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Effect of Steric Factor on Mesomorphic Stability, II: Binary Mixtures of Homologues of 4-(4′-Substituted Phenylazo)-1-naphthyl-4″-alkoxybenzoates

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Sixteen mesomorphic derivatives of the title compounds have been investigated for their phase behavior. These compounds constitute four homologous series that differ from each other by the substituent X. The latter varies between CH_3O, CH_3, Cl, and NO_2, and the number (n) of carbons in the alkoxy chain varies, within a homologous series, between 8, 10, 12, and 14. All possible binary mixtures made from any two homologues were prepared and characterized for their mesophase behavior by differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Phase diagrams for the 24 binary combinations were constructed to investigate the effect of inclusion of the 1,4-naphthalene moiety, as well as the variation in the alkoxy chain length, on the mesomorphic properties in mixed systems.

Keywords: steric factor; binary mixtures; 4-(4′-substituted phenylazo)-1-naphthyl-4″-alkoxybenzoates

INTRODUCTION

Earlier studies, in our laboratory, on the phase behavior of mixtures of various mesogens [1–8] showed the formation of mesomorphism in mixed systems by mixing compounds where none, one, or both components are mesogens. For eutectic compositions, which possess low melting temperatures, increase or decrease of the mesomorphic ranges and thermal stabilities and studies of the factors that influence mesomorphic properties have received great attention. We have reported

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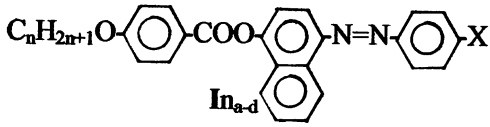
[8,9] homologous series of the azo-esters of the type 4-(4′-substituted phenylazo) phenyl 4″-alkoxy benzoates and evaluated their mesomorphic properties in pure [9] and mixed states [8]. A vast number of mesogenic compounds, containing a 1,4-, 1,5-, or 2,6-naphthalene moiety in the core system, have been reported [10–22].

In continuation of our studies of the structure–property relationships of ester-based mesogens, we reported [1] four homologous series of azo-esters containing a naphthalene moiety and investigated the effect of a laterally fused naphthalene ring on mesomorphism. The effect of replacing the central benzene ring in a previous series [9] by a 1,4-naphthalene moiety [1] on their mesogenic properties in the pure state was compared. As an extension of this work, we report here the investigation of the phase behavior in binary mixtures of homologues of the previously prepared [1] four homologous series $\mathbf{I}n_{\mathrm{a-d}}$. Each binary mixture is made from any two homologues bearing the same substituent X, but of different alkoxy chain lengths.



I8, n = 8; **I**10, n = 10; **I**12, n = 12; **I**14, n = 14
a, X = CH_3O; b, X = CH_3; c, X = Cl; d, X = NO_2

EXPERIMENTAL

Chemicals were purchased from the following companies: Aldrich, Wisconsin, USA; E. Merk, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

Preparation of Materials

All compounds investigated in this article were prepared according to the method previously described [1].

Physical Characterization

Calorimetric measurements were carried out using a PL-DSC from Polymer Laboratories, England. The instrument was calibrated for temperature, heat, and heat flow according to the method recommended by Cammenga et al. [23]. The measurements were carried

out for small samples (2–3 mg) placed in sealed aluminum pans. All of the thermograms have been achieved at a heating rate of 10°C/min in an inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and types of mesophases identified for compounds prepared with a standard polarized-light microscope (Wild, Germany) attached to a homemade hot stage.

For phase diagrams, binary mixtures of any two homologues, covering the whole composition range, were prepared by melting the appropriate amounts of each component, stirring to give a well-mixed blend, and then cooling with stirring to room temperature. The temperatures obtained for the prepared blends, as measured by both DSC and PLM, agreed within 2–3°C. In the phase diagrams, constructed by plotting transition temperatures versus mixture composition, the symbol "□" denotes nematic–isotropic and "○" solid–mesophase transitions.

RESULTS AND DISCUSSION

Transition temperatures as measured by DSC and identified by PLM, for all of the compounds investigated, are summarized in Table 1. In the table, the subscripts C, N, and I denote solid, nematic, and isotropic, respectively. As shown in this table, all derivatives irrespective of the substituent X or the length of the alkoxy chain, *n*, possess an enantiotropic nematic phase as the only mesophase observed.

TABLE 1 Transition Temperatures (°C) of the Homologous Series (**I***n*$_{a–d}$)

Compound number	X	T_m ($T_{C\text{-}N}$)	T_c ($T_{N\text{-}I}$)
I8$_a$	CH_3O	112.7	178.1
I10$_a$		108.6	167.3
I12$_a$		104.8	153.0
I14$_a$		109.6	142.5
I8$_b$	CH_3	139.0	149.8
I10$_b$		105.7	148.2
I12$_b$		115.0	139.1
I14$_b$		121.9	137.3
I8$_c$	Cl	106.1	160.5
I10$_c$		98.8	138.9
I12$_c$		105.8	128.9
I14$_c$		97.4	130.1
I8$_d$	NO_2	152.2	184.8
I10$_d$		121.4	177.6
I12$_d$		130.4	168.1
I14$_d$		131.2	161.0

Binary Mixtures of Electron-Releasing-Substituted Homologues

Figure 1a–f represents diagrams constructed for the six possible binary combinations prepared from the methoxy-substituted homologues $\mathbf{I}8_a$–$\mathbf{I}14_a$. Irrespective of the difference between the alkoxy chain length of the two components in any binary system investigated, all mixtures of the homologues $\mathbf{I}_a$ possess only the nematic phase, and their nematic–isotropic transition temperatures ($\boldsymbol{T}_C$) vary more or less linearly with composition. This behavior shows that, irrespective of the alkoxy chain length, all components investigated form an ideal mixed nematic phase, especially in the last three binary mixtures comprising the higher homologues $\mathbf{I}10_a$–$\mathbf{I}14_a$. Conversely, the solids of the individual homologues of $\mathbf{I}_a$ seem to differ from each other in their crystalline structure that is disturbed by the gradual addition of one component to the other. In such case, a solid solution is formed from the two components within a certain range of composition represented by the smooth variation of $\boldsymbol{T}_m$ with composition. Such a smooth composition dependence of $\boldsymbol{T}_m$ is dependent upon the alkoxy chain length, n, as well as the difference in n, (see Fig. 1). Thus, when the difference in n is 2 (e.g., in the mixtures $\mathbf{I}8_a/\mathbf{I}10_a$, $\mathbf{I}10_a/\mathbf{I}12_a$), there exist narrow ranges of solubility. Increasing the difference and/or the value of n increases the composition range where solid solution occurs to the extent that in the mixture $\mathbf{I}12_a/\mathbf{I}14_a$ solubility is extended to cover the whole range of composition (Fig. 1f). The range of composition over which solubility of homologues of I_a in each other decreases in the order $\mathbf{I}10_a/\mathbf{I}14_a > \mathbf{I}8_a/\mathbf{I}14_a > \mathbf{I}8_a/\mathbf{I}12_a > \mathbf{I}8_a/\mathbf{I}10_a \approx \mathbf{I}10_a/\mathbf{I}12_a$.

Similar behavior was observed for the mixtures of the methyl-substituted homologues, Fig. 2a–f; that is, all diagrams exhibit the nematic as the only mesophase observed. The nematic–isotropic transition temperatures ($\boldsymbol{T}_C$) varies linearly with composition, irrespective of the alkoxy chain length. On the other hand, the solid phase of mixed systems showed a composition range of solubility, dependent on n and difference in n between the two components of the mixture. Again, the composition range of solubility increases as n and/or difference in n increases to the extent that it covers the whole composition range in the last mixture ($\mathbf{I}12_b/\mathbf{I}14_b$) (see Fig. 2f). Similar solid-phase behavior was observed by Dave et al. [24] for the binary mixtures of the asymmetrical 4-decyloxyphenylazo-4′-(2-methyl-butyloxybenzene and 4-nitrophenyl-4′-decyloxy benzoate. But, in such a binary system of dissimilar mesogens, Dave gave no comments about such linear range of dependence; on the contrary he considered it as eutectic behavior. It should be mentioned here that evidence for the formation of the solid

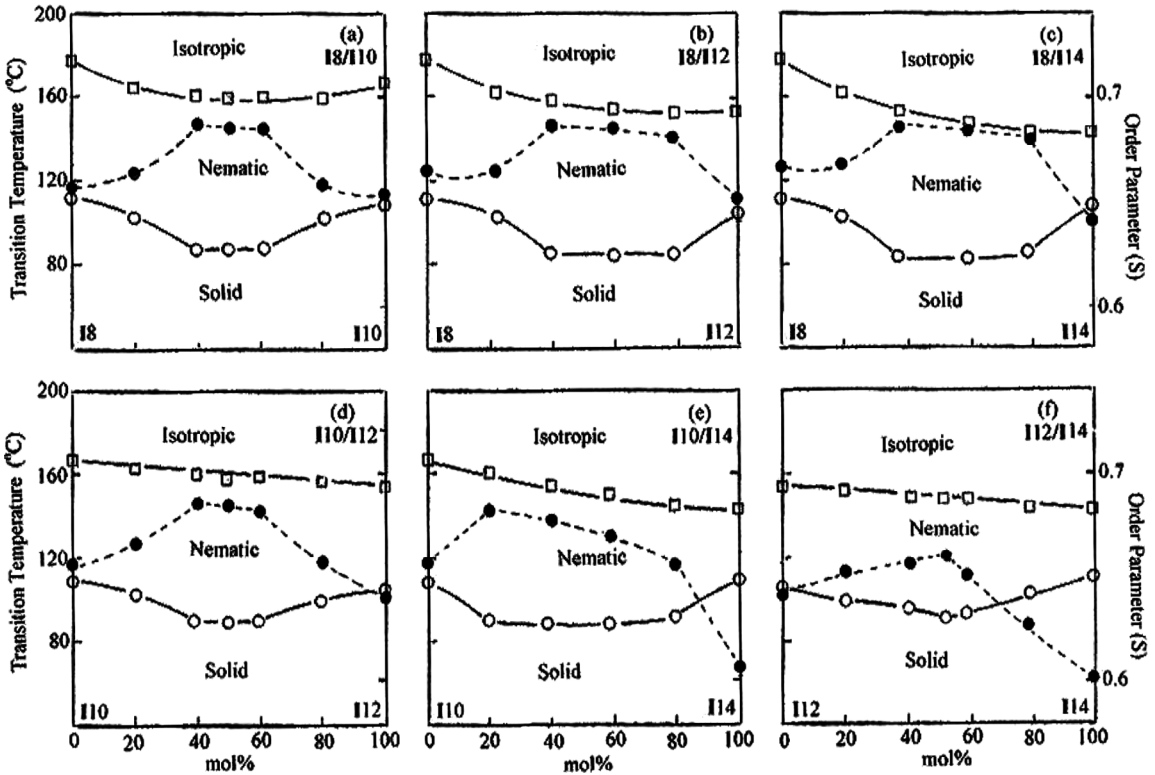


FIGURE 1 Phase diagrams for the binary mixtures of the methoxy-substituted homologues: (a) $\mathbf{I}8_a/\mathbf{I}10_a$, (b) $\mathbf{I}8_a/\mathbf{I}12_a$, (c) $\mathbf{I}8_a/\mathbf{I}14_a$, (d) $\mathbf{I}10_a/\mathbf{I}12_a$, (e) $\mathbf{I}10_a/\mathbf{I}14_a$, and (f) $\mathbf{I}12_a/\mathbf{I}14_a$. The calculated S-values are included as the solid circles.

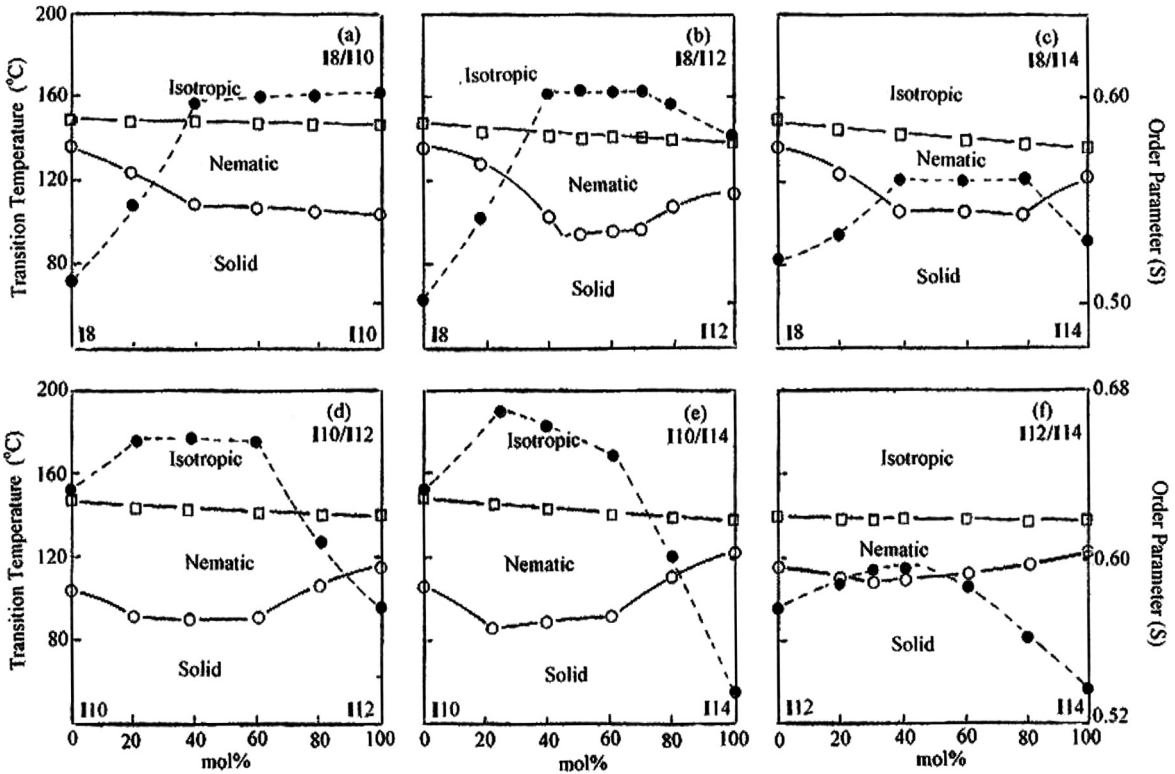


FIGURE 2 Phase diagrams for the binary mixtures of the methyl-substituted homologues: (a) $\mathbf{I}8_b/\mathbf{I}10_b$, (b) $\mathbf{I}8_b/\mathbf{I}12_b$, (c) $\mathbf{I}8_b/\mathbf{I}14_b$, (d) $\mathbf{I}10_b/\mathbf{I}12_b$, (e) $\mathbf{I}10_b/\mathbf{I}14_b$, and (f) $\mathbf{I}12_b/\mathbf{I}14_b$. The calculated S-values are included as the solid circles.

solution is that DSC thermograms within this linear range of composition dependence of $\boldsymbol{T}_{\mathrm{m}}$ showed only one endothermic peak of fixed melting point. Generally, the formation of a heterogeneous eutectic mixture is characterized by one endothermic peak corresponding to its $\boldsymbol{T}_{\mathrm{m}}$ transition, whereas two endothermic peaks are observed for other compositions.

Binary Mixtures of Electron-Withdrawing-Substituted Homologues

The binary phase diagrams of mixtures of homologues of the remaining series, $\mathbf{I}_c$ and $\mathbf{I}_d$, are respectively depicted in Figs. 3 and 4. The binary mixtures of the chloro-substituted homologues (Fig. 3) behave to a great extent like those of the methoxy- and methyl-substituted analogues. Again, in all the binary combinations, the nematic is the only mesophase, enantiotropically, observed with stability ($\boldsymbol{T}_{\mathrm{C}}$) that almost varies linearly with composition. Their solid–mesophase transitions ($\boldsymbol{T}_{\mathrm{m}}$) also show linear composition dependencies within a certain intermediate range of composition, indicating the partial solubilities of one component in the other.

The first three binary combinations of the nitro-substituted homologues, namely $\mathbf{I}8_{\mathrm{d}}/\mathbf{I}10_{\mathrm{d}}$, $\mathbf{I}8_{\mathrm{d}}/\mathbf{I}12_{\mathrm{d}}$, and $\mathbf{I}8_{\mathrm{d}}/\mathbf{I}14_{\mathrm{d}}$, which have $\mathbf{I}8_{\mathrm{d}}$ as a common component, again exhibit partial solubility in their solid mixtures. In the remaining three binary systems, namely, $\mathbf{I}10_{\mathrm{d}}/\mathbf{I}12_{\mathrm{d}}$, $\mathbf{I}10_{\mathrm{d}}/\mathbf{I}14_{\mathrm{d}}$, and $\mathbf{I}12_{\mathrm{d}}/\mathbf{I}14_{\mathrm{d}}$, their components are soluble in all proportions. This again indicates that solid-phase solubility increases with an increase of the alkoxy chain length. Like the homologues $\mathbf{I}_{\mathrm{a}}$–$\mathbf{I}_{\mathrm{c}}$, pure and mixed homologues of $\mathbf{I}_{\mathrm{d}}$ exhibit the enantiotropic nematic phase as the only mesophase observed, and in all cases, irrespective of the alkoxy chain length, the nematic–isotropic transition temperatures ($\boldsymbol{T}_{\mathrm{m}}$) varies, more or less, linearly with compositions.

The unusual solid-phase behavior exhibited by all binary systems investigated can be attributed to the presence of the lateral naphthalene moiety. This may lead, as a result of increasing intermolecular distances by steric effect, to comparable cohesive forces between molecules of individual components, and a solid solution is produced. Furthermore, the laterally protruded naphthalene moieties hinder rotation around the $\mathrm{O}-\mathrm{C}_{10}\mathrm{H}_6-\mathrm{N}$ bonds, thus prohibiting conjugation between the substituent X and the remainder of the molecule. This, consequently, diminishes the effect of various substitutions, thus increasing the possibility of solid-phase dissolution, as well as nematic-phase formation in pure and mixed systems.

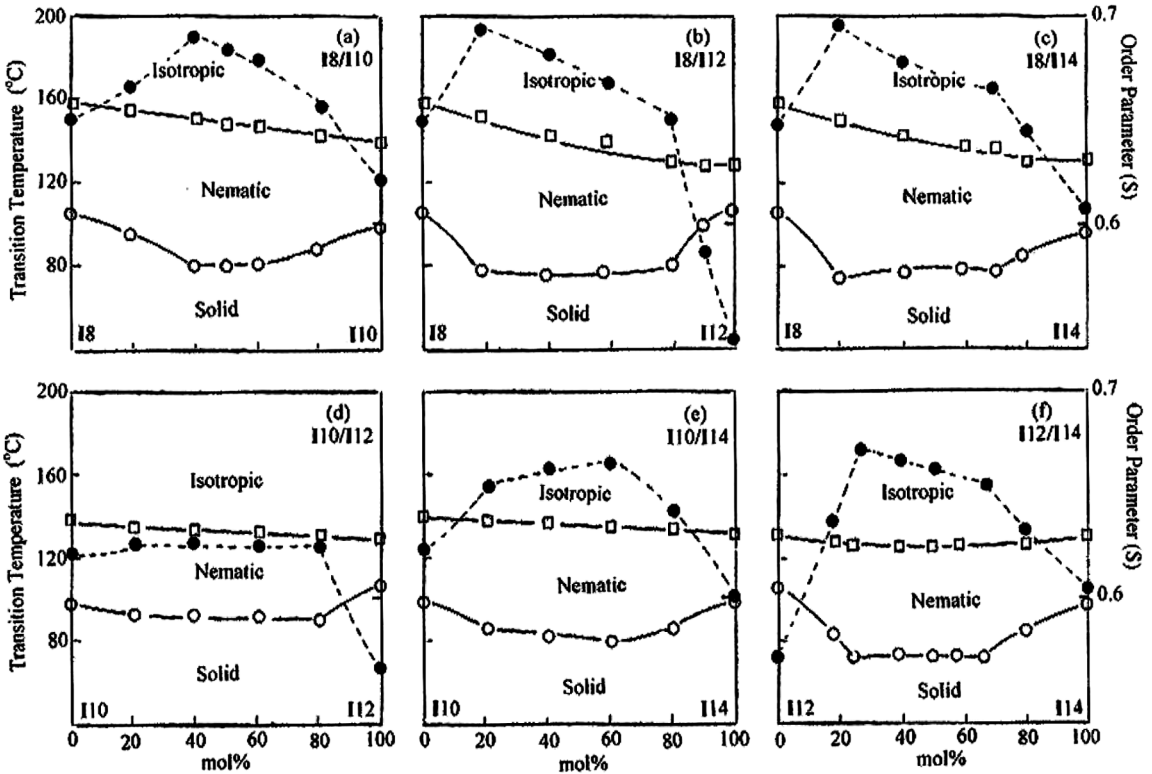


FIGURE 3 Phase diagrams for the binary mixtures of the chloro-substituted homologues: (a) $\mathbf{I}8_c/\mathbf{I}10_c$, (b) $\mathbf{I}8_c/\mathbf{I}12_c$, (c) $\mathbf{I}8_c/\mathbf{I}14_c$, (d) $\mathbf{I}10_c/\mathbf{I}12_c$, (e) $\mathbf{I}10_c/\mathbf{I}14_c$, and (f) $\mathbf{I}12_c/\mathbf{I}14_c$. The calculated S-values are included as the solid circles.

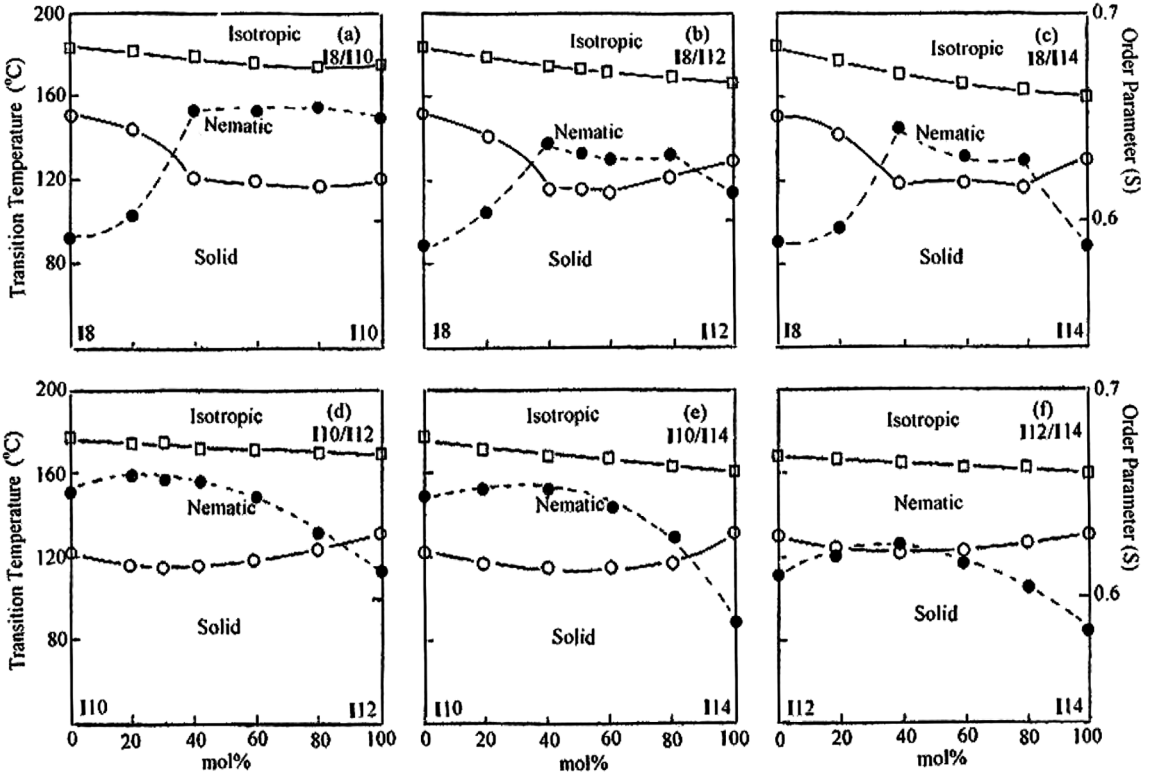


FIGURE 4 Phase diagrams for the binary mixtures of the nitro-substituted homologues: (a) $\mathbf{I}8_d/\mathbf{I}10_d$, (b) $\mathbf{I}8_d/\mathbf{I}12_d$, (c) $\mathbf{I}8_d/\mathbf{I}14_d$, (d) $\mathbf{I}10_d/\mathbf{I}12_d$, (e) $\mathbf{I}10_d/\mathbf{I}14_d$, and (f) $\mathbf{I}12_d/\mathbf{I}14_d$. The calculated S-values are included as the solid circles.

Nematic Order Stability and Mixture Composition

As mentioned by Gray [25], in the crystals of a nematogenic compound, the molecules lie parallel to one another and each molecule is locked in a regular geometric arrangement. In the nematic melt, only the parallel arrangement persists, the molecules are free to move, and the positions of the ends of the molecules are disorganized. The lateral, planar, and terminal cohesions must weaken profoundly at the solid–nematic transition. Now, although it is difficult to imagine substantial variations in the nature of layer crystal lattices upon melting, a nematogenic arrangement may change greatly from the crystal of one homologue to that of the next, and not necessarily in any regular fashion. Nevertheless, the exact arrangements of the molecules in the crystal will determine the strength of the lateral and planar attractions that must weaken at the melting point, and therefore the melting points of nematogenic compounds will depend on the exact nature of the crystal packing. These facts have encouraged us to apply Eq. (1), deduced by Hikmet and Lub [26], to evaluate the nematic order parameter (S) for the investigated mixtures at their melting points as a function of mixture composition:

$$S = \left[1 - 0.98\left(\frac{T_m}{T_C}\right)\right]^{0.22} \quad (1)$$

The calculated S-values are included in their corresponding phase diagrams as the solid circles. In this way, one may investigate the composition dependence of the nematic mesophase arrangement just at the melting temperature without giving a chance for the molecules to move. In the relation used, Eq. (1), the melting temperature ($\boldsymbol{T}_m$) replaces T. Assuming an uncertainty in measuring the transition temperatures ($\boldsymbol{T}_m$ or $\boldsymbol{T}_C$) equals ± 1 K, the expected uncertainty in S does not exceed ± 0.002.

As expected, the nematic order parameter, S, at $T = \boldsymbol{T}_m$, varies with composition in a fashion coincident with that of $\boldsymbol{T}_m$, except that S is higher for mixtures with lower $\boldsymbol{T}_m$. This may be explained by the fact that the order parameter (S) for a mesophase decreases by increase of temperature. Thus, for the mixtures of homologues (Figs. 1–4) let us start with the binary mixtures of the methoxy-substituted homologues (Fig. 1a–f) as an example. The addition of one homologue to the other, up to a certain composition, is accompanied by a drop in $\boldsymbol{T}_m$ and a consequent increase in S. This means that the presence of each component facilitates the formation of the mesophase by weakening the cohesive forces within the crystal lattice. Within the intermediate

composition range, S (at $\boldsymbol{T}_{\mathrm{m}}$) varies more or less gradually with composition, indicating the compatibility of the molecular arrangements of both components either in the solid or in the nematic phase. These findings add extra evidence for the formation of solid solution within this intermediate range of composition. In case of mixtures, where their components are of incompatible crystal structures, a eutectic point is observed associated with a peak value of S. Binary mixtures of other homologues (Figs. 2–4) behave in similar ways but to varying extents.

CONCLUSION

Binary mixtures were independently prepared from various homologues of the four homologous series 4-(4′-substituted phenylazo)-1-naphthyl-4″-alkoxybenzoates and characterized for their phase behaviour. Irrespective of the substituent X or alkoxy chain length, pure and mixed homologues were found to be nematogenic. Furthermore, in all phase diagrams investigated, the nematic–isotropic transition temperatures ($\boldsymbol{T}_{\mathrm{C}}$) were found to vary almost linearly with composition. On the other hand, the composition dependencies of the solid–nematic transition temperatures ($\boldsymbol{T}_{\mathrm{m}}$) of the binary mixtures investigated were found to form a solid solution through a composition range dependent on the alkoxy chain length n and the difference in n between the two components of the mixture. Such unusual binary solid-phase behavior would definitely be attributed to the steric effect of the 1,4-naphthalene moiety included in the core of compounds investigated.

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