

Table VII. Resonance Energies for Benzene (Referenced to $[\infty]$ Annulene/Polyene)

basis set	energy, kcal/mol			
	BA ref		BE ref	
	HF	MP2	HF	MP2
STO-3G	31.1	23.8	52.4	35.1
6-31G	29.3	17.2	40.5	24.2
6-31G*	26.6	27.6	37.1	33.5

of about $C=C$ and $C-C = 1.36 \pm 0.02$ and $1.44 \pm 0.02 \text{ \AA}$.^{106,107}

The distortional energies in *trans*-polyacetylene (bond equalized to bond alternate) on a per π -electron basis have been reported¹¹¹ as 3.56 (HF/STO-3G), 1.89 (MP2/STO-3G), 1.96 (HF/6-31G), 1.16 (MP2/6-31G), and 1.75 kcal/mol (HF/6-31G*). Although the geometrical treatment is somewhat different,¹¹¹ these values may be compared with our results for [18]annulene: 1.98 (HF/STO-3G), 0.14 (MP2/STO-3G), 0.91 (HF/6-31G), and 1.17 kcal/mol (HF/6-31G*). These values are significantly smaller than those given for *trans*-polyacetylene, and it therefore appears that while the bond lengths in the $[N = 4n + 2]$ annulenes are close to the limiting value, the distortional energies have not converged to the result for $N \rightarrow \infty$ at [18]annulene, which therefore suggests a more delocalized electronic structure for [18]annulene than for *trans*-polyacetylene.

The resonance energies discussed in an earlier section were reference to finite polyenes (Table II), but in fact HMO schemes have been developed which effectively utilize an $[\infty]$ annulene/polyene for the reference energy. By making use of the total energy per unit cell obtained in the crystal orbital calculations on polyacetylene, it is possible to develop an $[\infty]$ annulene/polyene reference energy for use in more detailed resonance energy calculations.¹¹⁴ While such a scheme cannot be used with molecules not based on $(C_2H_2)_n$ structures or on annulenes which suffer from angle strain or the presence of nonbonded interactions without correction factors, it is directly applicable to benzene, and the results are summarized in Table VII. The values obtained using BA *trans*-polyacetylene for the reference energy may be most

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appropriately compared with the resonance energies based on finite polyenes as these latter reference molecules are also bond-alternate. It may be seen that the HF results are comparable but the MP2 values are much reduced in the $[\infty]$ annulene/polyene scheme—with the exception of the results obtained with the 6-31G* basis set, which show little sensitivity to the inclusion of electron correlation effects. This latter result is surprising, as the HF/6-31G* energy for the reaction 3 benzene \rightarrow [18]annulene was noted to be in error by about 30 kcal/mol, and this discrepancy was previously ascribed to the neglect of electron correlation effects.

4. Origin of Basis Set and Electron Correlation Effects in Extended Conjugated Systems. The origin of these effects (discussed above and previously) has been considered by a number of authors.^{26-36,111,112} It is generally agreed that these deficiencies operate in concert to favor localized over delocalized structures, particularly in extended systems.

From a consideration of the Viral theorem,¹¹⁵ it becomes clear that the kinetic energy (KE) and the potential energy (PE) are too low in magnitude in the delocalized structure when a comparison is made with its localized counterpart in the presence of deficiencies in the basis set and neglect of electron correlation effects. As the electrons are more mobile in the delocalized structure, it is not surprising to find that they should execute a more complicated motion with higher KE to avoid one another than is necessary in the localized structure. Clearly a flexible basis set with additional nodes in the atomic functions and correlation of the motions of the electrons will serve to facilitate the necessary increase in KE in the delocalized structure. On the other hand, the PE suffers in the structure with the more mobile electrons because its orbitals are less localized, and thus the necessity for the electrons to occupy different regions of space and instantaneously correlate their motions becomes crucial. The PE of the localized structure will not be as sensitive to these effects, and in order to correctly treat the two cases in a balanced manner, it is clear that detailed basis sets and the inclusion of electron correlation effects will be critical.

Supplementary Material Available: Computer printout of coordinates and distance matrices (24 pages). Ordering information given on any current masthead page.

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Magnetotropism of Biphenylene and Related Hydrocarbons. A Circuit Current Analysis

Jun-ichi Aihara

Contribution from the Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422, Japan. Received May 29, 1984

Abstract: A general formula for ring currents induced in a polycyclic conjugated system was derived graph-theoretically. This formula is applicable to all planar carbocyclic and heterocyclic conjugated systems. Ring currents (i.e., bond currents in our terminology) are therein expressed as a superposition of currents induced in all possible π -electron circuits. Here, π -electron circuits signify ring components defined in Sachs' graph theory. It was proved that $[4n + 2]$ -membered and $[4n]$ -membered circuits in a polycyclic system are always diatropic and paratropic, respectively. Biphenylene and related hydrocarbons illustrate this magnetotropic behavior well. Benzenoid atropism in dicycloocta[1,2,3,4-def:1',2',3',4'-jkl]biphenylene was found to arise from the cancellation of currents induced in numerous $[4n + 2]$ -membered and $[4n]$ -membered circuits. London susceptibility can likewise be partitioned among the π -electron circuits.

Our interest in aromaticity and antiaromaticity has centered on the associated magnetotropism.¹⁻¹⁰ Monocyclic aromatic and

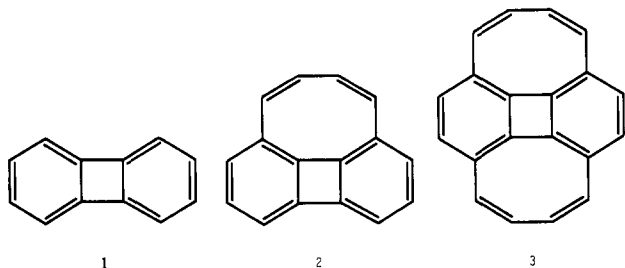
antiaromatic systems give rise to diamagnetic and paramagnetic ring currents, respectively.^{3,6,7,11-13} Systems formed by the fusion

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(4) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 1633.

of $[4n + 2]$ -membered rings, such as naphthalene and anthracene, sustain strong diamagnetic ring currents along the periphery.¹⁴⁻¹⁷ Interestingly, systems formed by the fusion of two $[4n]$ -membered rings again seem to sustain diamagnetic ring currents along the periphery.⁵⁻⁷ Butalene and bicyclo[6.2.0]decapentaene belong to systems of this type. They are predicted to be diatropic but thermodynamically antiaromatic.^{5-7,18,19} Most experimentalists have defined aromatic compounds as diatropic cyclic molecules in which all the ring atoms are involved in a single conjugated system.²⁰ It is clear that this definition is never satisfactory for polycyclic systems.

If fused systems contain both $[4n + 2]$ -membered and $[4n]$ -membered rings, a much more complicated situation arises. It is not easy to predict by intuition the sign and the magnitude of their magnetotropism. Biphenylene (**1**), cycloocta[def]biphenylene (**2**), and dicycloocta[1,2,3,4-def:1',2',3',4'-jkl]biphenylene (**3**) are typical examples.^{2,10,19-22} Especially, **3** is an unusual hydrocarbon in which the eight-membered rings retain strongly antiaromatic ring current behavior, while the neighboring benzene rings have virtually no ring currents.^{23,24}



In this paper, we introduce the concept of circuit currents to analyze the magnetotropism of such polycyclic conjugated systems and elucidate graph-theoretically the origin of their complex response to an external magnetic field.

Graph Theory of Circuit Currents

In 1979 we devised a graph-theoretical formula for London (or ring currents) susceptibility of a cyclic conjugated hydrocarbon with no bond alternation.² It was later modified to evaluate London susceptibilities of bond-alternate hydrocarbons.⁵ The modified formula was found to be general in the sense that it can be applied not only to bond-alternate hydrocarbons but also to heterocycles. It is expressed as follows.

A given carbocyclic or heterocyclic system with N conjugated atoms is denoted by G . Suppose that M π -electron circuits can be chosen from G . Here, π -electron circuits signify ring components defined in Sachs' graph theory²⁵⁻²⁷ and will often be abbreviated simply to circuits. Note that such π -electron circuits have been referred to as π -electron rings in our previous papers.¹⁻¹⁰ Our graph-theoretical formula for London susceptibility, χ_G , is then written in the form:⁵

$$\chi_G = -2 \left(\frac{e}{c\hbar} \right)^2 \beta S_i^2 \sum_{i=1}^M \sum_{j=1}^N \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \prod_{(st)}^{r_i} k_{st} \quad (1)$$

Here, r_i is the i th circuit chosen from G ; $P_G(X)$ is the characteristic polynomial for G ; $P_G'(X)$ is the first derivative of $P_G(X)$ with respect to X ; $P_{G-r_i}(X)$ is the characteristic polynomial for a sub-system of G , obtained by deleting the i th circuit and all π bonds incident to it from G ; X_j is the energy of the j th π -electron molecular orbital, obtained by solving the equation $P_G(X) = 0$; g_j is the occupation number for the j th π -electron molecular orbital; S_i is the area of the i th circuit; k_{st} is the resonance integral parameter for a π bond between the s th and t th atoms; (st) runs over all π bonds constituting the i th circuit; β is the resonance integral for each carbon-carbon π bond in benzene; and e , c , and \hbar are the standard constants with these symbols.

As shown in eq 1, London susceptibility is an additive function of π -electron circuits. It can be partitioned among the circuits. Therefore, the i th circuit susceptibility, i.e., the susceptibility contribution of the i th circuit, can be defined as

$$\chi_i = -2 \left(\frac{e}{c\hbar} \right)^2 \beta S_i^2 \sum_{j=1}^N \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \prod_{(st)}^{r_i} k_{st} \quad (2)$$

When there are degenerate orbitals, some corrections to eq 2 are needed according to the procedure described previously.⁸ Circuit susceptibility has been referred to as ring susceptibility in our papers.^{2,6-8,10}

The i th circuit susceptibility is reasonably associated with a current induced in the i th π -electron circuit,¹⁰ which is here termed the i th circuit current.²⁹ The i th circuit current, I_i , can then be defined by

$$I_i = \frac{c\chi_i H}{S_i} = -2 \frac{e^2 H}{c\hbar^2} \beta S_i \sum_{j=1}^N \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \prod_{(st)}^{r_i} k_{st} \quad (3)$$

where H is the intensity of the external magnetic field. This is a generalized formula for circuit currents, applicable to all kinds of planar conjugated systems. The magnitude of each circuit current is thus controlled by the area of the circuit times the product of the resonance integral parameters around the π bonds of the circuit. Accordingly, the intensities of the currents induced in large circuits must be more sensitive to bond alternation as a consequence of the greater number of resonance integral parameters entering the product.

The circuit current induced in benzene, I_0 , is calculated as

$$I_0 = -\frac{2}{9} \frac{e^2 H}{c\hbar^2} \beta S_0 \quad (4)$$

where S_0 is the area of the benzene ring. By the use of I_0 as a unit for I_i , I_i is rewritten as

$$I_i = 9 \frac{S_i}{S_0} I_0 \sum_{j=1}^N \frac{g_j P_{G-r_i}(X_j)}{P_G'(X_j)} \prod_{(st)}^{r_i} k_{st} \quad (5)$$

It should be noted that the term circuit current given above is not identical with the term ring current chemists have been using for a couple of decades. The latter term signifies an overall current induced in a given π bond. It is here termed a bond current in order to discriminate it from the circuit current defined by eq 3. The bond current flowing at a given π bond is equal to the sum of all circuit currents flowing there. Mathematically, this is true since the magnetic field we usually apply is very weak and can be treated as a small perturbation.²

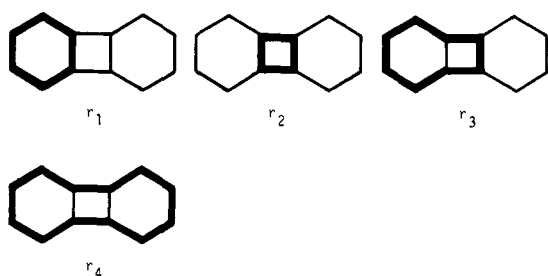
Calculation of Circuit Currents

As a result of applying this circuit current analysis, biphenylene (**1**) and two related hydrocarbons (**2**, **3**) were selected as potentially interesting species. The latter two compounds were recently prepared by Wilcox et al.¹⁹⁻²²

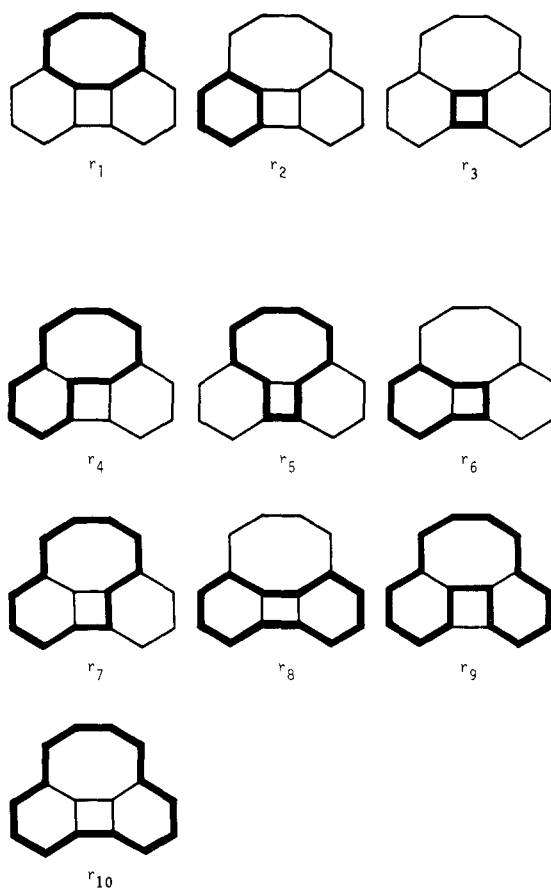
In performing circuit current calculations, all carbon-carbon π bonds in **1**–**3** were assumed to be equal in length and all four- and six-membered rings regular in shape. Molecular geometries of **2** and **3** were then depicted in such a manner that one or two

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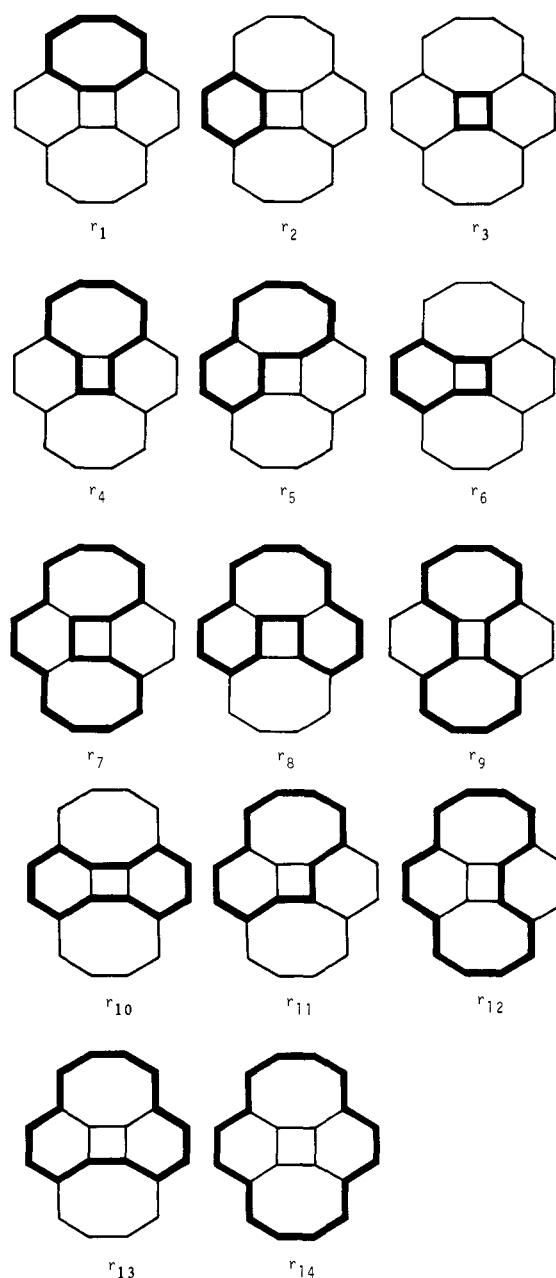
(a) Biphenylene



(b) Cycloocta[def]biphenylene



(c) Dicycloocta[1,2,3,4-def:1'.2',3',4'-jk1]biphenylene

Figure 1. Geometrically nonidentical π -electron circuits.

appropriate centrosymmetric octagons are attached exactly to the biphenylene structure formed by one square and two regular hexagons. Geometrically unidentical π -electron circuits are shown and numbered in Figure 1. The remaining circuits are omitted from it. The number of identical circuits is instead given in Table I for each circuit shown in Figure 1.

Calculated magnetic properties of nonbenzenoid species are often extremely sensitive to the degree of sophistication of the molecular orbital (MO) method used to compute them.³⁰⁻³² We adopt here what might be regarded as the best MO method available within a Hückel framework. It is a self-consistent Hückel

method, i.e., an iterative $\beta\omega'\omega''$ Hückel method.^{23,24,30-37} Its utility has repeatedly been verified by Gayoso, Mallion, Wilcox, and others.^{23,24,30-37} They found that the self-consistent Hückel method is best suited for computing magnetic properties of nonbenzenoid hydrocarbons.^{23,24,30-32,35-37} Wilcox et al. showed that it is one of the best MO methods for biphenylenoid hydrocarbons.^{23,24,37}

In this approach, each resonance integral parameter is expressed as a function of the bond order

$$k_{st} = \exp(0.6327p_{st} - 0.4218) \quad (6)$$

where p_{st} is the bond order for the s - t π bond. This function is essentially the same as Wilcox's function,^{23,24,37} which was taken from the bond order-bond length correlation of Dewar and

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Table I. Circuit Currents and Circuit Susceptibilities for Biphenylene and Related Hydrocarbons

circuit type	no. of identical circuits	circuit current, I_0	circuit susceptibility, χ_0
Biphenylene (1)			
r_1	2	1.084	1.084
r_2	1	-0.129	-0.049
r_3	2	-0.198	-0.275
r_4	1	-0.278	-0.664
Cycloocta[def]biphenylene (2)			
r_1	1	-0.232	-0.411
r_2	2	1.146	1.146
r_3	1	-0.156	-0.060
r_4	2	-0.195	-0.541
r_5	1	0.047	0.101
r_6	2	-0.218	-0.302
r_7	2	-0.029	-0.092
r_8	1	-0.279	-0.666
r_9	1	-0.182	-0.687
r_{10}	1	0.136	0.564
Dicycloocta[1,2,3,4-def:1',2',3',4'-jkl]biphenylene (3)			
r_1	2	-0.194	-0.343
r_2	2	1.246	1.246
r_3	1	-0.183	-0.070
r_4	2	0.095	0.204
r_5	4	-0.216	-0.597
r_6	2	-0.246	-0.341
r_7	2	0.079	0.356
r_8	2	-0.212	-0.798
r_9	1	-0.144	-0.565
r_{10}	1	-0.292	-0.695
r_{11}	4	-0.035	-0.110
r_{12}	2	-0.162	-0.797
r_{13}	2	0.145	0.602
r_{14}	1	-0.057	-0.338

Gleicher.³⁸ Equation 6 is set so as to make the benzene carbon-carbon bond lengths reproduced exactly.

Coulomb integral parameters are set equal to zero, since the present hydrocarbons are all alternant with uniform charge distribution. Therefore, the Hückel method we adopt is formally identical with that of Coulson and Golebiewski.^{39,40} MO calculations were iterated until resonance integrals were made self-consistent with the corresponding bond orders. The obtained wave functions were used to calculate circuit currents by means of eq 5.

Results and Discussion

The calculated circuit currents are listed in units of I_0 in Table I. The plus and minus signs indicate diatropism and paratropism, respectively. The most interesting feature of these circuit currents is that $[4n + 2]$ -membered and $[4n]$ -membered circuits are always diatropic and paratropic, respectively. There are no exceptions. As far as π -electron circuits are concerned, the sign of magnetotropism thus seems to be predictable with confidence. This constitutes the Hückel-like rule of magnetotropism.

We previously proved that annulenes with $4n + 2$ π electrons exhibit a net rise in energy when they are subjected to a magnetic field.^{3,6,7,12} The Hückel-like rule of magnetotropism can again be proved theoretically. Total π -electron energy of an alternant hydrocarbon, placed in a magnetic field, is known to be roughly proportional to the logarithm of the field-dependent Z^* value^{1,2,41}

$$Z^* = |P_G(i) + H^2 \sum_i \left(\frac{eS_i}{c\hbar} \right)^2 P_{G-r_i}(i) \prod_{(st)}^{r_i} k_{st}| - H^2 \sum_i' \left(\frac{eS_i}{c\hbar} \right)^2 |P_{G-r_i}(i)| \prod_{(st)}^{r_i} k_{st} + H^2 \sum_i'' \left(\frac{eS_i}{c\hbar} \right)^2 |P_{G-r_i}(i)| \prod_{(st)}^{r_i} k_{st} \quad (7)$$

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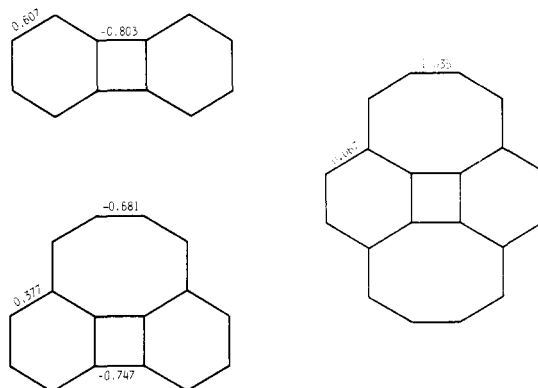


Figure 2. Bond currents in units of I_0 .

where $i = (-1)^{1/2}$, the single prime means summation over all $[4n + 2]$ -membered circuits, and the double prime means summation over all $[4n]$ -membered circuits.

The above expression for Z^* clearly indicates that all $[4n + 2]$ -membered circuits make the negative contribution to the thermodynamic stability when they are subjected to a magnetic field. Therefore, they make the negative contribution to the London susceptibility, which is the second derivative of the total π -electron energy with respect to the field strength.^{1,2} This means that $[4n + 2]$ -membered circuits bear diamagnetic circuit currents. Conversely, eq 7 indicates that all $[4n]$ -membered circuits make the positive contribution to the thermodynamic stability when they are subjected to a magnetic field. Therefore, they make the positive contribution to the London susceptibility. This means that $[4n]$ -membered circuits bear paramagnetic circuit currents. Such a structural dependence of Z^* gives the very reason why the magnetotropic analogue of the Hückel rule holds true for polycyclic conjugated hydrocarbons.

The above rather simple proof is applicable to all neutral alternant hydrocarbons and presumably to most neutral nonalternant hydrocarbons. It is not applicable to ionic or charged species because eq 7 is not defined for them.⁴¹ On the basis of this rule, all six-, ten-, fourteen-, and eighteen-membered circuits in Figure 1 can be said to be diatropic in nature, and all four-, eight-, twelve-, and sixteen-membered circuits in it are paratropic in nature. All circuits of the same shape happen to be similar in current intensity.

If Kekulé structures cannot be written for $G-r_i$, the circuit current induced in r_i is very small, and so is the circuit susceptibility. Remember that r_i stands for the i th circuit. For example, r_7 in cyclooctabiphenylene (2) and r_{11} in dicyclooctabiphenylene (3) are such examples. This feature, however, seems to be limited to alternant hydrocarbons only. In the case of nonalternant hydrocarbons, there often are odd-membered circuits in which large circuit currents are magnetically induced.⁴²

The calculated bond currents are presented in Figure 2. They agree exactly with the values obtained by means of the traditional London-McWeeny method.^{23,24,30-32,35-37,43} In principle, there is no rule for determining the sign of each bond current in a polycyclic system. Each bond current is given as a superposition of the currents induced in the circuits which share the very π bond in common. Related circuits vary from bond to bond. It is for this reason that the sign of a given bond current cannot be predicted readily. Furthermore, the sign often depends upon how to take into account the degree of bond alternation.^{30-32,41} It is in marked contrast to the sign of each circuit current, which is independent of the bond alternation introduced. Wilcox et al. stated that the calculated ring current (i.e., bond current) is a complex function of both the individual rings and the global connectivity of the molecule.³⁷ More accurately, it is a complex function of both the individual circuits and the way of introducing bond alternation.

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Dicyclooctabiphenylene (**3**) is one of the rare hydrocarbons in which the benzene rings have virtually no bond current.^{23,24} Benzenoid atropism in **3** can now be interpreted as follows. There are ten types of circuits which share every benzene ring. Three of them are diatropic, the remaining seven being paratropic. Large diatropism is predicted to arise from r_2 , r_7 , and r_{13} , while large paratropism is predicted to arise from r_5 , r_6 , r_8 , r_{10} , r_{11} , r_{12} , and r_{14} . Two identical circuits of the r_5 type can be chosen from **3**, in such a manner that they span the same benzene ring. The same is true for r_8 and r_{11} . Therefore, r_5 , r_8 , and r_{11} must be counted twice to evaluate the bond currents around each benzene ring. It follows that there are three diatropic and ten paratropic circuits in all.

As a result of the three diamagnetic circuit currents quenched mostly by the ten paramagnetic circuit currents, hydrocarbon **3** is expected to show neither marked upfield nor downfield shifts of the benzenoid protons. This was ascertained by NMR spectroscopy. All bond currents calculated for **3** are quite consistent with chemical shifts of all the protons.^{23,24} Such a consistency is also found for biphenylene (**1**) and cyclooctabiphenylene (**2**).^{21-24,37} Benzenoid diatropism in the series **1**, **2**, **3** is seen to decrease as the further annelation of cyclooctatetraene rings introduces a greater number of large $[4n]$ -membered π -electron circuits spanning the benzenoid rings.

The importance of a peripheral circuit has often been stressed for predicting not only aromaticity but also magnetotropism in a polycyclic conjugated system.⁴⁴⁻⁴⁶ The present analysis, however, clarified that a peripheral circuit is merely one of many circuits which contribute to magnetotropism and that a given peripheral bond current is again a combination of numerous circuit currents. As stated by Wilcox et al.,²³ perturbation by the central substructure is so great as to remove any simple predictive capability based upon periphery.

Circuit susceptibilities are also listed in Table I. London susceptibility of benzene, χ_0 , is a unit for them. The sum of all circuit susceptibilities for a given conjugated system is nothing other than London susceptibility for the system.² This way of evaluating London susceptibility resembles Gayoso's graph-theoretical one⁴⁷ based on Randić's conjugated circuit theory,⁴⁸⁻⁵⁰ in that both ascribe London susceptibility to the π -electron circuits or the like. London susceptibilities of **1**, **2**, and **3** are 0.905, -0.739,

and -4.240, respectively, in units of χ_0 .

In general, large circuits contribute much less to the thermodynamic stability or instability of a polycyclic system, because both the absolute value of $P_{G-r_i}(i)$ and the product of the resonance integral parameters around the bonds of r_i are very small for large circuits. On the other hand, the factor of the circuit area squared appears in the expression for circuit susceptibility (eq 2). Owing to this factor, large circuits contribute much more to the value of London susceptibility. The circuit area squared is unrelated to the energy of a cyclic conjugated system within a Hückel framework. Therefore, London susceptibility is not always good as a criterion for determining the degree of aromatic stabilization. Diamagnetic susceptibility exaltation^{51,52} is physically identical with London susceptibility, so it likewise reflects magnetotropism of large π -electron circuits to a greater extent. Hydrocarbons **1-3** seem to be considerably stabilized by bond alternation, whereas London susceptibility increases abruptly in this order: **1** < **2** < **3**. In fact, kinetic or apparent stability decreases in the same order,²¹⁻²⁴ but it is obvious that the order of thermodynamic stability cannot be estimated from it.

Concluding Remarks

The general graph-theoretical formula for circuit currents (eq 5) was presented in this paper. The series of related polycyclic hydrocarbons **1-3** was adopted to test the utility of this formula. The unusual magnetotropism of these compounds was interpreted successfully in terms of their circuit currents. Thus, eq 5 proved very useful for establishing the structure-magnetotropism correlation for polycyclic conjugated systems. This fact encourages us to extend the same circuit current analysis to a wide variety of polycyclic conjugated systems, both in the neutral and ionic states. Bond currents obtained by means of eq 5 are of course identical with those obtained by means of Pople's original method.^{10,53}

By the way, any monocyclic conjugated system exhibits only one circuit current, which constitutes all the bond currents. If a given conjugated system is bicyclic, the peripheral circuit current may often be predominant in its magnetotropic behavior. For butalene and bicyclo[6.2.0]decapentaene, the sign of each bond current is really determined by that of the peripheral circuit current.⁴² They are then expected to be diatropic as a whole.

Registry No. **1**, 259-79-0; **2**, 39873-27-3; **3**, 10454-31-6.

(44) See, e.g.: Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448.

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