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How Do Proton Chemical Shifts Reflect Aromaticity ? Graph Theory of the Secondary Magnetic Field Due to Ring Currents

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A secular determinant for a polycyclic conjugated molecule, combined with a test dipole, is definable as a function of the applied magnetic field. It was found that this determinant can be expanded graph-theoretically into a characteristic polynomial. A secondary magnetic field is brought about by so-called ring currents. A new formula for evaluating the secondary field was derived by applying Newton's method to this polynomial. This formula indicates that the secondary field at any point in the molecular plane is given exactly as a sum of the contributions of all π-electron circuits. The contribution of each π-electron circuit is expressible in terms of a pure geometric factor and an aromatic stabilization energy assigned to the circuit. The secondary field and then the proton chemical shifts can thus be related to aromaticities of individual π-electron circuits. Magnetotropism of most polycyclic conjugated molecules can be rationalized in this manner. π-Electron circuits which share the conjugated atom nearest to a given proton dominate the chemical shift. In general, a peripheral π-electron circuit contributes modestly to the overall thermodynamic stability of a molecule, but contributes much to the secondary fields at attached protons.

It is well-known that ring currents are induced in an aromatic hydrocarbon on application of an external magnetic field.[1,2] Ring currents are equivalent to magnetic shells, and the field at an attached proton consequently differs from the applied field owing to the resultant secondary field.[3-6] A significant part of the deshielding of aromatic protons is presumed to be due to ring current effects.[3-7] The deshielding can be estimated from what we call proton chemical shifts, i.e., shifts in the magnetic resonance peaks of the protons.[6]

In 1958, the secondary magnetic field was formulated independently by Pople and McWeeny within the Hückel framework.[4-6,8,9] The problem of finding a secondary field differs somewhat from that of finding London susceptibility, i.e., magnetic susceptibility associated with ring currents.[2] Pople managed to expand London's field-dependent secular determinant[2] into a characteristic polynomial, and solved the problem.[4] McWeeny introduced an infinitesimal test dipole into an aromatic molecule placed in the magnetic field, and evaluated the coupling energy between the dipole and the induced current distribution in the molecule.[5,6,8,9] The secondary field experienced by the dipole was obtainable from it. McWeeny employed the perturbational technique of Coulson and Longuet-Higgins[10] to derive the secondary field.

In 1979 Sachs' graph theory[11-14] proved very useful for expanding the field-dependent secular determinant for an aromatic molecule straightforwardly into a characteristic polynomial. We succeeded in devising the graph-theoretical formulas of London susceptibility and ring currents for cyclic conjugated systems.[15-26] Our graph-theoretical formula of London susceptibility established the existence of a distinct relationship between aromatic stabilization and diamagnetic susceptibility exaltation.[15,20,21] Diamagnetic susceptibility exaltation is an experimental manifestation of London susceptibility.

Sachs' graph theory[11-14] can likewise be used to formulate the secondary magnetic field experienced by the test dipole in a polycyclic aromatic molecule. McWeeny's secular determinant for such a system[5] can be expanded graph-theoretically into the characteristic polynomial. The secondary field at any proton can then be deduced without using any complicated perturbational technique. In this paper we present the graph-theoretical formulas thus obtained for ring currents and secondary fields. They are expressed in terms of pure geometric factors and circuit currents[24,25] or circuit resonance energies.[20,21] As will be seen, this kind of formulation is very useful for answering the question as to why and how proton chemical shifts reflect aromatic stabilization of a cyclic conjugated system.

General Terminology and Notation

Some unfamiliar terms and symbols are surveyed beforehand. A given conjugated molecule is denoted by G, which is assumed to have N conjugated atoms. In this paper, we deal only with cyclic conjugated molecules. If G is cyclic in geometry, one or more cyclic paths can be chosen from it. Such cyclic paths are termed π-electron circuits,[25,27] which are identical with ring components in Sachs' graph theory.[11-14] All possible cyclic paths in G constitute an entire set of π-electron circuits. The tth π-electron circuit is denoted by r_t. For example, seven π-electron circuits can be chosen from the acenaphthylene conjugated system. They are two six-membered, one five-membered, one ten-membered, and two nine-membered circuits, together with one eleven-membered peripheral circuit. $G-r_t$ represents the subsystem of G, obtained by deleting from G the tth π-electron circuit and all π bonds incident to it.[11-14]

Some geometric factors are then defined to characterize the individual π-electron circuits. The origin of the coordinates is usually set at the point in the molecular plane where the secondary magnetic field is to be evaluated. The signed area of the triangle formed by the origin and the i-j π bond is denoted by s_{ij}. It is counted positive if i→j is right-handed about the unit vector normal to the molecular plane.[2,4–6] Then, the following two quantities, S_t and F_t, are defined for the tth π-electron circuit:

$$S_t = \sum_{(ij)}^{r_t} s_{ij} \tag{1}$$

$$F_t = \sum_{(ij)}^{r_t} s_{ij} f_{ij} \tag{2}$$

Here, (ij) stands for the i-j π bond. It runs over all π bonds forming the tth π-electron circuit. The absolute value of S_t is equal to the area of the tth π-electron circuit.[2,4–6] f_{ij} is defined for (ij) as follows:

$$f_{ij} = \frac{1}{d_i^3} + \frac{1}{d_j^3}, \tag{3}$$

where d_i and d_j are the distances of atoms i and j, respectively, from the origin.

The polynomial obtained by expanding the Hückel secular determinant for G is termed the characteristic polynomial for G. This polynomial is denoted by $P_G(X, B)$ because the coefficients in it depend upon the applied magnetic field B. $P_{G\text{-}r_t}(X, B)$ represents a characteristic polynomial for $G-r_t$. Roots of the equation $P_G(X, B)=0$ represent the energies of N π-electron molecular orbitals in G. They are given relative to α, in units of β, where α and β are the standard Coulomb and resonance integrals, respectively.

When the external magnetic field is absent, the resonance integral for the i-j π bond is expressed in the form:

$$\beta_{ij}^{\circ} = k_{ij}\beta, \tag{4}$$

where k_{ij} is the resonance integral parameter which depends upon the bond type and bond order. The wth largest root of the equation $P_G(X,0)=0$, i.e., the energy of the wth π-electron molecular orbital in the absence of the external field is denoted by X_w. The number of π-electrons present in the wth molecular orbital is denoted by g_w. $Q_{G\text{-}r_t}(X)$ is defined by[25]

$$Q_{G-r_t}(X) = \frac{P_{G-r_t}(X,0)}{P_G'(X,0)} \prod_{(ij)}^{r_t} k_{ij}, \tag{5}$$

where (ij) runs over all π bonds forming the tth π-electron circuit. $P_G'(X,0)$ is the first derivative of $P_G(X,0)$ with respect to X. Finally, e, c, $\hbar$, and μ_0 are the standard constants with these symbols.

Graph-Theoretical Formulation of the Secondary Magnetic Field

The strength of the secondary magnetic field due to ring currents was formulated in the following manner. A given cyclic conjugated molecule G is placed in the magnetic field **B**, which is assumed to be perpendicular to the molecular plane, i.e., $\mathbf{B}=B\mathbf{n}$, where $\mathbf{n}$ is the unit vector normal to the molecular plane. An infinitesimal test dipole of moment $\mathbf{m}=m\mathbf{n}$ is introduced at a given point in the plane of G, this point being chosen as origin of the coordinates. The entire system now consists of the molecule G and the test dipole D. The resonance integral for the i-j π bond becomes[5,6]

$$\beta_{ij} = \beta_{ij}^{\circ} \exp\left[\frac{ies_{ij}}{\hbar}\left(B+\frac{\mu_0 m}{4\pi}f_{ij}\right)\right]. \tag{6}$$

It is to be noted that Eq. 6 represent the general form of off-diagonal elements of the secular determinant for this complex system. The diagonal elements remain the same as those of the secular determinant for the conjugated molecule alone.[2,6,15] Such a secular determinant can be expanded into a characteristic polynomial without difficulty.

As in the case of the system with no test dipole,[15,21] Sachs' graph theory[11–14] is applicable, and every coefficient in the polynomial is expressed as a combination of cyclic products of resonance integrals. Such cyclic products can be classified into two groups. The first group consists of cyclic products of two resonance integrals associated with individual π bonds. They take the general form $\beta_{ij}\beta_{ji}$, which in this case is associated with the i-j π bond. The second group consists of cyclic products of more than two resonance integrals associated with individual π-electron circuits. They take the general form $\beta_{op}\beta_{pq}\cdots\beta_{uv}\beta_{vo}$, which in this case is associated with a π-electron circuit formed by atoms o, p, q, ⋯, u, and v. This indicates that if one or more π-electron circuits can be chosen from the molecule, there always are cyclic products of more than two resonance integrals corresponding to them all.

The following two relationships can be deduced with regard to these cyclic poducts of resonance integrals:

$$\begin{aligned}\beta_{ij}\beta_{ji} &= \beta_{ij}^{\circ}\beta_{ji}^{\circ}\\ &= k_{ij}^2\beta^2\end{aligned} \tag{7}$$

$$\begin{aligned}&\beta_{op}\beta_{pq}\cdots\beta_{uv}\beta_{vo} + \beta_{ov}\beta_{vu}\cdots\beta_{qp}\beta_{po}\\ &= 2\beta_{op}^{\circ}\beta_{pq}^{\circ}\cdots\beta_{uv}^{\circ}\beta_{vo}^{\circ}\cos\left[\frac{e}{\hbar}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)\right]\\ &= 2k_{op}k_{pq}\cdots k_{uv}k_{vo}\beta^{z_t}\cos\left[\frac{e}{\hbar}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)\right].\end{aligned} \tag{8}$$

Here, z_t is the number of atoms constituting the tth π-electron circuit. Since the applied field and the test dipole can be treated as small perturbations, Eq. 8 can be approximated to:

$$\begin{aligned}&\beta_{op}\beta_{pq}\cdots\beta_{uv}\beta_{vo} + \beta_{ov}\beta_{vu}\cdots\beta_{qp}\beta_{po}\\ &= 2k_{op}k_{pq}\cdots k_{uv}k_{vo}\beta^{z_t}\left[1-\frac{e^2}{2\hbar^2}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)^2\right].\end{aligned} \tag{9}$$

We have previously investigated the magnetic response of a conjugated molecule, not combined with a test dipole.[15–26] In this case, Eq. 7 remains unchanged, but the value of m in Eqs. 8 and 9 vanishes, so that

$$\begin{aligned}&\beta_{\mathrm{op}}\beta_{\mathrm{pq}}\cdots\beta_{\mathrm{uv}}\beta_{\mathrm{vo}}+\beta_{\mathrm{ov}}\beta_{\mathrm{vu}}\cdots\beta_{\mathrm{qp}}\beta_{\mathrm{po}}\\&=2k_{\mathrm{op}}k_{\mathrm{pq}}\cdots k_{\mathrm{uv}}k_{\mathrm{vo}}\beta^{z_t}\left[1-\frac{e^2}{2\hbar^2}(BS_t)^2\right].\end{aligned}\tag{10}$$

A characteristic polynomial for the molecule alone is expressed in the form:[15,16,19]

$$P_{\mathrm{G}}(X,B)=P_{\mathrm{G}}(X,0)+\frac{e^2}{\hbar^2}\sum_t^{\mathrm{G}}(BS_t)^2P_{\mathrm{G}-\mathrm{r}_t}(X,0)\prod_{(\mathrm{ij})}^{\mathrm{r}_t}k_{\mathrm{ij}}.\tag{11}$$

It is noteworthy that Eq. 9 can be derived formally by replacing BS_t in Eq. 10 by $BS_t+(\mu_0 m/4\pi)F_t$. This indicates that the characteristic polynomial for the present system can likewise be derived by replacing BS_t in Eq. 11 by $BS_t+(\mu_0 m/4\pi)F_t$:

$$\begin{aligned}P_{\mathrm{G+D}}(X,B)&=P_{\mathrm{G}}(X,0)\\&+\frac{e^2}{\hbar^2}\sum_t^{\mathrm{G}}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)^2P_{\mathrm{G}-\mathrm{r}_t}(X,0)\prod_{(\mathrm{ij})}^{\mathrm{r}_t}k_{\mathrm{ij}},\end{aligned}\tag{12}$$

where G+D stands for the whole system consisting of the molecule G and the test dipole D.

By solving the equation $P_{\mathrm{G+D}}(X,B)=0$ by means of the Newton method, energies of the π-electron molecular orbitals in the whole system can be obtained, each as a function of the field strength B. When there are no degenerate orbitals in G, the energy of the wth π-electron molecular orbital is given in the form:

$$\begin{aligned}\varepsilon_w(B)&=\alpha+X_w(B)\beta\\&=\alpha+\beta\left[X_w^\circ-\frac{e^2}{\hbar^2}\sum_t^{\mathrm{G}}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)^2Q_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ)\right].\end{aligned}\tag{13}$$

Here, $X_w(B)$ is the wth largest root of the equation $P_{\mathrm{G+D}}(X,B)=0$. If there are degenerate orbitals in G, $X_w(B)$ for them must be evaluated by the procedure described in Refs. 16 and 22.

Toal π-electron energy of the whole system becomes

$$\begin{aligned}E_{\mathrm{G+D}}(B)&=\sum_{w=1}^{\mathrm{N}}g_w\varepsilon_w(B)\\&=\sum_{w=1}^{\mathrm{N}}g_w\left\{\alpha+\beta\left[X_w^\circ-\frac{e^2}{\hbar^2}\sum_t^{\mathrm{G}}\left(BS_t+\frac{\mu_0 m}{4\pi}F_t\right)^2Q_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ)\right]\right\},\end{aligned}\tag{14}$$

where g_w is the occupation number for the wth orbital.

It is readily seen that Eq. 14 contains the term linear in m. This term represents the coupling energy between the test dipole and the secondary magnetic field.[5,6] Therefore, it can be identified with $-mB'$, where B' is the secondary field at the position where the test dipole is placed. Then, the strength of the secondary magnetic field is given by

$$\begin{aligned}B'&=-\left[\frac{\partial}{\partial m}E_{\mathrm{G+D}}(B)\right]_{m=0}\\&=\frac{\mu_0 e^2B}{2\pi\hbar^2}\beta\sum_t^{\mathrm{G}}F_tS_t\sum_{w=1}^{\mathrm{N}}g_wQ_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ),\end{aligned}\tag{15}$$

This graph-theoretical formula is in marked contrast to McWeeny's one expressed in terms of imaginary bond-bond polarizabilities,[5,6] and had an advantage in that the secondary field can be related to the molecular geometry straightforwardly.

We have previously shown that London susceptibility and ring currents can both be partitioned exactly among the constituent π-electron circuits.[16,19–26] Equation 15 clearly indicates that the secondary field can also be partitioned among the π-electron circuits. This is expressed explicitly as

$$B'=\sum_t^{\mathrm{G}}\gamma_t,\tag{16}$$

where γ_t stands for the contribution of the tth π-electron circuit:

$$\gamma_t=\frac{\mu_0 e^2B}{2\pi\hbar^2}\beta F_tS_t\sum_{w=1}^{\mathrm{N}}g_wQ_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ).\tag{17}$$

As shown previously,[24,25] a bond current, i.e., a ring current flowing through a given π bond, is expressed as a sum of the contributions of π-electron circuits sharing the very π bond in common. The current contribution of the tth π-electron circuit is called the tth circuit current, which is given by[24,25]

$$\begin{aligned}I_t&=-\frac{2e^2B}{\hbar^2}\beta S_t\sum_{w=1}^{\mathrm{N}}g_wQ_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ)\\&=\frac{9I_0S_t}{S_0}\sum_{w=1}^{\mathrm{N}}g_wQ_{\mathrm{G}-\mathrm{r}_t}(X_w^\circ),\end{aligned}\tag{18}$$

where I_0 is the bond current induced in benzene under the same experimental condition, and S_0 is the area of the benzene ring. Using this expression for circuit currents, Eq. 15 is rewritten as

$$B'=\frac{\mu_0}{4\pi}\sum_t^{\mathrm{G}}I_tF_t.\tag{19}$$

The secondary field thus is a function of not only all circuit currents in G but also all F_t values. The quantity F_t is purely geometric in nature, depending merely upon the shape and the location of the tth π-electron circuit with respect to the origin, i.e., the position where the secondary field is evaluated.

In 1958, McWeeny derived the formula similar to, but not the same as, Eq. 19.[5,6,28–30] It is expressed analogously as

$$B'=\frac{\mu_0}{4\pi}\sum_{t'}^{\mathrm{G}}\bar{I}_{t'}\bar{F}_{t'},\tag{20}$$

where t' runs over all rings in G, but not over π-electron circuits, $\bar{I}_{t'}$ is the current contribution of the tth ring, and $\bar{F}_{t'}$ is the quantity analogous to $F_{t'}$, but defined for the t'th ring. Here, the term "ring" has the usual meaning in chemistry. It is used in such a manner that the acenaphthylene conjugated system consists of one five-membered and two six-membered rings. It is worth noting that Eqs. 19 and 20 represent two different physical aspects of the secondary field. Both ring currents and secondary fields can thus be partitioned not only among the constituent rings but also among the π-electron circuits.

Relationship between the Secondary Field and Aromaticity

We have developed the graph theory of aromaticity, in which the resonance energy arising from cyclic π-electron conjugation is defined graph-theoretically.[13,21,31,32] This type of resonance energy, $\mathrm{RE_G}$, has ben recognized as a reasonable index for determining the degree of aromatic stabilization. In 1981, we found that the resonance energy can be estimated as[20,21]

$$\mathrm{RE_G} \approx \sum_{t}^{\mathrm{G}} \rho_t, \tag{21}$$

where t runs over all π-electron circuits in G, and

$$\rho_t = -\,2\beta \sum_{w=1}^{\mathrm{N}} g_w Q_{\mathrm{G}-r_t}(X_w^\circ). \tag{22}$$

The quantity denoted by ρ_t can obviously be attributed to the tth π-electron circuit, and can be interpreted as a contribution of the tth π-electron circuit to the overall resonance energy, which we term the tth circuit resonance energy. The same quantity has previously been called the tth ring resonance energy.[20,21] Thus, the resonance energy can be partitioned among the π-electron circuits. In other words, the overall resonance energy is given approximately by adding up all the circuit resonance energies defined by Eq. 22. In general, circuit resonance energy is positive for $(4n+2)$-membered carbocyclic circuits, and negative for $(4n)$-membered carbocyclic circuits.[25,27]

By the use of Eq. 22, Eq. 15 can be rewritten as

$$B' = -\,\frac{\mu_0 e^2 B}{4\pi\hbar^2} \sum_{t}^{\mathrm{G}} A_t \rho_t, \tag{23}$$

where A_t is the pure geometric factor defined by $F_t S_t$. This expression is nothing other than what we wanted to derive in this paper. It clearly shows that the secondary field at any position is associated with the resonance energy or the extra thermodynamic stability due to aromaticity. Exactly speaking, the secondary field reflects not only all geometric factors denoted by A_t but also all circuit resonance energies. Both quantities are mathematically independent to each other within a Hückel framework.

Unfortunately, the interrelation between the resonance energy and the secondary field is never straightforward. As shown in Eq. 23, the secondary field is a function of all A_t values and all circuit resonance energies. If all A_t values were equal, B' would be proportional to the overall resonance energy. However, such a situation never occurs. Therefore, the secondary field cannot be predicted easily from the resonance energy and the molecular geometry.

Every A_t value is strongly dependent upon the distance from the origin and the shape of the π-electron circuit. Since the value of A_t is large for nearby π-electron circuits, it is quite possible that for many condensed aromatic hydrocarbons the secondary field is dominated primarily by the π-electron circuits which share the carbon nearest to the origin, i.e., the carbon to which a given proton is attached.

In a previous paper,[25] we proved that $(4n+2)$-membered circuits are diatropic in nature while $(4n)$-membered circuits are paratropic in nature. In the case of alternant hydrocarbons, smaller $(4n+2)$- and $(4n)$-membered circuits sustain stronger diamagnetic and paramagnetic currents, respectively. Therefore, if one or more $(4n+2)$-membered circuits can be chosen from a given conjugated hydrocarbon, in such a manner that they contain the carbon nearest to the origin, a proton at the origin will exhibit a downfield shift in the NMR spectrum. However, if one or more $(4n)$-membered circuits can also be chosen in the same manner, a downfield shift will be suppressed to some extent, or a net upfield shift will sometimes occur. This constitutes the very reason why typical aromatic compounds exhibit large downfield shifts of the constituent protons. There are no $(4n)$-membered circuits in catacondensed benzenoid hydrocarbons, so all protons necessarily exhibit downfield shifts.

Benzene is monocyclic in geometry, so only one π-electron circuit can be chosen from the conjugated system. The circuit resonance energy defined by Eq. 22 is $-2/9\beta$ or -0.2222β for it. The value of A_t is -5.28731×10^{-10} m at any benzene proton. Accordingly, using the strength of the secondary field at benzene protons, B_0, Eq. 23 is rewritten as

$$B' = -\,0.85110 \times 10^{10} B_0 \sum_{t}^{\mathrm{G}} A_t \rho_t, \tag{24}$$

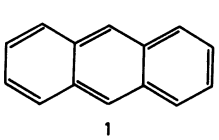
where

$$B_0 = -\,9.3500 \times 10^{-12} \frac{\mu_0 e^2 B}{\hbar^2}. \tag{25}$$

We will use Eq. 24 in what follows.

Secondary Fields in Anthracene

Anthracene **1** and dicycloocta[1,2,3,4-*def*: 1′,2′,3′,4′-*jkl*]biphenylene **2** illustrate the utility of the above



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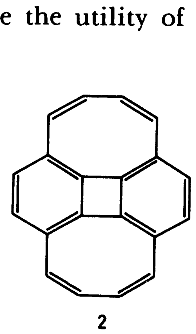

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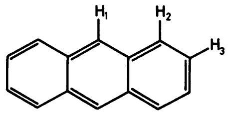
Table 1. Secondary Fields and Related Quantities for Anthracene **1**



$t^{a)}$	$I_t/I_o$$^{b)}$	$\rho_t/(-\beta)$$^{c)}$	$A_t/10^{-10}\,\mathrm{m}$$^{d)}$	$\gamma_t/B_o$$^{e)}$
		Proton 1		
1	0.3550	0.07889	−1.0395	0.0698
2	0.3617	0.08038	−5.2873	0.3617
3	0.3550	0.07889	−1.0395	0.0698
4	0.3125	0.03472	−12.6536	0.3739
5	0.3125	0.03472	−12.6536	0.3739
6	0.2478	0.01836	−22.0990	0.3453
		Proton 2		
1	0.3550	0.07889	−0.2461	0.0165
2	0.3617	0.08038	−1.0395	0.0711
3	0.3550	0.07889	−5.2873	0.3550
4	0.3125	0.03472	−2.5712	0.0760
5	0.3125	0.03472	−12.6536	0.3739
6	0.2478	0.01836	−19.7187	0.3081
		Proton 3		
1	0.3550	0.07889	−0.1045	0.0070
2	0.3617	0.08038	−0.3747	0.0256
3	0.3550	0.07889	−5.2873	0.3550
4	0.3125	0.03472	−0.9584	0.0283
5	0.3125	0.03472	−11.3241	0.3346
6	0.2478	0.01836	−17.2996	0.2703

a) Circuit number. b) Circuit current defined by Eq. 9. c) Circuit resonance energy defined by Eq. 13. d) Geometric factor defined in Eq. 14. e) Contribution to the secondary field, defined by Eq. 8.

theory. In general, calculated magnetic properties are often very sensitive to the degree of sophistication of the molecular orbital (MO) method for computing them.[33] The MO model employed here is an iterative $\beta\omega'\omega''$ method,[34,35] which is a kind of self-consistent Hückel method. This method has successfully been applied to many conjugated hydrocarbons.[33–37] Compounds **1** and **2** are both alternant hydrocarbons in the neutral state, so all Coulomb integrals remain unchanged by application of this method. Resonance integrals are all functions of the bond order. The resonance integral parameter employed is of the form:[25]

$$k_{ij} = \exp\,(0.6327p_{ij} - 0.4218), \tag{26}$$

where p_{ij} is the bond order for the i-j π bond. MO calculations were iterated until resonance integrals were made self-consistent with the corresponding bond orders.

Anthracene **1** is a typical catacondensed aromatic hydrocarbon. Three rings in it are assumed to be regular hexagons with all edge lengths equal to the carbon-carbon bond lengths of benzene (139.65 pm).[38] All carbon-hydrogen bond lengths are set equal to 108.5 pm.[38] There are three non-identical protons and six π-electron circuits in the conjugated system. They are numbered as shown in Table 1 and Fig. 1. Positions of all non-identical protons were succesively taken as origin of the coodinates, and the secondary fields and related quantities were calculated using Eqs. 15—25. All the numerical results are presented in Table 1 and Fig. 3.

As shown in Table 1, all π-electron circuits in anthracene contribute to the increase in the secondary field at any proton. This corresponds to the fact that they are all $(4n+2)$-membered circuits. It is clear that not all π-electron circuits contribute much to the secondary field at a given proton. In general, each π-electron circuit contributes much to the secondary fields at the protons located around it.

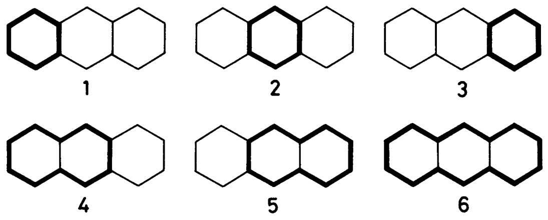


Fig. 1. π-Electron circuits in anthracene **1**.

Proton 1 in anthracene is predicted to suffer the secondary field of 1.594 B_o, which is comparable to the value obtained by the simple Hückel method, 1.707 B_o.[38] This indicates that this proton must exhibit a fairly large downfield shift in the NMR spectrum as long as local anisotropic effects[7] are not very unusual. π-Electron circuits 2, 4, 5, and 6 contribute almost equally to the secondary field although the circuit resonance energy decreases in this order. The decrease in the circuit resonance energy is obviously compensated by the increase in the geometric factor. These π-electron circuits share the carbon atom to which proton 1 is attached. The contribution of the peripheral π-electron circuit is far from negligible owing to the very large geometric factor.

π-Electron circuits which do not share the carbon nearest to proton 1 have much smaller geometric factors than those of circuits 2, 4, 5, and 6. Therefore, they contribute much less to the secondary field at proton 1. It is in marked contrast to the overall resonance energy, which is determined primarily by smaller π-electron circuits. Therefore, it is obvious that the relationship between the overall resonance energy and the secondary field is considerably obscured by the geometric factors which are unrelated to the thermodynamic stability. This supports Mallion's view that

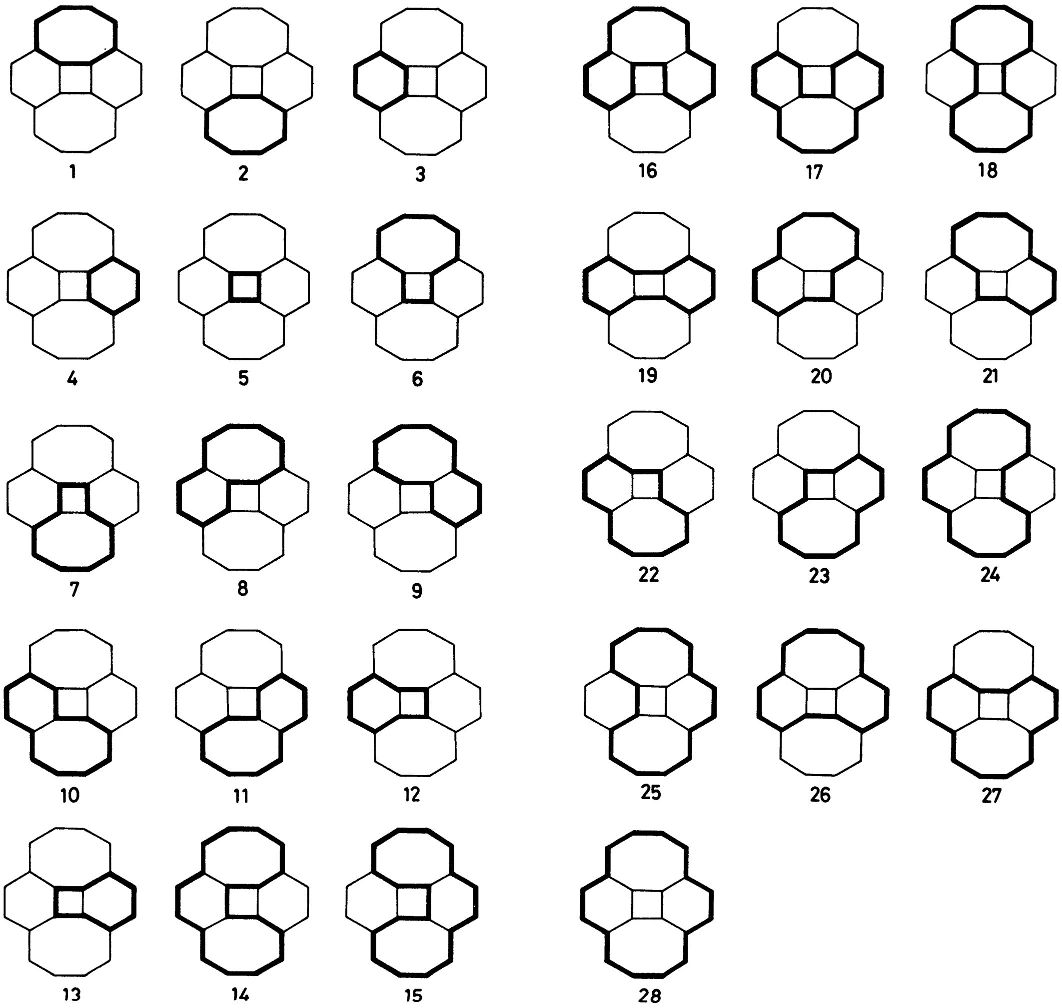


Fig. 2. π-Electron circuits in dicyclooctabiphenylene 2.

the graph-theoretical and geometric contributions to ring-current intensities are disentangled.[9]

The situation is essentially the same for protons 2 and 3. Protons 2 and 3 are predicted to suffer the secondary fields of 1.201 B_0 and 1.021 B_0, respectively. They are also comparable to the values calculated by the simple Hückel method, 1.387 B_0 at proton 2 and 1.197 B_0 at proton 3.[38] π-Electron circuits which share the carbon atom nearest to each of these protons again contribute primarily to the secondary field.

Every circuit current is proportional to the circuit area and the circuit resonance energy defined by Eq. 22. Thus, it is not influenced by the value of A_i, and independent of the distance from the origin.

Haigh et al. obtained the following regression line between experimental proton chemical shifts and the corresponding B'/B_0 ratios for a number of condensed benzenoid hydrocarbons:[38]

$$\delta = 5.66 + 1.56\frac{B'}{B_0} \tag{27}$$

This is based on the secondary fields calculated by the simple Hückel method. The regression line has not been obtained with the fields calculated by the iterative $\beta\omega'\omega''$ method, but Eq. 27 is not too bad to predict the proton chemical shifts from them. Protons 1, 2, and 3

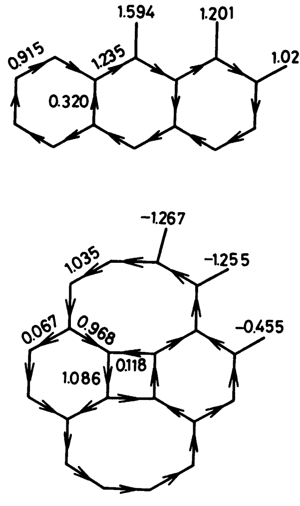
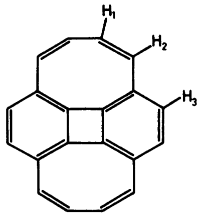


Fig. 3. Bond currents in units of I_0 and secondary magnetic fields in units of B_0: anthracene (upper) and dicyclooctabiphenylene (lower).

Table 2. Secondary Fields and Related Quantities for Dicyclooctabiphenylene **2**



t[a)]	I_t/I_o[b)]	$\rho_t/(-\beta)$[c)]	$A_t/10^{-10}\,\mathrm{m}$[d)]	γ_t/B_o[e)]
		Proton 1		
1	−0.1937	−0.02432	−10.7103	−0.2217
2	−0.1937	−0.02432	−0.3989	−0.0083
3	1.2461	0.27692	−0.2364	0.0557
4	1.2461	0.27692	−0.4605	0.1085
5	−0.1829	−0.10560	−0.0522	−0.0047
6	0.0946	0.00976	−13.3320	0.1107
7	0.0946	0.00976	−0.7781	0.0065
8	−0.2155	−0.01729	−17.4168	−0.2563
9	−0.2155	−0.01729	−18.0374	−0.2654
10	−0.2155	−0.01729	−1.2791	−0.0188
11	−0.2155	−0.01729	−1.8997	−0.0280
12	−0.2463	−0.03952	−0.5154	−0.0173
13	−0.2463	−0.03952	−0.8257	−0.0278
14	0.0785	0.00384	−29.5686	0.0967
15	0.0785	0.00384	−30.5857	0.1001
16	−0.2118	−0.01248	−25.4408	−0.2703
17	−0.2118	−0.01248	−3.4767	−0.0369
18	−0.1441	−0.00816	−25.1670	−0.1748
19	−0.2916	−0.02717	−1.9857	−0.0459
20	−0.0349	−0.00246	−20.2653	−0.0424
21	−0.0349	−0.00246	−20.9721	−0.0439
22	−0.0349	−0.00246	−1.8850	−0.0039
23	−0.0349	−0.00246	−2.5918	−0.0054
24	−0.1619	−0.00730	−32.7440	−0.2036
25	−0.1619	−0.00730	−33.8474	−0.2104
26	0.1448	0.00775	−28.6023	0.1885
27	0.1448	0.00775	−4.3957	0.0290
28	−0.0570	−0.00214	−42.1213	−0.0766
		Proton 2		
1	−0.1937	−0.02432	−10.2776	−0.2127
2	−0.1937	−0.02432	−0.5205	−0.0108
3	1.2461	0.27692	−0.1986	0.0468
4	1.2461	0.27692	−1.0395	0.2450
5	−0.1829	−0.10560	−0.0806	−0.0072
6	0.0946	0.00976	−12.9638	0.1076
7	0.0946	0.00976	−1.0848	0.0090
8	−0.2155	−0.01729	−16.6349	−0.2448
9	−0.2155	−0.01729	−18.9640	−0.2791
10	−0.2155	−0.01729	−1.3648	−0.0201
11	−0.2155	−0.01729	−3.6939	−0.0544
12	−0.2463	−0.03952	−0.5649	−0.0190
13	−0.2463	−0.03952	−1.7295	−0.0582
14	0.0785	0.00384	−28.5993	0.0936
15	0.0785	0.00384	−32.4166	0.1061
16	−0.2118	−0.01248	−26.5595	−0.2822
17	−0.2118	−0.01248	−5.7763	−0.0614
18	−0.1441	−0.00816	−24.7661	−0.1720
19	−0.2916	−0.02717	−3.4520	−0.0798
20	−0.0349	−0.00246	−19.6069	−0.0410
21	−0.0349	−0.00246	−22.2596	−0.0466
22	−0.0349	−0.00246	−2.2148	−0.0046
23	−0.0349	−0.00246	−4.8675	−0.0102
24	−0.1619	−0.00730	−32.0549	−0.1993
25	−0.1619	−0.00730	−36.1958	−0.2250
26	0.1448	0.00775	−30.1409	0.1987
27	0.1448	0.00775	−7.2357	0.0477
28	−0.0570	−0.00214	−44.7227	−0.0814
		Proton 3		
1	−0.1937	−0.02432	−2.2196	−0.0459
2	−0.1937	−0.02432	−0.9267	−0.0192
3	1.2461	0.27692	−0.1677	0.0395
4	1.2461	0.27692	−5.2873	1.2461
5	−0.1829	−0.10560	−0.0676	−0.0061
6	0.0946	0.00976	−3.0808	0.0256
7	0.0946	0.00976	−1.5067	0.0125
8	−0.2155	−0.01729	−3.9381	−0.0580
9	−0.2155	−0.01729	−18.1185	−0.2666
10	−0.2155	−0.01729	−1.9147	−0.0282
11	−0.2155	−0.01729	−16.0951	−0.2368
12	−0.2463	−0.03952	−0.4755	−0.0160
13	−0.2463	−0.03952	−7.5657	−0.2544
14	0.0785	0.00384	−8.8313	0.0289
15	0.0785	0.00384	−32.0725	0.1049
16	−0.2118	−0.01248	−25.2920	−0.2687
17	−0.2118	−0.01248	−22.5380	−0.2394
18	−0.1441	−0.00816	−7.6661	−0.0532
19	−0.2916	−0.02717	−13.4285	−0.3105
20	−0.0349	−0.00246	−5.0395	−0.0105
21	−0.0349	−0.00246	−21.1905	−0.0443
22	−0.0349	−0.00246	−2.7349	−0.0057
23	−0.0349	−0.00246	−18.8859	−0.0395
24	−0.1619	−0.00730	−10.4452	−0.0649
25	−0.1619	−0.00730	−35.6569	−0.2217
26	0.1448	0.00775	−28.6042	0.1886
27	0.1448	0.00775	−25.5690	0.1685
28	−0.0570	−0.00214	−43.8909	−0.0799

a)—e) See Table 1, footnotes a)—e).

are predicted from Eq. 27 to resonate at δ 8.15, δ 7.53, and δ 7.25, respectively. They are well compared to the experimental values, δ 8.36 for proton 1, δ 7.93 for proton 2, and δ 7.39 for proton 3.[38)]

Secondary Fields in Dicyclooctabiphenylene

Secondary fields in dicyclooctabiphenylene **2** can be evaluated in the same manner. One four-membered and two six-membered rings in it are assumed to be regular in shape. Two eight-membered rings are made centrosymmetric in such a manner that they are attached closely to the biphenylene structure. All carbon-carbon bond lengths are assumed to be equal to those of benzene (139.65 pm).[38)] All carbon-hydrogen bond lengths are again assumed to be 108.5 pm.[38] There are three non-identical protons and 28 π-electron circuits in all. They are numbered as shown in Table 2 and Fig. 2. All the numerical results are also presented in Table 2 and Fig. 3.

In contrast to anthracene, not all π-electron circuits contribute to the increase in the secondary field at a given proton. Since the geometric factor of any π-electron circuit has the same sign, the sign of the contribution depends upon the sign of the circuit resonance energy. As stated before, the circuit resonance energy is positive for all $(4n+2)$-membered circuits and negative for all $(4n)$-membered circuits. There are no odd-membered π-electron circuits in dicyclooctabiphenylene. Accordingly, all $(4n+2)$-membered π-electron circuits contribute to the increase in the secondary field at all protons, while all $(4n)$-membered π-electron circuits contribute to the decrease in it.

Circuits 3, 4, 6, 7, 14, 15, 26, and 27 are the $(4n+2)$-membered ones. When these π-electron circuits share the carbon atom nearest to a given proton, they contribute much to the increase in the secondary field thereat. Other π-electron circuits are the $(4n)$-membered ones. When these π-electron circuits share the carbon atom nearest to a given proton, they generally contribute much to the decrease in the secondary field. The contribution of the peripheral π-electron circuit is not negligible owing to the very large geometric factor.

Circuits 20—23 are exceptional, in that they contribute little to the secondary field. When any of these π-electron circuits is deleted from the entire conjugated system, Kekulé structures cannot be written for the residual system. In general, such π-electron circuits have very small positive or negative resonance energy,[39] so it follows that they little contribute to the secondary field.

Circuits 2 and 4 are also exceptional in another sense. For example, circuit 4 contributes much to the secondary fields at protons 1 and 2 although these protons are not attached to this π-electron circuit. This is due to the exceptionally large circuit resonance energy. These exceptions suggest that the secondary field and the proton chemical shift cannot always be inferred from the nearby bond currents.

Protons 1 and 2 are predicted to experience the secondary fields of $-1.267\ B_0$ and $-1.255\ B_0$, respectively, which indicates that these protons must exhibit fairly large upfield shifts in the NMR spectrum. Proton 3 is predicted to suffer a secondary field of $-0.455\ B_0$, which indicates that this proton must exhibit a slightly upfield shift. This is in good agreement with experiment. According to Wilcox and Farley,[36] the two benzene rings in 2 are esssentially atropic, while the two eight-membered rings are highly paratropic.

Protons 1, 2, and 3 in dicyclooctabiphenylene are predicted from Eq. 27 to resonate at δ 3.68, δ 3.70, and δ 4.95, respectively. They are again in good agreement with the experimental values, δ 3.63 for proton 1, δ 3.59 for proton 2, and δ 4.55 for proton 3.[36] It seems that Eq. 27 is still very applicable to the results obtained by use of the iterative $\beta\omega'\omega''$ method. However, this may be due to the fact that both anthracene and dicyclooctabiphenylene happen to be alternant hydrocarbons with uniform charge distribution. Local anisotropic effects[7] appear fairly uniform over all conjugated atoms and bonds.

Concluding Remarks

It was in 1961 that Elvidge and Jackman put forward the proposal that a molecule should be defined as aromatic if it will sustain an induced diamagnetic ring current.[40] They implied that the proton chemical shifts may be taken to be a quantitative measure of aromaticity. An NMR criterion has since been established according to which downfield proton chemical shifts indicate aromaticity while upfield proton chemical shifts indicate antiaromaticity. However, it has not at all been clear why the molecules which exhibit downfield proton chemical shifts have strong conjugative stabilization.[41]

In this paper, we proved that proton chemical shifts are really related to aromatic stabilization, but clarified that proton chemical shifts of a polycyclic conjugated system are never proportional to the degree of aromatic stabilization. The calculated secondary magnetic field was a function of both the circuits resonance energies and the pure geometric factors. It is now clear that marked downfield proton chemical shifts are associated with one or more π-electron circuits which contribute much to aromatic stabilization.

Gayoso[42] and Gomes and Mallion[43] have attempted to estimate magnetic properties of cyclic conjugated hydrocarbons by means of Randić's conjugated circuit theory.[44] The present approach gives a physical basis for these attempts.

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