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The average shapes of flexible mesogenic molecules On the choice of reference frame

A. Emerson[a]; G. R. Luckhurst[a]; R. W. Phippen[b]
[a] Department of Chemistry, University of Southampton, Southampton, England [b] IBM United Kingdom Ltd., UK Scientific Centre, Winchester, England

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The average shapes of flexible mesogenic molecules

On the choice of reference frame

by A. EMERSON and G. R. LUCKHURST*
Department of Chemistry, University of Southampton,
Southampton SO9 5NH, England

and R. W. PHIPPEN
IBM United Kingdom Ltd., UK Scientific Centre, Athelstan House,
St Clement Street, Winchester SO23 9DR, England

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The flexibility of most mesogenic molecules creates a problem when we wish to consider their shape, especially as the anisotropy in this is often invoked to explain liquid-crystalline behaviour. It has been suggested that images constructed from the average positions of atoms in the molecule with superimposed ellipsoids representing the mean square displacements of the atoms could present one solution to the problem. However, the nature of the image necessarily depends on the choice of the reference frame set in the molecule. Here we show how the images change as the atoms used to define the reference frame move along a single heptyl chain attached to a mesogenic core in both the isotropic and nematic phases. The appearance of the images and how they change with phase and reference frame are discussed in general terms. In addition, the possible relationship between the images and the order parameters for axes set in the same reference frame as that used to construct the image is explored. The significance of the fluctuational ellipsoids is also considered although they appear only to influence the order parameters at second order.

1. Introduction

The majority of mesogenic molecules are flexible, usually because they contain one or more alkyl chains which can adopt numerous conformations [1]. In spite of this the chemical structures of such molecules are often shown with the alkyl chains in their all-*trans* conformation, which is clearly an oversimplification. At the other extreme molecular theories of chain ordering can be used to obtain the complete conformational distribution [2] although this surfeit of information may be extremely hard to appreciate. To overcome both of these difficulties we have proposed a procedure with which to visualize the average shape of a flexible molecule, in a form analogous to a conventional chemical structure [3]. To construct these images the coordinates of each atom in the molecule are averaged over all conformations. The average coordinates of those atoms which are bonded chemically are then linked together to give an average structure with a familiar appearance. However, in order that this image is not taken to imply that the molecule exists exclusively in this structure, ellipsoids are centred on each atom with dimensions which reflect the extent of the fluctuations away from the average location of the atom. These fluctuational ellipsoids also define, in some way, the extremes of the molecular shape and its anisotropy which is important in determining the liquid-crystalline properties.

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* Author for correspondence.

The nature of the images obtained with this procedure was illustrated for the hexyl and heptyl members of the homologous series of 4-*n*-alkyl-4′-cyanobiphenyls. The reference frame used to define the atomic coordinates was located with its origin at the 4 position in a phenyl ring with the z axis along the para axis and the y axis in the plane formed by the origin and the first two carbon atoms in the chain. However, it was noted that the average structure calculated would change with the location of the reference frame. For example, with the original choice of frame the fluctuational ellipsoid for the terminal carbon atom in the alkyl chain is dominant, whereas if the frame had been located in the three carbon atoms at the end of the chain then the mesogenic group would have had the largest ellipsoid. Here we show how the image representing the average structure of a flexible molecule changes with the location of the reference frame and consider how such images might be employed to understand certain aspects of liquid-crystalline behaviour.

2. Calculation of the average structure

In order to illustrate the large changes in the average structure caused by varying the location of the reference frame we consider the nematogen 4-*n*-heptyl-4′-cyanobiphenyl. The molecular flexibility is taken to result from conformational changes associated entirely with the terminal alkyl chain. To describe these we use the Flory rotameric state model in which the chain can adopt a discrete number of conformations [4]. The average coordinates of an atom i are then

$$\bar{\mathbf{r}}_i=\sum_n p_n\mathbf{r}_i^n, \tag{1}$$

where $\mathbf{r}_i^n$ is the location of this atom in the nth conformer whose probability is p_n. The mean square displacements of an atom away from this average position are calculated from [3]

$$\sigma_i^2=\sum_n p_n(\mathbf{r}_i^n\mathbf{r}_i^n-\bar{\mathbf{r}}_i\bar{\mathbf{r}}_i). \tag{2}$$

This tensor is not necessarily diagonal in the reference frame and so it is diagonalized and the principal elements or eigenvalues of the tensor are used to construct an ellipsoid with its semi-axes equal to σ_i. The orientation of the fluctuational ellipsoid in the reference frame is determined from the eigenvectors for σ_i^2. We note that the fluctuational ellipsoids are necessarily symmetric because they are related to an even power of the atomic displacement. However the weighted distribution of an atom about its mean position will not, in general, be symmetric. This is especially true within a liquid crystal phase where the more anisotropic conformers are favoured. The problem of reflecting this asymmetric distribution in the fluctuational shape is one which we intend to address elsewhere.

According to the Flory model the internal energy of a conformer, needed to calculate p_n, is given by

$$U_{\text{int}}(n)=N_{\text{g}}E_{\text{tg}}+N_{\text{g}\pm\text{g}\mp}E_{\text{g}\pm\text{g}\mp}, \tag{3}$$

where N_{g} is the number of a gauche links in a conformer and $N_{\text{g}\pm\text{g}\mp}$ is the number of $\text{g}^{\pm}\text{g}^{\mp}$ sequences. The ability of a conformer in the isotropic phase is then

$$p_n=Z^{-1}\exp\{-U_{\text{int}}(n)/kT\}, \tag{4}$$

where Z is the conformational partition function

$$Z=\sum_{n}\exp\{-U_{\mathrm{int}}(n)/kT\}. \tag{5}$$

Those conformers in which atoms overlap are excluded from the calculation. Within the nematic phase the conformational distribution is changed by the presence of the potential of mean torque or ordering potential which favours the more elongated conformers. This modified conformational distribution function is given by the Emsley–Luckhurst theory [5] as

$$p_n=Q_n\exp\{-U_{\mathrm{int}}(n)/kT\}/\sum_{n}Q_n\exp\{-U_{\mathrm{int}}(n)/kT\}. \tag{6}$$

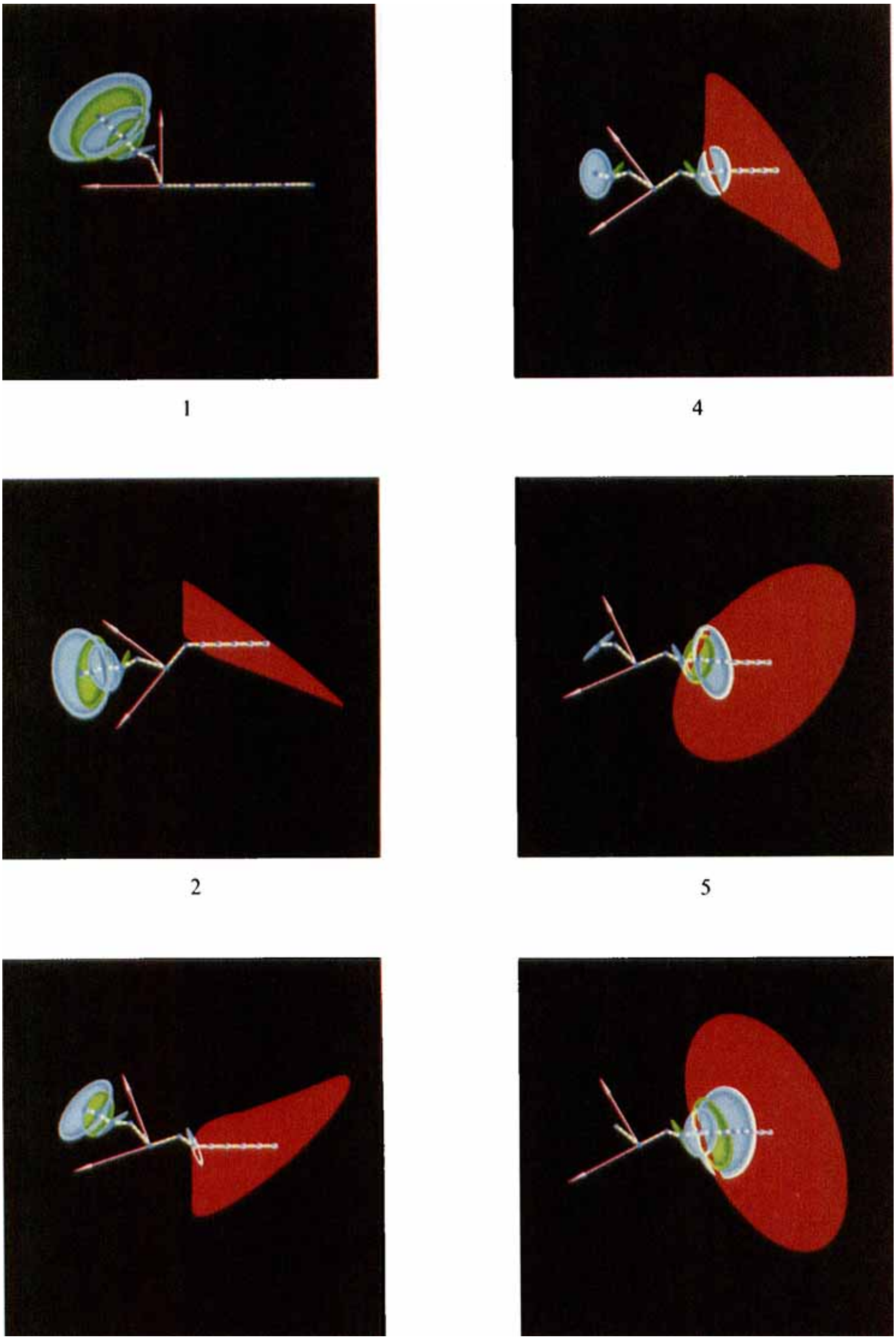
Here the new term Q_n is the orientational partition function for the nth conformer and is related to the potential of mean torque, $U_{\mathrm{ext}}(n,\omega)$, by

$$Q_n=\int\exp\{-U_{\mathrm{ext}}(n,\omega)/kT\}\,\mathrm{d}\omega, \tag{7}$$

where ω denotes the orientation of the director in a molecular frame. In the Emsley–Luckhurst–Stockley theory [2] the potential $U_{\mathrm{ext}}(n,\omega)$ is taken to be second rank and the coefficients determining its strength are constructed by assuming group additivity. For an alkylcyanobiphenyl these groups may be taken to be the cyanobiphenyl mesogenic core and the carbon–carbon bonds in the alkyl chain. Their strength parameters, X_a and X_c, can be estimated by fitting the order parameters for the C–D bonds in the alkyl chain, determined from deuterium NMR experiments [6]. Within our calculations E_{tg}/kT and $E_{\mathrm{g}\pm\mathrm{g}\mp}/kT$ have been set equal to 1·0 and 4·0, respectively; these are typical values. The ratio X_c/X_a is taken to be 0·3, again a typical value and X_a/kT has been varied to control the overall strength of the potential of mean torque for the various conformers. Our results are shown for a value of X_a/kT equal to 1·0 which corresponds to a reduced temperature, T/T_{NI}, of 0·64. This particularly low reduced temperature was chosen because we wished to emphasize the changes in the average structure caused by the ordering potential of the nematic phase.

The atoms represented in the average structure are the carbon atoms of the alkyl chain and to calculate their coordinates we take the chain to have a regular tetrahedral geometry. The hydrogen atoms are not included, partly to simplify the calculations but primarily to avoid complicating the final image. Representation of the cyanobiphenyl group presents a problem which we did not encounter in our previous study because the coordinates of the cyanobiphenyl did not change in the reference frame used [3]. This is not the case when the frame is fixed in the alkyl chain and so we need to decide how to picture the mesogenic core. Again to simplify both the calculations and the resultant image we have decided to represent the core by just five atoms positioned on the para axis. The spacing between these was chosen to equal the length of a carbon–carbon bond so that the lengths of the core and such a bond are in approximately the correct proportion.

Finally, the orientation of the reference frames used to define the atomic coordinates in the various conformers were located with three consecutive carbon atoms in the chain. We label these atoms $N-1$, N and $N+1$. The bond between atoms $N-1$ and N defines the z axis, the y axis is orthogonal to the plane formed by the three atoms and the x axis is orthogonal to both y and z. The reference frame employed in our original study corresponds to $N=1$, the first atom in the alkyl chain when $N-1$ is the



1 4

2 5

3 6

Figure 1. The average structures constructed for 4-*n*-heptyl-4′-cyanobiphenyl in the isotropic phase by using different sets of atoms to locate the reference frame (centred on $N=1$ to 6), along the heptyl chain.

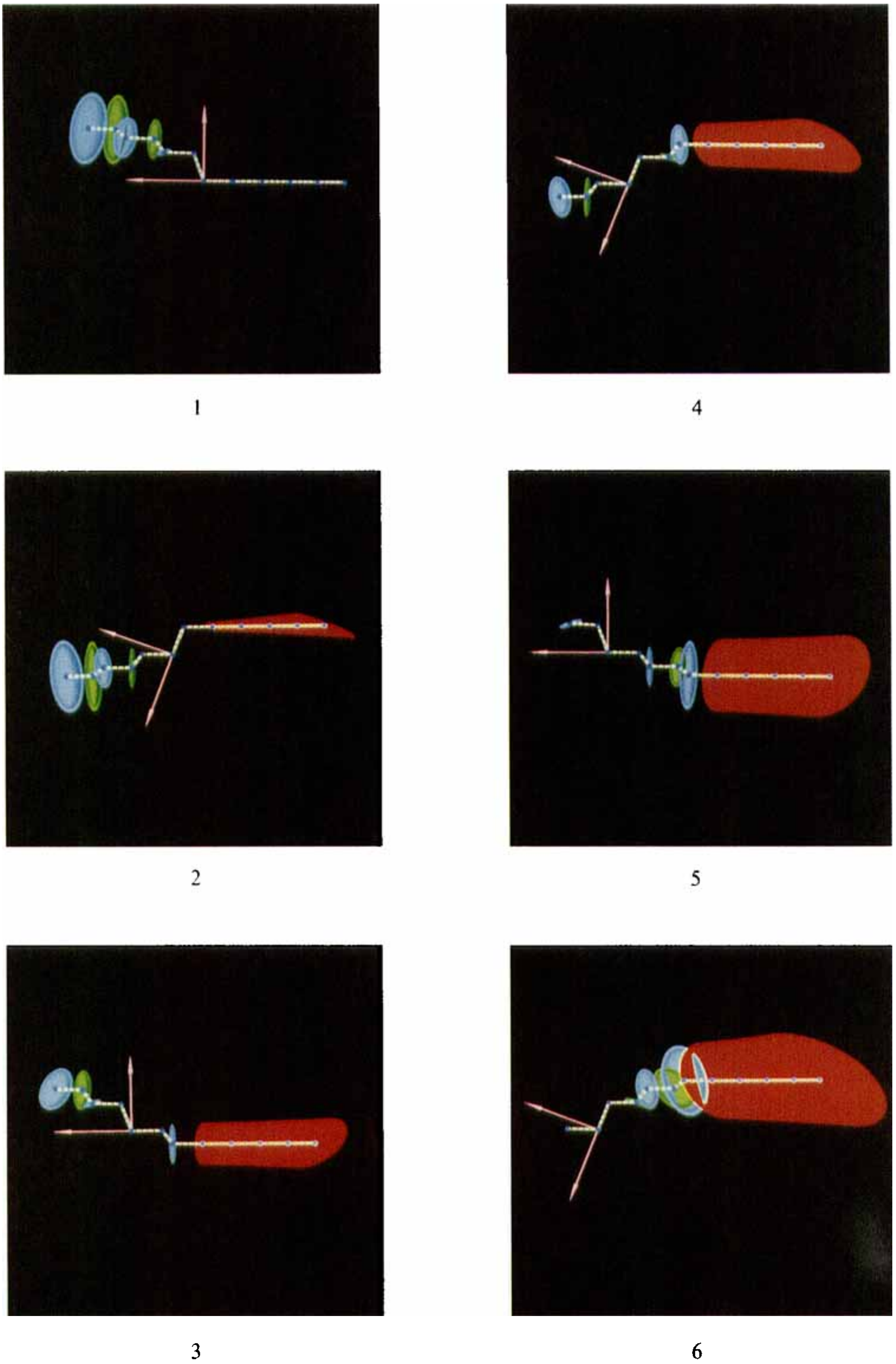


Figure 2. The average structures constructed for 4-*n*-heptyl-4′-cyanobiphenyl in the nematic phase at a reduced temperature, T/T_{NI} of 0·64 for different sets of atoms (centred on $N = 1$ to 6) used to locate the reference frame along the heptyl chain.

atom at position 4 in the phenyl ring. N can take values up to one less than the number of carbon atoms needed to locate the reference frame. For 4-*n*-heptyl-4′-cyanobiphenyl there are then six possible reference frames and we show the images constructed from these in the following section.

3. Images of the average structures and their fluctuational ellipsoids

The images showing the average structures and the associated fluctuational ellipsoids were constructed using WINSOM, a solid modelling software package developed at the IBM UK Scientific Centre. They were then visualized on an IBM 5080 Model 1 display whose screen was photographed to produce the images shown in figures 1 and 2 for the isotropic and nematic phases, respectively. These images are viewed looking down the y axis onto the xz plane formed by the average positions of the atoms and with the fluctuational ellipsoids superimposed. In order to reveal these average atomic positions the half of each ellipsoid above the xz plane was removed and the remaining half represented by a shell. This representation has the additional advantage that it is also possible to see the fluctuational ellipsoids even if they overlap significantly, as in the isotropic phase. We found that the five ellipsoids used to represent the mesogenic core did not always overlap completely to give a continuous surface as expected from this group. In consequence we have employed a linear interpolation procedure to create such a surface for the core and it is these which are shown. For ease of visualization the atoms and ellipsoids are coloured. Thus all of the atoms are blue while the bonds linking them are banded in pink and green with the number of bands proportional to the length of the bond. The composite fluctuational shape for the mesogenic core is shown in orange while the ellipsoids on alternate atoms in the alkyl chain are alternately coloured blue and green.

Before we consider the differences in the average structures produced by changing the reference frame and the phase, it is appropriate to comment on certain common features. The coordinates for the three atoms used to define the reference frame cannot change with the conformation and so there are no fluctuational ellipsoids; in addition, the two bond lengths in the average structure are unchanged. The atoms attached to those defining the reference frame can only adopt three positions within the Flory model and so these have fluctuational ellipses rather than ellipsoids. The five atoms defining the core remain collinear irrespective of the reference frame; in the images shown the line joining these five atoms is always horizontal. In general, as the distance of an atom from the reference frame increases so its fluctuational ellipsoid grows and the average bond lengths to its neighbours decrease. The fluctuational ellipsoid for the mesogenic group tends to dominate the average structure, especially in the isotropic phase, because the coordinates of the atoms at the end of the core furthest removed from the point of attachment to the chain necessarily undergo large conformational changes. In addition, the overall fluctuational shape for the mesogenic core has an asymmetric, often conical appearance which reflects the differential movement of the five atoms constituting the core.

The manifest changes in the images on going from the isotropic to the nematic phase (see figures 1 and 2) reflect the alteration in the conformational distribution produced by the nematic potential of mean torque. Thus, the more anisotropic conformers are favoured in the nematic phase. In consequence the average structures appear more linear and longer; in addition, the fluctuational ellipsoids are smaller because the molecule tends to adopt a reduced number of conformers which in turn have similar elongated shapes.

4. An interpretation of the average structures

We now turn to the challenging task of relating the images obtained using different reference frames to some observable property of the liquid crystal. We should emphasize that we do not expect to establish formal relationships between the average structures and liquid-crystalline behaviour. Indeed the development of a rigorous molecular theory of liquid crystals is still a topic of considerable debate. Our aim here, therefore, is to present semi-quantitative arguments to suggest ways in which the images which we have constructed might be used to understand some aspects of liquid crystals. Perhaps the most characteristic of these properties is the long range orientational order which may be defined with a set of order parameters [7]. The second rank quantity

$$S=\overline{P_2(\cos\beta)}, \tag{8}$$

where β is the angle made by a molecular axis with the director, is possibly the most important, partly because it is available from experiment and partly because it is normally dominant. For a non-rigid particle β fluctuates because of molecular reorientation and changes in the conformation. Within the context of the rotameric state model these two contributions to the order parameter can be separated, as Emsley and Luckhurst [5] have shown. Thus

$$S=\sum_n p_n S_n, \tag{9}$$

where S_n is the order parameter of a given axis in a rigid sub-unit of conformer n. This order parameter is related to the potential of mean torque, $U_{\text{ext}}(n\,\omega)$, experienced by the conformer via

$$S_n=Q_n^{-1}\int P_2(\cos\beta)\exp\{-U_{\text{ext}}(n,\omega)/kT\}\,\mathrm{d}\omega. \tag{10}$$

In the limit of low orientational order this expression can be simplified by expanding the exponentials and truncating the expansion after the first non-trivial term. This gives

$$S_n=-(1/4\pi kT)\int P_2(\cos\beta)U_{\text{ext}}(n,\omega)\,\mathrm{d}\omega, \tag{11}$$

which proves to be a reasonable approximation in the nematic phase close to the transition. The potential of mean torque can be expanded, quite generally, in a basis of modified spherical harmonics

$$U_{\text{ext}}(n,\omega)=-\sum_{L(\text{even}),\,m}\varepsilon^n_{L,m}C^*_{L,m}(\omega), \tag{12}$$

where $\varepsilon^n_{L,m}$ is an irreducible spherical tensor determining the strength of the ordering potential for the nth conformer. This basis set is of particular value because of the orthogonality of the modified spherical harmonics which leads to the simple result

$$S_n=\varepsilon^n_{2,0}/5kT \tag{13}$$

for the second rank order parameter. It is determined, in this low order limit, by just one of the coefficients in the formal expansion of the potential of mean torque [8]. This second rank coefficient $\varepsilon^n_{2,0}$ is the component of the interaction tensor corresponding to the axis whose order parameter is being evaluated. The conformationally averaged order parameter is then

$$S=\sum_n p_n \varepsilon^n_{2,0}/5kT; \tag{14}$$

that is the order parameter is determined by the average of the component $\varepsilon^n_{2,0}$ over all of the conformers; in general

$$\bar{\varepsilon}_{2,m}=\sum_n p_n \varepsilon^n_{2,m}. \tag{15}$$

It is frequently argued that the dominant factor influencing the alignment of molecules in a liquid crystal is the anisotropy of the repulsive forces. If this is the case then the shape anisotropy should make a major contribution to the interaction tensor $\varepsilon^n_{2,m}$ for a given conformation. In consequence we should expect the conformational average $\bar{\varepsilon}_{2,m}$ to be related to the average shape of the molecule. We should also recall that the interaction tensor $\varepsilon^n_{2,m}$ will change with the molecular frame in which it is evaluated, just as the order parameter will vary with the location of the sub-unit within the molecule. In the same way, we should expect these variations to be reflected by the changes in the average shape of the molecule as the reference frame in which it is calculated varies. Thus, the images which we have obtained from the average positions of the atoms should be of value in understanding the variation of the ordering of different rigid sub-units in the molecule. However, before we explore this association for images which we have constructed, it may be helpful to consider the frame dependence of the interaction tensors $\bar{\varepsilon}_{2,m}$ averaged over all of the conformers.

Within the Emsley–Luckhurst–Stockley theory [2], the interaction tensors $\varepsilon^n_{2,m}$ are related to the group interaction parameters X_a and X_c together with the conformational geometry; however, we need not be concerned with the form of this relationship here. The components of the tensor $\varepsilon^n_{2,m}$ for a particular conformer n depend on the orientation of the reference frame in which the tensor is expressed. They do not, of course, depend on the origin of this frame since $\varepsilon^n_{2,m}$ is a purely anisotropic tensor. Initially it might be surprising, therefore, to see that the average structures shown in figures 1 and 2 clearly vary with the location of the reference frame in the alkyl chain. This apparent paradox is resolved relatively easily. The dependence stems from the fact that we need to use a consistent reference frame in which to calculate $\varepsilon^n_{2,m}$ for all of the conformers. Here we chose to define the reference frame in terms of the positions of three adjacent atoms. These give the orientation of the reference frame which determines the components $\varepsilon^n_{2,m}$, but, again the values of these are independent of the origin of the frame which need only be located in the space defined by the three atoms. The particular selection of these three atoms, and hence the reference frame, also determines the extent to which the tensor $\varepsilon^n_{2,m}$ varies with the conformation. For example, since $X_a > X_c$ location of the reference frame within the mesogenic group necessarily results in a smaller dependence on the conformation than if the frame was located at the end of the alkyl chain. In consequence the conformationally averaged tensor $\bar{\varepsilon}_{2,m}$ will depend on the location of the reference frame. Such a dependence seems to imply that the choice of origin determines $\bar{\varepsilon}_{2,m}$ but this is clearly not the case; it is simply the choice of the three atoms used to define the orientation of the reference frame which is of importance.

The irreducible spherical components of the conformationally averaged interaction tensors in the reference frame and in principal axis system, for the isotropic and nematic phase.

Atoms defining the reference frame	Isotropic					Nematic				
	Reference frame			Principal frame		Reference frame			Principal fram	
	$\bar{\varepsilon}_{2,0}/kT$	$\bar{\varepsilon}_{2,\pm 1}/kT$	$\bar{\varepsilon}_{2,\pm 2}/kT$	$\bar{\varepsilon}_{2,0}/kT$	$\bar{\varepsilon}_{2,\pm 2}/kT$	$\bar{\varepsilon}_{2,0}/kT$	$\bar{\varepsilon}_{2,\pm 1}/kT$	$\bar{\varepsilon}_{2,\pm 2}/kT$	$\bar{\varepsilon}_{2,0}/kT$	$\bar{\varepsilon}_{2,\pm 2}/$
412†	6·64	∓0·88	1·25	6·78	1·19	9·93	∓1·27	1·80	10·11	1·72
123	−0·18	∓2·10	2·97	5·00	0·86	−0·37	∓4·15	5·86	9·88	1·68
234	4·91	∓0·74	1·05	5·04	0·99	9·70	∓1·37	1·95	9·93	1·86
345	0·08	∓1·81	2·55	4·26	0·85	−0·05	∓4·18	5·90	9·89	1·85
456	4·14	∓0·68	0·95	4·28	0·90	9·66	∓1·24	1·75	9·84	1·68
567	0·18	∓1·38	1·95	3·23	0·70	−0·36	∓3·96	5·60	9·44	1·60

† N.b. Here, 4 denotes the atom in the phenyl ring to which the heptyl chain is attached.

To illustrate the dependence of the interaction tensor $\bar{\varepsilon}_{2,m}$, averaged over all conformers, on the choice of the three atoms used to define the reference frame we show in the table the components in the reference frame and in the principal axis system, for both the isotropic and the nematic phase. As we have seen, the interaction tensor always enters the calculations via a Boltzmann factor and so is scaled with kT; it is these scaled values which are listed in the table. In an arbitrary axis system there are five independent components of $\bar{\varepsilon}_{2,m}$ corresponding to $m=2$, 1, 0, -1 and -2. In the principal axis system for the average tensor, there are just two independent elements $\bar{\varepsilon}_{2,0}$ and $\bar{\varepsilon}_{2,2}$ $(\equiv\bar{\varepsilon}_{2,-2})$; $\bar{\varepsilon}_{2,0}$ determines the alignment of the long molecular axis while $\bar{\varepsilon}_{2,2}$ reflects the biaxiality in the molecular interactions. As we can see within both phases the averaged tensor in the reference frame and in its principal axis system vary with the choice of the three atoms used to define this reference frame; we emphasize again that this dependence results because for every conformer the components of the tensor naturally vary with the orientation of the reference frame and because the conformational dependence of $\varepsilon^{n}_{2,m}$ is determined by the atoms defining the frame.

The tensors clearly exhibit some interesting trends and it is appropriate to comment on these. We begin by noting that in the reference frame some of the interaction tensor components are related $(\bar{\varepsilon}_{2,1}=-\bar{\varepsilon}_{2,-1};\bar{\varepsilon}_{2,2}=\bar{\varepsilon}_{2,-2})$ and so there are just three independent components; this results because the y axis is always a principal axis for the averaged tensor. The odd components $\bar{\varepsilon}_{2,\pm1}$ are seen to alternate in magnitude as the reference frame is moved along the alkyl chain in both the isotropic and nematic phases; similar variations occur in the value of $\bar{\varepsilon}_{2,0}$. These alternations result from an essentially geometric effect, for the principal components of the averaged interaction tensor do not show any such dramatic fluctuations. In other words, it occurs because the orientation of the reference frame alternates with respect to the principal axis system; thus they are approximately parallel when an odd-numbered atom is at the centre of the three used to define the reference frame but inclined when an even atom is at the centre. Such trends are more apparent for the nematic phase because the ordering potential restricts the most populated conformers to those which are elongated. Another consequence of this is the relatively modest reduction of the principal tensor component $\bar{\varepsilon}_{2,0}$ as the atoms defining the frame move from the beginning to the end of the chain. In contrast, in the isotropic phase, where the conformational averaging is far more extensive, $\bar{\varepsilon}_{2,0}$ exhibits a significant reduction as the reference frame moves to the end of the chain. Unlike $\bar{\varepsilon}_{2,0}$, the biaxiality in the conformationally averaged tensor $\bar{\varepsilon}_{2,\pm2}$ does not vary significantly with the location of the reference frame in the chain. However, the biaxiality is larger in the isotropic phase than the nematic. As we shall see, all of these variations in the conformationally averaged interaction tensor with the location of the reference frame and the nature of the phase are reflected by the images of the averaged structures.

We now return to the relationship between the orientational order parameters and the images which we have constructed. The order parameters for methylene units along an alkyl chain in a liquid crystal are most readily obtained from deuterium NMR spectroscopy [6]. Such experiments yield the order parameters for the C–D bonds in the chain but they are not the most appropriate for this discussion because these bond directions are not available explicitly in the images. However, it is possible, under certain conditions, to extract the order parameters, S_{CC}, for the carbon–carbon bonds along an alkyl chain [9] and these do form part of the images; indeed they define the z axis in the reference frame. As the order parameters S_{CC} have been determined from NMR studies of the nematic phase it is appropriate to consider the images calculated from this phase. That is, the conformational distribution used in the averaging procedure (see equations (1) and (2)) is the one calculated for the nematic phase by inclusion of the rotational partition function [2, 5]. Strictly, however, in the low order limit the Q_n are all equal, to 4π, and so the conformational distributions in the isotropic and nematic phases are identical (see equations (4) and (6)). None the less, at this stage the arguments concerning the images and their interpretation are intended to be illustrative and so we shall use the average skeletal structures calculated with the nematic conformational distribution. These are shown in figure 2 and we can see that for the images with N odd the z axis of the reference frame is more or less parallel to the major axis of the average structure. In addition, the molecular length corresponding to this axis is essentially unchanged as the atoms used to define the reference frame is moved towards the end of the alkyl chain. Similarly for the even positions the length of the major molecular axis in the average structure is independent of the location of the reference frame and approximately equal to that for the odd positions. However, the orientation of the z axis with respect to the major axis of the structure is quite different. The angle between the two axes is about 60° for even positions whereas for the odd positions of the reference frame it is only about 10°. There is, therefore, a large geometric difference between the z axes in the images constructed with the reference frames centred on odd and even carbon atoms. The shape anisotropy is largely independent of the location of the frame and so any difference in the S_{CC} order parameters must result predominantly from geometric effects. In fact such effects may be significant as we can see from the following idealized example. For a cylindrically symmetric molecule the order parameter, S_{aa}, for an arbitrary axis is related to that, S, for the symmetry axis by

$$S_{aa} = SP_2(\cos\theta), \tag{16}$$

where θ is the angle between a and the symmetry axis. The order parameter S_{aa} is then a maximum when θ is zero, decreases with increasing θ, vanishes when θ is 54·73° then becomes negative and finally reaches a limiting value of $-S/2$. The same qualitative behaviour is expected even when the molecule is not strictly cylindrically symmetric. From the images we would anticipate, therefore, that the order parameters S_{CC} for the carbon–carbon bonds along the chain would be large and positive for the odd positions but small and negative for the even positions with little attenuation as the frame is moved to the end of the chain. This dramatic odd–even alternation is indeed what is found for the S_{CC} of 4-*n*-octyl-4′-cyanobiphenyl [9] and there is every reason to expect this behaviour to obtain for the heptyl homologue for which we have obtained the images.

This clear distinction between images, constructed with the central atom of the three used to locate the reference frame on odd and even positions in the alkyl chain, disappears when we consider those for the isotropic phase. The differences in the angle between the major axis of the average structure and the carbon–carbon bond are certainly large for $N = 1$ and 2 but then it is rapidly attenuated as the reference frame is moved along the chain. In addition, there is also a reduction in the molecular length corresponding to the major axis as the frame is moved towards the end of the chain. From the images, therefore, we would expect that the odd–even alternation would be significantly reduced when the conformational distribution approaches that for the isotropic phase. Unfortunately, although it is possible to measure the field-induced order parameters for the C–D bonds in the isotropic liquid of a nematogen close to the phase transition [10], there is insufficient information with which to determine the S_{CC}.

5. The fluctuational ellipsoids and their significance

As we have seen, it is relatively straightforward to understand the significance of the average atomic positions and hence the average shape of a mesogenic molecule, at least in the low order limit. This does not appear to be the case for the deviations of the atoms away from their average positions as visualized by the fluctuational ellipsoids. Here we explore, in an essentially qualitative manner, a possible relationship between these ellipsoids and the segmental order parameters. Our starting point is the expression in equation (9) for the conformationally averaged order parameter for an arbitrary molecular axis which, with the help of equations (6) and (10), we write as

$$S=\frac{\sum\limits_{n}\exp\{-U_{\mathrm{int}}(n)/kT\}\int P_2(\cos\beta)\exp\{-U_{\mathrm{ext}}(n,\omega)/kT\}\,\mathrm{d}\omega}{\sum\limits_{n}\exp\{-U_{\mathrm{int}}(n)/kT\}\int\exp\{-U_{\mathrm{ext}}(n,\omega)/kT\}\,\mathrm{d}\omega}. \tag{17}$$

Here we emphasize that β is the angle made by the chosen axis set in some rigid sub-unit of the flexible molecule and that the potential of mean torque, $U_{\mathrm{ext}}(n,\omega)$, is expressed using a reference frame in the same sub-unit. This choice of frame determines the magnitude of the components of the interaction tensors, $\varepsilon^{n}_{L,m}$ (see equation (12)) which also vary with the molecular conformation. This conformational dependence in equation (17) for the order parameter enters through the Boltzmann factor and so the conformational average of the interaction tensors themselves can only be obtained in the low order limit (see equation (14)). In first order these averages were, it was argued, related to the average structure of the flexible molecule. To obtain quantities related to the fluctuations of the atoms away from this average structure we clearly need to take the expansion to second order. This can be achieved by expressing the conformational average of the exponential in terms of cumulants [11]. Taking the cumulant expansion of equation (17) to second order gives

$$S=\frac{\int P_2(\cos\beta)\exp\{-\bar{U}_{\mathrm{ext}}(\omega)/kT+[\overline{U^2_{\mathrm{ext}}}(\omega)-\bar{U}^2_{\mathrm{ext}}]/2k^2T^2\}\,\mathrm{d}\omega}{\int\exp\{-\bar{U}_{\mathrm{ext}}(\omega)/kT+[\overline{U^2_{\mathrm{ext}}}(\omega)-\bar{U}^2_{\mathrm{ext}}(\omega)/2k^2T^2\}\,\mathrm{d}\omega}, \tag{18}$$

where the bar indicates a conformational average of the potential of mean torque, over a distribution which is strictly that for the isotropic phase. That is

$$\bar{U}_{\mathrm{ext}}(\omega)=Z^{-1}\sum_{n}\exp\{-U_{\mathrm{int}}(n)/kT\}U_{\mathrm{ext}}(n,\omega) \tag{19}$$

and

$$\overline{U^2_{\mathrm{ext}}}(\omega)=Z^{-1}\sum_{n}\exp\{-U_{\mathrm{int}}(n)/kT\}U^2_{\mathrm{ext}}(n,\omega), \tag{20}$$

where the conformational partition function is given by equation (5). The first term in the cumulant expansion is determined by the conformational average of the interaction tensors. It is, therefore, related to the average structure of the flexible mesogenic molecule as we have argued previously. The second term is determined by the mean square fluctuation of the potential of mean torque away from its average value. We might speculate that it is this second order term which is reflected by the fluctuational ellipsoids. However, the exact nature of the relationship is not clear. If we write the potential of mean torque as an expansion in modified spherical harmonics (see equation (12)) then the first term in the cumulant expansion is

$$\bar{U}_{\text{ext}}(\omega) = -\sum_{L(\text{even}),m} \bar{\varepsilon}_{L,m} C^{*}_{L,m}(\omega) \tag{21}$$

and the second term, with which we are concerned, is

$$\overline{U^{2}_{\text{ext}}(\omega)} - \bar{U}^{2}_{\text{ext}}(\omega) = \sum_{\substack{L,l' \\ m,m'}} \{\overline{\varepsilon_{L,m}\varepsilon_{L',m'}} - \bar{\varepsilon}_{L,m}\bar{\varepsilon}_{L',m'}\} C^{*}_{L,m}(\omega) C^{*}_{L',m'}(\omega). \tag{22}$$

It is the mean square fluctuations in the interaction tensors which we expect to be related to the fluctuational ellipsoids shown in figures 1 and 2.

To explore the influence of the fluctuations on the orientational order it is helpful to replace the product of modified spherical harmonics by a single spherical harmonic so that the angular dependence of the second cumulant is more explicit. Thus,

$$\overline{U^{2}_{\text{ext}}(\omega)} - \bar{U}^{2}_{\text{ext}}(\omega) = \sum_{\substack{L,L' \\ m,m'}} \{\overline{\varepsilon_{L,m}\varepsilon_{L',m'}} - \bar{\varepsilon}_{L,m}\bar{\varepsilon}_{L',m'}\} \sum_{J=L-L'}^{L+L'} \times C(LL'J,00) C(LL'J,mm') C^{*}_{J,m+m'}(\omega), \tag{23}$$

where $C(LL'J,mm')$ is a Clebsch–Gordan coefficient [7]. The relative influence of the first and second order cumulants clearly depends on their signs as well as their magnitudes. For example, if the terms have opposite signs the first order cumulant will enhance the orientational order while the second term will decrease it. Given the relatively complicated expression for the second cumulant (in equation (23)) it is helpful to illustrate this point with a simple example. We consider a cylindrically symmetric molecule in which the conformational change does not alter the shape but just the anisotropy of the molecule. Accordingly, terms in equation (23) vanish unless m is equal to zero. In addition we restrict the potential to just second rank terms as in the Maier–Saupe theory [12]. Then the first cumulant is

$$\bar{U}_{\text{ext}}(\omega) = -\bar{\varepsilon}_{2,0} P_2(\cos\beta) \tag{24}$$

and the second is found to be

$$\overline{U^{2}_{\text{ext}}(\omega)} - \bar{U}^{2}_{\text{ext}}(\omega) = (\overline{\varepsilon^{2}_{2,0}} - \bar{\varepsilon}^{2}_{2,0})\{(1/5) + (2/7)P_2(\cos\beta) + (18/35)P_4(\cos\beta)\}, \tag{25}$$

after evaluating the Clebsch–Gordan coefficients. In this simple example if $\bar{\varepsilon}_{2,0} > 0$, as expected for linear molecules, then the first order cumulant favours alignment of the symmetry axis parallel to the director and so gives a positive order parameter. However, the second cumulant will not favour alignment parallel to the director because the mean square fluctuation $(\overline{\varepsilon^{2}_{2,0}} - \bar{\varepsilon}^{2}_{2,0})$, is positive and so this will reduce the order parameter produced by the first cumulant. The extent of this reduction will grow with the mean square fluctuation which should be related to the size of the fluctuational ellipsoid, which in this simple example degenerates to a line. It seems reasonable that, in the main, such arguments should hold for conformers of arbitrary shape. If this is the case then the larger the fluctuational ellipsoids the smaller will be the orientational order parameters, at least in second order. We should emphasize, however, that there does not appear to be a formal relationship between the average structures and the orientational ordering. The semi-quantitative arguments which we have presented here are intended simply to be suggestive.

Assuming the qualitative validity of these arguments, we can now use them to reconsider the images for 4-*n*-heptyl-4′-cyanobiphenyl in the nematic phase. As we have seen, the lengths of the skeletal structures are essentialy independent of the location of the reference frame although the orientation of this direction with respect to the carbon–carbon bond defining the z axis does alternate. This, we argued, was responsible for the alternation in the order parameters S_{CC} although in first order these were not attenuated as the bond approached the end of the chain. Such a result does not hold in second order for, as we can see from the images in figure 2, the envelope surrounding the fluctuational ellipsoids for an image increases dramatically in size as the three atoms used to define the reference frame are moved along the chain towards the methyl group. We might expect, therefore, that some attenuation in the alternation of the S_{CC} should be observed and this does seem to be the case [9]. The increase in the magnitude of all of the ellipsoids (or the attenuation) appears to be monotonic in the nematic phase. However, in the isotropic phase, the dimensions of the envelope surrounding the ellipsoids have a tendency to be paired ($N = 5$ with 6 and $N = 3$ with 4). Unfortunately there are no experimental results against which to test the implications of such pairings of the fluctuational ellipsoids on the order parameters S_{CC}.

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