Atomistic Simulations of a Thermotropic Biaxial Liquid Crystal

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We have performed molecular dynamics simulations of a 2,5-bis-(p-hydroxyphenyl)-1,3,4-oxadiazole mesogen (ODBP-Ph-C7) at a fully atomistic level for a range of temperatures within the region that has experimentally been assigned to a biaxial nematic phase. Analysis of the data shows that the simulated nematic phase is biaxial but that the degree of biaxiality is small. The simulations show also the formation of ferroelectric domains in the nematic where the molecular short axis is aligned with the oxadiazole dipoles parallel to each other. Removal of electrostatic interactions leads to destabilization of ferroelectric domains and destabilization of the biaxiality. An additional simulation shows the slow growth of a mesophase directly from the isotropic fluid over a period of approximately 50 ns. This is the first time this has been achieved within the framework of an all-atom model.

Predicted theoretically by Freiser more than 30 years ago [1], the phenomenon of nematic biaxiality has been observed in both lyotropic [2] and polymeric liquid crystals [3]. However, until recently biaxiality has remained elusive for thermotropic nematogens. A large variety of synthetic strategies have been employed to engineer new molecules, which could potentially exhibit orientational order along two perpendicular axes [4–7]. Although each strategy showed some merit, none of these succeeded in producing a verifiable biaxial phase. Recently this situation changed with both Madsen et al. [8] and Acharya et al. [9] reporting strong experimental evidence to have discovered the first biaxial phase in low molecular weight thermotropic liquid crystals based on molecules with an oxadiazole core (Fig. 1). These molecules are neither calamitic (rodlike) nor discotic (dislike) but belong to a third group of thermotropic mesogens known as bend-core mesogens [10]. Earlier theoretical work had predicted that bend-core systems could form mesophases [11]. However, the bend angle of the oxadiazole systems does not correspond to that predicted by theory, and at this stage it is not possible to attribute biaxial ordering in oxadiazole mesogens purely to molecular shape. It should also be noted that experiments to characterize the biaxial nematic phase further are not easy, since it is found to be stable only at high temperatures, which makes analysis difficult [8].

This Letter aims at analyzing the reported biaxial liquid crystalline phase of ODBP-Ph-C7 (Fig. 1) using an atomistic simulation approach for the molecule and investigating the forces responsible for its formation. Simulation allows us to observe the evolution of the biaxial phase and study the structure of the phase itself at a molecular level.

Results are obtained from classical molecular dynamics simulations carried out with 256 molecules in a cubic simulation box at five state points corresponding to temperatures assigned experimentally to lie within the biaxial nematic region: 448, 458, 468, 478, and 488 K. The calculations use an all-atom molecular dynamics simulation approach adopting the same methodology outlined in full in previous studies of the mesogen PCH5 [12,13]. In brief, the simulations used a harmonic force field of the OPLS-AA form obtained from a combination of ab initio quantum calculations to parametrize internal degrees of freedom and small molecule simulations to refine parameters for nonbonded terms [14,15]; employed partial electronic charges with an Ewald sum treatment of electrostatics; made use of the SHAKE procedure to constrain bond lengths with a time step of 2 fs; and were carried out in the constant-NpT ensemble using a Nosé-Hoover thermostat and a Hoover barostat coupled to a leap frog integrator. Simulations were started from an idealized perfectly aligned pseudonematic starting configuration with perfect order ($Q_{00}^2 = \langle S_2 \rangle = 1$, $Q_{22}^2 = 1$) at a gas phase density, compressed rapidly to liquid state density and equilibrated at a pressure of 1 bar. Additional simulations were started from an isotropic configuration with $Q_{00}^2 = \langle S_2 \rangle = 0$ at gas phase density. This was also compressed rapidly to liquid phase density and equilibrated to form an isotropic liquid phase.

The molecular orientation was calculated on the basis of three different criteria: (a) orthogonal vectors representing the three principal inertia axes of the molecule were obtained by diagonalizing the inertia tensor; (b) three orthogonal vectors were obtained from the central oxadiazole ring, with the ring long axis pointing along the nitrogen-nitrogen vector and the short axis pointing along

![Molecular structure and experimental transition temperatures of ODBP-Ph-C7.](image-url)
the system using spheroids [16] and a biaxial Gay-Berne [17], predict a
cules. For example, single site biaxial potentials, such as from the three molecular axes (axial order parameter for the long axis, By convention, Z Allen [16] we also calculate the biaxial order parameter for the molecule as a whole.

Table I suggests that the biaxiality of the core is imposed not depend significantly on the definition of the axes in the system to equilibrate. In Table I we give the mean values for each order parameter calculated from the final 3.5 ns of simulation for 5 temperatures. The system is seen to remain nematic and biaxial between 448 and 488 K, which covers the experimental range where biaxiality has been reported [8,9], with order parameters decreasing slightly as temperature is increased over this range. The measured biaxiality is small but sufficiently high to indicate a small degree of orientational order for the short axis within the phase. The fact that the values of <S^zzz>, <S^yzy>, and Q^zz do not depend significantly on the definition of the axes in Table I suggests that the biaxiality of the core is imposed on the molecule as a whole.

It should be stressed that the values for Q^zz are <0.2 in all cases. Such values are smaller than expected from previous simulations of idealized models for biaxial molecules. For example, single site biaxial potentials, such as spheroids [16] and a biaxial Gay-Berne [17], predict a

<table>
<thead>
<tr>
<th>Temperature/(K)</th>
<th>&lt;S^zzz&gt;</th>
<th>&lt;S^yzy&gt;</th>
<th>Q^zz</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>0.73 ± 0.02</td>
<td>0.27 ± 0.02</td>
<td>0.11 ± 0.03</td>
</tr>
<tr>
<td>458</td>
<td>0.74 ± 0.02</td>
<td>0.23 ± 0.03</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>468</td>
<td>0.71 ± 0.02</td>
<td>0.24 ± 0.02</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>478</td>
<td>0.68 ± 0.02</td>
<td>0.22 ± 0.02</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>488</td>
<td>0.65 ± 0.02</td>
<td>0.22 ± 0.02</td>
<td>0.09 ± 0.03</td>
</tr>
</tbody>
</table>

FIG. 2. Uniaxial order parameters calculated for the molecular long axis, <S^zzz> (top line), short axis, <S^yzy> (middle line), and biaxial order parameter (Q^zz) (bottom line) at 468 K. (a) Top graph—system grown from a perfectly aligned nematic; (b) system grown from the isotropic phase.

TABLE I. Mean order parameters for a series of simulation temperatures. Values are calculated from using definition (a) and (c)(ii) for the three molecular axes. Values for (c)(ii) are included in parentheses.
cently performed atomistic simulations [18]. The value of \( \langle S_i^2 \rangle = 0.2 \pm 0.02 \) for E7 is comparable to that seen in this work, while the value of \( \langle Q_z^2 \rangle = 0.06 \pm 0.03 \) is clearly considerably less. Here, however, we can deduce that the relatively large value of \( \langle S_i^2 \rangle \) for the E7 simulation is due to the central dipoles being aligned. A more quantitative measure of this is provided by calculating the biaxial parameter \( \eta \). Here, \( \eta = (q_{yy} - q_{xx})/q_{zz} \), where \( q_{zz} \geq |q_{yy}| \geq |q_{xx}| \) for eigenvalues of the ordering tensor of a chosen axis. For ODBP-Ph-C\(_7\), the ordering tensor for the long molecular (inertia) axes at 468 K yields a value of \( \eta = 0.16 \pm 0.04 \), whereas for E7 the value of \( \eta \) is 0.03 ± 0.02. With this evidence, it seems quite clear that the orientational order in ODBP-Ph-C\(_7\), although small, is fundamentally different to that in a uniaxial liquid crystal with local biaxial fluctuations. Madsen et al. [8] have measured a value of \( \eta \) in their NMR study by using quadrupolar splitting from a probe molecule of hexamethylbenzene dissolved in ODBP-Ph-C\(_7\). In their work a value of \( \eta \) of 0.11 is measured. This measurement arises from the biaxial ordering of the probe molecule within the phase itself. We would expect a slightly higher phase biaxiality from the actual ODBP-Ph-C\(_7\) molecules. As noted in [19], \( \eta \) values are expected to depend on the axis chosen within the molecule. In our work, larger values of \( \eta \) are available if other axes are chosen, e.g., a value of \( \eta = 0.3 \pm 0.1 \) is measured for the short axis at 468 K.

Turning to the interactions responsible for biaxiality, it has been suggested that the dipole across the center of the oxadiazole ring is important in stabilizing a biaxial phase. To this end it is interesting to note the formation of small ferroelectrically ordered domains in the sample. These are shown clearly in Fig. 3, where the color coding shows domains where the center dipoles are aligned. A more quantitative measure of this is provided by calculating the distance dependent pairwise dipole correlation function, \( g_1(r) = \langle \cos(\theta_{ij}) \rangle \), for all molecular pairs \( i \) and \( j \) at a separation \( r \) for angles \( \theta_{ij} \) between the short molecular axes (Fig. 4). Here, distances are measured with respect to the center of the oxadiazole ring. The peak in \( g_1(r) \) between \( 4.2 \) and \( 14.6 \) Å indicates a preference for a parallel arrangement of the core dipoles at these distances. [The sharp negative signal in \( g_1(r) \) over a very small range of \( r \) at \( \approx 3.3 \) Å occurs because two cores with parallel dipoles cannot approach this close without unfavorable steric repulsion.]

To test whether the small ferroelectric domains arise from preferential packing of the core or from electrostatics, we carried out additional simulations in which partial charges were removed from the system for further simulations at 468 K. The immediate influence of the removal of charges is a slight stabilization of the nematic phase, with the uniaxial order parameter from the long inertia axis increasing slightly to 0.8; accompanied by a decrease in \( \langle Q_z^2 \rangle \) to 0.07 and a decrease in \( \eta \) for the long axis to 0.03. The change in density accompanying the removal of charges is very small (<0.1%) (from 1.049 to 1.048 g cm\(^{-3}\)). As shown in Fig. 4 the reduction in biaxiality is associated with a destabilization of the ferroelectric domains. It therefore seems likely that ferroelectric parallel alignment of the cores helps in the stabilization of the biaxial nematic in ODBP-Ph-C\(_7\). Possibly this is due to favorable quadrupolar stacking of the molecular cores. Reintroduction of the charges leads to a recovery of the original domains and order parameters over a 8 ns period.

In recent experimental work, Göritz and Goodby have reported that oxidazole compounds can show interesting behavior with the formation of chiral domains of opposite handedness, as seen via optical microscopy [20]. We have therefore carried out extended simulations to study the
behavior of ODBP-Ph-C₇ on cooling by taking an equilibrated isotropic liquid phase and quenching into the mesophase regime. The time evolution of the order parameters from this simulation is shown in Fig. 2. Here, growth of a liquid crystalline mesophase takes place over approximately 50 ns, (corresponding to approximately 12 CPU years on our parallel opteron computer system used for this work). To our knowledge this is the first time growth of a liquid crystal phase has been achieved for an all-atom liquid crystal model. The time scale for the orientational transition is very similar to that seen in the work of Berardi et al. who considered the orientational melting of a nematic to an isotropic phase close to the clearing point [21]; and is considerably longer than that required for united-atom [22] or coarse-grained simulation models [23].

The value of $\langle S^Z_2 \rangle$ at the end of the run are typical of those expected experimentally for a nematic system. Viewing the snapshot in Fig. 3 shows that the phase has formed into two distinct ferroelectric domains in quenching. For this simulation, we have calculated the chirality for each molecule by means of the scaled chirality index, $G_{0S}$ [24]. Although individual molecular conformations are strongly chiral, the overall chirality cancels out through conformational averaging. Within the simulation error bars we can detect no difference in the chirality for the two domains formed. It should be stressed, of course, that the two domains seen here are limited by the size of the simulation box, $=(64 \AA)^3$, which is very small compared to the domains seen experimentally.

Summary.—We have simulated the nematic phase of the molecule ODBP-Ph-C₇ at an all-atom simulation level for 256 molecules. The results show that the degree of biaxiality is small in this molecule as measured by the biaxial order parameter $\langle Q^2_{22} \rangle$. However, we find that the biaxiality seen in this system is genuine and fundamentally different from the local biaxial fluctuations that arise in uniaxial systems. This is highlighted by comparisons of $\langle Q^2_{22} \rangle$ and the phase biaxiality $\eta$ from simulations of the uniaxial mixture, E7. The discovery of ferroelectric domains in this system is a surprising result. On removal of electronic charges these domains are destabilized, with a correspond-