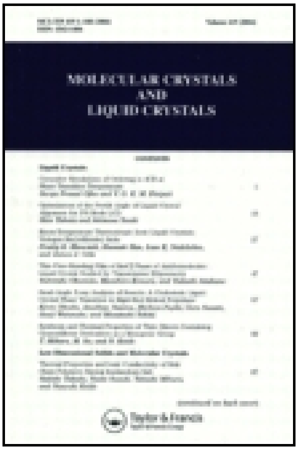

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Mesomorphic Properties And Molecular Structure of Four Closely Related Compounds

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Version of record first published: 04 Oct 2006.

To cite this article: M. Mitra , R. Paul & S. Paul (1989): Mesomorphic Properties And Molecular Structure of Four Closely Related Compounds, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 177:1, 71-80

To link to this article: http://dx.doi.org/10.1080/00268948908047771

Mol. Cryst. Liq. Cryst., 1989, Vol. 177, pp. 71–80
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Printed in the United States of America

Mesomorphic Properties And Molecular Structure of Four Closely Related Compounds

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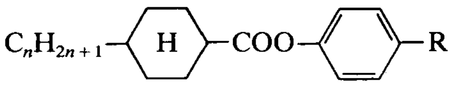
(Received May 14, 1988; in final form May 25, 1989)

In this paper we have reported the results of X-ray diffraction studies on magnetically aligned samples of four closely related compounds. These compounds are (1) *p*-methoxy phenyl trans-4-pentyl cyclohexane carboxylate (2) *p*-propoxy phenyl trans-4-pentyl cyclohexane carboxylate (3) *p*-ethoxy phenyl *trans*-4-butyl cyclohexane carboxylate and (4) *p*-cyano phenyl *trans*-4-pentyl cyclohexane carboxylate. Structural parameters and orientational order parameters of the compounds have been determined at different temperatures. The way in which the molecules are stacked has been discussed.

Keywords: X-ray Study, Molecular Parameters, Nematogens

1. INTRODUCTION

As a part of an extensive program aiming at a better understanding of the molecular structure and the mesomorphic properties of liquid crystals, X-ray diffraction measurements have been made on (I) *p*-methoxy phenyl *trans*-4-pentyl cyclohexane carboxylate (MPPCC), (II) *p*-propoxy phenyl *trans*-4-pentyl cyclohexane carboxylate (PPPCC), (III) *p*-ethoxy phenyl *trans*-4-butyl cyclohexane carboxylate (EPBCC) and (IV) *p*-cyanophenyl *trans*-4-pentyl cyclohexane carboxylate (CPPCC) having the following structural formulae



I. $n = 5$, $R = OCH_3$

II. $n = 5$, $R = OC_3H_7$

III. $n = 4$, $R = OC_2H_5$

IV. $n = 5$, $R = CN$.

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These are polar molecules. The ways in which polar molecules can overlap to form bilayer structures have recently been the subject of many investigations. In this context present study is of interest. From the X-ray diffraction photographs of magnetically aligned samples, structural parameters and orientational order parameters of these compounds have been determined and the ways in which the molecules are stacked are being discussed.

2. EXPERIMENTAL PROCEDURE

Purified and recrystallised samples were supplied to us by M/s. Hoffmann-La-Roche and Co., Basel, Switzerland. The transition temperatures as observed by us are

(1) Solid $\underset{\sim 11^\circ C}{\overset{40.7^\circ C}{\rightleftharpoons}}$ Nematic $\overset{71.1^\circ C}{\rightleftharpoons}$ Isotropic

(2) Solid $\underset{37^\circ C}{\overset{43.3^\circ C}{\rightleftharpoons}}$ Nematic $\overset{71.1^\circ C}{\rightleftharpoons}$ Isotropic

(3) Solid $\underset{\sim 11^\circ C}{\overset{36.3^\circ C}{\rightleftharpoons}}$ Nematic $\overset{74.6^\circ C}{\rightleftharpoons}$ Isotropic

(4) Solid $\underset{\sim 11^\circ C}{\overset{47^\circ C}{\rightleftharpoons}}$ Nematic $\overset{78.7^\circ C}{\rightleftharpoons}$ Isotropic

The melting behaviour of the samples were examined using a polarising microscope with a hot stage (Metler FP80/82). These temperatures agreed well with the supplied values (Hoffmann-La-Roche Catalogue) except that for all the compounds supercooled nematic phases were observed. The transition temperatures reported by Beens et al.[1] are slightly different from our findings.

The textures of the compounds were observed under polarizing microscope. The observations were performed under crossed polarizers with magnification 150 X and samples were taken between two coverslips. The four samples showed typical nematic textures throughout the whole mesomorphic range indicating the presence of only nematic phase.

A detailed description of the experimental set up used for the X-ray diffraction study is given elsewhere.[2] The specimen was enclosed in a thin-walled glass capillary of 1 mm. diameter. The capillary containing the sample was inserted in a brass block. The temperature of the block was controlled within ± 0.5°C by a temperature controller (Indotherm 401). Diffraction photographs were taken at ~4.5°C intervals. Magnetic field of 0.65 T was applied to align the sample. The sample was at first heated to the isotropic phase and magnetic field was applied parallel to the capillary axis. The substance was then allowed to cool to the desired temperature in the presence of the magnetic field. After the temperature had stabilized the X-ray tube was switched on. Photographs were taken at various constant temperatures, increasing the temperature each time, until the compound had gone well into the isotropic phase, all the while maintaining the magnetic field. Since we do not have any thermostatic arrangement with cooling facilities in our laboratory we could not take photographs below room temperature.

In order to determine various parameters, the photographs were scanned, both linearly and circularly by an optical microdensitometer (VEB Carl Zeiss, Jena Model 100) equipped with an auto recording facility. Sample to film distance was determined by taking X-ray diffraction photographs of aluminium powder.

3. RESULTS AND DISCUSSIONS

The outer equatorial arcs on X-ray diffraction photographs arise from the intermolecular spacings perpendicular to the long axes of the molecules. We obtain the average intermolecular spacing using the formula $2D \sin\theta = 1.117\lambda$ based on the arrangement of cylindrical symmetry.[3] *D* values are found to be within a few percent of 5 Å. The temperature dependence of *D* of all the compounds are shown in Fig. 1. The experimental uncertainty in *D* is ±.05 Å. *D* values are found to increase with temperature for all the compounds except for the compound III. For this

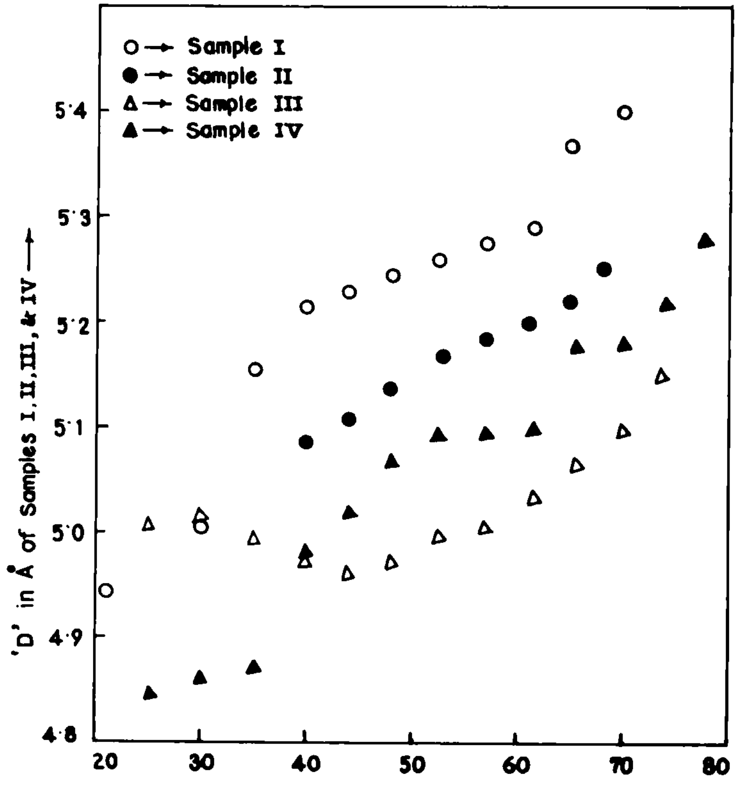

FIGURE 1 Variation of *D* with temperature.

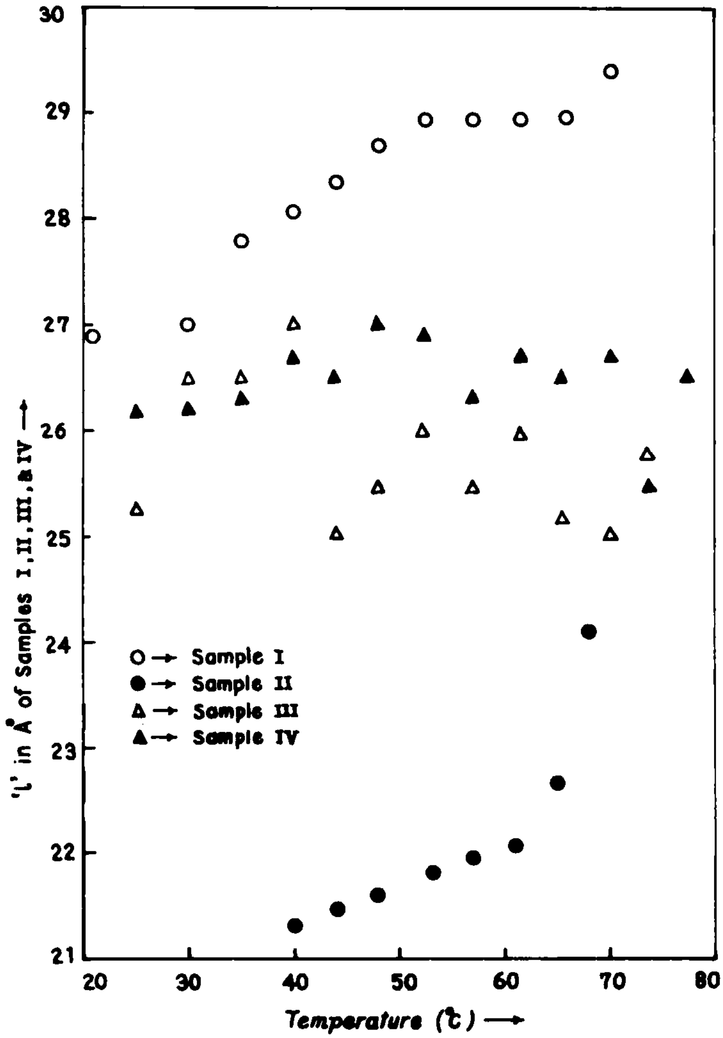

FIGURE 2 Variation of *l* with temperature.

compound *D* decreases with temperature up to 44°C and then begins to increase in the conventional way. Anomalous behaviour at this temperature was also observed in the values of density and refractive index for this compound.[4] Molecular packing in the crystalline state may explain such behaviour. Crystal structure of this compound therefore is of special interest and we plan to investigate it in future. Temperature dependence of *D* for the other three compounds have almost the same pattern.

The Bragg angle corresponding to the inner ring in the X-ray diffraction pattern gives the value of *l*, the apparent molecular length ($2l \sin\theta = \lambda$).[3] Variation of *l* with temperature for all the compounds are shown in Fig. 2. For the compound

III, the value of l rises abruptly to 27 Å at 40°C then decreases to 23.5 Å at 44°C. Temperature dependence of l for the other three compounds is also irregular. l values for the compounds at 48.5°C are 28.7 Å, 21.5 Å, 22.5 Å and 27 Å respectively. Near solid-nematic transition temperatures these values are 26.8 Å, 21.3 Å, 25.4 Å and 26.3 Å respectively. The molecular lengths (L) on molecular model using a stereo model unit (Prentice Hall Inc, N.Y.) in the most elongated configuration are ~19 Å, 21 Å, 18.5 Å and 17.6 Å respectively. It appears that, except for compound II, all molecules form associations in the mesophase, a phenomenon observed frequently in other nematic liquid crystals.[5–9] We have tried to visualize how this association occurs in these compounds. It seems that in samples I, III and IV dipole-induced dipole interactions between neighbouring molecules are responsible for the formation of association. In compounds I & III, the dipolar part $C^+ = 0^-$ of molecule A induces dipole moment in the aromatic ring of the neighbouring molecule B. Similarly $C^+ = 0^-$ dipole of molecule B induces dipole moment in the phenyl ring of molecule A. Thus a pair of dipole-induced dipole interactions bind two neighbouring molecules to form association. The phenyl ring is easily polarizable due to delocalization of Π-electrons in the system. The ratios of the model length of dimers to that of respective monomers come out to be 1.56 and 1.26 for sample I and sample III respectively. The experimentally obtained ratios, as indicated above, are 1.51 and 1.22 respectively, showing good agreement with the proposed interaction for molecular association. Similarly, in the case of sample IV, a pair of dipole-induced dipole interactions between $C^+ \equiv N^-$ part of one molecule with the phenyl ring of the neighbour cause the formation of association. The ratio of the length of model dimer such formed to that of the monomer comes out to be about 1.56 whereas the experimentally determined ratio is 1.50. All of these compounds have rather long aliphatic chain at one end any twisting of the chain in the dimer may reduce its affective length, thus bringing value of the ratios closer to the experimentally observed ones. The reason for compound II not to form associations is not clear, however, only this molecule (among the four studied in this paper) has sizeable flexible groups on both ends, presumably hindering the formation of associations with neighbouring molecules. Also, only compound II does not show much supercooling of the nematic phase. It may be that the formation of associations of molecules in the other compounds retard the crystallization process and hence all of them show significant supercooling.

Crystal structure of the compound IV has been determined by Baumeister et al.[10] Molecular packing in the solid state shows the presence of such interactions. For the other three compounds structural analysis have not been done as yet.

3.1. Orientational order parameters

The intensity $I(\psi)$ around the diffuse equatorial arc is related to the distribution function $f_d(\beta)$ as follows[11]

$$I(\psi) = C\int_{\beta=\psi}^{\beta=\pi/2} f_d(\beta)\,\sec^2\psi[\tan^2\beta - \tan^2\psi]^{-1/2}\sin\beta\, d\beta \qquad (1)$$

where $f_d(\beta)$ describes the distribution function for the orientation β of a local cluster of molecules which are assumed to have mutually perfect alignment and is expected to be the same as the singlet distribution function $f(\beta)$. This integral equation, though appears formidable, can be transformed into a much simpler equation[12]

$$I(\psi) = C \int_0^{\pi/2} f_2\,(\alpha,\psi)\,\sin\alpha d\alpha \qquad (2)$$

by substituting $\sin\alpha = \cos\beta \sec\psi$. This equation in turn can be solved for $f_1(\alpha,\psi)$ by series method.

Order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ have been calculated from the normalized distribution function and compared with the mean field results. For a system of rigid

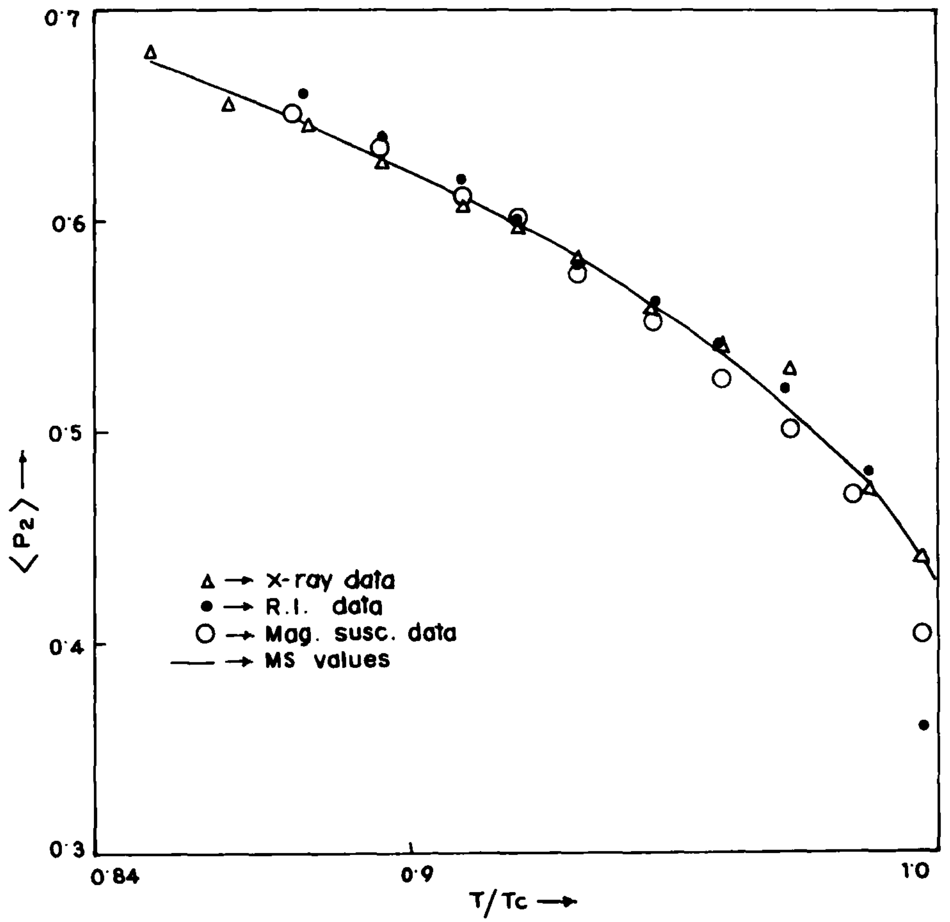

FIGURE 3 Plot of $\langle P_2\rangle$ against reduced temperature for compound I.

rods the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are defined by

$$\langle P_L \rangle = \int_0^{\pi/2} P_L(\cos\beta)\, f(\beta)\, \sin\beta d\beta$$

with $L = 2, 4$.

Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated from $f(\beta)$ at different temperatures for all the compounds are shown in Fig. 3 to 6 and Fig. 7. The experimental errors in order parameters values have been estimated, from the uncertainties of $I(\psi)$ values, to be ±.02 for both $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The experimental $\langle P_2 \rangle$ values are in good agreement with the Maier-Saupe[13] theoretical values. But $\langle P_4 \rangle$ values are significantly lower than the theoretical values. Such behaviour of $\langle P_4 \rangle$ has been observed by others.[5,6,14–16] This discrepancy remains unexplained. The figures show that for all the compounds values of $\langle P_2 \rangle$ determined from magnetic susceptibility and refractive index measurements[17,18] near the clearing tem-

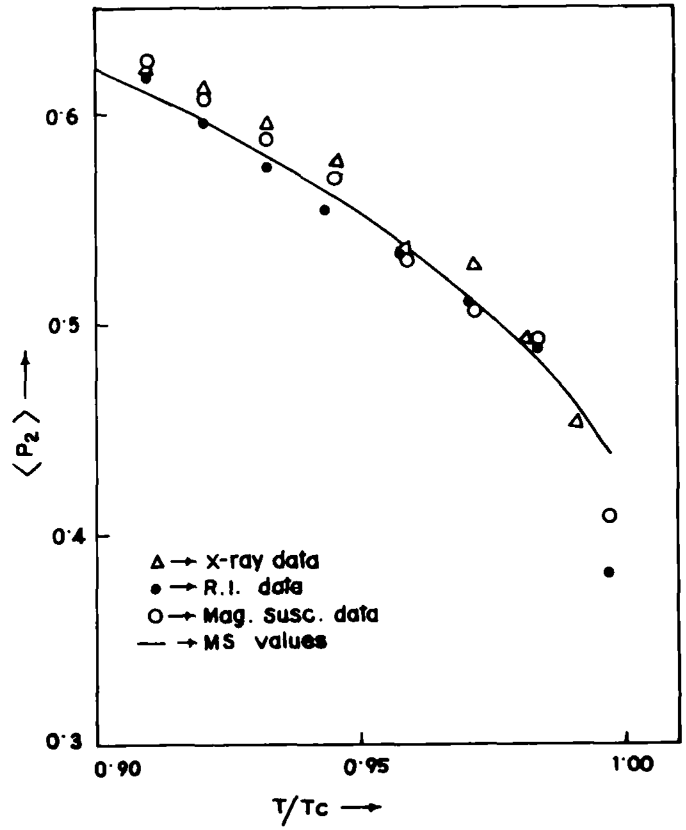

FIGURE 4 Variation of $\langle P_2 \rangle$ with reduced temperature for compound II.

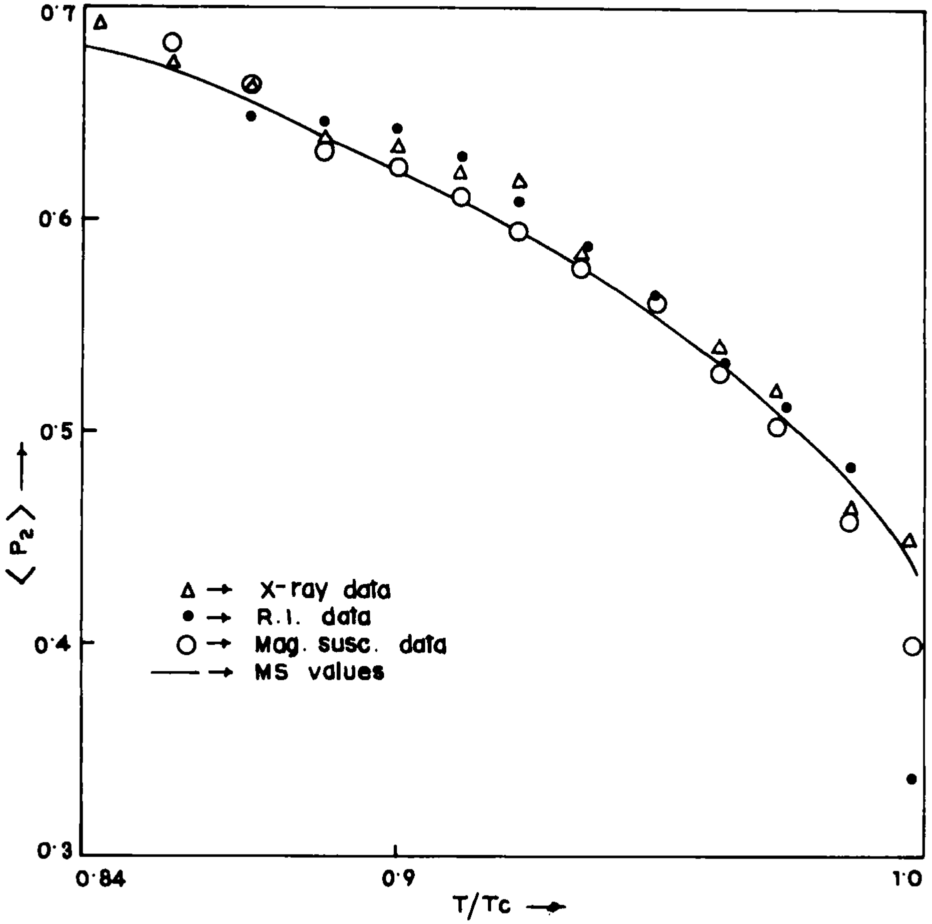

FIGURE 5 Plot of $\langle P_2 \rangle$ against reduced temperature for compound III.

perature are lower than the theoretical values, whereas for X-ray measurements this is not the case. This apparent contradiction between order parameter values obtained from X-ray diffraction on one hand and those obtained from our other experimental measurements on the other hand, has also been observed in BBBA.[14] This contradiction may be the result of different types of approximations and averaging involved in calculating orientational order parameter from experimental data obtained from X-ray studies in one hand, and birefringence and magnetic susceptibility measurements on the other hand.

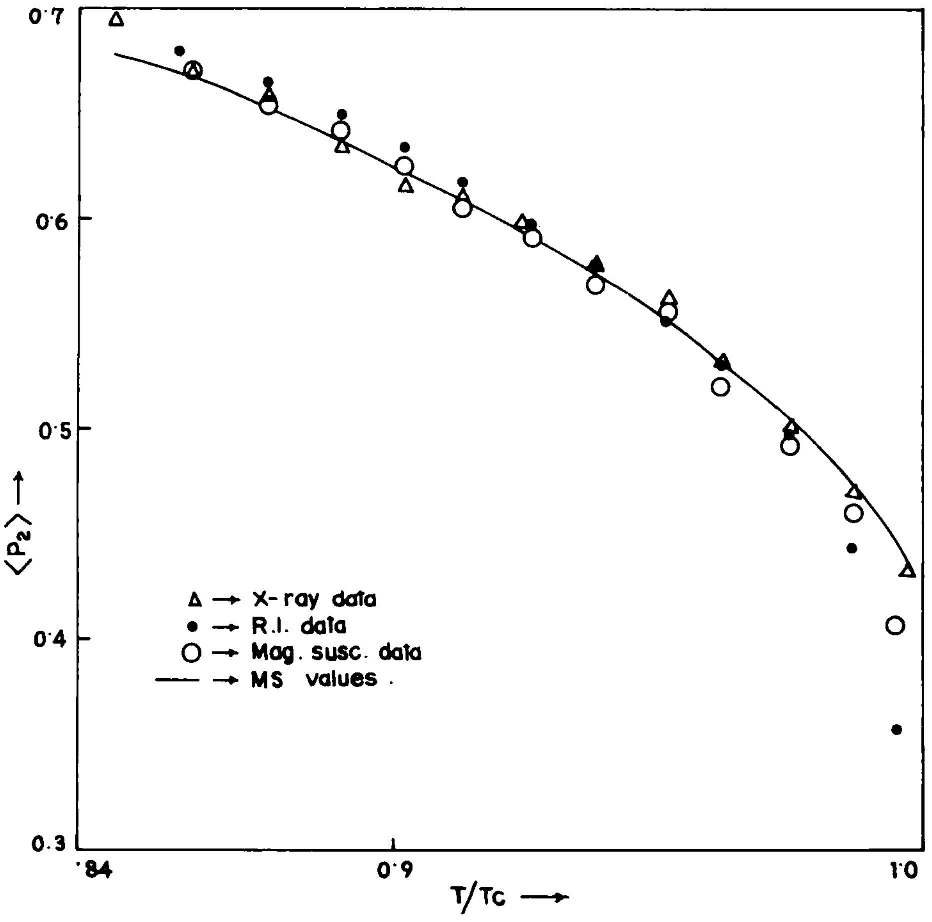

FIGURE 6 Variation of $\langle P_2 \rangle$ with reduced temperature for compound IV.

Acknowledgement

We are thankful to Mr. S. K. Sarkar for help in experimental work. We are thankful to the University Grants Commission, New Delhi for financial assistance, award of a research fellowship to one of us (MM). We also record our thanks to the Government of West Bengal for a grant for the procurement of the Optical Densitometer. We are also thankful to Hoffmann-La-Roche & Co., Basel, Switzerland for kindly donating the four liquid crystal samples.

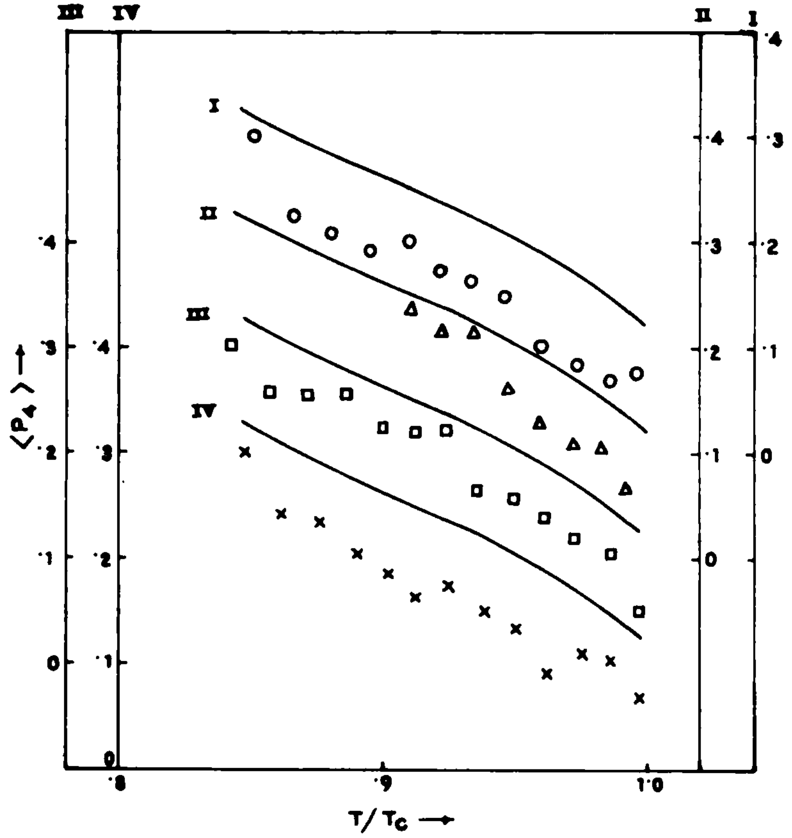

FIGURE 7 Plot of $\langle P_4 \rangle$ against reduced temperature.

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