Supporting Information: Closed-shell paramagnetic porphyrinoids

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Some remarks regarding the gauge origin

The magnetizability cannot be uniquely divided into paramagnetic and diamagnetic contributions when using perturbation-dependent London orbitals,[1] because they depend on the magnetic field, the gauge origin, and the origin of the Cartesian coordinate system. After evaluating the atomic integrals, the gauge origin vanishes, whereas the dependence on the origin of the Cartesian coordinate system remains. Thus, the individual contributions to the total magnetizability depend on the Cartesian origin even though the total magnetizability is unaffected by shifting the origin.[1] One usually divides the magnetizability into a diamagnetic part that depends only on the ground-state wave function and a paramagnetic contribution that comprises response terms due to the external magnetic field. The same principle has also been used for partitioning magnetic shielding tensors and magnetically induced current densities into diamagnetic and paramagnetic contributions.[2] The paramagnetic contribution to nuclear magnetic shielding tensors can though be accurately determined by combining calculations with and without London orbitals. The diamagnetic contribution is obtained with conventional basis sets and the total shielding with the perturbation-dependent basis functions. The paramagnetic shielding is the difference between the two contributions.[3,4]

Aromatic pathways

The term *aromatic pathways* is used in this context to describe the anticipated π electron conjugation pathway for isophlorin. For the antiaromatic porphyrinoids, 20 π electron are generally assumed to participate in the conjugation pathway making the molecule antiaromatic according to Hückel's π electron count rule. However, current density calculations show that all 28 π electrons sustain the ring current.

It is possible to calculate electron mobility or aromatic pathways using magnetically induced current densities,[5] by explicit numerical integration over the current flow passing selected bonds. In this way a clear picture of the preferred current pathway within a molecule can be obtained as shown

for example for porphyrins[6] and isophlorins.[7] Aromatic pathways are not experimentally measurable but provide a helpful concept for understanding the aromatic character of the investigated molecules. Figure 1 shows as an example the calculated current pathway for dioxa-dithia isophlorin. For further details see Ref. 7.
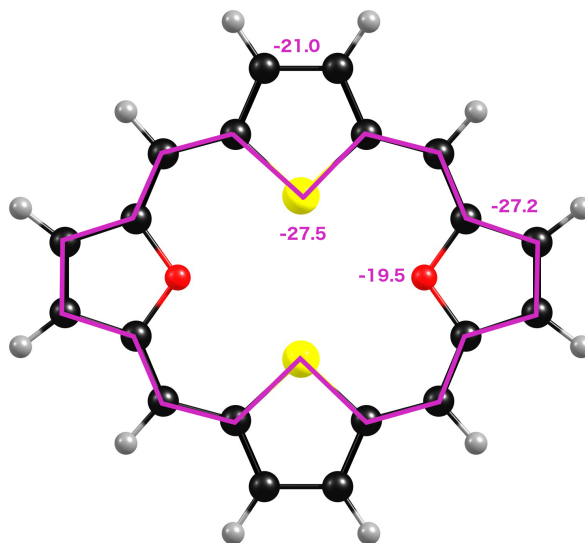

Fig. 1 Calculated current pathway for dioxa-dithia isophlorin indicated in pink. The integrated current strength susceptibility for selected bonds are given in nA/T. All valence π electrons sustain the ring current as the current strength along the inner and outer pathways are almost equal.

Computational details

Magnetizabilities at the HF and DFT levels we calculated using Gaussian 09 version D.01.[8] Magnetizabilities at the local MP2 level were obtained using MOLPRO version 2015.1[9,10] Perturbation-dependent London orbitals were employed in all calculations.[1,11] The def2-TZVP basis sets were used in the DFT and HF calculations,[12] whereas the MP2 calculations

were performed with the cc-pVDZ basis sets.[13] The ring-current strength susceptibilities calculated at the DFT level using the B3LYP functional [14–16] are taken from Refs. 7, 17, and 18. Here, the ring-current strength susceptibilities [5,19] have been integrated using current density susceptibilities calculated at the HF and MP2 levels using Turbomole 7.1 and the def2-TZVP basis sets.[20,21]

To check whether the investigated molecules have a significant multi-reference character, we carried out complete active space (CASSCF) calculations with 7 electrons in 10 molecular orbitals (MO) as well as calculations at the quasi-degenerate second order perturbation theory (XMC-QDPT2) level for compound VII[22] using the 6-31G(d,p) basis set.[23,24] Molecule VII has the largest current strength susceptibility of the investigated porphyrinoids and is therefore the most antiaromatic molecule among the studied molecules according to the ring current criterion. State-averaged calculations were performed for compound VII by averaging over the four lowest states using an effective Hamiltonian that included 30 states. The CASSCF and XMC-QDPT2 calculations were performed with the Firefly program package.[25] At the XMC-QDPT2 level, the vertical excitation energies of the lowest singlet (S_1) and triplet (T_1) states of molecule VII are 0.81 eV and 0.52 eV, respectively. A similar excitation energy of 0.45 eV was obtained for the lowest singlet state of molecule VII at the time-dependent density functional theory (TDDFT) level.[26,27]

Detailed references

The complete Gaussian and MOLPRO references are given here.[28,29]

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Table 1 Comparison of the calculated ring-current strength susceptibilities (in nA/T) and magnetizabilities (in a.u.) for the studied compounds I-VII calculated at different levels of theory. The diatropic and paratropic contributions to the total ring-current strength susceptibilities are also reported.

Molecule	Ring-current strength susceptibility			Magnetizability
	Diatropic	Paratropic	Total	Total ($\chi_d + \chi_p$)
DFT/B3LYP/TZVP				
I	21.0	-22.1	-1.1	-35.2
II	20.1	-27.5	-7.4	-21.8
III	14.7	-49.7	-35.0	25.4
IV	11.7	-64.2	-52.5	44.4
V	11.2	-73.7	-62.5	65.9
VI	9.1	-85.9	-76.8	90.2
VII	7.1	-152.1	-145.0	204.9
HF/TZVP				
I	22.1	-22.4	-0.3	-38.4
II	21.7	-24.1	-2.4	-36.3
III	18.9	-27.5	-8.6	-23.9
IV	19.6	-33.5	-13.9	-19.2
V	17.9	-33.8	-15.9	-11.6
VI	16.2	-31.9	-18.5	-14.0
VII	14.7	-35.4	-20.7	-3.8
MP2/TZVP				
I	22.3	-22.9	-0.6	-39.5
II	21.3	-25.7	-4.2	-32.3
III	17.2	-34.7	-17.5	-8.7
IV	15.8	-44.5	-28.7	7.11
V	14.8	-42.2	-27.4	15.8
VI	12.3	-47.2	-34.9	21.8
VII	10.5	-59.1	-48.6	48.3