

Molecular dimensions and elastic constants of nematic liquid crystals

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A discussion is given of the molecular factors that influence the elastic constants. For relatively rigid molecules the ratio K_3/K_1 varies parallel to the molecular length/width ratio. However, this trend is reversed if flexible alkyl chains are incorporated in the molecular structure. The ratio K_2/K_1 is rather constant for various nematogenic compounds.

Introduction

The bulk elastic properties associated with curvature of the director \vec{n} of a nematic liquid crystal can be described by three elastic constants. These constants are associated with the restoring torques opposing splay (K_1), twist (K_2) and bend (K_3) of the director pattern. The elastic distortion free energy density is given by [1]:

$$F_d = \frac{1}{2} [K_1 (\nabla \cdot \vec{n})^2 + K_2 (\vec{n} \cdot \nabla \times \vec{n})^2 + K_3 (\vec{n} \cdot \nabla \vec{n})^2]. \quad (1)$$

In this paper we shall pay attention to the molecular factors that influence these elastic constants. In particular we shall consider the possible relations between the ratios K_3/K_1 and K_2/K_1 and the molecular dimensions.

It is only during the last few years that systematic studies of the relation between molecular structure and elastic constants have been made [2-6]. The ratio K_3/K_1 has been found to vary considerably, in contrast to the results for K_2/K_1 . For the nematogenic compounds studied up to now one has:

$$0.5 < K_3/K_1 < 3.0,$$

$$0.5 < K_2/K_1 < 0.8.$$

However, it should be said that the range of compounds studied is much smaller in the latter case. Reliable measurements of K_2 are still scarce.

The ratio K_3/K_1 depends in general somewhat on the temperature. This temperature dependence is absent or very small when $K_3 \approx K_1$, and is stronger the more K_3 and K_1 differ from each other [2]. It is often assumed that

$K_1 \sim S^2$, where S is the nematic order parameter. However, such a proportionality would lead to ratios of elastic constants independent of the temperature, and therefore cannot be generally valid. In fact theoretical models that predict $K_1 \sim S^2$, also predict $K_3 = K_1$. For a further discussion of the temperature dependence we refer to [7].

K_3/K_1 and molecular length/width ratio

Intuitively one would expect relations between the elastic constants and the molecular dimensions, as we shall illustrate using a strongly simplified model. We shall take the molecules as rigid and cylindrically symmetric so that they can be represented by rods of length L and width W . Moreover, we assume ideal order ($S = 1$). Let the distance between the centers of neighbouring molecules in the direction of \vec{n} be denoted by z_0 , and perpendicular to \vec{n} by x_0 or y_0 . For a close-packed nematic liquid we then can take approximately

$$z_0/x_0 = z_0/y_0 \approx L/W. \quad (2)$$

Introducing a distortion of \vec{n} , neighbouring molecules will have slightly different preferred directions making an angle θ with each other. The elastic distortion free energy density then will be given by $\frac{1}{2}K_1(\theta/W)^2$ for a splay distortion, by $\frac{1}{2}K_2(\theta/W)^2$ for a twist distortion, and by $\frac{1}{2}K_3(\theta/L)^2$ in the bend configuration. (Note that the elastic constants have the dimension of energy/length). Thus we find

$$K_1:K_2:K_3 = 1:1:(L/W)^2. \quad (3)$$

Results analogous to Eq. (3) have been derived by various authors in a more sophisticated and sometimes better acceptable way [8,9,10]. The weakness of these lattice models lies in the assumption of a particular configuration of the molecules. However, the results of a more general calculation of the elastic constants by Priest [11] confirm the dependence of K_3/K_1 on L/W , albeit in a more complicated form.

In the case of some relatively rigid molecules the ratio K_3/K_1 indeed increases if the molecular length is increased, as illustrated in Fig. 1. *p*-Azoxyanisole (PAA), although different in bridging group from the other compounds, fits in with the general trend. Furthermore, if for MBBA the width is increased by adding an *ortho*-hydroxy group, K_3/K_1 decreases from 1.35 to

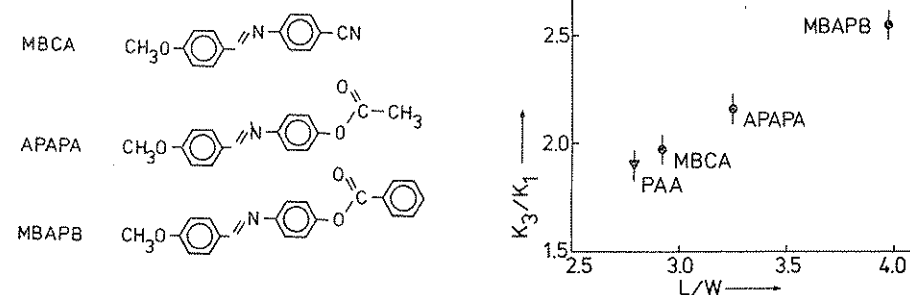


Fig. 1. Variation of K_3/K_1 with L/W for some relatively rigid molecules (ref. [13]).

1.06 (at $T/T_{NI} = 0.96$) [5]. These experiments are at least qualitatively in agreement with the theoretical ideas discussed above.

Rather different results have been obtained for some homologous series [2,5]. If the length of the alkyl chain is increased, the ratio K_3/K_1 is found to decrease. In this way rather low values of K_3/K_1 (even smaller than unity) have been obtained. Qualitatively this can be explained as follows [2]. Compared with more rigid molecules the flexible alkyl chains hinder a sliding of the molecules along each other (see Fig. 2). This means that neighbouring molecules have an enhanced preference to be with their aromatic cores close to each other. Thinking of clusters of several molecules this could

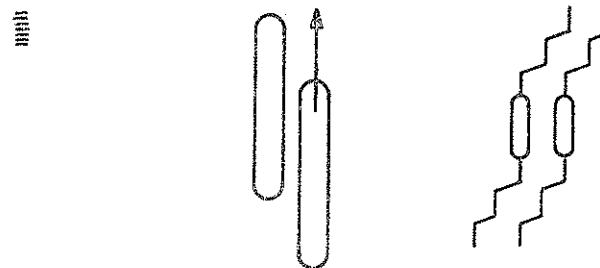


Fig. 2. Sliding of rigid molecules and molecules with flexible groups along each other.

lead to an effective width, with L/W_{eff} possibly smaller than one. Some preliminary calculations along this line [12] indicate that with reasonable parameters indeed values of $K_3/K_1 \approx 0.5$ can be reached. This effect should be distinguished from pretransitional smectic behaviour. In that case much larger numbers of molecules are arranged in smectic-like layers, leading to a strong increase of K_3 . Anyhow, these results for K_3/K_1 emphasize the importance of incorporating the flexibility of the alkyl chains somehow in molecular theories of the nematic phase.

K_2/K_1 and the cylindrical symmetry of the molecules

The fact that in Eq. (3) $K_2 = K_1$ is in the usual models a consequence of the assumption that the spatial dependence of the intermolecular potential can be separated from the rotational dependence. In combination with the cylindrical symmetry of the molecules, this makes the intermolecular interactions the same for a twist and a splay distortion. With the more complete theory of Priest [11] one obtains, however, $K_2 < K_1$. Moreover, in agreement with the experiments, for realistic length/width ratios K_2/K_1 is predicted to be only slightly dependent on L/W .

In the spirit of the above discussion one might wonder whether a stronger variation of K_2/K_1 will be found if the assumption of cylindrical symmetry of the molecules is dropped. In that case one could expect this ratio to be influenced by the degree of "flatness" of the molecules. We have investigated this question experimentally by measuring the elastic constants for three compounds with a very similar molecular structure, but a different degree of

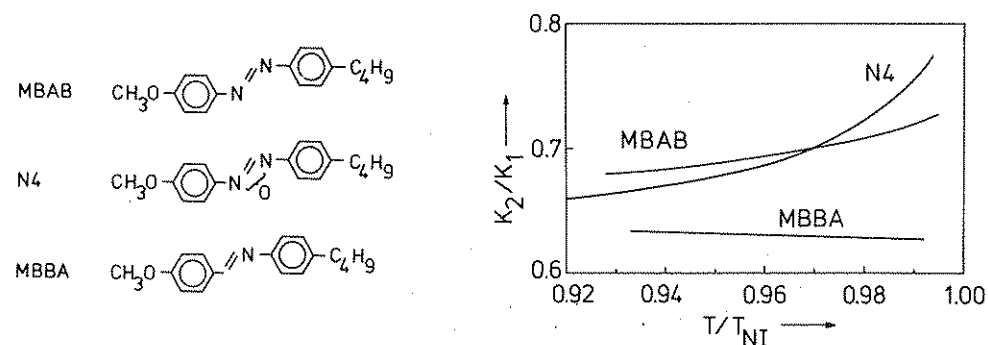


Fig. 3. The ratio K_2/K_1 for three compounds with a rather different degree of flatness.

flatness. The results, obtained via the well-known Frederiks-thresholds, are given in Fig. 3. MBAB is planar, N4 has an angle of about 20° between the planes of the two benzene rings, while for MBBA this angle is of the order of 45° . Within the experimental accuracy of about 5-10% the ratio K_2/K_1 is nevertheless very similar. The same applies to K_3/K_1 . The constancy of K_2/K_1 probably indicates that the nematogenic molecules can indeed be considered as effectively cylindrically symmetric.

Conclusions

For various electro-optic applications of nematic liquid crystals one is interested in sharp thresholds. This property is largely determined by ratios of elastic constants, for which now some general rules can be given. High values of K_3/K_1 are obtained with relatively rigid molecules with a high L/W ratio. Low values of K_3/K_1 are found when long alkyl chains are incorporated in the molecular structure. The ratio K_2/K_1 seems to be rather constant, and a high value of K_3/K_2 (important for the cholesteric-nematic transition) must be obtained via compounds with a high K_3/K_1 .

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