

Molecular flexibility and orientational statistics of liquid crystals: Raman study of 7-CB and 8-OCB

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(Received 7 August 1980; accepted 2 September 1980)

The Raman depolarization ratios of the $\text{-C}\equiv\text{N}$ vibrational band of 7-CB and 8-OCB have been measured in the aligned liquid crystal and isotropic phases. The temperature dependence of the absolute orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been evaluated for the mesophases of both compounds. A comparison of their $\langle P_4 \rangle$ values in the nematic phase with those determined by Miyano for 5-CB suggests that molecular flexibility is an important factor that serves to lower $\langle P_4 \rangle$ well below the predictions of mean field theories.

INTRODUCTION

The molecules in thermotropic liquid crystals are normally assumed to be elongated rigid rods possessing cylindrical symmetry. In the uniaxial nematic phase the molecular ordering can then be specified completely, in principle, given the knowledge of the orientational distribution function¹ $f(\cos\theta)$. One would thus like to obtain through experiments as complete information as possible about $f(\cos\theta)$. However, only the first two moments of $f(\cos\theta)$ have been easily accessible hitherto for practical measurements. These are given by

$$\langle P_2(\cos\theta) \rangle = \int_{-1}^1 f(\cos\theta) P_2(\cos\theta) d(\cos\theta), \quad (1)$$

$$\langle P_4(\cos\theta) \rangle = \int_{-1}^1 f(\cos\theta) P_4(\cos\theta) d(\cos\theta); \quad (2)$$

here $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$ are the second and fourth order Legendre polynomials, respectively, and the angular brackets denote averaging over all the molecules in the medium. An experimental determination of these two orientational order parameters, designated hereafter as $\langle P_2 \rangle$ and $\langle P_4 \rangle$, is of considerable interest from the standpoint of the statistical theories proposed for the molecular order in liquid crystals.

The anisotropies in various microscopic and macroscopic properties of liquid crystals have been extensively studied in the past in order to determine the variation of $\langle P_2 \rangle$, both with temperature and molecular structure.² Relatively little is known as yet about the behavior of $\langle P_4 \rangle$ in most liquid crystals. Recently, it was demonstrated that polarized Raman scattering can simultaneously yield the absolute values of both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in uniaxial liquid crystals.³⁻⁵ A puzzling result that emerged from the Raman studies is that $\langle P_4 \rangle$ could assume negative values in some cases, especially within a temperature range close to the nematic-isotropic transition. Although this behavior is yet to be reconciled with predictions based on mean field theories, some speculations were put forward regarding its possible origin.¹ In their earliest study, Jen *et al.*⁶ sug-

gested that negative $\langle P_4 \rangle$ values may be rationalized if the flexibility of mesogenic molecules is taken into account—a feature that is ignored in theoretical calculations which assume the molecules to be rigid rods. The molecular flexibility is enhanced by increasing the alkyl end-chain length. It is thus of interest to examine the behavior of $\langle P_4 \rangle$ in closely related or homologous mesogens in order to assess the influence of molecular structure on this order parameter. With this motivation, we have studied by Raman scattering the variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in two related cyanobiphenyl liquid crystals, viz., 7-CB (4,4'-*n*-heptylcyanobiphenyl) and 8-OCB (4,4'-*n*-octyloxycyanobiphenyl). For 7-CB our $\langle P_4 \rangle$ values are consistently lower than those determined earlier by Heger.⁴ A comparison of our $\langle P_4 \rangle$ results for 7-CB and 8-OCB with Miyano's data⁵ on 5-CB (4,4'-*n*-pentylcyanobiphenyl) suggests that molecular flexibility is an important factor that serves to lower $\langle P_4 \rangle$ well below the predictions of mean field theories.

EXPERIMENTAL

The transition temperatures of 7-CB and 8-OCB were determined from thermal microscopy. Their respective nematic-isotropic transition temperatures (T_{NI}) were 353.1 and 314.8 °K. The smectic A-nematic transition temperature (T_{AN}) of 8-OCB was 340 °K. The oriented liquid crystal samples, ~100 μ in thickness, were held between glass cover slips or optically polished fused quartz plates. Homogeneous alignment was achieved by oblique vacuum coating of a SiO layer on the inner surfaces of the windows. Homeotropic alignment was obtained by evaporating on the surfaces a dilute solution of cetyl trimethylammonium bromide in chloroform. The alignment of the samples was checked using a polarizing microscope. The sample cell was imbedded in a heated copper block and its temperature could be maintained at any desired value to within ± 0.2 °C.

Raman scattering experiments were performed in the backscattering geometry (180° scattering angle). The spectra were excited by ~100 mW at 6328 Å from a He-Ne laser. The scattered radiation was dispersed by a double grating monochromator and detected by a cooled photomultiplier tube (RCA-8852) in conjunction with a photon counting system. The experimentally measured

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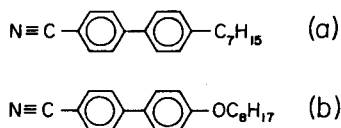


FIG. 1. Molecular structures: (a) 7-CB and (b) 8-OCB.

Raman depolarization ratios were corrected for the unequal response of the monochromator for the two different polarizations of the scattered radiation. The $\langle P_2 \rangle$ values were also measured independently by the method of infrared dichroism,⁷ employing unpolarized radiation and homeotropically aligned samples. Other details of our equipment and experimental procedure have been described elsewhere.^{7,8}

RESULTS AND DISCUSSION

The molecular structures of 7-CB and 8-OCB are shown in Fig. 1. It is reasonable to assume that in both cases the molecular long axis coincides with the line joining the centers of the two benzene rings. The intramolecular vibration corresponding to the $-\text{C}\equiv\text{N}$ stretch band also lies along the same axis. Our Raman and infrared experiments utilized this strong, isolated band in the spectra of both mesogens. In the infrared experiment, if R denotes the ratio of the integrated absorbance of this band in the homeotropically aligned mesophase to that in the isotropic phase, it is easily shown that⁷

$$\langle P_2 \rangle = (1 - R) \quad (3)$$

From the integrated intensity under the Raman band profile, we obtained the three depolarization ratios^{3,5}

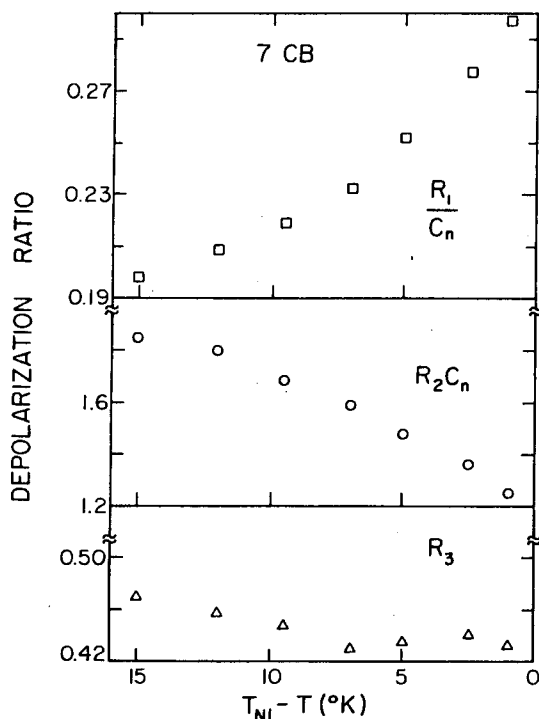
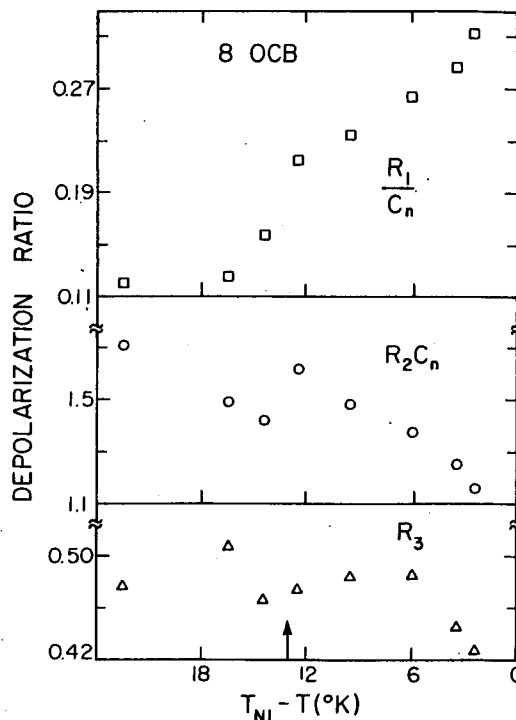


FIG. 2. Corrected depolarization ratios of 7-CB.

FIG. 3. Corrected depolarization ratios of 8-OCB. The arrow indicates T_{AN} .

R_1 , R_2 , and R_3 in the liquid crystalline phases:

$$R_1 = I_{yz}/I_{xx}, \quad R_2 = I_{xy}/I_{yy}, \quad R_3 = I_{yz}/I_{xx} \quad (4)$$

where the first subscript denotes the polarization of the scattered light and the second refers to that of the incident light in the laboratory frame of axes (x , y , z), the liquid crystal being aligned parallel to the z axis. For the isotropic phase, $R_{1,iso} = R_1 = R_2$. For the liquid crystalline phases, we duly corrected the observed depolarization ratios R_1 and R_2 in order to take account of the solid angle changes and transmission loss at the sample-cell interface.^{3,9} The corrected ratios are denoted by R_1/C_n and R_2C_n , where

$$C_n = [(n_x + n_e)/(n_x + n_o)]^2 \quad (5)$$

here n_x is the refractive index of the sample cell window and n_e and n_o represent, respectively, the ordinary and extraordinary refractive indices of the liquid crystalline sample. The pertinent refractive indices of 7-CB and 8-OCB were obtained by extrapolating the data of Karat and Madhusudana¹⁰ to the Stokes-shifted wavelength of the $-\text{C}\equiv\text{N}$ Raman band. The final computation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at each temperature was carried out following an iterative method, as described by Miyano.⁵

Figures 2 and 3 show the corrected depolarization data for the liquid crystalline phases of 7-CB and 8-OCB, respectively. Their respective $R_{1,iso}$ values are 0.378 and 0.332. The calculated values of $\langle P_2 \rangle$ as a function of temperature for both mesogens are shown in Fig. 3. For comparison, we have included the birefringence data of Karat and Madhusudana,¹⁰ normalized to the

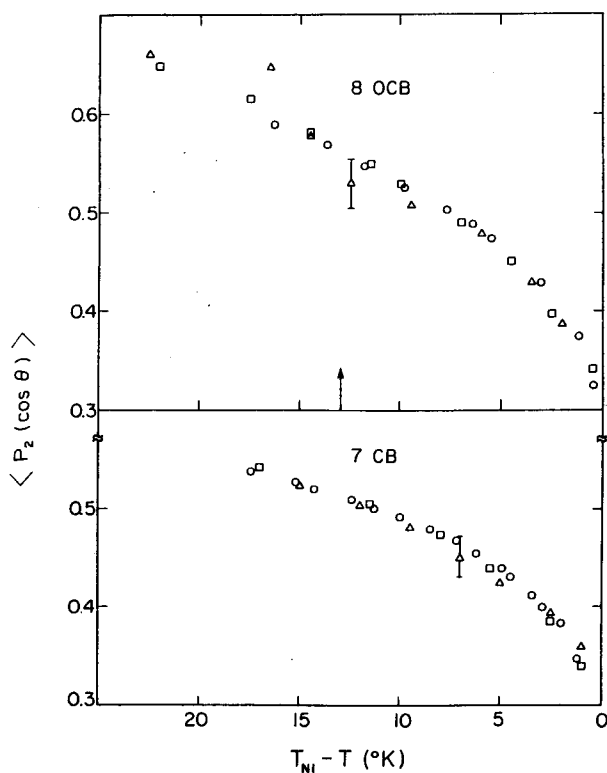


FIG. 4. Temperature dependence of $\langle P_2(\cos\theta) \rangle$ in 7-CB and 8-OCB. Triangles: Raman results; squares: infrared results; circles: birefringence data (Ref. 10). The arrow indicates T_{AN} of 8-OCB.

$\langle P_2 \rangle$ value obtained from our infrared measurements at the midpoint of the nematic range. There is close agreement between the $\langle P_2 \rangle$ values derived from our infrared and Raman measurements on the one hand, and the birefringence data on the other.

The $\langle P_4 \rangle$ results for 7-CB and 8-OCB are shown in Fig. 5. Also shown here is the corresponding result obtained by Miyano⁵ from a study of the $-\text{C}\equiv\text{N}$ Raman line of 5-CB. All three mesogens have identical cyanobiphenyl rigid cores, but differ in their end-chain length. Furthermore, the flexible parts of the molecular end group are identical for both 8-OCB and 9-CB, i.e., C_8H_{17} . This is because in 9-CB the first methylene group which is linked to the phenyl ring is essentially

TABLE I. Calculated Raman tensor parameters a and b of the $-\text{C}\equiv\text{N}$ band of 7-CB at different temperatures.

$T_{NI}-T(^{\circ}\text{K})$	a	b
1.0	-0.186	0.129
2.5	-0.184	0.127
5.0	-0.159	0.095
7.0	-0.135	0.065
9.5	-0.156	0.091
12.0	-0.157	0.092
15.0	-0.166	0.104

immobile. To this extent, there is a further justification for intercomparing the data on 8-OCB, 7-CB, and 5-CB. At any given relative temperature ($T_{NI}-T$) within the nematic range these data demonstrate for the first time the decrease in $\langle P_4 \rangle$ with an increase in end-chain length. In view of the indicated experimental uncertainties in $\langle P_4 \rangle$, this observed trend is necessarily qualitative. The broken curve which depicts Miyano's results on 5-CB is based on an extrapolation to zero sample thickness, while our data on 7-CB and 8-OCB pertain to a sample thickness of $\sim 100 \mu$. However, the reported thickness dependence of the depolarization ratios is quite small⁵ and the above conclusion would remain valid even if our data were extrapolated to zero sample thickness.

From Figs. 4 and 5, we note that in the smectic A phase of 8-OCB both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ register an increase. This reflects the greater degree of orientational order expected for this phase as compared to the nematic phase.

Our $\langle P_4 \rangle$ results on 7-CB differ from those reported earlier by Heger.⁴ In the latter case, the estimated $\langle P_4 \rangle$ values are all higher than those reported for 5-CB even very close to T_{NI} . This is in marked contrast with the trend seen in Fig. 5 with increasing chain length. Heger's $\langle P_4 \rangle$ values were calculated under the assumption that the Raman tensor of the $-\text{C}\equiv\text{N}$ band is uniaxial within the molecular frame of reference.¹¹ Our calculated tensor parameters a and b for 7-CB and 8-OCB are shown in Tables I and II, respectively. These results show that the relevant Raman tensor is biaxial for both cases, in accord with Miyano's data⁵ on 5-CB as well. We therefore feel that the above assumption and the less straightforward experimental geometry adopted by Heger could have caused significant departures in his estimates of $\langle P_4 \rangle$. On the other hand, we note that Heger's $\langle P_2 \rangle$ re-

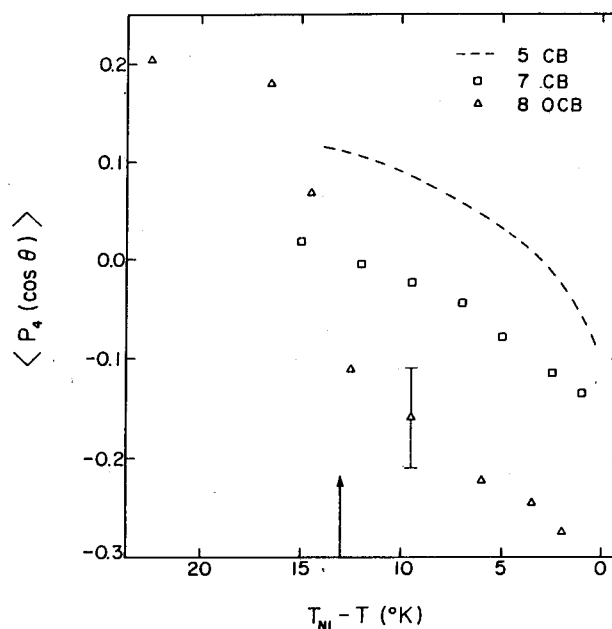


FIG. 5. Temperature dependence of $\langle P_4(\cos\theta) \rangle$ in 5-CB (Ref. 5), 7-CB, and 8-OCB. The arrow indicates T_{AN} of 8-OCB.

TABLE II. Calculated Raman tensor parameters a and b of the $-\text{C}\equiv\text{N}$ band of 8-OCB at different temperatures.

$T_{\text{NI}} - T$ (°K)	a	b
2.0	-0.240	0.319
3.5	-0.239	0.318
6.0	-0.248	0.333
9.5	-0.227	0.298
12.5	-0.204	0.260
14.5	-0.186	0.232
16.5	-0.185	0.231
22.5	-0.156	0.188

sults are in reasonable agreement with ours. This is consistent with the fact that the experimental uncertainties associated with the Raman technique always cause a much smaller percentage error in $\langle P_2 \rangle$ than in $\langle P_4 \rangle$.

Within a homologous series of liquid crystals, $\langle P_2 \rangle$ is known to exhibit the well known odd-even effect.¹² A similar effect is yet to be established in the case of $\langle P_4 \rangle$ for any homologous series. We note, however, that the results in Fig. 5 are not complicated by any possible odd-even effect, inasmuch as 8-OCB can be regarded as equivalent to 9-CB with regard to the flexible part of the molecule.

Any evaluation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ which relies on the optical or dielectric anisotropy of the medium must, in principle, include appropriate corrections for local field effects. A satisfactory theoretical estimate of these effects in liquid crystals remains as yet a difficult problem. However, based on other available empirical evidence Jen *et al.*³ concluded that such corrections should not significantly alter the results obtained by the Raman technique. They attribute this to the notion that the short range correlations between molecules are essentially insensitive to temperature changes. We note that with the geometry adopted for our infrared measurements, possible local field corrections to $\langle P_2 \rangle$ are expected⁷ to be well within 2%. Thus, the agreement seen in Fig. 4 between the $\langle P_2 \rangle$ results of both our Raman and infrared data indicates that the necessary corrections to the Raman measurements are again well within the experimental uncertainties.

In conclusion, the present study demonstrates the influence of increasing end-chain length and hence molecular flexibility on $\langle P_4 \rangle$. It is of interest to extend these experiments to other mesogenic molecules which possess the same end alkyl groups, but a more elongated rigid core structure. In this context, a study of the corresponding homologs of 4,4'-*n*-alkylcyanoterphenyl series of liquid crystals would be especially relevant.

ACKNOWLEDGMENTS

The authors thank Professor S. Chandrasekhar for his keen interest in this investigation. Our thanks are due to Mr. B. V. Nataraja for computational assistance and to Dr. B. K. Sadashiva for providing the liquid crystalline samples. One of us (S.V.) is grateful to Professor A. K. Ramdas for his hospitality at Purdue University during the progress of this work. S.N.P. acknowledges U.G.C. and N.C.E.R.T. for the award of a fellowship.

¹E. B. Priestley and P. J. Wojtowicz, in *Introduction to Liquid Crystals*, edited by E. B. Priestley, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1974), Chaps. 3, 4, and 6.

²For a review, see P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University, London, 1974).

³S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestley, *J. Chem. Phys.* **66**, 4635 (1977).

⁴J. P. Heger, *J. Phys. (Paris) Lett.* **36**, 209 (1975).

⁵K. Miyano, *J. Chem. Phys.* **69**, 4807 (1978).

⁶S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestley, *Phys. Rev. Lett.* **31**, 1552 (1973).

⁷J. R. Fernandes and S. Venugopalan, *J. Chem. Phys.* **70**, 519 (1979); *Mol. Cryst. Liq. Cryst.* **35**, 113 (1976).

⁸S. Venugopalan and S. N. Prasad, *J. Chem. Phys.* **72**, 4153 (1980); S. N. Prasad, Ph.D. thesis, University of Mysore (to be submitted).

⁹M. Lax and D. F. Nelson, *Phys. Rev. B* **4**, 3694 (1971); see also, *Proceedings of the Third Rochester Conference on Coherent and Quantum Optics*, edited by L. Mandel and E. Wolf (Plenum, New York, 1973), pp. 415-445.

¹⁰P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.* **36**, 51 (1976); **47**, 21 (1978).

¹¹J. P. Heger, Ph.D. thesis, École Polytechnique Fédérale de Lausanne, 1976 (unpublished).

¹²See, for example, S. Chandrasekhar, *Liquid Crystals* (Cambridge University, Cambridge, England, 1975), pp. 51-54.