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M. K. Das [a] & R. Paul [a]

[a] Department of Physics, University of North Bengal, Siliguri, 734430, India

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Determination of Bend to Splay Elastic Constant Ratio (K_3/K_1) of Several Nematogens and Applicability of Spherocylindrical Model

M. K. DAS and R. PAUL

Department of Physics, University of North Bengal, Siliguri-734430, India

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In the present work we have tried to test the theory of elastic constants of nematogens given by Priest, assuming spherocylindrical shape of the molecules. The bend (K_3) to splay (K_1) elastic constant ratios of four closely related nematic liquid crystals, having cyclohexane carboxylate core, have been determined by us using Freedericksz transition in a magnetic field. The length and width of the molecules and the order parameters $\bar{P}_2$ and $\bar{P}_4$, required for the theoretical calculations, have been estimated from our earlier X-ray studies on these compounds. The experimental values of the ratio K_3/K_1 for three of these compounds agree quite well with those calculated from the spherocylindrical model. The fourth nematogen, for which the agreement is poor, shows anomalous temperature variation of density and hence the rigid spherocylindrical model is not probably applicable to it. We have also measured K_3/K_1 for *n*-pentyl cyanobiphenyl (5CB), and have shown that the X-ray experimental data implies that $\bar{P}_4$ is positive even near the nematic-isotropic transition temperature for 5CB, which is at variance with some experimental Raman scattering results. Finally, the K_3/K_1 ratios for pentyloxy cyanobiphenyl (5OCB) at different temperatures obtained experimentally by Bradshaw *et al.* have been compared with those calculated from spherocylindrical model using our X-ray data.

Keywords: nematogen, elastic constants, spherocylindrical model

1. INTRODUCTION

The most important application of liquid crystals is in the field of display devices. The usefulness of a liquid crystal in a display device depends, among other things, on its elastic properties. There are three so-called Frank elastic constants characteristic of nematic liquid crystals, namely, splay (K_1), twist (K_2) and bend (K_3) elastic constants. One of the most convenient methods of determining elastic constants is from Freedericksz transition, where an electric or magnetic field is applied to deform a thin layer of surface aligned nematogenic sample. Depending on the geometry of the arrangement, splay, twist or bend elastic constant can be determined from Freedericksz transition.[1]

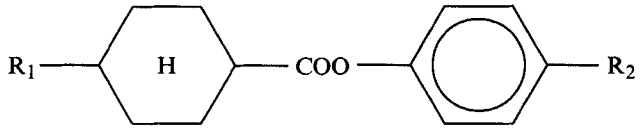
Apart from the above mentioned practical implication, there are other reasons for the determination of the elastic constants. There are several theories[2–6] of elastic constants of nematogens, but probably the simplest one is due to Priest,[4] who has expressed K_1, K_2 and K_3 in terms of the ratios of the order parameters $\bar{P}_2$ to $\bar{P}_4$, and of

the length to width of the molecules, assumed to be spherocylinders. In our laboratory, using X-ray diffraction technique, we have determined $\bar{P}_2$, $\bar{P}_4$ and apparent molecular length of a larger number of nematic liquid crystals[7]. Hence, it is of great interest to us to find how well these parameters, applied to Priest's theory, reproduce the elastic constant values. With this view in mind we have determined the splay to bend elastic constant ratios of four nematogens of a nearly homologous series, the compounds been studied earlier in our laboratory by Mitra *et al.*[8-11] They have measured refractive indices,[10-11] magnetic susceptibility anisotropy[8] and density[8-10] of these nematogens over their entire mesomorphic temperature range. X-ray diffraction studies have also been carried out by them to determine the order parameters $\bar{P}_2$ and $\bar{P}_4$, as well as the apparent molecular length.[9]

We have also determined the splay to bend elastic constant ratios of a much studied liquid crystal compound, viz., *n*-pentyl cyanobiphenyl (5CB), which have been reported by several authors,[12-16] in order to get an estimate of our experimental precision. Furthermore, the sign of $\bar{P}_4$ for 5CB, as obtained from Raman scattering experiments, is reported to be negative,[17-18] whereas it is positive from our X-ray measurements.[19] So it is of great significance to determine the ratio K_3/K_1 experimentally, since it depends on the sign of $\bar{P}_4$ according to the theory of Priest.[4]

2. EXPERIMENTAL

The molecular structure of the four compounds studied are given below:



I $R_1 = C_5H_{11}$, $R_2 = OCH_3$

II $R_1 = C_5H_{11}$, $R_2 = OC_3H_7$

III $R_1 = C_4H_9$, $R_2 = OC_2H_5$

IV $R_1 = C_5H_{11}$, $R_2 = CN$

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).
IV *p*-cyanophenyl *trans*-4-pentyl cyclohexane carboxylate (CPPCC).

All the compounds were obtained from M/S Hoffman – La Roche & Co, Basel, Switzerland in pure form and were used without further purification. The transition temperatures observed by us under a polarizing microscope equipped with Mettler FP

80/82 hot stage are as follows:

I MPPCC $\mathrm{K} \underset{\sim 11.5^{\circ}\mathrm{C}}{\overset{40.7^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \overset{71.1^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{I}$

II PPPCC $\mathrm{K} \underset{37.0^{\circ}\mathrm{C}}{\overset{43.3^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \overset{71.1^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{I}$

III EPBCC $\mathrm{K} \underset{\sim 11^{\circ}\mathrm{C}}{\overset{36.3^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \overset{74.6^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{I}$

IV CPPCC $\mathrm{K} \underset{\sim 11^{\circ}\mathrm{C}}{\overset{47.0^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \overset{78.7^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{I}$

The liquid crystal samples were filled in a specially surface treated glass cell of thickness of about 160 μm. Depending upon the surface treatment, either planar or homeotropic alignment were produced. The cells were examined under a polarising microscope to check the uniformity of alignment before using in the experiment. The cells were placed in a brass thermostat with glass windows. The temperature of the thermostat was kept constant within $\pm 0.2^{\circ}\mathrm{C}$ during the experiment using a temperature controller Indotherm-457. The sample cell with the thermostat was placed in a magnetic field with relevant geometry[1] for the measurement of splay and bend elastic constants. A polarized light beam from sodium vapour lamp was passed through the cell and a crossed analyser before entering a photomultiplier tube (RCA 931). The current output from the photomultiplier tube was amplified and measured. The magnetic field was measured with the help of a calibrated hall probe. The critical magnetic field for the Freedericksz transition could be observed quite accurately (within 0.5%) from the sudden change in the current from the photomultiplier tube. The relevant elastic constant K_i ($i = 1, 3$) was calculated from the well known equation

$$K_i = H_c^2 d^2 \Delta\chi / \pi^2,$$

where H_c is the critical field with geometry relevant for the particular elastic constant measurement, d the thickness of the sample and $\Delta\chi$ the magnetic susceptibility anisotropy. We had to work with rather thick samples, because of the limitation of the magnetic field available to us. We decided to present our data as the ratio of the elastic constants K_3/K_1, which avoids errors arising from different parameters viz. density and magnetic susceptibility anisotropy.

3. RESULTS AND DISCUSSIONS

The splay to bend elastic constants for 5CB were measured by us and these values are compared with those obtained by other workers[12–16] to check the accuracy of our measurements. The ratios K_3/K_1 for 5CB at four different temperatures have been compared in Table 1. It can be seen that our K_3/K_1 values are within the range of reported values and agree quite well ($\pm 4\%$) with the recent values of Hakemi.[13] Hence

TABLE I

Experimental and calculated values of the ratio K_3/K_1 at different temperatures for 5CB. The theoretical values were calculated using the values of $\bar{P}_4/\bar{P}_2$ from different methods

	Experimental						Calculated with $\bar{P}_4/\bar{P}_2$ from		
							X-ray diffraction	Raman Scattering experiment	
Temp. in °C	Hakemi* (a)	Karat* (b)	Hara* (c)	Madhusudana* (d)	Bradshaw* (e)	Present work	Our work (f)	Dalmolen* (g)	Miano* (h)
25.6	1.25	1.35	1.30	1.332	1.331	1.29	1.24	1.21	1.13
31.0	1.24	1.15	1.22	1.17	1.236	1.21	1.20	1.08	1.02
32.6	1.22	1.11	1.14	1.09	1.236	1.20	1.18	1.04	0.95
34.0	1.18	1.07	1.07	—	1.193	1.14	1.18	0.98	0.82

* Interpolated values from their experimental data. (a) Reference 13 (b) Reference 12 (c) Reference 14 (d) Reference 16 (e) Reference 15 (f) Reference 19 (g) Reference 17 (h) Reference 18.

our experimental values seem to be within the tolerable limits of the data available in the literature.

We have tried to test the theory of elastic constants given by Priest,[4] assuming spherocylindrical shape for the molecules. According to this theory

$$K_1 = \bar{K}(1 + \Delta - 3\Delta'\gamma) \tag{1a}$$

$$K_2 = \bar{K}(1 - 2\Delta - \Delta'\gamma) \tag{1b}$$

$$K_3 = \bar{K}(1 + \Delta + 4\Delta'\gamma) \tag{1c}$$

where

$$\bar{K} = (K_1 + K_2 + K_3)/3 \tag{2a}$$

$$\gamma = \bar{P}_4/\bar{P}_2 \tag{2b}$$

$$\Delta = (2R^2 - 2)/(7R^2 + 20) \tag{2c}$$

$$\Delta' = (9/16)(3R^2 - 8)/(7R^2 + 20) \tag{2d}$$

$$R = (L - D)/D, \tag{2e}$$

L and D being overall length and diameter of the spherocylinder respectively. For any reasonable length to diameter ratio Δ and Δ' are positive, hence, if $\bar{P}_4/\bar{P}_2 > 0$ then $K_3 > K_1 > K_2$. We have estimated values of L and D as follows. The apparent molecular length obtained from our X-ray data[9] was taken as L. Then, assuming a simple tetragonal lattice, with L as the longest axis and taking the value of density from our previous publications[8-10], the value of D was calculated. Since, in the mesophase, the molecules are not closely packed, we have not tried *hcp* or some other densely packed lattice system. In general, both L and D are functions of temperature, however, for CPPCC the variations of $L$and D are negligible over the mesomorphic temperature range and hence Δ and Δ' may be taken as constants independent of temperature in this case. The orientational order parameters of these compounds $\bar{P}_2$ and $\bar{P}_4$ have already been determined by us from X-ray diffraction studies.[9] From Equations 1a and 1c

$$K_3/K_1 = (1 + \Delta + 4\Delta'\gamma)/(1 + \Delta - 3\Delta'\gamma) \tag{3a}$$

$$= (1 + 4\delta)/(1 - 3\delta) \tag{3b}$$

$$\approx (1 + 7\delta) \tag{3c}$$

Where $\delta = \Delta'\gamma/(1 + \Delta)$. The last step in Equation 3 follows from the fact that in the present case of CPPCC $\delta \ll 1$ (δ ranges between .02 and .052). Figure 1 shows the variation of K_3/K_1 with δ for CPPCC, which is almost linear with a slope of 8.0 instead of 7.0 as predicted from Equation 3c. The agreement is surprisingly good considering

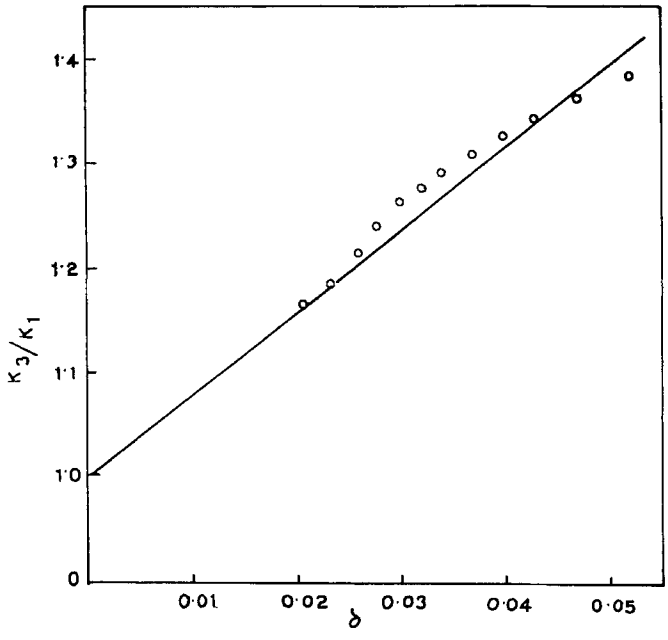


FIGURE 1 Values of K_3/K_1 versus $\delta(=\Delta'\gamma/(1+\Delta)$ for CPPCC, o, experimental values; full line, linear fit.

the approximations involved in the theory. In Figure 2, we have compared our experimental K_3/K_1 ratios at different temperatures with those calculated from Priests theory[4] using our data[8-10] for L, D, $\bar{P}_2$ and $\bar{P}_4$. As expected, the agreement for CPPCC is the best, while those for MPPCC and PPPCC are reasonable. The disagreement with Priest's theory is most pronounced for EBPCC, which shows an anomalous density variation with temperature.[10] This anomalous behaviour may have contributed to the disagreement with the theory of Priest,[4] since rigid spherocylinders should not show any anomalous temperature variation of density. So, the spherocylindrical model is not applicable in the case of EBPCC. The ratio K_3/K_1 decreases with increasing value of the L/D, as it should according to Priest,[4] the apparent molecular length to width ratios (L/D) for MPPCC, PPPCC, EPBCC and CPPCC at $T = T_{NI} - 1.1°C$ are given in Table II. The experimental and calculated K_3/K_1 ratios at the same temperature are also shown in the table for the help in comparison.

There are very few experimental methods that provide the value of $\bar{P}_4$. We have determined $\bar{P}_4$ for a large number of nematogens from X-ray diffraction studies.[7] Raman scattering experiments can also give $\bar{P}_4$ values. Some of the $\bar{P}_4$ values obtained from Raman scattering are negative, while all the $\bar{P}_4$ values obtained by us from X-ray studies are positive. It can be easily seen from Equation 1 that if $\bar{P}_4 > 0$ then $K_3/K_1 > 1$ and if $\bar{P}_4 < 0$ then $K_3/K_1 < 1$ ($\bar{P}_2$ is always positive). Hence, the value of K_3/K_1 is an indicator of the sign of $\bar{P}_4$. Both Miyano[8] and Dalmolen[17] have reported negative $\bar{P}_4$ values for 5CB near its nematic- isotropic temperature, while our X-ray data[19] yields positive $\bar{P}_4$ values throughout the mesomorphic range. In Table I we have given the calculated values of K_3/K_1 according to Priest's theory, taking L and D from our

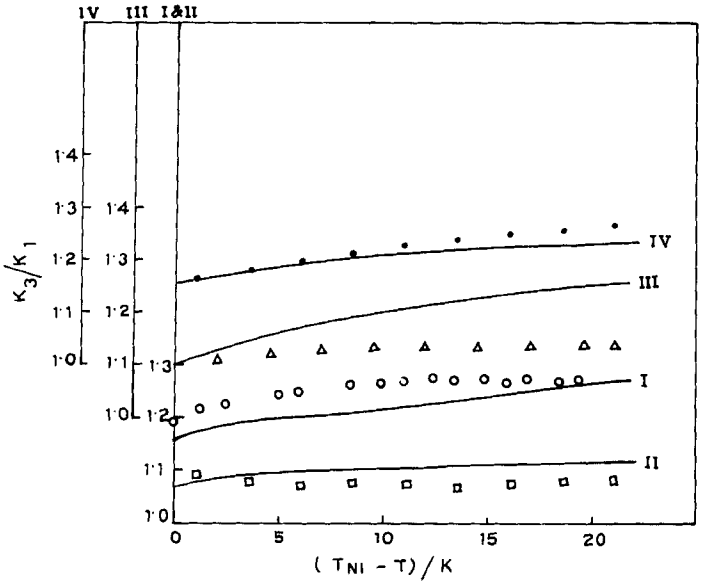


FIGURE 2 Ratio of the bend to splay elastic constant ratio K_3/K_1 as functions of relative temperature for I MPPCC (○); II PPPCC (□); III EPBCC (△); and IV CPPCC (●). Continuous curves correspond to the theoretical calculation of Priest [4], using our X-ray data (Ref. 8,9,10).

TABLE II

The L/D and K_3/K_1 values for different compounds at a relative temperature $(T_{NI} - T) = 1.1°C$

Compounds	L/D	K_3/K_1 values from	
		Experiment	Calculation (Equation 3b)
MPPCC	4.994	1.205	1.189
CPPCC	4.440	1.164	1.175
EPBCC	4.278	1.114	1.120
PPPCC	3.585	1.091	1.076

X-ray[19] and density[15] data, and taking γ from (i) our X-ray data,[19] (ii) Dalmolen *et al.* Raman scattering data[17] and (iii) Miyano's Raman scattering data.[18] The ratio K_3/K_1 calculated completely with our experimental (X-ray) data agree quite well with actual experimental K_3/K_1 values for all temperatures given in the same table, whereas, the K_3/K_1 calculated with $\bar{P}_4/\bar{P}_2$ values from Raman scattering experiments disagree with the actual experimental values near the nematic-isotropic transition temperatures. At 34°C, which is about 1°C below the transition temperature, none of the experimental K_3/K_1 values is less than 1, whereas both the calculated K_3/K_1 using Raman scattering data are less than 1 (since $\bar{P}_4$ are negative). Since experimental K_3/K_1 is always greater than one, it indicates that $\bar{P}_4$ is always positive for 5CB in agreement with our X-ray data.[19] Moreover, recent observation on 5CB by both Luminiscence and Raman

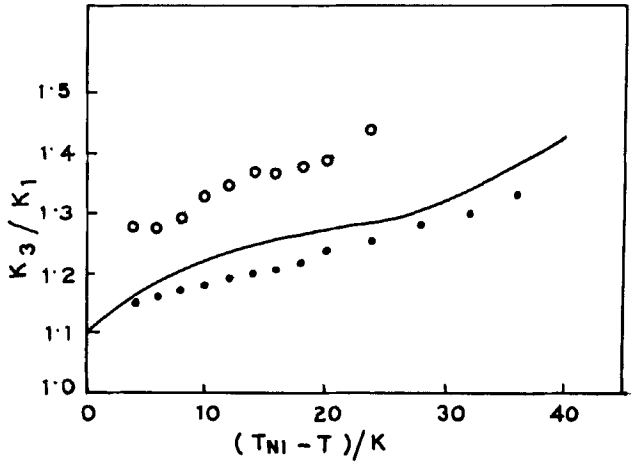


FIGURE 3 Ratio of the bend and splay elastic constant K_3/K_1 as function of relative temperature for 5OCB. ○ data from electrical measurement (Ref. 15). ● data from magnetic measurement (Ref. 15). Continuous curve correspond to the theoretical calculation of Priest [4], using our X-ray experimental data (Ref. 22).

scattering studies, show positive $\bar{P}_4$ values throughout the entire mesomorphic range.[20] It may be mentioned that recently Wilson and Allen[21] have shown from computer simulation of liquid crystal formation in semiflexible system of hard spheres, that $\bar{P}_4$ values are always positive for such system.

Lastly, we have tried to calculate the K_3/K_1 values of 4-*n*-pentyloxy cyanobiphenyl (5OCB) for different temperatures whose X-ray work[22] have been done in our laboratory. The density and experimental K_3/K_1 values from both electric and magnetic measurements of this compound have been reported by Bradshaw *et al.*[15] Our K_3/K_1 values calculated from Priest theory are in agreement with those obtained from magnetic measurement (Figure 3).

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