A P P E N D I X   I

ELASTICITY AND ORIENTATIONAL ORDER IN SOME CYANOBIPHENYLS:

REANALYSIS OF THE DATA

A.1   INTRODUCTION

The elastic constants of several cyanobiphenyls were measured in our laboratory some years ago and published in three earlier papers (Karat and Madhusudana 1976, 1977, 1978). The measurements were made by using the Freedericksz transition technique, and in analyzing the results to get the absolute values of the elastic constants, some data then available in the literature was made use of. It turns out that the normalizing constants that were used based on the available data are in considerable error, as has in fact been pointed out by several authors recently (Schad et al. 1979, Litster 1980, Schad and Osman 1981, Bunning et al. 1981). 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 the 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.

A.2   RESULTS AND CALCULATIONS

In an experiment using the Freedericksz transition technique,

the elastic constant K_{ii} is given by

$$K_{ii} = \frac{\Delta \chi H_c^2 d^2}{\pi^2} \tag{1}$$

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_c 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 the experiments, accurate values of H_c were determined at different temperatures for samples of known thickness d. $\Delta\chi$ values were not known at the time of the experiments, and the following arguments were used 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. $\Delta K = 118.6 \times 10^{-6}$ cgs units was used. This value is

given in a review article by Lansdale (1937) and reproduced in a book by Davies (1967). It is now clear that this value does not correspond to the definition of the anisotropy, and referring back to the paper by Krishnan et al. (1933), in which the original experimental data have been given, ΔK of biphenyl is only about 54×10^{-6} cgs units. Here AK 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 previously has a large error. In the past few years there have been a few independent determinations (Schad et al. 1979, Sherrell and Crellin 1979, Buka and Jeu 1982) of the diamagnetic anisotropy of alkyl cyanobiphenyls (nCB). Sherrell and Crellin (1979) have measured ΔX_m for five members of the series ($n = 5$ to 9). However, subsequent measurements on 7CB (Schad et al. 1979) and on 5CB and 7CB (Buka and Jeu (1982) yield values of ΔX_m which are about 7-10% lower than those given by Sherrel and Crellin (1979), and in fact Bunning et al. (1981) have themselves used the data of Buka and Jeu (1982) for their analysis of the elastic constants of 5CB. Further, our own calculations of ΔX_m for the homologues $n = 5$ to 8 which we shall describe presently yield values which are again lower than those given by Sherrell and Crellin (1979). Therefore it would appear reasonable to suppose that the lower values given by Schad et al. (1979) and Buka and de Jeu (1982) are more accurate.

ΔX_m can be calculated from Eq. (2) if one had reliable data on ΔX_{om}, S and ρ. Flygare (1974) has proposed an empirical scheme to evaluate ΔX_{om} of organic molecules by using the additivity of anisotropic bond susceptibilities. The method has been applied to evaluate ΔX_{om} of several mesogenic compounds (Sherrel and Crellin 1979, Ibrahim and Haase 1979, Leenhouts et al. 1979) and is expected to yield values to well within an accuracy of $\sim 5\%$ for the cyano biphenyl compounds. We have used this procedure to calculate ΔX_{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 are taken from earlier publications (Karat and Madhusudana 1976, 1978) and the values are in excellent agreement with subsequent measurements by others (Horn 1978, Dunmur et al. 1978). Applying the Vuks formula (Vuks 1966, Chandrasekhar and Madhusudana 1969 and Madhusudana 1980) we can express the order parameter as,

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

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
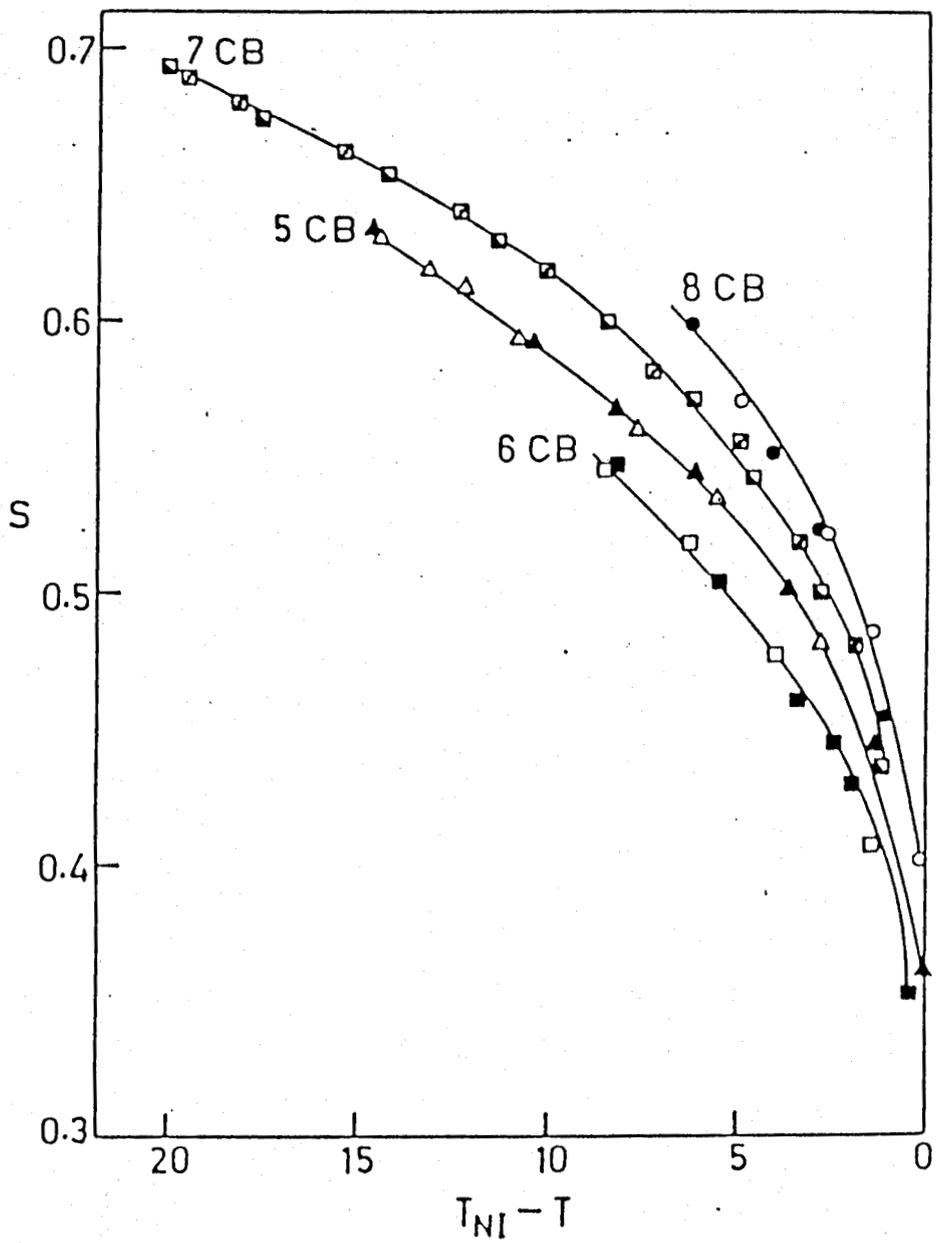
available, $\Delta\alpha$ is not known in any of these cases. Karat and Madhusudana (1979) have used Heger's (1975) Raman measurements of the absolute values of S of 7CB to estimate $\bar{\alpha}/\Delta\alpha$ for that compound. The $\Delta\alpha$ values for all the other homologues could then be estimated by suitably adding the incremental values corresponding to CH_2 groups. However, subsequent measurements (Constant and Decoster 1982, and Bunning et al. 1981) have shown that Heger's values for 7CB are too low, by 25%. For this reason, we now used Miyano's (1978) 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 by Karat and Madhusudana (1976). The values are listed in Table I. The recalculated values of S for nCB, $n = 5$ to 8, are shown in Fig. 1. The order parameters of 7CB and 8CB have been recently determined by Constant and Decoster (1982) using Raman measurements, and our values agree with their data obtained from the $C \equiv N$ band quite well, the former being $3 - 4\%$ lower than the latter.

ΔX_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 (1982) at lower temperatures, but our values tend to be lowered by $\sim$3-4% as T_{NI} is approached. On the other hand, for 7CB the two sets of data agree well close

TABLE 1

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

|	ΔX_{om} x 10^7 cgs units	$\bar{\alpha}/\Delta\alpha$ for $\lambda\,5893\,\overset{\circ}{A}$
5CB	1.76	1.55
6CB	1.83	1.64
7CB	1.53	1.71
8CB	1.61	1.81
8OÇB	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.

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, $\Delta X_m / (n_e^2 - n_o^2) / (\overline{n^2} - 1)$ does not remain constant but tends to increase by a few per cent as T_{NI} is approached for both 5CB and 7CB. This point was also noted for the case of 5CB by Bunning et al. (1981). On the other hand, with the data of Schad et al. (1979) on ΔX_m of 7CB, the above mentioned ratio does not show any systematic variation with temperature. Further, $(n_e^2 - n_o^2) / (\overline{n^2} - I$ is found to be proportional to the order parameters determined by the Raman measurements on the $C \equiv N$ band of 5CB (Miyano 1978), 7CB and 8CB (Constant and Decoster 1982) to within experimental errors. Consequently we believe that we can rely on the ΔX_m values calculated by us.

Using the density data given by Dunmur and Miller (1979) one can evaluate the anisotropy of the volume diamagnetic anisotropy AX [see Eq. (2)]. In conjunction with the Freedericksz threshold measurements (Karat and Madhusudana 1976, 1977) the absolute values of the elastic constants can now be obtained; the results for K_{11}, K_{22} and K_{33} of nCB 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. (1981), who have directly used the ΔX_m data of Buka and de Jeu (1982) in their analysis. In view of the possible errors in the various input parameters in the two analyses, this agreement in the absolute
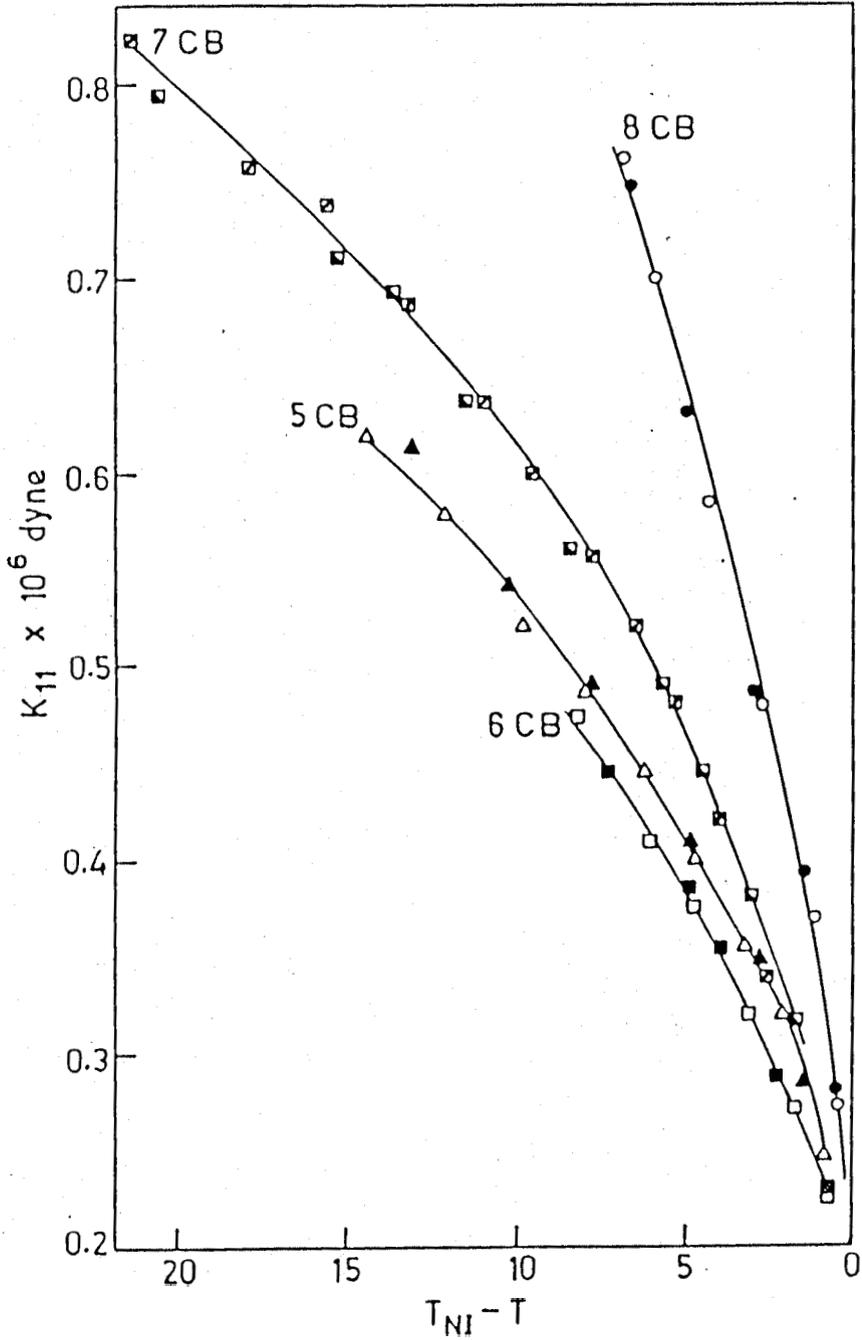
Figure 2

Variation of the splay elastic constant as a function of the relative temperature in the nematic phase of 'I¹-n-alkyl-4-cyanobiphenyls. Results of independent experiments have been marked separately.
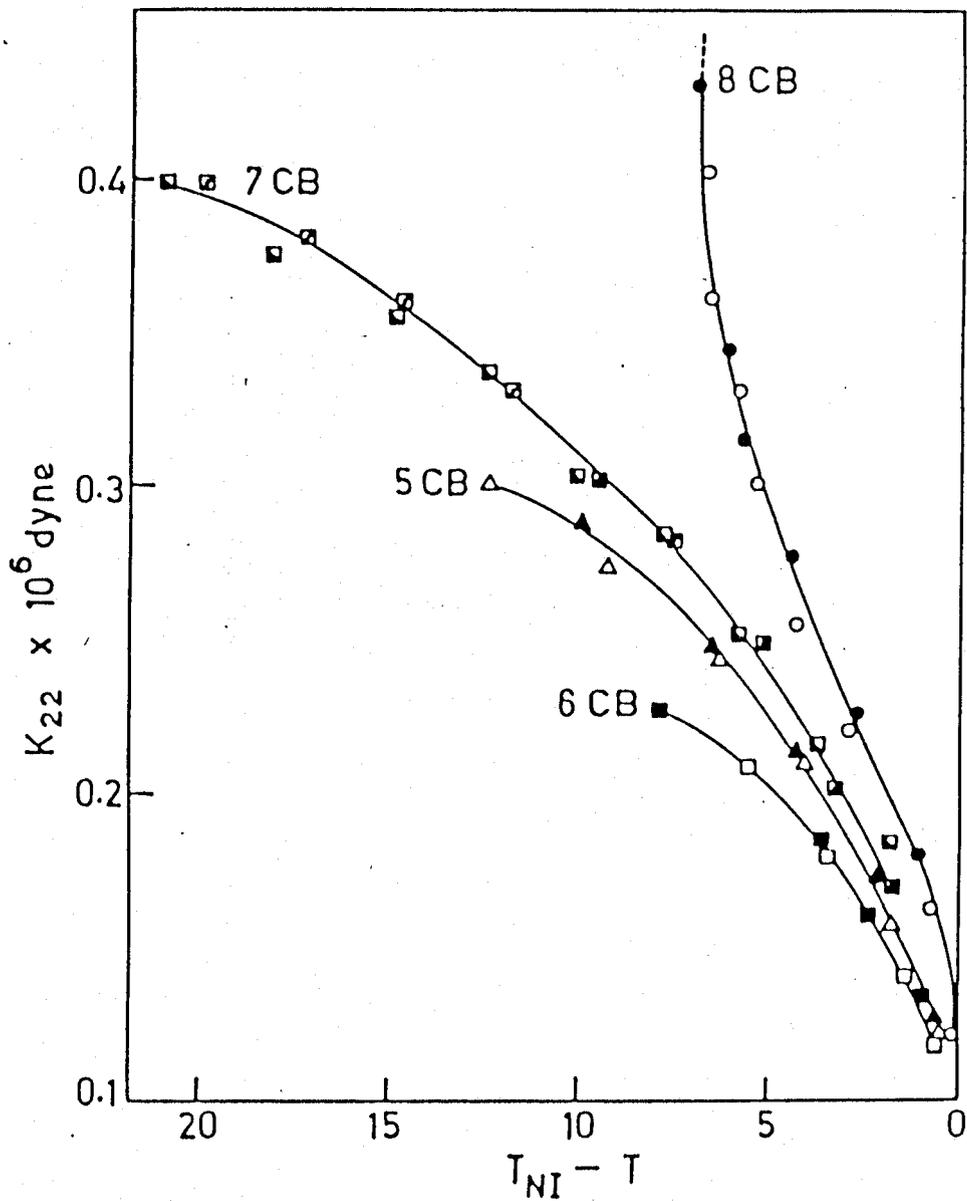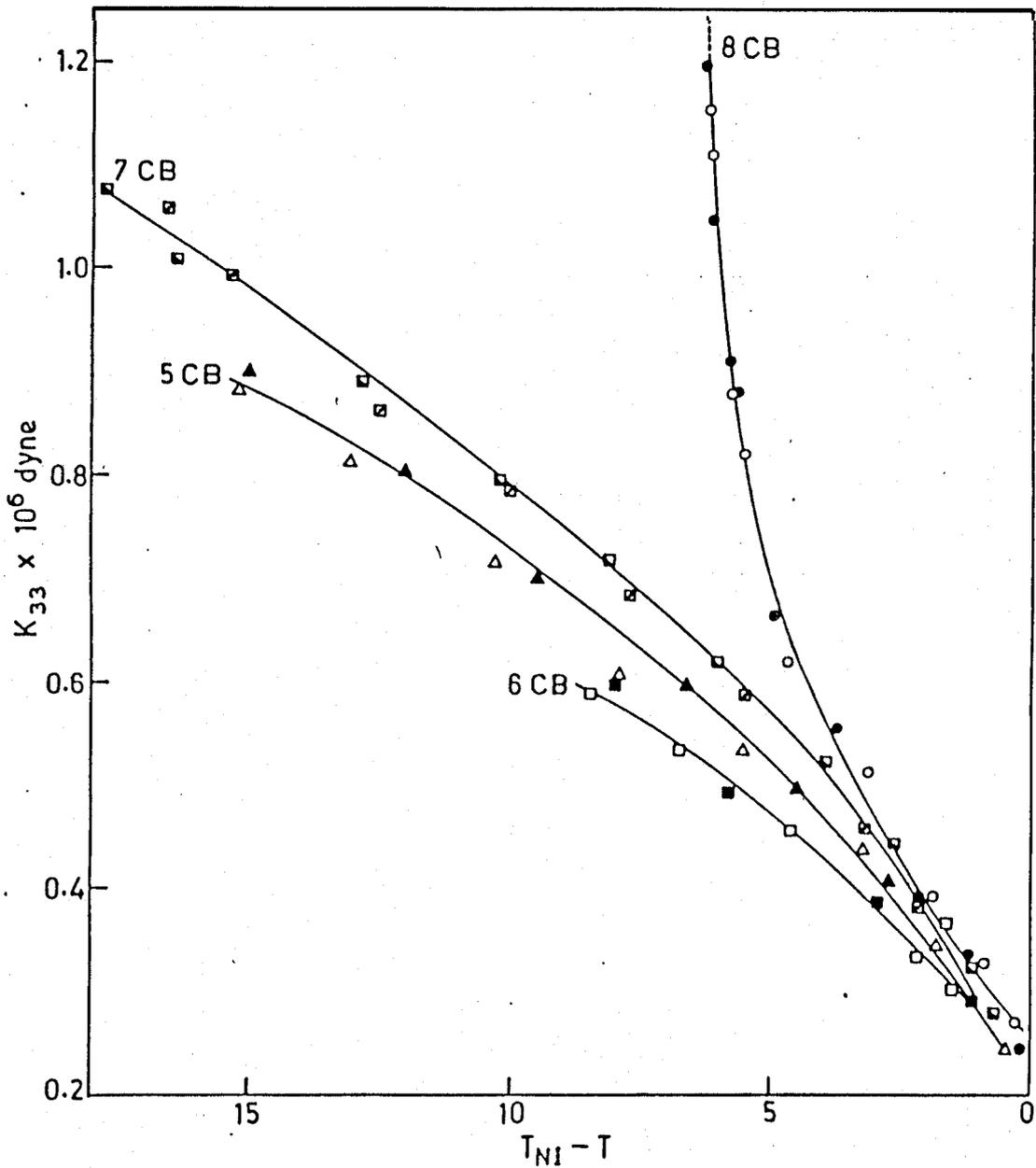
Figure 3

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.
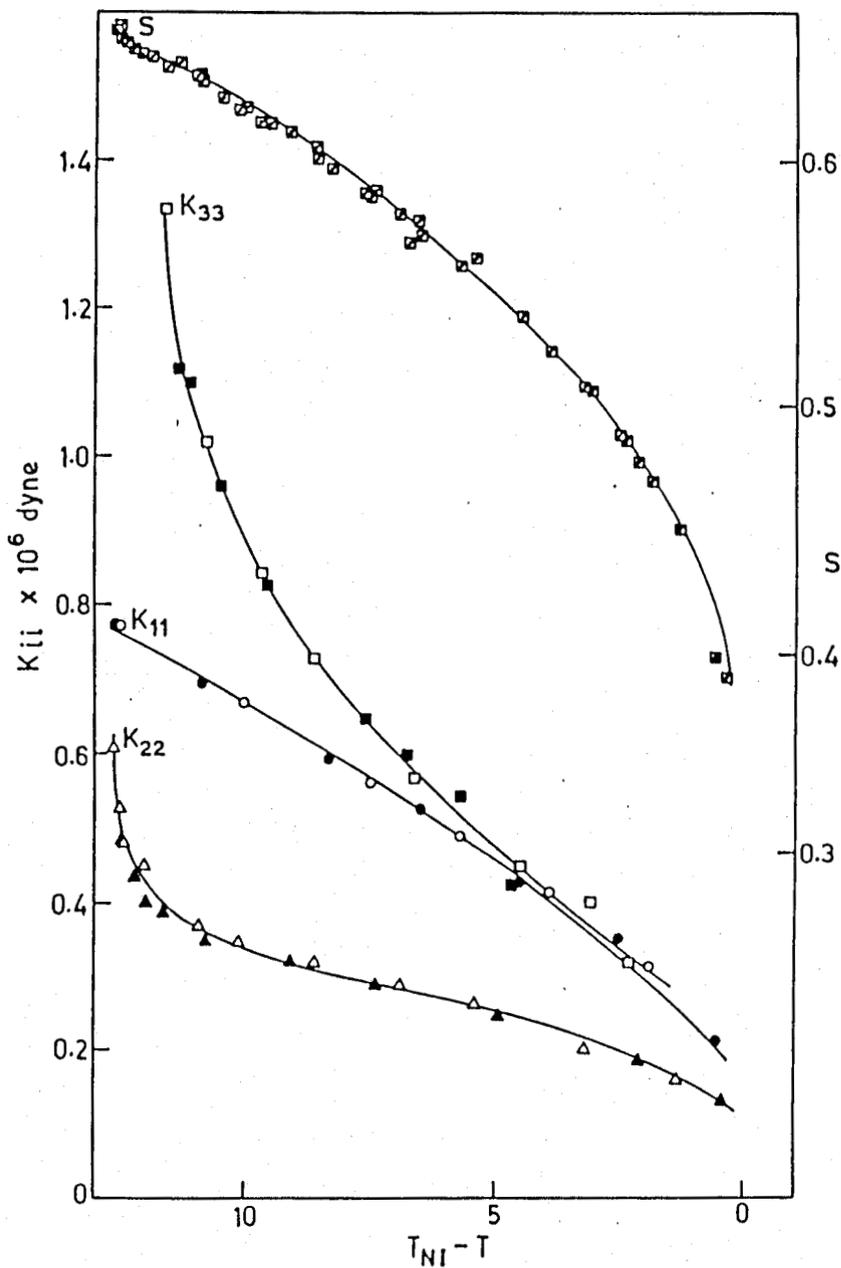
Figure 4

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.

values can be considered to be quite good. Schad and Osman (1981) have listed $K_{11}/\Delta\chi$, $K_{22}/\Delta\chi$ and $K_{33}A$ of 7CB determined by 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 twist distortion, which was developed by Madhusudana et al. (1973) and used in measurements by Karat and Madhusudana (1977). No other measurements of K_{22} are available for comparison.

The order parameters and elastic constants of 80CB were similarly recalculated and are presented in Fig. 5. The K_{11} value close to the smectic-nematic transition point of this compound agrees reasonably well with the value obtained on the basis of an analysis of X-ray scattering experiments on the smectic A phase of this compound (Litster 1980).

A.3. CONCLUSION

In conclusion, we believe that the recalculated absolute values of the order parameters and splay and bend elastic constants are accurate to about ±5%. The twist elastic constant is intrinsically more difficult to measure (Madhusudana et al. 1973), 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 by Karat and Madhusudana (1976, 1977, 1978), since they were based on the relative rather than the absolute values.

Figure 5

Variation 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.

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