Influence of chirality on phase transitions in ferroelectric liquid crystals

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Influence of chirality on phase transitions in ferroelectric liquid crystals†

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The transition temperatures between various smectic liquid crystal phases are determined as a function of the enantiomeric excess for three different chiral–racemic systems (i.e. binary mixtures consisting of a chiral enantiomer and its racemate). It is shown that transitions involving a ferroelectric phase occur in the chiral compounds at higher temperatures compared to their racemates, the temperature shift being proportional to the square of the enantiometric excess. In contrast, for transitions between two non-ferroelectric phases no difference between the chiral and the racemic compounds is found. Various reasons for the experimental behaviour are discussed. A chirality dependence of the transition temperature is also observed for the smectic A–isotropic transition.

1. Introduction

Smectic liquid crystal phases [1] possess, in addition to the nematic-like parallel orientational order of the rod-like molecules, a long range positional order in at least one dimension resulting in a layered structure. There are two subgroups of smectic phases: orthogonal phases, in which the director (the average direction of the long molecular axes) is parallel to the normal vector of the layer planes, and tilted phases, in which the director is inclined by a tilt angle θ to the layer normal. Due to different kinds of the in-plane molecular ordering there exists a large variety of both orthogonal and tilted smectic phases, the simplest (and most frequent) examples are smectic A (orthogonal) and smectic C (tilted), which possess within their layers only a liquid-like short range positional order. Often both phases occur in one compound, smectic A then being the high temperature phase to smectic C.

If a tilted smectic liquid crystal phase is composed of chiral (optically active) molecules, a unique coupling between macroscopic electric properties and molecular symmetry properties can be observed; the presence of chiral molecules leads to the appearance of a spontaneous electric polarization and ferroelectric properties [2]. As a second consequence of the molecular chirality some tilted smectic phases exhibit a helical superstructure in the director field. The periodicity of the helix is usually several micrometres and the molecular short range order is the same as in the non-chiral phases.

The appearance of the spontaneous polarization in tilted smectics is due to the combination of the monoclinic phase symmetry with the chiral (i.e. without a mirror plane) molecular symmetry leading to a polar overall symmetry of the point group C_2.

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Since one condition for the occurrence of the spontaneous polarization is the lack of mirror symmetry, non-chiral compounds and racemates (i.e. 1:1 mixtures of chiral antipodes) do not show a spontaneous polarization. On the other hand, all smectic liquid crystal phases can occur for non-chiral as well as for chiral molecules. Thus, every tilted smectic phase can exist in two modifications, namely with (chiral compound) or without (non-chiral or racemic compound) a spontaneous polarization. This behaviour illustrates also that ferroelectric liquid crystals are improper ferroelectrics [3], i.e. the transition to the ferroelectric phase in chiral compounds is not driven by the polarization but by molecular interactions which are present also in non-chiral or racemic compounds.

In this paper we consider chiral–racemic systems, i.e. binary mixtures of a chiral compound with its corresponding racemate. By preparing mixtures with different amounts of enantiometric excess the chirality, and accordingly the spontaneous polarization, can be varied continuously from zero (the value for the racemate) to the value for the optically pure enantiomer, while all properties not depending on the chirality are maintained, e.g. a chiral compound and its racemate show the same sequence of smectic phases in the same temperature regions. Thus, chiral–racemic systems are excellent model systems with which to study the relation between chirality and ferroelectric properties as well as to investigate the influence of the ferroelectricity on the liquid-crystalline properties, e.g. the smectic phase transitions.

In our study we consider the influence of the spontaneous polarization on phase transitions in chiral–racemic systems. Considering, for example, S_C–S_A transition, the amount of the spontaneous polarization is, to a first approximation, linearly coupled to the tilt angle of the S_C phase, i.e. polarization and tilt are nearly proportional to each other [4]. As stated already in 1975 by Meyer *et al.* [5], the tilt–polarization coupling should result in a small shift of the S_C–S_A transition temperature, because, compared to the racemate, the spontaneous polarization in the S_C phase of the chiral compound stabilizes the tilted structure. The same behaviour can be expected at transitions between two tilted phases possessing different molecular ordering in the smectic planes, e.g. S_G–S_C. In this case, the polarization is, in addition to the coupling to the tilt, coupled to the in-plane order (the S_G phase will show the larger polarization even if the tilt remains constant) and the S_G phase in the chiral compound will be stabilized by the spontaneous polarization compared to the S_G phase of the racemate. However, because of the relatively low values of the spontaneous polarization in many ferroelectric liquid crystals this effect is expected to be very small. Until recently, only for one type of ferroelectric phase transition, S_C–S_A, do a few experimental indications [6] exist for the chirality dependence of the transition temperature and nothing was known about transitions involving other (more ordered) ferroelectric smectic phases. On the other hand, in recent years there has been considerable progress in the preparation of liquid crystals with large values of the spontaneous polarization [2(b),(c)]. Among the compounds showing the highest values are esters of chlorocarboxylic acids [7] which exhibit a rich smectic polymorphism [7(c)] and are easily prepared. Recently, we have presented a detailed study [8] of a chiral–racemic system of one of these high polarization compounds (designated as A7 in this paper). Our results [8] have shown that the temperatures of the S_C–S_A and S_G–S_C transitions depend significantly on the enantiomeric excess.

In this paper, we present results obtained on two other chiral–racemic systems showing S_G–S_A, S_B–S_A, and S_E–S_B transitions. We also give a more detailed presentation of the results of our previous study [8] as far as the chirality dependence of
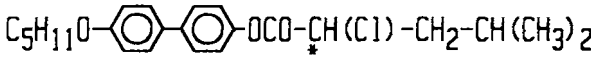
the transition temperatures is concerned. We show, that the transition temperatures of the S_C–S_A, S_G–S_C and S_G–S_A transitions are dependent on the enantiomeric excess whereas the transition temperatures of the S_B–S_A and S_E–S_B transitions are independent of the enantiomeric excess. Thus, our results seem to indicate a general difference between smectic phase transitions involving tilted phases and transitions involving only orthogonal phases.

2. Experimental

The three compounds studied here belong to two homologous series of ferroelectric liquid crystals described in [7(c)]. The structural formula and transition temperatures are shown in the table. The compounds were prepared in both their optically active configurations starting from L- or D-configured amino acids. The amino acids were transformed into the corresponding chloro acids according to a procedure given by Fu *et al.* [9]. The transformation can be conducted without measurable racemization [9]. The chloro acids were then combined with the corresponding 4-hydroxy-4'-alkyloxybiphenyls. The substances were purified by recrystallization until the differences in the transition temperatures of two optical antipodes became of the order of 0·1 K. The $S_{B(cryst)}$, S_E and S_G phases possess a pronounced in-plane positional order of the molecules and are often designated as crystal phases [1(b)]. However, because of their significant layer structure we maintain the designation as smectic liquid crystal phases.

The racemates and the mixtures with different amounts of enantiomeric excess were prepared by mixing corresponding amounts of the two antipodes. This way of preparing the racemates is preferable to a synthesis using a racemic starting material because we can exclude any impurity effects resulting from different synthetic routes. The transition temperatures of the pure compounds and the chiral–racemic mixtures were determined by the observation of the texture changes at the transitions using a polarizing microscope and a Mettler hot stage.

Structures and transition temperatures.

A7 $C_7H_{15}O$–⬡–⬡–OCO–$\overset{*}{C}H(Cl)$–$CH(CH_3)_2$

L–A7: S_G 71·2°C S_C 73·15°C S_A 81·7°C I
D–A7: S_G 71·1°C S_C 73·10°C S_A 81·7°C I

A6 $C_6H_{13}O$–⬡–⬡–OCO–$\overset{*}{C}H(Cl)$–$CH(CH_3)_2$

L–A6: S_G 77·6°C S_A 83·3°C I
D–A6: S_G 77·7°C S_A 83·3°C I

B5 $C_5H_{11}O$–⬡–⬡–OCO–$\overset{*}{C}H(Cl)$–CH_2–$CH(CH_3)_2$

L–B5: S_E 62·9°C S_B 71·3°C S_A 74·5°C I
D–B5: S_E 63·0°C S_B 71·4°C S_A 74·5°C I

3. Results

The compounds exhibit the following phase sequences: compound A7: S_G–S_C–S_A–I; compound A6: S_G–S_A–I; compound B5: S_E–$S_{B(cryst)}$–S_A–I. S_A, $S_{B(cryst)}$, and S_E denote orthogonal phases whereas S_C and S_G are tilted. Thus, the transitions in A7 and A6 involve tilted smectic phases possessing a spontaneous polarization (in chiral samples) whereas the transitions in B5 are between orthogonal smectic phases which do not possess a spontaneous polarization. Figure 1 shows the transition temperatures for the S_C–S_A, S_G–S_C, and S_G–S_A transition as a function of the enantiomeric excess. The transition temperature depends significantly on the enantiomeric excess and shows a minimum for the racemic mixtures: in the racemates the S_C–S_A transition occurs 0·8 K
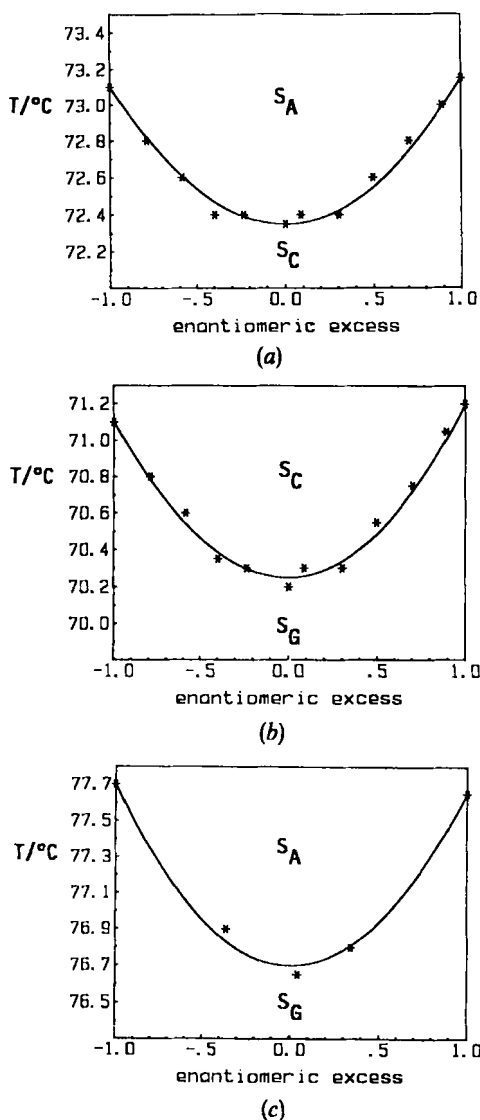

Figure 1. Chirality dependence of the transition temperatures; (a) S_C–S_A, compound A7; (b) S_G–S_C, compound A7; (c) S_G–S_A, compound A6. The enantiomeric excess is the difference between the mole fractions of the L- and D-enantiomers ($x_{ee} = x_L - x_D$).
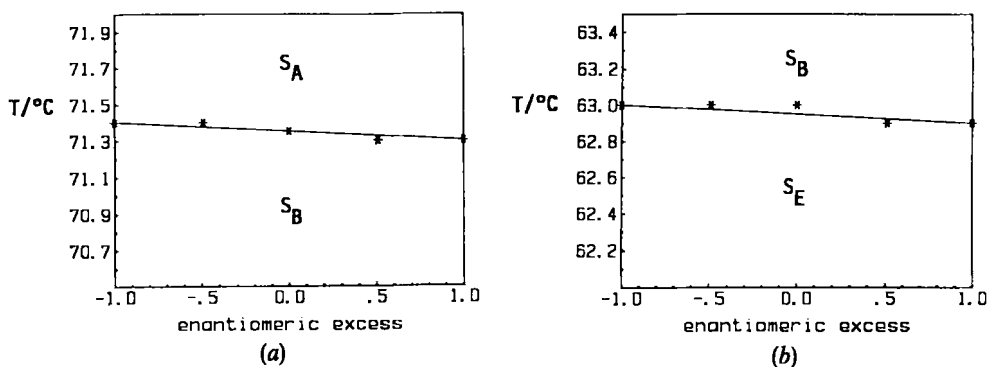
Figure 2. Chirality dependence of the transition temperatures; (a) S_B–S_A; (b) S_E–S_B, compound B5.

lower, the S_G–S_C and S_G–S_A transition 1·0 K lower than in the corresponding pure optically active enantiomers. The temperature difference $T - T_{rac}$ varies non-linearly with the amount of enantiomeric excess. A quadratic fit (i.e. assuming $T - T_{rac}$ to be proportional to the square of the enantiomeric excess) gives a fair description of the experimental values.

The dependence of the transition temperatures on the enantiomeric excess is most clearly seen in a contact preparation of two optical antipodes. Figure 4(a) shows a contact preparation of L- and D-configurated A7 at a temperature about 0·4 K below the S_C–S_A transition temperature of the optically active enantiomers. The S_C and S_A phases of our compounds may be distinguished under the polarizing microscope by their different birefringence colours [7 (d)]. In the margins of the contact preparation (high enantiomeric excess) the S_C phase is seen while in the middle (low enantiomeric excess) the S_A phase still exists (note the sharp phase boundary between the two phases indicating the first order nature of the S_C–S_A transition [7 (d)] in these compounds).

If the temperature shifts of the S_C–S_A, S_G–S_C, and S_G–S_A transitions in the chiral–racemic systems are really due to the stabilization effect of the spontaneous polarization, then transitions not involving ferroelectric phases should behave differently. Indeed we find that, within the limits of our experimental resolution, the transition temperatures of the $S_{B(cryst)}$–S_A and S_E–$S_{B(cryst)}$ transitions of the compound B5 (involving only orthogonal and thus non-ferroelectric phases) do not depend on the enantiomeric excess (see figure 2). As we discuss later, this observation for a compound possessing a structure very similar to those of compounds A7 and A6 gives strong support for the assumption that the chirality dependence of the transition temperatures in A7 and A6 is really due to the spontaneous polarization of the S_G and S_C phases.

4. Discussion

Summarizing our experimental results we observe in chiral–racemic systems a shift of the smectic phase transition temperatures to higher values with increasing enantiomeric excess for all cases in which a spontaneous polarization is present, regardless of whether the order parameter of the transition consists of the tilt angle (S_C–S_A), the in-plane positional order (S_G–S_C), or a combination of both parameters (S_G–S_A). If a ferroelectric phase is not involved ($S_{B(cryst)}$–S_A, S_E–$S_{B(cryst)}$), the transition temperatures are independent of the enantiomeric excess.

In the following, we discuss reasons other than the spontaneous polarization which might be responsible for our experimental observations. For example, it might be that

transitions showing a change of the tilt angle are influenced in some way by the chirality (apart from the effect of the spontaneous polarization) whereas transitions characterized mainly by a change of the in-plane order are not. In this case we would expect only a small effect for the S_G–S_C transition (X-ray investigations indicate only a minor change of the smectic layer thickness at the S_G–S_C transition of A7 corresponding to a tilt change of about 5° [10]). As we have described, we find experimentally a significant shift of the transition temperature, similar to the S_C–S_A and S_G–S_A transitions. The S_G–S_C transition is, in a way, the tilted analogue to the $S_{B(cryst)}$–S_A transition, in both cases the primary order parameter is described by the in-plane positional ordering of the molecules. The important difference for our study is that at the S_G–S_C transition a change of the spontaneous polarization occurs, whereas at the $S_{B(cryst)}$–S_A transition a spontaneous polarization is not present.

Another possibility to be considered is an influence on the transition temperatures resulting from the helical super-structure occurring in some tilted smectic phases of chiral molecules. The reciprocal of the helical pitch [11] and the spontaneous polarization [8, 11] in a chiral–racemic system were shown to vary nearly linearly with the enantiomeric excess. Thus, reciprocal pitch and spontaneous polarization behave in a very similar way for a chiral racemic system and an influence of the helical superstructure on the transition might be very difficult to separate from the influence of the spontaneous polarization. However, there are some reasons why such an influence of the helical structure is probably not present in our experiment. The measurements are made on thin samples in which, due to surface effects, the helical structure is more or less suppressed. Accordingly, we observe only fragmentarily the so-called dechiralization lines in the S_C phase of our sample indicating that the helical structure is almost completely suppressed. Moreover, in the S_G phase we do not observe, even in thick samples, any indication of a helical structure. Therefore, at least for the S_G–S_A transition any effect resulting from a helix formation can be excluded. If for the S_C–S_A and S_G–S_C transitions such an effect would exist because of a helix formation in the S_C phase, it should for the S_G–S_C transition (helical to uniform) be opposite to the S_C–S_A transition (uniform to helical). Experimentally, both transitions show a temperature shift in the same direction.

Our experimental results are qualitatively in agreement with the predictions of Landau theoretical models [12] of the S_C–S_A transition in ferroelectric liquid crystals. If only the simplest case is considered, i.e. if the Landau free energy contains only terms describing a simple bilinear coupling between polarization and order parameter and all effects not due to the polarization are neglected, the shift of the transition temperature is predicted to be [13]

$$T - T_{rac} = \frac{C^2 \chi}{a}. \tag{1}$$

Here, C is the bilinear order parameter–polarization coupling constant and χ is the dielectric susceptibility for the fixed order parameter. The parameter a is the coefficient of the second order term in the Landau expansion series (physically, a is a measure of the linear susceptibility of the order parameter with respect to a conjugate field). Concerning equation (1), it is of no consequence whether the Landau model describes a first order or a second order transition (i.e. whether the coefficient of the fourth order term has a negative or a positive sign). The equation for $T - T_{rac}$ is the same in both cases, provided that the nature of the transition does not change with the enantiomeric excess. If we assume that in a chiral–racemic system the coupling constant C varies

linearly with the enantiomeric excess [8], i.e. $C = C^* x_{ee}$, where C^* is the coupling constant of the optically pure enantiomer and x_{ee} is the mole fraction of the enantiomeric excess, then the transition temperature should vary with the square of the enantiomeric excess,

$$T - T_{rac} = \frac{C^{*2}\chi}{a} x_{ee}^2. \qquad (2)$$

For the S_C–S_A transition of the compound A7 the simple Landau model predicts a difference in the transition temperatures of racemate and chiral enantiomer of 2·9 K [8] which is at least of the same order of magnitude as the experimental value of 0·8 K.

A more comprehensive Landau model, given by Carlsson *et al.* [12(d)], which takes into account the helical superstructure, the non-linear relation between polarization and tilt, and a flexoelectric coupling between polarization and helix, predicts the temperature difference between racemate and optical active enantiomer [12(d)] to be

$$T - T_{rac} = \frac{1}{a}\left[\frac{\Lambda^2}{K} + \left(C + \frac{\Lambda\mu}{K}\right)^2 \bigg/ \left(\frac{1}{\chi} - \frac{\mu^2}{K}\right)\right]. \qquad (3)$$

Here, Λ is the coefficient of the Lifshitz term describing the helical superstructure, K is an elastic constant, and μ is the flexoelectric coupling constant (setting Λ and μ equal to zero reduces equation (3) to equation (1)). Whether the inclusion of the helical structure and of the flexoelectric coupling into the theory results in an increase or a decrease of the predicted temperature shift compared to the pure polarization effect, depends on the signs of the various coefficients which are, at least partly, not known for our compounds. Thus, it may be that the discrepancy between the experimental value (0·8 K) and the value predicted by the simplest theoretical model (2·9 K) is due to the neglecting of the helical structure in the S_C phase, although, as we have described, the comparison between the S_C–S_A and the S_G–S_C transition does not support this assumption. Furthermore, Carlsson *et al.* give in their theoretical study [12(d)] a quantitative estimate for the influence of helix formation on the S_C–S_A transition temperature. They find that the difference T(with helix) $- T$(without helix) is of the order of 10^{-3} K indicating that the influence of the helix is probably negligible. Another complication for the comparison between theory and experiment comes from the recent observation that the nature of the transition might change with varying enantiomeric excess. Calorimetric measurements have shown that the S_C–S_A transition in compound A7 is weakly first order in the chiral enantiomer and second order (in the
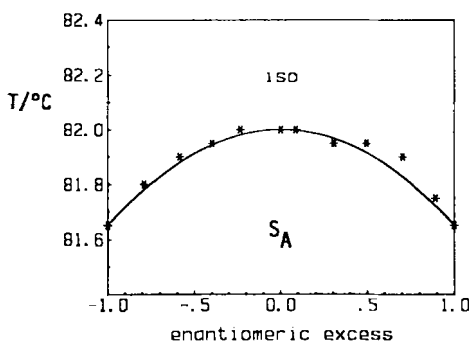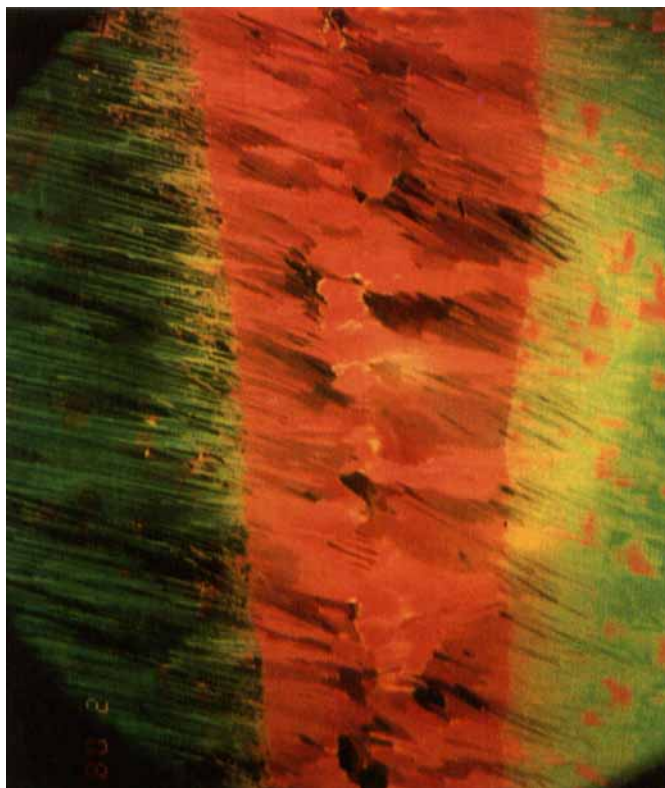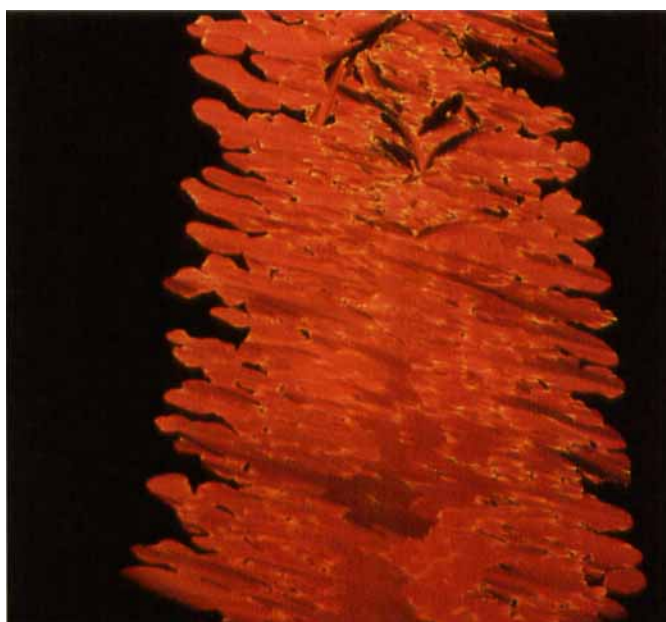

Figure 3. Chirality dependence of the smectic A–isotropic transition temperature, compound A7.

(a)

(b)

Figure 4.   Optical textures of a contact preparation of the L- and D-configured enantiomers of
compound A7 (the mole fraction of the enantiomeric excess varies continuously from -1
at the left margin over 0 in the middle to $+1$ at the right margin; (a) S_C–S_A transition
($T = 72 \cdot 7°C$), the S_A phase can be distinguished by its red birefringent colour from the green
appearing S_C phase; (b) S_A–I transition ($T = 81 \cdot 9°C$).

immediate vicinity of a tricritical point) in the racemate [14]. Therefore, we cannot expect equations (1)–(3) to give an exact description of the experimental result. To describe such a behaviour by Landau theory, we should introduce a chirality dependence of the coefficient of the fourth order term of the Landau free energy equation. From the molecular point of view, the reason for the change in the nature of the S_C–S_A transition of A7 in a chiral–racemic system, as well as the origin of the first order S_C–S_A transitions in general, is not clarified. Although the behaviour of A7 indicates, at first sight, that a first order S_C–S_A transition might appear because of a large spontaneous polarization, recent results [15] have shown that a first order transition also occurs in systems with zero polarization.

However, because of the various arguments described here it seems to us that the spontaneous polarization is at least one of the dominant parameters responsible for the transition temperature shift in our chiral–racemic systems. A final proof would consist of the preparation of a compound possessing a similar molecular structure to A7 and a considerably lower dipole moment (e.g. the chlorine at the chiral centre should be replaced by a methyl group). Then, the shift of the transition temperatures in a chiral–racemic system of this compound should be significantly smaller than in A7 (provided that the new compound also exhibits S_G, S_C, and S_A phases and that the transition entropies are of the same order of magnitude as for A7).

Finally, we want to report another observation probably not connected with the ferroelectric properties; for all of the three compounds we observe a chirality dependence of the temperature of the smectic A–isotropic transition which occurs in the racemic mixtures 0·2–0·3 K higher than in the optically active enantiomers (see figures 3 and 4(b)). Obviously, a racemic material adopts a smectic A arrangement rather than an optically active compound. This behaviour may be due to steric packing effects which might show up at the transition from the isotropic to a layered phase (but not at a transition between two layered phases).

In conclusion, we have shown that in chiral–racemic systems the transition temperatures for ferroelectric smectic phases show a dependence on the chirality. The shift of the transition temperature varies with the square of the enantiomeric excess. For transitions between two non-ferroelectric smectic phases a chirality dependence of the transition temperature is not observed indicating that the temperature shift may be due to the spontaneous polarization of the tilted smectic phases.

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