Molecular Statistical Theory of Nematic Liquid Crystals
II. Relation between Elasticity and Orientational Order

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A relationship is derived between curvature, elasticity and orientational order in nematic liquid crystals on the basis of the molecular statistical theory developed in Part I. Calculations show that the elastic moduli of *p*-azoxyphenetole should be greater than those of *p*-azoxyanisole, in quantitative agreement with the values reported by the Orsay Group. The theoretical temperature variation of the elastic moduli is also in accord with the available data.

Introduction

It is now well established that the elastic properties of nematic liquid crystals are described adequately by the phenomenological theory developed by Zocher, Oseen & Frank (see Frank, 1958). According to this theory, the free energy per unit volume of a liquid crystal of a given configuration relative to the state of uniform orientation can be expressed as

$$\delta F = \tfrac{1}{2}\left[k_{11}\left(\frac{\partial L_x}{\partial x}\right)^2 + k_{22}\left(\frac{\partial L_x}{\partial y}\right)^2 + k_{33}\left(\frac{\partial L_x}{\partial z}\right)^2 \right],$$

where $\partial L_x/\partial x$, $\partial L_x/\partial y$ and $\partial L_x/\partial z$ denote respectively the splay, twist and bend components of curvature at any point, the curvature being defined with respect to a right-handed cartesian coordinate system XYZ with the Z axis parallel to the preferred direction at the origin, and $\mathbf{L}$ is the unit vector representing the preferred direction. [A fourth term was introduced by Frank, but it does not in fact contribute to the volume energy (Ericksen, 1962) and is therefore neglected in the present discussion]. Experimentally, the principal elastic moduli k_{11}, k_{22} and k_{33} are found to have values $\sim 10^{-6}$ dyne. Frank has remarked that the elastic co-efficients should give 'unusually direct information regarding the mutual orienting effect of the molecules'.

In a previous paper (Chandrasekhar & Madhusudana, 1971, hereafter referred to as part I) a molecular statistical theory of orientational order in nematic liquid crystals was developed which led to a satisfactory quantitative explanation of the thermodynamic properties of a few compounds (Chandrasekhar & Madhusudana, 1970). In the present communication, we apply the theory to find an expression for the elastic coefficients in terms of the constants of the intermolecular potential function and the orientational order parameters. The dependence of elasticity on orientational order has been discussed previously by Saupe

(1960*a*). Our expression for the elastic moduli reduces to the form arrived at by Saupe when the potential function is restricted to the principal term in the dispersion energy.

Free energy of deformation

We consider first a homogeneous undeformed liquid crystal with the director along OZ. The mutual energy of interaction of a pair of molecules in the nematic assembly is given by a relation of the form

$$U_{ij} = -(l_i + m_i\cos^2\theta_j + n_i\cos^4\theta_j + \ldots), \quad (1)$$

where l_i, m_i, n_i etc. are power series in $\cos^2\theta_i$, θ being the angle which the long axis of the molecule makes with OZ. Using the mean-field approximation, the total energy of interaction of the molecule i with all its neighbours is

$$U_i = \sum_j U_{ij} = -V^{-3}[L_i + M_i\overline{\cos^2\theta} + N_i\overline{\cos^4\theta} + \ldots] \quad (2)$$

the orientation dependent part of which is given by equation (16) of part I. The Helmholtz free energy per mole due to orientational order is

$$F_s = \frac{NkT}{n}\left[\tfrac{1}{2}(a\overline{\cos^4\theta} + b\overline{\cos^2\theta} - c) \right. $$
$$\left. -\log\int_0^1 \exp(a\cos^4\theta_i + b\cos^2\theta_i)\mathrm{d}(\cos\theta_i) \right]$$

where N/n is the effective number of independent molecular entities per mole and a, b, c have the same significance as in part I; n is a numerical factor (of the order of 2–3) to allow for short range orientational order which may be regarded as the effective number of perfectly aligned molecules per cluster.

Let the liquid crystal be subject to a uniform twist about OX. Suppose that the ith molecule, or, more accurately, the ith cluster, is centred at the origin of the coordinate system. If the X coordinate of the jth cluster

is x_j, the director at that point is inclined at an angle qx_j with respect to OZ, where q is the twist per unit length. (In Frank's notation, $q = -\partial L_y/\partial x$.) If θ'_j is the angle which the major axis of the jth cluster makes with the director at that point, (1) may be written as

$$U_{ij} = -[l_i + m_i \cos^2(\theta'_j + qx_j) + n_i \cos^4(\theta'_j + qx_j) + \ldots] .$$

Now,

$$\cos^2(\theta'_j + qx_j) \simeq \cos^2 \theta'_j - q^2 x_j^2 (2 \cos^2 \theta'_j - 1) - 2qx_j \sin \theta'_j \cos \theta'_j ,$$

$$\cos^4(\theta'_j + qx_j) \simeq \cos^4 \theta'_j - q^2 x_j^2 (8 \cos^4 \theta'_j - 6 \cos^2 \theta'_j) .$$

Since we are dealing with very small deformations, the magnitude of the director may be assumed to be unchanged, so that

Using the mean-field approximation as before

$$U_i + \delta U_i \simeq -V^{-3}[L_i + M_i \times \{\overline{\cos^2 \theta} - q^2 \gamma_{22}(nV/N)^{2/3}(2\overline{\cos^2 \theta} - 1)\} + N_i\{\overline{\cos^4 \theta} - q^2 \gamma_{22}(nV/N)^{2/3} \times (8\overline{\cos^4 \theta} - 6\overline{\cos^2 \theta})\} + \ldots]$$
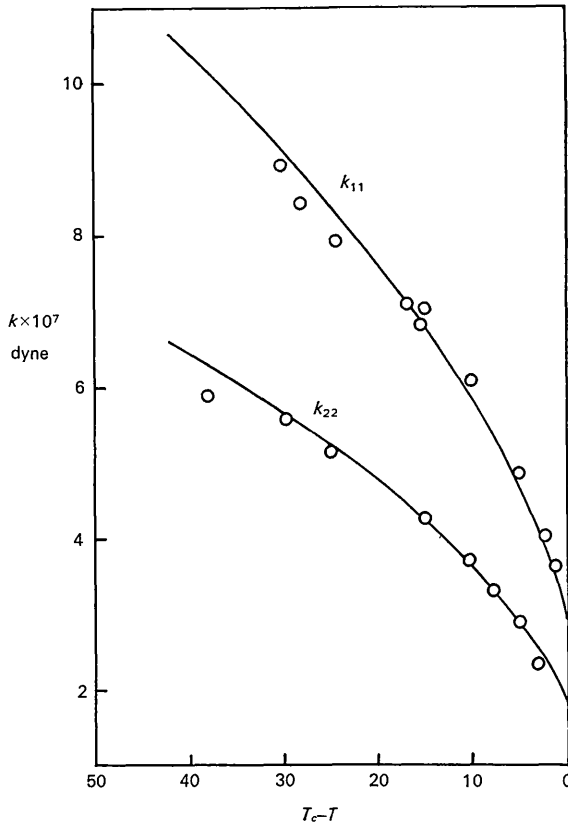

Fig. 1. Elastic moduli of p-azoxyanisole. The curves represent theoretical variation and the circles experimental data.

$$\overline{\cos^2 \theta'_j} = \overline{\cos^2 \theta} ,$$

$$\overline{\cos^4 \theta'_j} = \overline{\cos^4 \theta}$$

and

$$\overline{\sin \theta'_j \cos \theta'_j} = 0 .$$

where γ_{22} is a constant which depends on the (positional) molecular distribution function in the nematic structure.

$\delta U_i/U_i \simeq 10^{-6}$ or less for deformations ordinarily encountered in experiment. The orientation dependent part of the potential energy of the molecule in the deformed liquid crystal may therefore be written to a very good approximation as

$$U_i + \delta U_i = -V^{-3} B\{s_1 - 2q^2 \gamma_{22}(nV/N)^{2/3} s_1\} \times \left(\frac{3 \cos^2 \theta_i - 1}{2}\right) - V^{-3} D$$
$$\times \left[\{s_1 - 2q^2 \gamma_{22}(nV/N)^{2/3} s_1\} \left(\frac{5 \cos^4 \theta_i - 1}{4}\right) + \{s_2 - q^2 \gamma_{22}(nV/N)^{2/3} \times (8s_2 - 5s_1)\} \left(\frac{3 \cos^2 \theta_i - 1}{2}\right)\right]$$

which vanishes in the isotropic phase. B and D are the constants of the intermolecular potential function given by equation (16) of part I. Neglecting the volume change due to deformation, it is readily shown that the extra free energy per cm^3

$$\delta F_s \simeq \frac{q^2}{2} \gamma_{22} \left(\frac{N}{n}\right)^{1/3} V^{-10/3} s_1\{2Bs_1 + 5D(2s_2 - s_1)\} .$$

But, by definition, the free energy of twist

$$\delta F_s = \tfrac{1}{2} k_{22} q^2 ,$$

so that

$$k_{22} = \left(\frac{N}{n}\right)^{1/3} \gamma_{22} V^{-10/3} s_1\{2Bs_1 + 5D(2s_2 - s_1)\} . \quad (3)$$

Similar expressions with different γ's are obtained for the splay and bend moduli k_{11} and k_{33} respectively.

The factor γ is of the order of unity, as will be clear from the following approximate calculation for a simple cubic arrangement of the clusters. Considering nearest neighbours only, $x_j^2 = (nV/N)^{2/3}$; taking the average over the six nearest neighbours, $\overline{x_j^2} = \tfrac{1}{3}(nV/N)^{2/3}$, so that $\gamma_{22} = \tfrac{1}{3}$. Substituting this value in equation (3) gives $k_{22} = 3 \cdot 3 \times 10^{-7}$ for p-azoxyanisole (PAA) at $T_c - T = 5°C$, which compares very favourably with the observed value of 3×10^{-7} dyne (Saupe, 1960b; Orsay Group, 1970). However, for such an arrangement $\gamma_{33} = \gamma_{22}$ and $k_{33} = k_{22}$, whereas in fact $k_{33} = 3 \cdot 8 k_{22}$ for PAA (Saupe, 1960b). In the actual nematic structure, which has a cylindrically symmetric distribution, it is evident that γ_{33} should be significantly higher than γ_{22}. Further, since $\overline{x_j^2}$ will be slightly greater for a splay deformation than for a twist, k_{11} may be ex-

pected to have a value between k_{22} and k_{33}, as is indeed found to be the case experimentally (Saupe, 1960b).

Application to p-azoxyanisole and p-azoxyphenetole

For a comparison of the elastic moduli of PAA and p-azoxyphenetole (PAP) we make the reasonable assumption that the molecular distributions in the two compounds are similar. [The difference in the density is, in any case, accounted for explicitly in equation (3)]. Using the values B, D and n of PAA and PAP (see part I), and putting $\gamma_{22} = 0.300$ for both compounds, s_1, s_2 and k_{22} have been calculated for the temperatures for which data are available. Wherever transition temperatures T_c have not been specifically mentioned by the authors, the values of Chatelain & Brunet-Germain (private communication; see Chandrasekhar & Madhusudana, 1969) have been used. The results are presented below in terms of the relative temperature $T_c - T$:

	$T_c - T$	s_1 (theor.)	s_2 (theor.)	$k_{22} \times 10^7$ dyne (theor.)	(expt.)
PAA	5°C	0·422	0·328	2·95	2·89*
					3·1†
PAP	18°C	0·632	0·530	7·03	7·1†

* Saupe (1960b).
† Orsay Liquid Crystal Group (1970).

The temperature variation of the elastic moduli of PAA are shown in Fig. 1 along with data of Saupe (1960b) for k_{11} and those of Freedericks & Zwetkoff (1934; see Saupe, 1960b) for k_{22}. Here $\gamma_{11} = 0.481$, and $\gamma_{22} = 0.300$ as before.

The general agreement can be seen to be very good, showing that the approximations made in the calculations are justified. The results also seem to provide further confirmation of the validity of the statistical theory developed in part I.

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Thermal Expansion of LiF by X-ray Diffraction and the Temperature Variation of its Frequency Spectrum

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The coefficients of thermal expansion of LiF are determined at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are obtained for the variation of lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The energy of formation of Schottky pairs is found to be 2·42 eV. The Grüneisen constant y is found to decrease with temperature. The mean frequency of the vibrational spectrum is found to decrease with temperature and the variation between 300 and 1000°K is about 13%.

Introduction

The thermal expansion of LiF has been investigated mainly by Eucken & Dannöhl (1934), Sharma (1950) and Pathak, Pandya & Ghadiali (1963). The first two investigations are by macroscopic methods while the last one is by X-ray method.

It was shown in our previous paper (Pathak & Vasavada, 1970, to be called paper I hereafter) that values of the linear thermal expasion of NaCl, KCl and CsBr obtained by different workers agree at lower temperatures but show wide discrepancies at higher temperatures. The same feature can also be seen from Table 1 in the case of LiF.