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Chain Ordering and Sm–N Transition in Different Members of the Homologous Series 4-(4′-*n*-Alkoxy Benzylideneamino) Biphenyls

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Our extension of Marcelja's theory of nematic-isotropic transition to the smectic A phase is used to calculate the smectic A–nematic (Sm–N) transition temperatures for the homologous series 4-(4′-*n*-alkoxy benzylideneamino) biphenyls. In a mean field calculation, explicit inclusion of the conformational energies of the alkyl chain of a molecule in the partition function shows an even-odd effect generally observed in experiments on Sm–N transitions. It is found that the members of this series showing the smectic phase will have first order Sm–N transitions and the transition entropies for individual members are calculated.

Recently we[1] have been able to extend McMillan's[2] theory of the smectic A phase in such a way so as to incorporate the effects of the end chain conformation. This extension has enabled us to study thermodynamic properties of individual members of a homologous series in the smectic phase along with its phase diagram. This method has also made it possible for us to obtain for the first time the even-odd effect as is generally observed in Sm–N transitions. In reference 1 we have studied the oft used series of PAA where we have

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obtained a second order Sm–N transition, as is actually observed in experiments.

In the present paper we have chosen the homologous series 4-(4′-*n*-alkoxy benzylideneamino) biphenyls[3] for the following reasons. First, unlike the PAA series this series has alkyl chains only at one end of the rigid part of the molecule. Secondly, the ratio T_{SN}/T_{NI} for this series is greater than 0.88 and this according to both McMillan[2] and Lee *et al.*,[4] should produce first order Sm–N transition. Our purpose is to test whether in our model the Sm–N transitions are first or second order for each member of the homologous series.

Computations for the homologous series 4-(4′-*n*-alkoxy benzylideneamino) biphenyls indeed show first order Sm–N transitions for the experimentally observed smectic phases and ΔS_{SN}, the change in entropy at the Sm–N transitions, increases very rapidly with N, the number of segments in the end chain. We also obtain an even-odd effect in Sm–N transitions, (though this has not yet been experimentally detected in this particular series) and the general features of a phase diagram, viz., a gradual rise in T_{SN} with N is well reproduced. A plot of ΔS_{SN} against T_{SN}/T_{NI} shows that the results compare very favourably with those of McMillan[2] and of Lee[4] *et al.*

METHOD

In order to include the effects of conformational energies of the alkyl end chains in our calculation, we follow reference (1), and for simplicity start with a Kobyashi type intermolecular potential without its short range central force term. This is sufficient to ensure the formation of a smectic phase. We can easily generalize this interaction to more complex cases.

We now write down the energy of the rigid and the chain parts of a molecule in the mean field of other molecules.

Energy of the rigid part is written as

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

For a chain segment in a particular conformation of the chain

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

In the above expressions $C_a(N)$ and $C_c(N)$ are respective volume fractions of the rigid parts and the chains, V_{aa}, V_{ac}, V_{cc} and V_{ca} are the coupling constants which are determined as in reference (1) and also in Marcelja's work[5] on N–I transitions, η_a, η_c and σ are the order parameters obtained by self consistent solutions of the equations,

$$\eta_a = \langle P_2(\cos\theta)\rangle \qquad \text{(for the rigid parts)}$$

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

$$\eta_c = \frac{1.88}{N}\left\langle \sum_{i=1}^{N} P_2(\cos\theta i)\right\rangle \qquad \text{(for the chain part)}$$

$$= \frac{1.88}{Z_c}\sum_{\substack{\text{all initial}\\ \text{Conf. orient}}}\!\!\sum\ \sum_{i=1}^{N}\int_0^d P_2(\cos\theta i)\exp[-(E_c + V_{\text{int}})/KT]\,dz \tag{3b}$$

and

$$\sigma = \left\langle P_2(\cos\theta)\cos\frac{2\pi z}{d}\right\rangle \qquad \text{(a mixed order parameter)}$$

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

which couples the translational order to the orientational order. Z_a and Z_c are the corresponding partition functions. U_{int} in equation (3b) is the conformation internal energy of a chain. The parameter α has been introduced to make the layering interaction strength different from that of the orientational interaction, namely, V_{aa}, V_{ac}, etc. The value of α is obtained by fitting with experimental data and is kept fixed for all members in a homologous series. Addition of chain segments is taken care of by volume fractions.

Now we have five parameters V_{aa}, V_{cc}, V_{ac}, V_{ca} and α to be fixed. For $\sigma = 0$, the mesophase is nematic, and only the four parameters V's are relevant in the nematic phase. These are determined following the procedures given in reference (1). The values of the four parameters are $V_{aa} = 4030.0$ Cal/mole, $V_{ac} = 7980.6$ Cal/mole, $V_{cc} = 680.0$ Cal/mole and $V_{ca} = 575.8$ Cal/mole.

The remaining parameter α was fixed ($\alpha = 0.66$) from the S–N transition temperature of the fifth member of the homologous series 4-(4′-*n*-alkoxy benzylideneamino) biphenyls.

With all the five parameters thus fixed we evaluate the T_{SN}'s and T_{NI}'s for all the members. For each temperature self consistent solutions of the order parameters are found and the free energy evaluated using the expression,

$$\begin{aligned} F_s = \tfrac{1}{2}\big[&C_a(N)V_{aa}\big(\eta_a^2 + \alpha\sigma^2\big) + C_c(N)V_{ac}\big(2\eta_a\eta_c \\ &-\eta_a\eta_{c0} + \alpha\sigma^2\big) + (N-2)C_c(N)V_{cc}\big(\eta_c^2 + \eta_{c0}^2\big) \\ &+2(N-1)C_a(N)V_{ca}\eta_a\eta_{c0}\big] - KT\ln\big[Z_aZ_c/Z_c(0)\big] \end{aligned} \quad (4)$$

Comparing the free energies we obtain the S–N and N–I temperatures.

RESULTS

The results are shown in Figures (1) and (2). The $T_{\rm NI}$'s shown in Figure (1) are only slightly different from an exact Marcelja[5] type calculation because of a slight difference in the treatment of the initial chain segment as explained in reference (1).

It is found that the $T_{\rm SN}$'s of even members lie on a smooth curve well above a similar curve for odd members (Figure 1). Alternations in $T_{\rm SN}$ is in the same sense as in $T_{\rm NI}$. It is evident that for the first four members $T_{\rm SN}$'s lie below the solidification temperature and therefore no smectic phase is observed. It is also to be noted that the generally observed feature of a phase diagram of a homologous series, namely, a gradual rise in $T_{\rm SN}$ with N (the number of carbon atoms in the end chain) is well reproduced in our result. Though in this particular homologous series no even-odd effect has yet been detected (so far as we know) our Marcelja type calculation shows such an alternation, though the points oscillate roughly equally about the mean points observed experimentally.

At present we are looking into the matter of this rather large oscillation in $T_{\rm SN}$'s. Preliminary calculations show that if the orientation independent term in the Kobayashi two particle interaction ($V_{12}(r) = u(r) + W(r)P_2(\cos_{12})$) is taken into consideration the oscillation is considerably suppressed. The equation (1) is then modified as

$$\begin{aligned} E_a = -\Big[&\Big\{C_a(N)V_{aa}\Big(\eta_a + \alpha\sigma\cos\frac{2\pi z}{d}\Big) + C_c(N) \\ &\times V_{ac}\Big(\eta_c + \alpha\sigma\cos\frac{2\pi z}{d}\Big)\Big\}P_2(\cos\theta) \\ &+\delta\alpha(C_a(N)V_{aa} + C_c(N)V_{ac})\tau\cos\frac{2\pi z}{d}\Big] \end{aligned}$$

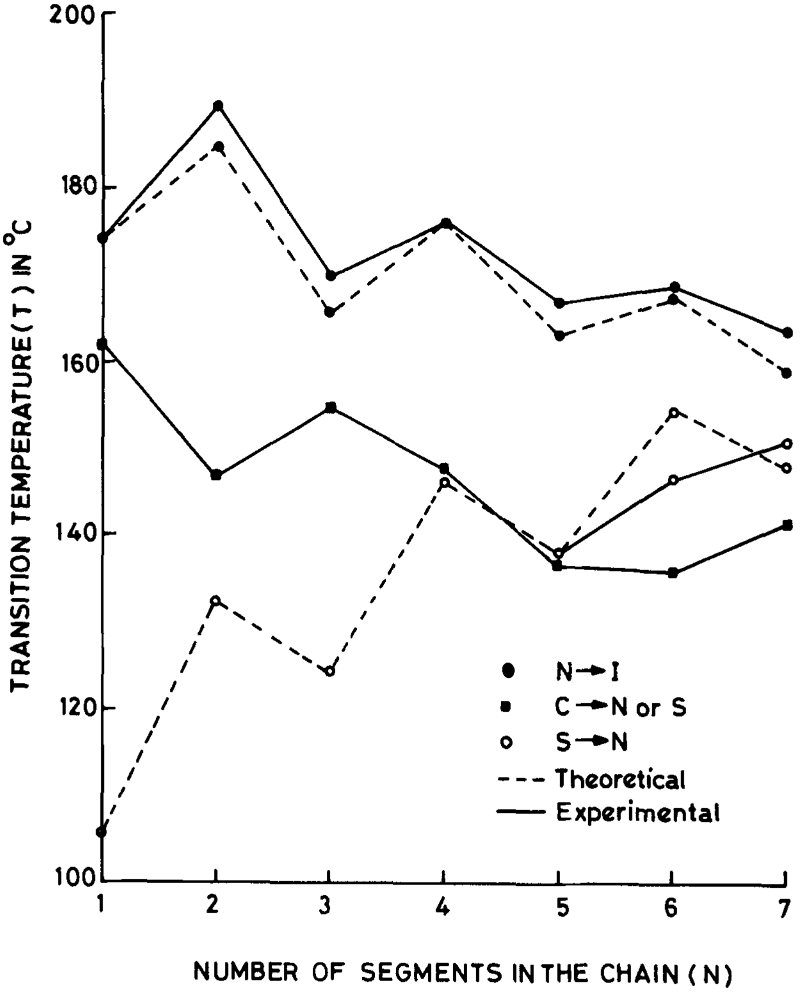

FIGURE 1 Transition temperatures are plotted against the number of segments in the chain for the first seven members of the homologous series 4-(4′-*n*-alkoxy benzylideneamino) biphenyls.

where τ is $\langle\cos(2\pi z/d)\rangle$, the layering order parameter (as in McMillan's work[2]) and δ is a parameter which gives the relative coupling strength of the orientation independent and orientation dependent terms in the Kobayashi potential. The details of the calculation and results will be published in a separate paper.

A plot of ΔS_{SN} against T_{SN}/T_{NI} (Figure 2b) shows that the results compare very favourably with those of McMillan and of Lee *et al.*

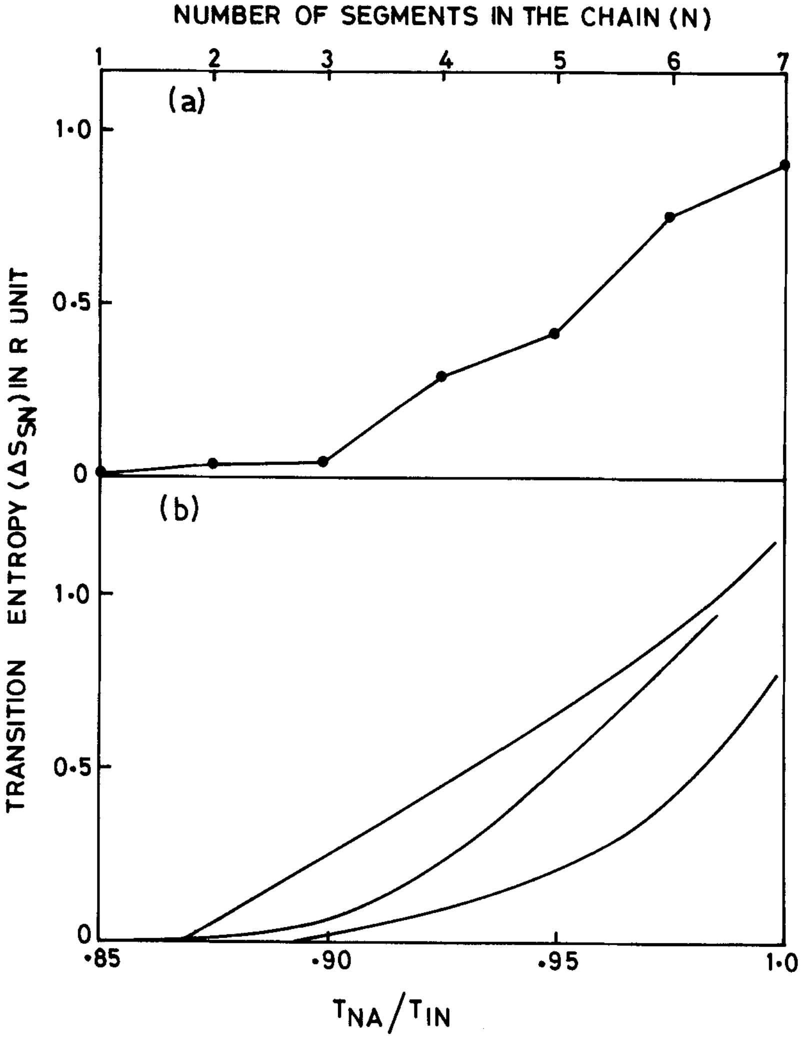

FIGURE 2 (a) Smectic A–nematic transition entropy versus the number of segments in the end chain. (b) Smectic A–nematic transition entropy versus ratio of transition temperatures T_{SN}/T_{NI}. Upper curve–McMillan, middle curve–present work, lower curve–Lee *et al.*

Figure 2(a) shows that up to $N = 3$, $\Delta S_{SN} < 0.1$ and from $N = 4$, ΔS_{SN} increases very rapidly. Since the first member which shows the smectic phase is $N = 5$, all the experimentally observed members of this series will have first order S–N transitions. It will be of interest to know whether these results are confirmed experimentally.

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References

1. C. D. Mukherjee, B. Bagchi, T. R. Bose, D. Ghosh, M. K. Roy and M. Saha, *Phys. Lett.*, **A92**, 403 (1982).
2. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971), ibid. **A6**, 936 (1972).
3. G. W. Gray, Advances in Liquid Crystals Vol. 2, (Edited by G. H. Brown, Academic press, New York, 1976).
4. F. T. Lee, H. T. Tan, Y. M. Shis and C. W. Woom, *Phys. Rev. Lett.*, **31**, 1117 (1973).
5. S. Marcelja, *J. Chem. Phys.*, **10**, 3599 (1974).