

Detailed Procedures for Computing Some Graph-Theoretically

Defined Quantities

In this Supplementary Information, we show explicitly how to use our graph-theoretical formulae (eqs 1-3) to obtain circuit currents (CCs), ring current (RC), and magnetic resonance energy (MRE) of a polycyclic \square system.

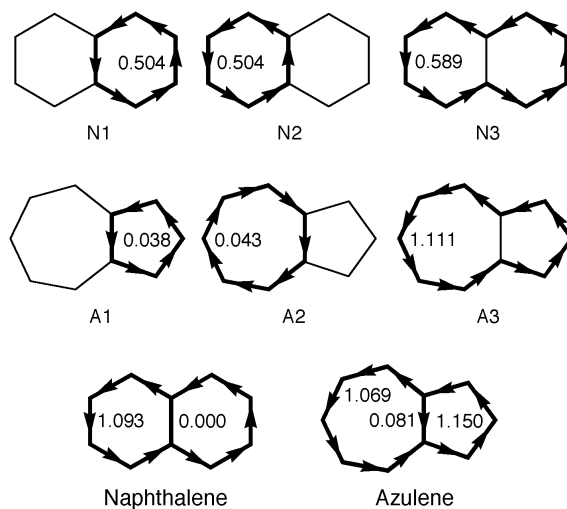


Figure S1. Circuit currents and ring currents induced in naphthalene and azulene.

As indicated in Figure S1, three circuits can be chosen from the naphthalene \square system (G), which are denoted by N1, N2, and N3. Sets of carbon atoms that form circuits N1, N2, and N3 are denoted by $r(N1)$, $r(N2)$, and $r(N3)$, respectively. $G-r(N1)$ and $G-r(N2)$ are identical with the butadiene \square system. By definition, a characteristic polynomial is a polynomial obtained by expanding a Hückel secular determinant. Characteristic polynomials for G, $G-r(N1)$, $G-r(N2)$, and $G-r(N3)$ are given as:

$$P_G(X) = X^{10} - 11X^8 + 41X^6 - 65X^4 + 43X^2 - 9$$

$$P_{G-r(N_1)}(X) = X^4 - 3X^2 + 1$$

$$P_{G-r(N_2)}(X) = X^4 - 3X^2 + 1$$

$$P_{G-r(N_3)}(X) = 1$$

Then,

$$P_G'(X) = 10X^9 - 88X^7 + 246X^5 - 260X^3 + 86X$$

The energies of the occupied π molecular orbitals in naphthalene (G) correspond to five positive zeroes of $P_G(X)$, which are 2.302776, 1.618034, 1.302776, 1.000000, and 0.618034. Inserting these polynomials and π orbital energies into eq 1, we obtain the following A_i values:

$$A_{N_1} = 0.11197, A_{N_2} = 0.11197, \text{ and } A_{N_3} = 0.06542$$

These values represent the circuit resonance energies (CREs) in units of $|\beta|$ for the three circuits. In general, larger circuits exhibit smaller CREs. According to eq 2, magnetic resonance energy (MRE) for naphthalene is given as the sum of all these A_i values:

$$\text{MRE}/|\beta| = 0.11197 + 0.11197 + 0.06542 = 0.28936$$

We next calculate the intensities of three circuit currents induced in naphthalene by inserting the A_i values into eq 3:

$$I_{N_1} = 4.5 \times 0.11197 I_0 (S_{N_1}/S_0) = 0.504 I_0$$

$$I_{N_2} = 4.5 \times 0.11197 I_0 (S_{N_2}/S_0) = 0.504 I_0$$

$$I_{N_3} = 4.5 \times 0.06542 I_0 (S_{N_3}/S_0) = 0.589 I_0$$

Note that $S_{N_1} = S_{N_2} = S_{N_3}/2 = S_0$. These circuit currents are graphically summarized in Figure S1, where counterclockwise and clockwise currents indicate diatropicity and paratropicity, respectively. The overall ring current or π current density is obtained by superposing these three circuit currents. The π -current density thus obtained for

naphthalene is exactly the same as that calculated using a standard Hückel-London method.^{S1}

Three circuits, A1, A2, and A3, can be chosen from the azulene π system. Circuit currents calculated for azulene are added in Figure 1S. Here, A1 and A2 are assumed to be of regular polygon. The π -current density in azulene obtained by superposing these circuit currents is exactly the same as that reported previously.^{S2} MRE for azulene is 0.12596 $|\mu|$, which indicates that this molecule is much less aromatic than naphthalene. For naphthalene, all the three circuits contribute almost equally to aromaticity. In the case of azulene, however, the peripheral ten-site circuit contributes predominantly to aromaticity, because it is the only conjugated circuit^{S3} in this molecule. Three circuits in naphthalene are all conjugated circuits.

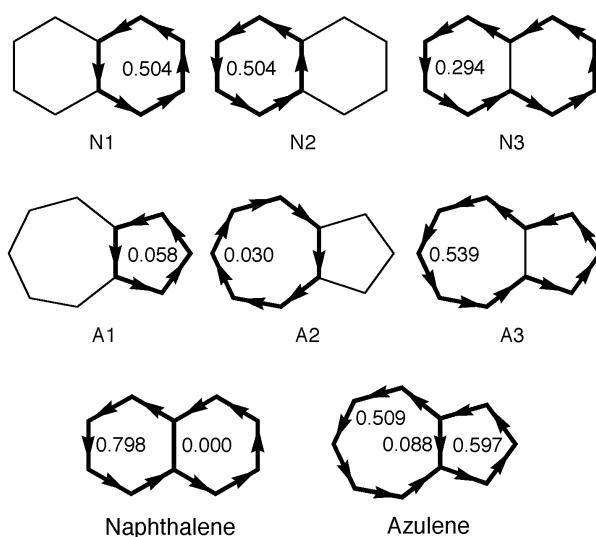


Figure S2. Geometry-independent circuit currents and ring currents in naphthalene and azulene.

Geometry-independent circuit currents and ring currents can be obtained by setting $S_i=S_0$ for all circuits in eq 3. Those for naphthalene and azulene are graphically shown in Figure S2. It is noteworthy that, although the authentic ring current induced along the

periphery of azulene is as strong as that of naphthalene, the geometry-independent ring current in azulene is appreciably smaller than that in naphthalene. Thus, geometry-independent ring current reflects the degree of aromaticity through the related CRE values.

Bond resonance energy (BRE) for a given π -bond, e.g., the π -bond formed by carbon atoms 5 and 10 in Figure S3, is calculated in the following manner. The resonance integral between carbon atoms 5 and 10 is set equal to $\pm i\beta$, where β is the standard resonance integral between two adjacent carbon atoms. The resulting secular determinant is given in Figure S3. The total π -binding energy for this hypothetical system (G') is obtained by solving this secular equation, which is 13.416408 β . The total π -binding energy obtained by solving the authentic Hückel secular equation is 13.683239 β . The BRE for the 5-10 bond is given as the difference between these two π -binding energies (0.266832 β).

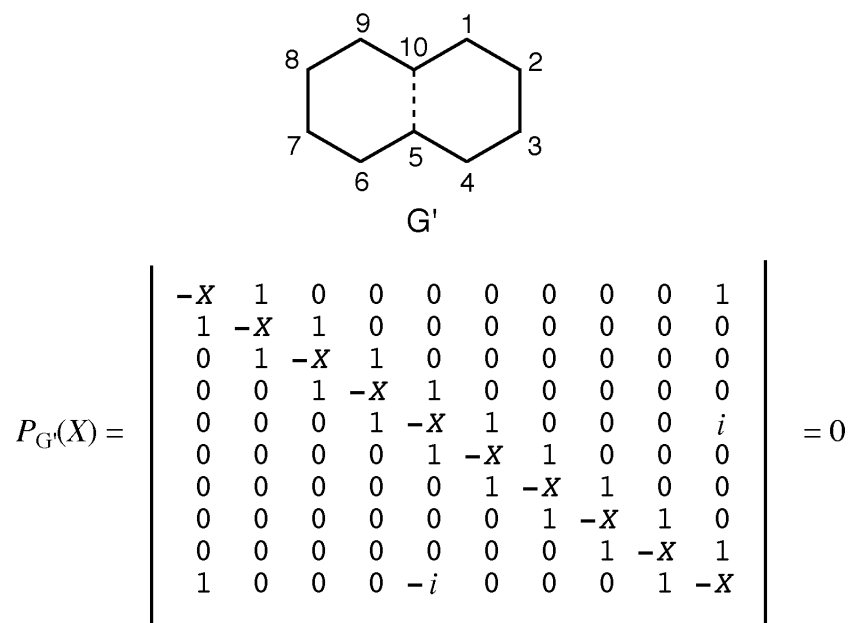


Figure S3. Secular determinant constructed to obtain the BRE for the 5-10 bond in naphthalene.

The BREs for all π -bonds in naphthalene and azulene are presented in Figure S4. Note that the BRE for the π -bond shared by two benzene rings in naphthalene is very large because it is shared by two six-site circuits, each with a large positive CRE. In marked contrast, that for the π -bond shared by five- and seven-membered rings is very small. This is because the corresponding five- and seven-site circuits are almost non-aromatic with very small positive and negative CREs, respectively. Thus, the BRE concept is very useful for exploring main aromatic conjugation pathways in a polycyclic π system. As far as peripheral π -bonds are concerned, BRE is roughly proportional to the intensity of the geometry-independent circuit current.

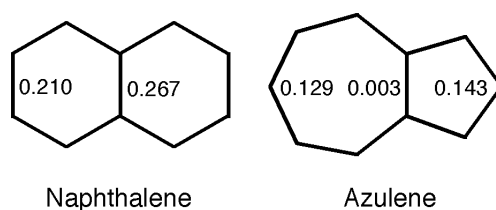


Figure S4. BREs for all π -bonds in naphthalene and azulene.

References

- (S1) McWeeny, R. *Mol. Phys.*, 1958, **1**, 311.
- (S2) Pople, J. A. *Mol. Phys.*, 1958, **1**, 175.
- (S3) Randic, M. *J. Am. Chem. Soc.*, 1977, **99**, 444.