Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 16 Nov 2012.

To cite this article: A. Zawadzki & H. G. Walton (2012): Measurements of the Splay and Bend Elastic Constants of 4′-Butyl-4-heptyl-bicyclohexyl-4- carbononitrile, CCN47, Molecular Crystals and Liquid Crystals, 569:1, 10-14

To link to this article: http://dx.doi.org/10.1080/15421406.2012.691070

Mol. Cryst. Liq. Cryst., Vol. 569: pp. 10–14, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.691070

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Measurements of the Splay and Bend Elastic Constants of 4′-Butyl-4-heptyl-bicyclohexyl-4-carbononitrile, CCN47

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We report measurements of the splay and bend elastic constants of 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47). We find K11 to be largely constant across the nematic range, with a value of ∼10 pN. K33 has a slightly lower value with K33/K11 ∼ 0.9 pN far from the transition to the SmA. In the vicinity of the SmA phase, K33 diverges with critical exponent $\gamma = -0.6$, with K33/K11 exceeding 5 close to the transition.

Keywords Bend; elastic constant measurement; nematic liquid crystal; splay

1. Introduction

Accurate values for the elastic constants of nematic liquid crystals are of considerable practical important as these parameters allow for the accurate prediction of a range of static continuum properties [1]. The liquid crystalline material 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47) offers several features useful for experimental studies including a large, negative, dielectric permittivity ($\Delta\varepsilon \sim -6$ at 35°C), a nematic phase just above room temperature, and a phase transition to a smectic A phase below this. Several investigators have reported novel or unusual phenomena associated with this material including observations of the electric field phase diagram [2], the quenching of nematic order in aerosil dispersions [3], the electro-optics of CCN47 molecules bonded to palladium nanoparticles [4], and novel surface anchoring effects in the smectic phase [5]. Recently, Dhara et al. [6] have reported a pronounced, temperature driven, homeotropic-to-planar, bistable anchoring transition for CCN47 on perfluoropolymer surfaces and described some device applications of this effect. With these reports in mind, we hope it may be useful to put accurate elastic constant data for CCN47 into the literature.

Dhara and Madhusudana [7] have previously reported permittivity data for CCN47 and provided some measurements of the bend elastic constant K33, acquired using an optical technique. We note what appears to be a typo on the axis labels of their paper, with K33 values seemingly divided by a factor of 10 (alongside the factor of 10 discrepancy with the measurements in this paper, the authors replot the K33 values from Schad and Osman [8] for a second compound—CCH7—on their same graph, again with a factor of 10 discrepancy).

This work is has not been published elsewhere and has not been submitted simultaneously for publication elsewhere.

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We are not aware that the values of the splay constant, K11, have been previously reported for CCN47. In addition, we provide more a detailed analysis of the divergence of K33 in the vicinity of the transition to the smectic A (SmA) phase. We determine elastic constants to an accuracy of order 5% via a capacitance-measurement technique [9,10]. For much of the nematic range, we find the splay constant is marginally larger than bend (K11 ∼10 pN and K33/K11 ∼0.9). In the vicinity of the transition to the SmA phase, we observe a pronounced divergence of K33, with the K33/K11 ratio diverging strongly.

2. Results and Discussion

The chemical structure of CCN47 (supplied by Merck, Southampton, UK) is shown in Fig. 1. The phase transition temperatures are: Cr 28 SmA.30.6 N 59.7 I.

The bend elastic constant, K33, of a negative dielectric anisotropy material can be determined from a measurement of the Freédericksz threshold voltage, V_c, in an untwisted, homeotropically aligned cell using

$$V_c = \pi \left(\frac{K_{33}}{\varepsilon_0 \Delta\varepsilon} \right)^{1/2}, \tag{1}$$

where ε_0 is the permittivity of free space and $\Delta\varepsilon = (\varepsilon_\perp - \varepsilon_{//})$ is the dielectric anisotropy of the nematic.

The splay elastic constant K11 can be determined from the behavior of a cell's capacitance at voltages above the threshold. At these higher voltages, the liquid crystal director tilt, θ, varies with position through the cell, from $\theta = 0$ (here defined as homeotropic) at the cell surfaces to a maximum tilt, θ_m, at the cell center. The tilt at any particular position is dictated by the applied voltage, V, the elastic constant anisotropy $\kappa = \text{K11/K33}$, and the normalized dielectric anisotropy $\gamma = (\varepsilon_\perp - \varepsilon_{//})/\varepsilon_\perp$ of the material. A knowledge of tilt at every position basically amounts to a knowledge of the local permittivity at that position, and so appropriately integrating the tilt across the cell yields a value for the total cell capacitance, C. Following through the details of this procedure [11] results in two coupled equations for C and V. Here, C_0 is the empty cell capacitance.

$$\frac{C_0}{C} = \frac{\int_0^{\theta_m} \left[\frac{[1+\kappa \sin\sin^2\theta]}{(1+\gamma \sin^2\theta)(\sin^2\theta_m - \sin^2\theta)} \right]^{1/2} d\theta}{\int_0^{\theta_m} \left[\frac{(1+\gamma \sin^2\theta)(1+\kappa \sin^2\theta)}{\sin^2\theta_m - \sin^2\theta} \right]^{1/2} d\theta}, \tag{2}$$

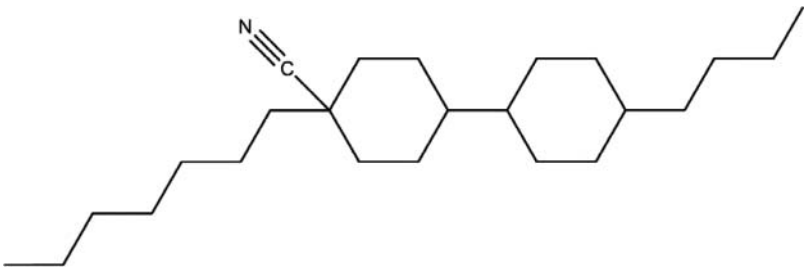

Figure 1. Chemical structure of 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47).

$$\frac{V}{V_c} = \frac{2}{\pi}\left(1+\gamma\sin^2\theta_m\right)^{1/2}\int_0^{\theta_m}\left[\frac{\left[1+\kappa\sin\sin^2\theta\right]}{\left(1+\gamma\sin^2\theta\right)\left(\sin^2\theta_m-\sin^2\theta\right)}\right]^{1/2}d\theta. \qquad (3)$$

Equations (2) and (3) suffice to determine the capacitance versus voltage behavior of an (untwisted) liquid crystal cell once the elastic constant anisotropy (κ), normalized dielectric anisotropy (γ), and threshold voltage (V_c) are fixed. Equivalently, measurements of the *C-V* curve provide information on κ, γ, V_c through Equations (2) and (3).

To achieve accurate measurements of capacitance in our work, sample cells were constructed from indium tin oxide (ITO)-coated glass, spaced 25 μ apart using hard-tempered aluminum foil (Goodfellow, Cambridge). Homeotropic alignment was achieved by spin coating the alignment layer JALS2017 (JSR, Japan). Close to V_c, capacitance values were recorded at 10 mV increments, allowing approximately 1 hour for the cell to equilibrate between each voltage increment. Errors due to fringing fields at cell edges were minimized by patterning the ITO electrodes with a guard ring structure. Electrical measurements were carried out at 4 kHz using an Agilent E4980A LCR meter. Sample temperatures were controlled to an accuracy of 0.1°C using a purpose built heating stage. Typical empty cell capacitances were of order 25 pF. Any variation of empty cell capacitance with temperature was recorded. Typical variation was less than 2 fF $^{\circ}C^{-1}$.

Figure 2 shows typical measured data for our CCN47 samples. Measured capacitance values have been normalized by the empty cell capacitance and plotted as relative permittivity on the *y*-axis.

Measured capacitance data were fitted numerically to Equations (2) and (3) using routines written in MATLAB, treating γ, κ, and V_c as fitting parameters. In brief, the method consists of taking starting guesses for γ, κ, and V_c, together with measured capacitance values C_m taken at measurement voltages, V_m. Substitution of γ, κ, V_c, and C_m into Equation (1) yields a value for $\mathrm{Sin}^2\,\theta_m$. Substituting this into Equation (2) then yields a calculated voltage, V_n. The values of γ, κ, and V_c are varied iteratively until a best fit is secured between V_m and V_n. The line fit in Fig. 2 is a typical example of a final fit. Figure 3 shows the residuals for the fit in Fig. 2. Typically, residuals in our measurements were 0.5 mV or better.

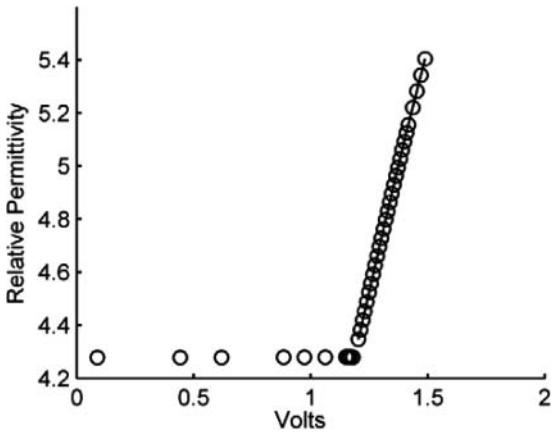

Figure 2. Measured values of relative permittivity of CCN47 versus voltage at $(T_{NI} - T) = 16.4$°C with curve fitted using equations (2) and (3) as described in main text.

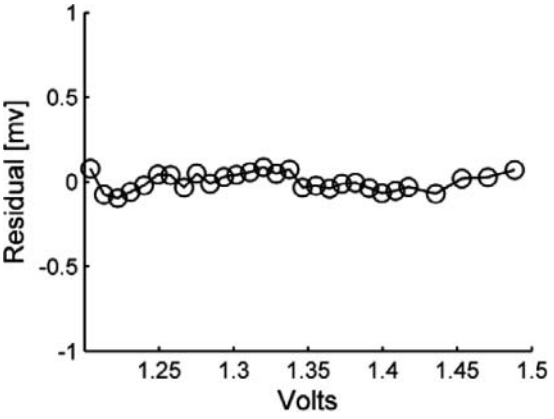

Figure 3. Residuals for curve fit in Fig. 2.

Figure 4 shows the measured values of the splay and bend elastic constants of CNN47. Far from the smectic transition, we observe a K11 slightly above K33 (K11/K33 ∼0.9). Close to the SmA a strong divergence of K33 is observed. Such a divergence is due to the presence of pretransitional smectic order, since the layered structure of smectics expels bend (and twist) [12]. No such effect is seen for the splay elastic constant.

De Gennes has suggested [13] that the divergence of K33 is of the form

$$K33 = K33^{(0)} + At^{\gamma},$$

where t is reduced temperature $(T_{\mathrm{SmA}} - T)/T$, A is a constant, and γ is a critical exponent. $K33^{(0)}$ is the "bare," purely nematic, value of the bend constant and the At^{γ} term corresponds to the extra stiffness imparted by the presence of pretransitional smectic layering. Based on an analogy with superconductors, De Gennes suggested γ should have the universal value –0.66. The precise determination of γ is a delicate matter [14] in part requiring

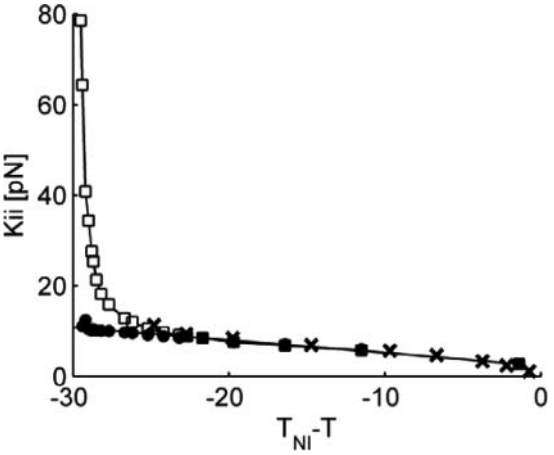

Figure 4. Measured values of K11 (•) and K33 (□) of 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile. K33 values of reference [7] have been multiplied by 10 (see explanation in main text) and replotted (x). Curves are guides for the eye.

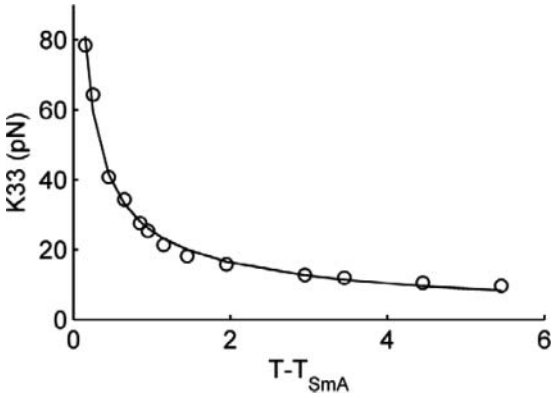

Figure 5. K33 values in the vicinity of the transition to smectic A and theoretical fit with critical exponent $\gamma = -0.6$.

precision measurements of transition temperatures. In our experiments we were limited to a temperature resolution of 0.1°C and could not determine K33 extremely close to the SmA. Nevertheless, as shown in Fig. 5, we achieve a good fit to the data with $\gamma = -0.6$.

3. Conclusion

We have applied the technique of numerically fitting measured capacitance-voltage data to extract elastic constants for the material CCN47. We achieve a measurement accuracy of approximately 5% on measured values of K11 and K33. We find K11 to be largely constant across the nematic range, with a value of ∼10 pN. K33 has a slightly lower value (K33/K11 ∼ 0.9 pN) far from the transition to the SmA. In the vicinity of the SmA, K33 diverges with critical exponent $\gamma = -0.6$, with K33/K11 exceeding 5 close to the transition.

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