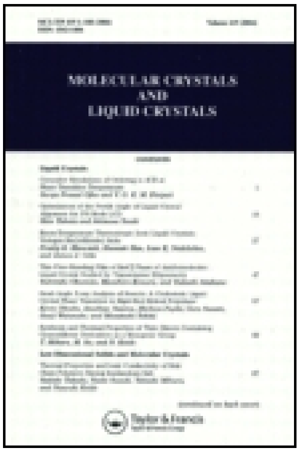

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A New Kind of A-A Transition: Studies on Binary Mixtures of Terminally Substituted Cyano and Nitro Compounds

R. Shashidhar [a] , B. R. Ratna [a] & S. Krishna Prasad [a]
[a] Raman Research Institute, Bangalore, 560080, India
Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. Volume 102 (Letters), pp. 105-111
0140-6566/84/1024-0105$18.50/0

A NEW KIND OF A-A TRANSITION: STUDIES ON BINARY MIXTURES OF TERMINALLY SUBSTITUTED CYANO AND NITRO COMPOUNDS

R.Shashidhar, B.R.Ratna and S.Krishna Prasad
Raman Research Institute, Bangalore 560080, India

(Received for Publication May 11, 1984)

Abstract. High pressure, Xray and miscibility studies on binary mixtures of terminally substituted cyano and nitro compounds have led to the observation of two kinds of A-A transitions, viz., A_d-A_d and A_d-A_1, the former being observed for the first time. The signatures of these transitions, which are not observable either optically or by differential scanning calorimetry, are seen dramatically in the smectic A - nematic phase boundary in the P-T plane. Xray results show that the A_d-A_d transition is from a partially bilayer smectic A with a temperature-independent layer spacing to one with a temperature-dependent layer spacing.

It is now well known[1] that several polymorphic forms of smectic A exist, viz., A_1, A_2, A_d and $\tilde{A}$. Direct transitions between all these forms (except the A_d-$\tilde{A}$ transition) have been observed either in single component systems or in binary systems.[2] We have studied, by miscibility, high pressure and Xray techniques, binary mixtures of terminally substituted cyano and nitro compounds with a view to seeing if the A_d phases exhibited by these compounds are isomorphous.

The compounds studied are 4-nitrophenyl-4'-(4"-n-hexyloxybenzoyloxybenzoate (or 6 ONPBB) and p-nonyloxybenzoyloxy-p'-cyanoazobenzene (or 9 OBCAB) whose molecular structures are given in Figure 1. 6 ONPBB exhibits A_d and N phases while 9 OBCAB shows A_1, N_{re}, A_d and N phases with increasing temperature (N and N_{re} standing for nematic and reentrant nematic).

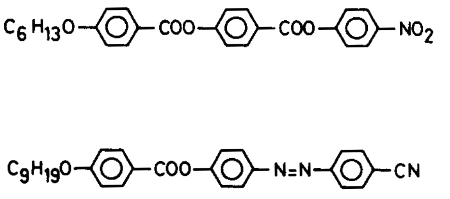

Figure 1 Molecular structures of 6 ONPBB (top) and 9 OBCAB (bottom).

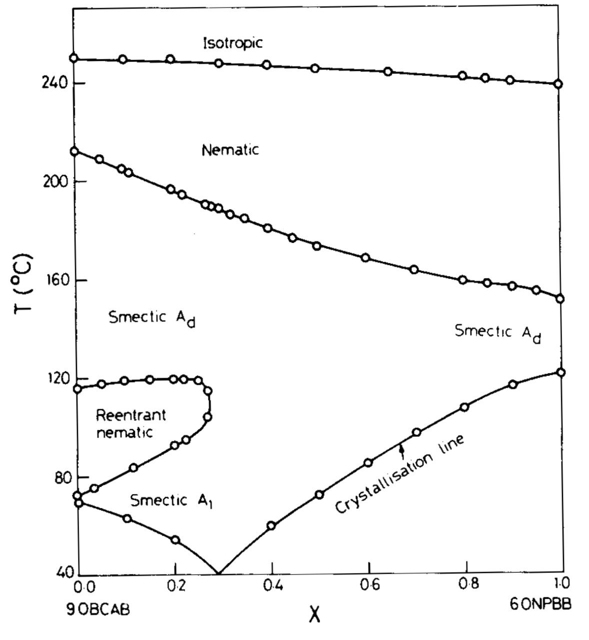

Figure 2. Temperature-concentration (T-X) diagram of binary mixtures of 6 ONPBB and 9 OBCAB. X is the mole fraction of 6 ONPBB in the mixture.

The temperature concentration diagram is shown in Figure 2.[3] It is interesting to note that the N_{re} phase is completely bounded and does not exist for 6 ONPBB molar concentrations (X) > 0.29. The two A_d phases as well as the A_1 phase appear to be isomorphous, no transitions between these phases being observable either optically or by differential scanning calorimetry (DSC). (A somewhat similar situation has been observed before by Hardouin et al.[2] where A_d and A_1 phases seemed to be continuously miscible.) Since we know from our earlier studies on 9 OBCAB[4,5] that the pressure behaviour of the A phase should be strongly related to the extent of interdigitation of the molecules in the layer, we decided to conduct a detailed pressure study of the A-N transition in 6 ONPBB/9 OBCAB mixtures.

Pressure Studies: The A-N transitions at high pressures were detected by the optical transmission technique using an optical high pressure cell.[4,6] The accuracy of pressure measurement was ±1 bar while that of temperature measurement was ±0.05^{o}C. Figures 3(a)-(d) show the P-T diagrams for 4 binary mixtures, viz., for X = 0.22, 0.45, 0.60 and 0.70, where X is the mole fraction of 6 ONPBB in the mixtures. The P-T diagram of the X = 0.22 mixture (Fig. 3a) is very similar to that of pure 9 OBCAB,[5] the A_1-N_{re} line is straight while the A_d phase is completely bounded. It is easy to see by extrapolating the A_1-N_{re} and N_{re}-A_d lines to negative pressures that we should arrive at a situation wherein the N_{re} phase ceases to exist between the A_1 and A_d phases resulting in a direct A_1-A_d transition at about -0.2 kbar. (In the case of pure 9 OBCAB[5] such a transition can be expected to occur at a still lower (negative) pressure, viz., -1.7 kbar). We can therefore infer that with increasing X, the pressure at which the A_1-A_d transition occurs should also increase and as a consequence the A_1-A_d transition should exist at atmospheric pressure for X > 0.29 at which the N_{re} phase ceases to exist (see Fig.2). For X = 0.45 (Fig. 3b) the A-N boundary shows a drastic change of slope at 0.3 kbar. We ascribe this to the intersection of the A_1-A_d line with the A_d-N and A_1-N phase boundaries. For X = 0.6 (Fig.3c) the A-N boundary shows two kinks, one at 0.41 kbar and the other at 0.08 kbar. The kink at 0.41 kbar can be associated, as in the case of the X = 0.45 mixture, with the intersection of the A_1-A_d boundary with the A_d-N and A_1-N boundaries. The second kink at 0.08 kbar, which is somewhat less pronounced, should be due to the meeting of another phase boundary with the A_d-N boundary. We associate this kink as being due to the existence of an A_d-A_d transition in the P-T plane. We shall show presently by Xray diffraction experiments that this A_d-A_d transition does exist even at atmospheric pressures. The same type of behaviour is again seen for the X = 0.80 mixture (Fig. 3d). It must be mentioned that although the signatures

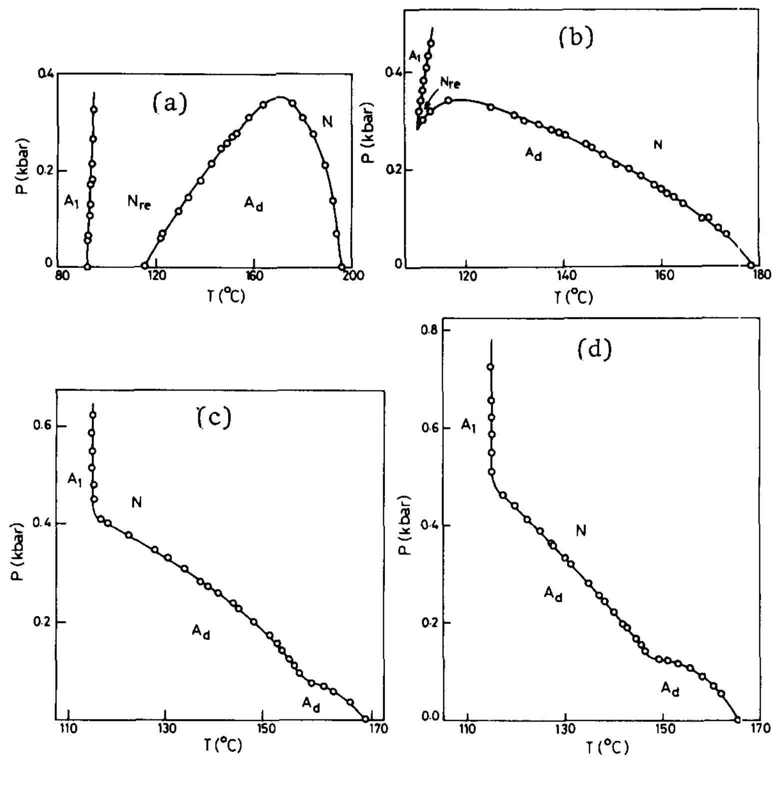

Figure 3. P-T diagrams of 6 ONPBB/9 OBCAB mixtures for different values of X; (a) 0.22, (b) 0.45, (c) 0.60 and (d) 0.70.

of the A_1-A_d and A_d-A_d transitions are seen dramatically in the A-N phase boundary in the P-T plane, both these transitions per se are unobservable either optically or by DTA experiments at high pressure showing thereby that these should be second order transitions.

Xray Results: We have determined by Xray diffraction experiments on oriented samples, the precise smectic A layer spacing as a function of temperature for different concentrations. We shall give here only two representative diagrams which illustrate the important results.

The temperature variation of the layer spacing (d) in the different A phases of the pure compounds 6 ONPBB and 9 OBCAB is already known from our previous Xray experiments. For 9 OBCAB d is independent of temperature in the A_1 phase ($d \simeq 0.96\ell$) while it varies quite appreciably ($d \simeq 1.07\ell$ to 1.14ℓ) with temperature in the A_d phase.[7] On the other hand in the case of the A_d phase of 6 ONPBB d is independent of temperature ($d \simeq 1.04\ell$)[8]. With these facts in mind we shall now examine the d vs. temperature curves for two concentrations, viz., X = 0.7 and 0.8 (Figs. 4a and 4b).

It is seen that for X = 0.7 (Fig. 4a) d is initially constant with respect to temperature but starts increasing beyond 118.2°C. This increasing trend is continued up to 138.0°C after which d again becomes independent of temperature. The d vs. temperature curve for X = 0.8 (Fig. 4b) also shows exactly similar features. From these curves we

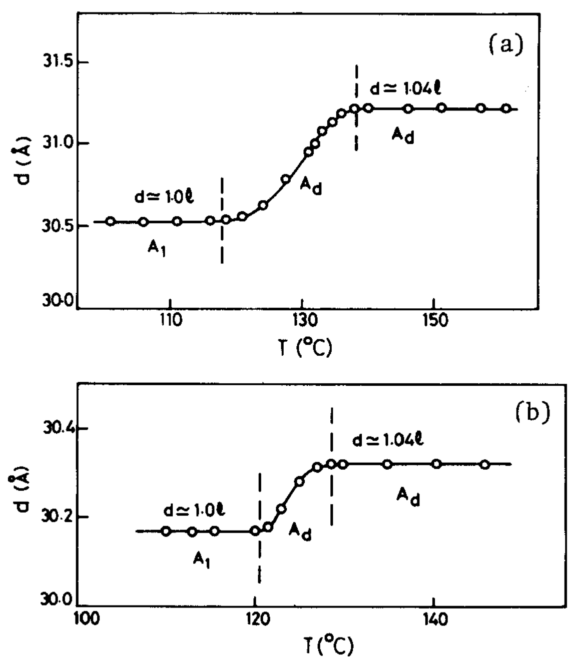

Figure 4. Temperature variation of the smectic A layer spacing (d) for (a) X = 0.7 and (b) X = 0.8.

can therefore identify three kinds of A phases - (i) the A_1 phase ($d \simeq 1.0\ell$) at low temperatures with a temperature-independent layer 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 ($d \simeq 1.04\ell$). Thus we have seen the A_1-A_d and A_d-A_d transitions, the latter being observed for the first time. It must also be remarked that this appears to be the only instance of an A-A transition being observed in binary systems wherein both the compounds have their bridging dipoles oriented additive with respect to the polar end group.

Similar Xray studies for several other concentrations have allowed us to obtain the A_1-A_d and A_d-A_d transition temperatures as functions of concentration at atmospheric pressure. The resulting plot is shown in Figure 5 which gives both the A_1-A_d and A_d-A_d phase boundaries in the T-X diagram.

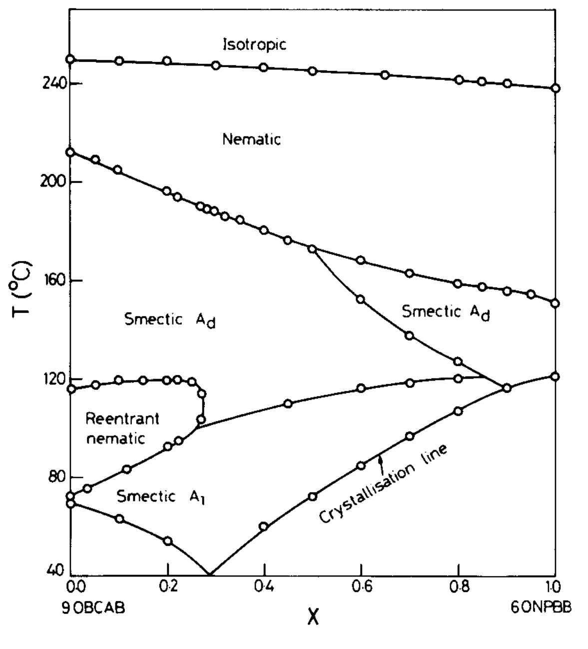

Figure 5. T-X diagram showing the A_1-A_d and A_d-A_d phase boundaries.

We are presently conducting high pressure Xray studies to monitor these transitions in the P-T plane. We are also conducting dielectric studies to see if these transitions manifest in the dielectric properties. The results of these investigations will be published elsewhere.

Acknowledgement: We wish to thank Professor S.Chandrasekhar for his interest in this work and for discussions.

References

1. See e.g., A.M.Levelut, R.J.Tarento, F.Hordouin, M.F.Achard and G.Sigaud, Phys.Rev. A24 2180 (1981).
2. For comprehensive reviews on the different types of A-A transitions observed so far see F.Hardouin, A.M.Levelut, M.F.Achard and G.Sigaud, J.Chim.Phys. 80, 53 (1983) and Nguyen Huu Tinh, J.Chim.Phys. 80, 83 (1983); see also N.V.Madhusudana, B.S.Srikanta and M.Subramanya Raj Urs, Mol.Cryst.Liquid Cryst., 97, 49 (1983).
3. G.Heppke and S.Pfeiffer (Private communication).
4. R.Shashidhar, Mol.Cryst.Liq.Cryst. 98, 13 (1983).
5. S. Krishna Prasad,R.Shashidhar, K.A.Suresh, A.N.Kalkura, G.Heppke and R.Hopf, Mol.Cryst.Liq. Cryst. 99, 185 (1983).
6. A.N.Kalkura, R.Shashidhar and M.Subramanya Raj Urs, J.Physique, 44, 51 (1983).
7. K.A.Suresh, R.Shashidhar, G.Heppke and R.Hopf, Mol.Cryst.Liq.Cryst. 99, 51 (1983).
8. B.R.Ratna, R.Shashidhar, S.Krishna Prasad, G.Heppke and S.Pfeiffer, to be presented at the Tenth International Liquid Crystal Conference, York, U.K., July 1984.