Supporting Information

Aromatic Character of Irregular-Shaped Nanographenes

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■ SSEs for All Benzene Rings in Irregular-Shaped PAHs.

Superaromatic stabilization energy (SSE) for a given benzene ring in a PAH molecule represents the degree of local aromaticity in the ring.[S1-S3] SSEs for all non-identical benzene rings in fundamental irregular-shaped PAHs studied are summarized in Figures S1-S5. Note that SSE is the only local aromaticity index not disturbed by the aromaticity of adjacent benzene rings.[S1]

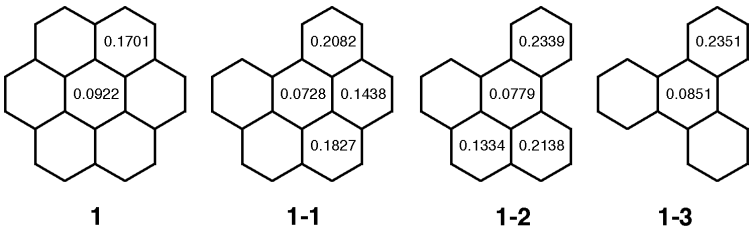


Figure S1. SSEs in units of $|\beta|$ for non-identical benzene rings in coronene (**1**) and its stepwise degradation products.

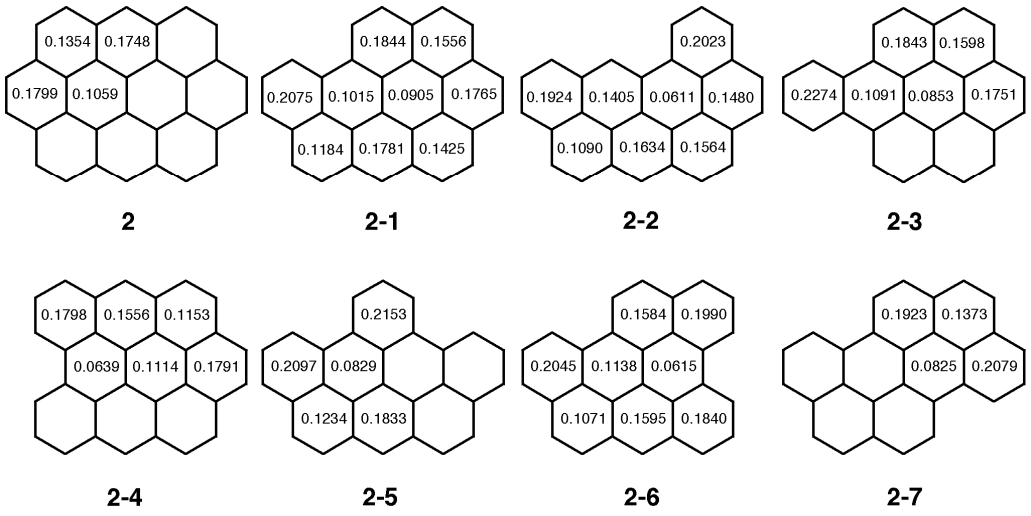


Figure S2. SSEs in units of $|\beta|$ for non-identical benzene rings in ovalene (**2**) and its stepwise degradation products.

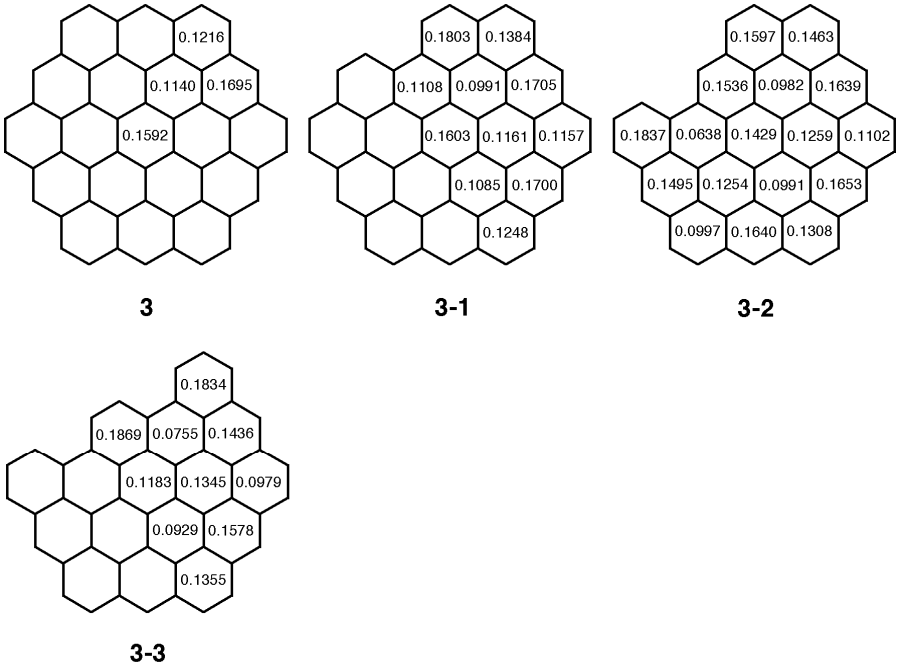


Figure S3. SSEs in units of $|\beta|$ for non-identical benzene rings in circumcoronene (**3**) and its stepwise degradation products.

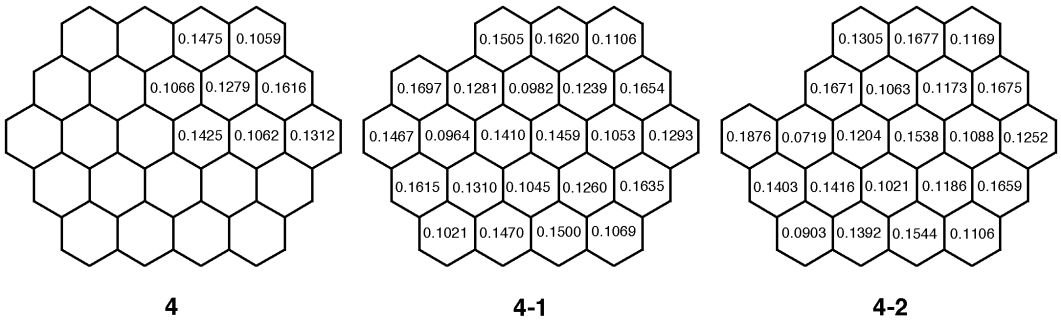


Figure S4, Part 1. SSEs in units of $|\beta|$ for non-identical benzene rings in circumovalene (**4**) and its stepwise degradation products.

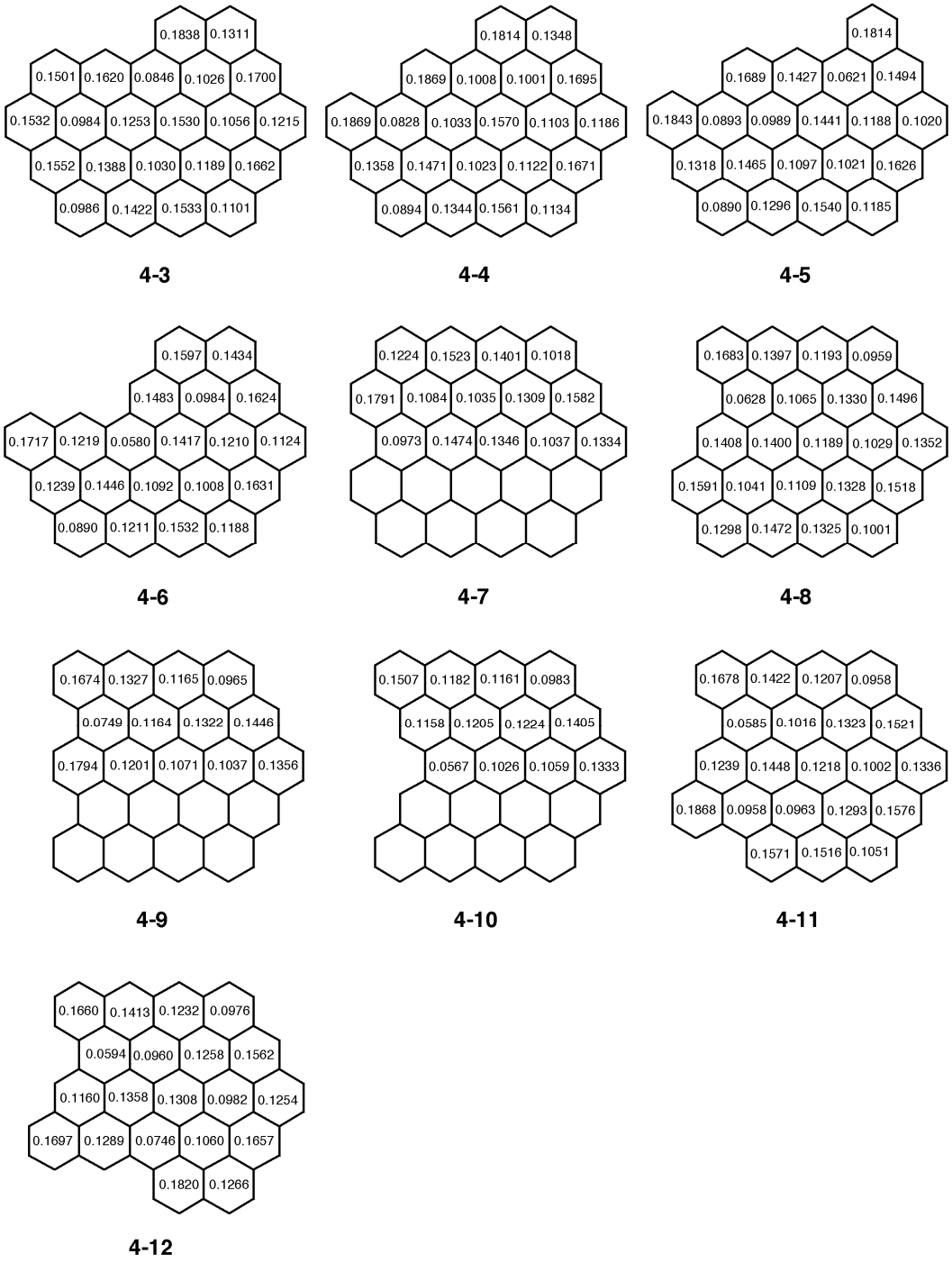


Figure S4, Part 2. SSEs in units of $|\beta|$ for non-identical benzene rings in circumovalene (**4**) and its stepwise degradation products.

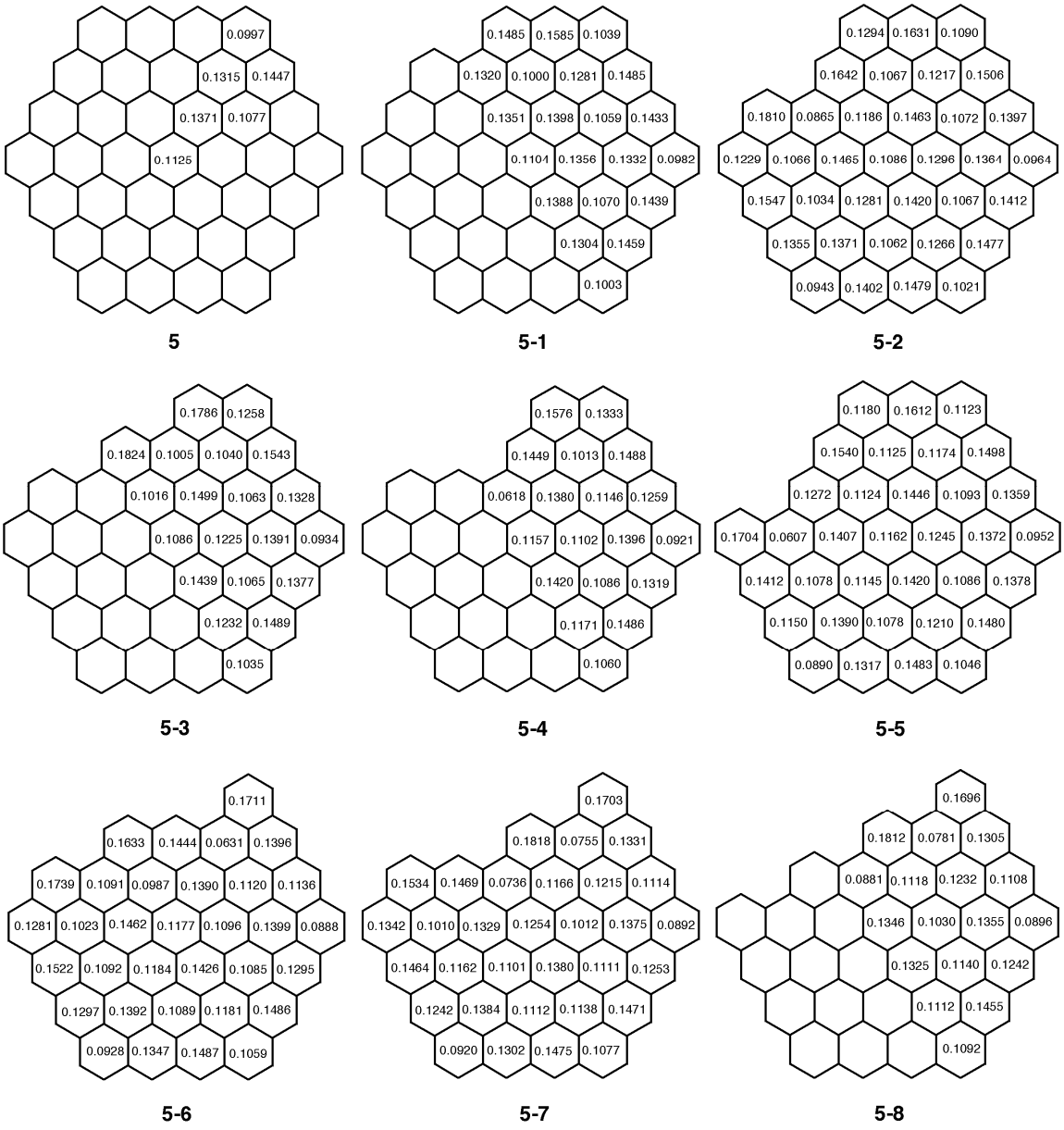


Figure S5. SSEs in units of $|\beta|$ for non-identical benzene rings in circum-circumcoronene (**5**) and its stepwise degradation products.

■ Aromaticity Patterns of Irregular-Shaped Giant PAHs.

Aromaticity patterns for a giant zigzag-edged PAH (D_{6h}-$C_{216}H_{36}$, **10**) and 14 stepwise degradation products are shown in Figure S6. As stated in the text, the introduction of an irregular edge into the upper part of **10** markedly disturbs the aromaticity pattern near the edge, but the disturbance is rather limited to nearby benzene rings. Therefore, if the π-system is sufficiently or moderately large, the disturbance by the upper irregular edge will never extend

to lower benzene rings. Benzene rings far from the upper irregular edge almost remain unaffected, retaining a honeycomb-like texture of the parent PAH molecule.

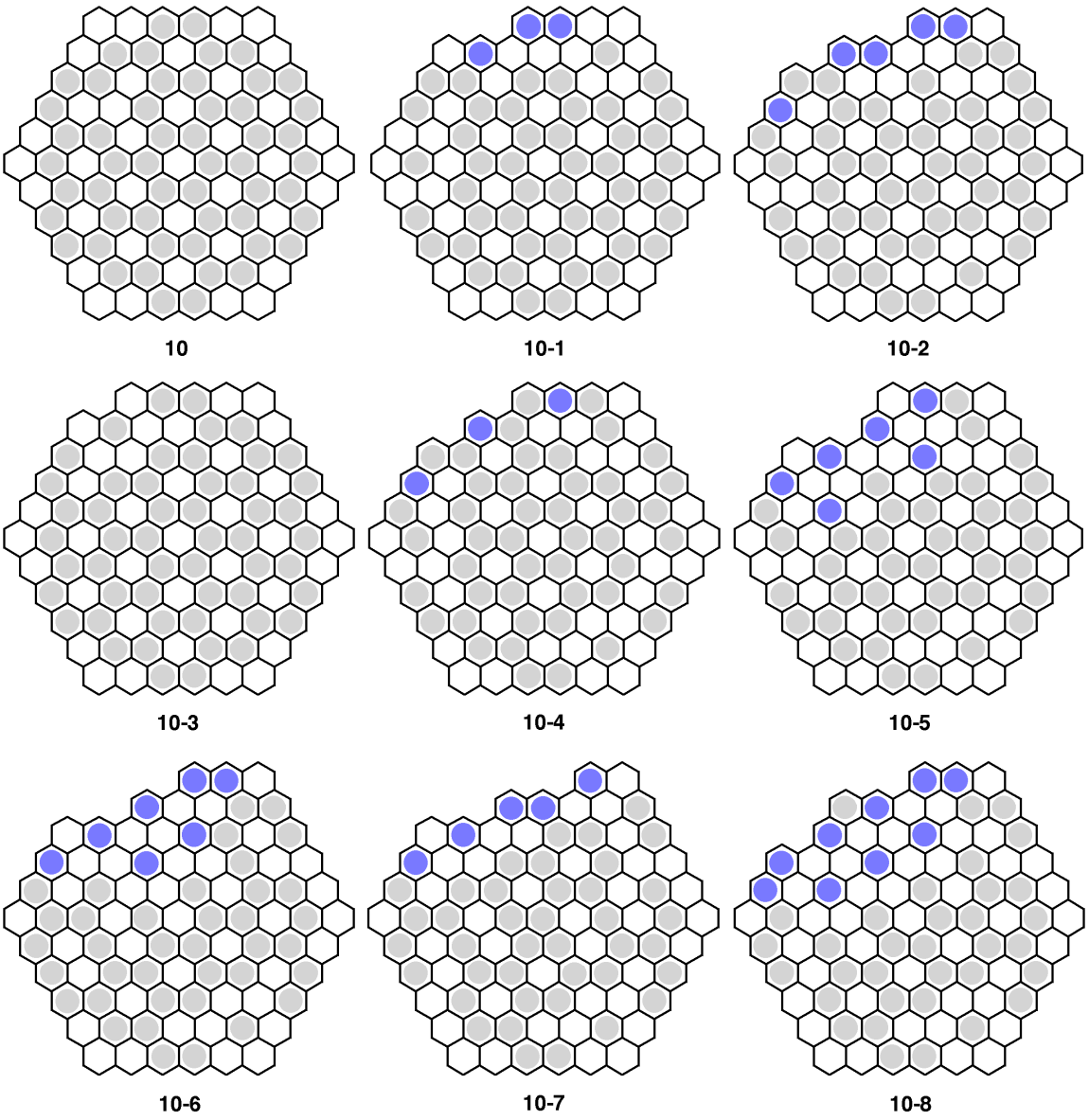


Figure S6, Part 1. Aromaticity patterns of giant zigzag-edged D_{6h}-$C_{216}H_{36}$ (**10**) and its degradation products. Indigo, blue, and gray filled circles indicate benzene rings with SSEs larger than 0.18, 0.14, and 0.12 $|\beta|$, respectively.

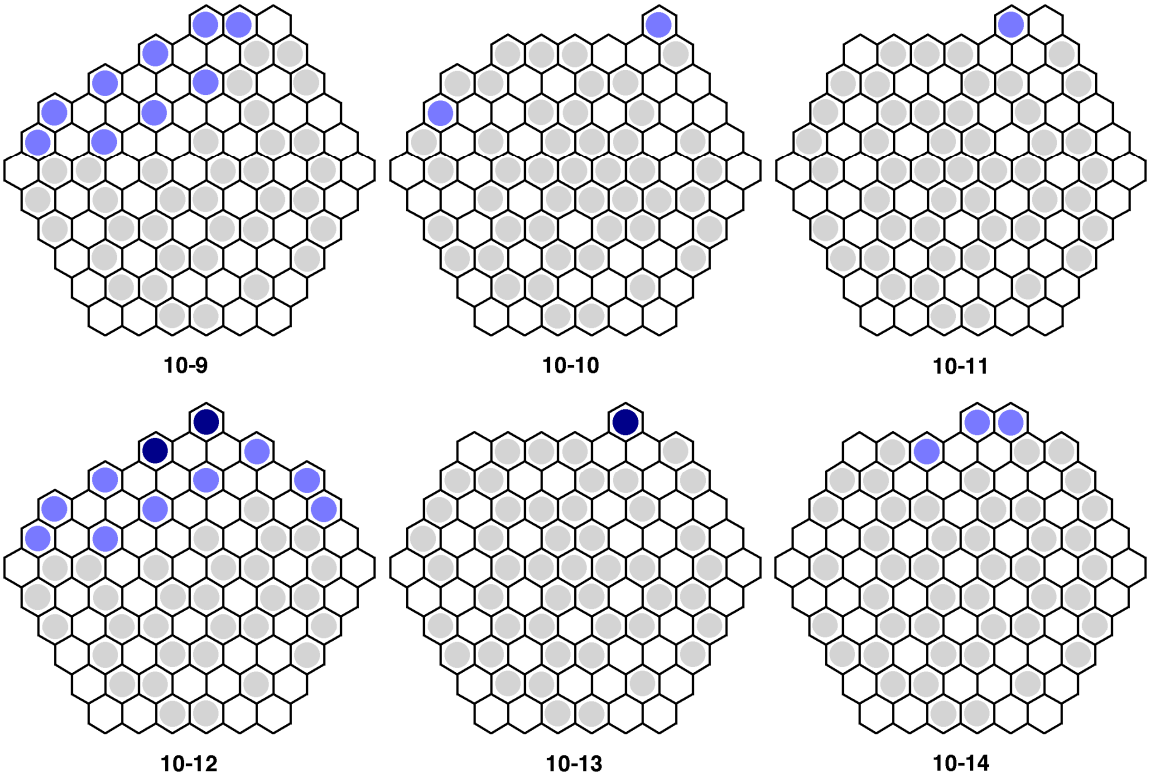


Figure S6, Part 2. Aromaticity patterns of giant zigzag-edged D_{6h}-$C_{216}H_{36}$ (**10**) and its degradation products. Indigo, blue, and gray filled circles indicate benzene rings with SSEs larger than 0.18, 0.14, and 0.12 $|\beta|$, respectively.

■ **SSEs for All Benzene Rings in Arbitrarily Shaped Nanographenes.**

SSEs for all non-identical benzene rings in arbitrarily shaped nanographenes **11**-**13** are summarized in Figure S7.

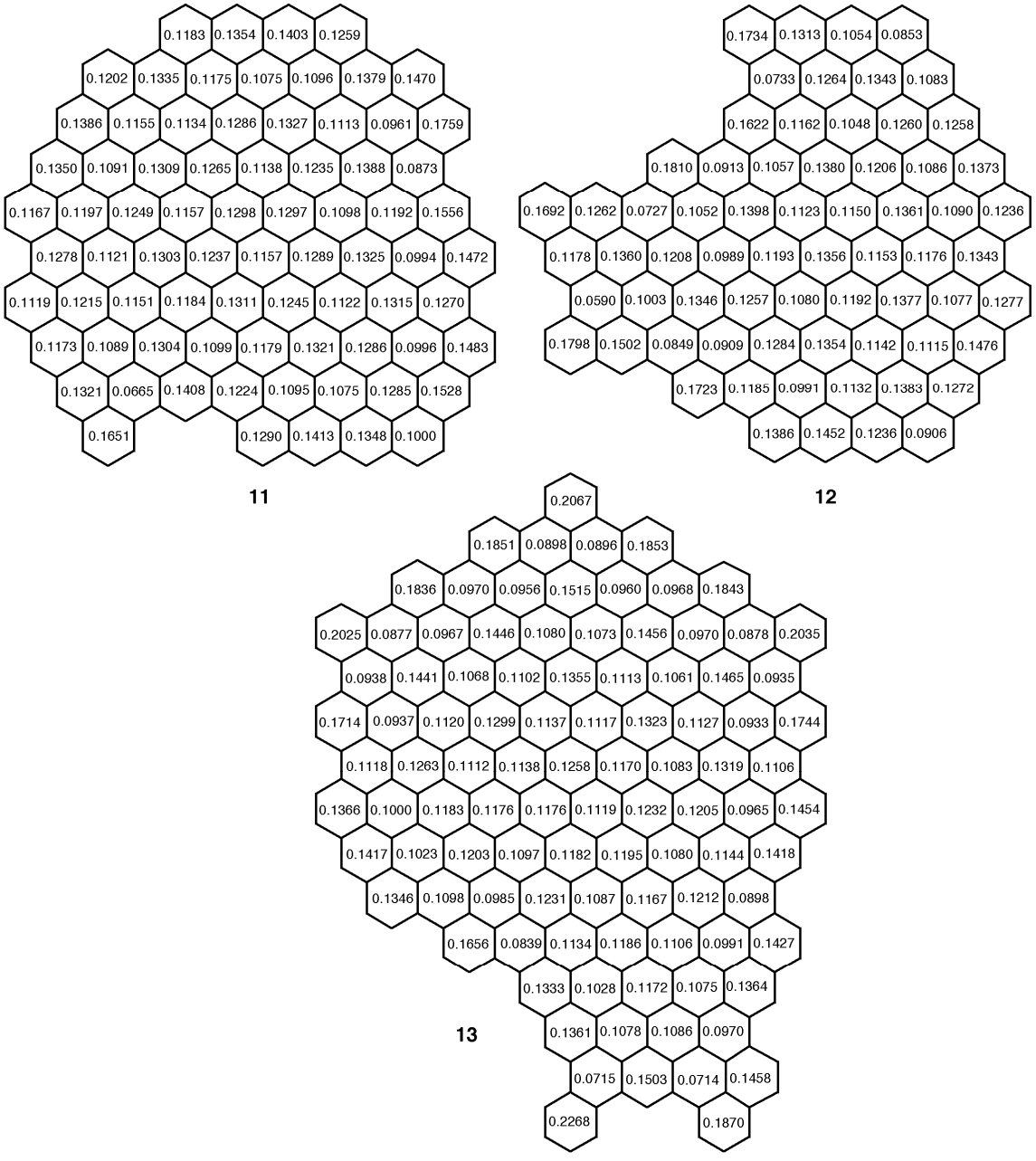
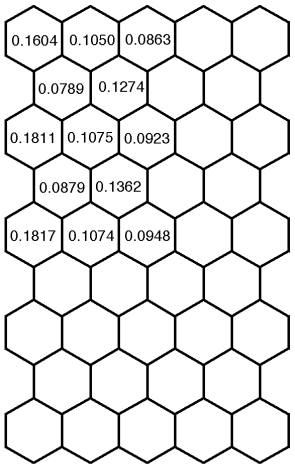


Figure S7. SSEs in units of $|\beta|$ for all benzene rings in three arbitrarily shaped nanographenes.

■ **SSEs for All Benzene Rings in (5a,5z)Periacene.**

SSEs for all non-identical benzene rings in (5a,5z)Periacene **14** are summarized in Figure S8.



14

Figure S8. SSEs in units of $|\beta|$ for non-identical benzene rings in [5a,5z]periacene.

REFERENCES

(S1) Aihara, J.; Makino, M.; Sakamoto, K. Superaromatic Stabilization Energy as a Novel Local Aromaticity Index for Polycyclic Aromatic Hydrocarbons. *J. Phys. Chem. A* **2013**, *117*, 10477-10488.

(S2) Aihara, J.; Makino, M. Constrained Clar Formulas of Coronoid Hydrocarbons. *J. Phys. Chem. A* **2014**, *118*, 1258-1266.

(S3) Sakamoto, K.; Nishina, N.; Enoki, T.; Aihara, J. Aromatic Character of Nanographene Model Compounds. *J. Phys. Chem. A* **2014**, *118*, 3014-3025.