Characteristic Polynomial Expression and Integral Expression for Imaginary Bond-Bond Polarizability. Rules for London Susceptibility and for Ring Current

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The McWeeny theory for calculating magnetic properties of conjugated hydrocarbons is studied from a graph-theoretical point of view. Imaginary bond-bond polarizability is expressed in terms of characteristic polynomial. The expression clarifies the dependence of imaginary bond-bond polarizability on the structure. It is shown that the expression enables one easily to derive the equations for the quantity proved in two previous papers. The characteristic polynomial expression for imaginary bond-bond polarizability is rewritten in Coulson's integral form. The rules for London susceptibility and for ring current are proved from the integral expression.

The application of the graph theory[1] in the Hückel molecular orbital (HMO) theory enabled one mathematically to prove statements valid for a large class of unsaturated conjugated systems which clarify that there are close relationships between the chemical properties of a conjugated hydrocarbon and the topologies.[2] One of the most significant achievements is the proof of the Hückel rule, which states that cyclic conjugation of the π-electron system causes drastically different effects on the thermodynamic stability, depending on the size of the circuit.[3]

The HMO method with London's approximations[4] for calculating magnetic properties of conjugated hydrocarbons was established in differents forms by Pople[5] and by McWeeny.[6] Pople calculated ring currents from a knowledge of the field-dependent secular determinant (characteristic polynomial) while McWeeny used the usual perturbation method and expressed the magnetic susceptibility due to π-electrons (London susceptibility) in terms of imaginary bond-bond polarizability.

Although Pople did not give an explicit expression for London susceptibility (and ring current), some time ago Aihara[7] was able to express London susceptibility in terms of a characteristic polynomial and showed that the London susceptibility of a polycyclic conjugated molecule can be given as a sum of the circuit susceptibilities over all the circuits found in the system. By using Coulson's integral method[8] the present author proved a rule for London susceptibility valid for any alternant polycyclic conjugated system which states that the sign of the circuit susceptibility for a circuit in the system is determined by the number of carbon atoms in the circuit.[9] This rule has very similar aspects to Hückel rule for thermodynamical stability.[10]

The McWeeny method has been widely applied to conjugated systems by a large number of authors.[11] However the properties of imaginary bond-bond polarizability had not been studied. Recently the present author clarified the dependence of imaginary bond-bond polarizability on the mode of branching[12] and the role of "acyclic" bond in the magnetic properties of conjugated molecules.[13] Although the McWeeny theory has also been pointed out to have some topological aspects associated with a spanning tree,[6,14] the close relationship between London susceptibility and the circuit found in the Pople-Aihara theory is not known in the McWeeny theory.

The purpose of this paper is to clarify the dependence of magnetic properties on the circuit in the McWeeny method.[15] In the first part of the present paper 1) imaginary bond-bond polarizability will be expressed in terms of a characteristic polynomial and 2) it will be shown that the characterist polynomial expression for imaginary bond-bond polarizability enables one to derive easily the equations proved in two previous papers. In the second part 3) imaginary bond-bond polarizability will be represented in Coulson's integral form and the rules for London susceptibility and for ring current will be proved.

Characteristic Polynomial Expression for Imaginary Bond-Bond Polarizability

In McWeeny's perturbation approach, the partial London susceptibility for the J-th MO, χ_J, of a polycyclic conjugated system is given by[6]

$$\chi_J=2\beta(e/\hbar c)^2\Big(\sum_{(rs)}P_{J,rs}S_{rs}^2 + \sum_{(rs)}\sum_{(tu)}\beta\pi_{J,(rs)(tu)}S_{rs}S_{tu}\Big), \tag{1}$$

where β is the field-free resonance integral, which is assumed to be equal for all the bonds in the molecule; e, $\hbar$, and c are the usual fundamental constants with these symbols; S_{rs} is the signed area of the triangle formed by an arbitrary origin and bond r–s; the sum $\sum_{(rs)}$ runs over all the bonds in the molecule; $P_{J,rs}$ is the partial Coulson bond order for the J-th MO;[8] $\bar{\pi}_{J,(rs)(tu)}$ is the partial imaginary bond-bond polarizability given by[6]

$$\bar{\pi}_{J,(rs)(tu)}=\sum_{K(\neq J)}\frac{(C_{rJ}C_{sK}-C_{sJ}C_{rK})(C_{tK}C_{uJ}-C_{uK}C_{tJ})}{(X_J-X_K)\beta}, \tag{2}$$

where X_J and C_{rJ} are the J-th eigenvalue (in units of β) and the eigenvector of the field-free Hückel Hamiltonian matrix, respectively.

In the later discussions attention should be paid to the order of the suffices in $\bar{\pi}_{J,(rs)(tu)}$ since

$$\bar{\pi}_{J,(rs)(tu)} = -\bar{\pi}_{J,(rs)(tu)} = -\bar{\pi}_{J,(rs)(tu)}. \tag{3}$$

The sign of χ_J is not dependent on the order of the suffices in the right-hand side of Eq. 1 because of Eq. 3 and $S_{sr} = -S_{rs}$.

Following Aihara,[7] in Pople's approach,[5] the London susceptibility of a polycyclic conjugated system is expressed in terms of a characteristic polynomial as follows:

$$\begin{aligned}\chi_J &= \sum_j 2\beta(e/\hbar c)^2 (P(G\ominus C_j; X_J)/P'(G; X_J)) S(C_j)^2 \\ &= \sum_j \chi_J(C_j).\end{aligned} \tag{4}$$

In Eq. 4 G is the graph representing the system; the sum runs over all the circuits found in G; $G\ominus C_j$ is a subgraph of G obtained by deleting circuit C_j and all the bonds incident to C_j from G; $P(G;X)$ and $P(G\ominus C_j;X)$ are the field-free characteristic polynomials of G and of $G\ominus C_j$, respectively; $P'(G;X)$ is the first derivative of $P(G;X)$ with respect to X; $S(C_j)$ is the area of C_j; $\chi_J(C_j)$ denotes the contribution of a circuit C_j to the London susceptibility of the system (circuit susceptibility).

For example, the London susceptibility of naphthalene is given by a sum of the circuit susceptibilities over three circuits C_1, C_2, and C_3 shown in Fig. 1. The circuit C_3 is produced by the fusion of two rings (fundamental circuits) R_1 and R_2 (see Fig. 1).

Equation 4 shows that the factor determining the magnetic properties of a polycylcic conjugated system is not the rings but the circuits. In other words, it shows that every circuit in the system acts as a driving force for the induction of ring current. The number of the modes of cyclic conjugation of the π-electrons is the number of the circuits found in the system. This aspect resembles Randić's "conjugated circuit" based on classical valence bond method.[16]

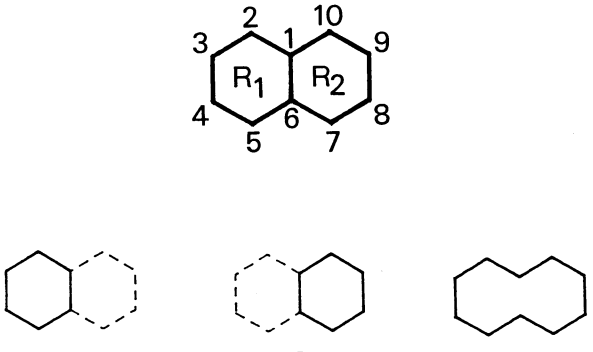

Fig. 1. Two rings and three circuits in naphthalene.

The expression for London susceptibility in McWeeny's theory, namely Eq. 1, is based on the concept "bond" while that in the Pople-Aihara theory, namely Eq. 4, is based on the concept "circuit." Since the two equations are obtained with the same approximations (London's approximations), they are equivalent mathematically.[17] Therefore comparison of the two equations will enable us to express imaginary bond-bond polarizability in terms of a characteristic polynomial. Before doing so, however it is necessary to express the London susceptibility in terms of the ring area $S(R_j)$ because the two equations are expressed in terms of the different area terms, that is, Eq. 1 is expressed in terms of triangle area S_{rs} while Eq. 4 is expressed in terms of the circuit area $S(C_j)$. Fortunately we have a unitary transformation devised by McWeeny,[6,14] which enables one to rewrite Eq. 1 in a form suitable for our purpose.

Due to McWeeny's unitary transformation we can obtain the transformed Hamiltonian matrix in which the elements for "circuit-completing" bonds for a chosen spanning tree[18] depend on an applied magnetic field but the other elements are independent of the field. From the transformed Hamiltonian matrix for a chosen spanning tree T we obtain in stead of Eq. 1 the following equation:

$$\begin{aligned}\chi_J = 2\beta(e/\hbar c)^2 (&\sum_j (P_{J,(b_j)} + \beta\bar{\pi}_{J,(b_j)(b_j)}) S(C_j)^2 \\ &+ 2\sum_j \sum_{k(>j)} (-1)^{\zeta} \beta\bar{\pi}_{J,(b_j)(b_j)} S(C_j) S(C_k)).\end{aligned} \tag{5}$$

In Eq. 5 C_j denotes a circuit completed by inserting a "circuit-completing" bond b_j for T; the sum is over all the "circuit-completing" bonds for T; ζ is a topological quantity defined as

$\zeta = 0$ if the direction of the bond b_j in the circuit C_j is identical with that of the bond b_k in the circuit C_k,
$\zeta = 1$ otherwise. (6)

It should be noted that the circuits appearing in Eq. 5 are only the circuits completed by inserting the "circuit-completing" bonds for a chosen spanning tree although all the circuits of the original graph appears in Eq. 4. The number of the "circuit-completing" bonds for a spanning tree for a polycyclic conjugated system equals the number of the rings (fundamental circuits) of the system. After representing the circuit area $S(C_j)$ in Eqs. 4 and 5 in terms of the ring area $S(R_j)$ and by equating the coefficients of $S(R_j)^2$ or $S(R_j)S(R_k)$ in the two equations, we can obtain the following equations:

$$P_{J,rs} + \beta\bar{\pi}_{J,(rs)(rs)} = \sum_j^{rs\,\in\,C_j} (P(G\ominus C_j; X_J)/P'(G; X_J)), \tag{7}$$

and

$$\beta\bar{\pi}_{J,(rs)(tu)} = \sum_j^{rs,\ tu\,\in\,Cj} (-1)^{\eta} (P(G\ominus C_j; X_J)/P'(G; X_J)), \tag{8}$$

In Eq. 7 the sum $\sum_{j}^{rs\in C_j}$ runs over all the circuits which pass through the bond r–s. In Eq. 8 the sum $\sum_{j}^{rs,tu\in C_j}$ runs over all the circuits which pass through the two bonds r–s and t–u and

$\eta=0$ if the directions of $r\rightarrow s$ and $t\rightarrow u$ are same in the circuit C_j

$\eta=1$ if they are different.

Further, by substituting the following equation[19)]

$$P_{J,rs}=(P(G\ominus e_{rs};X_J)+\sum_{j}^{rs\in C_j} P(G\ominus C_j;X_J))/P'(G;X_J), \tag{9}$$

into Eq. 7 we find that

$$\beta\bar{\pi}_{J,(rs)(rs)}=-P(G\ominus e_{rs};X_J)/P'(G;X_J), \tag{10}$$

where $G\ominus e_{rs}$ is a subgraph of G obtained by deleting bond (edge) r–s and all the bonds incident to e_{rs} from G. Figure 2 shows a subgraph $G\ominus e_{23}$ for bond 2-3 of naphthalene.

Let us take naphthalene as an example in order to illustrate the above procedure. Figure 3 shows a spanning tree for naphthalene, $T1$. The "circuit-completing" bonds for $T1$ are bonds 2-3 and 6-1. Insertion of bond 6-1 into $T1$ completes circuit C_2 (ring R_2) and that of bond 2-3 completes circuit C_3 which contains two rings R_1 and R_2 (see Fig. 1). If the spanning tree $T1$ is chosen, then in McWeey's method χ_J of naphthalene is given by (see Eq. 5):

$$\begin{aligned}\chi_J=2\beta(e/\hbar c)^2\{&(P_{J,23}+\beta\bar{\pi}_{J,(23)(23)})(S(R_1)+S(R_2))^2\\&-2\beta\bar{\pi}_{J,(23)(61)}(S(R_1)+S(R_2))S(R_2)\\&+(P_{J,61}+\beta\bar{\pi}_{J,(61)(61)})S(R_2)^2\},\end{aligned} \tag{11}$$

where the negative sign before the second term is due to the fact that the direction of 2→3 is anticlockwise in circuit C_3 but the direction of 6→1 is clockwise in circuit C_2 (see Figs. 1 and 3).

In Pople's method χ_J of naphthalene is expressed as a sum of the partial circuit susceptibilities for three circuits, C_1, C_2, and C_3:

$$\chi_J=\chi_J(C_1)+\chi_J(C_2)+\chi_J(C_3). \tag{12}$$

The explicit expressions for $\chi_J(C_1)$, $\chi_J(C_2)$, and $\chi_J(C_3)$ will be obvious. For example, from Eq. 4 $\chi_J(C_3)$ is

$$\begin{aligned}\chi_J(C_3)=2\beta(e/\hbar c)^2&(P(G\ominus C_3;X_J)/P'(G;X_J))\\&(S(R_1)+S(R_2))^2.\end{aligned} \tag{13}$$

By equating the coefficients of $S(R_j)S(R_k)$ in Eqs. 11 and 12 we obtain the following equations:

$$P_{J,23}+\beta\bar{\pi}_{J,(23)(23)}=(P(G\ominus C_1;X_J)+P(G\ominus C_3;X_J))/P'(G;X_J), \tag{14}$$

$$\beta\bar{\pi}_{J,(23)(61)}=P(G\ominus C_1;X_J)/P'(G;X_J), \tag{15}$$

$$P_{J,61}+\beta\bar{\pi}_{J,(61)(61)}=(P(G\ominus C_1;X_J)+P(G\ominus C_2;X_J))/P'(G;X_J). \tag{16}$$

It can be ascertained that the equations obtained for $T1$, namely Eqs. 14—16, are the examples of Eqs. 7 and 8. Even if the other spanning tree is chosen, we can ascertain the validity of Eqs. 7, 8, and 10.

The Eqs. 7, 8, and 10 are the desired equations. Equation 7 shows that the quantity $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$ for bond r–s is expressed as a sum of the characteristic polynomials of the subgraphs $G\ominus C_j$ over all the circuits passing through bond r–s. Equation 8 shows that the partial imaginary mutual bond-bond polarizability for two bonds r–s and t–u, $\beta\bar{\pi}_{J,(rs)(tu)}$, is expressed as a sum of the characteristic polynomials of the subgraphs $G\ominus C_j$ over all the circuits passing through the two bonds r–s and t–u. Equation 10 shows that the partial imaginary self bond-bond polarizability for bond r–s is expressed in terms of the characteristic polynomial of the subgraph $G\ominus e_{rs}$.

Although the imaginary bond-bond polarizability represents the imaginary part of the change of Coulson's bond order due to an applied magnetic field, we can find from Eqs. 7 and 8 a similarity between the two quantities $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$ and $\beta\bar{\pi}_{J,(rs)(tu)}$ that the two quantities are expressed in terms of the same type of characteristic polynomial such as $P(G\ominus C;X)$.[13)] Further it is seen from Eqs. 8 and 10 that the imaginary mutual bond-bond polarizability and the imaginary self bond-bond polarizability are different quantities because the former is associated with the subgraph $G\ominus C_j$ but the latter is associated with the subgraph $G\ominus e_{rs}$.

From Eqs. 7, 8, and 10 we can clarify the dependence of imaginary bond-bond polarizability on the topologies (circuit and connectivity). Let us first consider the properties related to the circuit. Equation 7 shows that the quantity $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$ for the bond r–s consists of the contributions of all the circuits passing through the bond r–s, and Eq. 8 shows that the partial imaginary mutual bond-bond polarizability $\beta\bar{\pi}_{J,(rs)(tu)}$ for bonds r–s and t–u consists of the contributions of all the circuits passing through the two bonds r–s and t–u. Although, as seen from Eq. 1, two quantities $P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}$ and $\beta\bar{\pi}_{J,(rs)(tu)}$ represent the contribution of a

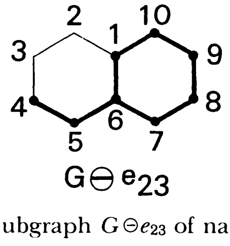

Fig. 2. Subgraph $G\ominus e_{23}$ of naphthalene.

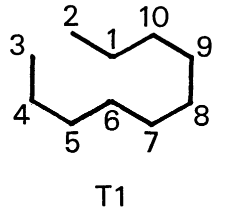

Fig. 3. Spanning tree, $T1$, for naphthalene.

bond to London susceptibility, it is interesting that the two quantities themselves show the circuit dependence mentioned above.

In a previous paper[13] we classified bonds into "acyclic" and "cyclic" and pointed out the importance of this classification in the study of magnetic properties of conjugated molecules. We proved that for an "acyclic" bond r–s,

$$P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}=0, \tag{17}$$

and

$$\bar{\pi}_{J,(rs)(vw)}=0, \tag{18}$$

where v–w is an arbitrary bond but not equal to r–s. The set of Eqs. 17 and 18 shows that an "acyclic" bond makes no contribution to London susceptibility and to ring current. Since an "acyclic" bond, by definition, has no circuits passing through it,[13] from Eqs. 7 and 8 we can easily obtain Eqs. 17 and 18.

The branching in a graph is one of the important factors determining the physical and chemical properties of unsaturated hydrocarbons.[2] Figure 4 shows two modes of branching in the graph representing a conjugated molecule. Since the difference in the modes of branching appears in the difference of the circuits passing through the bonds, Eqs. 7 and 8 give the imformation on the dependence of imaginary bond-bond polarizability on branching.

Let C be a circuit which passes through bond r–s in G1 shown in Fig. 4. Then the circuit C necessarily passes through bond s–t in G1 also and the directions of $r\rightarrow s$ and of $s\rightarrow t$ are the same in the circuit C. Therefore we obtain from Eqs. 7 and 8

$$\beta\bar{\pi}_{J,(vw)(rs)}=\beta\bar{\pi}_{J,(vw)(st)}, \tag{19}$$

$$P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}=P_{J,rs}+\beta\bar{\pi}_{J,(st)(st)}, \tag{20}$$

$$P_{J,rs}+\beta\bar{\pi}_{J,(rs)(rs)}=\beta\bar{\pi}_{J,(rs)(st)}, \tag{21}$$

where v–w is an arbitrary bond except the bonds in G1. In a similar way, it follows from Eqs. 7 and 8 that for vertices r', s', t', and u' in subgraph $G2$ shown in Fig. 4

$$\beta\bar{\pi}_{J,(vw)(r's')}=\beta\bar{\pi}_{J,(vw)(s't')}+\beta\bar{\pi}_{J,(vw)(s'u')}, \tag{22}$$

$$P_{J,r's'}+\beta\bar{\pi}_{J,(r's')(r's')}=\beta\bar{\pi}_{J,(r's')(s't')}+\beta\bar{\pi}_{J,(r's')(s'u')}, \tag{23}$$

where v–w is an arbitrary bond except the bonds in $G2$. The above five equations show the dependence of imaginary bond-bond polarizability on the mode of branching. Although Eqs. 19—23 were proved in a previous paper,[12] as seen above, Eqs. 7 and 8 provide an easier way to derive Eqs. 19—23 than that used in Ref. 12.

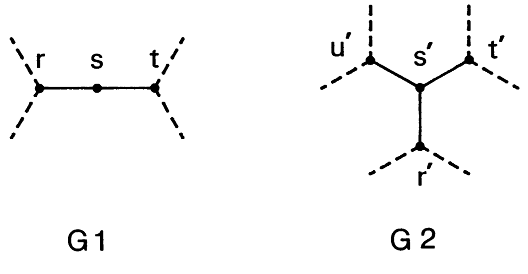

Fig. 4. Subgraphs G1 and G2.

Integral Expressions for Imaginary Bond-Bond Polarizability. Rules for London Susceptibility and for Ring Current

Coulson's integral representation technique[8] has been shown to be very powerful in the study of the dependence of the HMO π-electron indices on the structure of the conjugated molecule.[2] The characteristic polynomial expression for imaginary bond-bond polarizability obtained above is the first step for obtaining the integral expression for the quantity.

It follows from Eqs. 7, 8, and 10 that

$$P_{rs}+\beta\bar{\pi}_{(rs)(rs)}=\sum_{J} g_J \sum_{j}^{rs\in C_j}(P(G\ominus C_j;X_J)/P'(G;X_J)), \tag{24}$$

$$\beta\bar{\pi}_{(rs)(tu)}=\sum_{J} g_J \sum_{j}^{rs,tu\in C_j}(-1)^{\eta}(P(G\ominus C_j;X_J)/P'(G;X_J)), \tag{25}$$

and

$$\beta\bar{\pi}_{(rs)(rs)}=-\sum_{J} g_J P(G\ominus e_{rs};X_J)/P'(G;X_J), \tag{26}$$

where g_J is the occupation number of the J-th MO. According to the same procedure as in Ref. 9, for closed shell molecules Eqs. 24—26 can be written in the integral form as follows:

$$P_{rs}+\beta\bar{\pi}_{(rs)(rs)}=(-1/\pi)\sum_{j}^{rs\in C_j}\int_{-\infty}^{\infty}(P(G\ominus C_j;iy)/P(G;iy))dy, \tag{27}$$

$$\beta\bar{\pi}_{(rs)(tu)}=(-1/\pi)\sum_{j}^{rs,tu\in C_j}(-1)^{\eta}\int_{-\infty}^{\infty}(P(G\ominus C_j;iy)/P(G;iy))dy, \tag{28}$$

and

$$\beta\bar{\pi}_{(rs)(rs)}=(1/\pi)\int_{-\infty}^{\infty}(P(G\ominus e_{rs};iy)/P(G;iy))dy. \tag{29}$$

With the quantity $F(C)$ defined as[9]

$$F(G,C)=\int_{-\infty}^{\infty}(P(G\ominus C;iy)/P(G;iy))dy, \tag{30}$$

Eqs. 27 and 28 are written as follows:

$$P_{rs}+\beta\bar{\pi}_{(rs)(rs)}=(-1/\pi)\sum_{j}^{rs\in C_j}F(G,C_j), \tag{31}$$

and

$$\beta\bar{\pi}_{(rs)(tu)}=(-1/\pi)\sum_{j}^{rs,tu\in C_j}(-1)^{\eta}F(G,C_j). \tag{32}$$

It was shown that if the system G is alternant, the sign of $F(G,C)$ is determined only by the size of the circuit, $N(C)$:[9]

$$F(G,C)\begin{cases}<0 & \text{if } N(C)=4n+2\\ >0 & \text{if } N(C)=4n.\end{cases} \tag{33}$$

This equation means that the contribution of a $(4n+2)$-membered circuit is diamagnetic and that of a

$(4n)$-membered circuit is paramagnetic.

In a similar fashion it can be shown from Eq. 29 that the sign of the imaginary self bond-bond polarizability is always positive

$$\bar{\pi}_{(rs)(rs)} > 0\,, \tag{34}$$

where we used the fact that β is negative. This result was already obtained in another manner.[12]

If we remember that bond current for bond r–s (ring current) is expressed in terms of imaginary bond-bond polarizability as follows:[20]

$$Q(rs) = (P_{rs} + \beta\bar{\pi}_{(rs)(rs)})\, S_{rs} + \sum_{(tu)} \beta\bar{\pi}_{(rs)(tu)}\, S_{tu}\,, \tag{35}$$

it is seen from Eqs. 31 and 32 that the driving forces for the bond current for bond r–s are the presence of the circuits which contain the bond r–s. In other words, cyclic conjugation is the basis for the induction of bond current.

From Eqs. 31—33 we can obtain the rule for imaginary bond-bond polarizability which states that

(1) $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}$ is expressed as a sum of the contributions over all the circuits passing through bond r–s and the sign of the contribution of a circuit is determined only by the size of the circuit as shown in Eq. 33.

(2) $\beta\bar{\pi}_{(rs)(tu)}$ is expressed as a sum of the contributions over all the circuits passing through two bonds r–s and t–u, and the sign of the contribution of a circuit is determined only by the size of the circuit as shown in Eq. 33.

From this rule we can predict the sign of the imaginary bond-bond polarizability by counting the size of the circuit only. For example, it is seen for naphthalene that

$$P_{23} + \beta\bar{\pi}_{(23)(23)} > 0\,,$$
$$\beta\bar{\pi}_{(23)(61)} > 0\,,$$

because the circuits passing through 2-3 are C_1 and C_3, the circuit passing through 2-3 and 6-1 is C_1, $N(C_1)=6$ and $N(C_3)=10$. Similarly we can predict that the signs of $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}$ and $\beta\bar{\pi}_{(rs)(tu)}$ for any bond in a catacondensed benzenoid hydrocarbon are positive (diamagnetic) because all the circuits found in a catacondensed benzenoid hydrocarbon are $(4n+2)$-membered circuits.

Since London susceptibility and bond current are expressed in terms of $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}$ and $\beta\bar{\pi}_{(rs)(tu)}$ (see Eqs. 1 and 35), we can obtain the rules for London susceptibility and for bond current. For example, we can predict for a catacondensed benzenoid hydrocarbon that the London susceptibility and the bond current for any bond are diamagnetic because all the contributions of the circuits in the system to $P_{rs}+\beta\bar{\pi}_{(rs)(rs)}$ and $\beta\bar{\pi}_{(rs)(tu)}$ are diamagnetic. This is in agreement with experimental results.[21]

Concluding Remarks

By using the equality of the expressions for London susceptibility in two different methods (McWeeny and Pople–Aihara), imaginary bond-bond polarizability was expressed in terms of characteristic polynomial (see Eqs. 7, 8, and 10). It was shown that the characteristic polynomial expressions for imaginary bond-bond polarizability reveal the dependence of the quantity on the structures such as circuit and branching and that the equations proved in previous papers[12,13] can easily be derived from these expressions. The integral expressions for imaginary bond-bond polarizability (see Eqs. 27—29) were obtained from Eqs. 7, 8, and 10. It was shown that Eqs. 27—29 give a rule for imaginary bond-bond polarizability (and for London susceptibility and for ring current) of any alternant conjugated systems.

Equations 7, 8, and 10 hold only for nondegenerate molecular orbitals because Eqs. 4 and 5 do not hold for degenerate molecular orbitals. However, Eqs. 27—29 are valid for neutral alternant conjugated systems even with degenerate orbitals provided that they have filled bonding and empty antibonding molecular orbitals.[9]

In the present paper we neglect the effect of bond alternation. Since $[4n]$-annulene without bond alternation has nonbonding molecular orbitals, the rule proved in this paper cannot be applied to the system. However it has been reported that $[4n]$-annulene with bond alternation which has no nonbonding orbitals bears a paramagnetic ring current.[22] Further we can find the numerical results by Aihara for biphenylene, cycloocta[*def*]biphenylene and dicycloocta[1,2,3,4-*def*: 1′,2′,3′,4′-*jkl*]biphenylene with bond alternation, which show that circuit susceptibilities for the $(4n+2)$-membered circuits in these systems are diamagnetic and those for the $(4n)$-membered circuits are paramagnetic.[23] Accordingly it seems that the introduction of bond alternation changes the magnitude of a circuit susceptibility but does not change its sign.

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