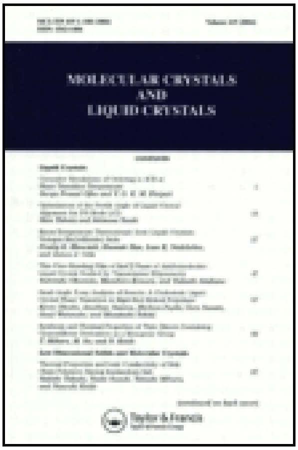

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Shape Parameters and Uniaxial Deformability of Mesogenic Dimers with Flexible Spacers

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To cite this article: H. S. Serpi & D. J. Photinos (2000): Shape Parameters and Uniaxial Deformability of Mesogenic Dimers with Flexible Spacers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 205-216

To link to this article: http://dx.doi.org/10.1080/10587250008023178

Mol. Cryst. and Liq. Cryst., 2000, Vol. 352, pp. 205-216
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Printed in Malaysia

Shape Parameters and Uniaxial Deformability of Mesogenic Dimers with Flexible Spacers

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We introduce a set of statistical shape parameters that quantify the concept of the "average shape" of flexible molecules in isotropic and in nematic media. These shape parameters are obtained as conformational averages of geometrical tensors constructed from the relative positions and orientations of the sub-molecular units. The deformability of the average molecular shape is quantified in terms of the variation of the respective shape parameters under the action of an ordering field. The quantification of shape and deformability is applied to the description of dimers consisting of two rod-like mesogenic units connected by an alkyl spacer.

Keywords: nematic; dimers; molecular shape parameters; conformational average

1. INTRODUCTION

Dimer mesogens typically consist of two mesogenic cores, of the calamitic or discotic type, tethered by a flexible hydrocarbon spacer. They have been extensively studied [1-7] in connection with the molecular modelling of liquid crystalline polymers and with the design of novel mesophases. Depending on the structure of the mesogenic cores and their linkage to the spacer, various types of dimer mesogens can be formed, exhibiting different macroscopic properties and mesophase stability. Furthermore, the stability depends not only on the length of the spacer but also on whether the spacer chain consists of an even or odd number of segments (chain parity effects) [1,3,5].

For the description of dimers it is necessary, in addition to the characteristics of the two mesogenic cores forming the dimer, to take into account the intramolecular interactions of the cores and their relative configurations, i.e. the conformations of the spacer chain. In most cases of interest the set of relevant conformations is enormous. It is therefore desirable to look into the possibility of obtaining useful insights not directly from the conformations but from a smaller set of quantities describing conformation-weighted molecular attributes of the dimer. The purpose of the present work is to introduce such quantities, to be referred to as "shape parameters", and to identify the ones that are more sensitive to the mesogenic properties of dimers. These parameters, being of statistical nature, are in general expected to depend on the temperature as well as on the type and strength of molecular organisation in the bulk phase. We therefore study the variation of the shape parameters with ordering strength. The variation provides, in turn, a measure of the deformability of the "average" dimer under the action of the ordering constraints. Our considerations are restricted to symmetric dimers with rigid-rod mesogenic units. We focus particularly on the effects of varying the length of the alkyl spacer and of changing the mode of core-spacer linkage. The approach, however, can be used more generally to describe a variety of flexible mesogens.

The shape parameters are defined in section 2 and their relevance to molecular shape and ordering is presented. Their values for typical dimers, both in the isotropic phase and in the uniaxial nematic phase, are calculated in section 3. The results are discussed in section 4 and the conclusions are stated in section 5.

2. THEORY

We consider a symmetric dimer with two rod-like mesogenic cores represented by the unit vectors $\mathbf{L}$ and $\mathbf{L}'$ and interacting with the molecules of a solvent only via hard body repulsive forces. The relative configuration of the cores is determined by the conformational state n of the spacer. The segments of the spacer chain normally have an appreciable contribution to the interaction of the dimer with its surroundings [2,6]. For simplicity, however, this contribution can be neglected in comparison with the interactions of the mesogenic cores. Within such simplification, the shape of the dimer is adequately described for any conformational state by providing the corresponding directions of the core vectors $\mathbf{L}$, $\mathbf{L}'$ and the connecting vector $\vec{r}$ (Fig.1c). Accordingly, any physical quantities referring to the state of a single molecule can be determined from these three vectors.

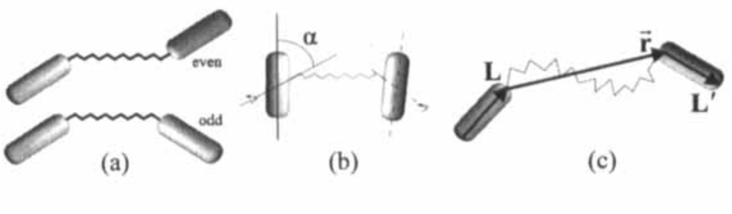

FIGURE 1 Generic structures of symmetric dimers with rod-like mesogenic cores. (a) Terminal linkage with even and odd spacers in the most extended (*all-trans*) conformation. (b) Lateral linkage at an angle α; spacer in *all-trans* conformation. (c) Core directions, $\mathbf{L}$, $\mathbf{L}'$ and spacer end-to end vector $\vec{r}$ for a terminally linked dimer.

A fundamental quantity describing the behaviour of the dimer in a spatially uniform solvent is the average volume $\overline{V}$ that is excluded to a solvent molecule because of the presence of the dimer molecule. This quantity depends on $\mathbf{L}$, $\mathbf{L}'$, $\vec{r}$ and is obtained by averaging the solvent-dimer excluded volume over the positions and orientations of the solvent. The average excluded volume $\overline{V}$, being a scalar quantity, can be put in the form of a tensor expansion as follows,

$$\overline{V} = \sum_{(\ell)} A_{\ell}(\mathbf{L},\mathbf{L}',\vec{r}) \cdot \langle B_{\ell} \rangle \quad , \qquad (1)$$

where $\langle B_{\ell} \rangle$ is a tensor of rank ℓ, averaged over the positions and orientations of the solvent molecule. and A_{ℓ} is a tensor of rank ℓ which can be formed from the vectors $\mathbf{L}$, $\mathbf{L}'$, $\vec{\mathbf{r}}$. The dot indicates a scalar product of the two tensors and the summation runs over all ranks ℓ.

In the isotropic phase of the solvent

$$\overline{V} = A_0 < B_0 >_{iso} \tag{2}$$

since all the components of the higher rank tensors $< B_\ell >$ vanish as a result of the orientation-independent averaging. In the above equation $< \ >_{iso}$ indicates averaging in the isotropic phase of the solvent.

In the nematic phase [6], all the odd rank components vanish because of the apolar averaging. The leading anisotropic contributions come from the second rank tensors, with the successive contributions becoming negligible with increasing tensor rank. Accordingly, the interaction of the dimer with a nematic solvent is reasonably described by a truncated expansion of the form

$$\overline{V} \approx A_0 < B_0 >_{nem} + A_2 \cdot < B_2 >_{nem} \tag{3}$$

where $< \ >_{nem}$ indicates averaging in the nematic phase of the solvent.

A good quantitative description of the ordering of dimers in a nematic solvent can be achieved with the so-called modular approach [2,6,8,9]. The modular form of A_2 in the present case consists of the sum of two second rank terms describing the independent interaction of the two mesogenic cores with the aligning field of the solvent. Aside from that, A_2 contains no information on the shape of the dimer. Such information is contained in the scalar contribution A_0, to which we now focus our attention.

The basic non-trivial scalar quantities that can be formed from the unit vectors $\mathbf{L}$, $\mathbf{L}'$ and the core-core vector $\vec{\mathbf{r}}$ are the following five:

$$r, \quad \mathbf{L}\cdot\mathbf{L}', \quad \mathbf{L}\cdot\vec{\mathbf{r}}+\mathbf{L}'\cdot\vec{\mathbf{r}}, \quad (\mathbf{L}\times\mathbf{L}')\cdot\vec{\mathbf{r}} \quad \text{and} \quad (\mathbf{L}\times\vec{\mathbf{r}})\cdot(\mathbf{L}'\times\vec{\mathbf{r}}),$$

where account has been taken of the symmetric structure of the dimer which implies invariance with respect to the simultaneous replacements $\mathbf{L} \to -\mathbf{L}'$, $\mathbf{L}' \to -\mathbf{L}$ and $\vec{\mathbf{r}} \to -\vec{\mathbf{r}}$. All the other scalar quantities that can be formed from $\mathbf{L}$, $\mathbf{L}'$, $\vec{\mathbf{r}}$, are obtained as powers or products of the above five scalars. The particular combination in which such quantities enter in the expression of A_0 depends on the details of the size and shape of the mesogenic units and of the solvent molecules. The values of the five scalar quantities, and of their combinations, generally depend on the conformation of the dimer. When averaged over all the conformations, each of these scalars produces a shape parameter. The conformational averaging can be carried out in the isotropic as well as in the ordered phase of the solvent. Comparison of the conformational averages in the two phases reveals the changes induced on the average shape of the dimer as a result of its ordering within the solvent.

The conformational averaging in the isotropic phase is done by assigning to each conformation n of the spacer a statistical weight

$$\mathcal{W}(n) = \exp(-E(n)/kT) \quad , \qquad (4)$$

where E(n) is the conformational energy of the spacer. In the ordered phase there is an additional weight factor which depends on the orientation of the mesogenic cores relative to the ordered solvent. According to the modular scheme [2,6,9], this weight factor is given by the expression

$$\mathcal{W}'(\mathbf{L},\mathbf{L}') = \exp(W^{*}\{3/2[(\mathbf{L}\cdot\mathbf{z})^{2} + (\mathbf{L}'\cdot\mathbf{z})^{2}] - 1\}) \quad , \qquad (5)$$

where W^{*} measures the strength of the ordering of the solvent phase ($W^{*}=0$ in the isotropic phase) and $\mathbf{z}$ is along the nematic director. The averaging is done simultaneously over the conformations of the spacer, weighted according to Equation 4, and the orientations of a dimer-fixed molecular frame relative to a frame of phase-fixed axes, weighted according to Equation 5.

Each of the basic shape parameters reflects certain features of the "average" molecular shape. Specifically, $<r>$ gives the average distance between the linkage points of the spacer and is therefore related to the average length of the dimer. The relative elongation is given by the scaled parameter $SP_1 = <r>/r_{max}$, where r_{max} is the maximal extension of the spacer, i.e. the value of r in the all-trans conformation of the spacer.

The mutual alignment of the two mesogenic cores is conveyed by the shape parameter $SP_2 = <\mathbf{L}\cdot\mathbf{L}'>$. The respective values range from 1, for parallel-core conformations, to −1 for antiparallel. Since the ordering in the nematic phase is apolar, i.e. invariant with respect to inversions of the direction of either of the vectors $\mathbf{L}$, $\mathbf{L}'$, a relevant measure of mutual alignment in the presence of direction-inversion symmetry is provided by the shape parameter $SP_3 = < 3/2\,(\mathbf{L}\cdot\mathbf{L}')^2 - 1/2 >$.

The degree of colinearity of the cores with the core-core vector is conveyed by $SP_4 = < \mathbf{L}\cdot\bar{r} + \mathbf{L}'\cdot\bar{r} > / 2r_{max}$. The values of SP_4 range from +1 (for perfect colinearity) to −1 (for fully extended spacer and with the two cores back-folded along $\bar{r}$).

The above four shape parameters cannot make direct distinctions between planar conformations, i.e. with $\mathbf{L}$, $\mathbf{L}'$, $\bar{r}$ contained in a single plane, and non-planar ones. The extent of non-planarity of the average molecular shape is reflected on $< (\mathbf{L}\times\mathbf{L}')\cdot\bar{r} >$ which receives contributions only from non-planar conformations. This shape parameter indicates also the possible lack of a plane of symmetry of the averaged dimer shape. For dimers exhibiting such a plane of symmetry (normally the plane of the all-trans conformation of the spacer) this shape parameter vanishes, in which case the degree of non-planarity is conveyed primarily by $SP_5 = < ((\mathbf{L}\times\mathbf{L}')\cdot\bar{r})^2 > / r_{max}^2$.

Finally, $SP_6 = < (\mathbf{L}\times\bar{r})\cdot(\mathbf{L}'\times\bar{r}) > / r_{max}^2$ gives a combined measure of planarity and colinearity.

3. CALCULATIONS

Calculations of the basic shape parameters introduced in the previous section are performed for model dimers consisting of an alkyl spacer and two rod-like mesogenic cores. The spacer is linked either at the end of the rod axis (terminal linkage, Fig. 1c) or laterally at an angle α to that axis (lateral linkage, Fig. 1b).

The conformations of the spacer are generated according to the standard 3-state RIS scheme [8,9]. Conformations leading to self-intersections of the dimer molecule are rejected. In all the calculations the dihedral angle for gauche rotations is set at 113°, and the *gauche-trans* energy difference is set at $E_{tg}/kT = 1.0$. The value of 112.5° is used for the C-C-C bond angle. The C-C bond length is taken to be 1.53Å and the united CH_2 atoms are assigned a van der Waals radius of 1.68Å. For the detection of self-intersections within the dimer, the mesogenic cores are treated as spherocylinders of diameter 6Å and total length 12Å.

Calculations are done both for the isotropic phase of the solvent ($W^*=0$) and for the nematic phase for different values of the ordering strength W^*. The spacer length, measured by the number N of carbons in the spacer chain, was varied from N=5 to N=12. The results presented here are for dimers with terminal linkage or with lateral linkage at an angle $\alpha=60^\circ$.

Figure 2 shows the results of the calculations of the basic shape parameters of dimers in an isotropic solvent as a function of spacer length. The same shape parameters have been calculated for dimers in the nematic solvent, as a function of the ordering strength W^* of the solvent. The results for dimers with spacer lengths N=10, 11 are plotted in Figure 3. The probability distribution of the relative orientations $\mathbf{L}\cdot\mathbf{L}'$ of the mesogenic cores has also been calculated for the terminally linked dimers with N=10 and 11 in the isotropic solvent and is shown in Figure 4.

4. DISCUSSION

The results of the calculations lead to the following inferences regarding the shape and deformability of the dimers studied.

The reduced spacer length SP_1 decreases with increasing N in the isotropic phase (Fig. 2a). In the nematic phase SP_1 is essentially independent of W^* (Fig. 3a) in the case of lateral linkage. In the case of terminal linkage opposite trends of variation are exhibited depending on the parity of N. The increase of SP_1 for N=10 is consistent with the favouring of more extended conformations on increasing the strength of nematic ordering. By contrast, the decrease of SP_1 for N=11 reflects the favouring of "U"-shaped conformations. This is in accord with the dependence of SP_4 on W^* (Fig 3b), from which it follows that $\vec{r}$ tends to be, on the average, at right angles to the mesogenic cores in the case of lateral linkage whereas it tends to align with the cores in the case of linear linkage with the N=10 spacer. For N=11, $\vec{r}$ tends to form large angles with the cores on increasing W^*. The odd-even trends observed for these shape parameters, as well as for others to be discussed below, are related to the geometry of the fully extended (*all trans*) conformation of the spacer (Fig. 1a). For even N the two ends are parallel and therefore can align simultaneously in the nematic medium whereas for odd N the two ends are at an angle, thus producing a less directional structure.

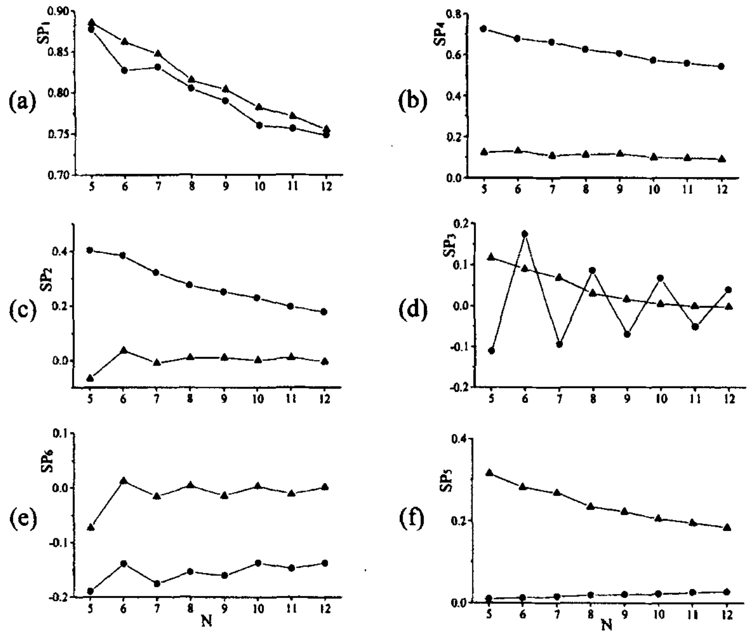

FIGURE 2 Calculated dependence of the shape parameters $SP1=\langle r\rangle/r_{max}$, $SP2=\langle L\cdot L'\rangle$, $SP3=\langle 3/2(L\cdot L')^2-1/2\rangle$, $SP4=\langle L\cdot\vec{r}+L'\cdot\vec{r}\rangle/2r_{max}$, $SP5=\langle((L\times L')\cdot\vec{r})^2\rangle/r_{max}^2$ and $SP6=\langle(L\times\vec{r})\cdot(L'\times\vec{r})\rangle/r_{max}^2$ on the spacer length N (number of carbons in the alkyl chain) in the isotropic phase. Dots correspond to terminally linked dimers and triangles correspond to lateral linkage at α=60°.

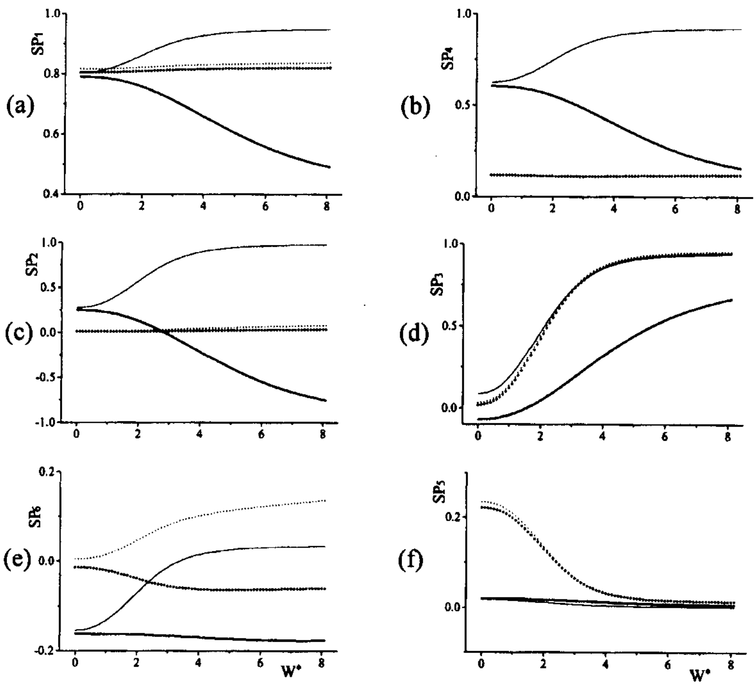

FIGURE 3 Calculated dependence of the shape parameters SP1 - SP6 on the strength W* of the ordering in the nematic solvent for terminally linked dimers (continuous lines) and laterally linked ones at α=60° (dotted lines) and for spacer lengths of N=10 (fine lines) and N=11 (bold lines).

The shape parameter that shows most dramatically the odd-even alternations in the isotropic phase is SP3 shown in Figure 2d. The effect is large for the dimers with terminal linkage and practically disappears for lateral linkage with α=60°. This shape parameter is a most sensitive indicator of the orientability of the dimers in the nematic field. Its odd-even alternations are further enhanced on increasing the strength W* of the orienting field (Fig. 3d). It is perhaps noteworthy that the odd-even alternations are not reflected on the values of $<\mathbf{L}\cdot\mathbf{L}'>$ in the isotropic environment (Fig. 2c). This result is readily explained with the help of the probability distributions of $\mathbf{L}\cdot\mathbf{L}'$ shown in Figure 4. Although the distributions are qualitatively different for N=10 and 11, the resulting average values of $<\mathbf{L}\cdot\mathbf{L}'>$ do not differ substantially due to cancellations between negative and positive contributions. Such cancellations do not occur when evaluating the second moment $<(\mathbf{L}\cdot\mathbf{L}')^2>$ which produces the shape parameter SP_3 of Figure 2d.

Some effects of parity alternations are exhibited by SP_6 in Figure 2e. In the nematic phase this parameter shows different behaviour depending on parity and type of linkage. In particular it tends to vanish for even spacers with terminal linkage, indicating the favouring of essentially collinear configurations of $\mathbf{L}$, $\mathbf{L}'$, $\hat{\mathbf{r}}$. For odd spacers with terminal linkage it remains nearly constant at a small negative value indicating the favouring of "U"-shaped configurations. For lateral linkage this shape parameter starts out from essentially vanishing values for both N=10 and 11 and grows slowly with W^* in opposite directions. It grows positive for N=10, indicating the favouring of a statistically planar, oblique "H"-like configuration of the vectors $\mathbf{L}$, $\mathbf{L}'$, and $\hat{\mathbf{r}}$, with $\mathbf{L}$, $\mathbf{L}'$ showing a slight preference to mutually parallel disposition. The negative values for N=11 are indicative of the favouring of a similar H-shaped arrangement only with slight preference for antiparallel disposition of $\mathbf{L}$, $\mathbf{L}'$.

The tendency towards a planar arrangement of the dimer, on increasing W^*, is clearly indicated by the plots of the SP_5 in Figure 3f. This parameter, which is a measure of the non-planarity of the dimer shape, is essentially zero for all the terminally linked dimers, both in the isotropic (Fig 2f) phase and in the nematic (Fig. 3f), for any value of W^*. For lateral linkage, on the other hand, it starts out at some appreciable value in the isotropic phase, indicating considerable non-planarity. It then decreases rapidly with increasing W^*, for odd and even spacers alike.

As shown in Figure 3a, b and c, the shape parameters SP_1, SP_4 and SP_2 are essentially unaffected by the ordering field in the case of laterally linked dimers. In other words, these dimers behave as 'non-deformable' with respect to those shape parameters. A similar behaviour is observed in Figure 3f for the shape parameter SP5 of the terminally linked dimers.

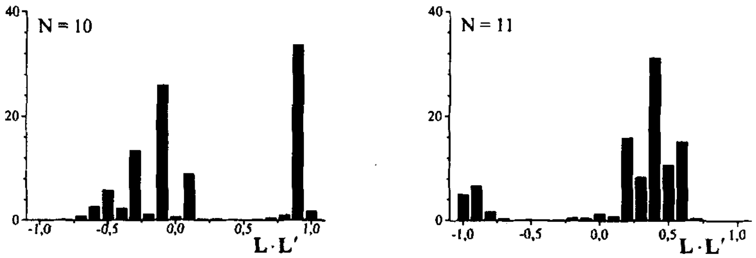

FIGURE 4 Calculated probability distribution of L·L' for terminally linked dimers with N=10 and N=11 in the isotropic phase.

5. CONCLUSIONS

The essential features of the conformationally averaged shape of mesogenic dimers, both in isotropic and in nematic media, can be described in terms of a small number of shape parameters. The combined information obtained from the calculated shape parameters indicates that on increasing the strength of nematic ordering all dimers tend to a planar average shape. For terminally linked dimers this shape is elongated or "U"-like for even or odd spacers respectively. For laterally linked dimers the predominant shape is "H"-like.

Acknowledgements

This research is supported by the TMR Programme under contract FMRX CT97 1021 and by the Educational and Initial Vocational Training Program on Polymer Science and Technology - 3.2a, 33H6.

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