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Tricritical behaviour of the smectic A to smectic C* transition for binary liquid crystal mixtures

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The tricritical behaviour for the smectic A (S_A) to chiral smectic (S_C^*) or smectic C (S_C) phase transition of four binary liquid crystal systems was investigated by ^{13}C NMR spectroscopy. The compounds 4′-(2-chloro-3-methylpentanoyloxy)-4-hexyloxy-1,1′-biphenyl (denoted C6) and 4′-(2-chloro-3-methylpentanoyloxy)-4-octyloxy-1,1′-biphenyl (C8) were used in their enantiomeric (L) and racemic (DL) forms. L-C6 and L-C8 exhibit a chiral smectic C (S_C^*) to S_A phase transition, and DL-C6 and DL-C8 exhibit a S_C to S_A transition, which are first order. Information about the orientational ordering of the aromatic core of C6 and C8 was obtained from measurements of ^{13}C chemical shifts. C6 displays a significant jump at the phase transition, whereas the discontinuity of C8 is much weaker. The enantiomeric and racemic forms have similar order parameters and phase behaviour. Various mixtures of C6 and C8 with 4-butyloxyphenyl-4′-decyloxybenzoate ($\overline{10}O\overline{4}$), which has a second order S_C to S_A transition, show a crossover from a first order to a continuous second order transition via a tricritical point. The tricritical mole fraction X_{TCP} of $\overline{10}O\overline{4}$ in the mixtures was found to be 0·14 ± 0·01 for DL-C6 and 0·13 ± 0·01 for L-C6. For mixtures containing C8, the tricritical mole fractions were much smaller, and it was found that $X_{TCP} \leqslant 0{\cdot}02$ for DL-C8 and $X_{TCP} \leqslant 0{\cdot}03$ for L-C8.

1. Introduction

The phase transition behaviour of the nematic (N) phase to the smectic A (S_A) phase has been studied extensively [1]. The S_A to smectic C (S_C) phase transition has been of considerable interest also [1–12]. Besides the nematic phase, the S_A and the S_C phases are the most common thermotropic liquid crystalline phases. These phases can be formed by rod-like molecules in a temperature range that is specific for each compound. In nematic and smectic phases, on average, the molecular long axes align in the same direction in small domains. To describe this phenomenon, a director **n** was introduced to denote the average direction of molecular alignment. Referring to this director, an order parameter S was defined. For biaxial flexible molecules this order parameter has to be described by the Saupe ordering matrix [13]

$$S_{\alpha\beta} = \frac{1}{2}\langle 3l_\alpha l_\beta + \delta_{\alpha\beta}\rangle. \tag{1}$$

Here $l_\alpha l_\beta$ denotes the product of the direction cosines of angles between two molecular axes α, β and the director, and $\delta_{\alpha\beta}$ is the Krönecker delta. The angular brackets characterize time and ensemble average. Expansion of the potential of mean torque in terms of the spherical harmonics results in up to five different order parameters that have to be used to describe the total orientational ordering of certain molecular segments. However, for molecules of molecular segments having a D_2 symmetry, only two order parameters S_{zz} and $S_{xx} - S_{yy}$ have to be considered. Smectic phases have partial positional order in addition to the orientational order found in nematics; i.e. the molecules arrange in layers so that a mass density wave parallel to the layer normal is formed. This additional positional ordering was explained in a theory by McMillan [14]. In the S_A phase the director and the mass density vector are parallel, whereas in the S_C phase the director is tilted away by an angle θ. Molecules that contain a chiral centre form the chiral smectic C (S_C^*) phase instead of the S_C phase, in which the director precesses around the mass density vector. One complete rotation is called the pitch p, which is a compound-specific property. However, the microscopic ordering in S_C and S_C^* is the same.

It is well known that approximately symmetrical linear molecules which contain terminal polar groups and chain branching on one side and a long alkyl or alkoxy chain on the other are likely to exhibit a S_C phase [15]. The existence of a chiral centre leads to the formation of the S_C^* phase, the ferroelectricity of which was

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predicted by Meyer *et al.* [16]. In the S_C^* phase, the lateral dipole moments of the molecules will align macroscopically along the same direction under the influence of an external electric field. This property makes chiral smectogens suitable for the surface stabilized ferroelectric liquid crystal (SSFLC) display [17], a new type of electro-optic device which has bistability and very short switching times.

Since the early 1970s, the S_A to S_C phase transition has attracted considerable attention. Initially it was unclear whether this transition is helium-like, as it was first proposed by de Gennes [18], or mean-field-like. Later-on, extensive calorimetric studies by Huang and coworkers confirmed that not only the S_A to S_C [19], but also the S_A to S_C^* [20] phase transition can be characterized more accurately by the mean-field model. As a result, in analogy to the Landau model, the free energy density g in the vicinity of a S_A to S_C transition can be expanded in terms of an order parameter ψ [21]

$$g = \left(\frac{T}{T_{\text{trans}}} - 1\right)\psi^2 + b\psi^4 + c\psi^6 \qquad (2)$$

where b and c are expansion coefficients, and ψ has the form

$$\psi = \theta \exp(i\phi). \qquad (3)$$

Here, θ is the tilt angle and ϕ is the azimuthal direction of the director. According to Huang and Viner [21], $b > 0$ describes a second order transition and $b < 0$ a first order transition. At the crossover, $b = 0$ characterizes a tricritical point (TCP) [21]. It has been found that the S_A to S_C or S_C^* transition for most compounds is a second order transition.

In 1986, two research groups discovered a new series of ferroelectric liquid crystals with very promising electric properties, such as extremely high spontaneous polarization and dielectric constants in their S_C^* phase [4, 22–29]. These liquid crystals are esters of differently branched α-chloro acids and 4-*n*-alkoxy-4′-hydroxybiphenyl. Since the discovery of these new liquid crystals, a lot of work regarding orientational ordering of these compounds and the nature of the S_A to S_C (S_C^*) phase transition have been performed [5, 6, 8–11]. From these results, relations between order parameters, molecular structures and phase behaviour have been obtained. In this laboratory, one and two dimensional ^{13}C NMR spectroscopy has been used for both kinds of investigations. Several studies on the behaviour of these chloroesters have been carried out, in which either the chiral part was modified or the length of the alkoxy chain was varied [12, 30–32]. In particular, the homologous series of 4′-(2-chloro-4-methylpentanoyloxy)-4-alkyloxybiphenyl and 4′-(2-chloro-3-methylpentanoyloxy)-4-alkyloxybiphenyl are of considerable interest because some members in this series show first order S_A to S_C^* transitions [5, 24]. For simplicity, they are denoted as B*n* and C*n*, respectively [24], where *n* is the number of carbon atoms in the alkyl chain (see figure 1). The (2*S*, 3*S*) compounds are referred to as L isomers for C*n*, and their racemic mixtures as DL isomers.

It has been found that mixing these compounds with a liquid crystal that displays a continuous S_A to S_C phase transition leads to a crossover from discontinuous to continuous behaviour via a critical point [11, 32]. This provides the possibility to obtain insight about tricritical behaviour in general. For this purpose, binary mixtures of B*n* and C*n* with 4-butyloxyphenyl-4′-decyloxybenzoate, denoted $\overline{10}\mathrm{O}\overline{4}$ (see figure 2), have been studied [11, 32–34].

In a previous investigation [32], we have used ^{13}C NMR spectroscopy to observe the behaviour of the S_A to S_C phase transition of DL-B7 and DL-C7 and their mixtures with $\overline{10}\mathrm{O}\overline{4}$. In this work, results of a study on the S_A to S_C phase transition of DL-C6 and DL-C8 as well as the S_A to S_C^* phase transition of L-C6 and L-C8 and their mixtures with $\overline{10}\mathrm{O}\overline{4}$ are reported and compared with those obtained for DL-C7.

2. Experimental

According to procedures in the literature [22–25, 35–37], C6 and C8 were synthesized using L- and DL-isoleucine, 1,1′-biphenol and 1-bromohexane or 1-bromooctane as starting materials, which were purchased from Aldrich Chemical Co. and used without further purification. The amino acids were transformed to α-chloro acids by diazotization and coupled with the

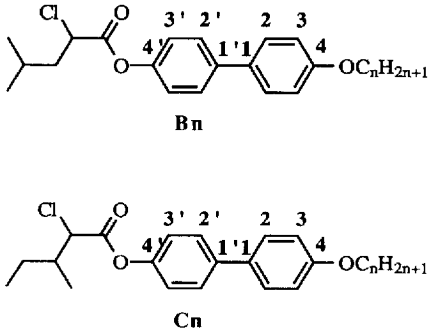

Figure 1. Molecular structures of the liquid crystals B*n* and C*n* (*n* = 6, 7 and 8).

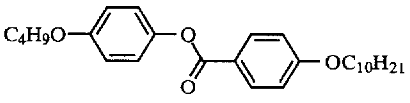

Figure 2. Molecular structure of $\overline{10}\mathrm{O}\overline{4}$, used for the preparation of binary liquid crystal mixtures.

monoalkylated biphenol using dicyclocarbodiimide (DCC) as carbonyl activator and dehydrating agent and 4-pyrrolidinopyridine as nucleophilic catalyst. The liquid crystals were purified by column chromatography using silica gel as stationary phase and chloroform as eluent, and were recrystallised from hexane. The purity of L-C6, DL-C6, L-C8 and DL-C8 was verified by proton NMR in isotropic solutions and by examining their transition temperatures under the polarizing microscope.

Information about the core parameter was obtained from ^{13}C NMR experiments on bulk liquid crystal samples at 125·7 MHz on a Varian VXR-500S spectrometer equipped with a Sun/360 workstation. A 5 mm indirect detection probe, manufactured by Nalorac Cryogenics Corp., was used to obtain optimal proton decoupling. The sample tube was spun at 8 Hz to avoid the development of a spinning vortex. In every experiment, the temperature was lowered from the isotropic phase of the liquid crystal until the sample started to crystallize. Spectra were acquired in temperature intervals of 0·1°C in regions of phase transitions and in 0·5°C steps otherwise. For each temperature two sets of spectra were taken, one with 24 transients to equilibrate the system to the new temperature, and another with 72 transients for the actual chemical shift measurements. Data processing was performed on a Sun 3/60 workstation and also on a Sun Sparc Station 5.

The ^{13}C NMR experiments were performed for 20 and 22 different compositions for DL-C6 and L-C6, covering a mole fraction of $X(\overline{10}O\bar{4})$.

3. Results and discussion

Because of the large positive diamagnetic anisotropy of the biphenyl unit, the director of the studied liquid crystals aligns parallel with the magnetic field $\mathbf{B}_o$. This means that the layer normals are orthogonal to $\mathbf{B}_o$ for the S_A phase. It was shown in this laboratory before that the director in the S_C phase also aligns with the magnetic field so that the layers are tilted with respect to $\mathbf{B}_o$ [36]. As a result, the tilt angle θ cannot be observed directly. Due to this phenomenon, the complex order parameter ψ is not used to describe the ordering of the S_C phase aligned in a high magnetic field. Instead, the orientational ordering can be simply described in analogy to the S_A phase by the Saupe order parameter matrix, where $S = 1$ refers to perfect alignment in a crystal and $S = 0$ an isotropic liquid [13].

Because of the macroscopic alignment of the director with respect to $\mathbf{B}_o$ the ^{13}C NMR signals for the aromatic carbons are relatively sharp, with linewidths on the order of about 65 Hz in the S_A phase. The peaks also remain relatively sharp in the S_C phase. However, the S_C^* phase of L-C7 seems to retain the alignment of the layer normal of the S_A phase due to its unusually tight pitch p, so that even the high magnetic field (11·07 T) of our NMR instrument was insufficient to unwind the helical structure of the S_C^* phase [12, 32]. As a result, the ^{13}C NMR spectrum shows very broad and overlapping peaks due to partial powder pattern characteristics [37].

It is known that many physical properties of homologous liquid crystals, such as phase transition temperatures, show one trend for compounds with alkyl chains containing odd numbers of carbon atoms, and show a different trend for compounds with even numbered chains (the odd–even effect). Thus, L-C6 and L-C8 exhibit a S_C^* phase which have longer pitches and, unlike L-C7, their helical alignment of the director is unwound by the high magnetic field of the NMR instrument because of the inverse proportionality between $\mathbf{B}_o$ and p [38]. Therefore, the ^{13}C peaks remain sharp in the S_C^* phase for L-C6 and L-C8, displaying about the same linewidths as the corresponding racemic mixtures in their S_C phase.

For L-C6 and L-C8, the linewidths of the 3′-carbon peak in the S_C^* phase is about 90 Hz and could be readily used for chemical shift measurements (figure 3). The slightly larger linewidth in the S_C phase compared to the S_A phase may be related to a decrease in the relation times.

In order to determine the order parameters of individual molecular segments in a liquid crystal, knowledge about their symmetry is required. For our compounds, the aromatic core is rigid and thus can be used to define the axis system in the molecular frame. Since the biphenyl group contains a twofold rotational axis, only two elements of the Saupe order parameter matrix have to be considered to describe the orientational ordering of each phenyl ring, namely S_{zz} and $S_{xx} - S_{yy}$ component does not show a significant temperature dependence [39], S_{zz} is sufficient for the description of the change in orientational ordering with temperature in the observed liquid crystalline phases. It was shown in this laboratory previously [12, 39] that the order parameter S_{zz} of the aromatic core of liquid crystals, which is often simplified as S, is related to the ^{13}C chemical shift by

$$S = \alpha(\delta_{\text{obs}} - \delta_{\text{iso}}) + \beta \qquad (4)$$

where δ_{obs} is the observed ^{13}C chemical shift and δ_{iso} chemical shift of the respective atom in the isotropic liquid. Thus, the empirical constants α and β describe the orientational ordering of particular atoms corresponding to an observed chemical shift. Their values have been determined for all four different aromatic carbon atoms in A7, B7 and C7 [12, 32, 33] using a procedure combining the techniques of variable angle spinning and separated local field spectroscopy (VAS/SLF) [40]. It was found that S values for both rings in each compound at a given temperature were the same within experimental error. This is expected because the C_2 axes of the two phenyl rings are colinear. Therefore, in this study, only the data for the 3′ carbon was used for calculations of the order parameter. For the previous work by Bräuniger [32, 33] the constants in equation (4) for the 3′ carbon are $\alpha = 0{\cdot}028 \pm 0{\cdot}004$ and $\beta = -0{\cdot}01 \pm 0{\cdot}01$. These values are assumed to be the same for L-C6, DL-C6, L-C8 and DL-C8. For all the four compounds it was found that the order parameter increases with decreasing temperature, lying in the range between 0·64 and 0·70 for the S_A phase, and between 0·70 and 0·78 for the S_C (S_C^*) phase. The temperature dependence is larger in the S_C (S_C^*) phase than in the S_A phase.

The values of S were plotted as a function of temperature for each mixture. Examples of these plots are given in figures 4–7. For the S_A to S_C (S_C^*) phase transition, the change in the order parameter is designated ΔS. The value of ΔS is larger than zero for first order transitions, and decreases with addition of more and more $\overline{10}O\overline{4}$ until it reaches zero for a continuous second order transition. Usually a range of coexistence of the S_A and S_C (S_C^*) phases, predicted by the Landau–de Gennes model for first order transitions, appeared over a temperature range of about 1 K for the pure compounds (see figure 3). In these cases, the transition temperature was determined as the arithmetic average of the first and last temperature of the range of coexistence. To be more quantitative, the curve for the temperature dependence of the order parameter in the S_C (S_C^*) phase for each mixture was then fitted to an empirical relation known

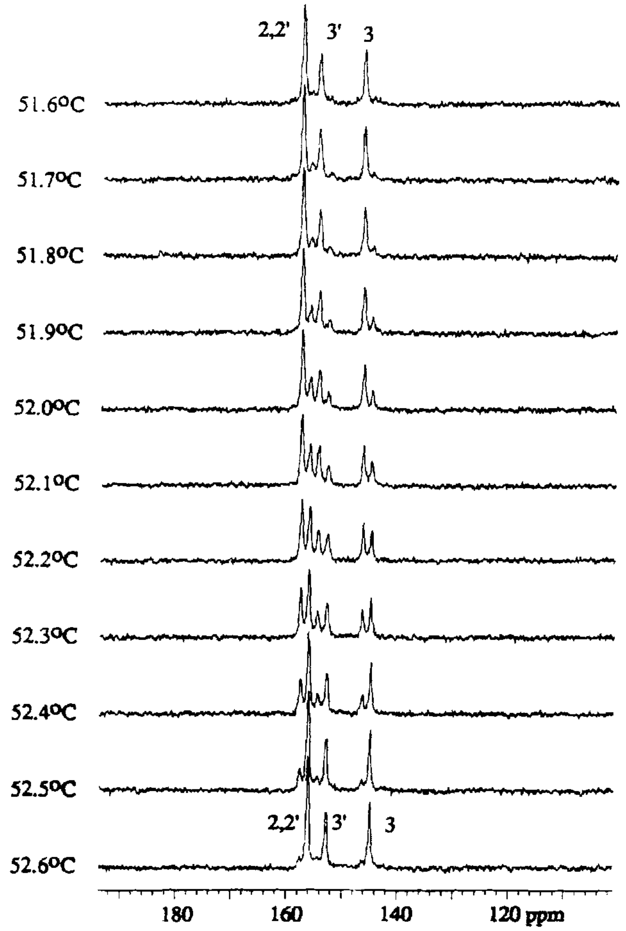

Figure 3. S_A to S_C phase transition in DL-C6, monitored by ^{13}C NMR. The coexistence of the two phases over a small temperature range, as predicted for first order transitions by the Landau–de Gennes theory, is verified by the coexistence of two peaks at different chemical shifts for the same corresponding carbon atom.

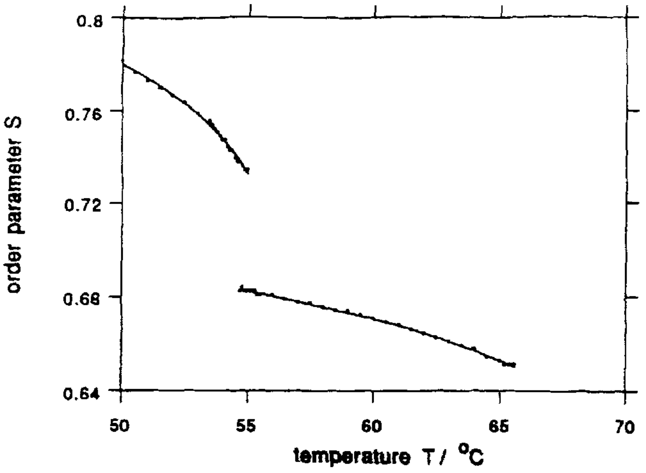

Figure 4. Temperature dependence of the core order parameter for pure L-C6, exhibiting a first order S_A to S_C^* phase transition.

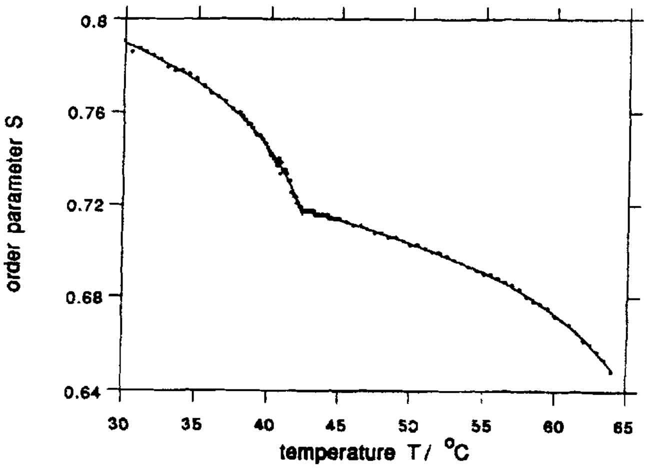

Figure 5. Temperature dependence of the core order parameter for a mixture of $X(\overline{10}O\overline{4}) = 0{\cdot}142$ in L-C6, showing a second order S_A to S_C^* phase transition.

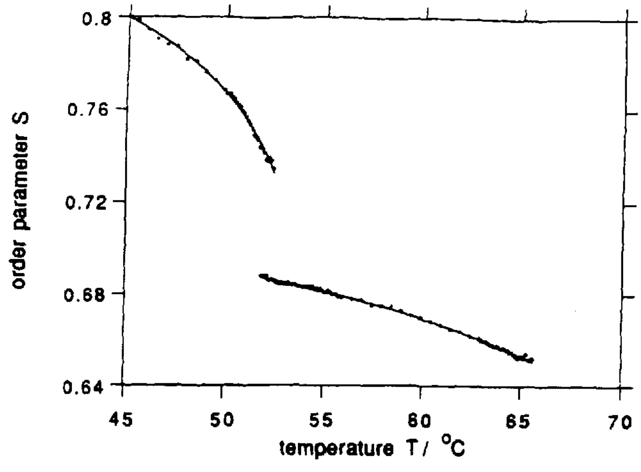

Figure 6. Temperature dependence of the core order parameter for pure DL-C6, exhibiting a first order S_A to S_C phase transition.

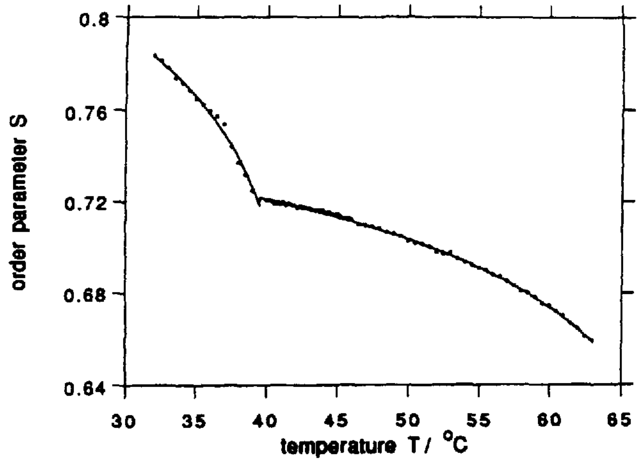

Figure 7. Temperature dependence of the core order parameter for a mixture of $X(\overline{10}O\overline{4}) = 0{\cdot}145$ in DL-C6, showing a second order S_A to S_C^* phase transition.

as the Haller equation

$$S = S_0\left(1 - \frac{T}{T_0}\right)^f. \qquad (5)$$

Although this equation was originally derived for nematics, it turned out to fit the data of the compounds under investigation very well. The quantities S_0, T_0 and f were treated as empirical constants, where T_0 has a slightly higher value than T_{C-A} and characterizes pretransitional behaviour [41]. The other two constants S_0 and f can be attributed to an equilibrium order parameter and how fast the system approaches equilibrium, respectively. Evaluation of the empirical constants by a least squares fit allows us to calculate ΔS for the transition temperature. Results of ΔS for mixtures of $\overline{10}O\overline{4}$ with L-C6 and DL-C6 plotted against the mole fraction are given in figures 8 and 9. It is found that the jump in the order parameter, ΔS, is linear for these compounds, and the intersection of the first linear segment of the plot can be extrapolated to give the tricritical mole fraction $X_{TCP}(\overline{10}O\overline{4})$. This procedure implies that enough data points should be available to obtain a reasonable linear fit. Using this procedure, the values of $X_{TCP}(\overline{10}O\overline{4})$ in the L-C6 and DL-C6 systems were determined graphically in the plots depicted in figures 8 and 9, respectively. The scattering of the data points might result from errors occurring in the Haller fits. Although the individual errors in the empirical constants S_0, T_0 and f are usually smaller than 1 per cent, the error in ΔS mainly depends on the error propagation and thus can have larger values. The overall error in $X_{TCP}(\overline{10}O\overline{4})$ are determined by the accuracy of the linear fit and thus is directly related to the correction coefficients. According to figures 8 and 9,

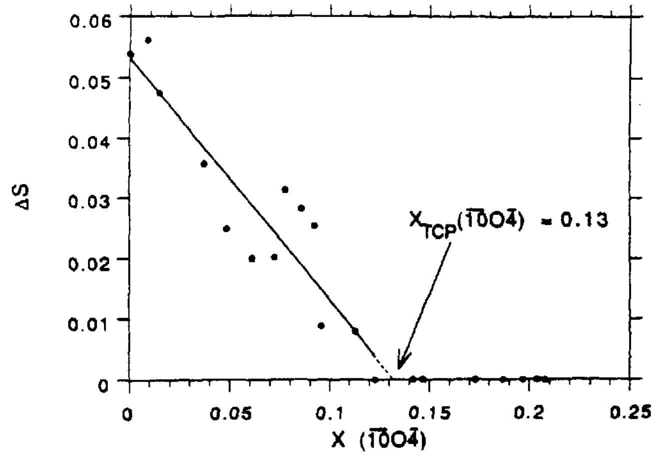

Figure 8. Determination of the tricritical mole fraction of $\overline{10}O\overline{4}$ in the L-C6 system.

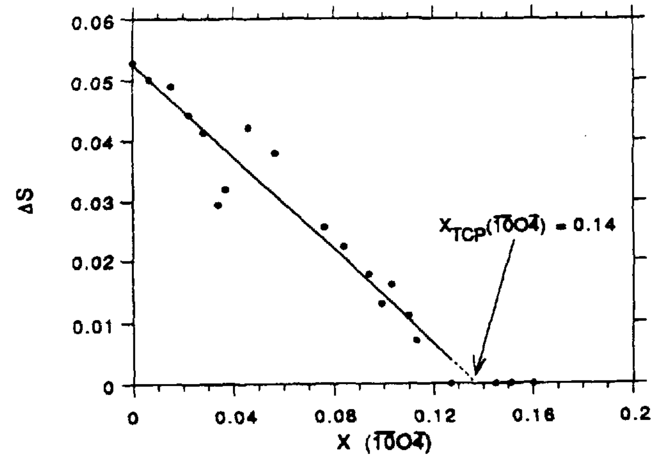

Figure 9. Determination of the tricritical mole fraction of $\overline{10}O\overline{4}$ in the DL-C6 system.

the determination of $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4})$ in the L-C6 and DL-C6 systems resulted in $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) = 0{\cdot}13 \pm 0{\cdot}01$ and $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) = 0{\cdot}14 \pm 0{\cdot}01$, respectively. L-C8 and DL-C8 show a much smaller jump in the order parameter, so that the tricritical mole fractions were much smaller. As a matter of fact, experiments with only six different binary mixtures for each of these two compounds were enough to pass the tricritical point. The $X(\overline{10}\mathrm{O}\overline{4})$ value did not exceed 0·03 for the L-C8 system and 0·025 for the DL-C8 system. Because it was difficult to run more than five significant mole fraction increments below these values, the determination of X_{TCP} for L-C8 and DL-C8 was less accurate. Hence, it was only possible to estimate their values from the obtained NMR spectra. Thereby, the tricritical mole fractions were determined to be $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) \leqslant 0{\cdot}03$ for the L-C8 system and $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) \leqslant 0{\cdot}02$ for the DL-C8 system.

4. Conclusions

One-dimensional ^{13}C NMR spectroscopy has been used to monitor the order parameter of the aromatic core in several binary liquid crystal mixtures composed of the smectogens L-C6, DL-C6, L-C8 and DL-C8 with $\overline{10}\mathrm{O}\overline{4}$. Although the $\mathrm{S_A}$ to $\mathrm{S_C}$ ($\mathrm{S_C^*}$) phase transition is continuous for most systems, the studied compounds exhibit a weak discontinuous phase transition in their pure forms. Addition of various amounts of $\overline{10}\mathrm{O}\overline{4}$, a compound that displays a continuous $\mathrm{S_A}$ to $\mathrm{S_C}$ transition, leads to a crossover from first to second order transitional behaviour via a tricritical point. The corresponding tricritical mole fractions were determined. They turned out to be $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) = 0{\cdot}13 \pm 0{\cdot}01$ for the L-C6/$\overline{10}\mathrm{O}\overline{4}$ system and $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) = 0{\cdot}14 \pm 0{\cdot}01$ for the DL-C6/$\overline{10}\mathrm{O}\overline{4}$ system. The discontinuity of L-C8 and DL-C8 was already small in their pure forms. As a result, it was found that $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) \leqslant 0{\cdot}03$ for the L-C8/$\overline{10}\mathrm{O}\overline{4}$ system and $X_{\mathrm{TCP}}(\overline{10}\mathrm{O}\overline{4}) \leqslant 0{\cdot}02$ for the DL-C8/$\overline{10}\mathrm{O}\overline{4}$ system. In comparison, the value of X_{TCP} ($\overline{10}\mathrm{O}\overline{4}$) for the DL-C7/$\overline{10}\mathrm{O}\overline{4}$ system determined from ^{13}C NMR measurements was $0{\cdot}13 \pm 0{\cdot}01$ [32], which differs slightly from the value of 0·106 for the L-C7/$\overline{10}\mathrm{O}\overline{4}$ system determined from calorimetric study [11]. We were not sure whether or not this was caused by a slightly different behaviour of the racemic mixture DL-C7 compared with the optically pure compound L-C7 [32]. From the present results, we conclude that X_{TCP} for optically pure compounds and their racemic mixtures do not differ within experimental error. The difference observed for the C7/$\overline{10}\mathrm{O}\overline{4}$ system [11, 32] possibly reflects the uncertainties in different experimental techniques.

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