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Supramolecular liquid crystals in binary and ternary systems

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ABSTRACT

Five, new laterally methyl-substituted, pyridine-based derivatives (**I**8–**I**16) having molecular formula 4-$C_nH_{2n+1}O{-}C_6H_4COOC_6H_3(2\text{-}CH_3){-}N{=}N{-}C_5H_4N$, with n varies between 8 and 16 carbons, were prepared and investigated for their mesophase behavior by differential scanning calorimetry (DSC) and polarized light microscopy (PLM). All prepared homologues were found to be smectogenic, possessing the smectic C mesophase. Binary mixtures, covering the whole concentration range, were independently prepared from corresponding isomers, one from series **I***n* and the other from series **II***n*, in which the methyl group is introduced this time into position-3. All mixtures were similarly characterized and their binary-phase diagrams constructed, from which the eutectic composition of each pair of isomers was determined. The increased stability of the SmC phase of mixtures is a consequence of the enhanced lateral molecular forces between the two components of the mixture.

Hydrogen-bonded 1:1 associates, formed between each of the derivatives (**I**8–**I**16) and 4-alkoxybenzoic acids (**III***m*), were prepared and similarly characterized to investigate the effect of lateral methyl orientations on the stability of the mesophases induced by intermolecular hydrogen bonding. All complexes prepared were investigated for their mesophase behavior by DSC and PLM and found to possess SmC as the only mesophase observed. The formation of the hydrogen-bonded complexes was confirmed by constructing their binary phase diagrams with the acid that cover the whole range of concentration of the two complements.

Finally, the formation of the hydrogen-bonded complexes between the eutectic mixtures of two pyridine-based isomers (**I**/**II**) and 4-alkoxybenzoic acids (**III***m*) was confirmed by constructing their apparent binary phase diagrams (actually of three components) with the acid (**III**) that cover the whole range of concentration of the two components (eutectic **I**/**II** and **III**).

1. Introduction

Interests in liquid crystalline materials have expanded greatly in recent years because of their optical properties. They can be found in a wide spectrum of applications: signpost panels, digital watches, calculators, cell phones, laptop displays, etc. Nearly all the devices used in our daily life nowadays use a liquid crystal display. Liquid crystal materials for device applications are mostly mixtures, usually of eutectic composition. Generally, lateral substitution decreases the thermal stability of both solid and mesophases [1–6]. Supramolecular liquid crystals are frequently induced, through hydrogen bonding, between aromatic carboxylic acids, as proton donor, and pyridine-based components, as proton acceptor [7–15]. We have previously reported [16–18] the preparation and characterization of some supramolecular, hydrogen-bonded, complexes between derivatives of pyridylazophenyl substituted benzoates (as proton-acceptors) and 4-alkoxybenzoic acids (as the proton donors).

Thus, to reduce the melting points of those previously [16] investigated supramolecular complexes, attempts were made [19,20] by introducing lateral methyl group into position-3 of the central benzene ring of the pyridine-based component of the complex [16–18]. In another investigation, we have observed [21] that the mesophase stability is differently affected by the spatial orientation of the methyl group substituted once in position-2 and another in position-3 of the central benzene ring in another group of azo-ester derivatives, namely, 4-(4′-substituted phenylazo)-2 (or 3-)-methyl phenyl)-4″-alkoxy benzoates [21]. It was found that lateral methyl substitution in position-2, with respect to the ester group, furnishes compounds mesomorphically more stable, compared with their isomers, methyl-substituted in position-3. These results have encouraged us to extend our investigation towards preparation and characterization of another group of isomers **I***n* in which the methyl group is laterally oriented by an angle different from that of the previously investigated [20] ones, **II***n*.

Binary mixtures of liquid crystalline materials can often lead either to a new liquid crystal phases, not observed in the corre-

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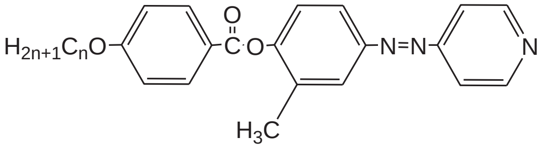
sponding pure components, or to the extension of the temperature range over which their mesophases are stable [22,23]. The enhancement of the liquid crystalline region often occurs because of the depression of the melting point, which reaches a minimum at the eutectic composition. However for certain materials, it is possible to observe, beside the melting point depression, liquid crystal phases that are formed via tailoring the molecular interaction between the components of the mixture thus increasing the stability of the induced mesophase, i.e., increasing the mesophase-isotropic transition temperature [24–28].

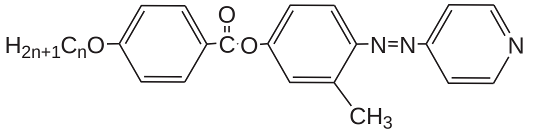
The goal of the present study is, first, to prepare a new group of pyridine based derivatives (**I**8–**I**16) and investigate their mesophase behavior via differential scanning calorimetry (DSC) and polarized-light microscopy (PLM).



I*n*

I*8*, $n = 8$, **I***10*, $n = 10$, **I***12*, $n = 12$, **I***14*, $n = 14$, **I***16*, $n = 16$

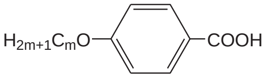
The second aim is to investigate their ability towards supramolecular hydrogen-bond formation with 4-alkoxybenzoic acids, in comparison with those of their 3-methyl-substituted isomers, **II***n* [20]. A third aim is to investigate, individually, the binary-phase behavior of each two pair of isomers, one from each group, **I** and **II**, aiming to elucidate their eutectic compositions.



II*n*

II*8*, $n = 8$, **II***10*, $n = 10$, **II***12*, $n = 12$, **II***14*, $n = 14$, **II***16*, $n = 16$

Finally, it is planned to investigate again the ability of each eutectic mixture towards the formation of the three-component supramolecular hydrogen-bonded complexes with 4-alkoxybenzoic acids, **III***m*, aiming to obtain complexes with lower melting point and greater mesophase stability.



III*m*

III*6*, $m = 6$, **III***8*, $m = 8$, **III***10*, $m = 10$, **III***12*, $m = 12$ and **III***16*, $m = 16$.

2. Experimental

The molecular formulae of the newly prepared pyridine-based derivatives (**I**8–**I**16) were confirmed via elemental analyses, ^{1}H NMR, and mass spectroscopy. The results were in agreement, within the permissible limits, with the structures assigned.

Infrared absorption spectra were measured with a Perkin-Elmer B25 spectrophotometer, and ^{1}H NMR spectra with a Varian EM 350L.

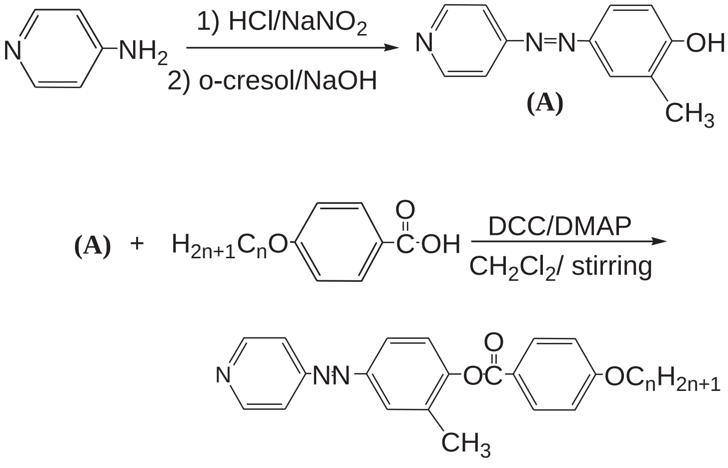
Calorimetric measurements were carried out using a PL-DSC of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al. [29]. DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All of the thermograms have been achieved at a heating rate of 10 °C/min in an inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and type of mesophase identified for the newly prepared pyridine-based derivatives (**I***n*) and their complexes with the acids (**III***m*), using a standard polarized light microscope PLM (Wild, Germany) attached to a home made hot-stage. The temperature is measured by a thermocouple placed just beside the sample and attached to temperature controller made by Brookfield, England.

The purity of samples prepared were checked with thin-layer chromatography using TLC-sheets coated with silica gel (E. Merck), whereby spots were detected by a UV-lamp. All the new derivatives (**I***n*) were found to be TLC pure.

2.1. Preparation of materials

The pyridine-based azo dyes (**I***n*) were prepared according to the following scheme:



(**I***n)*

2.1.1. Preparation of 4-(4′-pyridylazo)-2-methylphenol (A)

This was prepared according to the method described by Zhang and coworkers [30] from 4-aminopyridine and o-cresol. The yield of the crude product was 62%, and melts at 232.6 °C.

2.1.2. Preparation of 4-(4′-pyridylazo-2-methylphenyl)-4″-alkoxy-benzoates (*I**n*)

This was prepared by the method previously described [16] for the preparation of the laterally neat analogues. The solids (≈45% yield) obtained were crystallized from ethanol and found to be TLC pure and possess sharp melting temperatures as measured by DSC and are given in Table 1. Elemental analyses were conducted for these newly prepared compounds and the results (as given in Table 1) were consistent with structures proposed.

2.1.3. Preparation of supramolecular complexes

For the preparation of the supramolecular complexes (**I***n*/**III***m* or **I***n*/**II***n*/**III***m*), binary mixtures of any two complimentary components, were prepared in a 1:1 molar ratio by melting the appropriate amounts of each component, stirring to give an intimate blend, and then cooling with stirring to room temperature.

For the construction of binary phase diagrams, the mixtures of the two components were prepared to cover the whole range of composition. Transition temperatures obtained for all prepared blends, were measured by DSC and phases identified by PLM. 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.

Table 1
Elemental analyses, transition temperatures (°C), and transition enthalpies (kJ/mol), for the pyridine-based derivatives **I***n*.

Comp. no.	*n*	Analys. (found) Calc.			Transition temperatures			
		C	H	N	T_{Cr-C}	ΔH_{Cr-C}	T_{C-I}	ΔH_{C-I}
I8	8	(72.81) 72.78	(6.97)7.01	(9.44)9.43	91.9	40.66	(82.5)	0.78
I10	10	(73.57) 73.54	(7.40)7.45	(8.88)8.37	85.8	61.11	(82.4)	0.45
I12	12	(74.25) 74.22	(7.78)7.83	(8.38)8.37	73.5	41.04	83.1	0.28
I14	14	(74.86)747.82	(8.13)8.18	(7.94)7.93	79.5	74.82	84.2	0.97
I16	16	(75.40) 75.36	(8.44)8.49	(7.54)7.53	83.2	77.90	(79.1)	1.00

T_{Cr-C}: crystal to SmC transition; T_{C-I}: SmC to isotropic transition (monotropic).

3. Results and discussion

3.1. Confirmation of molecular structure

The molecular formulae of the newly prepared pyridine-based homologues (**I***n*) were confirmed via elemental analyses, IR, ^{1}H NMR, and mass spectra. Elemental analyses and infrared spectra were in agreement with the proposed formulae. ^{1}H NMR data showed expected integrated aliphatic–aromatic ratios. Mass spectra indicated exact molecular masses for the whole molecular structures and expected fragmentation.

3.2. Phase behavior

3.2.1. Pyridine-based molecules

Transition temperatures and transition enthalpies of the prepared pyridine-based derivatives (**I***n*) are given in Table 1. As can be seen from Table 1, except for the homologues **I**12 and **I**14, other members of the series exhibit monotropic SmC mesophase. The melting temperatures vary irregularly, as usual, with the increase of the alkoxy-chain length (*n*). Alternatively, the monotropic isotropic-to-SmC transition decreases with the increase of *n*. The homologues **I**12 and **I**14 were found to exhibit a narrow range of an enantiotropic SmC phase, namely ≈10 and 5 °C, respectively. Comparison of the data of the corresponding isomers in group **I***n* and the previously investigated group **II***n* [20] revealed that, the position and/or orientation of the lateral methyl group on the central benzene ring has but a slight effect on both melting points and smectic C stability between each pair of isomers. The SmC phase, as identified by PLM, of the derivatives **I**6–**I**16 was confirmed by constructing their binary phase diagrams with the purely smectogenic (SmC) acid components **III**14 and **III**16, as will be discussed later.

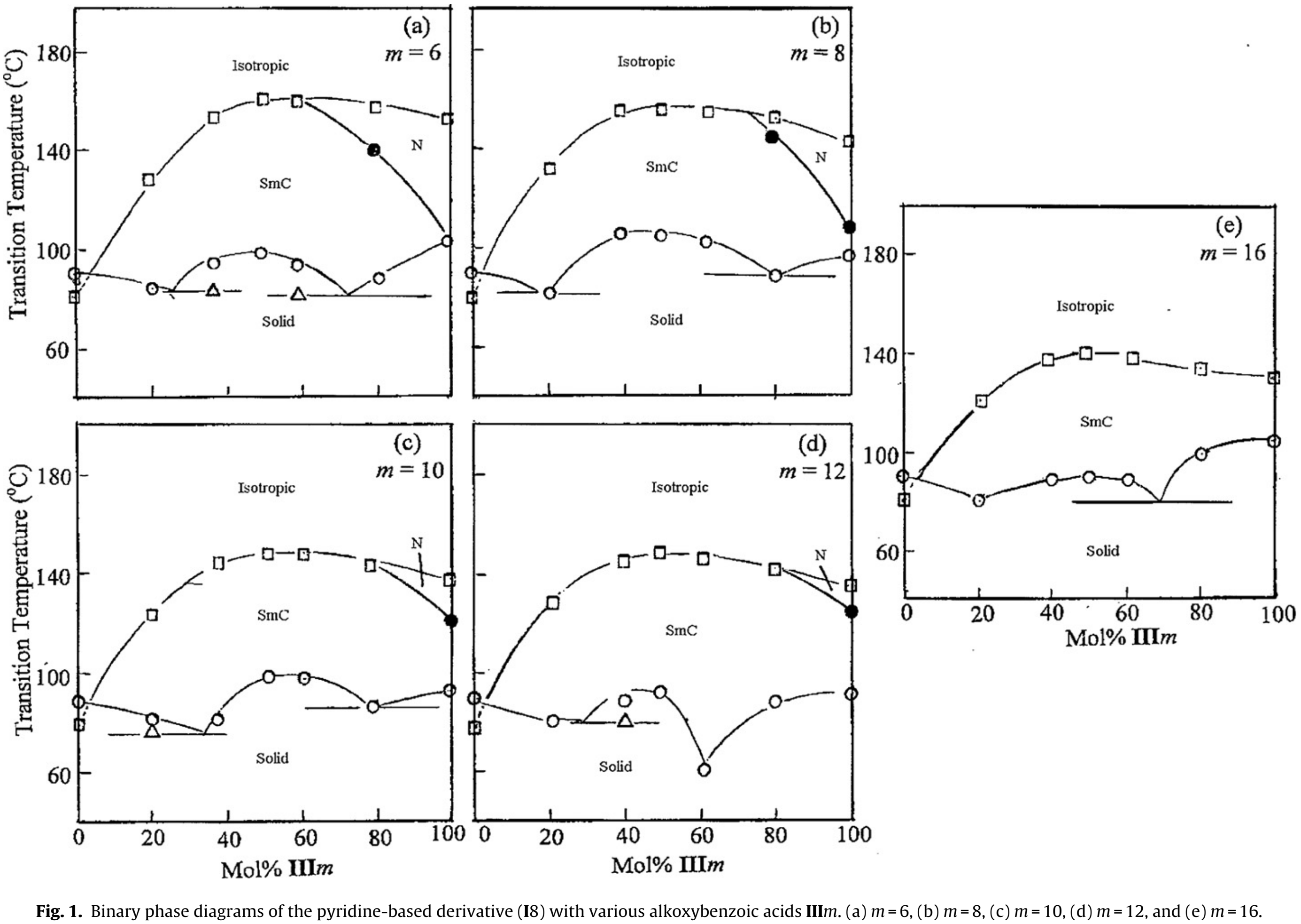


Fig. 1. Binary phase diagrams of the pyridine-based derivative (**I**8) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

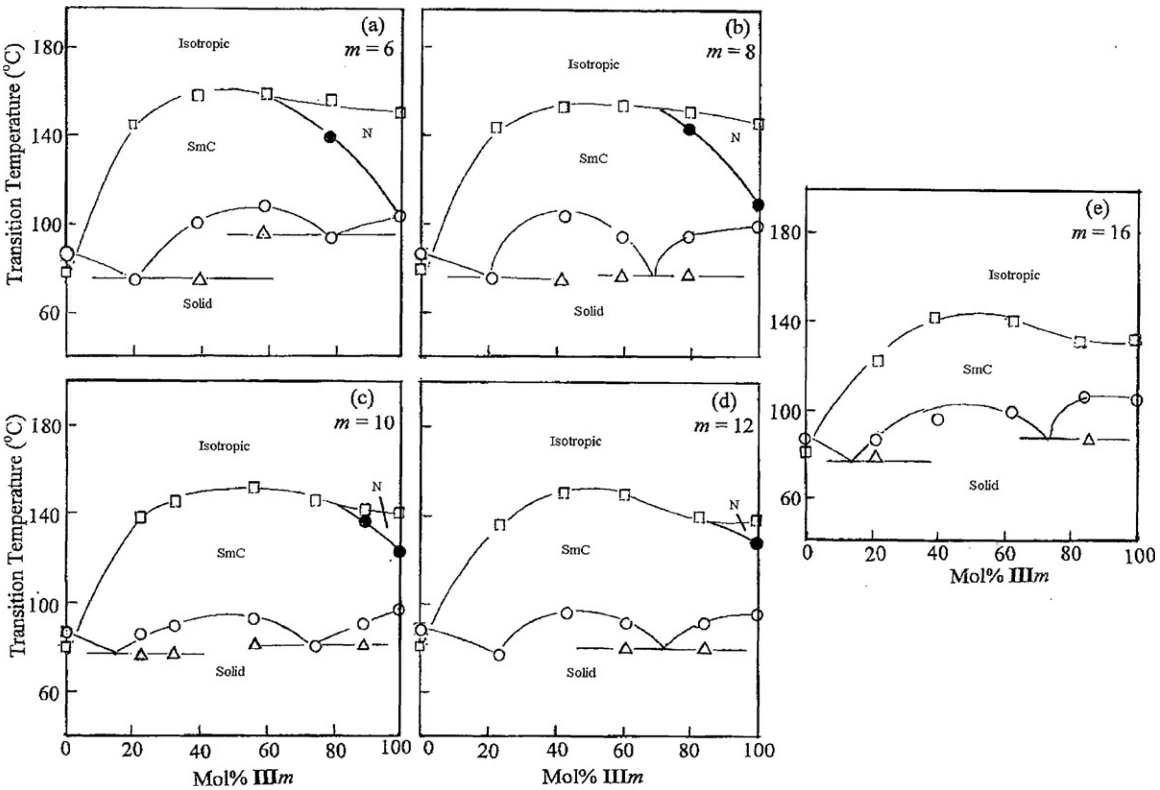


Fig. 2. Binary phase diagrams of the pyridine-based derivative (**I**10) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

Table 2
Transition temperatures (°C), transition enthalpies (kJ/mol) of the 1:1 supramolecular complexes (**I***n*/**III***m*).

System	*n*	*m*	T_{Cr-C}	ΔH_{Cr-C}	T_{C-I}	ΔH_{C-I}
I8/**III**6	8	6	99.4	44.1	161.4	4.0
I8/**III**8		8	106.4	30.2	158.8	4.6
I8/**III**10		10	104.8	57.6	153.8	4.0
I8/**III**12		12	94.7	52.8	151.1	3.9
I8/**III**16		16	90.5	51.4	144.0	3.4
I10/**III**6	10	6	109.2	36.0	162.4	3.1
I10/**III**8		8	105.8	43.5	157.1	3.3
I10/**III**10		10	94.4	54.0	153.7	3.0
I10/**III**12		12	96.3	64.2	151.8	3.1
I10/**III**16		16	99.6	54.7	145.7	7.0
I12/**III**6	12	6	117.0	43.6	151.2	2.4
I12/**III**8		8	97.8	56.7	154.9	4.1
I12/**III**10		10	100.2	54.3	153.1	4.2
I12/**III**12		12	97.3	82.1	151.0	3.4
I12/**III**16		16	104.8	74.6	146.7	5.3
I14/**III**6	14	6	96.2	77.4	149.7	2.9
I14/**III**8		8	88.3	59.5	148.1	3.4
I14/**III**10		10	93.0	82.9	145.8	3.9
I14/**III**12		12	98.7	84.7	142.0	10.1
I14/**III**16		16	99.0	61.6	140.2	13.1
I16/**III**6	16	6	104.4	64.7	146.1	4.1
I16/**III**8		8	100.1	55.7	151.6	5.0
I16/**III**10		10	107.8	52.0	146.1	7.9
I16/**III**12		12	103.2	55.6	142.1	8.3
I16/**III**16		16	109.7	67.0	141.2	12.0

Table 3
Eutectic composition, eutectic transition temperatures and enthalpies for the system **I***n*/**II***n*.

System	*n*	Mol% **I***n*	T_{Cr-C}	ΔH_{Cr-C}	T_{C-I}	ΔH_{C-I}
I8/**II**8	8	53.4%	71.1	27.4	85.7	0.3
I10/**II**10	10	48.8%	65.3	19.6	85.2	0.3
I12/**II**12	12	41.3%	68.1	36.6	81.9	0.6
I14/**II**14	14	72.3%	71.3	28.1	80.3	2.0
I16/**II**16	16	73.4%	70.1	636	79.4	1.3

*3.2.2. Supramolecular hydrogen-bonded complexes (**I**n/**III**m)*

Let us first investigate the binary phase behavior of this system, in order to confirm complex formation between the pyridine-based derivatives (**I***n*) and 4-alkoxybenzoic acids (**II***m*). Figs. 1–5 represent binary phase diagrams of the pyridine-based components (**I**8–**I**16) with five homologues of 4-alkoxybenzoic acids (**III***m*). As can be seen from these figures, the nematic phase of the nematogenic acid **III**6 and the polymorphic acids **III**8–**III**12 disappear upon the addi-

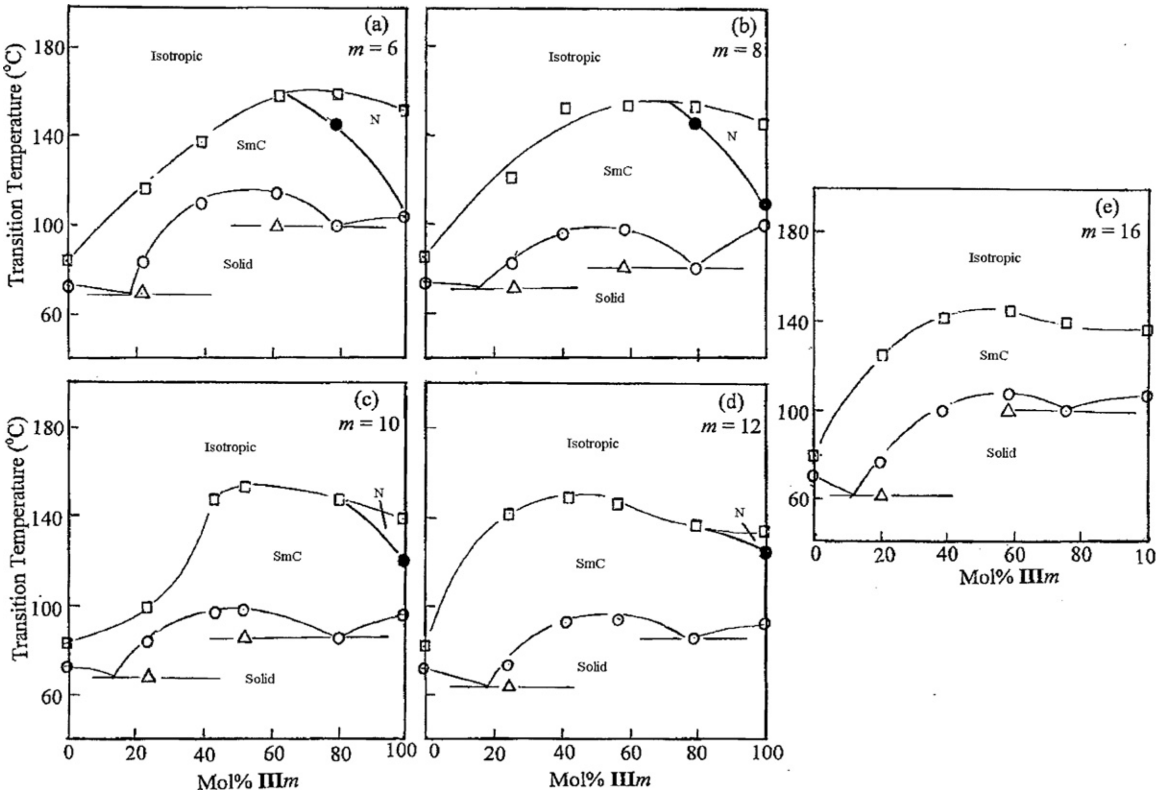


Fig. 3. Binary phase diagrams of the pyridine-based derivative (**I**12) with various alkoxybenzoic acids **III***m*. (a) $m = 6$, (b) $m = 8$, (c) $m = 10$, (d) $m = 12$, and (e) $m = 16$.

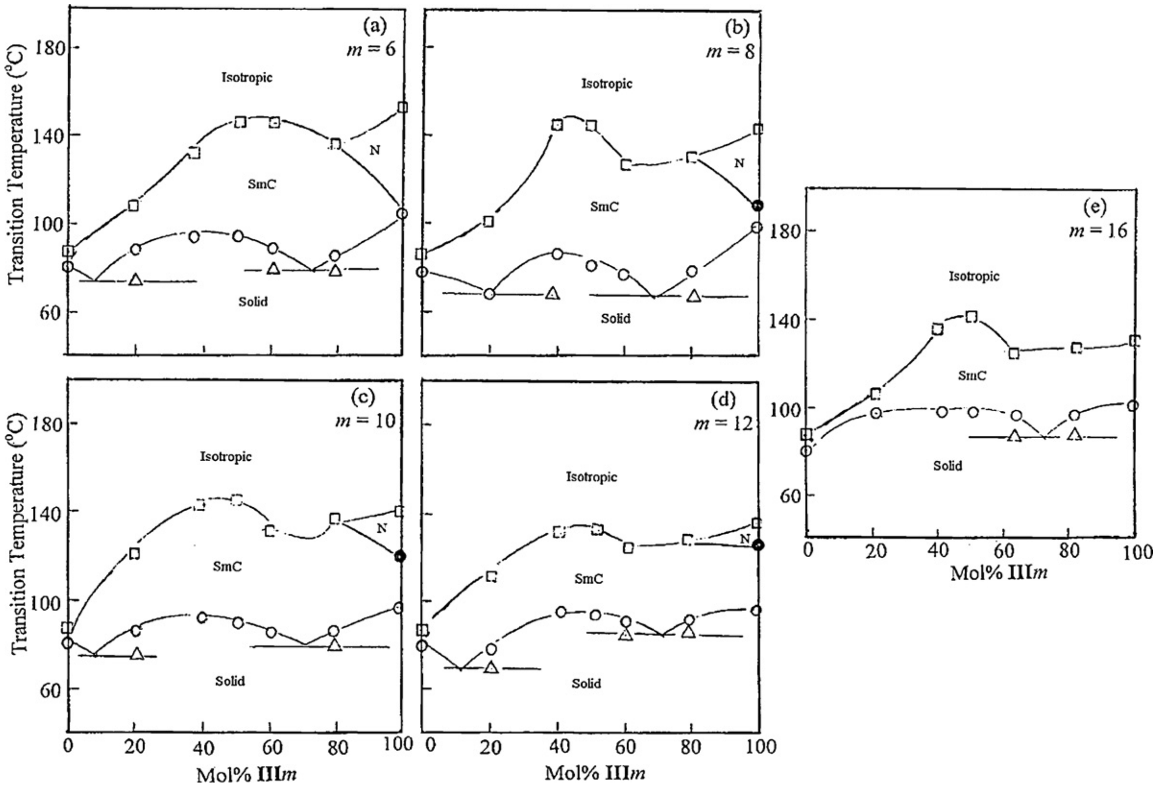


Fig. 4. Binary phase diagrams of the pyridine-based derivative (**I**14) with various alkoxybenzoic acids **III***m*. (a) $m = 6$, (b) $m = 8$, (c) $m = 10$, (d) $m = 12$, and (e) $m = 16$.

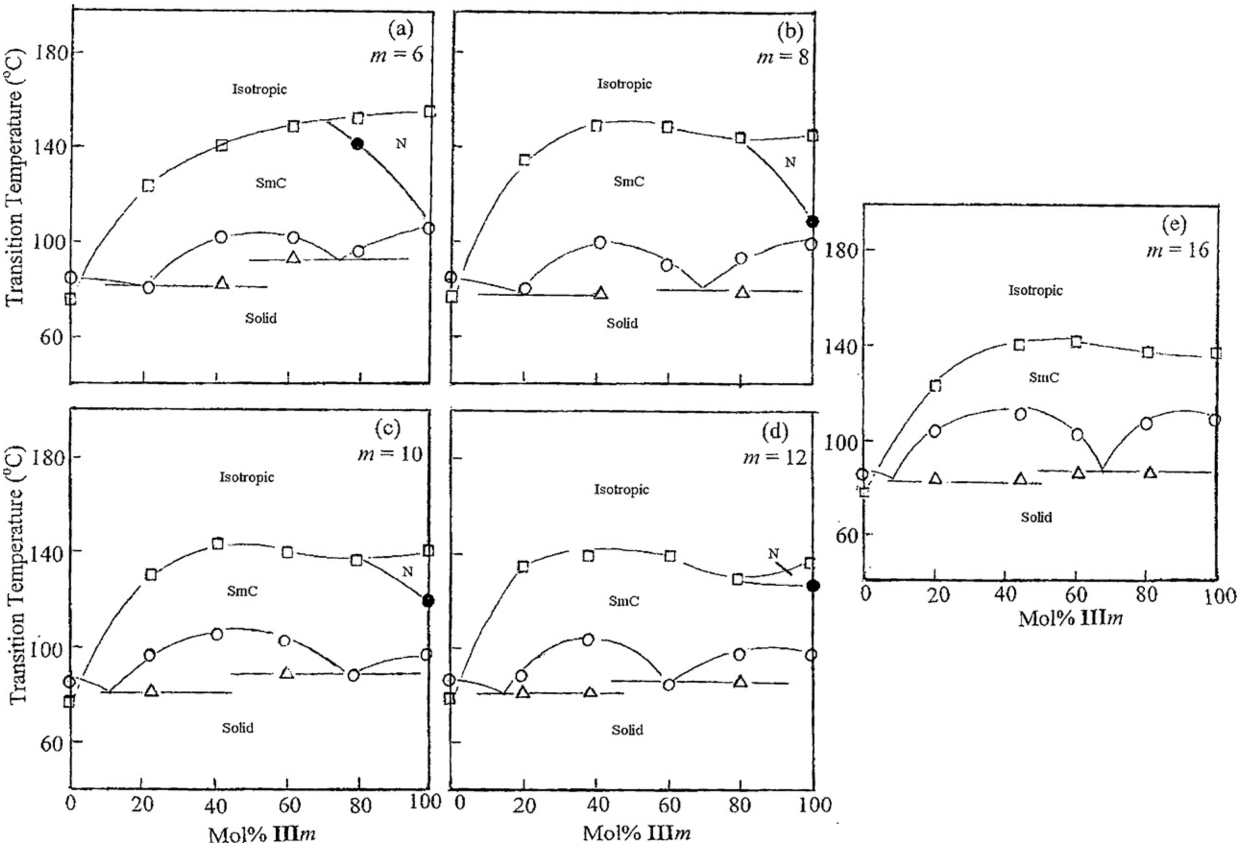


Fig. 5. Binary phase diagrams of the pyridine-based derivative (**I**16) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

tion of the base **I**8 in an amount that decreases (from 40 to 20 mol% of **I***n*) with the increase of the length of the alkoxy-chain of the acid component (*m*). Alternatively, the enantiotropic SmC phase of all acid homologues is retained in their binary mixtures throughout almost the whole composition range, confirming the SmC nature of the mesophase exhibited by newly prepared derivatives, **I**8–**I**16. In each case, complex formation either in the solid or the SmC phase is evidenced by the formation of two eutectic compositions, one

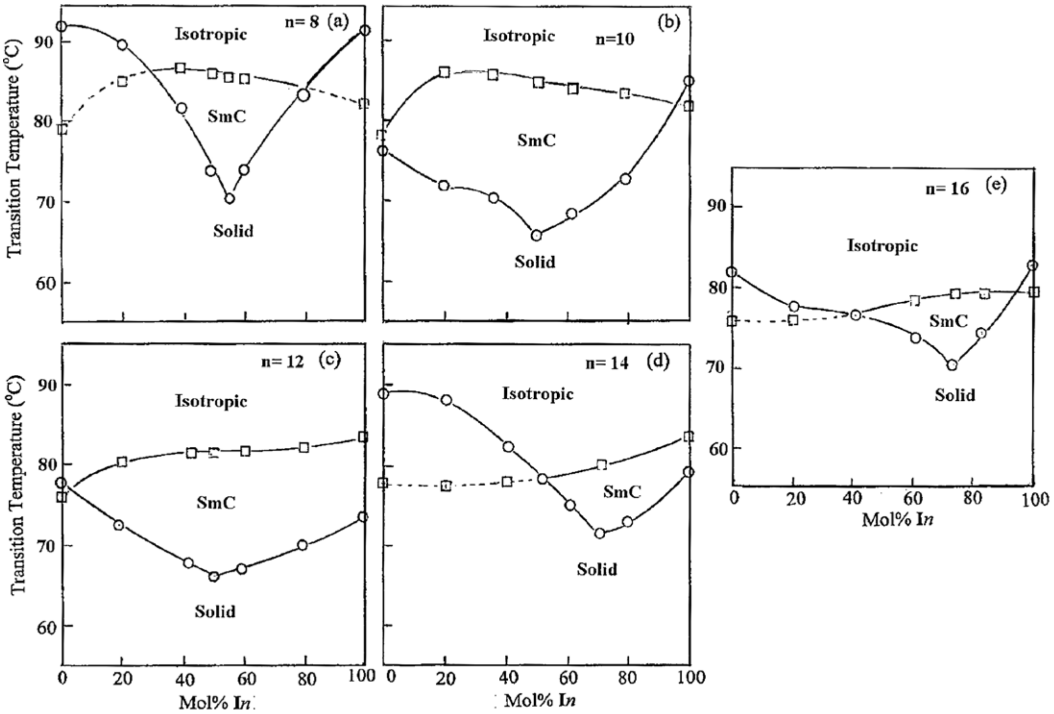


Fig. 6. Binary phase diagrams of the two pyridine based isomers (**I***n*/**II***n*). (a) *n* = 8, (b) *n* = 10, (c) *n* = 12, (d) *n* = 14, and (e) *n* = 16.

Table 4
Transition temperatures (°C), transition enthalpies (kJ/mol) of the 1:1 supramolecular complexes (**I***n*/**II***n*/**III***m*).

Complex	*n*	*m*	T_{Cr-C}	ΔH_{Cr-C}	T_{C-I}	ΔH_{C-I}
I8/**II**8/**III**6	8	6	86.2	20.9	159.3	2.4
I8/**II**8/**III**8		8	97.7	84.6	157.7	3.4
I8/**II**8/**III**10		10	88.2	46.2	152.5	3.1
I8/**II**8/**III**12		12	97.8	69.9	149.4	2.9
I8/**II**8/**III**16		16	84.5	59.7	140.2	3.6
I10/**II**10/**III**6	10	6	96.0	35.7	155.0	1.5
I10/**II**10/**III**8		8	86.0	50.7	152.0	2.8
I10/**II**10/**III**10		10	92.0	62.5	151.0	2.9
I10/**II**10/**III**12		12	94.0	51.5	152.0	3.0
I10/**II**10/**III**16		16	92.0	56.9	142.0	6.6
I12/**II**12/**III**6	12	6	98.0	39.6	150.0	3.3
I12/**II**12/**III**8		8	92.0	74.9	150.0	3.9
I12/**II**12/**III**10		10	92.0	48.3	142.0	1.8
I12/**II**12/**III**12		12	94.0	55.3	142.0	4.4
I12/**II**12/**III**16		16	96.0	76.7	137.0	9.0
I14/**II**14/**III**6	14	6	85.7	60.7	148.3	2.5
I14/**II**14/**III**8		8	81.8	86.6	146.3	3.1
I14/**II**14/**III**10		10	90.1	61.3	144.1	3.6
I14/**II**14/**III**12		12	94.8	71.8	136.1	4.2
I14/**II**14/**III**16		16	92.6	84.1	139.5	2.1
I16/**II**16/**III**6	16	6	97.2	36.2	148.6	4.1
I16/**II**16/**III**8		8	85.9	48.7	140.4	2.7
I16/**II**16/**III**10		10	92.0	61.8	137.0	5.9
I16/**II**16/**III**12		12	93.0	61.1	135.0	8.2
I16/**II**16/**III**16		16	101.0	59.5	132.0	8.2

preceding and the other following the 1:1 molar ratio. Complex formation is continued in the mesophase since the stability of the mesophase is greatly enhanced again at the 1:1 molar ratio. Similar behavior is observed (Figs. 2–5) for the binary mixtures of the other homologues (**I**10–**I**16) with the five homologues of the acid **III**6–**III**16, whereby all diagrams exhibit enhanced SmC stability for the 1:1 complexes in all the systems **I***n*/**III***m*.

Having been confirmed, all possible 1:1 complexes made from each of the homologues **I***n* with each of the acids **III***m* were prepared and characterized for their phase behavior by DSC and the type of the mesophase identified by PLM. The results are collected in Table 2. Irrespective of the length of the alkoxy chain, on either side of the complex, SmC mesophase is the only mesophase observed in all of the complexes investigated, the stability of the SmC mesophase was found to decrease slightly with the increase of *n* or *m*. The melting point of the complex, on the other hand, was found to vary irregularly, as usual, but with small variations with either *n* or *m*.

3.2.2.1. Supramolecular complexes of three components. It was planned to apply the triangle of composition [31,32] to the ternary systems **I***n*/**II***n*/**III***m* in order to elucidate the eutectic composition of these ternary systems. In this method, the composition triangle is constructed by locating each of the eutectic compositions of the three individual binary mixtures (**I***n*/**II***n*, **I***n*/**III***m*, and **II***n*/**III***m*) on its corresponding side and connecting each one to the opposing apex (representing the third pure component **III***m*, **II***n*, and **I***n*, respectively). The point of intersection of the three inner connecting lines gives the eutectic composition of the ternary system concerned. Practically, it was observed that this method is not applicable to cases exhibiting strong intermolecular interaction, such as hydrogen bonding. In the present case there are strong intermolecular interactions, via hydrogen bonding, within two of the three binary mixtures, namely **I***n*/**III***m* and **II***n*/**III***m*, which constitute two sides of composition triangle; in each case, instead, not only one but two eutectic points were observed one precedes and the other follows the 1:1 composition. The third side of the triangle represents the binary mixtures of the two pyridine-based isomers (**I***n* and **II***n*) which exhibits but relatively weak lateral interaction between the two methyl groups protruded by different angles within the two isomers. This type of interaction practically has lead to one eutectic composition only. Accordingly, we have decided to start first with elucidating the eutectic composition of each pair of isomers (**I***n*/**II***n*). The corresponding binary phase diagrams are represented graphically in Fig. 6. The eutectic compositions and their phase transitions and enthalpies are given in Table 3. As can be seen from Fig. 6, except for the binary mixture **I**14/**II**14, there is slight enhancement of the SmC stability for each of the binary systems (**I***n*/**II***n*). This may indicate that the smectic arrangement of the two isomeric molecules in the mixture is made face to face allowing the two molecules to be laterally closer leading to such slight SmC enhancement.

Being determined, each of the eutectic mixture (**I***n*/**II***n*) was first prepared and then mixed, alternatively, with each of the acid components, **III***m*. The apparent binary phase diagrams (**I***n*/**II***n* as one component and **III***m* as the second) were constructed and represented graphically in Figs. 7–11, for *n* = 8, 10, 12, 14, and 16 carbons, respectively. As can be seen from these figures, in all ternary systems investigated, the eutectic mixture (**I***n*/**II***n*), acting as one component, is strongly hydrogen-bonded to the acid component regardless of the length of the alkoxy group attached to either side of the complex. These results add more evidence that the pyridine-based constituents (**I***n* and **II***n*) of each eutectic mixture (**I***n*/**II***n*) do sterically interact in favor of SmC arrangement, as deduced before from their binary phase diagrams in Fig. 6. Also deduced from Figs. 7–11, that the formation of the 1 (acid): 1 (mixed bases) complexes is evident, in the solid phase, by the two eutectic compositions, one preceding and the other following the 1:1 molar ratio; and in the mesophase by the enhanced SmC stability at the same composition. Furthermore, in all cases, independent of *n* or *m*, all the 1:1 complexes are purely smectogenic exhibiting SmC as the only mesophase. This again indicates that the SmC is the mesophase observed in pure pyridine-based components, 4-alkoxy benzoic acid, and their binary and ternary supramolecular complexes. On the other hand, the nematic phase of the lower acid homologues (**III**6–**III**12) disappears completely upon addition of the eutectic mixture in a mol% that is decreased by the increase of *m*.

Comparison of the mesomorphic data for the complexes **I***n*/**II***n*/**III***m* (Table 4) with those of their corresponding binary complexes **I***n*/**III***m* (Table 2), indicates that the addition of the second

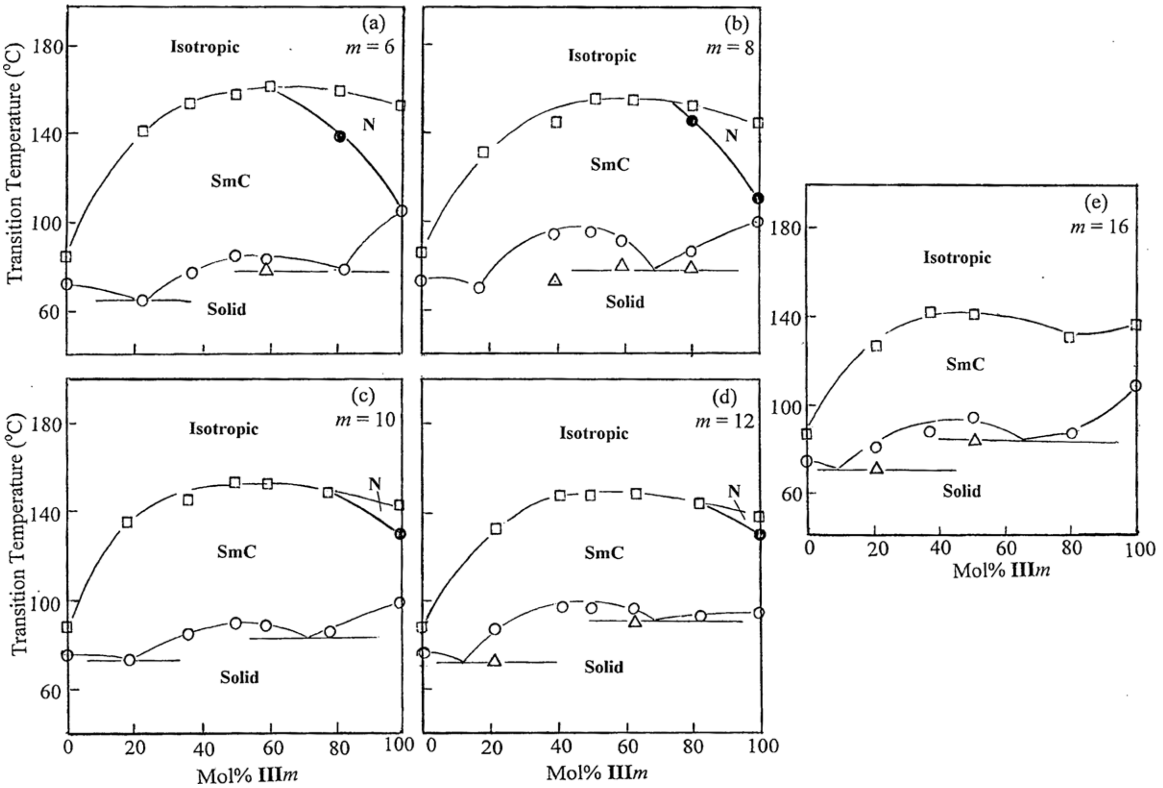


Fig. 7. Binary phase diagrams of the eutectic (**I**8/**II**8) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

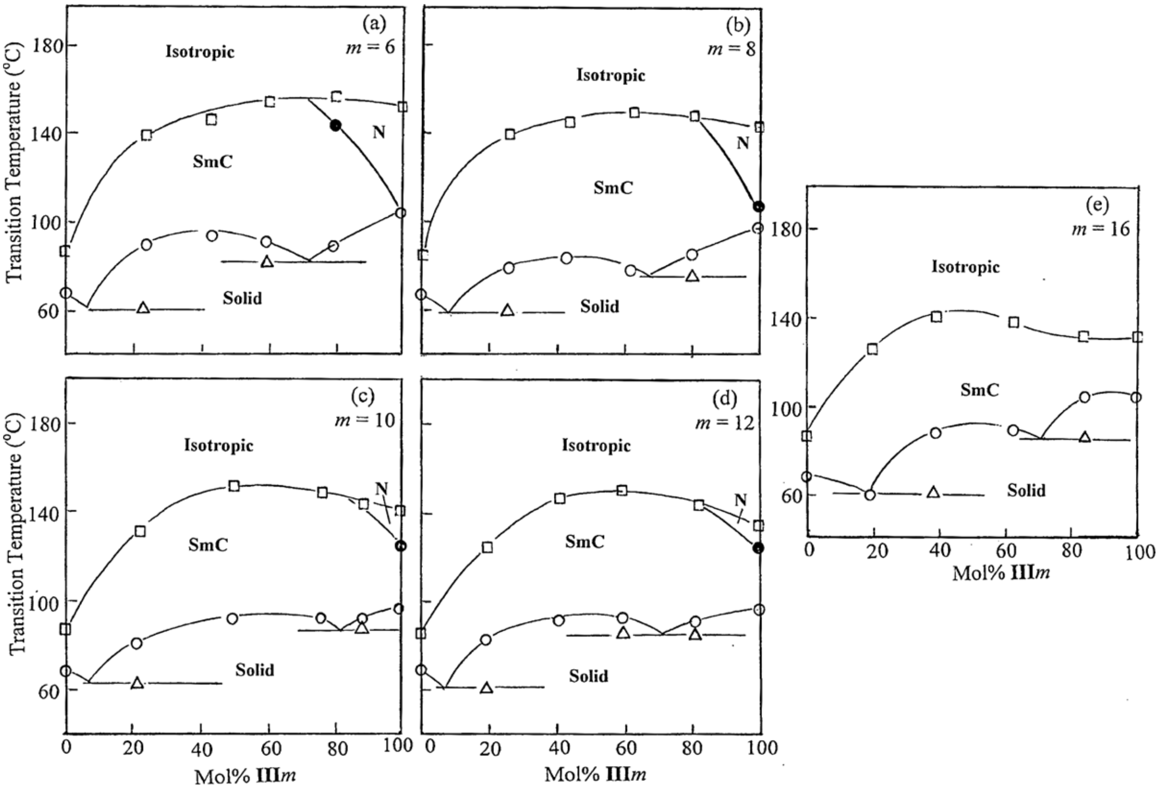


Fig. 8. Binary phase diagrams of the eutectic (**I**10/**II**10) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

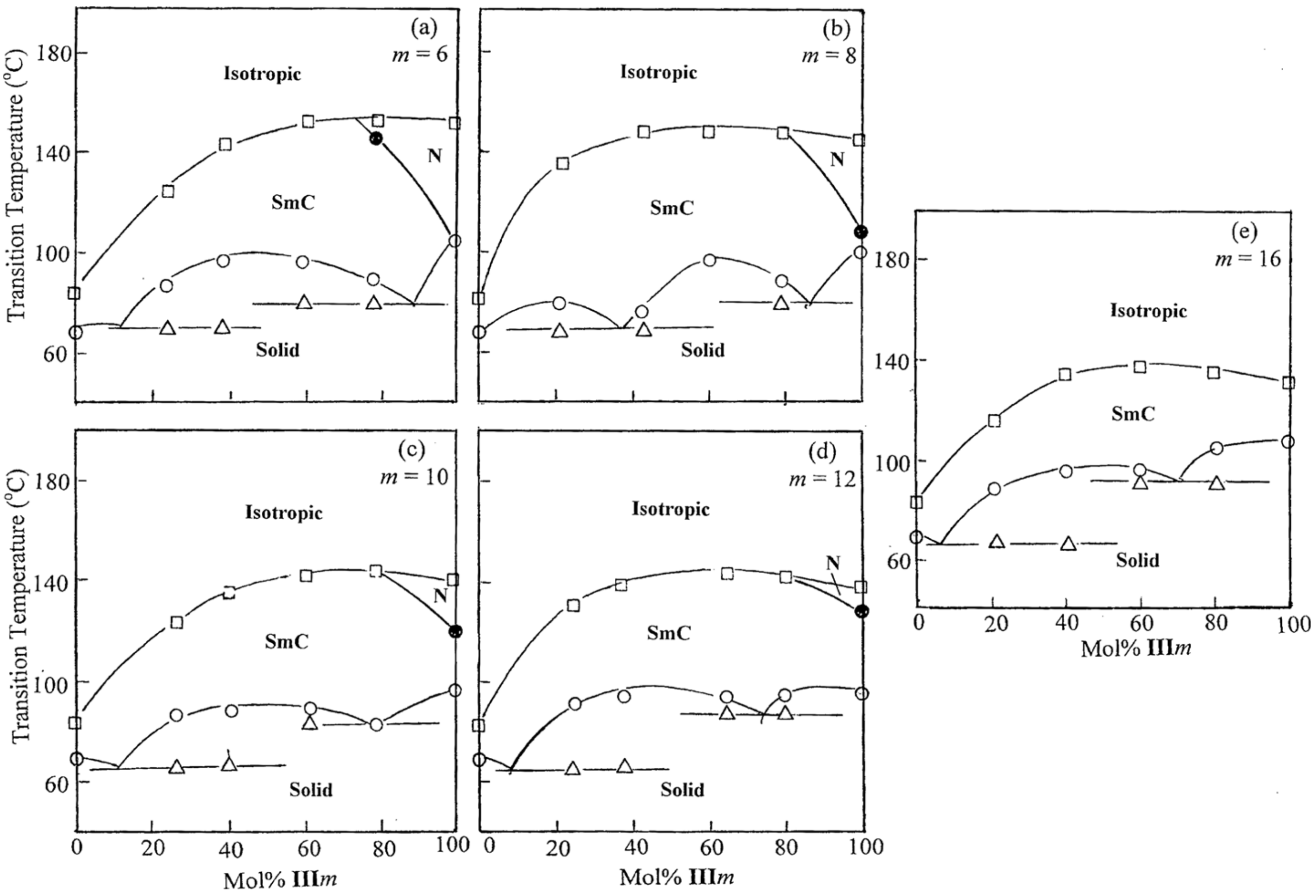


Fig. 9. Binary phase diagrams of the eutectic (**I**12/**II**12) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

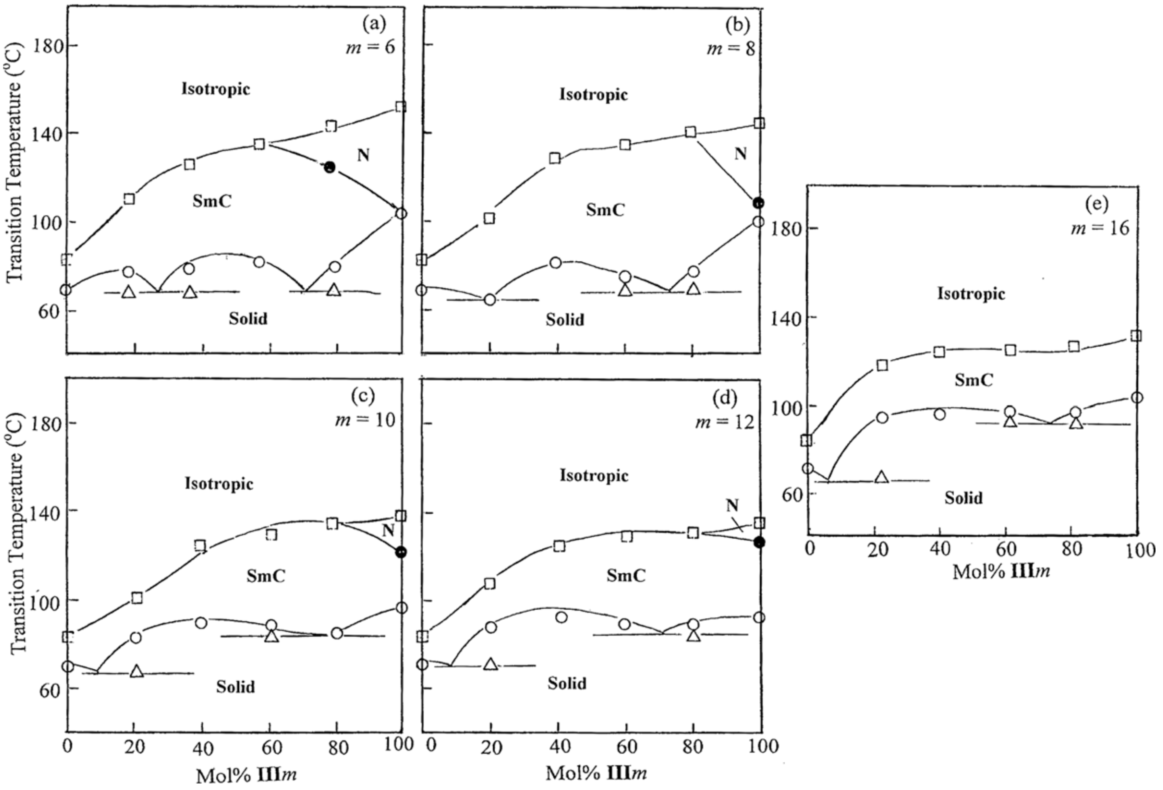


Fig. 10. Binary phase diagrams of the eutectic (**I**14/**II**14) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

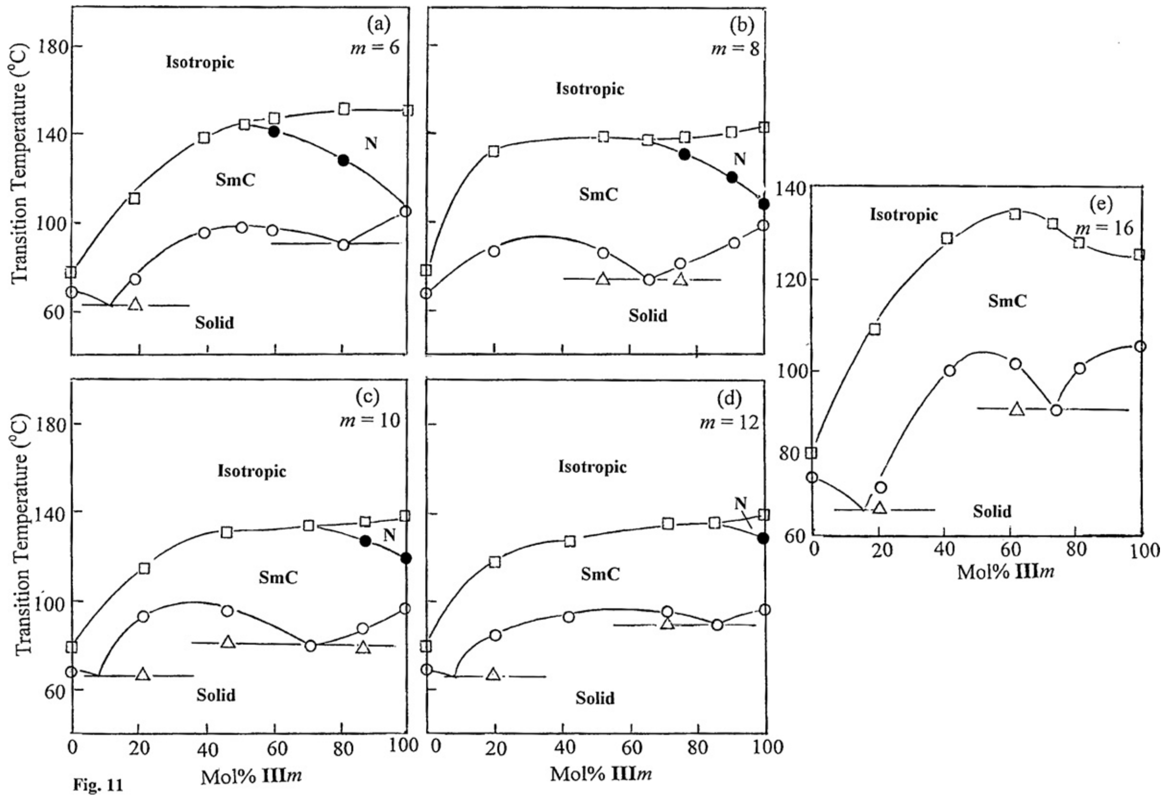


Fig. 11. Binary phase diagrams of the eutectic (**I**16/**II**16) with various alkoxybenzoic acids **III***m*. (a) *m* = 6, (b) *m* = 8, (c) *m* = 10, (d) *m* = 12, and (e) *m* = 16.

isomeric pyridine-based component **II***n* to the binary complexes **I***n*/**III***m* does not greatly influence the SmC stability. The difference between the SmC stability of the two complexes is small and decreases further upon increase of *m*. This again, as pointed out above, indicates that the addition of one isomer to the other does not disturb the smectic arrangement of the system.

4. Conclusions

The effect of introducing a lateral methyl group, of different orientation, into the pyridine-based azo-dye derivatives of the type 4-(4′-pyridylazo-2 (or 3-)-methylphenyl)-4″-alkoxy benzoates, **I***n* and **II***n*, on the formation, stability, and type of the mesophase observed in the prepared derivatives was investigated. The terminal alkoxy group in both series of compounds varies between 8, 10, 12, 14, and 16 carbons. Two groups of hydrogen-bonded supramolecular complexes were investigated for their mesophase behavior. In both groups of complexes, five homologues of the 4-alkoxybenzoic acids, **III**6–**III**16, were used and the 1:1 molar complex formation was confirmed by constructing their binary phase diagrams. In the first group of complexes, **I***n*/**III***m*, the two components are a pyridine-based homologue (**I***n*) and a homologue of the acids (**III***m*). In the second group of complexes, the pyridine-based components, **I***n*/**II***n*, were the eutectic mixture of two corresponding isomers from series **I** and **II**. The study revealed the following:

1. As evidenced from their binary-phase diagrams, irrespective of the alkoxy-chain length, *n* or *m*, 1:1 hydrogen-bonded complexes (***I****n*/**III***m*) are formed with reasonable range and stability in all systems investigated that possesses the SmC mesophase as the only mesophase observed.
2. Comparison between the present results and those previously reported [20] for the differently methyl-oriented derivatives (**II***n*) revealed that position and/or orientation of the lateral methyl group on the central benzene ring of the pyridine-based compounds do not affect significantly either the melting point or the mesophase stability of their hydrogen-bonded associates with 4-alkoxybenzoic acids.
3. Except for the binary phase **I**14/**II**14, there are but slight enhancements of the SmC stability of each of the binary systems (**I***n*/**II***n*) indicating that the arrangement of molecules within the mesophase is in favor of SmC formation.
4. The binary phase diagrams of the three-component complexes, **I***n*/**II***n* as one component and **III***m* as the second, revealed that the addition of the isomer **II***n* to the complex **I***n*/**III***m* almost does not affect the stability of the hydrogen-bonded complex. This again indicates that the position (or orientation) of the lateral methyl group does not disturb smectic arrangements either in the pure pyridine-based component or in its hydrogen-bonded complexes.

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