Topological reference systems

Takayuki OHMAE

Department of Human Nutrition, Faculty of Nursing and Human Nutrition, Yamaguchi Prefectural University, 3-2-1 Sakurabatake, Yamaguchi City, Yamaguchi 753-8502 Japan
ohmae@yamaguchi-pu.ac.jp

A topological reference system is a theory that allows the visualization of the effects of a ring structure on the energy stabilization of π-electron conjugated systems. In this study, the original paper was reconfigured to introduce the definition of the topological reference system and practical calculation method.

Key Words: Aromaticity, Resonance energy, Reference system, Visualization, Topology.

1. Introduction

When discussing the aromaticity of a ring π-electron conjugated compound, the resonance energy, $E_\pi^{res.}$, is defined as per Equation 1.

$$E_\pi^{res.} \equiv E_\pi^{real} - E_\pi^{ref.} \qquad (1)$$

However, here, E_π^{real} represents the total actual π-electron energy of a ring π-electron conjugated system, and $E_\pi^{ref.}$ represents the total π-electron energy of a hypothetical reference system of that ring π-electron conjugated system. The selection of the reference system is arbitrary, and various $E_\pi^{res.}$ values have been suggested to solve a variety of problems [1].

Among these various $E_\pi^{res.}$ values, the topological resonance energy (heretofore referred to as TRE) defines the hypothetical π-electron conjugated system as a reference system with all of the effects of ring structure removed from the ring π-electron conjugated system. Because it has a wide application range and clarity in physical imaging, it has been applied to various problems and produced satisfactory results [2]. However, $E_\pi^{res.}$ with TRE is only effective for a thermodynamic aromaticity of the ring π-electron conjugated system in question and cannot be applied to other problems in kinetic aromaticity related to the chemical reactivity influenced by the electron distribution of the system. In addition, many of the $E_\pi^{res.}$ values in the reference system are hypothetical and cannot examine the relationship between the structural and physical properties based on the electron distribution.

The kinetic and thermodynamic aromaticity can be discussed by comparing the quantum chemistry indices that are involved in the reactivity of the reference and the real ring π-electron conjugated systems, such as π-electron density and polarizability. Expanding the TRE theory will be an interesting topic. In addition, if the TRE reference system can be visualized, it becomes possible to expand the graphical discussion used widely in the TRE research area to the reference system, thereby deepening understanding of the true nature of aromaticity. However, thus far, these attempts have only been performed in graphical research with partial aromaticity by Gutman [3].

Therefore, in this report, TRE is reformulated using the propagator method based on the Hückel approximation in the next chapter, and through this process, the topological reference system (hereinafter referred to as TRS), a hypothetical concept that allows visualization, is proposed. Then, the quantum chemistry indices of the TRS are defined by the propagator from the analogical inferences with the real π-electron conjugated system. In addition, a general expression for the TRS quantum chemistry index for a simple ring π-electron conjugated

system is obtained in Chapter 3. To more appropriately use TRS in the π-electron conjugated system for a complicated structure, the TRS quantum chemistry index is calculated from the results of the TRS molecular orbital calculation by Hückel with visualization as a concrete structure, and the method is introduced in Chapter 4.

2. Topological reference system
2.1. Propagator method

First, the propagator method based on the Hückel approximation used in the TRE re-formulation, is summarized in accordance with Aono *et al.* [4]. The propagator, $G(z)$, is defined as Equation 2 below.

$$(z - H)G(z) = 1 \qquad (2)$$

In Equation 2, z is an energy parameter and H is a Hamiltonian, which describes the system. Here, if the complete orthonormal system of H, or a pair of $\{\,|\,n>\}$ that satisfies below is known,

$$H|n\rangle = \epsilon_n|n\rangle \qquad (3)$$
$$\langle n|m\rangle = \delta_{nm} \qquad (4)$$
$$\sum_n |n\rangle\langle n| = 1 \qquad (5)$$

$G(z)$ can be expressed as Equation 6 below by subtracting Equation 5 from Equation 2.

$$G(z) = \sum_n \frac{|n\rangle\langle n|}{z - \epsilon_n} \qquad (6)$$

Now, assuming that the π-electron in the π-electron conjugated system in discussion can be described well by the Hückel Hamiltonian shown by Equation 7,

$$H = \sum_s |s\rangle\alpha_s\langle s| + \sum'_{st}|s\rangle\beta_{st}\langle t|, \quad (7)$$

and considering a situation where the system consists of atoms that are all the same, the Coulomb integral, α_s, and the resonance integral, β_{st}, in Equation 7 can be expressed as below.

$$\alpha_s = \alpha = 0 \qquad (8)$$
$$\beta_{st} = \beta = 1 \qquad (9)$$

The Hückel Hamiltonian in Equation 7 is now simplified as Equation 10 below.

$$H = \sum'_{st}|s\rangle\langle t| \qquad (10)$$

However, the prime symbols at the summation symbols in Equations 7 and 10 indicate that the sum is between adjacently-bonded atoms. In addition, in the discussion below, the basis function in each atom of the π-electron conjugated system is hypothesized as a complete orthonormal system that satisfies Equations 3 to 5.
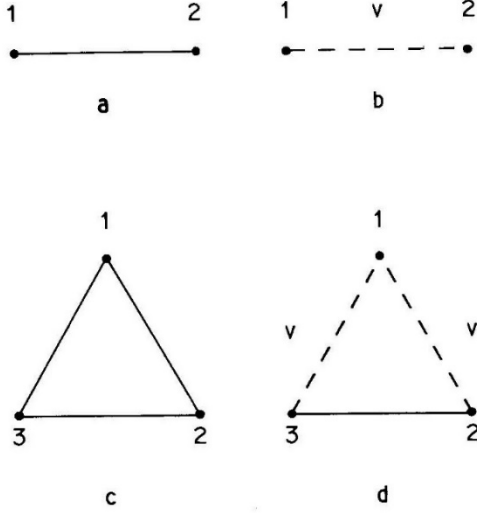
Fig.1 Schematic diagrams of molecules.
a: Diatomic molecule, b: nonperturbative diatomic molecule, c: triatomic ring molecule,
d: nonperturbative triatomic ring molecule.

Consider a diatomic molecule (Figure 1a) well-described by Hückel Hamiltonian theory in Equation 10. According to Equation 6, the diagonal element in the atomic orbital display for the 0th order propagator for the atom 1 in this diatomic molecule, $G_2^0(1)$, namely the propagator of a nonperturbative system with no interaction between atoms 1 and 2, v, (Figure 1b) is expressed simply as Equation 11 below.

$$G_2^0(1) = \frac{1}{z} \tag{11}$$

According to the self-consistent perturbation theory by Anderson [5], the diagonal element in atom 1 of the correct diatomic molecule that has incorporated v to the infinite dimension, $G_2(1)$, can be given by Equation 12 below.

$$G_2(1) = G_2^0(1) + G_2^0(1)v_{12}G_2^0(2)v_{21}G_2(1) \tag{12}$$

Combining Equations 11 and 12 gives Equation 13

$$G_2(1) = [\, G_2^0(1)^{-1} - v_{12}G_2^0(2)v_{21} \,]^{-1} \;=\; \frac{z}{z^2-1} \tag{13}$$

The pole in Equation 13 represents the Hückel molecular orbital energy. However, here, v_{12} and v_{21} are both 1 to maintain consistency with the substitution of Equation 9. In addition, $G_2^0(1) = G_2^0(2)$ as noted.

Integrating the obtained propagator by the path integral formulation C that may contain the pole corresponding to the occupied orbital inside, all π energy, E_π, π-electron density, q_r, bond order, p_{st}, and an atom's self-polarizability, π_{rr}, are obtained as below.

$$E_\pi = \sum_s \frac{1}{2\pi i} \int_c \, dz \, z G(s) \tag{14}$$

$$q_r = \frac{1}{2\pi i} \int_c \, dz \, G(r) \tag{15}$$

$$p_{st} = \frac{1}{2\pi i} \int_c \, dz \, G(s,t) \tag{16}$$

3

$$\pi_{r,r} = \frac{1}{2\pi i} \int_c dz\, G(r)G(r) \qquad (17)$$

However, the integral symbols in Equations 14 to 17 can also indicate the spin total. In addition, one needs to pay attention that, as the definition from Equation 16 using the propagator shows, p_{st} which was thought to be an index showing the bond strength, is only the probability amplitude between the atoms st. As described later, the bond strength between the atoms st must be defined as a quantity related to the bond energy. To minimize the impact to the traditional discussion, instead of p_{st}, an index showing the bond strength is defined in the next equation. However, here, a_{ts} indicates an element between ts in the adjacent matrix [6].

$$q_{st} = \frac{1}{2\pi i} \int_c dz\, G(s,t)a_{ts} \qquad (16a)$$

In a real π-electron conjugated system, it is apparent that the values of Equations 16 and 16a match.

2.2. Topological reference system

To simplify the discussion, please consider a three-membered ring in Figure 1c. Considering Figure 1d as a nonperturbative system and according to the self-consistent perturbation theory by Anderson, the diagonal element for atom 1 of the propagator for this three-membered ring, $R_3(1)$, can be given as Equation 18, which is similar to Equation 12.

$$R_3(1)^{-1} = R_3^0(1)^{-1} - v_{12}R_3^0(2)v_{21} - v_{13}R_3^0(3)v_{31} - v_{12}R_3^0(2,3)v_{31} - v_{13}R_3^0(3,2)v_{21} \qquad (18)$$

However, $R_3^0(2,3)$ and $R_3^0(3,2)$ in Equation 18 indicate nondiagonal elements between atoms 2 and 3 of the propagator in Figure 1d. In addition, each of the propagators of the nonperturbative system that appear on the right of Equation 18 are given as below [4].

$$R_3^0(1) = \frac{1}{z} \qquad (19)$$

$$R_3^0(2) = R_3^0(3) = \frac{z}{z^2-1} \qquad (20)$$

$$R_3^0(2,3) = R_3^0(3,2) = \frac{1}{z^2-1} \qquad (21)$$

Substituting Equations 19 to 21 to Equation 18 gives Equation 22 below.

$$R_3(1) = \frac{(z+1)(z-1)}{(z+1)^2(z-2)} \qquad (22)$$

However, here, v is 1 again.

Looking at Equation 18, one needs to consider the physical meaning of each item that configures the propagator of the three-membered ring once again. Figure 2 shows each item on the right of Equation 18 schematically. From this figure, it is clear that the fourth and fifth items on the right of Equation 18 reflect the ring structure of the three-membered ring. TRE assumes that the reference system is the system with all the interaction propagation effects that have reflected the removed ring structure [2], and when the propagator with the fourth and fifth items on the right of Equation 18 is removed, $R_3^{ref.}(1)$, is obtained experimentally, and Equation 23 below is obtained.

$$R_3^{ref.}(1) = \frac{(z+1)(z-1)}{z(z+\sqrt{3})(z-\sqrt{3})} \qquad (23)$$

It is important to note that the pole of this propagator correctly matches the answer of the TRE reference polynomial expression for the three-membered ring [7] as well as the fact that Equation 23 matches the propagator of the central location of the chain π-electron conjugated system composed of five atoms. From this, when calculating the diagonal element of the propagator for the ring π-electron conjugated system, not only can the propagator showing the TRE reference system be obtained by removing all the items that reflect the ring structure from the equation corresponding to Equation 18, but a practical calculation method, such as TRS electron density shown in Chapter 4, can also be devised.
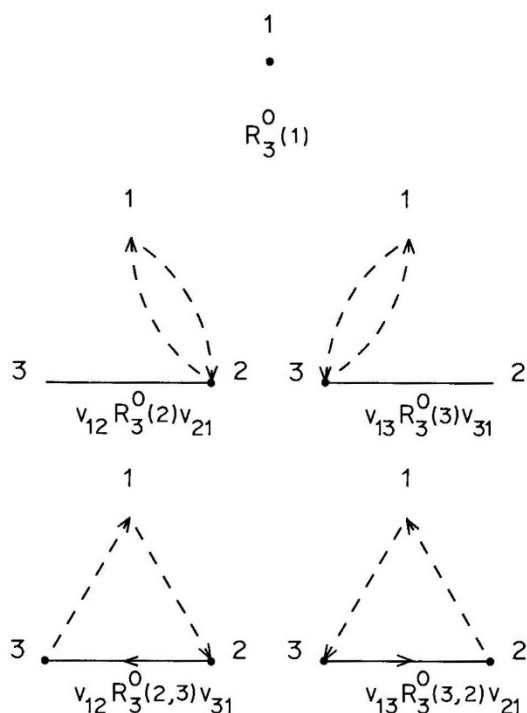

Fig.2　Schematic diagrams of the interactions between 1 and 2-3 subsystems. Broken lines indicate perturbations.

Once the propagator is obtained, the quantum chemistry index of the system in consideration can be calculated simply using the relational expression of Equations 14 to 17. In other words, if one can assume the TRS as the hypothetical system with all of the effects of the ring interaction propagation removed from the real system and obtain one pair of propagators that describes the TRS, the effects of the ring structure on various physiochemical qualities of the system can be considered using the propagators describing the real system and TRS.

Now, let us obtain the nondiagonal element of the propagator between atoms 1 and 2 in TRS, $R_3^{\text{ref.}}(1,2)$; Equation 23 shall be integrated later. Considering Figure 1d as a nonperturbative system here as well, Equation 25 is obtained from the Dyson formula [8] (Equation 24).

$$\boldsymbol{G} = \boldsymbol{G}^0 + \boldsymbol{G}^0 \boldsymbol{v} \boldsymbol{G} \tag{24}$$

$$R_3(1,2) = R_3^0(1)v_{12}R_3(2) + R_3^0(1)v_{13}R_3(3,2) \tag{25}$$

Furthermore, Equations 26 and 27 are obtained from Equation 24.

$$R_3(2) = R_3^0(2) + R_3^0(2)v_{21}R_3(1,2) + R_3^0(2,3)v_{31}R_3(1,2) \qquad (26)$$

$$R_3(3,2) = R_3^0(3,2) + R_3^0(3)v_{31}R_3(1,2) + R_3^0(3,2)v_{21}R_3(1,2) \qquad (27)$$

Substituting Equations 26 and 27 into Equation 25 gives $R_3(1,2)$ as Equation 28 below

$$R_3(1,2) = R_3(1)[v_{12}R_3^0(2) + v_{13}R_3^0(3,2)] \qquad (28)$$

Therefore, substituting $R_3(1)$ on the right of Equation 28 with $R^{ref.}_3(1)$ that has the effects of ring structure removed gives Equation 29 giving the nondiagonal element of the propagator of TRS for the three-membered ring.

$$R_3^{ref.}(1,2) = R_3^{ref.}(1)[v_{12}R_3^0(2) + v_{13}R_3^0(3,2)] \qquad (29)$$

Substituting Equations 19 to 21 into Equation 29 gives Equation 30.

$$R_3^{ref.}(1,2) = \frac{z+1}{z(z+1)(z-1)} \qquad (30)$$

However, here, v is 1 again.

　　Table 1 shows the calculated results in quantity, such as all π-electron energy, for the TRS of the three-membered ring obtained above.

Table 1　Quantum chemistry indices for the three-membered ring and the TRS ($\alpha=0$, $\beta=1$)

	Cation	Anion
$E_\pi{}^{real}$	4	2
$E_\pi{}^{ref.}$	$2\sqrt{3}$	$2\sqrt{3}$
TRE	0.54	-1.46
q_1	2/3	4/3
$q_1{}^{ref.}$	2/3	4/3
p_{12}	2/3	1/3
$p_{12}{}^{ref.}$	$(\sqrt{3}+1)/3$	$(\sqrt{3}-1)/3$
q_{12}	2/3	1/3
$q_{12}{}^{ref.}$	$1/\sqrt{3}$	$1/\sqrt{3}$
$\pi_{1;1}$	8/27	∞
$\pi_{1;1}{}^{ref.}$	$2\sqrt{3}/9$	$2\sqrt{3}/9$

As a result, the values of TRE, q_{12}, and $\pi_{1;1}$ show that the ring interaction gives thermodynamic stability, stronger bonding between adjacent atoms, and stability for addition reactions to the cations in the three-membered ring. However, one should note here that the self-polarizability is an index that shows the instability of a π-electron conjugated system [9]. Furthermore, the calculated results for the anions in the three-membered ring have shown that the ring interaction has an opposite effect to the system from cations. In addition, as Table 1 shows, one should note that there is a relationship shown as below [10] between the indices that show all the π-electron energy, electron density, and bond strength in both real systems and TRS.

$$E_\pi = \sum_r q_r\,\alpha + \sum'_{s,t} q_{st}\,\beta \qquad (31)$$

The relationships of $R_3(1) = R_3(2) = R_3(3)$ and $R_3^{ref.}(1) = R_3^{ref.}(2) = R_3^{ref.}(3)$ were used when calculating E_π^{real} and E_π^{ref}. Furthermore, $q_{st}^{ref.}$ was defined as the following equation.

$$q_{st}^{ref.} = \frac{1}{2\pi i} \int_c dz \, [G(s,t)a_{ts}]^{ref.}$$

(32)

Here, $[\cdots]^{ref.}$ means that the ring effects are all removed from […]. In $q_{st}^{ref.}$ for the three-membered ring, the second item within the brackets in the right of Equation 29 is removed by this operation.
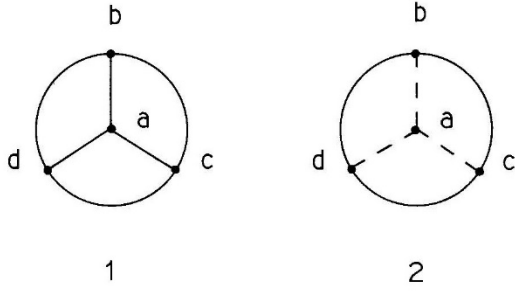

Fig.3   Schematic diagrams of a polycyclic molecule and its nonperturbative system. Broken lines indicate perturbations.

Now, expand the above discussion and consider how to obtain the diagonal element of the propagator describing the TRS of a general polycyclic π-electron conjugated system. But as has been mentioned earlier, the nondiagonal element is easily obtainable from the diagonal element, and so its discussion is omitted here.

Now, the polycyclic π-electron conjugated system of interest has a configuration of only three adjacent atoms bonded, and so it is enough to consider the system shown in Figure 3.1. Taking Figure 3.2 as the nonperturbative system of Figure 3.1 and applying Equation 24 gives Equations 33 to 34c below.

$$G(a) = G^0(a) + G^0(a)v_{ab}G(b,a) + G^0(a)v_{ac}G(c,a) + G^0(a)v_{ad}G(d,a)$$

(33)

$$G(b,a) = G^0(b)v_{ba}G(a) + G^0(b,c)v_{ca}G(a) + G^0(b,d)v_{da}G(a)$$

(34a)

$$G(c,a) = G^0(c)v_{ca}G(a) + G^0(c,b)v_{ba}G(a) + G^0(c,d)v_{da}G(a)$$

(34b)

$$G(d,a) = G^0(d)v_{da}G(a) + G^0(d,b)v_{ba}G(a) + G^0(d,c)v_{ca}G(a)$$

(34c)

From these equations, it is clear that the diagonal element for the atom a of the propagator of the system in Figure 3.1 can be given by the following equation.

$$G(a)^{-1} = G^0(a)^{-1} - v_{ab}G^0(b)v_{ba} - v_{ac}G^0(c)v_{ca} - v_{ad}G^0(d)v_{da}$$
$$-v_{ab}G^0(b,c)v_{ca} - v_{ac}G^0(c,b)v_{ba} - v_{ab}G^0(b,d)v_{da}$$
$$-v_{ad}G^0(d,b)v_{ba} - v_{ac}G^0(c,d)v_{da} - v_{ad}G^0(d,c)v_{ca}$$

(35)

It is clear that the effects of the interaction propagation of the ring with the atom a of this system are shown by the six items, the fifth to the tenth items in the right of Equation 35, by a similar operation as Figure 2. These items need to be removed first, and then the same operation is repeated for atoms b, c, and d that are bonded to the atom a to remove all the interaction propagation effects periodically. Then, the propagator that describes the TRS of a

general polycyclic system is given by Equation 36 below.

$$G^{ref\cdot}(a)^{-1} = G^0(a)^{-1} - v_{ab}G^{0,ref\cdot}(b)v_{ba} - v_{ac}G^{0,ref\cdot}(c)v_{ca} - v_{ad}G^{0,ref\cdot}(d)v_{da} \quad (36)$$

However, here, superscript 0 indicates the nonperturbative system of Figure 3.2, and $G^{0,ref\cdot}(s)$ indicates a diagonal element of the TRS propagator in atom s of the nonperturbative system.

3. Application to simple systems
3.1. Hückel annulenes

Consider a Hückel annulene that has n-number of the same atoms with the basis function in-phase and adjacent (Figure 4a). Figure 4a shows a configuration in which a carbon atom is arranged in a π-electron conjugated system using 2p-orbitals, without any elemental limitation, except that all basis functions are adjacent and in-phase. Furthermore, the symmetry shows that all atoms in this cyclic π-electron conjugated system are equivalent. However, the atoms have been numbered clockwise from the arbitrary atom for convenience.

To investigate the effects of a ring structure on various physical and chemical properties in this π-electron conjugated system, it is hypothesized that the system is well-described by the Hamiltonian of Equation 10. Under this approximation, the diagonal elements of propagators for the Hückel annulene, $R_n^H(1)$, and TRS, $R_n^{H,ref\cdot}(1)$, are obtained as Equations 37 and 38 using the same methods as for Equations 18, 22, and 23.

$$R_n^H(1) = [\ G_n^0(1)^{-1} - v_{12}G_n^0(2)v_{21} - v_{1n}G_n^0(n)v_{n1}$$
$$-v_{12}G_n^0(2,n)v_{n1} - v_{1n}G_n^0(n,2)v_{21}]^{-1} \quad (37)$$

$$R_n^{H,ref\cdot}(1) = [\ G_n^0(1)^{-1} - v_{12}G_n^0(2)v_{21} - v_{1n}G_n^0(n)v_{n1}]^{-1} \quad (38)$$

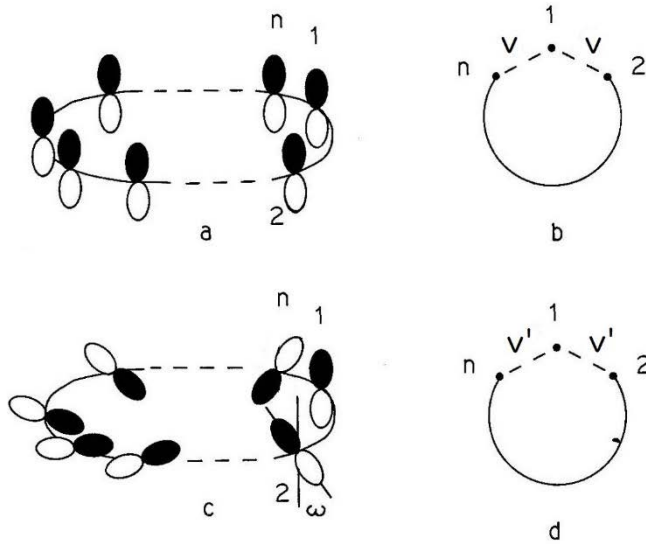**Figure 4   Diagrams of annulenes with the same type of atoms and bonding lengths. a: Hückel annulene, b: nonperturbation system of Hückel annulene, c: Möbius annulene, and d: nonperturbation system of Möbius annulene.**

Figure 4 shows that $G_n^0(1)$ is a single atom propagator, and $G_n^0(2)$ and $G_n^0(n)$ are the diagonal elements for the atoms at the end of the linear π-electron conjugated system that is made up of (n-1) number of the same atoms. In addition, $G_n^0(2,n)$ and $G_n^0(n,2)$ are the nondiagonal elements between the atoms at both ends of the linear π-electron conjugated system that is

made up of (n-1) number of the same atom. There are known general equations for these propagators using a trigonometric function, which can be used to obtain a general equation for the quantum chemistry indices defined by Equations 14–17.

$$G_n^0(1) = G_1(1) = \frac{\sin\theta}{\sin 2\theta} \tag{39}$$

$$G_n^0(2) = G_n^0(n) = G_{n-1}^L(1) = \frac{\sin(n-1)\theta}{\sin n\theta} \tag{40}$$

$$G_n^0(2,n) = G_n^0(n,2) = G_{n-1}^L(1, n-1) = \frac{\sin\theta}{\sin n\theta} \tag{41}$$

Notably, the superscript, *L*, implies a chain molecule. In addition, a situation without bond alternation was considered to simplify the discussion; however, this limitation can be easily removed [11].

Substituting Equations 39–41 into Equations 37 and 38 and simplifying it gives Equations 42 and 43.

$$R_n^H(1) = -\frac{\cos\frac{n\theta}{2}}{2\sin\theta\sin\frac{n\theta}{2}} \tag{42}$$

$$R_n^{H,ref.}(1) = \frac{\sin n\theta}{2\sin\theta\cos n\theta} \tag{43}$$

Note that the range of θ is as follows.

$$-\pi \leq \theta < \pi \tag{44}$$

In addition, $v = 1$ was set as before. Similarly, the nondiagonal terms can be obtained as follows.

$$R_n^H(1,2) = -\frac{\cos(\frac{n}{2}-1)\theta}{2\sin\theta\sin\frac{n\theta}{2}} \tag{45}$$

$$R_n^{H,ref.}(1) = \frac{\sin(n-1)\theta}{2\sin\theta\cos n\theta} \tag{46}$$

Substituting Equations 42–46 into Equations 17 and 32 and integrating them gives the quantum chemistry indices of the Hückel annulene as follows.

$$E_n^H = 4\sin\frac{2m\pi}{n}\cot\frac{\pi}{n}, M = 4m \tag{47a}$$

$$= 4\sin\frac{(2m+1)\pi}{n}\csc\frac{\pi}{n}, M = 4m+2 \tag{47b}$$

$$E_n^{H,ref.} = 2\sin\frac{m\pi}{n}\csc\frac{\pi}{2n}, M = 2m \tag{48}$$

$$q_1^H = q_1^{H,ref.} = \frac{2m}{n}, M = 2m \tag{49}$$

$$p_{12}^H = q_{12}^H = \frac{2}{n}\sin\frac{2m\pi}{n}\cot\frac{\pi}{n}, M = 4m \tag{50a}$$

$$= \frac{2}{n}\sin\frac{(2m+1)\pi}{n}\csc\frac{\pi}{n}, M = 4m+2 \tag{50b}$$

$$p_{12}^{H,ref.} = \frac{1}{n}\sin\frac{m\pi}{n}\{\csc\frac{\pi}{2n} + (-1)^{m-1}\sec\frac{\pi}{2n}\}, M = 2m \tag{51}$$

$$q_{12}^{H,ref.} = \frac{1}{n}\sin\frac{m\pi}{n}\operatorname{cosec}\frac{\pi}{2n}, M = 2m \tag{52}$$

$$\pi_{1;1}^{H} = \frac{1}{3}\left(1 - \frac{1}{n^2}\right) + \frac{4}{n^2}\sum_{j=1}^{m}\cot\frac{2\pi j}{n}\operatorname{cosec}\frac{2\pi j}{n}, M = 4m + 2 \tag{53}$$

$$\pi_{1;1}^{H,ref.} = \frac{1}{n^2}\sum_{j=0}^{m-1}\cot\frac{(2j+1)\pi}{2n}\operatorname{cosec}\frac{(2j+1)\pi}{2n}, M = 2m \tag{54}$$

$$TRE^{H} \equiv E_n^{H} - E_n^{H,ref.}$$

$$= -8\sin\frac{2m\pi}{n}\cos en\frac{\pi}{n}\sin\frac{3\pi}{4n}\sin\frac{\pi}{4n}, M = 4m \tag{55}$$

$$= 8\sin\frac{(2m+1)\pi}{n}\operatorname{cosec}\frac{\pi}{n}\sin^2\frac{\pi}{4n}, M = 4m + 2 \tag{56}$$

Although the details are described in the original report [12], these results enable us to investigate the effects of the ring structure on the thermodynamic stability and chemical reactivity within the same theoretical framework. Notably, TRE^H represents the TRE of a Hückel annulene.

3.2. Möbius annulene

Next, consider a Möbius annulene in which the basis function of an n-number of the same atom numbered as in Figure 4c is tilted by $\omega = \pi / n$ relative to an atom with a lower number and coupled via σ-bond. Similarly, it was hypothesized that the Hamiltonian, described in Equation 10, adequately represents this system. However, as previously discussed, the basis function is tilted by
π /n for coupling in a Möbius annulene, and note that the sign for the resonance integral between atoms 1 and n is the inverse of the one between other atoms (Equation 57).

$$v'_{1n} = v'_{n1} = -1 \tag{57}$$

Taking the nonperturbative system of the Möbius annulene as the one illustrated in Figure 4d and considering the relationship between Equations 37, 38, and 57, the diagonal elements of the propagator for the Möbius annulene and the TRS atom 1 can be obtained as follows.

$$R_n^{M}(1) = [\, G_n^0(1)^{-1} - v'_{12}G_n^0(2)v'_{21} - v'_{1n}G_n^0(n)v'_{n1}$$
$$-v'_{12}G_n^0(2,n)v'_{n1} - v'_{1n}G_n^0(n,2)v'_{21}]^{-1} \tag{58}$$

$$R_n^{M,ref.}(1) = [\, G_n^0(1)^{-1} - v'_{12}G_n^0(2)v'_{21} - v'_{1n}G_n^0(n)v'_{n1}]^{-1} \tag{59}$$

Here, apart from the size of the resonance integral, the propagators of the nonperturbative system described in Equations 58 and 59 are identical to those shown in Equations 39–41, enabling the following results.

$$R_n^{M}(1) = \frac{\sin\frac{n\theta}{2}}{2\sin\theta\cos\frac{n\theta}{2}} \tag{60}$$

$$R_n^{M,ref.}(1) = \frac{\sin n\theta}{2\sin\theta\cos n\theta} \tag{61}$$

In addition, the nondiagonal elements of R_n^{M} and $R_n^{M,ref}$ are obtained as follows.

$$R_n^{M}(1,2) = R_n^{M}(1)[v'_{12}G_n^0(2) + v'_{1n}G_n^0(2,n)] = \frac{\sin\left(\frac{n}{2}-1\right)\theta}{2\sin\theta\cos\frac{n\theta}{2}} \tag{62}$$

$$R_n^{M,ref.}(1,2) = R_n^{M,ref.}(1)v'_{12}G_n^0(2) = \frac{sinn\theta}{2sin\theta cosn\theta} \tag{63}$$

Notably, the range of θ is again the range of Equation 44. In addition, when obtaining Equations 62 and 63, $v'_{12} = 1$ and $v'_{1n} = -1$ were substituted to maintain consistency with Equation 10.

Calculating the quantum chemistry indices for the Möbius annulene using the propagators yields the following results.

$$E_n^M = 4\sin\frac{2m\pi}{n}\operatorname{cosec}\frac{\pi}{n}, M = 4m \tag{64a}$$

$$= 4\sin\frac{(2m+1)\pi}{n}\cot\frac{\pi}{n}, M = 4m+2 \tag{64b}$$

$$E_n^{M,ref.} = 2\sin\frac{m\pi}{n}\operatorname{cosec}\frac{\pi}{2n}, M = 2m \tag{65}$$

$$q_1^M = q_1^{M,ref.} = \frac{2m}{n}, M = 2m \tag{66}$$

$$p_{12}^M = q_{12}^M = \frac{2}{n}\sin\frac{2m\pi}{n}\operatorname{cosec}\frac{\pi}{n}, M = 4m \tag{67a}$$

$$= \frac{2}{n}\sin\frac{(2m+1)\pi}{n}\cot\frac{\pi}{n}, M = 4m+2 \tag{67b}$$

$$p_{12}^M = -p_{1n}^M = q_{12}^M = -q_{1n}^M \tag{68}$$

$$p_{12}^{M,ref.} = -p_{1n}^{M,ref.} = \frac{1}{n}\sin\frac{m\pi}{n}\{\operatorname{cosec}\frac{\pi}{2n} + (-1)^m\sec\frac{\pi}{2n}\}, M = 2m \tag{69}$$

$$q_{12}^{M,ref.} = -q_{1n}^{M,ref.} = \frac{1}{n}\sin\frac{m\pi}{n}\operatorname{cosec}\frac{\pi}{2n}, M = 2m \tag{70}$$

$$\pi_{1;1}^M = \frac{4}{n^2}\sum_{j=0}^{m-1}\cot\frac{\pi}{n}(2j+1)\operatorname{cosec}\frac{\pi}{n}(2j+1), M = 4m \tag{71}$$

$$\pi_{1;1}^{M,ref.} = \frac{1}{n^2}\sum_{j=0}^{m-1}\cot\frac{\pi}{2n}(2j+1)\operatorname{cosec}\frac{\pi}{2n}(2j+1), M = 2m \tag{72}$$

$$TRE^M \equiv E_n^M - E_n^{M,ref.}$$

$$= 8sin\frac{2m\pi}{n}cosen\frac{\pi}{n}sin^2\frac{\pi}{n}, M = 4m \tag{73}$$

$$= -8sin\frac{(2m+1)\pi}{n}cosec\frac{\pi}{n}sin\frac{3\pi}{4n}, M = 4m+2 \tag{74}$$

4. Practical calculation method

As previously stated, for simple systems such as Hückel and Möbius annulenes, the true system and its TRS are described via a simple propagator, allowing for generic calculation. However, when the structure of the π-electron conjugated system in consideration is complex, not only does obtaining the quantum chemistry indices by integrating the propagator become challenging but obtaining the propagator itself also becomes complicated. Therefore, this section describes a more simplified method for determining the quantum chemistry indices of the TRS of a general π-electron conjugated system. This method was devised based on the assembly method for a propagator under the Hückel approximation introduced in Section 2. No corrections to the Hückel molecular orbital method [13] program (hereinafter, HMO method) were added, and the quantum chemistry indices of the TRS of the π-electron conjugated system can be obtained simply by changing the angle of view.

First, let us revise the method for obtaining the diagonal elements from an atomic orbital

function expression (hereinafter, AO expression) for the propagator under the Hückel approximation describing the TRS, using the three-membered ring that was examined in detail in Section 2. According to Aono *et al.* [4], the diagonal elements, $R_3(l)$, in AO expression for the propagator in atom 1 in the three-membered ring (Figure 1c) are obtained using Equation 18 by considering Figure 1d as a nonperturbative system. In addition, Equation 75 gives the TRS propagator, $R_3^{ref}(1)$, by removing the components that reflect the ring structure from the right-hand side of Equation 18.

$$R_3^{ref.}(1)^{-1} = R_3^0(1)^{-1} - v_{12}R_3^0(2)v_{21} - v_{13}R_3^0(3)v_{31} \tag{75}$$

Disregard that Equation 75 is a hypothetical TRS propagator and examine the right-hand side explicitly. Thereafter, it should be noticed that the right-hand side of Equation 75 yielded the diagonal elements of a propagator under the Hückel approximation in atom 3 at the center of a chain molecule composed of five similar atoms with no bonding alternation (Figure 5a), and with a nonperturbative system shown in Figure 5b.
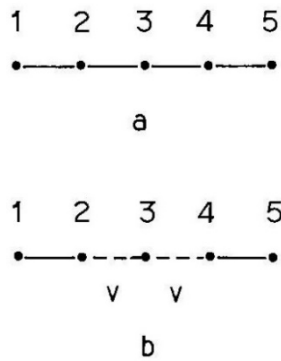

Figure 5   Five atomic linear π-electron conjugated systems and its nonperturbative systems.

Alternatively, the following relationship is established.

$$L_5(3) = \frac{z^4-2z^2+1}{z^5-4z^3+3z} = \frac{(z^2-1)^2}{(z^3-3z)(z^2-1)} \tag{76a}$$

$$= \frac{z^2-1}{z^3-3z} = R_3^{ref.}(1) \tag{76b}$$

In addition, the following relationship is clearly established for Equation 29.

$$R_3^{ref.}(1,2) = R_3^{ref.}(1)[v_{12}R_3^0(2) + v_{13}R_3^0(3,2)]$$

$$= L_5(3)[v_{34}L_5^0(4) + v_{32}L_5^0(2,1)]$$

$$= L_5(3,4) + L_5(3,1) \tag{77}$$

Note that $L_n(s,t)$ in Equations 76 and 77 indicate the s,t-elements of the propagator of the linear π-electron conjugated system composed of n-number of atoms.

From the aforementioned equations, we examined the modifications from Equation 76a to

12

Equation 76b. Noticeably, this modification and the arbitrary elements, $G(a,b)$, of the propagator under the Hückel approximation are expressed as Equation 78 using the LCAO coefficients, $C_{s,i}$, and orbital energy, ε_i, of the HMO.

$$G(a,b) = \sum_i \frac{c_{ai}^* c_{bi}}{z - \epsilon_i} \tag{78}$$

Information regarding the TRS of the three-membered ring can be extracted using the calculation results of the HMO of the five atomic linear π-electron conjugated systems and the following method.

Step A. In the HMO of the five atomic linear π-electron conjugated systems, ignore the orbital whose LCAO coefficient of atom 3 in the TRS of the three-membered ring is 0.

Step B. As the orbital energy of the orbital that remained by Step A gives the orbital energy of the TRS of the three-membered ring, use this value to calculate the total energy of the TRS, $E^{ref.}$, and TRE.

Step C. Using the LCAO coefficient of atom 3 in the five atomic chain molecule in the orbital that remained by Step A, calculate the electron density, $q^{ref.}$, self-polarizability, $\pi^{ref.}_{1;1}$, and frontier electron density, $f_1^{(E),ref.} f_1^{(N),ref.}$, for the atom 1 of the TRS of the three-membered ring.

Step D. Using the LCAO coefficients of the atoms 1, 3, and 4 of the five atomic linear π-electron conjugated systems that remained by Step A, calculate the bond order, p_{12}^{ref}, between the atoms 1 and 2 of the TRS of the three-membered ring and an index showing the bond strength, q_{12}^{ref}.

These four steps were used to calculate the quantum chemistry indices of the TRS of the three-membered ring using the HMO method results for the five atomic linear π-electron conjugated systems. The HMO method was used to calculate the five numbered atomic linear π-electron conjugated systems (Figure 5a, Table 2). Step A was followed in this case, and the orbitals with zero LCAO coefficient for atom 3 indicated by the broken line were ignored. The orbital energies for the remaining HMO orbitals were 1.7321, 0.0000, and −1.7321, in decreasing order of energy using the resonance integral as the unit. Step B shows that the HMO energy of the TRS of the three-membered ring obtained using Equation 76b is reproduced within the range of significant digits. Further, Step C was performed to calculate the quantum chemistry indices for when only the orbital of the TRS of the cation of the three-membered ring (the orbital with the orbital energy of 1.7321) is doubly occupied, and when two orbitals of the TRS of the anion of the three-membered ring (the orbitals with the orbital energies of 1.7321 and 0.0000) are doubly occupied. The quantum chemistry indices for the presence of two and six electrons in the five atomic linear π-electron conjugated systems were calculated (Table 1) within the range of significant digits. Note that $p_{12}^{ref.}$ is obtained by $p_{34} + p_{31}$ or $p_{32} + p_{35}$ of the five atomic chain molecules.

Table 2   HMO calculation results for five atomic linear π-electron conjugated systems

Position	Orbital energies				
	1.7321	1.0000	0.0000	-1.0000	-1.7321
	LCAO coefficients				
1	0.2887	0.5000	-0.5774	-0.5000	0.2887
2	0.5000	0.5000	0.0000	0.5000	-0.5000
3	0.5774	0.0000	0.5774	0.0000	0.5774
4	0.5000	-0.5000	0.0000	-0.5000	-0.5000
5	0.2887	-0.5000	-0.5774	0.5000	0.2887

The above steps are easily generalized, and the steps for obtaining a branched π-electron conjugated system that corresponds to the TRS of a more complicated cyclic π-electron conjugated system are as follows.

Step 1. From the bonding of the atoms of the true system for obtaining the TRS, consider the nonperturbative system in which the ring structure's bonding is removed.

Step 2. Sequentially restore the bonding that was cut in Step 1 to obtain a subsystem with similar number of bonds as the bonding that was removed.

Step 3. Superimpose the subsystems obtained from Step 2 onto the atom considered in Step 1.

Step 3a. If the ring structure remains in the structure obtained in Step 3, look for a branch structure connecting the atom examined in Step 1 and ring structure. Repeat Steps 1–3 for the atom connecting this branch and ring structures, and replace the ring structures with the branch structures.

Step 4. Determine the HMO of the resulting structure and the quantum chemistry indices of the TRS by following the aforementioned Steps A–D.

As an example of these generalized steps, Figure 6 shows the steps in obtaining the branched π-electron conjugated system corresponding to the TRS of α-phase in naphthalene. Refer to the original report [14] for a discussion on the practicality of this method.
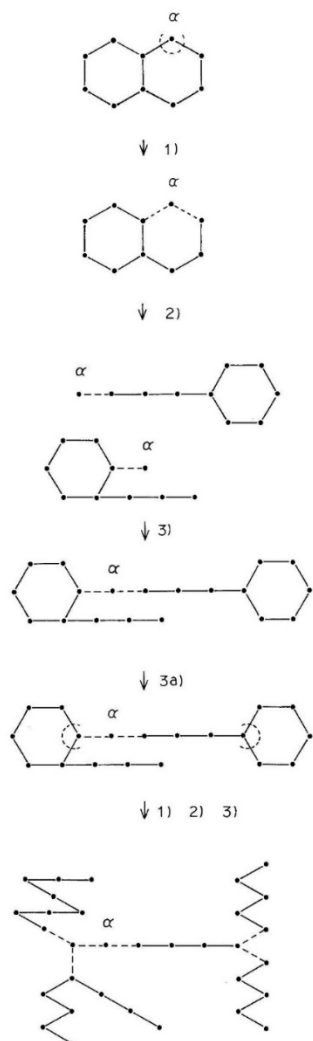

Figure 6   Branched π-electron conjugated system corresponding to the TRS of α-phase in naphthalene.

5. Conclusions

The concept of aromaticity has been employed in understanding the properties and the reaction mechanisms of molecules. This concept is defined by the ring structure's energy stabilization of the system. A hypothetical reference system is frequently used as the basis to decide the stabilization and used in the concepts of delocalization and resonance. However, these reference systems are different from the ones used in defining the aromaticity, and can be visualized, making it possible to discuss the effects of the ring structure on the electron density, which should result in a more meaningful comprehension of the aromaticity-based reaction mechanisms.

The method for the topological reference system we developed enabled us to visualize the reference system of the topological resonance energy with an excellent property as the index defining the energetic aromaticity. It also enables the study of the effects of the ring structure on the chemical reactivity of a cyclic π-electron conjugated system and the effects of ring structure in the transition state on the selectivity of chemical reactions. The theory reported here was constructed using the Hückel approximation; however, by increasing the degree of the Hamiltonian approximation, it is possible to obtain results comparable to those obtained by computation chemistry with a higher degree of approximation [15,16].

References and Notes
[1] N. Trinajistic, "Chemical graph theory", 2nd rev.ed., CRC Press, Inc., Boca Raton, (1992) pp.125-160.
[2] J. Aihara, *J. Am. Chem. Soc.,* **98**, 2750(1976); J. Aihara, *Bull. Chem. Soc. Jpn.,* **89**, 1425(2016).
[3] I. Gutman, *Bull. Soc. Chim. Beograd,* **43**, 191(1978).
[4] S. Aono, K. Nshikawa, *Bull. Chem. Soc. Jpn.,* 53, 3418(1980).
[5] P. W. Anderson, *Phys. Rev.,* **105**, 1388(1957).
[6] T. Ohmae, *J. Chem. Soc. Jpn.,* **1998,** 157(1998). (In Japanese.)
[7] O. Oka, H. Takashima, J. Aihara, *Chemistry*, 40(1), Appendix 1(1985). (In Japanese.)
[8] S. Aono, "Electronic states of molecules", KYORITSU SHUPPAN CO., LTD, (1986) pp.235-237.
[9] A. Streitwieser, Jr., "MOLECULAR ORBITAL THEORY FOR ORGANIC CHEMISTS", John Wiley & Sons, Inc., (1961) p.113.
[10] A. Streitwieser, Jr., "MOLECULAR ORBITAL THEORY FOR ORGANIC CHEMISTS", John Wiley & Sons, Inc., (1961) p.56.
[11] S. Aono, T. Ohmae, K. Nishikawa, *Bull. Chem. Soc. Jpn.,* **54**, 1645(1081).
[12] T. Ohmae, *J. Chem. Soc. Jpn.,* **1996,** 16(1996). (In Japanese.)
[13] For example, S. Satoh, Y. Satoh, "Chemical Programming with Excel VBA", BAIFUKAN CO., LTD, (2002) pp.150-154. (In Japanese.)
[14] T. Ohmae, *J. Chem. Soc. Jpn.,* **1996,** 120(1996). (In Japanese.)
[15] P. B. Karadakov, B. VanVeller, Chem. Commun., **57**, 9504(2021).
   https://doi.org/10.1039/D1CC03701C.
[16] L. Reuter, A. Lüchow, Nat. Commun., 12, 4820(2021).
   https://doi.org/10.1038/s41467-021-25091-8.

List of our papers on topological reference systems. (In Japanese.)
• T. Ohmae, *J. Chem. Soc. Jpn.,* **1995,** 948(1995).
• T. Ohmae, *J. Chem. Soc. Jpn.,* **1996,** 16(1996).
• T. Ohmae, *J. Chem. Soc. Jpn.,* **1996,** 116(1996).

- T. Ohmae, *J. Chem. Soc. Jpn.,* **1996,** 334(1996).
- T. Ohmae, *J. Chem. Soc. Jpn.,* **1998,** 157(1998).
- T. Ohmae, *Bull. Yamaguchi Pref. Univ. Fac. Human Life Sci.,* **25,** 1(1999).
- T. Ohmae, *Bull. Yamaguchi Pref. Univ. Fac. Human Life Sci.,* **28,** 35(2002).
- T. Ohmae, M, Hoshi, Y. Imai, *Bull. Fac. Nursing and Nutrition Yamaguchi Pref. Univ.,* **11,** 29(2018).