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Elasticity and Orientational Order in Some trans-p-n-Alkoxy-α-methyl Cyanophenyl Cinnamates

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Elasticity and Orientational Order in Some *trans-p-n*-Alkoxy-α-methyl Cyanophenyl Cinnamates

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The splay (k_{11}), twist (k_{22}) and bend (k_{33}) elastic constants determined by the Freedericksz method and the orientational order parameters (s) derived from optical measurements in the nematic phase of six homologues of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates (*n* OMCPC) are reported. The data close to the nematic-isotropic transition point (T_{NI}) are compared with T_{NI} and the heats of transition (ΔH). The temperature-variation of elastic constants is discussed in terms of existing theories. The pretransitional increase in the twist and bend constants near the nematic-smectic A transition point (T_{NA}) of 10 OMCPC has also been analysed.

INTRODUCTION

In continuation of our experimental studies on the elasticity and orientational order in nematic liquid crystals,[1–3] we report in this paper the results on *n* OMCPC.[4] These compounds are colourless and stable, and have the highly polar nitrile group at one end of the molecule (Figure 1). They also have relatively low melting points (Figure 2). The compounds with $n \geq 2$ are mesomorphic. The third, fifth, sixth and seventh members are monotropic nematic, the second, fourth, eighth, ninth and tenth members enantiotropic nematic, the last homologue exhibiting a monotropic smectic phase also. We have studied compounds with $n = 2$, 3, 4, 8, 9 and 10, since only these members exhibit the nematic phase over reasonably large temperature ranges.

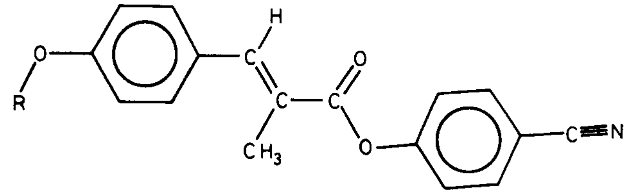

FIGURE 1 Structural formula of *trans*-*p*-*n*-alkoxy-α-methyl cyanophenyl cinnamate.

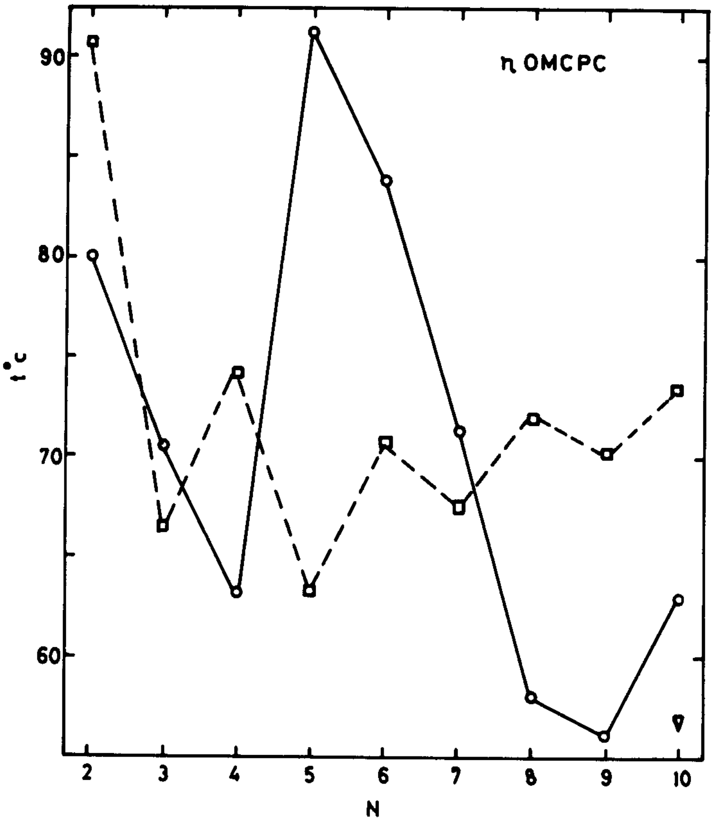

FIGURE 2 Melting points (circles), nematic-isotropic transition points (squares) and smectic-nematic transition points (inverted triangles) of *trans*-*p*-*n*-alkoxy-α-methyl cyanophenyl cinnamates.

EXPERIMENTAL

The elastic constants were determined using the Freedericksz transition method. The refractive indices for three wavelengths were determined by the prism method. The densities of two compounds, viz., 2 OMCPC and 8

OMCPC were measured at one temperature using the capillary method. All the experimental details have been given in our earlier publications[1–3] and will not be repeated here. Since the materials supercooled considerably in the nematic phase, the measurements were made while cooling the samples. The viscosity of the esters is quite high as evidenced by the fact that the time taken by the sample to relax back after the deforming magnetic field is removed is somewhat long. Hence care was taken to see that the sample was in the magnetic field for a sufficiently long time (~ 1 min) before taking the measurements.

RESULTS

The refractive indices for three wavelengths are given in Table I. The Vuks formula[5,6] can be used to calculate the average polarizabilities (α) from the measured values of refractive indices and densities in 2 OMCPC and 8 OMCPC. Assuming a uniform increment of $[(\alpha_8 - \alpha_2)/6]$ in α on going from one to the next higher homologue of the series, α can be estimated for all the other compounds. The Vuks formula can now be reused[2] to calculate the temperature variation of density in all the cases. The results are shown in Figure 3.

We can now calculate the anisotropy of polarizability of the nematic medium. If we also know the anisotropy $\Delta\alpha$ for a perfectly oriented medium with $s = 1$, we can calculate the s-value at any temperature. Fernandes and Venugopalan[7] have recently determined the orientational order in 8 OMCPC using IR dichroic measurements. We can normalize our data on this compound with the IR values by choosing $\alpha/\Delta\alpha = 1.35$ for λ 5893 Å. The values

TABLE I

Refractive indices of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates

$T_{NI} - T$ °C	λ 5461 Å n_o	λ 5461 Å n_e	λ 5893 Å n_o	λ 5893 Å n_e	λ 6328 Å n_o	λ 6328 Å n_e
			(i) 2 OMCPC			
0.5 (I)[a]	1.555	1.704	1.549	1.691	1.543	1.682
1.3 (II)[a]	1.553	1.709	1.546	1.697	1.540	1.689
2.7 (I)	1.549	1.720	1.543	1.706	1.538	1.695
3.8 (II)	1.547	1.725	1.541	1.712	1.535	1.701
6.2 (I)	1.545	1.734	1.538	1.721	1.533	1.710
7.4 (II)	1.544	1.738	1.537	1.724	1.532	1.714
10.6 (I)	1.542	1.747	1.536	1.733	1.531	1.722
13.0 (II)	1.540	1.753	1.534	1.738	1.529	1.727

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

TABLE I (continued)

$T_{NI} - T$ °C	λ 5461 Å n_o	n_e	λ 5893 Å n_o	n_e	λ 6328 Å n_o	n_e
14.9 (I)	1.540	1.757	1.534	1.742	1.529	1.732
18.0 (II)	1.539	1.763	1.533	1.748	1.528	1.737
20.0 (I)	1.539	1.767	1.533	1.752	1.528	1.741
23.6 (II)	1.538	1.773	1.532	1.758	1.527	1.746
26.4 (I)	1.538	1.778	1.532	1.762	1.527	1.751
29.2 (II)	1.537	1.782	1.531	1.766	1.527	1.755
31.7 (I)	1.537	1.786	1.531	1.770	1.527	1.758
34.0 (II)	1.537	1.789	1.531	1.773	1.527	1.761
37.2 (I)	1.537	1.794	1.531	1.778	1.527	1.766
40.0 (II)	1.537	1.797	1.531	1.781	1.527	1.769
(ii) 3 OMCPC						
0.3 (I)	1.559	1.696	1.553	1.683	1.548	1.672
2.3 (II)	1.555	1.707	1.548	1.695	1.543	1.686
3.8 (I)	1.552	1.715	1.546	1.703	1.540	1.694
4.2 (II)	1.552	1.717	1.545	1.704	1.540	1.693
6.9 (II)	1.549	1.726	1.543	1.713	1.538	1.703
8.2 (I)	1.548	1.730	1.542	1.717	1.537	1.707
9.7 (II)	1.547	1.734	1.541	1.721	1.536	1.710
13.1 (I)	1.546	1.743	1.540	1.728	1.535	1.718
13.9 (II)	1.546	1.744	1.539	1.730	1.535	1.720
18.3 (II)	1.544	1.753	1.538	1.739	1.533	1.727
22.9 (II)	1.544	1.761	1.538	1.746	1.533	1.735
25.6 (I)	1.543	1.764	1.537	1.750	1.533	1.739
28.1 (II)	1.543	1.768	1.537	1.753	1.533	1.742
32.6 (II)	1.543	1.774	1.537	1.759	1.533	1.748
(iii) 4 OMCPC						
−0.2 (I)	1.592		1.584		1.578	
0.6 (II)	1.552	1.677	1.546	1.665	1.540	1.657
0.8 (I)	1.548	1.686	1.542	1.670	1.537	1.665
2.3 (II)	1.546	1.692	1.540	1.680	1.535	1.670
2.7 (I)	1.544	1.697	1.538	1.685	1.533	1.675
4.6 (II)	1.542	1.703	1.536	1.691	1.531	1.682
5.7 (I)	1.540	1.709	1.534	1.697	1.529	1.688
7.6 (II)	1.539	1.714	1.533	1.701	1.528	1.691
9.0 (I)	1.538	1.720	1.532	1.707	1.527	1.697
11.4 (II)	1.537	1.724	1.531	1.711	1.526	1.701
12.6 (I)	1.536	1.728	1.530	1.715	1.526	1.705
14.8 (II)	1.536	1.731	1.530	1.718	1.525	1.708
16.2 (I)	1.535	1.735	1.529	1.722	1.525	1.712
18.1 (II)	1.535	1.738	1.529	1.724	1.524	1.715
20.1 (I)	1.534	1.743	1.528	1.729	1.524	1.718
22.9 (II)	1.534	1.747	1.528	1.732	1.524	1.722
24.5 (I)	1.533	1.750	1.528	1.736	1.524	1.726
27.6 (II)	1.533	1.754	1.528	1.740	1.523	1.729
28.9 (I)	1.533	1.756	1.528	1.742	1.523	1.731
32.4 (II)	1.533	1.761	1.527	1.746	1.523	1.735

TABLE I (continued)

$T_{NI} - T$ °C	λ 5461 Å n_o	n_e	λ 5893 Å n_o	n_e	λ 6328 Å n_o	n_e
			(iv) 8 OMCPC			
−1.1 (I)	1.569		1.562		1.556	
−0.6 (II)	1.569		1.562		1.556	
0.4 (I)	1.533	1.643	1.527	1.633	1.523	1.627
1.2 (II)	1.529	1.652	1.524	1.642	1.520	1.634
3.1 (I)	1.526	1.663	1.520	1.653	1.516	1.645
3.9 (II)	1.525	1.666	1.519	1.656	1.515	1.648
6.7 (II)	1.522	1.677	1.517	1.666	1.513	1.657
6.9 (I)	1.522	1.676	1.516	1.666	1.513	1.657
9.2 (II)	1.520	1.683	1.515	1.672	1.512	1.664
10.7 (I)	1.520	1.687	1.515	1.675	1.510	1.667
12.4 (II)	1.519	1.691	1.514	1.679	1.511	1.670
14.8 (I)	1.518	1.695	1.513	1.684	1.509	1.674
15.9 (II)	1.518	1.698	1.513	1.686	1.509	1.677
19.2 (I)	1.517	1.703	1.512	1.691	1.509	1.683
20.3 (II)	1.517	1.706	1.512	1.693	1.509	1.685
24.6 (II)	1.517	1.713	1.512	1.700	1.508	1.690
26.6 (I)	1.517	1.716	1.512	1.702	1.508	1.693
29.4 (II)	1.516	1.719	1.512	1.707	1.508	1.697
			(v) 9 OMCPC			
−1.1 (I)	1.565		1.558		1.552	
−0.3 (II)	1.564		1.558		1.552	
0.9 (I)	1.528	1.642	1.523	1.632	1.519	1.624
1.0 (II)	1.527	1.645	1.521	1.634	1.518	1.626
3.4 (I)	1.523	1.655	1.518	1.645	1.514	1.638
3.8 (II)	1.522	1.656	1.517	1.647	1.513	1.639
6.1 (I)	1.520	1.665	1.515	1.654	1.514	1.638
7.6 (II)	1.519	1.669	1.514	1.658	1.510	1.650
9.1 (I)	1.518	1.673	1.513	1.662	1.510	1.654
11.1 (II)	1.517	1.677	1.513	1.666	1.509	1.658
12.8 (I)	1.517	1.681	1.512	1.670	1.508	1.661
14.4 (II)	1.516	1.684	1.512	1.672	1.508	1.664
16.8 (I)	1.516	1.688	1.511	1.677	1.508	1.669
19.0 (II)	1.515	1.691	1.511	1.680	1.507	1.671
21.9 (I)	1.515	1.696	1.511	1.685	1.507	1.676
23.7 (II)	1.515	1.699	1.511	1.687	1.507	1.678
			(vi) 10 OMCPC			
0.8 (I)	1.525	1.631	1.519	1.623	1.515	1.614
1.6 (II)	1.522	1.637	1.517	1.627	1.513	1.620
2.0 (I)	1.521	1.639	1.516	1.628	1.512	1.621
6.7 (II)	1.514	1.659	1.509	1.649	1.505	1.641
7.1 (I)	1.513	1.661	1.509	1.650	1.504	1.642
9.9 (II)	1.512	1.667	1.507	1.657	1.503	1.649
13.0 (II)	1.511	1.674	1.506	1.663	1.503	1.655
15.3 (II)	1.510	1.678	1.505	1.667	1.502	1.659

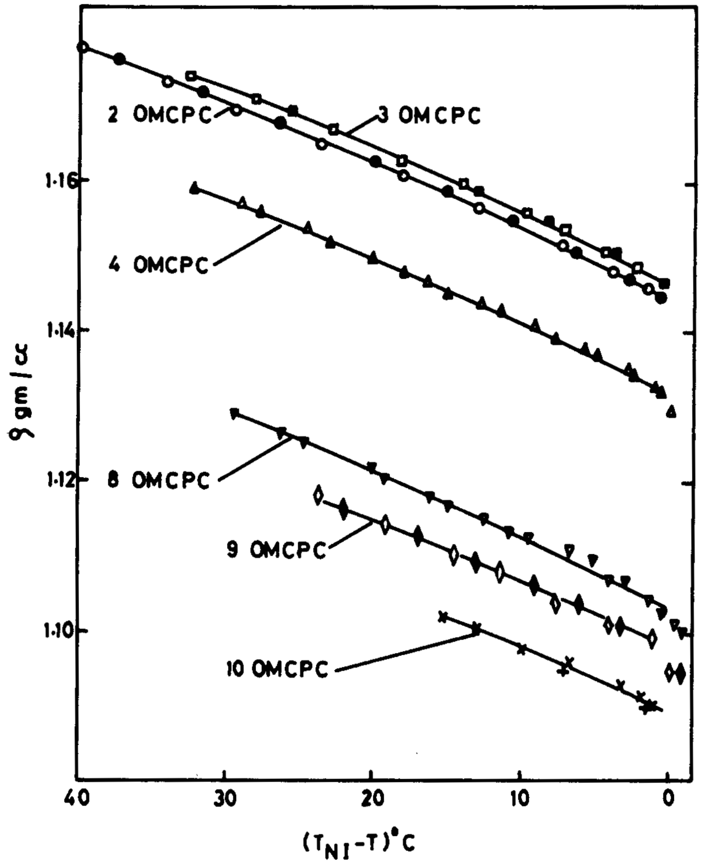

FIGURE 3 Variation of density, as derived from optical measurements, in the nematic phase of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates as a function of the relative temperature. Results of independent measurements have been marked separately. Each symbol represents a value averaged over three wavelengths.

for other wavelengths are in turn obtained by normalizing the order parameter with that calculated for $\lambda 5893$ Å at the lowest temperature of measurement.[1] The $\Delta\alpha$ values for the other compounds of the series are obtained by calculating the incremental values of $\Delta\alpha$, using bond polarizabilities of C—C and C—H bonds as described in an earlier publication.[1] The order parameters, averaged over the measurements on three wavelengths, are shown in Figure 4 for all the compounds.

We need the *volume* diamagnetic anisotropy $\Delta\chi$ of the nematic medium to obtain the elastic constants from the measured values of the Freedericksz threshold magnetic field. $\Delta\chi$ has not been measured for these compounds, but we can express it in terms of s the order parameter, ρ the density and

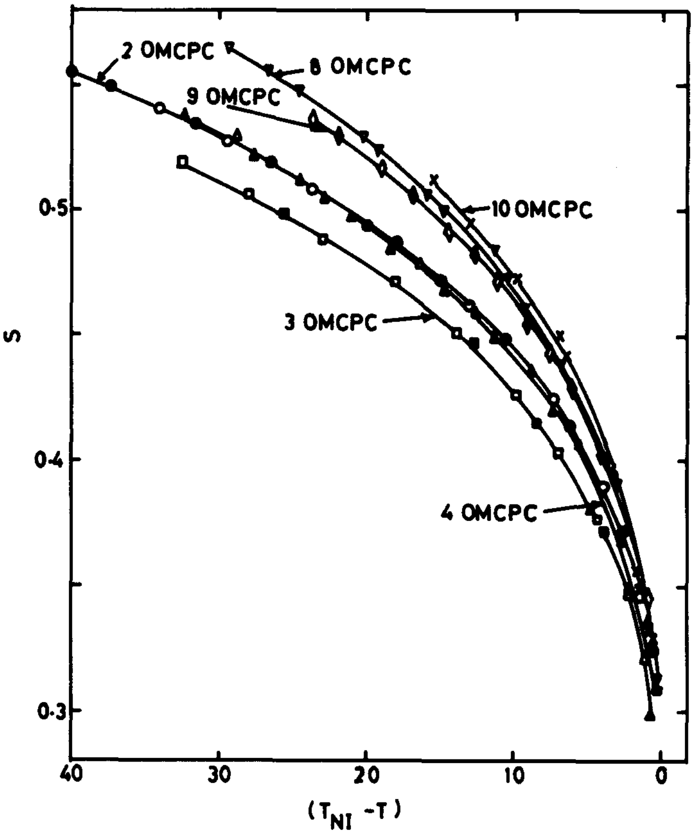

FIGURE 4 Variation of the order parameter as a function of the relative temperature in the nematic phase of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates. The values for λ5461 Å and λ6328 Å have been normalized with that of λ5893 Å at the lowest temperature. The averaging has been done as in Figure 3.

ΔK the anisotropy of magnetic susceptibility of a *gram molecule* of a perfectly oriented medium with $s = 1$. If we further assume that the magnetic anisotropy is essentially determined by the aromatic part of the molecule, ΔK is a constant for all the homologues.[1,2] We can hence calculate $k_{ii}/\Delta K$. The splay, twist and bend constants so obtained are displayed in Figures 5, 6 and 7 respectively. For the sake of comparison of the different properties, we have also plotted in Figure 8 T_{NI} (in °C), ΔH, the order parameters and elastic constants at $T_{NI} - 3°$.

Some salient features of the results are described below and discussed in terms of prevalent theories:

T_{NI} alternates (Figure 2), the compounds with an even number of carbon atoms having higher values, as is to be expected for alkoxy compounds.

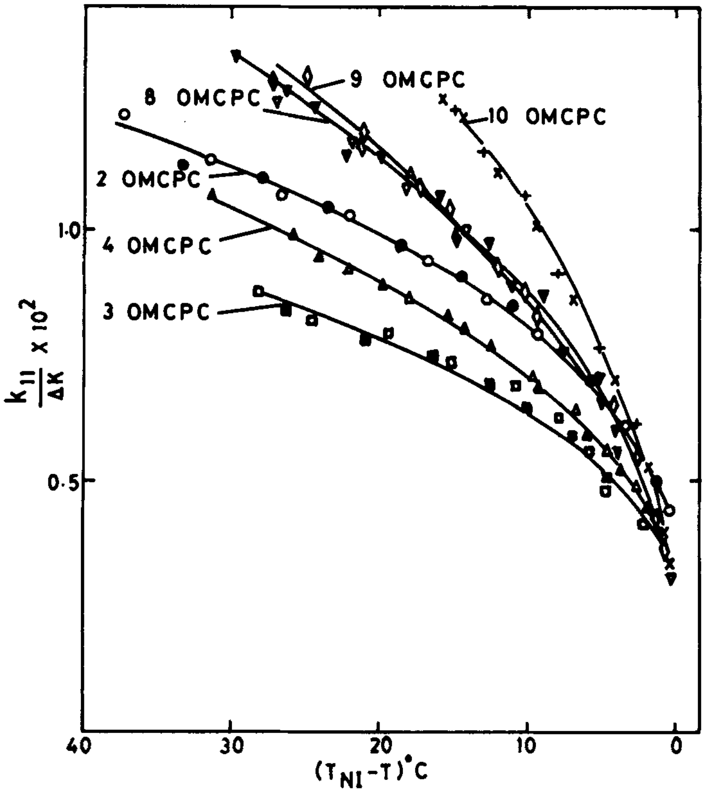

FIGURE 5 Variation of the splay elastic constant as a function of the relative temperature in the nematic phase of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates. The results of independent measurements have been marked separately.

The heat of the N–I transition, ΔH, also shows an alteration. However, there is a considerable increase in the value between 4 OMCPC and 8 OMCPC, unlike in the case of T_{NI}.

The order parameter (s) behaves in a manner similar to the heat of transition.

All the three elastic constants also exhibit alternation in both the groups (the second, third and fourth members in the first group and eighth, ninth and tenth members in the second) (Figure 8). However, the detailed behaviour is different in the three cases.

Considering temperatures close to T_{NI}, the bend constant decreases considerably between the second and third members, but there is hardly any increase between the third and fourth members despite the fact that both T_{NI} and s show considerable increases between the latter two homologues. A similar decrease between the eighth and ninth members and a levelling

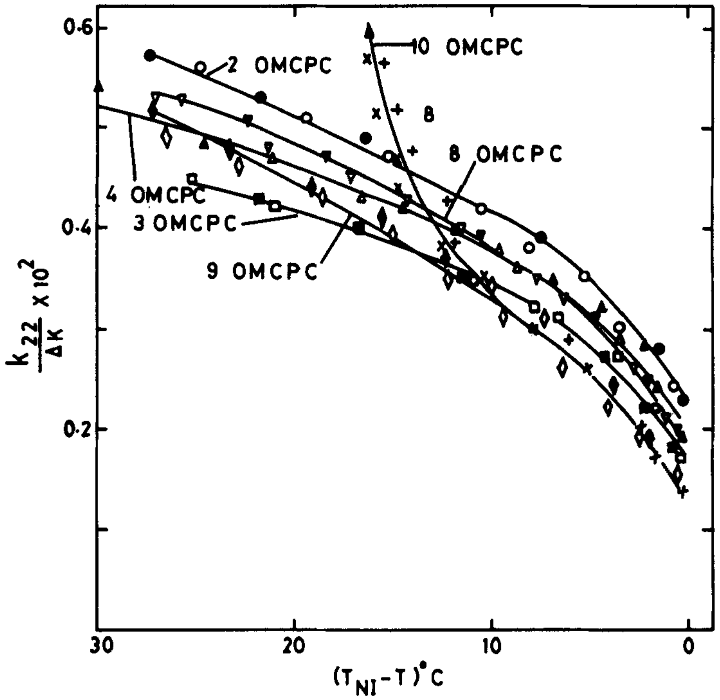

FIGURE 6 Variation of the twist elastic constant as a function of the relative temperature in the nematic phase of *trans*-*p*-*n*-alkoxy-α-methyl cyanophenyl cinnamates. The results of independent measurements have been marked separately.

off between ninth and tenth members is also seen. The tenth member exhibits the smectic *A* phase at lower temperatures and k_{33} increases rapidly as the temperature approaches the S_A—N transition point (Figure 7). The twist elastic constants of the second group of compounds behave in a similar manner. On the other hand, the splay constant increases considerably between the ninth and tenth members. Thus, very close to T_{NI}, $k_{11} > k_{33}$ for 10 OMCPC, which is reminiscent of the behaviour of 8CB.[3] It is also seen in Figure 8 that both k_{33} and k_{11} increase considerably between 4 OMCPC and 8 OMCPC.

We have also calculated the temperature dependence of the ratios of elastic constants for all the compounds except 10 OMCPC which exhibits the smectic A phase. In both 4 OMCPC and 8 OMCPC (k_{11}/k_{22}) decreases with increase of temperature. In all other cases, this ratio is roughly temperature-independent. The ratios (k_{33}/k_{11}) and (k_{33}/k_{22}) decrease with increase of temperature in all the cases. Further, though the ratios at any given relative temperature are comparable for neighbouring homologues, they

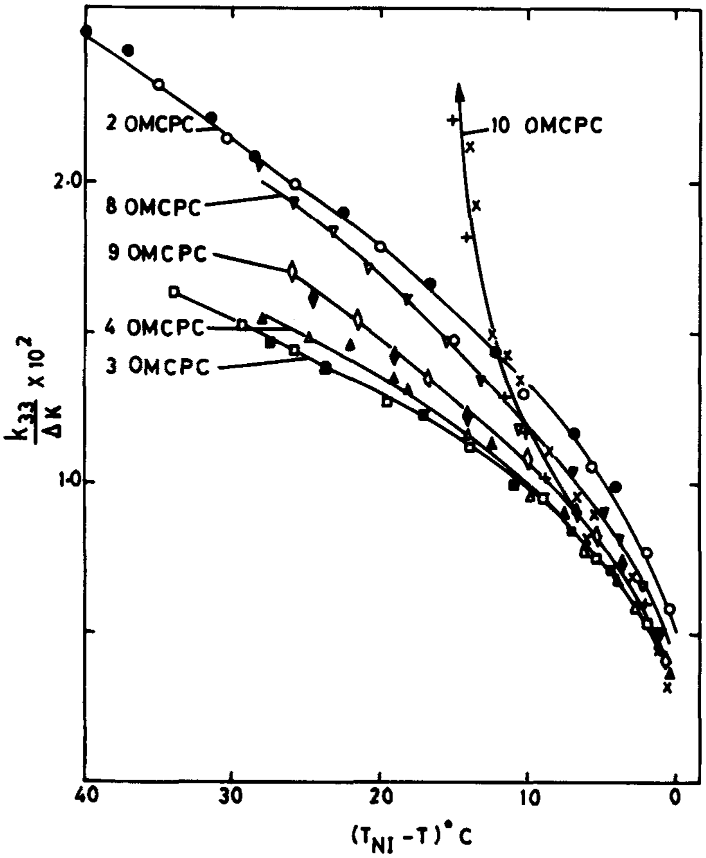

FIGURE 7 Variation of the bend elastic constant as a function of the relative temperature in the nematic phase of *trans-p-n*-alkoxy-α-methyl cyanophenyl cinnamates. The results of independent measurements have been marked separately.

are by no means constant throughout the series, unlike in the case of alkyl cyanobiphenyls.[2] The trend is also at variance with the results on non-polar compounds[8] in which (k_{33}/k_{11}) decreases continuously as the series is ascended. Another point of interest is that, at any given relative temperature, (k_{33}/k_{22}) has the lowest value in the case of 4 OMCPC.

Fitting the data on elastic constants to a formula of the type $(k_{ii}/\Delta K) = Cs^x$, we get the numbers listed in Table II. We note that the index for k_{33} is considerably greater than 2 in all the cases, while for k_{11} and k_{22}, it is around 2 for the homologues up to 8 OMCPC. However, it may be noted that in the case of 4 OMCPC, the x-value for k_{22} is significantly less than 2.

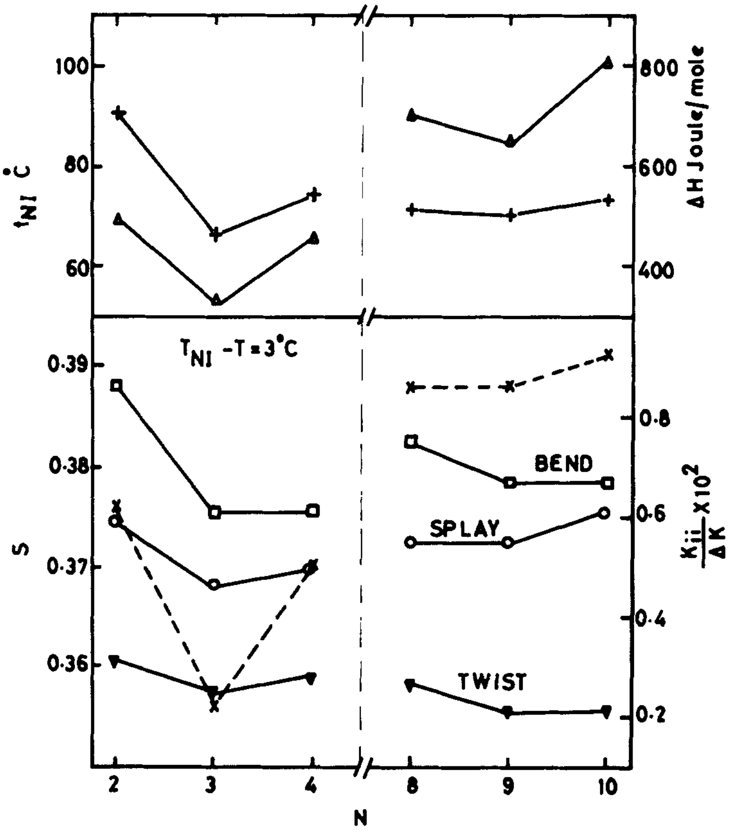

FIGURE 8 The nematic-isotropic transition points (+), the heats of transition (△), the order parameters (x), splay elastic constants (○), twist elastic constants (▽) and bend elastic constants (□) of *trans*-*p*-*n*-alkoxy-α-methyl-cyanophenyl cinnamates as functions of the number of carbon atoms in the end chain. The parameters plotted in the lower section of the figure are those at $T_{NI} - T = 3°C$.

TABLE II

Experimental data fitted to the equation $k_{ii}/\Delta K = Cs^x$

	$k_{11}/\Delta K$		$k_{22}/\Delta K$		$k_{33}/\Delta K$	
	C	x	C	x	C	x
2 OMCPC	3.77	1.90	2.00	1.92	12.46	2.76
3 OMCPC	3.27	1.92	1.76	1.95	8.42	2.55
4 OMCPC	3.64	1.98	1.50	1.67	7.94	2.52
8 OMCPC	4.65	2.20	1.60	1.87	9.70	2.73
9 OMCPC	5.74	2.45	2.23	2.47	9.05	2.77
10 OMCPC	6.36	2.43	—	—	—	—

COMPARISON WITH PRIEST'S THEORY

We can qualitatively understand these results in terms of Priest's theory of elasticity of nematic liquid crystals.[9] This theory is based on the mean field approximation and the specific results which can be compared with the experimental data are expressible as follows:

$$\begin{aligned} k_{11}/\bar{k} &= (1 + \Delta) - 3\Delta'(\bar{P}_4/\bar{P}_2) + \cdots \\ k_{22}/\bar{k} &= (1 - 2\Delta) - \Delta'(\bar{P}_4/\bar{P}_2) + \cdots \\ k_{33}/\bar{k} &= (1 + \Delta) + 4\Delta'(\bar{P}_4/\bar{P}_2) + \cdots \end{aligned} \tag{1}$$

where $\bar{k} = \frac{1}{3}(k_{11} + k_{22} + k_{33})$ is the average elastic constant, Δ and Δ' are molecular parameters depending on the nature of the compound and $\bar{P}_2 = s$ is the average second order Legendre polynomial while $\bar{P}_4$ is the average fourth order Legendre polynomial. Higher order terms ($\bar{P}_6$ etc.) should be included in principle, but it can be expected that their contributions will become progressively smaller.

Since the derivation of Eqs. (1) is based on the mean field theory, $\bar{k} \propto \bar{P}_2^2$, apart from a slight volume-dependence. The analysis of our data shows that only in the case of 4 OMCPC it comes close to this behaviour, and in all other cases the variation of $\bar{k}$ is much stronger. The molecules in this series of compounds have the strongly polar nitrile group at one end and in this case neighbouring molecules will have a strong antiparallel correlation[10] resulting in a bilayer structure.[11] Consequently the short-range order effects, both orientational and translational, are likely to be strong and the mean field theory can be expected to be inadequate. As we have mentioned earlier, 10 OMCPC shows a smectic A phase and in 9 OMCPC itself the deviation from the mean field index is quite large (see Table II).

Both Δ and Δ' in Eqs. (1) turn out to be positive,[3] and hence it is easy to understand the usually observed ordering $k_{33} > k_{11} > k_{22}$ in terms of Eqs. (1), as $(\bar{P}_4/\bar{P}_2)$ is also usually positive. Both theoretical estimates[12] and experimental data based on Raman scattering[13] and neutron scattering[14] studies show that the ratio $(\bar{P}_4/\bar{P}_2)$ decreases with increase of temperature, and particularly so close to T_{NI}. Consequently, it follows from Eqs. (1) that k_{33} varies more rapidly than $\bar{k}$ with temperature, i.e., the index x is much larger than 2 for k_{33} (see Table II). Further, Priest[8] has estimated that $\Delta \simeq 0.2$ and $\Delta' \simeq 0.05$ and hence it is obvious from Eq. (1) that k_{22} is also very much affected by the variation of $(\bar{P}_4/\bar{P}_2)$. In fact it should vary more slowly than $\bar{k}$. Hence, as in 4 OMCPC, the index x for k_{22} can be even less than 2 (Table II). Another result that follows from Eq. (I) is that k_{11} varies slower than $\bar{k}$ with temperature, which is again in accord with the experimental results (Table II).

Since $(\bar{P}_4/\bar{P}_2)$ decreases rapidly as we go close to T_{NI}, k_{33} and k_{11} approach each other. In the case of 10 OMCPC, k_{11} has a value greater than that of k_{33} very close to T_{NI}. We had noted a similar trend in the case of 8CB also.[2] This is easily understood in terms of Eq. (1) if $(\bar{P}_4/\bar{P}_2)$ becomes negative close to T_{NI}. Indeed Raman scattering[15] and fluorescence[16] experiments have clearly indicated a reversal of sign of $\bar{P}_4$ as T_{NI} is approached in a few cases (including 5CB).

We tried to make a quantitative fit of the data to Eq. (1) to estimate $(\bar{P}_4/\bar{P}_2)$. However this yielded values of $\bar{P}_4$ which are considerably larger than the values measured on other systems.[13] In any case since the interpretation of Δ and Δ' in terms of intermolecular attraction and repulsion interactions is not obvious, we do not report the results here. Priest[9] has also considered a model in which the intermolecular attractions are completely ignored and the medium is assumed to be an assembly of hard spherocylinders. He has shown that both Δ and Δ' can be related with R, the length to breadth ratio of the spherocylinders. In this case we have only two adjustable parameters, viz., R and $(\bar{P}_4/\bar{P}_2)$ and at each temperature we have estimated these numbers by a least squares fitting procedure from the measured values of the three elastic constants. It is again found that $(\bar{P}_4/\bar{P}_2)$ has values which are much larger than the experimental values, and moreover that R decreases with increase of temperature. The latter result can be interpreted to mean that R does not represent the length to breadth ratio of a single molecule but a similar ratio for a short-range ordered group. In other words, it can be equated to $\xi_{\parallel}/\xi_{\perp}$ where $\xi_{\parallel}$ is the correlation length of the cybotactic group along a direction parallel to the director and $\xi_{\perp}$ is that perpendicular to the director. This trend of $\xi_{\parallel}/\xi_{\perp}$ decreasing with temperature was noted by us in the case of alkyl cyanobiphenyl series also.[2] We should also mention that near T_{NI}, 4 OMCPC has the lowest value of R.

We shall now point out some other aspects of our measurements. We have already stated that s, ΔH and k_{33} increase substantially between 4 OMCPC and 8 OMCPC. The fifth, sixth and seventh homologues form monotropic nematic phases (Figure 2). It is also evident from the figure that the melting point of the crystal steadily decreases between the second and fourth homologues and then increases drastically between the fourth and fifth members and thereafter again decreases steadily till the ninth member. We believe that the crystal structure changes considerably between the fourth and fifth homologues. Thus the two groups of compounds studied may have very different crystal structures. This would also lead to a difference in the structure of short-range order in the two groups. This may account for the observed differences in the properties between 4 OMCPC and 8 OMCPC.

We have already noted that 4 OMCPC has the lowest values of R as well as the indices x. This homologue also shows a slightly anomalous value of the density. The temperature variations of density are shown in Figure 3. Normally, the addition of a CH_2-group would tend to reduce the density of the liquid crystal. However, we see that between 2 OMCPC and 3 OMCPC there is actually a small increase in the density at the same relative temperature. This may be related with the considerable reduction in T_{NI} itself between them (Figure 2). The density drops considerably between 3 OMCPC and 4 OMCPC and the drop appears to be somewhat more than what one would expect from the addition of a CH_2-group and the increase in T_{NI} between the two compounds. Thus the structure of 4 OMCPC appears to be slightly less closely packed than in the other two cases. The densities of the second group of compounds show the normal trend.

A-N TRANSITION IN 10 OMCPC

The last aspect that we will discuss concerns the pretransitional increases in the twist and bend elastic constants of 10 OMCPC. This compound exhibits a nearly second order smectic A-nematic phase transition, even though T_{AN}/T_{NI} is only 0.95. As we approach the phase transition point from above, the smectic-like short range order builds up strongly and k_{22} and k_{33} shoot up. de Gennes[17] and McMillan[18] pointed out the analogy between S_A—N transition and superconductor-normal transition and their analyses show that the twist and bend constants can be expressed in the form

$$k_{ii} = k_{ii}^{\circ} + D(T - T_{AN}^{*})^{-\gamma}, \qquad i = 2 \text{ or } 3 \tag{2}$$

where k_{ii}° is the background term due to the orientational order, D a constant depending on the material, γ the critical index and T_{AN}^{*} the A–N transition point if it is a second order transition. If the transition is weakly first order, T_{AN}^{*} is slightly less than the transition point. $\gamma = 0.5$ if the mean field theory[18] is valid, but if the A–N transition is analogous to the helium case,[17] $\gamma = 0.66$. As we have explained in a previous paper,[3] our experimental set-up was by no means adequate for determining the critical indices precisely, as the temperature control and measurement are not sufficiently accurate. Nevertheless, we analysed the data in terms of Eq. (2). We also assumed that $k_{ii}^{\circ} \propto \bar{P}_2^2$ for both k_{22} and k_{33} even though, as we have discussed in this paper, the index is different from 2 in both cases. The results are:

$$\gamma = 0.56 \text{ in the case of } k_{22} \quad \text{and}$$
$$0.64 \text{ in the case of } k_{33}.$$

The value of γ is lower for k_{22} than for k_{33}. This result, which we had noted in our earlier paper on other systems,[3] may be partly due to the incorrect background terms used; as we have discussed earlier, k_{33} is expected to vary much more strongly with the orientational order parameter than k_{22} does.

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