

Thermal behavior of binary mixtures of isomers of different molecular structures and different lateral substituent positions

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Abstract Binary systems comprising two laterally substituted azo/ester isomers, namely 2- (or 3-) methyl-(or fluoro-) substituted phenyl 4'-(4"-alkoxy phenylazo) benzoates (In_{a-d}), were thermally investigated by differential scanning calorimetry (DSC) and the phases identified by polarized light microscopy (PLM). The phase diagrams constructed were made from isomeric components that differ in the relative positions of the lateral substituent attached to the individual components. Another binary phase diagram was formed from the 3-fluoro phenyl-4'-(4"alkoxyphenylazo) benzoates (In_d) and their isomers 4-(3fluorophenylazo)-phenyl-4'-alkoxybenzoates ($\mathbf{II}n$). The latter two components differ from each other in the location inversion of the ester group, as well as in the exchange of the terminal substituents. For mixtures In_a/In_b , the CH₃ group distributed SmA arrangement. In the mixtures of the two structurally different isomers, In_d/IIn , the addition of one component to the other resulted in a pronounced decrease in the stability of all mesophases.

Keywords 2-Substituted phenyl 4'-(4''-alkoxy phenylazo)benzoates \cdot 3-Substituted phenyl 4'-(4''-alkoxy phenylazo)benzoates \cdot Phase transitions \cdot Binary phase diagrams

Introduction

It is already known that materials maintain the liquid crystalline property over a wide range of temperatures that can be used in various electro-optical applications, such as liquid–

H. A. Ahmed hadyelrahman@yahoo.com crystal displays, optical switch, filter, magnetic fluid films; the mesomorphic properties of liquid crystals are largely affected by the change in their molecular structure [1]. Mesophase characteristics of mesogens may be greatly modified upon the mixing of individual components. Many series of dimeric liquid crystals have been reported [2-5], and all of these compounds may be termed symmetric, with identical mesogenic moieties, or nonsymmetric dimers, with different mesogenic units. In both the cases, the specific interactions between the two mesogenic groups do lead to a significant variation in the mesophase behavior of such materials [2-5]. Earlier studies [6-16] have shown the emergence of the mesophase upon mixing the compounds where none, one, or both components of the mixture are mesogens. Generally, it has been reported that the central linkages and the terminal groups play important roles in the formation, type, thermal stability, and temperature range of the mesophase of the liquid crystalline compound [17–19]. Azobenzene group represents very comfortable fragments to design and synthesize new structures, giving stable mesophases often with very interesting polymorphism [20-23]. Liquid crystalline materials containing an azo group [24] in the mesomeric core are attractive with regard to studying their optical property. The ester group is commonly used, since it offers the advantage such as stability over other linking groups. On the other hand, the physical properties of a mesogen are strongly influenced when a lateral group is appended to a mesogenic core. From the steric point of view, a lateral substituent effectively widens the core and increases the intermolecular separation. This leads to a reduction in the lateral interactions [25], and consequently, the mesophase stability is reduced. Generally, both lateral substitution and mixing two or more individual components decrease the thermal stability of both solid and mesophases [6–9, 15, 26]. The binary mixtures of mesogens have provided better

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formulations for applications in different field [27], so the study of mixtures of liquid crystalline compounds is a subject of considerable interest.

One way to achieve low melting point 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 [28–30] This is because under such condition, the mesophase-to-isotropic line is usually straight or slightly enhanced, and the temperature range of the mesophase is consequently greater for the eutectic mixture than for either pure component.

Based on the types of the two components used, one can formulate different types of binary mixtures of components of close molecular formulae except the difference in polarity and/or position of the lateral substituent, X. The aim of the present work was to investigate the mesophase behavior of two types of binary mixtures made from the previously prepared [31, 32] two isomeric series 2- (or 3-) methyl-(or fluoro-) substituted phenyl 4'-(4"-alkoxy phenylazo) benzoates, In_{a-d} , and 4-(3-fluorophenylazo)phenyl-4'-alkoxybenzoates, IIn, which differ from each other in the location inversion of the ester group, as well as in the exchange of the position of terminal substituents, where n is the number of carbon atoms in the compound. The first type of mixtures is made from two positional isomers, e.g., In_a and In_b ; both components of the mixture bear alkoxy groups of the same chain length. The second type of mixtures will be made from the components one from the homologous series In_d and the other from series IIn; in this case, the components of the mixture differ from each other in the relative position of the terminal alkoxy chain, as well as in the inversion of COO- group. In this case, the two series of components represent extremes in conjugative interactions between the terminal alkoxy group and the ester moiety. Such mixtures aim to achieve a reasonable balance between improving mesomorphic properties and retaining advantageous physical properties of the laterally similarly substituted components.



In order to investigate the mesophase behavior in mixed systems, it is enough to investigate binary mixtures of isomeric components that bear alkoxy chain of the same length, but differ in the relative positions of the lateral substituent attached to the individual components. This still leads to a great number of phase diagrams, so it seems reasonable to investigate, as examples, the mixtures with isomeric components bearing the same alkoxy chain lengths, namely $I6_a/I6_b$, $I12_a/I12_b$, $I6_c/I6_d$, and $I12_c/I12_d$ for first type of mixtures and $I8_d/II8$, $I12_d/II12$ for the second type of mixtures.

Experimental

Chemicals used were of very pure grades. Ethyl-4-amino benzoate (Aldrich (Wisconsin, USA), 99 %) and substituted phenols (99 %), 1-bromo-n-alkane (98 %), dicyclohexylcarbodiimide (DCC, 99 %), and 4-(dimethylamino) pyridine (DMAP, 98 %) were purchased from the following companies: Fluka, Buchs, Switzerland; MP Biomedicals, Inc., Illkirch, France; BDH, Poole, England; Aldrich, Wisconsin, USA; and E. Merck, Darmstadt, Germany.

Preparation of materials

Compounds discussed in this paper, In_{a-d} and IIn, were prepared by the methods previously described [31, 32], according to the following Schemes 1 and 2.

Preparation of ethyl-4-hydroxyphenylazo benzoate (A)

Ethyl-4-amino benzoate (0.01 mol) was dissolved in concentrated hydrochloric acid and cooled in ice-salt bath to 0 °C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.03 mol) was added dropwise with stirring. During the addition, the temperature did not exceed 2 °C. After the complete addition, the cold mixture was added dropwise to an ice-cold solution of phenol (0.01 mol) in sodium hydroxide (0.03 mol). The mixture was further stirred by magnetic stirrer at 0 °C for one hour and then acidified with dilute hydrochloric acid. The solid separated was filtered and crystallized twice from ethanol. The product was of thin-layer chromatography (TLC) pure and gave melting point 163 °C that agreed with that reported in the literature [33].

Preparation of ethyl 4-n-alkoxy phenylazo benzoates (Bn)

Ethyl-4-hydroxyphenylazo benzoate (0.001 mol) was dissolved in alcoholic KOH (0.02 mol) to which the appropriate amount of 1-bromo-n-alkane (0.0012 mol) was added dropwise while stirring. Stirring was continued at Scheme 1 Steps for the preparation of compounds In_{a-d}



In_{a-d}

a, X = 2–CH₃; b, X = 3–CH₃; c, X = 2–F; d, X = 3–F





room temperature (25 °C) for 2 days. The solid separated was filtered off, the solution evaporated, and the residue crystallized twice from ethanol. The products were of TLC pure and give transition temperatures as given in the literature [34].

Preparation of 4-n-alkoxy phenylazo benzoic acids (An)

The esters (Bn) were hydrolyzed to the corresponding acids by refluxing in aqueous ethanolic potassium hydroxide for 24 h and then acidified by dilute HCl to give the corresponding acids. Again, the products were crystallized twice from ethanol to give TLC pure solids that give transition temperatures agreed with those reported in the literature [35].

Preparation of 2-(or 3-)-substituted phenyl-4'-nalkoxyphenylazo benzoates (In_{a-d})

Molar equivalents of 4-n-alkoxy phenylazo benzoic acid (An) and 2-(or 3-)-substituted phenol (0.001 mol each) were dissolved in 25 mL of dry methylene chloride. To the resulting mixture, dicyclohexylcarbodiimide (DCC, 0.002 mol) and few crystals of 4-(dimethylamino) pyridine

Comp No.	$T_{ m Cr-A}$	$T_{ m Cr-C}$	$T_{ m Cr-N}$	$T_{ m A-N}$	T _{A-I}	T _{C-I}	T _{N-I}
I 6 _a	_	_	117 (91.8)	-	_	_	139 (4.1)
$\mathbf{I}6_b$	92 (89.5)	_	-	110 (2.9)	_	_	162 (1.4)
$\mathbf{I}6_c$	90 (52.7)	_	_	110 (1.5)	_	_	146 (5.3)
$\mathbf{I}6_d$	108 (43.8)	_	_	117 (0.9)	_	_	154 (8.3)
$\mathbf{I} \mathcal{B}_d$	104 (20.3)	_	_	124 (1.9)	_	_	136 (4.9)
$\mathbf{I}/2_a$	109 (85.6)	_	_	_	132 (2.6)	_	-
$\mathbf{I}/2_b$	100 (64.2)	_	_	_	114 (2.68)	_	-
$\mathbf{I}/2_{c}$	97 (49.6)	_	_	_	118 (6.5)	_	-
$\mathbf{I}/2_d$	113 (22.1)	_	_	_	130 (6.5)	_	-
H 8	_	98 (35.8)	_	_	_	124 (1.8)	-
II 12	_	93 (42.1)	-	_	_	132 (6.1)	-

 Table 1
 Transition temperatures (°C) and (transition enthalpy, kJ/mol) of compounds, In_{a-d} [31] and IIn [32]

Cr-A denotes the transition from solid to the SmA phase. Cr-C denotes the transition from solid to the SmC phase. Cr-N denotes the transition from solid to the N phase. A-N denotes the transition from SmA to the N phase. A-I denotes the transition from SmA to the isotropic phase. C-I denotes the transition from SmC to the isotropic phase. N-I denotes the transition from nematic to the isotropic phase

Fig. 1 Binary phase diagrams of corresponding isomers for different lateral methylsubstituted analogues a $I6_a/I6_b$ and b $I/2_a/I/2_b$; the symbol *open circle* denotes solid-tomesophase, *filled diamond* SmA-to-N, *open square* mesophase-to-isotropic transition, and "..." eutectic temperature. *SmA* smectic A phase; *N* nematic phase



(DMAP), as a catalyst, were added and the mixture was stirred at room temperature (25 $^{\circ}$ C) for 3 days. The solvent was distilled off and the residue crystallized twice from ethanol.

Preparation of 4-(3'-fluoro phenylazo)-phenol (**B**)

One molar equivalent of the 3-fluoro aniline in ice-cold dilute hydrochloric acid is diazotized with cold sodium nitrite solution and then added slowly to a cold phe-nol/sodium hydroxide solution (1:1). The solid product obtained was filtered and recrystallized twice from glacial acetic acid to give a TLC pure compound. The melting points of the prepared azo dyes were in a good agreement with those reported in the literature [36].

Preparation of 4-(3-fluorophenylazo)-phenyl-4'alkoxybenzoates, **II**n

Molar equivalents of the 4-(3'-fluoro phenylazo)-phenol (**B**) and 4-n-alkoxybenzoic acid were dissolved in dry methylene chloride. To the resulting solution, 2 molar equivalents of dicyclohexylcarbodiimide (DCC) and few crystals of 4-(dimethylamino)-pyridine (DMAP), as a catalyst, were added and the solution was left to stand for 72 h at room temperature (25 °C) with stirring. The solid separated was then filtered off and the solution evaporated. The obtained solid residue was recrystallized twice from acetic acid and twice from ethanol to give TLC pure products.

The resulting compounds were of thin-layer chromatography (TLC) pure and exhibited phase transition temperatures agreed with those reported previously [31, 32].

Binary mixtures were prepared by mixing accurately weighed samples of the appropriate amounts of the individual components, melting them together (at ≈ 150 °C) to give an intimate mixture (± 1 % in composition), and then cooled to room temperature (25 °C) while stirring.

Physical characterization

Calorimetric measurements were carried out using a differential scanning calorimeter, PL–DSC, of Polymer Laboratories, England. The instrument was calibrated for temperature, heat, and heat flow according to the method recommended by Cammenga, et al. [37]. DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All measurements were achieved at a heating rate of 10 °C min⁻¹ in inert atmosphere of nitrogen gas (10 mL min⁻¹). All weighed samples were made using an ultra-microbalance, England, with accuracy ± 0.0001 .

Transition temperatures were checked and the types of mesophase identified for all compounds prepared and their mixtures with a standard polarized light microscope PLM (Wild, Germany) attached to a homemade hot-stage. The temperature is measured by thermocouple attached to a Brookfield temperature controller, England. Measurements were made twice and the results have standard uncertainty in transition temperature within ± 0.2 °C. Transition temperatures obtained for all prepared blends, as measured by both DSC and PLM, were found to be within 2–3 °C.

The purity of samples prepared were checked with thinlayer chromatography using TLC sheets coated with silica gel (E. Merck), whereby spots were detected by a UV lamp.

Fig. 2 Binary phase diagrams of corresponding isomers different lateral fluoro-substituted analogues **a** I_{c}/I_{d_d} and **b** $I/2_c/I/2_d$; the symbol *open circle* denotes solid-to-SmA, *filled diamond* SmA-to-N, *open square* mesophase-to-isotropic transition, and "..." eutectic temperature. *SmA* smectic A phase, *N* nematic phase

Results and discussion

Mesophase behavior of pure components

In our previous study [31, 32], transition temperatures, measured as the first heating by DSC and PLM, as given in Table 1, revealed that in the group I_{a-d} only I_{a} is purely nematogenic, while the remaining analogues I_{b-d} are dimorphic showing smectic A (SmA) and nematic phases. Conversely, all members of group $I/2_{a-d}$ are purely smectogenic possessing the SmA phase. On the other hand, all homologues of the other series, $\mathbf{II}n$, are purely smectogenic exhibiting smectic C (SmC) phase. Generally, the mesophase stability is augmented by an increase in the polarity and/or polarizability of the mesogenic part of the molecule. It was found that [31], when comparison is made between the differently substituted positional isomers within the series In_{a-d} , the stability and types of the mesophase produced are dependent on two factors. First, the dipole moment of the mesogenic portion of the molecule is affected remarkably, dependent on the position to which the polar group is introduced. The second factor is a steric one that varies according to the size and position of the substituent.

Binary mixtures of positional isomers

All phase diagrams of binary mixtures are constructed from experimental data; Fig. 1 shows two examples of binary mixtures of two laterally methyl-substituted positional isomers, where the mixtures are formed once from the two corresponding lower homologues $I6_a/I6_b$ and another from their higher homologues $I/2_a/I12_b$. As can



Fig. 3 Binary phase diagrams of two structurally different isomers a $I8_d/II8$ and b $I12_d/II12$; the symbol open circle denotes solid-to-mesophase, open triangle SmC-to-SmA, filled diamond SmA-to-N, open square mesophase-to-isotropic transition, and "..." eutectic temperature. SmA smectic A phase, SmC smectic C phase; N nematic phase





Fig. 4 DSC curves for mixture compositions a $I12_a/I12_b$ (80 mol% of $I12_a$) and b $I8_d/II8$ (89 mol% of II8): (1) first heating cycle and (2) first cooling one

be seen from Fig. 1a, the addition of the 2-CH₃-substituted analogue ($I6_a$) to its 3-CH₃-substituted isomer ($I6_b$), both bearing similar alkoxy chain length, resulted in a

reasonable decrease in the melting temperature. The eutectic mixture (52 mol% of $I6_a$) of this system ($I6_a/I6_b$) exhibits a wide nematic temperature range, 59.0 °C. With respect to the nematic dependence on composition, it can be observed from Fig. 1a that the nematic stability varies regularly with composition. This behavior reveals that ideal nematic arrangements are exhibited by molecules of the two isomeric components, as confirmed by the nearly linear dependency of T_{N-I} on composition. On the other hand, the addition of about 52 mol% of $I6_a$ to $I6_b$ completely destroys the SmA phase of the dimorphic isomer $I6_b$.

In the binary phase diagram of the corresponding higher homologues, $II2_a/II2_b$ (Fig. 1b), the SmA mesophase is observed to cover the whole composition range. The eutectic composition at 52 mol% of $II2_a$ exhibits a SmA phase with a temperature range (≈ 21 °C). Although both components possessed the potential for mesophase formation, the addition of the component $II2_a$ to its isomer $II2_b$ resulted in a notable decrease from the linearity dependence. This behavior reveals that the CH₃ steric effect in different positional isomers on the SmA arrangement leads them to disrupt to some extent the SmA phase of each other upon addition.

Two examples of the binary phase diagrams of two fluoro homologues In_c/In_d ($I\delta_c/I\delta_d$ and $I/2_c/I/2_d$) are represented graphically in Fig. 2. Examining these diagrams revealed that the addition of one positional isomer to the other is accompanied by a wide temperature range as a result of melting point depression at the eutectic composition. In both binary systems, linear dependences were observed for the N and SmA mesophases. This behavior may be attributed to the negligible steric effect of the small fluorine atom.



Fig. 5 Polarized optical micrographs images of $I6_a/I6_b$, 33 mol% of $I6_a$, **a** SmA phase at 93 °C, **b** nematic phase at 140 °C, $I/2_d/II/2$, 45 mol% of II/2, **c** SmA phase at 110 °C, and $I8_d/II8$, 89 mol% of II8, **d** SmC phase at 113 °C

Binary mixtures of structurally different isomers

Based on the types of the two components used, one can formulate a second type of binary mixture of two isomeric components that differ from each other in the position of the terminal groups (F and RO), as well as in the inversion of the ester COO-group. Thus, both mixtures are formed between 3-fluoro phenyl-4'-(4"-alkoxy phenylazo) benzoates (In_d) and their isomers 4-(3-fluoro phenylazo)-phenyl-4'-alkoxybenzoates (IIn), n = 8 and 12 carbons. Transition temperatures and transition enthalpies of compounds In_{a-d} [31] and IIn [32] are collected in Table 1. As can be seen from Table 1, the homologues (II8 and II12) are purely smectogenic exhibiting a wide SmC temperature range. With respect to the other components ($I8_d$ and $I12_d$), the lower homologue is dimorphic possessing SmA and nematic mesophases, while the higher one, $I12_d$, is purely smectogenic exhibiting only the SmA phase. Figure 3 collects the phase diagrams constructed for the resulting two binary systems, $I8_d/II8$ and its homologous system $I12_d/$ II12. As can be seen from Fig. 3, the addition of one component to the other resulted in a decrease in the stability of both mesophases (SmA, N, or SmC). Also shown from Fig. 3, the binary systems, In_d/IIn , exhibit eutectic compositions dependent upon the alkoxy chain length, but both eutectics melt at relatively low temperature, ≈ 70 °C.

Figure 4 presents, as examples, the DSC curves of the mixture compositions $I12_a/I12_b$ (80 mol% of $I12_a$) and $I8_d/I18$ (89 mol% of II8). Mixtures prepared in the present work display a pronounced thermal stability, when heated. Thus, when the samples were subjected to repeated heating/cooling cycles, the DSC profiles exhibited similar behaviors.

Representative examples of polarizing optical microscopic images of the mesophases are shown in Fig. 5. Figure 5a, b shows images of SmA phase and schlieren texture of nematic phase of the dimorphic mixture $I6_a/I6_b$ (33 mol% of $I6_a$). While mixture $I12_d/II12$ (45 mol% of II12) exhibits only SmA phase (Fig. 5c), $I8_d/II8$ (89 mol% of II8) exhibits only SmC phase (Fig. 5d).

Conclusions

Two types of binary phase diagrams were constructed; the first is made from two laterally substituted azo/ester isomers, namely 2- (or 3)-substituted phenyl 4'-(4"-alkoxy phenylazo) benzoates (In_{a-d}). The second is formed between 3-fluoro phenyl-4'-(4"-alkoxy phenylazo) benzoates (In_d) and their isomers 4-(3-fluoro phenylazo)-phenyl-4'-alkoxybenzoates (IIn).

Examining these diagrams revealed that:

- For (n = 12), the CH₃ groups in the different positional isomers affect sterically the SmA arrangement in the mixture (In_a/In_b), thus disrupting, to some extent, the SmA phase of each other upon mixing.
- In mixtures of the fluoro-substituted isomers (In_c/In_d), linear composition dependences were observed for both the N and SmA mesophases. This behavior is attributed to the negligible steric effect of the small fluorine atom.
- For mixtures of the structurally different isomers, In_d/ IIn, the addition of one component to the other resulted in a decrease in the stability of all mesophases (SmA, N, or SmC). Their eutectic compositions vary with the alkoxy chain length.

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