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A New Measure of Aromatic Stabilization: Resonance Energy per π Bond (REPB)

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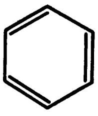
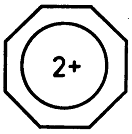
Synopsis. A concept of resonance energy per π electron appears unsuitable for representing the aromatic stabilization of a conjugated compound. If the resonance energy is divided by the number of π bonds constituting π rings in the conjugated system, though, a reasonable index is obtained for the same purpose.

In 1971, Hess and Schaad[1] interpreted Dewar's theory of aromaticity[2] by means of the HMO theory. They defined the aromatic resonance energy of a conjugated compound as the difference between the HMO π energy and the π energy of a "localized structure" obtained in an additive manner using the empirical π bond energies. Here, a "localized structure" signifies an olefinic reference structure which is hypothetically free from aromaticity. They further showed that if the resonance energy is divided by the number of π electrons in the compound, a quantity is obtained which correlates well with the experimental stability.[1] This was termed "resonance energy per π electron (REPE)". In previous papers,[3] we succeeded in formulating a characteristic polynomial for a "localized structure" of a conjugated compound, and analytically reproduced the resonance energies of Hess and Schaad without any parametrization. Of course, our resonance energies are Dewar-type.[1–3] In this note, we wish to point out that the definition of REPE should be modified in line with our exact resonance energies.

(I)



(II)



(III)

(IV)

First, one should remember that Hess and Schaad defined REPE in order to overcome the wide variation in the size of conjugated systems usually compared.[1] This means that the REPE was presented as a better way of comparing resonance energies of various compounds. However, one finds that when the concept of REPE is extended to ionic conjugated systems, a serious ambiguity arises. For example, the resonance energies of the cyclobutadiene dianion(I), benzene(II), and the cyclooctatetraene dication(III) must be divided by the same number of π electrons, *i.e.*, six, to obtain their REPE values. This procedure is obviously in contradiction to the original intention of Hess and Schaad.[1] As has been suggested above, they intended to reflect the size of a conjugated system in the resonance energy by defining REPE. Therefore, the divisor should be changed if the size of a conjugated system is changed. Logically it should not depend upon the ionicity of a conjugated system.

According to the same definition of REPE, the resonance energies of benzene(II) and butalene(IV) must also be divided by the same number of π electrons, *i.e.*, six, in order to obtain their REPE values. Although butalene has one more π bond than benzene, the sizes of their conjugated systems have been tacitly considered to be identical.[1] We might say that the number of π electrons does not always reflect the size of a conjugated system, even if it is a neutral compound. Such an aspect of REPE is found among many sets of conjugated compounds.

We verified previously that aromaticity arises exclusively from a set of π rings in a conjugated system.[3] It is obvious that even if side chains and the like are conjugated with the main part of a cyclic conjugated system, they are absolutely olefinic. We might say that these side chains are neither stabilized or destabilized by the overall resonance energy. The role of the side chains is to somewhat modify the resonance energy of a π ring system (*i.e.*, a set of π rings in the conjugated system). The resonance energy obtained should, therefore, be attributed exclusively to the π rings or their constituents (*i.e.*, π bonds constituting these π rings). This fact is also inconsistent with the previous definition of REPE.

In order to avoid such REPE-based difficulties, we propose a new quantity which supposedly represents the actual stability of a conjugated system. It is defined as the Dewar-type resonance energy, divided by the number of π bonds which form a π ring system of a conjugated compound, and is termed "resonance energy per π bond" or REPB for short. As is indicated in this definition, the π bonds involved here are limited to those constituting cyclic components of Sachs graphs (*i.e.*, subgraphs of a molecular graph originally introduced by Sachs[4]).

It is noteworthy to see that, as an index of the size of a π ring system, the number of π bonds in it is preferable to the number of π electrons. It is nothing other than all the π bonds in the π ring system which must be sustained by the overall resonance energy. In this sense, the REPB reflects the size of a π ring system. The resonance energy has thus been assigned to individual π bonds forming a π ring system. Such a consideration appears to support our definition of REPB.

Table 1 contains 18 examples of conjugated compounds, shown with their values for REPE and REPB. When a conjugated system is neutral and monocyclic, REPE exactly agrees with REPB. However, when a conjugated system is ionic or polycyclic, the two quantities generally disagree. The deviation of REPE from REPB is never small for most conjugated compounds. One can see by using REPB that substituents such as a vinyl group do not stabilize a cyclobutadiene ring so

Table 1. REPE and REPB values in units of β for 18 conjugated systems

Compound	Resonance energy[a)]	REPE $\times 10^3$	REPB $\times 10^3$	$100\times\dfrac{(\text{REPE}-\text{REPB})}{\text{REPB}}$
Cyclobutadiene	−1.226	−306.6	−306.6	0.0
Tetravinylcyclobutadiene	−0.703	−58.6	−175.7	−66.6
Cyclobutadiene dianion	0.305	50.8	76.1	−50.0
Cyclopentadienyl anion	0.317	52.8	63.3	−16.7
Benzene	0.273	45.4	45.4	0.0
Styrene	0.249	31.2	41.5	−24.8
Cycloheptatrienyl cation	0.225	37.6	32.2	16.7
Cyclooctatetraene dication	0.186	30.9	23.2	33.3
Butalene	−0.604	−100.7	−86.3	16.7
Pentalene	−0.215	−26.9	−23.9	12.5
Calicene	0.433	54.2	54.2	0.0
Fulvalene	−0.299	−29.9	−29.9	0.0
Azulene	0.151	15.1	13.7	10.0
s-Indacene	0.055	4.6	3.9	16.7
Naphthalene	0.389	38.9	35.3	10.0
Anthracene	0.475	33.9	29.7	14.3
Pyrene	0.598	37.4	31.5	18.8
Coronene	0.947	39.5	31.6	25.0

a) Ref. 3.

dramatically. This is in marked contrast to the prediction based on the REPE values.[5)]

So far, such a discrepancy has not been noticed, partly because the degree of aromaticity cannot be measured quantitatively, and partly because scarcely no resonance energies have been estimated for ionic species.[6)] Furthermore, the resonance energies published for neutral species are all empirical ones, in the sense that they are based on empirical π bond energies.[1,2)] Now the situation has been totally changed. We have shown that Dewar-type resonance energies can be exactly calculated for any conjugated systems, including ions, as long as the HMO theory is used.[3)] Accordingly, a measure of the aromatic stabilization should also be refined in harmony with the exactness of these resonance energies. This is exactly why REPE must be replaced by REPB. If a more detailed discussion of aromaticity is made in the future, it should be based on the values for REPB. The same definition of REPB can be applied to any Dewar-type resonance energies.[1–3)]

References

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6) Here, the resonance energies are restricted to those of the Dewar type. The only previous attempt to estimate the resonance energies of ionic species was made by the present author [J. Aihara, *Bull. Chem. Soc. Jpn.*, **49**, 1427 (1976)].