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The Resonance Energies of Polyacenes and Related Compounds

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

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The resonance energies of polyacenes were determined on the basis of the additive principle of π-bond energies in nonaromatic compounds. The additive components in the total π-energies for these compounds were reasonably estimated from the infinitely large polyacene. The calculated resonance energies appear to be much improved as compared with those calculated by Hess and Schaad.

In 1965, Dewar and Gleicher, using the semi-empirical SCF-MO method, found that the bond energies of acyclic polyenes are additive.[1-3] Therefore, we can readily calculate the total energy of any acyclic polyene by summing the energies of all its bonds. Using these additive bond energies, we can also calculate the reference energies of cyclic polyenes, and hence obtain their resonance energies. Here, the reference energy is defined as the energy which the compound in question would possess if it were absolutely olefinic in nature. These resonance energies were the first aromaticity indices which correlated very well with the experimental stability for a wide range of conjugated hydrocarbons.[4,5]

Subsequent HMO calculations, carried out by Hess and Schaad,[6-8] have produced results which nicely parallel the corresponding results of the SCF-MO approach. They classified the carbon-carbon bonds of acyclic polyenes into eight types, five types of double bonds and three types of single bonds, depending upon the number of attached hydrogens. The additive π-bond energies were then assigned to these types of π-bonds. These energies were used to calculate the reference energies of cyclic polyenes.

However, it must be noted that the additive bond energies have been, in all cases, somewhat arbitrarily determined from some groups of acyclic polyenes. Although the agreement between the calculated resonance energies and the experimental stabilities is generally good, the use of these fixed bond energies might sometimes cause a considerable ambiguity in the obtained resonance energies, especially for the larger conjugated systems.[9,10] With this in view, we reexamined the reference energies for the linear polyacenes within the framework of the HMO theory; we would now like to point out that the HMO resonance energies hitherto published for the polyacenes[6,7] appear to be considerably larger than what they should be. The classification of π-bonds made by Hess and Schaad[6] is assumed throughout this article.

Results and Discussion

It is widely known that the linear annellation of unsaturated six-membered rings yields a series of hydrocarbons (polyacenes) which show a decreasing stability as the number of rings is increased.[11,12] According to Clar,[11,12] every polyacene is stabilized primarily by a single aromatic sextet. One sextet is shared among all the rings by migrating from one ring to the other. This means a dilution of the sextet. The benzenoid character decreases with the length of polyacene. Such an aspect of polyacenes can be adequately visualized with the help of Herndon's resonance theory.[13,14]

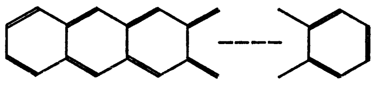
In 1973, Herndon succeeded in applying the resonance-theoretical approach to the evaluation of Dewar-type resonance energies. According to his theory, the resonance energy (E_R) for $[N]$acene, which contains N six-membered rings, is expressed as follows:

$$E_R([N]\text{acene}) = \frac{2[N\gamma_1+(N-1)\gamma_2]}{N+1}, \qquad (1)$$

where γ_1 denotes the resonance interaction between two Kekulé structures related by a permutation of three double bonds within a six-membered ring, and where γ_2 denotes the resonance interaction related by a permutation of five double bonds within a periphery of two annellated rings.

On this basis, the resonance energy for an infinitely large polyacene (I) can readily be given as:

$$E_R(\text{I}) = 2(\gamma_1+\gamma_2). \qquad (2)$$



(I)

The limiting resonance energy of polyacene is thus a finite quantity, *i.e.*, twice the sum of the resonance energy of benzene and that of the ten-membered ring. It is, hence, assumed with little difficulty that the reference energy of any polyacene can be estimated from the infinitely large polyacene because the resonance energy per π-electron (REPE) is considered to be zero. The use of an infinitely large species as a reference compound has been successfully demonstrated for the monocyclic conjugated systems.[10,15]

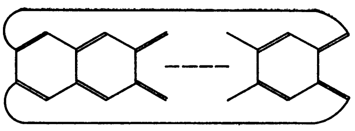
The unit energy (E_U) of polyacene is defined as the increment of the π-energy of the reference structure associated with every additional six-membered ring. All the energies will hereafter be given in units of β. The total π-energy (E_{HMO}) of $[N]$acene is analytically expressed in this form:[16,17]

$$E_{HMO}([N]\text{acene}) = 2+2\sum_{m=1}^{N}\sqrt{9+8\cos\frac{m\pi}{N+1}}. \qquad (3)$$

With the use of this expression, the unit energy of polyacene is given by the following expression:

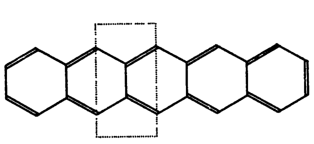
$$\begin{aligned} E_U(\text{polyacene}) &= \lim_{N\to\infty}\frac{2}{N}\sum_{m=1}^{N}\sqrt{9+8\cos\frac{m\pi}{N+1}} \\ &= 2\int_0^1\sqrt{9+8\cos\pi x}\,dx \\ &= 5.6113421\ldots\ldots. \end{aligned} \qquad (4)$$

In this connection, it is noteworthy that the unit



(II)

energy of polyacene does not necessarily depend upon the boundary conditions of the infinitely large polyacene. The hypothetical cyclic polyacene (II) has the same unit energy as that of the linear polyacene. It is clear that there is no aromatic sextet in any Kekulé structure of the cyclic polyacene. All six-membered rings in it are "empty" in Clar's sense.[11,12] According to Herndon's resonance theory,[13,14] the cyclic polyacene of any size must have zero resonance energy because neither γ_1-type nor γ_2-type interactions are present in it. This fact strongly suggests that the E_U(polyacene)-value, obtained in this manner, is free from aromaticity.



(III)

The unit structure corresponding to the unit energy of polyacene is illustrated in III as the portion of pentacene enclosed in the dotted line. As in the case of the cyclic polyacene, the unit structure of the infinitely large polyacene is considered to be a combination of two CH=C bonds, two CH–C bonds, and one C–C bond. In other words, the unit energy of polyacene is written as:

$$E_U(\text{polyacene}) = 2E_{CH=C} + 2E_{CH-C} + E_{C-C}\,, \tag{5}$$

where $E_{CH=C}$ is the additive π-bond energy of the CH=C bond, E_{CH-C} is that of the CH–C bond, and E_{C-C} is that of the C–C bond.

For this reason, the use of Kekulé structure of Type I is recommended for estimating the resonance energy for any polyacene. If it is employed as a reference structure, all the polyacene unit structures in it are structurally the same and are expressed by Eq. (5). Although there are N other Kekulé structures for [N]-acene, they are disregarded in the following calculations. It appears safe to arbitrarily adopt one Kekulé structure as a representative of all, as it has been reported that in no cases were the additive energies of the resonance structures of the same compound significantly different.[6]

The actual polyacene cannot, however, be constructed with the unit structures of the above type only. For example, pentacene is composed of four polyacene unit structures and the residual parts on both edges. If the residual parts are combined, they form a geometry of benzene. Therefore, the canonical structure of Type I for [N]acene corresponds to the sum of the $N-1$ polyacene unit structures and the reference structure of benzene. The π-energy of the reference structure (E_A) of benzene has already been calculated from the unit energy of the infinitely large annulene,[10] that is:

$$\begin{aligned} E_A(\text{benzene}) &= 3(E_{CH=CH} + E_{CH-CH}) \\ &= 7.6394373\ldots\ldots\,, \end{aligned} \tag{6}$$

where $E_{CH=CH}$ is the additive π-bond energy of the CH=CH bond and where E_{CH-CH} is that of the CH–CH bond. Accordingly, the additive energy, *i.e.*, the reference energy, of [N]acene is written in this form:

$$E_A([N]\text{acene}) = (N-1)E_U(\text{polyacene}) + E_A(\text{benzene})\,. \tag{7}$$

Using this expression for the reference energy, the resonance energy of [N]acene is given by:

$$E_R([N]\text{acene}) = E_{HMO}([N]\text{acene}) - E_A([N]\text{acene})\,. \tag{8}$$

The obtained resonance energies of polyacenes and related compounds are all listed in Table 1.

As may easily be seen, the total resonance energy of polyacene is a slowly varying function of N, and it appears to converge to some value near 0.460. These

TABLE 1. RESONANCE ENERGIES OF POLYACENES AND RELATED CONPOUNDS IN UNITS OF β

Species	E_{HMO}	E_A	E_R	REPE
Benzene	8.0000	7.6394	0.3606 (0.39)	0.0601 (0.065)
Naphthalene	13.6832	13.2508	0.4325 (0.55)	0.0432 (0.055)
Anthracene	19.3137	18.8621	0.4516 (0.66)	0.0323 (0.047)
Tetracene	24.9308	24.4735	0.4574 (0.75)	0.0254 (0.042)
Pentacene (III)	30.5440	30.0848	0.4592 (0.84)	0.0209 (0.038)
Hexacene	36.1560	35.6961	0.4598	0.0177
Heptacene	41.7675	41.3075	0.4600	0.0153
Octacene	47.3789	46.9188	0.4601	0.0135
Nonacene	52.9903	52.5302	0.4601	0.0121
Decacene	58.6017	58.1415	0.4601	0.0110
Compound IV	30.0785	30.0848	−0.0063 (0.37)	−0.0003 (0.017)
Azulene	13.3635	13.2508	0.1127 (0.23)	0.0113 (0.023)
Naphthalene-2,3-quinododimethide	15.532*	15.525	0.007 (0.093)	
Anthracene-2,3-quinododimethide	21.133*	21.137	−0.004 (0.169)	
Tetracene-2,3-quinododimethide	26.741*	26.748	−0.007 (0.253)	
Pentacene-2,3-quinododimethide (V)	32.351*	32.359	−0.008 (0.338)	

Total HMO π-energies marked with asterisks were taken from Ref. 19.

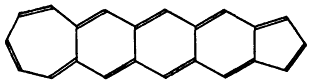
resonance energies are in marked contrast to those determined by Hess and Schaad,[6,7] which are placed in parentheses in Table 1. The latter resonance energies increase with an increase in the number of six-membered rings. This discrepancy between the two sets of resonance energies correspondingly expands on going to higher polyacenes. As a result, our resonance energy of pentacene (0.4592) is about a half of theirs (0.84), although the resonance energies of benzene are similar to each other.

This discrepancy in energy is mainly due to the difference between the π-energies of the polyacene unit structure as estimated by them and by us. The π-energy of the unit structure is calculated to be 5.5248 with the use of the π-bond energies determined by Hess and Schaad.[6] For reference, their additive π-bond energies are 2.1083 for the CH=C bond, 0.4362 for the CH–C bond, and 0.4358 for the C–C bond. Since the π-energy of the same unit structure is 5.6113 according to Eq. (4), the energy difference of 0.0865 is every time added to their resonance energy of polyacene. The most important point is that, if their π-bond energies are used, the limiting REPE amounts to as much as 0.0216; any higher polyacene must be as stable as azulene (REPE=0.023).

On the contrary, it is noticeable that the resonance energies determined by us are approximately constant from anthracene to decacene. Such a tendency of the resonance energies is in good accord with Clar's aromatic sextet theory.[11,12] The constancy of the total resonance energies apparently reflects the presence of a single aromatic sextet in every polyacene. The increment in the resonance energy from benzene to decacene is only 27.6 percent of the resonance energy of benzene. Such a small increment might be attributed to the resonance interactions among all possible Kekulé structures.

In this relation, it is interesting to see that the limiting resonance energy estimated by Herndon's method [Eq. (2)] is about twice as much as ours. Although we premised Herndon's resonance theory in evaluating the polyacene unit energy, the HMO resonance energies for the individual polyacenes are considerably different from the predictions of his theory. However, we might say that the two series of resonance energies of polyacenes are fairly consistent with each other in the sense that the REPE-values, which are closely associated with the stability of the compounds, rapidly converge to zero on going to higher polyacenes.

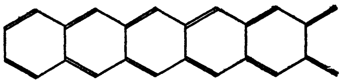
The validity of the polyacene unit energy, as estimated by us, is further supported by the plausible estimate of the resonance energies of some other polyacene analogues. Compound IV is one of the structural isomers of pentacene. This not-yet-isolated compound has been of theoretical interest, because its lowest energy state is supposedly a triplet.[18] As long as the spin states are disregarded, this compound possesses the same reference energy as pentacene. It can, then, be predicted to have the resonance energy of 0.3716 by using the π-bond energies of Hess and Schaad,[6] while it is much reduced to −0.0063 by using the present reference energy of pentacene. According to the PMO method,[3] when the essentially single bond is introduced between carbon atoms of a like parity in an alternant annulene, it leads to no first-order change in π-energy. In this sense, Compound IV should have the resonance energy similar to that of [22]annulene (0.0954).[10] In addition, there is no aromatic sextet in any of the resonance structures of this compound. These facts are evidently favorable to our resonance energy for this compound.



(IV)

The resonance energy ratio of azulene to benzene is 0.59 according to the calculations made by Hess and Schaad.[6] It is reduced by our treatment to 0.3127, which is in good agreement with Herndon's prediction (0.38).[13] The SCF-MO calculations performed by Dewar and de Llano[2] also favor our resonance energy of azulene. They showed azulene to have 19.4 percent of the resonance energy of benzene. Non-alternant hydrocarbons, such as Compound IV and azulene, are thus found to possess much less aromatic character than the isomeric benzenoid species. At the same time, it is suggested that the aromatic sextet in the classical resonance structure is the main origin of the aromaticity.

On the other hand, Gleicher *et al.* showed that the overall results of HMO calculations for quinododimethides with the use of the method and π-bond energies of Hess and Schaad are gratifying.[19] Nevertheless, the results concerning the series of polyacene-2,3-quinododimethides were disturbing. Although only a single classical structure can be written for each of these compounds, there is a steady increase in the REPE. Thus, pentacene-2,3-quinododimethide (V) is predicted to possess half the aromatic character associated with pentacene itself.



(V)

This problem can also be solved with the present unit energy of pentacene as follows. Note that there are $N-1$ polyacene unit structures in [N]acene-2,3-quinododimethide ([N]AQDM). Therefore, a correction must be made, at least, for the additive energy of this portion. As was mentioned above, the additive energy of the polyacene unit structure determined with the use of the π-bond energies of Hess and Schaad[6] differs by 0.0865 from that determined from Eq. (4). With this unit-energy difference, the reference energy of the entire compound can be approximately modified to this form:

$$E_{\mathrm{A}}([N]\mathrm{AQDM}) = E_{\mathrm{HS}}([N]\mathrm{AQDM}) - 0.0865(N-1). \quad (9)$$

Here, E_{HS} signifies the reference energy determined according to the method of Hess and Schaad. The resonance energies refined with Eq. (9) are much more acceptable, because the corresponding REPE values are all negligibly small. This is in good accord with the fact that there is no aromatic sextet in the resonance structure of any polyacene-2,3-quinododimethide. Furthermore, the present resonance energies parallel fairly well the results of the SCF-MO calculations carried out by Gleicher *et al.*[19]

In conclusion, the well-established additivity of the π-bond energies of nonaromatic polyenes allowed us to take an infinitely large polyacene as a reference compound in estimating the aromatic character of a given polyacene. The present approach appears to be superior to the original method of Hess and Schaad when both are applied to polyacenes and related compounds. As has been pointed out in previous papers,[10,15] the discrepancy between the resonance energies of Hess and Schaad and ours is attributable to the differently determined π-bond energies. They determined the π-bond energies from acyclic polyenes of a medium size. Slight energy deviations from ours have been magnified in larger compounds, and have sometimes become comparable to the resonance energies themselves. The polyacene series is a good example of how small errors in the π-bond energies can easily produce spurious results by a cumulative effect. Our simplified model neglected all effects arising from bond alternation. It is hoped that the gross features of the aromatic character of these compounds are not changed by them.

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