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Modelling a nematic liquid crystal

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The bulk phase liquid crystalline behaviour of a cyclic siloxane with a pentamethylcyclosiloxane core and biphenyl-4-allyloxybenzoate mesogens (BCS) was studied using molecular dynamics (MD) and wide angle X-ray analysis. This material exhibits partial crystallinity at room temperature and liquid crystalline behaviour above 120°C. For the MD simulations an ensemble of 27 molecules with 135 mesogenic units was simulated and a molecular mechanics force field was used to model the structural anisotropy of the siloxane molecules. Simulations were carried out both at room temperature and at an elevated temperature (425 K). Room temperature simulations showed that, contrary to our initial assumptions, the low energy molecular conformations were not cylindrical but splayed in shape. During the simulation a smectic-like, tilted layer structure was found to evolve for the cluster when full atom potentials were used, while no such development was observed when electrostatic interactions were neglected. The presence of a tilted layered structure was also suggested by the X-ray data. These results indicate that long range electrostatic interactions are significant for the molecular system under study. In order to calculate the orientational order parameter, the orientation of the molecular axis had to be determined. This was achieved by describing the mesogen shapes to be ellipsoidal and defining the principal axis of the ellipsoids to be the molecular directors. By sampling over 200 ps of simulation at 425 K, the time averaged order parameter (S) was calculated. The calculated S of 0·36 was comparable to the value of 0·4–0·45 found from the experimental data. Apart from providing insight into the relative importance of the various competing forces in the formation of the liquid crystalline phase, these simulations are also expected to be useful in predicting the mesophase behaviour of liquid crystalline systems.

1. Introduction

Side chain liquid crystals based on small siloxane rings [1] have generated considerable interest as model multifunctional materials for optical applications. In addition to exhibiting fast alignment kinetics under applied electric fields [2, 3], these low molecular weight compounds can readily form glass phases. The combination of glass-forming ability and low molecular weight (which gives rise to low melt viscosity) makes these liquid crystalline compounds particularly attractive as matrices for non-linear optical chromophores. The liquid crystalline order can be easily vitrified, thus preserving field-induced alignment in the chromophores, and the low melt viscosity aids in the processibility. Of these cyclic siloxanes [1], we have been particularly interested in a pentamethylcyclosiloxane compound with biphenylbenzoate mesogens (BCS) (see figure 1) [3, 4] which exhibits nematic mesophase behaviour above 120°C [2, 3].

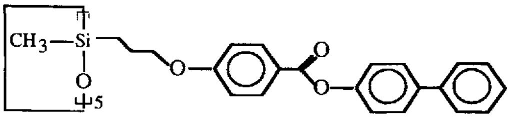

Figure 1. Schematic of cyclic siloxane with pentamethylcyclosiloxane core and biphenyl-4′-allyloxybenzoate mesogens.

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In the present paper we report our recent efforts in modelling BCS. In general, computer simulation studies of liquid crystals have focused on representing molecules by simple models [5–7] and are based on the assumption that the overall molecular shape and size determine the stability of the mesophases. For most cases these simulations take into account only excluded volume effects (the short range interactions are represented by 'hard' or 'soft' non-spherical potentials), but sometimes long range interactions are also included by using simple potentials. Although such models have been fairly successful in explaining broad features of the liquid crystalline phase, it has been evident from some recent studies [8, 9] that other factors, such as molecular flexibility, and variation in the polarizability, also contribute to anisotropic intermolecular interactions. These interactions favour orientational ordering and give rise to mesophase behaviour in molecules. The relative importance of the various contributions is dependent on the molecular structure, in which case a detailed potential energy function, such as the one provided in molecular mechanics, is needed to relate the structure with the phase behaviour. A major drawback of performing atomistic simulations using a molecular mechanics force field is the large computational effort involved, making it difficult to study a large number of molecules. However, with advances in computational capabilities and algorithm development, such larger scale simulations are now feasible and in the present study we report atomistic simulations on a cluster of BCS molecules.

Our initial studies [4] were concentrated on developing a suitable molecular model based on low energy conformations derived from molecular dynamics (MD) and semi-empirical quantum mechanical calculations. These studies were limited to single molecules and intermolecular interactions were taken into account by using periodic boundary conditions. Of the various possible conformations for BCS, a cylindrical conformation was found to be of the lowest energy [4].

In the present study we have extended our MD study to the investigation of the mesophase by analysing a molecular cluster at two different temperatures, one in the nematic range and another below the crystalline/nematic phase transition temperature. The purpose of these simulations is twofold: to determine the low energy molecular conformations by using explicit intermolecular interactions, and to develop an approach to study mesophase behaviour. Furthermore, such simulations are expected to support our efforts to develop a quantitative basis for structure–property relationships of these liquid crystalline materials and also to lay the foundation for future phase transition studies. Along with the molecular modelling, we also report results from X-ray diffraction analysis carried out at 100°C which is below the crystalline to nematic transition temperature [2].

2. X-ray diffraction

Figure 2 shows a wide angle X-ray pattern at 100°C. The pattern was obtained using synchrotron radiation from the Cornell High Energy Synchrotron Source (CHESS). The sample was aligned in the nematic phase using an electric field and then cooled to 100°C. Details of the experimental set-up are described elsewhere [2, 3]. The X-ray pattern showed several interesting features. All the prominent features of the high temperature nematic phase [2, 3] were still present. However, in most cases, the reflections were much sharper than those of the nematic phase. Some additional reflections were also found to be present. Although the sharp reflections indicate partial crystallinity, the absence of three-dimensional reflections ($h \neq 0, k \neq 0$ and $l \neq 0$) indicates that the material does not have long range three-dimensional positional correlation.

An interesting feature of the diffraction pattern is the four point pattern seen at small angles (see figure 3 (*a*)). This pattern is also observed in the nematic phase [3] and is considered to be indicative of the formation of cybotactic groups where domains with smectic C-like ordering are present [10]. At low temperatures ($\approx$ 100°C, see figure 2) these groups become fairly rigid and a tilted layered structure such as the one represented schematically in figure 3 (*b*) develops. The boundary planes in cybotactic groups (shown by the dotted lines in figure 3 (*b*)) have significantly different electron density than the layers themselves. These boundary planes define layers which extend normal to the plane of the paper and are arranged in all possible orientations about the alignment axis (in this case taken to be the *x* axis).

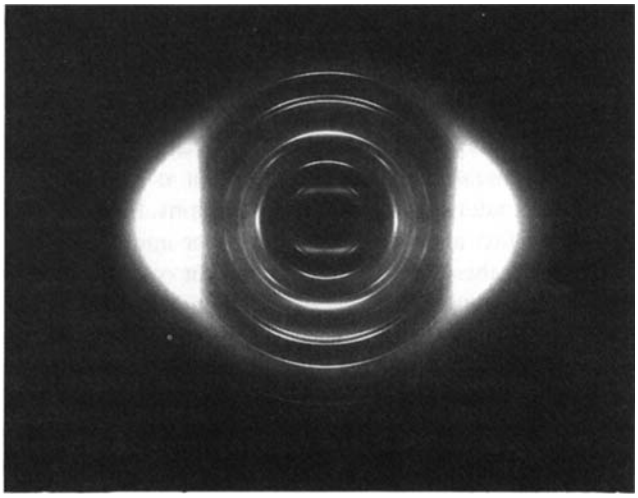

Figure 2. X-ray diffraction pattern of the sample at 100°C aligned with electric field of 10 KHz. The field direction is parallel to the meridian.

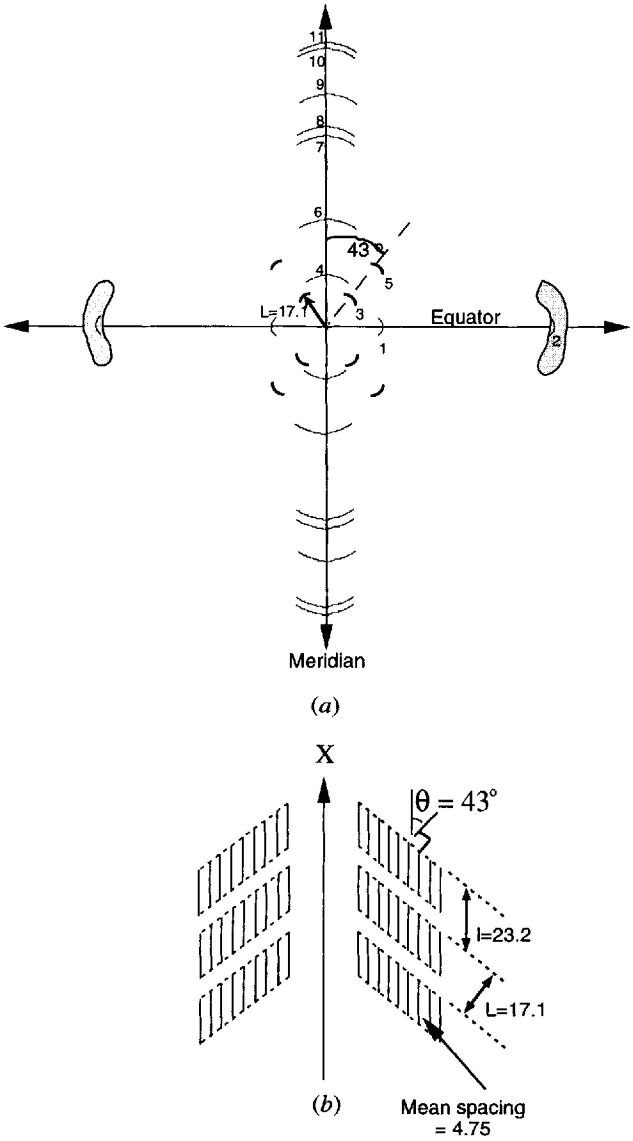

Figure 3. A schematic diagram showing (*a*) the various features of the X-ray diffraction pattern and (*b*) the layered structure.

Although in general cybotactic groups need to have only two parallel boundary planes, the sharpness of the four point pattern indicates that in the present case several groups are stacked together sharing boundary planes so as to form larger units. From reflection 3 (see figure 3 (*a*)), the periodicity (L) of this layered structure was measured to be 17·1 Å. A higher order ($n = 2$) reflection with $d = 8{\cdot}49$ Å (reflection 5) was also observed from this system of planes. The degree of arcing of reflections 3 and 5 is an indication of the perfection with which the layers are oriented. Their narrowness indicates that there is a significant long range orientational order between the layers. At the same time, the absence of reflections corresponding to $h \neq 0$, $k \neq 0$, $l \neq 0$ indicates very little lateral registry between the layers. The angle (θ) between the meridian and reflections 3 and 5 was measured to be 43°. This angle corresponds to the angle between the molecular axis and the normal to the boundary plane. From the values of L and θ, the repeat unit along the long axis (l) was calculated to be 23·2 Å. This is about half the length (45 Å) of a BCS molecule in the cylindrical conformation [4]. Therefore, the layers can be considered to be made of mesogens separated at the boundary plane by siloxane rings.

The wide angle crescent (4–5·5 Å) on the equator is characteristic of the average lateral packing of the mesogens [3]. The crescent is diffuse and wide. Its diffusiveness indicates that there is short range packing order between the mesogens, whereas the wide arc indicates that there is a large degree of misorientation about the alignment axis. In addition to the crescent, there are two more reflections on the equator with *d*-spacings of 9·91(1) and 4·75(2) Å. Frozen-in mesogens with longer range positional order could be contributing to the 4·75 Å reflection which is overlapped by the wide angle crescent. Its sharpness indicates that, unlike the nematic phase where all the mesogens have short range order, the low temperature phase has some mesogens with long range positional order. Although the occurrence of the reflection with 9·91 Å *d*-spacing cannot be unambiguously resolved, it can be attributed to the siloxane rings which are approximately of the same dimensions. A factor that supports this hypothesis is the observation of this reflection in electrically and magnetically aligned samples, but not in fibre samples [11]. The rings, which are electrostatically charged units, can be better aligned in the presence of a field, thereby giving rise to relatively longer range positional order in electrically and magnetically aligned samples.

Sharp reflections with *d*-spacings of 11·6(4), 7·8(5), 6·76(6), 5·79(7), 5·56(8), 4·78(9), 3·91(10) and 3·87(11) Å were observed on the meridian. The reflections with *d*-spacings 11·6, 7·8, 5·79, 4·78 and 3·87 Å can be referred to as the 2nd–6th order reflections from a repeat unit of 23·2 Å. These higher order reflections have also been observed in the nematic phase [12], although the shape of the reflections is different. At high temperatures, the reflections are disc-like, indicating cylindrical averaging of the mesogens, whereas at low temperatures they become like arcs, representing mesogen misorientation about the axis of alignment. The periodic reflections can be due to molecules arranged as strings parallel to the director with the centre of masses of the mesogens spaced with a periodicity of 23·2 Å. The reflections with 5·56 and 3·91 Å *d*-spacings can be considered as the 3rd and 4th order reflections from a repeat unit of 16·5 Å. A 16·5 Å length corresponds to the $O{-}C_6H_4{-}COO{-}C_6H_4C_6H_5$ segment, which is the rigid segment of the mesogen and of higher electron density than the rest of the mesogen. It is not very surprising to see only third and fourth order reflections from the rigid segment because the third and fourth order reflections from the mesogens ($l = 23{\cdot}2$ Å, figure 2) have also been observed to be of higher intensity. This is found to be the case also for diffraction data taken from powder samples at room temperature, and for magnetically aligned samples at high temperature [11].

3. Molecular dynamics

3.1. *Computational details*

The large scale simulations discussed in this paper were run on Sandia's nCUBE 2 machine, a 1024-processor distributed-memory parallel computer capable of 1–2 Gflops. The computations discussed were performed with a widely used MD package known as CHARMM [13] and a parallel molecular simulation code called ParBond [14]. Both codes use molecular mechanics force fields and model molecules via empirical equations for covalent 2-, 3-, and 4-body interactions (bond, angle, dihedral, improper forces) and pair-wise van der Waals and Coulombic (non-bonded) forces. The potential energy function used is given by

$$\begin{aligned}E_{\text{total}} = {} & \sum_{\text{bonds}} k_{\text{b}}(r - r_{\text{eq}})^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_{\text{eq}})^2 \\ & + \sum_{\text{dihedrals}} k_\phi(1 + \cos(n\phi - \delta)) \\ & + \sum_{\text{impropers}} k_\omega(\omega - \omega_{\text{eq}})^2 \\ & + \sum_{i,j>i} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \qquad (1)\end{aligned}$$

where k_{b}, k_θ, k_ϕ and k_ω are force constants representing bond stretching, bond bending, torsional motion and improper torsional motion respectively and A_{ij} and B_{ij} are non-bonded parameters derived from atom polarizabilities and effective number of outer shell electrons.

The results from the two codes were compatible since ParBond can compute CHARMM force fields. Full molecular flexibility was allowed as no geometric constraints were enforced on the molecular model and the parameters from QUANTA/CHARMm [15] were used. In all the simulations a 0·001 picosecond (ps) integration time step was used. A three-dimensional lattice with 135 mesogenic units was generated and the starting molecular conformation was taken to be cylindrical, based on results from our earlier study [4].

The degree of alignment in a liquid crystalline material can be defined by its microscopic order parameter which is a measure of the orientational distribution of its molecules. For rigid molecules of arbitrary shape, the order parameter is a tensor quantity $S_{ij}^{\alpha\beta}$ [16] where $\alpha\beta$ (x, y, z) refer to the laboratory fixed axes, ij refer to the molecular axes, and $S_{ij}^{\alpha\beta} = \frac{1}{2}\langle 3i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij}\rangle$. $S_{ij}^{\alpha\beta}$ is symmetric in $\alpha\beta$ and ij and is also a traceless tensor with respect to either pair, i.e. $S_{ij}^{\alpha\alpha} = S_{ii}^{\alpha\beta} = 0$. In the uniaxial nematic case, assuming that the nematic director is along z, the only non-zero components of the ordering matrix are $S_{ij}^{zz} = -2S_{ij}^{xx} = -2S_{ij}^{yy}$. Therefore the state of alignment of uniaxial rigid molecules can be fully described by calculating the scalar order parameter S,

$$S = \tfrac{3}{2}\langle\cos^2\theta_i\rangle - \tfrac{1}{2}$$

where θ_i is the angle between the long axis of molecule i and the nematic director.

For non-rigid models, namely for real molecules, the definition of the molecular frame, i.e. the molecular long axis, is difficult. In principle, separate order parameters should be defined with respect to the rigid core and the covalent bonds of the alkyl segment as these would be different due to their difference in flexibility. However, a more commonly used procedure is to define the molecular axes to be identified with the axes of symmetry of the molecule.

In the present case, the mesogens were assumed to be ellipsoidal with cylindrical symmetry and a single order parameter representing the average value of the angle between the symmetry axis of any individual mesogen and the macroscopic symmetry axis was considered to be sufficient for describing the alignment of the system. It is not inappropriate to treat the mesogens as uniaxial as they mainly execute rotational motion about their long axis and not their short axis. Although based on the structure of the mesogen, which has a hard segment at the centre and alkyl segments on both ends, the molecular shape was chosen to be ellipsoidal rather than cylindrical, the choice of this particular shape did not affect the results, since we were primarily concerned with the scalar order parameter which was calculated from the angle between the molecular axis and nematic director.

In order to assign ellipsoidal shape to the mesogens we had to measure the length (a), breadth (b) and width (c) of individual mesogens. This was done by first determining the centroid of the mesogen based on the position of all its atoms and then defining the origin to be at the centroid. After searching for the furthermost atom (i) from the origin, the primary axis was defined by a line segment with its centre at the origin and end points at atom (i) and an equidistant point reflected through the origin. The molecule was then rotated such that the primary axis coincided with the z axis and a search was made to find the position of an atom (j) furthermost from the z axis. The position of atom (j) was projected on the x–y plane, and the secondary axis or the mesogen width was defined by the line segment between this projected point and an equidistant point reflected about the origin. The molecule was further rotated so that the secondary axis was on the x–z plane. Then a search was made along a small solid angle about the y axis for the atom (k) furthest away from the z axis. The tertiary axis or the mesogen breadth was defined by a line segment between the projection of atom (k) on the y axis and its reflection about the origin. The ratios a/b and a/c were measured to evaluate the various mesogenic shapes. The nematic director was taken to be the mean molecular director for all the mesogens in the system. Due to the weak coupling between the rings and the mesogens and the flexible nature of the rings [4], the main contribution to the liquid crystallinity was assumed to be from the mesogen–mesogen interactions and the orientational order of the system (S) was taken to be approximately equal to that of the mesogens.

3.2. *MD at 300 K*

In a molecular mechanics force field, the computational work involved in evaluating the non-bonded interactions for a molecular system with N atoms increases as O (N^2). Therefore, it is common to introduce non-bonded cut-offs which define distances such that non-bonded interactions between pairs of atoms greater than these distances are neglected. Although the use of this method increases computational efficiency, discontinuities in the forces at the cut-off can lead to non-conservation of energy, while neglecting structure stabilizing interactions beyond cut-offs can give rise to conformational effects. Since Coulombic forces converge more slowly than van der Waals forces, these effects can be non-trivial for molecular systems such as BCS, where the electrostatic interactions are significant [4]. In the present case we evaluated the effect of two different cut-offs (10 Å and 15 Å) on the energy of a single molecule of BCS. The structural consequences, which are more difficult to detect than the energetic effects, were not studied in detail. The variation in the potential energy during the time of simulation is shown in figure 4. It was found that during a 100 ps simulation (after a 5 ps heating and 20 ps equilibration phase), the use of a 10 Å cut-off gave rise to non-conservation in the energy. Therefore, for all the subsequent runs a 15 Å cut-off was used which was observed to be energetically stable. Also, with the shorter cut-off, a time delayed effect in the evolution of equilibration structures was observed, indicating the presence of conformational effects.

In the starting configuration (see figure 5 (a)), 27 molecules (total of 6750 atoms) with 135 mesogens (each molecule has five attached mesogens) were arranged in a lattice such that the separation distances between the rings were 23 Å along x, 11·5 Å along y and 16·5 Å along z, with the long axis of the molecules along x. These dimensions were based on our earlier results [4] and were derived from distances corresponding to the minimum energy between two molecules as determined by Lennard–Jones and Coulombic interactions. On assuming a relevant correlation length of about 15 Å as is indicated by the stability of the potential energy with a 15 Å cut-off (see figure 4), it can be seen that all the neighbouring molecules of the central molecule which are within a radius defined by this correlation length are included in the cluster. Thus it is expected that there is no significant effect of the finite system size on the conformation of the central molecule. However, the cut-offs were studied for isolated molecules and were probably too inaccurate to account for all relevant long range interactions. Therefore, results from these simulations with free boundaries were compared with those using periodic boundary conditions (pbc) where the sample box is surrounded by exact replicas of itself.

To study the relative importance of various long and short range interactions in determining the molecular packing, several simulations were carried out. In each case, the energy of the molecular system was first minimized at 0 K and then the system was slowly heated to 300 K over a 100 ps time period. It was equilibrated at 300 K for 200 ps, and simulations were again carried out for another 200 ps. The analysis was carried out over this final stage, which is referred to as the simulation stage. The position coordinates were saved every 1 ps and 200 snapshots were analysed during the simulation stage. Figure 5 shows snapshots during the simulation under different conditions. For clarity, in all cases except the first, only the ring positions are shown. It was found that the long axis of the mesogens which were originally all aligned along x, were now distributed about x with an order parameter of 0·31. Also, the rings which were arranged in a rectangular lattice in the starting configuration (see

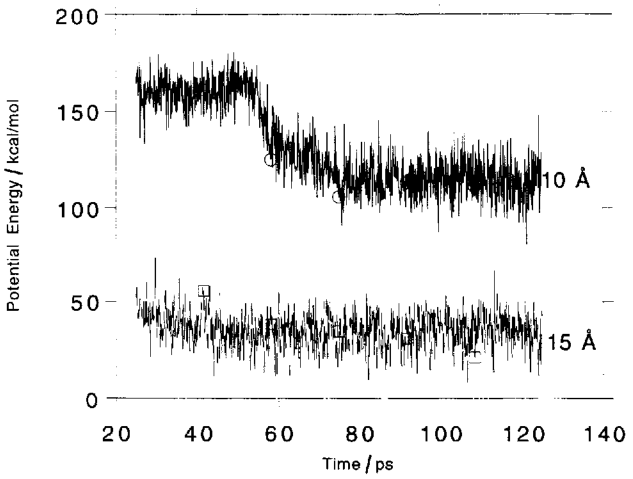

Figure 4. Effect of the non-bonded cutoff distance on the potential energy.

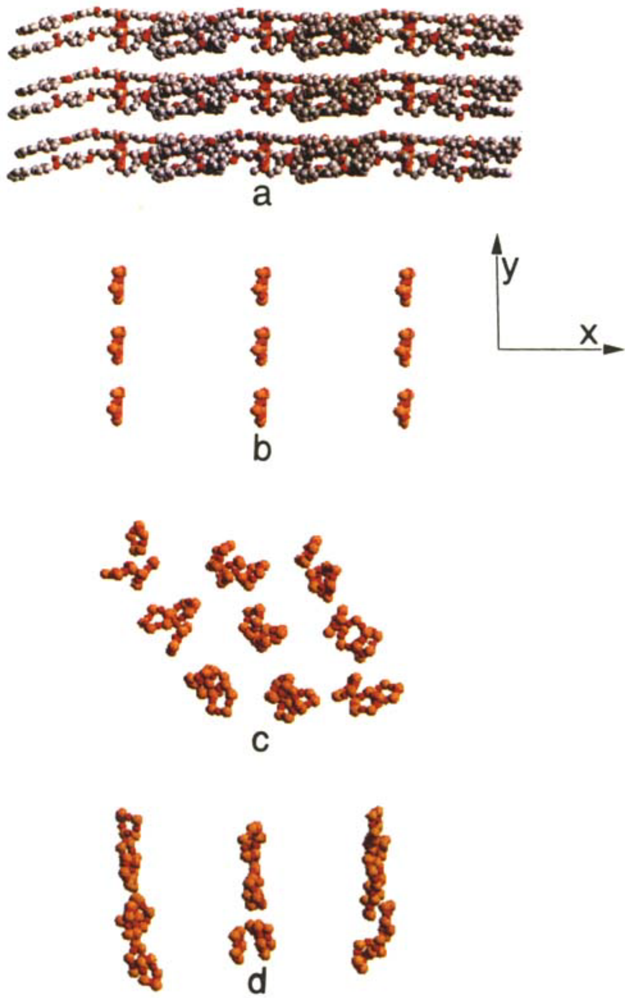

Figure 5. Snapshots showing the molecular cluster (*x*–*y* projection) during simulation at 300 K. Silicon atoms are shown in orange, oxygen in red and carbon in grey. (*a*) Starting position, (*b*) starting ring positions, (*c*) ring positions during simulation with electrostatic interactions included, (*d*) ring position during simulation with electrostatic interactions excluded.

figures 5 (*a*) and (*b*)), formed a rhombohedral arrangement during the simulation (see figure 5 (*c*)). The rings were now aligned such that they formed three sets of vertical layers normal to the plane of the paper and inclined to the *x* axis at 45°. Such a tilted molecular packing scheme where the boundary planes (made of siloxane rings) makes an angle with the mean direction of the molecular axis (taken to be the *x* axis) is consistent with the X-ray results described in the previous section (see figure 3). These results indicate that the molecular modelling study was successful in reproducing some of the salient features of the molecular packing present in the material. There is indirect evidence from some of our earlier simulations [4] that electrostatic interactions between various groups (the siloxane ring and the ester group in the mesogens) could be responsible for such a molecular packing. In order to verify this assumption, simulations were carried out without the inclusion of electrostatic interactions. As shown in figures 4 (*c*) and (*d*), a large difference was observed between the packing in the cases with and without electrostatic interactions. In the later case, no obvious tilt formation was observed. These simulations suggest that electrostatic interactions may be responsible for the tilted layer structure observed in the material.

In order to get an estimate of the molecular shape of the low energy conformations, the conformation of the central molecule in the cluster was analysed during the simulation. It was found that, due to the flexibility about the alkyl spacers, the configuration changes from the initial cylindrical shape to a more splayed-like conformation.

Due to the flexible nature of the molecule, a single parameter was not found to be sufficient in defining the degree of alignment of the various segments. Therefore, instead of considering the whole molecule as a single unit, each individual side chain ($((CH_2)_2–O–C_6H_4–COO–C_6H_4–C_6H_5)$) was taken to be an independent mesogenic segment and its shape was determined by approximating an ellipsoid around it. A large degree of variation was observed in the mesogen shape. Figure 6 shows a histogram of the *a/b* ratios corresponding to all the mesogens in 200 snapshots. The largest group of mesogens had an *a/b* ratio between 2·6 and 2·8, although quite a few had ratios as low as 1·2, indicating that even in the mesogen segment, a wide range of flexibility is present. It should be noted that the *a/b* ratio of the mesogens of the starting cylindrical model was 3·0.

Simulations with pbc did not show the development of the tilted structure, indicating that while using pbc, the shape of the simulation box is very critical and should be commensurate with the periodicity of the phase being studied. In the absence of a priori knowledge about the periodicity present in the system, it may be more appropriate to use free boundaries and a large cluster so that the system-size effects are small. At the same time it should be kept in mind that the calculated order parameters and the nematic–isotropic transition temperatures for the systems modelled with free boundaries will be smaller than those for the real molecular systems.

3.3. *MD at 425 K*

In order to estimate the molecular shape and the orientational order parameter in the nematic phase, simulations were carried out at 425 K. This temperature is approximately in the centre of the nematic range. A 100 ps heating time, a 200 ps equilibration time and 100 ps simulation time protocol was used. The molecular director was determined for each mesogen and the orientational order parameter was calculated throughout the simulation. The mean and median values of the order parameter,

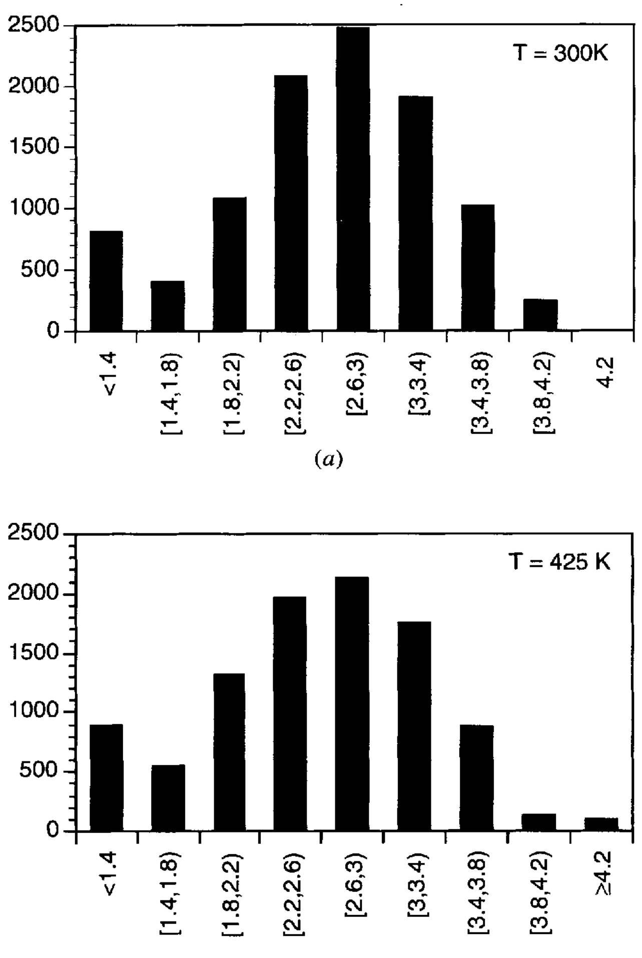

Figure 6. A histogram showing the variation in *a/b* ratios of the mesogens during a 200 ps simulation at (*a*) 300 K and (*b*) 425 K.

averaged over the final 200 ps, were found to be 0·35 and 0·36, respectively. These values although a little smaller (expected due to the use of free boundaries) than the experimental values of 0·4–0·45 [2] still compare reasonably well. It was observed that, compared to the simulations at 300 K, the population of mesogens with higher values of *a/b* was reduced.

4. Conclusions

X-ray results indicate that the material is partially crystalline at 100°C. Under an applied electric field, the mesogens are aligned along the field with a significant misorientation about the alignment axis. The molecules can be considered to be arranged as strings parallel to the alignment axis forming smectic C-like layers with their boundary planes inclined at an angle to the director axis.

By simulating a three-dimensional molecular cluster of BCS molecules, low energy conformations of the molecules in the presence of intermolecular interactions could be identified. It was found that, contrary to our previous assumptions [4], the low energy molecular conformations were not cylindrical but splayed in shape. Results from the MD simulations were consistent with the X-ray data and indicated that electrostatic interactions were mainly responsible for the tilted layer structure. The calculated order parameters were found to have values comparable to the experimental values [2]. Most of the simulations were done with free boundaries and future studies will include larger molecular systems which are expected to have smaller boundary effects. The results from the MD study presented here are to be used to form the basis for subsequent studies of the temperature dependence of the orientational order present in the material. In a broader sense, calculations such as these have wide ranging applications. Along with providing a systematic study of the relative importance of the various competing forces (steric repulsion, attractive forces, long range electrostatic interactions, etc.) in the formation of a liquid crystalline phase, they can also be used to predict phase behaviour prior to synthesizing the materials.

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