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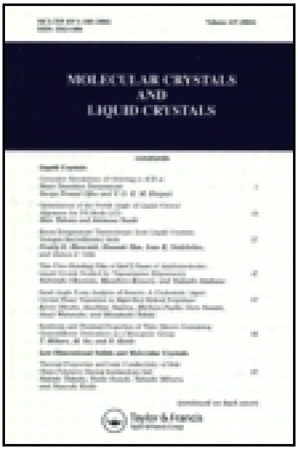

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Influence of Polar End Groups on Induced Smectic Phase Appearance

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Influence of Polar End Groups on Induced Smectic Phase Appearance

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Twenty binary mixtures of a polar and a non-polar α,α'-dimethylbenzalazine were prepared in order to study the influence of the polar end group on smectic phase induction. No EDA-complex formation was detected, and only strongly polar groups like —CN, —NO_2, —NCS, —CF_3, —Cl, —Br, —$COCH_3$, which increase the dipole moment along the molecular axis of the polar component, gave rise to induced smectic phases (always S_A phases).

Voluminous polar end groups and/or those with a weak dipole moment or that increase the component of the molecular dipole moment perpendicular to the molecular axis (*i.e.*, —H, —F, —CH_3, —OCH_3, —NH_2, —OH, —SH, —$COOCH_3$, —$OCOCH_3$, —$OCOC_6H_5$, —$N(CH_3)_2$) make it more difficult for suitable molecular interactions that give rise to smectic phases to occur, and no induced smectic mesophase appears.

Keywords: mixtures, induced smectic phase, polar end groups.

INTRODUCTION

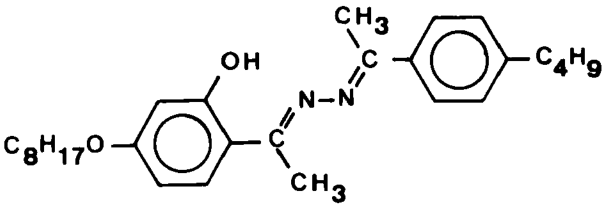
Since Dave *et al.* reported the first example of enhanced stability of a smectic phase that was present in one of the components of a binary mixture,[1] numerous papers have revealed a large number of binary systems with this behavior, even when none of the components exhibits a smectic phase (the term "induced phase" is used in both cases). In order to explain this phenomenon, many models have been proposed, but no definite criteria for the occurrence of this effect have been presented up to now.

Either EDA complex formation[2,3] or dipole interactions[1,4,5] have usually been invoked by way of explanation, depending on the mixture. However, other authors have suggested that the molecular framework may play an important role[6,7] or that there may be a relation between the appearance of this phenomenon and a potential bilayer arrangement in the pure components.[8]

Although induced smectic phases (ISP) mostly occur when one of the components has a strong polar group, such as —NO_2 or —CN, there are also some examples in the literature of mixtures with ISP whose components do not have this kind of group.[9,10]

The aim of this paper is to study in a systematic way the influence of the polar end group on the appearance of ISP and to propose the most suitable type of molecular interactions which explain the results obtained.

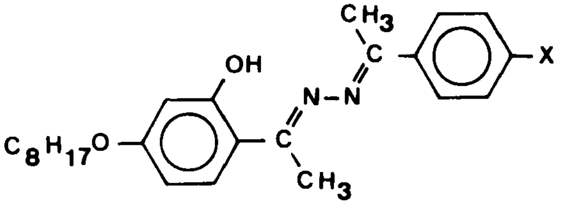
In order to carry out this study, twenty binary mixtures of a terminal-polar and terminal-non polar compound were prepared and characterized.
4′-*n*-butyl-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine was used as terminal-non polar component in all mixtures:



(C₄)

SKETCH 1

Eighteen different 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines



(X)

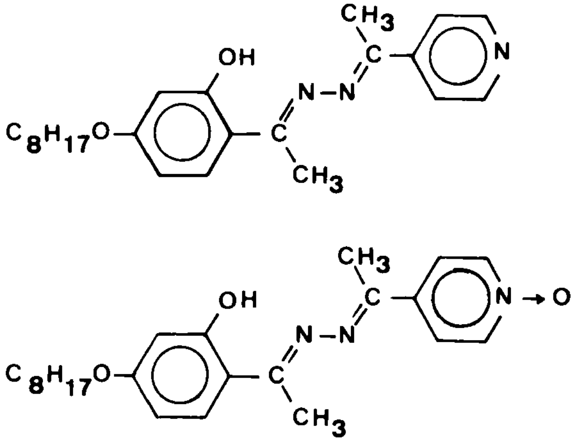
X: H, F, Cl, Br, CN, NO_2, CH_3, OCH_3, $N(CH_3)_2$,

CF_3, NCS, OH, NH_2, SH, $OCOCH_3$, $OCOC_6H_5$,

$COOCH_3$, $COCH_3$

SKETCH 2

and the related α,α′-dimethyl-2-hydroxy-4-*n*-octyloxy-benzylidene-4′-pyridylmethylenehydrazine and its N-oxide were used as terminal polar components.



(Py)

(Py→O)

SKETCH 3

The structural similarity of the components as well as the large number of groups used, enabled us to draw conclusions about the effect of the terminal polar substituents on smectic phase induction.

EXPERIMENTAL

1. Components

All the compounds used in this work were synthesized by us according to methods described previously.[11,12] The phase transition temperatures are listed in Table I.

2. Mixtures

Samples for phase diagrams were prepared by weighing the appropriate amounts of each component and mixing with stirring in the isotropic phase for 1 min. The mixture was then allowed to cool. This operation was repeated twice.

Transition temperatures and enthalpies were measured by Differential Scanning Calorimeter (Perkin-Elmer DSC-2). The heating rate was 10 K/min. The apparatus was calibrated by measuring the known melting point and heat of fusion of indium (429.6 K, 6.8 cal/g).

Phase textures and transition temperatures were studied using a MEIJI Polarizing Microscope equipped with a Mettler FP82 hot stage and FP80 central processor.

RESULTS AND DISCUSSION

For the sake of simplification each mixture is represented by a notation *A*:*B* where:

A: corresponds to the apolar component which remains unchanged and is represented by C_4.

B: corresponds to the polar component represented by X, Py or Py → O.

TABLE I

Phase transition temperatures for the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines (X), the α,α′-dimethyl-2-hydroxy-4-*n*-octyloxybenzylidene-4′-pyridylmethylenehydrazine (Py) and its N-oxide (Py → O) used for preparing the binary mixtures.

Compounds		Transition temperatures (K)
X:	C_4H_9	C 333.6 N 390.3 I
	H	C 358.8 I
	F	C 370.2 N 380.4 I
	Cl	C 380.9 N 408.2 I
	Br	C 382.7 N 408.2 I
	CN	C 373.8 N 433.2 I
	NO_2	C 371.0 N 419.5 I
	CH_3	C 361.6 N 397.3 I
	OCH_3	C 374.2 N 417.1 I
	$N(CH_3)_2$	C 384.0 C′ 406.4 N 417.4 I
	CF_3	C 347.4 C′ 376.6 S_A 394.3 I
	NCS	C 373.3 S_A 374.4 N 440.6 I
	OH	C 405.2 C′ 412.2 I
	NH_2	C 382.6 I 354.2 N[a]
	SH	C 371.8 C′ 380.4 N 400.3 I
	$OCOCH_3$	C 366.5 N 416.6 I
	$OCOC_6H_5$	C 381.3 N 467.0 I
	$COOCH_3$	C 399.8 N 428.6 I
	$COCH_3$	C 376.8 C′ 385.5 N 423.5 I
....		
Py		C 366.1 I
Py → 0		C 408.3 C′ 422.9 I

[a] Monotropic transition. Optical microscopic data.

1. Mixtures that show ISP

Seven of the twenty polar components used gave rise to ISP; these were the compounds with terminal groups —NO_2, —CN, —NCS, —CF_3, —Cl, —Br and —$COCH_3$ (see Figures 1–4).

In all seven mixtures, only a S_A phase was observed, together with a nematic phase. This smectic phase is very thermally stable and is enantiotropic. In this mesophase we could observed the beautiful focal conic or fan-shaped textural characteristics of the S_A phase.

The strongly polar groups —NO_2 and —CN give IS_AP even with small amounts of the polar components (approx. 10%) (see Figure 1).

The inductive effect of the NO_2-component is greater than that of CN, and the system C_4:NO_2 exhibits wider temperature and composition ranges of IS_AP than the mixture C_4:CN (60 K, 90:10–20:80 and 40 K, 90:10–40:60 respectively). Compositions higher than 40% in the CN-component do not give rise to IS_AP.

Interactions between the —CN group and the —C=N— azine bonds probably make formation of a suitable layer arrangement characteristic of a S_A mesophase more difficult.

The three least strongly polar groups: —Cl, Br and —$COCH_3$ show similar behavior. The mixtures with these polar components need higher mole fractions

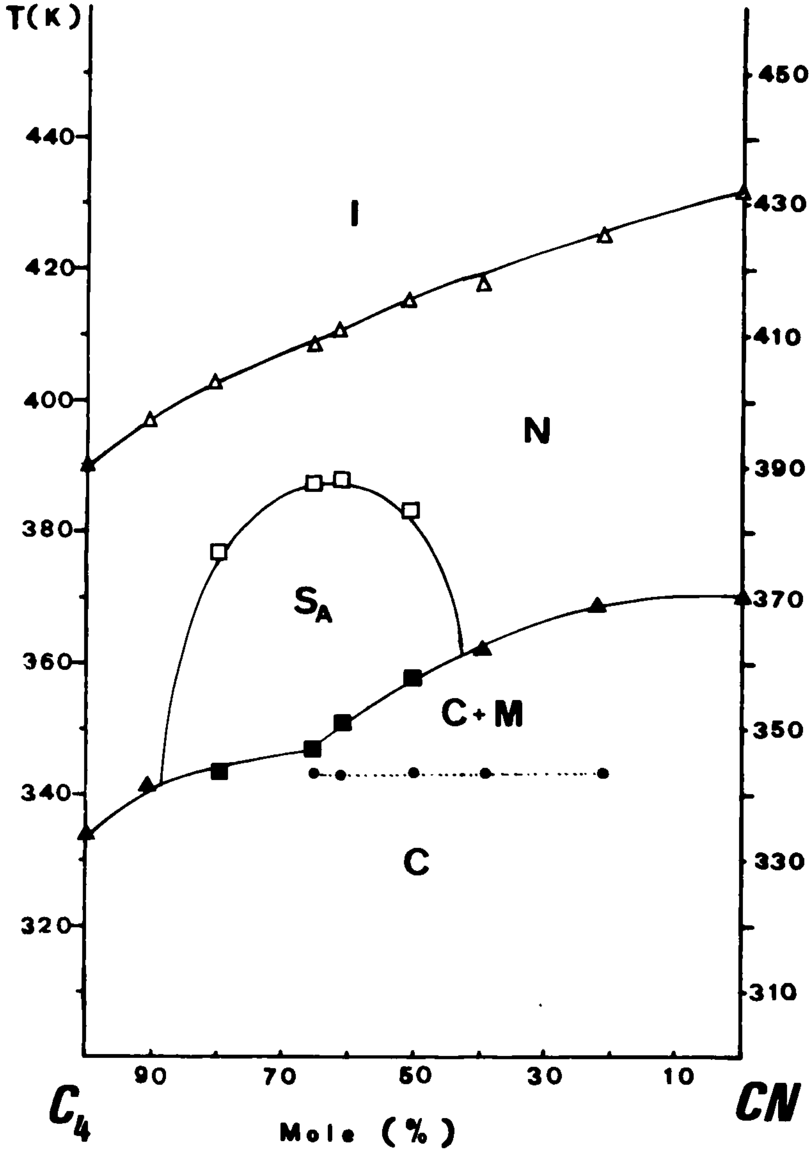


FIGURE 1 Phase diagram of the binary mixture C_4:CN.

of the polar compound to give rise to IS_AP (approx. 25%) (see Figures 2–3). These binary systems show similar maximum temperature ranges of IS_AP (approx. 20 K) and the S_A phase is located in the concentration range from 75% to 20% of the polar component.

The compounds with smectic phases (S_A) (groups —NCS and —CF_3), also give rise to ISP, but only a S_A mesophase appears (see Figure 4).

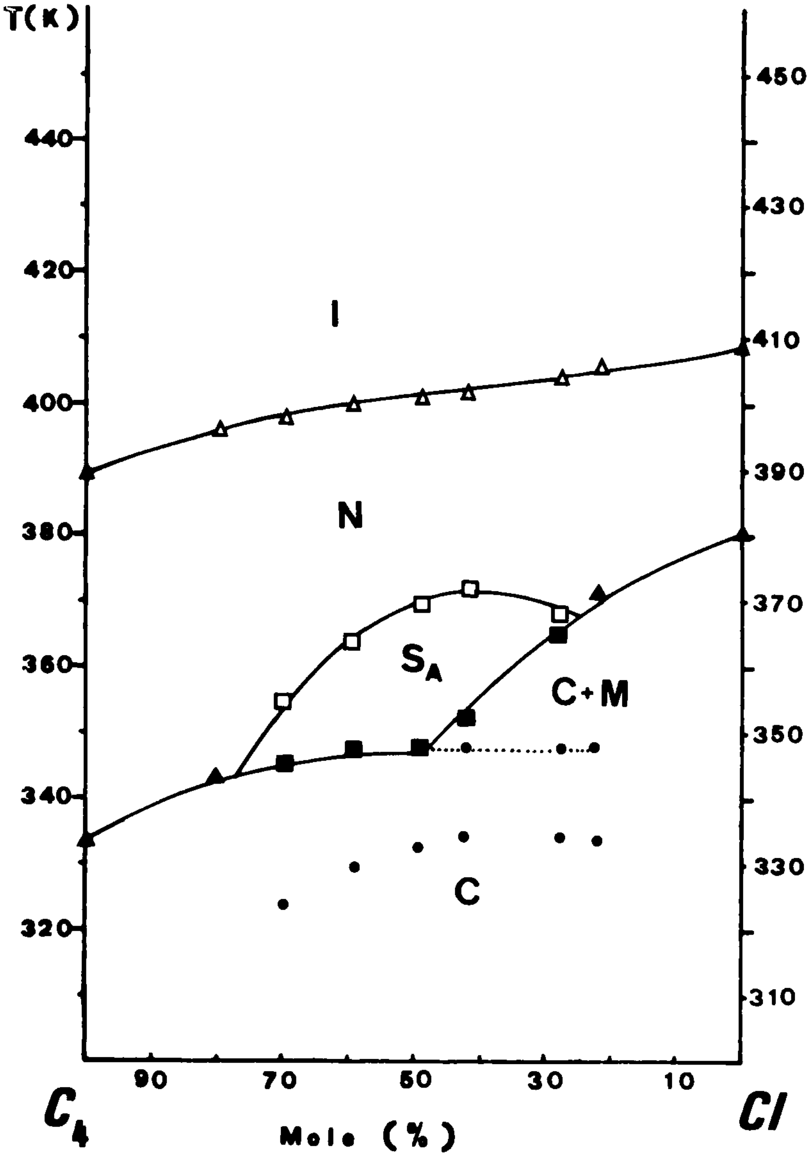


FIGURE 2 Phase diagram of the binary mixture C_4:Cl.

The S_A phase shown by the NCS-component is stabilized in the mixture C_4:NCS. The maximum thermal stability occurs at about the 40:60 composition, with a S_A–N transition temperature approximately 33 K higher than that of the pure component.

The component with the group —CF_3 shows a S_A phase that is stabilized over only about 10 K in the mixture C_4:CF_3. In order to prove the inductive effect of

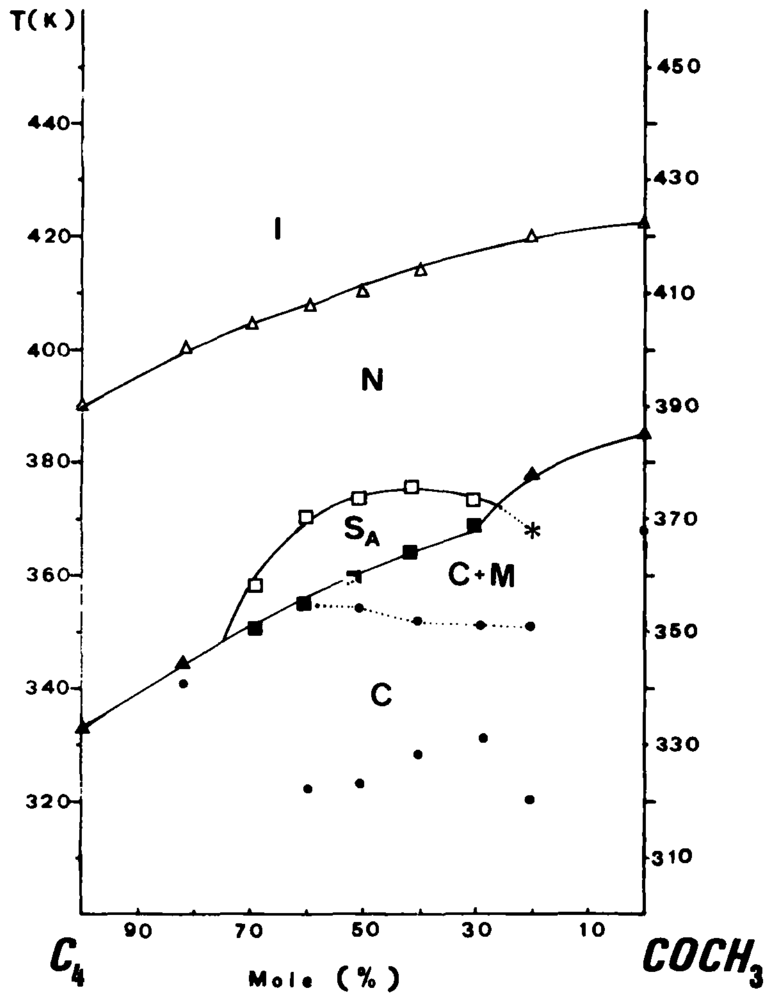


FIGURE 3 Phase diagram of the binary mixture C_4:$COCH_3$.

this group, we synthesized the analogue 4-*n*-butyloxy-2-hydroxy-4′-trifluoromethyl-α,α′-dimethylbenzalazine (represented by CF_3/OC_4). This compound does not form liquid crystals (C 407.2K I), but when it is mixed with the terminal non-polar component C_4, it gave rise to IS_AP (see Figure 5).

As happened with —CN and —NO_2, these strongly polar groups (—NCS and —CF_3) also gave rise to IS_AP with small amounts (approx. 10%) of the polar component.

A comparative study of the diagrams shows that the widest composition ranges of S_A phase correspond to the systems C_4:NCS and C_4:CF_3 (90:10–0:100), followed by the C_4:NO_2 system (90:10–20:80).

The widest temperature range of IS_AP is shown by the mixture C_4:NO_2 (approx. 55 K at 50:50).

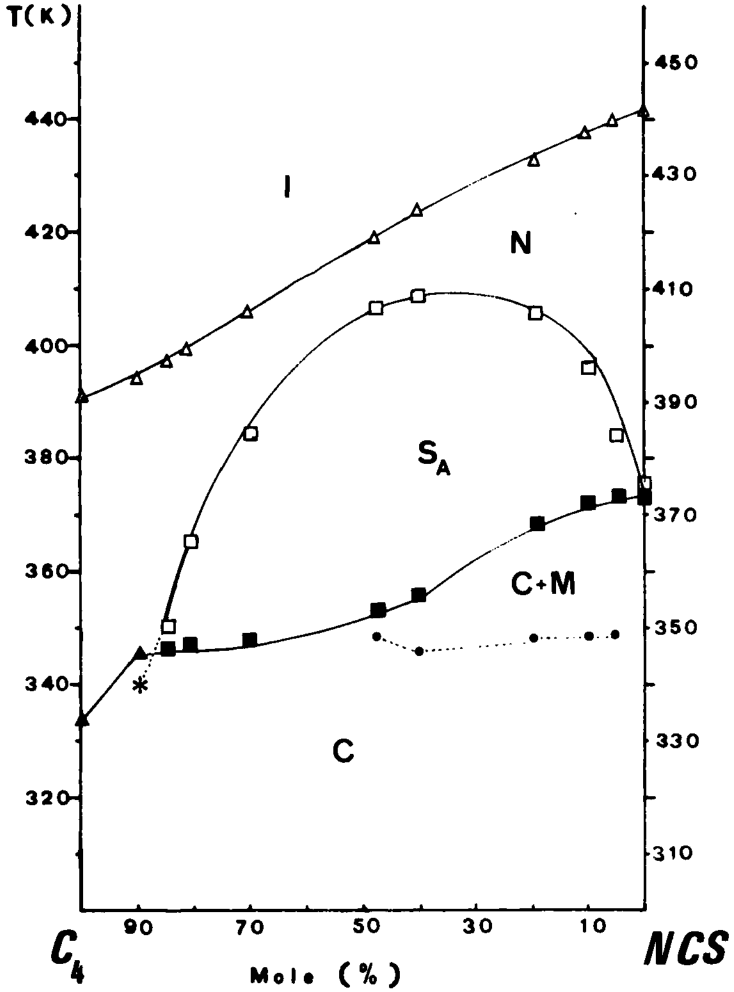


FIGURE 4 Phase diagram of the binary mixture C_4:NCS.

However, the compound with the group —NCS is the one that gives rise to the most stable S_A phase (407 K).

The biggest area of S_A phase is displayed by the system C_4:NCS followed by that for C_4:NO_2.

2. Mixtures that do not show ISP

The compounds with end groups: —F, —CH_3, —OCH_3, —$N(CH_3)_2$, —$OCOCH_3$, —$OCOC_6H_5$, —$COOCH_3$, —SH, —NH_2, —OH, —H and the azines derived from pyridine did not give rise to ISP.

Most of these compounds (X: —F, —CH_3, —OCH_3, —$COOCH_3$, —$OCOCH_3$, —$OCOC_6H_5$, —$N(CH_3)_2$ and —SH) mix well with the other component and give phase diagrams similar to the one shown in Figure 6.

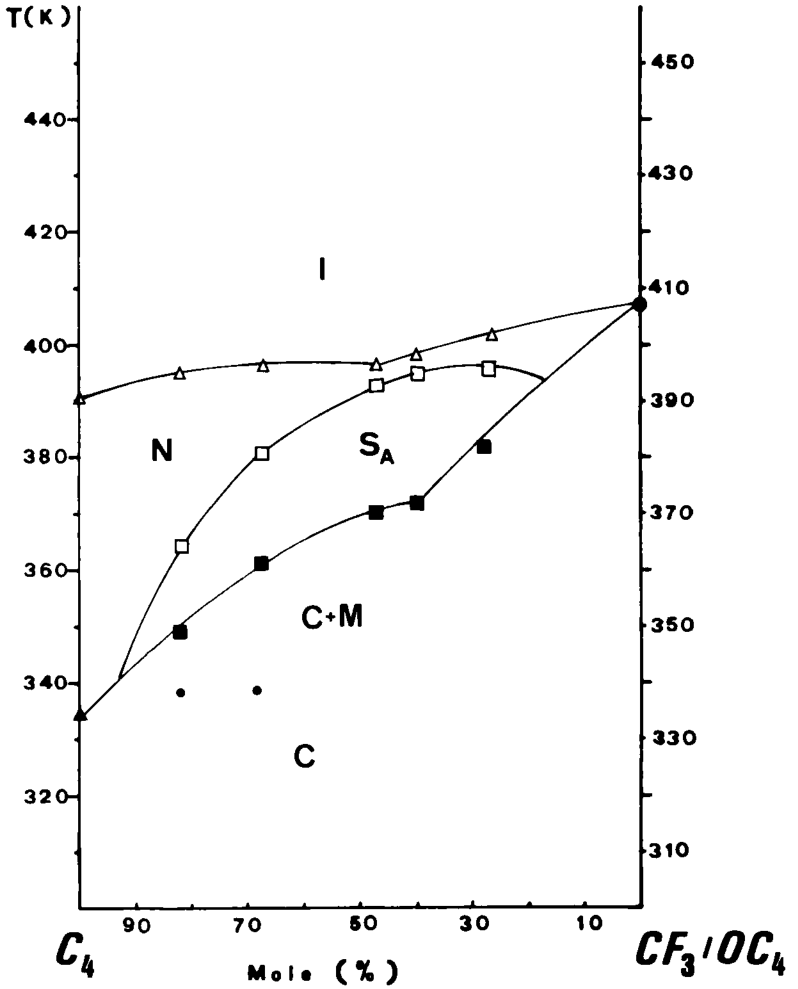


FIGURE 5 Phase diagram of the binary mixture C_4:CF_3/OC_4.

However, for the mixtures C_4:NH_2, C_4:H and C_4:Py, there are some binary proportions, generally with a majority of the polar component, for which the components do not mix. C + N → C + I → I transitions were observed under the microscope for these mixtures. The phase diagrams of these systems are similar to the one in Figure 7, which corresponds to the mixture C_4:NH_2.

Unsatisfactory mixing of the components was observed over the whole composition range for the mixtures of C_4:OH and C_4:Py → 0.

As can be seen with this group of mixtures, when one of the components does not form liquid crystals, the mixture obtained is unsatisfactory.

The effects that hinder mesomorphic behavior of the pure compounds are probably the same as those which cause the components to mix badly.

The different behavior of the systems C_4:OH, C_4:NH_2 and C_4:SH is noteworthy.

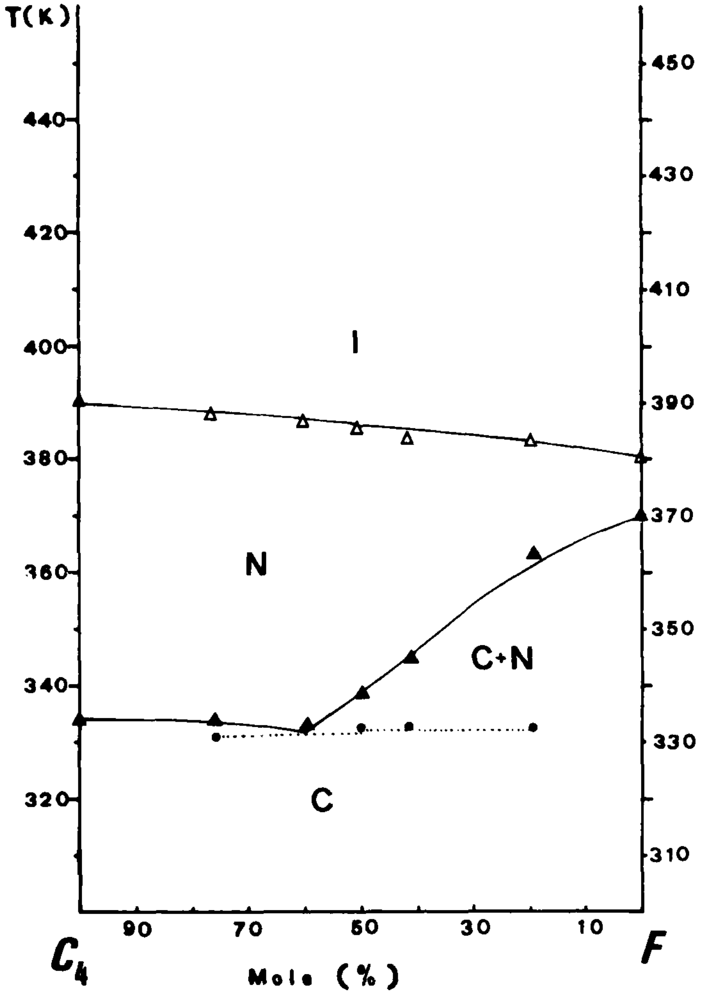


FIGURE 6 Phase diagram of the binary mixture C_4:F.

These polar end groups can form intermolecular hydrogen bonds of very similar structural characteristics. However, the different strengths of these bonds[13]

$$R—OH >> R—NH_2 > R—SH$$

appears to determine whether a good (—SH) or a bad mixture (in some proportions with $—NH_2$ and in all the range with —OH) was obtained.

3. Molecular interactions in these mixtures

Some of the binary systems studied here can be classified as donor-acceptor (D-A) or donor-donor (D-D) systems.

D-A = $C_4:NO_2$, C_4:NCS, C_4:CN, $C_4:CF_3$, $C_4:COCH_3$, $C_4:COOCH_3$

D-D = $C_4:N(CH_3)_2$, $C_4:NH_2$, C_4:SH, $C_4:OCOCH_3$, $C_4:CH_3$, $C_4:OCH_3$, . . .

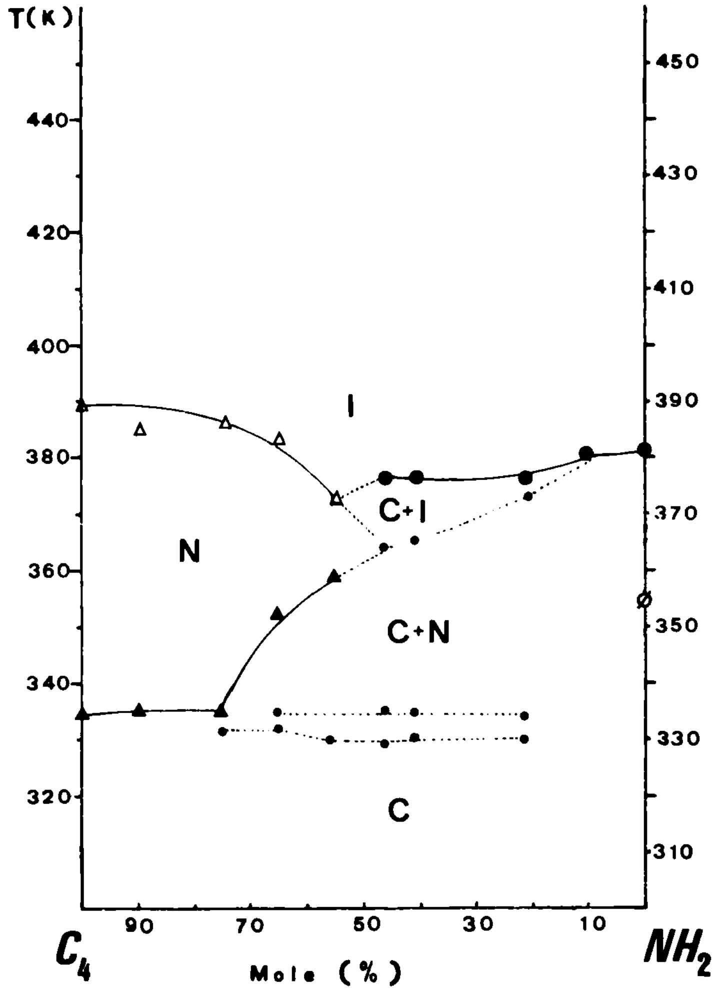


FIGURE 7 Phase diagram of the binary mixture C_4:NH_2.

According to the charge-transfer interaction model of Park *et al.*,[2] the D-D systems should not give ISP, while the D-A systems should.

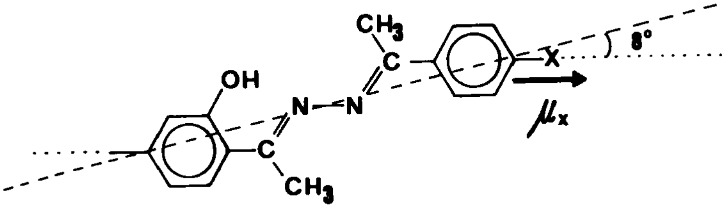
None of our D-D mixtures exhibited ISP. On the other hand, most of the D-A mixtures show IS_AP. Therefore EDA complex formation might be thought to take place. However, no color changes in the mixtures or optical absorption bands in the visible region were detected for these systems.

Likewise, other D-A mixtures (NO_2:$N(CH_3)_2$, CN:$N(CH_3)_2$, CF_3:$N(CH_3)_2$ NCS:$N(CH_3)_2$ and $COCH_3$:$N(CH_3)_2$) studied by the contact method did not show ISP.

These results lead us to conclude that very probably EDA complex formation does not give rise to the IS_AP in these binary mixtures.

However, dipole and steric interactions do seem to account for many of the results obtained. MNDO calculations for both conformations of 2-hydroxy-4-methoxy-α,α′-dimethylbenzalazine were carried out, and there showed that the molecular dipole moment of the molecule is nearly perpendicular to the plane defined by the hydroxylic aromatic ring, with a very small component in the $C_{1'}$–$C_{4'}$ direction.

All the binary mixtures with IS_AP show in their polar components an end group with a strong dipole moment ($\mu > 1.5$ D for benzene-derivatives)[14] in the $C_{Ar} \rightarrow X$ direction: —CN, —NO_2, —NCS, —CF_3, —Cl, —Br and —$COCH_3$).



SKETCH 4

These groups increase the axial component of the molecular dipole moment moving it out of the perpendicular. This greater dipole moment along the axis of the molecule gives rise to important dipole-induced dipole intermolecular interactions which may force the central parts of the molecules to lie side by side, allowing a layer arrangement characteristic of smectic phases.

However, when, due to the strength or direction of the end group dipole moment, the perpendicular component of the molecular dipole moment predominates, and/or the volume of this group makes these interactions more difficult, no ISP appears (*e.g.*, —F, —$COOCH_3$, —$N(CH_3)_2$, —$OCOCH_3$, —$OCOC_6H_5$, etc.)

No X-ray measurements on the systems reported in this paper could be made, so it is not possible to say which kind of S_A arrangement these mixtures show, and whether a S_A polymorph-polar end group relationship exists.

Neither S_A–S_A transition peaks on DSC nor significant texture changes on microscopy were detected in any mixture; however, a study of the ΔS_{S-N}-composition behavior of the mixtures reveals differences.

TABLE II

Transition entropies of the S_A–N transition of the mixtures C_4:NCS and C_4:CN.

Mixture	Mole fraction of C_4	ΔS_{S-N} (J/mol.K)
C_4:NCS	0.800	0.19
	0.703	0.39
	0.485	0.72
	0.389	0.74
	0.191	0.37
	0.098	0.23
C_4:CN	0.795	0.29
	0.650	0.62
	0.612	0.75
	0.502	0.26

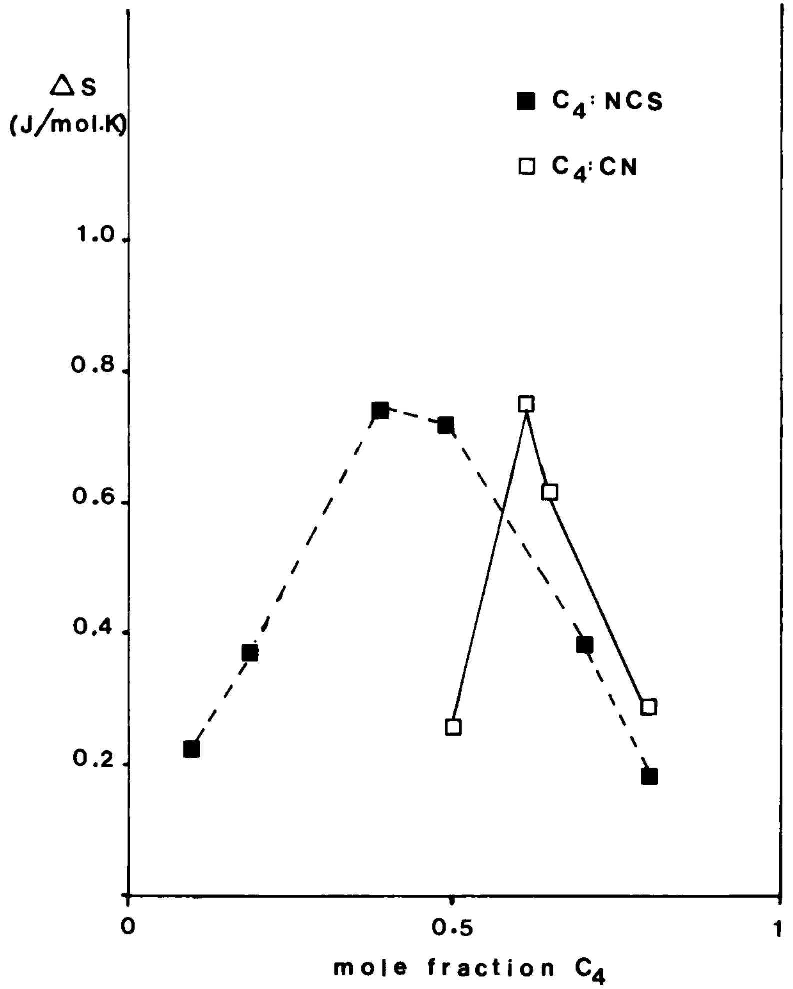


FIGURE 8 Transition entropies for the S_A–N transitions of the mixtures C_4:NCS and C_4:CN.

Thus, while the C_4:NCS system shows a gradual change in the ΔS_{S-N} values with mole fraction, a rapid decrease was observed for C_4:CN and C_4:NO_2 (see Table II and Figure 8). Dunmur *et al.*[15] attributed such a rapid decrease to a change in the nature of the S–N transition when the mixture composition varies.

If this in fact happens, two different S_A polymorphs could exist in the C_4:CN system, while only one kind of S_A should be exhibited by the mixture C_4:NCS.

However, more appropriate measurements must be made in order to confirm this theory for these mixtures.

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