Investigation of the chirality dependence of thermal properties in chiral-racemic mixtures of the cholesteric ester CE6

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Investigation of the chirality dependence of thermal properties in chiral-racemic mixtures of the cholesteric ester CE6

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A scanning adiabatic calorimetric technique has been used to study the thermal properties of the chiral and racemic liquid crystal CE6 and the phase diagram covering the cholesteric phase, the three blue phases and the isotropic phase. The purpose of this investigation is to study thermal properties of liquid crystals as a function of chirality, while all other parameters remain constant. Results for the temperature and the chirality dependence of the enthalpy and of the heat capacity are reported. The latent heats between the cholesteric phase and BPI and between the different blue phases change slightly as a function of the chirality. The total heat of transition at the isotropic phase boundary is independent of the chirality, but with decreasing chirality, we observe a large increase in the latent heat and, correspondingly, a decrease in the pretransitional contribution. These experimental facts are in qualitative agreement with the predictions of a Landau–de Gennes theory for blue phases.

1. Introduction

In recent years, investigations of the blue phases of cholesteric liquid crystals have been in progress [1–6], and it has been established that cholesteric liquid crystals with a short pitch may form up to three distinct blue phases: two cubic phases (BPI and BPII) and one amorphous phase (BPIII). Theoretical BP diagrams have been constructed by Grebel, Hornreich and Shtrikman (abbreviated as GHS theory) [7], who have studied the influence of adding a chiral term to the Landau–de Gennes free energy [8] of the nematic phase. For small chirality (i.e. the coefficient of the chiral term), this term leads to the normal low temperature cholesteric phase. For high chirality, however, phases with various cubic symmetries, blue phases, become energetically preferable near the cholesteric–isotropic phase boundary. The theoretically obtained phase diagrams, in which the phase transition temperature is plotted versus chirality (treated here as an independent thermodynamic parameter), show clearly how the blue phases appear and become wider in temperature range as chirality increases.

The behaviour of the entropy jump at the ordered–disordered phase boundary has been calculated in the GHS theory as a function of the chirality for several cases, for example, for a direct cholesteric to isotropic phase transition as well as for several cubic (BP) to isotropic phase transitions [7]. Therefore, we have investigated experimentally the chirality dependence in terms of the character and the properties of the phase transition from the ordered to the disordered phase. Below, we will give a detailed comparison between the theoretical calculations and our experimental findings.

One important question that arises from the GHS phase diagrams is whether there should exist universal features associated with the appearance of blue phases. Theoretically, a variation of the chirality alone causes the appearance of the blue

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phases. For several years, the effect of chirality on blue phases has been studied by mixing nematic compounds with chemically different materials [9–11]. But in these cases, it may be hard to separate out the effect of the chirality as such. A procedure which avoids this complication is to combine both left- and right-handed (or alternatively, chiral and racemic) versions of the same cholesteric material in a mixture. To a good approximation, the resulting mixtures will vary only in chirality, that is, only in the size of the chiral Landau coefficient. The other Landau coefficients will remain essentially unchanged, since, except for chirality, the two components are chemically identical.

Phase diagrams of chiral–racemic mixtures, observed by optical methods, have been reported previously [12–13], but uncertainty remains, for example, about the order of the transitions. Therefore, we report here high resolution adiabatic scanning calorimetric results concerning the thermal properties (enthalpy and specific heat) along the phase boundaries for chiral–racemic mixtures of S-$(+)$-4-(2-methylbutyl)phenyl 4-decyloxybenzoate (CE6) [14].

2. Experimental method

The chiral liquid crystal CE6 and its racemate CE6R were obtained from Merck Ltd., England, and used as received. CE6 is a member of a homologous series containing chiral alkyl and achiral alkoxy end chains.

CE6 has the following chemical formula:
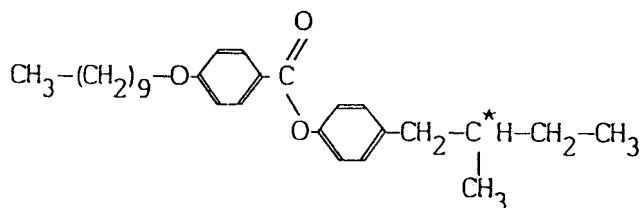
Following the binding conditions to the asymmetric C atom (marked with * in the chemical formula), the molecule will be called left- or right-handed.

The measurements have been carried out by adiabatic scanning calorimetry. The calorimeter consists of three stages. The calorimeter as a whole is submerged in a water thermostat. For the outer stage (stage 3), we obtain a temperature stability of the order of 10 mK. For measuring and controlling the temperatures of the different shields, a scanning digital multimeter set-up and programmable power sources, connected with a microcomputer, were used [15]. As a result, the temperature of the sample can be kept constant within 0·1 mK during at least 1 day. The measuring cell has a maximum sample volume of about 4 cc. Heating as well as cooling runs have been carried out at very slow scanning rates, typically of the order of 50 mK h^{-1}. With a constant heating (cooling) power, P, applied to the sample from the time t_s and during a period of several days, the experimental curve of temperature versus time, $T(t)$, results directly in the enthalpy of the sample

$$H(T) = H(T_s) - P(t - t_s).$$

The heat capacity $C_p^{tot}(T)$ is given by

$$C_p^{tot}(T) = \frac{P}{\dot{T}},$$

$\dot{T}$ can be obtained by numerical differentiation from the direct experimental data for $T(t)$. The $C_p^{tot}(T)$ value has to be transformed by subtracting the heat capacity of the

sample holder and by normalizing to one mol of sample. It is also possible to obtain values for latent heats, when they are present, for a given phase transition. If a first order transition occurs at T_{tr}, the temperature will be essentially constant for a time interval $\Delta T = \Delta H_L(T_{tr})/P$, with ΔH_L the latent heat. For mixtures, one does not expect the transition to take place at a single temperature T_{tr}, but over a finite temperature range ΔT.

3. Results and discussion

We have investigated the temperature dependence of the enthalpy and of the specific heat in 11 mixtures of chiral CE6 and its racemate CE6R with the following concentrations of chiral material: 100, 95·2, 90·5, 80·8, 69·7, 61·2, 51·0, 40·0, 25·0, 12·0 and 0 per cent. The termperature range covered lies between 20°C and 50°C; in this range we could observe, depending on the concentration of chiral material, maximally five phase transitions: crystalline to cholesteric, cholesteric to BPI, BPI to BPII, BPII to BPIII and BPIII to isotropic liquid. Upon cooling, a cholesteric to smectic A, followed by a smectic A to crystalline transition showed up.

Here we concentrate on the blue phases and the transitions to the cholesteric and isotropic phase. A phase diagram showing transition temperatures *versus* mol fraction of chiral material for CE6 has been given in figure 1.

When we compare this phase diagram with the one obtained by Yang and Crooker using an optical method [13], we see a different behaviour in the shape of the isotropic phase boundary. In our measurements, the transition temperature to the isotropic phase is almost independent of chirality, whereas Yang observes in his optical measurements a shift of about 0·6°C over the whole range. The same discrepancy exists
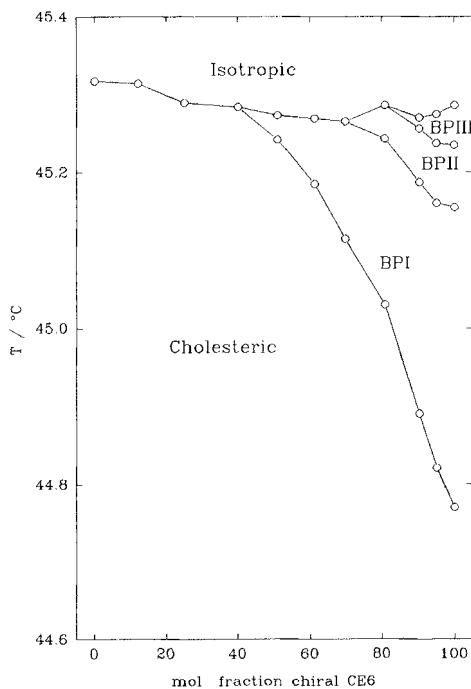

Figure 1. Phase diagram showing transition temperatures versus mol fraction of chiral material for CE6.

for measurements involving CE4 [15]. An explanation for this deviation can possibly be found in the different size of the samples and the corresponding inequality of the surface to volume ratio. Moreover, the thermal history of the sample under investigation seems to be of some importance: heating the sample far into the isotropic phase sometimes caused a slight shift of the temperature of the phase transition. On the other hand, when we normalize the phase diagram relative to the isotropic transition temperature and compare this with the phase diagram of Yang and Crooker [13], there is a good correspondence between the two diagrams. The general features which are confirmed, are the following:

(a)   BPI appears at the lowest chirality, followed by BPII and BPIII at higher chiralities.

(b)   The temperature width of each of the three blue phases increases with chirality. We have no evidence of a shrinking and disappearance of BPII as was found by Yang and Crooker for CE4, close to the 100 per cent chiral mixture [13].

It should be emphasized, however, that the first aim of these thermal measurements was not the detailed study of the phase diagram: optical observation may be more adapted for this purpose as it gives direct information on the structure and it is certainly less time consuming. The unique feature of the scanning adiabatic calorimeter is that it can measure the heats of transition and that it can disentangle the first and second order contributions.

Let us first of all consider the heats of transition concerning the cholesteric to blue phase and the blue phase to blue phase transitions. From a detailed analysis of the enthalpy versus temperature curves (for typical examples, see figures 2 to 4), it can be
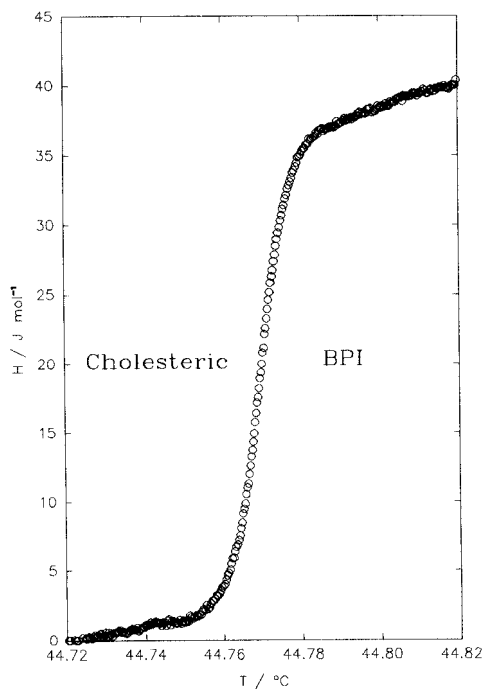

Figure 2.   Detailed plot of the enthalpy near the cholesteric to BPI transition for 100 per cent chiral CE6. For clarity, a large background contribution has been subtracted from the data.

Figure 3. Detailed plot of the enthalpy near the BPI to BPII transition for 100 per cent chiral CE6. For clarity, a large background contribution has been subtracted from the direct data.

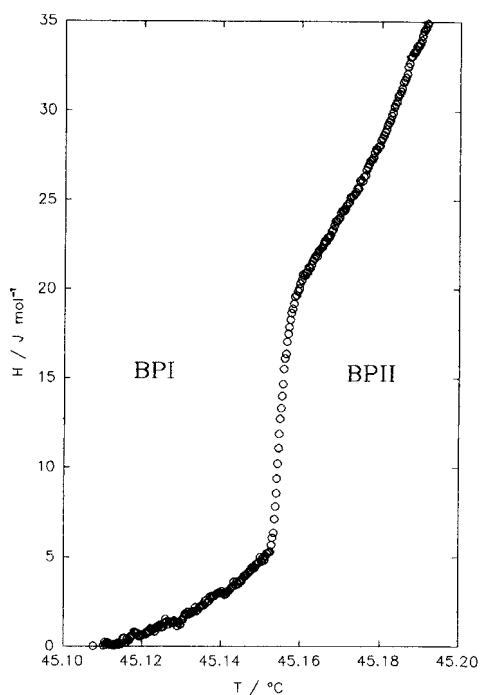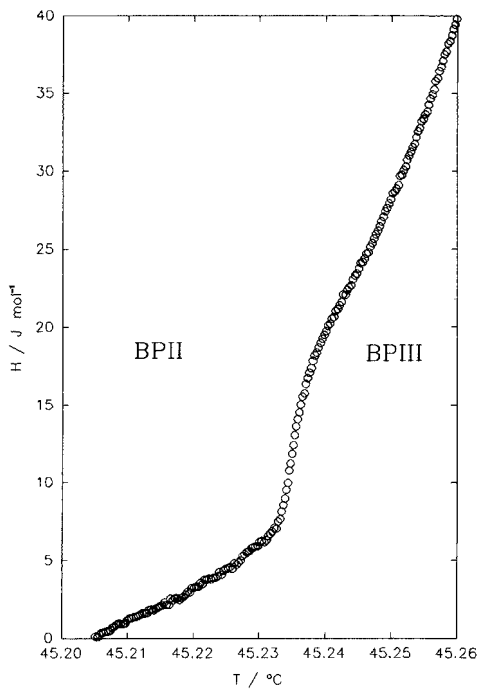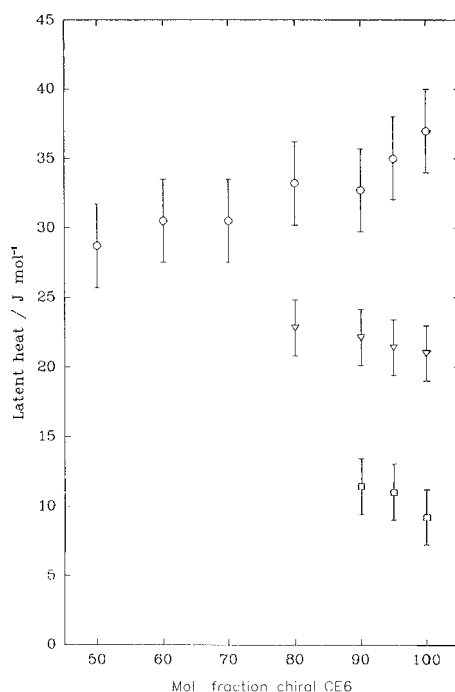Figure 4. Detailed plot of the enthalpy near the BPII to BPIII transition for 100 per cent chiral CE6. For clarity, a large background contribution has been subtracted from the direct data.

Table 1. Latent heats of the blue phase transitions as a function of the chirality.

% chiral CE6	$\Delta H/\text{J mol}^{-1}$ Ch–BPI	$\Delta H/\text{J mol}^{-1}$ BPI–BPII	$\Delta H/\text{J mol}^{-1}$ BPII–BPIII
100	37	21	9
95	35	21	11
90	33	22	11
80	33	23	—
70	31	—	—
60	31	—	—
50	29	—	—

Figure 5. Chirality dependence of the latent heats of transition for the various blue phases: BPII–BPIII ($\square$), BPI–BPII ($\triangledown$) and Ch–BPI ($\bigcirc$).

clearly seen that all transitions are first order. It should be noted that, for display reasons, a large part of the regular linearly-temperature-dependent part of the enthalpy has been subtracted from the direct data. In table 1, a summary is given for the values of the latent heats of the various transitions as a function of the chirality. From the graphical representation of these data in figure 5, it is clear that the latent heat of the cholesteric to BPI transition increases with the chirality, whereas for the two other transitions (BPI–BPII and BPII–BPIII), a decrease is suggested, although it hardly exceeds the experimental uncertainty.

The transitions from the cholesteric phase to BPI, from BPI to BPII and from BPII to BPIII give only minor enthalpy or entropy changes compared to those that occur for the transition to the isotropic phase. This may be illustrated by figures 6 (a) and (b) for 100 per cent chiral CE6 and by figures 7 (a) and (b) for the racemic mixture. The

(a)

(b)
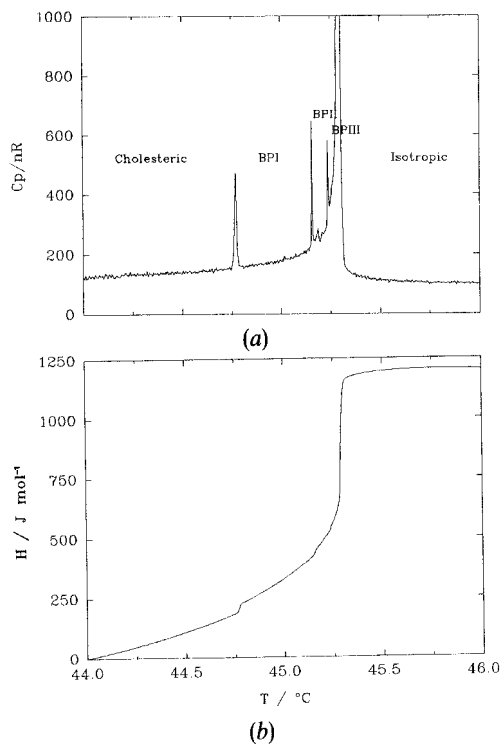
Figure 6. (*a*) General overview for the specific heat per mol in 100 per cent chiral CE6 for the temperature range covering all phase transitions involving blue phases and (*b*) the corresponding enthalpy plot for 100 per cent chiral CR6.
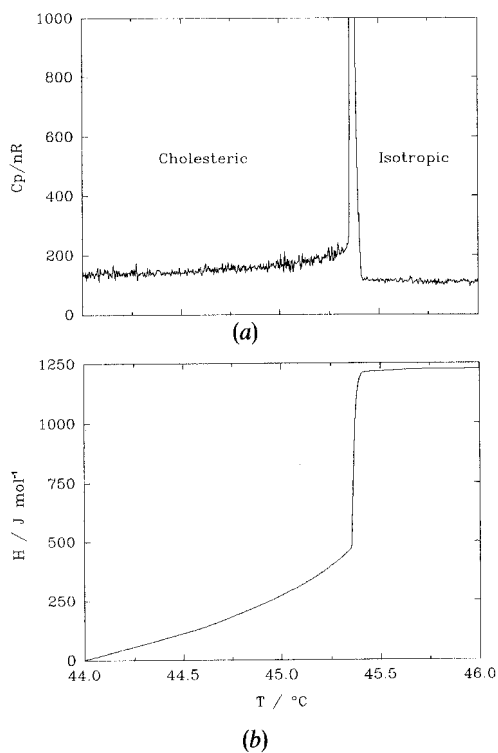

(a)

(b)

Figure 7. (*a*) General overview for the specific heat per mol in racemic CE6 and (*b*) the corresponding enthalpy plot for racemic CE6.

Table 2. Transition heats for the isotropic to ordered phase transition for CE6 as a function of the chirality.

% chiral CE6	$\Delta H_{total}/\text{J mol}^{-1}$	$\Delta H_{latent}/\text{J mol}^{-1}$	$\Delta H_{pretr}/\text{J mol}^{-1}$
0	1110	720	390
12	1090	680	410
25	1110	640	470
40	1100	630	470
50	1110	640	470
60	1110	570	540
70	1110	490	620
80	1100	470	630
90	1090	420	670
100	1110	400	710

curvature of the C_p curves is a measure of the fluctuation pretransitional contribution, while the steps in the H curves indicate the magnitude of the latent heat. The results of the data analysis are summarized in table 2 and should be interpreted in the following way:

ΔH_{total} represents the total enthalpy difference between subsequent phases, determined by extrapolation of the enthalpy behaviour from both phases to the transition temperature. This ΔH_{total} includes all pretransitional effects together with the latent heats.

ΔH_{latent} represents the total latent heat, determined from the linear parts in the enthalpy versus temperature curves. It includes the latent heats of the various blue phase transitions.

ΔH_{pretr} represents the difference between ΔH_{total} and ΔH_{latent}.

The data of table 2 are graphically drawn in figure 8: as a function of the chirality the latent heat decreases, but the pretransitional part increases, so that their sum is essentially constant. This result seems to contradict at first sight the DSC results of Tanimoto et al. [16], who claim that mixtures of CE6 with respectively 0, 50 and 100 per cent chiral concentration have the same latent heat value of 1070 ± 50 J mol^{-1}. But taking into account that the DSC technique is unable to disentangle the latent heat from the pretransitional part, their result probably has the same meaning as our ΔH_{total}, giving then a very good agreement with our mean value of 1100 J mol^{-1}.

4. Comparison with GHS theory

We will now compare our data with the Landau–de Gennes type of theory as worked out by Grebel, Hornreich and Shtrikman [7]. In this approach, gradients and fluctuations in the order parameter are not taken into account, and consequently the heats of transition are pure latent heats. The results from [7] can be summarized as follows.

The entropy jump between the cholesteric and the isotropic phase is given by

$$\Delta S_{IC} = 16\frac{df_C}{dt}\bigg|_{t=t_{IC}} = \begin{cases} \frac{1}{4}[2 + 3(1 + \frac{1}{3}\kappa^2)^{1/2} - (1 + \frac{1}{3}\kappa^2)^{3/2}] & \text{if } \kappa \leqslant 3 \\ 0 & \text{if } \kappa > 3 \end{cases} \quad (1)$$

Note that ΔS has been normalized so that $\Delta S_{IC}(\kappa=0) = \Delta S_R = 1$. κ is the chirality parameter, which is inversely proportional to the pitch, but the coefficient is material-
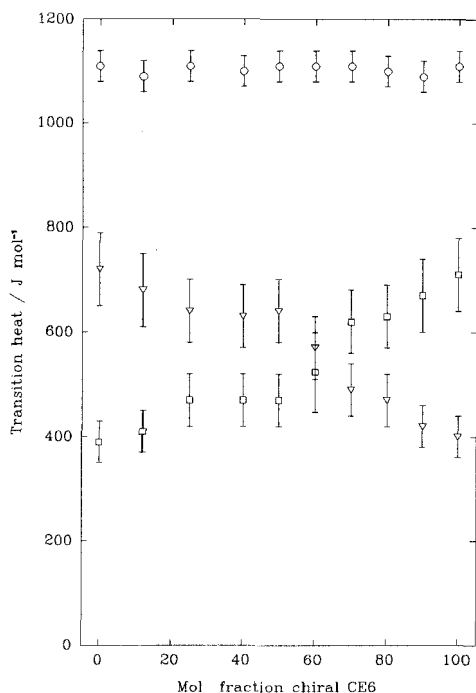
Figure 8. Transition heats for the isotropic to ordered phase transition in CE6 as a function of the chirality: pretransitional heat ($\square$), total heat ($\bigcirc$) and latent heat (∇).

Table 3. Values for the entropy jumps between the isotropic and several cubic phases [7].

Phase transition	κ†	ΔS
I–O^5	> 0·939	0·61
I–O^2	Intermediate	0·78
I–O^8	Intermediate	0·55

† The exact minimum value of κ for the existence of the cubic phase is model dependent for O^2 and O^8. The value for O^5 is obtained when harmonics are excluded.

dependent and not known *a priori*. For $\kappa > 3$, the value of ΔS_{IC} becomes zero and the phase transition has then changed its character from first to second order. But for sufficiently high values of the chirality parameter, intermediate phases are energetically more favourable and a first order phase transition from the isotropic to some other ordered phase is possible. In the high chirality limit ($\kappa \to \infty$), a cubic O^5 structure shows up for $\kappa > 0\cdot939$. But for finite chirality, other cubic structures can have lower free energies than O^5 in regions of the (κ, t) plane. Inclusion of three or four harmonics in the order parameter results in cubic structures other than O^5 (bcc O_a^8, O_b^8, O_c^8 and sc O^2) becoming thermodynamically stable. Within the framework of the GHS theory [7], normalized values of the entropy jump have been calculated for the IC, IO^2, IO^5 and IO^8 transitions. The results for the isotropic to cubic phase transitions are summarized in table 3. It should be noted that a direct IO^8 transition is not possible within this framework when all seven phases ($I, O^2, O^5, O_a^8, O_b^8, O_c^8, C$) are allowed.

For clarity, the following identifications between experiment and theory have been generally accepted: BPI has been identified with the O^8 symmetry group, BPII has been identified with the O^2 symmetry group. The O^5 symmetry group, which appears also in the theoretical phase diagrams, has until now not been observed experimentally. It should be emphasized that BPIII does *not* have the O^5 structure [17–19], although the theoretical phase diagram invites us to interpret O^5 in this way for $\kappa > 1.5$.

To compare the experimental results with those calculations, a few adaptations have to be made. We normalized the latent heat value for the IC transition in the racemic CE6 to 1. Moreover, since we have no clear relationship between the experimental value of the pitch of CE6 and the reduced chirality parameter in the GHS theory, we have extrapolated the latent heat values to the chirality where they should become zero, using equation (1). For CE6, the transition from the ordered to the isotropic phase should have no latent heat for a (hypothetical) 186 per cent chiral mixture. This assumption is only valid if the chirality is the only parameter which determines the nature of the phase transition to the isotropic phase. With this scaled chirality parameter, we obtain the result that the first cubic phase shows up experimentally for $\kappa = 0.7$. This agrees well with the theoretical prediction for the appearance of the first cubic phase. So the scaling of the chirality of our system in this way seems to be quite acceptable.

As one can see in figure 9, there is a rough qualitative agreement between theory and experiment in the sense that the entropy change between the isotropic and the ordered phase (cholesteric or blue phase) decreases with increasing chirality. Further, it may be emphasized that the free energy differences between the various cubic structures are very
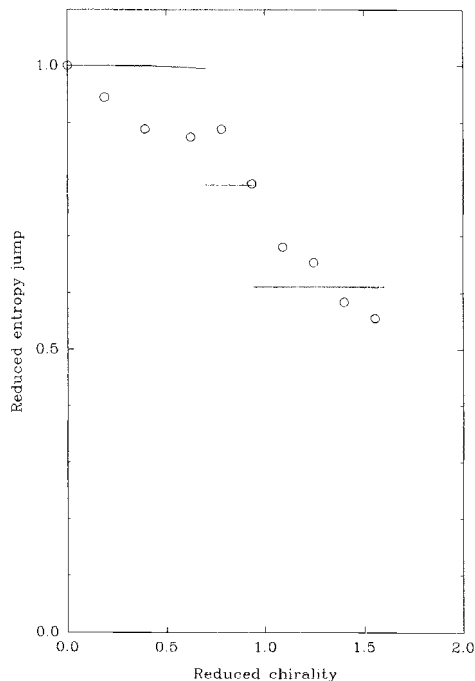
Figure 9. Comparison of the experimental entropy jumps (calculated from direct enthalpy data) for the ordered to disordered phase transition as a function of the chirality in mixtures of chiral and racemic CE6 (open circles) with the calculated entropy jumps from GHS theory [7] (full line).

small. Thus, terms which have been neglected in the Landau free energy density, since they did not play any significant role for the calculation of some physical quantities, could have an important effect on the phase diagram. Because of the absence of BPIII and of a direct IO^8 phase transition in the theoretical phase diagram, a complete and quantitative comparison between theory and experiment is not possible.

5. Summary and conclusions

In this paper, we have reported high resolution adiabatic scanning calorimetric data for chiral–racemic mixtures of CE6 for a temperature range covering all phase transitions involving the (maximal) three blue phases occurring in this material.

The purpose of this investigation was to study thermal properties of a liquid crystal as a function of chirality, while all other parameters remain constant. The results can be summarized in the following way. The latent heats of the cholesteric–blue phase transition depend on the chirality, whereas those of the blue phase–blue phase transitions are within experimental error independent of the chirality. On the other hand, we observe, with decreasing chirality, a large increase in the latent heat and, correspondingly, a decrease in the pretransitional contributions to the total heat of transition at the isotropic phase boundary. The total enthalpy difference between both phases, however, is independent of chirality.

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