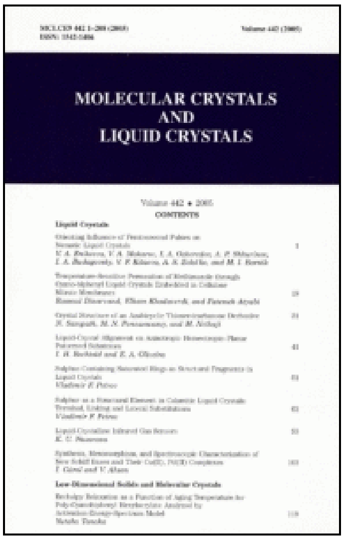

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Bend and Splay Elastic Constants of a Discotic Nematic

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Bend and Splay Elastic Constants of a Discotic Nematic

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We report the dielectric constants and the splay and bend elastic constants of hexa-n-dodecanoyloxy truxene in the nematic phase, which occurs between two columnar phases. The dielectric anisotropy is positive. The elastic constants are $\sim 10^{-7}$ dyne, which is of the same order as for nematics of rod-like molecules. Further, $k_{33} > k_{11}$, probably as a consequence of the columnar short range order in the medium.

Keywords: bend elastic constant, splay elastic constant, discotic nematic, dielectric constants

INTRODUCTION

Relatively few disc-like molecules are known to exhibit the nematic phase. Figure 1 gives a schematic illustration of the structure of the discotic nematic (N_D): in contrast to the classical nematic of rod-like molecules, the director now represents the preferred orientation of the *short* molecular axis. Consequently the medium is optically and diamagnetically negative. However, the dielectric anisotropy depends on the detailed molecular structure and may be positive, as has been found to be the case for hexa-heptyloxybenzoate of triphenylene (H7OBT).[1]

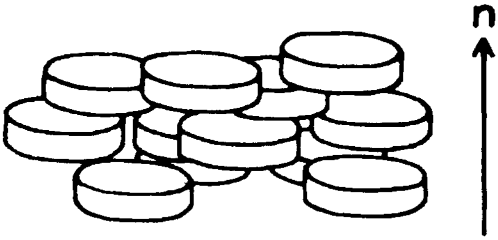

FIGURE 1 Schematic diagram showing the arrangement of disc-like molecules in the nematic state.

The mechanical properties of the N_D phase are evidently of much interest. For example, if the properties of the medium are determined by long range order alone, it is expected that $k_{11} > k_{33}$ for disc-like molecules, and vice versa for rod-like molecules.[2,3] Nematics of rod-like molecules have been studied very extensively, but to our knowledge there has been only one elastic constant measurement in the N_D phase, viz., k_{11} of H7OBT.[1]

In this paper, we report measurements of k_{11} and k_{33} of a truxene compound which exhibits a nematic phase in an 'inverted' sequence between two columnar phases.

EXPERIMENTAL

The compound studied was hexa-n-dodecanoyloxy truxene (C_{12}HATX) whose structure is shown in Figure 2. It was synthesized by one of us (C.D.) employing a procedure published elsewhere.[4] The phase transitions exhibited by the compound are:

$$K \xrightarrow[(28100)]{57^\circ C} N_D \xleftrightarrow[(620)]{84^\circ C} D_{rd} \xleftrightarrow{107^\circ C} D_{ho} \xleftrightarrow{249^\circ C} I$$

$$N_D \xrightarrow[(970)]{54^\circ C} D_{hd}$$

The numbers in brackets are the heats of transition in J/mole measured with a Perkin-Elmer DSC IV unit. We have used the Freed-

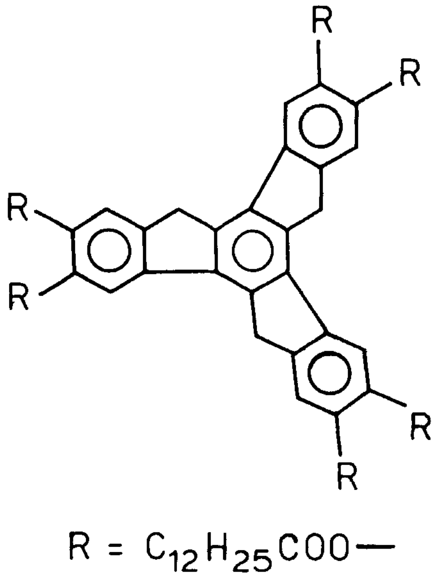

FIGURE 2 Structural formula of hexa-n-dodecanoyloxy truxene (C_{12}HATX).

ericksz transition technique for determining the elastic constants. The diamagnetic anisotropy of C_{12}HATX has not been measured. We have determined the dielectric anisotropy in the nematic phase, and used electric fields in conjunction with magnetic fields to measure the elastic constants. $\epsilon_{\parallel}$ and $\epsilon_{\perp}$, the principal dielectric constants of the medium, were measured at 1592 Hz using a Wayne-Kerr bridge (Model No. B642). For this purpose, the sample was taken between two indium tin oxide (ITO) coated plates. The $\epsilon_{\parallel}$ measurement requires homeotropic alignment of the director whereas $\epsilon_{\perp}$ requires homogeneous alignment. The alignment procedure is described below.

Homeotropic alignment was obtained quite easily by taking the sample between two clean glass plates or ITO-coated plates. On the other hand, homogeneous alignment was more difficult to achieve. It has been reported[1,5] 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 C_{12}HATX. The aromatic cores of the molecules appeared to have a strong affinity for the SiO surface. We therefore treated the obliquely SiO-coated plates 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 homogeneous alignment of C_{12}HATX.

For determining the splay elastic constant, a homogeneously aligned sample was prepared between two ITO-coated plates as described in the previous paragraph. The Freedericksz threshold voltage (V_{th}) was determined by detecting the deformation optically. The splay elastic constant is given by[1]

$$k_{11} = \frac{\Delta\epsilon V_{th}^2}{4\pi^3(300)^2} \tag{1}$$

where V is the RMS voltage of the applied AC field whose frequency was 1000 Hz. 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.

It is necessary to use homeotropically aligned samples to measure k_{33}. Since $\Delta\epsilon > 0$, a transverse field is required to deform the sample, but it is difficult to get a uniform electric field in this direction. However, since the anisotropy of diamagnetic susceptibility ($\Delta\chi$) of C_{12}HATX may be expected to be negative we could use a magnetic field (H) instead. The sample had to be aligned such that its undistorted director is parallel to H to produce the Freedericksz transition. Since $\Delta\chi$ of C_{12}HATX is not known, we also used an electric field E applied parallel to H to determine $\Delta\chi$.[6] In the absence of E, if the threshold magnetic field is H_0, k_{33} is given by

$$k_{33} = \frac{\Delta\chi d^2 H_0^2}{\pi^2} \tag{2}$$

where d is the sample thickness. If the threshold value of the magnetic field is H_1 in the presence of the electric field, we can write

$$\Delta\chi = \frac{\Delta\epsilon E^2}{4\pi}(H_1^2 - H_0^2)^{-1} \tag{3}$$

If the undistorted director n_0 is aligned exactly parallel to H, the azimuthal angle of the distorted director can take all possible values with equal probability. This degeneracy leads to the formation of 'umbilics' in the sample above the threshold field.[7] The sample was aligned with reference to H to yield the maximum number of umbilics.

RESULTS AND DISCUSSION

The temperature variations of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ are shown in Figure 3. $\Delta\epsilon > 0$ and its value remains practically independent of temperature. The nematic phase in C_{12}HATX occurs far below the D_h-isotropic transition temperature and it is to be expected that the orientational order parameter, and hence $\Delta\epsilon$, hardly vary with temperature. The positive sign of $\Delta\epsilon$ is interesting. The induced dipolar contribution to $\Delta\epsilon$ may be expected to be negative for the disc-like molecules. The permanent dipoles associated with the ester groups are responsible for the positive sign of $\Delta\epsilon$. It should be noted that the triphenylene compound H7OBT, which has similar ester linkage groups, also shows positive $\Delta\epsilon$.[1] 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 $\epsilon_{\parallel}$. The positive contribution

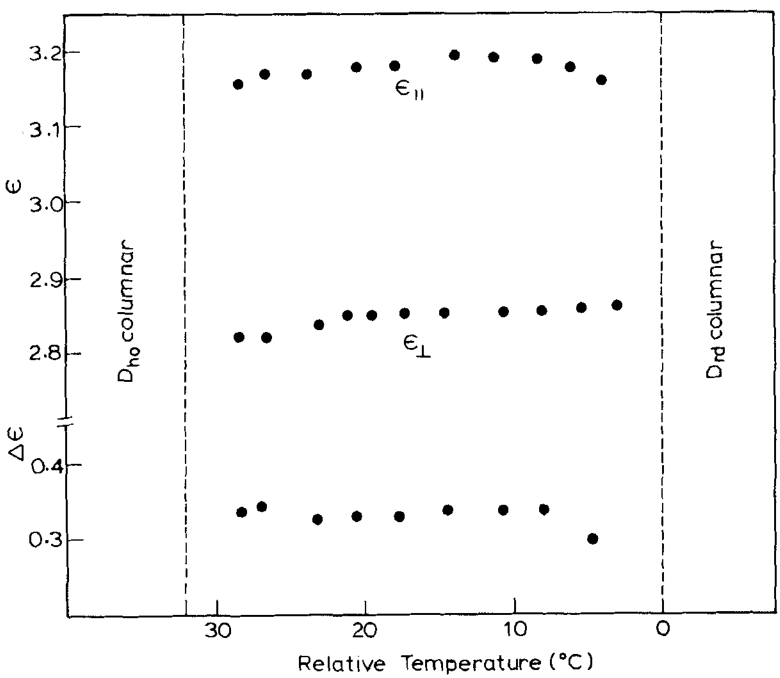

FIGURE 3 Temperature variations of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ in the nematic phase of C_{12}HATX.

arises from the reorientation of the ester dipoles along with the side chains of the molecules.

The temperature variation of the splay elastic constant is shown in Figure 4. In the lower temperature part of the nematic range, k_{11} has a practically constant value $\simeq 3.5 \times 10^{-7}$ dyne. This is of the same order of magnitude as in nematics of rod-like molecules, as already found for H7OBT by Mourey *et al.*[1] k_{11} tends to decrease as the $N_D - D_{rd}$ transition point is approached.

The temperature variation of the bend elastic constant is similar to that of k_{11} (Figure 5). It is interesting to note that $k_{11}/k_{33} < 1$. As mentioned in the introduction, if the elastic properties of the medium were determined by long range orientational order alone, we should have obtained $k_{11}/k_{33} > 1$. Clearly the short range columnar order, which should be present in the nematic, gives rise to the reverse trend. Such a short range cybotactic order has been found in other disc-like compounds by Levelut.[8] The reversal of the trend in k_{11}/k_{33} in C_{12}HATX is similar to that in nematics of rod-like molecules with smectic-like cybotactic groups.[9,10] The *decrease* of both k_{11} and k_{33} on approaching the $N_D - D_{rd}$ transition temperature is somewhat surprising. This trend perhaps arises from the building up of cybotactic groups with a rectangular lattice at the expense of those with the more compact hexagonal lattice as the temperature increases.

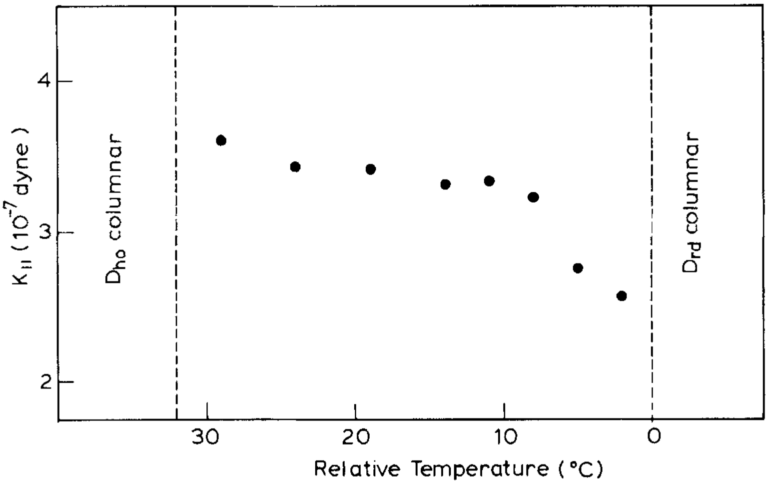

FIGURE 4 Temperature variation of the splay elastic constant in the nematic phase of C_{12}HATX.

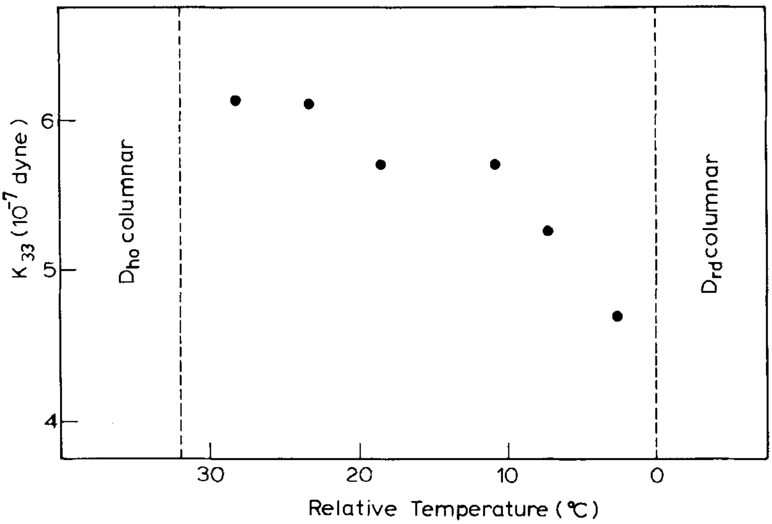

FIGURE 5 Temperature variation of the bend elastic constant in the nematic phases of C_{12}HATX.

The value of $\Delta\chi$ calculated using Eq. (3) is $\simeq -0.8 \times 10^{-7}$ cgs units, and is practically independent of temperature.

References

1. B. Mourey, J. N. Perbet, M. Hareng and S. Le Berre, *Mol. Cryst. Liq. Cryst.*, **84**, 193 (1982).
2. K. Sokalski and Th. W. Ruijgrok, *Physica*, **113A**, 126 (1982).
3. Y. Singh and K. Singh, *Phys. Rev.*, **33A**, 3481 (1986).
4. C. Destrade, J. Malthete, Nguyen Huu Tinh and H. Gasparoux, *Phys. Lett.*, **78A**, 82 (1980).
5. C. Vauchier, A. Zann, P. Le Barney, J. C. Dubois and J. Billard, *Mol. Cryst. Liq. Cryst.*, **66**, 103 (1981).
6. H. J. Deuling, in Solid State Physics, Suppl. 14, Ed. L. Liebert (Academic, New York, 1978) p. 77.
7. A. Rapini, *J. Phys.*, **34**, 629 (1973).
8. A. M. Levelut, *J. Chimie Phys.*, **80**, 149 (1983).
9. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **40**, 239 (1977).
10. B. W. Van der Meer, F. Postma, A. J. Dekker and W. H. de Jeu, *Mol. Phys.*, **45b**, 1227 (1982).