SUPPORTING INFORMATION

FOR

The Effect of π-system Extension on the Ionization Energy of the Planar Blatter Radical: Experimental and Theoretical Studies

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Table of Context

1. Ultraviolet photoelectron spectra. Magnified Figure 2 in the main text

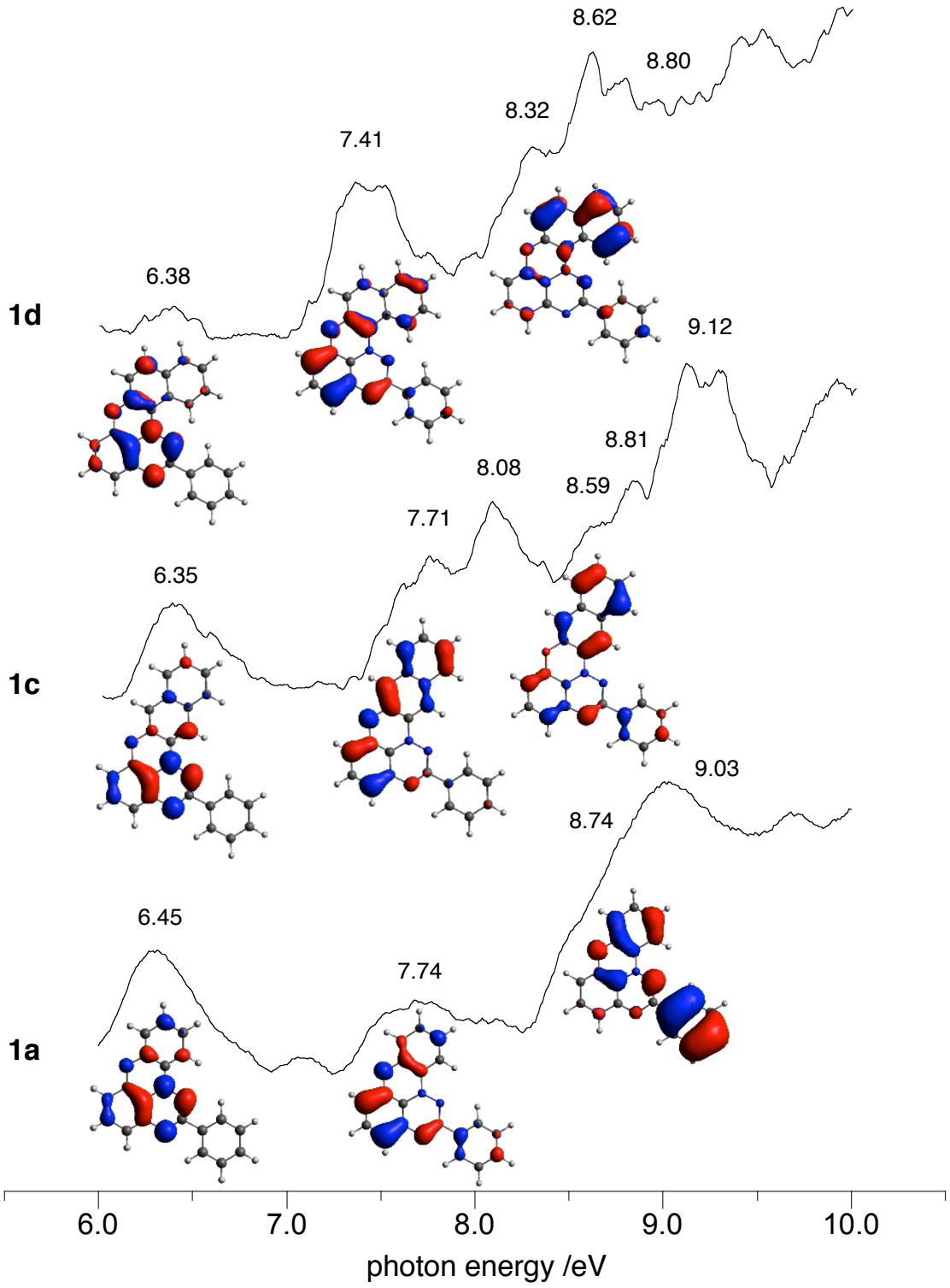


Figure S1. UV-photoelectron spectra for radicals **1a**,[1] **1c**, and **1d**.

2. Computational details and results

All calculations were performed using the Gaussian 09[2] computational package. Geometry optimizations were carried out with the UCAM-B3LYP[3-6] functional and the triple-ζ 6-311G(d,p) basis set.[7] Frequency calculations were performed for the optimized geometries in order to verify that the stationary points obtained were true energy minima. Atomic pin densities summed up to heavy atoms in series **1** were obtained using Barone basis set[8] at the UCAM-B3LYP/EPR-III//UCAM-B3LYP/6-311G(d,p) level of theory in benzene dielectric medium requested with the SCRF(IEFPCM, Solvent=Benzene) keyword (IEFPCM, the default PCM model).[9,10] Visualization of molecular orbitals was done with Avogadro software.[11,12]

a) Geometry optimization

The CAM-B3LYP/6-311G(d,p) optimized geometrical parameters (selected bond lengths and angles) for **1a**–**1h** are presented in Table S1 and compared with X-ray diffraction (XRD) data for **1a** [13] and **1c**.[14] A graphical comparison of the experimental (XRD) and DFT computed bond lengths in **1a** and **1c** is shown in Figure S2. Results show that DFT underestimates the bond lengths by about 0.011 Å, which within the experimental error of ±0.01 Å for **1a** and ±0.02 and ±0.03 Å for **1c**.

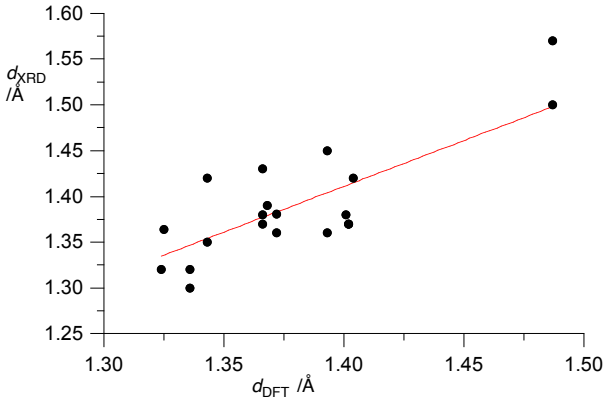
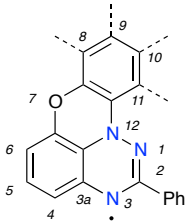


Figure S2. Correlation of the experimental and calculated bond distances *d* in **1a** and **1c**. Best fit line: $d_{XDR} = 0.0110(8) + d_{DFT}$, $r^2 = 0.66$.

Table S1. UCAM-B3LYP/6-311G(d,p) and XRD molecular geometrical parameters for radicals **1**.



Bond length and angle	**1a**	XRD [a]	**1b**	**1c**	XRD [b]	**1d**	**1e**	**1f**	**1g**	**1h**
11a-12 /Å	1.404	1.42	1.402	1.402	1.37	1.412	1.405	1.402	1.415	1.405
12-1/ Å	1.343	1.35	1.344	1.343	1.42	1.345	1.345	1.343	1.345	1.344
1-2/ Å	1.336	1.32	1.336	1.336	1.30	1.335	1.335	1.336	1.335	1.335
2-2Ph/ Å	1.487	1.50	1.488	1.487	1.57	1.487	1.488	1.487	1.487	1.487
2-3 /Å	1.325	1.364	1.325	1.324	1.32	1.323	1.325	1.325	1.323	1.325
3-3a /Å	1.366	1.38	1.366	1.366	1.43	1.366	1.365	1.366	1.366	1.366
3a-3a^1 /Å	1.401	1.38	1.401	1.402	1.37	1.402	1.401	1.402	1.402	1.401
3a^1-6a /Å	1.393	1.36	1.392	1.393	1.45	1.389	1.388	1.393	1.389	1.392
6a-7 /Å	1.368	1.39	1.370	1.366	1.37	1.364	1.368	1.367	1.364	1.368
7-7a /Å	1.372	1.381	1.372	1.372	1.36	1.371	1.374	1.372	1.370	1.372
12-1-2 /^{o}	116.1	114.1	116.1	116.2	112.3	117.1	116.2	116.1	117.0	116.1
1-2-3 /^{o}	127.2	130.2	127.3	127.1	134.0	127.4	127.3	127.2	127.3	127.2
6a-7-7a /^{o}	118.2	118.5	118.2	118.9	120.3	118.3	120.1	118.6	118.3	118.7
3a^1-12-11a /^{o}	118.7	118.6	118.5	119.2	122.2	118.9	119.2	118.9	118.9	118.9

[a] Ref. [13] est uncertainty 0.01. [b] Ref.[14] est uncertainty 0.02 and 0.03.

b) Ionization Energies (IE_n)

Vertical IE_n were calculated using two methods at the UCAM-B3LYP/6-311G(d,p) level of theory.

In the first, frequently used method[15-17] the lowest ionization energy (IE_1) was calculated as $\Delta E_{SCF} = E_{SCFcation} - E_{SCFradical}$ for fully optimized radical in its ground state and the cation at the radical geometry (single point calculations). Higher vertical ionization energies (IE_n) were obtained as a sum of ΔE_{SCF} and $E_{TD\text{-}DFT(n)}$, where the latter is the E_n excitation energy calculated with the TD method for the cation at the radical geometry. The TD method takes into account also low-lying ionic states and this approach has been demonstrated to be particularly reliable for obtaining accurate ionization energies.[18,19]

In the second method, vertical ionization energies (IE_n) are calculated based on Koopmans' theorem[20] and "shifted eigenvalue" correction.[21] In this formalism adopted for analysis of open-shell molecules, the first ionization energy: $IE_1^{KS} = -\varepsilon_{SOMO}^{KS}$ where ε_{SOMO}^{KS} is the Kohn-Sham energy of the highest occupied MO (SOMO) of the radical in its ground state, obtained with the unrestricted method (UCAM-B3LYP/6-311G(d,p)). Following the Stowasser and Hoffmann suggestion,[21] ionization energies for the first and higher ionization can be calculated from Kohn-Sham orbital energy corrected by a constant factor x as $IE_n = -\varepsilon_{HOMO-n+1}^{KS} + x_{\Delta ESCF}$, where the $\varepsilon_{HOMO-n+1}^{KS}$ for n>1 is obtained for fully geometry-optimized radical, using restricted open-shell method (RO-CAM-B3LYP/6-311G(d,p)). The "shifted eigenvalue" correction is calculated as $x_{\Delta ESCF} = IE_1^{ref(\Delta ESCF)} - IE_1^{KS}$ using theoretical first ionization energy as the reference ($IE_1^{ref(\Delta ESCF)} = \Delta E_{SCF} = E_{SCFcation} - E_{SCFradical}$, *vide supra;* then $x_{\Delta ESCF} = IE_1^{ref(\Delta ESCF)} - IE_1^{KS}$).[22]

Table S2. Theoretical ionization energies for radical **1b** obtained with the CAM-B3LYP/6-311G(d,p) method.

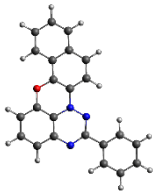
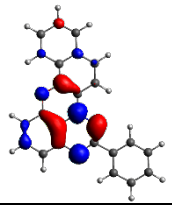
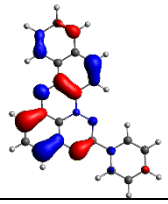
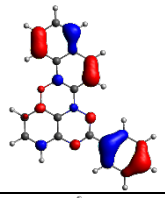
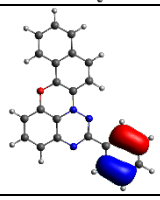
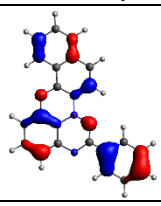
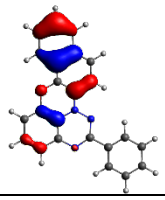
 **1b,** MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.252$ /eV
 H(S)OMO	6.267	6.015	6.267
 HOMO -1	7.052	7.128	7.380
 HOMO -2	8.315	7.974	8.227
 HOMO -3	8.323	8.338	8.591
 HOMO -4	8.701	8.399	8.652
 HOMO -5	8.836	8.589	8.841

Table S3. Assignment of experimental ionization energies (*IE*n) for radical **1c**. Theoretical values were obtained with the CAM-B3LYP/6-311G(d,p) method.

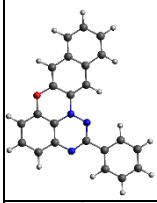
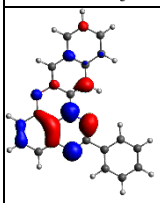
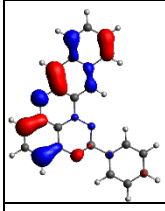
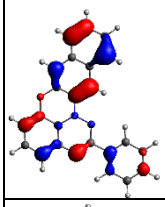
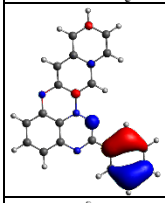
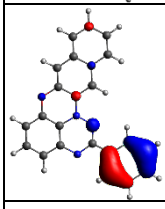
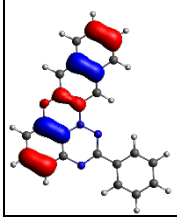
 **1c,** MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.245$ /eV	Exp. IE /eV
 H(S)OMO	6.393	6.148	6.393	**6.35**
 HOMO -1	7.323	7.286	7.531	**7.71**
 HOMO -2	7.992	7.660	7.905	**8.08**
 HOMO -3	8.311	8.243	8.489	**8.59**
 HOMO -4	8.479	8.404	8.650	**8.81**
 HOMO -5	8.719	8.833	9.078	**9.12**

Table S4. Assignment of experimental ionization energies (*IE*n) for radical **1d**. Theoretical values were obtained with the CAM-B3LYP/6-311G(d,p) method.

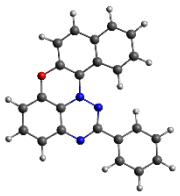
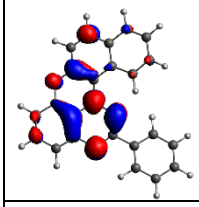
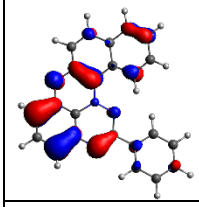
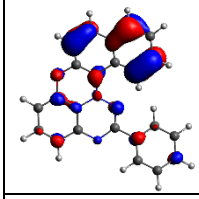
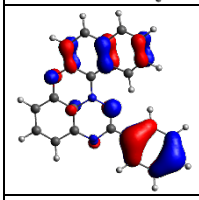
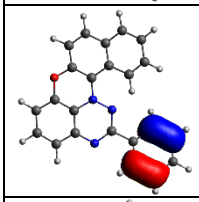
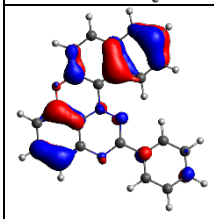
 **1d,** MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.257$ /eV	Exp. IE /eV
 H(S)OMO	6.282	6.025	6.282	**6.38**
 HOMO -1	7.066	7.144	7.401	**7.41**
 HOMO -2	8.337	7.990	8.246	**8.32**
 HOMO -3	8.371	8.158	8.415	**8.62**
 HOMO -4	8.487	8.381	8.638	**8.80**
 HOMO -5	8.917	8.689	8.945	**8.80**

Table S5. Theoretical ionization energies for radical **1e** obtained with the CAM-B3LYP/6-311G(d,p) method.

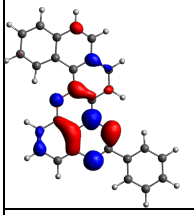
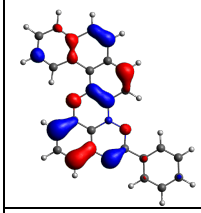
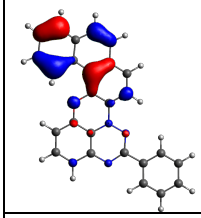
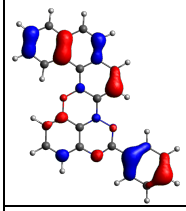
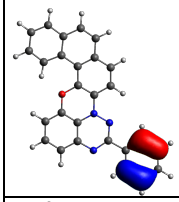
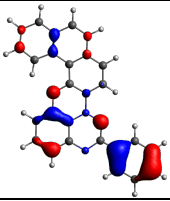
1e, MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.219$ /eV
 H(S)OMO	6.238	6.020	6.238
 HOMO -1	7.037	7.131	7.350
 HOMO -2	8.225	7.750	7.969
 HOMO -3	8.287	7.944	8.163
 HOMO -4	8.338	8.336	8.555
 HOMO -5	8.646	8.391	8.609

Table S6. Theoretical ionization energies for radical **1f** obtained with the CAM-B3LYP/6-311G(d,p) method.

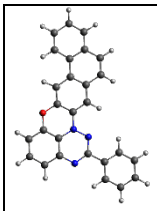
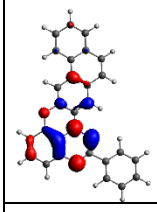
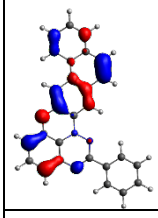
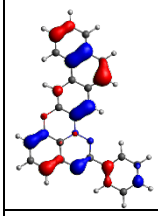
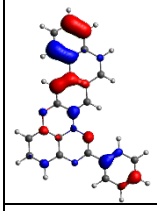
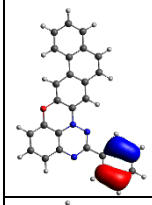
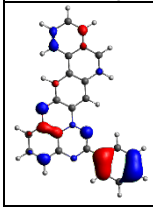
 **1f,** MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF}$ = 0.208 /eV
 H(S)OMO	6.313	6.105	6.313
 HOMO -1	7.174	7.145	7.353
 HOMO -2	8.012	7.658	7.866
 HOMO -3	8.164	8.043	8.251
 HOMO -4	8.388	8.331	8.539
 HOMO -5	8.619	8.399	8.607

Table S7. Theoretical ionization energies for radical **1g** obtained with the CAM-B3LYP/6-311G(d,p) method.

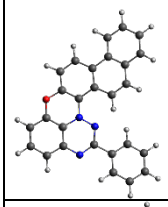
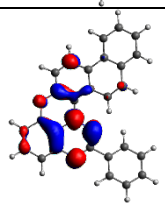
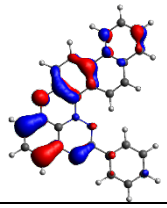
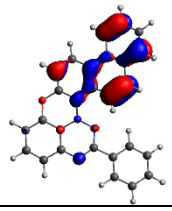
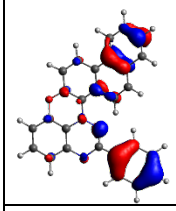
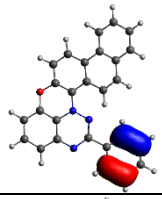
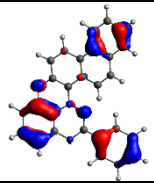
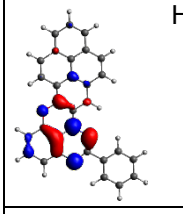
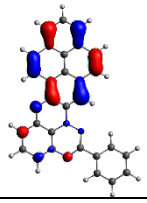
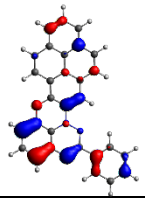
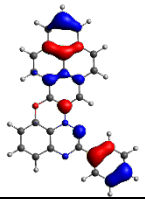
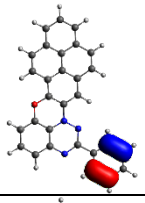
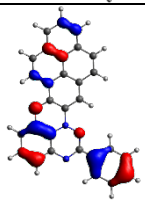
1g,  Type of MO	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.205$ /eV
H(S)OMO 	6.278	6.073	6.278
HOMO -1 	7.082	7.168	7.373
HOMO -2 	8.019	7.526	7.732
HOMO -3 	8.282	8.037	8.243
HOMO -4 	8.366	8.380	8.585
HOMO -5 	8.426	8.447	8.652

Table S8. Theoretical ionization energies for radical **1h** obtained with the CAM-B3LYP/6-311G(d,p) method.

1h, MO Type	Method 1 $\Delta E_{SCF}+E_{TD\text{-}DFT}$ /eV	$-\varepsilon^{KS}$ /eV	Method 2 $-\varepsilon^{KS} + x_{\Delta SCF}$ $x_{\Delta SCF} = 0.183$ /eV
 H(S)OMO	6.249	6.066	6.249
 HOMO -1	6.964	6.813	6.995
 HOMO -2	7.680	7.510	7.693
 HOMO -3	7.789	8.142	8.324
 HOMO -4	8.500	8.376	8.558
 HOMO -5	8.515	8.406	8.589

Correlation of experimental and theoretical ionization energies IE_n.

Experimentally established ionization energies were correlated with those DFT calculated using two methods. The initial fitting of the datapoitns to a linear function $y = ax + b$ gave slopes near unity and errors greater than the difference from slope unity:

Method 1: IE_n (DFT) = 0.11(37)+0.965(46)×IE_n (UVPES), $r^2 = 0.965$.

Method 2: IE_n (DFT) = –0.11(26)+1.006(31)×IE_n (UVPES), $r^2 = 0.984$.

Therefore, slopes were assumed unity and the datapoins were fitted to the function: $y = x + b$. Results are shown in Figures S3 and S4.

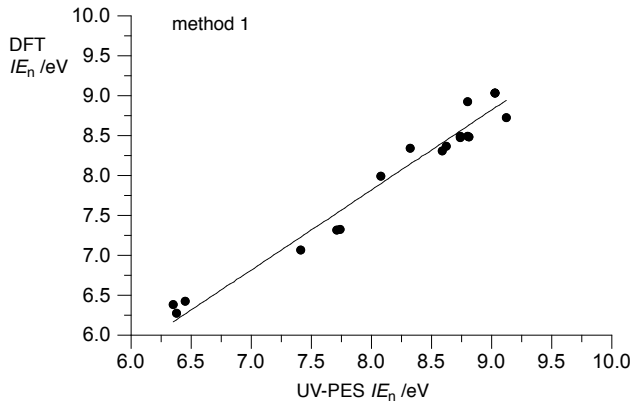


Figure S3. Correlation of ionization energies IE_n obtained for radicals **1a**, **1c** and **1d** form UV-PES measurements and DFT calculations using method 1 (as $IE_n = \Delta E_{SCF} + E_{TD\text{-}DFT}$). Best-fit function IE_n (DFT) = –0.181(41)+IE_n (UVPES), $r^2 = 0.964$.

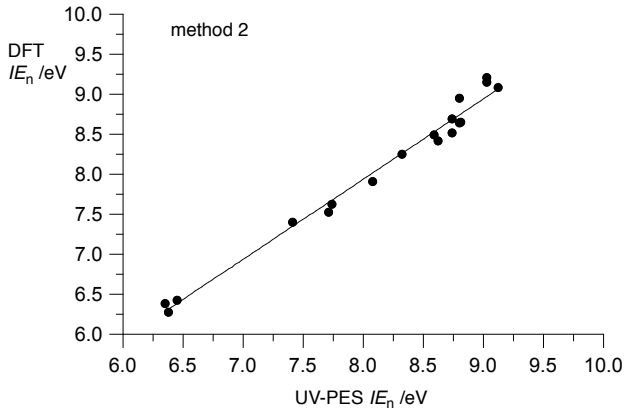


Figure S4. Correlation of ionization energies IE_n obtained for radicals **1a**, **1c** and **1d** from UV-PES measurements and DFT calculations using method 2 (as $-\varepsilon^{KS} + x_{\Delta SCF}$). Best-fit function IE_n (DFT) = –0.06(3)+IE_n (UVPES), $r^2 = 0.984$.

c) Electrostatic potential surface maps

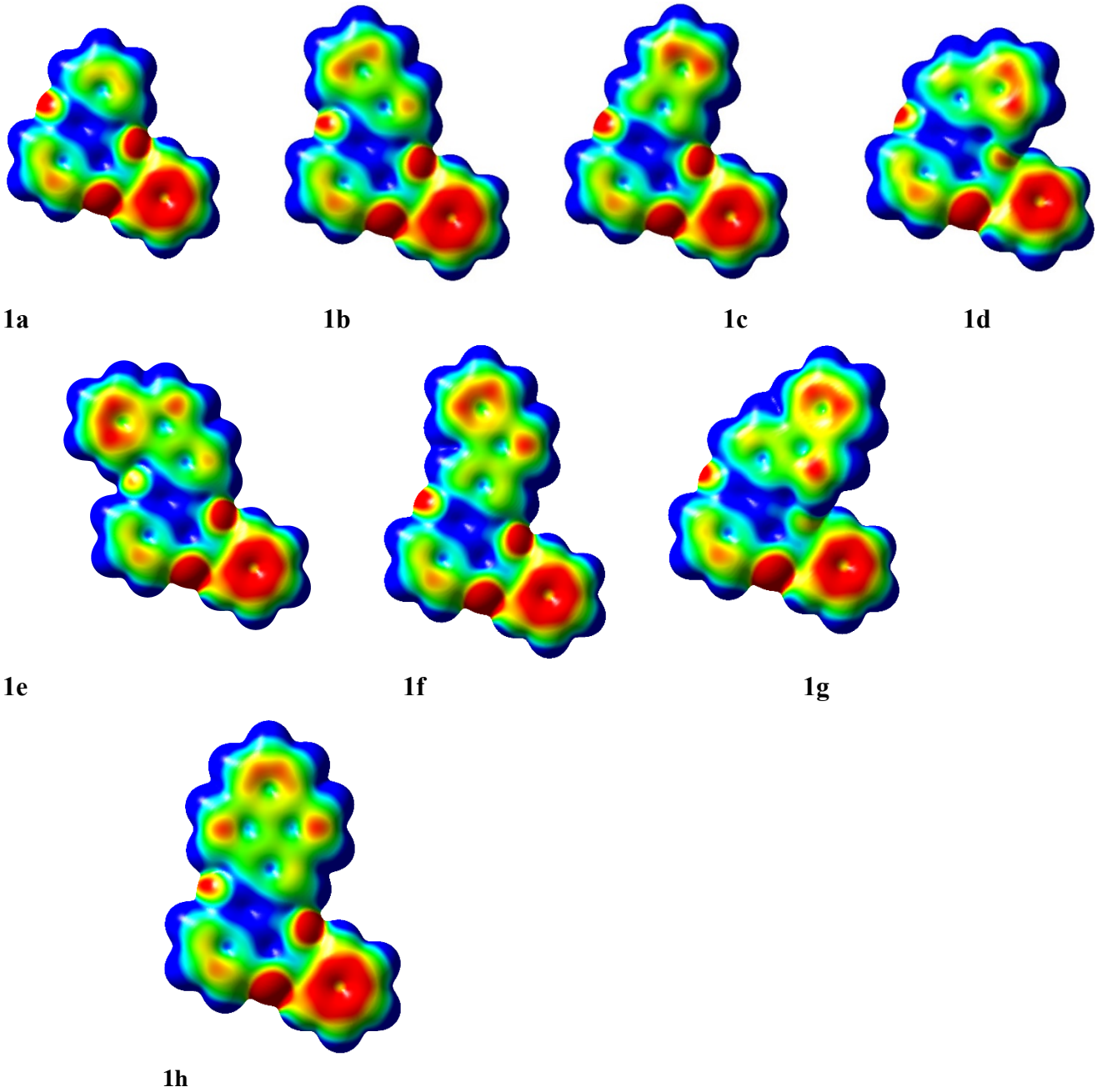


Figure S5. Electrostatic Potential Surface maps at the 0.004 electron/bohr^3 isodensity surface. Electrostatic potential iso-contour level from +12.55 (red) to -12.55 (blue) kcal/mole. UCAM-B3LYP/6 311G(d,p) level of theory.

d) spin delocalization

Spin delocalization parameter RDV (Radical Delocalization Value) was calculated according to the formula:[23]

$$RDV = \sum_{i=1}^{n} (\rho_i)^2$$

where spin concentration ρ_i on each heavy atom i (hydrogen atoms summed up to heavy atoms) is obtained with the UCAM-B3LYP/EPR-III//UCAM-B3LYP/6-311G(d,p) level of theory either in vacuum or in benzene dielectric medium requested with the SCRF(IEFPCM, Solvent=Benzene) keyword (IEFPCM, the default PCM model).[9,10]

For the purpose of this work, the inverse is reported: $RDV^{-1}=1/RDV$, since now the larger value corresponds to a greater delocalization. Results are shown in Table S9.

e) Spin density maps

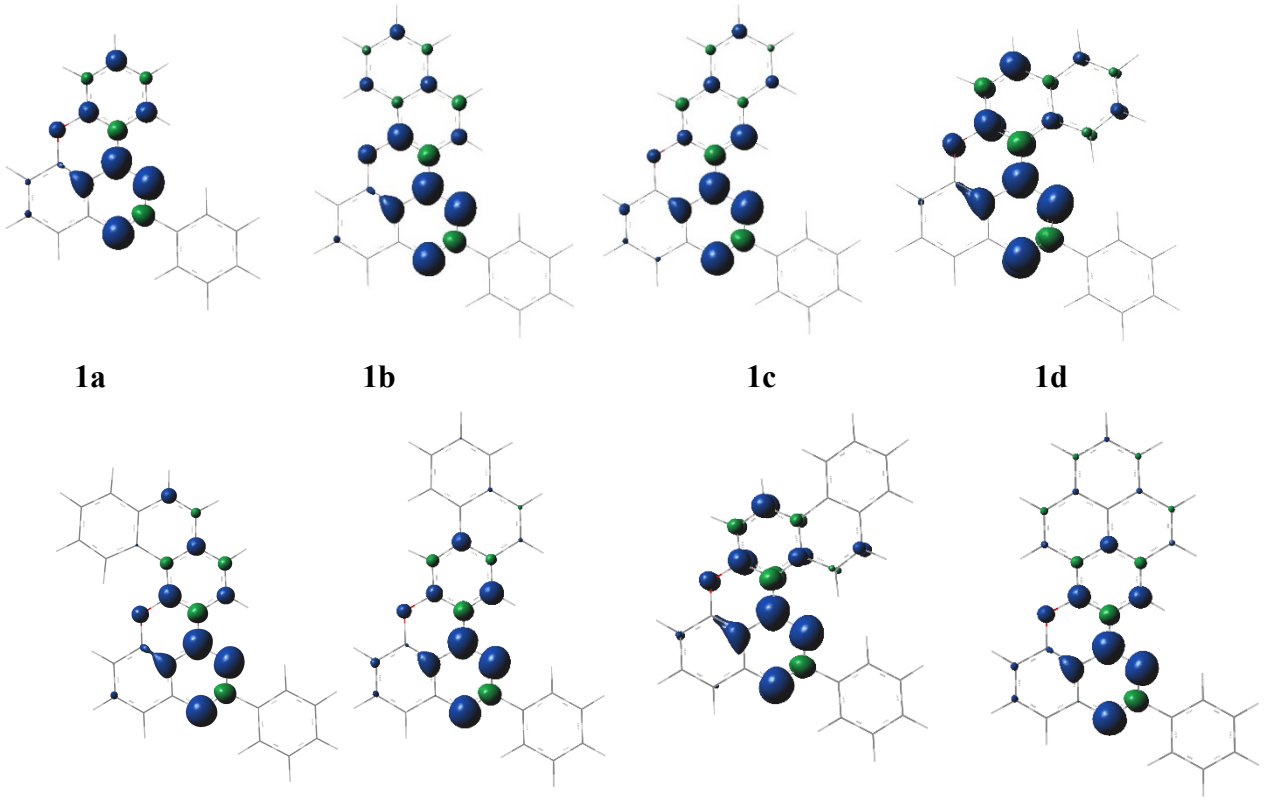


Figure S6. Spin Density Maps at the 0.004 electron/bohr^3. UCAM-B3LYP/6 311G(d,p) level of theory.

f) Summary of computational results

Computational results are summarized in Table S9.

Table S9. Summary of DFT-derived pertinent molecular parameters for radicals **1**.

Radical	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
ΔE_{SCF} (IE_1) [a] /eV	6.432	6.267	6.393	6.282	6.238	6.313	6.278	6.249
$\varepsilon_{\alpha HOMO}$ [a] /eV	-6.113	-6.015	-6.148	-6.025	-6.020	-6.105	-6.073	-6.066
$\varepsilon_{\alpha LUMO}$ [a] /eV	-0.350	-0.484	-0.463	-0.436	-0.434	-0.452	-0.421	-0.912
$\Delta E_{\alpha HOMO-\alpha LUMO}$ /eV	5.763	5.531	5.684	5.589	5.586	5.653	5.652	5.154
RDV^{-1}, [b]								
vacuum	3.809	3.832	3.789	3.628	3.893	3.906	3.718	3.877
benzene	3.873	3.894	3.847	3.688	3.952	3.969	3.775	3.937

[a] $\Delta E_{SCF} = E_{SCFcation} - E_{SCFradical}$; obtained at the UCAM-B3LYP/6-311G(d,p) level theory. [b] UCAM-B3LYP/EPR-III//UCAM-B3LYP/6-311G(d,p); see section 2.d.

g) Atomic coordinates for CAM-B3LYP/6-311G(d,p) optimized geometry and total energy

1b

C	1.01022100	3.60160200	-0.00000500
C	1.02569300	2.22549500	-0.00000500
C	-0.17345000	1.51811200	-0.00000200
C	-1.41145900	2.17353000	0.00000100
C	-1.41230300	3.57554900	0.00000000
C	-0.21970600	4.26633900	-0.00000300
H	1.94853700	4.13953600	-0.00000700
H	-2.36773400	4.08229600	0.00000100
H	-0.22826100	5.34918300	-0.00000400
C	-2.45126400	0.13260700	0.00000000
C	-3.70373300	-0.66989300	-0.00000100
C	-3.67135100	-2.06332700	-0.00002400
C	-4.93548700	-0.01873400	0.00002200
C	-4.85045000	-2.79065300	-0.00002400
H	-2.71559100	-2.56835100	-0.00004300
C	-6.11310200	-0.74880500	0.00002300
H	-4.94707500	1.06237900	0.00003900
C	-6.07483400	-2.13622200	-0.00000100
H	-4.81394100	-3.87357200	-0.00004300
H	-7.06543500	-0.23204200	0.00004100
H	-6.99632500	-2.70644400	-0.00000100
C	1.05140300	-0.54216200	0.00000100
C	2.21469900	0.19596800	-0.00000200
N	-0.17818600	0.13216700	-0.00000200
N	-1.31972500	-0.57682200	-0.00000200
N	-2.57145200	1.45204800	0.00000300
C	3.52696500	-1.85473100	0.00000600
C	2.31330700	-2.58741800	0.00000900
H	2.35484400	-3.66988900	0.00001300
C	1.10915500	-1.95365000	0.00000600
H	0.17581500	-2.49565000	0.00000900
C	3.47979400	-0.43765800	0.00000100
C	4.68717500	0.30094100	-0.00000200
H	4.63921800	1.38096300	-0.00000500
C	4.78974700	-2.48996500	0.00000800
H	4.82566900	-3.57337400	0.00001100
C	5.94355800	-1.75743300	0.00000300
H	6.90468000	-2.25696300	0.00000400
C	5.88952400	-0.34819000	0.00000000
H	6.81038800	0.22222700	-0.00000300
O	2.22702000	1.56751600	-0.00000700

E_{tot}= -1124.00243617 au

1c

C	0.15130800	4.17753200	-0.00000300
C	0.52309200	2.85175300	-0.00000500
C	-0.45432900	1.85947600	-0.00000300
C	-1.81975400	2.17813600	0.00000200
C	-2.18216200	3.53197600	0.00000400
C	-1.20713200	4.50600600	0.00000200
H	0.92158100	4.93684000	-0.00000500
H	-3.23599500	3.77484500	0.00000700
H	-1.49258500	5.55052800	0.00000500
C	-2.30669900	-0.06019400	-0.00000100
C	-3.31267200	-1.15554200	-0.00000200
C	-2.92513700	-2.49440900	-0.00003000
C	-4.66991900	-0.84064300	0.00002700
C	-3.87931900	-3.49878700	-0.00003000
H	-1.87206100	-2.73843500	-0.00005300
C	-5.62186200	-1.84735100	0.00002700
H	-4.95822400	0.20140300	0.00004700
C	-5.23026400	-3.17889200	-0.00000100
H	-3.56737800	-4.53643100	-0.00005300
H	-6.67459800	-1.59110200	0.00005000
H	-5.97537500	-3.96567900	-0.00000100
C	1.24941000	0.16348000	-0.00000300
C	1.66183400	-1.14143600	0.00000200
C	2.21456700	1.20960200	-0.00000600
C	3.03693600	-1.46566400	0.00000400
H	0.91350300	-1.92039100	0.00000600
C	3.54323400	0.92174600	-0.00000400
C	3.99556600	-0.41970500	0.00000200
H	4.25000900	1.74191700	-0.00000600
N	-0.10705500	0.51936900	-0.00000400
N	-1.03091700	-0.45610400	-0.00000400
N	-2.75750100	1.18517400	0.00000300
C	5.37032900	-0.74951900	0.00000300
C	5.77379900	-2.05589300	0.00000700
H	6.82992000	-2.29690500	0.00000500
C	3.48625100	-2.80796900	0.00001000
H	2.75045300	-3.60391300	0.00001500
C	4.82177700	-3.09673600	0.00001200
H	5.15505600	-4.12734500	0.00001800
H	6.10070300	0.05148700	-0.00000200
O	1.85127400	2.53278700	-0.00001100

E_{tot}= -1124.00294972 au

1d

C	1.27914700	4.13007200	0.00648900
C	1.39407600	2.76209900	-0.09240500
C	0.27329400	1.95023200	0.02681100
C	-1.00282500	2.50373100	0.20155000
C	-1.10929700	3.89782400	0.30776800
C	0.01543900	4.68798200	0.21425500
H	2.16694800	4.74044000	-0.08777400
H	-2.09588800	4.31862900	0.44619300
H	-0.07676600	5.76412300	0.29215700
C	-1.89599600	0.41607000	0.01146900
C	-3.08468600	-0.47262800	-0.08446900
C	-2.97282200	-1.78298100	-0.54682000
C	-4.33644200	0.01463000	0.28475800
C	-4.09462000	-2.59222400	-0.63126500
H	-2.00422100	-2.15640300	-0.85069800
C	-5.45498100	-0.79916900	0.20495100
H	-4.41115700	1.03658900	0.63018400
C	-5.33791600	-2.10445300	-0.25262500
H	-3.99837400	-3.60732600	-0.99775600
H	-6.42316900	-0.41202000	0.49937000
H	-6.21383200	-2.73909100	-0.31781400
C	1.67126600	-0.01906500	-0.07046300
C	1.93792300	-1.42510900	0.09732000
C	2.74021500	0.84458600	-0.24703100
C	3.28608300	-1.86924900	-0.03704300
C	4.05974000	0.38749600	-0.36327200
C	4.32592500	-0.94207000	-0.28280000
H	4.83234000	1.12782900	-0.52247800
H	5.34102900	-1.30624900	-0.38298700
N	0.38444900	0.56237100	-0.04234300
N	-0.72000800	-0.19924200	-0.13294200
N	-2.10863000	1.70296700	0.23035900
C	3.59361600	-3.24189600	0.10844400
C	2.62710800	-4.15629700	0.40933700
H	2.87646400	-5.20409700	0.52351700
C	0.96386600	-2.40314800	0.42911300
H	-0.05780100	-2.09612800	0.56047900
C	1.30303200	-3.72012800	0.58431200
H	0.53221500	-4.43458200	0.84728200
H	4.62602700	-3.54934000	-0.01277800
O	2.61608000	2.20714100	-0.33533800

E_{tot}= -1123.99249408 au

1e

C	0.43720600	3.41947700	0.00000500
C	0.34691600	2.04576100	-0.00000100
C	-0.89958100	1.43408700	0.00000200
C	-2.08599000	2.17854100	0.00000800
C	-1.98134100	3.57647800	0.00001300
C	-0.73955100	4.17479800	0.00001200
C	-3.26613800	0.21781000	0.00000000
C	-4.57171000	-0.49518200	-0.00000500
C	-4.63694200	-1.88745500	-0.00004200
C	-5.75477100	0.24075400	0.00002800
C	-5.86411600	-2.53030800	-0.00004600
H	-3.71903900	-2.45833200	-0.00007000
C	-6.98068400	-0.40492600	0.00002500
H	-5.69065800	1.32000600	0.00005600
C	-7.03957800	-1.79160100	-0.00001200
H	-5.90369000	-3.61310400	-0.00007600
H	-7.89447200	0.17727100	0.00005100
H	-7.99872000	-2.29589900	-0.00001500
C	0.17834400	-0.71466600	0.00000300
C	0.09767400	-2.11044400	0.00001500
C	1.41547300	-0.07623400	-0.00000100
C	1.24898200	-2.84107400	0.00002200
H	-0.87923300	-2.56782600	0.00002000
C	2.62966700	-0.80709500	0.00000300
C	2.51079600	-2.22191600	0.00001600
N	-0.99663600	0.05577900	-0.00000200
N	-2.18730300	-0.56932600	-0.00000400
N	-3.29433100	1.54275200	0.00000700
C	3.97344600	-0.21966400	-0.00000500
C	3.67766800	-3.04810300	0.00002500
C	4.91010500	-2.51196400	0.00002100
C	5.09228700	-1.09312400	0.00000500
O	1.49061000	1.29534400	-0.00001000
H	-0.66607200	5.25514700	0.00001600
H	-2.89547900	4.15438900	0.00001700
H	1.41126000	3.88958100	0.00000400
H	1.20251900	-3.92309300	0.00003200
C	6.40001900	-0.57486600	-0.00000100
C	6.63059000	0.77560600	-0.00001900
C	5.53897700	1.64691700	-0.00003100
C	4.25094100	1.16574900	-0.00002500
H	7.22892000	-1.27362400	0.00000800
H	7.64252200	1.16201300	-0.00002300
H	5.70258200	2.71798700	-0.00004700
H	3.44141300	1.87037800	-0.00003600
H	3.53815500	-4.12267400	0.00003500
H	5.79088600	-3.14353400	0.00002900

E_{tot}= -1277.58711128 au

1f

C	-1.10930900	4.22671100	-0.00000400
C	-0.64059200	2.93220800	-0.00000700
C	-1.54239200	1.87040600	0.00000200
C	-2.92744600	2.08653600	0.00001400
C	-3.38897200	3.40994500	0.00001900
C	-2.48853800	4.45339300	0.00000900
C	-3.24599400	-0.18267700	0.00000600
C	-4.16802700	-1.34964700	-0.00000100
C	-3.68194300	-2.65597500	-0.00004200
C	-5.54485800	-1.13619100	0.00002900
C	-4.55883700	-3.72847100	-0.00005300
H	-2.61358800	-2.82063100	-0.00006700
C	-6.41936500	-2.21085400	0.00001900
H	-5.90916500	-0.11824400	0.00005800
C	-5.92978700	-3.50961000	-0.00002200
H	-4.17086800	-4.74014300	-0.00008600
H	-7.48825700	-2.03370800	0.00004300
H	-6.61447000	-4.34954200	-0.00003100
C	0.28271200	0.31159600	0.00000100
C	0.80511300	-0.95881700	0.00001500
C	1.16137300	1.41583300	-0.00001200
C	2.19335500	-1.16930100	0.00001500
H	0.12332600	-1.79671300	0.00002800
C	2.51480300	1.22670000	-0.00001500
C	3.07381000	-0.06463400	-0.00000200
N	-1.09700100	0.55934200	0.00000000
N	-1.94432600	-0.48314800	-0.00000300
N	-3.78832600	1.02582200	0.00001900
C	4.50635100	-0.29797600	-0.00000500
C	5.45096800	0.74678000	-0.00003000
C	2.72330500	-2.50086000	0.00003600
C	4.98353300	-1.62813400	0.00001800
C	4.05320200	-2.71861200	0.00003900
C	6.37042400	-1.86831800	0.00001900
C	6.79947600	0.48909500	-0.00003000
C	7.26763600	-0.83143800	-0.00000500
H	7.50423300	1.31178100	-0.00005100
H	8.33256200	-1.02948600	-0.00000500
H	6.71946800	-2.89482300	0.00003800
H	4.44619700	-3.72883100	0.00005600
H	2.02628000	-3.33072400	0.00005000
O	0.70856500	2.71136100	-0.00002200
H	-2.85055700	5.47391200	0.00001200
H	-4.45783900	3.57449100	0.00002800
H	-0.39777700	5.04133100	-0.00001200
H	5.11863600	1.77602600	-0.00005100
H	3.13088000	2.11418900	-0.00002500

E_{tot}= -1277.59379656 au

1g

C	2.40859300	-4.20844700	0.07645200
C	1.46647200	-3.21413800	-0.05794500
C	1.82979100	-1.87905400	0.06497000
C	3.16754600	-1.51103000	0.26681100
C	4.11910600	-2.53098400	0.40982300
C	3.73731000	-3.85172100	0.31982100
C	2.56757700	0.67266800	0.00882600
C	2.94417100	2.10573300	-0.11949900
C	2.03006200	3.05548600	-0.57358400
C	4.23622000	2.50781500	0.21177600
C	2.40328200	4.38506600	-0.68819500
H	1.03141700	2.74134400	-0.84548100
C	4.60433300	3.83894300	0.10052800
H	4.93814500	1.75963700	0.55349600
C	3.68985600	4.78141400	-0.34921900
H	1.68724600	5.11478700	-1.04709400
H	5.61057800	4.14186800	0.36448700
H	3.97967100	5.82174100	-0.43849000
C	-0.49122400	-1.21675000	-0.08395900
C	-0.77745600	-2.56254000	-0.28112100
N	0.87875500	-0.86615200	-0.03497000
N	1.26942300	0.41388400	-0.16528400
N	3.52916000	-0.19427300	0.28152500
O	0.17506800	-3.54585400	-0.34572800
H	4.47930800	-4.63325800	0.42595400
H	5.14851900	-2.24124600	0.57088700
H	2.10104900	-5.24076200	-0.02057500
C	-6.13451100	2.01197700	0.24428400
C	-4.84843100	2.40475900	0.50623700
C	-3.77708800	1.49930600	0.38371300
C	-4.01962600	0.16650900	-0.00475600
C	-5.35282300	-0.20711400	-0.27174800
C	-6.38396300	0.69118000	-0.15235100
C	-2.43579500	1.90476700	0.65323400
C	-2.90160300	-0.75903600	-0.11500100
C	-1.57380900	-0.29536200	0.08030100
C	-1.38924400	1.06789000	0.49707800
C	-2.08472500	-3.00969300	-0.43427900
C	-3.12174800	-2.12202500	-0.37983800
H	-2.26242700	2.92090400	0.98936400
H	-6.95328300	2.71478200	0.33868300
H	-4.63491700	3.42319900	0.81059400
H	-5.58488300	-1.21354700	-0.59042800
H	-7.39730400	0.37554100	-0.36943300
H	-0.39205000	1.41685800	0.69447200
H	-2.24086000	-4.06701700	-0.60143200
H	-4.12575800	-2.49593000	-0.51224200

E_{tot}= -1277.58147672 au

1h

C	-1.10929500	4.15305900	-0.00000300
C	-0.71148400	2.83527700	-0.00000500
C	-1.66674100	1.82257300	-0.00000200
C	-3.03844800	2.11023200	0.00000400
C	-3.42895100	3.45641000	0.00000700
C	-2.47497200	4.45120900	0.00000300
C	-3.47298500	-0.13897000	-0.00000100
C	-4.45364900	-1.25724000	-0.00000200
C	-4.03568900	-2.58693800	-0.00004300
C	-5.81772600	-0.97349300	0.00003700
C	-4.96663200	-3.61288200	-0.00004400
H	-2.97728500	-2.80665300	-0.00007600
C	-6.74645900	-2.00169800	0.00003800
H	-6.12944800	0.06177900	0.00006800
C	-6.32456500	-3.32393000	-0.00000300
H	-4.63109400	-4.64315300	-0.00007700
H	-7.80479300	-1.76961700	0.00007000
H	-7.05149600	-4.12756400	-0.00000400
C	0.08028600	0.17305400	-0.00000200
C	0.51558200	-1.14360300	0.00000400
C	1.00535600	1.22095000	-0.00000600
C	1.87422300	-1.43960500	0.00000500
H	-0.22655000	-1.92811400	0.00000800
C	2.37490600	0.96451200	-0.00000500
C	2.81558000	-0.38111800	0.00000100
N	-1.28822700	0.49111900	-0.00000300
N	-2.18883500	-0.50597400	-0.00000600
N	-3.95325100	1.09581500	0.00000600
C	3.34766400	2.02166000	-0.00001000
C	4.20986000	-0.66737700	0.00000200
C	5.15228800	0.39060600	-0.00000300
C	4.66714800	1.74280300	-0.00000800
H	2.99633900	3.04397800	-0.00001500
H	5.39360700	2.54751100	-0.00001200
C	2.35641400	-2.79299100	0.00001100
C	4.65622800	-2.01256300	0.00000900
C	3.67713400	-3.06454300	0.00001400
C	6.02691800	-2.27036400	0.00001100
C	6.51354200	0.08688700	0.00000000
C	6.94335700	-1.23060600	0.00000600
H	7.23573500	0.89531200	-0.00000500
H	8.00432200	-1.44966100	0.00000700
H	6.37103800	-3.29834900	0.00001700
H	4.02667400	-4.09067700	0.00001900
H	1.62831000	-3.59583400	0.00001500
O	0.62392700	2.53871400	-0.00001200
H	-2.78336200	5.48920300	0.00000500
H	-4.48761100	3.67740500	0.00001100
H	-0.35695500	4.93013200	-0.00000600

E_{tot}= -1353.79843221 au

3. References

(1) Hande, A. A.; Darrigan, C.; Bartos, P.; Baylère, P.; Pietrzak, A.; Kaszyński, P.; Chrostowska, A. UV-Photoelectron spectroscopy of stable radicals: The electronic structure of planar Blatter radicals as materials for organic electronics *Phys. Chem. Chem. Phys.* submitted.

(2) Gaussian 09, Revision D.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian, Inc., Wallingford CT, 2013. Gaussian, Inc., Wallingford CT 2013.

(3) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior, *Phys. Rev. A* **1988**, *38*, 3098–3100.

(4) Becke, A. D. Density Functional Thermochemistry. III. The Role of Exact Exchange, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(5) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density, *Phys. Rev. B* **1988**, *37*, 785–789.

(6) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP), *Chem. Phys. Lett.* **2004**, *393*, 51–57.

(7) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions, *J. Chem. Phys.* **1980**, *72*, 650–654.

(8) Barone, V. Structure, Magnetic Properties and Reactivities of Open-Shell Species from Density Functional and Self-Consistent Hybrid Methods In *Recent Advances in Density Functional Methods*; Chong, D. P., Ed.; World Scientific Publ. Co.: Singapore, 1996; Vol. 1, p 287-334.

(9) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. PCM model, *J. Chem. Phys.* **2002**, *117*, 43-54, and references therein.

(10) Barone, V.; Cossi, M.; Tomasi, J. A new definition of cavities for the computation of solvation free energies by the polarizable continuum model, *J. Chem. Phys.* **1997**, *107*, 3210-3221.

(11) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform., *J. Chemoinform.* **2012**, *4*, 1–17.

(12) Avogadro: An Open-Source Molecular Builder and Visualization Tool. Version 1.2.0. Http://Avogadro.Cc/.

(13) Kaszynski, P.; Constantinides, C. P.; Young, V. G., Jr. The Planar Blatter Radical: Structural Chemistry of 1,4-Dihydrobenzo[*e*][1,2,4]triazin-4-yls, *Angew. Chem. Int. Ed.* **2016**, *55*, 11149 –11152.

(14) Bartos, P.; Young, V. G., Jr.; Kaszyński, P. Ring-Fused 1,4-Dihydro[1,2,4]triazin-4-yls through Photocyclization, *Org. Lett.* **2020**, *22*, 3835–3840.

(15) Bartnik, R.; Baylère, P.; Chrostowska, A.; Galindo, A.; Leśniak, S.; Pfister-Guillouzo, G. Flash Vacuum Thermolysis of 1-Azabicyclo[1.1.0]butanes. Photoelectron Spectrum of 3-Phenyl-2-azabuta-1,3-diene, *Eur. J. Org. Chem.* **2003**, *2003*, 2475-2479.

(16) Chrostowska, A.; Matrane, A.; Maki, D.; Khayar, S.; Ushiki, H.; Graciaa, A.; Belachemi, L.; Guillemin, J.-C. Are Unsaturated Isocyanides so Different from the Corresponding Nitriles?, *ChemPhysChem* **2012**, *13*, 226-236.

(17) Vu, T. Y.; Chrostowska, A.; Huynh, T. K. X.; Khayar, S.; Dargelos, A.; Justyna, K.; Pasternak, B.; Leśniak, S.; Wentrup, C. New Reactions of N-tert- Butylimines; Formation of N-Heterocycles by Methyl Radical Elimination on Flash Vacuum Thermolysis of N -Benzylidene- and N -(2-Pyridylmethylidene)-tert -butylamines *Chem. Eur. J.* **2013**, *19*, 14983-14988.

(18) Lemierre, V.; Chrostowska, A.; Dargelos, A.; H., C. Calculation of Ionization Potentials of Small Molecules: A Comparative Study of Different Methods, *J. Phys. Chem. A* **2005**, *109*, 8348–8355.

(19) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules, *J. Chem. Phys.* **1998**, *109*, 8218-8224.

(20) Koopmans, T. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms, *Physica* **1934**, *1*, 104-113.

(21) Stowasser, R.; Hoffmann, R. What Do the Kohn–Sham Orbitals and Eigenvalues Mean?, *J. Am. Chem. Soc.* **1999**, *121*, 3414–3420.

(22) Mazière, A.; Chrostowska, A.; Darrigan, C.; Dargelos, A.; Graciaa, A.; Chermette, H. Electronic structure of BN-aromatics: Choice of reliable computational tools, *J. Chem. Phys.* **2017**, *147*, 164306.

(23) De Vleeschouwer, F.; Chankisjijev, A.; Yang, W.; Geerlings, P.; De Proft, F. Pushing the Boundaries of Intrinsically Stable Radicals: Inverse Design Using the Thiadiazinyl Radical as a Template, *J. Org. Chem.* **2013**, *78*, 3151-3158.