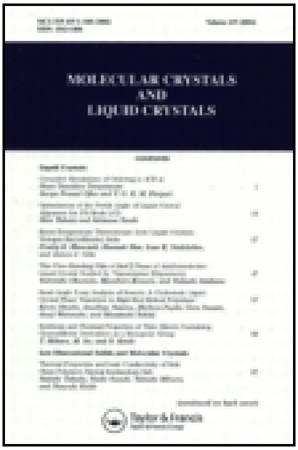

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Sonali Ghosh, Pradip Mandal, Sukla Paul, Ranjit Paul & Mary E. Neubert (2001): Small Angle X-Ray Diffraction Study for the Determination of Structural Parameters of Two Mesomorphic Compounds Having Smectic C Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 703-710

To link to this article: http://dx.doi.org/10.1080/10587250108025349

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 703-710
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Small Angle X-Ray Diffraction Study for the Determination of Structural Parameters of Two Mesomorphic Compounds Having Smectic C Phase

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X-ray diffraction study was carried out for the pentyl and octyl members of the series 4-n-alkoxy phenyl 4′-n octyloxy benzoate (PPOB and OPOB in short). The first shows S_C, S_A and N phases while the second compound has only S_C and N phases. The transition temperatures were determined by studying texture under polarizing microscope. Apparent molecular length in nematics, layer line spacings in smectics, tilt angle in S_C, inter molecular distances and orientational order parameters were determined from X-ray diffraction patterns of aligned samples at different temperatures. Temperature variation of the orientational order parameters agree fairly well with Maier-Saupe theory in the nematic phase and with McMillan's theory in the smectic phase with tilt angle correction in S_C. Discontinuities of $<P_2>$and $<P_4>$- at S_AN in PPOB and at S_C -N transitions indicate that the transitions are of the first order.

Keywords: X-ray diffraction; tilt angle; smectic C; orientational order parameters

INTRODUCTION

X-ray diffraction was carried out for the pentyl and the octyl members of the series 4-n alkoxy phenyl 4′-n octyloxy benzoate (PPOB and OPOB in short) at different temperatures with samples aligned by a magnetic field. The first compound shows a variety of mesogenic phases namely S_C, S_A and N while the second compound has S_C and N phases. We have undertaken this study to get information about the order of phase transitions S_C-S_A, S_A-N and S_C-N from the molecular parameters determined from X-ray diffraction patterns. Both PPOB and OPOB have been extensively studied by a number of workers [1-7] who have reported phase transition temperatures and calorimetric data. No X-ray diffraction data are available. Structural formula of the compounds are:

(I) PPOB : $H_{17}C_8O{-}C_6H_4{-}COO{-}C_6H_4{-}OC_5H_{11}$

(II) OPOB : $H_{17}C_8O{-}C_6H_4{-}COO{-}C_6H_4{-}OC_8H_{17}$

EXPERIMENTAL

Transition temperatures

Transition temperatures of the compounds were determined with a polarizing microscope fitted with a Mettler FP80/82 thermosystem. Both the compounds showed marble texture in their nematic phase, S_C showed broken focal conic texture and S_A of PPOB had focal conic fan texture. The S_C–S_A transition temperature of PPOB was accurately determined from the homeotropically aligned sample which showed Schlieren texture in S_C phase. Transition temperatures (°C) thus determined are:

(I) PPOB : K 58 (48) S_C 61.3 S_A 65.5 N 85 I

(II) OPOB: K62.5 (48) S_C 71.3 N 90.5 I

X-ray study

X-ray diffraction photographs were taken throughout the mesomorphic range using Nickel filtered CuKα radiation in presence of a magnetic field to align the sample. The details of our experimental set up has been given in our previous publication[8]. The photographs were scanned circularly and linearly by a microdensitometer Zeiss MD100.

RESULTS AND DISCUSSIONS

The X-ray diffraction photographs of nematic and smectic phases in our present study were exactly as expected for aligned samples. These x-ray diffraction patterns were analysed to determine apparent molecular length (l) in nematic phase, layer spacings (d) in smectic phases, intermolecular distance (D) and orientational order parameters ($<P_2>$ and $<P_4>$) using the procedure reported previously[9-11]. Intermolecular distance (D) is almost constant (~5 Å) in all phases for both the compounds. The variation of apparent molecular length (l) and layer thickness (d) with temperature for PPOB and OPOB are shown in Figure 1 and Figure 2 respectively. The apparent molecular length in the nematic phase of PPOB changes from 29 Å to 26 Å, while that of OPOB varies from 31.5 Å to 30 Å as the temperature increases. The model length (L) of PPOB and OPOB in their fully extended form are 29.2 Å and 32.8 Å repectively. Hence, it is clear that these molecules do not form associations in the nematic phase. The temperature variation of l is probably due to the increased vibration of the alkoxy chain as the temperature increases. The layer thickness in the S_A phase of PPOB is almost equal to its model length and is temperature independent. This shows that PPOB has a monolayer S_A phase. Layer spacings in the S_C phases of both the compounds decrease with decreasing temperature. This is due to the increase in the tilt angle (θ_t) as the temperature is reduced. The tilt angle is calculated from the equation $\theta_t = \cos^{-1}(d/L)$, where L is the molecular model length in the fully extended form. The tilt angle is about 21° at 58° C for PPOB. In OPOB, the tilt angle increases from 12° to 25° as the temperature decreases.

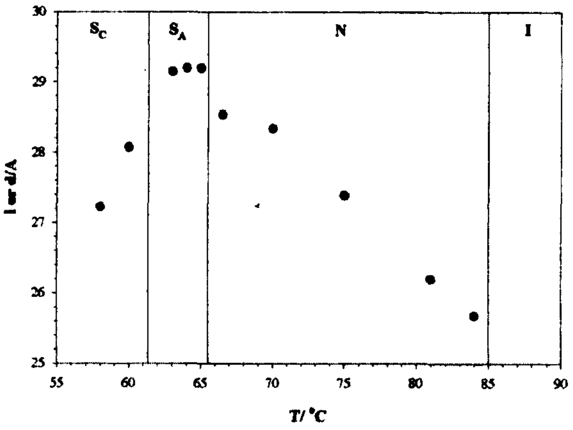

FIGURE 1. Variation of l or d with temperature for PPOB.

Orientational distribution function and hence the orientational order parameters were determined from the X-ray intensity data using a method described earlier[10-11]. Experimental values in the nematic phase agree well with those calculated from Maier-Saupe theory, as shown in Figure 3 and Figure 4 for PPOB and OPOB respectively. The x-ray photographs in the S_C phase of both the compounds were similar to those obtained from aligned S_A samples. This indicates that in our samples the director is randomly oriented in a cone about the layer normal, which is in the direction of the applied

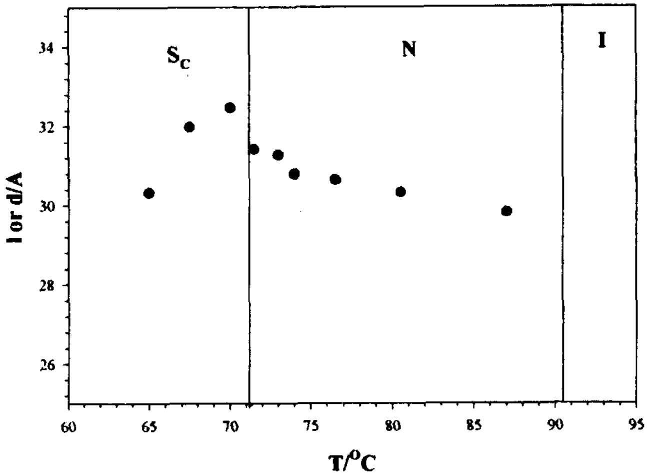

FIGURE 2. Variation of l or d with temperature for OPOB.

magnetic field. Following a procedure described by Paul et al [12] , the order parameters in the S_C phase have been calculated after taking into

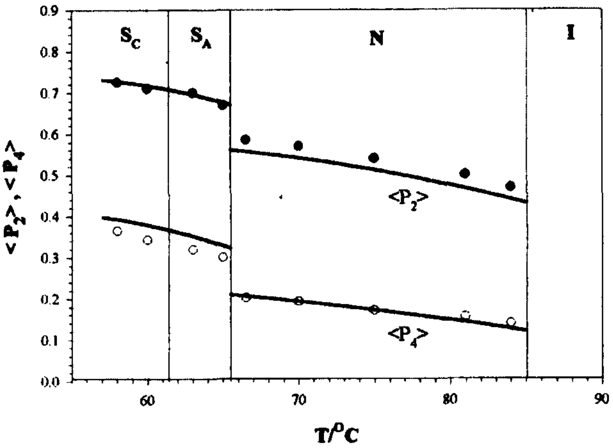

FIGURE 3. Variation of order parameter with temperature for PPOB. Solid line from McMillan theory.

account the values of the tilt angle. We have tried to fit the experimental order parameter values in smectic phases with those calculated from McMillan's theory[13]. The results are shown in Figure 3 and Figure 4 for PPOB and OPOB repectively. The parameters of the McMillan potential, which give the best fit to the experimental data, are $\delta = 0.9$ and $\alpha = 0.325$ for PPOB and $\delta = 0.5$ and $\alpha = 0.412$ for OPOB. As is expected the α value is greater for the homologue having longer alkoxy chain. Also the order parameter seems to change smoothly across the S_A - S_C transition in PPOB, indicating that this transition is probably of the second order. Order parameter values, however, change

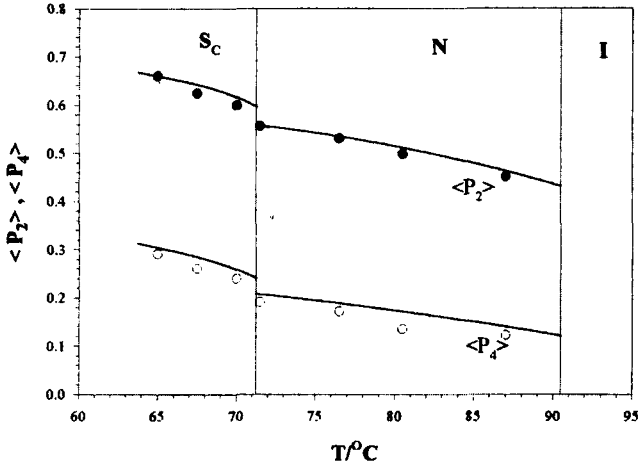

FIGURE 4. Variation of order parameters with temperature for OPOB. Solid line from McMillan theory.

abruptly at the N - S_C transition in OPOB and N - S_A transition in PPOB. This is in agreement with calorimetric measurements of Demus et al [2]. From their experimental values of ΔH for PPOB they found that S_C - S_A is also of weaky first order. Thoen et al [3] observed both of these transitions to be of second order. Extensive calorimetric measurements by different workers [14-18] in different compounds have established that S_C-S_A phase trasition is of second order, well described by the mean field theory of Landau. From the variation of l,d and D we are unable to draw any conclusion about the order of the phase transitions in these compounds.

Acknowledgments

This work has been partly financed by D.S.T,, New Delhi and one of the authors (SG) thanks D.S.T, New Delhi for the award of a research fellowship.

References

[1] J. Mathete, J. Billard, J. Canceil, J. Galeard, J. Jacques, *J. Phys.* (Paris), Suppl, **37**, C3 1 (1976).

[2] D. Demus, J. H. Deutscher, D. Marzoko, A. Weigeleleen, in *Liquid Crystals*, Proc. Int. Conf. Bangalore, Ed. S. Chandrasekhar, Heyden Press, 97 (1980).

[3] J. Thoen, R. Parret, *Liq. Cryst.*, **5**, 479 (1989).

[4] D. Jadzyn, P. Kedziora, *Mol. Cryst. Liq. Cryst.* **145**, 17 (1987).

[5] H. Kresse, G. Pelzl, *Phys. Status Solidi*, **A57**, K 149 (1980).

[6] M. E. Neubert, M.R. Jirousek, C.A. Hanlon, *Mol. Cryst. Liq. Cryst*, **133**, 223 (1986).

[7] R. T. Klingbiel, D.T. Genova, T.R. Criswel, J.P. Van Meter, *J. Am. Chem. Soc*, **96**, 7651 (1974).

[8] B. Jha, S. Paul, R. Paul and P. Mandal, *Phase Transitions.* **15**, 39, (1989).

[9] A. de Vries, *Mol. Cryst. Liq. Cryst*, **10**, 219 (1970).

[10] A. J. Leadbetter, E. K. Norris, *Mol. Phys*, **44**, 139 (1981).

[11] B. Bhattacharjee, S. Paul and R. Paul, *Molecular Phys.*, **44**, 139 (1981).

[12] R. Paul, B. Jha and D.A. Dunmur, *Liquid Crystals*, **13**, 629 (1993).

[13] W.L. McMillan, *Phys. Rev* **A6**, 936 (1972).

[14] C. C. Huang and J. M. Viner, *Phys. Rev.* **A25**, 3385 (1982).

[15] R. J. Birgenau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu and J. Goodby, *Phys. Rev.* **A27**, 1251 (1983).

[16] M. Meichle and C. W. Garland *Phys. Rev.*, **A27**, 1251 (1983).

[17] J. Thoen and G. Seynaeve, *Mol. Cryst. Liq. Cryst.*, **127**, 229 (1985).

[18] C. C. Huang in *Theory and Applications of Liquid Crystals*, eds J. L. Erickeen and D. Kinderlehrer, (Sprringer-Verlag, New York, 1987).