# Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures III. Binary mixtures of alkoxyphenyl arylates and arylalkoxybenzoates

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# Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures
# III. Binary mixtures of alkoxyphenyl arylates and arylalkoxybenzoates†

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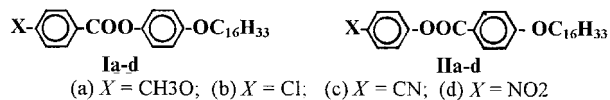Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

4-Substituted phenyl-4-hexadecyloxybenzoates and 4-hexadecyloxyphenyl-4-substituted benzoates were prepared and thermally characterized by differential scanning calorimetry. Transition temperatures were identified by polarized-light microscopy. Substituents were chosen to cover a wide range of electronic and dipolar characteristics. Binary mixtures of different components were prepared and similarly characterized to construct their phase diagrams. In mixtures of the 4-CN and 4-NO$_2$ analogues, enhanced SmA mesophases were found when either of these esters was mixed with one of the methoxy analogues. A weak molecular complex is proposed to account for this non-ideal solution behaviour. Linear or slightly enhanced mixture behaviours were found for the nitro or cyano derivatives when mixed with each other. The results are interpreted in terms of electronic, dipolar, and molecular interactions.

## 1. Introduction

Liquid crystals and their mixtures offer good opportunity to investigate molecular structure–mesomorphism relationships. Most binary mesophase systems exhibit eutectic behaviour in their solid–mesophase transition temperatures ($T_m$), whereas their mesophase–isotropic transition temperatures ($T_c$) vary linearly with composition [2]. However, non-linear behaviours have been reported for some mixtures when one component was a chloro- [3] or nitro- [3, 4] substituted liquid crystal. A structure rationale was postulated [4] based on dipolar characteristics of the constituent molecules. Furthermore, Labes and coworkers [5, 6] and Oh [7] have found that cyano-terminated liquid crystals are often successful in promoting enhanced mesomorphic behaviour in mixed liquid crystals. In mixtures of 4-substituted phenyl-4-decyloxybenzoates, enhanced smectic A, SmA, mesophases were found [8] for nitro esters when mixed with methyl or methoxy esters, while linear, ideal mixture behaviour was found for the nitro ester when mixed with the cyano ester. In the former case, a π-molecular complex was proposed [8] to account for the non-ideal solution behaviour.

The object of this work is to investigate the mesomorphic behaviour in binary mixtures of the previously prepared two isomeric series [1], **Ia-d** and **IIa-d**, which differ from each other in the location inversion of the carboxylic groups. The substituents (CH$_3$O, Cl, CN, and NO$_2$) were chosen to cover a wide range of electromeric and dipolar characteristics. These two series of compounds represent extremes in conjugative interactions between the terminal substituent, $X$, and the remainder of the molecule.

$$X-\bigodot-COO-\bigodot-OC_{16}H_{33} \qquad X-\bigodot-OOC-\bigodot-OC_{16}H_{33}$$

$$\textbf{Ia-d} \qquad\qquad\qquad \textbf{IIa-d}$$

(a) $X$ = CH3O; (b) $X$ = Cl; (c) $X$ = CN; (d) $X$ = NO2

Phase diagrams for various combinations were constructed to investigate the dependence of the mesogenic behaviour upon the electronic nature of the terminal substituent $X$ as well as its location with respect to the ester carbonyl group.

## 2. Experimental

The preparation of the materials, **Ia-d**, and **IIa-d**, has been described in a previous paper [1]. Calorimetric measurements were performed on a Polymer Laboratories Differential Scanning Calorimeter (PL-DSC, England) with nitrogen as a purge gas. Typical heating

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rates were 10 K min$^{-1}$, and sample masses were 1–2 mg. The 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).

For the phase diagrams, binary mixtures of any two components selected from series **I** and **II**, covering the whole range of composition, were prepared by melting, stirring to give an intimate blend, and then cooling while stirring in air to room temperature. The transition temperatures obtained for the prepared mixtures, as measured by both techniques, agreed within 2–3°C. In the phase diagrams, constructed by drawing the transition temperatures versus composition, the symbol '□' denotes solid–mesophase transition or mesophase–mesophase transition, '○' mesophase–isotropic transition, '×' solid–solid transition, and '△' eutectic or pretectic temperatures.

## 3.   Results and discussion

It is already known that materials which retain liquid crystalline character over a wide range of temperatures are preferred. Also, that one way to achieve this property is to use the corresponding possibly eutectic mixtures of materials exhibiting liquid crystallinity in their pure state, particularly when the molecules in question resemble one another structurally. This is because under such conditions the mesophase–isotropic transition line is usually straight or slightly enhanced and the temperature range of the mesophase is consequently greater for the eutectic mixture than for either component. The isomers **Ia-d** and **IIa-d** obviously provide a favourable system for this purpose. The transition temperatures $T_m$ and $T_c$ for compounds of the two series in the pure state, as reported in a previous paper [1], are summarized in the table. As shown from this table, the first two members of series **I** (**Ia** and **Ib**) are not mesomorphic. Their corresponding isomers in series **II**, i.e. **IIa** and **IIb**, are monotropic. The cyano and nitro analogues in both series were found to be enantiotropic. 'Mesophase'–isotropic transition temperatures $T_c$ for the non-LC (**Ia** and **Ib**) and the monotropic (**IIa** and **IIb**) analogues could be estimated from their binary phase diagrams

with one of the enantiotropes by the extrapolation method of Bogojawlensky and Winogradow [9]. The visible portions of the mesophase–isotropic transition lines are only slightly curved, and the extrapolated values, that lead to accepted results, are supported by the concordant results obtained from two or more different systems. Average values are included in the table.

### 3.1.   *Binary mixtures of enantiotropes*

Let us begin with the phase diagrams of the possible binary mixtures prepared from the four enantiotropes **Ic,d** and **IIc,d**; six possible binary systems could be obtained. Four of them are mixtures of one cyano and one nitro derivative, these are **Ic/Id**, **IIc/IId**, **Ic/IId**, and **IIc/Id**; their phase diagrams are illustrated in figures 1 (*a–d*) respectively. The remaining two binary mixtures, which are composed of either mixtures of the two cyano isomers, **Ic/IIc**, or of the two nitro analogues, **Id/IId**, gave the phase diagrams shown in figures 2 (*a, b*) respectively. Referring to figures 1 (*a–d*) and 2 (*a, b*) the phase diagrams for mixtures of the cyano and nitro compounds are of simple eutectic type with a smectic A composition [8, 10]. Above 60 mol % of **Id** in its binary phase diagrams [figures 1 (*a*), 1 (*d*) and 2 (*b*)] there is a region of a second smectic phase, SmC. The diagrams also emphasize the presence of a eutectic composition at about 50 mol % in the mixtures **IIc/IId**, **Ic/IIc** and **Id/IId** (figure 1 (*b*), 2 (*a*) and 2 (*b*)). In the other three mixtures, namely **Ic/Id**, **Ic/IId** and **IIc/Id**, the eutectic composition was observed at about 1 : 2 molar ratio. Any differences among the phase diagrams must have their roots in the nature of electronic interactions within their individual molecules. Since the cyano and nitro substituents are both electron-withdrawing, it follows that if they are attached to the similar ends of the two molecules (as in **Ic** and **Id**, or in **IIc** and **IId**), they will similarly interact electronically within the mesogenic group of the molecule, and their binary mixtures (**Ic/Id**, **IIc/IId**) tend to show ideal solution behaviour, as seen in figures 1 (*a, b*). Conversely, if substituents are introduced to opposite ends of the molecules (as in series **I** and **II**), their electronic interaction with the ester

Table.   Transition temperatures for compounds **Ia-d** and **IIa-d**. Values given in parentheses are those determined by extrapolation.

| Substituent $X$ | Compound No. | $T_m/°C$ | $T_c/°C$ | Compound No. | $T_m/°C$ | $T_c/°C$ |
|---|---|---|---|---|---|---|
| CH$_3$O | **Ia** | 90·9 | (81) | **IIa** | 96·1 | (80)[a] |
| Cl | **Ib** | 103·1 | (75) | **IIb** | 84·7 | (71)[a] |
| CN | **Ic** | 88·2 | 106·8 | **IIc** | 85·4 | 96·3 |
| NO$_2$ | **Id**[b] | 82·4 | 91·7 | **IId** | 79·4 | 88·7 |

[a] Corresponding values for the two monotropes **IIa** and **IIb** as determined on cooling are 75 and 73·4°C, respectively.
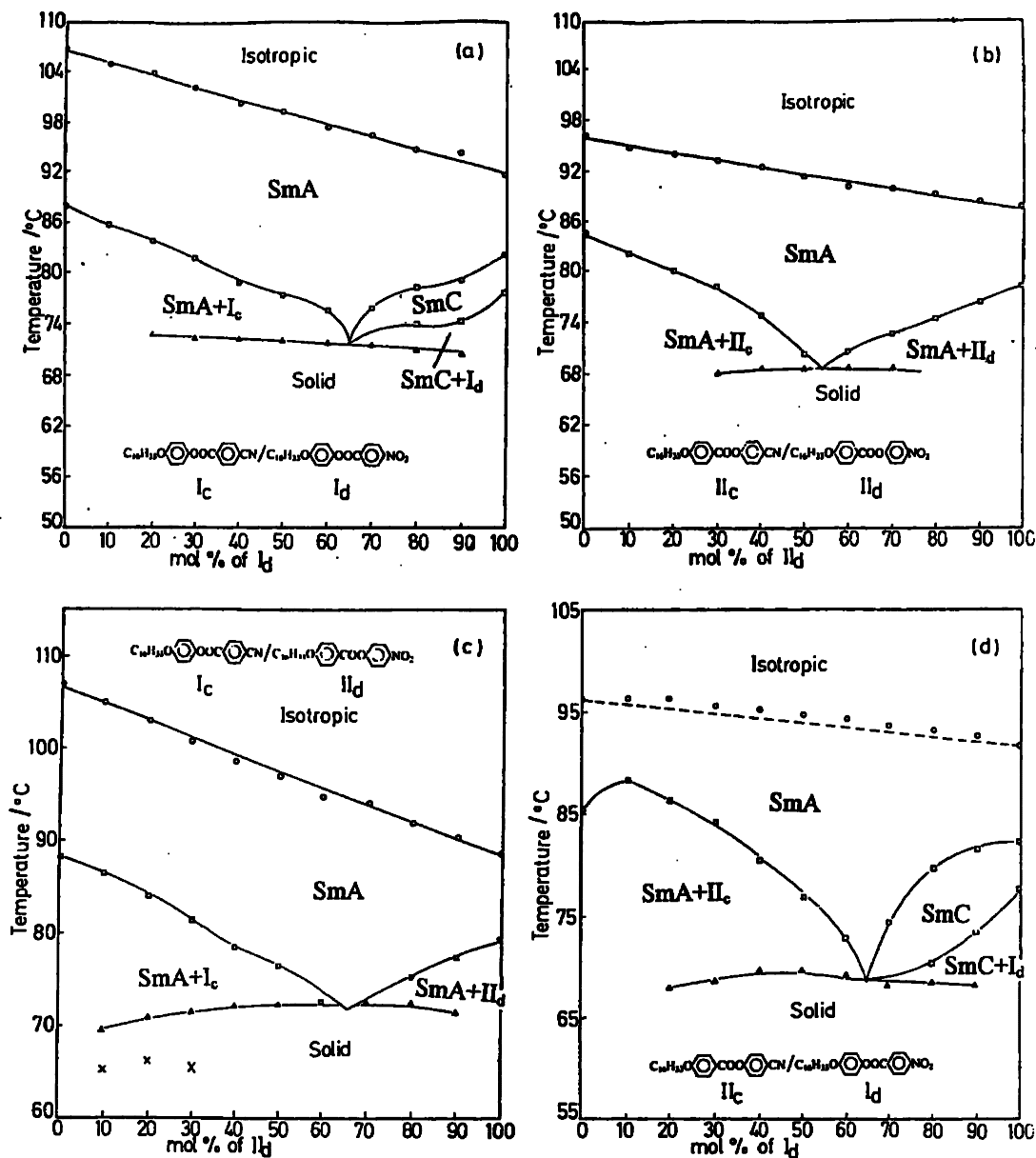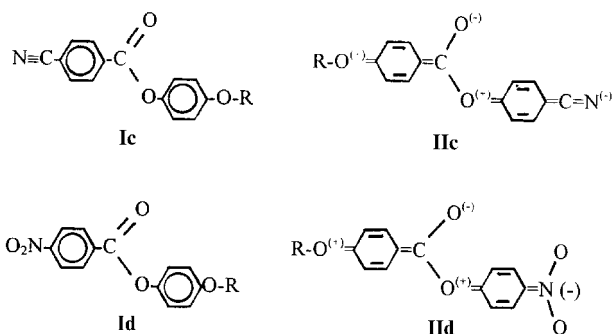[b] For compound **Id** transition temperatures, Cr–SmC and SmC–SmA, are 78·2 and 82·4°C, respectively.

Figure 1.   Phase diagrams of the binary mixtures (*a*) **Ic/Id**, (*b*) **IIc/IId**, (*c*) **Ic/IId** and (*d*) **IIc/Id**.

carbonyl, through the intervening benzene ring, will be different [1].



Thus, if the substituents are in the benzoyl moiety, i.e. **Ic** or **Id**, there will be a competitive mutual conjugative interaction in both sides of the molecule. In the corresponding isomers, **IIc** or **IId**, it is possible that conjugative interactions may take place simultaneously through the intervening phenylene rings of the molecule, forming a quadripole [1].

If differences between the electronic interaction within the molecule of **I** compared with that of **II** would lead to differences in the mode of interactions between molecules of **I** and **II** in the mesophase of their mixtures, one would expect that the cyano and nitro mixed systems would exhibit enhanced mesophase–isotropic transition
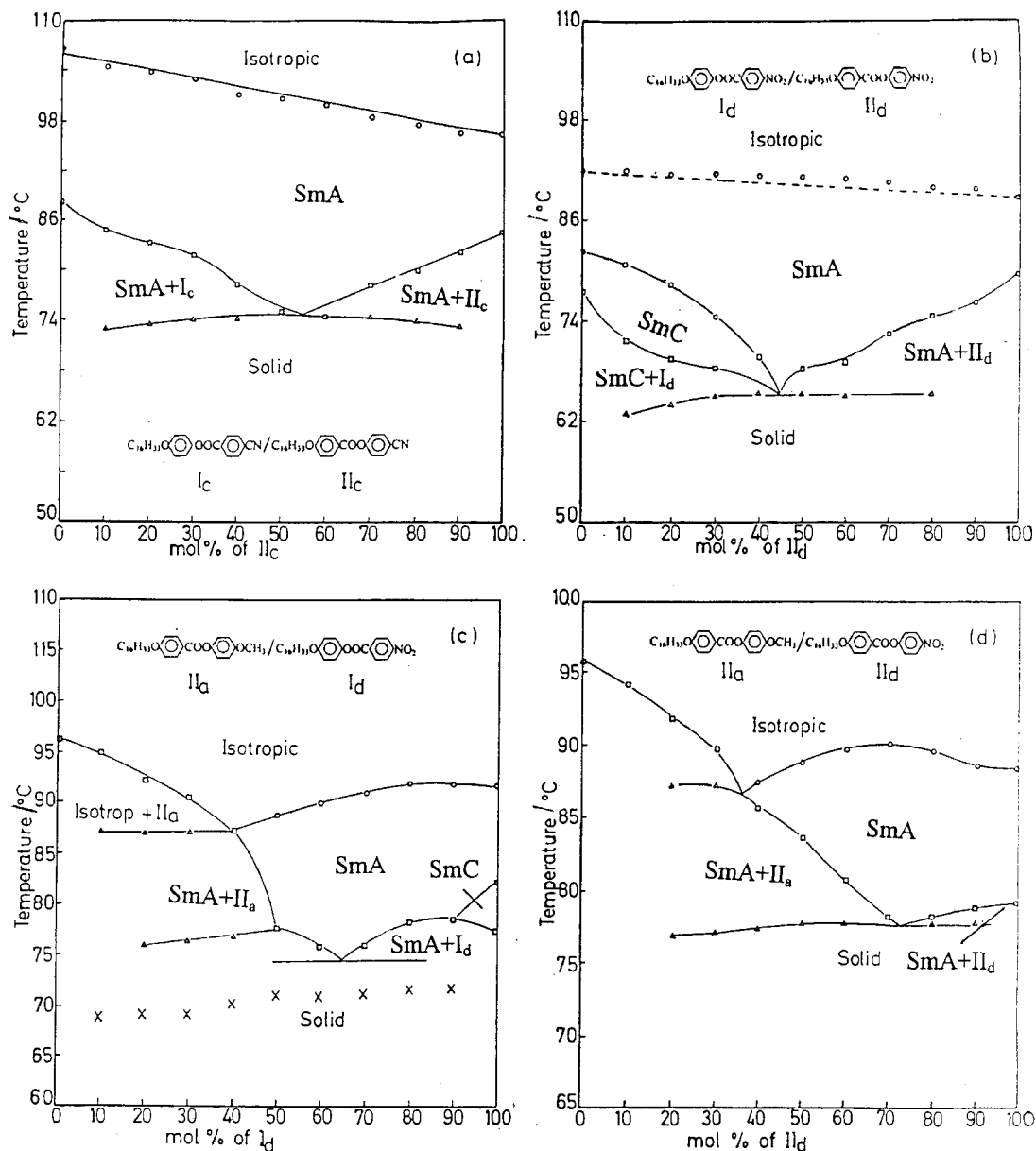
Figure 2. Phase diagrams of the binary mixtures (*a*) **Ic/IIc**, (*b*) **Id/IId**, (*c*) **IIa/Id** and (*d*) **IIa/IId**.

temperatures. The reverse was found to be the case, that is, such systems showed linear composition–dependencies in **Ic/IId** and **Ic/IIc** [figures 1 (*c*) and 2 (*a*)], or slight enhancement in **Id/IIc** and **Id/IId** [figures 1 (*d*) and 2 (*b*)] of their mesophase–isotropic transition temperatures. Such behaviour may lead to the conclusion that the mode of interaction between molecules of the nitro and cyano analogues in the **I/I** or **II/II** mixtures does not differ greatly from that between **I/II** or **II/I**.

Furthermore, comparison of the liquid crystalline ranges $\Delta T$ ($= T_c - T_m$) reveals that the extent of anisotropic stability of these mixtures at their eutectic

composition decreases in the order:

$$\mathbf{Id/IId} > \mathbf{Ic/IIc} > \mathbf{Ic/Id} > \mathbf{Id/IIc} > \mathbf{Ic/IId} > \mathbf{IIc/IId}$$
$$\Delta T = 26{\cdot}1 \quad 25{\cdot}8 \quad 25{\cdot}4 \quad 25{\cdot}0 \quad 22{\cdot}7 \quad 22{\cdot}6 \quad (^{\circ}C)$$

The difference between the highest (26·1°C for the eutectic **Id/IId**) and the lowest (22·6°C for the eutectic **IIc/IId**) $\Delta T$ values is again small enough to add extra evidence for the great similarity between the cyano and nitro groups, on the one hand, and between their molecules in series **I** and **II** on the other, in regard to their molecular interactions in their pure and mixed states.

### 3.2. *Mixtures of electron-donating and electron-withdrawing substituted derivatives*

The phase diagrams constructed for binary mixtures of components bearing the electron-donating group ($CH_3O$), i.e. **Ia** and **IIa**, with another bearing the electron-withdrawing groups (CN or $NO_2$), i.e. **Ic,d**, **IIc,d**, are presented in figures 2(c, d) and 3(a–d). An important consideration in figures 2(c, d) and 3(b) is that enhancement of the smectic A mesophase–isotropic transition is produced by the non-enantiotropic components **Ia** and **IIa**. This is reminiscent of some earlier work by Schroeder and Schroeder [11] on other systems. The eutectic composition of the binary system **IIa/Id**

appears to be very close to a 1:2 molar ratio; 1:3 for the system **IIa/IId**, 1:1 for the system **IIa/IIc**, and 1:4 for the mixture **Ia/IId**. On the other hand, complex compositions in the mesophase (to-isotropic) of the binary systems **IIa/Id**, **IIa/IId**, and **Ia/IId** appear to be very close to molar ratios 1:4, 1:3, and 1:4, respectively.

The fact that the solid phase behaviour can be drastically different in mixtures differing only in component structure is evident in comparing the mixtures **Ia/IId** [figure 3(b)] and **Ia/Id** [figure 3(d)]; both binary mixtures contain **Ia** as a common component. In spite of the fact that the second component in both mixtures is the nitro-containing ester, **IId** or **Id**, the COO ester
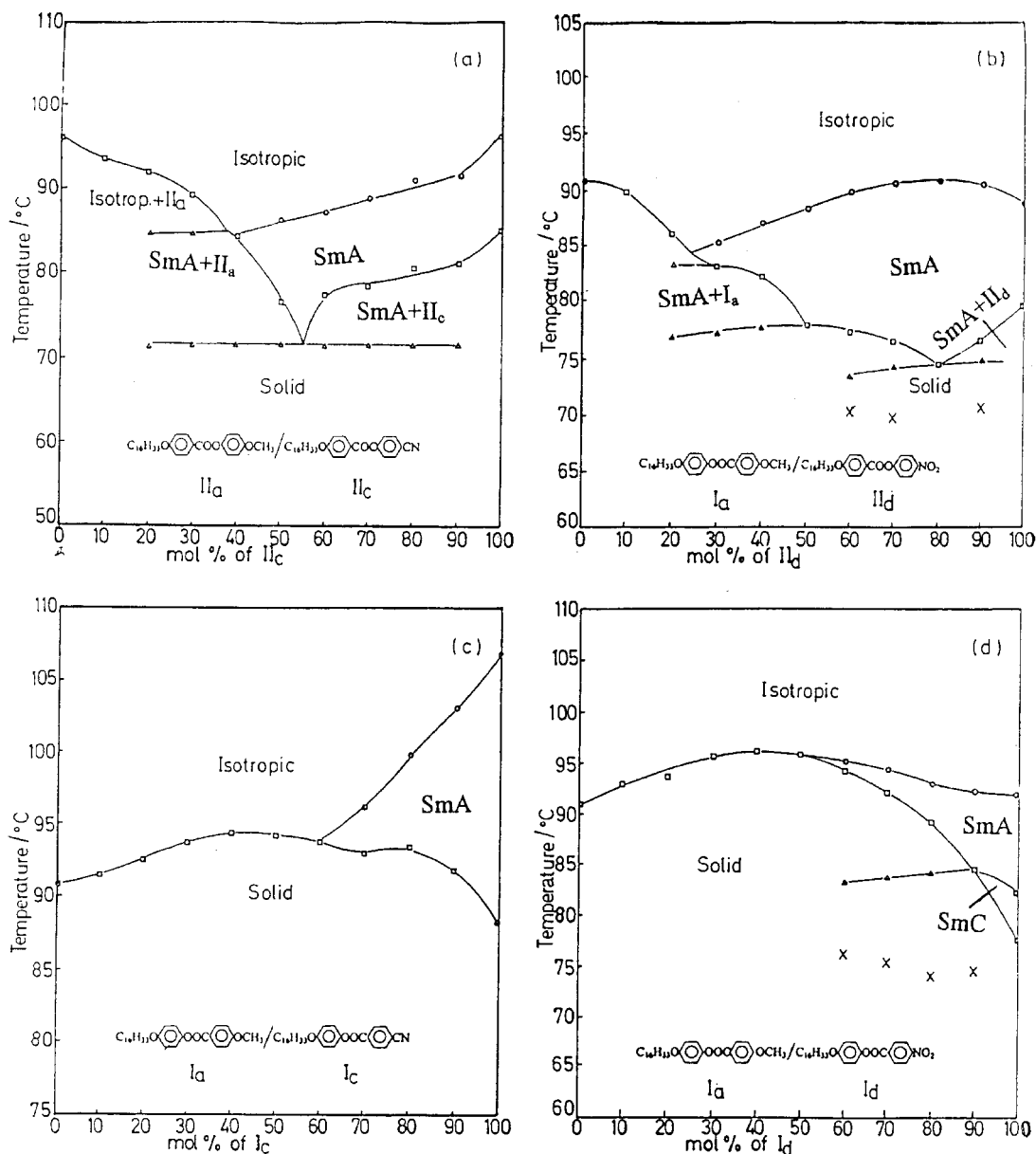


Figure 3.  Phase diagrams of the binary mixtures (a) **IIa/IIc**, (b) **Ia/IId**, (c) **Ia/Ic** and (d) **Ia/Id**.

linkage connecting the aromatic rings in **IId** leads to simple eutectic behaviour in the former case, whereas the inverted OOC ester linkage in the otherwise closely related molecule **Id** leads to the formation of a molecular compound and to a totally different phase behaviour in the latter case. The same can be said with respect to the two binary mixtures **Ia/Ic** [figure 3(c)] and **IIa/IIc** [figure 3(a)]. The only difference between these two mixtures is the location inversion of the ester group. In the former system, substituents *X* are *para* to the ester carbonyl group, while in the latter, substituents are in the phenolic moiety of the esters. In such systems, it is clear that differences in the mode of electronic interactions within the molecules result in drastic differences in the molecular interactions between different molecules when substituents are of different electronic properties. This is in accordance with the conclusions drawn by Dewar and Goldberg [12] which indicated that mutual conjugation between the carbonyl group and the terminal *para* substituent on an aromatic ring is important in this regard.

From the observation of the phase diagrams in figures 3(a–d), it is clear that there is a relationship between the non-linear thermal behaviour in the binary liquid crystal system and the smectic layering of the constituent molecules. This can be explained as an electronic phenomenon and not a geometric one, which is only apparent since the structural difference in the two molecules comprises one small terminal substituent (CH$_3$O, and CN or NO$_2$). This is obvious from a general examination of the **Ia/Id**, **Ia/IId**, **Ia/Ic**, and **IIa/IIc** sets of phase diagrams. Non-linear behaviour (which arises when A-B interactions are significantly different from interactions between the molecules of pure components A-A or B-B) is to be anticipated when molecules of different layering arrangements are mixed together. Griffin *et al.* [13] have predicted that the cyano and nitro compounds will exhibit a bimolecular smectic structure. From a consideration of terminal groups which promote non-linear thermal behaviour, i.e. CN and NO$_2$, it is believed that the electron-withdrawing nature of these substituents is responsible for this behaviour. Bimolecular smectics are a result of molecular complexing [14, 15] in pure components. For the cyano and nitro compounds, **Ic,d** and **IIc,d**, the most satisfactory model is a bimolecular one [13] as shown:
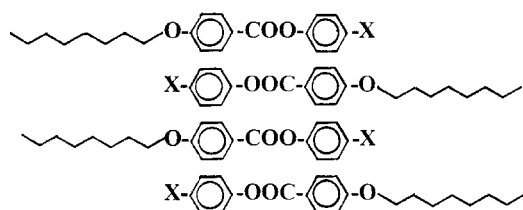
where *X* = CN or NO$_2$.

On the other hand, the effect of the methoxy group in **Ia** and **IIa** seems explicable in terms of a shielding effect on the oxygen lone pairs by an insulator, the methyl group. The repulsive forces involving the oxygen lone pairs are thereby substantially reduced; the lack of strong repulsive forces simply allows a close approach of the neighbouring molecules, thus increasing bonding forces. These strong forces will be associated with high melting points and melting enthalpies [1] in such a way that no mesophase is detected on heating. In these compounds, the melting of the crystals occurs at a higher temperature than does the breakdown of the mesomeric forces and there is insufficient molecular anisotropy to cause the formation of a mesophase.

Binary mesophase systems in which a bimolecular smectic is mixed with one which significantly peturbs its molecular anisotropy will exhibit non-linear thermal behaviour, i.e. non-ideal solution behaviour. Such a perturbation would be found in mixing compounds with electron-rich aromatic rings (which can successfully compete for molecular complexation) with an electron-deficient ring of another molecule. Thus the A-B interactions are considerably different from the A-A or B-B interactions. In such cases, non-linear thermal behaviour is found.

Likewise, one should expect that mixtures of compounds with similar smectic layering characteristics, such as **Ic** and **Id** [figure 1(a)] or **IIc** and **IId** [figure 1(b)], should exhibit thermal behaviour which is linear with concentration, as pointed out above.

Comparison between the LC-ranges ($\Delta T = T_c - T_m$) of these groups of binary mixtures reveals that the extent of anisotropic stability at their eutectic compositions decreases in the order:

$$\textbf{Ia/IId} > \textbf{IIa/Id} > \textbf{IIa/IIc} > \textbf{IIa/IId} > \textbf{Ia/Ic} > \textbf{Ia/Id}$$
$$\Delta T = \quad 16{\cdot}5 \qquad 16{\cdot}1 \qquad 15{\cdot}1 \qquad 12{\cdot}3 \qquad — \qquad — \qquad (°C)$$

The last two mixtures [figures 3(c, d)] do not show eutectic compositions. It can also be seen from this comparison that the greatest anisotropic stability is observed in cases where each substituent is introduced to opposite ends in the two components of the mixture, i.e. **Ia/IId** and **IIa/IId**.

### 3.3. *Mixtures of non-LC with enantiotropes*

Figures 3(c, d) and 4(a, b) illustrate the phase diagrams of binary mixtures composed of one enantiotrope (**Ic** or **Id**) and a non-liquid crystalline compound (**Ia** or **Ib**). It can be seen from these figures that the perturbation of smectic layering is so strong that even eutectic compositions could not be observed. Furthermore, complete destruction of the layers is effected by the addition of less than 40 mol% of the non-LC component to the enantiotrope. In such cases, the melting point of the
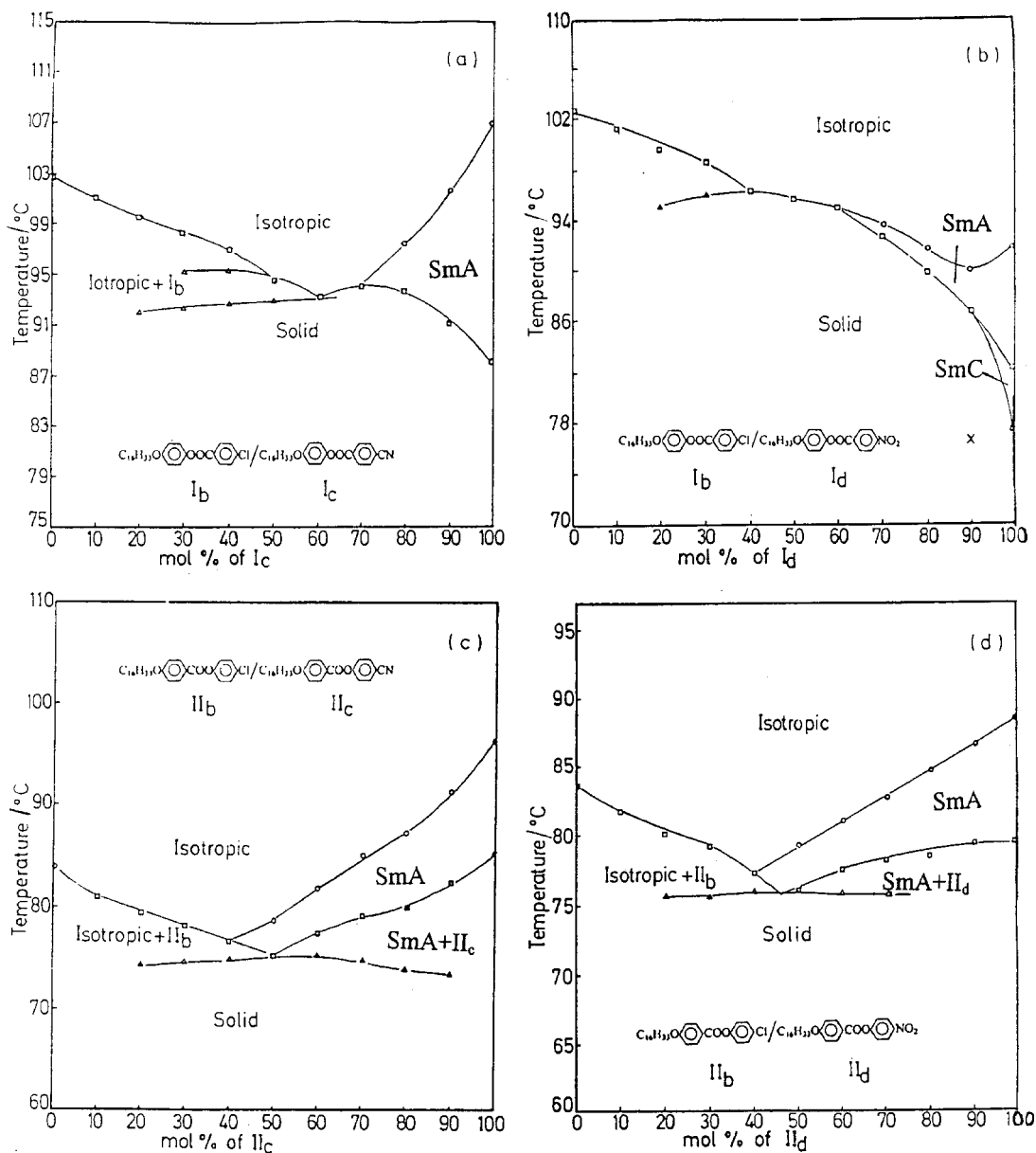
Figure 4. Phase diagrams of the binary mixtures (*a*) **Ib/Ic**, (*b*) **Ib/Id**, (*c*) **IIb/IIc** and (*d*) **IIb/IId**.

mixture lies far above the extrapolated $T_c$ values of the non-LC components **Ia** and **Ib**, which are 81 and 75°C, respectively (see the table). In the case of mixtures **Ia/Ic** [figure 3(*c*)] and **Ia/Id** [figure 3(*d*)], complex formation in the solid phase appears to be very close to a 2 : 1 molar ratio; two parts of the non-LC component (**Ia**) and one part of the enantiotrope (**Ic** or **Id**). It should be noted again that in either mixture, both components are substituted in the carboxylic acid residue of the ester.

On the other hand, enantiotropes with electron-withdrawing groups attached to the phenolic moiety of the molecule, e.g. **IId**, when mixed with the non-LC

component **Ia**, which bears an electron donating group attached to the carboxylic group moiety, result in a phase diagram that shows an enhanced mesophase [see figure 3(*b*)]. This again supports the hypothesis that electronic interaction within the molecule of each component would, in one way or another, affect the molecular interaction in their binary mixtures.

### 3.4. *Mixtures of monotropes and enantiotropes*

The monotropic components **IIa** and **IIb**, when mixed with an enantiotropic component, result in a phase diagram that shows a eutectic composition and a range of smectic mesophase. Phase diagrams for mixtures of

the monotrope **IIa** with the enantiotropes **Id**, **IId**, and **IIc**, are depicted in figures 2(c, d) and 3(a), respectively. The other monotrope **IIb** was used to prepare binary mixtures with the active enantiotropes **IIc** and **IId**, and their phase diagrams are illustrated in figures 4(c, d), respectively. Contrary to the component **IIa**, which bears the electron-donating CH$_3$O group, compound **IIb** bears the electron-attracting Cl. This expectedly results in a linear mesophase behaviour, with the enantiotropes **IIc** and **IId**, which bear the electron-attracting, CN and NO$_2$, groups, respectively. This mesophase is completely perturbed by the addition of an amount of **IIb** greater

than 60 mol % [figures 4(c, d)]. Herein, mixtures composed of more than 60 mol % of **IIb** (which possesses a relatively high melting point) will have melting points higher than the extrapolated $T_c$ value of **IIb** (see the table) and thus show no mesophase.

### 3.5. *Binary mixtures of the monotropes and/or non-LC*

Figures 5(a–d), represent the phase diagrams constructed for binary mixtures prepared from any two of the monotropes **IIa,b**, and the non-LCs **Ia,b**. It can be seen from figures 5(a, b) that in each of the mixtures **Ia/IIa** and **Ib/IIb**, although there is a monotropic
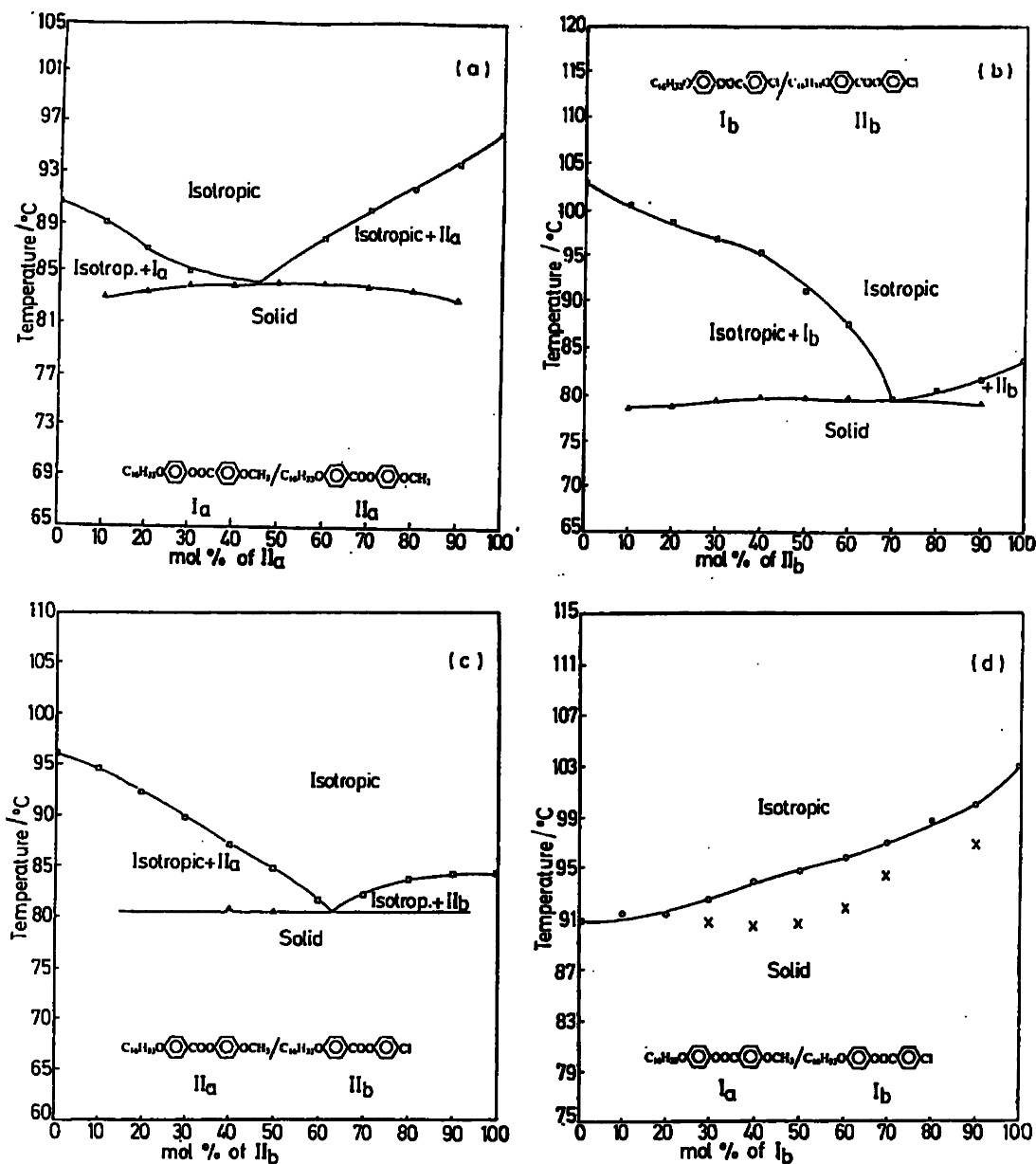


Figure 5. Phase diagrams of the binary mixtures (a) **Ia/IIa**, (b) **Ib/IIb**, (c) **IIa/IIb** and (d) **Ia/Ib**.

component, i.e. **IIa** or **IIb**, their mixtures showed no mesophase on heating. Both diagrams are of simple eutectic type and possessed their eutectic compositions at approximately 1 : 1 and 2 : 1 molar ratios, respectively. Similarly, investigation of the binary mixtures of the two monotropes **IIa** and **IIb** resulted in a phase diagram of simple eutectic type which showed no mesomorphic region [figure 5 (*c*)]. In each of the three diagrams the melting point of the eutectic composition is higher than the extrapolated $T_c$ values of its pure components, thus no mesophase is detected on heating.

The last diagram [figure 5(*d*)] illustrates the phase behaviour of the binary mixtures of the two non-LC components, **Ia** and **Ib**. It is clear from this figure that all mixtures throughout the whole range of composition melted directly to the isotropic liquid with nearly linear composition dependence, and in most cases these mixtures underwent modification in their crystal structure before melting. It seems interesting to investigate phase behaviour on cooling of all systems that do not show mesophases on heating; supercooling may allow the formation of a mesophase, suggesting an investigation of molecular interaction between molecules of these types. This is planned for a subsequent study.

## 4.  Conclusions

The aryl-arylate esters **Ia-d** and **IIa-d** represent model compounds for investigation of the electronic interaction between the *para* substituents (through the intervening benzene rings) and the central carboxyl group. Such interactions, which differ according to the electronic nature of the substituent as well as to its location with respect to the ester carbonyl group, have led to a significant variation in mesophase behaviour of the individual components [11] and, consequently, to a difference in the behaviour of their binary mixtures. Substituents with similar electronic nature, i.e. CN or $NO_2$ groups, whether they are attached to the benzoyl or phenolic moiety of the ester, resulted in compounds that gave, in their binary mixtures, phase diagrams of similar characteristics. That

is, all these diagrams exhibit eutectic behaviour in their solid–anisotropic transition temperatures, and a linear or slightly enhanced behaviour in their mesophase–isotropic transition temperatures. Alternatively, mixtures of derivatives bearing substituents with opposite mesomeric effects, e.g. $CH_3O$ and CN ($NO_2$ or Cl), gave phase diagrams that differed greatly, dependent on the electronic nature of the substituent as well as its location inversion. It has also been found that monotropic or non-LC components disturb to a great extent the mesophase stability of the enantiotropes.

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