The Origin of Aromaticity

This problem is one of the histories of organic chemistry. Many researchers have proposed their own understanding methods aiming at solution.[1] However, it is not heard that the problem of the origin why aromatic property exists was solved.

In fact, if the basic concepts of quantum mechanics are applied, comparatively easily, almost all problems are understandable and thus seem to be already solved. But those ideas have not arrived to organic chemists. I will explain as intelligibly as possible.

1. Fundamental Problem of Aromatic Property

(Those who are familiar with aromaticity may skip this part.)

Benzene

In order to clarify the main problems of aromaticity, the features of benzene and cyclobutadiene are taken as typical examples of aromaticity and antiaromaticity. Benzene is the most typical example of 4N+2 systems which have aromatic properties.[2] Figures 1 and 2 show Hückel π-molecular orbitals with energy-levels of benzene and referential hexatriene, respectively.[3]

$$\varepsilon_5 = \alpha - 2\beta$$
$$\psi_5 = \frac{1}{\sqrt{6}}(\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6)$$

$$\varepsilon_4 = \alpha - \beta$$
$$\psi_4 = \frac{1}{2}(\chi_2 - \chi_3 + \chi_5 - \chi_6)$$

$$\varepsilon_5 = \alpha - \beta$$
$$\psi_5 = \frac{1}{\sqrt{12}}(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6)$$

$$\varepsilon_2 = \alpha + \beta$$
$$\psi_2 = \frac{1}{\sqrt{12}}(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6)$$

$$\varepsilon_3 = \alpha + \beta$$
$$\psi_3 = \frac{1}{2}(\chi_2 + \chi_3 - \chi_5 - \chi_6)$$

$$\varepsilon_1 = \alpha + 2\beta$$
$$\psi_1 = \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)$$
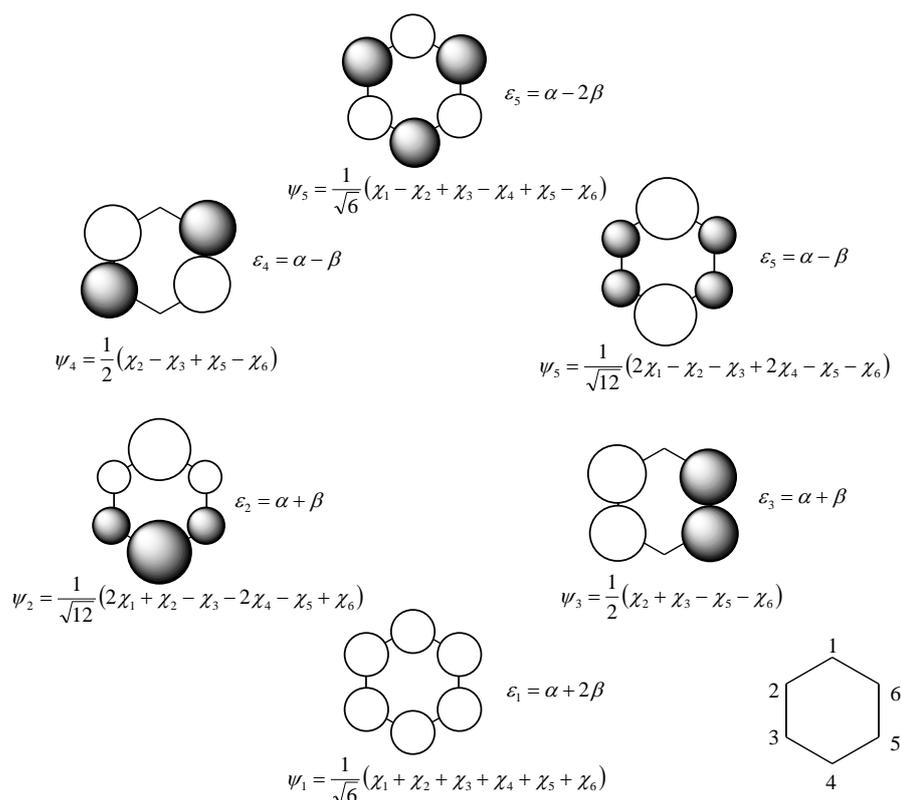
Fig.1. The Hückel molecular orbitals (HMOs) and energies of benzene.

White circles express the phase of +, a black ones express the phase of -,

and a size expresses the size of the absolute value of the coefficient.

The occupied orbitals of benzene are ψ_1, ψ_2, and ψ_3 and every pair of π electrons occupies them.

Clearly, benzene is chemically and thermodynamically stable compared with the referential chain-like (linear) unsaturated hydrocarbon: π electron energy of benzene is $6\alpha+8\beta$. Let's look at corresponding hexatriene.

ψ_1, ψ_2, and ψ_3 in hexatriene are occupied orbitals. The energy of ψ_1 becomes high about -0.2β above that of benzene. The energy of π electrons is $6\alpha+6.99\beta$ ψ_1, and that is higher than benzene by -1.01β (α and β are negative constants).

Although the energy sum of ψ_2 of benzene and ψ_3 is $2\alpha+2\beta$, that of ψ_2 and ψ_3 of hexatriene is $2\alpha+1.692\beta$, and the energy of benzene becomes low about 0.31β. In addition to the lower ψ_1, other energy-levels of other occupied orbitals in benzene are lower than those of hexatriene, the π electron energy in benzene becomes very low as a whole.

$$\varepsilon_6 = \alpha - 1.802\beta \qquad \psi_6$$
$$= 0.232\chi_1 - 0.418\chi_2 + 0.521\chi_3 - 0.521\chi_4 + 0.418\chi_5 - 0.232\chi_6$$

$$\varepsilon_5 = \alpha - 1.247\beta \qquad \psi_5$$
$$= 0.418\chi_1 - 0.521\chi_2 + 0.232\chi_3 + 0.232\chi_4 - 0.521\chi_5 + 0.418\chi_6$$

$$\varepsilon_4 = \alpha - 0.445\beta \qquad \psi_4$$
$$= 0.521\chi_1 - 0.232\chi_2 - 0.418\chi_3 + 0.418\chi_4 + 0.232\chi_5 - 0.5218\chi_6$$

$$\varepsilon_3 = \alpha + 0.445\beta \qquad \psi_3$$
$$= 0.521\chi_1 + 0.232\chi_2 - 0.418\chi_3 - 0.418\chi_4 + 0.232\chi_5 + 0.5218\chi_6$$

$$\varepsilon_2 = \alpha + 1.247\beta \qquad \psi_2$$
$$= 0.418\chi_1 + 0.521\chi_2 + 0.232\chi_3 - 0.232\chi_4 - 0.521\chi_5 - 0.418\chi_6$$

$$\varepsilon_1 = \alpha + 1.802\beta \qquad \psi_1$$
$$= 0.232\chi_1 + 0.418\chi_2 + 0.521\chi_3 + 0.521\chi_4 + 0.418\chi_5 + 0.232\chi_6$$
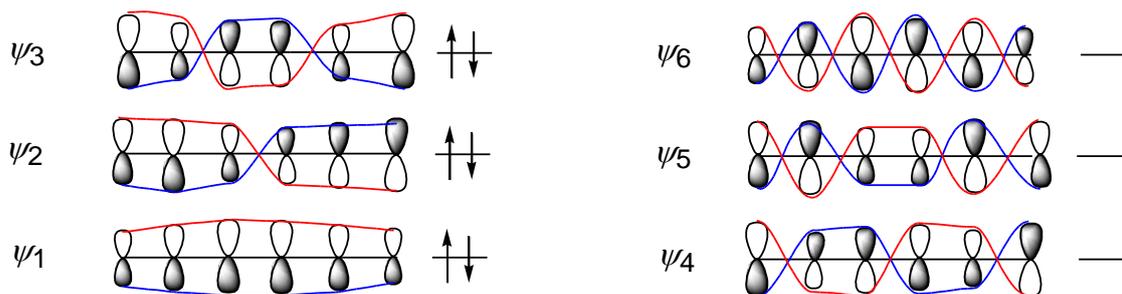

Fig.2. Hückel MOs of hexatriene.

Cyclobutadiene

Let's see cyclobutadiene which is a typical example of 4*N* systems which have antiaromatic properties. Figures 3 and 4 show the molecular orbitals and their energy-levels in cyclobutadiene and butadiene, respectively.

Except the lowest occupied orbital (ψ_1), the orbitals are doubly degenerated in the cyclic system (Fig. 3). The highest occupied molecular orbitals (HOMOs) are ψ_2, and ψ_3. Since electrons occupy dispersedly ψ_2, and ψ_3 (triplet state i.e. biradical), the stabilization energy by the chemical bonding does not take place. The case that two electrons occupy ψ_2 or ψ_3 (singlet state) is considered; there is an energy fall by a chemical bond. But is should be pointed out that since the bond distance between the bonding carbons is shortened, i.e., the geometry is changed, this is not the same system as cyclobutadiene.[4]

When two electrons go into the doubly degenerated orbitals the energy of the triplet state is generally lower. But since there is an energy fall by a chemical bond in the singlet state, it cannot be easily determined which is thermodynamically more stable as the ground state. Moreover, since it is easy to become the triplet state (biradical) even if it takes the singlet state, chemical activity seems to be highly "labile" for chemists.

$$\varepsilon_4 = \alpha - 2\beta$$

$$\psi_4 = \frac{1}{2}\left(\chi_1 - \chi_2 + \chi_3 - \chi_4\right)$$

$$\varepsilon_2 = \alpha$$

$$\psi_2 = \frac{1}{2}\left(\chi_1 + \chi_2 - \chi_3 - \chi_4\right)$$

$$\varepsilon_3 = \alpha$$

$$\psi_3 = \frac{1}{2}\left(\chi_1 - \chi_2 - \chi_3 + \chi_4\right)$$

$$\varepsilon_1 = \alpha + 2\beta$$

$$\psi_1 = \frac{1}{2}\left(\chi_1 + \chi_2 + \chi_3 + \chi_4\right)$$
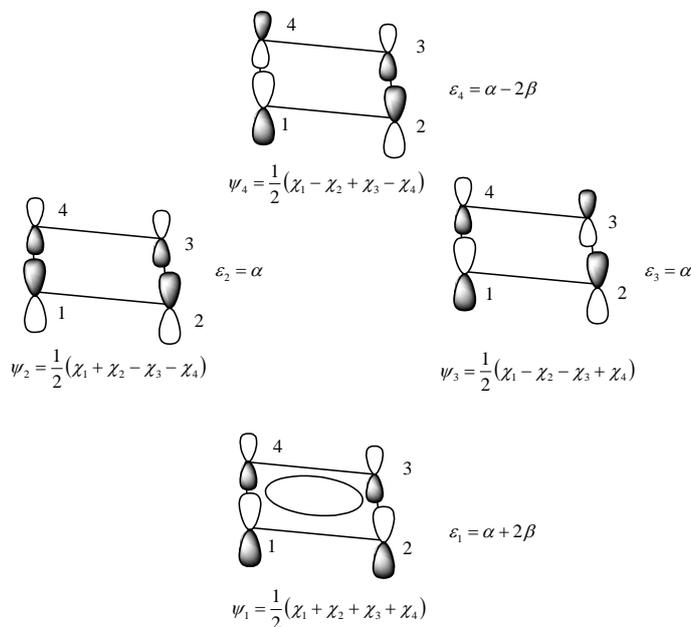
Fig. 3. The HMOs of cyclobutadiene. See that the lowest and the highest orbitals are not degenerated and the other orbitals are doubly degenerated.

The energy when an electron occupies the *i*-th orbital of HMO (ε^i) in cyclobutadiene is given by the following formula.

$$\varepsilon^i = \int \psi_i H \psi_i d\tau = \int \left(c_1^i \chi_1 + c_2^i \chi_2 + c_3^i \chi_3 + c_4^i \chi_4\right) H \left(c_1^i \chi_1 + c_2^i \chi_2 + c_3^i \chi_3 + c_4^i \chi_4\right) d\tau$$

$$= (c_1^i)^2 \int \chi_1 H \chi_1 d\tau + 2c_1^i c_2^i \int \chi_1 H \chi_2 d\tau + 2c_1^i c_3^i \int \chi_1 H \chi_3 d\tau + 2c_1^i c_4^i \int \chi_1 H \chi_4 d\tau +$$

$$2c_2^i c_3^i \int \chi_2 H \chi_3 d\tau + 2c_2^i c_4^i \int \chi_2 H \chi_4 d\tau + 2c_3^i c_4^i \int \chi_3 H \chi_4 d\tau + (c_4^i)^2 \int \chi_4 H \chi_4 d\tau$$

$$= (c_1^i)^2 H_{11} + 2c_1^i c_2^i H_{12} + 2c_1^i c_3^i H_{13} + 2c_1^i c_4^i H_{14} + (c_2^i)^2 H_{22} + 2c_2^i c_3^i H_{23} +$$

$$2c_2^i c_4^i H_{24} + (c_3^i)^2 H_{33} + 2c_3^i c_4^i H_{34} + (c_4^i)^2 H_{44} \qquad (\Theta\ H_{rs} = H_{sr})$$

1

Here, H is the Hückel Hamiltonian.

Well, according to the supposition of the HMO method, $H_{11}=H_{22}=H_{33}=H_{44}=\alpha$, $H_{12}=H_{23}=H_{34}=H_{41}=\beta$ and other H_{rs} are zero. So,

$$\varepsilon^i = (c_1^i)^2\alpha + 2c_1^i c_2^i \beta + 2c_1^i c_4^i \beta + (c_2^i)^2\alpha + 2c_2^i c_3^i \beta + (c_3^i)^2\alpha + 2c_3^i c_4^i \beta + (c_4^i)^2\alpha$$
$$= \left((c_1^i)^2 + (c_2^i)^2 + (c_3^i)^2 + (c_4^i)^2\right)\alpha + 2\left(c_1^i c_2^i + c_1^i c_4^i + c_2^i c_3^i + c_3^i c_4^i\right)\beta \qquad\qquad 2$$

is obtained. If the coefficients of ψ_2 or ψ_3 are substituted, the coefficient of β will be 0 and understandably, the stabilization by bond formation will not be given. Those orbitals are nonbonding ones which have neither contribution nor rebounding in the π bond formation and those energy levels are set to α.

The lowest HMO energy of cyclobutadiene is $\alpha+2\beta$. So, it comes out and 0.382β becomes lower compared to that of butadiene. In the case of butadiene, since the movement range of the π electrons is restricted within that from C_1 to C_4, the energy goes up that much due to the uncertainty principle.

ψ_2 or ψ_3 of cyclobutadiene are degenerated and have the energy value of α. Contrary to this, in case of butadiene since regions between C_1 and C_2 and between C_3 and C_4 of ψ_2 are bonding with energy of $\alpha+0.618\beta$, 0.618β lower compared to that of cyclobutadiene.

Cyclobutadiene has the lowest energy level of $\alpha+2\beta$, however, ψ_2 and ψ_3 have no contribution to π bond formation causing a high π electron energy.

$$\varepsilon_4 = \alpha - 1.618\beta \qquad \psi_4 = 0.371\chi_1 - 0.601\chi_2 + 0.601\chi_3 - 0.371\chi_4$$
$$\varepsilon_3 = \alpha - 0.618\beta \qquad \psi_3 = 0.601\chi_1 - 0.371\chi_2 - 0.371\chi_3 + 0.601\chi_4$$
$$\varepsilon_2 = \alpha + 0.618\beta \qquad \psi_2 = 0.601\chi_1 + 0.371\chi_2 - 0.371\chi_3 - 0.601\chi_4$$
$$\varepsilon_1 = \alpha + 1.618\beta \qquad \psi_1 = 0.371\chi_1 + 0.601\chi_2 + 0.601\chi_3 + 0.371\chi_4$$
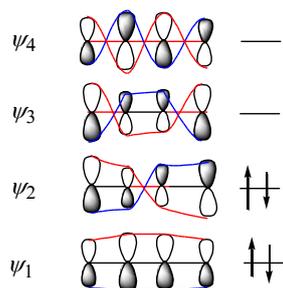
Fig.4. HMO orbitals of butadiene

If cyclobutadiene is referred, it may turn out that the thermodynamical energy is "unusually" high as it may come from the image of the word of "an antiaromatic series". But, it may not bet so. The HMO energy is $4\alpha+4\beta$ and this is equivalent to the π electron energy of two ethylene molecules. That is, it is the level that two ethylene units do not only conjugate (the π energy of ethylene is $2\alpha+2\beta$ per piece).

However, since the 2nd and 3rd π MOs are degenerated, cyclobutadiene becomes triplet state (biradical) causing chemical reactivity very high. Therefore, cyclobutadiene tends to give chemists the impression of being unusually unstable.

2. Problems Which Should be Solved

1. The HMO method computes the magnitude of aromaticity quantitatively.[1] Then, what does the HMO method calculate?

2. The lowest and the highest energy of HMO of a circular configuration system do not degenerate, while other orbitals doubly degenerate, and the reason why such degeneration is resolved in chain structure.

3. The reason why the lowest energy of HMO of a circular configuration takes a constant value ($\alpha+2\beta$) independently of the size of the circular system, and why the highest energy is set to be $\alpha-2\beta$.

4. Although it is considered that it is the cause of aromatic stability that the lowest energy takes the steady value of $\alpha+2\beta$ in both $4N+2$ and $4N$ system, such an effect does not take place in $4N$ system. What is the reason?

5. Are those problems and the answers generalizable?

3. The Concept of "Stability" in Chemistry Has Two Meanings

Cyclobutadiene is well known as very "unstable".[5] That a substance is "stable" means that the substance does not change. Namely, the state that a substance does not change is simply called "stable" and if not so, "unstable". However, being low in energy is also called "stable". The thermodynamical low state of energy is called stable (thermodynamically stable), whereas a high

state is called unstable (thermodynamically unstable): this may cause confusion. For example, the compounds **a** and **b** which are the isomers of benzene (**c**) change with heating etc. to **c** (a does not necessarily result in **c** through **b**). Although the total energy of **b** is lower than **a**, **b** changes to **c** easily. On the other hand, although the total energy of **a** is higher than **b,** changing to **c** is not easy. If these facts are denoted by a graph, it will become as it is shown in Fig. 5.
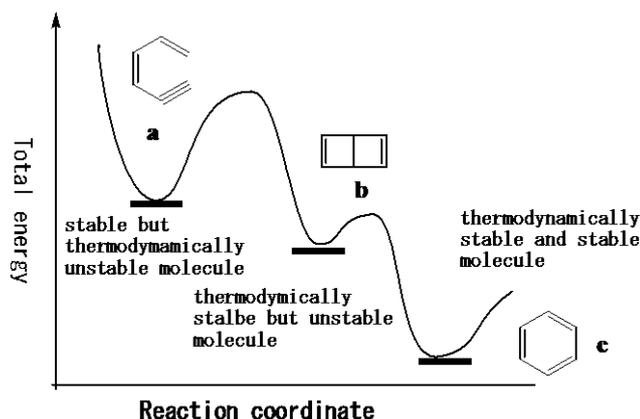

Fig. 5. Molecular stability and thermodynamical stability

Among these three molecules, **a** is stable as a molecule since it chemically is not easy to change but thermodynamically unstable whereas **b** is thermodynamically more stable than **a** but chemically unstable. **c** can be said to be "thermodynamically" and chemically stable.

Here it should be recalled that when arguing about the stability of aromatic compounds, only thermodynamics stability should be discussed, because, the problem of aromatic property is related with one molecule, and if it includes the chemical stable and unstable problem, the elements more than molecule-itself are involved. Again, aromaticity is a problem of a single molecule.

4. Standard of Stability

Chemical standard of aromaticity may be linear unsaturated hydrocarbon with the same number of double bonds. In the case of benzene, the reference compound is 1, 3, 5-hexatriene and for cyclobutadiene, it is butadiene. When using a molecular orbital theory, to make it stricter, various methods of defining aromaticity are proposed.[1] The methods may be effective if one quantitatively considers the aromaticity of an unknown aromatic compound. But it may not be effective to solve essential problems of aromaticity. Namely, the problem here is why a difference arises in the π electron energy between the cyclic-conjugated and linearly conjugated structures in the same carbon number. In other words, what we must clear is to explain *conceptually* the difference of the π electron energy between the cases where the movement range of the π electrons is limited to be linear and that is annular.

5.What Does HMO Calculate? (Answer to the problem 1)

π Electron energy of HMO can explain aromaticity quantitatively. This means that HMO will link with the elucidation of the cause of aromaticity directly. Thus we need to know what the HMO method calculates.

The energy of HMO has already become clear as it is "the kinetic energy of the π electrons in the potentials averaged from nuclei and other electrons[6]." Refer to the following document for more information.

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Thus, it may be said that the problem of aromatic property is a problem of being high or low of the kinetic energy of π electrons.

6. Kinetic Energy of the Lowest-Level Electrons in Annular Movement is in the State of 0 (Answer to Problem 3)

The kinetic energy of the π electrons in the lowest HMO of any annular unsaturated hydrocarbon serves as zero theoretically. This is because in HMO, it is assumed that the potentials from nuclei and other electrons are constant. Moreover, since kinetic energy is certainly a positive value, 0 is the lowest value. Generally, the lowest energy of HMO of annular unsaturated hydrocarbon is $\alpha+2\beta$ independently of the size of annular system. This value corresponds to the zero kinetic energy.[4] I will explain somewhat in detail.

Movement of a π electron of a cyclic conjugated system turns into circumference movement in a classic image. Generally the quantum mechanical energy of the lowest level in circumference movement is certainly zero. This is clear from the uncertainty relation: since there is no restraint to circumference movement, it turns out as Δq=infinity in the relationship, $\Delta p \cdot \Delta q > \hbar/2$, resulting in that the quantity of momentum itself approaches 0. Those who are against this idea because it is refuted as "Δp=0 is not that the quantity of momentum is 0 but the ambiguity of quantity of momentum being taken out" may refer to the comment of the uncertainty relation and energy shown in **1220**. The following comment, which explains the relationship between the region of a particle movement and its energy may also be useful as shown in **1230**.

What I want to emphasize is that the π electrons in the lowest orbital do not move in the annular conjugated system. This solves the riddle why the lowest HMO energy of annular unsaturated hydrocarbon is $\alpha+2\beta$ irrespective of the size of annular system. In the case of the even number atoms, there is no degeneration also in the orbital of the highest energy level. In this orbital, the π electrons are completely localized on each atom and it is thought that there is no circumference movement (since the π electrons are localized, the kinetic energy become large due to the uncertainty principle). The energy when π electrons localize completely is $\alpha-2\beta$. See, β is a negative value.

The resolution for the orbital of the highest energy level comes out. It may be mentioned that this

result is given when the LCAO method is used since LCAO adds a restriction on the solution (this may not be worried much).

7. General Consideration: Meaning of Degeneration and Non-Degeneration   (Answer to the problem 2)

Let us consider generally the meaning of degeneration and non-degeneration of HMOs in annular conjugated unsaturated systems. The HMO energy of the j-th orbital (ε_j) is expressed as a function of the number (n) of carbon atoms as Eq. 3.

$$\varepsilon_j = \alpha + 2\beta \cos\left(\frac{2\pi}{n}j\right) \qquad j = 0, \pm 1, \pm 2, \cdots, \left(\frac{n}{2}\right) \qquad for\ even\ n$$

$$\left\{ j = 0, \pm 1, \pm 2, \cdots, \pm \left(\frac{n-1}{2}\right) \qquad for\ odd\ n \qquad \right\} \qquad 3$$

The lowest energy level is $j = 0$. Since cos of the right-hand side is set to 1 whenever it substitutes $j = 0$ for Eq. 3, it becomes $\alpha + 2\beta$. This is not related to the number (n) of a ring.

The orbitals other than the lowest and highest energy-level in the case of the even number are doubly degenerated. Since they have two degrees of freedom, this is a natural consequence: classically, being clockwise movement and counterclockwise movement. It should be recalled that the same situation appears in the annular momentum in atomic orbitals.

The magnetic quantum number (m) of an atomic orbital is a quantum number of circumference movement about the z axis. Since there is no circumference movement when m is zero, a wave function does not degenerate taking a constant (therefore, kinetic energy is 0). Other orbitals take quantum number (m) as ± 1, ± 2, .. and the $\pm$ sign corresponds to the same meaning of j in Eq. 3.

Here, it must be mentioned that an actual annular unsaturated hydrocarbon system, since nuclear potential is not constant, the kinetic energy of π electrons in the lowest energy level does not become 0, but it was pointed out that the π electron energy at that energy in benzene becomes low unusually if compared with those of other energy levels.[6]

8. The Reason Why the Degenerated Orbitals in Annular Systems Resolve in Linear Systems (answer to the problem 2)

The HMO method obtains the kinetic energy and the orbital of π electrons by solving the Hückel Schrödinger equation based on the LCAO approximation. The Schrödinger equation of annular movement of electrons can be solved analytically. If these results are compared with those of the HMO method, the reason why the degenerated orbitals in annular systems resolve in linear systems may be understood.[6] The details are as follows.
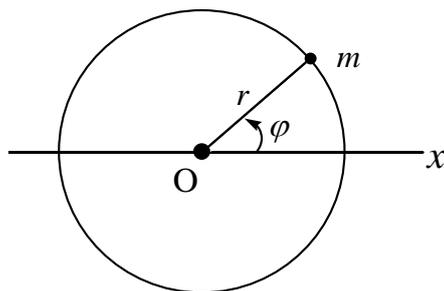
Fig.6. Circumference movement by two-dimensional polar coordinates. *m* is electronic mass, O is the center of circumference movement, *r* is the distance to the electron, and *φ* is angle between *x*-axis and *r*.

Let us consider the case that an electron moves circularly in a fixed potential ($\bar{U}$). To obtain the energy and orbital of the electron, the Schrödinger equation to be solved is,

$$E\psi = \left(-\frac{h^2}{8\pi^2 mr^2}\frac{d}{d\phi^2} + \bar{U}\right)\psi \qquad 4$$

The orbital and its energy (E_j) is analytically given as,

$$E_j = \frac{j^2 h^2}{2mL'^2} + \bar{U} \qquad j = 0, \pm 1, \pm 2, \pm 3 \cdots \qquad 5$$

where *L'* is the circumference of the ring. The wave functions are generally expressed as $\psi = (2\pi)^{-1}\exp(\pm ip\varphi)$, but are transformed to more understandable forms,

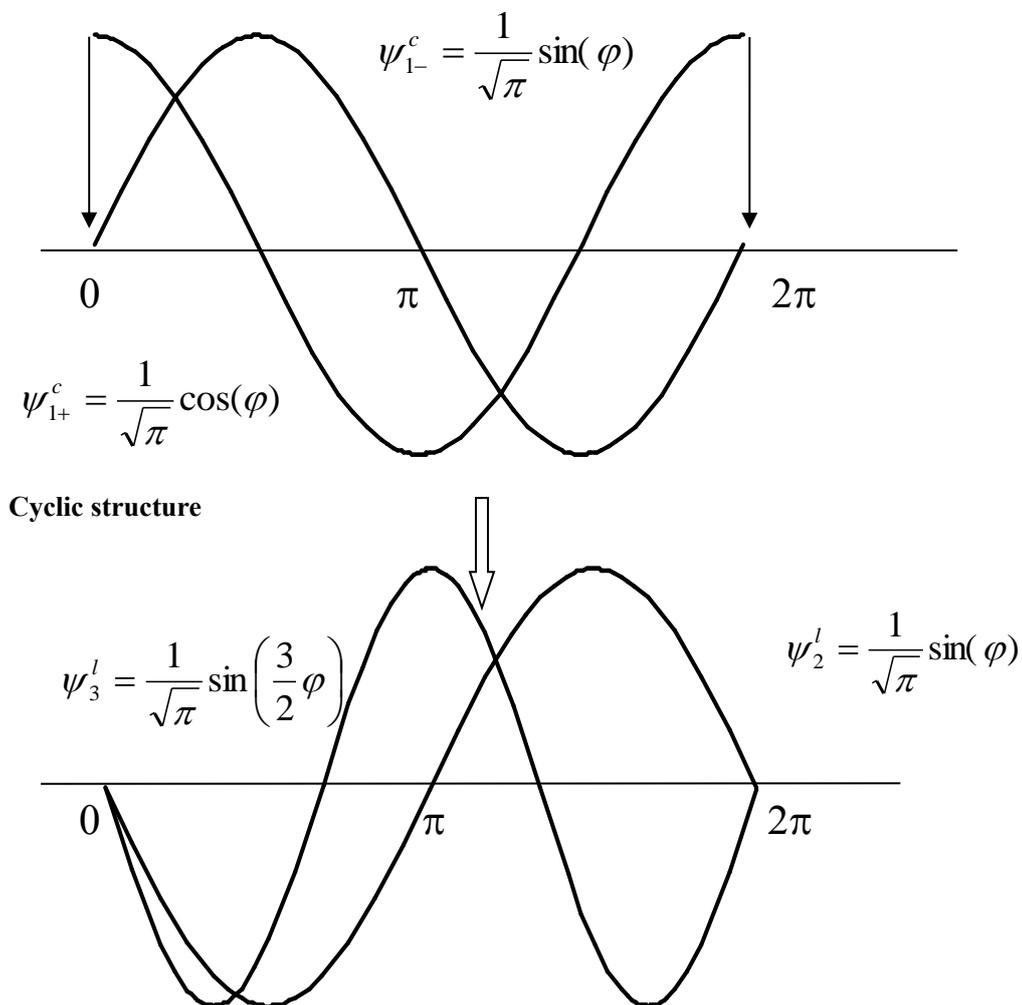$$\psi_0 = \frac{1}{\sqrt{2\pi}} \qquad \text{for } j = 0, \qquad 6$$

$$\psi_{j+} = \frac{1}{\sqrt{\pi}}cos(j\phi) \qquad \text{for positive } j, \qquad 7$$

$$\psi_{j-} = \frac{1}{\sqrt{\pi}}sin(j\phi) \qquad \text{for negative } j. \qquad 8$$

From Eq. 5, it turns out that the lowest orbital (*j*= 0) is not degenerated in agreement with the result of HMO. The wavefunction is also a constant and the electrons in it have zero value in the kinetic energy. [7] Other orbitals are doubly degenerated and are expressed as cos and sin functions. They are in good accordance with the results of HMO.

The change to linear structure from a circular one is equivalent to installing an infinite potential wall at zero (or 2π). That is, in chain structure, electrons cannot get out from the end of the chain; this means that there exists a high potential wall. The wave of the particle must shrink at 0 or 2π, i.e., the wavefunction is necessarily zero there.

If the wavefunction must take at 0 or 2π (Fig. 7), the phase of one of energetically equivalent wavefunctions (cos function) increases by one. The sign wavefunction does not change.

$$\psi^c_{1-} = \frac{1}{\sqrt{\pi}}\sin(\varphi)$$

$$\psi^c_{1+} = \frac{1}{\sqrt{\pi}}\cos(\varphi)$$

Cyclic structure

$$\psi^l_3 = \frac{1}{\sqrt{\pi}}\sin\left(\frac{3}{2}\varphi\right)$$

$$\psi^l_2 = \frac{1}{\sqrt{\pi}}\sin(\varphi)$$

Chain structure

Fig.7. Why the doubly degenerated states in cyclic system are resolved into two energetically different states in linear system. The linear system corresponds to the state of the cyclic system in which an impenetrable barrier is placed at 0 (or 2π). In this situation the wave function must shrink to zero at 0 and 2π, forming a sinusoidal function with a higher quantum number.

Since phase change is adding restriction to the range of electron's existence, the energy of the wave function becomes high. This is the reason why degenerated wavefunctions in a ring structure are resolved in a chain structure.

9. Concerning the Infinite Linearly Conjugated Systems (Answer to Problems 3 and 5)

Let's see the case of the infinite linear unsaturated hydrocarbon for comparison. The orbital energy

(ε_j) of level j in the linear unsaturated hydrocarbon which consists of n numbers of carbon atoms is given by Eq. 9 (be cautious of j beginning from 1).

$$\varepsilon_j = \alpha + 2\beta\,cos\left(\frac{\pi}{n+1}j\right) \qquad j = 1, 2, \cdots, n \qquad\qquad 9$$

The energy value of the lowest energy level ($j= 1$) is higher than $\alpha+2\beta$. If n is increased, the energy approaches to $\alpha+2\beta$. This is because the movement range of π electrons becomes large, and is the result of the uncertainty principle also agreeing with the principle. That is, the orbital energy of the lowest energy level of circumference movement is in agreement with the orbital energy which does not have restriction in the movement range. This means that there is no restraint in movement of the π electrons in the lowest-energy orbital of a cyclic conjugation system.

10. Electron Configurations (Answers to Problems 4 and 5)

The energy of the j-th orbital in annular or linear unsaturated hydrocarbons is expressed by Eq. 3 or Eq. 9, respectively. The number of π electrons is n the same as N.

4N system

J-value for HOMO is $\frac{4N}{4}=N$ and the number of the circle is 4N. Here, j increases as 0, ± 1, $\pm 2 \cdot \cdot$. If $j=\pm N$ is substituted in Eq. 1,

$$\varepsilon_{homo} = \alpha + 2\beta\,cos\left(\pm\frac{2\pi}{4N}N\right) = \alpha \qquad\qquad 10$$

is obtained. HOMOs serves as nonbonding orbitals which are degenerated, and since the coefficient of β is 0, two electrons in these orbitals have no contribution to the chemical bond. Therefore, the π-electron energy becomes high compared with the linear unsaturated compound of the same carbon number as shown next.

Contrarily to this, j-value for HOMO in the linear structure is $\frac{4N}{2} + 1 = 2N + 1$. The number of the chain is 4N. It should be noted that j starts as 1, 2, 3, … If $j=2N$ and $n=4N$ are substituted in Eq.9,

$$\varepsilon_{homo} = \alpha + 2\beta\,cos\left(\frac{(2N+1)\pi}{4N+1}\right) \qquad\qquad 11$$

is obtained. The value of the cos function takes some value more than 0 and less than 1; the coefficient of β is not zero. Namely, the HOMO is a bonding orbital.

4N+2 system

J-value for HOMO is $\frac{4N}{4}=N$ and the number of the circle is 4N+2. They are substituted in Eq. 2 to give,

$$\varepsilon_{homo} = \alpha + 2\beta\,cos\left(\pm\frac{2\pi}{4N+2}N\right) = \alpha + 2\beta\,cos\left(\frac{N\pi}{2N+1}\right) \qquad\qquad 12$$

Since the cos function never gives 0, the doubly degenerated HOMOs are bonding causing the π

electron energy low. 4 Electrons occupy the HOMOs lowering the π electron energy in addition to occupying the lowest orbital with $\alpha+2\beta$. This lowers the energy of the cyclic system more than corresponding linear system.

If $2N+1$ and $n=4N+1$ are substituted in Eq. 9 for linear system,

$$\varepsilon_{homo} = \alpha + 2\beta \cos\left(\frac{(2N+1)\pi}{4N+3}\right) \qquad 11$$

is obtained. This orbital also is bonding one. If $\frac{N}{2N+1}$ and $\frac{2N+1}{4N+3}$ are compared, the value of the former is always less than the latter. So, the π electron energy of the annular system is always lower than that of the linear system.

Hobey obtained the $4N/4N+2$ rule mathematically. [8] The physical meanings for his results were given.[6] Those who are interested may refer to the literature already given.

11. What is Aromaticity

The kinetic energy of the lowest π molecular orbital of a cyclic conjugation system is in the state of 0. This is the main cause of the stability of an annular unsaturated system. However, HOMOs in the 4N system, are inevitably nonbonding and doubly degenerated where two electrons occupy them dispersedly causing the state of biradical. Since they are nonbonding orbitals, electrons in HOMOs do not contribute to the energy fall of π electrons, making the energy of the system high compared to the reference system. Moreover, since the molecule has radical character, chemical reactivity becomes high. This is the reason why $4N$ systems are thermodynamically and chemically unstable.

On the other hand, the cause of the aromatic stability of $4N+2$ systems is that there is an orbital of the zero kinetic energy due to cyclic conjugation. Contrary to $4N$ systems, HOMOs of $4N+2$ systems are bonding orbitals. Although they are doubly degenerated, four electrons may occupy them with pairing and contributing to energy stabilization of π electrons.

If those mentioned above are made simpler, it turns out as "the aromatic property of an unsaturated hydrocarbon of circular configuration is brought forth by the zero kinetic energy in the lowest π electron orbital. But in $4N$ systems, two electrons occupy nonbonding HOMO orbitals producing biradical character as well as no binding energy. This cancels the effect of the zero kinetic energy".

References

1. Mimkin, V. I.; Glukhovtsev, M. N.; Simkin, Ya. B., "Aromaticity and Antiaromaticity," John Wiley & Sons, Inc., New York, 1994.
2. When the number of a ring is $4N+2$ ($N=$ 1, 2, 3 ..) in the cyclic conjugated compounds, the compounds are chemically more stable than those of linear with the same number of unsaturated bonds and are called to be aromatic, whereas the compounds of the series of $4N$ is

called antiaromatic because of being unstable. This rule is the Hückel rule or the $4N/4N+2$ rule. This is one of the most important concepts in organic chemistry.

3. There are many books on HMO. We recommend you the following URL explained including the physical meaning of HMO (currently in Japanese).

    https://www.aromaticity.org/ Tutorial/Elementary/EO2-3.html

4. In chemistry, even if a molecule has some structural changes, it is the same molecule, but when applying a molecular orbital method, the molecule which changes structurally must be considered as a different system. In this case, cyclobutadiene with regular tetragon (D_{4h}) structure and that of rectangle (D_{2h}) structure are different molecules in quantum chemistry.

5. Emerson, G. F.; Watts, L.; Pettit, R. , *J. Am. Chem. Soc.* **1965**, *87*, 131.

6. Ichikawa, H.; Sakata, K., *Int. J. Quam. Chem.*, **2002**, **87**, 135-144.

7. The reason why the kinetic energy of the wavefunction of a constant is zero: if the wave-function $\psi(r,\varphi)=K$ (constant) is applied to the general method of obtaining the expectation value in quantum mechanics,

$$E\psi(r,\phi) = \int K^* \left(-\frac{h^2}{8\pi^2 m r^2}\frac{d}{d\phi^2} + \bar{U} \right) K d\tau = K^* K U$$

    is obtained to show that the contribution of the differential par is null.

8. Hobey, W. D. *J. Org. Chem.* **1972**, *37*, 1137.