



Supporting Information

for

Hidden aromaticity behind paratropic ring currents in oxoverdazyl and benzotriazinyl radicals

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Quantum chemical calculation details

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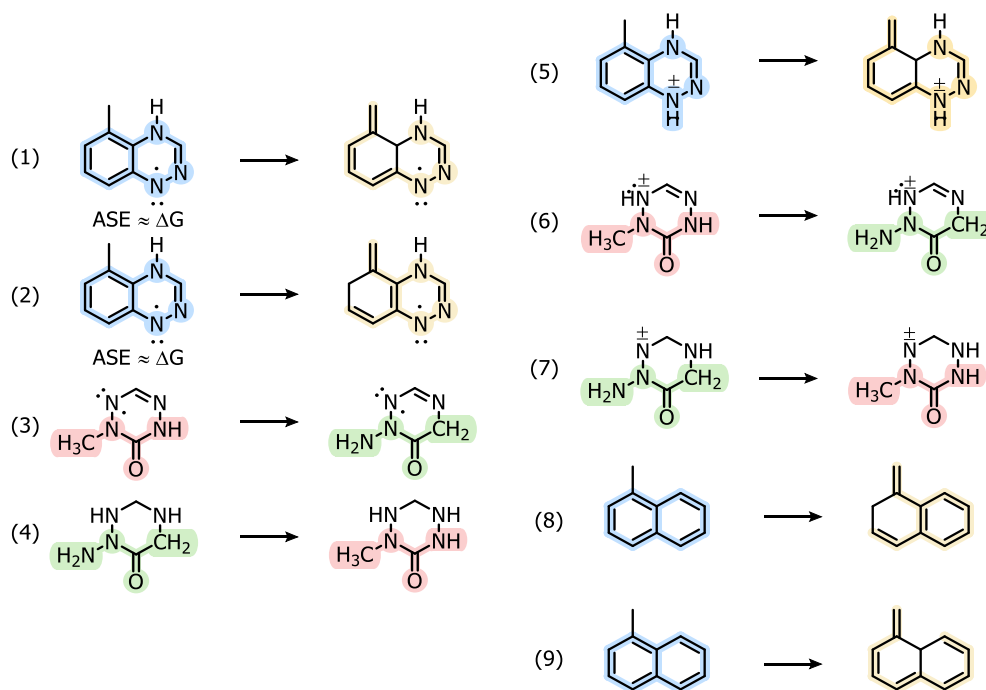
1. Computational data

Quantum chemical calculations were performed using ORCA 5.0.4 [1,2]. Initial geometries were optimized and frequencies were calculated at the r²SCAN-3c level of theory [3], verifying minima with zero imaginary frequencies [4]. Next, the geometries were improved at the MP2/def2-TZVP level of theory, single-point energies were obtained at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory [5,6]. At the MP2 level of theory, the RIJCOSX approximation was used together with the auxiliary basis sets def2/J and def2-TZVP/C. At the DLPNO-CCSD(T) level of theory, the RIJK approximation was used together with the auxiliary basis sets aug-cc-pVTZ/C and aug-cc-pVTZ/JK, and the TightSCF keyword was applied. In both cases, the FROZENCORE approximation, which is enabled by default in ORCA 5.0.4, was employed.

In all cases where energetic parameters were considered, the following expression for Gibbs free energy of formation was used:

$$\Delta G_f(X) = \Delta G_f(\text{r2SCAN} - 3\text{c}) - E_{\text{SPE}}(\text{r2SCAN} - 3\text{c}) + E_{\text{SPE}}(\text{DLPNO} - \text{CCSD(T)/aug} - \text{ccpVTZ}).$$

NICS values were calculated at the PBE0(D4)/pcseg-2//MP2/def2-TZVP level of theory. ACID diagrams were obtained at the B3LYP/6-31G(d)//MP2/def2-TZVP level of theory and visualized in AICD-3.0.4 program [7]. Magnetic field is directed towards the viewer, POV is placed on the Z-axis. Electron Density of Delocalized Bonds (EDDB) calculations were performed with runEDDB [8] (<https://aromaticity.uj.edu.pl/runeddb/>). The electron density was calculated in ORCA 6.1.0, at the B3LYP/def2-TZVP theory level.



Scheme S1: Isodecemic reaction equations.

Table S1. Energies of optimized structures (isodesmic reactions) with the number of imaginary frequencies. Calculated at DLPNO-CCSD(T)/aug-ccpVTZ//MP2/def2-TZVP level of teory.

compound	Number of imaginary frequencies.	SPE E _h	G E _h	H E _h
benzotriazinyl_anion_parent.xyz	0	-433.8457978	-433.7542291	-433.7141444
benzotriazinyl_cation_parent.xyz	0	-433.5693641	-433.47184	-433.432739
benzotriazinyl_parent.xyz	0	-433.8021352	-433.7086096	-433.6680698
eq1_eq2_reactant.xyz	0	-473.0488915	-472.9293368	-472.885224
eq1_product.xyz	0	-472.9955681	-472.8770696	-472.8331284
eq2_product.xyz	0	-473.0064105	-472.8888758	-472.8437889
eq3_product.xyz	0	-410.8350878	-410.7539498	-410.7142978
eq3_reactant.xyz	0	-410.8692523	-410.7875564	-410.748856
eq4_product.xyz	0	-412.6863575	-412.5614497	-412.521265
eq4_reactant.xyz	0	-412.6807036	-412.5572988	-412.5170149
eq5_anion_product.xyz	0	-473.0591678	-472.9407558	-472.8981795
eq5_anion_reactant.xyz	0	-473.0918236	-472.9741825	-472.9306
eq5_cation_product.xyz	0	-472.7468868	-472.6243427	-472.5818108
eq5_cation_reactant.xyz	0	-472.8205712	-472.697143	-472.6543904
eq6_anion_product.xyz	0	-410.915033	-410.8339454	-410.7946585
eq6_anion_reactant.xyz	0	-410.9210591	-410.8405121	-410.8006009
eq6_cation_product.xyz	0	-410.5642363	-410.4840085	-410.444465
eq6_cation_reactant.xyz	0	-410.5914093	-410.5080623	-410.469535
eq7_anion_product.xyz	0	-412.6424202	-412.5219374	-412.4818318
eq7_anion_reactant.xyz	0	-412.65275	-412.5327427	-412.4925899
eq7_cation_product.xyz	0	-412.4046048	-412.2834923	-412.2410415
eq7_cation_reactant.xyz	0	-412.3964376	-412.2747817	-412.2336705
verdazinium_parent.xyz	0	-371.3360443	-371.2801644	-371.2448856
verdazyde_parent.xyz	0	-371.6832422	-371.6302155	-371.593841
verdazyl_parent.xyz	0	-371.6300276	-371.5763512	-371.5398186
eq8_eq9_reactant_amenapht	0	-424,4220283	-424,2837485	-424,241332
eq8_product_iso1amenapht	0	-424,385587	-424,2484788	-424,2060576
eq9_product_iso2amenapht	0	-424,3386739	-424,2028023	-424,1603729

Table S2. Set of calculated NICS values for compounds. Calculated at PBE0(D4)/pcsSeg-2// MP2/def2-TZVP level of theory.

compound	nics(0)	Nics(1)	nics(1) _{zz}
benzotriazinyl_anion_parent.xyz	11.3	6.2	21.8
benzotriazinyl_cation_parent.xyz	-5.7	-10.3	-26.7
benzotriazinyl_parent.xyz	8.3	2.7	10.2
eq1_eq2_reactant.xyz	8.4	2.7	10.5
eq1_product.xyz	-1.4	-3.4	-4.8
eq3_product.xyz	4.6	0.6	3.7
eq3_reactant.xyz	3.5	0.5	3.3
eq4_product.xyz	-2.6	-1.0	2.0
eq4_reactant.xyz	-0.8	-0.8	3.0
verdazinium_parent.xyz	2.7	-3.1	-6.4
verdazyde_parent.xyz	4.0	3.6	12.3
verdazyl_parent.xyz	3.5	0.8	3.2

Table S3. EDDB analysis of parent benzotriazinyl radical.

	Total	per atom
ED_G population:	10.95	0.68
- alpha spin:	5.97	0.37
- beta spin:	4.98	0.31
EDLB_G population:	3.58	0.22
- alpha spin:	2.41	0.15
- beta spin:	1.16	0.07
EDDB_G population:	7.37	0.46
- alpha spin:	3.56	0.22
- beta spin:	3.82	0.24

Table S4. EDDB analysis of parent benzotriazinyl radical with tracking through the heterocyclic ring.

	Total	per atom:
ED_P population:	6.48	1.08
- alpha spin:	3.44	0.57
- beta spin:	3.04	0.51
EDLB_P population:	4.39	0.73
- alpha spin:	3.1	0.52
- beta spin:	1.29	0.22
EDDB_P population:	2.09	0.35
- alpha spin:	0.34	0.06
- beta spin:	1.74	0.29
Cyclic Delocal. Index (CDI):		0.22
- alpha spin:		0.03
- beta spin:		0.16

Table S5. EDDB analysis of parent oxoverdazyl radical with tracking through the heterocyclic ring.

	Total	per atom
ED_P population:	6.95	1.16
- alpha spin:	3.97	0.66
- beta spin:	2.98	0.5
EDLB_P population:	4.4	0.73
- alpha spin:	3.23	0.54
- beta spin:	1.17	0.19
EDDB_P population:	2.56	0.43
- alpha spin:	0.74	0.12
- beta spin:	1.82	0.3
Cyclic Delocal. Index (CDI):		0.13
- alpha spin:		0.03
- beta spin:		0.1

2. References

- (1) Neese, F. *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606. doi:10.1002/wcms.1606
- (2) Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78. doi:10.1002/wcms.81
- (3) Grimme, S.; Hansen, A.; Ehlert, S.; Mewes, J.-M. *J. Chem. Phys.* **2021**, *154*, 064103. doi:10.1063/5.0040021
- (4) Kesharwani, M. K.; Brauer, B.; Martin, J. M. L. *J. Phys. Chem. A* **2015**, *119*, 1701–1714. doi:10.1021/jp508422u
- (5) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101. doi:10.1063/1.4821834
- (6) Liakos, D. G.; Guo, Y.; Neese, F. *J. Phys. Chem. A* **2020**, *124*, 90–100. doi:10.1021/acs.jpca.9b05734
- (7) Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758–3772. doi:10.1021/cr0300901
- (8) Szczepanik, D. W.; Andrzejak, M.; Dominikowska, J.; Pawełek, B.; Krygowski, T. M.; Szatyłowicz, H.; Solà, M. *Phys. Chem. Chem. Phys.* **2017**, *19*, 28970–28981. doi:10.1039/C7CP06114E