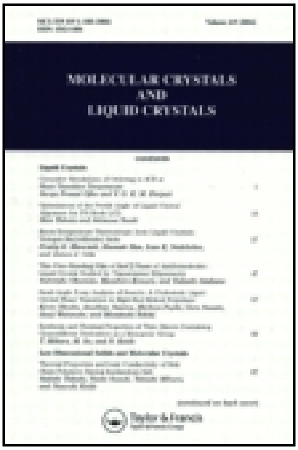


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# Induced Smectic Phases in Binary Mixtures of a Compound Having a Weakly Polar End Group and a Compound Having a Non-polar End Group

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# Induced Smectic Phases in Binary Mixtures of a Compound Having a Weakly Polar End Group and a Compound Having a Non-polar End Group

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We have studied the phase diagram of binary mixtures of 4′-n-heptyl-4-bromobiphenyl (a non-mesomorphic compound having a weakly polar terminal group) and 4,4′-di-n-heptyloxyazoxybenzene (a mesomorphic compound having a non-polar terminal group). The mixture exhibits an induced smectic A phase over a wide composition range and also an induced smectic E phase over a narrow composition range. X-ray studies show that the molecular arrangement in the smectic A phase is monolayer for all compositions.

We have also observed defects of strength ±2 and ±3/2 in the nematic phase in a certain composition range of the mixture.

## INTRODUCTION

Park, Bak and Labes[1] found that binary mixtures of nematogenic compounds, one with a strongly polar terminal group and the other with a non-polar terminal group, give rise to an induced smectic phase over a range of composition. Later investigations[2-14] have shown a large number of examples of induced smectic phases in binary mixtures of nematogenic compounds. In most cases the induced phase is of the smectic A type, and we shall confine our remarks to this type of phase induction. By and large, the rule appears to be that the smectic A ($S_A$) phase is induced in binary mixtures of a compound with a strongly polar terminal group and a compound with a non-polar terminal group. In terms of the structure the $S_A$ phase is induced in binary mixtures of a nematogen with a potential bilayer molecular arrangement (i.e., layer spacing greater than molecular length) and a nematogen with a potential monolayer arrangement.[3] However, exceptions to the rule have been reported by MacMillan and Labes[15] and by the present author.[16] The former[15] has reported an induced $S_A$ phase in mixtures of two compounds each having a polar terminal group and the latter[16] in mixtures of a compound with a weakly polar terminal group and a compound with a non-polar terminal group. This paper reports another case of an exception to this rule, viz., the occurrence of an induced $S_A$ phase in binary mixtures of a non-mesomorphic compound with a weakly polar terminal group, viz., 4′-n-heptyl-4-bromobiphenyl (7BB) and a mesomorphic compound with a non-polar terminal group, viz., 4,4′-di-n-heptyloxyazoxybenzene (HOAB). The mixtures exhibit the $S_A$ phase over a wide range of composition and also smectic E phase over a narrow range of composition. We find that the molecular structure of the induced $S_A$ phase to be strictly monolayer at all compositions.

## EXPERIMENTAL

*Binary mixtures.* The compound 7BB was prepared in our laboratory. HOAB was obtained from Eastman Kodak Co. The transition temperatures, on heating, are given below:

7BB : K 94°C I

HOAB : K 74°C $S_C$ 95.2°C N 124°C I.

The transition temperatures of the mixtures were determined using a Leitz Ortholux polarising microscope (Model 11 POL-BK) in conjunction with a Mettler hot stage (FP52) and checked using a differential scanning calorimeter (Perkin-Elmer, DSC-2). Textures were studied using the same polarizing microscope and hot stage facility.

*X-ray studies.* The sample was held in a Lindemann capillary and its temperature was controlled and maintained to ±0.25°C. In the $S_A$ phase the experiments were on monodomain samples obtained by heating the sample to nematic or isotropic phase and cooling at a slow rate to $S_A$ phase in a magnetic field of strength 5 Kgauss. The X-ray diffraction maxima were recorded photographically using a flat plate camera and $CuK_\alpha$ radiation reflected from a bent quartz crystal monochromator (Carl Zeiss, Jena). The film was positioned at the focus of the monochromator. The relative accuracy in the layer spacing determination is estimated to be better than ±0.1 Å.

## RESULTS AND DISCUSSION

The phase diagram of the mixtures of 7BB and HOAB is given in Figure 1. All the transition points shown in the figure are obtained on heating. In the pure state 7BB is non-mesomorphic and HOAB exhibits smectic C and nematic phases. The mixture shows an induced $S_A$ phase in the range of about 10–70 weight per cent (wt %) of 7BB. The induced $S_A$ phase is very stable and occurs enantiotropically. In this phase, we could observe beautiful focal conic or fan shaped textures characteristic of the $S_A$ phase. In the narrow range of about 60–70 wt % of 7BB the mixtures exhibit another more ordered smectic phase below the $S_A$ phase. This phase exhibits arced focal conic fan texture typical of the smectic E phase.

The X-ray studies on well aligned samples of binary mixtures of different concentrations varying from 10–70 wt % of 7BB confirm the existence of $S_A$ phase. The X-ray reflections are very sharp which permits accurate determination of layer spacing (d). Figure 2 shows the measured d values in the $S_A$ phase plotted as a function of concentration. The expected effective molecular length (l) at any concentration was calculated using the relation $l = X_1L_1 + X_2L_2$ where $X_1$, $X_2$ are the mole fractions of the components and $L_1$, $L_2$ are the

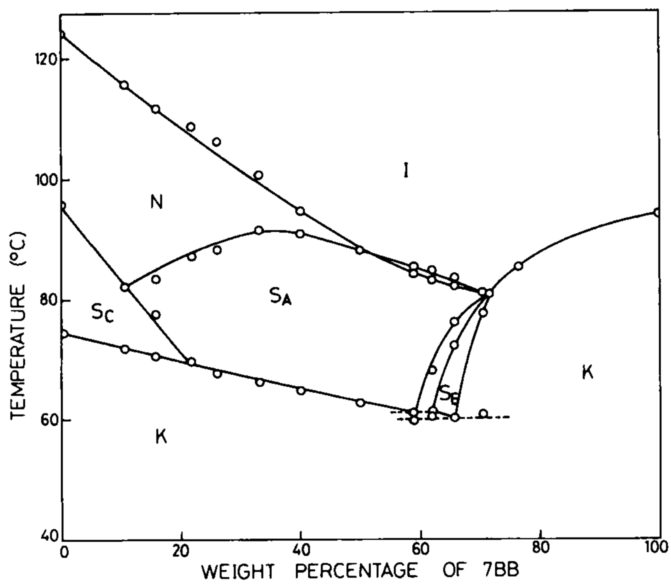


FIGURE 1 Phase diagram of mixtures of 7BB and HOAB.

molecular lengths estimated using Dreiding models of the components. Figure 2 also shows the l values plotted as a function of concentration. Comparison of the two curves clearly shows that at any concentration the d values are always lower than the l values which means that the $S_A$ phase has only monolayer molecular arrangement.

Our results show that 7BB with a terminal group which is not as strongly polar as cyano or nitro group induces $S_A$ phase. The X-ray results show that 7BB, HOAB mixtures form only monolayer $S_A$ phase. HOAB can be considered as a donor molecule, but 7BB is not strictly an acceptor molecule. Therefore it is difficult to explain the occurrence of induced $S_A$ phase in this mixture using the models of charge transfer interaction[1] or of dipole induced lamellar structure[2] or of packing of monolayer, bilayer mesogens.[3] Previously[16] we have reported induced $S_A$ phase in cholesteryl chloride, HOAB mixture which is also an example of a binary system of a compound with a weakly polar terminal group and a compound with a non-polar terminal group. Thus the exact nature of the interaction giving raise to the induced $S_A$ phase is not clear and the phenomenon continues to be an intriguing one, calling for more studies to find a general explanation.

Figure 3 shows a +3/2 and a −3/2 defect observed in a mixture of 15.7 wt % of 7BB in HOAB at 108°C. Such defects were observed on cooling from the isotropic phase to nematic phase and were very stable. We were also able to observe defects of strength ±2 but they

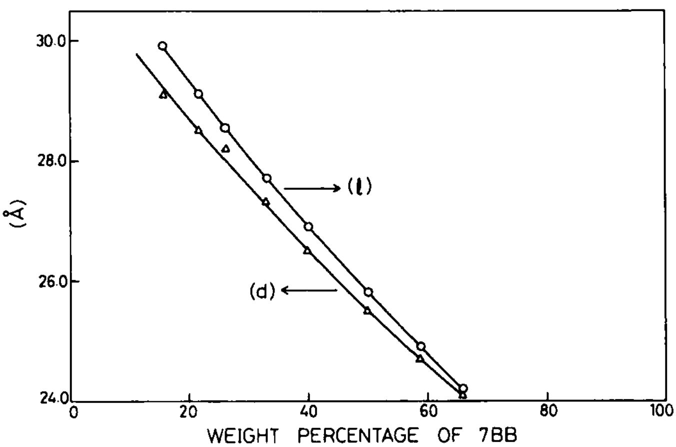


FIGURE 2 The layer spacing (d) obtained from experiments in the $S_A$ phase and the expected effective molecular length (l) for 7BB, HOAB mixtures.

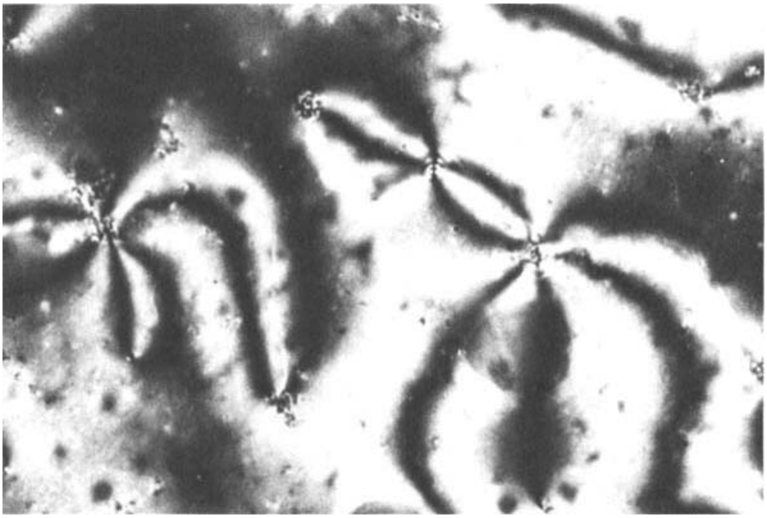

FIGURE 3 A +3/2 and a −3/2 defect observed using a polarising microscope. Magnification, ×400.

were not that stable and in course of time dissociated into two like defects of ±1 strength. Robinson et al.[17] appear to be the first to observe[18] +2 high strength defects in spherulitic texture of lyotropic cholesterics. Recently high strength defects have been reported even in thermotropics.[19,20] In these studies, the high strength defects were observed in nematogens mixed with plate like molecules[19] or in nematogens mixed with a lyotropic liquid crystal.[20] Interestingly, we find a rod-like molecule, viz., 7BB mixed with a mesogen, viz., HOAB can also result in high strength defects.

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