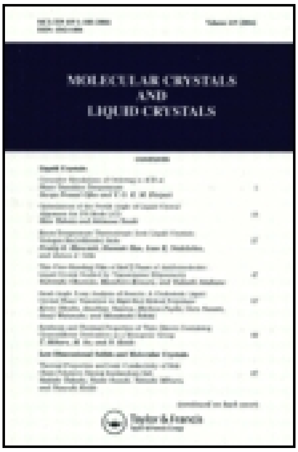

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: A. V. Doshi, D. A. Odedara & R. B. Patel (2012): Mesomorphism of Binary Systems of Nonmesogenic Compounds, Molecular Crystals and Liquid Crystals, 552:1, 97-103

To link to this article: http://dx.doi.org/10.1080/15421406.2011.604589

Mol. Cryst. Liq. Cryst., Vol. 552: pp. 97–103, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.604589

Mesomorphism of Binary Systems of Nonmesogenic Compounds

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Three binary systems, each consisting of two nonmesogenic compounds, viz. p-tolual-p-phenetidine (M.P. 108.5°C) [A] as the common component, and Methyl p-(p′-n-butyloxy benzoyloxy) benzoate (M.P. 119.0°C) [B_1], Ethyl-p-(p′-n-butyloxy benzoyloxy) benzoate (M.P. 94.0°C) [B_2], and n-Butyl p-(p′-n-butyloxy benzoyloxy) benzoate (M.P. 130.0°C) [B_3] as the second component, respectively, are studied with a view to understand the effect of terminal groups on nematic and/or smectic mesomorphism. Latent transition temperatures (LTT) of the constituent components A, B_1, B_2, and B_3 were determined by extrapolation. Binary system ($A + B_1$) induces a nematogenic mesophase while binary systems ($A + B_2$) and ($A + B_3$) both induce a smectic mesophase in addition to a nematic mesophase. Phase diagrams of the binary systems under investigation are plotted for the mole percent of component (A) versus the transition temperatures of each binary system as determined from polarizing optical microscopy. The texture of the nematic mesophase is of threaded type and that of the smectic mesophase is focal-conic fan shaped of the type smectic-A. Components A, B_1, B_2, and B_3 were prepared by established methods. Analytical data support the structure of molecules under investigation. Melting points of the constituent components match with data reported earlier.

Keywords Mixed mesomorphism, mixed melt, meshophase, smectic, nematic

Introduction

Some nonmesogenic substances have the potential to exhibit mesomorphic behavior; however, the mesophase does not appear because the temperature of the transition lies below the normal melting point. Such substances in their binary mixtures with another nonmesomorphic substance can give rise to "mixed liquid crystal" formation over a range of temperature and composition. The range of composition over which the mesophase exists depends upon the degree of similarity in shape, size, polarity, and polarizability of the components to cause anisotropic intermolecular forces of attractions of suitable magnitude, which can keep properly aligned molecules and/or a sliding layered arrangement of molecules in the binary mixture. Naturally, a search for their virtual transition temperatures by extrapolation is of great importance.

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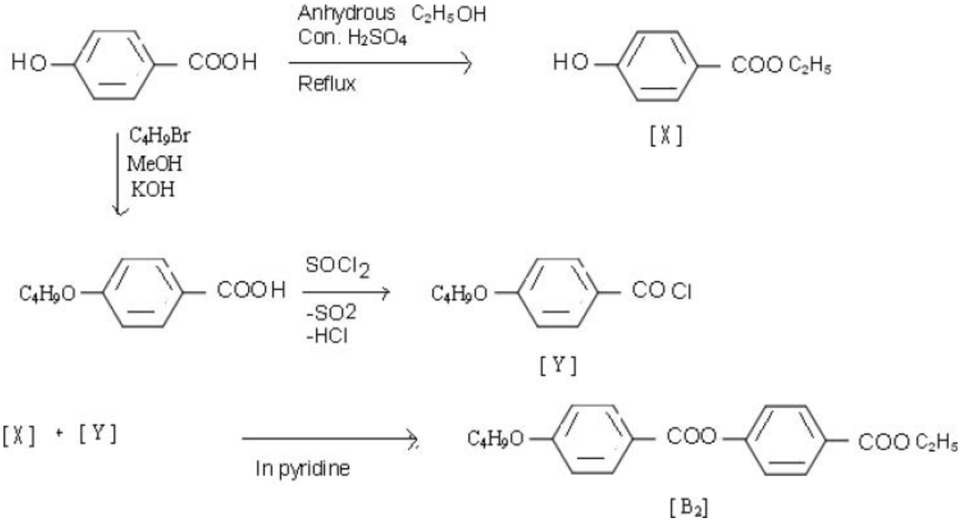
Experimental

Preparation

The common component (A) of the binary system *p*-tolual-*p*-phenetidine was prepared by refluxing equimolar proportions of *p*-tolualdehyde and *p*-phenetidine in alcohol for 2–3 h by an established method [1].

The uncommon components were prepared by the method described by Lohar and Doshi et al. [2–10] as shown in Scheme 1.



Scheme 1.

Similarly, methyl-*p*[*p*′-*n*-butyloxy benzoyloxy] benzoates [B_1] and *n*-butyl-*p*[*p*′-*n*-butyloxy benzoyloxy] benzoates [B_3] were synthesized according to Scheme 1.

Method

Transition temperatures of the binary systems (i) $A + B_1$, (ii) $A + B_2$, and (iii) $A + B_3$ and of pure substances A, B_1, B_2, and B_3 are determined by polarizing optical microscopy.

Preparation of Binary Mixtures

Binary mixtures of the binary systems (i) $A + B_1$, (ii) $A + B_2$, and (iii) $A + B_3$ were prepared by the established method of Lohar and Doshi et al. [2–10].

Results and Discussion

Binary systems $A + B_1$, $A + B_2$, and $A + B_3$ consist of *p*-tolual-*p*-phenetidine as a common component. The components under discussion are originally non-mesomorphic,

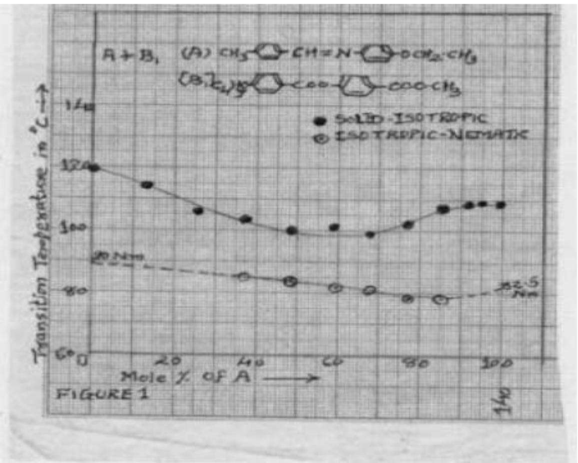


Figure 1. Phase diagram 1.

but monotropic nematic mesomorphism in the case of binary system A + B_1 and smectic mesophase in addition to nematic mesophases in the case of binary systems A + B_2 and A + B_3 are induced monotropically and enantiotropically, respectively. The respective phase diagrams of the binary systems are shown in Figs 1–3, drawn from Tables 1–3. The range of composition over which nematic and smectic mesophases appear in a binary mixture are represented in Table 4, as determined from the respective phase diagrams of the binary systems (Figs 1–3).

The components of binary systems under discussion individually do not form mesophases either monotropically or enantiotropically, but binary mixtures exhibit mixed mesomorphism over a range of composition and temperature, at constant pressure. Such components are highly crystalline and are not readily supercooled from the amorphous melt, which results in monotropic behavior. The net intermolecular forces of attraction generated are anisotropic and of suitable magnitude within a definite range of composition

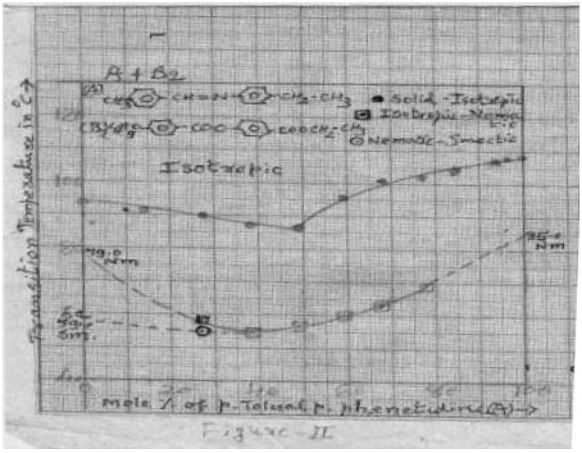


Figure 2. Phase diagram 2.

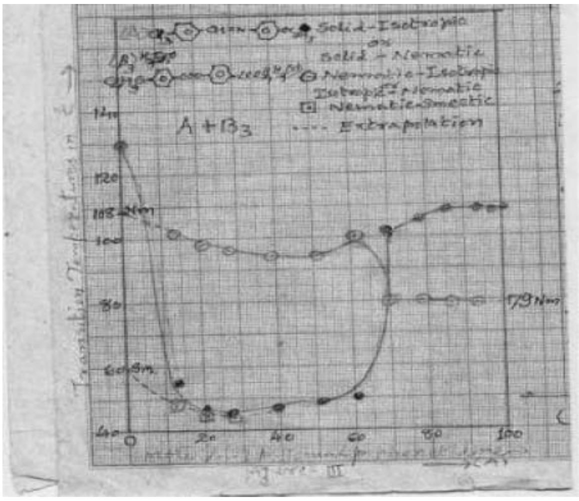


Figure 3. Phase diagram 3.

and temperatures (Table 4) as a consequence of similarity in molecular shape, size, polarity, polarizability, and factors conducive to molecular alignment at an angle less than 90° to the plane of the surface to cause mesophase formation. Intermolecular forces of adhesion may cause a layered arrangement of molecules and hence form a smectogenic phase in addition to a nematogenic mesophase as observed in the case of binary systems A + B_2 and A + B_3. In the case of the present study, a common component *p*-tolual-*p*-phenetidine (A) and added components B_1, B_2, and B_3 possess two phenyl rings linked through a central bridge and a rod-like shape with common $-OC_4H_9$ terminal chains. Component (A) of a binary system has highly polar and polarizable right terminal end group $-OC_2H_5$. The

Table 1. Transition Temperatures of Binary system 1

		Transition temperatures in °C		
Sr. No.	Mole % A	Sm	Nm	Isotropic
1.	0.0	—	—	119.0
2.	13.25	—	—	114.0
3.	25.35	—	—	106.0
4.	37.16	—	(85.0)	106.0
5.	48.48	—	(83.5)	100.0
6.	59.41	—	(82.0)	100.0
7.	68.0	—	(81.0)	99.0
8.	76.81	—	(78.0)	102.0
9.	84.68	—	(78.3)	107.5
10.	92.04	—	—	108.0
11.	95.14	—	—	108.0
12.	100.0	—	—	108.5

Note: () indicates monotropic.

Table 2. Transition Temperatures of Binary system 2

		Transition temperatures in °C		
Sr. No.	Mole % A	Sm	Nm	Isotropic
1.	0.0	—	—	94.0
2.	13.71	—	—	92.0
3.	26.44	(55.0)	(57.0)	90.0
4.	37.94	—	(55.0)	88.0
5.	44.52	—	(56.6)	87.0
6.	58.95	—	(61.0)	96.0
7.	67.36	—	(62.7)	101.0
8.	76.75	—	(67.0)	102.0
9.	85.03	—	—	105.0
10.	92.86	—	—	107.0
11.	96.5	—	—	108.5
12.	100.0	—	—	108.5

Note: () indicates monotropic.

changing part of all the binary systems A + B_1, A + B_2, and A + B_3 involves different right-side terminals of the molecules B_1, B_2, and B_3 viz. $-COOCH_3$, $-COOCH_2CH_3$, and $-COOCH_2CH_2CH_2CH_3$, respectively. These end groups are polarizable and polar, which gradually increase the length of the molecules and hence result in an increase in the length to breadth ratio. Consequently, intermolecular end-to-end and lateral forces of attractions, and molecular polarizability increases from $B_{1\rightarrow}$ $B_{2\rightarrow}$ B_3 in combination with

Table 3. Transition Temperatures of Binary system 3

		Transition temperatures in °C		
Sr. No.	Mole % A	Sm	Nm	Isotropic
1.	0.0	—	—	130.0
2.	12.5	(48.0)	55.0	102.0
3.	20.69	(45.0)	46.0	98.0
4.	27.4	(44.0)	45.0	96.0
5.	38.88	—	47.0	94.0
6.	50.78	—	48.0	94.0
7.	60.75	—	50.0	100.0
8.	69.37	—	(80.0)	102.0
9.	78.31	—	(80.0)	105.0
10.	86.38	—	(79.0)	108.0
11.	93.23	—	(79.0)	108.5
12.	96.71	—	—	108.0
13.	100.0	—	—	108.5

Note: () indicates monotropic.

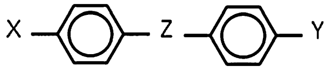
Table 4. Mole % of component (A) over which mesomorphism exists

		Mesophase range in mole %	
Sr. No.	Binary system	Smectic	Nematic
(i)	$A + B_1$	—	37.0–84.5
(ii)	$A + B_2$	27.5–38.0	27.5–78.0
(ii)	$A + B_3$	13.5–40.0	13.5–93.0

the end groups $-OC_2H_5$ and $-CH_3$ of component (A). Thus, resultant intermolecular forces of adhesion in the mixed melt are generated which are anisotropic and of suitable magnitude to cause a statistically parallel orientational order of molecules in all the binary systems, and intermolecular anisotropic forces of attractions are further strengthened to cause a lamellar molecular arrangement. Hence, binary system $A + B_1$ induces a monotropic nematic mesophase, binary system $A + B_2$ induces a monotropic smectic and nematic mesophases, and binary system $A + B_3$ induces monotropic smectic, as well as monotropic and enantiotropic nematic mesophases within a definite range of temperature and composition. The intermolecular forces of adhesion for the binary mixtures of binary systems $A + B_1$, $A + B_2$, and $A + B_3$ in a mixed melt within some range of composition other than that mentioned in Table 4 are not anisotropic and of suitable magnitude, which do not induce any mesophase but pass directly into the isotropic liquid state from the solid state, i.e., mesophase exhibition is restricted for such binary mixtures in which molecules are disaligned under the influence of applied heat.

Both constituent components of all the three binary systems under present investigation are chemically similar, and the melting point of the solid phase of the binary mixture falls below the mesophase to amorphous liquid transition temperature of the mixed liquid crystal phase, a temperature that lies between the two pure components. Such a mixture exhibits

Table 5. Comparison of LTT of component (A) and (B) of binary system

					LTT in °C				
					Present work		Doshi and Odedra		Doshi and Lohar, Joshi, Ganatra, Patel
S. No.		X	Z	Y	Sm	Nm	Sm	Nm	Nm
1.	(A)	CH_3	$-CH{=}N-$	OC_2H_5	—	82.5	—		90.0, 86.5,
					—	85.0	—	93.0	87.0, 84.0
					—	79.0	—	80.0	102.0
									—
2.	(B_1)	C_4H_9O	$-COO-$	$COOCH_3$	—	90.0	58.0	88.0	—
							71.0	88.0	
3.	(B_2)	C_4H_9O	$-COO-$	$COOC_2H_5$	59.0	79.0	60.0	78.0	—
							62.0	80.0	
4.	(B_3)	C_4H_9O	$-COO-$	$COOC_4H_9(n)$	60.0	108.0	66.0	100.0	—
							69.0	100.0	

enantiotropic liquid crystal properties as observed in case of binary system A + B_3. The binary phase diagrams (Figs 1–3) further suggest that when one of the components of a binary system is an ester, it induces mesomorphism. Induction of a smectic mesophase is more common.

Latent transition temperatures (LTTs) derived by extrapolation for the components A, B_1, B_2, and B_3 are quite agreeable to the values of LTT reported earlier for the same components. Thus, the concurrent values of LTT for the nonmesomorphic substances put the extrapolation method on more sound ground. Values of LTT as determined and shown in Table 5 are concurrent with permissible variation, though the first component of a binary system changed. Thus, the present investigation supports the view that the nonmesomorph is structurally similar to nonmesomorphic first or common component, and possesses sufficiently polar groups. Of course, for greater dependability of the extrapolation method, the eutectic points in such binary systems should preferably be in equilibrium with the anisotropic liquids and the terminal groups of the nonmesomorphs should be sufficiently polar. The evidence obtained by the present study raises the reliability and credibility of the extrapolation method to determine LTT of a non-mesomorph.

Conclusion

The present investigation supports the views that:

- The intermolecular forces of adhesion between similar and dissimilar molecules are anisotropic and of suitable magnitude that can restrict the molecules to disalign causing the formation of mesophases a binary system.
- LTT determination of a nonmesogenic substance by extrapolation of a transition curve of a phase diagram of a binary system can be done. Thus, the extrapolation method acquires more reliability and credibility by the present investigation.

Acknowledgments

The authors give thanks to ex. Professor and Head, Dr. R. A. Vora, of the Department of Applied Chemistry, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara, for his valuable cooperation and suggestions in the work.

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