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Kinetic Instability of Nonbenzenoid Aromatic Hydrocarbons

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Aromatic hydrocarbons have thermodynamically stable cyclic conjugated systems. There is a tacitly accepted view that not only aromatic stabilization but also kinetic stability arise from the same cyclic conjugation of π electrons. In order for this view to be examined criticaly, two reactivity indices, *i.e.*, localization energy and superdelocalizability, were adopted for a variety of cyclic conjugated hydrocarbons, and were compared with those defined for their olefinic reference structures. Interestingly, it was found that chemical reactivity of some constituent carbons might often overcome aromatic stabilization of an entire conjugated system. Not a few nonbenzenoid aromatic hydrocarbons were predicted to have reactive carbons which are olefinic in reactivity. These hydrocarbons constitute unstable aromatic compounds. Thus, it has been clarified that thermodynamic and kinetic stabilities do not always concur in the case of nonbenzenoid hydrocarbons.

An aromatic compound is thermodynamically stable by definition.1) It is supposed to be more stable than its olefinic reference structure with "localized" π bonds.1,2) The resonance energy defined in our graph theory of aromaticity is an excellent index of such thermodynamic stability.3–5) If a given cyclic conjugated system has a large positive resonance energy, it is considered thermodynamically stable and aromatic.1–5) The predicted aromaticity is due entirely to stabilization by cyclic conjugation.4)

Our experience tells us that thermodynamic and apparent stabilities of a cyclic conjugated system are closely related to each other. This implies that a thermodynamically stable compound usually has a large kinetic stability. There has been a widely accepted view that aromatic compounds must be stable in a commonplace sense. Thus, thermodynamic stability has long been confused with kinetic stability when one has to decide as to whether a given compound is aromatic or not. Many compounds have been classified as aromatic because of their isolability or low chemical reactivity,1–5) which are terms of kinetic stability.

Exactly speaking, whether a compound is isolable or not depends not only on the thermodynamic stability, but also on the stability of possible conversion products.6) A compound predicted to be thermodynamically stable may not be isolable because it can go to still more stable species. Conversely, a high-energy compound may be apparently stable if it has no easy conversion routes available.6) In principle, all possible reaction paths must be considered to predict kinetic or chemical stability of a cyclic conjugated system.

In fact, all aromatic compounds are neither chemically stable, nor all antiaromatic compounds chemically unstable.6) Although calicene is predicted to exhibit aromatic stabilization,2–5,7) it has neither been observed nor isolated. Dimethylenecyclohexadienes are not antiaromatic species,2–5,8) but they are not isolable. These notable exceptions suggest that chemical stability of a compound might sometimes be determined by factors other than thermodynamic stability. So far there have been few systematic analyses of kinetic stability or instability of cyclic conjugated systems.

The purpose of this paper is to examine kinetic stability of typical aromatic hydrocarbons in conjunction with their aromaticity. I point out that thermodynamic and kinetic stabilities do not always concur in the case of nonbenzenoid aromatic hydrocarbons, and that not a few aromatic hydrocarbons are obviously unstable due to high reactivity toward some kinds of reagents. In order for this feature to be seen explicitly, two reactivity indices, *i.e.*, localization energy9,10) and superdelocalizability10,11) are adopted for 42 conjugated hydrocarbons, and are compared with those defined for their olefinic reference structures.

Theoretical Background

The sign and the magnitude of our resonance energy3–5) are used as an index of aromaticity for cyclic conjugated systems. The degree of aromatic stabilization is given by the resonance energy, divided by the energy of the olefinic reference structure, and then multiplied by 100.12,13) This quantity is termed a percent resonance energy (%*RE*). Compounds listed in Table 2 are arranged in order of decreasing percent resonance energy. An aromatic compound is said to have as much thermodynamic stability as its resonance energy.

It is impossible to devise a good single index of kinetic stability because there are very many reactions associated with cyclic conjugated systems. In this sense, thermodynamic stability is a much simpler concept than kinetic stability. As will be seen, Wheland's localization energy9,10) and Fukui's superdelocalizability10,11) are suitable for surveying one aspect of kinetic stability. These reactivity indices have been defined to elucidate reactivity of conjugated hydrocarbons toward electrophiles and nucleophiles.

Electrophilic substitution, as well as electrophilic addition, involves a reaction with an electrophilic species. Electrophile addition results in a new conjugated system of one less atom and two less π electrons, which is termed a σ complex or Wheland intermediate. Localization energy and superdelocalizability are primary indices when the transition state resembles the σ complex. Abundant evidence has been reported to support the formation of a σ complex as a key intermediate in aromatic substitution.10)

The reactivity will be different for different hydrocarbons, and also for different positions of attachment of the electrophile in a given hydrocarbon in which there are two or more nonequivalent positions. A conjugated system of a given σ complex is denoted by G-v, where G is a conjugated system of the starting hydrocarbon, and v is a carbon to which the electrophile is attached. Localization energy corresponding to this σ complex with a +1 formal charge is denoted by $L_G(\mathrm{v},+1)$. It is defined by[9,10]

$$L_G(\mathrm{v}, +1) = E_G(0) - E_{G-\mathrm{v}}(+1), \tag{1}$$

where $E_G(0)$ is a total π-electron energy of the starting hydrocarbon with zero formal charge, and $E_{G-\mathrm{v}}(+1)$ is that of the σ complex with a +1 formal charge. Localization energy is thus a measure of the energy change on going from a given hydrocarbon to the σ complex. Smaller localization energies indicate more susceptible carbons.

Superdelocalizability is another measure of the energy difference between a given hydrocarbon and the σ complex. A possible importance of hyperconjugation through the electrophile-substituted methylene group is stressed in the derivation of superdelocalizability.[11] For a hydrocarbon with N conjugated carbons it is defined by[10,11]

$$S_G(\mathrm{v}, +1) = \sum_{i=1}^{N} \frac{g_i P_{G-\mathrm{v}}(X_i)}{X_i P_G'(X_i)}. \tag{2}$$

Here, $P_G(X)$ and $P_{G-\mathrm{v}}(X)$ are characteristic polynomials for G and G-v, respectively; X_i is the ith energy coefficient, *i.e.*, the ith largest root of the equation $P_G(X)=0$; and g_i is the corresponding occupation number. Superdelocalizability and localization energy are highly correlative with each other.[10]

The fact that stability is always relative leads us to the concept of reference states. We have been using a reference polynomial defined graph-theoretically to describe an olefinic reference structure of a cyclic conjugated system,[3-5,13-17] and interpreted it as a characteristic polynomial for the reference structure. This type of polynomial is denoted by $R_G(X)$. Exactly speaking, $R_G(X)$ is not a characteristic polynomial for the reference structure because it is not a polynomial obtained by expanding the secular determinant; an appropriate secular determinant cannot be defined within the framework of our graph theory.[3-5] Therefore, our olefinic reference structure is hypothetical in nature.

Nevertheless, it is very true that the reference polynomial can be viewed in many respects as a characteristic polynomial for this hypothetical reference structure. Many features of the reference polynomials for cyclic conjugated hydrocarbons are really those of acyclic polyenes:

(a) $R_G(X)$ can be defined in the same manner as a characteristic polynomial for acyclic polyenes,[3] namely,

$$R_G(X) = X^N + \sum_{k=1}^{[N/2]} (-1)^k p(k) X^{N-2k}, \tag{3}$$

where $p(k)$ is the number of ways of choosing k disjoint π bonds from a conjugated system G, and $[N/2]$ is a maximum integer not larger than $N/2$.

(b) The Hess-Schaad reference structure[2] can be considered as an olefinic structure in the singlet ground state since it is constructed using π bonds scissored from acyclic polyenes in the singlet ground state. The energy of this Hess-Schaad reference structure can be reproduced by means of $R_G(X)$, on the assumption that the reference structure defined by this polynomial is in the singlet ground state.[3,16]

(c) The energy levels given as roots of the equation $R_G(X)=0$ satisfy the pairing theorem.[3,4,18] The charge distribution estimated from $R_G(X)$ is uniform over the entire conjugated system.[17] These facts imply that our hypothetical reference structure is a kind of alternant hydrocarbon. Acyclic polyenes are all alternant hydrocarbons.

(d) Neither diamagnetic susceptibility exaltation nor diatropicity are expected in this type of reference structures.[15] The same is true for acyclic polyenes. The above features strongly support our view that $R_G(X)$ is a good characteristic polynomial for the hypothetical reference structure, and that the reference structure defined by $R_G(X)$ is very olefinic in nature. Therefore, we can safely assume that $R_G(X)$ practically represents an olefinic reference structure of a cyclic conjugated system. This interpretation has been consistent with every phase of aromatic chemistry.

On this theoretical basis, we can define reactivity indices for an olefinic reference structure of a cyclic conjugated system. Localization energy for the olefinic reference structure defined by $R_G(X)$ can be defined by

$$L_G{}^\circ(\mathrm{v}, +1) = E_G{}^\circ(0) - E_{G-\mathrm{v}}{}^\circ(+1), \tag{4}$$

where $E_G{}^\circ(0)$ and $E_{G-\mathrm{v}}{}^\circ(+1)$ are the total π-electron energies of the reference structures of G and G-v, respectively. In the same manner, superdelocalizability for the reference structure can be defined by

$$S_G{}^\circ(\mathrm{v}, +1) = \sum_{i=1}^{N} \frac{g_i R_{G-\mathrm{v}}(X_i{}^\circ)}{X_i{}^\circ R_G'(X_i{}^\circ)}, \tag{5}$$

where $X_i{}^\circ$ is the ith largest root of the equation $R_G(X)=0$. $L_G{}^\circ(\mathrm{v},+1)$ and $S_G{}^\circ(\mathrm{v},+1)$ are reactivity indices which the system G would have if it were free of aromaticity. They are expected to represent the tendency of the reference structure to undergo electrophilic reactions.

Reactivity indices can likewise be defined to describe the tendency to undergo nucleophilic substitution (or addition) reactions. In this case, the intermediate σ complex must have a -1 formal charge. Its total π-electron energy is denoted by $E_{G-\mathrm{v}}(-1)$, where v is a carbon to which the nucleophile is attached. Localization energy related to this σ complex is defined by[9,10]

$$L_G(\mathrm{v}, -1) = E_G(0) - E_{G-\mathrm{v}}(-1). \tag{6}$$

The corresponding superdelocalizability is defined by[10,11]

$$S_G(\mathrm{v}, -1) = \sum_{i=1}^{N} \frac{(g_i-2) P_{G-\mathrm{v}}(X_i)}{X_i P_G'(X_i)}. \tag{7}$$

For alternant hydrocarbons, such as acyclic polyenes and benzenoid hydrocarbons, $L_G(\mathrm{v},-1)=L_G(\mathrm{v},+1)$ and $S_G(\mathrm{v},-1)=S_G(\mathrm{v},+1)$, so the nucleophilic reactivity is identical with the electrophilic one. As mentioned before, olefinic reference structures of cyclic conjugated hydrocarbons can also be considered as a kind of alternant hydrocarbons. For these reference structures, indices of nucleophilic reactivity are exactly the same as those of electrophilic reactivity. Therefore,

$$L_G{}^\circ(\mathrm{v}, -1) = L_G{}^\circ(\mathrm{v}, +1) \tag{8}$$

and

$$S_G{}^\circ(\mathrm{v}, -1) = S_G{}^\circ(\mathrm{v}, +1). \tag{9}$$

Localization energy and superdelocalizability can be regarded as indices of kinetic stability (or instability) common to cyclic and acyclic conjugated systems. These indices can be applied equally to aromatic, antiaromatic, and nonaromatic systems to see their electrophilic and nucleophilic reactivities. Whatever the reaction products may be, highly reactive compounds must be very unstable in a kinetic sense. This is a primary reason to choose localization energy and superdelocalizability for the present study of kinetic stability.

Reactivity indices for the olefinic reference structures will give reasonable criteria for estimating the effect of aromaticity on the electrophilic and nucleophilic reactivities. In order to see possible interrelation between aromaticity and reactivity, it is instructive to evaluate the reactivity indices relative to those for the olefinic reference structures, namely,

$$\Delta L_G(\mathrm{v}, \pm 1) = L_G(\mathrm{v}, \pm 1) - L_G{}^\circ(\mathrm{v}, \pm 1), \tag{10}$$

and

$$\Delta S_G(\mathrm{v}, \pm 1) = S_G(\mathrm{v}, \pm 1) - S_G{}^\circ(\mathrm{v}, \pm 1). \tag{11}$$

These differences in reactivity index can naturally be ascribed to aromaticity, *i.e.*, cyclic π-electron conjugation of the type $\beta_{ij}\beta_{jk}\cdots\beta_{pq}\beta_{qi}$, where β's are resonance integrals between bonded carbons.[14,15] $\Delta L_G(\mathrm{v}, \pm 1)$ and $\Delta S_G(\mathrm{v},\pm 1)$ are hence interpreted as a portion of contribution of aromaticity to kinetic stability. If a given constituent carbon has a small $\Delta L_G(\mathrm{v},\pm 1)$ value or a large $\Delta S_G(\mathrm{v},\pm 1)$ value, it must be olefinic in reactivity.

Results and Discussion

Conjugated carbons in hydrocarbons are classified as shown in Fig. 1. Edge carbons, *i.e.*, exomethylene carbons, are called primary carbons. Carbons shared by two π bonds are called secondary carbons. When a given carbon is shared by three π bonds, it is called a tertiary carbon. Primary, secondary, and tertiary carbons are denoted by Pn, Sn, and Tn, respectively, where the suffixes n indicate nonequivalent carbons.

First, stability considerations are made on the basis of localization energies. Localization energies calculated for all carbons in 42 conjugated hydrocarbons are listed in Tables 1 and 2. Ethylene (**1**), butadiene (**2**), and hexatriene (**3**) in Table 1 are nonaromatic species. In these polyenes, constituent carbons have a variety of localization energies. It is clear that, even in a single conjugated hydrocarbon free of aromaticity, carbons are quite diverse in reactivity. Edge carbons have considerably smaller localization energies than inner carbons. Kinetic stability of a conjugated hydrocarbon is determined by the most reactive carbons. For acyclic polyenes, electrophilic and nucleophilic reactivities are determined primarily by the edge or primary carbons. Each acyclic polyene is identical with its olefinic reference structure.[3-5] Therefore, kinetic stability expressed in terms of localization energy is the same for the two structures.

Table 1. Localization energies for acyclic polyenes

Compound	v	$L_G(\mathrm{v}, \pm 1)$
Ethylene (**1**)	P1	2.000
Butadiene (**2**)	P1	1.644
	S1	2.472
Hexatriene (**3**)	P1	1.524
	S1	2.516
	S2	2.159

Let us examine reactivities of cyclic conjugated systems listed in Table 2. Localization energies for the olefinic reference structures, $L_G{}^\circ(\mathrm{v},\pm 1)$, are now useful for analyzing those for real conjugated systems, $L_G(\mathrm{v}, \pm 1)$, in detail. As in the case of acyclic polyenes, $L_G{}^\circ(\mathrm{v},\pm 1)$ is very small at primary carbons, ranging from 1.22 to 1.48. Secondary carbons have $L_G{}^\circ(\mathrm{v},\pm 1)$ in the range 1.85—2.40, and tertiary carbons in the range 2.33—3.00. Among tertiary carbons, those next to primary carbons have $L_G{}^\circ(\mathrm{v},\pm 1)$ larger than 2.81, and those surrounded by three tertiary carbons have $L_G{}^\circ(\mathrm{v},\pm 1)$ less than 2.41. The values of $L_G{}^\circ(\mathrm{v},\pm 1)$ at primary carbons never overlap with those at secondary and tertiary carbons. Secondary carbons scarcely overlap with tertiary carbons in this sense. Thus, it is obvious that $L_G{}^\circ(\mathrm{v},\pm 1)$ is determined by the type of the carbon. If a given conjugated hydrocarbon were deprived of aromaticity, electrophilic and nucleophilic reactivities would be determined primarily by the molecular geometry. Such regularity of the $L_G{}^\circ(\mathrm{v},\pm 1)$ values further supports the validity of these reference indices.

Benzenoid hydrocarbons **5**—**11** and **14** are highly aromatic since they have large percent resonance energies. These compounds have positive $\Delta L_G(\mathrm{v},\pm 1)$ values at all constituent carbons, so they must be much less reactive than their olefinic reference structures. This means that all the carbons are stabilized by aromaticity, *i.e.*, cyclic π-electron conjugation. All carbons in benzene (**5**) have the same $L_G(\mathrm{v},\pm 1)$ value of 2.536 and the same $\Delta L_G(\mathrm{v},\pm 1)$ value of 0.273. These large values show that benzene is kinetically very stable in accord with its chemical behavior. Naphthalene (**8**) and other condensed benzenoid hydrocarbons are predicted to be a little more reactive than benzene since some of the secondary carbons have smaller $L_G(\mathrm{v},\pm 1)$ values; when $L_G(\mathrm{v},\pm 1)$ is small at carbon v, $\Delta L_G(\mathrm{v},\pm 1)$ usually is small there. Smaller $\Delta L_G(\mathrm{v},\pm 1)$ values naturally indicate enhanced olefinic reactivity. In fact, when appropriate reagents coexist with these compounds, they are not so stable as benzene. In the case of biphenyl (**6**), triphenylene (**7**), naphthelene (**8**), phenanthrene (**9**), and anthracene (**14**), not only substitution but also addition products are formed by reaction with molecular chlorine.[19]

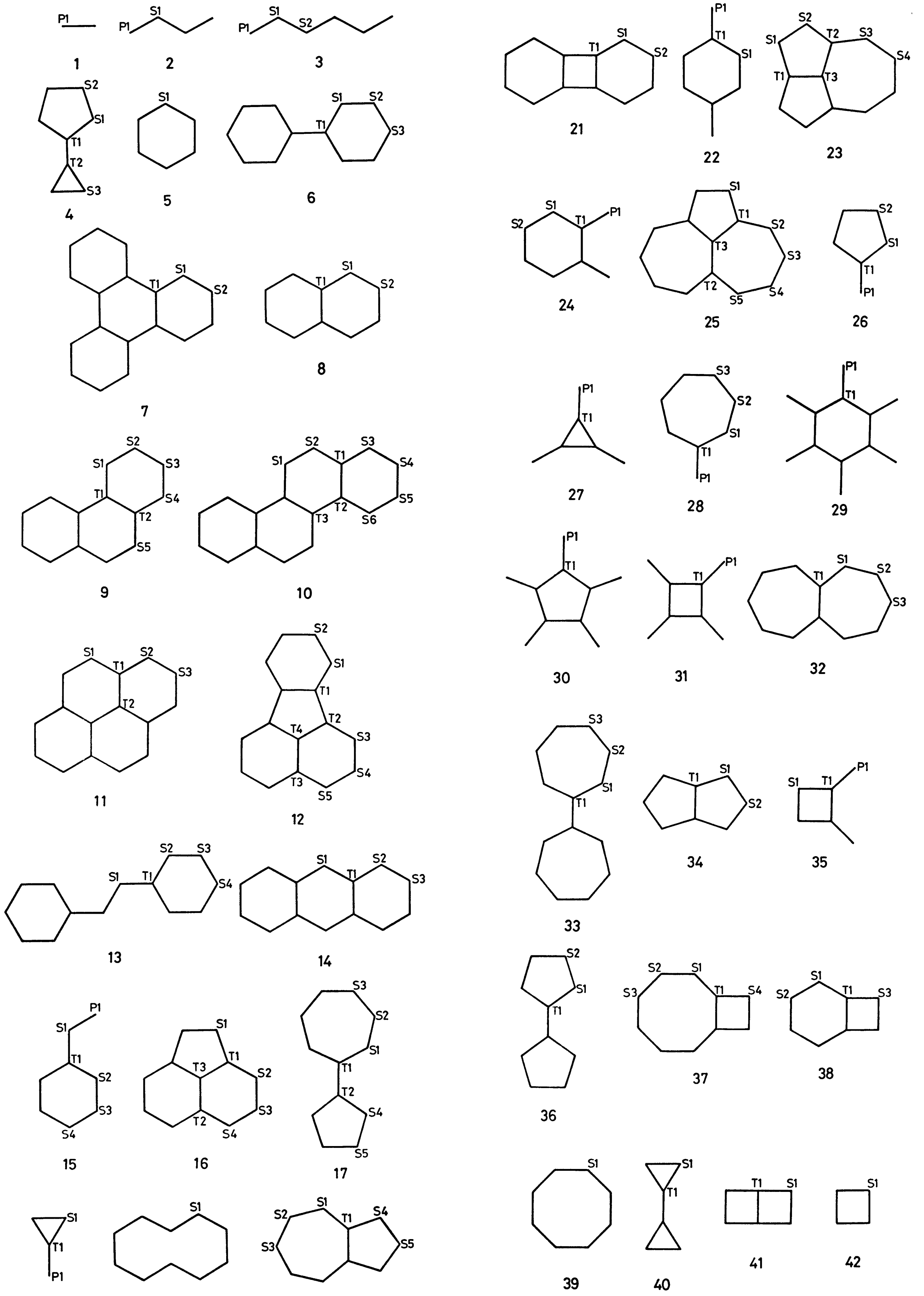

Fig. 1. Conjugated hydrocarbons investigated.

TABLE 2. LOCALIZATION ENERGIES FOR CYCLIC CONJUGATED HYDROCARBONS

Compound	%*RE*	v	$L_G°(v, \pm 1)$	$L_G(v, +1)$	$\Delta L_G(v, +1)$	$L_G(v, -1)$	$\Delta L_G(v, -1)$
Calicene (**4**)	4.13	S1	1.940	1.998	0.058	2.728	0.788
		S2	2.081	2.078	−0.003	3.005	0.924
		S3	1.858	2.863	1.005	2.022	0.164
		T1	2.569	2.467	−0.102	3.703	1.134
		T2	2.350	3.703	1.353	2.467	0.117
Benzene (**5**)	3.53	S1	2.263	2.536	0.273	2.536	0.273
Biphenyl (**6**)	3.16	S1	2.105	2.400	0.295	2.400	0.295
		S2	2.298	2.544	0.246	2.544	0.246
		S3	2.156	2.447	0.291	2.447	0.291
		T1	2.690	2.919	0.229	2.919	0.229
Triphenylene (**7**)	3.01	S1	2.111	2.378	0.267	2.378	0.267
		S2	2.189	2.477	0.288	2.477	0.288
		T1	2.559	2.881	0.322	2.881	0.322
Naphthalene (**8**)	2.92	S1	2.102	2.299	0.197	2.299	0.197
		S2	2.220	2.480	0.260	2.480	0.260
		T1	2.667	3.056	0.389	3.056	0.389
Phenanthrene (**9**)	2.89	S1	2.122	2.365	0.243	2.365	0.243
		S2	2.182	2.453	0.271	2.453	0.271
		S3	2.212	2.497	0.285	2.497	0.285
		S4	2.086	2.317	0.231	2.317	0.231
		S5	2.109	2.298	0.189	2.298	0.189
		T1	2.556	2.889	0.333	2.889	0.333
		T2	2.639	3.007	0.368	3.007	0.368
Chrysene (**10**)	2.81	S1	2.312	2.351	0.219	2.351	0.219
		S2	2.065	2.254	0.189	2.254	0.189
		S3	2.073	2.302	0.229	2.302	0.229
		S4	2.205	2.492	0.287	2.492	0.287
		S5	2.172	2.448	0.276	2.448	0.276
		S6	2.111	2.349	0.238	2.349	0.238
		T1	2.638	3.022	0.384	3.022	0.384
		T2	2.548	2.902	0.354	2.902	0.354
		T3	2.522	2.822	0.300	2.822	0.300
Pyrene (**11**)	2.73	S1	2.099	2.274	0.175	2.274	0.175
		S2	1.995	2.190	0.195	2.190	0.195
		S3	2.263	2.549	0.286	2.549	0.286
		T1	2.648	2.966	0.318	2.966	0.318
		T2	2.467	2.908	0.441	2.908	0.441
Fluoranthene (**12**)	2.64	S1	2.109	2.371	0.262	2.371	0.262
		S2	2.176	2.435	0.259	2.435	0.259
		S3	2.001	2.465	0.464	2.465	0.464
		S4	2.276	2.503	0.227	2.503	0.227
		S5	1.969	2.341	0.372	2.078	0.109
		T1	2.531	2.781	0.250	2.781	0.250
		T2	2.585	2.734	0.149	2.734	0.149
		T3	2.719	3.064	0.345	3.064	0.345
		T4	2.406	2.715	0.309	3.021	0.615
Stilbene (**13**)	2.61	S1	2.104	2.157	0.053	2.157	0.053
		S2	2.051	2.318	0.267	2.318	0.267
		S3	2.309	2.548	0.239	2.548	0.239
		S4	2.113	2.379	0.266	2.379	0.266
		T1	2.758	2.989	0.231	2.989	0.231
Anthracene (**14**)	2.52	S1	1.922	2.013	0.091	2.013	0.091
		S2	2.059	2.231	0.172	2.231	0.172
		S3	2.189	2.423	0.234	2.423	0.234
		T1	2.661	3.025	0.364	3.025	0.364

Table 2. (Continued)

Compound	%RE	v	$L_G^\circ(\mathrm{v}, \pm 1)$	$L_G(\mathrm{v}, +1)$	$\Delta L_G(\mathrm{v}, +1)$	$L_G(\mathrm{v}, -1)$	$\Delta L_G(\mathrm{v}, -1)$
Styrene (**15**)	2.45	P1	1.610	1.704	0.094	1.704	0.094
		S1	2.448	2.424	−0.024	2.424	−0.024
		S2	2.120	2.370	0.250	2.370	0.250
		S3	2.297	2.546	0.249	2.546	0.249
		S4	2.175	2.424	0.249	2.424	0.249
		T1	2.711	2.960	0.249	2.960	0.249
Acenaphthylene (**16**)	2.18	S1	2.056	2.124	0.068	2.124	0.068
		S2	1.958	2.525	0.567	1.999	0.041
		S3	2.282	2.513	0.231	2.513	0.231
		S4	1.958	2.417	0.459	1.969	0.011
		T1	2.634	2.812	0.178	2.812	0.178
		T2	2.727	3.066	0.339	3.066	0.339
		T3	2.355	2.566	0.211	3.135	0.780
Sesquifulvalene (**17**)	1.73	S1	1.915	2.454	0.539	1.964	−0.049
		S2	2.075	2.781	0.706	2.073	−0.002
		S3	2.010	2.601	0.591	2.035	0.025
		S4	1.882	1.972	0.090	2.506	0.624
		S5	1.991	2.062	0.071	2.715	0.724
		T1	2.516	3.361	0.845	2.471	−0.045
		T2	2.424	2.471	0.047	3.361	0.937
Triafulvene (**18**)	1.29	P1	1.435	0.962	−0.473	2.962	1.527
		S1	2.071	2.134	0.063	2.134	0.063
		T1	2.899	2.962	0.063	2.962	0.063
[10]Annulene (**19**)	1.25	S1	2.157	2.317	0.160	2.317	0.160
Azulene (**20**)	1.14	S1	2.020	2.551	0.531	1.929	−0.091
		S2	2.197	2.341	0.144	2.341	0.144
		S3	2.070	2.730	0.660	1.988	−0.082
		S4	1.973	1.924	−0.049	2.600	0.627
		S5	2.212	2.362	0.150	2.362	0.150
		T1	2.585	2.736	0.151	2.736	0.151
Biphenylene (**21**)	0.75	S1	2.128	2.408	0.280	2.408	0.280
		S2	2.219	2.352	0.133	2.352	0.133
		T1	2.605	2.522	−0.083	2.522	−0.083
3,6-Dimethylene-1,4-cyclohexadiene (**22**)	0.62	P1	1.298	1.204	−0.094	1.204	−0.094
		S1	2.136	2.197	0.061	2.197	0.061
		T1	2.965	3.026	0.061	3.026	0.061
Cyclopent[*cd*]azulene (**23**)	0.62	S1	2.085	2.352	0.267	1.970	−0.115
		S2	2.056	1.972	−0.084	2.382	0.326
		S3	2.038	2.553	0.515	1.988	−0.050
		S4	2.151	2.638	0.487	2.077	−0.074
		T1	2.557	2.479	−0.078	3.048	0.491
		T2	2.597	3.042	0.445	2.486	−0.111
		T3	2.355	2.313	−0.042	2.882	0.527
5,6-Dimethylene-1,3-cyclohexadiene (**24**)	0.60	P1	1.329	1.233	−0.096	1.233	−0.096
		S1	2.016	2.076	0.060	2.076	0.060
		S2	2.232	2.291	0.059	2.291	0.059
		T1	2.907	2.966	0.059	2.966	0.059
Cyclopenta[*ef*]heptalene (**25**)	0.56	S1	2.052	2.014	−0.038	2.491	0.439
		S2	2.031	2.204	0.173	1.934	−0.097
		S3	2.122	2.061	−0.061	2.463	0.341
		S4	2.144	2.436	0.292	2.060	−0.084
		S5	2.009	1.937	−0.072	2.221	0.212
		T1	2.564	2.505	−0.059	2.981	0.417
		T2	2.600	2.995	0.395	2.513	−0.087
		T3	2.334	2.801	0.467	2.319	−0.015

Table 2. (Continued)

Compound	%*RE*	v	$L_G^\circ(\mathrm{v}, \pm 1)$	$L_G(\mathrm{v}, +1)$	$\Delta L_G(\mathrm{v}, +1)$	$L_G(\mathrm{v}, -1)$	$\Delta L_G(\mathrm{v}, -1)$
Fulvene (**26**)	0.27	P1	1.291	2.230	0.939	0.994	−0.297
		S1	1.982	2.002	0.020	2.002	0.020
		S2	2.220	2.240	0.020	2.240	0.020
		T1	2.974	2.994	0.020	2.994	0.020
[3]Radialene (**27**)	0.12	P1	1.473	1.459	−0.014	1.459	−0.014
		T1	2.819	2.828	0.009	2.828	0.009
Heptafulvene (**28**)	0.09	P1	1.223	1.006	−0.217	1.897	0.674
		S1	1.931	1.940	0.009	1.940	0.009
		S2	2.258	2.267	0.009	2.267	0.009
		S3	2.107	2.116	0.009	2.116	0.009
		T1	2.997	3.006	0.009	3.006	0.009
[6]Radialene (**29**)	0.06	P1	1.468	1.464	−0.004	1.464	−0.004
		T1	2.828	2.837	0.009	2.837	0.009
[5]Radialene (**30**)	0.00	P1	1.468	1.468	0.000	1.468	0.000
		T1	2.828	2.828	0.000	2.828	0.000
[4]Radialene (**31**)	−0.73	P1	1.468	1.504	0.036	1.504	0.036
		T1	2.830	2.758	−0.072	2.758	−0.072
Heptalene (**32**)	−0.89	S1	1.982	1.660	−0.322	2.193	0.211
		S2	2.175	2.032	−0.143	2.032	−0.143
		S3	2.034	1.715	−0.319	2.337	0.303
		T1	2.568	2.427	−0.141	2.427	−0.141
Heptafulvalene (**33**)	−1.20	S1	1.900	1.513	−0.387	1.949	0.049
		S2	2.045	1.626	−0.419	2.248	0.203
		S3	1.988	1.586	−0.402	2.088	0.100
		T1	2.472	2.029	−0.443	2.919	0.447
Pentalene (**34**)	−2.02	S1	2.024	2.380	0.356	1.538	−0.486
		S2	2.247	2.027	−0.220	2.027	−0.220
		T1	2.616	2.401	−0.215	2.401	−0.215
Dimethylenecyclobutene (**35**)	−2.21	P1	1.371	1.612	0.241	1.612	0.241
		S1	2.144	1.982	−0.162	1.982	−0.162
		T1	2.899	2.736	−0.163	2.736	−0.163
Fulvalene (**36**)	−2.28	S1	1.906	1.987	0.081	0.987	−0.919
		S2	2.024	2.236	0.212	1.452	−0.572
		T1	2.471	3.091	0.620	1.855	−0.616
Bicyclo[6.2.0]decapentaene (**37**)	−3.46	S1	2.064	2.191	0.127	2.191	0.127
		S2	2.228	2.046	−0.182	2.046	−0.182
		S3	2.161	2.112	−0.049	2.112	−0.049
		S4	2.176	1.839	−0.337	1.839	−0.337
		T1	2.676	2.215	−0.461	2.215	−0.461
Benzocyclobutene (**38**)	−3.65	S1	2.127	2.261	0.134	2.261	0.134
		S2	2.255	2.173	−0.082	2.173	−0.082
		S3	2.209	1.661	−0.548	1.661	−0.548
		T1	2.719	2.326	−0.393	2.326	−0.393
Cyclooctatetraene (**39**)	−5.80	S1	2.197	1.602	−0.595	1.602	−0.595
Triafulvalene (**40**)	−5.81	S1	1.925	1.035	−0.890	2.114	0.189
		T1	2.461	1.464	−0.997	3.464	1.003
Butalene (**41**)	−7.31	S1	2.261	2.061	−0.200	2.061	−0.200
		T1	2.797	2.193	−0.604	2.193	−0.604
Cyclobutadiene (**42**)	−23.46	S1	2.398	1.172	−1.226	1.172	−1.226

Especially, carbon S1 in anthracene is very reactive and olefinic since $L_G(\mathrm{S1},\pm1)$ and $\Delta L_G(\mathrm{S1},\pm1)$ are very small. All other carbons in benzenoid hydrocarbons have $\Delta L_G(\mathrm{v},\pm1)$ in the range 0.172—0.441.

Fluoranthene (**12**) contains a five-membered ring, but this is similar in reactivity to benzenoid hydrocarbons. All constituent carbons are highly stabilized by aromaticity. The same is true for the second member of aromatic annulenes, [10]annulene (**19**). All carbons are moderately stabilized. However, this compound is far from isolable because of heavy steric hindrance.$^{20)}$

Stilbene (**13**) and styrene (**15**) are aromatic compounds, but can be regarded as substituted ethylenes. Carbons at ethylenic portions have small $L_G(\mathrm{v},\pm1)$ values and small positive or negative $\Delta L_G(\mathrm{v},\pm1)$ values, and tend to undergo addition reactions. They are located outside of the aromatic rings. Acenaphthylene (**16**) is olefinic in reactivity at carbon S1. In accord with this, $L_G(\mathrm{S1},\pm1)$ and $\Delta L_G(\mathrm{S1},\pm1)$ are very small. Biphenylene (**21**) has small positive resonance energy. However, $\Delta L_G(\mathrm{T1},\pm1)$ is negative, suggesting that carbon T1 is highly destabilized by the antiaromatic central four-membered ring. Several addition reactions are known to occur around this ring.$^{21)}$

Other nonbenzenoid hydrocarbons generally have reactive carbons with smaller localization energies. Azulene (**20**) has long been recognized to be the first example of nonbenzenoid aromatics. This compound undergoes various electrophilic and nucleophilic substitution reactions only under mild conditions.$^{22)}$ These observations may be rationalized by the negative values of $\Delta L_G(\mathrm{S1},-1)$, $\Delta L_G(\mathrm{S3},-1)$, and $\Delta L_G(\mathrm{S4},+1)$. These negative values, however, indicate that azulene is more reactive than its olefinic reference structure. In fact, oxidative decomposition and hydrogenation easily take place.$^{23)}$

Two asymmetric fulvalenes **4** and **17** are predicted to be highly aromatic with large resonance energies. However, there is no experimental evidence for aromatic stabilization.$^{24)}$ Calicene (**4**) has defied all attempts of isolation. Both compounds are supposed to be very olefinic in reactivity; either $\Delta L_G(\mathrm{v},+1)$ or $\Delta L_G(\mathrm{v},-1)$ is small or negative at each carbon. Therefore, all carbons must be very reactive toward electrophiles or nucleophiles. We might say that the entire π-electron frameworks of these fulvalenes are really aromatic but very unstable.

All radialenes **27** and **29**—**31**, fulvenes **18**, **26**, and **28**, and dimethylenecyclohexadienes **22** and **24** are all predicted to be essentially nonaromatic with small percent resonance energies. They have one or more primary carbons, at which $L_G(\mathrm{v},\pm1)$ is very small as in the case of acyclic polyenes. Secondary and tertiary carbons are also olefinic with $\Delta L_G(\mathrm{v},\pm1)\approx0$. These compounds are very olefinic in their chemical behavior. Triafulvene (**18**) and dimethylenecyclohexadienes are too reactive to be isolated in any form. The same is true for dimethylenecyclobutene (**35**). This compound does readily polymerize in the presence of air.$^{25)}$ Conjugated hydrocarbons with exomethylene groups are thus extremely reactive. Benzene, fulvene, and dimethylenecyclobutene form an interesting set of isomers, being respectively aromatic, nonaromatic, and antiaromatic, but the first species alone is of great kinetic stability.

Cyclopent[*cd*]azulene (**23**) and cyclopenta[*ef*]heptalene (**25**) are substantially nonaromatic. These nonalternant hydrocarbons are not highly symmetric in shape, so they necessarily have reactive carbons with negative $\Delta L_G(\mathrm{v},+1)$ or $\Delta L_G(\mathrm{v},-1)$ values. These carbons determine the degree of kinetic stability associated with electrophilic and nucleophilic reactivities.

In marked contrast to asymmetric fulvalenes, symmetric fulvalenes **33**, **36**, and **40** are all typically antiaromatic; either $\Delta L_G(\mathrm{v},+1)$ or $\Delta L_G(\mathrm{v},-1)$ at each carbon takes a large negative value. Therefore, they are predicted to be much more reactive than their olefinic reference structures. This is in agreement with their chemistry.$^{24)}$ Triafulvalene (**40**) has not been isolated yet. Other antiaromatic hydrocarbons belong to the group of such chemically very unstable species. Among them are heptalene (**32**), pentalene (**34**), bicyclo[6.2.0]decapentaene (**37**), benzocyclobutene (**38**), cyclooctatetraene (**39**), butalene (**41**), and cyclobutadiene (**42**). They tend to polymerize readily, or are obtained as a dimer which may arise by way of a self-Diels-Alder reaction. Some carbons in each of these hydrocarbons again have small localization energies together with large negative $\Delta L_G(\mathrm{v},+1)$ or $\Delta L_G(\mathrm{v},-1)$ values. This indicates that antiaromatic instability itself is relaxed by forming appropriate σ complexes. Especially, all carbons in cyclooctatetraene, butalene, and cyclobutadiene have negative $\Delta L_G(\mathrm{v},\pm1)$ values.

We have been examining the values of $L_G(\mathrm{v},\pm1)$ and $\Delta L_G(\mathrm{v},\pm1)$ to discuss the discrepancy between aromaticity and kinetic stability. Essentially the same discussion can be made using Fukui's concept of superdelocalizability, $S_G(\mathrm{v},\pm1)$.$^{10,11)}$ The magnitude of superdelocalizability for the olefinic reference structure of a cyclic conjugated hydrocarbon, $S_G{}^\circ(\mathrm{v},\pm1)$, depends primarily on the type of the carbon.$^{26)}$ Although there are several exceptions, $S_G{}^\circ(\mathrm{v},\pm1)$ is larger at primary carbons than at secondary carbons, and at secondary carbons than at tertiary carbons. If a given carbon v is stabilized by the cyclic conjugation of π electrons, $S_G(\mathrm{v},\pm1)$ becomes smaller than $S_G{}^\circ(\mathrm{v},\pm1)$, so the difference $\Delta S_G(\mathrm{v},\pm1)$ becomes negative in sign. When $S_G(\mathrm{v},\pm1)$ is large at carbon v, $\Delta S_G(\mathrm{v},\pm1)$ usually is large there. Reactive carbons specified in terms of $S_G(\mathrm{v},\pm1)$ and $\Delta S_G(\mathrm{v},\pm1)$ are essentially the same as those specified in terms of $L_G(\mathrm{v},\pm1)$ and $\Delta L_G(\mathrm{v},\pm1)$. Such a parallelism can be rationalized partly by noting that $L_G(\mathrm{v},\pm1)$ is theoretically interrelated with $S_G(\mathrm{v},\pm1)$.$^{27)}$

In brief, benzenoid hydrocarbons, fluoranthene, and [10]annulene are thermodynamically stable with large $\%RE$ values, and are predicted to be rather resistant to electrophiles and nucleophiles. Stilbene, styrene, acenaphthylene, azulene, biphenylene, cyclopent[*cd*]azulene, cyclopenta[*ef*]heptalene, dimethylenecyclohexadienes, radialenes, and asymmetric fulvalenes must be very reactive toward electrophiles and/or nucleophiles whether these hydrocarbons are aromatic with positive resonance energies or not. All other hydrocarbons investigated must be much more reactive than nonaromatic polyenes. This aspect of kinetic stability or instability is in good agreement with their chemical behavior.[28]

Concluding Remarks

Thermodynamic stability of a cyclic conjugated system may correlate with its kinetic stability. However, there are such notable exceptions as aromatic compounds for which all synthetic attempts failed. These compounds must have conversion routes to others with still larger kinetic stability. The present approach complements the stability considerations based solely on aromaticity. Using the concepts of localization energy and superdelocalizability, we found that the kinetic stability of a cyclic conjugated system can be conjectured well from its electrophilicity and nucleophilicity. In this sense, localization energy and superdelocalizability are representative indices of kinetic stability. $\Delta L_G(\mathrm{v},\pm 1)$ and $\Delta S_G(\mathrm{v},\pm 1)$ serve as indices of olefinic reactivity. Highly electrophilic and/or nucleophilic carbons were shown to be very olefinic in reactivity. Therefore, hydrocarbons having such carbons are reluctant to retain their original cyclic conjugated systems. When they are attacked by an electrophile or a nucleophile, reaction paths to compounds other than substitution products will be chosen preferentially.

Most nonbenzenoid hydrocarbons have reactive carbons whether they are aromatic or not. In these hydrocarbons not only aromaticity but also reactivity are induced by the same cyclic interactions of π electrons. Many of the anomalies found in the aromaticity-stability relationship can be rationalized in this manner. Examination of reactivities other than electrophilic and nucleophilic ones would further clarify the essence of kinetic stability. In view of excellent correlation between calculated reactivity indices and chemical behavior, we emphasize that aromatic compounds are quite diverse in kinetic stability. Thermodynamic and kinetic stabilities do not always concur in the case of nonbenzenoid hydrocarbons. Some compounds may appear to be chemically stable because their conjugate acids and bases are both stable.[1] According to the present approach, these will be predicted to be reactive and unstable.

If only cyclic unsaturated compounds characterized by low chemical reactivity and high thermodynamic stability are regarded as aromatic compounds, they will be limited to benzenoid hydrocarbons and some semibenzenoids such as fluoranthene. All carbons in these compounds are really stabilized by the cyclic π-electron conjugation. Most nonbenzenoid hydrocarbons will become nonaromatic in this sense. However, we choose to call them unstable aromatic compounds, retaining the original definition of aromaticity based on thermodynamic stability.

It is interesting to see that the most reactive carbons sometimes vary on going from a real conjugated system to its olefinic reference structure. However, the most reactive carbons in benzenoid hydrocarbons usually remain the same in their olefinic reference structures. This indicates that aromaticity, *i.e.*, cyclic π-electron conjugation, scarcely affects relative reactivities of constituent carbons in these compounds.

Finally, one comment must be made concerning the π-electron densities. Localization energy and superdelocalizability are applicable only to the reaction with an electrophile or a nucleophile for which the transition state resembles the σ complex. If the transition state occurs early in the same reaction, that is, if the transition state resembles the initial reactants, the π-electron densities will be a primary index.[10,29] Here, an electrophile or a nucleophile acts as an opposite-charge-seeking species. It follows that if the reaction proceeds via an early transition state, any nonalternant hydrocarbon would be more reactive than its olefinic reference structure, where the charge distribution is uniform as in the case of alternant hydrocarbons.[17] This implies that nonalternant hydrocarbons must be more reactive toward electrophiles and nucleophiles than alternant hydrocarbons including acyclic polyenes. This is possibly another reason why many nonalternant hydrocarbons are much more reactive than are predicted from their resonance energies.

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