With use of FAB mass spectrometry, ions characteristic of molecular weight are produced for times ranging from minutes to ca 1 h on samples of 1–50 nmol of highly polar compounds. Thus, conditions suitable for carrying out high-resolution measurements exist. With use of an MS 50 instrument, a resolving power of 80 000 has been obtained. In favorable cases, the intensities of ions characteristic of molecular weight are sufficient to permit precise mass determination (e.g., the antibiotic erythromycin), despite the reduction in the number of ions reaching the collector when operating under high-resolution conditions.

Molecules which do not readily act as proton donors or acceptors are less well suited to examination by FAB mass spectrometry. Thus, we find that structurally informative ions are not produced from nonpolar hydrocarbons with high sensitivity even under a variety of conditions (samples loaded in glycerol, trigol, Nujol, silicone oil, or as a solid). We conclude that FAB mass spectrometry represents a major advance in the study of relatively polar molecules, and appears likely to largely supersede field desorption in this area.

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Unified Theory of Aromaticity and London Diamagnetism

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Abstract: The concepts of aromaticity and London diamagnetism were unified into a single theoretical framework. It was then found that a simple relationship exists between the magnitude of the diamagnetic susceptibility due to ring currents and that of the resonance energy due to aromaticity. However, this relationship does not guarantee the proportionality of the susceptibility to the resonance energy. Therefore, it is sometimes dangerous to regard the sign of the susceptibility as an indication of aromaticity or antiaromaticity. The heptalene dianion and bicyclo[6.2.0]decapentaene were predicted to be diatropic but antiaromatic compounds.

In 1961 Elvidge and Jackman suggested that the magnitude of the ring current might be used as a measure of aromaticity of the molecule.[2] An NMR criterion of aromaticity has since been advanced according to which diamagnetic ring currents indicate aromaticity while paramagnetic ring currents indicate antiaromaticity.[3-5] The contribution of ring currents to the magnetic susceptibility is called the London diamagnetism.[6] In 1968 Dauben et al. employed the London diamagnetism as a reliable criterion of aromaticity.[6,7]

However, it was not at all clear that molecules with diamagnetic ring currents also have strong conjugative stabilization.[5,8] In 1966 Abraham and Thomas[9] pointed out that there is little connection between the ring currents and the resonance energy defined by Dewar et al.[10] Labarre and Crasnier[8] and Haddon[11] stressed that it is impossible to link the ring current criterion of aromaticity to the resonance energy or the reactivity of the molecule.

Such a perplexing situation had not changed until the graph theory of aromaticity[12,13] was developed extensively. This theory was found to reproduce analytically the resonance energy of Dewar's type. Furthermore, by the use of the theory, I could prove that both the London diamagnetism and the resonance energy have the same root in the cyclic conjugation of π electrons.[14,15] We are now ready to examine the magnetic criterion of aromaticity in detail. In this paper, I would like to show that the analytic expression of London diamagnetism has a close resemblance in nature to that of the resonance energy. This enables us to clarify the theoretical basis of London diamagnetism as a measure of aromatic stabilization and the limit of its utility. The Hückel molecular orbital model is used throughout this paper.

Theory

Let a characteristic polynomial for the conjugated system G be denoted by $P_G(X)$, and the corresponding reference polynomial $R_G(X)$ can be written formally in this form:[12,13,16]

$$R_G(X) = P_G(X) - \Delta P_G(X) \qquad (1)$$

$R_G(X)$ has been interpreted as a characteristic polynomial for the olefinic reference structure of G. Let the jth largest root of the equation $P_G(X) = 0$ be denoted by X_j, and this represents the jth π-electron orbital energy of G. By the use of Newton's method for numerically solving algebraic equations, the corresponding root X_j^0 of the equation $R_G(X) = 0$ can be expressed approximately as

$$X_j^0 \approx X_j + \frac{\Delta P_G(X_j)}{P_G'(X_j)} \qquad (2)$$

where $P_G'(X)$ is the first derivative of $P_G(X)$ with respect to X. X_j^0 represents the jth π-electron orbital energy of the reference structure. The validity of eq 2 depends upon the magnitudes of all the $\Delta P_G(X_j)/P_G'(X_j)$ values. Fortunately, they are commonly

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very small, so we might say that eq 2 holds well for most conjugated systems. See, e.g., Table III in ref 15.

The jth orbital resonance energy RE_j is defined as the energy difference between the jth π-electron orbitals in G and in its reference structure,[15] namely,

$$\mathrm{RE}_j = X_j - X_j^0 \approx -\frac{\Delta P_G(X_j)}{P_G'(X_j)} \qquad (3)$$

The overall resonance energy RE of the conjugated system G is then approximated as

$$\mathrm{RE} = \sum_{j=1}^{N} g_j RE_j \approx -\sum_{j=1}^{N} \frac{g_j \Delta P_G(X_j)}{P_G'(X_j)} \qquad (4)$$

where N denotes the number of conjugated atoms, and where g_j is the number of π electrons in the jth orbital. All these resonance energies are given in units of β, which is the absolute value of the resonance integral β.

For simplicity, we first consider the conjugated hydrocarbons with no alteration of π bond lengths. In the case of monocyclic and bicyclic hydrocarbons, $\Delta P_G(X)$ can be written simply as[15,17]

$$\Delta P_G(X) = P_G(X) - R_G(X) = -2\sum_{i}^{G} P_{G-r_i}(X) \qquad (5)$$

where $G - r_i$ is a subsystem of G, obtained by deleting from G the ith π-electron ring r_i and all π bonds adjacent to r_i, and where i runs over all π-electron rings in G. Here, a π-electron ring is identical with a ring component defined in Sachs' graph-theoretical theorem.[18,19] If $G = r_i$, $P_{G-r_i}(X) = 1$ by definition.[18,19] The resonance energy can now be approximated as

$$\mathrm{RE} \approx 2\sum_{j=1}^{N}\sum_{i}^{G} g_j Q_{G-r_i}(X_j) \qquad (6)$$

where

$$Q_{G-r_i}(X) = \frac{P_{G-r_i}(X)}{P_G'(X)} \qquad (7)$$

If there are degenerate orbitals with the energy X_{j*} in G, the expression for their orbital resonance energies becomes

$$\mathrm{RE}_{j*} \approx \pm\left[\frac{2}{U_G(X_{j*})}\sum_{i}^{G} P_{G-r_i}(X_{j*})\right]^{1/2} + \frac{U_G'(X_{j*})}{U_G(X_{j*})^2}\sum_{i}^{G} P_{G-r_i}(X_{j*}) - \frac{1}{U_G(X_{j*})}\sum_{i}^{G} P_{G-r_i}'(X_{j*}) \qquad (8)$$

where $U_G(X)$ is defined by

$$P_G(X) = U_G(X)(X - X_{j*})^2 \qquad (9)$$

When a pair of degenerate orbitals are full, the contributions from the first term of eq 8 are cancelled out.

The resonance energy in the form of eq 6 can be divided among the π-electron rings. The ith ring resonance energy, i.e., the resonance energy of the ith π-electron ring, is then given by

$$\mathrm{RE}^{(i)} \approx 2\sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \qquad (10)$$

All these expressions also apply to pericondensed tricyclic hydrocarbons, such as acenaphthylene, aceheptylene, and cyclopent[*cd*]azulene.

On the other hand, the diamagnetic susceptibility due to ring currents is nothing other than a measure of London diamagnetism.[6] For any conjugated hydrocarbon with no bond alternation, the jth orbital susceptibility χ_j was previously defined as[15]

$$\chi_j = -2\sum_{i}^{G} Q_{G-r_i}(X_j)\Theta_i^2 \qquad (11)$$

where

$$\Theta_i = eS_i/\hbar c \qquad (12)$$

Here, S_i is the area enclosed by r_i, and e, $\hbar$, and c are the standard constants with these symbols. The overall susceptibility due to ring currents, χ_π, is[15]

$$\chi_\pi = \sum_{j=1}^{N} g_j \chi_j = -2\sum_{j=1}^{N}\sum_{i}^{G} g_j Q_{G-r_i}(X_j)\Theta_i^2 \qquad (13)$$

All these susceptibilities are given in units of β.

If there are degenerate orbitals in G, their orbital susceptibilities are given by[15]

$$\chi_{j*} = \frac{U_G'(X_{j*})}{U_G(X_{j*})^2}\sum_{i}^{G} P_{G-r_i}(X_{j*})\Theta_i^2 - \frac{1}{U_G(X_{j*})}\sum_{i}^{G} P_{G-r_i}'(X_{j*})\Theta_i^2 \qquad (14)$$

By the way, eq 8 was derived by analogy with the derivation of this expression.

The diamagnetic susceptibility in the form of eq 13 can also be divided among the π-electron rings. The ith ring susceptibility, i.e., the susceptibility attributable to the ith π-electron ring, is given by[15]

$$\chi_\pi^{(i)} = -2\Theta_i^2 \sum_{j=1}^{N} \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \qquad (15)$$

We have been dealing with conjugated systems with no bond alternation. If all bond parameters (k) in G are not equal to unity, $P_{G-r_i}(X)$ and $P_{G-r_i}'(X)$ in eq 5–15 must be multiplied by the product of bond parameters of all π bonds around r_i.[21]

It is now easy to show the existence of correlation between the magnitude of the resonance energy and that of the susceptibility due to ring currents. Comparing eq 10 and 15, we see that the ith ring resonance energy is evidently related to the ith ring susceptibility; the two quantities differ only by the factor $-\Theta_i^2$. This relationship indicates that the sign of any ring susceptibility is opposite to that of the resonance energy of the same ring. Since $(4n + 2)$-membered rings have positive ring resonance energies,[15,22] they must have negative ring susceptibilities. Conversely, $4n$-membered rings have negative resonance energies,[15,22] so they must have positive ring susceptibilities. This is the primary reason why London diamagnetism is commonly a manifestation of aromaticity.[6,7] It has been established that aromatic character of the molecule can be equated well with the sign and the magnitude of the resonance energy adopted in this paper.[12-16,22]

However, the sign of the overall susceptibility (χ_π) does not always differ from that of the overall resonance energy (RE). If the two quantities have the same sign, the weighting factors $-\Theta_i^2$ will be obviously responsible for it. This effect can be visualized as follows. RE is a simple sum of the ring resonance energies. By substituting eq 10 in eq 13, χ_π can also be expressed in terms of the same ring resonance energies, namely,

$$\chi_\pi \approx -\sum_{i}^{G} \mathrm{RE}^{(i)}\Theta_i^2 \qquad (16)$$

where each ring resonance energy is counted with a different weight. This expression indicates that larger rings contribute much more to χ_π than to RE, because each of the weighting factors is proportional to the corresponding ring area squared. Therefore, in the case of conjugated systems with two or more π-electron rings, the magnitude of χ_π often becomes far from proportional to that of RE;[15] this means that it is not always safe to regard the sign of χ_π as an indication of aromaticity or antiaromaticity.

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Table I. Resonance Energy and Susceptibility of the Heptalene Dianion (1), Each as a Function of k

k	RE, β	$RE^{\#}, \beta$	$\chi_\pi, \Theta_0^2\beta^a$
0.00	0.128	0.104	−0.811
0.10	0.093	0.077	−0.809
0.20	0.055	0.046	−0.808
0.30	0.015	0.011	−0.805
0.40	−0.027	−0.029	−0.800
0.50	−0.072	−0.076	−0.794
0.60	−0.118	−0.129	−0.787
0.70	−0.165	−0.191	−0.779
0.80	−0.212	−0.264	−0.769
0.90	−0.260	−0.350	−0.759
1.00	−0.308	−0.455	−0.748

[a] $\Theta = eS_0/\hbar c$, where S_0 is an area of the benzene ring.

Table II. Resonance Energy and Susceptibility of Bicyclo[6.2.0]decapentaene (2), Each as a Function of k

k	RE, β	$RE^{\#}, \beta$	$\chi_\pi, \Theta_0^2\beta^a$
0.00	0.159	0.129	−0.651
0.10	0.108	0.088	−0.646
0.20	0.053	0.041	−0.637
0.30	−0.005	−0.011	−0.625
0.40	−0.066	−0.070	−0.608
0.50	−0.129	−0.137	−0.587
0.60	−0.194	−0.212	−0.559
0.70	−0.261	−0.298	−0.523
0.80	−0.327	−0.396	−0.478
0.90	−0.394	−0.509	−0.422
1.00	−0.461	−0.642	−0.352

[a] See Table I, footnote a.

Thus, eq 16 shows the limits of the utility of χ_π as a measure of aromaticity. Even though there are degenerate orbitals in G, eq 16 holds.

As far as monocyclic conjugated systems are concerned, correlation between RE and χ_π is usually very good. From eq 16 we obtain

$$\chi_\pi \approx -\mathrm{RE}\Theta_i^2 \tag{17}$$

In this connection, Haddon[23] and later I[24] presented a similar relationship between RE and χ_π for aromatic annulenes. What I derived is[24]

$$\chi_\pi \approx -0.81\mathrm{RE}\Theta_i^2 \tag{18}$$

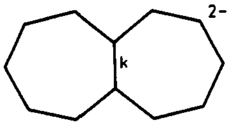
Here, the proportionality constant (0.81) deviates slightly from unity, but still lies in the acceptable range. In the case of oxocarbon conjugated systems, eq 17 holds very well.[25] These facts show that the quantity χ_π/Θ_i^2, rather than χ_π itself, is a good measure of aromaticity for monocyclic conjugated systems.

Proton chemical shifts have been used to estimate the aromatic character of cyclic conjugated systems.[2-5,26] A current induced in the ith π-electron ring is given as the first derivative of the ith ring susceptibility with respect to the ring area.[26] Therefore, the sign of the ring current, i.e., its direction, is naturally opposite to the sign of the ring resonance energy. This provides a theoretical justification for the utility of proton chemical shifts as a conventional criterion of aromaticity. However, it is again quite possible that larger π-electron rings dominate the chemical shifts.

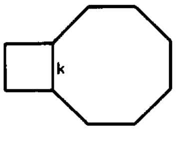
We have confined ourselves to monocyclic, bicyclic, and pericondensed tricyclic hydrocarbons. For other polycyclic systems, some correction terms must be added to eq 5[12,13] and, hence, to eq 6–10 and 16. However, a major part of RE can still be described by eq 6 in its original form. The necessity of additional terms in eq 6–10 implies that the relationship in the form of eq 16 becomes gradually ambiguous on going to tetracyclic and more highly polycyclic hydrocarbons.

Aromatic Character of the Heptalene Dianion and Bicyclo[6.2.0]decapentaene

Let us apply the above theory to the heptalene dianion (**1**) and bicyclo[6.2.0]decapentaene (**2**), and examine the theory a bit further. These two compounds have been considered aromatic[27,28] because of their diatropicity.[4,29] Compound **1** indeed has relatively small alternation of the peripheral π bonds, together with a rather elongated central π bond.[28] For these reasons, it has been believed that the peripheral conjugated systems determine the aromaticity of these compounds.[27,28] In order to look over the situation, their resonance energies and susceptibilities were calculated, each as a function of a bond parameter of the central π bond (k). They are listed in Tables I and II. For simplicity, all π bonds were assumed to have the same lengths.



1



2

For both of these compounds, agreement between RE and RE# is very good over the entire range of the k value, where RE# signifies the resonance energy estimated by means of eq 6. When the k value is very small, resonance energies of these compounds are positive. However, they are negative for the realistic k values (i.e., $0.5 \leq k \leq 1.0$). Contrary to the aromaticity considerations based on the chemical shifts,[27,28] this indicates that the compounds must be antiaromatic. For the heptalene dianion, RE vanishes near $k = 0.34$, while RE# vanishes at essentially the same k value (i.e., $k = 0.33$). For bicyclo[6.2.0]decapentaene, RE and RE# vanish at $k = 0.29$ and 0.28, respectively. These results show that RE# is really a good substitute for the exact resonance energy.

On the other hand, these two compounds always have negative susceptibilities due to ring currents, indicating that their conjugated systems are diamagnetic independently of the k value. The observed chemical shifts are consistent with these susceptibilities, and are therefore in apparent disagreement with the antiaromatic character predicted from the resonance energies. We might say that these compounds are diatropic[29] but antiaromatic in nature. It is noteworthy that diatropicity and antiaromaticity coexist in a single conjugated system. This has been the origin of confusion brought about by the organic chemists.[27,28] The reason why such a discrepancy occurred between RE and χ_π is now evident. The weighting factors $-\Theta_i^2$ are primarily responsible for it. This kind of situation scarcely appears in the case of monocyclic conjugated systems.[23-25]

Concluding Remarks

The concepts of aromaticity and London diamagnetism were unified into a single theoretical framework. It was then found that there obviously exists an explicit relationship between the magnitude of RE and that of χ_π. This relationship is relatively simple, but does not guarantee the proportionality of χ_π to RE. Therefore, as suggested by Abraham and Thomas,[9] it is in the detection of aromaticity rather than in the measurement of the degree of aromatic character that the magnetic criterion of aromatic character is most useful. However, it is dangerous to overestimate its ability to predict aromaticity.

Acknowledgment. The use of the facilities of the Hokkaido University Computing Center is gratefully acknowledged.

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