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Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures VI [1]. The effect of molecular length

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The apparent solution dipole moments of compounds based on 4,4′-di-substituted phenyl benzoate ($ROC_6H_4COOC_6H_4X$), **I**, where X is a cyano group and R a terminal linear alkyl chain ranging from C_{12} to C_{20}, were determined in cyclohexane at 30°C. The compounds were also thermally characterized by polarized light microscopy and differential scanning calorimetry. Phase diagrams were constructed for various binary mixtures prepared from any two homologues of series **I** as well as for every one of them with the nitro analogue **II**, where X is a nitro group and $R = C_{16}H_{33}$. The study was undertaken in order to investigate the effect of the alkyl chain length on the mesophase behaviour. In order to assess the influence of structural variation in the central mesogenic group on the mesophase stability of pure and mixed compounds, the investigation was extended to cover binary mixtures of any two of the three compounds: analogue **II** ($X = OC_{16}H_{33}$), and the symmetric dialkoxy substituted phenyl esters $(C_{16}H_{33}OC_6H_4COO)_2A$, where A is the 1,4-phenylene group (**IV**) or 4,4′-biphenylene (**V**).

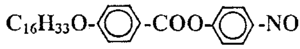
1. Introduction

It is well known that the stability of a mesophase in liquid crystals depends primarily on the anisotropy of intermolecular forces. As a result of lateral attractions, rod-shaped molecules tend to adopt a parallel arrangement. Attempts to correlate the mesophase stability with molecular structure, in a mesomorphic system, are based on considerations of the nature and magnitude of intermolecular forces favouring such lateral associations. However, recent work [1–5] has led to the conclusion that intermolecular forces, due to dipole–dipole attractions and others, are not the only factors important in determining mesophase stability. Conversely, enhanced intermolecular attractions may lead to a decrease in the stability of the mesophase [3, 6, 7].

The extension of a terminal n-alkyl chain substituent, in a homologous series, gives rise to a gradient in the liquid crystal transition temperatures [8, 9]. In the lower homologues of a series a nematic mesophase appears, and if the terminal chain length increases there is a tendency for a smectic A phase to appear. On the other hand, replacement of the phenylene by a biphenylene group raises both transition temperatures—the melting (T_m) and clearing (T_c) points—and broadens the mesophase range. This is not surprising in view of the greater molecular rigidity and polarizability of the biphenylene group [10, 11] compared with the phenylene group.

The goal of the present work is first to examine a series of model compounds, **Ia–d** (see structures below), where X = CN and R changes from n-$C_{12}H_{25}$ to $C_{20}H_{41}$, in an attempt to investigate the effect of the terminal chain length on the liquid crystalline phase stability in their pure states and in their binary mixtures—with each other as well as with their nitro analogue **II**.

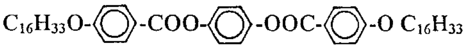
Ia, $R = C_{12}H_{25}$; Ib, $R = C_{14}H_{29}$; Ic, $R = C_{16}H_{33}$; Id, $R = C_{20}H_{41}$



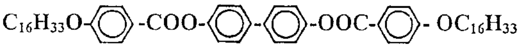
II

Secondly, it is to extend our investigation to another group of compounds (**III–V**) in order to correlate changes in the central group length with the liquid crystalline behaviour of these compounds as well as their possible binary mixtures.

III



IV



V

2. Experimental

The preparation of the compounds **Ia–d** and **II–V**, was described in previous work [3, 10]. Calorimetric

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measurements were performed on a Polymer Laboratories differential scanning calorimeter (PL-DSC, England) with nitrogen as purge gas. Typical heating 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 an FB 52 hot-stage equipped with an FB 80 central processor (Mettler, Switzerland).

For the construction of phase diagrams, binary mixtures of any two components covering the whole range of composition were prepared by melting, stirring to give an intimate blend and then cooling to room temperature while stirring in air. 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, ◇ is mesophase–isotropic transition, × is solid–solid transition, and △ denotes eutectic temperatures.

Dipole moments were calculated from measurements of the dielectric constant, density, and refractive index for dilute solutions in cyclohexane at 30°C. The symbols have the following meaning: ${}_{\mathrm{D}}P_2$ is the molar deformation polarization of the solute obtained by extrapolating the measured molar refraction for the sodium D-line to infinite wavelength; $P_{2\infty}$ is the molar polarization of the solute at infinite dilution, taken as the average of that determined graphically and those calculated from the equations of Hedestrand [12] and Palit and Banerjee [13]; μ(D) is the dipole moment determined by the refractivity method from

$$\mu(\mathrm{D}) = 0.01273[(P_{2\infty} - {}_{\mathrm{D}}P_2)T]^{1/2}.$$

On the basis of precessions of ± 0.0005 in dielectric constants, ± 0.0001 in refractive indices, and $\pm 0.02\%$ in solution concentrations, the dipole moment values are believed reliable to ± 0.05 D.

3. Results and discussion

The 4-substituted phenyl esters of 4-alkoxybenzoic acids, **Ia–D** and **II**, provide an excellent system which can be used to study the role of both terminal groups on mesophase stability in their pure or mixed systems. The effect of substituents, covering a wide range of electronic nature, was studied in detail in previous papers [1–5]. In this work we extend the study to investigate the effect of the alkoxy chain length on the phase behaviour of binary mixtures.

The nature and length of the central mesogenic group in the phenyl benzoate ester systems are also of great importance. These can be studied by (i) taking both terminal groups in the phenyl benzoate molecule as $C_{16}H_{33}O$ (**III**) and increasing the central group by another $-C_6H_4COO-$ group (giving **IV**), and (ii) replacing the central phenylene group in **IV** by a biphenylene group, to give **V**.

3.1. *Effect of alkyl chain length*

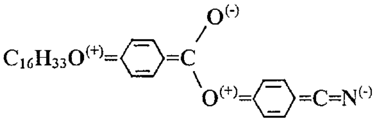
Since the mesophase stability of a liquid crystalline compound depends upon the intermolecular interactions in which dipole–dipole attraction plays an important role, it seemed worthwhile to examine, firstly, the effect of alkyl chain length on the dipole moment of each member of the homologous series **Ia–d**. Thus, the apparent solution dipole moments of these compounds were measured at 30°C in cyclohexane; the results, as calculated by the Hedestrand [12], Palit and Banerjee [13], and graphical methods, are summarized in table 1. Corresponding data for the nitro analogue [2] are included for comparison.

As can be seen from table 1, the dipole moments of all members of the homologous series **Ia–d** are virtually the same, irrespective of the length of the alkyl chain. These results are in accordance with the fact that the alkoxy groups are of the same polarity regardless of length and, at the same time, do not affect the extent of conjugative interactions between the alkoxy oxygen and the ester carbonyl group through the intervening phenylene group. Consequently, increasing chain length, within our investigated range of carbon atoms, has no influence on the resultant dipole moment of the whole molecule.

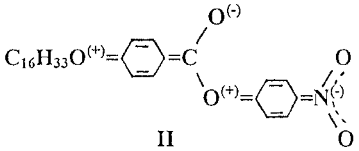
Table 1. Polarization data for compounds **Ia–d**, **II** and **III** in cyclohexane at 30°C.

		$P_{2\infty}/\mathrm{cm}^3$				
Compound	${}_{\mathrm{D}}P_2/\mathrm{cm}^3$	Hedestrand	Palit–Banerjee	Graphical	Average	μ (D)
Ia	119.92	817.66	801.00	817.60	812.09	5.83
Ib	146.23	835.19	822.79	835.14	831.04	5.80
Ic	176.48	875.15	862.64	875.09	870.96	5.84
Id	205.91	896.51	879.12	896.41	890.68	5.80
II	163.39	836.51	819.13	836.41	830.68	5.73
III	151.71	294.95	296.57	297.95	297.49	2.67

With regard to the nitro derivative **II**, its apparent solution moment in cyclohexane ($\mu = 5.73$ D) is found to be close to that of its cyano analogue (**Ic**, $\mu = 5.84$ D). This is expected in view of the fact that the two groups are of comparable electronic character. Moreover, the same conjugative interaction between the cyano or nitro groups and the ester oxygen atom, as well as the mesomeric interaction between the alkoxy oxygen and the ester carbonyl group, has led to this high dipole moment.



Ic



II

In order to investigate the effect of alkyl chain length on phase behaviour, DSC analyses were carried out for compounds **Ia–d** and **II**; the results are given in table 2. The phase transitions were identified with the aid of a polarized light microscope. In a series of type **I**, the mesophase–isotropic transition temperature (T_c) rises with increasing chain length. In the lower homologues a nematic mesophase appears [14], while in the higher ones there is a tendency for a smectic A phase to appear. Furthermore, in compound **Id** ($R = C_{20}H_{41}$) a solid–solid transition was observed at about 79°C. On the other hand, the observed increase in T_m and T_c with alkoxy chain length has been attributed by Gray and Winsor [14] to the fact that lateral attraction grows stronger as the alkoxy group is lengthened, while the terminal attraction (all members of the series are of the same dipole moment value, $\mu \approx 5.8$ D) grows relatively weaker. The net result would be a rising mesophase–isotropic curve which levels off as the series terminates at 12 carbon atoms.

Table 2. Transition temperatures (°C) and enthalpy of transitions (kJ mol^{-1}) for compounds **Ia–d** and **II–V**.

Compound	T_M	ΔH_m	T_c	ΔH_c	ΔT
Ia	74.6	41.5	90.7	3.8	16.1
Ib	76.3	46.5	92.9	4.0	16.6
Ic	85.4	61.1	96.3	5.7	10.9
Id	86.4	65.1	96.4	5.4	10.0
II	79.4	54.5	88.7	3.6	9.3
III	95.8	67.4	(78.3)[a]	—	—
IV	110.2	61.6	156.9	11.8	46.7
V	124.0	60.5	227.5	13.0	103.5

[a] On cooling.

Regarding the cyano (**Ic**) and the nitro (**II**) analogues, one might expect that in view of the similar dipolar and mesomeric character of the terminal cyano and nitro groups, a similar phase behaviour would take place. Experimental results, as shown in table 2, showed that the temperatures and enthalpies of transitions are lower for the nitro than for the cyano analogue. This may be explained in terms of the differences encountered in their steric interactions. The nitro group in **II** being bulkier than the cyano, results in a decrease in the extent of lateral association, either in the solid or the mesophases, and thereby lowers both T_m and T_c (and their corresponding ΔH values) compared with those of the cyano analogue **Ic**.

One obvious way of achieving liquid crystallinity over a wide range of temperature is to use eutectic mixtures of materials forming liquid crystals. Thus, the phase diagrams for various possible binary combinations of the cyano derivatives **Ia–d**, as well as for their mixtures, individually, with the nitro analogue **II**, were constructed to investigate the effect of the alkoxy chain length on the phase behaviour of these mixtures.

Let us begin with the phase diagrams of the possible binary mixtures prepared from any two of the four enantiotropes **Ia–d**; six systems could be obtained as represented graphically in figures 1 (*a–f*); all of them are of simple eutectic type with a smectic A as the mesophase. Since all members of series **I** bear, on one side, the same polar compact cyano group, and on the other side an alkoxy group (C = 12 to 20) of equal polarity, their mixtures are expected to show ideal solution behaviour in their mesophase–isotropic transition temperatures. A general consideration of figures 1 (*a–f*) emphasizes the presence of a eutectic mixture, the composition of which is dependent on the difference in the number of carbon atoms in the alkoxy group between the two components of the mixture. The greater the difference in chain length, the greater is the deviation of the eutectic composition from the 1 : 1 molar ratio. These figures also show that the extent of mesophase stability ($\Delta T = T_c - T_m$) at the eutectic compositions decreases in the order:

$$\begin{array}{lcccccc} & \mathbf{Ia/Id} > & \mathbf{Ia/Ib} > & \mathbf{Ib/Id} \approx & \mathbf{Ib/Ic} > & \mathbf{Ic/Id} \approx & \mathbf{Ia/Ic} \\ \Delta T & 32 & 30 & 28 & 28 & 27 & 27\ (^\circ\mathrm{C}). \end{array}$$

The difference between the highest (32°C for the eutectic **Ia/Id**) and the lowest (27°C for the mixtures **Ic/Id** and **Ia/Ic**) ΔT values is small enough to conclude that the mesophase stability of any of these eutectic mixtures is only slightly dependent upon the length of the alkyl chain, within the investigated range of chain lengths. These results may show that, since each member of the series possesses the same mesogenic group ($OC_6H_4COOC_6H_4CN$), they all exhibit equal end-to-end

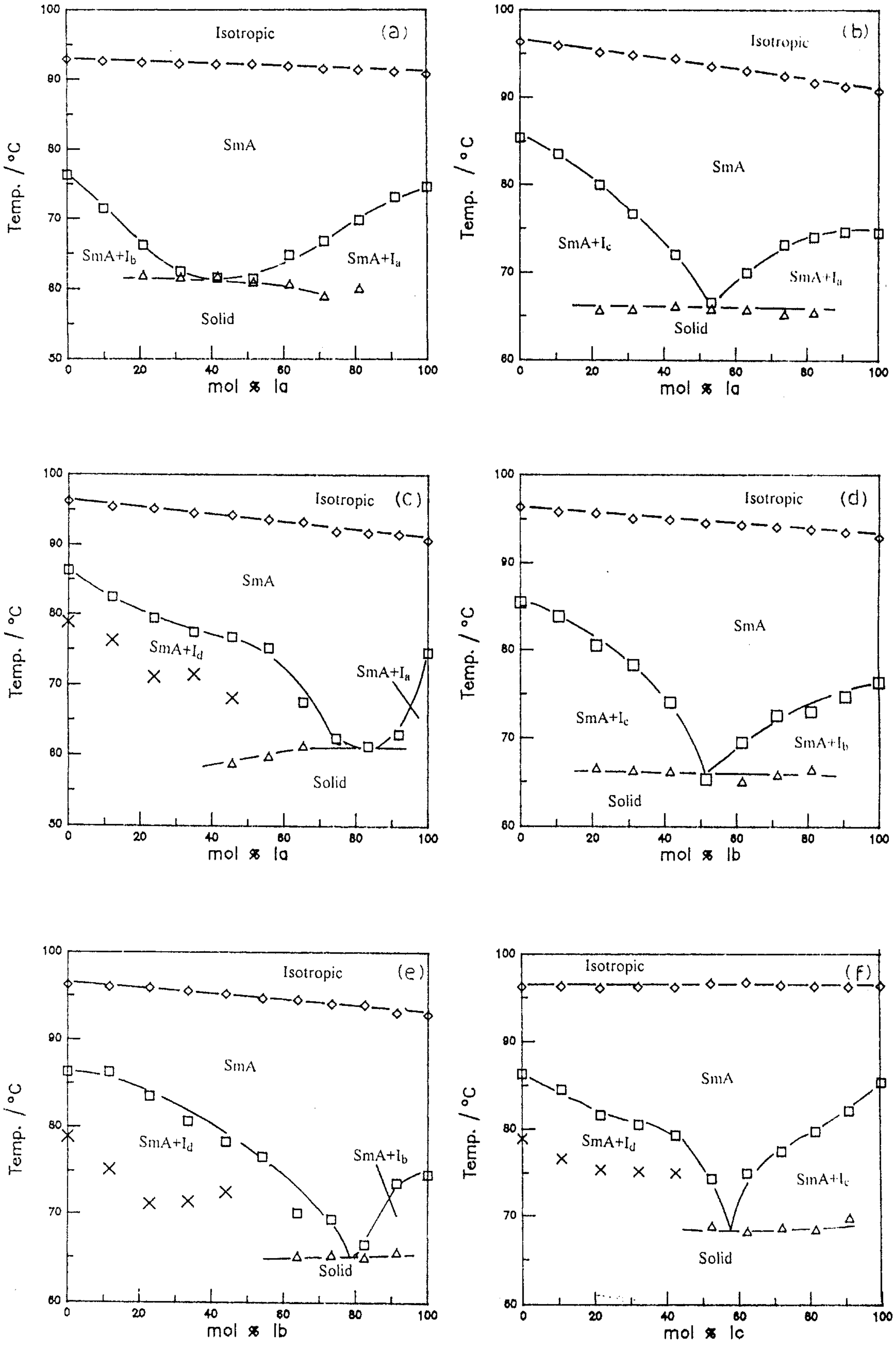


Figure 1. Binary phase diagrams for the binary mixtures (*a*) **Ia/Ib**, (*b*) **Ia/Ic**, (*c*) **Ia/Id**, (*d*) **Ib/Ic**, (*e*) **Ib/Id**, and (*f*) **Ic/Ib**.

interactions. Furthermore, according to Gray [14] the strength of lateral association does not increase significantly upon increasing the number of carbon atoms in the alkoxy group beyond 12. Taking both factors together, this would result in a closely related mesophase stability of their eutectic mixtures. Alternatively, the mixing of two structurally similar components with similar polarities (see table 1) but with different alkoxy chain length, would slightly perturb the smectic arrangements of molecules resulting in mixtures with different eutectic compositions. When the mixture is prepared from two components bearing alkoxy groups with similar chain lengths, e.g. C_{12}/C_{14} (**Ia/Ib**) or C_{14}/C_{16} (**Ib/Ic**), the eutectic composition was observed to be close to the 1 : 1 molar ratio. As the difference increases, perturbation increases and the molar ratio changes to be richer in the component bearing the shorter alkoxy chain.

We turn now to mixtures of components bearing two different terminal polar substituents, i.e. compound **II** with each member of series **I**. Four binary phase diagrams can be constructed and are represented graphically in figures 2 (*a–d*). As mentioned before, the cyano and nitro groups are of similar electronic nature and of nearly the same polarity, hence mixtures of their compounds are expected to behave ideally. That is, they exhibit eutectic behaviour in their solid–mesophase transition temperatures T_m, whereas their mesophase–isotropic transition temperatures T_c vary linearly with composition. The effect of changing the length of the alkoxy group in series **I** on the phase behaviour of its mixtures with **II** is reflected in two independent phenomena, namely, the composition and the mesophase stability of the eutectic mixtures. The extent of the anisotropic stability ΔT of these mixtures at their eutectic compositions decreases

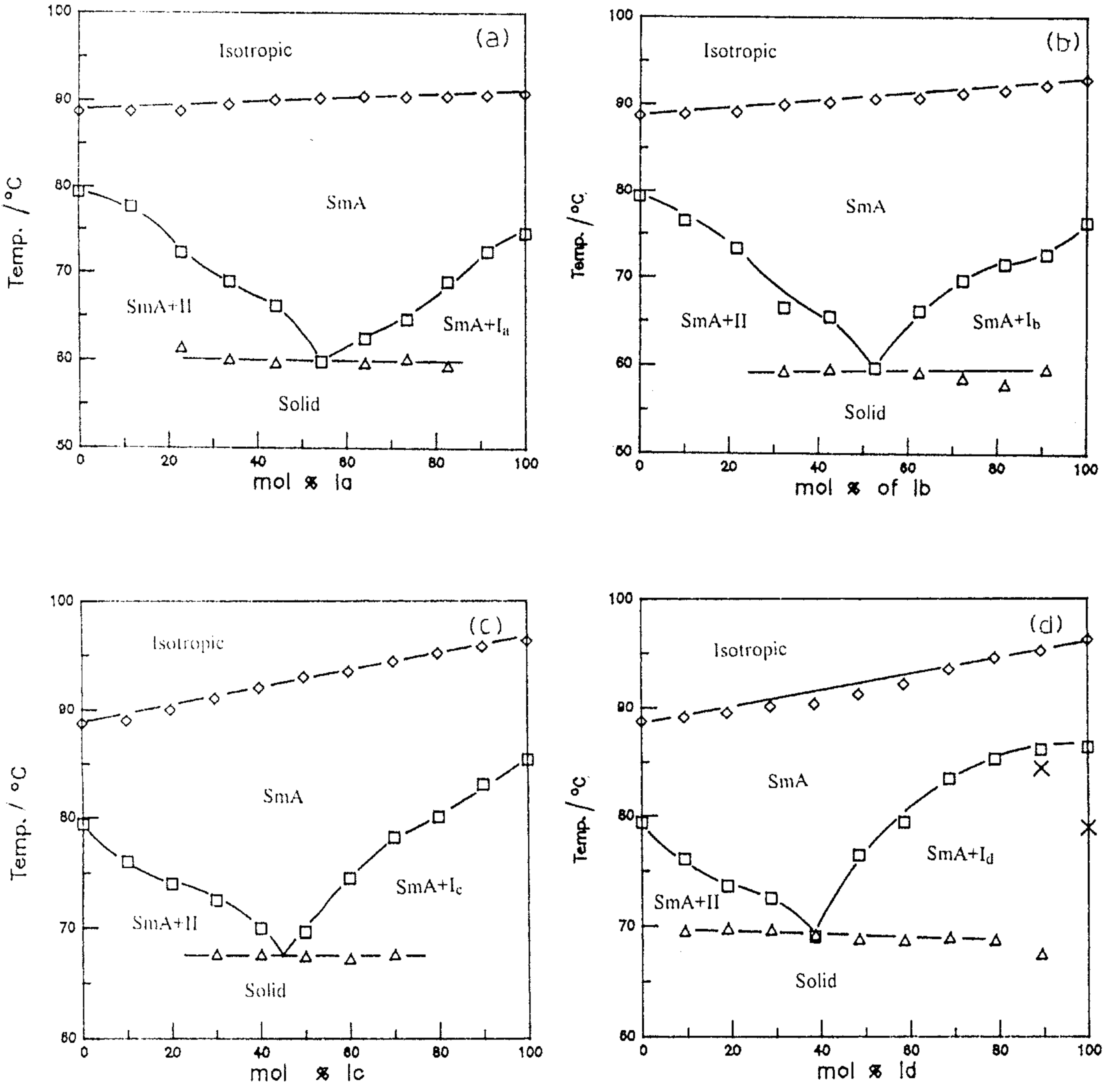


Figure 2. Binary phase diagrams for the binary mixtures (*a*) **Ia/II**, (*b*) **Ib/II**, (*c*) **Ic/II** and (*d*) **Id/II**.

in the order:

$$\mathbf{Ib/II} \approx \mathbf{Ia/II} > \mathbf{Ic/II} \approx \mathbf{Id/II}$$
$$\Delta T \quad 31 \qquad 30 \qquad 25 \qquad 25 \quad (^\circ\mathrm{C}).$$

Again, the differences are quite small, adding extra evidence that the length of the alkyl chain in compounds of comparable polarities does not greatly affect the stability of the mesophase of eutectic mixtures with a structurally similar compound.

Regarding these eutectic compositions, it is observed in figures 2 (*a–d*) that they are close to the 1 : 1 molar ratio when the alkoxy groups of each component of the mixture are of comparable length, while they deviate from 1 : 1 molar when the difference in chain length becomes more pronounced.

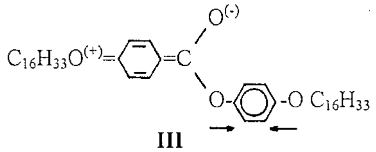
It should be mentioned here that the mesophase stability of the eutectic mixture of a cyano with a nitro compound is somewhat greater than for the corresponding cyano/cyano eutectics bearing similar alkyl groups. This may be attributed [3, 4] to the difference encountered in the steric effect of the linear cyano and the bulkier nitro groups.

Finally, compound **Id** (C = 20) exhibits a solid–solid modification at about 79°C. This solid–solid transition is retained in its mixtures with any other derivatives (**Ia–c** or **II**) up to the eutectic composition, see figures 1 (*c*, *e*, *f*) and 2 (*d*). In all these mixtures the solid–solid transitions are at temperatures above the eutectic points. This proves that any binary mixture containing **Id**, having a composition richer in **Id** than the eutectic, and at a temperature between the eutectic and the clearance, is a mixture of smectic A mesophase and pure solid **Id**.

3.2. *Effect of mesogenic group length*

In order to investigate the effect of enlarging the central mesogenic group on the phase behaviour of the phenyl benzoate system, it was planned to determine first the dipole moments of compounds **III–V**, all of them bearing two terminal $C_{16}H_{33}O$ groups. Unfortunately, except for 4-hexadecyloxyphenyl-4-hexadecyloxy benzoate (**III**), the solubility of these derivatives in non-polar solvents was too poor to prepare a solution with the concentration necessary to determine their apparent solution moments. Alternatively, the respective strength of intermolecular association occurring individually within these three molecules (**III–IV**) may be tentatively deduced if one considers their transition temperatures, T_m and T_c. DSC analyses were therefore carried out, with the results given in table 2.

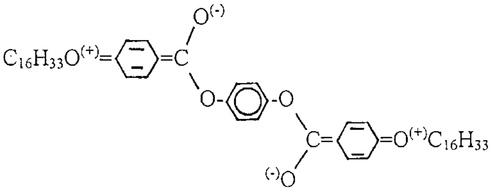
In the molecule of the 4,4′-dialkoxy phenyl benzoate **III**, conjugative interactions take place through one side of the molecule; that is, between the alkoxy oxygen and the *para*-located carbonyl ester. On the other side, competitive mesomeric interactions occur between the oxygen atom of the alkoxy group and the ester oxygen atom through the intervening benzene ring.



III

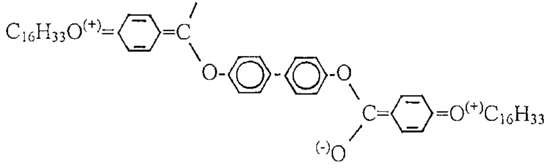
Such half-way conjugation results in a molecule possessing a relatively small dipole moment ($\mu = 2.67$ D), see table 1. Accordingly, weak intermolecular forces are expected, resulting in a relatively low melting point (95.8°C). Compound **III** is monotropic with T_c and T_m, on cooling, equal to 85.6 and 783.°C, respectively.

Replacement of the phenyl benzoate group in **III** by the 1,4-phenylene dibenzoate in **IV** results in a molecule that exhibits conjugative interactions on both sides of the molecules. Such increased polarization is definitely associated with stronger intermolecular forces either in the solid or mesophases. Compound **IV** is an enantiotrope that melts to a smectic A mesophase at 110.2°C ($\Delta H = 61.6\,\mathrm{kJ\,mol^{-1}}$) and changes to the isotropic liquid at 156.9°C ($\Delta H = 11.8\,\mathrm{kJ\,mol^{-1}}$).



IV

Similar mesomeric interactions are encountered in compound **V**. It is well known [11, 15] that the addition of more phenyl rings into a mesogenic compound increases the range of the liquid crystalline phase, as well as of transition temperatures and enthalpies. Replacement of the central phenylene group in **IV** by the more polarizable biphenylene group in **V** increases the polarity and polarizability of the molecule and, consequently, the strength of the intermolecular association. The result is the increase of T_m from 110.2°C to 124.0°C ($\Delta H = 60.5\,\mathrm{kJ\,mol^{-1}}$), and T_c from 156.9°C to 227.5°C ($\Delta H = 13.0\,\mathrm{kJ\,mol^{-1}}$).



V

At this stage, it seemed interesting to investigate the phase behaviour of binary mixtures prepared from compounds **III–V** which exhibit a wide range of polarity and considerable difference in their intermolecular forces. Three phase diagrams were constructed and are illustrated in figures 3 (*a–c*). As expected, figure 3 (*a*) shows that the mixture of the two structurally and electronically similar molecules **IV** and **V** behaves ideally, showing its eutectic composition at 31 mol % of **V** and its eutectic mesophase stability, $\Delta T = 80$°C.

At the other extreme, figure 3 (*b*) represents the phase diagram of binary mixtures of molecules **III/V** exhibiting extreme polarity and mesophase stability. This mixture gave a system that exhibits phase separation, in either the solid or liquid phases. The incompatibility of these two molecules seems to be so strong that the stable mesophase of **V** ($\Delta T = 103.5$°C) is completely disrupted upon addition of more than 20 mol % of the monotrope **III**.

Figure 3 (*c*) represents an intermediate situation, the binary mixtures of the monotrope **III** with the enantiotrope **IV**; the smectic A mesophase is observed up to ≈ 90 mol % of **III**. The eutectic composition lies around 80 mol % of **III** and is of relatively low mesophase stability, $\Delta T \approx 18$°C.

4. Conclusion

The effect of molecular length on the phase behaviour of LC compounds and of their binary mixtures comprises:

(1) The effect of terminal chain lengths. In our range (C_{12} – C_{20}) no pronounced differences were observed either in the mode of phase behaviour or on the mesophase stability of the eutectic mixtures. The only effect observed was on the

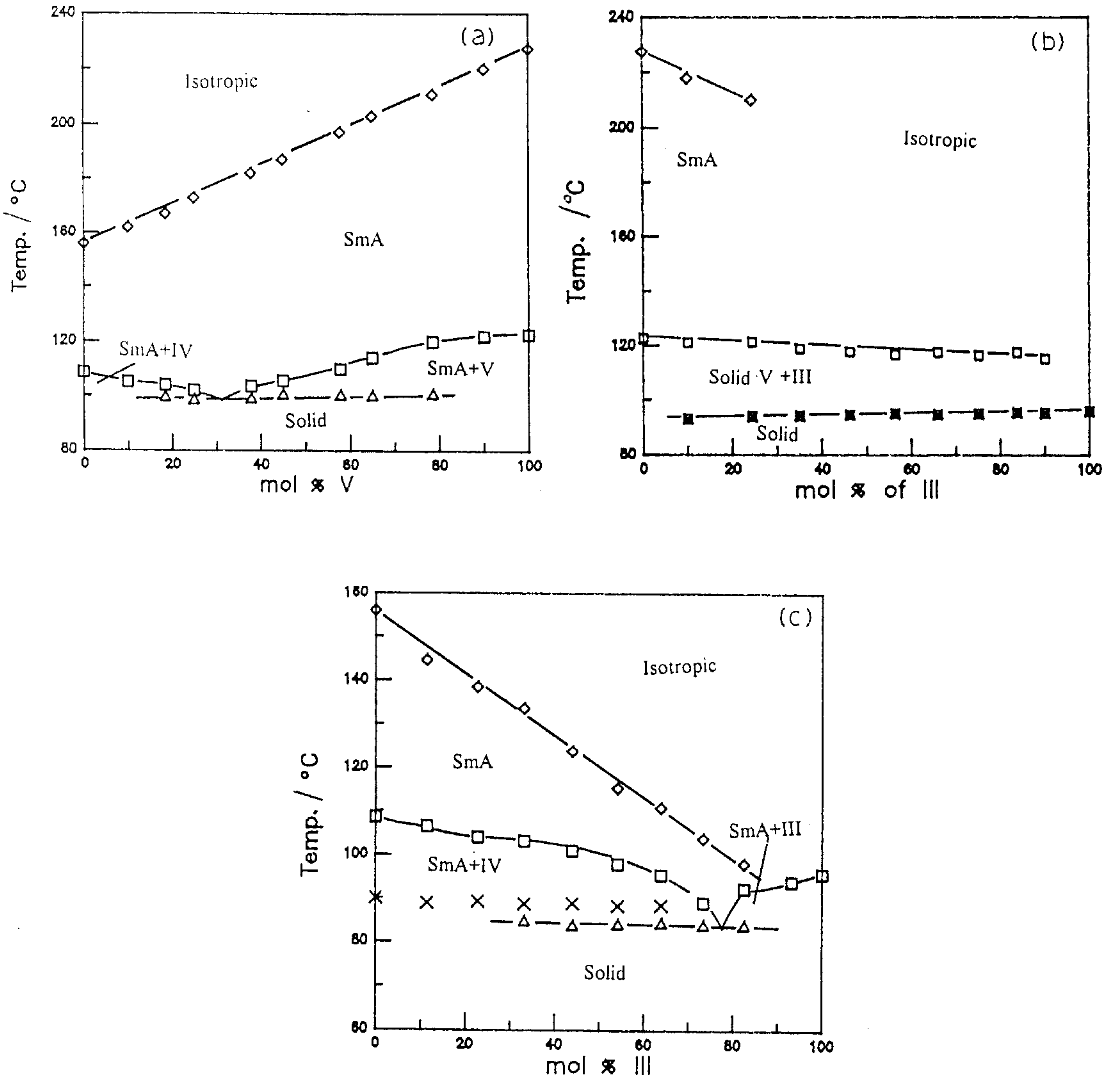


Figure 3. Binary phase diagrams for the binary mixtures (*a*) **IV/V**, (*b*) **III/V**, (*c*) **III/IV**.

eutectic compositions, which vary according to differences in the length of chain attached to both components of the mixture.

(2) The effect of variation in the central mesogenic group lengths. Since the stability of the LC molecule increases upon introducing an extra phenylcarboxylate group (for compound **IV**) (into the phenyl benzoate molecule **III**), as well as upon replacing the phenylene group by biphenylene group (for compound **V**), the result is an extreme variation in the phase behaviour of the binary mixtures of such compounds.

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