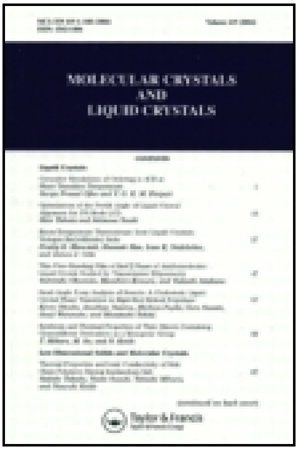

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Additive Partial Chiral Properties of a Thermotropic Liquid Crystal with Two Chiral Centers

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To cite this article: I. Dierking , F. Gießelmann & P. Zugenmaier (1996): Additive Partial Chiral Properties of a Thermotropic Liquid Crystal with Two Chiral Centers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 79-90

To link to this article: http://dx.doi.org/10.1080/10587259608042235

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 79–90
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Additive Partial Chiral Properties of a Thermotropic Liquid Crystal with Two Chiral Centers

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(Received December 14, 1994; in final form December 14, 1994)

Temperature dependent measurements of the pitch of the cholesteric phase and the spontaneous polarization of the smectic C^* phase are presented for five configurations of a thermotropic liquid crystal with two chiral centers. The temperature dependent chiral properties of the two diastereoisomers (S,S)-M96 and (S,R)-M96 are additively composed by the partial contributions of the individual chiral centers, determined from the partially racemic configurations. Mixtures of the diastereoisomers exhibit a mole fraction weighted additivity of the chiral properties.

Keywords: Smectic C^*, chirality, diastereoisomers, spontaneous polarization, cholesteric pitch.

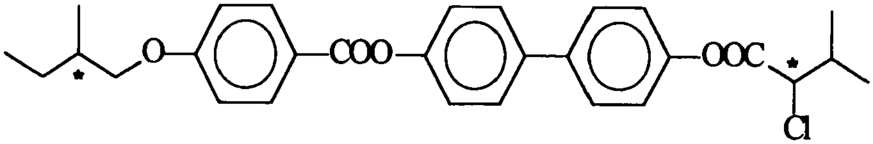
INTRODUCTION

Chiral properties of liquid crystalline phases such as the pitch of the cholesteric phase and the spontaneous polarization of the smectic C^* phase are characterized by their absolute values and their signs, in general positive for right handed and negative for left handed quantities. The absolute value of chiral properties is usually found to be temperature dependent, whereas only few compounds are known where the sign is a function of temperature. These compounds are shown to exhibit temperature induced cholesteric twist inversions[1–9] or polarization sign reversals[10–18]. Generally, it is found that liquid crystalline properties of mixtures of different compounds do not behave additively, whereas mixtures of two enantiomers of a compound may reveal linear additive chiral properties as the cholesteric pitch[19] or the spontaneous polarization of the S_C^* phase[20]. The properties of diastereoisomers and their partially racemic configurations as well as mixtures of diastereoisomers represent a case in between. On the one hand diastereoisomers are different compounds with different physical properties, on the other hand they represent systems that deviate very little from each other.

Recently, Kuball *et al.*[21,22] have demonstrated for induced cholesteric phases, that the helical twisting power (HTP) is not very sensitive with respect to the local order parameters S^* and D^*, where S^* describes the local orientational order of the molecule fixed x_3^* axis with respect to the optical axis and D^* gives a measure for the deviation of rotational symmetry of the molecules around the x_3^* axis. They demonstrated that the HTP is strongly dependent on the direction of the orientation axis x_3^* relative to the molecular skeleton. Varying the direction of the orientation axis by different substitution of the chiral guest molecules, they have shown that additivity rules only hold if the orientation axis is the same for the molecules compared[22]. In the case of the configurations of a rod-like molecule investigated here with two chiral centers on opposite ends of the more or less linear molecular skeleton, we believe that these conditions approximately hold, even though different molecules are compared.

EXPERIMENTAL

A benzoic acid biphenyl ester (M96) of the general formula



was investigated in five configurations, namely: (S, S), (S, R), (S, RS_{rac}), (RS_{rac}, S) and (RS_{rac}, R). The synthesis, characterization and general data has been reported elsewhere.[8,9] The compounds exhibit the general phase sequence

$$I \leftrightarrow BP \leftrightarrow N^* \leftrightarrow S_C^* \leftrightarrow (S_G^*) \leftrightarrow \text{Cryst.}$$

where the blue phase (BP) is missing for the (S, S) and (S, RS_{rac}) configurations. The temperature dependence of the cholesteric pitch was determined by the color change method[4,23] using 10 μm commercially available liquid crystal cells (E.H.C. Ltd.) and was checked by the Cano-Grandjean method[24,25] as well as by measurements of the selective reflexion wavelength. The handedness of the helicoidal cholesteric structure was determined by optical rotation measurements.[26]

The temperature dependence of the spontaneous polarization P_s was obtained by the well known triangular wave method[27] with 4 μm LC cells and the sign of P_s introduced according to the conventions by Clark and Lagerwall.[28] For completeness of the characterization, the temperature dependence of the (non-chiral) parameters as tilt angle Θ and the effective rotational viscosity γ_{eff} were also determined. Tilt angles Θ were estimated from X-ray measurements of the layer spacings d_{SC}^* of the S_C^* phase, divided by the length of the molecules taken from molecular modelling calculations as $d = 26.7$ Å ($\Theta = \arccos(d_{SC}^*/d)$). Effective rotational viscosities γ_{eff} were estimated from the polarization reversal current measurements according to Escher *et al.*[29]

EXPERIMENTAL RESULTS AND DISCUSSION

Keating[30] has derived from a simple model of the cholesteric phase that the twisting power P^{-1} can in first approximation be regarded as a linear function of temperature, disregarding temperatures in the vicinity of phase transitions. The partial twisting power $p_{i,j}^{-1}$ of a chiral element j of a molecule i can thus be written as

$$p_{i,j}^{-1} = a_{i,j}T + b_{i,j} \tag{1}$$

with i: molecular index, j: chiral center index, $a_{i,j}$ and $b_{i,j}$: coefficients and T: absolute temperature. The macroscopic twisting power P_i^{-1} of molecule i is given by the sum of

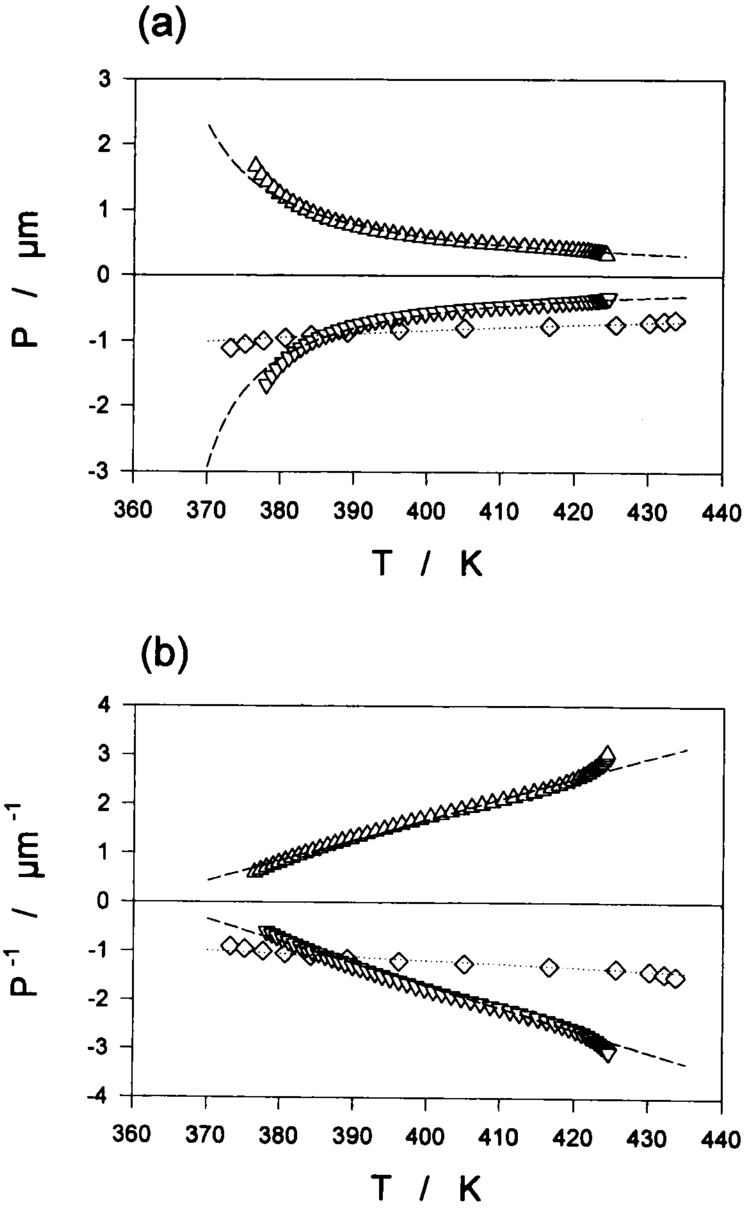


FIGURE 1 Temperature dependence of (a) the cholesteric pitch P and (b) the twisting power P^{-1} of the partially racemic configurations (S, RS_{rac})-M96 (◇), (RS_{rac}, S)-M96 (Δ) and (RS_{rac}, R)-M96 (∇). The dotted and dashed lines represent a linear best-fit, disregarding temperatures in the vicinity of the phase transitions.

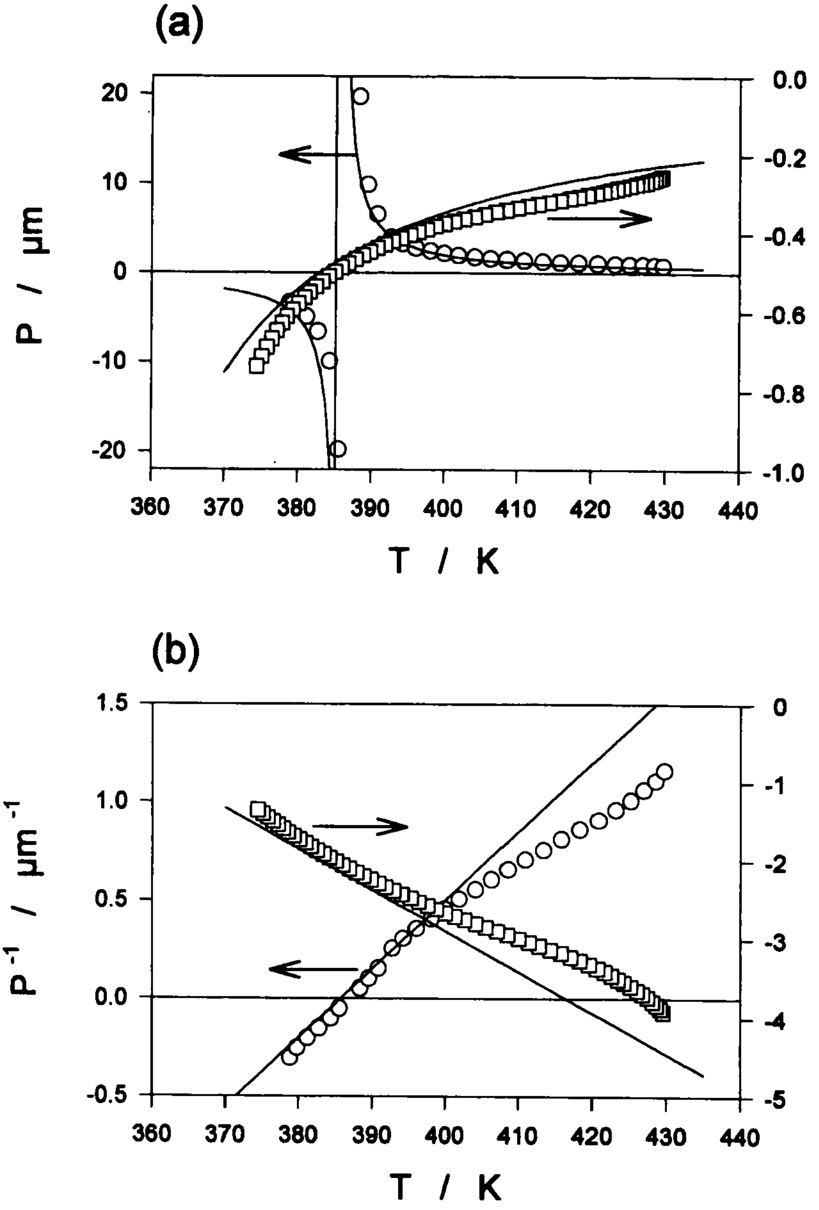


FIGURE 2 Temperature dependence of (a) the cholesteric pitch P and (b) the twisting power P^{-1} of the diastereoisomers (S, S)-M96 (○) and (S, R)-M96 (□). Solid lines represent the additively calculated temperature dependence according to Equation (2).

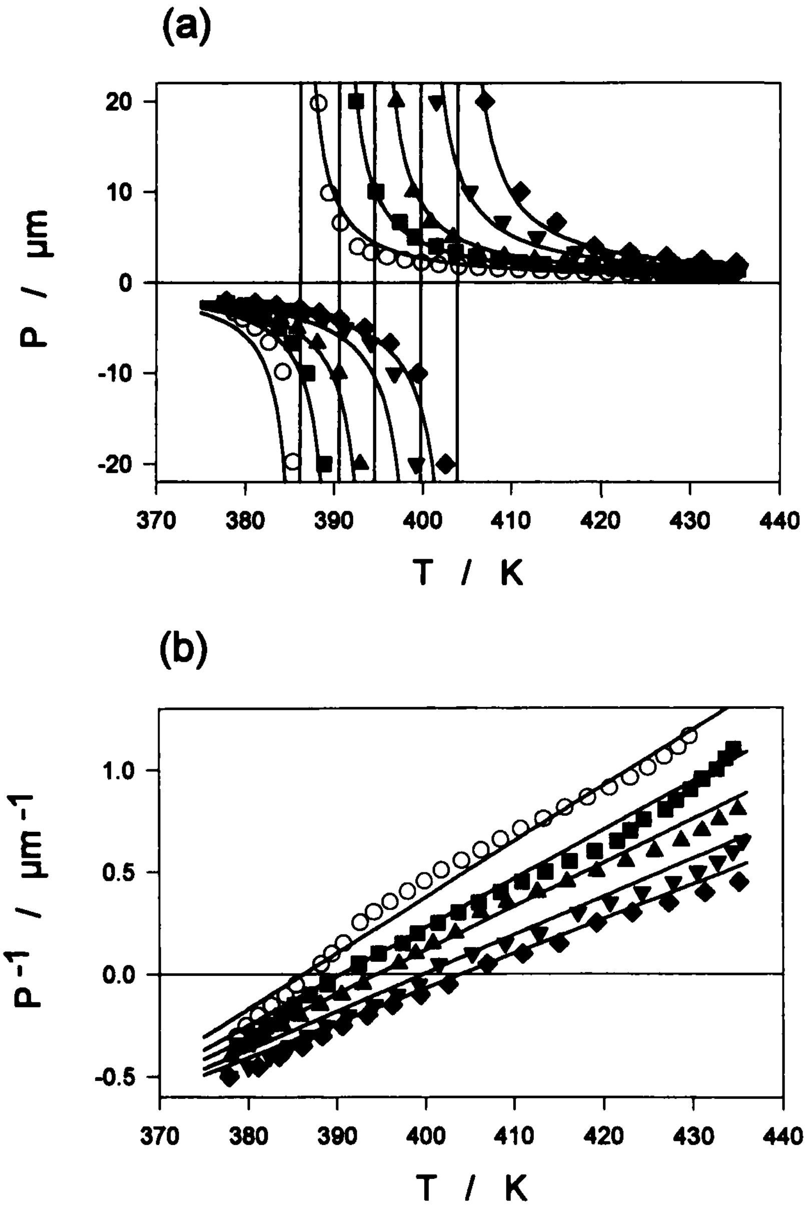


FIGURE 3 Temperature dependence of (a) the cholesteric pitch P and (b) the twisting power P^{-1} of mixtures of the two diastereoisomers (S, S)-M96 and (S, R)-M96 with (○) 100%-, (■) 95.0%-, (▲) 91.3%-, (▼) 87.5%- and (◆) 85.0%-(S, S)-M96. Solid lines represent the calculated temperature dependence according to Equation (3).

the partial twisting powers $p_{i,j}^{-1}$ of the individual chiral elements

$$P_i^{-1} = \sum_j p_{i,j}^{-1} = \sum_j (a_{i,j}T + b_{i,j}) \qquad (2)$$

if the chiral elements are regarded as independent, i.e. without any intramolecular coupling. Extension of the additivity of partial chiral contributions to mixtures, yields a macroscopic twisting power of

$$P^{-1} = \sum_i x_i P_i^{-1} = \sum_i x_i \left(\sum_j p_{i,j}^{-1}\right) = \sum_i x_i \left(\sum_j (a_{i,j}T + b_{i,j})\right) \qquad (3)$$

by weighing the individual contributions of different compounds i with their mole fraction x_i. The validity of Equation (2) has been shown in an earlier work[9], where the temperature induced cholesteric twist inversion of single component systems was treated in terms of additive partial twisting powers as demonstrated in Figure 1 and Figure 2. From measurements of the temperature dependence of the cholesteric pitch (Figure 1a), and the twisting power (Figure 1b), of the partially racemic configurations (S, RS_{rac})-M96 (◇), (RS_{rac}, S)-M96 (Δ) and (RS_{rac}, R)-M96 (∇) the temperature dependence of the pitch (Figure 2a) and twisting power (Figure 2b) of the dias-

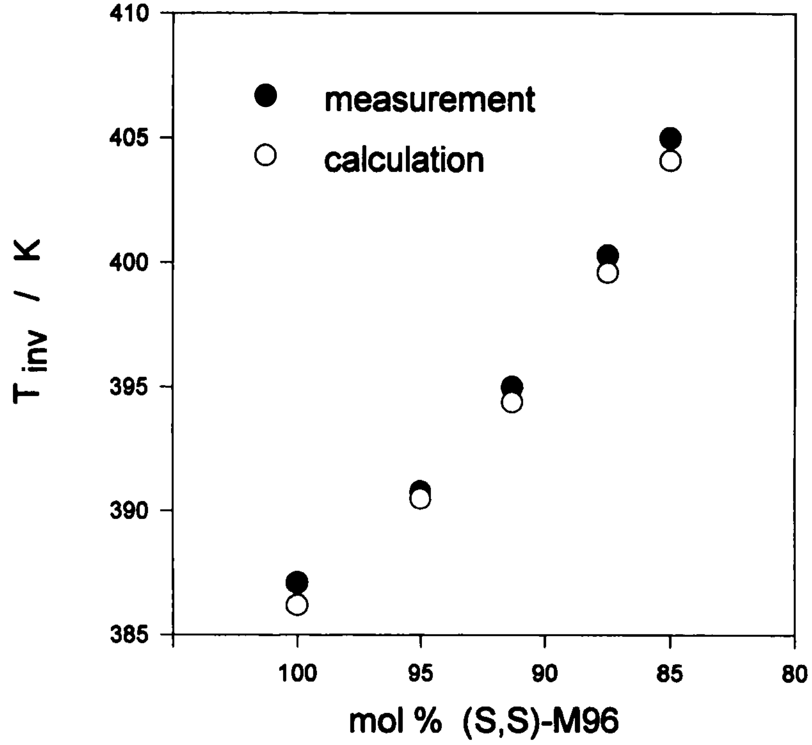


FIGURE 4 Dependence of the twist inversion temperature T_{inv} on the mole fraction of (S, S)-M96 for the binary (S, S)-M96/(S, R)-M96) mixtures. (●) measured values and (○) calculated values from Equation (3).

tereoisomers (S, S)-M96 (○) and (S, R)-M96 (□) can be predicted by use of Equation (2). In the figures, the dotted lines represent the contribution of chiral center "1", the dashed line that of chiral center "2" and the solid line the sum of both (Equation (2)).

Figure 3 depicts the temperature dependence of the cholesteric pitch (Figure 3a) and the twisting power (Figure 3b) for different mixtures of the diastereoisomers (S, S)-M96 and (S, R)-M96. The solid lines represent the calculated temperature behaviour according to Equation (3), clearly demonstrating the validity of approximate additivity. As expected, the different mixtures exhibit a shift in the twist inversion temperature T_{inv} to higher temperatures with increasing mole fraction of (S, R)-M96. The experimentally determined twist inversion temperatures compare well to the calculated ones (Equation (3)), as depicted in Figure 4.

Following the same considerations as above for the temperature dependence of the cholesteric twisting power, Equation (2) and (3) can analogously be extended to the temperature dependence of the spontaneous polarization of the ferroelectric smectic C^* phase

$$P_s^{(i)}(T) = \sum_j P_s^{(i,j)}(T) \tag{4}$$

Equation (4) describes the temperature dependence of the spontaneous polarization of diastereoisomer *i* in terms of additive partial contributions of chiral centers *j*. Extension

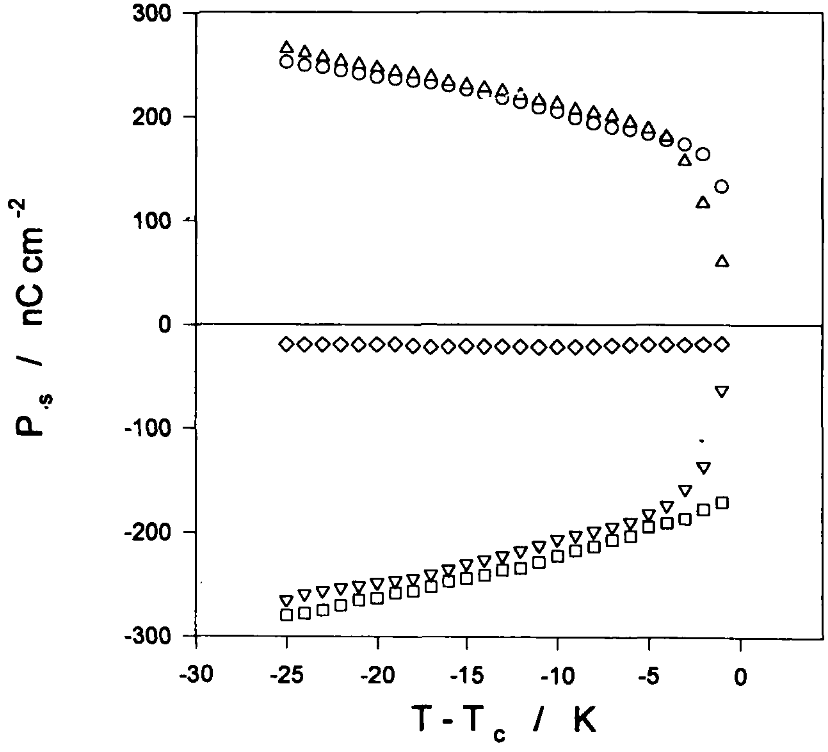


FIGURE 5 Reduced temperature dependence of the smectic C^* spontaneous polarization for the partially racemic configurations (◇) (S, RS_{rac})-M96, (△) (RS_{rac}, S)-M96, (▽) (RS_{rac}, R)-M96 and the diastereoisomers (○) (S, S)-M96 and (□) (S, R)-M96.

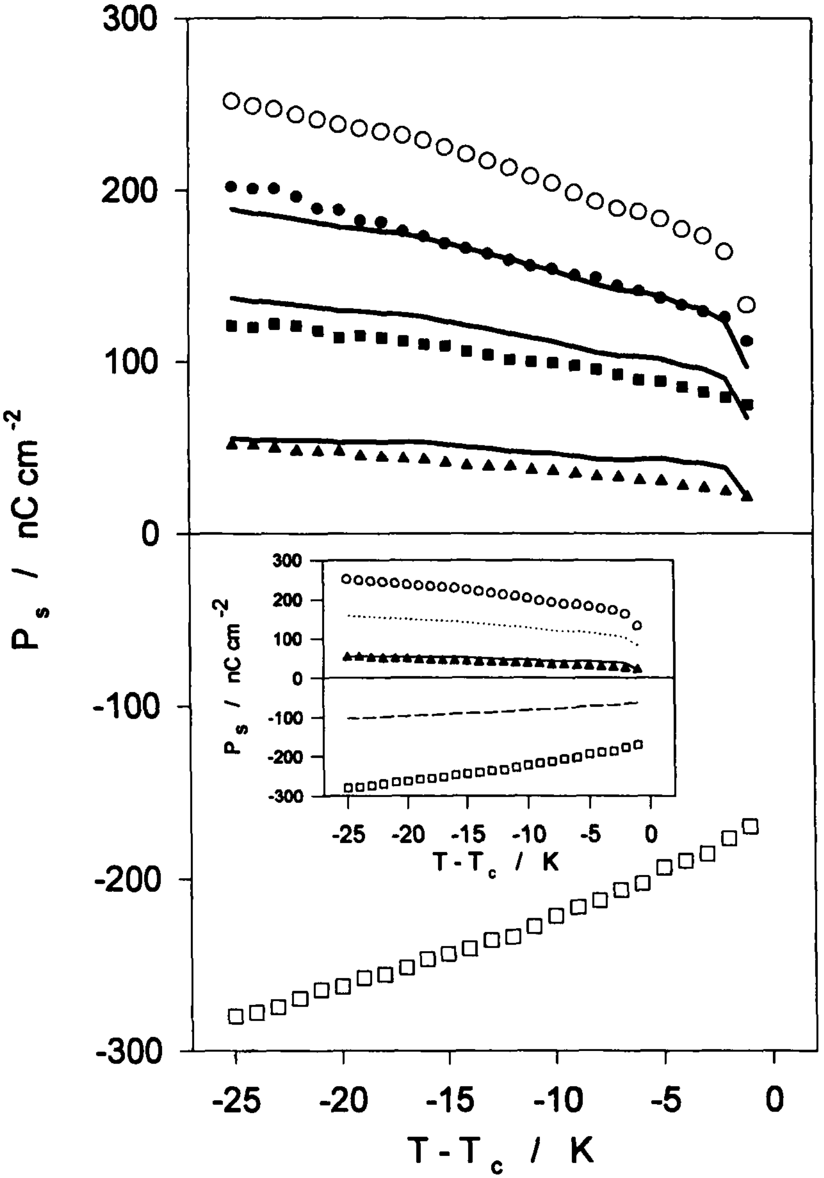


FIGURE 6 Reduced temperature dependence of the smectic C* spontaneous polarization for some mixtures of the diastereoisomers (S, S)-M96 and (S, R)-M96. (○) 100%-, (●) 88.1%-, (■) 78.4%-, (▲) 63.1%- and (□) 0%-(S, S)-M96. The solid lines represent the results of the calculation according to Equation (5). The inlet demonstrates the contributions of the two diastereoisomers: 63.1% (S, S)-M96 as dotted line and 36.9% (S, R)-M96 as dashed line.

to mixtures of the two diastereoisomers yields

$$P_s(T) = \sum_i x_i P_s^{(i)}(T) = \sum_i x_i \left(\sum_j P_s^{(i,j)}(T) \right) \tag{5}$$

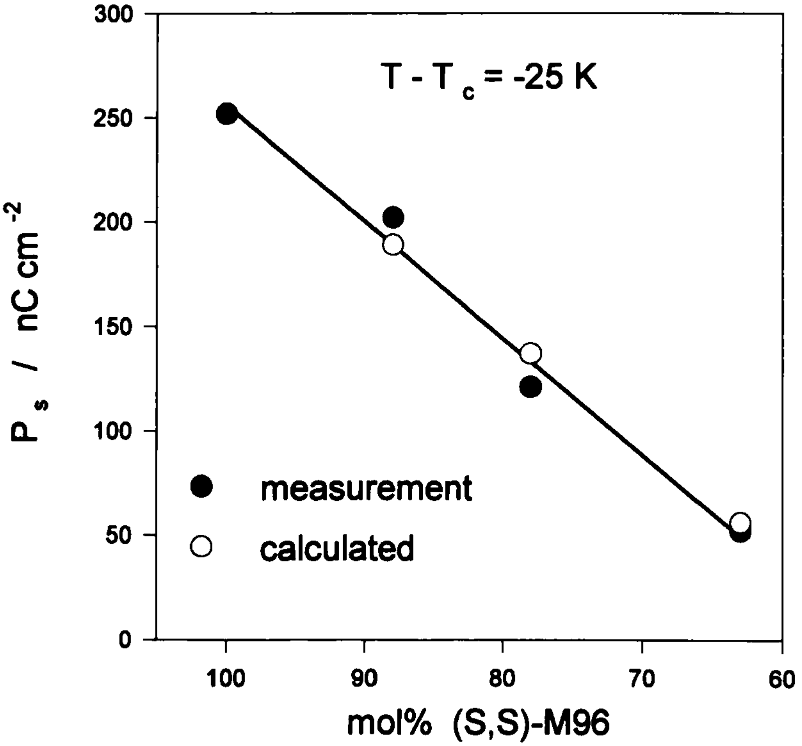


FIGURE 7 Dependence of the spontaneous polarization for a certain reduced temperature $T - T_c = -25$ K as a function of the mole fraction of (S, S)-M96. (●) measurement and (○) calculated from Equation (5).

However the spontaneous polarization of (S, RS_{rac})-M96 (◇ in Figure 5) is quite small as compared to the other configurations. Therefore, Equation (4) should only be discussed qualitatively. Figure 5 depicts the temperature dependence of the spontaneous polarization for the five different configurations investigated. It is clear, that the values for (S, S)-M96 (○) result from additive contributions of (S, RS_{rac})-M96 (◇) and (RS_{rac}, S)-M96 (Δ), as well as the values for (S, R)-M96 (□) are a sum of contributions from (S, RS_{rac})-M96 (◇) and (RS_{rac}, R)-M96 (∇).

Measurements on mixtures of the diastereoisomers (S, S)-M96 (○) and (S, R)-M96 (□) are depicted in Figure 6, reflecting the approximate additivity proposed in Equation (5). The inlet in Figure 6 demonstrates the contributions of the two diastereoisomers, 63.1% (S, S)-M96 as dotted line and 36.9% (S, R)-M96 as dashed line. Solid lines in Figure 6 represent calculated values according to Equation (5). Figure 7 illustrates a linear variation of the spontaneous polarization with changing mole fractions of the two diastereoisomers for a fixed reduced temperature $T - T_c = 25$ K. Experimental and calculated values again compare well.

Figure 8 and Figure 9 depict the temperature dependence of the tilt angle Θ of the S_C^* phase and the effective rotational viscosity γ_{eff}, respectively. Since these parameters

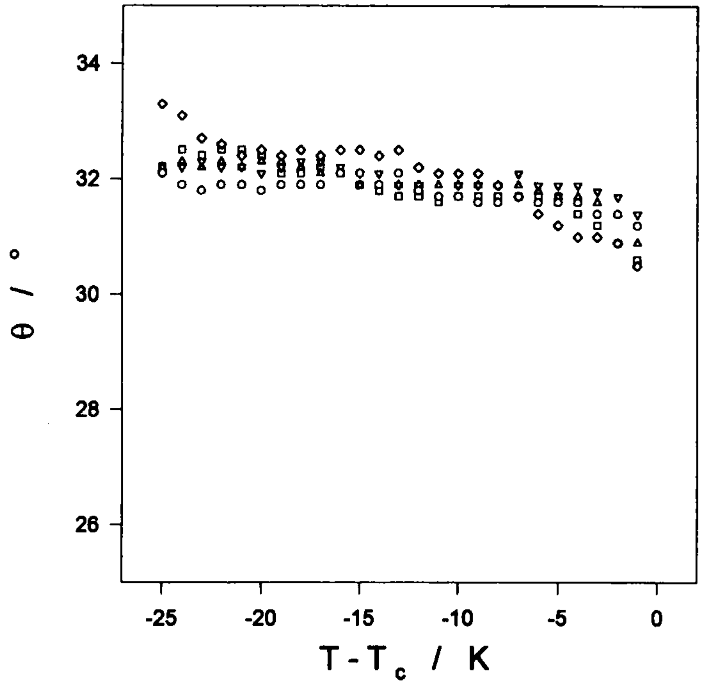


FIGURE 8 Reduced temperature dependence of the smectic C^* tilt angle Θ, estimated from small angle x-ray diffraction data. (◇) (S, RS$_{rac}$)-M96, (Δ) (RS$_{rac}$, S)-M96, (∇) (RS$_{rac}$, R)-M96, (○) (S, S)-M96 and (□) (S, R)-M96.

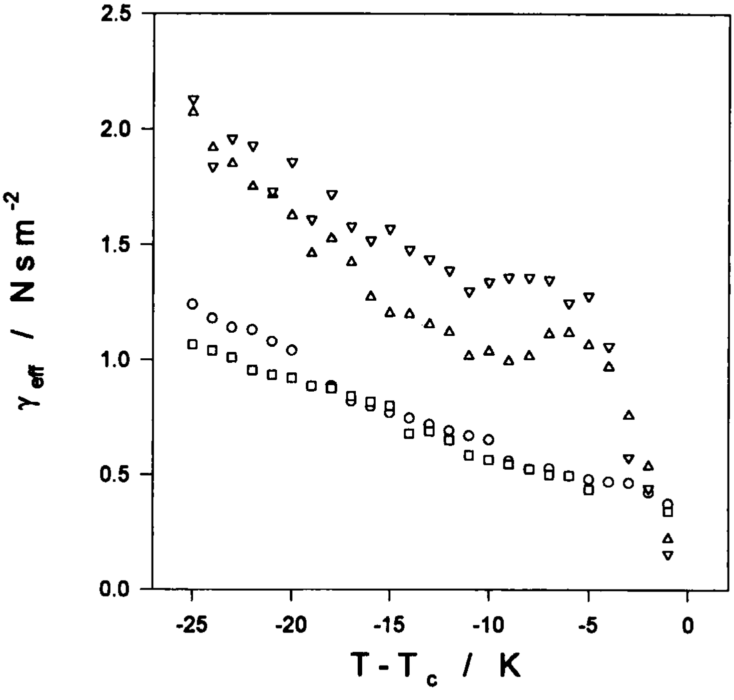


FIGURE 9 Reduced temperature dependence of the effective rotational viscosity γ_{eff} of the smectic C^* phase for (Δ) (RS$_{rac}$, S)-M96, (∇) (RS$_{rac}$, R)-M96, (○) (S, S)-M96 and (□) (S, R)-M96 as estimated from measurements of the polarization reversal current.

are non-chiral in character, a large deviation of values is not expected for the different configurations. Indeed, the tilt angles are almost independent of temperature and all the values determined are in the same order of magnitude.

CONCLUSION

Macroscopic chiral properties as the cholesteric pitch and the spontaneous polarization of the S_C^* phase of two diastereoisomers with two chiral centers can be predicted from measurements of the partial chiral properties determined for partially racemic configurations. Measurements of the same parameters for different mixtures of these diastereoisomers exhibit a mole fraction weighted additivity.

The demonstrated additivity of partial chiral contributions of chiral centers within a molecule cannot be considered as a generally valid principle, but is likely to be restricted to molecules of very similar constitution.

Acknowledgments

This work was supported by a grant from the Deutsche Forschungsgemeinschaft.

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