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

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To cite this Article Nessim, Refaat I. , Naoum, Magdi M. and Nessim, Maher I.(2005) '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', Liquid Crystals, 32: 7, 867 — 876

To link to this Article: DOI: 10.1080/02678290310001481117

URL: http://dx.doi.org/10.1080/02678290310001481117

Liquid Crystals, Vol. 32, No. 7, July 2005, 867–876

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

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(*Received 20 February 2003; in final form 17 April 2003*)

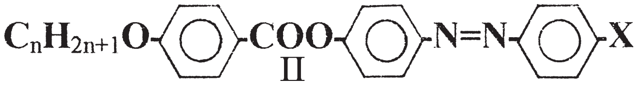
Binary mixtures formed from components of the five homologous series of the 4-(4-substituted phenylazo)phenyl-4-alkoxybenzoates **I**a-e were prepared and their mesophase behaviour characterized. Transition temperatures of the mixtures prepared were measured by differential scanning calorimetry and identified by polarizing optical microscopy. Each binary combination was made from components bearing a terminal alkoxy group with the same number of carbon atoms (kept constant at $n=6$, 8, 10, 12, 14 or 16), while the other substituent (X) was different—CH_3O, CH_3, Cl, NO_2, or CN. Phase diagrams were constructed for the various systems in order to investigate the effect of the terminal substituent X, as well as of the alkoxy chain length, on the phase behaviour of mixed systems.

1. Introduction

It is well established that the stability of a mesophase in a liquid crystalline compound depends primarily on the anisotropy of intermolecular forces. As a result of lateral attractions, rod-shaped molecules tend to adopt a parallel arrangement. Generally, the stability of a mesophase should be greater, the greater the lateral adhesion of the rod-shaped molecules; this in turn would be augmented by an increase of the polarity or polarizability of the mesogenic part of the molecule. Of course, the terminal substituents can affect the polarizability of the aromatic ring to which they are attached; in addition, they may interact with the lateral portion of an adjacent molecule. As the polarity of the group increases, the clearing temperature (T_C) seems also to increase. This is attributed [2, 3] to increased intermolecular attractions with increasing polarity and polarizability of the substituent.

In previous work [1], the effect of a small compact terminal substituent (X) and an alkoxy terminal group of varying chain length on the mesophase stability of 4-(4-substituted phenylazo)pheny1-4-alkoxybenzoates, **I**6a-e–**I**16a-e was investigated. Generally, in the phenyl benzoate system, liquid crystallinity is more persistent as mutual conjugation between the substituent and the ester C–O group is increased. A change in the degree of conjugation will alter both the polarizability and the resultant dipole moment of the molecule; the latter due to an effect on the mesomeric moment. A decrease in the polarizability will lead to a decrease in the dispersion forces, and consequently to a decrease in the thermal stability of the mesophase.

The purpose of the present work is to extend our investigation to binary mixtures of the previously [1] prepared six series of compounds, **I**6a-e–**I**16a-e, that differ from each other in the chain length of the alkoxy group. The substituents X in each series were chosen to cover a wide range of dipolar and electronic characteristics, representing extremes in the conjugated interactions between X and the phenylazo group.



I*n*a-e

I6, $n=6$; **I**8, $n=8$; **I**10, $n=10$; **I**12, $n=12$; **I**14, $n=14$; **I**16, $n=6$

a, $X=CH_3O$; b, $X=CH_3$; c, $X=Cl$; d, $X=NO_2$; e, $X=CN$

For Part XIII, see ref. [1].

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290310001481177

2. Experimental

Chemicals were purchased from Aldrich, Wisconsin, USA; E. Merck, Darmstadt, Germany; and Fluka, Buchs, Switzerland. All the compounds discussed in this paper were prepared according to the method previously described [1].

Calorimetric investigations were made using a Polymer Laboratories (England) differential scanning calorimeter, PL-DSC, with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultra pure metals, a value of $28.45\,\mathrm{J\,g^{-1}}$ being used for the enthalpy of fusion of indium. Typical heating rates were $10\,\mathrm{K\,min^{-1}}$, with a sample mass of 2–3 mg. Transition temperatures were identified with a standard polarizing optical microscope (C. Zeiss, Germany), attached to a FB 52 hot stage equipped with a FB 80 central processor (Mettler, Switzerland).

Thin layer chromatography, for checking the purity of samples, was performed with TLC sheets coated with silica gel (E. Merck); spots were detected by UV irradiation. Silica gel (No. 6634, E. Merck) was used for column chromatography.

3. Results and discussion

Five different homologous series, **I**a–**I**e, of the compounds of type **I**, were prepared in which the terminal group X was varied from one series to another, between CH_3O, CH_3, Cl, NO_2, and CN, respectively. The homologues with n=6, 8, 10, 12, 14 and 16 were investigated for their phase transitions. Transition temperatures of these compounds in their pure states, as reported previously [1, 4–6] are summarized in table 1. In this table the following symbols are given for the various transition temperatures: crystal–SmA ($T_{\text{C-A}}$), crystal–nematic ($T_{\text{C-N}}$), SmA–nematic ($T_{\text{A-N}}$), SmA–isotropic ($T_{\text{A-I}}$), nematic–isotropic ($T_{\text{N-I}}$), and the mesomorphic range ($\Delta T = T_C - T_m$). As can be seen from the table, the methoxy and methyl (i.e. electron-releasing) substituted homologues in the six series (**I**6–**I**16) possess only the nematic phase (N). The chloro

Table 1. Transition temperatures and mesophase ranges (in °C) for compounds **I***n*a-e
$4\text{-}C_nH_{2n+1}O\text{–}C_6H_4\text{–}COO\text{–}C_6H_4\text{–}N\text{–}N\text{–}C_6H_4\text{–}X\text{-}4$.

Compound	n	X	$T_{\text{C-A}}$	$T_{\text{C-N}}$	$T_{\text{A-N}}$	$T_{\text{A-I}}$	$T_{\text{N-I}}$	ΔT°C
I6a	6	CH_3O	—	122.8	—	—	225.8	133.0
I6b		CH_3	—	103.5	—	—	227.8	124.3
I6c		Cl	114.9	—	145.6	—	241.0	126.1
I6d		NO_2	103.6	—	240.5	—	254.7	151.1
I6e		CN	110.0	—	151.8	—	266.4	156.4
I8a	8	CH_3O	—	117.9	—	—	233.5	115.6
I8b		CH_3	—	107.5	—	—	208.9	101.4
I8c		Cl	107.6	—	179.3	—	224.2	116.6
I8d		NO_2	99.9	—	237.9	—	249.9	150.1
I8e		CN	93.0	—	191.7	—	257.5	164.5
I10a	10	CH_3O	—	137.8	—	—	220.9	83.1
I10b		CH_3	—	105.0	—	—	188.1	83.1
I10c		Cl	123.9	—	—	210.9	—	87.0
I10d		NO_2	102.6	—	—	230.9	—	128.3
I10e		CN	105.1	—	223.0	—	243.5	138.4
I12a	12	CH_3O	—	130.7	—	—	209.3	78.6
I12b		CH_3	—	98.9	—	—	183.9	85.0
I12c		Cl	120.1	—	—	197.7	—	77.6
I12d		NO_2	86.5	—	—	221.9	—	135.4
I12e		CN	93.6	—	228.0	—	232.0	138.4
I14a	14	CH_3O	—	114.6	—	—	196.7	82.1
I14b		CH_3	—	96.1	—	—	179.9	83.8
I14c		Cl	104.3	—	—	193.4	—	89.1
I14d		NO_2	93.5	—	—	215.3	—	122.2
I14e		CN	98.4	—	—	226.6	—	128.2
I16a	16	CH_3O	—	124.2	—	—	192.1	67.9
I16b		CH_3	—	98.8	—	—	170.6	91.8
I16c		Cl	105.3	—	—	186.0	—	80.7
I16d		N_2O	101.8	—	—	210.9	—	109.1
I16e		CN	97.3	—	—	220.7	—	123.4

analogues, $\mathbf{I}_c$, exhibit the SmA phase, as the only mesophase, at and after $n=10$. Lower homologues ($\mathbf{I}6_C$ and $\mathbf{I}8_C$) exhibit the SmA phase together with a nematic range that decreases as *n* increases.

The nitro and cyano (i.e. electron-withdrawing) substituted analogues exhibit the SmA and N mesophases, but to varying extents dependent on the length of the alkoxy chain (*n*). Generally all compounds investigated possess higher melting (T_m) and clearing (T_C) temperatures with decreasing mesomorphic range (ΔT), for any derivative, as the chain length is increased.

3.1. *Binary mixtures of electron-releasing substituted compounds* (Ia,b)

The phase diagrams constructed for the six binary mixtures, prepared from the methoxy and the methyl-substituted derivatives in each of the six series **I**6–**I**16, are illustrated in figure 1. As can be seen, each diagram, irrespective of the alkoxy chain length, exhibits gradual variation of the solid–mesophase transition temperatures (T_m) with composition, and nearly linear composition dependence of their mesophase–isotropic transition temperature (T_C). This behaviour indicates that both substituents exert similar effects in each of the molecules being mixed. Furthermore, in all diagrams, the nematic phase was the only mesophase observed.

3.2. *Mixtures of electron-withdrawing substituted analogues* (Ic-e)

From the three electron-withdrawing (Cl, NO_2, and CN) substituted analogues (**I**c, **I**d, and **I**e), three possible binary systems (**I**c/**I**d, **I**c/**I**e, and **I**d/**I**e) could be investigated for each of the six series (**I**6–**I**16). Figures 2–4 represent the phase diagrams of these three binary systems, respectively. Each of the phase diagrams of the nitro and cyano binary systems (figure 4) shows nearly ideal solution behaviour in their mixed solid, mesophase, and isotropic phases. These results reflect the similar behaviour effected by substituents of closely related electronic nature [7]. Both components of the mixture exhibit polymorphic phase behaviour (SmA and N) in their lower (**I**6 and **I**8) homologues, while for higher homologues (**I**14 and **I**16) only the SmA phase is observed. Diagrams for intermediate homologues (**I**10 and **I**12) showed a small composition range of the N phase that decreases as *n* increases. The gradual variation with composition of the melting point (T_m) of the nitro compounds on the addition of the cyano analogues, without passing a eutectic composition, suggests the formation of solid solutions. This has been observed before [7] for the correspondingly substituted 1,4-phenylene bis(4-substituted benzoates). In either case, this indicates the resemblance of solid crystal structure between the nitro and cyano-substituted derivatives bearing an alkoxy group of the same length. Such similar and strong intermolecular attractions are retained in the mesophase, whether it is nematic or smectic.

Figures 2 and 3 illustrate the phase diagrams of the **I**c/**I**d, and **I**c/**I**e systems. Since in both systems, the cloro derivative **I**c is common, and the nitro and cyano groups are of similar electronic nature, similar phase behaviour was observed for both systems. As mentioned above, the nitro, cyano, and chloro analogues exhibit SmA as well as N mesophases in their **I**6 and **I**8 series, and only the SmA phase in the higher **I**14 and **I**16 series. Consequently, mixed systems of the nitro or cyano with the chloro analogue showed SmA and N phases throughout the whole composition range in their lower (**I**6 and **I**8) homologues, and only the SmA phase in their higher (**I**14 and **I**16) homologues. For the intermediate homologues (**I**10 and **I**12), the two systems **I**c/**I**d, and **I**c/**I**e behave differently. In the former, only SmA is observed covering the whole composition range, while in the latter a narrow nematic temperature range is observed up to the addition of less than 20 mol% of **I**c.

With respect to the solid–mesophase transitions, both systems exhibit eutectic behaviour up to the homologues **I**12, whereas solid solutions are formed for higher homologues (**I**14 and **I**16), as indicated by the gradual variation of T_m with composition. This again reflects the similarity of crystal structure and molecular forces existing within the solid phase in each pair of components of the higher homologues at and after $n=14$. In all cases, the mesophase–isotropic temperature, T_C, varies more or less linearly with composition.

3.3. *Mixtures of compounds bearing electron-releasing with those bearing electron-withdrawing substituents*

Figures 5–10 represent the phase diagrams constructed for binary mixtures of components—one bearing an electron-donating (CH_3O, or CH_3) group, i.e. **I**a or **I**b; and the other bearing an electron-withdrawing (Cl, NO_2, or CN) group, i.e. **I**c, **I**d, or **I**e. The phase diagrams of the binary mixtures composed from the CH_3O- or CH_3-substituted compounds as the first component, and the chloro derivative as the second are shown in figures 5 and 6, respectively. Since there is a difference in the electronic nature between the chlorine atom, on the one hand, and the CH_3O or CH_3 groups, on the other, complex phase diagrams are obtained. This is attributed to differences in the phase behaviour of the pure components. As mentioned above, the methoxy and methyl analogues are

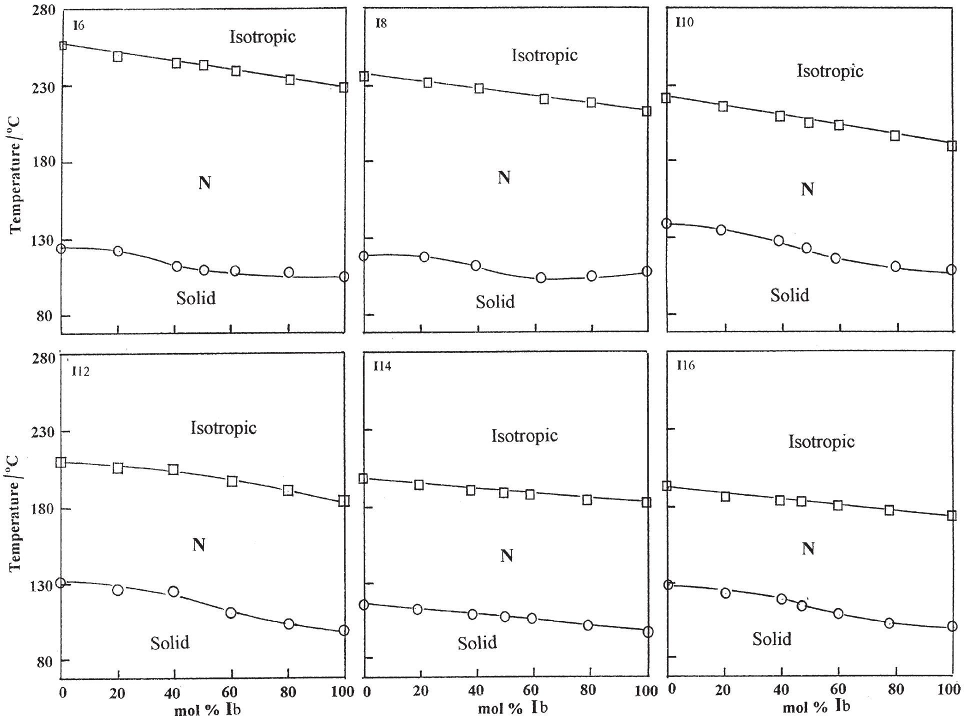


Figure 1. Binary phase diagram for the system **I**a/**I**b for n=6, 8, 10, 12, 14 and 16.

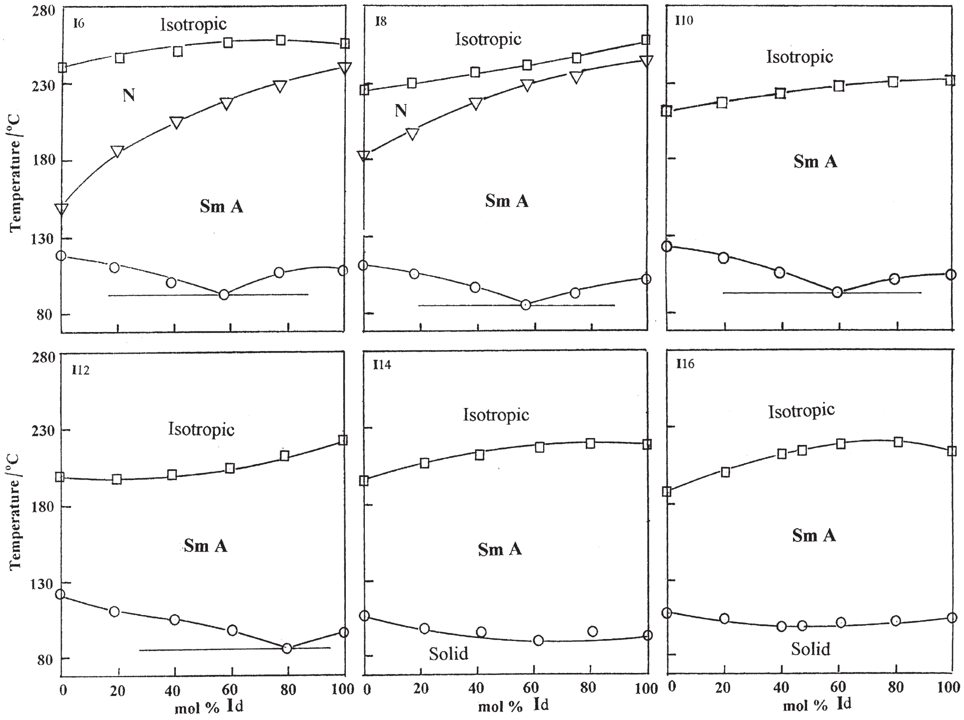


Figure 2. Binary phase diagram for the system **I**c/**I**d, for n=6, 8, 10, 12, 14 and 16.

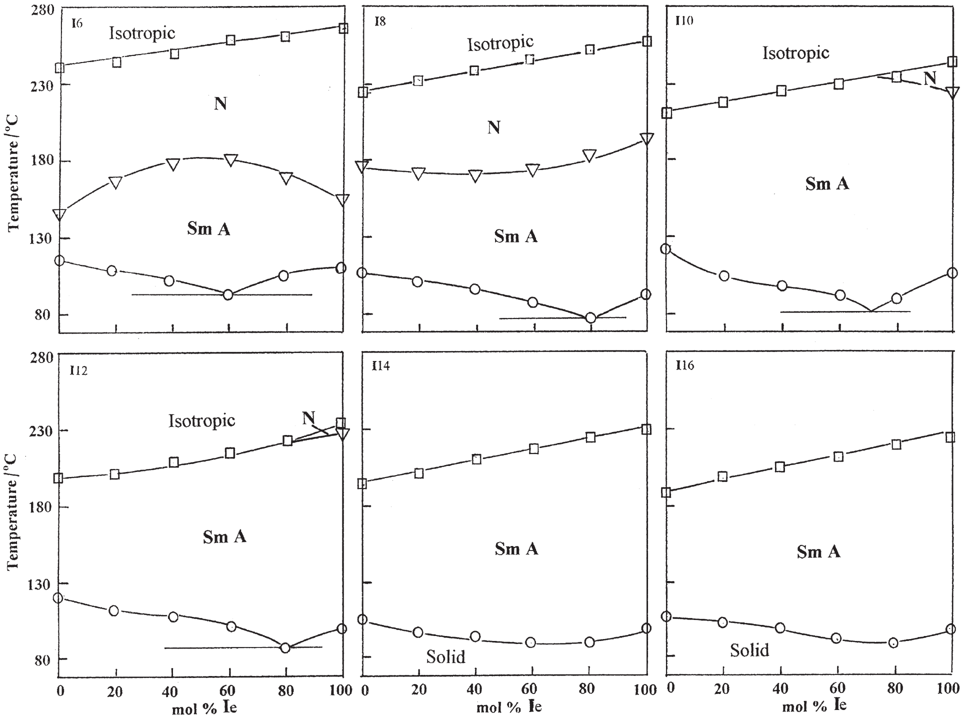


Figure 3. Binary phase diagram for the system **Ic**/**Ie**, for n=6, 8, 10, 12, 14 and 16.

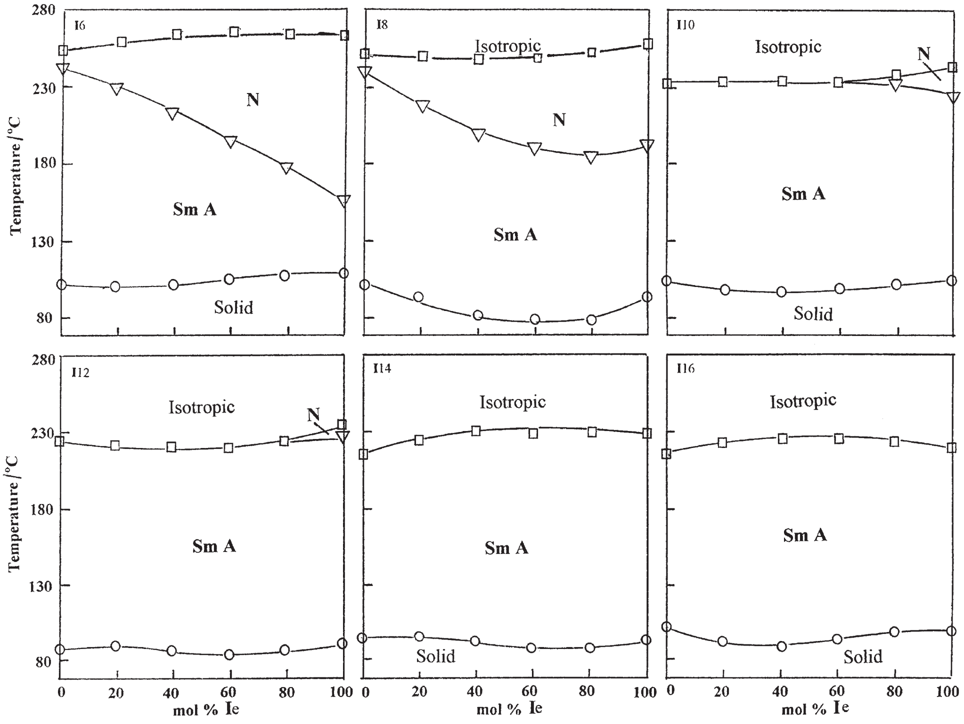


Figure 4. Binary phase diagram for the system **Id**/**Ie**, for n=6, 8, 10, 12, 14 and 16.

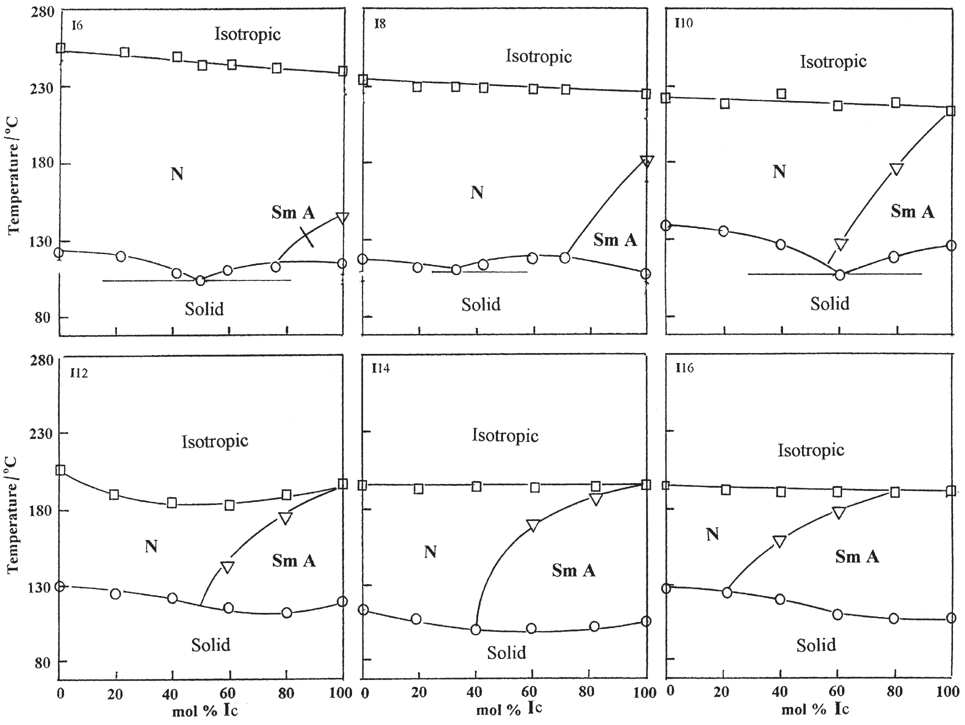


Figure 5. Binary phase diagram for the system **Ia**/**Ic**, for $n=6$, 8, 10, 12, 14 and 16.

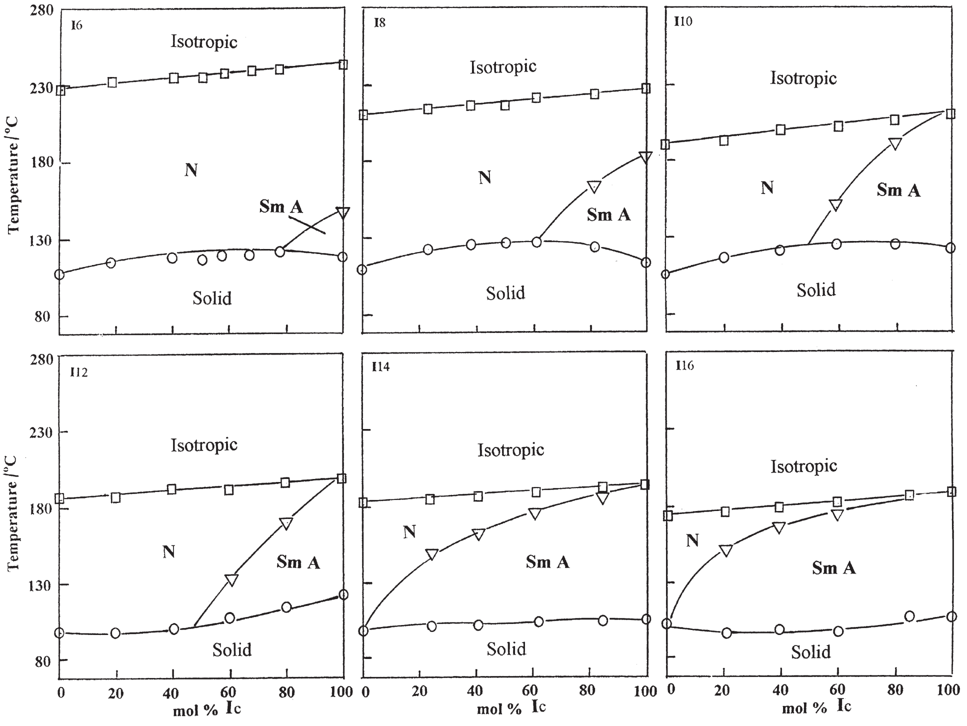


Figure 6. Binary phase diagram for the system **Ib**/**Ic**, for $n=6$, 8, 10, 12, 14 and 16.

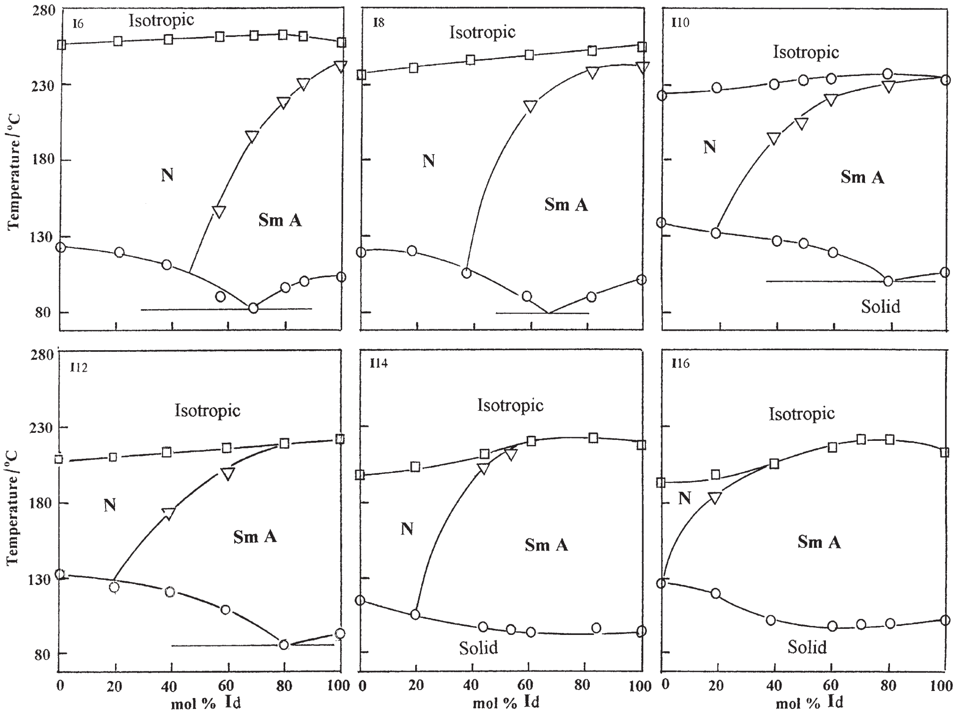


Figure 7. Binary phase diagram for the system **I**a/**I**d, for n=6, 8, 10, 12, 14 and 16.

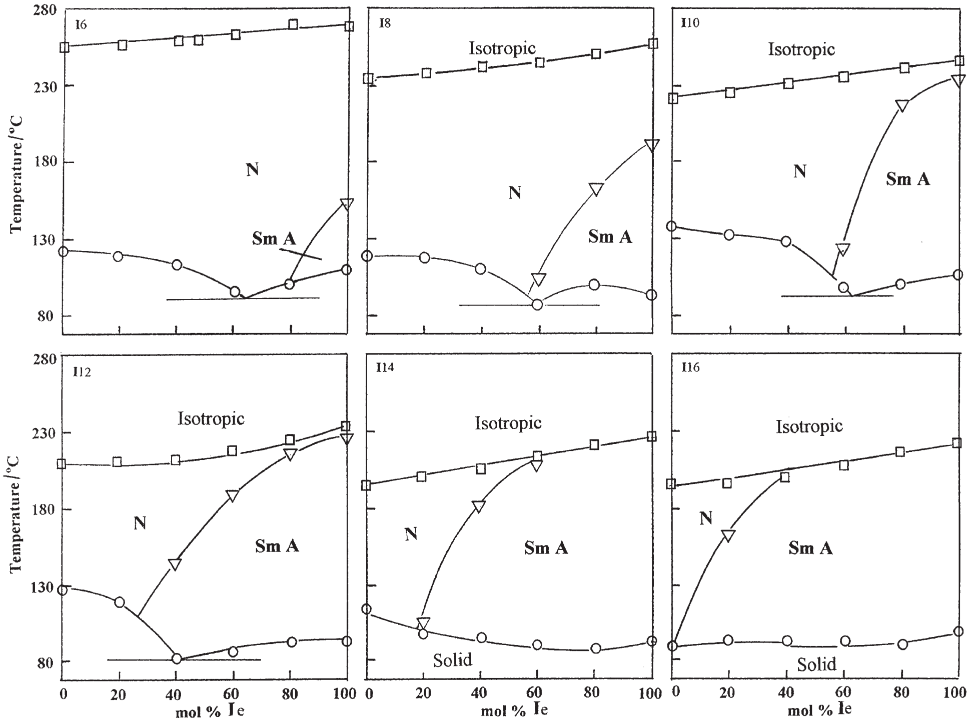


Figure 8. Binary phase diagram for the system **I**a/**I**e, for n=6, 8, 10, 12, 14 and 16.

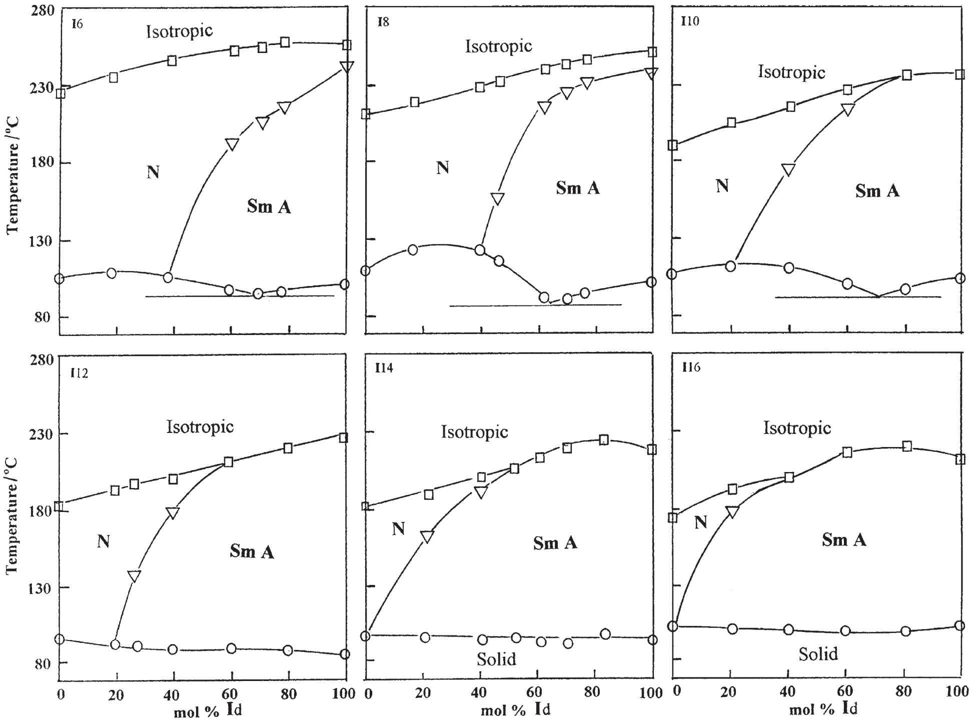


Figure 9. Binary phase diagram for the system **Ib**/**Id**, for n=6, 8, 10, 12, 14 and 16.

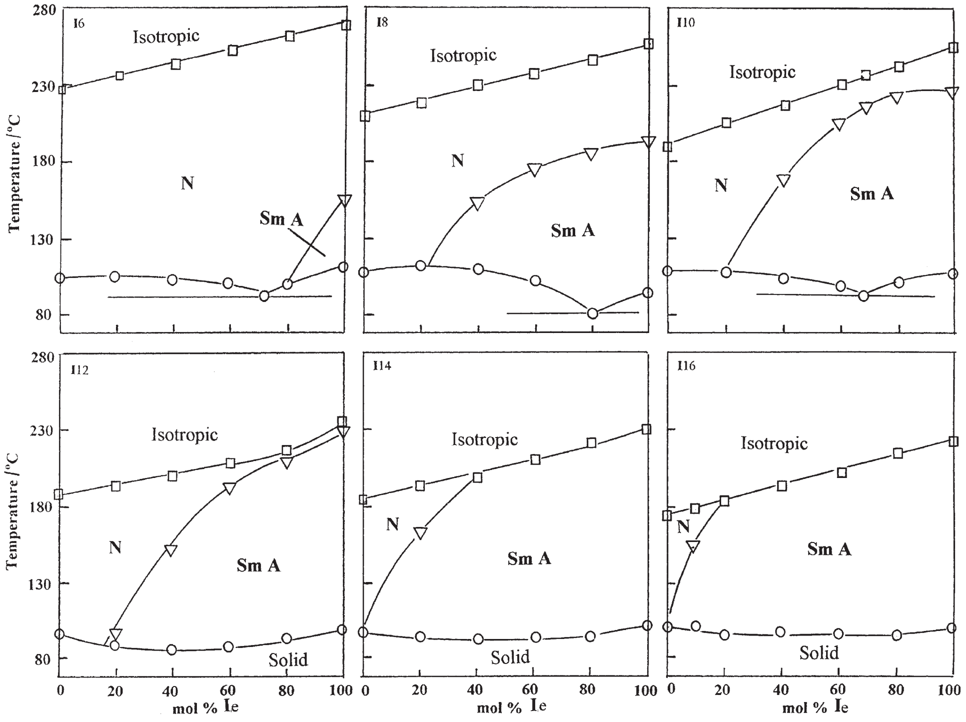
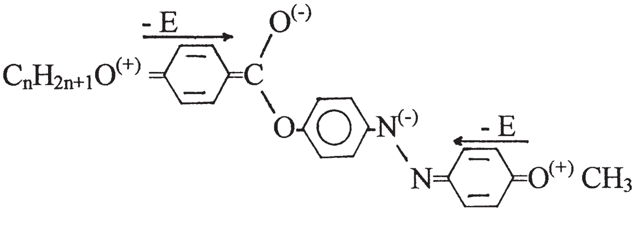


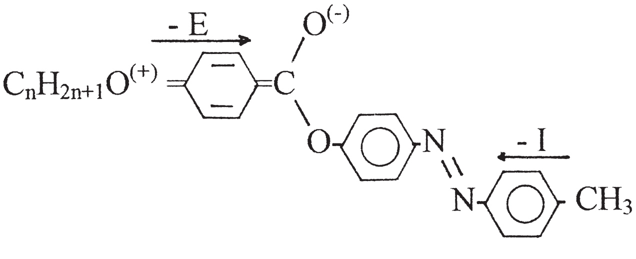
Figure 10. Binary phase diagram for the system **Ib**/**Ie**, for n=6, 8, 10, 12, 14 and 16.

monomorphic, irrespective of the alkoxy chain length, i.e. exhibiting only the N phase. The chloro derivatives, on the other hand, are polymorphic, exhibiting in addition to the SmA phase a decreasing temperature range of nematic, in their **I**6 and **I**8 homologues, but disappearing in the higher **I**10–**I**16 homologues. Consequently, their binary phase diagrams with the methoxy and methyl derivatives (figures 5 and 6, respectively) exhibit a SmA phase composition range that is increased with increasing alkoxy chain length, covering the whole concentration range in the binary system **Ib**/**Ic** at and after $n=14$. In the binary system **Ia**/**Ic**, a SmA composition range occurs up to 80 mol% of **Ia** at $n=16$. Another difference between these two systems is that the system **Ia**/**Ic** (figure 5) shows a eutectic composition up to the homologues **I**10, and thereafter the melting points T_m change gradually with composition. In the other system (**Ib**/**Ic** figure 6), a gradual variation of T_m with composition appeared, starting from the lowest homologues investigated, i.e. **I**6. This difference in behaviour can be attributed to the difference encountered in the electronic interactions between either of the two electron-donating (CH_3O or CH_3) groups with the remainder of the molecule. Thus, the methoxy group in **Ia** would lead to opposite conjugative interactions on each end of the molecule:



Formula 1.

While in **Ib** the methyl group affects the polarization of the molecule to a smaller extent via the inductive effect:

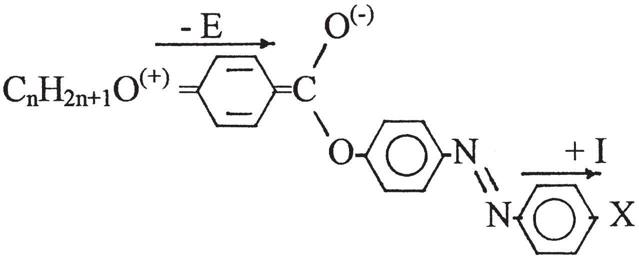


Formula 2.

The chlorine atom in **Ic** interacts by +I and −E effects on both sides of the molecule. Such effects would lead to a mild polarization, more or less compatible with that caused by the methyl group in **Ib**, thus forming with it solid solutions. The reverse holds good with the strong (−E) methoxy group that leads to compound **Ia** forming a heterogeneous solid mixture with **Ic**. This incompatibility diminishes as the alkoxy chain length increases, whereby a homogeneous solid solution is formed at and after $n=12$.

The phase diagrams for the lower series (**I**6–**I**10) of the binary mixtures of either the methoxy (**Ia**) or the methyl (**Ib**) substituted analogues with the nitro (**Id**) or cyano (**Ie**) derivatives (figures 7–10) are characterized by: (i) linear or nearly linear T_C–composition dependence, (ii) eutectic melting behaviour, and (iii) a large nematic mesophase with a SmA composition range that increases as n increases. For higher series (**I**12–**I**16), the clearing temperature suffers non-linear composition dependence due to the complexity of the mesophase at this transition. The SmA composition range increases while T_m varies regularly with composition. In all cases, the mesomorphic temperature ranges ($\Delta T = T_c - T_m$) decreases as the alkoxy chain length increases.

It may also be noted from figures 5–10 that all phase diagrams constructed for the binary systems composed from an electron-releasing substituted derivative with another bearing an electron-withdrawing group unexpectedly exhibit linear or near-linear T_C–composition dependence. The two electron-donating groups on each side of the molecules of **Ia** or **Ib** would lead to an increase of electron density at the mesogenic group, thus leaving the two terminals with positive charges (formulae 1 and 2). On the other hand, in the chloro, nitro, or cyano analogues (**Ic**–**Ie**), the electron-releasing nature of the alkoxy group, on one side of the molecule, would partly increase the electron density at the centre of the mesogenic group. The inductive withdrawing effect of the nitro (chloro, or cyano) group, on the other side of the molecule, would add little effect. The result is a relatively somewhat lower electron density at the centre of the mesogenic group of molecules bearing an electron-withdrawing substituent (formula 3) compared with those bearing electron-donating substituents:



Formula 3, X=Cl, NO_2, or CN.

Such Compounds, **I**a or **I**b as one component, and **I**c, **I**d, or **I**e as the other, when mixed together would have little affinity for one another to form a donor–acceptor complex. Consequently, their binary mixtures would exhibit more or less linear T_C–composition dependence (see figures 5–10).

4. Conclusions

Binary mixtures made from the 4-(4-substituted phenylazo)phenyl-4-alkoxybenzoates, were prepared and their phase transition temperatures characterized. Two types of substituents were used, viz. an alkoxy group of varying chain length and a small compact polar substituent X. All compounds investigated were found to possess high transition temperatures, indicating strong intermolecular association either in the solid or in the mesophase. The conjugation between the alkoxy and the ester carbonyl groups, on one side of the molecule, increases the polarity of the carbonyl oxygen and so stabilizes the mesophase. On the other side of the molecule, the varying electronic nature of the substituent X results in extremes in the electronic interactions between the substituent and the phenylazo group. Such differences lead to a significant variation in the mesophase behaviour in the pure components and, consequently, in their binary mixtures.

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