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A simple molecular theory of a nematic–nematic phase transition in highly polar compounds

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We have extended an earlier molecular model which was developed to explain the double reentrant sequence in highly polar compounds to predict the possibility of a nematic (N_1)–nematic (N_2) phase transition in such compounds. At moderate densities the dipolar interactions would give rise to an antiparallel near neighbour arrangement of the polar molecules while at higher densities, the dipole–induced dipole and chain–chain dispersion interactions give rise to a parallel configuration. The N_1–N_2 transition corresponds to a jump in the relative concentration of the two species. Using the mean field approximation we have calculated the phase diagram. The weak first order transition disappears above a critical point as a function of an appropriate parameter. We have also calculated the specific heat anomaly around the transition region.

1. Introduction

Mesomorphic compounds whose molecules have the strongly polar $-C{\equiv}N$ or $-NO_2$ end groups exhibit a variety of interesting phase transitions. Prost and co-workers [1, 2] have developed a rather successful Landau theory of these phase transitions using two competing order parameters. In particular, some compounds with cores having 2 or 3 phenyl rings exhibit the phenomenon of double reentrance [3]. There have also been several attempts to develop a molecular theory of this phenomenon [4–11]. A particularly simple model was proposed in a recent paper [11]. The permanent dipolar interaction favours an antiparallel arrangement between neighbouring molecules of the mesogen [12]. However, the strongest attractive interaction is between the aromatic cores of the molecules, which leads to the well known partial bilayer arrangement in which antiparallel neighbours have an overlap of the aromatic parts. The alkyl chains of the two molecules are on opposite sides of the core region (see figure 1) and hence do not have a significant interaction.

On the other hand, if the molecules are parallel, the permanent dipolar interaction is repulsive. However, the aromatic cores have strong polarizabilities and the induced dipole moment due to a neighbouring polar molecule would weaken the net dipole moment of any given molecule in this configuration (see figure 2). Further, the chains are now in close proximity and the dispersion interaction between them would favour this arrangement.

The dipolar interaction is $\propto 1/r^3$ while both the dipole-induced dipole and the dispersion interactions are $\propto 1/r^6$. Hence there can be a change from the antiparallel to the parallel configuration as the intermolecular separation is decreased below some value as the density is increased, i.e. as the temperature is lowered. The dipolar

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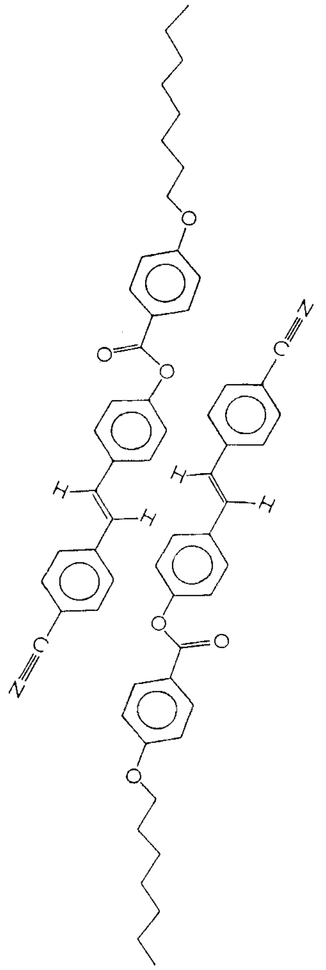

Figure 1. The antiparallel configuration of two octyloxybenzoyloxy cyano-stilbene (T8) molecules favoured at intermediate intermolecular separations (from [11]).

interactions are long range, and it may appear necessary to take into account the interactions between a given molecule and a large number of neighbours including distant ones. As we have shown earlier [11], calculations based on the summation of interactions of molecules in a hexagonal lattice lead to a result which is qualitatively similar to those obtained by considering just one pair of molecules, viz. that at intermolecular separations larger than some value, the antiparallel configuration is favoured while for smaller separations, the parallel configuration is preferred. This change in configuration was incorporated in [11] to account for many features of the phenomenon of double reentrance. In this case, there are two smectic phases, viz, the S_{A_d} phase with a partial bilayer spacing at higher temperatures and the S_{A_1} phase with a monolayer spacing at lower temperatures separated by a reentrant nematic phase. In fact it is also known that some polar compounds exhibit a smectic A to smectic A phase transition without any intervening nematic phase, like for example the S_{A_d}–S_{A_2} transition [13, 14]. The phenomenological Landau theory predicts the above transition as well as a nematic–nematic phase transition under certain conditions close to

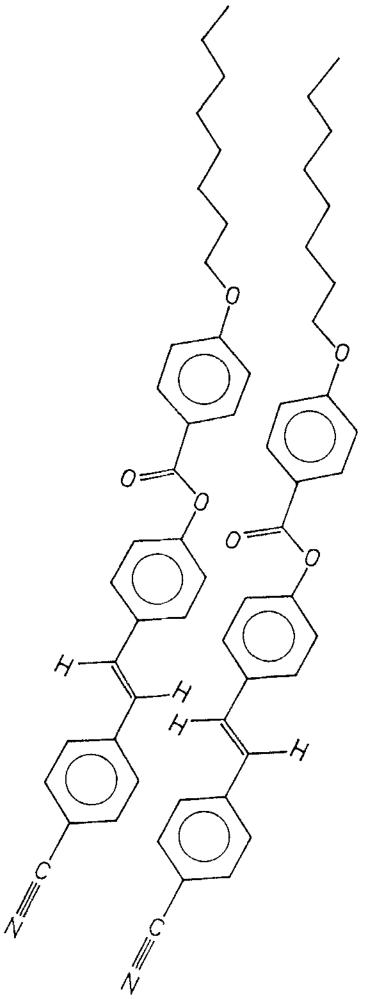

Figure 2. The parallel configuration of two T8 molecules favoured at relatively low values of intermolecular separation (from [11]).

the smectic S_{A_1}–S_{A_d} transition [15]. There has been a recent experimental report of such a possible N–N transition on the basis of a calorimetric study on a mixture of polar compounds [16]. In this paper, we have used the model described earlier to obtain solutions corresponding to a nematic–nematic phase transition. The relative concentration of the two configurations jump at the phase transition point. We have calculated the appropriate phase diagrams as well as the variation of specific heat in the phase transition region.

2. Theoretical model

For the sake of simplicity and in view of our earlier discussion regarding the dependence of the mutual configuration of near neighbours on intermolecular separation, we assume that the medium consists of pairs of molecules which have either an antiparallel (A) or parallel (P) configuration. In the former case, frustration effects can be expected to favour the formation of pairs. On the other hand, we may expect a large number of molecules to be associated in a P type configuration. A statistical mechanical description of the latter becomes quite complex and for the sake of simplicity, we assume that even the P-type configurations have only effective pairs, as in the earlier paper [11].

As we described earlier, the A-type configuration is favoured at lower densities and the P-type at higher densities. Again, for the sake of simplicity, following the approximation made in [11] we assume that the configuration energy difference has the following form:

$$\Delta E = E_{\mathrm{A}} - E_{\mathrm{P}} = R_1 k T_{\mathrm{NI}} \left(\frac{R_2}{T_{\mathrm{R}}} - 1 \right), \tag{1}$$

where k is the Boltzmann constant, E_{A} and E_{P} stand for the configurational energies of the A-type and P-type pairs respectively, T_{NI} is the nematic–isotropic transition temperature of the A type pairs, $T_{\mathrm{R}} = T/T_{\mathrm{NI}}$ is the reduced temperature, $R_1 k T_{\mathrm{NI}}$ is an interaction parameter and R_2 is the reduced temperature at which the density of the medium is such that ΔE becomes zero. For $T_{\mathrm{R}} > R_2$, the A-type configuration has the lower energy while for $T_{\mathrm{R}} < R_2$ the P-type configuration has the lower energy.

As the main interest in the present paper is to look for a nematic–nematic phase transition, we assume that the orientational potential of the two types of pairs are different. In the earlier paper in which the main interest was the double entrant phenomenon, they were assumed to be equal for the sake of simplicity. However it is clear from figures 1 and 2 that the geometrical parameters of the two configurations are so different that a relaxation of this condition is quite appropriate.

The medium is assumed to consist of a mixture of A-type and P-type pairs. Following the method of Humphries *et al.* [17] for the mean field molecular theory of mixtures, we write the orientational potential energy of the ith A-type pair as

$$U_{\mathrm{A}i} = -U_{\mathrm{AA}} X_{\mathrm{A}} S_{\mathrm{A}} P_2(\cos\theta)_{\mathrm{A}i} - U_{\mathrm{AP}} X_{\mathrm{P}} S_{\mathrm{P}} P_2(\cos\theta)_{\mathrm{A}i}, \tag{2}$$

where U_{AA} is the mean field interaction potential between two A-type pairs, U_{AP} that between A-type and P-type pairs, X_{A}, X_{P} and S_{A}, S_{P} are the mole fractions and the orientational order parameters of the A and P type pairs respectively. As usual, $P_2(\cos\theta)$ is the second Legendre polynomial.

Similarly for a P-type pair,

$$U_{\mathrm{P}j} = -U_{\mathrm{PP}} X_{\mathrm{P}} S_{\mathrm{P}} P_2(\cos\theta)_{\mathrm{P}j} - U_{\mathrm{PA}} X_{\mathrm{A}} S_{\mathrm{A}} P_2(\cos\theta)_{\mathrm{P}j}, \tag{3}$$

where U_{PP} is the interaction potential between two P-type pairs and the mutual interaction $U_{\mathrm{PA}} = U_{\mathrm{AP}}$.

Now we can write the internal energy of one mole of the pairs by averaging over the distribution functions

$$2U = \left(\frac{N X_{\mathrm{A}}}{2} \right) \overline{U_{\mathrm{A}i}} + \left(\frac{N X_{\mathrm{P}}}{2} \right) \overline{U_{\mathrm{P}j}} - N X_{\mathrm{P}} \Delta E, \tag{4}$$

where the bars indicate statistical averages, and the factor 2 on the left hand side reminds us that we have a mole of pairs. We have also added the concentration dependent part of the configurational energy. N is the Avogadro number.

The normalized orientational distribution functions of the A and P type of pairs are, respectively,

$$f_{\mathrm{A}i}(P_2(\cos\theta))=\frac{\exp\{-U_{\mathrm{A}i}/kT\}}{\int_0^1 \exp\{-U_{\mathrm{A}i}/kT\}d(\cos\theta_i)}, \tag{5}$$

$$f_{\mathrm{P}j}(P_2(\cos\theta))=\frac{\exp\{-U_{\mathrm{P}j}/kT\}}{\int_0^1 \exp\{-U_{\mathrm{P}j}/kT\}d(\cos\theta_j)}, \tag{6}$$

where k is the Boltzmann constant.

The molar entropy is given by

$$\begin{aligned}2S= -Nk\left[X_{\mathrm{A}}\int f_{\mathrm{A}i}\ln f_{\mathrm{A}i}d(\cos\theta)_{\mathrm{A}i}+X_{\mathrm{P}}\int f_{\mathrm{P}j}\ln f_{\mathrm{P}j}d(\cos\theta)_{\mathrm{P}j}\right]\\ -Nk(X_{\mathrm{A}}\ln X_{\mathrm{A}}+X_{\mathrm{P}}\ln X_{\mathrm{P}})\end{aligned} \tag{7}$$

in which the last term is the entropy of mixing.

The Helmholtz free energy is given by

$$F=U-TS. \tag{8}$$

Minimizing the free energy with respect to the order parameters, we get the usual consistency conditions

$$\overline{P_2(\cos\theta)_{\mathrm{A}i}}=\int_0^1 P_2(\cos\theta)_{\mathrm{A}i}f_{\mathrm{A}i}d(\cos\theta_i)=S_{\mathrm{A}} \tag{9}$$

and

$$\overline{P_2(\cos\theta)_{\mathrm{P}j}}=\int_0^1 P_2(\cos\theta)_{\mathrm{P}j}f_{\mathrm{P}j}d(\cos\theta_j)=S_{\mathrm{P}}. \tag{10}$$

The mole fraction X_{A} of the A-type pairs is found by minimizing the free energy with respect to X_{A}. We get

$$X_{\mathrm{A}}=\frac{1}{1+\frac{\mathrm{DFP}}{\mathrm{DFA}}\exp(\Delta E/kT)} \tag{11}$$

where DFA and DFP are the normalizing integrals in the denominators of equations (5) and (6) respectively.

For the sake of convenience we write $U_{\mathrm{PP}}=YU_{\mathrm{AA}}$. The solutions to the above equations which minimize the free energy define an appropriate thermodynamically stable phase. We get a nematic phase if $S_{\mathrm{A}}\neq 0$ and $S_{\mathrm{P}}\neq 0$ and the isotropic phase for $S_{\mathrm{A}}=S_{\mathrm{P}}=0$. The calculations have to be made numerically. This will be discussed in the next section.

2.1. *Specific heat at constant volume*

The molar specific heat at constant volume is given by

$$
\begin{aligned}
C_v &= \left[\frac{\partial}{\partial T}(U)\right]_v \\
&= -\frac{N}{2}\left[\frac{\partial X_A}{\partial T}\{U_{AA}X_AS_A^2 - U_{PP}X_PS_P^2 + U_{AP}S_AS_P(X_P - X_A)\}\right. \\
&\quad + \frac{\partial S_A}{\partial T}\{U_{AA}X_A^2S_A + U_{AP}X_AX_PS_P\} \\
&\quad \left. + \frac{\partial S_P}{\partial T}\{U_{PP}X_P^2S_P + U_{AP}X_AX_PS_A\}\right] \\
&\quad + N\Delta E\frac{\partial X_A}{\partial T}. \qquad (12)
\end{aligned}
$$

Note that in the above expression, we have not differentiated ΔE with respect to T. As we discussed in the introduction, ΔE is truly a function of intermolecular separation, or equivalently, the volume of the system. It is purely for the sake of convenience in calculation that ΔE was written as a function of temperature. As such in calculating C_v, in which the volume is held fixed, we do not differentiate ΔE with temperature. Expressions for $\partial S_A/\partial T$, $\partial S_P/\partial T$, and $\partial X_A/\partial T$ are obtained by differentiating with respect to T the equations (9), (10) and (11) respectively. The three derivatives are obtained by solving the three simulatneous equations. It is necessary to calculate the statistical averages $\langle P_2^2(\cos\theta)_A\rangle$ and $\langle P_2^2(\cos\theta)_P\rangle$ for this purpose.

3. Results and discussion

In order to proceed with the calculations, we have to make some assumption about U_{AP}. Humphries *et al.* used the well-known geometric mean approximation, i.e. $U_{AP} = (U_{AA}U_{PP})^{1/2}$. However, as they noted [18], most experimental phase diagrams on binary mixtures correspond to a value of U_{AP} less than the geometric mean value. In other words, if

$$U_{AP} = P(U_{AA}U_{PP})^{1/2} \qquad (13)$$

$(P-1)$ which is a measure of the deviation from the geometric mean rule is negative. In fact theories based on hard rod models of mixtures of rods with two different length to breadth ratios [19–21] appear to give rise to a phase boundary which would correspond to $P < 1$ in the context of the theory of Humphries *et al.* Palffy-Muhoray *et al.* [22] have extended the Humphries *et al.* model by taking into account the volume dependence of the potential functions. In this case, the chemical potentials of the two species have to be calculated to determine the phase diagram. Apart from getting a nematic–isotropic coexistence range they have also found a nematic–nematic coexistence at sufficiently low temperatures when the T_{NI} values of the two components differ considerably. Indeed, experiments on mixtures of two very dissimilar chemical species have shown such a coexistence [23, 24] of two nematic phases.

In our calculations we have used equation (13) with $P < 1$. We evaluate all the necessary integrals numerically by using a 32 point gaussian quadrature method in double precision. All temperatures are referred to the nematic–isotropic transition point $(T_{NI})_A$ of the A-type pairs, i.e. by using $U_{AA}/k(T_{NI})_A = 4{\cdot}541$ and $T_R = (T/T_{NI})_A$. At any reduced temperature T_R, consistent values of S_A and S_P are found as X_A is varied from 0 to 1 for the assumed set of the four parameters of the problem, viz. R_1, R_2, Y and P.

Calculations have been made for $R_1 = 15$ and $R_2 = 0{\cdot}6$, which are very reasonable values [11]. Naturally we can expect the nematic–nematic transition to take place at $T_R \simeq R_2$. We find that the transition occurs when the deviation from the geometric mean rule is quite significant. We made the calculations for Y ranging from 0·9 to 2. $Y<1$ signifies that $|U_{AA}| > |U_{PP}|$, i.e. the pure P-type species has a lower T_{NI} value than the A-type species. In this case the deviation from geometric mean rule should be quite large with $P \sim 0{\cdot}5$ in order to get the N_1–N_2 transition. For some values of the parameters, and in a narrow range of temperatures, we found that the free energy has two minima as X_A is varied, indicating the possibility of existence of two different nematic phases with different values of X_A. We illustrate this trend for $Y = 1{\cdot}4$ in figure 3. Indeed by a careful numerical calculation we find that at some temperature the two free energy minima become equal signifying a first order transition between the two nematic phases. As the two nematic phases have the same symmetry, we can expect either a first order phase transition or a continuous change over between them. As the parameter P is increased (keeping all other parameters fixed), the jump in X_A decreases, until we reach the critical point beyond which there is no phase transition separating the two nematic phases (see figure 4). We have also evaluated the heat of the N_1–N_2 transition. As we know, even the N–I transition is only weakly first order in nature. Understandably N_1–N_2 transition is found to be very much weaker than the N–I transition. In the range of our

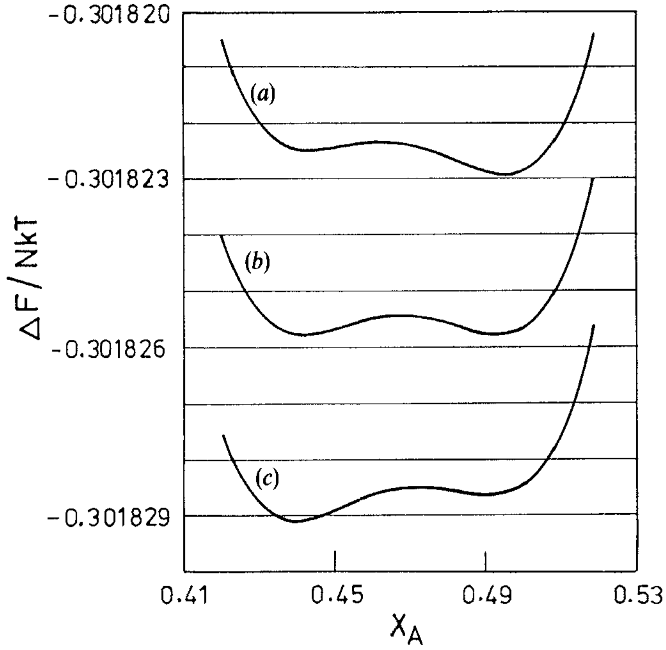

Figure 3. Molar Helmholtz free energy difference $\Delta F = F_{\text{nematic}} - F_{\text{isotropic}}$ plotted as a function of relative concentration of A-type of species (X_A) at three temperatures near $T_{N_1-N_2}$ for $Y = 1{\cdot}4$ and $P = 0{\cdot}6954$. (a) $T/T_{NI} = 0{\cdot}62659436$, (b) $T/T_{NI} = 0{\cdot}62659386$ and (c) $T/T_{NI} = 0{\cdot}62659340$.

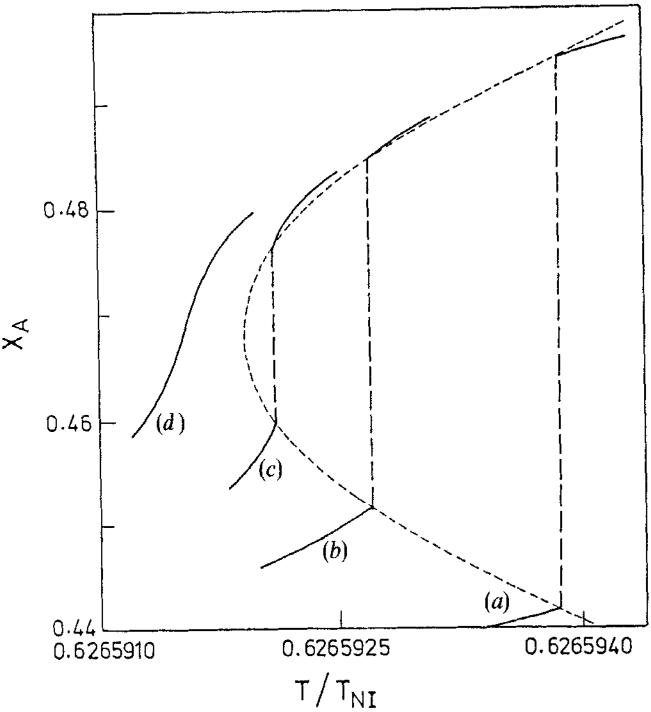

Figure 4. Relative concentration of A-type of species (X_A) plotted as a function of T/T_{NI} for $Y=1·4$. (*a*) $P=0·6954$, (*b*) $P=0·6956$, (*c*) $P=0·6957$, (*d*) $P=0·6958$.

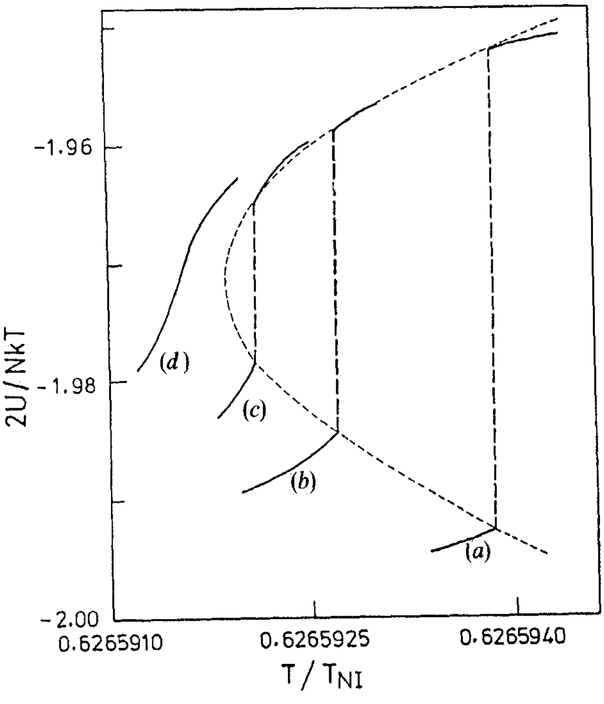

Figure 5. Internal energy per mole of pairs (2 *U*) plotted as a function of T/T_{NI} for $Y=1·4$ for different values of *P*. (*a*), (*b*), (*c*) and (*d*) have the same significance as in figure 4.

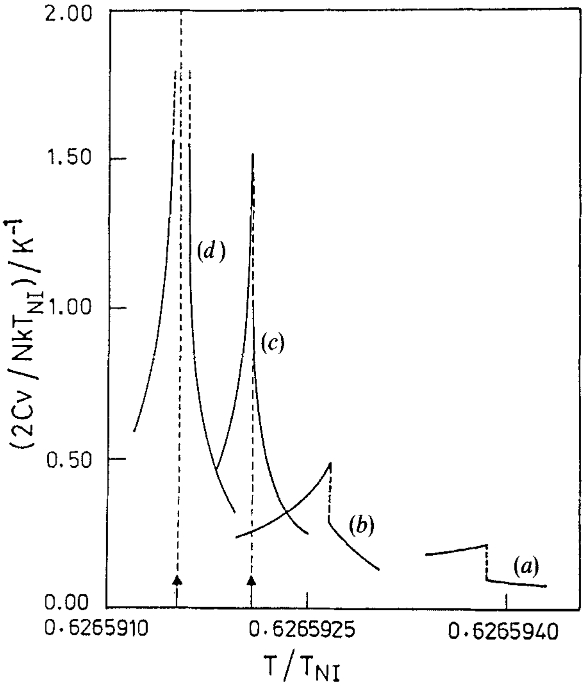

Figure 6. Specific heat at constant volume per mole of pairs ($2C_v$) plotted as a function of T/T_{NI} for $Y=1{\cdot}4$ for different values of P. (*a*), (*b*), (*c*) and (*d*) have the same significance as in figure 4.

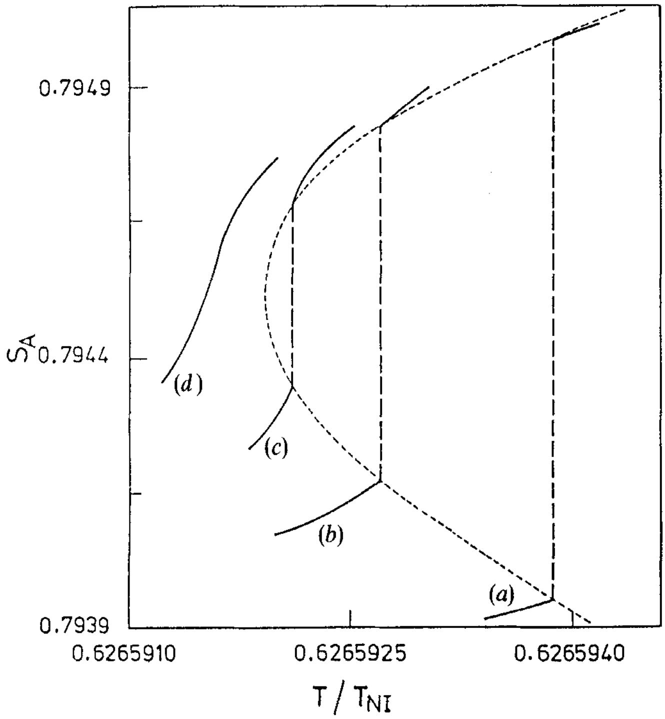

Figure 7. Order parameter of A-type of species (S_A) plotted as a function of T/T_{NI} for $Y=1{\cdot}4$ for different values of P. (*a*), (*b*), (*c*) and (*d*) have the same significance as in figure 4.

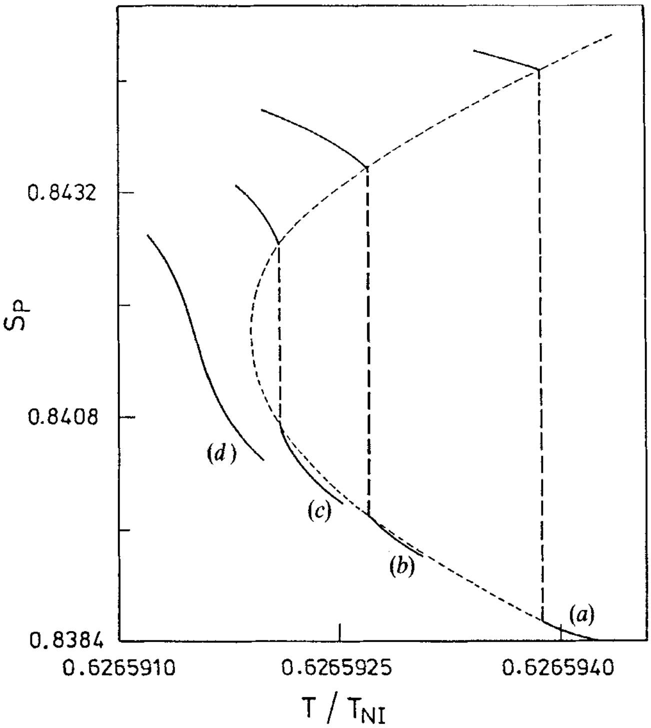

Figure 8. Order parameter of P-type of species (S_P) plotted as a function of T/T_{NI} for $y = 1{\cdot}4$ for different values of P. (a), (b), (c) and (d) have the same significance as in figure 4.

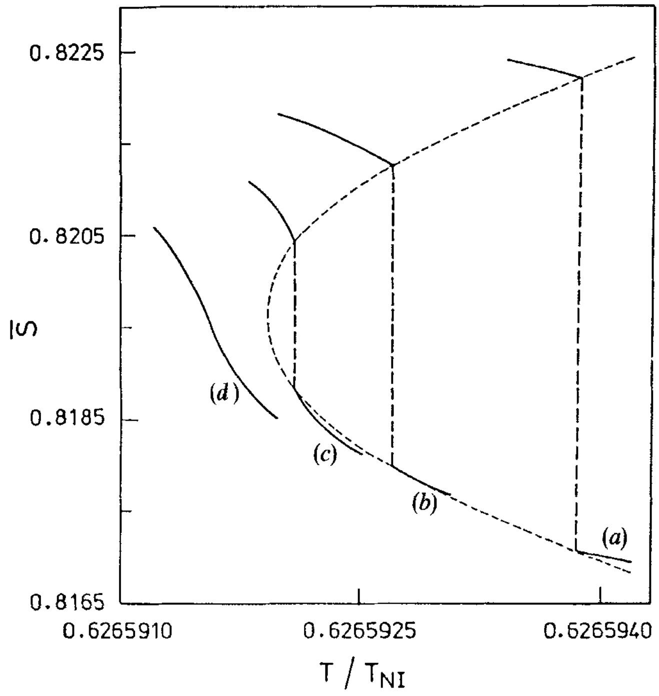

Figure 9. Averaged order parameter $\bar{S} = X_A S_A + X_P S_P$ plotted as a function of T/T_{NI} for $Y = 1{\cdot}4$ for different values of P. (a), (b), (c) and (d) have the same significance as in figure 4.

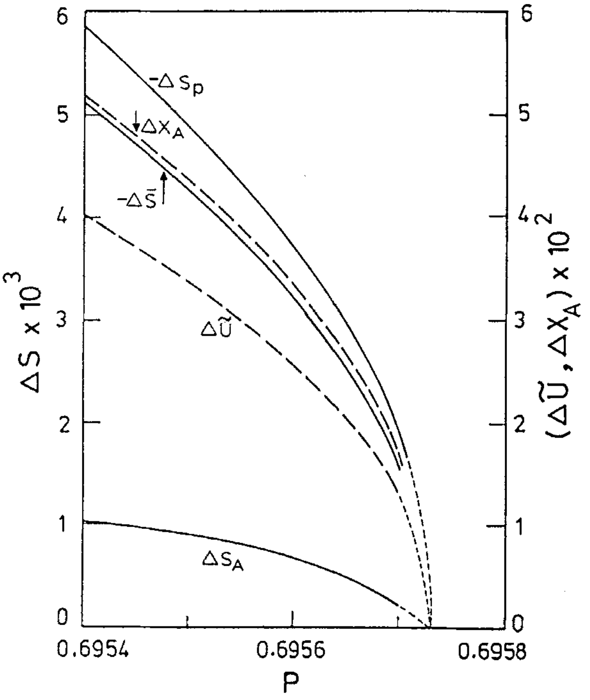

Figure 10. Variations of the jumps at $T_{N_1-N_2}$ in X_A, $\tilde{U}=2U/NkT$, S_A, S_P and $\bar{S}$ as functions of P for $Y=1{\cdot}4$. The jumps decrease continuously to zero as P approaches $P_{cr} \simeq 0{\cdot}69573$.

calculations, the highest heat of transition is ~50 joule mol^{-1}, i.e. an order of magnitude smaller than the corresponding value at the N–I transition (see figure 5). Consequently, the specific heat shows a strong peak as the transition point is approached from either side. As the critical point is approached, the sharpness of the peak increases further (see figure 6). We have shown the temperature variations of the order parameters S_A, S_P and $\bar{S}=X_AS_A+X_PS_P$ near the N_1–N_2 transition point in figures 7 to 9 respectively. For the sake of comparison, we have plotted in figure 10 jumps in various parameters like X_A, $\tilde{U}$, S_A, S_P and $\bar{S}$ as functions of P for $Y=1{\cdot}4$. All these jumps decrease continuously to zero as P approaches $P_{cr} \approx 0{\cdot}69573$.

When T is significantly less (greater) than $T_{N_1-N_2}$, $S_A > S_P$ ($S_P > S_A$). When $Y=0{\cdot}9$, $P_{cr} \approx 0{\cdot}531$. Further when $Y<1$, as P increases, T_R at $T_{N_1-N_2}$ increases. Note that the calculations are made in a very narrow range of T_R values and it is rather easy to miss this transition in the calculations. When $Y=0{\cdot}999$, P_{cr} increases to about $0{\cdot}5732$. T_R does not appear to change with P for this value of Y. On the other hand, when $Y>1$, we get N_1–N_2 transition for higher values of P, i.e. smaller deviation from the geometric mean rule. For example, when $Y=2$, $P_{cr} \simeq 0{\cdot}82$. We have shown the dependence of P_{cr} on Y in figure 11. For higher values of Y, there is a partial compensation of the lower pairing potential by the higher orienting potential of P type of pairs at higher temperatures. Similarly there is a compensation of potentials for the A type pairs also. The overall dissimilarity between the two types of configurations is thus reduced which may be responsible for the increase in P_{cr} towards the geometric mean value of 1 as Y is increased. Also when $Y>1$ the critical point is reached as P is increased as before, but

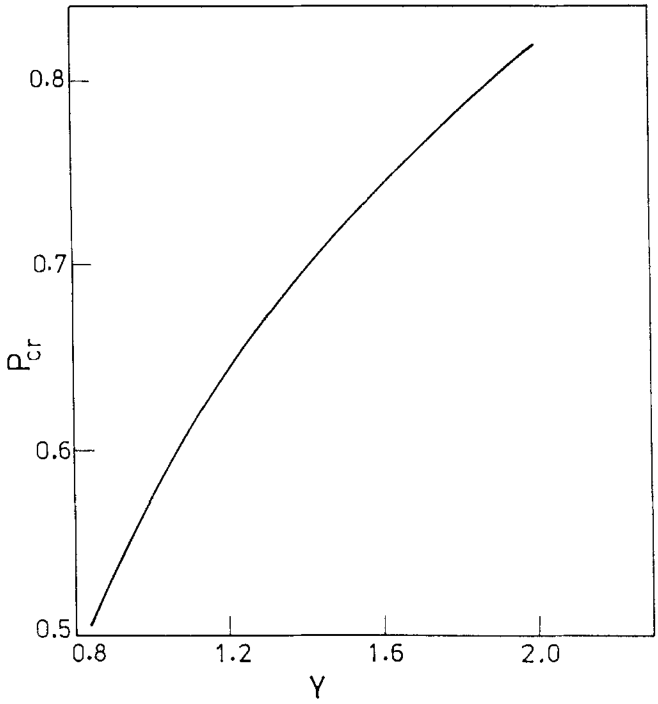

Figure 11. The critical value of P plotted as a function of Y.

the corresponding value of T_R at the N_1–N_2 transition decreases. Even though the P-type configuration is favoured to occur at lower temperatures, it is quite possible that the orientational potential U_{PP} may be considerably higher than U_{AA} of the A-type species, which are favoured to occur at higher temperatures. As we discussed in the introduction, the A-type configuration may actually occur as pairs due to frustration effects. The frustration effect may also effectively reduce the orientational potential between neighbouring A-type pairs. On the other hand, the P-type configuration should favour formation of large clusters which can enhance the orientational potential of the effective pairs used in our model.

In conclusion, we have extended our simple molecular theory of highly polar compounds to demonstrate the possibility of a nematic–nematic transition in such cases. Predictably, it is a very weak transition with a large variation of specific heat around the transition point. The transition disappears above a critical point. We are now extending these calculations to the smectic phases.

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