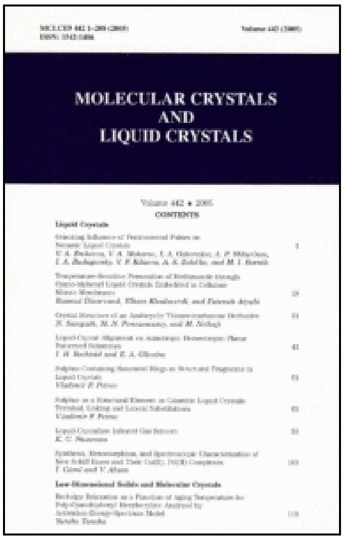

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Elasticity and Orientational Order in Some Cyanobiphenyls: Part IV. Reanalysis of the Data

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Elasticity and Orientational Order in Some Cyanobiphenyls: Part IV. Reanalysis of the Data

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We present revised *absolute* values of the elastic constants and order parameters of several cyanobiphenyls. The calculations make use of our earlier measurements of Freedericksz threshold fields and refractive indices, and corrected values of normalizing constants, particularly in respect of the anisotropy of magnetic susceptibility. The new values agree well with some recent measurements.

INTRODUCTION

The elastic constants of several cyanobiphenyls were measured in our laboratory some years ago and published in three earlier papers[1–3] (hereafter referred to as I, II and III). The measurements were made by using the Freedericksz transition technique, and in analyzing the results to get the absolute values of the elastic constants, we had to make use of some data then available in the literature. It turns out that the normalizing constants that we used based on the available data are in considerable error, as has in fact been pointed out by several authors recently.[4–7] The cyanobiphenyls are an important class of mesogens from the point of view of basic studies as well as applications, and it is not surprising that our data are being cited quite extensively in recent publications. We therefore felt it was necessary to point out these errors and to present revised values of the elastic constants and order parameters based on what we now believe to be the appropriate normalizing constants.

CALCULATIONS AND RESULTS

In an experiment using the Freedericksz transition technique, the elastic constant k_{ii} is given by

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

where $i = 1, 2$ and 3 correspond to splay, twist and bend, depending on the geometry of the initial alignment of the sample and the direction of the applied magnetic field H in relation to the bounding glass plates. H_0 is the magnetic field necessary to start a distortion, d the sample thickness and $\Delta\chi$ the anisotropy of the *volume* diamagnetic susceptibility of the sample. In our experiments, we determined accurate values of H_0 at different temperatures for samples of known thickness d. $\Delta\chi$ values were not known at the time of our experiments, and we used the following arguments to estimate the same. Firstly, one can write

$$\Delta\chi = \Delta\chi_m \rho = \Delta\chi_{om} S \rho \tag{2}$$

where $\Delta\chi_m$ is the anisotropy of the *mass* diamagnetic susceptibility of the medium; $\Delta\chi_{om}$ that for a perfectly ordered medium with the orientational order parameter $S = 1$, and ρ the density. Further, to a good approximation, $\Delta\chi_{om}$ can be assumed to be determined entirely by the aromatic core of the molecule. Then, one can write

$$\Delta\chi_{om} = \Delta K/M \tag{3}$$

where ΔK is the anisotropy of the susceptibility of one mole of biphenyl, and M the molecular weight of the given cyanobiphenyl compound. We used $\Delta K = 118.6 \times 10^{-6}$ cgs units, a value given in a review article by Lansdale[8] and reproduced in a book by Davies.[9] It is now clear that this value does not correspond to our definition of the anisotropy, and referring back to the paper by Krishnan *et al.*,[10] in which the original experimental data have been given, ΔK of biphenyl is only about 54×10^{-6} cgs units. Here ΔK is defined as $K_\parallel - K_\perp$, where $K_\parallel$ is the value measured along the long axis of the molecule and $K_\perp$ is the average value perpendicular to that axis. Hence the normalizing constant used by us in our earlier calculations[1-3] has a large error. In the past few years there have been a few independent determinations[4,11,12] of the diamagnetic anisotropy of alkyl cyanobiphenyls (nCB). Sherrell and Crellin[11] have measured $\Delta\chi_m$ for five members of the series ($n = 5$ to 9). However, two subsequent measurements[4,12] on 7CB and one[12] on 5CB yield values of $\Delta\chi_m$ which are about 7–10% lower than those given in Ref. 11, and in fact Bunning, Faber and Sherrell[7] have themselves used the data of Ref. 12 for their analysis of the elastic constants of 5CB. Further our own calculations of $\Delta\chi_m$ for the homologues $n = 5$ to 8 which we shall describe presently yield values which are again lower than those of Ref. 11. Therefore it would appear reasonable to suppose that the lower values given in Refs. 4 and 12 are more accurate.

$\Delta\chi_m$ can be calculated from Eq. (2) if one had reliable data on $\Delta\chi_{om}$, S and ρ. Flygare[13] has proposed an empirical scheme to evaluate $\Delta\chi_{om}$ of organic molecules by using the additivity of anisotropic bond susceptibilities. The method has been applied to evaluate $\Delta\chi_{om}$ of several mesogenic compounds[11,14,15] and is expected to yield values to well within an accuracy of ~5% for the cyanobiphenyl compounds. We have used this procedure to calculate $\Delta\chi_{om}$ for nCB ($n = 5$ to 8) and 8OCB, assuming an all-trans conformation of the alkyl chain. The calculated values are presented in Table I.

The principal refractive indices of all the above mentioned compounds were reported by us in our earlier publications[1,3] and the values are in excellent agreement with subsequent measurements by others.[16,17] Applying the Vuks formula[18–20] we can express the order parameter as

$$S = \left(\frac{\bar{\alpha}}{\Delta\alpha}\right)\frac{n_e^2 - n_o^2}{\overline{n^2} - 1} \tag{4}$$

where $\bar{\alpha}$ is the mean polarizability, $\Delta\alpha$ the anisotropy of polarizability of a perfectly oriented medium with $S = 1$, n_e and n_o stand for the extraordinary and ordinary refractive indices and $\overline{n^2} = (n_e^2 + 2n_o^2)/3$. Since the relevant measurements on crystals are not available, $\Delta\alpha$ is not known in any of these cases. In I, we used Heger's[21] Raman measurement of the absolute values of S of 7CB to estimate $\bar{\alpha}/\Delta\alpha$ for that compound. The $\Delta\alpha$ values for all the other homologues could then be

TABLE I

$\Delta\chi_{om}$ and $(\bar{\alpha}/\Delta\alpha)$ values of cyanobiphenyls

	$\Delta\chi_{om} \times 10^7$ c.g.s. units	$\bar{\alpha}/\Delta\alpha$ for λ5893 Å
5CB	1.76	1.55
6CB	1.83	1.64
7CB	1.53	1.71
8CB	1.61	1.81
8OCB	1.28	1.75

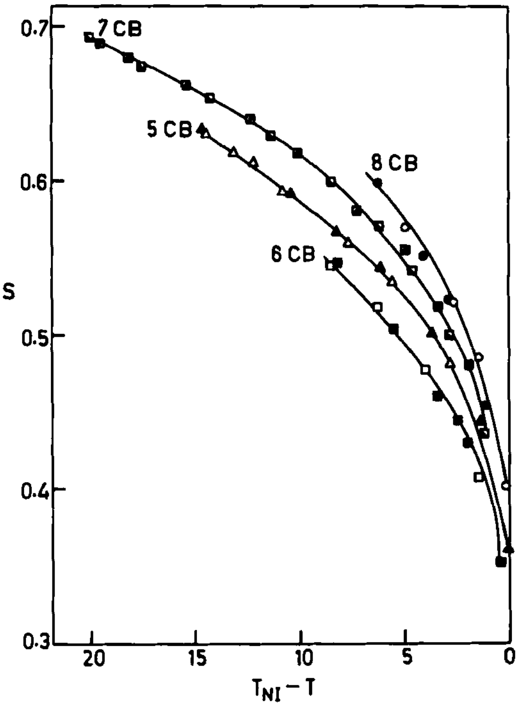

FIGURE 1 Variation of the order parameter as a function of the relative temperature in the nematic phase of 4'-*n*-alkyl-4-cyanobiphenyls. Results of independent experiments have been marked separately.

estimated by suitably adding the incremental values corresponding to CH_2 groups. However, subsequent measurements[22] (see also Ref. 7) have shown that Heger's values for 7CB are too low, by ~25%. For this reason, we now use Miyano's[23] Raman measurements on the absolute values S of 5CB to normalize our data on that compound and as we shall see presently this seems to yield satisfactory results. $\bar{\alpha}/\Delta\alpha$ for the other homologues can then be calculated by the procedure mentioned earlier and given in detail in I. The values are listed in Table I. The recalculated values of S for nCB, $n = 5$ to 8, are shown in Figure 1. The order parameters of 7CB and 8CB have been recently determined by Constant and Decoster[22] using Raman measurements, and our values agree with their data obtained from the C≡N band quite well, the former being 3–4% lower than the latter.

$\Delta\chi_m$ for the different homologues of nCB can now be evaluated using Eq. (2). For 5CB, the calculated values agree well with the experimental data of Buka and de Jeu[12] at lower temperatures, but our values tend to be lowered by ~3–4% as T_{NI} is approached. On the other hand, for 7CB the two sets of data agree well close to T_{NI}, but our values are higher at lower temperatures, the difference being ~4% at $T_{NI} - T \simeq 16°$. In other words, using the magnetic susceptibility data of Buka and de Jeu, $\Delta\chi_m/(n_e^2 - n_o^2)/(\overline{n}^2 - 1)$ does not remain constant but tends to increase by a few percent as T_{NI} is approached for both 5CB and 7CB. This point was also noted for the case of 5CB by Bunning *et al.*[7] On the other hand, with the data of Schad *et al.*[4] on $\Delta\chi_m$ of 7CB, the above mentioned ratio does not show any systematic variation with temperature. Further, $(n_e^2 - n_o^2)/(\overline{n}^2 - 1)$ is found to be proportional to the order parameters determined by the Raman measure-

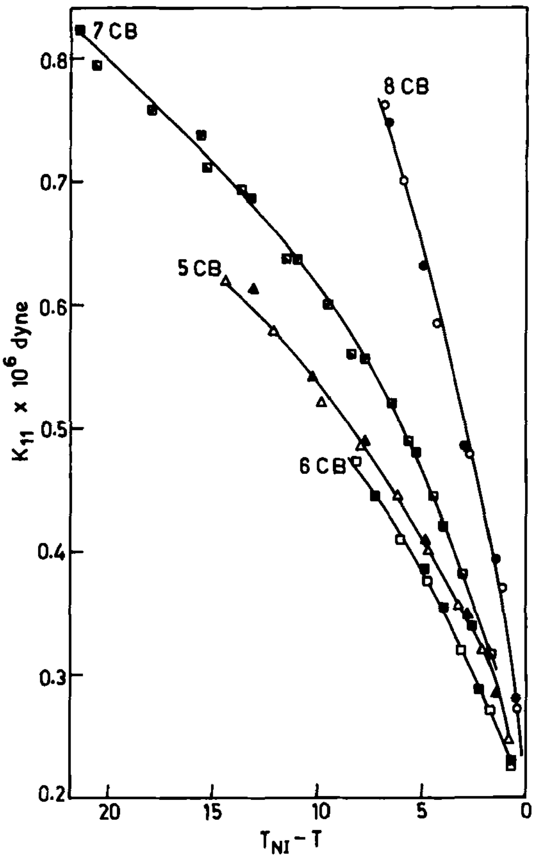

FIGURE 2 Variation of the splay elastic constant as a function of the relative temperature in the nematic phase of 4′-*n*-alkyl-4-cyanobiphenyls. Results of independent experiments have been marked separately.

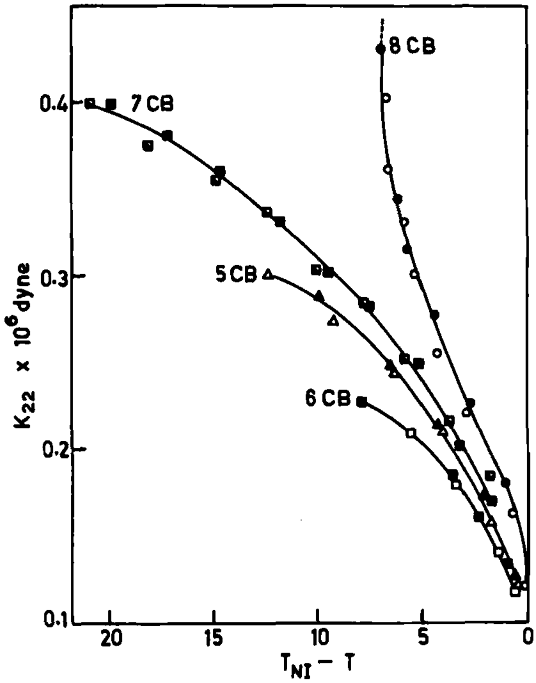

FIGURE 3 Variation of the twist elastic constant as a function of the relative temperature in the nematic phase of 4′-*n*-alkyl-4-cyanobiphenyls. Results of independent experiments have been marked separately.

ments on the C≡N band of 5CB,[23] 7CB[22] and 8CB[22] to within experimental errors. Consequently we believe that we can rely on the $\Delta\chi_m$ values calculated by us.

Using the density data given by Dunmur and Miller[24] one can evaluate the anisotropy of the *volume* diamagnetic anisotropy $\Delta\chi$ [see Eq. (2)]. In conjunction with our Freedericksz threshold measurements, [1,2] the *absolute* values of the elastic constants can now be obtained; the results for k_{11}, k_{22} and k_{33} of *n*CB are shown in Figures 2, 3, and 4 respectively.

Our values for k_{11} and k_{33} for 5CB are about 5–6% lower than those reported recently by Bunning *et al.*,[7] who have directly used the $\Delta\chi_m$ data of Buka and de Jeu[12] in their analysis. In view of the possible errors in the various input parameters in the two analyses, this agreement in the absolute values can be considered to be quite good. Schad and Osman[6] have listed $k_{11}/\Delta\chi$, $k_{22}/\Delta\chi$ and $k_{33}/\Delta\chi$ of 7CB determined by

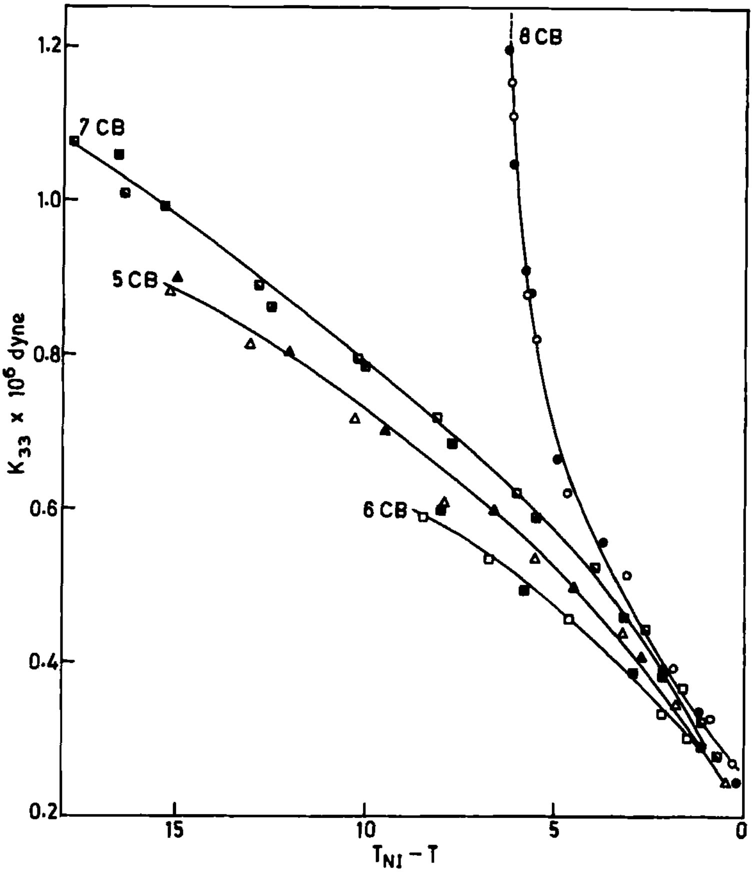

FIGURE 4 Variation of the bend elastic constant as a function of the relative temperature in the nematic phase of 4'-*n*-alkyl-4-cyanobiphenyls. Results of independent experiments have been marked separately.

them at several temperatures. The $k_{11}/\Delta\chi$ data agree with our values to within ~1%, while $k_{33}/\Delta\chi$ are lower by ~4%. However, as regards $k_{22}/\Delta\chi$, their values are higher by ~15–20%, even though they have used the technique of oblique incidence of the light beam to detect the twist distortion, which was developed by us[25] and used in our own measurements.[2] No other measurements of k_{22} are available for comparison.

The order parameters and elastic constants of 8OCB were similarly recalculated and are presented in Figure 5. The k_{11} value close to the smectic–nematic transition point of this compound agrees reasonably

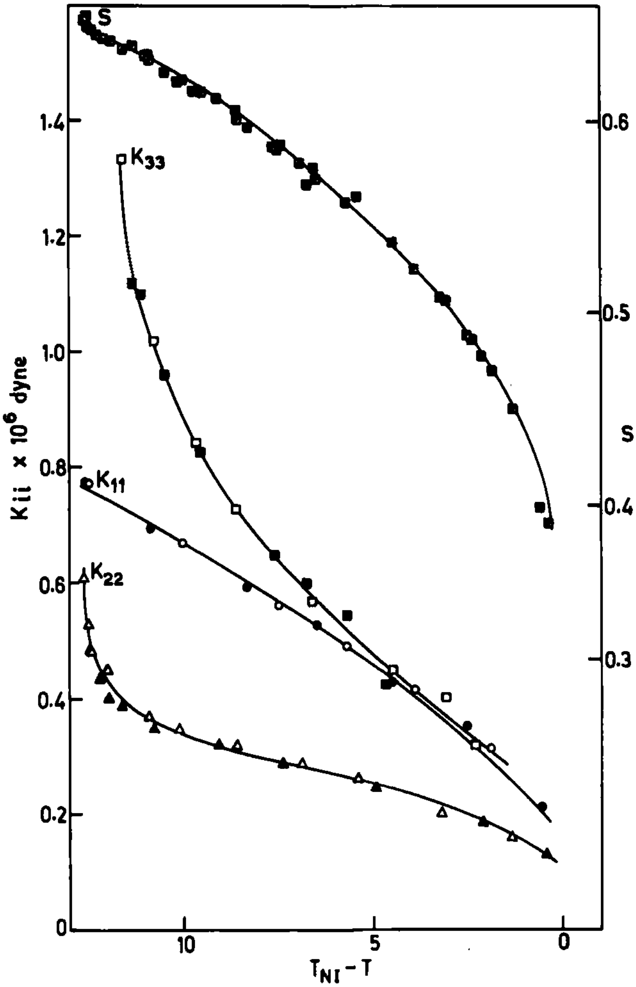

FIGURE 5 Variations of the order parameter and elastic constants as functions of the relative temperature in the nematic phase of 4′-*n*-octyloxy-4-cyanobiphenyl. Results of independent experiments have been marked separately.

well with the value obtained on the basis of an analysis of X-ray scattering experiments on the smectic A phase of this compound.[5]

CONCLUDING REMARKS

In conclusion, we believe that the recalculated absolute values of the order parameters and splay and bend elastic constants presented in this note are accurate to about ±5%. The twist elastic constant is intrinsically more difficult to measure,[25] and we believe the error in this case may be somewhat higher. However, it may be remarked that the present reanalysis of the data does not alter the discussions in I, II and III, since they were based on the relative rather than the absolute values.

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