Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Lateral protrusion and mesophase behaviour in pure and mixed states of model compounds of the type 4-(4'-substituted phenylazo)-2-(or 3-)methyl phenyl-4'-alkoxy benzoates

M. M. Naoum[a]; S. Z. Mohammady [§a]; H. A. Ahmed[a]
[a] Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

To cite this Article Naoum, M. M. , Mohammady §, S. Z. and Ahmed, H. A.(2010) 'Lateral protrusion and mesophase behaviour in pure and mixed states of model compounds of the type 4-(4'-substituted phenylazo)-2-(or 3-)methyl phenyl-4'-alkoxy benzoates', Liquid Crystals, 37: 10, 1245 — 1257

To link to this Article: DOI: 10.1080/02678292.2010.497228

URL: http://dx.doi.org/10.1080/02678292.2010.497228

Liquid Crystals,
Vol. 37, No. 10, October 2010, 1245–1257

Lateral protrusion and mesophase behaviour in pure and mixed states of model compounds of the type 4-(4′-substituted phenylazo)-2-(or 3-)methyl phenyl-4’-alkoxy benzoates

M.M. Naoum*, S.Z. Mohammady§ and H.A. Ahmed

Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

(*Received 14 December 2009; final version received 26 May 2010*)

Two groups of the title compounds were prepared and investigated for their mesophase formation and stability. Each group constitutes five homologous series that differ from each other by the polar substituent X (CH_3O, CH_3, H, Cl, and NO_2). Within each homologous series, the number (*n*) of carbons in the alkoxy chain varies between 8, 10, 12, 14 and 16. The difference between the two groups of compounds lies in the orientation protrusion of the lateral methyl group attached to the central benzene ring. In the first group (Group **I**) the methyl substituent, introduced into the *o*-position with respect to the ester group, makes an angle of 60° with the long axis of the molecule. In the other series of compounds (Group **II**), the orientation angle is 120° as it is introduced into the position-3. All possible binary phase diagrams could be constructed in which the two components are corresponding positional isomers from either group. The study aimed to investigate the effect of inclusion of the lateral methyl group, as well as its spatial orientation, on the mesomorphic properties of the produced derivatives in their pure and mixed states. The compounds prepared in both groups were characterised for their mesophase behaviour by differential scanning calorimetry and polarised light microscopy. The nematic phase is the mesophase observed in most of the compounds prepared and their binary mixtures.

Keywords: lateral substitution; binary mixtures; 4-(4′-substituted phenylazo)-2 (or 3-)-methyl phenyl)-4′-alkoxy benzoates

1. Introduction

Studies of the factors that influence mesomorphic properties have received considerable attention. We have previously studied structure–property relationships for homologous series of the azo ester of the type 4-(4′-substituted phenylazophenyl)-4′-alkoxy benzoates and evaluated their mesomorphic properties in pure [1] and mixed states [2]. Aiming to reduce their melting temperatures, we reported [3] another series of the azo ester mesogens, substituting the central 1,4-phenylene group with a laterally protruded 1,6-naphthalene, and investigated the steric effect exerted by the naphthalene protrusion on their mesomorphic properties, again in pure [3] and mixed states [4, 5]. In these mixed systems, binary mixtures were made once from any two homologues carrying the same polar group X [2, 4], and another from any two analogues of different X but of the same alkoxy group length [2, 5]. A third type of binary system [6] was made from two analogously terminally substituted compounds but of different mesogenic core, one is an azo ester and the other is a di-ester.

In view of the upsurge of interest in room temperature liquid crystalline materials, we continue here our work by investigating mixtures of liquid crystals of two positional isomers of the same skeletal structure bearing the same terminal (polar and alkoxy) groups but with the lateral methyl substituent protruded with different angles with respect to the long axis of the molecule. The azo ester molecule was chosen on the basis of its relatively high mesophase stability. Dye-containing materials can be applied to a wide variety of fields such as high technology and nanotechnology [7]. Azo-based dyes can improve the viewing angle and the order parameter in guest–host liquid crystal displays and can be used to obtain full colour reflective displays.

The study aimed to investigate first the effect of methyl-lateral substitution into the central benzene ring, and its different orientation, on the mesomorphic range and stability of the previously investigated azo esters [1]. Secondly, the aim was to investigate the effect of steric interaction that may be encountered between any two corresponding positional isomers from these two groups of compounds (**I** and **II**) on the mesomorphic properties of their binary mixtures.

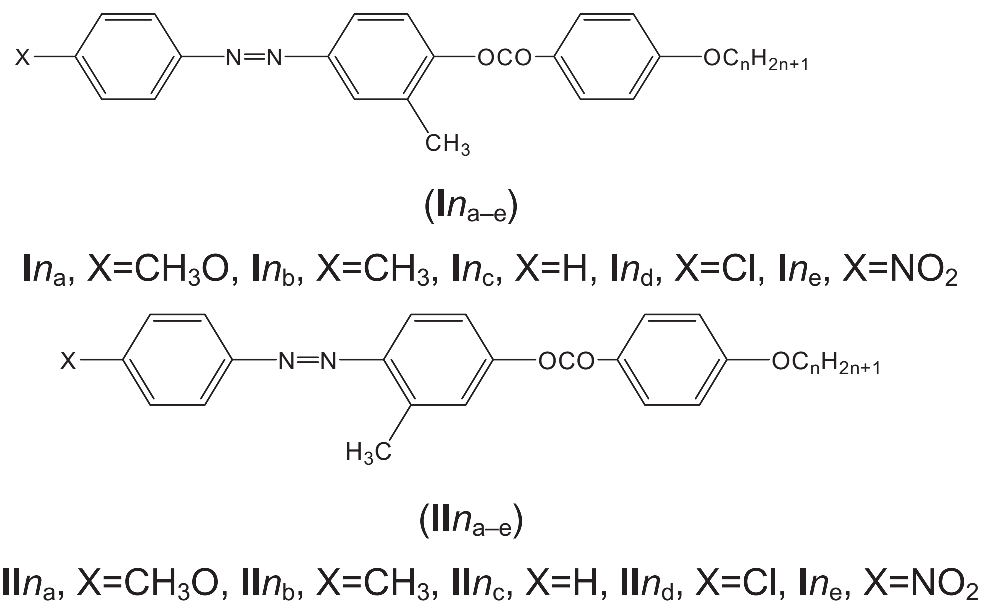
Substituents were chosen to cover a wide range of electronic and dipolar characteristics, and the length of the alkoxy group varied between eight and 16 carbon atoms. The methyl-lateral substituent was chosen on the basis of its mild polarity to affect greatly the polarity of any two positional isomers from both groups of compounds. Furthermore, different protrusion angles between the two isomers may lead to a further decrease in melting temperatures in their mixed systems.

---

*Corresponding author. Email: magdinaoum@yahoo.co.uk
§Present Address: Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University, Makkah, Saudi Arabia.

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678292.2010.497228
http://www.informaworld.com



($\mathbf{I}n_{a\text{–}e}$)

$\mathbf{I}n_a$, X=CH_3O, $\mathbf{I}n_b$, X=CH_3, $\mathbf{I}n_c$, X=H, $\mathbf{I}n_d$, X=Cl, $\mathbf{I}n_e$, X=NO_2

($\mathbf{II}n_{a\text{–}e}$)

$\mathbf{II}n_a$, X=CH_3O, $\mathbf{II}n_b$, X=CH_3, $\mathbf{II}n_c$, X=H, $\mathbf{II}n_d$, X=Cl, $\mathbf{I}n_e$, X=NO_2

Scheme 1. Molecular formulae for compounds $\mathbf{I}n_{a\text{–}e}$ and $\mathbf{II}n_{a\text{–}e}$.

2. Experimental

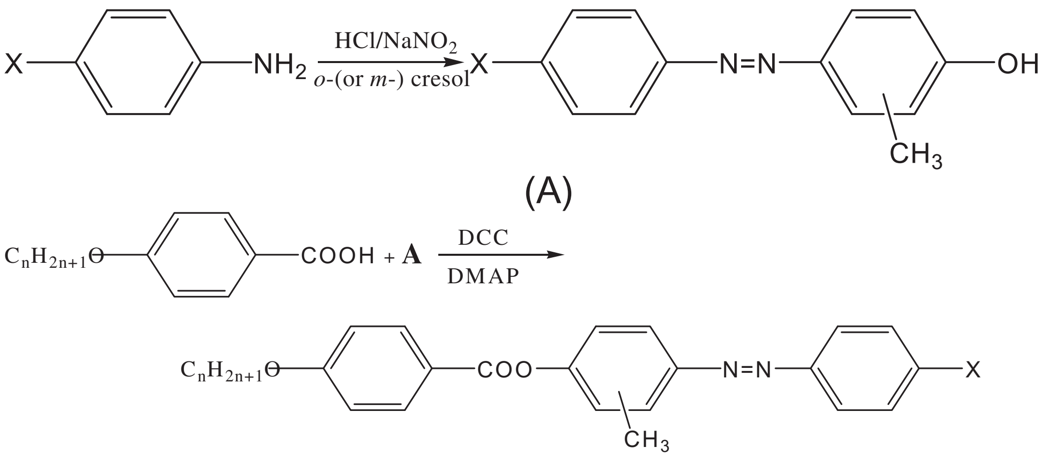
Chemicals were purchased from the following companies: Aldrich, Wisconsin, USA; E. Merck, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

2.1 Preparation of materials

Compounds $\mathbf{I}n_{a\text{–}e}$ and $\mathbf{II}n_{a\text{–}e}$ were prepared according the general procedure shown.

2.1.1 4-(4′-Substituted phenylazo)-2-(or 3-) methyl phenol (A)

One molar equivalent of the 4-substituted aniline in ice-cold dilute hydrochloric acid was diazotised with cold sodium nitrite solution and then added slowly to a cold 2- (or 3-) cresol/sodium hydroxide solution (1:1). The solid product was filtered and recrystallised twice from glacial acetic acid. The melting points of



$\mathbf{I}n_{a\text{–}e}$ or $\mathbf{II}n_{a\text{–}e}$

Scheme 2. General scheme for the preparation of compounds $\mathbf{I}n_{a\text{–}e}$ and $\mathbf{II}n_{a\text{–}e}$.

the prepared azo dyes were in good agreement with those reported in the literature [8].

*2.1.2 4-(4′-Substituted phenylazo)-2-(or 3-) methyl phenyl -4'- n –alkoxy benzoates, **I**n$_{a–e}$ (and **II**n$_{a–e}$)*

Molar equivalents of the 4-(4′-substituted phenylazo)-2-(or 3-) methyl phenol (A) and 4-*n*-alkoxybenzoic acid were dissolved in dry methylene chloride. To the resulting solution, dicyclohexylcarbodiimide (DCC) and 4-dimethylamino-pyridine (DMAP) were added and the solution was left to stand for 72 hours at room temperature with stirring. The separated solid was then filtered off and the solution evaporated. The obtained solid residue was recrystallised twice from acetic acid and twice from ethanol to give TLC-pure products.

2.2 Physical characterisation

Calorimetric measurements were carried out using a PL-DSC from Polymer Laboratories, Epsom, Surrey UK. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga *et al.* [9]. The measurements were carried out for small samples (2–3 mg) placed in sealed aluminium pans. All the thermograms were achieved at a heating rate of 10°C min^{-1} in an inert atmosphere of nitrogen gas (10 mL min^{-1}).

The transition temperatures were checked and the types of mesophases were identified for the compounds prepared and their binary mixtures using a standard polarised light microscope (Wild, Germany) attached to a homemade hot stage.

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

Infrared spectra (4000–400 cm^{-1}) were measured using a Perkin Elmer B25 spectrophotometer and ^{1}H NMR-spectra with a Varian EM 350L.

3. Results and discussion

The infrared spectra and elemental analyses for the compounds investigated were consistent with the structures assigned. ^{1}H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

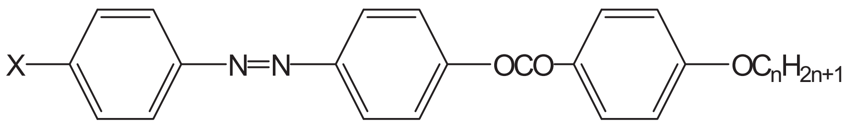
Almost identical infrared absorption spectra were observed for all corresponding analogues in the five series (**I***8*–**I***16*). The infrared absorption bands of the ester carbonyl group revealed that neither the length of the alkoxy group, C_8–C_{16}, in any of the homologous series, **I**$_{a–e}$, nor the substituent X in any group of derivatives bearing the same alkoxy group (specially in group **II)** has a significant effect on the absorption associated with the carbonyl group (1732–1734 cm^{-1}). These findings are in agreement with the data obtained previously for the laterally neat analogues **III** [1].

3.1 Mesophase behaviour

Since the mesophase stability of a liquid crystalline compound is mainly dependent on intermolecular attractions, in which molecular polarity plays a significant role, it has been shown that, in a series of compounds, the dipole moment of any compound is dependent upon the nature of the substituent [10]. A change in the extent of conjugation alters the polarisability and resultant dipole moment of the molecule. It has also been shown that the dipole moments of all members of a homologous series are virtually the same irrespective of the alkoxy chain length [11]. This result is in accordance with the fact that the alkoxy groups are of the same polarity regardless of the chain length, and at the same time, do not significantly affect the extent of conjugative interactions between the alkoxy oxygen and the ester carbonyl, as is observed from infrared measurements.

The transition temperatures and transition enthalpies as measured by differential scanning calorimetry (DSC) and the phases identified by polarised light microscopy (PLM) for compounds **I***n*$_{a–e}$ and **II***n*$_{a–e}$ are summarised in Tables 1 and 2, respectively.

The data in these tables reveal that all members of both groups, except the unsubstituted (**II**$_c$) and chloro-substituted (**II**$_d$) homologues of group **II**, are purely nematogenic. In general, the stability of the mesophase is augmented by an increase in the polarity or polarisability of the mesogenic part of the molecule. This was



III

Scheme 3. Molecular formula for compounds **III***n*$_{a–e}$.

Table 1. Phase transition temperatures (°C), enthalpy of transition (ΔH, kJ mol^{-1}) and $\surd \boldsymbol{T}_C$ for Group $\mathbf{I}n_{a–e}$.

Comp. No.	*n*	X	$\boldsymbol{T}_{S–N}$	$\Delta H_{S–N}$	$\boldsymbol{T}_{N–I}$	$\Delta H_{N–I}$	$\surd \boldsymbol{T}_C$
$\mathbf{I}8_a$	*8*	CH_3O	94.3	24.04	186.3	0.96	21.43
$\mathbf{I}8_b$		CH_3	79.7	24.49	160.3	1.35	20.81
$\mathbf{I}8_c$		H	71.7	26.07	89.7	0.63	19.05
$\mathbf{I}8_d$		Cl	87.8	41.47	162.9	1.14	20.87
$\mathbf{I}8_e$		NO_2	101.0	34.82	179.3	0.45	21.27
$\mathbf{I}10_a$	*10*	CH_3O	78.7	27.25	159.9	0.79	20.81
$\mathbf{I}10_b$		CH_3	79.9	26.69	149.6	1.49	20.56
$\mathbf{I}10_c$		H	79.7	26.28	88.2	0.23	19.00
$\mathbf{I}10_d$		Cl	88.3	26.78	152.1	1.38	20.62
$\mathbf{I}10_e$		NO_2	81.9	77.58	174.1	0.91	21.12
$\mathbf{I}12_a$	*12*	CH_3O	83.0	35.11	165.5	1.64	20.94
$\mathbf{I}12_b$		CH_3	77.2	24.06	119.5	2.38	19.81
$\mathbf{I}12_c$		H	74.1	20.04	87.5	0.41	18.98
$\mathbf{I}12_d$		Cl	80.9	21.11	142.3	1.05	20.38
$\mathbf{I}12_e$		NO_2	88.2	71.94	164.0	1.13	20.90
$\mathbf{I}14_a$	*14*	CH_3O	98.4	30.30	154.2	1.25	20.66
$\mathbf{I}14_b$		CH_3	76.5	22.07	111.7	2.67	19.61
$\mathbf{I}14_c$		H	67.3	44.64	70.0	0.84	18.52
$\mathbf{I}14_d$		Cl	80.2	50.16	140.7	1.13	20.34
$\mathbf{I}14_e$		NO_2	80.2	52.08	161.0	0.53	20.83
$\mathbf{I}16_a$	*16*	CH_3O	88.3	33.23	146.1	1.62	20.47
$\mathbf{I}16_b$		CH_3	77.2	24.45	103.5	1.19	19.4
$\mathbf{I}16_c$		H	71.4	55.26	76.6	0.97	18.7
$\mathbf{I}16_d$		Cl	81.7	31.81	130.1	0.76	20.01
$\mathbf{I}16_e$		NO_2	85.5	52.50	160.8	0.75	20.82

Table 2. Phase transition temperatures (°C), enthalpy of transition (ΔH, kJ mol^{-1}) and $\surd \boldsymbol{T}_C$ for Group $\mathbf{II}n_{a-e}$.

Comp. No.	*n*	X	$\boldsymbol{T}_{S–I}$	$\Delta H_{S–I}$	$\boldsymbol{T}_{S–N}$	$\Delta H_{S–N}$	$\boldsymbol{T}_{N–I}$	$\Delta H_{N–I}$	$\surd \boldsymbol{T}_C$
$\mathbf{II}8_a$	*8*	CH_3O	–	–	94.6	30.64	149.5	1.21	20.55
$\mathbf{II}8_b$		CH_3	–	–	99.1	31.09	175.1	1.08	21.17
$\mathbf{II}8_c$		H	94.1	39.71	–	–	–	–	–
$\mathbf{II}8_d$		Cl	99.8	19.56	–	–	–	–	–
$\mathbf{II}8_e$		NO_2	–	–	99.1	31.14	170.0	0.84	21.05
$\mathbf{II}10_a$	*10*	CH_3O	–	–	90.8	29.18	142.0	0.65	20.73
$\mathbf{II}10_b$		CH_3	–	–	74.9	42.97	174.4	1.07	21.15
$\mathbf{II}10_c$		H	93.7	38.53	–	–	–	–	–
$\mathbf{II}10_d$		Cl	106.5	17.34	–	–	–	–	–
$\mathbf{II}10_e$		NO_2	–	–	70.0	29.93	156.0	0.63	20.70
$\mathbf{II}12_a$	*12*	CH_3O	–	–	93.6	43.47	133.3	0.79	20.16
$\mathbf{II}12_b$		CH_3	–	–	86.5	43.33	162.3	1.31	20.86
$\mathbf{II}12_c$		H	84.9	41.71	–	–	–	–	–
$\mathbf{II}12_d$		Cl	108.3	15.81	–	–	–	–	–
$\mathbf{II}12_e$		NO_2	–	–	77.9	26.63	156.0	0.77	20.7
$\mathbf{II}14_a$	*14*	CH_3O	–	–	91.4	49.20	132.4	1,23	20.13
$\mathbf{II}14_b$		CH_3	–	–	85.3	44.88	153.9	1.50	20.66
$\mathbf{II}14_c$		H	87.1	51.75	–	–	–	–	–
$\mathbf{II}14_d$		Cl	83.0	29.70	–	–	–	–	–
$\mathbf{II}14_e$		NO_2	–	–	80.5	31.98	146.0	0.50	20.47
$\mathbf{II}16_a$	*16*	CH_3O	–	–	93.2	49.32	123.5	0.75	19.91
$\mathbf{II}16_b$		CH_3	–	–	88.0	49.37	148.2	1.55	20.52
$\mathbf{II}16_c$		H	91.9	64.58	–	–	–	–	–
$\mathbf{II}16_d$		Cl	115.0	28.38	–	–	–	–	–
$\mathbf{II}16_e$		NO_2	–	–	69.6	17.56	140.9	0.50	20.35

found to be true where, in both groups of compounds, **I***n*$_{a-e}$ and **II***n*$_{a-e}$, both the electron-donating (CH_3O and CH_3) and electron-withdrawing (NO_2) substituents enhance the nematic stability (T_{N-I}) over their unsubstituted analogues. Conversely, independent of the alkoxy chain length, the unsubstituted as well as the chloro-substituted homologues in series **II** are monotropically nematogenic. Such a destabilisation of the mesophase compared with the laterally neat analogues, **III**, is accordingly ascribed to the methyl-lateral substitution. On the other hand, the electron-donating methyl group introduced at the *ortho*-position-2 (**I**) with respect to the ester carbonyl enhances its polarisation compared to its isomer (**II**) where the methyl group is inserted at position-3. In the latter case, methyl-lateral substitution furnishes non-mesomorphic compounds with the less polar terminal H- and Cl- atoms.

It is well known that the relative strength of the lateral cohesive forces between molecules determines the type of the mesophase formed [12, 13]. Thus, the introduction of the lateral methyl group either in position-2 or position-3 weakens the lateral intermolecular cohesions compared with the laterally neat ones [1], whereby the nitro-substituted analogues of **III** exhibit the smectic A (SmA) and N phases in their lower homologues (n = 6 and 8 carbons) while the SmA mesophase is exhibited alone in the higher homologues (n = 10, 12, 14, and 16 carbons). The weak lateral cohesions in series **I** and **II** resulted in compounds that are purely nematogenic or at least monotropically nematogenic as pointed out above.

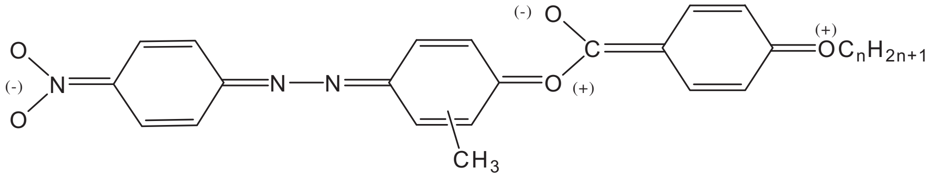
In the nitro analogues in both groups of compounds, **I***n*$_{a-e}$ and **II***n*$_{a-e}$, mesomeric interaction between the alkoxy oxygen and the ester carbonyl, on one side of the molecule, is augmented by the conjugated interaction between the ester oxygen and the nitro group via the phenylazo group, on the other side of the molecule.

This augmented polarisation should increase the polarity of the mesogenic portion as a whole, which in turn stabilises the mesophase. Conversely, there are opposing effects on each side of the molecule of the methoxy (**I**$_a$ or **II**$_a$) and the methyl (**I**$_b$ or **II**$_b$) analogues.

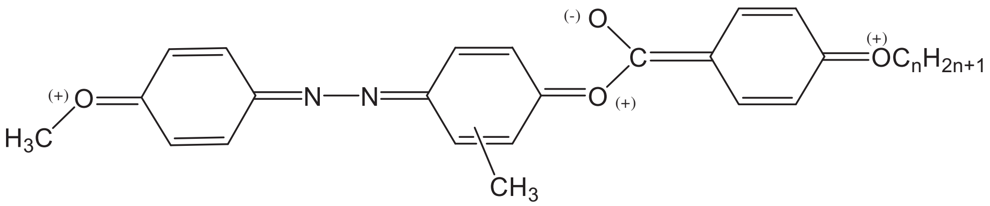
Accordingly they are expected to possess a lower dipolar character, which would lead to lower values for the nematic–isotropic transition temperature (T_C).

The substituent X attached to the mesomorphic compounds can be placed in the order of enhancing nematic stability of group **I** compounds as: $NO_2 > CH_3O > Cl > CH_3 > H$, for all homologues except for **I***8* and **I***12*, where the order $NO_2 > CH_3O$ is reversed. This latter order with the $NO_2 > CH_3O$ inversion is the same as that given in the nematic terminal group efficiency order for the laterally neat analogues **III** [1], as well as for a much wider range of substituents in a number of different mesogenic anils and other systems first reported by Gray [12] and later extended [13].

In order to investigate the effect of increasing the alkoxy chain length on the phase behaviour for the two investigated homologous series, the transition temperatures are plotted in Figures 1 and 2 for series **I** and **II**, respectively, against the length of the alkoxy group (n), with the remaining part of the molecule held constant. As shown from these figures, the solid–nematic transition temperatures change irregularly with



Scheme 4. Tautomerism in the derivatives **I***n*$_e$.



Scheme 5. Tautomerism in the derivatives **I***n*$_a$.

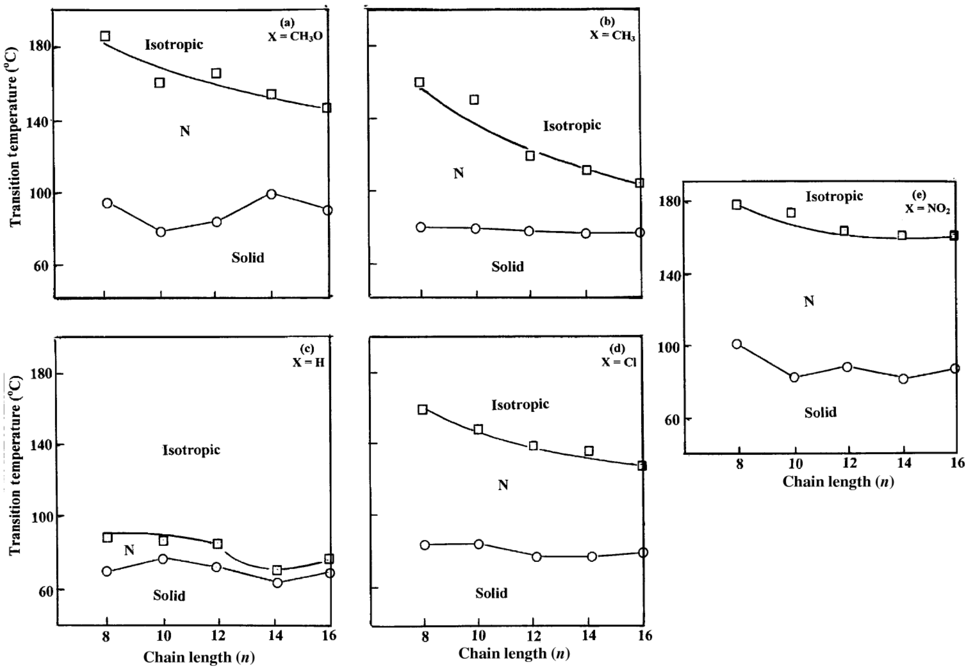


Figure 1. Effect of alkoxy chain length on the mesophase behaviour of the individual homologous series of group **I**. Note: ○ denotes solid–mesophase transition ($\mathbf{T}_m$) and □ denotes mesophase–isotrophic transition.

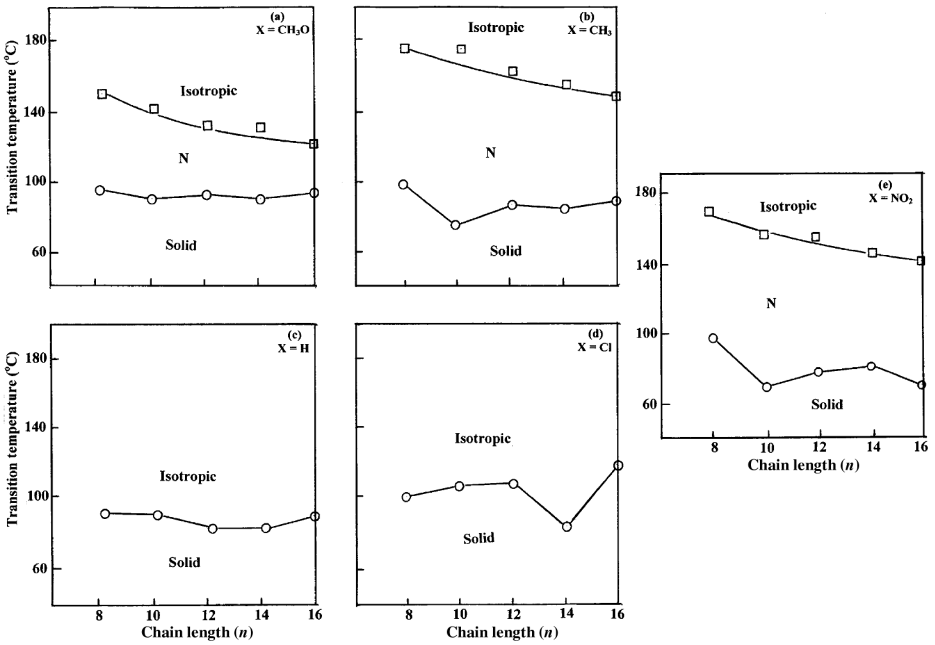


Figure 2. Effect of alkoxy chain length on the mesophase behaviour of the individual homologous series of group **II**. Note: ○ denotes solid–mesophase transition ($\mathbf{T}_m$) and □ denotes mesophase–isotrophic transition.

increase of the alkoxy chain length. If a nematogenic compound is melted, the molecules are free to move whereby the positions of their ends are disorganised, whereas the parallel alignment of the molecules persists. At the solid–nematic transition, cohesive forces weaken profoundly [12]. Thus, although substantial variation in the nature of layer crystal lattices upon melting is very improbable, nevertheless, a nematogenic arrangement may change greatly from the crystal of one homologue to another and not necessarily in a regular fashion. Certainly, the solid crystalline structure affects the strength of the intermolecular forces of attraction and, therefore, the melting point of the nematogenic compound will depend on the exact nature of the crystal packing.

Figure 1 shows that, irrespective of the substituent X, the nematic phase is the only mesophase observed for all homologues of group **I**, and that $\boldsymbol{T}_C$ decreases regularly with increasing alkoxy chain length. The increased alkyl chain length reduces the rod-shaped molecule's rigidity and, consequently, its ability to fit readily into the parallel arrangement within the nematic phase. The result is a decrease in the mesophase stability and a lower transition temperature. Because of the effect of the polar substituent X, which produces a high order of stability and consequently high transition temperatures, a long alkyl group would be relatively mobile, so that its disrupting effect increases with chain length beyond $n = 6$.

Further more, the nematic phase observed for all the homologues of series **I** may be attributed to their end-to-end intermolecular association as indicated by their high clearing enthalpies ($\Delta H_{N\text{–}I} = 0.4\text{–}2.67$ kJ mol^{-1}). This strong end-to-end association is a result of strong intermolecular mesomeric interaction between the alkoxy group oxygen and the ester carbonyl. In addition, the lateral interaction between every second molecule grows weaker upon increasing the alkoxy chain length, in addition to the steric effect of the lateral protrusion of the methyl group, leading to the formation of the nematic phase. Wide nematic ranges were observed for the strong electron-donating (CH_3O) and strong electron-withdrawing (Cl and NO_2) substituted derivatives, followed by the methyl-substituted homologues. The unsubstituted homologues are the poorest mesomorphic compounds.

This mesomorphic behaviour reveals that polar substituent, whether electron-donating or electron-withdrawing, is essential for mesophase formation. For series **II** (Figure 2) where the methyl group is in the *meta*-position, a different order is observed. As stated before, both the unsubstituted and chloro-substituted homologues exhibited a monotropic nematic phase independent of the alkoxy chain length. The nitro homologues showed the highest nematic stability with wide nematic temperature range, followed by the methyl and finally the methoxy. This irregular behaviour indicates that the nematic mesophase stability as well as the nematic temperature range is affected to different extents by each of three factors, namely, the polarity of the terminal group, the length of the alkoxy chain, and the position (or orientation) of the lateral methyl group. These three factors are collected in one figure by plotting the nematic stability ($\boldsymbol{T}_{N\text{–}I}$) against the alkoxy chain length for the corresponding homologous series from the three groups (**I**, **II** and **III**) in Figure 3.

As can be seen from Figure 3, the mesophase stability, whether smectic (▲) or nematic (□), of the laterally neat analogues, **III**, is much decreased as expected by lateral substitution in **I** (●) or **II** (○). The position of the lateral group is also important. Thus, the strong polar methoxy and nitro terminal substituents result in more nematic stability when the lateral methyl group is in position-2, i.e. **I** > **II**. The reverse holds true for the less polar methyl terminal substitution, whereby **II** > **I**. The chloro-substituted homologues of **II** are monotropically nematogenic, while those of **III** are smectogenic except for the lower homologue**, III***8*. No data are available for the terminally unsubstituted homologues of **III**.

3.2 Binary phase behaviour of isomeric analogues

It is already known that materials that retain liquid crystalline character over a wide range of temperatures are preferred for practical applications. One way to achieve this property is to use eutectic mixtures of materials exhibiting liquid crystallinity in their pure state, or at least when the molecules in question resemble one another structurally. This is because, under such a condition, the mesophase–isotropic line is usually straight or slightly enhanced, and the temperature range of the mesophase is consequently greater for the eutectic mixture than either component. Our investigated isomers, **I***n*$_{a\text{–}e}$ and **II***n*$_{a\text{–}e}$, provide a favourable system for such investigation.

3.2.1 Binary mixtures of isomers bearing electron-donating substituents

Figure 4(a–e) collects the phase diagrams constructed for the five binary systems prepared from the CH_3O-substituted isomers in each of the series **I***n*$_a$ and **II***n*$_a$, where *n* varies between 8 and 16, respectively. Figure 4 shows that, in all five systems, the nematic–isotropic transition temperatures vary, more or less, linearly with composition, while their mixed solid phase exhibits eutectic behaviour in their solid to nematic transition temperatures. This behaviour indicates that, irrespective of the length of the alkoxy chain, the nematic arrangement of molecules of one isomer is not disturbed by the addition of the other isomer. This in turn reveals that the different spatial orientation of the methyl groups has nothing to do with the nematic arrangements in both isomers. Such compatibility is not continued in the solid phase, where the different crystalline lattices of the two solid components form heterogeneous mixtures as indicated by the eutectic behaviour.

Similar behaviour was observed for the 4-methyl substituted analogues. Figure 5 illustrates the binary

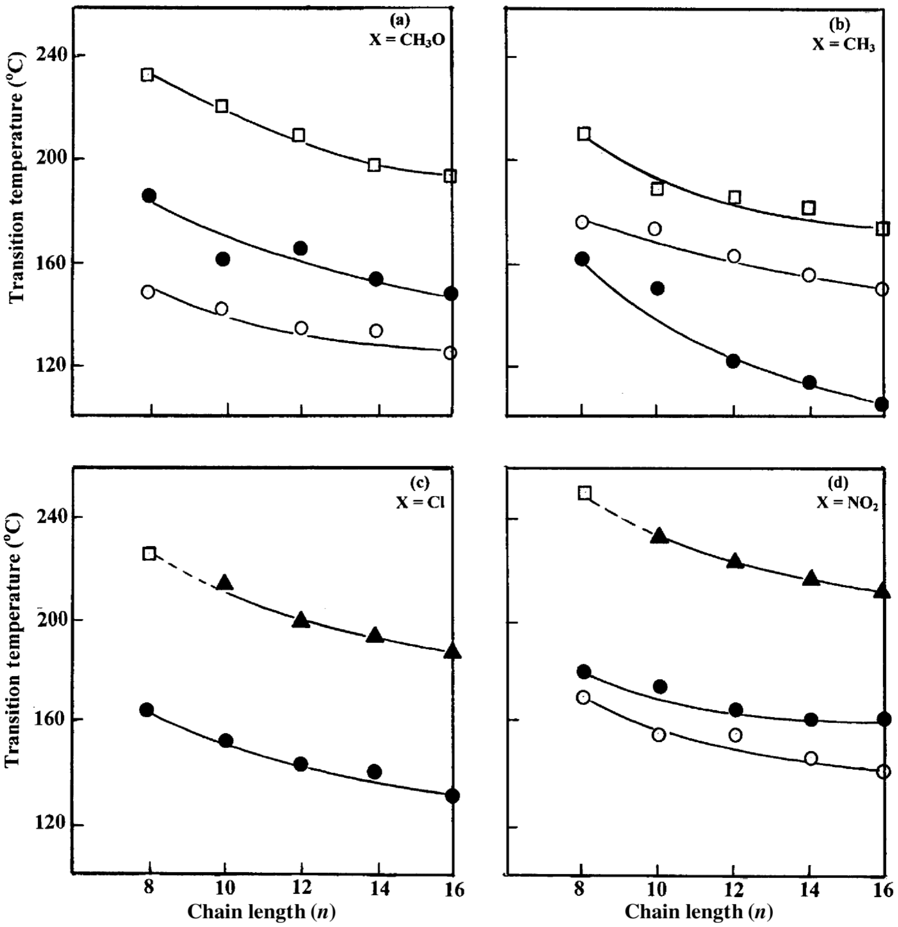


Figure 3. Comparative dependency on the alkoxy chain length of the nematic stability of Group **I** (●), Group **II** (○) and the laterally neat analogues **III** (□). The symbol (▲) is taken to represent the SmA stability of the smectogenic derivatives of the last group.

phase diagrams of corresponding isomers from the homologues **I**n_b and **II**n_b.

3.2.2 Binary mixtures of terminally unsubstituted isomers **I**n_c/**II**n_c

The phase diagrams of the five binary systems **I**n_c/**II**n_c are illustrated in Figure 6(a–e) for $n = 8$–14, respectively. Referring to Figure 6, in all the five binary systems one of the two components, **II**n_c, is monotropically nematogenic while the other, **I**n_c, is weakly nematogenic. Nevertheless, since both components pertain the linear requirement for mesophase formation, the addition of the monotropic component, **II**, to the nematogen, **I**, resulted in a linear T_C–composition dependency.

This behaviour indicates that, in spite of the difference in the lateral methyl group orientation, the compatibility of both molecules allows them to fit into a linear alignment. It can also be noted from Figure 6 that the amount of monotropic isomer **II** required to hide completely the enantiotropic nematic phase of **I** varies irregularly with increasing alkoxy chain length. It is evident that such composition depends mainly on the melting temperature of the monotropic isomer, **II**, which in turn varies irregularly with the alkoxy chain length as shown in Figure 2. The mole percentage (mol%) of **II**$_\mathrm{c}$ required to hide the nematic phase decreases according to the alkoxy chain length (n) in the order: $12 > 16 > 10 > 8 > 14$ carbons. With respect to their mixed solids, these systems were shown to exhibit eutectic behaviour irrespective of the alkoxy chain length, indicating the incompatibility of their crystalline lattices.

3.2.3 Binary mixtures of chloro- substituted isomers **I**n_d/**II**n_d

The phase behaviour of the binary systems made from the two isomers of the chlorosubstituted homologous series **I**n_d and **II**n_d is illustrated in Figure 7. Since

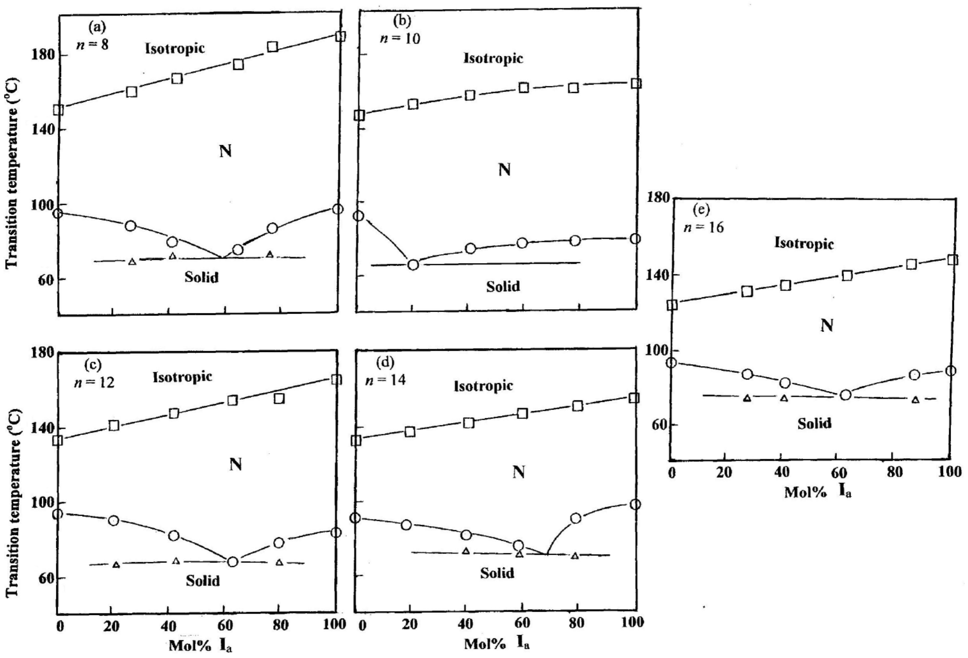


Figure 4. Binary phase diagrams of the corresponding isomers from the two methoxy-substituted homologous series **I***n*$_a$ and **II***n*$_a$. Note: ○ denotes solid–mesophase transition (T_m), □ denotes mesophase–isotrophic transition and Δ denotes eutectic temperature.

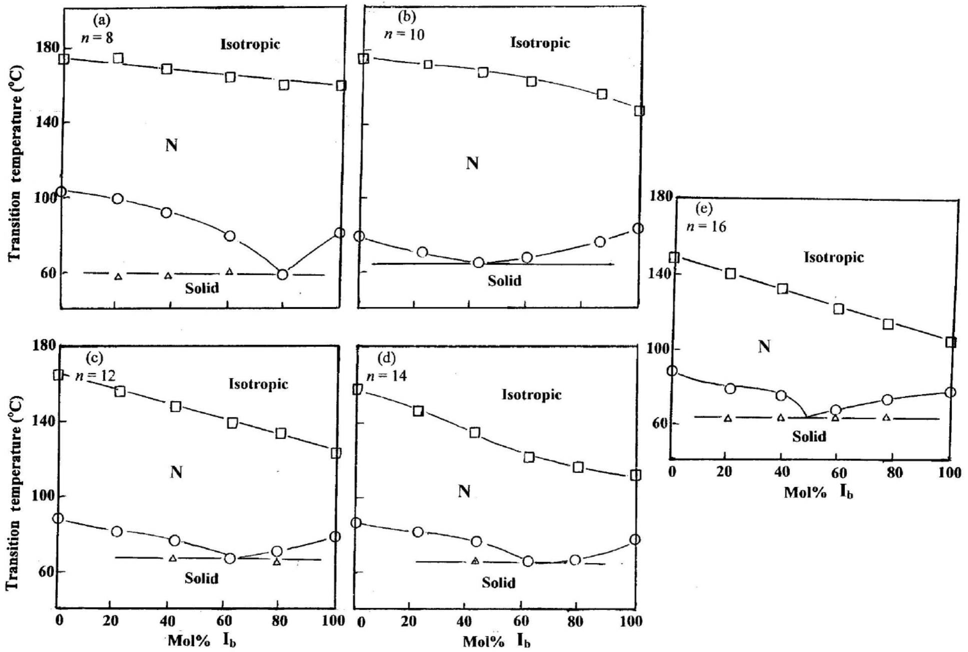


Figure 5. Binary phase diagrams of the corresponding isomers from the two methyl–substituted homologous series **I***n*$_b$ and **II***n*$_b$. Note: ○ denotes solid–mesophase transition (T_m), □ denotes mesophase–isotrophic transition and Δ denotes eutectic temperature.

all homologues of **I**$_d$ are non-mesomorphic while those of **II**$_d$ are monotropically nematogenic, the phase diagrams constructed for these systems resemble those of the terminally unsubstituted systems **I***n*$_c$/**II***n*$_c$ but to differing extents. Substitution with the electron-withdrawing chlorine atom enhances the nematic phase stability as well as the nematic range for Group **I** homologues, whereas those of Group **II** are all hidden. The addition of the isomer **II**$_c$ to the isomer **I**$_d$ disturbs its nematic arrangement and prevents the appearance

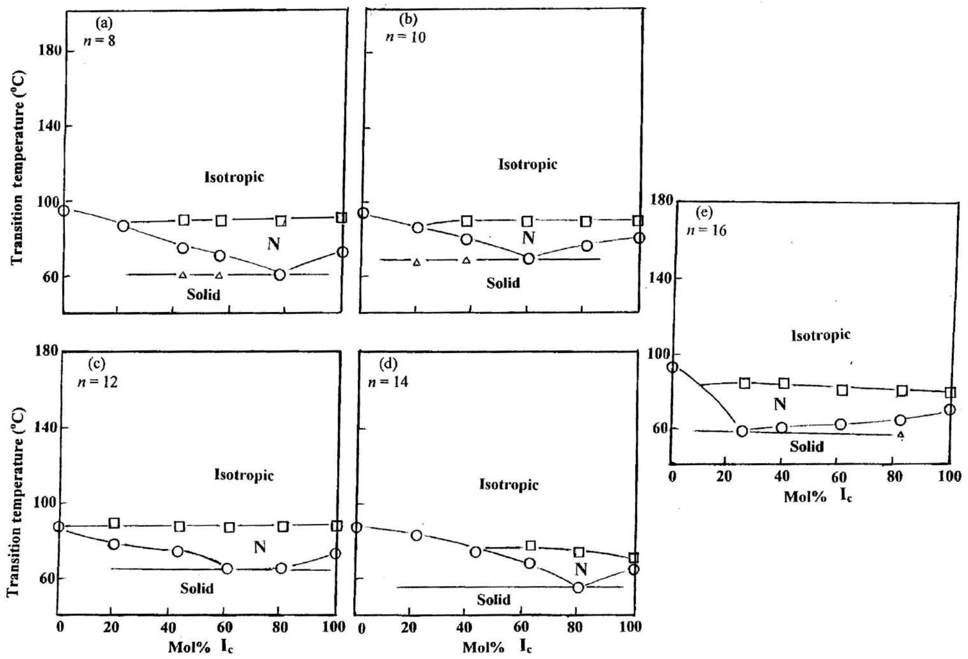


Figure 6. Binary phase diagrams of the corresponding isomers from the two terminally unsubstituted homologous series **I***n*$_c$ and **II***n*$_c$. Note: ○ denotes solid–mesophase transition (T$_m$), □ denotes mesophase–isotrophic transition and Δ denotes eutectic temperature.

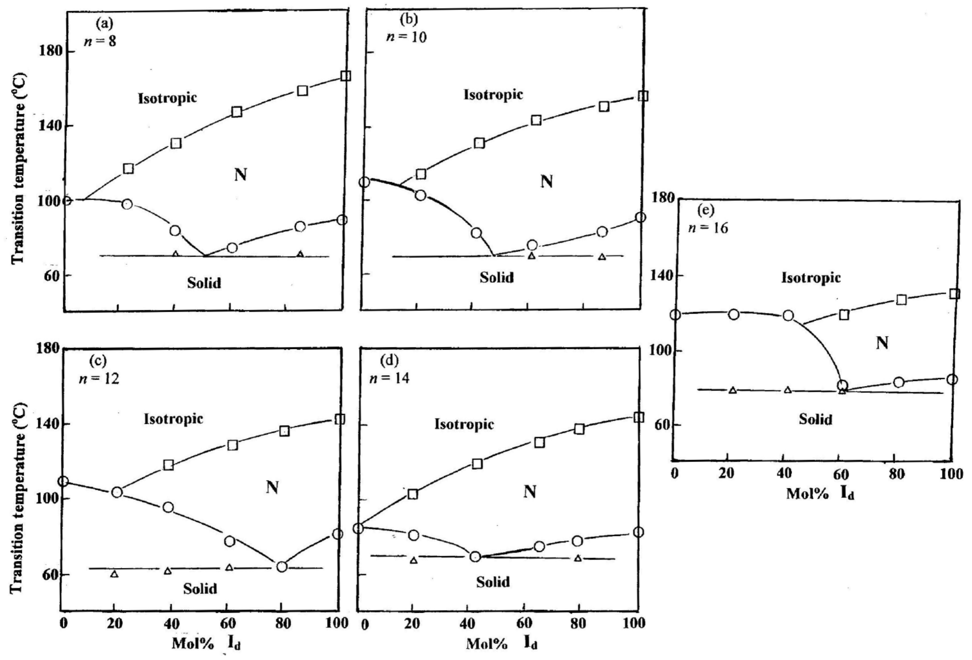


Figure 7. Binary phase diagrams of the corresponding isomers from the two chloro-substituted homologous series **I***n*$_d$ and **II***n*$_d$. Note: ○ denotes solid–mesophase transition (T$_m$), □ denotes mesophase–isotrophic transition and Δ denotes eutectic temperature.

of the nematic phase on heating by the addition of an amount of **II**$_d$ that varies irregularly with higher homologues. Such an amount of **II***n*$_d$ decreases with chain length in the order: 14 > 8 > 10 > 12 > 16 carbons.

3.2.4 Binary mixtures of nitro-substituted isomers **I***n*$_e$/**II***n*$_e$

Since the nitro group is the highest polar group under investigation, one would expect it to enhance the stability

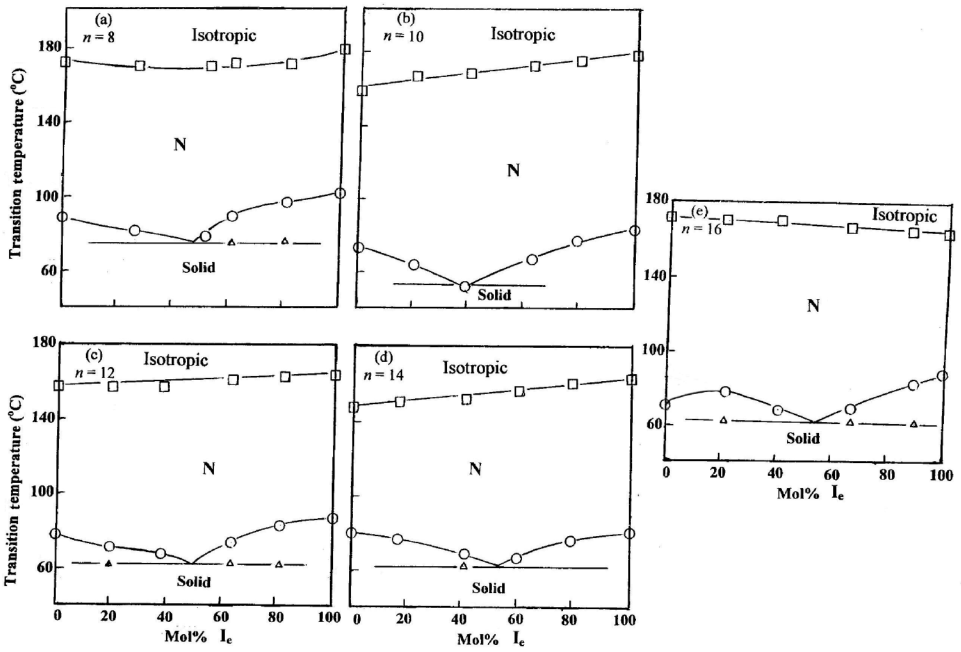


Figure 8. Binary phase diagrams of the corresponding isomers from the two nitro-substituted homologous series **I***n*$_e$ and **II***n*$_e$. Note: ○ denotes solid–mesophase transition (T_m), □ denotes mesophase–isotrophic transition and Δ denotes eutectic temperature.

(T_C) and temperature range ($\Delta T = T_C - T_m$) of the mesophase to greater extent. This was found to be the case, i.e. both isomers **I***n*$_e$ and **II***n*$_e$ exhibit a wide nematic range with high nematic stability (see Figures 1(e) and 2(e), respectively). Accordingly, the binary mixtures of each pair of isomers, as given in Figure 8, showed a relatively stable nematic phase with wide temperature range and which covers the whole range of composition. Figure 8 revealed that compatible nematic arrangements were exhibited by both isomers as evidenced by the linear, or nearly linear, T_C–composition dependency. Their mixed solids exhibit eutectic behaviour in which eutectic nematic ranges decrease with chain length (*n*) in the order: $10 > 16 > 12 > 8 \approx 14$ carbons; their nematic stability decreases in the order: $8 > 10 \approx 16 > 12 > 14$ carbons.

3.3 Clearing temperature and polarisability anisotropy of the C_{ar}–X bonds

The relationship between the stability of the mesophase, expressed as the clearing temperature, T_C, and the anisotropy of polarisability ($\Delta\alpha_X$) of bonds to small compact terminal substituent (C_{ar}–X) was studied by van der Veen [14]. The relationship has the form:

$$T_C \propto (\Delta\alpha_M + \Delta\alpha_X)^2 \qquad (1)$$

where T_C is measured in Kelvin. The term $\Delta\alpha_M$ is the anisotropy of the polarisability for all the molecular structure except the terminal substituent, X. Equation (1) can be put in the form [15]:

$$\sqrt{T_C} \propto (\Delta\alpha_M + \Delta\alpha_X) = a.\Delta\alpha_M + a.\Delta\alpha_X \qquad (2)$$

where '*a*' is the proportionality constant. Thus, if $\sqrt{T_C}$ is plotted against $\Delta\alpha_X$ for any series of liquid crystalline compounds, a straight line is expected, the slope of which equals '*a*' and intercept equals '$a.\Delta\alpha_M$'. Consequently, $\Delta\alpha_M$ will be given by: $\Delta\alpha_M$ = intercept/slope.

The $\sqrt{T_C}$ values are plotted as a function of $\Delta\alpha_X$ for series **I** and **II** in Figures 9 and 10, respectively. As shown in Figure 9, acceptable linear correlations were obtained for group **I** compounds whereby the slopes and intercepts, and consequently $\Delta\alpha_M$, were calculated by the method of least squares; the results of computation are given in Table 3.

Table 4 collects the $\Delta\alpha_M$ values of corresponding analogues of groups **I** and the laterally neat group **III** for the sake of comparison. Such a comparison reveals that the introduction of a lateral methyl group into the central benzene ring in position-2 with respect to the ester group enhances the polarisability of the ester group by positive inductive effect (+I) and consequently the polarisability anisotropy of the whole molecular structure except the substituent X, $\Delta\alpha_M$. This is evident from the greater $\Delta\alpha_M$ values for group **I** compounds compared with those of group **III**.

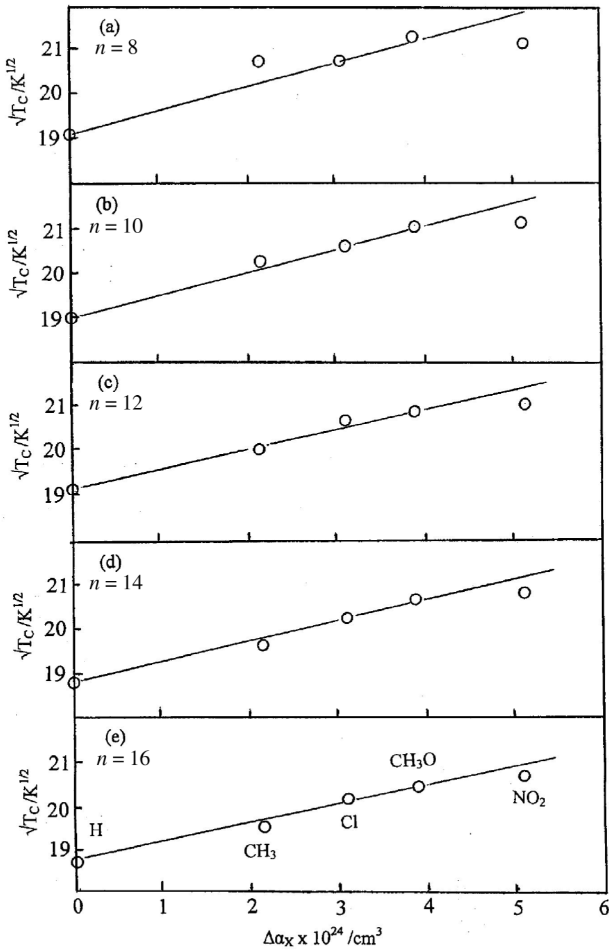


Figure 9. Dependence of the mesophase stability ($T_C^{1/2}$) on the polarisability anisotropy ($\Delta\alpha_X$) of the substituent (X) of the analogues of Group **I**.

With respect to group **II** compounds, as illustrated in Figure 10, the stability of their nematic mesophases were found to decrease slightly and in an irregular fashion with the increase of the polarisability anisotropy of the C_{ar}–X bonds. This means that the introduction of the lateral methyl group, this time into the position-3, results as concluded before in a disturbance of the nematic arrangement irrespective of the polarity of the whole molecule. The disturbance is so great that the nematic phase of the terminally unsubstituted and the chlorosubstituted homologues are only monotropic.

4. Conclusions

Two groups (**I** and **II**) of laterally methyl-substituted arylazophenyl-4-alkoxy benzoates were prepared and characterised for their mesophase behaviour. The difference between these two groups of compounds lies in the spatial orientation of the lateral methyl group. Two types of terminal substituents were used, namely, a small compact polar group, X, and an alkoxy group with varying chain length. In the first group of compounds, **I**, the methyl group is introduced into the

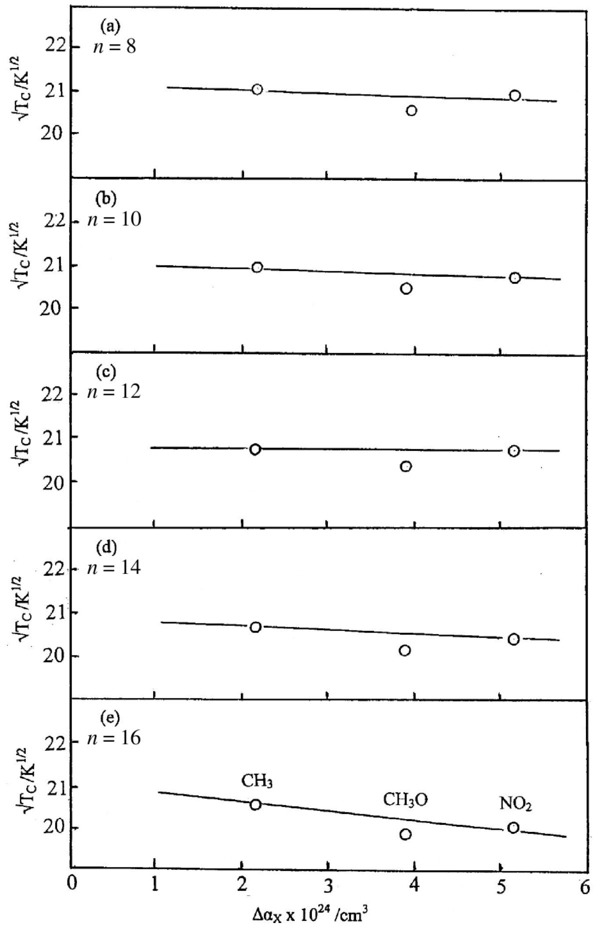


Figure 10. Dependence of the mesophase stability ($T_C^{1/2}$) on the polarisability anisotropy ($\Delta\alpha_X$) of the substituent (X) of the analogues of Group **II**.

Table 3. Slopes and intercepts of regression lines and $\Delta\alpha_M$ (in cm^3) for series **I***8*–**I***16*.

Series	*n*	Slope (× 10^{-23})	Intercept ($K^{1/2}$)	$\Delta\alpha_M$ x 10^{23}
I*8*	8	5.40	19.05	3.53
I*10*	10	4.70	19.0	4.02
I*12*	12	4.24	18.98	4.48
I*14*	14	5.10	18.52	3.66
I*16*	16	4.19	18.7	4.46

Table 4. Polarisability anisotropy, $\Delta\alpha_M \times 10^{23}$ cm^3, of series **I** and **III** [1] as a function of alkoxy chain length.

Series	$n = 8$	$n = 10$	$n = 12$	$n = 14$	$n = 16$
I*n*	3.53	4.02	4.48	3.66	4.46
II*n*	3.65	3.63	3.48	3.32	3.16

central benzene ring in position-2 with respect to the ester group, while in group **II** it is located in position-3. Binary mixtures were independently prepared for all corresponding isomers from the two series, covering the whole range of concentration, and similarly characterised and their binary phase diagrams constructed. The study revealed the following:

- All members of the first group (**I**$n_{\text{a–e}}$), irrespective of the polarity of the terminal substituent X or the length of the alkoxy group, were found to be purely nematogenic but of little stability compared with their laterally neat analogues. This means that the orientation of the lateral methyl group, as well as its electronic interaction with the remainder of the molecule, still maintain the mesophase stability.
- With respect to compounds of group **II**, it seems that the orientation of the methyl group is not in favour of mesophase formation so that it destabilises the nematic phase to the extent that all the terminally unsubstituted and chloro-substituted homologues are only monotropic.
- Extension of the terminal alkoxy chain gives rise to a decrease in the nematic–isotropic transition temperatures, suggesting that its effect becomes dominant over polarity variation.
- It was found that $\sqrt{T_C}$ for group **I** increases linearly with the polarisability anisotropy, $\Delta\alpha_X$, of the C_{ar}–X bond for all homologous series investigated. Conversely, for group **II**, $\sqrt{T_C}$ was found to decrease slightly and irregularly with $\Delta\alpha_X$, suggesting that the spatial orientation of the lateral methyl group plays an important role in the stability of the nematic phase.
- Irrespective of the alkoxy chain length or the polarity of the substituent X, all binary mixtures proved to exhibit the nematic phase.

References

[1] Nessim, R.I.; Naoum, M.M.; Mohamed, S.Z.; Nessim, M.I. *Liq. Cryst.* **2004**, *31*, 649–654.
[2] Nessim, R.I.; Naoum, M.M.; Nessim, M.I. *Liq. Cryst.* **2005**, *32*, 867–876.
[3] Mohammady, S.Z.; Nessim, R.I.; Shehab, O.R.; Naoum, M.M. *Liq. Cryst.* **2005**, *32*, 477–482.
[4] Mohammady, S.Z.; Nessim, R.I.; Shehab, O.R.; Naoum, M.M. *Mol. Cryst. Liq. Cryst.* **2006**, *451*, 53–64.
[5] Mohammady, S.Z.; Nessim, R.I.; Shehab, O.R.; Naoum, M.M. *Thermochim. Acta* **2006**, *449*, 61–66.
[6] Nessim, R.I. *Thermochim. Acta* **2005**, *439*, 142–150.
[7] Kato, T. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 513–514.
[8] Buckingham, J.B.; Macdonald, F. *Dictionary of Organic Compounds*, 6th ed., Suppl. 2; Chapman & Hall: London, 1997.
[9] Cammenga, H.K.; Eysel, W.; Gmelin, E.; Hemmiger, W.; Hoehne, G.W.H.; Sagre, S.M. *Thermochim. Acta* **1993**, *219*, 333–342.
[10] Naoum, M.M.; Saad, G.R.; Nessim, R.I.; Selger, H.; Abdel Aziz, T.A. *Liq. Cryst.* **1997**, *23*, 789–795.
[11] Saad, G.R.; Nessim, R.I. *Liq. Cryst.* **1999**, *26*, 629–636.
[12] Gray, G.W. *Molecular Structure and the Properties of Liquid Crystals*; London: Academic Press, 1962; pp 132, 174.
[13] Gray, G.W. In *The Molecular Physics of Liquid Crystals*: Luckhurst, G.R., Gray, G.W., Eds.; Academic Press: London, 1979; Chapters 1 & 2.
[14] Van der Veen, J. *J. Phys., Colloque C1* **1975**, *36*, 375–377.
[15] Naoum, M.M.; Saad, G.R.; Nessim, R.I.; Abdel Aziz, T.A. *Liq. Cryst.* **1998**, *25*, 73–83.