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Invited Lecture

Synthesis and liquid-crystalline properties of a homologous series of antiferroelectric liquid crystals and their respective racemates†

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New chiral, as well as racemic 1-methylalkyl terephthalidene-bis-aminocinnamates have been synthesized and their liquid-crystalline properties investigated. Generally, the chiral compounds possess the antiferroelectric S_D^* phase, whereas in the homologous series of racemates, the appearance of the S_O phase depends on the length of the alkyl chain. For racemic compounds derived from 2-alkanols with an odd number of carbon atoms, a S_O phase is generally observed. On the other hand when the number of carbon atoms is even, a S_C phase occurs. Moreover, in racemic 1-methylbutyl terephthalidene-bis-aminocinnamate, a S_C - S_O - S_C reentrant phase sequence has been established.

1. Introduction

X-ray and miscibility studies on the liquid-crystalline modifications of chiral, as well as racemic 1-methylheptyl terephthalidene-bis-aminocinnamate (M7TAC) led to the discovery of a novel smectic phase type (S_O), in 1983, by Levelut *et al.* [1]. As in the S_C phase, the molecules in the S_O phase are positionally disordered inside the smectic layers and tilted with respect to the layer normal. Later on, Galerne and Liebert showed that the structure of the S_O phase is distinguished from the S_C phase by an alternation of the tilt direction from one smectic layer to another, thereby forming a herringbone structure [2]. In the chiral S_D^* phase each individual layer possesses a spontaneous polarization perpendicular to the layer normal and to the tilt direction. Due to the alternation of the tilt direction the orientation of the spontaneous polarization also alternates from layer to layer and hence the S_D^* phase exhibits an antiferroelectric structure [3].

In addition to M7TAC, in which the occurrence of the S_O (or S_D^*) phase has been found to be independent of chirality, two other 1-methylalkyl terephthalidene-bis-aminocinnamates (alkyl = hexyl, propyl) have been investigated so far [4-7]. For the chiral 1-methylhexyl derivative (M6TAC), a S_D^* phase, which in the racemic mixture of both enantiomers is replaced by a S_C phase, and for the chiral 1-methylpropyl derivative (M3TAC), a S_C^* phase, in addition to a S_A phase, has been established.

A similar antiferroelectric phase (S_{CA}), additionally showing antiferroelectric switching behaviour, was observed in chiral 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC), in 1988, by Chandani *et al.* [8]. Recently, we have demonstrated through miscibility studies that S_O and S_{CA} belong to the same phase type [9, 10].

Here, the polymorphism, phase transition temperatures and transition enthalpies of several new chiral (alkyl = butyl, pentyl) as well as racemic (alkyl = propyl, butyl,

† Other parts of the lecture will be published elsewhere [10, 15].

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pentyl, hexyl, octyl, nonyl, decyl, undecyl) 1-methylalkyl terephthalidene-bis-aminocinnamates are presented and the influence of the alkyl chain length, as well as of the chirality, on the occurrence of the S_0 phase is discussed.

2. Experimental

The 1-methylalkyl terephthalidene-bis-aminocinnamates were prepared by esterification of 4-nitro-cinnamic acid with the respective chiral or racemic 2-alkanol, followed by reduction of the nitro group to amino and condensation of the 4-aminocinnamates with terephthalaldehyde according to descriptions given in [4].

Transition temperatures were determined optically using a Leitz SM-Lux-Pol polarizing microscope fitted with a Mettler FP 82 microheating stage and a Mettler FP 80 control unit. Transition enthalpies were obtained by DSC measurements using a Perkin-Elmer DSC 7. Miscibility studies were carried out by the contact method and, in some cases, in addition, by choosing specific concentrations. For these investigations (*R,R*)-M7TAC ($I-S_0-S_0^*$) and (*S*)-2f-6 ($I-S_C^*-S_M-S_I$) [11], which is an ester of (*S*)-2-chloro-4-methylbutanoic acid with 2-(4-hexyloxyphenyl)-5-(4-hydroxyphenyl) pyrimidine, have been used as reference compounds.

3. Results

The phase transition temperatures of the new 1-methylalkyl terephthalidene-bis-aminocinnamates were determined by optical microscopy. In order to classify the observed liquid-crystalline modifications, miscibility studies with (*R,R*)-M7TAC, which exhibits a S_0^* phase, and (*S*)-2f-6, which exhibits a S_C^* phase, have been carried out. As an example, the phase diagrams of rac-M4TAC/(*R,R*)-M7TAC and rac-

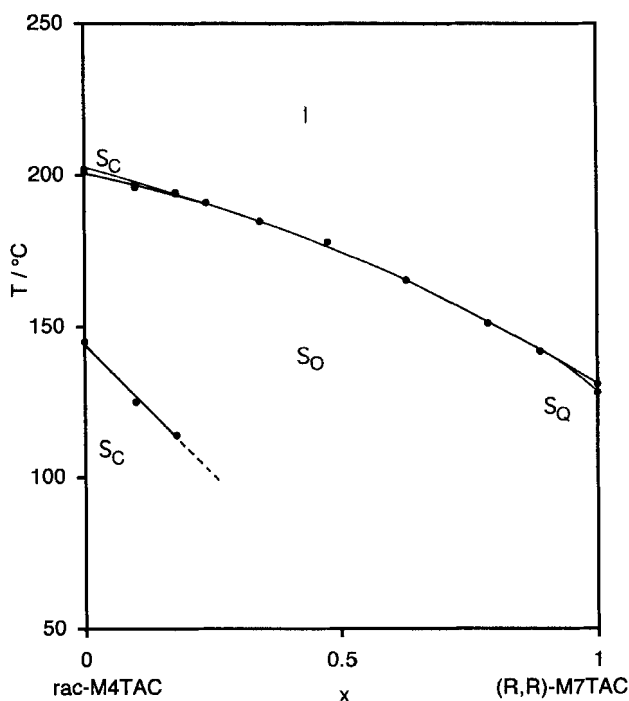


Figure 1. Phase diagram between rac-M4TAC and (*R,R*)-M7TAC.

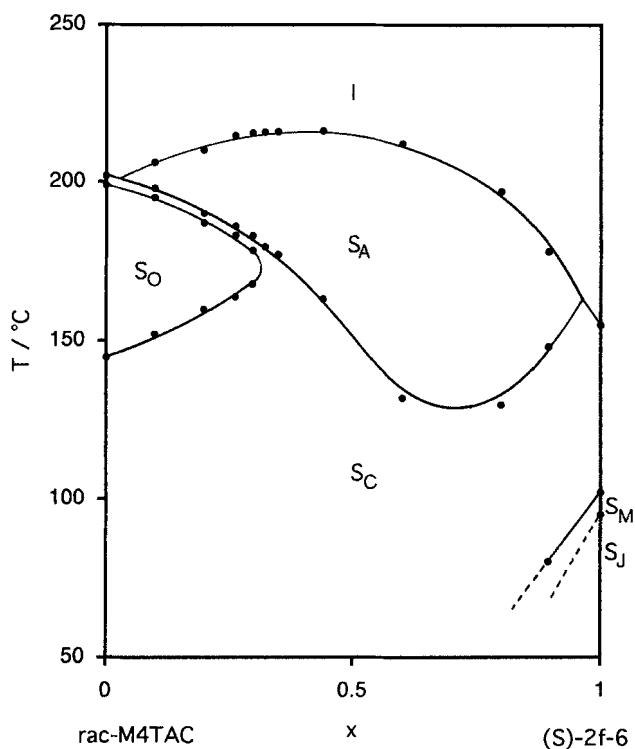
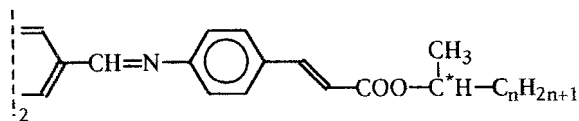


Figure 2. Phase diagram between rac-M4TAC and (S)-2f-6.

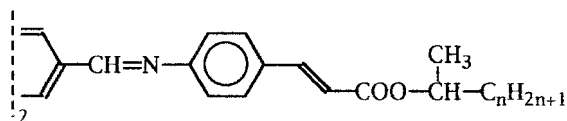
M4TAC/(S)-2f-6 are shown in figures 1 and 2, respectively. In figure 1, an uninterrupted miscibility between the S_0^* phase of (R,R)-M7TAC and one of the smectic modifications of rac-M4TAC is observed. As shown most clearly in the second phase diagram (see figure 2), the high as well as the low temperature phase of rac-M4TAC are uninterruptedly miscible with the S_C^* modification of (S)-2f-6. Thereby, a $S_C-S_O-S_C$ reentrant phase sequence, as observed so far only in a small concentration range of binary mixtures between chiral or non-chiral M7TAC and non-chiral M6TAC [5–7], is established for rac-M4TAC. In both phase diagrams (see figures 1 and 2), the $S_C-S_O-S_C$ reentrant phase sequence is maintained over a concentration range of about 20–30 mol%, where upon either the S_C or the S_O phase disappears.

The polymorphism, phase transition temperatures and transition enthalpies of the 1-methylalkyl terephthalidene-bis-aminocinnamates are given in table 1 (pure enantiomers) and table 2 (racemates). For the pure enantiomers, a S_0^* phase is observed, with the exception of the 1-methylpropyl derivative which exhibits S_C^* and S_A phases instead of the S_0^* phase. In the homologous series of racemates an odd–even effect appears for compounds with more than five carbon atoms in the alkyl chain: non-chiral compounds derived from 2-alkanols with an odd number of carbon atoms (M5TAC, M7TAC, M9TAC and M11TAC) possess a S_O phase whereas a S_C phase is observed when the number of carbon atoms of the 2-alkanol substituent is even (M6TAC, M8TAC and M10TAC). Comparing the pure enantiomers with their respective racemates, distinct influence of chirality on the occurrence of the S_O phase becomes obvious, for example M6TAC exhibits a S_0^* phase in its chiral form (see table 1) whereas in the racemate (see table 2) a S_C phase is observed.

Table 1. Polymorphism, transition temperatures ($^{\circ}\text{C}$) and in brackets the transition enthalpies (kJ mol^{-1}) of the chiral 1-methylalkyl terephthalidene-bis-aminocinnamates.

<i>n</i>	Compound	C	S_{O}^*	S_{Q}	S_{C}^*	S_{A}	I
2	(<i>S,S</i>)-M3TAC	● 151 [36]	—	—	● 223 [0·6]	● 236 [2·3]	●
3	(<i>R,R</i>)-M4TAC	● 131 [43]	● 192 [2·6]	—	—	—	●
4	(<i>R,R</i>)-M5TAC	● 107 [22]	● 167 [2·1]	—	—	—	●
5	(<i>R,R</i>)-M6TAC†	● 99 [21]	● 144 [2·2]	—	—	—	●
6	(<i>R,R</i>)-M7TAC	● 93 [18]	● 128 [1·6]	● 131 [0·4]	—	—	●

† Data from [5].

Table 2. Polymorphism, transition temperatures ($^{\circ}\text{C}$) and in brackets the transition enthalpies (kJ mol^{-1}) of the racemic 1-methylalkyl terephthalidene-bis-aminocinnamates.

<i>n</i>	Compound	C	S_{C}	S_{O}	S_{C}	S_{A}	I
2	rac-M3TAC	● 160 [30]	—	—	● 226 [0·9]	● 243 [2·4]	●
3	rac-M4TAC	● 137 [37]	● 145 [0·1]	● 201 [4·2]	● 202]†	—	●
4	rac-M5TAC	● 88 [18]	—	● 182 [4·5]	—	—	●
5	rac-M6TAC	● 85 [19]	—	—	● 175 [4·1]	—	●
6	rac-M7TAC	● 101 [33]	—	● 158 [3·6]	—	—	●
7	rac-M8TAC	● 87 [31]	—	—	● 153 [3·6]	—	●
8	rac-M9TAC	● 83 [32]	—	● 145 [3·6]	—	—	●
9	rac-M10TAC	● 98 [45]	—	—	● 135 [3·1]	—	●
10	rac-M11TAC	● 79 [54]	—	● 126 [2·1]	—	—	●

† DSC peaks for the $S_{\text{O}}-S_{\text{C}}$ and $S_{\text{C}}-I$ transitions could not be separated.

4. Discussion

Till now, only little is known about the relationship between molecular structure and the appearance of an antiferroelectric smectic phase. Recently, it has been pointed out that in homologous series of antiferroelectric liquid crystals, in which the length of the chiral chain is varied, quite often an alternation between S_{CA}^* and S_C^* phases occurs [12]. To explain this influence of the chiral chain length on the occurrence of the antiferroelectric phase, a model, which takes into account only steric interaction between molecules in neighbouring layers, has been proposed [13]. In the present study, we have established a similar odd–even effect for the racemic 1-methylalkyl terephthalidene-bis-aminocinnamates. Another remarkable feature observed for the S_{CA} phase is its stabilization in chiral racemic phase diagrams with increasing enantiomeric excess, an effect which is assumed to be caused by the increasing spontaneous polarization [12, 14]. Again, this behaviour is observed for the S_O phase exhibited by the compounds investigated. Probably, both spontaneous polarization as well as steric factor contribute to the stability of the S_O phase, although the relative roles of these factors is uncertain. Further studies are required to understand the origin of the herringbone structure on a molecular level.

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