Bull. Chem. Soc. Jpn., **65**, *1057—1061 (1992)*

A Computational Approach to the Structure and Motion of Hexakis(pentyloxy)triphenylene(THE5) in Discotic Mesophase

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(Received October 28, 1991)

A molecular dynamics simulation using the atom–atom potential was applied to THE5 of a disk-like mesogenic molecule. The calculations were carried out in a canonical (*NVT*) ensemble. The results show that the time-averaged molecular properties and molecular ordering are in agreement with experiment. The effects of molecular flexibility in side chains are clearly demonstrated in the profile of the order parameters of each C–H bond.

Hexakis(pentyloxy)triphenylene (THE5) exhibits a D_{ho} mesophase[1] in which disk-like molecules are stacked periodically in a column, the different columns being arranged in a hexagonal array.[2] The side chains bonded to the central core are in a relatively disordered state due to their flexibility. The order parameters of the rigid aromatic core and of the side chains of THE5 in the D_{ho} mesophase have been determined by ^{2}H NMR[3] and ^{13}C NMR[4] studies. The ordering of the side chain obtained from ^{2}H NMR was incompatible with that from ^{13}C NMR. Especially, the O–C_1 bond linked to the central core lays out of the core plane by ^{2}H NMR,[3,5] whereas the bond was fixed to lie on the same plane by ^{13}C NMR.[4] On the other hand, a semiempirical calculation gave rise to an apparent deviation of about 120° from the plane.[6] In order to evaluate the molecular structure in the discotic mesophase, it is necessary to take into account not only the intramolecular interaction, but also the intermolecular interaction for the stacking arrangement of mesogens in the column, which influence the molecular motion of the side chain. The molecular dynamics (MD) method is available to evaluate the molecular motion and ordering in consideration of these interactions.

We recently performed MD simulations based on the atom–atom potential for 4-alkyloxy-4-cyanobiphenyls (nOCB).[7] The calculated values were in agreement with the data for order parameters of a whole molecule, as well as of each C–H bond in the side chain. The anisotropies of the self-diffusion coefficients obtained in the nematic phase were consistent with the values found in the literature. Although the previous paper dealt with calamitic liquid crystal compounds with a lath-like molecular structure, the method can be used concerning the problem of discotic compounds.

We present a study of the MD simulation for THE5 to be assumed to be in the D_{ho} mesophase. The calculated results are compared with the experimental values.

Computation

The potential energy used in the MD simulation is

$$E = E_{ES} + E_{VDW} + E_{TORS}.$$

The Coulomb potential E_{ES} is

$$E_{ES} = Q_i Q_j / r,$$

where Q_i and Q_j are the atomic charges of atoms i and j, respectively, and r is the distance between atoms i and j. The atomic charges were calculated using the ab initio molecular orbital method (STO-3G) for an isolated molecule. The van der Waals term (E_{VDW}) and the torsion term (E_{TORS}) were calculated by using the potential of molecular mechanics MM2,[8]

$$E_{VDW} = 2.90 \times 10^5\, \varepsilon \exp(-12.50\, r/r_0) - 2.25\, \varepsilon\, (r_0/r)^6$$

and

$$E_{TORS} = \Sigma V_i\, (1 \pm \cos(i\omega)),$$

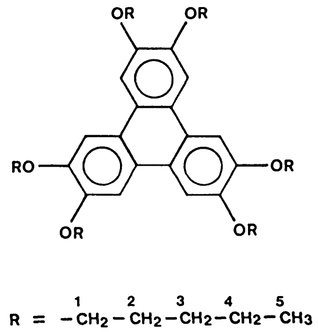
where ε, r_0 and V_i denote the constants for each set of atoms.[8] The methylene groups in the aliphatic chain were approximated as being united atoms.[7] The lengths and angles of the bonds[5] in the molecules were fixed throughout this simulation.

A canonical (*NVT*) ensemble was used for the MD simulation. A temperature of 380 K was chosen as experimentally indicating the D_{ho} mesophase. The periodic boundary condition was adopted for the unit cell. The equations of motion were integrated using a leapfrog scheme.[9] The MD run took fifty thousand time steps of two femtoseconds; during the initial three thousand steps, the calculation was carried out at a higher temperature (430 K) so as to avoid any dependence on the initial geometry.

All calculations were performed on a HITAC M-880/310 located in the Computer Centre of the University of Tokyo.

Results and Discussion

Calculation for Isolated Molecule. The chemical formula of THE5 is shown in Fig. 1. THE5 molecule consists of a triphenylene core and six pentyloxy chains. The pentyloxy chains were found to have disorder in the D_{ho} mesophase.[3,4] The conformation of the binding part linked to the core affects the structure of the chain. It is not clear from the experimental results whether the O–C_1 bond is fixed to the core plane or not. The THE5



$$R = \overset{1}{-CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

Fig. 1. Chemical formula and numbering of the carbons of THE5.

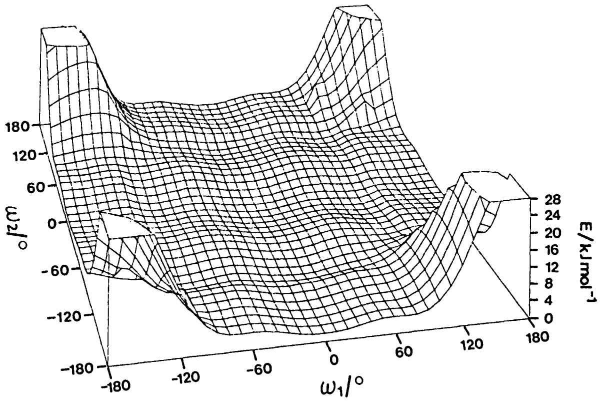


Fig. 2. Energy map against the torsional angles (ω_1 and ω_2) for the isolated BDE5 molecule by MM2.

molecule has threefold symmetry, and the chains belonging to the different phenyl rings are far away. A calculation involving the adjacent chains is sufficient to account for the stable conformation. 1,2-Bis(pentyloxy)benzene (BDE5) was selected as a model for a molecular mechanics MM2[8] calculation in order to elucidate the torsional behavior around the two C_{ar}–O bonds, as defined ω_1 and ω_2. The torsional angles (ω_1 and ω_2) are defined as zero when both O–C_1 bonds are spread on plane of the core, and are oppositely directed to each other. A positive value is relative to a clockwise rotation for both bonds. Figure 2 shows the energy map against two torsional angles (ω_1 and ω_2) of BDE5. The calculation suggests that the structure $\omega_1=\omega_2$ with 0° has the minimum energy. The energy minima are not very different from the global minimum. The structures in which one of the two chains stand at 90° are obtained as conformations with a local minimum. The structures with torsional angles of $\omega_1=\omega_2\simeq\pm 90°$ are also stable, in which the two bonds are situated anti-parallel to each other, and lying perpendicular to the phenyl ring. Although several structures with local minimum energy are obtained (Fig. 2), the energy barriers around angles ω_1 and ω_2 are relatively low. Nevertheless, structures with $|\omega_1|>100°$ and $|\omega_2|>100°$ are unstable, owing to a steric repulsion between the two chains.

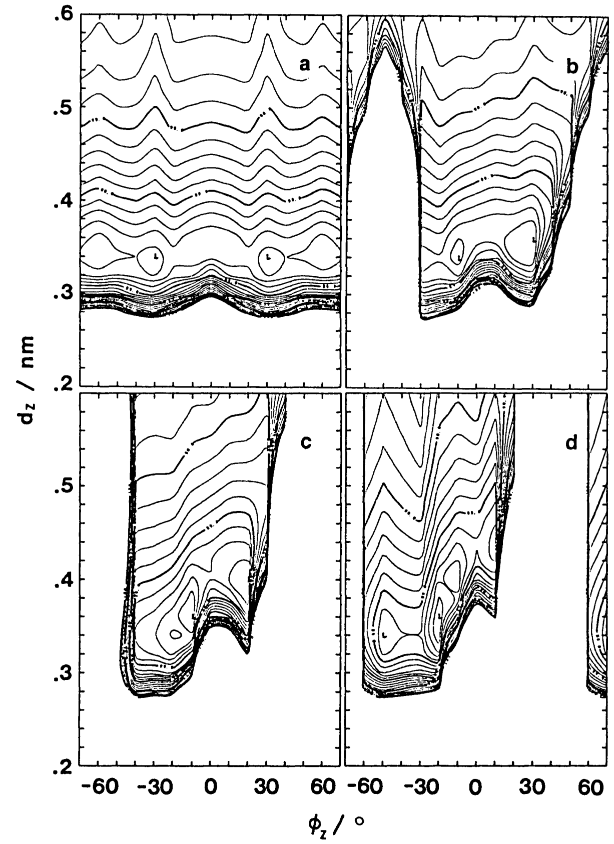


Fig. 3. Energy contour maps for a pair of THE5 molecules which are stacked in parallel with an intermolecular distance of d_z and an rotational angle of ϕ_z. Contour maps a, b, c, and d correspond to the torsional angles (ω_1 and ω_2) of 0, 30, 60, and 90 degrees, respectively.

Calculations for Dimer. Calculations for a pair of THE5 molecules were performed in order to evaluate the intermolecular distance of parallel-arranged molecules. The energy was calculated as a function of the intermolecular distance (d_z) and the rotational angle (ϕ_z). Figure 3 shows the energy contour maps, where a, b, c, and d indicate torsional angles (ω_1 and ω_2) of 0, 30, 60, and 90 degrees, respectively. The conformations, except for ω_1 and ω_2, in the pentyloxy chain were assumed to be all-*trans*. Taking into account the threefold symmetry of the THE5 molecule, the value of ϕ_z was taken to be from −60° to +60°. As shown in Fig. 3, the curves differ from one another according to the bending of the bonds from the triphenylene plane. This is caused by a steric repulsion of another chains. The intermolecular distance (0.36 nm) was measured by X-ray diffraction[1] and is approximately reproduced by the calculations for any conformer.

MD Simulation in D_{ho} Mesophase. The MD simulation starts from the state to be the D_{ho} mesophase. Nine columns, in each of which six molecules were stacked with an intermolecular distance 0.36 nm, were arranged hexagonally. An experimental value of 1.89

nm by X-ray diffraction2) was adopted for the intercolumner distance. The size of a unit cell including 54 molecules was thus fixed to be $5.682\times4.920\times2.154\ \mathrm{nm}^3$. The averaged pressure of the system was 0.8 MPa, and the anisotropy of pressure could not be recognized as being significant through a pronounced fluctuation in the pressure.

Figure 4a shows a *snapshot* taken at 380 K. In order to elucidate the positions of the triphenylene cores, a *snapshot* without the side chains is also shown in Fig. 4b. After equilibrium was reached in the system, the triphenylene cores retained the columitic arrangement. The self-diffusion coefficient (D), was calculated in order to evaluate the dynamical properties. D was obtained from the slope of the mean square displacement (MSD). We averaged the MSD at intervals of five thousand steps for the final forty thousand steps. These results are shown in Fig. 5. A value of $9.84\times 10^{-12}\ \mathrm{m^2\,s^{-1}}$ was obtained for the longitudinal diffusion coefficient along the director ($D_{/\!/}$). On the other hand, the diffusion perpendicular to the director is relatively faster ($D_{\perp}=1.89\times10^{-11}\ \mathrm{m^2\,s^{-1}}$). The values of $D_{/\!/}$ and $D_{\perp}$ in $\mathrm{D_{ho}}$ mesophase of THE8 or THE10 were reported.10) Although the calculated tendency of $D_{/\!/}< D_{\perp}$ coincides qualitatively with the experimental results, no large anisotropy was obtained in our simulation. The calculated order parameter ($S=0.95$) indicates a highly ordered core. This value agrees with the experimental results of $S=0.85\pm0.1$ by ^{13}C NMR4) for THE5 or $S=0.90$ by ^{2}H NMR.3,11) While the MD simulation was performed in a small system and over a fairly short time, the structures and motions of the core part in the $\mathrm{D_{ho}}$ phase are partly reproduced from the calculation.

It is known that the side chains are in disorder, contrary to the high order of the core in the $\mathrm{D_{ho}}$ mesophase. For example, the intercolumner distance (1.89 nm) measured by X-ray diffraction1) is shorter than the length for the structure of a fully extended (all-*trans*) conformation of the aliphatic chain. This can be accounted for by the disorder of the chain. Experimentally, the order parameters of the side chain ($S_{\mathrm{C\text{-}H}}$) were measured by ^{2}H NMR for THE5 in the $\mathrm{D_{ho}}$ mesophase.3) The value of $S_{\mathrm{C\text{-}H}}$ for each C–H bond can be calculated from the conformation of the pentyloxy chain, even though the methylene groups are treated as being the united atoms in the MD. Figure 6 shows the

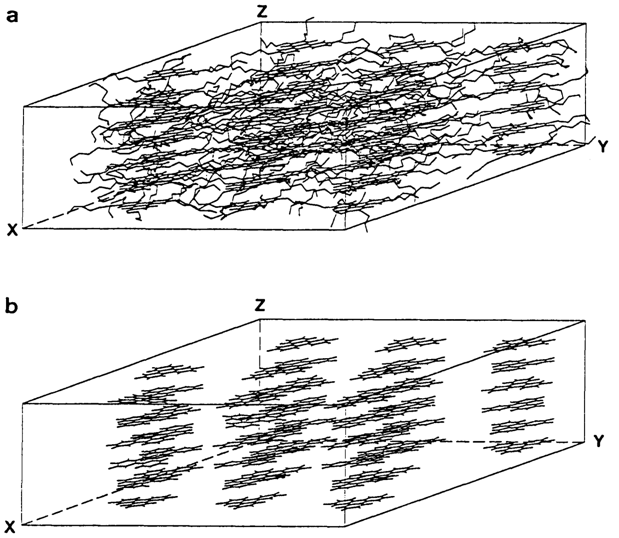


Fig. 4. *Snapshot* of 54 molecules in a unit cell at 380 K (a), and that without a side chain (b).

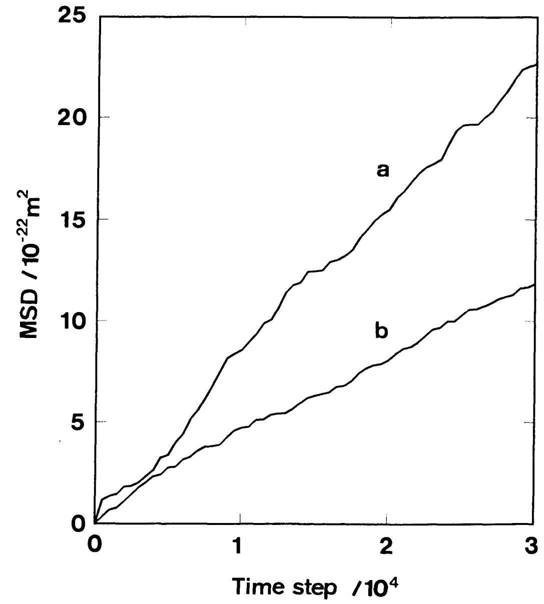


Fig. 5. Plots of MSD for the perpendicular (a) and parallel (b) compornents to the director.

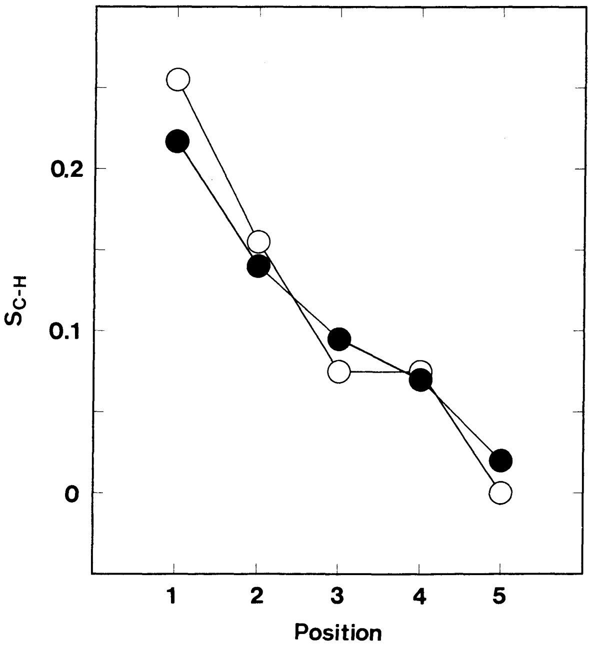


Fig. 6. Calculated (●) and experimental (○)3,5) order parameters ($S_{\mathrm{C\text{-}H}}$) against the bond position.

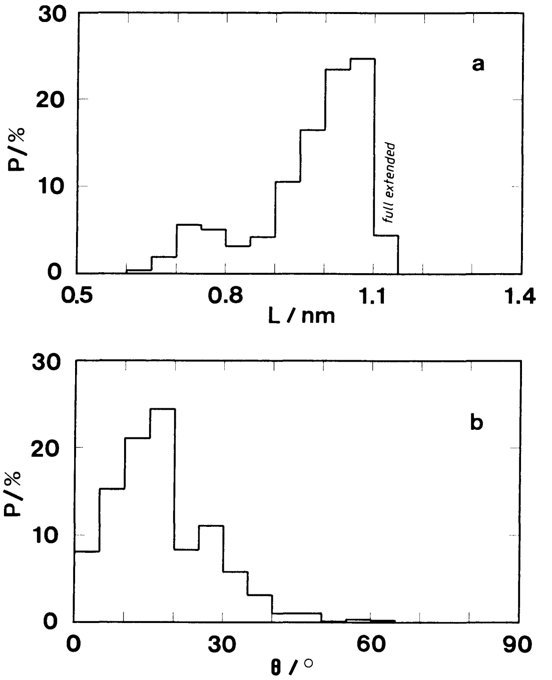


Fig. 7. Distributions of the length (a) and angle (b) from the core of the vector, which is defined from the center of triphenylene to the carbon of the methyl group.

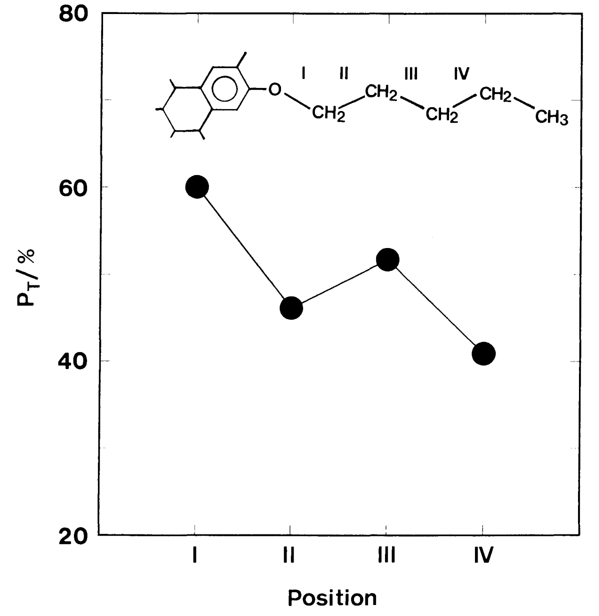


Fig. 8. Plot of the population of the *trans* conformation versus the bond position.

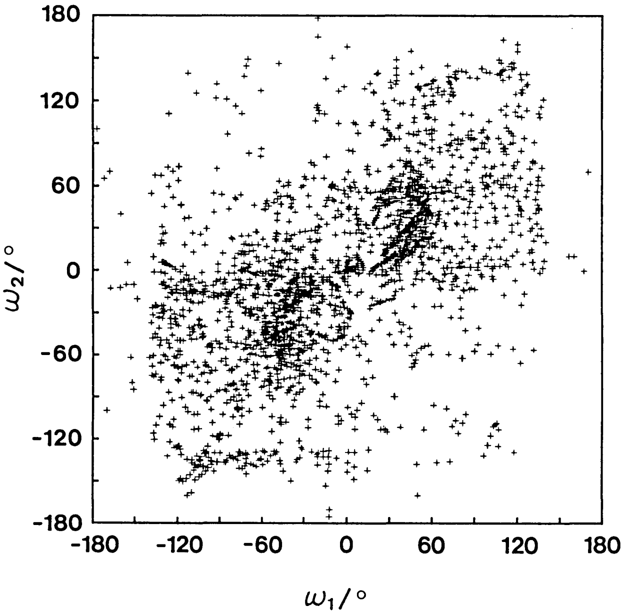


Fig. 9. Population of the torsional angles (ω_1 and ω_2) obtained by an MD simulation.

$S_{\mathrm{C-H}}$ calculated (closed circle) against the bond position. The values of $S_{\mathrm{C-H}}$ decrease stepwise along the aliphatic chain. This decrease is in good agreement with that of the experimental values (open circle). In rod-like liquid crystals, the simulated $S_{\mathrm{C-H}}$ also agrees with the experimental value. Thus, an MD simulation is well suited for evaluating the ordering, not only of the entire molecule, but also of the side chain. However, the agreement in the quantitative magnitude is inferior to the results of a mean field approximation.[5]

We defined the vector from the center of the triphenylene core to the carbon of the terminal methyl group. Figure 7a shows the distribution of the length of the vector. The wide distribution of the length calculated from the MD simulation implies that the pentyloxy chains are in a disordered state. Moreover, the major populations are found to be not more than an angle of 30° from the triphenylene plane, as shown in Fig. 7b. Thus, the structure is not a so-called *octopus-like* structure.

To discuss the conformation of the side chain, the probability of a *trans* conformer against the position of bonds is shown in Fig. 8. The populations are relatively large for the odd positions. This tendency is normally obtained for an anisotropic system, such as liquid crystals.[12] Figure 9 shows the populations of the two torsional angles around the C_{ar}–O bonds (ω_1 and ω_2). The simulated structures, in which the two chains are situated above and under the phenyl ring, are found more than the structures $\omega_1=\omega_2=0°$, which are inferred from a calculation for the model compound (BDE5). The angles ω_1 and ω_2 are distributed over a wide range; angles from 30° to 60° were obtained as the probable conformations. Similar results concerning the range of the torsional angles were reported for pyramidic hexakis(octyloxy)tribenzocyclononene in the mesophase by ^{2}H NMR.[13]

Although it is necessary to consider that the results are obtained under fairly restricted conditions, the molecular structures and motions of the disk-like compound in the D_{ho} mesophase were reproduced by an MD simulation using realistic molecules.

The authors are grateful to Professors Masatami Takeda and Keizo Suzuki of the Science University of Tokyo for their helpful discussions.

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