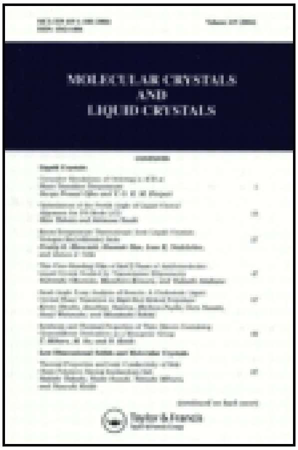

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# THE ORDER AND POLARISATION OF A SYSTEM COMPOSED OF BENT POLAR GAY-BERNE MOLECULES

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# THE ORDER AND POLARISATION OF A SYSTEM COMPOSED OF BENT POLAR GAY-BERNE MOLECULES

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*NVT molecular dynamics simulation are carried out to study the relation between the molecular shape and dipole moment to the liquid crystalline ordering for a system of coupled Gay-Berne molecules. These are dimers of two types of Gay-Berne particles coupled by a harmonic spring. The appearance of the polarisation and biaxiality together with the location of isotropic-nematic clearing temperature are reported for various combinations of position and direction of the dipole attached to the molecule.*

*Keywords*: bend molecule; electric polarisation; Gay-Berne model; MD simulation; phase biaxiality

## INTRODUCTION

In the field of liquid crystals, the shape of the constituent molecules has in general a special meaning because of the anisotropic interaction. For example, in antiferroelectric smectics, in which various interesting phenomena occur, the bend of the molecular ends are reported in the context of the stabilisation of the antiferroelectric phase [1–3]. Even for non-chiral liquid crystalline materials composed of banana-shaped molecules, ferro-and antiferro-electric phases are known to appear [4–5]. The permanent dipole moment attached to the molecules also influences the liquid crystalline behaviour. In practice, investigations of a system

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of molecules with an electric dipole [6–8] or quadrupole [9] have suggested interesting features. In a previous study, we have reported preliminary results for a system of coupled Gay-Berne [10–12] molecules by NVT molecular dynamics simulations [13]. Here, the molecular dynamics simulation of this system is carried out to study the effect of the shape and dipole moment of the molecule on the ordering and polarization of the system.

The molecules studied here consists of two Gay-Berne particles with different lengths coupled by a harmonic spring, where the length of the shorter one is twice the diameter $\sigma_0$ and the longer one three times, for modeling of the antiferroelectric material. The molecular bond angle is adjusted to take a given value in isolated state. The permanent dipole is attached to the molecule in various positions and directions of the moment in the molecule. The appearance of biaxiality and electric polarisation are shown to depend on the direction of the attached dipole, as well on the position of the dipole in the molecule.

In the following section, the system studied and the constituent molecules are introduced and the conditions of the simulation are explained. The results of the simulation are shown following this and finally the summary discussions are given.

## SYSTEM AND CONDITION OF SIMULATION

The system is composed of molecules, which are composed of two Gay-Berne particles. As shown in Figure 1, the interaction energy consists

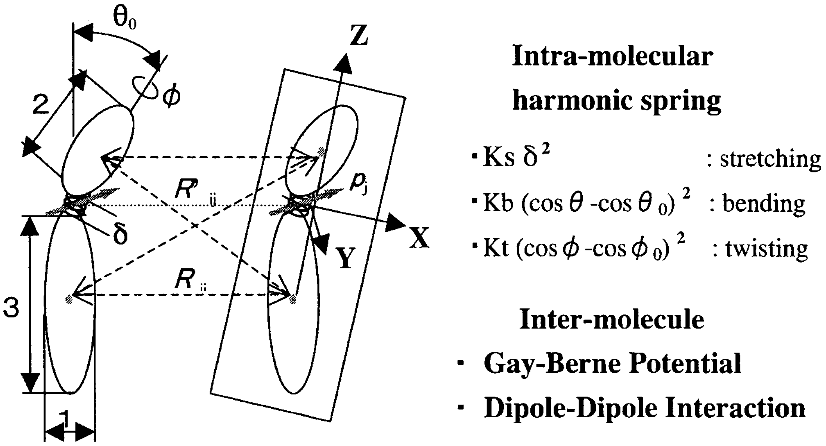

**FIGURE 1** Model of bent polar Gay-Berne molecule.

of the sum of the individual Gay-Berne potentials between particles of different molecules and of the dipole-dipole interaction together with the deformation energies of each molecule.

The interaction energy for the Gay-Berne potential is given by [10–12],

$$\mathrm{U}_{\text{G-B}} = 4\,\varepsilon(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}})[\{\sigma_{\mathrm{o}}/(R_{\mathrm{ij}} - \sigma(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}) + \sigma_{\mathrm{o}})\}^{12} \\ - \{\sigma_{\mathrm{o}}/(R_{\mathrm{ij}} - \sigma(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}) + \sigma_{\mathrm{o}})\}^{6}], \tag{1}$$

where $\boldsymbol{u}_{\mathrm{i}}$ is the unit vector denoting the direction of the symmetry axis of G-B particle i, $\boldsymbol{R}_{\mathrm{ij}} = \boldsymbol{R}_{\mathrm{i}} - \boldsymbol{R}_{\mathrm{j}}$ and $R_{\mathrm{ij}} = |\boldsymbol{R}_{\mathrm{i}} - \boldsymbol{R}_{\mathrm{j}}|$ with $\boldsymbol{R}_{\mathrm{i}}$ the position vector of centre of mass of G-B particle i. The potential well depth $\varepsilon(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}})$ and the inter-molecular separation $\sigma(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}})$ are given by

$$\varepsilon(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}) = \varepsilon_0\{1 - \chi^2(\boldsymbol{u}_{\mathrm{i}} \cdot \boldsymbol{u}_{\mathrm{j}})^2\}^{-1}\varepsilon_2(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}), \tag{2}$$

$$\sigma(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}) = \sigma_0[1 - (\chi/2)\{(\alpha\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{i}} + \alpha^{-1}\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{j}})^2/(1 + \chi\boldsymbol{u}_{\mathrm{i}} \cdot \boldsymbol{u}_{\mathrm{j}}) \\ + (\alpha\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{i}} - \alpha^{-1}\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{j}})^2/(1 - \chi\boldsymbol{u}_{\mathrm{i}} \cdot \boldsymbol{u}_{\mathrm{j}})\}]^{-1/2}, \tag{3}$$

with $\varepsilon_2(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}})$

$$\varepsilon_2(\boldsymbol{u}_{\mathrm{i}}, \boldsymbol{u}_{\mathrm{j}}, R_{\mathrm{ij}}) = [1 - (\chi'/2)\{(\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{i}} + \boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{j}})^2/(1 + \chi'\boldsymbol{u}_{\mathrm{i}} \cdot \boldsymbol{u}_{\mathrm{j}}) \\ + (\boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{i}} - \boldsymbol{R}_{\mathrm{ij}} \cdot \boldsymbol{u}_{\mathrm{j}})^2/(1 - \chi'\boldsymbol{u}_{\mathrm{i}} \cdot \boldsymbol{u}_{\mathrm{j}})\}]^{-1/2}, \tag{4}$$

respectively, where the parameters $\chi'$, $\chi$ and $\alpha$ are given by

$$\chi' = \{1 - (\varepsilon_{\mathrm{E}}/\varepsilon_{\mathrm{S}})\}/\{1 + (\varepsilon_{\mathrm{E}}/\varepsilon_{\mathrm{S}})\}, \tag{5}$$

$$\chi = \{(L_{\mathrm{i}}^2 - 1)(L_{\mathrm{j}}^2 - 1)/(L_{\mathrm{j}}^2 + 1)(L_{\mathrm{i}}^2 + 1)\}^{1/2}, \tag{6}$$

$$\alpha^2 = \{(L_{\mathrm{i}}^2 - 1)(L_{\mathrm{j}}^2 + 1)/(L_{\mathrm{j}}^2 - 1)(L_{\mathrm{i}}^2 + 1)\}^{1/2}, \tag{7}$$

where the G-B particle length $L_{\mathrm{i}}$ (in units of $\sigma_0$) is taken to be 2 if particle i is the shorter one and 3 if particle i is the longer one, and the value of $\varepsilon_{\mathrm{E}}/\varepsilon_{\mathrm{S}}$ is chosen to be 0.2.

The energy of the dipole-dipole interaction is given by

$$\mathrm{U}_{\text{D-D}} = \mu{\sigma_0}^3\{(\boldsymbol{p}_{\mathrm{m}} \cdot \boldsymbol{p}_{\mathrm{n}})/{\boldsymbol{R}'_{\mathrm{mn}}}^3 - 3(\boldsymbol{R}'_{\mathrm{mm}} \cdot \boldsymbol{p}_{\mathrm{m}})(\boldsymbol{R}'_{\mathrm{mn}} \cdot \boldsymbol{p}_{\mathrm{n}})/{\boldsymbol{R}'_{\mathrm{mn}}}^5\}, \tag{8}$$

where $\boldsymbol{p}_{\mathrm{i}}$ is the unit vector denoting the direction of the dipole of molecule m, $\boldsymbol{R}'_{\mathrm{mn}}$ is the relative position vector from the dipole m to the dipole n, and $R'_{\mathrm{mn}} = |\boldsymbol{R}'_{\mathrm{mn}}|$. The magnitude of the dipole-dipole interaction is taken as that $\mu/\varepsilon_0 = 0.05$.

The force constants for stretch, bend and twist of the molecular deformation, $\mathrm{K_s}$, $\mathrm{K_b}$, and $\mathrm{K_t}$ are taken as $5{\sigma_0}^{-2}$, 1.0 and 1.0, respectively, in units of $\varepsilon_0$. The system is composed of 512 molecules in the simulation box, whose size is $8.5\sigma_0$ in the $x$- and $y$-directions and $14.1\sigma_0$ in the $z$-direction. At each wall of the simulation box, the periodic boundary condition is applied.

First, the molecular positions were generated randomly in order that the molecules do not overlap each other in the simulation box at high temperature $T = 10$ (in the unit $\varepsilon/k_\mathrm{B}$, $k_\mathrm{B}$ is the Boltzmann constant), and relaxed over up to 100000 time steps. After that the temperature is reduced gradually to $T = 6$ during 300000 time steps. Then, by lowering the temperature in a similar manner step by step we study the behaviour of the system at various temperatures. The data are taken as averages over 1000 time steps at each temperature, as the variation of the state is not significant during this interval at each simulation.

The simulations are carried out for several molecular systems differing in the molecular bond angle, $\theta_0$, to study the effect of molecular shape. In addition, the position and direction of the dipole moment were also changed to study the effect of the polar group on the liquid crystal properties. The long axis, which is defined by the direction connecting the two centres of gravity of the constituent Gay-Berne particles, is taken as the Z-axis of the molecular coordinate system and molecular plane is in the XZ plane. The cases with values, $\theta_0 = 0^\circ$, $15^\circ$ and $30^\circ$, are studied. Several positions of the dipole moment attached to the molecule are chosen; the connecting point, a centre of gravity of the shorter Gay-Berne particle and the centre of the longer one. Two cases of the dipolar direction, along the Z and X axes, are studied.

## RESULTS

First, results of simulation at the system with $\theta_0 = 15^\circ$ and with dipole attached at the connecting point are explained. In Figure 2, snap shots projected on the $x$-$z$ plane of the system with dipole along the X axis are shown in isotropic phase ($T = 10$, (a)), nematic phase ($T = 3$, (b)) and smectic phase ($T = 0.2$, (c)).

Here the molecule is represented by a broken segment of a line, in which the portion of the light segment denotes the symmetry axis of the shorter Gay-Berne particle and the dark one is that of the longer Gay-Berne particle. The temperature dependences of the nematic order parameter $S(=\langle(3\cos^2\theta_i - 1)/2\rangle)$ with $\theta_\mathrm{i}$ the angle between director and i-th molecular symmetry axis, of biaxial one $S_b(= (3/2)\langle\sin^2\theta_i\cos^2\psi_i\rangle)$ with $\psi_\mathrm{i}$ the azimuthal angle, of the smectic order paramter $\sigma(=\langle(\cos(2\phi z_i'/d_0)(3\cos^2\theta_i - 1)/2\rangle)$ with $d_0$ the layer spacing and $z_\mathrm{i}'$ the coordinate of molecule i along the layer normal and of the magnitude of the polarisation $P(=\langle p_\mathrm{i}\rangle)$ are shown in Figure 3.

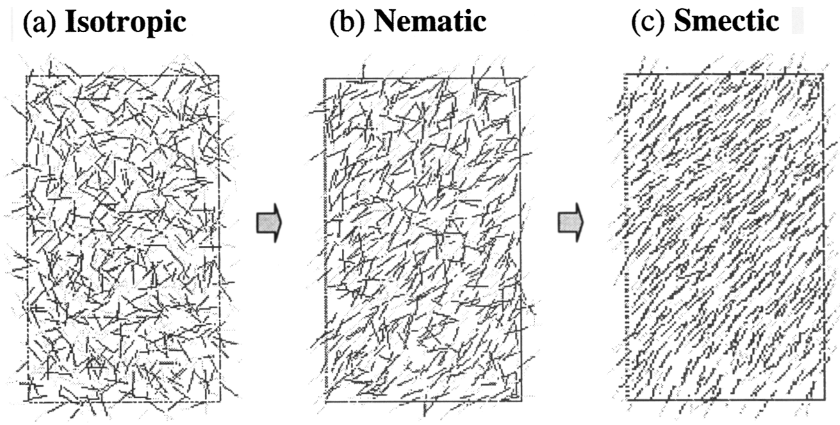

**FIGURE 2** Snap shots of the isotropic phase (a), nematic phase (b) and smectic phase (c).

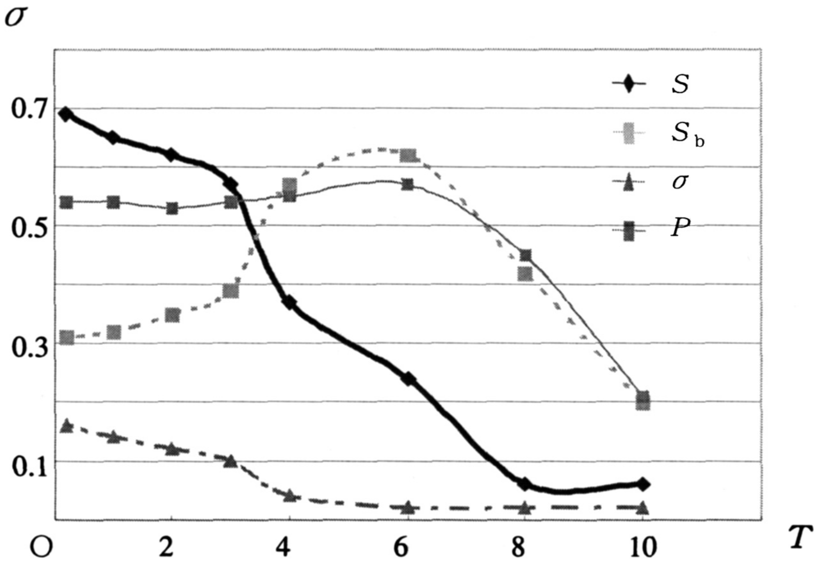

**FIGURE 3** Temperature dependences of the order parameters, where the dipole is attached at the connection point of X axis with $\theta_0 = 15^\circ$.

Two characteristic points should be noticed; (1) $S_b$ and $P$ appear even at high temperature, that is, the system shows biaxiality; (2) as the temperature is lowered, the nematic order S increases while $S_b$ decreases. These tendencies are observed commonly for systems with angles $\theta_0 = 0^\circ$

and 30°. Though the smectic order appears at the low temperature region, $\sigma$ is so small that a nematic-smectic phase transition temperature is not apparent.

In the system with the dipole along the Z axis, the temperature dependences of the order parameters are shown in Figure 4, where the clearing temperature is estimated as $T_c = 1.8$ which is compared to an estimate $T_c = 2.4$ in the case of the non-dipolar system [15]. Both the biaxial ordering and electric polarisation are quite small, at a fluctuation level in this case. Low smectic order appears also at the sufficiently low temperature region, in which the layer structure of smectic C type [6,7,13] is clearly observed in contrast with the case of the dipole along the X axis mentioned above where the layer ordering is of SmA type. Hence, the effect of the dipole along the Z axis is not so remarkable.

In the above simulations the dipole is attached at the connection point. In case the dipole is attached at the centre of gravity of the shorter constituent particle along the Z axis, an enhancement of nematic order due to the dipole has been reported [13]. Here, the simulation is carried out at the system with $\theta_0 = 15$, where the position of the dipole is changed to the centre of gravity of the shorter particle as this and the direction is in the X axis. The relations of the order paramters to the temperature

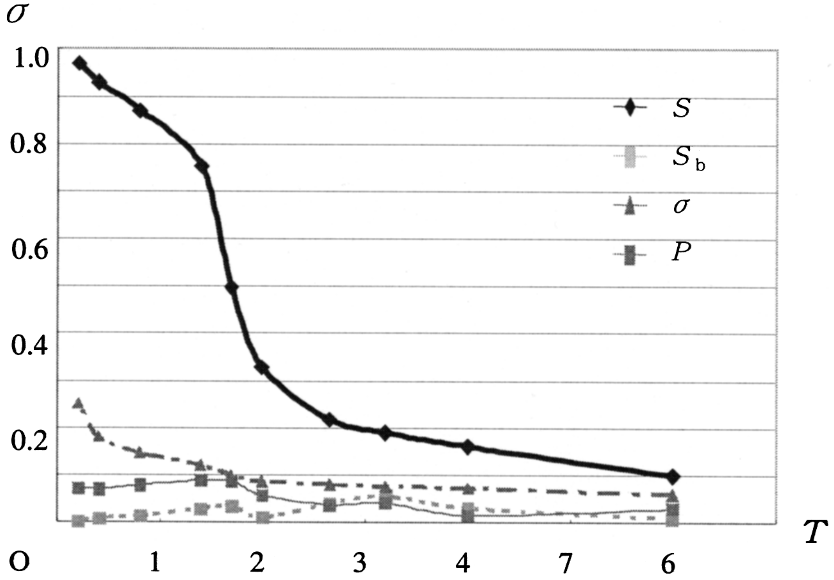

**FIGURE 4** Temperature dependences of order parameters, where the dipole is attached at the connection point in Z axis with $\theta_0 = 15°$.

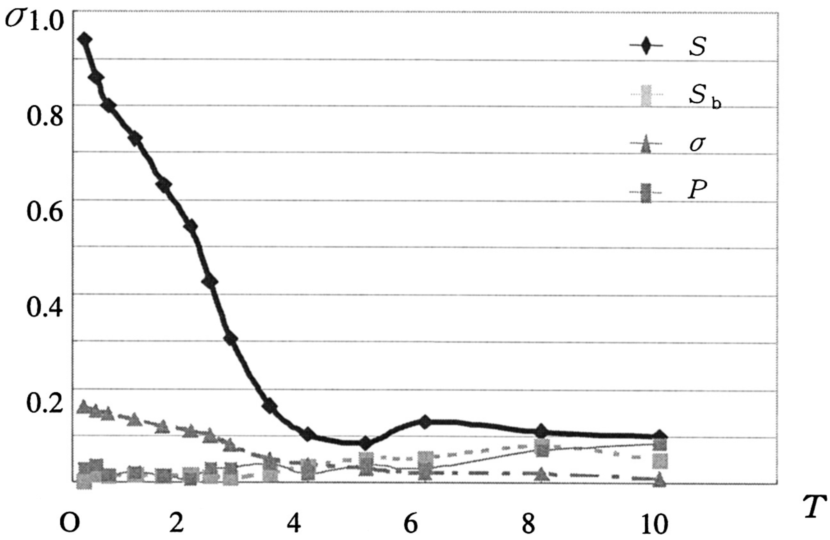

**FIGURE 5** Temperature dependences of the order parameters, where the dipole is attached at the centre of gravity of the shorter constituent particle along the X axis with $\theta_0 = 15°$.

are shown in Figure 5, in which $T_c$ is estimated to be 2.4, and neither the biaxiality nor the polarisation is observed.

These results are also similar for those in the case with zero dipole [15]. The simulation for the case with the dipole attached at the centre of gravity of the longer constituent particle shows similar behaviour to the above shorter case except for the enhancement of the nematic order, to some extent.

## SUMMARY

To elucidate the effect of the molecular shape and the dipole moment on the liquid crystalline ordering, NVT molecular dynamics simulation are carried out for a system of bent molecules which are dimers of two types of Gay-Berne particles coupled by a harmonic spring. The electric polarisation is observed exclusively for the system of molecules where the dipole is attached at the connection point along the X axis, while no sign of polarisation is deteted for any another case of combination of the position and direction. Biaxiality occurs accompanying the polarisation. The characteristic behaviour of biaxiality is noticed, where the biaxial order decreases as the temperature is lowered while the nematic order increases.

This relation seems to oppose the usual one where the biaxiality appears cooperatively to the nematic order for a system composed of long board-shaped molecules. The tendency observed in this simulation is considered to come from somthing like a frustration between the Gay-Berne potential and dipole-dipole interaction, which depends on the direction, and position of dipole at the molecule. In this respect, another type of combination of the position and direction of the dipole moment together with various strengths of dipole-dipole interaction should be tested systematically.

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