Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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R. Dbrowski[a]; B. Wayska[b]; B. Sosnowska[a]
[a] Military Technical Academy, 01-489, Warsaw, Poland [b] Warsaw Technical University, 02-524, Warsaw, Poland

To cite this Article Dbrowski, R. , Wayska, B. and Sosnowska, B.(1986) 'Creation of a nematic phase in mixtures of smectic A_1 phases', Liquid Crystals, 1: 5, 415 — 428
To link to this Article: DOI: 10.1080/02678298608086266
URL: http://dx.doi.org/10.1080/02678298608086266

LIQUID CRYSTALS, 1986, VOL. 1, NO. 5, 415–428

Creation of a nematic phase in mixtures of smectic A_1 phases

by R. DĄBROWSKI†, B. WAŻYŃSKA‡ and B. SOSNOWSKA†
† Military Technical Academy, 01-489 Warsaw, Poland
‡ Warsaw Technical University, 02-524 Warsaw, Poland

(*Received 20 January 1986; accepted 21 May 1986*)

Phase diagrams were determined for binary mixtures consisting of two 5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane compounds (*n*-DBT) or 4″-isothiocyanatophenyl 4-(trans-4′-*n*-decylcyclohexyl)benzoate and *n*-DBT. All compounds investigated have monolayer smectic A phases. A nematic phase in the upper temperature range and a nematic gap between two smectic regions also were observed, with the smectic layer spacing ratio, d/d', of 1·23 and 1·87 respectively. The variation of the enthalpy of transition with mixture composition in relation to changes of layer spacing ratio are also discussed for these systems.

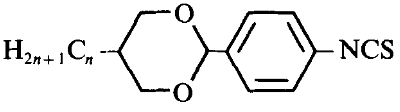
1. Introduction

The phenomenon of creating a new phase in liquid-crystalline mixtures is interesting from both the theoretical and the practical point of view. For instance, the possibility of creating a nematic phase in mixtures composed of smectic A phases is interesting as it finds application in large displays addressed with a laser beam. Nematics can easily be oriented in a relatively weak electric field as distinguished from smectics or isotropic liquids which are much less liable to orientation. Thus for this mentioned purpose smectic materials are required which reveal a nematic phase in a narrow temperature interval directly preceding the clearing temperature thus making it possible to obtain a uniformly oriented liquid-crystalline layer [1].

So far much attention has been devoted to the phenomenon of creating smectic phases in mixtures of nematic compounds; these are called induced smectic phases [2–7]. The opposite phenomenon, i.e. creation of a nematic phase in mixtures of smectics, has been observed in several instances [8–13] but conditions for its appearing have not been recognized. It is only recently that more systematic studies of binary systems consisting of smectic A_1 (monomolecular smectic layers) and A_d (partially bimolecular smectic layers) phases have been undertaken [14–16]. It has been shown [15, 16] that for mixtures consisting of a mesogen with smectic A_1 and nematic phases or only with the smectic A_1 phase and of a mesogen having smectic A_d and nematic phases the temperature range of the nematic phase is enhanced at the cost of the temperature range of the smectic phase when the spacing ratio of smectic layers measured for the pure components increases. When the limiting value of 1·36 to 1·46 of that ratio, depending on the chemical structure of the components, is exceeded, we observe an interruption of the continuity of the smectic regions. The concentration range in which the smectic A_d phase is observed becomes separated by a nematic gap from the concentration range in which the smectic A_1 phase is observed. It has been suggested [15] that such a behaviour may be observed in mixtures consisting of smectic A phases of the same kind. The aim of the present work was to determine the conditions which should be met by the components of a binary mixture consisting of smectic A_1 phases if the nematic phase was to appear in it, and to confirm the possibility of the nematic gap occurring in mixtures of smectic A_1 phases only.

2. Experimental

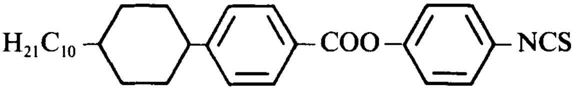
The phase diagrams have been determined for binary mixtures composed of compounds belonging to the 5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (*n*-DBT) homologous series (**1**)



(**1**)

n-DBT

as well as those of binary mixtures composed of compounds (**1**) and the ester (**2**)



(**2**)

10TPCHB

The transition temperatures and enthalpies of the compounds used in the present work are summarized in the table; the molecular lengths and smectic layer spacings are taken from [16] for compounds (**1**) and from [15] for compound (**2**). The procedure for preparing compounds (**1**) has been described in [17] and that for preparing compound (**2**) in [18]. Compounds (**1**) and (**2**) form monolayer smectic A phases. Compounds (**1**) reveal only the smectic phase in the members of the homologous series from $n = 2$ to 12; beginning with the $n = 4$ member the S_{A_1} phase is enantiotropic and lies in the temperature range from 35° to 80°C so they are a convenient object for the experiments conducted in the present work. Compound (**2**) reveals the S_{A_1} phase in a wide temperature range together with a nematic phase in a narrow temperature range. The phase diagrams of all the binary 4DBT–*n*-DBT and 10PCHB–*n*-DBT mixtures were determined by using a polarization microscope with a heated stage (VEB Analytic, Dresden). The phase transitions were observed in the heating and cooling cycles, the stage being heated to a temperature close to a transition temperature at a rate of 0·5°C min^{-1}. Several binary systems: 4DBT–6DBT, 4DBT–12DBT and 4DBT–10TPCHB were investigated using calorimetry with a Perkin–Elmer DSC 2. The measurements were made in a pure argon atmosphere.

The mixtures were prepared from weighed out portions of the pure components which were homogenized before the measurements by heating to a temperature several degrees above the transition to the isotropic phase, mixing and finally cooling. The first measurement was carried out with a heating rate of 10°C min^{-1} for the whole temperature range. The remaining two measurements were performed at a heating rate of 1·25°C min^{-1} starting from a temperature 10 K below the transition temperature.

3. Results

3.1. *Effect of the smectic layer spacing on the phase diagram*

Figure 1 shows the phase diagram of the 4DBT–6DBT two component system and figure 2 that of the 4DBT–12DBT system, determined by the calorimetry. These

Transition temperatures and enthalpies of transition, molecular lengths, *l*, and smectic layer spacings, *d*, for the compounds used to prepare the binary mixtures.

	Transitions temperatures/°C Transition enthalpies/kJ mole^{-1}							Moleculear dimensions	
					n-DBT				
n	C_1		C_2		S_{A_1}		I	*d*/nm	*l*/nm
2				74 23·4		54		1·53	1·74
3				79 20·8		65		1·66	1·90
4				61 18·8		76·5 3·9		1·82	1·98
5				60 18·3		79 4·1		1·96	2·13
6				34·5 22·9		79 4·0		2·11	2·23
7				52 30·6		82·5 3·3		2·20	2·37
8				47 26·3		81·5 4·0		2·36	2·48
9				56·5 38·6		81·5 4·1		2·53	2·62
10		52·5 7·5		61 31·0		79·5 3·8		2·63	2·73
12		31 3·1		70·5 33·6		78 4·1		2·97	2·99

					10TPCHB						
C_1		C_2		C_3		S_{A_1}		N		I	*d*	*l*
	60 0·9		84 17·7		95 28·1		179·5 0·74		201 1·71		3·21	3·39

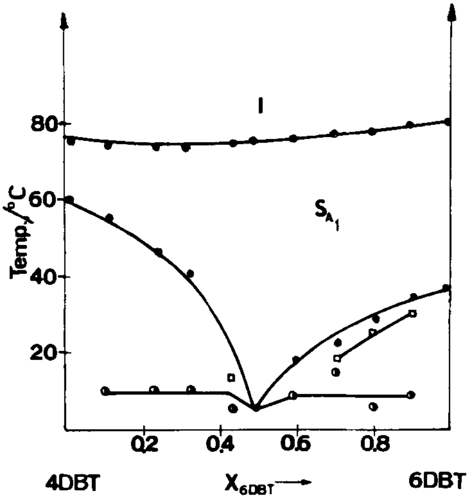


Figure 1. The phase diagram for a binary system composed of near members of the *n*-DBT homologous series.

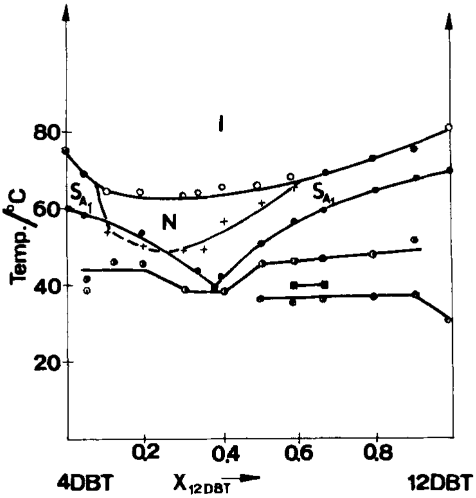


Figure 2. The phase diagram for a binary system composed of far members of the *n*-DBT homologous series. The phase transitions are marked: ●, end melting point; ⊗, smectic–isotropic transition, ○, nematic–isotropic transition; ×, smectic–nematic transition; □, ■, ⊙, transitions in the solid phase.

diagrams are in accord with those determined by the microscopy but reveal more details relating to the solid phase. Both binary mixtures yield simple eutectics like the remaining 4DBT–*n*-DBT combinations. Both branches of the melting curves (liquidus) are in agreement with the CSL (Le Chatelier, Schröder, van Laar) equation [19] for nearly all of the concentration range; the only exception is the region close to the eutectic point. In the two-phase region, solid plus mesophase, (C + S_A), in the concentration range of the 4DBT–6DBT mixture, x_{6DBT}, from 0·7 to 0·9 an additional exothermic phase transition is observed whose presence was not detected for pure 6DBT. In the concentration range of the 4DBT–12DBT mixture of x_{12DBT} from 0·5 to 1·0 a transition takes place in the solid phase which also occurs at a somewhat lower temperature for pure 12DBT. The solid phase, consisting of a mixture of 4DBT and 12DBT of composition close to that of the eutectic, begins to melt at a temperature lower than for the mixtures in the remaining concentration range. This is probably due to the vicinity of the melting point of the eutectic and the polymorphous transition in the solid phase which may favour the generation of the eutectic from a metastable solid in this temperature range.

Distinct differences between the phase diagrams of the 4DBT–6DBT and 4DBT–12DBT systems are observed at the isotropic liquid-mesophase transition. The isotropic transition temperatures for the 4DBT–6DBT mixtures lie in the vicinity of the straight line connecting those of the pure components whereas for the 4DBT–12DBT mixtures they lie significantly below this straight line and a fairly deep minimum is observed in the clearing curves for the mole fraction x_{12DBT} of 0·3. At the same time the nematic phase appears in this mixture for the mole fraction, x_{12DBT}, from 0·1 to 0·6. The stability of the smectic phase decreases more rapidly on the side of 4DBT excess than on the side of the excess of 12DBT in the mixture. Similar behaviour was also observed for the smectic A_1 and smectic A_d mixture for the pair of compounds 4DBT–8OCB [15]. This is probably also related with the fact that the change of density of 4DBT–12DBT mixtures is greater when a small quantity of

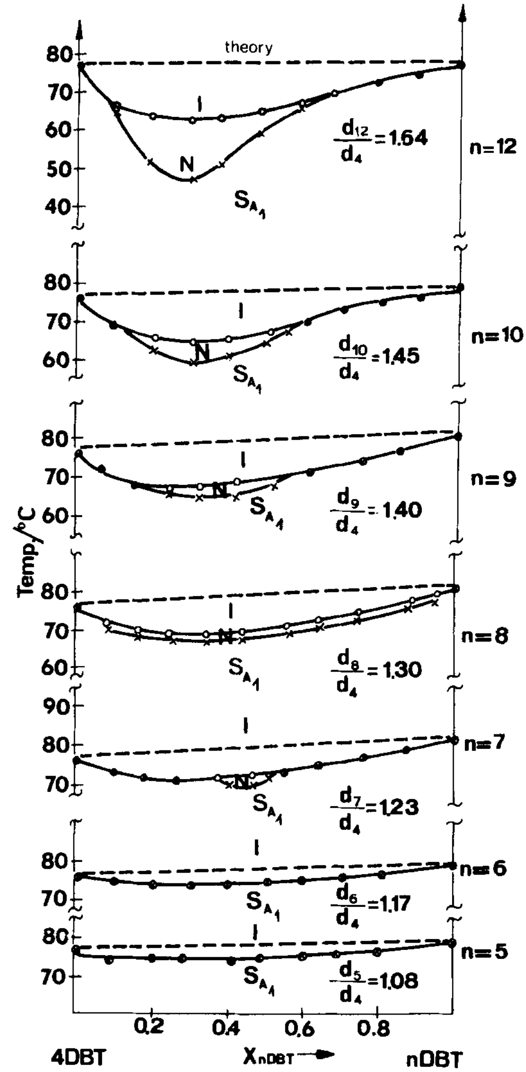


Figure 3. Influence of the smectic layer spacing ratio on the phase transitions in two component mixtures composed of members of the *n*-DBT homologous series, - - - - -, theoretical line for the S_{A_1} → I transitions.

12DBT is added to 4DBT that when a small quantity of 4DBT is added to pure 12DBT.

In figure 3 fragments of the phase diagrams of 4DBT–*n*-DBT binary mixtures relating to the S_A → I or N → I and S_A → N phase transitions are compared which are significant for the phenomenon studied here. From the data shown in figure 3 we see that a strong relationship exists between the stability of the smectic phase in the mixtures and the smectic layer spacing of the compounds making up these mixtures. The S_A → I transition temperatures for the 4DBT–5DBT and the 4DBT–6DBT binary mixtures with a small smectic layer spacing ratio, d_5/d_4, of 1·08 and, d_6/d_4, of 1·17, respectively, are close to the theoretical values, and the observed minima in the clearing curves are very weakly developed. As the spacing for the smectic layers of the second component of the mixture increases, the observed minimum systematically deepens. At the same time, beginning with $n = 7$, the nematic phase appears in the central region of the concentration range. For the 4DBT–7DBT system with d_7/d_4 equal to 1·23 the nematic phase occurs in a narrow range of concentrations and temperatures. As the smectic layer spacing increases, the region of the nematic phase created is enhanced. For the 4DBT–12DBT system, where d_{12}/d_4 equals 1·64, the nematic phase exists in 15°C range. With the increase of the spacing of the smectic layers of the compounds making up the mixture a change is observed in the symmetry of the region of occurrence of the induced nematic phase. For the first pair of compounds in which the nematic phase is observed this phase appears in the central region of the diagram. For the 4DBT–8DBT mixture the nematic phase also appears symmetrically in a very narrow temperature range but for a wide mole fraction range, $x_{8\mathrm{DBT}}$, of 0·1 to 0·9. For the subsequent pairs, the concentration interval in which the nematic phase is observed is smaller but the temperature range in which this phase is observed is much wider and the position of the smectic phase stability minimum is shifted more and more towards high concentrations of 4DBT. From the variation of the smectic phase stability in the mixtures with the increase of the smectic layer spacing ratio of compounds making up the mixture shown in figure 3 we can expect for the pairs of compounds: 3DBT–12DBT and 2DBT–12DBT a further deepening of the smectic phase stability minimum and even the occurrence of a nematic gap. Unfortunately the compounds 2DBT and 3DBT have monotropic smectic phases and their high melting points do not allow us to obtain mixtures which could be supercooled to temperatures at which the smectic–nematic phase transition takes place. This inconvenience has been partially overcome by preparing a 2DBT–4DBT binary mixture with a 1 : 1 molar ratio; this melts at 36°C and the smectic A_I–nematic transition occurs at 59°C. The smectic layer spacing in this mixture has been estimated as 1·66 nm which is an average value between those for 4DBT and 2DBT. By using this mixture as one component and 12DBT as the second component we determined accurately the limits of existence of the nematic phase (cf. figure 4). In this system the smectic phase stability minimum observed at $x_{12\mathrm{DBT}}$ of about 0·25 is very deep, the nematic phase exists in the temperature interval from 16° to 50°C. The estimated smectic layer spacing ratio, $d_{12}/d_{2,4}$, for this system is 1·78. We should expect therefore that for a mixture of two smectic A_I phases with the smectic layer spacing ratio larger than 1·78 a nematic gap will appear separating the smectic A_I regions of the components of this mixture. Indeed the binary mixture consisting of compounds 4DBT and 10TPCHB, where the smectic layer spacing ratio is 1·87, reveals such behaviour (cf. figures 5 (*a*), (*b*)). The phase diagram shown in figure 5 (*a*) is based on microscopic measurements, and that in figure 5 (*b*) on calorimetric studies. Both diagrams are in agreement except for the details regarding the polymorphic transitions in the solid phase which are more distinct in figure 5 (*b*) and for the region of existence of the smectic phase and the two-phase regions which are better seen in figure 5 (*a*). The microscopic method allows for a much more precise determination of the region of existence of the smectic phase than the calorimetry since the enthalpy of the nematic–smectic phase transition decreases in the 4DBT–10TPCHB mixture very rapidly to zero as the distance increases from the compositions with the excess of one component.

The binary system 4DBT–10TPCHB yields a simple eutectic. The 10TPCHB solubility curve changes its slope in the vicinity of 70°C, this is due to the polymorphic transition taking place in this compound. For $x_{10\mathrm{TPCHB}}$ from 0·2 to 0·6 in the mixture we observed only the nematic phase, even if the mixture was supercooled to

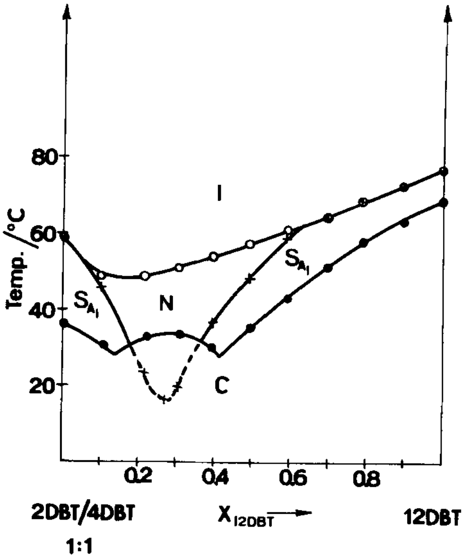


Figure 4. The phase diagram for a tricomponent system composed of the mixture 2DBT : 4DBT with a 1 : 1 molar ratio and 12DBT.

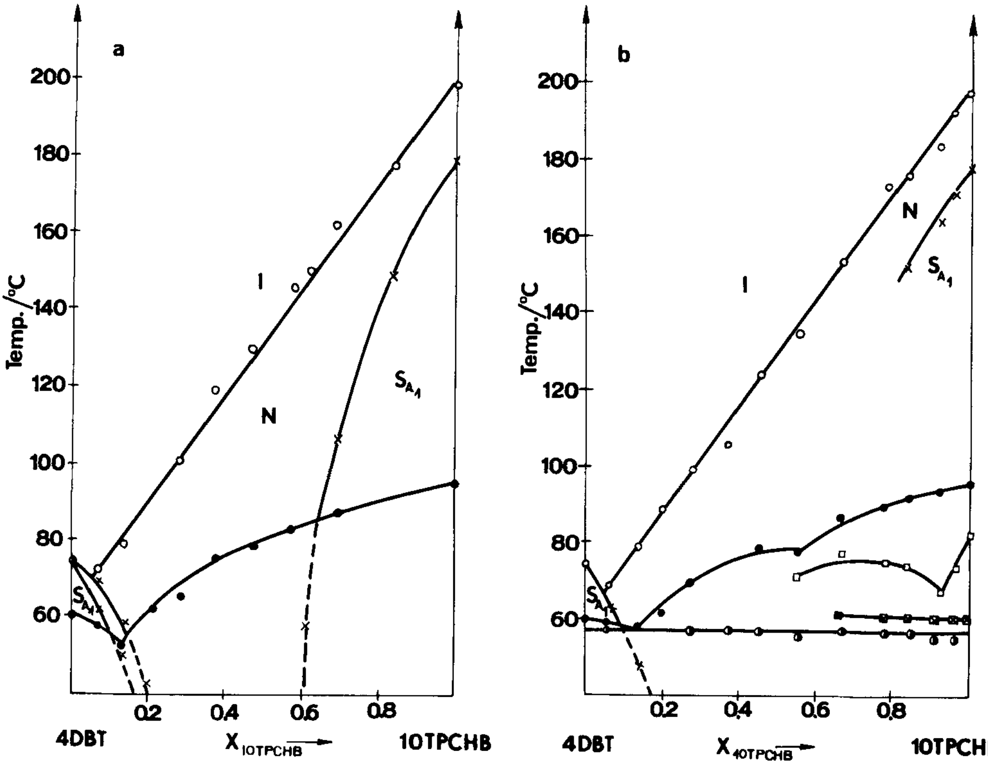


Figure 5. The phase diagram for the binary system composed of 5-*n*-butyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (4DBT) and 4″-isothiocyanatophenyl 4-(trans-4′-*n*-decylcyclohexyl)benzoate (10TPCHB): (*a*) obtained by microscopy; (*b*) obtained by calorimetry. Smectic layer spacing ratio $d_{10TPCHB} : d_{4DBT}$ is 1·87.

temperatures below 20°C. The wide interval of co-existence of the nematic and smectic phases both as regards temperature and concentration is a characteristic feature of the N → S_{A_1} interface in this system. This is particularly pronounced on the side of excess of 4DBT (cf. figure 5(*a*)). Such behaviour was also observed in the 4DBT–8OCB mixture, where 8OCB has a smectic A_d phase, in which a nematic gap separating the smectic A_1 and A_d regions also occurs. Thus the occurrence of large two-phase regions is a common feature of mixtures whose molecules differ significantly in length or reveal smectic layers of different spacing.

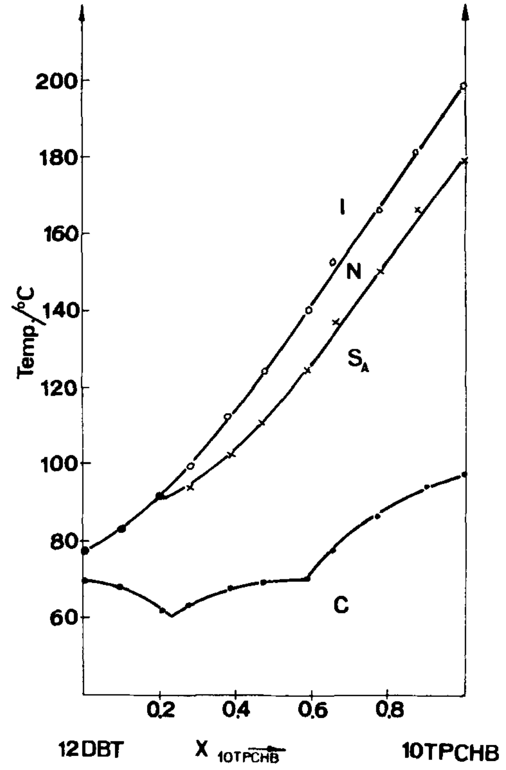


Figure 6. The phase diagram for a binary system composed of 5-*n*-dodecyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (12DBT) and 4″-isothiocyanatophenyl 4-(trans-4′-*n*-decylcyclohexyl)benzoate. Smectic layer spacing ratio $d_{10TPCHB}:d_{12DBT}$ is 1·14.

The molecules of 4DBT and 10TPCHB belong to different homologous series and differ as regards their chemical structure and shape. This is a factor which probably facilitates the observation of the nematic gap, however, for mixtures composed of smectic A_1 phases its significance seems to be minor, as can be concluded from the diagram for the mixture of 12DBT and 10TPCHB (cf. figure 6). This pair of compounds which is an equivalent of the 4DBT–10TPCHB system, but characterized by a smectic layer spacing ratio of 1·14, has clearing points and nematic–smectic transition temperatures approximating those of the ideal system.

3.2. *Effect of the smectic layer spacing ratio on the enthalpies of transition*

The variation of the enthalpy for the S_A → I transition with the composition of the 4DBT–6DBT mixture is shown in figure 7. The transition enthalpy of this mixture

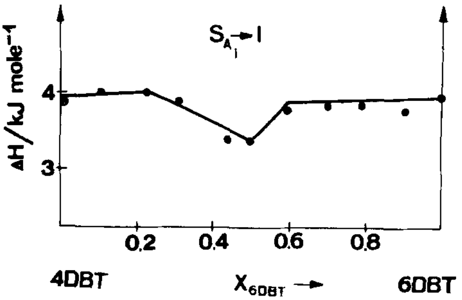


Figure 7. Enthalpies of the $S_{A_1} \rightarrow I$ transitions in two component mixtures composed of near members of the n-DBT homologous series.

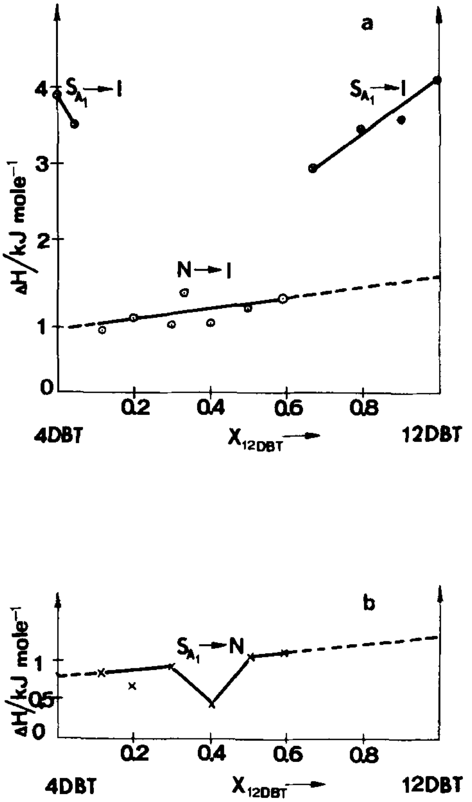


Figure 8. Enthalpies of (*a*) the $S_{A_1} \rightarrow I$, and the $N \rightarrow I$ phase transitions and (*b*) the S_{A_1}–N *transition in two component mixtures composed of far members of the* n-DBT homologous series.

varies additively except for the concentration region with x_{6DBT} from 0·4 to 0·5, where it assumes lower values. This indicates that the energy of the smectic lattice decreases in this region. The deviation from ideal behaviour is manifested in this region more explicitly by the lowering of the transition enthalpy than by the lowering of the transition to the isotropic phase (cf. figure 1). Hence, already in the binary mixture in which we have only the smectic phase more pronounced changes, observed in the diagram of the adjacent 4DBT–7DBT pair (cf. figure 7), can be anticipated from the lowering of the smectic lattice energy in the central part of the composition range. A different picture of the variation of the transition enthalpy is observed for the 4DBT–12DBT pair (cf. figure 8 (*c*)) in which the injected nematic phase exists. The phase transition $S_A \rightarrow I$ appears here in two different regions between which a N → I phase transition occurs. The $S_A \rightarrow I$ transitional enthalpy in both, purely smectic, regions varies with concentration similarly as it decreases with the increase of concentration of the second component of the mixture.

The values of the enthalpy of the N → I transition lie in the entire nematic concentration range, on one straight line; this proves that the character of the interactions does not change in the nematic phase with concentration. The linear dependence of ΔH_{NI} on composition allows us to extrapolate the value of ΔH_{NI} for the composition $x_{4DBT} = 1$ and $x_{12DBT} = 1$ and to estimate the enthalpies of the virtual N → I phase transitions in these two smectics as $0{\cdot}75\,kJ\,mole^{-1}$ and $1{\cdot}5\,kJ\,mole^{-1}$, respectively. These values are close to those estimated by a similar procedure for the 4DBT–8OCB system [15].

The enthalpy of the smectic–nematic phase transition in the 4DBT–12DBT mixture (cf. figure 8 (*b*)) is not linear in the composition but assumes a value half as small for the mole fraction x_{12DBT} of 0·4 as for the remaining compositions for which the S → N transition is observed. The mixture of this composition, which lies in the region of the minimum of the smectic phase stability (cf. figure 2), shows the lowest energy of molecular interaction in the smectic lattice. The value of the S → N transition enthalpy for the 4DBT–10TPCHB mixture, in which the nematic gap is observed, decreases very rapidly and vanishes at low concentrations (cf. figure 9 (*b*)). The S → N phase transition is already second order at mole fractions $x_{10TPCHB}$ of 0·2 or x_{4DBT} of 0·2. Similar regularities have also been observed for the mixture consisting of smectic A_1 and A_d with a nematic gap [16]. The clearing enthalpy of the 4DBT–10TPCHB system, which in the concentration range $x_{10TPCHB}$ from 0·1 to 1·0 is associated with the N → I phase transition, varies linearly with composition except for the region of concentrations close to the pure compounds.

4. Discussion and conclusions

The character of the phase diagrams of binary mixtures consisting of mesogens which are monomolecular smectic A phases depends on the ratio of smectic layer spacings for the pure mesogens. For monomolecular smectics in which the length of the molecule is approximately equal to the smectic layer spacing the ratio may be replaced by the ratio of lengths of the particular molecules. The increase of the difference of smectic layer spacing of the components making up the mixtures manifests itself initially by a minimum at the $S_{A_1} \rightarrow I$ phase transition followed by the appearance of the nematic phase, when the smectic layer spacing ratio is about 1·25, in the central part of the system. The concentration interval and especially the temperature interval in which this nematic phase is observed extends systematically and finally, at the smectic layer spacing ratio between 1·85 and 1·9, the smectic regions become separated by the nematic phase.

The observed smectic layer spacing ratio at which the nematic gap occurs in mixtures composed of *n*-DBT compounds or *n*-DBT and 10CHBT compounds is similar to that observed in smectic mixtures consisting of *n*-DBT and 12OCB [20] with d_{12OCB}/d_{7DBT} equal to 1·83 but greater than that observed in other mixtures of smectic

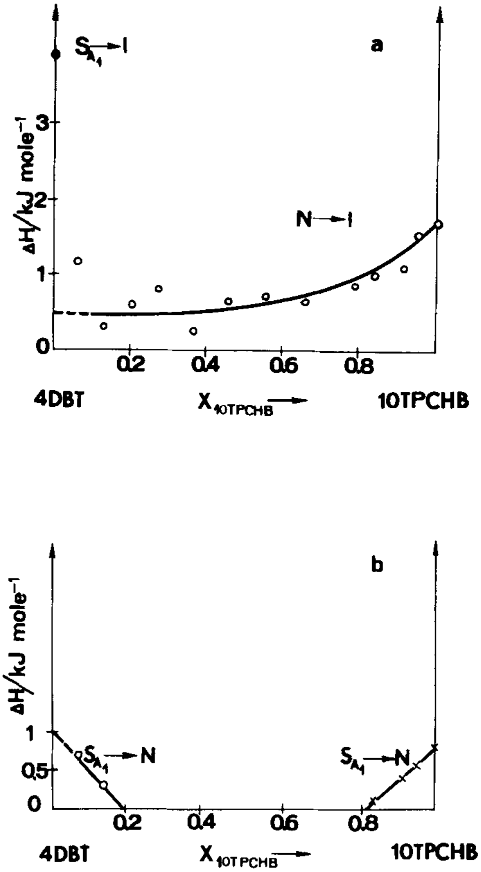


Figure 9. Enthalpies of (*a*) the S_{A_1} → I and the N → I transition and (*b*) the S_{A_1} → N transition of a binary system composed of 5-*n*-butyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane and 4″-isothiocyanatophenyl 4-(trans-4′-*n*-decylcyclohexyl)benzoate.

A_1 and A_d phases [15, 16]. The nematic phase and nematic gap are not created at some definit smectic layer spacing ratio since that ratio varies with the properties of the smectic phases of the components. The results of Ziemnicka *et al.* [14], who determined the properties of binary mixtures of 2-fluorenylmethylidine-4′-*n*-dodecylaniline (FC12A) and 4-*n*-butoxybenzylidene-4′-halogenoanilines (4OX) revealing an almost constant smectic layer spacing ratio, d_{FC12A}/d_{4OX}, of 1·75, also confirm this statement. The stability of the 4OX smectic phase varies in the order: X = Cl < Br < I. The temperature range in which the smectic layer exists in the mixtures of these compounds with FC12A decreases in the same order.

The nematic gap in the *n*-DBT series, which is the result of the impossibility of the smectic layer being formed in mixture of compounds, appears if the length of one molecule is almost double that of the other. This indicates that a system with isothiocyanate terminal group cannot yield smectic layers composed of a one longer and two shorter molecules alternately.

The interaction energy in the smectic layers composed of mixtures of S_{A_1} mesogens varies with the molecular length ratio. This manifests itself initially by the lowering of the enthalpy of the S_{A_1} → I phase transition in the central region of the concentration range. For mixtures in which the nematic phase is created the enthalpy of the $S_{A_1} \rightarrow N$ transition exhibits a minimum value in the vicinity of the central region of the concentration range. In a mixture in which the nematic gap occurs, the energy of the smectic lattice assumes zero values in the region neighbouring the nematic gap; the $S_{A_1} \rightarrow N$ phase transition is second order in this concentration region. The variations of the $S_{A_1} \rightarrow N$ enthalpy with composition in mixtures of smectic A_1 and A_d in systems with a nematic gap are identical. The rapid decrease of the molecular interactions in the smectic layers, in both types of mixtures, means that these molecules are no longer kept in constant position, in consequence they can migrate freely yielding a nematic.

The nematic phase observed in smectic mixtures described in [8–13] was referred to as 'stabilized intermediate nematic phase'. Its creation was assigned to the hypothetical phases of the pure compounds which are believed to exist in the metastable or unstable region [13]. The assumption that the lowering of the smectic phase stability in their mixtures with respect to that of the pure compounds reveals the internal latent features of the nematic phases of these compounds is justified for the series of *n*-DBT compounds. We found that the latent temperatures of the N → I phase transition for the *n*-DBT are fairly high. For instance, the hypothetical T_{NI} is 72°C and 74°C for 6DBT and 8DBT, respectively. These temperatures were determined by estimating the clearing temperatures of 6DBT–6CHBT and 8DBT–8CHBT binary mixtures and extrapolation to the concentrations $x_{6DBT} = 1$ and $x_{8DBT} = 1$. Compounds CHBT are nematics [17] whose geometrical structure resembles that of *n*-DBT. The good agreement between the N → I phase transition temperatures of the pure compounds of the *n*-DBT series determined in this way and those observed in their mixtures (cf. figure 3) supports this interpretation. Thus, smectic compounds may be considered as potential nematics. They may be converted into nematics if conditions are created that favour the decrease of the intermolecular forces in the smectic layer. This may be achieved by differentiating the lengths of the molecules, considered as single molecules or dimers, in the smectic layer. In view of the dimeric structure of many liquid-crystalline molecules, the spacing of the smectic layers of the pure compounds, which is easy to measure experimentally, is a better, and more general, parameter for predicting the properties of binary systems. All the cases so far observed for the creation of the nematic phase have been observed for mixtures composed of compounds differing in their smectic layer spacings. Hence, the nematic phases created from smectic compounds may be referred to as nematic phases created by depression of the smectic stability.

The nematic phases described in [8–13] were observed in smectic mixtures obtained from compounds which had different smectic phases. Generally one was a smectic A and the other was a smectic C. Thus it is justified to call this nematic phase an 'intermediate nematic phase', since it occurs between two different smectic phases. As regards the mixtures studied by us, the nematic phase appears between two smectic regions of the same kind, namely S_A, and so the term 'intermediate' seems to be misleading.

The phenomenon of creating a new phase is commonly called 'induction'. To date the term 'induced phase' was usually also related to the mechanism of intermolecular interaction which leads to a strong increase of the intermolecular forces in the smectic and nematic phases or only in the smectic phase which manifests itself by the maxima of the S → N or S → I transition temperatures in the central region of the concentration range. The nature of this specific intermolecular interaction is often connected with the complexing process of the EDA type [21]. The complexing process usually leads to the creation of smectic phases, but several cases of creating nematic phase have been described by Araya and Matsunaga [22]. Recently, [14], the term 'induced nematic phase' has been used for the nematic phase created between smectic phases.

Calorimetric investigations of smectic phases created from nematic compounds have shown that the enthalpies $\Delta H_{\mathrm{NS_A}}$ and ΔH_{NI} depend strongly on the composition of the mixtures and assume maximal values in the central region of the concentration range of the binary mixtures [23, 24]. When the nematic phase is created from smectic compounds, the enthalpy ΔH_{SN} decreases, as we have shown, and assumes minimal values in the central region of the concentration range. From the energetic point of view induction of the smectic phase from nematic compounds and that of the nematic phase from smectics are opposite processes and their mechanisms are different. Nevertheless it seems that it is right to use the term 'induced phase' in both cases if it is related to the creation of a new phase and not to the mechanism leading to that creation. The use of the term 'induced phase' in a more general sense also finds other justification. Cases are already known of enhancement of the smectic phase or creation of a new smectic phase with a characteristic stability maximum in compounds with the same character of polarity (that is both compounds are polar or both non-polar) [2, 25] for which the manifestation of a new, specific intermolecular interaction that does not occur between the molecules of the pure components is not expected. Considering these doubts, we wish to ask whether the term 'stabilized intermediate nematic phase', 'induced nematic phase' or 'nematic phase created by depressing the smectic stability' should be used to describe the nematic phase formed in the binary mixtures studied here.

References

[1] Dewey, A. G., 1980, *The Physics and Chemistry of Liquid Crystal Devices*, edited by G. J. Sprokel (Plenum Press), p. 219.

[2] Domon, H., and Billard, J., 1979, *J. Phys., Paris*, **40**, C3, 413.

[3] Engelen, B., and Schneider, F., 1978, *Z. Naturf. (a)*, **33**, 1077.

[4] Sharma, N. K., Pelzl, G., Demus, D., and Weisflog, W., 1980, *Z. phys. Chem.*, **281**, 579.

[5] Cladis, P. E., 1981, *Molec. Crystals liq. Crystals*, **67**, 177.

[6] Fukui, M., and Matsunaga, Y., 1981, *Bull. chem. Soc. Japan*, **54**, 3137.

[7] Sadowska, K. W., Żywociński, A., Stecki, J., and Dąbrowski, R., 1982, *J. Phys., Paris*, **43**, 1673.

[8] Pelzl, G., Bättger, U., and Demus, D., 1981, *Molec. Crystals liq. Crystals Lett.*, **64**, 283.

[9] Demus, D., Kölz, K. H., and Sackmann, H., 1972, *Z. phys. Chem.*, **249**, 217.

[10] Demus, D., Kunicke, G., Pelzl, G., Rohling, B., Sackmann, H., and Salffner, R., 1973, *Z. phys. Chem.*, **254**, 373.

[11] Demus, D., Richter, L., Rümp, C. E., Sackmann, H., and Schubert, M., 1975, *J. Phys., Paris*, **36**, C1, 349.

[12] Pelzl, G., Diele, G., Latif, L., Demus, D., Schäfer, W., and Zaschke, H., 1985, *Molec. Crystals liq. Crystals* (in the press).

[13] Arnold, H., and Sackmann, H., 1959, *Z. Elektrochem. Ber. Bunsenges.*, **63**, 1171.

[14] Ziemnicka, B., de Vries, A., Doane, J. W., and Arora, S. L., 1985, *Molec. Crystals liq. Crystals* (in the press).

[15] Dąbrowski, R., and Szulc, J., 1985, *J. Phys., Paris*, **45**, 1213.

[16] Czupryński, K., Dąbrowski, R., Baran, J., Przedmojski, J., and Żywociński, A., 1986, *J. Phys., Paris* (in the press).

[17] Dąbrowski, R., Dziaduszek, J., and Szczuciński, T., 1985, *Molec. Crystals liq. Crystals*, **124**, 241.

[18] Dąbrowski, R., Dziaduszek, J., Szczuciński, T., and Raszewski, Z., 1984, *Molec. Crystals liq. Crystals*, **107**, 411.

[19] van Laar, I., 1908, *Z. phys. Chem.*, **63**, 216; 1908, *Ibid.*, **64**, 257.

[20] Czupryński, K., and Dąbrowski, R., *Molec. Crystals liq. Crystals Lett.* (in the press).

[21] Demus, D., Hauser, A., Pelzl, G., Böttger, U., and Schönburg, S., 1985, *Crystal. Res. Technol.*, **20**, 381.

[22] Araya, K., and Matsunaga, Y., 1981, *Molec. Crystals liq. Crystals*, **67**, 153.

[23] Szabon, J., and Janossy, J., 1980, *Advances in Liquid Crystals Research and Applications*, edited by L. Bata (Pergamon Press and Akademai Kiado), p. 229.

[24] Boij, A., and Adomenos, P., 1983, *Fifth Conference Socialist Countries*, Odessa, Abstract D-4.

[25] Nguyen Huu Tinh, Hardouin, F., and Sigaud, G., 1980, *Molec. Crystals liq. Crystals Lett.*, **56**, 189.