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Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds II. Binary Systems of 4-n-Heptyloxyphenyl 4-[4-ethylcyclo-hexanoyloxy]-benzoate with Homologues of the n-Alkyl 4-[4-ethoxybenzylidene amino]-α-methylcinnamates

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Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds II.† Binary Systems of 4-*n*-Heptyloxyphenyl 4-[4-ethylcyclo-hexanoyloxy]-benzoate with Homologues of the *n*-Alkyl 4-[4-ethoxybenzylidene amino]-α-methylcinnamates

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To examine the influence of chemical structure on the occurrence of reentrant nematic phases in binary systems of terminal-nonpolar compounds, the phase diagrams of such systems were studied where the nematogenic component (*n*-heptyloxyphenyl 4-[4-ethylcyclohexanoyloxy]-benzoate) was the same and the smectogenic components were homologous *n*-alkyl 4-[4-ethoxybenzylidene-amino]-α-methylcinnamates (from C_2—C_{12}). It was found that reentrant nematic phases occur only for mixtures containing the higher homologues of the smectogenic series.

Keywords: reentrant nematic phase, binary mixtures, terminal non-polar compounds

1. INTRODUCTION

The occurrence of reentrant nematic phases (in the sequences N S_A N_{re} or N S_A N_{re} S_C) has been previously described for binary systems of terminal-nonpolar (t.n.p.) compounds[1,2,3] and recently a pressure-induced reentrant cholesteric phase has been observed in a ternary system of t.n.p. compounds.[4]

Because reentrance was originally found in terminal-polar (t.p.) systems, the first attempts at an explanation of this phenomenon were in terms of the interaction in systems of this type.[5] However, the occurrence of reentrant phases in t.n.p. systems indicates that a more general approach is necessary. A disturbance of the smectic layer order is a general condition for nematic reentrance. As shown in References 5 and 6 the stability of smectic layers can be strongly influenced by

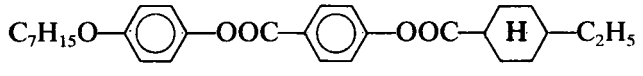
†Paper I in this series is reference 3.

steric factors and the molecular packing in smectic layers in mixed phases can be readily disturbed if the molecules of the two components have different shapes.

In order to study the influence of the molecular structure on reentrance in binary systems our investigations have been continued. Reentrant behaviour is often encountered in binary systems where one component has a nematic region over a large temperature range and does not possess a boundary with a S_A phase at lower temperatures. The S_A–N transition curve (T–x) starting from the second compound can fall steeply and attains a maximum concentration of the S_A phase region followed by a part where the slope of the curve changes sign. (See the binary systems in Reference 3.) In this paper binary systems are described where the *n*-heptyloxyphenyl 4-[4-ethylcyclohexanoyloxy]-benzoate was mixed with homologues of the *n*-alkyl 4-[4-ethoxybenzylidene amino]-α-methyl-cinnamates which have a S_A phase with a suitable temperature range.

2. SUBSTANCES

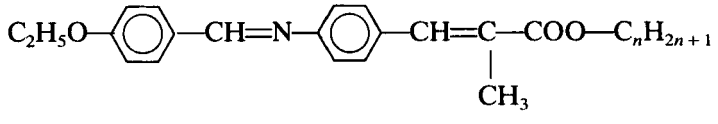
A: *n*-heptyloxyphenyl 4-[4-ethylcyclohexanoyloxy]-benzoate



K 62 (S_C 41.5) N 183 Is

This substance forms a nematic phase over a wide temperature range and in addition has a metastable S_C phase.

B1 . . . 12: *n*-alkyl 4-[4-ethoxybenzylideneamino]-α-methylcinnamates



	n	K	S_A	N	I_S
B2	2	• 92	(• 74)	• 121	•
B3	3	• 89	(• 80)	• 122	•
B4	4	• 55	• 75	• 87	•
B5	5	• 64	• 84	• 100	•
B6	6	• 60	• 81	• 89	•
B7	7	• 61.5	• 77	• 88	•
B8	8	• 57	• 77	• 85.5	•
B9	9	• 58	• 81	• 85	•
B10	10	• 58	• 80	• 81	•
B11	11	• 62	• 81	–	•
B12	12	• 62	• 74.5	–	•

3. PHASE DIAGRAMS

The phase diagrams (T–x diagrams) of the binary systems were studied by polarizing microscopy using both the contact method[9] and by determining transition temperatures of samples made up at specific concentrations.

For the A/B2 system, shown in Figure 1, the N to S_A transition appears only for the supercooled nematic phase (and is shown as a dotted line). This transition curve falls with increasing slope until it is virtually parallel to the temperature axis. The phase diagrams of the A/B3 and A/B4 systems are very similar to that of the A/B2 system (and are therefore not shown). In the A/B5 system no N_{re} phase

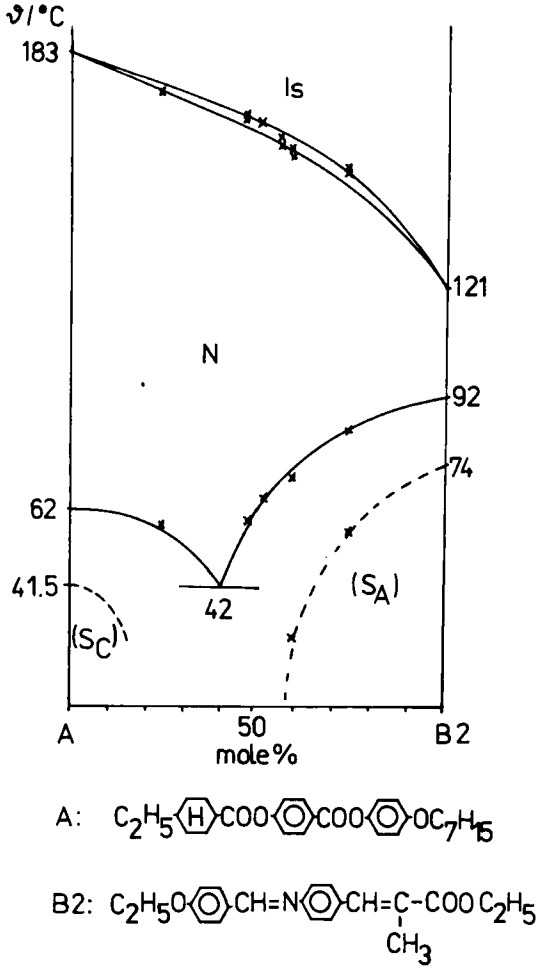
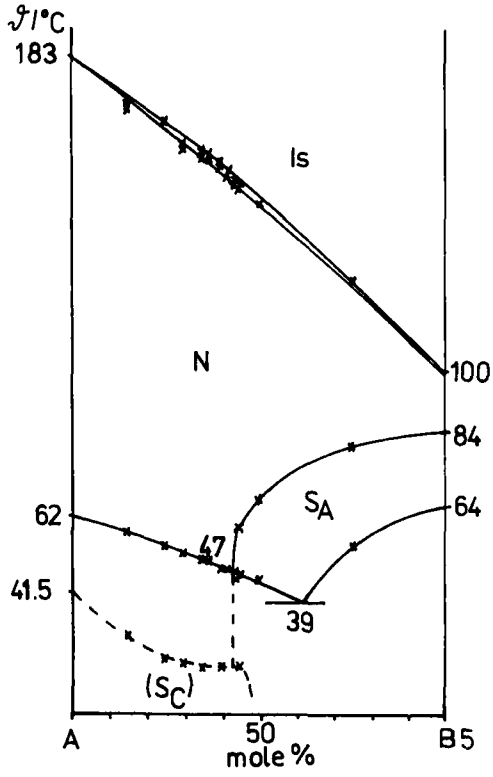


FIGURE 1 *The A/B2 system*
An S_A—N transition can be observed from the supercooled S_A phase and the transition curve falls steeply with concentration but no reentrant N phase could be detected.
The A/B3 and A/B4 systems have phase diagrams of a similar form.

appears. A metastable S_C phase, arising from the A component, on the left, extends over a wide concentration range and reaches the S_A phase extending from the B component on the right as shown in Figure 2.

The first example of a reentrant nematic phase occurs in the A/B6 system shown in Figure 3. A maximum appears in the S_A—N transition curve and the reentrant sequence, N S_A N_{re} S_C occurs. The A/B7 and A/B8 systems behave similarly, as shown in Figure 4. The S_A—N curve has a more pronounced maximum and a stable reentrant nematic phase occurs. Systems A/B9, A/B10 and A/B11 (shown in Figure 5) and A/B12 (described in Reference 3), also have reentrant nematic phases with



A: C_2H_5-(H)-COO-(O)-COO-(O)-OC_7H_{15}

B5: C_2H_5O-(O)-CH=N-(O)-CH=C(CH$_3$)-$COOC_5H_{11}$

FIGURE 2 *The A/B5 system*
A metastable S_C phase extends from the A component towards the S_A phase region. No reentrant nematic phase was found.

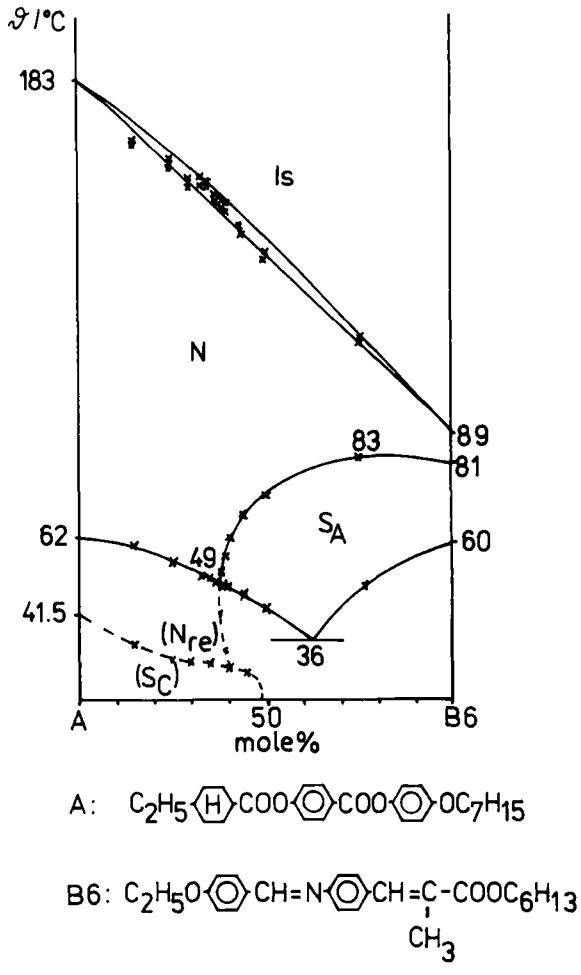


FIGURE 3 *The A/B6 system*
Nematic reentrance occus in the sequence N S_A N_{re} S_C and a maximum appears in the S_A—N transition curve.

stable regions of existence. In these four cases the S_C phase region does not extend to reach the S_A phase region, causing the phase sequence, N S_A N_{re} to occur.

4. DISCUSSION

The results presented here complete and extend the study of the reentrant phenomenon in t.n.p. systems outlined in Reference 3. In all of the systems examined, an extended S_A mixed phase region was found. The S_A—N transition curves have a region of steeply decreasing temperatures with increasing concentration of the

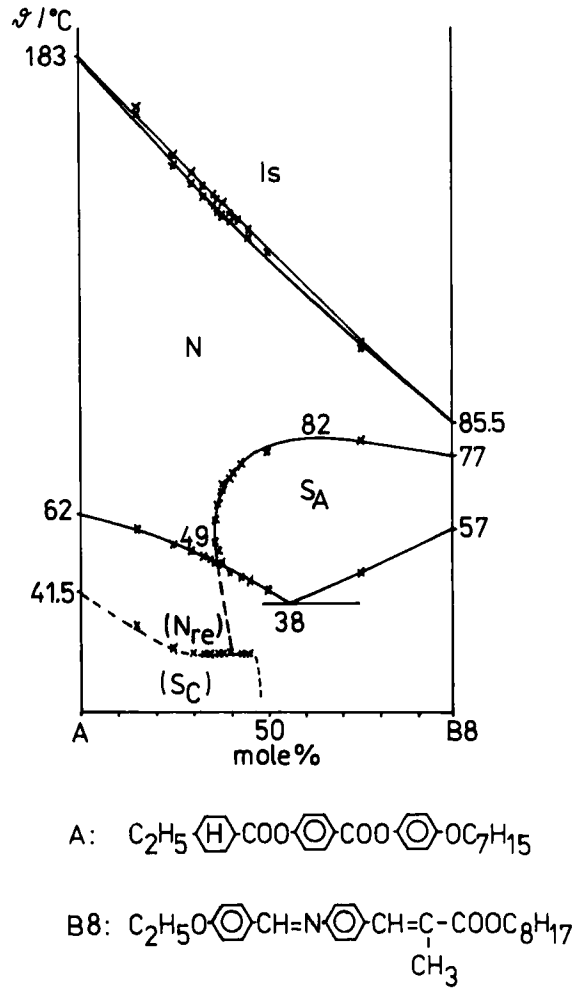
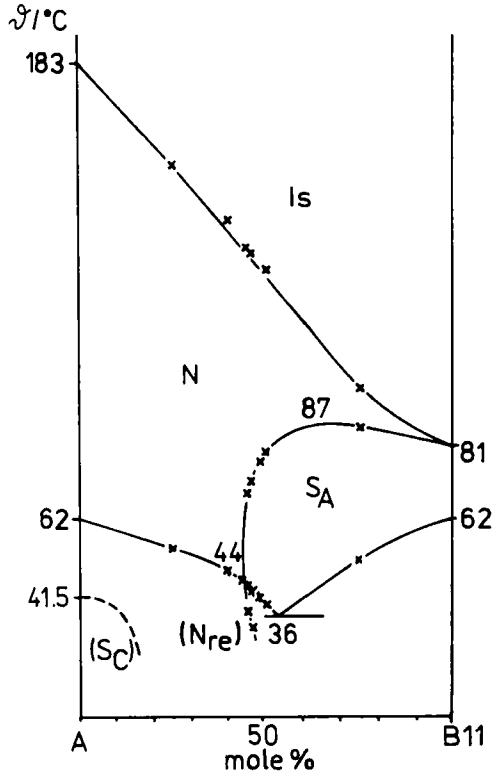


FIGURE 4 *The A/B7 and A/B8 systems*
Both systems show nematic reentrance similar to that shown in Figure 3. Here the maximum in the S_A—N transition curve is more pronounced.

nematogenic, A compound. In the A/B6 . . . 12 systems the slope of the transition curve changes sign and reentrant nematic phases appear.

In Figure 6 the maximum concentration of the A component in the S_A phase region is plotted against the number of C-atoms in the alkyl chains of the B homologues. At the maximum of this curve the molecular lengths of the A and B compounds are nearly the same and it is in this region where the nematic reentrance appears. This coincidence may be accidental, but the more favourable packing of molecules of nearly equal length within the smectic layers may well be responsible



A: C_2H_5-(H)-COO-(O)-COO-(O)-OC_7H_{15}

B11: C_2H_5O-(O)-CH=N-(O)-CH=$\underset{\underset{CH_3}{|}}{C}$-$COOC_{11}H_{23}$

FIGURE 5 *The A/B9, A/B10 and A/B11 systems*
All of these systems have a reentrant nematic phase. Note that the S_C phase region does not extend to reach the S_A phase and the sequence N S_A N_{re} occurs without an S_C phase.
The phase diagram of the A/B12 system (described in Reference 3) has a similar form.

for the extension of the S_A phase region. In systems of the type shown in Figure 1 the slope of the S_A—N transition curve at low temperatures is not observable. But in principle, a reentrance of the nematic phase at lower temperatures seems to be possible as shown in Figures 3, 4, 5 and 8 of paper I (Reference 3).

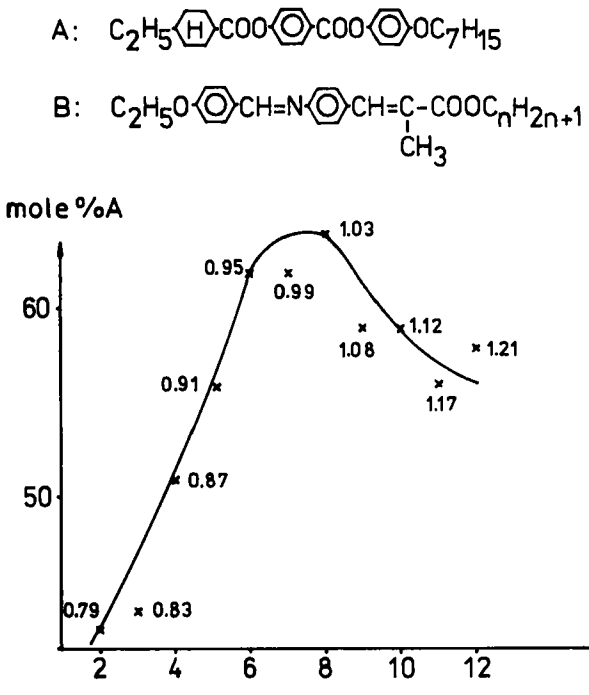


FIGURE 6 The concentration range of the S_A phase in mole % of the A component plotted against the number of carbon atoms (n) in the alkyl chain of the B components. For each mixture, the ratios of the molecular lengths of the two components is quoted (L_A/L_B). Note that at the maximum of this curve, the molecular lengths of the two components are nearly the same.

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