

Supplementary Information

The Behavior of a Paramagnetic System in Electric and Magnetic Fields as Exemplified by Revisiting $\text{Li@B}_{10}\text{H}_{14}$

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Table S1. Dipole moments, polarizability and first hyperpolarizability of Li@B₁₀H₁₄ (conformer A) evaluated by the MP2 and selected DFT methods using different basis sets. The orientation of the molecule is shown in Figure 1. All values are in a.u.

Method/basis set	μ_0	$\bar{\alpha}$	β_0	β_y	β_z	μ_y	μ_z	α_{xx}	α_{yy}	α_{zz}	β_{yxx}	β_{yyy}	β_{zxx}	β_{zyy}	β_{zzy}	β_{zzz}
MP2/FC/6-31+G(d)	2.562	140.7	1027	-108	-1021	1.232	2.247	135.5	145.4	141.1	-16	-79	-79	67	-85	-1690
MP2/FC/6-31++G(d,p)	2.570	140.7	970	-93	-966	1.233	2.255	136.2	145.2	140.8	-18	-68	-52	45	-69	-1603
MP2/FC/6-311+G(d)	2.555	142.1	916	-73	-913	1.228	2.241	137.4	146.9	142.1	-17	-63	-63	62	-41	-1521
MP2/FC/6-311++G(d,p)	2.555	142.0	863	-74	-860	1.226	2.242	137.6	147.0	141.3	-19	-64	-52	57	-41	-1437
MP2/FC/6-311++G(2d,p)	2.554	142.4	836	-75	-833	1.225	2.241	138.1	147.5	141.5	-19	-63	-51	59	-42	-1396
MP2/FC/aug-cc-pVDZ	2.548	143.9	867	-76	-864	1.223	2.235	139.4	148.8	143.4	-21	-66	-56	57	-40	-1441
MP2/full/aug-cc-pVDZ	2.541	143.9	869	-75	-866	1.221	2.228	139.4	148.8	143.4	-21	-66	-56	57	-39	-1444
CAM-B3LYP/6-31+G(d)	2.524	137.3	655	-87	-649	1.225	2.207	134.0	143.5	134.5	-13	-60	-57	57	-71	-1082
CAM-B3LYP/6-31++G(d,p)	2.508	138.6	630	-82	-625	1.223	2.190	135.5	144.6	135.6	-15	-56	-38	44	-65	-1048
CAM-B3LYP/6-311++G(d,p)	2.503	139.3	560	-68	-556	1.219	2.186	136.4	145.7	135.7	-15	-51	-39	50	-47	-938
CAM-B3LYP/6-311++G(2d,p)	2.499	139.5	554	-70	-550	1.219	2.182	136.6	145.9	135.8	-16	-51	-39	50	-49	-928
CAM-B3LYP/ 6-311++G(3df,3pd)	2.498	139.9	540	-68	-536	1.217	2.181	137.1	146.4	136.4	-17	-51	-40	47	-46	-901
B3LYP/6-31+G(d)	2.499	141.7	2011	-255	-1995	1.212	2.185	135.7	145.9	143.5	-20	-95	-98	-4	-310	-3223
B3LYP/6-31++G(d,p)	2.483	142.9	1919	-237	-1905	1.209	2.169	137.3	147.1	144.4	-23	-91	-78	-17	-281	-3080
B3LYP/6-311++G(d,p)	2.482	143.2	1645	-183	-1635	1.207	2.169	138.1	148.0	143.5	-21	-77	-74	11	-207	-2662
B3LYP/6-311++G(2d,p)	2.478	143.4	1621	-184	-1611	1.207	2.165	138.3	148.2	143.6	-22	-77	-73	11	-209	-2622
BHandHLYP/6-31+G(d)	2.558	136.0	867	-104	-861	1.233	2.241	132.4	141.6	134.1	-14	-63	-65	55	-97	-1424
BHandHLYP/6-31++G(d,p)	2.540	137.3	835	-96	-829	1.230	2.222	134.0	142.7	135.2	-16	-57	-46	42	-88	-1379
BHandHLYP/6-311++G(d,p)	2.529	138.0	741	-77	-737	1.226	2.212	134.9	143.9	135.3	-16	-52	-47	52	-60	-1234
BHandHLYP/6-311++G(2d,p)	2.526	138.2	731	-79	-727	1.226	2.208	135.1	144.0	135.5	-16	-53	-46	53	-62	-1217

Table S2. Dipole moments, polarizability and first hyperpolarizability of Li@B₁₀H₁₄ (conformer **B**) evaluated by the MP2 and selected DFT methods using different basis sets. The orientation of the molecule is shown in Figure 1. All values are in a.u.

Method/basis set	μ_0	$\bar{\alpha}$	β_0	β_z	μ_z	α_{xx}	α_{yy}	α_{zz}	β_{zxx}	β_{zyy}	β_{zzz}
MP2/FC/6-31+G(d)	3.610	187.3	20704	-20704	3.610	147.0	154.1	260.9	-2076	-1666	-30765
MP2/FC/6-31++G(d,p)	3.649	180.8	14005	-14005	3.649	146.5	153.7	242.3	-1763	-1448	-20131
MP2/FC/6-311+G(d)	3.676	181.9	17331	-17331	3.676	147.9	155.0	242.7	-1890	-1475	-25520
MP2/FC/6-311++G(d,p)	3.732	174.7	10653	-10653	3.732	147.1	154.3	222.8	-1498	-1177	-15080
MP2/FC/6-311++G(2d,p)	3.753	172.6	8578	-8578	3.753	146.9	154.6	216.2	-1342	-1083	-11871
MP2/FC/aug-cc-pVDZ	3.722	174.9	8411	-8411	3.722	148.6	156.1	220.1	-1389	-1117	-11512
MP2/full/aug-cc-pVDZ	3.716	175.3	8727	-8727	3.716	148.6	156.1	221.2	-1407	-1126	-12012
CAM-B3LYP/6-31+G(d)	3.869	165.6	12117	-12117	3.869	142.4	150.0	204.2	-1155	-1012	-18028
CAM-B3LYP/6-31++G(d,p)	3.865	166.2	11718	-11718	3.865	143.4	151.3	203.8	-1119	-1024	-17387
CAM-B3LYP/6-311++G(2d,p)	3.913	163.9	10289	-10289	3.913	143.9	152.1	195.9	-1002	-926	-15221
CAM-B3LYP/6-311++G(3df,3pd)	3.911	164.0	10075	-10075	3.911	144.2	152.4	195.4	-974	-913	-14905
B3LYP/6-31+G(d)	3.592	186.3	20258	-20258	3.592	147.5	154.7	256.8	-2012	-1636	-30115
B3LYP/6-31++G(d,p)	3.594	186.2	19606	-19606	3.594	148.3	156.0	254.3	-1961	-1651	-29064
B3LYP/6-311++G(d,p)	3.660	182.7	18877	-18877	3.660	148.4	156.3	243.5	-1823	-1543	-28095
B3LYP/6-311++G(2d,p)	3.664	182.8	18922	-18922	3.664	148.4	156.4	243.6	-1812	-1543	-28182
BHandHLYP/6-31+G(d)	3.804	169.8	15476	-15476	3.804	141.5	149.1	218.9	-1404	-1231	-23158
BHandHLYP/6-31++G(d,p)	3.800	170.6	15132	-15132	3.800	142.5	150.4	218.8	-1378	-1255	-22588
BHandHLYP/6-311++G(d,p)	3.848	168.3	13795	-13795	3.848	143.1	151.1	210.6	-1283	-1166	-20543
BHandHLYP/6-311++G(2d,p)	3.851	168.3	13729	-13729	3.851	143.1	151.2	210.5	-1269	-1161	-20452

Table S3. Cartesian coordinates of Li@B₁₀H₁₄ conformers A-F (optimized at the UMP2/6-31+G(d) level of theory; given in Å)

Conformer A

B	2.305493693	-0.902979850	-1.387449898
B	1.441021978	-2.386253005	-0.926687550
B	0.569151110	-0.907316972	-1.387449898
B	1.433628691	0.573607713	-0.948354120
B	2.879319018	-1.837200247	0.000000000
B	0.000000000	-1.844392353	0.000000000
B	0.000000000	0.000000000	0.000000000
B	2.870105046	0.007169090	0.000000000
H	2.973501220	-0.920372120	-2.400098548
H	1.443403672	-3.339751021	-1.677047099
H	-0.098761196	-0.928046169	-2.400098548
H	1.431297759	1.506783422	-1.690490063
H	3.910826463	-2.435407891	-0.024502455
H	-1.028506128	-2.447745600	-0.024502455
H	-1.039460627	0.583857835	-0.005047321
H	3.906635943	0.596212440	-0.005047321
B	1.432963374	0.839963721	0.754150657
B	1.441793354	-2.695069325	0.754972811
H	1.430214966	1.940273596	1.206304909
H	0.505839353	0.092569921	1.273167518
H	2.363809557	0.097210851	1.273167518
H	2.377162927	-1.959896664	1.274116667
H	0.502762775	-1.964578634	1.274116667
H	1.444573568	-3.808112309	1.175638903
Li	1.440120491	-2.025347789	-3.151756828

Conformer B

B	-0.870396000	0.000000000	-1.288229000
B	0.000000000	1.480102000	-0.817533000
B	0.870396000	0.000000000	-1.288229000
B	0.000000000	-1.480102000	-0.817533000
B	-1.443578000	0.930853000	0.083399000
B	1.443578000	0.930853000	0.083399000
B	1.443578000	-0.930853000	0.083399000
B	-1.443578000	-0.930853000	0.083399000
H	-1.577526000	0.000000000	-2.248554000
H	0.000000000	2.446205000	-1.514118000
H	1.577526000	0.000000000	-2.248554000
H	0.000000000	-2.446205000	-1.514118000
H	-2.472864000	1.531275000	0.121830000
H	2.472864000	1.531275000	0.121830000
H	2.472864000	-1.531275000	0.121830000
H	-2.472864000	-1.531275000	0.121830000
B	0.000000000	-1.737422000	0.913626000
B	0.000000000	1.737422000	0.913626000
H	0.000000000	-2.836812000	1.372468000
H	0.977497000	-1.013301000	1.391515000
H	-0.977497000	-1.013301000	1.391515000
H	-0.977497000	1.013301000	1.391515000
H	0.977497000	1.013301000	1.391515000
H	0.000000000	2.836812000	1.372468000
Li	0.000000000	0.000000000	2.993465000

Conformer C

B	-0.872945000	1.478089800	-0.457175460
B	0.000000000	2.960244787	0.000000000
B	0.872945000	1.478089800	-0.457175460
B	0.000000000	0.000000000	0.000000000
B	-1.441197000	2.409889651	0.911534290
B	1.441197000	2.409889651	0.911534290
B	1.426806000	0.549276363	0.941827490
B	-1.426806000	0.549276363	0.941827490
H	-1.584268000	1.489715011	-1.414880861
H	0.000000000	3.933426366	-0.688397272
H	1.584268000	1.489715011	-1.414880861
H	0.000000000	-0.947318073	-0.721935596
H	-2.468573000	3.015882519	0.959434669
H	2.468573000	3.015882519	0.959434669
H	2.466619000	-0.034843857	0.966556348
H	-2.466619000	-0.034843857	0.966556348
B	0.000000000	-0.259074271	1.713767706
B	0.000000000	3.181890577	1.729990893
H	0.000000000	-1.335797992	2.220454570
H	0.951364000	0.488060216	2.216946344
H	-0.951364000	0.488060216	2.216946344
H	-0.961006000	2.459001432	2.224784668
H	0.961006000	2.459001432	2.224784668
H	0.000000000	4.330080671	2.121147634
Li	0.000000000	3.616247654	3.948271217

Conformer D

B	0.873232595	1.464843299	-0.485841573
B	0.000000000	0.000000000	0.000000000
B	-0.870612212	1.452386363	-0.477296778
B	0.000000000	2.922328566	0.000000000
B	1.422645196	0.556959232	0.941914684
B	-1.445606654	0.504767335	0.916927176
B	-1.426059667	2.337460517	0.952917900
B	1.438240917	2.366889091	0.940328061
H	1.567720949	1.434746329	-1.456837963
H	0.014876322	-0.965908939	-0.735708531
H	-1.564233818	1.428028431	-1.447346878
H	-0.009152268	3.876143867	-0.713488670
H	2.461703106	-0.070830090	0.957495942
H	-2.462047686	-0.118332519	0.894971909
H	-2.462435203	2.927034796	0.970696964
H	2.476525829	2.954566073	0.936928503
B	0.000000000	3.180005827	1.710179891
B	-0.000196909	-0.305490515	1.707282076
H	-0.016643705	4.276127164	2.172496410
H	-0.918699584	2.419066424	2.226126255
H	0.954413593	2.472132505	2.227002370
H	0.916746127	0.427216867	2.241863905
H	-0.961887196	0.348284907	2.235284810
H	0.075144377	-1.450705986	2.085374141
Li	1.383085244	-1.671625296	0.380560969

Conformer E

B	-0.876496354	1.483670000	-0.461644542
B	0.000000000	0.000000000	0.000000000
B	0.848919710	1.483670000	-0.464392497
B	0.000000000	2.967340000	0.000000000
B	-1.422153254	0.558924000	0.945791778
B	1.399185735	0.574665000	0.965518485
B	1.399185735	2.392675000	0.965518485
B	-1.422153253	2.408416000	0.945791778
H	-1.570282804	1.483670000	-1.431766580
H	0.030279908	-0.945997000	-0.724626714
H	1.553275735	1.483670000	-1.452549246
H	0.030279908	3.913337000	-0.724626714
H	-2.456183936	-0.033829000	0.957443729
H	2.454078544	-0.027698000	0.925918409
H	2.454078545	2.995038000	0.925918409
H	-2.456183936	3.001169000	0.957443729
B	0.000000000	3.255778000	1.709371032
B	0.000000000	-0.288438000	1.709371032
H	0.009764437	4.366676000	2.135135216
H	0.941187050	2.533845000	2.255911530
H	-0.919084482	2.508223000	2.229828293
H	-0.919084482	0.459117000	2.229828293
H	0.941187050	0.433495000	2.255911530
H	0.009764437	-1.399336000	2.135135216
Li	3.118163951	1.483670000	-0.153734650

Conformer F

B	-0.873285053	1.479082391	-0.479397746
B	0.000000000	0.000000000	0.000000000
B	0.860857264	1.461081228	-0.453415804
B	0.000000000	2.944634283	0.000000000
B	-1.434552899	0.582520398	0.932275527
B	1.427183409	0.571347319	0.966483104
B	1.419118176	2.384571181	0.956996685
B	-1.433857276	2.426109072	0.917363781
H	-1.548003992	1.497475460	-1.463542008
H	0.010365383	-0.948132289	-0.721311195
H	1.562391427	1.471659257	-1.445915913
H	0.037746650	3.899936115	-0.746933220
H	-2.473170499	-0.002717267	0.935664463
H	2.466558364	-0.015557204	0.968770131
H	2.469290340	2.988735394	0.905388842
H	-2.455454712	3.039725563	0.900496900
B	0.000000000	3.275873586	1.693819015
B	-0.011918576	-0.254609823	1.709648131
H	0.011589568	4.404394350	2.074225566
H	0.939989778	2.567057419	2.241242471
H	-0.933782074	2.555231539	2.211779060
H	-0.946761977	0.497990528	2.208690406
H	0.916758408	0.474897728	2.243284825
H	-0.025336025	-1.351682640	2.169447857
Li	1.920064867	3.372209786	-1.059291458