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Resonance Energies of the Arenium Ions and Their Relevance to the Electrophilic Substitution Reactions

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Hyperconjugative interaction through the methylene group was incorporated in the framework of the Hückel molecular orbital model. Resonance energies of the arenium ions, derived from typical benzenoid hydrocarbons, were calculated using the graph theory of aromaticity. It was found that even a benzenium ion has a considerable degree of aromaticity. In general, the arenium ion with large localization energy has both large resonance energy due to hyperconjugation and large positive charge density at the methylene group. These two quantities are possibly responsible for the competition between substitution and addition reactions on the benzenoid hydrocarbons. An aromatic transition state tends to choose a reaction path to substitution products, at least, for these compounds.

It is widely known from the chemistry of aromatic hydrocarbons that solutions of these compounds in strong acidic media, such as concentrated sulfuric acid, show an intense color even if the pure compound is colorless.[1,2] The formation of an arenium ion, *i.e.*, a proton addition complex, is responsible for this phenomenon. An aromatic hydrocarbon is, therefore, characterized as a base, and the corresponding arenium ion as the conjugate acid. The cyclic π-electron system of an aromatic hydrocarbon is the electron source often sought not only by a proton but also by the reagent electrophile.[3,4] The arenium ions have been firmly established as intermediates in electrophilic substitution reactions, as well as numerous acid-catalyzed transformations of aromatics.[5,6] Thus, it is quite understandable that a considerable effort has been expended over the past years to elucidate the electronic structures of the arenium ions through their characterization by various theoretical as well as experimental methods.[1,2]

Above all, it has been argued that aromatic character of an aromatic hydrocarbon would be retained partly in the arenium ion.[7] This viewpoint is closely associated with possible hyperconjugation which should occur between the CH_2 group and the remaining π-electrons of the ring.[7,8] It has also been argued that the residual aromaticity in the arenium-type intermediate might be responsible for the occurrence of electrophilic substitution reactions.[4] The theoretical treatment of hyperconjugation shows that it should occur not only with the CH_2 group but also when one of the hydrogen atoms is replaced by any substituent group.[7,8] In this paper, I will first estimate the extent of hyperconjugation acting through the CH_2 group, and analyze in detail the electronic structure of arenium ions derived from typical benzenoid hydrocarbons. Our graph theory of aromaticity[9] will be applied to them to evaluate the resonance energies due to hyperconjugation. All the results will be examined in conjunction with the tendency of the benzenoid hydrocarbons to undergo electrophilic substitution reactions.


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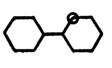
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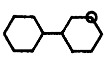
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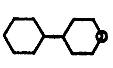
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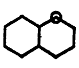
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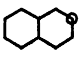
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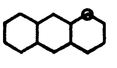
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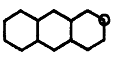
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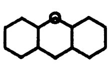
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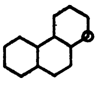
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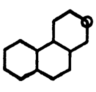
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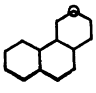
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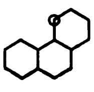
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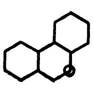
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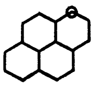
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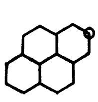
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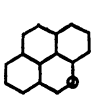
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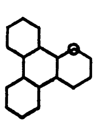
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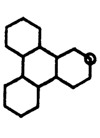
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Hyperconjugation through the CH_2 Group

The graph theory of aromaticity has been described several times,[9,10] so it is not repeated here. The theory is based on the simple Hückel molecular orbital (HMO) model. The addition of a proton to the aromatic hydrocarbon destroys the sp^2-hybridized valence state of one of the carbon atoms, denoted by C*, and converts it into an sp^3-hybridized tetrahedral valence state.[7,8] In the arenium ion thus formed, one finds a CH_2 group adjacent to the remaining π-electron system. One hydrogen is believed to be above and the other below the plane,[11] the two hydrogens being denoted by H′ and H″.

In order to keep the algebra as simple as possible, we take one of the methylene orbital ψ to be the composite bond orbital of π-symmetry,[12,13] namely,

$$\psi = \frac{1}{2}(\phi_1 - \phi_2), \tag{1}$$

where ϕ_1 and ϕ_2 are the σ-bond orbitals localized along the C*–H′ and C*–H″ bonds, respectively. This constitutes a quasi-π orbital which functions like a π orbital in linear combinations with the $2p_z$ orbitals of the ring carbon atoms, in such a way as to yield a partial restoration of cyclic conjugation. This is nothing other than hyperconjugative interaction.

In order to incorporate the methylene orbital of π-symmetry in the HMO bonding model, two parameters,

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h and k, must be determined for it. Here, h is related to the Coulomb integral for the quasi-π orbital, and k to the resonance integral for hyperconjugative interaction of this orbital with one of the adjacent $2p_z$ orbitals. By analogy with a hyperconjugative methyl orbital,3) the value $h=2.0$ and $k=0.7$ may be applied to the methylene quasi-π orbital, too. Haddon recently reexamined hyperconjugation through the methylene group,14) and suggested that a little smaller k value (≈ 0.5) might be more preferable for the methylene quasi-π orbital. At least, it gives a more reasonable diamagnetic anisotropy of cyclopentadiene.14)

Heilbronner *et al.* adopted the simple bond orbital model to analyze the photoelectron spectra of cyclic alkanes,13) and estimated the self-energy for the C–H bond orbital, A_{CH}, to be -15.67 eV and the cross term between two vicinal bond orbitals, $B_{\mathrm{CH,CH}}$, to be -2.19 eV. In the simple HMO model, the self-energy corresponds to the Coulomb integral and the cross term to the resonance integral. From Eq. 1 the self-energy for the methylene quasi-π orbital can be set equal to $A_{\mathrm{CH}}-B_{\mathrm{CH,CH}}=-13.48$ eV. This represents a Coulomb integral for the methylene quasi-π orbital. For aromatic hydrocarbons, the resonance integral between two adjacent $2p_z$ orbitals has been estimated to be -2.7—-3.0 eV.15) Then the Coulomb integral for each carbon $2p_z$ orbital lies in the -5.8—-6.5 eV range, depending upon the value adopted for the resonance integral. If we take all these numerical values into account, the $h=2.5$ value will become more suitable for the methylene quasi-π orbital.

TABLE 1. ENERGY SEPARATION BETWEEN TWO OCCUPIED π ORBITALS FOR THREE DIENES

Species	Experimental energy separation[a)] eV[b)]	HMO/β	
		$h=2.0$ $k=0.5$	$h=2.5$ $k=0.6$
1,4-Pentadiene	0.50	0.188	0.191
Cyclopentadiene	2.04	0.814	0.845
1,4-Cyclohexadiene	1.06	0.366	0.382

a) Ref. 16. b) 1 eV=9.6525×10^4 J/mol.

Once this h value is adopted, the k value must next be determined in harmony with it. The simplest way of doing so is to make reference to the energy separations between the first and second π orbitals in such hydrocarbons as 1,4-pentadiene (0.50 eV), cyclopentadiene (2.04 eV), and 1,4-cyclohexadiene (1.06 eV).16) The k value suitable for reproducing these energy separations were about 0.6. For this point, see Table 1. The set of HMO parameters suggested by Haddon, $h=2.0$ and $k=0.5$,14) can likewise reproduce these energy separations. Conversely speaking, this kind of reproducibility supports the existence of hyperconjugative interaction through the CH_2 group. The above two sets of HMO parameters were employed to calculate resonance energies of arenium ions. For simplicity, all discussion will be made using the results based on our way of parametrization (*i.e.*, $h=2.5$ and $k=0.6$).

Resonance Energies of the Arenium Ions

Table 2 contains resonance energies of nineteen arenium ions derived from seven benzenoid hydrocarbons, together with their localization energies.17) These resonance energies were calculated according to our graph theory of aromaticity.9,10) An aromatic compound is characterized by the positive resonance energy, the magnitude of which indicates the degree of aromatic stabilization.9,10,18) All energetic quantities are given in units of β or its absolute value β.

First, the simplest arenium ion, a benzenium ion, is predicted to have resonance energy of 0.094 β. If we adopt an effective β value reported for the resonance energies of benzenoid hydrocarbons ($\beta=3.562$ eV),18) this resonance energy corresponds to 7.7 kcal/mol.†† Resonance energy of benzene is 0.273 β or 20.8 kcal/mol,19,20) so the resonance energy of the benzenium ion amounts to about one-third that of benzene. Considering that benzene is one of highly aromatic compounds, the resonance energy of the benzenium ion is obviously far from negligible. Resonance energies of α-pyrone, γ-pyrone, furan, [10]annulene, and azulene are 0.044, 0.010, 0.010, 0.159, and 0.151, respectively, all in units of β.9) Thus, the benzenium ion is much more aromatic than some weakly aromatic compounds, such as pyrones and furan, and is comparable in aromaticity to [10]annulene and azulene if the molecular sizes are taken into consideration.21) As the benzenium ion is a monocyclic conjugated system, the whole resonance energy can be attributed to the hyperconjugative interaction through the CH_2 group; any resonance energy could not be anticipated without hyperconjugation.

In the case of polycyclic arenium ions, the situation is somewhat different. The contribution of the CH_2 group to aromaticity must be estimated relative to the resonance energy of some appropriate reference structure. A hypothetical compound with the same geometry but lacking conjugative interaction between the CH_2 group and the remaining π-electron system will serve for this purpose. The same structure has been used to calculate the localization energy.17) The increment of resonance energy on introducing the hyperconjugative interaction in this reference structure can be interpreted as resonance energy due to hyperconjugation or hyperconjugative resonance energy (HRE). The HRE's are also listed in Table 2. It should be stressed that these HRE's are never negligible, either. Many of the polycyclic arenium ions indeed have HRE's comparable to that of the benzenium ion.

Hyperconjugative Resonance Energy and Electrophilic Substitution Reactions

The occurrence of electrophilic substitution reactions has been long regarded as an excellent indication of aromaticity.3–16,22) However, we can easily show that

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†† 1 $\mathrm{cal_{th}}=4.184$ J.

TABLE 2. RESONANCE ENERGIES AND LOCALIZATION ENERGIES FOR TYPICAL ARENIUM IONS

Ion	LE[a)]/β		RE[b)]/β		HRE[c)]/β	
	h=0.0 k=0.0	h=2.5 k=0.6	h=2.0 k=0.5	h=2.5 k=0.6	h=2.0 k=0.5	h=2.5 k=0.6
Benzenium (1)	2.536	2.953	0.085	0.094	0.085	0.094
2-Biphenylium (2)	2.400	2.774	0.289	0.297	0.082	0.091
3-Biphenylium (3)	2.544	2.963	0.337	0.345	0.082	0.090
4-Biphenylium (4)	2.447	2.830	0.294	0.303	0.085	0.092
1-Naphthalenium (5)	2.299	2.638	0.244	0.250	0.052	0.058
2-Naphthalenium (6)	2.480	2.873	0.209	0.217	0.080	0.089
1-Anthracenium (7)	2.231	2.544	0.344	0.348	0.041	0.045
2-Anthracenium (8)	2.423	2.789	0.308	0.315	0.067	0.074
9-Anthracenium (9)	2.013	2.279	0.403	0.406	0.020	0.023
1-Phenanthrenium (10)	2.318	2.663	0.378	0.385	0.063	0.070
2-Phenanthrenium (11)	2.498	2.898	0.352	0.362	0.091	0.101
3-Phenanthrenium (12)	2.454	2.836	0.356	0.365	0.081	0.090
4-Phenanthrenium (13)	2.366	2.726	0.373	0.380	0.070	0.078
9-Phenanthrenium (14)	2.299	2.637	0.411	0.417	0.054	0.060
1-Pyrenium (15)	2.190	2.494	0.447	0.452	0.044	0.049
2-Pyrenium (16)	2.549	2.969	0.414	0.424	0.101	0.112
4-Pyrenium (17)	2.274	2.601	0.470	0.475	0.047	0.052
1-Triphenylenium (18)	2.378	2.743	0.550	0.558	0.078	0.086
2-Triphenylenium (19)	2.477	2.869	0.541	0.550	0.090	0.099

a) Localization energy. b) Resonance energy. c) Hyperconjugative resonance energy.

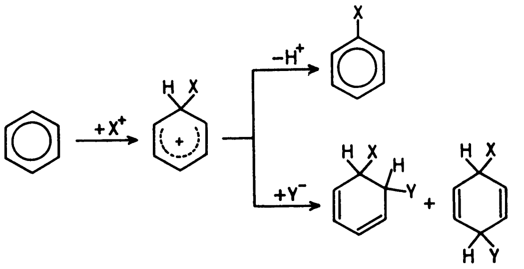
TABLE 3. POSITIVE CHARGE DENSITY IN THE METHYLENE QUASI-π ORBITAL FOR TYPICAL ARENIUM IONS

Ion	PCD[a)]	
	h=2.0 k=0.5	h=2.5 k=0.6
Benzenium (1)	0.146	0.139
2-Biphenylium (2)	0.129	0.124
3-Biphenylium (3)	0.147	0.140
4-Biphenylium (4)	0.133	0.128
1-Naphthalenium (5)	0.115	0.112
2-Naphthalenium (6)	0.137	0.132
1-Anthracenium (7)	0.106	0.104
2-Anthracenium (8)	0.128	0.124
9-Anthracenium (9)	0.083	0.084
1-Phenanthrenium (10)	0.118	0.114
2-Phenanthrenium (11)	0.140	0.154
3-Phenanthrenium (12)	0.133	0.128
4-Phenanthrenium (13)	0.124	0.119
9-Phenanthrenium (14)	0.115	0.112
1-Pyrenium (15)	0.101	0.099
2-Pyrenium (16)	0.147	0.140
4-Pyrenium (17)	0.111	0.108
1-Triphenylenium (18)	0.126	0.121
2-Triphenylenium (19)	0.137	0.131

a) Positive charge density in the methylene quasi-π orbital.

less aromatic compounds, in general, undergo electrophilic substitution reactions more rapidly. For example, furan undergoes substitution reactions much more rapidly than benzene when an appropriate electrophile attacks them.[23] In line with this, furan often reacts with electrophiles to form addition products.[23] Therefore, the tendency to undergo electrophilic substitution reactions is a vague criterion of aromaticity.[24]

In this connection, it seems quite likely that an electrophilic substitution reaction is not always an exothermic reaction. Let us consider the following pair of reactions: Suppose here that X and Y are hydrogen atoms. Heats of hydrogenation of benzene and 1,3-cyclohexadiene are 49.8 and 55.6 kcal/mol, respectively, in the gas phase.[25] 1,4-Cyclohexadiene also give a heat of hydrogenation comparable to that of 1,3-diene.[20] As stated before, benzene is highly aromatic with resonance energy of 20.8 kcal/mol.[19,20] If resonance energy of a given cyclic conjugated system were about 6 kcal/mol smaller than that of benzene, there would be no preference for substitution to addition reactions. Heats of reaction would become comparable for reactions of the types 2a and 2b. Many compounds are really considerably less aromatic than benzene.[9,10] Accordingly, such a situation might often be encountered even if X^+ and Y^- in Eq. 2 are replaced by an appropriate electrophile and nucleophile, respectively. In fact, it has been found that addition-accompanied substitution occurs in the chlorination of relatively simple benzenoid hydrocarbons, such as biphenyl and naphthalene.[26] As the situation is like this, the question may be raised why electrophilic substitution occurs preferentially.



(2a)

(2b)

By the way, localization energy (LE) has been successfully related to the rate of electrophilic substitution reaction.[3–6,17,27] The Wheland intermediate which appears during the reaction[17] is iso-π-electronic with a corresponding proton addition complex. According to the Hammond postulate,[28] the transition state must closely resemble the Wheland intermediate, because it is much higher in energy than the reactant and product. The effect of hyperconjugation has been neglected in the original LE theory,[3–6,17] but the present study shows that it must decrease the energy of the intermediate by 0.26—0.48 β (Table 2).

Now, let us return to the point. Stock suggested that the residual aromaticity in the transition state might be necessary for the occurrence of electrophilic substitution reactions.[4] The existence of this kind of resonance energy has already been clarified. The positive HRE is related exactly to the residual aromaticity. In this sence, Stock's suggestion appears to be worthy of serious consideration.

In order to obtain a clue to this problem, HRE was plotted against LE for the nineteen arenium ions (Fig. 1). Here and in Fig. 2, LE's defined for the systems with h=0.0 and k=0.0 are used. It was then found that HRE is closely related to LE, in such a manner that, when LE is large, HRE is large, too. This trend does not depend upon the type of the site to which a proton is attached. For example, the 9-anthracenium ion has both smaller LE and HRE than any other arenium ion investigated. The largest HRE is given by the 2-pyrenium ion, which necessarily has the largest LE. Since an electrophilic reaction takes place mostly *via* a Wheland intermediate with the smallest LE,[3–6] we might say that the reaction occurs mostly *via* the Wheland intermediate with the smallest HRE. This implies that most electrophilic reactions occur at the sites which are least favorable to the occurrence of substitution reactions.

This viewpoint is based on the fact that an aromatic species generally has not only thermodynamic but also kinetic stability.[29–31] In 1971, Hess and Schaad showed that the energy separation between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is a linear function of the resonance energy per π-electron (REPE) for a variety of benzenoid hydrocarbons.[18,29] The REPE is a measure of aromatic stabilization, normalized with respect to the number of π electrons. Recently, Haddon and Fukunaga found an analogous relationship for the annulenes.[30] It then follows that an aromatic compound with larger resonance energy tends to retain its cyclic conjugated system, resisting addition-type reactions. Assigning such an attribute to the arenium ion and Wheland intermediates, we can reasonably infer that a highly aromatic intermediate would tend to refrain from taking paths to addition products. Addition products obviously break the cyclic conjugated system of the intermediate. On the other hand, a poorly aromatic intermediate would be willing to take paths to addition products.

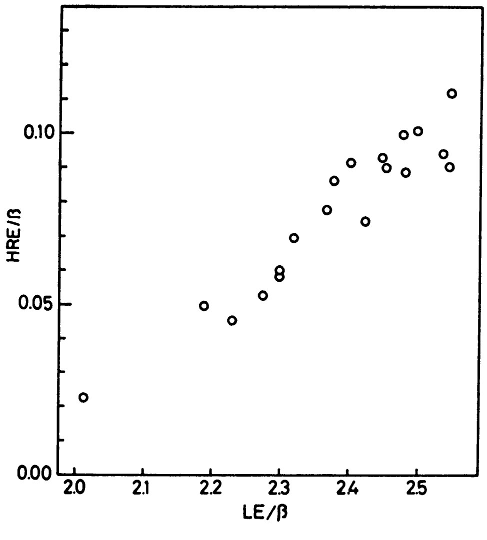


Fig. 1. Plot of hyperconjugative resonance energy (HRE) against localization energy (LE) for nineteen arenium ions.

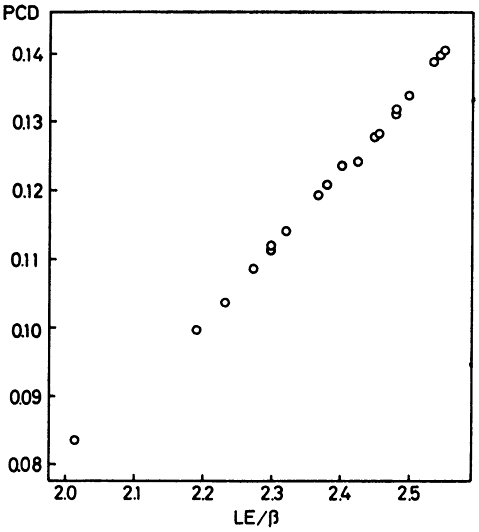


Fig. 2. Plot of positive charge density in the methylene quasi-π orbital (PCD) against localization energy (LE) for nineteen arenium ions.

The above inference is in fact supported by the work of de la Mare's group.[26] They studied the chlorination of benzenoid hydrocarbons with a molecular chlorine. The chlorine is a highly selective reagent.[32] It was found that significant proportions of by-products were formed by addition of chlorine or chlorine acetate derived from chlorine and acetic acid solvent.[26] There seems to be a general tendency for addition to become prominent as the reactivity of the hydrocarbon increases. Thus, the order of proportions of addition to substitution products was phenanthrene>naphthalene>triphenylene>biphenyl≫benzene. This is exactly the same order as that of the overall reaction rates.[26] Anthracene probably comes first.[3] It is widely known that the 9 position of anthracene has a greater tendency toward electrophilic addition than the 9 position of phenanthrene.[4,33] It has been accepted that the overall reaction rate is determined by the smallest LE conceivable in the compound.[3,4] A greater overall reaction rate corresponds to the smaller LE, and a greater proportion of the addition products to the smaller HRE. Competition between substitution and addition reactions can thus be related to the aromatic character of the Wheland intermediate.

Here, there is an exception to the order of experimental reaction rates; it is phenanthrene *vs.* naphthalene. LE of the 9-phenanthrenium ion is comparable to that of the 1-naphthalenium ion. However, the greater reactivity of phenanthrene than naphthalene is experimentally commonplace, and has been observed is several substitution reactions.[33] Unfortunately, this problem is beyond the scope of the HMO model, and should be treated by more sophisticated methods.[27]

Charge Density in the Methylene Quasi-π Orbital

When substitution occurs, the Wheland intermediate loses a proton to the nucleophile, and so reverts to an aromatic π-electron ring, now substituted with the electrophilic group.[3-6] It is noteworthy that salts of substituted benzenium ions can be isolated as crystalline materials or observed by spectroscopic techniques in non-nucleophilic solvents.[1,2,34] In this view, we may expect that, the greater the positive charge density (PCD) in the methylene orbital is, the easier should it be to remove hydrogen as a proton. If PCD is low in the methylene orbital, the chance that nucleophilic addition occurs to the remaining π-electron system would be great. In this connection, Dixon regarded the charge density on the protons of the CH_2 group as a measure of proton loss, leading to overall substitution.[12]

We can examine this effect by means of the present bonding model. Hyperconjugation permits a considerable migration of negative charge into the ring from the methylene quasi-π orbital. The PCD is induced as a result of partial equalization of the charge distribution. Table 2 and Fig. 2 indicate how the positive charge in the methylene quasi-π orbital correlates with LE for the benzenoid hydrocarbons studied. We see therefrom that PCD is almost linearly related to LE and, hence, to the overall reaction rate. This suggests that the leaving ability of hydrogen as a proton might be enhanced in the case of the arenium ions with large LE's. In other words, proton loss occurs more readily to restore the fully aromatic sextet when there is more extensive delocalization of the positive charge. This indicates that PCD reflects the magnitude of HRE straightforwardly. Accordingly, the tendency of a benzenoid hydrocarbon to undergo electrophilic substitution, predicted from the PCD, bears a close resemblance to the tendency predicted from the HRE. Both are naturally in good accord with experiment. The two effects seem to enhance cooperatively the preference for substitution reactions. In our chemical sence, it seems that HRE tends to avoid adding a nucleophile to the π-electron system, while PCD tends to eliminate a proton, both resulting in the same substitution reaction.

However, it should be stressed that HRE is not always a single determinant for the occurrence of substitution reactions. For example, pyrene is much more reactive than phenanthrene.[3,4,27,33] but the addition products have not been observed appreciably. Since HRE is at most 8 kcal/mol for any compound, the other factors, such as the size of an electrophile and a steric effect in the addition product, cannot be neglected in tracing a reaction path. By inspecting the molecular model, it was found that every ring in pyrene might be subject to some steric restriction when it undergoes an addition reaction. The restriction appears very severe in the case of addition reactions starting from the 1-pyrenium-type intermediate. In such a case, addition-elimination routes to substitution products become important.

Concluding Remarks

Three of the most characteristic properties of aromatic compounds are the thermodynamic stability, the diamagnetic susceptibility exaltation, and the tendency to undergo electrophilic substitution reactions. The first two properties can be analyzed consistently in terms of our graph theory of aromaticity.[9,10,35] For the first time, this theory succeeded in unifying the two concepts.[35] Along with these physical properties, the tendency to undergo electrophilic substitution reactions has been widely used as a purely chemical criterion of aromaticity.[22,36]

As stated before, this criterion is quite empirical. To make matters worse, it is not always related to aromaticity.[24,36] The tropylium ion, accepted as an example of a nonbenzenoid aromatic species, does not react with electrophiles.[36] On the contrary, a 2,3-dihydro-1,4-diazepinium ion undergoes many electrophilic substitution reactions, although it has no cyclic conjugated system.[36] In this sence, there is an obvious limitation in the present approach. It does not apply to the Wheland intermediates which are aromatically- or hetero-atom-stabilized species.[37] For example, the aromatically-stabilized intermediates are those derived from azulene and calicene. The azulenium and 2-calicenium ions are both Hückeloid aromatic cations with substituents. The hetero-atom-stabilized systems are exemplified by the Wheland intermediates derived from pyrrole and a 2,3-dihydro-1,4-diazepinium ion.

Electrophilic substitution is indeed a complicated chemical process.[5,6,38] To the best of my knowledge, there have been few logical approaches to the competition between substitution and addition reactions. Therefore, the present approach might be regarded as a first significant step forward, although its application is limited to benzenoid hydrocarbons. This approach not only unveiled some important features of aromatic substitution, but also enabled us to trace reaction routes to substitution products more closely than before. All the reasoning is relatively simple and understandable.

In summary, I have considered both the ability of the CH_2 group to function as a hyperconjugator and the ability to dissociate a proton. HRE represents the energy difference between a real hyperconjugative system and its hyperconjugative reference structure. Stock's suggestion that electrophilic substitution might occur *via* an aromatic transition state[4] has been verified and generalized in terms of HRE. It was theoretically conciliated with Dixon's measure of proton loss defined using PCD.[12] If the Wheland intermediate were absolutely olefinic in nature, a significant proportion of addition products would be obtained, because there is no tendency for polyenic cations to undergo electrophilic substitution reactions. In general, if the parent compound is not aromatic, the corresponding proton addition complex has no HRE. This might be the main reason why electrophilic substitution is limited mostly to aromatic compounds.

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