

Chapter 8

Experimental determination of the
splay and bend elastic constants
of a discotic nematic

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EXPERIMENTAL DETERMINATION OF THE SPLAY AND BEND ELASTIC CONSTANTS OF A DISCOTIC NEMATIC

8.1 INTRODUCTION

After the discovery of **discotic** mesomorphism by Chandrasekhar et al. [1], a large number of **discotic mesogens** have been synthesized. But relatively few of these exhibit the nematic phase. In contrast to the nematics of rod-like molecules, the director in a **discotic** nematic (N_b) represents the preferred orientation of the short molecular axis (Fig. 1). Consequently, the medium is optically and diamagnetically negative. The dielectric anisotropy can however be positive or negative depending on the detailed molecular structure.

The mechanical properties of the N_b phase are evidently of much interest. For example, if the properties of the medium are determined by long range order alone, the splay elastic constant K_1 is expected to be greater than the bend elastic constant K_3 in a **discotic** nematic. On the other hand, in a nematic of rod-like molecules K_3 is expected to be greater than K_1 , under the same condition [2,3]. Though nematics of rod-like molecules have been extensively studied, there have been only a few measurements of the elastic constants in the N_b phase

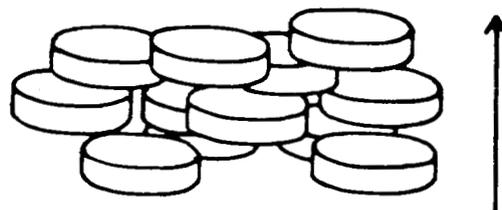


Fig.1. Schematic diagram showing the molecular arrangement in a discotic nematic.

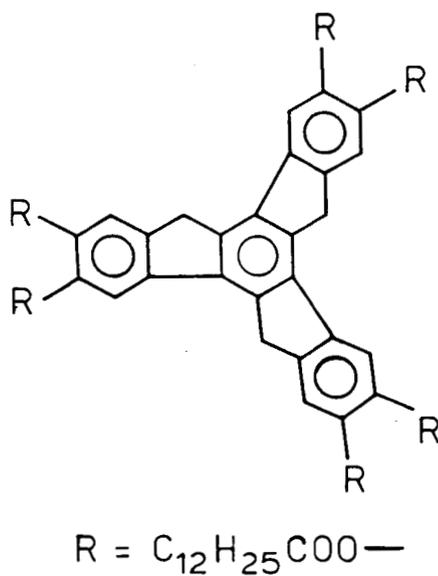
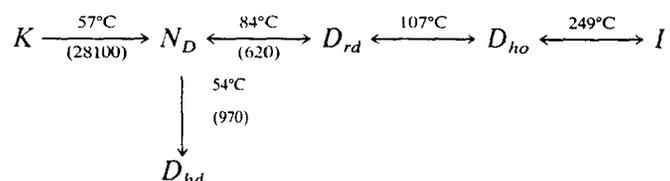


Fig.2. Structural formula of C₁₂HATX.

[4,5]. In this chapter we describe the experimental determination of the splay and bend elastic constants of a truxene derivative which exhibits a nematic phase in an 'inverted' transition sequence between two columnar phases.

8.2 EXPERIMENTAL

The compound studied was hexa-*n*-dodecanoyloxy truxene (C_{12} HATX) [6], whose structure is shown in Fig. 2. It was synthesized by C. Destrad and kindly given to us. The phase transitions exhibited by the compound are:



Here the symbols K , D_{hd} , D_{rd} and D_{ho} stand for the crystal, hexagonal disordered columnar, rectangular disordered columnar and hexagonal ordered columnar phases, respectively. The numbers in brackets are the heats of transition in J/mole measured with a Perkin - Elmer DSC IV unit.

1) Alignment of the sample

Homeotropic alignment was obtained easily by taking the sample between two clean glass plates or indium tin

oxide coated plates. On the other hand, homogeneous alignment was more difficult to achieve. It has been reported [7] that homogeneous alignment of some discotic nematics could be obtained by using glass plates with an oblique coating of silicon monoxide, as with nematics of rod-like molecules. However, such a treatment yielded only homeotropic alignment in the case of C₁₂HATX. The aromatic cores of the molecules appeared to have a strong affinity for the SiO surface. We therefore treated the plates with an oblique coating of SiO with octadecyl triethoxy silane, thus obtaining an aliphatic surface which can be expected to have the undulations of the underlying SiO coating. We found that this combined treatment results in a homogeneous alignment of C₁₂HATX.

2) Determination of the principal dielectric constants.

The principal dielectric constants ϵ_{\parallel} and ϵ_{\perp} were measured at 1592 Hz using a Wayne - Kerr bridge (8642). The ϵ_{\parallel} measurement requires a homeotropic alignment of the director and the ϵ_{\perp} measurement requires a homogeneous alignment. The procedure described in the previous section was used to produce the required alignment. Dispersion studies up to 13 MHz were carried out using a Hewlett - Packard impedance analyser (4192 A).

3) Determination of K_1 .

The splay elastic constant K_1 was measured using the Freedericksz transition method. The experimental set up is shown schematically in Fig.3. A homogeneously aligned sample was prepared between two indium tin oxide coated plates using the procedure described earlier. The cell thickness was measured using the channelled spectrum technique [8] and was found to be 29 μm . The cell was kept in a Mettler hot stage (FP 52) so that its temperature could be conveniently controlled. The sample was viewed under a polarizing microscope. Monochromatic light from a sodium vapour lamp was allowed to fall on the sample. The incident beam was linearly polarized with the plane of polarization making 45° with the undistorted director. The light emerging from the sample is elliptically polarized and by using a quarter wave plate with its fast axis parallel to the axis of the polarizer, it was converted into a linearly polarized beam. This emergent beam was then viewed through an analyser. The analyser was adjusted so that the field of view was dark. An AC electric field of 1 kHz frequency was applied between the two plates. The voltage was slowly increased till the field of view started to become bright, indicating the onset of a deformation of the director in the sample. The RMS value of the applied voltage in volts at which the

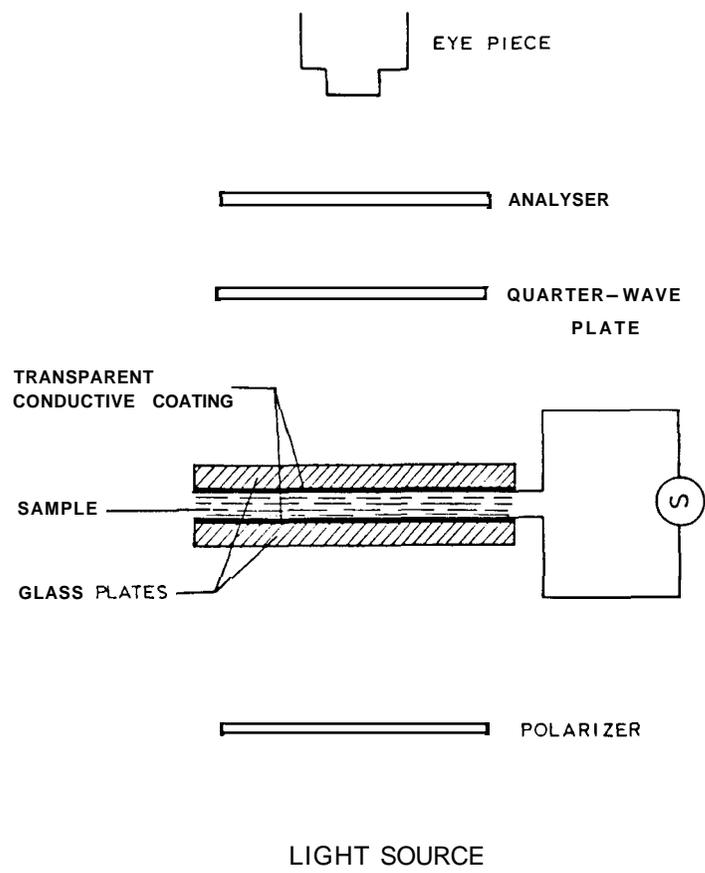


Fig.3. Schematic diagram of the experimental set up used to measure the splay elastic constant.

field of view started to become bright was taken as the threshold voltage V_{th} of the transition. The splay elastic constant was then determined using the relation

$$K_1 = \epsilon_a V_{th}^2 / [4 \pi^3 (300)^2] \quad (1)$$

We found that the anchoring for homogeneous alignment was not uniformly strong and after repeated deformations the alignment deteriorated in some regions. The measurements were made on selected regions which preserved the alignment during the course of the experiment.

4) Determination of K_3

It is necessary to use homeotropically aligned samples to measure K_3 . Since ϵ_a is found to be positive in C₁₂HATX, a transverse field is required to deform the sample. But it is difficult to get a uniform field in this direction. However, since the anisotropy of the diamagnetic susceptibility of this material can be expected to be negative, we could use a magnetic field applied parallel to \hat{n}_o , instead. The experimental set up is shown in Fig.4. The mirror M1 enables the linearly polarized light from a sodium lamp to fall normally on the sample. The emergent light is reflected by the mirror M2 and passes through the analyser A. It is then viewed through a low power microscop-

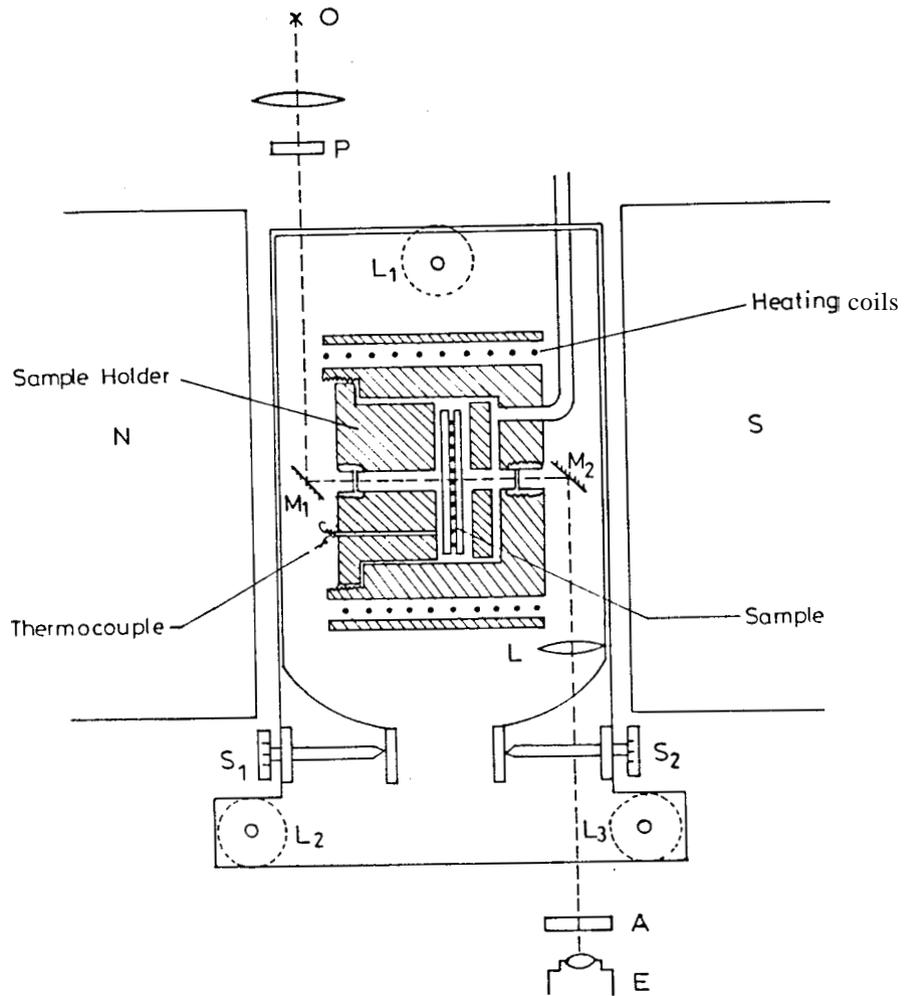


Fig.4. Schematic diagram of the experimental set up used to measure the bend elastic constant.

pe. The whole set up is mounted on a base provided with side screws S1 and S2 and levelling screws L1 ,L2 and L3, using which the sample can be aligned with the director parallel to the field direction. .

The existence of a critical field for the onset of the deformation requires \vec{H} to be parallel to the undistorted director. If this condition is satisfied then the azimuthal angle of the distorted director can take all possible values with equal probability and this degeneracy leads to the formation of umbilics [9] in the sample above the threshold. The sample was aligned with reference to the field direction to yield the maximum number of umbilics.

To measure the critical field, the polarizer and analyser were first adjusted to get a dark field of view. The magnetic field was then slowly increased till the field of view started to become bright. The corresponding value of the field is the critical value H_c for the onset of the deformation. The bend elastic constant is obtained from the relation

$$K_3 = \chi_a d^2 H_c^2 / \pi^2 \quad (2)$$

where χ_a is the diamagnetic anisotropy per unit volume.

Since χ_a of C₁₂HATX is not known, we used an electric field applied parallel to \vec{H} to determine χ_a . If H_1 is the critical field in the presence of the electric field E, then

$$\chi_a = \epsilon_a E^2 (H_1^2 - H_0^2)^{-1} / (4\pi) \quad (3)$$

8.3 RESULTS AND DISCUSSION

The temperature variation of $\epsilon_{||}$, ϵ_{\perp} and ϵ_a are shown in Fig.5. $\epsilon_a > 0$ and its value remains practically independent of the temperature. The nematic phase in C₁₂HATX occurs far below the D_n-isotropic transition temperature and it is to be expected that the orientational order parameter, and hence ϵ_a , hardly vary with temperature. The positive sign of ϵ_a is interesting. The induced dipolar contribution to ϵ_a may be expected to be negative for disc-like molecules. The permanent dipoles associated with the ester groups are responsible for the positive sign of ϵ_a . It should be noted that the triphenylene compound H7OBT, which has similar ester linkage groups, also shows positive ϵ_a [4]. Of course, it is very unlikely that the entire molecule can reorient about a long dimension, and indeed measurements up to 13 MHz did not yield any dispersion of $\epsilon_{||}$.

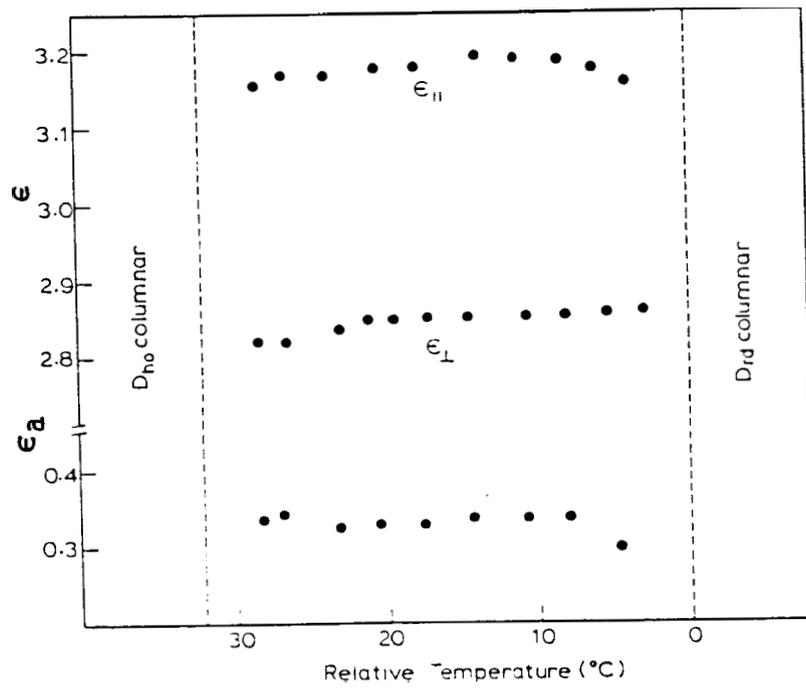


Fig.5. Temperature variation of $\epsilon_{||}$, ϵ_{\perp} and ϵ_a in the nematic phase of C₁₂HATX.

The temperature variation of the splay elastic constant is shown in Fig.6 . In the lower temperature part of the nematic range, K_1 has a practically constant value of about 3.5×10^{-7} dyne. This is of the same order of magnitude as in nematics with rod-like molecules, as already found for H7OBT by Mourey et al.[4]. K_1 tends to decrease as the N_D-D_{r,d} transition point is approached.

The temperature variation of the bend elastic constant is similar to that of K_1 (Fig.7). It is interesting to note that $K_1/K_3 < 1$. As mentioned earlier, if the elastic properties of the medium were determined by long range orientational order alone, we should have obtained $K_1 / K_3 > 1$. Clearly the short range columnar order, which should be present in the nematic-range, gives rise to the reverse trend. Such a short range cybotactic order has been found in other disc-like compounds by Levelut [11]. The reversal of the trend in K_1/K_3 in C₁₂HATX is similar to that in nematics of rod-like molecules with smectic-like cybotactic groups [12,13]. The decrease of both K_1 and K_3 on approaching the N_D-D_{r,d} transition temperature is somewhat surprising. This trend perhaps arises from the building up of cybotactic groups with rectangular lattice at the expense of those with the more compact hexagonal lattice as the temperature increases. The value of χ_a calc-

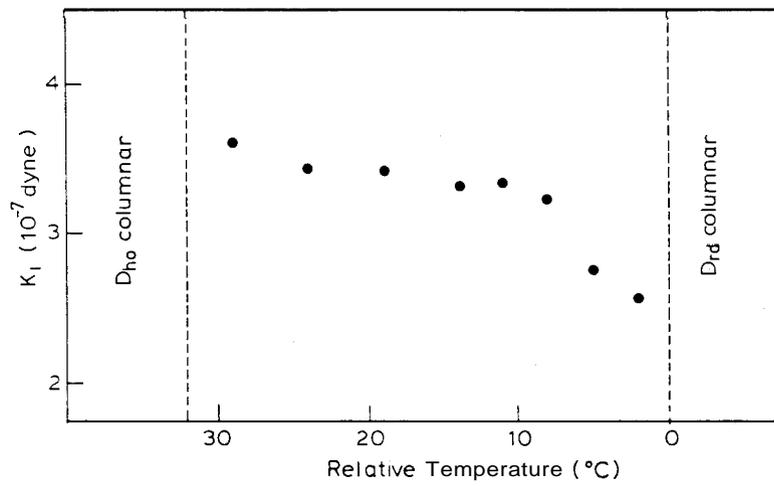


Fig.6. Temperature variation of the splay elastic constant of C₁₂HATX.

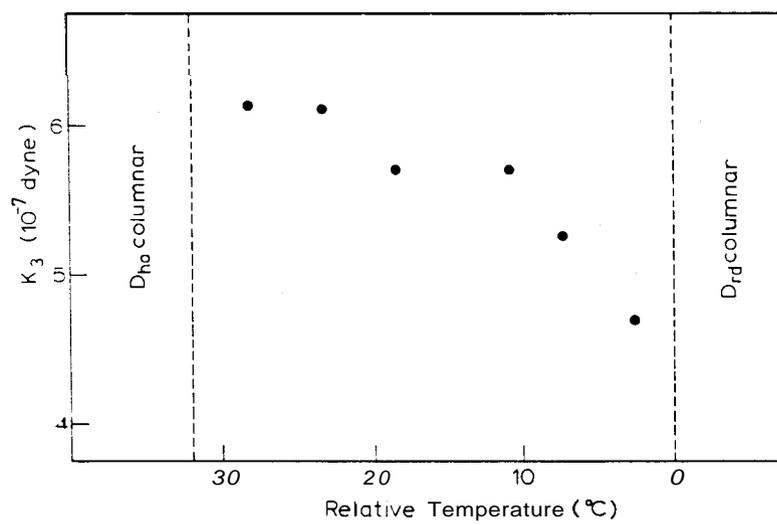


Fig.7. Temperature variation of the bend elastic constant of C₁₂HATX.

ulated using Eq.(3) is $\approx -0.8 \times 10^{-7}$ cgs units, and is practically independent of temperature.

We should mention here that recently Warmerdam et al.[5] have reported K_1 and K_3 of two homologues of C_{12} HATX, viz, C_{10} HATX and C_{14} HATX. C_{14} HATX shows a transition sequence identical to that exhibited by C_{12} HATX. C_{10} HATX also shows an 'inverted' transition sequence, but the re-entrant columnar phase is absent in this case. By measuring the variation of the transmitted light intensity, above the threshold of the Freedericksz transition, Warmerdam et al. obtained K_3/χ_a and K_1/K_3 . In both the compounds K_1/K_3 is found to vary from about 1.8 to 1 as the temperature is raised in the nematic phase. The value of K_3/χ_a is found to be comparable in the two compounds and increases slightly from about 4 to 4.5 cgs units with temperature across the nematic range. The estimated value of K_1/χ_a is also comparable in the two compounds. It decreases strongly from about 7 to 4.5 cgs units with increase of temperature.

We must point out that in our measurements as well as in those of Warmerdam et al. K_3/χ_a has been determined from the threshold of the Freedericksz transition in a homeotropically aligned sample. From the numbers quoted

above, it is clear that our values of K_3/χ_a are much larger than those obtained by Warmerdam et al. As mentioned earlier, we have used clean indium tin oxide coated glass plates to produce the homeotropic alignment, while in Ref.5 polyimide coated plates were used for the same purpose. A possible cause for the lower values of K_3/χ_a obtained by them is a relatively weaker anchoring at the polyimide coated plates. As described in the previous section, we have measured K_1 independently from the threshold of the Fredericksz transition in a homogeneously aligned sample and the anchoring in this case was not as strong as that in the case of homeotropic alignment. Indeed our K_1 values are lower than those obtained by Warmerdam et al. However, it should be noted that the discrepancy in the trend in K_1/K_3 arises mainly due to the larger K_3 values obtained by us rather than the smaller K_1 values. The ratio K_1/K_3 was obtained by Warmerdam et al. by studying the director distortion as a function of the field strength above the threshold of the Fredericksz transition. Since the method used by them is different from that employed by us, the cause for the difference in the trend in K_1/K_3 is not clear. It will be interesting to measure K_1/K_3 using the same technique in all these homologues.

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