Theor Chem Acc (2010) 126:339–349
DOI 10.1007/s00214-009-0692-z

REGULAR ARTICLE

# Theoretical basis for the correlation between energetic, magnetic, and electron density criteria of aromaticity: definition of molecular circuit electric conductance

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Received: 4 September 2009 / Accepted: 4 November 2009 / Published online: 22 November 2009

**Abstract** Using a semiclassical model, a theoretical basis for the correlation between energetic, magnetic, and electron density criteria of aromaticity has been established. The key quantity that links ring current intensity, topological resonance energy, and multicenter electron delocalization is the molecular circuit electric conductance, which is defined as the inverse of the resistance of the molecular circuit to the electron flow when an external electromotive force is exerted on it. The particular case of an external magnetic field applied perpendicularly to the molecular plane is employed here as source of the electromotive force. In addition, it is shown how aromatic stabilization can be estimated quantitatively by means of multicenter electron delocalization in PAHs and nitrogenated polyheterocyclic compounds.

**Keywords** Aromaticity · Ring electron current · Multicenter electron delocalization · Electric conductivity

## 1 Introduction

Since the introduction of aromaticity as the reason for the extra stabilization of some cyclic and polycyclic compounds, numerous criteria based on the calculation of different properties have been proposed for its estimation [1, 2]. This is one of the most controversial aspects of the aromaticity concept, a multiple number of properties that are unequivocally related to it but that sometimes leads to contradictory conclusions. Hence, it has been frequently stated that assessing the aromatic character of a given molecule cannot be done with a simple evaluation of a property or an index but requires considering different criteria simultaneously [3–6].

Among these criteria, those based on energetic [7–10] and magnetic properties [11–16] are probably the most recognized, although those based on direct measures of electron delocalization have gained importance in the last years [17, 18]. Indeed it has to be mentioned that geometry-based criteria [19] have been also extensively employed for estimating aromaticity with great success in particular cases. Unfortunately, geometry-based aromaticity indices lack of general application and depend strongly on the use of several parameters obtained from arbitrary reference systems. For these reasons, criteria based on magnetic, energetic, and electron density properties have gained on those based on molecular geometry.

Most of the determinations of the extra energetic stabilization of an aromatic system, such as the aromatic stabilization energy, ASE, also require using arbitrary reference systems [10]. This is an important drawback, since different references provide different results for the same aromatic system. However, not all the proposed methods for calculating the aromatic stabilization depend on the use of arbitrary reference molecules. It has been defined a quantity that do not rely on the choice of arbitrary reference molecules but depends exclusively on the bonding topology. This quantity is the topological resonance energy, TRE, and was put forward independently by Aihara [20] and Gutman et al. [21]. The limitation of the TRE is that it has been defined within the context of the Hückel molecular orbital theory, HMO. Although in principle it could be extended to more accurate quantum chemical methods, its application is at present just limited to the HMO level.

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However, the TRE has been shown to provide useful interpretations of many experimental evidences related to the aromaticity in polycyclic aromatic hydrocarbons, PAHs, and polyheterocyclic compounds. It has provided a theoretical background for linking magnetic and energetic aromaticity criteria [22]. Thus, using Hückel-London theory of diamagnetism, Aihara was able to embody mathematically the experimentally observed relation between magnetic susceptibility due to ring electron currents and energetic stabilization due to cyclic conjugation [23–26]. The latter is represented by the circuit resonance energy, CRE, [22] in the Aihara's formulation and the conjugated circuit energy, CCE [27, 28] in the Gutman's formulation. Both CRE and CCE are closely related and perfect correlation has been found between them [22]. The relevance of the works by Aihara, even when they have been carried out in the framework of the HMO theory, is reflected on the publication of numerous papers in top-ranked chemistry journals (see references above).

On the other hand, Bultinck et al. have proven very recently that at least in PAHs the nucleus independent chemical shift, NICS [11] calculated for a given benzene ring mainly results from the superposition of ring currents circulating around different circuits of benzene, naphtalene, anthracene, etc. [29]. They employed the correlation found between NICS and multicenter electron delocalization indices, *n*-DIs or MCIs, obtained by multivariate linear regression for their proof. Subsequently they have employed the parameters obtained from such correlation to reconstruct, in a series of benzenoid hydrocarbons, the ring current maps obtained from ab initio calculations [30]. Thus, the relation between multicenter electron delocalization and magnetic susceptibility due to ring currents has been already established in a heuristic manner.

The main aim of this work is to present a simple formulation merging the three main conceptual aspects of aromaticity, i.e., resonance energy, magnetic susceptibility due to ring currents and multicenter electron delocalization. In this paper, the physical meaning of the previously defined circuit resonance energy is investigated within the framework of the electromagnetism laws. Therefore, it is found that the CRE is in fact the circuit electric conductance. The connection between the aromatic stabilization and the electric and magnetic properties of aromatic systems is established using a semi classical model that merges classical electromagnetism laws with the Aihara's graph theory of ring-current diamagnetism. Some particular aspects of the magnetic behavior of planar annulenes, such as the effect of bond localization are rationalized with the model. Moreover, the physical origin of the correlation between multicenter electron delocalization and ring current maps in planar aromatic hydrocarbons is also rationalized within the same context. The main ideas obtained for these systems are in turn extrapolated to other polycyclic aromatic systems.

## 2 Molecular circuit electric conductance

Pauling compared for the first time the moving of electrons in a conductor with that of the electrons in a conjugated polybenzenoid to get an estimation of the magnetic anisotropy in these systems due to induced electron ring currents [31]. Therefore, he was able to predict the electron current intensity induced by a time-dependent magnetic field in aromatic molecules, such as anthracene by using the Maxwell's equations. Comparison with experimental results demonstrated that the analogy established by Pauling is perfectly valid. Here, we will follow a similar way to derive mathematical relations between resonance energy, circuit electric conductivity, and ring electron delocalization in cyclic planar aromatic molecules like benzene.

Thus, consider a time-dependent magnetic field, **B**, uniformly distributed around the area enclosed by a circuit and applied perpendicularly to the circuit plane. Combining the Faraday–Lenz and Ohm's laws one can express the intensity, *I*, of the ring electron current induced by **B** as in Eq. 1,

$$I = -k\frac{A}{L}S\frac{\partial \mathbf{B}}{\partial t} \tag{1}$$

where *L* is the circuit length, *A* is the conductor section and *S* and *k* are the enclosed area and the circuit electric conductivity, respectively. Equation 1 can also be expressed in terms of the electric conductance, *G*, which is represented by Eq. 2.

$$G = k\frac{A}{L} \tag{2}$$

If the circuit corresponds to the cyclic array of carbon–carbon bonds of a cyclic planar hydrocarbon like benzene, then Eq. 1 transforms into Eq. 3,

$$I = -k\frac{A}{r_{\mathrm{CC}}}\frac{S}{n}\frac{\partial \mathbf{B}}{\partial t} \tag{3}$$

where $r_{\mathrm{CC}}$ represents the averaged CC bond distance and *n* is the number of atoms in the ring.

On the other hand, the induced ring electron current, *I*, can also be expressed in terms of the diamagnetic susceptibility, $\chi_d$, the magnetization vector, **H**, and the enclosed area, *S*, as in Eq. 4,

$$I = \frac{\chi_d}{S}\mathbf{H} \tag{4}$$

which transforms into Eq. 5 by using the well-known relation between the magnetic fields, **B** and **H**.

$$I = \frac{\chi_d}{\mu_0(1+\chi_d)}\frac{\mathbf{B}}{S} \tag{5}$$

Considering that the averaged carbon–carbon bond distance keeps approximately constant for the series of cyclic planar hydrocarbons and that $A$ must be a common value, one can merge Eqs. 3 and 5 to get an expression of $\chi_d$ in terms of the ring area, the number of carbon atoms and the circuit electric conductivity.

$$\frac{\chi_d}{1+\chi_d} = -k\frac{S^2}{n}\frac{A}{r_{CC}}\frac{\mu_0}{\mathbf{B}}\frac{\partial \mathbf{B}}{\partial t} \tag{6}$$

Assuming that $\chi_d \ll 1$ and using the value of $\chi_d$ for the benzene ring as reference one obtains,

$$\chi_d = \frac{k}{k^0}\left(\frac{S}{S^0}\right)^2\frac{n^0}{n}\chi_d^0 \tag{7}$$

where the terms denoted by the superindex 0 are those corresponding to the benzene ring. It must be noticed that $\chi_d$ in Eq. 7 represents the contribution to the total magnetic susceptibility of the ring electron current induced by $\mathbf{B}$.

Molecular circuit electric conductivity in Eq. 7 is directly related with the aromatic stabilization of the ring. Therefore, using topological arguments and the extended formulation of the Hückel-London theory of diamagnetism [23, 24], $\chi_d$ and $I$ can be expressed in terms of the circuit resonance energy, CRE, introduced by Aihara [22]. These magnitudes adopt, respectively, the forms of Eqs. 8 and 9.

$$\chi_d = \frac{\mathrm{CRE}}{\mathrm{CRE}^0}\left(\frac{S}{S^0}\right)^2\chi_d^0 \tag{8}$$

$$I = \frac{\mathrm{CRE}\ S}{\mathrm{CRE}^0 S^0}I^0 \tag{9}$$

Since CRE and TRE are found to be proportional [32, 33], CREs could be replaced by TREs in Eqs. 8 and 9. By comparison between Eqs. 7 and 8 and taken into account the relation between $k$ and $G$, it can be established that the relative value of the circuit (or topological) resonance energy is equal to the relative electric conductance of the circuit. Thus, the following relation between circuit (or topological) resonance energies and molecular circuit electric conductance can be established.

$$\frac{\mathrm{CRE}}{\mathrm{CRE}^0} = \frac{G}{G^0} \tag{10}$$

It must be noticed that Eq. 10 is also consistent with the particular case of antiaromatic cycles. Antiaromatic systems display negative CRE (or TRE) values, which according to Eq. 10 lead to negative values of the electric conductance. This negative electric conductance could explain, within our semi classical model, why ring electron currents in these systems are magnetically induced in a paratropic sense instead of diatropic.

It is also interesting to investigate how the model reproduces the effects of bond localization on magnetically induced ring currents in $(4N+2)$ annulenes. Therefore, it has been shown that although ring current intensity decreases when strong bond localization is imposed on benzene, a strong diatropic current still survives [34–36]. On the contrary, ring currents tend to disappear for the series of large $D_{3h}$ planar annulenes, $C_nH_n$ ($n > 30$), with the occurrence of bond localization [37, 38]. The opposite behavior is found for the same series of compounds when bond delocalization is imposed by constraining the geometries to $D_{6h}$ symmetry, so a strengthening of the ring currents is found as $n$ growths [37, 38]. The circuit electric conductance should follow a similar behavior when bond localization is imposed. It must be taken into account, however, that the relation between circuit electric conductance and ring current intensity depends strongly on the circuit area, $S$.

$$\frac{I}{I^0} = \frac{G}{G^0}\frac{S}{S^0} \tag{11}$$

Approaching the ring area by the circle area, Eq. 11 can be transformed into Eq. 12.

$$\frac{I}{I^0} = \frac{G}{G^0}\left(\frac{n}{n^0}\right)^2 \tag{12}$$

Although $G$ has been defined in terms of the CRE (Eq. 10), it is preferred in the following discussion to rewrite it in terms of the CCE introduced by Gutman et al. [27, 28]. It must be noticed that both CRE and CCE represent the same entity, so that not only a perfect correlation has been found between them but also similar values are obtained for the same ring [22]. So, replacing the CREs by the CCEs in Eq. 10 and using the Newton–Rapshon method to calculate the roots for the reference polynomial employed in the calculation of the CCE (a similar procedure followed by Aihara to calculate the CREs [26]), one arrives to the following expression for the circuit electric conductance of a cyclic planar aromatic hydrocarbon,

$$\frac{G}{G^0} = -\frac{\beta}{\mathrm{CCE}^0}\sum_j \frac{P_C(x_j)}{P_{G'}(x_j)} \tag{13}$$

where $P_C$ represents the contribution to the characteristic polynomial from the cyclic array of atoms (the $n$—product of beta resonance integrals which results from the expansion of the secular determinant in the HMO approach). $P_{G'}$ is the first derivative of the characteristic polynomial and $x_j$ represent their roots (for details about the graph-theoretical treatment of the resonance energy see for instance references [22, 26–28]). In the case of annulenes with perfect bond delocalization $P_C$ is equal to 2 (the clock-wise plus the counterclock-wise $n$-product of beta resonance integrals) since all beta integrals are equivalent. Therefore, the ring current intensity adopts the following form.

$$\frac{I}{I^0} = -\frac{2\beta}{\mathrm{CCE}^0}\left(\frac{n}{n^0}\right)^2 \sum_j \frac{1}{P_{G'}(x_j)} \tag{14}$$

On the other hand, bond localization may be represented within the framework of the HMO approach by assuming the non-equivalency of beta integrals. This can be done in an arbitrary manner by considering that bond localization comes with a symmetrical reduction/increase of half ($n/2$) of the beta integrals by an amount of $\beta k$ (with $0 < k < 1$). This leads to the following expression for the ring current intensity in a $(4N + 2)$ annulene with bond localization,

$$\frac{I}{I^0} = -\frac{2\beta}{\mathrm{CCE}^0}\left(\frac{n}{n^0}\right)^2 (1+k)^{n/2}(1-k)^{n/2} \sum_j \frac{1}{P_{G'}(x_j)} \tag{15}$$

which can be rewritten as,

$$\frac{I}{I^0} = -\frac{2\beta}{\mathrm{CCE}^0}\left(\frac{n}{n^0}\right)^2 \mathrm{e}^{-an} \sum_j \frac{1}{P_{G'}(x_j)} \tag{16}$$

with $a = [\ln(1 + k) + \ln(1 - k)]/2$.

The ring current intensity in $(4N + 2)$ annulenes is then proportional to the function $f$ given by.

$$f = \left\{ \begin{array}{ll} n^2 & \text{delocalized bonds} \\ n^2 \mathrm{e}^{-an} & \text{localized bonds} \end{array} \right\} \tag{17}$$

The shape of $f$ is shown in Fig. 1 for values of $n$ comprised between 6 ($N = 1$, benzene) and 82 ($N = 20$, $C_{82}H_{82}$) in the case of delocalization and localization of bonds (with $k = 0.5$ for the latter). The behavior of this function seems to rule the trends followed by the current intensity along the series of $(4N + 2)$ annulenes. In the case of bond delocalization, the current intensity increases with $n^2$ in agreement with the well-known relation between resonance energy and ring size derived at the HMO level [39]. On the contrary, when bond localization is imposed and its effect on the values of the beta integrals considered, the current intensity decreases dramatically when $n$ is large, in agreement with the recently computed ring current maps of large $D_{3h}$ annulenes [38].

In connection with the discussion presented above, the relation between bond delocalization and resonance energy or in particular the relation between multicenter electron delocalization and topological resonance energy can be represented using multicenter electron delocalization indices. Hence, the resonance energies in Eq. 8 can be substituted for their expressions in terms of the normalized Giambiagi multicenter delocalization indices (or multicenter bond indices) [40] derived by Cioslowski et al. within the framework of the HMO theory for $(4N + 2)$ annulenes [41].

$$\chi_d = \frac{\Delta_n^{1/n}}{\Delta_{n^0}^{1/n^0}} \frac{n^0}{n} \left(\frac{S}{S^0}\right)^2 \chi_d^0 \tag{18}$$

In Eq. 18, the unnormalized multicenter index is denoted by $\Delta_n$. Merging Eqs. 7 and 18, one arrives to a mathematical relation between multicenter bonding and molecular circuit electric conductivity.

$$\frac{k}{k^0} = \frac{\Delta_n^{1/n}}{\Delta_{n^0}^{1/n^0}} \tag{19}$$

The electron current intensity per magnetic field unit circulating around the ring can also be expressed in terms of the normalized multicenter index.

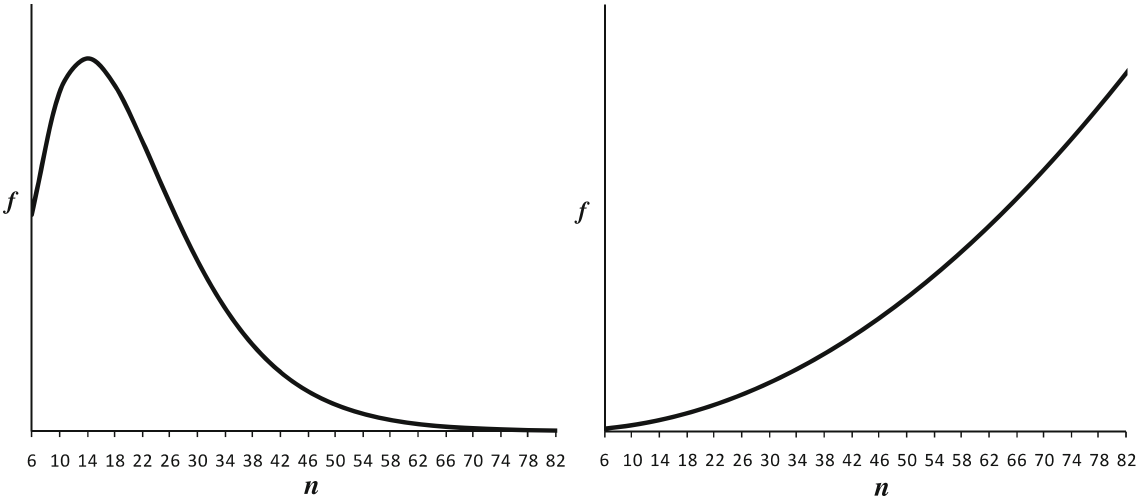


**Fig. 1** Shape of the function $f$ for the case of localized (**a**) and delocalized (**b**) bonds (see text for details). Scale of the axis $y$ in plot (**b**) is much larger than that in plot (**a**), first points ($n = 6$) are 15.2 and 36.0 for (**a**) and (**b**), respectively

$$I = \frac{\Delta_n^{1/n}}{\Delta_{n^0}^{1/n^0}} \frac{n^0}{n} \frac{S}{S^0} I^0. \quad (20)$$

## 3 Polycyclic and heterocyclic systems

Polycyclic aromatic molecules can be considered as systems composed by several ring circuits that are fused or superimposed. Aihara in its graph-theoretical interpretation of the Hückel-London theory of diamagnetism proved that for polycyclic aromatic hydrocarbons, PAHs, the magnetically induced ring electron current and then also properties associated to it are additive functions of their individual circuit components [22]. This has also been shown very recently using conjugated circuits [42]. Thus, the total susceptibility exaltation, ring current intensity and aromatic stabilization in a PAH can be partitioned into individual ring circuit contributions.

Aihara defined the circuit resonance energy, CRE, as the individual contribution of a circuit to the total resonance energy [22]. Thus, Eqs. 8–10 still hold for a given circuit $i$ in a PAH.

$$\chi_{d,i} = \frac{\mathrm{CRE}_i}{\mathrm{CRE}^0}\left(\frac{S_i}{S^0}\right)^2 \chi_d^0 \quad (21)$$

$$I_i = \frac{\mathrm{CRE}_i}{\mathrm{CRE}^0} \frac{S_i}{S^0} \chi_d^0 \quad (22)$$

$$\frac{\mathrm{CRE}_i}{\mathrm{CRE}^0} = \frac{G_i}{G^0} \quad (23)$$

Therefore, the relation between molecular circuit electric conductance and resonance energy derived in the previous section for monocyclic systems is perfectly valid for the individual circuits constituting a polycyclic system.

It must be noticed that the procedure followed to get the CREs in the Aihara's formulation is equivalent to the application of the superposition theorem to get the total current flow in electric circuit's theory. Thus, in order to get the $\mathrm{CRE}_i$ for a given ring circuit the remaining ring terms are removed from the characteristic polynomial, in other words a value zero is assigned to remaining rings. This allows calculating the $I_i$ corresponding to the ring circuit $i$, the summation of the electron currents of all the circuits passing through a given bond gives the total current circulating by the bond. On the other hand, when applying the superposition theorem the individual effect of each generator of a given electric circuit is calculated. All the generators other than the one being considered are removed; either short-circuited in the case of voltage generators or open circuited in the case of current generators. This means for our case (polycyclic molecules) that conductances zero are assigned to all the circuits other than the one being considered (which is equivalent to consider that the CREs are zero). The total current through a particular branch (bond) is then calculated by summing all the individual currents.

Unfortunately, the non-additive character of the normalized multicenter index prevents its use for the calculation of magnetic and electric properties in polycyclic systems, and then Eqs. 18–20 are not applicable in polycyclic systems. The nature of the index normalization is responsible of this non-additive character. Thus, the normalized multicenter index derived by Cioslowski et al. represents the geometric mean of the Coulson bond orders for a given ring [41]. Thus, the geometric mean of bond orders is expected to reflect properly the cyclic electron delocalization in monocyclic aromatic hydrocarbons where there is a one-to-one correspondence between bond order and ring index. However, such correspondence does not hold anymore when bonds support more than one ring circuit as in the case of polycyclic aromatic systems.

On the other hand, qualitative considerations expounded in the previous section about the relation between ring electron delocalization and circuit electric conductivity should still hold for polycyclic systems, but in this case, we need to look for a more appropriate normalization of the index. We have found that a simple reformulation of Eq. 19 provides satisfactory results for PAHs and some polyheterocyclic compounds. This reformulation has been done according to the following statements:

1. The electric conductivity through a given bond may be expressed by a summation of the electric conductivities of the circuits passing through the bond.
2. Monocyclic systems are particular cases of polycyclic systems, so that the expression of the circuit electric conductivity in PAHs must become Eq. 19 for the particular case of benzene.

Statement 1 is a consequence of the additive character of the induced electron currents in polycyclic systems (superposition theorem), whereas statement 2 is an obligated condition for the expression to be of general application. According to statements 1 and 2, an appropriate expression for the electric conductivity through a given bond is:

$$k = \sum_i w_i k_i \quad (24)$$

where $k_i$ is the expression of the circuit electric conductivity for isolated circuits (Eq. 19) and $w_i$ represents the weight of the circuit $i$ in the total electric conductivity or, in other words, how the electric conductivity changes when the circuit is incorporated in a polycyclic system. The summation runs over all the circuits passing through the bond.

Evidently, now the problem is to give form to the weight factors, $w_i$, in Eq. 24. A magnitude that can be suitable for this purpose is the unnormalized multicenter delocalization index. Some recent works by Bultinck and co-workers support the use of unnormalized multicenter indices to represent the weight factors. They have found using multivariate linear regression that the sum of multicenter delocalization indices calculated for the different circuits in a benzenoid hydrocarbon correlate well with topological resonance energies [43], NICS indices [29] and ring current

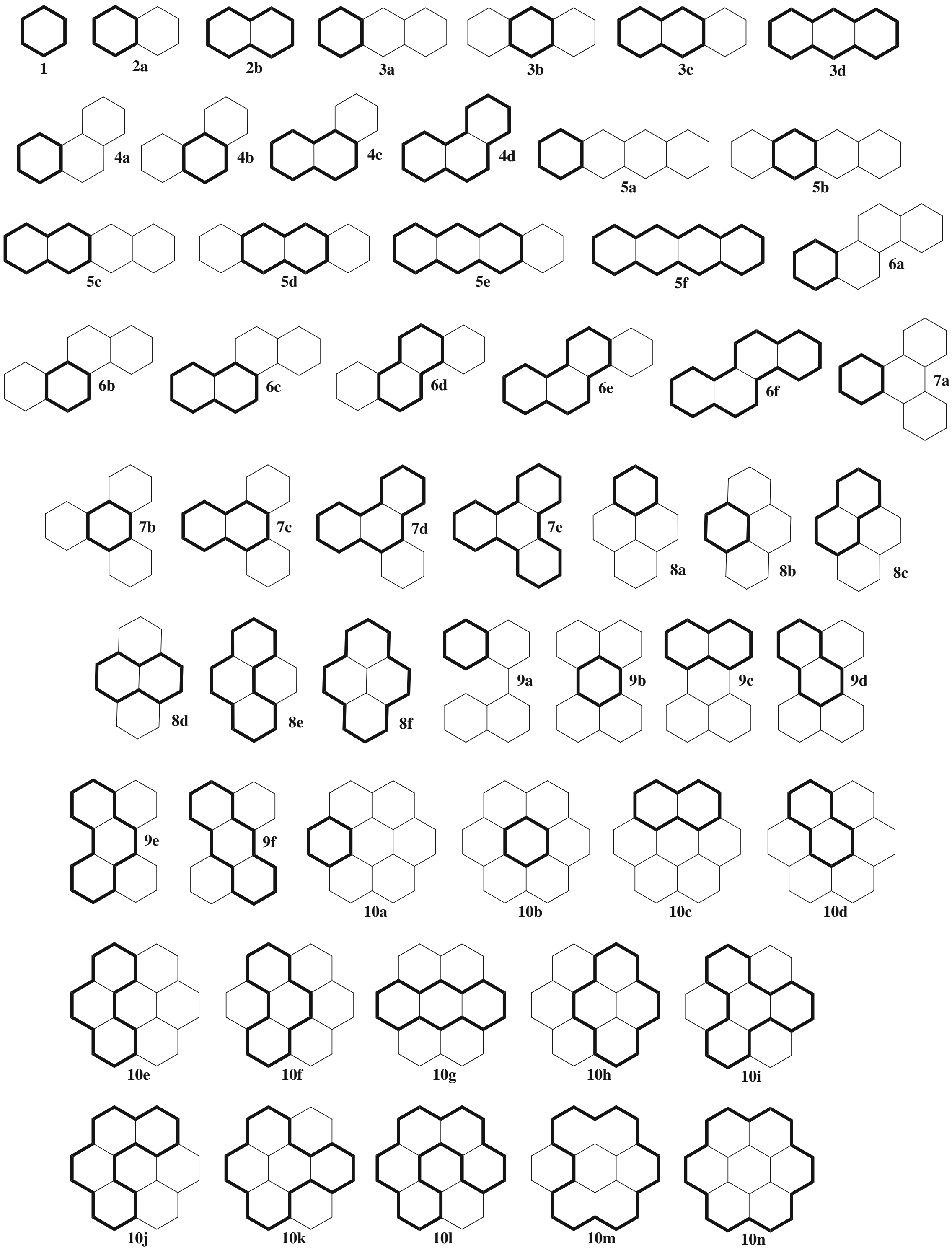


**Fig. 2** Ring circuits containing $4N + 2$ electrons for a series of ten PAHs

maps [30]. Therefore, based on their findings we propose to construct an ansatz for $w_i$ in terms of unnormalized multicenter indices.

$$w_i = \frac{\Delta_{n_i}}{(\Delta_{n^0})^{n_i/n^0}} \tag{25}$$

In Eq. 25, $w_i$ is given with respect to benzene (as all the properties considered here), so fulfilling the statement (2) for the case of benzenoid hydrocarbons (it adopts the value 1 for the case of benzene). The exponent is introduced in order to account for the size dependence of the multicenter index when $n_i$ is different from $n^0$.

Introducing Eqs. 25 and 19 into Eq. 24, one obtains an expression for the relative electric conductivity through a given bond in a polycyclic system.

$$\frac{k}{k^0} = \sum_i \frac{\Delta_{n_i}^{\frac{n_i+1}{n_i}}}{\Delta_{n^0}^{\frac{n_i+1}{n^0}}} \tag{26}$$

Additionally, approximated expressions for the ring current intensity, ring current diamagnetic susceptibility, and circuit resonance energy follow from Eq. 26.

$$I_i = \frac{\Delta_{n_i}^{\frac{n_i+1}{n_i}}}{\Delta_{n^0}^{\frac{n_i+1}{n^0}}} \frac{S_i}{S^0} \frac{n^0}{n_i} I^0 \tag{27}$$

$$\chi_{d,i} = \frac{\Delta_{n_i}^{\frac{n_i+1}{n_i}}}{\Delta_{n^0}^{\frac{n_i+1}{n^0}}} \left(\frac{S_i}{S^0}\right)^2 \frac{n^0}{n_i} \chi_d^0 \tag{28}$$

$$\mathrm{CRE}_i = \frac{\Delta_{n_i}^{\frac{n_i+1}{n_i}}}{\Delta_{n^0}^{\frac{n_i+1}{n^0}}} \frac{n^0}{n_i} \mathrm{CRE}^0 \tag{29}$$

Equations 28 and 29 will be employed here to check the reliability of expression 25.

In Table 1 are the values of $k_i$, $w_i$, and $\mathrm{CRE}_i$ obtained using Eqs. 25, 26 and 29, respectively, for all the aromatic circuits [containing $4N + 2$ pi electrons ($N = 1, 2, 3,\ldots$)] depicted in Fig. 2. CREs obtained with Eq. 29 are compared in the table with those calculated by Aihara at the HMO level [22] (Fig. 3).

Multicenter indices were obtained from one-electron density matrices calculated at the HMO and B3LYP/STO-3G levels (molecular geometries taken from reference [44]). The one-electron density matrix obtained from SCF calculations was projected onto the space formed by the $p_z$ orbitals, the axis $z$ being that perpendicular to the molecular plane. Multicenter indices so obtained reflect exclusively the $\pi$-electron delocalization. It must be remarked that HMO and SCF calculations (using minimal basis set) provided very similar results, so that only those obtained at the SCF level will be shown. Due to the high

**Table 1** Molecular circuit electric conductivities for hypothetical isolated rings, circuit weight factors, and circuit resonance energies for the circuits depicted in Fig. 2

| Ring | $k_i$[a] | $w_i$ | CRE (estimated) | CRE[b] |
|---|---|---|---|---|
| 1a | 1.000 | 1.000 | 0.222 | 0.222 |
| 2a | 0.913 | 0.580 | 0.118 | 0.112 |
| 2b | 0.933 | 0.499 | 0.062 | 0.065 |
| 3a | 0.875 | 0.450 | 0.088 | 0.090 |
| 3b | 0.865 | 0.419 | 0.081 | 0.063 |
| 3c | 0.898 | 0.341 | 0.041 | 0.035 |
| 3d | 0.913 | 0.282 | 0.024 | 0.027 |
| 4a | 0.938 | 0.683 | 0.142 | 0.141 |
| 4b | 0.808 | 0.279 | 0.050 | 0.052 |
| 4c | 0.874 | 0.260 | 0.030 | 0.027 |
| 4d | 0.904 | 0.243 | 0.021 | 0.019 |
| 5a | 0.854 | 0.388 | 0.074 | 0.086 |
| 5b | 0.839 | 0.349 | 0.065 | 0.052 |
| 5c | 0.881 | 0.282 | 0.033 | 0.027 |
| 5d | 0.874 | 0.260 | 0.030 | 0.020 |
| 5e | 0.894 | 0.210 | 0.018 | 0.015 |
| 5f | 0.906 | 0.169 | 0.011 | 0.013 |
| 6a | 0.930 | 0.648 | 0.134 | 0.132 |
| 6b | 0.839 | 0.350 | 0.065 | 0.066 |
| 6c | 0.892 | 0.320 | 0.038 | 0.037 |
| 6d | 0.823 | 0.143 | 0.016 | 0.012 |
| 6e | 0.865 | 0.131 | 0.011 | 0.008 |
| 6f | 0.889 | 0.120 | 0.008 | 0.006 |
| 7a | 0.953 | 0.749 | 0.159 | 0.165 |
| 7b | 0.717 | 0.136 | 0.022 | 0.024 |
| 7c | 0.814 | 0.128 | 0.014 | 0.010 |
| 7d | 0.860 | 0.122 | 0.010 | 0.007 |
| 7e | 0.887 | 0.116 | 0.008 | 0.005 |
| 8a | 0.904 | 0.545 | 0.109 | 0.099 |
| 8b | 0.814 | 0.292 | 0.053 | 0.051 |
| 8c | 0.869 | 0.246 | 0.029 | 0.019 |
| 8d | 0.821 | 0.139 | 0.015 | 0.006 |
| 8e | 0.894 | 0.208 | 0.018 | 0.013 |
| 8f | 0.903 | 0.238 | 0.020 | 0.013 |
| 9a | 0.898 | 0.526 | 0.105 | 0.102 |
| 9b | 0.691 | 0.109 | 0.017 | 0.022 |
| 9c | 0.916 | 0.417 | 0.051 | 0.054 |
| 9d | 0.784 | 0.088 | 0.009 | 0.004 |
| 9e | 0.831 | 0.075 | 0.006 | 0.001 |
| 9f | 0.831 | 0.075 | 0.006 | 0.001 |
| 10a | 0.851 | 0.381 | 0.072 | 0.067 |
| 10b | 0.770 | 0.209 | 0.036 | 0.030 |
| 10c | 0.853 | 0.205 | 0.023 | 0.015 |
| 10d | 0.818 | 0.134 | 0.015 | 0.005 |
| 10e | 0.854 | 0.110 | 0.009 | 0.005 |
| 10f | 0.839 | 0.086 | 0.007 | 0.002 |
| 10g | 0.839 | 0.086 | 0.007 | 0.001 |

**Table 1** continued

| Ring | $k_i$[a] | $w_i$ | CRE (estimated) | CRE[b] |
|---|---|---|---|---|
| 10h | 0.854 | 0.110 | 0.009 | 0.002 |
| 10i | 0.855 | 0.059 | 0.004 | 0.001 |
| 10j | 0.851 | 0.055 | 0.003 | 0.001 |
| 10k | 0.863 | 0.071 | 0.005 | 0.001 |
| 10l | 0.843 | 0.034 | 0.002 | 0.001 |
| 10m | 0.875 | 0.090 | 0.006 | 0.001 |
| 10o | 0.887 | 0.115 | 0.008 | 0.004 |

[a] Values relative to that of benzene

[b] Values taken from reference [22]

computational cost that requires the use of large basis sets in the calculation of multicenter indices of circuits containing a large number of centers we have employed a minimal basis set (STO-3G). It has been shown that the pseudo-$\pi$ approach [45], where carbon atoms are replaced by hydrogens and the STO-3G basis set is employed, applied on the calculation of multicenter indices provides accurate results [46]. However, its application is restricted to polycyclic aromatic hydrocarbons, so that we have not employed the pseudo-$\pi$ method here but used minimal basis set.

As one can see in Table 1, graphically represented in Fig. 3, there is a very good correspondence between estimated and calculated values, with the exception of large circuits of highly condensed PAHs such as perylene (9) and coronene (10), for which Eq. 29 overestimates the CRE values. This discrepancy is not significant for the calculation of topological resonance energies since the contribution to the aromatic stabilization of large circuits is negligible. However, it drives to important deviations in the calculation of ring currents and diamagnetic susceptibilities since these properties strongly depend on the circuit size. This can be observed in Fig. 4a, where the diamagnetic susceptibilities estimated using multicenter indices are compared with the London diamagnetic susceptibilities computed at the HMO level. As one can see, there is a very good correlation for the first 7 molecules, small deviations for molecules 8 and 9 and a dramatic deviation for molecule 10. Thus, contributions of large circuits are overestimated when the degree of ring condensation is high. On the contrary, the contributions of large circuits in molecules with lower degree of condensation are very well estimated using Eq. 28. This limits the use of Eq. 25 to the calculation of magnetic properties of polycyclic systems not displaying a large degree of condensation or the truncation of the calculations to circuits containing up to three benzene rings (see Fig. 4b), as performed by Bultinck et al. for the reconstruction of ring current maps in benzenoid hydrocarbons [30]. However, the fact that large circuits do not contribute significantly to the aromatic stabilization enables the use of Eq. 25 even for highly condensed polycyclic compounds. An extensive study of magnetically induced ring currents in highly condensed aromatic hydrocarbons has been performed by Fowler et al. [47–50].

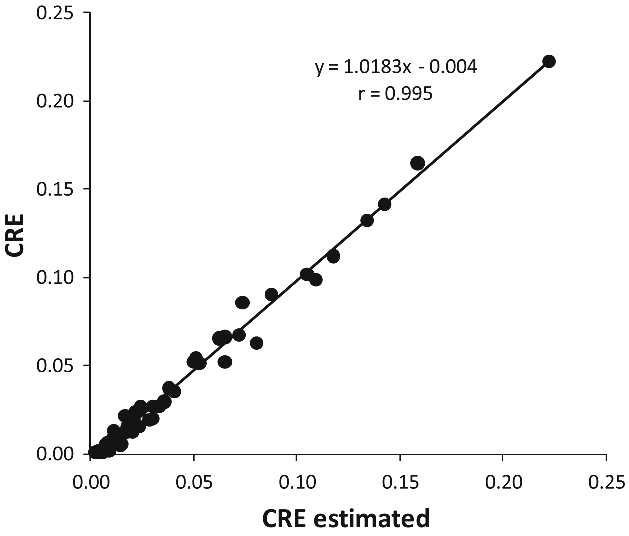


**Fig. 3** Representation of calculated (taken from reference [22]) versus estimated (using Eq. 29) cyclic resonance energies for the ring circuits depicted in Fig. 2

It must be noticed that relative $k_i$ values for hypothetical isolated rings do not change significantly along the series. Differences between rings containing the same number of centers come mainly from the value of $w_i$. This allows writing the topological resonance energy of a PAH as a multivariate equation,

$$\mathrm{TRE} \approx \mathrm{TRE}^0 \bar{k} \left[ \frac{1}{\left(\Delta_6^0\right)^{6/6}} \sum_i \Delta_6^i + \frac{1}{\left(\Delta_6^0\right)^{10/6}} \sum_j \Delta_{10}^j + \frac{1}{\left(\Delta_6^0\right)^{14/6}} \sum_k \Delta_{14}^k + \cdots \right] \qquad (30)$$

where terms in brackets multiplying each summation are the parameters obtained by multivariate linear regression in the work by Bultinck et al. [43], and $\bar{k}$ is the averaged conductivity for the hypothetical isolated rings (collected in Table 1).

We have also estimated the topological resonance energy of some polyheterocylic compounds such as carbazole, acridine and porphine (see Fig. 5). We have employed only nitrogenated compounds since the beta resonance integrals for nitrogen-carbon bonds are close to that of carbon–carbon bonds in both imine and amine nitrogen atoms [51]. So, they are expected to resemble as much as possible the behavior of the carbon–carbon bonds for the calculation of topological resonance energies. On

**Fig. 4** Representation of calculated (taken from reference [55]) versus estimated (using Eq. 28) total London diamagnetic susceptibilities, **a** including all the circuits, and **b** removing circuits containing more than three benzene rings in the highly condensed PAHs

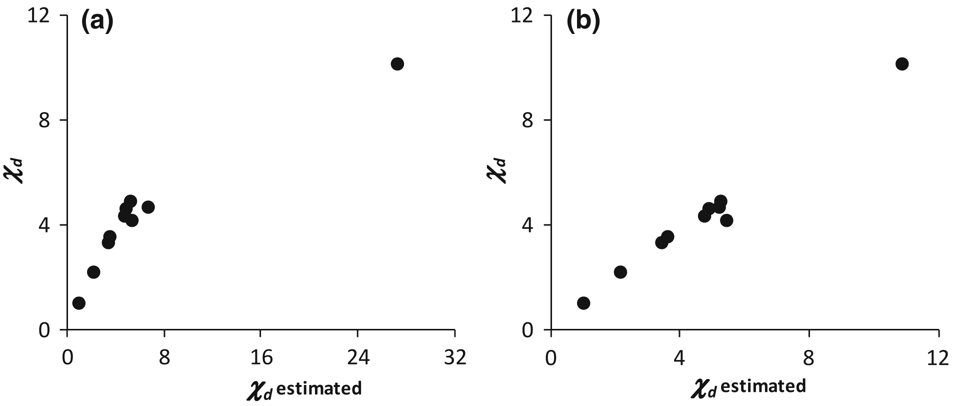
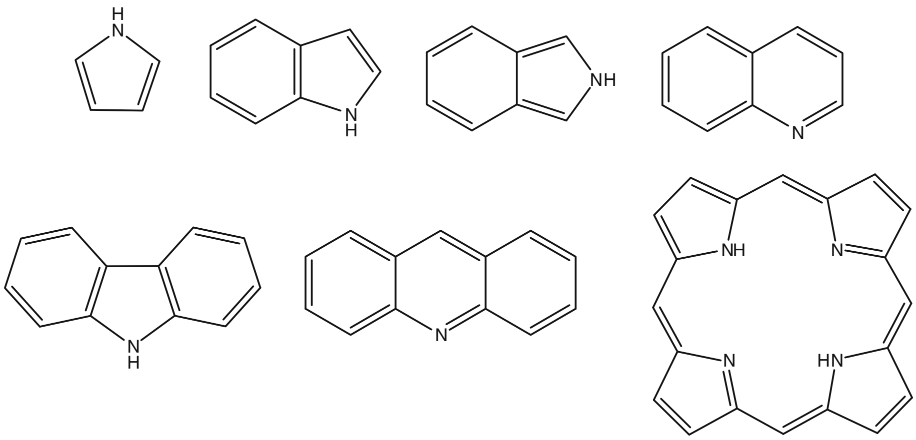


**Fig. 5** Heterocyclic compounds considered



the contrary, oxygen and sulphur atoms display beta resonance integrals with large deviations with respect to the carbon–carbon bonds [51], which prevent the application of the approaches expounded above. As one can see in Fig. 6, the correlation is quite good for these systems. Multicenter indices together with the approaches presented above can then be employed to estimate the total aromatic stabilization of nitrogenated aromatic systems containing either imine or amine nitrogen. We have also calculated the diamagnetic susceptibilities using Eq. 28 for the series of nitrogenated aromatic systems and compared them with the susceptibility exaltations reported for the same compounds in reference [52]. The value for porphine was taken from reference [53]. Susceptibility exaltations are mainly due to ring current susceptibilities [54], its use for heterocyclic compounds avoids the choice of a set of values for the beta and alpha resonance integrals in the calculation of the London susceptibilities at HMO level. As shown in Fig. 7 the correlation is also quite acceptable, this for the case of porphine reflects that the contribution of large circuits is not overestimated in this molecule.

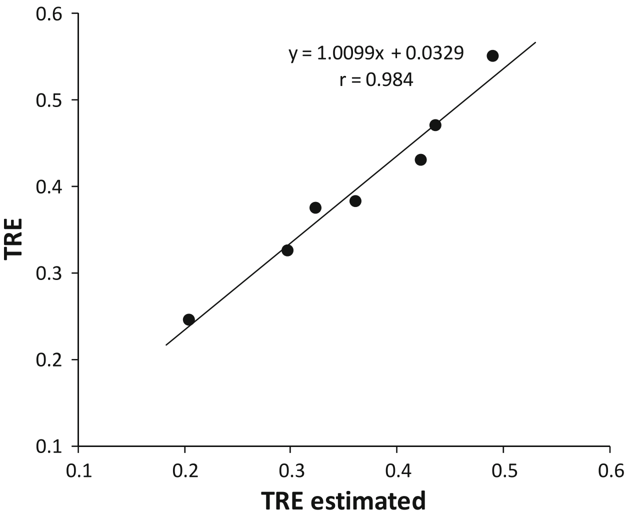


**Fig. 6** Representation of calculated (taken from reference [33]) versus estimated (using Eq. 29) topological resonance energies for the series of heterocyclic compounds depicted in Fig. 5

We would like to end the discussion about heterocyclic compounds with the particular case of constrained benzene ($D_{3h}$) (already discussed in the previous section). Although this is not a heterocyclic system, from the point of view of its bond symmetry it should be included within this class of compounds. Thus, the beta resonance integrals and bond orders are not equivalent as in the case of benzene ($D_{6h}$),

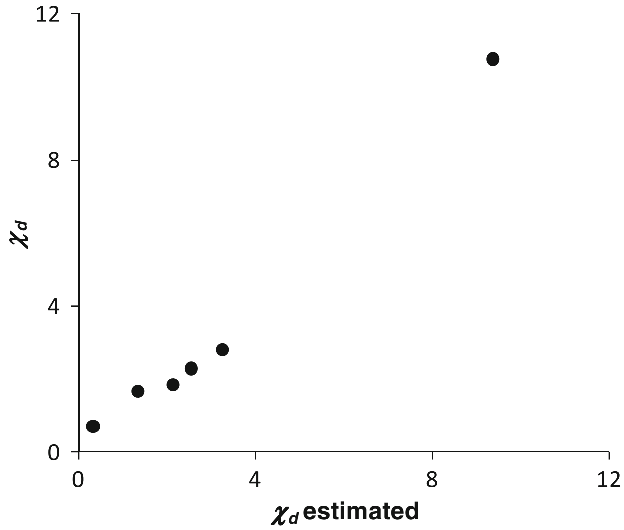


**Fig. 7** Representation of diamagnetic susceptibility exaltations (taken from references [52, 53]) versus estimated (using Eq. 28) total London diamagnetic susceptibilities for the series of heterocyclic compounds depicted in Fig. 5

and so Eq. 20 must be replaced by Eq. 27, which incorporates the weight factor, for the calculation of the ring current intensity. We have estimated the ratio between the current intensity in benzene ($D_{3h}$) and ($D_{6h}$) using Eq. 27 and taking the constrained geometry reported in reference [34] for benzene ($D_{3h}$). The value obtained (0.67) is close to that obtained between the maximum intensities, $j_{\max}$, (0.75) by Havenith et al. in the same work.

## 4 Concluding remarks

Solid theoretical foundation for the correlation between energetic, magnetic and electron density criteria of aromaticity has been provided by using a semiclassical model. The previous theoretical background provided by Aihara for the correlation between aromatic stabilization and magnetic susceptibility exaltation has been merged with a classical view of magnetically induced ring currents to define the molecular circuit electric conductance, a key quantity that allows linking resonance energies with ring electron currents and in turn with multicenter electron delocalization.

The application of the additive property allows defining the molecular circuit electric conductance also for a given circuit of a polycyclic system. Using approximated expressions, it is possible to estimate quantitatively the contribution of each ring circuit to the values of the topological resonance energies in PAHs and nitrogenated polyheterocyclic systems by means of multicenter electron delocalization.

**Acknowledgments** The author thanks the “Xunta de Galicia” for financial support as researcher in the “Isidro Parga Pondal” program.

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