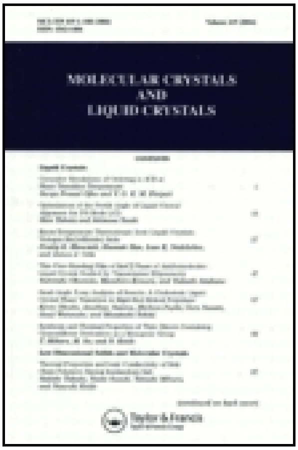

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Exhibition of Induced Mesophases in the Binary Systems Where Both the Components are Non-Mesogenic

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Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 43-54
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Exhibition of Induced Mesophases in the Binary Systems Where Both the Components are Non-Mesogenic

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Binary systems of two non-mesogens exhibiting mesomorphism are rare. In the present study few binary systems of non-mesogens exhibiting smectic and/or nematic mesophases are reported. One of the components is Schiff base having terminal isopropyl group and the other component contains an ester linkage. The binary systems of non-mesogens with terminal iso-propyl group having identical structures (homologues) also exhibit induced mesomorphism. Some of the binary compositions exhibit smectic phase at ambient temperature. The phase diagrams of the present study are discussed in detail and the common features emerging from the overall study are outlined.

Keywords: Induced Mesophases; Binary Systems; Non-mesogenic Components

INTRODUCTION

Early studies on binary mixtures have suggested the formation of mixed mesomorphism from the pairs of compounds which are non-mesogenic by themselves.[1-3] Bennet and Jones[4] reported that p-methoxybenzoic acid and p-ethoxybenzoic acid which are non-mesogenic, do exhibit nematice 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. Gupta and Vora[6] have reported number of binary mixtures where both the components are non-mesogenic exhibit mesomorphism with non-linear tendency of the transition temperature curve. Vora et al[7] observed the induced mesomorphism in the binary mixtures where both the components belong to different homologous series. One of the components possesses a nitro group while other component is an ester with $-CH_3$ or $-COOC_5H_4$ terminal group. Prajapati[8] reported the induction of smectic mesophase in the binary mixtures of esters having terminal broken

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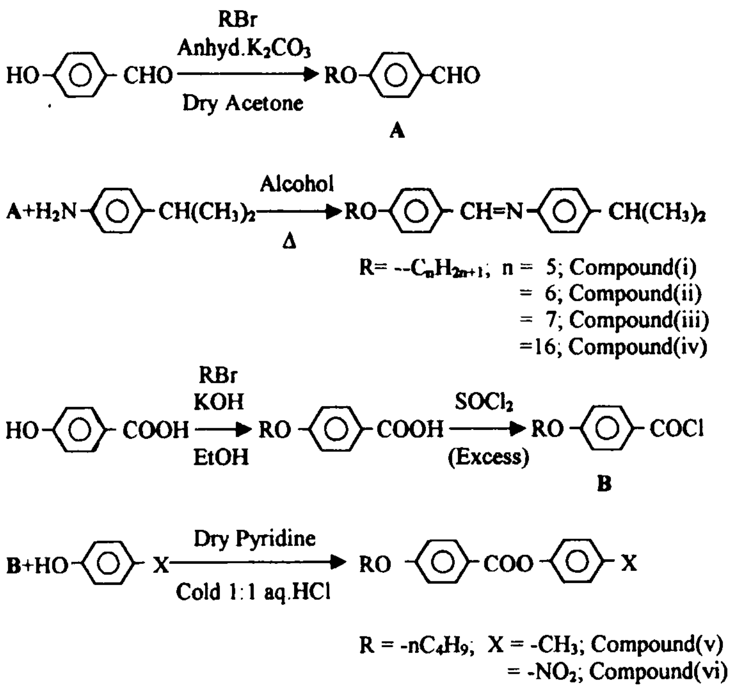
alkoxy chain in one of the component. Recently, Mahajan et al[9] have reported induction of mesophases by intermoleculor hydrogen bonding in few binary mixtures where both the components are non-mesogenic by themselves. Binary mixtures with both the components are non-mesogenic becomes an interesting and enlighting feature when they exhibit mesomorphism at ambient temperature. In the present study we report number of binary systems where two non-mesogens exhibit smectic and/or nematic mesophases at ambient temperature over a certain range of concentration.

EXPERIMENTAL

Preparation of compounds

The Scheme 1 shows the detail of synthetic route for the preparation of following compounds.



Scheme 1: Synthetic route to compound (i) to compound (vi)

(i). 4-n-Pentyloxybenzylidene 4'-iso-propylaniline(5BiPA)
(ii). 4-n-Hexyloxybenzylidene 4'-iso-propylaniline(6BiPA)
(iii). 4-n-Heptyloxybenzylidene 4'-iso-propylaniline (7BiPA) and
(iv). 4-n-Hexadecyloxybenzylidene 4'-iso-propylaniline (16BiPA) were synthesized by condensation of an appropriate 4-n-alkoxybenzaldehyde with 4-iso-propylaniline as described by Prajapati[8]
(v). 4 (4'-n-Butyloxybenzoyloxy) toluene (4BT) and
(vi). 4(4'-n-Butyloxybenzoyloxy) nitrobenzene (4BNB) were synthesized by the condensation of 4-n-butyloxybenzoylchloride with p-cresol and p-nitrophenol, respectively by following the procedure described by Dave and Vora.[10]

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 homogeneous mixture. The melt was quenched and the solid obtained was ground finely and was used for determining transition temperatures.

The transition temperatures were determined by using a Leitz Laborlux 12 POL microscope provided with a heating stage. The transition temperatures were determined on heating as well as cooling.

RESULTS AND DISCUSSION

The following six binary mixtures having both the components non-mesogenic are studied.

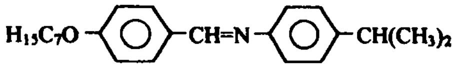
System I : 7 BiPA + 4BT
System II : 7 BiPA + 4BNB
System III : 16 BiPA + 4BNB
System IV : 5 BiPA + 4BNB
System V : 7 BiPA + 6BiPA
System VI : 7 BiPA + 16BiPA

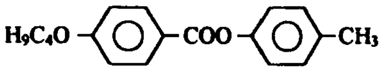
The transition temperatures of the systems I-VI are given in Table I-VI, respectively. The plots of transition temperatures versus mole percent are given in figure I-VI.

System I: 7BiPA + 4BT

Reference to binary phase diagram (Figure 1) shows that system is non-mesogenic when the concentration of 7BiPA is low but the monotropic smectic A phase is induced from 35.98 to 88.35 mole % concentration of 7BiPA. The smectic-isotropic transition temperatures curve is extrapolated on the side where monotropic nature is observed. The extrapolation method of finding a transition temperature is more reliable if monotropic mesophases are observed upto certain concentration range [6,7,11-14]. The latent transition temperature obtained by this method is 37.5^{0}C for 7BiPA.

Table-I: Transition temperatures of system-I

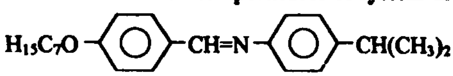
A: 

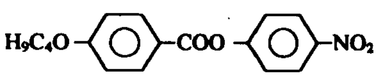
B: 

Mole % of A	S_A	I
00.00	-	79.0
07.77	-	74.0
17.39	-	58.5
26.53	-	56.0
35.98	(34.0)[a]	54.0
45.73	(34.5)	52.5
55.83	(39.5)	47.0
66.29	(39.0)	50.0
77.12	(37.5)	50.5
88.35	(37.5)	62.5
100.00	-	58.0

[a]values in the parenthesis indicate monotropy

Table-II: Transition temperatures of system-II

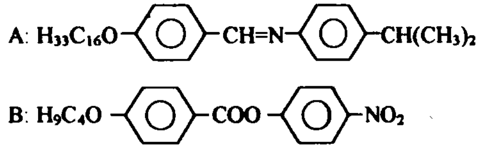
A: 

B: 

Mole % of A	Transition Temperatures		
	S_A	N	I
00.00	-	-	60.0
09.42	-	(44.5)[a]	60.0
18.92	-	(50.5)	65.0
28.60	41.5	-	71.5
38.39	49.5	-	76.0
48.32	51.0	-	77.0
58.36	42.5	-	75.5
68.57	*	-	74.0
78.90	36.5	-	73.5
89.39	37.0	-	70.5
100.00	-	-	58.0

[a]values in the parenthesis indicate monotropy,
*mixtures remain smectic on quenching even at 0^0C.

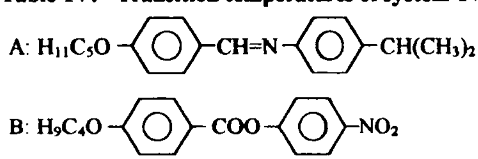
Table-III: Transition temperatures of system-III



Mole % of A	Transition Temperatures		
	S_A	N	I
00.00	-	-	60.0
07.03	-	(48.0)[a]	65.5
14.53	-	(52.0)	74.0
22.57	-	(54.5)	78.0
31.18	(56.0)	(60.5)	74.5
40.49	(60.0)	-	75.0
50.50	(59.0)	-	76.5
61.36	(58.5)	-	77.0
73.12	(57.5)	-	78.5
85.98	(57.0)	-	80.0
100.00	-	-	80.0

[a]values in the parenthesis indicate monotropy,

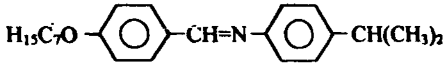
Table-IV: Transition temperatures of system-IV

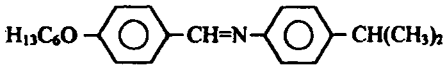


Mole % of A	Transition Temperatures		
	S_A	N	I
00.00	-	-	60.0
10.19	-	(42.0)a	61.0
20.30	-	(47.0)	57.0
30.40	(40.0)	(49.0)	56.0
40.45	36.0	-	62.5
50.48	28.5	-	65.0
60.46	*	-	65.0
70.40	*	-	66.0
80.30	39.0	-	67.5
90.19	58.0	-	64.0
100.00	-	-	60.0

[a]values in the parenthesis indicate monotropy.
*Mixtures remain smectic on quenching even at ^{0}C

Table-V: Transition temperatures of system-V

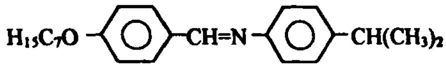
A: 

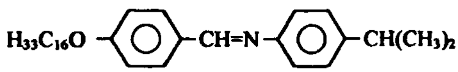
B: 

Mole % of A	Transition Temperatures	
	S_A	I
00.00	-	64.0
09.63	-	67.5
19.32	-	69.0
29.11	-	72.0
38.99	(50.5)[a]	71.5
48.96	(50.0)	70.0
58.97	(48.5)	65.0
69.10	(49.0)	60.5
79.31	(50.0)	56.5
89.60	(46.5)	57.0
100.00	-	58.0

[a]values in the parenthesis indicate monotropy,

Table-VI: Transition temperatures of system-VI

A: 

B: 

Mole % of A	Transition Temperatures	
	S_A	I
00.00	-	80.0
13.25	-	81.0
25.55	-	78.5
37.05	(58.0)[a]	74.0
47.80	(54.5)	69.0
57.88	(52.0)	60.0
67.34	(51.0)	58.5
76.22	(49.5)	57.0
84.60	(47.0)	58.0
92.52	-	59.5
100.00	-	58.0

[a]values in the parenthesis indicate monotropy.

System II: 7BiPA + 4BNB

The binary phase diagram (Figure 2) exhibits interesting behaviour. The two non-mesogens induced monotropic nematic phase when the concentration of 7BiPA is low (<20 mole %) whereas induced enantiotropic smectic A phase is appear with further increase in the concentration of 7BiPA. The enantiotropic smectic A mesophase persist even upto 89.39 mole % concentration of 7BiPA. This may be due to the marked depression in the melting point of the binary mixture from 18.9 to 89.39 mole % concentration of 7BiPA. In the region of 68.57 to 89.39 mole % concentration of 7BiPA the smA phase obtained at ambient temperature. The latent transition temperature obtained for 4BNB by extrapolation method is 40^0C.

System III: 16BiPA + 4BNB

Figure 3 shows that an induced monotropic nematic phase appears upto 31.18 mole % concentration of 16BiPA whereas SmecticA mesophase commences at this concentration as a monotropic phase and persist upto 85.98 mole % concentration of 16BiPA. The latent transition temperature obtained for 4BNB by extrapolation method is 40^0C and that of 16BiPA is 56.5^0C.

System IV: 5BiPA + 4BNB

Reference to phase diagram (Figure-IV) shows that the monotropic nematic phase is induced from 10.19 to 30.40 mole % concentration of 5BiPA and monotropic Smectic A appears at this concentration which becomes enantiotropic with further increase in the concentration of 5BiPA. The enantiotropic Smectic A phase persist upto 90.19 mole % concentration of 5BiPA. The system exhibits enantiotropic Smectic A phase at room temperature between 50.48 to 70.40 mole % concentration of 5BiPA.

The latent transition temperature obtained for 4BNB by extrapolation method is 40^0C. The value of latent transition temperature obtained in systems II-IV for 4BNB agree well with the value reported by Vora et al[7]

System V: 7BiPA + 6BiPA

Binary phase diagram (Figure V) exhibits an induced monotropic smectic A phase between 38.99 to 89.60 mole % concentration of 7BiPA. The latent transition temperature obtained by extrapolation for 7BiPA is 38^0C.

System VI: 7BiPA + 16 BiPA

The system exhibits induced monotropic smectic A phase between 37.05 to 84.60 mole % concentration of 7BiPA (Figure VI). Extrapolated latent transition temperature for 7BiPA is 39^0C.

In system I-IV one of the components is a Schiff base with terminal isopropyl group while the other is an ester with $-CH_3$ or $-NO_2$ terminal group. System I is purely monotropic smectogenic in nature whereas both smectic and nematic mesophases are induced in the systems II-IV

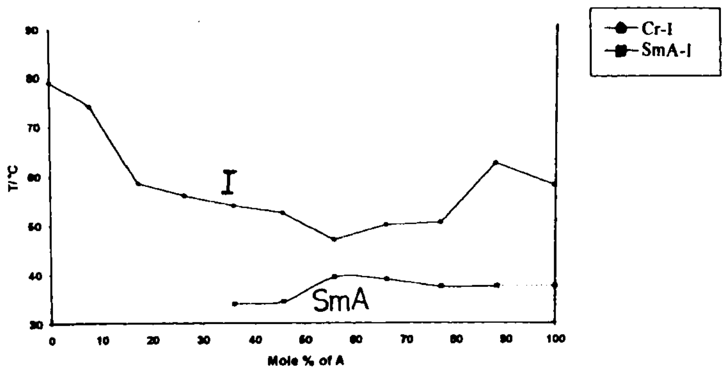


Figure 1: 7BiPA : 4BT(System-I)

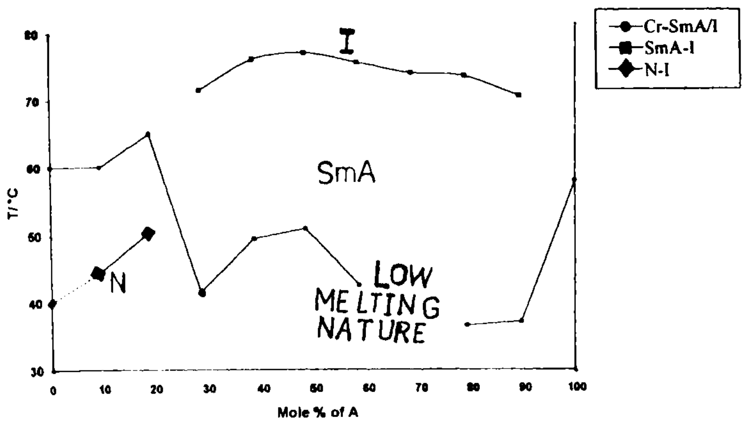


Figure 2: 7BiPA : 4BNB(System-II)

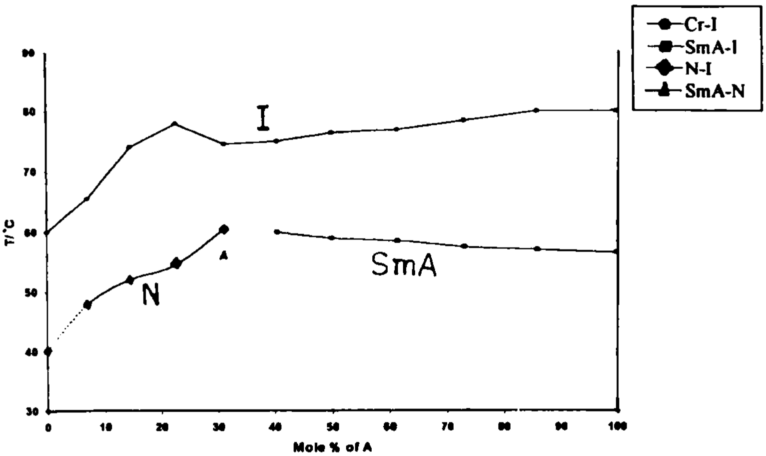


Figure 3: 16 BiPA : 4BNB(System-III)

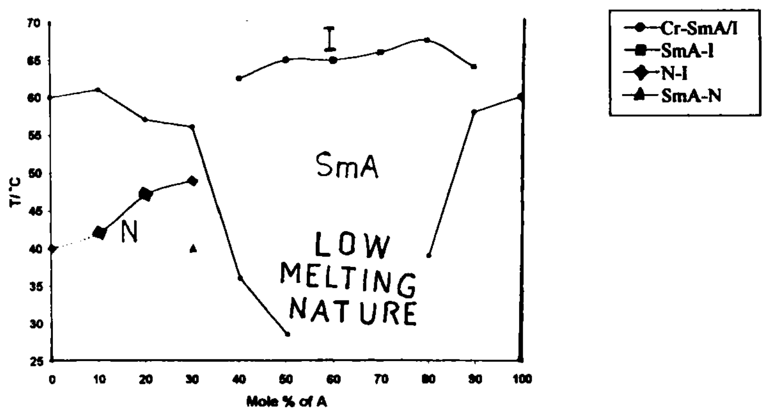


Figure 4: 5 BiPA : 4BNB(System-IV)

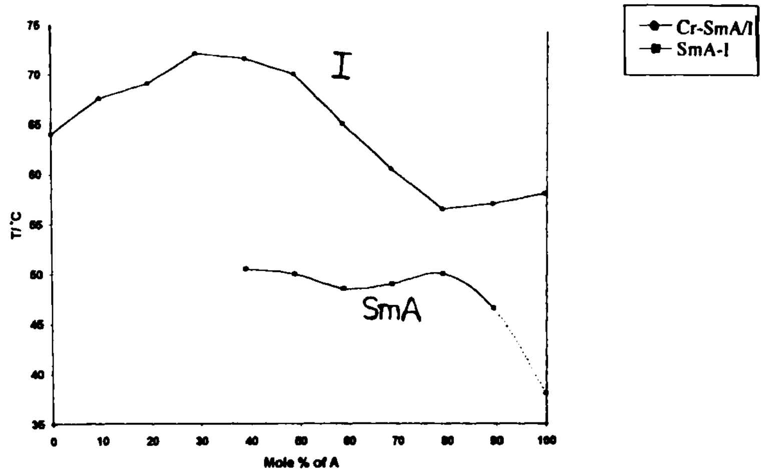


Figure 5: 7 BiPA : 6BiPA(System-V)

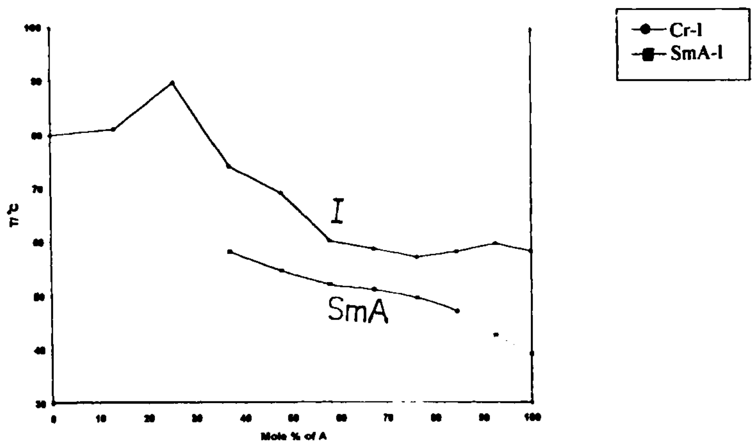


Figure 6: 7 BiPA : 16BiPA(System-VI)

This indicates that the terminal nitro group must be playing some role for the induction of both the phases in the binary systems II-IV. Some binary systems consisting non-mesogenic compounds are also reported in the literature[6,15] to give an induced smectic phase along with a nematic phase.

One of the components in binary systems II-IV is 4BNB while the other is a Schiff base with identical structure (homologous) to each other. In systems II and IV, monotropic nematic and enantiotropic SmA phase is observed whereas in system III both nematic and SmA mesophase observed are monotropic in nature. This suggests that terminal alkoxy group contributes towards the induction of an enantiotrotropic nature of smectic mesophase and to much longer alkoxy chain affects adversely for the induction of an enantiotropic smectic mesophase in the present investigation.

In systems V and VI both the components having identical chemical structures (homologous). Gupta and Vora[6] reported in their study that binary systems of non-mesogens having identical structures do not exhibit mesomorphism whereas a monotropic smectic A mesophase is observed in both the present systems V and VI.

The latent transition temperatures obtained for 7BiPA is 37.5, 38.0 and 39.0^{0}C respectively in three systems I, V and VI. The latent transition temperatures obtained for 4BNB is 40^{0}C in all the three systems II to IV. These values of latent transition temperatures obtined by extrapolation is almost the same in different systems indicates homogeniety of the mixtures and reliability of the extrapolation method.

The study provides number of binary systems of non-mesogens which exhibit mesophases at ambient termperatures.

CONCLUSION

The terminal nitro group is found to be responsible for the induction of both the nematogenic and smectogenic tendency in the present investigation of binary systems with two 'incompatible' components i.e. one with an azomethine central linkage and the other with an ester linkage. In the present work, even though the two components are 'compatible', i.e., both have central azomethine linkage, induced mesophases are exhibited by the binary systems.

Since number of composition of binary systems II and IV exhibit enantiotropic smectic A phase below room temperature they may have potential applications in display devices.

Acknowledgments
The authors are thankful to Head of the Applied Chemistry Department and Dean, Faculty of Technology and engineering for providing research facilities.

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