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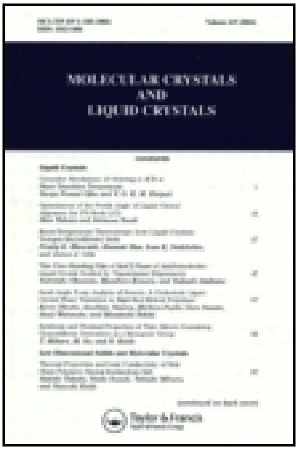

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Reentrant Nematic and Injected Smectic Behaviour in Binary Mixtures Including Those of Terminally Non-Polar Compounds

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Reentrant Nematic and Injected Smectic Behaviour in Binary Mixtures Including Those of Terminally Non-Polar Compounds[†]

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(*Received May 5, 1987*)

Some new examples of injected smectic behaviour for binary mixtures of strong terminally polar mesogens (CBs, PCHs, BCOs, and CCHs) with a range of terminally non-polar esters are presented. Variations in the strength of the injected behaviour are discussed. Examples of S_B as well as S_A injection occur.

Studies of mixtures of terminally non-polar 4,4″-dialkyl-2′-fluoro-*p*-terphenyls (I) with cyano-substituted mesogens are also described and provide an example of injection of S_A and S_E phases.

Of greater interest is the observation that binary mixtures consisting solely of homologues of (I) can exhibit reentrant nematic behaviour, providing further evidence that reentrant phenomena are not a special feature of terminally polar mesogens and their mixtures. An isomeric mixture of two compounds of structure (I) also gives an interesting case of an injected S_C phase, and enhanced S_C properties are recorded for other mixtures of homologues of (I).

Mixtures involving alkyl/alkoxy analogues of (I) also provide examples of S_C phase injection or enhancement, and in one case some evidence for injected S_I behaviour.

Keywords: mixtures of terminally non-polar mesogens, reentrant nematics, injected S_A *phases, injected* S_C *phases, lateral fluoro-substitution*

[†] Presented at the 11th International Liquid Crystal Conference, Berkeley, California, June 30–July 4, 1986.

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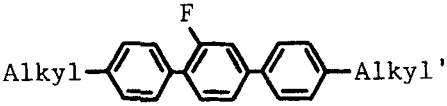
INTRODUCTION

Mixtures of terminally polar mesogens, e.g., 4-alkyl- or -alkoxy-4'-cyanobiphenyls (K/M or CB series) or *trans*-1-alkyl-4-(4'-cyanophenyl)cyclohexanes (PCH series) with esters or other terminally non-polar materials are of particular interest because of their improved multiplexing capability in electro-optical displays. A severe problem is however the occurrence of injected smectic phases in such mixtures. A range of examples of such binary mixtures is now described and the results provide information about the dependence of the strength of the smectic injection upon the structures of terminally polar components and esters of commercial interest.

Until reports by Demus *et al.*[1,2] of binary systems of terminally non-polar compounds exhibiting reentrant nematic behaviour, this phenomenon was thought to be a special feature of compounds with terminal polar groups[3] and their mixtures.[1,4,5,6] The occurrence of reentrant nematic phases in binary mixtures (including one simple homologous mixture) of terminally non-polar 4,4″-dialkyl-2'-fluoro-*p*-terphenyls of the general structure



was then reported by us at Berkeley in 1986, and the results for these and some terminal alkoxy analogues, together with interesting examples of S_C phase injection, are presented in this paper. Subsequently, Pelzl *et al.*[7] have reported further cases of reentrant nematic behaviour in a range of mixtures in which the two components are terminally non-polar, and structurally quite distinct.

RESULTS AND DISCUSSION

1. Binary mixtures of a terminally polar mesogen with a terminally non-polar mesogen

The classes of terminally polar mesogens (all cyano-compounds) and terminally non-polar mesogens (all esters) used in the studies are listed below.

Many binary mixtures of individual members from each of the two classes of mesogens, covering a range of different terminal alkyl groups

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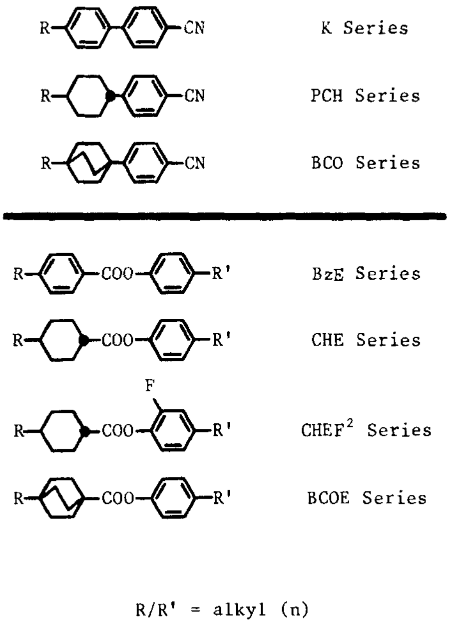

(R, R'), were examined. Figures 1 and 2 provide representative examples of the binary diagrams of state for one member of the K series with three of the esters. All these injected smectic phases appear to be S_{A_1}. In these and other similar diagrams of state throughout this paper, it is emphasized that most transitions for the mixtures gave two-phase regions, sometimes extending over as much as 3°, but to avoid unnecessary complications in the diagrams, these have not been shown. The points plotted relate to the mid-points of any two-phase regions.

Figure 1 shows the very rapid fall away in the S_{A_d}–N transition temperature of the biphenyl component (K27) as the amount of ester is increased, the occurrence of the narrow nematic window, and then the massive injection of the smectic phase (S_{A_1}) whose presence causes a slight rise in the $T_{N\text{-}I}$ values above that of the ester (5CHE5).

Similar features occur in Figure 2, but with the fluoro-substituted ester (5CHE5F^2), the S_A injection is small and occurs only at low temperatures. The injection of S_A phase with 5BCOE5 is much more marked and causes an elevation in $T_{N\text{-}I}$ over that of the pure ester.

As a basis for comparison of the extent of smectic phase injection with a given terminally polar mesogen and a particular terminally non-polar mesogen we may consider either:

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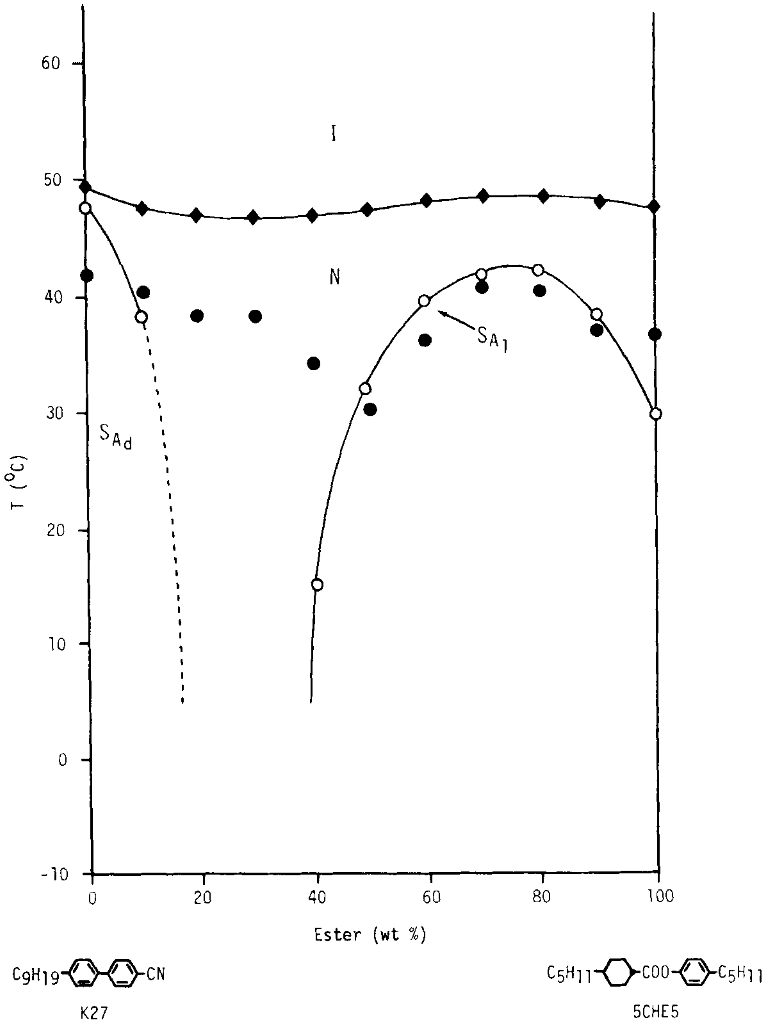

FIGURE 1 Phase diagram for the binary system K27/5CHE5. In this and other binary phase diagrams, two-phase regions are not shown. For simplicity, points denote midpoints of any two-phase regions. ● = C–S_A or N.

1. the difference between T_{N-I} and T_{S_A-N} at a fixed mol % of ester;
2. the ratio of T_{N-I} to T_{S_A-N} (in °K) at a fixed mol % of ester.

With reference to Figures 1 and 2 and similar data for the binary system K27 and 5BzE5, the following results are obtained:

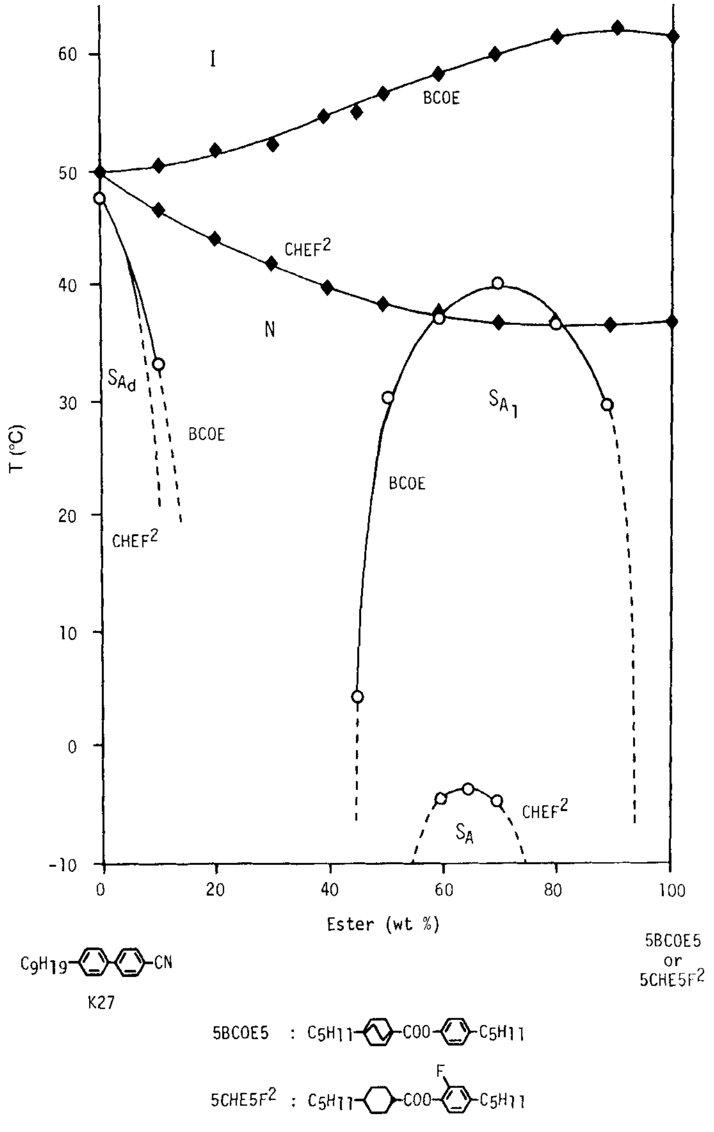

FIGURE 2 Phase diagrams for the binary systems K27/5BCOE5 and K27/5CHE5F^2.

70 mol % of Ester in K27

		5BzE5	*5CHE5*	*5BCOE5*	*5CHE5F^2*
(1)	$T_{N-I}-T_{S_A-N}$	6.3	6.5	19.8	41.4°
(2)	T_{N-I}/T_{S_A-N}	1.021	1.021	1.063	1.154

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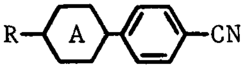
Either basis, (1) or (2), gives the same order of decreasing smectic phase injection for the common terminally polar component (K27) as the ester is varied

ORDER: 5BzE5 $\geq$ 5CHE5 > 5BCOE5 >> 5CHE5F[2]

Using PCH9 or BCO9 with the same esters as those used above gives this same order. This is also the case for individual members of the K, PCH, and BCO series of terminally polar mesogens with *n*-alkyl chains, other than C_9H_{19}, in binary mixtures with esters having C_5H_{11} chains at each end. The order of ester type is also preserved when esters with constant end chains other than C_5H_{11} are used in admixture with specific members chosen from the K, PCH or BCO series.

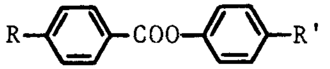
It is noted however, as shown in Figure 3, that when PCH9 is mixed with 5BCOE5, there is a relatively weak overall smectic injection, but two injected phases, S_A and S_B are involved. Even although the maximum T_{S_A-N} is well separated from T_{N-I}, a rise in the T_{N-I} line above the maximum in the injected smectic curve still occurs.

In summary, with



(K, PCH or BCO series)

we observe the *strongest* smectic injection with



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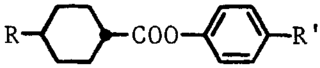
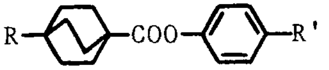
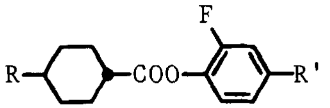


less with



and markedly *least* with



The suppression of smectic properties in pure mesogens[8,9,10] resulting from lateral fluoro-substitution appears to apply at least to some extent in these systems to injected smectic properties.

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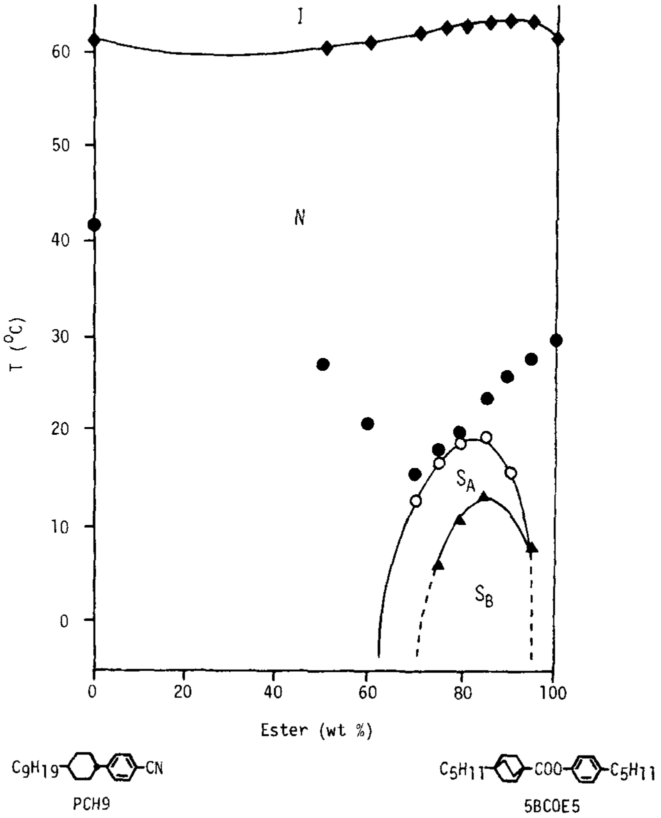

FIGURE 3 Partial phase diagram for the binary system PCH9/5BCOE5. ● = *C–N*.

The extent of smectic phase injection is in fact relatively *insensitive* to the length of the terminal alkyl chain (R) in the terminally polar component. For example:

K component ($R = C_7H_{15}$) + 5CHE5 (70 mol %)
$T_{N-I}/T_{S_A-N} = 1.017$
and $T_{N-I}-T_{S_A-N} = 5.3°$

K component ($R = C_9H_{19}$) + 5CHE5 (70 mol %)
$T_{N-I}/T_{S_A-N} = 1.021$
and $T_{N-I}-T_{S_A-N} = 6.5°$

The extent of smectic phase injection is however very *sensitive* to the alkyl chain length in the terminally non-polar ester component. This is made clear in Figure 4 where results are shown for K21 (R = C_7H_{15}) mixed separately with $CHEF^2$ esters with combinations of terminal alkyl groups *R* and *R'* varying in total carbon content from just 14 to 10. As can be seen, the variation in smectic injection is large, bearing in mind that for $5CHE5F^2$, *no* smectic injection was observed at any composition down to −20°C.

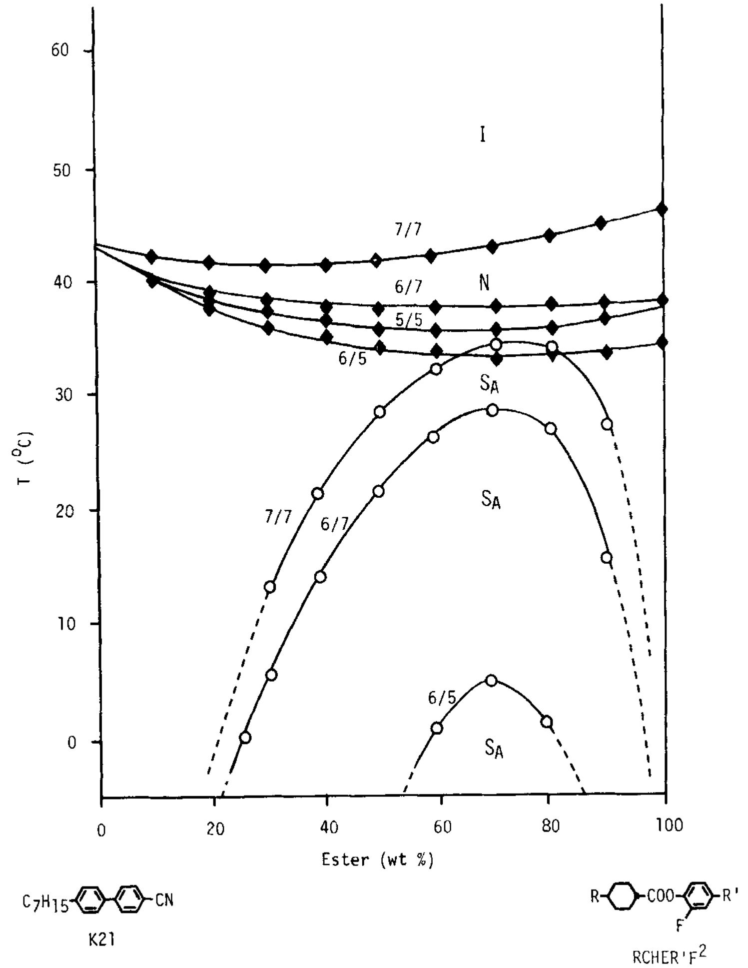

FIGURE 4 Phase diagrams for the binary systems K21/RCHER'F^2, where *R*/*R'* = 7/7, 6/7, 5/5, or 6/5. Note, no transitions involving S_A phases were observed down to −20°C for $5CHE5F^2$.

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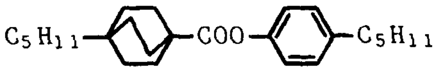
Based on the ratio T_{N-I}/T_{S_A-N}, the order of decreasing smectic injection that can be deduced from Figure 4 is:

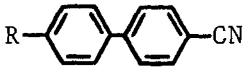
70 mol %	$7CHE7F^2$	≥	$6CHE7F^2$	>	$6CHE5F^2$	>>	$5CHE5F^2$
T_{N-I}/T_{S_A-N}	1.028		1.034		1.104		>1.219

Two additional carbons on each chain virtually negate the smectic-suppressing effect of the lateral fluoro-substituent in $5CHE5F^2$, implying that the suppression of injected smectic phases by a lateral fluoro-substituent in one component may not be so strong.

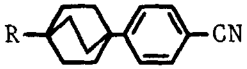
It is interesting to look now at varying the terminally polar component, whilst maintaining the terminally non-polar ester component constant at



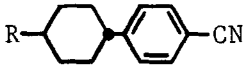
The terminally polar components used (R = C_9H_{19}) were:



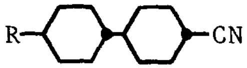
K



BCO



PCH



CCH

Results at two different mol % of ester are presented, and, based upon the ratio T_{N-I}/T_{S_A-N}, give the orders of decreasing smectic injection shown below.

70 mol % of 5BCOE5

	K	>>	BCO	≥	PCH	>	CCH
T_{N-I}/T_{S_A-N}	1.063		1.185		1.187		1.216

80 mol % of 5BCOE5

	K	>>	PCH	>	BCO	=	CCH
T_{N-I}/T_{S_A-N}	1.084		1.149		1.206		1.206

The most serious injection obviously occurs with the cyanobiphenyls (K series), but a defined order for the other terminally polar mesogens does not emerge from the data. The differences in order are a consequence of shifts (see below) in the positions of the maxima (with respect to the composition axis) from system to system.

Terminally polar mesogen	K	PCH	BCO	CCH
Mol % 5BCOE5 at maximum	70	83	73	80

Further binary mixtures with one or more than one laterally fluorinated component. We have already noted from the results for the binary system K21/5CHE5F[2], that the injected smectic phase is suppressed relative to that for mixtures of K21 with esters having no lateral fluoro-substituent. To examine whether this is a more general effect upon which we can rely, two further systems have been studied. These involve as the terminally non-polar component a 4,4″-di-*n*-alkyl-*p*-terphenyl[10] carrying a lateral fluoro-substituent in the 2′-position. In the pure mesogens of this family, this fluoro-substituent strongly suppresses smectic properties. For 2′-fluoro-4-*n*-pentyl-4″-*n*-propyl-*p*-terphenyl,[10] no smectic phases have been observed—see

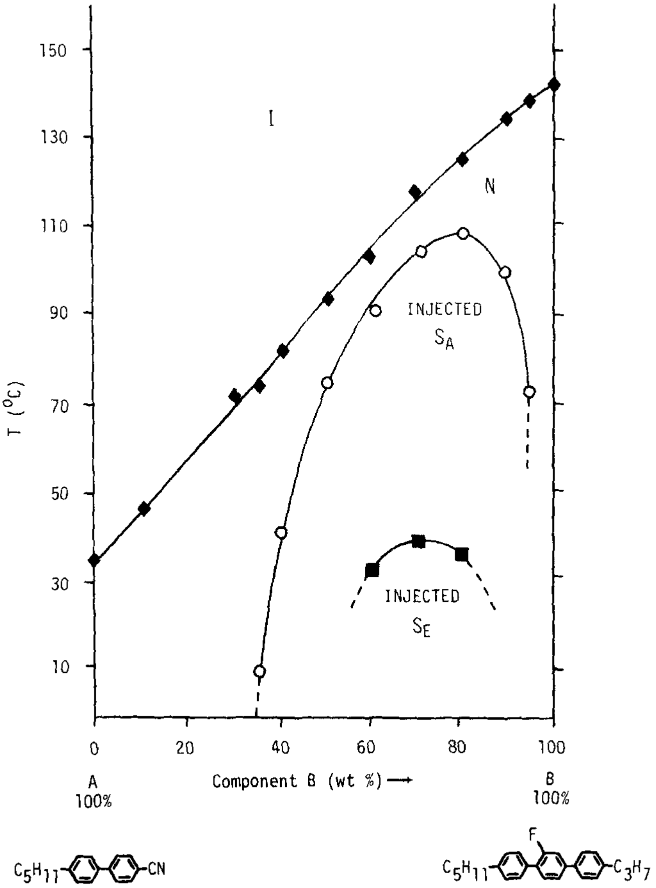


FIGURE 5 Phase diagram for the binary system of components A and B shown.

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Figure 5. However, as can be seen from Figure 5, although both components are nematogens, there is a very strong injection of S_A phase, such that at 80 wt % of B, $T_{N-I} - T_{S_A-N}$ is only 16° and $T_{N-I}/T_{S_A-N} = 1.04$. The failure of the laterally fluorinated terminally non-polar component to prevent injected smectic properties in the mixtures is further emphasized by the additional occurrence of a highly ordered injected S_E phase with a maximum $T_{S_E-S_A}$ transition at around 40°C.

The terminally polar component of the binary mixture was then made even less favourable to smectic behaviour by using 4-cyano-2-fluoro-4′-*n*-pentylbiphenyl.[9] The terminally non-polar component was kept the same as that for Figure 5. The diagram of state is shown in Figure 6. Although injected smectic A behaviour is less in this binary

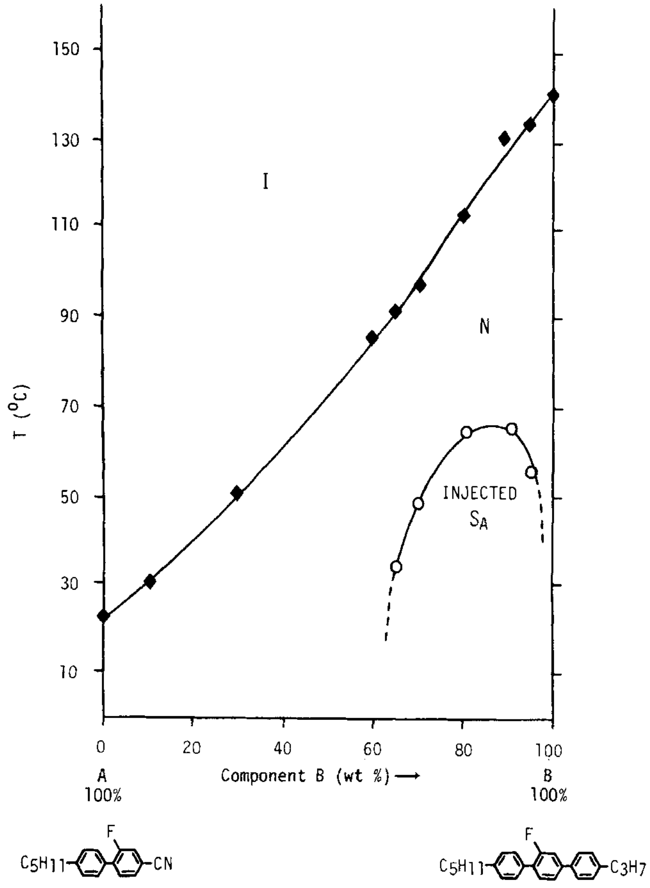

FIGURE 6 Phase diagram for the binary system of components A and B shown.

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system, it is still pronounced. At 80 wt % of B, $T_{N-I}-T_{S_A-N}$ is 50°C and $T_{N-I}/T_{S_A-N} = 1.15$. The injected S_E phase no longer occurs. However, even though both components are laterally fluorinated nematogens, the injected smectic phenomenon is still well in evidence, making it clear that lateral fluoro-substituents cannot be relied upon to play a dominant role in suppressing injected smectic phases in mixtures. Clearly, the effect varies from system to system.

Systems with no nematic window. Finally in this section of the paper, it is interesting to consider Figure 7, which gives the phase diagram of state for a longer chain member of the K series ($C_{10}H_{21}$). The stronger smectic characteristics (S_{A_d}) of the terminally polar component give rise to a continuum of S_A–N transitions from 10 to >90 wt % of the ester (7CHE7F^2) (S_{A_1}),i.e., no nematic window occurs.

There is therefore no evidence for any break or two phase region between the S_{A_d} and S_{A_1} phases. X-ray measurements[11] of layer spacings again reveal no discontinuity as we pass from the S_{A_d} to the S_{A_1} phase; the progression is gradual, though non-linear. Moreover,

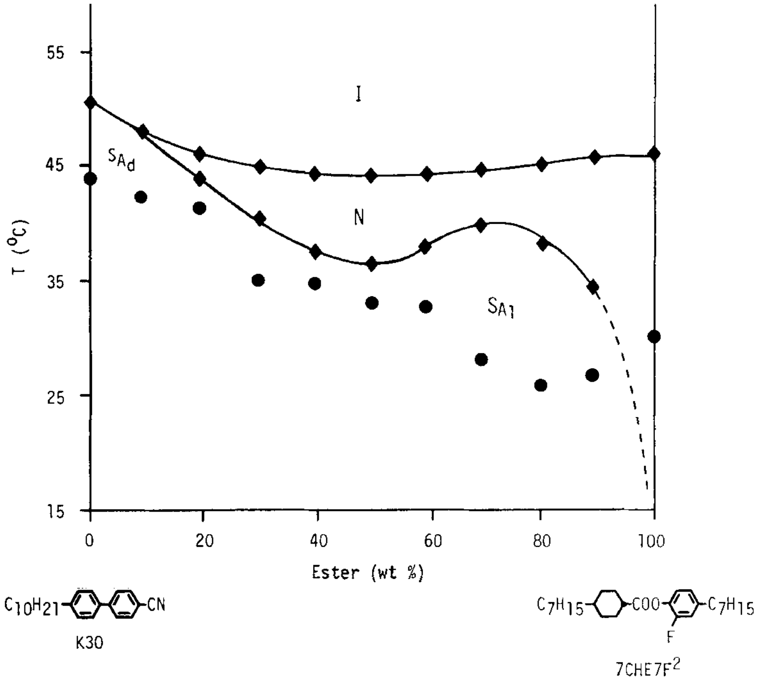

FIGURE 7 Phase diagram for the binary system K30/7CHE7F^2. ● = C–S_{A_d} or S_{A_1} or N.

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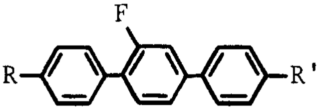
monitoring[12] of n_o, n_e, $\Delta\varepsilon$, $\varepsilon_\parallel$ and $\varepsilon_\perp$ for the smectic phases and of ΔH for the S_A–N transitions showed no irregularities with increasing concentration of ester from 10 to 90 wt %. There is therefore a continuum of smectic phase across the diagram of state, and the change from S_{A_d} to S_{A_1} phase appears to be a gradual one.

2. *Binary mixtures of terminally non-polar components*

Interesting observations relating to reentrant nematic behaviour and injected tilted smectic phases (S_C and S_I) are now described for binary mixtures of 4,4″-disubstituted 2′-fluoro-*p*-terphenyls[10] (I) in which the terminal substituents are such that the molecules are of a terminally non-polar nature.



(I)

R and/or R' = alkyl and/or alkoxy

The extent of the suppression of smectic properties brought about by the lateral fluoro-substituent in the pure mesogens (I) is shown by the following results for microscopically observed phases:

(I) *R*/*R*′ = 5/3†
C 50°C N 140.6°C I

(I) *R*/*R*′ = 5/3 (no lateral F substituent)
C 180°C S_E 200°C S_B 214°C S_A 218°C I

The unfluorinated analogue of (I) 5/3 is therefore strongly smectic, and exhibits no nematic phase at all.

From initial results for the homologous series of compounds (I), with *R* = *n*-alkyl and *R*′ kept constant at C_3H_7, we obtained the plot of transition temperatures against chain length of *R* shown in Figure 8.

As can be seen from Figure 8, the absence of an S_A phase for (I) 7/3 seems surprising. To throw light on this, some miscibility studies were undertaken from which we also hoped to obtain extrapolated

---

†Throughout the rest of this paper this notation will be used for the compounds (I): *R* = *n*-pentyl and *R*′ = *n*-propyl is (I) 5/3. (I) 50/3 is *R* = *n*-pentyloxy, *R*′ = *n*-propyl. (I) 10/3 is *R* = *n*-decyl, *R*′ = *n*-propyl

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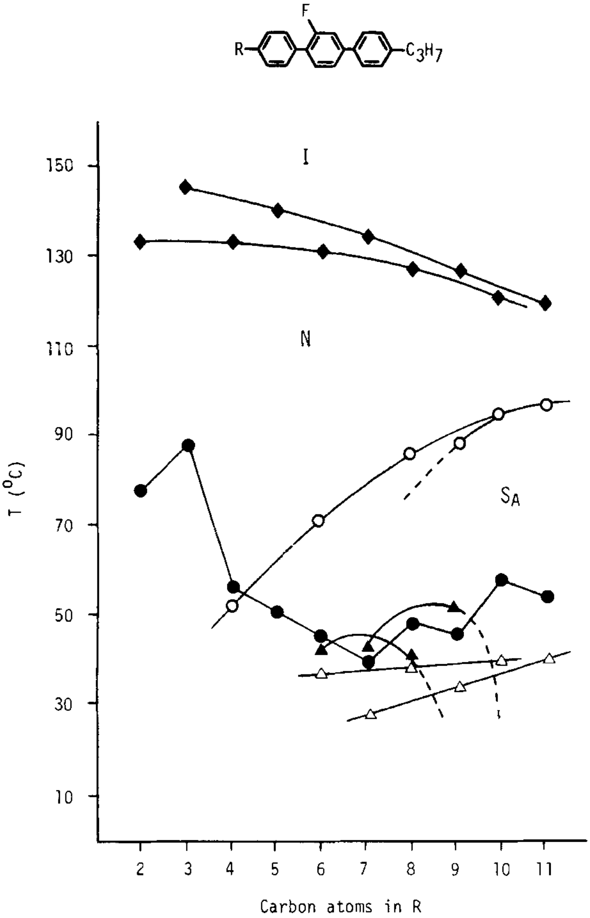

FIGURE 8 Original form of the plot of transition temperatures against number of carbon atoms in the *n*-alkyl group *R* for the terphenyl system shown. ▲ = S_C–S_A or *N*; △ = S_B–S_A or S_C; ● = crystal-mesophase.

transition temperatures for lower temperature smectic phases in each of (I) 5/3, and (I) 4/3 and confirmation of the seemingly parabolic nature of the S_C transition lines. Other features of Figure 8 seemed quite normal, e.g., the regularly alternating T_{N-I} values.

Figure 9 represents the binary diagram of state for mixtures of (I) 9/3 with (I) 7/3. As can be seen, the complete loss of all S_A properties at >60 wt % of (I) 7/3 follows the occurrence of injected N properties in the range 50–60 wt % of (I) 7/3. In this concentration range, the sequence of phases on cooling is

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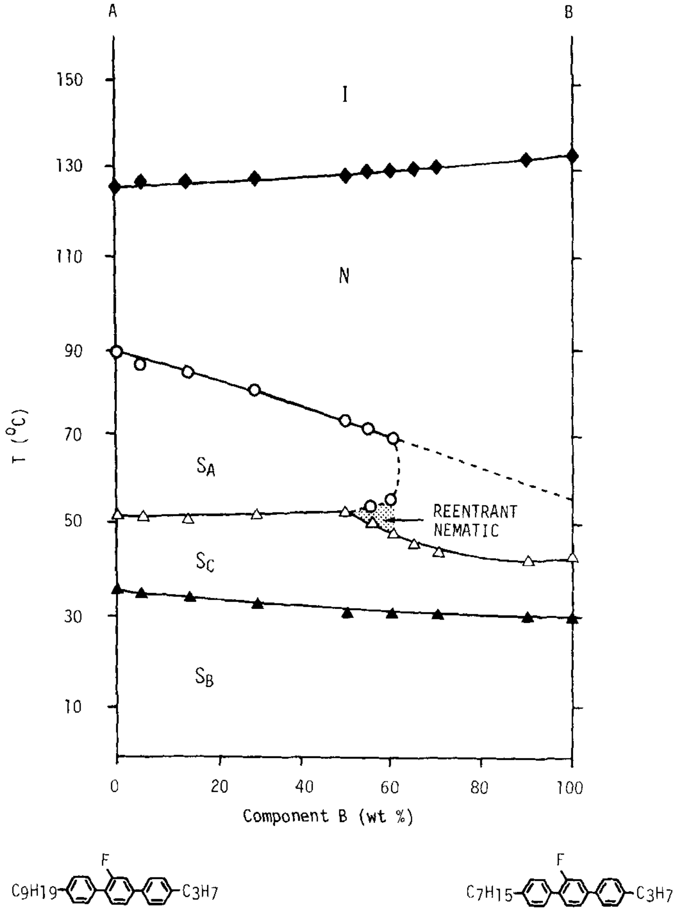

FIGURE 9 Phase diagram for the binary system of components A and B shown. The dashed line is an extrapolation to a hypothetical T_{S_A-N} for component B.

$$\mathrm{I} \longrightarrow \mathrm{N} \longrightarrow S_A \longrightarrow N_{re} \longrightarrow S_C \longrightarrow S_B$$

Note that the increasing temperatures of transitions to the S_C phase fall to some extent after the point at which N_{re} phases occur.

This therefore provides a further example of reentrant nematic behaviour in a binary system of two terminally non-polar mesogens, an example which is particularly striking because of the structural similarity between the two components, i.e., they are homologues differing only by two carbon atoms in the nature of R in structure (I).

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Returning to Figure 8, the failure of (I) 7/3 to exhibit S_A properties is now seen to be connected with the occurrence of the N_{re} phase in the mixtures. If we choose to ignore the reentrant behaviour and simply extrapolate the transition line formed by the T_{S_A-N} points for compositions up to 60 wt % of (I) 7/3 to 100 wt % of (I) 7/3, we obtain a hypothetical T_{S_A-N} for (I) 7/3. This temperature of 56°C does not relate to any real transition, nor should it be considered as a virtual value. It is the T_{S_A-N} value which (I) 7/3 might have been expected to have based on the behaviour of (I) 9/3, without taking into account the evidence provided by Figure 9 that shortening *R* from C_9H_{19} to C_7H_{15} simply and dramatically extinguishes the S_A properties and results in the cooling sequence

$$\mathrm{I} \longrightarrow \mathrm{N} \longrightarrow S_C \longrightarrow S_B$$

which persists for higher concentrations of (I) 7/3 in (I) 9/3.

Similar binary diagrams of state have been obtained for mixtures of (I) 7/3 with (I) 6/3, and (I) 10/3 with (I) 5/3 and 4/3; all show reentrant nematic properties.

In the case of mixtures of (I) 9/3 or 10/3 with (I) 5/3, the same behaviour occurs, but the reentrant nematic phases occur at much lower concentrations of the compound exhibiting no S_A phase, i.e., (I) 5/3. This range is from 10–20 wt % of (I) 5/3, and at >20 wt % the mixtures are purely nematic from their T_{N-I} in the range 130–140°C until they crystallise. Extrapolation of the line through the few T_{S_A-N} points across to 100 wt % of (I) 5/3 is rather long and steep in these cases, but indicates a hypothetical T_{S_A-N} for (I) 5/3 of <20°C. To obtain a better estimate of this hypothetical value, further binary diagrams of state were constructed, including that shown in Figure 10 for (I) 6/3 and (I) 5/3.

In this case, we could not obtain definite visual microscopic evidence for an N_{re} phase. In the appropriate region of the diagram [30 wt % of (I) 5/3], the thermal range of the S_A phase is quite short, restricting the temperature and composition ranges over which reentrant properties might be expected to occur. However, the same cutoff in S_A properties occurs, and extrapolation of the more gently sloping line through the T_{S_A-N} points gives a hypothetical T_{S_A-N} for pure (I) 5/3 of 16°C.

The enhanced S_C properties of the mixtures in Figure 10 up to about 30 wt % of (I) 5/3 is noted. After this, the T_{S_C-N} temperatures fall gradually, and extrapolation gives a hypothetical $T_{S_C-S_A}$ for (I) 5/3 of 13°C.

It is noted that extrapolation of the line through the $T_{S_B-S_C}$ points

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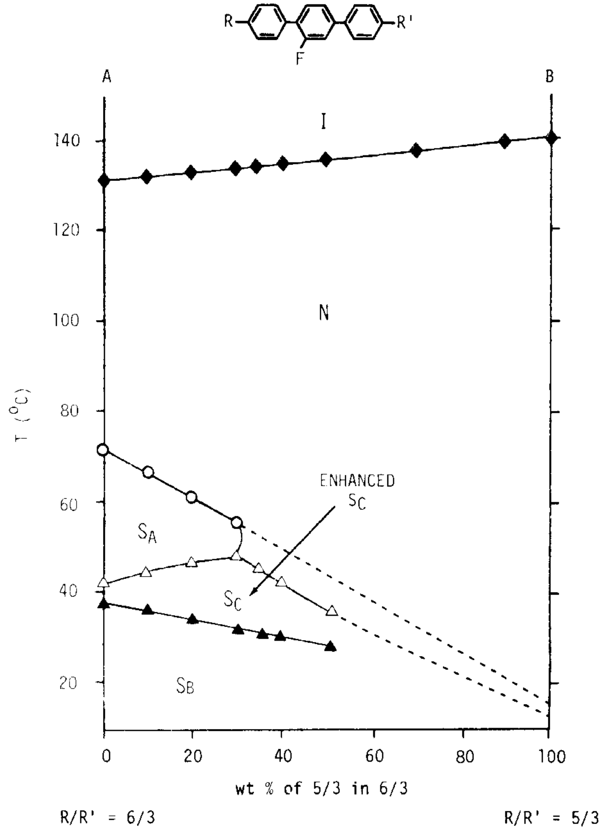

FIGURE 10 Phase diagram for the binary system of components A and B shown. The dashed lines are extrapolations to hypothetical $T_{S_C\text{-}S_A}$ and $T_{S_A\text{-}N}$ for component (I) 5/3.

in Figure 10 gives a virtual $T_{S_B\text{-}N}$ value of 20°C for pure (I) 5/3. Reference to Figure 8 shows that this is not an unreasonable value in relation to the monotropic transitions involving the S_B phases of (I) 7/3, 9/3 and 11/3. The transitions at 16°C and 13°C referred to above for (I) 5/3 relate to temperatures which cannot be achieved without prior crystallisation. Indeed, even if crystallisation could be prevented, the S_B phase would form at 20°C. They are again therefore regarded as hypothetical transitions, as they relate to S_A and S_C phases respectively which could only occur if a more ordered phase (S_B) did not intervene.

Finally, miscibility experiments produced a hypothetical $T_{S_C\text{-}S_A}$ of 25°C for (I) 4/3.

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It was then of interest to see whether these hypothetical values, i.e.,

T_{S_A-N}: 56°C for (I) 7/3
16°C for (I) 5/3
$T_{S_C-S_A}$: 13°C for (I) 5/3
$T_{S_C-S_A}$: 25°C for (I) 4/3

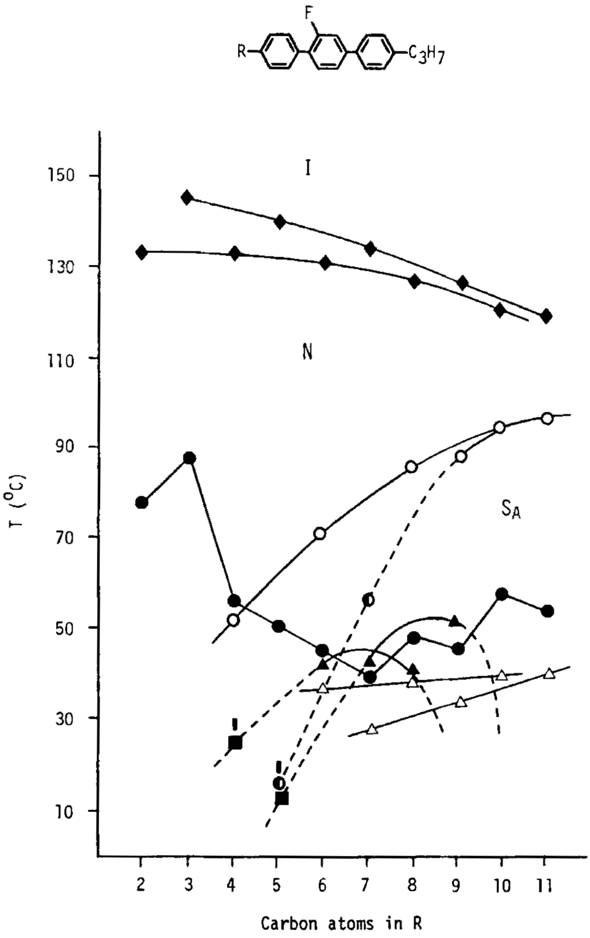

FIGURE 11 Final form of the plot of transition temperatures against number of carbon atoms in the *n*-alkyl group *R* for the terphenyl system shown. The diagram includes the points for four hypothetical transitions (see text) denoted ◐ or ■; ▮ = temperature of recrystallisation; other symbols are the same as those in Figure 8.

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would fit in the plot of transition temperatures against chain length in R given in Figure 8. The plot including these points is given in Figure 11, where connections to these points are shown in dashed lines. As can be seen, the fits are good giving

(a) a steeply rising T_{S_A-N} curve which includes the real T_{S_A-N} for (I) 9/3 and merges with the T_{S_A-N} line for members of the series with even R values;

(b) confirmation of two parabolic curves on which the $T_{S_C-S_A}$ values for the even and odd R members lie.

Although these values are hypothetical and in the case of T_{S_A-N} for (I) 7/3 can be shown not to occur in real terms, they do fit the plots well and suggest that if features of molecular structure and packing (which we do not understand) had not prevented phase formation or caused formation of an alternative phase, the transitions would have occurred.

A binary mixture of isomers of structure (I). The subtlety of the dependence of injected smectic properties on structure is shown particularly clearly by the binary diagram of state for components which are simply homologous isomers, i.e., for (I) 5/3 and (I) 3/5.

The phase sequences for the pure components observed by optical microscopy on cooling are:

(I) 3/5	I, N, S_A, S_B, crystallisation
(I) 5/3	I, N, crystallisation

As Figure 12 shows, there is once more a sudden cut-off in S_A properties, in this case, at concentrations of (I) 5/3 above 75 wt %. No reentrant nematic behaviour could in fact be observed microscopically, but again it is difficult to be certain that the phase is not present. Extrapolation of the curve through the T_{S_A-N} transition points confirms the hypothetical S_A–N transition for (I) 5/3 at 16°C (Figure 11). The salient feature of Figure 12 is however the injected S_C phase in a system consisting of two isomeric materials, neither of which possesses S_C properties. The injection is quite pronounced over a concentration range of about 25 wt % and suggests that mixtures of these isomers, particularly those consisting of about 70 wt % (I) 5/3 and 30 wt % (I) 3/5, have a markedly enhanced ability to form S_C phases. Extrapolation of the $T_{S_C-S_A}/T_{S_C-N}$ curve again confirms the hypothetical $T_{S_C-S_A}$ value of 13°C (Figure 11) for (I) 5/3.

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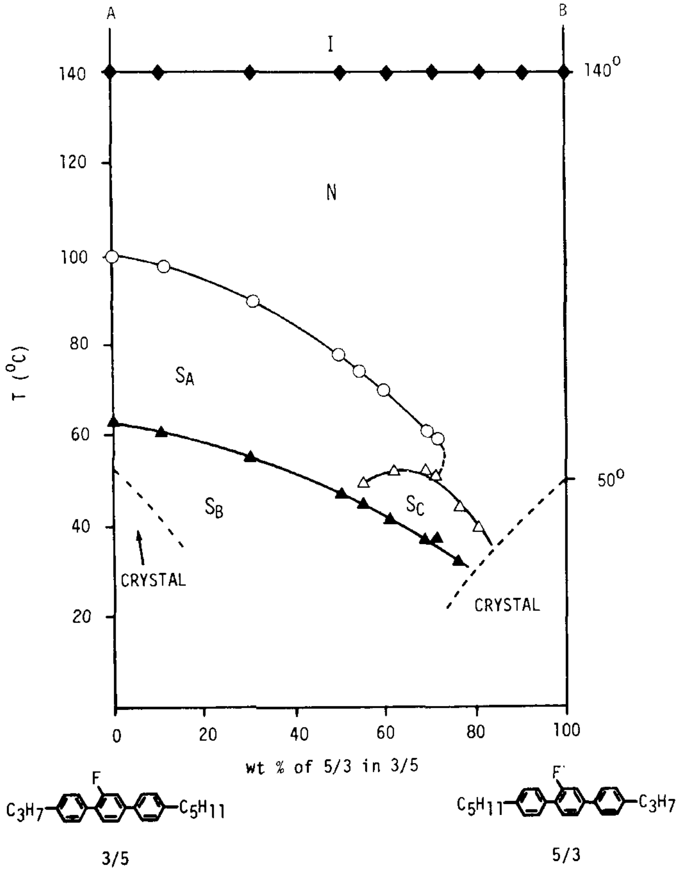

FIGURE 12 Phase diagram for the binary system of components A and B shown.

Further instances of injected S_C behaviour are provided by binary mixtures of (I) 10/3 and (I) 5/02, and (I) 10/3 and (I) 5/3. The diagram of state in the latter case is shown in Figure 13 as both these binary systems combine the features of reentrant nematic and injected S_C behaviour. Component (I) 10/3 with an S_B phase is obviously not a S_C system. The steep fall away in the T_{S_A-N} curve and the shortness of the $T_{S_C-S_A}$ curve make extrapolations to 100 wt % of (I) 5/3 uncertain, but confirm that the hypothetical T_{S_A-N} and $T_{S_C-S_A}$ values for pure (I) 5/3 are low.

Terminal alkyl/alkoxy systems. [(I), *R* or *R'* = alkoxy] Appropriate homologues of these series[10] exhibit S_C phases. Their

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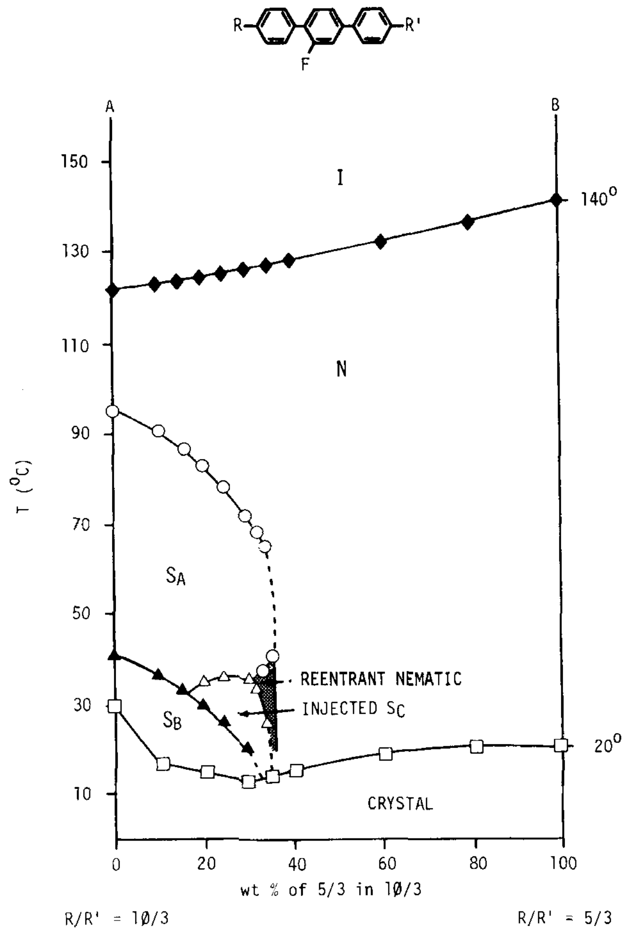

FIGURE 13 Phase diagram for the binary system of components A and B shown. ☐ = recrystallisation (cooling).

mixtures with one another and with terminal dialkyl analogues give further instances of enhanced S_C properties and of injected S_C phases in cases where neither component exhibits a S_C phase.

The S_C phases of the pure alkyl/alkoxy systems were readily observed by optical microscopy, but it was difficult in some cases to confirm their existence by X-ray diffraction. Tilt angles appear to be very low. Many miscibility studies were therefore carried out to confirm the presence of the S_C phase. One example is shown in Figure 14 and this allows attention to be drawn to a particularly interesting feature.

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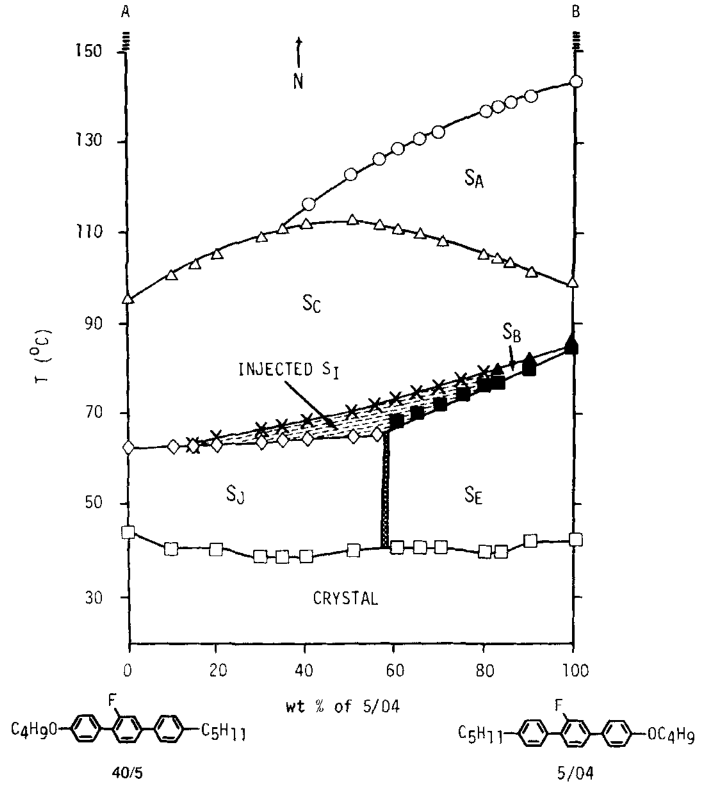

FIGURE 14 Phase diagram for the binary system of components A and B shown. The S_J phase is still to be confirmed by X-ray. □ = recrystallisation (cooling).

Figure 14 is unexceptional in that it confirms the S_C phase of compound (I) 5/04 based on the standard S_C material (I) 40/5 in which the S_C phase had been confirmed by other miscibility experiments. There is therefore a continuum of S_C properties across the diagram of state, and S_C phases are quite markedly enhanced in thermal stability at compositions around 50 wt % of (I) 5/04.

The interesting feature of Figure 14 is however the region of S_I phase between about 15 and 80 wt % of (I) 5/04. This can reasonably be said to be an injection of S_I properties, as both pure components give ordered crystal smectic phases below their S_C phases—S_J in the case of (I) 40/5 and S_B followed by S_E for (I) 5/04. Two-phase regions associated with the transitions bounding this band of S_I phase are fortunately very small, and the microscopic evidence for the S_I phase is quite definite. It is however stressed that the evidence that the

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injected phase is S_I rather than S_F is based entirely upon observation of microscopic textures, not upon X-ray data. A small biphasic region separates the S_I from the S_B phase on the right of the diagram; this is not shown in Figure 14. A narrow biphasic region separates the immiscible S_J and S_E phase. This occurs around 55–60 wt % of (I) 5/04.

Corrected transition temperatures. During the current research, many miscibility experiments have been carried out. As a result, it was found that S_B phases had been overlooked in the case of three fluoro-*p*-terphenyls reported in Table II of reference 10. The correct transition temperatures for these materials are given below:

Compound code	$C–S_B$ or S_A	$S_B–S_A$	$S_A–N$	$N–I$
(I) 2/5	47.0°C	64.0°C	90.0°C	128.7°C
(I) 3/5	55.0	61.0	99.5	141.5
(I) 4/5	68.0	(67.0)	106.8	131.2

EXPERIMENTAL

3. Materials

(a) Pure samples of the terminal cyano-substituted materials (Ks, PCHs, BCOs and CCHs) were obtained either from BDH Limited, Poole or from E. Merck, Darmstadt.

(b) Pure samples of the esters used in the binary mixtures were obtained from BDH Limited, Poole or synthesised by standard procedures from available acids and phenols.

(c) 4-Cyano-2-fluoro-4′-*n*-pentylbiphenyl[9] was an available material.

(d) 4,4″-Disubstituted-2′-fluoro-*p*-terphenyls of structure (I) have already been described[10] and were available. Further samples had to be prepared in some cases, and the synthetic route employed is shown in the following scheme.

By these methods, any combination of R and R' = alkyl or alkoxy can be obtained. Yields were in the range 30–60%.

All the materials of structure (I) employed in the mixture work were of established purity (tlc, glc, ^{1}H nmr, hplc). Infra-red, mass spectral and analytical data were in accordance with the required structures. Transition temperatures for the single component systems (I) have been reported in Reference 10.

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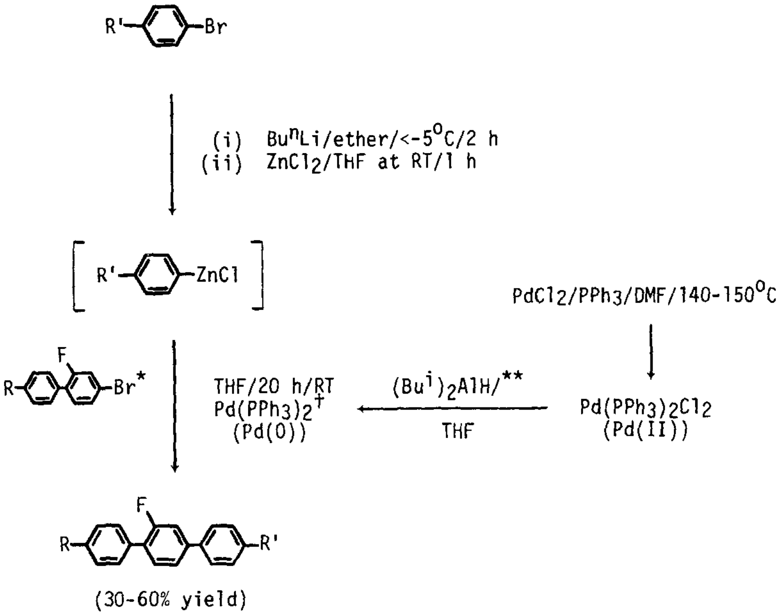
SYNTHETIC SCHEME

4,4"-Disubstituted *p*-terphenyls

(R/R' = Alkyl or Alkoxy)

All reactions under N_2 atmosphere



* From BDH Limited, Poole

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† Prepared *in situ* as shown

4. Mixtures and physical studies

The phase diagrams of the binary systems were obtained by determining the transition temperatures of samples made up at specific concentrations. Transition temperatures were measured by optical microscopy (Olympus BDSP 753 polarising microscope) in conjunction with a Mettler FP52 heated stage and a temperature control unit.

In some cases, calorimetry was used to confirm transition temperatures (Perkin-Elmer DSC-2C with data station).

CONCLUSIONS

Some structural factors influencing the injection of S_A phases in binary mixtures of terminally polar cyano-compounds and terminally non-polar materials have been examined and evidence has been found that lateral fluorination of one or both components of such mixtures cannot be relied upon to give mixtures free from injected S_A phases.

New examples of reentrant nematic phases in binary mixtures of terminally non-polar components are discussed: some of these systems also provide examples of injected or enhanced S_C behaviour. In one case the injection involves the S_I phase.

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