

Extended Range Ambient Temperature Nematic Mesophase in Binary Systems of *N*-(4-*n*-Alkoxybenzylidene)-4-*n*-alkylanilines

By D. L. FISHEL* and YING YEN HSU

(*Liquid Crystals Institute and the Department of Chemistry, Kent State University, Kent, Ohio 44242*)

Summary Markedly lowered solid-nematic transition temperatures and enhanced temperature range for nematic properties obtain in certain specific binary mixtures of *N*-(4-*n*-alkoxybenzylidene)-4-*n*-alkylanilines.

ATTEMPTED syntheses of novel compounds with low temperature solid-mesophase transitions and wide thermal stability for the mesophase have been recently reported.¹⁻⁴ Such compounds would greatly simplify fundamental investigations of mesophase structure and properties⁵ and

would provide materials for potential applications of unusual electro-optical effects.⁶ Mixed systems⁷ have also been investigated. We have discovered systems which are binary mixtures of compounds from the *N*-(4-*n*-alkoxybenzylidene)-4-*n*-alkylaniline series⁴ and which have extremely low temperature solid-nematic transitions and consequent wide range for nematic stability.

Pure *N*-(4-*n*-alkoxybenzylidene)-4-*n*-alkylanilines were prepared as previously described³⁻⁴ and recrystallized from ethanol or methanol. Table I presents transition tempera-

TABLE 1 Transition temperatures for N-(4-n-alkoxybenzylidene)-4-n-alkylanilines

Identification Code	Transition temperatures °C ^a	
	Solid-nematic	Nematic-Isotropic
1-2	32.5 ^b	56.5
1-3	44.6	61.2
1-4 ^c	20.0	47.3
1-5	39.3	64.0
1-7	25.5	61.4
2-4	35.5	79.0
3-5	32.6 ^d	71.6
3-7	29.2	69.0
3-8	36.0	64.4
3-9	29.5	69.0

^a Temperatures by differential thermal analysis. Phase contrast microscopy gave values within 2°. ^b Monotropic transition. ^c Previously reported by Kelker.² ^d Solid-Nematic transition (heating) cooling from isotropic liquid gives nematic-smectic B at 21.5° and smectic B solid at 13.5°.

tures for the pure anils used. Compounds are identified by designating the numbers of carbon atoms in the n-alkoxy- and n-alkyl-groups respectively, thus '3-5' refers to N-(4-n-propoxybenzylidene)-4-n-pentylaniline. A series of mixtures with known compositions were prepared for all pair-combinations of the compounds listed in Table 1, these binary systems all show minimum solid-nematic transitions for a short composition range near apparent 1:1 or 2:1 mole ratios. Data are given in Table 2 for those binary systems showing an extreme temperature lowering (solid-nematic transition below 0°C).

TABLE 2 Minimum-melting compositions and transition temperatures for binary systems of N-(4-n-alkoxybenzylidene)-4-n-alkylanilines^a

Components A/B	Mol % A/B	Transition temperatures °C	
		Solid-nematic	Nematic-isotropic
1-2/3-5	50/50	-21.5	46.7
1-3/3-5	67/33	-23.0	58.5
1-4/3-5	67/33	-28.5	50.0
1-4/3-7	50/50	-36.5	57.0
1-4/2-4	67/33	-17	56
1-4/3-9	50/50	-11	54.3
1-4/1-7	50/50	-1	49.8
2-4/3-7	50/50	-4.5	72.5
3-5/3-9	50/50	-1.8	63
1-3/3-8	50/50	-10	52.5

^a Nematic mesophases for the first four systems are stable over two months at -10°.

¹ G. W. Gray, "Liquid Crystals 2," Gordon and Breach, London, 1969, Part 1, p. 143.

² H. Kelker and B. Scheurle, *Angew Chem*, 1969, **81**, 903.

³ J. B. Flannery and W. Haas, *J Phys Chem*, 1970, **74**, 3611.

⁴ D. L. Fishel, Y. Y. Hsu, P. R. Patel, and M. A. Flandera, *J Phys Chem*, submitted for publication.

⁵ J. J. Visintainer, J. W. Doane, and D. L. Fishel, *Mol Cryst and Liq Cryst*, 1971, **13**, 69. A. De Vries, *Mol Cryst and Liq Cryst*, 1970, **11**, 361. E. Sackmann, S. Meiboom, and L. C. Synder, *J Amer Chem Soc*, 1968, **90**, 2183.

⁶ G. H. Heilmeyer and L. A. Zanon, *Appl Phys Lett*, 1968, **13**, 91. L. K. Vistin and A. P. Kapustin, *Optika i Spektroskopiya*, 1968, **24**, 650. *Chem Abs*, 1968, **69**, 31,212z.

⁷ D. Demus, *Z Naturforsch*, 1967, **22a**, 285.

A cold-stage polarizing microscope was used to examine the first four binary systems of Table 2 in greater detail. The onset of melting corresponds closely ($\pm 2^\circ\text{C}$) with differential thermal analysis data but it was not possible to determine the temperature range for melting owing to experimental problems (fogging and water contamination) during these initial measurements. The solid phase appeared to be isomorphous over the whole range of compositions (continuous solid solution). The partial phase diagram for system 1-4/3-7 (Figure) is typical for

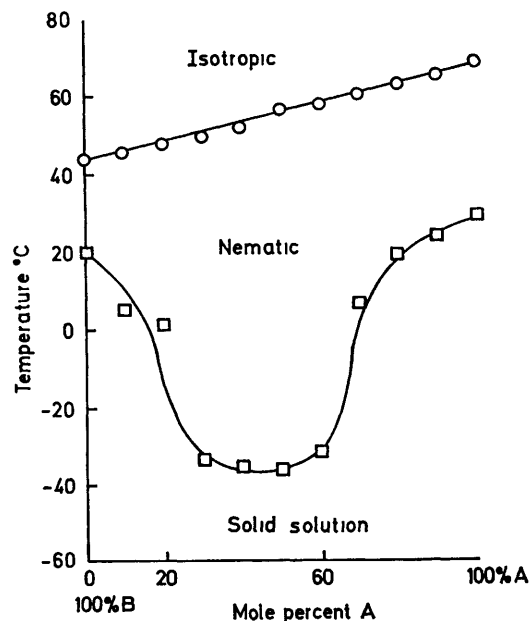


FIGURE Partial phase diagram for the binary system N-(4-n-propoxybenzylidene)-4-n-heptylaniline (A) and N-(4-methoxybenzylidene)-4-n-butylaniline (B).

these binary systems, the solid nematic curve shows a marked minimum whereas the nematic-isotropic curve is nearly a straight line or is curved slightly upward. This greatly extends the temperature range for stable mesophase behaviour.

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