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

Temperature Variation of the Layer Spacing in the Smectic A, Reentrant Nematic and Reentrant Smectic A Phases of 9 OBCAB

K. A. Suresh [a] , R. Shashidhar [a] , G. Heppke [b] & R. Hopf [b]

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

[b] Universitärer Forschungschwerpunkt-UF1, der Technische Universität Berlin, Sekr C2, Strasse des 17 Juni 135, D-1000, Berlin 12, Federal Republic of Germany

Version of record first published: 17 Oct 2011.

To cite this article: K. A. Suresh , R. Shashidhar , G. Heppke & R. Hopf (1983): Temperature Variation of the Layer Spacing in the Smectic A, Reentrant Nematic and Reentrant Smectic A Phases of 9 OBCAB, Molecular Crystals and Liquid Crystals, 99:1, 249-253

To link to this article: http://dx.doi.org/10.1080/00268948308072046

Mol. Cryst. Liq. Cryst., 1983, Vol. 99, pp. 249–253
0026-8941/83/9904–0249/$18.50/0

Printed in the United States of America

Temperature Variation of the Layer Spacing in the Smectic A, Reentrant Nematic and Reentrant Smectic A Phases of 9 OBCAB†

K. A. SURESH‡, R. SHASHIDHAR‡, G. HEPPKE§ and R. HOPF§

‡Raman Research Institute, Bangalore 560 080, India; §Universitärer Forschungschwerpunkt-UF1, der Technische Universität Berlin, Sekr C2, Strasse des 17 Juni 135, D-1000 Berlin 12, Federal Republic of Germany

(Received February 28, 1983)

Precise X-ray determinations have been made of the temperature variation of the layer spacing in the smectic A, reentrant nematic and reentrant smectic A phases of a pure reentrant mesogen, *viz.*, 4-nonyloxy-benzoyloxy-4′-cyanoazobenzene (9 OBCAB). The higher temperature smectic phase is (partially) bilayer in nature, the extent of the overlap increasing with decrease of temperature. The reentrant smectic A has a monolayer structure whose spacing is temperature independent. The change from the bilayer to monolayer arrangement is a continuous process which commences in the reentrant nematic phase and continues right through it.

INTRODUCTION

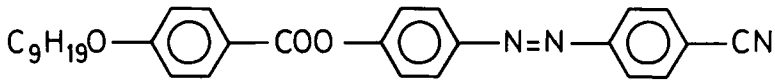
Reentrant behavior in liquid crystals[1,2] is exhibited by compounds having a highly polar cyano or nitro group attached to one end of the molecule which results in strong antiparallel near neighbor correlations.[3] This, in turn, leads to a bilayer structure in which the molecules are interdigitated.[4] The study of the extent of overlap and its dependence on temperature is, therefore, of considerable importance in understanding the reentrant phenomenon at a molecular level. There have been a few studies on the temperature variation of the smectic A layer spacing in reentrant mesogens and the results appear to depend on the compound. In mixtures of N-*p*-

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

cyanobenzylidene-*p*-*n*-octyloxyaniline (CBOOA) and N-(*p*-hexyloxybenzylidene)-*p*-aminobenzonitrile (HBAB) the layer spacing (d) shows a small increase with decreasing temperature.[5] In both 4-cyanophenyl-3′-methyl-4′(4″-*n*-undecylbenzoyloxy) benzoate (11CPMBB) and its next higher homologue 12 CPMBB, the *d* value decreases first over a part of the A phase and then increases with decrease of temperature.[6] In the case of 4-*n*-octyloxybenzoyloxy-4′-cyanostilbene (T_8) which exhibits both reentrant nematic (N_{re}) and reentrant smectic A (A_{re}) phases it was found that in the high temperature (partially) bilayer A phase the *d* value decreases with decrease of temperature while it is independent of temperature in the A_{re} phase, the periodicity in this phase corresponding to the molecular length.[7,8] Some measurements of *d* were also made in the N_{re} phase of T_8. However, these measurements were restricted to temperatures very close to the A-N_{re} and N_{re}-A_{re} transitions and hence it is not clear if the development of the monolayer phase from the bilayer phase is a continuous or abrupt process. We have carried out accurate determination of *d* in another pure reentrant mesogen, *viz.*, 4-nonyloxybenzoyloxy-4′-cyanoazobenzene (9 OBCAB), not only in the two A phases but also in the N_{re} phase. As far as we are aware, these are the first extensive measurements of *d* in the N_{re} phase.

EXPERIMENTAL

The compound 9 OBCAB has the following structural formula:



It was synthesized in the manner described elsewhere.[9,10] The transition temperatures, as determined using a polarizing microscope equipped with a Mettler FP52 hot stage, are given below.

K		A_{re}		N_{re}	*A*	*N*	*I*
·	94.0°C	(· 70.9°C)	·	116.0°C	· 212.4°C	· 242.9°C	·

The X-ray diffraction maxima were recorded photographically using a flat plate camera and CuKα radiation reflected from a bent quartz crystal monochromator (Carl Zeiss, Jena). The film was positioned at the focus of the monochromator. The sample was taken in powder form in a 0.5 mm

diameter Lindemann capillary which was then evacuated and sealed. The temperature of the sample was maintained to ±0.25°C. The sample was aligned using ≈5 KGauss magnetic field (H). The relative accuracy in the layer spacing determination is estimated to be ±0.1 Å. After each set of measurements, the transition temperatures of the sample were redetermined to ensure that they had not undergone any change and thereby there was no decomposition of the sample.

RESULTS AND DISCUSSION

Typical X-ray diffraction photographs in the A, N_{re} and A_{re} phases are shown in Figure 1. It is seen that both the A and the A_{re} phases give rise to extremely sharp X-ray reflections. In the N_{re} phase, the arcs are more diffuse, but nevertheless very strong cybotactic smectic ordering exists which permits accurate determination of d in the N_{re} phase.

The temperature variation of d in the A, N_{re} and A_{re} phases is shown in Figure 2. Owing to the limitation of our experimental set up, we have measured d only up to 150°C in the A phase, although the A phase exists till 212.4°C. The value of d at the highest temperature that we have measured is 36.0 Å and it decreases gradually with decreasing temperature.

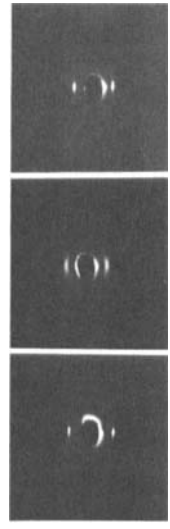


FIGURE 1 X-ray diffraction photographs of 9 OBCAB in (a) smectic A phase at 140°C, (b) reentrant nematic phase at 100°C, and, (c) reentrant smectic A phase at 68°C.

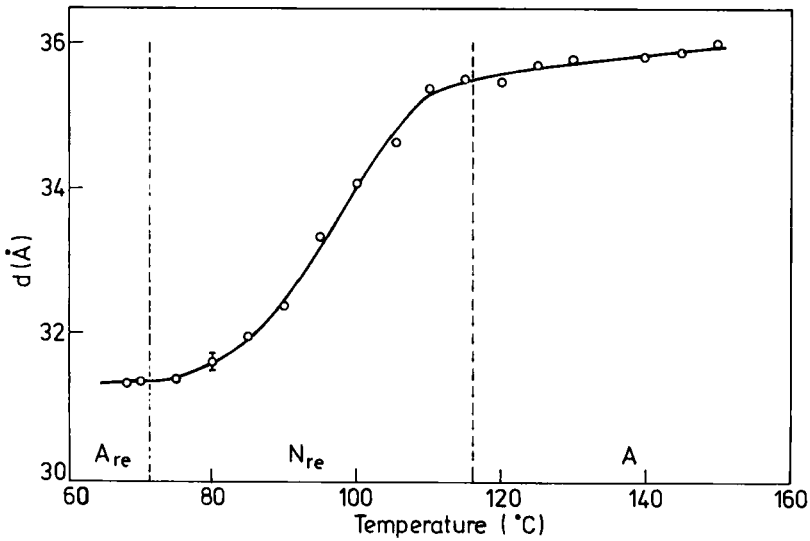


FIGURE 2 Variation of the layer thickness (d) with temperature for 9 OBCAB.

Since the molecular length (l) of 9 OBCAB measured in its most extended conformation using the Dreiding model is 33 Å, the high temperature A phase can be classified as the partially bilayer (A_d) phase. The d value in the A_{re} phase is, however, temperature independent and the d/l value in this phase corresponds to ≈ 0.95 showing thereby that this is a monolayer phase. In the N_{re} phase, close to the A-N_{re} transition, the structure is still partially bilayer. But the d value decreases quite rapidly in the N_{re} phase and close to the N_{re}-A_{re} transition the structure is monolayer. Thus, our results show that in 9 OBCAB the change from bilayer to monolayer is a continuous process which commences in the N_{re} phase and continues right through it.

Acknowledgment

We are grateful to Professor S. Chandrasekhar for his keen interest and encouragement during this work.

References

1. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975); P. E. Cladis, R. K. Bogardus, W. B. Daniels and G. N. Taylor, *Phys. Rev. Lett.*, **39**, 720 (1977).
2. N. V. Madhusudana, B. K. Sadashiva and K. P. L. Moodithaya, *Curr. Sci.*, **48**, 613 (1979); F. Hardouin, G. Sigaud, M. F. Achard and H. Gasparoux, *Phys. Lett.*, **71A**, 347 (1979). For a complete list of pure compounds which exhibit the reentrant polymorphism

see G. Sigaud, Nguyen Huu Tinh, F. Hardouin and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **69**, 81 (1981).
3. N. V. Madhusudana and S. Chandrasekhar, Proceedings of the International Liquid Crystals Conference, Bangalore, 1973, *Pramana Suppl.*, **1**, 57.
4. A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray and A. Mosley, *J. de Physique*, **40**, 375 (1979).
5. D. Guillon, P. E. Cladis and J. Stamatoff, *Phys. Rev. Lett.*, **41**, 1598 (1978).
6. S. Chandrasekhar, K. A. Suresh and K. V. Rao, in 'Liquid Crystals', Proc. Int. Liquid Crystals Conference, Bangalore, 1979, Ed. S. Chandrasekhar (Heyden, London, 1980), p. 131.
7. A. M. Levelut, F. Hardouin and G. Sigaud, in 'Liquid Crystals', Proc. Int. Liquid Crystals Conf., Bangalore, 1979, Ed. S. Chandrasekhar (Heyden, London, 1980) p. 143.
8. F. Hardouin and A. M. Levelut, *J. de Physique*, **41**, 41 (1980).
9. G. Heppke, R. Hopf, B. Kohne and K. Praefcke, in 'Advances in Liquid Crystal Research and Applications,' Proc. Third Liquid Crystal Conference of Socialist Countries, Budapest, 1979, Ed. L. Bata (Pergamon Press, 1980) p. 141.
10. G. Heppke, R. Hopf, B. Kohne and K. Praefcke, *Z. Naturforsch*, **35b**, 1384 (1980).