Simple Topological Theory of Aromaticity for Annulenes and Radialenes

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(Received January 5, 1980)

Synopsis. Simple theory of aromaticity for annulenes and radialenes is developed by means of generalized total π-electron energy indexes, and is used to rationalize thermochemical stability and diamagnetic susceptibility exaltation of these compounds.

Total π-electron energy, E_π, is one of the fundamental quantities in chemistry of conjugated compounds. It is essential to the estimation of their thermochemical stability and reactivity. Molecular orbital (MO) theory has so far provided much information concerning total π-electron energies of conjugated hydrocarbons.[1] In parallel with this, a considerable amount of effort has been devoted to correlating the total π-electron energy E_π with particular structural features of a conjugated system.[2] Coefficients of the Hückel MO characteristic polynomial P(X) also reflect E_π in a like manner.[2-5] They can easily be evaluated by inspection of a molecular geometry.[5-7] Hosoya *et al.* previously proposed a modified topological index for E_π as a function of most coefficients of $P(X)$.[3] We later generalized it so as to include contributions from all the coefficients.[4] Our generalized total π-electron energy index Z^* is formally defined as

$$Z^* = |P(\mathrm{i})|, \tag{1}$$

where $\mathrm{i}=\sqrt{-1}$. In the case of alternant hydrocarbons, Z^* exactly agrees with Hosoya's modified topological index.[3,4] The total π-electron energy can nicely be approximated as[4]

$$E_\pi \approx E_\pi^* = 6.0846 \log Z^*, \tag{2}$$

in units of β. In this note I would like to show that Eqs. 1 and 2 are very useful for elucidating aromatic character of annulenes and radialenes.

Table 1. π-Electron energies per unit structure of annulenes ($2E_\pi/N$) in units of β

N	Z^*	$2E_\pi/N$	
		$2E_\pi^*/N$	Hückel MO
4	5.00	2.1265	2.0000
6	20.00	2.6387	2.6667
8	45.00	2.5148	2.4143
10	125.00	2.5518	2.5889
12	320.00	2.5405	2.4880
14	845.00	2.5441	2.5680
16	2205.00	2.5429	2.5137
18	5780.00	2.5433	2.5595
20	15125.00	2.5432	2.5255
22	39605.00	2.5432	2.5552
24	103680.00	2.5432	2.5319
26	271445.00	2.5432	2.5527
28	710645.00	2.5432	2.5358
30	1860500.00	2.5432	2.5511
∞	∞	2.5432	2.5465

First, the Z^* value of [N]annulene is given in a general form as

$$Z^* = \frac{1}{\sqrt{5}}\left(\frac{1+\sqrt{5}}{2}\right)^{N+1} - \frac{1}{\sqrt{5}}\left(\frac{1-\sqrt{5}}{2}\right)^{N+1} - 2(-1)^{N/2}. \tag{3}$$

Derivation of this expression is based on the recursion formula for obtaining topological indexes of annulenes.[8] Individual Z^* values are presented in Table 1. Since E_π^* represents estimated total π-electron energy of [N]-annulene, the π-electron energy per annulene unit structure is given as $2E_\pi^*/N$. This quantity corresponds to a sum of π-electron energies of the C=C bond and its adjacent C–C bond in the canonical structure.[9,10] As easily seen from Table 1, the $2E_\pi^*/N$ value oscillates about the limiting value of 2.5432β. This limiting value is an estimated π-electron energy per unit structure for an infinitely large annulene, which is evidently free from aromaticity.

Accordingly, annulenes with $2E_\pi^*/N < 2.5432\beta$ are predicted to be aromatic, and those with $2E_\pi^*/N > 2.5432\beta$ to be antiaromatic. Although these predictions seem very rough, they are in good accord with Hückel's $(4n+2)$ rule of aromaticity.[11] All annulenes predicted to be aromatic possess $(4n+2)$ π-electrons, and those predicted to be antiaromatic possess $4n$ π-electrons. Such a way of aromaticity consideration is exactly the same as those presented by Aihara,[10] Cocordano,[12] and Haddon.[13] The Hückel MO π-electron energies per unit structure are favorably compared with the $2E_\pi^*/N$ values in Table 1. Another important point is that the π-electron energy per unit structure becomes nearly constant for annulenes with $N \geq 20$. This aspect of our total π-electron energy index Z^* is quite consistent with the finding of Dewar *et al.*[14] and Hess and Schaad[9] that bond energies are additive for nonaromatic species.

Next, the Z^* value of [N]radialene is expressed as

$$Z^* = \begin{cases} (1+\sqrt{2})^{N+1} + (1-\sqrt{2})^{N+1} - 2(-1)^{N/2} & \text{for } N = 2n \\ \{[(1+\sqrt{2})^{N+1} + (1-\sqrt{2})^{N+1}]^2 + 4\}^{1/2} & \text{for } N = 2n+1, \end{cases} \tag{4}$$

where n is an integer. Derivation of this expression is also based on the recursion formula for obtaining topological indexes of radialenes.[8] Individual Z^* values are listed in Table 2. A radialene unit structure is a combination of the CH_2=C bond and its adjacent C–C bond in the canonical structure.[9,10] Unlike annulenes, radialenes appear substantially olefinic in nature except for slightly antiaromatic [4]radialene. All the π-electron energies per unit structure (E_π^*/N) are very close to the limiting value of 2.3290β. Comparison with MO π-electron energies per unit structure[9,10,14] supports nonaromatic character of radialenes thus predicted. These results are of course

Table 2. π-Electron energies per unit structure of radialenes (E_π/N) in units of β

N	Z^*	E_π/N	
		E_π^*/N	Hückel MO
3	14.14	2.3333	2.4335
4	32.00	2.2896	2.4142
5	82.02	2.3291	2.4320
6	200.00	2.3335	2.4335
7	478.00	2.3290	2.4320
8	1152.00	2.3285	2.4319
9	2786.00	2.3290	2.4320
10	6728.00	2.3291	2.4320
11	16238.00	2.3290	2.4320
12	39200.00	2.3290	2.4320
13	94642.00	2.3290	2.4320
14	228488.00	2.3290	2.4320
15	551614.00	2.3290	2.4320
∞	∞	2.3290	2.4320

consistent with our graph theory of aromaticity.[15]

An NMR criterion of aromaticity has also been used according to which diamagnetic ring currents indicate aromaticity while paramagnetic ring currents indicate antiaromaticity.[16] We can show that such a magnetic criterion of aromaticity is identical with the above energetic criterion. When an external magnetic field, H, is applied perpendicularly to the molecular plane, our total π-electron energy index of [N]annulene becomes[17]

$$Z^* = \frac{1}{\sqrt{5}}\left(\frac{1+\sqrt{5}}{2}\right)^{N+1} - \frac{1}{\sqrt{5}}\left(\frac{1-\sqrt{5}}{2}\right)^{N+1} - 2(-1)^{N/2}\cos\Theta_N H, \quad (5)$$

where $\Theta_N = 2\pi e S_N/hc$. Here, S_N is the area enclosed by the [N]annulene ring, and e, h, and c are the standard constants with these symbols. When $N=4n+2$, the applied magnetic field decreases Z^*, so it decreases E_π^*. Conversely, when $N=4n$, the applied magnetic field increases both Z^* and E_π^*. Thus the effect of the magnetic field H on [$4n+2$]annulenes is exactly opposite to that on [$4n$]annulenes. This gives the reason why [$4n+2$]annulenes are diamagnetic while [$4n$]annulenes are paramagnetic.[16] Note that the second derivative of the total π-electron energy with respect to H gives the magnetic susceptibility of a conjugated system.[17] It should be noted that the sign of the susceptibility obtained from Eq. 5 agrees with experiment, so does the sign of the ring current.[16]

On the other hand, for [N]radialene in the magnetic field,

$$Z^* = \begin{cases} (1+\sqrt{2})^{N+1} + (1-\sqrt{2})^{N+1} - 2(-1)^{N/2}\cos\Theta_N H & \text{for } N = 2n \\ \{[(1+\sqrt{2})^{N+1} + (1-\sqrt{2})^{N+1}]^2 + 4\cos^2\Theta_N H\}^{1/2} & \text{for } N = 2n+1. \end{cases} \quad (6)$$

When N is even, the field effect on [N]radialene is in principle analogous to that on [N]annulene, but the former is much smaller than the latter. When N is odd, the field effect is essentially negligible. These suggest that marked diamagnetic susceptibility exaltation cannot be anticipated for radialenes. This is in harmony with their olefinic character.[9,10,14,15] We have thus been able to elucidate two major features of aromaticity, *i.e.*, specific stability and enhanced diamagnetism, in terms of our generalized total π-electron energy index Z^*.

Since 1971, Hosoya and coworkers have been interpreting various molecular properties in terms of topological indexes.[3,6,8,18] The present theory of aromaticity can hence be regarded as a practical extension of their topological chemistry. Simplicity and elegance are characteristics common to all these works.

References

1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y. (1961); L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y. (1966); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y. (1969).

2) References in this field have been exhaustively collected in: I. Gutman, *Match*, **4**, 195 (1978).

3) H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37 (1975).

4) J. Aihara, *J. Org. Chem.*, **41**, 2488 (1976).

5) J. Aihara, *J. Am. Chem. Soc.*, **98**, 6840 (1976).

6) H. Hosoya, *Theor. Chim. Acta.* **25**, 215 (1972).

7) A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta*, **26**, 67 (1972),

8) H. Hosoya, *Fibonacci Quart.*, **11**, 255 (1973).

9) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305, 2413 (1971).

10) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).

11) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **78**, 628 (1932).

12) M. Cocordano, *C. R. Acad. Sci., Ser. C*, **284**, 441 (1977).

13) R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722 (1979).

14) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

15) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976); I. Gutman, M. Milun, and N. Trinajstić, *ibid.*, **99**, 1692 (1977).

16) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Top. Curr. Chem.*, **16**, 103 (1971); F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972).

17) J. Aihara, *J. Am. Chem. Soc.*, **101**, 558, 5913 (1979).

18) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971); H. Hosoya, K. Kawasaki, and K. Mizutani, *ibid.*, **45**, 3415 (1972); H. Hosoya and M. Murakami, *ibid.*, **48**, 3512 (1975); H. Hosoya and K. Hosoi, *J. Chem. Phys.*, **64**, 1065 (1976); I. Gutman, T. Yamaguchi, and H. Hosoya, *Bull. Chem. Soc. Jpn.*, **49**, 1811 (1976).