February, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 517—520 (1975) 517

Resonance Energies of Annulenes and Radialenes

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

(Received July 10, 1974)

Resonance energies of annulenes and radialenes were estimated on the basis of the π-bond energies of infinitely large annulene and radialene, respectively. The widely accepted Hückel's $(4n+2)\pi$ rule was verified for annulenes, whereas radialenes were substantially nonaromatic regardless of the number of π-electrons.

Though the Hückel molecular orbital (HMO) model has shown a great degree of success in the interpretation of gross electronic structures of conjugated systems,[1] the extension of this approach has given rather limited agreement. In particular, it was recently shown that the delocalization energy is not useful in predicting the relative stability of benzenoid and nonbenzenoid hydrocarbons.[2]

In 1965, Dewar and Gleicher, using the semiempirical SCF-MO method, have found that the bond energies of acyclic polyenes are additive.[3] Adopting this principle, Hess and Schaad defined the HMO resonance energy as the difference between the total HMO π-energy and the additive contribution obtained by summing individual π-bond energies.[4] An excellent correlation between the resonance energies calculated in this manner and the observed stability and chemical behavior of many cyclic polyenes was obtained.

We also verified the additivity of π-bond energies of linear polyenes on the basis of the total HMO π-energies of infinitely large annulene and polyene.[5] The most striking advantage of our treatment was that the somewhat arbitrary assignment of values for eight types of π-bond energies made by Hess and Schaad[4] was completely avoided. In order to extend our understanding of aromatic stabilization of cyclic systems within the framework of the HMO theory and without additional assumptions, the same idea was applied to two typical cyclic systems; annulenes and radialenes.

Results and Discussion

It is generally accepted that sufficiently large annulene is considered to suffer from bond alternation, and is almost nonaromatic cyclic polyene.[6,7] It is hence assumed without difficulty that the additive contribution to the total π-energy of any annulene can be estimated from the π-energy of infinitely large annulene. When the classical resonance structure is written for annulene, it is a cyclic chain composed of unit structures, each of which involves the CH=CH bond and the adjacent CH–CH bond. The π-energy of the unit structure (E_U) is then evaluated by dividing the total HMO π-energy of [infinity]-annulene by half the number of carbon atoms. With the use of Hess and Schaad's notation,[2,4] it is expressed as follows:

$$E_U(\text{annulene}) = E_{22} + E_{12} = \frac{8}{\pi}, \tag{1}$$

where E_{22} and E_{12} signify the π-bond energies of the CH=CH and CH–CH bonds, respectively.

The ability to calculate accurately in an additive manner the total π-energy of linear polyene[5] allows us to calculate the additive contribution to the total π-energy of annulene. The additive contribution to the total π-energy of annulene as is defined as the π-energy of the localized structure of annulene is simply expressed as follows:

$$E_A([N]\text{-annulene}) = \frac{N}{2}(E_{22}+E_{12}) = \frac{4N}{\pi}, \tag{2}$$

where N is the number of carbon atoms in annulene.

The resonance energy (E_R) of annulene is hence obtained by substracting E_A from the total HMO π-energy (E_{HMO}), that is,

$$E_R([N]\text{-annulene}) = E_{HMO}([N]\text{-annulene}) - E_A([N]\text{-annulene}). \tag{3}$$

The resonance energies determined by using Eq. (3) as well as E_{HMO} and E_A are all listed in Table 1. REPE denotes resonance energy per π-electron. The geometry of the annulenes investigated is tacitly assumed to be planar with constant resonance integrals over all carbon-carbon bonds.

As is easily seen, the total resonance energy oscillates about zero-axis, approaching zero with increasing N. All [4n]-annulenes are correctly predicted to be

TABLE 1. RESONANCE ENERGIES OF ORDINARY ANNULENES IN UNITS OF β

N	E_{HMO}	E_A	E_R	REPE
4	4.0000	5.0930	−1.0930	−0.2732
6	8.0000	7.6394	0.3606	0.0601
8	9.6569	10.1859	−0.5291	−0.0661
10	12.9443	12.7324	0.2119	0.0212
12	14.9282	15.2789	−0.3507	−0.0292
14	17.9758	17.8254	0.1505	0.0107
16	20.1094	20.3718	−0.2625	−0.0164
18	23.0351	22.9183	0.1168	0.0065
20	25.2550	25.4648	−0.2098	−0.0105
22	28.1067	28.0113	0.0954	0.0043
24	30.3830	30.5577	−0.1747	−0.0073
26	33.1849	33.1042	0.0807	0.0031
28	35.5010	35.6507	−0.1497	−0.0053
30	38.2671	38.1972	0.0699	0.0023
32	40.6127	40.7437	−0.1310	−0.0041
34	43.3518	43.2901	0.0617	0.0018
36	45.7202	45.8366	−0.1164	−0.0032
38	48.4383	48.3831	0.0552	0.0015
40	50.8248	50.9296	−0.1048	−0.0026

antiaromatic with negative resonance energies. The [$4n+2$]-annulenes are predicted to be aromatic up to [infinity]-annulene. Hückel's famous ($4n+2$)π rule which states that [$4n+2$]-annulenes will possess relative electronic stability[8] has been nicely verified in this manner. Above all, it must be noted that, though our present results are in fair agreement with earlier theoretical studies on annulenes,[4,9–12] our simple approach is best grounded on the additivity of π-bond energies of the nonaromatic reference structure.

Dewar and Gleicher predicted that the critical size of annulene at which the bond alternation occurs is between [22]- and [26]-annulene, which was supported by some experimental evidence.[7,13] Though we can not predict the critical size of annulene at which Hückel's ($4n+2$)π rule ceases to hold, their statement seems to be quite consistent with our results as higher annulenes with an REPE less than 0.004 β are considered to be substantially nonaromatic in accordance with the interpretation of the additivity of π-bond energies of acyclic polyenes made by Hess and Schaad.[4] When Hess and Schaad's π-bond energies are employed to calculate the π-energy of the reference structure, the limiting REPE of annulene amounts to 0.0053 β.[14] This suggests that sufficiently large annulenes are still aromatic with resonance energies of about $0.0053N\beta$, which is in contradiction to the premise that higher annulenes should be nonaromatic. In our case, the resonance energy of [$4n+2$]-annulene diminishes monotonously as n increases.

Similar results can be obtained by taking linear polyene as a reference compound for annulene. According to the procedure given in the previous paper,[5] the additive contribution to the total π-energy of annulene may be rewritten as follows:

$$E_R([N]\text{-annulene}) = E_{HMO}([N]\text{-polyene}) - 2E_{23} + 2E_{22} + E_{12}$$

$$= E_{HMO}([N]\text{-polyene}) + 2 - \frac{4}{\pi} \ . \qquad (4)$$

The list of resonance energies derived from Eq. (4) was omitted here because of their close resemblance to those in Table 1.

On the other hand, the potential utility of the Möbius conformation of annulene in ring-opening reactions has been pointed out by Zimmerman.[15] The Möbius cyclic system is a singly twisted cyclic polyene in which there is only one side of the π-surface.[16] Craig and Paddock also considered the possibility of the Möbius conformation for cyclic phosphonitrilic derivatives.[17]

The resonance energies of the Möbius systems of annulenes were calculated by assuming the same reference structures as those of ordinary annulenes, although the additive principle of π-bond energies may be somewhat obscured for these systems. The change in resonance integrals with twisting was neglected to simplify the calculation. The obtained resonance energies of the Möbius systems are shown in Table 2. They were found to have positive resonance energies when they have $4n$ π-electrons. The resonance energies were negative for the systems with ($4n+2$) π-electrons. The aromaticity is thus determined by the converse of Hückel's ($4n+2$)π rule in agreement with the conclusion lead by Heilbronner.[16]

Table 2. Resonance energies of Möbius-type annulenes in units of β

N	E_{HMO}	E_A	E_R	REPE
4	5.6569	5.0930	0.5639	0.1410
6	6.9282	7.6394	−0.7112	−0.1185
8	10.4525	10.1859	0.2666	0.0333
10	12.3107	12.7324	−0.4217	−0.0422
12	15.4548	15.2789	0.1759	0.0147
14	17.5251	17.8254	−0.3002	−0.0214
16	20.5033	20.3718	0.1315	0.0082
18	22.6851	22.9183	−0.2332	−0.0130
20	25.5698	25.4648	0.1050	0.0053
22	27.8206	28.0113	−0.1907	−0.0087
24	30.6452	30.5577	0.0874	0.0036
26	32.9430	33.1042	−0.1613	−0.0062
28	35.7256	35.6507	0.0749	0.0027
30	38.0575	38.1972	−0.1397	−0.0047
32	40.8092	40.7437	0.0655	0.0020
34	43.1669	43.2901	−0.1233	−0.0036
36	45.8949	45.8366	0.0582	0.0016
38	48.2728	48.3831	−0.1103	−0.0029
40	50.9820	50.9296	0.0524	0.0013

As a further application, we may compare the total HMO π-energies and the additive contributions of π-bond energies for radialenes. Radialenes form an apparently very dissimilar series of conjugated polyenes containing a ring of carbon atoms, each doubly bound to a methylene group. In other words, radialenes are all composed of the same unit structures, each involving a CH_2=C bond and an adjacent C–C bond. Therefore, the numbers of the single and double carbon-carbon bonds are the same, and are equated to M. If the π-bonds are localized as in the classical resonance structure, the total π-energy of [M]-radialene should be given by (in Hess and Schaad's notation[2,4]):

$$E_A([M]\text{-radialene}) = M(E_{22'} + E_{10}) \ , \qquad (5)$$

where E_{22}' and E_{10} denote the π-bond energies of the CH_2=C and C–C bonds, respectively.

In order to determine the π-energy of the radialene unit structure, we employed the same procedure as used for annulenes. Here, radialenes are assumed to be coplanar with the rings forming regular polygons and free from ring strains. The general HMO solution for radialene was presented by Hess and Schaad.[4] According to them, the m-th orbital energy of [M]-radialene is expressed in units of β as follows:

$$\varepsilon_m([M]\text{-radialene}) = \cos\lambda_{Mm} + (\cos^2\lambda_{Mm} + 1)^{1/2} \ , \qquad (6)$$

where

$$\lambda_{Mm} = \frac{2m\pi}{M} \qquad m = 0, 1, 2, \cdots\cdots, (M-1) \ . \qquad (7)$$

As in the case of annulene, if the radialene ring is large enough, it can be considered as a nonaromatic cyclic polyene. The π-energy of the unit structure of radialene is therefore estimated at the nonaromatic limit as

$$\begin{aligned} E_U(\text{radialene}) &= E_{22'} + E_{10} \\ &= \lim_{M\to\infty} \frac{2}{M} \sum_{m=0}^{M-1} [\cos \lambda_{Mm} + (\cos^2 \lambda_{Mm} + 1)^{1/2}] \\ &= 2\int_0^1 [\cos 2\pi x + (\cos^2 2\pi x + 1)^{1/2}]\mathrm{d}x \\ &= 2.4320134\cdots\cdots . \end{aligned} \tag{8}$$

The numerical estimation of the unit energy was made by the double-precision computation. The π-energy of the reference structure of $[M]$-radialene is equated to $2.4320134M\beta$. Table 3 shows the resonance energies of radialenes based on this value, *i.e.*, the differences between the total HMO π-energies and the additive contributions defined by Eq. (5).

Table 3. Resonance energies of radialenes in units of β

M	E_{HMO}	E_{A}	E_{R}
3	7.3006	7.2960	0.00452
4	9.6569	9.7281	−0.07119
5	12.1602	12.1601	0.00009
6	14.6011	14.5921	0.00904
7	17.0241	17.0241	0.00000
8	19.4548	19.4561	−0.00129
9	21.8881	21.8881	0.00000
10	24.3203	24.3201	0.00019
11	26.7521	26.7521	0.00000
12	29.1841	29.1842	−0.00002
13	31.6162	31.6162	0.0
14	34.0482	34.0482	0.0
15	36.4802	36.4802	0.0
16	38.9122	38.9122	0.0
17	41.3442	41.3442	0.0
18	43.7762	43.7762	0.0
19	46.2083	46.2083	0.0
20	48.6403	48.6403	0.0
30	72.9604	72.9604	0.0
40	97.2805	97.2805	0.0
50	121.6007	121.6007	0.0

In contrast to annulenes, the agreement between the total π-energies and the additive contributions for radialenes is surprisingly excellent for all M's. All REPE's range between -0.00890β for $M=4$ and 0.00075β for $M=3$. This implies that they are to be considered nonaromatic regardless of the number of the π-electrons, and supports strongly that our way of determining the π-energy of the unit structure is quite reasonable. Radialenes can therefore be well represented in terms of localized single and double bonds in accordance with more elaborate calculations carried out by Dewar and his collaborators.[7,18]

If Table 3 is further examined in detail, it is found that the resonance energies are slightly negative for $M=4$, 8, and 12, and that they are slightly positive for $M=6$ and 10. This behavior of the resonance energies tempts us to present a new version of Hückel's $(4n+2)\pi$ rule for radialenes, in which the number of π-electrons (n) should be replaced by the number of methylene groups (M). However, the applicability of this rule fades very rapidly with increasing M. The additivity of π-bond energies are perfect for radialenes with M-values more than 12, though they are chemically of little importance. These aspects of the resonance energies of radialenes have so far been disregarded because of the tiny deviation of the total HMO π-energies from the additive contributions. The resonance energies of radialenes calculated by Hess and Schaad[4] were all negative as the sum of $E_{22'}$ and E_{10} (2.4358β) was slightly larger than the corresponding value calculated by us.

We have assumed in the present treatment that the geometries of annulenes and radialenes are all planar with constant resonance integrals. This is, however, exactly true only for the six-membered ring systems when they are substantially aromatic with little bond-order fluctuation. In most cases, ring strain and H–H nonbonded repulsions become significant; they would tend to destabilize both small and large rings relative to the six-membered rings. On the other hand, the introduction of bond alternation would often reduce the π-energy of the system. These effects were completely neglected in our simplified approach modeled after Hess and Schaad's.[4] Nevertheless, it must be noted that the resonance energies obtained here still appear to be much improved as an aromaticity index of the compound, and should be utilized, instead of the delocalization energies, to discuss the stability of these cyclic systems.

In conclusion, the well-established additivity of π-bond energies of nonaromatic polyenes allowed us to take infinitely large annulene and radialene as reference compounds in estimating the aromaticity of a given annulene and radialene. Such a procedure removed the difficulty encountered in evaluating the resonance energies of these compounds within the framework of the HMO theory. It is noticeable that the concept of aromaticity thus derived does not violate the simplicity and straightforwardness of the HMO theory, and may be considered as a practical extension of the HMO theory.

We are grateful to the Hokkaido University Computing Center for the use of their FACOM 230-60 on which all the calculations were performed.

References

1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y. (1961).

2) B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 2413 (1971).

3) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965).

4) B. A. Hess, Jr. and L. J. Schaad, *ibid.*, **93**, 305 (1971).

5) J. Aihara, This Bulletin, **47**, 3169 (1974).

6) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England (1969).

7) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

8) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **72**, 310 (1931).

9) T. M. Krygowski, *Tetrahedron Lett.*, **1970**, 1311.

10) I. Gutman, M. Milun, and N. Trinajstic, *Croat. Chem. Acta*, **44**, 207 (1972).

11) W. D. Hobey, *J. Org. Chem.*, **37**, 1137 (1972).

12) H. P. Figeys, *Tetrahedron*, **26**, 5225 (1970).

13) F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

14) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).

15) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

16) E. Heilbronner, *Tetrahedron Lett.*, **1964**, 1923.

17) D. P. Craig and N. L. Paddock, "Nonbenzenoid Aromatics," Vol. 2, ed. by J. P. Synder, Academic Press, New York, N. Y. (1971), Ch. 5.

18) M. J. S. Dewar and C. De Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).