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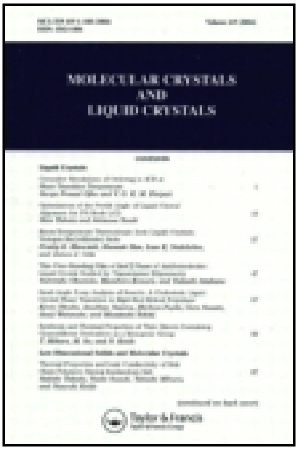

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Computer Simulations of Mesogenic Molecules Using Realistic Atom-Atom Potentials

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Computer Simulations of Mesogenic Molecules Using Realistic Atom-Atom Potentials

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Molecular dynamics simulations are reported for an atom-based model of the mesogen *trans*-4-(*trans*-4-n-pentylcyclohexyl)cyclohexylcarbonitrile (CCH5). Atom-atom potential functions take account of intermolecular contributions to the potential energy and internal molecular structure is modelled by a standard empirical force field. The calculations are carried out in the isothermal-isobaric ensemble at a range of temperatures, and the results provide predictions for phase behaviour and orientational ordering which are in good agreement with experiment. Time-averaged molecular properties are calculated from the simulation data. We discuss the possible uses of this technique in the study of liquid crystalline systems and in the prediction of the phase behaviour of real molecules.

INTRODUCTION

During the last decade considerable progress has been made in the computer simulation of liquid crystals.[1] Work on a variety of *hard-nonspherical* models has been successful in showing the importance of excluded volume effects in the promotion of mesogenic behaviour and confirms that liquid-crystalline behaviour can be understood in terms of the simplest of models.[2]

Although hard-repulsive interactions play a dominant role in determining phase behaviour, it is clear from experiment that a number of other factors may also be important.[3] For real molecules it is likely that molecular shape, charge distribution and polarizability anisotropy will all have some effect on phase behaviour, and that the extent of this influence will vary from molecule to molecule. The assessment of the importance of each of these factors provides a major challenge for the computer simulator.[4]

Recently, we have been involved in the development of realistic computer models for liquid crystal molecules. Our initial studies[5,6] have concentrated on computing intermolecular interaction energies and preferred dimer configurations for pairs of mesogenic molecules, using complex atom-atom potentials. By employing potential functions on each atom, a complex molecular potential may be built which models faithfully the detailed structural anisotropy of real molecules. Our results indicate that we are able to successfully model both dipole-dipole and orientational cor-

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relations which exist in dilute solutions of anisotropic molecules.[5,6,7] However both experiment and calculation agree in predicting that strong angular correlation between molecular pairs is not necessarily associated with stable mesophase behaviour.[6,8] Phase behaviour appears to be most strongly dependent on molecular packing within the bulk fluid.

In the present work we extend our study of model mesogens to the investigation of the bulk mesophase. Molecular dynamics calculations are carried out for a *realistic* model of the molecule *trans*-4-(*trans*-4-n-pentylcyclohexyl)cyclohexylcarbonitrile (CCH5). We use the same atom-atom potentials employed in our previous studies on pairs of molecules, and allow for molecular flexibility through the use of a standard molecular mechanics force-field. Molecular properties are calculated for the isotropic and nematic phases shown by our model, and we assess the possibilities and limitations of this approach in the study of liquid crystal phase stability.

COMPUTATIONAL DETAILS

In this study mesogenic molecules are represented as flexible entities composed of a series of atom-based potential functions. We employ the united atom approximation throughout, replacing hydrogen atoms attached to non-electronegative atoms with extended atoms. Thus for CCH5 a 19-site model is used (Figure 1). The potential energy function employed is the AMBER potential,[10,11]

$$E_{\text{total}} = \sum_{\text{bonds}} K_r(r - r_{eq})^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}(1 + \cos(n\phi - \gamma)) + \sum_{i<j} \left(\frac{q_i q_j}{R_{i,j}} + \frac{A_{i,j}}{R_{i,j}^{12}} - \frac{C_{i,j}}{R_{i,j}^{6}} \right), \quad (1)$$

where K_r, K_θ and V_n are force constants representing bond stretching, bond bending and torsional motion respectively. $R_{i,j}$ is the distance between atoms i and j, $A_{i,j} = (A_{i,i} \cdot A_{j,j})^{1/2}$, and $C_{i,j} = (C_{i,i} \cdot C_{j,j})^{1/2}$. $A_{i,i}$ and $C_{i,i}$ can be expressed in terms of Lennard-Jones ε and σ parameters: $A_{i,i} = 4\varepsilon_{i,i}\sigma_{i,i}^{12}$, $C_{i,i} = 4\varepsilon_{i,i}\sigma_{i,i}^{6}$.[12]

As in our previous work on CCH5[5] we use non-bonded parameters derived from Monte Carlo simulations of simple organic liquids.[13] Partial charges were obtained from minimal basis set SCF calculations on energy minimised structures of CCH5 using the program GAMESS.[14] Merger of the AMBER force-field with the OPLS non-bonded potential functions due to Jorgensen has already been considered.[15] Use of OPLS potentials requires that the AMBER 1,4 non-bonded interactions are scaled by dividing by a factor of 8.0 for Lennard-Jones terms. The force-field parameters used in this study are given in the appendix. Trial molecular mechanics calculations indicated that the global energy minimum for CCH5 was in good agreement with crystal structure data, and that conformational energy differences for fragments of CCH5 were close to those given by MM2.[16]

Differentiation of equation (1) provides the force acting on each atom at a given

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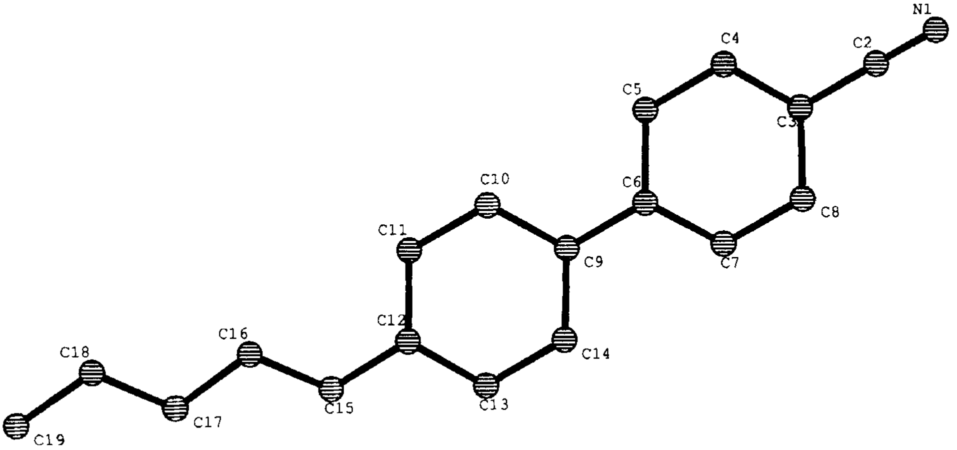

FIGURE 1 United atom model for a molecule of *trans*-4-(*trans*-4-n-pentylcyclohexyl)cyclohexylcarbonitrile, CCH5.

time. Newton's equations of motion were solved using the molecular dynamics module of the program AMBER.[10] The time-evolution of the system is carried out using the *leapfrog* algorithm, and we make use of the SHAKE method[17] to remove high frequency bond-stretching motion, allowing the use of a 3 fs time-step. A non-bonded cutoff of 8Å was used and the calculations were carried out at constant temperature and zero pressure. Calculations were carried out on the Bristol University IBM 3090-150 VF computer. The computationally expensive calculation of non-bonded interactions proved to be well-vectorizable.

Initial calculations were carried out on 64 molecules of CCH5 to provide preliminary information about phase behaviour. Cubic periodic boundary conditions were employed, together with isotropic pressure scaling of the system. We make use of both isotropic and nematic-like starting configurations. Our main production runs were carried out on a system of 128 molecules in a cuboidal box with lengths in the ratio 1:1:2.

RESULTS AND DISCUSSION

Initial calculations involved a series of fairly short simulation runs (200–500 ps) starting from both an initially well-aligned sample of 64 molecules with an order parameter of 0.8 and also from a randomly oriented sample of the same size. We follow Eppenga and Frenkel[18] in calculating the order parameter S as minus twice the middle eigenvalue of the ordering tensor whose components are,

$$Q_{\alpha\beta} = \frac{1}{N}\sum_i (3u_{i\alpha}u_{i\beta} - \delta_{\alpha\beta})/2 \qquad (2)$$

where $\mathbf{u}_i$ is a unit vector along the long axis of the moment of inertia ellipsoid for

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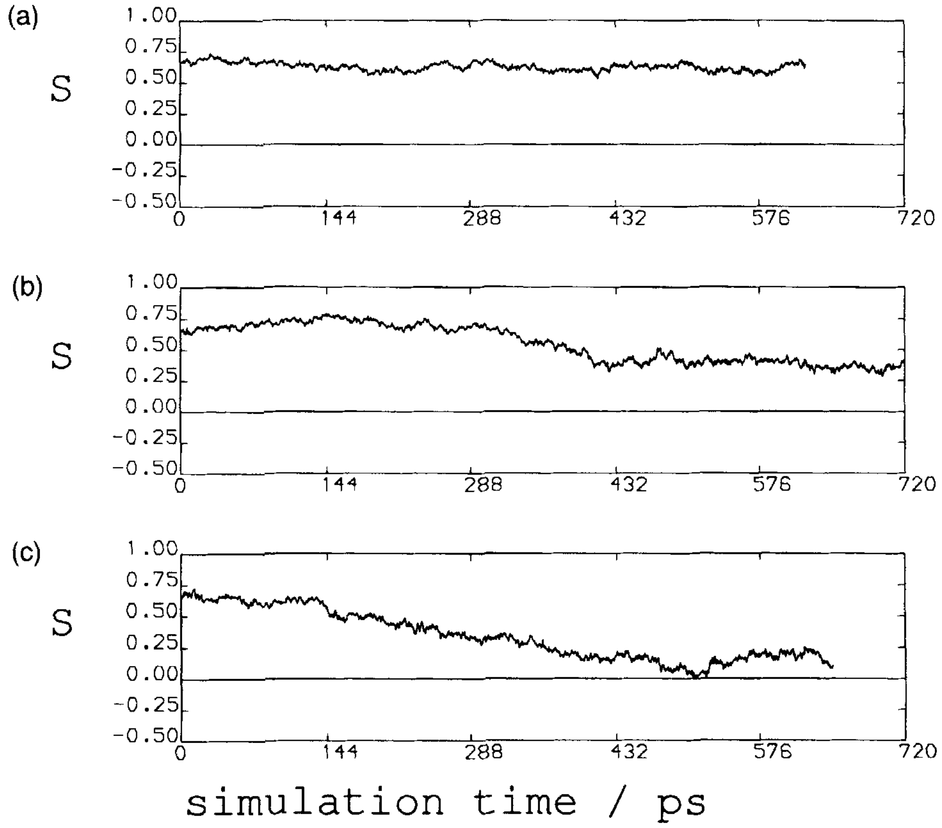

FIGURE 2 The decay of uniaxial order parameter S in simulations of 128 molecules of CCH5 at different temperatures: a) 350 K; b) 370 K; c) 390 K.

each molecule i. Runs were carried out at 10 K intervals in the region 290–400 K. At high temperatures (400 K), decay of orientational order occurred fairly rapidly within 200 ps. At lower temperatures, 330–360 K, the behaviour of the system was extremely sluggish, and there were clear indications that problems were being caused by too small a system size. Below 330 K, the system freezes. Although there were some signs of the tilted layer structure exhibited in the crystal structure of CCH5,[9] it proved impossible to enter the solid phase slowly enough to avoid the freezing-in of considerable molecular disorder.

Calculations starting from a well-aligned sample carried out at 290 K, showed no sign of freezing over a period 550 ps. After an initial decay of the orientational order parameter to a value of 0.6, the system appeared to equilibrate at an order parameter of 0.8. Observation of snapshots taken from this run show the presence of translational order. The behaviour was tentatively assigned to the formation of a super-cooled smectic phase.

Following our initial calculations three longer runs were carried out on a sample of 128 molecules. A starting configuration with $S = 0.65$, was generated by duplicating an equilibrated box of 64 particles along the director axis (z-axis). Sim-

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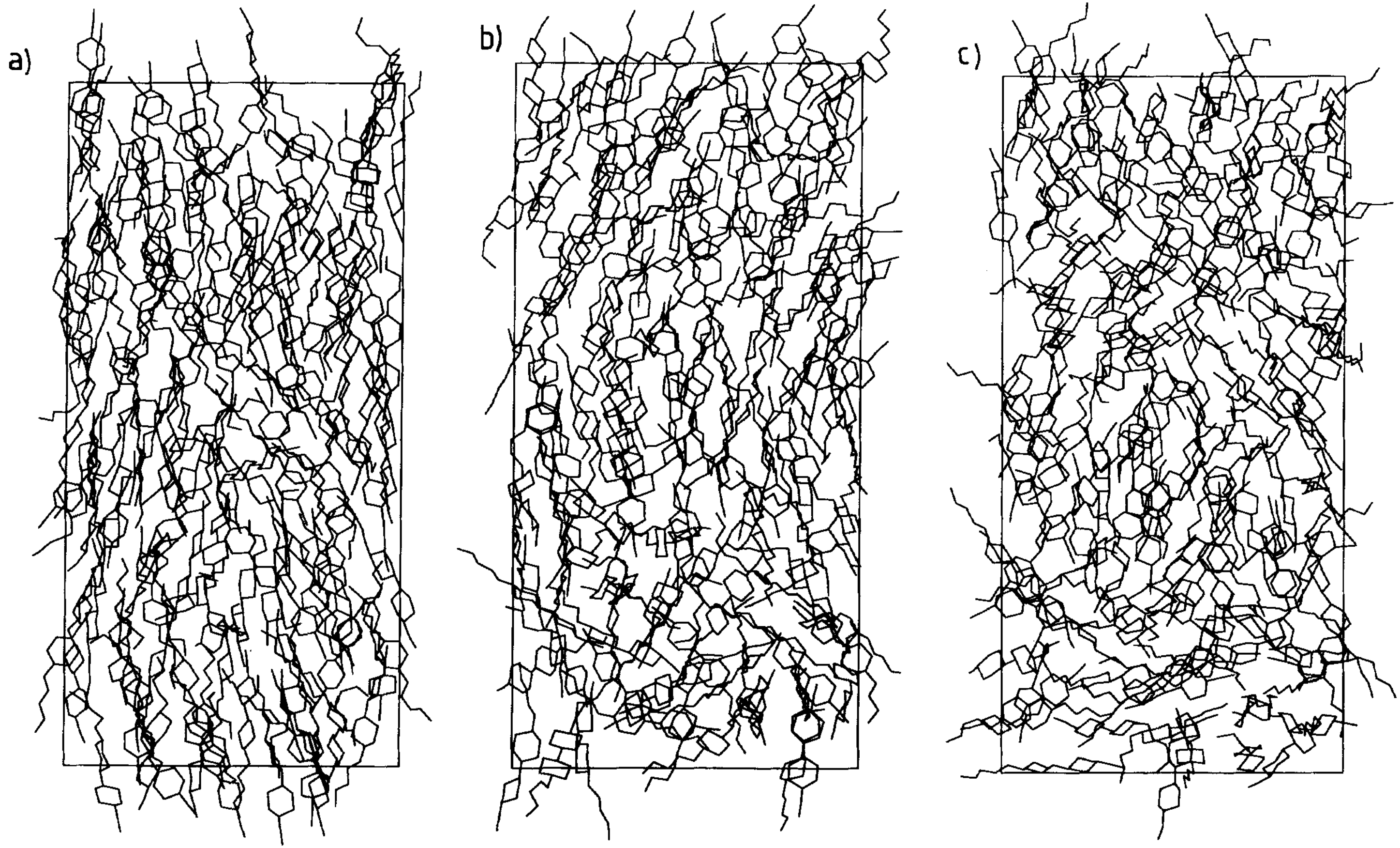

FIGURE 3 Snapshots from simulations of CCH5 at different temperatures. a) Nematic phase at 350 K, $S = 0.64$. b) Nematic phase at 370 K, $S = 0.39$. c) Isotropic phase at 390 K, $S = 0.18$.

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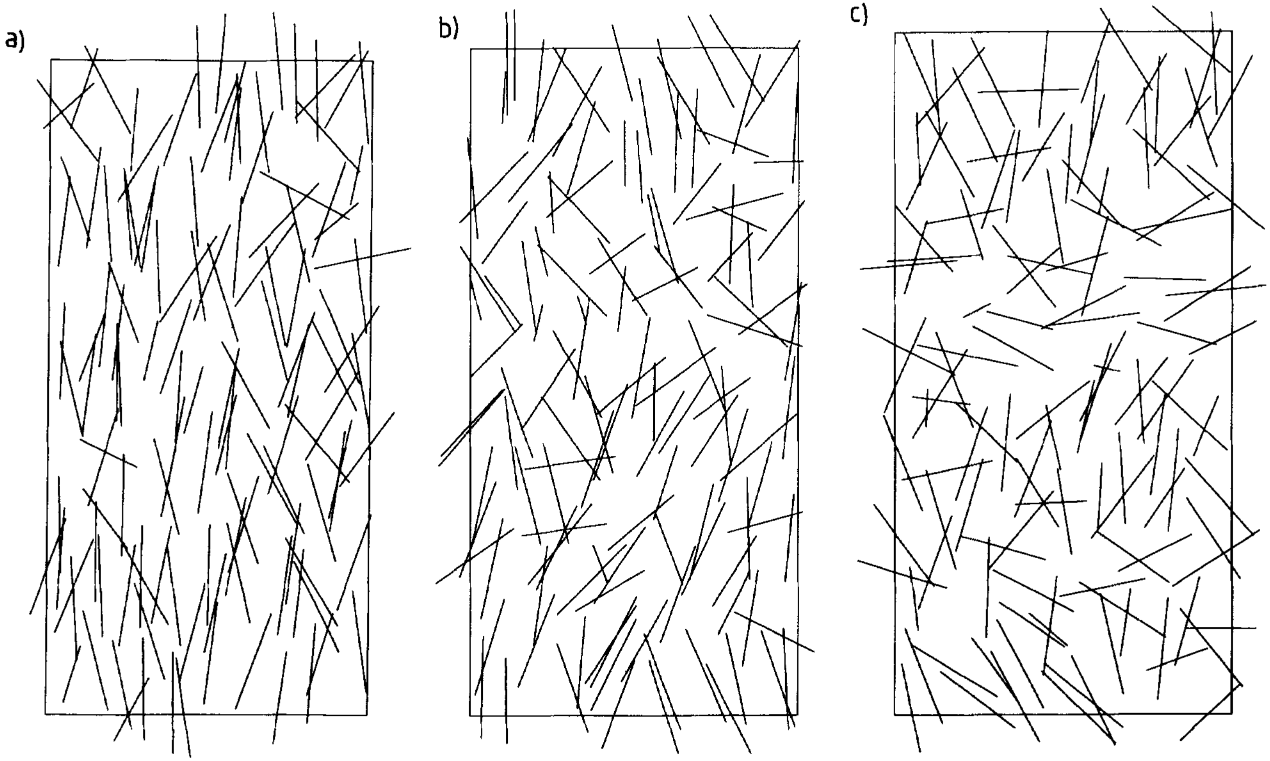

FIGURE 4 Snapshots from simulations of CCH5 at different temperatures showing the alignment of the principal moment of inertia axis for each molecule. a) Nematic phase at 350 K, $S = 0.64$. b) Nematic phase at 370 K, $S = 0.39$. c) Isotropic phase at 390 K, $S = 0.18$.

TABLE I

Diffusion coefficients, mean order parameter, and mean density for simulations of CCH5

T / K	$\overline{D}$ / 10^{-9} m^2 s^{-1}	$D_{\parallel}$ / 10^{-9} m^2 s^{-1}	$D_{\perp}$ / 10^{-9} m^2 s^{-1}	S	ρ / kg m^{-3}
350	0.313	0.554	0.192	0.62	916.1
370	0.703	1.076	0.517	0.38	881.9
390	1.067	1.230	0.986	0.14	854.3

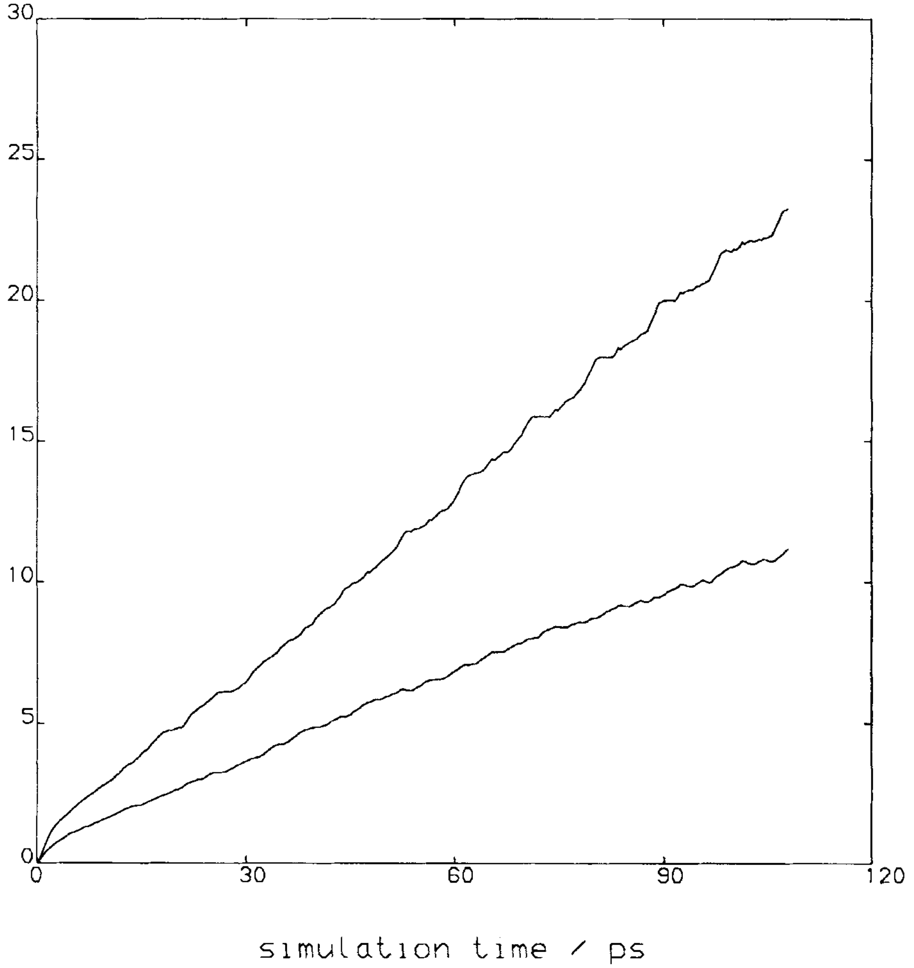

FIGURE 5 Mean square displacements of CCH5 molecules averaged over the final 216 ps of the 370 K simulation, units of Å^2.

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TABLE II

Mean Length *a*, width *b*, and breadth *c*, of molecular moment of inertia ellipsoids for CCH5

T/K	*a*/Å	*b*/Å	*c*/Å
350	9.80	2.06	1.12
370	9.73	2.09	1.18
390	9.66	2.11	1.27

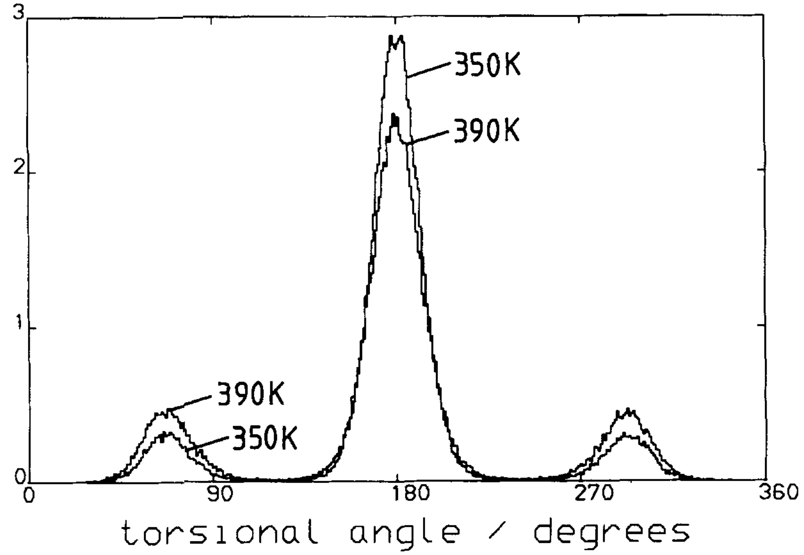

FIGURE 6 Distribution of the dihedral angle C16-C17-C18-C19 for CCH5 at 350 and 390 K, (arbitrary units).

ulations were carried out at 350 K, 370 K and 390 K. The decay of S is shown in Figure 2 for these three runs, and snapshots of sample configurations are shown in Figures 3 and 4. At 390 K, the order parameter decays over a period of approximately 500 ps to give an isotropic liquid. At 350 and 370 K a nematic phase is clearly visible. In the most ordered system (350 K) some indication of local smectic ordering can be seen in Figure 4a. For comparison the nematic range for real CCH5 is 335–358 K. The mean values of the order parameter averaged over the final 216 ps of each run are given in Table I. The value of $S = 0.14$ at 390 K is too low for a nematic phase but is indicative of the pretransitional order parameter fluctuations which occur in an isotropic liquid.

In constant volume, constant energy simulations, diffusion coefficients can be calculated either from the velocity autocorrelation function or from molecular mean-square displacements. In our isothermal-isobaric simulations we can only make approximate estimates of diffusion coefficients, both because of the (small) systematic differences between ensembles and because box-size fluctuations are superimposed on molecular displacements, worsening the statistics. Nonetheless, we have calculated the diffusion coefficients as a guide to the true values and as a

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check that the system remains fluid throughout the simulation runs. At each temperature we average the mean square displacements over the final 216 ps of the run. In Figure 5 we plot the mean square displacements parallel and perpendicular to the director for our system at 370 K. The form of the curve indicates that displacements should be monitored out to time intervals of at least 60 ps. Diffusion and orientational order are closely coupled in the nematic phase; strong evidence of this has appeared in simulations of hard ellipsoids,[20] and is also observed in this work. Corresponding diffusion coefficients $D_{\|}$ and $D_{\perp}$ and the mean value $\bar{D} = (D_{\|} + 2D_{\perp})/3$, are given in Table I. A substantial decrease in diffusion is seen as the nematic phase is entered from above. Diffusion is favoured parallel to the director as expected, even for the 390 K run where fluctuations in orientational order still occur in the isotropic phase.

The mean length, width and breath of the molecular moment of inertia ellipsoids have been calculated, and are given in Table II. They indicate that an elongation of the molecular long axis occurs, as temperature is decreased. Calculation of the dihedral distribution $s(\phi)$ for torsional angles in the alkyl chain, confirms a broader distribution of dihedral angles in the high temperature phase (Figure 6). It has been predicted by theory that a quenching of torsional angle distributions should occur in the nematic phase.[19] Calculations of the effective potential of mean torque $v(\phi) = -k_BT \ln s(\phi)$ from our measured $s(\phi)$ indicate that an effect of this kind is seen, i.e. the differences in distributions are not simply attributable to the differences in temperature. More detailed investigations of this phenomenon will form the subject of a further communication.

CONCLUSIONS

The work presented here is preliminary in the sense that only three state points are studied in detail. However, the implications of the approach taken here are far reaching. Calculations such as these should be able to provide both predictions of molecular properties and approximate predictions of phase behaviour prior to synthesis. They therefore have a role in the molecular engineering of new materials.

In addition to their use as an experimental tool, realistic simulations of mesogens have considerable potential from the point of view of theory. Despite numerous studies, the role played by molecular structure in the formation of liquid crystal phases is still poorly understood. The relative importance of steric repulsions, attractive forces and charge effects in specific molecules are not clear. Realistic simulations open the way to a systematic study of these factors. Molecular correlations of structurally similar molecules with different phase behaviour can be studied at the molecular level, providing information about intermolecular interactions. Tuning of interactions by the removal of partial charges or the artificial raising of torsional barriers are easily carried out, allowing the study of the importance of dipolar effects or molecular flexibility in isolation from other factors.

The drawback of these calculations is seen in the cost involved. This work has been limited to relatively small system sizes (64–128 molecules) and to fairly short run times (< 750 ps), because of the large amounts of computer time involved. In this study a total CPU time in excess of 800 hours was required on an IBM 3090

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processor. Conversion of molecular collision times of hard particles into molecular units suggest that run times well in excess of 1 ns may be required in order to see the spontaneous formation of orientationally ordered mesophases from the isotropic phase. Runs of this length are within reach, but require dedicated computer resources. Close to phase transitions the behaviour of the system becomes sluggish. A series of long runs on large systems are required in order to pin down transition temperatures with any degree of certainty. This study suggests that such runs for realistic models of the kind studied here are currently beyond the reach of modern computers.

APPENDIX: SIMULATION DATA

TABLE III

Assignment of atom-types and partial charges for extended atoms in CCH5

atom name	atom type	partial electronic charge
N1	NZ	-0.20576
C2	CZ	0.06299
C3	CH	0.04664
C4	C2	0.029485
C5	C2	0.006045
C6	CH	0.01575
C7	C2	0.006045
C8	C2	0.029485
C9	CH	0.01379
C10	C2	-0.005225
C11	C2	-0.003155
C12	CH	0.01544
C13	C2	-0.003155
C14	C2	-0.005225
C15	C2	-0.00253
C16	C2	-0.00060
C17	C2	0.00191
C18	C2	0.00689
C19	C3	-0.00881

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TABLE IV

Bond stretching parameters

bond	K_r/kcal mol^{-1}Å^{-2}	r_{eq}/Å
CH-CH	260.0	1.526
CH-C2	260.0	1.526
CH-C3	260.0	1.526
C2-C2	260.0	1.526
C2-C3	260.0	1.526
CH-CZ	374.0	1.466
CZ-NZ	1330.9	1.164

TABLE V

Bond bending parameters

angle	K_θ/kcal mol^{-1}rad^{-2}	θ_{eq}/°
CH-CH-C3	63.0	111.5
CH-CH-C2	63.0	111.5
CH-CH-CH	63.0	111.5
C2-CH-C2	63.0	111.5
CH-C2-CH	63.0	112.4
CH-C2-C2	63.0	112.4
CH-C2-C3	63.0	112.4
C3-C2-C2	63.0	112.4
C2-C2-C2	63.0	112.4
C2-CH-CZ	63.0	111.5
CH-CZ-NZ	57.6	180.0

TABLE VI

Torsional parameters

torsion	$\frac{V_n}{2}$/kcal mol^{-1}	γ	n
X-CH-CH-X	2.0	0	3
X-CH-C2-X	2.0	0	3
X-C2-C2-X	2.0	0	3

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TABLE VII

Improper torsional parameters

torsion	$\frac{V_n}{2}$/kcal mol^{-1}	γ	n
X-C2-CH-X	2.0	180	3
X-CH-CH-X	2.0	180	3

TABLE VIII

Nonbonded parameters

atom	$A_{i,i}$/kcal mol^{-1}Å^{12}	$C_{i,i}$/kcal mol^{-1}Å^{6}
CH	3393741.3	1024.1
C2	5934641.1	1673.7
C3	8801374.5	2482.1
CZ	3248063.4	1168.0
NZ	944298.4	801.3

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