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Splay and Bend Elastic Constants in 7CB and 8CB

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Splay and Bend Elastic Constants in 7CB and 8CB

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Measurements of splay (K_{11}) and bend (K_{33}) elastic constants in 7CB and 8CB are reported. The method involves measurement of voltage dependence of capacitance and K_{11} is obtained directly from the Freedericksz threshold voltage. K_{33} is extracted from the nature of the $C-V$ curve by a method first suggested by Uchida and Takahashi[4]. Our results are in good quantitative agreement with the available results.

Keywords: Nematic, splay, bend, elastic constants

INTRODUCTION

Over the past decade several authors have reported the measurements of the splay and bend elastic constants, K_{11} and K_{33} respectively, in the cyano-biphenyl compounds. Notable among these are the measurements by Madhusudana and Pratibha[1] and Bradshaw *et al.*[2] (Madhusudana and Pratibha did not actually make the measurements themselves but reanalyzed the data obtained by Karat and Madhusudana[3]). These authors used either a magnetic field or an electric field to induce Freedericksz transition. The distortions were monitored either by an optical method or by measurement of capacitance. K_{33}/K_{11} and K_{11} in all cases were obtained by a multiparameter computer fit to the data for fields (electric or magnetic) exceeding the Freedericksz threshold. Bradshaw *et al.*[2] have discussed at length the relative advantages and disadvantages of using a magnetic or an electric field and we have no intention of repeating the same. The results quoted in Reference 2 where electric and magnetic fields were used in two separate sets of experiments to determine K_{11} and K_{33}, are not always in good agreement with each other. In particular, the disagreement between the values of K_{11} obtained by the two methods differ by about 7% in 7CB and 4–8% in 8CB. The corresponding differences for K_{33} are about 6–9% and 5–20% respectively. It must however be noted that the difference in the methods in Reference 2 are more profound than just that of electric and magnetic fields. One method used an electric field, capacitance and homogeneous alignment whereas the other method used a magnetic field, optical method and homeotropic alignment. The large error in K_{33} in 8CB is perhaps a consequence of poor temperature measurement by these authors. We shall compare our results with the results Bradshaw *et al.* obtained by the electric field method.

In this paper we report measurements of K_{11} and K_{33} in 7CB and 8CB as a function of temperature. A capacitance measurement method using an electric field has been used and the Freedericksz threshold voltage and hence the splay elastic constant K_{11} is measured directly. The ratio K_{33}/K_{11} and hence K_{33} is obtained by a method first suggested by Uchida and Takahashi[3] which eliminates the need for going into a multiparameter least square fit. We demonstrate in this paper that this approach provides us with a simple yet reliable method of measuring these two elastic constants.

THE PRINCIPLE OF THE METHOD

The splay elastic constant K_{11} is related to the Freedericksz threshold voltage V_{th} by the relation[5]

$$K_{11} = \varepsilon_0 \Delta\varepsilon / \pi^2 V_{th}^2 \tag{1}$$

where ε_0 = permittivity of free space and $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, the dielectric anisotropy of the sample. As described in the next section, V_{th} was extracted directly from the C–V data. The method of determination of $\Delta\varepsilon$ is elaborated below.

The exact relationship between the cell capacitance C and the voltage V applied across the cell was obtained by Gruler[6]

$$\frac{V}{V_{th}} = \frac{2}{\pi}(1+\gamma\sin^2\phi_m)^{1/2}\int_0^{\phi_m}\left[\frac{(1+\kappa\sin^2\phi)}{(1+\gamma\sin^2\phi)(\sin^2\phi_m-\sin^2\phi)}\right]^{1/2}d\phi \tag{2}$$

and

$$\frac{C}{C_\perp} = \frac{\displaystyle\int_0^{\phi_m}\left[\frac{(1+\kappa\sin^2\phi)(1+\gamma\sin^2\phi)}{(\sin^2\phi_m-\sin^2\phi)}\right]^{1/2}d\phi}{\displaystyle\int_0^{\phi_m}\left[\frac{(1+\kappa\sin^2\phi)}{(1+\gamma\sin^2\phi)(\sin^2\phi_m-\sin^2\phi)}\right]^{1/2}d\phi} \tag{3}$$

where $\kappa = K_{33}/K_{11} - 1$, $\gamma = \varepsilon_\parallel/\varepsilon_\perp - 1$, ϕ is the tilt angle made by the director with a direction parallel to the cell walls and ϕ_m is the tilt angle at the centre of the cell. These equations can be combined to yield[4]

$$\frac{C-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}(1+\gamma\sin^2\phi_m)^{1/2}\frac{V_{th}}{V}\int_0^{\sin\phi_m}\left[\frac{(1+\kappa x^2)(1-x^2)}{(1+\gamma x^2)(\sin^2\phi_m-x^2)}\right]^{1/2}dx. \tag{4}$$

When the applied voltage is much higher than the threshold voltage, the director at the centre of the cell becomes perpendicular to the cell walls and $\phi_m = \pi/2$. Then the above equation reduces to

$$\frac{C-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}(1+\gamma)^{1/2}\frac{V_{th}}{V}\int_0^1\left[\frac{(1+\kappa x^2)}{(1+\gamma x^2)}\right]^{1/2}dx \tag{5}$$

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or dividing by γ

$$\frac{C-C_\perp}{C_\parallel - C_\perp} = C_R = 1 - \frac{2}{\pi}(1+\gamma)^{1/2}\frac{V_{th}}{V}\int_0^1 \left[\frac{(1+\kappa x^2)}{(1+\gamma x^2)}\right]^{1/2} dx \tag{6}$$

where C_R may be called the reduced capacitance. $C_\parallel$ is the capacitance of the cell when the nematic is homeotropically oriented, i.e., the value of C in the limit $1/V \to 0$.

Thus Equation (5) predicts that a plot of $(C-C_\perp)/C_\perp$ against $1/V$ for $V \gg V_{th}$ should be linear and the extrapolated vlaue of the ordinate for $1/V \to 0$ should directly provide the value of $\gamma = \Delta\varepsilon/\varepsilon_\perp$. This procedure for obtaining γ was first suggested by Meyerhofer.[7] The slope of C_R vs. $1/V$ graph, for $V \gg V_{th}$ should therefore be a straight line if Equation (6) is to hold good and is given by

$$\alpha = \frac{2}{\pi}(1+\gamma)^{1/2} V_{th}\int_0^1 \left[\frac{(1+\kappa x^2)}{(1+\gamma x^2)}\right]^{1/2} dx \tag{7}$$

A linear regression performed on the C_R vs. $1/V$ data would yield α. The equation can be easily solved to yield κ and hence K_{33} if K_{11} is known.

DETAILS OF THE EXPERIMENTAL METHOD AND THE RESULTS

We used a Hewlett–Packard gain phase/impedance analyser HP 4194A and an LCR meter HP 4284A to measure the capacitance of the sample cell filled with a nematic. (The HP 4194A is an efficient device for measurement and analysis of components and circuits, featuring a wide range of frequencies—100 Hz to 40 MHz for impedance measurement. Both 4194A and 4284A employ the so called "auto balancing bridge method" to measure both the real and complex parts of the impedance simultaneously). The sample cell consisting of two *optically flat* ITO coated glass plates with a spacing of 30 microns, had brushed polyimide treatment to ensure planar orientation. The sample cells, which were of very high precision, were not fabricated in this laboratory but were obtained from Asulab Inc., Switzerland. A PID temperature controller was used to control the temperature and a stability of ± 0.1°C could be achieved. The temperature was measured with a Chromel-Alumel thermocouple along with an HP 3458A DMM. The orientation of the nematic within the cell was checked by using a Leitz polarizing microscope and all over the cell it was indeed found to be planar. The checking of the uniformity of the thickness of the cell was made by observing the cell in sodium light, and as far as we could check, there was no visible deviation from uniformity. The samples were obtained from the BDH and were used without further purification.

The probe voltages of the HP 4194A and the HP 4284A provided the aligning a.c. electric fields. In case of the former instrument this could be varied from 10 mV to 1 V r.m.s. in discrete steps of 1 mV. The HP4194A was programmed and both instruments were used in the $C_p - G$ mode. In the neighbourhood of the Freedericksz transition readings were taken at intervals of 2 mV. The longest integration time (100 msec) was used for each voltage and an average of 256 readings were taken. Each time after

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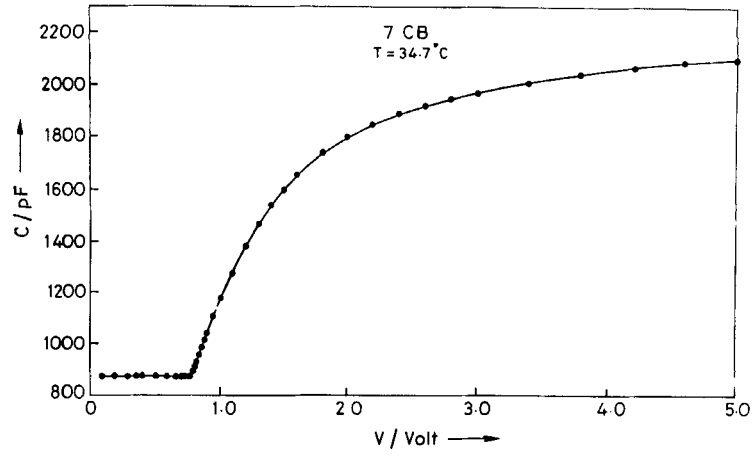

FIGURE 1 A typical appearance of capacitance-voltage curve for 7CB (at 34.7°C).

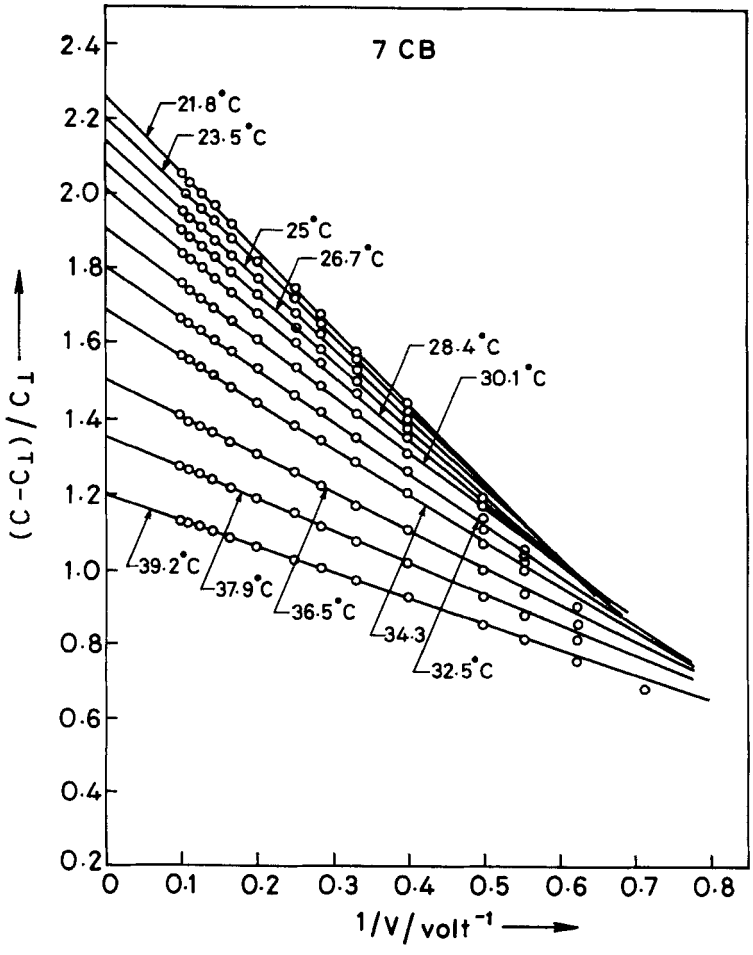

FIGURE 2 The ratio $(C - C_\perp)/C_\perp$ plotted against V^{-1} in 7CB for different temperatures and extrapolated to $V^{-1} \to 0$.

changing the voltage V, a delay of 120 seconds was allowed to enable the distortions to stabilize before any reading was taken. Fairly sharp transitions were obtained at all temperatures (Figure 1) and from the data we could directly determine the threshold voltage V_{th}. Readings were taken by approaching the transition both from above and below V_{th}. There was no evidence of any hysteresis and the uncertainty in the value of V_{th} was always found to be within ± 4 mV. Thus with the threshold voltage generally ranging from 650 mV to 800 mV the maximum uncertainty in the value of V_{th} was about

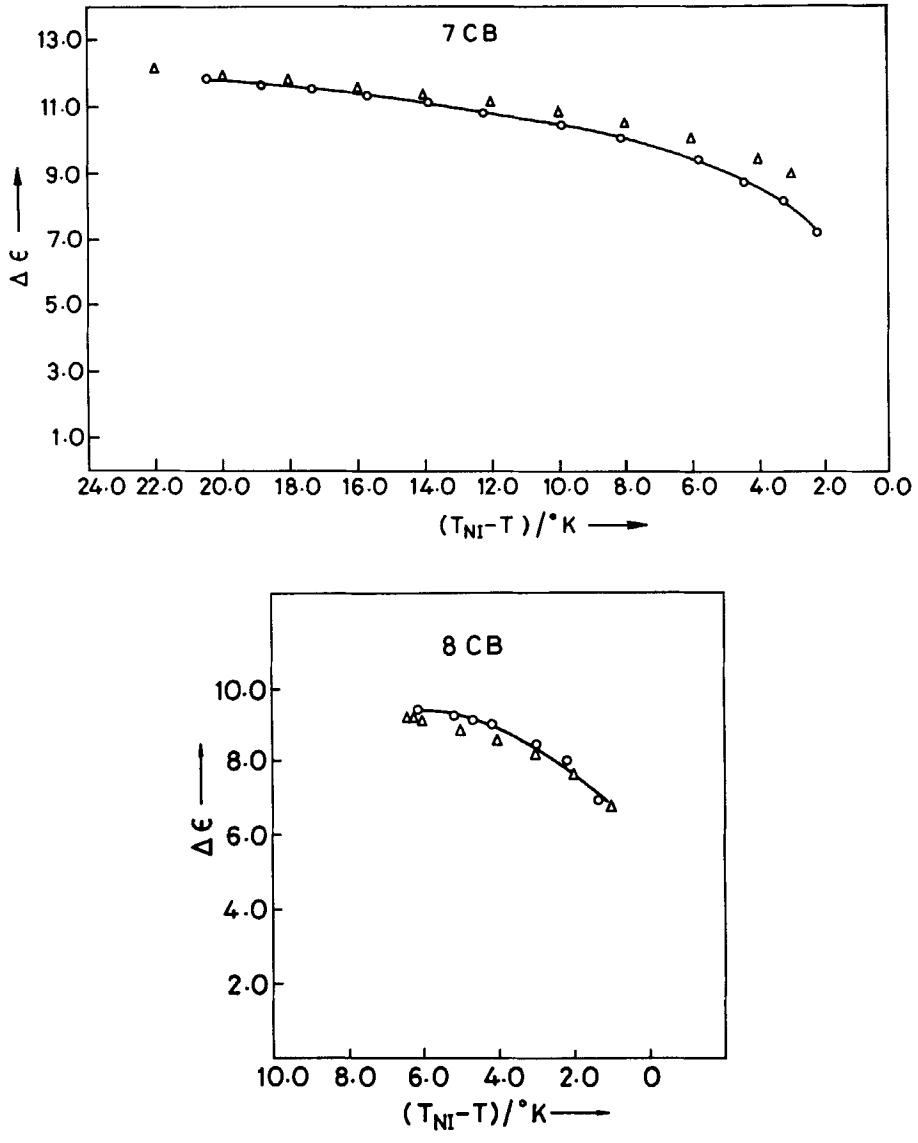

FIGURE 3 (a) and 3 (b) The dielectric anisotropy $\Delta\varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp})$ plotted against $(T_{NI} - T)$ for 7CB and 8CB. 0 → our results, Δ → results of Bradshaw *et al.*[2]

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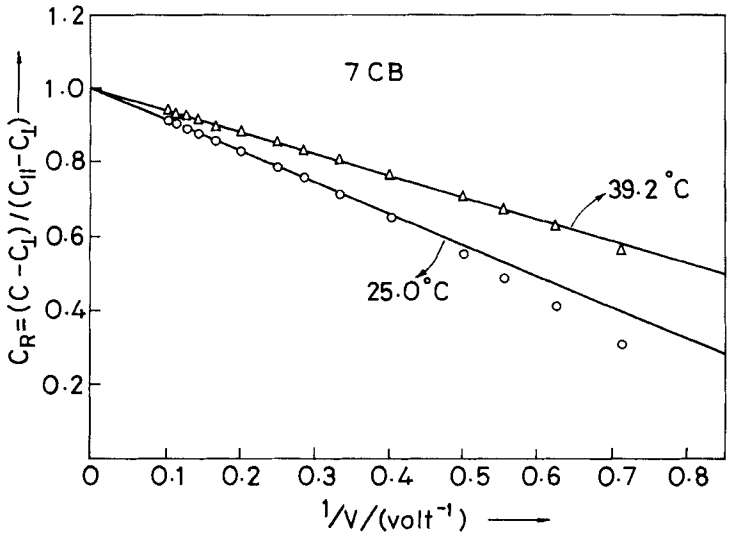

FIGURE 4 The reduced capacitance $C_R = (C - C_\perp)/(C_\parallel - C_\perp)$ plotted against V^{-1} for 7CB at two temperatures. The graphs demonstrate the linearity of the fit for $V^{-1} < 0.4$ Volt^{-1}.

0.6%. A comparison of the cell capacitance for $V < V_{th}$ with the empty cell capacitance yielded directly the dielectric constant $\varepsilon_\perp$.

For aligning voltages in excess of 1 V r.m.s. we used the HP 4284A LCR meter and readings were taken for voltages upto 10 to 20 V r.m.s. In all cases a spot frequency of 1 kHz was used.

Figure 2 shows the plot of $(C - C_\perp)/C_\perp$ vs. $1/V$ at eleven temperatures in 7CB. It is clear from these plots that for $V > 2.5$ volts $(C - C_\perp)/C_\perp$ is essentially a linear function of $1/V$. It is worth pointing out in this connection that if Equation (2) is solved for ϕ_m as a function of V/V_{th} with approximate input values of γ and κ, one obtains $\phi_m = \pi/2$ for $V/V_{th} > 5$. The intercepts on the y-axis were obtained from a linear regression analysis of these data and $\gamma = \Delta\varepsilon/\varepsilon_\perp$ was thus directly obtained. The dielectric anisotropy $\Delta\varepsilon$ thus obtained are plotted as a function of $(T_{NI} - T)$ for 7CB and 8CB in Figure (3a) and (3b) respectively and a comparison is made with the results obtained by Bradshaw *et al.* [2].

Figure 4 shows a plot of $C_R = (C - C_\perp)/(C_\parallel - C_\perp)$ vs. $1/V$ for two temperatures in 7CB and as expected the linearity is very good for $V > 2.5$ Volts. K_{11} is determined as a function of temperature using Equation (1) and the results for 7CB and 8CB are plotted in Figure 5 and Figure 6 respectively. Comparison is again made with the results obtained by Madhusudana and Pratibha[1] and Bradshaw *et al.*[2] (electric field method). It is apparent that in the case of 7CB our K_{11}, while differing with that in Reference 2 by 12–16%, agrees fairly well with that in Reference 1. It is believed that rubbed polyimide normally produces a surface pretilt of about 1^0 which lowers the value of K_{11} by about 5%. It seems that brushed polyimide behaves in a similar way and this may partly explain the disagreement of our results for K_{11} in 7CB with those of Reference 2. In case of 8CB, the agreement with both references in good and no systematic deviation resulting from the lowering of threshold voltage (due to brushed polyimide coating), if any, is seen. In particular, our results in 8CB are closer to those of

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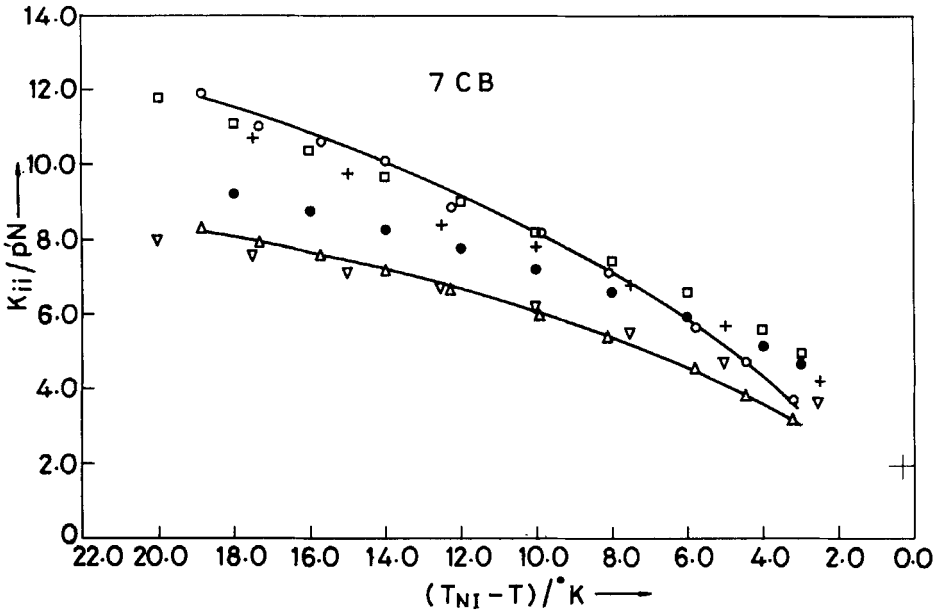

FIGURE 5 K_{11} and K_{33} for 7CB plotted against $(T_{NI} - T)$. For K_{11}: Δ, our results, ∇, Reference 1, ●, Reference 2. For K_{33}: ○, our results, + – Reference 1, □, Reference 2. Our $T_{NI} = 42.4°C$.

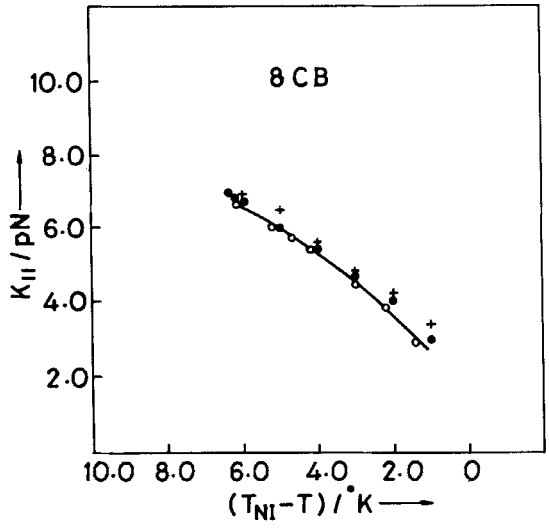

FIGURE 6 Temperature dependence of K_{11} for 8CB. Our results (○) are compared with those of Reference 1 (+) and Reference 2 (●). Our $T_{NI} = 39.2°C$.

Bradshaw *et al.* while the results obtained by Madhusudana and Pratibha are on the slightly higher side.

The slope α of the $(C_R - 1/V)$ graphs for different temperatures were obtained by a linear regression. Equation (7) was then solved for $\kappa = K_{33}/K_{11}$. In Figure 7a and 7b

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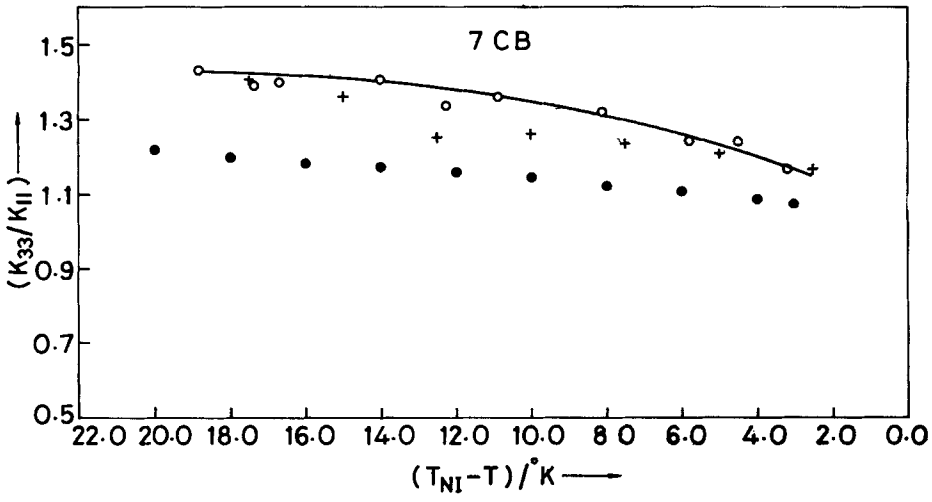

FIGURE 7(a) Temperature dependence of K_{33}/K_{11} for 7CB. Our results (○) are compared with those of Reference 1 (+) and Reference 2 (●).

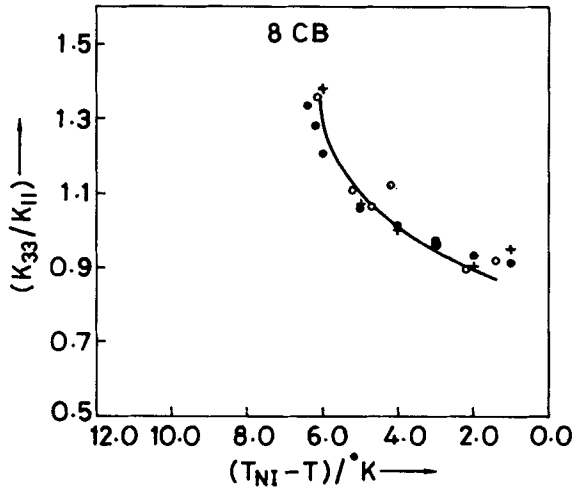

FIGURE 7(b) Temperature dependence of K_{33}/K_{11} for 8CB. Our results (○) are compared with those of Reference 1 (+) and Reference 2 (●).

we have plotted the values of κ against $(T_{NI} - T)$ for 7CB and 8CB respectively and comparison is made with results of References 1 and 2. It is clear from Figure 7a that in case of 7CB our κ is considerably higher than those reported in both references for which the surface pretilt presumably is to be blamed. On the other hand, κ for 8CB agrees fairly well with results of both references except perhaps very close to T_{NI}. K_{33} (obtained from the values of K_{11} and κ) for 7CB are also depicted in Figure 5 while that for 8CB are plotted in Figure 8. As is clear from the diagrams, the values of K_{33} in 7CB are in fairly good agreement with both these works and the difference is only about

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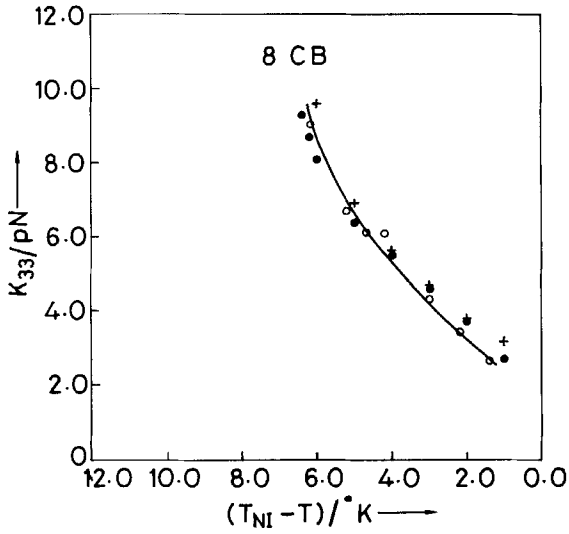

FIGURE 8 Temperature dependence of K_{33} for 8CB. Our results (○) are compared with those of Reference 1 (+) and Reference 2 (●).

5% except at points close to T_{NI}. In case of 8CB, our results are once again in good agreement with the results of the References 1, 2 with no systematic deviation anywhere. We trust our results for K_{11} to be accurate to within 4% and K_{33} to within 5%. Bradshaw *et al.*[2] have reported that in the capacitance measurement method using an electric field, application of a high voltage sometimes introduced defects which were slow to disappear subsequently. These authors therefore had to be cautious for taking measurements for $V > 2V_{th}$. We would like to emphasize that nowhere in the course of our experiments did we notice any such effect. The difficulty encountered by Bradshaw *et al.*[2] at high voltages is probably attributable to the zero pretilt SiO_x alignment used by them.

CONCLUSION

We have therefore illustrated that by using the method suggested by Uchida and Takahashi,[4] it is possible to extract the bend elastic constant K_{33} fairly easily and accurately provided of course one knows K_{11} with a good degree of accuracy. We are aware of the fact that Equation 7 is not particularly sensitive to K_{33}/K_{11}; typically an error of 1% in α leads to an error of about 10% in K_{33}/K_{11}. The linear regression performed on the $C_R - 1/V$ data, however, always exhibited a very high degree of goodness of fit and we estimate that the error in α in any case is at most 0.3%. We believe that if one is able to measure V_{th} with the same degree of precision as we have able to do, there is no need to enter into a multiparameter least square programme. The accuracy of our measurement of V_{th} is attributed to the high quality of the sample cells (which led to the sharp and reproducible threshold voltages) and the precision of the HP4194A impedance analyser which was used to monitor the transitions.

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