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Phase behaviour of binary mixtures of LC compounds of different molecular structure and comparable molecular length
I. 4-(4′-Substituted phenylazo)phenyl-4″-alkoxybenzoates and 4-(4′-substituted phenyl carbonyloxy)phenyl-4″-alkoxybenzoates

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Abstract

Phase diagrams were constructed for the various binary systems made from compounds of structurally different mesogens; one component is from the five homologous series 4-(4′-substituted phenylazo)phenyl-4″-alkoxybenzoates ($\mathbf{I}_{a\text{–}e}$) and the other from the similarly substituted homologous series 4-(4′-substituted phenyl carbonyloxy)phenyl-4″-alkoxy benzoates ($\mathbf{II}_{a\text{–}e}$). Transition temperatures of all mixtures prepared were measured by differential scanning calorimetry and identified by polarized light microscopy. Polarity and polarizability of the investigated compounds could be varied by changing the substituent X (CH_3O, CH_3, Cl, CN and NO_2), which covers a wide range of polarity, and the alkoxy-chain length, which varied between 6, 8, 14, or 16 carbons.

Keywords: Binary phase diagrams; Arylazo phenyl arylates; Unsymmetrical bis-1,4-phenylene arylates

1. Introduction

Substantial impetus has been provided for the systematic investigation of the relationships between molecular structure and liquid crystallinity. Since no single material yet discovered has a satisfactory nematic range for device application, all currently marketed devices contain mixtures of liquid crystals. Trial-and-error attempts to find eutectics in homologous series or using compounds of differing molecular structure have met with reasonable success [1]. In view of the growing upsurge of interest in room-temperature liquid crystalline materials, we are continuing our works towards investigating mixtures of liquid crystals of structurally dissimilar structures. The ester group was selected as a basic linkage, in both components, since it offers stability advantage over other linking groups.

It has been previously shown [2,3] that introducing a third phenylene ring into a two-ring liquid crystalline compound enhances both solid and mesophase stabilities, i.e. both melting (T_m) and clearing (T_C) temperatures. Thus, introducing the phenylazo [2] or the phenyl carbonyloxy [3] groups into the phenyl benzoate molecule, to give compounds **I** and **II**, respectively, has shown to raise both T_m and T_C. We have reported binary systems of structurally similar mesogens, where both components of a system bear different X but of the same alkoxy group [2,4–7] or they are homologues of the same series that bear the same substituent, X [8]. The phase diagrams obtained, in most of the cases, did not show eutectic points which was attributed to the close similarity in the solid crystalline structure of nearly all members of one and the same series of compounds (**I** or **II**). Continuing our research in this field, we report here binary systems consisting of the structurally dissimilar mesogens (**I** and **II**) but both components bear the same substituents X and R.

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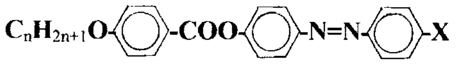
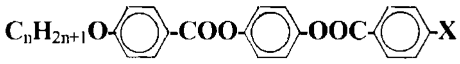


In_{a-c}



IIn_{a-c}

n = 6, 8, 14, 16

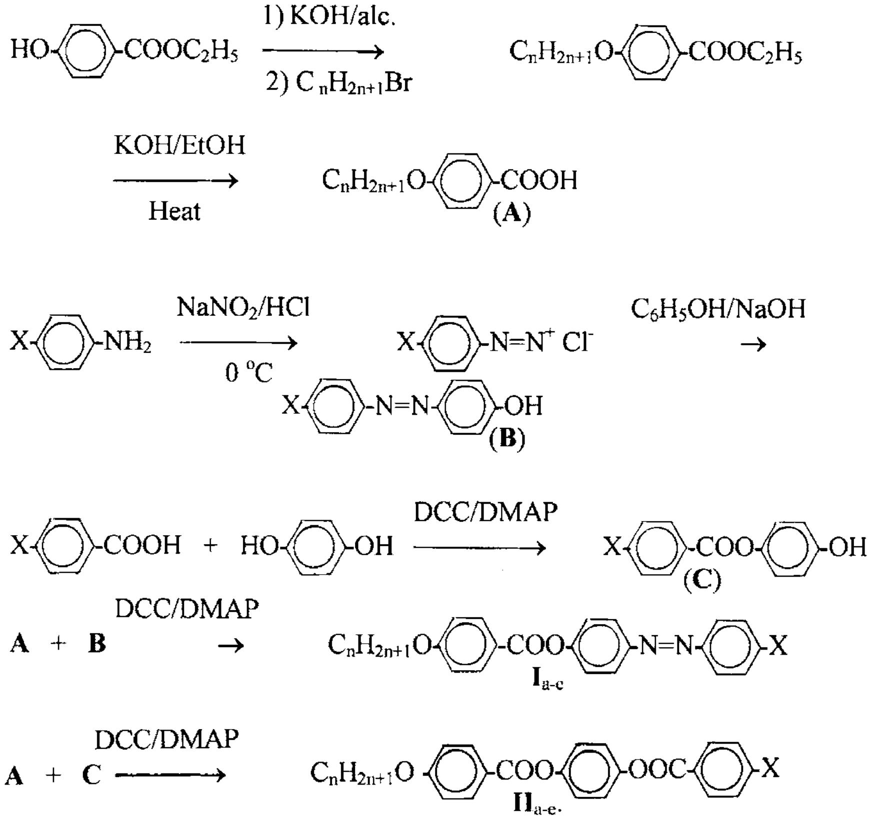
a, X = CH_3O; b, X = CH_3; c, X = Cl; d, X = CN; e, X = NO_2

2. Experimental

Chemicals were purchased from the following companies: Aldrich, Wisconsin, USA; E. Merck, Darmstadt, Germany; Fluka, Buchs, Switzerland.

2.1. Preparation of materials

All compounds discussed in this paper, $\mathbf{I}_{a-e}$ and $\mathbf{II}_{a-e}$, were prepared by the method previously described [2,3], according to the following scheme:



The resulting compounds were TLC pure and exhibited phase transition temperatures agreed with those reported previously [2,3,9–18].

2.2. Physical characterization

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^{-1} was used for the enthalpy of fusion of indium. Typical heating rates were 10 K min^{-1}, and a sample mass was 2–3 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).

Thin-layer chromatography was performed with TLC sheets coated with silica gel (E. Merck); spots were detected by UV irradiation.

The type of mesophase was identified using polarized light microscopy by the contact method with standard materials.

3. Results and discussion

Five different homologous series of each of the compounds of type **I** or **II** were prepared in which the terminal group X was respectively varied between CH_3O, CH_3, Cl, CN and NO_2. The homologues (n = 6, 8, 14 and 16) prepared were investigated for their phase transitions. Transition temperatures of these compounds in their pure states, as reported previously [2,3] are summarized in Tables 1 and 2, respectively. In these tables the following symbols are given for

Table 1
Transition temperatures and mesomorphic ranges (in °C) for compounds **I**$n_{a\text{–}e}$ 4-$C_nH_{2n+1}O—C_6H_4—COO—C_6H_4—N{=}N—C_6H_4$–X-4

Compound	n	X	$T_{C\text{-}A}$	$T_{C\text{-}N}$	$T_{A\text{-}N}$	$T_{A\text{-}I}$	$T_{N\text{-}I}$	ΔT	Ref.
I6_a	6	CH_3O	–	122.8	–	–	255.8	133.0	[2,9]
I6_b		CH_3	–	103.5	–	–	227.8	124.3	[2,9]
I6_c		Cl	114.9	–	145.6	–	241.0	126.1	[2,10]
I6_d		CN	110.0	–	151.8	–	266.4	156.4	[2,11]
I6_e		NO_2	103.6	–	240.5	–	254.7	151.1	[2]
I8_a	8	CH_3O	–	117.9	–	–	233.5	115.6	[2,9]
I8_b		CH_3	–	107.5	–	–	208.9	101.4	[2,9]
I8_c		Cl	107.6	–	179.3	–	224.2	116.6	[2,10]
I8_d		CN	93.0	–	191.7	–	257.5	164.5	[2,11]
I8_e		NO_2	99.9	–	237.9	–	249.9	150.1	[2]
I14_a	14	CH_3O	–	114.6	–	–	196.7	82.1	[2]
I14_b		CH_3	–	96.1	–	–	179.9	83.8	[2]
I14_c		Cl	104.3	–	–	193.4	–	89.1	[2]
I14_d		CN	98.4	–	–	226.6	–	128.2	[2]
I14_e		NO_2	93.5	–	–	215.3	–	122.2	[2]
I16_a	16	CH_3O	–	124.2	–	–	192.1	67.9	[2]
I16_b		CH_3	–	98.8	–	–	170.6	71.8	[2]
I16_c		Cl	105.3	–	–	186.0	–	80.7	[2]
I16_d		CN	97.3	–	–	220.7	–	123.4	[2]
I16_e		NO_2	101.8	–	–	210.9	–	109.1	[2,11]

the various transition temperatures: crystal-smectic A ($T_{C\text{-}A}$), crystal-nematic ($T_{C\text{-}N}$), SmA-nematic ($T_{A\text{-}N}$), SmA-isotropic ($T_{A\text{-}I}$), nematic-isotropic ($T_{N\text{-}I}$) and the mesomorphic range ($\Delta T = T_C - T_m$). As can be seen from Table 1, the methoxy and methyl (i.e., electron-releasing) substituted homologues in the four series (**I**6–**I**16) possess only the nematic phase (N). The chloro analogues exhibit the SmA phase, as the only mesophase, at and after $n = 10$. Lower chloro-substituted homologues (**I**6_C and **I**8_C) exhibit the SmA phase together with a nematic range that decreases as n increases.

The nitro- and cyano (i.e., electron-withdrawing) -substituted analogues exhibit the SmA and N mesophases as the chloro derivatives but to varying extents dependent on the length of the alkoxy-chain (n). Generally all compounds investigated possess high melting (T_m) and clearing (T_C) temperatures with mesomorphic range (ΔT), for any derivative, decreases as the chain length is increased.

For the other series of compounds (**II**$n_{a\text{–}e}$), as can be seen from Table 2, the methoxy- and methyl (electron-donating) -substituted homologues in the four series (**II**6–**II**16) were found to possess only nematic phase (N). The nitro and cyano (electron-withdrawing) analogues, on the other hand, exhibit the smectic A phase (SmA) in addition to the nematic, which are exhibited in the lower homologues (**II**$6_{d\&e}$ and **II**$8_{d\&e}$) as the only mesophase. The chloro homologues (**II**$_c$), with intermediate electronic nature, occupy intermediate position, i.e., the lower homologues (**II**6_c and **II**8_c) exhibit only the nematic phase, while their higher homologues (**II**14_c and **II**16_c) exhibit smectic A phase together with small range of nematic; these nematic ranges are 9.3 and 2.5 °C, respectively. It can also be seen from Table 2 that all compounds investigated are again of high melting (T_m) and clearing (T_C) points, and that the mesomorphic range ($\Delta T = T_C - T_m$) for any derivative decreases as the chain length of the alkoxy group is increased. Furthermore, within any series, the cyano derivative possesses the greatest mesomorphic range, while the chloro analogue exhibits the lowest value.

In order to make a comparison of the mesomorphic thermal stability of molecules of type **I** with those of type **II**, the mesophase–isotropic transition temperatures (T_C) of the individual derivatives in series **I** were plotted (in Fig. 1) against those of the correspondingly substituted analogues

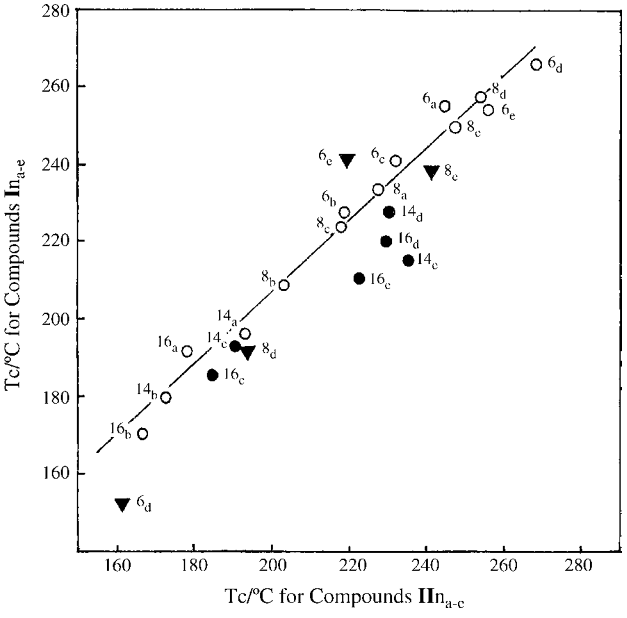


Fig. 1. Correlation between the mesophase stability of compounds from series **I** with those of the correspondingly substituted derivatives from series **II**: (◯) $T_{N\text{-}I}$, (●) $T_{A\text{-}I}$, and (▽) $T_{A\text{-}N}$.

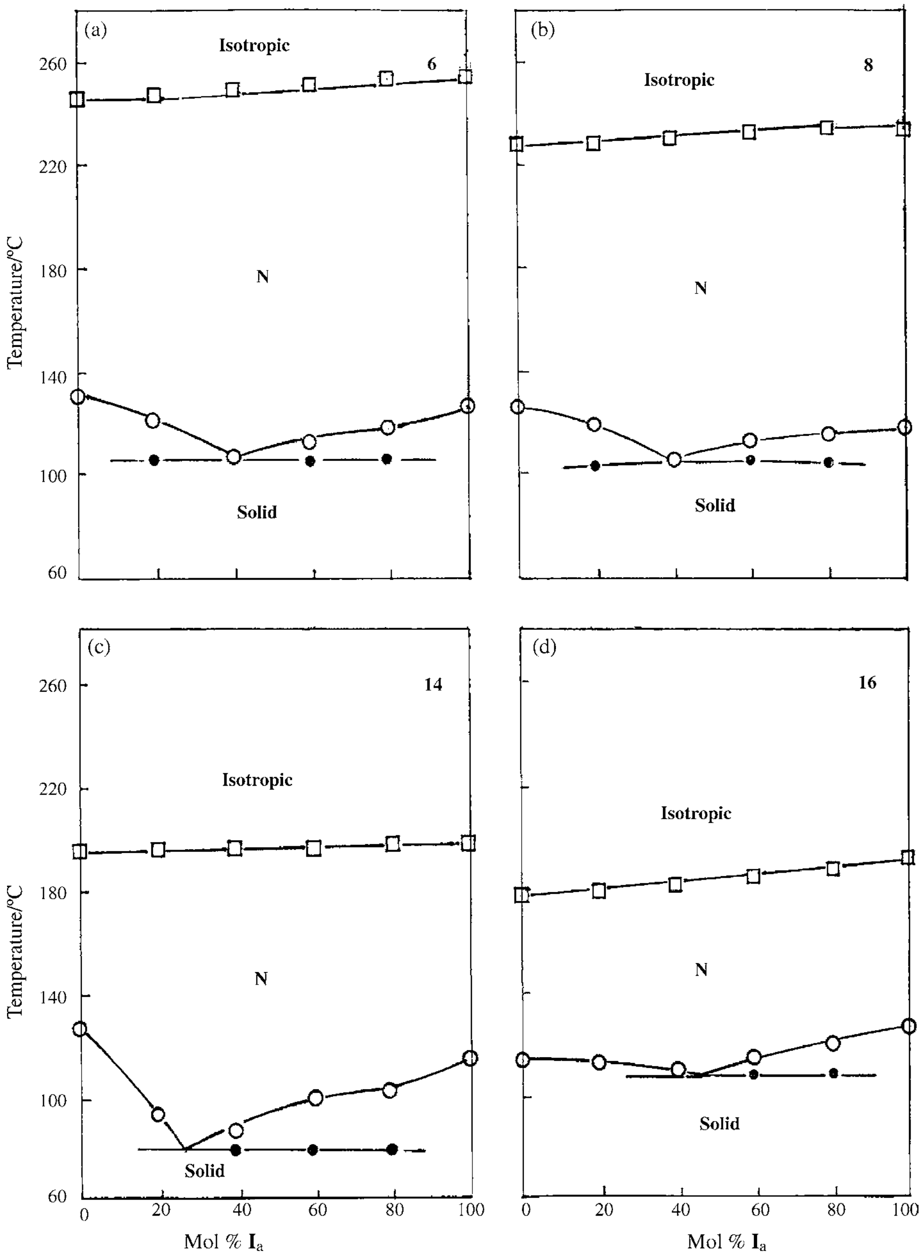


Fig. 2. Binary phase diagram for the system **I**$_a$/**II**$_a$: (a) $n = 6$, (b) $n = 8$, (c) $n = 14$ and (d) $n = 16$.

Table 2
Transition temperatures and mesomorphic ranges (in °C) for compounds **II**$n_{a–e}$ 4-$C_nH_{2n+1}O—C_6H_4—COO—C_6H_4—OOC—C_6H_4$–X-4

Compound	n	X	$T_{C\text{-}A}$	$T_{C\text{-}N}$	$T_{A\text{-}N}$	$T_{A\text{-}I}$	$T_{N\text{-}I}$	ΔT	Ref.
II6$_a$	6	CH_3O	–	129.9	–	–	244.6	114.7	[3,12]
II6$_b$	6	CH_3	–	119.9	–	–	218.9	99.0	[3]
II6$_c$	6	Cl	–	165.4	–	–	231.7	66.3	[3]
II6$_d$	6	CN	146.7	–	161.1	–	268.6	121.9	[3,14]
II6$_e$	6	NO_2	165.4	–	219.0	–	256.7	91.3	[15–17]
II8$_a$	8	CH_3O	–	126.3	–	–	227.7	101.4	[12]
II8$_b$	8	CH_3	–	107.2	–	–	203.3	96.1	[18]
II8$_c$	8	Cl	–	165.2	–	–	218.0	52.8	[18]
II8$_d$	8	CN	145.2	–	193.0	–	253.9	108.7	[14]
II8$_e$	8	NO_2	168.2	–	241.0	–	246.7	78.5	[17]

Table 2 (*Continued*)

Compound	*n*	X	$T_{\text{C-A}}$	$T_{\text{C-N}}$	$T_{\text{A-N}}$	$T_{\text{A-I}}$	$T_{\text{N-I}}$	ΔT	Ref.
II14_a	14	CH_3O	–	125.6	–	–	193.2	67.6	[3]
II14_b	14	CH_3	–	105.0	–	–	172.5	67.5	[3]
II14_c	14	Cl	157.4	–	180.9	–	190.2	32.8	[3]
II14_d	14	CN	138.6	–	–	230.2	–	91.6	[3]
II14_e	14	NO_2	160.0	–	–	235.1	–	75.1	[3]
II16_a	16	CH_3O	–	115.5	–	–	178.1	62.6	[3]
II16_b	16	CH_3	–	109.1	–	–	166.5	57.4	[3]
II16_c	16	Cl	157.2	–	182.1	–	184.6	27.4	[3]
II16_d	16	CN	136.5	–	–	229.7	–	93.2	[3]
II16_e	16	NO_2	159.4	–	–	222.2	–	62.8	[3]

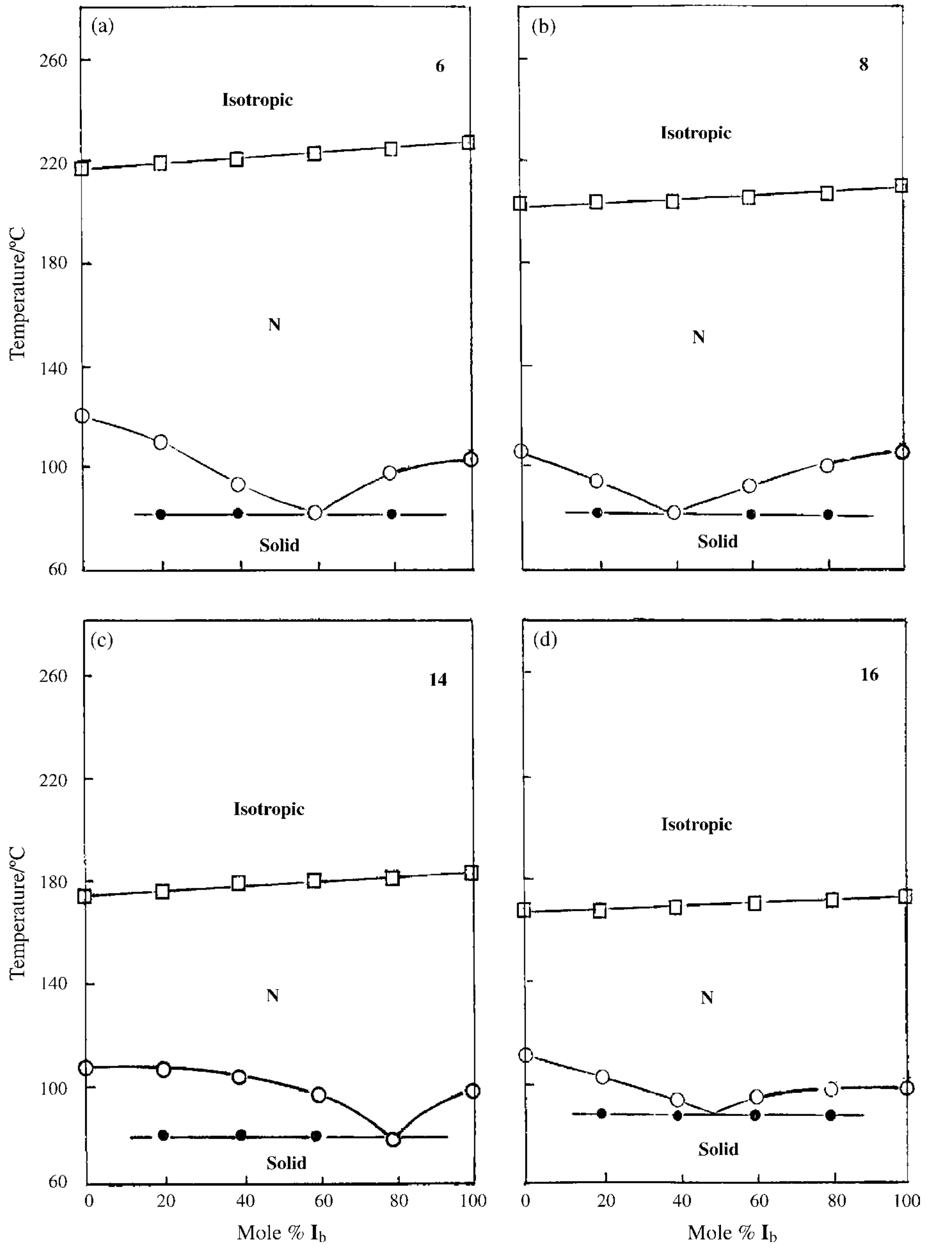


Fig. 3. Binary phase diagram for the system I_b/II_b: (a) $n = 6$, (b) $n = 8$, (c) $n = 14$ and (d) $n = 16$.

from series **II**. As can be seen from Fig. 1, except for the higher homologues ($n = 14$ and 16) of the cyano- and nitro-substituted derivatives, the correlation is linear with slope = 0.94 and correlation coefficient 0.984. These eight derivatives, four from each series, are found to possess the Sm A phase as the only mesophase. A slope of ≈1 for correlating the nematic-isotropic transition temperatures, $T_{\text{N-I}}$, of corresponding derivatives in both series, revealed that the nematic group efficiency are nearly of the same order in both types of molecules. For both groups of compounds, **I** and **II**, the nematic thermal stability generally decreases in the order:

$$\text{CN} > \text{NO}_2 > \text{CH}_3\text{O} > \text{Cl} > \text{CH}_3.$$

On the other hand, the scattered data obtained for correlating the Sm A stability (i.e., $T_{\text{A-N}}$ or $T_{\text{A-I}}$), indicate that substitution with CN or NO_2 groups in either molecules resulted in compounds that behave differently in promoting the Sm A phases.

*3.1. Binary mixtures of similarly substituted components from series **I** and **II***

In this group of binary systems, phase diagrams are constructed for mixtures made from one component from each group, **I** and **II**, but both components bears the same substituent X and of the same alkoxy-chain length, *n*.

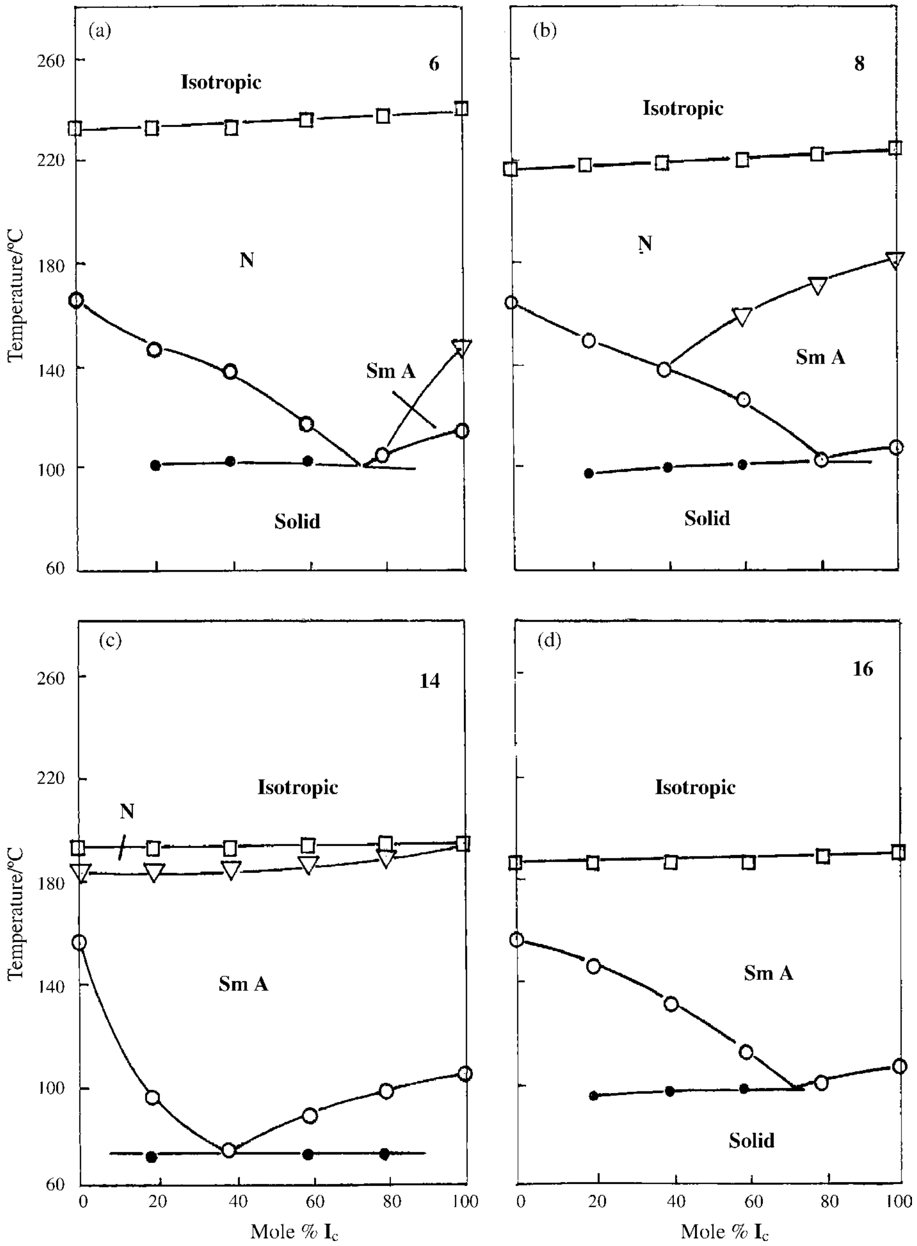


Fig. 4. Binary phase diagram for the system $\mathbf{I}_c/\mathbf{II}_c$: (a) $n = 6$, (b) $n = 8$, (c) $n = 14$ and (d) $n = 16$.

3.1.1. Binary mixtures of electron-releasing substituted analogues (I_a/II_a and I_b/II_b)

The phase diagrams constructed for the four binary mixtures made from each of the four methoxy-substituted homologues $\mathbf{I}_a$ from group **I** with the similarly substituted analogues from group **II**, i.e. $\mathbf{II}_a$, are illustrated in Fig. 2. Similar phase diagrams, constructed for the methyl-substituted homologues are given in Fig. 3. As can be seen from both figures, each diagram, irrespective of the alkoxy-chain length, exhibits a eutectic behaviour in their solid-nematic transition temperature and a linear T_C-composition dependence. This behaviour indicates that either substituent (CH_3O or CH_3) exerts similar effects in each of the two molecules (**I** or **II**) being mixed. Furthermore, in all eight diagrams, illustrated in Figs. 2 and 3, irrespective of the alkoxy-chain length, the nematic phase is the only phase observed throughout the whole range of composition.

3.1.2. Binary mixtures of electron-withdrawing substituted analogues (I_c/II_c, I_d/II_d and I_e/II_e)

Figs. 4–6 represent the phase diagrams of the other three binary systems, namely $\mathbf{I}_c/\mathbf{II}_c$, $\mathbf{I}_d/\mathbf{II}_d$ and $\mathbf{I}_e/\mathbf{II}_e$, respectively. Each of the four diagrams of the chloro-substituted components (Fig. 4) shows linear composition dependence of the mesophase–isotropic transition temperature (T_C), and a eutectic behaviour in their solid-mesophase transition tem-

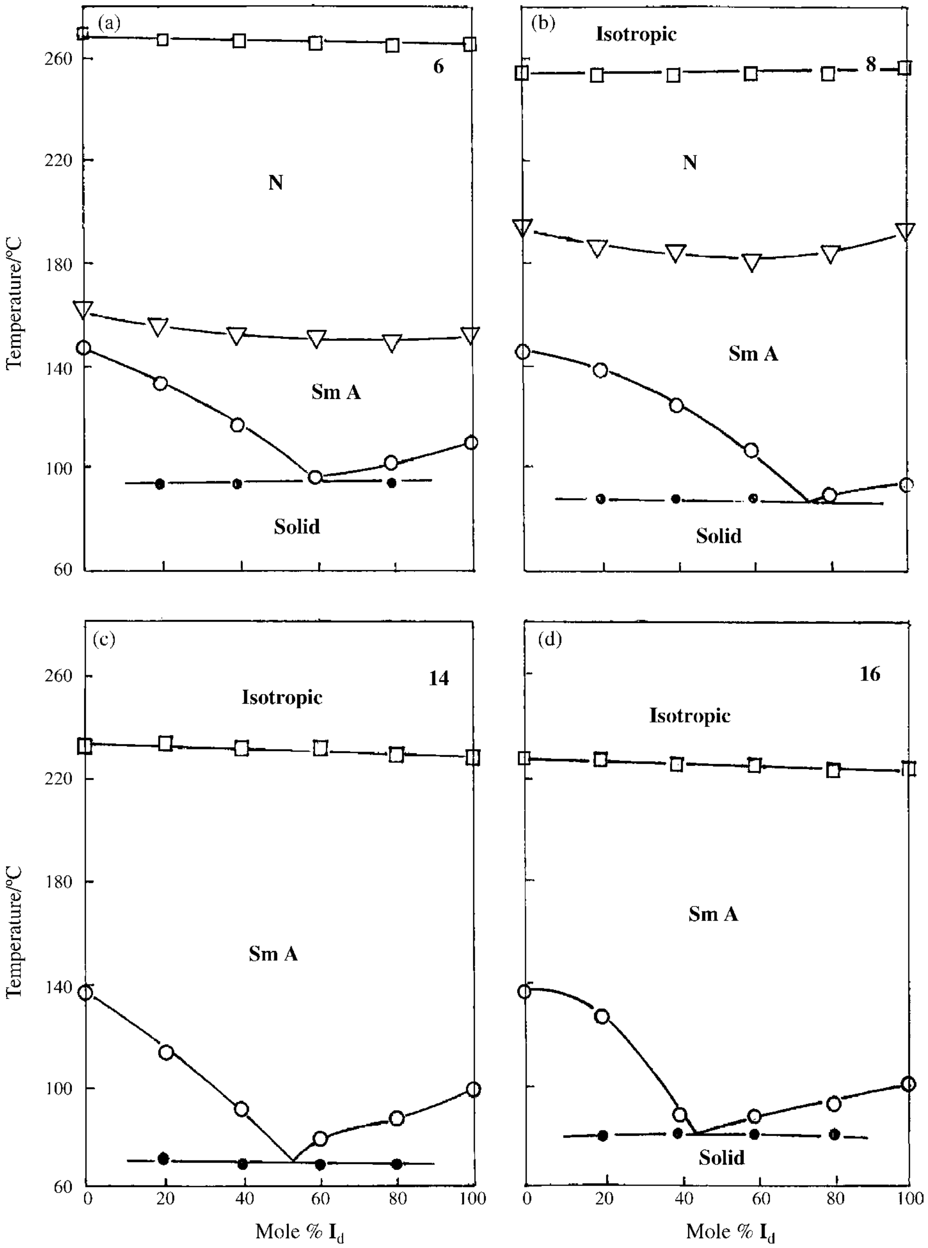


Fig. 5. Binary phase diagram for the system $\mathbf{I}_d/\mathbf{II}_d$: (a) $n = 6$, (b) $n = 8$, (c) $n = 14$ and (d) $n = 16$.

peratures (T_m). Since the homologous series of $\mathbf{I}_c$ exhibits polymorphic phase behaviour (Sm A and N) in their lower ($\mathbf{I}6_c$ and $\mathbf{I}8_c$) homologues, and only Sm A mesophase in their higher ($\mathbf{I}14_c$ and $\mathbf{I}16_c$) ones, whereas, the corresponding homologues of $\mathbf{II}_c$ showed their Sm A phase in the $\mathbf{II}14_c$ homologue and becomes the only mesophase in $\mathbf{II}16_c$, their mixed systems with **I** exhibit a large composition range of nematic with a small Sm A range in their mixtures of lower homologues ($\mathbf{I}6_c/\mathbf{II}6_c$ and $\mathbf{I}8_c/\mathbf{II}8_c$). The smectic A phase increases to cover the whole composition range in the higher homologous mixed systems ($n = 14$ and 16 carbons).

Figs. 5 and 6 illustrate the last two systems, i.e., mixtures of components bearing the electron-withdrawing cyano and nitro substituents, respectively. Since, the cyano and nitro groups are of similar electronic nature, similar phase behaviour was observed for corresponding phase diagrams. As can be seen from Tables 1 and 2, the nitro and cyano analogues in both groups of compounds (**I** and **II**) exhibit Sm A as well as N mesophases in their lower ($n = 6$ and 8) homologues, while only the Sm A phase is observed in their higher ($n = 14$ and 16) ones. Consequently, mixed systems showed Sm A and N phases throughout the whole composition range, in the lower ($n = 6$ and 8) homologous systems, and only the Sm A phase in their higher ($n = 14$ and 16) ones. Both systems ($\mathbf{I}_d/\mathbf{II}_d$ and $\mathbf{I}_e/\mathbf{II}_e$), irrespective of the alkoxy-chain length, exhibit eutectic behaviour on their solid-mesophase transitions.

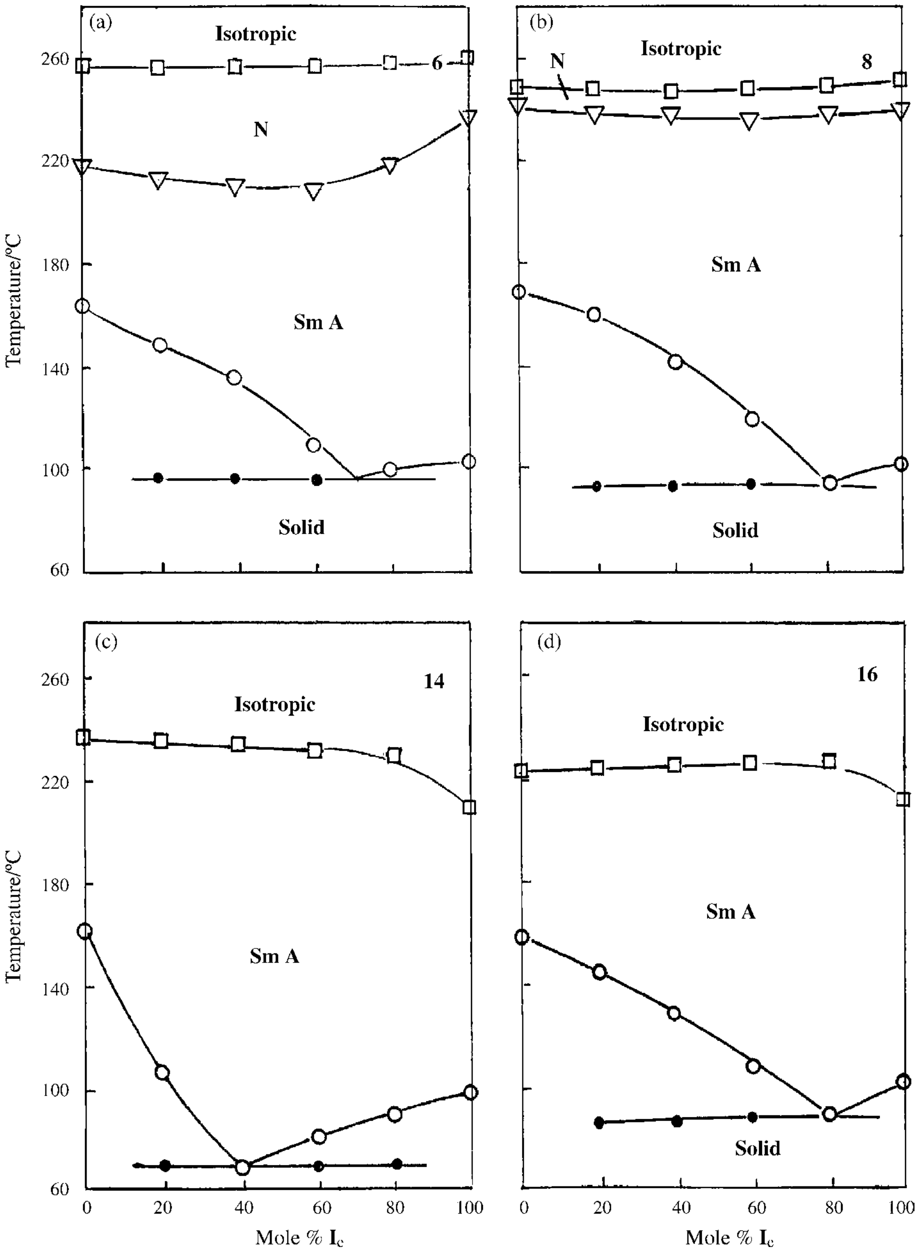


Fig. 6. Binary phase diagram for the system $\mathbf{I}_e/\mathbf{II}_e$: (a) $n = 6$, (b) $n = 8$, (c) $n = 14$ and (d) $n = 16$.

4. Conclusions

In spite of the difference in core structure, and consequently, in the conjugative interactions between the substituent X and the remainder of the molecular structure, between analogously substituted analogues of compounds **I** and **II**, their binary mixtures showed ideal mesophase behaviour. That is, in all the systems investigated, irrespective of substituent X or alkoxy-chain length, their mesophase–isotropic transition temperatures (T_C) vary linearly with composition. This is in accordance with the above findings that the mesophase group efficiency in both series **I** and **II** are of the same order. On the other hand, in contrast to binary mixtures prepared from components of the same group (i.e., **I** or **II**), the mixed systems **I/II** exhibit eutectic behaviour for their solid-mesophase transition temperatures (T_m) indicating the formation of heterogeneous solid mixtures. This result revealed that the difference encountered in their core structures gives different solid crystalline structures, and their mixed solids form heterogeneous mixtures. The reverse holds good for mixtures of the same core structures, i.e., components of the same series **I** or **II**. In either case [4,5,7], T_m varies gradually with composition, especially when the substituents X in both component of the mixture are of the same electronic nature, i.e. of electron-withdrawing or electron-releasing nature, or if the alkoxy group is of long chain length ($n \geq 14$).

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