Supplementary information:

Theoretical investigation of paramagnetic group 13 diazabutadiene radicals: Insights into the prediction and interpretation of EPR spectroscopy parameters

Heikki M. Tuononen*[a] and Andrea F. Armstrong[b]

[a] Department of Chemistry, University of Jyväskylä

P.O. Box 35, FIN-40014 Jyväskylä, Finland

E-mail: hetuonon@cc.jyu.fi

Tel: +358-14-260-2613

Fax: +358-14-260-2501

[b] Department of Chemistry, McMaster University

1280 Main St. W., Hamilton, Ontario, Canada L8S 4M

Table S1 Calculated hyperfine coupling constants of monocyclic group 13 diazabutadiene radicals **6-M$^{R}_{X}$** [a]

(R–DAB)$MX_2^{\bullet}$	R	M	^{14}N	^{1}H	X
M = ^{27}Al	H	–6.9	2.9	–7.1	8.3
X = ^{19}F	Me	–7.5	3.7	–6.2	8.8
	^{t}Bu	–7.4	3.7	–6.3	9.7
	Ph	–7.1	3.6	–6.7	8.3
M = ^{27}Al	H	–7.4	3.0	–7.1	1.5
X = ^{35}Cl	Me	–8.1	3.7	–6.2	1.5
	^{t}Bu	–8.2	3.8	–6.2	1.6
	Ph	–7.7	3.6	–6.7	1.4
M = ^{27}Al	H	–7.6	3.0	–7.0	5.7
X = ^{79}Br	Me	–8.2	3.8	–6.2	6.2
	^{t}Bu	–8.4	3.8	–6.2	7.1
	Ph	–7.8	2.7	–6.7	5.5
M = ^{27}Al	H	–8.2	3.0	–6.9	6.3
X = ^{127}I	Me	–8.7	3.8	–6.1	7.3
	^{t}Bu	–8.9	3.9	–6.1	10.0
	Ph	–8.4	3.7	–6.6	6.8
M = ^{69}Ga	H	–23.2	3.4	–7.0	8.0
X = ^{19}F	Me	–25.4	4.2	–6.0	8.6
	^{t}Bu	–25.2	4.2	–6.1	9.7
	Ph	–24.1	4.1	–6.6	8.0
M = ^{69}Ga	H	–22.8	3.5	–6.8	1.5
X = ^{35}Cl	Me	–24.9	4.3	–5.9	1.5
	^{t}Bu	–25.2	4.4	–6.0	1.7
	Ph	–23.6	4.2	–6.5	1.4

Table S1 Continued

(R–DAB)$MX_2^{\bullet}$	R	M	^{14}N	^{1}H	X
M = ^{69}Ga	H	–22.9	3.6	–6.8	6.0
X = ^{79}Br	Me	–25.0	4.3	–5.9	6.5
	^{t}Bu	–25.3	4.5	–5.9	7.5
	Ph	–23.6	4.3	–6.4	5.8
M = ^{69}Ga	H	–23.9	3.6	–6.7	8.3
X = ^{127}I	Me	–25.5	4.4	–5.8	9.1
	^{t}Bu	–25.8	4.5	–5.8	11.9
	Ph	–24.2	4.3	–6.3	8.9
M = ^{115}In	H	–35.7	3.7	–6.6	5.2
X = ^{19}F	Me	–39.6	4.6	–5.7	5.3
	^{t}Bu	–39.2	4.5	–5.8	6.1
	Ph	–37.3	4.5	–6.2	4.9
M = ^{115}In	H	–32.1	3.8	–6.6	1.0
X = ^{35}Cl	Me	–35.8	4.7	–5.6	1.0
	^{t}Bu	–36.5	4.6	–5.7	1.1
	Ph	–33.7	4.6	–6.2	1.0
M = ^{115}In	H	–30.6	3.8	–6.6	4.5
X = ^{79}Br	Me	–33.9	4.7	–5.6	4.6
	^{t}Bu	–34.7	4.7	–5.7	5.1
	Ph	–31.6	4.6	–6.2	4.1
M = ^{115}In	H	–29.0	3.9	–6.5	6.6
X = ^{127}I	Me	–31.8	4.7	–5.3	7.2
	^{t}Bu	–32.8	4.7	–5.7	8.9
	Ph	–29.8	4.6	–6.1	7.0

[a] Values reported in Gauss (1G = 0.1mT).

Table S2 Calculated hyperfine coupling constants of dimeric group 13 diazabutadiene diradicals **7-M$^{R}_{X}$** [a]

[(R–DAB)MX]$_2^{\bullet\bullet}$	R	M	^{14}N	^{1}H	X
M = ^{27}Al	H	5.5	1.6 / 1.9	–3.8 / –3.9	14.0
X = ^{19}F	Me	2.8	2.0 / 2.3	–3.1 / –2.7	13.2
	^{t}Bu	5.3	2.1 / 2.3	–3.0 / –2.7	14.4
	Ph	4.3	1.8 / 2.1	–2.4 / –2.6	9.2
	Ph (C_{2h})	0.7	1.9	–2.9	10.0
M = ^{27}Al	H	5.9	1.6 / 1.9	–3.8 / –3.9	2.1
X = ^{35}Cl	Me	3.5	2.0 / 2.3	–3.1 / –2.7	1.9
	^{t}Bu	5.1	2.2 / 2.3	–3.0 / –2.7	2.1
	Ph	4.5	1.9 / 2.0	–2.4 / –2.5	1.3
	Ph (C_{2h})	1.3	1.9	–2.9	1.4
M = ^{27}Al	H	6.1	1.5 / 1.9	–3.8 / –3.9	9.2
X = ^{79}Br	Me	3.9	2.0 / 2.3	–3.1 / –2.7	8.9
	^{t}Bu	5.2	2.2 / 2.3	–3.0 / –2.7	9.3
	Ph	4.7	1.89/ 2.0	–2.4 / –2.5	5.1
	Ph (C_{2h})	1.7	1.9	–2.9	5.9
M = ^{27}Al	H	6.3	1.6 / 1.9	–3.8 / –3.9	11.5
X = ^{127}I	Me	4.1	2.0 / 2.3	–3.1 / –2.7	11.3
	^{t}Bu	5.3	2.1 / 2.3	–3.0 / –2.7	13.2
	Ph	4.2	1.8 / 2.0	–2.3 / –2.5	5.1
	Ph (C_{2h})	1.8	1.9	–2.9	6.7
M = ^{69}Ga	H	7.3	1.8 / 2.0	–3.9 / –4.0	12.6
X = ^{19}F	Me	4.0	2.3 / 2.5	–3.1 / –2.6	12.4
	^{t}Bu	8.1	2.3 / 2.5	–3.0 / –2.7	13.4
	Ph	4.3	1.8 / 2.1	–2.4 / –2.6	9.1
	Ph (C_{2h})	-1.0	2.1	–2.9	9.5
M = ^{69}Ga	H	10.6	1.9 / 2.1	–3.9 / –4.0	2.0
X = ^{35}Cl	Me	7.1	2.3 / 2.6	–3.0 / –2.6	1.9
	^{t}Bu	10.3	2.4 / 2.5	–3.0 / –2.6	2.0
	Ph	6.0	1.9 / 2.2	–2.3 / –2.6	1.2
	Ph (C_{2h})	1.7	2.1	–2.8	1.4

Table S2 Continued

$[(R–DAB)MX]_2^{\bullet\bullet}$	R	M	^{14}N	^{1}H	X
M = ^{69}Ga	H	11.6	1.9 / 2.1	–3.9 / –4.1	8.3
X = ^{79}Br	Me	8.3	2.4 / 2.6	–3.0 / –2.6	8.2
	^{t}Bu	10.9	2.4 / 2.5	–2.9 / –2.6	8.8
	Ph	6.3	1.9 / 2.1	–2.3 / –2.4	4.1
	Ph (C_{2h})	2.9	2.2	–2.8	5.6
M = ^{69}Ga	H	12.7	1.9 / 2.1	–3.9 / –4.0	10.4
X = ^{127}I	Me	9.5	2.3 / 2.6	–3.0 / –2.6	10.3
	^{t}Bu	11.2	2.4 / 2.5	–3.0 / –2.6	12.5
	Ph	10.8	1.9 / 2.2	–2.3 / –2.6	4.6
	Ph (C_{2h})	3.6	2.1	–2.8	6.6
M = ^{115}In	H	7.4	1.9 / 2.0	–3.9 / –4.0	8.1
X = ^{19}F	Me	2.3	2.4 / 2.6	–2.6 / –2.9	7.6
	^{t}Bu	16.9	2.3 / 2.5	–2.6 / –2.9	10.7
	Ph	6.5	2.0 / 2.2	–2.2 / –2.7	5.1
	Ph (C_{2h})	4.3	2.2	–2.6	5.7
M = ^{115}In	H	13.2	1.9 / 2.1	–3.9 / –4.0	1.4
X = ^{35}Cl	Me	7.6	2.5 / 2.6	–2.6 / –2.9	1.3
	^{t}Bu	11.9	2.4 / 2.5	–2.6 / –2.9	1.5
	Ph	10.6	2.1 /2.3	–2.2 / –2.6	0.8
	Ph (C_{2h})	4.3	2.2	–2.6	0.9
M = ^{115}In	H	14.7	2.0 / 2.1	–3.9 / –4.0	5.6
X = ^{79}Br	Me	9.4	2.5 / 2.6	–2.6 / –2.9	5.3
	^{t}Bu	18.8	2.1 / 2.3	–2.7 / –2.9	6.7
	Ph	12.5	2.3	–2.2 / –2.6	3.3
	Ph (C_{2h})	5.7	2.0 / 2.1	–2.6	3.6
M = ^{115}In	H	17.8	2.0 / 2.1	–3.9 / –4.0	7.8
X = ^{127}I	Me	12.1	2.5 / 2.6	–2.6 / –2.9	7.8
	^{t}Bu	20.1	2.4 / 2.5	–2.7 / –2.8	9.8
	Ph	15.9	2.2 / 2.3	–2.3 / –2.4	3.9
	Ph (C_{2h})	8.5	2.3	–2.6	4.5

[a] Values reported in Gauss (1G = 0.1mT).

Table S3 Calculated and experimental geometrical parameters of monocyclic group 13 diazabutadiene complexes **6-M$^{R}_{X}$** [a]

Parameter	**Al$^{Ph}_{I}$** Calc.	**Al$^{Dipp}_{I}$** Exptl.[b]	**Ga$^{tBu}_{I}$** Calc.	**Ga$^{tBu}_{I}$** Exptl.[b]	**Ga$^{Ph}_{I}$** Calc.	**Ga$^{Dipp}_{I}$** Exptl.[c]	**In$^{Ph}_{Cl}$** Calc.	**In$^{Dipp}_{Cl}$** Exptl.[d]
r MN	1.918	1.889	1.965	1.931	1.971	1.945	2.164	2.193
r NC(1)	1.332	1.337	1.328	1.337	1.329	1.339	1.328	1.331
r NC(2)	1.421	1.445	1.475	1.488	1.418	1.437	1.418	1.439
r C(1)C(1*)	1.399	1.409	1.398	1.450	1.399	1.404	1.402	1.384
r MX	2.507	2.514	2.537	2.531	2.517	2.519	2.337	236.4
∠ XMX*	116.2	110.8	115.1	109.3	117.1	112.3	117.5	111.5
∠ XMN	112.8	114.2	113.1	114.8	112.8	114.0	113.7	112.3
∠ MNC(1)	110.2	108.9	108.3	109.6	110.2	109.1	110.5	110.9
∠ NMN	85.7	87.4	85.8	87.1	84.0	85.7	78.5	77.0
∠ MNC(2)	129.5	130.5	130.9	129.6	128.6	129.2	129.0	128.6
∠ NC(1)C(1*)	116.9	116.7	118.8	116.9	117.8	117.6	120.2	119.8

[a] Average values of experimental parameters are reported. [b] Reference 11e. [c] Reference 11d. [d] Reference 11h.

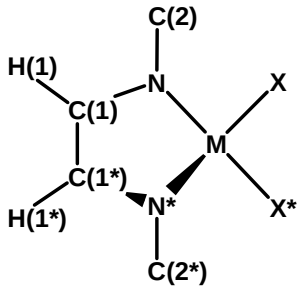

Table S4 Calculated and experimental geometrical parameters of dimeric group 13 diazabutadiene diradicals **7-M$^{R}_{I}$** [a]

Parameter	**Ga$^{tBu}_{I}$** Calc.	**Ga$^{tBu}_{I}$** Exptl.[b]	**Ga$^{Ph}_{Br}$** Calc.	**Ga$^{Dipp}_{Br}$** Exptl.[c]	**Ga$^{Ph}_{I}$** Calc.	**Ga$^{Dipp}_{I}$** Exptl.[c]	**In$^{Dipp}_{Cl}$** Calc.	**In$^{Dipp}_{Cl}$** Exptl.[d]
r MM*	2.433	2.423	2.454	2.466	2.462	2.576	2.742	2.727
r MX	2.618	2.617	2.377	2.374	2.586	2.586	2.387	2.409
r MN(1)	1.986	1.968	1.999	1.982	2.000	1.997	2.198	2.168
r MN(2)	1.997	1.966	-	-	-	-	-	-
r N(1)C(1)	1.327	1.334	1.331	1.343	1.332	1.336	1.330	1.324
r N(2)C(2)	1.328	1.322	-	-	-	-	-	-
r C(1)C(2)	1.397	1.395	1.392	1.385	1.391	1.411	1.394	1.410
r N(1)C(3)	1.475	1.483	1.405	1.434	1.405	1.445	1.399	1.444
r N(2)C(4)	1.472	1.484	-	-	-	-	-	-
∠ XMM*	119.4	115.2	112.5	113.2	112.3	113.8	114.9	118.8
∠ N(1)MN(2)	84.2	85.2	82.7	83.9	82.8	84.0	77.4	78.7
∠ N(1)MM	97.2	116.3	124.0	123.2	123.8	121.8	125.2	122.2
∠ N(2)MM	128.8	124.8	-	-	-	-	-	-
∠ C(1)N(1)M	115.4	109.0	109.6	134.2	109.6	109.9	110.1	110.2
∠ C(2)N(2)M	109.2	108.8	-	-	-	-	-	-
∠ C(1)C(2)N(2)	118.5	118.7	118.1	118.1	118.8	117.4	120.6	120.4
∠ C(2)C(1)N(1)	118.8	118.0	-	-	-	-	-	-
∠ MN(1)C(3)	130.0	131.2	129.7	131.0	129.8	131.8	128.4	130.2
∠ MN(2)C(4)	127.7	131.1	-	-	-	-	-	-
d XMM*X*	81.7	72.8	180.0	180.0	180.0	180.0	180.0	180.0

[a] Average values of experimental parameters are reported. [b] Reference 11e. [c] Reference 11d. [d] Reference 11f.