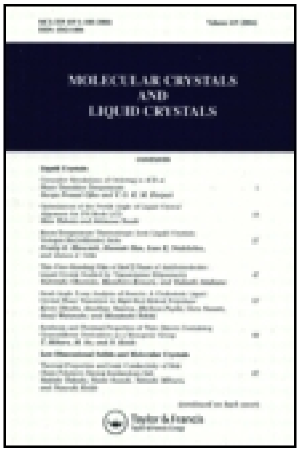

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Exhibition of Non-Linear Behaviour and Smectic and Nematic Mesophases in the Binary Systems Where Both the Components are Non-Mesogenic

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Exhibition of Non-Linear Behaviour and Smectic and Nematic Mesophases in the Binary Systems Where Both the Components are Non-Mesogenic

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Binary systems of two non-mesogens exhibiting polymesomorphism are rare. In the present study three binary systems of non-mesogens exhibiting smectic and/or nematic mesophases are reported. One of the component is Schiff base and possesses strongly polar nitro end group. The transition temperature curves exhibit non-linear behaviour. In another binary system where one of the component exhibit monotropic nematic phase, induced smectic mesophase is observed and the monotropic nematic phase is converted to enantiotropic phase in certain concentration range. The binary systems of non-mesogens having identical structures (homologues) do not exhibit mesomorphism. Binary systems, where both the components are homologues and one of them is monotropic nematic, then, ideal behaviour is observed in their mixed mesomorphism.

INTRODUCTION

Early studies of Vorländer and Gahren[1] and Bogojawlensky and Winogradow[2] have suggested the formation of mixed mesomorphism from the pairs of compounds which are non-mesogenic by themselves. Walter[3] reported enantiotropic mixed mesomorphism within certain range of concentration in the study of two non-mesogenic aromatic acids. Bennett and Jones[4] showed that *p*-methoxybenzoic acid and *p*-ethoxybenzoic acid which are high melting and non-mesogenic by

TABLE I

Binary system Ia:
p-nitrobenzylidene-*p*′-*n*-hexyloxyaniline:
p(*p*′-*n*-butoxy benzoyloxy) toluene

Mole percent of BBT	Transition temperatures °C	
	Nematic	Isotropic
0.00	—	94.0
11.82	(85.0)[a]	92.0
22.38	(85.0)	89.5
32.94	(83.0)	83.5
44.28	64.0	82.0
52.95	64.0	79.0
63.04	63.0	72.0
72.80	63.0	68.0
82.54	—	73.5
89.75	—	77.0
100.00	—	79.0

[a] Values in parentheses indicate monotropy.

themselves, do exhibit nematic mesophase in their binary mixtures. Lohar[5] has confirmed this result and showed that mixtures of the two acids exhibit mixed mesomorphism over a small range of temperature and concentration. Walter[3] has suggested that substances which do not individually form mesophases but exhibit mixed mesomorphism in

TABLE II

Binary system IIa:
p-nitrobenzylidene-*p*′-*n*-pentyloxyaniline:
p(*p*′-*n*-butoxy benzoyloxy) toluene

Mole percent of BBT	Transition Temperatures °C		
	smectic	Nematic	Isotropic
0.00	—	—	89.0
13.23	—	(78.0)[a]	87.0
21.54	—	(77.0)	83.5
31.91	—	75.0	77.0
42.70	(58.5)	60.0	77.0
52.13	(55.0)	60.5	72.5
61.97	(48.0)	65.0	69.0
71.92	—	(65.0)	70.0
81.12	—	(63.0)	73.0
90.15	—	—	77.5
100.0	—	—	79.0

[a] Values in the parentheses indicate monotropy.

TABLE III

System Ic:
p-nitrobenzylidene-*p*′-*n*-pentyloxyaniline:
p-(*p*′-*n*-pentyloxybenzoyloxy) toluene

Mole percent of PBT	Transition Temperatures °C		
	smectic	Nematic	Isotropic
0.00	—	—	89.0
10.88	—	(76.5)[a]	87.5
20.79	—	(76.0)	82.0
31.58	(60.0)	63.0	78.0
40.74	55.0	64.0	76.0
51.83	51.0	61.0	71.5
60.80	50.0	58.0	69.0
71.01	52.0	54.0	65.5
80.95	—	(56.0)	64.0
100.0	—	—	70.0

[a] Values in the parentheses indicate monotropy.

binary mixtures, are generally very crystalline and are not readily supercooled, therefore, monotropic liquid crystals which might have been expected for them by reason of their chemical constitution remain latent.

No extensive studies have been made for mixed liquid crystals of smectic type. Dave *et al.*,[6] studied binary systems comprising of a

TABLE IV

System IIa:
p(*p*′-*n*-hexyloxy benzoyloxy) toluene:
p-nitro benzylidene-*p*′-*n*-hexyloxyaniline

Mole percent of HBT	Transition Temperatures °C		
	smectic	Nematic	Isotropic
0.00	—	—	94.0
10.47	—	(85.0)[a]	91.0
20.46	—	(86.0)	89.0
31.55	73.5	76.0	85.0
41.55	65.0	74.0	83.0
49.68	55.0	70.0	80.0
61.29	52.0	70.0	77.0
70.63	52.0	61.0	71.0
76.29	53.0	56.0	68.0
90.30	—	59.0	62.5
100.0	—	(51.0)	64.0

[a] Values in the parentheses indicate monotropy.

TABLE V

System IIb
p-nitrobenzylidene-*p*′-*n*-hexyloxy aniline:
p-nitro benzylidene-*p*′-*n*-butoxyaniline

Mole percent of NBHA	Transition Temperatures °C	
	Nematic	Isotropic
0.00	(69.5)[a]	79.0
23.69	68.0	71.0
38.21	64.0	72.0
58.97	(75.0)	80.0
76.86	—	89.5
100.0	—	94.0

[a] Values in the parentheses indicate monotropy.

TABLE VI

System IIc
p-nitro benzylidene-*p*′-*n*-pentyloxy aniline:
p-nitro benzylidene-*p*′-*n*-butoxy aniline

Mole percent of NBPA	Transition Temperatures °C	
	Nematic	Isotropic
0.00	(69.5)[a]	79.0
20.17	(69.0)	73.5
39.58	63.0	67.0
58.51	(68.0)	77.5
78.80	—	85.0
100.0	—	89.0

[a] Values in the parentheses indicate monotropy.

TABLE VII

System IIIa:
p-nitrobenzylidene-*p*′-*n*-hexyloxyaniline:
p-nitrobenzylidene-*p*′-pentyloxyaniline

Mole percent of NBHA	Melting Points °C
0.00	89.0
21.94	83.0
39.19	80.0
60.02	84.0
79.96	90.0
100.0	94.0

smectogen and a non-mesogen. Mixed smectic liquid crystals was obtained over a range of concentration and temperatures. Recently some binary systems have been reported where smectic mesophase is induced in the mixed liquid crystals.[7-10]

In the present study we report number of binary systems where two non-mesogens exhibit smectic and nematic mesophases over a certain range of concentration and temperature.

EXPERIMENTAL

1. Preparation of compounds

(i) *p*-Nitro benzylidene-*p*′-*n*-butoxy aniline (NBBA)
(ii) *p*-Nitro benzylidene-*p*′-*n*-pentyloxy aniline (NBPA) and
(iii) *p*-Nitro benzylidene-*p*′-*n*-hexyloxy aniline (NBHA) were synthesized as described by Vora and Dixit.[11]
(iv) *p*(*p*′-*n*-butoxybenzoyloxy)toluene (BBT)
(v) *p*(*p*′-*n*-pentyloxybenzoyloxy) toluene (PBT) and
(vi) *p*(*p*′-*n*-hexyloxybenzoyloxy) toluene (HBT) were synthesized as described by Dave and Vora.[12]

2. Preparation of mixtures

Both the components were weighed accurately in known proportion and melted together in fusion tubes. The mixtures were thoroughly mixed to obtain a homogenous mixture. The melt was quenched and the solid obtained was ground finely and was used for determining transition temperatures.

TABLE VIII

System IIIb:
p(*p*′-*n*-butoxybenzoyloxy) toluene:
p(*p*′-*n*-pentyloxybenzoyloxy) toluene

Mole percent of BBT	Melting Points °C
0.00	70.0
22.41	66.0
42.64	69.0
61.05	72.0
81.26	77.0
100.00	79.0

3. Determination of transition temperatures

The transition temperatures were determined by using a polarising Mettler FP-2 microscope equipped with a hot stage.

The transition temperatures were determined on heating as well as cooling.

The transition temperatures are given in Tables I to VIII.

RESULTS AND DISCUSSION

Three different types of binary systems are studied.

System I: Both the components are non-mesogenic and one of the components possesses strongly polar terminal nitro group.

Ia: NBHA + BBT
Ib: NBPA + BBT
Ic: NBPA + BBT

In the above three systems both the components belong to two different homologous series.

System Ia: One of the Components is an ester while the other is a Schiff base with polar end nitro group.

The transition temperatures of the binary system are plotted against the mole percent concentration of component BBT. (Figure 1). As the concentration of NBHA decreases, monotropic nematic mesophase

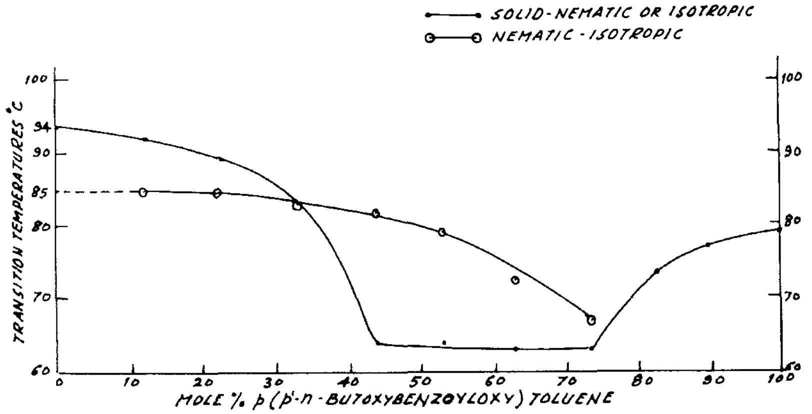


FIGURE 1 $p(p'$-n-Butoxybenzoyloxy) toluene: p-nitro benzylidene-p'-n-hexyloxy aniline.

appears which becomes enantiotropic with further decrease in the concentration of NBHA. As the concentration of NBHA decreases below 32 mole percent, the system again becomes non-mesogenic. The region where system exhibits enantiotropic nematic mesophase, the crystal to mesomorphic transitions are much more depressed and the curve becomes almost a parabola. The nematic–isotropic curve shows falling tendency from right to left. The nematic–isotropic transition temperature curve is extrapolated on the side where monotropic nematic phase is observed. The extrapolation method of finding a transition temperature is more reliable if monotropic mesophases are observed upto certain concentration range.$^{6,13-15}$ The latent transition temperature obtained by this method is 85 °C for NBHA.

System Ib: NBPA + BBT

The binary phase diagram (Figure 2) exhibits interesting behaviour. The two non-mesogens exhibit nematic and smectic mesophases in the mixed state over a certain range of concentration. The induced smectic mesophase appears in the central portion of the phase diagram as a monotropic phase. The monotropic nematic mesophase observed at the two extremes of the phase diagram becomes enantiotropic in the central part suggesting that 65 to 35 mole percent composition of the mixture is more mesogenic. Nematic–isotropic transition temperature curve exhibits non-linear behaviour. The latent transition temperature obtained for NBPA by extrapolation method is 74.5 °C.

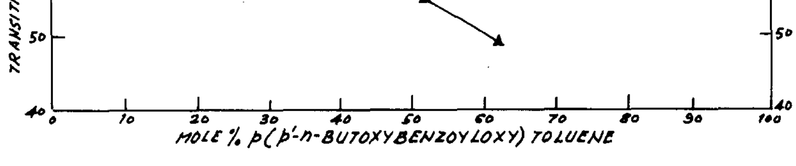


FIGURE 2 $p(p'$-n-butoxybenzoyloxy) toluene: p-nitro benzylidene-p'-n-pentyloxy aniline.

System Ic: NBPA + PBT

The binary phase diagram (Figure 3) exhibits monotropic and enantiotropic smectic and nematic mesophases. The nematic–isotropic and smectic–nematic transition temperature curves show non-linear behaviour. The latent transition temperatures obtained for PBT and NBPA by extrapolation method are 41.0 °C and 72.5 °C respectively.

System II: One of the components is monotropic nematic and other is non-mesogenic.

System IIa: HBT + NBHA

One of the components possesses strongly polar terminal nitro group. The monotropic nematic phase of HBT becomes enantiotropic nematic even with as low as 7.5 mole percent concentration of NBHA (Figure 4). The enantiotropic smectic mesophase appears at the 25 mole percent concentration of NBHA and continues upto about 68 mole percent of NBHA. The transition temperature curves exhibit non-linear behaviour. The latent transition temperature obtained by extrapolation for NBHA is 82 °C.

System IIb: NBBA + NBHA

Both the components have strongly polar end nitro group. The monotropic nematic phase of NBBA becomes enantiotropic nematic, again monotropic nematic and finally system becomes non-mesogenic as the concentration of NBHA increases (Figure 5). Extrapolated latent transition temperature for NBHA is 84.5 °C. The transition temperature curve exhibits linear behaviour.

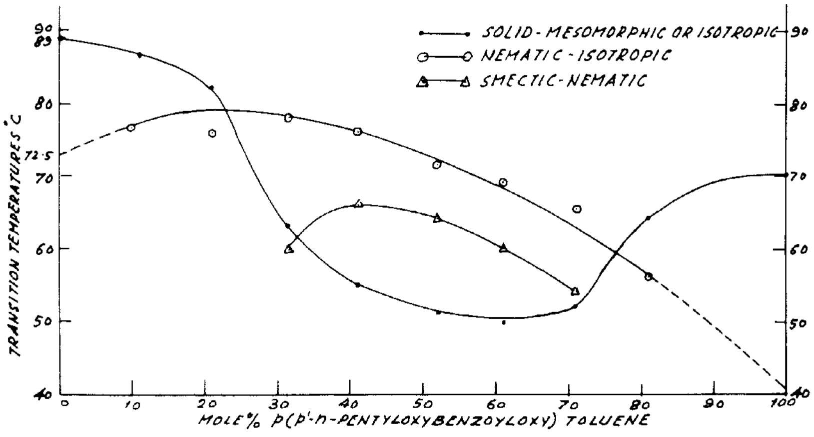


FIGURE 3 *p*(*p*′-*n*-pentyloxybenzoyloxy) toluene: *p*-nitro benzylidene-*p*′-*n*-pentyloxy aniline.

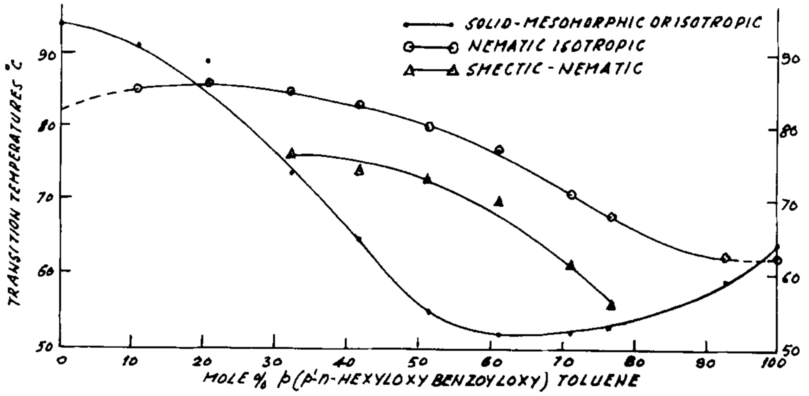


FIGURE 4 *p*(*p*'-*n*-hexyloxybenzoyloxy) toluene: *p*-nitro benzylidene-*p*'-*n*-hexyloxy aniline.

System IIc: NBPA + NBBA

This binary system also has both the components with strongly polar nitro end group and both the components are homologues. The behaviour of the binary phase diagram is similar to the System IIb (Figure 6).

System III: Two non-mesogenic homologues.

System IIIa: NBHA + NBPA

Both the components have strongly polar terminal nitro group and the mixture does not exhibit mixed mesomorphism.

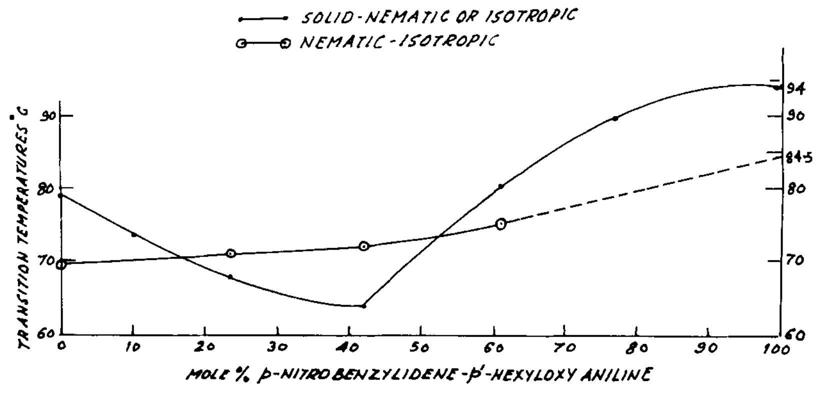


FIGURE 5 *p*-nitro benzylidene-*p*'-hexyloxy aniline: *p*-nitro benzylidene-*p*'-*n*-butoxy aniline.

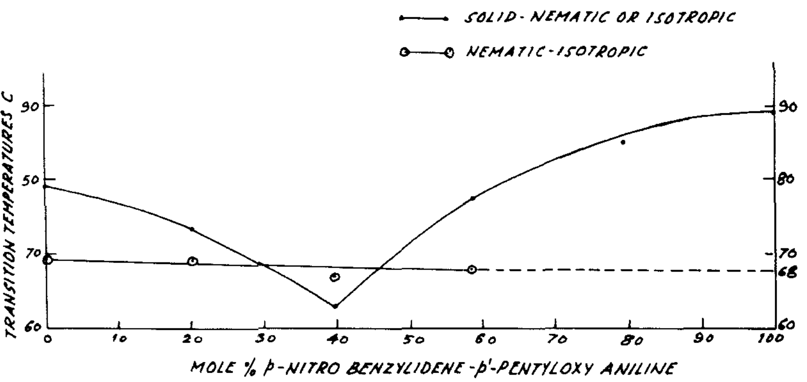


FIGURE 6 *p*-nitro benzylidene-*p*'-*n*-pentyloxy aniline: *p*-nitro benzylidene-*p*'-*n*-butoxy aniline.

System IIIb: BBT + PBT

Both the components have alkoxy group at one end and methyl group at the other end. No mixed mesomorphism is observed in the binary system.

The binary phase diagrams of systems Ia to Ic (Figures 1 to 3) are of interest as mesomorphism is observed even though both the components are non-mesogenic by themselves. Recently some binary systems consisting non-mesogenic compounds are known to give an induced smectic phase along with a nematic phase.[16] In the systems Ib and Ic induced smectic mesophase is observed along with a nematic mesophase. One of the components, in all the three binary systems

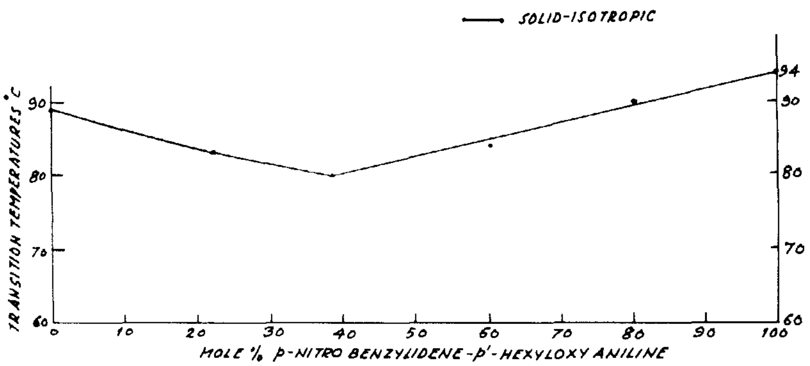
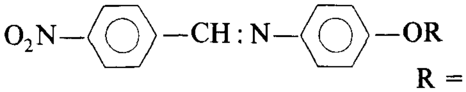
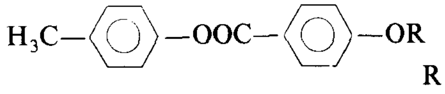


FIGURE 7 *p*-nitro benzylidene-*p*'-*n*-hexyloxy aniline: *p*-nitro benzylidene-*p*'-*n*-pentyloxy aniline.

possesses strongly polar terminal nitro group and both the components differ in their central linkages. The structures of both the components are given below.



R = $-C_4H_9, -C_5H_{11}, -C_6H_{13}$.



R = $-C_4H_9, -C_5H_{11}, -C_6H_{13}$

The gradual increase in mesogenic character is observed as we proceed from system Ia to Ic. Interesting part is that both the components are members of two homologous series. The components of system Ia have even end alkoxy groups; system Ib has odd and even alkoxy end groups while system Ic has both the alkoxy groups with odd members. This suggests that end odd alkoxy group also contributes towards the inducement of smectic mesophase along with other factors like terminal nitro group and the nature of central linkage.

The non-linear behaviour of the binary phase diagrams where one of the components has strong polar end group have been reported by various workers.[6,17–20] Vora and Dixit[9] have also reported such binary systems when both the components are mesogenic as well as when one of the components is non-mesogenic.

In the present study we have observed such behaviour, that is, induction of smectic and nematic mesophase with non-linear tendency of the transition temperature curve.

In the system IIa, one of the components exhibiting a monotropic nematic phase has a strongly polar nitro group. The system exhibits

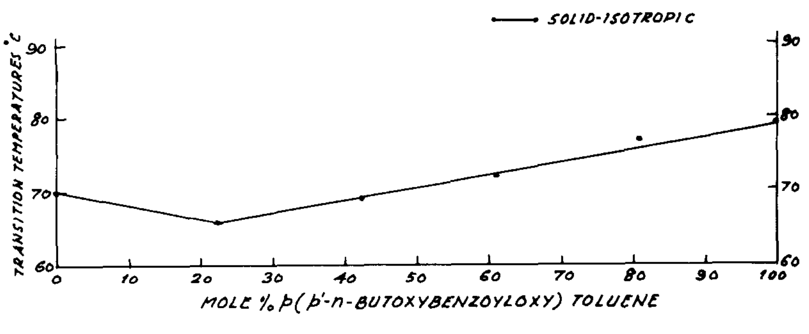


FIGURE 8 *p*(*p*'-*n*-butoxybenzoyloxy) toluene: *p*(*p*'-*n*-pentyloxy-benzoyloxytoluene.

induced enantiotropic smectic phase, enhanced nematic phase and non-linear behaviour of phase diagrams. The systems IIb and IIc exhibit ideal behaviour where both the components are homologues with terminal nitro group. Vora and Dixit[9] have tried to explain such behaviour by proposing a modified model of molecular arrangement by taking into account the molecular packing and dipole interactions for mesogenic–mesogenic and non-mesogenic–mesogenic systems. The explanation can also be extended to present systems. Systems of type III provides interesting results. The non-mesogenic compounds exhibiting mixed mesomorphism with other non-mesogenic compounds having different chemical structure do not exhibit mixed mesomorphism with their own non-mesogenic homologues. This indicates that the structural dissimilarity such as central linkages and end groups play very important role in such systems. Dave *et al.*[14,21] have pointed out that dissimilarity in structures depresses the melting points much more than isomorphous substances in binary systems.

The latent transition temperatures obtained for NBHA is 85° and 82°C respectively in two systems (Ia and IIa). The latent transition temperatures obtained for NBPA is 72.5° and 74.5°C in system Ib and Ic. These values of latent transition temperatures obtained by extrapolation is almost the same in different systems indicates homogeniety of the mixtures and reliability of the extrapolation method. The latent transition temperature values of these compounds also match with the values obtained by extrapolating nematic–isotropic transition temperature curves of both the homologous series.[11,12]

The depression in melting point is quite good and number of composition exhibit mesophases at ambient temperatures.

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