Structure and molecular ordering extracted from residual dipolar couplings: A molecular dynamics simulation study

Baltzar Stevensson
Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

Andrei V. Komolkin
Physics Institute, St-Petersburg State University, 198904 Saint Petersburg, Russia

Dick Sandström and Arnold Maliniak
Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

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A molecular dynamics (MD) simulation, based on a realistic atom–atom interaction potential, was performed on 4-n-pentyl-4′-cyanobiphenyl (5CB) in the nematic phase. The analysis of the trajectory was focused on the determination of molecular structure and orientational ordering using nuclear dipole–dipole couplings. Three sets of couplings were calculated: $^{13}$C–$^{13}$C, $^{13}$C–$^1$H, and $^1$H–$^1$H. These dipolar couplings were used for investigation of the biphenyl and the ring–chain fragments in 5CB. The models employed in the analysis were based on the rotational isomeric state (RIS) approximation and the maximum entropy (ME) approach. The main questions addressed in this article are: (i) How sensitive are the various sets of dipolar couplings to the long-range orientational order and molecular conformation? (ii) Which model predicts a molecular structure that is in best agreement with the true conformation? Computer simulation is an attractive method to address these questions since the answer is provided: we know the true orientational order and the molecular structure. We found that all sets of dipolar couplings analyzed using the two models predict correct orientational order for the biphenyl fragment. The structure of this moiety was unambiguously determined in all analyses except for the ME method applied on the $^{13}$C–$^{13}$C couplings. The RIS approximation failed to discriminate between a large range of possible structures of the ring–chain fragment. © 2001 American Institute of Physics. [DOI: 10.1063/1.1337046]

I. INTRODUCTION

Studies of molecular structure, orientational order, and dynamics in liquid–crystalline systems are of utmost importance in exploring the fundamental physics of these phases. Such investigations are also motivated by the spectacular technical applications of liquid crystals, mainly in display technology. Liquid crystals are usually formed by rod-like or disk-like molecules and are characterized by long-range orientational order. This order originates from the anisotropic nature of the intermolecular interactions. Furthermore, there exists a strong coupling between the orientational order and the molecular conformation.¹

Nuclear magnetic resonance (NMR) is an established tool for studies of partially ordered systems.²,³ In particular, the through-space magnetic dipole–dipole (DD) interactions have proven to be of great importance.⁴ These interactions depend on the spin–spin distances and on the orientations of the internuclear vectors with respect to the external field. This means that the DD coupling is a valuable probe of long-range order and molecular structure. Several NMR experiments have recently been developed that make it possible to measure both heteronuclear and homonuclear dipole–dipole interactions in concentrated liquid–crystalline systems with high accuracy. A variety of methods based on heteronuclear local field spectroscopy can be used for estimating $^{13}$C–$^1$H DD couplings (see, e.g., Ref. 5 and references therein). Natural-abundance double-quantum $^{13}$C NMR is able to provide $^{13}$C–$^{13}$C through-space couplings,⁶,⁷ and proton NMR may, especially when combined with partial deuteration,⁸,⁹ yield $^1$H–$^1$H dipolar couplings.¹⁰ Furthermore, measurements of one-bond $^{13}$C–$^1$H residual dipolar couplings have attracted a considerable amount of attention for structure determination of proteins¹¹,¹² and carbohydrates¹³,¹⁴ dissolved in aqueous diluted liquid crystals.

To extract useful information about conformation and order from the experimental DD couplings in a flexible molecule, we need a model that takes both whole molecule motion and internal degrees of freedom into account. Several such approaches have been considered for the interpretation of NMR data in general, and of nuclear spin dipolar couplings in particular.¹ The simplest possible model assumes that only a small set of minimum-energy structures is populated. This is often called the rotational isomeric state (RIS) approach. More realistic models allow for continuous bond rotations.

From the discussion above, two important questions emerge: (1) Which type of dipolar couplings should we try to measure in order to determine the long-range orientational order and torsion angle distributions with highest possible accuracy? (2) Which theoretical model predicts a molecular

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¹Author to whom correspondence should be addressed. Electronic mail: arnold.maliniak@physc.su.se

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structure that is closest to the true one? The second question would be insignificant if all approaches predicted the same conformation from a given set of DD interactions. As we will demonstrate in this paper, this is not always the case. These questions can, at least partially, be addressed by computer calculations since the simulations contain essentially complete information about the orientational order and molecular structure.

Computer simulation is an increasingly important tool for studies of ordered media. Previously, we have reported several molecular dynamics (MD) simulations of liquid-crystalline phases formed by 4-n-pentyl-4'-cyanobiphenyl (5CB). In these investigations, a large number of static and dynamic molecular characteristics were extracted from the trajectories. The present work deals with various sets of dipolar couplings calculated from an MD simulation of a nematic phase. The molecule 5CB is once again used as a model compound because it has been extensively studied in the past. Thus, there exists a considerable amount of data to compare our results with. Three DD data sets ([13C–H], [13C–[13C], and [H–H]) are used to test the rotational isomeric state and maximum entropy (ME) models which attempt to extract molecular torsion angles and long-range orientational order. Both these methods have previously been employed in experimental NMR studies of 5CB and related molecules in the nematic phase. The strength of using computer simulation is quite obvious: (i) All possible dipolar couplings may be calculated from the trajectory. (ii) Rigorous tests of theoretical approaches for analyzing DD couplings are straightforward to perform since the results they produce can be compared with the simulated counterparts. Similar studies of solute molecules dissolved in Gay–Berne liquid crystals have been presented elsewhere. There, however, only spin–spin couplings between protons were considered.

We will focus on the interring and ring–chain torsion angles (φ1 and φ2 in Fig. 1) in our conformational analysis of 5CB. The structure of these fragments has been thoroughly investigated in the nematic phase by means of NMR. These studies indicate that the angle φ1 is around 35°, and that φ2 is equal to 90° (i.e., that the aliphatic chain orients perpendicularly to the ring plane).

The outline of this paper is as follows. Details of the computer simulation are described in Sec. II. In Secs. III and IV we calculate order parameters and dipolar couplings from the MD trajectory. The methods used for interpretations of DD couplings are summarized in Sec. V. Finally, we test the theoretical models of obtaining orientational order, torsion angles, and their distributions from simulated dipolar couplings in Sec. VI.

II. COMPUTATIONAL DETAILS

The MD simulation of the nematic liquid crystal was performed in a cubic box containing 120 5CB molecules. The side length of the box was 36.47 Å, corresponding to a density of 1.02 g cm⁻³. The temperature was kept constant (NVT ensemble) at 300 K by using a weak coupling to an external heat bath. The coupling parameter (19.7 fs) was chosen to be much longer than the integration step and significantly shorter than the simulation length. The equations of motion were solved using the Verlet leap frog integration algorithm with a time step of 2 fs. The length of the entire simulation was 2 ns and the final analysis was performed on a trajectory of 600 ps, comprising 15 000 sets of coordinates. Initially, a rectangular simulation cell was created and the 5CB molecules were placed in five layers with the para axes oriented parallel to the long axis of the box. The vertical orientations of the molecules were altered in order to prevent a net dipole moment from occurring. This initial configuration corresponds to a perfectly ordered smectic A phase. During the equilibration procedure the system was compressed until the experimental density was reached. The CH, CH₂, and CH₃ groups were treated as single interaction centers (united atoms) which results in 19 sites per molecule. The interring and ring–chain torsion angles were modeled using a potential function of the form

$$V(\phi) = V_2(1 + A \cos 2\phi) + V_4 \cos 4\phi,$$

with the force constants $V_2 = 5.85$, $V_4 = 5.10$ kJ mol⁻¹, and $A = -1$ for φ1. The corresponding parameters for φ2 are $V_2 = 30$, $V_4 = 0$ kJ mol⁻¹, and $A = 1$. These potential functions were estimated from analyses of 1H NMR data recorded in 4-methoxy-4'-cyanobiphenyl for φ1 and in 5CB for φ2. Note that Eq. (1) describes the total intramolecular potential for φ1 and φ2, i.e., no nonbonded (Lennard-Jones and electrostatic) interactions were used for these torsion angles. The potential proposed by Ryckaert and Bellemans was used to model the torsion angles in the alky chain. All other interaction parameters are identical to those used in our previous simulations of 5CB.

III. ORDER PARAMETERS FROM THE MD SIMULATION

The long-range orientational order present in liquid-crystalline systems is usually described in terms of second-rank order parameters. The first step towards the determination of these quantities from a computer simulation is to define a molecular-fixed coordinate frame. For a flexible molecule like 5CB, the most convenient choice of this frame is that corresponding to the principal axis system of the moment of inertia tensor I. This frame is calculated for every molecule at each time step, and the long-molecular axis (or z axis) corresponds to the smallest eigenvalue of I.

The second step is to find the director frame of the liquid crystal. The instantaneous orientation of the nematic director n can be determined by constructing a general Cartesian ordering matrix $Q_{ij}$ with elements $
\[ Q_{zz}^{\mu \nu} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} (3 \cos \beta_{z\mu} \cos \beta_{z\nu} - \delta_{\mu \nu}), \]

where \( N \) is the number of molecules in the simulation cell, and \( \beta_{z\mu} \) is the angle between the long molecular axis \( z \) and the \( \mu \) axis fixed in the simulation cell. The diagonalization of \( Q_{zz} \) gives three eigenvalues and the nematic director is the eigenvector associated with the largest eigenvalue.

Having located the molecular frame and the director, it is possible to calculate the molecular ordering matrix \( S \), with its principal values defined by

\[ S_{aa} = \left( \frac{1}{3} (3 \cos^2 \beta_a - 1) \right), \]

where the angular bracket denotes a time and ensemble average, and \( \beta_a \) is the angle between the director and the molecular-fixed principal axis \( a \) \((a=x,y,z)\). Since \( S \) is traceless, it is sufficient to specify two of the three diagonal elements. The MD simulation of 5CB resulted in the following time-averaged order parameters: \( S_{zz} = 0.50 \pm 0.05 \) and \( S_{xx} - S_{yy} = 0.03 \pm 0.03 \). These values are in reasonable agreement with previously reported data obtained from NMR experiments.\(^7\,10\)

**IV. CALCULATION OF THE DIPOlar COUPLINGS**

The through-space magnetic dipolar coupling between spins \( i \) and \( j \), with magnetogyric ratios \( \gamma_i \) and \( \gamma_j \), is (in rad s\(^{-1}\)) given by

\[ D_{ij} = - \frac{\mu_0}{8 \pi} \gamma_i \gamma_j \hbar \left( 3 \cos^2 \theta_{ij} - 1 \right) r_{ij}^{-3}, \]

where \( r_{ij} \) is the spin–spin distance, and \( \theta_{ij} \) is the angle between the spin–spin vector and the external field. In our analysis below, we assume that the director and magnetic field directions coincide. The angular bracket in Eq. (4) indicates that the DD couplings in liquid crystals are averaged over both molecular tumbling and any internal bond rotations.

The MD trajectory was used to calculate the \(^{13}\)C–\(^1\)H, \(^{13}\)C–\(^{13}\)C, and \(^1\)H–\(^1\)H dipolar interactions in 5CB. The potential model employed in the simulation is based on united atoms, which means that no hydrogen atoms were included. Instead, the hydrogen positions were calculated from the carbon coordinates using the parameters in Table I. The simulated DD couplings collected in Table II have been averaged according to molecular symmetry. The full (unsymmetrized) set of dipolar couplings can be obtained from the authors. The errors reported in Table II were estimated by averaging each DD coupling over all molecules in the simulation box, followed by an average over the entire trajectory. The \(^{13}\)C–\(^1\)H and \(^1\)H–\(^1\)H DD couplings calculated from the trajectory are in agreement with experimentally determined couplings.\(^7\,10\,25\,34\) This indicates that our force field adequately describes the structure and order of the liquid crystal.

A consequence of not explicitly including protons in the MD simulation is that vibrational contributions to the \(^1\)H–\(^1\)H and \(^{13}\)C–\(^1\)H couplings are neglected.

**V. METHODS USED FOR ESTIMATING MOLECULAR STRUCTURE AND ORDER FROM THE SIMULATED DIPOlar COUPLINGS**

In order to derive the molecular conformation and order parameters from the simulated DD couplings, we used the following relationship:\(^3\)

\[ D_{ij} = - \frac{\mu_0}{8 \pi} \gamma_i \gamma_j \hbar \left( 3 \cos^2 \theta_{ij} - 1 \right) r_{ij}^{-3} \cos \left( \phi_a \right) \sin \left( \phi_a \right) \]

where \( \theta_{ij} \) \((a=x,y,z)\) are angles between the spin–spin vector and the molecular-fixed axes.

If the dipolar coupling is between spins in different molecular fragments, \( r_{ij} \), \( S_{ab} \), \( \theta_{ij} \), and thus the DD coupling in Eq. (5) become dependent on molecular structure (below described by the internal angle \( \phi \)). The motionally averaged dipolar coupling can in this case be expressed as

\[ D_{ij} = \int D_{ij}(\phi) P(\phi) d\phi. \]

The torsion angle probability \( P(\phi) \) in Eq. (6) is defined as the ensemble average over the singlet orientational distribution function (ODF), \( P(\beta, \gamma, \phi) \)

\[ P(\phi) = Z^{-1} \int \int P(\beta, \gamma, \phi) \sin \beta d\beta d\gamma, \]

where \( \beta \) and \( \gamma \) are Euler angles relating the director frame to the molecular frame, and \( Z \) is a normalization factor. The ODF contains complete information about the orientational order and structure of the molecular fragment. The conformation-dependent orientational order parameters are also given by ensemble averages according to

\[ S_{ab}(\phi) = Q(\phi)^{-1} \int \int D^2_{0,0}(0, \beta, \gamma) P(\beta, \gamma, \phi) \sin \beta d\beta d\gamma, \]

where \( Q(\phi) \) is the \( \phi \)-dependent orientational partition function and \( D^2_{m,0}(\alpha, \beta, \gamma) \) are second-rank Wigner functions which define the relative orientations of the molecule and

### Table I. Geometrical parameters used in the analysis of the dipolar couplings.

<table>
<thead>
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<th>Bonds</th>
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</thead>
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</tr>
<tr>
<td>C2–C3</td>
<td>1.395</td>
</tr>
<tr>
<td>C3–H3</td>
<td>1.085</td>
</tr>
<tr>
<td>C5–C8</td>
<td>1.531</td>
</tr>
<tr>
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<td>C14–C15</td>
<td>1.535</td>
</tr>
<tr>
<td>C14–H14</td>
<td>1.100</td>
</tr>
<tr>
<td>C11,C14,C15</td>
<td>110.8</td>
</tr>
<tr>
<td>C15,C14,H14</td>
<td>109.1</td>
</tr>
<tr>
<td>C11,C14,H14</td>
<td>109.1</td>
</tr>
<tr>
<td>H14,C14,H14</td>
<td>109.8</td>
</tr>
</tbody>
</table>

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director. The relationship between the elements of the ordering matrix, \( S_{ab} \), and \( D_{ij}^{\beta\gamma}(0, \beta, \gamma) \) can be found in Ref. 35.

A brief description of the methods we have used for analyzing the simulated dipolar couplings in 5CB is given in the following discussion.

### A. Order parameters of the phenyl rings

The dipolar couplings within the aromatic rings do not depend on any torsion angle. Therefore, an analysis of the DD couplings within these rigid fragments results in a set of local order parameters reflecting the orientational order of the two individual rings.

### B. The rotational isomeric state (RIS) approach

This method is based on the assumption that the molecule (or molecular fragment) under consideration jumps between a small number of symmetry-related structures, and that the probabilities of the different conformations are independent of the overall molecular orientation. It is also assumed that the jumps are much faster than the inverse of the dipolar couplings \( D_{ij}^{\beta\gamma} \). Analysis using this model yields a set of the orientational order parameters and discrete torsion angles.

### C. The maximum entropy (ME) analysis

The maximum entropy method allows for continuous bond rotations and is therefore more physically sound than the RIS model. Another advantage is that the ME approach does not require any assumptions about the form of the singlet orientational distribution function. Instead, it is expressed as:

\[
P^{\text{ME}}(\beta, \gamma, \phi) = Z^{-1} \exp \left( -\sum_{i,j} \lambda_{ij} D_{ij}(\beta, \gamma, \phi) \right),
\]

where \( \lambda_{ij} \) are adjustable parameters that can be determined by bringing calculated DD couplings into agreement with those obtained from the MD simulation. There are, however, two potential problems associated with the ME method. First, the torsion angle distribution \( P^{\text{ME}}(\phi) \) obtained by combining Eqs. (7) and (9) depends on the orientational ordering. It tends to flatten with decreasing order, and \( P^{\text{ME}}(\phi) \) becomes completely \( \phi \) independent in the isotropic liquid phase where all order parameters (and thus all dipolar couplings) are identically zero. Second, it is not obvious which, and how many, \( \lambda_{ij} \) parameters one should use in the construction of \( P^{\text{ME}}(\beta, \gamma, \phi) \).
VI. ANALYSIS OF THE SIMULATED DIPOLAR COUPLINGS

We shall now apply the methods described in Sec. V to the simulated dipolar couplings in 5CB. The strategy used in the analysis is to fit the couplings in Table II to Eq. (5). The fitting program, which is based on a Monte Carlo subroutine, minimizes the weighted sum error

$$\text{fitting error} = \sqrt{\frac{1}{N} \sum_{i,j} \left[ \frac{D_{ij}^{\text{sim}} - D_{ij}^{\text{calc}}}{D_{ij}^{\text{calc}}} \right]^2},$$

where N is the number of the dipole–dipole couplings, and $D_{ij}^{\text{sim}}$ and $D_{ij}^{\text{calc}}$ are the simulated and calculated dipolar couplings, respectively. All geometrical parameters used in the analysis of the DD couplings are collected in Table I.

We will treat the aromatic rings, the biphenyl core, and the ring-chain fragments separately.

A. The rigid phenyl rings

We start the analysis by considering the dipolar couplings within the two aromatic rings (denoted A and B in Fig. 1). Two separate local axis systems may be attached to the rings, with the $z_{\sigma}$ axes in the direction of the para axes, and the $y_{\sigma}$ axes normal to the ring planes ($\sigma = \text{A, B}$). The aromatic moieties are assumed to have perfect hexagonal symmetry. The orientational order parameters estimated from the 13C–1H, 13C–13C, and 1H–1H dipolar couplings predict correct $\phi_1$ angles within 1°. The estimated local order parameters from all three data sets are in agreement with the values calculated directly from the trajectory.

The normalized torsion angle distribution obtained from the simulation $P^{\text{sim}}(\phi_1)$ is shown in Fig. 2 (solid line). The positions of the maxima are at $\phi_1 \approx \pm 31^\circ$ and $\phi_1 \approx \pm 149^\circ$. The distribution is not exactly symmetric about 0° and 90°, as it should be for 5CB. This is because the computer simulation does not sample the whole conformational space properly.

In order to estimate the structure of the biphenyl core from the simulated DD couplings, we must include not only the intraring but also the interring dipolar couplings in the analysis. Equation (5) can be simplified if one knows the location of all principal axes of S. From symmetry arguments the $z_{\text{biph}}$ axis is easily identified (see Fig. 1). The $x_{\text{biph}}$ axis can, to a good approximation, be fixed in the plane bisecting the ring planes.10,37

1. RIS analysis of $\phi_1$

The RIS approach assumes that only four symmetry-related conformations are appreciably populated [$\phi = \pm \phi_1$ and $\pm (\pi - \phi_1)$], and that there are no geometrical or motional differences between the two rigid rings. Thus, in this analysis there are three parameters to vary ($S_{zz}$, $S_{xx} - S_{yy}$, and $\phi_1$), and by fitting the simulated sets of DD couplings to Eq. (5) (neglecting the off-diagonal elements in the S matrix) we obtained the results given in Table III. The torsion angle extracted from the 1H–1H dipolar couplings deviates 4° from the maximum in $P^{\text{sim}}(\phi_1)$, while the 13C–13C and 13C–1H couplings predict correct $\phi_1$ angles within 1°. The estimated local order parameters from all three data sets are in agreement with the values calculated directly from the trajectory.

In order to investigate the sensitivity of the dipolar interactions to the interring angle, we fixed $\phi_1$ and varied $S_{zz}$ and $S_{xx} - S_{yy}$, so as to minimize the target function in Eq. (10). This procedure was repeated for many equally spaced $\phi_1$ values, and the fitting error versus $\phi_1$ is shown in Fig. 3. It is clear that the 1H–1H dipolar couplings in the biphenyl fragment are most sensitive to the interring angle.

2. ME analysis of $\phi_1$

The first step in the maximum entropy approach is to decide which dipolar couplings to include in the construction of $P^{\text{ME}}(\beta, \gamma, \phi_1)$. Guided by several tests, we used four DD

![Fig. 2. Normalized $\phi_1$ torsion angle distribution functions from: the trajectory (solid), and the ME analyses of 1H–1H (dashed) and 13C–1H (dotted) DD couplings.](Image)
couplings in the analysis of the biphenyl fragment, two intraring and two interring couplings. We tried to reduce the number of adjustable parameters to three, but this attempt failed since it resulted in large fitting errors and poor distribution functions. Including five or more $\lambda_{ij}$ parameters did not improve the fits.

The $^{13}\text{C}--^{13}\text{C}$ dipolar couplings were not sensitive enough to build a ME torsion angle distribution in agreement with the simulated result. These couplings yielded a $P_{\text{ME}}(\phi_1)$ with a maximum at $0^\circ$. The other two data sets produced the distributions shown in Fig. 2. The optimized $\lambda_{ij}$ parameters are collected in Table IV. Clearly, the $^{13}\text{C}--^{1}\text{H}$ and $^{1}\text{H}--^{1}\text{H}$ dipolar couplings result in interring probabilities with maxima and minima close to those found in $P_{\text{sim}}(\phi_1)$.

The most complete description of orientational order in a liquid crystal is provided by the singlet orientational distribution function which, for the biphenyl moiety, depends on $\beta$, $\gamma$, and $\phi_1$. To facilitate a comparison between MD and ME ODFs, we determined $P_{\text{ME}}(\beta)$ by integrating $P_{\text{ME}}(\beta, \gamma, \phi_1)$ over $\gamma$ and $\phi_1$. A time-averaged $P_{\text{sim}}(\beta)$ was obtained by calculating the distribution function for the para axis with respect to the nematic director. The two probabilities obtained by the ME method from the $^{13}\text{C}--^{1}\text{H}$ and $^{1}\text{H}--^{1}\text{H}$ dipolar couplings are compared to the true distribution in Fig. 4, and a good agreement is observed. The $^{13}\text{C}--^{13}\text{C}$ maximum-entropy ODF agrees also with $P_{\text{sim}}(\beta)$ when the dependence of $\gamma$ and $\phi_1$ is integrated out.

### C. The ring–chain fragment

The normalized torsion angle distribution obtained from the simulation $P_{\text{sim}}(\phi_2)$ is shown in Fig. 5 (solid line). The positions of the maxima are at $\phi_2 = \pm 90^\circ$. The distribution is not symmetric about $0^\circ$ which, again, is a result of insufficient MD sampling.

The conformation and order of the ring-chain fragment is studied by considering dipolar couplings within ring B, and couplings between ring B and the first CH$_2$ group in the alkyl chain. In the analysis of the $^{13}\text{C}--^{1}\text{C}$ spin–spin interactions, it is necessary to include dipolar couplings between C15 and the ring carbons. A local axis system was fixed in ring B with the $z_B$ axis pointing along the para axis, and the $x_B$ axis in the ring plane. Note that the local ordering tensor for the ring–chain fragment is not diagonal in this frame.

#### 1. RIS analysis of $\phi_2$

We follow the approach taken in Sec. VI B 1 and assume that only four minimum-energy conformations are populated. Both order parameters and direction cosines in Eq. (5) are

![FIG. 3. Fitting error dependence of the $\phi_1$ torsion angle obtained using the RIS model.](image1)

![FIG. 4. The orientational distribution functions $P(\beta)$ calculated from the trajectory for the para axis (solid line), and from the ME analyses of $^{1}\text{H}--^{1}\text{H}$ (dashed) and $^{13}\text{C}--^{1}\text{H}$ (dotted) DD couplings in the biphenyl fragment.](image2)

![FIG. 5. Normalized $\phi_2$ torsion angle distribution functions from: the trajectory (solid), the ME analyses of $^{1}\text{H}--^{1}\text{H}$ (dashed), $^{13}\text{C}--^{1}\text{H}$ (dotted), and $^{13}\text{C}--^{13}\text{C}$ (dash dotted) DD couplings.](image3)

### TABLE IV. Values of $\lambda_{ij}$ parameters obtained from the ME analysis of dipolar couplings in the biphenyl fragment. The reported values are products of fitted $\lambda_{ij}$ parameters and the corresponding dipolar coupling.

<table>
<thead>
<tr>
<th>$^{1}\text{H}--^{1}\text{H}$</th>
<th>$^{13}\text{C}--^{1}\text{H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>$j$</td>
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<tr>
<td>3</td>
<td>4</td>
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</tr>
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<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>

Fitting error: 0.0066

Fitting error: 0.0099
The maximum entropy distributions extracted from the $^{1}$H–$^{1}$H, $^{13}$C–$^{1}$H, and $^{13}$C–$^{13}$C DD couplings are compared to $P^\text{sim}(\phi_2)$ in Fig. 5. The optimized $\lambda_{ij}$ parameters are collected in Table V. The maxima of the ME torsion angle distributions are located at $\phi_2 \approx \pm 90^\circ$, which agree with the simulated probability function. The distribution extracted from the $^{1}$H–$^{1}$H couplings is much broader than the simulated. The $P^\text{ME}(\phi_2)$ distributions are significantly flatter than $P^\text{sim}(\phi_2)$, which is in accordance with the ME principle which results in the flattest possible single molecule ODF consistent with the dipolar couplings used in the analysis.\(^{20}\) A previous ME analysis of experimental $^{1}$H–$^{1}$H dipolar couplings in the ring-chain fragment of 4-chloroethylbenzene resulted in a torsion angle distribution with maxima at $\phi_2 = 0$ and $90^\circ$.\(^{38}\) By comparison with molecular orbital calculations,\(^{39}\) the peak at $\phi_2 = 0^\circ$ was regarded as being rather unlikely due to electron–electron repulsions.

The $P^\text{ME}(\beta)$ probabilities for the ring–chain fragment (not shown) are similar to those depicted in Fig. 4, demonstrating that the ME method predicts correct orientational order.

### VII. SUMMARY

We have, in this article, presented results from a molecular dynamics (MD) simulation of a nematic liquid crystal formed by 4-$n$-pentyl-$4'$-cyanobiphenyl (5CB). The simulation was performed using a detailed atom–atom interaction model. The aim was to estimate the long-range orientational order and molecular structure from an analysis of the simulated dipolar couplings. Three sets of spin–spin couplings were calculated: $^{13}$C–$^{13}$C, $^{13}$C–$^{1}$H, and $^{1}$H–$^{1}$H. These couplings were used for investigations of the biphenyl and ring-chain fragments in 5CB. Two methods were employed in the analysis: (i) the rotational isomeric state (RIS) approximation, and (ii) the maximum entropy (ME) method. In the RIS approach it is assumed that only the minimum-energy discrete structures are populated. The internal motion between these structures is described by jumps. In the ME method, dipolar couplings are used for construction of the singlet ODF which means that this model, in contrast to the RIS approximation, allows for continuous bond rotations.

The most important conclusions of our study may be summarized as follows:

(i) All three DD data sets predict correct long-range orientational order of the biphenyl fragment. This holds true for both the RIS and the ME method.

(ii) The analysis using the RIS model fails in an unambiguous estimation of the structure and orientational order of the ring–chain fragment.

(iii) The correct interring angle is recovered from all analyses, except when interpreting the $^{13}$C–$^{13}$C dipolar couplings using the ME approach.

(iv) The fitting errors are more sensitive to the interring torsion angle for the $^{1}$H–$^{1}$H and $^{13}$C–$^{1}$H couplings, and less sensitive for the $^{13}$C–$^{13}$C interactions.

(v) In the case of $\phi_1$ and $\phi_2$ in 5CB, the ME approach seems to produce more reliable results for the molecular structure compared to the RIS approximation. The ME torsion angle distributions for $\phi_2$ are, however, not suitable for interpretation of the dipolar couplings in the ring–chain fragment.

### TABLE V. Values of $\lambda_{ij}$ parameters obtained from the ME analysis of dipolar couplings in the core-chain fragment. The reported values are products of fitted $\lambda_{ij}$ parameters and the corresponding dipolar coupling.

<table>
<thead>
<tr>
<th>$^{1}$H–$^{1}$H</th>
<th>$^{13}$C–$^{1}$H</th>
<th>$^{13}$C–$^{13}$C</th>
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<tbody>
<tr>
<td>$i$</td>
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<td>9</td>
<td>14</td>
<td>0.144</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>0.405</td>
</tr>
</tbody>
</table>

Fitting error: 0.011 Fitting error: 0.017 Fitting error: 0.0096
flatter than the true (simulated) one. This is consistent with the well-known problems associated with the ME method.

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