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Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures

XI. Binary mixtures of unsymmetrical 1,4-phenylene bis-(4-substituted benzoates)[†]

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Binary mixtures formed from components of the four series of unsymmetrical 1,4-phenylene bis-4-substituted benzoates, in which one substituent is a terminal alkoxy group with a number of carbon atoms kept constant (at $n = 6, 8, 14$ and 16) while the other substituent (X) ranges through CH_3O , CH_3 , Cl , CN and NO_2 , were prepared and characterized for their mesophase behaviour. Transition temperatures of the mixtures prepared were measured by differential scanning calorimetry and identified by polarizing optical microscopy. Phase diagrams for the various binary combinations were constructed to investigate the dependence of the phase behaviour of mixed systems upon the electronic nature of the terminal group X , as well as on the chain length of the alkoxy group. The results are discussed in terms of mesomeric and polarizability effects.

1. Introduction

Liquid crystalline phenomena are exhibited by compounds having rigid, polar, and rod-shaped molecules, which tend to orient with their long axes parallel owing to forces of mutual attraction. On heating such a substance, the crystalline solid melts to an anisotropic liquid (the mesophase) in which adjoining molecules lie parallel to one another. As is true for other solids, the melting point of a mesomorphic compound is depressed by the addition of another substance, and a mixed mesophase results in which the liquid crystalline range begins at a lower temperature. If the added substance is structurally dissimilar to the host compound and does not show a mesophase, only a small amount suffices to destroy liquid crystallinity of the host because of its disrupting effect on the mesophase [2]. If however, it is structurally similar, liquid crystallinity may persist to a high concentration of the second component and, in fact, over all compositions if both components are mesomorphic [3–5]. This is understandable in that rod-shaped, polar molecules, which meet the fundamental criteria for liquid crystallinity, would be expected to adapt more readily to parallel alignment in a mixed mesophase than would bulky, non-polar molecules.

Most binary mesophase systems exhibit mesophase-isotropic transition temperatures (T_c) that are linearly dependent on composition; in some cases, however, there are exceptions. Binary mesophase systems, in which a bimolecular smectic is mixed with one that perturbs the molecular complexing of the pure bimolecular smectic, will exhibit non-linear thermal behaviour. An example would be found in the addition of compounds with electron-rich aromatic rings, which can successfully compete for molecular complexation with an electron-deficient ring of another molecule [4, 5]. On the other hand, one would expect that compounds with similar smectic layering characteristics should, when mixed with each other, exhibit thermal behaviour that is linear with concentration.

In previous studies [4, 5], the effect of terminal substituent and inversion of the central $-\text{COO}-$ group on the mesophase stability of unsymmetrically di-substituted phenyl benzoates and their binary mixtures, was investigated. Generally the stability of the mesophase is greater, the greater the lateral adhesion of the rod-shaped molecules in question which, in turn, is greater the greater the polarity and/or the polarizability of the central part of the molecule. Introducing a second $-\text{C}_6\text{H}_4\text{COO}-$ group to the phenyl benzoate molecule would definitely enhance both these factors. *p*-Phenylene-di-*n*-alkoxybenzoates have been shown to exhibit mesophases with broad ranges terminating at high temperatures [6–8]. The

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[†] For part X, see reference [1].

introduction of very different alkoxy groups, e.g. CH₃O and *n*-C₈H₁₇O [9], or the replacement of one alkoxy end group by Cl, NO₂, or CN [7] would greatly affect the mesophase stability of the compound. Such systems would, therefore, be excellent for an extensive study of the effects of structural changes on the mesophase behaviour of pure compounds or their mixed systems.

The objective of this work is to investigate the mesomorphic behaviour in binary mixtures of the previously prepared [1] four series of compounds (**I6–I16**) that differ from each other in the chain length of the alkoxy group. The substituents were chosen to cover a wide range of electronic and dipolar characteristics representing extremes in the conjugated interactions between the substituent *X* and the carbonyl group.

Ia-e

I6, *n* = 6; **I8**, *n* = 8; **I14**, *n* = 14; **I16**, *n* = 16
 a, *X* = CH₃O; b, *X* = CH₃; c, *X* = Cl; d, *X* = CN; e, *X* = NO₂

2. Experimental

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

2.1. Preparation of materials

2.1.1. 4-*n*-Alkoxybenzoic acids

Ethyl-4-*n*-alkoxybenzoates were first prepared from ethyl-4-hydroxybenzoate and the appropriate 1-bromo-*n*-alkane; the esters were then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described previously [4]. The resulting acids were TLC pure and exhibited phase transition temperatures agreeing with those reported in the literature [10].

2.1.2. 4-*n*-Alkoxybenzoyl chlorides

These were prepared from the acids by heating with excess thionyl chloride under reflux for 5 h. The unused thionyl chloride was removed under vacuum to give the acid chloride as residue.

2.1.3. 4-Hydroxyphenyl 4-*n*-alkoxybenzoates

One molar equivalent of the 4-*n*-alkoxybenzoyl chloride in dry pyridine was added drop-wise to a solution of hydroquinone in dry pyridine over a period of 1 h and the resulting mixture was heated overnight with stirring at 60°C. The products were fractionally crystallized from ethanol to separate the mono- (more soluble) from the di-esters (less soluble). Both products were column purified over silica gel using dichloromethane as the eluent, and finally recrystallized from ethanol. The products had melting points that agreed with those reported in the literature [9, 11].

2.1.4. 1,4-Phenylene-bis-4-substituted benzoates

One molar equivalent of the 4-substituted benzoyl chloride in dry pyridine was added drop-wise with stirring to a solution of 4-hydroxyphenyl 4-*n*-alkoxybenzoate in dry pyridine and the reaction was continued as described in the previous section. The products, after two recrystallizations from acetic acid, were TLC pure, and gave melting points that agreed with those reported previously [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, and a value of 28.45 J g⁻¹ was used for the enthalpy of fusion of indium. The typical heating rate was 10 K min⁻¹, and a sample mass was 2–3 mg. Transition temperatures were identified with a standard polarized-light microscope (C. Zeiss, Germany), attached to a FB 52 hot stage equipped with a FB 80 central processor (Mettler, Switzerland).

Thin layer chromatography 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

It is known that one way to prepare a liquid crystalline material that retains its mesophase over a wide range of temperature, starting at low temperature, is to use eutectic mixtures of compounds exhibiting liquid crystallinity in their pure state. It was therefore decided to examine the mesophase behaviour of various binary combinations made from members of the four series (**I6a–e–I16a–e**). Transition temperatures of these compounds in their pure states, as reported previously [1, 9, 12–14], are summarized in the table. The methoxy and methyl (electron-donating) substituted homologues in the four series (**I6–I16**) possess only the nematic phase (N). The nitro and cyano (electron-withdrawing) analogues, on the other hand, exhibit a smectic A phase (SmA) in addition to the nematic phase, in the lower homologues (**I6** and **I8**) only. The chloro derivatives, with intermediate electronic nature, occupy an intermediate position; i.e. the lower homologues (**I6c** and **I8c**) exhibit only the nematic phase, while their higher homologues (**I14c** and **I16c**) exhibit the SmA phase together with small nematic range; these nematic ranges are 9.3 and 2.5°C, respectively. In the table the following symbols are given for the various transition temperatures: crystal–smectic A ($T_{C,A}$), crystal–nematic ($T_{C,N}$), smectic A–nematic ($T_{A,N}$), smectic A–isotropic ($T_{A,I}$), and nematic–isotropic ($T_{N,I}$). It can be seen from the table

Table. Transition temperatures and mesophase (in °C) range for compounds (**16a-e**–**116a-e**). For key, see text.

4-C _n H _{2n+1} O-C ₆ H ₄ -COO-C ₆ H ₄ -OOC-C ₆ H ₄ -X-4									
Compound	<i>n</i>	<i>X</i>	<i>T</i> _{C-A}	<i>T</i> _{C-N}	<i>T</i> _{A-N}	<i>T</i> _{A-I}	<i>T</i> _{N-I}	Δ <i>T</i>	Ref.
16a	6	CH ₃ O	—	129.9	—	—	244.6	114.7	[9]
16b	6	CH ₃	—	119.9	—	—	218.9	99.0	[1]
16c	6	Cl	—	165.4	—	—	231.7	66.3	[1]
16d	6	CN	146.7	—	161.1	—	268.6	121.9	[13]
16e	6	NO ₂	165.4	—	219.0	—	256.7	91.31	[12]
18a	8	CH ₃ O	—	126.3	—	—	227.7	101.4	[9]
18b	8	CH ₃	—	107.2	—	—	203.3	96.1	[14]
18c	8	Cl	—	165.2	—	—	218.0	52.8	[14]
18d	8	CN	145.2	—	193.0	—	253.9	108.7	[13]
18e	8	NO ₂	168.2	—	241.0	—	246.7	78.5	[14]
114a	14	CH ₃ O	—	125.6	—	—	193.2	67.6	[1]
114b	14	CH ₃	—	105.0	—	—	172.5	67.5	[1]
114c	14	Cl	157.4	—	180.9	—	190.2	32.8	[1]
114d	14	CN	138.6	—	—	230.2	—	91.6	[1]
114e	14	NO ₂	160.0	—	—	235.1	—	75.1	[1]
116a	16	CH ₃ O	—	115.5	—	—	178.1	62.6	[1]
116b	16	CH ₃	—	109.1	—	—	166.5	57.4	[1]
116c	16	Cl	157.2	—	182.1	—	184.6	27.4	[1]
116d	16	CN	136.5	—	—	229.7	—	93.2	[1]
116e	16	NO ₂	159.4	—	—	222.2	—	62.8	[1]

that all compounds investigated are of high melting (*T_m*) and clearing (*T_c*) points, and that the mesophase range (Δ*T* = *T_m* – *T_c*) for any derivative decreases as the chain length of the alkoxy group is increased. Furthermore, within any series, the cyano derivative possesses the greatest mesomorphic range, while the chloro analogue exhibits the lowest value.

3.1. Binary mixtures of electron-releasing substituted compounds (**1a,b**)

Figure 1(a–d) represents the phase diagrams constructed for the four binary mixtures prepared from the methoxy and methyl substituted compounds in the four series **16** to **116**, respectively. All the diagrams are remarkably similar, each exhibits eutectic behaviour in their solid–mesophase transition temperatures (*T_m*), while their mesophase–isotropic transition temperatures (*T_c*) vary more or less linearly with composition, irrespective of the alkoxy chain length, indicating that this exerts a similar effect in the molecules being compared. In all four diagrams, only the nematic phase was observed. Such simple binary phase behaviour is expected since both components bear a substituent with compatible electronic nature, i.e. both have an electron-donating nature. It can also be seen from figure 1 that the mesomorphic range (Δ*T* = *T_m* – *T_c*) decreases as the alkoxy chain length is increased. This suggests that as the alkoxy end group becomes larger, its diluent effect becomes dominant over polarity variation within the centres of the molecules.

3.2. Mixtures of electron-withdrawing substituted derivatives (**1c-e**)

For each of the four series, three possible binary systems could be obtained from the three electron-withdrawing (Cl, CN, and NO₂) substituted derivatives (**1c**, **1d**, and **1e**). The phase diagrams of the binary mixtures **1c/1d**, **1c/1e**, and **1d/1e** are illustrated in figures 2–4, respectively. Referring to figure 4, the phase diagrams of the nitro and cyano derivatives each show near-ideal solution behaviour in the mixed solid, mesophase, or liquid phase. These results reflect the nearly similar behaviour effected by substituents of closely related electronic nature. Both components of the mixture exhibit polymorphic phase behaviour in their lower (**16d,e** and **18d,e**) homologues; that is, each melts to a SmA phase that transforms to nematic at higher temperature and thence to the isotropic liquid. For the higher (**114d,e** and **116d,e**) homologues only SmA phases are observed. The gradual increase in the melting point of the nitro-terminated derivatives by the addition of the cyano compound suggests the formation of solid solutions. This indicates the resemblance of crystal structure between the solid nitro and cyano substituted derivatives bearing the same alkoxy group. Such similar, and strong, intermolecular attractions are retained in the mesophase, whether it is nematic or smectic. It can further be noted from figure 4 that the mesomorphic range decreases as the alkoxy chain is lengthened. This finding again reveals that, for a given system with definite polarity interactions, the diluent effect upon increasing alkoxy chain

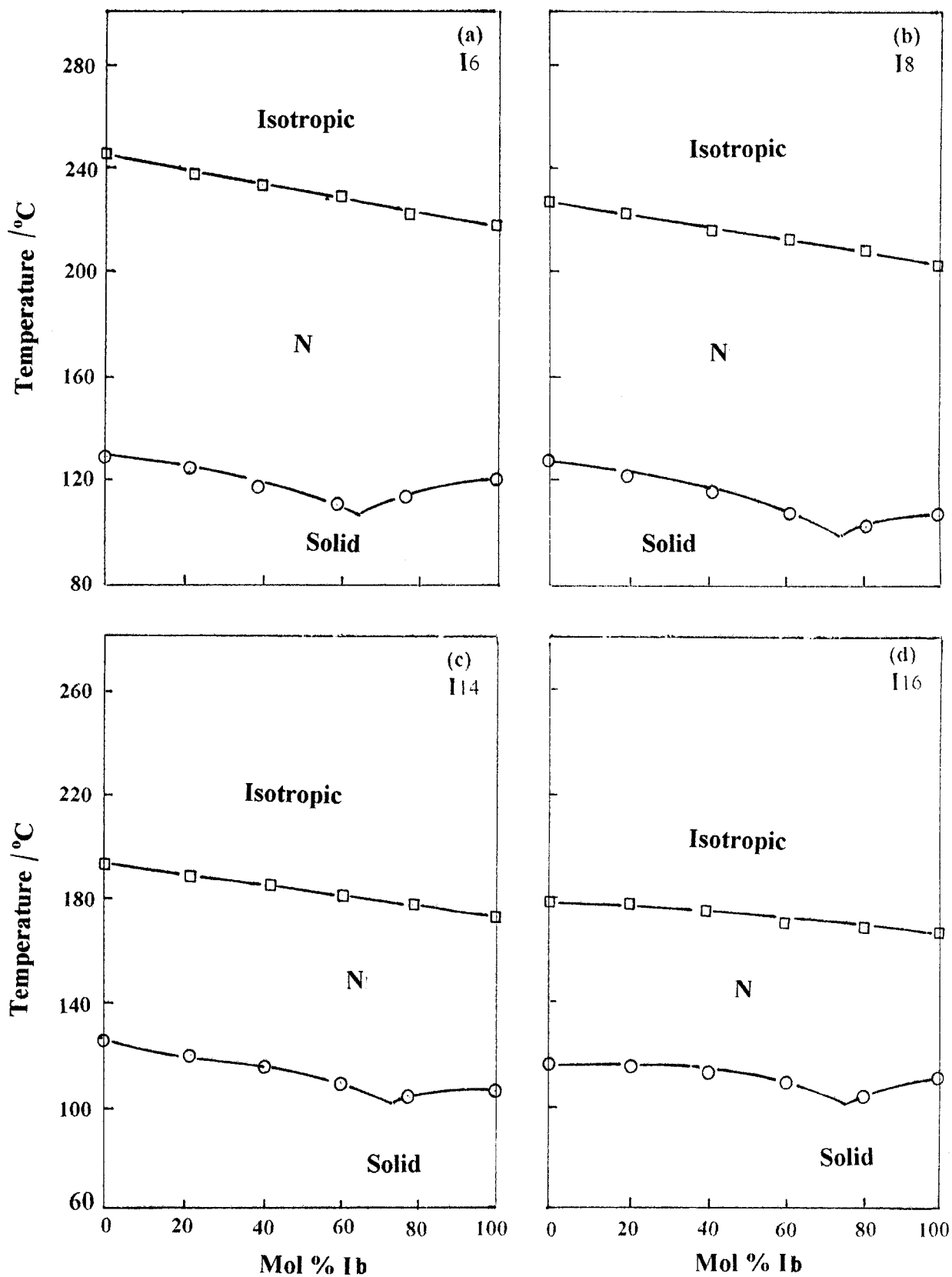


Figure 1. Phase diagrams for the binary mixtures of the methoxy and methyl substituted derivatives: (a) **I6a/I6b**, (b) **I8a/I8b**, (c) **I14a/I14b**, (d) **I16a/I16b**.

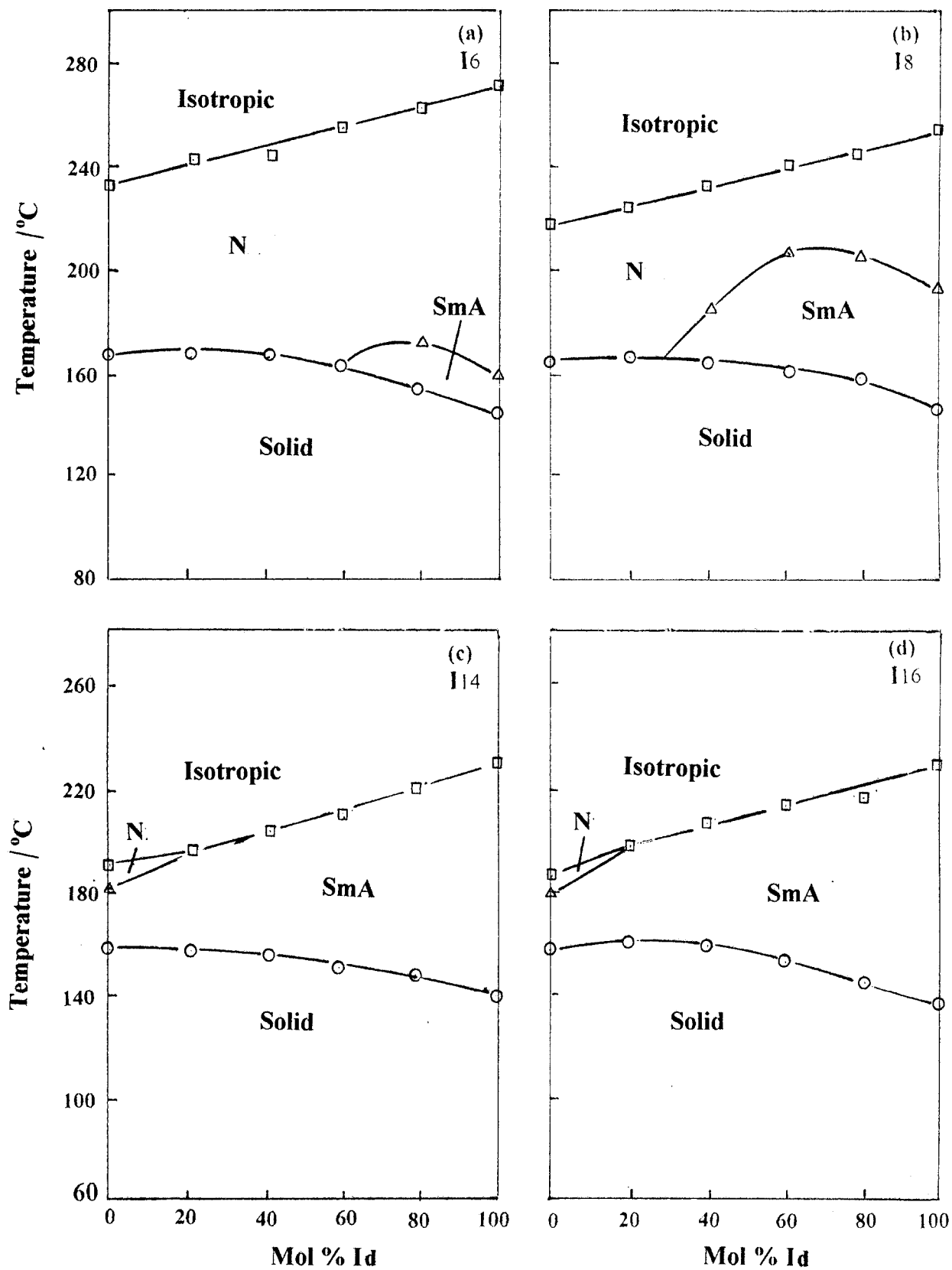


Figure 2. Phase diagrams for the binary mixtures of the chloro and cyano substituted derivatives: (a) I6c/I6d, (b) I8c/I8d, (c) I14c/I14d, (d) I16c/I16d.

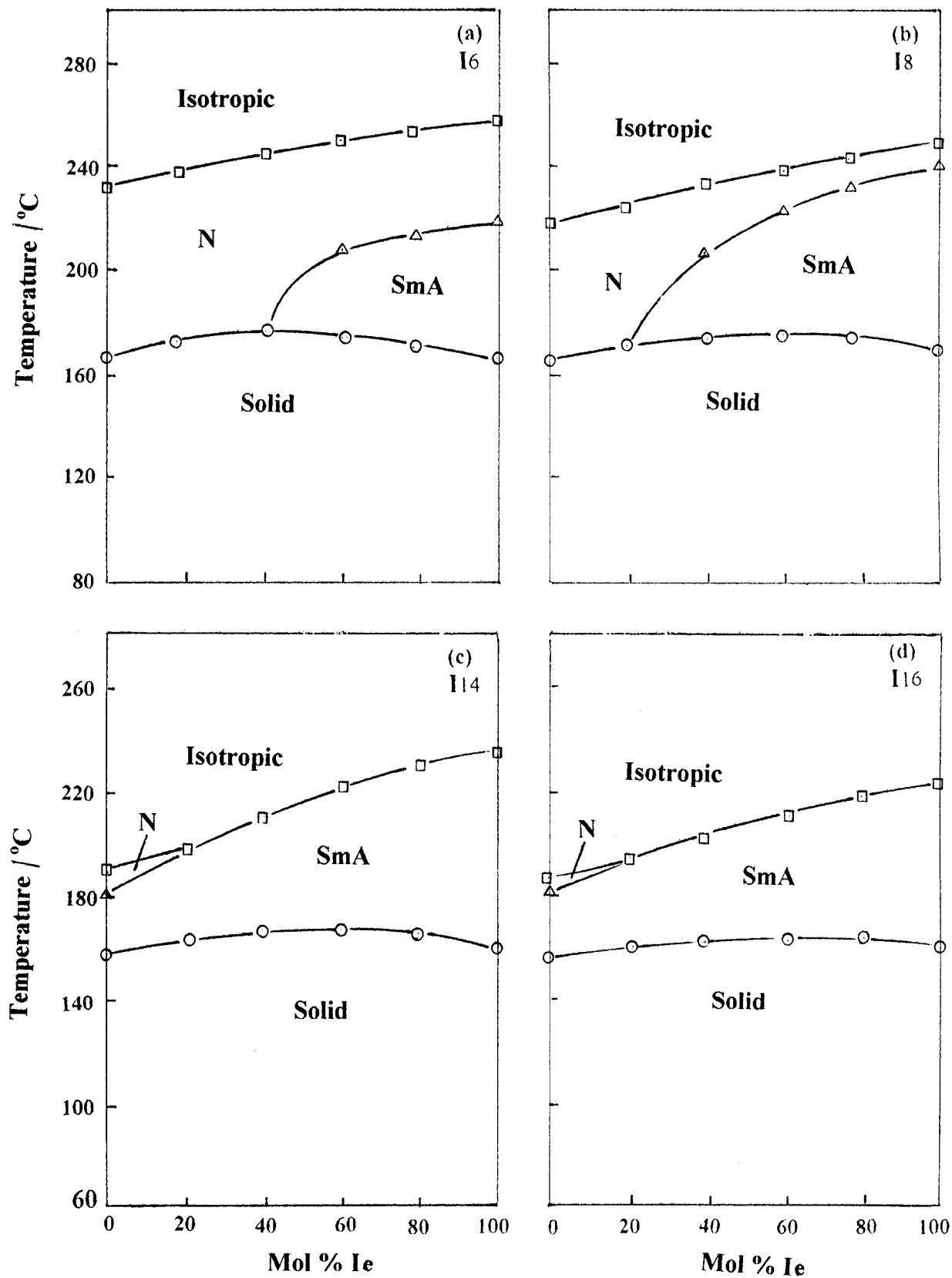


Figure 3. Phase diagrams for the binary mixtures of the chloro and nitro substituted derivatives: (a) I6c/I6e, (b) I8c/I8e, (c) I14c/I14e, (d) I16c/I16e.

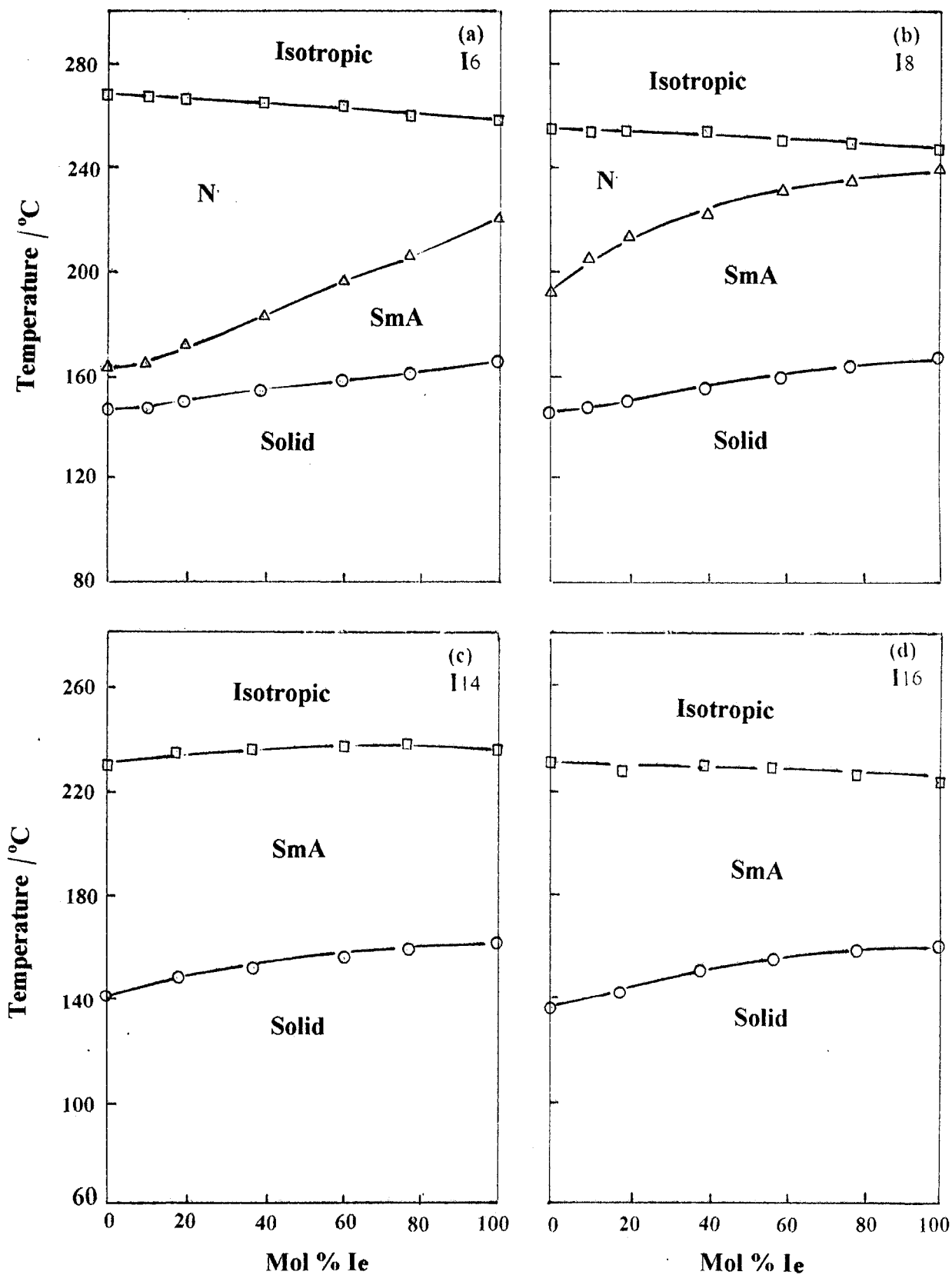


Figure 4. Phase diagrams for the binary mixtures of the cyano and nitro substituted derivatives: (a) I6d/I6e, (b) I8d/I8e, (c) I14d/I14e, (d) I16d/I16e.

length becomes dominant over polarity variation within molecules of this particular binary system.

In the other two systems, **Ic/IId** and **Ic/Ie**, the chloro derivative **Ic** is common (figures 2 and 3). Since there exists a difference in the electronic nature between the chlorine atom, from one side, and the cyano or nitro group, from the other side, complex phase diagrams are obtained. This is attributed to differences in the phase behaviour of the pure components. As mentioned above, the cyano and nitro analogues exhibit SmA and N mesophases in their **I6** and **I8** series, and only the SmA phase in the other **I14** and **I16** series. The chloro derivatives are monomorphic exhibiting only the N phase in their **I6** and **I8** analogues, while the higher **I14** and **I16** analogues are polymorphic, exhibiting, in addition to the SmA phase, a narrow temperature range nematic. Consequently, their binary phase diagrams (figure 2) with the cyano derivatives, i.e. **Ic/IId**, exhibit a small composition range of smectic A phase that is destroyed by the addition of 40 and 70 mol % of **Ic** in the series **I6** and **I8**, respectively. In the higher series, the nematic phase of **Ic** disappears on the addition of ≈ 20 mol % of **IId**. In all cases T_c varies almost linearly with composition, whereas a gradual increase in T_m of **Ic** is observed upon the addition of **IId**. This again reflects the resemblance of the crystal structures and molecular forces existing within the solid phase in each pair of components, and the similarity between the crystal lattices of the solids and the molecular arrangements in the mesophase to which they melt.

Similar phase behaviour was observed in the case of the binary mixtures **Ic/Ie** formed from the chloro and nitro substituted derivatives (figure 3), except that the SmA mesophase of the nitro component **Ie** is retained up to the addition of 60 and 80 mol % of **Ic** in the lower two series **I6** and **I8**, respectively.

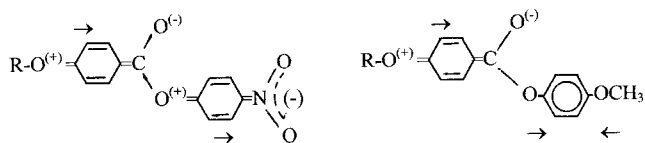
3.3. Mixtures of compounds bearing electron-withdrawing and electron-donating groups

The phase diagrams constructed for binary mixtures of components one bearing electron-donating (CH_3O or CH_3) groups, i.e. **Ia** and **Ib**, and the other bearing electron-withdrawing (Cl, CN, or NO_2) groups, i.e. **Ic**, **IId**, or **Ie**, are presented in figures 5–10. Figures 5 and 6, which illustrate the phase diagrams of binary mixtures composed from the CH_3O or CH_3 substituted compounds, as one component, and the chloro derivative as the second, show that they are of typical eutectic type with almost linear T_c -composition dependence. This indicates that the similar electronic nature of the two electron-donating groups (CH_3O or CH_3) would have similar effects on their mixed phase behaviour with the chloro analogue **Ic**. Furthermore, it can be observed from figures 5 and 6, that in the lower **I6** and **I8** series,

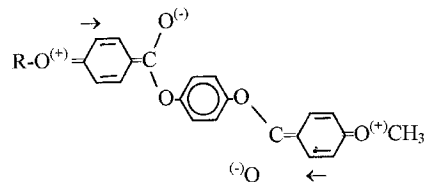
only nematic phase ranges were observed, while in the higher series, nematic phases are produced with a small composition range of SmA mesophase. In the **I14** series the SmA mesophase of the chloro derivative **I14c** totally disappeared upon the addition of ≈ 20 mol % of **I14a** or **I14b**. In the higher series, **I16**, the SmA mesophase of **I16c** is retained up to the addition of ≈ 40 mol % of **I16a** or **I16b**.

As for the mixtures of either **Ia** or **Ib** with **IId** or **Ie** (figures 7–10) the diagrams for the lower series (**I6** and **I8**) are characterized by (i) linear T_c -composition dependence, (ii) eutectic melting behaviour, (iii) largely nematic mesophase, with small composition ranges of SmA, for mixtures possessing low concentrations of **Ia** or **Ib**. For the higher series (**I14** and **I16**), the clearing points suffers a non-linear composition dependence due to the complexity of the mesophase. The range of composition for the SmA mesophase increases and the solids exhibit eutectic behaviour. In all cases, the mesomorphic temperature range decreases as the alkoxy chain length increases.

Irrespective of the alkoxy chain length, all phase diagrams (figures 5–10) constructed for binary systems composed from an electron-donating substituted component (i.e. electron-rich) with another bearing an electron-withdrawing group (i.e. electron-deficient), unexpectedly exhibit negligible deviation from the linear T_c -composition dependence. In contrast, in simpler molecules, namely, 4-substituted phenyl 4'-alkoxybenzoates [5], the difference between the nitro and methoxy substituted derivatives, with respect to the mesomeric interaction within the molecule, has led to a significant difference in the electron density on the mesogenic portion of the molecule concerned, and consequently to a significant positive deviation in their mixtures. The latter indicates the formation of a donor-acceptor complex between electron-rich and electron deficient molecules.



In our investigated compounds, both electron-donating, the CH_3O (or CH_3) and alkoxy, groups on both sides of the molecule would lead to an increase of electron density at the centre of the mesogenic group, thus leaving the two terminals with nearly equal positive charges.



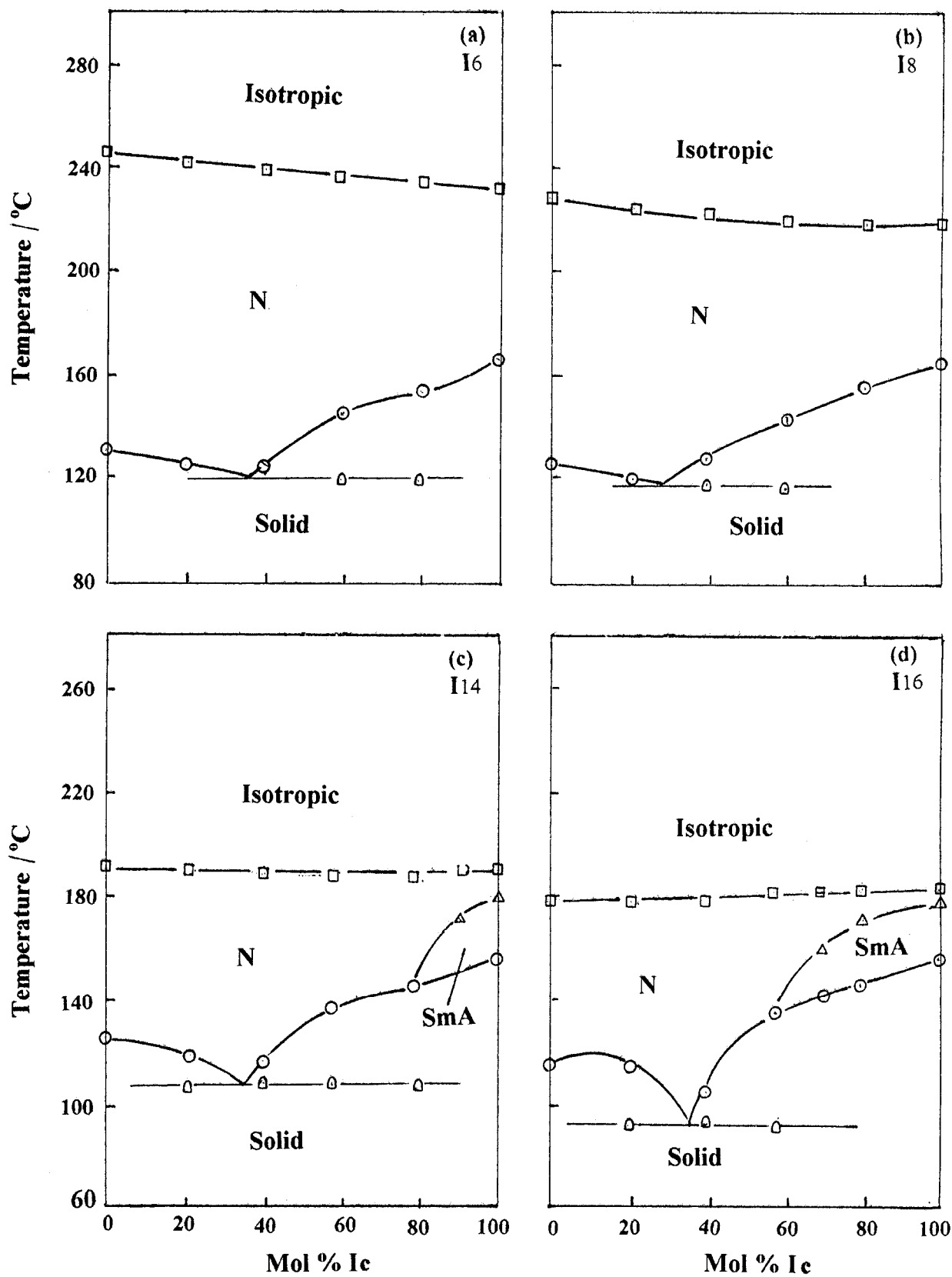


Figure 5. Phase diagrams for the binary mixtures of the methoxy and chloro substituted derivatives: (a) I6a/I6c, (b) I8a/I8c, (c) I14a/I14c, (d) I16a/I16c.

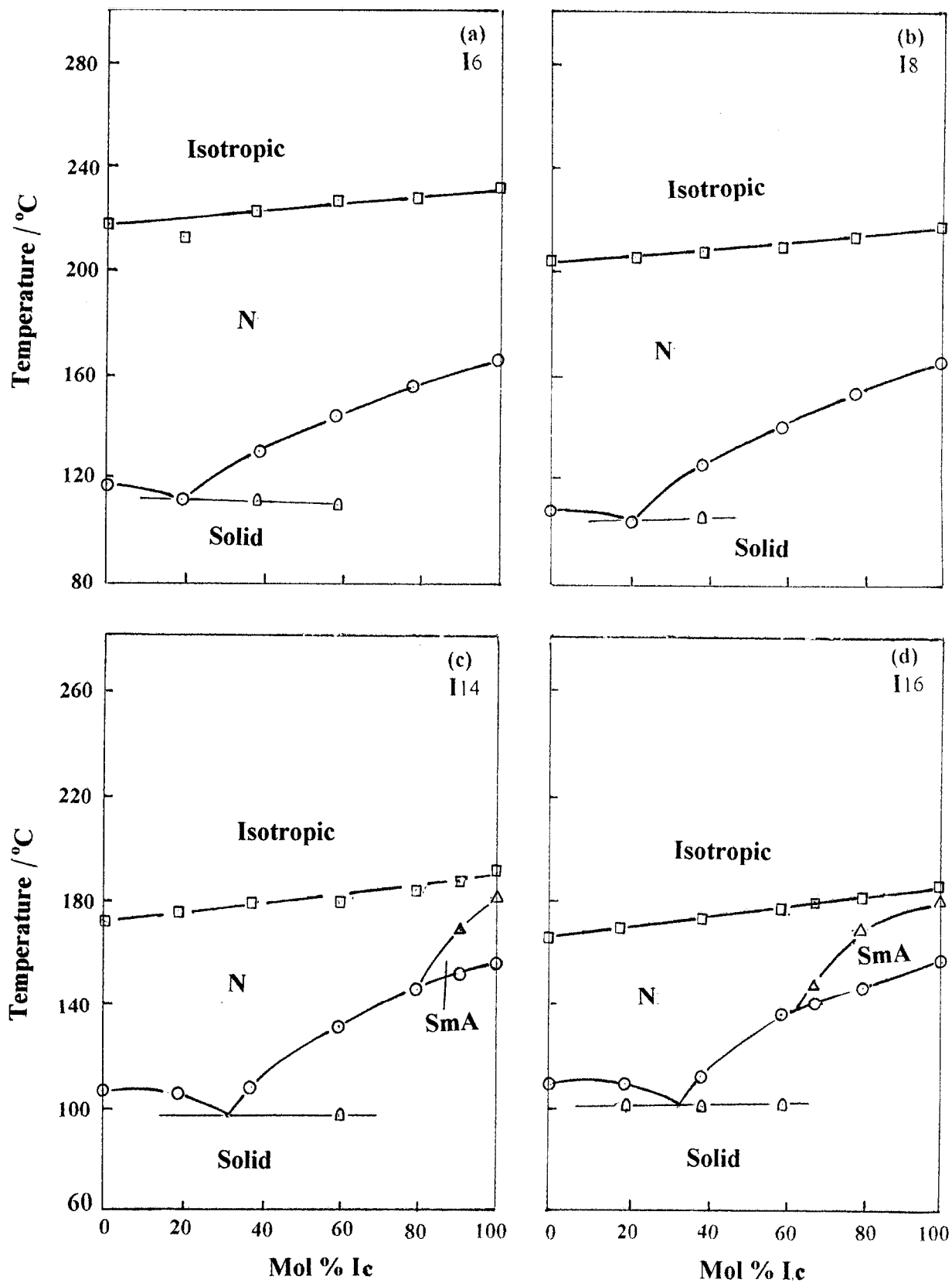


Figure 6. Phase diagrams for the binary mixtures of the methyl and chloro substituted derivatives: (a) 16b/16c, (b) 18b/18c, (c) 114b/114c, (d) 116b/116c.

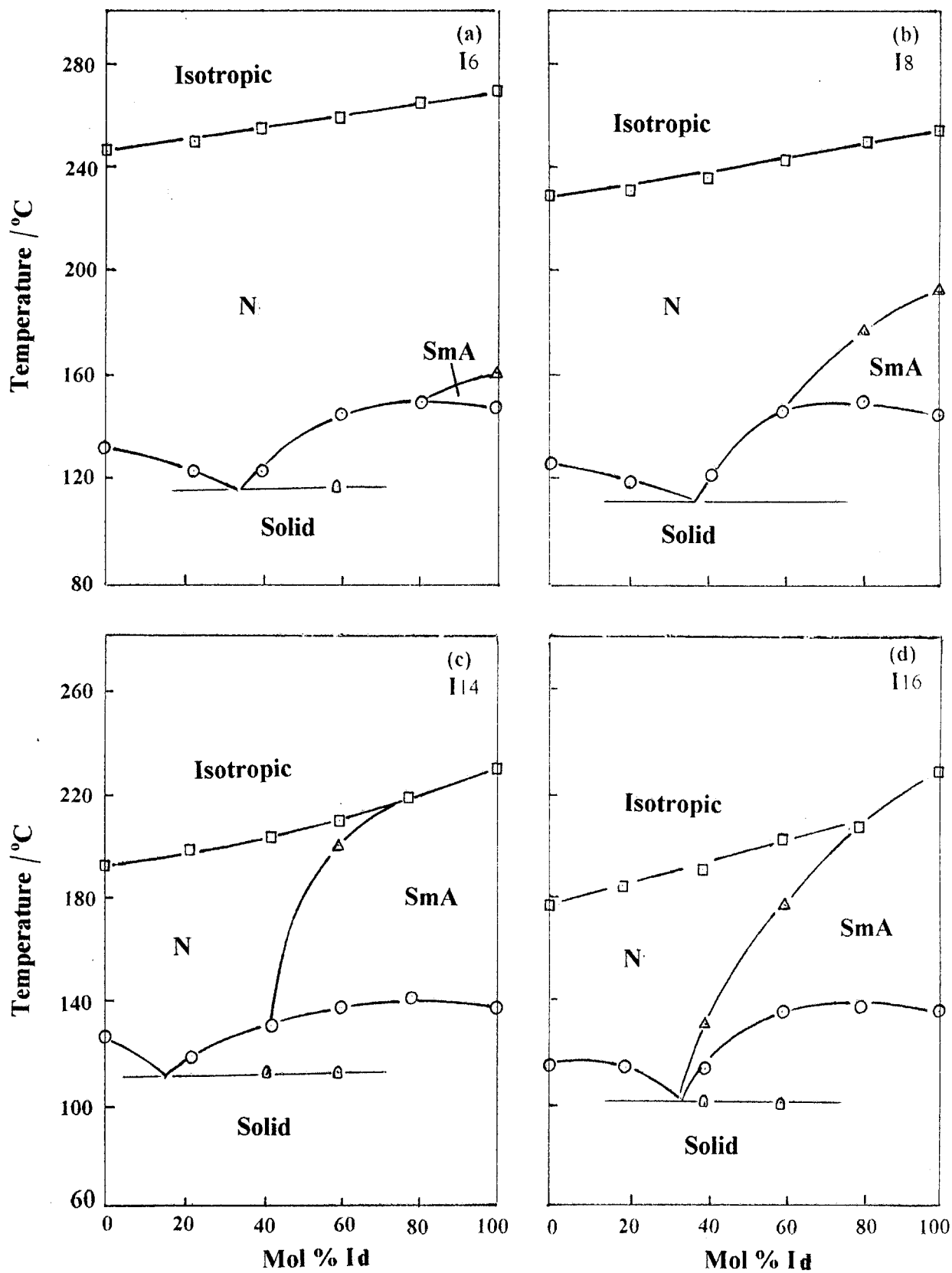


Figure 7. Phase diagrams for the binary mixtures of the methoxy and cyano substituted derivatives: (a) I6a/I6d, (b) I8a/I8d, (c) I14a/I14d, (d) I16a/I16d.

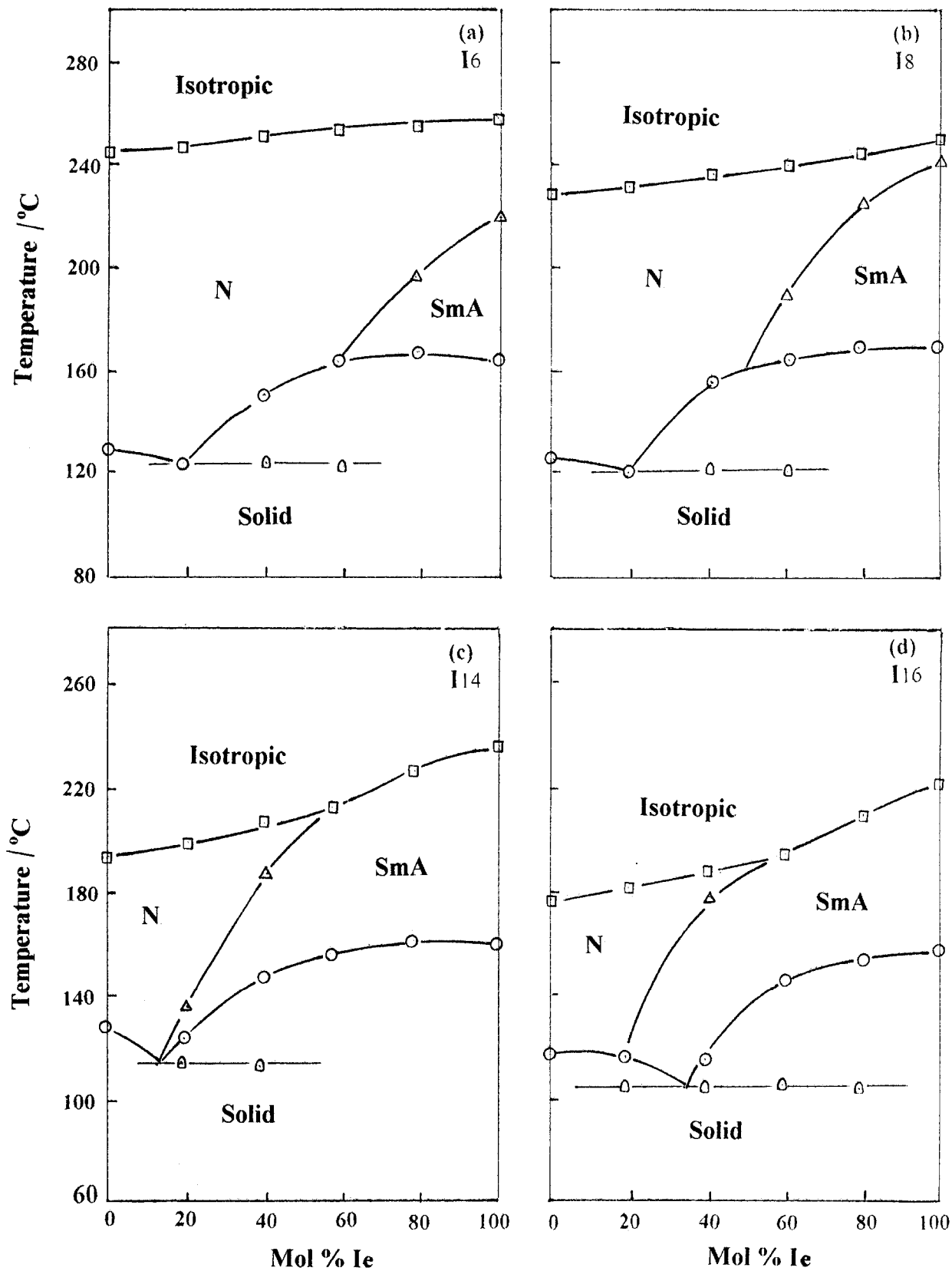


Figure 8. Phase diagrams for the binary mixtures of the methoxy and nitro substituted derivatives: (a) **I6a/I6e**, (b) **I8a/I8e**, (c) **I14a/I14e**, (d) **I16a/I16e**.

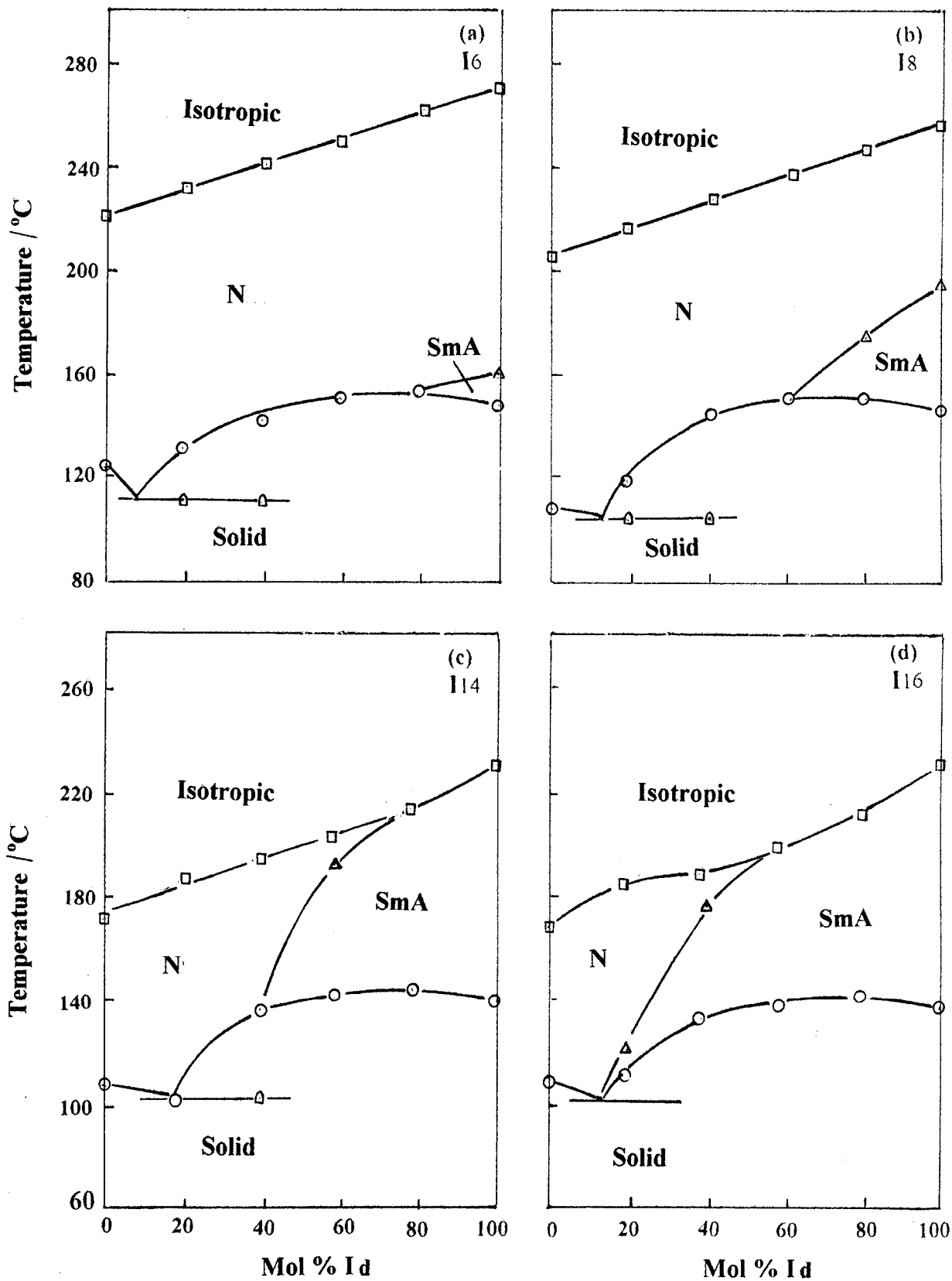


Figure 9. Phase diagrams for the binary mixtures of the methyl and cyano substituted derivatives: (a) I6b/I6d, (b) I8b/I8d, (c) I14b/I14d, (d) I16b/I16d.

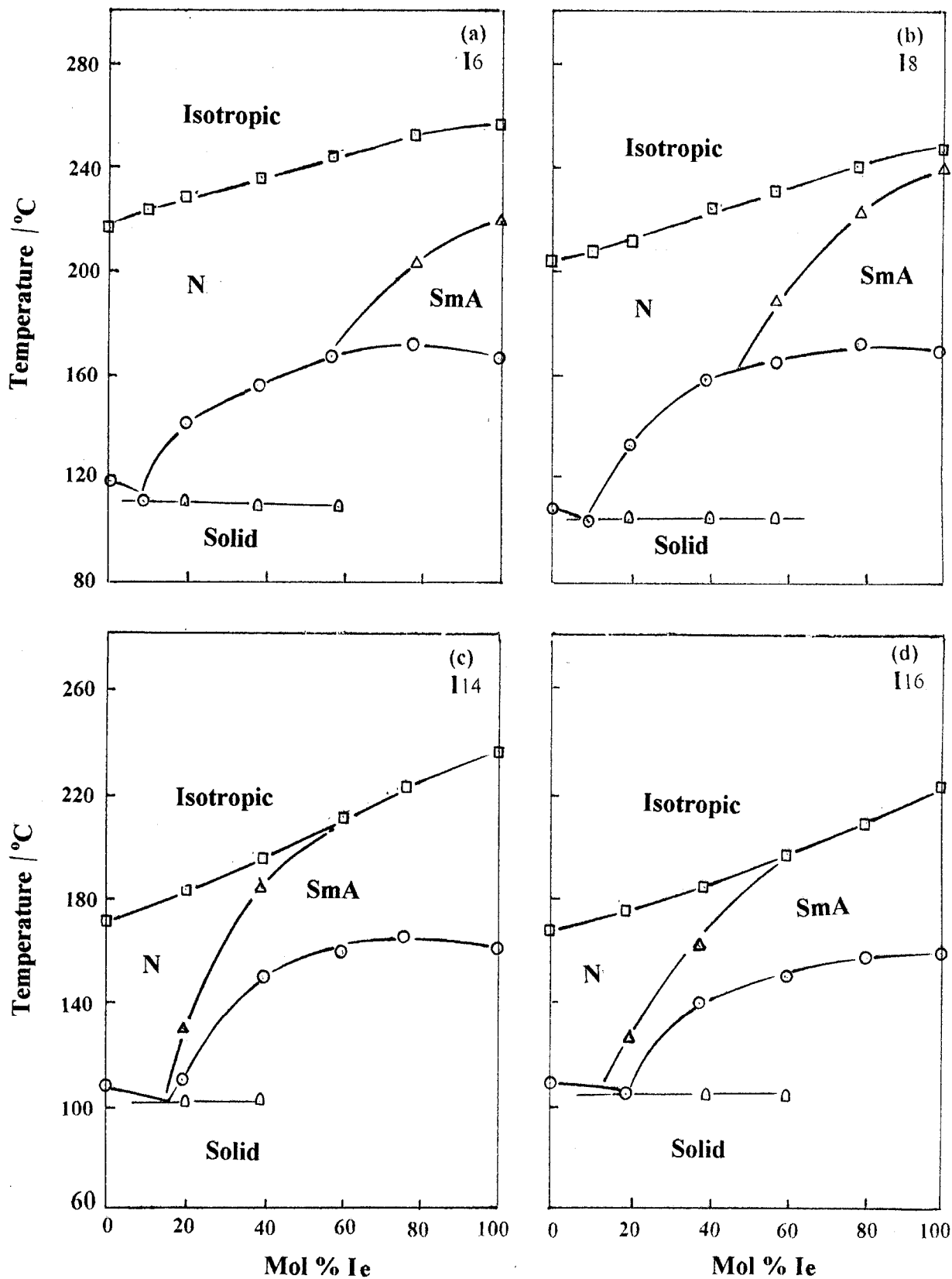
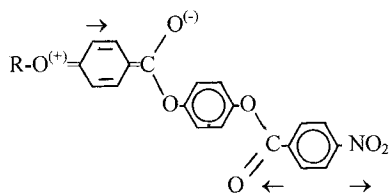


Figure 10. Phase diagrams for the binary mixtures of the methyl and nitro substituted derivatives: (a) I6b/I6e, (b) I8b/I8e, (c) I14b/I14e, (d) I16b/I16e.

On the other hand, in the nitro, chloro, or cyano derivatives (**Ie**, **Ic**, or **Id**), the electron-releasing nature of the alkoxy group, on one side of the molecule would increase, to smaller extent, the electron density at the centre of the mesogenic group; while competitive interactions between the nitro (chloro or cyano) group and the second carbonyl group, on the other side of the molecule, will add no further effect. The result is a relatively lower electron density in the case of the electron-withdrawing substituted compounds compared with those bearing the electron-donating substitutions.



Such compounds, when mixed together, are expected to have too little affinity to one another to form a donor-acceptor complex. Consequently, their binary mixtures would exhibit more or less linear T_c -composition dependence, as is observed from figures 5–10.

4. Conclusion

Binary mixtures were prepared from the unsymmetrical 1,4-phenylene bis-(4-substituted benzoates), and characterized for their phase transition temperatures. Two types of substituent were used, viz. an alkoxy group of varying length and a small compact polar group, X . All the compounds investigated were found to possess high transition temperatures, indicating strong intermolecular association in either the solid or mesophases. The conjugation between the alkoxy and the first 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. 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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