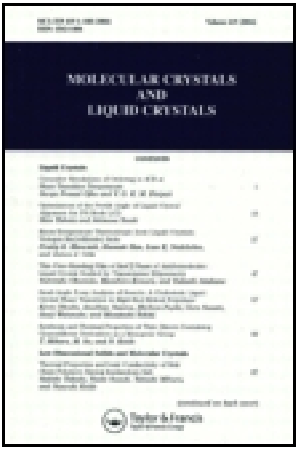

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 28 Mar 2007.

To cite this article: J. S. Dave , P. R. Patel & K. L. Vasanth (1969): Mixed Mesomorphism in Binary Systems Forming Smectic-Nematic Phases, Molecular Crystals, 8:1, 93-100

To link to this article: http://dx.doi.org/10.1080/15421406908084900

Molecular Crystals and Liquid Crystals. 1969. Vol. 8, pp. 93–100

Mixed Mesomorphism in Binary Systems Forming Smectic-Nematic Phases

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Abstract—A number of binary systems have been investigated with *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline — a mesomorphic component exhibiting both smectic and nematic phases — and other non-liquid crystalline solutes. When the transition temperatures of such binary systems are plotted against the mole per cent composition of the liquid crystalline component, two types of curve are obtained:

(1) A usual curve where the transition lines are depressed regularly and (2) a rising curve exhibiting only a smectic phase and a maximum. The latter type of curve indicates an enhancement in the smectic thermal stability while the former shows a decrease in the mesomorphic thermal stability during the course of mixed liquid crystal formation; the range of temperature over which the nematic phase exists increases at the cost of the smectic mesophase. It is observed that in such a binary mixture, if at least the first few compositions chosen melt to give the isotropic liquid at a temperature higher than the mesomorphic-isotropic liquid transition temperature of the pure liquid crystalline component, the mesomorphic-isotropic liquid transition curve exhibits a maximum and the mixture exhibits only a smectic phase.

Binary systems in which one or both the components are nematic liquid crystal have been investigated.[1–6] Such mixtures possess a pronounced ability to form homogeneous nematic melts over a range of temperature and concentration. The authors[7] have investigated mixed mesomorphism in the binary mixtures wherein one of the components is a pure smectic mesomorph and the other a non-liquid crystalline Schiff's base. Arnold and Sackmann[8] who studied the miscibility of the smectic phase of one compound with the nematic phase of the other compound have stated that the nematic liquids and smectic liquids are not continuously miscible. Little work seems to have been done pertaining to the effect of dissolution of a non-liquid crystalline substance in a mesomorphic component exhibiting both smectic and nematic phases. An attempt is made here to explore the possibility and the extent of mixed liquid crystal formation in such mixtures. As the liquid crystalline component is a polymesomorph, the mixed liquid crystal formation here can conveniently be called mixed polymesomorphism.

Results and Discussion

During the present investigation, the following binary systems (Table 1) are studied where *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline is a mesomorph exhibiting both smectic and nematic phases; the other component is a non-mesomorphic Schiff's base.

TABLE 1

Component A: *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline (a polymesomorphic liquid crystal)	
Component B:	m.p. °C
1. *p*-Anisal-*p*-phenetidine (monotropic nematic)‡	128.5
2. *p*-Anisal-*p*-anisidine	147.0
3. *p*-Dimethylaminobenzal-*p*-phenetidine	148.0
4. *p*-Anisal-*p*-chloroaniline	92.0
5. *p*-Anisal-*p*-bromoaniline	120.0
6. *p*-Nitrobenzal-*p*-phenetidine	123.5
7. *p*-Nitrobenzal-*p*-chloroaniline	132.0
8. *p*-Nitrobenzal-*p*-bromoaniline	163.0

‡ Transition temperature — 122 °C.

A nematic mesophase consists of rod-shaped molecules having translational freedom but only a restricted rotational freedom and thus possesses a domain structure wherein the molecules lie parallel to one another. Any other substance dissolved in such a liquid would be in an anisotropic environment and affect its mesomorphic properties. Dave and Dewar[5] and Dave and Lohar[6] in their study of mixed liquid crystal formation in the nematic phase have stated that the transition lines of binary systems in the phase diagrams stand as a measure of the tendency of the non-mesomorphic component towards mixed mesomorphism; thereby they have deduced different values of group slopes for various endgroups present in the non-mesomorphic component. The lower slope value indicates a greater tendency of the non-mesomorphic component towards mixed mesomorphism and vice versa.

A smectic mesophase is known to be a system of stratified structure in which rod-shaped molecules lie parallel in each stratum. The mesomorphic substance viz. *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline selected in this study, first melts at 101 °C giving rise to a stratified structure of the smectic phase and at 111.0 °C, it changes to a more mobile nematic phase; finally it becomes a clear liquid at 111.5 °C. These changes are reversible and before crystallization it gives one monotropic smectic phase at 95 °C. A non-mesomorphic substance dissolved in such a liquid should affect the mesomorphic properties of the smectic and nematic mesophases in an interesting manner. When solid-mesomorphic, mesomorphic-mesomorphic and mesomorphic-isotropic transition temperatures of these binary systems are plotted against mole per cent composition of the mesomorphic component, i.e. component A, two distinct types of phase diagram are obtained:

(i) a phase diagram having two transition curves, the lower one showing the smectic-nematic transition and the upper one marking the mesomorphic-isotropic transition (Figs. 1 and 2),

(ii) a phase diagram possessing a single smectic-isotropic transition curve exhibiting a maximum (Fig. 3).

In the case of the phase diagrams of the binary systems of the first type, the mesomorphic-isotropic transition temperatures lie on a gradually depressing curve. The transition curve is almost linear and compares with the transition curves obtained in the study of mixed mesomorphism in a pure nematic phase.[5,6]

The smectic-nematic transition temperatures in the first five systems lie on a regularly falling curve; the transition curve falls gradually in the phase diagrams of the binary systems where it cuts the melting point curve to the left of the eutectic (Fig. 1) and it is rather steep when it cuts the melting point curve to the right of the eutectic (Fig. 2).

The phase diagrams of the first five binary systems reveal that the nematic phase region increases at the cost of the smectic phase region as the concentration of the non-mesomorphic component increases. This may be attributed to the change in the molecular arrangement of the smectic phase due to the movement of the molecules in the direction of their long axes. At this stage the molecules must be slipping out of the characteristic layers of the smectic phase but remain parallel to one another in spite of their end positions being disturbed, thus giving a nematic phase. As the smectic-nematic transition curve continues, a state is reached when the smectic phase altogether disappears and the solid mixture passes directly into the nematic phase.

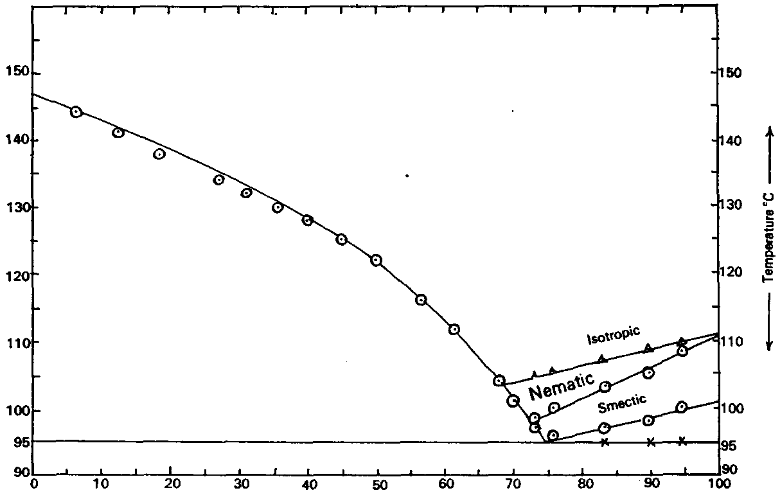

Figure 1. *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline: *p*-anisal-*p*-anisidine

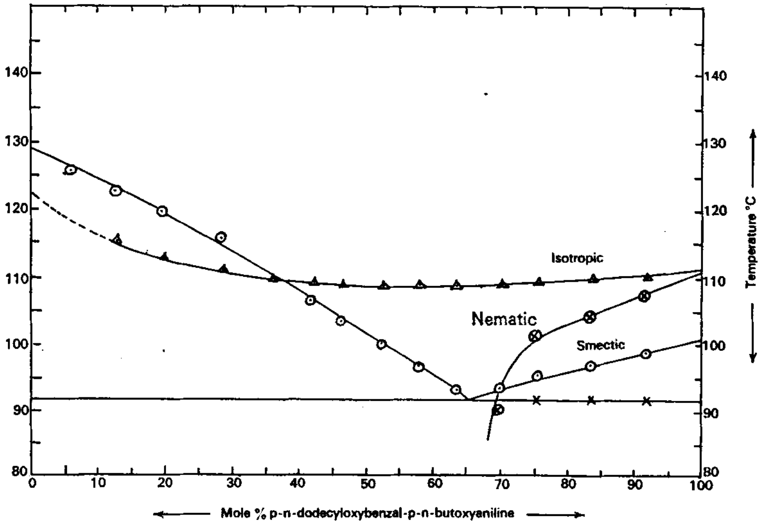

Figure 2. *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline: *p*-anisal-*p*-phenetidine

In the case of the phase diagrams of the binary systems of the second type (Fig. 3), the smectic-isotropic transition curve exhibits a convexity. It is interesting to note that in this case the nematic phase present in the pure *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline is eliminated by the addition of the non-mesomorphic nitro-compounds and the solid mixture passes to a pure smectic phase which in turn transforms to the isotropic liquid. In the smectic mesomorphic state of such systems, a condition is reached so that the molecules of the strata are not slipping away from their layers to form a nematic phase, but the thermal vibrations bring about the disruption of the parallel orientation of the molecules, to give rise to an isotropic liquid. Due to the high dipole moment of the nitro-compounds operating in the direction of the major molecular axis and thus supporting the terminal cohesive forces, the thermal agitation may result in the disruption of the smectic phase to give the isotropic liquid at a temperature higher than that of the mesomorphic-isotropic transition point of the pure liquid crystal.

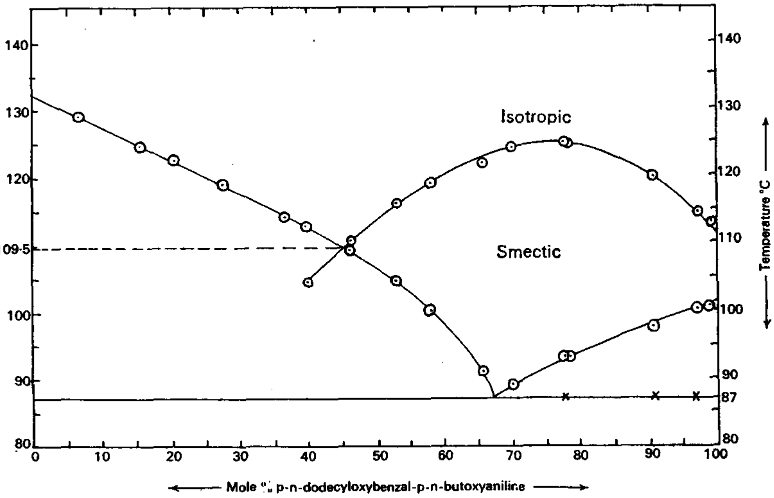

Figure 3. *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline: *p*-nitrobenzal-*p*-chloroaniline

The melting points, smectic-nematic points and the mesomorphic-isotropic temperatures of all the binary systems are recorded in Tables 2, 3, and 4 respectively.

Comparison of the phase diagrams of the first five binary systems with those of systems 6, 7 and 8 shows that if at least the first few chosen compositions of a binary mixture melt to an isotropic liquid at a temperature higher than the mesomorphic-isotropic temperature of the pure liquid crystalline component and the mesomorphic-isotropic transition curve exhibits a maximum, then probably the mixture will exhibit only a smectic phase.

Experimental

p-*n*-dodecyloxybenzaldehyde was prepared by the method given by Gray and Jones[9] and *p*-*n*-butoxyaniline by the method of Gutekunst and Gray.[10] Equimolecular quantities of *p*-*n*-dodecyloxybenzaldehyde and *p*-*n*-butoxyaniline were condensed to yield

TABLE 2 Solid to liquid or mesomorphic transition temperatures (°C) for the binary systems. The eutectic temperatures and the melting points of pure components are direct experimental values. The other temperatures are read from the phase diagrams.

Sr. No.‡	Mole % *p-n*-Dodecycloxybenzal -*p-n*-butoxyaniline (A)														Eutectic	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole %(A)	Temp. (°C)
1	128.5	123.5	119.0	114.0	107.8	101.0	95.0	93.0	94.4	95.6	97.0	98.2	99.5	101.0	65.5	91.5
2	147.0	142.2	137.5	133.0	128.0	122.0	113.5	101.0	95.0	96.5	97.5	98.6	99.8	101.0	75.0	95.0
3	148.0	144.0	139.5	134.4	128.0	120.8	112.5	104.5	100.5	96.5	97.8	98.8	99.8	101.0	80.0	96.5
4	92.0	87.6	82.0	78.0	82.5	86.2	89.5	93.0	94.5	96.2	97.5	99.0	100.0	101.0	27.0	76.5
5	120.0	115.2	108.8	100.6	93.0	87.5	87.5	91.8	94.0	95.6	97.5	98.8	100.0	101.0	57.0	85.5
6	123.5	120.8	117.4	113.0	107.5	101.0	92.5	91.2	93.0	94.5	96.2	98.0	99.5	101.0	63.0	89.0
7	132.0	127.0	122.0	117.2	112.5	106.5	98.5	89.0	91.5	94.0	96.0	98.0	99.5	101.0	67.0	87.0
8	163.0	157.5	152.5	147.0	141.5	134.8	120.8	90.0	93.0	95.0	97.0	98.5	100.0	101.0	68.2	89.0

TABLE 3 Smectic-nematic transition temperatures (°C) for the binary systems. The values are read from the phase-diagrams. The smectic-nematic transition temperature for the pure compound is a direct experimental value. The values in the parentheses show the monotropic transition temperatures.

Sr. No.‡	Mole % *p-n*-Dodecycloxybenzal -*p-n*-butoxyaniline (A)									Triple Point.	
	50	60	70	75	80	85	90	95	100	Mole % (A)	Temp. (°C)
1	—	—	(90.0)	100.0	103.0	104.8	106.5	109.0	111.0	70.5	93.0
2	—	—	—	99.5	101.5	103.8	106.0	108.2	111.0	72.5	98.0
3	—	—	(97.0)	(100.0)	102.5	104.8	107.0	108.6	111.0	75.5	100.2
4	(82.5)	96.0	102.5	104.5	106.5	107.5	108.5	109.5	111.0	53.5	87.5
5	(84.5)	96.5	102.5	104.0	—	—	—	—	111.0	46.5	87.0
6	—	—	—	—	—	—	—	—	—	—	—
7	—	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—	—

TABLE 4 Mesomorphic-isotropic transition temperatures (°C) for the binary systems. The values are read from the phase diagrams. The mesomorphic-isotropic transition temperature for the pure compound is a direct experimental value. The values in the parentheses show the monotropic transition temperatures.

Ser. No.‡	Mole % *p-n*-Dodecycloxygenzal-*p-n*-butoxyaniline (A)											Triple Point.	
	20	30	40	50	60	70	75	80	85	90	95	100	Mole % (A)	Temp. (°C)
1	(112.5)	(110.6)	109.0	108.5	108.0	108.5	108.5	108.8	109.0	109.5	110.4	111.5	37.0	109.5
2	—	—	—	—	—	104.0	105.2	106.5	107.5	108.8	110.4	111.5	68.5	103.5
3	—	—	—	(106.2)	(107.0)	108.0	108.5	109.0	109.5	110.0	110.5	111.5	66.0	107.5
4	(75.0)	84.0	90.5	96.0	101.0	104.5	106.0	107.5	109.0	110.0	110.5	111.5	23.8	79.0
5	—	—	(89.5)	91.0	101.5	105.0	106.5	107.8	109.0	109.8	110.5	111.5	42.5	91.5
6	—	(108.5)	116.5	122.5	126.0	127.0	126.5	125.0	122.5	119.5	115.8	111.5	33.2	111.2
7	—	—	(104.2)	113.5	120.0	124.0	124.8	124.2	123.0	120.5	116.5	111.5	45.0	109.5
8	—	—	—	—	124.0	127.0	127.0	126.2	124.5	121.0	116.5	111.5	59.0	123.0

‡ Serial Nos. refer to the compounds given in Table 1.

the Schiff's base, *p*-*n*-dodecyloxybenzal-*p*-*n*-butoxyaniline.[11] The product crystallized from ethyl alcohol as colourless flakes.

The binary mixtures were investigated by using a Leitz Ortholux Polarizing Microscope equipped with a heating arrangement.[11]

Acknowledgment

The authors express their thanks to Prof. S. M. Sethna for his interest in the work.

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