

# Possibility of mesophase formation in some model compounds based on the *N*-aryl benzamide group

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## Abstract

Five series of *N*-aryl-4-alkoxybenzamides [RO–C<sub>6</sub>H<sub>4</sub>–CONH–C<sub>6</sub>H<sub>4</sub>–X] were prepared where the terminal alkoxy group (RO) possesses a number of carbon atoms (*n*) that varies between 8, 10, 12, 14, or 18 carbons, while the other terminal substituent (X) alternatively changes from CH<sub>3</sub>O, CH<sub>3</sub>, H, Cl, and NO<sub>2</sub>. The terminal group X was introduced once in position 4- with respect to the anilide C=O group, furnishing, as expected, linear molecules, and others in the 2- (or 3-) positions aiming to induce some steric hindrance to the linear association of the rod-shaped molecules, specially in the solid phase. Further replacement of the anilide-H atom with a methyl (CH<sub>3</sub>) group was performed into the unsubstituted derivatives (X=H) in order to disrupt any unfavourable hydrogen bonding between any two neighbouring molecules. Compounds prepared were characterized by elemental analyses, infrared, and <sup>1</sup>H NMR spectra, and their phase behaviour investigated by differential scanning calorimetry and polarized-light microscopy. The results were discussed in terms of mesomeric, steric, polarity, and polarizability effects. Independent of the polarity or position of the substituent X, all compounds prepared were found to be non-mesomorphic. The *N*-methyl derivative (that excludes the possibility of hydrogen-bond formation) was also found to be non-mesomorphic. In all five series of compounds, their tendency to form a mesophase (smectic or nematic) was estimated from their binary phase diagrams with either of the smectogenic compound, 4-*n*-C<sub>16</sub>H<sub>33</sub>O–C<sub>6</sub>H<sub>4</sub>–COO–C<sub>6</sub>H<sub>4</sub>–OOC–C<sub>6</sub>H<sub>4</sub>–CN, or the nematogenic compound, 4-*n*-C<sub>16</sub>H<sub>33</sub>O–C<sub>6</sub>H<sub>4</sub>–COO–C<sub>6</sub>H<sub>4</sub>–OOC–C<sub>6</sub>H<sub>4</sub>–CH<sub>3</sub>. Dipole moment calculations for the core structure (benzanilide) revealed that such a group of compounds exists in a non-linear, non-planar conformation.

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## 1. Introduction

Organic compounds that form mesophases upon melting (thermotropic) are those having either linear (calametic) or disk-like (discotic) molecules. Calametic liquid crystals are characterized by being long, narrow, and rod-shaped molecules. Both permanent dipoles and polarizable moieties are required. The thermal stability of the mesophase formed depends, to a great extent, on subtle structural, steric, and electronic effects within the central and terminal groups. Attempts to correlate the mesophase stability with molecular structure, in liquid crystalline compounds, are based on considerations of the

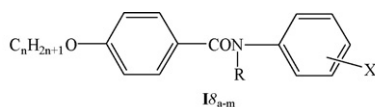
nature and magnitude of the intermolecular forces that favour the lateral association of their rod-shaped molecules. However, intermolecular forces due to dipole–dipole interactions have showed [1–9] to be not the only factors important in promoting mesophase stability. Linking groups that maintain rigidity and linearity of the molecules are satisfactory in this respect. The ester group (COO) is one of the most commonly used linking units in liquid crystals since it is relatively stable. Mutual conjugation within the ester moiety, in the phenyl benzoate molecule, and the rings leads to some double bond character and the mesophase becomes more persistent when the mutual conjugation between the substituents and the ester carbonyl (or oxygen) is increased [10]. The anilide linking group, in the benzanilide system (I) furnishes compounds that are more or less electronically and sterically similar to the ester group. It has been mentioned [11,12] that replacement of the ester group (COO) with an anilide group (CONH) enhances the nematic transition temperature ( $T_{N-I}$ ) by about 16 °C. Carboxylic acid

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derivatives, such as the anilide, hinder rotation around the single bond, therefore, possess higher transition temperatures [11]. Nevertheless, the number of amide-based liquid crystals is small since amides have often comparatively high melting temperatures and mesophases cannot be observed. Unfortunately, little attention has been paid to investigate such group of compounds.

The purpose of the present study is to investigate, first, the effect of the polarity of the substituent X as well as the length of the alkoxy-chain R on the mesophase formation of compounds of type I. Secondly, is to test the steric factors, due to *ortho*-, *meta*-, or *N*-substitution of the anilide, that may affect, specially in the solid phase, the strength of lateral association or any unfavourable H-bond formation. Terminal substituents can both attract and repel one another in different molecules. They can also affect the polarizability of the aromatic rings to which they are attached. In addition, terminal substituents may interact with the lateral portion of an adjacent molecule.



$n = 8, 10, 12, 14, \text{ or } 18,$

R = H, a, X = 4-CH<sub>3</sub>O; b, X = 4-CH<sub>3</sub>; c, X = H; d, X = 4-Cl; e, X = 4-NO<sub>2</sub>; f, X = 3-CH<sub>3</sub>O; g, X = 2-CH<sub>3</sub>O; h, X = 3-CH<sub>3</sub>; i, X = 2-CH<sub>3</sub>; j, X = 3-Cl; k, X = 2-Cl; l, X = 3-NO<sub>2</sub>; and m, X = 2-NO<sub>2</sub>  
n, R = CH<sub>3</sub>, n = 18, X = H

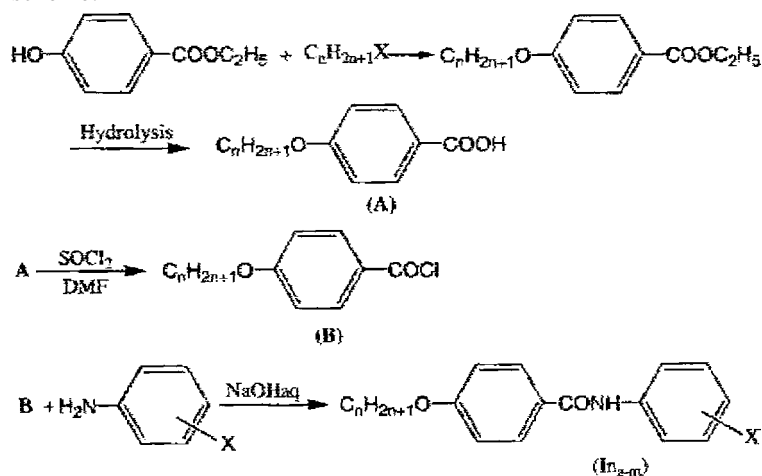
Substituents were chosen to cover a wide range of steric and electronic nature, which represent extremes in conjugated interaction with the central linking group via the intervening benzene rings.

## 2. Experimental

Chemicals were purchased from the following companies; M.B. Biomedicals Inc., France; Sigma–Aldrich Chemie, GMBH, Germany; Fluka Chemie AG, Switzerland; and BDH LTD, England.

### 2.1. Preparation of materials

All compounds were prepared according to the following scheme:



#### 2.1.1. 4-*n*-Alkoxybenzoic acid (A)

Ethyl 4-*n*-alkoxybenzoate were first prepared from ethyl 4-hydroxybenzoate and the appropriate 1-bromo-*n*-alkane; the esters were then saponified to the corresponding acid using aqueous KOH, by the method previously described [10,13]. The resulting acids were TLC pure and exhibited phase transition temperatures agreed with those reported in the literature [10,13].

#### 2.1.2. *N*-Aryl-4-*n*-alkoxybenamides (In<sub>a-m</sub>)

To 0.005 mol of the acid, 2 drops of dimethylformamide (DMF) were added followed by 4 ml thionyl chloride and the mixture warmed carefully on a water bath for 20 min. After cooling to room temperature, 20 ml of dichloromethane were added (solution I). In a separate Erlenmeyer flask, 0.01 mol of the amine was dissolved in 20 ml of dichloromethane. To the resulting mixture, 20 ml of 25% aqueous NaOH solution were added and the two-phase mixture cooled in an ice-bath (solution II). The dilute acid chloride solution (solution I) was added, in 1 ml portions with vigorous swirling, to the amine solution (II) and cooling after each addition in the ice-bath. The upper aqueous layer was checked with pH paper after each addition to ensure that the pH of the aqueous layer remained over 10. After the addition was complete, the Erlenmeyer flask was swirled vigorously at room temperature for 10 min and left overnight with stirring. The dichloromethane (lower) layer was separated and washed with 15 ml 5% aqueous HCl solution followed by 15 ml of water. After evaporating the dichloromethane solution to dryness, the solid residue was crystallized twice from aqueous ethanol and third from acetone–petroleum ether, if necessary. The resulting anilides were TLC pure and exhibited phase transition temperatures as summarized in Table 1.

### 2.2. Physical characterization

Infrared spectra were measured (4000–400 cm<sup>-1</sup>) with a Perkin-Elmer B25 spectrophotometer, and <sup>1</sup>H NMR-spectra with a Varian EM 3501.

Table 1  
Melting temperatures ( $T_m$ , °C), melting enthalpies ( $\Delta H_m$ , kJ/mol), and freezing temperatures ( $T_f$ , °C) of the homologous series (**I** $n_{a-e}$ )

Compound no.	$n$	Substituent X	On heating		On cooling	
			$T_m$ (°C)	$\Delta H_m$ (kJ/mol)	$T_f$ (°C)	$\Delta H_f$ (kJ/mol)
<b>I</b> 8 <sub>a</sub>	8	–OCH <sub>3</sub>	159.2	36.65	142.6	–35.07
<b>I</b> 8 <sub>b</sub>		–CH <sub>3</sub>	154.0	40.36	145.8	–38.14
<b>I</b> 8 <sub>c</sub>		H	150.0	54.98	129.8	–52.15
<b>I</b> 8 <sub>d</sub>		–Cl	178.7	23.03	171.8	–20.90
<b>I</b> 8 <sub>e</sub>		–NO <sub>2</sub>	150.0	19.68	137.1	19.68
<b>I</b> 10 <sub>a</sub>	10	–OCH <sub>3</sub>	148.2	22.0	135.3	–15.73
<b>I</b> 10 <sub>b</sub>		–CH <sub>3</sub>	148.3	25.12	136.1	–22.76
<b>I</b> 10 <sub>c</sub>		H	132.5	33.19	120.8	–31.03
<b>I</b> 10 <sub>d</sub>		–Cl	179.8	12.52	174.3	–11.07
<b>I</b> 10 <sub>e</sub>		–NO <sub>2</sub>	141.8	14.93	129.8	–14.28
<b>I</b> 12 <sub>a</sub>	12	–OCH <sub>3</sub>	147.5	16.95	128.0	–9.63
<b>I</b> 12 <sub>b</sub>		–CH <sub>3</sub>	143.3	27.57	112.3	–25.67
<b>I</b> 12 <sub>c</sub>		H	137.0	28.39	119.6	–24.14
<b>I</b> 12 <sub>d</sub>		–Cl	174.3	5.29	168.0	–5.15
<b>I</b> 12 <sub>e</sub>		–NO <sub>2</sub>	133.5	11.73	108.0	–8.09
<b>I</b> 14 <sub>a</sub>	14	–OCH <sub>3</sub>	150.0	23.88	135.1	–16.12
<b>I</b> 14 <sub>b</sub>		–CH <sub>3</sub>	142.8	28.26	132.8	–27.86
<b>I</b> 14 <sub>c</sub>		H	140.5	32.36	126.9	–31.30
<b>I</b> 14 <sub>d</sub>		–Cl	172.9	17.18	163.1	–15.0
<b>I</b> 14 <sub>e</sub>		–NO <sub>2</sub>	96.1	24.18	74.9	–22.51
<b>I</b> 18 <sub>a</sub>	18	–OCH <sub>3</sub>	140.8	34.68	129.5	–18.08
<b>I</b> 18 <sub>b</sub>		–CH <sub>3</sub>	133.1	28.28	124.9	–25.05
<b>I</b> 18 <sub>c</sub>		H	131.2	30.83	114.7	–28.10
<b>I</b> 18 <sub>d</sub>		–Cl	120.2	9.89	99.5	–9.09
<b>I</b> 18 <sub>e</sub>		–NO <sub>2</sub>	118.6	10.75	111.3	–8.58

Calorimetric investigations were made using Polymer Laboratories (England) differential scanning calorimeter, PL-DSC, with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultra-pure metals, and a value of 28.45 J g<sup>–1</sup> was used for the enthalpy of fusion of indium. Typical heating rates were 20 K min<sup>–1</sup>, and a sample mass was 2–3 mg. Transition temperatures were identified with a standard polarized-light microscope (Wild, Switzerland), attached to a home-made hot-stage.

Thin layer chromatography (TLC) was performed with TLC-sheets coated with silica gel (E. Merck); spots were identified with uv-illumination.

### 3. Results

Transition temperatures ( $T_m$ ) and transition enthalpies ( $\Delta H_m$ ), as measured by DSC, for all compounds investigated are summarized in Table 1.

Since identical infrared absorption spectra were observed for all corresponding members in the five series (**I**8, **I**10, **I**12, **I**14, and **I**18), the absorption frequencies for compounds of series **I**8, with their assignments, are given as representative examples, in Table 2.

Infrared spectra and elemental analyses for compounds investigated were consistent with the structures assigned. H<sup>1</sup> MNR data observed showed expected integrated aliphatic-to-aromatic proton ratios.

Table 2  
Characteristic infrared absorption frequencies (in cm<sup>–1</sup>) for compounds **I**8<sub>a–m</sub> in KBr

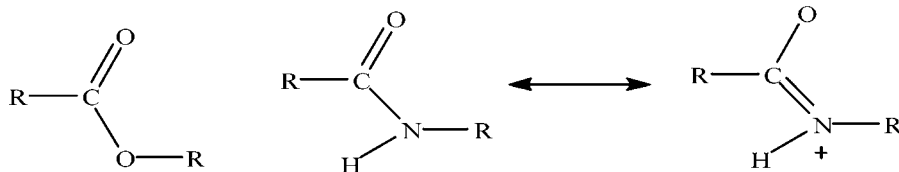
Compound no.	X, R	$\nu_{N-H}$	$\nu_{C=O}$	$\nu_{C-N}$	$\nu_{NO_2}$
<b>I</b> 8 <sub>a</sub>	4-OCH <sub>3</sub> , H	3310	1636	1404	–
<b>I</b> 8 <sub>b</sub>	4-CH <sub>3</sub> , H	3302	1639	1435	–
<b>I</b> 8 <sub>c</sub>	H, H	3317	1643	1435	–
<b>I</b> 8 <sub>d</sub>	4-Cl, H	3333	1651	1435	–
<b>I</b> 8 <sub>e</sub>	4-NO <sub>2</sub> , H	3340	1659	1342	1504
<b>I</b> 8 <sub>f</sub>	2-OCH <sub>3</sub> , H	3325	1643	1435	–
<b>I</b> 8 <sub>g</sub>	3-CH <sub>3</sub> , H	3286	1643	1435	–
<b>I</b> 8 <sub>h</sub>	2-CH <sub>3</sub> , H	3310	1636	1451	–
<b>I</b> 8 <sub>i</sub>	3-Cl, H	3310	1643	1435	–
<b>I</b> 8 <sub>j</sub>	2-Cl, H	3310	1643	1435	–
<b>I</b> 8 <sub>k</sub>	3-NO <sub>2</sub> , H	3333	1659	1350	1512
<b>I</b> 8 <sub>l</sub>	2-NO <sub>2</sub> , H	3356	1674	1435	1497
<b>I</b> 8 <sub>m</sub>	H, CH <sub>3</sub>	–	1635	1470	–

### 4. Discussion

#### 4.1. Infrared spectra

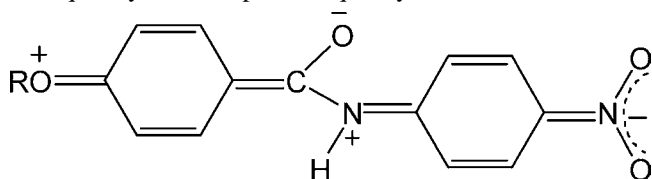
The almost identical infrared spectra observed for all homologues, bearing the same substituent X, in the five series of compounds, revealed that the mesomeric shift of: (i) the anilide C=O group, attached to the 4-position with respect to the alkoxy group, and (ii) the aniline –C<sub>6</sub>H<sub>4</sub>NH– bridge attached to the 4- (2- or 3-) position to the substituent X are not significantly affected by the length of the alkoxy-chain ( $n=8, 10, 12, 14,$

or 18). Generally, the anilide C=O group absorbs at lower frequency compared with the ester C=O group [14]. This indicates that replacement of the –O– bridge in an ester by a –NH– bridge decreases the double bond character of the C=O bond and, consequently, lowers its absorption frequency. This can be explained considering the inductive (electron-withdrawing) and resonance effects. These two effects operate in opposite manners to influence the C=O stretching frequency. First, an electronegative element may tend to draw-in the electrons between the carbon and oxygen atoms, through its electron-withdrawing effect, so that the C=O bond becomes somewhat stronger. A high frequency (high energy) absorption then results, as in the case of the ester analogues [9]. Second, the unpaired electrons on the nitrogen, in the anilide analogues, can conjugate with the carbonyl group, resulting in an increased single bond character and a lowering of the C=O absorption frequency. Oxygen is more electronegative than nitrogen, and the first effect dominates in an ester to raise the carbonyl frequency. In an anilide, the second effect is dominant since nitrogen is not as electronegative as oxygen and more willingly back-donates its unshared electrons, resulting in an absorption frequency lower than that of the ester.



It has to be mentioned that the conjugative interaction between the oxygen atom of the 4-alkoxy group and the anilide carbonyl in our investigated group of compounds (**I**<sub>a-m</sub>) decreases the possibility of conjugation between the amide-N and the amide carbonyl.

As can be seen from Table 2, for a group of the anilide compounds bearing the same alkoxy group, e.g., **I**<sub>8-a-n</sub>, the anilide C=O absorption frequencies are influenced by the nature and position of the polar group X. This could be attributed to their inductive effect (through the –C<sub>6</sub>H<sub>4</sub>NH– bridge) on the extent of polarization of the anilide C=O group. Thus, due to the variation in the electronic (and steric in the 2- and 3-substituted derivatives) nature of X, its mesomeric interaction with the remainder of the molecule is expected to be somewhat different. Thus, in the electron-withdrawing (4-NO<sub>2</sub>) substituted homologues, conjugative interaction takes place between the substituent X and the lone pair of the anilide nitrogen via the intervening benzene ring, leading to an increase in the double bond character of the anilide C=O group by a positive inductive effect (+I). Consequently, its absorption frequency is increased.



Conversely, the electron-donating (CH<sub>3</sub>O or CH<sub>3</sub>) substituent, supplies electrons to the carbonyl bond, via negative

inductive effect thus, weakens the C=O bond and lowers the force constant and absorption frequency.

The charged (mesomeric) form of the anilide analogues may lead to strong intermolecular hydrogen bonding. Generally, hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the stretching force constant. This results in a lowering of the absorption frequency.

It can be noted from Table 2 that compounds bearing the electron-withdrawing (4-NO<sub>2</sub>) group have their anilide carbonyls that absorb at 1659–1674 cm<sup>-1</sup>. This may be attributed to the mesomeric interactions affected by the two terminal (nitro and alkoxy) groups on both sides of the molecule; that is between the alkoxy oxygen and the anilide C=O, on one side, and between the nitro group and the anilide nitrogen, on the other side. Thus, while the conjugated interaction in the former increases the single bond character of the C=O, hence lower its force constant and consequently, its absorption frequency, the latter raises, by the electron-withdrawing inductive effect, the C=O stretching frequency and a value of 1659 cm<sup>-1</sup> is observed.

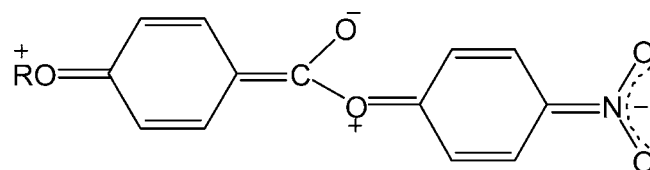
Conversely, in the derivatives bearing the electron-releasing (4-CH<sub>3</sub>O, and 4-CH<sub>3</sub>) substituents, opposite interactions on



both sides of the molecule results in compounds that absorb at lower frequencies (1636 and 1639 cm<sup>-1</sup>, respectively). The 4-chloro-homologues (**I**<sub>h</sub>) absorb at intermediate frequencies (1651 cm<sup>-1</sup>).

#### 4.2. Phase behaviour

The most common type of molecules that forms liquid crystal phases, is linear rod-shaped molecules, i.e., one molecular axis is much longer than the other two. The recipe of such molecule is two or more ring structures, linked via rigid linking groups plus hydrocarbon chain at one or both ends. Alternatively, a polar group can replace one of the chain groups. The investigated anilides of the type **I** satisfy these criteria. The ester linkage, in the phenyl benzoate molecule, contains no multiple bonds in the chain of atoms linking the two benzene rings, however, conjugative interactions within the ester moiety and the rings do lead to some double bond character. Hence, the mesophase becomes more persistent when the phase stability effect of the mutual conjugation between substituents and the ester C=O and O is increased.



Expectedly, the anilide linkage, sterically and electronically, behaves in a similar manner to the ester group. Mesomeric interaction in the nitro-substituted benzanilide molecule, as an example, is represented above.

It is known that significant strong forces between linear or rod-shaped molecules give rise to an ordered parallel arrangement that would be retained after melting at  $T_m$ . That is, if the intermolecular forces (arising from dipole–dipole, dipole-induced dipole interactions, as well as dispersion forces and hydrogen bonding) are strong enough, linear association of the molecules will be affected and retained after melting at  $T_m$  [10]. At this temperature, a liquid crystalline phase is formed so long as the required parallelism for the anisotropic property of such a compound is satisfied and the obtained mesophase exists over an interval of temperatures until the clearance temperature  $T_C$  is reached. At this stage, transition from the mesophase to the isotropic liquid takes place. If, however, the intermolecular forces are not sufficiently strong to maintain linear association of molecules, the required parallelism for liquid crystal formation will be disrupted. Alternatively, it may happen that the association, in the solid crystal phase, is so strong (as evidenced by high melting temperatures and enthalpies) that, by the time the solid reaches its melting point,  $T_m$ , the thermal fluctuations are too intense to permit any preferred substantial order (i.e., parallel alignment of molecules) to remain within the fluid. In such cases, the solid passes directly into the isotropic liquid at its melting point,  $T_m$ . In such compounds, the melting of crystals occurs at a higher temperature than does the breakdown of the mesomorphic forces. Hence, there will be insufficient molecular anisotropy to allow the formation of the mesophase on heating. On the other hand, the possible super-cooling effect (i.e., solidification at significantly lower temperature than  $T_m$ ) would allow the persistence of the ordered alignment of the molecules and the appearance of a monotropic mesophase, only during cooling.

4-Substituted derivatives of the anilide **I** were prepared and their phase behaviour investigated by differential scanning calorimetry (DSC) and detected by polarized-light microscopy (PLM). The results as given in Table 1, irrespective of the length of the alkoxy-chain ( $n = 8–18$ ) or the polarity of the substituent X, that none of the linearly (4-) substituted derivatives was found to exhibit any type of mesophase. This may be attributed, as inferred above, to the strong intermolecular interaction in the solid phase (evidenced by their high melting temperatures,  $T_m$ , and enthalpies,  $\Delta H_m$ ). Such strong intermolecular forces of attraction are due to the strong terminal as well as lateral forces. Upon melting, both types of forces break down, due to the strong thermal agitation, and this results in a completely disordered molecules with respect to one another. At such high temperatures, the solid passes directly to the isotropic liquid.

#### 4.2.1. Super-cooling effect

If we assume that our group of compounds satisfies the requirements for mesophase formation and the negative results are due only to the strong intermolecular association in the solid state, super-cooling effect would definitely be of help in this respect. The effect of possible super-cooling on the mesophase

formation was investigated by determining (via DSC measurements) the phase transitions during the cooling cycle from the isotropic melts. The results were included in Table 1. In spite of the strong super-cooling accompanying the solidification of the melts at  $T_f$ , again, no mesophases were detected, in any of the derivatives. This indicates the relatively poor stability of any probable mesophase ( $T_C$ ) above the freezing temperatures at  $T_f$ .

#### 4.2.2. Effect of lateral substitution

Lateral substituents (in the 2- or 3-positions) are, generally, used to modify the mesophase morphology and consequently its physical properties. As far as the substituents, which occupy positions along the sides of the long molecules, are concerned, it has been made clear [15–19] that lateral substitution decreases the thermal stability of both solid and mesophases. In addition, the introduction of the lateral substituent (in the 2- or 3-positions) would be expected to contribute to the molecular dissymmetry and possibly leads to lower crystal-mesophase transition temperatures ( $T_m$ ). Long narrow molecules will be forced apart so reducing the intermolecular lateral attractions. The stability of both solids and mesophases depends, to a greater or lesser extent, on these cohesive forces to maintain the parallel alignment of the linear molecules. Therefore, lateral substitution will decrease both melting ( $T_m$ ) and clearing ( $T_C$ ) temperatures. Hence, the homologues of the 2- and 3-substituted derivatives were prepared and their phase behaviour similarly investigated via DSC and PLM. The results obtained, as included in Table 1, revealed that although the melting temperatures of the 2- and 3-substituted homologues are significantly reduced compared with their 4-substituted analogues, again no mesophase was observed. This may add further evidence to the poor stability of the mesophase.

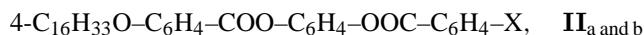
#### 4.2.3. Estimation of the type and stability of the latent mesophase

When two mesomorphic compounds are mixed together, the melting points and mesophase transition temperatures are depressed. On the other hand, binary mixtures, of certain non-mesomorphic compounds with a mesomorphic one, frequently, exhibit mesophases that are sometimes enantiotropic and in other time only monotropic. Obviously, the non-mesomorphic compound should consist of molecules that are structurally compatible with the mesomorphic molecular arrangement, and the most favourable conditions would arise with molecules that are long and lath-shaped, as is expected for our groups of compounds. In the work of Bogavlensky and Winogradov [20], reference was made to the latent mesomorphic property of the non-mesomorphic component of the binary mixture. The possibility of the occurrence of liquid crystalline properties, in a mixture, therefore resolves itself into a question whether the solid–liquid transition temperature of the mixture occurs at enough low temperature for the anisotropic arrangement of suitably shaped molecules to persist.

Even if the solid mixture melts to an isotropic liquid, it is possible that the two-component melt may crystallize less readily than would the melts of either of the two pure components. That is, quite marked super-cooling of the melt may

take place, and when the temperature falls, the molecules may adapt themselves in an anisotropic arrangement over a range of temperatures below the melting point of the mixture. The mixture will then exhibit a monotropic mesophase. In order to investigate the type and stability of the latent (nematic or smectic) mesophase, the mesophase-isotropic transition temperatures ( $T_C$ ) for the investigated compounds could be estimated from their binary phase diagrams with compounds exhibiting enantiotropic mesophases, by the method of Bogavlenky and Winogradov [20]. The linearly substituted (4-) derivatives (i.e., X = 4-CH<sub>3</sub>O, 4-CH<sub>3</sub>, H, 4-Cl, and 4-NO<sub>2</sub>) were chosen to account for optimum requirements (expected lath-shaped conformation) to the mesophase formation. The other components of the binary mixture should be one possessing a nematic phase only and the other possessing the smectic phase only. That is one compound should be a nematogen and the other is a smectogen. It would have been better to use the closest structure to our group of compounds, i.e., substituted phenyl benzoate. Unfortunately, 4-substituted phenyl-4'-alkoxybenzoates [21] are either monotropic nematogens (the methoxy and methyl derivatives) or monotropic smectogen (the nitro and cyano

derivatives). Other alternatives were chosen to be the methyl and cyano substituted derivatives of compound **II** having the general formula:



The first (the 4-methyl derivative **II<sub>a</sub>**) is purely nematogenic, having a nematic stability ( $T_{N-I}$ ) = 166.5 °C, while the second (the 4-cyano derivative **II<sub>b</sub>**) is purely smectogenic, having SmA stability ( $T_{A-I}$ ) = 229.7 °C.

#### 4.2.4. Tendency of the 4-substituted anilides to form a smectic mesophase

The tendency of the linearly (4-) substituted 4-alkoxy benzanilides, **II<sub>a-e</sub>**, to adapt their molecules within a smectic A mesophase could be investigated by constructing their binary phase diagrams with the smectogen 4-*n*-C<sub>16</sub>H<sub>33</sub>O-C<sub>6</sub>H<sub>4</sub>COOC<sub>6</sub>H<sub>4</sub>OOC<sub>6</sub>H<sub>4</sub>-CN-4, **II<sub>b</sub>**.

4.2.4.1. Effect of polar substituents. Figs. 1–4, represents the binary phase diagrams for compounds bearing different substituents, X, and of alkoxy-chain length  $n = 8, 10, 12,$  and 18

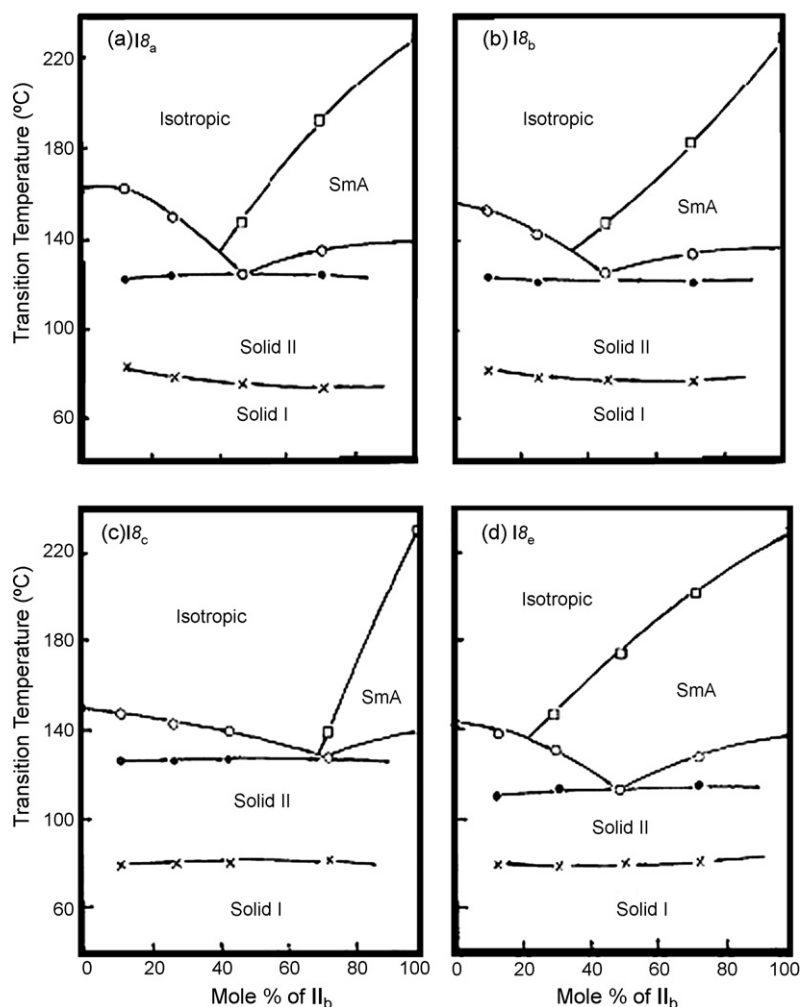


Fig. 1. Binary phase diagram of the smectogenic derivative **II<sub>b</sub>** with the *N*-4-substituted phenyl-4'-*n*-octyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

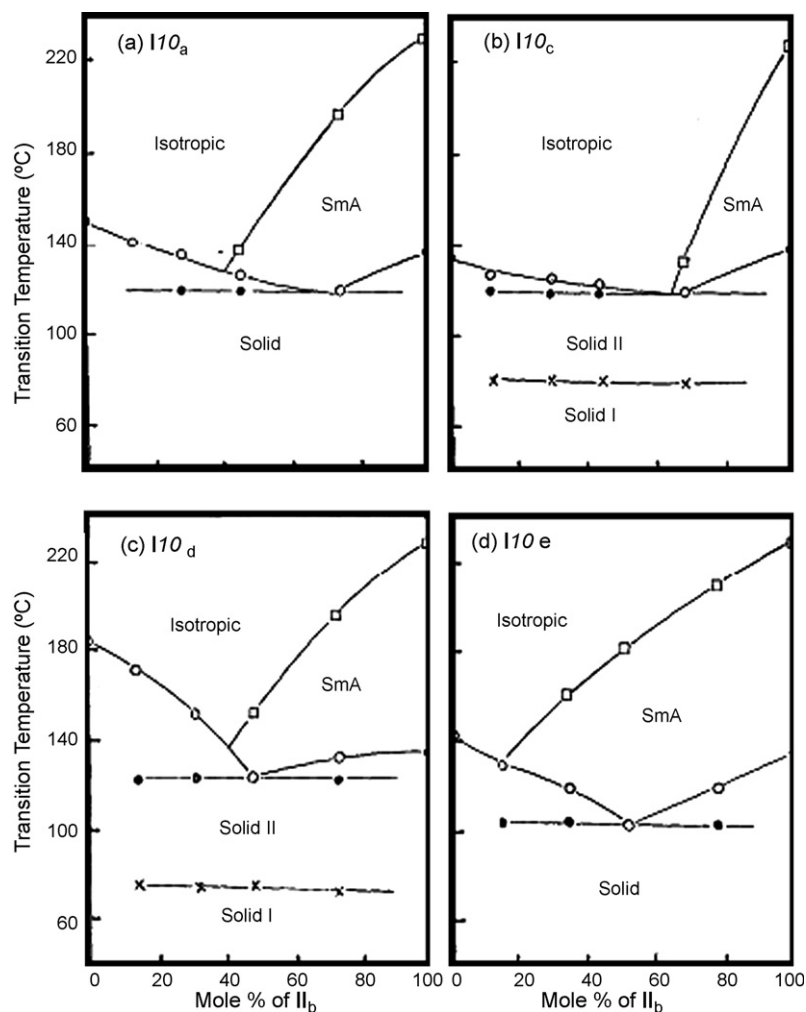


Fig. 2. Binary phase diagram of the smectogenic derivative  $\mathbf{II}_b$  with the *N*-4-substituted phenyl-4'-*n*-decyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) H, (c) 4-Cl, and (d) 4-NO<sub>2</sub>.

carbons, respectively. As can be seen from Fig. 1, for all of the octyloxy ( $n = 8$ ) analogues, irrespective of the polarity of the substituent X, the binary solid mixtures exhibit two types of solid modifications, denoted in the figure as solid I and solid II as the temperature increases, respectively. The binary mixtures with  $\mathbf{II}_b$  of the unsubstituted derivative  $\mathbf{I8}_c$ , as well as the substituted (methoxy, methyl, and nitro) analogues, exhibit eutectic compositions at about 72, 46, 46, and 48 mol% of  $\mathbf{II}_b$ , respectively. In all four systems, the addition of  $\mathbf{I8}_c$  to  $\mathbf{II}_b$  disrupts the SmA arrangement of the molecules of  $\mathbf{II}_b$  but to varying extents, depending upon the substituent X. For the unsubstituted derivative  $\mathbf{I8}_c$ , no more than 30 mol% were enough to disrupt completely the smectic A alignment of the molecules of  $\mathbf{II}_b$ . This percent increases to about 60, 62, and 78 mol% of the methoxy,  $\mathbf{I8}_a$ , methyl,  $\mathbf{I8}_b$  and nitro,  $\mathbf{I8}_e$  analogues, respectively. These findings indicate that both types of the polar substituents (i.e., either electron-donating or electron-withdrawing) facilitate the linear arrangement of the anilide molecules within the smectic A mesophase of  $\mathbf{II}_b$ . Furthermore, it can be observed from Fig. 1 that the most polar (nitro) derivative possesses the highest tendency towards smectic A mesophase formation (up to 78 mol%). That is, the tendency for smectic A mesophase formation increases in

the order:



Fig. 2 represents the corresponding binary phase diagrams for the mixtures of  $\mathbf{II}_b$  with the decyloxy ( $n = 10$ ) analogues. In these systems, only the unsubstituted ( $\mathbf{I10}_c$ ) and the chloro-substituted ( $\mathbf{I10}_d$ ) derivatives, both, showed two solid modifications. Again, the four derivatives ( $\mathbf{I10}_a$ ,  $\mathbf{I10}_c$ ,  $\mathbf{I10}_d$ , and  $\mathbf{I10}_e$ ), each exhibits a eutectic composition at about 71, 49, 63 and 50 mol% of  $\mathbf{II}_b$ , respectively. With respect to the smectic A mesophase formation, again the unsubstituted ( $\mathbf{I10}_c$ ) possesses the least tendency towards smectic A phase formation. It disrupts the mesophase completely upon the addition of about 30 mol% of  $\mathbf{I10}_c$ . The nitro-substituted derivative,  $\mathbf{I10}_e$ , on the other hand, possesses the greatest tendency towards smectic A mesophase formation, i.e., up to 84 mol% addition of  $\mathbf{I10}_e$ . The chloro ( $\mathbf{I10}_c$ ) and methoxy ( $\mathbf{I10}_a$ ) substituted analogues occupy intermediate positions. Again, the tendency for smectic mesophase formation increases in the order:



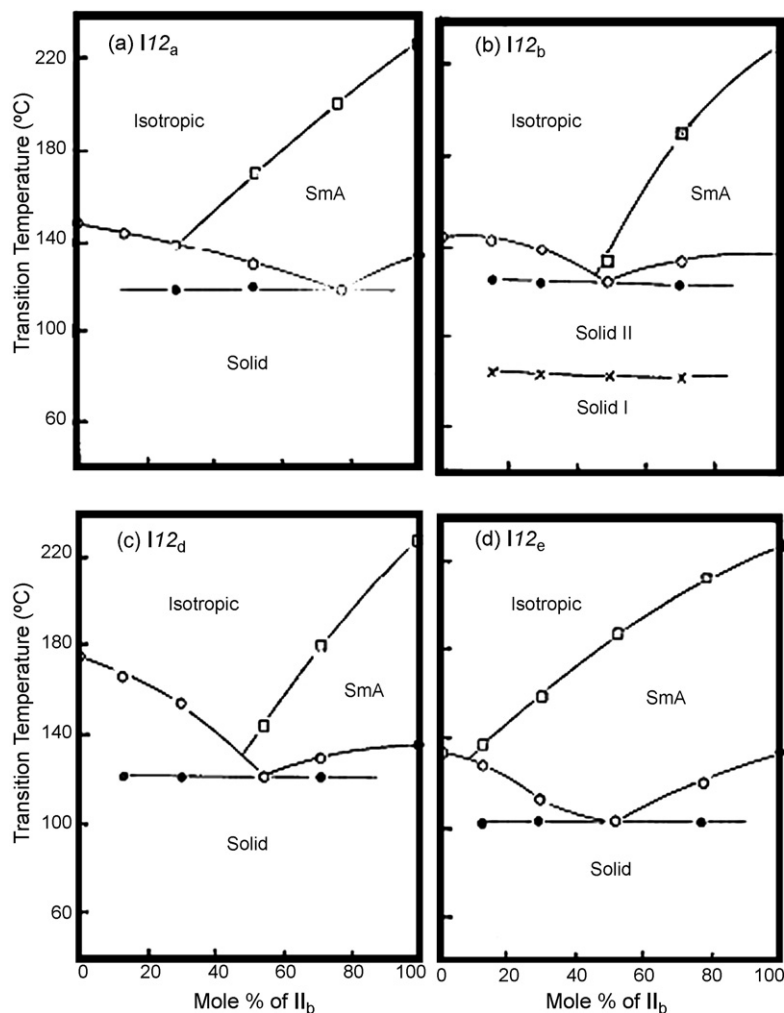
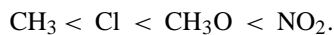


Fig. 3. Binary phase diagram of the smectogenic derivative **II**<sub>b</sub> with the *N*-4-substituted phenyl-4'-*n*-dodecyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) 4-Cl, and (d) 4-NO<sub>2</sub>.

Comparable results were obtained with the dodecyloxy ( $n = 12$ ) analogues. Thus, as can be seen from Fig. 3, eutectic compositions were detected in all four systems. Smectic A mesophases were observed in the four systems investigated, but to varying extents dependent upon the polarity of the substituent X. The tendency of smectic A mesophase formation again increases in the order:

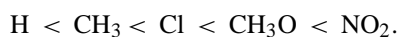


The binary phase diagrams for the mixtures of the analogues **I/8** with the smectogen **II**<sub>b</sub> are depicted in Fig. 4. As can be seen from this Figure, none of the four systems investigated showed but one solid modification. On the other hand, all binary mixtures, independent of the substituent on component **I** possess eutectic composition at about 77, 57, 54, and 57 mol% of **II**<sub>b</sub>, with the analogues **I/8**<sub>a</sub>, **I/8**<sub>b</sub>, **I/8**<sub>c</sub>, and **I/8**<sub>e</sub>, respectively. Again, the smectic A mesophase of **II**<sub>b</sub> extends upon the addition of component **I**, to varying extents dependent on the polarity of the substituent X on **I**. The tendency for smectic A mesophase

formation decreases in the order:



General conclusions that can be drawn from Figs. 1–4 are: (i) Two solid modifications were observed in the binary mixtures of the lower homologues (**I/8**), whereby they form independent of the substituent X, whereas in those of the highest homologues (**I/8**), only one solid modification was observed. (ii) In all systems investigated, independent of either X or  $n$ , the components **I**<sub>*n*-e</sub> form eutectic mixtures with the smectogen **II**<sub>b</sub>. (iii) The tendency for smectic A mesophase formation in compounds having the formula **I** is enhanced by substitution, either with an electron-withdrawing substituent or with an electron-donating one. The effect in the former case, on the tendency of smectic A mesophase formation, is more pronounced than that in the latter. A general order for smectic A formation, irrespective of the alkoxy-chain length (between 8 and 18) is given by:





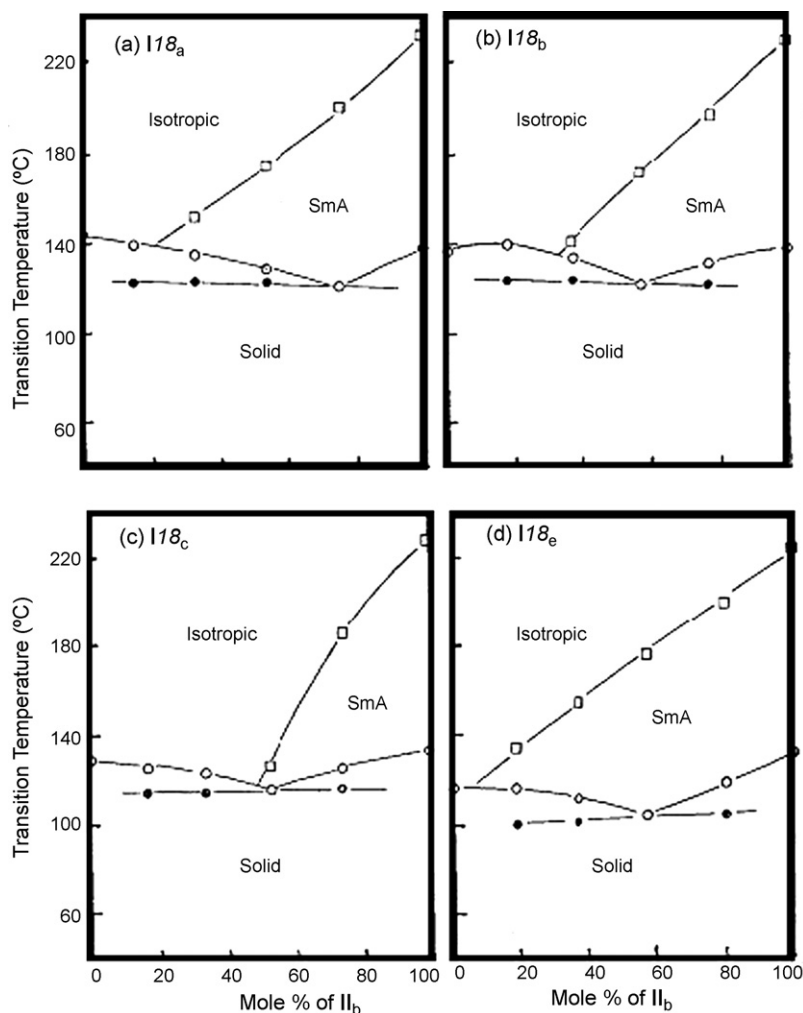
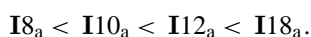


Fig. 4. Binary phase diagram of the smectogenic derivative **II<sub>b</sub>** with the *N*-4-substituted phenyl-4'-*n*-octadecyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

**4.2.4.2. Effect of alkoxy-chain length.** The effect of increasing the length of the alkoxy-chain on the tendency of the smectic A mesophase formation in binary mixtures with the smectogen **II<sub>b</sub>**, was investigated. Figs. 5–7, represent the binary phase diagrams of **II<sub>b</sub>** with the most electron-withdrawing (nitro) substituted, and the most electron-releasing (methoxy) substituted derivatives, as well as with the unsubstituted derivatives, respectively.

Fig. 5, which represents the binary phase diagrams for the methoxy-substituted homologues **I<sub>n<sub>a</sub></sub>** with the smectogen **II<sub>b</sub>**, shows that only the shortest (*n* = 8) alkoxy homologue exhibits two mixed-solid phase modifications, together with a eutectic composition at about 46 mol% of **II<sub>b</sub>**. The other three systems (where *n* = 10, 12, and 18 carbons), each, exhibits only one solid modification and eutectic compositions at 72, 76, and 76 mol% of **II<sub>b</sub>**, respectively. The tendency to form a smectic A mesophase increases, as the alkoxy-chain increases in length, in the order:



The corresponding binary phase diagrams for the 4-nitro substituted homologues with **II<sub>b</sub>** are depicted in Fig. 6. As can be seen from this figure, solid phase modifications are observed only with the shortest homologue (*n* = 8). All binary mixtures (with **II<sub>b</sub>**) exhibit eutectic compositions. Again, the tendency towards smectic A mesophase formation increases with increasing the alkoxy-chain length.

The binary phase diagrams for the unsubstituted homologues (**I<sub>c</sub>**) with the smectogen **II<sub>b</sub>** are represented graphically in Fig. 7. Solid modifications were observed only in the case of the lower homologues **I8** and **I10**. It obeys the same general smectic A order of formation, that increases with increase of the alkoxy-chain length.

#### 4.2.5. Tendency of 4-substituted anilides to form a nematic mesophase

The tendency of the linearly (4-) substituted derivatives of the 4-alkoxy benzanilides, **I<sub>n<sub>a-e</sub></sub>**, to adapt their molecules within a nematic phase could be investigated by constructing their binary phase diagrams with the nematogen C<sub>16</sub>H<sub>33</sub>O–C<sub>6</sub>H<sub>4</sub>COOC<sub>6</sub>H<sub>4</sub>OOCC<sub>6</sub>H<sub>4</sub>–CH<sub>3</sub>-4, **II<sub>a</sub>**.

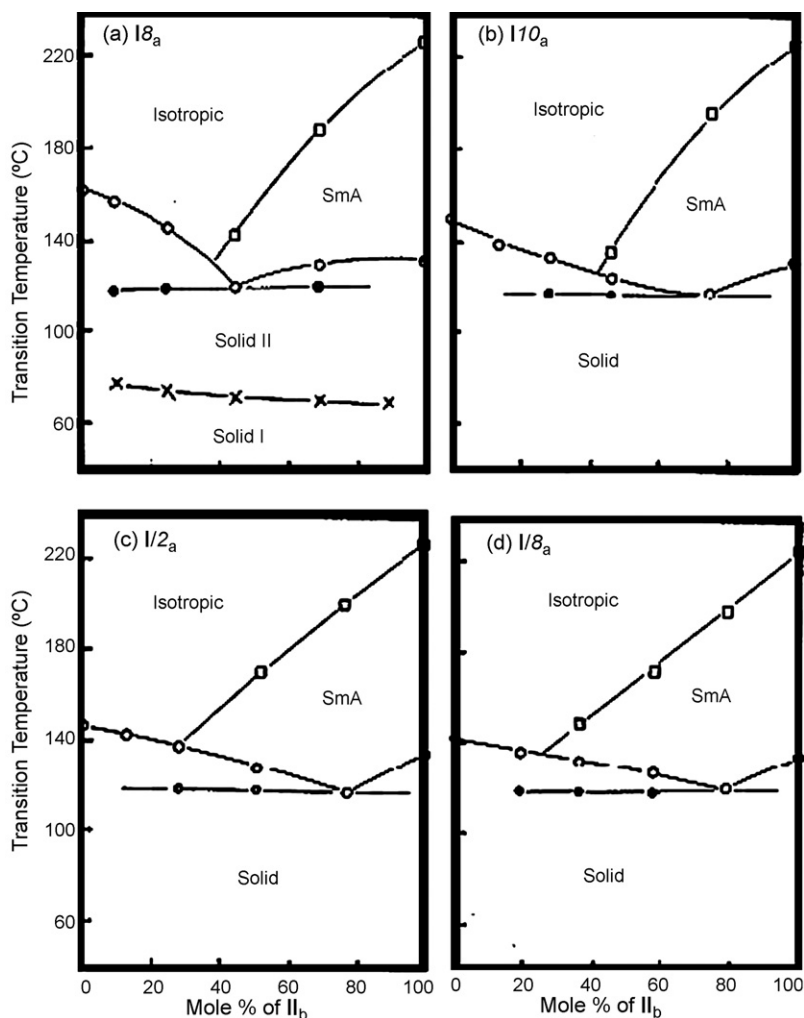
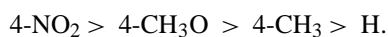


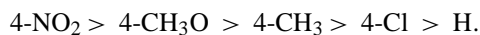
Fig. 5. Binary phase diagram of the smectogenic derivative  $\text{II}_b$  with the *N*-4-methoxy phenyl-4'-*n*-alkoxy benzamide, (a)  $n=8$ , (b)  $n=10$ , (c)  $n=12$ , and (d)  $n=18$ .

#### 4.2.5.1. Effect of polar substituents on the tendency towards nematic phase formation.

In order to investigate the effect of the polar substituent, X, on the tendency of the molecules on **I** to adapt themselves within a nematic ordering, four groups of binary phase diagrams (Figs. 8–11) were constructed. Within a group of diagrams, the alkoxy-chain length was kept constant while the polar group X is varied. Fig. 8 represents the phase diagrams constructed for the four binary systems of octyloxy ( $n=8$ ) analogues of **I**, bearing the same alkoxy-chain but differ in their polar groups, with the nematogen,  $\text{II}_a$ . As can be seen from Fig. 8, irrespective of the polarity of the substituent X, the nematic ordering of the molecules of  $\text{II}_a$  is gradually disrupted by the addition of the molecules of **I** to an extent dependent upon the polarity of X. For example, the nematic order of  $\text{II}_a$  is retained up to the addition of 78 mol% of the nitro derivative,  $\text{I}8_c$ , whereas the unsubstituted analogue,  $\text{I}8_c$ , destroys completely the nematic arrangement of  $\text{II}_a$  upon addition of only 33 mol% of  $\text{I}8_c$ . One may conclude from Fig. 8 that the tendency of the molecules of **I** to adapt themselves within the nematic arrangement of  $\text{II}_a$  decreases in the order:



This order is coincident with that deduced for their tendency to adapt within a smectic A arrangement. The other groups of diagrams (Figs. 9–11) represent the corresponding diagrams for the  $\text{I}10$ ,  $\text{I}14$ , and  $\text{I}18$  analogues with  $\text{II}_a$ , respectively. As can be seen from these figures, irrespective of the alkoxy-chain length, the tendency for compounds  $\text{I}_{a-e}$  towards nematic phase adaptation decreases in the following order:



That is substitution with either an electron-withdrawing or an electron-donating group increases the tendency of molecules of **I** to adapt within nematic arrangement. The un-substituted derivatives,  $\text{I}_c$ , possess the least tendency.

#### 4.2.5.2. Effect of alkoxy-chain length on the tendency towards nematic order adaptation.

In this part of the study other groups of binary phase diagrams were constructed (Figs. 12–15). In each group of diagrams, the substituent, X, is kept constant, while the alkoxy-chain length is varied. Fig. 15(a–d), for example, represents the binary phase diagrams constructed for the four methoxy-substituted homologues ( $\text{I}8_a$ – $\text{I}18_a$ ) with  $\text{II}_a$ . These figures revealed that, the nematic ordering of  $\text{II}_a$  is retained up to

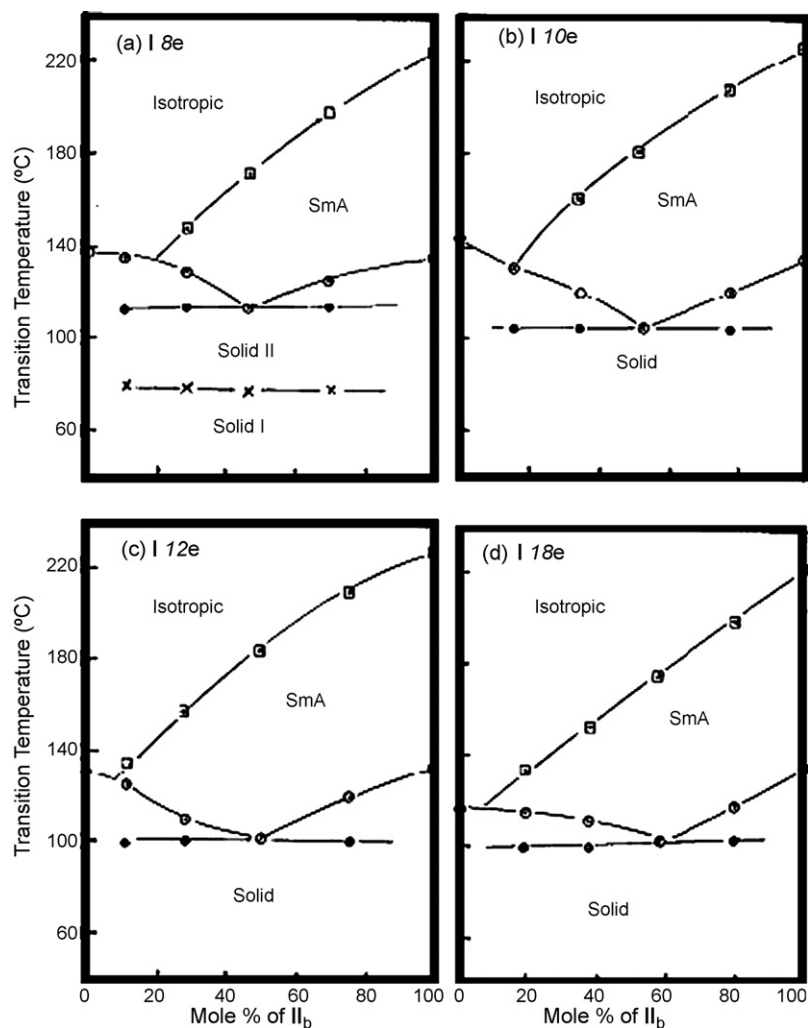


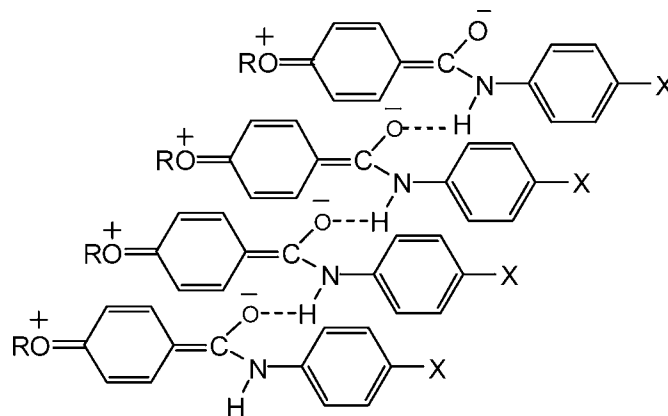
Fig. 6. Binary phase diagram of the smectogenic derivative  $\text{II}_b$  with the *N*-4-nitro phenyl-4'-*n*-alkoxy benzamide, (a)  $n = 8$ , (b)  $n = 10$ , (c)  $n = 12$ , and (d)  $n = 18$ .

the addition of 42.6, 53, 46.5, and 42.6 mol% of  $\text{I8}_a$ ,  $\text{I10}_a$ ,  $\text{I14}_a$ , and  $\text{I18}_a$ , respectively. For the methyl-substituted analogues, the tendency towards nematic phase formation, as measured by the mol% addition of **I**, were found to be, respectively, 38.7, 49.1, 51.7, and 51.9 mol%. For the nitro-substituted analogues the tendency for nematic order adaptation is 86.6, 49.3, 44, and 42.6 mol%, respectively. As can be deduced from Figs. 12–15, there is no regular trend for the variation of the tendency towards nematic ordering with increasing alkoxy-chain length,  $n$ . It seems that it increases first with “ $n$ ” up to a value of “ $n$ ” dependent on the polarity of the substituent, X, then decreases. This trend may be attributed to the increased tendency towards smectic A phase formation, as the alkoxy-chain length increases, accompanied with a decreasing tendency towards nematic phase formation, with increasing the alkoxy-chain length.

#### 4.3. Mesophase behaviour of the *N*-methyl derivative ( $\text{I18}_m$ )

As mentioned before, strong intermolecular forces result from strong polarization of the anilide C=O group as evidenced from their infrared spectra (Table 2). These strong intermolec-

ular forces may arise from a hydrogen-bonding between two or more neighboring molecules.



In order to investigate the influence of intermolecular hydrogen bond formation on the tendency of mesophase formation, the *N*-methyl analogue of the unsubstituted derivative ( $\text{I18}_n$ , X = H) was prepared, as an example, and similarly investigated. The DSC and infrared data for the *N*-methyl homologue ( $\text{I8}_m$ ) are included in their corresponding tables. As can be seen from these

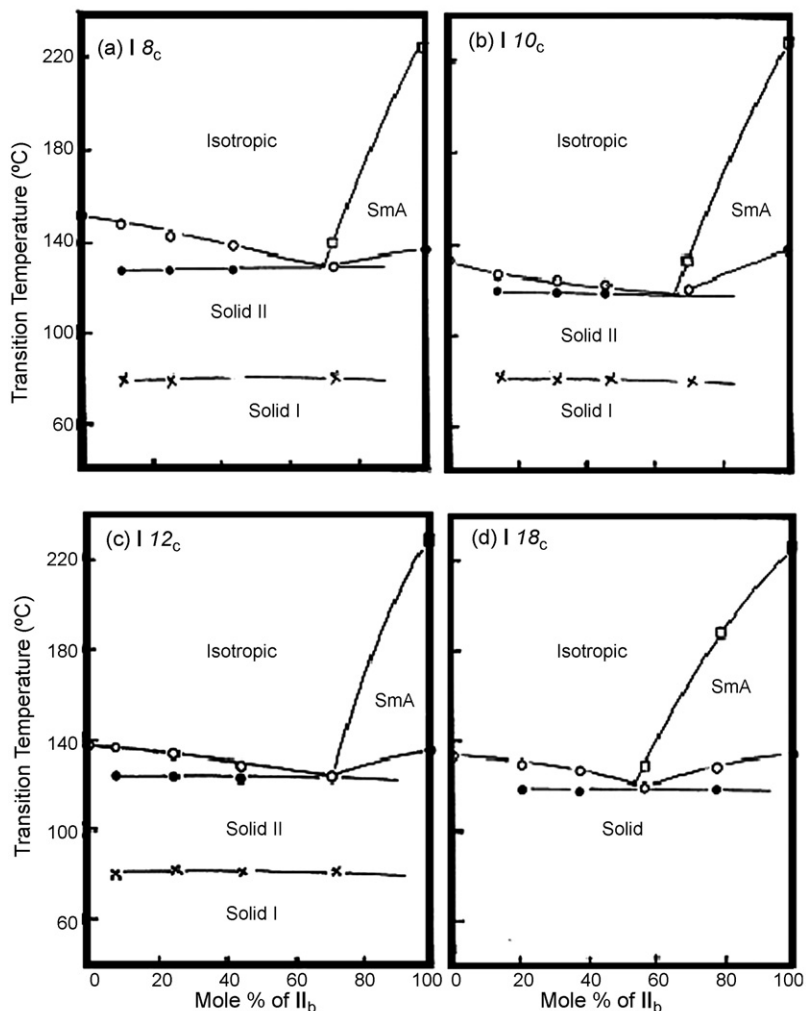


Fig. 7. Binary phase diagram of the smectogenic derivative  $\text{II}_b$  with the *N*-phenyl-4-*n*-alkoxy benzamide, (a)  $n = 8$ , (b)  $n = 10$ , (c)  $n = 12$ , and (d)  $n = 18$ .

tables, there is still no mesophase observed, either on melting the solid crystals, or cooling the isotropic melts. This means that a new factor, other than hydrogen bonding still exists.

#### 4.4. Estimation of the linearity and/or planarity of the anilide molecule

The only possible reason left for the poor ability of the molecule of compounds  $\text{In}_{a-e}$  to form a mesophase is that its mesogenic portion, i.e., the benzanilide moiety, is non-linear and/or non-planar. To elucidate the exact conformation of the molecules of compounds  $\text{In}_{a-e}$ , it is possible to estimate the extent of linearity and/or planarity, an essential criteria for mesophase formation, in the core molecule, namely, benz-4-substituted anilides ( $\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_4\text{-X-4}$ ). This can be realized by calculating the resultant dipole moment of the molecule, by the vector summation method of bond moments, for all possible conformations starting from a planar one by rotating the  $\text{Ar-N-H}$  grouping around the carbamoyl  $\text{C-N}$  bond, and comparing the results with the observed dipole moments, as collected from the literature [22,23].

##### 4.4.1. Vector summation of bond moments

For the deduction of the most probable conformation of the anilides ( $\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_4\text{-X-4}$ ) molecule, the vector summation method of bond moments for each of the 4-substituted benzanilides (4- $\text{CH}_3\text{O}$ , 4- $\text{CH}_3$ , 4- $\text{Cl}$ , H, and 4- $\text{NO}_2$ ) is established. The 4-substituted benzanilides were chosen as they represent the core structure of the investigated anilides,  $\text{In}_{a-e}$ . The fixed set of reference axes, which is chosen for the benzanilide molecule, has as shown in Fig. 16, its origin at the nitrogen atom of the carbamoyl group,  $y$ -axis along the  $\text{C-N}$  bond of this group,  $x$ -axis in the plane of the molecule, and the  $z$ -axis perpendicular to the plane constituting the whole molecule. Also indicated in Fig. 16 are the bond moments and bond angles as taken from the literature [22,23]. Starting with the anilide aryl group in plane while the anilide-H atom protruding out-of-plane, and rotating the  $\text{H-N-Ar}$  group around the  $\text{C-N}$  bond by an angle that varies between 0 and  $360^\circ$ , the various possible conformations could be calculated. It should be mentioned here that the remaining part of the molecule is planar for reasons of conjugation between the carbonyl and alkoxy groups via the attached phenyl ring. The dipole moment components along the

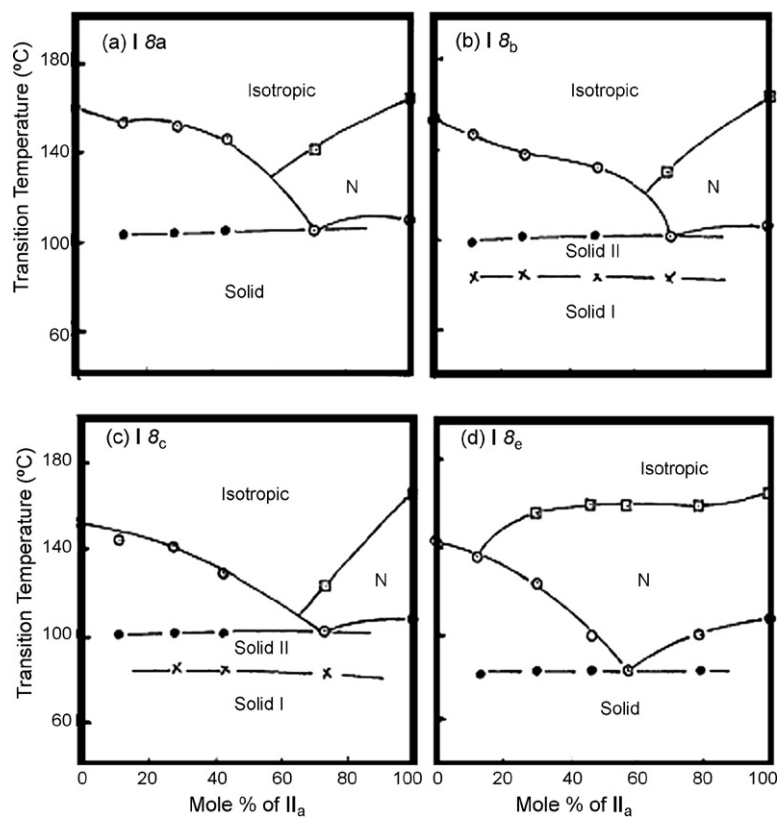


Fig. 8. Binary phase diagram of the nematogenic derivative  $II_a$  with the  $N$ -4-substituted phenyl-4'- $n$ -octyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

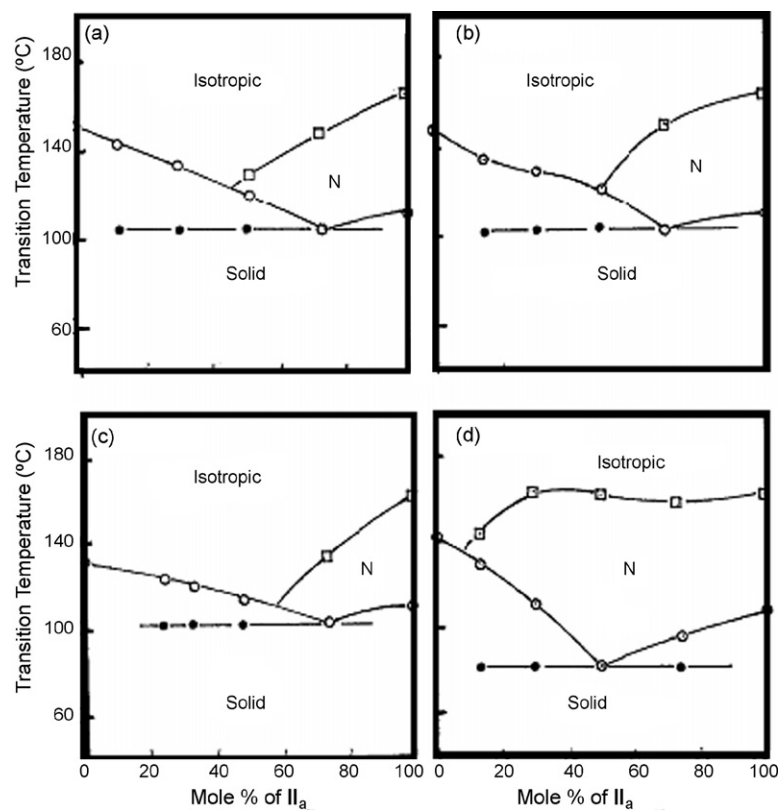


Fig. 9. Binary phase diagram of the nematogenic derivative  $II_a$  with the  $N$ -4-substituted phenyl-4'- $n$ -decyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

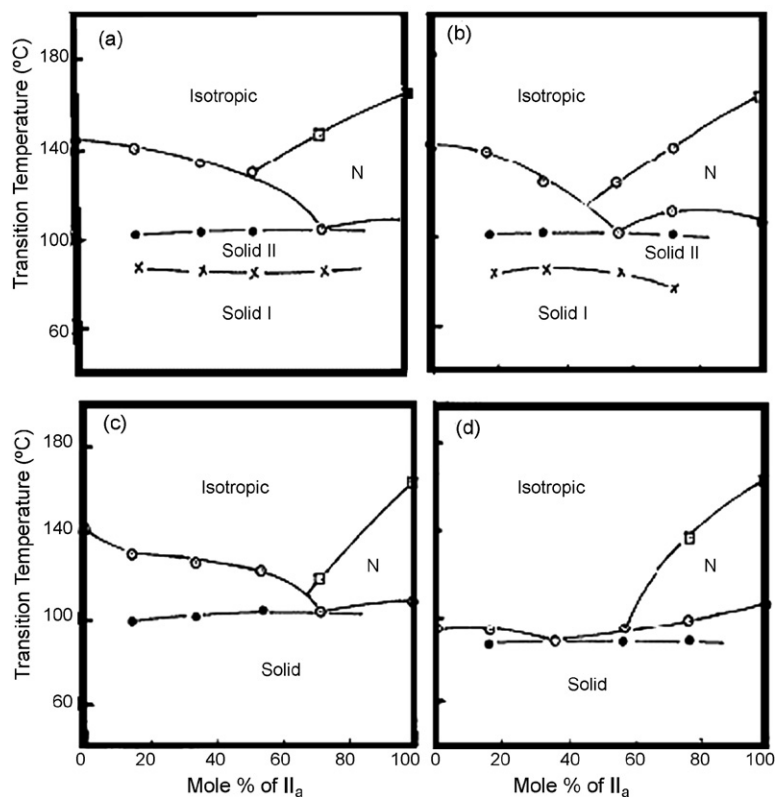


Fig. 10. Binary phase diagram of the nematogenic derivative  $\text{II}_a$  with the *N*-4-substituted phenyl-4'-*n*-tetradecyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

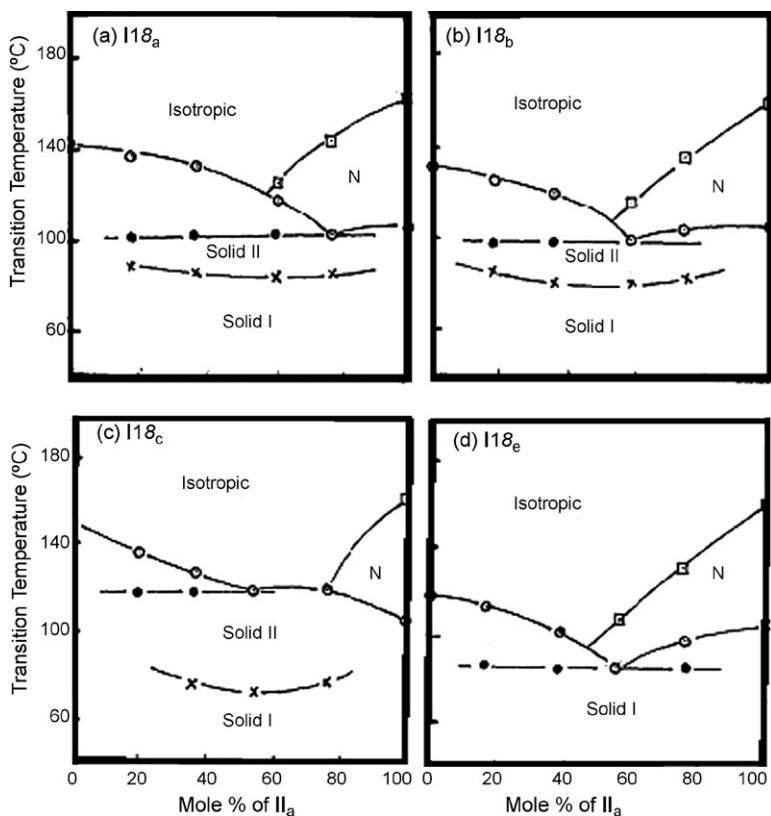


Fig. 11. Binary phase diagram of the nematogenic derivative  $\text{II}_a$  with the *N*-4-substituted phenyl-4'-*n*-octadecyloxy benzamide, (a) 4-OCH<sub>3</sub>, (b) 4-CH<sub>3</sub>, (c) H, and (d) 4-NO<sub>2</sub>.

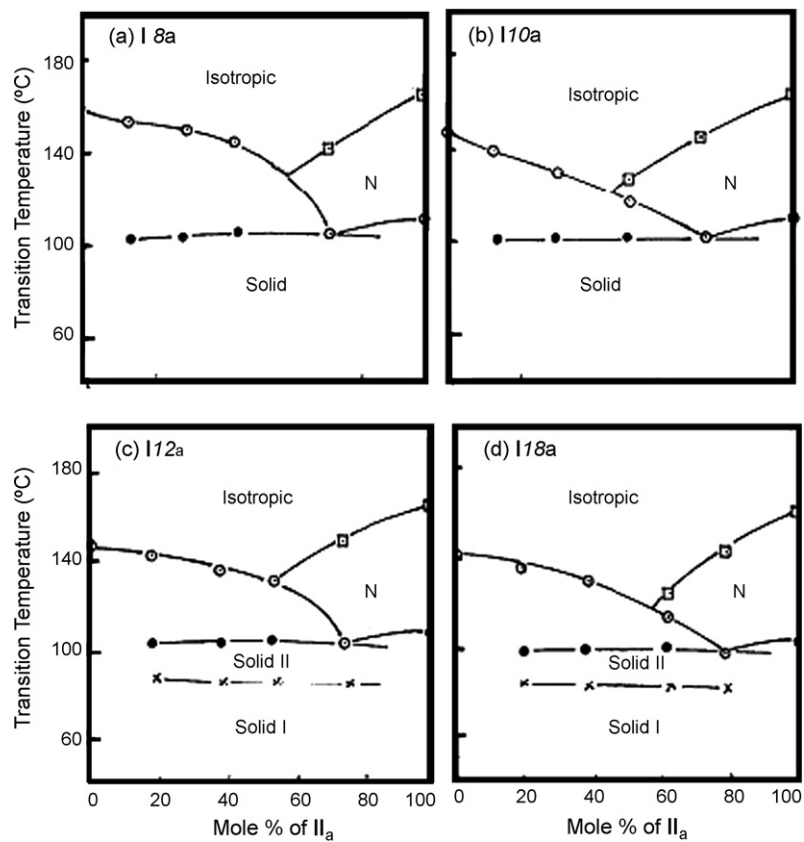


Fig. 12. Binary phase diagram of the nematogenic derivative  $II_a$  with the *N*-4-methoxy phenyl-4'-*n*-alkoxy benzamide, (a)  $n = 8$ , (b)  $n = 10$ , (c)  $n = 12$ , and (d)  $n = 18$ .

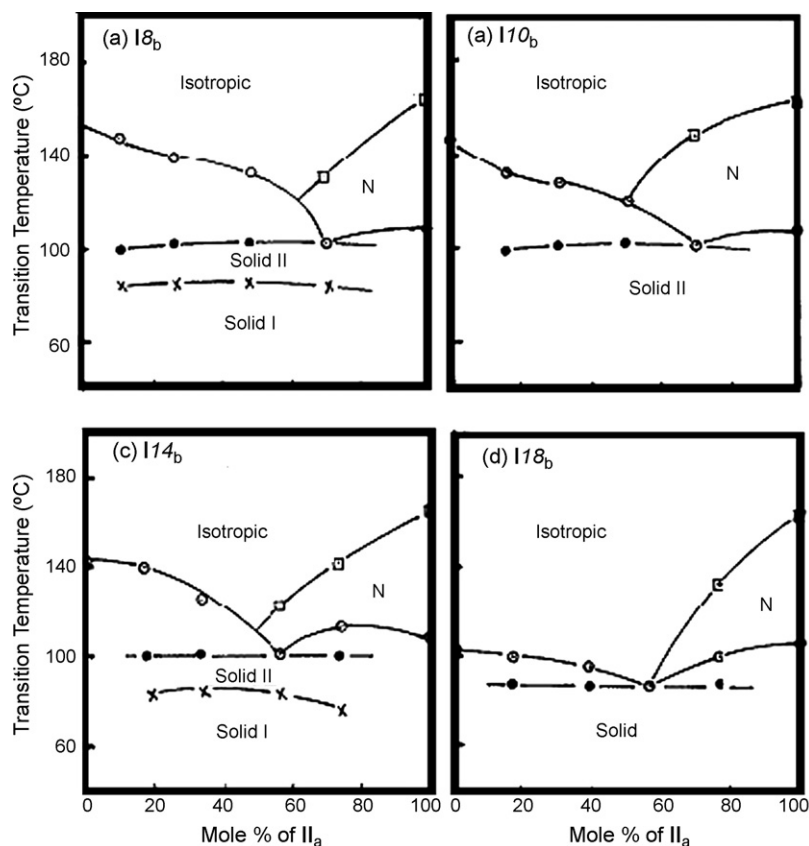


Fig. 13. Binary phase diagram of the nematogenic derivative  $II_a$  with the *N*-4-methyl phenyl-4'-*n*-alkoxy benzamide, (a)  $n = 8$ , (b)  $n = 10$ , (c)  $n = 14$ , and (d)  $n = 18$ .

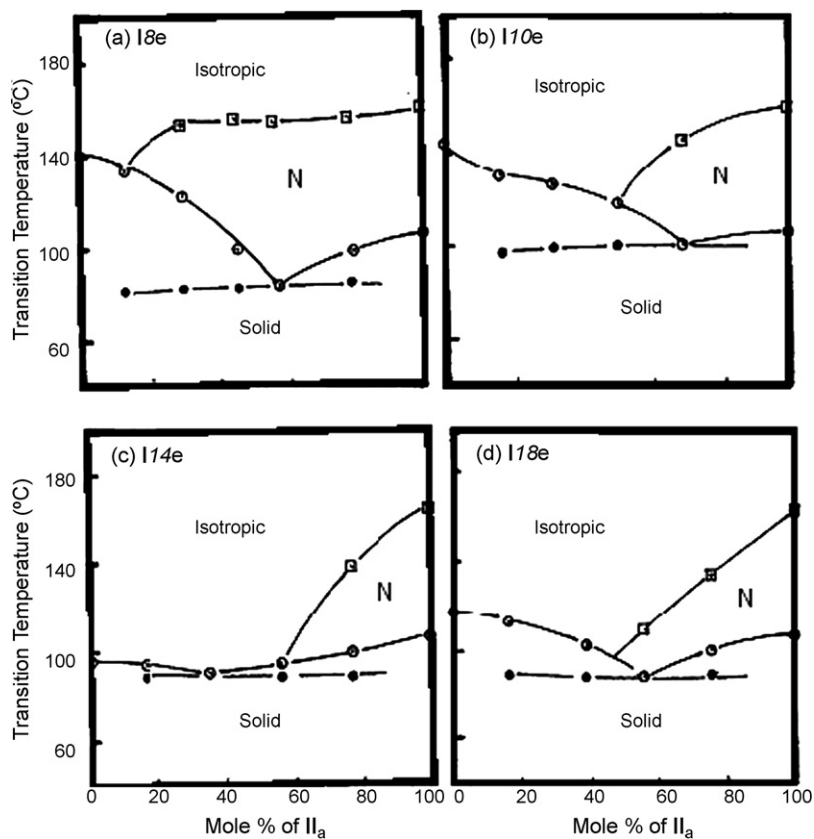


Fig. 14. Binary phase diagram of the nematogenic derivative  $II_a$  with the *N*-4-nitro phenyl-4'-*n*-alkoxy benzamide, (a)  $n=8$ , (b)  $n=10$ , (c)  $n=14$ , and (d)  $n=18$ .

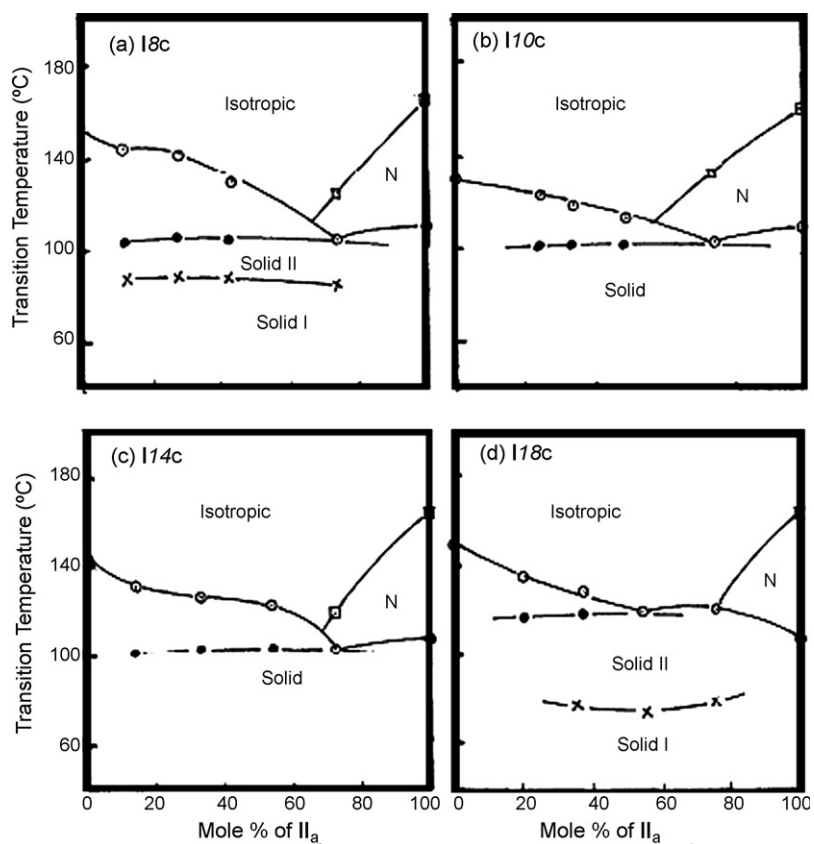


Fig. 15. Binary phase diagram of the nematogenic derivative  $II_a$  with the *N*-4-phenyl-4'-*n*-alkoxy benzamide, (a)  $n=8$ , (b)  $n=10$ , (c)  $n=14$ , and (d)  $n=18$ .





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