

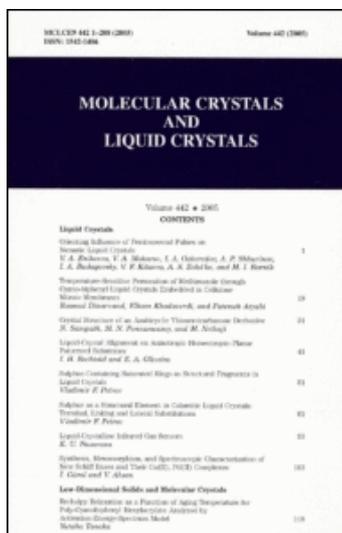
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# Theory of Birefringence of Nematic Liquid Crystals

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**Abstract**—A theory of the birefringence of nematic liquid crystals is developed taking into account the intermolecular potential energy arising from dipole-dipole, anisotropic dispersion, induction and repulsion interactions. The potential energy exhibits a dependence on molecular orientation and is expressible as  $-(u_0 + u_1 \cos \theta + u_2 \cos^2 \theta + u_4 \cos^4 \theta + u_6 \cos^6 \theta + \dots)$  where  $\theta$  is the angle which the long axis of the molecule makes with the uniaxial direction of the liquid crystal. The birefringence of the medium is evaluated in terms of the Boltzmann distribution of the oriented molecules. The theory explains the experimentally observed result that the temperature coefficient of the extraordinary index is large and negative whereas that of the ordinary index is small and positive. Analysis of the data on *p*-azoxyanisole and *p*-azoxyphenetole shows that dispersion and repulsion forces play a predominant role in determining the temperature variation of the birefringence.

Assuming that the molecular librations in the liquid crystal can be represented by a system of harmonic oscillators, the rms librational amplitude is evaluated for *p*-azoxyanisole from recent measurements of the ultrasonic velocity. The increase in the rms amplitude with temperature in the nematic range is found to be in good agreement with that obtained directly from the experimental data on birefringence.

## 1. Introduction

Nematic liquid crystals are optically uniaxial, positive and strongly birefringent. Their refractive indices are very sensitive to temperature, the temperature coefficient being about a hundred times greater than that for a solid crystal. The ordinary index

increases when the liquid crystal is heated, whereas the extraordinary index decreases; thus the birefringence falls rapidly with rise of temperature. At the nematic-liquid transition point there is a discontinuous change in the refractive indices and the birefringence drops abruptly to zero.

A theory of the optical behaviour of the liquid crystalline phase was proposed by Born.<sup>1,2</sup> It would follow from his theory that the transition to this phase takes place at the critical temperature corresponding to the "polarization catastrophe" in a medium consisting of permanent electric dipoles. However, as is well known from the work of Onsager<sup>3</sup> such a catastrophe is not expected to occur. Born also derived the expression

$$\frac{1}{3\rho_1} \left( \frac{n_e^2 - 1}{n_e^2 + 2} + 2 \frac{n_o^2 - 1}{n_o^2 + 2} \right) = \frac{1}{\rho_2} \frac{n_i^2 - 1}{n_i^2 + 2} \quad (1)$$

where  $\rho_1$  and  $\rho_2$  are respectively the densities of the liquid crystalline and isotropic phases,  $n$  the refractive index, the suffixes  $e, o$  and  $i$  denoting extraordinary, ordinary and isotropic. The refractive indices of *p*-azoxyanisole at several wavelengths and temperatures have been found to satisfy this expression approximately.<sup>4,5</sup>

The chemical evidence for the dependence of mesomorphic behaviour on factors such as molecular shape, polarizability and dipole moment have been discussed at length by Brown and Shaw<sup>6</sup> and by Gray.<sup>7</sup> Brown and Shaw<sup>6</sup> (p. 1055) have remarked that "compounds exhibiting mesomorphism have molecules that are elongated, and in some cases flattened as well, and which possess one or more polar groups". Gray<sup>7</sup> (p. 149) has also stated that "to constitute a potentially mesomorphic system, the long narrow molecules must have permanent dipole moments and must be highly polarizable". However, from his own investigations on the mesomorphism and chemical constitution of a wide range of isomorphous compounds, Gray has concluded that the contribution of dipole-dipole forces to nematic stability is comparatively small.

The first attempts to deduce the degree of molecular order in the nematic liquid crystal from its physical properties were by

Zwetkoff<sup>8</sup> and by Chatelain.<sup>9</sup> Maier and Saupe<sup>10-13</sup> have developed a theory of the nematic state in which they have assumed that the orientational potential energy of this phase is determined entirely by dispersion forces. The theory leads to a universal curve for the molecular orientation factor as a function of  $TV^2/T_cV_c^2$ , where  $T$  and  $V$  are the temperature and molar volume in the nematic phase,  $T_c$  and  $V_c$  the corresponding values at the nematic-isotropic transition point. However, significant deviations from a common curve have been observed experimentally.<sup>39</sup> One of the reasons for their ignoring the contribution of dipoles to the orientational potential energy was that ferroelectricity had not been observed in liquid crystals. The early experiments to detect free charges on the surface of the liquid crystal, carried out with a view to testing Born's dipole theory, had yielded negative results.<sup>14,15</sup> Recent investigations appear to show the existence of the hysteresis loop and of polarized domains,<sup>16-21</sup> but the question of ferroelectricity in nematic liquid crystals has not yet been settled unequivocally.

In view of this recent evidence for the possible existence of oriented dipoles in nematic liquid crystals, we proposed an elementary theory of the birefringence of the nematic state, postulating that the intermolecular interactions are predominantly of the dipole-dipole type.<sup>22</sup> We present here a general theory taking into account not only the dipole-dipole interactions, but also the *anisotropic* dispersion, induction and repulsion forces, all of which will, no doubt, contribute to the orientational potential energy. Comparison of the theory with experiment shows quite conclusively that our earlier assumption is not valid and that, in fact, repulsion and dispersion forces play a very important role in determining the temperature variation of the birefringence.

## 2. The Intermolecular Potential Energy

It is well-known from the work of Keesom<sup>23</sup> and London<sup>24</sup> that the predominant interactions between organic molecules

consist of dispersion, dipole-dipole, induction and repulsive forces. We work out below these interactions for an assembly of anisotropic molecules in the ordered nematic state and obtain the result that the potential energy of any molecule is a function of its orientation with respect to the mean direction of the molecules in the medium. In Section 3 we determine the principal polarizabilities of the medium, and hence the birefringence, in terms of the probability distribution of the molecular orientations.

For a pair of molecules the mutual potential energy is a function of the molecular orientations with respect to the intermolecular radius vector  $\mathbf{r}_{ij}$ , but for an assembly  $\mathbf{r}_{ij}$  itself assumes diverse directions. Hence, it is convenient to assume a space fixed coordinate system, and, in such a case, the potential energy will be a function not only of the orientations of the molecules but also of the distribution of  $\mathbf{r}_{ij}$ . In a solid crystal, the molecular arrangement is defined by the crystal structure, but in a liquid crystal it can assume diverse complexions. Therefore, to evaluate the average orientational potential energy, we shall first average over all possible distributions of  $\mathbf{r}_{ij}$ . The essential characteristic of a liquid crystal is that its molecular distribution function is anisotropic (see, for example, Landau and Lifshitz<sup>25</sup>). In the optically uniaxial oriented nematic state the average distribution function should exhibit cylindrical symmetry, as has been confirmed by recent X-ray studies.<sup>40,41</sup> If the direction cosines of  $\mathbf{r}_{ij}$  are  $\alpha_{rij} \beta_{rij} \gamma_{rij}$ ,

$$\left. \begin{aligned} \overline{\alpha_{rij}^2} + \overline{\beta_{rij}^2} + \overline{\gamma_{rij}^2} &= 1 \\ \overline{\alpha_{rij}^2} &= \overline{\beta_{rij}^2} \neq \overline{\gamma_{rij}^2}, \quad \text{or} \quad \overline{\alpha_{rij}^2} = \overline{\beta_{rij}^2} = \frac{1}{2}(1 - \overline{\gamma_{rij}^2}) \\ \overline{\alpha_{rij} \beta_{rij}} &= \overline{\beta_{rij} \gamma_{rij}} = \overline{\gamma_{rij} \alpha_{rij}} = 0 \\ \overline{\alpha_{rij}^4} &= \overline{\beta_{rij}^4} \neq \overline{\gamma_{rij}^4}, \\ \overline{\alpha_{rij}^2 \beta_{rij}^2} &\neq \overline{\beta_{rij}^2 \gamma_{rij}^2} = \overline{\gamma_{rij}^2 \alpha_{rij}^2}, \text{ etc.} \end{aligned} \right\} \quad (2)$$

## 2.1. DIPOLE-DIPOLE INTERACTION

We shall assume that the dipole moment of the molecule is directed along its long axis. This assumption is justifiable since NMR studies<sup>26</sup> (see also Maier and Saupe<sup>11</sup>) indicate that the molecule rotates about its long axis, so that only the component of the dipole moment along this axis is effective.

We shall choose a space fixed coordinate system  $XYZ$ , the  $Z$  axis being the optic axis of the medium. The interaction energy between two identical dipoles of moment  $\mu$  is given by

$$U_{ij}^{\text{dip}} = \frac{\mu^2}{r_{ij}^3} (\mathbf{e}_i \cdot \mathbf{e}_j - 3\mathbf{e}_i \cdot \mathbf{e}_{rij} \mathbf{e}_j \cdot \mathbf{e}_{rij})$$

where  $\mathbf{e}_i$ ,  $\mathbf{e}_j$  and  $\mathbf{e}_{rij}$  are the unit vectors of the dipoles and  $\mathbf{r}_{ij}$  respectively. Therefore

$$U_{ij}^{\text{dip}} = \frac{\mu^2}{r_{ij}^3} [(\alpha_i \alpha_j + \beta_i \beta_j + \gamma_i \gamma_j) - 3(\alpha_i \alpha_{rij} + \beta_i \beta_{rij} + \gamma_i \gamma_{rij}) \times (\alpha_j \alpha_{rij} + \beta_j \beta_{rij} + \gamma_j \gamma_{rij})]$$

where  $\alpha_i \beta_i \gamma_i$ ,  $\alpha_j \beta_j \gamma_j$  and  $\alpha_{rij} \beta_{rij} \gamma_{rij}$  are the direction cosines of  $\mathbf{e}_i$ ,  $\mathbf{e}_j$  and  $\mathbf{e}_{rij}$  respectively. Averaging over  $\mathbf{r}_{ij}$  and transforming to polar coordinates, i.e.,  $\alpha = \sin \theta \cos \phi$ ,  $\beta = \sin \theta \sin \phi$  and  $\gamma = \cos \theta$ , we have

$$U_{ij}^{\text{dip}} = -(\mu^2/r_{ij}^3)D[2 \cos \theta_i \cos \theta_j - \sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j)]$$

where  $D = (3\overline{\gamma_{rij}^2} - 1)/2$ . In the optically uniaxial nematic state we may suppose that for every  $\theta_i$ ,  $\phi_i$  and  $\theta_j$ ,  $\cos(\phi_i - \phi_j)$  can have both positive and negative values, i.e., the azimuthal orientations  $\phi_j$  and  $\phi_j + \pi$  are equally probable. Hence the average potential energy per dipole pair making angles  $\theta_i$ ,  $\theta_j$  is

$$U_{ij}^{\text{dip}} = -\frac{2\mu^2 D}{r_{ij}^3} \cos \theta_i \cos \theta_j \quad (3)$$

For a spherically symmetric distribution  $D = 0$  and  $U_{ij}^{\text{dip}}$  vanishes, but if oriented domains exist  $D$  cannot vanish.

## 2.2. DISPERSION FORCES

The expression for the dispersion energy between a pair of anisotropic molecules possessing cylindrical symmetry has been derived for the first time very recently by van der Merwe.<sup>27</sup> In the general case, each molecule may be associated with three mutually perpendicular dipole oscillators so that the energy involves nine interactions. We have derived the expression for the potential energy of an assembly of molecules taking into account nine interactions per pair, but the theoretical treatment is so cumbersome that we discuss here only a simplified model in which each molecule is associated with a single oscillator parallel to its long axis. We have verified that both models give the same functional dependence of the potential energy on  $\theta_i, \theta_j$ .

The interaction potential energy between two dipole oscillators is given by

$$V_{ij} = \frac{q^2}{r_{ij}^3} (\mathbf{r}_i \cdot \mathbf{r}_j - 3\mathbf{r}_i \cdot \mathbf{e}_{rij} \mathbf{r}_j \cdot \mathbf{e}_{rij})$$

where  $q$  is the charge,  $\mathbf{r}_i$  and  $\mathbf{r}_j$  are the position vectors of the charges with respect to their equilibrium positions and  $\mathbf{e}_{rij}$  is the unit vector of  $\mathbf{r}_{ij}$ . When the molecules are infinitely far apart and in their ground states, their energy corresponding to the unperturbed state is  $E_{00} = \frac{1}{2}\hbar\nu_i + \frac{1}{2}\hbar\nu_j = \hbar\nu_1$ , where  $\nu_1$  is the frequency of the oscillator. As the molecules approach each other the system is perturbed owing to the effect of  $V_{ij}$ . Since  $V_{ij}$  is an odd function of  $\mathbf{e}_i$  and  $\mathbf{e}_j$  (the unit vectors of  $\mathbf{r}_i$  and  $\mathbf{r}_j$ ) the first order perturbation energy vanishes and the second order perturbation energy, which is the dispersion energy, turns out as

$$U_{ij}^{\text{disp}} = - \left( \frac{q^2}{r_{ij}^3} \right)^2 \sum_{n_i} \sum_{n_j} \frac{(\mathbf{r}_i \cdot \mathbf{r}_j - 3\mathbf{r}_i \cdot \mathbf{e}_{rij} \mathbf{r}_j \cdot \mathbf{e}_{rij})_{n_i n_j}^2}{(E_{n_i n_j} - E_{00})}$$

where  $n_i$  and  $n_j$  are the quantum states of the two oscillators. For a linear harmonic oscillator, at most one term survives having a non-zero matrix element  $(0 | \xi | 1) = (2\beta_1)^{-1/2}$  connecting its ground state with its first excited state; all other

terms  $(0 | \xi | n)$  vanish, where  $\xi$  is the position coordinate and  $\beta_1 = C_1/h\nu_1$ ,  $C_1$  being the stiffness constant. Hence

$$U_{ij}^{\text{disp}} = - \left( \frac{q^2}{r_{ij}^3} \right)^2 \frac{(\mathbf{e}_i \cdot \mathbf{e}_j - 3\mathbf{e}_i \cdot \mathbf{e}_{rij} \mathbf{e}_j \cdot \mathbf{e}_{rij})^2}{2h\nu_1(2\beta_1)^2} \quad (4)$$

which is valid for an oscillator with a single electron. If  $f$  is the oscillator strength of the molecule, (4) has to be multiplied by  $f^2$ . As the polarizability  $\alpha_1 = fq^2/C_1$ ,  $\beta_1 = fq^2/\alpha_1 h\nu_1$ . Also, since  $\nu_1 = (q/2\pi)(f/m\alpha_1)^{1/2}$ , where  $m$  is the mass of the electron,

$$\left( \frac{f^2 q^4}{8h\nu_1 \beta_1^2} \right) = \frac{q\hbar}{16\pi} \left( \frac{f}{m} \right)^{1/2} \alpha_1^{3/2} = g, \quad \text{say.} \quad (5)$$

Hence

$$U_{ij}^{\text{disp}} = - \frac{g}{r_{ij}^6} (\mathbf{e}_i \cdot \mathbf{e}_j - 3\mathbf{e}_i \cdot \mathbf{e}_{rij} \mathbf{e}_j \cdot \mathbf{e}_{rij})^2$$

Averaging over  $\mathbf{r}_{ij}$  as before, introducing polar coordinates and averaging over  $\phi$  (i.e.,  $\overline{\sin \phi} = \overline{\cos \phi} = 0$ ;  $\overline{\sin^2 \phi} = \overline{\cos^2 \phi} = \frac{1}{2}$ , etc.), the average potential energy per pair of molecules making angles  $\theta_i, \theta_j$  is

$$\begin{aligned} U_{ij}^{\text{disp}} = & - \frac{g}{r_{ij}^6} \left[ \left( \frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2} \overline{\alpha_{rij}^4} + \frac{9}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} \right) \right. \\ & \times (1 - \cos^2 \theta_i - \cos^2 \theta_j + \cos^2 \theta_i \cos^2 \theta_j) \\ & + 9\overline{\alpha_{rij}^2 \gamma_{rij}^2} (\cos^2 \theta_i + \cos^2 \theta_j) \\ & \left. + (1 - 6\overline{\gamma_{rij}^2} - 18\overline{\alpha_{rij}^2 \gamma_{rij}^2} + 9\overline{\gamma_{rij}^4}) \cos^2 \theta_i \cos^2 \theta_j \right] \quad (6) \end{aligned}$$

When the two molecules are aligned parallel to each other and end on,  $\gamma_{rij} = 1$ ;  $\alpha_{rij} = \beta_{rij} = 0$ ;  $\cos \theta_i = \cos \theta_j = 1$ ; and

$$U_{ij}^{\text{disp}} = - \frac{4g}{r_{ij}^6}$$

When they are parallel to each other and broad side on

$\cos \theta_i = \cos \theta_j = 1$ ;  $\gamma_{rij} = 0$ ; and

$$U_{ij}^{\text{disp}} = -\frac{g}{r_{ij}^6}$$

When the two molecules can take all possible orientations  $\gamma_{rij} = 1$ ;  $\alpha_{rij} = \beta_{rij} = 0$ ;  $\overline{\cos^2 \theta_i} = \overline{\cos^2 \theta_j} = \frac{1}{3}$ ; and

$$U_{ij}^{\text{disp}} = -\frac{2}{3} \frac{g}{r_{ij}^6}$$

These results are identical with those of van der Merwe when in his equations we substitute  $\alpha_{\perp} = 0$ .

If the molecular distribution function is spherically symmetric, (6) reduces to an expression very similar to that derived by Maier and Saupe<sup>11</sup> except that our theory involves the molecular parameters more explicitly.

### 2.3. INDUCTION EFFECT

Again, as in the foregoing calculations, we shall assume for the sake of simplicity that  $\alpha_{\perp} = 0$ .

$$\begin{aligned} U^{\text{ind}}(\mu_i, \alpha_j) &= -\frac{1}{2} \alpha_{1j} E_{1j}^2 \\ &= -\frac{1}{2} \alpha_{1j} \frac{\mu_i^2}{r_{ij}^6} (\mathbf{e}_i \cdot \mathbf{e}_j - 3\mathbf{e}_i \cdot \mathbf{e}_{rij} \mathbf{e}_j \cdot \mathbf{e}_{rij})^2 \end{aligned} \quad (7)$$

where  $E_{1j}$  is the field at  $j$  due to the dipole  $i$ . We have a similar expression with  $i$  and  $j$  interchanged, so that

$$U_{ij}^{\text{ind}} = U^{\text{ind}}(\mu_i, \alpha_j) + U^{\text{ind}}(\mu_j, \alpha_i)$$

Since (7) and (4) are closely similar,  $U_{ij}^{\text{ind}}$  becomes identical with (6) except that  $g$  has to be replaced by  $\alpha_{\perp} \mu^2$ .

### 2.4. REPULSION ENERGY

The repulsion energy between atoms with spherically symmetric charge distributions may be expressed as  $b \exp(-ar)$ . Hitherto no attempts have been made to calculate the repulsive potential energy of an assembly of non-spherical molecules as a function of their relative orientations. To evaluate the orientation dependent potential energy we consider a simplified model

consisting of identical linear molecules each of which is replaced by three centres of repulsion, two near the ends of the molecule and one at its centre. Most of the common nematic substances (e.g., *p*-azoxyanisole, *p*-azoxyphenetole) have molecules which are very nearly symmetrical about the centre and, therefore, we shall assume that the centres of repulsion near the ends of the molecule are identical but different from that at the middle.

We denote the repulsion centres at the middle of the molecules *i* and *j* by  $C_{1i}$ ,  $C_{1j}$ , and those at the ends by  $C_{2i}$ ,  $C_{3i}$  and  $C_{2j}$ ,  $C_{3j}$ . Let  $C_{1i}$  be chosen as the origin of the coordinate system so that  $\overrightarrow{C_{1i}C_{1j}} = \mathbf{r}_{ij}$ , and let  $C_{1i}C_{2i} = C_{1j}C_{2j} = l$ . The coordinates of the six repulsion centres are:

$$\begin{aligned} &C_{1i}(0, 0, 0); \quad C_{2i}(l\alpha_i, l\beta_i, l\gamma_i); \quad C_{3i}(-l\alpha_i, -l\beta_i, -l\gamma_i); \\ &C_{1j}(\mathbf{r}_{ij}\alpha_{rij}, \mathbf{r}_{ij}\beta_{rij}, \mathbf{r}_{ij}\gamma_{rij}); \quad C_{2j}(\mathbf{r}_{ij}\alpha_{rij} + l\alpha_j, \mathbf{r}_{ij}\beta_{rij} + l\beta_j, \\ &\quad \mathbf{r}_{ij}\gamma_{rij} + l\gamma_j) \quad \text{and} \quad C_{3j}(\mathbf{r}_{ij}\alpha_{rij} - l\alpha_j, \mathbf{r}_{ij}\beta_{rij} - l\beta_j, \\ &\quad \mathbf{r}_{ij}\gamma_{rij} - l\gamma_j) \end{aligned}$$

$$\begin{aligned} U_{ij}^{\text{rep}} = &U(C_{1i}C_{1j}) + U(C_{1i}C_{2j}) + U(C_{1i}C_{3j}) + U(C_{2i}C_{1j}) \\ &+ U(C_{2i}C_{2j}) + U(C_{2i}C_{3j}) + U(C_{3i}C_{1j}) + U(C_{3i}C_{2j}) \\ &+ U(C_{3i}C_{3j}) \end{aligned} \quad (8)$$

We represent the centre-centre, end-end and centre-end interactions by the interaction constants  $a_1$ ,  $b_1$ ;  $a_2$ ,  $b_2$ ; and  $a_3$ ,  $b_3$  respectively. Therefore

$$U(C_{1i}C_{1j}) = b_1 \exp(-a_1 r_{ij})$$

$$\begin{aligned} U(C_{2i}C_{2j}) = &b_2 \exp(-a_2[r_{ij}^2 + 2l^2 - 2l^2(\alpha_i\alpha_j + \beta_i\beta_j + \gamma_i\gamma_j) \\ &+ 2lr_{ij}\{\alpha_{rij}(\alpha_j - \alpha_i) + \beta_{rij}(\beta_j - \beta_i) \\ &+ \gamma_{rij}(\gamma_j - \gamma_i)\}]^{1/2}) \\ = &b_2 \exp\left[-a_2 r_{ij} \left\{1 + \frac{2l^2}{r_{ij}^2} - \frac{2l^2}{r_{ij}^2} f_1 + \frac{2l}{r_{ij}} f_2\right\}^{1/2}\right] \end{aligned}$$

$$\text{where } f_1 = \sum_{\alpha, \beta, \gamma} \alpha_i \alpha_j \quad \text{and} \quad f_2 = \sum_{\alpha, \beta, \gamma} \alpha_{rij}(\alpha_j - \alpha_i).$$

Defining  $f_3 = \sum_{\alpha, \beta, \gamma} \alpha_{rij} \alpha_i$ ,  $f_4 = \sum_{\alpha, \beta, \gamma} \alpha_{rij} (\alpha_j + \alpha_i)$  and  $f_5 = \sum_{\alpha, \beta, \gamma} \alpha_{rij} \alpha_j$ , we can similarly work out the other seven terms of (8). Summing all the nine terms, expanding the exponentials, averaging over  $r_{ij}$  and  $\phi$ , and rearranging terms, it can be shown that the average repulsion energy per pair of molecules making angles  $\theta_i$ ,  $\theta_j$  is expressible as

$$\begin{aligned} U_{ij}^{\text{rep}} &= (R_0 + R'_0 \cos^2 \theta_i + R''_0 \cos^4 \theta_i + \dots) \\ &\quad + \cos^2 \theta_j (R_2 + R'_2 \cos^2 \theta_i + \dots) \\ &\quad + \cos^4 \theta_j (R_4 + R'_4 \cos^2 \theta_i + \dots) + \dots \\ &= R_{0i} + R_{2i} \cos^2 \theta_j + R_{4i} \cos^4 \theta_j + \dots \quad \text{say.} \end{aligned} \quad (9)$$

It may be noted that  $U_{ij}^{\text{rep}}$  involves only the even powers of  $\cos \theta_i$  and  $\cos \theta_j$  and is symmetric in  $\theta_i$  and  $\theta_j$ . In (9) the expansion should be carried out at least up to terms involving  $r_{ij}^{-12}$ .

## 2.5. ORIENTATIONAL POTENTIAL ENERGY IN THE NEMATIC STATE

The total energy of interaction is

$$\begin{aligned} U_{ij} &= - \left[ \frac{g + \alpha_1 \mu^2}{r_{ij}^6} \left\{ \left( \frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2} \overline{\alpha_{rij}^4} + \frac{9}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} \right) (1 - \cos^2 \theta_i) \right. \right. \\ &\quad \left. \left. + 9 \overline{\alpha_{rij}^2 \gamma_{rij}^2} \cos^2 \theta_i \right\} - R_{0i} \right] - \left[ \frac{\mu^2}{r_{ij}^8} (3\overline{\gamma_{rij}^2} - 1) \cos \theta_i \right] \cos \theta_j \\ &\quad - \left[ \frac{g + \alpha_1 \mu^2}{r_{ij}^6} \left\{ \left( \frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2} \overline{\alpha_{rij}^4} + \frac{9}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} \right) (\cos^2 \theta_i - 1) \right. \right. \\ &\quad \left. \left. + 9 \overline{\alpha_{rij}^2 \gamma_{rij}^2} + (1 - 6\overline{\gamma_{rij}^2} - 18\overline{\alpha_{rij}^2 \gamma_{rij}^2} + 9\overline{\gamma_{rij}^4}) \cos^2 \theta_i \right\} - R_{2i} \right] \\ &\quad \times \cos^2 \theta_j + R_{4i} \cos^4 \theta_j + \dots \end{aligned} \quad (10)$$

$U_{ij}$  given by (10) represents the average energy due to all forces between two molecules in the medium inclined at  $\theta_i$ ,  $\theta_j$  with respect to the mean direction of the long axes of the molecules in the medium. The total interaction energy of the molecule  $i$

with all its neighbours  $j$  is

$$U_i = \sum_j U_{ij} \quad (11)$$

where the surrounding molecules  $j$  can take all possible orientations but subject to the Boltzmann distribution which, in turn, is determined by their energies  $U_j$ . If  $\overline{U_{ij}}$  is the value of  $U_{ij}$  averaged over all possible orientations of the molecules  $j$ , (11) may be written as

$$U_i = \sum_j \overline{U_{ij}},$$

where

$$\overline{U_{ij}} = \int_0^\pi U_{ij} \exp(-U_j/kT) \sin \theta_j d\theta_j / \int_0^\pi \exp(-U_j/kT) \sin \theta_j d\theta_j \quad (12)$$

$U_{ij}$  as given by (10) could be written as

$$U_{ij} = - (L_i + M_i \cos \theta_j + N_i \cos^2 \theta_j - R_{4i} \cos^4 \theta_j - \dots), \quad (13)$$

where  $M_i$  is directly proportional to  $\cos \theta_i$  and represents the total contribution of the dipole-dipole forces;  $L_i$  and  $N_i$  each consist of a sum of terms of even powers of  $\cos \theta_i$  and involve all forces other than dipole-dipole; and  $R_{4i}$ ,  $R_{6i}$ , etc. each consist of a sum of terms of even powers of  $\cos \theta_i$  and involve only repulsive forces.

Similarly,  $U_j$  in (12)

$$\begin{aligned} &= \sum_l U_{jl} \\ &= \sum_l - (L_j + M_j \cos \theta_l + N_j \cos^2 \theta_l - R_{4j} \cos^4 \theta_l - \dots). \end{aligned}$$

Since the expression is symmetrical in  $j$  and  $l$ , we may regroup the terms involving  $\theta_j$ 's so that

$$U_j = \sum_l - (L_l + M_l \cos \theta_j + N_l \cos^2 \theta_j - R_{4l} \cos^4 \theta_j - \dots).$$

Substituting for  $U_j$  in (12), expanding the exponentials up to terms involving  $r_{ji}^{12}$  and integrating,

$$\begin{aligned}
\overline{U}_{ij} = & - \left[ \frac{g + \alpha_1 \mu^2}{r_{ij}^6} \left\{ \frac{1}{2} (9\overline{\alpha_{rij}^4} + 9\overline{\alpha_{rij}^2 \beta_{rij}^2} + 3\overline{\gamma_{rij}^2} - 2) \right. \right. \\
& - \frac{1}{6} (9\overline{\alpha_{rij}^4} + 9\overline{\alpha_{rij}^2 \beta_{rij}^2} - 18\overline{\alpha_{rij}^2 \gamma_{rij}^2} + 3\overline{\gamma_{rij}^2} - 2) \\
& \times \left( 1 + \frac{1}{kT} \sum_l \frac{4N_l}{15} + \frac{1}{k^2 T^2} \sum_l \sum_{l'} \frac{2M_l M_{l'}}{15} \right) \left. \right\} \\
& - \left( R_0 + \frac{R_2}{3} + \frac{R_4}{5} + \dots \right) \left. \right] - \left[ \frac{\mu^2}{r_{ij}^3} (3\overline{\gamma_{rij}^2} - 1) \right. \\
& \times \left( \frac{1}{kT} \sum_l \frac{M_l}{3} + \frac{1}{k^2 T^2} \sum_l \sum_{l'} \frac{4M_l N_{l'}}{45} \right. \\
& \left. \left. - \frac{1}{k^3 T^3} \sum_l \sum_{l'} \sum_{l''} \frac{M_l M_{l'} M_{l''}}{45} \right) \right] \cos \theta_i - \left[ \frac{g + \alpha_1 \mu^2}{r_{ij}^6} \right. \\
& \times \left\{ -\frac{1}{2} (9\overline{\alpha_{rij}^4} + 9\overline{\alpha_{rij}^2 \beta_{rij}^2} - 18\overline{\alpha_{rij}^2 \gamma_{rij}^2} + 3\overline{\gamma_{rij}^2} - 2) \right. \\
& \left. + 3 \left( \overline{\gamma_{rij}^4} + \frac{1}{2} \overline{\alpha_{rij}^4} + \frac{1}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} - 2 \overline{\alpha_{rij}^2 \gamma_{rij}^2} - \frac{1}{2} \overline{\gamma_{rij}^2} \right) \right. \\
& \times \left( 1 + \frac{1}{kT} \sum_l \frac{4N_l}{15} + \frac{1}{k^2 T^2} \sum_l \sum_{l'} \frac{2M_l M_{l'}}{15} \right) \left. \right\} \\
& - \left( R'_0 + \frac{R'_2}{3} + \frac{R'_4}{5} + \dots \right) \left. \right] \cos^2 \theta_i + \left( R''_0 + \frac{R''_2}{3} + \frac{R''_4}{5} + \dots \right) \\
& \times \cos^4 \theta_i + \dots \tag{14}
\end{aligned}$$

Hence  $U_i = \sum_j \overline{U}_{ij}$  may be expressed as

$$- (u_0 + u_1 \cos \theta_i + u_2 \cos^2 \theta_i + u_4 \cos^4 \theta_i + \dots). \tag{15}$$

In order to bring out explicitly the dependence of  $U_i$  on temperature  $T$  and volume  $V$  ( $\propto r^3$ ) we may write

$$\left. \begin{aligned} u_0 &= \left( \frac{G_1}{V^2} + \frac{R_a}{V^4} \right) + \frac{G_2}{kT V^4} + \frac{G_3}{k^2 T^2 V^4}, \\ u_1 &= \frac{G_4}{kT V^2} + \frac{G_5}{k^2 T^2 V^4} + \frac{G_6}{k^3 T^3 V^4}, \\ u_2 &= \left( \frac{G_7}{V^2} + \frac{R_b}{V^4} \right) + \frac{G_8}{kT V^4} + \frac{G_9}{k^2 T^2 V^4}, \\ u_4 &= \frac{R_c}{V^4}, \text{ etc.} \end{aligned} \right\} \quad (16)$$

where  $G_1$  and  $G_7$  represent first order dispersion effects,  $G_2$  and  $G_8$  second order dispersion effects,  $G_4$  and  $G_6$  first and second order dipole effects respectively,  $G_3$ ,  $G_5$  and  $G_9$  dipole-dispersion cross terms, and  $R$ 's the repulsion terms which are assumed to vary as  $r^{-12}$ .

### 3. The Birefringence of the Nematic State

Let  $A$ ,  $B$ ,  $C$  be the principal polarizabilities of a molecule referred to its principal axes  $X'Y'Z'$ . Let  $XYZ$  be the fixed coordinate system,  $Z$  being so chosen as to coincide with the optic axis of the medium. If  $E_Z$  and  $E_X$  represent the components of the electric vector of the incident light wave, then the induced moments  $P_z$  and  $P_x$  are given by

$$\begin{aligned} P_z &= E_Z(A \cos^2 ZX' + B \cos^2 ZY' + C \cos^2 ZZ'), \\ P_x &= E_X(A \cos^2 XX' + B \cos^2 XY' + C \cos^2 XZ'), \end{aligned} \quad (17)$$

where

$$\begin{aligned} \cos^2 ZX' &= \sin^2 \theta \cos^2 \Psi, \\ \cos^2 ZY' &= \sin^2 \theta \sin^2 \Psi, \\ \cos^2 ZZ' &= \cos^2 \theta, \\ \cos^2 XX' &= (\cos \Psi \cos \phi \cos \theta - \sin \Psi \sin \phi)^2, \\ \cos^2 XY' &= (-\sin \Psi \cos \phi \cos \theta - \cos \Psi \sin \phi)^2, \\ \cos^2 XZ' &= \sin^2 \theta \cos^2 \phi, \end{aligned}$$

$\theta$ ,  $\phi$ ,  $\Psi$  being the Eulerian angles defining the orientations of  $X'Y'Z'$  with respect to  $XYZ$ .

To evaluate the polarizabilities  $\alpha_x$  and  $\alpha_z$ , it is necessary to average over all possible orientations taking into account the Boltzmann factor involving the potential energy of the molecule given by (15). The probable number of molecules having the orientation  $\theta$ ,  $\phi$ ,  $\Psi$  is hence given by

$$C_0 \exp\left(-\frac{U}{kT}\right) \sin\theta \, d\theta \, d\phi \, d\Psi$$

where  $C_0$  is a normalizing constant. Therefore

$$\alpha_x = \frac{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} C_0 P_x \exp\left(-\frac{U}{kT}\right) \sin\theta \, d\theta \, d\phi \, d\Psi}{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} C_0 E_x \exp\left(-\frac{U}{kT}\right) \sin\theta \, d\theta \, d\phi \, d\Psi} \quad (18)$$

Since the molecules are rotating about their long axes,  $\Psi$  can take all possible values, and similarly since the structure is symmetrical about the optic axis,  $\phi$  can also take all possible values. Integrating

$$\alpha_x = \alpha + (\alpha_{\parallel} - \alpha_{\perp}) \left( \frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \dots \right)$$

where  $\alpha_{\perp} = (A + B)/2$ ,  $\alpha_{\parallel} = C$ ,  $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ ,  $h_1 = u_1/kT$ ,  $h_2 = u_2/kT$ , etc.

Similarly

$$\alpha_z = \alpha - \frac{\alpha_{\parallel} - \alpha_{\perp}}{2} \left( \frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \dots \right)$$

Assuming the Lorenz-Lorentz relationship,

$$\frac{n_e^2 - 1}{n_e^2 + 2} = \frac{4\pi}{3} N \alpha_x, \quad (19)$$

$$\frac{n_o^2 - 1}{n_o^2 + 2} = \frac{4\pi}{3} N \alpha_z, \quad (20)$$

and

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{4\pi}{3} N_1 \alpha \quad (21)$$

where  $N$  and  $N_1$  are the number of molecules per cc in the liquid crystalline and liquid states respectively, we find that relation (1) derived by Born is satisfied.

It would be more realistic to assume the existence of an anisotropic polarization field in the liquid crystalline medium. The idea of such a field was first introduced in the theory of the Kerr effect in liquids.<sup>28,29</sup> The relation between the effective polarizabilities  $A'$ ,  $B'$ ,  $C'$  and  $A$ ,  $B$ ,  $C$  was found by considering an ellipsoidal cavity instead of a spherical one as in the Lorenz-Lorentz case.

Chatelain<sup>9</sup> has suggested that  $A'$ ,  $B'$ ,  $C'$  in the oriented nematic mesophase are given by

$$A' = A \left(1 - \frac{4\pi NA}{3}\right)^{-1}, \quad B' = B \left(1 - \frac{4\pi NB}{3}\right)^{-1}, \text{ etc.}$$

In general,  $\alpha'_{\parallel}$ ,  $\alpha'_{\perp}$  may be taken to be of the form

$$\alpha'_{\parallel} = \alpha_{\parallel}(1 - P_1 N \alpha_{\parallel})^{-1}, \quad \alpha'_{\perp} = \alpha_{\perp}(1 - P_2 N \alpha_{\perp})^{-1}$$

where  $P_1$ ,  $P_2$  are not necessarily equal to  $4\pi/3$ . Hence (19) and (20) reduce to

$$\left. \begin{aligned} n_e^2 - 1 &= 4\pi N \left[ \alpha' + (\alpha'_{\parallel} - \alpha'_{\perp}) \left( \frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \dots \right) \right] \\ n_o^2 - 1 &= 4\pi N \left[ \alpha' - \frac{(\alpha'_{\parallel} - \alpha'_{\perp})}{2} \left( \frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \dots \right) \right] \end{aligned} \right\} \quad (22)$$

Therefore (1) will be only approximately satisfied. It is seen that the extraordinary index consists of a sum of two terms both of which diminish with temperature. On the other hand the ordinary index consists of a difference of two similar terms. The experimentally observed fact that  $dn_e/dT$  is large and negative and  $dn_o/dT$  comparatively small and positive is thus readily

understood. From (22),

$$n_e^2 - n_0^2 = 4\pi N(\alpha'_{\parallel} - \alpha'_{\perp}) \left( \frac{h_1^2}{15} + \frac{2h_2}{15} + \frac{4h_3^2}{315} + \frac{4h_4}{35} + \dots \right)$$

Making use of (14), (15) and (16), we get

$$\begin{aligned} n_e^2 - n_0^2 = 4\pi N(\alpha'_{\parallel} - \alpha'_{\perp}) & \left[ \frac{1}{kT\bar{V}^4} \left( \frac{2R_b}{15} + \frac{4R_c}{35} + \dots \right) + \frac{2G_7}{15kT\bar{V}^2} \right. \\ & \left. + \frac{1}{k^2T^2\bar{V}^4} \left( \frac{2G_8}{15} + \frac{4G_7^2}{315} \right) + \frac{2G_9}{15k^2T^3\bar{V}^4} + \frac{G_4^2}{15k^4T^4\bar{V}^4} \right] \quad (23) \end{aligned}$$

#### 4. Temperature Variation of the Birefringence

A direct calculation of the birefringence from theory would require a knowledge of the molecular distribution function in the nematic state, the repulsive parameters, oscillator strengths etc. Not enough reliable information is available on these quantities for such a calculation to be carried out. Nevertheless it is possible to draw some important conclusions regarding the relative contributions of the different forces. To facilitate discussion we write below the separate contributions of the different forces to  $n_e^2 - n_0^2$ , bringing out explicitly their dependence on  $T$  and  $V$ :

$$\begin{aligned} (n_e^2 - n_0^2) \quad (\text{1st order dispersion}) & = \frac{N\chi_1}{T\bar{V}^2}, \\ (n_e^2 - n_0^2) \quad (\text{repulsion}) & = \frac{N\chi_2}{T\bar{V}^4}, \\ (n_e^2 - n_0^2) \quad (\text{2nd order dispersion}) & = \frac{N\chi_3}{T^2\bar{V}^4}, \\ (n_e^2 - n_0^2) \quad (\text{dispersion-dipole cross terms}) & = \frac{N\chi_4}{T^3\bar{V}^4}, \\ (n_e^2 - n_0^2) \quad (\text{dipole-dipole}) & = \frac{N\chi_5}{T^4\bar{V}^4}. \end{aligned}$$

where the  $\chi_1$  and  $\chi_2$  involve the molecular distribution function  $\chi_3$ ,  $\chi_4$  and  $\chi_5$  involve the molecular distribution function as well as summations over  $\cos \theta_i$  and its powers. (The induction terms, whose contribution may be expected to be small, have the same temperature dependence as the dispersion terms.) Thus the temperature variation of the birefringence is determined by the variation of  $N$  ( $\propto$  density  $\rho$ ),  $V$  ( $\propto \rho^{-1}$ ) and the  $\chi$ 's. A correction could be effected for the variation of  $N$  and  $V$  from the thermal expansion measurements. The correction is  $(\rho_0/\rho)^3$  for the first order dispersion term and  $(\rho_0/\rho)^5$  for all other terms,  $\rho_0$  being the density at the nematic-liquid transition point. However the fractional density change over the entire mesomorphic range is only of the order of 2–3%, so that we shall assume that a factor  $(\rho_0/\rho)^4$  is approximately adequate for all terms. To this approximation, therefore, we can eliminate the effect of thermal expansion and write

$$y = (n_e^2 - n_o^2)(\rho_0/\rho)^4 \approx \frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3} + \frac{D}{T^4},$$

where  $A$  represents the repulsion and first order dispersion terms,  $B$  the second order dispersion term,  $C$  the dipole-dispersion cross term and  $D$  the dipole-dipole term. Hence

$$\begin{aligned}
 m &= \frac{d \ln y}{d \ln T} \\
 &= [-AT^{-1} - 2BT^{-2} - 3CT^{-3} - 4DT^{-4} + dA/dT \\
 &\quad + T^{-1}dB/dT + T^{-2}dC/dT + T^{-3}dD/dT] \\
 &\quad \times [AT^{-1} + BT^{-2} + CT^{-3} + DT^{-4}]^{-1}
 \end{aligned} \tag{24}$$

Since the volume change is small, the molecular distribution function is not expected to vary appreciably with temperature except perhaps in the neighbourhood of the nematic-liquid transition, and hence  $A$  may be taken to be practically constant as it does not depend on  $\cos \theta_i$ . However  $B$ ,  $C$  and  $D$  will decrease with temperature as they involve summations over  $\cos \theta_i$  and its powers. In the next section we have evaluated the dependence of

$\overline{\theta^2}$  on temperature (see Fig. 3) and it may be shown that the resulting variation of  $\cos \theta$ , will be comparatively slow initially and will become increasingly faster with rise of temperature.

If the repulsion and first order dispersion effects predominate, i.e.,  $B$ ,  $C$  and  $D$  are negligible, it is seen from (24) that the minimum value of  $|m|$  will be 1.0, whereas if the dipole-dipole forces predominate, i.e.,  $A$ ,  $B$  and  $C$  are negligible, its minimum value will be 4.0. The actual slope of the  $\ln y - \ln T$  plot near the solid-nematic transition temperature should give an indication of the relative contributions of the different terms. As the temperature increases,  $|m|$  may be expected to increase owing to the increase of  $\overline{\theta^2}$ , gradually at first and rapidly as the temperature approaches the nematic-liquid transition point. We shall compare these conclusions with the experimental facts.

Using the density data (see Appendix) and the refractive index measurements of Chatelain and Germain,<sup>30</sup>  $y$  has been evaluated

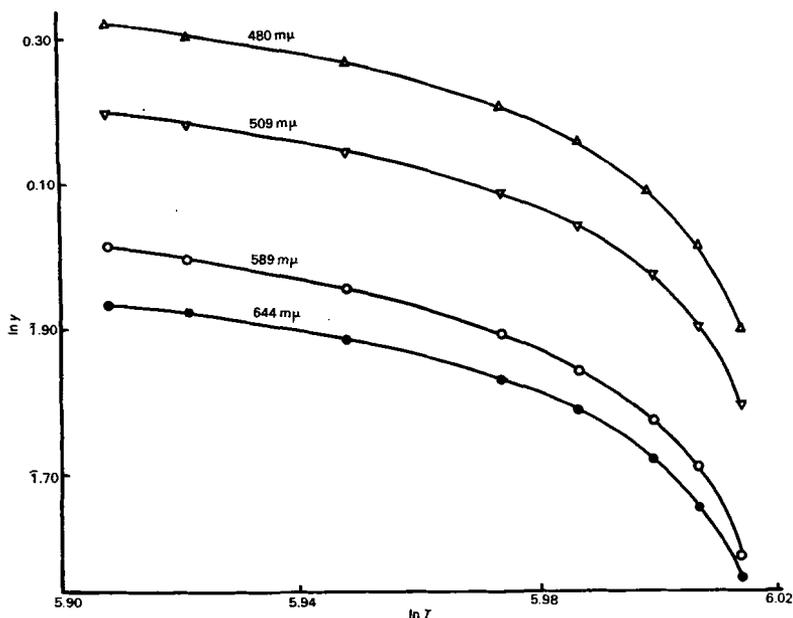
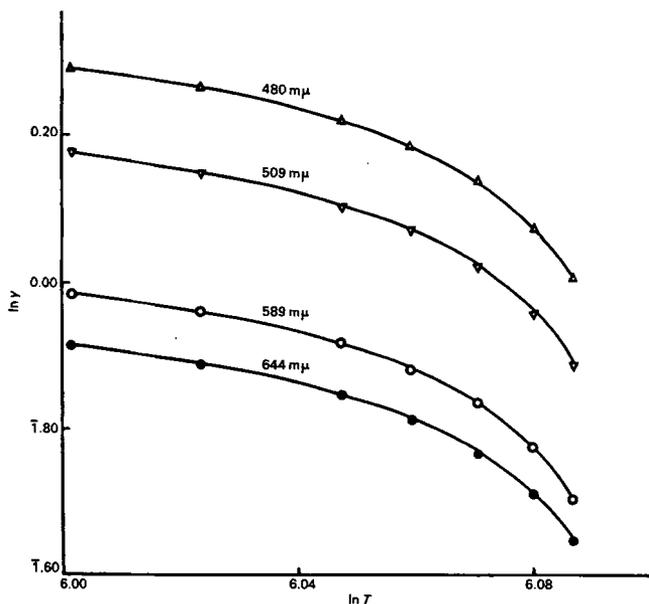


Figure 1.  $\ln y - \ln T$  plot for *p*-azoxyanisole


 Figure 2.  $\ln y$ — $\ln T$  plot for *p*-azoxyphenetole

at different temperatures for *p*-azoxyanisole and *p*-azoxyphenetole. The plot of  $\ln y$  versus  $\ln T$  for the two cases are shown in Figs. 1 and 2. There are small variations in the slopes for the different wavelengths and hence we give below the mean slope for each temperature range. The increase in the slope with temperature is seen to agree qualitatively with what has been discussed earlier.

<i>p</i> -azoxyanisole ( $T_c = 410^\circ\text{K}$ )		<i>p</i> -azoxyphenetole ( $T_c = 441^\circ\text{K}$ )	
Temp. range ( $T_c - T$ )	Mean slope $ m $	Temp. range ( $T_c - T$ )	Mean slope $ m $
42-37	1.13		
37-27	1.46	37-28	1.14
27-17	2.33	28-18	1.87
17-12	3.65	18-13	2.79
12-7	5.54	13-8	4.16
7-4	9.19	8-4	6.48
4-1	15.1	4-1	10.3

The fact that the initial value of  $|m|$  is only slightly greater than 1.0 in both cases shows *conclusively* that the temperature variation of the birefringence is determined mainly by the repulsion and dispersion forces. The result that the dipole-dipole forces do not make an important contribution is in general agreement with the observations of Gray<sup>7</sup> and of Maier and Saupe<sup>11</sup> regarding the stability of the nematic mesophase.

### 5. Molecular Librations

The orientational potential energy of the molecule given by (15) may be expressed approximately as  $U = -C_1(1 - C_2\theta^2)$ , where  $C_1$  and  $C_2$  are constants, so that  $dU/d\theta \propto \theta$ . Thus the molecules may be expected to execute rotational oscillations (librations) about the mean orientation. We shall suppose that the librations can be treated in terms of an Einstein model and assume the well-known relation  $\Theta \propto \rho^{-1/6}\beta^{-1/2}$ , where  $\Theta$  is the Einstein characteristic temperature,  $\rho$  the density and  $\beta$  the volume compressibility.<sup>31,32</sup> Since  $\beta = \rho^{-1}v^{-2}$ , where  $v$  is the velocity of the low frequency longitudinal elastic wave in the liquid crystal  $\Theta \propto \rho^{1/3}v$ . Cruickshank<sup>33,34</sup> has shown that when  $T \gg \Theta$ , which is certainly the case in our problem, the mean square librational amplitude

$$\overline{\theta^2} = h^2T/4\pi^2Ik\Theta^2,$$

where  $I$  is the moment of inertia of the molecule. Therefore

$$\overline{\theta^2} \propto T\rho^{-2/3}v^{-2}.$$

This result, though necessarily approximate, enables one to make a rough estimate of the variation of the librational amplitude with temperature from the available ultrasonic data.

The ultrasonic velocity in *p*-azoxyanisole in the nematic range has been measured by Gabrielli and Verdini,<sup>35</sup> by Hoyer and Nolle<sup>36</sup> and by Kapustin and Bykova<sup>37</sup>. The velocity decreases with rise of temperature, almost linearly at first and more rapidly as the temperature approaches the nematic-liquid transition point. Using the data of Kapustin and Bykova<sup>33</sup> the fractional variation

with temperature of  $\theta_{\text{rms}} = (\overline{\theta^2})^{1/2}$  has been calculated. (The velocity measurements extend from the nematic-liquid point  $T_c$  down to about  $12^\circ$  below  $T_c$ . Extrapolation over a few degrees was necessary at the lower temperatures, in which region, as already remarked, the velocity varies almost linearly with temperature.)

Earlier investigators<sup>9,11</sup> have expressed the degree of orientation of the molecules in terms of a factor  $S = (3 \overline{\cos^2 \theta} - 1)/2$ . It is readily shown that for rotational oscillations

$$S = \frac{1}{2} \{ \cos^2(2^{1/2} \theta_{\text{rms}}) + \cos(2^{1/2} \theta_{\text{rms}}) \}$$

Using this relation, the  $S$  factors obtained directly from the experimental data on birefringence<sup>12</sup> have been expressed as  $\theta_{\text{rms}}$  and are shown as points in Fig. 3. The curve in Fig. 3 presents  $\theta_{\text{rms}}$  calculated from ultrasonic data, and has been drawn by choosing the proportionality constant to fit the experimental value at one temperature. For comparison, we also give in Fig. 4

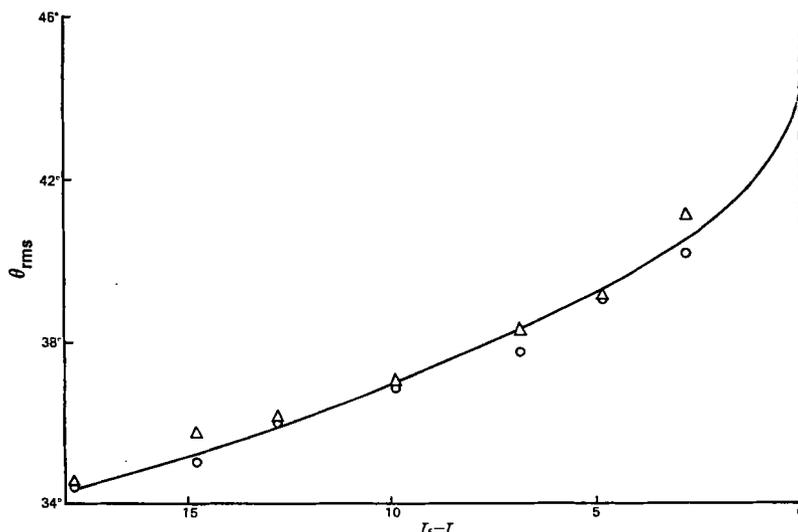


Figure 3. Variation of rms librational amplitude in *p*-azoxyanisole. Curve represents theoretical variation derived from ultrasonic velocity; points give the values obtained from birefringence,  $\Delta$   $\lambda 5890$ ,  $\circ$   $\lambda 5461$ .

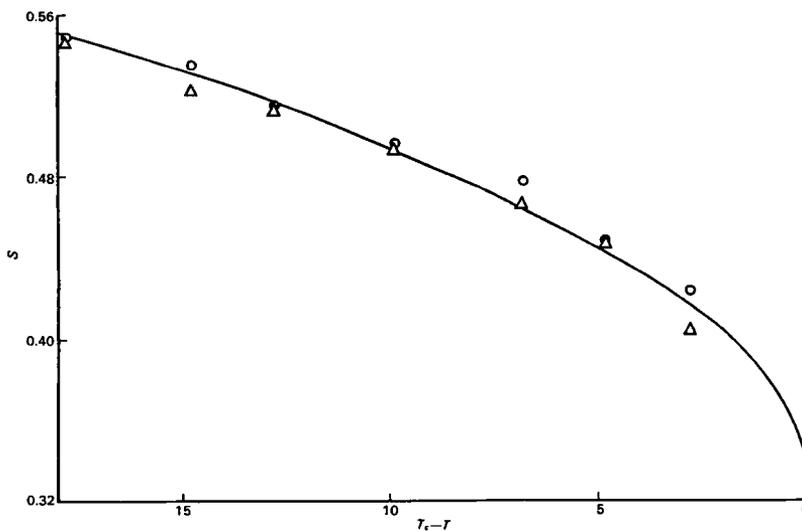


Figure 4. Variation of orientation factor  $S$  with temperature in *p*-azoxyanisole (see legend of Fig. 3).

the corresponding variation of  $S$ . The agreement is remarkably good over the entire nematic range. It is interesting to note that  $\theta_{\text{rms}}$  is only  $44^\circ$  at the upper transition temperature showing that the phase change is characterized by an abrupt collapse of the orientational order.

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### Appendix

Since the temperatures at which thermal expansion measurements have been carried out are not the same as those for which birefringence data are available some interpolation and extrapolation was necessary for the calculations. It was therefore found convenient to use empirical formulae to fit the observed thermal expansion data.

Accurate density measurements have been made by Maier and Saupe<sup>12</sup> for *p*-azoxyanisole. Their data are expressible by the

empirical equation

$$\rho = \rho_0 \left( 1 + \int_T^{T_c} \alpha dT \right) \quad (\text{i})$$

where 
$$\alpha = 12.65 \times 10^{-4} / (T_c - T)^{1/6} \quad (\text{ii})$$

Table I shows the agreement between the calculated and observed data.

TABLE I

$T_c - T$	$\rho_{\text{obs}}$	$\rho_{\text{calc}}$
30.8	1.1781	1.1779
25.8	1.1737	1.1737
20.8	1.1694	1.1694
15.8	1.1649	1.1650
13.8	1.1630	1.1631
11.8	1.1611	1.1612
9.8	1.1592	1.1593
7.8	1.1572	1.1572
5.8	1.1551	1.1551
3.8	1.1528	1.1529
2.8	1.1516	1.1517
1.8	1.1504	1.1504
0.8	1.1490	1.1490
0.3	1.1482	1.1482

The volume expansion coefficients of *p*-azoxyphenetole reported by Bauer and Bernamont<sup>38</sup> can be represented by the empirical formula

$$\alpha = \frac{1.303 \times 10^{-3}}{(T_c - T)^{1/6}} \quad (\text{iii})$$

It may be seen from Table II that the formula gives a good fit, the deviations being of the same order as the reported experimental error. The extrapolated values are likely to be quite accurate since the variation of  $\alpha$  is gradual in this region. The values of  $\rho/\rho_0$  shown in Table II are obtained using equations (i) and (iii).

TABLE 2

$T_c - T$	$\alpha_{\text{obs}} \times 10^3$	$\alpha_{\text{calc}} \times 10^3$	$(\rho/\rho_0)_{\text{calc}}$
20.8	0.94	0.93	1.0194
17.8	0.95	0.95	1.0169
15.8	0.97	0.96	1.0152
11.3	1.00	1.00	1.0113
7.5	1.04	1.04	1.0088
5.3	1.06	1.08	1.0065
3.1	1.14	1.14	1.0043
0.6	1.39	1.38	1.0009

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