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Induced Mesophases in Binary Systems of Non-Mesogens Where One of the Component is 1,2,4 Trisubstituted Benzene Derivatives

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Exhibition of mixed mesophases in binary systems where both the components are non-mesogens by themselves offer a very interesting study. In the present work four binary systems were studied where one of the components is non-mesogenic 1,2,4-trisubstituted benzene derivative while the other components are rod shaped non-mesogens. Induction of mesophases is observed in all the binary systems studied. Few compositions on cooling remain in liquid crystalline phase at the ambient temperatures for about 48 hours.

INTRODUCTION

Non-linear mesomorphic compounds have many applications. However, a majority of such compounds do not exhibit stable mesophases at ambient temperatures. On mixing such compounds with other rod-like compounds 'filled mesophases' may be obtained. With this in view, four binary systems were prepared where one of the components is swallow tailed/wedge shaped and the other component is rod-like. Both the components are non-mesogenic. Schiff bases and other compounds with nitro group have certain structural characteristics considered essential for the exhibi-

tion of mesophases in their binary mixtures. Hence, such compounds were selected for the present investigations.

EXPERIMENTAL

1. Preparation of compounds.

- (i) 4'-chloro-2,4-bis(4"-ethoxy benzoloxy) azobenzenes were synthesized by condensing 2 moles of 4-ethoxy benzolo acid with 1 mole of 2,4-dihydroxy 4'chloro azobenzene(1)
- (ii) 4-nitrobenzylidene 4' -n-hexyloxy aniline and
- (iii) 4-nitrobenzylidene -4'-methoxy aniline were synthesized as reported by Vora and Dixit (2)
- 4-(4'-n- butoxy benzoloxy) nitrobenzene was synthesized as described by Lohar and Dave for cinnamoyl derivatives(3)
- (v) 4-anisal 4'-chloroaniline was synthesized as described by Vora (4)

2. Preparation of Mixtures

In all the systems studied the 1,2,4-trisubstituted benzene is common component which is mixed with other rod shaped molecules.

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

The transition temperatures were determined by using Leitz Laborlux 12 POL microscope.

The transition temperatures are given in tables 1 to 4. The plots of transition temperatures versus mole percentage are given in figures 1 to 4.

Table: 1 System I

Mole % A	Transition Temperatures ^o C	
	Smectic	Isotropic
0.0		94.0
6.25	(92.0)*	94.0
13.04	(90.0)	98.0
19.23	(88.0)	99.0
27.56	(86.0)	104.0
37.50	(85.0)	116.0
47.80	(84.0)	120.0
58.18#	(76.0)	126.0
70.53#	(76.0)	126.0
84.30#	(68.0)	128.0
100.00		130.0

Table: 2 System II

Mole % A	Transition Temperatures ^o C		
	Smectic	Isotropic	
0.0		64.0	
5.92	(54.0)*	105.0	
12.41#	(58.0)	113.0	
18.52#	(59.0)	120.0	
26.92#	(62.0)	119.0	
36.00#	(62.0)	122.0	
46.41	(64.0)	124.0	
57.4	(112.0)	126.0	
69.85	~~~ ~~~	116.0	
83.7		128.0	
100.00		130.0	

^{*} values in the paranthesis indicate monotropy # monotropic phase persists upto 24-48 hours

Table: 3 System III

Mole % A	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0.0			98.0
3.34			88.0
7.26			88.0
11.11		(68.0)*	94.0
16.83		(70.0)	98.0
23.68		(72.0)	101.0
32.35	(68.0)*	(75.0)	121.0
42.52	(57.0)	(86.0)	124.0
55.94	(62.0)	(110.0)	124.0
94.32	(98.0)	(120.0)	126.0
100.00			130.0

Table: 4 System IV

Mole % A	Transition Temperatures ^o C		
	Smectic	Nematic	Isotropic
0.0			143.0
3.54	(105.0)*	135.0	141.0
7.72	(97.0)	135.0	137.0
11.63	(92.0)	131.0	136.0
17.50	(89.0)	(115.0)*	129.0
25.00	(78.0)	(101.0)	130.0
33.33	(66.0)		126.0
43.75	(88.0)		124.0
57.03			128.0
76.74			126.0
100.00			130.0

^{*} values in the paranthesis indicate monotropy

Figure - 1 System - 1

$$A = C_2H_5O \longrightarrow OOC \longrightarrow N=N \longrightarrow CI$$

$$OOC \longrightarrow OC_2II_5$$

$$B = H_{13}C_6O \longrightarrow N=CH \longrightarrow NO_2$$

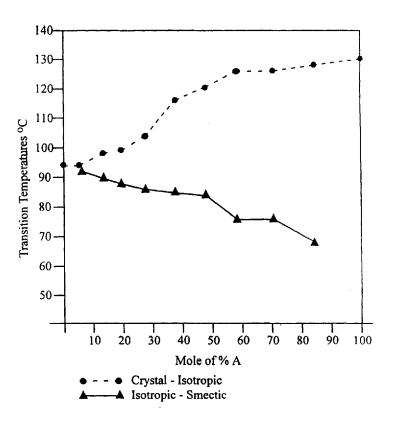


Figure - 2 System - II

$$A = C_2H_5O - OOC - N=N - OC_2H_5$$

$$OOC - OC_2H_5$$

$$B = H_9C_4O - OC_2 - NC_2$$

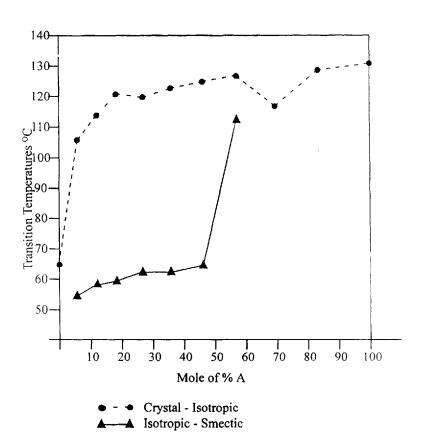


Figure - 3 System - III

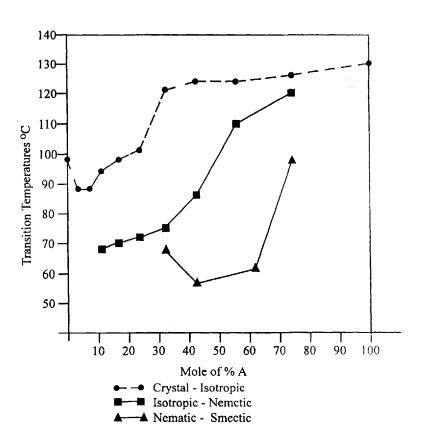
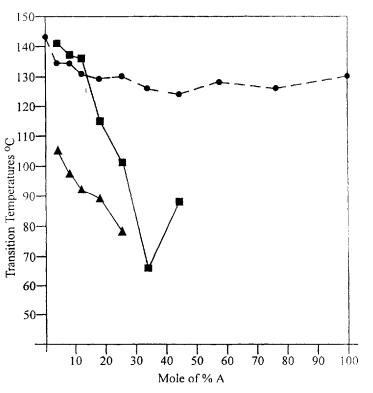


Figure -4 System - IV

$$A = C_2H_5O - \bigcirc \bigcirc \bigcirc - OOC - \bigcirc \bigcirc - N=N - \bigcirc \bigcirc - CI$$

$$OOC - \bigcirc \bigcirc - OC_2H_5$$

$$B = H_3CO - \bigcirc \bigcirc - N=CH - \bigcirc - NO_2$$



-- Mesomorphic/crystal - Isotropic

Mesomorphic - Isotropic

▲ A Nematic - Smectic

RESULTS AND DISCUSSION

In system I induced monotropic smectic phase is observed from 6 mole % of the swallow tailed compound and persists upto 83 mole%, whereas in system IV where the terminal hexyloxy group of component B of series I is replaced by methoxy group, induced nematic and smectic mesophyses are observed with 3.5mole% of the diester. Enantiotropic nematic phase is obtained with lower concentrations of diester which becomes monotropic in nature and persists upto 25mole% of diester. Enhanced mesomorphism in system IV may be attributed to the closer packing of the rod-shaped molecules with smaller methoxy group between the gaps of bulky terminal branches of diester as suggested by Haddawi et al (5,6) which may not be as effective with the longer hexyloxy group of schiff base in system I.

System III is less mesogenic as compared to sytem IV. In system III, the azomethine linkage of component B is reversed and the terminal nitro group is replaced by chloro group. Nitro group is more conducive to induced mesomorphism as compared to chloro group. This may be the reason behind the low mesogenicity of system III as against that of system IV. System II is the least mesogenic. Here the component B contains an ester linkage in place of an azomethine linkage as in systems I,III & IV. This decreases the mesogenicity as compared to the other three systems.

The component A is common in all the systems studied, therefore the effect on the nature and the stability of induced mesophases may be attributed to the role of component B. The effective packing of component B in between the branching of component A will be responsible for the phase stability.

In few compositions of system I and II, the induced mesophases persists for about 24-48 hours at ambient temperatures. This highly super cooling

tendency may find applications. By selecting proper components the induced mesophase may be stabilized for longer periods without crystallization taking place.

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