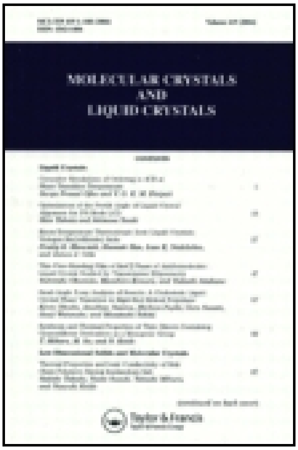

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Induced Smectic Mesomorphism in Binary Mixtures of Cholesteryl Chloride and 4,4′-diheptyloxyazoxybenzene

K. A. Suresh [a]
[a] Raman Research Institute, Bangalore, 560080, India
Version of record first published: 17 Oct 2011.

Mol. Cryst. Liq. Cryst., 1983, vol. 97, pp. 417–421
0026-8941/83/9704-0417/$18.50/0

Induced Smectic Mesomorphism in Binary Mixtures of Cholesteryl Chloride and 4,4′-diheptyloxyazoxybenzene*

K. A. SURESH
Raman Research Institute, Bangalore 560080, India

(Received August 15, 1982; in final form October 25, 1982)

We report here the occurrence of an 'Induced Smectic A' phase in binary mixtures of cholesteryl chloride (ChCl) and 4,4′-diheptyloxyazoxybenzene (HOAB). It is interesting to find that cholesteryl chloride, which is not as strongly polar as cyano- or nitro group containing aromatic nematogens, gives rise to the induced smectic phase.

X-ray studies on ChCl, HOAB and their mixtures show that neither the pure compounds nor the mixtures have a bilayer arrangement of molecules. The interesting result is obtained that in a 12 mole pct ChCl in HOAB mixture, which exhibits a twisted smectic C phase and a skew-cybotactic cholesteric phase, the tilt angle varies with temperature, although in the corresponding smectic C and skew-cybotactic nematic phases of pure HOAB, the tilt angle is independent of temperature.

INTRODUCTION

There have been many studies[1-6] on phase diagrams of binary mixtures of nematogenic compounds, one of which consists of aromatic molecules having cyano or a similarly strong polar end group, whereas the other consists of molecules without such a strong polar end group. These studies have shown that such mixtures exhibit an induced smectic A (A) phase over a range of compositions, though the pure compounds themselves do not exhibit the A phase. In this paper we report a study on the phase diagram of mixtures of cholesteryl chloride (ChCl) and 4,4′-diheptyloxyazoxybenzene (HOAB). Our studies show that mixtures in a certain composition range exhibit an induced A phase though neither of the components

*Presented at the IX International Liquid Crystal Conference, Bangalore, 1982.

has an appreciably strong polar end group. This is an interesting result from the point of view of the various models[1-3] proposed to explain the occurrence of the induced A phase.

We have carried out x-ray measurements to ascertain the type of molecular arrangement in the mesophase. We find that neither ChCl nor HOAB form bilayers. We have also carried out x-ray studies on a mixture of 12 mole pct ChCl in HOAB. We find that, in the twisted smectic C (C*) and in the skew-cybotactic cholesteric (Ch_{sc}) phase of this mixture, the tilt angle varies as a function of temperature although in the corresponding smectic C (C) and skew cybotactic nematic (N_{sc}) phases of pure HOAB the tilt angle is independent of temperature.[7]

EXPERIMENTAL

Binary mixtures: The components HOAB and ChCl were obtained from Eastman Kodak Co. and Riedel-de Haen respectively. The transition temperatures were checked and found to be in good agreement with reported values. Hence the samples were used without further purification. The transition temperatures of the mixtures were obtained using a Mettler hot stage (Model FP 52) in conjunction with a polarizing microscope. The transition temperatures were also checked using a differential scanning calorimeter (Perkin-Elmer DSC-2).

X-ray studies: The sample was taken in powder form in a 0.5 mm Lindemann capillary and its temperature was controlled and maintained to ±0.25 °C.

The layer spacing was determined photographically using flat plate camera and CuK_α radiation reflected from a bent quartz crystal monochromator (Carl Zeiss Jena). The film was placed at the focus of the monochromator. The diffraction rings were quite sharp. The diameters of the rings were measured using an accurate comparator. The relative accuracy in the layer spacing is estimated to be about ±0.1 Å.

RESULTS AND DISCUSSION

The phase diagram of the mixtures of HOAB and ChCl is shown in Figure 1. In the pure state ChCl shows a monotropic cholesteric (Ch) phase and HOAB shows the C and N_{sc} phases. The mixture shows an induced A phase for mole percentages in the range of 10–50 of ChCl. The A–Ch transition curve peaks around the composition of 30 mole pct of ChCl. The

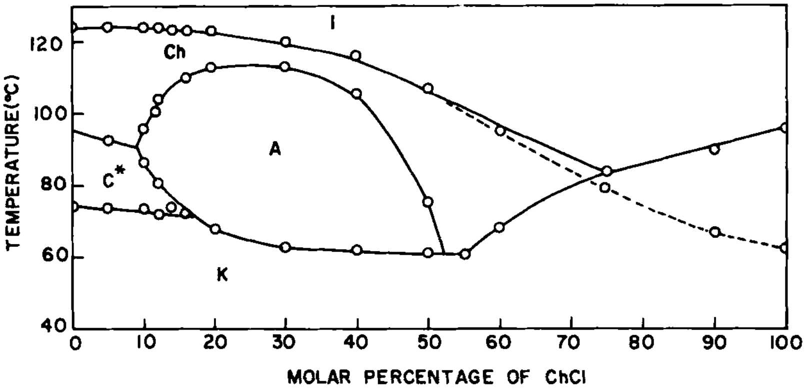

FIGURE 1 Phase diagram of mixtures of HOAB and ChCl. The dotted line indicates isotropic-cholesteric transition on cooling.

induced A phase is very stable and occurs enantiotropically. In this phase, for certain compositions, the sample has a strong tendency to align homeotropically. We could also observe the focal conic or fan shaped textures typical of the A phase. Mixtures with 50–75 mole pct of ChCl exhibit enantiotropic Ch phase, and for higher concentrations of ChCl, the mixture has only a monotropic Ch phase. For a narrow range of about 10–20 mole pct of ChCl the mixture shows a C* phase, an induced A phase and a Ch_{sc} phase.

The layer spacing d measured for various concentrations are given in Table 1. The molecular lengths (1) of HOAB and ChCl calculated using Dreiding models, and the expected effective molecular length for different concentrations are also shown in the table. A comparison of the experimental and calculated values clearly shows that the pure components or their mixtures do not form bilayer molecular arrangement.

TABLE I

Percentage of ChCl in HOAB	Experimental d (Å)	Calculated 1 (Å)
0	23.4[a]	32
12	29.3[b]	30.5
30	26.8[b]	28
50	25.1[b]	26
72	22.4[c]	23.0
100	17[c]	19.5

Measured in (a) smectic C phase, (b) smectic A phase, and (c) cholesteric phase.

Park, Bak, and Labes[1] have suggested that the induction of the A phase is due to charge transfer interaction between the components, while Oh[2] proposed a dipole induced lamellar structure. Griffin[3,8] found that mixing a monolayer mesogen with a bilayer mesogen results in the induction of the A phase. Our results show that cholesteryl chloride is not a 'bilayer mesogen' as defined by Griffin[8] nor is it as strongly polar as cyano- or nitro group containing aromatic nematogens. HOAB can be considered as a donor molecule, but ChCl is not strictly an acceptor molecule. As such, we do not have clear evidence for charge transfer. Thus, the occurrence of the induced smectic phase between HOAB and ChCl is unusual.

Figure 2 shows d measured as a function of temperature for a mixture of 12 mole pct ChCl. In the induced A region d is equal to 29.3 Å and invariant with temperature. In the C* as well as the Ch_{sc} phases d does vary with temperature. Assuming this d variation as solely due to the variation of the tilt of the molecules in the layer and taking the molecular length to be equal to 29.3 Å, the tilt angle at various temperatures has been evaluated. In the C* phase d varies from about 29.3 Å to 27.5 Å (or the tilt angle from about 0° to 20°) and in the Ch_{sc} phase d varies from about 29.3 Å to 28.4 Å (or the tilt angle from about 0° to 14°).

For a mixture of 30 mole pct ChCl, which does not exhibit the C* phase, d is invariant with temperature in the A phase and practically so in the Ch_{sc} phase.

In pure HOAB the tilt angles are about 45° in the C phase and about 40° in the N_{sc} phase and are independent of temperature;[7] whereas in a mixture

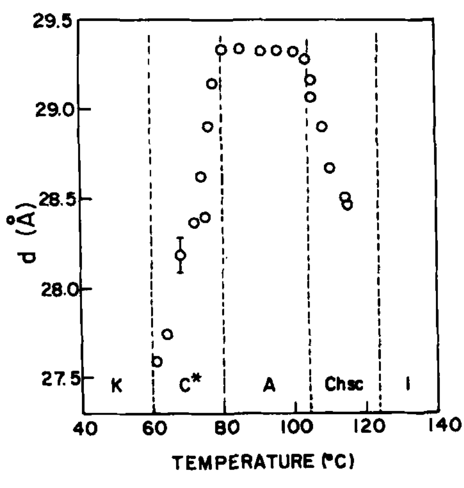

FIGURE 2 The layer spacing d (Å) as a function of temperature for a mixture of 12 molar percent ChCl in HOAB.

of 12 mole pct ChCl in HOAB, in the corresponding phases, the tilt angles are much smaller and temperature dependent. This marked difference in the behavior in the tilt angle on addition of a mere 12 mole pct of ChCl into HOAB is obviously related to the occurrence of the induced A phase. The tilt angle which is zero in the induced A phase increases in the adjacent C* and Ch_{sc} phases on either side. The reason for this is not yet clear to us.

Acknowledgments

I am very grateful to Prof. S. Chandrasekhar for several useful suggestions and discussions. I would also like to thank Dr. N. V. Madhusudana and Dr. V. Surendranath for many helpful discussions.

References

1 J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).
2 C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).
3 A. C. Griffin and J. F. Johnson, *J. Am. Chem. Soc.*, **99**, 4859 (1977).
4 B. Engelen, G. Heppke, R. Hopf, and F. Schneider, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 193 (1979).
5 L. J. Yu and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **54**, 1 (1979).
6 K. P. L. Moodithaya and N. V. Madhusudana, Proc. Int. Liquid Crystals Conf., Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London (1980) p. 297.
7 K. A. Suresh and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **40**, 133 (1977).
8 A. C. Griffin, T. R. Britt, N. W. Buckley, R. F. Fisher, S. J. Havens, and D. W. Goodman, 'Liquid Crystals and Ordered Fluids, Vol. 3, Eds. J. F. Johnson and R. S. Porter, (Plenum Press, New York) (1978) p. 61.