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Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XII. Binary mixtures of homologues of unsymmetrical 1,4-phenylene bis (4-substituted benzoates)

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Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures
XII. Binary mixtures of homologues of unsymmetrical 1,4-phenylene bis(4-substituted benzoates)

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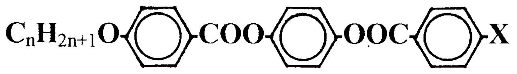
Twentyfour liquid crystalline esters of the type 4-(n-$C_nH_{2n+1}O$)$C_6H_4COOC_6H_4OOCC_6H_4$-X-4 have been investigated for their phase behaviour. These compounds constitute six homologous series that differ from each other by the substituent X. The latter varies between CH_3O, CH_3, Cl, CN, NO_2, and n-$C_nH_{2n+1}O$, and the number (n) of carbons varies, within a homologous series, between 6, 8, 14, and 16. All possible binary mixtures made from any two homologues were prepared and characterized for their mesophase behaviour by differential scanning calorimetry and polarizing optical microscopy.

1. Introduction

In a previous study in this laboratory [1], the effect of a small compact terminal substituent X on the mesophase behaviour of compounds of type **I** was investigated. Molecules of type **I** (see formula below) represent extremes in conjugative interaction between the substituent X and the ester carbonyl group to which it is attached via the intervening phenylene group. In another study [2], all possible binary combinations made from components bearing a different substituent X, but of the same alkoxy chain length, were similarly investigated. The results [1, 2] revealed that all the compounds are mesomorphic and possess high solid–mesophase (T_m) and mesophase–isotropic (T_C) transition temperatures, indicating the existence of strong intermolecular forces of association, either in the solid or in the mesophases. Irrespective of chain length, the binary mixtures showed linear, or nearly linear, T_C–composition dependency.

On the other hand, variation of T_m with composition was found to depend mainly on the difference in the electronic nature of the substituent attached to either component of the binary mixture investigated. Thus, eutectic behaviour was observed for mixtures of components one bearing an electron-withdrawing (Cl, CN, or NO_2) substituent, and the other bearing an electron-releasing (CH_3O or CH_3) one. In contrast, binary mixtures of components bearing substituents of similar electronic nature showed, in addition to ideal mesophase solution behaviour, an ideal solid solution behaviour.

These findings indicated that such substituents result in compounds that possess compatible crystalline solid and mesophase structures. However, binary mixtures of a component bearing the CH_3O group with another bearing the CH_3 group (both electron-donating), are exceptions. These mixtures showed eutectic solid behaviour, indicating that these two components are of different crystalline structure as a result of the difference in intramolecular conjugative interaction within either molecule.



Ia-f
I6, $n = 6$; **I**8, $n = 8$; **I**14, $n = 14$; **I**16, $n = 16$
a, $X = CH_3O$; b, $X = CH_3$; c, $X = Cl$; dx = CN; e, $X = NO_2$;
f, $X = C_nH_{2n+1}O$

The objective of this work is to extend the later investigation [2] to examine the phase behaviour of other possible binary combinations made from any two homologues bearing the same substituent X, but of different alkoxy chain length (n).

2. Experimental

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

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2.1. *Preparation of materials*

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

2.2. *Physical characterization*

Calorimetric investigations were made using a Polymer Laboratories (England) differential scanning calorimeter, PL-DSC, with nitrogen as purge gas. The instrument was calibrated from the melting points of ultra-pure metals, using a value of 28.45 J g^{-1} for the enthalpy of fusion of indium. Typical heating rates were 10 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).

In the accompanying phase diagrams the symbol '○' denotes solid mesophase transition, '□' denotes mesophase–isotropic transition, '△' denotes Sm–N transition, and '●' the mesomorphic range (ΔT).

3. Results and discussion

Six different homologous series, **I**a to **I**f, of esters were prepared in which the terminal group X was varied between CH_3O, CH_3, Cl, CN, NO_2, and n-$C_nH_{2n+1}O$. The homologues ($n = 6$, 8, 14, and 16) prepared were investigated for their phase transitions. Transition temperatures of the other homologues were collected from the literature [3–5].

It is of interest to consider first the effect of increasing the alkoxy chain length, in each homologous series, on the phase transitions. In figure 1, transition temperatures are plotted against length of the alkoxy group (n) with the remaining part of the structure held constant. These plots show that, irrespective of the substituent X, the mesophase–isotropic (T_C) as well as the solid–mesophase (T_m) transition temperatures decrease regularly with increasing alkoxy chain length. These results are unsurprising and in accord with previous observations [6]. The increased alkyl chain length reduces the rod-shaped molecule's rigidity and, consequently, its ability to fit readily into the parallel molecular arrangement of the mesophase. The result is a decrease in mesophase stability and a lower transition temperature. Because of the effect of the substituent X, which produces a high order of stability and, consequently, high transition temperatures, even a very long alkyl group would be relatively mobile, so that their disrupting effect continues to increase with chain length beyond $n = 6$.

As shown in figure 1, in the two homologous series **I**a and **I**b, which respectively bear the electron-donating CH_3O and CH_3 substituents, only the nematic phase is observed up to the highest chain length investigated ($n = 16$). This may be attributed to their end-to-end intermolecular association as indicated by their high clearing enthalpies ($\Delta H_C = 1.2$–1.7 kJ mol^{-1}). These enthalpies are not significantly affected with increase in chain length [1]. This strong end-to-end association is a result of strong intramolecular mesomeric interaction between the CH_3O group and the ester carbonyl leading to the association represented in figure 2. In such a case, lateral interaction between every second molecule grows weaker

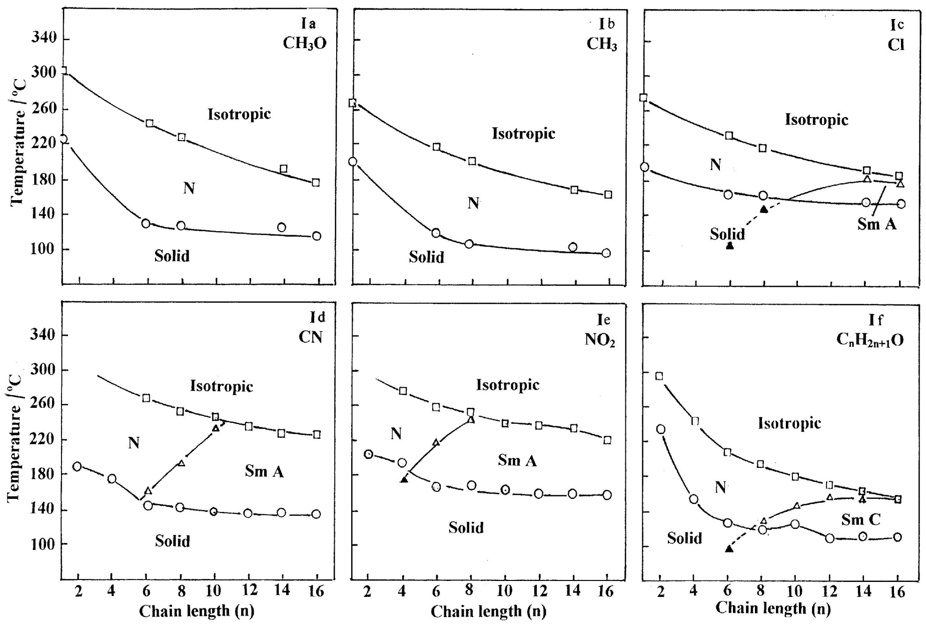
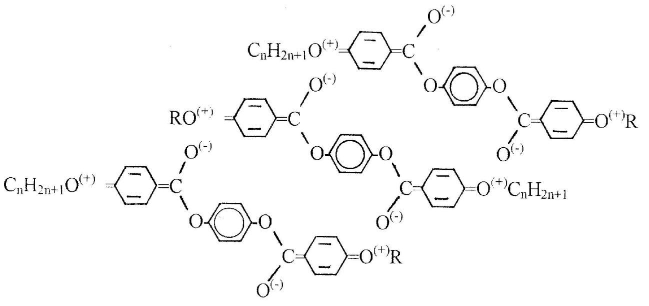
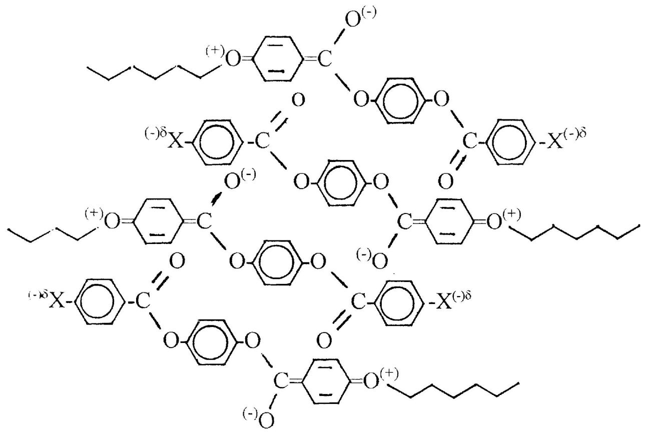


Figure 1. Dependence of transition temperatures on alkoxy chain length in the variously substituted homologous series **I**a, **I**b, **I**c, **I**d, **I**e, and **I**f.



R = CH_3 or C_nH_{2n+1}

Figure 2. Mode of intermolecular association in the alkoxy-substituted homologues, **I**a and **I**f.



X = Cl, CN, or NO_2

Figure 3. Mode of intermolecular association in the electron-withdrawing-substituted homologues, **I**c, **I**d and **I**e.

upon increasing the alkoxy chain length, leading to the formation of the nematic phase.

The methyl group, in **I**b, interacts only by the inductive effect, resulting in somewhat weaker forces, but sufficient to produce the nematic phase.

In the chloro derivatives **I**c, in addition to the nematic phase observed in the lower homologues ($n = 6$ and 8), the higher homologues exhibit the smectic A phase. The relatively high ΔH_C value ($\approx 0.93\,\mathrm{kJ\,mol^{-1}}$) for the lower homologue ($n = 6$), which reflects the strong intermolecular association, increases with increasing chain length [1] up to $\approx 2.7\,\mathrm{kJ\,mol^{-1}}$ for **I**16c as a result of increased lateral association and leads to the appearance of the smectic A phase.

The first two homologues ($n = 2$ and 4) of the cyano-substituted series (**I**d) exhibit only the nematic phase. but at and after $n = 6$, the smectic A phase is also observed, becoming the only mesophase at $n = 12$. In the lower homologues, the relatively small alkoxy group furnishes poor insulation against terminal attractions that preclude a smectic phase. As the size of the alkoxy group increases, in the higher homologues, these forces decrease while lateral intermolecular attractions (between the polymethylene chains) aggregate and a smectic phase appears. A comparison of the effect of the electron-withdrawing (Cl, CN, and NO_2) groups in the analogues **I**c–**I**e, respectively, with the electron-releasing CH_3O substituent in **I**a, on the mesophase stability of these compounds was made. This revealed that, due to the opposite effects on the polarity of the ester carbonyl group to which substituent is attached, in either case, there is a strong tendency in the NO_2 (and to a less extent in the CN and Cl) derivatives to lose molecular pairing [7, 8]; an anti-parallel alignment of molecules then occurs (see figure 3) and a smectic A phase is formed upon increasing the alkoxy-chain length, to an extent dependent on the polarity of the group.

For the nitro-substituted homologues ($\mathbf{I}_e$), the derivative with $n = 2$ shows only a nematic phase; the smectic A appears at $n = 4$ as a monotropic phase, while the nematic phase disappears with $n = 10$. The strong repulsive forces between the electron-attracting CN or (NO_2) terminal groups lead to relatively weak end-to-end association, a pre-requisite for smectic phase formation. Increasing chain length is associated with increasing lateral association, leading to smectic A phase appearance.

All homologues of the symmetrical 1,4-phenylene bis-(4-alkoxybenzoates), **I**f, with chain length up to 14 carbons, show the nematic phase. Homologues with $n = 8$ [9] and $n = 14$ carbons exhibit, in addition to the nematic phase, a smectic C phase. The smectic C phase alone is observed for the C_{16} homologue; a monotropic smectic C phase is also observed for the C_6 homologue [4]. Smectic C phases, for the newly prepared homologues, were identified by their textures as well as by mixing with the known homologue **I**8f (see figure 6). Although a similar intramolecular conjugative interaction exists in series **I**f to that in **I**a, the long chains on both sides of the molecule strengthen the lateral association that leads to the formation of the tilted smectic C phase (see figure 2).

Usually the smectic–nematic transition temperature curve initially rises steeply, with increasing chain length, as the increased lateral attractions resist the movement of molecules from one layer to another thus forming a smectic structure. However, an opposing effect occurs; namely, an increasing tendency for inter-penetration of the layers as the terminal alkyl chains grow longer and more flexible. The gradual rise in the latter portion of the curve (figure 1, **I**c–**I**f), can be explained by other ordinarily predominant effects. The relationship $\Delta H = T\Delta S$ holds at the smectic nematic transition, so that an increase in the transition temperature T with chain length indicates an increase in $\Delta H/\Delta S$. ΔH and ΔS reflect the changes occurring in the intermolecular forces and in the mesophase order, on passing from the smectic to the nematic mesophases, respectively. With successive addition of CH_2 units to the *n*-alkoxy end groups, intermolecular attractive forces increase in both mesophases, but more so in the more highly ordered, less mobile smectic phase, resulting in an increase in ΔH with chain length. There is also an increase in ΔS, as chain extension contributes more additional order to the well-organized smectic 'lattice' than to the relatively open molecular arrangement of the nematic phase. The enthalpy effect predominates, and the net result is an increasing transition temperature T.

3.1. *Binary mixtures of electron-releasing-substituted homologues*

Figures 4(*a–f*) represent the phase diagrams constructed for the six possible binary combinations prepared from the four methoxy-substituted analogues **I**6a–**I**16a. Irrespective of the difference between the alkoxy chain length of the two components in any binary system, all mixtures possess only the nematic mesophase, and their solid–nematic (T_m) as well as nematic isotropic (T_C) transition temperatures vary more or less linearly with composition. It can also be seen from figure 4 that, in all cases, the mesomorphic range ($\Delta T = T_C - T_m$) varies regularly with composition without passing a maximum, indicating the formation of ideal solid solutions. This finding, together with the regular T_m–composition dependence, shows that, irrespective of the alkoxy chain length, all pure solid homologues of this series are of similar crystalline structure and of comparable intermolecular forces of association. As pointed out above, these forces are strong enough to be significantly influenced by chain length and to produce a smectic phase.

The corresponding binary phase diagrams of the homologous series **I**b are represented graphically in figures 5(*a–f*). Since each of the homologues in this series bears the electron-donating CH_3 group, they were expected to give similar binary phase behaviour to those of series **I**a. In contrast, except for the last mixture (**I**14b/**I**16b), these systems exhibit eutectic solid behaviour. This was shown by its ΔT–composition dependence that passes through a maximum in the first five mixtures but varies regularly with composition in the last one. Such behaviour may be explained in terms of intermolecular forces existing in their solid states. Since the CH_3 group is of less electron-donating character than the CH_3O group, intermolecular forces in compounds **I**b are weaker than those in **I**a, as shown by their low T_m values. Such weak forces are significantly influenced by the increase in chain length, resulting in compounds with different crystalline structure, depending on chain length; consequently their mixtures exhibit eutectic behaviour. As the chain length increases to $n = 14$ and 16, in the last two homologues, the intermolecular forces become comparable and their mixed solids behave ideally. As for the binary phase diagrams of the methoxy-substituted homologues, the phase diagrams of the **I**b homologues are characterized by the nematic phase as the only mesophase, and by a nearly linear T_C–composition dependence.

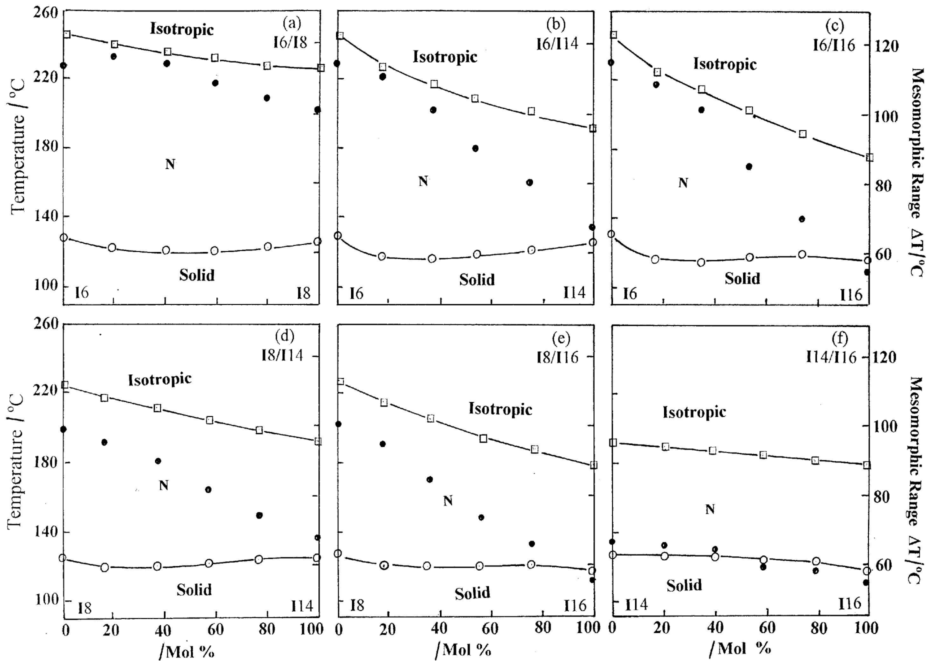


Figure 4. Binary phase diagrams for mixtures of the methoxy-substituted homologues: (*a*) **I**6a/**I**8a, (*b*) **I**6a/**I**14a, (*c*) **I**6a/**I**16a, (*d*) **I**8a/**I**14a, (*e*) **I**8a/**I**16a and (*f*) **I**14a/**I**16a.

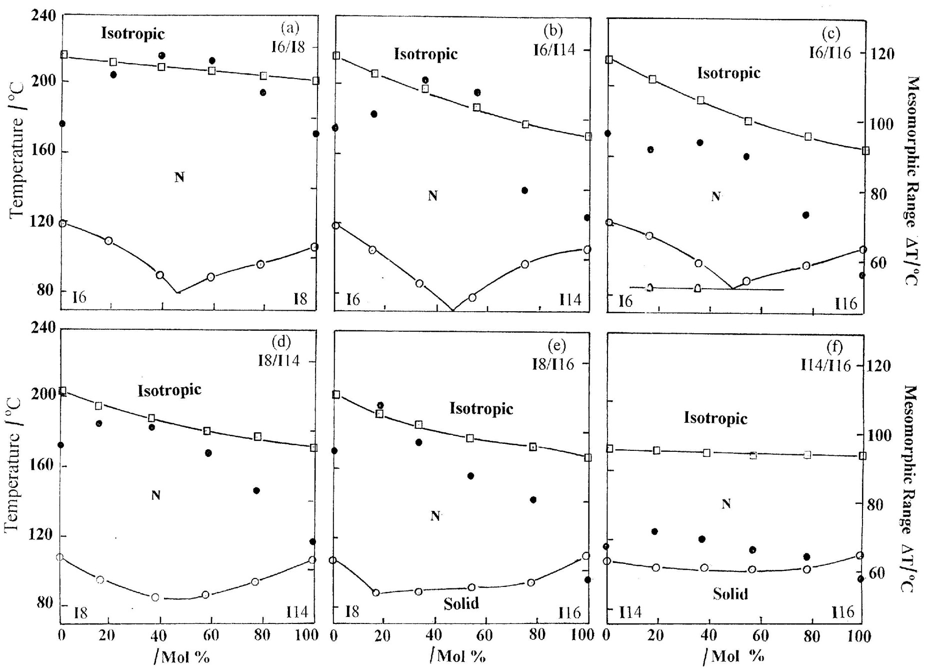


Figure 5. Binary phase diagrams for the mixtures of the methyl-substituted homologues: (*a*) I6b/I8b, (*b*) I6b/I14b, (*c*) I6b/I16b, (*d*) I8b/I14b, (*e*) I8b/I16b and (*f*) I14b/I16b.

Since the alkoxy group in the **I**f homologues affects their behaviour to an extent different from those in **I**a, their binary phase diagrams are expected also to be different. Figures 6 (*a–f*) show the binary phase diagrams constructed for the binary systems of homologues **I**f. Except for the binary mixture **I**14f/**I**16f, all the systems are found to exhibit eutectic behaviour indicating that, in mixtures possessing either of the lower homologues

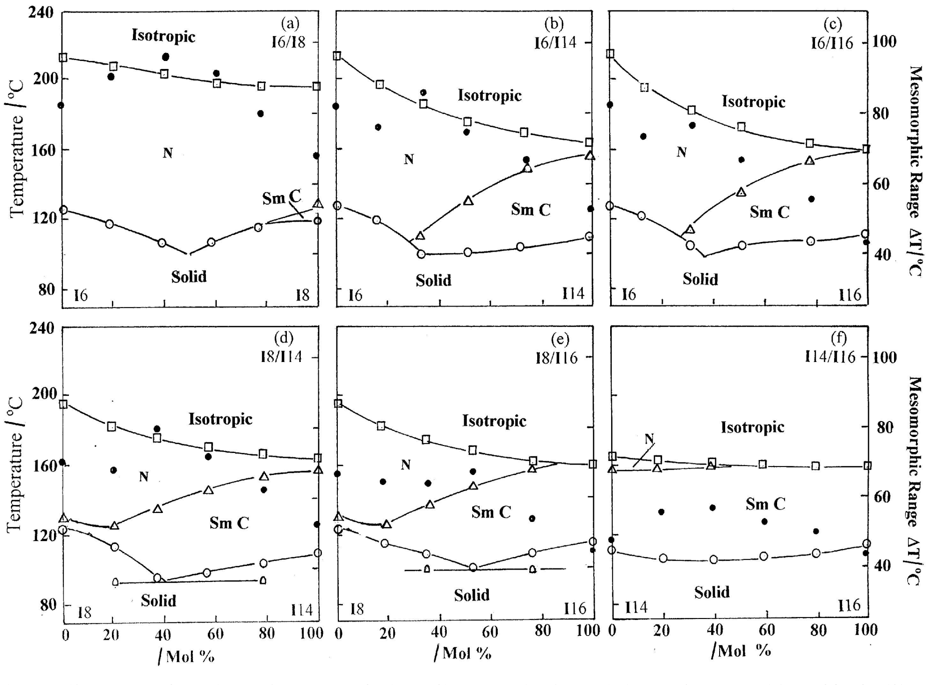


Figure 6. Binary phase diagrams for the mixtures of the alkoxy-substituted homologues: (*a*) I6f/I8f, (*b*) I6f/I14f, (*c*) I6f/I16f, (*d*) I8f/I14f, (*e*) I8f/I16f and (*f*) I14/I16.

C_6 or C_8, each component of these mixtures exhibits a different crystalline structure. Conversely, the ideal solid solution behaviour observed for the binary mixture of the higher homologues ($n = 14$ and 16) shows that the increase in intermolecular forces induced by lengthening the alkoxy group levelled off after $n = 14$ carbons. It is also observed from figure 6 that all the binary systems investigated exhibit the smectic C and nematic phases to varying extents.

3.2. *Binary mixtures of electron-withdrawing-substituted homologues*

Since the chlorine atom interacts mesomerically as an electron-releasing group and inductively as electron-attracting group, it occupies an intermediate position between the electron-donating (CH_3O and CH_3) and electron-attracting (CN and NO_2) substituents. The six possible binary phase diagrams, made from the four chlorine-substituted homologues, are represented collectively in figures 7(*a–f*). All the phase diagrams show ideal solution behaviour, either in the solid or the mesophase. This reflects the very similar behaviour of all the components. Since the lower homologues, **I**6c and **I**8c, do not exhibit a smectic phase, their binary mixtures show only a nematic phase. On the other hand, the binary mixtures of the higher (**I**14c and **I**16c) two homologues show both smectic A and nematic mesophases throughout the whole composition range, figure 7(*f*); the two homologues form ideal solutions either in the solid, smectic or nematic phase, again indicating similar effects on intermolecular forces induced by the C_{14} and C_{16} alkoxy chains. In the remaining diagrams 7(*b–e*), the smectic A phase of the higher homologues ($n = 14$ or 16) is totally destroyed by the addition of the lower homologues ($n = 6$ or 8) in an amount dependent on chain length.

Similarly, either of the electron-withdrawing groups (CN and NO_2) affects the binary phase behaviour, but to a different extent, in favour of smectic A formation; see figures 8(*a–f*) and 9(*a–f*). Mixtures of the lower homologues ($n = 6$ and 8) exhibit both smectic A and nematic mesophases throughout the whole composition range, while those of the higher homologues ($n = 14$ and 16) possess only the smectic A phase. Mixtures of other homologues display the smectic A phase within a certain range of composition. The nitro group is found to be more efficient than the cyano, in promoting the smectic phase, while the mesomorphic range (ΔT) in the cyano analogues is wider than in the nitro compounds.

4. Conclusion

Binary mixtures were independently prepared from the various homologues of the unsymmetrical 1,4-phenylene bis(4-substituted benzoates), and characterized for their phase behaviour. Two types of substituent were used: an alkoxy group of varying chain length and a small compact polar group, X. All the compounds investigated were found to possess high transition temperatures,

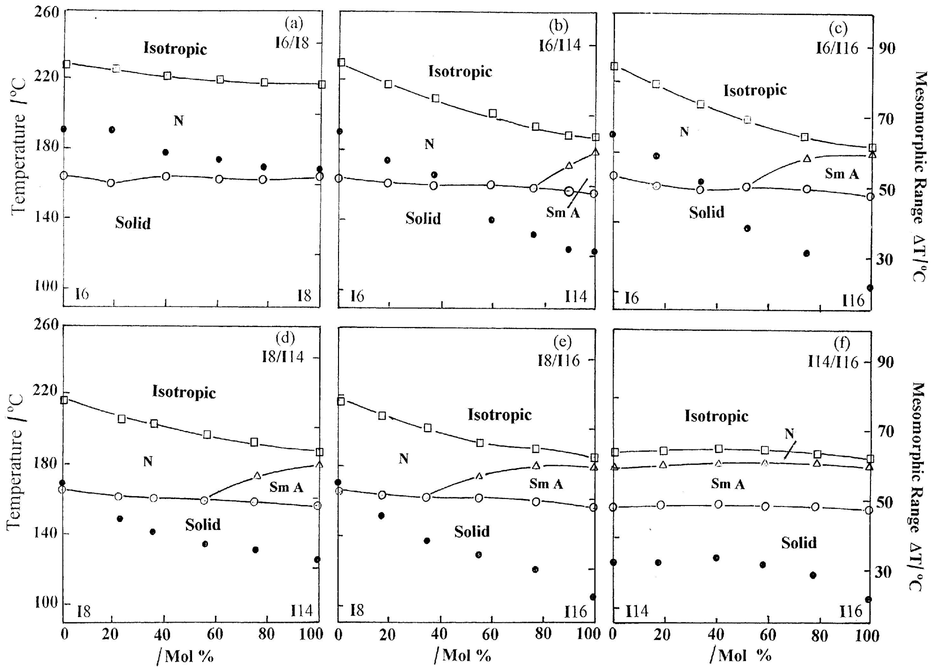


Figure 7. Binary phase diagrams for the mixtures of the chloro-substituted homologues: (*a*) **I**6c/**I**8c, (*b*) **I**6c/**I**14c, (*c*) **I**6c/**I**16c, (*d*) **I**8c/**I**14c, (*e*) **I**8c/**I**16c and (*f*) **I**14c/**I**16c.

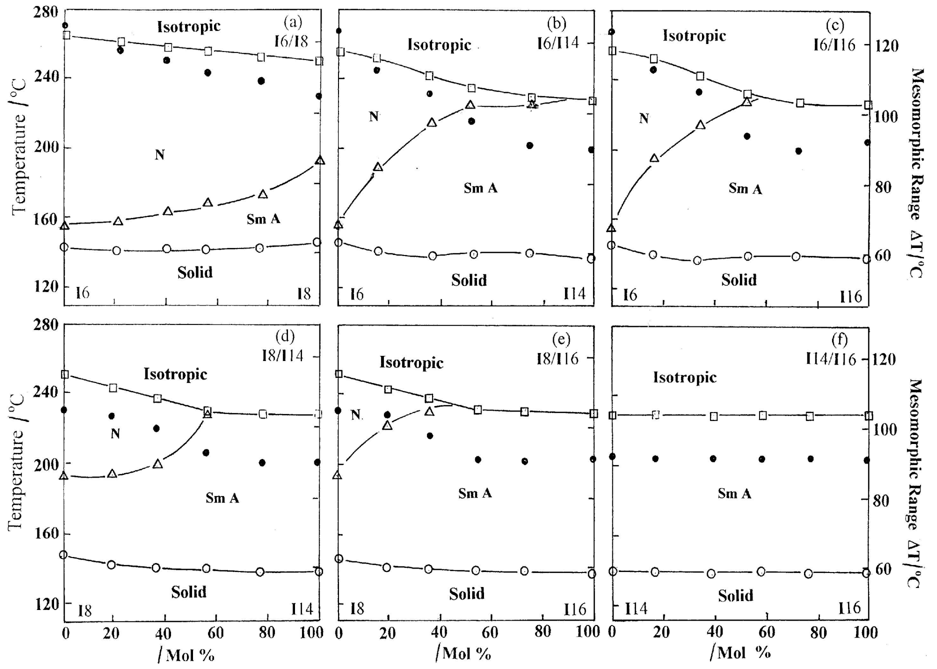


Figure 8. Binary phase diagrams for the mixtures of the cyano-substituted homologues: (*a*) I6d/I8d, (*b*) I6d/I14d, (*c*) I6d/I16d, (*d*) I8d/I14d, (*e*) I8d/I16d and (*f*) I14d/I16d.

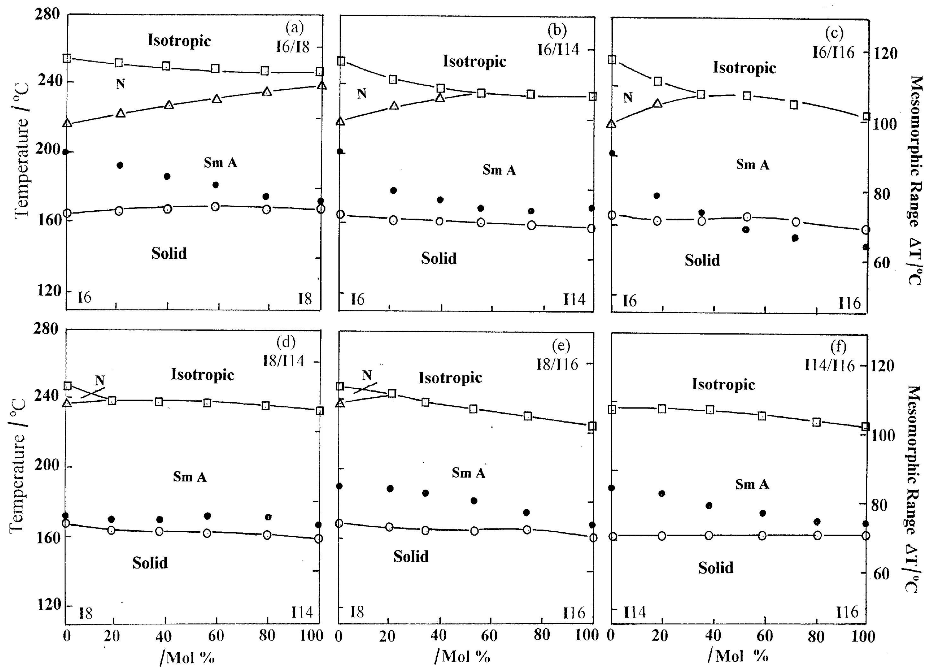


Figure 9. Binary phase diagrams for the mixtures of the nitro-substituted homologues: (*a*) I6e/I8e, (*b*) I6e/I14e, (*c*) I6e/I16e, (*d*) I8e/I14e, (*e*) I8b/I16b and (*f*) I14e/I16e.

indicating strong intermolecular forces of association either in the solid or mesophases. Conjugation between the alkoxy and one of 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 second ester carbonyl group. The effect of increasing chain length on the mesophase behaviour, either of pure homologues or of their binary mixtures, was found to depend significantly on the electronic nature of the substituent *X*.

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