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

Experimental Studies on a Terminally Nitro Substituted Compound with a Latent Reentrant Nematic Phase

B. R. Ratna [a], S. Krishna Prasad [a], R. Shashidhar [a], G. Heppke [b] & S. Pfeiffer [b]

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

[b] Technische Universität Berlin, ER11, Strasse des 17 Juni 135, D-1000 Berlin 12, Germany

Version of record first published: 17 Oct 2011.

To cite this article: B. R. Ratna , S. Krishna Prasad , R. Shashidhar , G. Heppke & S. Pfeiffer (1985): Experimental Studies on a Terminally Nitro Substituted Compound with a Latent Reentrant Nematic Phase, Molecular Crystals and Liquid Crystals, 124:1, 21-26

To link to this article: http://dx.doi.org/10.1080/00268948508079462

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 21–26
0026-8941/85/1244–021/$15.00/0

Printed in the United States of America

Experimental Studies on a Terminally Nitro Substituted Compound with a Latent Reentrant Nematic Phase†

B. R. RATNA, S. KRISHNA PRASAD, R. SHASHIDHAR

Raman Research Institute, Bangalore 560 080, India

and

G. HEPPKE and S. PFEIFFER

Technische Universität Berlin, ER11, Strasse des 17 Juni 135, D-1000 Berlin 12, Germany

(*Received September 30, 1984; in final form November 19, 1984*)

In this paper we present the results of our high pressure, miscibility and X-ray studies on 4-nitrophenyl-4′-(4″-n-hexyloxybenzoyloxy)benzoate in which the longitudinal components of the bridging dipoles are oriented additive with respect to the nitro end group dipole. The results show that this compound has latent reentrant polymorphism.

INTRODUCTION

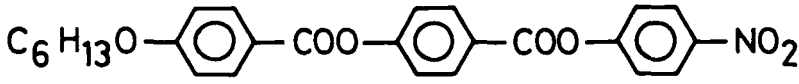
Only a few triaromatic compounds with a nitro end group are known to exhibit reentrant nematic behavior.[1–3] In all of them, the longitudinal components of the dipole moments of the bridging groups oppose that of the nitro end group dipole. As yet no case has been found of reentrant polymorphism in a nitro compound in which the bridging and the end dipoles are additive. In this paper we present X-ray, high pressure and miscibility studies on a triaromatic com-

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

pound, viz, 4-nitrophenyl-4′-(4″-n-hexyloxybenzoyloxy)benzoate, hereafter abbreviated as 6 ONPBB, in which all the dipoles are additive. The results show that this compound has a *latent* reentrant nematic phase.

EXPERIMENTAL

The compound 6 ONPBB has the following molecular structure:



It exhibits the smectic A-nematic (A-N) transition at 151.5°C and the nematic-isotropic (N-I) transition at 238.4°C.

In order to characterize the smectic A phase X-ray studies have been conducted on magnetically oriented samples. Copper K_α radiation reflected from a flat graphite monochromator was incident on the sample. The diffraction spots which lie in the equatorial plane were recorded photographically on a flat film. The temperature of the sample was maintained constant to within 100 mK during an exposure. The relative accuracy in the layer spacing measurement is ± 0.1 Å.

The smectic A-nematic phase boundary in the pressure-temperature plane was studied using an optical high pressure cell with sapphire windows.[4] The sample was isolated completely from the pressure transmitting fluid (plexol) by an elastomer material (fluran). The transition temperatures were determined by varying the temperature at a constant pressure and monitoring the changes in the intensity of laser light transmitted by the sample. Pressures were read using a Heise Gauge to a precision of ± 1 bar while the transition temperatures were determined to a precision of ± 0.1°C.

Miscibility studies were conducted with 4-cyanophenyl 4′-(4″-n-nonyloxybenzoyloxy)benzoate (9 OCPBB) which exhibits the following sequence of transitions:[5] I 227.3 N 192.7 A_d 116.7 N_{re}.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the layer spacing (d) versus temperature in the smectic A phase of 6 ONPBB. The value of d remains unchanged

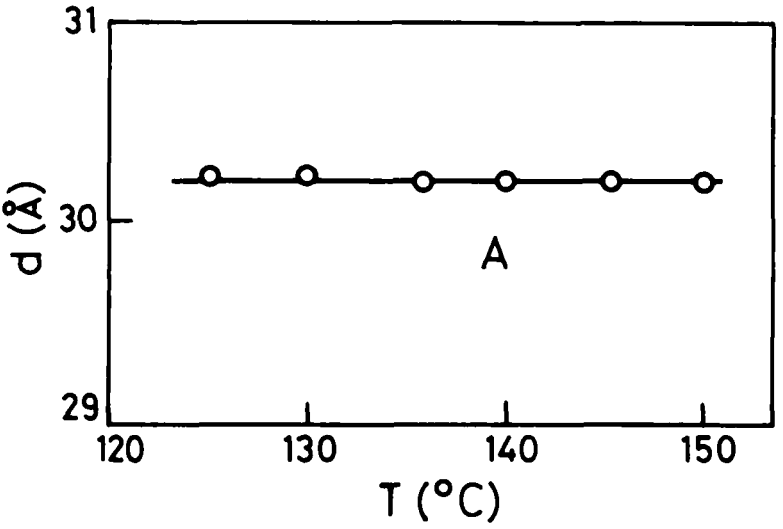


FIGURE 1 Temperature variation of layer spacing in the S_A phase of 4-nitrophenyl-4'-(4"-n-hexyloxybenzoyloxy)benzoate (6 ONPBB).

throughout the smectic phase. We have measured the length of the molecule using the Dreiding model as 29 Å which gives a d/1 ratio of about 1.04. Therefore we classify the smectic A phase as a partially bilayer (A_d) phase.

In Figure 2 we show the pressure-temperature diagram of 6 ONPBB showing the A-N boundary. (Since the maximum working temperature in our high pressure cell is about 250°C, we have not followed the N-I transition at high pressures.) It is seen that the A-N phase boundary which has a negative slope even at 1 bar curls towards the pressure axis with increasing pressure and the reentrant nematic phase is observed in the pressure range 175–214 bar. Crystallization prevents the observation of the N_{re} phase for pressures below 175 bar. We also identified the reentrant nematic phase at high pressures by optical microscopic observation. By fitting the experimental data to a general equation of a conic section we find that the A-N phase boundary has an elliptic shape. This is in agreement with our earlier observation on a number of reentrant nematogens.[6] The fitted elliptic curve is shown as a solid line in Figure 2. It cuts the temperature axis at 103°C which is the virtual N_{re}-A transition at 1 bar. The fact that this compound exhibits the reentrant nematic phase at high pressure supports the X-ray result, namely, the A phase of this compound is a partially bilayer phase.

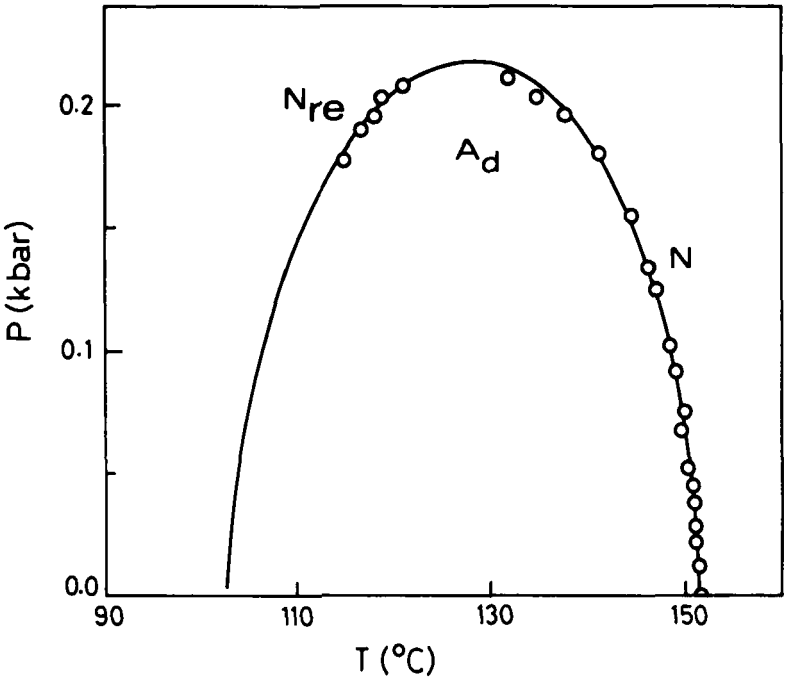


FIGURE 2 P-T diagram of 6 ONPBB showing the A-N phase boundary. The solid line is a computer fit of the data to the general equation of a conic section (see text).

The results of our miscibility studies are given in Figure 3. Since 9 OCPBB exhibits a reentrant nematic phase while 6 ONPBB has an inherent reentrant nematic behavior (as seen by the pressure studies), one would expect the smectic A phases of the two compounds to be miscible. But we see from Figure 3 that this is not the case, the two A_d phases are in fact *separated* in the concentration range $0.3 < X < 0.44$, where X is the mole fraction of 9 OCPBB in the mixture. It may be recalled that we had previously observed a similar instance of the A_d phases of terminally substituted nitro and cyano compounds being incompatible and leading to an A_d-A_d transition.[7] It is of interest to note that the N_{re} phase is seen even for mixtures rich in 6 ONPBB. The crystallization line, which cuts the A-N_{re} portion of the phase boundary for $X < 0.1$ prevents the occurrence of N_{re} phase for concentrations $X < 0.1$. An extrapolation of the A-N_{re} phase boundary to $X = 0$ gives the virtual A-N_{re} transition temperature of 105°C for 6 ONPBB which is in reasonable agreement with the value (103°C) obtained from pressure studies. It is thus clear that the occurrence of reentrant nematic behavior (at atmospheric pressure) in terminally

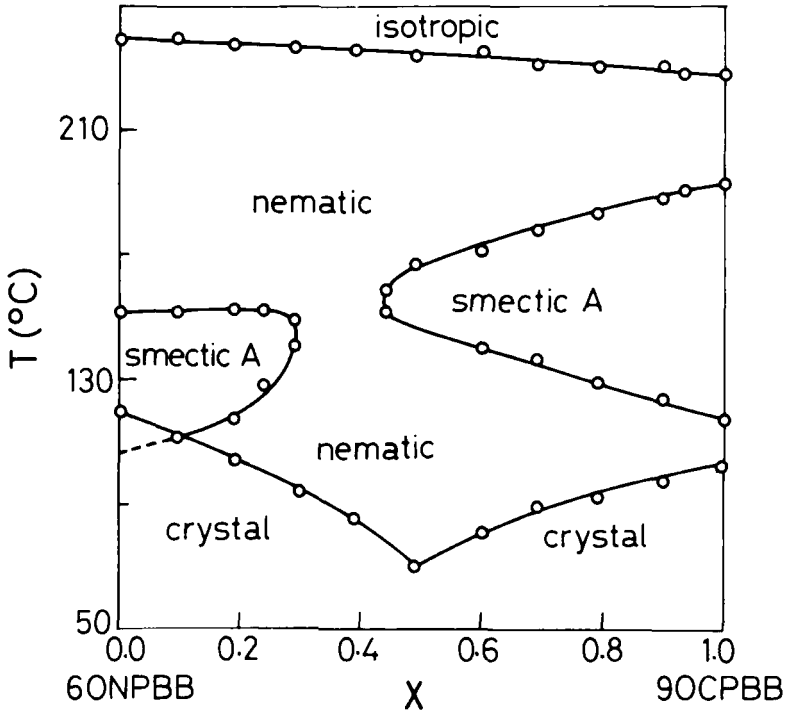


FIGURE 3 Temperature-concentration diagram (1 bar) for binary mixtures of 6 ONPBB and 9 OCPBB. X is the mole fraction of 9 OCPBB in the mixture.

nitro substituted compounds in which the longitudinal components of the bridging dipoles are additive with respect to the nitro end group is a distinct possibility. Further studies on similar substances will be of great interest.

Acknowledgment

We wish to thank Professor S. Chandrasekhar for discussions. One of us (S. P.) acknowledges the financial support of the Gesellschaft von Freunden der Technischen Universität Berlin. Thanks are also due to Dr. K. A. Suresh for his help in carrying out the X-ray studies. We are grateful to the referee for suggestions.

References

1. For a detailed account of the various compounds exhibiting the reentrant nematic behaviour, see Nguyen Huu Tinh, *J. Chim. Phys.*, **80**, 83 (1983).
2. Nguyen Huu Tinh, F. Hardouin and C. Destrade, *J. Physique*, **43**, 1127 (1982).

3. Nguyen Huu Tinh, H. Gasparoux and J. Malthete, *Proc. Fourth European Winter Conference*, Bovec, Yugoslavia, March 1984.
4. A. N. Kalkura, 'High Pressure Optical Studies on Liquid Crystals,' Ph.D. Thesis, University of Mysore 1982.
5. G. Heppke and U. Müller (unpublished.).
6. A. N. Kalkura, R. Shashidhar and M. Subramanya Raj Urs, *J. Physique*, **44**, 51 (1983).
7. R. Shashidhar, B. R. Ratna and S. Krishna Prasad, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 105 (1984).