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

IV. Dependence of T_c on the anisotropy of polarizability of the aryl–*X* bond

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Transition temperatures of binary mixtures of the two series, 4-hexadecyloxyphenyl-4′-substituted benzoates (**I**a-d) and 4-substituted phenyl-4′-hexadecyloxybenzoates (**II**a-d), have been determined on cooling and the phase diagrams compared with those previously obtained on heating. T_c values for the monotropes and the non-LC analogues have been evaluated by extrapolation. Examination of both series revealed that the square root of T_c is related to the polarizability anisotropy, $\Delta\alpha_X$, of the C_{Ar}–X bond, except for the methoxy derivatives.

1. Introduction

In previous work [1, 2], the effect of inverting the central –COO– group and terminal substituent, *X*, on the mesophase stability of 4-hexadecyloxyphenyl-4′-substituted benzoates, **I**a-d, and 4-substituted phenyl-4′-hexadecyloxy benzoates, **II**a-d, as well as of their binary mixtures, was investigated. In the phenyl benzoate ester system, liquid crystallinity is more persistent as the mutual conjugation between the 4-substituent and the ester –CO– group and/or the ester oxygen atom is increased. A change in the degree of conjugation will alter both polarizability and the resultant dipole moment of the molecule; the latter is due to an effect on the mesomeric moment. A decrease in the polarizability will lead to a decrease in the dispersion forces, and consequently to a decrease in the thermal stability of the liquid crystalline phases. To realize this dependence, van der Veen [3] has used a relation to study the dependence of the mesomorphic–isotropic temperature, T_c, on the anisotropy of polarizability of bonds to small, compact terminal substituents, i.e. of the C_{Ar}–X bond, on the basis of the molecular statistical theory of Maier and Saupe [4]. Van der Veen, with some assumptions, arrived at a relation which could be applied to any mesomorphic series of compounds differing only in the terminal substituent. This relation has the form:

$$T_c \approx \Delta\alpha_M^2 + 2\Delta\alpha_M\Delta\alpha_X + \Delta\alpha_X^2. \tag{1}$$

The term $\Delta\alpha_M$ is the anisotropy of polarizability ($\alpha_{\|}$-$\alpha_{\perp}$) for all of the molecular structure except the terminal substituent, *X*. The polarizability anisotropy of the C_{Ar}–X bond, $\Delta\alpha_X$, was calculated using the data of Le Fevre and co-workers [5–7].

In equation (1), van der Veen assumed that if $\Delta\alpha_M$ is much larger than $\Delta\alpha_X$, the anisotropic–isotropic transition temperature, T_c, should show a linear dependence on $\Delta\alpha_X$, i.e.

$$T_c \approx 2\Delta\alpha_X. \tag{2}$$

More accurately, equation (1) may be re-written as:

$$T_c^{1/2} \approx \Delta\alpha_M + \Delta\alpha_X. \tag{3}$$

Thus, if $T_c^{1/2}$ values are plotted against the anisotropy of polarizability $\Delta\alpha_X$ of the substituent, a straight line is expected with an intercept equal to $\Delta\alpha_M$.

The purpose of the present work is first to examine the mesophase behaviour of the binary mixtures previously reported [2] for the two series **I**a-d and **II**a-d during the cooling cycle, in order to throw more light on the effect of the electronic nature of substituent *X* on such behaviour. Secondly, it is to test the applicability of the relation derived by van der Veen [3] and examined later by Griffin [8] to both series which represent extremes in conjugated interactions between the 4-substituent, *X*, and the remainder of the molecule. It was decided to test this relation using T_c values obtained on both heating and cooling, bearing in mind that in the case of non-LC derivatives (**I**a,b) and monotropes (**II**a,b)

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T_c values could be tentatively deduced by the extrapolation method [9] of binary phase diagrams using an enantiotrope.

2. Experimental

The preparation and characterization of compounds **I**$_{a-d}$ and **II**$_{a-d}$ have been described in a previous paper [1]. Calorimetric investigations were made using a Differential Scanning Calorimeter, PL-DSC, (Polymer Laboratories, England). Typical cooling rate was 10 K min^{-1}, and sample masses were 1–2 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).

For phase diagram data, 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. Transition temperatures during the cooling cycle were measured both by DSC and microscopy and found to agree within 2–3°C.

3. Results and discussion

The transition temperatures T_m and T_c which were previously [1] measured on heating, together with those obtained on cooling are listed in tables 1 and 2. As these tables show, the first two members of series **I** (**I**$_a$ and **I**$_b$) are not mesomorphic, whereas the corresponding isomers in series **II** (**II**$_a$ and **II**$_b$) are monotropic. The cyano and nitro analogues in both series are enantiotropic. T_c values for the non-LC (**I**$_a$ and **I**$_b$) and the monotropic analogues (**II**$_a$ and **II**$_b$) were estimated from their binary phase diagrams (constructed on heating and on cooling with one of the enantiotropes) by the extrapolation method of Bogojawlensky and Winogradow [9].

3.1. *Binary phase behaviour*

Except for the binary mixtures of any two enantiotropes, the phase diagrams of binary mixtures obtained on cooling are represented graphically in figures 1–7. Corresponding heating curves previously obtained [2] are also shown in these figures for the sake of comparison.

3.1.1. *Mixtures of methoxy-bearing derivatives and enantiotropes*

The phase diagrams constructed on heating and cooling for binary mixtures of components bearing the electron-donating group CH_3O, i.e. **I**$_a$ and **II**$_a$, with another bearing the electron-withdrawing groups CN and NO_2, i.e. the enantiotropes **I**$_c$, **I**$_d$ and **II**$_c$, **II**$_d$, are presented in figures 1–3.

An examination of the phase diagrams of the binary mixtures composed of the monotrope **II**$_a$ and the enantiotropes **I**$_d$, **II**$_d$, and **II**$_c$ [figures 1 (*a–d*) and 2 (*a*, *b*)] indicates that cooling curves possess an expanded liquid crystalline phase to cover the whole composition range, as compared with the corresponding heating curves. Furthermore, the eutectic compositions do not change significantly on the cooling curves from those observed on heating. On the other hand, an enhancement of the smectic A mesophase is produced by the monotrope **II**$_a$ when mixed with the nitro analogues **I**$_d$ and **II**$_d$ [see figures 1 (*b*, *d*)], while a corresponding linear dependence is obtained when **II**$_a$ is mixed with the cyano analogue **II**$_c$. Such behaviour is ascribed [2] to differences in the steric effect between the cyano (in **II**$_c$) and the nitro (in **I**$_d$ and **II**$_d$) groups. The bulkiness and non-linearity of

Table 1. Transition temperatures of compounds **I**$_{a-d}$.

		Heating			Cooling		
Substituent *X*	Compound	T_m/°C	T_c/°C	$T_c^{1/2}$/K$^{1/2}$	T_m/°C	T_c/°C	$T_c^{1/2}$/K$^{1/2}$
OCH_3	**I**$_a$	90·9	(81)	(18·82)	84·1	(74·6)	(18·65)
Cl	**I**$_b$	103·1	(75)	(18·66)	95·2	(69·1)	(18·50)
CN	**I**$_c$	88·2	106·8	19·49	79·1	104·2	19·43
NO_2	**I**$_d$	82·4	91·8	19·10	67·9	90·0	19·06

Table 2. Transition temperatures of compounds **II**$_{a-d}$.

		Heating			Cooling		
Substituent *X*	Compound	T_m/°C	T_c/°C	$T_c^{1/2}$/K$^{1/2}$	T_m/°C	T_c/°C	$T_c^{1/2}$/K$^{1/2}$
OCH_3	**II**$_a$	96·1	(80·0)	(18·79)	63·5	75·0	(18·66)
Cl	**II**$_b$	84·7	(71·0)	(18·55)	64·0	73·4	(18·62)
CN	**II**$_c$	85·4	96·3	19·22	67·6	90·2	19·06
NO_2	**II**$_d$	79·4	88·7	19·02	62·4	87·0	18·95

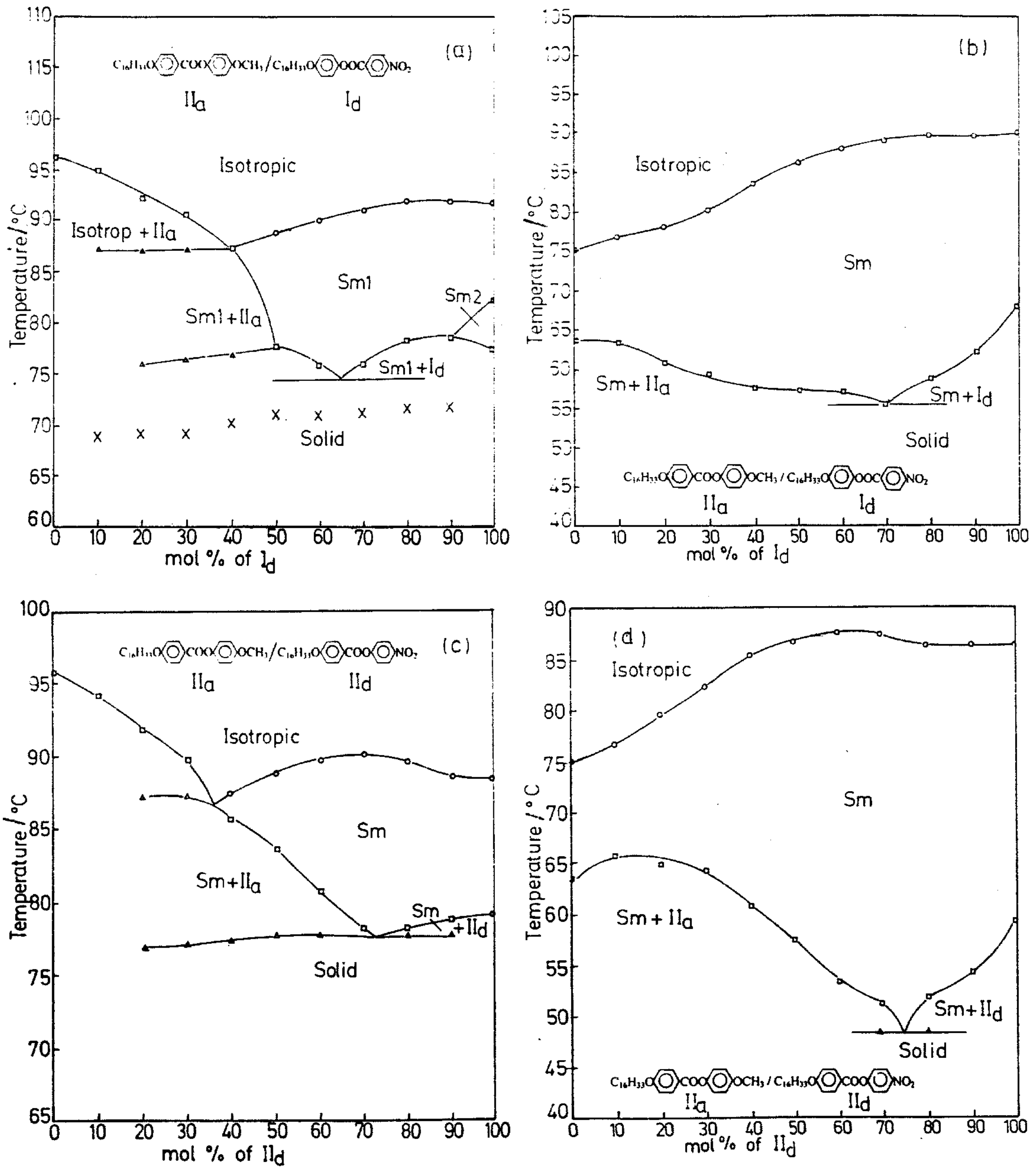


Figure 1. Phase diagrams of the binary mixtures **IIa**/**Id** and **IIa**/**IId**, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

the nitro group may lead to an enhanced dipole–dipole interaction which in turn leads to positive deviations from the ideal behaviour, as observed for the mixtures **IIa**/**Id** and **IIa**/**IId**. It may be further noticed from figures 1 (*a*–*d*), that the extent of mesophase enhancement observed on cooling is much more than that observed on heating. The clearing temperatures on heating, T_c, are higher than those detected on cooling; such higher thermal agitation energy would definitely affect the complex formation responsible for mesophase enhancement.

A consideration of the phase diagrams [figures 2 (*c*, *d*) and 3 (*a*–*d*)] that represent the binary mixtures **Ia**/**Id**, **Ia**/**IId**, and **Ia**/**Ic**, respectively, reveals that the perturbation of the smectic layering (on cooling) of the enantiotrope **IId** by the non-LC analogue **Ia** is much less than that observed with the other enantiotropes, **Ic** and **Id**. This adds extra evidence [1] for the greater mesomorphic stability of the smectic layering of the nitro and cyano isomers in series **II** compared with series **I**.

Comparison between the LC-ranges ($\Delta T = T_m - T_c$) determined on cooling, for this group of binary mixtures, which are in general greater than those determined on heating [2], reveals that the extent of anisotropic stabilities at their eutectic compositions, which are

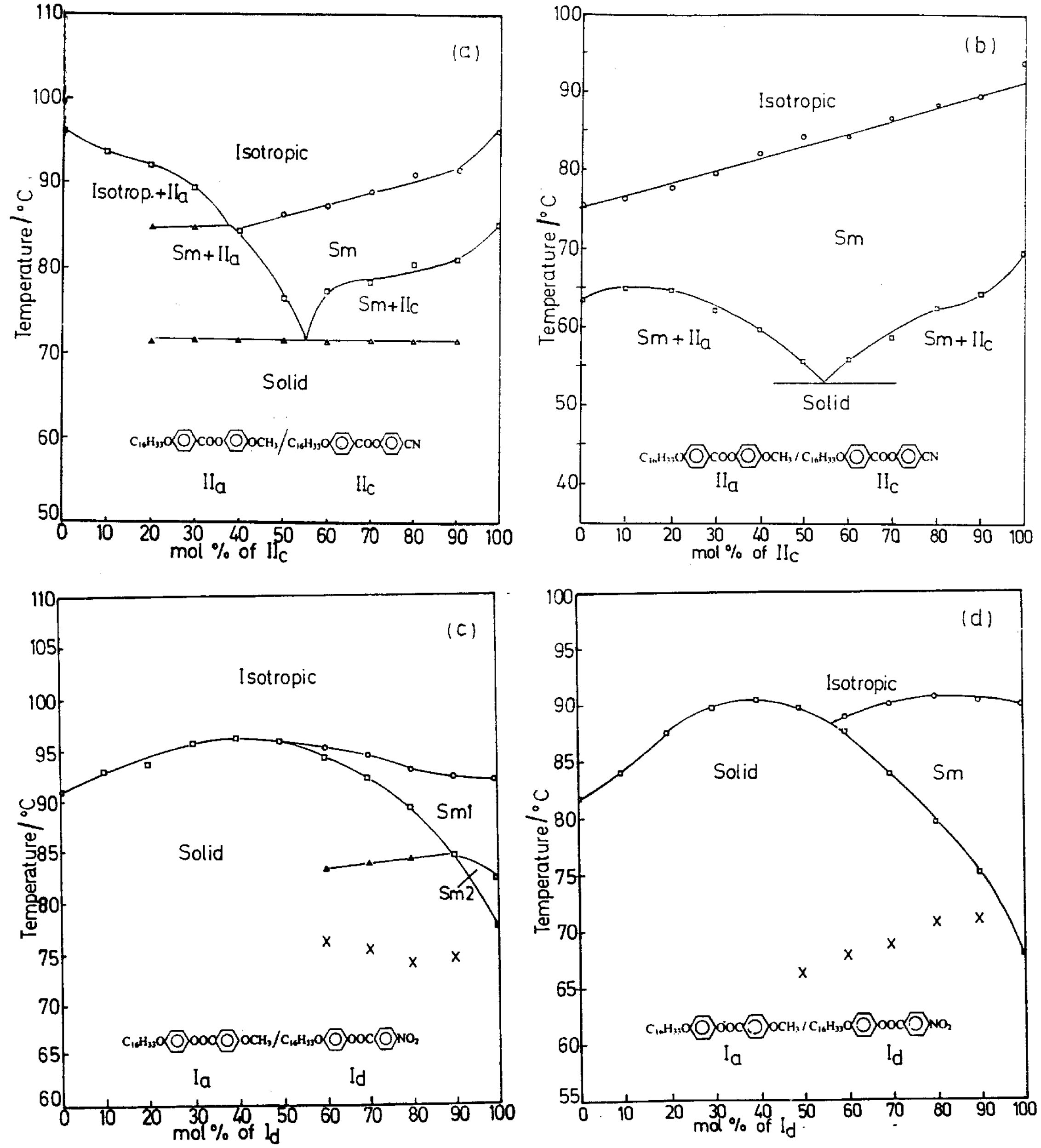


Figure 2. Phase diagrams of the binary mixtures **IIa/IIc** and **Ia/Id**, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

computed from the corresponding curves, decreases in the order

	IIa/IId >	**Ia/IId** >	**IIa/Id** >	**IIa/IIc** >	**Ia/Ic** >	**Ia/Id**
ΔT	38·5	34·0	33·9	30·5	—	—

As observed on heating, this comparison reveals that greater anisotropic stability is observed in the cases where each substituent is introduced into opposite ends in the two components of the mixtures, i.e. **Ia/IId** and **IIa/Id**. A better order of mesomorphic stability was observed on cooling than on heating for the mixture of the monotrope **IIa** with the most stable enantiotrope **IId**.

The last two mixtures (**Ia/Ic** and **Ia/Id**), consisting of the non-LC component **Ia** and the enantiotrope **Ic** or **Id** did not show eutectic compositions. In these mixtures, complete destruction of the smectic layering in **Ic** or **Id** is effected by the addition of less than 40 mol % of the non-LC component **Ia**.

3.1.2. *Mixtures of chlorine-bearing derivatives and enantiotropes*

The heating and cooling phase diagrams constructed for the binary mixtures of each of the chloro derivatives **Ib** or **IIb** with one of the enantiotropes **Ic**, **Id** or **IIc**, **IId**,

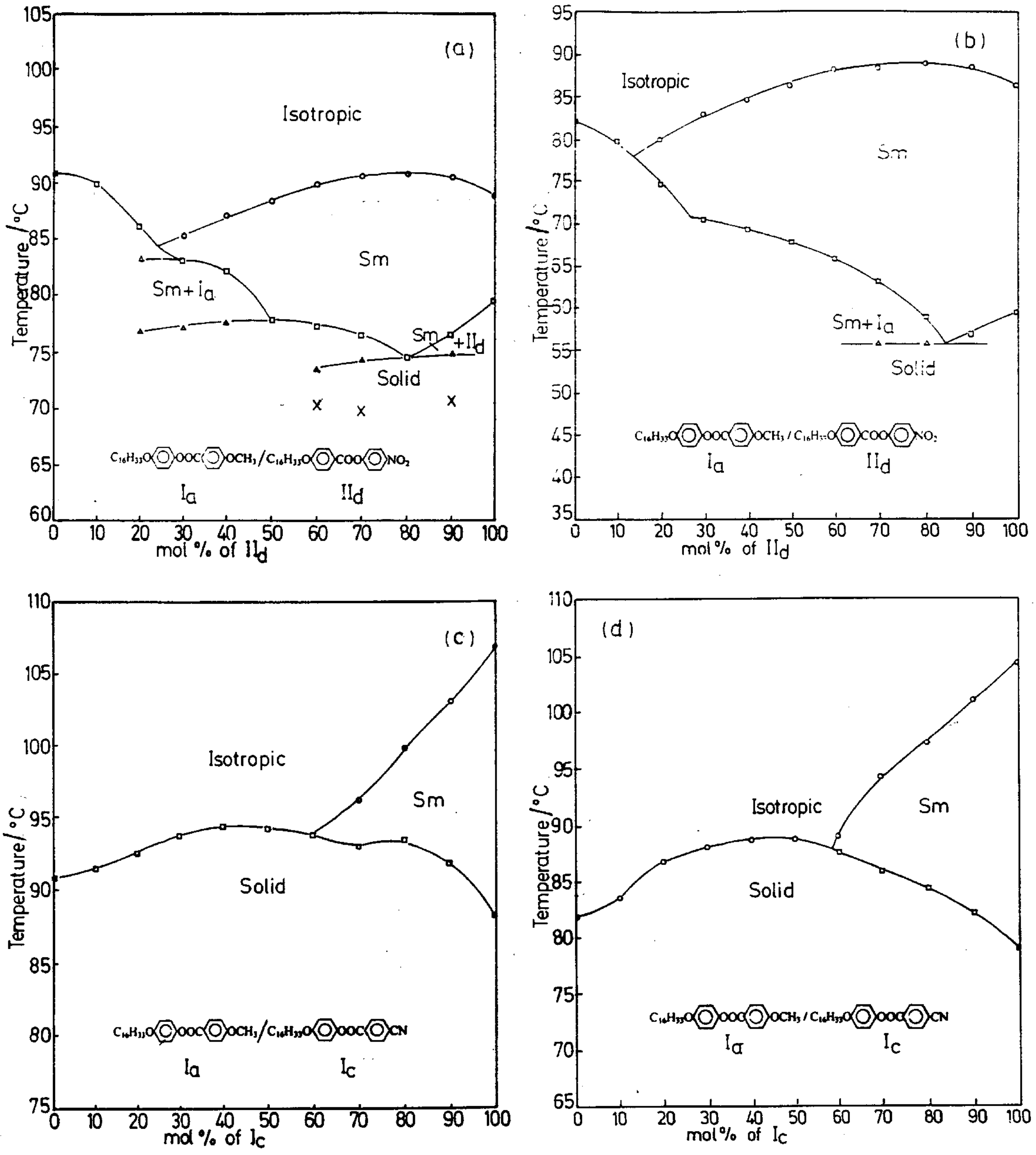


Figure 3. Phase diagrams of the binary mixtures $\mathbf{I_a}$/$\mathbf{II_d}$ and $\mathbf{I_a}$/$\mathbf{I_c}$, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

respectively, are illustrated in figures 4 and 5. As can be seen from figure 4, the perturbation of the smectic layering in $\mathbf{I_c}$ or $\mathbf{I_d}$ by the addition of the non-LC component $\mathbf{I_b}$ is so strong that even the eutectic composition could not be observed, on either heating or cooling. In both cases, the melting points of the mixtures are far above the extrapolated T_c values of $\mathbf{I_b}$, which are 75 and 69·1°C, determined on heating and cooling, respectively.

On the other hand, the monotropic isomer $\mathbf{II_b}$, when mixed with an enantiotrope $\mathbf{II_c}$ or $\mathbf{II_d}$, results in phase diagrams (figure 5) that show eutectic compositions at 60 and 50 mol % of $\mathbf{II_b}$, respectively, and a range of smectic mesophase which is expanded on cooling to cover the whole composition range. The mesophase stability ($\Delta T = T_c - T_m$) at their eutectic compositions on cooling, of the mixtures $\mathbf{II_b}$/$\mathbf{II_c}$ and $\mathbf{II_b}$/$\mathbf{II_d}$, are 22·6 and 26·0°C, respectively. Contrary to the other monotrope $\mathbf{II_a}$ that bears the electron-donating CH_3O group, the component $\mathbf{II_b}$ that bears the electron-attracting chlorine atom, results in a linear T_c-composition dependence with either of the enantiotropes $\mathbf{II_c}$ or $\mathbf{II_d}$, which bear also the electron-attracting cyano or nitro group. This is more obvious in the cooling curves, figures 5(*b*, *d*). The

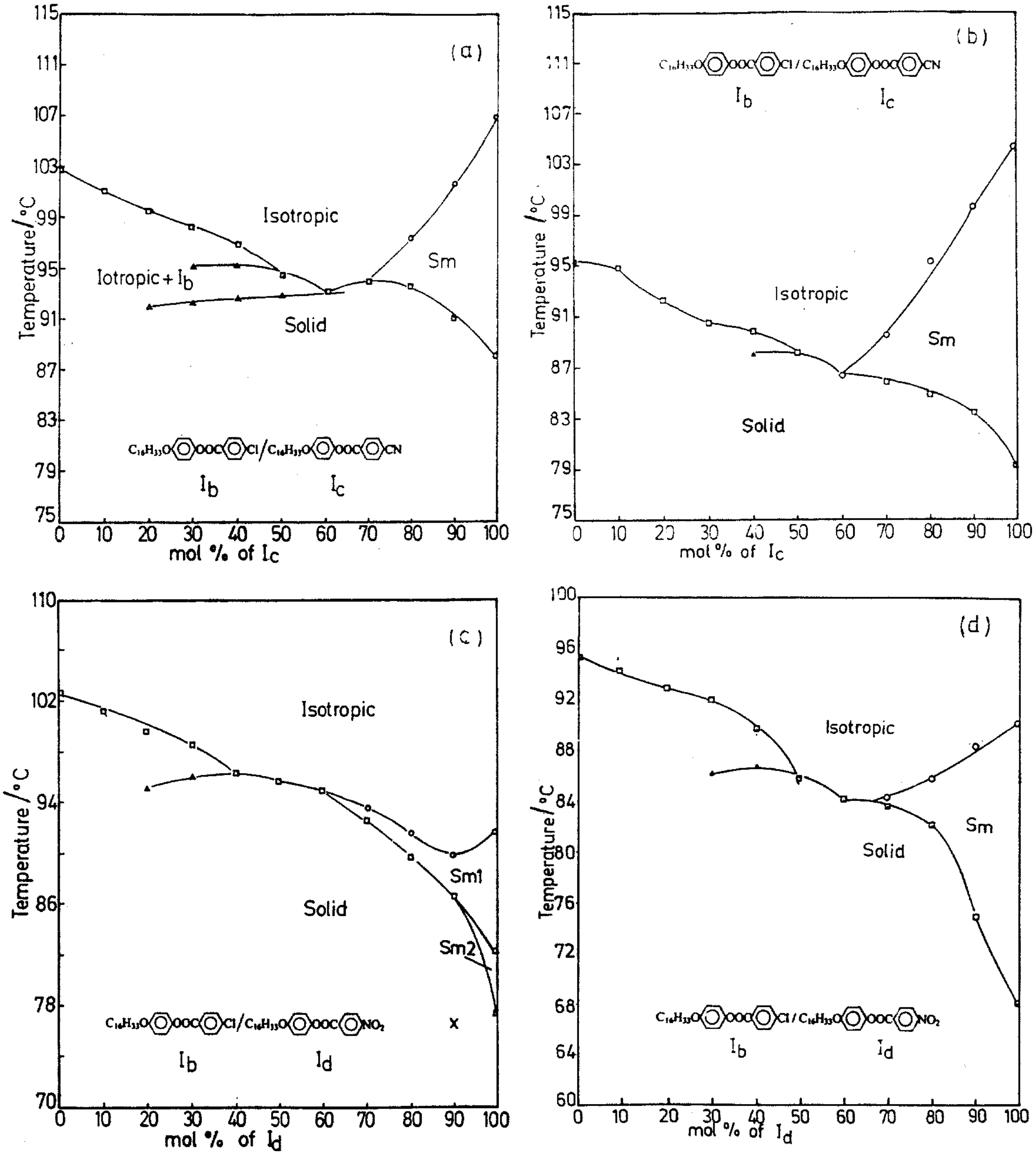


Figure 4. Phase diagrams of the binary mixtures **I**b/**I**c and **I**b/**I**d, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

heating-T_c value for **II**b, as deduced from figures 5 (*a*) or 5 (*c*) by extrapolation, is 71°C.

3.1.3. *Binary mixtures of the chloro and or methoxy compounds*

Figures 6 and 7 represent the phase diagrams constructed for the binary mixtures **I**a/**II**a, **I**b/**II**b and **II**a/**II**b, **I**a/**I**b, respectively. It can be seen from figure 6 that there is no mesophase on heating in either of the mixtures **I**a/**II**a and **I**b/**II**b, despite the fact that both of the components **II**a or **II**b is monotropic. Cooling, however, results in liquid crystalline formation (see figure 6) which is completely perturbed by the addition of an amount of the non-LC components **I**a or **I**b greater than 70 or 40 mol %, respectively.

On the other hand, the binary mixtures of the monotropes, **II**a with **II**b, gave phase diagrams of simple eutectic type on heating as well as on cooling. However, in the former case no mesophase is formed [figure 7 (*a*)], whereas in the latter a mesophase that covers the whole range of composition [figure 7 (*b*)] is observed having a stability (ΔT) at its eutectic composition of ≈13·9°C.

The phase behaviour of the binary mixtures of the two non-LC components, **I**a with **I**b, as illustrated in

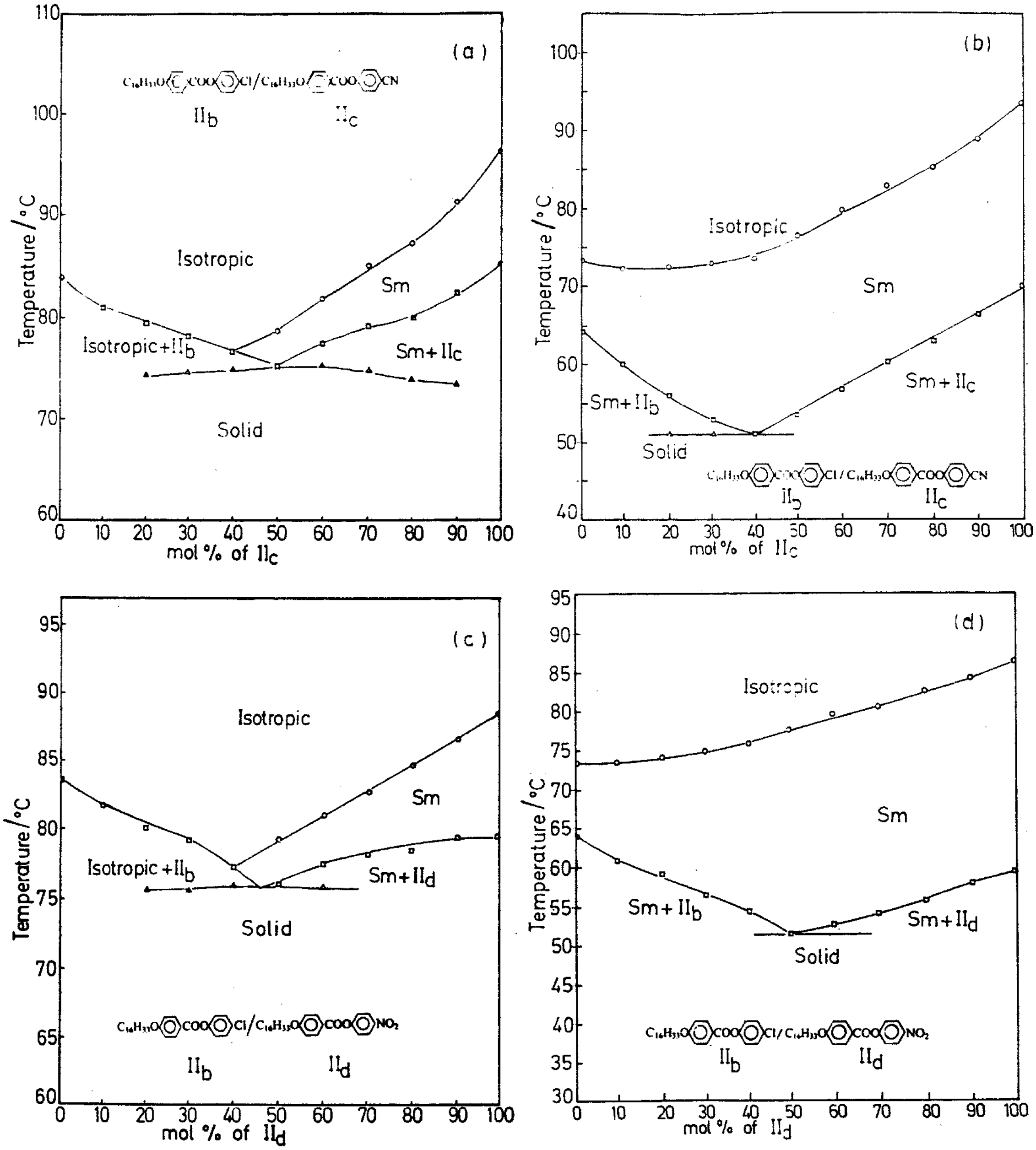


Figure 5. Phase diagrams of the binary mixtures $\mathbf{II_b}$/$\mathbf{II_c}$ and $\mathbf{II_b}$/$\mathbf{II_d}$, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

figures 7 (*c*, *d*), reveals that all mixtures melt directly to the isotropic phase and crystallize directly to the solid with roughly a linear dependence of T_c upon composition. It might be further noticed that on heating, solid mixtures undergo crystalline modifications before melting which are not evident on cooling. It seems that, on cooling, some time is required for the crystallized solid to attain its stable modification.

3.2. *Clearing temperatures and bond polarizabilities*

The determination of the semi-axes (b_1, b_2, and b_3) of a molecular polarizability ellipsoid requires a knowledge of the molar Kerr constant (K_m), the electronic polarization (P_E), and the molecular anisotropy (δ^2_∞). The relations required for such calculations are given elsewhere [10]. Alternatively, these axes can be calculated as the summation of bond and group polarizabilities (b_L, b_T, and b_V) of the individual groups and bonds constituting the molecular structure. If differences are observed between values calculated by the two methods, these may be ascribed to the polarizability exaltations, $\Sigma\Delta b$, associated with mesomeric interactions. For instance, in the *para* substituted toluenes, 4-$CH_3C_6H_4X$, the molecular polarizability tensor could be specified

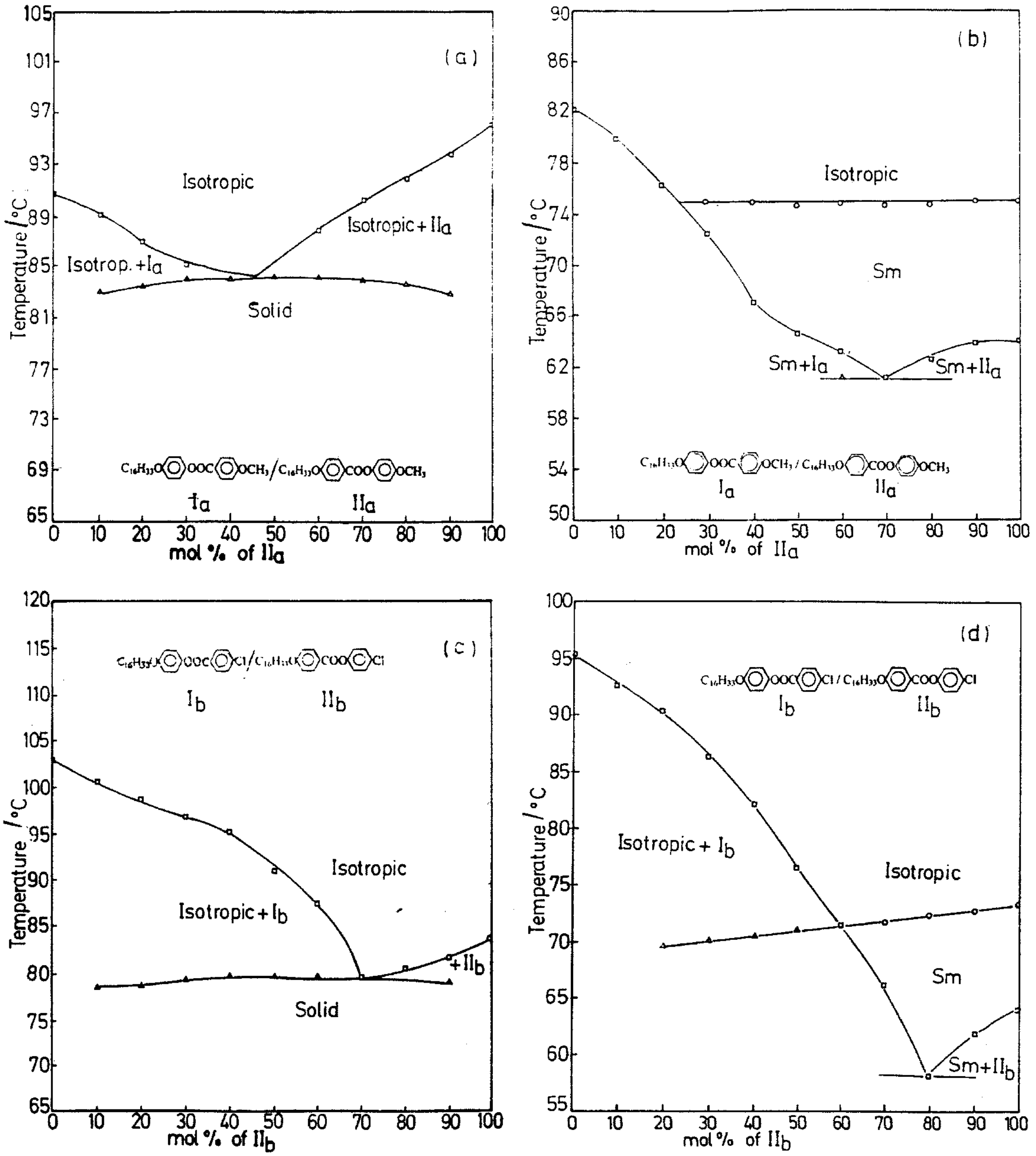


Figure 6. Phase diagrams of the binary mixtures **Ia/IIa** and **Ib/IIb**, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

[6] from the additivity of C_6H_4, C_{Ar}–CH_3, and the appropriate C_{Ar}–X group polarizabilities, if the assumption is made that the group polarizabilities are not significantly perturbed through interactions between the methyl group and the 4-X substituent. However, in the case of 4-cyano- and 4-nitro-toluenes, the predicted Kerr constant is less than that observed. This was attributed [6] to the electromeric interaction between the methyl group and its *para* (-E) substituent which results in an augmented polarizability above that predicted by additivity of the C_6H_4, C_{Ar}–CH_3, and C_{Ar}–NO_2 (or CN) group polarizabilities. Similarly, for 4-substituted anisoles, Le Fevre and co-workers [7] have calculated the polarizability enhancements, $\Sigma\,\Delta b$, from the relationship:

$$\sum \Delta b = (b_1 + b_2 + b_3)_{\text{obs}} - \sum (b_L + b_T + b_V)_{\text{calc}}. \quad (4)$$

These are regarded as corrections to the b_{xx} terms arising from the electromeric interaction occurring predominantly along the 1,4-axis of the ring. Unfortunately, the molecular anisotropy data (δ^2_∞) were not available for 4-substituted anisoles in order to estimate their individual b_1, b_2, and b_3 values or, consequently, the polarizability components b_L, b_T, and b_V of the C_{Ar}–X bonds. Alternatively, in a rough manner, b_1, b_2, and b_3,

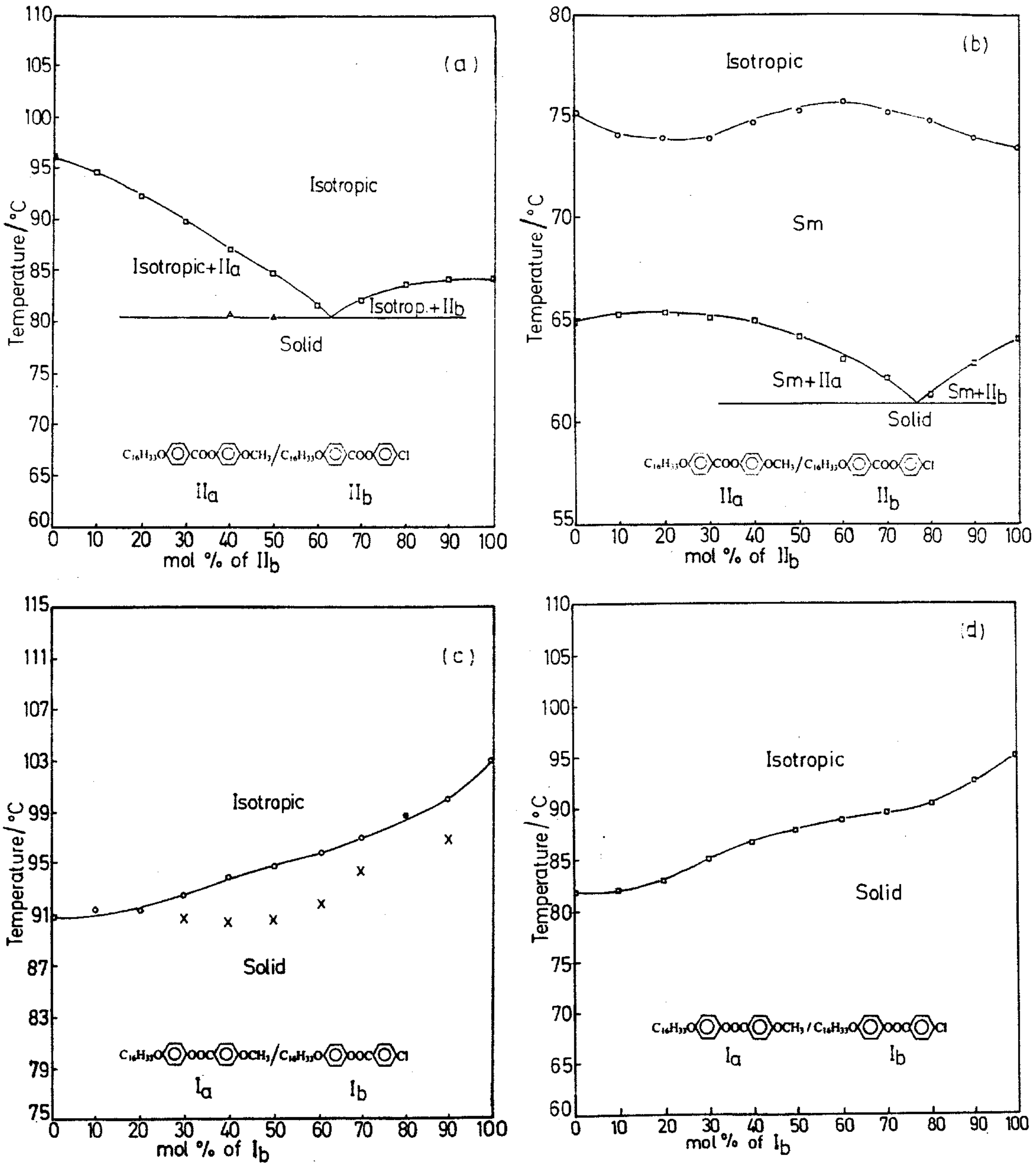


Figure 7. Phase diagrams of the binary mixtures $\mathbf{II_a}/\mathbf{II_b}$ and $\mathbf{I_a}/\mathbf{I_b}$, on heating (*a*, *c*) and on cooling (*b*, *d*), respectively.

which are the molecular polarizabilities in the direction of the dipole, in-plane perpendicular, and out-of-plane perpendicular (vertical), respectively, may be calculated if we assume that they are proportional to the dipole moment components (μ_1, μ_2, and μ_3) in the direction of these three perpendicular axes, respectively. That is,

$$\frac{b_1}{\mu_1}=\frac{b_2}{\mu_2}=\frac{b_3}{\mu_3}.$$

Thus, calculating the sum ($b_1+b_2+b_3$), from the experimental P_E values [7], using the equation

$$P_E=4\pi N(b_1+b_2+b_3)/9 \qquad (5)$$

and also the dipole moment components (μ_1, μ_2, and μ_3) from the measured dipole moment and its dihedral angles, θ and ϕ [7], using the equations:

$$\mu_1=\mu_{\text{obs}}\cos\theta \qquad (6)$$

$$\mu_2=\mu_{\text{obs}}\sin\theta\cos\phi \qquad (7)$$

$$\mu_3=\mu_{\text{obs}}\sin\theta\sin\phi \qquad (8)$$

one may estimate the individual molecular polarizabilities (b_1, b_2, and b_3). Subsequently, the polarizabilites (b_L, b_T, and b_V) of the C_{Ar}–X bond can be computed from the relations:

$$b_L(C_{Ar}\text{–}X) = b_1(\text{obs.}) - b_1(\text{anisole}) + b_L(\text{C–H}) \quad (9)$$

$$b_T(C_{Ar}\text{–}X) = b_2(\text{obs.}) - b_2(\text{anisole}) + b_T(\text{C–H}) \quad (10)$$

$$b_V(C_{Ar}\text{–}X) = b_3(\text{obs.}) - b_3(\text{anisole}) + b_V(\text{C–H}) \quad (11)$$

and the anisotropy polarizabilities ($\Delta\alpha'_X$) of the C_{Ar}–X bonds, taking into consideration the mesomeric interactions with the 4-OCH_3 substituent, are thus calculated as:

$$\Delta\alpha'_X = b_L(C_{Ar}\text{–}X) - b_V(C_{Ar}\text{–}X). \quad (12)$$

Conversely, assuming that the group polarizabilities of the molecule $CH_3OC_6H_4X$ are not perturbed by an electronic interaction between the CH_3O group and the substituent X, the anisotropic polarizabilities ($\Delta\alpha_X$) of the C_{Ar}–X bond were calculated from measurements of substituted benzene [5] in the non-polar solvent CCl_4, on the basis of the relations:

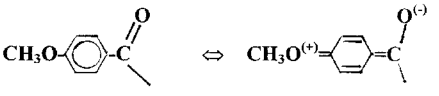
$$b_L(C_{Ar}\text{–}X) = b_1(C_6H_5X) - b_L(C_6H_5) \quad (13)$$

$$b_T(C_{Ar}\text{–}X) = b_2(C_6H_5X) - b_T(C_6H_5) \quad (14)$$

$$b_V(C_{Ar}\text{–}X) = b_3(C_6H_5X) - b_V(C_6H_5). \quad (15)$$

Hence, the $\Delta\alpha'_X$ and $\Delta\alpha_X$ were calculated from the data given by Le Fevre and co-workers [5–7] and the results are given in tables 3 and 4, respectively.

In order to apply equation (3) to the two series **Ia-d** and **IIa-d** one would expect a better correlation between $T_c^{1/2}$ of compounds **Ia-d** with $\Delta\alpha_X$ rather than with $\Delta\alpha'_X$. This is because, except for **Ia**, the substituent X will not interact electromerically with the CO group situated *para* to it [1]. This was found to be true; if one considers figure 8, a good correlation was obtained except for **Ia**. In the latter case, the excess mesomeric effect, encountered between the CH_3O and the *para* CO groups,



would lead to a greater polarizability and, hence, to a large $\Delta\alpha_X$ value. This could, conversely, be estimated from figure 8 by interpolation to be $3{\cdot}1 \times 10^{-24}\,\text{cm}^3$, as a $\Delta\alpha_X$ correct value for the CH_3O group, when substituted *para* to a carbonyl group.

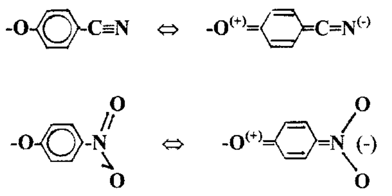
Table 3. Polarizability enhancement ($\Sigma\Delta b$), group semi-axes polarizabilities (b_L, b_V), and polarizability anisotropy ($\Delta\alpha'_X$), of the C_{Ar}–X bond based on measurements of substituted anisoles in CCl_4 [7].

Substituent X	10^{24} $\Sigma\Delta b/\text{cm}^3$	10^{24} b_L/cm^3	10^{24} b_V/cm^3	10^{24} $\Delta\alpha'_X/\text{cm}^3$
OCH_3	−0·11	3·62	2·80	0·92
Cl	0·66	4·67	1·56	3·11
CN	0·60	6·17	1·05	5·12
NO_2	2·46	6·96	2·38	4·58

Table 4. Group semi-axes polarizabilities (b_L, b_V), and polarizability anisotropy ($\Delta\alpha_X$) of the C_{Ar}–X bond based on measurements of substituted benzenes in CCl_4 [5].

Substituent X	10^{24} b_L/cm^3	10^{24} b_V/cm^3	10^{24} $\Delta\alpha_X/\text{cm}^3$
OCH_3	3·73	2·87	0·86
Cl	4·30	1·50	2·80
CN	5·70	1·45	4·25
NO_2	5·61	1·90	3·71

With respect to series **IIa-d**, the reverse seems true, that is a better correlation is obtained between $T_c^{1/2}$ values and $\Delta\alpha'_X$, rather than with $\Delta\alpha_X$, since in this series of compounds, the substituent X is located *para* to the ester oxygen atom. This would lead to an enhancement of polarizabilities,



The deviation from linearity observed for the derivative **IIa** is attributed to an inaccuracy in calculating $\Delta\alpha'_X$ for the C_{Ar}–OCH_3 bond. The latter was calculated on the

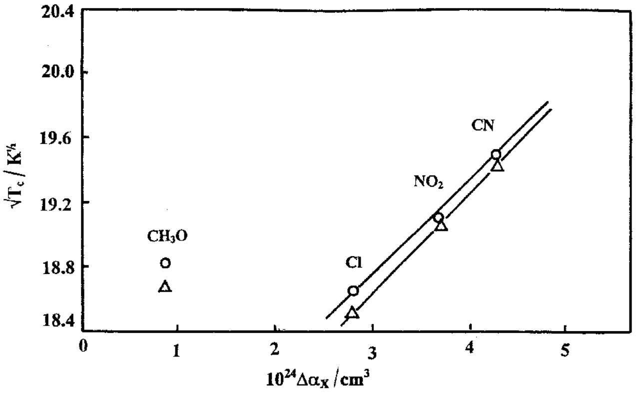


Figure 8. Dependence of the square root of T_c of series **Ia-d** on the anisotropy of polarizability ($\Delta\alpha_X$) of the C_{Ar}–X bonds.

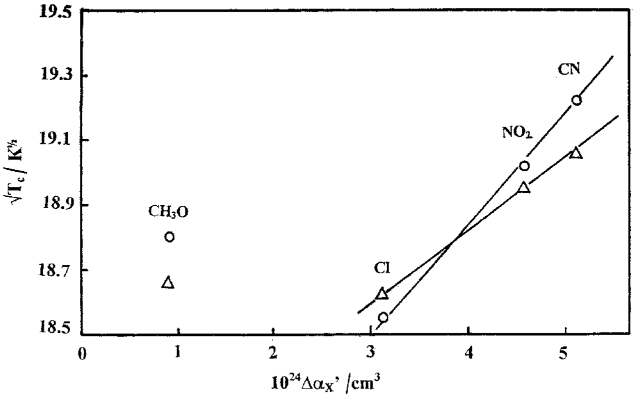


Figure 9. Dependence of the square root of T_c of series **IIa-d** on the anisotropy of polarizability ($\Delta\alpha_X$) of the C_{Ar}–X bonds.

basis of measurements of anisole and not of the dimethoxybenzene in CCl_4 [7]. A corrected $\Delta\alpha_X'$ value for the 4-methoxy analogue could be estimated, by interpolation in figure 9, to be $3{\cdot}2 \times 10^{-24}\,cm^3$.

4. Conclusions

The two series **Ia-d** and **IIa-d** represent extremes in conjugative interactions between the terminal substituent X and the remainder of the molecule. Such differences would lead to a significant variation in the mesophase behaviour of either pure components of their binary mixtures. Examination of the phase diagrams of mixtures composed of the monotropes **IIa** or **IIb** with one of the enantiotropes revealed that the cooling curves possess expanded LC-ranges to cover the whole composition range, as compared with the corresponding heating curves. While, on heating, the binary mixtures of the two monotropes (**IIa**/**IIb**) together gave a phase diagram that shows no mesophase, on cooling, the mesophase covers the whole range of composition.

On the other hand, it was found that $T_c^{1/2}$ is related to the polarizability anisotropy, $\Delta\alpha_X$, of the C_{Ar}–X bond. The T_c values for the non-LC analogues, **Ia** and **Ib**, as well as the on-heating values for the monotropes **IIa** and **IIb**, have been evaluated by the method of extrapolation of their binary phase diagrams with an enantiotrope. For series **Ia-d**, a good correlation could be drawn between $T_c^{1/2}$ and $\Delta\alpha_X$, as calculated from substituted benzenes, while for compounds **IIa-d**, a better correlation was obtained with $\Delta\alpha_X'$ as evaluated from substituted anisoles. The methoxy substituents in **Ia** and **IIa**, which interact strongly with the remainder of the molecular π-electronic system, are notable exceptions.

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