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# On the Role of the Quadrupole-quadrupole Interaction in the Molecular Arrangements in Crystalline Benzene

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It has been said that, in a typical aromatic crystal, quadrupole-quadrupole interaction makes only a negligible contribution to the lattice energy[1-3] and the equilibrium molecular orientation. On the other hand, Kihara[4-6] indicated, after using his molecular models, which simulate magnetically the electric multipoles of actual molecules, that the structure of a molecular crystal corresponds to a minimum of the electrostatic energy between the molecules when the molecules have simple shapes and sufficiently strong electric multipoles. We cannot, therefore, neglect the quadrupole-quadrupole interaction energy against the van der Waals dispersion energy, because only the relative smallness of the former against the latter does not generally justify the discarding of the former.

The crystal packing problem of benzene has been discussed by several authors[1-3,7-8] in terms of the intermolecular potential functions. These authors calculated the dependency of the potential energy of this crystal with respect to the class of the structural variation, in which the molecules are rotated in only small angles from the equilibrium structure, with a preservation of the space-group symmetry. They have obtained a successful explanation in terms of the van der Waals dispersion energy only. However, in principle, we must start to consider the molecular packing problem in two interacting molecules; we must calculate the most stable relative arrangement of the two molecules when the intermolecular distance is known, and then construct the whole crystal from this pair. This is related to the phenomena of condensation and crystallization.

## Calculation and Results

One of the two molecules is set on the point of the origin of the cartesian coordinate, while the position of the other is expressed by $P(\theta,\theta',\varphi,\varphi',\gamma,R)$, as is shown in Fig. 1.

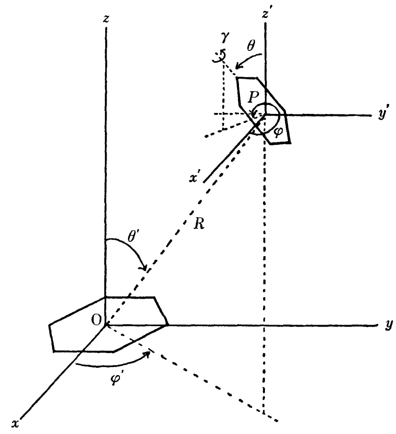

Fig. 1. Geometrical representation of two benzene molecules in interaction.

The intermolecular potential, $v(R)$, is expressed by the sum of the interatomic potentials, $v(r_j)$, as follows:

$$v(R) = \sum_j v(r_j) = \sum_j (b_j \exp(-c_j r_j) - a_j/r_j^6), \qquad (1)$$

where the summation, $j$, is extended to all pairs of atoms in the two molecules. The three parameters, $a_j$, $b_j$, and $c_j$, were derived from Bartell's function in a way fully described in the text (*cf.* Table 1).[9] A part of the potential energy surface obtained is indicated

Table 1. Parameter set

| | $a_j$ | $b_j$ | $c_j$ |
|---|---|---|---|
| C···C | 298.0 | $237.0\times10^3$ | 4.32 |
| C···H | 121.0 | $31.4\times10^3$ | 4.20 |
| H···H | 49.2 | $6.60\times10^3$ | 4.08 |

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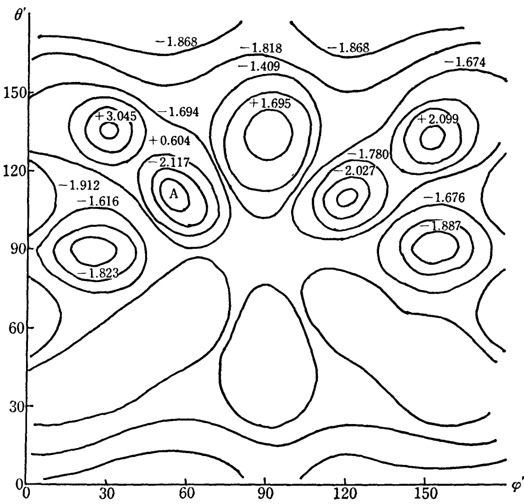

Fig. 2. θ'-φ' energy surface between two benzene molecules. The values in the figure are the minimum with regard to θ, φ, and γ and expressed in kcal/mol unit.

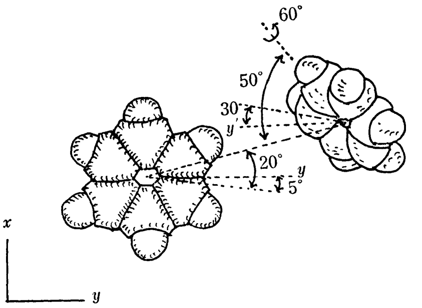

Fig. 3. The most stable orientation of two benzene molecules when $R$=5.13Å.

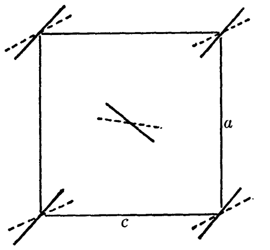

Fig. 4. Diagram of the crystal structure of benzene projected down the $b$-axis. —— : experimental; ······ our calculation.

in Fig. 2, where $R$ is set at 5.13 Å, the shortest intermolecular distance in the benzene crystal at −3°C. The relative molecular orientation corresponding to the $A$ position in Fig. 2 is indicated in Fig. 3. The corresponding packing in the crystal is indicated by the dashed line in Fig. 4. Thus, it can be observed in Fig. 4 that the molecular packing derived from the two molecules is not consistent with the experimental one, indicating that other types of intermolecular force are acting in addition to the van der Waals interaction.

There are two types of such intermolecular forces. One is the non-additive contribution to Eq. (1), but this is small because of the relatively higher symmetry of the benzene molecules.[10] The other is the quadrupole-quadrupole interaction. The benzene molecules have quadrupole moments[11] perpendicular to the molecular plane:

$$q_{//} = -(5.6\pm2.8)\times10^{-26}\ \mathrm{cm}^2\ \mathrm{e.s.u.}$$

The quadrupole-quadrupole interaction is expressed as follows:

$$\begin{aligned} Q_{ab} = 3qq'[&1-5(\cos^2\theta+\cos^2\theta')+17\cos^2\theta\cos^2\theta' \\ &+2\sin^2\theta\sin^2\theta'\cos^2(\varphi-\varphi') \\ &+16\sin\theta\sin\theta'\cos\theta\cos\theta'\cos(\varphi-\varphi')]/4R^5. \qquad (2) \end{aligned}$$

Here, the $q$'s are the observed quadrupole moments of the benzene molecule and the θ's and φ's are correlated to the θ's, φ's, and γ in Fig. 1.

The most favourable relative arrangement of two quadrupoles can easily be calculated to be the one in which the molecular planes make a 90° angle. This is almost entirely consistent with the experimental molecular arrangement in the crystal.[12]

Thus, it is necessary, in studying the molecular packing in the benzene crystal, to introduce the quadrupole-quadrupole interaction. The calculated quadrupole-quadrupole interaction energy is −0.95——0.86 kcal/mol at the equilibrium arrangement; this value is attractive.

All the numerical calculations in this paper were done at Computer Center of Tohoku University, using a NEAC 2200 model 700—500 Computer system.

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