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Improved Resonance Energies of Nonalternant Hydrocarbons. An ω-Technique Approach

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The ω-technique of Wheland and Mann was introduced into the graph theory of aromaticity in order to improve the resonance energies of nonalternant hydrocarbons. For these compounds, the ω-technique resonance energy was more or less smaller than the resonance energy calculated on the basis of the simplest Hückel MO model. Especially, several compounds thus far considered to be aromatic were predicted to be substantially olefinic with much reduced resonance energies. They are calicene, sesquifulvalene, azulene, dibenzo[*cd,gh*]pentalene, and cyclohepta[*def*]fluorene. Many aspects of their chemistry were evidently consonant with the improved resonance energies. Possible limitation of the use of electrophilic substitution as a criterion of aromaticity was discussed. Resonance energies of alternant hydrocarbons are not modified by application of the ω-technique.

The graph theory of aromaticity[1-4] has proved very successful in rationalizing aromatic character of a wide variety of cyclic conjugated compounds. A theoretical relationship between diamagnetic susceptibility exaltation and aromatic stabilization has also been verified by means of this theory.[5] The graph theory of aromaticity in its original form is based on the simplest Hückel molecular orbital (HMO) model.[1-5] In this model the assumption is tacitly made that the Coulomb integral α is a constant characteristic of an atom and independent of a conjugated system in which it appears. A standard value of α for sp^2 carbon atoms may be denoted by α_0. This assumption is indeed reasonable for alternant hydrocarbons, each with a uniform charge distribution.

However, a simple argument[6] shows that a carbon atom in a conjugated hydrocarbon on which the charge density q is not equal to unity cannot really have $\alpha=\alpha_0$. If $q<1$, the net positive charge means that the screening seen by any one electron is reduced and the Coulombic attraction to the nucleus is increased. The Coulomb integral for such a carbon atom should have a more negative value. Conversely, a carbon atom with a net negative charge should have a less negative value of α. Wheland and Mann proposed that the value of α should be linearly related to the charge on the atom concerned, namely,[7]

$$\alpha_s = \alpha_0 + (1-q_s)\omega\beta_0, \tag{1}$$

where ω is a dimensionless parameter whose value may be so chosen as to give the best agreement with experiment, β_0 a standard value of the resonance integral between two bonded sp^2 carbon atoms, and the subscript s used to represent the s-th carbon atom.

The value appropriately selected for the ω parameter apparently allows for an average effect of other electrons. We might say that, with one empirical parameter, this ω-technique introduces some electron repulsion within the framework of the simple HMO model.[6] The use of this technique has been shown to lead to improved calculated energy values for nonalternant hydrocarbons and conjugated cations.[6-8] In this paper I would like to revise the graph theory of aromaticity[1-5] by means of the ω-technique, and present improved resonance energies of typical nonalternant hydrocarbons in conjunction with their chemistry.

Theory

One first obtains the charge distribution of a conjugated hydrocarbon according to the simplest HMO model. This charge distribution is used to calculate new α_s's according to Eq. 1, and the new charge distribution is calculated. This process is continued until the charge distribution no longer changes, that is, the system is self-consistent.[6,7] The value of ω is taken to be 1.40 as usual.[8] On the other hand, an olefinic reference structure constructed graph-theoretically for any conjugated hydrocarbon can be regarded as a kind of alternant hydrocarbon.[1] The charge density is correspondingly equal to unity on each carbon atom of the reference structure.[9] The total π-electron energy of the reference structure was termed the reference energy.[1] It can hence be calculated without regard to the charge distribution of the reference structure. In other words, the reference energy of a conjugated hydrocarbon is independent of the ω parameter. Thus the ω-technique resonance energy of any conjugated hydrocarbon can be calculated relative to the reference energy based on the simplest HMO model.

Results and Discussion

Resonance energies thus calculated for 40 nonalternant hydrocarbons are listed in Table 1. They are compared therein with the resonance energies calculated on the basis of the simplest HMO model.[1,4] First of all, it is noteworthy that the total π-electron energy of any nonalternant hydrocarbon increases by application of the ω-technique. This might imply that the effect of electron repulsion is to diminish the resonance energy of a conjugated system because the reference energy remains unchanged. Consequently, when the absolute value of the resonance energy is small, the sign of the resonance energy is often changed by application of the ω-technique. Such compounds are **1**—**5**, **17**, **19**, and **31**.

Here a new measure of aromatic stabilization is adopted, which is defined as 100 times the resonance energy, divided by the reference energy.[10] It is termed the percent resonance energy (%*RE*). This quantity nicely gives the degree of stabilization with which a conjugated system behaves aromatically as a whole.

Table 1. Resonance energies of 40 nonbenzenoid hydrocarbons

Compound	Simplest HMO		ω-Technique	
	$RE^{a,b)}$	$\%RE^{c)}$	$RE^{a)}$	$\%RE^{c)}$
1	0.063	1.29	−0.145	−2.96
2	0.020	0.27	−0.082	−1.10
3	0.009	0.09	−0.052	−0.52
4	0.005	0.04	−0.036	−0.29
5	0.009	0.12	−0.005	−0.06
6	0.000	0.00	0.000	0.00
7	−0.461	−5.81	−0.607	−7.66
8	0.433	4.13	0.038	0.36
9	−0.299	−2.28	−0.367	−2.81
10	0.272	1.73	0.023	0.15
11	−0.218	−1.20	−0.261	−1.43
12	−0.215	−2.02	−0.411	−3.85
13	0.151	1.14	0.055	0.42
14	−0.141	−0.89	−0.252	−1.60
15	0.354	2.18	0.319	1.96
16	0.339	1.80	0.317	1.69
17	0.101	0.62	−0.030	−0.18
18	0.106	0.56	0.014	0.07
19	0.055	0.34	−0.056	−0.35
20	0.106	0.55	0.065	0.33
21	0.398	1.82	0.334	1.53
22	0.134	0.55	0.110	0.45
23	0.372	1.70	0.317	1.45
24	0.376	1.72	0.312	1.43
25	0.222	1.16	0.062	0.32
26	0.247	1.13	0.063	0.29
27	0.230	0.95	0.152	0.62
28	0.217	0.99	0.131	0.60
29	0.214	0.98	0.117	0.54
30	0.122	0.56	0.034	0.16
31	0.035	0.14	−0.078	−0.32
32	0.578	2.64	0.567	2.59
33	0.418	1.92	0.326	1.49
34	0.400	1.64	0.340	1.39
35	0.416	1.71	0.382	1.54
36	0.558	2.28	0.552	2.26
37	0.310	1.42	0.275	1.26
38	0.508	1.85	0.423	1.54
39	0.506	1.84	0.434	1.58
40	0.522	1.90	0.425	1.55

a) Resonance energy. b) References 1 and 4. c) Percent resonance energy.


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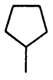
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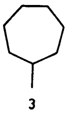
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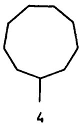
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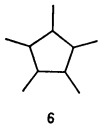
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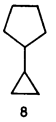
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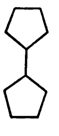
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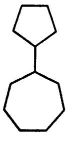
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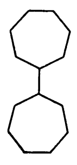
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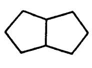
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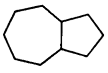
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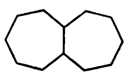
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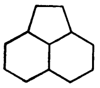
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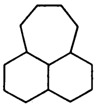
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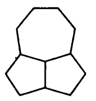
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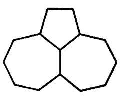
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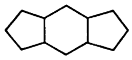
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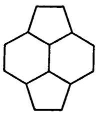
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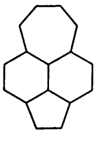
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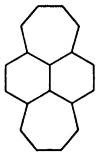
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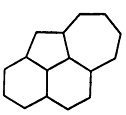
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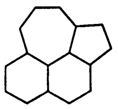
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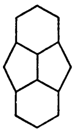
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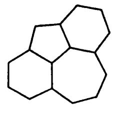
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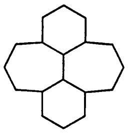
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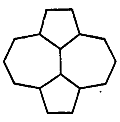
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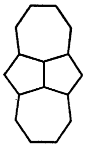
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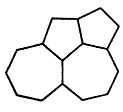
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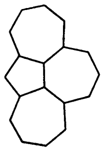
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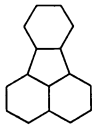
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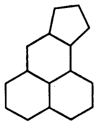
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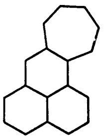
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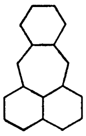
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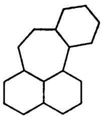
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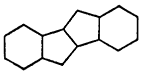
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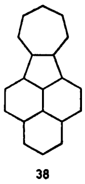
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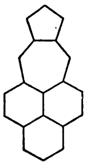
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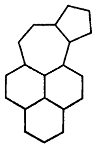
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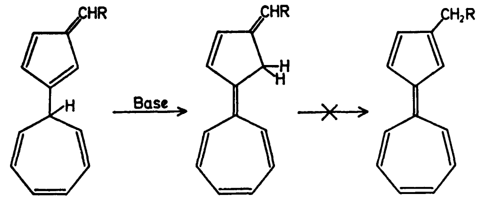
Note that the $\%RE$ neither depends upon the number of π electrons[11] nor upon the number of π bonds[12] in a conjugated system. By examining $\%RE$ values in Table 1 in detail, we can safely say that compounds with $\%RE<0.50$ might be regarded as olefinic species.

When one or more aromatic sextets[13–17] can be chosen from a nonalternant hydrocarbon, it may be called a semibenzenoid hydrocarbon.[18] Such semibenzenoid hydrocarbons are **15**, **16**, **20**—**24**, and **32**—**40**. For these compounds, a decrease in resonance energy is rather modest. Therefore, previous aromaticity considerations[1,4,11,15,17–19] are still applicable to them. They are not repeated here.

On the other hand, when a conjugated system is a combination of odd-membered π rings only, a pronounced decrease in resonance energy occurs by application of the ω-technique. Among them the following five fully nonbenzenoid hydrocarbons are particularly noteworthy: calicene (**8**), sesquifulvalene (**10**), azulene (**13**), dibenzo[*cd,gh*]pentalene (**25**), and cyclohepta[*def*]fluorene (**26**). These compounds have been predicted to be moderately aromatic on the basis of the simplest HMO model,[1,4,11] whereas the present approach predicts them to be substantially nonaromatic with markedly reduced resonance energies. We can show below that these ω-technique resonance energies are indeed in excellent agreement with experiment.

Both calicene (**8**) and sesquifulvalene (**10**) have so far had significant $\%RE$ values.[1,11] Sesquifulvalene is known,[20] but it is not stable, polymerizing even at 30 °C. Calicene itself is not known, but a number of substituted calicene derivatives are now known.[21] Some of them, as well as sesquifulvalene, readily form adducts with tetracyanoethylene.[22] These polyene-like features of asymmetric fulvalenes are obviously consistent with the smaller $\%RE$ values. Some calicene derivatives have very large dipole moments,[23] and some have electronic spectra strongly dependent upon the solvent as might be expected for a dipolar species.[24] Such a nonuniform charge distribution in a conjugated system decreases the resonance energy when the ω-technique is applied to it.



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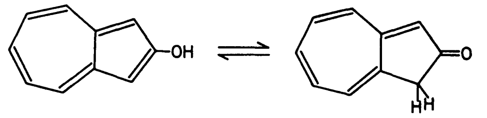
The prototropic rearrangement of 3-cycloheptatrienylfulvenes (**41**) gives the conjugated heptafulvenes (**42**) instead of the sesquifulvalene (**43**).[22,25] Here, R is an alkyl or an aryl group. An aromatic compound might be defined as a compound which tends to maintain its cyclic conjugated system since it has a larger binding energy than the olefinic reference structure. According to this definition, sesquifulvalenes can be classified as olefinic species. Compounds of the type **41** are obviously reluctant to attain a sesquifulvalene conjugated system. Neither triafulvalene (**7**) nor its derivatives have been prepared. The other symmetric fulvalenes **9** and **11** are extremely reactive.[22] Resonance energies of these fulvalenes were also decreased considerably. The same is true for triafulvene (**1**), which is not known yet.

Azulene has been a classical example of a nonbenzenoid aromatic compound. Let the ratio of the resonance energy of azulene to that of the isomeric naphthalene be denoted by *r*. The *r* value based on the ω-technique resonance energies is about one-eighth, which is comparable to that of Dewar and de Llano calculated using the SCF resonance energies.[26] However, it is in poor accord with the *r* value of Hess and Schaad based on the simplest HMO model.[11] It must be noted here that they did not take the effect of electron repulsion into consideration,[11] but Dewar and de Llano did.[26] Azulene has a dipole moment of 1.0 D with the five-membered ring negative,[27] so the ω-technique resonance energy is aparently preferable as long as it is consistent with its chemistry. Thus azulene appears to have a small positive resonance energy, much less than that of naphthalene.

An experimental support for an olefinic nature of azulene is afforded by the occurrence of valence tautomerism of the simple derivatives in solution. 2-Hydroxyazulene (**44**) partly undergoes valence tautomerization to the nonaromatic heptafulvene derivative (**45**).[28] 4,8-Dimethyl-6-hydroxyazulene (**46**) coexists in solution with the tautomeric troponoid species (**47**),[29] in which an azulenoid bicyclic conjugated system is missing.



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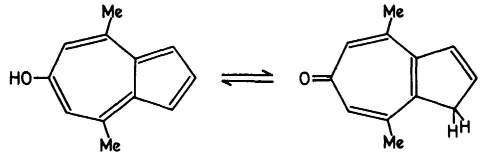

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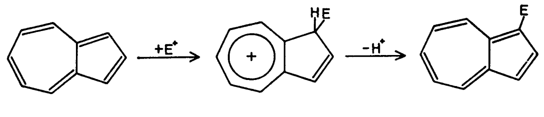
In this context, it should be remembered that 9-anthranol coexists in solution with anthrone.[30] Resonance energies of these two isomers are presumably similar to each other.[31] By analogy with this, the enol forms of hydroxyazulenes **44** and **46** must be as aromatic as the keto forms **45** and **47**, respectively. However, the latter keto forms are olefinic, so must be the former azulenoid species.

Substituted calicenes and sesquifulvalenes are protonated in acidic media to form cyclopropenium and tropylium cations, respectively.[22] Azulene itself is readily protonated, the proton adding in the 1-position of the five-membered ring to form an azulenoid cation.[32] Such a high basicity of a conjugated system is often an indication of aromaticity of the protonated species.[33] Conversely, calicene, sesquifulvalene, and azulene are not typically aromatic, in the sense that they are reluctant to maintain their original conjugated systems in acidic media.

Dibenzo[*cd,gh*]pentalene (**25**) and cyclohepta[*def*]-fluorene (**26**) have not been prepared yet. Although a dianion of **25** is known,[34] attempts to prepare the neutral hydrocarbon were unsuccessful. Such synthetic inaccessibility is not congruent with large resonance energies previously reported for them.[4] The ω-technique resonance energies are both very small in good accord with their chemistry. For these compounds, only two Kekulé structures can be written with a central double bond fixed in each Kekulé structure.

The occurrence of electrophilic substitution was a long-standing criterion of aromaticity. Azulene and some calicene derivatives undergo electrophilic substitution reactions.[35,36] This chemical feature has been used as an irrefutable evidence of aromaticities of these compounds.[11] Electrophilic substitution usually occurs *via* a Wheland-type reaction intermediate.[37] In the case of azulene and calicenes, Wheland-type reaction intermediates are shown below:



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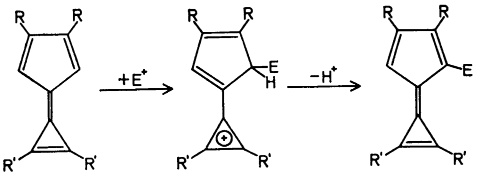
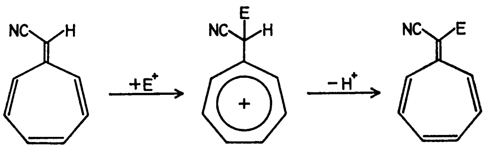


51 52 53

Here, E^+ is indicative of an electrophile.

However, it must be stressed that many olefinic compounds are now known to undergo electrophilic substitution reactions.[38] Such olefinic compounds are metal β-diketonates,[39] 2,3-dihydro-1,4-diazepinium salts,[38,40] 1,2-dihydropyrimidinium salts,[41] open-chain diazapolymethinium salts,[42] Nickel 1,19-dimethyltetradehydrocorrin salts,[43] 8-cyanoheptafulvene,[44] and ethylenic compounds such as vinyl ethers and vinyl sulfides.[45] For all these compounds, a Wheland-type intermediate is either a hetero-atom-stabilized carbonium ion or an aromatically-stabilized carbonium ion.[46] Therefore, specific stabilization of a reaction intermediate appears to be the most important condition for the occurrence of electrophilic substitution on polyenic compounds. For vinyl ethers and vinyl sulfides, a substitution reaction proceeds *via* a hetero-atom-stabilized carbonium ion.[45] 8-Cyanoheptafulvene (**54**) can be regarded as a trisubstituted ethylene. This compound undergoes several electrophilic substitution reactions at the *exo*-methylene group.[44] Each reaction intermediate is obviously an aromatically stabilized tropylium cation (**55**).



54 . 55 56

It is an interesting fact that a Wheland-type intermediate for azulene (**49**) is quite similar to that for 8-cyanoheptafulvene (**55**). Both are evidently stabilized by an aromatic tropylium structure. This analogy strongly suggests that aromaticity of azulene, if any, may not be necessary in order for substitution reactions to proceed on it. Calicenes undergo electrophilic substitution reactions *via* aromatically-stabilized cyclopropenium ion (**52**),[36] but this does not warrant aromaticities of the starting materials, either. Thus the occurrence of electrophilic substitution does not exclude the possibility that the starting material is olefinic as in the case of diazapolymethinium salts[40–42] and 8-cyanoheptafulvene.[44]

Further examination of various electrophilic substitution reactions disclosed the fact that, in general, less aromatic compounds are more favorable to such reactions. There have been several kinetic studies of electrophilic substitution reactions on monocyclic conjugated compounds.[47] For these compounds, the following order of reactivity has universally been established: benzene<thiophene<selenophene<tellurophene<furan<pyrrole.[47] If these compounds are arranged in an ascending order of aromaticity, this order is exactly reversed,[1,48] except for pyrrole which is much more aromatic than furan in all respects.[49]

When all or part of resonance energy is lost to form a Wheland-type reaction intermediate, the degree of destabilization of the intermediate necessarily depends upon the degree of aromaticity of the starting material. As stated above, it also depends upon the nature of the intermediate itself. One obvious conclusion which may be drawn here is that ready occurrence of electrophilic substitution is often inconsistent with high aromaticity. Benzene is then most aromatic and least reactive toward electrophiles. On the other hand, a Wheland-type intermediate for pyrrole is a highly stable azacarbonium ion,[50] *i.e.*, a kind of hetero-atom-stabilized carbonium ion,[46] so the reactivity is much greater than might be expected from its aromaticity. Thus there are not a few difficulties in using electrophilic substitution as a criterion of aromaticity.

Concluding Remarks

The graph theory of aromaticity based on the simplest HMO model[1–4] is free from any parametrization. In the present approach, only one parameter (*i.e.*, ω) had to be introduced in it to improve the resonance energies of nonalternant hydrocarbons. However, the revised theory can still retain all the simplicity and elegance as long as the accepted ω value of 1.40 is used.[6–8] The ω-technique resonance energies of nonbenzenoid hydrocarbons are more or less smaller than those calculated on the basis of the simplest HMO model.[1,11] In this paper, resonance energies of five nonbenzenoid hydrocarbons which are markedly sensitive to the ω-technique were analyzed in detail in conjunction with their chemistry. This analysis clearly indicated the inadequacy of the simplest HMO model, with all Coulomb integrals set equal, for dealing these nonalternant hydrocarbons. Conversely, it has firmly been established that the ω-technique resonance energies are in much better agreement with experiment.

The ω-technique approach can in principle be applied to all conjugated systems and to all cyclic conjugated ions alike. However, when a charge distribution in the reference structure is not uniform, the reference energy must be calculated self-consistently by iteratively evaluating all the Coulomb integrals[9] according to Eq. 1. The original reference energy cannot be used in this case. It goes without saying that the resonance energy of any alternant hydrocarbon remains unchanged even if the ω-technique is applied to it.

It should be pointed up that the empirical theory of aromaticity, developed by Hess and Schaad,11,48) can also be improved by application of the ω-technique. The ability to calculate in an additive manner the total π-electron energy of any acyclic polyene allowed them to calculate the reference energy of a cyclic conjugated system, and hence to obtain the resonance energy. Since acyclic polyenes are all alternant hydrocarbons, their additive π-bond energies11) are not modified by application of the ω-technique. They can still be used to estimate reference energies. Accordingly, the Hess-Schaad resonance energy of a cyclic conjugated hydrocarbon is given as the difference between the total π-electron energy based on the ω-technique and the original reference energy.

When such a modified Hess-Schaad method is applied to nonalternant hydrocarbons, most results presented in this paper can be reproduced. Hess-Schaad resonance energy of azulene is changed from 0.23β to 0.14β, about one-fourth the resonance energy of naphthalene.11) The r value becomes much closer to that estimated in this paper, and also to that estimated using the SCF resonance energies.26)

Finally, another way of improving the graph theory of aromaticity1–5) may be to include the overlap integrals S into HMO calculations.51) Inclusion of overlap changes the spacing of energy levels. However, total π-electron energies and resonance energies do not seem to be affected significantly.6)

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