Supplementary Information

A new architecture of high spin organics based on Baird's rule of 4n electron triplet aromatics

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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] Density functional theory computations have been performed with the hybrid B3LYP and OLYP functionals. Both functionals contain the correlation correction of Lee, Yang and Parr.[2] B3LYP includes Becke's exchange functional (that contains approximately 20% exact Hartree-Fock exchange).[3] B3LYP is parameterized against experimental data, mainly atomization and ionization energies and atomic energies.[4] OLYP differs from B3LYP in that it contains the optimized OPTX exchange functional rather than the B88 exchange.[5] In this way we tried also to obviate a possible overestimation of the relative stability of higher multiplicity states because of the high content of exact exchange in the B3LYP functional. The main problem, however, is that density functional methods in general are not considered suitable to accurately evaluate quantitatively the relative energy of molecules with different spin multiplicity (and are susceptible to spin contamination, which could result in artefactual energetics and geometries).[6]

That spin contamination can occur at all is due to the fact that in unrestricted methodologies the $\hat{S}^2$ and the Hamilton operator do not commute. States of highest multiplicity show usually only small spin contamination because admixture of higher multiplicity states is not possible, of course. Hence, spin contamination may signal the breakdown of a single reference description for the "wave function" (actually density matrix in case of DFT): only the dynamic part of the electron correlation is taken into account, the so-called "static" electron correlation, which comes from the admixture of states of different (i.e. higher) multiplicity, is neglected.

The MCSCF calculations started from a canonical RHF basis calculated in a previous run on the closed shell singlet biscyclopentadienyl cation **4** (Figure S1 and Table S1). To obviate SCF convergency issues, the basis sets in the CASSCF calculations have been successively projected to larger basis sets, beginning with STO-3G -> 4-31G -> 6-31G*. The whole π electron subspace was taken as the active space. The Frost-Musulin memnonic for the $C_5H_5^+$ monomer suggests that the 4 electrons in this cation are distributed among five orbitals. Hence, we have to use 8 electrons in 10 orbitals as active space for the dyads. This method establishes the correct order of states of different spin multiplicity in terms of the state "purity", which is achieved by evaluating all possible electron configurations as individual wave function references and for a given variational subspace, i.e. the "static" electron correlation). In order to do this, we have increased the maximum possible wave function reference configurations to 50,000. To retrieve also the dynamical correlation, we used perturbative MP2 corrections of the multi-determinant CASSCF wave function with a chosen cutoff for the CI coefficient of 0.02. This results in less than 1,000 configurations for each species **1-3** to be taken into account in the multi-reference MP2 single point calculation.

Dunning's correlation consistent cc-pVTZ and cc-pVDZ basis sets have been applied in the coupled cluster theory computations, where possible.[7] While the major part of (dynamic) electron correlation is retrieved already by CCSD with doubly excited Slater determinants, the inclusion of perturbative triples allows to take into account also part of the static correlation even though the method is still a single reference approach.[8] The QCISD method is size-consistent due to the quadratic terms in the

expansion (in contrast to CI) and is tantamount to a truncated CCSD series.[9] Because second order analytic derivatives are available in GAUSSIAN, geometry optimizations have been facilitated at this level of theory.

The vertical excitation spectra were computed starting from the geometry of quintet **1** with the (U)CIS (with a UHF reference) and TDDFT methods. The latter does not work for the dyad species, i.e. the first excited singlet state has an imaginary excitation energy, and the Tamm-Dancoff approximation (TDA), equivalent to CIS within a linear response Hartree-Fock formalism,[10] with which one may possibly overcome this problem, was not at our disposal with the GAUSSIAN version (C01) we have employed.

To obtain broken symmetry DFT solutions as input for the geometry optimizations of the open shell singlet polyads, we have also performed stability calculations on the closed shell singlet stationary points that we located on the PES's. Spin densities shown in Fig. 1 are computed at UB3LYP/6-311G* level (with a broken symmetry solution for the open shell singlet **3**). Such DFT (i.e. single determinant) spin densities were evaluated against CASSCF spin densities: as long as there is no complete breakdown of the single-determinant approach, UB3LYP spin densities have been found to perform well.[11]

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 (for the rotation around the CC single bond). Furthermore, intrinsic reaction coordinate computations (IRC) have been carried out to verify that the located transition structures pertain to the correct minima.

For the GIAO magnetic shielding computations (with the gauge-independent atomic orbitals method), the SCF and MP2/6-31G* methods have been employed. NICS plots are based on HF isotropic shielding values.

Spin pairing in states of higher multiplicity leads to a state of lower multiplicity (by reduction of the total spin by 1). This is possible only, when there is a conical intersection of the potential energy surfaces pertaining to the two multiplicities and which allows to judge, in principle, the kinetic stability of the highest multiplicity spin isomer. We located a conical intersection geometry (and where the Born-Oppenheimer approximation breaks down) by a CASSCF calculation. Furthermore, this spin pairing may result in structures which have a higher relative stability with respect to the maximum multiplicity state (because of an additional CC bond formed in these species). Appropriate derivatization strategies, however, can be employed to change this thermodynamic order of stability and establish the maximum multiplicity state as thermodynamic ground state. These results will be published elsewhere.

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

References:

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Section B: Structure and Energetics of Dyads at B3LYP (also c.f. full text in paper)

142.4 143.1
142.2 150.3
142.4 143.1

1, Q (C_2)

-4.6   -4.6

142.5 143.2 142.4
142.4 141.3 149.8
140.8 147.2 149.6 143.2 142.1
142.4

2,T (C_1)

+15.4   -4.7

143.4 149.4
142.3 149.9 149.1 139.2
141.9 144.4 140.2 143.6
142.2 142.1

3,S (o.s., C_1)

+15.4   +15.4

134.4 148.3
145.9
156.3 145.2
134.9

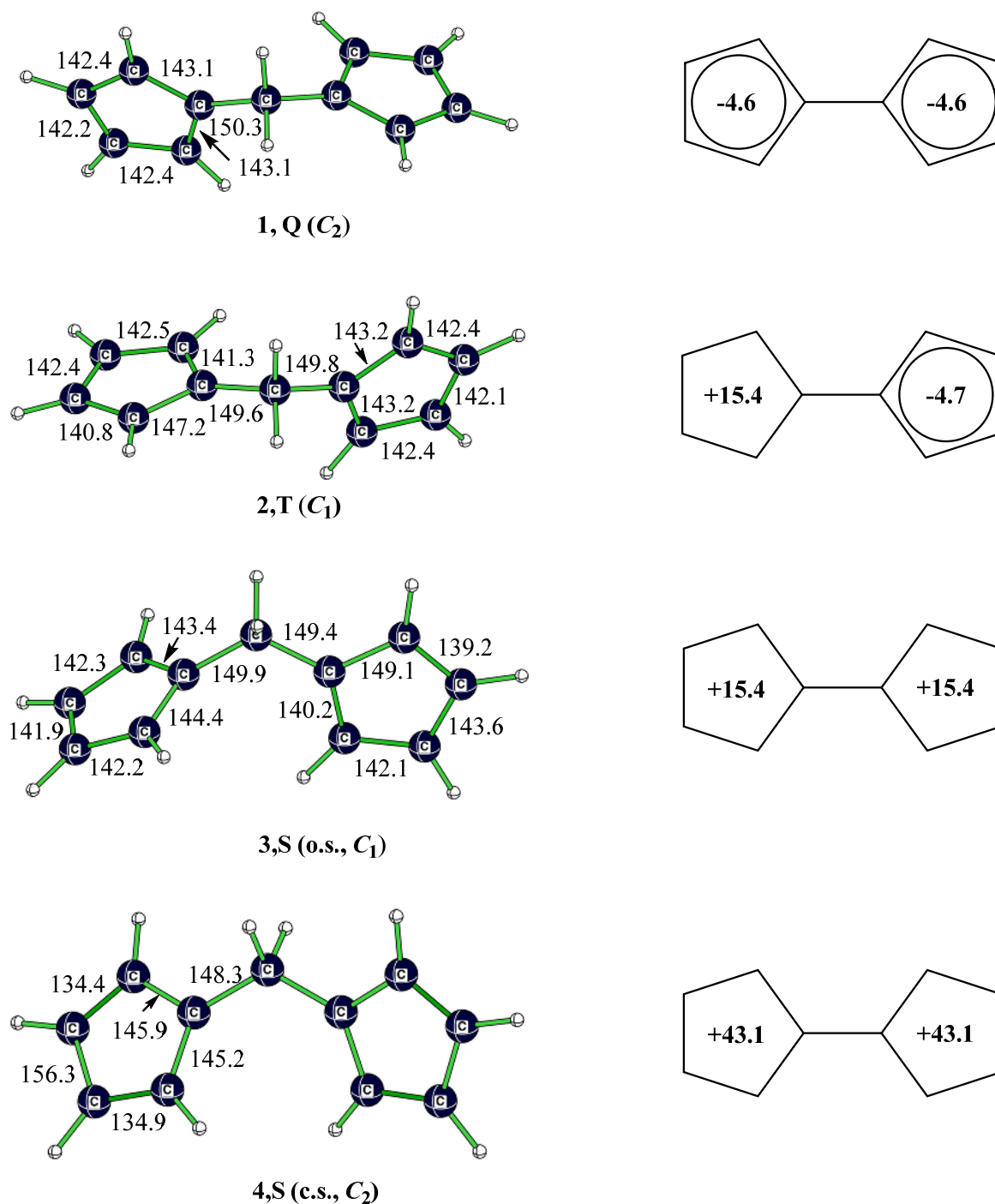**4,S (c.s., C_2)**

+43.1   +43.1

Figure S1. Dyads at B3LYP/6-311G* level. NICS(0) are computed at B3LYP/6-31G*//B3LYP/6-311G*. Bond lengths are given in pm (c.s. = closed shell, o.s.= open shell "broken symmetry" (BS) solution).