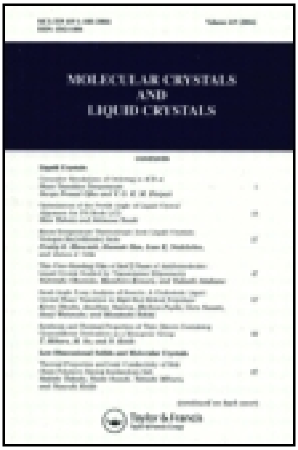

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The Elastic Constants of Hybrid Mixtures for Multiplexed Twisted Nematic Displays

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The Elastic Constants of Hybrid Mixtures for Multiplexed Twisted Nematic Displays

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Nematic liquid crystal mixtures with a low ratio of k_{33}/k_{11} and reasonably low k_{11} are particularly important for improving the performance of complex, highly multiplexed twisted nematic displays. Measurements of the splay and bend elastic constants of a series of hybrid mixtures containing terminally cyano substituted nematogens and various non-cyano substituted esters are reported. The results are analysed to show the relative importance of various aspects of the molecular structure of the esters.

Keywords: twisted nematic displays, elastic constants

INTRODUCTION

Twisted nematic liquid crystal displays are now a well-established technology, and further improvements in their performance are being constantly sought. The majority of twisted nematic displays are multiplexed—from a low level of 1 : 2 to 1 : 4 in watches and calculators up to 1 : 64 in complex alpha-numeric displays. The properties of liquid crystal materials which affect the multiplexing performance are therefore of great importance. This paper will consider the splay and bend elastic constants (k_{11} and k_{33}) of nematic materials as both of these are crucial to the multiplexing performance of twisted nematic displays.

(i) Splay elastic constant (k_{11})

The threshold voltage V_c of a twisted device is given by

$$\epsilon_0(\epsilon_{\parallel} - \epsilon_{\perp})V_c^2 = \pi^2\left(k_{11} + \left[\frac{1}{4}(k_{33} - 2k_{22})\right]\right) \qquad (1)$$

However, for most nematic materials the term in square brackets is found to be small compared with k_{11} and equation (1) can be simplified to give

$$\epsilon_0(\epsilon_{\|} - \epsilon_{\perp})V_c^2 = \pi^2 k_{11} \,. \tag{2}$$

Therefore, the splay elastic constant and the permittivity anisotropy $(\epsilon_{\|} - \epsilon_{\perp})$ determine the threshold voltage of the device, and as V_c is usually fixed by the particular voltage source used to drive the display, a knowledge of these parameters is important.

(ii) The ratio of bend to splay elastic constants (k_{33}/k_{11})

The level of multiplexing possible in a twisted nematic display is related to the steepness of the electro-optic response curve which is determined by the following combination of permittivities and elastic constants:[1]

$$\text{Steepness} \propto \frac{1}{(\epsilon_{\|} - \epsilon_{\perp})/\epsilon_{\perp} + 5/8\,(k_{33}/k_{11})} \tag{3}$$

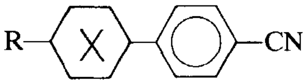
Although in principle $(\epsilon_{\|} - \epsilon_{\perp})/\epsilon_{\perp}$ can be lowered to improve the steepness, this approach is limited by the necessity mentioned above of being able to operate the display at certain fixed (and usually low) voltages. Therefore, we need materials with low (k_{33}/k_{11}) to improve the multiplexing capability.

EXPERIMENTAL METHOD

The splay and bend elastic constants (k_{11} and k_{33}) were determined from the detailed analysis of the capacitance-voltage characteristic of a 25 μm thick nematic layer with initial homogeneous alignment (zero tilt and twist) distorted by an alternating electric field applied normal to the layer. The low voltage capacitance together with the empty capacitance gave $\epsilon_{\perp}$ repeatable to within 0.5%, and $\epsilon_{\|}$ was estimated from the high field data using a 1/V extrapolation.[2] The capacitance-voltage data, $\epsilon_{\perp}$ and the estimated $\epsilon_{\|}$ value were fitted to the continuum theory by a nonlinear least squares fitting program to determine the "best" fit values of the three parameters $(k_{33} - k_{11})/k_{11}$, threshold voltage (V_c), and $\gamma = (\epsilon_{\|} - \epsilon_{\perp})/\epsilon_{\perp}$. This gave k_{33}, k_{11} and γ to within 5%, 2% and 1%, respectively. To achieve this accuracy an automated system measured the change in capacitance to within 0.01% and the voltage to 10^{-4} V. Equilibrium readings were ensured by increasing the voltage in steps and having a sequence of pauses totalling 2 hours just above V_c. The quality of the alignment was checked by observation of the threshold sharpness of the capacitance/voltage curve and it was found that the increase in the reduced capacitance as the bias voltage was increased to just below threshold $[C(V_c^{(-)}) - C_\perp]/[C_\| - C_\perp]$ was less than 0.03%. Thirty data points in the voltage range V_c to $2V_c$ were used and these gave residuals (the deviations between the fitted curve and experimental data points) of less than 10^{-4} V, which represents the resolution of the voltage measurements. The measurements were made in the temperature range from 0°C to 100°C with the temperature stabilized to within 0.1°C.

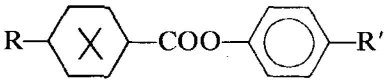
Nematic materials used

Low values of k_{33}/k_{11} are found in hybrid mixtures[3] formed by combining strongly polar materials containing terminal cyano groups,

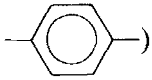


(I)

together with weakly polar, or non-polar materials, of which the esters



(II)

are the best known example. For the type I material we used ZLI 1289, a convenient mixture (available from E Merck) containing cyanobiphenyls ( = ) and phenylcyclohexanes ( = ) with alkyl groups $R = C_2H_5$ and C_4H_9.

These short, even alkyl groups are useful for generating a low threshold voltage[4] and reducing the possibility of an unwanted injected smectic A phase. A standard concentration of 30% (molar) of a variety of type II ester materials was added to ZLI 1289. The esters used and their acronyms are shown in Table I, and the clearing points of the resulting hybrid mixtures are shown in Table II. Usually the clearing points of the hybrid mixtures were spread because of the widely different clearing points of the components, therefore T_{NI}

TABLE I

Esters used in hybrid mixtures

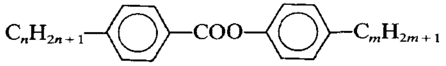
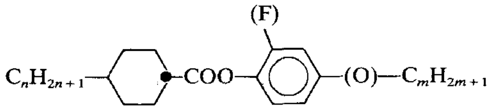
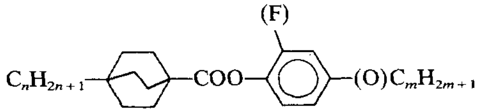
Structure	Acronym	Homologues studied
	Men.m	Me2.2, Me3.3, Me3.5 Me3.7, Me7.3, Me5.5, Me5.7 Me7.7, Me9.9
	(F)Den.(O)m	De5.5, De5.04, FDe5.5
	(F)BCOn.(O)m	BCO5.5, BCO5.04, FBCO5.5

TABLE II

Thermal and dielectric data for the mixtures

		Dielectric data and V_c at 0.90 T_{NI}		
Ester in mixture	T_{NI} (°C)	$\epsilon_\perp$	$(\epsilon_\parallel - \epsilon_\perp)$	V_c
none (ZLI 1289)	67	6.1	13.4	0.772
Me2.2	40	6.3	12.5	0.782
Me3.3	46.5	5.9	11.4	0.837
Me3.5	47	5.7	11.3	0.888
Me3.7	48	5.5	10.7	0.933
Me7.3	47.5	5.5	10.7	0.909
Me5.5	49	5.5	10.7	0.923
Me5.7	50	5.3	10.5	0.989
Me7.7	51	5.1	10.0	1.077
Me9.9	52.5	—	—	—
De5.5	56	5.0	9.3	0.985
De5.04	68	5.4	9.0	1.005
FDe5.5	49.5	5.4	9.6	0.939
BCO5.5	64	5.0	9.2	0.979
BCO5.04	77.5	5.3	8.7	1.005
FBCO5.5	62	5.3	9.0	0.964

represents the mid-point of the biphasic region. Injected smectic A phases were found only in the two mixtures containing Me7.7 and Me9.9.

The variations explored fall into the following three categories:

(i) Different lengths of alkyl chains in the phenyl benzoate ester series are used, covering the range of materials Me2.2 to Me9.9.

(ii) The ring in the acid moiety is varied whilst keeping the alkyl chains fixed at $R = C_5H_{11}$. This covers the Me5.5, De5.5 and BCO5.5 esters.

(iii) Three different phenol moieties are considered—the alkyl, alkoxy and fluoro substituted alkyl phenols. The alkyl group is $R = C_5H_{11}$, with $R = C_4H_9O$ being used as the equivalent alkoxy group. Two groupings are covered in this variation:

De5.5, De5.04 and FDe5.5

and BCO5.5, BCO5.04 and FBCO5.5

ELASTIC CONSTANT RESULTS

(i) Variable alkyl chains (Men.m)

Figures 1 and 2 show k_{11} and k_{33}/k_{11} respectively for hybrid mixtures containing phenyl benzoate esters with a range of alkyl chains from C_2H_5 up to C_9H_{19}; ZLI 1289 is also shown for reference. Providing

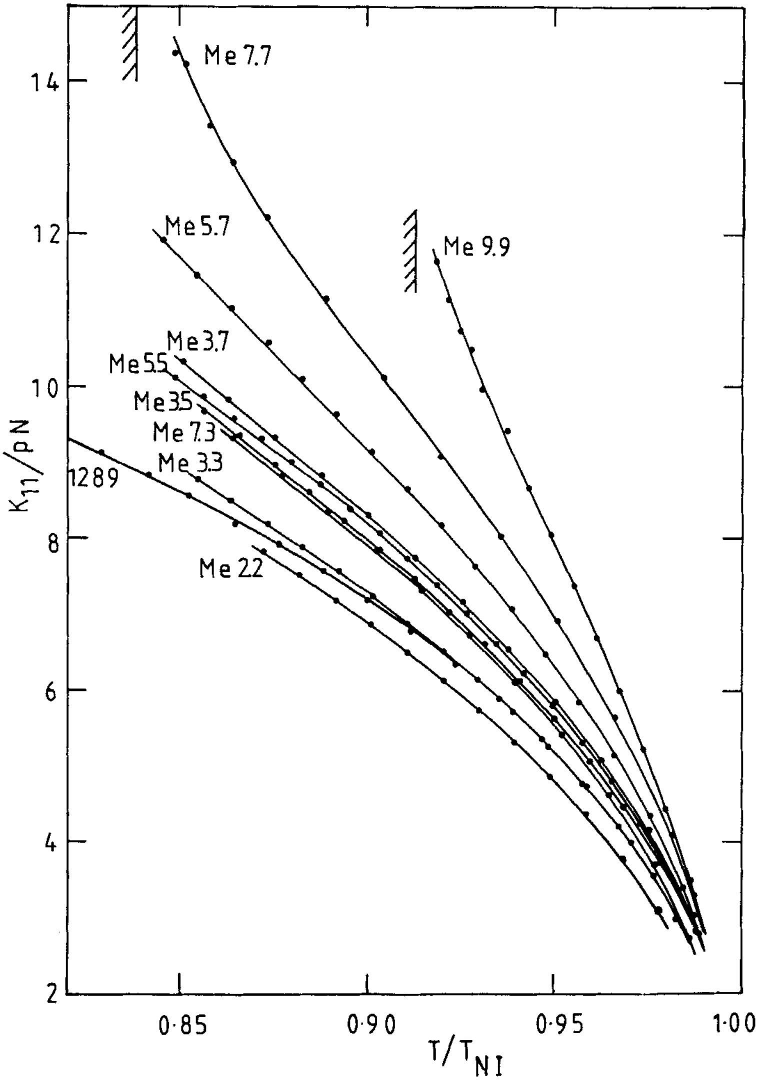


FIGURE 1 Splay elastic constants (k_{11}) for hybrid mixtures containing ZLI 1289 and a range of Men.m esters; pure ZLI 1289 is also shown for comparison.

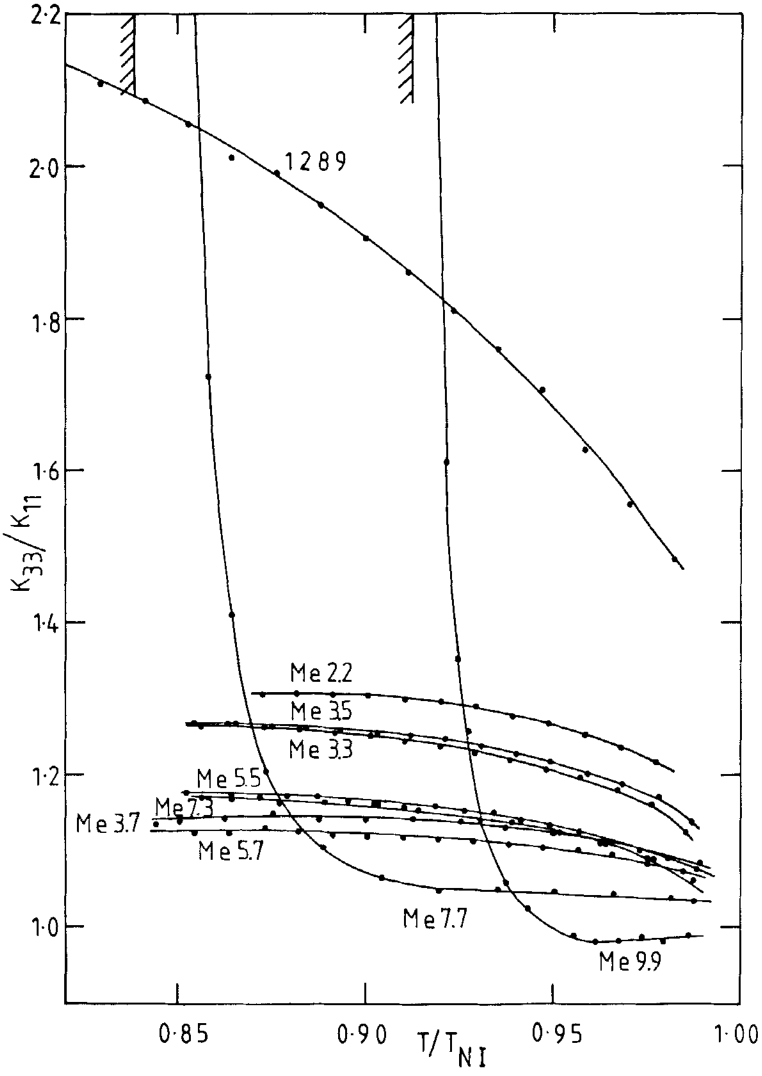


FIGURE 2 Ratio of bend to splay elastic constants (k_{33}/k_{11}) for hybrid mixtures containing ZLI 1289 and a range of Men.m esters; pure ZLI 1289 is also shown for comparison.

the alkyl chains on the phenyl benzoate esters are short, there is little or no increase in k_{11} for the hybrid mixtures compared to pure ZLI 1289. Alkyl chains longer than C_3H_7 cause a progressive increase of k_{11} until Me9.9 shows $k_{11} \approx 80\%$ larger than for ZLI 1289. It is clear therefore, that for low threshold voltage mixtures, esters with short alkyl chains should be used, with Me2.2 and Me3.3 being noticeably superior to the rest. An increase in k_{11} just above the injected smectic A phase is observed in the mixtures containing Me7.7 and Me9.9. This has also been found in other hybrid mixtures.[5] The threshold voltages at 0.90 T_{NI} are given in Table II and show similar values for the hybrid mixture containing Me2.2 and for ZLI 1289. It is also noticeable that $(\epsilon_{\parallel} - \epsilon_{\perp})$ is lowered only slightly by adding the shorter chain esters. This is undoubtedly a consequence of the reduction in anti-parallel ordering of the cyano molecules as the non-polar esters are added.

The ratio k_{33}/k_{11}, given in Figure 2, shows a marked general reduction for the hybrid mixtures compared with ZLI 1289; this is consistent with previous findings for hybrid mixtures[3] and is mainly attributable to a lowering of k_{33}. There is also a small variation in k_{33}/k_{11} between the different hybrid mixtures with the reduction in k_{33}/k_{11} as the alkyl chains are lengthened arising from a small increase in k_{11}. Close to the injected smectic A phase in the hybrid mixtures containing Me7.7 and Me9.9 pre-transitional effects dominate and k_{33}/k_{11} increases significantly.

(ii) The comparison of different rings in the acid moiety (Figure 3) shows very small differences ($\approx$ 5%) in k_{11}. At low temperatures BCO5.5 shows the lowest k_{11}, which perhaps reflects the smaller (dS/dT) observed in the cyano bicyclo [2.2.2] octane derivatives.[6] All of the hybrid mixtures containing the 5.5 esters show an increase of about 10% in k_{11} compared with ZLI 1289. The elastic constant ratio (k_{33}/k_{11}) does show a significant dependence on the ring used, varying from $\approx$ 1.30 for BCO5.5 to $\approx$ 1.25 for De5.5 down to $\approx$ 1.15 for Me5.5. This result is again reminiscent (though smaller in magnitude) of the trend found in the corresponding cyano derivatives.[6]

(iii) Finally we have examined the effect of changing the phenol moiety from alkyl, to alkoxy or to alkyl with a fluoro substituent in the phenyl ring. Figures 4 and 5 shows the results for the De and BCO series respectively. Both systems show the same trend of an increase in k_{11} compared with ZLI 1289 with the fluoro esters showing the least effect. The ratio (k_{33}/k_{11}) does increase progressively by a total of 10% in going from the alkyl through the alkoxy to the fluoro derivative.

DISCUSSION OF RESULTS

Several clear guidelines emerge from our results for the design of practical mixtures for multiplexed twisted nematic displays. Firstly a

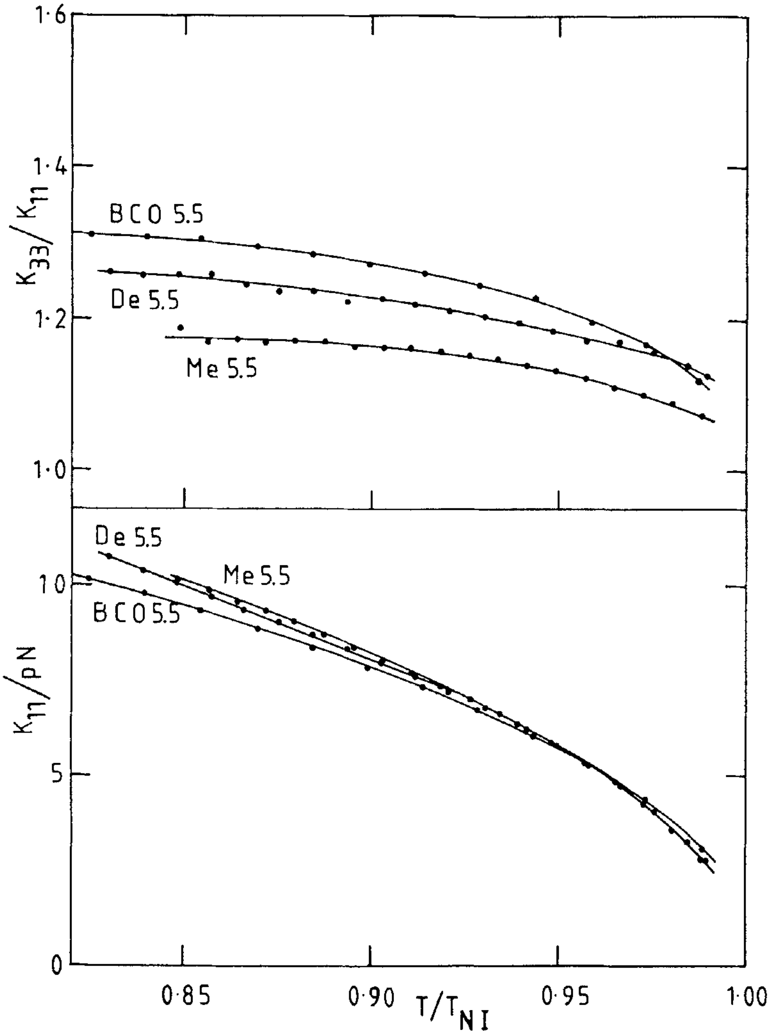


FIGURE 3 Splay elastic constants (k_{11}) and the ratio of bend to splay elastic constants (k_{33}/k_{11}) for hybrid mixtures containing ZLI 1289 and esters with different rings in the acid moiety.

low threshold voltage is achieved by using either short alkyl chain esters or by using fluorinated di-alkyl esters. It is particularly interesting that when very short alkyl chains are used (eg Me2.2 and Me3.3) the hybrid mixtures (which contain only 70% (molar) of ZLI 1289) show a threshold voltage almost identical to pure ZLI 1289.

A good performance at high levels of multiplexing requires a low value of k_{33}/k_{11} and consistent with earlier results on strongly polar materials[7] and on weakly polar materials,[8] a low k_{33}/k_{11} can be achieved by using esters with long alkyl chains. However, there are also other trends which are useful in the selection of suitable esters. By varying the rings in the acid moiety, there is the following trend for k_{33}/k_{11}

phenyl < cyclohexyl < bicyclo [2.2.2] octyl

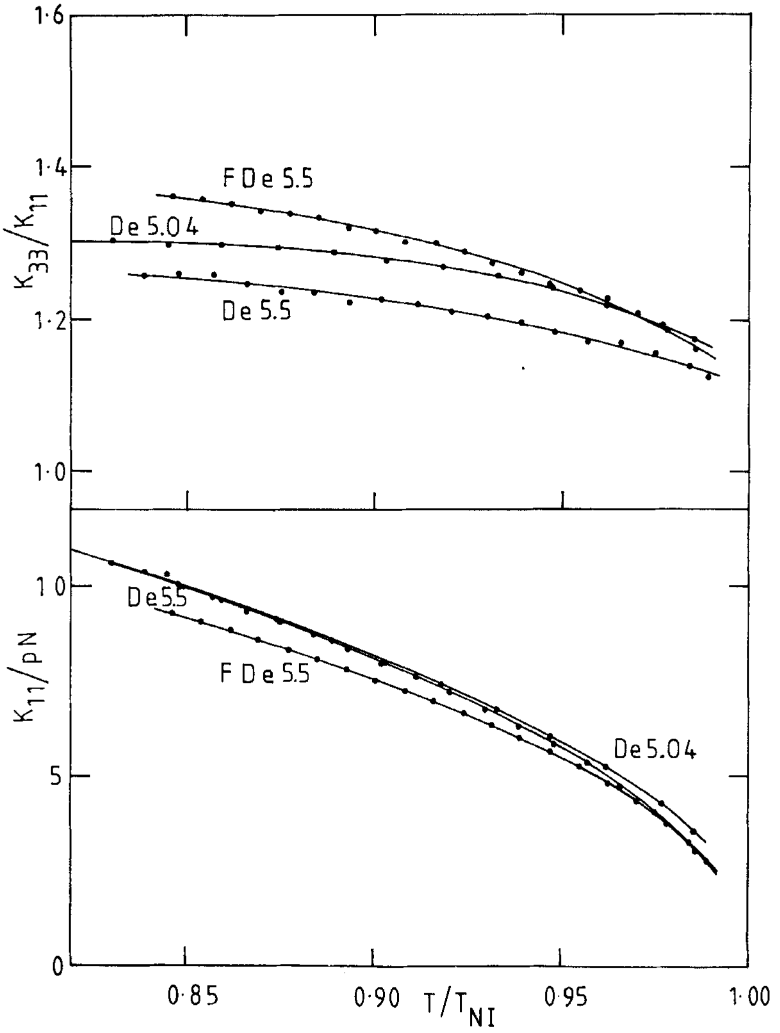


FIGURE 4 Splay elastic constants (k_{11}) and the ratio of bend to splay elastic constants (k_{33}/k_{11}) for hybrid mixtures containing ZLI 1289 and esters with different phenol moieties from the De series.

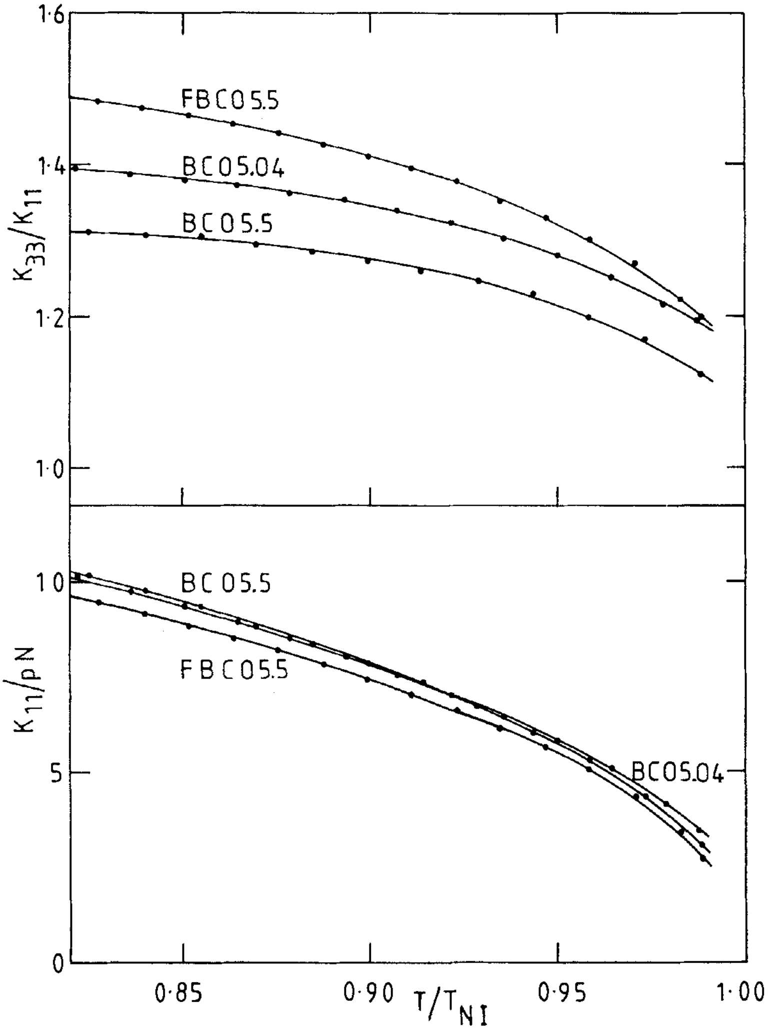


FIGURE 5 Splay elastic constants (k_{11}) and the ratio of bend to splay elastic constants (k_{33}/k_{11}) for hybrid mixtures containing ZLI 1289 and esters with different phenol moieties from the BCO series.

and by varying the phenol moiety the following trend is observed for k_{33}/k_{11}

alkyl < alkoxy < fluorinated alkyl.

It is interesting to correlate these results with the relative strengths of the smectic tendencies expected in the various systems. It has been observed that well away from the pre-transitional region the elastic constants are strongly influenced by the amount of smectic-like local ordering;[9] increasing order increases k_{11} and lowers k_{33}/k_{11}. It has been suggested[5] that for the lowest values of k_{33}/k_{11}, a nematic mixture is required that does not have a pre-transitional smectic region but is otherwise as close as possible to the injected smectic phase in order to maximise the smectic-like local ordering. We see that this is exactly the situation with hybrid mixtures containing the longer chain phenyl benzoate esters, a fact put to good use in the formulation of practical mixtures suitable for high level multiplexing.[10]

We also note that introducing the fluorine substituent decreases k_{11} and increases k_{33}/k_{11}, consistent with the fact that the fluorine substituent is known to suppress the smectic phase[11] and therefore is likely to reduce the smectic-like local ordering in the hybrid mixtures.

CONCLUSIONS

The splay and bend elastic constants of a wide range of hybrid mixtures made from a variety of esters have been examined. Guidelines have been found which relate the structure of the ester to the performance of the hybrid mixtures in multiplexed twisted nematic displays.

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