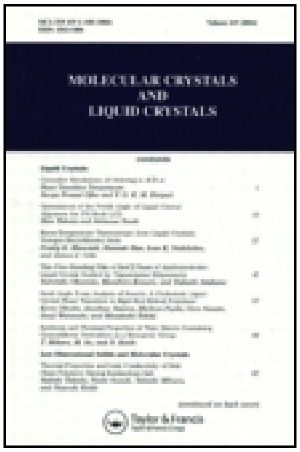

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Reentrant Nematic phases in Binary Systems of Terminal-Nonpolar Compounds

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Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds

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The phase diagrams of nine binary systems containing reentrant nematic phases in the sequence N_{re} S_A N and S_C N_{re} S_A N are presented. In these mixtures both components are of the terminal-nonpolar type. X-ray diffraction studies of three systems were carried out. The relationship between the form of the phase diagrams and the chemical nature and polymorphism of the separate components is discussed.

1. INTRODUCTION

For some years it appeared that reentrant phenomena are a special feature of compounds with terminal polar groups and their mixtures. We have, however, recently found that reentrant nematic (N_{re}) phases can also occur in binary systems of terminal-nonpolar compounds.[1,2]

In this paper we describe further examples of binary systems of this type.

2. EXPERIMENTAL

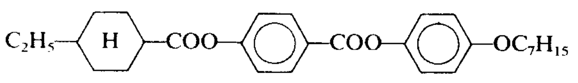
The phase diagrams of the binary systems were studied by means of a polarizing microscope using the contact method[3] and by determining transition temperatures of samples made up at specific concentrations. In some cases calorimetry was used to detect particular phase transitions. For the calorimetric measurements a differential scanning calorimeter (DSC-2, Perkin-Elmer) was used. X-ray investigations were performed with either a photographic flat film method using oriented samples or with a small angle diffractometer.

3. SUBSTANCES

We used original substances and the syntheses are described in the cited papers.

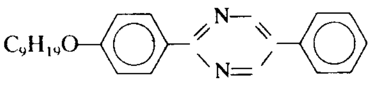
In some cases the transition temperatures determined by microscopic observations differ slightly (but not significantly) from the values reported in the literature.

C 1 4-*n*-heptyloxy-phenyl 4-[4-ethyl-cyclohexanoyloxy]benzoate



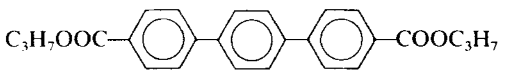
Cr 61.5 (S_C 41.5) N 183 Is[4]

C 2 5-phenyl-2-[4-*n*-nonyloxyphenyl]-pyrimidine



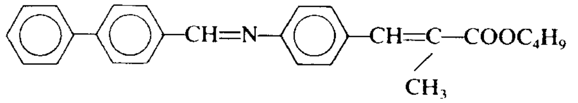
Cr 101 N 109.5 Is[5]

C 3 di-*n*-propyl *p*-terphenyl-4,4′-dicarboxylate



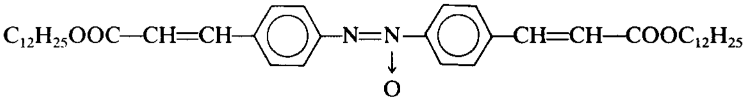
Cr 122 S_E 137.1 S_A 239 Is[6]

C 4 *n*-butyl-4-[4-phenyl-benzylideneamino]-α-methylcinnamate



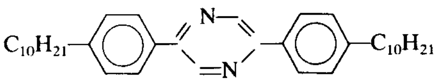
Cr 94.2 S_B 103.5 S_A 153.5 N 156.5 Is[7]

C 5 di-*n*-dodecyl-[4,4′-azoxycinnamate]



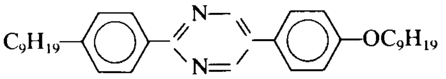
Cr 102 S_C 156.5 S_A 159.5 Is[8]

C 6 2,5-bis-[4-*n*-decylphenyl]-pyrazine



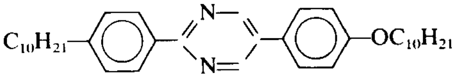
Cr 112 (S_X 106) S_C 170.5 Is[9]

C 7 2-[4-*n*-nonylphenyl]-5-[4-*n*-nonyloxyphenyl]-pyrimidine



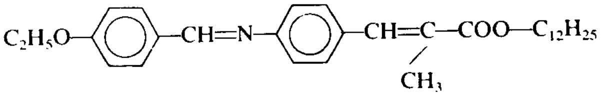
Cr 94 (S_G 89) S_F 131 S_C 176.5 S_A 188.5 Is[10]

C 8 2-[4-*n*-decylphenyl]-5-[4-*n*-decyloxyphenyl]-pyrimidine



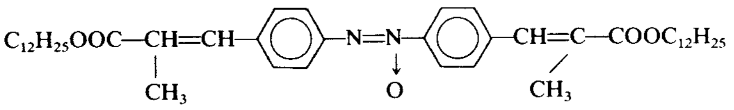
Cr 88 S_G 117 S_F 133 S_C 179.5 S_A 183 Is[10]

C 9 *n*-dodecyl 4-[4-ethoxybenzylideneamino]-α-methylcinnamate



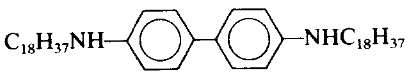
Cr 69 S_A 81 Is[7]

C 10 di-*n*-dodecyl-[4,4′-azoxy-α-methylcinnamate]



Cr 79 S_C 83.7 S_A 87.9 Is[7]

C 11 4,4′-bis-[4-*n*-octadecylamino]-biphenyl



Cr 105 S_I 112 Is[11]

Cr:	Crystalline solid
N:	nematic
S_A, S_B, S_C, S_G, S_F:	smectic A . . . . . F
Is:	isotropic liquid

The numbers between the phase symbols are the transition temperatures (°C). Brackets denote monotropic transitions.

4. PHASE DIAGRAMS

The temperature/composition phase diagrams of nine binary systems (nos. 1, 2, . . .) were investigated and are shown in the Figures 1 to 9. The dotted curves indicate phase transitions in the supercooled state.

In all binary systems studied, the first component (A) is a nematogenic compound C1 or C2. The compound C1 forms a nematic phase over a wide temperature range and in addition has a metastable S_C phase. The second component, B forms one or more smectic phases (C3–C11).

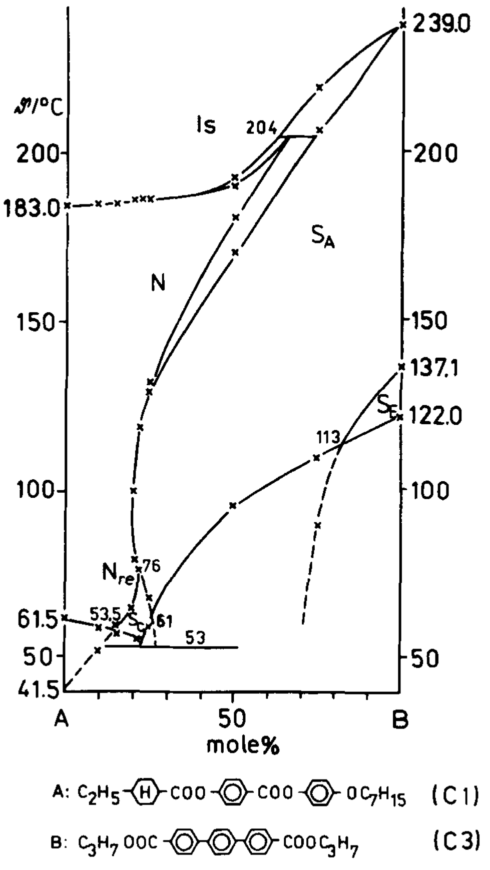


FIGURE 1 Binary system 1

In three binary systems (1, 2, and 3) the component C1 was combined with a smectic dimorphic compound: C3 (S_A, S_E), C4 (S_A, S_B), C5 (S_A, S_C) giving phase diagrams shown in Figures 1 to 3. The common feature is the appearance of the S_A phase over a large range of both concentration and temperature. The other smectic phases (S_E, S_B, S_C) are restricted to mixtures with higher concentrations of component B. A further common feature is the occurrence of an N_{re} phase over a small concentration interval. On cooling the N_{re} phase, an S_C phase is formed. In contrast to the situation shown in Figure 1, in the mixture 2 and 3, the S_C phase region of compound C1 is not continuous with the S_C phase region occurring below the N_{re} phase.

In the binary system 4 (Figure 4) the nematic compound is the pyrimidine derivative C2. The smectic component C6 forms an S_C

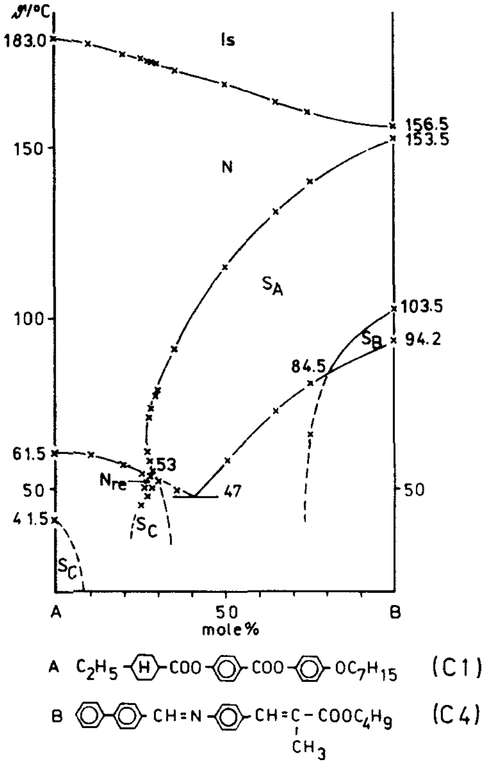


FIGURE 2 Binary system 2

phase and a further low temperature smectic phase but does not form an S_A phase. Nevertheless a similar type of a phase diagram is observed, characterized by an extended region of an intermediate S_A phase at the center of the concentration range and by the occurrence of a metastable N_{re} phase (83–85 mole-% C2). The monotropic smectic low temperature phase of the compound C6 could not be classified because this phase crystallized immediately after formation (for both the pure compound and binary mixtures).

In the binary systems 5 and 6 (Figures 5 and 6†) the B components are the homologous C7 and C8 pyrimidine derivatives. Both exhibit smectic tetramorphism in the sequence S_A S_C S_F S_G. In both binary systems the tilted smectic phases S_C, S_F, S_G only occur in mixtures containing high concentrations of the B component whereas the S_A

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†Part of diagram 6 has been previously presented in Ref. 2.

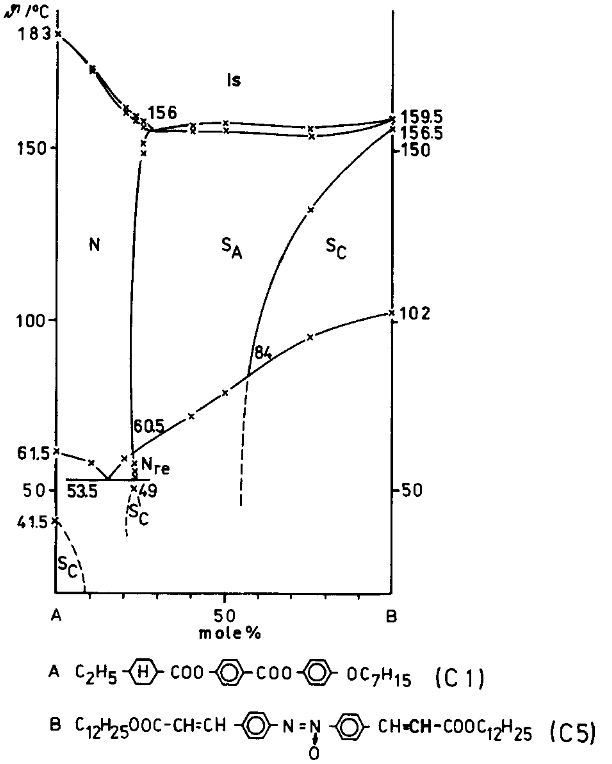

FIGURE 3 Binary system 3

phase region is extended over a large range of concentration and temperature as found in systems 1 and 4.

In system 5 the N_{re} phase occurs only on supercooling (89 to 90 mole-% C2). At middle concentrations in system 5 an intermediate S_E phase occurred over a wide concentration range. This S_E phase was identified from microscopic observations by its characteristic paramorphic fan texture with stripes and concentric arcs[12] and from X-ray investigations.[13]

In system 6 a stable N_{re} phase occurs (81 to 84 mole-% C1). On cooling the N_{re} phase transforms into a S_C phase. A maximum in the melting curve was found, which indicates a complex formation in the solid state. The melting curve was determined by calorimetric and X-ray measurements because the melting was difficult to detect by microscopic investigations. The transition temperature obtained by calorimetric measurements are shown as circles.

In the binary systems 7 and 8 (Figures 7 and 8) the clearing points

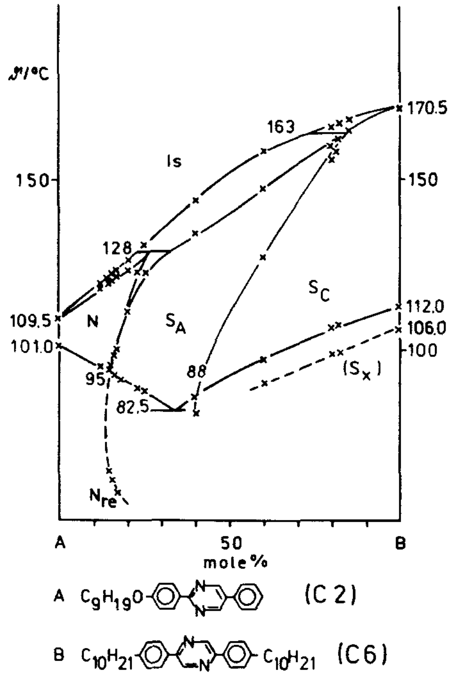

FIGURE 4 Binary system 4

of the B component are relatively low. The broad S_A phase regions have a maximum in the transition curve S_A–N. This points to an induced S_A phase at the center of the concentration range.

A much more complex type of phase diagram occurs for system 9 (Figure 9) where the B component only possesses a S_I phase. There are two intermediate phases S_A and S_C and the N_{re} phase, occurring between 75 and 77 mole-% C1, is stable.

5. X-RAY INVESTIGATIONS

X-ray investigations on system 6 have been previously reported.[2] There was clear corroborative evidence of the microscopically observed phase sequence, N S_A N_{re} S_C.

In system 7, X-ray investigations were performed on samples in the concentration range of the N_{re} phase (56 mole-% C1, see the arrow in Figure 7), using a small angle diffraction equipment. Figure 10 shows the diffracted intensity between 1° and 2° for the N, S_A, and N_{re} phase. The scattering intensity of the three phases was recorded

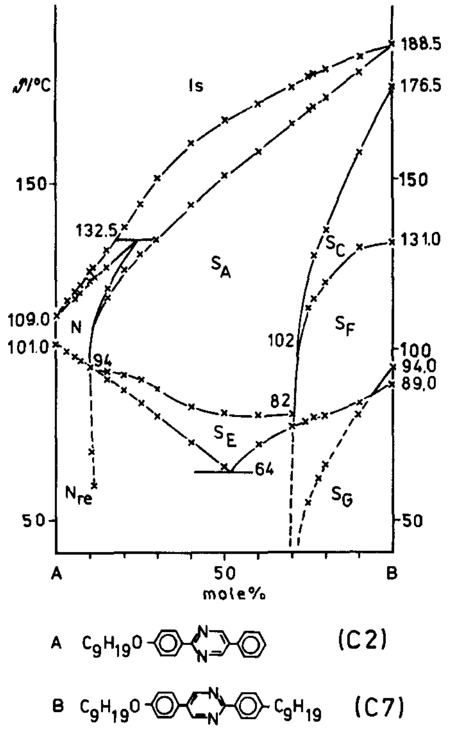

FIGURE 5 Binary system 5

with the same amplification. At high temperatures the nematic phase gave only weak diffuse scattering. Approaching the N → S_A transition the intensity increases. The S_A phase gave the characteristic strong Bragg peak from the layer spacing. In the diffraction pattern of the N_{re} phase, the Bragg peak is broadened indicating the degeneration of the layer order, but the scattering intensity is still high compared with that given by the higher temperature nematic phase. This is obviously due to the presence of some kind of cybotactic organization.

Figure 11 presents the scattering curves in nematic mixtures near the maximum concentration of the S_A mixed phases (59 mole-% C1, see arrow in Figure 7). Between 120°C and 80°C there is only the usual diffuse scattering of nematic phases. From 76°C the scattering intensity distinctly increases and reaches a maximum at about 50°C. On further cooling the intensity decreases again.

These results indicate the existence of a smectic-like ordering in the nematic phases as the N–S_A transition is approached, in all parts of the region of the apex.

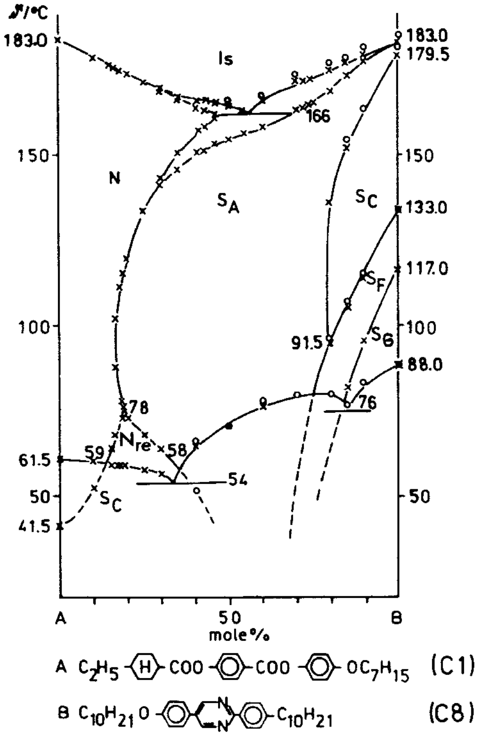

FIGURE 6 Binary system 6

Such smectic-like ordering has also been invoked to explain anomalies in dielectric measurements near the S_A–N transition.[14]

Using Bragg's law the *d*-value of the S_A phase was calculated. The spacing obtained of 33.9 Å is virtually the same as averaged molecular length $\bar{L}$ ($\bar{L} = x_A L_A + x_B L_B$) = 35.1 Å. The difference can be credibly explained by the non-rigid nature of the long aliphatic chains. From the diffuse scattering in the N and N_{re} phase *d*-values of 34.1 Å resp. 33.7 Å for the smectic-like cybotactic groups could be deduced.

Figures 12 and 13 show the small-angle scattering curves for system 9, for corresponding concentration and temperature regions. In Figure 12 (78 mole-% C1) the phase sequence N, S_A, N_{re}, S_C (indicated by the arrow in Figure 9) was traversed by the measurements. As we approach the N → S_A and the N_{re} → S_A transition the scattering intensity clearly increases. In Figure 13 (79.5 mole-% C1) the scattering curves are presented when the nematic region near the apex of the S_A–N

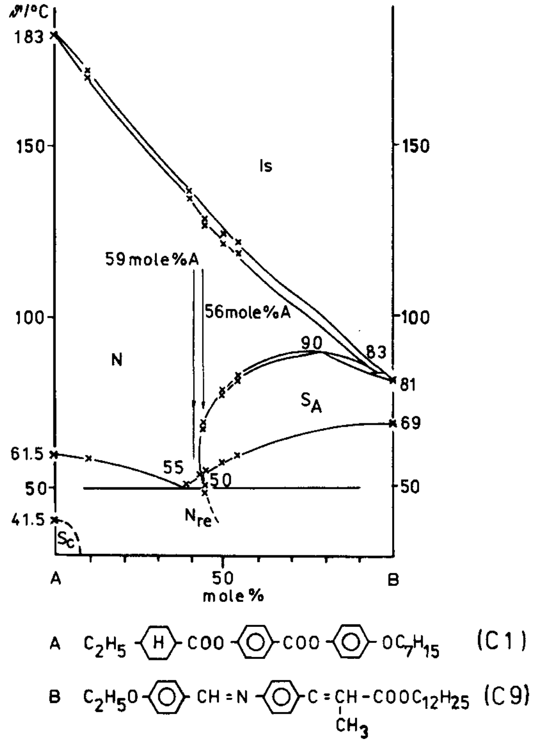

FIGURE 7 Binary system 7

curve is crossed (arrow in Figure 9). On cooling from 120°C to 96°C a continuous increase of the scattering intensity is observed. The intensity reaches a maximum at about 96°C and then decreases on further cooling.

In this binary system the *d*-value of the S_A phase (38 Å) also agrees very well with the averaged molecular length $\bar{L} = 39$ Å. The *d*-values of the smectic cybotactic groups calculated from the diffuse scattering curves of the nematic phase have nearly the same value (37.7 Å).

If we assume that the molecules in S_A are arranged perpendicular to the layer planes and the chain conformation is not too different in the S_A and S_C phases, the tilt angle, β of the S_C phase can be calculated from the position of the scattering peak in Figure 12 (69°C)

$$\cos\beta = d_{S_C}/d_{S_A}$$

This calculation gives a value for the tilt angle of 13°.

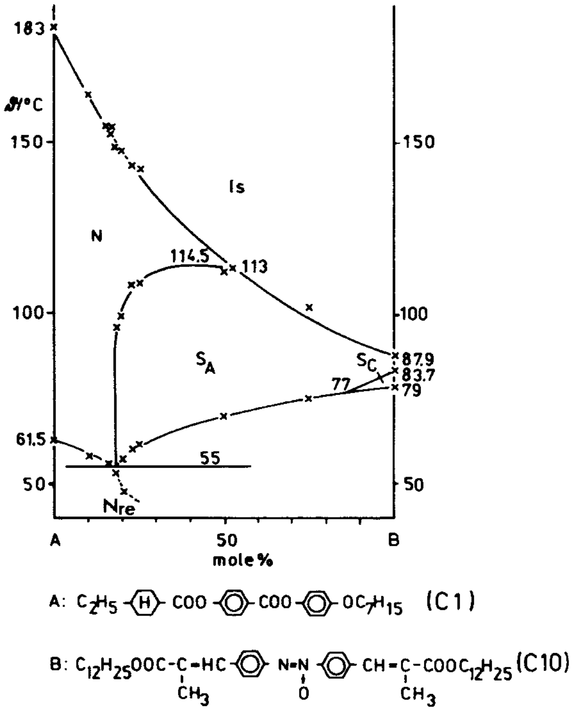

FIGURE 8 Binary system 8

6. DISCUSSION

The nematic reentrant phenomenon has been previously found in both one and two-component systems of strongly polar compounds. These substances were terminal-polar (t.p.) compounds. The systems described here show that reentrant behaviour can occur also in binary mixtures where both compounds are of a terminal-non-polar (t.n.p.) type.

The systems examined contained different types of mesogen. The component A forms a stable nematic phase, but not an S_A phase (compounds C1 and C2). These nematic phases were found to persist over a large supercooled region. For the second component, B, substances with a different pattern of polymorphism, mostly involving S_A phases were used.

In those binary systems containing compounds which did not themselves form S_A phases, the mixed S_A phase occurs in the centre of the phase diagram (systems 4 and 9). In the other systems where one of the components itself forms an S_A phase, the mixed S_A phase

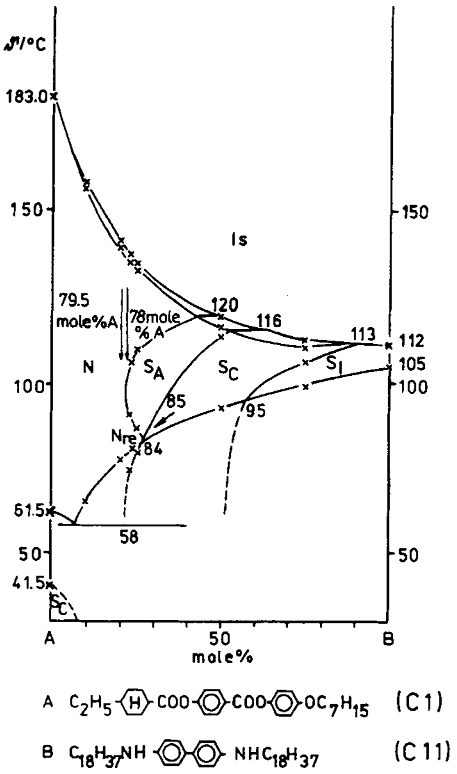

FIGURE 9 Binary system 9

region extends continuously from the edge of the phase diagram as in Figure 14.

This general pattern of behaviour has been often observed. Together with our results it was found in binary systems which combine:-

a) two t.p. compounds (the first system with nematic re-entrance was of this kind).[15]
b) one t.p. compound and one t.n.p. compound with two different cases
    (1) the mixed phase is starting from the S_A phase of the t.p. compound† (see Refs. 16, 17, and 18),
    (2) the mixed phase is starting from the S_A phase of the t.n.p. compound.[1]
c) two t.n.p. compounds.[1,2]

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†In the binary systems of this type additionally an induced S_A phase is observed at middle concentrations.[16,17,18]

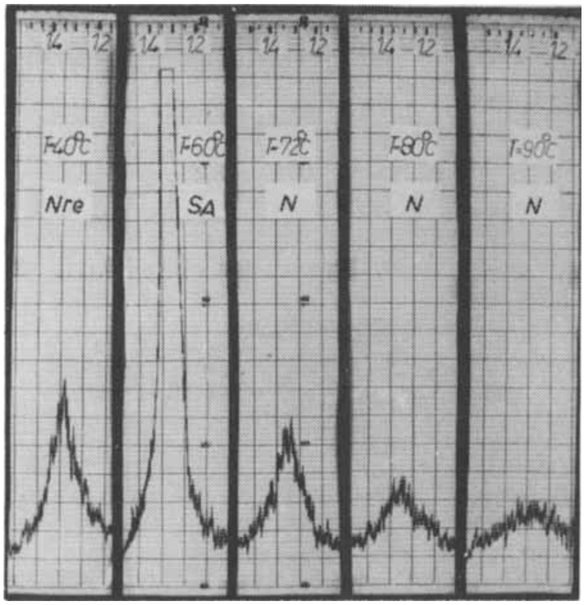

FIGURE 10 Scattering intensity curves in the Bragg angle region between 1 and 2° in the N, S_A, and N_{re}, S_C phase of the binary mixture C1/C9 containing 56 mole-% C1.

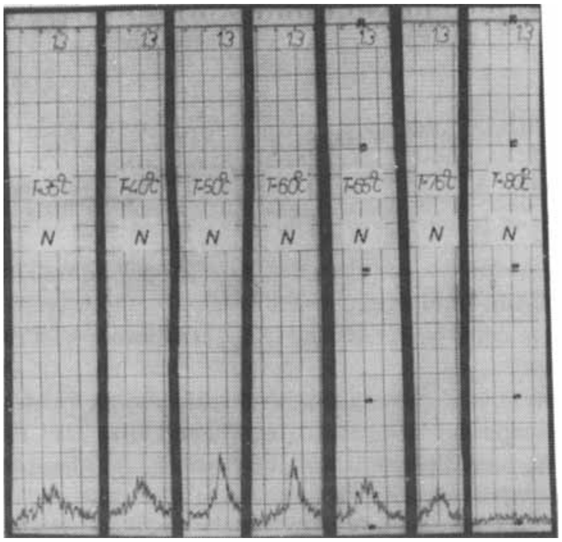

FIGURE 11 Scattering intensity curves in the Bragg angle region between 1 and 2° in the nematic phase of the binary mixture C1/C9 containing 59 mole-% C1.

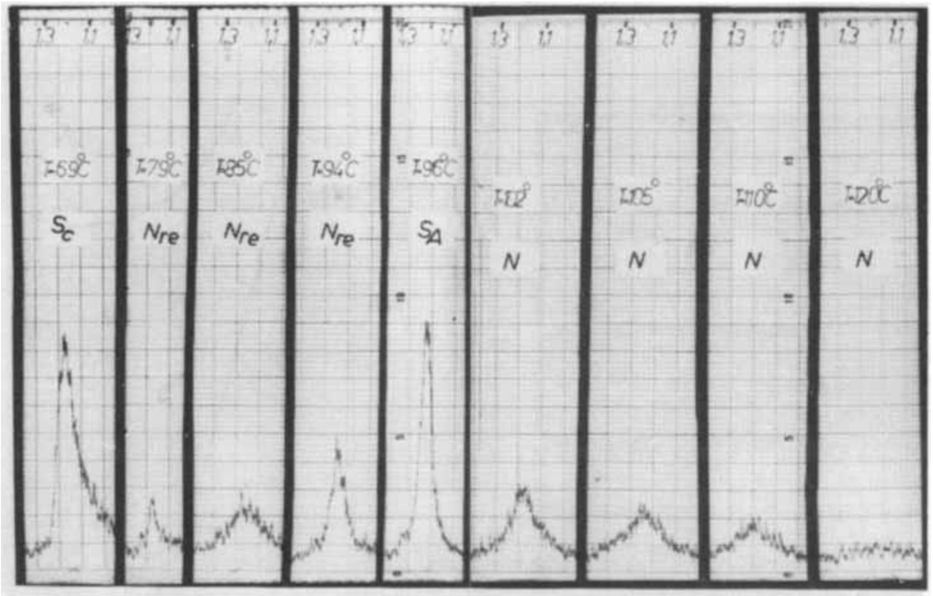

FIGURE 12 Scattering intensity curves in the Bragg angle region between 1 and 2° in the N, S_A, N_{re}, and S_C phase of the binary mixture C1/C11 containing 78 mole-% C1.

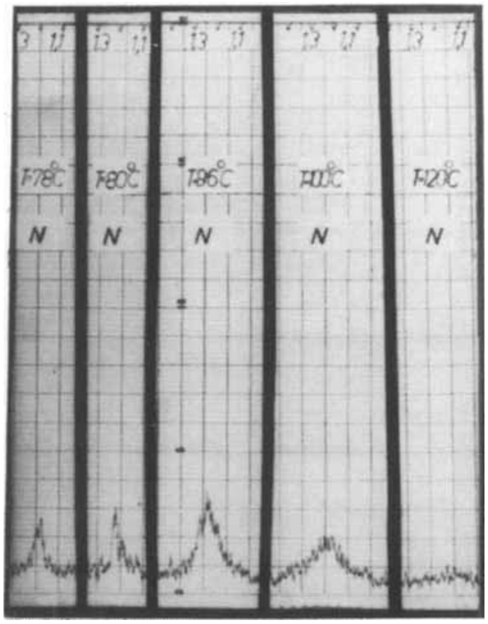

FIGURE 13 Scattering intensity curves in the Bragg angle region between 1 and 2° in the nematic phase of the binary mixture C1/C11 containing 79.5 mole-% C1.

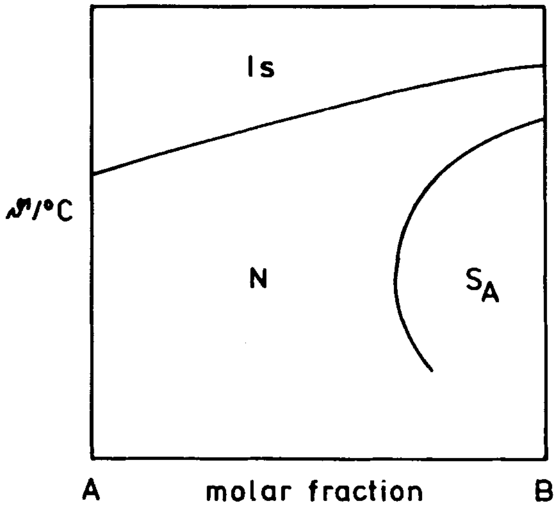

FIGURE 14 General shape of the S_A-N transition curve.

Because of the dominant role of t.p. compounds, a strong polarity of the molecules was assumed to be necessary for nematic reentrance to occur. The S_A phases between two nematic phases are S_{A_d} phases with a ratio d/L 1.1–1.6 (layer distance (d), molecular length (L)). The relative proportions of monomer and dimer molecules determines this ratio.[19,20] Its shift with temperature can lead to an unfavourable packing in the S_A phase and hence cause a nematic reentrance.[21]

The conception of monomer–dimer equilibrium as an explanation for reentrance should be also applicable to S_A mixtures of type b1 where the concentration of monomers and dimers changes as the t.n.p. component is added. The interactions and the layer ordering are determined by the composition of a three component system consisting of monomers, dimers, and individual molecules of the t.n.p. compound.

The available experimental data of mixed S_{A_d} phases indicate that the layer distance decreases with increasing concentration of the t.n.p. compound.[16,19,20]

This monomer–dimer relation may be not predominant in systems of the type b2 and there is no reason to think that it occurs in t.n.p. systems of the type c. Indeed in such a system a monolayer type was found over the whole range of the S_A mixed phase.[1] Furthermore, in the reentrant region of the S_A phase of the systems 7 and 9 a monolayer was also observed (see section 5).

Some phase diagrams of our t.n.p.–t.n.p. mixtures point to a reentrant behaviour in induced S_A phase systems and such behaviour was first described in t.n.p.–t.p. combinations.[16] An isolated S_A phase with a high thermal stability was found at middle concentrations (intermediate phases). A second type with induced S_A phases corresponds to Figure 14. It shows a S_A phase starting from the t.n.p. compound and a maximum in the S_A–N transition curve.[1,16,18]

In our t.n.p.–t.n.p. combinations the system shown in Figure 3 of Ref. 1, the system 7 and in a modified way (because S_A–isotropic transitions take place) systems 3 and 8 belong to this type. Perhaps also in some other systems (for example 1 or 6) the broad S_A mixed phase region is connected with inducing effects.

The X-ray diffraction studies of the reentrant region N S_A N_{re} as well as in the nematic phase near the apex of the transition curves, point to continuous transitions into monolayer S_A phases of a weak smectic order. The S_A–N and N_{re}–S_A phase transitions could not be observed by calorimetric measurements even at the highest sensitivity of the instrument.

The occurrence of a transition curve S_A–N is to be expected in binary systems if the mixing components exhibit the polymorphism, N and N S_A, respectively. But the occurrence of a nematic reentrance is a more sensitive situation. As can be seen in our examples there is a great variation of the shape of the individual S_A–N transition curves.

Reentrance may be favoured by a mixed phase field S_A extended in temperature and concentration without transition to other smectic and solid phases at lower temperatures. As can be seen, in some systems the reentrant region is a supercooled phase field (systems 3, 4, 5, 8). In the systems 1, 2, and 3 the stability of the N_{re} region is restricted by the adjacent S_C phase. In this context we are reminded of the occurrence of nematic reentrance in some binary systems with very complicated forms of phase diagrams.[22]

The results, discussed here, point to a more general view of the reentrant phenomenon. A monomer–dimer equilibrium is only one possibility for the generation of a steric situation in a S_A phase system which produce layers with low order and favours the reentrance of a nematic phase. In our t.n.p.–t.n.p. system one component at least was an unsymmetrical compound. Therefore, an unfavourable packing of the rigid and flexible parts of the molecules may determine whether reentrance occurs in each particular system. Indeed, recently it was shown by Dowell[23] on the basis of molecular lattice theory, that differences in the steric (hard-repulsive) packing of the rigid cores and of the partially flexible tails are sufficient to give rise to a stable N_{re} phase.

References

1. G. Pelzl, S. Diele, I. Latif, W. Weißflog and D. Demus, *Cryst. Res. Technol.*, **17**, K78 (1982).
2. S. Diele, G. Pelzl, I. Latif and D. Demus, *Mol. Cryst. Liq. Cryst. Letters*, **92**, 27 (1983).
3. H. Sackmann and D. Demus, *Z. Phys. Chem.* (Leipzig) **222**, 143 (1963).
4. H.-J. Deutscher, M. Körber, H. Altmann and H. Schubert, *J. Prakt. Chem.*, **321**, 969 (1979).
5. H. Zaschke and H. Schubert, *J. Prakt. Chem.*, **315**, 1113 (1973).
6. H. Schubert, H.-J. Lorenz, R. Hoffmann and F. Franke, *Z. Chem.*, **6**, 337 (1966).
7. G. Pelzl and H. Sackmann, *Symposium Farad. Soc.*, No. 5, 68 (1971).
8. D. Vorländer, *Z. Phys. Chem.*, **A126**, 449 (1927).
9. H. Schubert, R. Hacker and K. Kindermann, *J. Prakt. Chem.*, **37**, 12 (1968).
10. S. Diele, D. Demus, A. Echtermeyer, U. Preukschas and H. Sackmann, *Acta Physica Polonica*, **A55**, 125 (1979).
11. N. K. Sharma, W. Weißflog, L. Richter, S. Diele, B. Walter, H. Sackmann and D. Demus, *Advances in Liquid Crystal Research and Applications*, Edit. by L. Bata, Vol. 1, p. 3 (1980).

12. D. Demus and L. Richter, *Textures of Liquid Crystals*, Second Edition, Leipzig, 1978, p. 167–169.
13. I. Latif, *Dissertation A*, Halle /S., 1984.
14. B. R. Ratna, R. Shashidhar, M. Bock, A. Göbl-Wunsch and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **99**, 285 (1983).
15. P. E. Cladis, *Phys. Rev. Letters*, **35**, 48 (1975).
16. B. Engelen, G. Heppke, R. Hopf and F. Schneider, *Mol. Cryst. Liq. Cryst. Letters*, **49**, 193 (1977).
17. G. Pelzl, U. Böttger and D. Demus, *Cryst. Res. Technol.*, **16**, K67 (1981).
18. S. Takenaka, H. Nakai and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **100**, 299 (1983).
19. S. Diele, U. Baumeister and D. Demus, *Z. Chem.*, **21**, 28 (1981).
20. P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, **59**, 63 (1980).
21. L. Longa and W. H. de Jeu, *Phys. Rev.*, **A26**, 1632 (1982).
22. G. Pelzl, U. Böttger and D. Demus, *Mol. Cryst. Liq. Cryst. Letters*, **64**, 283 (1981).
23. F. Dowell, *Phys. Rev.*, **A28**, 3526 (1983), and **31**, 3214 (1985).