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Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 29 Aug 2007.

To cite this article: P. P. Karat & N. V. Madhusudana (1976): Elastic and Optical Properties of Some 4'-n-Alkyl-4-Cyanobiphenyls, *Molecular Crystals and Liquid Crystals*, 36:1-2, 51-64

To link to this article: <http://dx.doi.org/10.1080/00268947608084830>

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Elastic and Optical Properties of Some 4'-*n*-Alkyl-4-Cyanobiphenyls

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(Received December 5, 1975, in final form April 28, 1976)

The bend elastic constants (k_{33}) and order parameters (S) derived from optical measurements in the nematic phase of pentyl, hexyl, heptyl and octyl cyanobiphenyls (5CB, 6CB, 7CB and 8CB respectively) are reported. The odd-even effect is clearly seen in the k_{33} values of all four compounds and in the S values of the first three. 5CB, 6CB and 7CB show only the nematic mesophase but their elastic constants indicate the existence of smectic-like short range order. For example, even the lowest homologue, 5CB, does not obey the law $k_{33} \propto S^2$ given by the mean field theory. 7CB has about the same order parameter as 5CB but a much higher elastic constant. 8CB, which shows a smectic A phase as well, exhibits a lower k_{33} than 7CB near the nematic-isotropic transition point but a pronounced pretransitional increase near the A-N transition.

INTRODUCTION

The elastic constants of nematic liquid crystals are particularly sensitive to the order in the mesophase. Mean field theories^{1,2} predict that $k_{ii} \propto S^2$ where k_{ii} stand for the elastic constants and S for the long range orientational order parameter, ignoring a volume-dependent term which does not contribute much to the variation of k_{ii} . If the nematic phase goes over to a smectic A phase at a lower temperature, the bend and twist deformations become difficult due to the build-up of smectic-like short range order. As a consequence, the corresponding elastic constants exhibit pretransition anomalies as the nematic-smectic A transition point is approached.³⁻⁵ We have undertaken the experimental determination of the elastic constants of several compounds with a view to studying these aspects of the problem. In the present communication we report the bend elastic constants and the order parameters derived from refractive indices of the pentyl, hexyl, heptyl and octyl cyanobiphenyls. These are colourless, exceptionally stable room

temperature liquid crystals⁶ and, because of their strong positive dielectric anisotropy, they are very useful in applications for display devices.

There has been one earlier study on the elastic constants of a homologous series of compounds by Gruler,⁷ but these compounds exhibit a smectic C type of short range order, whereas the compounds used in the present investigation exhibit a smectic A type of short range order.

EXPERIMENTAL

All the compounds used in this investigation were synthesized in our chemistry laboratory. Of the four compounds studied, the first three homologues (5CB, 6CB and 7CB) exhibit only the nematic mesophase, while the octyl derivative (8CB) exhibits both the smectic A and the nematic mesophases. The relevant phase transition points are collected in the following table.

TABLE I
Transition points of 4'-n-alkyl-4-cyanobiphenyls

	K-A or K-N	A-N	N-I
5CB	22.4°C	—	34.5°C
6CB	13.8°C	—	28.8°C
7CB	28.5°C	—	41.9°C
8CB	20.5°C	33.3°C	40.1°C

K = Crystal; A = Smectic A; N = Nematic;
I = Isotropic.

Bend elastic constants

We used the well known Freedericksz transition technique, in which the magnetic field H_0 necessary to start a distortion in a homeotropically aligned sample with its undistorted director set perpendicular to the applied field is measured. The bend elastic constant is given by

$$k_{33} = \frac{\Delta\chi H_0^2 d^2}{\pi^2} \quad (1)$$

where $\Delta\chi$ is the anisotropy of the *volume* diamagnetic susceptibility of the medium and d the thickness of the sample. We can write $\Delta\chi = \Delta\chi_{\text{om}} \rho S$, where S is the degree of the orientational order of the medium, ρ its density and $\Delta\chi_{\text{om}}$ the anisotropy of the *mass* susceptibility of the perfectly oriented medium with $S = 1$. Then we can re-express (1) as

$$(k_{33}/\Delta\chi_{\text{om}}) = (H_0^2 S \rho) d^2 / \pi^2. \quad (2)$$

Since the magnetic susceptibility data are not available for these compounds, we have estimated $\Delta\chi_{\text{om}}$ from the magnetic data on biphenyl as we shall explain later. Also, as we shall show in the later discussion, the temperature variation of the order parameter and the density can be derived from optical measurements.

The sample was taken between two optical flats (~ 2 mm thick) separated by mylar spacers. $25\text{ }\mu\text{m}$ thick samples were adequate for measurements on the three lower homologues. In the case of 8CB, $\sim 50\text{ }\mu\text{m}$ thick samples were needed to keep the values of H_0 within the maximum field attainable with our magnet, as the bend constant becomes very large near the *A-N* transition point in this case (see Eq. 1). Glass plates treated with a dilute aqueous solution of a cleaning agent (Teepol, BDH India Ltd.), and subsequently dried, were enough to homeotropically align 6CB, 7CB and 8CB samples. However, in the case of 5CB it was necessary to treat the glass plates with a dilute solution of cetyl trimethyl ammonium bromide in chloroform to get a good alignment. The specimen was mounted in a copper block whose temperature could be maintained at any desired value (to an accuracy of $\sim 0.02^\circ\text{C}$) above the ambient by means of an electric oven. The sample chamber was filled with nitrogen and the temperatures were measured by means of a copper-constantan thermocouple which was calibrated against a thermometer provided with a hot stage microscope used for melting point determinations. The field was applied by means of an electromagnet and was calibrated with a Gaussmeter (Model 750, Radio Frequency Laboratories, USA). For a correct determination of the true Freedericksz transition field H_0 , it is essential to maintain the undistorted director exactly normal to the applied field. This was ensured by adjusting the orientation of the sample chamber by means of suitable screws to get the maximum number of inversion walls in the field of view, with an applied field above H_0 . The distortion was detected optically by viewing the medium between crossed polaroids through a low power microscope. The actual thickness of the sample was always measured by using channelled spectrum from an air gap in the sample.

Refractive indices

The principal indices of refraction of the medium were determined by the prism method. Carefully selected glass plates, which had plane parallel surfaces were used in making the low-angled ($5\text{--}6^\circ$) prisms. The liquid crystal was aligned with its director parallel to the refracting edge by unidirectional rubbing of the glass surfaces. The indices were measured for three wavelengths ($\lambda 5461\text{ }\text{\AA}$, $\lambda 5893\text{ }\text{\AA}$ and $\lambda 6328\text{ }\text{\AA}$) by means of a precision goniometer-spectrometer (Prazisionsmechanik, East Germany) reading to $2''$ of arc.

TABLE II
Refractive indices of 4'-*n*-alkyl-4-cyanobiphenyls
(i) 5CB

$(T_{NI} - T)$ in °C	$\lambda 5461 \text{ \AA}$		$\lambda 5893 \text{ \AA}$		$\lambda 6328 \text{ \AA}$	
	n_o	n_e	n_o	n_e	n_o	n_e
14.6 (II) ^a	1.536	1.739	1.532	1.727	1.528	1.719
14.4 (I)	1.536	1.737	1.532	1.726	1.528	1.717
13.1 (I)	1.537	1.734	1.532	1.723	1.528	1.714
12.2 (II)	1.538	1.733	1.533	1.722	1.528	1.713
10.7 (I)	1.539	1.727	1.533	1.716	1.530	1.708
10.3 (II)	1.539	1.727	1.534	1.716	1.530	1.708
8.2 (II)	1.540	1.721	1.535	1.711	1.531	1.702
7.6 (I)	1.541	1.718	1.536	1.707	1.531	1.698
6.0 (II)	1.542	1.714	1.536	1.703	1.532	1.695
5.4 (I)	1.542	1.712	1.537	1.701	1.533	1.693
3.5 (II)	1.544	1.703	1.539	1.693	1.535	1.685
2.8 (I)	1.546	1.699	1.541	1.685	1.537	1.680
1.4 (II)	1.550	1.689	1.544	1.679	1.540	1.672
0.1 (II)	1.557	1.670	1.551	1.662	1.547	1.656

^a I and II in parentheses refer to two independent measurements.

(ii) 6CB

$(T_{NI} - T)$ in °C	$\lambda 5461 \text{ \AA}$		$\lambda 5893 \text{ \AA}$		$\lambda 6328 \text{ \AA}$	
	n_o	n_e	n_o	n_e	n_o	n_e
8.4 (I)	1.540	1.703	1.535	1.692	1.531	1.684
8.1 (II)	1.540	1.703	1.535	1.692	1.531	1.684
6.3 (I)	1.542	1.695	1.537	1.686	1.533	1.679
5.4 (II)	1.543	1.693	1.538	1.683	1.534	1.675
3.9 (I)	1.545	1.687	1.540	1.677	1.536	1.669
3.4 (II)	1.546	1.683	1.541	1.673	1.537	1.666
2.5 (I)	1.547	1.679	1.542	1.670	1.538	1.663
1.9 (II)	1.548	1.675	1.543	1.667	1.539	1.659
1.3 (I)	1.550	1.671	1.545	1.662	1.541	1.654
0.4 (II)	1.555	1.659	1.550	1.651	1.545	1.654

RESULTS

a) *Order parameters* Two independent sets of measurements of refractive indices were made on separate samples for each compound and the values are given in Table II. The birefringence in the nematic phase of these colourless compounds lies in the range 0.1–0.2.

TABLE II (continued)

(iii) 7CB

$(T_{\text{NI}} - T)$ in °C	$\lambda 5461 \text{ \AA}$		$\lambda 5893 \text{ \AA}$		$\lambda 6328 \text{ \AA}$	
	n_o	n_e	n_o	n_e	n_o	n_e
20.0 (II)	1.523	1.719	1.519	1.709	1.516	1.701
19.4 (I)	1.524	1.718	1.519	1.707	1.516	1.699
18.2 (I)	1.524	1.716	1.519	1.705	1.516	1.697
17.4 (II)	1.524	1.714	1.520	1.704	1.516	1.696
15.1 (I)	1.524	1.710	1.520	1.700	1.517	1.692
14.3 (II)	1.525	1.708	1.520	1.698	1.517	1.690
12.4 (I)	1.525	1.705	1.520	1.695	1.517	1.687
11.3 (II)	1.525	1.702	1.521	1.692	1.518	1.685
10.0 (I)	1.526	1.699	1.521	1.689	1.518	1.682
8.5 (II)	1.527	1.696	1.522	1.686	1.519	1.679
7.2 (I)	1.527	1.692	1.523	1.682	1.519	1.675
6.2 (II)	1.528	1.689	1.524	1.680	1.520	1.672
4.9 (I)	1.529	1.685	1.525	1.675	1.521	1.668
4.5 (II)	1.530	1.682	1.526	1.673	1.522	1.665
3.3 (I)	1.532	1.677	1.527	1.667	1.524	1.660
2.9 (II)	1.533	1.673	1.528	1.664	1.525	1.657
2.0 (I)	1.535	1.669	1.530	1.660	1.526	1.653
1.2 (II)	1.539	1.658	1.533	1.651	1.529	1.645

(iv) 8CB

$(T_{\text{NI}} - T)$ in °C	$\lambda 5461 \text{ \AA}$		$\lambda 5893 \text{ \AA}$		$\lambda 6328 \text{ \AA}$	
	n_o	n_e	n_o	n_e	n_o	n_e
6.3 (II)	1.525	1.682	1.520	1.673	1.517	1.666
5.1 (I)	1.526	1.676	1.521	1.667	1.518	1.659
4.2 (II)	1.527	1.672	1.523	1.663	1.520	1.657
3.0 (II)	1.529	1.667	1.525	1.658	1.521	1.651
2.7 (I)	1.530	1.666	1.524	1.657	1.521	1.651
1.5 (I)	1.532	1.659	1.527	1.651	1.523	1.643
1.2 (II)	1.535	1.653	1.530	1.645	1.526	1.639
0.2 (I)	1.537	1.643	1.533	1.636	1.529	1.630
-0.2 (I)	1.572		1.566		1.560	

We use the Vuks' relation,^{8,9} which is known to yield good results,^{10,11} to derive the polarizabilities from the refractive indices. The relation is

$$\frac{4\pi}{3} v\alpha_i = \frac{n_i^2 - 1}{n^2 + 2} \quad (3)$$

where v is the number of molecules per unit volume, α_i is a principal polarizability of the medium, n_i the corresponding refractive index and

$\overline{n^2} = \frac{1}{3} \sum_i n_i^2$. The order parameter is then given by

$$S = (\alpha_e - \alpha_o)/\Delta\alpha \quad (4)$$

where the subscripts *e* and *o* stand for extraordinary and ordinary, and $\Delta\alpha$ is the anisotropy of polarizability of the perfectly oriented medium with $S = 1$. We need the density data to derive the polarizabilities at different temperatures. Since experimental density data are not available, we derive the relative variation of the density from the relation

$$\rho = \frac{3M}{4\pi N\bar{\alpha}} \frac{\overline{n^2} - 1}{\overline{n^2} + 2} \quad (5)$$

where M is the molecular weight, N the Avogadro number and $\bar{\alpha}$ the average polarizability.

The absolute densities were measured approximately at room temperature for 5CB and 7CB which exhibit the nematic phase at that temperature, using a small specific gravity bottle (~ 0.5 cc in volume). The density was calibrated against that of double-distilled water. The absolute values are expected to be accurate to about $\pm 0.1\%$.

$\bar{\alpha}_{5CB}$ and $\bar{\alpha}_{7CB}$ can now be evaluated using eqn. (5). The average polarizabilities of 6CB and 8CB are estimated by adding to $\bar{\alpha}_{5CB}$ and $\bar{\alpha}_{7CB}$ the polarizability of a CH_2 group, which is equal to $(\bar{\alpha}_{7CB} - \bar{\alpha}_{5CB})/2$. The density at any temperature can now be calculated with the aid of Eq. (5). (The density of 6CB was also independently measured by weighing a small length (~ 1 cm) of the liquid crystal taken in a capillary tube. The calculated and measured values agree quite well.) The densities at room temperature and the average polarizabilities are tabulated below.

The temperature variation of the densities of all the four compounds as functions of $(T_{NI} - T)$ are shown in Figure 1. For each compound, the relative values are estimated to be accurate to better than 0.0005 units. We have also evaluated the molar volumes $V (= M/\rho)$ of the four compounds:

	5CB	6CB	7CB	8CB
$T_{NI} - T = 5^\circ\text{C}$	244.5 cc	259.9 cc	277.3 cc	293.0 cc

TABLE III

	ρ at 25°C	$\bar{\alpha} \times 10^{24} \text{ cm}^3$		
		$\lambda 5461 \text{ \AA}$	$\lambda 5893 \text{ \AA}$	$\lambda 6328 \text{ \AA}$
5CB	1.023	33.2	32.9	32.6
6CB	1.012	35.0	34.7	34.4
7CB	1.010	36.8	36.4	36.1
8CB	0.995	38.6	38.2	37.9
(at 35°C)				

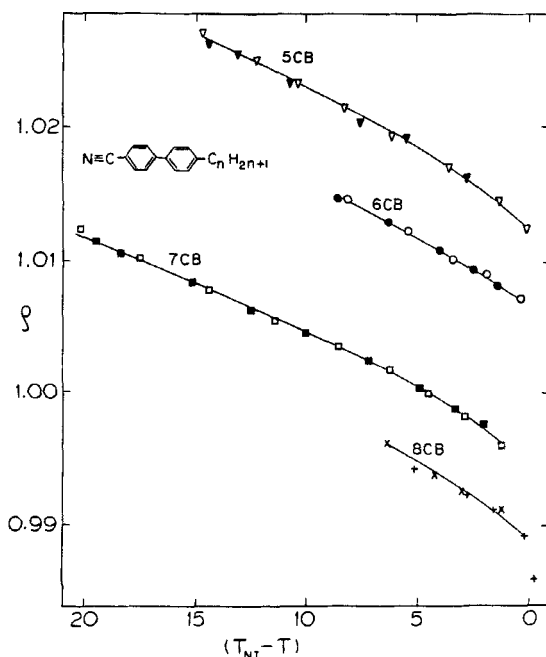


FIGURE 1 Variation of density, as derived from optical measurements, in the nematic phase of 4'-*n*-alkyl-4-cyanobiphenyls as a function of the relative temperature. Results of two independent experiments have been marked separately. Each symbol represents a value averaged over three wavelengths.

It is seen that the increment in V is somewhat larger on going from the even to the next higher odd member than from the odd to the even member, as a consequence of the alternation in T_{NI} (see Table I).

Using (3), (4) and (5) we can write

$$S = \frac{n_e^2 - n_o^2}{n^2 - 1} \left(\frac{\bar{\alpha}}{\Delta\alpha} \right). \quad (6)$$

It is obvious from Eq. (5) that we have to know the values of $(\bar{\alpha}/\Delta\alpha)$ for the different wavelengths to be able to derive independent values of S from the measurements on those wavelengths.

There has been a recent determination of the absolute values of S in 7CB using Raman depolarization measurements.¹² The relative values agree with our data quite well; for example, with $(\bar{\alpha}/\Delta\alpha) = 1.34$ for $\lambda 5893 \text{ \AA}$, the agreement is better than $\pm 2\%$ throughout the nematic range.

We will now make an approximate calculation of the absolute values of the order parameters of the other three compounds. In this series of compounds, only one end has the alkyl chain. We can see from Table III that $\bar{\alpha}$ varies by

about 5% between successive members of the series. $\Delta\alpha$ is expected to alternate, taking higher values in the case of odd members. As we have already seen, our data on 7CB can be normalized with the Raman measurements. This yields $\Delta\alpha_{7\text{CB}} = 27.2 \text{ \AA}^3$ for $\lambda 5893 \text{ \AA}$. The increment in $\Delta\alpha$ between successive members of the homologous series is calculated as follows: From any given member of the series, a CH_2 -group has to be added to get the next member. This means that one C—C bond and two C—H bonds make extra contributions to the anisotropy of polarizability of the new compound compared to that of the previous one. Assuming, for the sake of simplicity, an all-*trans* configuration of the chain, the extra C—C bond makes a large angle with the long axis of the molecule if the new member is an even member. (Again for the sake of simplicity, the molecular long axis is assumed to coincide with the long axis of the aromatic part.) For an odd member, the last C—C bond almost coincides with the long axis. Knowing the anisotropy of polarizability of the C—C and C—H bonds, we can calculate the increment to the longitudinal component of the polarizability by using the relation $\delta\alpha_{\parallel} = \sum \gamma \cos^2 \beta$ where the summation extends over all the principal polarizabilities γ of all the additional bonds and β the angle that the corresponding principal direction makes with the long axis of the molecule.¹³ The increment to the transverse polarizability of the molecule, viz., $\delta\alpha_{\perp}$ can be calculated by a similar procedure. The result of these calculations is that $\delta(\alpha_{\parallel} - \alpha_{\perp}) = \delta(\Delta\alpha) \simeq 0.27 \text{ \AA}^3$ when going from an even to the next higher odd member of the series, while it is $\simeq -0.10 \text{ \AA}^3$ while going from an odd to the next higher even member. Using these values, we have calculated the approximate values of the order parameters of this series. The *S*-values calculated from the index data on the different wavelengths have been normalized at the lowest temperature for which the measurement is available for each compound. The temperature variations of *S* thus derived agree to within $\pm 1\%$. (The good agreement can also be taken as an evidence for the validity of the application of the Vuks' relation to nematic compounds.) The *S*-values averaged over three wavelengths are shown in Figure 2. The data are also shown at $T_c - T = 2^\circ\text{C}$ in Figure 5. It is noteworthy that the *S*-value alternates for the first three members, but *increases* between the 7th and 8th members, contrary to the prevalent trend. (The initial alternation as well as the increase for 8CB of the *S*-values are not very strong, possibly since even the lowest member itself has 5 carbon atoms in the chain.) While this result has to be confirmed by an independent experiment like for instance NMR, it would appear that this increase in the orientational order is connected with 8CB exhibiting the smectic phase at lower temperatures.

b) *Elastic constants* Using the relation (2) we can now evaluate $k_{33}/\Delta\chi_{\text{om}}$. If ΔK is the anisotropy of the susceptibility of a gram-molecule of the sub-

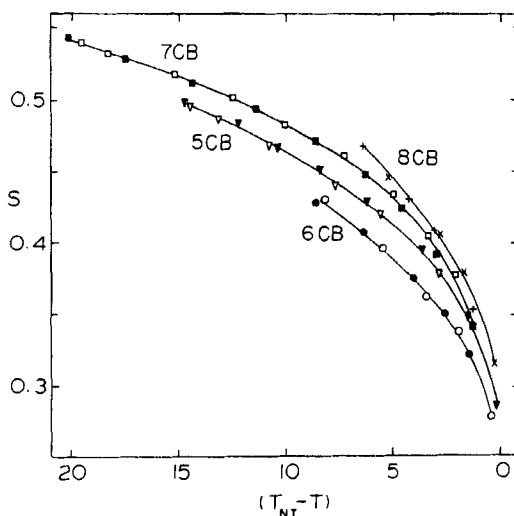


FIGURE 2 Variation of the order parameter as a function of the relative temperature in the nematic phase of 4'-*n*-alkyl-4-cyanobiphenyls. The values for λ_{5461} Å and λ_{6328} Å have been normalized with that of λ_{5893} Å at the lowest temperature. The averaging has been done as in Figure 1.

stance, $\Delta\chi_{om} = \Delta K/M$. Assuming that the anisotropy of susceptibility is essentially determined by the aromatic part of the molecule, ΔK is a constant for all the members of the series. The measurements on biphenyl give $\Delta K = 118.6 \times 10^{-6}$ c.g.s. units.¹⁴ Assuming this value for all the compounds, we have evaluated the absolute values of k_{33} (Figure 3). The alternation in k_{33} is clearly seen near the nematic-isotropic transition temperature. However, the curve for 8CB shoots up as one approaches the smectic-nematic transition point. Since the full variation over the entire temperature range cannot be included in the figure in the last case, we have separately shown it in Figure 4 where the bend constant has been plotted against $\log(T - T_{AN})$.

DISCUSSION

To facilitate comparison of the data for the different members, we have shown in Figure 5 the order parameters and elastic constants at $(T_{NI} - T) = 2^\circ\text{C}$. We have also plotted T_{NI} versus chain length in the figure. Firstly we notice that the order parameters of these compounds are fairly low. However, the k_{33} of even 6CB, which is the lowest in the series, is more than twice that of MBBA at the same relative temperature.¹⁵⁻¹⁷ It is also higher than that of PAA,¹⁸ a compound with a much higher *N-I* transition point. These facts

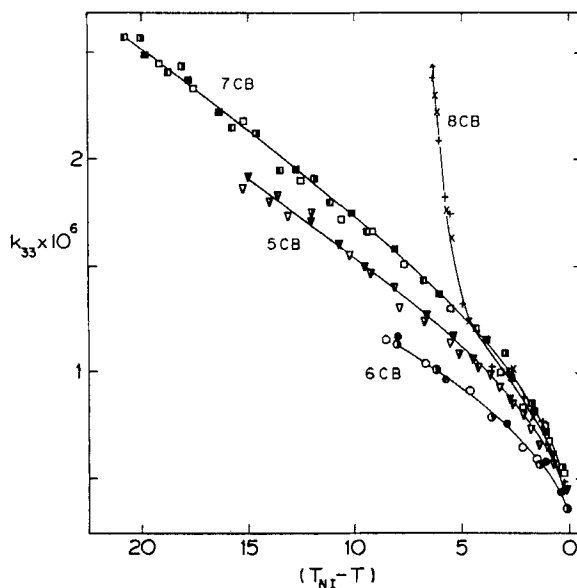


FIGURE 3 Variation of the bend elastic constant as a function of the relative temperature in the nematic phase of 4'-*n*-alkyl-4-cyanobiphenyls. The results of independent experiments have been marked separately.

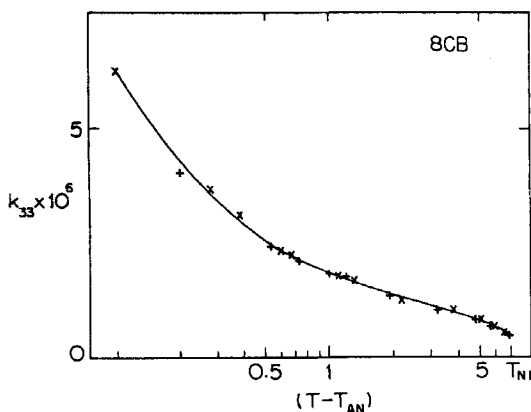


FIGURE 4 Temperature variation of the bend elastic constant of 4'-*n*-octyl-4-cyanobiphenyl.

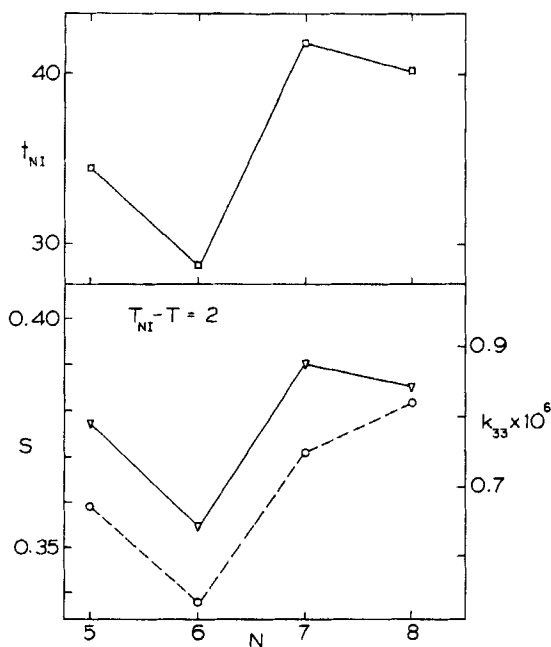


FIGURE 5 The nematic-isotropic transition points (upper section of the diagram), the order parameters and the bend elastic constants (dashed lines and full lines respectively, in the lower section of the diagram) as functions of the number of carbon atoms in the alkyl chain of 4'-*n*-alkyl-4-cyanobiphenyls.

already indicate that cyanobiphenyls have considerable smectic-like short range order.

One expects that the various physical properties of the nematic phase alternate as one ascends the homologous series, in view of the differences in the configuration of the end chain. In the even members of the series, the final C—C bond of the alkyl chain makes, on the average, a large angle with the long axis of the molecule, thus reducing the anisotropy of the molecule and thereby lowering T_{NI} as well as the order parameter. On the other hand, in the odd members the final segment is oriented nearly parallel to the long axis on the average thus enhancing the anisotropy of the molecule, T_{NI} and the order parameter. A detailed statistical thermodynamic treatment of the effect of end-chain conformations on the properties of the nematic phase has been given by Marcelja,¹⁹ using the mean field theory. The fact that in the present series, the order parameter of the 8th member does not follow this trend indicates that near neighbour correlations play a prominent role and that the mean field theory may not be adequate.

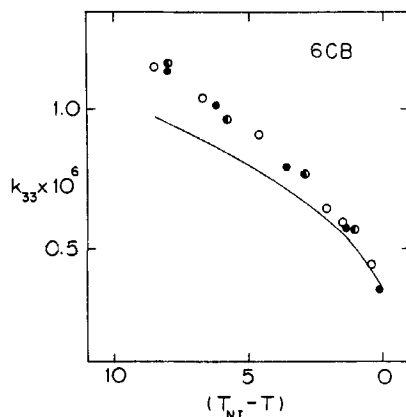


FIGURE 6 Comparison of the temperature variation of the bend elastic constant with the prediction of the mean field theory. Circles represent the experimental values for 4'-n-hexyl-4-cyanobiphenyl. The curve represents the theoretical variation according to the relation $k_{33} \propto S^2$.

An interesting feature of the data presented above is that even in the cases of 5CB and 6CB the prediction of mean field theories^{1,2} that $k_{33} \propto S^2$ is not satisfied (Figure 6). A least squares fitting of the data for a law of the type $k_{33} \propto S^\gamma$ indicates that $\gamma \approx 2.4$ –2.6. The molecules of this series of compounds are strongly polar, a nitrile group with a dipole moment of about 4 debyes attached practically parallel to the long axis of the molecule at one end. In such a case, there should be a strong antiparallel correlation amongst the neighbouring molecules.²⁰ Indeed recent X-ray studies of Leadbetter *et al.*²¹ have shown that these compounds give rise to meridional reflections with a repeat unit along the texture axis of about 1.4 molecular lengths, the corresponding correlation length being about 4–5 repeat units. This indicates that there is a smectic A type of short range order in the medium, wherein each layer is made up of two molecules which lie with their polar ends interdigitated because of strong antiparallel correlations. Hence the relation predicted by the mean field theory is no longer valid.

The bend constant which describes the elasticity corresponding to the gradient along the director of the distortion is far more sensitive to short-range order structure than the other two elastic constants.¹⁸ Thus, for instance, Gruler finds that even in *p*-azoxyanisole k_{33} does not follow the mean field theory, while k_{11} does. On the other hand, in the case of MBBA, Haller¹⁵ and independently Poggi *et al.*¹⁶ who used the optical technique to detect the critical field found that the mean field theory is valid for k_{33} . (However Greulich *et al.*¹⁷ who used electrical conductivity measurements to determine k_{33} of the same compound found that the mean field theory is not valid.)

Another noteworthy result of the present study is that even though 7CB has practically the same orientational order as 5CB at any given relative temperature near T_{NI} (see Figure 5), it has a higher value of the elastic constant. This immediately suggests a stronger smectic-like short range order in 7CB. In fact it is estimated from the correlation lengths that in 5CB the ordered regions may contain about 100 molecules while in 7CB the number is ~ 150 .²¹ The larger values of k_{33} in 7CB can be understood in terms of the greater smectic-like short-range order, since the contribution to k_{33} from this type of short range order is given by $k_{33} \propto \xi$ where ξ is a measure of the correlation length, or the size of the smectic-like domains.³

Even though 8CB actually exhibits the smectic A phase and its orientational order is also somewhat higher, its bend constant is slightly *lower* than that of 7CB near the *N-I* transition point (see Figure 5). At the moment, we can only speculate on the possible reason for this unexpected behaviour. Firstly, the structure of the double-molecular layer itself appears to be practically the same as in the lower homologues: for instance, X-ray evidence²² indicates that the ratio of the layer thickness to the molecular length is practically unaltered. The higher value of the orientational order parameter in the nematic phase of 8CB appears to indicate a stronger antiparallel correlation in this case. This could be expected to give rise to a somewhat larger in-plane or transverse correlation length (ξ_{\perp}) compared to 7CB. However, close to the *N-I* transition point the overall smectic-like short range order must be lower than in 7CB, since the bend elastic constant has a lower value. It probably means that the longitudinal correlation length (ξ_{\parallel}) is smaller in 8CB than in 7CB close to the *N-I* point.³ In other words, we believe that $\xi_{\parallel}/\xi_{\perp}$ decreases when we go from 7CB to 8CB. (This can be tested by a measurement of k_{22} , which we have undertaken.) This decrease should be connected with the orientation of the end-group which makes a large angle with the director. (The next member of the series, viz., 9CB, for which the conditions for the formation of a smectic phase are more favourable, the *A-N* point occurs just three degrees below the *N-I* point.⁶) As the temperature of 8CB in the nematic phase is lowered, both the correlation lengths (which are proportional to each other) increase, finally giving rise to the smectic phase. As the *A-N* transition entropy in 8CB is extremely low the bend constant shows a very strong pretransition enhancement (see Figure 4).

The strong tendency to form double molecular layers due to antiparallel correlations between neighbours might also explain the experimentally observed fact that 8CB, 9CB, 4'-octyloxy-4-cyanobiphenyl as well as CBOOA tend to have an almost second-order *A-N* transition, even though T_{AN}/T_{NI} in all these cases is rather high compared to the value predicted by the mean field theory.²³

Finally, there is a close correlation between the bend constant and the

nematic-isotropic transition temperature. As can be clearly seen in Figure 5, there is a strong similarity in the alternation of these two properties.

Thus, it appears that the detailed nature of the short-range structure will have a predominant influence over the bend elastic constants of nematic liquid crystals. We have undertaken the measurements of the other elastic constants of these compounds to elucidate these points further.

Acknowledgements

We are deeply indebted to Professor S. Chandrasekhar for several useful discussions. Our thanks are also due to Dr. V. Surendranath, Mr. B. K. Sadashiva and Mr. M. R. Subrahmanyam for the chemicals.

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