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Generalized Graph-theoretical Formula for London Diamagnetism

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Synopsis. The previous graph-theoretical formula for London diamagnetism was improved so as to include all kinds of cyclic conjugated systems. Bicyclo[6.2.0]decapentaene was then found to be diatropic but antiaromatic even though the central π bond was elongated.

Diamagnetic susceptibility due to ring currents is one of the key quantities in aromatic chemistry.[1] In 1937 London formulated it in quantum-mechanical terms,[2,3] so it has been called the London diamagnetism.[1] Recently I reformulated it[4,5] by means of Sachs' graph-theoretical theorem.[6] The obtained formula enabled us to estimate susceptibility contributions from individual π-electron rings in a conjugated system.[5] However, I later found that this formula was applicable only to conjugated hydrocarbons with no bond alternation. In this note, I would like to generalize the graph-theoretical formula for London diamagnetism so as to include not only conjugated hydrocarbons with appreciable bond alternation but also heterocycles.

Let us consider the conjugated system G placed perpendicularly in the external magnetic field H. The ith π-electron ring in G is denoted by $\mathrm{r_i}$, which is identical with the ith ring component in Sachs' theorem.[6,7] The area of $\mathrm{r_i}$ is denoted by $S_{\mathrm{r_i}}$. For simplicity, we define

$$\Theta_{\mathrm{r_i}} = \frac{eS_{\mathrm{r_i}}}{\hbar c}, \tag{1}$$

where e, $\hbar$, and c are the standard constants with these symbols. A characteristic polynomial for G is a function of H, so it is denoted by $P_{\mathrm{G}}(X,H)$.[6,7] When there is no external field, the contribution of $\mathrm{r_i}$ to the coefficients of the characteristic polynomial is given by[7]

$$C(\mathrm{r_i}, 0) = 2\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}. \tag{2}$$

Here, k_{s} is a Hückel bond parameter for the sth π bond in G, and s runs over all π bonds in $\mathrm{r_i}$. If the field H is applied to G, it should become[4,5]

$$C(\mathrm{r_i}, H) = 2\cos(\Theta_{\mathrm{r_i}}H)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}. \tag{3}$$

With this expression in mind and by analogy with Hosoya's way of expanding Hückel secular determinants,[8] $P_{\mathrm{G}}(X,H)$ can be expanded as

$$\begin{aligned} P_{\mathrm{G}}(X,H) &= R_{\mathrm{G}}(X) - 2\sum_{\mathrm{i}}^{\mathrm{G}} R_{\mathrm{G-r_i}}(X)\cos(\Theta_{\mathrm{r_i}}H)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}} \\ &\quad + 2^2\sum_{\mathrm{i<j}}^{\mathrm{G}} R_{\mathrm{G-r_i-r_j}}(X)\cos(\Theta_{\mathrm{r_i}}H)\cos(\Theta_{\mathrm{r_j}}H)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}\prod_{\mathrm{s}}^{\mathrm{r_j}} k_{\mathrm{s}} \\ &\quad - \dots . \end{aligned} \tag{4}$$

Here, $R_{\mathrm{G}}(X)$ is a reference polynomial defined for G, *i.e.*, a characteristic polynomial for the olefinic reference structure of G;[5,6,9] G-$\mathrm{r_i}$ is a subgraph of G, obtained by deleting $\mathrm{r_i}$ and all π bonds adjacent to it; G-$\mathrm{r_i}$-$\mathrm{r_j}$ is a subgraph of G, obtained by deleting a pair of disjoint π-electron rings $\mathrm{r_i}$ and $\mathrm{r_j}$ and all π bonds adjacent to $\mathrm{r_i}$ and/or $\mathrm{r_j}$; the first summation is practiced over all π-electron rings, and the second one over all possible pairs of disjoint π-electron rings.

Since the applied field H can be treated as a small perturbation,

$$\cos(\Theta_{\mathrm{r_i}}H) \approx 1 - \frac{1}{2}\Theta_{\mathrm{r_i}}{}^2H^2. \tag{5}$$

By applying this approximation to Eq. 4, the following expression can be derived:

$$\begin{aligned} P_{\mathrm{G}}(X,H) &= R_{\mathrm{G}}(X) - 2\sum_{\mathrm{i}}^{\mathrm{G}} R_{\mathrm{G-r_i}}(X)\left(1-\frac{1}{2}\Theta_{\mathrm{r_i}}{}^2H^2\right)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}} \\ &\quad + 2^2\sum_{\mathrm{i<j}}^{\mathrm{G}} R_{\mathrm{G-r_i-r_j}}(X)\left(1-\frac{1}{2}\Theta_{\mathrm{r_i}}{}^2H^2\right)\left(1-\frac{1}{2}\Theta_{\mathrm{r_j}}{}^2H^2\right) \\ &\quad \times \prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}\prod_{\mathrm{s}}^{\mathrm{r_j}} k_{\mathrm{s}} - \dots \\ &= P_{\mathrm{G}}(X,0) + H^2\sum_{\mathrm{i}}^{\mathrm{G}} P_{\mathrm{G-r_i}}(X,0)\,\Theta_{\mathrm{r_i}}{}^2\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}. \end{aligned} \tag{6}$$

In deriving the last expression, we used the relationship in this form:

$$\begin{aligned} P_{\mathrm{G}}(X,0) &= R_{\mathrm{G}}(X) - 2\sum_{\mathrm{i}}^{\mathrm{G}} R_{\mathrm{G-r_i}}(X)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}} \\ &\quad + 2^2\sum_{\mathrm{i<j}}^{\mathrm{G}} R_{\mathrm{G-r_i-r_j}}(X)\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}\prod_{\mathrm{s}}^{\mathrm{r_j}} k_{\mathrm{s}} - \dots . \end{aligned} \tag{7}$$

This is nothing other than a generalized form of Hosoya's formula for obtaining $P_{\mathrm{G}}(X,0)$.[8]

After a simple treatment of Eq. 6, analogous to that presented in Ref. 5, the diamagnetic susceptibility attributable to the mth orbital is given by

$$\chi_{\mathrm{m}} = -2\beta\sum_{\mathrm{i}}^{\mathrm{G}} \frac{P_{\mathrm{G-r_i}}(X_{\mathrm{m}}^{\circ},0)}{P_{\mathrm{G}}'(X_{\mathrm{m}}^{\circ},0)}\,\Theta_{\mathrm{r_i}}{}^2\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}, \tag{8}$$

where X_{m}° is the mth largest root of the equation $P_{\mathrm{G}}(X,0)=0$. Then, the overall susceptibility due to ring currents is

$$\chi = 2\sum_{\mathrm{m=1}}^{\mathrm{m_0}} \chi_{\mathrm{m}}. \tag{9}$$

Here, $\mathrm{m_0}$ indicates the highest occupied orbital. Unfortunately, Eq. 8 does not hold for degenerate orbitals. In this case, $P_{\mathrm{G}}(X,0)$ is rewritten as

$$P_{\mathrm{G}}(X,0) = U_{\mathrm{G}}(X)(X-X_{\mathrm{m}^*}{}^{\circ})^2, \tag{10}$$

where m* indicates the degenerate orbitals. According to the mathematical treatment similar to that of Pullman and Pullman,[3] the diamagnetic susceptibility attributable to each of these orbitals becomes

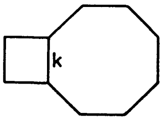
$$\chi_{\mathrm{m}^*} = \frac{U_{\mathrm{G}}'(X_{\mathrm{m}^*}{}^{\circ})V_{\mathrm{G}}(X_{\mathrm{m}^*}{}^{\circ}) - U_{\mathrm{G}}(X_{\mathrm{m}^*}{}^{\circ})V_{\mathrm{G}}'(X_{\mathrm{m}^*}{}^{\circ})}{U_{\mathrm{G}}(X_{\mathrm{m}^*}{}^{\circ})^2}, \tag{11}$$

where

$$V_{\mathrm{G}}(X) = \sum_{\mathrm{i}}^{\mathrm{G}} P_{\mathrm{G-r_i}}(X,0)\,\Theta_{\mathrm{r_i}}{}^2\prod_{\mathrm{s}}^{\mathrm{r_i}} k_{\mathrm{s}}. \tag{12}$$

Now the graph-theoretical formulation of London diamagnetism has been completed. We can easily evaluate the susceptibility of any cyclic conjugated system by means of these expressions, but without any knowledge of graph theory. They are really applicable to any kind of conjugated systems, including heterocycles.

As an example, it is instructive to calculate the susceptibility of the bicyclo[6.2.0]decapentaene conjugated system (I). Oda *et al.* showed that this compound has relatively small alternation of the peripheral π bonds and a rather elongated central π bond.10) Therefore, the susceptibility was calculated as a function of the bond parameter of the central π bond (k). The susceptibilities obtained according to Eq. 8 are 0.352 for $k=1.00$, 0.422 for $k=0.90$, 0.478 for $k=0.80$, 0.523 for $k=0.70$, 0.559 for $k=0.60$, and 0.587 for $k=0.50$, all in units of $\Theta_0{}^2\beta$. Here, Θ_0 is $e/\hbar c$, multiplied by the area of the benzene ring, and $\beta=|\beta|$. In this connection, the resonance energies due to aromatic stabilization9) are -0.642 for $k=1.00$, -0.509 for $k=0.90$, -0.396 for $k=0.80$, -0.298 for $k=0.70$, -0.212 for $k=0.60$, and -0.137 for $k=0.50$, all in units of β. These results clearly indicate that the bicyclo[6.2.0]decapentaene conjugated system is diamagnetic but antiaromatic in nature. This conclusion is independent of the magnitude of the k value. Therefore, we might say that this compound is a diatropic antiaromatic compound. Diatropicity has been supported by experiment.10) It is noteworthy that diatropicity and antiaromaticity coexist in such a bicyclic conjugated system.



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References

1) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, "Nonbenzenoid Aromatics," ed by J. P. Snyder, New York, N. Y. (1971), Vol. II, Chap. 3.

2) F. London, *J. Phys. Radium*, **8**, 397 (1937).

3) B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie Organique," Masson et Cie, Paris (1952), Chap. 9.

4) J. Aihara, *J. Am. Chem. Soc.*, **101**, 558 (1979).

5) J. Aihara, *J. Am. Chem. Soc.*, **101**, 5913 (1979).

6) H. Sachs, *Publ. Math.* (*Debrecen*), **11**, 119 (1964); A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta*, **26**, 67 (1972).

7) J. Aihara, *J. Am. Chem. Soc.*, **98**, 6840 (1976).

8) H. Hosoya, *Theor. Chim. Acta*, **25**, 215 (1972).

9) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976); I. Gutman, M. Milun, and N. Trinajstić, *ibid.*, **99**, 1692 (1977).

10) C. Kabuto and M. Oda, *Tetrahedron Lett.*, **1980**, 103; M. Oda and H. Oikawa, *ibid.*, **1980**, 107.