Bull. Inst. Chem. Res., Kyoto Univ., Vol. 50, No. 5, 1972

Molecules and Structure of Regular Molecular Assembies. I. Ring Forming Ellipse

Yuzuru HIRAGI*

Received August 21, 1972

For the elucidation of the relation between characters of molecules such as shapes and positions of the bonding sites, and the structure of their regular assemblies, a ring composed of identical ellipse was investigated as the simplest case. It was shown that the radius of ring and the number of the constituent ellipse were dependent on the length of the major and minor axes, and the position of the bonding site of the ellipse.

INTRODUCTION

Under a suitable condition, most of molecules as well as ions and atoms aggregate together forming the regular molecular assemblies. The most typical example is crystal; other types of assemblies are often observed among biological systems where biological macromolecules are heaped up into regular structures after the manner somewhat different from the ordinary crystals and compose the biological entities or organellas. Plant viruses such as tobacco mosaic virus, spherical viruses such as polyovirus, organellas such as bacterial flagella or microtubules in sperms, muscles, subunit containing enzymes and biological membranes are examples of these assemblies.

Although not yet adequately established, it seems that the structures of these biological systems would closely relate to their functions. Study of the mechanisms defining the structure would, therefore, more helpful for the understanding of the relation of the structure to the functions. What is that define the structure of the assemblies? For the simple ionic crystals such as NaCl, CsCl and ZnS (sphalelite) type crystals, the structures are defined by the ratio of ionic radii of anion to cation.[1] Even for the rather complex crystals such as nitrate of alkali metals or carbonate of alkali earth metals, the ratio of ionic radii plays the important role for the composition of the crystal structures,[2] although reason is still unexplained.

In the case of the assemblies of macromolecules, it is very difficult to explain clearly the influence of the properties of molecules on the structure of assemblies. Nevertheless, it is doubtless that the characters of the molecules such as the length and direction of the bonds, shape of the molecules, and the distribution of charge in the molecules govern the structure.

Little effort has been made to elucidate the relation between the structure of the assemblies and characters of the molecules. One of a very few trial was reported by Niggli[3,4] who first investigated the relation between the number and positions of the bonding site of circle molecule, and the structure of the two dimensional lattice of these

* 柊　弓絃: Laboratory of Physical Chemistry of Enzymes, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

molecules. However, there has not yet been the trial to connect the parameters expressing the properties of molecules to structure parameters such as lattice constants. As the first step for the trial, a simplest case including the relation between the ring composed of the elliptic molecules and the constituent ellipse will be discussed in the present paper.

THEORETICAL

General Expression

Let a point 0 be a point in a closed plane curve expressed by the position vector $\boldsymbol{X}=x\boldsymbol{e}_1+y\boldsymbol{e}_2$ and origin of the coordinates be at 0. If the curve $\boldsymbol{X}$ together with 0 is so moved as to be 0 on the another curve $\boldsymbol{R}=x_R\boldsymbol{e}_1+y_R\boldsymbol{e}_2$, the curve will be expressed by $\boldsymbol{X}+\boldsymbol{R}$ instead of $\boldsymbol{X}$. Rotate the closed curve counter-colckwise about the translated point 0′ by α and denote this $\boldsymbol{X}'=x'\boldsymbol{e}_1+y'\boldsymbol{e}_2$ (see Fig. 1). Then $\boldsymbol{X}'$ is given as

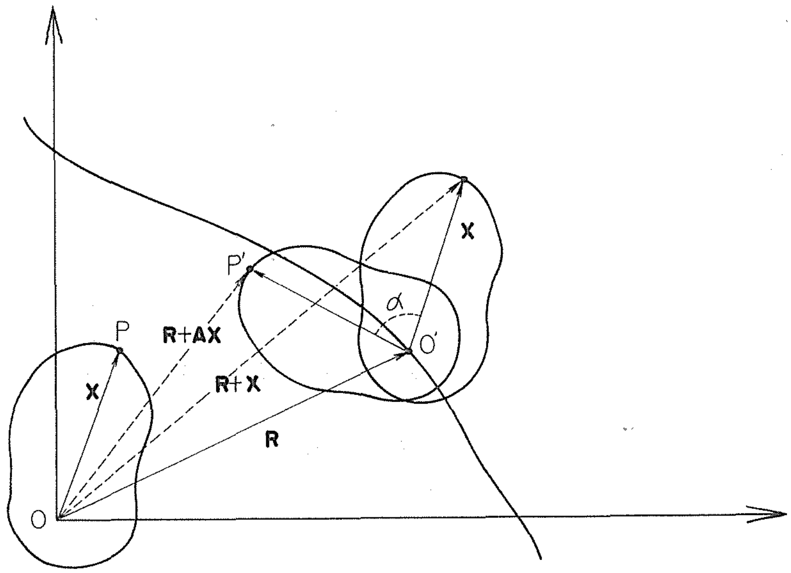

Fig 1. Closed curve at origin and those on the another curve $\boldsymbol{R}$.

$$\boldsymbol{X}'=\boldsymbol{R}+\boldsymbol{A}\boldsymbol{X}, \tag{1}$$

where

$$\boldsymbol{A}=\begin{pmatrix}\cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha\end{pmatrix}. \tag{2}$$

Ellipse on Ring

We now consider such case that $\boldsymbol{X}$ is an ellipse whose center at origin and is moved by R to the positive direction along x axis and revolved counterclockwise about the origin by Θ (see Fig. 2).

Let now $\boldsymbol{R}$ be a ring of radius R and $\boldsymbol{X}'$ a ellipse of center on the ring. Then we can fully express the above system in Eq. (1), if we make $\alpha=\Theta$ with which $\boldsymbol{R}$ is

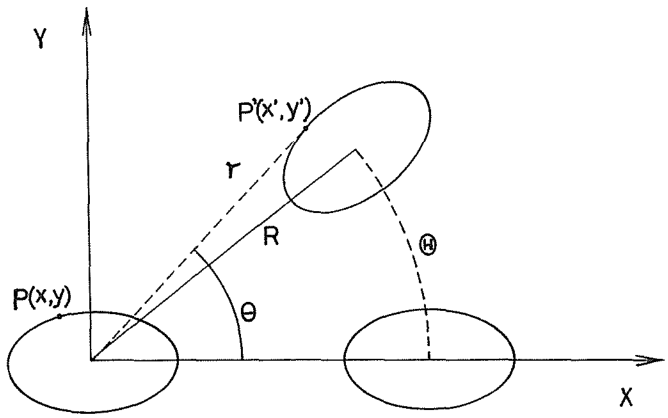

Fig. 2. Ellipse after moved by R along x axis and revolved about the origin by Θ.

exprssed in polar co-ordinate system as

$$\boldsymbol{R}=\begin{pmatrix} x_R \\ y_R \end{pmatrix} = \begin{pmatrix} R\cos\Theta \\ R\sin\Theta \end{pmatrix}. \tag{3}$$

Accordingly

$$\boldsymbol{A}=\begin{pmatrix} \cos\Theta & -\sin\Theta \\ \sin\Theta & \cos\Theta \end{pmatrix}. \tag{4}$$

In general, the closed curves are not given in the form of the function of (x', y') but by that of $(x\ y)$. For expressing $\boldsymbol{X}'$ by the function of (x', y') and (x_R, y_R), therefore, it is necessary to express (x, y) with $(x'\ y')$ and (x_R, y_R). Rewriting Eq. (1), we obtain

$$\boldsymbol{X}=\boldsymbol{A}^{-1}(\boldsymbol{X}'-\boldsymbol{R}), \tag{5}$$

where $\boldsymbol{A}^{-1}$ is the inverse matrix of $\boldsymbol{A}$ and presently

$$\boldsymbol{A}^{-1}=\begin{pmatrix} \cos\Theta & \sin\Theta \\ -\sin\Theta & \cos\Theta \end{pmatrix}. \tag{6}$$

If we represent a point on the ellipse $\boldsymbol{X}'$ in polar co-ordinates as

$$\boldsymbol{X}'=\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} r\cos\theta \\ r\sin\theta \end{pmatrix}, \tag{7}$$

we can express the rectangular co-ordinates of $\boldsymbol{X}$ with r, θ, R and Θ by substituting Eqs. (3), (6) and (7) into Eq. (5). Then we obtain,

$$\begin{cases} x=r\cos(\theta-\Theta)-R \\ y=r\sin(\theta-\Theta) \end{cases}. \tag{8}$$

As the ellipes $\boldsymbol{X}$ is expressed by the following equation:

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}=1, \tag{9}$$

we can express the ellipse X' as

$$\frac{\{r\cos(\theta-\Theta)-R\}^2}{a^2}+\frac{\{r\sin(\theta-\Theta)\}^2}{b^2}=1. \tag{10}$$

Ellipses Arranged in Ring

Let us now consider where n ellipses are so arranged that they compose a ring of radius R* (see Fig. 3).

We easily obtain that the value of Θ, which is the co-ordinate of the center of the ellipes, of the i th ellipse from that of on X axis is $\frac{2(i-1)}{n}\pi$, where i is $n \geqq i \geqq 1$. In this circumstance, each ellipse must contact with both side of neighbours. The contact point with i th and $i+1$ th ellipse will be given by solving the following simultaneous equations:

$$\begin{cases} \dfrac{\left\{r\cos\left(\theta-\dfrac{2(i-1)}{n}\pi\right)-R\right\}^2}{a^2}+\dfrac{\left\{r\sin\left(\theta-\dfrac{2(i-1)}{n}\pi\right)\right\}^2}{b^2}=1, \\ \dfrac{\left\{r\cos\left(\theta-\dfrac{2i}{n}\pi\right)-R\right\}^2}{a^2}+\dfrac{\left\{r\sin\left(\theta-\dfrac{2i}{n}\pi\right)\right\}^2}{b^2}=1. \end{cases} \tag{11}$$

Both equations are satisfied at $\theta=\frac{2i-1}{n}\pi$, indicating the co-ordinate of θ at contact point. Substituting this value into Eq. (11), we obtain

$$\frac{\left(r\cos\frac{1}{n}\pi-R\right)^2}{a^2}+\frac{\left(r\sin\frac{1}{n}\pi\right)^2}{b^2}=1. \tag{12}$$

Since each ellipse contact with its neighbour the two root of Eq. (7) should be the same. Therefore the discriminant of Eq. (12) should be zero.
Namely,

$$D=b^4R^2\cos^2\frac{1}{n}\pi-\left(a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi\right)b^2(R^2-a^2)=0, \tag{13}$$

therefore

$$R^2=\frac{a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi}{\sin^2\frac{1}{n}\pi}. \tag{14}$$

As R is positive,

$$R=\frac{\sqrt{a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi}}{\sin\frac{1}{n}\pi}. \tag{15}$$

Substituting Eq. (15) into Eq. (12) we obtain the radius of contact point r_c.
Namely,

$$r_c=\frac{b^2\cot\frac{1}{n}\pi}{\sqrt{a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi}}. \tag{16}$$

* The distance from origin to the center of the ellipses.

Since n should not be less than 2 for making a ring, $\sin\frac{1}{n}\pi$ and $\cot\frac{1}{n}\pi$ should have positive value. Therefore both R and r_c are also positive.

Thus we can express the radius of the ring, R and the co-ordinats of contact points of the ellipses, r_c and θ with a, b and n. In other words, radius of ring and the co-ordinates of contact points are defined by the shape and number of constituent ellipse.

As the i th ellipse contact with both $(i-1)$ th and $(i+1)$ th ellipses, the co-ordinates of the two contact points should be $\left(r_c, \frac{2i-1}{n}\pi\right)$ and $\left(r_c, \frac{2i+1}{n}\pi\right)$, being given r_c by Eq. (16).

CHARACTERS OF RING-FORMING ELLIPSE

We have seen that the ring was defined by the number and coefficients of the ellipse. Let us next consider the characters of the ellipse forming such a ring.

From the equation (8), the position of the contact point A (see Fig. 4) on the ellipse are given as

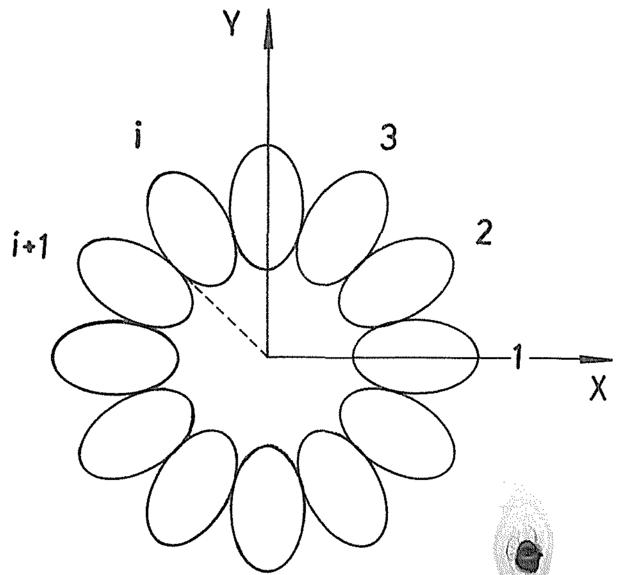

Fig. 3. Ellipse arranged in ring. The center of the first one is on x axis.

$$x_c = r_c\cos(\theta-\Theta) - R = r_c\cos\frac{1}{n}\pi - R$$

$$= \frac{-a^2\sin\frac{1}{n}\pi}{\sqrt{a^2\sin^2\frac{1}{n}\pi + b^2\cos^2\frac{1}{n}\pi}}, \tag{17}$$

and

$$y_c = r_c\sin(\theta-\Theta)$$

$$= \frac{b^2\cos\frac{1}{n}\pi}{\sqrt{a^2\sin^2\frac{1}{n}\pi + b^2\cos^2\frac{1}{n}\pi}}. \tag{18}$$

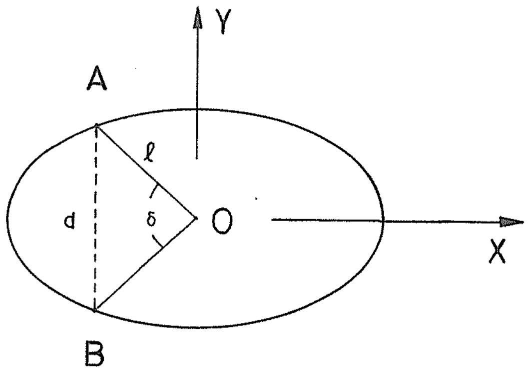

Fig. 4. Explanation of A, B, l and d at the ring forming ellipse. Origin of the co-ordinate of the contact points A and B, which is expressed by Eqs. (11) and (12), is at 0, the center of the ellipse.

Another contact point B is, therefore, has the co-ordinate $(x_c, -y_c)$. Denoting by l the lenght of the contact point to the center, (see Fig. 4) we obtain

$$l=\sqrt{x_c^2+y_c^2}=\sqrt{\frac{a^4\sin^2\frac{1}{n}\pi+b^4\cos^2\frac{1}{n}\pi}{a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi}}\,. \tag{19}$$

Let $\angle$AOB be δ. Then,

$$\cos\delta=\frac{x_c\cdot x_c+y_c\cdot(-y_c)}{\sqrt{x_c^2+y_c^2}\sqrt{x_c^2+y_c^2}}=\frac{x_c^2-y_c^2}{x_c^2+y_c^2}$$

$$=\frac{a^4\sin^2\frac{1}{n}\pi-b^4\cos^2\frac{1}{n}\pi}{a^4\sin^2\frac{1}{n}\pi+b^4\cos^2\frac{1}{n}\pi}\,. \tag{20}$$

And as the distance between A and B, denoting this by d, is $2y_c$, we obtain

$$d=2y_c=\frac{2b^2\cos\frac{1}{n}\pi}{\sqrt{a^2\sin^2\frac{1}{n}\pi+b^2\cos^2\frac{1}{n}\pi}}\,. \tag{21}$$

DISCUSSIONS

From the above arguments, it is apparent that the number of identical elliptic molecules having two symmetrical bonding (or contact) site compose a ring. Equations (17) and (18) mean that the radius of the ring and the number of the constituent molecules is defined by a, b and the location of the bonding site on the surface of molecules. Namely, structure of the regular aggregate is determined by the intrinsic nature of the molecules. Although even the tertiary structure of the molecules are restricted by the steric hindrance of constituent atomic groups, this case suggests that the regular assembly or quarternary structure of macromolecules would more directly affected by the character, especially shape, of molecules.

Although the argument is restricted to two dimentional case, this is directly appricable to the ring composed of the molecule of ellipse of gyration. We may be able to apply this to the study of the biological macromolecules composing a ring appearanced organellas. Suppose that they cannot minutely observe in an electron microscope because either the organella or component molecules is too delicate to be treated with fixing reagents, and we only can measure, in an optical microscope, the outside radius, $(R+a)$, and the inside radius, $(R-a)$, and hence obtain the length of R and a. Nevertheless, we can obtain either n, for example, by some chemical titration method, or ratio of a to b by the hydrodynamic measurements. Even if the thickness of the ring cannot be microscopically measured, we can obtain the length a and b from both chemical and hydrodynamic data.

AKNOWLEDGMENT

The author is grateful to Professor T. Ooi and Dr. K. Nishikawa for discussions.

REFERENCES

(1) F. Hund, "Theorie des Aufbaues der Materie", B. G. Teubner, Stuttgart, 1961, Chapter 2.
(2) L. Pauling, "The Nature of the Chemical Bond" 3rd Ed., Cornel Univ. Press, Ithaca, N. Y., 1960, Chapter 13.
(3) P. Niggli, *Zeit. f. Krist.*, **65**, 391 (1927).
(4) P. Niggli, *ibid.*, **68**, 404 (1928).