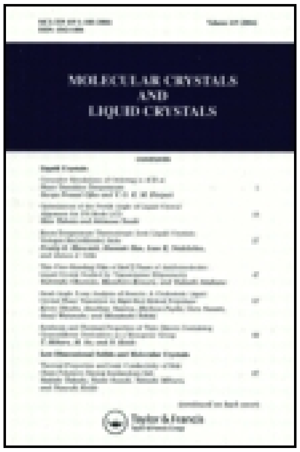

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Even-Odd Effect in Nematic Isotropic Transitions of Liquid Crystals Composed of Molecules with Terminal Phenyl Rings

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Even-Odd Effect in Nematic Isotropic Transitions of Liquid Crystals Composed of Molecules with Terminal Phenyl Rings

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The unusually pronounced even-odd effect in nematic isotropic transitions observed in liquid crystalline compounds with terminal phenyl ring is reproduced in a mean field model. Calculations are presented for the first five members of ω-phenylalkyl 4-(-*p*-cyanobenzylideneamino) cinnamates. The conformational and dispersion energies for the rigid part and the terminal ring of a molecule in the field of other molecules are considered but the aliphatic chain anisotropic interaction is neglected for simplicity. The chain conformations, however, directly influence the relative configuration of the central rigid part and the terminal ring and as a result the longitudinal polarizability of the molecules changes.

Keywords: even-odd effect, terminal phenyl ring, mean-field theory

Thermotropic liquid crystals are often formed by linking a central mesogenic unit composed of benzene rings to flexible chain parts, which are normally alkyl chains, attached directly to the rigid part

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or via an oxygen atom. Each alkyl or alkoxy chain is made up of N segments where N is the number of carbon atoms in the chain. The liquid crystalline properties of such a homologous series are found to depend critically on the number of carbon atoms in the chain. For example, there is an even-odd alternation of the nematic isotropic transition temperature within a homologous series and also a decrease in the magnitude of alternation when the series is ascended. There are, however, certain samples,[1,2] having bulky ester phenyls at the end of the alkyl chains, for which this even-odd effect is unusually large. In a few cases this extremely large even-odd effect can even give rise to an alternation in phase type[1] as one ascends such a homologous series. Here we describe a simple model to calculate the phase diagram for such a homologous series where the nematogens are composed of flexible molecules with large terminal benzene ring.

Marcelja[3] developed a theory for non-rigid mesogens in the molecular mean field approximation. He gave a realistic treatment of the role of the flexible alkyl end chain in a molecule which quite successfully generates the even-odd effect commonly observed. Unlike the samples treated by Marcelja which had a rigid part and a flexible chain the molecules being considered here are made up of three components, viz., the rigid core, the chain and the terminal benzene ring (henceforth called the 'bob'). The two ends of a flexible hydrocarbon alkyl chain is attached to the rigid segment and the bob. In the present model, we assume, for the sake of simplicity, that the chain part interacts weakly as compared to the other two parts. The present sample can thus be treated as a 'two component' system as was done by Marcelja. There is however an important difference. For evaluating the orientation order of the chain part, Marcelja does not consider all possible orientations of the chains with respect to the mean field. In his self consistent calculation, the rigid part order parameter is first calculated in one interaction. Three discrete directions, which simulate the order parameter, are then selected. The order parameter of the chain part is calculated by placing the chains at the end of the rigid part only along the above mentioned three directions and taking into account all the possible chain conformations. This crude approximation is justified because of the smallness of contribution by the chains to the mean field. In the present case the 'bob' part cannot be assumed to play such a subservient role as the bobs presumably interact quite strongly with the neighbouring molecules. In a recent work Luckhurst[4] considered all orientations as well as all conformations of the chain part and reproduced the even-odd effect for samples with a rigid part and alkyl chains at the ends. A method similar to Luckhurst's but with a further modification to include the rotation of a molecule around its own axis (chosen along the rigid part) has been adopted in our present work.

With the simplifying assumption mentioned earlier (neglecting the chain interaction) the system can be considered to be composed of molecules with two parts interacting with all other similar molecules via a Maier–Saupe dispersion force. The dispersion energy of a molecule in a particular conformation can be written as,

$$E_{\text{dis}} = -[X_a P_2(\cos\theta_a) + X_b P_2(\cos\theta_b(\phi))] \tag{1}$$

where the subscripts 'a' and 'b' stand for rigid and bob components of the molecule respectively and the angles θ_a and θ_b are the respective spherical polar angles between a component and the direction of the field. X_a and X_b are the interaction strength parameters. The angle ϕ refers to the angle of rotation of the bob about the rigid part. When the mesophase contains a mixture of different rod like molecules then the molecular field experienced by one molecule will depend both on the order parameter of the other species as well as the strengths of the anisotropic interactions and the composition. So by analogy with the rigorous result for multicomponent mixtures[3,5] the strength parameters are given by,

$$X_a = V_{aa} C_a(N)\, V_a^{-1} \eta_a + V_{ab} C_b(N)\, V_b^{-1} \eta_b \tag{2a}$$

$$X_b = V_{ab} C_a(N)\, V_a^{-1} \eta_a + V_{bb} C_b(N)\, V_b^{-1} \eta_b \tag{2b}$$

where $C_a(N)$ and $C_b(N)$ are the corresponding volume fractions of the Nth member of the homologous series and V_a, V_b are the molecular volumes of the two basic components. The values of these quantities are available from tabulation. V_{aa}, V_{bb} and V_{ab} are the coupling constants which result from core–core, bob–bob and core–bob or bob–core interaction respectively. These three are unknown quantities. But according to Berthelot's combining rule[5] for the binary mixtures of nematogenic molecules we have,

$$V_{ab} = (V_{aa} \times V_{bb})^{1/2}$$

Therefore only two of them remain as adjustable parameters which are fixed from the nematic isotropic transition temperatures of two members of the homologous series. Using the above relation, the ratio of the strength parameters, X_a/X_b, reduces to $(V_{aa}/V_{bb})^{1/2}$

and so it is independent of the temperature and the number of the members in the homologous series. So this ratio is constant for a homologous series.

The order parameters of the two components at a particular temperature, T, are obtained as a solution of the self-consistent equations,

$$\eta_a = \frac{1}{z} \sum_{\substack{\text{all}\\\text{conf}}} \int_0^{2\pi} \int_0^1 P_2(\cos\theta_a) \exp[-(E_{\text{dis}} + E_{\text{con}})/\text{KT}]\, d(\cos\theta)\, d\phi \tag{3a}$$

$$\eta_b = \frac{1}{z} \sum_{\substack{\text{all}\\\text{conf}}} \int_0^{2\pi} \int_0^1 P_2(\cos\theta_b(\phi)) \exp[-(E_{\text{dis}} + E_{\text{con}})/\text{kT}]\, d(\cos\theta)\, d\phi \tag{3b}$$

where E_{con} is the conformational internal energy of the molecule and z is the partition function.

Now we have to find θ_b and E_{con} for each of the possible conformations. The conformations are generated using internal angles and the corresponding orientations with the lab-frame are calculated for a given ϕ. For this we have adopted the convention of Flory which is stated clearly in Reference 6. The summation over the three discrete directions (cf Ref. 6) have been replaced by the continuous distribution of the rigid part. So a full self-consistency would require the summation in the order parameter equations to extend, with the proper weight factor, over all possible orientations of the molecules. For each temperature, the self-consistent solution of the order parameters are found and the Helmholtz free energy per particle for identifying a stable solution is given by,

$$F = (X_a\eta_a + X_b\eta_b)/2 - \text{kT}\ln(Z/Z_I) \tag{4}$$

where Z_I is the partition function in the isotropic phase which is obtained by setting the anisotropic part of the interaction equal to zero.

The calculated nematic isotropic transition temperatures of the homologous series of ω-phenylalkyl (4-*p*-cyanobenzylideneamino) cinnamates are compared with the experimentally observed values in Figure 1. The estimated volumes of the rigid and bob parts are 413.9A^3 and 108.5A^3 respectively together with the volume value of 27A^3 for

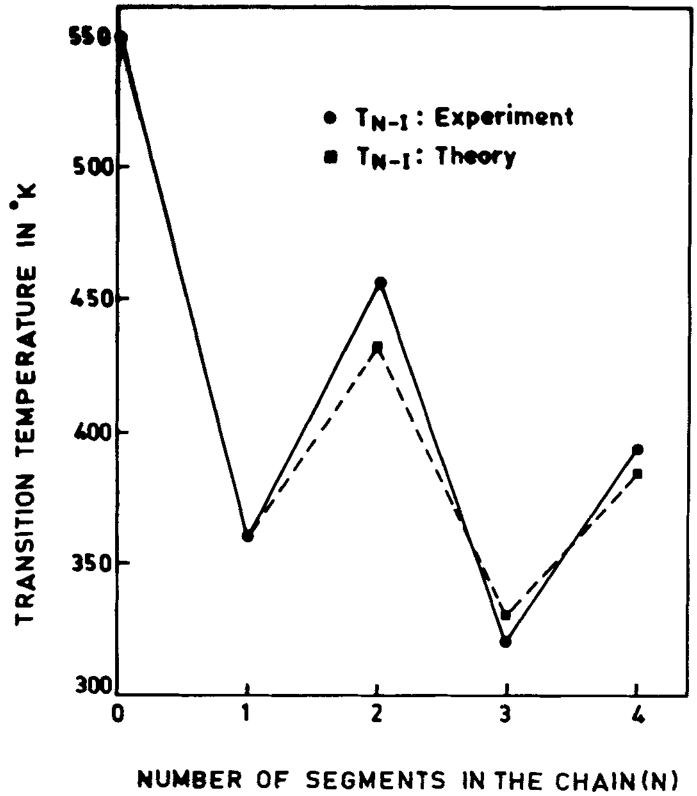

FIGURE 1 Plot of nematic–isotropic transition temperature against number of methylene groups (N) in the chain of ω-phenylalkyl 4-*p*-cyanobenzylideneamino cinnamates.

each chain segment. The values of coupling constants viz., V_{aa}, V_{bb} and V_{ab}, obtained by fitting the nematic isotropic transition temperature of the first and second members of this homologous series, are 1928950.0, 48922.2 and 307194.5 respectively in C.G.S. units. The ratio of the strength parameters is constant throughout the calculation and its value for this homologous series is 6.279.

In conclusion we would like to mention that this is possibly the first calculation where the generally observed features of a phase diagram of a ω-phenylalkyl cinnamate sample, namely a high alternation in the nematic–isotropic transition temperature and a diminution in the alternation as the series is ascended, is well reproduced. The calculated transition points are seen to be only about 20°–10°K off the experimental values. Here, throughout the calculation, the energy values of the gauche states of the chain segments which are used correspond to those of a polyethylene chain. But these states are energetically more difficult to attain owing to a possible steric overlap of the bulky phenyl ring at the end of the alkyl chain. This may be a reason for the small deviation from the experimental results. Another probable reason which is well established from the work of McColl and Shih,[7] is that a purely attractive pair potential of the dispersion force may not be adequate in explaining the alternation of nematic isotropic transition temperature. At present we are trying to extend this model to the smectic phase by introducing the orientation independent term in the Kobayashi type of pair interaction. Preliminary calculations show that this model is able to predict an alternation between homologues giving both smectic and nematic phases and those giving only smectic phase as the series is ascended. The details of the calculation and results will be published in a separate paper.

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