Modeling EPR parameters of nitrogen containing conjugated radical cations

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SUPPLEMENTARY INFORMATION:

Table S1. Theoretical isotropic hyperfine coupling constants (G) of ^{1}H nuclei of the conjugated radical cations at the following levels: PBE0/N07D, B3LYP/6-31G*, B3LYP/N07D, B3LYP/TZVP, and B3LYP/EPR-III. All calculations were carried out on the geometries optimized at B3LYP/6-31G*.

		a_{iso} (theoretical)					
		PBE0	B3LYP				
no.	nuclei	N07D	6-31G*	N07D	TZVP	EPR-III	a_{iso} (exptl.)[a]
1	H_1	+1.3	+1.1	+1.1	+1.1	+1.1	0.9
	$H_{3,4}$	–2.8	–3.1	–3.1	–2.9	–3.0	3.6
	$6H_\beta$	+15.8	+16.9	+17.0	+16.9	+18.2	16.0
2	$H_{3,4}$	–3.0	–3.2	–3.2	–3.0	–3.2	3.4
	$6H_\beta$	+15.4	+16.5	+16.6	+16.4	+17.8	16.0
	$3H_{\beta'}$	–2.1	–1.9	–1.9	–1.9	–2.0	1.5
3	$H_{1,4}$	–9.4	–10.3	–10.1	–9.7	–9.8	7.94
	$H_{2,3,5,6}$	–3.3	–3.7	–3.7	–3.4	–3.4	3.13
4	$H_{2,3,5,6}$	–2.9	–3.2	–3.2	–2.9	–3.0	2.85
	$6H_\beta$	+7.9	+8.5	+8.3	+8.1	+8.8	8.03
5	$H_{1,4}$	–8.4	–9.1	–8.9	–8.6	–8.6	7.17
	$H_{2,3}$	–3.7	–4.0	–4.0	–3.7	–3.8	3.99
	$H_{5,8}$	–0.4	–0.5	–0.5	–0.5	–0.5	0.75
	$H_{6,7}$	–1.6	–1.7	–1.7	–1.6	–1.7	1.38
6	$H_{2,3}$	–3.4	–3.8	–3.7	–3.4	–3.5	3.70
	$H_{5,8}$	–0.7	–0.7	–0.7	–0.7	–0.7	0.92
	$H_{6,7}$	–1.5	–1.6	–1.6	–1.5	–1.6	1.42
	$6H_\beta$	+6.8	+7.1	+7.0	+6.9	+7.4	6.90
7	$H_{1,5}$	–3.7	–4.2	–4.1	–3.9	–3.9	3.37
	$H_{2,6}$	–5.4	–5.6	–5.5	–5.2	–5.4	4.64
	$H_{3,7}$	–0.5	–0.7	–0.7	–0.7	–0.8	1.08
	$H_{4,8}$	–6.6	–6.9	–6.8	–6.2	–6.4	6.25
8	$H_{2,6}$	–4.7	–4.9	–4.9	–4.5	–4.7	4.34
	$H_{3,7}$	–0.9	–1.1	–1.1	–1.1	–1.1	1.30
	$H_{4,8}$	–6.2	–6.6	–6.5	–5.9	–6.1	6.02
	$6H_\beta$	+2.2	+2.4	+2.3	+2.3	+2.4	2.21
9	$H_{1,4,5,8}$	–0.3	–0.4	–0.4	–0.3	–0.3	0.66
	$H_{2,3,6,7}$	–1.8	–1.9	–1.9	–1.8	–1.9	1.71
	$H_{9,10}$	–7.3	–7.9	–7.8	–7.4	–7.5	6.49
10	$H_{1,4,5,8}$	–0.4	–0.5	–0.5	–0.5	–0.5	0.62
	$H_{2,3,6,7}$	–1.7	–1.8	–1.8	–1.7	–1.8	1.38
	$6H_\beta$	+5.7	+5.9	+5.9	+5.8	+6.3	6.20
11	$H_{3,3'}$	–1.1	–1.2	–1.2	–1.1	–1.2	2.39[b]
	$H_{4,4'}$	–2.1	–2.2	–2.1	–2.0	–2.1	0.65[b]
	$H_{5,5'}$	–3.1	–3.4	–3.4	–3.1	–3.2	2.81
	$H_{6,6'}$	+0.003	–0.1	–0.1	–0.1	–0.1	0.23
	$2H_\beta$	+22.2	+23.7	+23.4	+22.7	+24.4	24.24
12	$H_{3,3'}$	–0.6	–0.8	–0.8	–0.7	–0.8	2.54[b]
	$H_{4,4'}$	–2.7	–2.9	–2.8	–2.6	–2.7	0.58[b]
	$H_{5,5'}$	–2.8	–3.1	–3.0	–2.8	–2.9	2.89
	$H_{6,6'}$	–0.5	–0.6	–0.6	–0.5	–0.5	0.36
	$2H_\beta/2H_\beta$	+1.3/+5.3	+1.4/+5.6	+1.4/+5.5	+1.4/+5.4	+1.5/+5.8	6.98[c]
13	$H_{1,1'}$	–4.7	–5.2	–5.0	–4.8	–4.9	4.06
	$H_{2,2',6,6'}$	–1.8	–2.0	–2.0	–1.8	–1.8	1.61
	$H_{3,3',5,5'}$	–1.4	–1.6	–1.5	–1.4	–1.4	1.45
14	$H_{2,2',6,6'}$	–1.4	–1.6	–1.6	–1.5	–1.5	1.33
	$H_{3,3',5,5'}$	–1.5	–1.7	–1.6	–1.5	–1.5	1.57
	$6H_\beta$	+4.0	+4.2	+4.1	+4.0	+4.4	3.99
15	$H_{1,3,6,8}$	–2.3	–2.6	–2.6	–2.3	–2.4	1.93
	$H_{2,7}$	–5.4	–5.9	–5.8	–5.6	–5.6	4.52
	$H_{4,5,9,10}$	–0.4	–0.4	–0.4	–0.4	–0.4	0.41
16	$H_{1,3,6,8}$	–2.0	–2.3	–2.2	–2.0	–2.0	1.83
	$H_{4,5,9,10}$	–0.4	–0.4	–0.4	–0.3	–0.3	0.40
	$6H_\beta$	+4.3	+4.6	+4.5	+4.4	+4.8	4.39
17	$H_{1,3,4,6,7,9}$	–7.3	–7.4	–7.3	–6.7	–7.0	6.45
	$H_{2,5,8}$	+3.0	+2.6	+2.5	+2.3	+2.4	1.78

Table S1. *(cont.)*

		a_{iso} (theoretical)					
		PBE0	B3LYP				
no.	**nuclei**	**N07D**	**6-31G***	**N07D**	**TZVP**	**EPR-III**	a_{iso} **(exptl.)**[a]
18	$H_{1,7}$	–3.2	–3.2	–3.1	–2.8	–2.9	2.43
	$H_{2,8}$	+1.8	+1.6	+1.5	+1.4	+1.5	0.99
	$H_{3,9}$	–3.9	–3.9	–3.8	–3.6	–3.8	3.58
	$H_{4,10}$	+2.0	+1.8	+1.7	+1.6	+1.7	1.17
19	$H_{2,7}$	–4.5	–4.6	–4.4	–4.2	*d*	3.94
	$H_{3,8}$	+1.4	+1.2	+1.1	+1.0	*d*	0.74
20	$H_{1,8}$	–1.2	–1.1	–1.1	–1.0	–1.1	1.61
	$H_{2,7}$	–0.6	–0.8	–0.8	–0.8	–0.8	0.44
	$H_{3,6}$	–3.1	–3.2	–3.2	–2.9	–3.1	3.27
	$H_{4,5}$	+1.0	+0.8	+0.8	+0.7	+0.8	0.66
	H_{9}	–8.8	–9.4	–9.3	–8.9	–9.0	9.02
21	$H_{1,8}$	–0.9	–1.0	–0.9	–0.9	*d*	1.14
	$H_{2,7}/H_{4,5}$	–0.5/+0.8	–0.7/+0.7	–0.7/+0.6	–0.7/+0.6	*d*	0.49[c]
	$H_{3,6}$	–2.5	–2.6	–2.5	–2.4	*d*	2.50
	H_{9}	–7.3	–7.9	–7.8	–7.4	*d*	7.41
22	$H_{1,2}$	–4.1	–4.7	–4.6	–4.2	–4.2	4.35
	$6H_{\beta}/6H_{\beta}$	+6.9/+8.3	+7.1/+8.8	+7.1/+8.7	+7.0/+8.7	+7.6/+9.4	8.15[c]
23	$12H_{\beta}$	+3.2	+3.4	+3.4	+3.3	+3.6	3.28
	$12H_{\beta}$	+2.8	+3.1	+3.0	+3.0	+3.2	2.84
24	$2H_{\alpha}$	–9.3	–10.0	–9.8	–9.6	–9.5	9.58
	$2H_{o}$	–5.5	–5.6	–5.5	–5.0	–5.2	5.82
	$2H_{m}$	+2.1	+1.7	+1.6	+1.4	+1.5	1.52
	H_{p}	–10.0	–10.2	–10.2	–9.3	–9.8	9.58
25	$2H_{\alpha}$	–9.5	–10.0	–9.9	–9.6	–9.5	10.23
	$2H_{o}$	–5.8	–5.7	–5.7	–5.3	–5.5	6.42
	$2H_{m}$	+2.7	+2.2	+2.2	+2.0	+2.1	2.06
26	$2H_{o}$	–4.9	–4.9	–4.8	–4.4	–4.6	5.21
	$2H_{m}$	+1.8	+1.4	+1.3	+1.2	+1.2	1.36
	$6H_{\beta}$	+10.8	+11.1	+11.2	+11.0	+11.9	12.22[b]
	$3H_{\beta'}$	+11.0	+11.4	+11.6	+11.5	+12.5	9.97[b]
27	$4H_{\alpha}$	–6.8	–7.4	–7.2	–7.0	–7.0	5.88
	$H_{2,3,5,6}$	–1.8	–2.0	–2.0	–1.9	–2.0	2.13
28	$4H_{\alpha}$	–5.9	–6.6	–6.3	–6.2	–6.1	5.10
	$12H_{\beta}$	+1.2	+1.3	+1.3	+1.3	+1.4	1.53
29	$2H_{\alpha}$	–5.9	–6.5	–6.2	–6.1	–6.0	5.16
	$H_{2,6}$	–2.5	–2.5	–2.6	–2.4	–2.5	2.65
	$H_{3,5}$	–1.0	–1.4	–1.3	–1.2	–1.3	1.46
	$6H_{\beta}$	+8.1	+8.3	+8.4	+8.2	+9.0	7.75
30	$H_{2,3,5,6}$	–1.7	–1.9	–1.9	–1.8	–1.8	1.98
	$12H_{\beta}$	+7.1	+7.3	+7.4	+7.2	+7.8	6.74
31	$H_{3,6}$	+1.6	+1.2	+1.6	+1.0	+1.4	0.34
	$12H_{\beta}$	+3.6	+4.2	+3.8	+4.1	+4.0	3.76
	$12H_{\beta'}$	+2.2	+3.7	+2.3	+3.5	+2.5	2.56
32	$4H_{arom}$	–1.7	–1.9	–1.9	–1.7	–1.8	2.01
	$8H_{\beta}$	+9.9	+10.3	+10.3	+10.2	+11.0	9.75
	$8H_{\gamma}$	–0.2	–0.1	–0.1	–0.1	–0.2	0.17
33	$12H_{\beta,ax}$	+4.1	+4.4	+4.3	+4.2	+4.6	4.22
	$12H_{\beta,eq}$	+0.9	+0.9	+0.9	+0.9	+1.0	0.97
34	$24H_{\beta}$	+3.6	+2.9	+2.9	+2.8	+3.0	2.81
35	$4H_{\alpha}$	–4.3	–4.7	–4.6	–4.5	–4.4	3.97
	$H_{2,2',6,6'}$	–1.0	–1.1	–1.2	–1.1	–1.1	1.08
	$H_{3,3',5,5'}$	–1.1	–1.3	–1.3	–1.2	–1.2	1.62
36	$H_{2,2',6,6'}$	–0.6	–0.8	–0.8	–0.7	–0.8	0.73
	$H_{3,3',5,5'}$	–1.4	–1.5	–1.5	–1.4	–1.4	1.65
	$12H_{\beta}$	+5.0	+5.1	+5.2	+5.1	+5.5	4.70
37	H_{α}	–10.7	–11.0	–11.0	–10.6	–10.7	10.98
	$2H_{o}/2H_{o}$	–3.8/–3.5	–3.7/–3.5	–3.6/–3.3	–3.4/–3.1	–3.5/–3.2	3.46[c]
	$2H_{m}/2H_{m}$	+1.8/+2.0	+1.5/+1.7	+1.5/+1.6	+1.4/+1.5	+1.4/+1.6	1.31[c]
	$2H_{p}$	–5.4	–5.5	–5.4	–5.0	–5.2	4.86

Table S1. *(cont.)*

		a_{iso} (theoretical)					
		PBE0	B3LYP				
no.	nuclei	N07D	6-31G*	N07D	TZVP	EPR-III	a_{iso} (exptl.)[a]
38	H_{α}	–9.8	–10.4	–10.3	–9.9	–10.0	11.06
	$H_{1,1'}$	+1.9	+1.6	+1.5	+1.4	+1.4	0.93
	$H_{2,2'}$	–5.1	–5.1	–5.1	–4.6	–4.9	4.73
	$H_{3,3'}$	+1.5	+1.2	+1.1	+1.0	+1.1	1.14
	$H_{4,4'}$	–3.3	–3.2	–3.1	–2.9	–3.0	3.19
39	$6H_o$	–2.5	–2.4	–2.3	–2.1	–2.2	2.26
	$6H_m$	+1.7	+1.5	+1.5	+1.3	+1.4	1.22
	$3H_p$	–3.6	–3.6	–3.6	–3.3	–3.4	3.27
40	$H_{1,2}$	–5.2	–5.6	–5.5	–5.2	–5.1	6.53
	$H_{3,6}$	–1.9	–2.2	–2.2	–2.0	–2.1	0.92
	$H_{4,5}$	–5.3	–5.7	–5.7	–5.3	–5.5	5.80
41	$H_{1,8}$	–1.6	–1.6	–1.5	–1.4	–1.5	1.73
	$H_{4,5}$	+0.9	+0.7	+0.7	+0.6	+0.7	0.55
	$H_{3,6}$	–2.4	–2.5	–2.4	–2.3	–2.4	2.31
	$6H_{\beta}$	+7.5	+7.7	+7.7	+7.6	+8.2	8.22
42	$4H_o$	–1.9	–1.8	–1.8	–1.6	–1.7	1.37
	$4H_o$	–1.6	–1.5	–1.5	–1.3	–1.4	1.07
	$4H_m/4H_m$	+1.3/+0.8	+1.1/+0.7	+1.1/+0.7	+1.1/+0.6	+1.1/+0.7	0.48[c]
	$4H_p$	–2.3	–2.2	–2.2	–2.0	–2.1	1.86
43	$H_{2,5,9,12}$	+1.1	+1.1	+1.1	+1.1	+1.2	0.62
	$H_{3,4,10,11}$	–1.5	–1.6	–1.6	–1.4	–1.5	1.43
	$H_{7,14}$	+0.9	+0.8	+0.7	+0.6	+0.6	<0.1
	$2H_{\beta}$	+0.1	+0.1	+0.1	+0.1	+0.1	<0.1
44	$H_{2,5,9,12}$	+1.6	+1.6	+1.5	+1.5	+1.6	0.90
	$H_{3,4,10,11}$	–1.4	–1.5	–1.5	–1.3	–1.4	1.45
	$4H_{\beta}$	+1.0	+1.0	+1.1	+1.0	+1.2	0.76
45	$H_{2,12}$	+1.4	+1.5	+1.5	+1.5	+1.6	1.54
	$H_{5,9}$	+1.6	+1.7	+1.7	+1.7	+1.8	1.74
	$H_{3,11}$	–0.02	–0.01	–0.01	–0.02	–0.02	2.03
	$H_{4,10}$	–0.1	–0.1	–0.1	–0.1	–0.1	2.10 [b]
	H_7	–1.7	–1.8	–1.7	–1.7	–1.8	<0.05 [b]
	H_{14}	–1.9	–1.9	–1.8	–1.8	–1.9	0.09
	$2H_{\beta}$	+19.9	+20.6	+20.7	+20.6	+22.1	21.82
	$2H_{\beta}$	+0.5	+0.4	+0.4	+0.4	+0.4	0.59
	H_{γ}	–2.2	–2.2	–2.2	–2.1	–2.3	2.46
	H_{γ}	–1.2	–1.2	–1.2	–1.2	–1.2	1.29
46	$H_{2,5,9,12}$	+1.4	+1.4	+1.5	+1.5	+1.6	1.54[e]
	$H_{3,4,10,11}$	–0.1	–0.3	–0.2	–0.2	–0.1	1.88[b,e]
	$H_{7,14}$	–1.7	–1.6	–1.6	–1.6	–1.7	0.12[b]
	$4H_{\beta}$	+6.4	+6.6	+6.6	+6.6	+7.1	7.18[e]
	$4H_{\gamma}$	+0.7	+0.8	+0.8	+0.8	+0.9	0.51[e]
47	$H_{2,5,9,12}$	+1.6	+1.7	+1.7	+1.7	+1.9	1.72
	$H_{3,4,10,11}$	–0.04	–0.03	–0.03	–0.03	–0.03	1.89[b]
	$H_{7,14}$	–1.7	–1.7	–1.6	–1.6	–1.7	<0.2[b]
	$6H_{\beta}$	+11.3	+11.7	+11.8	+11.7	+12.7	12.13
48	$4H_o$	–2.3	–2.2	–2.1	–2.0	–2.1	2.5
	$4H_m$	+1.2	+1.0	+1.0	+0.9	+1.0	1.0
	$2H_p$	–3.4	–3.4	–3.4	–3.1	–3.3	3.4
49	$2H_o$	–1.9	–1.8	–1.8	+1.7	–1.8	2.4
	$4H_m$	+0.7	+0.7	+0.7	+0.8	+0.7	0.76
	$2H_p$	–3.1	–3.2	–3.1	–2.9	–3.0	3.2
50	$2H_o$	–2.4	–2.3	–2.3	–2.1	–2.2	2.6
	$4H_m$	+1.1	+0.9	+0.8	+0.8	+0.8	0.8
	$2H_p$	–3.6	–3.6	–3.6	–3.3	–3.5	3.5
	$2H_{\beta,ax}$	+4.6	+4.5	+4.6	+4.5	+4.9	4.7
	$2H_{\beta,eq}$	+1.8	+1.8	+1.8	–1.8	+1.9	1.8

[a] The corresponding references are the same as those provided for ^{14}N nuclei in Table 1. [b] The assignment of the experimental hfccs to these nuclei is expected to be exchanged taking into account the present theoretical calculations. [c] Those nuclei have not been taken into consideration in the regression analysis because of uncertainty in the assignation. [d] EPR-III basis set is not parameterized for third row nuclei. [e] Averaged values for two pairs protons.

Figure S1. Plot of theoretical *vs* experimental $a_{iso}(^{14}N)$ of the conjugated radical cations, calculated at the following levels: PBE0/N07D, B3LYP/6-31G*, B3LYP/N07D, B3LYP/TZVP, and B3LYP/EPR-III. (a) In the whole range; (b) in the range 0 – 10 G. Linear fits are represented by solid lines.

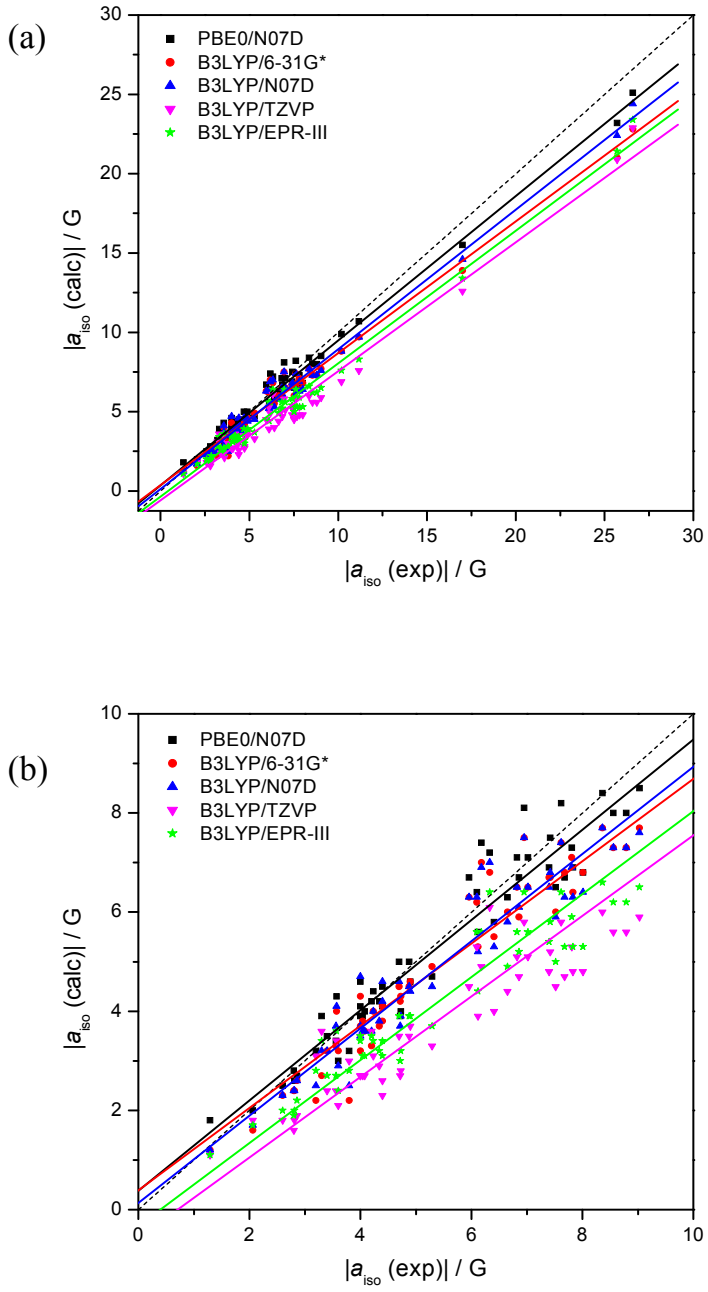


Figure S2. Plot of theoretical *vs* experimental $a_{iso}(^1H)$ of the conjugated radical cations, calculated at the following levels: PBE0/N07D, B3LYP/6-31G*, B3LYP/N07D, B3LYP/TZVP, and B3LYP/EPR-III. (a) In the whole range; (b) in the range 0 – 14 G. Linear fits are represented by solid lines.

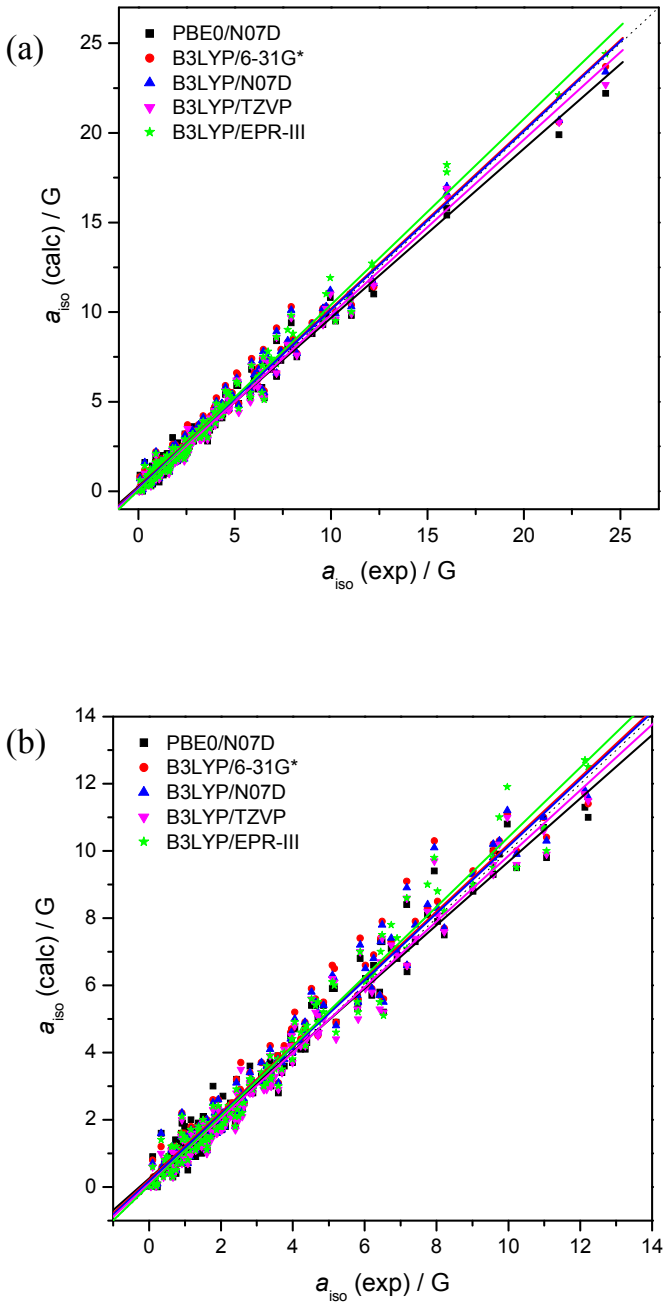
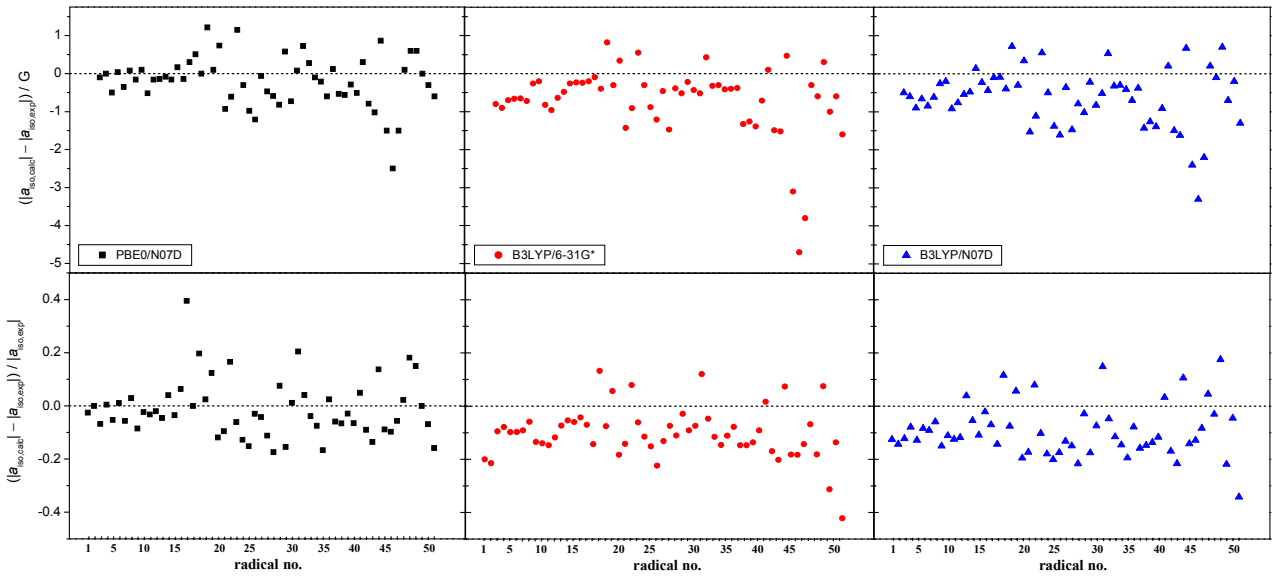


Figure S3. Absolute (top) and relative (bottom) deviation of the calculated $a_{iso}(^{14}N)$ of the conjugated radical cations computed at the following levels: PBE0/N07D, B3LYP/6-31G*, B3LYP/N07D, B3LYP/TZVP, and B3LYP/EPR-III.



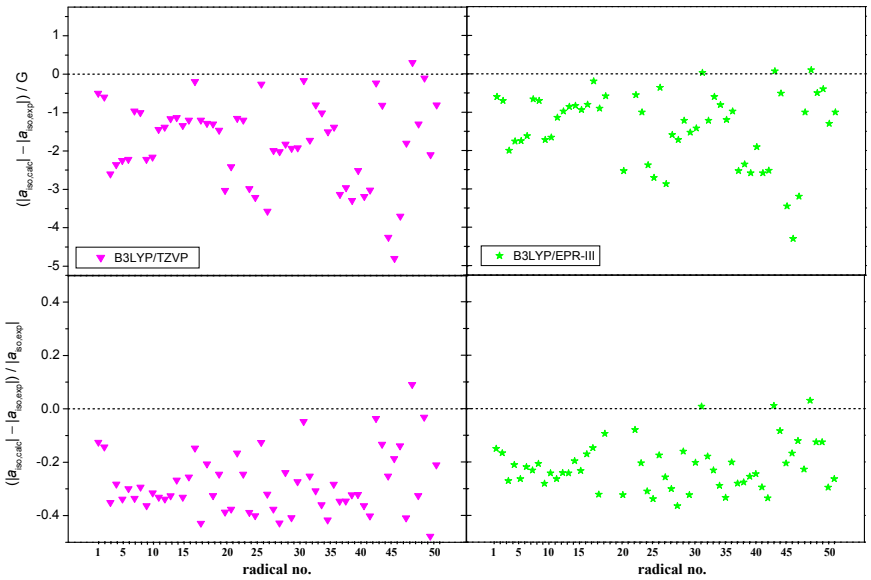


Table S2. Regression analysis for predictions of ^{1}H hfccs (G).

Level of theory	intercept	slope	R^2	N	|min|	|max|	max. absolute error	MAD[a]	range/MAD
PBE0/N07D	0.2459	0.9433	0.9819	165	0.003	22.2	2.0	0.39	56.92
B3LYP/6-31G*	0.2127	0.9983	0.9815	165	0.01	23.7	2.4	0.40	59.25
B3LYP/N07D	0.1704	0.9969	0.9832	165	0.01	23.4	2.2	0.37	63.24
B3LYP/TZVP	0.0896	0.9766	0.9838	165	0.02	22.7	1.8	0.34	66.76
B3LYP/EPR-III	0.0421	1.0370	0.9840	160	0.02	24.4	2.2	0.37	65.95

[a] MAD (Mean Absolute Deviation) $= \frac{1}{N}\sum_{i}^{N}\left|a_{iso}(calc) - a_{iso}(exp)\right|$.

Figure S4. Plot of selected NBO of radicals **43** (top), **46** (center) and **47** (bottom), computed at B3LYP/cc-pVTZ//B3LYP/6-31G* level of theory.

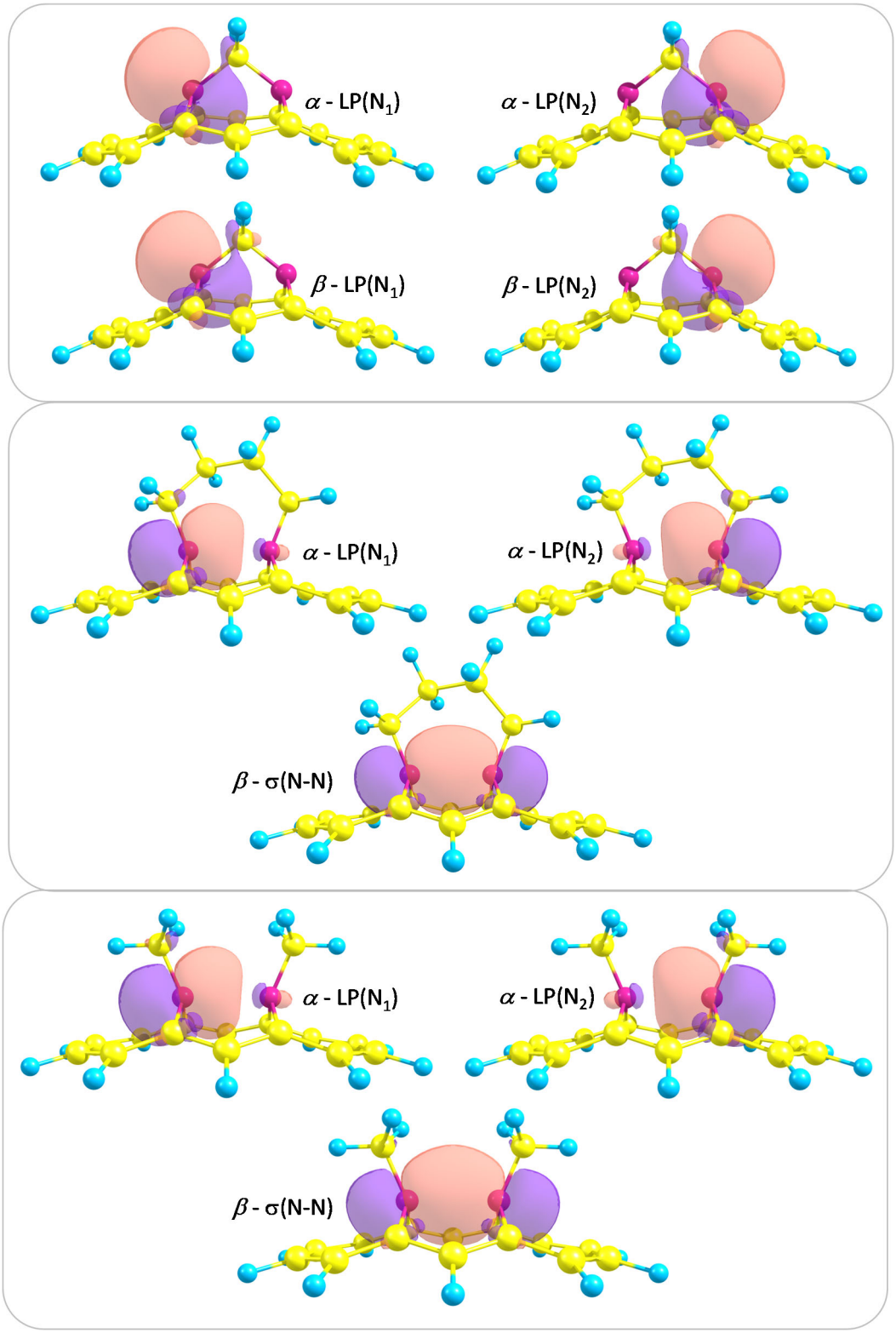


Figure S5. Plot of N atomic contributions to positive density deformations (contour = 0.001 a.u.) of radicals **43** (top), **46** (center) and **47** (bottom), computed at B3LYP/cc-pVTZ//B3LYP/6-31G* level of theory.

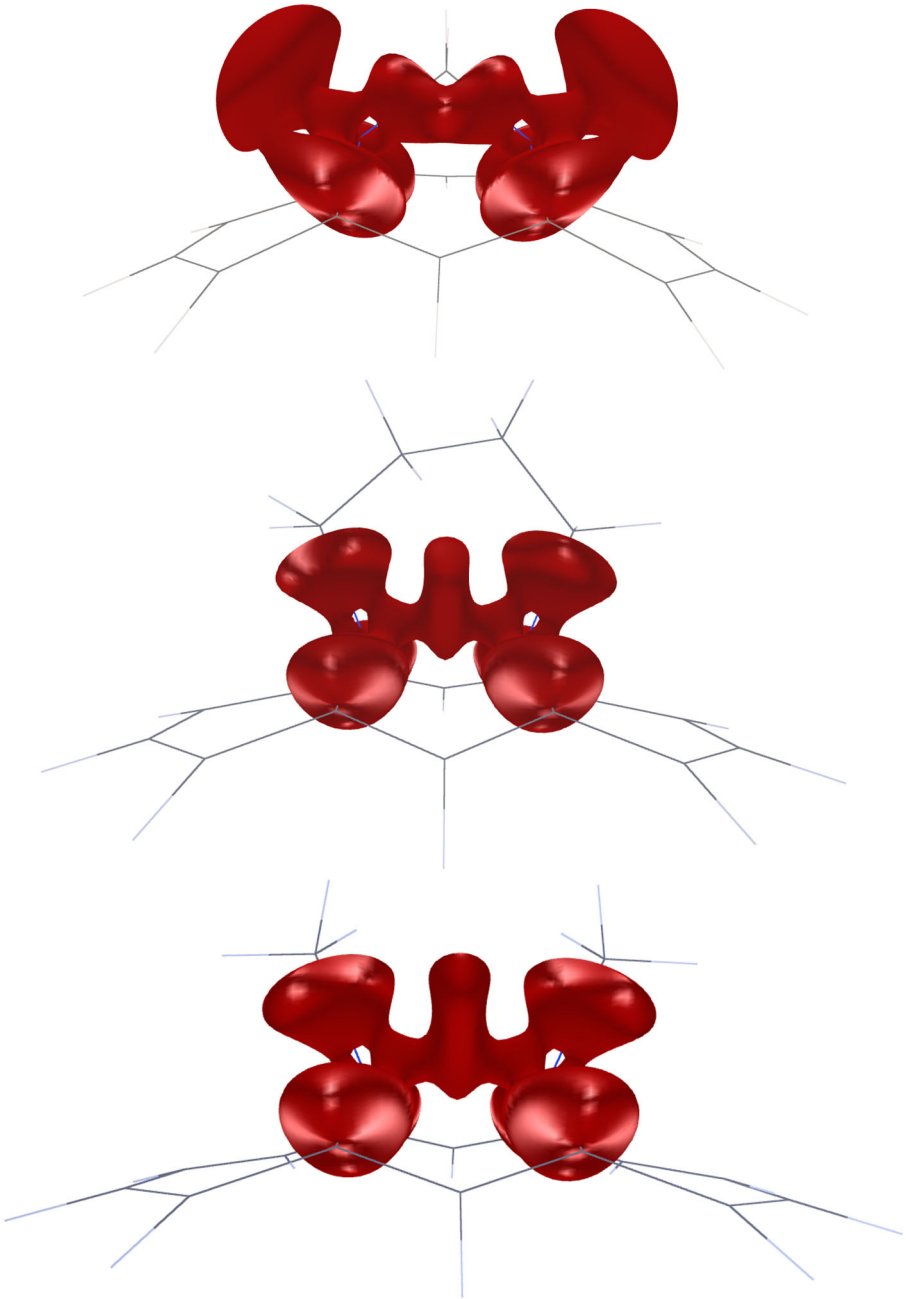


Figure S6. Plot of spin densities (contour = 0.005 a.u.) of radicals **43** (top), **46** (center) and **47** (bottom), computed at PBE0/N07D//B3LYP/6-31G* level of theory.