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Understanding the dependence of the transitional properties of liquid crystal dimers on their molecular geometry

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The characteristic feature of liquid crystal dimers, in which two mesogenic groups are linked by a flexible spacer, is often thought to be the strong odd–even effect exhibited by their transitional properties. That is, the nematic–isotropic transition temperature and the entropy of transition are large for dimers with an even number of groups in the spacer in comparison with those for neighbouring dimers with an odd number of groups. However, the magnitude of the odd–even effect along a homologous series of dimers is found to depend strongly on the nature of the link between the mesogenic group and the spacer. This dependence is thought to originate in the variation of the molecular geometry with the linking group, a view which is supported by detailed molecular field theory calculations involving all of the conformational states. Here we are concerned with developing a more transparent understanding of this geometrical effect using a simple model of the dimers in which all of the conformational states are replaced by just two, a linear and a bent conformer. The model has been found to exhibit a strong odd–even effect as well as a nematic–nematic transition when the bond angle is tetrahedral. We have used this model to explore the dependence of the transitional properties of liquid crystal dimers on their geometry by varying the bond angle of the bent conformer. The behaviour predicted by the model for the nematic–isotropic transition is found to be in qualitative agreement with experiment. In addition, the nematic–nematic transition is observed to exhibit a critical behaviour as the bond angle is increased. At the other extreme, when the bond angle is reduced to its limiting value of 90° there is a very strong first order transition between a discotic and a calamitic nematic.

1. Introduction

Liquid crystal dimers in which two mesogenic groups are linked by a flexible spacer are of considerable interest not only because of the dramatic odd–even effect exhibited by their transitional properties, but also because their behaviour parallels that found for semi-flexible main chain polymers, e.g. [1]. Thus, the nematic–isotropic transition temperature is significantly larger for dimers with an even number of atoms in the spacer than for those with an odd number, although the difference decreases with increasing spacer length. In contrast, the difference in the entropy of transition, which is higher for even than for odd dimers, is apparently unattenuated as the length of the spacer increases to about twelve methylene groups. Although such behaviour is recognised as being archetypal of liquid crystal dimers, it is important to note that the magnitude of the odd–even effect is dependent on the nature of the link between the mesogenic unit and the alkyl spacer. For example, if the methylene link in the α,ω-bis(4-cyanobiphenyl-4′-yl)alkanes is replaced by an ether link, then the alternations in both T_{NI} and $\Delta S/R$ are significantly reduced [2]. Further, if the ether linkage is replaced by a carbonate group, then the alternation in T_{NI} is essentially removed and only a small alternation in $\Delta S/R$ remains, although the transitional entropy is larger than for a monomer [3]. This often profound dependence of the transitional properties for liquid crystal dimers on the nature of the link has been attributed to a change in the molecular geometry [3]. For example, the difference in the angle between the two mesogenic groups for odd and even dimers with the chain in the all-transconformation decreases along the series of links: methylene, ether and carbonate. At a more quantitative level, calculations based on the Marcelja–Luckhurst theory for nematogens composed of flexible molecules reveal that a change in the $\hat{CXC}$ angle where X is CH_2 or O, from 113·5° to 126·4°, which are typical values, is

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sufficient to explain the change in the transitional behaviour [4]. This result has been confirmed for a more realistic parametrisation of the potential of mean torque for each conformer using the surface tensor approach [5].

Although such detailed calculations are of considerable value, it is of interest to see if simpler models can also account for the influence of these geometrical differences. We have developed a generic model incorporating the essential physics of the problem with which to understand the unusual transitional properties of liquid crystal dimers [6]. In this, the numerous conformational states in which real dimers can exist are replaced by just two. In one, the linear conformer, the mesogenic groups are parallel, while in the other, the bent conformer, they are inclined with respect to each other at a tetrahedral angle. The behaviour of the system is then effectively determined by the relative amounts of the conformers in the isotropic phase, although in the nematic phase the composition will change because the conformers may interconvert and the nematic phase favours the linear conformer. The system is found to behave qualitatively like real methylene linked dimers, in that when the molar fraction of the bent conformer is high, the entropy of transition is low as for odd dimers, and as the mol fraction is decreased, there is a critical value at which the entropy of transition jumps to a value characteristic of even dimers. In addition, for very high concentrations of the bent conformer, the system exhibits a nematic–nematic transition which is reminiscent of the behaviour found for certain semi-flexible main chain polymers with an odd spacer [7]. Here we use this model to explore the influence of the geometry of liquid crystal dimers on their transitional properties. An important parameter within the model is the angle between the mesogenic groups in the bent conformer. This was not varied in our original calculations, but we have now studied the influence of this geometrical parameter on the transitional properties and we present our results for different bond angles. At first sight it might seem that the bond angle could be identified with that between the mesogenic groups for liquid crystal dimers. This is certainly the case when the chain adopts a tetrahedral geometry and the angle between the long axis of the mesogenic group and the first link in the chain is also tetrahedral. However, when the chain angles are tetrahedral, but the angle made by the first link in this with the mesogenic group is not, then the angle between the mesogenic groups adopts more than just the two values (109° and 180°) found for the tetrahedral geometry. As the angle between the mesogenic group and the first link in the chain deviates from 109°54′, so the range of angles between the mesogenic groups grows, adopting values which depart to a greater extent from the initial bond angle. In consequence, mapping the results obtained for the simple model onto the behaviour of real liquid crystal dimers will become more problematic as the bond angle deviates from the tetrahedral angle. Nonetheless, the results obtained for the model are of interest in their own right and will reflect to a varying extent the transitional properties of real dimers.

2. The background theory

We begin by describing the model [6] in a little more detail and quantitatively. The molar Helmholtz free energy for this binary mixture of bent (b) and linear (l) conformers is

$$A/RT = -\ln[g_l Q_l + g_b \exp(-\Delta E/k_B T) Q_b] + \frac{1}{2}\left[x_l \sum_m (-)^m \tilde{X}^l_{2m} \bar{C}^l_{2-m} + x_b \sum_m (-)^m \tilde{X}^b_{2m} \bar{C}^b_{2-m}\right]. \quad (1)$$

In this expression Q_b is the orientational partition function for the bent conformer,

$$Q_b = \int \exp[-U_b(\omega)/k_B T]\,d\omega, \quad (2)$$

where the potential of mean torque is

$$U_b(\omega) = -\sum_m (-)^m X^b_{2m} C_{2-m}(\omega). \quad (3)$$

Here X^b_{2m} is the interaction tensor controlling the strength of the molecular field tending to orient the molecules, the tilde in equation (1) indicates that the tensor is divided by $k_B T$ and $C_{2m}(\omega)$ is a second rank modified spherical harmonic with ω defining the orientation of the director in a molecular frame. There are similar expressions for the linear conformer. The ordering tensor of the bent conformer $\bar{C}^b_{2m}$, is related to the potential of mean torque by

$$\bar{C}^b_{2m} = Q_b^{-1} \int C_{2m}(\omega) \exp[-U_b(\omega)/k_B T]\,d\omega. \quad (4)$$

The mol fraction of the bent conformer is denoted by x_b and is given by

$$x_b = g_b \exp(-\Delta E/k_B T) \times Q_b/[g_l Q_l + g_b \exp(-\Delta E/k_B T) Q_b]; \quad (5)$$

the orientational partition functions enter this expression because the ordering potential in the nematic phase can change its composition [8]. In fact, in the nematic mixture, the linear conformer is favoured because its orientational partition function is greater than that for the bent conformer. In the isotropic phase the orientational partition functions are equal (to 4π) and the mol fraction of the bent conformer reduces to

$$x_b^0 = g_b \exp(-\Delta E/k_B T)/[g_l + g_b \exp(-\Delta E/k_B T)]. \tag{6}$$

Here ΔE is the difference in the internal energy between the two conformers and g_b is a degeneracy factor. This is introduced to allow for the observation that for real dimers with a tetrahedral geometry for the spacer, about 75% of all conformers have the mesogenic groups tilted with respect to each other irrespective of the spacer length or parity. It is the energy differences between the conformers which favour the linear form for even dimers and the bent form for the odd. These energy differences vary significantly depending on the conformers involved; within the model this is allowed for, albeit crudely, by ΔE which can be thought of as some average internal energy difference. For even dimers ΔE is positive so that x_b^0 will be small, while for odd dimers ΔE is negative and so x_b^0 will be large. In the calculations it is convenient to assume that the conformational Boltzmann factor, $\exp(-\Delta E/k_B T)$ does not change with temperature. With this approximation the mol fraction of the bent conformer in the nematic phase can be rewritten as

$$x_b = x_b^0 Q_b/(x_l^0 Q_l + x_b^0 Q_b). \tag{7}$$

The dependence of the transitional properties on the molecular geometry of the dimers is contained in the interaction tensors X_{2m}^l and X_{2m}^b. This dependence takes a relatively simple form if we assume a segmental approach in which the total interaction tensor for a conformer is written as a tensorial sum of the interaction tensors of the component mesogenic groups [9]. For the linear conformer, in a frame with the z axis parallel to the symmetry axis of the mesogenic groups, the only non-zero component is

$$X_{20}^l = 2X_a, \tag{8}$$

where X_a is the irreducible spherical tensor component for a single mesogenic group. The subscript 'a' was first introduced by Marcelja [9] in his theory of nematics composed of non-rigid molecules to denote a mesogenic group, because at that time they were essentially composed of aromatic moities. For the bent conformer the non-zero components are

$$X_{20}^b = X_a(1 - 3\cos\theta)/2$$

and

$$X_{22}^b = (3/8)^{1/2} X_a(1 + \cos\theta), \tag{9}$$

where θ is the angle between the two mesogenic groups which we shall refer to as the bond angle, the x axis bisects this and the z axis is in the molecular plane and orthogonal to x. The maximum molecular biaxiality occurs for the tetrahedral angle ($\theta = \cos^{-1}(-1/3)$) when one of the cartesian components vanishes and the other two are equal but opposite in sign. At this point the irreducible components of the interaction tensor are

$$X_{20}^b = X_a \qquad X_{22}^b = X_a/6^{1/2}. \tag{10}$$

As the bond angle between the mesogenic groups is increased, so X_{20}^b also increases and the biaxiality X_{22}^b decreases until the limiting value for θ of 180° is reached, at which point X_{22}^b vanishes and X_{20}^b adopts the value for a rod of $2X_a$. For real liquid crystal dimers, the angle is usually equal to or greater than the tetrahedral value, although it should certainly be possible to introduce links which would reduce the angle. In fact this is also a situation of some interest which can be considered using our model; decreasing the bond angle again reduces the molecular biaxiality and a limiting case is reached when the particles regain their cylindrical symmetry. This occurs when the mesogenic groups are orthogonal, that is θ is 90°, but now the particle is disc-like rather than rod-like. Such changes are not immediately apparent from the irreducible components given in equation (9) because, for bond angles less than the tetrahedral value, the interaction tensor for the conformer tends to be cylindrically symmetric about the y axis, orthogonal to the two mesogenic groups. If this is now labelled as the z axis, the irreducible spherical tensor components become

$$X_{20}^b = -X_a \qquad X_{22}^b = -(3/8)^{1/2} X_a \cos\theta, \tag{11}$$

and the biaxiality of the disc-like conformer vanishes when the two mesogenic groups are orthogonal. The same series of changes then recur as the bond angle is further reduced from 90° to zero.

The interaction parameter X_a is strongly temperature dependent because it is related to the orientational order within the nematic phase. In fact within the molecular field approximation, X_a is directly proportional to the conformationally averaged second rank order parameter for the mesogenic groups [6]

$$X_a = \varepsilon_{aa}\langle \bar{P}_2 \rangle, \tag{12}$$

where ε_{aa} is a measure of the spatially averaged anisotropic interaction between two mesogenic groups. The weighted average of the order parameter for these is defined by

$$\langle \bar{P}_2 \rangle = x_l \bar{P}_2^l + x_b \bar{P}_2^b, \tag{13}$$

where $\bar{P}_2^l$ and $\bar{P}_2^b$ denote the order parameters for the mesogenic groups within the linear and bent conformers, respectively. These order parameters are obtained from the ordering tensors of the two conformers, calculated from equation (4). However, this dependence of X_a on $\langle \bar{P}_2 \rangle$, is not needed to determine the entropy of transition or the order parameters at the nematic–isotropic transition; it is used only to obtain the temperature dependence of the order parameters and the composition within the nematic phase [10] and, as we shall see, to locate the nematic–nematic transition.

Finally, the theory is also used to evaluate the molar entropy change at the nematic–isotropic transition. This is given by

$$\Delta S/R = -\left(\frac{1}{2}\right)\left[x_{\mathrm{l}}^{\mathrm{N}}\sum_{m}(-)^{m}\tilde{X}_{2m}^{\mathrm{lN}}\bar{C}_{2-m}^{\mathrm{lN}} + x_{\mathrm{b}}^{\mathrm{N}}\sum_{m}(-)^{m}\tilde{X}_{2m}^{\mathrm{bN}}\bar{C}_{2-m}^{\mathrm{bN}}\right] + (x_{\mathrm{b}}^{\mathrm{N}}-x_{\mathrm{b}}^{\mathrm{I}})\Delta\tilde{E}^{\mathrm{N}}, \qquad (14)$$

where the labels N and I denote the values in the nematic and isotropic phases, respectively, at the nematic–isotropic transition. The last term in this equation results from the change in the composition $(x_{\mathrm{b}}^{\mathrm{N}}-x_{\mathrm{b}}^{\mathrm{I}})$ caused by the onset of orientational order within the nematic phase.

Before we consider the predictions of this molecular field theory in the following section, we describe briefly how the nematic–isotropic transition is located and how the transitional entropy, $\Delta S/R$, and the average order parameter for the mesogenic groups $\langle\bar{P}_2\rangle_{\mathrm{N}}$, at the transition are evaluated. We begin the calculations by selecting values for the bond angle θ of the bent conformer, the conformational degeneracy factors, g_{l} and g_{b}, and the scaled conformational energy difference, $\Delta E/k_{\mathrm{B}}T$. The following calculations are then performed for a range of values of the scaled interaction parameter, $\tilde{X}_{\mathrm{a}}$. For each value of $\tilde{X}_{\mathrm{a}}$, the scaled interaction tensors $\tilde{X}_{2m}^{\mathrm{l}}$ (see equation (8)) and $\tilde{X}_{2m}^{\mathrm{b}}$ (see equation (9)) are evaluated for the linear and bent conformers, respectively. The ordering tensors, $\bar{C}_{2m}^{\mathrm{l}}$ and $\bar{C}_{2m}^{\mathrm{b}}$, are then determined by taking the appropriate orientational Boltzmann averages (see equation (4)). These calculations also involve the evaluation of the two orientational partition functions, Q_{l} and Q_{b}. From these we can determine the mol fractions of the two conformers in the nematic phase (see equations (6) and (7)). There is now sufficient information to calculate the molar free energy of the nematic phase from equation (1) and to determine the value of $\tilde{X}_{\mathrm{a}}$ when it is equal to the free energy of the isotropic phase

$$A_{\mathrm{I}}/RT = -\ln\{4\pi[g_{\mathrm{l}} + g_{\mathrm{b}}\exp(-\Delta E/k_{\mathrm{B}}T)]\}. \qquad (15)$$

At this value of $\tilde{X}_{\mathrm{a}}$ we already know the quantities needed to evaluate the transitional entropy from equation (14). All that remains is the conformationally averaged order parameter $\langle\bar{P}_2\rangle_{\mathrm{N}}$ at the nematic–isotropic transition (see equation (13)). To evaluate this, the ordering tensors at the transition, $\bar{C}_{2m}^{\mathrm{lN}}$ and $\bar{C}_{2m}^{\mathrm{bN}}$ are transformed to give the order parameters $\bar{P}_2^{\mathrm{lN}}$ and $\bar{P}_2^{\mathrm{bN}}$, for the axes parallel to the mesogenic groups constituting the dimer.

3. Results and discussion

We shall begin our discussion of the results obtained for this model with the dependence of the average mesogenic order parameter at the nematic–iostropic transition, $\langle\bar{P}_2\rangle_{\mathrm{N}}$, and the entropy of transition on the composition in the isotropic phase. Here we use this composition as some measure as to whether the model corresponds to an even dimer (x_{b}^{0} less than some critical value) or an odd dimer, where x_{b}^{0} is greater than this critical value. The composition of the isotropic phase is changed by varying the energy difference ΔE between the two conformers. For a given ΔE and hence isotropic composition, the Boltzmann factor $\exp(-\Delta E/k_{\mathrm{B}}T)$ is then held constant which ignores, therefore, the small temperature dependence resulting from $1/k_{\mathrm{B}}T$, but facilitates the calculations. For comparison we show in figures 1(*a*) and 2(*a*) the results for the transitional order parameter and the entropy of transition, respectively, obtained for the tetrahedral geometry. We see that as the mol fraction of the bent conformer in the isotropic phase increases, so too does the average order parameter for the mixture at the transition. However, at a critical value of x_{b}^{0} which is approximately 0·97, the order parameter falls to a very small value, expected for such a high concentration of bent particles. Entirely analogous behaviour is observed for the entropy of transition which essentially parallels $\langle\bar{P}_2\rangle_{\mathrm{N}}$ (see figure 1(*a*)). Within this model, therefore, we see that below the critical composition the transitional entropy is small, as for odd dimers, and above it $\Delta S/R$ is dramatically higher, as for even dimers. At first sight the increase in the orientational order as the concentration of the bent conformer in the isotropic phase increases may seem surprising. It can, however, be understood in the following way. The introduction of bent conformers to a system of linear conformers will, necessarily, lower the nematic–isotropic transition temperature. At the transition, the bent conformer is converted to the linear form because the resulting increase in conformational free energy is compensated for by the decrease in the orientational free energy. This conversion of bent to linear conformer then increases the transition temperature of the mixture, but because the temperature is fixed the reduced temperature, T/T_{NI}, must fall and so the orientational order increases. As the amount of bent conformer increases, so the effect is enhanced because the depression of the nematic–isotropic transition is greater. This process continues until a concentration of bent conformer is reached at which the orientational free energy is insufficient to compensate for the growth of

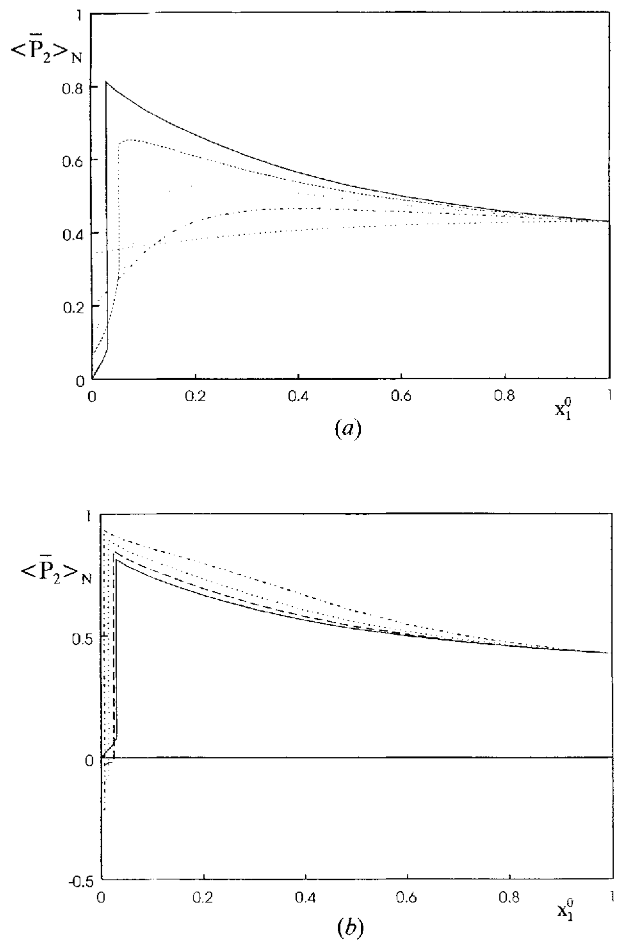


Figure 1. The dependence of the average mesogenic order parameter $\langle \bar{P}_2 \rangle_N$ at the nematic–isotropic transition on the mol fraction, x_1^0, of the linear conformer in the isotropic phase calculated for different values of the bond angle for the bent conformer; (*a*) equal to and greater than the tetrahedral value 109·48° (——), 112° (– – –), 115° (······), 120° (··–··–) and 140° (• • • • •); (*b*) equal to and less than the tetrahedral value 109·48° (——), 108° (– – –), 105° (······) and 90° (··–··–).

conformational free energy and no significant change in composition occurs; at this point the average orientational order at the transition remains small.

We now turn to the change in this composition dependent behaviour for the transitional entropy and the average mesogenic order parameter at the nematic–isotropic transition for differing bond angles. As before, we have calculated each quantity as a function of the concentration of the bent conformer in the isotropic phase. We shall start with the change in this behaviour as the angle between the two mesogenic groups is increased from the tetrahedral value. As θ is increased, so the biaxiality of the interaction tensor will decrease and the major component will increase (see equation (9)).

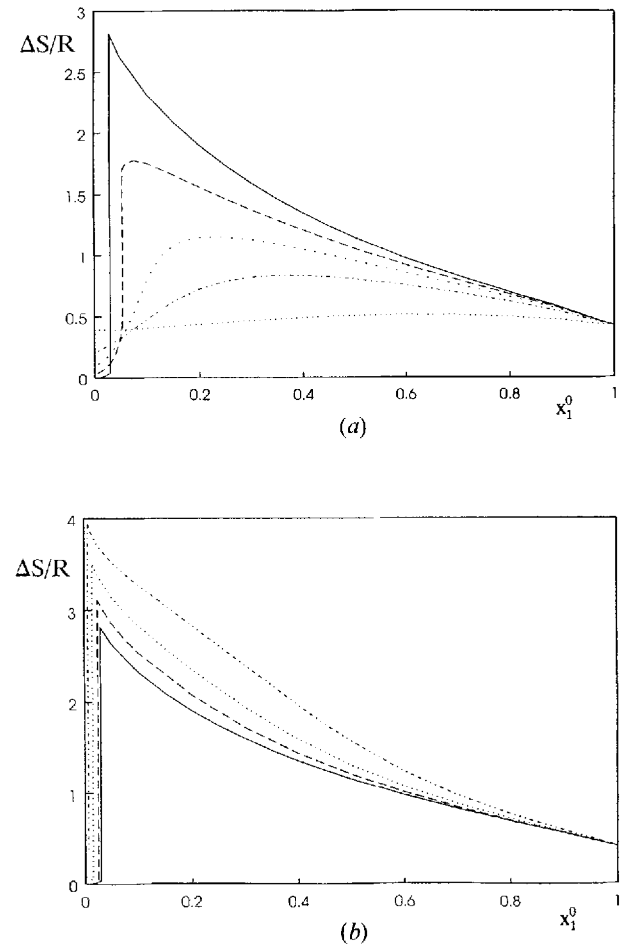


Figure 2. The variation of the nematic–isotropic transitional entropy, $\Delta S/R$, with the mol fraction, x_1^0, of the linear conformer in the isotropic phase calculated for differing values of the bond angle for the bent conformer; (*a*) equal to and greater than the tetrahedral value 109·48° (——), 112° (– – –), 115° (······), 120° (··–··–) and 140° (• • • • •); (*b*) equal to and less than the tetrahedral value 109·48° (——), 108° (– – –), 105° (······) and 90° (··–··–).

We expect, therefore, that the influence of the bent conformer on the transitional properties will be smaller than for the tetrahedral geometry, for the same isotropic composition. Thus the depression of the nematic–isotropic transition temperature of the linear conformer by the addition of the bent will be smaller and the orientational partition function for the two conformers will become similar, so that the compositional change at the onset of orientational order will be reduced. Our results for the compositional dependence of the transitional entropy and the average at the transition of the order parameter are shown in figures 1 (*a*) and 2 (*a*), respectively. Since the behaviour of $\Delta S/R$ parallels that of $\langle \bar{P}_2 \rangle_N$, we shall confine our discussion to the influence of the bond angle on the average order parameter. When

θ is increased to just 112°, there is only a slight deviation from the behaviour found for the tetrahedral geometry, provided the concentration of the bent conformer is small. However, as x_b^0 grows, so too does the deviation, and the transitional order parameter passes through a sharp maximum before falling steeply to the low value anticipated for a bent conformer. The nematic–isotropic transition in the limit that x_b^0 tends to unity is then weakly first order; a result confirmed by the transitional entropy (see figure 2(*a*)). The variation of $\langle \bar{P}_2 \rangle_N$ with the composition of the mixture differs from that found when θ is 109·48°, first because there is a maximum and not a cusp and secondly because the concentration of bent conformer at which the order parameter falls steeply is lower. For a bond angle of 115°, there is a larger and more significant deviation from the behaviour found for the tetrahedral bond angle. Thus, with increasing concentration of the bent conformer the transitional order parameter increases only slightly above the value found for the pure linear conformer. It then passes through a fairly broad maximum before falling quite gradually and continuously to the value expected for the pure bent conformer. This trend with increasing bond angle continues, and for 120° the average order parameter barely increases above the value expected for the linear conformer before falling continuously to that for the bent conformer. When the bond angle is 140°, the difference in the interaction tensors for the two conformers is relatively small; this is apparent from their similar transitional order parameters (see figure 1 (*a*)). In consequence there is little change in the composition of the mixture at the transition to the nematic phase and so the average transitional order parameter, $\langle \bar{P}_2 \rangle_N$, falls slightly with increasing concentration of the bent conformer in the isotropic phase. This change in the transitional behaviour with the increase in the bond angle in the bent conformer is entirely consistent with that for liquid crystal dimers where an increase in the angle between the mesogenic group and the first chain segment away from the tetrahedral value reduces the odd–even behaviour, also in a dramatic manner. It is significant that although the transitional entropy has a far less dramatic dependence on composition for large bond angles, corresponding to a reduction in the odd–even effect, its value is larger than for the linear conformer alone; such behaviour resembles that observed for the carbonate linked cyanobiphenyl dimers [3]. However, the difficulty of mapping the geometry of the various conformers of the liquid crystal dimers onto that of the two conformers in our simple model prevents any quantitative comparison.

We shall now consider the change in the transitional behaviour predicted by the model when the bond angle of the bent conformer undergoes a negative deviation from the tetrahedral value. The results for the average mesogenic order parameter, $\langle \bar{P}_2 \rangle_N$, at the transition and the entropy of transition, $\Delta S/R$, are shown as a function of the molar fraction of the bent conformer in the isotropic phase in figures 1 (*b*) and 2 (*b*), respectively. As before we shall only consider the behaviour of $\langle \bar{P}_2 \rangle_N$, since this reflects that of $\Delta S/R$. For a bond angle of 108°, we see that for small amounts of the bent conformer there is little change in the orientational order. However, there is an increase in $\langle \bar{P}_2 \rangle_N$ above the value for the tetrahedral geometry and this increase grows with the amount of the bent conformer in the isotropic phase. The average order parameter passes through a maximum value at a cusp in the plot and then drops dramatically to a negative value for large x_b^0. At first sight the negative order parameter may seem unusual, but is, in fact, quite straightforward. It results because for a discotic nematic the order parameter for the near symmetry axis is positive, as for rods, but now the mesogenic groups are orthogonal to the symmetry axis and so their order parameters are negative. In addition the cusp is found to occur at larger mol fractions of bent conformer. As the bond angle between the mesogenic groups is decreased further, so these changes continue until the limiting value of 90° is reached. At this point, the average orientational order parameter at the transition grows significantly until it passes through a high maximum at a very large mol fraction of the bent conformer in the isotropic phase (~ 0·99). The order parameter then drops catastrophically to a negative value of about −0·21 which is to be expected since, for cylindrically symmetric discs, the transitional order parameter for the symmetry axis is the Maier–Saupe value of 0·429, and so the order parameter for an axis orthogonal to the symmetry axis is just −1/2 this value, that is −0·215.

These changes in the transitional properties as the bond angle is decreased from the tetrahedral value to the limiting angle of 90° are very much in accord with our expectations. For the case when the two conformers are either rods ($\theta = 0°$) or discs ($\theta = 90°$), the difference in their interaction tensors is very large ($X_{20}^{1} = 2X_a$ and $X_{20}^{b} = X_a$, see equations (8) and (11)), and so the difference in the orientational partition functions is also considerable. It is this difference which is responsible for the ready conversion of the bent to the linear conformer with the onset of orientational order in the nematic phase, since it is the linear conformer which has the largest orientational partition function—that is, until the concentration of the bent or disc-shaped conformer is so high that a discotic nematic results, for then X_a is negative. Associated with the change in the composition of the mixture is a large jump in both the orientational order parameter, $\langle \bar{P}_2 \rangle_N$, for the mixture and the transitional entropy (see figures 1 (*b*) and 2 (*b*)). An equivalent explanation of such behaviour for rod-like and disc-like conformers is, as we have seen, provided by the following arguments. The addition of the disc-like conformer to its rod-like counterpart causes a significant depression of the nematic–isotropic transition. At the transition, however, the disc-like conformer is largely converted to the rod-like conformer with the consequent increase in the conformational free energy being provided by the decrease in the orientational free energy. The extent of this conversion is particularly pronounced because of the considerable difference in the orientational partition functions for the two conformers. This change in composition increases the nematic–isotropic transition temperature which effectively decreases the reduced temperature for the system and so increases the orientational order at the transition, as well as the transitional entropy. Of course, for extremely large concentrations of the disc-like conformer in the isotropic phase, the gain in orientational free energy at the nematic–isotropic transition is insufficient to convert the disc-like to the rod-like conformer and so the transition is somewhat weaker (see figure 2 (*b*)).

As far as we are aware, no dimers have been prepared with sufficiently small bond angles between the mesogenic group and the first link in the spacer to exhibit the dramatic odd–even effects predicted by our model. However, there are star-like trimers which conform to certain features of the model; in a star-like trimer, three mesogenic groups are linked symmetrically via flexible spacers to a central phenyl ring [11]. The three-fold symmetry of such molecular structures suggests that they should form discotic liquid crystals, whereas in practise they behave like calamitics [11]. Presumably, as for our model, the flexible spacers adopt conformations in which all three mesogenic groups can be parallel, the increase in the conformational free energy being compensated for by the decrease in the orientational free energy.

One of the intriguing features of the behaviour predicted by this model, when the bond angle for the bent conformer is tetrahedral, is the occurrence of a nematic–nematic transition when the mol fraction of the linear conformer is very small, just 0·01 [6]. The two nematic phases differ both in their compositions and the orientational order, with the low temperature phase having a much higher concentration of the linear conformer and a higher order. It is of some interest to investigate how this transition depends on the bond angle for the bent conformer. It is not possible to locate the nematic–nematic transition using the same strategy as for the nematic–isotropic transition, because the free energies of the two nematic phases cannot be obtained independently. To achieve this it is necessary to assume a particular dependence of the strength parameter, X_a, on the average order parameter, $\langle \bar{P}_2 \rangle$, and in our previous study X_a was taken to be linear in $\langle \bar{P}_2 \rangle$ [6] (see equation (12)). With this assumption the calculations were performed as we had described in § 2 for a given value of $\tilde{X}_a$; then once the average order parameter has been evaluated, the scaled temperature $T^*(\equiv k_B T/\varepsilon_{aa})$ corresponding to particular values of $\langle \bar{P}_2 \rangle$, x_b and x_l is obtained from equation (12). As we shall see, at certain scaled temperatures the average order parameter can, in addition to a zero value, adopt two, three or even four non-zero values. The relative thermodynamic stability of the phases corresponding to these different values of the order parameter is determined by evaluating the Helmholtz free energy; that is, from equation (1) in which the scaled interaction tensors, $\tilde{X}^{l}_{2m}$ and $\tilde{X}^{b}_{2m}$, are calculated from $\langle \bar{P}_2 \rangle$ via equations (8), (9) and (12). The nematic–nematic and nematic–isotropic transitions are then located by determining the scaled temperatures at which the free energies of the phases are equal.

The results of these calculations are shown in figure 3 as the dependence on the scaled temperature, T^*, of the conformationally averaged order parameter of the mesogenic groups in the two conformers, $\langle \bar{P}_2 \rangle$, and the mol fraction of the linear conformer, x_l. In all of the calculations the mol fraction of the linear conformer in the isotropic phase was given the low value of 0·01 and the degeneracy factors g_l and g_b were set equal to 0·25 and 0·75, respectively. We begin by considering the predictions for a bent conformer with a bond angle of 112°. The scaled nematic–isotropic transition temperature for the pure linear conformer is predicted to be 0·4406 [6] and we expect the addition of a high concentration of the bent conformer to produce a large depression of the transition. This is indeed the case, as we can see from figure 3 (*a*), for T^*_{NI} of the mixture is just 0·146. In addition the transition is weak, with an average order parameter of about 0·14 which compares with a value of 0·429 for the pure linear conformer. In keeping with the weakness of the first order nematic–isotropic transition, the mol fraction of the linear conformer changes by a very small amount at the transition. As the temperature is lowered, the order parameter increases, but with an unexpected upward curvature at a scaled temperature of 0·12; this is associated with an analogous growth in the mol fraction of the linear conformer. Then, just below this temperature region, there is a strong first order nematic–nematic transition at which the order parameter, $\langle \bar{P}_2 \rangle$, jumps by about 0·3. There is a corresponding large growth in the mol fraction of the linear conformer from 0·13 to 0·75. Such changes are in keeping with our previous calculations for the bent conformer with a tetrahedral geometry; however, for this system, the nematic–isotropic transition was weaker and the nematic–nematic transition was stronger [6]. This change in behaviour is to be expected because as the bond angle of the bent conformer increases, so it becomes more like the linear conformer which will weaken

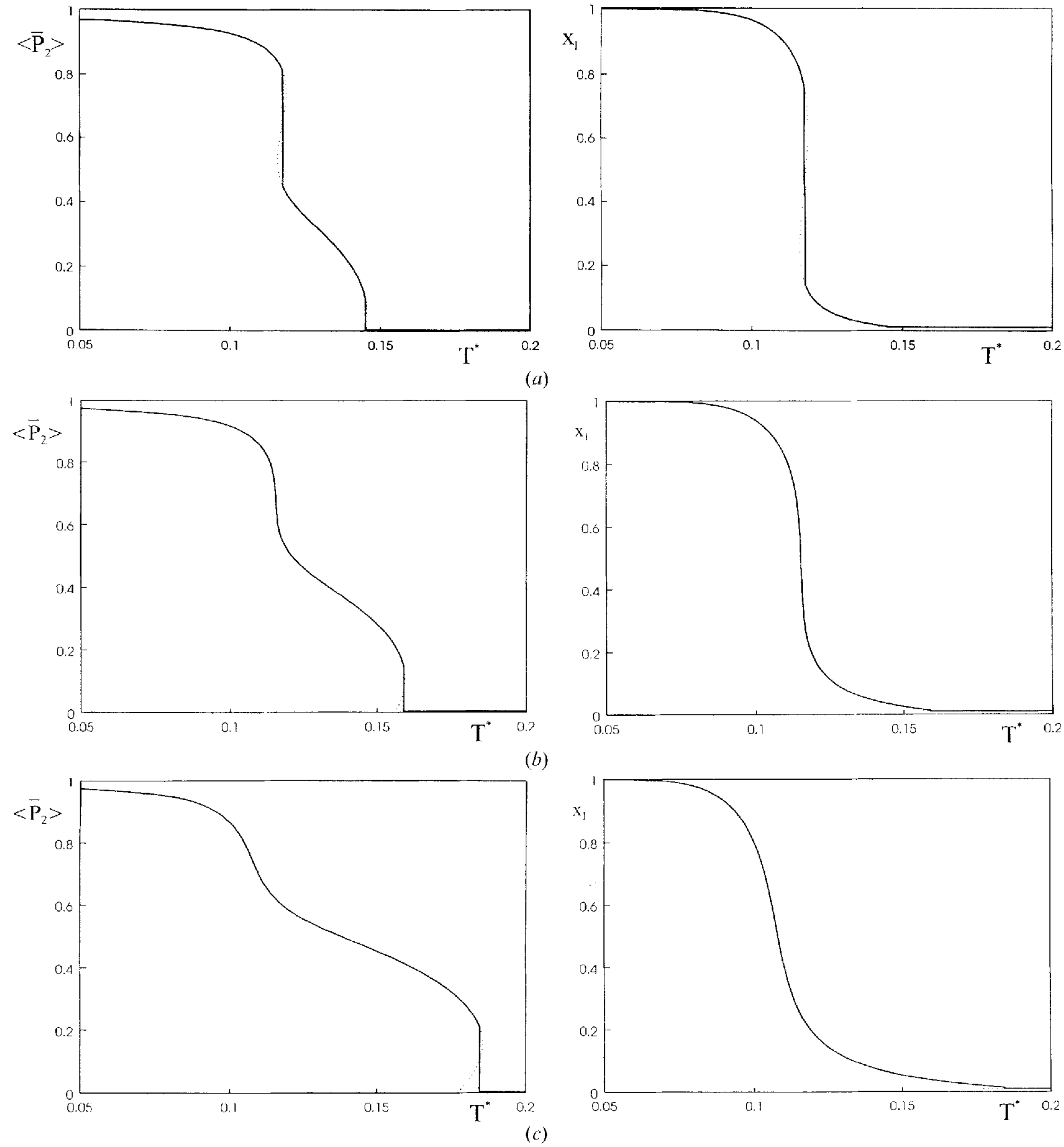


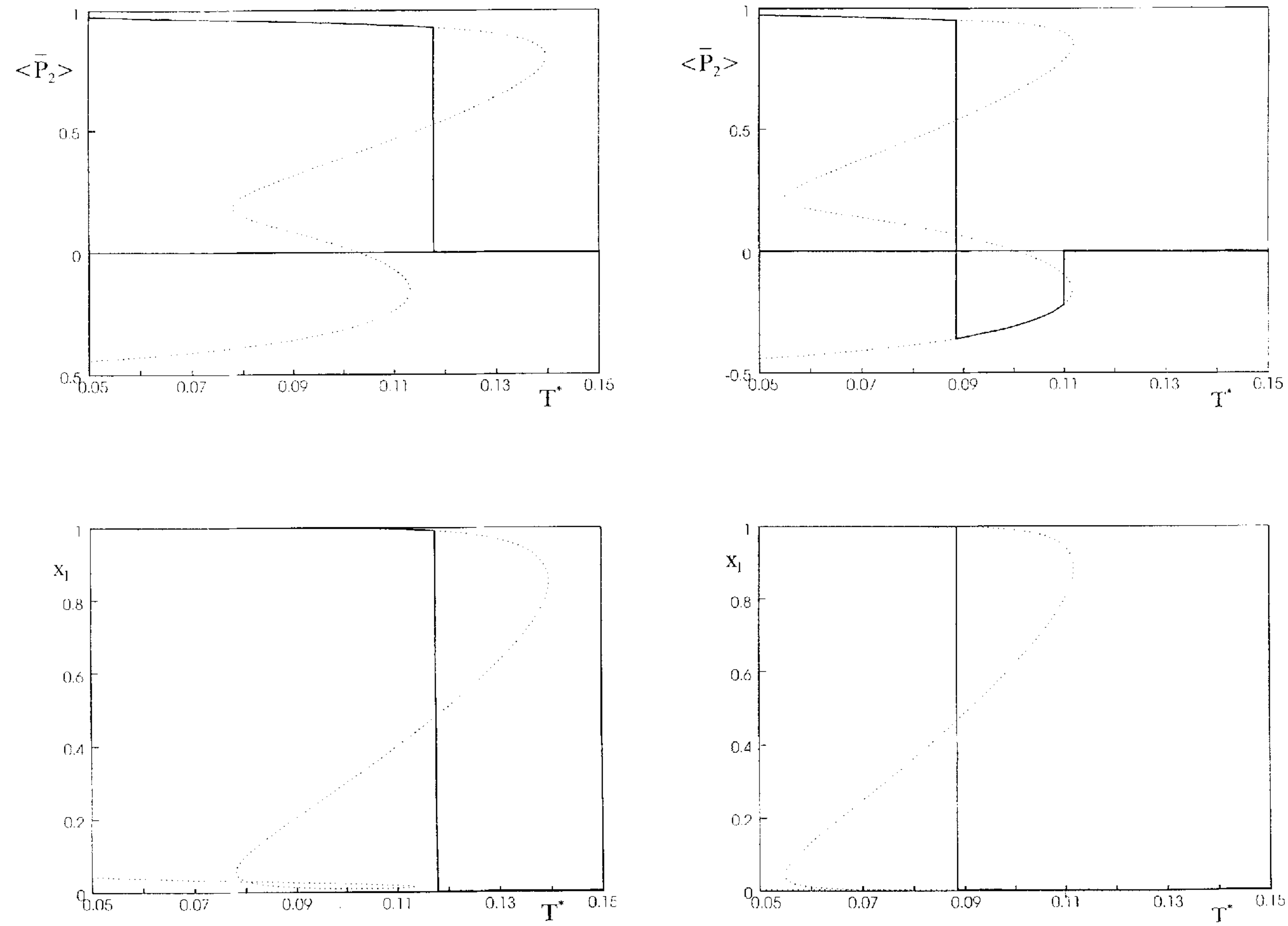
Figure 3. The dependence of the conformationally averaged order parameter for the mesogenic groups, $\langle \bar{P}_2 \rangle$, and the mol fraction of the linear conformer, x_l, on the scaled temperature, $T^*(\equiv k_B T/\varepsilon_{aa})$. In these calculations the mol fraction of the linear conformer in the isotropic phase was 0·01 and the bond angle, θ for the bent conformer was (*a*) 112°, (*b*) 115° and (*c*) 120°.

the nematic–nematic transition and strengthen the nematic–isotropic.

Such changes prove to be rather sensitive to the bond angle especially for the nematic–nematic transition, as the analogous calculations with θ of 115° show (see figure 3 (*b*)). The scaled nematic–isotropic transition temperature has increased, as has its strength, reflected by the jump in $\langle \bar{P}_2 \rangle$, although the change in the mol fraction of the linear conformer at the transition remains rather small. On lowering the temperature, the order parameter grows, again with a strong upward curvature at the same scaled temperature of about 0·12 , but this growth is not followed by a nematic–nematic transition. Instead, both the average order parameter, $\langle \bar{P}_2 \rangle$, and the mol fraction of the linear conformer increase continuously, but rapidly at a reduced temperature of 0·11. This trend continues and when the bond angle has increased to 120°, the nematic–isotropic temperature is higher and the transition is stronger as we can judge from the results in figure 3 (*c*). However, the change in the composition of the mixture at this transition remains small. As the scaled temperature is lowered, the mol fraction of the linear conformer grows with the rate of change being greatest at T^* of about 0·1, although the temperature range over which the majority of this change takes place has increased. There is an analogous maximum in the rate of change of the average order parameter, although the magnitude of the change in $\langle \bar{P}_2 \rangle$ itself has decreased.

From these results we see that the nematic–nematic transition is predicted to exhibit a critical behaviour as the bond angle of the bent conformer increases. That is, the strength of the nematic–nematic transition weakens as the bond angle increases from the tetrahedral value, until the difference in the two nematic phases disappears. The critical value of the bond angle is between 112° and 115°; for larger values of the bond angle, the average orientational order parameter increases continuously with decreasing temperature, although there is a temperature range over which the rate of change is especially large. However, the magnitude of the overall change in $\langle \bar{P}_2 \rangle$ also decreases with increases in the bond angle of the bent conformer. Associated with these changes in the average order parameter are comparable variations in the mol fraction of the linear conformer. Analogous critical behaviour for a nematic–nematic transition has been predicted by Govind and Madhusudana [12] based on an early model for double re-entrant behaviour [13]. In the model, there are again two conformers which are allowed to interconvert, but now both are linear with different anisotropic interaction parameters, and the factors controlling the extent of the interconversion via the orientational partition functions are the relative magnitudes of the interaction parameters for the two like interactions and the one mixed interaction. The quantity playing the same role as the bond angle in our model is the extent to which the mixed interaction deviates from the geometric mean of the two like interactions. With negative deviations from the geometric mean combining rule, a nematic–nematic transition is observed, but only over a very narrow range of values for the mixed anisotropic interaction. Associated with such changes are equally small variations in the orientational order and composition of the two nematic phases involved in the transition.

Finally, we consider the limiting case for the bent conformer when the bond angle is 90°, since with the segmental approach which we are using, the bent conformer is equivalent to a disc (see equation (11)). In principle mixtures of rod-like and disc-like molecules can form a biaxial nematic phase [14]. However, for the extreme compositions of the conformational mixture which we consider, it is safe to ignore this possibility and so we restrict our attention to the uniaxial nematic phases. The behaviour predicted by our molecular field theory for a mixture with a mol fraction of just 0·01 of linear conformers in the isotropic phase is shown in figure 4 (*a*). The presence of such a high concentration of disc-like conformers produces a large depression of the nematic–isotropic transition temperature from the value expected for pure rod-like conformers, and this is indeed observed. However, when the transition to the nematic phase does occur, it is strongly first order with an average order parameter at the transition, $\langle \bar{P}_2 \rangle_N$, of approximately 0·95. This very large value occurs because, at the transition, essentially all of the disc-like conformers are converted to their rod-like counterparts. As we have seen, this effectively increases the nematic–isotropic transition temperature which decreases the reduced temperature and so increases the orientational order. The dotted lines in figure 4 (*a*) show the behaviour of the unstable ordered phase; the average order parameter for the mesogenic groups is seen to become negative, corresponding to a nematic composed of disc-like conformers. However, the difference in the conformational free energy for the rod-like and disc-like conformers is insufficient to overcome the orientational free energy of the system of rod-like conformers. In an attempt to stabilise the discotic nematic with respect to the calamitic nematic, we have reduced the mol fraction of the linear conformer in the isotropic phase to 0·001 which is equivalent to increasing the conformational free energy difference. The results of our calculations are shown in figure 4 (*b*), which displays a quite fascinating behaviour. Again the high concentration of the bent conformer depresses the nematic–isotropic transition which occurs at a scaled temperature of about 0·11. The average orientational order for the mesogenic groups is negative corresponding to the formation of a discotic nematic; this is as expected for an essentially pure system of disc-like conformers. Similarly the mol fraction of the linear conformer does not change at this nematic–isotropic transition. As the scaled temperature is lowered, the orientational order of the discotic nematic increases with a negligible change in the mol fraction of the linear conformer. Then, just below a reduced temperature of 0·09, there is an extremely strong first order transition from the discotic nematic to a calamitic nematic phase. As we can see from the data in figure 4 (*b*), essentially all of the disc-like conformers are converted to their rod-like counterparts. In consequence the effective nematic–isotropic transition temperature is increased, the reduced temperature decreases dramatically and the



(*a*) (*b*)

Figure 4. The dependence of the average orientational order parameter for the mesogenic groups, $\langle \bar{P}_2 \rangle$, and the mol fraction of the linear (or rod-like) conformer, x_l, on the scaled temperature, T^*, for a mixture of rod-like and disc-like conformers with the mol fraction of the rod-like conformer in the isotropic phase of (*a*) 0·01 and (*b*) 0·001.

average order parameter increases almost to its limiting value of unity.

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