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On the Even Odd Effect in Smectic-Nematic Transitions†

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An extension of an earlier work by the present authors on the even-odd effect in smectic A-nematic (S-N) transition is presented. The earlier model showed too large an alternation in T_{SN}. In the present work the mean field is modified by including the contribution from the orientation independent term of the Kobayashi pair potential. Numerical calculations on three homologous series with alkyl chains, namely 4-(4′-n-alkoxybenzylideneamino) biphenyls, (p′-n-alkoxybenzoyloxy) acetophenones and PAA show a marked diminution in alternation of T_{SN}. The present mean field, though a definite improvement over the earlier one, is still found to be inadequate quantitatively, especially for samples with very small or virtually nonexistent alternation in T_{SN}. It seems that a purely attractive pair potential may not be adequate in explaining this aspect of S-N transition. A possible role of repulsive interaction in suppressing this 'even-odd' amplitude is discussed.

INTRODUCTION

In an earlier work,[1] the present authors extended Marcelja's[2] model to S-N transitions in order to treat individual members of a homologous series in both smectic and nematic phases. Taking into account the chain conformations explicitly the T_{SN}'s and T_{NI}'s of the first seven members of the two series namely PAA[1] and 4-(4′-n-Alkoxy Benzylideneamino) biphenyls[3] were calculated. For the latter series the transition entropies were also calculated for individual members

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so as to test whether the transition is a first order transition or a second order one. One shortcoming of the model, as mentioned in reference 3, is that the calculated alternation in T_{SN} were found to be large contrary to experimental observations. In each case the alternation in T_{SN} was larger than the alternation in T_{NI} while experiments show a general damping of alternation in T_{SN}. In the present work we have modified the earlier mean field by incorporating the contribution from the orientation independent part of the Kobayashi potential and calculated the T_{NI}'s and T_{SN}'s for the first few members of three homologous series, namely, 4-4′-n-alkoxy benzylideneamino) biphenyls,[4] p-(p′-n-alkoxybenzoyloxy) acetophenones[5] and PAA.[6] A comparison with the earlier model shows a marked diminution of alternation in T_{SN}.

METHOD

Following reference 1 we consider the mean field experienced by a molecule to be consisting of two parts—one for the rigid cores and the other for the end chains. A straightforward generalization of the mean field of reference 1, taking into account the contribution from the orientation-independent term of the Kobayashi two particle potential $V_{12}(r) = U(r) + W(r)P_2(\cos\theta_{12})$ gives the energy E_a of the rigid part as

$$E_a = -[(C_a(N)V_{aa}(\eta_a + \alpha\sigma\cos(2\pi z/d)) + C_c(N)V_{ac}(\eta_c + \alpha\sigma\cos(2\pi z/d)))P_2(\cos\theta) + \delta\alpha(C_a(N)V_{aa} + C_c(N)V_{ac})\tau\cos(2\pi z/d)] \quad (1)$$

The term involving τ (McMillan layering order parameter) comes from the orientation-independent term U(r). This is exactly similar to the inclusion of this contribution in McMillan's mean field for the smectic A phase.[7] The suffixes '*a*' and '*c*' have been introduced to denote entities pertaining to the rigid and the chain parts respectively.

As in the earlier works,[1,3] we neglect, for simplicity, the terms involving smectic order parameters in the energy E_c of the chain and can write

$$E_c = -(1.88/N)[C_c(N)V_{cc}\eta_c + C_a(N)V_{ca}\eta_a]\sum_{i=1}^{N} P_2(\cos\theta_i) \quad (2)$$

In the above expressions $C_a(N)$ and $C_c(N)$ are the respective volume fractions of the rigid parts and the chains with N carbon atoms; V_{aa}, V_{ac}, V_{cc} and V_{ca} are the coupling constants to be determined as in reference (1). The parameter δ is the relative coupling strength of the orientation independent and orientation dependent terms in the Kobayashi potential. As explained in reference 1, the parameter α, though reminiscent of McMillan's 'length parameter,' has been introduced mainly on a phenomenological basis. In McMillan's work this α is related to the Fourier transform of the radial part of the intermolecular interaction and varies from one member to the other while in the present case we keep it fixed for all members and addition of chain segments is taken care of by volume fractions. The order parameters η_a, η_c, σ and τ can be obtained from the self consistent solution of the following equations.

$$\eta_a = \frac{1}{Z_a}\int_0^1\int_0^d P_2(\cos\theta)\exp[-E_a/kT]d(\cos\theta)dz \tag{3a}$$

$$\eta_c = \frac{1.88}{Z_c}\sum_{\substack{all\\conf.}}\sum_{\substack{initial\\orient}}\sum_{i=1}^{N}\int_0^d P_2(\cos\theta_i)\exp[-(E_c + V_{int})/kT]dz \tag{3b}$$

$$\sigma = \frac{1}{Z_a}\int_0^1\int_0^d P_2(\cos\theta)\cos(2\pi z/d)\exp[-E_a/kT]d(\cos\theta)dz \tag{3c}$$

$$\tau = \frac{1}{Z_a}\int_0^1\int_0^d \cos(2\pi z/d)\exp[-E_a/kT]d(\cos\theta)dz \tag{3d}$$

Z_a and Z_c are the partition functions corresponding to the rigid part and the chain part respectively. V^1_{int} is the conformation energy of a chain.

Out of the six parameters V_{aa}, V_{ac}, V_{ca}, V_{cc}, α and τ the first four are determined, as in reference,[1] by using T_{NI}'s while the last two are fixed by fitting T_{SN}'s of the first two members of the homologues for which experimental data are available. With all the parameters thus fixed the T_{NI}'s and T_{SN}'s are evaluated for the first seven members of the three series mentioned earlier. The free energy expression

for identifying a stable solution is given by

$$F = -kT \ln (Z_a) + C_a(N)V_{aa}[\eta_a^2 + \alpha\sigma^2 + \delta\alpha\tau^2]/2$$
$$+ C_c(N)V_{ac}[\eta_a(2\eta_c - \eta_{co}) + \alpha\sigma^2 + \delta\alpha\tau^2]/2$$
$$+ (N\text{-}1)N_c[C_a(N)V_{ca}\eta_a\eta_{co} + C_c(N)V_{cc}(\eta_c^2 + \eta_{co}^2)/2]$$
$$- N_c\, kT \ln [Z_c/Z_c(o)] \qquad (4)$$

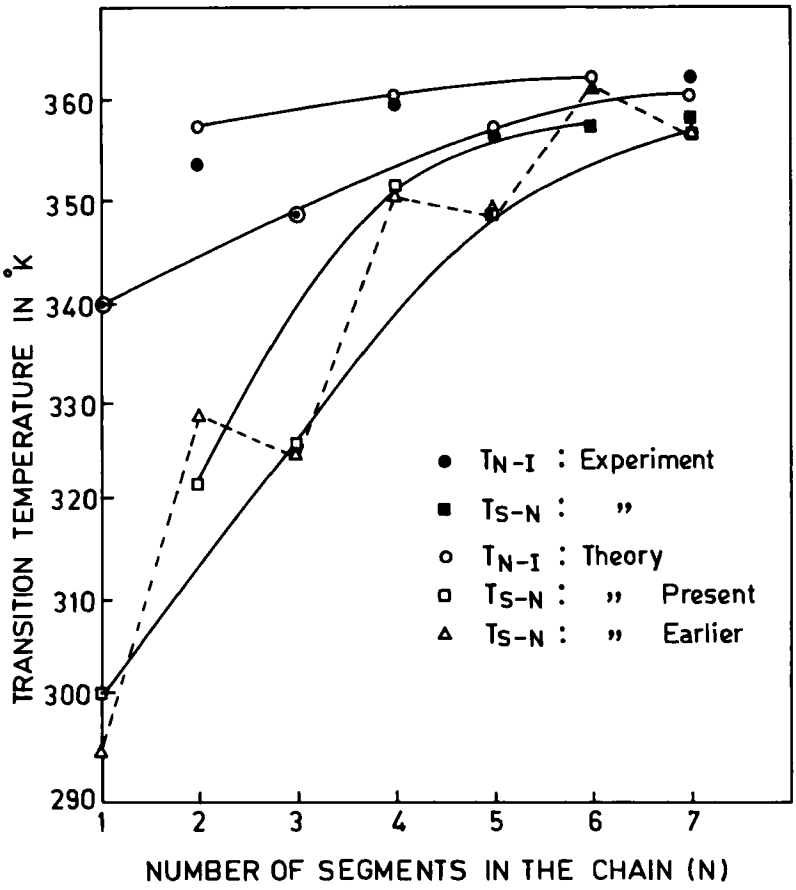

FIGURE 1 Variation of transition temperature in the homologous series of p-(p'-n-alkoxybenzoyloxy) acetophenones. Earlier theory $\alpha = 0.73$; Present theory $\alpha = 0.25$, $\delta = 1.05$.

where N and N_c are the number of the segments in the chain and the number of chains in the molecule respectively, η_{co} signifies chain ordering for a noninteracting chain due to the ordering of the rigid part from zero to η_a and $Z_c(o)$ is the corresponding partition function for the end chains.

RESULTS

Figure 1 shows the calculated transition temperatures (both T_{NI}'s and T_{SN}'s) for the first seven members of the series p-(p'-n-alkoxybenzoyloxy) acetophenones. Transition temperatures of the odd and the even members are joined by smooth curves. The fitted values of V_{aa} = 3066.0 cal/mole, V_{ac} = 7663.5 cal/mole, V_{ca} = 450.0 cal/mole and V_{cc} has been taken to be = 680.0 cal/mole. α and δ obtained by fitting T_{SN}'s of the fifth and the sixth members are 0.25 and 1.05 respectively. The calculated T_{SN} for the seventh member is seen to be about 2°K below the experimental value. For comparison the results of the earlier model are also shown. It is evident that alternation is somewhat reduced.

The calculated transition temperatures of the series 4-(4'-n-alkoxybenzylideneamino) biphenyls are shown in Figure 2. The fitted values of V_{aa} = 4030.0 cal/mole, V_{ac} = 7980.0 cal/mole, V_{ca} = 575.8 cal/mole, α = 0.15 and δ = 1.82. The alternation in T_{SN} is considerably reduced compared to the results of the earlier model. It is to be noted that the experimental T_{SN}'s of the different members fall on a single smooth line irrespective of odd or even members. The complete absence of alternation is however not reproduced in this model.

Figure 3 shows similar results for PAA series. The values of the constants for this series are V_{aa} = 3680.0 cal/mole, V_{ac} = 7992.0 cal/mole, V_{ca} = 540.0 cal/mole, α = 0.2 and δ = 0.83. Because of the fact that the seventh member is actually the smallest member of the series for which T_{SN} has been measured experimentally, we did not fix α and δ for this series. To fix them we would have to consider the eighth member but only at the cost of as much as three times the computation time for the seventh member. Only to test the influence of the orientation independent term we calculated transition temperatures with several pairs of values of α and δ. A typical set of results are shown in Figure 3 indicating clearly that the present model can successfully account for at least a part of the diminution of 'even-odd' effect in S-N transition.

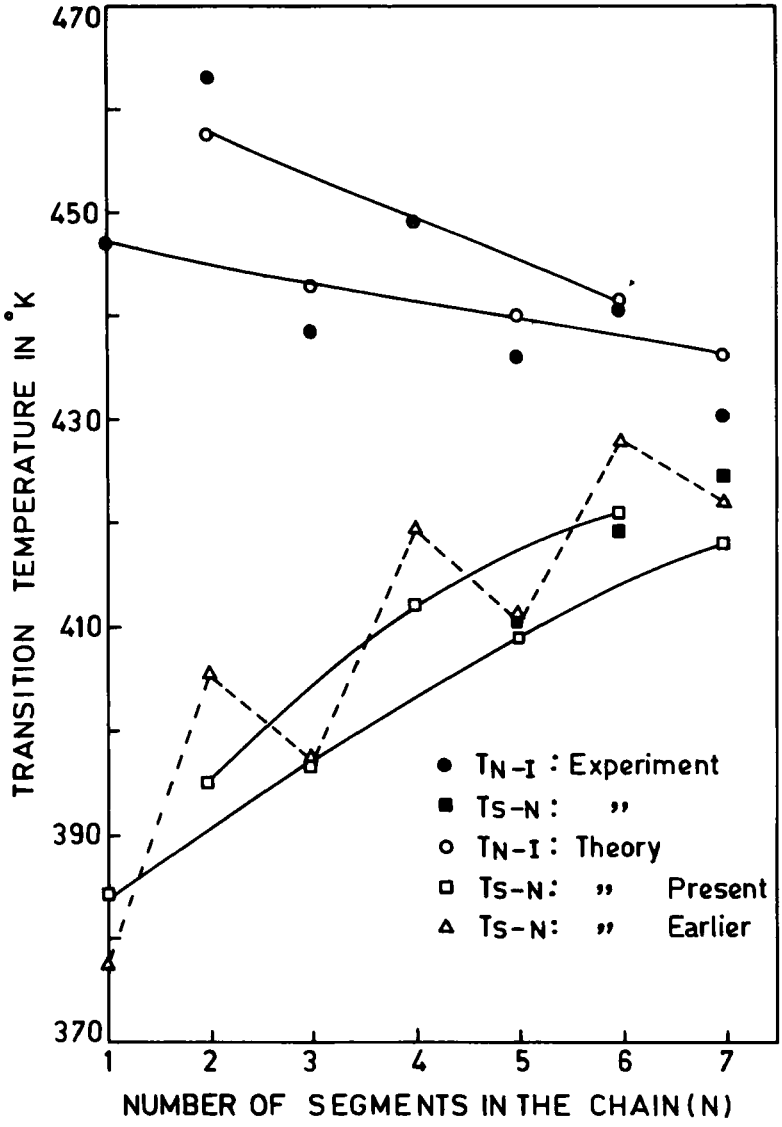

FIGURE 2 Variation of transition temperature in the homologous series of 4-(4′-n-alkoxybenzylideneamino) biphenyls. Earlier theory $\alpha = 0.66$; Present theory $\alpha = 0.15$, $\delta = 1.82$.

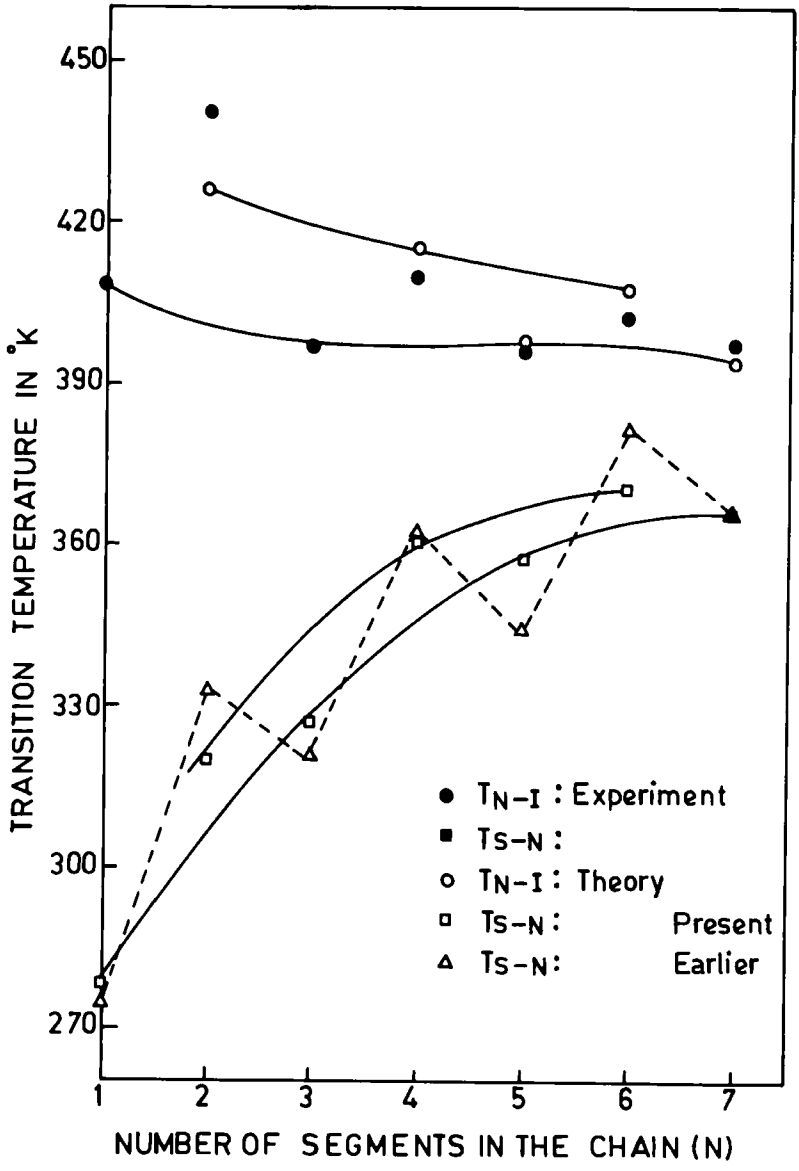

FIGURE 3 Variation of transition temperature in the homologous series of PAA. Earlier theory $\alpha = 0.45$; Present theory $\alpha = 0.2$, $\delta = 0.83$.

CONCLUSION

In Marcelja's model[2] for molecules with alkyl chains, successive C—C bonds contribute differently to the axial polarizability as the dihedral angle between them is about 68°. This is in fact the cause of alternation in T_{NI}'s. In our extension[1] of Marcelja's work to the smectic phase the alternation in T_{SN}'s arises because of the same reason. The mean field in that work contains contributions from the orientation dependent part only of the Kobayashi potential. The phase transition temperatures (T_{SN}'s) thus had a near total dependence on orientation ordering. The T_{SN}'s being lower than the T_{NI}'s, the chains have a greater probability of being in an all-trans state in the smectic phase. The difference in contributions to the axial polarizability by the successive C—C bonds is therefore enhanced in smectic phase. This naturally gave rise to a larger alternation in T_{SN}. The present model incorporates a part of the pair interaction which is orientation independent. This in a sense frees the S-N transition from the total dependence on orientation. This is manifested in the marked reduction of even-odd effect in the calculated S-N transition temperatures. This diminution has been obtained in the new model for all the three series studied. It is generally observed in experiments that the 'even-odd' effect in the S-N transition is less pronounced compared to the N-I transition. In this respect the present generalization shows a better agreement with experiments. It should however be pointed out that for samples with steeply rising T_{SN} with N the alternation in T_{SN} is experimentally observed to be quite small and in certain cases e.g., sample 4-(4′-n-alkoxybenzylideneamino) biphenyls it is altogether absent.[4] This complete absence of 'even-odd' effect was not reproduced in the present model. It seems that a purely attractive pair potential of the Kobayashi type may not be adequate in explaining this aspect of S-N transition. A possible role of 'Steric intermolecular interactions' (repulsive forces) in suppressing the alternation in T_{SN} is being investigated. As the molecules are packed in a layer in the smectic phase there is considerable lateral steric repulsion between the molecules.[8] It is quite likely that those conformations for which the chain segments deviate much from the molecular axis (defined by the central line through the rigid part) are suppressed due to the lateral repulsion by the neighboring molecules. A similar idea has been utilized in the 'Kink' model for membranes[9] where it is argued that the conformations which tend to preserve the linearity of the chain are only allowed. Once this restriction of linearity is imposed on the conformations the successsive members of a homologous series will

contribute similarly to the axial polarizability and hence a suppression of alternation in T_{SN} should result. The details and results of such a calculation will be published in a separate paper.

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