Orientational order and tricritical behavior in the trans-p-n-alkoxy-α-methyl-p'-cyanophenyl cinnamate (n-OMCPC) series of liquid crystals

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The temperature dependence of the orientational order parameter S has been evaluated from their infrared spectra for six homologues of the n-OMCPC (trans-p-n-alkoxy-α-methyl-p'-cyanophenyl cinnamate) series of liquid crystals with $n = 7$–12, where n is the number of carbon atoms in the end alkyl chain. The even–odd effect of the S values in the nematic phase is rather weak for homologues 7–10. In homologues 10–12, the changes of S at the transitions have been correlated with their thermodynamic behavior. The smectic A–nematic (A–N) and nematic–isotropic (N–I) transitions in several binary mixtures of 11 with 8, 10, and 12 have been studied by differential scanning calorimetry. With decreasing average alkyl chain length in the mixtures, the nematic range becomes extended and the enthalpy of the A–N transition is found to decrease. We deduce that the tricritical point in the A–N transition occurs when the reduced temperature $T_R = T_{AN}/T_{NI} = 0.94 \pm 0.005$. The triple point between A, N, and I phases has also been observed in an 11–12 mixture at the mole percent ratio of ~27:73.

I. INTRODUCTION

Many physical properties of liquid crystals exhibit marked changes within a homologous series as the length of the end alkyl chains of the molecules is varied. The even–odd effects in the nematic–isotropic transition temperature[1,2] (T_{NI}) as well as the entropy[1] and orientational order parameter[3] (S) at T_{NI} are some well known examples of such a behavior. Following the recent theoretical studies of Marcelja[4] and Pink[5], who showed that the even–odd effect originates primarily from the various conformations adopted by the hydrocarbon end chains of the molecules, there is now a renewed interest in investigating the orientational order and phase transitions in different homologous series, both in the pure compounds and their binary mixtures.[6-8] In comparison to the pure compounds, binary mixtures have the added advantage that their average alkyl chain length may be varied in a continuous manner over any desired range.[9] This property of mixtures has also proved to be a convenient method of studying the tricritical behavior of the smectic A–nematic (A–N) transition in a few cases.[7,8]

In this paper, we report the results of an infrared study of the even–odd effect in the orientational order of some homologues of the *trans-p-n*-alkoxy-α-methyl-*p'*-cycnophenyl cinnamate (n-OMCPC) series of liq-

uid crystals. These compounds possess stable, colorless mesophases at relatively low temperatures.[10] The birefringence and elastic constants of some members of this series have been studied recently.[11] We have determined the temperature dependence of the S values in six homologues, the number of carbon atoms, n, in their alkyl chain varying from 7 to 12. As will be seen later, our results on the orientational order of these pure compounds as also their phase diagram prompted us to study the enthalpy of the A–N transition in several binary mixtures of these homologues. Based on these calorimetric measurements, we have obtained evidence for tricritical behavior of the A–N transition in the mixtures. These results are also presented and discussed here.

II. EXPERIMENTAL

The liquid crystals used in these experiments were synthesized and purified in our chemistry laboratory.[10] The transition temperatures of the compounds studied are listed in Table I. For infrared measurements, the samples were homeotropically aligned between NaCl windows and the alignment was preserved in the smectic phase as well for compounds 10–12. We observed that the smectic phases of these three compounds were optically uniaxial. This coupled with the fact that all these

TABLE I. Transition temperatures (in °K) of the n-OMCPC homologues studied. Monotropic transitions are indicated by asterisks. The transitions not applicable to a given homologue are left blank. T_c represents A–I or N–I transition as the case may be.

| Alkyl chain | Short notation for the homologue | Crystal to | | | | T_c | |
		A	N	I	A–N	A–I	N–I
C_7H_{15}	7	...	...	344.2	...	...	340.5*
C_8H_{17}	8	...	331.0	...	...	...	345.0
C_9H_{19}	9	...	329.0	...	...	...	343.3
$C_{10}H_{21}$	10	...	335.8	...	330.6*	...	346.6
$C_{11}H_{23}$	11	...	343.0	...	343.1*	...	346.7
$C_{12}H_{25}$	12	338.0	...	...	...	349.5	...

smectic phases show a simple fan shaped texture[10] shows that they are all of the smectic A type. As the samples were homeotropically aligned, unpolarized radiation could be used in all the measurements. Other advantages of this technique as well as our experimental procedure are fully described in our earlier work.[12,13] As the mesophases could be supercooled considerably, the S values were obtained from spectra taken while cooling the samples.

The technique of randomly polishing NaCl surfaces on chamois leather[12] did not yield well aligned samples of the lower homologues of this series with n values below 7. Our attempts at inducing uniform homeotropic alignment by treating the NaCl surfaces with a dilute solution of cetyl trimethyl ammonium bromide in chloroform were also unsuccessful. It is for this reason that our order parameter measurements had to be restricted to the higher homologues of this series.

Differential scanning calorimetric (DSC) measurements were performed using a Perkin–Elmer calorimeter (Model DSC–2). The transition temperatures were determined from the onset of the endotherms during heating cycles and are nominally accurate to ± 0.5 °C; in the case of very weak A–N transitions the accuracy is ±1 °C. An indium calibration standard was used for calculating the enthalpies of the A–N transitions. As this transition does not supercool perceptibly, enthalpy data were obtained during both heating and cooling cycles and the average values are quoted here. A full scale range of 0.5 or 0.2 mcal/sec was used during these measurements in order to facilitate more accurate estimates of the usually low enthalpy of the A–N transition.

III. RESULTS AND DISCUSSION

A. Orientational order

For deducing the S values, we utilized the strong, isolated and well defined –C≡N absorption band exhibited by all the compounds and evaluated the integrated absorbance of this band, corrected for the effects of finite spectral slit width.[14] If R denotes the ratio of the absorbance in the homeotropically aligned mesophase to that in the isotropic phase, it can be shown that the orientational order parameter is given by[12]

$$S = (1 - R)/(1 - \tfrac{3}{2}\sin^2\alpha) , \qquad (1)$$

where α is the angle between the transition dipole moment of the band and the long axis of the molecule. The n-OMCPC molecule may adopt either of two different conformations[10] as shown in Fig. 1. Assuming that the long axis of the molecule lies along the line joining the centers of the two benzene rings,[12] it is seen that α is ~18.4° for conformer I and ~4° for conformer II. Although the presence of conformer II cannot be entirely ruled out, Sadashiva has indicated[10] that conformer I is sterically more favored and that free rotation around
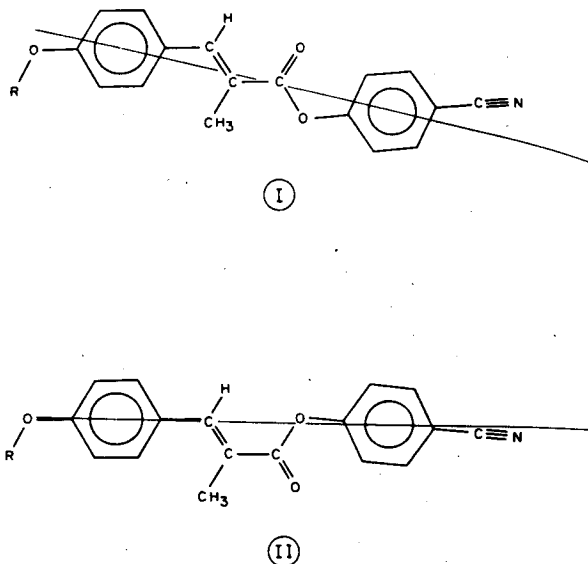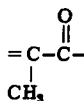
$$= \overset{O}{\overset{\|}{\underset{\underset{CH_3}{|}}{C}}} - \overset{}{C} -$$

FIG. 1. Molecular structure and two possible conformations of the rigid part of $trans$-p-n-alkoxy-α-methyl-p'-cyanophenyl cinnamates (n-OMCPC). The long axis of the molecule is taken to be the line joining the centers of the two benzene rings. The alkyl chain (C_nH_{2n+1}) is denoted by R.

is not too likely since the single bond has some double bond character due to resonance. For this reason, we have taken α to be 18.4° and calculated the S values assuming that the population of conformer II is negligible in the mesophases. This assumption, of course, remains to be verified by other methods such as x-ray diffraction which can determine the average breadth of the molecules in the mesophases and hence the preferred conformation. In any case, this question is important only with regard to the magnitude of the correction factor due to α, as seen from the denominator of Eq. (1). Thus, should subsequent x-ray studies indicate that our assumption is not justified, then given a knowledge of the relative abundances of the two conformers, it is a simple matter to accordingly scale down the S values determined by us. But for this consideration, our experimental geometry leads to the absolute values of S as other corrections due to the anisotropy in the refractive indices and the polarizability of the liquid crystalline medium are known to be well below our normal experimental error.[12] The calculated S values are estimated to be accurate to well within 5%.

Figures 2 and 3 show the temperature dependence of S for compounds 7–9 and 10–12, respectively. In the nematic phases of compounds 7–9, it is seen that as usual the S values decrease monotonically as T_c is approached. 10 OMCPC exhibits a monotropic A–N transition 16 °K below T_{NI}. It is seen from Fig. 3 that in this case the change in S at T_{AN} is hardly discernible. This is in accord with our calorimetric measurement discussed below, which gives a rather low value of ~1.0 cal/mole for the enthalpy of this transition.

On the other hand, there is a fairly large and abrupt

change in S at the monotropic $A-N$ transition of 11 OMCPC, characteristic of a distinctly first order transition; the enthalpy of this transition is also found to be nearly 40 times larger when compared to 10 OMCPC.

12 OMCPC exhibits only a smectic A mesophase. The observed S values in this case, even close to the isotropic transition are accordingly much higher than those obtained near T_{NI} in the other compounds studied here.

It is of interest to compare the S values of all these mesogens at a common relative temperature in the vicinity of the isotropic transition. Figure 4 shows these data 2° below the respective isotropic transition temperature in each case. Here each S value corresponds to the average of three independent measurements. Accordingly, the error limit on these values is within ~3%. The isotropic transition temperatures of the compounds are also shown for comparison. For compounds 8–10, Karat[11] has determined the relative S values from birefringence measurements. We have compared his data with ours, after normalizing the two sets of data for 9 OMCPC. Within the accuracy of the present measurements, a reasonable agreement exists between both sets of data for compounds 8–10.

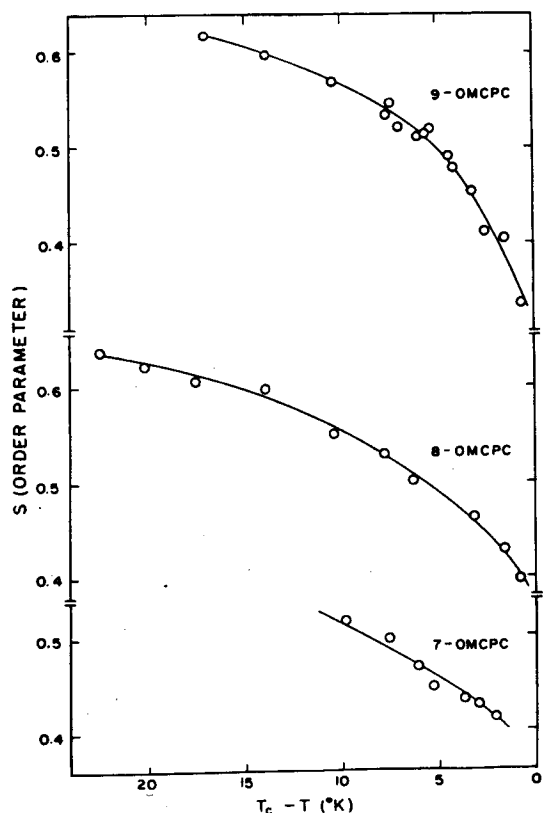For compounds 7–10, it is seen that the trend of even-odd effect in S values is at best very weak. Their re-
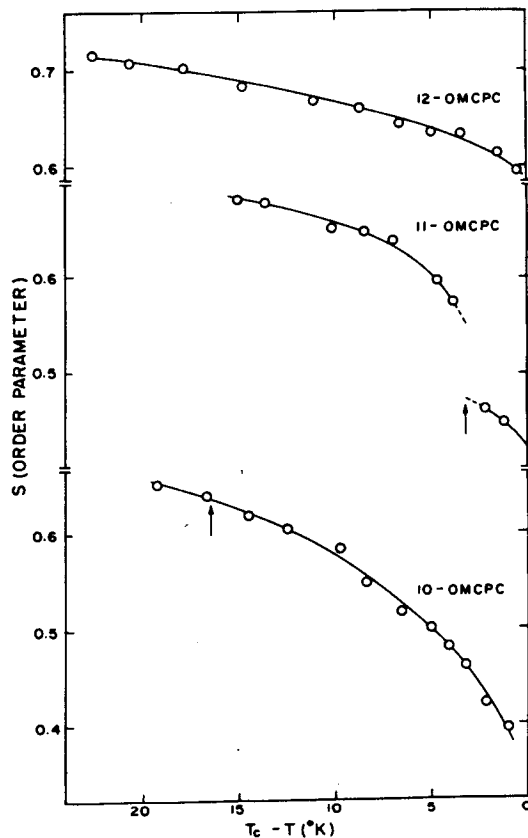

FIG. 3. Variation of S in the smectic A and nematic phases of 10 and 11 and in the smectic A phase of 12. The arrows show the $A-N$ transition points.
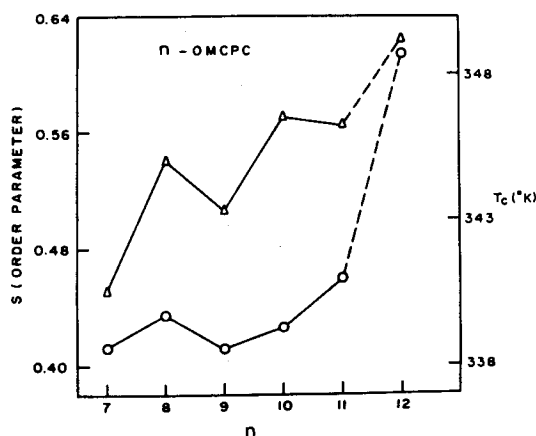

FIG. 4. Variation of S (circles) and the isotropic transition temperature, T_c (triangles), with the number of carbon atoms in the alkyl chain. The ordinate marks corresponding to T_c are shown on the right vertical axis. The S values are referred to a common relative temperature of $(T_c - 2)$ °K. The variation from 11 to 12 is shown by broken lines as 12 exhibits only the smectic A phase.

FIG. 2. Variation of S in the nematic phase of compounds 7–9.

spective T_{NI} values also show a similar behavior. As this series possesses an alkoxy end group, it is understandable that among these four compounds, the odd members may have slightly lower S values than the even members.[4,5] Even so, the observed variation in S is admittedly comparable to the maximum possible error limit on these data. This is not entirely surprising considering that the end chains are already quite long for the homologues considered here and that the even–odd effect progressively diminishes for higher homologues within any series. Furthermore, the even–odd effect in T_{NI} itself is seen to be quite small for compounds 7–11. A more pronounced even–odd effect in T_{NI} and relative S values has been observed in the lower homologues of this series.[10,11]

In Fig. 4, the S value is seen to increase on going from 10 to 11. This behavior is at variance from the pattern exhibited by the lower odd homologues. At $T_c - 2$, 11 OMCPC is barely 1.6 °K above T_{AN}. The presence of near neighbor correlations resulting in short range smecticlike order within the nematic phase is very probably the explanation for the anomalous increase in this case. Evidently, predictions based on mean-field theories[4,5] cannot account for the effects arising from such interactions.

B. Tricritical behavior

Considerable interest has been evinced recently in tricritical $A-N$ transitions. By varying a parameter related to the molecular packing or intermolecular interactions, the character of the $A-N$ transition can be made to evolve in a continuous manner from first to second order. For this purpose, concentration serves as a convenient variable in binary mixtures,[9] whereas pure compounds require the application of high pressures.[15-18] At the tricritical point, where the lines of first and second order transitions meet, the enthalpy of

the transition vanishes and the first order transition yields place to one of critical behavior. Our results on the variation of S values at T_{AN} as also the phase diagram of compounds 9–12 led us to investigate the thermodynamic behavior of binary mixtures of these homologues. Based on the theories proposed by McMillan[19] and Lee et al.,[20] a tricritical point in the $A-N$ transition is expected to occur at the reduced temperature $T_R = T_{AN}/T_{NI} \sim 0.88$. From Table I it is seen that T_R decreases on going from 11 to 10, their respective values being 0.99 and 0.95. It was also noted earlier that the enthalpy of the $A-N$ transition decreases drastically while going from 11 to 10, i.e., as the alkyl chain length decreases. These factors suggest that one may be observing here a tricritical behavior which can be studied in further detail by varying the average alkyl chain length in a continuous manner. Thus binary mixtures of 10 or 11 with lower homologues may reveal, at atmospheric pressure, the presence of a tricritical point at an appropriate ratio in the phase diagram of the mixtures. In fact, some homologues in this series with n values below 10 might conceivably have second order $A-N$ transitions which are not observed presumably because of the intervention of the solid phase. Another noteworthy feature from Table I is that the nematic range decreases on going from 10 to 11 and disappears altogether for 12. Here again, the phase diagram of binary mixtures of 11 and 12 may reveal, at atmospheric pressure, the existence of a triple point between the smectic A, nematic and isotropic phases.

Motivated by these considerations, we performed calorimetric measurements on several binary mixtures wherein 11 was one component while the other was 12, 10, or 8 as the case may be. If A and B denote the two components and χ_A and χ_B their respective mole percent concentration in the mixture, the average number of carbon atoms in the alkyl chain is given by

$$n_a = \frac{\chi_A n_A + \chi_B n_B}{100} , \qquad (2)$$

where n_A and n_B are the respective number of carbon atoms in the alkyl chain of the pure homologues. The different mixtures studied and their n_a and T_R values are summarized in Table II. Figure 5 shows their transition temperatures T_{AN} and T_{NI} as a function of n_a. The transition temperatures of the relevant pure compounds are also shown for comparison. It is interesting to note that although data corresponding to three separate families of mixtures are being compared they all point to a common trend when the average chain length or n_a is considered to be the variable, i.e., the nematic range increases as n_a decreases. Also, as expected, T_R is seen to diminish as n_a is lowered in the mixtures and this indicates an approaching tricritical point in the $A-N$ transition. The anticipated triple point between the smectic A, nematic, and isotropic phases is seen to occur in an 11–12 mixture at the mole percent ratio of ~27:73.

When compared to T_{AN}, the variation of T_{NI} in all three families of mixtures is much smaller. This is not surprising considering that the T_{NI} values of the

TABLE II. Mixtures investigated and their corresponding n_a and T_R values. A and B denote the two components and χ_A and χ_B their respective mole percent concentration in the mixture.

$A-B$	χ_A	χ_B	n_a	T_R
	26.5	73.5	11.74	1.0
11–12	53.3	46.7	11.47	0.996
	75.1	24.9	11.25	0.992
	0.0	100.0	11.00	0.990
	28.6	71.4	10.71	0.983
10–11	52.4	47.6	10.48	0.977
	70.3	29.7	10.30	0.971
	100.0	0.0	10.0	0.954
	5.2	94.8	10.84	0.987
	7.2	92.8	10.78	0.985
	9.0	91.0	10.73	0.983
8–11	13.2	86.8	10.60	0.980
	19.0	81.0	10.43	0.972
	22.4	77.6	10.33	0.970
	35.3	64.7	9.94	0.947
	37.4	62.6	9.88	0.933

relevant pure compounds are themselves quite close to each other.

It is of interest to examine the specific manner in which the enthalpy of the $A-N$ transition (ΔH_{AN}) varies against T_R as the tricritical point is approached. In Fig. 6 the ΔH_{AN} values obtained in 8–11 and 10–11 mixtures are plotted as a function of T_R. In the case of the mixtures, the ΔH_{AN} values pertain to the appropriate average molar weight for any given composition of the mixture. To the extent that ΔH_{AN} varies against T_R in a nonlinear fashion, the present results are in qualitative agreement with the theory proposed by Lee et al.[20] Our extrapolated data show that the $A-N$ transition would become second order for $T_R = 0.94 \pm 0.005$. In order to ascertain this, we investigated an 8–11 mixture with a T_R value of 0.933. The $A-N$ transition in this case was detected only as a feeble discontinuity in the baseline of the DSC trace, thus indicating that the transition is of second order. The corresponding ΔH_{AN}, if any, was indeed too small to be measured within the accuracy of the DSC-2. The T_{AN} and T_{NI} values of this mixture were also confirmed through microscopic observation using a hot stage.

Our T_R value at the tricritical point is considerably higher than that predicted by theory. Similar deviations have been reported earlier in a few other cases as well. For example, Johnson et al.[8] obtained a value of 0.96 from studies on binary mixtures of another series. Using hydrostatic pressure rather than the concentration of mixture as the variable, T_R values of 0.92 and 0.90 were reported in two instances.[15,16] In certain other cases, however, pressure as well as concentration de-
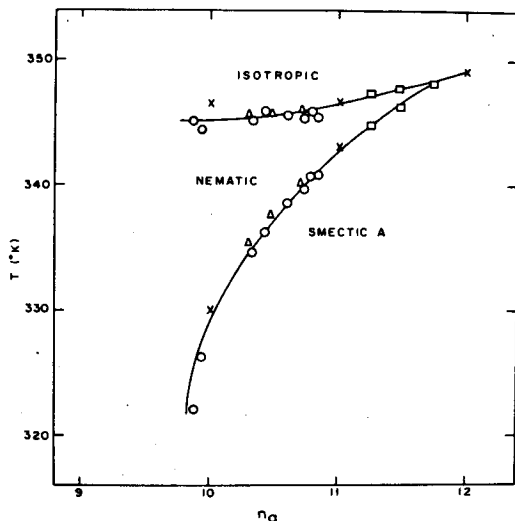

FIG. 6. Variation of ΔH_{AN} with T_R in 8–11 and 10–11 mixtures. Experimental uncertainties in the three lowest enthalpy values are also indicated.

FIG. 5. Variation of T_{AN} and T_{NI} in three families of mixtures as a function of the average number of carbon atoms, n_a, in the alkyl chain. The transition temperatures of the pure compounds are also shown for comparison. Circles: 8–11 mixtures; triangles: 10–11 mixtures; squares: 11–12 mixtures; crosses: pure compounds.
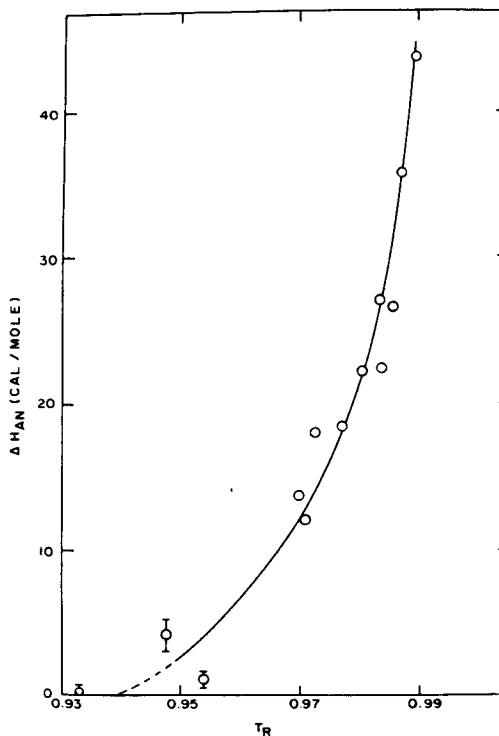
pendent studies have yielded T_R values in very close agreement with theory.[7,17,18] Such differences amongst different homologous series on the one hand, and between theory and experiment on the other, remain to be explained satisfactorily. In this respect, differences between the rigid core sizes of mesogenic molecules may be a relevant factor in determining the exact tricritical behavior observed in each series.

IV. CONCLUSIONS

The results of this study emphasize the close link that exists between the molecular ordering and thermodynamic behavior of mesophases. The even–odd effect in both S and T_{NI} is not very pronounced in the higher homologues we have investigated, as they all possess relatively long alkyl end chains. Nevertheless, the observed discontinuities in S values at the $A-N$ transition clearly reflect the enthalpy of this transition in the two homologues 10 and 11. The calorimetric results on binary mixtures show the presence of a concentration dependent triple point between A, N, and I phases. In addition, a tricritical point is shown to occur in the $A-N$ transition at a reduced temperature of $\simeq 0.94$. Further studies of the critical exponent as well as the fluctuations in concentration and order parameter in the vicinity of this tricritical point would be of considerable interest.

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