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Exact Relationship between Resonance Energies and Ring Currents of Aromatic Annulenes

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Synopsis. Haddon's analytical relationship between the resonance energies and the ring currents of $(4n+2)\pi$-electron annulenes was decidedly improved by means of the graph theory of aromaticity.

An NMR criterion of aromaticity has widely been accepted according to which diamagnetic ring currents indicate aromaticity while paramagnetic ring currents indicate antiaromaticity.[1-2] However, it had not been clear that this magnetic criterion is equivalent to the energetic definition of aromaticity[3] until we previously proved that the diamagnetic susceptibility of a cyclic conjugated system[4,5] strongly reflects its conjugative stabilization.[6] In the case of annulenes, the sign of the susceptibility exactly accords with that of the resonance energy due to aromaticity.[7-10]

Recently, Haddon reported an analytical relationship between the resonance energies (*RE*s) and the reduced ring currents (*RC*s) of $(4n+2)\pi$-electron annulenes.[11] He adopted my former method (denoted by A-I)[7,8] to estimate the resonance energies, and found that the relationship takes the form

$$RE = \frac{\pi^2}{3S}RC, \tag{1}$$

where S is the area of the annulene ring, and RC the reduced ring current related linearly to the ring current intensity, I, in this manner:

$$I = \left[8\pi^2 c\left(\frac{e}{hc}\right)^2 H\right] RC. \tag{2}$$

Here, H is the applied magnetic field (taken perpendicular to the molecular plane), and the other symbols have their usual meaning.

The A-I method is one of the analytical methods for estimating the resonance energy of a cyclic conjugated system.[7,8] The π-bond energy of an infinitely large cyclic polyene is therein utilized in the definition of an olefinic reference structure. However, I have not been using this method since another method (denoted by A-II) was devised by means of graph theory.[8] At present, the A-II method appears to be physically much more sound and meaningful.[6,8-10] Accordingly, Haddon's treatment of ring currents[11] can naturally be improved on the basis of the A-II method. This is shown below.

Theory and Discussion

According to the A-II method,[8-10] a characteristic polynomial for an olefinic reference structure of a conjugated hydrocarbon can be written as

$$R(X) = X^N + \sum_{k=1}^{[N/2]} (-1)^k p(k) X^{N-2k}, \tag{3}$$

where N is the number of sp^2-carbon atoms in a conjugated system, $p(k)$ the number of ways of choosing k disjoint π bonds from the conjugated system,[12] and $[N/2]$ the maximum integer not larger than $N/2$. The resonance energy can be defined as the difference between the total π-electron energy of a conjugated system and that of its reference structure given by Eq. 3, and this is termed the A-II resonance energy.[8]

There are five kinds of $(4n+2)\pi$-electron annulenes; $[4n+2]$annulenes, $[4n]^{2+,2-}$annulenes, $[4n+1]^-$annulenes, and $[4n+3]^+$annulenes. These are all aromatic.[8-10] Fortunately, A-II resonance energies (RE^*) of these annulenes can be expressed analytically in the form[10]

$$RE^* = \frac{4(1-\cos\theta)\beta}{\sin 2\theta} \quad ([4n+2]\text{annulenes}) \tag{4a}$$

$$= \frac{4(1-\cos\theta)\beta}{\tan 2\theta} \quad ([4n]^{2+,2-}\text{annulenes}) \tag{4b}$$

$$= \frac{2(1-\cos\theta)\beta}{\sin\theta} \quad ([4n+1]^-\text{annulenes and } [4n+3]^+\text{annulenes}). \tag{4c}$$

Here, $\theta = \pi/2N$. On the other hand, the reduced ring currents are given by[11,13]

$$RC = \frac{2S\beta}{N^2 \sin 2\theta} \quad ([4n+2]\text{annulenes}) \tag{5a}$$

$$= \frac{2S\beta}{N^2 \tan 2\theta} \quad ([4n]^{2+,2-}\text{annulenes}) \tag{5b}$$

$$= \frac{S\beta}{N^2 \sin\theta} \quad ([4n+1]^-\text{annulenes and } [4n+3]^+\text{annulenes}). \tag{5c}$$

Combining Eq. 4 with Eq. 5, we obtain

$$RE^* = \frac{2N^2 RC}{S}(1-\cos\theta), \tag{6}$$

for all kinds of $(4n+2)\pi$-electron annulenes. It should be stressed that this is a single exact relationship found between the A-II resonance energies and the ring currents of aromatic annulenes.

In order to visualize the physical image of this relationship, let us expand the cosine in it into a corresponding power series as follows:

$$RE^* = \frac{\pi^2}{4S}RC\left(1 - \frac{\pi^2}{48N^2} + \frac{\pi^4}{5760N^4} - \cdots\right). \tag{7}$$

Cleraly for large N it is possible to truncate Eq. 7 at the first term. Even for benzene ($N=6$), the error due to such truncation is less than one percent. Adopting this simplification, we obtain for the A-II resonance energy

$$RE^* = \frac{\pi^2}{4S}RC. \tag{8}$$

This expression is quite similar to Haddon's one (Eq. 1), but the proportionality constant is reduced to three-fourths. This is due to the fact that the A-I resonance energy is about 33 percent larger than the

A-II resonance energy for all aromatic annulenes, both neutral and ionic.[8] However, this difference is never a triviality. Considering that the A-II resonance energy only is closely related to the magnetic property of a cyclic conjugated system,[6] it will be evident that Eq. 8 is much more preferable to Eq. 1. In other words, Eq. 8 represents a more realistic relationship between the resonance energies and the ring currents of $(4n+2)\pi$-electron annulenes.

By the way, the diamagnetic susceptibility(χ_π) of an annulene conjugated system[5] is given by

$$\chi_\pi = \frac{SI}{cH}. \tag{9}$$

The following relationship then holds for aromatic annulenes:

$$\chi_\pi = 32\left(\frac{e}{hc}\right)^2 S^2 RE^*. \tag{10}$$

This expression indicates that the susceptibility is proportional both to the resonance energy and to the area of the annulene ring squared.

Concluding Remarks

The behavior of the ring current in relation to the A-II resonance energy has been considered above in the hypothetically bond-equalized case. The entire analysis has been simple and exact. As pointed out by Haddon,[11] encouraging evidence for Eqs. 1 and 8 has already been published in the case of aromatic bisdehydroannulenes,[14] for which proton chemical shifts nicely correlate with Hess-Schaad resonance energies.[15] However, any analytical relationship between resonance energies and ring currents cannot be obtained for antiaromatic annulenes, because bond alternation plays a crucial role in these compounds.[16]

Finally, it must be noted that Eq. 8 does not imply that a theoretical relationship must exist between the resonance energies and the ring currents of $(4n+2)\pi$-electron annulenes. It simply indicates the A-II resonance energy evaluated relative to the magnitude of the ring current. The close relationship found between these two quantities might have been regarded as superficial if a theoretical relationship between aromaticity and diamagnetism has not been established.[6]

Addendum. The realness of the roots of the same polynomial as Eq. 3 has already been proved by Heilmann and Lieb.[17] This proof warrants the realness of the A-II resonance energy. Professor L. J. Schaad kindly brought my attention to the Heilmann-Lieb paper.

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