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Why Does the Hückel Rule Hold for a Variety of Monocyclic Conjugated Systems?

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Hückel's $4n+2$ rule is shown to be applicable to diverse monocyclic π systems by means of graph theory and frontier orbital theory. All monocyclic $(4n+2)$-π-electron systems are proved to have both kinetic and thermodynamic stabilities. They are predicted to be diatropic in nature.

In 1931 Hückel presented so-called Hückel molecular orbital (HMO) theory.[1] He applied it to annulene π systems, and established the well-known Hückel rule for aromaticity, according to which all annulenes with $4n+2$ π electrons are predicted to be chemically stable or aromatic, and all annulenes with $4n$ π electrons are predicted to be rather reactive or antiaromatic. The Hückel rule is applicable not only to neutral annulenes but also to annulene ions.[1–3] Hückel suggested that it is also applicable to such heteroconjugated systems as pyridine and pyrrole.[1] As a matter of fact, the Hückel rule has been successfully applied to many monocyclic heteroconjugated systems and their ions.[4]

Hückel pointed out that the highest occupied molecular orbitals (HOMO's) of $[4n+2]$annulene are completely filled.[1] He then associated the closed-shell π system with the stability or aromaticity of an entire conjugated system. The HOMO's of $[4n+3]$annulene cations and $[4n+1]$annulene anions are also completely filled. In contrast to them, the HOMO's of $[4n]$annulene are relatively high in energy, and not completely filled. Hückel predicted that it must be reactive for this reason.[1]

A number of attempts have been made to test the validity of the Hückel rule. Various perturbational MO methods have been used to explain stabilization or destabilization of annulenes due to cyclic conjugation.[5–8] Breslow compared the energy of a cyclic π system with that of an open-chain reference system.[9] The applicability of the Hückel rule to annulenes has been confirmed by these attempts.

Dewar et al. devised an olefinic reference system of the same geometry as a real π system, using such bonds as scissored off from acyclic π systems,[10] and evaluated the so-called Dewar resonance energy relative to the energy of such a reference system. Hess and Schaad defined this type of resonance energy within the framework of HMO theory.[11,12] Aihara found that for monocyclic π systems Dewar resonance energy is definable using π bond energies of infinitely large cyclic π systems.[13] Two research groups formulated the Dewar resonance energy graph-theoretically.[14–18] All these attempts revealed that very many heterocyclic compounds obey the Hückel rule.

However, it has not been clarified yet whether or not the Hückel rule is applicable to all monocyclic π systems conceivable. There has been no general proof for the validity of the Hückel rule. This paper aims at elucidating the applicability and the physical meaning of the Hückel rule by means of graph theory[14–20] and frontier orbital theory.[7,21–23] The HMO model is used throughout this paper. Arbitrary integers are represented by N, m, n, p, or q.

Kinetic Aspect of the Hückel Rule

First, an aromatic molecule must be chemically stable or preferably unreactive. This kind of stability has been referred to as kinetic stability. We show below that the Hückel rule can be used reasonably to predict the kinetic stability of any monocyclic π system.

A given monocyclic π system formed by N conjugated atoms is denoted by G. We assume that there is no substituent in G. A characteristic polynomial $P_G(X)$ for G can be obtained by means of Sachs graph theory.[14–20] A reference polynomial $R_G(X)$ is a characteristic polynomial constructed graph-theoretically for a hypothetical olefinic reference structure of G.[14–18] Both $P_G(X)$ and $R_G(X)$ are the polynomials of degree N. The reference structure defined by $R_G(X)$ is assumed to have exactly the same geometry as G. However, the π bonds in it are tacitly assumed to have the same π bond energies as the analogous π bonds in acyclic polyenes.

For monocyclic π systems, $P_G(X)$ is obtainable simply by subtracting a constant from $R_G(X)$, namely,[14–18]

$$P_G(X) = R_G(X) - K_G, \tag{1}$$

where $K_G>0$ is the constant given by

$$K_G = 2\prod_{(ij)}^{G} k_{ij}. \tag{2}$$

Here, k_{ij} is the Hückel parameter for the i–j π bond, and (ij) runs over all π bonds in G. The curves $Y=P_G(X)$ and $Y=R_G(X)$ coincide exactly in the X–Y plane by displacing the former curve upward by K_G. There are N zeroes in $P_G(X)$ and $R_G(X)$, which represent the energies of N molecular orbitals (MO's) in G and its reference structure, respectively.[14–18] For example, K_G is 1.3122 for 1,4-dihydropyrazine, and $P_G(X)$ and $R_G(X)$ are

$$P_G(X) = X^6 - 3X^5 - 2.99X^4 + 10.86X^3 + 2.3644X^2 - 7.86X - 0.3744, \tag{3}$$

$$R_G(X) = X^6 - 3X^5 - 2.99X^4 + 10.86X^3 + 2.3644X^2 - 7.86X + 0.9378. \tag{4}$$

Here, the Hückel parameters of Hess, Schaad, and Holyoke[11] were used. The curves $Y=P_G(X)$ and $Y=R_G(X)$ for this eight-π-electron system are drawn in Fig. 1.

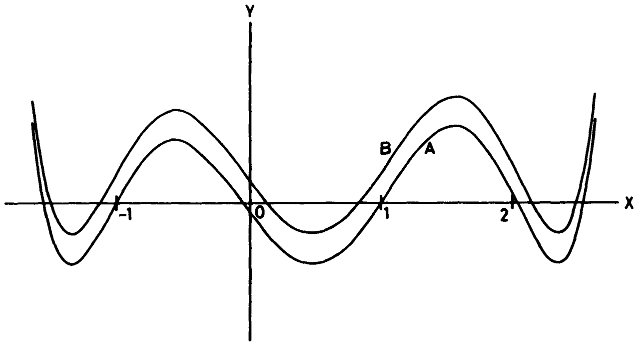

Fig. 1. The curves $Y=P_G(X)$ (A) and $Y=R_G(X)$ (B) for 1,4-dihydropyrazine.

Fikui et al.[7,21–23] named the HOMO and the lowest unoccupied molecular orbital (LUMO) frontier MOs, the energies and phases of which are closely related to the reactivity of the molecule. The HOMO and the LUMO contribute much more to such reactivity indices as superdelocalizabilities than any other MO's.[22] Therefore, it is instructive to examine the locations of these MO's in the energy scale.

The mth largest root X_m of the equation $P_G(X)=0$ represents the energy of the mth MO in G. The mth largest root $X_m{}^\circ$ of the equation $R_G(X)=0$ represents the energy of the mth MO in an olefinic reference system of G.[14–18] In general, positive and negative roots correspond to bonding and antibonding MOs, respectively. As can be seen from Fig. 1, the following two inequalities hold:

$$\begin{aligned} X_m > X_m{}^\circ \text{ for } m = 2p+1 \\ X_m < X_m{}^\circ \text{ for } m = 2p \end{aligned} \tag{5}$$

It is clear from Eq. 5 that the HOMO of a monocyclic $(4n+2)$-π-electron system is always lower in energy than that of the olefinic reference system, but that the LUMO is always higher in energy than that of the reference system. Such a $(4n+2)$-π-electron system must have much smaller superdelocalizabilities than its olefinic reference system defined by $R_G(X)$. This indicates that a $(4n+2)$-π-electron system must be much more resistant both to electrophilic and nucleophilic substitutions than a hypothetical olefinic system of the same geometry (i.e., the reference system). On the other hand, a monocyclic $4n$-π-electron system has a higher HOMO and a lower LUMO, both of which contribute much to the increase in reactivity. It has thus been confirmed that the Hückel rule holds in a kinetic sense for all kinds of monocyclic π systems. Therefore, it is very possible that most monocyclic species classified as aromatics are less reactive than those classified as antiaromatics.

Figure 1 shows that even if the $(2p)$th and $(2p+1)$th MO's of a monocyclic π system are degenerate in energy, the $(2p+1)$th and $(2p+2)$th MO's are never degenerate. If the $(2p+1)$th and $(2p+2)$th MO's were degenerate, the corresponding roots of the equation $R_G(X)=0$ would become complex numbers. This never occurs since the realness of these roots has been proved mathematically.[24] Therefore, a monocyclic conjugated species with $4n+2$ π electrons always has a closed-shell π system with a doubly occupied HOMO. As mentioned, Hückel showed that $[4n+2]$annulene has a closed-shell π system.[1] The present graph-theoretical analysis happens to constitute an extension of this viewpoint to all monocyclic conjugated systems. There is no open-shell $(4n+2)$-π-electron system as far as monocyclic conjugated molecules are concerned.

A singly occupied molecular orbital (SOMO) is also one of the frontier orbitals.[7,22,23] As seen above, Hückel's original interpretation of aromaticity is based on the kinetic instability of an open-shell π system with SOMO's.[1] It is very true that an open-shell π system is very reactive. Aside from $[4n]$annulenes, however, there are few monocyclic systems with SOMO's. Even in $[4n]$annulenes the degeneracy of the SOMO's are in fact lifted by the introduction of bond-length alternation. Since most heterocyclic systems with $4n$ π electrons have no degenerate SOMO's, the interpretation of antiaromaticity in terms of SOMO's is of limited use.

Thermodynamic Aspect of the Hückel Rule

Ideally, an aromatic molecule must exhibit not only kinetic but also thermodynamic stabilities.[3–9] Haddon and Fukunaga showed that $[4n+2]$annulenes meet the thermodynamic and kinetic criteria of aromatic character.[25] We next prove that any monocyclic $(4n+2)$-π-electron system is thermodynamically stabilized by cyclic conjugation. Fukui's frontier MO theory[7] is again useful for this purpose.

The Schrödinger equation defined in HMO theory for a linear π system is essentially of one-dimensional character, and can formally be reduced to the one-dimensional form:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dX^2}\Psi(X) + \{V(X) - E\}\Psi(X) = 0, \tag{6}$$

where $\Psi(X)$ is the eigenfunction (i.e., the MO), E is the eigenvalue (i.e., the energy of the MO), $V(X)$ is the electrostatic potential felt by an electron, m is the mass of an electron, and $\hbar$ is the Planck constant divided by 2π. The interatomic distances and the form of $V(X)$ can in principle be chosen in such a manner that Eq. 6 yields the Hückel secular determinant for a given linear π system. In other words, $V(X)$ may be an unrealistic function as far as Eq. 6 reproduces the Hückel matrix elements within the Hückel approximation. $V(X)$ may be assumed to be a differentiable function. In this treatment, we tacitly use hypothetical one-dimensional AO analogues as the LCAO basis functions.

Such a Schrödinger equation is mathematically identical with the eigenvalue problem of the Sturm-Liouville type.[26] The mth eigenfunction obtained by solving this problem has $m-1$ zeroes in the defined region. In the present case, the mth eigenfunction corresponds to the mth MO of a linear π system, which necessarily has $m-1$ nodes. The number of nodes increases one by one on going to higher MOs. Accordingly, LCAO coefficients of the $(2p+1)$th MO have the same sign at the two edge atoms, whereas those of the $(2p)$th MO at the edge atoms differ in sign. This sign rule holds for all kinds of linear π systems.

Fukui indicated that any conceivable division of benzene into two fragments produces segments whose HOMO and LUMO overlap in-phase at the original two junctions.[7] HOMO–LUMO interactions then give rise to stabilization by cyclic conjugation. We adopt this way of reasoning. An arbitrarily chosen monocyclic π system is first divided into two segments, both of which are linear conjugated subsystems. These two segments are assumed to have an even number of π electrons. Figure 2 shows the case in which a monocyclic aromatic molecule is divided into two segments, the one with two conjugated atoms and two π electrons and the other with the remaining conjugated atoms and π electrons.

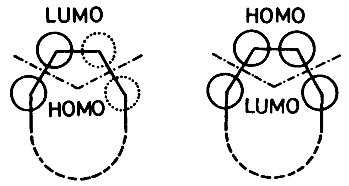

Fig. 2. Stabilizing HOMO–LUMO interactions in a monocyclic $(4n+2)$-π-electron system.

It follows that if the HOMO and the LUMO concerned are the $(2p+1)$th MO of one segment and the $(2q+1)$th MO of the other segment, respectively, both MO's overlop in-phase at the original two junctions. If the HOMO and the LUMO are the $(2p)$th MO of one segment and the $(2q)$th MO of the other segment, respectively, both MO's overlap in-phase, too. Then, the entire cyclic π system is predicted to gain stabilization energy by HOMO–LUMO interactions. Such a situation occurs only if the entire cyclic system has $4n+2$ π electrons.

On the other hand, if the HOMO and the LUMO concerned are the $(2p)$th MO of one segment and the $(2q+1)$th MO of the other segment, respectively, both MO's do not overlap in-phase at one of the junctions. In this case, the HOMO of the latter segment necessarily does not overlap in-phase with the LUMO of the former segment, either. The entire cyclic π system is predicted not to be stabilized by HOMO–LUMO interactions. Such a situation occurs only if the entire cyclic π system have $4n$ π electrons.

We can also assume that an odd number of π electrons reside at each segment.[5,7] This time the SOMO's of the two segments become interacting frontier MO's. Exactly the same proof can be achieved for the thermodynamic aspect of the Hückel rule by examining whether or not a phase dislocation occurs between the SOMO's at the original two junctions. Unless the total number of π electrons is equal to $4n+2$, the two SOMO's do not overlap in-phase at one of the junctions.

The above frontier MO analyses apply not only to all neutral monocyclic species but also to all charged ones. It is monocyclic $(4n+2)$-π-electron systems alone that are stabilized by HOMO–LUMO interactions. This is the very reason why the Hückel rule can be interpreted in thermodynamic terms. We can safely say on this basis that all kinds of $(4n+2)$-π-electron systems are thermodynamically stable.

Thermodynamic stability of a molecule due to cyclic conjugation is given numerically by the graph-theoretically defined resonance energy, RE.[14–18] It is defined as the difference in total π-electron energy between a given conjugated system and its reference system. RE is expressed explicitly as

$$\mathrm{RE} = \sum_{m=1}^{N} g_m(X_m - X_m^\circ), \tag{7}$$

where g_m is the occupation number for the mth MO. The mth orbital resonance energy, ORE_m, is defined as[27]

$$\mathrm{ORE}_m = X_m - X_m^\circ. \tag{8}$$

Since Eq. 5 holds, ORE_m is positive if $m=2p+1$, and negative otherwise. Therefore, the HOMO resonance energy of a $(4n+2)$-π-electron system is positive, whereas that of a $(4n)$-π-electron system is negative. RE is obtainable by adding up twice the orbital resonance energies of all occupied MO's.[27]

Figure 1 indicates that $P_G(X)$, in general, has a rather steep gradient at $X=X_1$ and X_N, compared to those at other zeroes of $P_G(X)$. This implies that the absolute values of ORE_1 and ORE_N are in general smaller than those of other orbital resonance energies. ORE_1 always has a small positive value. ORE_m is positive in sign if m=even, and negative otherwise. Except the cases of m=1 and N, the absolute values of the orbital resonance energies are rather comparable with each other. This might be understandable from Fig. 1. Since any monocyclic π system behaves as such, the sign of the overall resonance energy (i.e., RE) is determined primarily by the sign of the HOMO resonance energy, i.e., the orbital resonance energy of the HOMO.

We have calculated RE's of many monocyclic heteroconjugated systems.[14,18] Resonance energies and orbital resonance energies for four typical monocyclic π systems are listed in Table 1. Here, the Hückel parameters determined by Hess, Schaad, and Holyoke were employed.[11] For all these molecules, the sign of RE is really determined by the sign of HOMO resonance energy. No exceptions were found in accordance with the above frontier MO analyses. As predicted by the frontier MO analyses, monocyclic ($4n+2$)-π-electron systems alone have positive RE due to cyclic conjugation. There seems to be no monocyclic aromatic species which has a destabilized HOMO and no monocyclic antiaromatic species which has a stabilized HOMO.

For most neutral monocyclic systems, all bonding MO's are filled, and all antibonding MOs vacant. For these systems, aromaticity can be estimated by comparing the values of $|P_G(i)|$ and $|R_G(i)|$, where $i=\sqrt{-1}$.[15,28] If $|P_G(i)|>|R_G(i)|$ for a given species G, it is aromatic thermodynamically. Logarithms of $|P_G(i)|$ and $|R_G(i)|$ are roughly proportional to the total π-electron energies of G and its olefinic reference structure, respectively.[15] K_G increases or decreases the value of $|P_G(i)|$ according to the Hückel rule. If G has $2n+1$ bonding MO's with $4n+2$ π electrons, K_G makes $|P_G(i)|$ larger than $|R_G(i)|$, and positive RE results. There are no exceptions.

Table 1. Orbital Resonance Energies of Monocyclic π Systems

m	X_m	X_m°	ORE_m/β[a]
A. 1,4-Dihydropyrazine (RE=−0.132β)			
1	2.547	2.494	0.053
2	2.034	2.146	−0.112
3	1.000	0.833	0.167
4	−0.047	0.127	−0.174
5	−1.000	−1.121	0.121
6	−1.534	−1.479	−0.055
B. Imidazole (RE=0.196β)			
1	2.366	2.334	0.032
2	1.064	1.270	−0.206
3	0.633	0.361	0.272
4	−0.892	−0.706	−0.186
5	−1.292	−1.380	0.088
C. Pyrimidine (RE=0.193β)			
1	1.749	1.704	0.045
2	0.961	1.248	−0.287
3	0.915	0.578	0.337
4	−0.535	−0.268	−0.267
5	−0.727	−0.923	0.196
6	−1.604	−1.578	−0.026
D. Azepine (RE=−0.288β)			
1	2.398	2.381	0.017
2	1.600	1.719	−0.119
3	1.247	1.057	0.190
4	−0.021	0.210	−0.231
5	−0.445	−0.653	0.208
6	−1.476	−1.374	−0.102
7	−1.802	−1.841	0.039

a) β is an absolute value of β.

Magnetotropic Aspect of the Hückel Rule

It has widely been accepted that aromatic and antiaromatic annulenes are diatropic and paratropic, respectively.[29] Magnetotropism of annulens is simply determined by the number of π electrons. Therefore, it is predictable from the Hückel rule. Let us examine whether or not the magnetotropism of an arbitrarily chosen monocyclic π system is predictable from the Hückel rule.

When the magnetic field is applied to a monocyclic π system, only the term K_G in $P_G(X)$ changes.[16,27,30] All coefficients of $R_G(X)$ are not dependent upon the external field. If the field is perpendicular to the molecular plane, K_G is expressed as

$$K_G = 2\cos\left(\frac{eSB}{\hbar}\right)\prod_{(ij)}^{G} k_{ij}, \tag{9}$$

where B is the field strength, S is the area of the ring, and e is the charge of an electron.

Since K_G slightly decreases in the magnetic field, $P_G(X)$ displaces slightly downward toward the location of $R_G(X)$. Accordingly, every MO with positive orbital resonance energy is destabilized by the field, whereas every MO with negative orbital resonance energy is stabilized by the field. The former MO contributes to the exaltation of molecular diamagnetism.[27,31] The latter MO is paramagnetic in nature, decreasing molecular diamagnetism. The HOMO of a monocyclic system with $4n+2$ π electrons is always diamagnetic or diatropic in nature. These magnetic effects arise from the ring current induced in a cyclic system.

Haddon[32] and Aihara[33] proved that the ring current intensity is proportional to the product of the resonance energy and the ring area for all aromatic annulenes and annulene ions. Aihara extended this idea to all monocyclic π systems, and found that the induced ring current is approximately proportional to the resonance energy, multiplied by the area of the ring.[34] Since it has been proved that monocyclic systems with $4n+2$ π electrons have positive RE, they all are necessarily diatropic. Those with $4n$ π electrons have negative RE, so they must be paratropic. Thus, magnetotropism is an excellent index for determining the degree of aromatic stabilization. Conversely, the Hückel rule can be used assuredly to determine the sign of magnetropism for all monocyclic π systems.

Concluding Remarks

The Hückel rule has been used successfully to identify innumerable monocyclic π systems as aromatic or antiaromatic species. The above treatments based on graph theory and frontier orbital theory revealed novel physical implications of the Hückel rule, and justified well the use of it. It has been established that any monocyclic $(4n+2)$-π-electron system has not only kinetic but also thermodynamic stabilities. The sign of the overall resonance energy is determined simply by the number of π electrons. Ichikawa and Ebisawa[35] recently found a nice correlation between the Hückel resonance energy[11] and the kinetic energy of π electrons.

If a given monocyclic molecule has a singly twisted π system (i.e., a Möbius ring system),[36] the sign of K_G in Eq. 2 becomes negative.[17,37] The curve $Y=P_G(X)$ for a Möbius system displaces upward from the curve $Y=R_G(X)$. When a $(4n+2)$-π-electron Möbius system is divided into two segments, a phase dislocation occurs between the frontier MO's of the two segments. For a $(4n)$-π-electron Möbius system, however, it does not occurs. The Hückel rule is thus reversed. Any Möbius system with $4n+2$ π electrons then becomes antiaromatic, and any Möbius system with $4n$ π electrons aromatic.

The Hückel rule and the above explanation of it do not apply to highly charged molecules since electrostatic interactions are far from being balanced. Thus, such species as tetraanions and tetracations of monocyclic π systems may be very unstable even if they have $4n+2$ π electrons. We might say that the Hückel rule is universally applicable as far as intramolecular electrostatic interactions are well-balanced.

If the Hückel rule seems not to be applicable to a given neutral molecule, the validity of its bonding scheme, rather than that of the Hückel rule, should be questioned. For example, phosphole does not behave like an aromatic molecule although it appears to be iso-π-electronic with pyrrole.[4] Cyclophosphazene of any size is neither aromatic nor antiaromatic.[38] Its diamagnetic susceptibility can be estimated additively with respect to constituent atoms and bonds.[39] There must be no cyclic conjugation in these compounds, and the Hückel rule is not applicable.

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