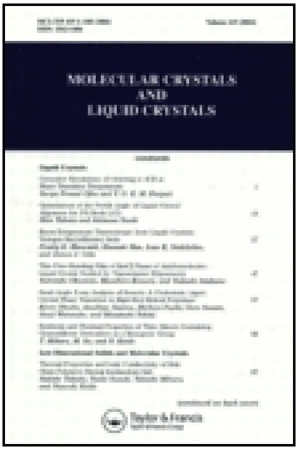

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Microscopic Order Parameter of Two Nematogenic Compounds using X-Rays

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X-ray diffraction patterns from two different nematic samples viz (i) 1-hexyl-4-(4-isothiocyanatophenyl) bicyclo [2,2,2] octane and (ii) 4′-(pentyloxy)-4-biphenyl carbonitrile, were recorded using Laue type of arrangement, consisting of flat 2D- image plate detector. Using these recorded data and employing three different models orientational order parameter [1] $\langle P_2 \rangle$ and the higher order parameter $\langle P_4 \rangle$, have been computed and analyzed. The order parameters estimated from X-ray method is also compared with that obtained from optical method.

Keywords: orientational order parameter; X-ray diffraction pattern

INTRODUCTION

The orientational order parameter of nematic liquid crystals determines the materials usefulness in electro-optical displays and hence there is a continued interest amongst various investigators to compute the order parameter. This parameter can be evaluated by various methods viz., Optical, NMR, X-ray etc. The earlier works of the determination of

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the order parameter using X-rays are due to Falgueirettes [1], Delord and Falgueirettes [2], de Vries [3], Leadbetter and Norris [4], Baumann *et al*. [5], Somashekar *et al*. [6] and Divya *et al*. [7]. The simplest approach is that of Leadbetter [8] which leads to the classical formula

$$I(\phi) = \int_0^{\pi/2} f(\beta) \sec^2 \phi \left(\tan^2 \beta - \tan^2 \phi\right)^{-1/2} \sin \beta d\beta \quad (1)$$

which relates the variation of scattered intensities I(ϕ) around the wide angle arc and the degree of orientational distribution function f(β) of the molecules. The higher the degree of orientational order the more the scattered intensity, which is concentrated on the equator. The orientational distribution function f(β) and the order parameter have been determined by various numerical and series expansion methods [9–11]. Deutsch [12] has shown Eq. (1) can be analytically inverted which leads to general expression for the second rank order parameter i.e., $\langle P_2 \rangle$ and also one or even more of the higher rank terms of order parameter i.e., $\langle P_4 \rangle$, $\langle P_6 \rangle$, etc. Davidson *et al*. [13], here afterwards called Levelut method, have developed a simple analytical calculation of Eq. (1) which leads to a series expression. Also, they have shown it that single intensity measurement at a temperature in the nematic phase can lead to the evaluation of f(β). By employing these methods we have computed the order parameter of two nematic compounds viz, (i) 1-hexyl-4-(4-isothiocyanatophenyl) bicyclo [2,2,2] octane (HIPBO) and (ii) 4′-(pentyloxy)-4-biphenyl carbonitrile (5OCB), using good quality X-ray intensity data. The estimated values are also compared with that determined from optical method [7,14].

EXPERIMENTAL

The nematic compounds 5OCB and HIPOB used in this investigation were supplied by M/s Aldrich Chemical Company (USA). Using Ortho plan Leitz polarizing microscope in conjunction with a hot stage the nematic – isotropic transition temperatures of these two samples were determined and are respectively 68.5 and 86°C. These values are in good agreement with the standard values. X-ray diffraction experiments on these two samples were performed using a rotating anode X-ray generator (RIGAKU, ULTRA 18). For X-ray recording the samples were taken in a capillary tube of 1 mm diameter and were placed in a chamber whose temperature can be controlled between 25 and 150°C using PID (proportional integrator detector) controller. A constant magnetic field of strength 0.6 T was used to orient the samples. The X-ray diffraction patterns from these samples were recorded at different temperatures in the nematic phase using Laue type of arrangement, consisting of 2D-image plate detector (MARS RESEARCH). Recorded data contain X-ray intensity at each pixel of the detector. The sample to detector distance was 250 mm and exposure time was set for 30 minutes. The temperature was controlled to an accuracy of $\pm 0.01^{\circ}$C. Using the supplied X-ray software, the recorded X-ray intensity data were sorted as a function of the arc angle ϕ. The wavelength of the X-rays used was 1.5418 Å (Cu K). The intensity versus arc angle data were obtained by integrating the diffused reflections over an annular ring centered on these reflections. Such Intensity data were obtained at various temperatures in the nematic phase of the samples in steps of 2°C per minute. One of these image plate recordings at various temperatures is given in Figure 1.

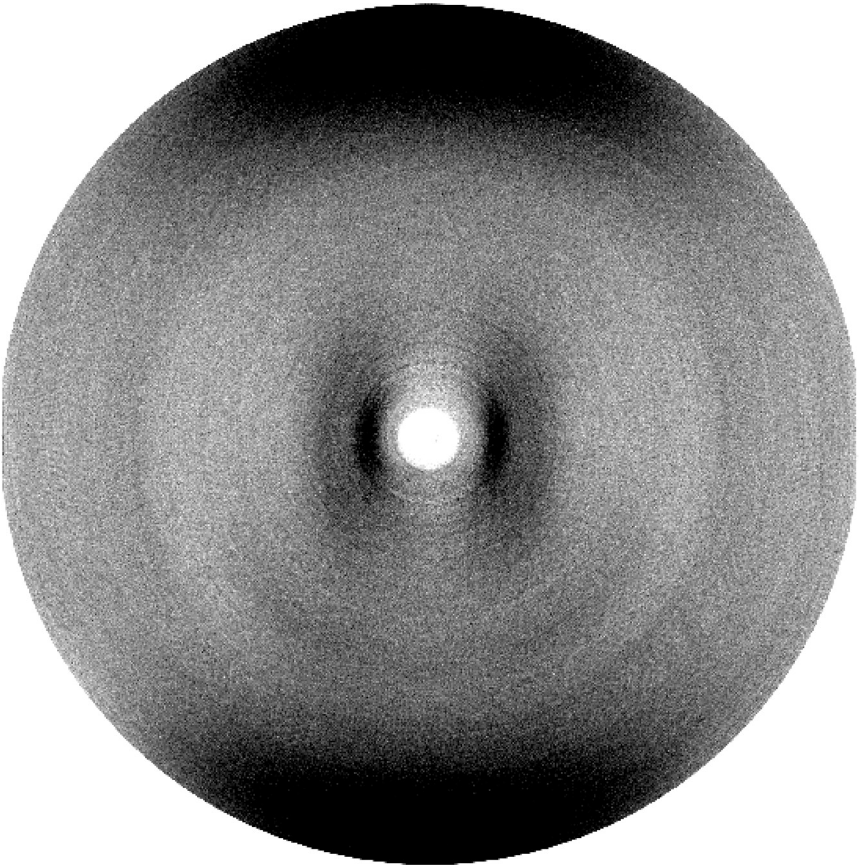


FIGURE 1 X-ray diffraction pattern from 5OCB at temperature 50 degree C.

3. ANALYSIS OF X-RAY INTENSITY DATA

Equation (1) can be used to estimate orientational order parameter $\langle P_2 \rangle$ and also higher order parameter $\langle P_4 \rangle$ Kelkar and Paranjape [15] have inverted Eq. (1) to estimate the distribution function. Later Deutsch [12] has analytically inverted Eq. (1) to determine f(β) and hence the orientational order parameters using the following equations.

$$\langle P_2 \rangle = 1 - \frac{3}{2} N \int_0^{\pi/2} I(\phi) \Big[\sin^2\phi + (\sin\phi \cos^2\phi) \times \log\{(1 + \sin\phi/\cos\phi\} \Big] d\phi \qquad (2)$$

and $N = \int_0^{\pi/2} I(\phi) d\phi$

$$\langle P_4 \rangle = 1 - \frac{1}{N} \int_0^{\pi/2} I(\phi) \left[\sin^2\phi \frac{105}{16} \cos^2\phi \frac{15}{24} \right] + \sin\phi \ln\{1 + \sin\phi/\cos\phi\} \left[\frac{105}{16} \cos^4\phi - \frac{15}{4} \cos^2\phi \right] d\phi \qquad (3)$$

Leadbetter also suggested during the same time a numerical method using truncated Legendre polynomials and corresponding expression of I(ϕ) is given by

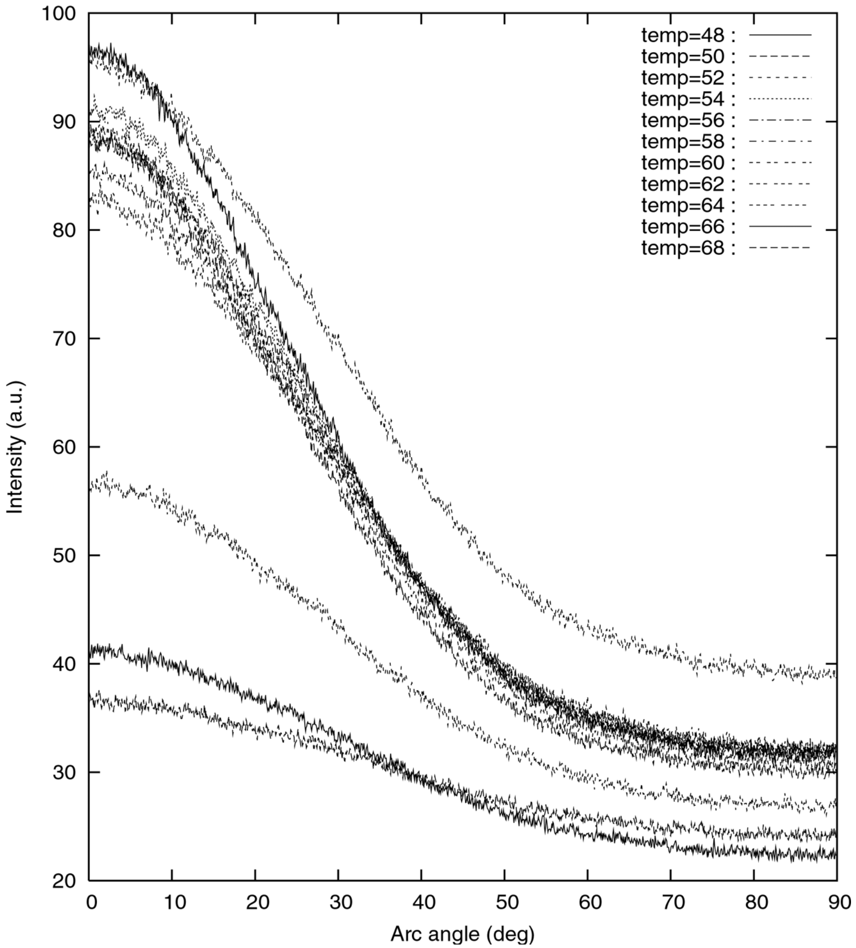
$$I(\phi) = f_0 + \frac{2}{3} f_2 \cos^2\phi + \frac{8}{15} f_4 \cos^4\phi + \frac{16}{35} f_6 \cos^6\phi + \frac{128}{315} f_8 \cos^8\phi + \frac{256}{693} f_{10} \cos^{10}\phi + \cdots \qquad (4)$$

Levelut group [16] also reported a novel method of inverting Eq. (1) wherein there is only one independent parameter which determines the distribution function f(β) and hence the orientational order parameter. The equation used by them for I(ϕ) is given by

$$I(\phi) = \frac{1}{Z} \left[1 + \frac{2m}{3} \cos^2\phi + \frac{4m^2}{15} \cos^4\phi + \frac{8m^3}{105} \cos^6\phi + \frac{16m^4}{945} \cos^8\phi + \cdots \right], \qquad (5)$$

where $Z = 4\pi \int_0^1 \exp(mx^2) dx$ is the normalization constant. The constant m in Levelut approach and the constant 'f' in Leadbetter approach is related to the order parameter via the orientational distribution functions. These are given by

$$S = (3\langle \cos^2\beta \rangle - 1)/2 \qquad (6)$$



(a)

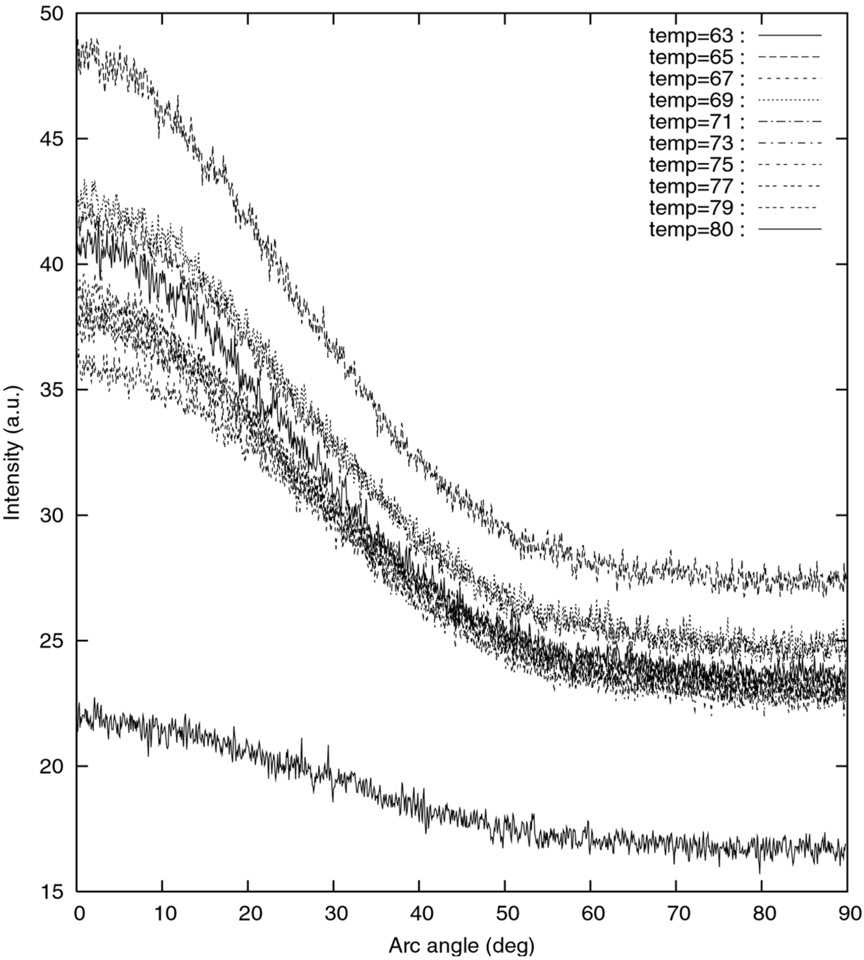
FIGURE 2 Averaged intensity versus arc angle for (a) 5OCB and (b) HIPBO.

$$\langle \cos^2 \beta \rangle = \frac{J_2(m)}{J_0(m)} \tag{7}$$

The relation involving ‘f’ is given by

$$\langle \cos^2 \beta \rangle = \sum f_{2i}/(2i+3) \Big/ \sum f_{2i}/(2i+1) \tag{8}$$

Presently, we have estimated the orientational order parameter and higher order Parameter, using Eqs. (1–7). Necessary programs were



(b)

FIGURE 2 Continued.

written in Fortran77 language and these were run on a Linux supported PC.

RESULTS AND DISCUSSION

We have computed orientational order parameter $\langle P_2 \rangle$ and higher order parameter $\langle P_4 \rangle$ using experimental X-ray data and Eqs. (1–6). Raw X-ray intensity data were corrected for Lorentz Polarization factors. Such computations were carried out for both the samples at different temperatures in the nematic phase. The goodness of the computed parameters was checked by recomputing the intensity profile using the above equations and in all our calculation it turned out to be less than 1 percent of the mean value of the X-ray data. In fact, such is the advantage and accuracy of the X-ray method for the estimation of the order parameter, which is absent in many of other methods. X-ray intensities along the arc-angle are measured for two compounds at different temperatures, in four quadrants and the

TABLE 1 Orientation Order Parameter $\langle P_2 \rangle$ Obtained at Different Temperatures in the Nematic Phase of 5OCB

TC	Leadbetter	Deutsch	Levelut
48	0.712	0.637	0.529
50	0.709	0.629	0.514
52	0.703	0.617	0.494
54	0.699	0.612	0.484
56	0.691	0.599	0.459
58	0.687	0.591	0.445
60	0.678	0.573	0.410
62	0.669	0.559	0.383
64	0.661	0.534	0.345
66	0.650	0.520	0.309
68	0.612	0.450	0.169

TABLE 2 Orientation Order Parameter $\langle P_2 \rangle$ Obtained at Different Temperatures in the Nematic Phase of HIPBO

T°C	Leadbetter	Deutsch	Levelut
63	0.734	0.668	0.587
65	0.718	0.643	0.538
67	0.707	0.641	0.506
69	0.703	0.619	0.494
71	0.702	0.617	0.473
73	0.695	0.607	0.453
75	0.690	0.598	0.447
77	0.688	0.595	0.441
79	0.678	0.574	0.313
81	0.656	0.534	0.281
83	0.616	0.482	0.156

average intensity versus arc angle are given in Figures 2(a) and 2(b). Tables 1 and 2, show the orientational order parameter $\langle P_2 \rangle$ obtained from Leadbetter (B) Deutsch (C) and Levelut (D), methods using the averaged X-ray intensity data given in Figures 2(a) and 2(b). It is evident from these tables, that analytical method of inverting Eq. (1) by Deutsch is more appropriate than the values of $\langle P_2 \rangle$ over estimated in the case of Leadbetter technique and under estimated in the case of Levelut method. The discrepancy in Leadbetter and Levelut computations lies because of the fact that the methods involve a truncation of the series which results in the serious error in the estimated values of $\langle P_2 \rangle$. Such a problem does not arise in Deutsch method, since we can reduce this error by rechecking the computed X-ray intensity values with that of experimental X-ray intensities, using the analytical solutions rather than truncated series function.

A comparison of the temperature variation of $\langle P_2 \rangle$ obtained from Deutsch method with the Maier-Saupe theory (M-S model) indicates that near the nematic-isotropic transition temperature, the M-S model

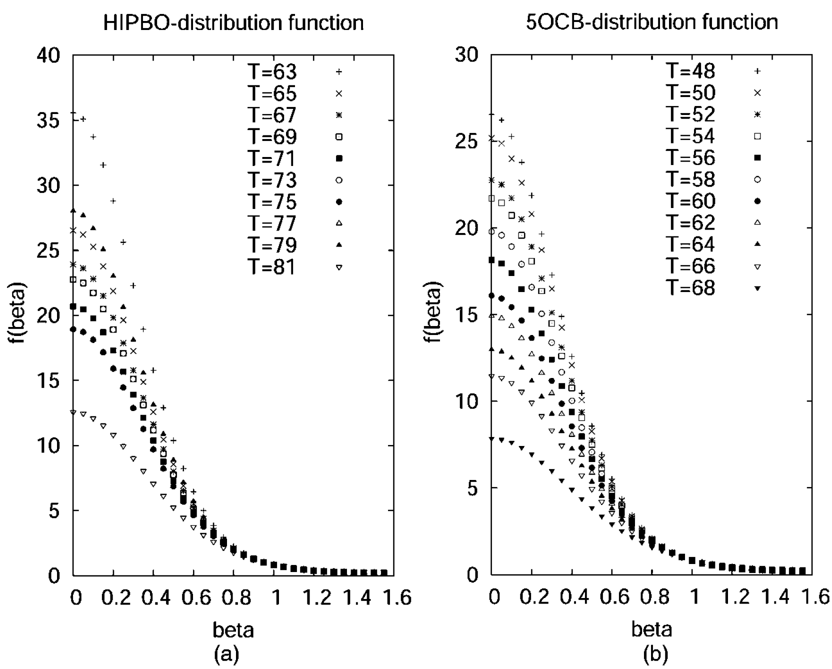


FIGURE 3 Variation of distribution function in the case of (a) HIPBO and (b) 5OCB.

predicts a value of 0.38 for $\langle P_2 \rangle$ where as in our computation the values turn out to be 0.45 and 0.48 respectively for HIPBO and 5OCB. For the sake of completeness, we have reproduced here the distribution function calculated using Deutsch method forHIPBO and 5OCB in Figures 3(a) and (b). Further, a comparison of $\langle P_2 \rangle$ estimated from refractive index data using Neugebauer relations with that obtained from X-ray data (in Deutsch method) is given in Figures 4(a) and (b). It is evident from these figures that optical method of $\langle P_2 \rangle$ are lower compared to X-ray method. The reason for such a debacle lies in the following:

(i) point dipole approximation used in Neugebauer method may not be of good local field approximation. Also, this method is sensitive to accuracy of density measurements as pointed out by Madhusudana [17].

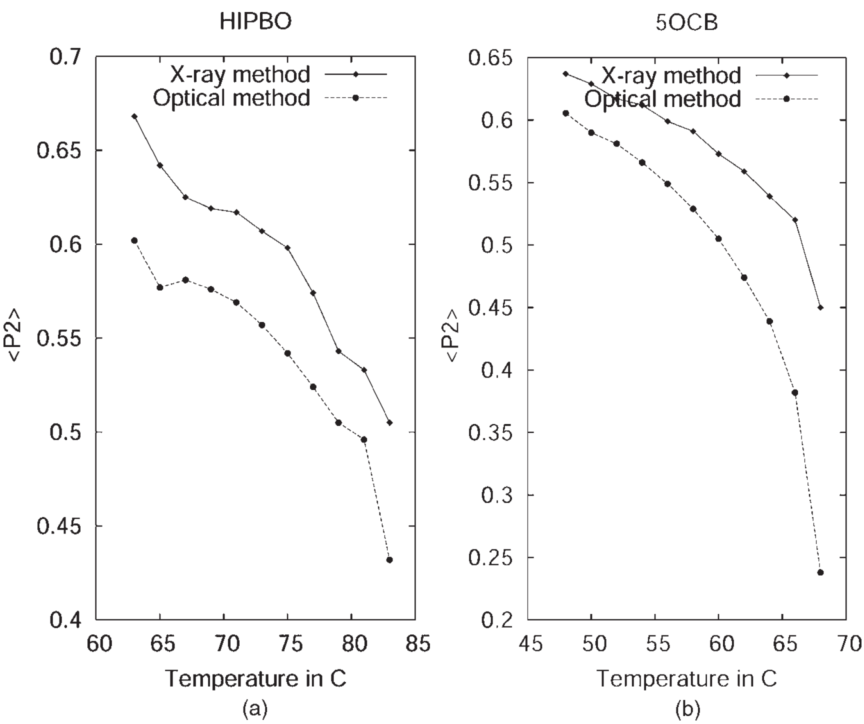


FIGURE 4 Variation of order parameter with temperature in the case of (a) HIPBO and (b) 5OCB.

(ii) The averaging procedure involved in these two methods are different. It is macroscopic averaging in optical method and microscopic averaging in X-ray technique [18].

According to P. G. de Gennes [18] based on a theoretical model, higher order parameter is found to obey the following relation:

$$\langle P_4 \rangle \geq (35P_2^2 - 10P_2^2 - 7)/18 \tag{9}$$

Presently, estimated values of $\langle P_4 \rangle$ and $\langle P_2 \rangle$ along with the theoretical estimates of HJL and MS theory are given in Figure 5. An examination of Figure 5 indicates that $\langle P_4 \rangle$ values computed from X-ray data using Deutsch method lie very close to the values estimated using the Eq. (9). This evidently indicates that pair correlations are important in these nematic systems and they have a profound influence on the interpretation of the data (all based on one-particle approximation). It is also observed that the values of $\langle P_4 \rangle$ obtained from X-ray data lie below the predicted value of MS-theory which indicates the θ fluctuations are not large as expected from the theory.

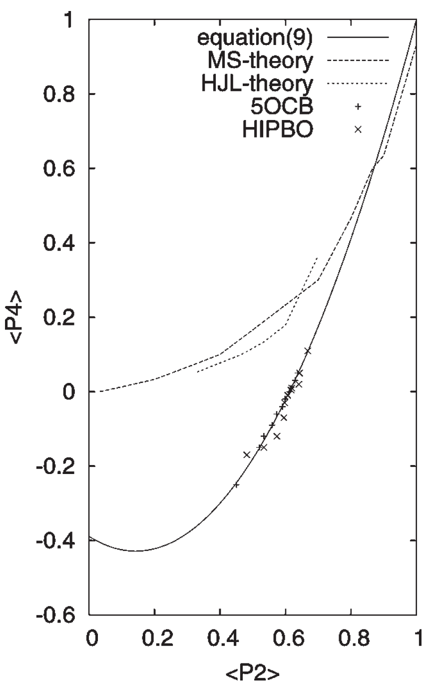


FIGURE 5 Variation of ⟨P4⟩ with ⟨P2⟩.

CONCLUSIONS

In this paper, we have recorded X-ray diffraction patterns from two nematogenic compounds in the nematic phase at different temperatures. By circular scanning of the diffused ring, we have computed the orientational order and we find that this method is more logical and is in agreement with the theoretically predicted values of $\langle P_4 \rangle$ using Eq. (9) and nearly those of HJL-theory.

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