, whereas smectic C_{α} and smectic C_{γ} phases were suppressed. X-ray studies of the effect on the layer spacing in the smectic A phase of increasing the long alkyl branch of one series of compounds are included. Results of polarisation studies on some chiral analogues are also reported.

INTRODUCTION

The existence of zigzag ordered smectic C phases (S_{Calt}) in non-chiral compounds has been known for many years. These type of compounds were first reported by Levelut¹ *et al.*, and also occur in dimers² and in some polymers³. More recently Nishiyama and Goodby produced a swallow-tailed compound⁴ which showed complete miscibility with the S_C^*A phase of a standard compound. This work proposed that the incidence of the S_{Calt} phase was due to the formation of molecular pairs which was due to the overall molecular geometry and not necessarily as a direct result of the chirality of the species. In order to investigate this situation further, a number of series of compounds, in which there was a systematic variation of the three alkyl chain lengths, were synthesised and their phase behaviour determined The number of bonds in the linking group X was also varied from single to double to triple bond. The basic structure of the compounds investigated is shown below.



The structural variations investigated were:

- 1. The number of bonds in the linking group X.
- 2. The length of the single alkoxy chain R
- 3. The lengths of the two arms of the branched alkyl chain n and m

The nature of the smectic C phase was determined initially by miscibility studies with a known compound $10b1M7^5$ (see figure 2) which showed both the S_C^* and $S_C^*_A$ phases and then by contact studies with other members of the series.

<u>Synthesis</u>

The general synthetic route to the series of compounds of interest is shown in Scheme 1. Methyl 4-hydroxycinnamate was alkylated with the corresponding alkyl bromide in the presence of potassium carbonate, and the free acid was obtained by hydrolysis of the methyl ester with sodium hydroxide in a mixture of water and ethanol. 4-Hydroxybiphenyl-4'-carboxylic acid was esterified with the required alcohol in the presence of diethylazodicarboxylate (DEAD) and triphenylphosphine in equimolar quantities. The final products were obtained by the reaction of the 4-alkoxycinnamic acids with alkyl 4-hydroxybiphenyl-4'-carboxylate in the presence of DCC and a catalytic amount of DMAP.

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Transition temperatures were determined by optical polarising microscopy, using a Leitz SM-Lux-Pol microscope fitted with a Mettler FP82 heating stage and a Mettler FP800 control unit. DSC was performed using a Perkin Elmer DSC 7.



SCHEME 1

The compounds with a single bond in place of the double bond (9Chbp33 and 9Chbp16(R)) were synthesised from the corresponding nonyloxy acid prepared from methyl 3-(4-hydroxyphenyl)propionate. The compounds with the triple bond (9Ctbp33 and 9Ctbp16(R)) were available from previous work at Hull^{6,7}

RESULTS

1. Variation in the linking group X.

Three compounds were synthesised and their phase properties are shown in figure 1 The single (9Chbp33) and triple bond (9Ctbp33) linked compounds exhibited monotropic transitions, whereas the double bond compound (9Cbp33) exhibited enantiotropic phase behaviour. As a consequence of this study compounds with a double bond linking group were used for the study of the effects of the variation of the three alkyl chain lengths.



FIGURE 1 The transition temperatures of the three compounds 9Chbp33, 9Cbp33 and 9Ctbp33

The nature of the smectic C phase was determined initially by miscibility studies with a known compound 10b1M7 and then by contact studies with other members of the series.

Mixture 9Cbp25 and 10b1m7



10**b1m7**(S)



FIGURE 2: The binary phase diagram of 10b1m7 and 9Cbp25

2. Variation of n and m for a constant R.

$2.1 \text{ R} = C_9 H_{19}, n = 2, m = 1-6.$

Table 1 shows the transition temperatures of the series 9Cbp2m as determined by thermal optical microscopy. These results are shown graphically in figure 3.

m	1	2	3	4	5	6
Iso-S _A	178.4	156.4	140	133.6	130.1	127.6
ΔH kJ/mol	4.13	3.24	2.86	2.51	2.44	2.45
S_A-S_C	150.7	136		117 ^②	114	111.4
ΔH kJ/mol	0.29	0.66			0.51	0.45
SA-SCalt			127	118.9 ^①		
ΔH kJ/mol			1.14	1.09		
S _C -S _{Calt}		126.5		116.7 [©]	113.4	110.4
ΔH kJ/mol		0.19			0.26	0.25 ^③
mpt	132.3	121.9	109	98.5	89.6	81.7
ΔH kJ/mol	23	27.05	24.03	19.47	18.01	26.24

⁽¹⁾On heat cycle only ⁽²⁾On cool cycle only ⁽³⁾ appears to be two transitions at slow heating rates

TABLE 1 The transition temperatures and heats of transition of the series 9Cbp2m



FIGURE 3 A plot of the transition temperatures of the series 9Cbp2m

Both smectic C_{alt} and smectic C phases are obtained in these compounds. In some cases the smectic C transition supercools slightly and is seen on heating the sample and not on cooling. The differential scanning calorimetry thermograms of this series are shown in figure 4. The supercooling effect in the S_C to S_{Calt} transition can be clearly seen. No odd even effects are seen in the transition temperatures.

The effect on the layer spacing of increasing m for this series is shown in figure 5. For each increase in length by one methylene unit (m = 1, 2, ..., 6), there is an increase in the layer spacing of 0.066 nm which is equivalent to half the length of one methylene unit, for the all *trans* conformation. This suggests some interdigitation of the molecules in their layers. This effect will be discussed in detail at a later date. Plate 1 shows the texture of the smectic C_{alt} phase as seen on thermal optical microscopy.

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FIGURE 4: Differential scanning calorimetry traces of the series 9Cbp2m, showing the supercooling effect on the smectic C - C_{alt} transition.



FIGURE 5: The layer spacing in the smectic C phase of the series 9Cbp2m determined by X-ray scattering.

$2.2 \text{ R} = C_9 H_{19}, n = 3, m = 1-6.$

The transition temperatures of the series 9Cbp3m as determined by thermal optical microscopy are shown in table 2 and graphically in figure 6. When $m \ge n$, these compounds were found to exhibit smectic A and smectic C_{alt} phases. However for m = 1, smectic A and smectic C phases are seen.

m	1	2	3	4	5	6
Iso-S _A	167	140	126	120.2	114.7	108.9
ΔH kJ/mol	3.53	2.86	2.07	1.73	0.17	1.3
S _A -S _C	149					
∆H kJ/mol	0.49					
SA-SCalt		127	112	103.3	96.1	91.4
∆H kJ/mol		1.14	0.97	0.87	0.75	0.75
mpt	120.3	109	106.5	95.4	82.8	73.6
ΔH kJ/mol	21.29	24.03	20.81	21.6	19.46	18.03

 TABLE 2
 The transition temperatures and enthalpies of the series 9Cbp3m



FIGURE 6 A plot of the transition temperatures of the series 9Cbp3m

$2.3 \text{ R} = \text{C}_9\text{H}_{19}, \text{ n} = \text{m} = 2-5.$

These swalle	ow tail com	pounds were	prepared and	their trans	sition tempe	ratures	are sho	wn
in table 3.	Unlike the	swallow tail	compounds	prepared	previously,	in this	series	the
length of the	e swallow ta	il was altered	l to give both	shorter ar	nd longer ch	ain varia	ants.	

n = m	2	3	4	5
S _A -Iso	156.4	126	112.1	110.6
∆H kJ/mol	3.24	2.07	1.34	1.27
SA-SCalt		112	94.3	78
ΔH kJ/mol		0.97	0.8	0.15
$S_A - S_C$	136			
ΔH kJ/mol	0.66			
S_{Calt} - S_{C}	126,5			
∆H kJ/mol	0.19			
mpt	121.9	106.5	82.8	54.4
ΔH kJ/mol	27.05	20.8	20.23	2.49

TABLE 3 The transition temperatures and enthalpies of transitions for the 9Cbpmm series



FIGURE 7 A plot of the transition temperatures of the series 9Cbpmm

At longer chain lengths again only zigzag ordered smectic C_{alt} phases are seen. It should be noted that in all cases the temperatures of the transitions, isotropic to smectic A, and smectic A to smectic C (both types), follow smooth curves, it is just the nature of the structure of smectic C phase that changes.

<u>**3**. $\mathbf{R} = \mathbf{C}_{\mathbf{p}}\mathbf{H}_{2\mathbf{p}+1}, \mathbf{p} = 6,7,8,9,10,11,12,14, \mathbf{n} = \mathbf{m} = 4$ </u>

The transition temperatures of the series RCbp44 are shown in table 4 along with the enthalpies of transition. Two new phases were discovered in these systems, denoted by X and Y in table 4 below. These phases have long range order and were marked by unusual supercooling effects and slow rates of transition.

p	6	7	8	9	10	11	12	14
Iso - S _A	133.6	125	118	112.1	106			-
∆H kJ/mol	4.1	2.28	2.63	1.35	0.79			
X/Y - Iso						100	100	9 7
∆H kJ/mol						1.92	2.22	35.04
Iso/S _A -X					90.6	89	86	86.1
∆H kJ/mol					0.64	0.057	0.052	-
X - Y						82	85	86.1
∆H kJ/mol						1.07	1.18	1.6
Y/X- S _{Calt}					84	72		
∆H kJ/mol					0.64	-		
S _A - S _C		95.5	98		90.6			
∆H kJ/mol		-	0.33		0.93			
SA/SC - SCalt			95.9	94.3	90.5			
∆H kJ/mol			0.17	0.80	-			
mpt	129	110.5	97	82.8		82	100	101
∆H kJ/mol	22.06	20.91	26.61	20.26		22.53	34.66	35.7

TABLE 4 The transition temperatures and enthalpies of the series RCbp44



FIGURE 8 A plot of the transition temperatures of the series RCbp44

The phases identified as X and Y have not been fully categorised. On optical microscopy the phase X appears as a slow growing mosaic texture at the A - C transition for the decyloxy homologue. The texture of the X phase is shown in plates 2 and 3. On further cooling the mosaic texture changes to that of the smectic Calt phase with both 2 and 4 brush defects being observed in the schlieren texture. On heating of the smectic Calt phase, the X phase reappears. Rapid cooling of the smectic A phase of the decyloxy homologue produces a direct transition to the smectic C phase and a further transition to the smectic Calt phase. In the undecyloxy homologue the X phase is stable on cooling but can change to the optically extinct Y phase or to the S_{Calt} phase. These latter transitions are monotropic and recrystallisation tends to occur simultaneously. At longer chain lengths the X phase is not stable and rapidly undergoes the transition to the Y This grows into the X phase in well defined shapes usually octagonal or phase. rectangular, and in the undecyloxy and dodecyloxy compounds it exhibits no shear birefringence and is viscous. In the tetradecyloxy homologue a weakly birefringent texture can be seen, and when pressure is applied to the cover slip shear birefringence is seen. Plate 4 shows the Y phase growing into the X phase of the dodecyloxy homologue. The X and Y phases are miscible across all the later members of the series. Further investigations including X-ray measurements are currently in progress into the structure of these phases and the results will be published in a further communication.



PLATE 1: Photomicrograph (x100) of the S_{Calt} phase of compound 9Cbp26. See Color Plate II.



PLATE 2: Photomicrograph (x100) of the X phase of compound 10Cbp44. See Color Plate III.



PLATE 3: Photomicrograph (x100) of the X phase of compound 11Cbp44. See Color Plate IV.



PLATE 4: Photomicrograph (x100) of the Y phase growing into the X phase of compound 12Cbp44. See Color Plate V.

4 Chiral compounds

Chiral versions of two of the compounds described above were synthesised as well as two other chiral examples based on the same core structure. Again it was found that the compounds based on 4-hydroxycinnamic acid exhibited more stable enantiotropic phases than the compounds based on 4-hydroxyphenylpropiolate or 4-hydroxyphenylpropionate. As with the non-chiral compounds, it was found that increasing the length of the lateral branched carbon chain increases the incidence of alternating tilted phases with the corresponding loss of the ferroelectric smectic C* phase. The results found are shown in figure 9 for the nonyloxy homologues.



FIGURE 9 The transition temperatures of the chiral compounds.

The magnitude of the spontaneous polarization for these compounds was measured using the triangular wave method. As the length of the lateral branch at the chiral centre was increased from 1 to 2 to 3 carbon atoms the maximum value of the Ps obtained fell and the threshold switching voltage in S_C^*A phase increased, to over 400 Vpp. All values were measured in 4 µm cells.

compound	n	m	phase behaviour
9Cbp14(<i>R</i>)	1	4	Iso - 163 - S_A^* - 146.5 - S_C^* - 127 - $S_C^*_{\gamma}$ - 127 - $S_C^*_A$ - 110.5 - K
9Cbp16(<i>R</i>)	1	6	Iso - 152 - S_A^* - 142 - S_C^* - 120 - $S_C^*_{\gamma}$ - 115 - $S_C^*_A$ - 96 - K
9Cbp26(<i>R</i>)	2	6	Iso - 120 - S_A^* - 106 - S_C^* - 105.7 - S_C^*A - 90 - K
9Cbp36(<i>R</i>)	3	6	Iso - 116 - S_A^* - 97 - S_C^*A - K

TABLE 5: the transition temperatures of the chiral compounds synthesised



FIGURE 10 The spontaneous polarisation of the chiral compounds

Figure 10 shows the determination of the value of the spontaneous polarisation for the four compounds as a function of temperature. It is interesting to note that as the lateral branch length increases the polarisation decreases, which contradicts models of the development of the spontaneous polarisation based on steric interactions at the chiral centre (i.e., steric hindrance). However accompanying the decrease in the polarisation there is an increase in the threshold voltages i.e., the antiferroelectric state becomes

stabilised with increasing lateral branch length. The reorientational switching times of these compounds were found to be in the region of 10-20 μ s. A decrease in the longer alkyl chain attached to the chiral carbon from six to four carbon atoms (9Cbp14(*R*)) gave a small increase in the maximum Ps values obtained which is related to dilution effects. All chiral centres were (*R*) configuration.

DISCUSSION

Non chiral compounds.

Some general trends in properties can be discerned from these results. As the size of the branched chain is increased there is an increase in the stability of the alternating tilt smectic C_{alt} phase, and as the size of the non-branched chain is increased there is initially an increase in the smectic C_{alt} transition temperatures and then two soft crystal phases, X and Y are interjected.

It has been found previously that there is a strong odd-even effect of the size of the lateral branch with the formation of smectic C_{alt} and smectic C phases in both chiral and racemic systems. This was not observed in any of the systems reported here. The temperatures of the transitions usually follow smooth curves and only the nature of the smectic C phase obtained alters, giving the smectic C phase for short (methyl) branches and smectic C_{alt} at longer branch lengths. With n = 1 and m = 2, 3 no odd-even effect is seen. When the shorter alkyl chain is methyl the normal smectic C phase is observed, when it is ethyl both types of smectic C occur, and when the shorter alkyl chain is propyl only smectic C_{alt} phases are obtained.

The stability of the phases is influenced to a large extent by the character of the linking group X. When $X = -CH_2-CH_2$ - (ethyl) the transitions are of lower temperature and monotropic. There is free rotation around this bond and the increased number of conformations possible may reduce the mesomorphic character of the compound either through an increase in the apparent width of the molecule, a decrease in linearity or the linkage could be effectively reducing the size of the rigid core by removal of the terminally associated phenyl group from the core, both physically and because of a decrease of electron delocalisation over this area, i.e., conjugation.

In comparison the $-CH_2=CH_2$ - (ethene) linkage has a high barrier to rotation from the *trans* conformation and delocalisation (and hence polarisation) of electrons is possible through the double bond from the phenyl group. Thereby giving a long rigid core which is bent. The -C=C- (ethyne) linkage again allows delocalisation but is linear, this may have the effect of increasing the core interactions and hence the melting point so that the phase transitions are monotropic. The strong localisation of electrons in the triple bond may also have the effect of reducing the transition temperatures.

The first series described here are 9Cbp2m, 9Cbp3m and 9Cbpmm. These all have S_C phases when m = 1. When m = 2 both types of S_C phase are observed and when m = 3 then only S_{Calt} phases are seen. When $m \ge 3$ and n = 2 then there is a very short S_C phase present. For m = 4 the S_C phase is only seen on cooling as the S_{Calt} transition supercools.

Chiral compounds

In chiral compounds the transition from S_C^* to S_C^*A often goes via an $S_C^*\gamma$ phase. This phase was not seen in any of the non-chiral or racemic compounds investigated. Although the compound 9Cbp26 showed two signals in the DSC at the transition at low heating rates it was not possible to resolve these and miscibility studies with a standard chiral compound does not suggest that the presence of an $S_{C\gamma}$ phase is a likely explanation.

CONCLUSION

It is again shown here that non-chiral compounds can exhibit alternating tilt smectic phases. These results on the non-chiral and racemic compounds would seem to suggest that the nature of the smectic C phase is dependent on more than one factor. For instance the results suggest that the incidence of alternating tilt smectic C phases is due to steric factors (the size of the branched alkyl chain groups) and that the incidence of the more 'unstructured' smectic C phases α and γ is due to other factors such as dipolar contributions. The presence of moderated smectic A phases is described in terms of the incommensurability of two layer spacings and this applies also to the smectic C phase (I. Nishiyama, J. W. Goodby ref. 4). In these compounds it can be imagined that the two incommensurate layer spacings relate to the length of the molecules which is moderated by the bulky nature of the lateral alkyl branch and the length of the dipolar molecular pairs which are formed by the chiral compounds.

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