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A visual representation for the shapes of flexible mesogenic molecules

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A visual representation for the shapes of flexible mesogenic molecules[†]

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The shapes of most mesogenic molecules vary as a result of internal motions whose magnitude changes discontinuously at the transition to the isotropic phase. Here we propose a visual representation for such flexible molecules which shows their average chemical structure together with the extent of the fluctuations away from this.

The vast majority of liquid-crystalline compounds are composed of flexible molecules and for most of these their non-rigidity results from the rotational isomerization of one or more alkyl chains. For thermotropic liquid crystals of low molar mass the chains are usually at the terminal positions of a semi-rigid aromatic core [1], although it has recently been shown that relatively long alkyl chains may also be introduced into a lateral position without destroying the liquid-crystalline behaviour [2]. Indeed several alkyl chains have been attached to both terminal and lateral positions to give the so-called phasmidic [3] and biforked liquid crystals [4]. In addition a chain may be used to link two mesogenic units together and, as with the main chain liquid crystal polymers, the properties of these materials are found to depend strongly on the number of carbon atoms in the flexible spacer and its parity [5]. Chains are also used in side chain liquid crystal polymers to attach mesogenic units to the polymer backbone [6]. Finally, alkyl chains occur widely in lyotropic liquid crystals where they usually form the hydrophobic part of the amphiphilic molecule. In many, if not all, of these examples the alkyl chains play an essential role in establishing liquid-crystalline behaviour as well as contributing to the mesogenic properties.

The investigation, both experimental and theoretical, of the conformations adopted by the flexible chains is a particularly difficult task, especially as the conformation of a molecule is usually strongly coupled to its orientation [7]. In consequence, the conformational distribution changes discontinuously at the transition to the liquid-crystalline phase and may vary significantly with further reduction in temperature [8, 9]. The populations of the various conformers and their variation cannot be measured directly, although this information can be extracted from the orientational order parameters determined at positions along the alkyl chains, usually by deuterium N.M.R. spectroscopy [8, 9]. However, a model is then required to relate the order

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parameter profile to the conformational distribution. In developing such models the alkyl chain is usually assumed to exist in a discrete set of conformers, characterized by trans and gauche arrangements about C–C bonds as proposed by Flory [10], and so the observed order parameters for each C–D bond direction are given by

$$S_{\mathrm{CD},i} = \sum_n p_n S^n_{\mathrm{CD},i}. \qquad (1)$$

Here $S^n_{\mathrm{CD},i}$ denotes the order parameter for the C–D bond at the ith site in the nth conformer and p_n is the normalized probability for that conformer. We can see, therefore, that the conformational distribution is combined with the order parameter for the appropriate conformer, and so to separate them a model is needed with which to calculate these order parameters. One such model has been developed by Emsley *et al.* [8] and it has been used successfully to account for the order parameter profiles of certain 4-*n*-alkyl-4′-cyanobiphenyls [9]. Fitting the model to the experimental data allows the unknowns occurring in the theory to be determined. These may then be used to calculate the conformational distribution within the isotropic and nematic phases, the changes in this distribution are predicted to be significant, especially for those compounds with an alkyl chain linking two mesogenic groups [11].

Although the complete set of conformational probabilities contains all of the information needed to calculate conformational averages, it is often difficult to appreciate their significance, especially when the number of conformers is large. For example, there are 729 conformers for 4-*n*-octyl-4′-cyanobiphenyl and, within the Flory rotameric state model, this number is trebled each time a methylene group is added to the chain. We have attempted to solve the problem of how to present such large tabulations of conformational probabilities, in a readily assimilated form, by constructing an image which illustrates not only the average structure of the flexible molecule but also the extent of the conformational fluctuations away from this. We have explored several visual representations for such an average structure and here we present one which seems to be especially promising.

In arriving at our particular choice we decided that the image should retain the appearance of a chemical structure with its atoms linked by bonds. We shall illustrate the implementation of the scheme by using the 4-*n*-alkyl-4′-cyanobiphenyls as examples because the parameters governing their orientational order and conformational distributions are known [9]. The mean position of a carbon atom in the chain is defined as the average,

$$\bar{\mathbf{r}}_i = \sum_n p_n \mathbf{r}^n_i, \qquad (2)$$

over all conformations, where $\mathbf{r}^n_i$ denotes the position vector for the ith atom in conformer n. Next, we must select a reference frame in which to write the atomic coordinates $\mathbf{r}^n_i$ and for the 4-*n*-alkyl-4′-cyanobiphenyls we place z parallel to the para axis of the biphenyl group, x orthogonal to the plane formed by the first two segments of the chain and y orthogonal to x and z. The origin is located in the 4 position of the phenyl ring and the frame so formed is shown in figure 1. Although this choice may seem natural for a single alkyl chain attached to a single mesogenic core it is not unambiguous. The problem of locating the reference frame is highlighted when we come to consider molecules with a flexible spacer linking two mesogenic groups, where placing the frame in one of these groups would destroy the obvious molecular symmetry. However, locating the frame in a central methylene group or groups would result in particularly large fluctuations of the mesogenic groups away from the

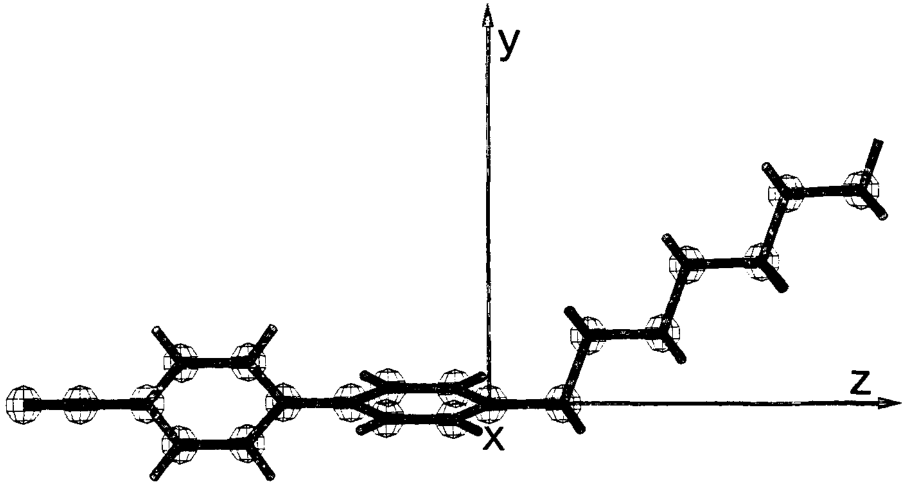


Figure 1. The reference frame, *xyz*, chosen for the 4-*n*-alkyl-4′-cyanobiphenyls.

average structure. In consequence, selecting a frame which minimizes the extent of the conformational fluctuations could have certain advantages. It might also be of value not to fix the reference frame to a rigid molecular fragment but to allow it to change with the conformer, so as to reflect some conformational property. For example, the principal axes of the inertial tensor or the molecular field interaction tensor [8] may provide a better representation of the molecular shape, although for the mesogens considered here there would be little difference between these frames and that which we have chosen. It is also important to realise that the selection of the reference frame will, almost certainly, be influenced by the specific property of the liquid crystal which we are attempting to relate to the molecular shape. Thus, location of the frame in a particular methylene group may be of value when trying to understand the variation of the orientational order along the alkyl chain. These various possibilities need to be explored and such a study is underway.

The image formed from the average positions of the carbon atoms in the chain is, of course, incomplete for it does not reveal in any direct manner the fluctuations of the atoms away from these positions. To quantify the extent of such conformational changes we have also calculated the mean square displacement,

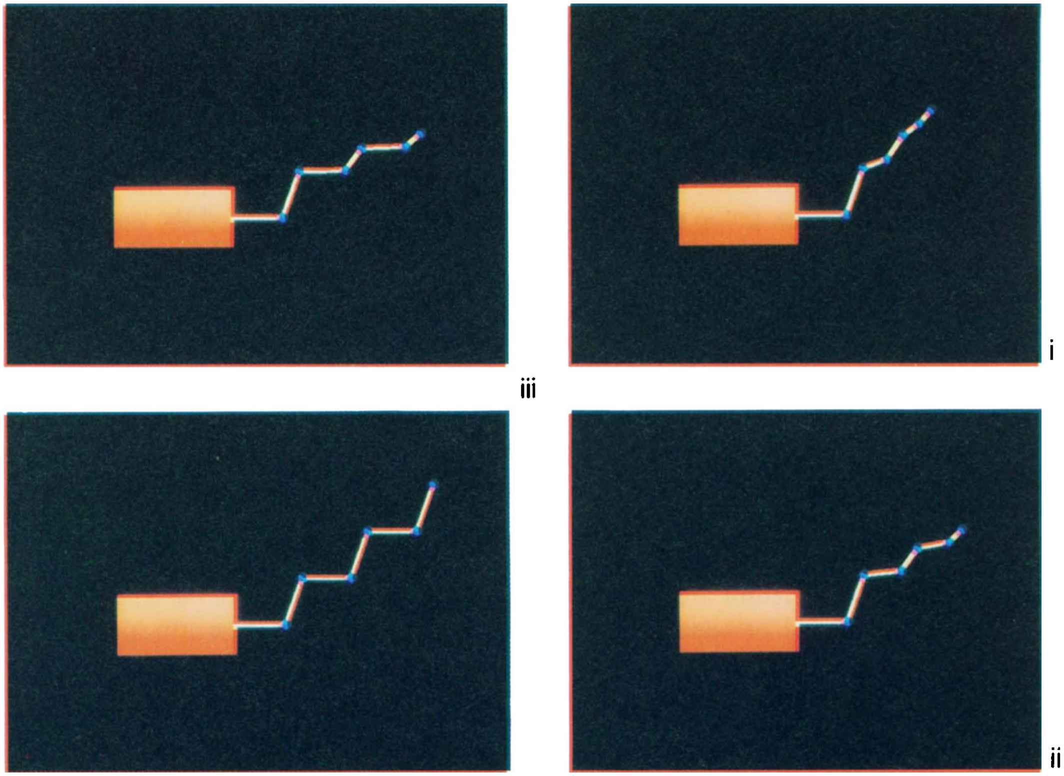
$$\sigma_i^2 = \sum_n p_n(\mathbf{r}_i^n \mathbf{r}_i^n - \bar{\mathbf{r}}_i \bar{\mathbf{r}}_i), \qquad (3)$$

for the *i*th atom. The principal axis system for the displacement tensor, σ_i^2, is not necessarily parallel to the reference frame and so it is located by diagonalizing σ_i^2. The eigenvalues of the tensor are then used to construct an ellipsoid with the lengths of its three orthogonal, principal axes equal to σ_i. The orientation of these principal axes in the reference frame is given by the eigenvectors obtained when diagonalizing σ_i^2. This ellipsoidal representation of the conformational fluctuations of an atom away from its equilibrium position has much in common with the thermal ellipsoids used to show the much smaller atomic motion within a crystal [12].

The probabilities of the conformers needed to evaluate the averages for the 4-*n*-alkly-4′-cyanobiphenyls were obtained by using the model developed by Emsley *et al.* [8], and we shall not repeat the details of the calculation here. The internal or conformational energy of the alkyl chain is given, in the Flory rotameric state model, by the number of gauche linkages, N_g, and the number of $g^{\pm} g^{\mp}$ sequences $N_{g^{\pm} g^{\mp}}$ thus

$$U_{\mathrm{int}}(n) = N_g E_{tg} + N_{g^{\pm} g^{\mp}} E_{g^{\pm} g^{\mp}} . \tag{4}$$

The energy parameters occur in the calculation as the Boltzmann factors E_{tg}/kT and $E_{g^{\pm} g^{\mp}}/kT$; strictly they vary with temperature but this variation was ignored and these scaled parameters were given the typical values of 1·0 and 4·0, respectively [10]. The mesogenic core, like each carbon–carbon bond, was taken to be cylindrically symmetric and the ratio of their interaction parameters X_c/X_a governing the potential of mean torque responsible for ordering each conformer was set equal to 0·3 [9]. The carbon–hydrogen bond interactions [9] were not included in our calculations. The alkyl chain was taken to adopt a regular tetrahedral structure, with the carbon atoms occupying sites on a diamond lattice, since this simplifies the calculation without compromising any of the ideas concerning the molecular shape which we wish to illustrate. The calculations were performed for differing values of the reduced temperature, T/T_{NI}, where the nematic–isotropic transition temperatures were predicted by a molecular field theory [13]. The average positions and the displacement ellipsoids for the carbon atoms in the alkyl chain were obtained for the hexyl and heptyl members of the homologous series of 4-*n*-alkyl-4′-cyanobiphenyls.



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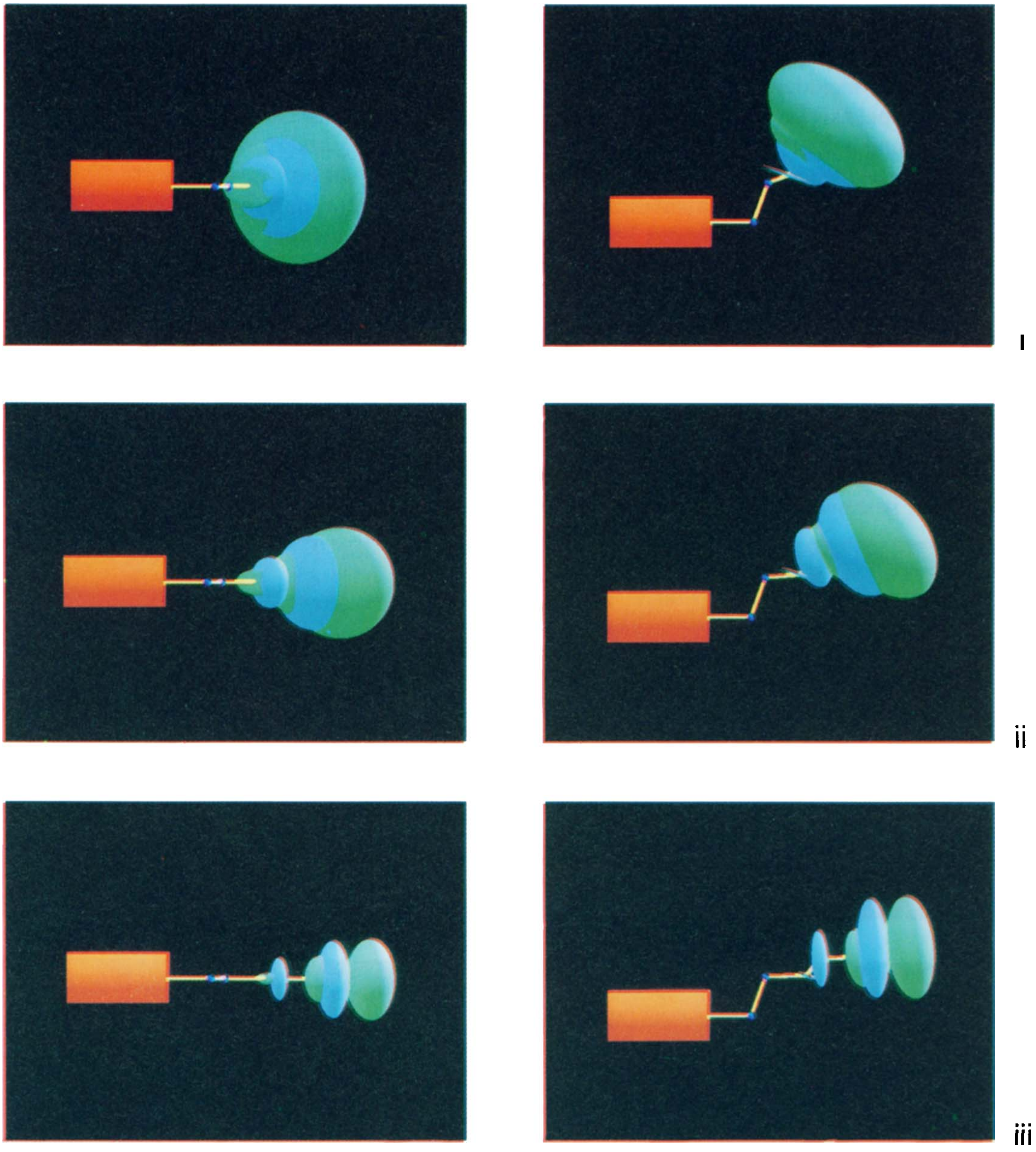
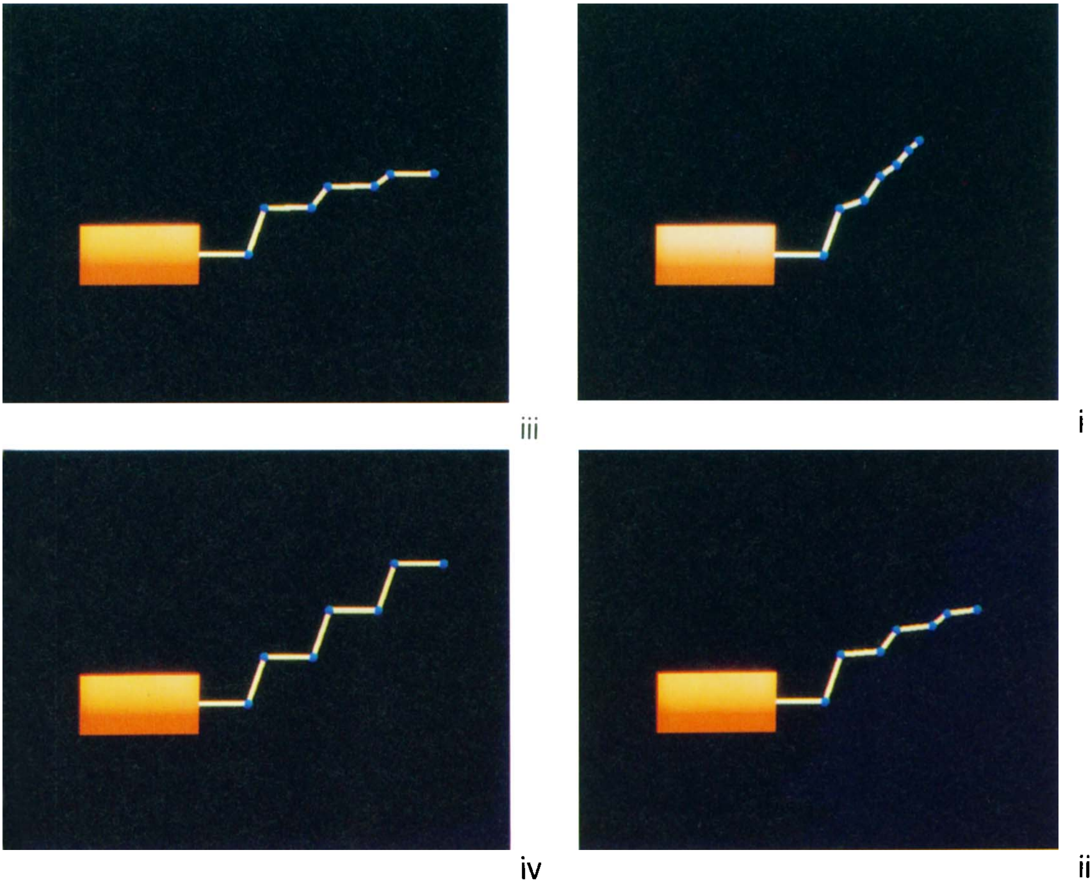


Figure 2. (*a*) The average positions of the carbon atoms in the alkyl chain of 4-*n*-hexyl-4′-cyanobiphenyl calculated for the isotropic phase at the nematic-isotropic transition (i) and in the nematic phase at reduced temperatures of 0·85 (ii) and 0·55 (iii); the all-trans conformation (iv) is also shown for comparison. (*b*) The displacement ellipsoids have been added to these average positions and two views, along the x and y axes, of the resultant structures are shown.

With this model and within the reference frame which we have defined, the average x coordinate, $\bar{r}_{x,i}$, for every carbon atom in the chain is zero. This situation obtains because the conformers related by the transformations $g^{\pm} \rightarrow g^{\mp}$ occur with equal probabilities while the x coordinates for each atom change sign. The average of $r_{x,i}$ vanishes therefore since the x coordinates in the all-trans conformer, which is the only one not included in the transformations, are already zero. Similarly the x axis is a principal axis for the mean square displacement tensor, $\boldsymbol{\sigma}_i^2$, for although the $r^n_{x,i}$ change sign under the transformation $g^{\pm} \rightarrow g^{\mp}$ the coordinates $r^n_{y,i}$ and $r^n_{z,i}$ remain unchanged. In consequence the averages σ^2_{xy} and σ^2_{xz}, defined by equation (3), vanish.

The results of our calculations are shown in figures 2 (*a*) and (*b*) for 4-*n*-hexyl-4′-cyanobiphenyl and in figures 3 (*a*) and (*b*) for the heptyl member of this homologous series. These average chemical structures correspond to the isotropic phase, at the nematic–isotropic transition, the nematic phase at a reduced temperature of about 0·85 and the particularly low value of approximately 0·55, which was chosen to emphasise the structural variations with temperature. The all-trans conformers for the two chain lengths are also included in figures 2 (*a*) and 3 (*a*) for comparison. The images for the average structures, with and without the displacement ellipsoids, were produced on an IBM 5080 Model 1 display using WINSOM, a solid modelling software package developed at the IBM (U.K.) Scientific Centre. The rigid mesogenic core is shown as the red cylinder, the carbon atoms in the chain are shown as small



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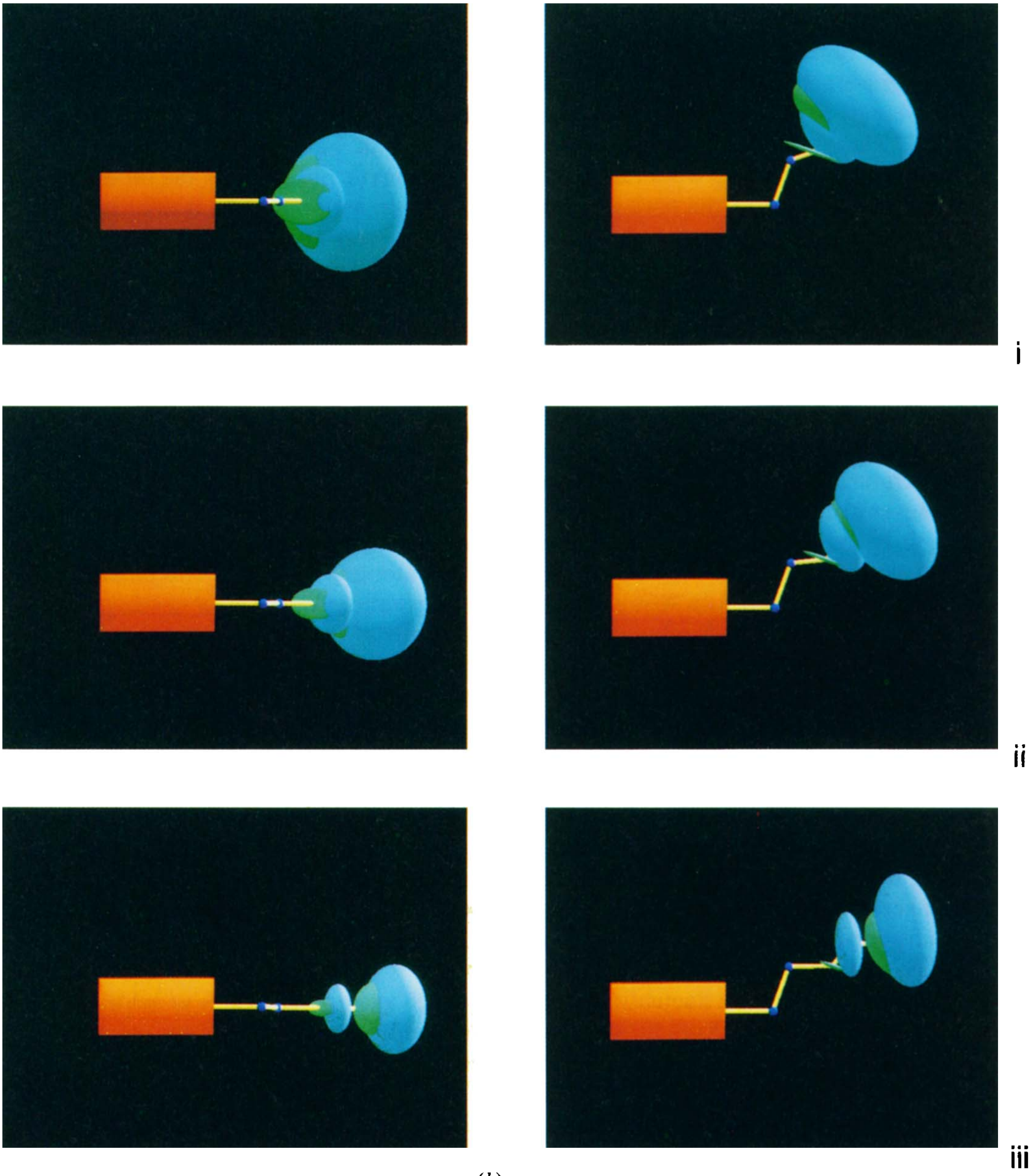

(*b*)

Figure 3. (*a*) The average locations of the carbon atoms in the alkyl chain of 4-*n*-heptyl-4′-cyanobiphenyl calculated for the isotropic phase at the nematic-isotropic transition (i) and at reduced temperatures of 0·85 (ii) and 0·55 (iii) within the nematic phase; the all-trans conformation (iv) is shown for comparison. (*b*) The displacement ellipsoids have been superimposed on these average positions and two views, along the x and y axes, of the composite structures are shown.

blue spheres and the linking carbon–carbon bonds as yellow lines (*cf.* figures 2 (*a*) and 3 (*a*)). The displacement ellipsoids are drawn alternately in green and blue along the chain so as to simplify the identification of the ellipsoids and to clarify their location on particular atoms. Two views of the resultant images, along the x and y axes, are shown in order to reveal the average molecular shape and the anisotropy of the displacement ellipsoids. In all of these images the size of the chain has been enlarged with respect to the core because our primary concern is with the average shape of the chain. The average positions of the carbon atoms in both chains change quite dramatically on passing from the isotropic to the nematic phase. Thus the tilt of the chain with respect to the core decreases, making the molecules less biaxial in the nematic phase. This difference in the orientation of the core and the chain is apparent from combined X-ray and optical studies of the molecular tilt angles in the smectic C phase [14], although such investigations are unable to detect the change in the relative orientation of the core and chain at the transition to the isotropic phase. The effective length of the bonds also increases, although those bonds essentially parallel to the core are more elongated than the others. There is also a tendency for the length of the bonds in these two sets to diminish as their distance from the core increases. As the temperature is lowered the effective chain length increases; indeed, at a reduced temperature of about 0·55 it is essentially equal to that of the all-trans conformer. However at the more usual, higher reduced temperature (~0·85) the average chain length is about 1 Å shorter than that of the fully extended chain; the extent of this shortening does increase with the number of carbon atoms in the chain. This difference in length is in accord with X-ray diffraction determinations of the layer spacings for smectic A phases, which often differ from the length of the all-trans conformer by approximately 2 Å [15]. The average structures shown in figures 2 (*a*) and 3 (*a*) illustrate in a very direct manner the change in both the molecular shape and dimensions brought about by the orientational ordering potential within the liquid crystal phase. We also note that the average positions for the carbon atoms common to both the hexyl and heptyl chains are essentially identical at the same reduced temperatures (*cf.* figures 2 (*a*) and 3 (*a*)). The sole difference between the two chains would seem to be in the position of the additional carbon atom in the heptyl chain. Such similarities in the average structures of the alkyl chains for neighbouring members of an homologous series lend support to a method of assigning deuterium quadrupolar splittings along a deuteriated alkyl chain based on comparisons with earlier members of the series [16].

We turn now to the fluctuations away from such average structures as evidenced by the displacement ellipsoids, which are shown centred on the respective atoms in figures 2 (*b*) and 3 (*b*). We begin with their appearance in the isotropic phase: the most obvious feature is the increase in size of the ellipsoid with increasing separation from the core which occurs as a result of the concerted displacements of preceding atoms. The first two atoms of the chain are fixed by our choice of reference frame and the third atom fluctuates the least from its average position; in fact the displacement ellipsoid is an ellipse in the plane formed by the three positions allowed for this atom. The remaining ellipsoids are essentially oblate with their minor axes tilted significantly away from the z axis, indeed almost parallel to the direction adopted by the average chain. Within the nematic phase the size of the displacement ellipsoids is reduced to an extent which decreases on lowering the temperature. In addition the orientation of the principal axes in the reference frame changes significantly until at the lowest reduced temperature these axes are essentially parallel to the reference frame. Such variations do not occur for the displacement ellipsoid for the third atom in the chain although its size does decrease dramatically with temperature. The size of the ellipsoids also increases with the separation of the atom from the core, as in the isotropic phase; this monotonic variation of the magnitude of the fluctuations along the alkyl chain is in accord with the analogous change in deuterium spin lattice relaxation times along the chain in 4-*n*-pentyl-4′-cyanobiphenyl [17]. Unlike the average positions of comparable atoms in the two chains there is a noticeable difference in the fluctuational ellipsoids, at the same reduced temperature. These differences are seen most clearly at the lowest reduced temperature, of 0·55, when the ellipsoids on adjacent atoms are reasonably well separated. The displacements of the carbon atoms in the hexyl chain appear to be larger than their counterparts in the longer, heptyl chain. Indeed even the terminal atom on the hexyl chain undergoes larger fluctuations away from its average position than that in the heptyl chain. Such differences might well be reflected in the deuterium N.M.R. spin lattice relaxation times although the measurements necessary to test this do not appear to have been made.

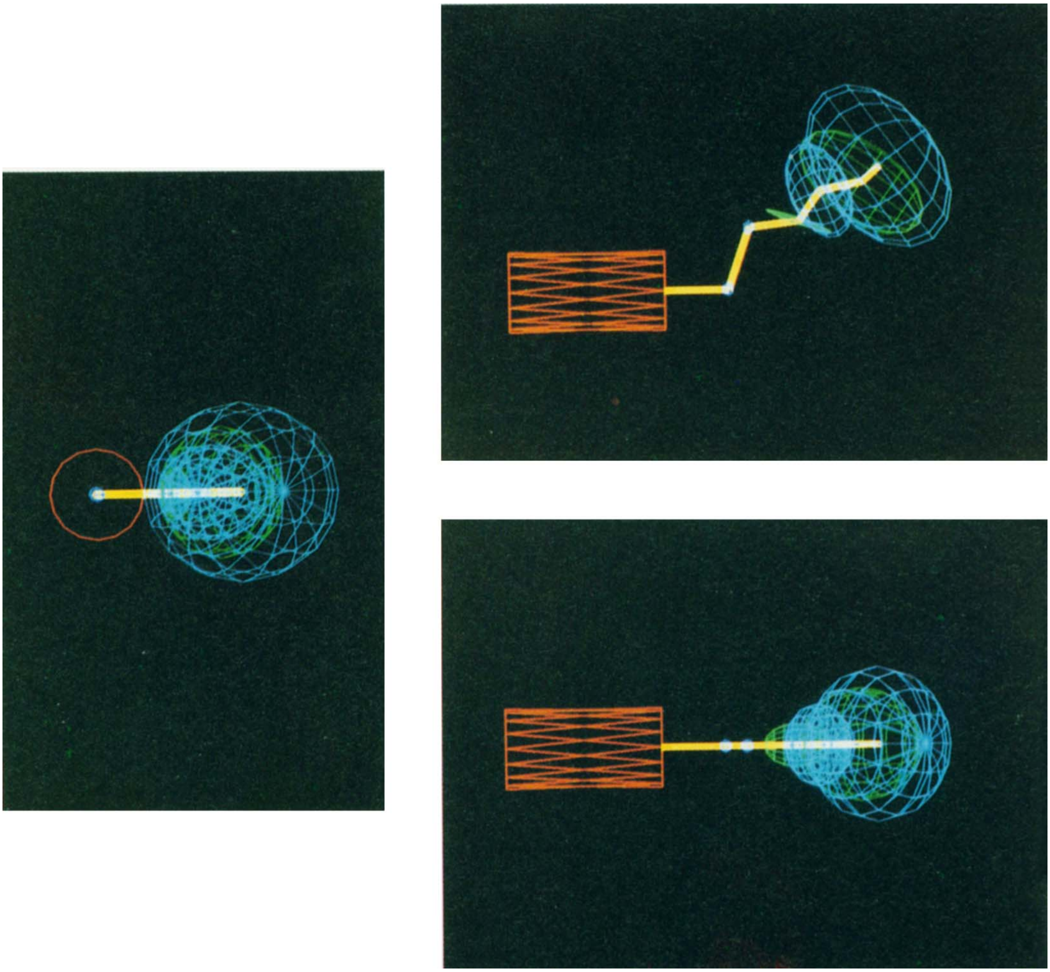

Figure 4. The images, taken along the x, y and z axes, constructed from faceted surfaces using vector graphics for 4-*n*-hexyl-4′-cyanobiphenyl in the nematic phase at a reduced temperature of approximately 0·85.

Although the solid images chosen to represent the average positions of the carbon atoms and their conformational fluctuations have many advantages, there are also disadvantages associated with them. For example, they cannot be rotated in real time on the IBM 5080 display and, perhaps more importantly, it is not possible to discern the shapes of ellipsoids when they overlap significantly. We have, therefore, considered an alternative form with which to show the displacement ellipsoids, based on the use of vector graphics to create a faceted surface to outline their shapes. An example of this construction, again drawn on an IBM 5080 display but now produced with the WGS three-dimensional vector graphics package, is shown in figure 4 for 4-*n*-hexyl-4′-cyanobiphenyl in the nematic phase at a reduced temperature of about 0·85. The two views, along the x and y axes comparable to those in figure 2 (*b*), are shown together with a third view along the z axis; the same colour coding is used as for the solid images. This form of presentation is particularly good for the view along the x axis where the four ellipsoids with their differing sizes and orientations are clearly apparent. These can be seen for the other two views but not quite so well because of the higher density of lines defining the faceted surface; indeed, for the image taken along the z axis it is especially difficult to locate the ellipsoids on their respective carbon atoms. However, it does emphasize, quite starkly, the fact that the core and chain are not collinear.

Finally we note that, although the scheme which we have developed to display the structures of non-rigid molecules has been applied to mesogenic compounds, we are aware that molecular flexibility is of importance in many other areas of science and we expect the representation, based on average atomic coordinates with their associated displacement ellipsoids, to be of value for these areas also.

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