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Effect of Electric Field on the Nematic–Isotropic Phase Transition of Compounds with a Strong Longitudinal Dipole Moment†

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We present calculations on the effect of an external electric field on the nematic–isotropic transition of compounds with strong longitudinal dipole moments. In such compounds neighbouring molecules have antiparallel correlations. We use the Bethe cluster model and the constant coupling approximation in our calculations. Assuming reasonable values of the dipole moment and polarizabilities of the molecules, it is predicted that the nematic-(field induced) paranematic transition becomes continuous for an internal field $E \simeq 3250$ esu, when the transition point is ~ 6 °K above the field-free value.

INTRODUCTION

The effect of an external orienting field on the nematic-isotropic transition is of considerable interest since a critical point in the nematic to the field-induced paranematic phase transition is expected to occur at sufficiently high fields.[1-3] The models proposed up to now are limited to using a Maier–Saupe type mean field approximation and calculations on the effect of an external magnetic field on the relatively weak diamagnetic anisotropy or an electric field on the

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polarizability anisotropy of (non-polar) molecules. Experiments[4,5] *using strong magnetic fields have shown that the transition point is* increased slightly, though the prospect of reaching the critical point by this technique appears to be remote in view of the weakness of the diamagnetic anisotropy.

Many nematogenic materials which have the strongly polar cyano group at one end have been synthesized in the past few years. Assuming that they can be purified of ionic impurities so that heating due to ionic conduction as well as problems due to electrohydrodynamic instabilities can be eliminated, application of strong electric fields to such compounds appears to be a feasible method of attaining the critical point. Indeed some early experiments[6] have already shown that the transition point can be shifted by ~ 1°K in such systems. In this paper, we present calculations on the effect of electric fields on the NI transition of such compounds.

For several reasons, such a calculation is not as simple as that on the effect of a magnetic field: (i) The neighbouring molecules of the strongly polar compounds have antiparallel correlations,[7,8] which is now an experimentally well established[9] fact; (ii) the actual electric field which is effective in orienting the molecules because of its interaction with the polarizability anisotropy is different from the field effective in orienting the dipole moment, and both are different from the external field due to the polarization of the medium.[10] Indeed there is no exact theory available for the calculation of these 'effective' fields in a strongly anisotropic medium;[11] (iii) since the electric field necessary to observe a change in the transition point is quite strong, the 'effective' fields mentioned above will have a nonlinear dependence on the applied field;[10] even though the dominant contributions may still be expected to be from the linear terms.

We use the Bethe cluster model to take into account the antiparallel correlations between neighbouring molecules, and use the constant coupling approximation for making calculations. In the present paper, we avoid the problem of connecting the 'effective' field with the external field by presenting all the calculations in terms of the effective field itself.

THEORETICAL MODEL

We consider a Bethe cluster of $(z + 1)$ molecules, and take the mutual interaction energy of the central molecule i and one of the nearest neighbours, j, to be of the form[7,8]

$$E(\cos\theta_{ij}) = A^*P_1(\cos\theta_{ij}) - B^*P_2(\cos\theta_{ij}) \qquad (1)$$

where θ_{ij} is the angle between the long axes of the molecules i and j, and $P_1(\cos\theta_{ij})$ and $P_2(\cos\theta_{ij})$ are Legendre polynomials of order one and two respectively. The positive sign of the $P_1(\cos\theta_{ij})$-term favours an antiparallel arrangement of neighbouring (polar) molecules. As usual, we assume that no two nearest neighbours of the central molecule are nearest neighbours of each other.

An external electric field E_{ext} applied along the director produces an 'effective' field E at the site of a given molecule. One has to usually distinguish between the directing field E_d which is effective in orienting the permanent dipole moment of the molecule and the internal field E_i which is effective in producing the induced dipole moments in the molecules,

$$\mathbf{E}_d = \mathbf{E}_c + \boldsymbol{f} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}_d \tag{2}$$

where $\mathbf{E}_c$ is the cavity field, and the second term is the reaction field due to the polarizability $\boldsymbol{\alpha}$ of the molecule, $\boldsymbol{f}$ being called the reaction field factor, which depends on the dielectric constants of the medium (see Eq. 15). The potential energy of the dipole $\boldsymbol{\mu}$ is given by

$$U_{\mu} = -\boldsymbol{\mu} \cdot \mathbf{E}_d \tag{3}$$

The internal field is given by

$$\mathbf{E}_i = \mathbf{E}_d + \overline{\mathbf{R}} \tag{4}$$

where $\overline{\mathbf{R}}$ is the average reaction field due to the orientation of the permanent dipole moment in the external field

$$\overline{\mathbf{R}} = \boldsymbol{f} \cdot (\boldsymbol{\mu} + \boldsymbol{\alpha} \cdot \overline{\mathbf{R}}) \tag{5}$$

and the potential energy of the molecule due to the induced polarization is given by[1]

$$U_{\text{induced}} = -(\mathbf{E}_c \cdot \boldsymbol{\alpha} \cdot \mathbf{E}_i) \tag{6}$$

As we mentioned earlier, a calculation of $\mathbf{E}_d$ and $\mathbf{E}_i$ as functions of $\mathbf{E}_{\text{ext}}$ is rather intricate and we shall not take it up in the present paper. Instead we shall simply write the orientational potential energy of the molecule j due to the electric field in the form

$$V_h(\cos\theta_j) = -E\mu_{\text{eff}} P_1(\cos\theta_j) - \frac{E^2}{2}\alpha P_2(\cos\theta_j) \tag{7}$$

where E is an 'effective' electric field. In general it depends on E_{ext}, the anisotropic dielectric constants and polarizabilities, the dipole moments of the molecule and the order parameters of the system. For the sake of simplicity, we have also assumed that the same value of E can be used in both the terms of Eq. (7), which may be taken to mean that μ_{eff} is different from the actual dipole moment μ of the molecule. We shall use eqs. (1) and (4) to estimate a value of (E_{ext}/E) towards the end of the paper.

The potential energy of an outer molecule j due to its interactions with the rest of the medium is taken to be of the form

$$\begin{aligned} V_m(\cos\theta_j) = {} & -B_1P_1(\cos\theta_j) - B_2P_2(\cos\theta_j) \\ & -B_3P_3(\cos\theta_j) - B_4P_4(\cos\theta_j) \end{aligned} \tag{8}$$

As has been discussed elsewhere,[8] the results obtained by using terms up to $P_4(\cos\theta)$ in V_m satisfy thermodynamic consistency much better than the ones with terms only up to $P_2(\cos\theta)$. $B_1 = B_3 = 0$ in the field free case, as the nematic is not a ferroelectric. We use the constant coupling approximation,[10,12] which implies the following consistency conditions:

$$\begin{aligned} & \int P_n(\cos\theta_i)F_1(\cos\theta_i)\,d(\cos\theta_i) \\ & = \int\int\int P_n(\cos\theta_j)F_{12}(\cos\theta_{ij})\,d(\cos\theta_i)\,d(\cos\theta_j)\,d(\varphi_i - \varphi_j) \end{aligned} \tag{9}$$

where $F_1(\cos\theta_i)$ and $F_{12}(\cos\theta_{ij})$ are the one and two particle distribution functions given by

$$\begin{aligned} F_1(\cos\theta_i) &= \frac{1}{Z_1}[g(\cos\theta_i)]^{z/z-1}h(\cos\theta_i), \\ F_{12}(\cos\theta_{ij}) &= \frac{1}{Z_{12}}f(\cos\theta_{ij})g(\cos\theta_i)g(\cos\theta_j) \\ & \quad \times h(\cos\theta_i)h(\cos\theta_j) \end{aligned} \tag{10}$$

where

$$Z_1 = \int [g(\cos\theta_i)]^{z/z-1} h(\cos\theta_i)\, d(\cos\theta_i)$$

$$Z_{12} = \int\int\int f(\cos\theta_{ij})\, g(\cos\theta_i)\, g(\cos\theta_j)\, h(\cos\theta_i) \times h(\cos\theta_j)\, d(\cos\theta_i)\, d(\cos\theta_j)$$

$$g(\cos\theta_i) = \exp[-V_m(\cos\theta_i)/kT],$$

$$h(\cos\theta_i) = \exp[-V_h(\cos\theta_i)/kT],$$

and

$$f(\cos\theta_{ij}) = \exp[-E(\cos\theta_{ij})/kT].$$

Equation (9) generally admits more than one solution. The equilibrium degree of order is determined by choosing that solution which minimizes the Helmholtz free energy given by

$$\frac{F}{NkT} = (z-1)\ln Z_1 - \frac{z}{2}\ln Z_{12}. \tag{11}$$

The internal energy is given by

$$\frac{U}{N} = \frac{z}{2}\left[A^*\langle P_1(\cos\theta_{ij})\rangle - B^*\langle P_2(\cos\theta_{ij})\rangle\right] - E\mu_{\mathrm{eff}}\langle P_1(\cos\theta_i)\rangle - \frac{E^2}{2}\Delta\alpha\langle P_2(\cos\theta_i)\rangle \tag{12}$$

where

$$\langle P_n(\cos\theta_{kl})\rangle = \int\int\int P_n(\cos\theta_{kl})\, F_{12}(\cos\theta_{kl}) \times d(\cos\theta_k)\, d(\cos\theta_l)\, d(\varphi_k - \varphi_l) \tag{13}$$

The method of calculation

For the purpose of making calculations, we assume $\mu_{\mathrm{eff}} = 5$ Debye, $\alpha = 50$ Å^3, and $z = 4$. Further, we also assume that $A^*/B^* = 0.5$ and $B^* = 585 \times 10^{-16}$ erg which leads to $T_{\mathrm{NI}} = 325$ K. All the integrations have been evaluated on a computer using a 16-point Gaussian quadrature method. For a given value of the effective field E and temperature T, calculations are made as follows. B_1, B_2, B_3 and B_4 are

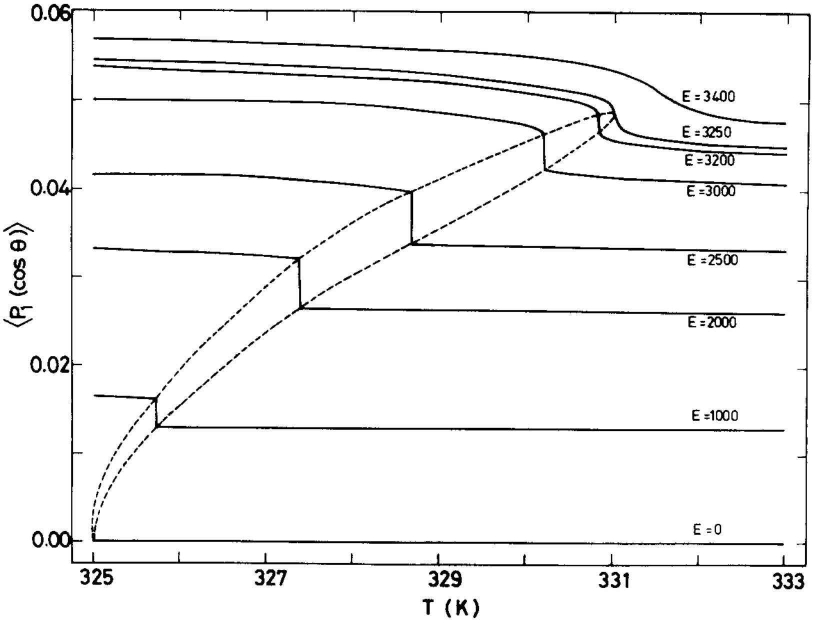

FIGURE 1 Variation of $\langle P_1(\cos\theta)\rangle$ as a function of temperature T for various values of the electric field E.

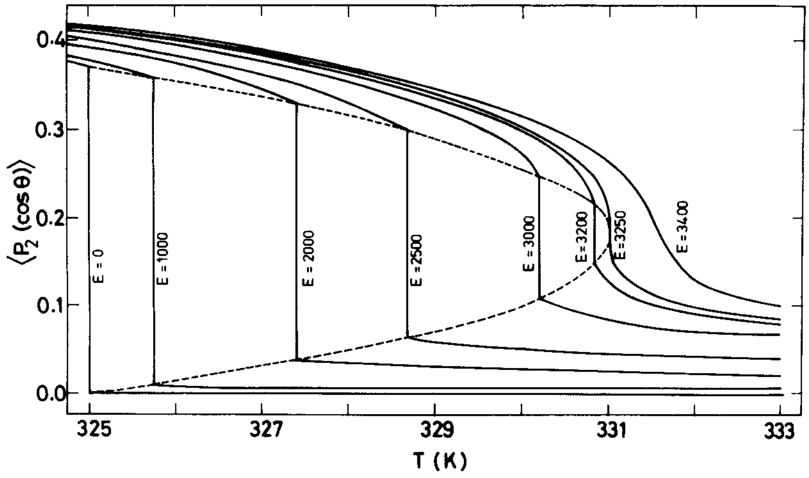

FIGURE 2 Variation of $\langle P_2(\cos\theta)\rangle$ as a function of temperature T for various values of the electric field E.

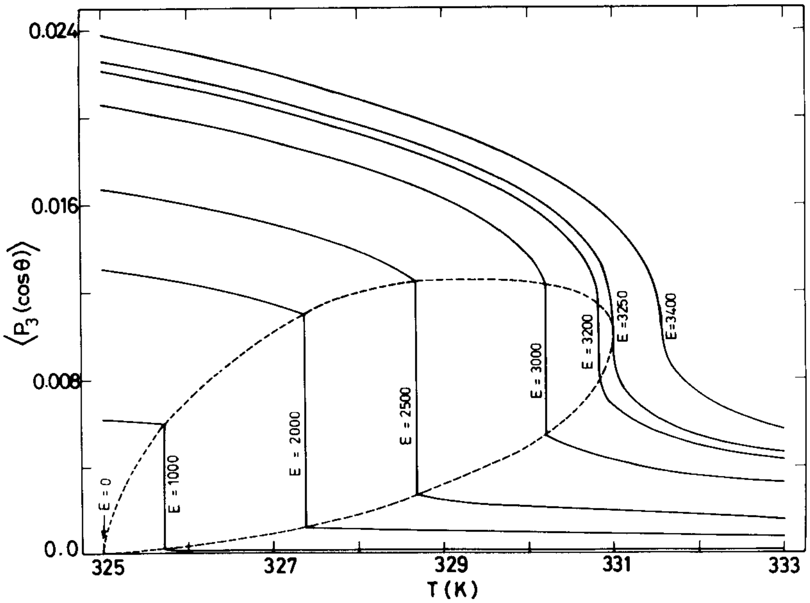

FIGURE 3 Variation of $\langle P_3(\cos\theta)\rangle$ as a function of temperature T for various values of the electric field E.

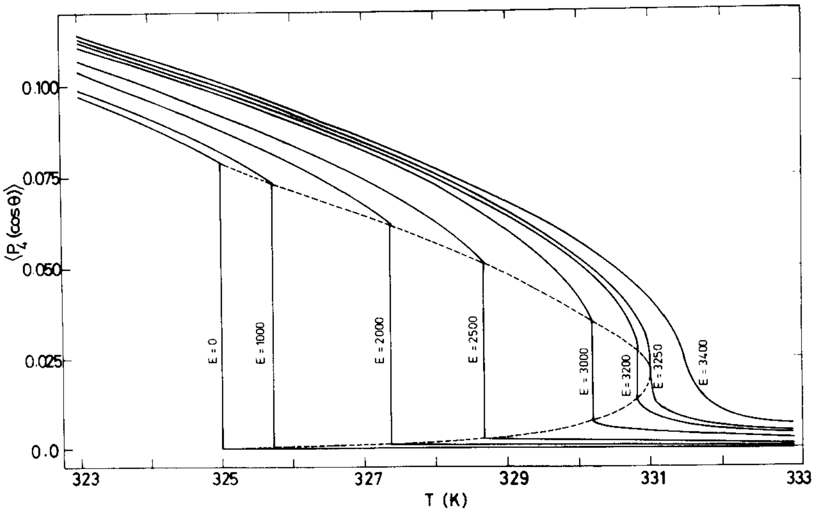

FIGURE 4 Variation of $\langle P_4(\cos\theta)\rangle$ as a function of temperature T for various values of the electric field E.

calculated by satisfying Eq. (9) for $n = 1, 2, 3$ and 4. For the field free system ($E = 0$), $B_1 = B_2 = B_3 = B_4 = 0$ is a possible solution which describes the isotropic phase. For $E \neq 0$, the isotropic phase no longer exists, since the field induces an orientational order. At any given values of E and T, the stable phase is determined by that set of B coefficients which minimizes the Helmholtz free energy (Eq. 11). The temperature at which the free energies of the nematic and paranematic phases become equal is the transition temperature T_{NP}. For $T < T_{NP}$ the nematic phase is stable while for $T > T_{NP}$ the paranematic phase is stable. We have made calculations for a range of values of E from 0 to 3400 esu.

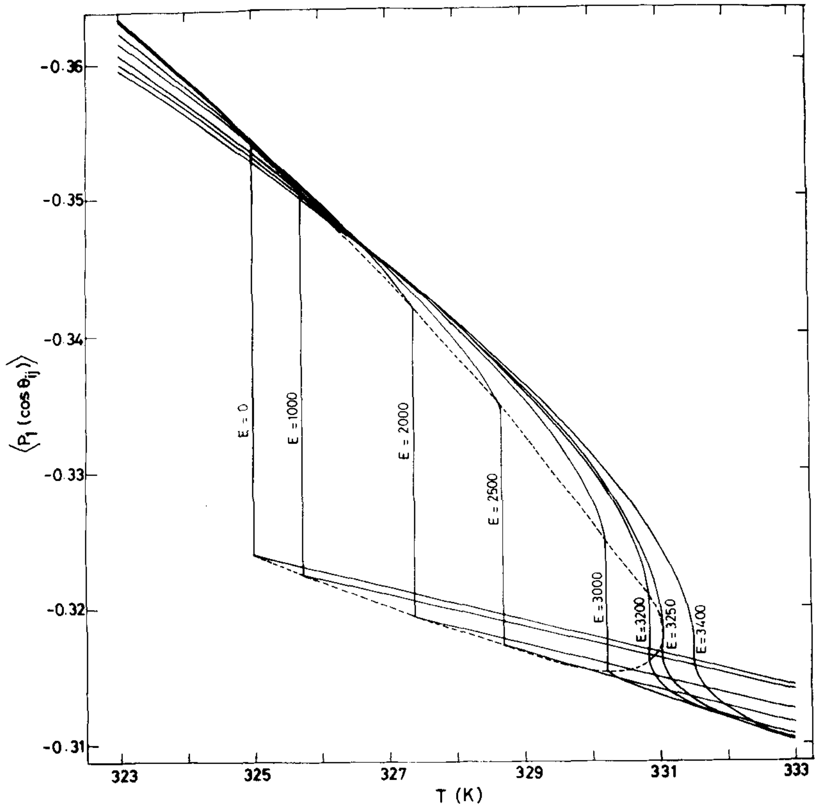

FIGURE 5 Variation of $\langle P_1(\cos\theta_{ij})\rangle$ as a function of temperature T for various values of the electric field E.

RESULTS AND DISCUSSION

$\langle P_1(\cos\theta)\rangle$, $\langle P_2(\cos\theta)\rangle$, $\langle P_3(\cos\theta)\rangle$, $\langle P_4(\cos\theta)\rangle$, $\langle P_1(\cos\theta_{ij})\rangle$, $\langle P_2(\cos\theta_{ij})\rangle$ and U/NB^* are plotted as functions of temperature for various values of the effective field E in Figures 1 to 7 respectively. E^2 is plotted against $T_{NP}(E) - T_{NP}(0)$ in Figure 8. From the figures, we notice the following points. At any given temperature, except $|\langle P_1(\cos\theta_{ij})\rangle|$ all the other order parameters increase with E. At low temperatures, $|\langle P_1(\cos\theta_{ij})\rangle|$ *decreases* with E, since the permanent dipoles would prefer to align along the direction of the external field. However, as the temperature is increased, the rate of decrease of $|\langle P_1(\cos\theta_{ij})\rangle|$ is slower if E is larger, so that at higher temperatures, as the electric field is increased, $|\langle P_1(\cos\theta_{ij})\rangle|$ increases (Figure 5). At these temperatures the nematic phase is stabilized by the external field which gives rise to a considerable increase in the value of $\langle P_2(\cos\theta_{ij})\rangle$ (Figure 6) because of the $\frac{1}{2}\Delta\alpha E^2$ term in the potential energy. This in turn results in an increase of $|\langle P_1(\cos\theta_{ij})\rangle|$. As E increases the strength of the transition comes down. Except the field-induced order parameters $\langle P_1(\cos\theta)\rangle$ and $\langle P_3(\cos\theta)\rangle$, the other order parameters of the nematic phase at T_{NP} decrease with increasing E. $\langle P_1(\cos\theta)\rangle$ and

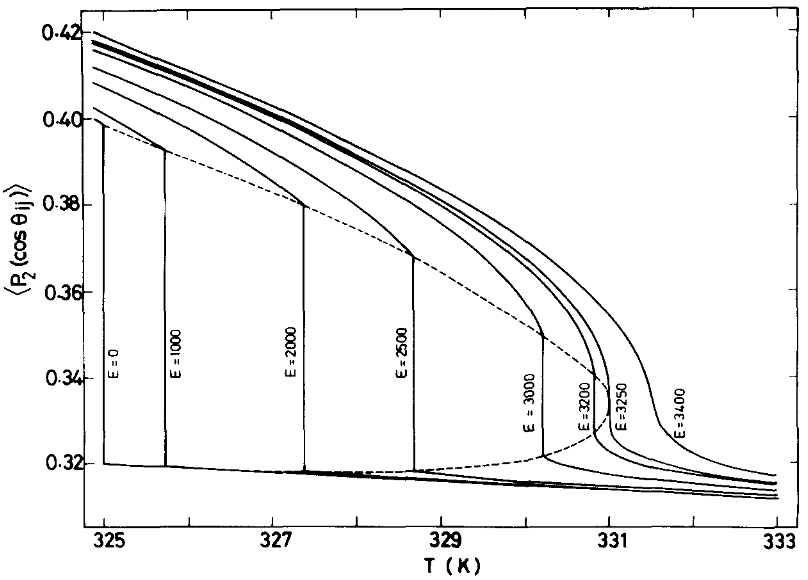

FIGURE 6 Variation of $\langle P_2(\cos\theta_{ij})\rangle$ as a function of temperature T for various values of the electric field E.

$\langle P_3(\cos\theta)\rangle$ are zero in the absence of an external field and hence can only increase when an external field is applied. The jump in $\langle P_2(\cos\theta)\rangle$, $\langle P_4(\cos\theta)\rangle$, $\langle P_1(\cos\theta_{ij})\rangle$ and $\langle P_2(\cos\theta_{ij})\rangle$ and U/NB^* at T_{NP} decrease as E increases and for $E_c \simeq 3250$ esu, the NP transition takes a second order character. The jumps in the field-induced order parameters $\langle P_1(\cos\theta)\rangle$ and $\langle P_3(\cos\theta)\rangle$ at T_{NP} increase at first and then decrease to zero as E is increased to 3250 esu. The transition point itself increases with increase of E, and for E taking the critical value $E_c = 3250$ esu, $T_{\mathrm{NP}}(E_c) - T_{\mathrm{NP}}(\mathrm{O}) \simeq 6°$. The plot of $T_{\mathrm{NP}}(E) - T_{\mathrm{NP}}(\mathrm{O})$ versus E^2 (Figure 8) deviates somewhat from a straight line, since (a) the dipolar energy (which is $\propto E$) and (b) near neighbour interactions have been taken into account in the calculations.

As we have discussed earlier, our calculations have been made at various values of an 'effective field' E. In order to estimate the external field corresponding to the effective field, it is simpler to

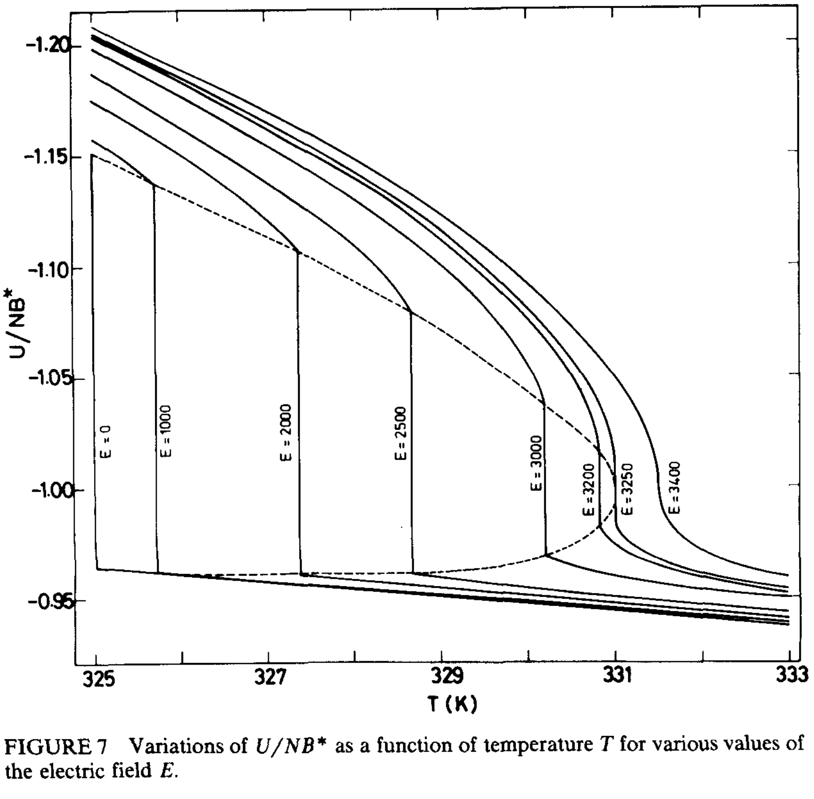

FIGURE 7 Variations of U/NB^* as a function of temperature T for various values of the electric field E.

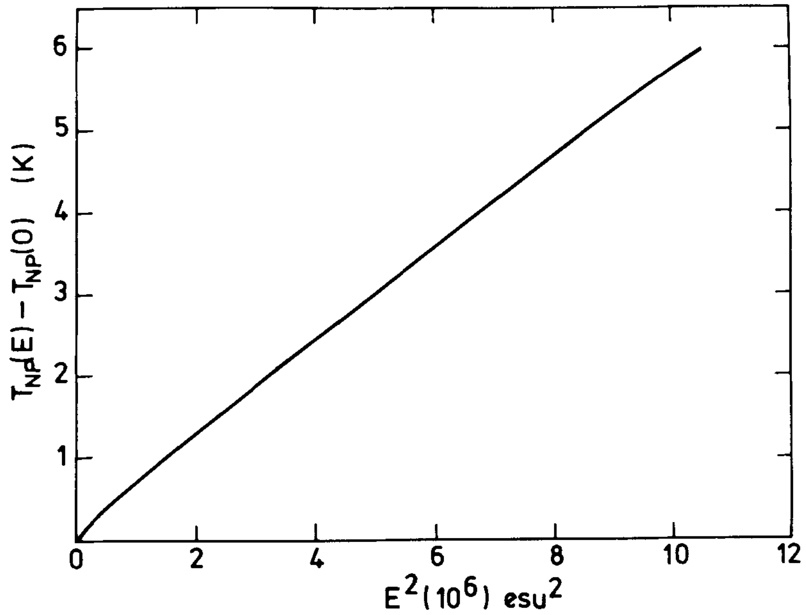

FIGURE 8 Variation of $[T_{NP}(E) - T_{NP}(O)]$ as a function of E^2.

evaluate E_d (Eq. 2), especially if we assume following Maier and Meier,[13] that only the average values of ϵ and α need be used. This is an extension of the Vuks' formula[14] which assumes that the cavity field is isotropic in organic molecular crystals, which is not too bad an approximation for a system of rod-like molecules.[11] In that case

$$E_d = \frac{3\bar{\epsilon}}{2\bar{\epsilon}+1}\frac{1}{1-f\bar{\alpha}}E_{\text{ext}} \tag{14}$$

where

$$f = \frac{4\pi N}{3}\frac{2(\bar{\epsilon}-1)}{2\bar{\epsilon}+1} \tag{15}$$

Using $\bar{\epsilon} = 10$, $\bar{\alpha} = 50 \times 10^{-24}$ *cc* and $N = 2 \times 10^{21}/cc$ $E_d \simeq 2.2E_{\text{ext}}$.

It is much more difficult to exactly evaluate (E_iE_c) of Eq. (6), since the reaction field $\bar{R}$ due to the permanent dipoles contributes to E_i (Eq. 4). However a simple calculation shows that $\sqrt{(E_iE_c)}$ is of the same order as E_d when the temperature is close to T_{NI} (i.e., $T_{NP}(O)$). With $E = 2.2E_{\text{ext}}$, the calculated value of $\Delta T/E_{\text{ext}}^2 \simeq 3.6 \times 10^{-6}$

K/(esu)^2 for relatively weak fields (< 1000 esu) and is reduced to $\sim 2.7 \times 10^{-6}$ K/(esu)^2 when the field is much stronger. This is of the order of the experimental value[6] which is $\simeq 5 \times 10^{-6}$ K/(esu)^2 for a compound with a cyano end group.

In conclusion, our calculations show that it may be a feasible proposition to try to observe the electric-field induced critical point of the nematic-paranematic transition in compounds with a strongly polar cyano end group.

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