Bend and splay elastic constants of diheptylazoxybenzene

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In this study we report the values of the bend (K_3) and splay (K_1) elastic constants of the nematic liquid crystal diheptylazoxybenzene, using a Fréedericksz-transition technique. Both the bend and the splay constants were measured over a range of temperatures approaching the nematic–smectic-A (NA) transition. The ratios of K_3/K_1 follow the trend of increasing towards the NA transition, which makes the conditions favorable, in the homeotropic geometry, for striped instabilities to set in. The value of K_3/K_1 for our material is fairly small at higher temperatures when compared to similar materials, which is consistent with the decreasing of K_3/K_1 with an increasing alkyl-chain length. The bend critical exponent ρ_3 was determined to be 0.68 ± 0.04, which is in close agreement with a prediction of de Gennes [Solid State Commun. **10**, 753 (1972)]. The effect of the nematic range on this critical exponent is examined in terms of a critical-multicritical crossover.

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INTRODUCTION

There have been numerous theoretical and experimental projects done in recent years to understand the critical behavior of the nematic–smectic-A (NA) transition [1]. In spite of these efforts, there is not yet a theoretical or experimental consensus about the universality class of these transitions. Based on the Ginsburg-Landau model, de Gennes predicted that the NA transition is in the same universality class as the three-dimensional XY (3D-XY) model. The 3D-XY model developed by de Gennes [2], Dasgupta and Halperin [3], and Helfrich [4] predicts the bend exponent ($\rho_3 = \nu_\parallel$) to have a value of 0.67. In a review of the NA transition, Lubensky [1] proposed two possibilities for a 3D system with finite splay elasticity, and isotropic critical point (same universality class as type II superconductors) describable by an inverted XY model with the critical exponents for the correlation length $\nu_\parallel = \nu_\perp = 0.67$, or an anisotropic critical point whose universality class is not yet known and its critical exponents not yet predicted other than that $\nu_\parallel = 2\nu_\perp$. Mean-field theories predict an isotropic divergence of the correlation length with the two exponents $\nu_\parallel = \nu_\perp = 0.5$. In spite of extensive experimental studies, there is still a controversy about the exact nature of the critical exponents associated with this transition.

Although de Gennes's continuum model of the liquid crystals seems to qualitatively predict the behavior of the elastic constants through the NA phase transition, the interpretation of the elastic constants in terms of molecular theories still remains an outstanding problem in this field. McMillan [5] and Kobayashi [6] independently predicted the existence of a tricritical point and suggested, based on mean-field models, that the nature of NA transition depends on the nematic range of the material. Among the molecular statistical treatment of NA transition, both the Meyer-Lubensky model (ML) and the Kobayashi-McMillan model (KM) predict a tricritical point, where the NA transition changes its nature from first order to a second-order transition. This is either due to the coupling between the two translational order parameters in the smectic phase (ML) or that between a translational order parameter and the nematic orientational order parameter (KM). Experimentally, tricritical points have been shown to exist, but the actual ratio of T_{NA}/T_{NI} (where T_{NA} and T_{NI} are the nematic–smectic-A and the nematic-isotropic transition temperatures, respectively) at which these occur are higher than that predicted by mean-field theoretical models [7–9]. The interpretations of the KM model, for example, predict the occurrence of a tricritical point at the reduced transition temperature, $t_{NA-NI} = T_{NA}/T_{NI} = 0.88$, which is very different from the experimentally observed cases. The nCB series have been found to have a tricritical point at $t_{NA-NI} = 0.99$ [10], whereas a mixture of C_7 and C_8, with a mole fraction of C_8 equal to 0.464 was found to have a tricritical point at $t_{NA-NI} = 0.976$ [10]. For this case, the birefringence was measured as a function of temperature for mixtures of C_7 and C_8 with different concentrations and these results seem to verify a coupling of the kind described by the KM model [10]. The occurrence of the tricritical point very close to the nematic-isotropic transition does support the coupling between a smectic order parameter and the nematic order parameter, S, which varies strongly in the region close to the NI transition [11].

It has also been suggested [12,13] that measurements of ρ_2, ρ_3, and other exponents on materials with different spans of t_{NA-NI} are essential. Although the effect of decreasing nematic range has been demonstrated for the specific-heat exponent α [7,8], the susceptibility exponent γ [9], and the twist exponent ρ_2 [12], there have not been enough recent Fréedericksz-transition data since the understanding of the crucial role of strong anchoring conditions [14], to evaluate a similar effect on ρ_3. Being a member of the DnAOB homologous series with both its neighbors exhibiting nematic and smectic-A phases, diheptylazoxybenzene is a good candidate for such an in-

vestigation. It has a positive magnetic anisotropy and a rather narrow nematic range, $t_{NA-NI}=0.956$. Previous work on these materials and their mixtures has been reported [14–17]. Very recently, the critical behavior of the twist and the bend elastic coefficients of D6AOB have been studied by light scattering and magnetic-field deformation study [12,18]. This sixth homolog has a wide nematic range with $t_{NA-NI}=0.885$, which makes our material an ideal system for comparison of the effects of the nematic range on the NA transition and the critical exponents.

In this paper we report measurements of the bend and splay elastic constants of the liquid-crystal diheptylazoxybenzene (C_7), using a magnetic-field-induced Fréedericksz transition [19]. Most reported measurements of the splay constants have been done in the bend geometry with the splay constant of nematic liquid crystals being extracted by a theoretical fit to the transmitted intensity data. We have measured the splay elastic constants in the splay geometry itself with a homogeneous sample and believe this to be more accurate than the other method. We have also measured the splay constants at different temperatures along with the bend critical exponent. K_1 is an important parameter in determining the nature of the NA critical point [1]. Careful measurements of the splay and the bend constants were made in the nematic–smectic-A phase-transition (NA-transition) region. Precise temperature control enabled us to study the divergence of the bend elastic constant due to the appearance of smectic fluctuations near the phase-transition region and thus measure the bend critical exponent (ρ_3). Comparing the value of ρ_3 of C_7 with other materials, it is not clear how this exponent depends on the nematic range. If, in fact, it does increase with the nematic range, then the measured exponents of materials with narrow ranges could be only apparent values due to the critical-tricritical crossover.

THEORY

The Fréedericksz transition at the critical magnetic field H_c marks the onset of the field-induced deformation. The bend elastic constant (in cgs units) is related to the bend threshold field by

$$K_3 = \left[H_c \frac{d}{\pi} \right]^2 \chi_a , \qquad (1)$$

where d is the sample thickness and χ_a is the anisotropic magnetic susceptibility at that temperature [20]. We used the values of magnetic susceptibility for C_7 measured by de Jeu and Claassen [16].

To examine pretransitional effects in the nematic phase, the bend and the twist elastic constants can be expressed in terms of a background term in the absence of smectic-A order-parameter fluctuations and a temperature sensitive term in the presence of smectic-A order-parameter fluctuations as follows [21]:

$$K_3 = K_{30} + \frac{k_B T}{24\pi} q_0^2 \xi_\parallel , \qquad (2)$$

$$K_2 = K_{20} + \frac{k_B T}{24\pi} q_0^2 \frac{\xi_\perp^2}{\xi_\parallel} , \qquad (3)$$

where k_B is the Boltzmann constant and $\xi_\parallel$ and $\xi_\perp$ are the correlation lengths parallel and perpendicular to the director, respectively; q_0 is the smectic layer spacing. The smectic-like fluctuations renormalize the bend and the twist according to that the second terms in the above equations increase rapidly as the transition is approached. Thus K_2 and K_3 are expected to show anomalous behavior at NA transition. On the other hand, K_1 is not expected to show pretransitional increase since the splay deformation of the director (equivalent to the undulations of the smectic layers) is allowed in the smectic-A and the nematic phases.

The temperature dependence of the correlation lengths defined by Eqs. (2) and (3) are written in terms of the reduced temperature $t = (T - T_{NA})/T_{NA}$ as [1]

$$\xi_\parallel = \xi_\parallel^0 t^{-\rho_3} , \qquad (4)$$

$$\xi_\perp = \xi_\perp^0 t^{-[(\rho_2 + \rho_3)/2]} , \qquad (5)$$

where $\xi_\parallel^0$ and $\xi_\perp^0$ are bare correlation lengths, and ρ_2 and ρ_3 are critical exponents for the twist and the bend elastic constants; i.e., $K_3 \sim \xi_\parallel \sim t^{-\rho_3}$ and $K_2 \sim t^{-\rho_2}$. This describes the behavior of the bend elastic constant in the vicinity of the NA transition, where smectic-like fluctuations are dominant. The divergence of the bend elastic constant has the same exponent as the correlation length parallel to the director.

EXPERIMENT

The cell was made of two square pieces of glass cut out from microscope slides with sides of 1 and $\frac{1}{2}$ in. The smaller piece was centered on the larger piece separated by a thin wire spacer of 151 μm thickness. The cells for the experiment were prepared by us in a clean bench environment. The homeotropic cells were prepared with the silane surface treatment [22], whereas the homogeneous samples were prepared by baking a monolayer of poly butylene tetraphthalate dissolved in a solution of tetrachloroethane and chlorophenol onto the cell plates and then rubbing the baked-on layer in one direction [23]. The liquid-crystal material was synthesized and recrystallized from ethanol by Sandra Keast and Dr. Mary Neubert of the Liquid Crystal Institute at Kent State University. We further filtered the material through 0.2-μm filters before filling our sample cells. Since the nematic phase of the C_7 was above room temperature, filling of the cells was done at about 60 °C and then the cells were sealed with the epoxy. This procedure caused problems with the epoxy (Torr Seal) not curing well; in fact, we observed a gradual migration of the epoxy into the liquid crystal. In order to prevent the direct contact of the epoxy with the liquid-crystal material, we used Indium metal to seal the gap around the cell before applying the epoxy. This stopped the migration of the epoxy and

confirmed our suspicion that the C_7 at temperatures higher than 50 °C reacted with the epoxy. We used a 151-μm spacer in all the cells. Both homeotropic and homogeneous orientations were confirmed by viewing under a polarizing microscope. The cells were also verified to be free from dust particles. We assume strong anchoring exists in both samples. Recent light scattering experiments by Johnson and Vithana [18] have shown that the silane surfactant procedure that we have used here produces strong anchoring in the nearest homolog of our compound, C_6.

For all the three experiments, the cell was housed in a solid aluminum block which acted as a thermostat and had a thermistor embedded in it and heater tapes uniformly distributed. This block was housed inside an outer hollow aluminum box, also with heaters and a thermistor and was temperature controlled separately. The outer box was controlled to ±0.01 K, whereas short-term fluctuations of the inner thermostat were better than ±0.3 mK. The temperatures were controlled using a computer-based controlling algorithm. We used a Keithley Model 199 digital multimeter with a scanner to measure the voltage drop across the two thermistors and a Macintosh IIci personal computer (PC) calculated the voltage required to maintain the desired temperature based on the monitoring of the actual temperature. An NB-MIO-16XL circuit board then put out the necessary analog voltage to control two programmable Kepco power supplies which in turn supplied the needed voltages to the inner and the outer thermostats, respectively.

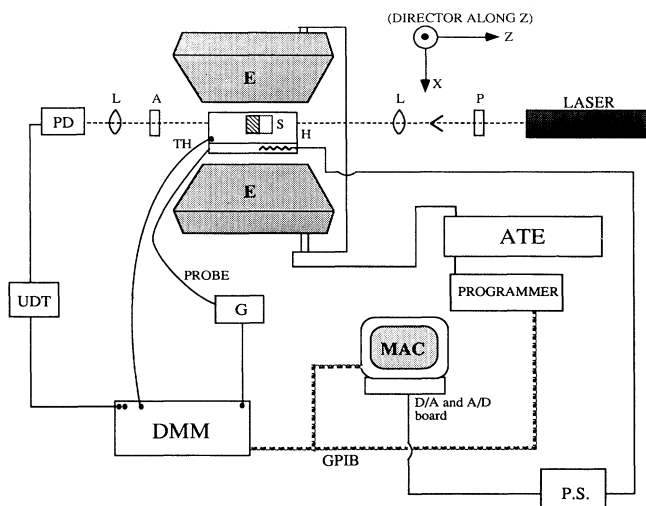The experimental setup used to detect the magnetically induced Fréederickz transition (the bend geometry) is
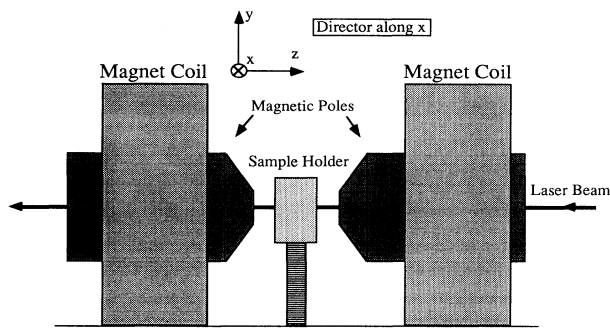

FIG. 2. The splay geometry (side view).

shown in Fig. 1. A polarized Melles-Griot He-Ne laser of 3 mW power was used. The polarizer and the analyzer were crossed at ±45° relative to the vertical axis for the bend experiment and at vertical and horizontal for the splay. The transmitted light intensity was monitored by a photodiode whose output was also measured by the Keithley 199 digital multimeter. Figure 2 shows the geometry for the splay experiment.

The Fréedericksz experiment was controlled and the data collected by the same Macintosh IIci via an IEEE bus system. Control of the magnetic field was achieved by programming the current of a Kepco ATE 36-30 power supply, through a Kepco SN-488 programmer. The current stability through the electromagnet was ±0.0009 A, which is equivalent to ±0.16 G at the threshold positions. The step rate of the current was timed by the internal clock of the PC. Different ramp rates were tried and the rate used for data collection was 1.58 G/min. The magnetic field was calibrated by ramping the current both up and down and the difference was taken into account while Fréedericksz threshold fields were measured.

FIG. 1. The experimental arrangement for the Fréedericksz transition (bend geometry). PD, photodiode; P, polarizer; A, Analyzer; S, sample; L, lens; TH, thermistors; H, heaters; G, gaussmeter; UDT, United Detector Technology photometer; MAC, Macintosh IIci; E, Electromagnet; PS, voltage-controlled power supply for heaters; DMM, Keithley digital multimeter; ATE, current-controlled Kepco power supply for the electromagnet. GPIB denotes a general-purpose interface bus, DA is a digital-to-analog converter, and AD is an analog-to-digital converter.

RESULTS

The bend elastic constant

Our Fréedericksz-transition data for the bend geometry were fitted by a single power-law equation, which is derived from Eqs. (1), (2), and (4):

$$H_c^2 = A T t^{-p_3} + B , \qquad (6)$$

where A and B are constants,

$$A = \frac{\pi k_B q_0^2 \xi_\parallel^0}{24 d^2 \chi_a} \qquad (7)$$

and

$$B = \frac{K_{30} \pi^2}{\chi_a d^2} . \qquad (8)$$

The result of nonlinear least-squares fit of the Fréedericksz threshold fields versus the reduced temperature to Eq. (6) on a log-log graph is shown in Fig. 3. Our best-fit values give us a χ^2 of 1 and an exponent p_3 of
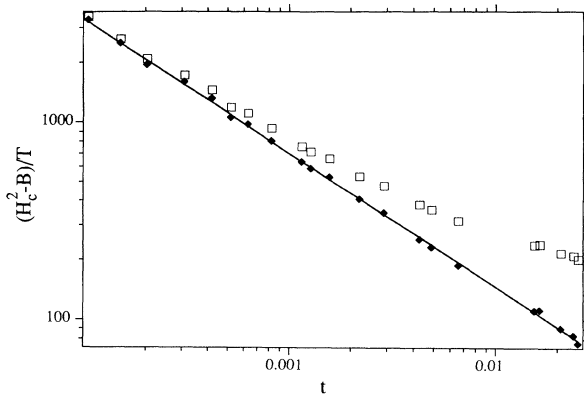
FIG. 3. Log-log plot of bend data (closed diamonds) with the theoretical fit (solid line) to Eq. (6). Overlay plot of the data with the background factor (B) subtracted (open squares) is also shown. The best-fit values to Eq. (6) are $T_c = 327.881$ K; $A = 0.62716 \times 10^2$; $B = 0.42104 \times 10^5$; $\rho_3 = 0.68$.

0.68 ± 0.04. We applied the range shrinking technique (data points were removed one at a time at the high-field end and the remaining data fitted, then the procedure was repeated for the low-field end) to our data which indicated the stability of the fitting parameters and the χ^2 value over a decade. This test indicates that the critical exponent is stable within the range of our error bar. We did not test for the change in the transition temperature (T_c) with magnetic field since Gooden et al. showed that such a correction is negligible in their compounds [24]. It has also been confirmed [25] that the effect of magnetic field on transition temperature, $T_c(H)$, is never more than ± 1 mK at the maximum field values (1 kG) used in our experiments. We did not monitor the phase-transition temperature on a daily basis but fitted T_c as a parameter and the value obtained is in agreement to within 5 mK of the measurement of T_c at the end of the experiment using light scattering. In addition, we tested our data by fixing the parameter T_c at 5 mK above our best-fit value for T_c and fitted the data to Eq. (6) to obtain a value for the critical exponent ρ_3. We repeated this test by fixing T_c at 5 mK below our best-fit value and obtained another value for ρ_3. These tests gave us the range of variation in our exponent value to be ± 0.001, due to a possible drift of T_c up to ± 5 mK (which is a typical value). This variation of our exponent is much less than our error bar and thus confirming that the correction due to the daily drift in T_c is negligible in our case.

Our value for the bend exponent is in good agreement with de Gennes's theoretical predictions and some of the earlier work done on 4-(n-octyloxy)-4'-cyanobiphenyl (8OCB), 4-n-pentylphenylthiol-4'-n-octyloxybenzoate ($\overline{8}$S5), 4-n-hexyloxybenzoate ($\overline{6}$09), and 4-n-nonylphenyl-4'-n-pentylbenzthiolate (9S5) [24], however, it does not agree with the bend exponent of Dihexylazoxybenzene (C_6) recently measured to be 0.825 [18]. Our data were taken over a wide range of temperatures well into the nematic phase, whereas the data on C_6 were taken over a very narrow range of temperature with a concentration of

points in the $t < 0.01$ region. A value of $\rho_3 > 0.8$ has been found for wide nematic range nonpolar materials [18], but ours does not fall under that category since $t_{\text{NA-NI}} = 0.956$, as opposed to 0.885 for C_6.

The unchanging part of the bend constant, K_{30} is calculated from Eq. (8):

$$K_{30} = \frac{\chi_a B d^2}{\pi^2} = 9.816 \times 10^{-13} \text{ N} .$$

We calculated the bare correlation length $\xi_\parallel^0$ to be 2.74 Å from $\xi_\parallel^0 = A 24 d^2 \chi_a / \pi k_B q_0^2$, where A is the constant obtained from fitting our data to Eq. (6) and q_0 is 0.17 ± 0.005 Å^{-1} [26].

Our value for the bare correlation length parallel to the director is of the same order as that of C_6 [18]. There are no published x-ray measurements of C_7 with which to compare. At present, we do not have a value for the critical exponent, ρ_2 associated with the divergence of the twist constant. In recent years it has been shown for some materials that the two correlation length exponents differ by a small but definite amount, indicating the nematic–smectic-A critical point to be anisotropic [1], that is, $\rho_2 \neq \rho_3$. In most reported cases, the twist exponent ρ_2 has values between 0.5 and 0.67.

The splay elastic constants

In the geometry shown in Fig. 2, we measured the splay elastic constants, by the Frēedericksz-transition method. The splay constants at various temperatures were calculated from an equation similar to Eq. (1). Our splay data show that K_1 is only slightly temperature dependent (see Fig. 4). This again, is in good agreement with other splay constant measurements [27]. K_1 seems to be independent of the correlation length as expected.

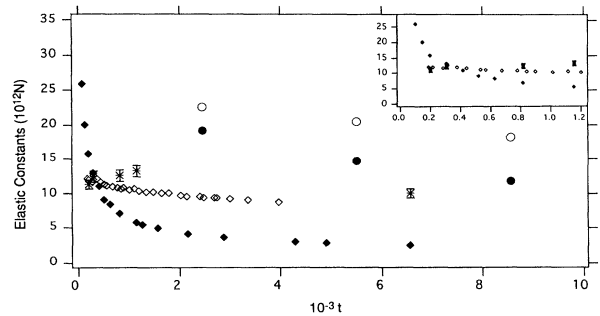We have also performed a light scattering study of C_7

FIG. 4. The bend (closed triangle) and the splay (open triangle) elastic constants of C_7 as a function of reduced temperature $t = (T - T_c)/T_c$. A few splay constants (stars) calculated from δ vs H_c^2 plot of the birefringence data from our bend Frēedericksz transition experiment are shown. The bend (closed circle) and the splay (open circle) elastic constants calculated by us from the data provided in Ref. [14] are also shown. (In order to plot these, we have used $T_c = 53.9\,°C$ reported in Ref. [16] by the same authors).

which will be reported elsewhere. The measurement of the twist elastic constant (K_2) we obtained from the light scattering experiment is in good agreement with magnitude of this constant in other liquid crystals. In all reported cases, the twist elastic constant is found to be the smallest of all three elastic constants.

The striped phase

Figure 4 shows the bend and the splay elastic constants as a function of reduced temperature, t. The ratio of the two elastic constants K_1/K_3 is about 3.9 in the higher-temperature end of the graph and reduces to less than 1 when the phase transition is approached (as $t \rightarrow 0$). In this region (at temperatures close to T_{NA}), when the field is increased further than the bend Fréedericksz threshold, the homogeneous distortion becomes energetically unfavorable and the stripe phase sets in [28,29]. Our experimental observations confirmed this, as explained below.

We encountered the periodically distorted stripe phase which has been reported by many experimentalists [24,30], as we got closer to the NA transition in the bend geometry. In fact, the appearance of these instabilities prevented us from getting meaningful data in the region $T - T_c < 30$ mK. We also observed a type of instability in our data from one of our homeotropic cells (not the sample in which we measured the elastic constants), as yet unreported by anyone. These "new stripes" appeared at about $T - T_{NA} = 9$ K at a field higher than the bend Fréedericksz threshold. We observed a diffraction pattern along a direction parallel to the field (along x in Fig. 1). These stripes were concluded to be in a direction perpendicular to the field and the director (along y in Fig. 1), as opposed to the often reported stripes which are parallel to the field. The difference in the two threshold fields (i.e., the Fréedericksz and the stripes) became less as we got closer to the NA phase transition, but we could not
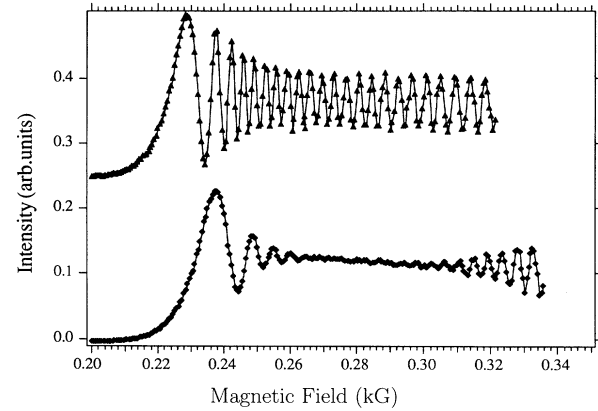

FIG. 5. Fréederickz-transition raw data on a sample different from the one used for data in Fig. 3. The intensity of the two runs are offset on an arbitrary scale. The upper plot is that of a normal Fréederickz data run while the lower one shows the onset of the "new stripes" when the normal birefringent oscillations disappear.

observe them clearly in the region close to the phase transition to be able to conclude if there is a boundary between the two different striped regimes. Figure 5 shows the experimental data of a normal Fréedericksz run and one in which these "new stripes" occurred. Although it is apparent that these instabilities appear at temperatures far from the NA transition unlike those observed by experimentalists so far, we are not yet able to conclude the nature of these instabilities. An interesting observation is that these new instabilities are quenched when the field is increased sufficiently above their threshold and the familiar oscillations due to birefringence set in again. The exact nature of these instabilities is currently under investigation in our laboratory.

TABLE I. Elastic constants for some nematic liquid crystals (10^{-12} N).

Material	K_1	K_2	K_3	K_3/K_1	Reference	T (°C)	T_c (°C)
MBBA				1.25	[31]	32.3	47
	7.1[i]	4.0[ii]	9.2[i]	1.3	i and ii[32]	~24	47
PAA	6.9[i]	3.8[iii]	11.9[i]	1.72	iii [32]	~122	135.5
5CB	4.0		4.85	1.21	[33]	38.1	35.1
6CB	3.3		3.75	1.14	[33]	32.2	29.2
7CB	4.65		5.0	1.08	[33]	45.3	42.3
8CB	4.7		4.6	0.98	[33]	42.8	39.8[a]
9CB	4.55		4.4	0.97	[33]	50.3	50.1[a]
5OCB	3.0		3.85	1.28	[33]	72.3	68.3
6OCB	3.7		4.35	1.18	[33]	80.8	76.8
7OCB	3.4		3.65	1.07	[33]	78.9	74.9
8OCB	4.5		4.75	1.06	[33]	83.8	79.8[a]
C_3				1.37	[14]	39.6	60.4
C_4				0.98	[14]	17.0	31.9
C_5				0.75	[14]	25.1	67.5
C_6				0.61	[14]	21.1	17.0[a]
C_7				0.65	[14]	56.7	53.9[a]
C_7	8.98±0.13		2.40±0.03	0.27	This work	57	54.9[a]
C_8				0.53	[14]	65.1	64.5[a]

[a]These are nematic–smectic-A transitions.

DISCUSSION AND CONCLUSIONS

Table I shows the values of all three elastic constants for some nematic liquid crystals. It can be seen that some liquid crystals have $K_3 > K_1$, whereas some others have $K_3 < K_1$. It has been shown that materials with small alkyl-chain length fall under the first category and material with long alkyl-chain length in the second category. Ours clearly belongs to the second case as can be expected from its structure. Bradshaw et al. [33] measured splay and bend constants for the homologous series alkyl- and alkoxy-cyanobiphenyls. From their data, it can be seen that as one goes up the homologous series to the higher members, the ratio of K_3 / K_1 decreases. de Jeu and Claassen [14] showed that the elastic ratio K_3 / K_1 decreases along the homologous series DnOAB and that K_1 and K_3 become greater with increasing alkyl-chain length. They claimed difficulty in obtaining strong anchoring with the homeotropic samples of C_7 and thus their bend constants for this liquid crystal were measured from the birefringence data on the planar samples. These measurements of K_1 and K_3 were made over the entire nematic range with the points being about a degree apart (see Fig. 4, where a few data points from Ref. [14] are plotted). de Jue and Claassen [14] did not set out to measure the bend exponent and thus their temperature measurements did not have to be as precise as ours. In fact, the exact temperature at which the NA transition was observed during their experiment is not reported in their paper [14]. Since our goal was to monitor the behavior of the elastic constants close to the NA transition, a direct comparison of the two works is not possible. de Jeu and Claassen's elastic constants seem to be somewhat higher than ours. But we conclude that our results are self-consistent for the following reason. We calculated a few values for K_1 (also shown in Fig. 4) from the birefringence of our bend Fréedericksz data from a homeotropic sample and these are in good agreement with our K_1 values measured independently from the splay Fréedericksz experiment using a homogeneous sample.

Variation of the ratio of bend to the splay constant with the alkyl-chain length is attributed to changes of the correlation lengths parallel and perpendicular to the director ($\xi_\parallel, \xi_\perp$), due to the presence of smectic fluctuations [14]. This pretransitional smectic order occurs when the transition is (almost) second order, which gives rise to the anomalous increase in the bend and the twist constant just above the transition, since the bend and the twist deformations are practically ruled out in the smectic-A phase. Some of the data reported in Table I seem to be collected at temperature ranges where smectic-A enhancement had not kicked in yet.

Our sample has a ratio of $t_{\text{NA-NI}} = 0.956$, where C_6 has a ratio of 0.885. The behavior suggested by these ratios is verified by the earlier experimental measurements of dielectric anisotropies and diamagnetic susceptibilities in these liquid crystals. According to de Jeu, Goossens, and Bordewijk [17] and Achard et al. [34] C_6 has practically a second-order transition whereas C_7 has a weakly-first-order transition and the next member in the series C_8 has a clearly-first-order transition. These would support our conclusion that the pretransitional effects in the two liquid crystals C_6 and C_7 are of different nature. This would explain the difference in the values of the bend critical exponent in the two cases. The influence of the nematic range, especially the value of $t_{\text{NA-NI}}$, on the critical behavior of the bend elastic constant, needs a sys-

TABLE II. Variation of critical exponents $\nu_\perp$ and $\nu_\parallel$ with the nematic range. FT denotes Fréedericksz transition and LS denotes light scattering.

Material	$T_{\text{NA}}/T_{\text{NI}}$	$\nu_\perp$	$\nu_\parallel = \rho_3$	Technique	Reference
XY Model		0.67	0.67	Theory	
8CB	0.977		1.0 ± 0.1	FT	[37]
		0.51 ± 0.04	0.67 ± 0.03	x ray	[38]
		0.49 ± 0.04	0.70 ± 0.03	x ray	[39]
		0.53 ± 0.06	0.72 ± 0.05	LS	[39]
9S5	0.964		0.68 ± 0.02	FT	[24]
8OCB	0.962		0.67 ± 0.05	FT	[24]
		0.58 ± 0.04	0.71 ± 0.04	x ray	[39]
		0.61 ± 0.05	0.75 ± 0.04	LS	[39]
C_7	0.956		0.68 ± 0.04	FT	This work
CBOOA	0.94		0.65	FT	[27]
		0.66 ± 0.05		LS	[40]
		0.62 ± 0.04	0.70 ± 0.04	x ray	[41]
$\overline{8}$S5	0.933		0.68 ± 0.03	FT	[24]
		0.68 ± 0.04	0.83 ± 0.03	x ray	[39]
		0.73 ± 0.06	0.89 ± 0.05	LS	[39]
40.7	0.926	0.65 ± 0.02	0.78 ± 0.02	LS	[42]
C_6	0.885		0.825 ± 0.005	FT	[18]
		$0.74 \pm 0.02^*$		LS	[12]
		0.65 ± 0.03	0.75 ± 0.03	x ray	[43]

*Calculated from ρ_2 and ρ_3 values reported in Ref. [12], using $\nu_\perp = (\rho_2 + \rho_3)/2$.

tematic investigation.

Previous experimental data [35] have shown that in a homologous series with decreasing chain length the ratio $t_{\text{NA-NI}}$ decreases and the change in the nematic order at the NA transition also decreased. These trends were as predicted by the microscopic theory [5,6]. A recent theoretical treatment [36] of the critical behavior above the nematic–smectic-A phase transition has shown that as the NA transition is approached, there are extended crossover regions from isotropic behavior to an anisotropic fixed point and that the largest anisotropy should occur for systems with the smallest range of the nematic phase (i.e., large $t_{\text{NA-NI}}$). Based on their model the authors predict that K_1 will be smaller for systems with larger $t_{\text{NA-NI}}$ [36]. A comparison of our value of K_1 with that of 4-(n-octyl)-4'-cyanobiphenyl (8CB) and 8OCB (both of which have larger value of $t_{\text{NA-NI}}$ than C_7) seem to be in agreement with this prediction (see Tables I and II).

Table II shows the exponents for different materials measured by various techniques. Existing Fréedericksz-transition data do not show an obvious trend of bend exponent with decreasing $t_{\text{NA-NI}}$ ratio (see Fig. 6). It is clear that more experimental work is needed on nematic crystals with different nematic ranges. Tricritical behavior which seems to occur with decreasing nematic range is driven by the coupling between nematic and smectic order parameter, in the absence of the saturation of the nematic order parameter before the NA transition. There is enough experimental evidence to conclude that the critical-tricritical crossover has a significant effect on the measured exponents if $t_{\text{NA-NI}} > x$, x being a lower limit which needs to be established. However, the differences among the same critical exponent for the same material measured by different experimental techniques still remain unaccounted for. At this point in the development of theoretical models, none seem to be entirely correct in predicting the critical exponents, only the hyperscaling relation, $2v_\perp + v_\parallel = 2 - \alpha$, holds for most materials suggesting some underlying universal behavior. The first generation of experiments to measure the bend and the twist exponents seem to have been performed on materials that are in the middle of the critical to tricritical crossover region. It is imperative that the future experiments be done on materials with $t_{\text{NA-NI}} < 0.9$ in order to develop a complete picture of this complicated phenomenon. The question remains open as to how the tricritical fluctuations affect the bend exponent; i.e., how the bend exponent evolves between the critical and tricritical regions.
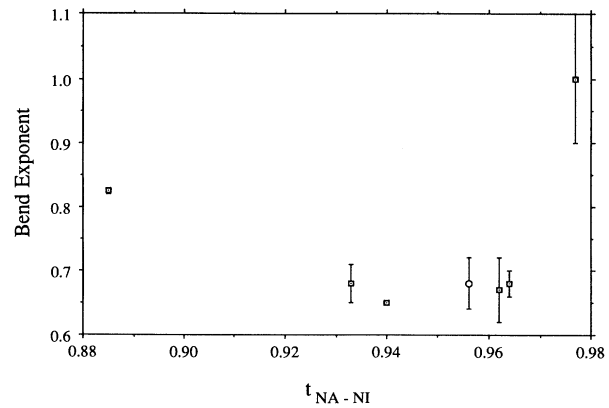

FIG. 6. Bend critical exponents (ρ_3) against $t_{\text{NA}-\text{NI}}$ from Fréedericksz-transition data in Table II, shown as squares. Our bend critical exponent is displayed as an open circle.

SUMMARY

We found the bend elastic constant to diverge at the NA transition with an exponent of 0.68 ± 0.04, in agreement with the predictions of the 3D-XY model. Whether the behavior of NA transition of diheptylazoxybenzene agrees completely with the 3D-XY model can only be confirmed if we have the critical exponent for the twist elastic constant available. Our value for the ratio of the bend and the splay elastic constants near the NA phase transition and the appearance of the striped instabilities, are consistent with our present understanding of the dependence of director stability on the material constants [28].

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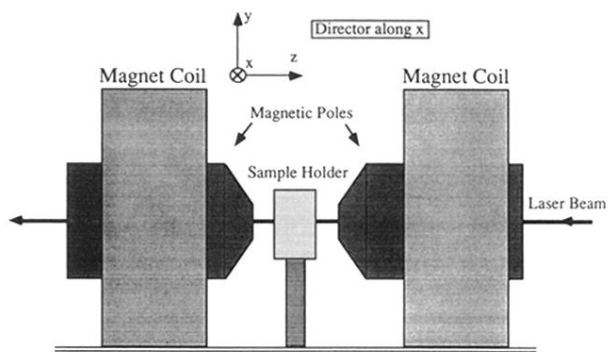[43] Li Chen, J. D. Brock, J. Huang, and Satyendra Kumar, Phys. Rev. Lett. **67**, 2037 (1991).

FIG. 2. The splay geometry (side view).