

*Supporting Information*

## Open-Shell Doublet Character in a Hexaazatrinaphthylene Trianion Complex

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### Experimental and Computational Details: General Considerations

**Synthesis.** The synthesis of **1**-toluene was carried out using standard Schlenk and glovebox techniques in an inert atmosphere of nitrogen or argon. Solvents (toluene, THF) were dried by refluxing either over potassium for at least three days, before being distilled and stored for 48 hours over activated 4 Å molecular sieves or a potassium mirror. All the solvents were degassed prior to use. Benzene-d<sub>6</sub> was degassed and refluxed over molten potassium for three days before being vacuum transferred into an ampoule and stored in a glovebox. 5,6,11,12,17,18-Hexaazatrinaphthylene was synthesized according to a literature procedure.<sup>1</sup> [Mg(nacnac)]<sub>2</sub> was synthesized using a modified literature procedure, using KC<sub>8</sub> in place of the potassium mirror. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University, U.K.<sup>2</sup>

**X-ray crystallography.** The crystal and molecular structure of **1**-toluene was determined by mounting a single crystal on an Agilent Technologies SuperNova diffractometer, using MoK $\alpha$  radiation. The structure was solved with SHELXS using direct methods; refined was achieved with SHELXL using least squares minimization.<sup>3</sup> The asymmetric unit contains a toluene molecule of solvation which is disordered over six sites and located on a special position. This molecule was modeled free from special position constraints with one-sixth occupancy; the C<sub>6</sub> ring was modeled as a regular hexagon with constrained C–C bond lengths of 1.390 Å; the C – CH<sub>3</sub> bond was set to 1.498 Å and was left isotropic.

**EPR spectroscopy.** The CW X-band spectrum of **1**-toluene were recorded as a solid (powder) and a solution ( $2 \times 10^{-4}$  M in THF) using a Bruker EMX Micro X-Band spectrometer at 293 K. Three freeze-pump cycles were done for the THF prior to sample preparation. The experimental  $g_{\text{iso}}$  values 2.0072 G (powder) and 2.0070 G (THF) were corrected with respect to the Bruker strong pitch (2.0028 G) to give  $g_{\text{iso}}$  values of 2.0033 G and 2.0031 G the for powder and solution samples, respectively.

**NMR, IR and Electronic spectroscopy.** The electronic absorption spectrum of **1**-toluene was measured on  $3.6 \times 10^{-5}$  M THF solution using a PerkinElmer Lambda-1050 spectrometer in the range 300-2000 nm. NMR spectra were acquired on a Bruker Avance III 400 MHz spectrometer. The FTIR spectrum was recorded on Perkin Elmer Spectrum RX1 Spectrometer in Nujol mull on KBr discs.

**DFT and TD-DFT Calculations.** All calculations used Gaussian 09,<sup>4</sup> Turbomole 6.3<sup>5</sup> and ORCA<sup>6</sup> programme packages, whereas the visualizations of molecular orbitals and spin densities were done with Gview.<sup>7</sup> The geometries of HAN, the simplified model systems **1a** with  $S = 1/2$  and **1a** with  $S = 3/2$  were fully optimized in  $D_{3h}$ ,  $C_1$ , and  $C_3$  point groups, respectively, using the B3LYP exchange-correlation functional<sup>8</sup> in conjunction with two different triple- $\zeta$  valence quality basis sets, namely, 6-311G\*\* and def2-TZVP.<sup>9,10</sup> The simplified system **1a** was modified from the crystal structure by removing methyl groups from nacnac backbones and replacing the Dipp groups with phenyl substituents. For the B3LYP/6-311G\*\* optimized structures, frequency analyses were performed to ensure that they correspond to true minima (no imaginary frequencies) on the potential energy hypersurface. All DFT calculations were performed using unrestricted formalism.

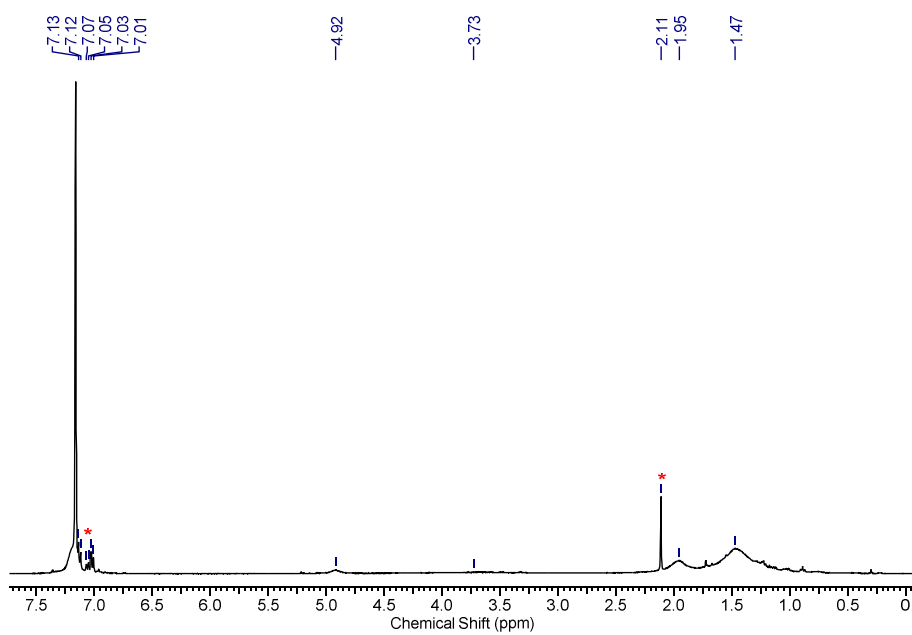
To assign the experimentally observed electronic transitions of **1**-toluene at the UV/vis/NIR region (200-1700 nm), a single point time-dependent density functional theory (TD-DFT) calculation was done in a

medium for the gas phase optimized geometry (B3LYP/6-311G\*\*) of **1a** with  $S = 1/2$  at the CAM-B3LYP/6-31+G\*/THF level of theory.<sup>11</sup> The solvent effect was modelled using the integral equation formalism variant of the polarisable continuum model (IEFPCM) as implemented in Gaussian09, and default solvent parameters were employed for THF.<sup>4</sup> The lowest 50 excited states were considered in TD-DFT calculations. The simulated spectra were constructed by fitting the excitation energy of each electron excitation to a Gaussian function with a full width at half maximum of 58.70 nm and 80.05 nm for the regions 300-599 nm and 600-1700 nm, respectively. Only electron excitations with oscillator strengths greater than 0.001 were considered in the simulation. A TD-TDF calculation and spectrum simulation were also carried out for **1a** with  $S = 3/2$ , using the same procedure as for doublet state. However, only one full-width half-maximum (58.70 nm) was used for the quartet state in the simulation.

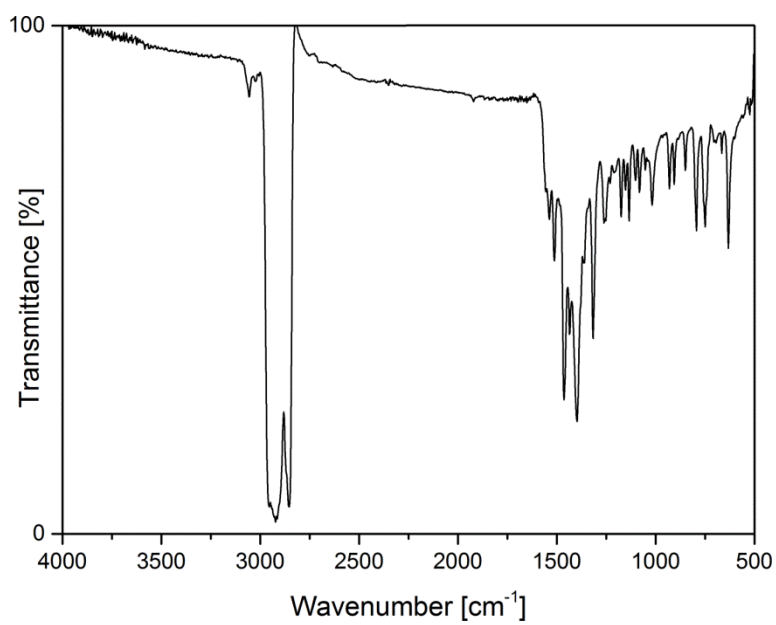
**CAS calculations.** Single-point complete active space (CAS) calculations in conjunction with 6-311G\*\* basis set were performed for the B3LYP/6-311G\*\* optimized geometry of the simplified model system with  $S = 1/2$ .<sup>12</sup> Quasi-restricted orbitals from B3LYP/311G\*\* calculations were used as starting orbitals in CAS calculations.<sup>13</sup> Four active spaces were used: CAS(3,3), CAS(5,5), CAS(7,7) and CAS(9,9). Starting orbitals included in the active space were determined by the basis of their composition, by visual inspection and by testing different combinations of starting orbitals. It was found that including the  $\pi$ -type orbitals of HAN-ligand into the active space yields the lowest energy solutions. The lowest energy solutions were obtained by including the  $\pi$ -type and  $\pi^*$ -type orbitals of the [HAN]<sup>3-</sup> ligand into the active space.

Based on the CAS calculations, the total wave function of **1a** ( $S = 1/2$ ) can be represented as the linear combination of five Slater determinants that form three configurations:  $(292)^2(293)^1(294)^0$ ,  $(292)^0(293)^1(294)^2$ , and  $(292)^1(293)^1(294)^1$ . These configurations are shown in Figure 3. The last electronic configuration must be written as a linear combination of three Slater determinants that differ only in the spin state of the electrons ( $\alpha\alpha\beta$ ,  $\alpha\beta\alpha$ , and  $\beta\alpha\alpha$ ). This ensures that the last electronic configuration is also a true eigenstate of both  $S_z$  and  $S^2$  operators. The contribution of each configurations to the total wave function of **1a** ( $S = 1/2$ ) can be determined by the weights of configurations, *i.e.* the squares of configuration interaction coefficients. The weights are given in Table S6 and, for example, the first, second and third configurations contribute 73 %, 10% and 9 % to the total wave function of **1a** ( $S = 1/2$ ) at the CAS(9,9) level of theory.

**Synthesis of 1-toluene.** [Mg(nacnac)g]<sub>2</sub> (200 mg, 0.23 mmol) and 5,6,11,12,17,18-hexaazatrinaphthalene (HAN, 59 mg, 0.15 mmol) were combined as solids and toluene (20 ml) was added at room temperature, resulting in the immediate formation of a dark red-brown solution. The solution was stirred for 18 h and filtered. The filtrate was concentrated *in vacuo* until a red/brown solid began to precipitate from solution, which was re-dissolved by heating briefly the solution to reflux. Slow cooling to room temperature followed by storage at 0°C for 24 h yielded dark brown crystals, which were subsequently isolated and identified to be **1-toluene**. A second crop of crystals was obtained by concentrating the filtrate and storing the solution for a further 24 h at 0°C, giving a total yield of 165 mg, or 64%. Anal. Calc. for C<sub>118</sub>H<sub>143</sub>Mg<sub>3</sub>N<sub>12</sub>: C 78.63 %; H 8.00 %; N 9.33 %. Found: C 78.49 %; H 8.15 %; 9.21 %. <sup>1</sup>H NMR (400.07 MHz, benzene-d<sub>6</sub>, 296 K),  $\delta$ /ppm: 7.16 (br, under residual solvent resonance), 7.13-7.01 (toluene CH resonances), 4.92 (br), 3.73 (very br), 2.11 (toluene CH<sub>3</sub> resonance) 1.95 (br), 1.47 (br). IR ( $\tilde{\nu}$ /cm<sup>-1</sup>): 3056 (w), 1540 (w), 1515 (m), 1436 (s), 1398 (s), 1317 (s), 1258 (w), 1173 (w), 1154 (w), 1336 (w), 1104 (w), 1081 (w), 1055 (w), 1018 (w), 930 (w), 905 (w), 849 (w), 795 (w) 749 (w) 700 (w), 664 (w), 632 (w).



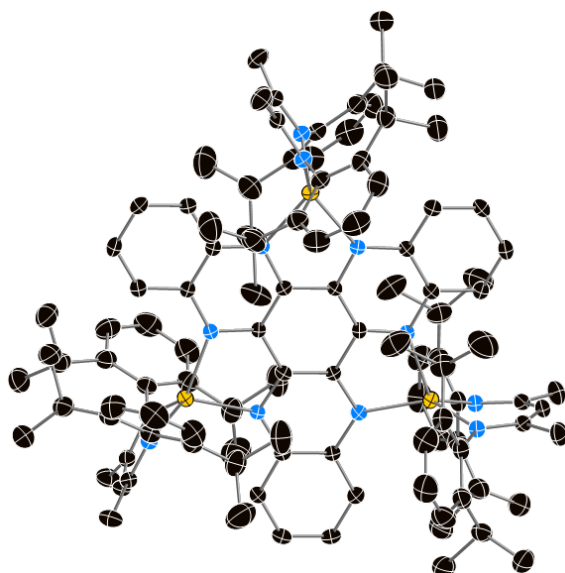
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1**-toluene in benzene- $\text{d}_6$ . \* = toluene of solvation.



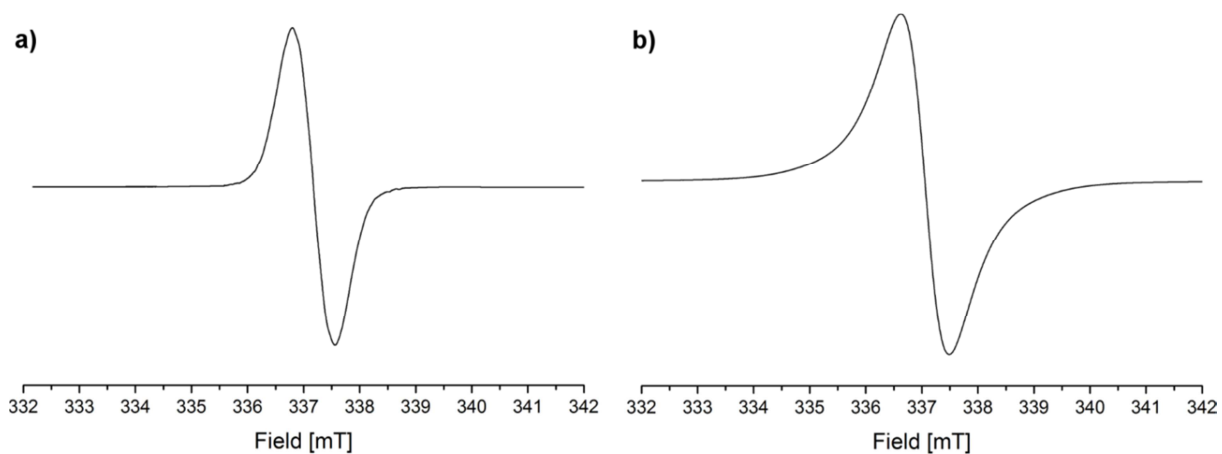
**Figure S2.** IR spectrum of **1**-toluene as a Nujol mull.

**Table S1.** Crystal data and structural refinement for **1**-toluene.

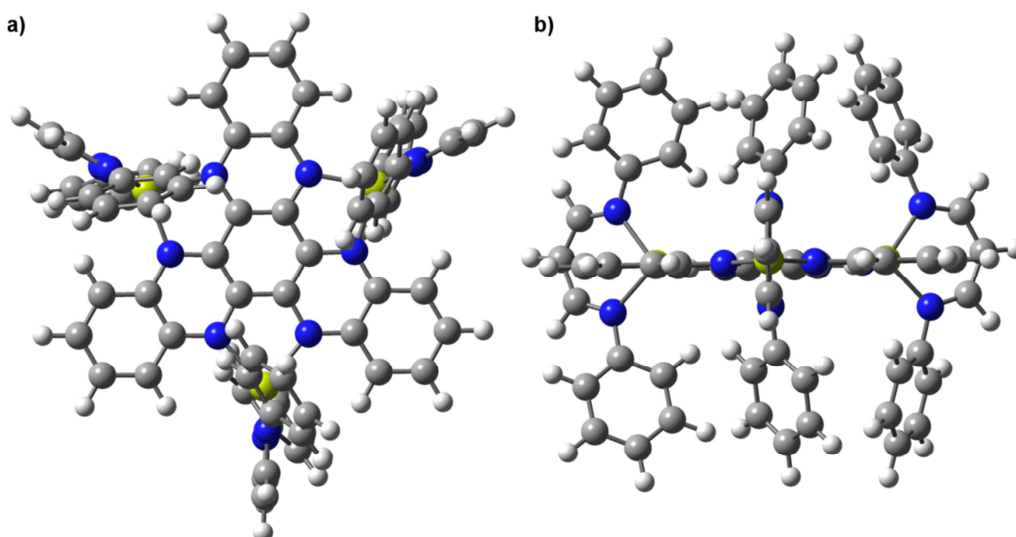
CCDC ref. code	1047819
Formula	C <sub>118</sub> H <sub>143</sub> N <sub>12</sub> Mg <sub>3</sub>
FW	1802.37
Crystal system	Hexagonal
Space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>
<i>a</i> /Å	15.9267(3)
<i>b</i> /Å	15.9267(3)
<i>c</i> /Å	24.0860(9)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	120
<i>V</i> /Å <sup>3</sup>	5291.1(3)
<i>Z</i>	2
Crystal size/mm <sup>3</sup>	0.6 × 0.6 × 0.4
2 $\theta$ range/°	6.766 to 52.744
Reflections collected	44033
Independent reflections, <i>R</i> (int)	3690
Completeness/%	99.8
Data/restraints/parameters	3690/3/230
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.118
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0555, <i>wR</i> <sub>2</sub> = 0.0231
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0687, <i>wR</i> <sub>2</sub> = 0.1548



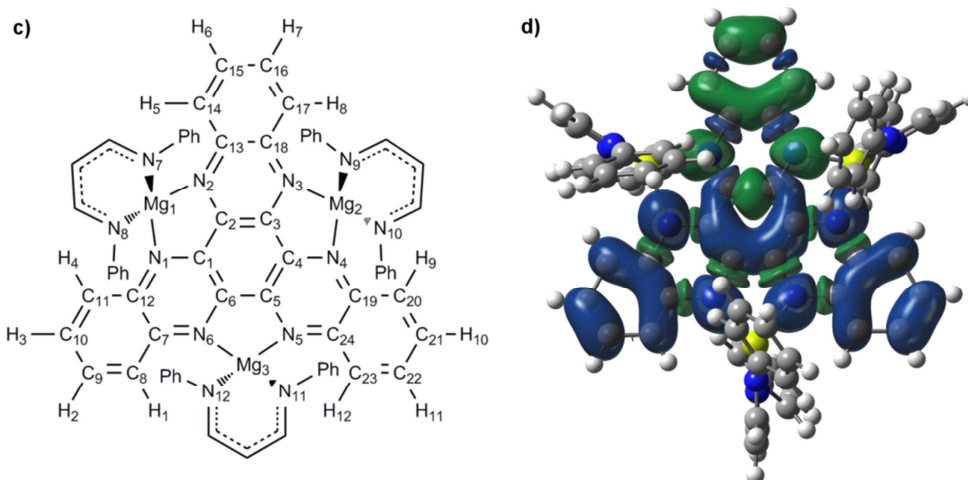
**Figure S3.** Thermal ellipsoid representation (50% probability) of the molecular structure of **1**. Yellow = Mg; blue = nitrogen; black = carbon.



**Figure S4.** a) Solution-state X-band EPR spectrum of **1**-toluene at 293 K in THF: mod. amp. = 1.0 G, lw = 7.73 G, and  $g_{\text{iso}} = 2.0031$  G. b) Powder X-band EPR spectrum of **1**-toluene at 293 K: mod. amp. = 1.0, lw = 8.59 G, and  $g_{\text{iso}} = 2.0033$  G.



**Figure S5.** Two views of the B3LYP/6-311G\*\* optimized geometry of **1a** with  $S = 1/2$ . Yellow = Mg; blue = nitrogen; black = carbon; white = hydrogen.



**Figure S6.** Left: numbering of atoms in the model system **1a**. Right: spin density for **1a** with  $S = 1/2$  calculated at the B3LYP/6-311G\*\* level of theory: blue =  $\alpha$  spin density; green =  $\beta$  spin density.

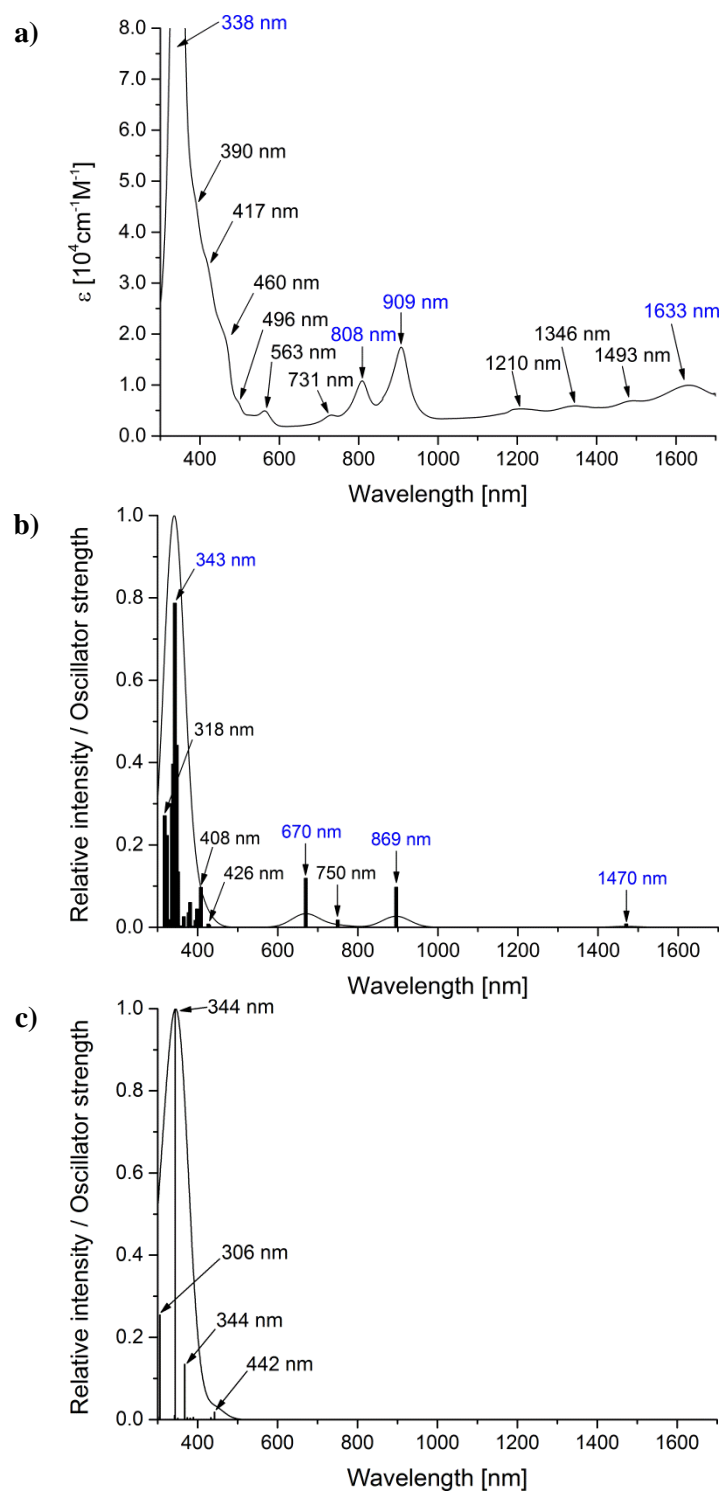
**Table S2.** Selected experimental (**1**) and calculated (B3LYP) bond lengths (Å) and angles (°) for **1a**. For numbering of atoms see Figure S6.

Bond	<b>1a (S=1/2)</b>					<b>1a (S=3/2)</b>			
	Exp.	6-311**	Exp.-Calc.	def-TZVP2	Exp.-Calc.	6-311**	Exp.-Calc.	def-TZVP2	Exp.-Calc.
N <sub>1</sub> -C <sub>1</sub>	1.359(3)	1.376	-0.017	1.373	-0.014	1.369	-0.010	1.366	-0.007
N <sub>2</sub> -C <sub>2</sub>	1.359(3)	1.362	-0.003	1.357	0.002	1.367	-0.008	1.364	-0.005
N <sub>3</sub> -C <sub>3</sub>	1.359(3)	1.363	-0.004	1.358	0.001	1.369	-0.010	1.366	-0.007
N <sub>4</sub> -C <sub>4</sub>	1.359(3)	1.374	-0.015	1.371	-0.012	1.367	-0.008	1.364	-0.005
N <sub>5</sub> -C <sub>5</sub>	1.359(3)	1.351	0.008	1.346	0.013	1.369	-0.010	1.366	-0.007
N <sub>6</sub> -C <sub>6</sub>	1.359(3)	1.350	0.009	1.345	0.014	1.367	-0.008	1.364	-0.005
N <sub>1</sub> -C <sub>12</sub>	1.385(3)	1.380	0.005	1.376	0.009	1.377	0.008	1.373	0.012
N <sub>2</sub> -C <sub>13</sub>	1.391(3)	1.376	0.015	1.373	0.018	1.376	0.015	1.372	0.019
N <sub>3</sub> -C <sub>18</sub>	1.385(3)	1.378	0.007	1.374	0.011	1.377	0.008	1.373	0.012
N <sub>4</sub> -C <sub>19</sub>	1.391(3)	1.377	0.014	1.374	0.017	1.376	0.015	1.372	0.019
N <sub>5</sub> -C <sub>24</sub>	1.385(3)	1.391	-0.006	1.387	-0.002	1.377	0.008	1.373	0.012
N <sub>6</sub> -C <sub>7</sub>	1.391(3)	1.389	0.002	1.386	0.005	1.376	0.015	1.372	0.019
N <sub>1</sub> -Mg <sub>1</sub>	2.076(2)	2.081	-0.005	2.068	0.008	2.093	-0.017	2.081	-0.005
N <sub>2</sub> -Mg <sub>1</sub>	2.071(2)	2.091	-0.020	2.081	-0.010	2.088	-0.017	2.076	-0.005
N <sub>3</sub> -Mg <sub>2</sub>	2.076(2)	2.097	-0.021	2.087	-0.011	2.093	-0.017	2.081	-0.005
N <sub>4</sub> -Mg <sub>2</sub>	2.071(2)	2.075	-0.004	2.063	0.008	2.088	-0.017	2.076	-0.005
N <sub>5</sub> -Mg <sub>3</sub>	2.076(2)	2.094	-0.018	2.082	-0.006	2.093	-0.017	2.081	-0.005
N <sub>6</sub> -Mg <sub>3</sub>	2.071(2)	2.089	-0.018	2.077	-0.006	2.088	-0.017	2.076	-0.005
N <sub>7</sub> -Mg <sub>1</sub>	2.0442(18)	2.078	-0.034	2.068	-0.024	2.078	-0.034	2.066	-0.022
N <sub>8</sub> -Mg <sub>1</sub>	2.0442(18)	2.080	-0.036	2.068	-0.024	2.076	-0.032	2.065	-0.021
N <sub>9</sub> -Mg <sub>2</sub>	2.0442(18)	2.078	-0.034	2.068	-0.024	2.078	-0.034	2.066	-0.022
N <sub>10</sub> -Mg <sub>2</sub>	2.0442(18)	2.080	-0.036	2.068	-0.024	2.076	-0.032	2.065	-0.021
N <sub>11</sub> -Mg <sub>3</sub>	2.0442(18)	2.073	-0.029	2.063	-0.019	2.078	-0.034	2.066	-0.022
N <sub>12</sub> -Mg <sub>3</sub>	2.0442(18)	2.075	-0.031	2.063	-0.019	2.076	-0.032	2.065	-0.021
C <sub>1</sub> -C <sub>2</sub>	1.440(4)	1.430	0.010	1.426	0.014	1.430	0.010	1.427	0.013
C <sub>2</sub> -C <sub>3</sub>	1.407(4)	1.416	-0.009	1.415	-0.008	1.418	-0.011	1.416	-0.009
C <sub>3</sub> -C <sub>4</sub>	1.440(4)	1.430	0.010	1.426	0.014	1.430	0.010	1.427	0.013
C <sub>4</sub> -C <sub>5</sub>	1.407(4)	1.404	0.003	1.401	0.006	1.418	-0.011	1.416	-0.009
C <sub>5</sub> -C <sub>6</sub>	1.440(4)	1.459	-0.019	1.458	-0.018	1.430	0.010	1.427	0.013
C <sub>6</sub> -C <sub>1</sub>	1.407(4)	1.404	0.003	1.401	0.006	1.418	-0.011	1.416	-0.009
C <sub>7</sub> -C <sub>12</sub>	1.412(4)	1.427	-0.015	1.424	-0.012	1.430	-0.018	1.427	-0.015
C <sub>13</sub> -C <sub>18</sub>	1.412(4)	1.429	-0.017	1.426	-0.014	1.430	-0.018	1.427	-0.015
C <sub>19</sub> -C <sub>24</sub>	1.412(4)	1.427	-0.015	1.424	-0.012	1.430	-0.018	1.427	-0.015
<b>Angle</b>									
N <sub>1</sub> -Mg <sub>1</sub> -N <sub>2</sub>	81.21(9)	81.779	-0.569	82.148	-0.938	81.952	-0.742	85.359	-4.149
N <sub>3</sub> -Mg <sub>2</sub> -N <sub>4</sub>	81.21(9)	81.748	-0.538	82.114	-0.904	81.952	-0.742	85.359	-4.149
N <sub>5</sub> -Mg <sub>3</sub> -N <sub>6</sub>	81.21(9)	81.289	-0.079	81.639	-0.429	81.952	-0.742	85.359	-4.149
N <sub>7</sub> -Mg <sub>1</sub> -N <sub>8</sub>	96.17(10)	94.467	1.703	94.996	1.174	94.646	1.524	95.184	0.986
N <sub>9</sub> -Mg <sub>2</sub> -N <sub>10</sub>	96.17(10)	94.460	1.710	94.990	1.180	94.646	1.524	95.184	0.986
N <sub>11</sub> -Mg <sub>3</sub> -N <sub>12</sub>	96.17(10)	94.753	1.417	95.313	0.857	94.646	1.524	95.184	0.986

**Table S3.** Calculated (B3LYP) isotropic hyperfine coupling constants (in MHz) and Mulliken spin density for 1a with  $S = 1/2$ . The numbering of atoms is presented in Figure S6.

	IHCC		Mulliken spin density	
	6-311**	def-TZVP2	6-311**	def-TZVP2
<b>Mg<sub>1</sub></b>	0.10	0.35	-0.000	-0.001
<b>Mg<sub>2</sub></b>	0.33	0.44	-0.003	-0.002
<b>Mg<sub>3</sub></b>	2.55	2.18	0.003	-0.003
<b>N<sub>1</sub></b>	8.73	9.31	0.235	0.232
<b>N<sub>2</sub></b>	-7.72	-7.78	-0.201	-0.190
<b>N<sub>3</sub></b>	-7.54	-7.60	-0.195	-0.184
<b>N<sub>4</sub></b>	8.93	9.50	0.241	0.238
<b>N<sub>5</sub></b>	8.04	8.40	0.232	0.225
<b>N<sub>6</sub></b>	8.25	8.60	0.239	0.231
<b>C<sub>1</sub></b>	-2.29	-1.17	0.097	0.090
<b>C<sub>2</sub></b>	3.06	2.47	0.000	0.010
<b>C<sub>3</sub></b>	3.15	2.56	0.001	0.011
<b>C<sub>4</sub></b>	-3.11	-1.94	0.007	0.081
<b>C<sub>5</sub></b>	-10.28	-9.56	0.031	0.024
<b>C<sub>6</sub></b>	-11.19	-10.35	0.024	0.019
<b>C<sub>7</sub></b>	-7.87	-6.95	0.018	0.021
<b>C<sub>8</sub></b>	-0.65	-0.56	0.027	0.021
<b>C<sub>9</sub></b>	0.51	0.92	0.044	0.047
<b>C<sub>10</sub></b>	-0.58	-0.59	0.034	0.034
<b>C<sub>11</sub></b>	0.25	0.72	0.037	0.032
<b>C<sub>12</sub></b>	-8.62	-8.32	0.012	0.017
<b>C<sub>13</sub></b>	7.24	6.47	-0.007	-0.009
<b>C<sub>14</sub></b>	-0.30	-0.51	-0.027	-0.019
<b>C<sub>15</sub></b>	0.35	0.19	-0.026	-0.027
<b>C<sub>16</sub></b>	-0.30	-0.40	-0.032	-0.033
<b>C<sub>17</sub></b>	0.28	0.00	-0.020	-0.012
<b>C<sub>18</sub></b>	6.51	5.86	-0.013	-0.017
<b>C<sub>19</sub></b>	-9.34	-8.92	0.007	0.009
<b>C<sub>20</sub></b>	0.81	1.22	0.043	0.039
<b>C<sub>21</sub></b>	-1.20	-1.15	0.027	0.028
<b>C<sub>22</sub></b>	1.14	1.50	0.051	0.054
<b>C<sub>23</sub></b>	-1.22	-1.09	0.021	0.013
<b>C<sub>24</sub></b>	-7.15	-6.34	0.024	0.030
<b>H<sub>1</sub></b>	-2.49	-2.19	-0.002	-0.001
<b>H<sub>2</sub></b>	-3.23	-3.29	-0.003	-0.003
<b>H<sub>3</sub></b>	-2.60	-2.42	-0.002	-0.002
<b>H<sub>4</sub></b>	-3.01	-2.88	-0.003	-0.002
<b>H<sub>5</sub></b>	2.30	2.02	0.002	0.001
<b>H<sub>6</sub></b>	1.98	1.85	0.002	0.001
<b>H<sub>7</sub></b>	2.36	2.19	0.002	0.002
<b>H<sub>8</sub></b>	1.97	1.74	0.002	0.001
<b>H<sub>9</sub></b>	-3.33	-3.16	-0.003	-0.002
<b>H<sub>10</sub></b>	-2.25	-2.11	-0.002	-0.002
<b>H<sub>11</sub></b>	-3.61	-3.63	-0.003	-0.003
<b>H<sub>12</sub></b>	-2.17	-1.90	-0.002	-0.001





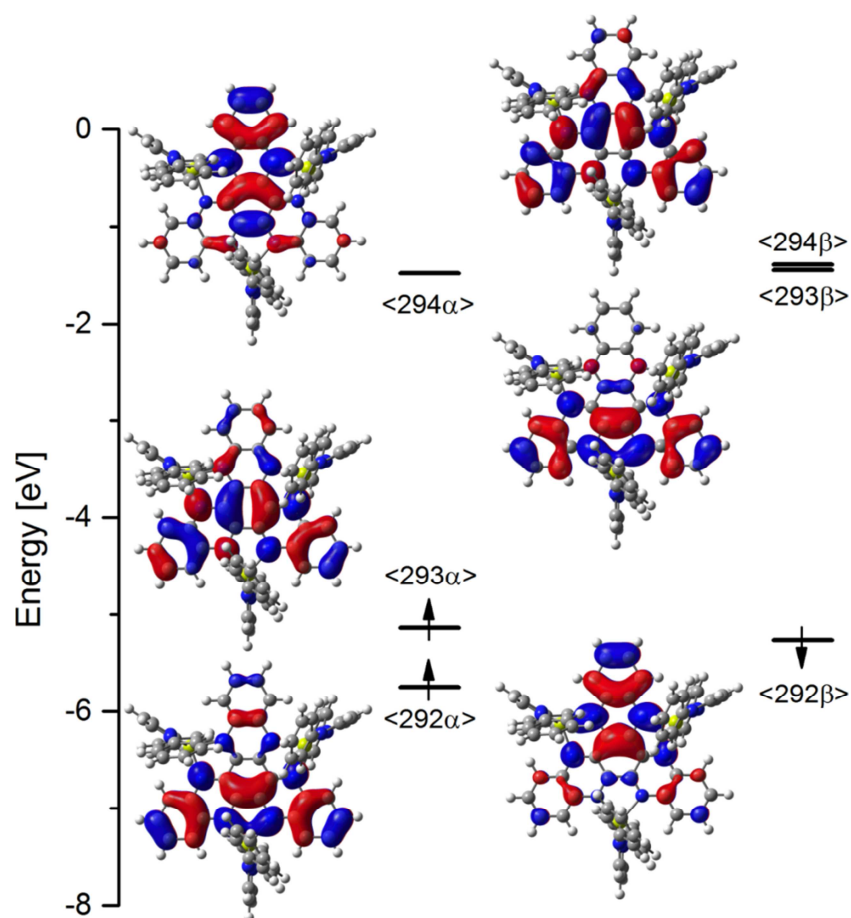
**Figure S7.** a) Experimental electronic absorption spectrum for **1**-toluene in THF solution. b) Simulated spectrum for **1a** ( $S = 1/2$ ) and calculated electron excitations with oscillator strengths (black bars). c) Simulated spectrum for **1a** ( $S = 3/2$ ) and calculated electron excitations along with oscillator strengths (black bars).

The simulated spectra and calculated oscillator strengths were scaled to one and the original oscillator strengths of electron absorptions are presented in Table S5. The well-resolved electron transitions found in experimental spectrum and their corresponding calculated values are marked in blue.

**Table S4.** Calculated (CAM-B3LYP/6-31+G\*/THF) electron transitions, their contributions, wavelengths and oscillator strengths for **1a** with  $S = 1/2$ , with the corresponding well-resolved maxima (1633, 909 nm, 808 nm, and 338 nm) in the experimental electronic absorption spectrum of **1-toluene**.<sup>a</sup>

Transition ( <b>1a</b> )	Contribution/% ( <b>1a</b> )	$\lambda/\text{nm}$ ( <b>1a</b> )	$f$ ( <b>1a</b> )	$\lambda_{\text{exp}}/\text{nm}$ ( <b>1-toluene</b> )
293 $\alpha$ $\rightarrow$ 294 $\alpha$	73	1470	0.008	1633
292 $\beta$ $\rightarrow$ 294 $\beta$	23			
292 $\beta$ $\rightarrow$ 294 $\beta$	71	896	0.097	909
293 $\alpha$ $\rightarrow$ 294 $\alpha$	23			
292 $\alpha$ $\rightarrow$ 294 $\alpha$	85	670	0.119	808
293 $\alpha$ $\rightarrow$ 298 $\alpha$	12	343	0.787	338
293 $\alpha$ $\rightarrow$ 303 $\alpha$	12			
290 $\alpha$ $\rightarrow$ 294 $\alpha$	11			
290 $\alpha$ $\rightarrow$ 297 $\alpha$	10			
290 $\beta$ $\rightarrow$ 297 $\beta$	9			
289 $\alpha$ $\rightarrow$ 295 $\alpha$	6			
289 $\beta$ $\rightarrow$ 295 $\beta$	6			
290 $\beta$ $\rightarrow$ 294 $\beta$	5			

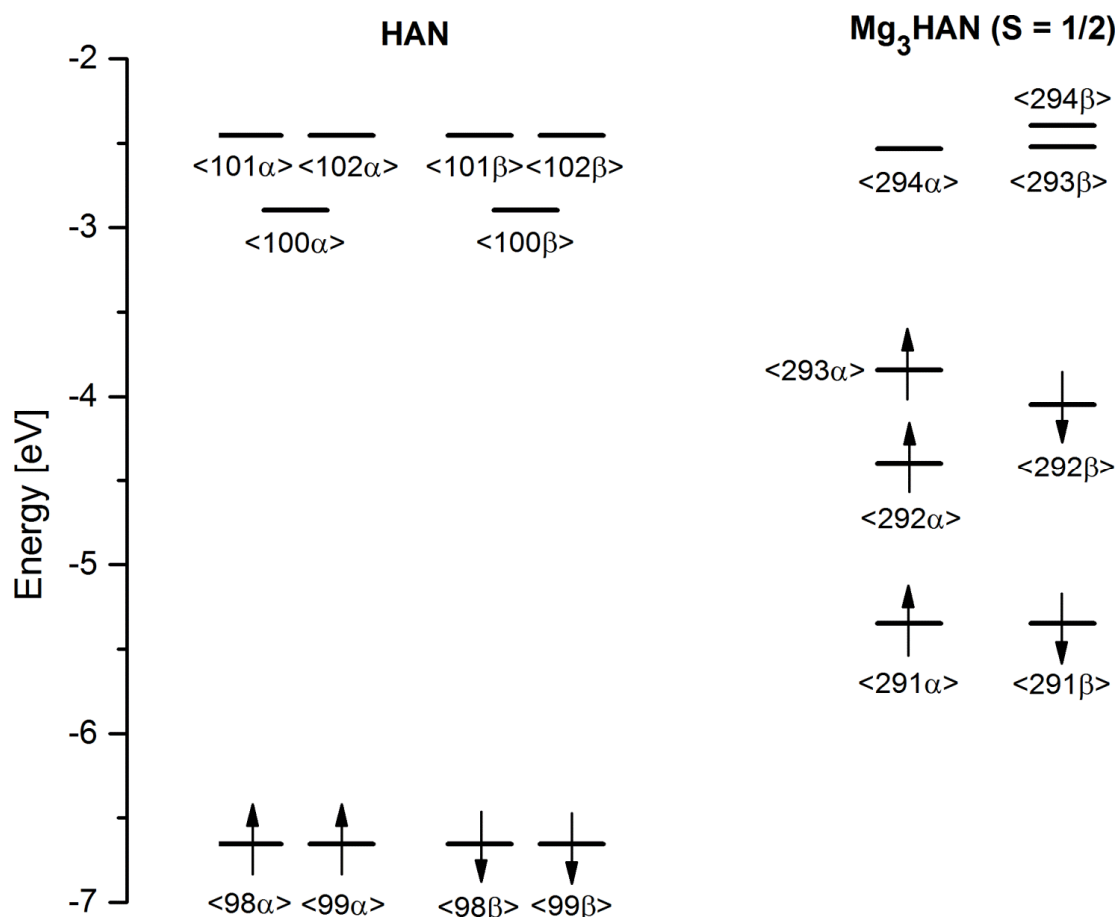
<sup>a</sup> Only transitions that contribute more than 5% are listed. The MOs associated with the characteristic transitions (292 $\beta$  $\rightarrow$ 294 $\beta$ , 293 $\alpha$  $\rightarrow$ 294 $\alpha$ , and 292 $\alpha$  $\rightarrow$ 294 $\alpha$ ) of the radical are shown in Figure S8.



**Figure S8.** Selected frontier MOs for **1a** with  $S = 1/2$  calculated the CAM-B3LYP/6-31+G\*/THF level of theory.

**Table S5.** Calculated (CAM-B3LYP/6-31+G\*) electron excitations and their corresponding oscillator strengths used in the simulated electronic absorption spectra for **1a** with  $S = 1/2$  and  $S = 3/2$ .

$S = 1/2$			$S = 3/2$		
State	$\lambda/\text{nm}$	$f$	State	$\lambda/\text{nm}$	$f$
1	1470	0.008	6	442	0.043
2	896	0.097	7	442	0.043
3	750	0.017	8	433	0.011
4	670	0.119	9	433	0.011
9	429	0.005	11	389	0.013
10	426	0.008	12	389	0.012
11	408	0.097	15	382	0.008
12	401	0.001	16	382	0.008
13	399	0.044	19	374	0.011
14	396	0.006	20	374	0.011
15	395	0.017	21	374	0.007
18	386	0.003	22	368	0.317
19	381	0.060	23	368	0.249
20	380	0.003	24	368	0.003
21	378	0.035	25	368	0.222
25	366	0.026	26	368	0.290
26	360	0.003	28	351	0.008
27	352	0.004	29	351	0.008
28	351	0.134	30	350	0.002
32	348	0.015	34	344	2.358
33	348	0.442	35	342	0.023
34	347	0.160	36	342	0.024
35	346	0.336	42	306	0.600
36	344	0.023	43	306	0.599
37	343	0.562	44	305	0.016
38	343	0.787			
39	341	0.012			
40	340	0.077			
41	339	0.396			
42	336	0.300			
44	326	0.019			
45	323	0.223			
46	323	0.012			
47	318	0.271			



**Figure S9.** B3LYP/6-311G\*\* molecular orbital energies in eV and orbital occupations for HAN (left) and **1a** ( $S = 1/2$ ) (right).

**Table S6.** Natural orbital occupation numbers (NOONs) of **1a** ( $S = 1/2$ ) and the weight of leading configurations in the ground-state wave function. Configurations  $(292)^2(293)^1(294)^0$ ,  $(292)^0(293)^1(294)^2$  and  $(292)^1(293)^1(294)^1$  are shown in Figure 3.

NO	NOON				Configuration	Weight/%			
	CAS(3,3)	CAS(5,5)	CAS(7,7)	CAS(9,9)		CAS(3,3)	CAS(5,5)	CAS(7,7)	CAS(9,9)
289	-	-	-	1.97	$(292)^2(293)^1(294)^0$	0.73	0.73	0.74	0.73
290	-	-	1.98	1.96	$(292)^0(293)^1(294)^2$	0.13	0.13	0.12	0.10
291	-	1.97	1.96	1.95	$(292)^1(293)^1(294)^1$	0.14	0.12	0.09	0.09
292	1.60	1.61	1.64	1.67					
293	1.00	1.00	1.00	1.00					
294	0.40	0.39	0.36	0.34					
295	-	0.04	0.04	0.05					
296	-	-	0.03	0.05					
297	-	-	-	0.03					

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**XYZ-Coordinates (B3LYP/6-311G\*\*)****Mg3HAN (S = 1/2)**

E = -3918.62696834 (6-311G\*\*)

E = -3919.0349764 (def2-TZVP)

NIMAG = 0

Mg	-3.315838	-2.242997	-0.023267	C	3.250424	3.838290	-0.088920
N	-2.761442	-0.221334	-0.092367	H	2.654770	4.745003	-0.093259
N	-1.257994	-2.500622	-0.090269	C	2.592234	2.595653	-0.085795
N	-4.400270	-2.975174	1.593940	N	-4.573660	-3.076425	-1.451877
C	-1.404511	-0.094201	-0.097211	C	-4.236763	-3.031222	-2.829307
C	-0.615139	-1.286108	-0.095920	C	-4.029307	-4.056080	-5.019563
C	-0.468405	-3.629334	-0.097089	H	-4.145711	-4.925921	-5.656821
C	-1.050713	-4.909345	-0.103706	C	-3.508017	-2.874127	-5.541035
H	-2.132592	-4.988510	-0.106901	H	-3.227393	-2.813797	-6.586120
C	-0.268148	-6.054605	-0.109637	C	-3.340440	-1.773956	-4.701577
H	-0.743689	-7.028650	-0.115180	H	-2.934873	-0.847390	-5.092315
C	1.126313	-5.955463	-0.110102	Mg	-0.258609	4.001845	-0.021520
H	1.739405	-6.848618	-0.116000	N	-0.404801	5.309373	1.589564
C	1.725944	-4.703049	-0.104106	C	-0.451511	7.309734	0.184725
H	2.807778	-4.618702	-0.108019	H	-0.454591	8.390071	0.251580
C	0.955261	-3.531659	-0.096792	C	-0.528427	4.814596	2.913416
C	-6.135866	-3.982870	0.197763	C	-1.535402	4.829646	5.121498
H	-7.082239	-4.503326	0.269117	H	-2.247770	5.257182	5.818632
C	-3.906644	-2.838272	2.917149	C	-0.743434	3.750356	5.507529
C	-3.424167	-3.721845	5.125297	H	-0.825688	3.341596	6.507951
H	-3.447143	-4.551734	5.823152	C	0.148278	3.195875	4.590338
C	-2.871444	-2.502115	5.509866	H	0.771639	2.355490	4.874875
H	-2.474290	-2.372500	6.509957	N	-0.398627	5.497487	-1.456975
C	-2.826653	-1.453492	4.592114	C	-0.515847	5.172604	-2.832883
H	-2.400480	-0.497645	4.875800	C	-1.502632	5.472576	-5.029876
N	1.213851	2.533050	-0.083342	H	-2.204730	5.990898	-5.673828
N	-1.509449	2.327034	-0.088288	C	-0.717556	4.441521	-5.541054
C	0.644944	1.280238	-0.092403	H	-0.795405	4.160103	-6.584767
C	-0.780819	1.176848	-0.094873	C	0.160030	3.767972	-4.692907
C	-2.881369	2.216619	-0.094646	H	0.776473	2.962154	-5.075470
C	-3.687910	3.370517	-0.097406	Mg	3.602988	-1.760721	-0.008144
H	-3.205474	4.342083	-0.097706	N	4.775362	-2.301387	1.617330
C	-5.068526	3.277256	-0.102626	C	6.564175	-3.230618	0.233572
H	-5.669745	4.178865	-0.105301	H	7.509371	-3.752133	0.311827
C	-5.687810	2.018999	-0.105797	C	4.383962	-1.960582	2.938520
H	-6.768865	1.944615	-0.111057	C	4.851110	-1.075753	5.148860
C	-4.918852	0.868117	-0.103374	H	5.556626	-0.645877	5.851436
H	-5.395899	-0.106216	-0.109163	C	3.523366	-1.269662	5.523945
C	-3.512508	0.934414	-0.097244	H	3.192468	-1.004274	6.521305
N	1.578403	-2.288559	-0.087877	C	2.623345	-1.799918	4.600650
N	2.778712	0.156995	-0.080172	H	1.586829	-1.957554	4.877149
C	0.786063	-1.194189	-0.093492	N	4.972373	-2.399645	-1.427713
C	1.429652	0.115701	-0.089966	C	4.758829	-2.147109	-2.807796
C	3.382720	1.407711	-0.084246	C	5.520900	-1.433431	-4.998309
C	4.780644	1.512459	-0.086076	H	6.319877	-1.068600	-5.634485
H	5.372009	0.602809	-0.088466	C	4.245416	-1.629041	-5.523320
C	5.407227	2.751344	-0.088344	H	4.047854	-1.429225	-6.570013
H	6.489022	2.810690	-0.090168	C	3.223623	-2.073152	-4.685653
C	4.635788	3.916993	-0.089650	H	2.225459	-2.229165	-5.079252
H	5.117114	4.888144	-0.092327	C	5.949610	-2.892418	1.445133
				H	6.501469	-3.168725	2.346137
				C	6.111093	-2.977379	-1.065333
				H	6.770974	-3.314495	-1.867391
				C	5.280044	-1.410379	3.867695
				H	6.304542	-1.214703	3.573042

C	3.046450	-2.139990	3.319949	C	-0.428209	4.521359	5.533048
H	2.346222	-2.571151	2.613545	H	-0.530168	4.254729	6.578548
C	-3.931720	-3.894620	3.840822	C	0.395253	3.774394	4.692224
H	-4.319253	-4.860853	3.539327	H	0.945513	2.925388	5.082151
C	-3.335329	-1.618526	3.308128	N	1.418635	-2.405609	0.090901
H	-3.314417	-0.793299	2.605500	N	2.791046	-0.031906	0.089752
C	0.254169	3.718640	3.305785	C	0.707831	-1.235583	0.097436
H	0.962044	3.293944	2.602974	C	1.424258	0.001847	0.096969
C	-1.437140	5.355219	3.836446	C	3.463336	1.168154	0.097402
H	-2.089999	6.165858	3.534343	C	4.870760	1.194194	0.103183
C	-1.411236	5.832988	-3.688599	H	5.407765	0.251614	0.105970
H	-2.059483	6.606384	-3.293339	C	5.564802	2.392039	0.108974
C	0.259781	4.125646	-3.352620	H	6.648474	2.387245	0.113977
H	0.957653	3.609081	-2.702989	C	4.866661	3.607456	0.109960
C	-3.697457	-1.849880	-3.359550	H	5.407879	4.546256	0.115603
H	-3.581822	-0.983991	-2.717236	C	3.481893	3.611257	0.105054
C	-4.384799	-4.140409	-3.676514	H	2.939729	4.551000	0.109449
H	-4.747536	-5.078672	-3.273129	C	2.751163	2.407980	0.098277
C	5.777884	-1.681958	-3.653166	N	-2.792636	-0.025770	0.090901
H	6.762845	-1.483436	-3.246903	N	-1.423155	-2.401163	0.089752
C	3.474406	-2.327750	-3.341484	C	-1.423962	0.004792	0.097436
H	2.679227	-2.693022	-2.701095	C	-0.710530	-1.234367	0.096969
C	-5.526424	-3.650986	1.413537	C	-0.720016	-3.583414	0.097402
H	-6.058537	-3.975607	2.310402	C	-1.401178	-4.815299	0.103183
C	-5.671636	-3.732219	-1.097790	H	-2.485978	-4.809069	0.105970
H	-6.303845	-4.109526	-1.904367	C	-0.710834	-6.015279	0.108974
C	-0.456914	6.621008	1.403387	H	-1.256822	-6.951370	0.113977
H	-0.489745	7.247618	2.297301	C	0.690818	-6.018380	0.109960
C	-0.449672	6.776898	-1.108760	H	1.233234	-6.956489	0.115603
H	-0.475411	7.509269	-1.918431	C	1.386494	-4.821036	0.105054

**Mg3HAN (S = 3/2)**

E = -3918.62339196 (6-311G\*\*)

E = -3919.03041196 (def2-TZVP)

NIMAG = 0

Mg	0.000000	4.008963	0.017433	C	0.709791	-3.586568	0.098277
N	1.374001	2.431378	0.090901	N	-0.028091	5.307968	-1.604203
N	-1.367891	2.433070	0.089752	C	-0.181912	4.814317	-2.925594
N	-0.018789	5.518230	1.442159	C	-1.179092	4.885766	-5.136695
C	0.716131	1.230791	0.097436	H	-1.858113	5.357297	-5.838697
C	-0.713729	1.232520	0.096969	C	-0.462430	3.752021	-5.513776
C	-2.743319	2.415259	0.097402	H	-0.569666	3.344068	-6.512152
C	-3.469582	3.621105	0.103183	C	0.386287	3.142720	-4.590632
H	-2.921787	4.557455	0.105970	H	0.951237	2.259829	-4.868201
C	-4.853967	3.623240	0.108974	Mg	3.471864	-2.004482	0.017433
H	-5.391652	4.564125	0.113977	N	4.788322	-2.742843	1.442159
C	-5.557479	2.410924	0.109960	C	6.299622	-3.721624	-0.213641
H	-6.641113	2.410233	0.115603	H	7.192268	-4.329212	-0.288434
C	-4.868387	1.209779	0.105054	C	4.597504	-2.464943	2.820262
H	-5.411146	0.270380	0.109449	C	5.420301	-1.826490	5.012364
C	-3.460954	1.178587	0.098277	H	6.250039	-1.543129	5.650707
C	0.073210	7.316445	-0.213641	C	4.129716	-1.889840	5.533048
H	0.153074	8.393293	-0.288434	H	3.949787	-1.668226	6.578548
C	-0.164048	5.214027	2.820262	C	3.071094	-2.229496	4.692224
C	-1.128364	5.607363	5.012364	H	2.060704	-2.281532	5.082151
H	-1.788631	6.184257	5.650707	N	4.610881	-2.629657	-1.604203
				C	4.260277	-2.249618	-2.925594
				C	4.820743	-1.421759	-5.136695
				H	5.568612	-1.069476	-5.838697
				C	3.480560	-1.475535	-5.513776
				H	3.180881	-1.178688	-6.512152

C	2.528532	-1.905895	-4.590632
H	1.481451	-1.953709	-4.868201
Mg	-3.471864	-2.004482	0.017433
N	-4.769533	-2.775387	1.442159
C	-6.372832	-3.594821	-0.213641
H	-7.345341	-4.064080	-0.288434
C	-4.433455	-2.749083	2.820262
C	-4.291937	-3.780873	5.012364
H	-4.461408	-4.641129	5.650707
C	-3.701507	-2.631519	5.533048
H	-3.419619	-2.586503	6.578548
C	-3.466347	-1.544898	4.692224
H	-3.006217	-0.643856	5.082151
N	-4.582790	-2.678312	-1.604203
C	-4.078365	-2.564699	-2.925594
C	-3.641651	-3.464007	-5.136695
H	-3.710499	-4.287822	-5.838697
C	-3.018131	-2.276486	-5.513776
H	-2.611214	-2.165379	-6.512152
C	-2.914819	-1.236825	-4.590632
H	-2.432688	-0.306119	-4.868201
C	-5.899903	-3.371290	1.083743
H	-6.553721	-3.715659	1.887735
C	-5.743729	-3.293669	-1.427485
H	-6.290208	-3.587986	-2.326085
C	-4.649313	-3.846080	3.668788
H	-5.066572	-4.761796	3.266377
C	-3.824994	-1.601433	3.349674
H	-3.656634	-0.744642	2.706633
C	-1.006147	5.949463	3.668788
H	-1.590551	6.768678	3.266377
C	0.525615	4.113258	3.349674
H	1.183438	3.539059	2.706633
C	3.299378	-2.511825	3.349674
H	2.473196	-2.794417	2.706633
C	5.655459	-2.103383	3.668788
H	6.657123	-2.006882	3.266377
C	5.210334	-1.797699	-3.854465
H	6.249383	-1.709845	-3.559012
C	2.911622	-2.286267	-3.308758
H	2.168512	-2.637696	-2.601924
C	0.524154	3.664672	-3.308758
H	1.200056	3.196834	-2.601924
C	-1.048314	5.411131	-3.854465
H	-1.643922	6.267047	-3.559012
C	-4.162020	-3.613432	-3.854465
H	-4.605461	-4.557202	-3.559012
C	-3.435776	-1.378405	-3.308758
H	-3.368568	-0.559138	-2.601924
C	0.030328	6.795111	1.083743
H	0.059006	7.533519	1.887735
C	0.019463	6.621050	-1.427485
H	0.037817	7.241473	-2.326085

C	5.869575	-3.423821	1.083743
H	6.494716	-3.817860	1.887735
C	5.724266	-3.327381	-1.427485
H	6.252391	-3.653487	-2.326085

### HAN

E = -1250.60123760 (6-311G\*\*)

NIMAG = 0

C	0.718337	1.268023	0.000000
C	-0.718337	1.268023	0.000000
C	1.457308	-0.011914	0.000000
C	0.738971	-1.256109	0.000000
C	-0.738971	-1.256109	0.000000
C	-1.457308	-0.011914	0.000000
N	1.368654	-2.416229	0.000000
C	2.718068	-2.395928	0.000000
C	3.433969	-1.155952	0.000000
N	2.776843	0.022825	0.000000
N	-1.368654	-2.416229	0.000000
C	-2.718068	-2.395928	0.000000
C	-3.433969	-1.155952	0.000000
N	-2.776843	0.022825	0.000000
N	-1.408188	2.393404	0.000000
N	1.408188	2.393404	0.000000
C	0.715901	3.551880	0.000000
C	-0.715901	3.551880	0.000000
C	-3.441174	-3.617628	0.000000
C	-4.853545	-1.171330	0.000000
C	-1.412371	4.788958	0.000000
C	1.412371	4.788958	0.000000
C	4.853545	-1.171330	0.000000
C	3.441174	-3.617628	0.000000
C	4.812776	-3.598818	0.000000
C	5.523056	-2.368577	0.000000
C	-0.710280	5.967395	0.000000
C	0.710280	5.967395	0.000000
C	-4.812776	-3.598818	0.000000
C	-5.523056	-2.368577	0.000000
H	-2.874145	-4.540489	0.000000
H	-5.369251	-0.218838	0.000000
H	-2.495106	4.759327	0.000000
H	2.495106	4.759327	0.000000
H	5.369251	-0.218838	0.000000
H	2.874145	-4.540489	0.000000
H	-5.367339	-4.530295	0.000000
H	-6.607020	-2.383104	0.000000
H	5.367339	-4.530295	0.000000
H	6.607020	-2.383104	0.000000
H	1.239681	6.913399	0.000000
H	-1.239681	6.913399	0.000000