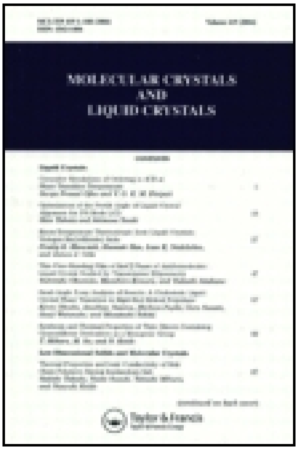

Molecular Crystals and Liquid Crystals

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

A_d-A_d Transition in a Binary Liquid Crystal System

R. Shashidhar [a] , B. R. Ratna [a] & S. Krishna Prasad [a]

[a] Raman Research Institute, Bangalore, 560 080, India

Version of record first published: 20 Apr 2011.

To cite this article: R. Shashidhar , B. R. Ratna & S. Krishna Prasad (1985): A_d-A_d Transition in a Binary Liquid Crystal System, Molecular Crystals and Liquid Crystals, 130:1-2, 179-193

To link to this article: http://dx.doi.org/10.1080/00268948508079509

Mol. Cryst. Liq. Cryst., 1985, Vol. 130, pp. 179–193
0026-8941/85/1302–0179/$20.00/0

A_d-A_d Transition in a Binary Liquid Crystal System†

R. SHASHIDHAR, B. R. RATNA and S. KRISHNA PRASAD
Raman Research Institute, Bangalore 560 080, India

(*Received December 20, 1984*)

Miscibility, high pressure, Xray and dielectric studies on binary mixtures of terminally nitro and cyano substituted compounds are presented. The results show the existence of the A_d - A_d transition which occurs from a partially bilayer phase with a temperature-dependent layer spacing to another with a temperature-independent layer spacing.

1. INTRODUCTION

While studying the phase diagram of binary mixtures of 4-n-pentylphenyl-4′-cyanobenzoyloxybenzoate and terephthal-bis-4-n-butylaniline, Sigaud et al.[1] found evidence of a transition between two optically identical smectic A phases: Xray studies[2] showed that this was a transition from a monolayer phase (A_1) to a bilayer phase (A_2). Subsequent studies have revealed several other types of A-A transitions, viz., A_1 - $\tilde{A}$, $\tilde{A}$ - A_2, A_d - A_1 and A_d - A_2.[3] The possibility of a transition between a partially bilayer A_d phase and another A_d phase with a different molecular overlapping was considered by Levelut et al.[4] though they did not find such a transition. Recently we reported[5] preliminary evidence for A_d - A_d and A_d - A_1 transitions in binary mixtures of 4-nitrophenyl-4′-(4″-n-hexyloxybenzoyloxy) benzoate (or 6 ONPBB) and p-nonyloxybenzoyloxy-p′-cyanoazobenzene (or 9 OBCAB). In this paper we report the results of our detailed high pressure, Xray and dielectric studies on this binary system.

---

†Presented at the Tenth International Liquid Crystal Conference, York, 1984.

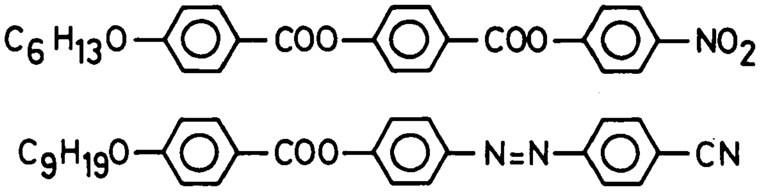

FIGURE 1 Molecular structures of 6 ONPBB (top) and 9 OBCAB (bottom).

2. THE COMPOUNDS

The molecular structures of 6 ONPBB and 9 OBCAB are given in Figure 1. The former compound, which is a terminally nitro substituted compound exhibits A_d and N phases while the latter one which has a terminally cyano end group shows A_1, N_{re}, A_d and N phases (N and N_{re} stand for nematic and reentrant nematic respectively). The transition temperatures for the two compounds are listed in Table I.

3. EXPERIMENTAL

The transition temperatures at high pressure were determined by the optical transmission technique using an optical cell with sapphire windows. Details of the high pressure set up have been described elsewhere[6,7] and will not be repeated here. Pressures were measured to a precision of ±1 bar while the transition temperature at any pressure was determined to a precision of 0.05°C.

TABLE I

Transition Temperatures of 6 ONPBB & 9 OBCAB

Compound	Transition	Temperature (°C)
6 ONPBB	$K - A_d$	124.0
	$A_d - N$	151.5
	$N - I$	238.4
9 OBCAB	$K - N_{re}$	91.0
	$N_{re} - A_d$	116.1
	$A_d - N$	212.4
	$N - I$	249.5
	$(A_1 - N_{re})$	72.4

( ) denotes that the transition is monotropic

Xray studies were performed on magnetically oriented samples contained in 0.5 mm Lindemann glass capillaries, using Copper K_α radiation reflected from a bent quartz crystal monochromator and a flat photographic film. The stability of the sample temperature during any exposure (typically 20–30 minutes) was ±0.1°C. The relative accuracy in the determination of the temperature variation of the layer spacing is reckoned to be ±0.1 Å or better.

The low frequency dispersion of $\epsilon_\parallel$ (measuring field parallel to the uniaxial direction) was studied using a Hewlett Packard Impedance analyser (4192A). The sample was typically 50–100 μm thick and was aligned by a 15 kG magnetic field. The temperature of the sample was maintained constant to ±25 mK during the dispersion measurements.

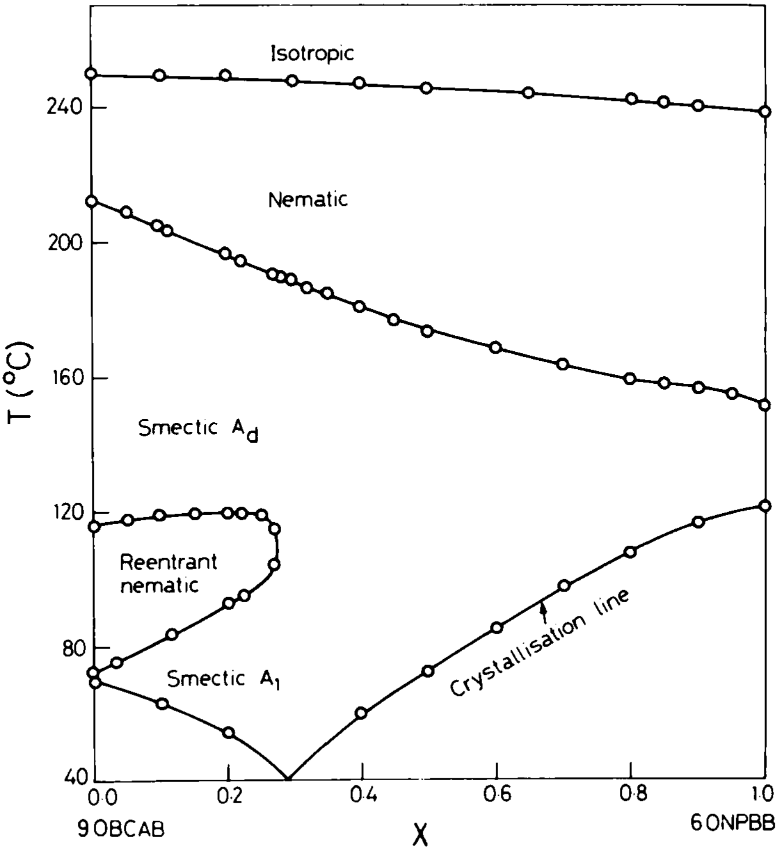

FIGURE 2 Temperature-concentration (T-X) diagram of binary mixtures of 6 ONPBB and 9 OBCAB. X is the mole fraction of 6 ONPBB in the mixture.

4. RESULTS AND DISCUSSION

The temperature-concentration (T-X) diagram of binary mixtures of 6 ONPBB and 9 OBCAB is shown in Figure 2. It is seen that the reentrant nematic phase is completely bounded in the T-X plane and does not exist for 6 ONPBB concentrations (X) > 0.29, and that the two A_d phases as well as the A_1 phase *appear* to be isomorphous, no transitions between these phases being observable optically or by DSC. A somewhat similar situation has been observed by Hardouin et al.[3,8] wherein the A_1 and A_d phases appeared to be continuously miscible without a phase transition. Since we know from our earlier pressure studies[9] that the pressure behavior of the A-N phase boundary is strongly related to the interdigitation of the molecules in the A phase, we took up a detailed high pressure study of the A-N transition in 6 ONPBB/9 OBCAB mixtures.

Pressure studies

The pressure-temperature (P-T) diagrams of the two pure compounds are shown in Figure 3(a) and 3(h) while figures 3(b)–(g) give those for mixtures with X = 0.22, 0.45, 0.6, 0.7, 0.8 and 0.9 respectively. For 9 OBCAB (Figure 3a) the A_1 - N_{re} phase boundary is a straight line while the A_d phase is bounded. It is easy to see by extrapolating the A_1 - N_{re} and N_{re} - A_d phase boundaries to negative pressures that at a pressure of about -1.7 kbar the N_{re} phases should cease to exist resulting in a direct A_1 - A_d transition. In the case of the X = 0.22 mixture (Figure 3b), such a transition is expected to take place at nearly -0.2 kbar. We can therefore infer that the pressure at which the A_1 - A_d transition occurs increases with X. For X > 0.29 (the concentration at which N_{re} phase ceases to exist at 1bar) the transition should occur at atmospheric pressure. Indeed for X = 0.45, the presence of this transition is manifested dramatically on the A-N phase boundary (Figure 3c) as an abrupt change in slope at ~0.3 kbar. Thus one can see that even though the A_1 - A_d phase boundary itself is not observed (by optical transmission technique) in the P-T plane, it leaves its signature on the A-N phase boundary. In Figure 3d we have shown the P-T diagram for X = 0.6. Here again we observe a kink at ~0.4 kbar which we associate with the ending of the A_1 - A_d transition. In addition we see a second kink at ~0.08 kbar which we associate with the existence of an A_d - A_d line below that pressure. Similar features are observed for X = 0.7 and X = 0.8 (Figures 3e and 3f) mixtures also, the range of the high temper-

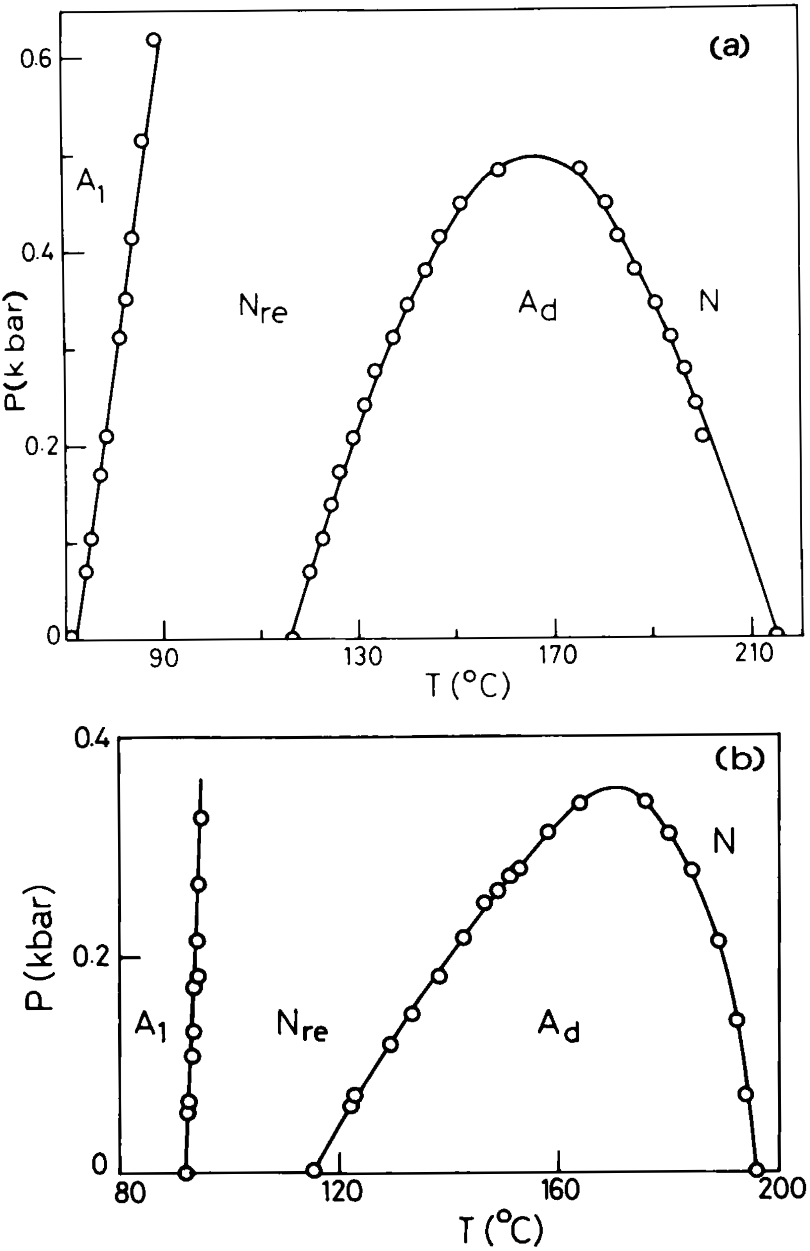

FIGURE 3 Pressure-temperature (P-T) diagrams of 6 ONPBB/9 OBCAB mixtures showing the smectic A–nematic phase boundary for different molar concentrations (X) of 6 ONPBB. The values of X for the mixtures are (a) 0 or pure 9 OBCAB, (b) 0.22, (c) 0.45, (d) 0.6, (e) 0.7, (f) 0.8, (g) 0.9 and (h) 1.0 or pure 6 ONPBB.

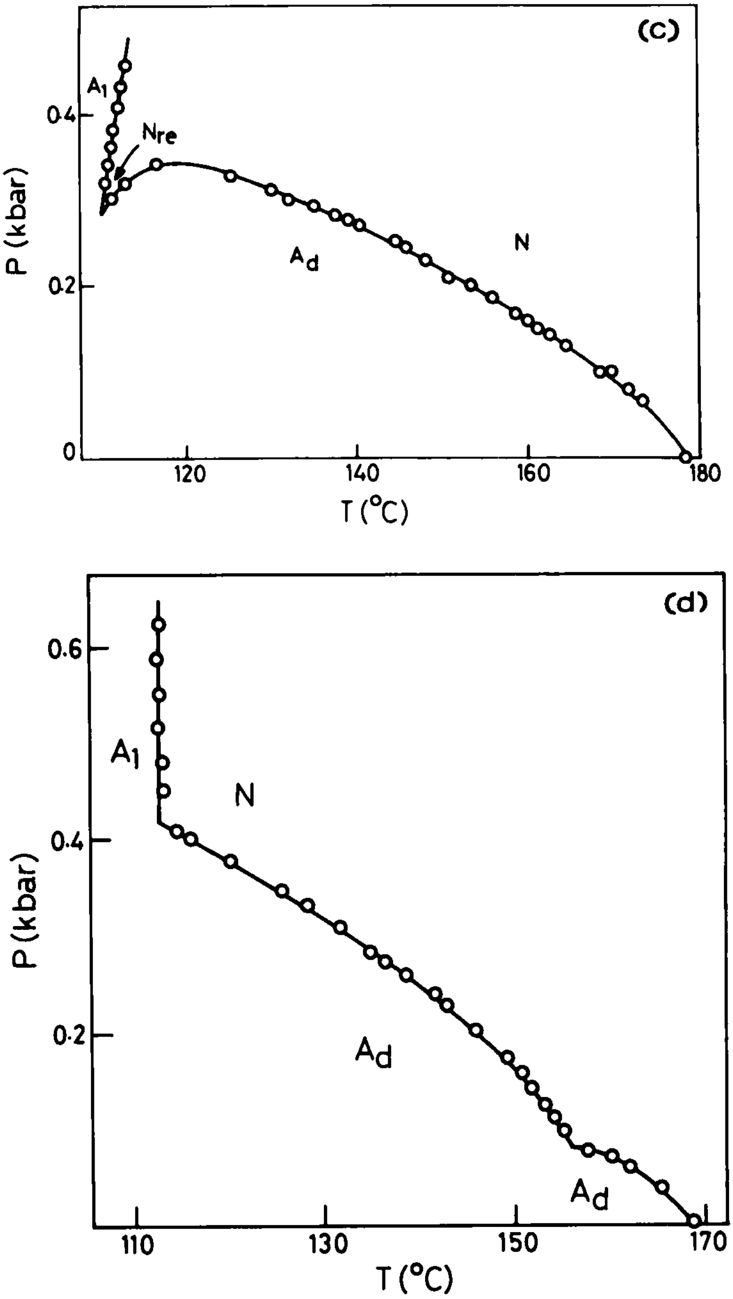

FIGURE 3 (*Continued*)

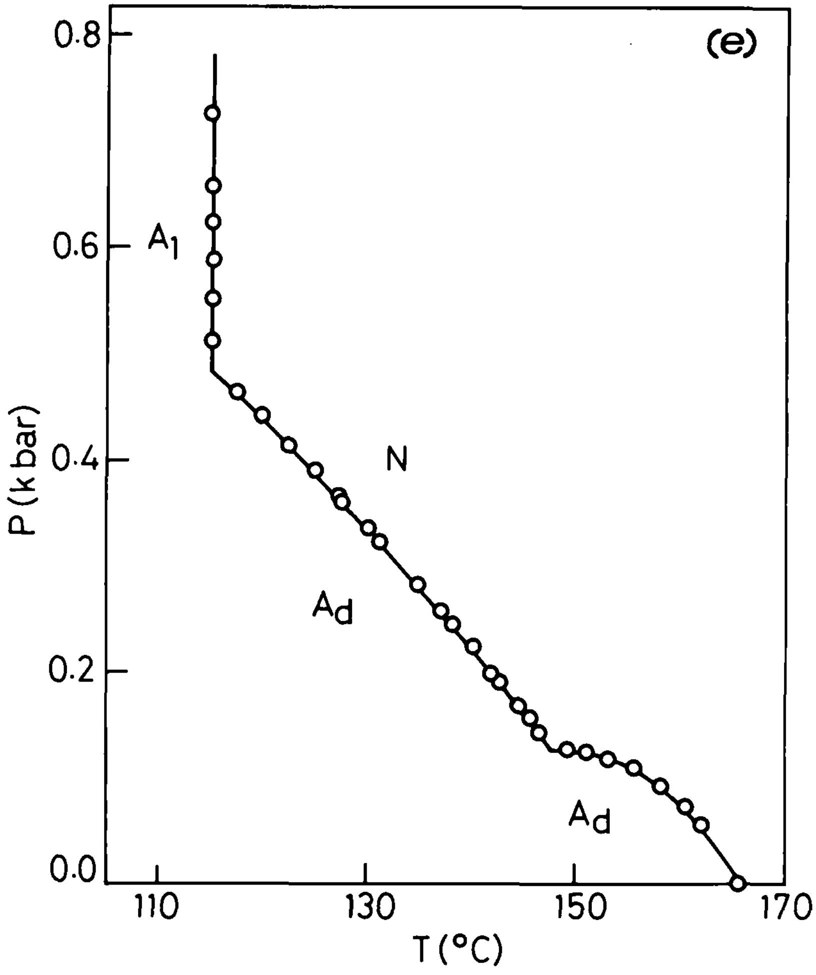

FIGURE 3 (*Continued*)

ature A_d phase increasing at the expense of that of the low temperature one. For X = 0.9 (Figure 3g) both kinks are absent showing thereby that the A_d - A_d and A_d - A_1 transitions do not exist for this concentration. In fact the P-T diagram resembles that of 6 ONPBB (Figure 3h).

The topology of the P-T diagrams in Figures 3c–f near the points at which the A_1 - A_d and A_d - A_d lines meet the A - N phase boundary clearly shows that these points should be bicritical in nature. In fact similar bicritical points have already been observed in the T-X plane.[3,10]

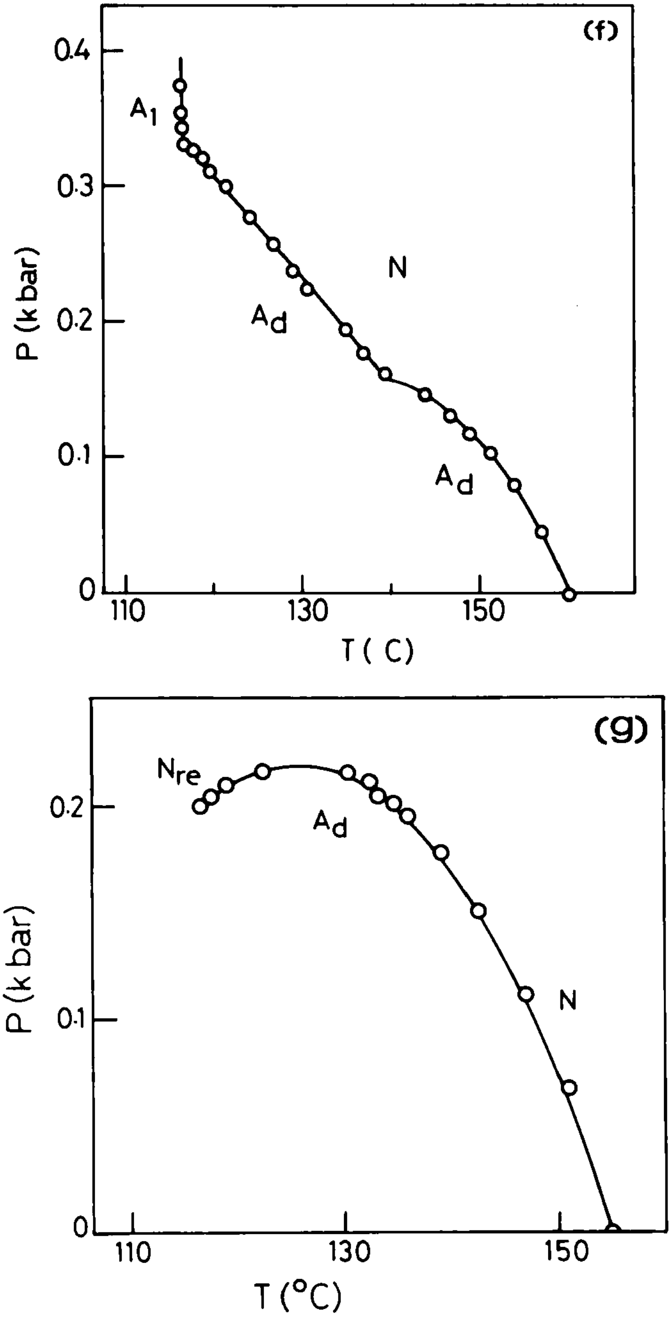

FIGURE 3 (*Continued*)

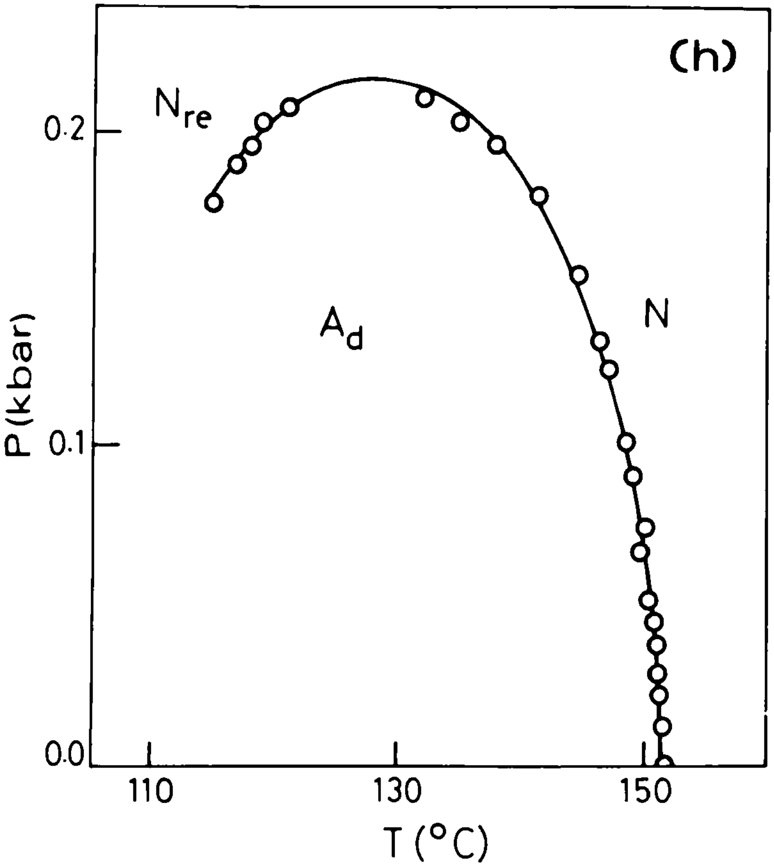

FIGURE 3 (*Continued*)

Xray studies

Precise determination of the thermal evolution of the smectic A layer spacing is of great importance in locating transitions between two types of A phases. In fact recently Hardouin et al.[11] observed that in several members of the DB_nOCl series the A_d - A_2 transition was not seen either as a textural change or in DSC traces, the only hint in favor of its existence being the change of slope observed in the temperature variation of the layer spacing. We have carried out a precise layer spacing (d) determination as a function temperature for X = 0.4, 0.55, 0.59, 0.72 and 0.79 mixtures with a view to locating the A_1 - A_d and A_d - A_d transitions at atmospheric pressure.

The temperature variation of d in the A phases of the pure compounds 9 OBCAB and 6 ONPBB is known from our previous Xray experiments.[12–14] For 9 OBCAB, d is independent of temperature in the A_1 phase and varies quite appreciably in the A_d phase. In the case of 6 ONPBB, d is practically independent of temperature in the entire A_d phase. With these facts in mind we shall now examine the d vs. temperature curves for the mixtures. For X = 0.4 (Figure 4a) the layer spacing is constant with respect to temperature up to 105°C

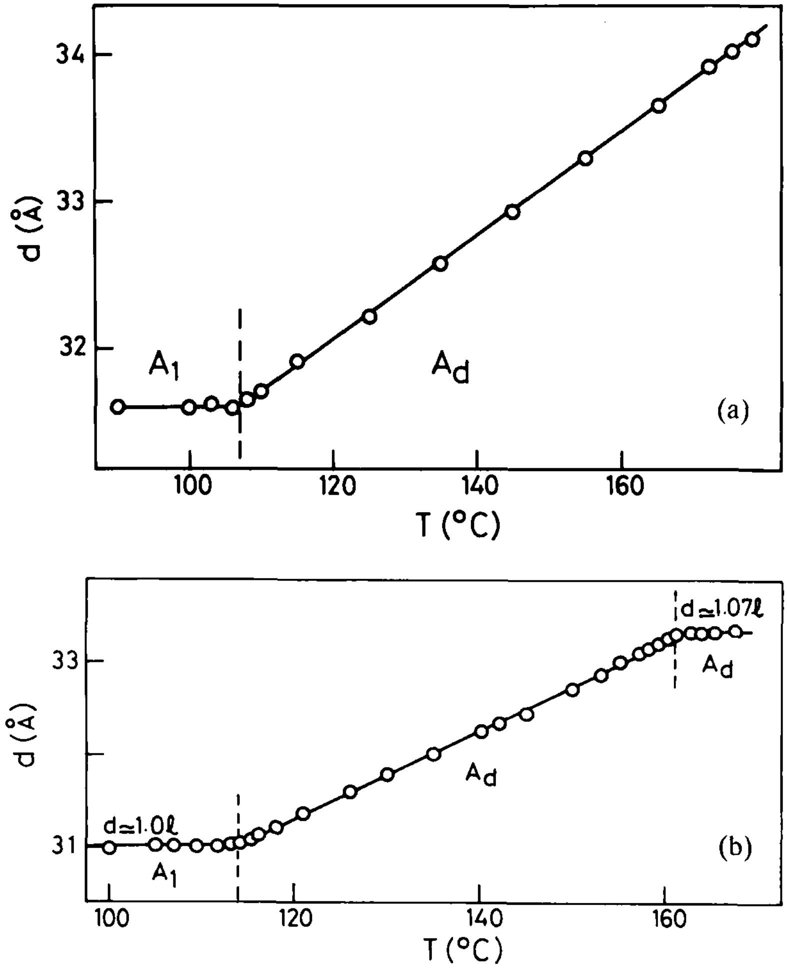

FIGURE 4 Temperature variation of the smectic A layer spacing (d) for 6 ONPBB–9 OBCAB mixtures. The values of X are (a) 0.4, (b) 0.55, (c) 0.59, (d) 0.72 and (e) 0.79.

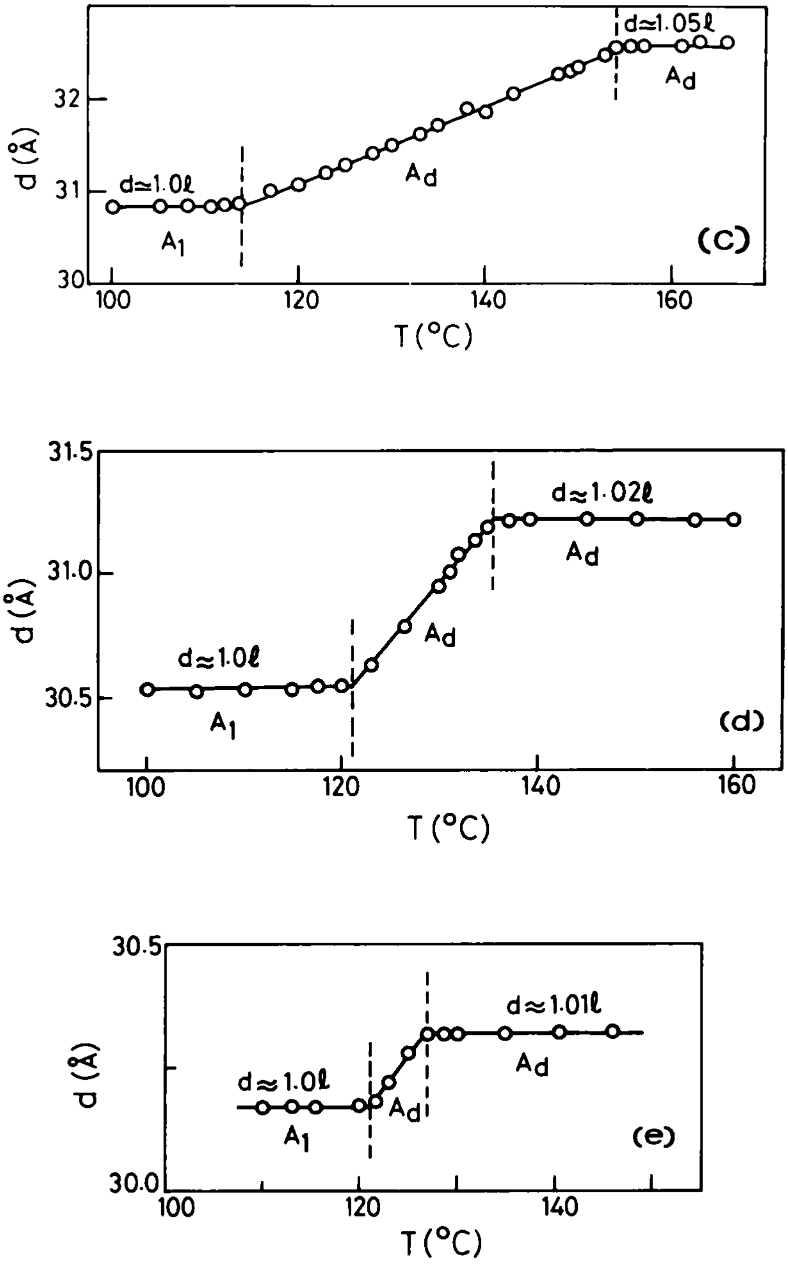

FIGURE 4 (*Continued*)

after which it suddenly starts increasing linearly right upto the A-N transition temperature. The point at which d develops the temperature dependence is identified as the A_1 - A_d transition. For the X = 0.55 mixture (Figure 4b) d vs. temperature curve exhibits a change of slope at *two* points. Initially d is temperature independent, but starts increasing with increasing temperature at 114°C. The increase in d continues till 161°C after which d again becomes independent of temperature. Essentially the same behavior is seen for X = 0.59, 0.72, and 0.79 (Figures 4c–4e respectively) also. From these curves we can therefore identify three kinds of A phases: (i) the A_1 phase ($d \simeq 1.0l$) at low temperatures with a temperature-independent layer

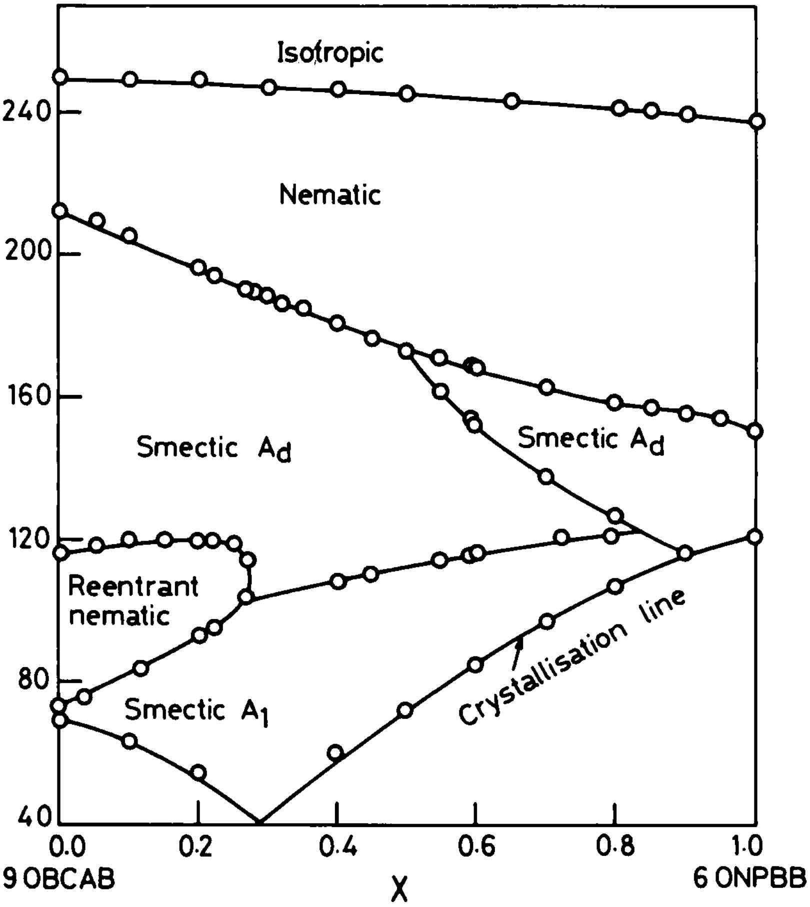

FIGURE 5 T-X diagram of 6 ONPBB - 9 OBCAB mixtures showing the A_l - A_d and A_d - A_d phase boundaries.

spacing, (ii) the A_d phase with a temperature-dependent layer spacing and (iii) another A_d phase at higher temperatures which is characterised by a temperature-independent layer spacing. Thus we have identified the A_1 - A_d and A_d - A_d transitions in these mixtures. These transition temperatures were used to map the A_1 - A_d and A_d - A_d boundaries in the T-X plane. The resulting phase diagram is given in Figure 5. It is seen that the range of the intermediate A_d phase decreases with X while that of the higher temperature phase increases, a fact which is borne out by the results of both high pressure and Xray studies.

Dielectric relaxation studies

The potentiality of using dielectric relaxation as a method to show the existence of the different polymorphic forms of the A phase has recently been demonstrated by Druon and Wacrenier.[15] We have carried out low frequency dielectric relaxation studies of $\epsilon_{\parallel}$ for a representative mixture, $X = 0.6$. Figure 6 shows the plot of f_R vs. 1/T, f_R being the relaxation frequency. It is seen that the activation energy (W) is distinctly different in the nematic, A_1 and the two A_d phases.

Thus, our high pressure, Xray and dielectric studies have shown the existence of the A_1 - A_d and A_d - A_d transitions in binary mixtures of 6ONPBB and 9OBCAB. As far as we are aware, this appears to be the only instance of an A-A transition being observed in a binary system wherein both the constituent compounds have the longitudinal components of the bridging dipoles oriented additive with respect to that of the end group dipole. The occurrence of the A_d - A_d transition is not altogether unexpected—several phase diagrams are known[4,14,16] wherein two A_d phases are separated in the temperature-concentration plane implying thereby that there may be two kinds of A_d phases.

It may be recalled that the problem of A_d - A_1 transition has been discussed theoretically by Prost[17] and more recently by Prost and Barois[18] who have argued that since the A_1 and A_d phases have the same symmetry, any phase transition between them has to be first order except possibly at a critical point like the one in a liquid-vapour system. One would therefore expect a discontinuity in the layer spacing at this transition. But within our experimental accuracies, we do not see such a discontinuity in the layer spacing at either the A_1 - A_d or the A_d - A_d transition, although we do observe a break in the thermal expansion at these transitions. To this extent these transitions are somewhat unusual. This also leads us to conclude that the dif-

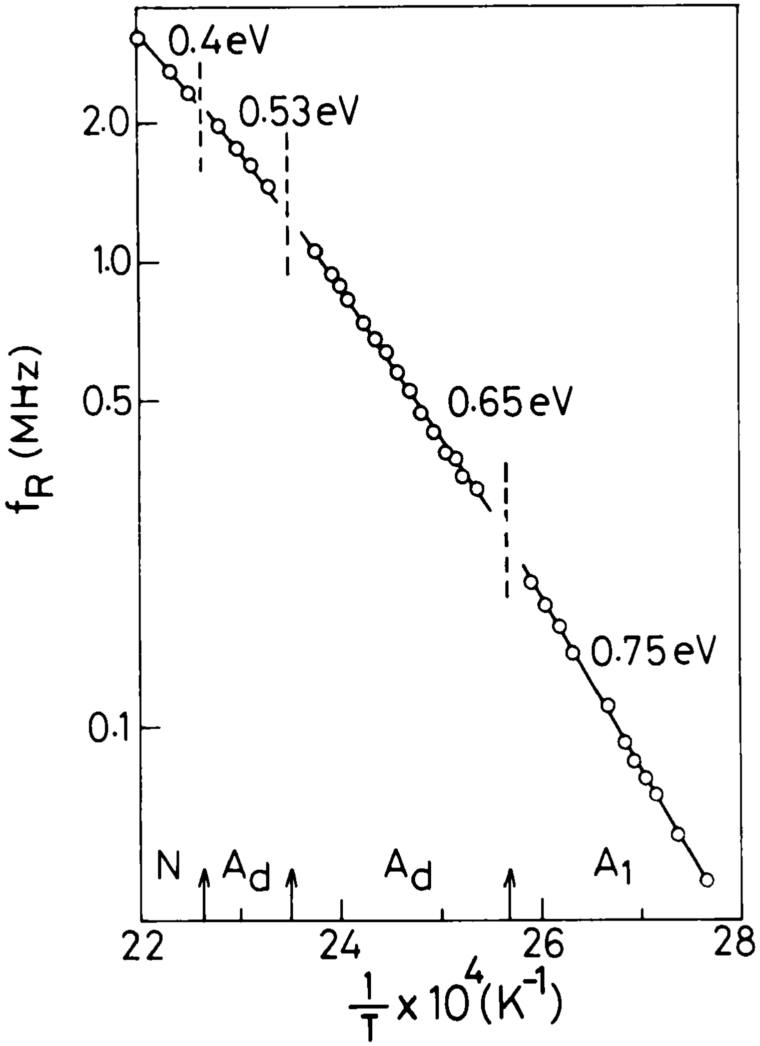

FIGURE 6 Plot of relaxation frequency (f_R) vs. 1/T for X = 0.6 mixture.

ferences between the A_1 and the two A_d phases should be quite subtle. Clearly, more experiments are needed to understand these differences.

Acknowledgment

The authors are thankful to Professor S. Chandrasekhar for useful discussions. The help of Mr. V. N. Raja and Mr. C. Nagabhushan in some measurements is gratefully acknowledged. Thanks are also due to Dr. J. Prost for comments.

References

1. G. Sigaud, F. Hardouin, M. F. Achard and H. Gasparoux, *J. Physique*, **40** C3-356 (1979).
2. F. Hardouin, A. M. Levelut, J. J. Benattar and G. Sigaud, *Solid State Commun.*, **33** 337 (1980).
3. For a comprehensive review on transitions between different types of A phases see F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *J. Chim. Phys.*, **80**, 53 (1983); see also N. V. Madhusudana, B. S. Srikanta and M. Subramanya Raj Urs, *Mol. Cryst. Liq. Cryst.*, **97**, 49 (1983).
4. A. M. Levelut, R. J. Tarento, F. Hardouin, M. F. Achard and G. Sigaud, *Phys. Rev.*, **A24**, 2180 (1981).
5. R. Shashidhar, B. R. Ratna and S. Krishna Prasad, *Mol. Cryst. Liq. Cryst. Letters*, **102**, 105 (1984).
6. A. N. Kalkura, R. Shashidhar and M. Subramanya Raj Urs, *J. Physique*, **44**, 51 (1983).
7. A. N. Kalkura, 'High Pressure Optical Studies on Liquid Crystals' Ph.D. Thesis, University of Mysore, 1982.
8. F. Hardouin, A. M. Levelut, G. Sigaud, M. F. Achard, Nguyen Huu Tinh and H. Gasparoux in 'Symmetries and Broken Symmetries in Condensed Matter Physics,' Ed: N. Boccara, IDSET, Paris, p. 231 (1981).
9. S. Krishna Prasad, R. Shashidhar, A. N. Kalkura, K. A. Suresh, G. Heppke and R. Hopf, *Mol. Cryst. Liq. Cryst.*, **99**, 13 (1983).
10. J. Prost, *Advances in Physics*, **33**, 1 (1984).
11. F. Hardouin, M. F. Achard, C. Destrade and Nguyen Huu Tinh, *J. Physique*, **45**, 765 (1984).
12. K. A. Suresh, R. Shashidhar, G. Heppke and R. Hopf, *Mol. Cryst. Liq. Cryst.*, **99**, 249 (1983).
13. G. Heppke and R. Hopf (Unpublished).
14. B. R. Ratna, S. Krishna Prasad, R. Shashidhar, G. Heppke and S. Pfeiffer, Presented at the X Int. Liq. Cryst. Conference, York, July 1984, *Mol. Cryst. Liq. Cryst.*, (in press).
15. C. Druon and J. M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **98**, 201 (1983).
16. B. R. Ratna, R. Shashidhar and S. Somasekhar (Unpublished).
17. J. Prost, in 'Liquid Crystals of One- and Two-Dimensional Order,' Eds.: W. Helfrich and G. Heppke, Springer-Verlag, (Berlin, Heidelberg, New York) p. 125, 1980.
18. J. Prost and P. Barois, *J. Chim. Phys.*, **80**, 65 (1983).