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: 28 Mar 2007.

To cite this article: H. Hakemi, E. F. Jagodzinski & D. B. Dupré (1983): Temperature Dependence of the Anisotropy of Turbidity and Elastic Constants of Nematic Liquid Crystal Mixture E7, Molecular Crystals and Liquid Crystals, 91:1-2, 129-136

To link to this article: http://dx.doi.org/10.1080/00268948308083080

Mol. Cryst. Liq. Cryst., 1983, Vol. 91, pp. 129–136
0026-8941/83/9102-0129$18.50/0

Printed in the United States of America

Temperature Dependence of the Anisotropy of Turbidity and Elastic Constants of Nematic Liquid Crystal Mixture E7

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(*Received July 15, 1982; in final form September 20, 1982*)

The three principal elastic constants, K_{11}, K_{22} and K_{33} of the eutectic nematic liquid crystal mixture E7 have been determined as a function of temperature by following changes in the anisotropy of turbidity of a magnetically aligned specimen. The agreement with values of K_{22} obtained by a previous capacitance-voltage method is excellent, whereas the values of K_{11} and K_{33} derived from the absorption coefficients are systematically higher.

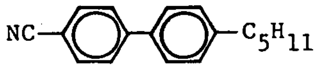
INTRODUCTION

Eutectic nematic liquid crystal mixtures have important applications in electrooptical devices due to their stability, fast response time, and large nematic range which includes room temperature. The three principal elastic moduli K_{11}, K_{22} and K_{33} corresponding to modes of splay, twist and bend, respectively, of the director of the liquid crystal are also fundamental parameters in the design aspects of such switching devices. Low values of the ratio of the bend to splay elastic constants, K_{33}/K_{11}, are particularly sought in materials for displays with large information content.

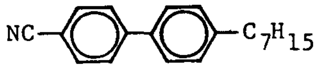
The temperature dependence of K_{11}, K_{22} and K_{33} has been measured by following changes in the anisotropy of turbidity through the major part of the nematic range of E7, the first eutectic liquid crystal widely used in electrooptic displays.

EXPERIMENTAL SECTION

The nematic eutectic mixture E7 was obtained from BDH Chemicals Ltd. and used without further purification. This mixture consists of three alkycyanobiphenyls and one alkylcyanoterphenyl with the following molecular structures:



(5CB)



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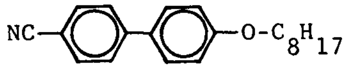

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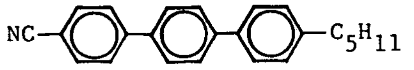

(5CT)

The mixture, as received, was determined by polarization microscopy to clear over the temperature range of 61.0°C to 62.5°C (±0.1°C) with the latter taken as the nematic-isotropic transition temperature, T_{NI}, in this study. The solid-nematic transition occurs around −10°C which is below the capabilities of our temperature control apparatus.

Determination of the three primary elastic constants from the anisotropy of turbidity has been discussed elsewhere[1,2] and requires precise measurements of the total scattering cross section (or turbidity) of a well oriented nematic thin film in three special geometries: (1) $\mathbf{k} \parallel \mathbf{v}_0$; (2) $\mathbf{k} \perp \mathbf{v}_0$, $\mathbf{i} \perp \mathbf{v}_0$ and (3) $\mathbf{k} \perp \mathbf{v}_0$, $\mathbf{i} \parallel \mathbf{v}_0$, where $\mathbf{k}$ is the propagation direction of an incident laser beam polarized in the $\mathbf{i}$ direction and $\mathbf{v}_0$ is the mean direction of the nematic director orientation defined by a strong magnetic field. Experimentally, the absorption coefficients, σ_i, in the selected geometries corresponding to cases $i = 1$, 2, and 3 are measured according to: $\sigma_i = (ln\ I_i^0 - ln\ I_i)/l$, where I_i^0 and I_i are the light intensities of the isotropic phase and nematic phase, respectively, and l is the sample thickness.

The beam of a 7 mW He-Ne laser was passed through a polarization rotator and a series of intercavity and exit mirrors that establish the three required geometries. The details of the method and experimental procedure are discussed in our previous publication[2] and Ref. (1).

The temperature dependence of the anisotropy of turbidity in each geometry was determined on E7 contained in teflon sealed rectangular optical cells with inside thicknesses of $l = 0.1$ and 0.2 cm. The sample cell was placed in a temperature control unit designed to fit between the pole faces of a 14 kG electromagnet which was used to establish the alignment direction ($\mathbf{v}_0$) of the liquid crystal. The temperature of the cell was controlled to ±0.1°C by a constant temperature circulator and measured digitally with a thermocouple placed in direct contact with the sample cell. Temperature range of this study was −0.5°C to 63.0°C.

RESULTS AND DISCUSSION

The variation of the absorption coefficients, σ_i, of E7 in the three geometries is shown in Figure 1 as a function of the relative temperature, $\Delta T = (T_{NI} - T)$ in °C. The σ_i data reported here are only for the sample thickness of $l = 0.2$ cm as some inconsistency was found with the thinner ($l = 0.1$ cm) cell with the values of σ_1. The inconsistency in data obtained in geometry 1 could be due to static orientational defects at the glass walls which would have a more significant influence on extraneous light scattering in the thinner cell. If a surface parallel attachment of the liquid crystal is preponderant in these clean but otherwise untreated cells, measurements in geometry 1 would be more likely

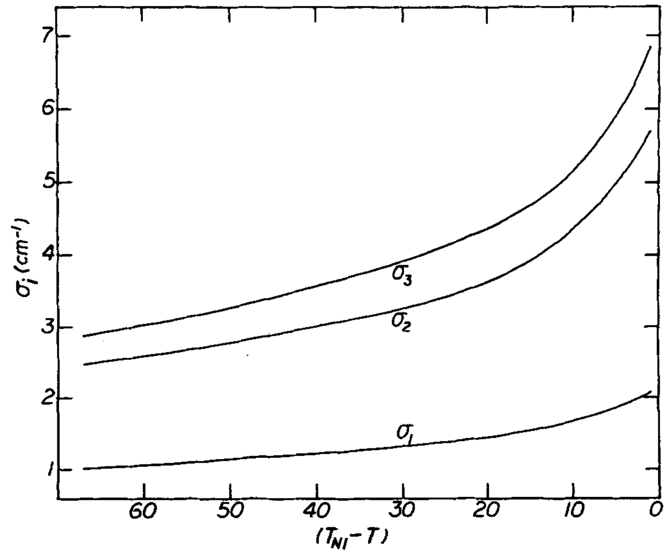

FIGURE 1 Absorption coefficients, σ_1, σ_2 and σ_3, as a function of relative temperature, $\Delta T = (T_{NI} - T)$ for eutectic, nematic mixture E7.

to detect these defects as the magnet field is perpendicular to the larger surfaces of the cell in this configuration [*Cf.* Figure 1 of Ref. (2)].

For purposes of data processing, the σ_i values recorded in 0.5°C increments were fitted to a four constant polynomial of the form:

$$y = B_0 + B_1x + B_2x^2 + B_3x^3$$

where y is the absorption coefficient σ_i and x is ΔT. The constants B_0, B_1, B_2, B_3, were obtained by using least square adjustments and are listed in Table I along with similar polynomial fits to other derived constants of this article. The temperature dependence of σ_2 and σ_3 is found to be more significant than that of σ_1.

Numerical evaluations of K_{11}, K_{22}, and K_{33} were performed by a computer search routine[2] which finds the K_{ii} values for the best fit between experimental and theoretical[1] values of the ratios of σ_1/σ_2 and σ_1/σ_3. Refinement of this routine now allows an accuracy in the determination of the elastic constants of 10%, so far as the method is precise. Systematically higher values of the K_{ii} as compared with those obtained by the Frederik's distortion method were noted in previous utilizations of this procedure[1,2] and other light scattering methods.[3] At this time there is no definitive resolution of the origin of the discrepency. Weak surface anchorage of the liquid crystal which would lead to

TABLE I

Polynomial fits to the temperature dependence of the absorption coefficients, refractive indices and elastic constants of E7: $y = B_0 + B_1x^2 + B_2x^2 + B_3x^3$

y	x	B_0	B_1	B_2	B_3
σ_1	$(T_{NI} - T)$	$+2.14$ $(\pm 2 \times 10^{-2})$	-7.2×10^{-2} $(\pm 5 \times 10^{-3})$	$+2.7 \times 10^{-3}$ $(\pm 3 \times 10^{-4})$	0
σ_2	$(T_{NI} - T)$	$+5.96$ $(\pm 5 \times 10^{-2})$	-2.4×10^{-1} $(\pm 1 \times 10^{-2})$	$+9 \times 10^{-3}$ $(\pm 9 \times 10^{-4})$	-2×10^{-4} $(\pm 2 \times 10^{-5})$
σ_3	$(T_{NI} - T)$	$+7.19$ $(\pm 8 \times 10^{-2})$	-3.0×10^{-1} $(\pm 2 \times 10^{-2})$	$+1.2 \times 10^{-2}$ $(\pm 1 \times 10^{-3})$	-2×10^{-4} $(\pm 3 \times 10^{-5})$
n_o	$(T_{NI} - T)$	$+1.530$ $(\pm 4 \times 10^{-4})$	-2×10^{-3} $(\pm 1 \times 10^{-4})$	$+1 \times 10^{-4}$ $(\pm 7 \times 10^{-6})$	0
n_e	$(T_{NI} - T)$	$+1.650$ $(\pm 9 \times 10^{-4})$	$+6.1 \times 10^{-3}$ $(\pm 2 \times 10^{-4})$	-2×10^{-4} $(\pm 2 \times 10^{-5})$	0
K_{11}	$t_r = T/T_{NI}$	-39.7 (± 6.8)	$+111.0$ (± 15.0)	-70.4 (± 8.3)	0
K_{22}	$t_r = T/T_{NI}$	-8.18 (± 1.08)	$+25.0$ (± 2.4)	-16.6 (± 1.3)	0
K_{33}	$t_r = T/T_{NI}$	-12.9 (± 9.6)	$+68.6$ (± 21.3)	-54.7 (11.7)	0

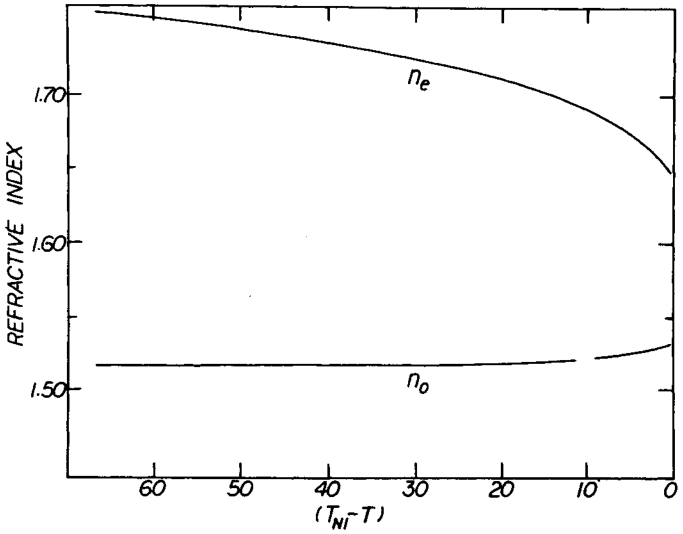

FIGURE 2 Temperature dependence of the ordinary (n_o) and extraordinary (n_e) refractive indices of E7. Interpolation of the data of Ref. (4) to 6328 Å and scaled according to $\Delta T = (T_{NI} - T)$ (°C).

low values of the K_{ii} by the Frederik's distortion can apparently be ruled out as tests are available and have been applied to check for weak anchoring. The possible neglect of volume changes in the theory of equilibrium, field induced distortions of the director pattern have been suggested but not quantitatively explored.[3]

Additional input to the computer routine is the ordinary and extraordinary refractive indices: n_o and n_e, respectively. The values of n_o and n_e of E7 at 6328 Å were deduced from data in the literature.[4] Interpolation of the dispersion data to the wavelength of the He-Ne laser was first performed and the temperature dependence of n_o and n_e scaled according to $\Delta T = (T_{NI} - T)$ (Figure 2). Polynomial lease square fits to this data are presented in Table 1.

The temperature dependence of K_{11}, K_{22} and K_{33} is presented in Figure 3 and Table II as a function of the reduced temperature $t_r = T/T_{NI}$ (in °K/°K). Constants of polynomial fits to this data are listed in Table I. The elastic moduli are also compared with the average value $\bar{K} = 1/3(K_{11} + K_{22} + K_{33})$ and two indicator ratios K_{33}/K_{11} and K_{22}/K_{11} are tabulated.

As expected, all three elastic constants decrease with increasing temperature and exhibit the relative order $K_{33} > K_{11} > K_{22}$.

Some limited data on the temperature dependence of the elastic con-

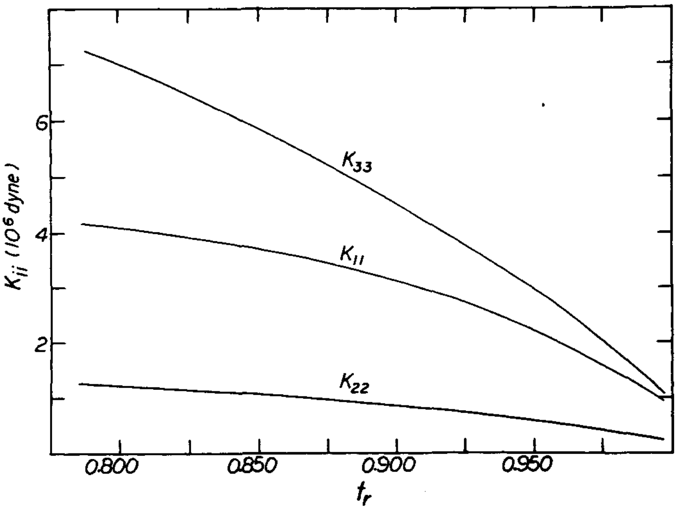

FIGURE 3 Elastic constants of E7 as a function of reduced temperature $t_r = T/T_{NI}$ (°K/°K).

stants of E7 obtained by capacitance-voltage measurements on a twisted nematic preparation are available for comparison.[5] Whereas our data for K_{22} are in excellent agreement with these measurements, K_{11} and K_{33} values reported here are consistently larger. The average values $\bar{K}$, obtained by the procedure of this article, are also larger (by a factor of 2) than those derived from Ref. (5). The ratio of K_{22}/K_{11} in both procedures is constant as a function of temperature. K_{33}/K_{11}, however, decreases as the nematic-isotropic transition is approached.

Our previous study[2] of the temperature dependence of the anisotropy of turbidity of a homologous series of *n*-alkylcyanobiphenyls (*n*-CB with $n = 5,6,7,8$) yielded absolute values of the elastic constants that were systematically higher than those obtained from field distortion methods. Ratios of K_{33}/K_{11} and K_{22}/K_{11} were however in satisfactory agreement among the various measurements.

The above ratios are frequently discussed in attempts to correlate molecular structural factors with macroscopic elasticity of liquid crystals. A definite theoretical development of the elastic constants in terms of microscopic molecular parameters has yet to emerge. One would expect the molecular elongation to be a fundamental determinant in any such theory. The statistical theories of Priest[6] and van der Meer and Vertogen[7] represent this aspect in a manner amenable to direct comparison with the dimensions of a constituent liquid crystal molecule. Theory for example predicts that K_{33}/K_{11} should increase as

TABLE II

Temperature dependence of the elastic constants of E7

	(10^6 dyne)					
$t_r = T/T_{NI}$	K_{11}	K_{22}	K_{33}	$\bar{K}$	K_{33}/K_{11}	K_{22}/K_{11}
0.9955	0.82	0.24	0.91	0.66	1.12	0.29
0.9925	1.00	0.25	1.18	0.81	1.12	0.25
0.9880	1.18	0.29	1.46	0.98	1.24	0.25
0.9850	1.30	0.32	1.70	1.11	1.30	0.25
0.9775	1.56	0.38	1.98	1.31	1.27	0.24
0.9700	1.83	0.43	2.41	1.56	1.31	0.24
0.9555	2.22	0.55	2.91	1.89	1.31	0.25
0.9405	2.43	0.65	3.29	2.13	1.35	0.27
0.9245	2.67	0.73	3.70	2.37	1.38	0.27
0.9105	3.03	0.79	4.26	2.69	1.41	0.26
0.8960	3.14	0.85	4.63	2.87	1.47	0.27
0.8810	3.26	0.93	4.98	3.08	1.53	0.28
0.8660	3.50	1.02	5.34	3.29	1.52	0.29
0.8510	3.72	1.09	5.73	3.51	1.54	0.29
0.8360	3.90	1.12	6.30	3.83	1.62	0.29
0.8210	3.96	1.12	6.60	3.89	1.67	0.28
0.8120	4.04	1.16	6.84	3.92	1.69	0.29

the length to width (L/D) ratio of the molecule (taken as a rigid rod) increases. (This is true so long as $\bar{P}_4/\bar{P}_2 > 0$, which is not always the case. $\bar{P}_n$ is the average value of the *n*th Legendre polynomial describing orientational order in the liquid crystal.) K_{33}/K_{11} has in fact been found to increase when the rigid core of structurally similar thermotropic liquid crystals is elongated.[8,9] A decrease of this ratio is observed however with homologous series involving para-substituted *n*-alkyl chains.[8,9] In the latter case rotational isomers of the alkyl part of the molecule increase the width as well as the length of the molecule as the number of methylene carbons is increased. There are further complications in determining L/D of a responding unit when strong polar moieties (such as cyano groups) are presented that can lead to molecular pairing.[10]

We find that the ratio K_{33}/K_{11} is larger for the eutectic mixture E7 at most reduced temperatures than values obtained for either of the components 5CB and 7CB in our previous examination of the turbidity anisotropy procedure. This could be due to the longer molecular axial ratio of the terphenyl component, 5CT. The terphenyl compound is present to only 8% by weight in the mixture[5] however and no data on the elastic constants of the 80CB compound is currently available. A fundamental flaw in the theories sited[6,7] which are truncated developments in *n*th order Legendre polynomials was recently pointed out.[11]

We hesitate therefore to make further speculation about the molecular basis of the values of the elastic constants that we find for E7, particularly as it is a multicomponent mixture with undoubtedly more complicated interactions among molecules.

Acknowledgments

This work was supported in part by the National Science Foundation under grant DMR-7903760 and the National Institutes of Health under grant HL-24364. The authors wish to thank Drs. M. G. Pellat and C. R. P. Wilcox of BDH Chemicals Ltd. for the supply of the E7 liquid crystalline mixture.

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