

MOLECULAR STRUCTURE AND ELASTIC CONSTANTS OF NEMATIC LIQUID CRYSTALS

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Received 21 March 1979

The elastic constants are reported of a number of nematic liquid crystals with relatively rigid molecular structures. The data prove conclusively, that the ratio of the bend and splay elastic constants K_3/K_1 increases with increasing length to width ratio.

According to the continuum theory [1] of nematic liquid crystals, the bulk elastic properties can be described by three elastic constants, associated with the restoring forces opposing splay (K_1), twist (K_2) and bend (K_3) distortions. The distortion free energy density is

$$F_{\text{dist}} = \frac{1}{2} [K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2] . \quad (1)$$

Here \mathbf{n} , the director, indicates the preferred direction of the long axes of the molecules. The continuum theory has been very successful in explaining the phenomenological properties of nematic liquid crystals. On the other hand relatively little attention has been paid so far to the relationship between elasticity and molecular structure. Systematic studies have been reported [2,3] for some homologous series, in which case K_3/K_1 was found to decrease with increasing length of the alkylene chain. This result is somewhat surprising, as various theoretical approaches predict that K_3/K_1 should increase with increasing length to width ratio of the molecules. In this paper we present systematic results for K_3/K_1 of some nematics with rigid molecular structures, differing in length to width ratio. The results can be well described in terms of existing theoretical models. We conclude, that earlier results for homologous series are "special" in the sense that other effects, associated with the flexibility of the alkylene chains, come into play.

The compounds studied are *p*-methoxybenzylidene-

p'-cyanoaniline (MBCA), anisylidene-*p*-aminophenylacetate (APAPA) and *p*-methoxybenzylidene-*p'*-aminophenylbenzoate (MBAPB). Table 1 lists the molecular structures, the crystal-nematic and nematic-isotropic transition temperatures. The materials were purified by several recrystallizations from methanol.

The elastic constants have been measured by following optically the Frederiks transition of uniformly aligned samples in a magnetic field. In this way a critical field H_c is measured, which marks the onset of the distortion:

$$(H_c)_i = (\pi/d)(K_i/\Delta\chi)^{1/2}, \quad i = 1, 2, 3 . \quad (2)$$

Here d is the thickness of the layer and $\Delta\chi$ the anisotropy of the magnetic volume susceptibility. The twist critical field was measured using conoscopy [4] and the splay and bend critical fields by recording the intensity of a laser beam traversing the nematic layer [5]. Strong anchoring of the molecules at the sample boundaries and a precise position of the field relative to the director was ensured, as described in previous papers [6,7].

First we shall consider the ratios of the elastic constants. In table 2 we have collected K_3/K_1 and K_2/K_1 of the compounds studied, all taken at the same reduced temperature, i.e. at $T/T_c = 0.95$, where T_c is the nematic-isotropic transition temperature. In order to relate these ratios to the overall molecular shape, we have calculated the length to width ratio of the molecules. First the lengths L were obtained from molecular models and the molecular volumes V from tabulated Van der Waals radii and bond lengths [8]. Assuming that

Table 1
Molecular structures of the compounds studied.

		nematic range (°C)
MBCA		106-118.0
APAPA		82-111.0
MBAPB		119-177.7

the molecules can be represented by spherocylinders, i.e. cylinders capped with hemispheres at both ends, then the widths W and parameters $R = (L - W)/W$ can also be found (see table 2). The results indicate that K_3/K_1 is related to the molecular length to width ratio, as is shown also in fig. 1. The corresponding quantities of *p*-azoxyanisole (PAA) [7] have also been included in the figure. Like the other compounds considered, the molecular structure of PAA is relatively rigid. However, the bridging group, connecting the two benzene rings is totally different. Nevertheless PAA fits the trend observed for the Schiff's bases quite well.

Using the thickness d , which was measured interferometrically, the individual $K_i/\Delta\chi$ can be calculated (see fig. 2). MBAPB could only be measured up to $T/T_c = 0.94$, since the materials used for the preparation of the sample cells could not stand higher temperatures. We note, that the values of $K_i/\Delta\chi$ for MBAPB are lower than the corresponding quantities of APAPA and MBCA. This is probably mainly due to a difference in $\Delta\chi$. As a MBAPB molecule contains three benzene rings, we can expect that $\Delta\chi$ is approximately 1.5

Table 2
Ratio's of the elastic constants at $T/T_c = 0.95$, molecular volumes V and lengths L . $R + 1$ is the overall length to width ratio.

	K_3/K_1	K_2/K_1	V (Å ³)	L (Å)	R
MBCA	1.97	0.64	233	14.2	1.92
APAPA	2.16	0.71	258	15.7	2.25
MBAPB	2.55	0.71	317	19.1	2.98

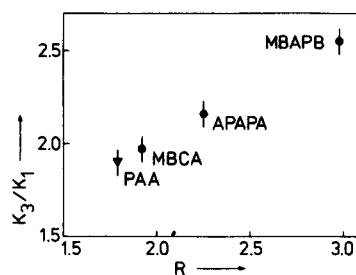


Fig. 1. Ratio of the bend and splay elastic constants K_3/K_1 ($T/T_c = 0.95$) versus R , where $R + 1$ is the molecular length to width ratio.

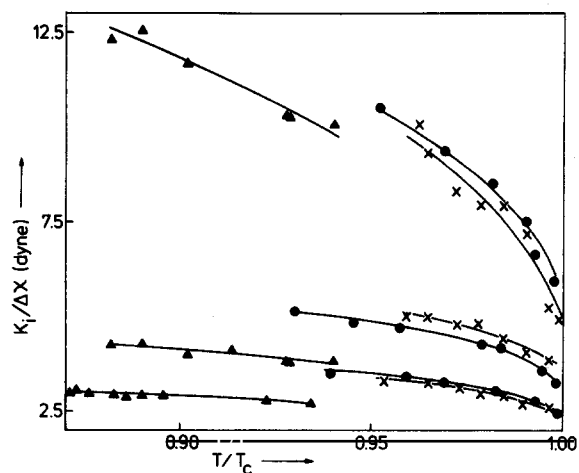


Fig. 2. $K_i/\Delta\chi$ as a function of reduced temperature T/T_c ($K_3/\Delta\chi > K_1/\Delta\chi > K_2/\Delta\chi$). \times , MBCA; \bullet , APAPA; \blacktriangle , MBAPB.

times greater than this quantity for the other compounds.

When discussing the results in terms of existing theories, we have to rely on models that take into account the characteristic elongated shape. This excludes a discussion in terms of the calculations of Nehring and Saupe [9], which are based on the Maier-Saupe [10] theory. Priest [11] has extended these calculations, still assuming axial symmetry of the molecules, but including higher order terms in the intermolecular potential. He has obtained the result

$$\begin{aligned} K_1/\bar{K} &= 1 + \Delta - 3\Delta' \langle P_4 \rangle / \langle P_2 \rangle + \dots, \\ K_2/\bar{K} &= 1 - 2\Delta - \Delta' \langle P_4 \rangle / \langle P_2 \rangle + \dots, \\ K_3/\bar{K} &= 1 + \Delta + 4\Delta' \langle P_4 \rangle / \langle P_2 \rangle + \dots, \end{aligned} \quad (3)$$

where $\bar{K} = (K_1 + K_2 + K_3)/3$ and Δ and Δ' depend on molecular properties. The degree of orientational order of the nematic is described by the parameters $\langle P_{2n}(\cos \theta) \rangle$, where P_{2n} represents the Legendre polynomial of degree $2n$, the brackets denote a statistical average and θ is the angle between the long molecular axis and the director. In order to calculate Δ and Δ' , further assumptions have to be made. Representing the molecules by spherocylinders, interacting via a hard core repulsion, the result is [11]

$$\begin{aligned} \Delta &= (2R^2 - 2)/(7R^2 + 20), \\ \Delta' &= 27(R^2/16 - 1/6)/(7R^2 + 20), \end{aligned} \quad (4)$$

where $R + 1$ is the overall length to width ratio of the spherocylinders.

In fig. 3 the ratio's K_i/\bar{K} are plotted as a function of temperature for APAPA. K_1/\bar{K} and K_2/\bar{K} increase somewhat with increasing temperature, whereas K_3/\bar{K} decreases. Assuming that the molecules can be represented by hard spherocylinders, table 2 and eq. (4) show that Δ and Δ' are positive for the compounds studied. Since $\langle P_4 \rangle / \langle P_2 \rangle$ decreases with increasing temperature, eqs. (3) and (4) predict at least qualitatively the correct temperature dependence. The other Schiff's bases studied exhibit a similar temperature dependence.

Finally we have collected in table 3 experimental data of K_1/\bar{K} , K_3/\bar{K} and K_3/K_1 at $T/T_c = 0.95$ as well as the corresponding quantities calculated using eqs. (3) and (4). In the absence of measurements of $\langle P_4 \rangle$ for the compounds studied, we assume $\langle P_4 \rangle / \langle P_2 \rangle = 0.5$.

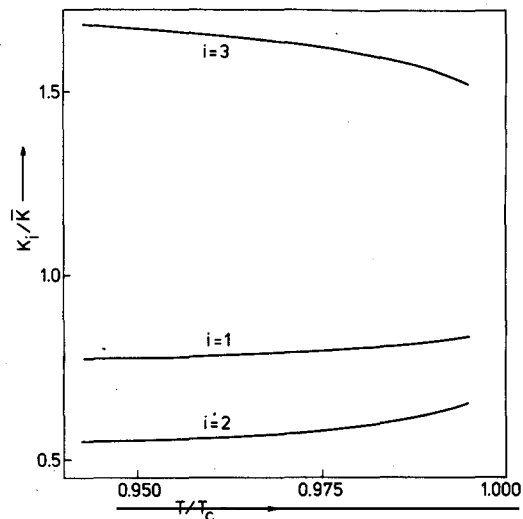


Fig. 3. Temperature dependence of the parameters K_i/\bar{K} for APAPA.

The table shows, that the experimentally observed trends agree with the trends calculated using eqs. (3) and (4). This is not true for K_2/\bar{K} . Previously [3] we have suggested that the ratio K_2/K_1 reflects the deviation from axial symmetry of the molecules, which is not incorporated in the calculations of Priest.

We conclude, that for rigid molecules K_3/K_1 increases with increasing length to width ratio, in agreement with theoretical predictions, which take account of the molecular shape. This result is in contrast with results obtained for molecules with flexible alkylene chains, where K_3/K_1 decreases with increasing chain length. In the latter case the molecular dimensions are not well defined. The suggestion has been raised [3]

Table 3
Experimental and theoretical values of K_1/\bar{K} , K_3/\bar{K} and K_3/K_1 at $T/T_c = 0.95$. The theoretical values were calculated using eqs. (3) and (4) with $\langle P_4 \rangle / \langle P_2 \rangle = 0.5$ and R -values taken from table 2.

	experiment			theory		
	K_1/\bar{K}	K_3/\bar{K}	K_3/K_1	K_1/\bar{K}	K_3/\bar{K}	K_3/K_1
MBCA	0.83	1.64	1.97	1.06	1.19	1.12
APAPA	0.77	1.67	2.16	1.04	1.29	1.24
MBAPB	0.70	1.79	2.55	1.00	1.45	1.45

that the effective molecular length to width ratio decreases with increasing chain length, as a result of the flexibility. However this decrease is probably not sufficient to account for the decrease of K_3/K_1 . Possible explanations are either an anomalous increase of K_1 similar as discussed by De Gennes [12] for nematic polymers or an anomalous decrease of K_3 , owing to the presence of banana-like shaped molecular conformations, as discussed by Gruler [13].

We thank H.J. Roebbers and J.J. Jonker for technical assistance and B.W. van der Meer for valuable discussions. This work was performed as a part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) with financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek" (ZWO).

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