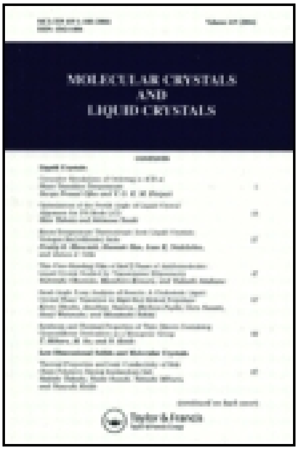

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Elasticity and Orientational Order in Some 4′-*n*-Alkyl-4-Cyanobiphenyls: Part II

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The splay and twist elastic constants (k_{11} and k_{22}) of pentyl, hexyl, heptyl and octyl cyanobiphenyls (5CB, 6CB, 7CB and 8CB respectively) have been determined by the Freedericksz transition method. The results are compared with the bend elastic constants (k_{33}) and order parameters (S) of these compounds reported by us in an ealier paper, as also with the heats of transition (ΔH) determined using a differential scanning calorimeter and the temperatures of transitions (T_{NI}). T_{NI} and k_{33} near T_{NI} exhibit alternation for all the four compounds. On the other hand, S, ΔH, and k_{11} and k_{22} near T_{NI} exhibit alternation only for the first three compounds and *increase* between 7CB and 8CB. It is concluded that ($\xi_{\perp}/\xi_{\parallel}$), the ratio of the transverse to the longitudinal correlation lengths of the smectic A type cybotactic order increases between 7CB and 8CB.

INTRODUCTION

The fifth to eighth homologues of 4′-*n*-alkyl-4-cyanobiphenyls are extremely stable, colourless room temperature liquid crystals.[1] Moreover, because of the strong positive dielectric anisotropy of these compounds arising from the nitrile group attached to the molecules, they are finding wide applications in display devices. In an earlier paper[2] (hereafter referred to as I) we presented the data on the bend elastic constants k_{33}, densities, refractive indices and the order parameters S derived from the refractive indices in the nematic phase of all the four compounds. We found that k_{33} near the nematic–isotropic transition point T_{NI} alternates in all the four compounds: k_{33} of 8CB was found to be lower than that of 7CB at the same relative temperature ($T_{NI} - T$) in spite of the fact that 8CB exhibits a smectic A phase with the smectic A–nematic transition point T_{AN} lying just 6.8° below T_{NI}. On the other hand, the order parameter increases between 7CB and 8CB. We interpreted this behaviour to mean that the ratio of the transverse to longitudinal correlation lengths ($\xi_\perp/\xi_\parallel$) of the smectic A like cybotactic groups *increases* between 7CB and 8CB. In fact, our data on k_{33} indicated that all the four compounds have considerable cybotactic order even near T_{NI}. Neighbouring molecules in such strongly polar compounds are expected to have antiparallel correlations.[3] The X-ray evidence on these compounds clearly indicates such an arrangement.[4,5] There is a tendency to form layers, each layer being made up of two molecules which lie with their polar ends interdigitated because of strong antiparallel correlations. The layer thickness is about 1.4 times the molecular length. Also the size of the cybotactic group was found from the X-ray studies to be larger in 7CB ($\simeq 150$ molecules) than in 5CB ($\simeq 100$ molecules). We could correlate the X-ray evidence with our k_{33} data.[2] In continuation of this work, we present in this communication experimental data on the splay (k_{11}) and twist (k_{22}) elastic constants of 5CB, 6CB, 7CB and 8CB. In addition, we have also measured the heat ΔH of the nematic–isotropic transition. We discuss the results in the light of our earlier observations.

EXPERIMENTAL

All the compounds used in the experiments were synthesized in our chemistry laboratory and their phase transition points were given in I.

Both the splay and twist elastic constants were determined by the Freedericksz transition method. Homogeneously aligned samples are necessary for both the measurements. Unidirectional rubbing of the glass plates was found to give a good alignment in all cases. If H_0 is the magnetic field necessary to start a distortion in the sample with the undistorted director set normal to H_0, we have

$$k_{ii} = \frac{\Delta\chi H_0^2 d^2}{\pi^2} \tag{1}$$

where $\Delta\chi$ is the anisotropy of the *volume* diamagnetic susceptibility of the medium and d the thickness of the sample. k_{ii} is the splay elastic constant if H_0 is normal to the bounding surfaces, and it is the twist elastic constant if H_0 is parallel to the bounding surfaces. The diamagnetic anisotropy data are not available for these compounds. Hence we write $\Delta\chi = \Delta\chi_{om}\rho S$ where ρ is the density of the medium and $\Delta\chi_{om}$ the anisotropy of the *mass* susceptibility of a perfectly oriented medium with $S = 1$. We can now rewrite (1) as

$$k_{ii} = \frac{\Delta\chi_{om} d^2}{\pi^2}(H_0^2 S\rho). \tag{2}$$

As explained in I, we have estimated $\Delta\chi_{om}$ from the susceptibility measurements on biphenyl, and the density and order parameter values have already been given in I, based on refractive index measurements.

The sample was mounted between two 2 mm thick optical flats separated by mylar spacers. The thickness of the sample was measured using channelled spectrum. Special precautions were taken to set the initial undistorted director orientational normal to the magnetic field. The sample was viewed through a low power microscope in sodium light. The experimental details have been given in I, and we mention below the special features of the experimental arrangements for the splay and twist elastic constant measurements:

Splay

In this case, as the light beam has to travel parallel to the magnetic field, the collimated light beam was deflected on to the sample by means of a suitable mirror. Since we measured only H_0, the Freedericksz transition field, it is necessary to use an optical set up sensitive to small changes in the phase retardation of the medium. The incident beam is polarized at 45° to the director. The beam is split into ordinary and extraordinary waves in the medium which travel with different velocities so that the outcoming beam will be elliptically polarized. This is converted back to linear polarization by a quarter wave plate which is set with one of its principal axes at 45° to the undistorted director. The outcoming beam can now be detected by means of a linear analyser whose azimuth can be suitably adjusted. The observations are made through a low power microscope into which the beam is deflected by means of a suitable mirror. The analyser is set initially to get a dark field of view and any small distortion in the medium brightens up the field of view.

Twist

The nematic liquid crystals have a high birefringence Δn. For the compounds investigated here $\Delta n \simeq 0.1$. In such a case, because of the "adiabatic theorem," the twist deformation cannot be detected optically by using a light beam travelling normal to the bounding surfaces. In order to overcome this difficulty, we have employed the simple technique of viewing the sample at an oblique angle[6] (Figure 1). In this case, the distortion can be easily detected by the optical set up described above.

The heat of the nematic–isotropic transition was measured by a Perkin Elmer differential scanning calorimeter, model DSC-2. The mass of the sample used was typically 5 mgms.

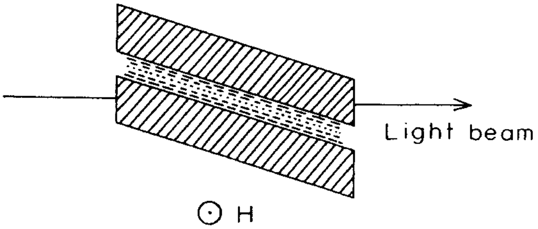

FIGURE 1 Schematic diagram of the experimental set up to determine twist elastic constant by the oblique incidence method.

RESULTS AND DISCUSSION

We have displayed in Figures 2 and 3 the splay and twist elastic constants. For the sake of comparison, we have also shown in Figure 4 the bend elastic constants. In Figure 5 we have plotted the nematic–isotropic transition points (T_{NI}), the heats of this transition (ΔH), and the order parameters (S), and all the elastic constants at $T_{NI} - 2°$. We summarize below the noteworthy features:

a) The transition temperatures and only k_{33} near T_{NI} exhibit alternation for all the four compounds.

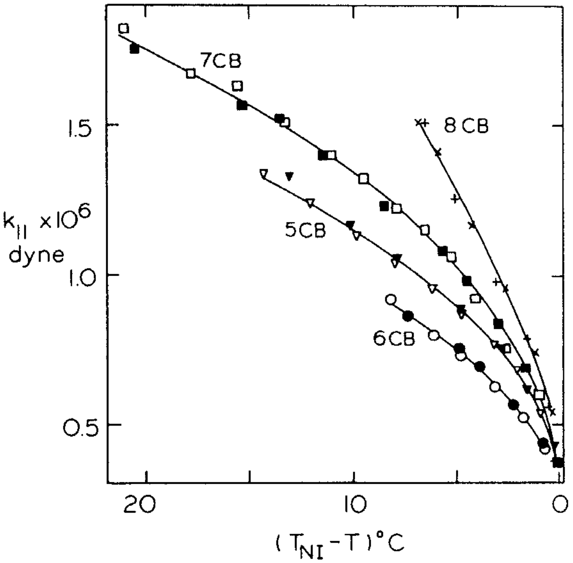

FIGURE 2 Splay elastic constants of 4′-n-alkyl-4-cyanobiphenyls as functions of the relative temperature. The results of independent experiments have been marked separately.

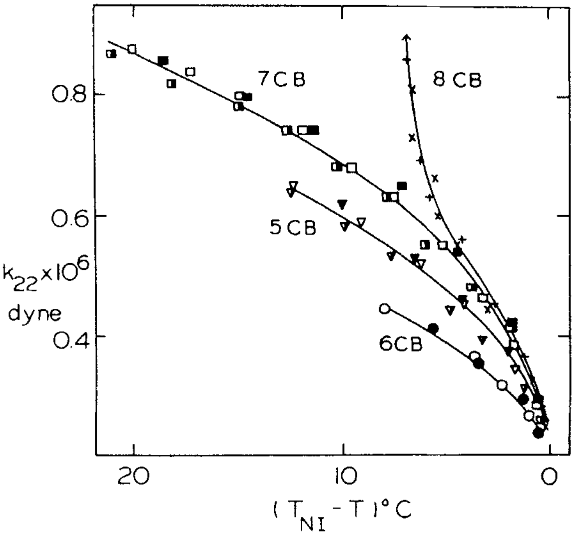

FIGURE 3 Twist elastic constants of 4′-*n*-alkyl-4-cyanobiphenyls as functions of the relative temperature. The results of independent experiments have been marked separately.

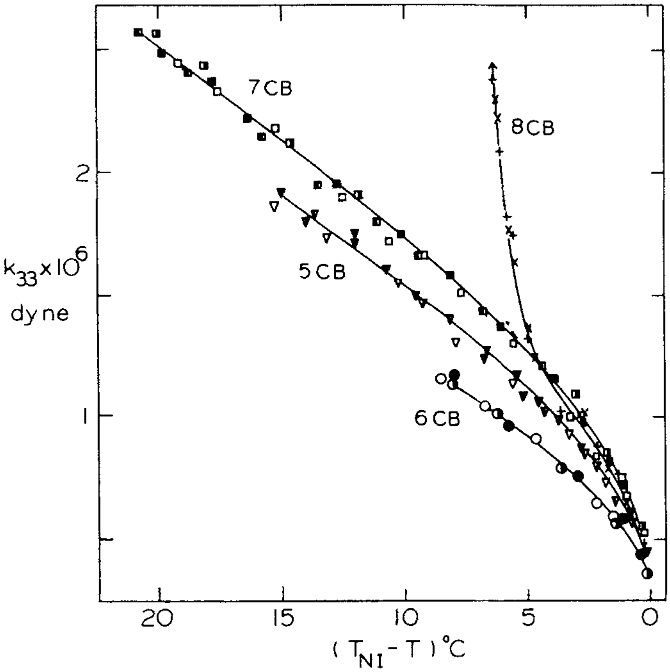

FIGURE 4 Bend elastic constants of 4′-*n*-alkyl-4-cyanobiphenyls as functions of the relative temperature. The results of independent experiments have been marked separately.

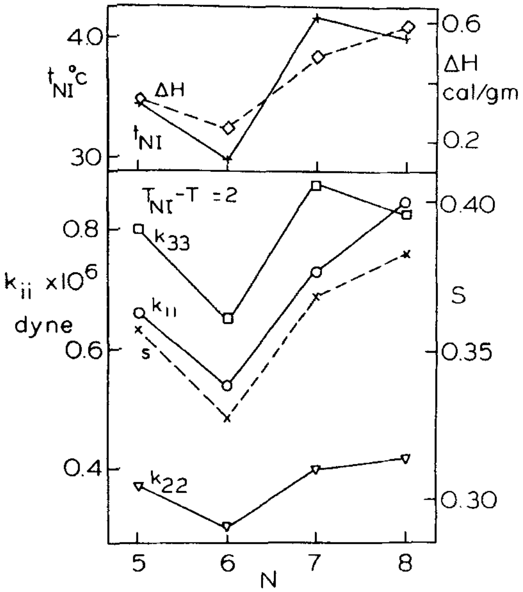

FIGURE 5 The nematic–isotropic transition points (+), heats of transition (◇), order parameters (×), splay elastic constants (○), twist elastic constants (▽) and bend elastic constants (□) of 4′-n-alkyl-4-cyanobiphenyls.

b) The order parameters, ΔH, k_{11} and k_{22} alternate only for the first three compounds, but increase between 7CB and 8CB.

c) In the case of 8CB, both k_{22} and k_{33} diverge as the nematic–smectic A transition point (T_{AN}) is approached.

d) For any given compound, the ratios of elastic constants do not remain constant with temperature.

Thus the mean field result that $k_{ii} \propto S^2$ (ignoring a volume-dependent term) does not hold good. We have fitted the experimental data to a formula of the type $k_{ii} = cS^x$, and the results are given in Table I. (The numbers given

TABLE I

	k_{11}		k_{22}		k_{33}	
	c	x	c	x	c	x
5CB	5.98	2.15	2.70	1.96	11.78	2.65
6CB	5.31	2.08	2.00	1.74	8.40	2.35
7CB	7.18	2.31	3.00	2.01	13.81	2.81
8CB	10.79	2.62				

in the table give the parameters for the best overall fit; a perfect fit is not obtained for most cases.) From the table we notice that among the first three homologues, there is an alternation in both c and x while in the case of k_{11} both these quantities increase between 7CB and 8CB. The exponent x is very close to 2 only for k_{22} in 5CB and 7CB. We also observe that for the twist elastic constant of 6CB, x is less than 2. We have no explanation for this peculiar result.

e) In 8CB a very unusual behaviour is observed. As we have noted earlier, k_{33} of 8CB near T_{NI} is lower than that of 7CB. On the other hand, k_{11} shows the reverse trend. In fact for 8CB k_{11} has a *larger* value than k_{33}, which is not a common behaviour. However, as the temperature is decreased, k_{33} rapidly increases becoming larger than k_{11} for temperatures lower than $(T_{NI} - 4.5°)$.

The increase in ΔH between 7CB and 8CB can be related with a similar increase in the order parameter between the two compounds. Based on the behaviour of k_{33} and S, we had surmised in our earlier paper[2] that $\xi_{\perp}/\xi_{\parallel}$ increases between 7CB and 8CB. This appears to be borne out by the increase of k_{11} and k_{22} between these two compounds. By the nature of the deformations involved, we can see that this trend is compatible with an increase in $\xi_{\perp}/\xi_{\parallel}$ between 7CB and 8CB.

Finally, the ratios of elastic constants have practically the same values at the same relative temperature $(T_{NI} - T)$ for all the first three compounds. This indicates that even though the absolute values of the cybotactic order are different in the different cases (as evidenced by the magnitudes of elastic constants as well as the X-ray results), the temperature variation of this order is similar in all the three compounds.

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