Mesophase stability in binary mixtures of monotropic nematogens

H.A. Ahmed*

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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Binary phase diagrams were constructed from laterally substituted methyl azo/ester derivatives, namely 4-(4′-substituted phenylazo)-3-methyl phenyl-4″-alkoxy benzoates (Bnazo). In this group of compounds the unsubstituted and chloro-substituted derivatives possess the nematic phase monotonically, while the nitro and methyl analogues are enantiotropically nematogenic. The binary phase diagrams constructed were made once from the monotropic nematogens with each other, and another with the enantiotropic nematogens. In both the cases enantiotropic nematic phase was observed that covers a wide range of composition. The mesophase behaviour of all binary mixtures was investigated by differential scanning calorimetry (DSC) and polarised light microscopy (PLM). The nematic phase was exhibited in all binary mixtures. Independent of the alkoxy chain length, the entropy change, $\Delta S_{ex}$ of the N–I transition of pure components was found to vary irregularly with the anisotropy of polarisability ($I_{ex}$) of the polar substituent, X.

Keywords: 4-(4′-substituted phenylazo)-3-methyl phenyl-4″-alkoxy benzoates; phase transitions; binary phase diagrams; anisotropy of polarisability

1. Introduction

Generally, liquid crystalline compounds are rod-like molecules with stable central linkages.[1] The ester carbonyl group is one of the most commonly used linking units since it is relatively thermally stable. [1–3] Azobenzene group represents very comfortable fragments to design and synthesise new structures, giving stable mesophases often with very interesting polymorphism.[4–7] Liquid crystalline materials, either low molar mass [8–11] or polymeric in nature,[12] containing an azo group in the mesomeric core are attractive with regard to studying their optical properties. Generally, it has been reported that the central linkages and the terminal groups play important roles in the formation, type, thermal stability and temperature range of the mesophase of the liquid crystalline compound.[13] Many series of dimeric liquid crystals have been reported.[8–11] All of these compounds may be termed symmetric, with identical mesogenic moieties, or non-symmetric dimers, with different mesogenic units. In both the cases, the specific interactions between the two mesogenic groups do lead to a significant variation in the mesophase behaviour of such materials.[8–11]

Mesophase characteristics of mesogens may be greatly modified upon mixing of individual components. Earlier studies [14–25] have shown that the emergence of the mesophase upon mixing compounds where none, one or both components of the mixture are mesogens.

In our laboratory, various types of binary mixtures, dependent on the two components of the mixture, were investigated. For such mixed systems, all components were of the same core structure, namely, phenylazo phenyl benzoates (X-C$_6$H$_4$-N=NC$_6$H$_4$-OCO-C$_6$H$_4$OR'). Binary mixtures were made once from any two homologues carrying the same terminal polar group X, [26,27] and another from any two terminally substituted analogues bearing different polar groups, X, but of the same alkoxy chain length.[26,28] A third type of binary system [29] was made from two analogously terminally substituted compounds but of different mesogenic core, one is an azo-ester and the other is the corresponding terminally substituted di-ester.

Going further in investigating mixtures of liquid crystalline components, two groups of positional isomers of the same skeletal structure, bearing the same terminal (polar and alkoxy) groups, but of lateral methyl substituent protruded with different angles with respect to the long axis of the molecule, were prepared, and their mesophase behaviour was investigated again in their pure and mixed states.[30] That is, binary mixtures were made from any two positional isomers, one from each group. In a more recent work,[31] the same core structure was used, but the difference between the two components of the binary mixtures lies in the polarity of the lateral substituent (CH$_3$ and Cl) attached to the same position of central benzene ring.

*Email: hadyelrahman@yahoo.com

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Generally, the physical properties of a nematogens are strongly influenced when a lateral substituent is appended to the mesogenic core. Lateral protrusion effectively widens the mesogenic core, thus increases intermolecular separation that leads to a reduction in the lateral association,[32] and hence the nematic phase stability is reduced.

In a previous work in our laboratory,[30] compounds \( \text{In}_{a-d} \) were prepared and characterised for their mesophase behaviour. It was found that, independent of the length of the terminal alkoxy chain, compounds \( \text{In}_{b-c} \) (X = H and Cl) possess a monotropic nematic phase, whereas, the electron-donating CH\(_3\) group in \( \text{In}_a \), or the electron-withdrawing NO\(_2\) substituent in \( \text{In}_d \) induces the nematic phase enantiotropically. The goal of the present study is to extend investigation to the binary phase behaviour of mixtures once prepared from two monotropic mesogens and another from a monotropic nematogen with an enantiotropic one.

\[ \text{In}_a, X=\text{CH}_3, \text{In}_b, X=\text{H}, \text{In}_c, X=\text{Cl}, \text{In}_d, X=\text{NO}_2 \]

2. Experimental

Compounds, \( \text{In}_{a-d} \), were prepared by the method described in a previous work.[30]

Calorimetric measurements were carried out using a differential scanning calorimeter, PL-DSC, of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al.[33] DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminium pans. All of the thermograms have been achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 ml/min).

Binary mixtures were prepared by mixing accurately weighed samples of the appropriate amounts of the individual components, melting them together to give an intimate mixture and then cooling to room temperature while stirring.

Transition temperatures were measured by DSC and the type of mesophase identified for all mixtures prepared with a standard polarised light microscope, PLM (Wild, Germany) attached to a home-made hot stage. The transition temperatures obtained for all prepared blends as measured by both DSC and PLM agreed within 2–3°C.

In the phase diagrams, constructed by plotting transition temperatures versus composition, the symbol ‘o’ denotes solid-to-nematic transition, \( T_{\text{Cr-N}} \), ‘□’ nematic-to-isotropic transition, \( T_{\text{N-I}} \), and ‘…’ eutectic temperature.

3. Results and discussion

Transition temperatures as measured by DSC and PLM are given in Table 1. The data in this table, which match those reported previously,[30] revealed that all members of group \( \text{In}_{a-d} \) are purely nematogenic, but the unsubstituted (\( \text{In}_b \)) and the chloro-substituted (\( \text{In}_c \)) homologues showed their nematic phase monotropically. In order to confirm the purity of prepared compounds, the elemental analysis data of \( \text{In}_{a-d} \), infrared (IR) and \(^1\)H-NMR data of \( \text{II}_{a-d} \) as representative compounds are collected in Tables 2–4, respectively. Generally, the mesophase stability is augmented by an increase in the polarity and/or polarisability of the mesogenic part of the molecule. Also it was reported [34] that the terminal substituent has relatively greater effect on the shape anisotropy of the unit to which it is attached and consequently the mesophase behaviour. The electron-donating (CH\(_3\)) and electron-withdrawing (NO\(_2\)) substituents (in \( \text{In}_a \) or \( \text{In}_d \)) were found to enhance the nematic stability (\( T_{\text{N-I}} \)) over those of their unsubstituted analogues (\( \text{In}_b \)). This indicates that the polarity and/or polarisability play an important role in enhancement mesophase stability. On the other hand, the data in Table 1, when compared with those reported for their corresponding laterally neat analogues,[35] revealed that lateral methyl substitution on the central ring in position 3 is accompanied with an increase of the double bond character of the C=O group and, in addition to its special effect, consequently, furnishes poor mesomorphic compounds specially in the less polar terminal H- and Cl-substituents.

It is already known that materials that retain their liquid crystalline character over a wide range of temperatures are preferred for practical applications. One way to achieve this property is to use eutectic mixtures of materials exhibiting liquid crystallinity in their pure state, or at least when molecules in question resemble one another structurally. Under such condition, the mesophase-to-isotropic line is usually straight or even enhanced and the temperature range of the mesophase is greater for the eutectic mixture than either pure components.

Since the unsubstituted (\( \text{In}_b \)) and Cl-substituted (\( \text{In}_c \)) homologues are only monotropically
nematogenic, it is interesting to investigate if there are enhancements of the nematic stability and temperature ranges when they are mixed with each other or with their structurally comparable enantiotropic nematogenic analogues, bearing the terminal CH₃, in I₈ₐ, or NO₂, in I₈ₐ, groups. In order to confirm that molecules of the monotropic nematogens I₈ₐ or I₈ₐ fit readily in the nematic

Table 1. Phase transition temperatures (°C), enthalpy of transition (ΔHᵢ₋₄, kJ/mole) and transition entropy (ΔSᵢ₋₄, J mol⁻¹ K⁻¹), for compounds I₈ₐ–d.

| Comp. No. | N | X  | T_cr-I   | T_cr-N   | Tᵢ₋₄   | ΔHᵢ₋₄ | ΔSᵢ₋₄ |
|-----------|---|----|-----------|-----------|--------|-------|-------|
| I₈ₐ       | 8 | CH₃| 99.1      | 175.1     | 1.08   | 2.41  |
| I₈ₐ       | 8 | H  | 94.1      | —         | (88.0) | (0.76) | (2.10) |
| I₈ₐ       | 8 | Cl | 99.8      | —         | (95.7) | (0.20) | (0.54) |
| I₈ₐ       | 8 | NO₂| —        | 99.1      | 170.0  | 0.84  | 1.89  |
| I₁₀ₐ      | 10| CH₃| —        | 74.9      | 174.4  | 1.07  | 2.38  |
| I₁₀ₐ      | 10| H  | 93.7      | —         | (90.5) | (0.53) | (1.46) |
| I₁₀ₐ      | 10| Cl | 106.5     | —         | (93.7) | (0.17) | (0.46) |
| I₁₀ₐ      | 10| NO₂| —        | 70.0      | 156.0  | 0.63  | 1.47  |
| I₁₂ₐ      | 12| CH₃| —        | 86.5      | 162.3  | 1.31  | 3.01  |
| I₁₂ₐ      | 12| H  | 84.9      | —         | (83.2) | (1.13) | (2.81) |
| I₁₂ₐ      | 12| Cl | 108.3     | —         | (93.2) | (0.16) | (0.44) |
| I₁₂ₐ      | 12| NO₂| —        | 77.9      | 156.0  | 0.77  | 1.79  |
| I₁₄ₐ      | 14| CH₃| —        | 85.3      | 153.9  | 1.50  | 3.51  |
| I₁₄ₐ      | 14| H  | 87.1      | —         | (83.4) | (0.73) | (2.05) |
| I₁₄ₐ      | 14| Cl | 83.0      | —         | (80.2) | (0.19) | (0.54) |
| I₁₄ₐ      | 14| NO₂| —        | 80.5      | 146.0  | 0.50  | 1.19  |
| I₁₆ₐ      | 16| CH₃| —        | 88.0      | 148.2  | 1.55  | 3.68  |
| I₁₆ₐ      | 16| H  | 91.9      | —         | (83.1) | (0.74) | (2.08) |
| I₁₆ₐ      | 16| Cl | 116.0     | —         | (113.5)| (0.25) | (0.65) |
| I₁₆ₐ      | 16| NO₂| —        | 69.6      | 140.9  | 0.50  | 1.21  |

Note: N, nematic; I, isotropic; and () monotropic.

Table 2. Elemental analysis of prepared compounds, I₈ₐ–d (4-CₙH₂n+1O-C₆H₄-COO-C₆H₃(3-CH₃)-N═N-C₆H₄-X-4).

| Comp No. | N | Substituent X | %C      | %H      | %N      | %Cl   |
|-----------|---|---------------|---------|---------|---------|-------|
| I₈ₐ       | 8 | CH₃           | 75.97 (75.95) | 7.45 (7.47) | 6.14 (6.11) | —     |
| I₈ₐ       | 8 | H             | 75.65 (75.50) | 7.26 (7.31) | 6.30 (6.32) | —     |
| I₈ₐ       | 8 | Cl            | 70.19 (70.21) | 6.49 (6.52) | 5.59 (5.85) | 7.42 (7.40) |
| I₈ₐ       | 8 | NO₂           | 68.66 (68.69) | 6.40 (6.38) | 8.59 (8.58) | —     |
| I₁₀ₐ      | 10| CH₃           | 76.50 (76.51) | 7.88 (7.87) | 5.76 (5.76) | —     |
| I₁₀ₐ      | 10| H             | 76.25 (76.24) | 7.67 (7.68) | 5.92 (5.93) | —     |
| I₁₀ₐ      | 10| Cl            | 71.08 (71.06) | 6.98 (6.96) | 5.55 (5.52) | 6.96 (6.99) |
| I₁₀ₐ      | 10| NO₂           | 69.59 (69.61) | 6.79 (6.82) | 8.13 (8.12) | —     |
| I₁₂ₐ      | 12| CH₃           | 76.90 (77.01) | 8.25 (8.22) | 5.42 (5.44) | —     |
| I₁₂ₐ      | 12| H             | 76.78 (76.77) | 8.07 (8.05) | 5.59 (5.60) | —     |
| I₁₂ₐ      | 12| Cl            | 71.82 (71.82) | 7.33 (7.35) | 5.22 (5.24) | 6.60 (6.63) |
| I₁₄ₐ      | 14| CH₃           | 77.47 (77.45) | 8.60 (8.54) | 5.14 (5.16) | —     |
| I₁₄ₐ      | 14| H             | 77.22 (77.24) | 8.37 (8.39) | 5.29 (5.30) | —     |
| I₁₄ₐ      | 14| Cl            | 73.37 (73.39) | 7.19 (7.22) | 5.88 (5.90) | —     |
| I₁₄ₐ      | 14| NO₂           | 72.49 (72.51) | 7.72 (7.70) | 4.50 (4.97) | 6.29 (6.30) |
| I₁₆ₐ      | 16| CH₃           | 75.75 (75.73) | 8.60 (8.59) | 4.78 (4.77) | —     |
| I₁₆ₐ      | 16| H             | 77.845 (77.85) | 8.82 (8.83) | 4.90 (4.91) | —     |
| I₁₆ₐ      | 16| Cl            | 77.67 (77.66) | 8.69 (8.69) | 5.05 (5.03) | —     |
| I₁₆ₐ      | 16| NO₂           | 73.14 (73.13) | 8.03 (8.01) | 4.73 (4.73) | 5.96 (6.00) |
arrangement of their structurally similar enantiotropic nematogenic analogues (I or II), the binary phase behaviour of the mixtures with other three types of components were investigated. In the first system (e.g., I8b/I8c and I16b/I16c), the binary mixtures were composed of the two monotropically nematogenic analogues, the second system (e.g., I8b/I10b and I8c/I10c) is a mixture of two homologues of each, and the third type (e.g., I8b/I8d and I10c/I10d) is their mixture with a corresponding enantiotropic nematogen.

3.1. Lateral substitution and entropy change of transition, ΔSN–I

The entropy of the nematic–isotropic transition was calculated for the two series I/a–d (Table 1) and II/a–d.[31] The difference between the two groups of compounds lies in the orientation protrusion of the laterally substituted methyl group into the central benzene ring. In the first group (Group I), the methyl substituent, introduced in position 3 with respect to the ester group, makes an angle of 120° with the long axis of the molecule. In the other group (Group II), the orientation angle is 60° since it is introduced in position 2.

The calculated entropies are represented graphically as a function of the anisotropy of polarisability (ΔαX) in Figure 1. As can be seen from the figure, the terminally unsubstituted isomers (I8b and I10b) showed that lateral substitution with the ortho-methyl group is associated with lower values of ΔSN–I than those of their corresponding laterally meta-substituted analogues, except for those bearing longer alkoxy chain length (n = 16). The decrease observed in ΔSN–I is presumably, in part, a reflection of the increase in biaxiality of the mesogenic group resulted from the flexible terminal alkoxy chain being less strongly anchored at its end, thus resulting in a decrease in the conformational entropy.[35]
changes in an irregular fashion with $\Delta \alpha_X$ upon increase of the alkoxy chain length ($n$). Such discrepancy may be attributed to the significant steric effect of the lateral substitution as well as their different electronic interaction with the central benzene ring; this consequently affects the polarisability of the molecule as a whole.

Upon terminal substitution with different polar groups, the behaviour became more complex, reflecting the variable extent of the strength of the mesomeric interaction within the mesogenic core resulting from the change in degree of conjugation. Hence, for the terminally 4-CH$_3$ substituted homologues in both the series $\text{II}_n$ and $\text{II}_n$ (Figure 1), their relative value of $\Delta S_{N-1}$ vary according to the length of the flexible part of the molecule, which definitely affects the lateral intermolecular interaction to a variable degree. That is for $n = 8–14$, the order of the decrease in $\Delta S_{N-1}$ is $\text{II}_{16_a} > \text{II}_{16_a}$, while for $n = 16$ is reversed, i.e., $\text{II}_{16_a} > \text{II}_{16_a}$. Terminal substitution by the 4-Cl group resulted in a big difference in $\Delta S_{N-1}$ values between the homologues; $\text{II}_{n}$ in all cases are greater than $\text{I}_{n}$. The low $\Delta S_{N-1}$ value of the chloro derivatives is attributed to the repulsive force contribution that predominates and consequently reduces $\Delta S_{N-1}$.

On the other hand, when comparison is made between members of any group of derivatives bearing the same lateral substituent (2-CH$_3$ or 3-CH$_3$) and the same terminal alkoxy group, the entropy change $\Delta S_{N-1}$ was found to decrease in an order that varies according to the nature of these substituents.

In summary, $\Delta S_{N-1}$ decreases according to the terminal polar substituent in the order:

**Group I: Lateral methyl group in m-position**

For $n = 8$, CH$_3 > H > NO_2 > Cl$

For $n = 10$, CH$_3 > H \approx NO_2 > Cl$

For $n = 12$, CH$_3 > H > NO_2 > Cl$

For $n = 14$, CH$_3 > H > NO_2 > Cl$

This comparison indicated that the introduction of a lateral substituent, whether it is in ortho or meta position with respect to the ester group, has led to an irregular $\Delta S_{N-1}$-$\Delta \alpha_X$ dependency; in other words, $\Delta S_{N-1}$
For $n = 16$, $CH_3 > H > NO_2 > Cl$

Group II: Lateral methyl group in o-position

For $n = 8$, $CH_3 > Cl > H > NO_2$
For $n = 10$, $CH_3 > Cl > NO_2 > H$
For $n = 12$, $CH_3 > NO_2 > Cl > H$
For $n = 14$, $CH_3 > Cl > H > NO_2$
For $n = 16$, $CH_3 > H > Cl > NO_2$

The low $\Delta S_{N-I}$ of some nitro and chloro derivatives is in accordance with the concept of repulsion, [36] adjacent molecules being forced apart, making the nematic arrangements more random and less anisotropic. Thus, in the case of these nitro derivatives the repulsive contribution predominates and consequently reduces $\Delta S_{N-I}$.

In order to investigate the effect of the size of terminal substituent on the mesophase behaviour of prepared compounds, the dependence of the nematic–isotropic transition temperature on the van der Waals radius of the terminal substituent, $X$, those for $I_{8a-d}$ and $I_{16a-d}$, as representative examples, is shown in Figure 2. It was obvious that the transition temperatures are less linearly dependent on the shape of the terminal substituent, irrespective of the alkoxy chain length. The terminally unsubstituted and chloro-substituted analogues are associated with lower values of $T_{N-I}$ than those of their corresponding terminally methyl and nitro-substituted analogues. This suggests that the shape of the compact terminal substituent ($X$) has insignificant effect on the shape anisotropy of the unit to which it is attached and consequently the mesophase stability.

### 3.2. Binary mixtures of monotropic nematogens

#### 3.2.1. Binary phase behaviour of the two monotropic nematogens bearing the same alkoxy chain, $In_b/In_c$

In order to test the ability of the two monotropic nematogenic homologues $In_b$ and $In_c$ to form the nematic phase in their own, their binary mixtures, covering the whole composition range, were first prepared then thermally and optically investigated to construct their binary phase diagrams. Figure 3 shows two examples, where the binary mixtures are formed from the two corresponding lowest homologues $I_{8b/I8c}$ and the $I_{16b/I16c}$.
are found to be enantiotropic, namely, \( \Delta n = 8 \) and \( \Delta n = 16 \). A scan of the phase diagram revealed that when adding the unsubstituted homologue ( \( I_{8d} \)) to its chloro-substituted analogue, \( I_{8c} \), the nematic phase starts to appear, enantiotropically, upon addition of about 20 mol% of the unsubstituted, \( I_{8c} \), to its chloro-substituted analogue, \( I_{8c} \). This range of composition is some what increased in the mixtures of their higher homologues, \( I_{16d}/I_{16c} \), to cover a range of 2–90 mol% of \( I_{16b} \). Eutectic mixtures in both the systems \( (I_{8b}/I_{8c} \) and \( I_{16b}/I_{16c} \)) showed to exhibit reasonable nematic temperature ranges, namely, 21.5°C and 27.5°C, respectively.

3.2.2.2. Mixtures of homologues of \( I_{n} \). Two examples of the binary phase diagrams of mixtures of two homologues of the chloro analogues \( (I_{8b}/I_{10c} \) and \( I_{8b}/I_{12c} \)) are represented graphically in Figure 5. As in the case of the mixtures of the terminally unsubstituted homologues \( (I_{8e}) \), the mixtures of homologues of \( I_{n} \) proved to exhibit nematic phase within a composition range dependent on \( \Delta n \). That is, this composition range increases from \( \approx 55 \) mol% (in the system \( I_{8b}/I_{10c} \)) to 75 mol% (for \( I_{8b}/I_{12c} \)) as \( \Delta n \) increases from 2 to 4 carbons. It is also evident from Figure 5 that the lower homologue \( (I_{8b}) \) is more effective in promoting the nematic phase. The nematic phase starts to appear enantiotropically by the addition of less than 5 mol% of the other homologue \( (I_{10c} \) or \( I_{12c} \)) to \( I_{8c} \).

3.2.3. Binary phase behaviour of the monotropic components \( (I_{8b} \) or \( I_{8c} \)) with their enantiotropic nematogenic (4-methyl and 4-nitro) substituted analogues

Since the 4-methyl \( (I_{8d}) \) and 4-nitro \( (I_{8d}) \) substituted homologues of group II are found to be enantiotropically nematogenic, they were chosen to be the second component in the binary mixtures with either of the two monotropic analogues \( (I_{8b} \) and \( I_{8c} \)), in order to investigate the effect of the former components to enhance the nematic phase in the latter ones.

3.2.3.1. Mixtures of \( I_{8a} \) with \( I_{8b} \). Figure 6 depicts graphical representation of the two binary systems \( I_{8b}/I_{8b} \) and \( I_{16b}/I_{16b} \). In both the components of the two mixtures the whole molecular structure is kept

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Figure 4. (colour online) Binary phase diagrams of two terminally unsubstituted \( (I_{8b}) \) homologues: (a) \( I_{8b}/I_{10b} \) and (b) \( I_{8b}/I_{16b} \).
constant except the 4-substituent, X. Two extreme chain lengths (\(n = 8\) and 16) were chosen to investigate the effect of the alkoxy chain length. It is clear from Figure 6 that, in both the examples investigated, the nematic temperature range of the enantiotropic nematogen, \(I_{na}\), decreases in almost linear fashion, indicating the compatibility of the two molecules, so that the inclusion of \(I_{nb}\) molecules into the nematic arrangement of \(I_{na}\) does not disturb the order significantly. Also observed from Figure 6 that the increase in \(n\) is accompanied by a reduction of the nematic composition range from \(\approx 95\) mol\% (for \(n = 8\)) to \(\approx 90\) mol\% (for \(n = 16\) carbons). Another effect of the alkoxy chain length is that the eutectic composition changes from \(\approx 68\) mol\% \(I_{8b}\) for the mixture of the lower homologues to \(\approx 47\) mol\% \(I_{16b}\) for the higher homologues.

3.2.3.2. Mixtures of \(I_{na}\) with \(I_{nc}\). The corresponding binary phase diagrams of \(I_{nc}\) with the strong nematogen \(I_{na}\) are given for two representative examples in Figure 7. The resemblance between the diagrams in Figures 6 and 7 revealed that the unsubstituted analogues \(I_{nb}\) behave mesomorphically nearly similar to those of their corresponding 4-chloro analogues, \(I_{nc}\). Again, the higher homologue is less nematogenic.

3.2.3.3. Mixtures of \(I_{nb}\) with \(I_{nd}\). Two examples were chosen for this group of binary mixtures, which again represent extremes in the alkoxy chain length (8 and 16 carbons). Figure 8 illustrates graphical representation of the two binary systems, \(I_{8b}/I_{8d}\) and \(I_{16b}/I_{16d}\). Again, as can be seen from Figure 7, the addition of more than 90 mol\% of the monotopic-nematogenic terminally unsubstituted homologues (\(I_{8b}\) or \(I_{16b}\))
does not disturb significantly the nematic arrangement of either I\textsubscript{8}d or I\textsubscript{16}d. That is, the enantiotropic nematic phase of I\textsubscript{8}d or I\textsubscript{16}d is retained in the mixtures up to the addition of more than 90 mol\% of the monotropic nematogens (I\textsubscript{8}b or I\textsubscript{16}b). On the other hand, the eutectic compositions of the solid mixtures possess small contents (less than 20 mol\%) of I\textsubscript{8}b or I\textsubscript{16}b.

3.2.3.4. Mixtures of I\textsubscript{n}c with I\textsubscript{n}d Figure 9 represents the binary phase diagrams of the monotropic nematogens (I\textsubscript{n}c) with the strong nematogens (I\textsubscript{n}d). As shown in Figure 9, similar behavior was observed for the binary mixtures of the (monotropic) 4-chloro with the (enantiotropic) 4-nitro-substituted analogues. Again, the lower homologue (I\textsubscript{8}c) proved to maintain the nematic arrangement of the nitro analogue (I\textsubscript{n}d) throughout nearly the whole composition range. Conversely, in these systems the eutectic composition possesses greater amounts (=60 mol\%) of the monotropic component (I\textsubscript{8}c or I\textsubscript{16}c).

4. Summary and conclusions

When comparison was made between the entropy change associated with the nematic-to-isotropic transition, $\Delta S_{N-I}$, for two groups of compounds bearing different lateral substituent (3-CH\textsubscript{3}, I\textsubscript{n}a-d and 2-CH\textsubscript{3}, I\textsubscript{n}a-d) keeping the alkoxy chain length constant, it was found that $\Delta S_{N-I}$ decreases in an order dependent on the nature of the two (terminal and lateral) substituents.
Three types of phase diagrams were constructed for binary mixtures made from the laterally 3-methyl substituted phenyl azo phenyl benzoates, namely, 4-(4’-substituted phenyl azo)-3-methyl phenyl-4”-alkoxy benzoates. All compounds are nematogenic, but all the terminally unsubstituted and 4-chloro-substituted homologues (for n = 8–16 carbons) where found to show their nematic phase monotropically. The other two homologous series bearing the 4-CH₃ and 4-NO₂ wing substituents are enantiotropically nematogenic. The binary phase diagrams were constructed to possess at least one monotropic nematogenic, thus these three types were made from:

(1) The monotropic nematogens Inb and Inc as the two components.

(2) Two monotropic nematogenic homologues.

(3) A monotropic nematogens (Inb or Inc) as the first component, while the second one is an enantiotropic nematogens (Ina or Ind).

In all three cases, enantiotropic nematic phases were observed that cover a wide range of composition showing eutectic concentration dependent on the two terminal substituents (RO and X). Also, all the systems studied showed enhanced behavior in the N–I curve, which is attributed to the fact that all of these binary systems consist of two structurally similar components.

**Supplemental data**

Supplemental data for this article can be accessed here.

**References**

[1] Gray GW. Molecular structure and properties of liquid crystals. New York (NY): Academic Press; 1962.

[2] Lu Z, Henderson PA, Paterson BJA, Imrie CT. Liquid crystal dimers and the twist-bend nematic phase. The preparation and characterisation of the α,ω-bis(4-cyanobiphenyl-4’-yl) alkaneedioates. Liq Cryst. 2014;41:471–483. doi:10.1080/02678292.2014.88803

[3] Podruczna M, Hofmańska A, Niezgoda I, Pociecha D, Galewski Z. Influence of terminal groups on liquid-crystalline polymorphism of selected azobenzene derivatives. Liq Cryst. 2014;41:113–125. doi:10.1080/02678292.2013.839834

[4] Alaasar M, Prehm M, Tschierske C. Influence of halogen substituent on the mesomorphic properties of five-ring banana-shaped molecules with azobenzene wings. Liq Cryst. 2013;40:656–668. doi:10.1080/02678292.2013.767949

[5] Alaasar M, Prehm M, Tschierske C. New azobenzene containing bent-core liquid crystals based on disubstituted resorcinol. Liq Cryst. 2014;41:126–136. doi:10.1080/02678292.2013.840393

[6] Yang C-A, Xie H, Chen S, Zhang H. Synthesis and phase structures of combined main-chain/side-chain liquid crystalline polymers with different-number azobenzene moiety in the side-chain based on mesogen-jacketed liquid crystalline polymers. Liq Cryst. 2013;40:1487–1502.

[7] Gutierrez-Cuevas KG, Larios-Lopez L, Julia Rodriguez-Gonzalez R, Donnio B, Navarro-Rodriguez D. On the liquid-crystalline properties of methacrylic polymers containing 4’-(4-alkoxyxenophenyl) azobenzene mesogens. Liq Cryst. 2013;40:534–545. doi:10.1080/02678292.2012.762124

[8] Hogan JL, Imrie CT, Luckhurst GR. Asymmetric dimeric liquid-crystals – the preparation and properties of the alpha-(4-cyanobiphenyl-4’-oxy)-omega-(4-normal-alkylaminebenzylidene-4-oxoxyhexanes. Liq Cryst. 1988;3:645–650. doi:10.1080/0267829880886408

[9] Attard GS, Date RW, Imrie CT, Luckhurst GR, Roskilly SJ, Seddon JM, Taylor L. Nonsymmetrical dimeric liquid-
[10] Imrie CT. Non-symmetric liquid crystal dimers: how to make molecules intercalate. Liq Cryst. 2006;33:1449–1485. doi:10.1080/02678290601140498

[11] Imrie CT, Henderson PA, Seddon JM. Non-symmetric liquid crystal trimers. First example triply-intercalated alternating smectic C phase. J Mater Chem. 2004;14:2486–2488.

[12] Imrie CT, Paterson BJA. Induction of liquid crystallinity in blends of amorphous side-chain polymers and their analogous copolymers. Macromolecules. 1994;27:6673–6676. doi:10.1021/ma000100a063

[13] Ahmed HA, Naoum MM, Saad GR. Effect of alkoxy chain length proportionation on the mesophase behaviour of terminally di-substituted phenylazo phenyl benzoates. Liq Cryst. 2013;40:914–921. doi:10.1080/02678292.2013.788739

[14] Dave JS, Vasant KL. Influence of molecular structure on liquid crystalline properties and phase transitions in mixed liquid crystals. Mol Cryst Liq Cryst. 1966;2:125–134. doi:10.1080/02678292.1966.1058725

[15] Dave JS, Patel PR, Vasant KL. Mixed mesomorphism in binary systems forming smectic-nematic phases. Mol Cryst Liq Cryst. 1969;8:93–100. doi:10.1080/02678292.1969.1058726

[16] Dave JS, Menon MR, Patel PR. Chiral phases induced by doping nonmesogenic component into mesogenic esters. Mol Cryst Liq Cryst. 2003;392:83–95. doi:10.1080/02678292.2003.1058731

[17] Vora RA, Gupta R, Patel K. Exhibition of induced mesophases in the binary systems where one or both the components are non-mesogenic. Mol Cryst Liq Cryst. 1991;209:251–263. doi:10.1080/02678292.1991.1058730

[18] Fujimura S, Yamamura Y, Hishida M, Nagatomo S, Saito K. Reentrant nematic phase in 4-alkyl-4-cyano-biphenyl (nCB) binary mixtures. Liq Cryst. 2014;41:927–932.

[19] Prasad A, Das MK. Determination of elastic constants of a binary system (7CBP+9-CN) showing nematic, induced smectic A(d) and re-entrant nematic phases. Liq Cryst. 2014;41:1261–1268. doi:10.1080/02678292.2014.915589

[20] Cvetinov M, Obadovic D, Stojanovic M, Lazar D, Vajda A, Eber N, Fodor-Csorba K, Ristic I. Mesophase behaviour of binary mixtures of bent-core and calamitic compounds. Liq Cryst. 2013;40:1512–1519. doi:10.1080/02678292.2013.822938

[21] Salud J, López DO, Diez-Berart S, de la fuente MR. Tests of the tricritical point in the smA-to-N phase transition of binary mixtures of butyloxybenzylidene octylcyanil and hexyloxybenzylidene octylcyanil. Liq Cryst. 2013;40:293–304. doi:10.1080/02678292.2012.742580

[22] Prajapati AK, Patel NS, Lad VG. Induction of chirality by doping mesogens with non-mesogenic chiral dopant. Mol Cryst Liq Cryst. 2000;348:41–51. doi:10.1080/00268949108036531

[23] Vora RA, Rajput SJ. Binary mesogenic systems comprised of ester mesogens and non-mesogens. Mol Cryst Liq Cryst. 1991;209:265–277. doi:10.1080/0268949108036201

[24] Govindaiah TN, Nagappa SPM, Mahadeva I, Sreepad HR. Induced chiral smectic phase in mixtures of mesogenic and non-mesogenic compounds. Mol Cryst Liq Cryst. 2011;548:55–60. doi:10.1080/00268949108036531

[25] Lohar JM, Dave JS. Emergence of smectic mesophase in binary mixtures of pure nematogens. Mol Cryst Liq Cryst. 1983;103:181–192. doi:10.1080/00268948308071049

[26] Nessim RI, Naoum MM, Nessim MI. Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XIV. Binary mixtures of 4-(4-substituted phenylazo) phenyl-4-alkoxybenzoates. Liq Cryst. 2005;32:867–876.

[27] Mohammady SZ, Nessim RI, Shehab OR, Naoum MM. Effect of steric factor on mesomorphic stability, II: binary mixtures of homologues of 4-4′-substituted phenylazo)-1-naphthyl-4′-alkoxybenzoates. Mol Cryst Liq Cryst. 2006;451:53–64. doi:10.1080/02678290601140498

[28] Mohammady SZ, Nessim RI, Shehab OR, Naoum MM. Phase behaviour of the binary mixtures of substituted analogues of LC compounds of the type 4-(4′-substituted phenylazo)-1-naphthyl-4′-alkoxybenzoates. Thermochim Acta. 2006;449:61–66. doi:10.1016/j.tca.2006.05.024

[29] Nessim RI. Phase behaviour of binary mixtures of LC compounds of different molecular structure and comparable molecular length: I. 4-(4′-substituted phenylazo)phenyl-4′-alkoxybenzoates and 4-(4′-substituted phenyl carbonylxy) phenyl-4′-alkoxybenzoates. Thermochim Acta. 2005;439:142–150.

[30] Naoum MM, Mohammady SZ, Ahmed HA. Lateral protrusion and mesophase behaviour in pure and mixed states of model compounds of the type 4-(4′-substituted phenylazo)-2-(or 3-methyl phenyl-4′-alkoxy benzoates. Liq Cryst. 2010;37:1245–1257. doi:10.1080/02678292.2010.497228

[31] Naoum MM, Fahmi AA, Alaaasr MA, Abdel-Aziz ME. Effect of lateral substitution of different polarity on the mesophase behaviour in pure and mixed states of 4-4′-substituted phenylazo)-2-substituted phenyl-4′-alkoxy benzoates. Liq Cryst. 2011;38:391–405. doi:10.1080/02678292.2010.550069

[32] Weissflog W, Demus D. New lateral long-chain substituted liquid crystals. Mol Cryst Liq Cryst. 1985;129:235–243. doi:10.1080/00268948308084178

[33] Cammenga HK, Eykel W, Gmelin E, Hemmiger W, Hoehe GWH, Sagre SM. The temperature calibration of scanning calorimeters: part 2. Calibration substances. Thermochim Acta. 1993;219:333–342. doi:10.1016/0040-6031(93)80510-H

[34] Yeap G-Y, Hng T-C, Yeap S-Y, Gorecka E, Itto MM, Ueno K, Okamoto M, Mahmood WAK, Imrie CT. Why do non-symmetric dimers intercalate? The synthesis and characterisation of the (-4-benzylidene-substituted-aniline-4′-oxy)-(2-methylbutyl-4′-(4′-phenyl)-benzoateoxy)alkanes. Liq Cryst. 2009;36:1431–1441. doi:10.1080/02678290903271504

[35] Nessim RI, Naoum MM, Mohamedi SZ, Nessim MI. Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XIII. 4-(4′-substituted phenylazo)phenyl 4′-alkoxybenzoates. Liq Cryst. 2004;31:649–654.

[36] Chandler D. Equilibrium structure and molecular motion in liquids acc. Chem Res. 1974;7:246–251. doi:10.1021/ar50080a002