The Elastic Constants of Nematic *n*-Hexylcyanobiphenyl Determined with the Capacitance Method

G. Czechowski, S. Czerkas[a], and J. Jadżyn
Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17, 60-179 Poznań, Poland
[a] Universität Bielefeld, Fakultät für Physik D2, Universitätstr. 25, 33501 Bielefeld, Germany
Reprint requests to Prof. J. J.; Fax: (61) 86-84-524; E-mail: jadzyn@ifmpan.poznan.pl

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The splay (K_{11}) and bend (K_{33}) elastic constants of *n*-hexylcyanobiphenyl (C_6H_{13}-Ph-Ph-C≡N) were determined from the voltage (U) dependence of the capacitance (C) of the planar nematic cell with a small molecular pretilt angle. The capacitance changes are due to distortion of the director **n** driven by the applied electric field. K_{11} was obtained from the Freedericksz threshold voltage (U_{th}) and K_{33} from the $C(U)$ dependence above the threshold voltage by means of the method proposed by Gruler et al. and Uchida et al. The significance of the pretilt angle in the determination of K_{33} is discussed.

Key words: Elastic Constants; Nematic; *n*-Hexylcyanobiphenyl; Pretilt Angle.

1. Introduction

Nematic liquid crystals have peculiar elastic properties, their understanding being an intriguing problem of basic research [1, 2]. The determination of their elastic constants is based on measurements of the distortion of the director **n** caused by an external electric or magnetic field. In principle, the elastic constants corresponding to the three basic distortions of the nematics: splay (K_{11}), twist (K_{22}) and bend (K_{33}), can be obtained from three independent experiments. In two of them, the electric field induces the director distortion in a planar (K_{11}) or twisted planar (K_{22}) cell, and in the third experiment a magnetic field causes the distortion in the homeotropic cell (K_{33}). In case of a strong anchoring of the nematic molecules at the cell surfaces, the distortions have a threshold character (Freedericksz transition). Then, the elastic constants K_{ii} ($i = 1, 2, 3$) can be calculated on the basis of the threshold value of the voltage (U_{th}) or magnetic field (B_{th}), provided the dielectric or magnetic anisotropy of the studied liquid crystal is known. Reliable determination of the elastic constants is not a simple task, and papers reporting the three elastic constants of a given nematic liquid crystal are rare.

Most papers on the elasticity of nematics concern the splay and bend constants only, since these constants govern such switching characteristics as the threshold voltage or the response time. Many experimental methods were elaborated for the determination of K_{11} and K_{33}. Most of them are based on optical or capacitate observations of the director distortion in a pre-oriented nematic cell [3 - 7].

In this paper we present the results of K_{11} and K_{33} measurements preformed for the nematic *n*-hexylcyanobiphenyl (6CB) by means of the capacitance method. The method consists in the analysis of the voltage dependence of the capacity of the planar nematic cell. In case of nematic liquid crystals with a positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp} > 0$ where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are permittivity measured, respectively, parallel and perpendicular to the macroscopic molecular ordering (the director **n**), the probing electric field **E** of a sufficient intensity causes a distortion of the director (Fig. 1). With increasing field intensity, the capacity of the cell increases from the initial value $C_{\perp}$, corresponding to $\mathbf{n} \perp \mathbf{E}$, to the final value $C_{\|}$, corresponding to $\mathbf{n} \parallel \mathbf{E}$. As mentioned above, the phenomenon has a threshold, i. e. the capacity does not depend on the voltage before the voltage reaches a characteristic value U_{th}. This value is the basic quantity for the calculation of the splay elastic constant:

$$K_{11} = \varepsilon_0 \Delta\varepsilon U_{\text{th}}^2 / \pi^2, \qquad (1)$$

where $\varepsilon_0 = 8.85$ pF/m.

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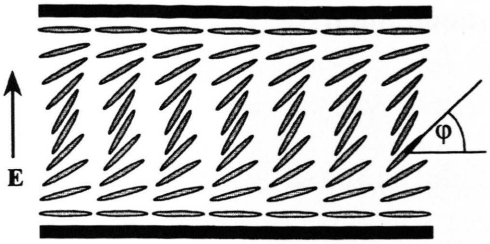

Fig. 1. Distortion of the director **n** in a planar nematic cell caused by voltages higher than the Freedericksz threshold value U_{th}.

The elastic constant K_{33} can be determined in the same experiment from the dependence of the cell capacitance on the voltage *above the threshold value.* The exact equation describing the $C(U)$ dependence was first obtained by Gruler, Scheffer, and Meier [8]. Next, Uchida and Takahashi [9] proposed a procedure for the K_{33} determination which eliminates the need of a multiparameter least squares fitting of the Gruler et al. equation to the experimental data. The final equation for the $C(U)$ dependence has the form [10, 11]

$$\frac{C(U)-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}\frac{U_{\text{th}}}{U}\left(1+\gamma\sin^2\varphi_{\text{m}}\right)^{1/2} \cdot \int_0^{\varphi_{\text{m}}}\left[\frac{(1+\chi\sin^2\varphi)(1-\sin^2\varphi)}{(1+\gamma\sin^2\varphi)(\sin^2\varphi_{\text{m}}-\sin^2\varphi)}\right]^{1/2}\cos\varphi \mathrm{d}\varphi, \tag{2}$$

where $\chi = -1 + K_{33}/K_{11}$, $\gamma = -1 + \varepsilon_\parallel/\varepsilon_\perp$, φ is the tilt angle between the director **n** and the cell walls and φ_{m} is the tilt angle at the center of the cell.

For voltages much higher than the threshold value, the director at the center of the cell becomes perpendicular to the cell walls and $\varphi_{\text{m}} = \pi/2$. Then (2) reduces to

$$\frac{C(U)-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}\frac{U_{\text{th}}}{U}(1+\gamma)^{1/2} \cdot \int_0^{\pi/2}\left(\frac{1+\chi\sin^2\varphi}{1+\gamma\sin^2\varphi}\right)^{1/2}\cos\varphi \mathrm{d}\varphi. \tag{3}$$

This equation predicts that for $U \gg U_{\text{th}}$ the dependence $(C(U) - C_\perp)/C_\perp$ on U^{-1} should be linear. The extrapolation of the dependence to $U^{-1} = 0$ leads directly to the value of $\gamma = \Delta\varepsilon/\varepsilon_\perp$, and the slope

$$\alpha = \frac{2\gamma}{\pi}(1+\gamma)^{1/2}U_{\text{th}}\int_0^{\pi/2}\left(\frac{1+\chi\sin^2\varphi}{1+\gamma\sin^2\varphi}\right)^{1/2}\cos\varphi \mathrm{d}\varphi \tag{4}$$

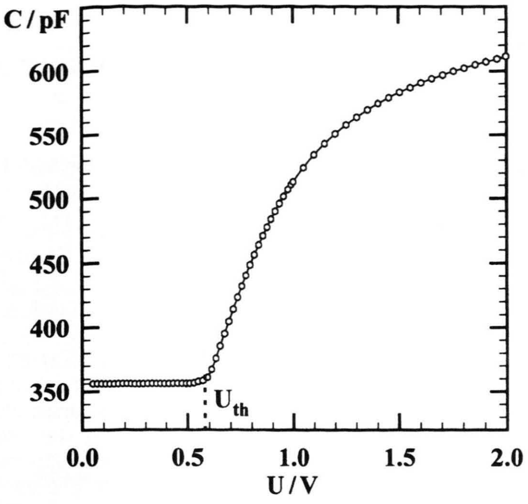

Fig. 2. The Freedericksz transition in the planar cell of the nematic 6CB at 22.5 °C.

contains only one unknown quantity: $\chi = -1 + K_{33}/K_{11}$. So, the K_{33} can be easily obtained since the constant K_{11} is known from (1).

2. Experimental

6CB (C_6H_{13}-Ph-Ph-C≡N) was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. Its isotropic to nematic phase transition occured at 29 °C. It was placed in the LINKAM cell consisting of two flat ITO coated glass plates with a spacing of 5 μm. Due to brushed polyimide treatment of the electrode surfaces, the nematic molecules were oriented planar to the electrodes. A sinusoidal voltage of the HP 4284A Precision LCR-meter up to 20 V_{rms}, at 1 kHz was applied to the probe, and the cell capacitance as a function of the applied voltage was recorded. The voltage step was 20 mV in the vicinity of the Freedericksz transition and 200 mV at the higher voltage. Figure 2 presents a typical low-voltage dependence $C(U)$ for 6CB at 22.5 °C.

3. Results and Discussion

The measured dependence of C on U for a planar 6CB nematic cell in the whole range of the applied voltages is depicted in Figure 3. In this range of U, the capacity of the cell changes from $C_\perp$ (for $U < U_{\text{th}}$) to close to $C_\parallel$ (for $U \gg U_{\text{th}}$).

Figure 4 presents the temperature dependence of the voltage threshold value U_{th} for the Freedericksz

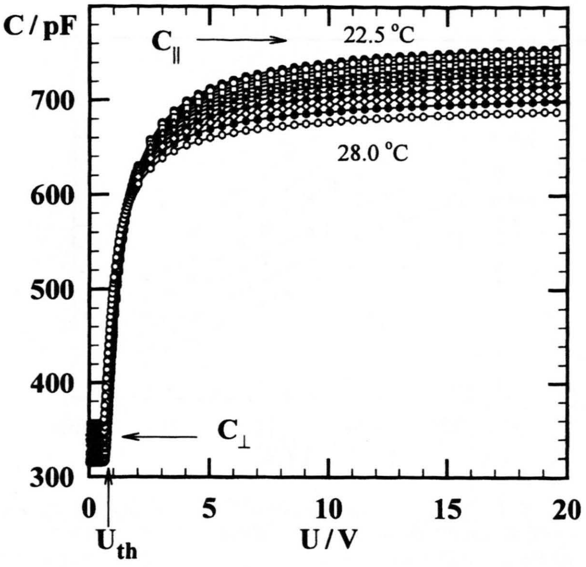

Fig. 3. Voltage dependence of the capacitance of the planar 6CB nematic cell at different temperatures (step 0.5 °C).

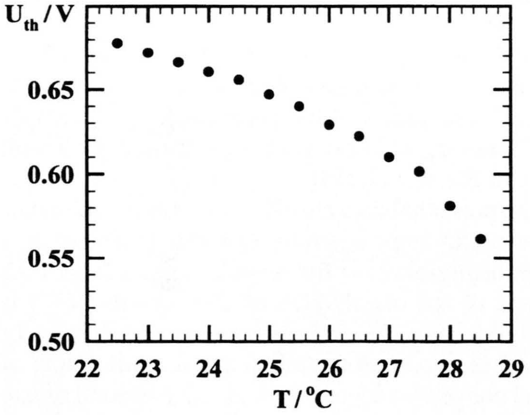

Fig. 4. Temperature dependence of the threshold voltage for the Freedericksz transition in the planar 6CB nematic cell.

transition in the 6CB planar cell, and Fig. 5 shows the dependence for the splay elastic constant K_{11} calculated from (1). The values of the dielectric anisotropy $\Delta\varepsilon$ of 6CB were taken from [12]. As seen in Fig. 5, the values obtained for K_{11} elastic constant agree very well with the results of Bradshaw et al. [13].

The distortion of the director **n** caused by voltages higher than the Freedericksz threshold value leads to an increase of the capacity of the planar nematic cell. According to (3), the theory predicts that for the voltages much higher than U_{th} the change of the cell capacity should be proportional to the reciprocal

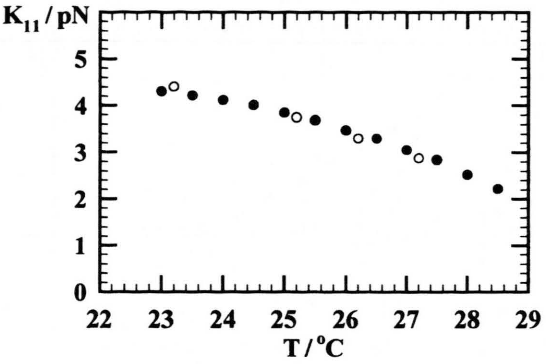

Fig. 5. Temperature dependence of the splay elastic constant of 6CB. The open points denote the results of Bradshaw et al. [13].

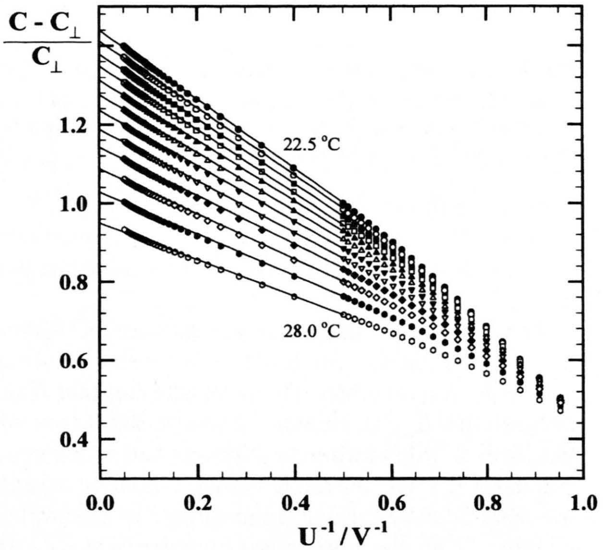

Fig. 6. Dependence of $(C - C_\perp)/C_\perp$ on U^{-1} for nematic 6CB at different temperatures (step 0.5 °C).

of U. The results presented in Fig. 6 show that this prediction is well fulfilled: for U higher than about 4 V the dependence $C(U^{-1})$ is linear with exception of the temperature region close to the nematic to isotropic transition where small deviations from linearity are observed.

The extrapolation of the linear dependences in Fig. 6 to $U^{-1} = 0$ leads to the value of $(C_\parallel - C_\perp)/C_\perp$, i. e. to $(\varepsilon_\parallel - \varepsilon_\perp)/\varepsilon_\perp$, the quantity which can be directly determined for example by the static dielectric measurements of the nematic sample oriented with a magnetic field. In Fig. 7 the values of $(\varepsilon_\parallel - \varepsilon_\perp)/\varepsilon_\perp$ obtained from the extrapolation are compared with those

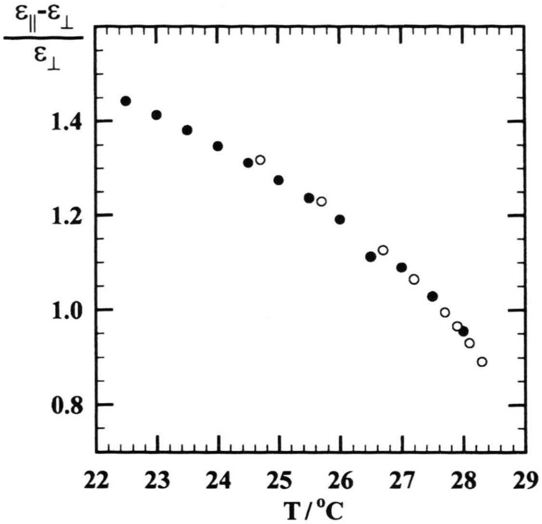

Fig. 7. Temperature dependence of $(\varepsilon_{\parallel} - \varepsilon_{\perp})/\varepsilon_{\perp}$ for 6CB determined by the extrapolation of $(C - C_{\perp})/C_{\perp}$ to U^{-1} (see (3) and Fig. 6) (full points), and measured on a sample oriented with a magnetic field (open points) [12].

obtained in direct dielectric measurements [12]. The perfect agreement of these two results is a good test for consistency of the experimental procedure and the theory.

The slope α of the linear dependence of $\frac{C-C_{\perp}}{C_{\perp}}$ on U^{-1}, as shows (4), leads to the value of $\chi = -1 + K_{33}/K_{11}$, and hence to the elastic constant K_{33}, because the K_{11} is known. However, the theory of Gruler et al. [8] is formulated for an ideal planar cell, where for $U < U_{\text{th}}$ the angle between the long axis of the nematic molecules and the surface of electrodes is zero. Then, the integration boundaries in (2 - 4) extend from zero to $\pi/2$. Still, a small pretilt angle of few degrees is always possible even for perfectly prepared surfaces, and this fact we take into account in the discussion of the experimental results. From a formal point of view, the consideration of the pretilt angle φ_0 consists in a change of the lower boundary of the integration in (2 - 4), as suggested by Zhou and Sato [11].

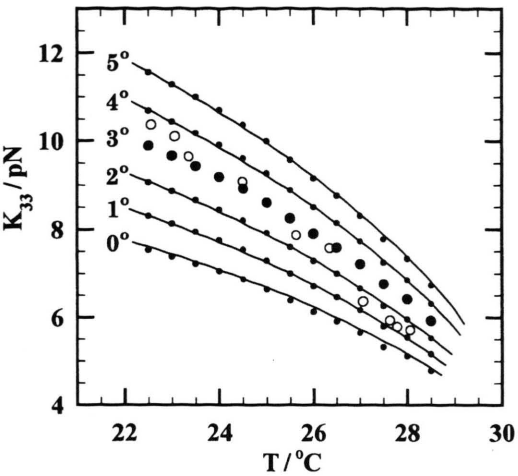

Fig. 8. Temperature dependence of the bend elastic constant of 6CB calculated with (4) for different values of the pretilt angle φ_0 (full circles). For $\varphi_0 \approx 3°$ the results are close to the Karat et al. results (open circles) [14].

Figure 8 presents the temperature dependences of the bend elastic constant of 6CB calculated with (4) for different values of the pretilt angle φ_0 (from 0° to 5°). For $\varphi_0 \approx 3°$ our results agree quite well with those of Karat et al. [14].

The presented data clearly show that the influence of the pretilt angle φ_0 on the calculated value of K_{33} is not negligible even for so small φ_0, for which the change of the initial value of the capacity $(C_{\perp})$ is negligible (Fig. 7). From the experimental point of view it is important to realize that a pretilt angle of about one or two degrees is in practice beyond of any control and detection, so the results presented in Fig. 8 show that the agreement of about 10% in the values of K_{33} determined in two independent experiments should be considered as quite satisfactory.

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