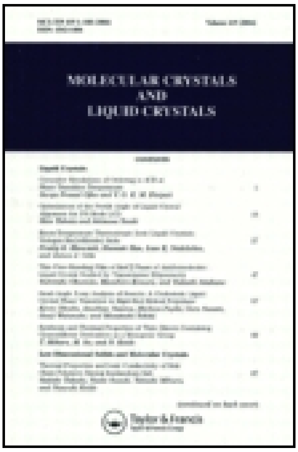

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Molecular Dynamics Simulations for Cyanobiphenyl Liquid Crystals

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MOLECULAR DYNAMICS SIMULATIONS FOR CYANOBIPHENYL LIQUID CRYSTALS

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Abstract A new approach has been used to perform detailed molecular dynamics simulations for several cyanobiphenyl liquid crystals. The molecular potential is obtained by considering the phenyl rings in the liquid crystal molecules as enlarged spherical extended atoms. This method allows more rapid simulations than those using full atom-atom potentials, without losing any structural or orientational information. To investigate the nematic properties of the cyanobiphenyl liquid crystals, we calculated the order parameters for the principle molecular axes, C-H bonds in the alkyl chains, and C-C bonds of the alkyl chains of four cyanobiphenyls, and compared the results with available experimental data. Diffusion coefficients in directions both parallel and perpendicular to the director have also been calculated. To study the conformational equilibria of the model systems, we have also calculated dihedral distribution functions for several of the relevant torsional angles.

INTRODUCTION

Because of the orientational ordering and structural anisotropy displayed by liquid crystal systems, their theoretical study is an interesting and challenging task. One of the earliest liquid crystal theories is the work by Maier and Saupe.[1,2] According to their theory, know as the mean field theory, the individual liquid crystal molecule is treated as a rigid rod which exists in an average potential field created by the molecules surrounding it. This technique was later improved by Marcelja[3] who included the effect of a flexible alkyl chain in his model liquid crystal molecules. Since these theories were created, more rigorous and complex treatments have been presented by several other groups.[4-7] All of these treatments are based upon the original method of Maier and Saupe. Each description considers that the orientation and conformation of the liquid crystal molecules are determined by their interaction with the average potential field created by the surrounding molecules. These theories only consider average inter and intra molecular interactions between individual molecules, allowing the solutions to be obtained in an analytical form. However, because of the many degrees of freedom associated with a flexible liquid crystal model, it is mathematically difficult to describe mean field models for arbitrary liquid crystal systems of varying size and complexity. These problems have limited the wide spread use of mean field theory as a practical tool for studying liquid crystal behavior in terms of structure-property relationships. Ideally, one would like to develop models for any liquid crystal relating the phase behavior and other important characteristics to their detailed structural composition; however, this is a very difficult problem which has not yet been solved.

Molecular dynamics (MD) simulations are an alternate method which can be used to describe the orientational and structural behavior of liquid crystals[8-23] and other ordered systems.[24-30] During molecular dynamics simulations, various combinations of bonded and non-bonded molecular potentials are used to construct a model liquid crystal molecule.[31] An ensemble of these molecules is then allowed to interact with one another for a specified length of time. By using special algorithms, the temperature and pressure can be held constant during a simulation, allowing a variety of ensemble types to be evaluated.[32,33] During the simulation, individual liquid crystal molecules are oriented by their anisotropic interactions with the molecules surrounding them. The physical forces responsible for orienting the individual liquid crystal molecules are conceptually very similar for both mean field theories and molecular dynamics simulations.

Spherocylindrical or ellipsoidal potential functions such as the Gay-Berne potential[17-21,31] have been used in many MD simulations. These types of potentials describe the interaction between liquid crystal molecules in terms of an orientational dependence and a positional dependence. Simulations of this type have been shown to display nematic and smectic like phases as well as first order nematic to isotropic phase transitions.[20,31] Although these studies demonstrate that the elongated shape of a liquid crystal molecule is capable of explaining orientational behavior and causing phase transitions, they are too simple to yield any practical information about how this behavior depends upon the detailed structural composition of the individual molecules.

With the development of more powerful and economical computers, more sophisticated algorithms have been developed which allow complex model systems to be described at the atomic scale in terms of stretching, bending, torsional, and non-bonded interactions. These new computer programs make it possible to study the orientational behavior and other anisotropic properties of liquid crystals in great detail. Simulations of this type are capable, in principle, of giving very specific information concerning orientational, structural, dynamical, and phase behavior, and how it is related to detailed molecular composition. Although modern MD techniques offer the benefit of atomic details, very few liquid crystal systems have been studied this way because of the extremely time consuming nature of the computations. Some liquid crystalline systems which have been studied at this level are: 4-*n*-pentyl-4'-cyanobiphenyl (5CB),[12] 4-*n*-pentyloxy-4'-cyanobiphenyl (5OCB),[13] and *trans*-4-(*trans*-4-*n*-pentylcyclohexyl)cyclohexylcarbonitrile (CCH5).[14,15]

With the aid of a supercomputer, molecular dynamics computer simulations of systems having approximately 20,000-30,000 atoms can be handled. However, many researchers only have access to a mainframe computer or dedicated workstation which is capable of simulating smaller systems (approximately 3000 atoms or less is within reach of many modern workstations). Given size limitations such as this, only the smallest liquid crystalline compounds can be systematically studied. In order to circumvent this problem, we have developed and tested a method which allows detailed structural and conformational information to be built into a simulation while delivering substantial time savings.[34] This paper uses the new method described above to investigate the orientational behavior of several cyanobiphenyl liquid crystals: 4-*n*-pentyl-4'-cyanobiphenyl (5CB), 4-*n*-hexyl-4'-cyanobiphenyl (6CB), 4-*n*-heptyl-4'-cyanobiphenyl (7CB), and 4-*n*-octyl-4'-cyanobiphenyl (8CB). In order to investigate these systems, order parameters for the principal molecular axis and individual segments in the alkyl chain will be calculated and compared with experiment. The conformation of the alkyl chains and the diffusional behavior of these simulated compounds will also be discussed.

COMPUTATIONAL DETAILS

The method we used to investigate the systems mentioned above is a hybridization of the full atom-atom simulation and a simplified spherocylindrical potential function. Our potential is constructed by treating all atoms except those occurring in phenyl rings with full bonded and non-bonded atom-atom interaction parameters, while treating the phenyl rings as single enlarged extended atoms which have a radius approximately equal to 1/2 the breadth of a phenyl ring (Figure 1 shows how 5CB is transformed from the full atom-atom potential to the pseudo 5CB potential).[34] This technique allows us to capture the most important orientational and structural aspects of the simulated systems while greatly reducing the computational time as compared to "full" simulations using all atomic details. Furthermore, the technique is easy to implement, and can be applied by using any of the existing MD simulation programs.

Although changing from a ring to a sphere seems quite dramatic, we would like to point out that in the "full" treatment of many MD simulations, each CH, CH_2, or CH_3 group is already treated as a spherical extended atom.

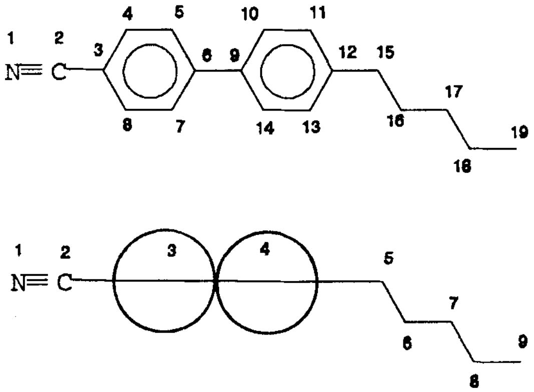

FIGURE 1 Schematic representation and numbering system for 5CB using a full atom-atom potential and the pseudo molecular potential.

Therefore, the simplification of a phenyl ring to a sphere does not represent a radical deviation from this approach. Furthermore, connecting six extended CH "atoms" to form a phenyl ring in the regular MD treatment does not consider the conjugation of the π-electrons, but the spherical "extended atom" simplification for the ring system does account for the conjugation to a good extent. The most convincing argument, however, is the proven success of the technique. When orientational, structural, and transport properties calculated using the two methods are compared, very little difference exists between the two systems, while only small amounts of conformational information are sacrificed due to the assumed spherical symmetry of the phenyl rings.[34] In addition, diffusional behavior for the pseudo ring simulation more closely matches experimental data than do many previous atom-atom simulations for 5CB or similar compounds. The most important advantage of this approach is the substantial savings in computation time. This is not only because six extended "atoms" in each phenyl ring are replaced by one large pseudo "atom," but also because a very large percentage of computer time in the full atom-atom simulation of a liquid crystal compound which contains aromatic rings is spent evaluating the tight inter-core interactions. The amount of time which is actually saved during the simulation depends upon the fraction of total atoms in the phenyl rings.

All of our calculations were performed on an IBM RS/6000 model 320H workstation operating at 13.5 MFLOPS using the program AMBER 4.0 (obtained from the University of California San Francisco, UCSF, School of Pharmacy). The model liquid crystal molecules were constructed using the pseudo ring approximation as explained above. Simulations for the systems, therefore, contained 9, 10, 11, and 12 "atoms" per molecule for the 5CB, 6CB, 7CB, and 8CB systems, respectively. The interactions between the atoms and molecules are computed, as they are for many MD simulations, using bending and torsional potentials, for covalently linked atoms, and non-bonded Lennard-Jones type potentials for non-covalently linked atoms. The total potential energy of the system is described by the 3N positions of its atoms:

$$\begin{aligned} V(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) &= \sum K_b(b-b_o)^2 + \sum K_\theta(\theta-\theta_o)^2 + \sum (1/2)V_n[1+\cos(n\phi-\delta)] \\ &+ \sum_{i=1,N}\sum_{j=1,N} [A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^{6} + q_iq_j/\epsilon r_{ij}] \end{aligned} \tag{1}$$

The covalent bond stretching energy for each bond in the system is given by the first sum, where K_b is the bond force constant, b is the instantaneous bond length, and b_o is the equilibrium bond length. The bond angle bending energy is given by the second sum, and is similar to the first term, where K_θ is the force constant for angle bending, θ is the instantaneous bond angle, and θ_o is the equilibrium bond angle. Dihedral torsional interactions, represented by the third sum, are also harmonic potentials like the first two, where V_n is the torsional barrier height, n is the periodicity of the rotational interaction, ϕ is the torsional angle, and δ is a phase angle. The constants A and C in the fourth sum are Lennard Jones coefficients, r_{ij}'s are interatomic distances, q is the electric charge on an atom, and ε is the dielectric permeability. The first three terms on the right hand side represent the total energy of covalently bonded interactions for the model system. The final term represents all non-bonded interactions. It is composed of core repulsion and dispersion factors as well as coulombic interactions.

By differentiating Eq. 1 with respect to $\mathbf{r}_i$, the force acting upon each atom in the system can be obtained. AMBER uses the leap frog algorithm[12,31] in order to obtain the atoms positions as a function of time. The algorithm SHAKE[32] was used to constrain all of the bond stretching modes. The time step used in our simulations was 3.0 fs. An isothermal-isobaric (NPT) ensemble at 300K and zero atmosphere was used for all systems.[33] Each simulation contained 80 molecules which were placed into a cubic box approximately 3.2 nm each side with periodic boundary conditions. The non-bonded cutoff radii we employed was 1.0 nm in all systems. Interaction parameters which were used in our simulations have been published previously.[34] It is important to note, however, that the radius and well depth of the pseudo ring potential were adjusted in order to give densities and core order parameters which are comparable to those obtained with a full atom-atom simulation at an equivalent temperature. All other atoms were treated routinely and taken either from AMBER or other published sources.[14] The simulations for 6CB, 7CB, and 8CB each ran for a total 500 ps. Statistics for all reported quantities were collected from 100 to 500 ps and are considered to be equilibrium statistics. The data for the 5CB simulation was taken from our previous paper.[34] Results for other cyanobiphenyls are similar; those for 7CB are shown in this paper as an example. Snapshots for the equilibrated 7CB system are shown in Figure 2.

DATA ANALYSIS

Orientational Ordering

In order to describe the orientational ordering of the simulated systems, order parameters for the principle molecular axis, S_{zz}, and for individual

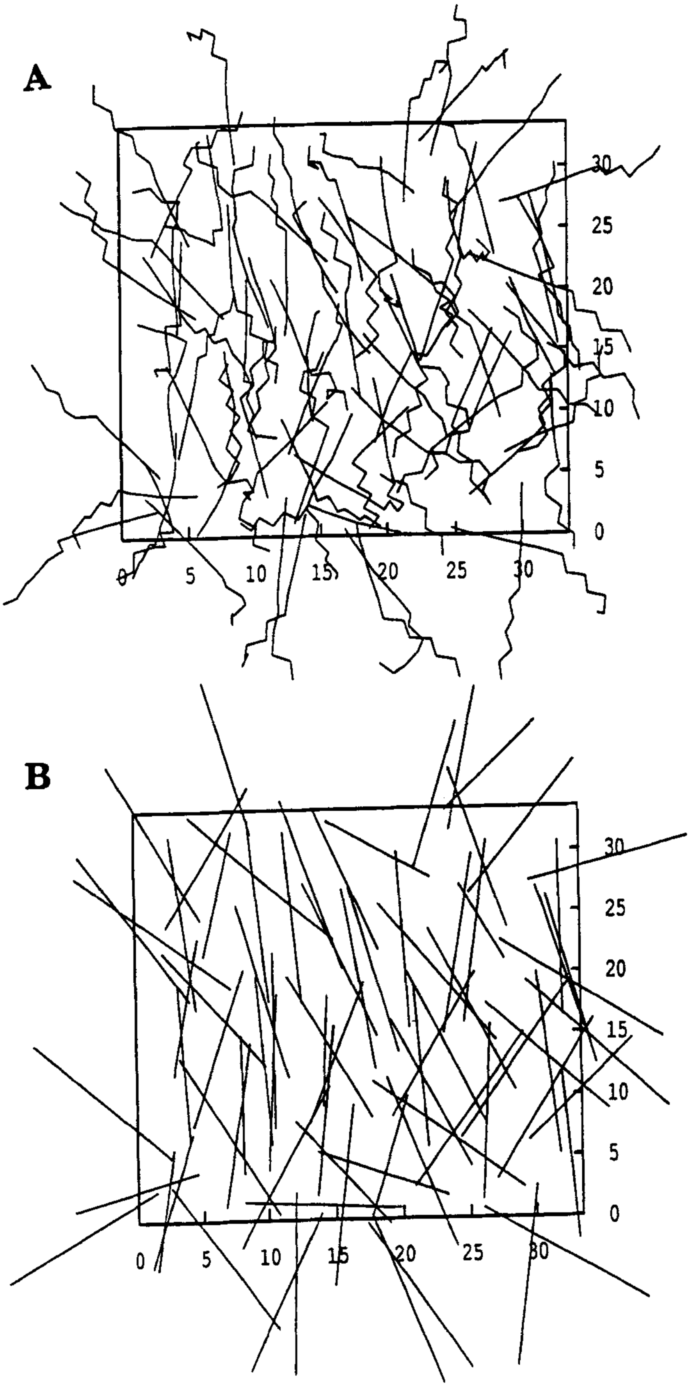

FIGURE 2 Snapshots for the equilibrated 7CB system. (A) All atoms; (B) Principal axis only.

segments of the alkyl chain were calculated. The ordering matrix for an arbitrary molecular coordinate system was originally described by Maier and Saupe[1,2] and is defined as:

$$S_{ij}=\frac{1}{2}<3\cos(\theta_i)\cos(\theta_j)-\delta_{ij}> \tag{2}$$

where θ_i and θ_j are the angles between the director, **n**, and the ith and jth molecular axis, respectively, δ_{ij} is the Kroenecker delta, and the angular brackets denote both an ensemble and a time average. Because the matrix is symmetrical and traceless, it contains at most 5 independent elements. These 5 elements give a complete description for the ordering of any rigid molecular segment with respect to a laboratory coordinate system having the director as its z axis.

The director, **n**, is found by diagonalization of the ordering tensor, **Q**, for the principle molecular axis, **a**. The long molecular axis, **a,** is in turn taken as the principle axis of the moment of inertia tensor for an individual molecule. The ordering tensor, **Q**, for the principle molecular axis is defined as:[35-37]

$$Q^{aa}_{\alpha\beta}=\frac{1}{N}\sum_{j=1}^{N}\frac{3}{2}a_{j\alpha}a_{j\beta}-\frac{1}{2}\delta_{\alpha\beta} \tag{3}$$

where N is the number of molecules, a_α and a_β are components of a unit vector, $\mathbf{a}_j$, associated with the long axes of the individual molecules, and $\delta_{\alpha\beta}$ is the Kroenecker delta. The detailed procedure for calculating the order parameters has been published previously,[14,15] and was also described in our earlier paper.[34]

Order parameters for the principle axis, for the CH bonds in the alkyl chain, and for the CC bonds in the alkyl chain have been calculated for each system. At 300K, the order parameters for the principle axes are: 0.56, 0.59, 0.58, and 0.72, for the 5CB, 6CB, 7CB, and 8CB, respectively. Although the temperature in our computations was fixed at 300 K, it does not necessarily represent the actual temperature accurately because MD calculations cannot yet predict correct nematic ranges. In order to compare the order parameters in the alkyl chain to experimental data, a temperate of $T - T_{NI} = 12$ K is chosen so that the experimental core order parameter for 5CB matches that from our calculated pseudo 5CB very closely. The CH order parameters for the calculated and experimental alkyl chains are shown in Table I. The CC order parameters calculated by both MD and mean field theories are shown in Table II.

TABLE I. Calculated and experimental S_{CH} values for the alkyl chains.

Carbon in chain	α	β	γ	δ	ε	ζ	η	ω
5CB calc.	-0.24	-0.22	-0.23	-0.16				-0.07
6CB calc.	-0.26	-0.24	-0.25	-0.19	-0.19			0.09
7CB calc.	-0.25	-0.23	-0.23	-0.18	-0.19	-0.16		-0.03
8CB calc.	-0.32	-0.29	-0.30	-0.23	-0.24	-0.20	-0.20	0.11
5CB exptl.	-0.22	-0.15	-0.16	-0.11				-0.08
6CB exptl.	-0.21	-0.15	-0.16	-0.13	-0.13			0.0
7CB exptl.	-0.24	-0.18	-0.19	-0.16	-0.16	-0.11		-0.07
8CB exptl.	-0.25	-0.15	-0.19	-0.19	-0.19	-0.15	-0.13	0.0

The agreement between the calculated and experimental data for the alpha and omega carbons is the best for 5CB, 6CB, and 7CB, with the order parameters for the carbons in the middle of the chain being somewhat more negative than the experimental data. The calculated data for 8CB have larger absolute values than the experimental data, but the reason is not clear. Most importantly, both the experimental and calculated data show that the CH order parameters do not decrease monotonically along the alkyl chains, but show an alternating odd-even effect for all compounds. Modification of the bonded potentials in the chain to allow more motional freedom might give better results for CH order parameters in future simulations. Although experimental data for CC order parameters do not exist to our knowledge, the agreement between those calculated from MD and mean field theory is quite reasonable, representing the correct trends and signs of the order parameters in the chain.

TABLE II. S_{CC} order parameters for the alkyl chain calculated from molecular dynamics (MD; this work) simulations and mean field theory (m. f. ; ref. 40). L = the next to the last carbon in the chain.

Bond	core-α	α-β	β-γ	γ-δ	δ-ε	ε-ζ	ζ-η	L-ω
5CB MD	0.57	-0.07	0.50	-0.06				0.38
6CB MD	0.54	-0.00	0.52	-0.0	0.39			0.02
7CB MD	0.54	-0.03	0.52	-0.01	0.38	0.03		0.29
8CB MD	0.65	-0.00	0.62	0.04	0.48	0.05	0.39	0.04
5CB m. f.	0.47	-0.03	0.35	-0.01				0.25
6CB m.f.	0.43	-0.01	0.32	0.02	0.23			0.02
7CB m.f.	0.51	-0.02	0.39	0.01	0.30	0.02		0.22
8CB m.f.	0.54	-0.01	0.42	0.04	0.33	0.06	0.25	0.05

Structure and Dynamics

Because liquid crystals have orientational ordering, the fluid properties observed for these compounds are anisotropic. The diffusion coefficient for a liquid crystal must, therefore, be considered as a tensor. According to the conventional notation, $D_{zz}=D_{\parallel}$, $D_{xx}=D_{yy}=D_{\perp}$, with all off-diagonal elements equal to zero. Because the cross section of a liquid crystal molecule is narrower along its long axis than it is along either of its short axes, diffusion

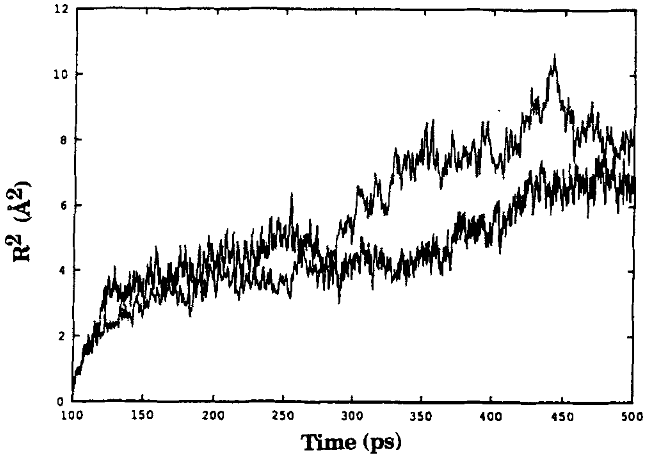

FIGURE 3 Mean square displacement for the 7CB system. Upper plot, parallel component. Lower plot, perpendicular component.

is favored along the direction parallel to the director. In order to monitor the diffusional behavior of our simulations, we have computed diffusion coefficients both parallel and perpendicular to the director. The diffusion coefficients $D_\parallel$ and $D_\perp$ were calculated as the slope of the mean square displacements (Figure 3):

$$D_{\alpha\alpha} = \lim_{t\to\infty} \frac{<\delta R_\alpha^2(t)>}{2t} \qquad (4)$$

where the mean square displacement is computed as

$$<\delta R_\alpha^2(t)> = \frac{1}{N}\sum_{i=1}^{N} [R_{\alpha i}(t) - R_{\alpha i}(0)]^2 \qquad (5)$$

with α=x,y,z. The results we have obtained for diffusion coefficients parallel and perpendicular to the director are as follows: $1.6\text{x}10^{-10}$ m²/s and $0.7\text{x}10^{-10}$ m²/s ($D_\parallel/D_\perp$=2.3) for 5CB, $1.3\text{x}10^{-10}$ m²/s and $0.9\text{x}10^{-10}$ m²/s ($D_\parallel/D_\perp$=1.4) for 6CB, $2.0\text{x}10^{-10}$ m²/s and $1.0\text{x}10^{-10}$ m²/s ($D_\parallel/D_\perp$=2.0) for 7CB, and $1.5\text{x}10^{-10}$ m²/s and $0.6\text{x}10^{-10}$ m^2/s ($D_\parallel/D_\perp=2.5$) for 8CB. The experimental values for 5CB are $D_\parallel=5.3\text{x}10^{-11}$, $D_\perp=4.1\text{x}10^{-11}$ m^2/s, and $D_\parallel/D_\perp=1.3$, at 298K.[41] The diffusion coefficients for other liquid crystal compounds also fall into the same range.[42] It should be mentioned here that experimental values for diffusion coefficients are not very exact and often vary by a factor of two or more when the same compound is measured by different methods. Although the diffusion coefficients calculated from our simulations are not very accurate, their order of magnitude is comparable to experimental diffusion coefficients, and to the calculated diffusion coefficients for other related compounds.[12-15] Also, they clearly show that diffusion parallel to the director is strongly favored. The lack of any regular trends with respect to the chain lengths is due to statistical uncertainty caused by the relatively small sizes of the systems.

We have accumulated statistics for the dihedral angle distributions of the alkyl chains in order to show that when using the pseudo ring potential, *trans-gauche* conformations for torsional bonds are reasonable (Figure 4). In our previous paper[34] we showed that the distribution functions for the dihedral angles in the alkyl chain of 5CB were very comparable when calculated with both the atom-atom potential and the pseudo ring potential. The only significant difference between these systems being the torsional rotation about the bond between the first and second methylene groups in the chain (atoms 5 and 6 in figure 1) which shows only trans conformations for the pseudo 5CB simulation. We believe that this is caused by steric repulsion between the pseudo ring (atom 4) and methylene number 3 (atom 7). This effect can also be seen in the dihedral distribution for the torsion around the corresponding bond in the chain of the 7CB simulation, which shows only *trans* probability.

CONCLUSION

By using the pseudo molecular potential we were able to study several

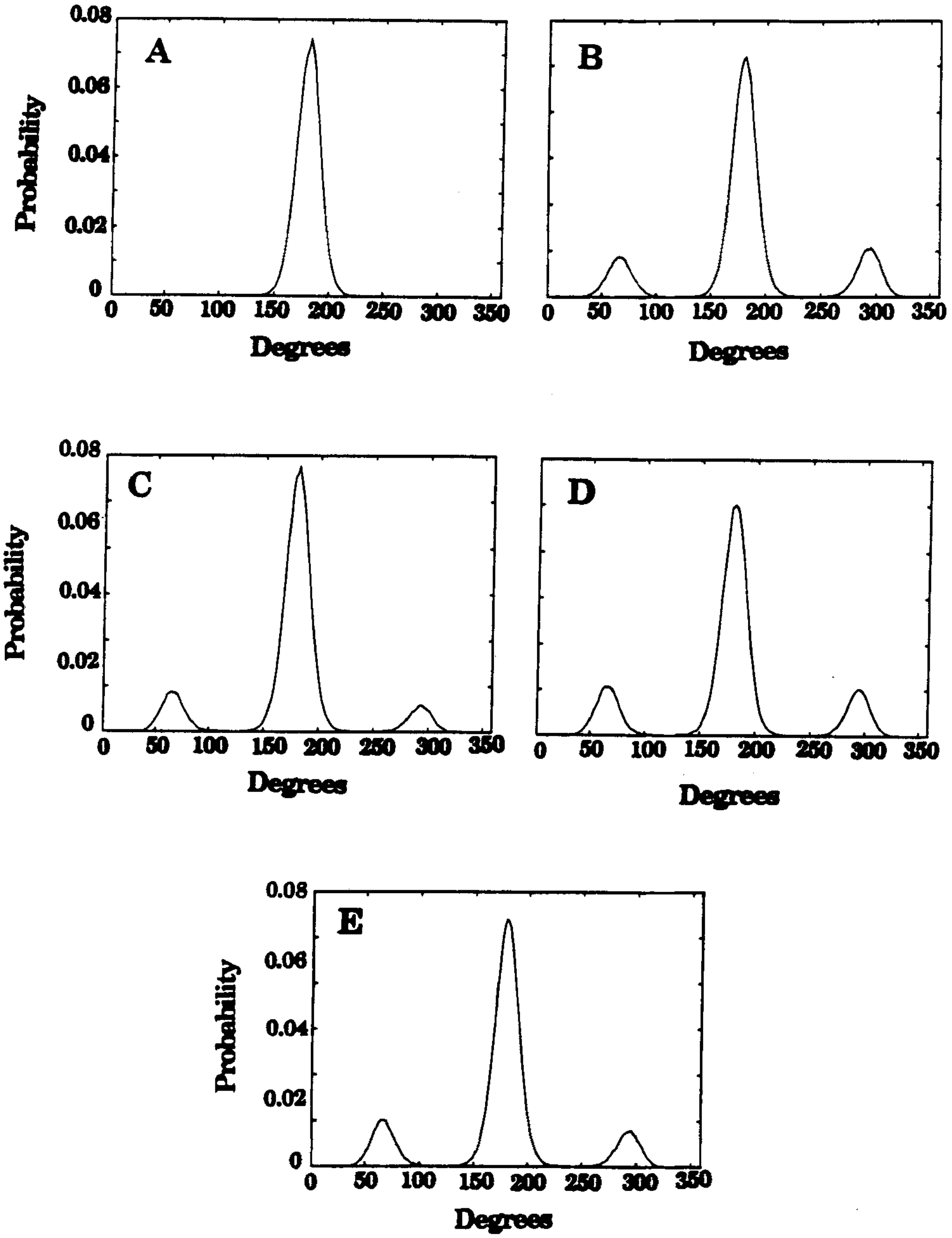

FIGURE 4 Dihedral distributions for torsional angles in the alkyl chain of 7CB (plots A-E run from the ring to the end of the chain).

members of the cyanobiphenyl series in a reasonably short time period. The orientational, structural, and conformational behavior for our simulated liquid crystals closely parallels that of the equivalent experimental system. Calculations of this type are, therefore, potentially very useful for the study of structure property relationships in more complex liquid crystal systems where full atom-atom potentials are too computationally intensive. By replacing all aromatic rings in a simulated molecule with single extended atoms, computational time can be reduced up to a factor of 4 when compared to the atom-atom method. Furthermore, all of the important structural features of the target molecule such as bond angles and torsional angles are conserved. This allows important information regarding detailed anisotropic contributions to observed properties to be investigated.

We consider the pseudo ring method to be reliable and effective when used to study liquid crystal systems. Considering the time savings gained when using the method, and the fact that any loss of structural information is relatively negligible, we believe that the possibility exists to extend the technique to other large systems such as proteins and polymers containing aromatic units. Because intermolecular interactions in systems of this type are often more dependent upon groups rather than individual atoms, the effect of replacing a rapidly moving aromatic ring with a sphere is not too dramatic, except that the speed of the simulation is greatly accelerated.

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