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On the Factors Determining the Molecular Arrangement in Crystalline Ethylene

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The orientation-dependent potential energy of the ethylene crystal was calculated using a somewhat modified expression for the dispersion energy in the case of non-axially symmetric molecules. It was concluded that the main force which determines the angle between the *bc* plane and the C=C bond axis in the ethylene crystal is the dispersion; on the other hand, it is the quadrupole-quadrupole interaction which determines the angle between the *ab* plane and the C=C bond axis. The expected molecular arrangement in the crystalline ethylene belongs to the space group $P2_1/n$, this is consistent with the conclusion obtained from the spectroscopic data.

Kihara[1–4] has suggested, in his brilliant models, that the molecular arrangement in some molecular crystals depends upon the electrostatic multipole interactions. On the other hand, Craig *et al.*[5,6] concluded that, in the benzene and the naphthalene crystals, the molecular arrangement depends upon a minimization of intermolecular hydrogen-hydrogen repulsions rather than upon the quadrupole-quadrupole and the dispersion energies.

In a previous paper[7] (designated I henceforth), we have found that the electrostatic multipole, the intermolecular hydrogen-hydrogen repulsion, and even the dispersion interaction energies seem to play an important role in determining the molecular arrangement. There remain some ambiguities in determining the factor effective for the molecular arrangement in molecular crystals. Therefore, it is necessary to investigate other molecular crystals from this point of view.

In the present investigation we have studied the refinement of the crystal structure of ethylene, of which both spectroscopic[8–13] and theoretical investigations using the non-bonded atom-atom pair potentials[14] have already been made. We have calculated the orientation dependence of the lattice energy of the crystalline ethylene by means of the same method as before (see I).

It was concluded that the main force which determines the angle between the *bc* plane and the C=C bond axis in the ethylene crystal is the dispersion interaction; on the other hand, it is the quadrupole-quadrupole interaction which determines the angle between the *ab* plane and the C=C bond axis. These results obtained were then compared with the results obtained by the use of the Lennard-Jones-type non-bonded atom-atom interaction potential. All the numerical calculations were made at Computer Center of Tohoku University.

Theoretical

Dispersion Energy. Since the ethylene molecule has a non-axial symmetry, the expression (1) of the dispersion energy for axially-symmetric molecules must be modified:

$$\begin{aligned} W_{\text{disp}} = -[(A-2B+C)\{&\sin\theta\sin\theta'\cos(\phi-\phi') \\ &- 2\cos\theta\cos\theta'\}^2 + 3(B-C)(\cos^2\theta+\cos^2\theta') \\ &+ 2(B+2C)]/R^6, \end{aligned} \qquad (1)^{[15]}$$

where $A=e^2\alpha_{\parallel}(QM)_{\parallel}/4$, $B=e^2\alpha_{\parallel}\alpha_{\perp}(QM)_{\parallel}(QM)_{\perp}/2\alpha_{\parallel}(QM)_{\perp}+\alpha_{\perp}(QM)_{\parallel}$, and $C=e^2\alpha_{\perp}(QM)_{\perp}/4$. $(QM)_{\parallel}$ and $(QM)_{\perp}$ are the quantum mechanically-calculable averages (see I).

In the non-axially symmetrical ethylene molecule, the three components of the molecular polarizability are written in terms of α_x, α_y, and α_z in the cartesian coordinate, where α_z is along the C=C bond; α_y, along the molecular plane, and α_x, along the axis perpendicular to it. $\alpha_{\parallel}$ and $\alpha_{\perp}$ may be expressed as follows:

$$\alpha_{\parallel} = \alpha_z;\ \alpha_{\perp} = (\alpha_x\cos\beta+\alpha_y\sin\beta)/2. \qquad (2)$$

β is the angle of the rotation of the molecular plane around the C=C bond axis. In the same way, the modified (QM)'s may be written as follows:

$$\left.\begin{aligned} &(QM)_{\parallel} = (QM)_z; \\ &(QM)_{\perp} = \{(QM)_x\cos\beta+(QM)_y\sin\beta\}/2 \end{aligned}\right\} \qquad (3)$$

Then, A, B, and C in Eq. (1) are replaced by new α's and (QM)'s. Thus, Eq. (1) has ben modified to be applicable to the case of non-axial symmetry.

Other Interactions. Quadrupole-quadrupole, the non-additive three body, and the overlap repulsion interactions are treated in exactly the same way as in I. The quadrupole moment of the ethylene molecule used in the present work is $\pm 1\times 10^{-26}$ e.s.u., which was determined approximately by Smith.[16,17]

The Axilrod and Teller expression for three-body interaction must be modified before it can be applied

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to the anisotropic molecule. This was done by Stogryn,[18] but the numerically-calculable form was not given there. This will be published elsewhere by the present authors in this series of investigations. At this time, therefore, we will content ourselves with discussing its order of magnitude.

Numerical Calculation

In Table 1, the calculated values of the (QM)'s and α's are indicated. The (QM)'s were calculated as usual (see I), while the α's were calculated by using bond polarizabilities[19].

Table 1. The anisotropies of quantum mechanically calculable average and polarizability of ethylene molecule. The C=C bond axis is along the z-axis

	(QM) a.u.	α cm^3
x	23.882	39.6×10^{-25}
y	18.560	33.8×10^{-25}
z	26.270	54.4×10^{-25}

We start from the structure determined by Bunn.[20] Consider three kinds of molecular rotation. The first is the deflection of the C=C bond axis from the *ab* plane, the second is the deflection of the molecular plane from the *bc* plane, and the last is the rotation of the molecular plane around C=C bond axis. These angles of rotations are indicated in terms of δ, γ, and β respectively (see Fig. 1). In Fig. 1, there are indicated the twelve first neighbour molecules. They are between 4.5 and 6.5 Å away from the central molecule, O. The second neighbours are between 7.4 and 12.9; the third, between 11.1 and 19.4; the fourth, between 15.0 and 25.8, and the fifth, between 19.1 and 32.3 Å, away from the O molecule. We calculated the dispersion and quadrupole-quadrupole interaction energy for the molecules up to fifth neighbours, but the repulsion energy for the first neighbours only.

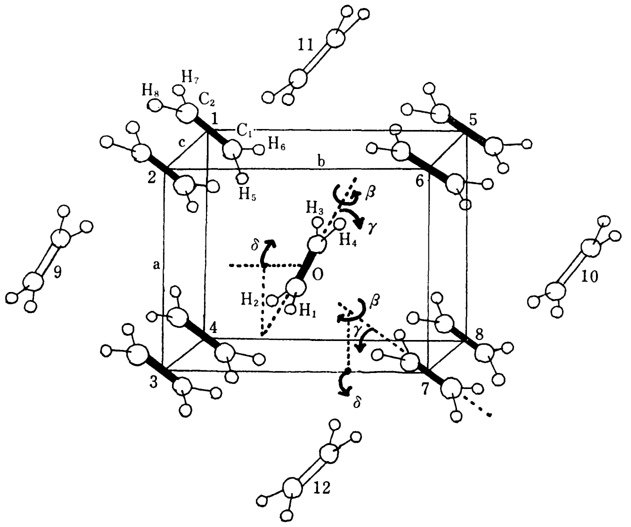

Fig. 1. The starting positions of carbon and hydrogen atoms in crystalline ethylene.
○…carbon atoms; ∘…hydrogens. a=4.89Å, b=6.46Å, and c=4.14Å.

Results and Discussion

Figure 2 indicates the β-dependency of the interaction energies when δ and γ are fixed at the values of Bunn's structure. The arrows show the values of β, which correspond to Bunn's structure and the spectroscopic structure.[13] From Fig. 2 it may be concluded that the factor determining the molecular orientation around the C=C bond axis is mainly the minimization of the dispersion energy. This confirms the non-axial symmetry of the polarizability of the ethylene molecule about the C=C bond axis.

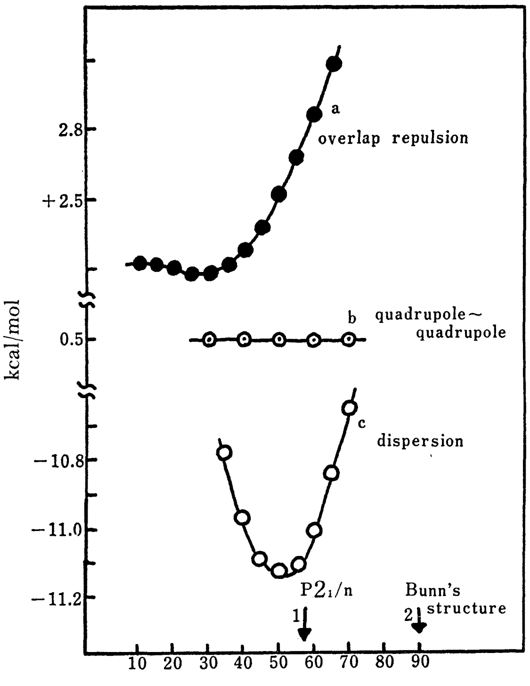

Fig. 2. Variations of interaction energies with the angle of rotation around the C=C bond axis.
a: overlap repulsion; b: quadrupole-quadrupole; c: dispersion interaction.
The arrows 1 and 2 indicate the values correspond to the spectroscopic and Bunn's structures, respectively.

Fixing the β value at the value indicated in Fig. 2, we calculated the δ- and γ-dependencies. The results are indicated in Fig. 3 and 4 respectively. The arrows in these figures also have the same meaning as in Fig. 2. It may be concluded from Fig. 3 that the dispersion interaction mainly determines the angle between the molecular plane and the *bc* plane. We have concluded from Fig. 4 that the angle between the C=C bond axis and the *ab* plane is mainly determined by the quadrupole-quadrupole interactions.

The above conclusions are also confirmed from another point of view. If we approximate the mo-

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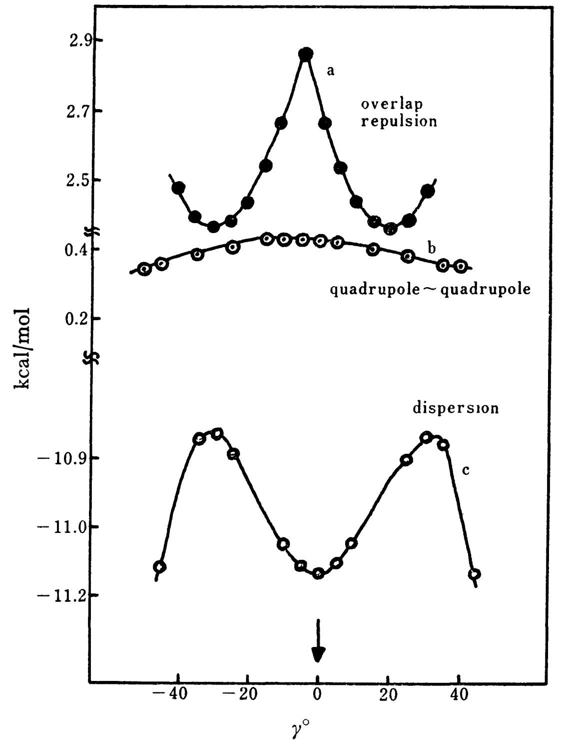

Fig. 3. Variations of interaction energies with the angle of deflection from *bc* plane.
a: overlap repulsion; b: quadrupole-quadrupole; c: dispersion interaction.

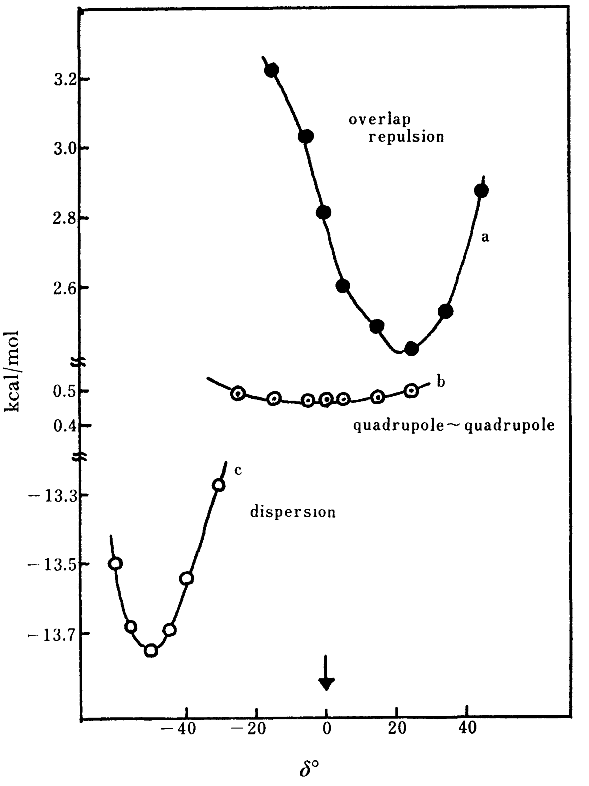

Fig. 4. Variation of interaction energies with the angle of deflection from *ab* plane.
a: overlap repulsion; b: quadrupole-quadrupole; c: dispersion interaction

lecular interaction by the non-bonded atom-atom interaction of the type of Lennard-Jones,

$$v(r) = \sum_j (b_j/r_j^{12} - a_j/r_j^{6}), \tag{4}$$

where the parameters, a_j and b_j, have been chosen[21] so as to give the best fit with second virial coefficient data of methane. The j summation is extended to all pairs of atoms in the two molecules. Equation (4) is further summed up to fifth neighbours in the crystal.

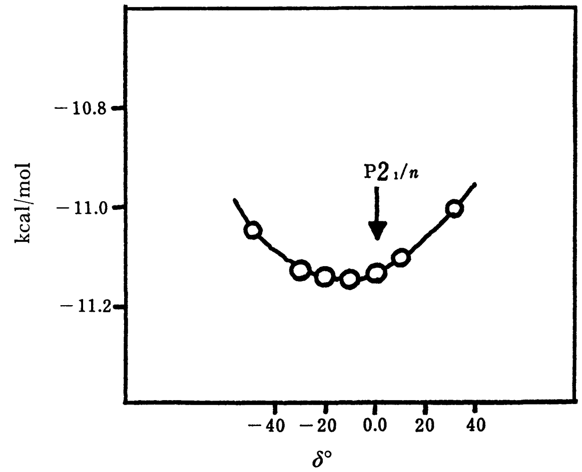

Fig. 5. Variation of Lennard-Jones interaction energy with the angle of deflection from *ab* plane.

Figure 5 indicates the δ-dependency of the $v(r)$. Since the deviation of δ from the experimental value is found to be about 10°, the interaction expressed by Eq. (4) can not explain the experimental δ value. Therefore, quadrupole-quadrupole interaction is necessary to explain the experimental δ value.

It can be concluded from the above results that the main force which determines the angle between the *bc* plane and the C=C bond axis in the ethylene crystal is the dispersion interaction; on the other hand, it is the quadrupole-quadrupole interaction which determines the angle between the *ab* plane and the C=C bond axis. It can also be concluded that the molecular orientation around the C=C bond axis is mainly determined by the dispersion interaction and that the angle of rotation around the C=C axis is nearly equal to the experimental one. This structure belongs to the $P2_1/n$ space group.

The role of the three-body interaction, which is estimated to be of the order of 0.2 kcal/mol if the ethylene molecule has spherical symmetry and which is too large to be neglected, may be important, since it is perhaps strongly orientation-dependent in such anisotropic molecules as ethylene. However, a good estimate of the accuracy of three-body interaction for asymmetric molecules is difficult to make at the present time and must remain a problem for the future.

The authors wish to thank Dr. Masamoto Iwaizumi for his helpful discussions.

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