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Molecular dynamic study of the odd-even effect in some 4-*n*-alkyl-4′-cyanobiphenyls

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Using a united atom model, we performed molecular dynamics (MD) simulations on the 4-*n*-alkyl-4′-cyanobiphenyl (nCB) liquid crystal homologous series for $n=5-9$ at a constant reduced temperature in the nematic phase. To evaluate the rotational diffusion coefficient (RDC), the second- and fourth-rank order parameters (OP's) and correlation time were calculated from MD trajectories. We analyzed the rotational viscosity coefficient (RVC) by using the Nemtsov-Zakharov and Fialkowski methods based on statistical-mechanical approaches. The simulated RDC, RVC, and OP's were found to be reasonable when compared with previous theoretical and experimental data. These quantities were also calculated for the rigid core and alkyl chain segments separately for each mesogen, to take a closer look at the molecule tail-chain flexibility. The properties calculated for a rigid core were compared with those for an alkyl chain, and satisfactory results were obtained. Odd-even effects for RDF, RVC, and molecular ordering parameters were calculated for five mesogens.

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I. INTRODUCTION

There has been a recent surge of interest in the 4-*n*-alkyl-4′-cyanobiphenyl (nCB) liquid crystals (LC's) due to their simple molecular structures as well as their increased use in technologically important applications. They are widely used in electro-optical display devices because they have strong positive dielectric anisotropy and a remarkably stable and colorless mesophase at room temperature [1]. An industrially crucial property of liquid crystals is the rotational viscosity coefficient (γ_1). Since on and off times of liquid crystal displays are proportional to this property [1], its computation for LC's has been the subject of much computer simulation research [2–13].

To investigate LC properties, molecular dynamics (MD) computer simulation is a powerful method. Many previous MD studies include the calculation of γ_1 restricted with the Gay-Berne model [2–6,11]. Recently, atomistic simulation has been utilized to calculate γ_1 [7–10,12,13]. The studies of the viscosity of LC model systems are based on two methods: equilibrium MD and nonequilibrium MD. Some viscosity calculations given by Sarman and co-worker were performed by an equilibrium Green-Kubo method and generally nonequilibrium MD approach [4–6,11]. Using atomistic simulation, Kuwajima and Manabe first evaluated γ_1 by nonequilibrium MD [8] while in some other papers it was calculated from the equilibrium MD trajectories [7,9,10,12,13].

In this paper we present the rotational viscosity and diffusion coefficients, the second- and fourth-rank order parameters as a function of C atom number in the alkyl chain for homologous series of 4-*n*-alkyl-4′-cyanobiphenyl from $n=5$ to 9 at a constant reduced temperature in nematic phase. We calculated the rotational viscosity coefficient (RVC) by the Nemtsov-Zakharov and Fialkowski methods based on statistical-mechanical approaches and the rotational self-diffusion coefficient (RDC) with an analysis of the MD trajectory after the manner of Refs. [7,9,10,12,13]. The angle χ between the final C-C bond of the alkyl chain and the long molecular axis corresponding to the minimum energy geometry was calculated. The computation of equilibrium molecular geometries was performed at the density functional B3LYP/6-31G(d) level. All other results of this study were obtained from MD simulations.

The conformation of the end chain causes pronounced alternations in certain physical properties as the number of -CH2- and -CH3 groups in an alkyl chain varies from odd to even in LC phases and this effect is known as the odd-even effect in a homologous series. The odd-even effect in nCB homologous series has been discussed experimentally and theoretically. Marcelja considered a statistical termodynamic treatment of the effect of end-chain conformations on the properties of the nematic phase by using mean-field theory [14]. Karat and Madhusudana have shown that the odd-even effects are especially noticeable at experimental splay, twist, and bend elastic constants, the clearing point, and the order parameter for the nCB members [15,16]. The Zvetkow twist viscosity measurements obtained from a plot of torque against angular frequency of the magnetic field and density measurements was reported for a series of cyanobiphenyl LC's by Siedler and co-workers [17]. Their results exhibit an odd-even variation at a given relative temperature. Marinelli and co-workers measured the odd-even effect in the experimental thermal conductivity and thermal diffusivity of aligned nCB samples with a photopyroelectric technique [18]. Although the alternations in experimental results have been the subject of a number of investigations, there so far does not appear to have been any MD treatment of odd-even effects in RVC, RDC, and order parameters (OP's) in the nematic phase of nCB homologous series. The first atomistic

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MD simulation of the odd-even effect has been reported by Berardi and co-workers. [19]. They investigated the odd-even effect in the biaxiality, the distribution functions of the inertia tensor anisotropy, and some molecular geometry parameters for the phenyl alkyl-4-(4′-cyanobenzylidene) aminocinnamate series.

Many works have pointed out that the LC molecule does behave as a structural unit composed of semiflexible and rigid components rather than a rigid rod. An NMR work has given that the rigid core of the 5CB molecule has a significantly higher order parameter than the flexible alkyl chain segment [20]. Kobayashi and co-workers have found that the mean order parameter for the chain was smaller than for the core subunit [21]. Booth and co-workers have represented from Raman results that the effective splay core viscosity is higher than the bulk viscosity, while the effective alkyl chain viscosity is lower and the alkyl chain of 5CB responds more rapidly to the electric field than the rigid core [22]. In a Fourier transform infrared (FTIR) study of 5CB, it has been shown that the rigid core of the nematic molecule moves as a unit and the phenyl chain reorients more rapidly than the core [23].

In this paper we present an atomistic MD study in which the odd-even effect in RVC, RDC, and OP's for 4-*n*-alkyl-4′-cyanobiphenyl homologous series containing an *n*-alkyl chain, as *n* varies from 5 to 9. Furthermore, atomistic MD simulation results for the second- and fourth-rank order parameters, rotational viscosity, and diffusion coefficient of the rigid-rod-like core and the semiflexible alkyl parts of each mesogen are separately computed.

The rest of the paper is organized as follows: we summarize the two statistical-mechanical approaches for the rotational viscosity in Sec. II while the details of simulation and rotational self-diffusion calculation are in Sec. III. We present results and a discussion in Sec. IV, and finally, we make some conclusions in the last section.

II. TWO STATISTICAL-MECHANICAL APPROACHES FOR THE ROTATIONAL VISCOSITY

One of the theoretical accounts used to understand the basic physics of the rotational viscosity of LC's, the Ericksen-Leslie theory, is based on the continuous hydrodynamics of uniaxial nematic LC's [9,24]. The six Leslie coefficients given by this theory, α_i ($i=1,\ldots,6$), satisfy the general Onsager-Parodi relation $\alpha_2+\alpha_3=\alpha_6-\alpha_5$, so that only five coefficients are independent. The coefficient $\gamma_1=\alpha_3-\alpha_2$ is defined as the rotational viscosity coefficient and has a very important role in liquid crystal applications [12,25,26].

The coefficient γ_1 has been calculated by several approaches [4,8,12]. According to an efficient microscopic approach, the rotational diffusion model is used to determine the dynamical properties of LC's. In this study, we calculated γ_1 by using the rotational self-diffusion coefficient from a microscopic viewpoint. We used Nemtsov-Zakharov (NZ) and Fialkowski (F) models based on different physical approximations. Zakharov and co-workers have already determined γ_1 by these two methods for 5CB [7,9] and 8OCB [27]. Cheung and co-workers have also used the same process for PCH5 [12].

Nemtsov and Zakharov proposed [28–30] a statistical-mechanical approach based on the random walk theory and Zubarev nonequilibrium statistical operator to calculate rotational viscosities. In the framework of this approach, the different correlations are considered. Consequently, according to the NZ approach, the γ_1 rotational viscosity of the uniaxial system formed by uniaxial molecules depends on the second-rank order parameter $\bar{P}_2$ and rotational self-diffusion coefficients $D_\perp$ corresponding to the molecular tumbling and takes the following form:

$$\gamma_1^{\mathrm{NZ}}=\frac{\rho k_{\mathrm{B}}T}{D_\perp}\left(\frac{\bar{P}_2^2(9.54+2.77\bar{P}_2)}{2.88+\bar{P}_2+12.56\bar{P}_2^2+4.69\bar{P}_2^3-0.74\bar{P}_2^4}\right), \tag{1}$$

where ρ is the number density of molecules, T is the temperature, and k_B is the Boltzmann constant.

As a second method, Fialkowski gave the general expressions of the viscosity coefficient in a biaxial nematic LC [31]. In this approach it is assumed that the velocity gradient field which rotates each molecule with a certain average angular velocity is low. Viscosity coefficients for a uniaxial system are derived from the limiting case of those for a biaxial system. Consequently, the F approach gives γ_1 for the uniaxial system of uniaxial molecules as

$$\gamma_1^{\mathrm{F}}=\frac{\rho k_{\mathrm{B}}T}{D_\perp}\left(\frac{70\bar{P}_2^2}{16\bar{P}_4+5\bar{P}_2+14}\right)\frac{1}{2}, \tag{2}$$

where $\bar{P}_4$ is the fourth-rank order parameter. According to Eqs. (1) and (2), γ_1 is inversely proportional to the rotational self-diffusion constant.

III. SIMULATION DETAILS AND ROTATIONAL SELF-DIFFUSION

In this paper, the MD simulations for nCB series ($n=5-9$) in the nematic phase were performed using the COGNAC 3.77[1] [32] molecular dynamics simulation program and AMBER[2] force field [33]. We used the united atom model in which each of the aliphatic CH_2 and CH_3 and the

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[1] Coarse-grained molecular dynamics program by NAgoya Cooperation contained in OCTA2002 software. OCTA is an integrated simulation system for soft materials developed by the joint project of industry and academia funded by Ministry of Economy, Trade and Industry, Japan. In Japanese, the word "OCTA" means growth for the future.

[2] Assisted model building with energy refinement.

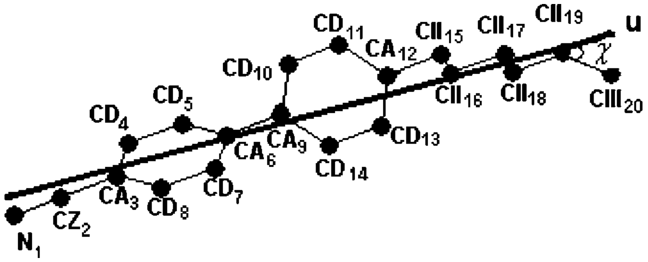

FIG. 1. The united atom model of 6CB. The long principal axis and the angle χ are also shown.

aromatic CH groups were treated as a single interaction center. In Fig. 1, the schematic united atom geometry for 6CB is illustrated. The consecutive members are created by adding one metil group to the alkyl chain of the former homolog. Therefore each of 5CB, 6CB, 7CB, 8CB, and 9CB molecules consists of 19, 20, 21, 22 and 23 interaction sites, respectively. The velocity verlet algorithm was applied to integrate the equations of motion with a time step of 1 fs. MD simulations were performed in the *N*-*P*-*T* ensemble using a Berendsen algorithm to control the temperature and pressure. An Ewald sum was carried out to evaluate electrostatic interactions with an Ewald convergence parameter of 0.3 Å^{-1} and 5 wave vectors in the x, y, and z directions. A $2.5\sigma_{ij}$ cutoff was imposed on the van der Waals interactions along with the long-range corrections for the energy, where σ_{ij} is a Lennard-Jones (LJ) parameter between interacting sites i and j.

In the initial configuration, a cubic fcc lattice of $N=64$ molecules was created at low density. After each system reached real density in Ref. [15] at the target temperature with a rapid compression, it was run at 1 atm pressure for simulation time of 1.6 ns. Odd-even effects were investigated at the temperatures given in Table I. The reduced temperature for four mesogens was taken as $T/T_{NI}=0.98$, but it was 0.99 for 9CB because of its rather short nematic range (1.5 K). The production time was different in each simulation, depending on the time interval in which the total energy remained stable (see Table I).

TABLE I. Temperatures and time periods of evaluation runs. The reduced temperatures are also reported.

	T (K)	T/T_{NI}	Production time (ps)
5CB	303	0.98	1450
6CB	296.5	0.98	700
7CB	310	0.98	900
8CB	307	0.98	1450
9CB	322	0.99	750

The AMBER-type force field is represented by

$$E_{\text{total}} = \sum_{\text{bonds}} K_r(r-r_{\text{eq}})^2 + \sum_{\text{angles}} K_\vartheta(\vartheta-\vartheta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}[1-\cos(n\phi-\delta_n)] + \sum_{i<j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_iq_j}{4\pi\pi_0 r_{ij}}\right], \tag{3}$$

where K_r and K_ϑ are force constants representing bond stretching, angle bending, and the rotational barrier, respectively; V_n is the torsional barrier height; n is the periodicity of the rotational interaction; r_{eq}, ϑ_{eq}, and ϕ are equilibrium values; δ and q are a phase angle and the electrostatic charge, respectively. The coefficients A_{ij} and B_{ij} are given by $A_{ij}=4\varepsilon_{ij}\sigma_{ij}^{12}$ and $B_{ij}=4\varepsilon_{ij}\sigma_{ij}^{6}$ where ε_{ij} and σ_{ij} are Lennard-Jones parameters for atoms i and j. All parameter sets [19,33,34] are listed in the Appendix.

It is possible to describe conveniently the molecular rotational motion using the normalized orientational time correlation function (TCF)

$$\mathbf{\Phi}_{00}^{2}(t) = \frac{\langle D_{00}^{2*}[\mathbf{\Omega}(0)]D_{00}^{2}[\mathbf{\Omega}(t)]\rangle}{\langle D_{00}^{2*}[\mathbf{\Omega}(0)]D_{00}^{2}[\mathbf{\Omega}(0)]\rangle}, \tag{4}$$

where Ω is the set of Euler angles that define the orientation of the molecular axes relative to the director frame. $D_{00}^{2}(\mathbf{\Omega})$ is a Wigner rotational matrix element of rank 2 and given by [12]

$$D_{00}^{2}[(\theta(t)\ ] = \frac{3}{2}\cos^2\theta - \frac{1}{2} = \frac{3}{2}(\mathbf{u}\cdot\mathbf{n})^2 - \frac{1}{2}, \tag{5}$$

where the molecular long axis $\mathbf{u}$ and the nematic director $\mathbf{n}$ are found from the simulation trajectories as described below. For flexible molecules, the molecular long axis $\mathbf{u}$ is defined as the long axis found from the inertial tensor:

$$I_{ab} = \sum_{i=1}^{N} m_i(r_i^2\delta_{ab} - r_{ia}r_{ib}) \quad \{a,b=x,y,z\}, \tag{6}$$

where r_i and m_i are the positions relative to the molecular center of mass and the masses of the atoms, respectively, and the sum runs over all the atoms in a particular molecule. The unit vector $\mathbf{u}$ is then the eigenvector corresponding to the smallest eigenvalue of I_{ab}.

The nematic director $\mathbf{n}$ is determined by diagonalization of the second-rank ordering tensor given by

$$Q_{ab} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{3}{2}u_{ia}u_{ib} - \frac{1}{2}\delta_{ab}\right), \tag{7}$$

and it is the eigenvector corresponding to the largest eigenvalue, where N is the number of molecules, u_{ia} and u_{ib} are components of a unit vector $\mathbf{u}_i$ associated with the molecular long axis found via the diagonalized moment of the inertia tensor [Eq. (6)]. In order to find second- and fourth-rank order parameters and also the time correlation function, the director of liquid crystal is calculated at each time step.

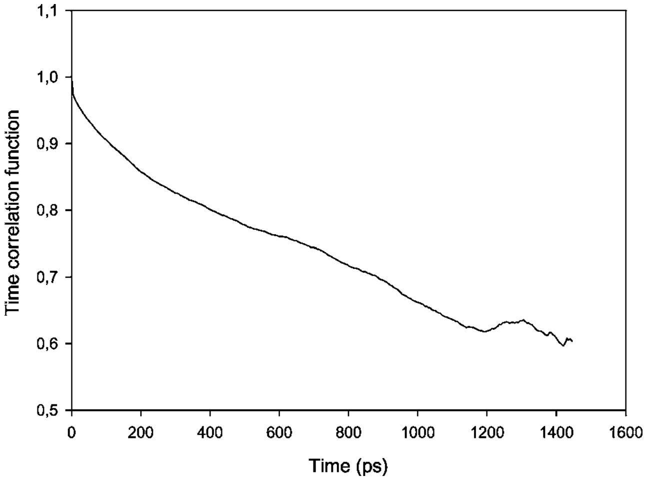

FIG. 2. Normalized orientational time correlation function $\Phi_{00}^{2}(t)$ for 5CB at 303 K.

By using the Wigner rotational matrix element $[D_{00}^{2}(\mathbf{\Omega})]$ obtained from Eq. (5) after calculating the **u** and **n** vectors, the TCF $\mathbf{\Phi}_{00}^{2}(t)$ is determined by Eq. (4). For symmetrical molecules in a uniaxial phase, $\mathbf{\Phi}_{00}^{2}(t)$ corresponds to the tumbling motion and can be written with a single-exponential approach:

$$\mathbf{\Phi}_{00}^{2}(t)=\mathbf{\Phi}_{00}^{2}(\infty)+[\mathbf{\Phi}_{00}^{2}(0)-\mathbf{\Phi}_{00}^{2}(\infty)]\exp\left(-\frac{t}{\tau_{00}^{2}}\right). \tag{8}$$

Once $\mathbf{\Phi}_{00}^{2}(t)$ is known from the MD trajectory via Eq. (4), it can be fitted to the single-exponential decay in Eq. (8) and then τ_{00}^{2} can be obtained. The second- and fourth-rank order parameters $\bar{P}_2$ and $\bar{P}_4$ are ensemble- and time-averaged values and calculated from the expressions

$$\bar{P}_2=\frac{3\,\overline{\cos^2\theta}-1}{2},\quad \bar{P}_4=\frac{35\,\overline{\cos^4\theta}-30\,\overline{\cos^4\theta}+3}{8}, \tag{9}$$

where $\cos\theta=\mathbf{u}\cdot\mathbf{n}$. The rotational self-diffusion coefficient describing molecular tumbling, $D_{\perp}$, can be found by

$$D_{\perp}=\left(6\tau_{00}^{2}\frac{7+5\bar{P}_2-12\bar{P}_4}{7+10\bar{P}_2+18\bar{P}_4-35\bar{P}_2^{2}}\right)^{-1}. \tag{10}$$

Then $D_{\perp}$ is substituted into Eqs. (1) and (2) to find the NZ and F rotational viscosity coefficients.

IV. RESULTS AND DISCUSSION

The $\Phi_{00}^{2}(t)$ functions of 5CB, 6CB, 7CB, 8CB, and 9CB have been computed at the reduced temperatures given in Table I. As an example, the TCF for 5CB at 303 K is drawn in Fig. 2. It can be seen that the first decay is not one exponential function, and so it does not correspond to the small step diffusion. Therefore, we fitted the TCF to the one-exponential function in Eq. (8) in a suitable time interval, giving the best regression parameter. As explained in Sec. III, the correlation times (τ_{00}^{2}), the rotational self-diffusion coefficients ($D_{\perp}$), and the mean second- and fourth-rank order parameters ($\bar{P}_2$ and $\bar{P}_4$) for each homologous were found from MD trajectories and used to determine the NZ and F rotational viscosities from Eqs. (1) and (2).

In this work, the equilibrium geometries of the lowest-energy conformation for nCB molecules were computed and verified by the following frequency analysis at the B3LYP/6-31G(d) level. Becke's three-parameter [35] and the Lee-Yang-Parr functionals [36] are used for the exchange and correlation energies, respectively. All calculations were performed using the GAUSSIAN 98 program package [37]. The hybrid functional B3LYP performs extremely well in predicting the structural parameters and vibrational frequencies of molecules [38]. To compute the angle χ between the final C-C bond of the alkyl chain and long principal axis for an isolated molecule, the moment of the inertia tensor for each member of the homologous series was calculated from the B3LYP atomic coordinates by using Eq. (6) and then **u** was determined after diagonalization. The long principal axis found for 6CB and the angle χ is illustrated in Fig. 1 as an example.

We also calculated the effective viscosities, the second- and fourth-rank order parameters, the correlation times, and

TABLE II. Rotational diffusion and viscosity coefficients and second and fourth-rank order parameters at T/T_{NI}=0.99 for 9CB and T/T_{NI}=0.98 for the others. n and V denote the number of C atoms in the alkyl chain and the volume of simulation cell, respectively.

n	χ^{a} (deg)	$\bar{P}_2$	$\bar{P}_4$	$S^{\text{expt,b}}$	V (10^{-27} m^3)	τ_{00}^{2} (ps)	$D_{\perp}$ (10^{8} s^{-1})	γ_1^{NZ} (mPa s)	γ_1^{F} (mPa s)	$\gamma_1^{\text{expt,c}}$ (mPa s)
5	8.4	0.35±0.03	0.05±0.03	0.36	25.58±0.10	2015	0.71	37.6±9.9	38.4±8.6	53.5
6	66.1	0.38±0.02	0.11±0.03	0.34	26.99±0.12	2977	0.58	46.9±8.2	47.2±7.0	66.4
7	13.2	0.39±0.01	0.18±0.03	0.37	28.79±0.13	3754	0.58	47.2±5.2	45.5±4.6	48.9
8	51.6	0.27±0.03	0.05±0.03	0.38	30.37±0.14	3143	0.55	28.4±8.1	25.1±6.6	70.4
9	17.1	0.42±0.02	0.15±0.03		32.09±0.16	4697	0.37	77.4±12.0	82.2±11.1	

[a] See Fig. 1.
[b] Reference [15].
[c] Reference [17].

TABLE III. Rotational diffusion and rotational viscosity coefficients and second- and fourth-rank order parameters of cyanobiphenyl groups of nCB at $T/T_{NI}=0.99$ for 9CB and $T/T_{NI}=0.98$ for the others.

	$\bar{P}_2$	$\bar{P}_4$	τ_{00}^2 (ps)	$D_\perp$ (10^8 s^{-1})	γ_1^{NZ} (mPa s)	γ_1^{F} (mPa s)
5CB	0.35±0.03	0.07±0.04	1475	1.07	25.2±7.1	25.2±6.2
6CB	0.36±0.03	0.10±0.03	1834	0.94	27.5±7.0	27.2±5.0
7CB	0.37±0.02	0.12±0.04	2273	0.81	32.0±5.8	31.4±5.3
8CB	0.23±0.04	0.06±0.05	1759	1.07	11.9±5.9	9.9±4.6
9CB	0.39±0.02	0.12±0.04	2065	0.84	31.2±6.9	32.0±6.2

the rotational self-diffusion coefficients of alkyl chain and rigid core parts of each molecule individually because of the importance of the tail flexibility on LC properties. Therefore, the segmental director and long axis were determined separately.

All computed results together with some published experimental data for five mesogens have been collected in Table II and those for cyanobiphenyl and alkyl parts in Tables III and IV, respectively.

The angle χ, the simulated second- and fourth-rank order parameters, and experimental order parameters [15] against C atom number (n) of the alkyl chain are plotted in Fig. 3. As shown, the angles χ are high at the even members and low at the odd members. Therefore, it can be concluded that in the even members of the series, the anisotropy of the molecule decreases because the final C-C bond of an alkyl chain makes on average a large angle with the long axis of the molecule whereas for the odd members the final methyl segment is oriented nearly parallel to the long axis of the molecule. These anisotropy changes for consequent members cause alternations of some physical properties. For instance, the order parameter [15], elastic constant [16], and T_{NI} phase transition temperature [15] have lower values in even members than in the adjacent odd members. On the other hand, the rotational viscosity and density become higher [17] for even members.

In Fig. 3, the experimental order parameters previously reported give an alternation, although 8CB does not follow this trend, indicating that near-neighbor correlations play a prominent role [16]. Although similar alternations have not been explicitly noticed in simulated order parameters, an odd-even effect can be mentioned if the standard deviations involved in Fig. 3 are taken into consideration. It is worthwhile to note that the simulated second-rank order parameters are of the same order of magnitude as the experimental values [15].

Figure 4 presents the isothermal rotational viscosities γ_1^{NZ}, γ_1^{F}, and γ_1^{expt} against the number of carbon atoms (n) in the alkyl chain. As shown, the experimental viscosity gives a periodic variation with maxima at 6CB and 8CB and minima at 5CB and 7CB [17]. However, a slight odd-even effect in simulated RVC's is produced only for the first three members when the standard deviations involved are considered. As is seen, the γ_1^{NZ} and γ_1^{F} values are found close to each other in this work in contrast to those in Refs. [9,12]. In these earlier papers, the factor of $1/2$ in the Fialkowski equation was not taken into account and this caused a misleading result indicating that the F theory gives higher γ_1 values than the NZ theory.

The dependence of the rotational diffusion coefficient on n is shown in Fig. 5. It illustrates that the rotational diffusion coefficients show an odd-even alternation similar to the behavior of the simulated rotational viscosities discussed above.

The odd-even effects in all simulated properties are more unclear than the experimental data available (see Figs. 3 and 4). This should be expected in MD simulation from the fact that the force field parameters, simulation time, and sample size are very effective in generating the physical properties of LC's. First, the force fields used in MD studies of LC's have not been derived to reproduce the order parameters and the rotational viscosity and diffusion coefficients. Second, the simulation time for LC's should be very long, due to the slow relaxation of LC properties. With reference to work

TABLE IV. Rotational diffusion and rotational viscosity coefficients and second- and fourth-rank order parameters of alkyl chain segments of nCB at $T/T_{NI}=0.99$ for 9CB and $T/T_{NI}=0.98$ for the others.

	$\bar{P}_2$	$\bar{P}_4$	τ_{00}^2 (ps)	$D_\perp$ (10^8 s^{-1})	γ_1^{NZ} (mPa s)	γ_1^{F} (mPa s)
5CB	0.16±0.05	0.00±0.04	203	8.13	0.9±0.7	0.7±0.6
6CB	0.24±0.04	0.05±0.04	667	2.69	5.4±2.0	4.6±1.6
7CB	0.19±0.04	0.05±0.04	553	3.49	2.8±1.4	2.2±1.0
8CB	0.21±0.04	0.03±0.05	592	2.93	3.8±1.6	3.2±1.3
9CB	0.24±0.02	0.06±0.04	633	3.02	4.3±1.0	3.6±0.8

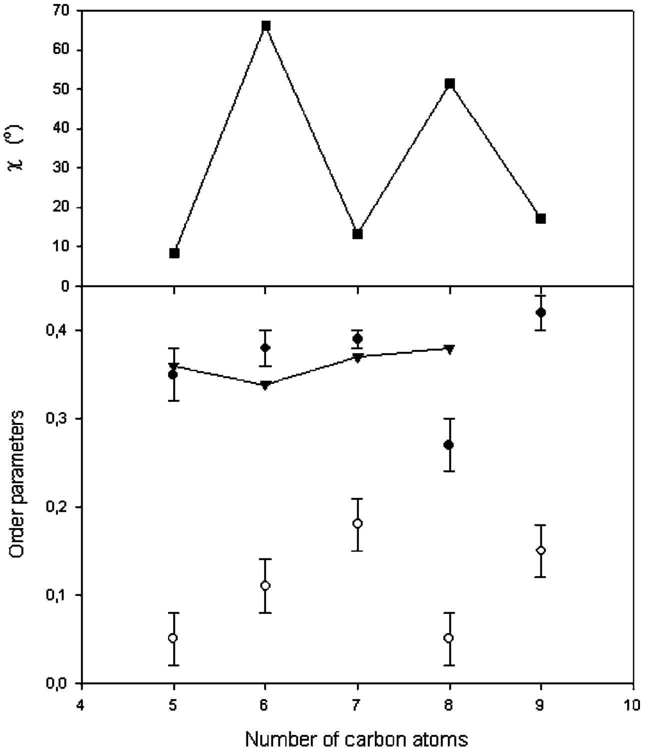

FIG. 3. The order parameters and the angle χ (■) plotted versus the number of C atoms, n, in the alkyl chain. Standard deviations for $\bar{P}_2$ (●) and $\bar{P}_4$ (○) are also included. The experimental order parameters S^{expt} (▼) are from Ref. [15]. The reduced temperatures are 0.99 and 0.98 for 9CB and the other mesogens, respectively. The lines have been drawn to aid the eye in observing any odd-even effects.

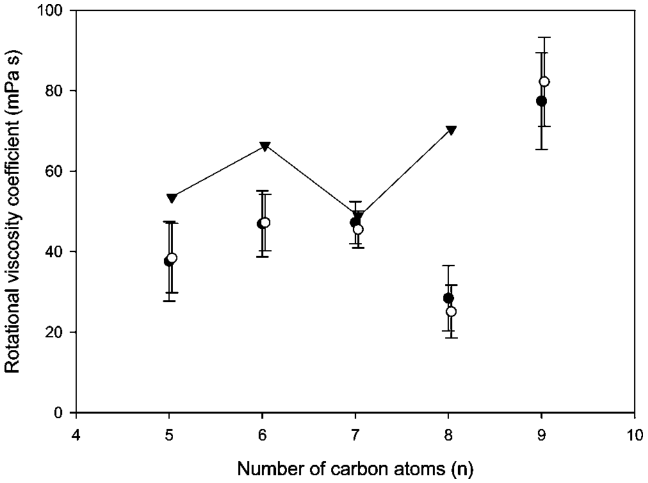

FIG. 4. The rotational viscosities versus the number of carbon atoms in the alkyl chain. γ_1^{NZ} (○) and γ_1^{F} (○) are from MD simulations with standard deviations, γ_1^{expt} (▼) are the experimental values from Ref. [17]. The points for the same n are displaced laterally for the sake of clarity. The reduced temperatures are 0.99 and 0.98 for 9CB and the other mesogens, respectively. The lines have been drawn to aid the eye in observing odd-even effects in experimental RVC's.

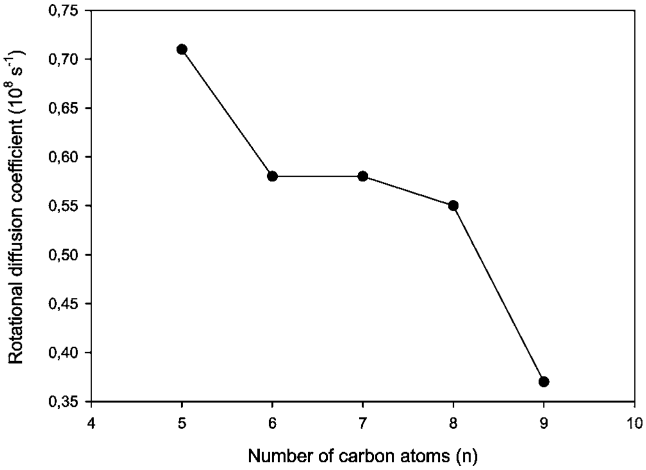

FIG. 5. Rotational diffusion coefficients from MD simulation versus n. The reduced temperatures are 0.99 and 0.98 for 9CB and the other mesogens, respectively.

performed by Berardi and co-workers [19] on phenyl alkyl-4-(4′-cyanobenzylidene) aminocinnamates, there is a need to carry out MD simulations lasting up to 40 ns in order to obtain the temperature dependence of LC properties. Third, to reproduce macroscopic properties by MD, the number of molecules should be increased considerably. However, the effect of the increment of system size on macroscopic properties is controversial; that is, size dependence was not obtained in some studies in contrast to others [19,39]. Small changes in rotational viscosities with system size were found previously for Gay-Berne systems [3].

Consequently, the MD simulation is not very successful in investigating the odd-even effect and the temperature dependence of physical properties [13,22,39] unless the simulation run times become very long, better force fields are used, and the system size is much increased. However, the simulated RVC's, RDC's, and OP's in this work are in the order of experimental results (see Table II). For example, the rotational diffusion coefficients for 5CB are in close agreement with the deuterium NMR results, $(0.5-1.5)\times 10^8$ s^{-1} [40]. Other methods as in Refs. [10,12] can be used to find better RVC results.

As seen in Tables III and IV, the order parameters and rotational viscosities of core parts of nCB homologous series are higher than the values of the corresponding alkyl chain. On the other hand, the core rotational diffusion coefficient is lower than the chain's. These results imply that the liquid crystal molecule does not behave as a rigid rod during reorientation. It is evident from the simulated RVC and RDC values that the alkyl part reorients faster than the core part. The overlap of π orbitals in the aromatic rings and the cyano group of an nCB molecule leads to the rigidity of the core. An alkyl chain is partially flexible since it costs a finite, but easily achievable, energy to make rotations about any carbon-carbon bond. The separate order parameters of the aliphatic chains and the core segments do not change seriously along the homologous series. The order parameters of the core segment for a mesogen and of the entire mesogen are close. Our simulated results for the alkyl and core parts are supported by the other studies [20–23].

V. CONCLUSION

We performed MD simulations for the five members of 4-*n*-alkyl-4′-cyanobiphenyl homologs at the reduced temperature in nematic phase. We calculated the rotational viscosity and diffusion coefficients and the second- and fourth-rank order parameters. The rotational viscosity coefficients are derived by means of the Nemtsov-Zakharov and Fialkowski methods. The NZ and F rotational viscosities are comparable with each other and in agreement with experiments. The simulated OP and RDC are also on the order of the corresponding experimental values. Odd-even effects in the OP's, RVC, and RDC are produced slightly. We also calculated the same properties for rigid rod and alkyl chain parts separately. The OP's and RVC of a rigid rod are higher than the chain values in contrast to the RDC. Therefore, it is evident that the flexible alkyl chain reorients much faster than the rigid core. This emphasizes that the liquid crystal molecule does not behave as a rigid unit during reorientation.

The angle between the final C-C bond of the alkyl chain and long principal axis for each isolated molecule was computed at the B3LYP/6-31G(d) geometry, and it was high for the even and low for the odd members.

In conclusion, the RDC, RVC, and OP's in this work are found to be reasonable. However, MD simulations performed by the more suitable force fields for LC's, high sample sizes, and long simulation times can be suggested to reproduce odd-even effects and temperature-dependent processes better. Furthermore, to get a better agreement with experiments the other methods [14] can be used in evaluation of the RVC.

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APPENDIX

The parameters used in the MD calculations are given in Table V [see Eq. (3)]. The force field parameters were taken from Refs. [19,33] and the partial charges were from Ref. [34].

TABLE V. Parameters used in the MD calculations.

Atom type	q (e)
N^1	−0.283
CZ^2	0.019
CA^3	0.010
CD^4	0.096
CD^5	0.024
CA^6	−0.018
CD^7	0.024
CD^8	0.096
CA^9	−0.043
CD^{10}	0.027
CD^{11}	0.005
CA^{12}	0.011
CD^{13}	0.005
CD^{14}	0.027

Atom type	Mass (amu)	A (kcal mol^{-1} Å^{12})	B (kcal mol^{-1} Å^{6})
N	10.01	755438.8	641.1
CZ	12.01	2381903.3	1007.3
CA	12.01	3572870.0	1284.8
CD	13.02	3572870.0	1284.8
CII	14.03	5934641.1	1673.7
CIII	15.03	8801374.5	2482.1

Bond	K_r (kcal mol^{-1} Å^{-2})	r_{eq} (Å)
CZ-N	600	1.150
CZ-CA	400	1.458
CA-CA	469	1.400
CD-CD	469	1.400
CA-CD	469	1.400
CA-CII	317	1.510
CII-CII	260	1.526
CII-CII	260	1.526

Angle	K_θ (kcal mol^{-1} rad^{-2})	θ_{eq} (deg)
N-CZ-CZ	57.6	180.0
CZ-CA-CD	70.0	120
CD-CA-CA	70.0	120
CD-CA-CII	70.0	120
CA-CD-CD	85.0	120
CD-CA-CD	85.0	120
CA-CII-CII	63.0	112.4
CII-CII-CII	63.0	112.4
CII-CII-CIII	63.0	112.4

Torsion	$V_n/2$ (kcal mol^{-1})	δ_n (deg)	n
N-CZ-CA-CD	0	0	0
X-CD-CD-*X*	5.3	180	2
X-CA-CD-*X*	5.3	180	2
X-CA-CA-*X*	5.3	180	2
X-CII-CA-*X*	0.0	0	2
X-CII-CII-*X*	2.0	0	3

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