BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 3169—3170 (1974)

On the Additivity of π-Bond Energies in Linear Polyenes

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

(Received May 24, 1974)

Synopsis. The additivity of π-bond energies in linear polyenes was confirmed by taking nonaromatic [infinity]-annulene and -polyene as reference compounds. The π-bond energies determined by Hess and Schaad were found to be oriented to polyenes of a medium size.

Dewar and his collaborators, using the LCAO–SCF–MO method, have found that the bond energies of acyclic polyenes are additive.[1,2] One can readily calculate the total energy of any acyclic polyene merely by summing the energies of all its bonds. Figeys applied the LCAO–BETA method to the calculation of the total energies of linear polyenes[3] and indicated that linear polyene can be represented in terms of localized single and double C–C bonds, in agreement with their finding.

In 1971, Hess and Schaad found that a similar treatment of the HMO π-energies allows the calculation of π-bond energies in a much simpler way.[4] They classified the single and double C–C bonds further into eight types according to the number of attached hydrogen atoms; they determined the corresponding eight π-bond energies, which are listed in Table 1.

TABLE 1. HMO π-BOND ENERGIES OF CARBON-CARBON BONDS OF ACYCLIC POLYENES CALCULATED BY HESS AND SCHAAD[4]

Designation	Type of bond	Calculated π-bond energy (β)
E_{23}	$H_2C{=}CH$	2.0000
E_{22}	$HC{=}CH$	2.0699
E_{22}'	$H_2C{=}C$	2.0000
E_{21}	$HC{=}C$	2.1083
E_{20}	$C{=}C$	2.1716
E_{12}	HC-CH	0.4660
E_{11}	HC-C	0.4362
E_{10}	C-C	0.4358

The total π-energy of any acyclic polyene was then found to be very accurately calculated with these π-bond energies in an additive manner. This means that the π-bonds in polyene are quite localized at the conventionally-written double bonds. In this connection, we reexamined the additivity of π-bond energies of linear polyenes within the framework of the HMO theory, and without any additional assumptions.

Results and Discussion

The total HMO π-energy (E_{HMO}) of linear polyene is calculated from the following simple expression:[5)

$$E_{\mathrm{HMO}}([\mathrm{N}]\text{-polyene}) = 2\operatorname{cosec}\frac{\pi}{2\mathrm{N}+2} - 2. \qquad (1)$$

Similarly, the total HMO π-energy of annulene is evaluated using the following expression:[5]

$$E_{\mathrm{HMO}}([\mathrm{N}]\text{-annulene}) = \begin{cases} 4\operatorname{cosec}\dfrac{\pi}{\mathrm{N}} & \text{for } [4n+2]\text{-annulene} \\ 4\cot\dfrac{\pi}{\mathrm{N}} & \text{for } [4n]\text{-annulene.} \end{cases} \qquad (2)$$

In the above expressions, N is the number of carbon atoms in linear polyene (1) or annulene (2). The energies obtained from the expressions (1) and (2) are given in units of β.

It is generally accepted that, as the ring of annulene becomes very large, the $(4n+2)$ π rule on aromaticity no longer operates, and the annulene is considered to be a nonaromatic cyclic polyene.[6] Assuming that the π-bond energies are additive, [infinity]-annulene can be employed as one of the reference compounds in determining the π-bond energies. When N is large enough, the total π-energy of [N]-annulene can be expressed with the use of Hess and Schaad's notation (See Table 1) as:

$$E_{\mathrm{HMO}}([\mathrm{N}]\text{-annulene}) \sim \frac{\mathrm{N}}{2}(E_{22}+E_{12}). \qquad (3)$$

Therefore, the π-bond energy of the unit structure in annulene, which is a combination of CH=CH and CH–CH bonds, is estimated at the nonaromatic limit as:

$$E_{22} + E_{12} = \lim_{\mathrm{N}\to\infty} \frac{E_{\mathrm{HMO}}([\mathrm{N}]\text{-annulene})}{\left(\dfrac{\mathrm{N}}{2}\right)} = \frac{8}{\pi} = 2.5464791\cdots\cdots . \qquad (4)$$

The same quantity can be derived from the following expression concerning linear polyenes:

$$E_{22} + E_{12} = \lim_{\mathrm{N}\to\infty} \{E_{\mathrm{HMO}}([\mathrm{N}+2]\text{-polyene}) - E_{\mathrm{HMO}}([\mathrm{N}]\text{-polyene})\} = \frac{8}{\pi} \qquad (5)$$

The coincidence between the above two values supports strongly the absence of aromaticity in large annulene, as was expected.[6] In this sense, Hess and Schaad's estimate of the limiting REPE (resonance energy per π-electron) of annulene at 0.0053β appears to be unlikely.[7]

On the other hand, the difference in the total HMO π-energies between [infinity]-annulene and the corresponding linear polyene is associated with the π-bond energy of the $CH_2{=}CH$ type (E_{23}). That is,

$$2E_{22} + E_{12} - 2E_{23} = \lim_{\mathrm{N}\to\infty} \{E_{\mathrm{HMO}}([\mathrm{N}]\text{-annulene}) - E_{\mathrm{HMO}}([\mathrm{N}]\text{-polyene})\} = 2 - \frac{4}{\pi} = 0.7267605\cdots\cdots \qquad (6)$$

Table 2. π-Energies in units of β of linear polyenes

N	E_{HMO}	E_{A}	$E_{\mathrm{HMO}}-E_{\mathrm{A}}$	E_{HS}	$E_{\mathrm{HMO}}-E_{\mathrm{HS}}$
4	4.4721	4.3662	0.1059	4.4660	0.0061
6	6.9879	6.9127	0.0752	7.0019	−0.0140
8	9.5175	9.4592	0.0584	9.5378	−0.0203
10	12.0533	12.0056	0.0477	12.0737	−0.0204
12	14.5925	14.5521	0.0403	14.6096	−0.0171
14	17.1335	17.0986	0.0350	17.1455	−0.0120
16	19.6759	19.6451	0.0308	19.6814	−0.0055
18	22.2191	22.1916	0.0276	22.2173	0.0018
20	24.7630	24.7380	0.0250	24.7532	0.0098
22	27.3073	27.2845	0.0228	27.2891	0.0182
24	29.8519	29.8310	0.0210	29.8250	0.0269
26	32.3969	32.3775	0.0194	32.3609	0.0360
28	34.9420	34.9239	0.0181	34.8968	0.0452
30	37.4873	37.4704	0.0169	37.4327	0.0546
32	40.0328	40.0169	0.0159	39.9686	0.0642
34	42.5783	42.5634	0.0150	42.5045	0.0738
36	45.1240	45.1099	0.0142	45.0404	0.0836
38	47.6698	47.6563	0.0134	47.5763	0.0935
40	50.2156	50.2028	0.0128	50.1122	0.1034
42	52.7615	52.7493	0.0122	52.6481	0.1134
44	55.3074	55.2958	0.0116	55.1840	0.1234
46	57.8534	57.8423	0.0111	57.7199	0.1335
48	60.3994	60.3887	0.0107	60.2558	0.1436
50	62.9455	62.9352	0.0103	62.7917	0.1538

Therefore, as long as the π-bond energies are additive, the total π-energy of linear [N]-polyene can reasonably be estimated by combining Eqs. (4) and (6) as follows:

$$E_{\mathrm{A}}(\text{[N]-polyene}) = \frac{\mathrm{N}}{2}(E_{22}+E_{12}) - (2E_{22}+E_{12}-2E_{23})$$

$$= \frac{4(\mathrm{N}+1)}{\pi} - 2. \tag{7}$$

Table 2 shows the total π-energies of linear polyenes estimated by using Eq. (7) (E_{A}), together with those estimated from Table 1 (E_{HS}).

As may easily be seen, the total HMO π-energies are excellently reproduced by the present treatment. It must be noted that E_{A} was derived simply on the assumption of the additivity of π-bond energies. Since there is no arbitrariness in deriving Eq. (7), E_{A} is a unique solution for linear polyene. The deviation of E_{A} from E_{HMO} is generally very small, and at its maximum at N=4, for which E_{A} is only 2.37 percent less than E_{HMO}. Even though every π-bond energy can not be evaluated by the present consideration, we can safely say that the additivity of π-bond energies was verified in this manner. The small energy difference between E_{A} and E_{HMO} might be considered as a kind of stabilization energy, though it is not well grounded. This apparent stabilization energy is a result of taking [infinity]- annulene and -polyene as reference compounds; it may be related to the stability of relatively small polyenes.[8] The energy difference diminishes gradually on going to longer polyenes.

In this sense, the total π-energies determined by using Hess and Schaad's π-bond energies (E_{HS}) appear to be influenced by the above effect. Since their intention was to attain the best additivity of π-bond energies for acyclic polyenes of a medium size,[4] the additivity itself is considerably better for polyenes with N-values less than 22. The energy deviation of E_{HS} from E_{HMO} is suppressed at less than 0.22 percent of the total π-energy in that range of N. However, we could not find any meaning in the energy deviation, as it is not systematic with respect to N. It is totally dependent on the choice of π-bond energies. Some parts of the energy deviation are possibly due to the arbitrary assignment of the value to two of the eight π-bond energies made by Hess and Schaad.[4] The energy deviation of E_{HS} from E_{HMO} as well as the percent energy deviation increases monotonously beyond N=22.

As is indicated in Eq. (4), the π-bond energy of the unit structure of annulene was estimated at 2.5465β, which is quite comparable to the value determined from Table 1 (2.5359β). On the other hand, the quantity defined by Eq. (6) (0.7268β) is somewhat larger than the corresponding value determined from Table 1 (0.6058β). Such a discrepancy is suggestive of the peculiar contribution of the edge double bonds in polyene.

The above discussion has been made on the basis of the simple HMO theory, in which the effect of bond alternation was completely disregarded for the sake of simplicity. As long as the effect of the more striking bond alternation near both edges of the polyene[5] is assigned simply to E_{23} only, it must be slightly larger than was expected by Hess and Schaad.[4] This fact also suggests that, when the additive π-bond energies derived from relatively small polyenes are used to spurious estimate the resonance energies of cyclic systems, spurious results might sometimes be produced.

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) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 692 (1965).
2) M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).
3) H. P. Figeys, *Tetrahedron*, **26**, 5225 (1970).
4) B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305 (1971).
5) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman, San Francisco, Calif. (1965).
6) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London (1969).
7) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).
8) See *e.g.*, "The Chemistry of Alkenes," edited by S. Patai, Interscience Publ., London (1964).