

ELASTIC CONSTANTS OF SOME NEMATIC LIQUID CRYSTALS WITH BANANA-SHAPED MOLECULES

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Results are given for the elastic constants in the nematic phase of some molecules with a curved (banana-like) molecular shape. In principle this could lead to a reduced bend elastic constant due to the possibility of adjusting to a bend deformation by a redistribution of the molecules. However, the elastic constants turn out to have quite normal values as compared with similar non-curved molecules.

Constraints on the preferred orientation of a nematic liquid crystal, given by the director \mathbf{n} , often force \mathbf{n} to be non-uniform. The associated elastic properties are described by three bulk curvature-elastic constants, corresponding to the restoring torques opposing splays (K_1), twists (K_2), and bends (K_3), respectively. The distortion free energy reads [1]

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

During the last decade numerous studies of the elastic properties of nematics have appeared [2], both from a more fundamental point of view and with applications in mind. In the latter case especially the quantity K_3/K_1 is relevant, which should be low to improve the threshold of twisted nematic displays [3]. In this letter we investigate the possibility to obtain low values for K_3 by taking molecules with an intrinsic bend (banana shape), that can adjust to a bend field [4]. In spite of theoretical estimates that this could be an important effect [5,6] the result is negative: the ratio K_3/K_1 is exactly as expected for similar rigid molecules without a banana form.

The formulae of the molecules investigated are given in the inset of fig. 1, where $n = 1, 5$ or 7 . The *para*-axes of the two benzene rings are not colinear. From electron diffraction measurements on the unsubstituted central ring system the angle between these

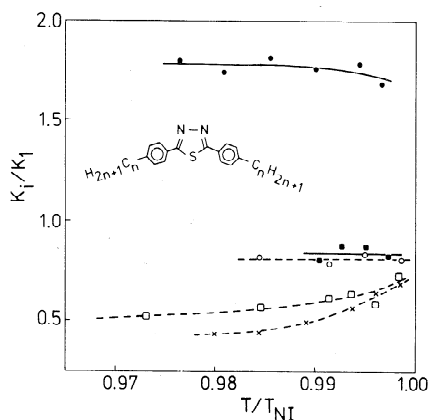


Fig. 1. K_3/K_1 (full line) and K_2/K_1 (broken line) versus reduced temperature; \bullet : $n = 1$, \blacksquare : $n = 5$, \times : $n = 7$.

axes is estimated to be 18° [7]. Hence especially for $n = 1$, where in contrast to $n = 5$ and 7 no different alkyl conformations can interfere, the molecule is a good model of a banana-shaped specimen. The compounds were obtained from Dr. J. van der Veen [8] (Philips Research Laboratories, Eindhoven, The Netherlands) and Dr. D. Demus [9] (Laboratory of Physical Chemistry, Martin-Luther-University, Halle, DDR). The transition temperatures are given in table 1.

The elastic constants were determined using the Freedericksz transition of samples of $80\text{--}100\ \mu\text{m}$ thickness in an external magnetic field [1,2]. The

Table 1

Transition temperatures of the compounds studied; K is crystal, S_C = smectic-C, N is nematic, I is isotropic; temperatures in degrees centigrade.

| n | T | | |
|---|---------------------------|-------------------|-------------|
| | K-S _C | S _C -N | N-I |
| 1 | 161.9-162.2 ^{a)} | | 172.6-172.8 |
| 5 | 90.9-91.2 | 123.1-123.4 | 164.8-165.2 |
| 7 | 79.8-80.1 | 148.6-148.8 | 158.0-158.2 |

^{a)} Transition from K to N.

deformation of the director was determined optically. In the case of the splay geometry by direct interference of a laserbeam, for the twist geometry by conoscopic observation of the sample. From a least-squares fit of the optical data to the theoretical formulas, $K_1/\Delta\chi$, K_3/K_1 and $K_2/\Delta\chi$ can be determined, where $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility. This procedure requires data of the refractive indices. These were obtained using an Abbe-refractometer for n_0 , while Δn was determined directly by interferometry. Details of the methods have been published elsewhere [10].

For $K_1/\Delta\chi$ and $K_2/\Delta\chi$ values were obtained in the order of 2-20 dyne. This is very similar to results for compounds with only two benzene rings [2]. As $\Delta\chi$ is roughly proportional to the number of aromatic rings, one expects $\Delta\chi$ values of about 1.5×10^{-7} CGS units [2]. This leads to values for K_1 and K_2 between 10^{-7} and 10^{-6} dyne. We conclude that K_1 and K_2 are not different from what is expected in analogy with more linear molecules.

In the absence of more detailed information on $\Delta\chi$ we concentrate on the ratios K_3/K_1 and K_2/K_1 , as displayed in fig. 1. From this figure we note two trends:

(1) $K_2/K_1 \approx 0.5-0.7$, more or less independent of the temperature and only slightly dependent on the value of n .

(2) K_3/K_1 decreases with increasing chain length as given by n .

Both trends are quite similar to results observed for several other series of compounds [2]. For relatively rigid molecules (no flexible alkyl chains) Leenhouts [10] has established empirically a proportionality

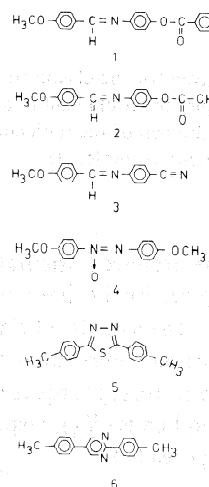
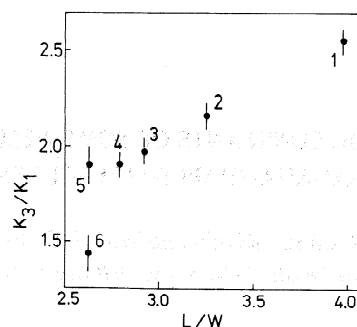


Fig. 2. K_3/K_1 and the length/width ratio of some nematics without flexible alkyl chains (1-4 from ref. [10]).

between K_3/K_1 and L/W , where L and W are the molecular length and width, respectively (see fig. 2). If we consider the compound with $n = 1$, one can estimate from space-filling molecular models $L/W \approx 2.6$. From fig. 2 we note that this fits in nicely with the trend observed for rigid molecules without a curved molecular shape.

Finally we compared the result of K_3/K_1 for $n = 1$ with that of a linear molecule with three aromatic rings (no. 6 in fig. 2). In this case L/W is very similar and K_3/K_1 is even slightly lower. In fact heterocyclic compounds often give a somewhat lower K_3/K_1 as compared with analogous compounds with benzene rings [3]. Without going into this problem, we conclude again that there is no reason to ascribe any special effect to the K_3/K_1 ratio of the banana-shaped analogue.

Helfrich [5] has given a theoretical estimate for the

effect on the elastic constants due to the molecular adjustment to a strain field. If the unadjusted modulus is denoted by \bar{K} , the result for the bend elastic constant is

$$K_3 = \bar{K}_3 / [1 + \beta^2 N^{-1/3} (\bar{K}_3 / 2k_B T)]. \quad (2)$$

Here β is the angle that expresses the curvature of the molecule, N is the number of molecules and k_B is Boltzmann's constant. With $\beta = 0.3$, $N = 10^{22} \text{ cm}^{-3}$, $\bar{K}_3 = 10^{-6} \text{ dyne}$, and $k_B T = 6 \times 10^{-14} \text{ erg}$, the adjustment of \bar{K}_3 turns out to be of the order of 5%. More sophisticated calculations by Gruler [6], that take the internal field correction, the elongated molecular shape, and the degree of order into account, predict the effect to be an order of magnitude larger. In contrast to these estimates we conclude from the present experimental results that the effect of adjustment of K_3 due to a redistribution of the molecules in a bend field, if any, must be small.

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