

## Molecular Shape and Structure of Regular Molecular Assemblies. II. The Geometrical Conditions for Two Dimensional Packings of the Elliptic Molecule

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The structure of two dimensional regular arrangement, namely crystal, of elliptic molecules in relation to their shape is discussed. Although lattice constants can be expressed as the functions of the elliptic parameters, they are not unequivocal unless the contact (or binding) sites on the ellipse are determined. The maximum and minimum area of the unit cell is, on the other hand, uniquely determined from the shape of the ellipse, and corresponding porosities are calculated to be 21.5 % and 9.31 % respectively. In both cases minimum value of lattice angle is  $90^\circ$ ; hence structure is exclusively determined as rectangular lattice.

### INTRODUCTION

It is intuitively understandable that the structure of a molecular assembly — one of the typical example is crystal — is determined by the shape of molecules and interacting forces among them. Few attempts have been made, nevertheless, to elucidate the relation between the structure of the assemblies and properties of the molecules; to make clear the influence of the molecular shape and intermolecular forces on the structure is by no means an easy task.

Only two series of works seem to trend to the approach of this problem. Niggli<sup>1,2)</sup> studied, for the first time, the relation between the number and positions of the bonding (or contact) sites of circles, and the structures of the two dimensional lattices. Another way of approach was made by Kihara<sup>3-6)</sup> who, by the use of molecular models, explained known and conjectured unknown crystal symmetry of simple molecular crystals. The method is conspicuous by the introduction of electric multipolar interactions as well as the molecular shape. Both methods, however, gave no quantitative geometrical relations between molecular shape and crystal structure.

In the preceding paper<sup>7)</sup>, as the simplest case of the relation between molecular shape and the structure (and form) of the regular molecular assemblies, the radius of a ring consisted of the identical ellipses was given as the function of the number of component ellipses, lengths of the ellipsoidal axes and the positions of the bonding sites. In the present paper the geometrical conditions for two dimensional array of elliptic molecules with the same orientation will be discussed under an assumption that the unit cell contains only one molecule.

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**THEORETICAL**

**General Expression**

The origin, O, of the coordinate axes is at the center of an ellipse, say  $E_0$ , and x- and y-axes coincide with semiaxes a and b of the ellipse, respectively. Let the coordinates of the centers,  $P_1$  and  $P_2$ , of  $E_1$  and  $E_2$ , two of the ellipses in contact with  $E_0$ , be  $P_1(A_1, B_1)$  and  $P_2(A_2, B_2)$  or  $P_1(a_0, \theta_1)$  and  $P_2(b_0, \theta_2)$  in the polar coordinates, respectively. Let the two primitive translational vectors of the unit cell of the two dimensional array be  $a_0 = \vec{OP}_1$  and  $b_0 = \vec{OP}_2$ . These circumstances should be easily understood from Fig. 1.

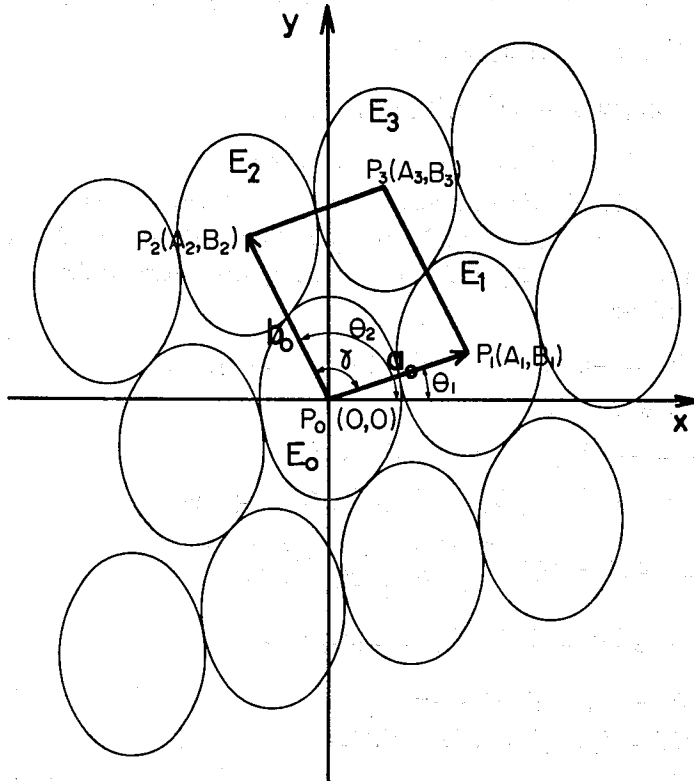


Fig. 1. Four nearest neighbor packing of ellipses.

Using the expressions of the ellipses,

$$\frac{(X-A_i)^2}{a^2} + \frac{(y-B_i)^2}{b^2} = 1, \quad i=1 \text{ and } 2 \quad (1)$$

and the conditions that  $E_i$ 's are in contact with  $E_0$

$$\frac{A_i^2}{4a^2} + \frac{B_i^2}{4b^2} = 1, \quad (2)$$

we obtain the following results:

$$A_i = \delta_i 2ab/D_i \quad \text{and} \quad B_i = \delta_i 2ab\theta_i/D_i \quad (3)$$

$$\text{with} \quad \begin{cases} \theta_i = \tan^{-1} a/b & \text{and} \quad D_i = \sqrt{b^2 + a^2\theta_i^2} \\ \delta_1 = 1 & \text{and} \quad \delta_2 = \begin{cases} 1 & \text{for } 0 < \theta_2 \leq \pi/2 \\ -1 & \text{for } \pi/2 < \theta_2 \leq \pi, \end{cases} \end{cases} \quad (4)$$

where we assumed without loss of generality that  $0 < \theta_1 \leq \pi/2$ ,  $0 < \theta_2 \leq \pi$  and  $\theta_1 < \theta_2$ . Hence the lattice constants are given by

$$a_0 = 2ab\sqrt{1 + \theta_1^2}/D_1 \quad \text{and} \quad b_0 = 2ab\sqrt{1 + \theta_2^2}/D_2 \quad (6)$$

$$\gamma = \theta_2 - \theta_1 \quad \text{and} \quad \cos \gamma = \delta_2(1 + \theta_1\theta_2)/\sqrt{(1 + \theta_1^2)(1 + \theta_2^2)}. \quad (7)$$

The area  $S$  of the unit cell is given by

$$S = a_0 b_0 \sin \gamma = 4a^2 b^2 \delta_2 (\theta_2 - \theta_1) / D_1 D_2. \quad (8)$$

### Maximum Unit Cell Area — Loose Packing

We now consider the dependence of area of unit cell and other parameters on  $\theta$ . Differentiating equation (8) with respect to  $\theta_1$  and  $\theta_2$ , we get the condition for the maximum  $S$ , its value  $S'$ , and other necessary quantities under an assumption that  $b \geq a$ , as follows:

$$\theta_1 \theta_2' = -b^2/a^2 \quad (\because \theta_2' < 0 \text{ or } \pi/2 < \theta_2 \leq \pi) \quad (9)$$

$$S' = 4ab \quad (10)$$

$$A_2' = -2a^2\theta_1/D_1 \quad \text{and} \quad B_2' = 2b^2/D_2 \quad (11)$$

$$a_0 = 2ab\sqrt{1 + \theta_1^2}/D_1 \quad \text{and} \quad b_0' = 2\sqrt{b^4 + a^4\theta_1^2}/D_1 \quad (12)$$

$$0 \leq \cos \gamma' = \frac{(b^2 - a^2)\theta_1}{\sqrt{(1 + \theta_1^2)(b^4 + a^4\theta_1^2)}} \leq \frac{b^2 - a^2}{a^2 + b^2}. \quad (13)$$

The center,  $P_3(A_3, B_3)$ , of  $E_3$  in Fig. 1 is given by

$$\begin{cases} A_3' = A_1 + A_2' = 2a(b - a\theta_1)/D_1 \\ B_3' = B_1 + B_2' = 2b(b + a\theta_1)/D_1. \end{cases} \quad (14)$$

They are found to satisfy the relation

$$\frac{A_3'^2}{8a^2} + \frac{B_3'^2}{8b^2} = 1. \quad (15)$$

Comparing this equation with Eq. (2), we see that  $E_3$  is not in contact with  $E_0$  as shown in Fig. 1. Thus we have the four nearest neighbor packing. The condition for the maximum value of  $\cos \gamma'$  (minimum  $\gamma'$ ) in Eq. (13) is obtained by differentiating  $\cos \gamma'$  with respect to  $\theta_1$  and it is

$$\theta_1 = -\theta_2' = b/a. \quad (16)$$

This result leads to the centered rectangular lattice.

**Minimum Unit Cell Area — Close Packing**

On the other hand, if  $\gamma$  becomes smaller (larger) than  $\gamma'$ ,  $E_2(E_3)$  approaches  $E_1(E_0)$  and finally comes in contact with  $E_1(E_0)$ , as shown in Fig. 2. In this case,

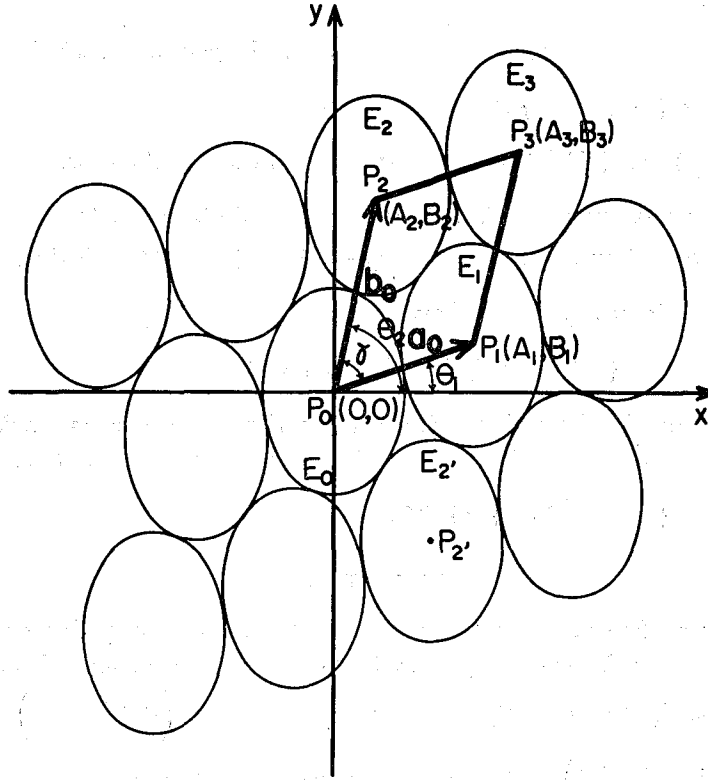


Fig. 2. Six nearest neighbor packing of ellipses.

we have the minimum  $S$ , the closest packing, and the six nearest neighbor packing. The necessary quantities in this case are calculated as follows:

$$\theta_2'' = b(\sqrt{3}b + a\theta_1)/a(b - \sqrt{3}a\theta_1) \tag{17}$$

$$S'' = 2\sqrt{3}ab \tag{18}$$

$$A_2'' = a(b - \sqrt{3}a\theta_1)/D_1 \quad \text{and} \quad B_2'' = b(\sqrt{3}b + a\theta_1)/D_1 \tag{19}$$

$$a_0 = 2ab\sqrt{1 + \theta_1^2}/D_1$$

$$\text{and } b_0'' = \sqrt{a^2(b - \sqrt{3}a\theta_1)^2 + b^2(\sqrt{3}b + a\theta_1)^2}/D_1 \tag{20}$$

$$0 < \cos \gamma'' = \frac{a(b - \sqrt{3}a\theta_1) + b(\sqrt{3}b + a\theta_1)\theta_1}{\sqrt{(1 + \theta_1^2)\{a^2(b - \sqrt{3}a\theta_1)^2 + b^2(\sqrt{3}b + a\theta_1)^2\}}} \leq \frac{3b^2 - a^2}{3b^2 + a^2} \tag{21}$$

The condition for the maximum value of  $\cos \gamma''$  (minimum  $\gamma''$ ) in this case is

$$\theta_1 = -\theta_2'' = \frac{\sqrt{3}b}{a}. \quad (22)$$

This structure has the centered rectangular lattice.

### Porosity

One of the important geometrical quantities is the porosity,  $e$ , which is defined as

$$e = \{1 - (\pi ab/S)\} \times 100\%. \quad (23)$$

From Eqs. (10) and (18), we have, regardless of the shape of ellipse,

$$\begin{aligned} \text{the maximum porosity: } e' &= (1 - \pi/4) \times 100\% = 21.5\% \\ \text{the minimum porosity: } e'' &= (1 - \pi/2\sqrt{3}) \times 100\% = 9.31\% \end{aligned} \quad (24)$$

and in general, from Eq. (8), we have

$$e = [1 - \{\pi D_1 D_2 / 4ab \delta_2 (\theta_2 - \theta_1)\}] \times 100\%. \quad (25)$$

The structure can be determined from porosity if  $a=b$  *i.e.* disk molecule. In this particular case, we may restrict  $\gamma$  within the range  $\pi/3 < \gamma \leq \pi/2$  and hence we have

$$e = \{1 - (\pi/4 \sin \gamma)\} \times 100\%. \quad (26)$$

### DISCUSSIONS

We now confine ourselves the discussions to the two interesting cases, namely loose and close packings. Ellipse itself has a symmetry of  $mm$ . Therefore, the bonding sites,  $C_i$ , on the ellipse should be given as  $C_i(\pm \frac{A_i}{2}, \pm \frac{B_i}{2})$  — and also  $C_3(\pm \frac{A_2 - A_1}{2}, \pm \frac{B_2 - B_1}{2})$  in the case of six nearest neighbor packing. The arrangement of the ellipse and lattice constants are uniquely determined from the positions of bonding sites if the elliptic parameters are fixed, or *vice versa*. We can obtain  $\theta_1$  from the coordinates of bonding sites. As we see in Eqs. (12) and (13), or (20) and (21), lattice constants  $a_0$ ,  $b_0$ , and  $\gamma$  are functions of single argument  $\theta_1$ . In contrast to these, the area of the unit cell and porosity are independent of  $\theta_1$ , or more properly bonding sites. They are determined solely by the shape of ellipse.

For the consideration of the arrangement of molecules, we must take not only the symmetry of the molecular shape but also the symmetry of the bonding sites into account. Ellipse cannot be arranged in the same orientation if the bonding sites are dissymmetrically distributed. To align the ellipse, which has the  $mm$  symmetry, bonding sites should be so located as to include the 2-fold or inverse symmetry. On the other hand nonsymmetrical molecules such as biological macromolecules can also arrange in the same orientation with the proper combination of shape and bonding sites. The fact that the existing biological molecular assemblies are in most case unidirectionally oriented, would suggest some simple integrating mechanism.

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**REFERENCES**

- (1) P. Niggli, *Zeit. f. Krist.*, **65**, 391 (1927).
- (2) *idem.*, *ibid.*, **68**, 404 (1928).
- (3) T. Kihara, *Acta Cryst.*, **16**, 1119 (1963).
- (4) *idem.*, *ibid.*, **21**, 877 (1966).
- (5) *idem.*, *ibid.*, **A26**, 315 (1970).
- (6) *idem.*, *ibid.*, **A31**, 718 (1975).
- (7) Yuzuru Hiragi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 584 (1972).