



## Molecular Crystals and Liquid Crystals

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M. M. Naoum<sup>a</sup>, A. A. Fahmi<sup>a</sup> & M. A. Alaasar<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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## Supramolecular Hydrogen-Bonded Liquid Crystals Formed from 4-(4'-Pyridylazophenyl)-4''-Substituted Benzoates and 4-Alkoxybenzoic Acids

M. M. Naoum, A. A. Fahmi, and M. A. Alaasar

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

*Phase diagrams of the binary mixtures of the title compounds were constructed to investigate the effect of different polar substituents, on the pyridine-based derivatives, as well as the alkoxy-chain length, on the acids, on the extent and stability of the supramolecular liquid crystal phases induced by intermolecular hydrogen bonding. None of the newly prepared pyridine-based derivatives is mesomorphic, but the hydrogen-bonded complexes are. The mixtures prepared were characterized for their mesophase behavior by differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Five pyridine-based derivatives (**Ia-e**), with molecular formula  $X-C_6H_4COOC_6H_4-N=N-C_5H_4N$ , were prepared that differ from each other by the substituent X. The latter varies between  $CH_3O$ ,  $CH_3$ , H, Br, and  $NO_2$ . Four 4-alkoxybenzoic acids ( $C_nH_{2n+1}OC_6H_4COOH$ , **II10–II18**) were used; the number of carbons (n) of their alkoxy groups varies between 10, 12, 14, and 18. Smectic C mesophase is induced in most of the binary mixtures investigated.*

**Keywords:** 4-alkoxybenzoic acids; 4-(4'-pyridylazophenyl)-4''-substituted benzoates; binary mixtures; supramolecular LCs

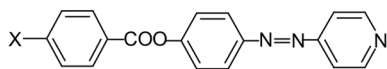
## INTRODUCTION

The role of hydrogen-bonding interaction in molecular recognition and self-assembly of liquid crystalline phases has been investigated in recent years and significant work has been conducted [1,2]. Rigid rod-shaped anisotropic molecules, appropriately functionalized by recognizable moieties, interact in the melt or in solution and lead to the formation of supramolecular complexes that may exhibit

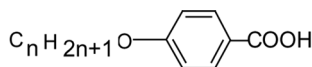
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Address correspondence to M. M. Naoum, Department of Chemistry, Faculty of Science Cairo University, P.O. Box 12613, Giza, Egypt. E-mail: magdinaoum@yahoo.co.uk

thermotropic liquid crystalline character. A number of supramolecular mesogenic materials have been induced by self-assembly through hydrogen bonding [2]. Following the first and well-established examples of liquid crystal formation [3] through the dimerization of aromatic carboxylic acids, several classes of compounds have been prepared by the interaction of complementary molecules, the liquid crystalline behavior of which is appreciably dependent on the structure of the resulting supramolecular system. Kato and Frechet [4] expanded the latter concept to include mixtures of 4-alkoxybenzoic acids and pyridine based compounds. A single hydrogen bond between the carboxyl and pyridine moieties was found [2] to be extremely fruitful for the formation of liquid crystals. Azo dye molecules, on the other hand, are attracting attention in both academic and application areas [5–9]. The aim of the present study is to combine the pyridyl and azo moieties in one single newly prepared pyridine-based azo dye (**I**<sub>a-e</sub>) and to investigate possible molecular self-assembly through hydrogen-bonding with 4-alkoxybenzoic acids (**II**10–**II**18).

(I<sub>a-e</sub>)

**I**<sub>a</sub>, X=CH<sub>3</sub>O, **I**<sub>b</sub>, X=CH<sub>3</sub>, **I**<sub>c</sub>, X=H, **I**<sub>d</sub>, X= Br, **I**<sub>e</sub>, X=NO<sub>2</sub>

(II<sub>n</sub>)

**II**10, *n*=10, **II**12, *n*=12, **II**14, *n*=14, **II**18, *n*=18

## EXPERIMENTAL

Chemicals 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.

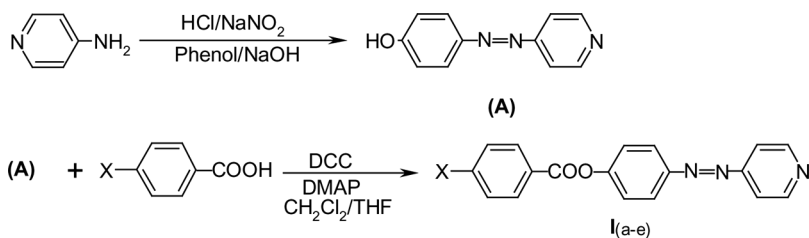
## Preparation of Materials

All benzoic acids (**II**10–**II**18) were prepared according to the methods previously described [10]. Transition temperatures of all acids, as given in Table 1, agreed with those reported before [10].

**TABLE 1** Phase Transition Temperatures (°C) of the Acids, **II10–II18**

| Compound number | <i>n</i> | <i>T</i> <sub>S-A</sub> | <i>T</i> <sub>A-N</sub> | <i>T</i> <sub>S-I</sub> | <i>T</i> <sub>N-I</sub> |
|-----------------|----------|-------------------------|-------------------------|-------------------------|-------------------------|
| <b>II10</b>     | 10       | 101                     | 122                     | –                       | 141                     |
| <b>II12</b>     | 12       | 93                      | 129                     | –                       | 137                     |
| <b>II14</b>     | 14       | 89                      | –                       | 133                     | –                       |
| <b>II18</b>     | 18       | 109                     | –                       | 126                     | –                       |

The pyridine-based azo dyes (**I<sub>a-e</sub>**) were prepared according to the following scheme:



### Preparation of 4-(4'-Pyridylazo)-phenol (A)

This was prepared according to the method described by Zhang *et al.* [11] from 4-aminopyridine and phenol. To a solution of 4.0 g (0.058 mol) of sodium nitrite in 20 ml water, 5.0 g (0.053 mol) phenol in 45 ml of 10% sodium hydroxide solution (0.1125 mol) was added with stirring while cooling both solutions to 0°C. The resulting solution was added to a cooled solution of 4-aminopyridine (6.0 g, 0.064 mol) in 25 ml (0.25 mol) concentrated hydrochloric acid and 16 ml water with stirring for 10 minutes below 0°C. Subsequently, a saturated solution of sodium carbonate was added to adjust the pH of the mixture to about 6. A yellow dye is formed which was filtered off and used for subsequent steps without purification. The yield of the crude product was 75%.

### Preparation of 4-(4'-Pyridylazophenyl)-4''-Substituted Benzoates (**I<sub>a-e</sub>**)

The azo **A** (0.60 g, 0.0027 mol) with its molar equivalent of the acid (**II**), 1.11 g (0.0054 mol) of dicyclohexyl carbodi-imide (DCC), and few crystals of the catalyst dimethylamino pyridine (DMAP), were dissolved in 100 ml (1:1) mixture of CH<sub>2</sub>Cl<sub>2</sub> and tetrahydro furan (THF); the mixture was left to stand, at room temperature with stirring, for at least 72 hrs. The solid was filtered off, washed with 20 ml CH<sub>2</sub>Cl<sub>2</sub>,

**TABLE 2** Melting Points (°C) and Melting Enthalpies of the Pyridine-Based Azo Dyes, **I<sub>a-e</sub>**

| Compound number      | X                 | <i>T<sub>m</sub></i> | $\Delta H_m$ (kJ/mol) |
|----------------------|-------------------|----------------------|-----------------------|
| <b>I<sub>a</sub></b> | CH <sub>3</sub> O | 170                  | 32.3                  |
| <b>I<sub>b</sub></b> | CH <sub>3</sub>   | 162                  | 31.5                  |
| <b>I<sub>c</sub></b> | H                 | 178                  | 20.1                  |
| <b>I<sub>d</sub></b> | Br                | 186                  | 11.3                  |
| <b>I<sub>e</sub></b> | NO <sub>2</sub>   | 205                  | 65.9                  |

and the filtrate allowed to evaporate. The residue was then soaked in methanol for 2 hrs with stirring and filtered. The solids (50% yield) obtained were found to be thin layer chromatography (TLC) pure and possess sharp melting temperatures as measured by differential scanning calorimetry (DSC) and are given in Table 2.

### Physical Characterization

Calorimetric measurements were carried out using a 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.* [12]. DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All of the thermograms have been achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and types of mesophases identified for mixtures prepared with a standard polarized light microscopy PLM (Wild, Germany) attached to a home-made hot-stage.

For phase diagrams, binary mixtures of any two complimentary components, covering the whole composition range, were prepared by melting the appropriate amounts of each component, stirring to give an intimate blend, and then cooling by stirring to room temperature. The temperatures obtained for the prepared blends, as measured by both DSC and PLM, agreed within 2–3°C. In the phase diagrams, constructed by plotting transition temperatures *versus* mixture composition, the symbol “○” denotes solid-mesophase, “□” mesophase-isotropic transitions, “●” mesophase-another mesophase, and, “▲” eutectic temperature.

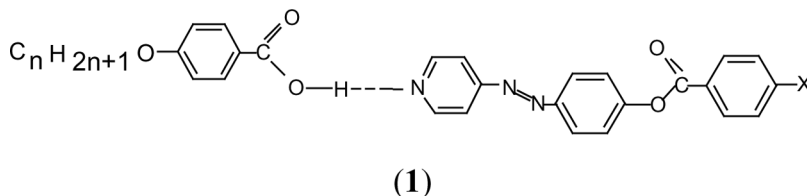
### Conformation of Molecular Structure

The molecular formulae of the newly prepared pyridine-based derivatives (**I<sub>a-e</sub>**) were conducted via elemental analyses, NMR, and mass

spectroscopy. The results were in agreement, within the permissible limits, with the proposed structures.

## RESULTS AND DISCUSSION

Generally, complementary components in a mixture employed for the formation of liquid crystals may be either mesomorphic or nonmesomorphic or both; however, novel liquid crystals can be obtained. Hydrogen bonding between the two components of the mixture leads to an elongation of the rigid-rod segment of the individual components as represented, for our investigated systems, by formula **1**.

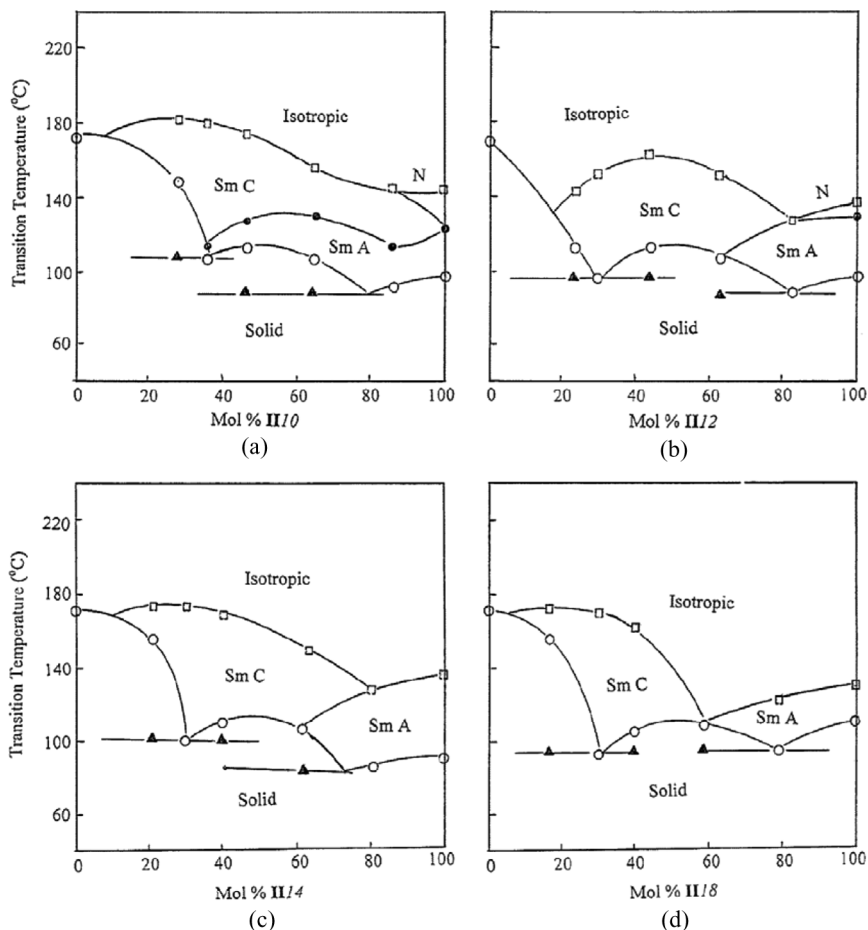


Transition temperatures of the investigated acids (**II10–II18**), as reported previously [10], are summarized in Table 1. Melting points and melting enthalpies of pyridine-based derivatives (**I<sub>a-e</sub>**) are given in Table 2. In the tables, the following symbols are used as subscripts to specify the various transition temperatures: solid (S), nematic (N), smectic A (A), smectic C (C), and isotropic (I). Transitions of solid to any liquid phase are also denoted as melting point ( $T_m$ ). It can be seen from the table that all of the pyridine-based compounds investigated are of high melting ( $T_m$ ) points, and none of them is mesomorphic.

As can be seen from Table 1, the lower homologs of the acids, **II10** and **II12**, are polymorphic that possess both nematic, N, and smectic A, Sm A, mesophases, while the higher homologs, **II14** and **II18**, are purely smectogenic possessing only SmA mesophase. This difference in behavior of the acids would definitely affect the mesophase behavior of their mixtures with the pyridine-based derivatives in a variable manner. The binary phase diagrams of the individual homologs of the acids (**II10–II18**) with the pyridine derivatives (**I<sub>a-e</sub>**) are represented graphically in Figures 1–5, respectively.

### Binary Mixtures of the Electron-Donating (CH<sub>3</sub>O or CH<sub>3</sub>) Substituted Derivatives (**I<sub>a</sub>** and **I<sub>b</sub>**) with the Four Homologs of the Acid

In hydrogen-bonded liquid crystals, phase behavior is related to the strength of the hydrogen bonds involved [13]. In the pyridine/acid

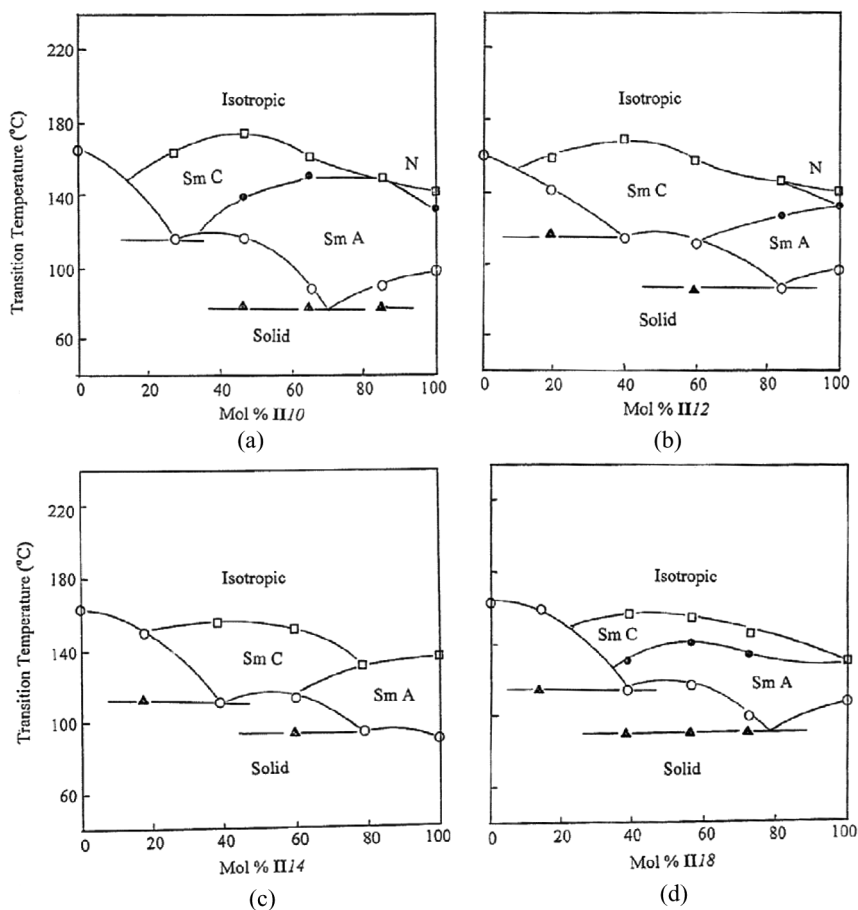


**FIGURE 1** Binary phase diagrams for the mixtures of 4-(4'-pyridylazo phenyl)-4''-methoxybenzoate, **I<sub>a</sub>**, with the four homologs of acids, (a) **II10**, (b) **II12**, (c) **II14**, and (d) **II18**.

complexes, the association is primarily affected by the acidity of the proton-donor, the acid, and the basicity of the pyridine derivative.

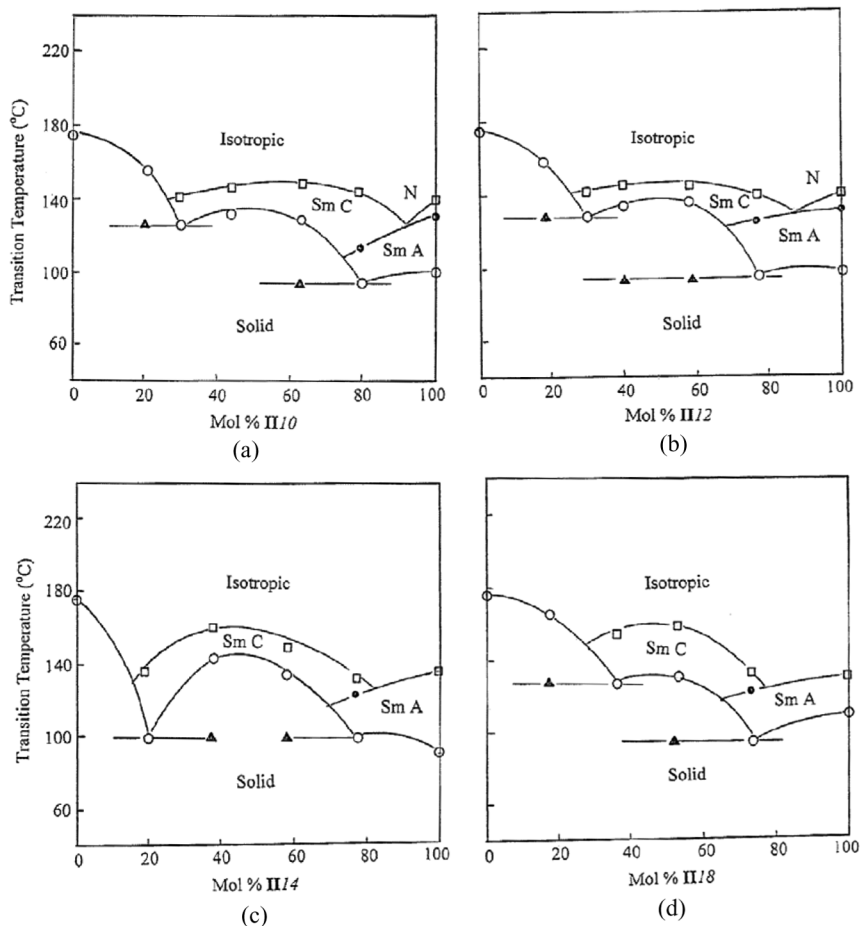
In order to obtain stoichiometric information on the binary mixtures made from the proton-donor (**II10–II18**) and the proton acceptor (**I<sub>a&b</sub>**) which is stabilized by the electron-donating ( $\text{CH}_3\text{O}$  and  $\text{CH}_3$ ) groups in the para-position, a series of hydrogen-bonded complexes was prepared using a varying mol% of **I<sub>a</sub>** or (**I<sub>b</sub>**) as proton acceptor, and each of the four acid homologs (**II10–II18**), individually, as proton donor.





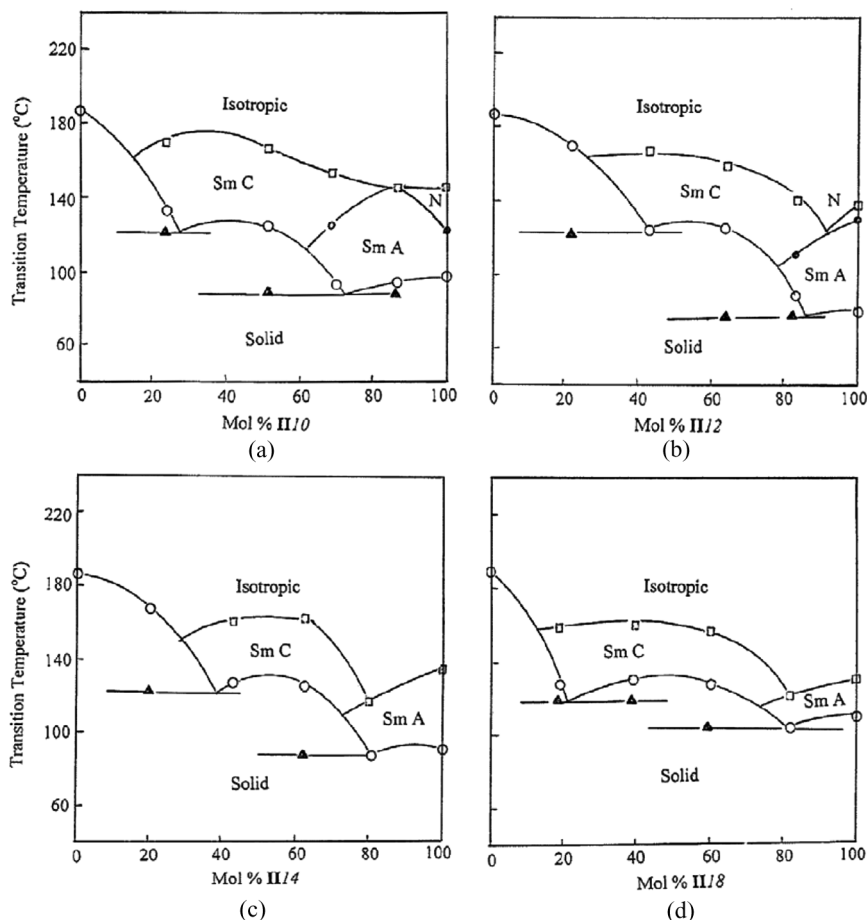
**FIGURE 2** Binary phase diagrams for the mixtures of 4-(4'-pyridylazo phenyl)-4''-methylbenzoate,  $I_b$ , with the four homologs of acids, (a)  $II/10$ , (b)  $II/12$ , (c)  $II/14$ , and (d)  $II/18$ .

Figures 1a–d represents the binary phase diagrams constructed for the four binary systems prepared from the methoxy-substituted pyridine derivative ( $I_a$ ) with the four acid homologs,  $II/10$ – $II/18$ , respectively. As can be seen from the figure, each homologs of the acid induces the SmC phase within the intermediate range of composition, with varying extents dependent on the length of the alkoxy chain. The nematic phase persists, in the lower homologs ( $II/10$  and  $II/12$ ) up to the addition of about 20 mol% of the nonmesomorphic component  $I_a$ . Evidence for the formation of liquid crystalline complexes in all four



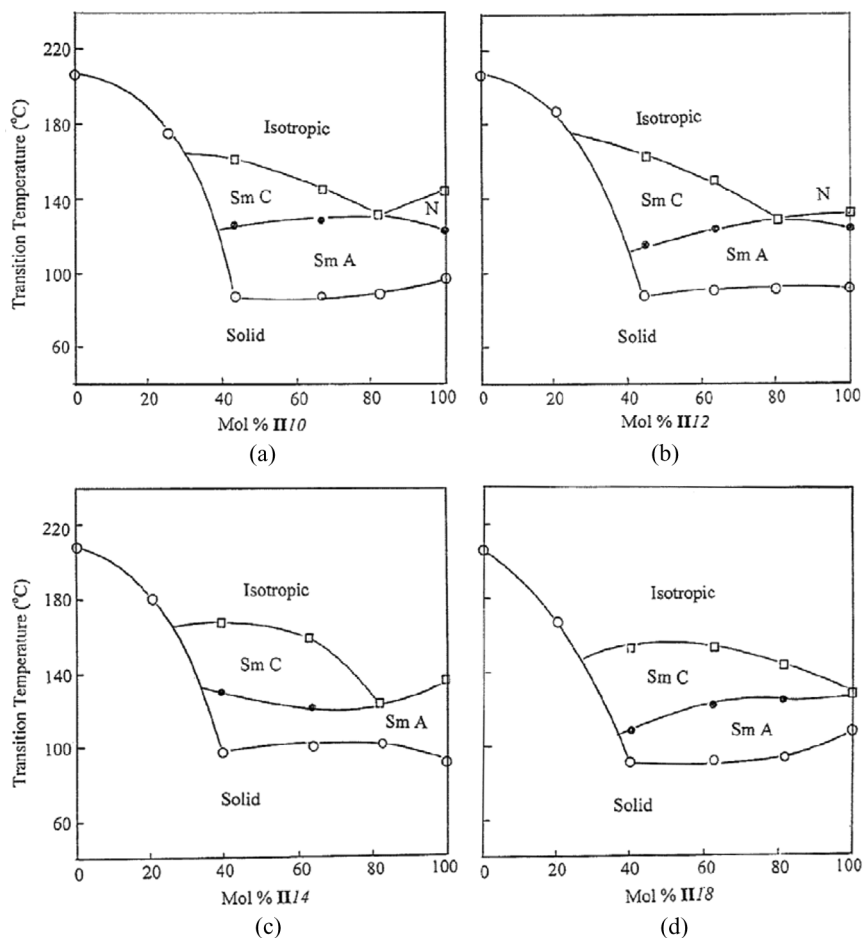
**FIGURE 3** Binary phase diagrams for the mixtures of 4-(4'-pyridylazo phenyl) benzoate, **I<sub>c</sub>**, with the four homologs of acids, (a) **II10**, (b) **II12**, (c) **II14**, and (d) **II18**.

systems by supramolecular hydrogen bonding in the 50 mol% mixture (1:1 complex) is provided by the existence of the two eutectic points before and after the 50 mol%, *i.e.*, at about 30 and 80 mol%. It can also be noted from Figure 1 that the mesophase characteristics of the 1:1 complex (at 50 mol% composition) varies according to the length of the alkoxy chain of the acid. Thus, for the lowest homolog (**II10**, Fig. 1a) the hydrogen bonded complex **I<sub>a</sub>/II10** melts at 114 °C to SmA, changes to SmC at 129 °C, and isotropizes at 171 °C. Increasing the alkoxy-chain



**FIGURE 4** Binary phase diagrams for the mixtures of 4-(4'-pyridylazo phenyl)-4''-bromobenzoate, **I<sub>d</sub>**, with the four homologs of acids, (a) **II/0**, (b) **II/2**, (c) **II/4**, and (d) **II/8**.

length of the acid to 12 carbons furnishes a complex that melts directly to a SmC mesophase at 116°C, and to the isotropic liquid at 163°C. The other two intermediate homologs of the acid, **II/4** and **II/8**, behave similarly to the latter; they melt at 112 and 110°C to the SmC phase and isotropize at 148 and 137°C, respectively. These results revealed that increasing the alkoxy-chain length of the proton-donor above 10 carbons results in a complex, with the methoxy-substituted proton-acceptor, **I<sub>a</sub>**, that is purely smectogenic exhibiting the SmC mesophase. Furthermore, an increase of the chain length is accompanied



**FIGURE 5** Binary phase diagrams for the mixtures of 4-(4'-pyridylazo phenyl) 4''-nitrobenzoate,  $I_e$ , with the four homologs of acids, (a)  $II_{10}$ , (b)  $II_{12}$ , (c)  $II_{14}$ , and (d)  $II_{18}$ .

by a destabilization of the SmC mesophase from 171 to 137°C, while the melting temperature is not significantly influenced by the length of the alkoxy chain; it varies irregularly between 110 and 114°C. It may also be added that the nematic phase observed for the lower acids ( $II_{10}$  and  $II_{12}$ ) disappears completely upon the addition of 20 mol% of the non-mesomorphic base  $I_a$ .

Investigation of the binary phase behavior of the methyl-substituted analog,  $I_b$ , with the four homologs of the acid ( $II_{10}$ – $II_{18}$ ), as

given in Figure 2, revealed that a supramolecular hydrogen-bonded complexes are formed between the proton-donors (*i.e.*, the acids) and the still strong proton-acceptor (*i.e.*, the base  $I_b$ ). In the present case, the strength of the proton-acceptor is evidently enhanced by the electron-releasing character of the 4-methyl group, as in the case of the 4-methoxy group but to a smaller extent. Complex formation is again evidenced by the existence of two eutectic points; one preceding and the other following the 1:1 molar ratio (see Figs. 2a–d). In this binary system, purely smectogenic (SmC) complexes are observed only for the complexes between  $I_b$  and the two intermediate homologs of the acid, **II12** and **II14** (Figs. 2b and c). The complexes of the other two acids (**II10** and **II18**) both exhibit polymorphic mesophases. Thus, while the lowest homolog (**II10**) of the acid forms a 1:1 complex which melts at 114°C to the SmA phase, changes to the SmC phase at 139°C, and isotropizes at 169°C, the highest homolog investigated (**II18**) melts first to a SmA at 119°C, transforms to the SmC phase at 138°C, and finally to the isotropic liquid at 156°C. It is worth mentioning that the nematic phase of the two lowest homologs of the acid (**II10** and **II12**) persists up to the addition of 20 mol% of  $I_b$ .

### Binary Mixtures of the Unsubstituted Derivative ( $I_c$ ) with the Four Homologs of the Acid

Turning now to the intermediate analog of the proton-acceptors that bears no substituent,  $I_c$ . The binary phase diagrams of  $I_c$  with the homologs of the acid (**II10**–**II18**) are represented graphically in Figures 3a–d, respectively. Examining the binary phase diagrams revealed that the proton-acceptor strength of the unsubstituted base is still adequate to be involved in a supramolecular hydrogen-bonded complex formation. This is again evidenced by the two eutectic points; the first lies around 30 mol% of the acid, while the second is found around 80 mol%. Compared with the electron-withdrawing substituents ( $CH_3O$  and  $CH_3$ ), the unsubstituted derivative ( $I_c$ ,  $X = H$ ) furnishes the correspondingly less stable SmC mesophase of its complexes with the homologs of the acid (**II10**–**II18**) as is evidenced by their relatively lower stability ( $T_{C-I}$ ) and mesomorphic range ( $\Delta T = T_{C-I} - T_{C-A}$ ), see Table 3. Furthermore, in the four diagrams of this system, the SmC phase is the only mesophase observed for the 1:1 complexes of all four homolog (see Fig. 3). The SmA phase persists up to the addition of about 30 mol% of the base  $I_c$ , while the nematic phase in the lower two homologs of the acid disappears completely by the addition of no more than 10 mol% of  $I_c$ .

**TABLE 3** Phase Transition Temperatures (°C) of the 1:1 Supramolecular Hydrogen-Bonded Complexes of the Systems **I/II**

| System                    | X                 | <i>n</i> | <i>T</i> <sub>S-A</sub> | <i>T</i> <sub>S-C</sub> | <i>T</i> <sub>A-N</sub> | <i>T</i> <sub>A-C</sub> | <i>T</i> <sub>C-I</sub> | Δ <i>T</i> |
|---------------------------|-------------------|----------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------|
| <b>I<sub>a</sub>/II10</b> | CH <sub>3</sub> O | 10       | 114                     | –                       | –                       | 129                     | 171                     | 42         |
| <b>I<sub>a</sub>/II12</b> |                   | 12       | –                       | 116                     | –                       | –                       | 163                     | 46         |
| <b>I<sub>a</sub>/II14</b> |                   | 14       | –                       | 112                     | –                       | –                       | 148                     | 36         |
| <b>I<sub>a</sub>/II18</b> |                   | 18       | –                       | 110                     | –                       | –                       | 137                     | 27         |
| <b>I<sub>b</sub>/II10</b> | CH <sub>3</sub>   | 10       | 114                     | –                       | –                       | 139                     | 169                     | 29         |
| <b>I<sub>b</sub>/II12</b> |                   | 12       | –                       | 116                     | –                       | –                       | 162                     | 46         |
| <b>I<sub>b</sub>/II14</b> |                   | 14       | –                       | 115                     | –                       | –                       | 152                     | 37         |
| <b>I<sub>b</sub>/II18</b> |                   | 18       | 119                     | –                       | –                       | 138                     | 156                     | 18         |
| <b>I<sub>c</sub>/II10</b> | H                 | 10       | –                       | 132                     | –                       | –                       | 148                     | 16         |
| <b>I<sub>c</sub>/II12</b> |                   | 12       | –                       | 138                     | –                       | –                       | 145                     | 7          |
| <b>I<sub>c</sub>/II14</b> |                   | 14       | –                       | 142                     | –                       | –                       | 156                     | 14         |
| <b>I<sub>c</sub>/II18</b> |                   | 18       | –                       | 130                     | –                       | –                       | 156                     | 16         |
| <b>I<sub>d</sub>/II10</b> | Br                | 10       | –                       | 124                     | –                       | –                       | 166                     | 42         |
| <b>I<sub>d</sub>/II12</b> |                   | 12       | –                       | 130                     | –                       | –                       | 165                     | 35         |
| <b>I<sub>d</sub>/II14</b> |                   | 14       | –                       | 132                     | –                       | –                       | 162                     | 30         |
| <b>I<sub>d</sub>/II18</b> |                   | 18       | –                       | 132                     | –                       | –                       | 158                     | 26         |
| <b>I<sub>e</sub>/II10</b> | NO <sub>2</sub>   | 10       | 87                      | –                       | –                       | 125                     | 155                     | 30         |
| <b>I<sub>e</sub>/II12</b> |                   | 12       | 94                      | –                       | –                       | 121                     | 159                     | 38         |
| <b>I<sub>e</sub>/II14</b> |                   | 14       | 98                      | –                       | –                       | 124                     | 163                     | 39         |
| <b>I<sub>e</sub>/II18</b> |                   | 18       | 92                      | –                       | –                       | 117                     | 155                     | 38         |

### Binary Mixtures of the Electron-Withdrawing (Br and NO<sub>2</sub>) Substituted Derivative (**I<sub>d</sub>** and **I<sub>e</sub>**) with the Four Homologs of the Acid

As it is well known, the remaining two substituents on the proton-acceptor, **I**, interact electronically, in different manners, with the rest of the molecule. Thus, while the nitro group, in **I<sub>e</sub>**, induces an electro-meric shift of electrons towards the nitro group, the bromine substituent interacts electronically with the remainder of the molecule in two opposing manners. In the first, it attracts the electrons by its inductive effect due to its relatively high electronegativity. While in the second, it induces an electro-meric shift of the electrons towards the pyridine-nitrogen. These two opposing effects may render the basicity of the molecule of **I<sub>d</sub>**, more or less, comparable with the unsubstituted analog, **I<sub>c</sub>**. Thus examining the binary phase diagrams of the bromo-substituted pyridine-based azo dye, **I<sub>d</sub>**, with the four homologs of the acid (**II10–II18**), as represented graphically in Figure 4, revealed that the basicity of **I<sub>d</sub>** is still adequate to form supramolecular hydrogen-bonded complexes at the 1:1 molar ratio. In each of the four phase diagrams of this system, **I<sub>d</sub>/II** two eutectic points were observed before

and after the 50 mol% composition. Such a complex is purely SmC independent of the length of the alkoxy chain of the acid. The stability of the phase and its temperature range are relatively high compared with those of the unsubstituted analog. This findings revealed that the electromeric donating character of the bromine atom with the rest of the molecule, overcomes its electron-withdrawing inductive effect, thus, rendering the molecule more basic compared with the unsubstituted analog. Accordingly, its hydrogen-bonded complexes with the acid homologs are more stable.

As expected for the nitro-substituted analog, its strong electron-withdrawing character will diminish the electron density on the pyridine-nitrogen and, consequently, its basicity and proton-acceptor capability. Hence, the possibility of hydrogen-bonded complex formation is accordingly reduced. This was found to be the case. As can be seen from Figure 5, which reproduces the binary phase diagrams of the system **I<sub>e</sub>**/**II** revealed that no complex formation was detected with all acid homologs, since only one eutectic point is observed in each diagram. The higher  $T_c$  ( $T_{C-I}$ ) and  $\Delta T$  ( $=T_{C-I} - T_{C-A}$ ) values for the 50 mol% composition (see Table 3) may be attributed to the possible anti-parallel alignment of the dipolar molecules that enhances the overall molecular length, and consequently its phase stability.

## CONCLUSIONS

Five pyridine-based azo dye derivatives of the type 4-(4'-pyridylazo phenyl)-4''-substituted benzoates, **I<sub>a-e</sub>**, in which the substituent varies between  $\text{CH}_3\text{O}$ ,  $\text{CH}_3$ , H, Br, and  $\text{NO}_2$  groups, respectively. Their molecular structures were checked via elemental analyses, NMR, and mass spectroscopy. The effect of the polarity of the substituent (electron donating or electron withdrawing) on supramolecular hydrogen-bonded complexing with four homologs of 4-alkoxybenzoic acids, **II10–II18**, was investigated by constructing their corresponding binary phase diagrams. The study revealed the following

1. All mixtures, in their intermediate composition ranges, showed an SmC mesophase.
2. Except for the nitro-substituted, the other analogs proved to form supramolecular hydrogen-bonded complexes in 1:1 molar ratio with all the investigated homologs of the acid.
3. Although the nitro-substituted analog did not show such a complex, its mixtures with the acids possessed stable SmC mesophases that could be attributed to an antiparallel alignment of the molecules.

## REFERENCES

- [1] Lehn, J. M. (1988). *Angew. Chem. Int. Ed. Engl.*, 27, 89.
- [2] Constantinos, M. P., & Dimitris, T. (2001). *Liq. Cryst.*, 28, 1127.
- [3] Bradfield, D. & Jones, B. (1929). *J. Chem. Soc.*, 2660; Gray, G. W., & Jones. B. *J. Chem. Soc.*, 4179.
- [4] Kato, T. & Frechet, M. J. (1989). *J. Am. Chem. Soc.*, 111, 8533.
- [5] Ruslim, C. & Ichimura, K. (1998). *Chem. Lett.*, 789.
- [6] Kozlovsky, M. V., Shibaev, V. P., Stakanov, A. I., Weyrauch, T., & Haase, W. (1998). *Liq. Cryst.*, 24, 759.
- [7] Shibaev, V. P., Kostomin, S. A., & Ivanov, S. A. (1996). In: *Polymers as Electrooptical and Photooptical Active Media*, Shibaev, V. P. (Ed.), Springer: Berlin, 37–110.
- [8] Herman, D. S., Rudquest, P., Ichumura, K., Kudo, K., Komitov, L., & Lagerwall, S. T. (1997). *Phys. Rev. E.*, 55, 2857.
- [9] Sasaki, T., Tkeda, T., & Ichumura, K. (1994). *J. Am. Chem. Soc.*, 116, 625.
- [10] Naoum, M. M., Saad, G. R., Nessim, R. I., Abdel Aziz, T. A., & Seliger, H. (1997). *Liq. Cryst.*, 23, 789.
- [11] Song, X., Li, J., & Zhang, S. (2003). *Liq. Cryst.* 30, 331.
- [12] Cammenga, H. K., Eysel, W., Gmelin, E., Hemmiger, W., Hoehne, G. W. H., & Sagre, S. M. (1993). *Thermochim. Acta.*, 219, 333.
- [13] Bernhardt, H., Weissflog, W., & Kresse, H. (1996). *Angew. Chem. Int. Ed. Engl.*, 35, 874.