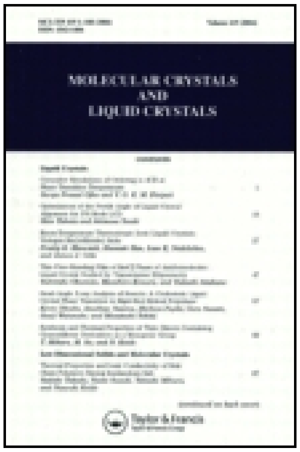

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Calorimetric Study of the Diastereomeric Interactions of Enantiomeric Iso-octyl-benzoyloxybenzoate Solutes with a Chiral Liquid Crystal

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Precision differential scanning calorimetric (DSC) analysis of the effect of doping cholesteryl nonanoate with the enantiomers of 4-(4-*n*-hexyloxybenzoyloxy)-isooctyl benzoate (R811 and S811) has been performed. Depressions of the enthalpies of both phase transitions, from crystalline to cholesteric and from cholesteric to isotropic phases, were found to be ~ 1.5 times greater for the samples of cholesteryl nonanoate doped with left-handed S811. Depressions of the temperatures of phase transitions are also more pronounced in the case of S811. Thus, the left-handed enantiomer S811 affects the molecular packing of cholesteryl nonanoate much more strongly than its right-handed counterpart R811. Remarkably, the difference between the enthalpy of melting of samples containing only 1 wt% of either enantiomer reaches ~ 20% of the enthalpy of fusion of pure cholesteryl nonanoate, indicating strong diastereomeric discrimination in the system. This calorimetric manifestation of diastereomer discrimination of S811 and R811 in cholesteryl nonanoate is in agreement with earlier observed non-symmetrical effects of these enantiomers on the pitch of cholesteric liquid crystals; that is the left-handed S811 enantiomer constricts the pitch nine times more strongly than the right-handed R811 expands the helix.

Keywords: Enantiomer; diastereomeric; liquid crystal; calorimetry; iso-octyl-benzoyloxybenzoate; enthalpy

INTRODUCTION

Solute – solvent chiral interactions have long been and continue to be an important focus of interest in liquid crystal research [1]. One can distinguish

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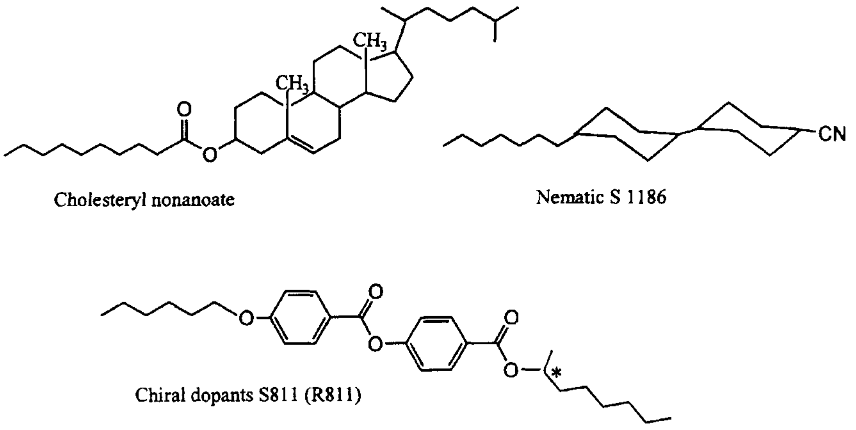
* Corresponding author.

three different cases of these interactions depending on whether only one or both components of a solute–solvent system are chiral. When a chiral solute is added to a non-chiral (nematic) liquid crystal, a macroscopic helicoidal array is established [2]. The screw sense of the twist is determined by the nature of the chiral additive, and enantiomeric solutes are known to produce helices of opposite handedness. This type of interaction is the most thoroughly studied, and the mechanism of chirality transfer from a chiral guest to a non chiral medium is satisfactorily understood [3, 4]. When achiral solutes are dissolved in chiral (cholesteric) liquid crystals (ChLC), they can perturb the helicoidal array of ChLC, resulting in visible changes in their apparent color. High sensitivity of this effect has made possible its application for the visual distinction between *cis*- and *trans*-isomers [5], and detection of vapors of volatile solvents [6–8]. According to some theoretical studies, a reverse influence of a cholesteric medium on a solute should also occur, resulting in "an induced deracemization of flexible solute conformers" [9, 10], but there has been no convincing experimental evidence of that phenomenon as yet. Experimentally, recent studies from these laboratories first presented some evidence for chiral induction in rigid rod solutes [11], but subsequently it was found that these effects could not be reproduced [12]. The third instance arises when both a solute and a solvent are chiral; the present work concerns this situation. Specific diastereomeric interactions between enantiomeric guests and a chiral medium have long been employed in the field of chiral recognition and separation, ChLC stationary phases being one of the examples. A recent study also reports on the stereoselective influence of cholesteric solvents on the kinetics of reactions involving enantiomeric solutes [13]. However, optical and calorimetric studies of diastereomeric interactions in cholesteric solvents are virtually unknown. Therefore, the behavior of enantiomers in ChLC is generally assumed to be similar to their behavior in non-chiral nematic LC; *i.e.*, enantiomers produce opposite but symmetrical shifts in the pitch. Recently, however, we observed a definite distinction in the behavior of certain enantiomers in ChLC based on cholesteryl esters [14]. For instance, R811 and S811 showed a marked non-symmetrical effect on the pitch: left-handed S811 constricted the pitch nine times more strongly than right-handed R811 expanded it. It occurred to us that the strong asymmetry in the helical twisting power of R811 and S811 in cholesteric matrices might be indicative of considerable differences in thermodynamic parameters of these solute–solvent systems. Precision DSC measurements were therefore undertaken to provide evidence of thermodynamic recognition of enantiomers R811 and S811 by the cholesteric matrix. In the previous study, two and three component cholesteric mixtures were employed. In order to simplify the interpretation of DSC data, in this work an individual cholesteric compound, cholesteryl nonanoate (CN), was used. This cholesteryl ester has been thoroughly studied and can serve as a model cholesteric phase [15].

EXPERIMENTAL

Cholesteryl nonanoate (CN) of 97% purity was obtained from Aldrich. The ester was recrystallized two times from *n*-pentyl alcohol, washed with ethanol, and vacuum dried at 50° prior to use. The specific optical rotation of CN, measured in methanol using a Perkin Elmer Lamda Spectropolarimeter was $\alpha_{25} = -30°$. R811 and S811 and the nematic liquid crystal 4-*n*-heptyl-4′-cyanobicyclohexyl (S1186), were purchased from EM Chemicals and used as received. Diagrams of the molecular structures of employed compounds are given in Figure 1. The samples were analyzed on a DSC Model 2950, manufactured by TA Instrument Co. Samples of CN doped with R811 or S811 were prepared by weighing specified amounts of CN and dopants into a vial, heating to the isotropic liquid and thoroughly mixing until dopants were completely dissolved. This visualization of solubility was performed on a Nikon polarizing microscope using a Mettler FP 82 hot stage. For DSC traces, three to eight mg samples were weighed to 0.1 mg and enclosed in aluminum crimped pans. The samples were then heated to



Cholesteryl nonanoate

Nematic S 1186

Chiral dopants S811 (R811)

FIGURE 1 Structures of the employed compounds.

the isotropic liquid at a scan rate of 5°/min, cooled to crystallize, and reheated to the isotropic liquid. The DSC runs for samples containing each concentration of a dopant were repeated at least five times, always using freshly prepared samples. The accuracy of transition heat measurements was calculated for each dopant concentration. For the solid crystal–cholesteric phase transition, accuracy within the 95% confidence interval is better than ± 10% and for the cholesteric phase–isotropic liquid transition is about ± 15%.

RESULTS AND DISCUSSION

DSC thermograms of CN doped with 2 wt.% of R811, 2 wt.% of S811, and of pure CN are shown in Figure 2. The shape of the DSC traces appears to be similar for all three samples, although the enthalpies and temperatures of phase transitions are somewhat different. An increase in the concentration of dopants leads to a proportional depression of both thermodynamic parameters, as illustrated in Figures 3 and 4. At low dopant concentration the difference between the values of the phase transition temperatures for CN/R811 and CN/S811 mixtures first fall in the range of experimental error

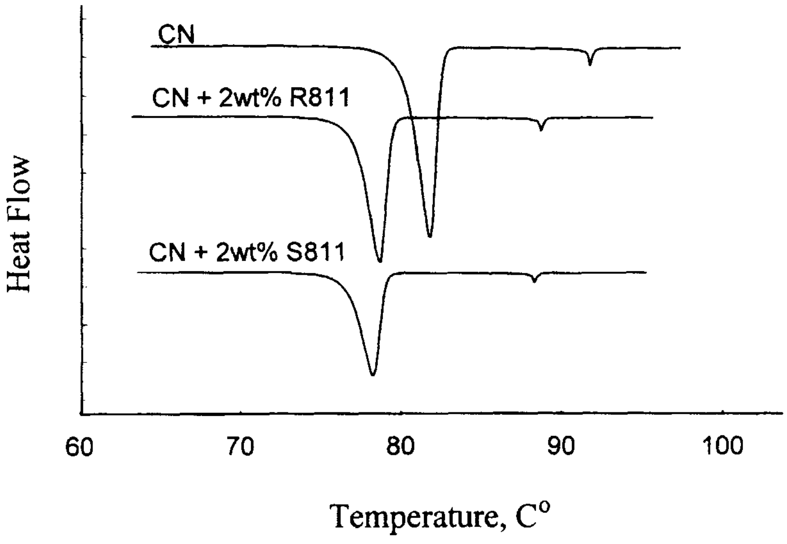


FIGURE 2 DSC traces of pure CN (upper curve), and CN doped with 2 wt.% of R811 (middle curve) and S811 (lower curve), respectively.

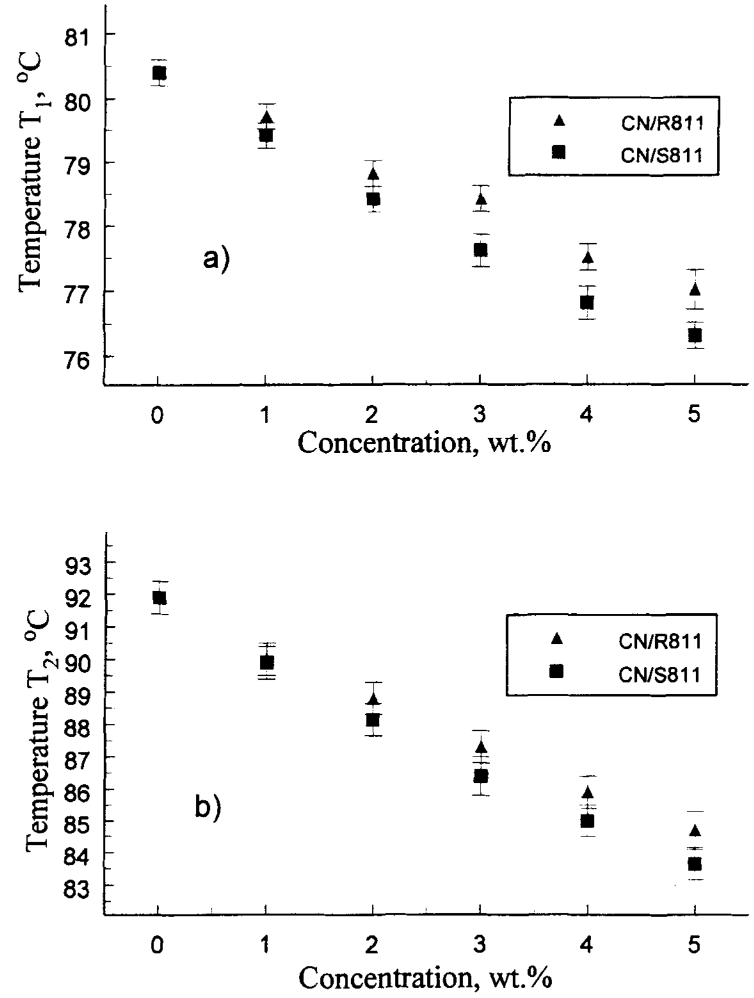


FIGURE 3 Phase transition temperature of cholesteryl nonanoate as a function of concentration of the enantiomeric dopants R811(-▲-) and S811(-■-): (a) crystal to cholesteric transition; (b) cholesteric to isotropic transition.

(0.95 confidence probability interval shown by error bars), but at higher concentrations (4 and 5 wt.%) the difference becomes statistically significant and one can discern a clear-cut tendency of S811 to more strongly depress the temperatures of phase transitions (Figs. 3a, b). The difference in enthalpy appears to be much more pronounced than the difference in temperature. For example, the enthalpies of the transition from the crystalline to cholesteric phase for CN doped with 1 wt.% of R811 and

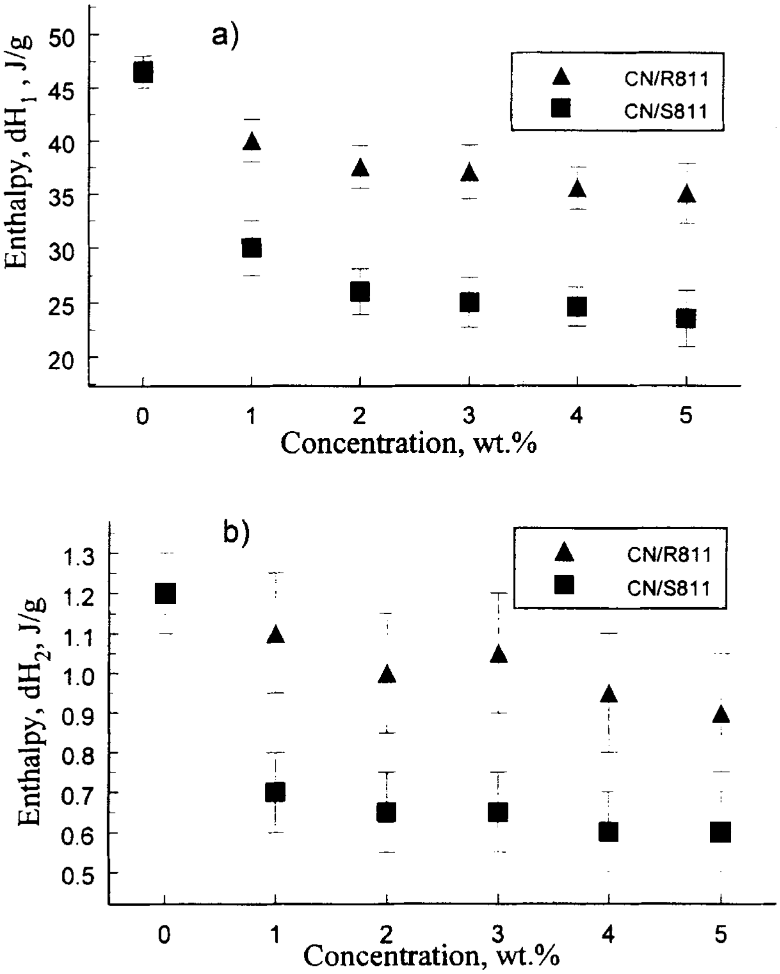


FIGURE 4 Phase transition enthalpy of cholesteryl nonanoate as a function of concentration of the enantiomeric dopants R811(-▲-) and S811(-■-); (a) crystal to cholesteric transition; (b) cholesteric to isotropic transition.

S811 are ~41 J/g and ~30 J/g respectively. Remarkably, the difference reaches ~20% of the enthalpy of fusion of pure cholesteryl nonanoate, indicating strong diastereomeric discrimination in the system. The enthalpy of the transition from the cholesteric to isotropic phase is also greater for a sample doped with R811 (1.0 J/g) than for that doped with S811 (0.67 J/g). These results imply that one enantiomer, namely left-handed S811, whose sign of optical rotation coincides with that of the cholesteric solvent, affects the molecular packing of CN much more strongly than its right-handed counterpart R811.

It is well known that the shape of the DSC melting endotherm of a crystalline compound is indicative of its purity [16]. At a low limit of concentration of "impurities" (usually up to 5 wt.%) the peak can be approximated by the Van't Hoff equation, which enables one to evaluate calorimetrically the purity of a sample and the depression of its melting point. The validity of this analysis is based on several assumptions; mainly that (i) the melt is an ideal solution in which the impurities are soluble; (ii) in the solid state the impurities are not soluble in the principal component. These two assumptions imply the absence of any specific interactions in the system. Thus, a disagreement between the amount of impurity calculated according to the Van't Hoff equation and the actual concentration of added R811 or S811 dopants can serve as further indirect evidence of specific diastreomeric interactions in the studied system. Therefore, an analysis of DSC data (using the TA dynamic calorimetric purity data analysis program-Purity 4.1A) was undertaken to monitor changes in calorimetric purity of CN with an increase in the concentration of enantiomeric dopants.

Interestingly, the DSC peaks of the second endothermic transition from the cholesteric to isotropic phase (second melting) do not lend themselves to an analysis according to the Van't Hoff equation. Although a depression in the temperature of the second melting clearly correlates with the concentration of dopants (as illustrated by Fig. 2) the "calorimetric purity" of all samples estimated from these endotherms invariably fall into the range of 99.90–99.98%. Apparently this transition does not satisfy the conditions necessary for the Van't Hoff analysis.

The purity of samples estimated from the first melting endotherm (a transition from solid crystalline to cholesteric phase) correlates with the actual amount of the added dopant. It is worth noting that the correlation is much better in the case of R811 than of S811. For instance, the purity of a sample containing 3 wt.% of R811 is estimated as 97.06 ± 0.20%, whereas the sample containing 4 wt.% of S811 is reported by the Data Analysis Program as 98.10 ± 0.2% pure. The same tendency continues in the whole range of dopant concentrations. In view of the previous comments on the validity of the Van't Hoff equation, one can conclude that the behavior of S811 in CN is further from the ideal than that of R811. Since S811 and R811 constitute an enantiomeric pair, the difference in their behavior in solution can be attributed to their specific diastereomeric interactions with chiral CN.

In order to further support the conclusion about diastereomeric discrimination of R811 and S811 in a cholesteric solvent CN, the behavior of these enantiomers in a nematic solvent S1186, has also been studied. In this non-chiral liquid crystal both enantiomers cause the **identical** depression in temperature and the enthalpy of phase transitions (the enthalpy of melting decreases approximately 3.8% for every 1 wt.% of either dopant), thus indicating that the observed effects in chiral CN are clearly of a diastereomeric nature.

The results of this work are in agreement with the earlier observed non-symmetrical effects of R811 and S811 enantiomers on the pitch of right- and left-handed cholesterics. The helical twisting power (HTP) of S811 is -13.1, whereas that of R811 is $+1.5\,\mu\mathrm{m}^{-1}$/wt. fraction; *i.e.*, when an equal amount of each enantiomer is added to a cholesteric solvent, the left-handed S811 enantiomer constricts the pitch nine times more strongly than the right-handed R811 expands it. To account for this asymmetry, a model has been proposed in which the effective HTP consists of two contributions [14]: one chiral (β_{chir}) and one geometrical (β_{geom}), where the chiral contribution, originating from the intrinsic molecular chirality has the same absolute value but opposite sign for R811 and S811 enantiomers. In view of the calorimetric manifestation of diastereomeric discrimination of these enantiomers in CN, the proposed relation $\beta^{\mathrm{R811}}_{\mathrm{chir}} = -\beta^{\mathrm{S811}}_{\mathrm{chir}}$ cannot be justified in spite of the good quantitative agreement of this model with the values of HTP of some enantiomers in steroidal cholesteric solvents. It appears that a higher absolute value of HTP of levorotatory S811 reflects the stronger diastereomeric interaction of this enantiomer with the levorotatory solvent CN, as confirmed by the present calorimetric study. Apparently the improved model should consider the HTP of the diastereomeric pairs S^-D^- and S^-D^+, formed by a levorotatory solvent molecule S^- and a molecule of either enantiomeric dopant D^- (S811) or D^+ (R811) rather than the HTP of the dopants themselves.

CONCLUSIONS

Depression of the enthalpy of phase transitions from crystalline to cholesteric and from cholesteric to isotropic phases was found to be ~ 1.5 times greater for the samples of cholesteryl nonanoate doped with left-handed S811. Depression of the temperatures of phase transitions is also more pronounced in the case of S811. The dissimilar behavior of S811 and R811 is in agreement with earlier observed non-symmetrical effects of these enantiomers on the pitch of liquid crystalline cholesteryl esters: the left-handed S811 enantiomer constricts the pitch ~ nine times more strongly than the right-handed R811 expands it. These results are indicative of a remarkable case of diastereomeric discrimination.

Acknowledgements

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