

Chemistry–A European Journal

Supporting Information

**Disclosure of Ground-State Zimmerman-Möbius
Aromaticity in the Radical Anion of [6]Helicene and
Evidence for 4π Periodic Aromatic Ring Currents in a
Molecular “Metallic” Möbius Strip**

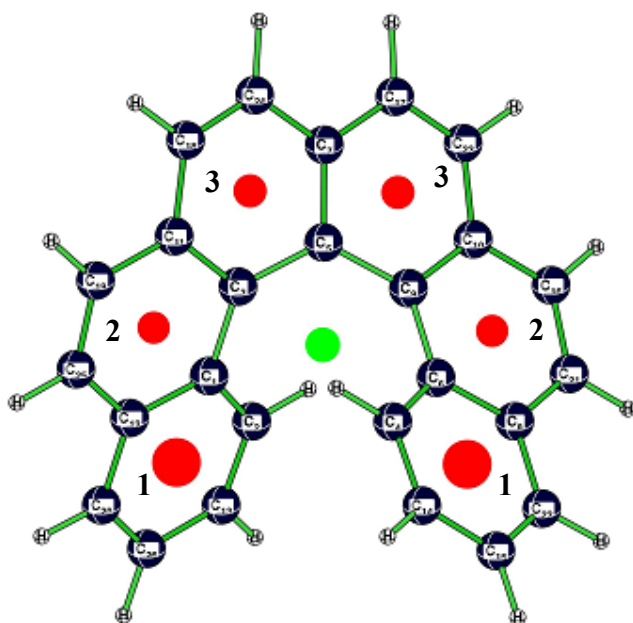
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1. Computational Methods

We used density functional theory for geometry optimization without any geometry restriction and computation of properties with the GAUSSIAN09 quantum chemistry program suite.^[1] Unless otherwise stated, B3LYP/6-31G* level had been used throughout, also to compute NMR shieldings, optical band gaps, optical rotations and first order electronic polarizabilities via coupled-perturbed Hartree-Fock (CPHF) calculations;^[2] with Becke's three parameter functional^[3] and the correlation correction of Lee, Yang and Parr,^[4] unless otherwise stated. Pople's et al valence split basis sets have been used throughout.^[5] All stationary points on their respective potential energy surfaces (PES) have been rigorously characterized by the number of imaginary frequencies in harmonic frequency calculations. Relative energies are zero-point energy (ZPE) corrected. Transition state structures have been matched to their pertaining minimum structures by an intrinsic reaction coordinate (IRC) following algorithm. Where applicable, configuration interaction singles (CIS) stability calculations have been performed to check the wave function stability. In order to take into account dispersion energy effects, Grimme's D3 semi-empirical dispersion energy correction has been used, together with Becke-Johnson damping, to facilitate convergence.^[6] Zhao and Truhlar's M06-2X functional has been used to validate several of the results.^[7] For **13**, M06 has also been employed for comparison.^[7] In all cases except metallic **13**, M06-2X gave results similar to those with B3LYP. For this particular species (and for **12** as reference) we used the HSE06 functional of Heyd-Scuseria-Ernzerhof,^[8] which uses an error-function screened Coulomb potential to calculate the exchange portion of the energy, and is based on a mixing scheme for Hartree-Fock exchange and Perdew-Burke-Ernzerhof (PBE) exchange in the short range.^[9] Magnetic shieldings have all been computed with the gauge-including atomic orbital (GIAO) method.^[10] NICS values have been computed in the respective geometric ring centers. Time-dependent (TD)-DFT computations were carried out to compute the electronic transitions to excited states. Cartesian coordinates of all species can be requested from the authors.

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2. Evaluation of individual six-ring's shielding contributions in hexahelicene



$$\sum_i \text{NICS}_i(0) = 2 * (\text{NICS}_1 + \text{NICS}_2 + \text{NICS}_3) = 1.6$$

$$(\text{NICS}_1 = 0.2, \text{NICS}_2 = 0.3, \text{NICS}_3 = 0.3)$$

Figure S11: If there was no global gap-crossing current in **1**, NICS(0) at the molecules' center should be approximately the sum of local shielding contributions from surrounding fused benzene rings. As the resulting value, though, is much smaller than that given in Figure 1, the above assumption has to be discarded.

3. Topological coupling of peripheral to central circuits in corannulene

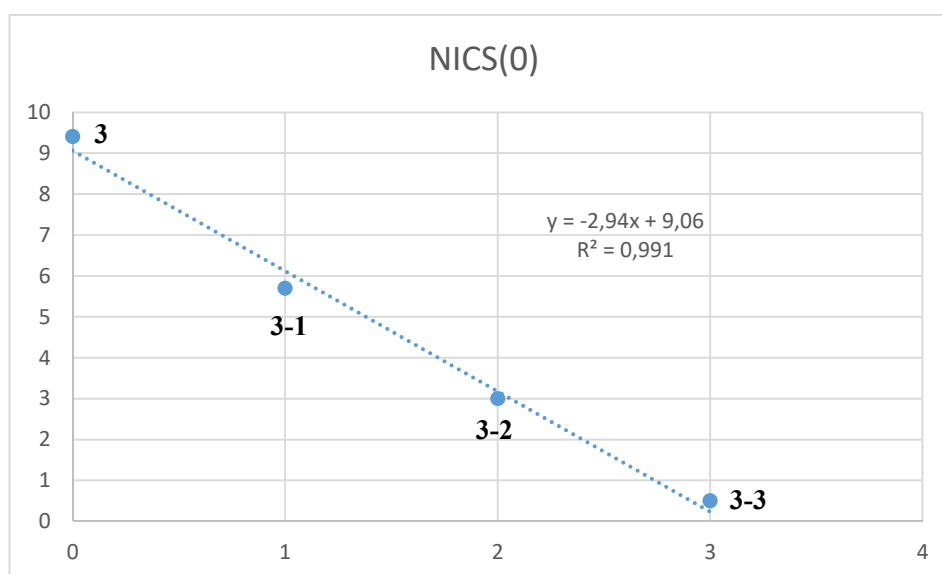
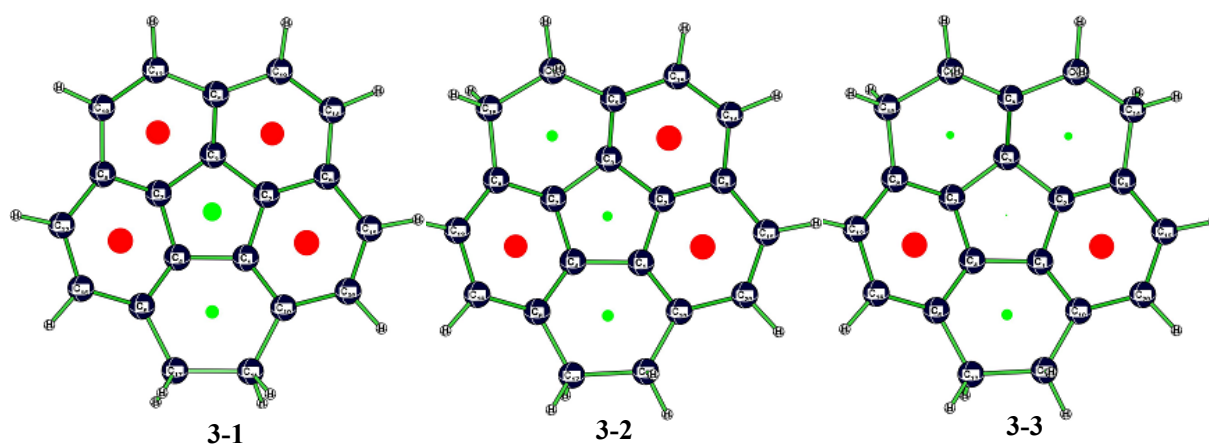


Figure SI2: Linear dependence of central NICS(0) value from number of partly hydrogenated peripheral benzene rings. Regression line with significance R is included in diagram below.

4. Homodesmotic equation for evaluation of aromatic stabilization energy of hexahelicene radical anion

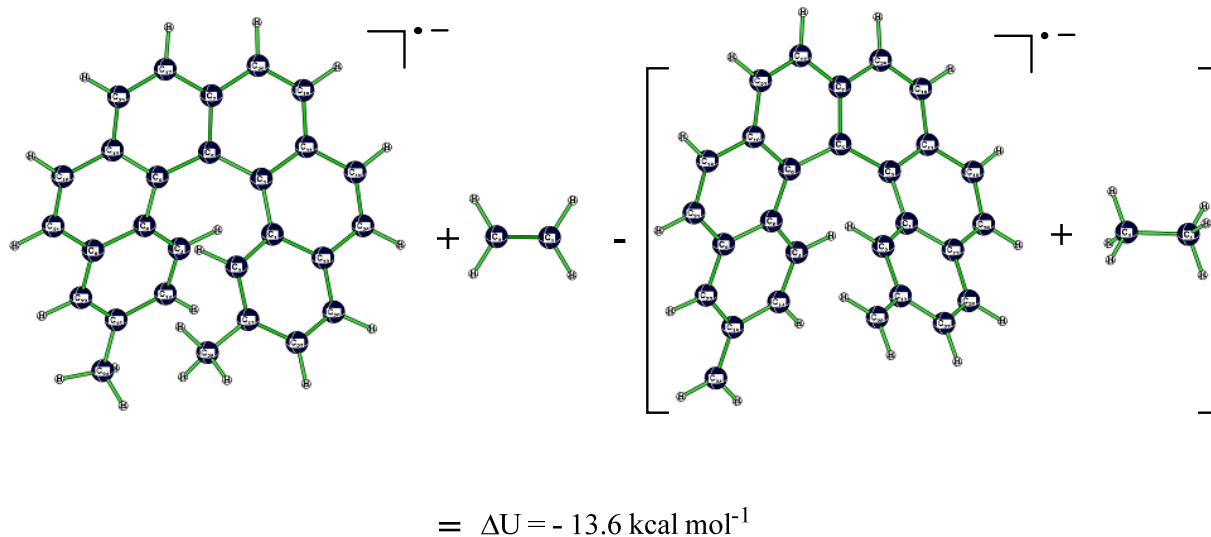


Figure S13: Homodesmotic equation calculated from absolute energies at B3LYP/6-311+G** to evaluate aromatic stabilization energy of [6]helicene radical anion **4** with balanced number of sp^2 and sp^3 carbons (and of double bond equivalents). The structure to the right has still some residual, but small, aromaticity: maximum NICS(0) value among six-rings is -3.8, average is -2.4 ppm.

5. Evaluation of aromatic stabilization energy of naphthalene radical anion by Schleyer-Pühlhofer method

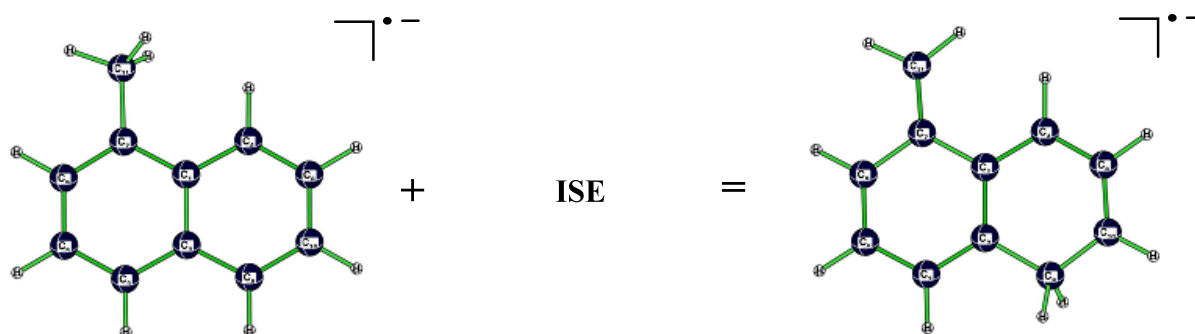


Figure S14: Evaluation of isomerization-stabilization energy (ISE) after Schleyer and Pühlhofer (ref. 49) for naphthalene radical anion **9** at B3LYP/6-311+G**.

6. Evaluation of aromatic stabilization energy of C_{2h} diaza-tetracene by Schleyer-Pühlhofer method

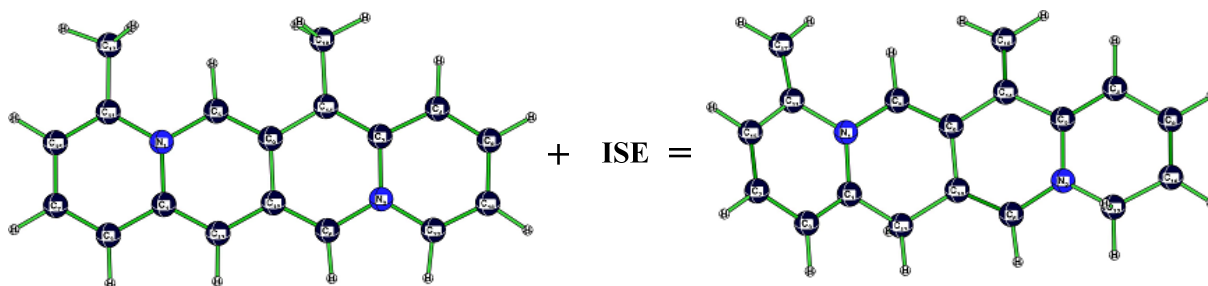


Figure S15: Evaluation of isomerization-stabilization energy (ISE) after Schleyer and Pühlhofer (ref. 49) for C_{2h} 1,10-diaza-tetracene at B3LYP/6-31G*.

7. Blocking of 4π -periodic ($4N+1$ π -electron) edge ring current in Möbius[16]cyclacene

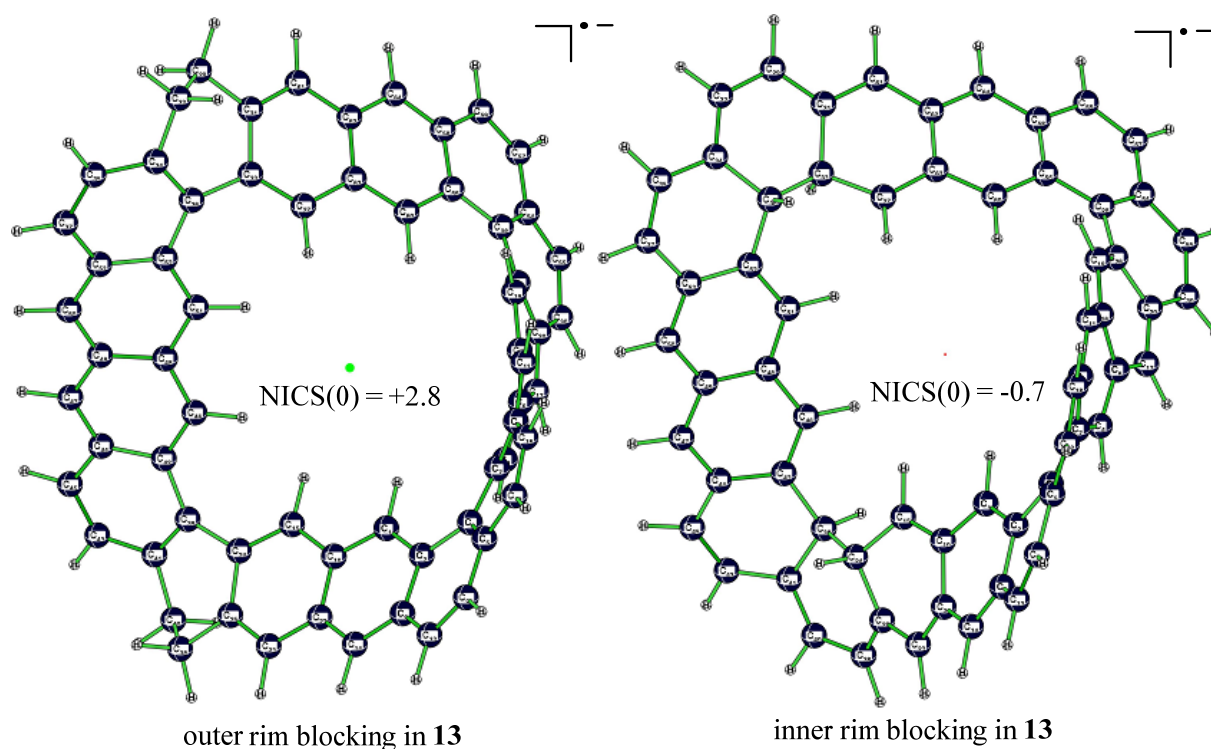


Figure SI6: Blocking of edge ring current in **13**: NMR calculation at M06-2X/6-31G*//M06-2X/6-31G* with GIAO method. At HSE06/6-31G*//HSE06/6-31G*, the corresponding values are -2.0 and -0.5, respectively.

8. Magnetic shielding computation for [6]helicene dianion

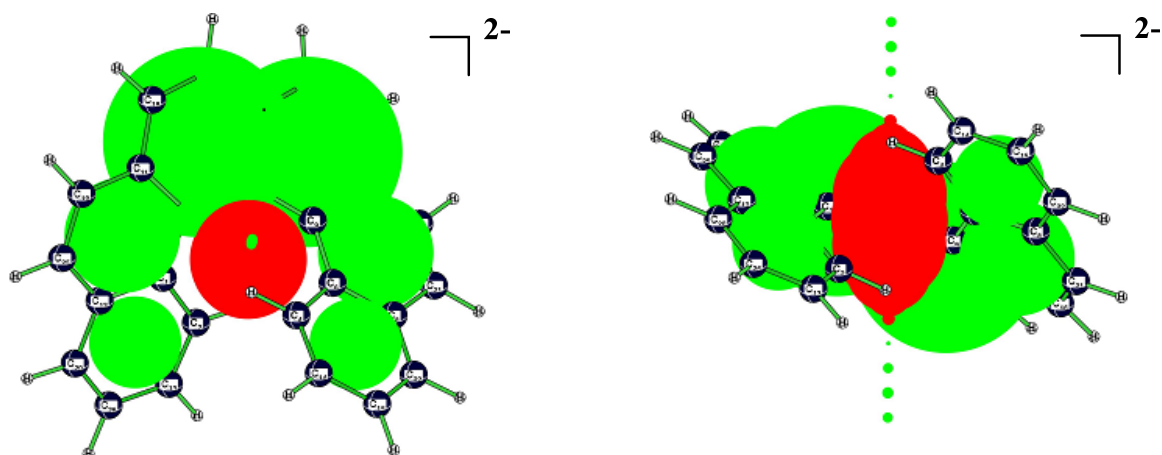


Figure S16: Depiction of NICS values in ring centers and center of the dianion computed at B3LYP/6-31G**/B3LYP/6-31G* (positive values = green, indicating paratropicity; negative values = red, indicating diatropicity).