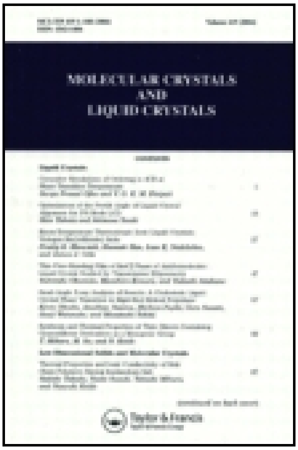

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# The Pair Intermolecular Interaction Energy of the Two Nematogenic Liquid Crystals

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# THE PAIR INTERMOLECULAR INTERACTION ENERGY OF THE TWO NEMATOGENIC LIQUID CRYSTALS

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Abstract. The dispersion term in the intermolecular potential calculated from the Rayleigh-Schrödinger perturbation theory exhibits the similar angle dependence as assumed by Maier-Saupe for the model system of MBBA.

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Intermolecular forces are essential for understanding the formation of long-range orientational order in nematogenic liquid crystals. A simple anisotropic pair potential used in molecular field theory is $U(r_{12}, \theta_{12}) = -U(r_{12})P_2(\cos\theta_{12})$, where U is scalar potential, $P_2(\cos\theta_{12})$ is second Legendre polynomial , $r_{12}$ and $\theta_{12}$ are the separation and the angle between molecules 1 and 2, respectively. It is worthwhile to examine whether an angular dependence of the anisotropic pair potential is actually valid or not by the calculation based on molecular orbital method.

In the present work we have calculated the interaction energies between selected model compounds of nematogenic liquid crystals, i.e., MBBA(N-(*p*-methoxybenzylidene)-*p*-butylaniline) and PPCHC(4′-pentyloxyphenyl *trans*-4-propylcyclohexanecarboxylate).

The intermolecular interaction energy is calculated by the method based on the Rayleigh-Schrödinger perturbation theory.[1,2,3] The interaction energy, $E_{int}$, is approximated by

$$E_{int} = E_{es} + E_{ind} + E_{dis} + E_{rep}$$

where $E_{es}$, $E_{ind}$, $E_{dis}$, and $E_{rep}$ are the electrostatic, the induction, the dispersion, and the valence repulsive energies, respectively. The electron net charges, the atomic dipoles, and the ionization potentials used in the calculation of the first three terms have been approximated by the CNDO/2 molecular orbital method.[4] The valence repulsive energy which is not included in the perturbation theory was estimated from the repulsive part of the Lennard-Jones(6-12) potential in which the coefficients of the repulsive terms were taken from Ref. 5. In the calculation of $E_{int}$, the geometry data of model MB for MBBA and model PP for PPCHC were taken from the standard parameters.[6]

Figure 1 shows the molecular formulae of MB and PP, and the coordinate system. The origins of the local coordinate systems for MB and PP were chosen at the midpoints of the C=N bond and the C-O bond, respectively.

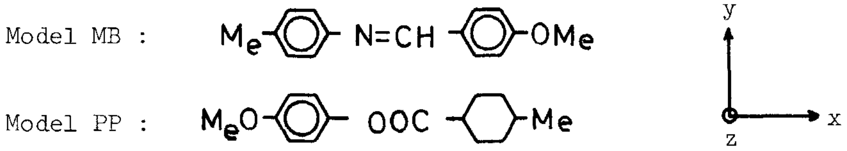

FIGURE 1. The molecular formulae of MB and PP.

The calculations of $E_{int}$ have been performed on the configurations of the $(MB)_2$ and the $(PP)_2$ systems obtained by the parallel separations of the second molecule with respect to the first one along the z-axis and then by clockwise rotations by the angle $\theta$ around the same z-axis in both the angles $\psi = 0^\circ$ and $\psi = 180^\circ$ around the same x-axis of this second molecule.

Figure 2 shows the dependences of $E_{int}$ on intermolecular distance, R, for $(MB)_2$ and $(PP)_2$ systems. The solid and dashed

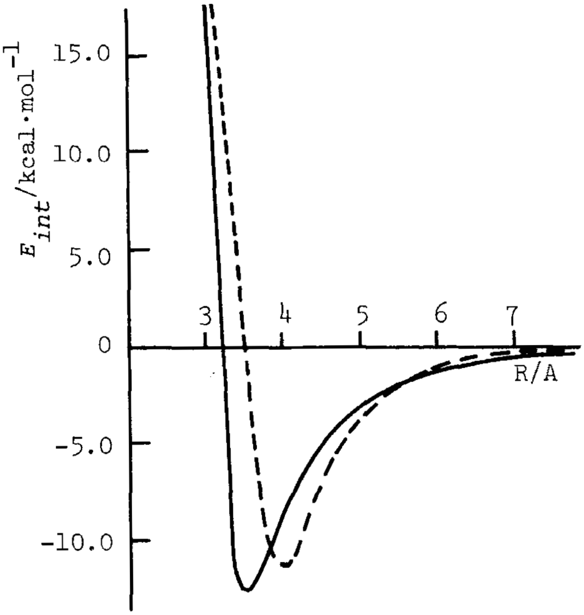

FIGURE 2. The dependences of $E_{int}$ on intermolecular distance. $(MB)_2$: ——— , $(PP)_2$: — — — —.

TABLE 1. The interaction energies and the $R_{min}$ of the $(MB)_2$ and the $(PP)_2$ systems.[a]

| System | θ | ψ | $E_{es}$ | $E_{ind}$ | $E_{dis}$ | $E_{rep}$ | $E_{int}$ | $R_{min}$ |
|---|---|---|---|---|---|---|---|---|
| $(MB)_2$ | 180° | 0° | 0.5 | -1.0 | -17.5 | 5.7 | -12.3 | 3.5 |
| $(PP)_2$ | 0° | 180° | 18.8 | -2.3 | -35.4 | 7.5 | -11.4 | 4.0 |

[a] The energies and the distances are given in kcal·mol$^{-1}$ and in Angstroms.

lines are $(MB)_2$ and $(PP)_2$ systems, respectively. In the figure, the angles $\theta$ and $\psi$ of the systems were fixed at the values of the energy minimum point through the parallel separations, that is, the second molecules of $(MB)_2$ and $(PP)_2$ systems were fixed at $\theta = 180^\circ$ and $\psi = 0^\circ$, $\theta = 0^\circ$ and $\psi = 180^\circ$, respectively. The value of $E_{int}$ in energy minimum for the $(MB)_2$ system is ca. 1.0 kcal·mol$^{-1}$ smaller than that of the $(PP)_2$. The value of R in energy minimum, $R_{min}$, of the $(MB)_2$ system is ca. 0.5A smaller than that of the $(PP)_2$. Table 1 lists the values of estimated $E_{es}$, $E_{ind}$, $E_{dis}$, $E_{rep}$, and $R_{min}$ in energy minimum for $(MB)_2$ and $(PP)_2$ systems. As apparently from the table, $E_{dis}$ shows the fairly large contribution on the attractive energy. This result is in agreement with the others.[2,3]

Figure 3 shows the $\theta$ angle dependences of $E_{dis}$ for $(MB)_2$ and $(PP)_2$ systems at the fixed $\psi$ and $R_{min}$ in energy minimum. The closed circles and triangles are the plots of $E_{dis}$ obtained from the calculation above mentioned as a function of the $\theta$ angles for $(MB)_2$ and $(PP)_2$, respectively. The solid lines in the figure show the $\theta$ angle dependences of $(3\cos^2\theta - 1)$ of the attractive potential proposed by Maier-Saupe.[7] The magnitude of $(3\cos^2\theta - 1)$ is normalized on that of $E_{dis}$ in each system. The $\theta$ angle dependence for the $(MB)_2$ system shown in Fig. 3 are good consistent with the solid line, however, the overall energy, $E_{int}$, did not show the angle dependence such as Fig. 3. On the other hand, the $\theta$ angle dependence for the $(PP)_2$ system deviates from the solid line over ca. $\theta = 90^\circ$. In the light of the above results, the $\theta$ angle dependence for the system of the MB molecule, which is like the hard rod with $C_2$ symmetry, is in accord with the Maier-Saupe theory.

The dependences of $E_{int}$ on horizontal displacement, $R_x$,

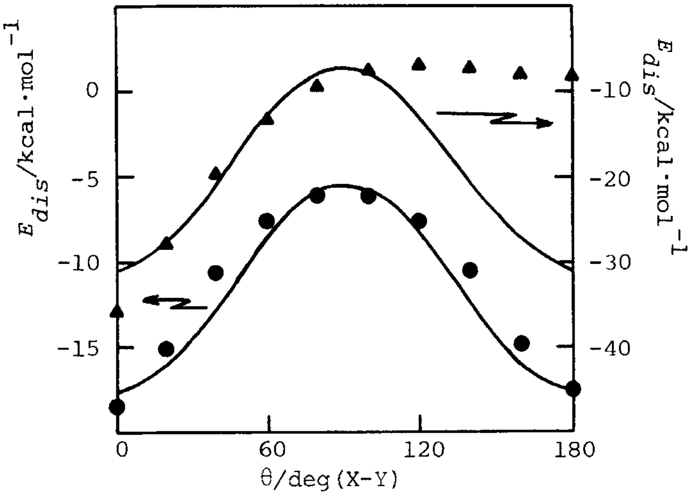

FIGURE 3. The θ angle dependences of $E_{dis}$. $(MB)_2$: ● , $(PP)_2$: ▲ .

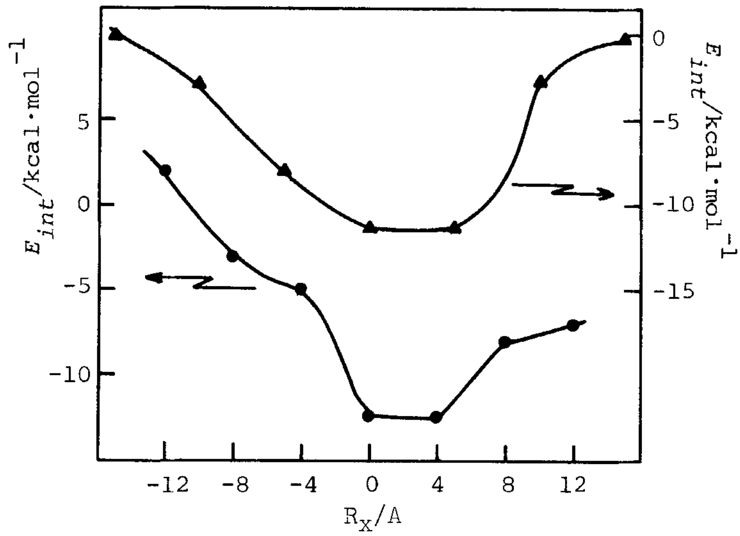

FIGURE 4. The dependences of $E_{int}$ on horizontal displacement. $(MB)_2$: ● , $(PP)_2$: ▲ .

for $(MB)_2$ and $(PP)_2$ systems are shown in Fig. 4, then $\theta$, $\psi$, and $R_{min}$ in each system were fixed at the values of the energy minimum. $R_x$ is the distance of the horizontal displacement of the second molecule of the systems with respect to the first one along the molecular axis, x-axis, of the local coordinate systems. As seen from the figure, the values of $E_{int}$ at the displacement from ca. 0 to +5A along the x-axis, which is about half lengths of the model molecules, do not effectively change in both the systems. Therefore, it may be considered that the second molecules easy transfer in the positive direction of the molecular axis.

Finally, these results obtained by the calculation will be essentially compared with the experimental ones such as the density, the order parameter, and etc. in the nematic state of liquid crystals. Further work on this problem is under way.

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