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

VII. Ternary mixtures of enantiotropes

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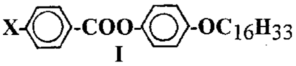
Transition temperatures of the ternary mixtures, prepared from compounds of the two series, 4-hexadecyloxyphenyl 4-substituted benzoates (**Ia**,**b**) and 4-substituted phenyl 4-hexadecyloxy benzoates (**IIa**,**b**) have been determined by differential scanning calorimetry and identified with polarized light microscopy. The cyano and nitro derivatives, in both series, were used because their molecules form enantiotropic phases. A new method was elaborated for the elucidation of the eutectic composition of any ternary system from the knowledge of the eutectic composition of the three individual binary mixtures.

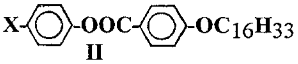
1. Introduction

Since the publication of Gray's monograph [1], there has been much interest in liquid crystals resulting from the discovery of their outstanding technological applications. Most of this work has been directed toward the synthesis of new compounds of variable practical value, to the study of their physical properties with a view to improving devices based on them, or to relating their mesophase stability to molecular structure [2–10]. Early studies [1] suggested that compounds tend to form liquid crystals if their molecules are rod-shaped and possess polar terminal groups. It was also suggested that the *p*-phenylene group might favour lateral attractions in molecules containing it, due to the presence of polarizable π-electrons, and through enhanced polarity as a result of conjugation with the attached polar groups.

The core of a mesogenic compound is often composed of aromatic rings joined through a linking group such as −COO−, −CH=CH−, −CH=N−, −N=N−, or −N=NO− [11]. Aromatic esters are known to be thermally stable; in addition, the conjugative interaction between the ester group and the benzene rings in a molecule such as phenyl benzoate leads to some double bond character and to a stiffer structure than might be expected. The 4-alkoxy phenyl ester of 4-substituted benzoic acids (**I**) and their corresponding isomers, 4-substituted phenyl esters of 4-alkoxy benzoic acids (**II**) provide excellent systems which are used to investigate the role of both terminal groups on mesophase stability, either in their pure state or in mixed systems. The effect of substituents, covering a wide range of electronic nature, on the mesophase behaviour of compounds of types **I** and **II** was previously [4–6] discussed in terms of dipolar and mesomeric effects. It was found [6] that the methoxy and chloro derivatives in series **I** are not mesomorphic, whereas their corresponding isomers in series **II** are monotropic. The cyano and nitro analogues in both series are enantiotropic. Furthermore, the mesophase behaviour of all possible binary combinations of any two components from both series, has been thoroughly investigated [7, 8]. The objective in this work is to extend these studies to investigate the mesophase behaviour of the liquid crystals (**Ia**,**b** and **IIa**,**b**) in their ternary systems to elucidate and characterize their eutectic mixtures.



I



II

Substituents with similar electronic nature, viz. CN or NO_2 groups, whether they are attached to the benzoyl or phenolic moiety of the ester, resulted [8] 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 behaviour in their mesophase–isotropic transition temperatures.

2. Experimental

The preparation and characterization of compounds **Ia**,**b** and **IIa**,**b** have been described previously [6]. Calorimetric investigations were made using a differential scanning calorimeter (PL-DSC, England) with nitrogen as a purge gas. A typical heating rate was 10 K min^{-1}, and sample masses were 2–3 mg. Transition temperatures

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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).

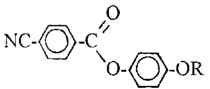
Binary mixtures were prepared by mixing the appropriate amounts of components, melting together with stirring, and then cooling to room temperature while stirring in air. The ternary mixtures for any system (**A**/**B**/**C**) were prepared in two steps. The eutectic mixture of the binary system **A**/**B** was first prepared, as a constant ratio mixture, then the component **C** was admixed to cover the whole **C**-composition range, i.e. from 0 to 100% of **C**. Secondly, the eutectic mixture **A**/**C** was first prepared, to which the component **B** was added in amounts varying from 0 to 100%. Thirdly, the eutectic **B**/**C** was prepared and component **A** was added.

Transition temperatures of the prepared mixtures, were measured both by DSC and polarized light microscopy and found to agree within 2–3°C.

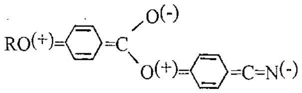
In the phase diagrams, constructed by plotting transition temperatures versus composition, the symbols 'o' denote solid–mesophase transitions, '◇' mesophase–isotropic transition, and '*x*' eutectic temperatures.

3. Results and discussion

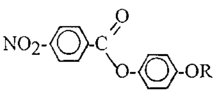
Before discussing the phase behaviour of ternary mixtures we must consider the characteristics of the pure components as well as their binary mixtures. The two molecules 4-hexadecyloxyphenyl 4-substituted benzoates (**I**) and 4-substituted phenyl-4-hexadecyloxybenzoates (**II**), which differ only in the location inversion of the ester $-COO-$ group, represent extremes in the conjugative interactions between the terminal substituents (X and $C_{16}H_{33}O$) and the other portion of the molecule.



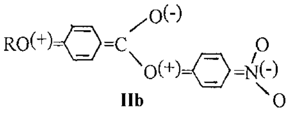
Ia



IIa



Ib



IIb

Thus if the substituent is in the benzoyl moiety (**Ia** and **Ib**) there will be competitive conjugative effects on both sides of the molecule. This will lead to relatively smaller dipole moments; these were measured [6] to be 3.87 and 3.60 D for compounds **Ia** and **Ib**, respectively. In the corresponding isomers, **IIa** and **IIb**, the conjugative interaction between the cyano (or nitro) group and the ester oxygen atom, as well as that between the alkoxy group oxygen and the ester carbonyl group, lead to higher dipole moments [6], which are 5.84 and 5.73 D, respectively.

These four derivatives were thermally characterized for their transition temperatures in their pure states (table 1) and in their binary mixtures (table 2). Differences between the conjugative interaction within a molecule of type **I** and that in a molecule of type **II**, as can be seen from the tables, have led to a variation in the mesophase behaviour both of the pure components and of their binary mixtures. It might be noted that although the dipole moments of compounds **IIa** (5.84 D) and **IIb** (5.73 D) are greater than their corresponding isomers **Ia** (3.87 D) and **Ib** (3.60 D), respectively, their crystal–mesophase, T_m, as well as their mesophase–isotropic, T_c, transition temperatures behave in an opposite manner. This may be explained in terms of repulsive forces. For compounds **IIa** and **IIb** repulsive contribution predominates and thereby lowers both T_m and T_c, as compared with the corresponding isomers **Ia** and **Ib**, see again table 1.

Furthermore, in view of the similar dipolar and mesomeric character of the terminal cyano and nitro groups, one might expect that, in one and the same series, a similar phase behaviour would take place. However, experimental results showed that the temperatures of transition are lower for the nitro than for the cyano analogues. This may be explained in terms of the differences encountered in their steric interactions. The nitro group in **Ib** or **IIb**, being bulkier than the cyano group, results in a decrease in the extent of lateral association of molecules, either in the solid or in the mesophase, and thereby lowers both T_m and T_c compared with those of the cyano analogues, see table 1.

With respect to their binary mixtures, comparison between the LC-ranges ($\Delta T = T_m - T_c$), determined for this group of binary systems [8], reveals that the extent

Table 1. Transition temperatures, mesophase stability, and dipole moment of the compounds investigated.

Compound	T_m/°C	T_c/°C	ΔT/°C	μ/D
Ia	88.2	106.8	18.6	3.87
Ib	78.2	91.7	13.5	3.60
IIa	85.4	96.3	10.9	5.84
IIb	79.4	88.7	9.3	5.73

Table 2. Eutectic compositions and phase transition temperatures of the binary systems investigated.

System (**A**/**B**)	%**A**	%**B**	T_m/°C	T_c/°C	ΔT/°C
Ia/Ib	33.0	67.0	76.2	97.1	20.9
Ia/IIa	42.0	58.0	74.8	99.8	25.0
Ia/IIb	35.0	65.0	69.9	94.3	24.4
Ib/IIa	60.0	40.0	70.4	95.0	24.6
Ib/IIb	53.0	47.0	64.9	90.8	25.9
IIa/IIb	43.5	56.5	68.7	91.5	22.8

of anisotropic stabilities at their eutectic compositions (table 2), which are computed from the corresponding binary phase diagrams, decreases in the order:

Ib/IIb > **Ia/IIa** > **Ib/IIa** ≈ **Ia/IIb** > **IIa/IIb** > **Ia/Ib**

Furthermore, it may be noticed that the range of mesophase stability (ΔT) increases from 9–18°C for the pure components to 20–26°C for their eutectic mixtures in binary systems.

Generally, the phase diagram of a binary system is constructed by plotting the transition temperatures versus the composition of the binary mixtures in a two-dimensional representation. Conversely, to construct the phase diagram of a ternary system, the composition will be represented by a triangle, while transition temperatures are plotted on the third dimension. In such cases, each apex of the triangle will represent one pure component, while each side represents the full range of composition of a binary mixture made from any two of these three components. Ternary mixture compositions will be given by points enclosed within the area of the triangle. A serious problem is raised: how to select the compositions necessary to elucidate their eutectic composition, and hence to characterize their phase behaviour. To do that, a reasonable way is to make use of the binary diagrams in the determination of their corresponding eutectic compositions, and hence their phase transition temperatures. Assume that for the ternary system **A**/**B**/**C**, the pure components **A**, **B**, and **C** are represented graphically by the apexes A, B, and C, respectively, on the triangle ABC. The compositions of their binary mixtures **A**/**B**, **A**/**C**, and **B**/**C**, are represented, respectively, by its sides AB, AC, and BC. If we locate the eutectic composition of each binary mixture on its corresponding side on the triangle of composition, and connect each apex representing a pure component to the opposite point representing the eutectic composition of the other two components, one would expect that these three inner connecting lines (a, b, and c) might intersect in one point that gives the eutectic composition of the ternary mixture **A**/**B**/**C**.

Experimentally, this idea can be verified by constructing the three individual phase diagrams by plotting the transition temperatures versus the compositions represented by the inner connecting lines a, b, and c. In such a way, the individual eutectic compositions, of these three selected ternary mixtures, would be determined. If the idea is correct, these three values will coincide with one another and with the point of intersection inside the triangle of ternary composition.

The four enantiotropes **Ia**,**b** and **IIa**,**b** seemed to us to be interesting components to realize our idea. In this case, four possible ternary systems, **Ia**/**Ib**/**IIa**, **Ia**/**Ib**/**IIb**, **Ia**/**IIa**/**IIb** and **Ib**/**IIa**/**IIb**, can be prepared from these four derivatives, which seem to be sufficient to verify our idea. For each of these four ternary mixtures the triangle of composition as well as the corresponding three phase diagrams covering the composition ranges represented by the inner lines a, b, and c, were constructed and are represented graphically in figures 1–4, for the four systems, respectively. The eutectic compositions of binary mixtures as represented on each side of the composition triangle were constructed from the corresponding binary phase diagrams [8].

As can be seen from figures 1–4, the eutectic composition of any ternary system can be safely determined from any one of the phase diagrams a, b, or c, which also match within ±0.5% that determined from the point of intersection of the inner three lines a, b, and c on the corresponding composition triangle. The results of computation are given in table 3, from which it can be seen that the range of the mesophase stability (ΔT)

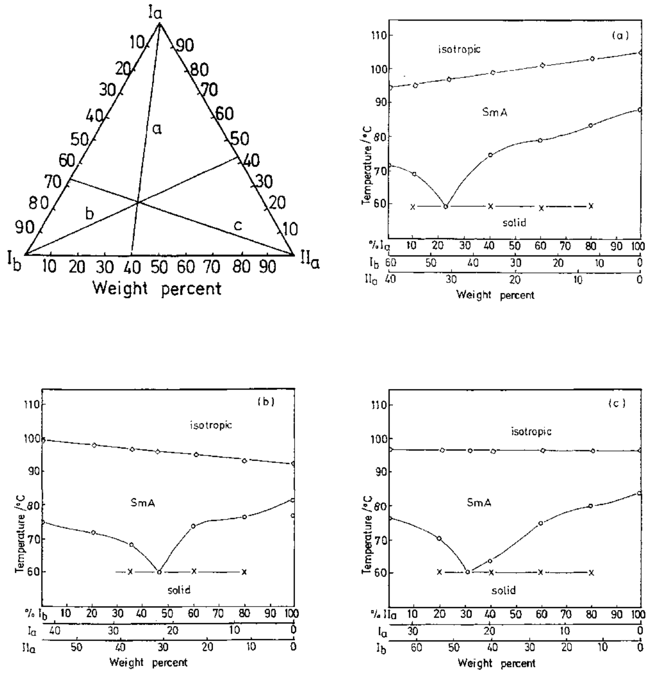


Figure 1. Composition triangle of the ternary system **Ia**/**Ib**/**IIa**, and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

Table 3. Eutectic composition and its phase transition temperatures of the ternary mixtures investigated.

System (**A**/**B**/**C**)	%A	%B	%C	T_m/°C	T_c/°C	ΔT/°C
Ia/Ib/IIa	22.5	46.5	31.0	60.5	96.5	36.0
Ia/Ib/IIb	20.6	41.8	37.6	62.5	94.2	31.7
Ia/IIa/IIb	23.5	33.5	43.0	58.8	94.8	36.0
Ib/IIa/IIb	39.0	26.5	34.5	61.0	92.8	31.8

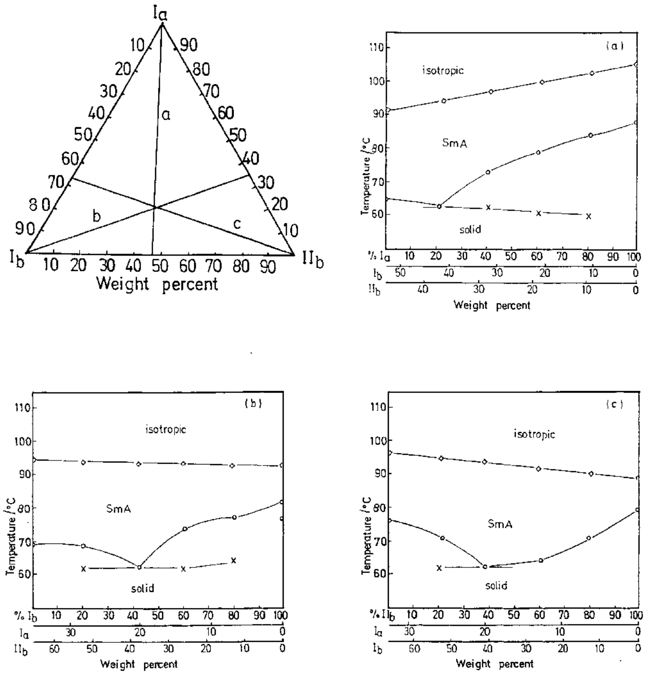


Figure 2. Composition triangle of the ternary system **Ia/Ib/IIb**, and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

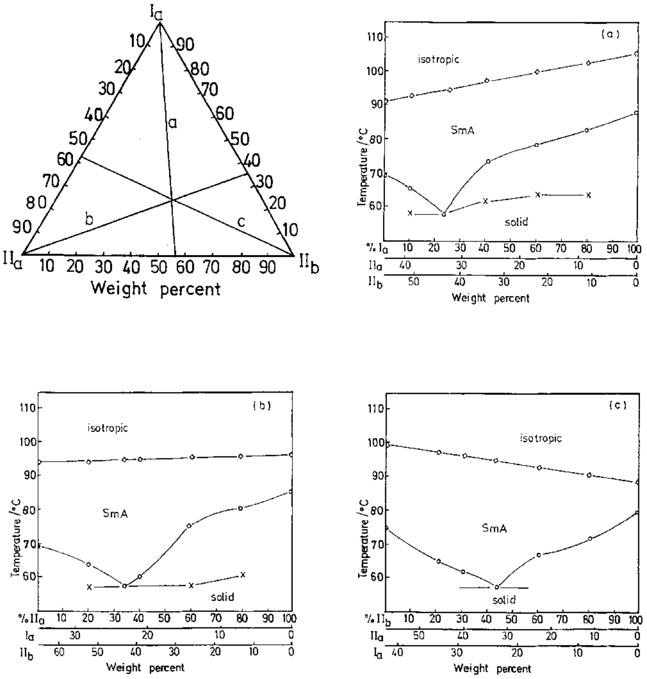


Figure 3. Composition triangle of the ternary system **Ia/IIa/IIb**, and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

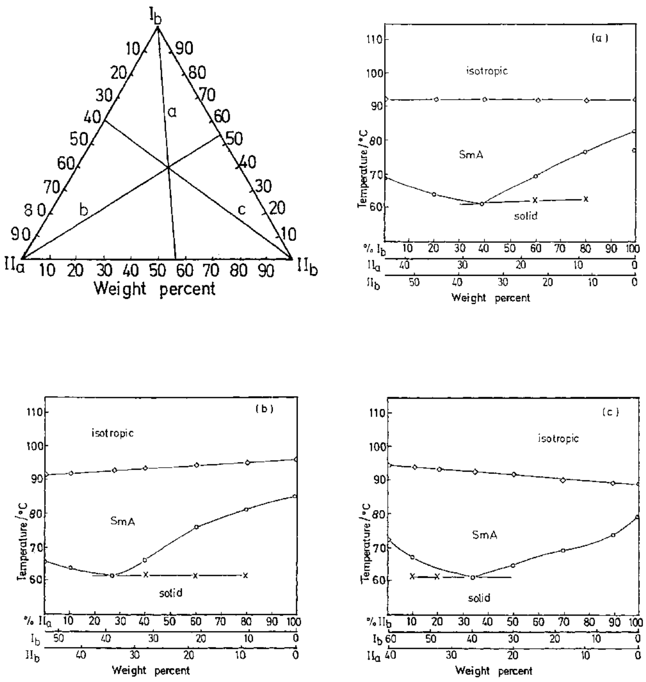


Figure 4. Composition triangle of the ternary system **Ib/IIa/IIb**, and ternary phase diagrams covering the composition ranges represented by the inner lines a, b, and c.

increases further from 20–26°C for the eutectic mixtures of binary systems, to 30–36°C for those of the ternary systems. Their ranges of stability decrease, for the four systems investigated, in the order:

Ia/IIa/IIb = Ia/Ib/IIa > Ia/Ib/IIb ≈ Ib/IIa/IIb.

The first two systems, with a mesophase stability of 36°C, have in common the binary mixture **Ia/IIa**, while the last two have the binary mixture **Ib/IIb** in common. This is expected, since the mesophases of the cyano derivatives in either series (**Ia** and **IIa**) are more stable than their corresponding nitro analogues as can be seen from table 1.

On the other hand, it may be observed from table 2 that the composition of the eutectic mixture of any binary system is richer in the component which has the lower melting point. Recalling table 1, the melting points of the compounds investigated increase in the order:

Ib < IIb < IIa < Ia.

In practice, any binary mixture is found to have its eutectic composition shifted toward the component according to the order:

Ib > IIb > IIa > Ia.

A similar order of composition is also applicable in case of the ternary systems investigated, as can be deduced from table 3. For example, in the ternary system **Ia/Ib/IIa**, the components composition at its eutectic decreases in the order:

	Ib >	**IIa** >	**Ia**
Composition	46.5	31.0	22.5 %
Melting point	67.8	85.4	88.2 °C

The other three systems behave in a parallel manner. This order of eutectic composition reflects the steric effect of the nitro group.

4. Conclusion

The cyano and nitro groups have similar electronic nature but differ in their steric effect. The electronic interaction between such substituents and the central carboxyl group differs according to its location with respect to the ester carbonyl group. This difference in the electronic interaction leads to a variation in the mesophase stability of the individual components and consequently in their binary or ternary mixtures. The CN and NO_2 substituents, whether they are attached to the benzoyl or the phenolic moiety of the ester, result in compounds that give in their binary or ternary mixtures, phase diagrams that exhibit eutectic behaviour in their solid–anisotropic transition temperatures, and linear composition dependences in their mesophase–isotropic transition temperatures. A new method has been adopted for the elucidation of the eutectic composition of ternary systems. The compositions of the eutectic mixtures investigated were found to progress in an order dependent on the melting points of the individual pure components.

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