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Mean field analysis of four liquid crystalline odd–even ester dimers*

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A mean field analysis is presented for four liquid crystalline ester dimers, D*n*, containing the dimethylbenzalazine mesogen, alkanedioyloxy flexible spacers from 7 to 10 carbon atoms and acetate terminal groups. The conformations of the dimers, in the RIS approximation, were generated from the known crystallographic coordinates of D8 and D9. The energy of each conformer is split into an internal (conformation dependent) part and an external (orientation dependent) part. After proper averaging over all orientations and conformations, the orientation–conformation partition function is evaluated and, from that, the Helmholtz free energy. A qualitative agreement between calculated and observed thermodynamic properties is obtained. In fact, the theoretical analysis correctly predicts strong odd–even fluctuations for the mesogenic group order parameter, S, as well as for transition entropy, ΔS_{NI}, and transition temperature, T_{NI}. The distribution of conformers is similar for dimers having the same parity of the spacer. For even dimers, the calculated fraction of linear extended conformers in the nematic phase at the N–I transition is around 47%, whereas it is less than 3.6% for odd dimers.

1. Introduction

In a previous paper [1] we have reported the synthesis of the four liquid crystalline ester dimers, D*n* (see scheme 1), containing the mesogenic group dimethylbenzalazine, and the X-ray crystallographic analysis of two of them (n=8, 9). The analysis showed that the odd dimer D9 adopts in the crystal phase a conformation with the two mesogenic groups parallel with respect to each other, as for the even dimer D8.

That result seemed rather unusual. In fact, the thermodynamic properties of D*n* dimers show strong odd–even fluctuations in nematic–isotropic transition temperatures and entropies, as expected. This apparent discrepancy and the detailed knowledge of the molecular structure of the dimers coming from the X-ray analysis, prompted us to perform a theoretical analysis of the liquid crystal phase of the four dimers. The results of this analysis are reported in the present paper.

Dimeric mesogens have been object of several theoretical investigations, mainly with reference to the series of α,ω-bis(4′-cyanobiphenyl-4-yl)alkanes and α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes [2]. Most of these investigations have been performed within the mean-field approach [3], either using the rotational isomeric state (RIS) approximation to evaluate the conformations accessible to the molecules or the model of full distribution of the torsional angles [2]. Moreover, a simplified, but physically deeper model, was developed, in which equilibrium between only two conformers (a linear and a bent one) is assumed to account for the observed odd–even effects. [4]

For the present analysis, we have followed the mean-field approach with the RIS approximation. We note that our analysis is the first one for full ester-type dimers and that the structural parameters of dimeric molecules were not assumed from more or less related compounds, but they have been taken from the X-ray analysis of the same compounds which are object of the theoretical analysis. This can be an important point since the results of the theoretical analysis can be significantly affected by the assumed structure of the mesogen and by other structural parameters such as the bond angles between the mesogen and the spacer [2].

2. Experimental

Conformations of dimers D*n* were generated using the geometry of the mesogenic group resulting from the crystal structure analysis of D8 and D9 [1]. Bond lengths and angles within the polymethylenic spacer, which can be affected by distortions due to thermal motion, were previously adjusted to their standard values [5]. In practice, for generating a conformer obtained by anticlockwise rotation of a molecular

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* Dedicated to Professor Augusto Sirigu on the occasion of his retirement.

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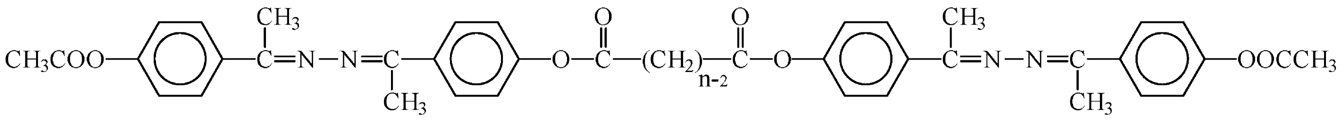


n = 7, 8, 9, 10

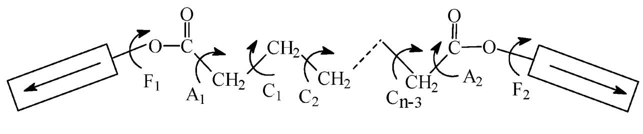
Scheme 1. Chemical diagram of D*n* dimers.

portion by φ angle around the chemical bond A–B, we have firstly moved the origin of the Cartesian coordinate system on the A atom and then we have chosen a new monometric orthogonal coordinate system (Z axis coincident with the bond A–B and oriented from A to B) then calculating the coordinates of all atoms relative to this system (x_0, y_0, z_0). For atoms of the molecular portion attached to B and involved in the rotation, the new coordinates (x_t, y_t, z_t) are given by the matrix relation:

$$\begin{pmatrix} x_t \\ y_t \\ z_t \end{pmatrix} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix}.$$

The relative orientation of the two mesogenic groups in the dimers is determined by the following Lagrangian coordinates (see scheme 2): torsions around the bonds from the mesogen to the alkyloxy O atoms, indicated by F_1 and F_2, respectively; torsions around the bonds from the carbonyl C atom to the first CH_2 group of the spacer, indicated by A_1 and A_2, respectively; torsions around CH_2–CH_2 bonds internal to the polymethylenic spacer, indicated by C_n (n=1, ..., 4 for D7, n=1, ..., 5 for D8, n=1, ..., 6 for D9 and n=1, ..., 7 for D10).

We have assumed a fourfold potential for F_1 and F_2 rotations (minima at ±60° and ±120°) [6], threefold for A_1 and A_2 (minimum at 180°, secondary minima at ±120° ($G^{\pm}$), energy difference of 4.28 kJ mol^{-1}) [5, 7] and threefold for C_n (minimum at 180°, secondary minima at ±120° ($G^{\pm}$), energy difference 1.63 kJ mol^{-1} for CH_2–CH_2 bonds adjacent to A_1 or A_2, 2.09 kJ mol^{-1} in all other cases) [5]. Conformations corresponding to sequences G^+G^- or G^-G^+ for consecutive CH_2–CH_2 bonds have been discarded since they give too short contacts between non-bonded C atoms of the chain [2c, 5]. However, given the complex structure of the mesogenic group, we found that this was not sufficient to discard all conformers with unacceptable contacts between non-bonded atoms, in particular in the case of highly folded conformers, so a direct check was performed on the distances between atoms of the two different mesogenic groups, discarding those conformers for which the minimum distance was less than 3.4 Å. In this way an additional number of 63, 47, 534 and 1036 conformers for D7, D8, D9 and D10, respectively, were discarded (see table 2 below).



Scheme 2. Definition of the conformational degrees of freedom for D*n* dimers.

3. Results and discussion

The thermodynamic properties of D*n* dimers related to the nematic–isotropic transition are summarized in table 1 (they have been adapted from Centore *et al.* [1]). The dimers show thermotropic nematic mesomorphism with odd–even fluctuations; this behaviour, which was first observed in the semiflexible main-chain polymers [8] for which dimers can be considered as models, is typical of nematogenic dimers and it has been observed in many systems [9].

We have generated all conformations of the dimers allowed by the RIS model, assuming conformational degrees of freedom and torsional potentials as described in section 2. The total number of conformations for each dimer is reported in table 2.

Table 1. Thermodynamic data of D*n* dimers (adapted from Centore *et al.* [1]).

	T_{NI}/K	T_{NI}/T_{NI} (D10)	$\Delta S_{NI}/R$
D7	494	0.992	0.97
D8	516	1.036	2.14
D9	487	0.978	0.99
D10	498	1	2.15

Table 2. Number of conformations in the RIS model for D*n* dimers.

Dimer	No. of conformations
D7	3761
D8	9185
D9	21 754
D10	52 772

For each conformation, the τ angle between the elongation axes of the two mesogenic groups of the molecule was calculated (the axes are schematically indicated by arrows in scheme 2). The elongation axis of each mesogen was assumed as the segment connecting the two phenyl C atoms bonded to O atoms.

The potential energy of the generic (*i*th) conformer is given by [3]

$$U(i) = U(i)_{\text{int}} + U(i)_{ext} \tag{1}$$

where $U(i)_{\text{int}}$ is the intramolecular conformational energy, evaluated using torsional potentials reported above, and $U(i)_{ext}$ is the external, intermolecular energy due to the mean field generated by all other molecules. For nematic liquid crystals, $U(i)_{ext}$ is orientation-dependent and, in the most simple model, a Maier–Saupe type expression involving only the mesogenic groups can be used [10, 11]

$$U(i)_{ext} = -X_a\left(1-\frac{3}{2}\sin^2\psi_i^1\right) - X_a\left(1-\frac{3}{2}\sin^2\psi_i^2\right) \tag{2}$$

in which ψ_i^1 and ψ_i^2 are the angles formed by mesogenic groups of the molecule with the director in the *i*th conformation. X_a is the parameter measuring the strength of interaction between the mesogenic groups and the external field.

Let us indicate with $\mathbf{a}_1$ and $\mathbf{a}_2$ unit vectors for the elongation axes of the first and second mesogen, respectively, while τ_{i} is the angle between the mesogens (*i*th conformer) and $\mathbf{n}$ is the unit vector corresponding to the nematic director (figure 1). Let us take, for the rigid spherical motion of the conformer in the external field, a Cartesian coordinate system with z axis coincident with the elongation axis of the first mesogen, the elongation axis of the second mesogen being in the *yz* plane, at τ_i angle with z; let $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ be, as usual, unit vectors for the axes of the Cartesian reference system. Finally, let (ϑ, φ) be the spherical polar coordinates of the director in this reference system.

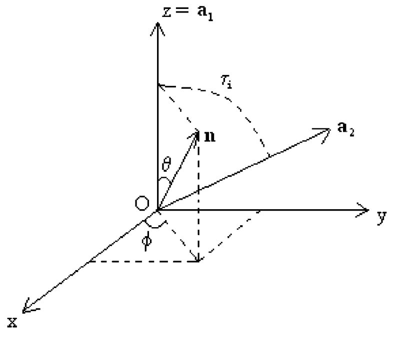


Figure 1. Reference systems for the dimers.

From figure 1 it follows that

$$\begin{aligned}
&\mathbf{a}_1 = \mathbf{k}\\
&\mathbf{a}_2 = \cos\left(\frac{\pi}{2}-\tau_i\right)\mathbf{j} + \sin\left(\frac{\pi}{2}-\tau_i\right)\mathbf{k} = \sin\tau_i\mathbf{j} + \cos\tau_i\mathbf{k}\\
&\mathbf{n} = \sin\vartheta\cos\varphi\,\mathbf{i} + \sin\vartheta\sin\varphi\,\mathbf{j} + \cos\vartheta\,\mathbf{k}
\end{aligned} \tag{3}$$

So we have [12]

$$\begin{aligned}
&\mathbf{n}\cdot\mathbf{a}_1 = \cos\vartheta\\
&\mathbf{n}\cdot\mathbf{a}_2 = \sin\vartheta\sin\tau_i\sin\varphi + \cos\vartheta\cos\tau_i.
\end{aligned} \tag{4}$$

All orientations of the conformer are obtained starting from this configuration by spherical rigid motion of $\mathbf{n}$ around O. During the motion, $U_{\text{int}}(i)$ is constant, whereas $U_{ext}(i)$, in general, is not.

The quantity $U_{ext}(i)$ depends, in general, on the solid angle Ω defining the orientation of the director with respect to the conformer and we must now try to get the explicit dependence. By substituting in equation (2) the angles between the director and the two mesogens given by equation (4) we have

$$\begin{aligned}
U_{ext}(i) = {} & -X_a\left(1-\frac{3}{2}\sin^2\vartheta\right)\\
& -X_a\left[1-\frac{3}{2}\sin^2\arccos(\sin\vartheta\sin\tau_i\sin\varphi\right.\\
& \left.+\cos\vartheta\cos\tau_i)\right]
\end{aligned} \tag{5}$$

or, putting

$$\beta = \arccos(\sin\vartheta\sin\tau_i\sin\varphi + \cos\vartheta\cos\tau_i), \tag{6}$$

$$\begin{aligned}
U_{ext}(i) &= -X_a\left(1-\frac{3}{2}\sin^2\vartheta\right) - X_a\left(1-\frac{3}{2}\sin^2\beta\right)\\
&= -2X_a + \frac{3}{2}X_a\left(\sin^2\vartheta + \sin^2\beta\right).
\end{aligned} \tag{7}$$

The rotational partition function of the *i*th conformer, Q_i, is given by

$$\begin{aligned}
Q_i &= \int_0^{2\pi}\int_0^{\pi} \mathrm{e}^{-\frac{U_{ext}(i)}{k_BT}}\sin\vartheta\,d\varphi\,d\vartheta\\
&= \mathrm{e}^{2X_a^*}\int_0^{2\pi}\int_0^{\pi}\mathrm{e}^{-\frac{3}{2}X_a^*\left(\sin^2\vartheta+\sin^2\beta\right)}\sin\vartheta\,d\varphi\,d\vartheta
\end{aligned} \tag{8}$$

The double integral on the right side is a function of the scaled interaction parameter X_a^* (i.e. $X_a^* = X_a/k_BT$ with k_B Boltzmann constant) and of the angle τ_i, $f_1\left(X_a^*, \tau_i\right)$, that is evaluated numerically. We note that for X_a=0 (isotropic phase), $f_1\left(X_a^*, \tau_i\right) = 4\pi$, as it must be [3].

The total conformational–orientation partition function, Z, is given by

$$Z = \sum_i e^{-\frac{U_{\text{int}}(i)}{k_B T}} Q_i = e^{2X_a^*} \sum_i e^{-\frac{U_{\text{int}}(i)}{k_B T}} f_1\left(X_a^*, \tau_i\right) \qquad (9)$$

The Boltzmann factors, $U_{\text{int}}(i)/k_B T$, have been evaluated at the experimental transition temperature of the dimer.

The statistical weight $p(i)$, for each conformation of dimers, has been calculated according to the relation

$$p(i) = \frac{e^{-\frac{U_{\text{int}}(i)}{k_B T}} Q_i}{Z}. \qquad (10)$$

In this approach, all conformations of dimers allowed by constraints of chemical connection between the two mesogens are generated; each conformation is weighted for its internal energy and for the relative orientation between the mesogenic groups (i.e. the angle τ_i).

In figure 2 is reported the average angle between mesogens, $<\tau>$, calculated according to the relation $\langle \tau \rangle = \sum_i p(i)\tau_i$, as a function of the scaled interaction parameter X_a^* for the dimers.

The first noteworthy feature is the similarity of the curves for dimers of the same parity and their qualitative difference for dimers of different parity. For $X_a^* = 0$ (isotropic phase), $<\tau>$ values are 107.81°, 109.18°, 102.29° and 105.19° for D7, D8, D9 and D10, respectively, and the corresponding distributions of conformers, reported in figures 3–4, look very similar for dimers of the same parity.

In the explored range of X_a^* values, the curves in figure 2 for D8 and D10 are above the curves for D7 and D9, indicating a more bent shape for odd dimers. The behaviour of the curves in figure 2 for high values of X_a^* is also noteworthy. Actually, for very strong fields, conformations with parallel arrangement of mesogens (low U_{ext}) become prevalent, independently

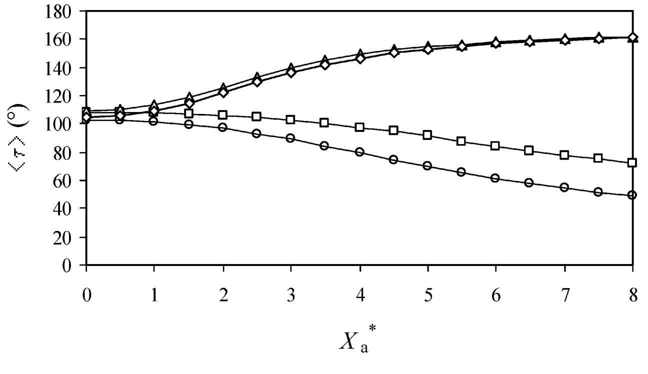


Figure 2. Plot of $<\tau>$ versus X_a^* for D7 (squares), D8 (triangles), D9 (circles) and D10 (diamonds).

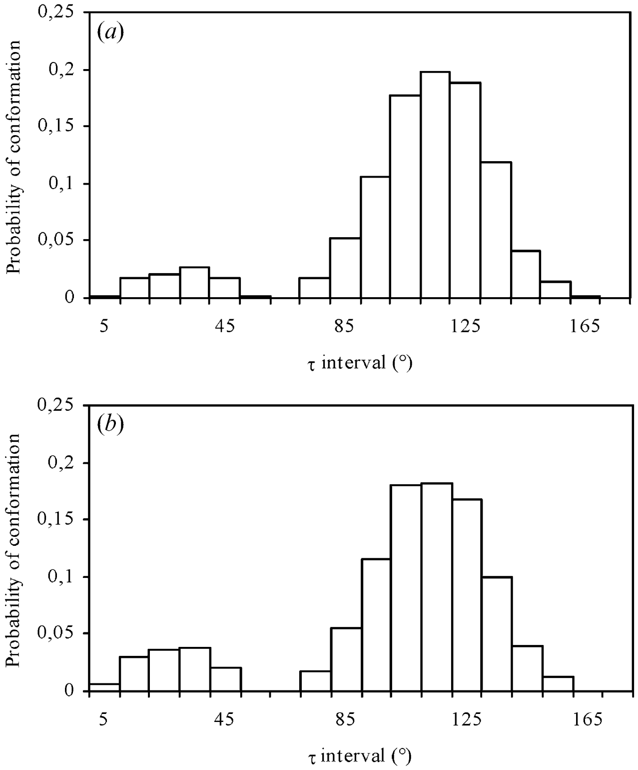


Figure 3. Histograms of the distribution of conformers for (a) D7 and (b) D9 (X_a=0).

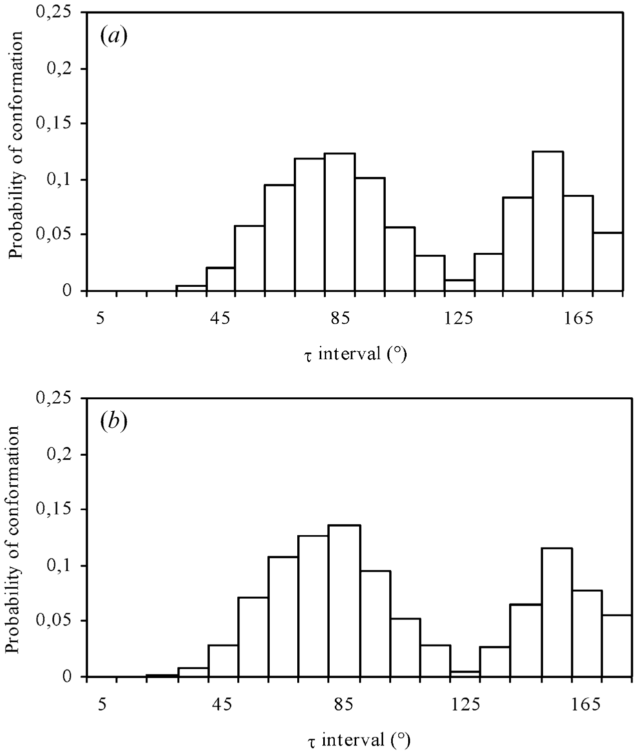


Figure 4. Histograms of the distribution of conformers for (a) D8 and (b) D10 (X_a=0).

from their internal energy; in the case of even dimers this corresponds mainly to select linear parallel conformers (i.e. those with τ close to 180°) and the corresponding asymptotic behaviour is toward high values of $<\tau>$. On the other hand, in the case of odd dimers, the distribution is strongly bimodal and conformers with τ close to 180° (i.e. linear parallel) and to 0° (i.e. parallel folded) are selected (figure 5), giving a (formal) average value not far from 90°. This qualitatively different behaviour, in turn, can be related to the fact that the number of linear parallel conformers is higher for even dimers than for odd ones, whereas, on the contrary, the number of parallel folded conformers is higher for odd dimers than for even. As an example, the number of conformers with $150° \leqslant \tau \leqslant 180°$ is 1.0% for D7 (0.69% for D9) and 26.2% for D8 (24.6% for D10), whereas the number of conformers with $0° \leqslant \tau \leqslant 30°$ is 4.9% for D7 (8.6% for D9) and only 0.05% for D8 (0.12% for D10). A linear parallel and a parallel folded conformer of D9 are reported in figure 6 as an example.

The orientational order parameter of the dimers, S, has been calculated according to the relation

$$S = \sum_i p(i) s_i \qquad (11)$$

with s_i the orientational order parameter of the ith conformer. The latter was calculated according to the relation

$$s_i = 1 - \frac{3}{2} \langle \sin^2 \vartheta \rangle_i \qquad (12)$$

where the bracket implies orientational average for one mesogenic group of the ith conformer. By substituting the proper Boltzmann factors, after simplification, we get the expression

$$s_i = 1 - \frac{3}{2} \frac{\int_0^{2\pi} \int_0^{\pi} \sin^3 \vartheta \, e^{-\frac{3}{2} X_a^* \left(\sin^2 \vartheta + \sin^2 \beta\right)} \, d\varphi \, d\vartheta}{\int_0^{2\pi} \int_0^{\pi} \sin \vartheta \, e^{-\frac{3}{2} X_a^* \left(\sin^2 \vartheta + \sin^2 \beta\right)} \, d\varphi \, d\vartheta} \qquad (13)$$

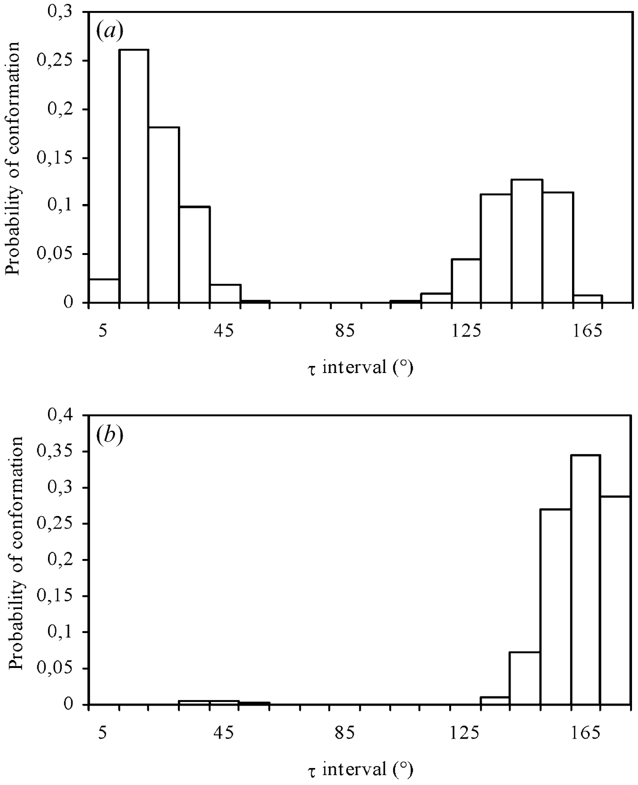


Figure 5. Histograms of the distribution of conformers for (a) D7 and (b) D8 ($X_a^* = 8.0$).

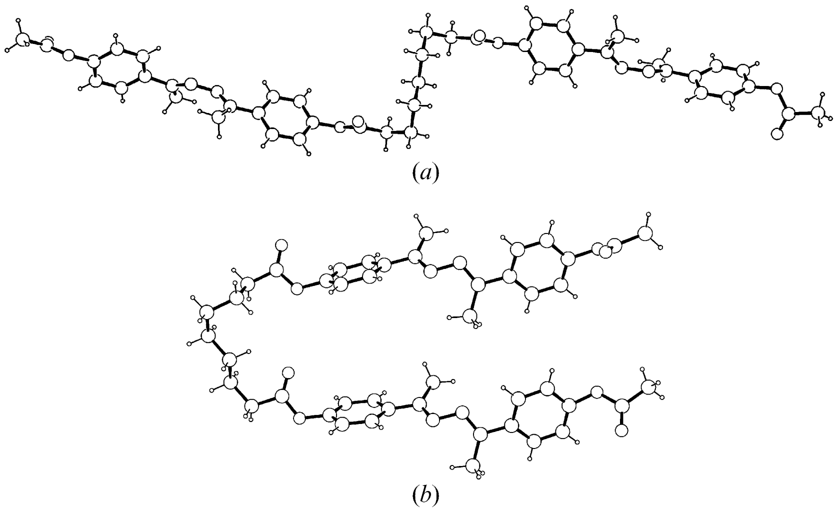


Figure 6. (a) A linear parallel conformer (τ=160.72°) and (b) a parallel folded conformer (τ=2.26°) for D9.

or

$$s_i = 1 - \frac{3f_2(X_a^*, \tau_i)}{2f_1(X_a^*, \tau_i)} \quad (14)$$

with the function

$$f_2(X_a^*, \tau_i) = \int_0^{2\pi}\int_0^{\pi} \sin^3\vartheta \, e^{-\frac{3}{2}X_a^*(\sin^2\vartheta + \sin^2\beta)} \, d\varphi \, d\vartheta \quad (15)$$

evaluated numerically. The dependence of S on X_a^* is reported in figure 7.

Again, we note the closeness of curves for dimers of the same parity when plotted against the scaled X_a^* parameter (this holds, in particular, for even dimers, analogously to the corresponding behaviour of $<\tau>$, cf. figure 2). The behaviour is very similar to the theoretical curves reported by Ferrarini *et al.* in their theory of dimers as mixtures of the linear and the bent conformers [4]. Clearly, in comparing figure 7 and figure 2 for odd dimers in the high X_a^* region, we must take into account the fact that the conformational distribution is bimodal (*vide supra*).

From figure 7 it follows that if one knows the orientational order parameter of the dimers, the values of X_a^* can be calculated and, from these, one could have access to the (calculated) statistical distribution of the conformers in the nematic phase. The value of X_a^* at the nematic–isotropic transition, X_a^{*NI}, can be estimated by the condition that the Helmholtz free energy (A) of the isotropic and nematic phases is equal, i.e.

$$\Delta A_{NI} = A_I - A_N = 0. \quad (16)$$

This condition, which is frequently used in the mean field analysis of liquid crystals [2b, 2c, 3, 4], corresponds to neglecting the (small) volume change at the N–I transition.

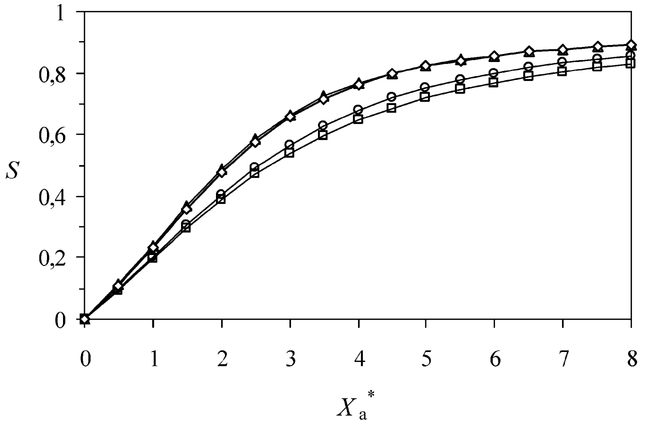


Figure 7. Plot of the orientational order parameter, S, versus X_a^* for D7 (squares), D8 (triangles), D9 (circles) and D10 (diamonds).

The Helmholtz free energy of the isotropic phase (per mol of compound) is

$$A_I = -RT \ln Z_I(X_a = 0) \quad (17)$$

and that of the nematic phase is [2c, 3]

$$A_N = -RT \ln Z_N - \frac{\langle \bar{U}_{\mathrm{ext}} \rangle}{2} \quad (18)$$

where the bar implies conformational average and the bracket orientational average).

The orientationally averaged external energy of the ith conformer, $<U_{ex}(i)>$, is obtained by averaging the expression of equation (7). After proper manipulations, the following expression is obtained:

$$\frac{\langle U_{ext}(i) \rangle}{k_B T_{NI}} = -X_a^* \left[\left(1 - \frac{3f_2(X_a^*, \tau_i)}{2f_1(X_a^*, \tau_i)} \right) + \left(1 - \frac{3f_3(X_a^*, \tau_i)}{2f_1(X_a^*, \tau_i)} \right) \right] \quad (19)$$

with

$$f_3(X_a^*, \tau_i) = \int_0^{2\pi}\int_0^{\pi} \sin^2\beta \sin\vartheta \, e^{-\frac{3}{2}X_a^*(\sin^2\vartheta + \sin^2\beta)} \, d\varphi \, d\vartheta. \quad (20)$$

The fully averaged external energy is given by the expression

$$\langle \bar{U}_{ext} \rangle = \sum_i p(i) \langle U_{ext}(i) \rangle. \quad (21)$$

So we have

$$\Delta A_{NI} = -RT \ln Z_I + RT \ln Z_N + \frac{1}{2} RT \langle \bar{U}_{ext} \rangle = 0. \quad (22)$$

In equation (22), the quantities Z_N and $<\bar{U}_{ext}>$ depend parametrically on X_a^*. Starting from $X_a^* = 0$, the expression is calculated for increasing values of X_a^* till it is equal to zero, and X_a^{*NI} is obtained. From the values of X_a^{*NI} it is possible to estimate the mesogenic group order parameter at the N–I transition, S [equations (11)–(15)], as well as other thermodynamic properties of the dimers, such as ΔS_{NI} and T_{NI}. These are evaluated using the following equations, adapted from Ferrarini *et al.* [2b]

$$T_{NI}^{calc} = \text{const} \frac{S}{V X_a^{*NI}} \quad (V = \text{molecular volume}) \quad (23)$$

$$\frac{\Delta S_{NI}^{calc}}{R} = \left(\frac{\langle \bar{U}_{\mathrm{int}}^I \rangle - \langle \bar{U}_{\mathrm{int}}^N \rangle}{RT_{NI}} \right) - \frac{1}{2} \frac{\langle \bar{U}_{ext} \rangle}{RT_{NI}}. \quad (24)$$

The transition temperatures have been scaled with the

Table 3. Calculated thermodynamic properties of D*n* dimers at the N–I transition.

D*n*	X_a^{*NI}	S	V/Å^3	$T_{NI}^c/T_{NI}^c(D10)$	$\Delta S_{NI}^c/R$
D7	1.730	0.338	953	0.89	0.60
D8	2.090	0.504	977	1.07	1.05
D9	1.924	0.389	1001	0.88	0.76
D10	2.168	0.511	1025	1	1.11

transition temperature of the D10 dimer and approximate molecular volumes have been estimated from the crystal structures of D8 and D9 dimers [1].

The calculated thermodynamic properties are summarized in table 3.

As can be seen, significant odd–even fluctuations are predicted for the mesogenic group order parameter, *S*. The pattern of the predicted order parameters is satisfying not only because the values are quite realistic both for odd members and for even ones [they can be compared, for example, with experimental values for the series of α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes] [4a] but also because some more subtle effects, such as the increase of the orientational order for odd members with increasing the spacer length, [9c, 9d], are apparently reproduced.

Odd–even fluctuations are also predicted for the transition temperatures, with the spanning of the fluctuations becoming reduced along the series, in accordance with the experimental data, and in the transition entropies, ΔS_{NI}. In the latter case, however, the quantitative agreement with experimental data is less satisfying, and the calculated values appear to be underestimated. This underestimation is present also in other mean-field RIS theoretical analyses of mesogenic dimers [2b] so it may reflect intrinsic limits of the model, as was already pointed out [2b]. We note, however, that the different degree of underestimation between even and odd dimers is somewhat reversed in our analysis as compared with similar analyses [2b]: this could be related, perhaps, to our choice of neglecting contributions to the potential of mean torque coming from the flexible spacer.

The contribution of the conformational entropy to the total transition entropy is small (below 5%), in agreement with other theoretical analyses of mesogenic dimers [2b].

The distributions of conformers in the nematic phase at nematic–isotropic transition, calculated assuming $X_a^{*NI}=1.73$ for D7, $X_a^{*NI}=2.090$ for D8, $X_a^{*NI}=1.924$ for D9 and $X_a^{*NI}=2.168$ for D10, are reported in figures 8 and 9.

They correspond, respectively, to $<\tau>=106.79°$ for D7 and 127.28° for D8 (for D9 and D10 the corresponding $<\tau>$ values are 97.19° and 124.41°, respectively). As can be seen, for odd dimers the distribution of conformers in the nematic phase is not very different from the isotropic phase. On the other hand, for even dimers a relevant increase of linear extended conformers and a reduction of bent conformers (i.e. those with τ around 80°) is observed in the nematic phase, as compared with the isotropic phase. As an example, the probability of conformers with $150° \leqslant \tau \leqslant 180°$ (i.e. linear extended) is only 3.5% for D7 and 2.2% for D9, whereas it is 46.6% for D8 and 46.9% for D10; in the isotropic phase ($X_a^*=0$) at the same temperature, the corresponding probabilities are 1.6% for D7 (1.2% for D9) and 26.2% for D8 (24.9% for D10).

4. Conclusion

In conclusion, although the assumptions of our model are very simple, the predictions are in reasonable

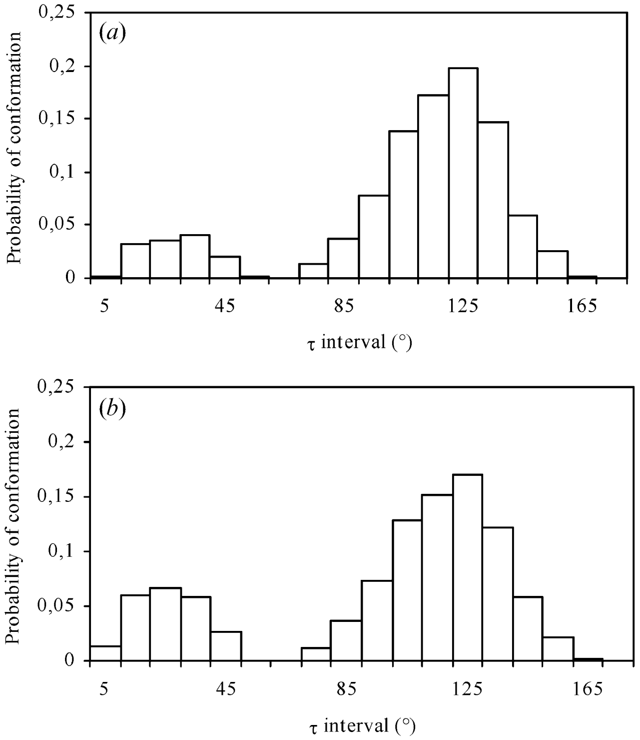


Figure 8. Histograms of the distribution of conformers for (a) D7 ($X_a^*=1.730$) and (b) D9 ($X_a^*=1.924$).

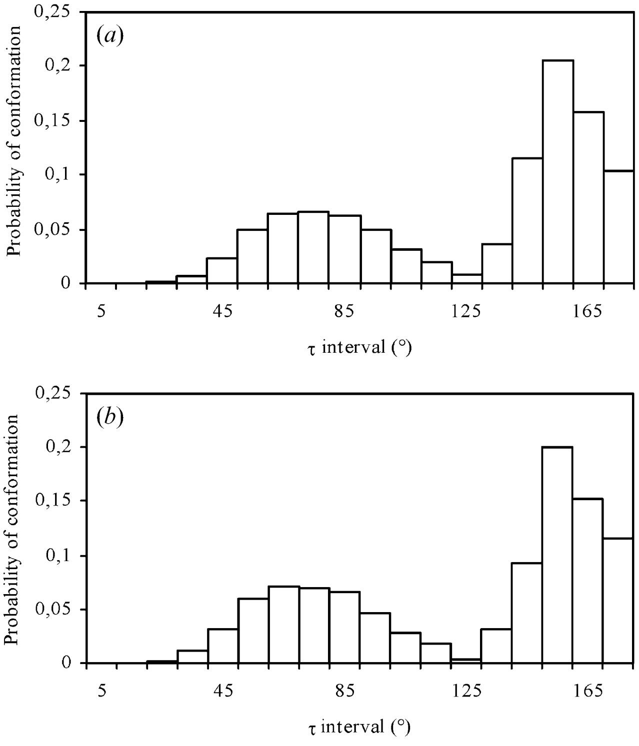


Figure 9. Histograms of the distribution of conformers for (a) D8 ($X_a^* = 2.090$) and (b) D10 ($X_a^* = 2.168$).

agreement with the experimental data and with the general model of LC dimers developed by Ferrarini *et al.* [4]. We stress, however, that our main interest is in a comparative analysis between D*n* dimers; to this respect, we think that all systematic errors present in the model should affect the results of the comparative analysis at a minor level.

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