Supplementary Information

A Study on the Aromaticity and Magnetic Properties of Triazolephorphyrazines

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In order to see how the eq 3 can be applied to polycyclic conjugated systems, let us calculate the circuit resonance energies of a phenanthrene conjugated system. A graph representing the conjugated system is here denoted by G.

A field-free characteristic polynomial for an entire conjugated system of phenanthrene is:

$$P_G(x) = x^{14}-16x^{12}+98x^{10}-297x^8+479x^6-407x^4-166x^2-25 \qquad (a)$$

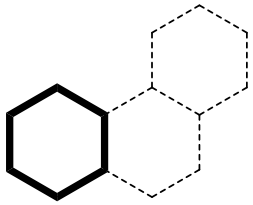
The largest seven eigenvalues, which correspond to the occupied molecular orbitals in phenanthrene (G) are:

2.434763802739; 1.950626891439; 1.516273666604; 1.305800277419; 1.142384405608; 0.769051520885; 0.605225071170

The first derivative of eq (a) is:

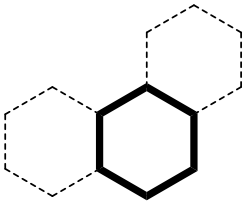
$$P_G`(x)= 14x^{13}-192x^{11}-980x^9-2376x^7+2874x^5-1628x^3-332x \qquad (b)$$

Six circuits, F1, F2, F3, F4, F5, and F6 can be chosen from the phenanthrene π system as shown in Figure S1. All the possible subgraphs and its characteristic polynomials are also added in Figure S1.



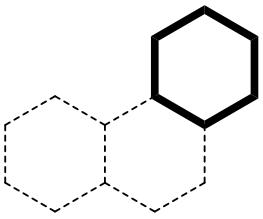
$P_{G\text{-}r(F1)}(x)=x^8-8x^6+19x^4-16x^2+4$

F1



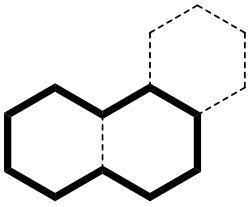
$P_{G\text{-}r(F2)}(x)=x^8-6x^9+11x^4-6x^2+1$

F2



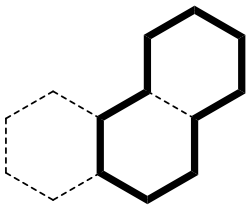
$P_{G\text{-}r(F3)}(x)=x^8-8x^6+19x^4-16x^2+4$

F3



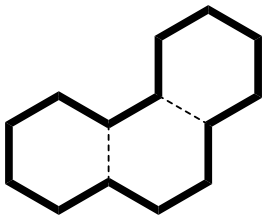
$P_{G\text{-}r(F4)}(x)= x^4-3x^2+1$

F4



$P_{G\text{-}r(F5)}(x)=x^4-3x^2+1$

F5



$P_{G\text{-}r(F6)}(x)=1$

F6

Fig. S1 Subgraphs of ***G*** for phenanthrene and its characteristic polynomials

Inserting the polynomials and π orbital energies into eq 3, we obtain the following A_i values:

A_{F1}=0.14135; A_{F2}=0.05197; A_{F3}=0.14135; A_{F4}=0.02672; A_{F5}=0.02672; A_{F6}=0.01926

These values represent the circuit resonance energies (CREs) in units of |β | for the six circuits. According to eq 2, magnetic resonance energy (MRE) for phenanthrene is obtained as the sum of all these A_i values:

MRE/|β | =0.14135+0.05197+0.14135+0.02672+0.02672+0.01926=0.40736

We next calculate the intensities of three circuit currents induced in phenanthrene by inserting the A_i values into eq 3. Here, we assum all hexagons are regular polygons and all CC bonds are equal to those in benzene. That is to say, we assumed that the ring area of every hexagon is 1 and that it is the same as benzene.

$I_{F1} = 4.5\times0.14135\ I_0\ (S_{F1}/S_0) = 0.63608\ I_0$

$I_{F2} = 4.5\times0.05197\ I_0\ (S_{F2}/S_0) = 0.23387 I_0$

$I_{F3} = 4.5\times0.14135\ I_0\ (S_{F3}/S_0) = 0.63608\ I_0$

$I_{F4} = 4.5\times0.02672\ I_0\ (S_{F4}/S_0) = 0.24048\ I_0$

$I_{F5} = 4.5\times0.02672\ I_0\ (S_{F5}/S_0) = 0.24048\ I_0$

$I_{F6} = 4.5\times0.01926\ I_0\ (S_{F6}/S_0) = 0.26001\ I_0$

We next calculate the *i*-th circuit-current susceptibility (CCS) in phenanthrene by inserting the A_i values into eq 4:

$CCS_{F1}=4.5\times1.0\times0.14135\ I_0\ (S_{F1}/S_0)^2 = 0.63608\chi_0$

$CCS_{F2}=4.5\times1.0\times0.05197\ I_0\ (S_{F2}/S_0)^2 = 0.23387\chi_0$

$CCS_{F3}=4.5\times1.0\times0.14135\ I_0\ (S_{F3}/S_0)^2 = 0.63608\chi_0$

$CCS_{F4}=4.5\times1.0\times0.02672\ I_0\ (S_{F4}/S_0)^2 = 0.48096\chi_0$

$CCS_{F5}=4.5\times1.0\times0.02672\ I_0\ (S_{F5}/S_0)^2 = 0.48096\chi_0$

$CCS_{F6}=4.5\times1.0\times0.01926\ I_0\ (S_{F6}/S_0)^2 = 0.78004\chi_0$

In general, ring current (RC) can be obtained by superposing all the circuit-currents. The RC values can be calculated in the following manner:

RC(A) = RC(C) = 0.63608+0.24048+0.26001=1.13657 I_0

RC(B) = 0.23387+ 0.24048+0.24048 +0.26001 = 0.97484 I_0

The induced π-electron currents in the phenanthrene π system are shown below in Figure S2.

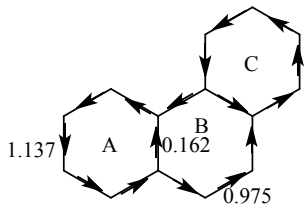


Fig. S2 Induced π-electron currents in phenanthrene.