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A correlation between short range smectic-like ordering and the elastic constants of nematic liquid crystals

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Résumé. — Nous avons mesuré les constantes élastiques de courbure (k_{33}) et de déformation en éventail (k_{11}) ainsi que l'amplitude de l'ordre local de type smectique (obtenu par des techniques de diffraction des rayons X) pour un large ensemble de nématogènes. Les résultats montrent une forte corrélation entre k_{33}/k_{11} et l'intensité de l'ordre local de type smectique. Cette corrélation s'applique à des nématogènes de structure tant bicouche que monocouche. Ces résultats s'interprètent en détail et de façon rationnelle en termes d'un modèle théorique récent qui permet le calcul des constantes élastiques en fonction de l'ordre local de type smectique.

Abstract. — The measurements of the bend (k_{33}) and splay (k_{11}) elastic constants and the amplitude of the smectic-like local ordering (obtained using X-ray diffraction techniques), have been made for a wide range of nematogens. The results reveal a strong correlation between k_{33}/k_{11} and the strength of the smectic-like local ordering. This correlation applies to nematogens with either bilayer or monolayer structures, irrespective of whether or not they exhibit a smectic phase. These results have been rationalized in more detail in terms of a recent theoretical model which calculated the elastic constants as a function of smectic-like local ordering.

Introduction.

The characteristics of display devices depend critically upon the physical properties of the liquid crystal employed. In particular the elastic constants together with the dielectric anisotropy are important as these determine the distortion of the liquid crystal layer when an electric field is applied. To formulate liquid crystals with elastic properties to meet device requirements it is desirable to understand the factors which determine the elastic constants.

In 1972, Gruler [1] postulated that the temperature variation of the elastic constants, observed in the homologous series of 4, 4'-di (n-alkoxy)-azoxy-benzenes, was attributable to changes in the local ordering of the nematic, including the possibility of regions with smectic-like ordering. Recent X-ray diffraction measurements [2] of the peak intensities of the meridional diffuse spot of terminally cyano substituted nematogens have shown a correlation between k_{33} and smectic-like local ordering. In this paper we present rather more detailed X-ray diffraction measurements of the smectic-like local ordering, together with elastic constants for a wider range of nematogens including those with bilayer and monolayer structures. The results confirm the correlation between smectic-like local ordering and the elastic constants and are rationalized in more detail in terms of a recent theory by van der Meer *et al.* [3].

1. Materials.

The structures and acronyms of the nematogens studied are shown in tables I and II. We have examined the pentyl and heptyl homologues of terminally cyano substituted nematogens with a variety of ring systems. For PECH we include the propyl homologue to allow comparisons to be made between two pairs of structural isomers of PCH and PECH. In addition we include measurements of 6CB and a mixture containing 6CB and 10CB which exhibits a smectic A phase.

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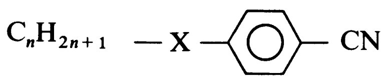
Table I. — *Terminally cyano substituted nematogens.*



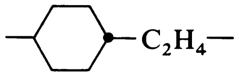
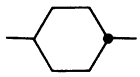
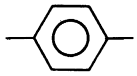
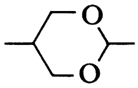
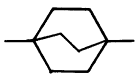
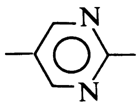
ACRONYM	X	*n*
PECH		3, 5, 7
PCH		5, 7
CB		5, 6, 7, E1 6-10 [70 : 30]
PDX		5
BCO		5, 7
PYR		5, 7

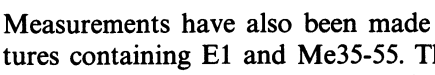
Table II. — *Hybrid mixtures* (*A* + *B*)

A. Terminally cyano substituted nematogens

E1		PCH analogue of EI	
5 CB	59 mol %	5 PCH	59 mol %
7 CB	41 mol %	7 PCH	41 mol %

B. Non-polar end group nematogen

Me35-55

	Me35	68 mol %
	Me55	32 mol %

Measurements have also been made on hybrid mixtures containing E1 and Me35-55. This combination shows an injected monolayer smectic A phase centred about the 55 mol. % Me35-55 composition [4]. For comparison we include measurements of the analogous 5-7 PCH/Me35-55 mixture which shows no injected smectic phase down to − 20 °C.

2. Experimental methods.

2.1 Elastic constant measurements. — The splay and bend elastic constants (k_{11} and k_{33}) were determined from the capacitance-voltage characteristics of a homogeneously aligned (zero twist and tilt) nematic layer, distorted by an electric field applied normal to the layer [5]. An automatic system was used to measure the change in capacitance to within 0.01 %, and the voltage to 10^{-4} V at various temperatures stabilized to 0.1 °C over a range of 0 °C to 100 °C. The capacitance-voltage data and the permittivity components were fitted to the continuum. theory by a three parameter, non-linear, least squares fitting programme to give k_{11}, k_{33} and k_{33}/k_{11} to within 2 %, 5 % and 3 % respectively. The deviations between the fitted curve and the experimental data points were found to be less than 10^{-4} V, which was representative of the resolution of the voltage measurements.

2.2 X-ray measurements. — The nematogens were held in a flat sample holder made of copper with 2 mm diameter beryllium windows giving a constant irradiated volume of 1 mm thickness. The temperature was stabilized to 0.1 °C.

Homogeneous alignment was obtained by cooling from the isotropic phase in the presence of a magnetic field of 0.7 T, and this field was then maintained throughout the experiment. CuKα (1.5 Å) radiation, monochromated by a graphite crystal and collimated to ~ 0.5 mm diameter, was applied in a direction normal to the magnetic field and the director **n**, as shown in figure 1*a*.

Flat plate photographs were taken to verify the quality of the nematic alignment and to determine the positions of the diffraction features. A diffraction pattern typical of the nematic phase is illustrated in figure 1*b*, and a major feature is the diffuse meridional peaks which vary markedly in strength and sharpness between nematogens. These meridional peaks arise from damped density waves [6] parallel to the director (**n**) and are indicative of short range smectic-like local ordering.

Measurement of the position of the maximum intensity ($S = 2 \sin \theta/\lambda$) of the first order meridional peak enables the wavelength of the density wave (the analogue of the layer spacing in a smectic) to be calculated from $d_{\parallel} = S_{\parallel}^{-1}$. For a monolayer structure the « layer spacing » is approximately equal

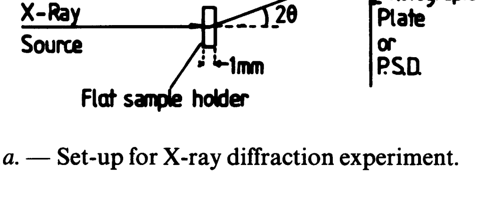


Fig. 1*a*. — Set-up for X-ray diffraction experiment.

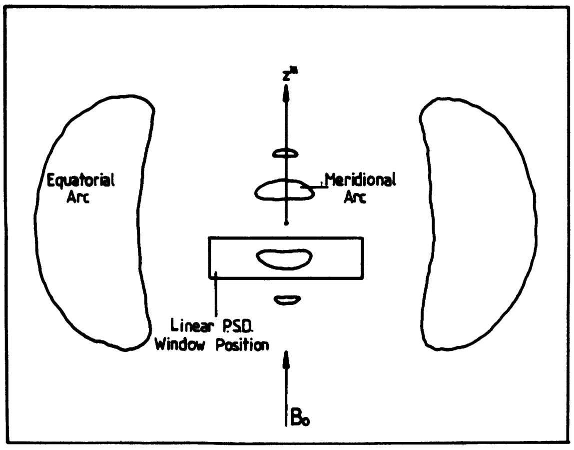


Fig. 1*b*. — Typical X-ray diffraction pattern for a nematogen.

to the molecular length (l) and it is somewhat greater than this for a bilayer structure, for example $d_{\parallel} \simeq 1.4\, l$ for the cyanobiphenyls [6].

The width of the diffuse peak along z is a measure of the correlation length of the smectic-like local ordering and typically the ordering extends over a few molecules. However, in the pre-transitional region close to the smectic phase the correlation length increases rapidly causing the formation of transient smectic regions which results in the meridional peaks becoming much sharper. Most of the measurements we report in this paper have been made on nematogens which show no smectic phases down to the temperature at which they solidify.

The integrated intensity (I) of the first order meridional peak is a measure of the strength of the smectic-like local ordering of the nematogen. This follows by analogy with the expression for the integrated intensity of the sharp first order meridional peak of the smectic A phase which is given by [6] :

$$I = C\tau^2 \mid F \mid^2 \tag{1}$$

where $\tau = \langle \cos (2\pi z/d_{\parallel}) \rangle$ is the amplitude of the smectic density wave, z is the axis normal to the layers (parallel to $\mathbf{n}$), F is the structure factor of a perfectly ordered layer and C is a constant. The same formula also applies to the nematic phase as a reduction in the correlation length to give a damped density wave does not affect the integrated intensity of the diffraction peak — it just reduces the sharpness.

The integrated intensity of the diffuse meridional peak of the nematogen was measured using a Marconi Avionics linear position sensitive detection system, the window position being shown in figure 1*b*. The intensities were normalized to the background scattering in the « wings » of the diffuse peak to allow a comparison between different samples. This gave normalized integrated intensities (I) reliable to about $\pm$ 20 %, after correction for air and sample holder scattering.

3. Results and discussion.

3.1 LAYER SPACINGS. — The values of $d_{\parallel}$ obtained from the X-ray diffraction photographs, together with molecular lengths (l) measured using CPK models, are shown in table III. It has previously been suggested [2], using the results in table III, that the anti-parallel local structures of PCH and BCO are characterized by partial core overlap unlike CB which exhibits complete core overlap [6]. The results in table III also suggest that the overlap for PDX and PYR might be even greater than for CB. The PECH results are particularly interesting since their layer spacings are approximately the same as those found for their PCH structural isomers despite the different positioning of the carbon atoms. This suggests that the most likely local packing is partial core overlap of just the cyano phenyl group as this would result in the same layer spacings for the two structural isomers.

The $d_{\parallel}$ values for the E1/Me35-55 mixtures show that the bilayer ordering of the para-cyano substituted nematogens is reduced to a monolayer structure with the addition of only 40 mol. % of a non-polar end group nematogen, as has been observed in other hybrid mixtures.

3.2 k_{33}/k_{11}. — The ratio k_{33}/k_{11} is shown as a function of ln I in figure 2. We have measured I for reduced temperatures in the range 0.96 to 0.99 but because the temperature dependence of I approaches the limit of precision of the measurements, no clear correlation with temperature is discernible. For this reason we show results just for 0.96 T_{NI}, except for 7 PYR which is shown at 0.98 T_{NI} (the lowest mea-

Table III. — *Layer spacings and molecular lengths* [Å]

Nematogens	l	$d_{\parallel}$
5CB	18	25
6CB	20	28
7CB	21	29
5PCH	18	26
7PCH	21	31
3PECH	18	27
5PECH	21	31
7PECH	24	41
5BCO	18	26
7BCO	21	29
7PYR	21	27
5PDX	18	22

E1 + x mol. % Me35-55		
x	l	$d_{\parallel}$
0	20	26
20	21 (*)	23
40	21 (*)	21
60	22 (*)	21
80	22 (*)	21
100	23	—

(*) Calculated assuming linear variation with composition.

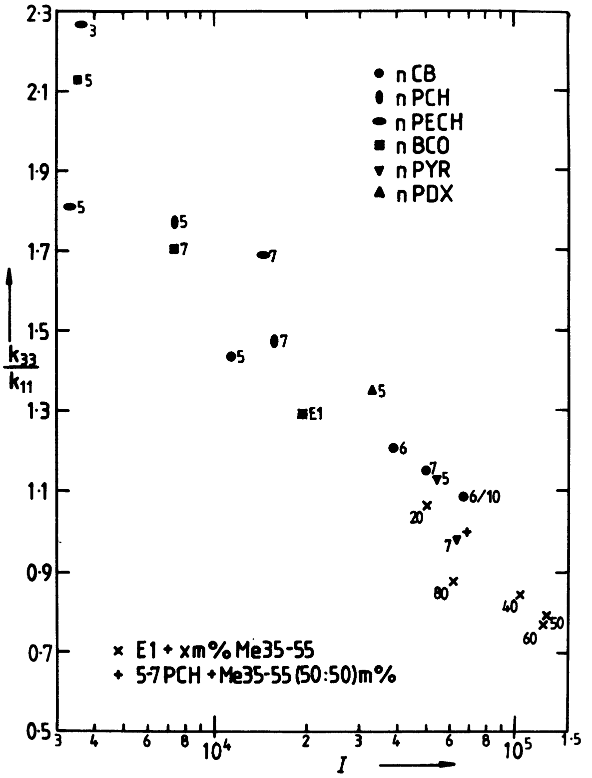


Fig. 2. — Dependence of k_{33}/k_{11} on ln I, at 0.96 T_{NI}.

surement temperature possible due to its high melting point).

A strong correlation between k_{33}/k_{11} and ln I is apparent. Indeed to a good approximation the elastic constant ratio varies linearly with ln I. Since I is related to the amplitude of the damped density wave (Eq. 1), these results suggest that a high k_{33}/k_{11} is associated with weak smectic-like local ordering.

Generally, nematogens with underlying smectic phases tend to exhibit stronger smectic-like local ordering, note for example the large value of ln I for the 6 CB/10 CB mixture compared with other cyanobiphenyl nematogens, and the increased ln I over the injected smectic phase in the E1/Me35-55 hybrid mixture. However, it is important to note that the smectic-like local ordering is not just a consequence of an underlying smectic phase as it occurs in all the nematogens we studied and most of these do not show smectic phases even at low temperatures.

Our results show that the correlation between k_{33}/k_{11} and the smectic-like local ordering applies to bilayer and monolayer nematogens, with or without smectic phases. Also the variation in k_{33}/k_{11} within a homologous series can be attributed to changes in smectic-like local ordering, since in line with the greater « smectic tendencies » of longer alkyl chains the smectic-like local ordering is found to increase with alkyl chain length.

The results for the structural isomers of PECH and PCH are particularly interesting, since consistent with their close structural resemblance most of their physical properties are very similar [7]. However, their elastic properties are remarkably different, for the PECH compounds k_{11} and k_{33}/k_{11} are approximately 50 % larger than for their PCH isomers. Our results, shown in figure 2, suggest that it might be the weaker smectic-like local ordering of PECH which is important, leading to an increased k_{33}/k_{11} compared with its PCH analogue.

The variation in the elastic constants across the phase diagram of the E1/Me35-55 hybrid mixtures can also be related to changes in the smectic-like local ordering. This is most clearly illustrated in figure 3 which shows k_{33}/k_{11} and ln I as a function of E1/Me35-55 composition. The decrease in k_{33}/k_{11} towards the centre of the phase diagram clearly correlates with an increase in the smectic-like local ordering.

A more quantitative rationalization of our results can be achieved using equation 1; if we define the distribution function along the z axis to be Gaussian, equation 1 becomes

$$I = C \mid F \mid^2 \exp(-4 \pi^2 \langle z^2 \rangle / d_{\|}^2) \quad (2)$$

where $\langle z^2 \rangle / d_{\|}^2$ is the normalized mean square displacement of the molecules in the z direction. From equation 2

$$\frac{\langle z^2 \rangle}{d_{\|}^2} = \frac{1}{4 \pi^2} (\ln C \mid F \mid^2 - \ln I) . \quad (3)$$

Using equation 3 we are now in a position to compare our results with the predictions of a recent theoretical model by van der Meer *et al.* [3]. By assuming distributed harmonic forces between the molecules they calculate the elastic constants of a nematogen with perfect orientational order, as a function of the strength of the smectic-like local ordering. They model this by defining the distribution function of the molecular centres, parallel to the director, to be Gaussian.

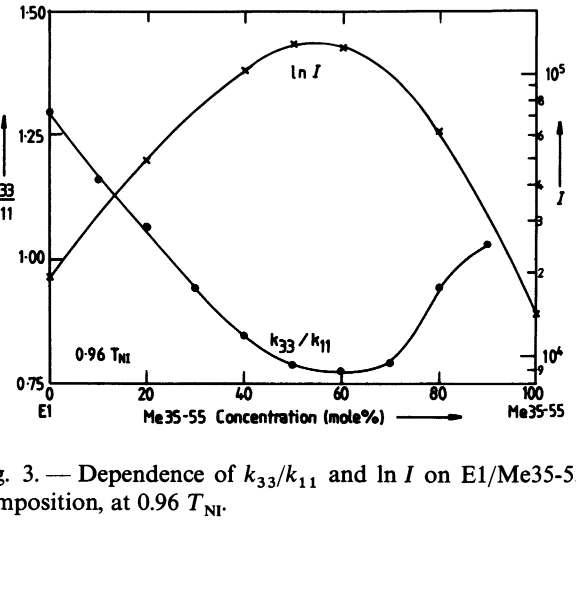


Fig. 3. — Dependence of k_{33}/k_{11} and ln I on E1/Me35-55 composition, at 0.96 T_{NI}.

Their theory predicts that

$$\frac{k_{33}}{k_{11}} = \frac{L^2}{W^2}\,\frac{4}{3}\,\frac{\langle be(\alpha)\rangle}{\langle st(\alpha)\rangle} \tag{4}$$

where L and W are the molecular length and width respectively, and α is the normalized displacement between molecules in a direction parallel to the director. $\langle be(\alpha)\rangle$ and $\langle st(\alpha)\rangle$ are the averages of functions of α and are related to the degree of smectic-like local ordering. An increase in the local ordering is simulated by increasing the intensity of the Gaussian distribution resulting in a decrease in $\langle be(\alpha)\rangle / \langle st(\alpha)\rangle$. Thus from equation 4 the theory predicts a reduction in k_{33}/k_{11} with increasing smectic-like local ordering.

Although the theory is for perfect ordering we feel justified in comparing it with our results because at an equal reduced temperature the order parameter (S) is found to be constant within a few per cent and so the general trend predicted by equation 4 is likely to be applicable to our results.

The ratio $\langle be(\alpha)\rangle / \langle st(\alpha)\rangle$ is approximately proportional to $\langle \alpha^2 \rangle$, the normalized mean square displacement, and so (4) becomes :

$$\frac{k_{33}}{k_{11}} \propto \frac{L^2}{W^2}\langle \alpha^2 \rangle . \tag{5}$$

The parameter $\langle \alpha^2 \rangle$ from van der Meer *et al.*'s theory can be equated to the quantity $\langle z^2 \rangle / d_{\parallel}^2$, and comparing (3) and (5) gives

$$\frac{k_{33}}{k_{11}} \propto \frac{L^2}{W^2}(\ln (C \mid F \mid^2) - \ln I) . \tag{6}$$

This result agrees well with our findings, shown in figure 2, of an approximately linear variation of k_{33}/k_{11} with $\ln I$. Correlations between k_{33}/k_{11} and L/W are not discernible from our results, probably because there is not a sufficient variation in L/W between the materials to show effects above the experimental scatter in the intensity.

3.3 k_{11} AND k_{33}. — Figures 4 and 5 show k_{11} and k_{33} as a function of $\ln I$, respectively. For the PECH materials both k_{11} and k_{33} are anomalously high [7]. and with the exception of the PECH materials we see that k_{33} is roughly linear with $\ln I$ and there is a marginal increase in k_{11} with $\ln I$. This indicates that the increase in k_{33}/k_{11} with decreasing smectic-like local ordering results predominantly from increasing k_{33}, with k_{11} having only a minor effect — this result is predicted by van der Meer *et al.*'s theory for nematogens with the same molecular interaction energy.

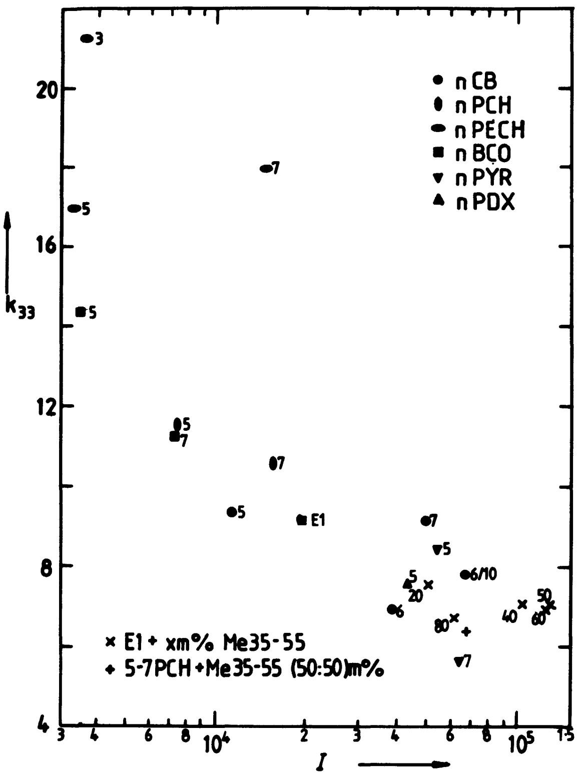


Fig. 4. — Dependence of k_{33} on $\ln I$, at 0.96 $T_{\rm NI}$.

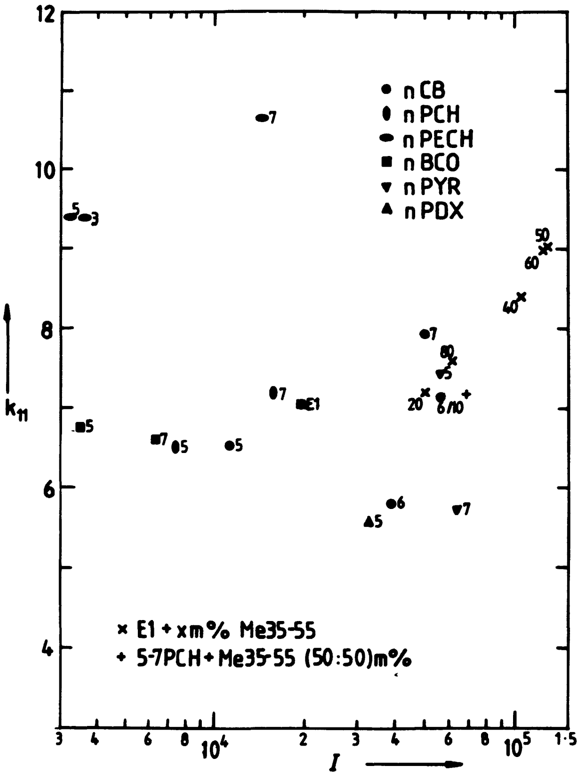


Fig. 5. — Dependence of k_{11} on $\ln I$, at 0.96 $T_{\rm NI}$.

4. Conclusion.

Measurements have been made of k_{11} and k_{33}, and the integrated intensity of the meridional X-ray peak (I) of a series of terminally cyano substituted nematogens and a set of hybrid mixtures. I is a measure of the amplitude of the nematic density wave parallel to **n**, and is related to the strength of the smectic-like local ordering. For all materials studied it has been found that k_{33}/k_{11} is approximately a linear function of ln I. This correlation, which was found to apply to homologous series, nematogens with different ring systems, and to hybrid mixtures, showed that a low k_{33}/k_{11} was associated with increased smectic-like local ordering. However, it was not found necessary for the nematogen to exhibit a smectic phase, indeed pre-transitional effects close to a smectic phase give quite different effects [8, 9]. The results suggest that it might be the weaker smectic-like local ordering of PECH which leads to its anomalously large k_{33}/k_{11} compared with that for its structural isomer PCH, since molecular aspects are similar. Also the results show that the large decrease in k_{33}/k_{11} on approaching the centre of the E1/Me35-55 phase diagram correlates with an increase in smectic-like local ordering. We have compared our results to the predictions of van der Meer *et al.*'s theory [3], and the predicted correlation between k_{33}/k_{11} and $\langle \alpha^2 \rangle$ (the mean square molecular displacement which we equate to $\langle z^2 \rangle / d_{\parallel}^2$) is substantiated. It has been observed that k_{11} perhaps increases slightly and k_{33} decreases significantly with increasing smectic-like local ordering, in accord with the prediction of van der Meer *et al.* In conclusion we have found that k_{33}/k_{11} predominantly depends upon the strength of the smectic-like local ordering, with changes in molecular aspects only having a minor direct effect.

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