SUPPORTING INFORMATION

Möbius-Hückel Topology Switching in an Expanded Porphyrin Cation Radical as Studied by EPR and ENDOR Spectroscopy

Klaus Möbius^{1,2}, Martin Plato¹, Gudrun Klihm², Christoph Laurich², Anton Savitsky², Wolfgang Lubitz², Bartosz Szyszko³, Marcin Stępień³ and Lechosław Latos-Grażyński³

¹ Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
² Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, 45470 Mülheim (Ruhr) Germany
³ Wydział Chemii, Uniwersytet Wrocławski, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Details of the DFT calculations of ¹⁴N- and ¹H hyperfine couplings of the cation radicals of the Möbius and Hückel conformers

All results of the DFT calculations of isotropic hfc's, a_nth, are compiled in tabular form, those of ¹⁴N nuclei, a_Nth, in Table S1, those of ¹H nuclei, a_Hth, in Table S2.

Case ¹⁾	Structure ²⁾	a_N^{th}/MHz			
		N ₃₄	N ₃₈	N ₃₃	N ₃₇
1	<i>T1-</i> 1	3.72	3.52	6.20	- 0.65
1	<i>T2-</i> 1	3.98	3.99	1.83	1.85*
2	<i>T1-</i> 1	3.64	3.56	6.12	- 0.68
2	<i>T1-</i> 1	2.64	3.01	4.62	- 0.17
5	<i>T2-</i> 1	3.25	3.26	1.44	1.45*
4	<i>T1-</i> 1	2.89	3.28	5.15	- 0.12
5	<i>T1-</i> 1	1.72	3.36	4.10	0.50
6	<i>T1-</i> 1	1.27	3.59	3.73	1.03
7	<i>T1-</i> 1	2.91	5.05	7.38	0.90

Table S1. ORCA-DFT results for isotropic ¹⁴N hyperfine coupling constants a_N th in cation radicals of Möbius and Hückel structures, *T1*-1 and *T2*-1, respectively.

¹⁾ Different program settings (functional, basis-set, etc.)

Case 1: B1LYP,¹ TZVP,² in gas phase, without geometry optimization

Case 2: B1LYP, TZVP, in gas phase, with geometry optimization in neutral singlet ground state,

Case 3: B3LYP,³ Def2-TZVP,⁴ otherwise same as Case 2,

Case 4: B3LYP, IGLO-III,⁵ otherwise same as Case 2,

Case 5: same as Case 3, but with geometry optimization in cation doublet state, spin unrestricted option, 6

Case 6: same as Case 5, in solvent CH_2Cl_2 (model COSMO⁷), with optimization result of Case 5,

Case 7: B3LYP, 6-31G**,^{3, 8} including geometry optimization and solvent CH_2Cl_2 (Test case for quality of basis set in predicting values of a_N^{exp}).

²⁾ initial geometries from optimized X-ray structures.⁹

* values practically pairwise equivalent for symmetry reasons.

Case ¹⁾	Structure ²⁾	a _H th/MHz		
		H(N ₃₄)	H(N ₃₈)	
1	<i>T1-</i> 1	- 4.58	- 5.12	
	<i>T2-</i> 1	- 4.97	- 4.99*	
2	<i>T1-</i> 1	- 4.71	- 5.17	
3	<i>T1-</i> 1	- 3.63	- 4.58	
	<i>T2-</i> 1	- 4.22	- 4.23*	
4	<i>T1-</i> 1	- 3.54	- 4.46	
5	<i>T1-</i> 1	- 2.56	- 5.13	
6	<i>T1-</i> 1	- 2.02	- 5.42	

Table S2. ORCA-DFT results for selected isotropic ¹H hyperfine coupling constants a_H^{th} in cation radicals of Möbius and Hückel structures, *T1*-1 and *T2*-1, respectively.

¹⁾ Different program settings (functional, basis-set, etc.), same as in Table S1.

²⁾ initial geometries from optimized X-ray structures.⁹

* values practically pairwise equivalent for symmetry reasons.

Case 6, which includes solvation effects by use of the COSMO model, does not give the anticipated improvement. It must be pointed out, that this calculation does not include any electrostatic effects from the counter-ion, which is expected to significantly stabilize the solute-solvent system. Case 7 clearly demonstrates that using the Gaussian basis 6-31G** is not the best choice for predicting hyperfine couplings, although it is quite frequently used for energy calculations (see stability aspects based on energy considerations below).

Aside from calculations of hyperfine couplings a_n for the various structures considered in Tables S1 and S2, additional important information concerning the structures' relative energetic stabilities is anticipated from the corresponding total energies (comprising electronic, nuclear and solvent contributions). Unfortunately, reliable values for such energies are difficult to assess theoretically for the cation state of **1** in liquid solution, where not only the dielectric properties of the solvent are expected to contribute significantly to the total energy of the solute-solvent system, but also the counter-ion. We do not expect the Coulomb interaction between the radical cations of

T1-1 and *T2*-1 and their counter anions to be of the same magnitude because of their different spatial arrangements in the solvent. This situation is not encountered in the neutral state of 1, where no electric charges, except for dielectric screening effects by the solvent, are operative. We therefore refrain from discussing in detail energy values of the cation state of 1, where the use of COSMO alone would lead to insignificant results. We prefer to supplement the energy calculations performed by Stępień et al.⁹ on the neutral state of 1. By using the functional/basis-set B3LYP/6-31G**, these authors find comparable energies for the conformers *T2*-1 and *T1*-1. However, the Hückel structure turns out to be more stable than the Möbius structure by 12.6 kJ·mol⁻¹.

Equivalent calculations performed with ORCA-DFT yielded exactly the same result as above. In addition, we included solvation effects using the COSMO model. This resulted in a reduction of the above value of $12.6 \text{ kJ} \cdot \text{mol}^{-1}$ to $7.7 \text{ kJ} \cdot \text{mol}^{-1}$. It confirms the expectation that the dielectric properties of the solvent lead to a significant decrease in the energy difference between *T2-1* and *T1-1*. COSMO, however, does not achieve a complete turn-around of the energy levels. This might be due to shortcomings of the COSMO model and/or to insufficient accuracy of the DFT results when using the B3LYP/6-31G** program settings.

References

- 1. A. D. Becke, J. Chem. Phys., 1996, **104**, 1040-1046.
- 2. A. Schafer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829-5835.
- 3. A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 4. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
- 5. W. Kutzelnigg, U. Fleischer and M. Schindler, in *NMR Basic Principles and Progress*, Springer Berlin Heidelberg, Editon edn., 1991, vol. 213, pp. 165-262.
- 6. F. Neese, WIREs Comput. Mol. Sci., 2012, 2, 73-78.
- 7. A. Klamt and G. Schüürmann, J. Chem. Soc., Perkin Trans. 2, 1993, 799-805.
- 8. R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, 54, 724-&.
- 9. M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz and L. Szterenberg, *Angew. Chem. Int. Ed.*, 2007, **46**, 7869-7873.