Indian Journal of Chemistry
Vol. 25A, May 1986, pp. 431-435

Induced Smectic Phases : Studies in Binary Mixtures of Alkylaminobiphenyls & Nonyloxycyanobiphenyl†

N K SHARMA* & R K BAMEZAI
Department of Chemistry, University of Jammu, Jammu (Tawi) 180 004

Received 22 *August* 1985; *revised and accepted* 10 *October* 1985

The diagrams of state of mixtures of 4,4'-bis-[*n*-alkylamino]biphenyls with 4-*n*-nonyloxy-4'-cyanobiphenyl are studied. The induced smectic phases of the type S_A, S_B and S_E have been observed. The induction may be due to the presence of amino and cyano end groups which imparts the molecules electron donor and electron acceptor properties respectively. The intermediate smectic phases of the type C and I have also been observed.

Many binary mixtures of liquid crystalline compounds are known where an increase in the clearing point temperatures in middle area of concentrations have been observed. Such enhanced phases are known as induced phases and have been of great interest[1-6]. Initially only smectic-A phase was known but recently induced smectic-B and smectic-E phases have also been observed[7]. Many theories have been proposed in order to explain their existence[3,8]. The appearance of these phases may be due to thermal stabilization of potential mesophases of component compounds by charge transfer interaction introduced on mixing[9]. This paper reports the formation of induced smectic-A, smectic-B and smectic-E phases between some members of the homologous series of 4,4'-bis[*n*-alkylamino]biphenyls (*n*-ABP, where n = 4,6,7 and 8) acting as electron donors and 4-*n*-nonyloxy-4'-cyanobiphenyl (9OCBP) acting as electron acceptor.

Materials and Methods

The diagrams of state of binary systems were studied with the help of a polarising microscope provided with a microheating stage by contact method[10] and/or by investigations of mixtures with known concentrations. The substances used in this work along with their polymorphy are given in Table 1. The experimental results agreed well with earlier reported results[11,12]. 9OCBP (BDH) was used as such. The compounds of homologous series of alkylaminobiphenyls were synthesized in our laboratory using standard procedures[12]. 9OCBP was one of the components of the binary system, the other component being a homologue of *n*-ABP (n = 4,6,7 and 8). The microphotographs were taken with the help of a camera attachment provided with an automatic light device.

Table 1—Compounds Used and Their Polymorphy

Sl No.	Compound	Structural formula	Polymorphy*
1.	4-*n*-Nonyloxy-4'-cyanobiphenyl (9OCBP)	$C_9H_{19}O\text{-}C_6H_4\text{-}C_6H_4\text{-}CN$	Cr 64.0 S_A 77.5 N 80.0 I_s
2.	4,4'-Bis[*n*-butylamino]biphenyl (4ABP)	$C_4H_9NH\text{-}C_6H_4\text{-}C_6H_4\text{-}NHC_4H_9$	Cr 60.7 N 97.0 I_s
3.	4,4'-Bis[*n*-hexylamino]biphenyl (6ABP)	$C_6H_{13}NH-C_6H_4-C_6H_4-NHC_6H_{13}$	Cr 93.7 N 103.0 I_s
4.	4,4'-Bis[*n*-heptylamino]biphenyl (7ABP)	$C_7H_{15}NH-C_6H_4-C_6H_4-NHC_7H_{15}$	Cr 97.0 (S_C 93.0) N 103.8 I_s
5	4,4'-Bis[*n*-octylamino]biphenyl (8ABP)	$C_8H_{17}NH-C_6H_4-C_6H_4-NHC_8H_{17}$	Cr 99.8 (S_I 99.0) S_C 110.5 N 110.9 I_s

*The abbreviations used are : Cr = Crystalline solid; S_A,S_B.........S_I = smectic modifications of the type A,B............I respectively; N = nematic phase; I_s = isotropic liquid;
The abbreviations in between the numbers (°C) indicate phase transitions in the liquid crystalline state. In parentheses are the transition temperatures of metastable liquid crystalline modifications.

†Presented as a poster at the 21st Annual Convention of Chemists, Calcutta, 1984.

Results and Discussion

System-1 (*4ABP/90CBP*)

Figure 1 shows an increase in N/I_s and S_E/I_s temperatures with a maximum at 123°C. Smectic-E phase appears in the middle composition range and covers the largest area. Growth of S_E starts in the form of lancets and mosaics. Although both the components of the binary system are nematogens yet no uninterrupted miscibility is observed between them. Miscibility in nematic phases is interrupted by the growth of induced smectic-E phase.

System 2 (*6ABP/90CBP*)

The binary diagram of state between 6ABP and 90CPB in the entire composition range is shown in Fig.2. This system shows the presence of smectic-E phase which occurs in typical fan-shaped concentric arc-ring like textures along with mosaic ones (Plate 1). Another region of induced phase of the type smectic-B appears at 115.5°C, in between nematic and smectic-E phases. This phase solidifies at 81.3°C. The nematic phase of either components are confined to a very small concentration regions.

System 3 (*7ABP/90CBP*)

A maximum in the clearing point temperature at 132.0°C shows S_A/isotropic transition (Plate 2) which is closely followed by smectic-E phase at 131.5°C on the side of 90CBP. The region of induced smectic-A phase is restricted due to the appearance of S_B, S_I and S_C phases as shown in Fig. 3. Induced smectic-B phase appears at 119.5° which is sandwiched between S_A and S_E. The transition from S_A to S_B is identifiable by the appearance and disappearance of transition lines when fan-shaped textures of S_A with small focal conics in domains ('scaly' fan texture) are converted into fan-shaped textures with diminished number of discontinuities (Plate 3). S_I phase appears at 104.4° while smectic-C phase appears as an intermediate at

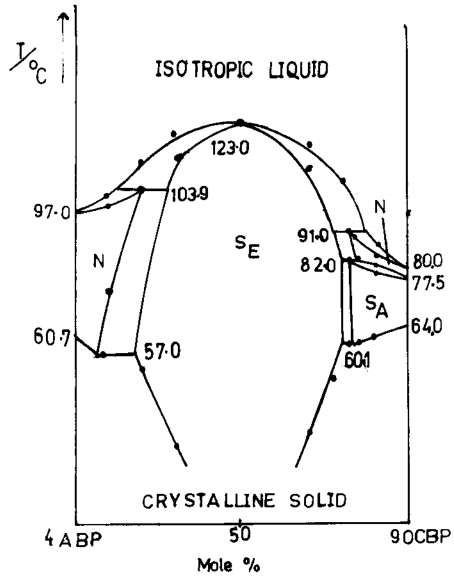

Fig. 1—Binary diagram of state between 4ABP and 90CBP

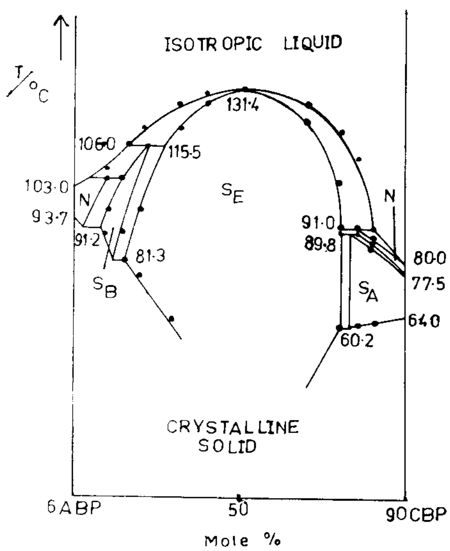

Fig. 2—Binary diagram of state between 6ABP and 90CBP

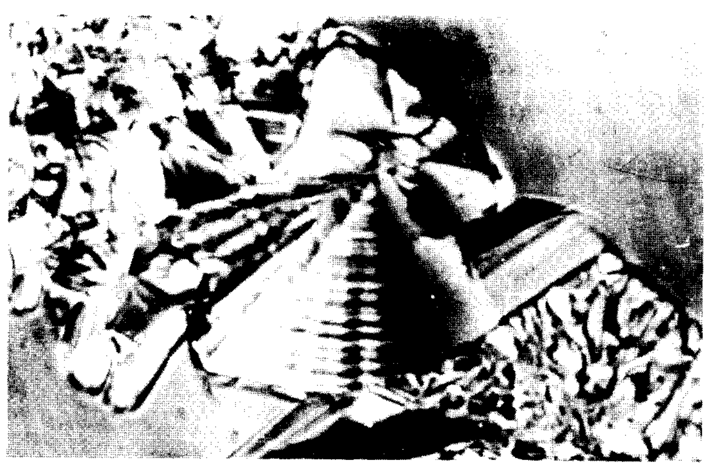

Plate 1—Induced smectic-E phase, a section showing concentric arc ring textures (130.5°C), crossed polarisers (× 150)

100.7°C. The heterogeneous region of smectic C and I phases is shown in Plate 4.

System 4 (8*ABP*/90*CBP*)

The diagram of state of this system (Fig. 4) shows results similar to those of system-3 (Plate 5) except in case of smectic-C which in this system appears in pure 8ABP. The smectic-I phase covers a larger area than that in system-3. The S_E, S_B, S_I phases appear through three phase reactions at 120.6°, 110.3° and 109.4°C respectively. The eutectic temperatures of these systems could not be determined as these did not crystallize even by keeping them in a refrigerator for a number of days.

Summarising the results obtained above, we conclude that the electron donor-acceptor interaction favours the formation of induced smectic phases of S_A, S_B and S_E types. It has been observed that these induced phases are stabilized by electron donor-acceptor interaction[7a,b]. Comparison of Figs 1 and 2 shows that in former smectic-E phase is induced while in the later smectic-B and especially smectic-E phase of

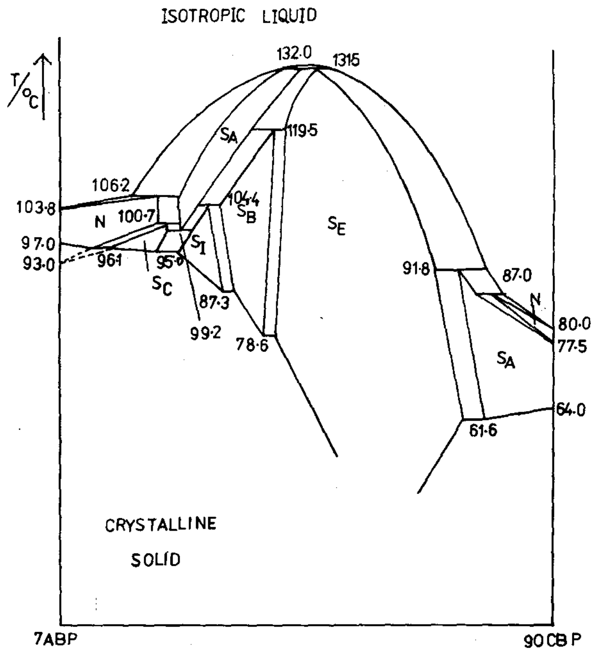

Fig. 3—Binary diagram of state between 7ABP and 90CBP.

Plate 2—Induced smectic-A phase, fan-shaped textures, (131.2°C), crossed polarisers (× 150)

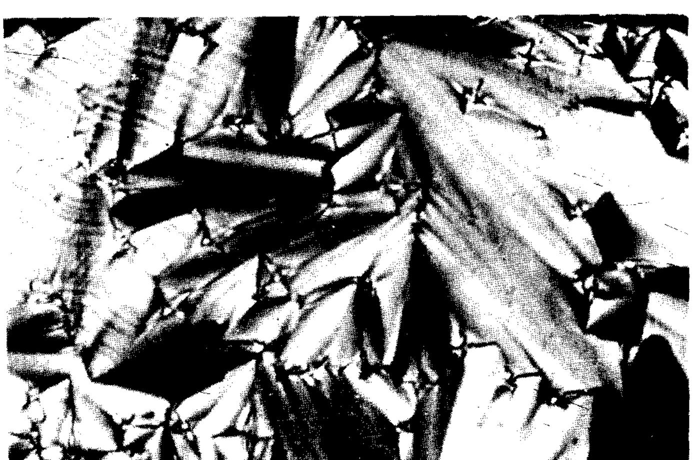

Plate 3—Induced smectic E and smectic B phases of 7ABP/90CBP, (118.2°C), crossed polarisers (× 150)

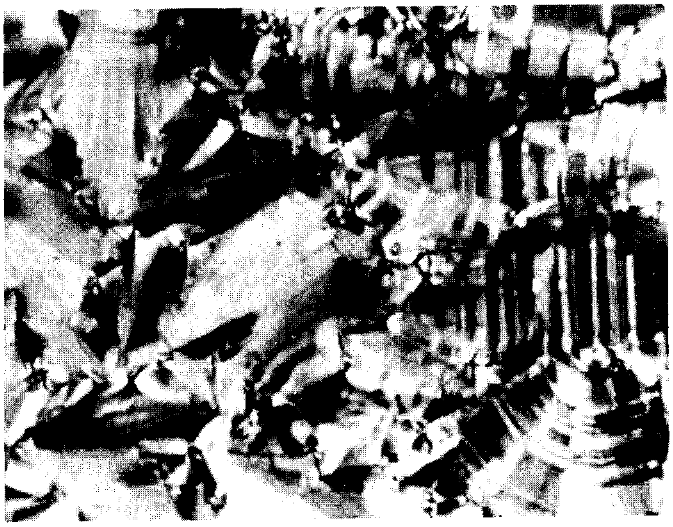

Plate 4—Broken fan shaped textures of Sc and divided fan shaped textures of Sɪ of 7ABP/9OCBP, 99.0°C (× 150)

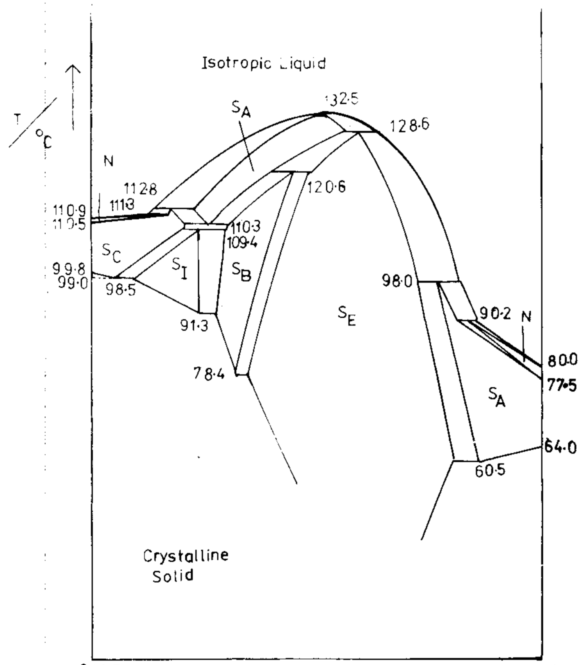

Fig. 4—Binary diagram of state between 8ABP and 9OCBP

high thermal stability are obtained. The ratio of smectic-E phase area to the total smectic phase area is relatively larger in all these systems. In Fig. 3 Sc phase appears as an intermediate but in Fig. 4 it appears in the pure component, 8ABP. The appearance of Sc phase in 7ABP/9OCBP system can be attributed to its presence as monotropic phase in 7ABP. The appearance of Sɪ modification in 7ABP/9OCBP system can be interpreted as higher members of 7ABP possess this low temperature modification[12]. Sɪ phase is further confirmed in 8ABP/9OCBP as it is observed as monotropic in 8ABP. Due to close relationship between smectic-I and smectic-B phases, the latter is observed in systems 3 and 4. It seems that the absence of smectic-I in 6ABP/9OCBP is mainly caused by Sʙ phase which appears at 115.5°, through $I_s + S_E \longleftrightarrow S_B$, has to its left side the nematic phase. The smectic-I phase has never been found in homeotropic textures[14]. It shows the textures of divided fan-shaped type. Sɪ modification is an equilibrium phase. On cooling the preparations Sɪ phase appears in between S_B and S_F phases according to Sackmann's rule.

If we consider the arithmatic mean of clearing point temperatures of pure components, it is seen that the thermal stability of induced phases in all these systems lie in the narrow range of 34.5° to 40.5°C, indicating that although amino group which is a good electron donor to favour induced smectic phases, it has a very small influence of change in the donor strength if one replaces 4ABP with 6ABP, 7ABP and finally with 8ABP.

Acknowledgement

One of us (RKB) is thankful to the University of Jammu, Jammu for providing a fellowship.

References

1 Dave J S, Patel K L & Vasanth K L, *Indian J Chem*, **4** (1960) 505.
2 Dave J S, Patel P R & Vasanth K L, *Molec Cryst Liq Cryst*, **8** (1969) 93.
3 Park J W, Bak C S & Labes M M, *J Am chem Soc*, **97** (1975) 4398.
4 Engelen B & Schneider F, *Z Naturf*, **33a** (1978) 1077.
5 Sharma N K, Pelzl G, Demus D & Weissflog W, *Z phys Chem* (*Leipzig*), **261** (1980) 579.
6 Araya K & Matsunaga Y, *Molec Cryst Liq Cryst*, **67** (1981) 153.
7 (a) Schneider F & Sharma N K, *Z Naturf*, **36a** (1981) 62.
(b) Schneider F & Sharma N K, *Z Naturf*, **36a** (1981) 1086.
8 Engelen B, Heppke G, Hopf R & Schneider F, *Ann Phys*, **3** (1978) 403.

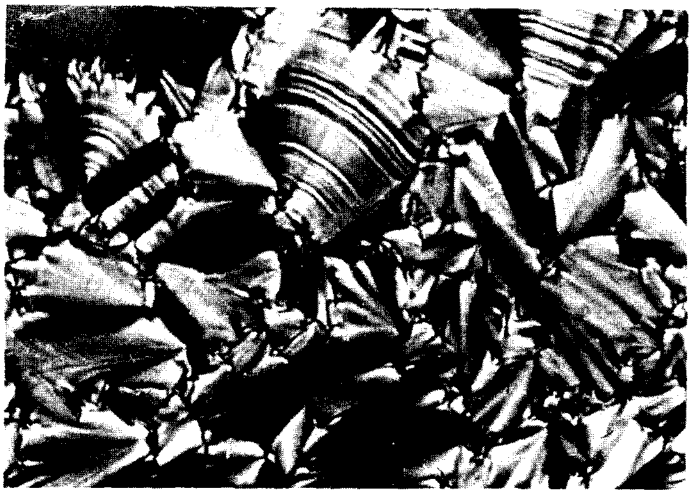

Plate 5—Induced smectic-A phase in fan shaped textures and induced smectic E phase in concentric arc ring like fan shaped textures of 8ABP/9OCBP (127°C), crossed polarisers (× 150)

9 Demus D, Pelzl G, Sharma N K & Weissflog W, *Molec Cryst Liq Cryst*, **76** (1981) 241.

10 Kofler L & Kofler A, *Thermo - Mikromethoden Zur Kennzeichnung Organischer Stoffe Und Stoffgemische* (Verlag Chemie, Weinheim) 1954.

11 *BDH Liquid Crystal material mannual* (1979).

12 Sharma N K, Weissflog W, Richter L, Diele S, Walther B, Sackmann H & Demus D, *Advances in liquid crystal research and applications*, edited by Lajos Bata (Pergamon Press, Oxford) 1980.

13 Demus D & Richter L, *Textures of liquid crystals* (Verlag fuer Grundstoffindustrie, Leipzig) 1980.

14 Sharma N K, *Indian J Chem*, **21A** (1982) 4.