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# Aromaticity of Monocyclic Ions

Jun-ichi Aihara
*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060*

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**Synopsis.** The infinitely-large annulenes with additional formal charges were employed as reference structures to evaluate the reference energies of monocyclic ions. On this basis, the Hückel (4r+2) rule of aromaticity was verified within the framework of the HMO theory. The results obtained agree well with the available experimental evidence.

The aromatic criterion of Hess and Schaad[1] has been very successful for interpreting the aromatic character of cyclic conjugated systems within the framework of the Hückel molecular orbital (HMO) theory.[2,3] The resonance energy of a compound is given by the difference between the total $\pi$-energy of the compound and the $\pi$-energy of a hypothetically non-aromatic reference structure with the same molecular geometry. In previous papers,[4,5] the author has reported that the $\pi$-energy of the reference structure could sometimes be estimated from infinitely-large species of the same type.

However, no one has attempted an analogous approach to the ionic species, although some cyclic ions, such as cyclopropenyl and cycloheptatrienyl ions, are known to be aromatic.[6-8] It is the purpose of this paper to show that the HMO theory can be used to analyze the aromaticity of some carbocyclic ions, provided the author's reformulation of the aromatic criterion is employed. The HMO theory in its simplest form is used. All energies are given in units of $\beta$.

## Theoretical

The total HMO $\pi$-energy of a monocyclic ion with a general formula of $C_nH_n{}^m$ is calculated by summing the $\pi$-energies of all its occupied levels. In the chemical formula, $n$ and $m$ respectively signify the numbers of carbon atoms and formal charges, the sign of $m$ being indicative of the type of charge. The total HMO $\pi$-energy of $C_nH_n{}^m$, $E_{\text{HMO}}$ $(n,m)$, is then expressed in the analytical form:[9]

$$E_{\text{HMO}}(n, m) = 2\sum_k g_k \cos\frac{2\pi k}{n}, \tag{1}$$

where $g_k$ is the number of electrons which are present in the $k$th orbital.

On the other hand, an infinitely-large annulene should be neither aromatic nor antiaromatic, even though it bears formal charges. It should be similar to a charged linear polyene. For this reason, the infinitely-large charged annulene was used as the non-aromatic basis for the evaluation of the aromatic stabilization of the $C_nH_n{}^m$ series. In this case, the ratio of the number of additional charges to the number of carbon atoms, $R$, in the infinitely-large system must be adjusted to that of the ion under consideration, *i.e.*, $m/n$. For example, the reference structure of a cycloheptatrienyl cation is to be derived from the infinitely-large annulene from which a seventh part of the occupied $\pi$-electrons are removed.

If $n$ is sufficiently large, Eq. 1 can be rewritten as:

$$\begin{aligned} E_{\text{HMO}}(n, m) &\approx 4n\sum_k \frac{1}{n}\cos\frac{2\pi k}{n} \\ &\approx 4n\int_{\text{occ.}} \cos 2\pi x\text{d}x \\ &= 4n\left\{\int_0^{1/4(1-m/n)} \cos 2\pi x\text{d}x + \int_{1/4(3+m/n)}^{1.0} \cos 2\pi x\text{d}x\right\} \\ &= \frac{4n}{\pi}\cos\left(\frac{m\pi}{2n}\right), \end{aligned} \tag{2}$$

where the integration is made over all occupied energy levels of $C_nH_n{}^m$. The regions of integration are indicated by arrows in Fig. 1. When $n$ approaches infinity, the integrated value becomes solely dependent upon the ratio $m/n$ and is denoted as $I(m/n)$.

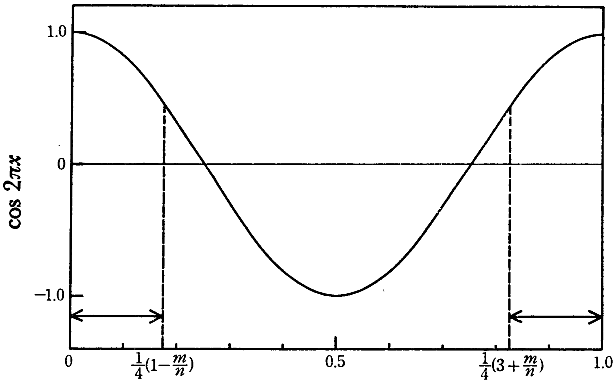

Fig. 1. The regions of integrations in Eq. 2.

Accordingly, the $\pi$-energy per $\pi$-bond, $E_{\text{U}}(m/n)$, for an infinitely-large annulene with $R=m/n$ is derived from Eq. 2 as follows:

$$\begin{aligned} E_{\text{U}}\left(\frac{m}{n}\right) &= \lim_{d\to\infty}\frac{E_{\text{HMO}}(nd, md)}{nd} \\ &= 4I\left(\frac{m}{n}\right) = \frac{4}{\pi}\cos\left(\frac{m\pi}{2n}\right). \end{aligned} \tag{3}$$

The limiting $\pi$-energy per $\pi$-bond is exact. From this expression, the infinitely-large annulene can be regarded as a kind of alternant hydrocarbon, *i.e.*,

$$E_{\text{U}}\left(\frac{m}{n}\right) = E_{\text{U}}\left(-\frac{m}{n}\right). \tag{4}$$

Consequently, the $\pi$-energy, $E_{\text{A}}(n,m)$, of the reference energy for $C_nH_n{}^m$ is defined as:

$$E_{\text{A}}(n, m) = nE_{\text{U}}\left(\frac{m}{n}\right) = \frac{4n}{\pi}\cos\left(\frac{m\pi}{2n}\right). \tag{5}$$

Such a derivation of the reference energy for a carbocyclic ion appears to be the best way imaginable at present, since the additive principle of localized $\pi$-bond

Table 1. Resonance energies of monocyclic ions in units of $|\beta|$

| Species | $E_{\mathrm{HMO}}$ | $E_{\mathrm{A}}$ | $E_{\mathrm{res}}$ | Character |
|---|---|---|---|---|
| Two-Electron System ($n-m=2$) | | | | |
| $C_3H_3^+$ | 4.0000 | 3.3080 | 0.6920 | Aromatic |
| $C_4H_4^{2+}$ | 4.0000 | 3.6013 | 0.3987 | Aromatic |
| Four-Electron Systems ($n-m=4$) | | | | |
| $C_3H_3^-$ | 2.0000 | 3.3080 | −1.3080 | Antiaromatic |
| $C_4H_4$ | 4.0000 | 5.0930 | −1.0930 | Antiaromatic |
| $C_5H_5^+$ | 5.2361 | 6.0546 | −0.8185 | Antiaromatic |
| $C_6H_6^{2+}$ | 6.0000 | 6.6159 | −0.6159 | Antiaromatic |
| Six-Electron Systems ($n-m=6$) | | | | |
| $C_4H_4^{2-}$ | 4.0000 | 3.6013 | 0.3987 | Aromatic |
| $C_5H_5^-$ | 6.4721 | 6.0546 | 0.4175 | Aromatic |
| $C_6H_6$ | 8.0000 | 7.6394 | 0.3606 | Aromatic |
| $C_7H_7^+$ | 8.9879 | 8.6892 | 0.2987 | Aromatic |
| $C_8H_8^{2+}$ | 9.6569 | 9.4106 | 0.2463 | Aromatic |
| Eight-Electron Systems ($n-m=8$) | | | | |
| $C_6H_6^{2-}$ | 6.0000 | 6.6159 | −0.6159 | Antiaromatic |
| $C_7H_7^-$ | 8.0978 | 8.6892 | −0.5914 | Antiaromatic |
| $C_8H_8$ | 9.6569 | 10.1859 | −0.5291 | Antiaromatic |
| $C_9H_9^+$ | 10.8229 | 11.2851 | −0.4621 | Antiaromatic |
| $C_{10}H_{10}^{2+}$ | 11.7082 | 12.1092 | −0.4010 | Antiaromatic |
| Ten-Electron Systems ($n-m=10$) | | | | |
| $C_8H_8^{2-}$ | 9.6569 | 9.4106 | 0.2463 | Aromatic |
| $C_9H_9^-$ | 11.5175 | 11.2851 | 0.2325 | Aromatic |
| $C_{10}H_{10}$ | 12.9443 | 12.7324 | 0.2119 | Aromatic |
| $C_{11}H_{11}^+$ | 14.0533 | 13.8631 | 0.1903 | Aromatic |
| $C_{12}H_{12}^{2+}$ | 14.9282 | 14.7583 | 0.1699 | Aromatic |

energies is not applicable due to the lack of definite classical resonance structures. The resonance energy, $E_{\mathrm{res}}$, for $C_nH_n^m$ is then given by the expression:

$$E_{\mathrm{res}}(n, m) = E_{\mathrm{HMO}}(n, m) - E_{\mathrm{A}}(n, m). \tag{6}$$

The results obtained are presented in Table 1.

## Results and Discussion

It is evident from Table 1 that the number of $\pi$-electrons is a significant factor which determines the aromaticity. All species with (4r+2) $\pi$-electrons are predicted to be aromatic, because they have positive resonance energies, where r is an integer. Conversely, all species with 4r $\pi$-electrons are predicted to be antiaromatic with negative resonance energies. Note that this result is the best verification of the Hückel (4r+2) rule of aromaticity within the Hückel theory.[10] These results are, of course, in qualitative agreement with the available experimental evidence.[6-8] In general, aromaticity or antiaromaticity decreases as the ring size increases.

Several years ago, Dewar and Venier defined a cyclic ion as being aromatic, if it has a greater $\pi$-energy than a corresponding open-chain system.[11] Their SCF-MO calculations appeared to be consistent with the predictions of the Hückel rule.[10] Subsequent free-electron molecular-orbital (FEMO) calculations, carried out by Hobey,[12] were also based on the same reference structures as were adopted by Dewar and Venier. However, one of the difficulties in using open-chain systems as reference structures appears to be that the molecular geometries and numbers of $\pi$-bonds are not preserved in them. To make the matter worse, the FEMO model cannot reproduce even the additivity of $\pi$-bond energies[1-5,11,13] for non-aromatic systems. However, the presently considered reference energies of monocyclic ions are free from these difficulties; the contributions from all $\pi$-bonds are counted in the present procedure. The HMO $\pi$-bond energies are sure to be additive in non-aromatic species.[1-5] For a general discussion, see Ref. 5.

Although our simple model neglects some significant effects arising from bond alternation and, more importantly, from interelectronic repulsion, the good agreement with experiment strongly suggests that the resonance energies obtained are good indices of aromaticity, at least, for the monocyclic ions investigated. It is expected that the gross features of the predicted aromatic character are not changed by these effects. On the contrary, it can be noted that the concept of aromaticity for ions thus introduced does not violate the simplicity and elegance of the HMO theory. Finally, it should be emphasized that the same approach can easily be extended to many other conjugated systems, as cited in Ref. 5.

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