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# Theoretical Relationship between Diamagnetic Susceptibility Exaltation and Aromatic Stabilization

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**Abstract:** The London theory of diamagnetism for aromatic compounds was reformulated by analogy with the graph theory of aromaticity. A relationship between diamagnetic susceptibility exaltation (DSE) and aromatic stabilization was theoretically clarified for these compounds. The role of the applied magnetic field was to make the total $\pi$-electron energy of a conjugated system slightly approach that of its olefinic reference structure. The total $\pi$-electron energy of the reference structure was free from the effect of the magnetic field. The DSE was found to reflect the sign of the resonance energy and, to a lesser extent, its magnitude. Now, we can safely use the DSE as a definite criterion of aromaticity.

Early in this century, Pascal found that, in general, the diamagnetic susceptibility of an organic compound is approximately an additive function of its constituent groups.[1] He constructed a system for estimating the diamagnetic susceptibility on this principle. However, benzene typically exhibited a rather larger susceptibility than was expected from a comparison with the values of alkenes. Many aromatic compounds were found to show an analogous response to the magnetic field. In this context, diamagnetic susceptibility exaltation (DSE) is defined as the difference between the susceptibility ($\chi$) found for a compound and that ($\chi_0$) for the olefinic reference structure.[2-4] Here, $\chi_0$ is the value estimated on Pascal's additive principle.

In 1936, Pauling pointed out that the DSE arises from a circulation of fully delocalized $\pi$ electrons (i.e., a ring current).[5] London developed a simple quantum mechanical description of this effect.[6,7] The contribution of fully delocalized $\pi$ electrons to the magnetic susceptibility is termed the London diamagnetism. It is nothing other than the origin of the DSE. The London diamagnetism is strongly anisotropic, being large in the direction perpendicular to the ring plane and small or zero in the plane.

It has widely been accepted that DSE is not only a manifestation of the presence of fully delocalized $\pi$ electrons in a compound but also a reliable criterion of aromaticity.[2-4] However, there have been no satisfactory theories which might justify a relationship between the DSE and the degree of aromatic stabilization. In this paper, I would like to develop the London theory of diamagnetism by analogy with the graph theory of aromaticity,[8-10] and present a theoretical basis for correlating the DSE concept with the theory of aromaticity. We hereafter refer to DSE only, and call it the diamagnetic susceptibility of a conjugated system for convenience's sake.

## Graph Theoretical Formulation of the London Theory

In the London theory for aromatic hydrocarbons,[6,7] the effect of a uniform, external magnetic field, with a component perpendicular to the ring plane, is to perturb the original "field-free" Hückel secular determinant by modifying all the off-diagonal matrix elements, $H_{ij}$, in the original AO basis, by a complex factor

$$\omega_{ij} = \exp(i\theta_{ij}H) \tag{1}$$

where

$$\theta_{ij} = \frac{2\pi e s_{ij}}{hc} \tag{2}$$

Here, $H$ is the magnitude of the component of the external magnetic field perpendicular to the ring plane, $e$, $h$, and $c$ are the standard constants with these symbols, and $s_{ij}$ is the signed (algebraic) area of the triangle formed by an arbitrary (but subsequently fixed) origin and atoms $i$-$j$ in the conjugated system. Since $s_{ij}$ is a signed area, $s_{ij} = -s_{ji}$, and therefore $\omega_{ij} = \omega_{ji}^*$.

Here, we consider the eigenvalue problem of conjugated hydrocarbons. To a first approximation, one may take $H_{ij}$ to have a common value $\beta$ for all C-C bonds. All the diagonal matrix elements, $H_{ii}$, may be set equal to $\alpha$. The Hückel secular equation can then be reduced to

$$|\omega_{ij} - X\delta_{ij}| = 0 \tag{3}$$

where $X$ is a dimensionless eigenvalue. It is linearly related to

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the energy eigenvalue $X_e$, namely,

$$X = \frac{X_e - \alpha}{\beta} \tag{4}$$

On expansion eq 3 leads to a polynomial in $X$, the coefficients all being expressible in terms of closed cyclic products of the type $\omega_{ij}\omega_{jk} \ldots \omega_{pq}\omega_{qi}$. Such products of more than two factors represent closed cycles of $\pi$ bonds (i.e., $\pi$ rings) in a conjugated system.[11] Every such product can be evaluated as

$$\omega_{ij}\omega_{jk} \ldots \omega_{pq}\omega_{qi} = \exp(i\Theta_\sigma H) \tag{5}$$

where the numerical value of $\Theta_\sigma$ is $(2\pi e S_\sigma / hc)$, in which $S_\sigma$ is the area enclosed by $\pi$ ring $\sigma$. Therefore

$$\omega_{ij}\omega_{jk} \ldots \omega_{pq}\omega_{qi} + \omega_{ji}\omega_{kj} \ldots \omega_{qp}\omega_{iq} = 2\cos(\Theta_\sigma H) \tag{6}$$

The simplest cyclic product is just

$$\omega_{ij}\omega_{ji} = 1 \tag{7}$$

which is independent of the magnetic field.

With eq 6 and 7 in mind, we can easily apply Sachs' graph theoretical theorem[12] to the reduced Hückel secular determinant (eq 3), and obtain a corresponding characteristic polynomial in the form

$$P(X,H) = X^N + \sum_{k=1}^{N} a_k(H) X^{N-k} \tag{8}$$

where

$$a_k(H) = \sum_{t \in T_k} (-1)^{n(t)} \prod_\sigma [2\cos(\Theta_\sigma H)] \tag{9}$$

Here, $N$ is the number of atoms in the entire conjugated system, $T_k$ is a set of all possible Sachs graphs, each containing $k$ atoms, $n(t)$ is the number of components of Sachs graph $t$, and $\sigma$ runs over all $\pi$ rings in the Sachs graph. If there are no $\pi$ rings (as in linear polyenes, for example), all coefficients of $P(X,H)$ are independent of the magnetic field.

The roots of the equation $P(X,H) = 0$ are arranged in decreasing order as

$$X(H) = X_1(H), X_2(H), \ldots, X_{N-1}(H), X_N(H) \tag{10}$$

The first $N/2$ roots represent the energies of the occupied $\pi$ molecular orbitals perturbed by the external magnetic field. The total $\pi$-electron energy of a conjugated system is

$$E_\pi(H) = 2 \sum_{k=1}^{N/2} X_k(H) \tag{11}$$

On the other hand, a characteristic polynomial for an olefinic reference structure,[8-10] which is needed for estimating aromatic stabilization of a conjugated system, can be defined as

$$\begin{aligned} R(X) &= X^N + \sum_{k=1}^{N} \left\{ \sum_{t \in T_k^*} (-1)^{n(t)} \right\} X^{N-k} \\ &= X^N + \sum_{r=1}^{N/2} (-1)^r p(2r) X^{N-2r} \end{aligned} \tag{12}$$

where $T_k^*$ is a set of all possible Sachs graphs, each containing $k$ atoms but no $\pi$ rings, and $p(2r)$ is the number of ways in which $r$ disjoint $\pi$ bonds are chosen from the conjugated system. The roots of the equation $R(X) = 0$ are supposed to represent the energies of the $\pi$ molecular orbitals which the compound would possess if it were absolutely olefinic in nature. Since all contributions of $\pi$ rings in the conjugated system are omitted from the coefficients of $R(X)$, the energy levels of the reference structure are necessarily independent of the magnetic field. This aspect of $R(X)$ is quite consistent with a supposedly olefinic nature of the reference structure. Note that the energy levels of linear polyenes are not field dependent.[6]

For example, $R(X)$ and $P(X,H)$ for azulene are respectively

$$R(X) = X^{10} - 11X^8 + 41X^6 - 61X^4 + 31X^2 - 2 \tag{13}$$

and

$$\begin{aligned} P(X,H) = R(X) &+ 2\cos(\Theta_5 H)\{-X^5 + 4X^3 - 3X\} \\ &+ 2\cos(\Theta_7 H)\{-X^3 + 2X\} - 2\cos[(\Theta_5 + \Theta_7)H] \end{aligned} \tag{14}$$

where $\Theta_5$ and $\Theta_7$ are the $\Theta_\sigma$ values for the five- and seven-membered ring, respectively. Thus, the additional terms which appear in $P(X,H)$ are all dependent on the applied magnetic field.

## The DSE Concept and Aromaticity

Next, let us consider the effect of the magnetic field on the total $\pi$-electron energy of a conjugated system. The total $\pi$-electron energy can be approximated in terms of a characteristic polynomial.[9] In the present case, it is expressed as

$$E_\pi(H) \approx 6.0846 \log |P(i,H)| \tag{15}$$

where $i = \sqrt{-1}$.

The total $\pi$-electron energy of a reference structure can analogously be estimated using the coefficients of $R(X)$, i.e.,

$$E_\pi{}^0 \approx 6.0846 \log |R(i)| \tag{16}$$

The resonance energy of a conjugated system is then given by[9]

$$\begin{aligned} \mathrm{RE}(H) &= E_\pi(H) - E_\pi{}^0 \\ &\approx 6.0846 \{\log |P(i,H)| - \log |R(i)|\} \end{aligned} \tag{17}$$

The values of $|R(i)|$ and $|P(i,H)|$ for azulene are calculated respectively as

$$\begin{aligned} |R(i)| = |i^{10} - 11i^8 + 41i^6 \\ - 61i^4 + 31i^2 - 2| = 147 \end{aligned} \tag{18}$$

and

$$\begin{aligned} |P(i,H)| &= |R(i) + 2\cos(\Theta_5 H)\{-i^5 + 4i^3 - 3i\} \\ &\quad + 2\cos(\Theta_7 H)\{-i^3 + 2i\} - 2\cos[(\Theta_5 + \Theta_7)H]| \\ &= \{\{|R(i)| + 2\cos[(\Theta_5 + \Theta_7)H]\}^2 \\ &\quad + \{16\cos(\Theta_5 H) - 6\cos(\Theta_7 H)\}^2\}^{1/2} \end{aligned} \tag{19}$$

The total change in energy for any applied field can now be visualized by combining such an expression for $P(i,H)$ with eq 15.

Since the applied field $H$ can be treated as a small perturbation, every cosine in $P(X,H)$ has a positive value and can be regarded as a monotonously decreasing function of $H$. Considering that the contribution of every $\pi$ ring in a conjugated system is expressed in the form of eq 6, the role of the external magnetic field is to reduce the contribution of all the $\pi$ rings to the total $\pi$-electron energy. In other words, it is obvious that the applied field makes the total $\pi$-electron energy slightly approach that of its reference structure.

By definition, the diamagnetic susceptibility of a conjugated system (i.e., DSE) is[6,7]

$$\chi_\pi = -\left[\frac{\partial^2}{\partial H^2} E_\pi(H)\right]_{H=0} \tag{20}$$

It can also be interpreted as

$$\chi_\pi = -\left[\frac{\partial^2}{\partial H^2} \mathrm{RE}(H)\right]_{H=0} \tag{21}$$

because the reference energy $E_\pi{}^0$ is not field dependent. The field dependence of the total $\pi$-electron energy near $H = 0$ can be expressed by

$$E_\pi(H) = E_\pi(0) - \frac{1}{2}\chi_\pi H^2 \tag{22}$$

This expression signifies that both the total $\pi$-electron energy and the resonance energy decrease in proportion to the field strength squared. Since an aromatic compound does not have a magnetic moment, the term proportional to $H$ is absent in eq 22. Accordingly,

$$\left[\frac{\partial}{\partial H}\mathrm{RE}(H)\right]_{H=0} = 0 \tag{23}$$

Now, we can verify that the diamagnetic susceptibility of a conjugated system really reflects its aromaticity. It can be seen from a combination of eq 15 with such an expression as eq 19 that the absolute value of the resonance energy monotonously decreases with increasing field strength. According to eq 21 and 22, the change in resonance energy for a given field is proportional to $\chi_\pi$. Since a term proportional to $H$ is missing in eq 22, the sign of $\chi_\pi$ must necessarily agree with that of the resonance energy. One should note that the Dewar-type resonance energy,[13] such as ours,[8-10] is an excellent index of aromaticity. Therefore, this result is in exact agreement with our empirical interpretation of $\chi_\pi$ as an aromaticity index.[2-4] We can now assuredly use the DSE (i.e., $\chi_\pi$) as a definite experimental criterion of aromaticity.

Furthermore, it is suggested from such expressions as eq 19 that, in general, the resonance energy of a more aromatic compound decreases more rapidly as the applied field is intensified. In other words, one may suspect that a compound with a larger resonance energy exhibits a larger susceptibility of the conjugated system. However, this is not always true. Since $\chi_\pi$ is a measure of the response of RE($H$) to $H$ near $H = 0$, it is not directly related to the value of RE(0). The resonance energy is not exactly proportional to $\chi_\pi$. This gives the reason why a linear polyacene has a larger susceptibility than its angulated isomers.[7] For example, the degrees of aromatic stabilization of tetracyclic benzenoid hydrocarbons are in the order[14] triphenylene (0.739) > chrysene (0.688) > benz[*a*]anthracene (0.643) > naphthacene (0.533). Here, the values in parentheses are resonance energies given in units of $\beta$. The susceptibilities of these conjugated systems are in the reverse order. They are 5.272 for triphenylene, 5.741 for chrysene, 5.696 for benz[*a*]anthracene, and 6.139 for naphthacene, all in units of $10^{-17}\beta$.[7] There are many such sets of conjugated systems whose susceptibilities[7] cannot be arranged in order of their resonance energies.[8] However, it goes without saying that the signs of resonance energies of these compounds are in accord with those of the susceptibilities.

## Concluding Remarks

As has been seen above, the diamagnetic susceptibility exaltation was found to reflect the sign of the resonance energy and, to a lesser extent, its magnitude. In any case, the applied magnetic field destabilizes a conjugated system of an aromatic compound, whereas it stabilizes that of an antiaromatic compound. Such a magnetic response is quite analogous to the substituent effect on a conjugated system. The introduction of appropriate substituents stabilizes an antiaromatic compound, but somewhat destabilizes an aromatic compound.[8a,15] On this basis, an aromatic compound might be defined as a conjugated compound which is destabilized by a small perturbation, such as an external magnetic field and an inductive effect of substituents. Bond alternation also tends to stabilize an antiaromatic or less aromatic compound, but somewhat destabilizes a highly aromatic compound. The magnitude of the susceptibility, as well as the resonance energy, is partially quenched if bond alternation occurs.[8,16]

We have considered the London theory of diamagnetism for conjugated hydrocarbons only. When a conjugated system in question has one or more heteroatoms, a reduced Hückel secular determinant in the form of eq 3 must be modified as follows. The off-diagonal matrix element corresponding to each heterobond is replaced by $k\omega_{ij}$, where $k$ is a heterobond parameter of the heterobond. The diagonal matrix element corresponding to each heteroatom is replaced by $(h - X)$, where $h$ is a heteroatom parameter of the heteroatom. The resultant determinant can be expanded into a polynomial in $X$ in the same manner as described previously.[10]

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