

Supplementary Information

4N electron aromatic cycles in polycyclic hydrocarbons

Michael Mauksch*^[a] and Svetlana B. Tsogoeva*^[b]

Section A: Computational Methods

All geometry optimizations have been performed without any geometry restrictions. The computations have been carried out with the GAUSSIAN09 program package.¹ In the density functional theory computations, we used a valence split 6-31G* basis set on all atoms. We have also performed wave function stability calculations on the minima in which antiaromaticity is converted to aromaticity (e.g. **3**), to ensure that we have found the correct electronic state.

Frequency calculations have been carried out to characterize rigorously stationary points on the potential energy surfaces by the number of imaginary frequencies. (Unscaled) zero point energy corrections (for the lowest vibrational quantum levels) have been applied to correct the energy of transition states. Furthermore, intrinsic reaction coordinate computations (IRC) have been carried out to verify that the located transition structures pertain to the correct minima. Charges have been taken from natural population analysis, unless stated otherwise.

For the DFT geometry optimizations and the magnetic shielding computations (with the gauge-independent atomic orbitals method), the B3LYP hybrid density functional has been employed, which includes Becke's exchange functional (that contains approximately 20% exact Hartree-Fock exchange)² together with the correlation correction of Lee, Yang and Parr.³ B3LYP is parameterized against experimental data, mainly atomization and ionization energies and atomic energies.

The HOMA geometric indices have been computed according to the formula

$$\text{HOMA} = 1 - 257.7/n * \sum_{i \rightarrow n} (1.388 - \text{BL})^{**2}$$

(BL = perimeter CC bond length). The normalization factor in front of the sum depends on the definition of the "optimal" bond length (here 1.388 Å).

Cartesian coordinates of all transition state structures may be requested from the authors.

Section B: Charge distribution of species **6** and **8**

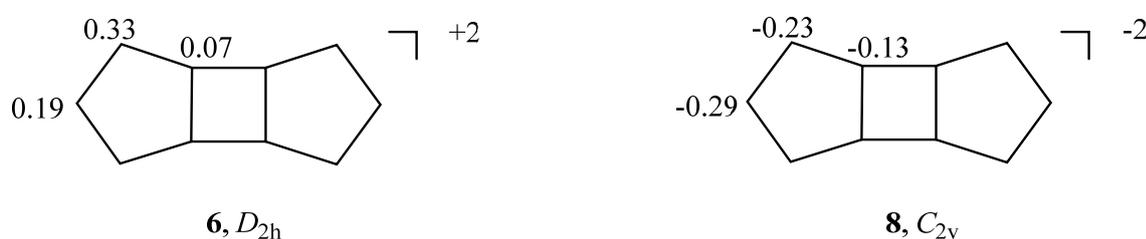


Figure S1. Natural charges (from natural population analysis) on carbons (with charges on hydrogen summed up) for species **6** and **8**.

The charge distributions in (see Figure S1) shows that the total charges on the five rings in **6** and **8** amounts to about +e and -e, respectively, while the charge density on the central 4-rings is small (i.e. 0.28 e and -0.52 e, respectively).

Section C: Reference structures for calculation of aromatic stabilization energy by the isomerization-stabilization method⁴

Figure S2 shows the minimum structures that have been employed to benchmark the isomerization-stabilization method for assessing aromatic stabilization energies in polycyclic compounds. Only Kekulé structures are used. For cyclobutadiene, this gives a unique result. For benzene already there are two possible locations of the sp^3 hybridised carbon atom: ortho or para to the exocyclic CC double bond. These two possibilities are comparable in energy but differ in their contribution from double bond conjugation: one reference has a solely linear conjugation, the other, expectedly less favorable, a cross conjugation.

To compute the ISE of pentalene, usually a reference is used in which the sp^3 carbon and the exocyclic CC double bond are direct neighbours on one of the pentalene rings.⁵ For instance, Xia, Zhu, Schleyer and co-workers employed a pentalene reference similar to the second one used by us (see Figure S2 at relative energy of -6.9 kcal/mol) and at B3LYP/6-311++G** level of theory to obtain -8.8 kcal/mol antiaromatic destabilization energy of pentalene. This would not, however, be possible when complete disruption of cyclic electron delocalization in species like **4** or **9**, with a central pentalene unit, is intended. Therefore we employed a reference in which the sp^3 carbon and the exocyclic bond are located on different rings. One can see, that in this case the destabilization due to antiaromaticity in parent pentalene becomes smaller (-3.5 vs. -6.9 kcal/mol), due to decreased thermodynamic stability of the reference with disrupted cyclic delocalization. One should therefore be aware that applying the ISE method to polycyclic compounds (which has, to the best of our knowledge, been done in this work for the first time) involves a certain ambiguity and has to be carried out very carefully. However, it gives at least a qualitative (or semi-quantitative) answer to the question whether a given polycyclic hydrocarbon is aromatic and to which extent it is stabilized (or destabilized) by cyclic electron delocalization.

The thermodynamic stability of the reference structures (see Figure S2-S5), and in which the cyclic delocalization is disrupted, differs sometimes considerably (see e.g. **r10-2** vs. **r10-1** in Figure S4 and cf. **r110-2** vs. **r110-1** in Figure S5) even if the structural modification may not appear dramatic. In the present case, for instance, **r110-2** and **r10-2** differ only in the positions of the two methyl groups. We reported here the larger ISE resulting value in the paper, because of the greater conformity with the benchmark for parent pentalene and species **4**, **9** and **11**. The amount of linear electron delocalization (or "conjugation") in these structures is different (depending on the available delocalization pathways). Also important could be, in principle, also the extent of antiaromaticity in the central cyclobutadiene rings of the reference structures denoted by a "-2" suffix: the less antiaromatic these rings are in the reference structures with otherwise disrupted cyclic delocalization, the smaller the obtained ISE value is expected to be. However, the NICS(1) values for the 4-rings in **r10-2** and **r110-2** are almost identical: +27.6 (NICS(1)_{zz} = +99.5) and +27.5 (NICS(1)_{zz} = +109.2), respectively. In this case, the influence of the different conjugation patterns appears to be dominating.

The number of possible reference structures becomes soon prohibitively large for the bigger molecules: e.g. for **10** and when non-Kekulé structures are included, the total combinatorial possible number of reference structures with maximally disrupted cyclic electron delocalization is 45! We did not explore the full configuration space of all these possible reference pairs because this would be outside of the scope of our present study, instead we intended to compare "families" of reference structure pairs with closely related substitution patterns: i.e. **4** and **9-11** which pertain to one of the pentalene benchmark in Figure S2 with ISE = + 3.5 and **5-8** which pertain to the other pentalene benchmark in Figure S2 with ISE = + 6.9).

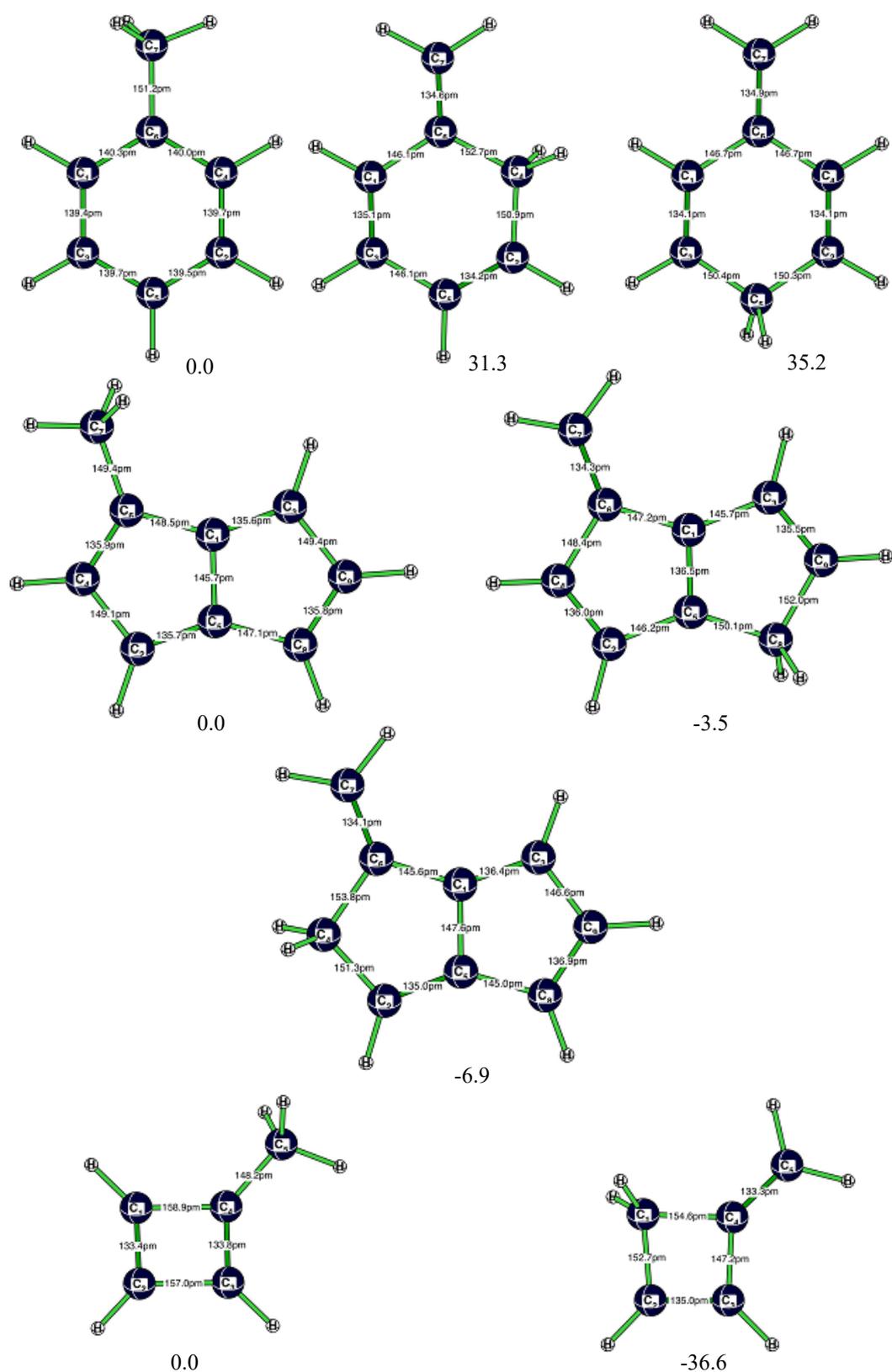


Figure S2. Reference structures at B3LYP/6-31G* (rel. Energies in kcal/mol) for the cyclic frameworks used in this work: benzene (top), pentalene (middle) and cyclobutadiene (bottom). Bond lengths are given in pm.

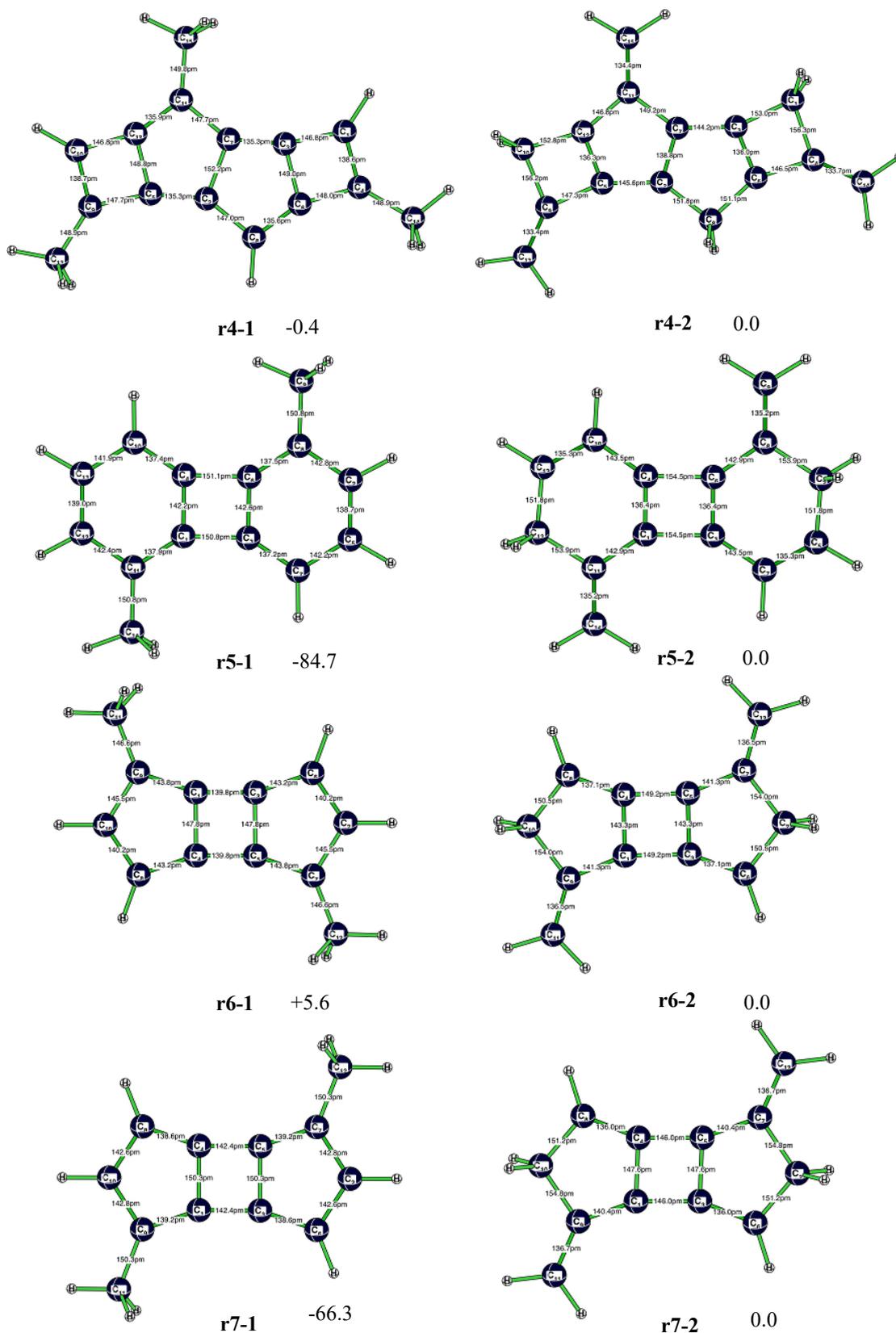


Figure S3. Reference structures at B3LYP/6-31G* (rel. Energies in kcal/mol as reported in the paper full text) for the polycyclic hydrocarbons **4-7** used in this work. For easy reference, all reference structures carry a "r" prefix before the species number from Figure 2. Suffix "-1" denotes the reference structure with intact cyclic delocalization, suffix "-2" denotes structure with maximally interrupted cyclic delocalization. Bond lengths are given in pm.

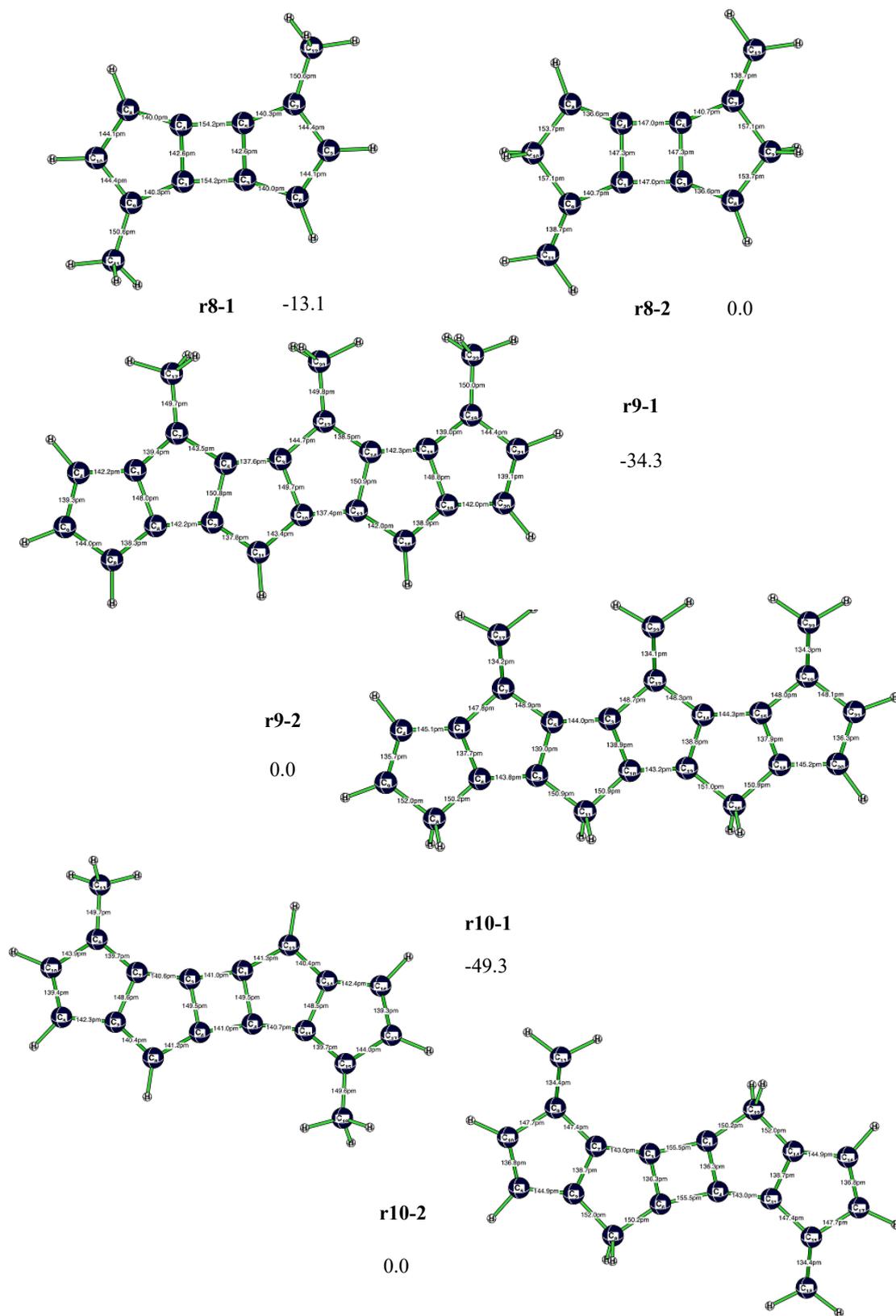


Figure S4. Reference structures at B3LYP/6-31G* (rel. Energies in kcal/mol) for the polycyclic hydrocarbons **8-10** used in this work. For easy reference, all reference structures carry a "r" prefix before the species number from Figure 2. Suffix "-1" denotes the reference structure with intact cyclic delocalization, suffix "-2" denotes structure with maximally interrupted cyclic delocalization. Bond lengths are given in pm.

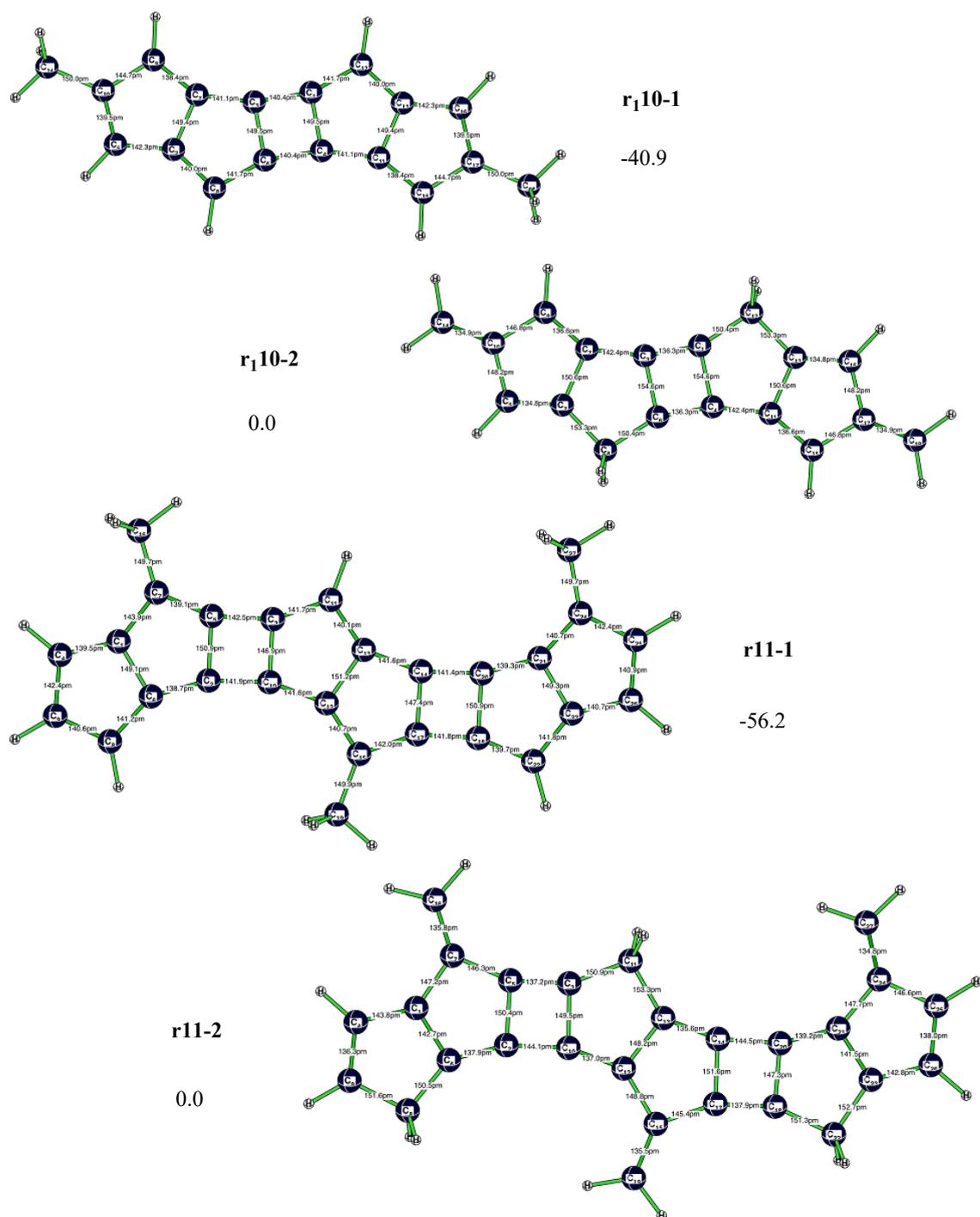


Figure S5. Reference structures at B3LYP/6-31G* (rel. Energies in kcal/mol) for the polycyclic hydrocarbons **10-11** used in this work. For easy reference, all reference structures carry a "r" prefix before the species number from Figure 2. Suffix "-1" denotes the reference structure with intact cyclic delocalization, suffix "-2" denotes structure with maximally interrupted cyclic delocalization. To distinguish between the two different reference structure pairs (cf. Figure S4) for compound **10**, an index is used. Bond lengths are given in pm.

References:

- 1 GAUSSIAN09, M. J. Frisch, et al., Gaussian Inc. Pittsburgh PA, 2008.
- 2 A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
- 3 C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.
- 4 P.v.R. Schleyer, F. Pühlhofer, *Org. Lett.*, 2002, **4**, 2873.
- 5 C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P.v.R. Schleyer, H. Xia, *Nature Chemistry*, 2012, **5**, 698.