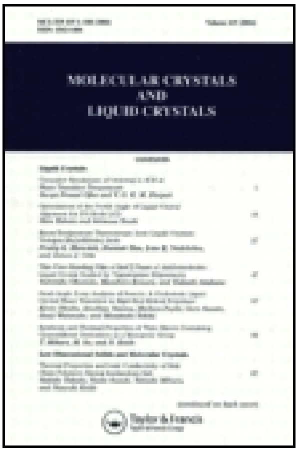

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Diminution of Even-Odd Alternation in Smectic-Nematic Transitions

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Diminution of Even-Odd Alternation in Smectic-Nematic Transitions

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The alternation in Smectic A-Nematic transition temperatures of the members of a homologous series is generally observed to be highly diminished and in some cases even absent, as compared to the Nematic-Isotropic transition temperatures. The earlier mean field model by some of the present authors showed on the contrary, an enhancement. This inadequency of the earlier model has been removed in this paper by explicitly taking into account a variation of McMillan's α parameter from member to member. The phase diagrams for the first seven members of the PAA series and of 4-(4′-*n*-2-(4′-*n*-alkoxy-benzylideneamino) biphenyls are presented which demonstrate the diminution. Further, some results of a model system are presented to bring out the fact that the diminution is actually due to the variation of α. A faster variation of α causing a steeper rise in A-N temperature entails a greater dampening of alternation.

Keywords: Smectic-Nematic transitions, chain molecules

INTRODUCTION

A molecular mean field theory of the even-odd effect in Nematic-Isotropic (N-I) phase transition for non-rigid mesogens taking into account the chain conformations explicitly was first developed by Marcelja.[1]

Marcelja's theory of N-I phase transition was extended to the case of Smectic A-Nematic (A-N) transition by Mukherjee *et al.*[2] However, the alternation in A-N transition temperatures obtained from the latter theory was found to be enhanced as compared to the alternation in N-I transition temperatures. This enhancement is quite contrary to the experimental observations where it is seen that the alternation is very much diminished or in some cases absent. A further attempt was made by including the contribution of the purely translational[3] term of the Kobayashi potential to the McMillan[4] mean field. Alternation in the latter case was smaller but was still much higher than that in the N-I transition. It looked as though a non-steric interaction in a conventional McMillan type model would be inadequate in reproducing the damping of alternation. In the present paper we show that a fast varying layering interaction can, so to say, stretch the alternation out. This

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has been conclusively established in the present work with the help of a model system by changing the steepness of the mean $T_{A\text{-}N}$ vs. n curve (where n is the number of segments in a chain).

THEORY

As in our earlier papers[2,3] we describe the orientation order of the central rigid part and the flexible chains by two different order parameters.

Orientation order parameter for the rigid part can be written as[2]

$$\eta_\alpha = \langle P_2(\cos\theta)\rangle \tag{1}$$

where θ is the angle between the rigid part and the mean field direction.

Orientational order parameter for the chain part is

$$\eta_c = \frac{1.88}{n}\left\langle \sum_{i=1}^{n} P_2(\cos\theta_i)\right\rangle \tag{2}$$

where θ_i is the angle made by the ith C—C bond with the mean field direction; n is the number of segments in the chain; 1.88 is the normalization factor of η_c for the all trans state.

The mixed order parameter[2] for the rigid part is defined as

$$\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle \tag{3}$$

where d is the layer spacing and the z-axis is chosen along the layer normal.

The energy of the rigid part of a molecule in the mean field due to the rigid parts and the chain parts of the rest of the molecules is given by,

$$\begin{aligned} E_a = &-[C_\alpha V_{\alpha\alpha}\{\eta_a + \alpha\sigma\cos(2\pi z/d)\} \\ &+ C_c V_{\alpha c}\{\eta_c + \alpha\sigma\cos(2\pi z/d)\}]P_2(\cos\theta) \end{aligned} \tag{4}$$

and the corresponding energy of the chain is

$$E_c = -(1.88)\sum_{i=1}^{n}[c_c V_{cc}\eta_c + C_\alpha V_{c\alpha}\eta_\alpha]P_2(\cos\theta_i) \tag{5}$$

Here the suffixes a and c stand for the rigid and chain part respectively; C_a and C_c are the corresponding volume fractions. V_{ij}'s are the coupling constants, where the first index refers to the entity (rigid and chain) experiencing the mean field and the latter index refers to the mean field producing entity.

In the earlier model[2] α was kept fixed for all the members and the effect of the addition of chain segments was thought to be taken care of by the volume fractions.

This was a deviation from McMillan's model where α was varied to span a homologous series. There was, however, no way in McMillan's model to assign values of α for individual members. In the present work an explicit way for the assignment of α from member to member is introduced.

From McMillan's theory we get

$$\alpha = 2\exp[-(\pi r_0/d)^2] \tag{6}$$

where r_0 is the length of the rigid part.

It is to be noted that for the sake of simplicity we have included the layering interaction in E_α only and do not define two different mixed order parameters for the rigid and the chain parts.

In the present theory we consider that the layer spacing d is equal to the average length of a molecule. This average length is given by

$$d = r_0 + \langle l_c \rangle \tag{7}$$

where $\langle l_c \rangle$ is the average length of a single chain. This average length has a rather strong temperature dependence due to the change of weightage of different conformations.

In the present work, d is explicity calculated taking into consideration all the possible chain conformations. It has been pointed out in some earlier studies[5,6] that in the application of McMillan model to ordinary smectics, α calculated from $T_{\text{A-N}}$ (using Equation 6) corresponds to a core length usually smaller than the geometrical size of the core i.e., the core length relevant to α is a fraction K_s of r_0, the geometrical length. So, in this model α is modified as[4,5]

$$\alpha = 2\exp[-(\pi r_0 K_s/d)^2] \tag{8}$$

r_0 and K_s are taken as constant for a given homologous series. K_s is determined from the experimental value of the $T_{\text{A-N}}$ of a chosen member of a homologous series and utilized unchanged for other members.

Following Flory[7] the matrix for transforming a vector in the frame attached to the $(i + 1)$th C—C bond to the (i)th C—C bond can be written as

$$T_i = \begin{bmatrix} \cos\delta & \sin\delta\cos\phi_i & \sin\delta\sin\phi_i \\ \sin\delta & -\cos\delta\cos\phi_i & -\cos\delta\sin\phi_i \\ 0 & \sin\phi_i & -\cos\phi_i \end{bmatrix}$$

where π—δ is the bond angle and ϕ is the dihedral angle for the ith chain segment. For trans(t) state $\phi = 0°$ and for the two gauche (g^+, g^-) states, ϕ is equal to $+120°$ and $-120°$, respectively. For a given conformation the component of the unit vector along the $(i + 1)$th C—C bond can be obtained in the rigid core frame by the following transformation

$$\begin{bmatrix} u_{i+1} \\ v_{i+1} \\ w_{i+1} \end{bmatrix} = T_1 \,.\,.\,.\,.\,.\, T_{i-1}\delta T_i \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

u_{i+1} is the projected length of the bond along the molecular axis.

Now, $\langle l_c \rangle$ can be calculated from the self consistent equation

$$\langle l_c \rangle = (1/Z_c) \sum_{\text{all conf.}} \sum_{i=1}^{n} u_i \exp(-U_{\text{int}}/KT) \tag{9a}$$

$$\langle l_i \rangle = m\langle l_c \rangle \tag{9b}$$

where, the interaction energy is

$$U_{\text{int}} = \sum_{i=1}^{n} E(\xi_{i-1}, \xi_i)$$

ξ represents any of the three states, t, g^+, g^- and m is the number of chains attached to the rigid part.

The values of the order parameters at a given temperature T can be obtained by self-consistent solutions of the following equations

$$\eta_a = (1/Z_\alpha) \int_0^1 \int_0^d P_2(\cos\theta)\exp(-E_\alpha/KT)\; d(\cos\theta)\; dz \tag{10a}$$

$$\eta_c = (1.88/n)(1/Z_c) \sum_{\text{all conf.}} \sum_{\substack{\text{initial} \\ \text{orientations}}} \sum_{i=1}^{n} \int_0^d P_2(\cos\theta_i) \cdot \exp\left[-(E_c + U_{\text{int}})/KT\right] dz \tag{10b}$$

$$\sigma = (1/Z_\alpha) \int_0^d \int_0^d P_2(\cos\theta)\cos(2\pi z/d)\exp(-E_a/KT)\; d(\cos\theta)\; dz \tag{10c}$$

Extending Marcelja's[1] calculation to smectic phase the free energy expression was obtained in the following way. The entropy difference per molecule in units of R, between an isotropic phase and a smectic phase is given by (using Equations (4) and (5))

$$\begin{aligned} TS = {} & -C_\alpha V_{\alpha a}(\eta_\alpha^2 + \alpha\sigma^2) - C_c V_{\alpha c}(\eta_\alpha \eta_c + \alpha\sigma^2) \\ & - 2(n-1)[C_c V_{cc}\eta_c^2 + C_\alpha V_{c\alpha}\eta_\alpha\eta_c] + KT \ln Z_\alpha + 2KT \ln (Z_c/Z_c(0)) \end{aligned}$$

where Z_α is the partition function of the rigid part; $Z_c(0)$ is the partition function of the end chain when $E_c = 0$ in Equation (5) i.e., in an isotropic phase; Z_c is the partition function of the end chains when the chain interaction is switched on ($E_c \neq 0$). The multiplying factor 2 in the third and last term indicates that we have considered here two end chains per molecule.

The internal energy consists of two parts. One part is the energy acquired as the rigid parts assume orientational order η_α and smectic order σ. Prior to the 'switching' on of the chain-chain interaction, chains acquire orientational order η_{c0} because the rigid parts, while being oriented towards the director, impart some orientational order to the chains attached to them.[1] Further, as the chain-chain interaction is swtiched on (i.e., $E_c \neq 0$) η_{c0} increases to η_c. This leads to the following expression of internal energy U.

$$\begin{aligned} U = & -\int_0^{\eta_\alpha} C_\alpha V_{\alpha\alpha}\eta \, d\eta - C_c V_{\alpha c}\int_0^{\eta_\alpha} (\eta_{c0}/\eta_\alpha)\eta \, d\eta - C_c V_{\alpha c}\int_0^{\sigma_\alpha} \alpha\sigma \, d\sigma \\ & - C_\alpha V_{\alpha\alpha}\int_0^{\sigma_\alpha} \alpha\sigma \, d\sigma - 2\int_{\eta_{c0}}^{\eta_c} [C_c V_{cc}\eta_c + C_\alpha V_{c\alpha}\eta_\alpha](n-1) \, d\eta_c \\ = & -0.5\, C_\alpha V_{\alpha\alpha}(\eta_\alpha^2 + \alpha\sigma^2) - 0.5\, C_c V_{\alpha c}(\eta_\alpha\eta_{c0} + \alpha\sigma^2) \\ & - 2(n-1)[0.5\, C_c V_{cc}(\eta_c^2 - \eta_{c0}^2) + C_\alpha V_{c\alpha}\eta_\alpha\eta_c - C_c V_{c\alpha}\eta_\alpha\eta_{c0}] \end{aligned}$$

The expression for the free energy is

$$\begin{aligned} F = & \; U - TS \\ = & \; 0.5\, C_\alpha V_{\alpha\alpha}(\eta_\alpha^2 + \alpha\sigma^2) + 0.5\, C_c V_{\alpha c}(2\eta_\alpha\eta_c - \eta_\alpha\eta_{c0} + \alpha\sigma^2) \\ & - KT \ln Z_\alpha + (n-1)C_c V_{cc}(\eta_c^2 + \eta_{c0}^2) + 2(n-1)C_\alpha V_{c\alpha}\eta_\alpha\eta_{c0} \qquad (11) \\ & - 2KT \ln [Z_c/Z_c(0)] \end{aligned}$$

RESULTS AND DISCUSSIONS

For a given temperature the set of self-consistent Equations (9a), (10a)–(10c) are solved iteratively. The stability of a phase is ascertained from the minimum of the free energy (Equation 11). $\eta \neq 0$, $\sigma = 0$ indicate a nematic phase while $\eta \neq 0$, $\sigma \neq 0$ indiate a smectic phase. The calculated values of $T_{\text{N-I}}$ and $T_{\text{A-N}}$ for the first seven members of the PAA series are shown in Figure 1. The values of the coupling constants were obtained from $T_{\text{N-I}}$'s of the first and third members (Reference 2 for details). For Equation (2) we obtained K_s by fitting the $T_{\text{A-N}}$ of the seventh member. The values of r_0 and the length of the one C—C bond were taken as 18.224 and 1.34 Å,[8] respectively. It is evident that if one connects the $T_{\text{A-N}}$'s of the odd members and the even members separately by two smooth curves the

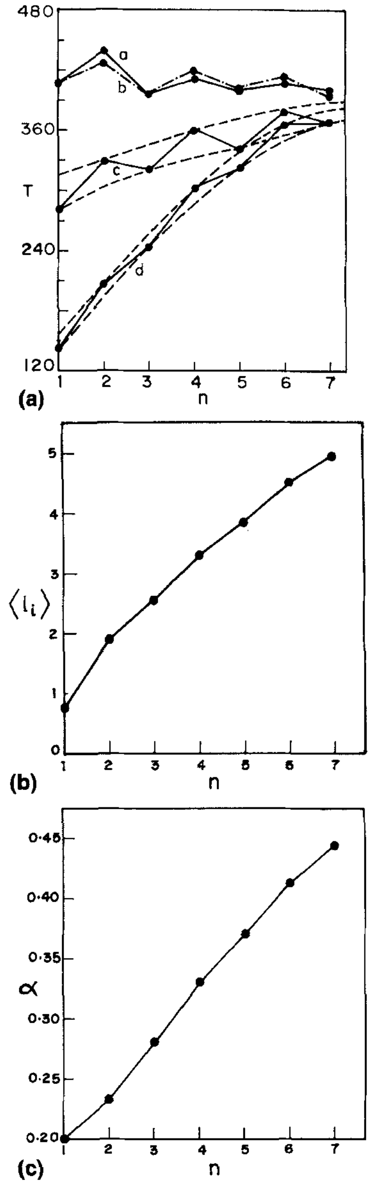

FIGURE 1 (a), PAA series. Solid curves: a. Experimental N-I phase diagram c. theoretical A-N phase diagram,[2] d. A-N phase diagram obtained in the present model. Dotted curve: b. Theoretical N-I phase diagram.[2] Broken curves are obtained by joining the even members or the odd members of the series. (b), $\langle l_i \rangle$ vs. n curve for the PAA series. (c), α vs. n curve for the PAA series.

separation between these two lines is much smaller than the separation obtained in the earlier studies (shown in Figure 1a). This separation may be taken to be a measure of the alternation amplitude which in the present case is considerably reduced. What is more noteworthy is that the present work is the first successful attempt in reproducing a $T_{A\text{-}N}$ alternation smaller than that of $T_{N\text{-}I}$ alternation.

The average chain length $\langle l_i \rangle$ and α at transition temperature of different members are shown in Figure 1b and Figure 1c, respectively.

The above mentioned success, though quite satisfactory raises a question which needs to be resolved. It is by now well established from the earlier works[1-3] that an increase in longitudinal polarizability of molecules increases the N-I transition temperature. In a PAA molecule with polymethylene chain in an all trans-state a C—C bond on each side is sequentially added alternatively along the molecular axis and then along a direction making an angle of 68° with the molecular axis as one ascends the series. This means that for some members (even members in this case) axial polarizability increases more than the odd members. It is however not true that the molecules are in an all trans-state but at small temperatures the all trans-state predominates over the gauche states and as a result the even-members have their axial polarizability increased more than their odd counterparts. As a result we have the even-odd effect. Now, if this be the case it is natural that $T_{\text{A-N}}$'s being lower than $T_{\text{N-I}}$'s we will have this effect enhanced. This is what is reflected in our earlier models. The apparent smoothness of the $T_{\text{A-N}}$ curves as observed in experiments which are also reproduced to a good extent in the present model is therefore to be understood inspite of the contrary possibility discussed above. A careful analysis of the present model led us to believe that an increase in α with addition of C—C bonds introduced in the present model causes a steep rise of A-N temperature while ascending the series. This steep rise stretches the curve which looks smoother. In order to check this conjecture two model systems were considered where one system differed from the other only by the length of the rigid part. The system with the smaller core length had a steeper α-variation as compared to that of the sample with the longer core length. The phase diagrams of both the systems were obtained as shown in Figure 2. It is apparent that the sample with a steeper rise of $T_{\text{A-N}}$ curve has an appreciably smoother $T_{\text{A-N}}$ curve.

It is to be pointed out that in presenting the results for the PAA series we have ignored the fact that the series shows smectic C and not a smectic A phase. For a direct comparison with earlier results we have chosen PAA. We have also considered 4-(4'-*n*-2-(4'-*n*-alkoxy-benzylideneamino) biphenyls which shows smectic A

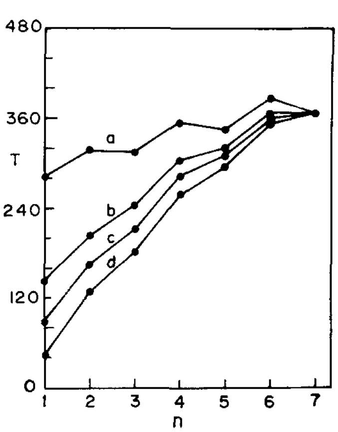

FIGURE 2 A-N phase diagrams for: a. $K_s = 0.4$, b. $K_s = 0.53$, c. $K_s = 0.6$, d. $K_s = 0.7$.

phase. The phase diagrams reproduced for the sample in the earlier model and in the present model are shown in Figure 3a. The present model shows clearly a dimunution of alternation in $T_{A\text{-}N}$ transitions. The average chain lengths and α at $T_{A\text{-}N}$ for each member of the series are shown in Figure 3b and Figure 3c.

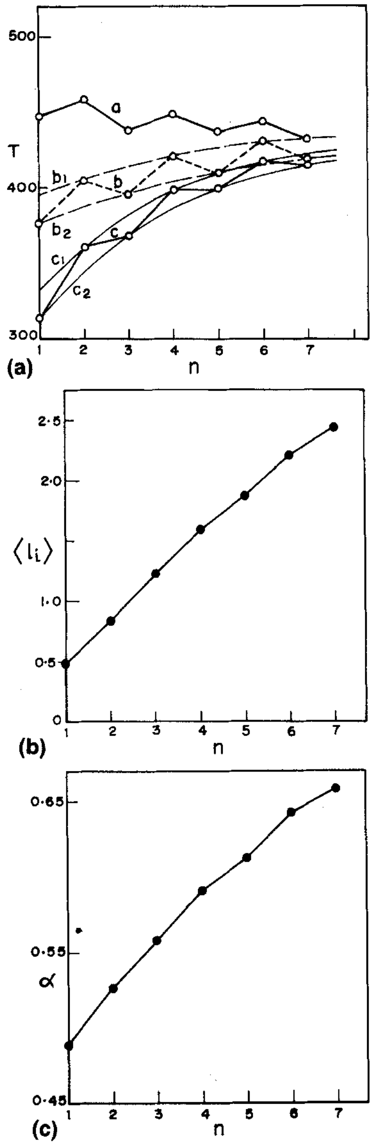

FIGURE 3 (a), 4-(4′-*n*-2-(4′-*n*-alkoxy-benzylideneamino) biphenyls. Solid curves: a. Experimental N-I phase diagrams, c. theoretical A-N phase diagram obtained in the present model, c1. curve obtained by joining the $T_{A\text{-}N}$s of the even members, c2. curve obtained by joining the $T_{A\text{-}N}$s of the odd members. Dotted curves: b. Theoretical A-N phase diagram,[2] b1. curves obtained by joining the $T_{A\text{-}N}$ *s* of the even members of the series, b2. curves obtained by joining the $T_{A\text{-}N}$ *s* of the odd members of the series. (b), $\langle l_i \rangle$ vs. *n* curve for the 4-(4′-*n*-2-4′-*n*-alkoxy-benzylideneamino) biphenyls. (c), α vs. *n* curve for the 4-(4′-*n*-4′-*n*-alkoxy-benzylideneamino) biphenyls.

CONCLUSION

With a simple modification of the earlier model by incorporating an explicit variation of α from member to member for the PAA series and 4-(4'-*n*-2-(4'-*n*-alkoxy-benzylideneamino) biphenyls we could reproduce the observed dampening of alternation of transition temperature in smectic A-nematic temperatures. It has also been shown with the help of model systems that the variation of α is indeed responsible for the smoothness of the $T_{\text{A-N}}$ curve. A check with some experimental phase diagrams corroborate our conclusion. It is seen that systems with steeper $T_{\text{A-N}}$ vs n curves seem to have the curve smoother as compared to the case of systems with comparatively flatter $T_{\text{A-N}}$ vs n curve. The mesogens 2-(4'-*n*-alkoxy-benzylideneamino) fluorenones[9] and 4-(4'-*n*-2-(4'-*n*-alkoxy-benzylideneamino) biphenyls[9] are examples of the former class while *n*-alkyl 4-(-*p*-methoxybenzylideneamino) cinamates[9] and *n*-alkyl 4-(-*p*-phenylbenzylideneamino) cinamates are of the latter category.

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