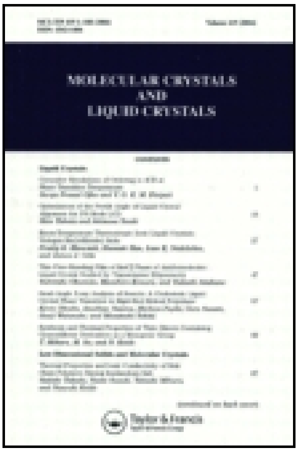


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Small Angle X-ray Scattering Studies on Smectic and Nematic Phases of a Toluidine Compound

P. K. Sarkar [a], S. Paul [a] & P. Mandal [a]

[a] Department of Physics, North Bengal University, Darjeeling, INDIA, PIN-734430

To cite this article: P. K. Sarkar, S. Paul & P. Mandal (1995): Small Angle X-ray Scattering Studies on Smectic and Nematic Phases of a Toluidine Compound, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 249-255

To link to this article: http://dx.doi.org/10.1080/10587259508041696

Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 249–255
Reprints available directly from the publisher
Photocopying permitted by license only

SMALL ANGLE X-RAY SCATTERING STUDIES ON SMECTIC AND NEMATIC PHASES OF A TOLUIDINE COMPOUND

P. K. SARKAR, S. PAUL AND P. MANDAL
Department of Physics, North Bengal University
Darjeeling, INDIA, PIN- 734430

Abstract X-ray diffraction studies on N,N'-Bis (p-butoxybenzylidine)-α,α'-bi-p toluidine [BBBT] in smectic and nematic phases have been reported. Apparent molecular length, average intermolecular distance in both the phases have been determined. Molecular organizations in the smectic phase has been discussed in relation to its packing in the crystalline state.[1]

INTRODUCTION

Polymorphism of a toluidine compound N,N'-Bis(p-butoxybenzylidine)-α,α'-bi-p-toluidine [BBBT in short] has been investigated by small angle X-ray scattering. It exhibits both smectic and nematic phases over a wide range of temperature. The molecular organizations in both the phases have been determined from X-ray photographs. Molecular and crystal structures of the compound had been determined earlier.[1] Packing of the molecules in the liquid crystalline as well as in the crystalline state has been discussed.

EXPERIMENTAL

Accurate phase transition temperatures were determined by studying textures under polarizing microscope using Mettler FP82 hot stage. Mosaic texture in smectic and marbled texture in nematic phase were observed.[1] Molecular formula and phase transitions temperatures (in degree centigrade) are given below:

$$(C_4H_9O-C_6H_4-CH=N-C_6H_4-CH_2-)_2$$

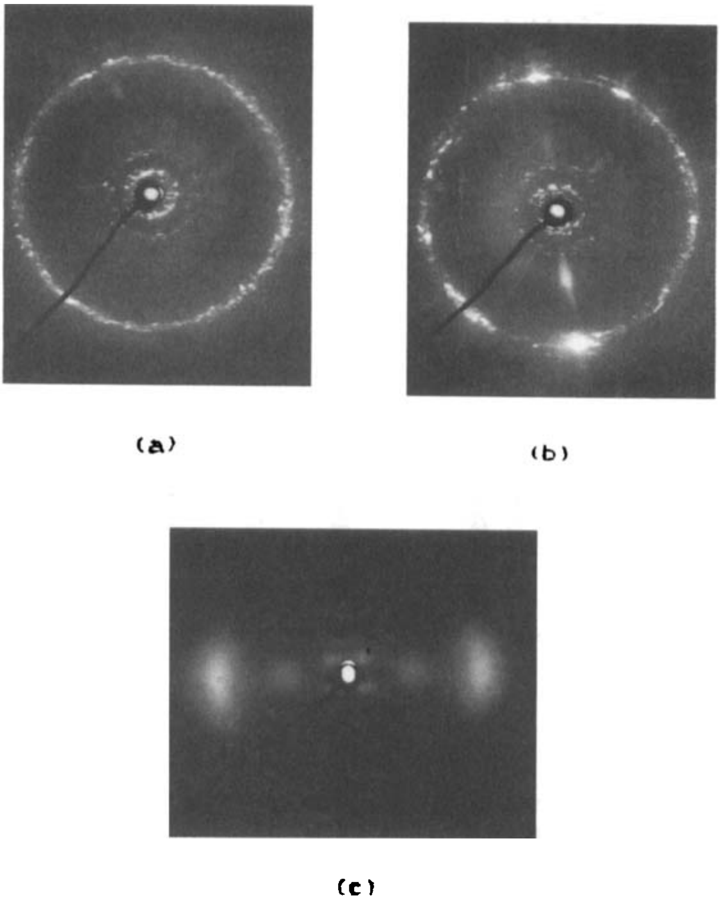
$$Cr \underset{145}{\overset{159}{\rightleftharpoons}} Sm \underset{172}{\overset{188}{\rightleftharpoons}} N \xleftrightarrow{293} I$$

Small angle X-ray photographs of both non-aligned and magnetically aligned samples were taken throughout the mesomorphic range. A high temperature camera[2] was used, samples were taken in Lindemann glass capillary of ~ 1.0 mm diameter and a temperature controller Indotherm 401D was used to control temperature within ± 0.5°C. We tried to get monodomain sample in smectic phase by very slow and regulated cooling from isotropic to smectic phase using only the capillary surface effect and also applying magnetic field of 0.5 Tesla. We also tried to align the sample by slow heating to smectic phase in presence of magnetic field. But we could produce only partial alignment. All photographs were taken with X-rays perpendicular to the magnetic field direction. In order to determine various parameters the photographs were scanned linearly by an optical densitometer (Carl Zeiss MD100).

RESULTS AND DISCUSSIONS

X-ray diffraction photographs in smectic phase have been given in Figures 1 (a) and (b). At temperature 160°C it shows two very closely spaced outer rings with d values of 4.44 and 4.55 Å along with four inner rings with d values of 11.97, 13.55, 21.47 and 29.90 Å. So the smectic layer spacing is 29.90 Å, since the innermost ring corresponds to the density variation along the smectic layers. However, the molecular model length of BBBT in all trans-conformations is 34.3 Å. So the molecules are tilted at an angle of 29.3° within the smectic layers. Presence of several rings indicate that there is long range three dimensional ordering. There is also indication of presence of pseudo-hexagonal symmetry within the layers in the photograph of partially aligned sample. All these features along with the observed texture suggest[3] that the phase is probably smectic H (or smectic H′) which is now also termed as crystal H phase because of its more crystal like character.[4,5] For precise identification of the phase one, however, needs to index photograph from a monodomain sample with X-rays parallel to smectic layer normal.

X-ray photograph in nematic phase is given in Figure 1(c). In addition to the outer crescent we observe that


(a) (b)

(c)

FIGURE 1 X-ray diffraction photographs of BBBT: (a) non aligned at 160°C, (b) aligned at 160°C and (c) aligned at 183°C.

the inner crescent splits into four distinct spots which indicate the presence of cybotactic groups. The boundary planes of these groups are found to be at an angle of $\sim 45°$ with the group director. The phase is, therefore, identified as skewed cybotactic nematic.[6]

We have also studied variation of different molecular parameters as a function of temperature. In smectic phase the d-values corresponding to the intermolecular distances do not change appreciably with temperature as shown in Figure 2. However, d-value corresponding to the smectic layer spacing increases appreciably. We can define a tilt angle $\beta_t = \cos^{-1}(d/L)$, where d is smectic layer spacing and L is model length of the molecules. in all trans-conformations. We find that β_t decreases from 33.8° to 24.6° with temperature.

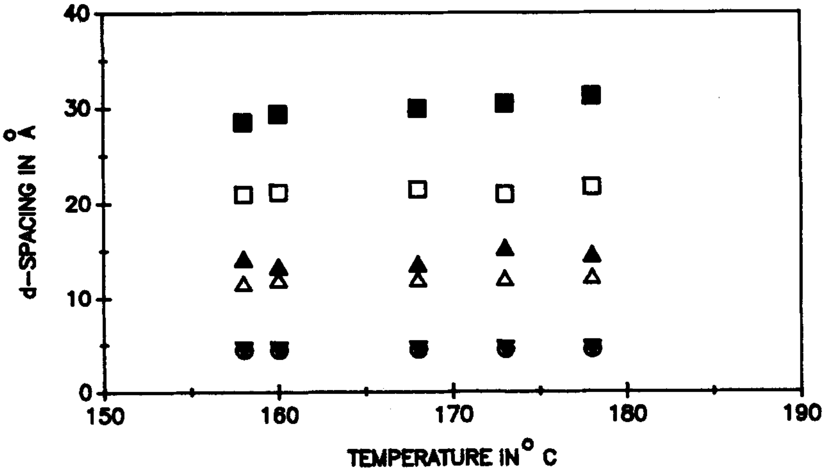


FIGURE 2 Variation of d-spacing with temperature in smectic phase.

The outer equatorial arc in the nematic phase arises from the intermolecular distances perpendicular to the director. The average intermolecular distance, D, is calculated using a modified Bragg's relation, $2D\sin\theta = 1.117\ \lambda$, obtained on the arguments of cylindrical symmetry of the molecules.[6] With temperature D is found to increase slightly, the variation being shown in Figure 3. The meridional scattering amplitude is obtained from the density variation along the director and gives information about the apparent molecular length, l, of the molecules. In this case Bragg's relation is used as such. We found that l increases by 4.4 Å as temperature changes from 178 to 278°C, shown in Figure 3. Corresponding change of tilt angle is from 49.7 to 41.1°.

We thus find that the molecular tilt angle in smectic and nematic phases decreases with temperature, but there is an abrupt increase in tilt angle at Sm - N transition.

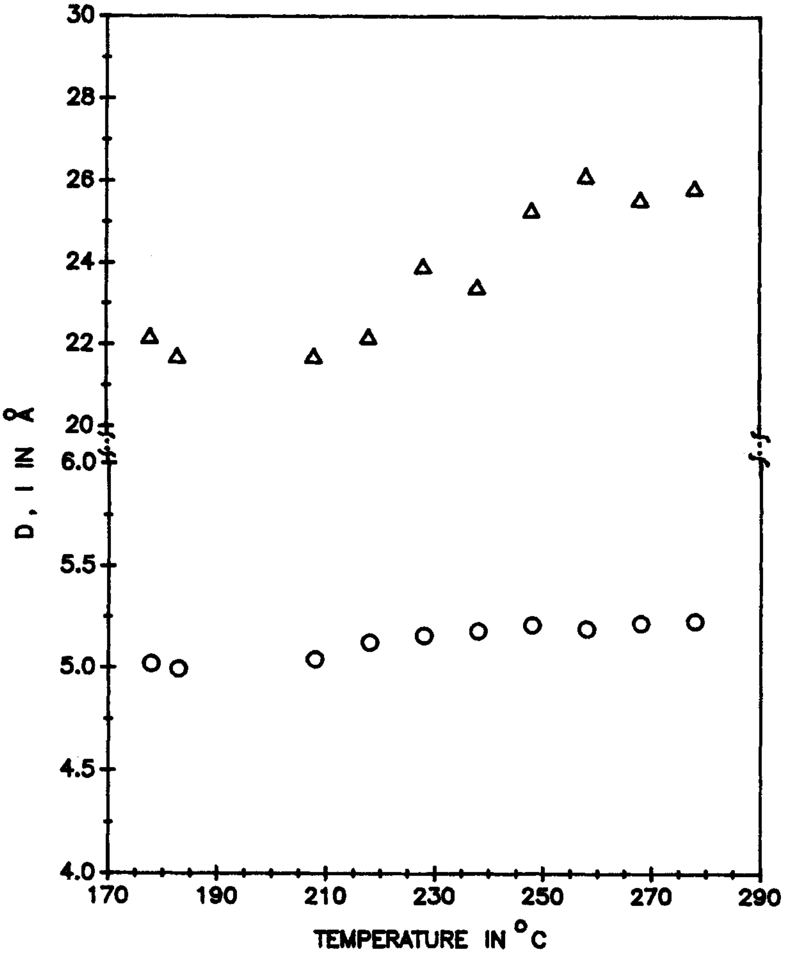


FIGURE 3 Variation of average intermolecular distance (D) and apparent molecular length (l) with temperature in nematic phase.

Although it is not yet possible to predict with certainty the existence of a definite phase from molecular shape and inter molecular interactions, molecular packing in the crystalline state may provide a better insight in understanding the solid - mesophase transitions.[7,8] It had been shown earlier[1] that the molecules in the crystalline state are arranged in layers and within a layer the molecules are tilted with respect to the layer normal. This arrangement is the classical solid state precursor of smectic phase. It may be mentioned here that in the compound BOCP, which exhibits only skewed cybotactic nematic phase, parallel imbricated mode of molecular packing was observed.[8]

BBBT molecules crystallize in triclinic system with cell parameters a=6.116, b=7.916, c=31.421Å and α=92.39, β=92.35, γ=96.59° and space group $P\bar{1}$. Also it is found that the molecular long axis defined as a best fitted line through all the atoms, makes an angle 32° with the layer normal. Comparing these values with the d-values and the tilt angle of the molecules in the smectic phase we like to infer that Cr - Sm transition is essentially of displacive type[9].

In order to get idea about the intermolecular forces responsible for mesophase stability, we calculated all the intermolecular distances less than 3.65Å. Distances between few carbon atoms of centro symmetrically related molecules are found to be less than the sum of their van der Waals' radii. Thus van der Waals interaction plays a significant role in molecular packing in the solid state which is also expected to be present in smectic phase. No intermolecular contact found to exist between the transverse dipole moments, though the tilting of the molecules within the smectic layers may be favoured by the longitudinal component of the dipoles.[10]

ACKNOWLEDGEMENT

P. K. Sarkar and P. Mandal are thankful to UGC, India, for a fellowship and financial assistance.

REFERENCES

1. P. Mandal, S. Paul, K. Goubitz and H. Schenk, Mol. Cryst. Liq. Cryst. (In press).
2. B. Jha, S. Paul, R. Paul and P.Mandal, Phase Trans., 15, 39 (1989).
3. P. Mandal, M. Mitra, S. Paul and R. Paul, Liq. Crystals, 2, 183 (1987)
4.a) P. S. Pershan, Structure of Liquid Crystal Phases, (World Scientific, New Jersy,1988), p. 62.
   b) G.W. Gray and J.N. Goodby, Smectic Liquid Crystals: Textures and Structures, (Leonard Hill, Glasgow, 1984), P. 105.
5. J. Doucet, The Molecular Physics of Liquid Crystals, Edited by G. R. Luckherst and G. W. Gray (Academic Press, New York, 1979), p. 317.
6. A. de Vries, Mol. Cryst. Liq. Cryst, 10, 31 & 219 (1970)
7. R. F. Bryan, Proceedings of the 14th IUCr, Perth, Australia (1987).
8. P.Mandal, S. Paul, H. Schenk and K. Goubitz, Mol. Cryst. Liq. Cryst, 210, 21 (1992) and references therein.
9. R. F. Bryan and P. G. Fourier, Mol. Cryst. Liq. Cryst, 60, 133 (1980).
10. N. V. Madhusudana, Liquid Crystals— Applications and Uses, edited by B. Bahadur (World Scientific, Singapore, 1990), p. 76.