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Singlet-Triplet Splittings and 1,2-Hydrogen Shift Barriers for Methylphenylborenide, Methylphenylcarbene, and Methylphenylnitrenium in the Gas Phase and Solution. What a Difference a Charge Makes

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1$^-$S

E(BPW91/cc-pVDZ) = -296.315 74 h
E(BPW91/aug-cc-pVDZ//BPW91/cc-pVDZ) = -296.344 05 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -24.6 kcal/mol (*n*-heptane) and -54.4 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

H	-2.335540	3.483004	0.000000
C	-2.011524	2.418721	0.000000
B	-0.446158	2.114654	0.000000
H	-2.483789	1.922604	0.888013
H	-2.483789	1.922604	-0.888013
C	0.000000	0.653978	0.000000
C	0.269863	-0.082498	-1.214217
C	0.269863	-0.082498	1.214217
C	0.745369	-1.395190	-1.210063
C	0.745369	-1.395190	1.210063
C	1.000776	-2.085662	0.000000
H	1.399874	-3.110873	0.000000
H	0.088836	0.414931	-2.182640
H	0.088836	0.414931	2.182640
H	0.919033	-1.905222	-2.174377
H	0.919033	-1.905222	2.174377

1⁻T

E(BPW91/cc-pVDZ) = -296.322 69 h
E(BPW91/aug-cc-pVDZ//BPW91/cc-pVDZ) = -296.347 40 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -23.8 kcal/mol (*n*-heptane) and -49.8 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

B	0.555530	2.049875	0.000000
C	0.000000	0.628352	0.000000
C	2.088353	2.513836	0.000000
H	2.654520	2.137543	0.890673
H	2.654520	2.137543	-0.890673
H	2.221834	3.618834	0.000000
C	-1.415000	0.329628	0.000000
C	0.846572	-0.549897	0.000000
C	-1.921924	-0.969218	0.000000
C	0.340081	-1.851500	0.000000
C	-1.055513	-2.095200	0.000000
H	-2.115090	1.182585	0.000000
H	1.940516	-0.409153	0.000000
H	-3.015083	-1.125181	0.000000
H	1.040033	-2.706510	0.000000
H	-1.454315	-3.121036	0.000000

1⁻‡

E(BPW91/cc-pVDZ) = -296.297 80 h
E(BPW91/aug-cc-pVDZ//BPW91/cc-pVDZ) = -296.325 04 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -24.7 kcal/mol (*n*-heptane) and -51.7 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

B	2.068415	0.062606	-0.628127
C	0.561250	0.048755	-0.298096
C	3.087926	-0.130370	0.464006
H	4.182774	-0.111176	0.283630
H	2.908444	1.065022	-0.123461
H	2.857702	-0.376780	1.539160
C	-0.239845	1.230488	-0.136301
C	-0.170065	-1.185734	-0.199829
C	-1.612883	1.184919	0.124245
C	-1.547763	-1.232898	0.039903
C	-2.299859	-0.048739	0.209181
H	0.257835	2.211611	-0.219605
H	0.386135	-2.131844	-0.310182
H	-2.169875	2.128837	0.257739
H	-2.051791	-2.212911	0.110475
H	-3.385867	-0.084319	0.384227

2S

E(BPW91/cc-pVDZ) = -309.518 15 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -5.4 kcal/mol (*n*-heptane) and -5.6 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -5.6 kcal/mol (*n*-heptane) and -5.9 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -5.8 kcal/mol (*n*-heptane) and -6.8 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

C	-1.894382	-0.627719	-0.375049
C	-0.517849	-0.271216	-0.150993
C	-2.913170	0.233950	0.255878
H	-3.850052	0.300190	-0.333973
H	-2.616776	1.234678	0.663926
H	-3.200755	-0.388401	1.143080
C	0.448774	-1.320389	-0.049234
C	-0.039484	1.078371	-0.131463
C	1.802379	-1.036569	0.136346
C	1.329705	1.351304	-0.049260
C	2.251067	0.300215	0.113066
H	0.083934	-2.355294	-0.100730
H	-0.754712	1.905297	-0.239344
H	2.525831	-1.855233	0.253991
H	1.686351	2.390563	-0.085426
H	3.323931	0.520514	0.202730

2T

E(BPW91/cc-pVDZ) = -309.529 90 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -4.7 kcal/mol (*n*-heptane) and -4.0 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -5.9 kcal/mol (*n*-heptane) and -6.5 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -6.0 kcal/mol (*n*-heptane) and -7.2 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

C	0.433231	1.894777	0.000000
C	0.000000	0.559498	0.000000
C	1.711809	2.619981	0.000000
H	2.328093	2.381759	0.898278
H	2.328093	2.381759	-0.898278
H	1.553381	3.717698	0.000000
C	-1.397580	0.230075	0.000000
C	0.936386	-0.533749	0.000000
C	-1.821708	-1.097910	0.000000
C	0.491306	-1.856357	0.000000
C	-0.886040	-2.153235	0.000000
H	-2.129067	1.049369	0.000000
H	2.013210	-0.316664	0.000000
H	-2.897843	-1.322004	0.000000
H	1.227162	-2.673382	0.000000
H	-1.227442	-3.197021	0.000000

2‡

E(BPW91/cc-pVDZ) = -309.506 78 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -5.4 kcal/mol (*n*-heptane) and -5.5 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -6.0 kcal/mol (*n*-heptane) and -6.8 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -6.6 kcal/mol (*n*-heptane) and -8.7 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

C	-1.949949	-0.458894	-0.458658
C	-0.529466	-0.213282	-0.198007
C	-2.868057	0.266291	0.336024
H	-3.947891	0.198467	0.107167
H	-2.679698	-0.940241	0.621950
H	-2.589636	1.048450	1.085353
C	0.373219	-1.300993	-0.062834
C	0.002615	1.104830	-0.180430
C	1.738994	-1.077994	0.143274
C	1.380084	1.320123	-0.037221
C	2.251470	0.232931	0.144548
H	-0.026146	-2.323473	-0.113102
H	-0.673433	1.961389	-0.316052
H	2.417590	-1.932383	0.275660
H	1.776475	2.345388	-0.052120
H	3.329272	0.404341	0.270968

3+S

E(BPW91/cc-pVDZ) = -325.972 08 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -27.5 kcal/mol (*n*-heptane) and -50.3 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -27.2 kcal/mol (*n*-heptane) and -49.8 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -27.2 kcal/mol (*n*-heptane) and -49.9 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

N	0.171125	1.867736	0.000000
C	0.000000	0.551840	0.000000
C	1.442263	2.494511	0.000000
H	1.442412	3.204099	0.862661
H	1.442412	3.204099	-0.862661
H	2.355547	1.869477	0.000000
C	-1.398754	0.139920	0.000000
C	1.038367	-0.470596	0.000000
C	-1.736370	-1.203741	0.000000
C	0.676244	-1.803570	0.000000
C	-0.701137	-2.168188	0.000000
H	-2.150334	0.940568	0.000000
H	2.097394	-0.185291	0.000000
H	-2.786292	-1.522188	0.000000
H	1.441953	-2.589902	0.000000
H	-0.964646	-3.236077	0.000000

3^{+}T

E(BPW91/cc-pVDZ) = -325.947 13 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -27.1 kcal/mol (*n*-heptane) and -49.8 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -27.2 kcal/mol (*n*-heptane) and -50.1 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -27.2 kcal/mol (*n*-heptane) and -50.3 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

N	0.298855	1.774250	0.000000
C	0.000000	0.493627	0.000000
C	1.243910	2.808753	0.000000
H	1.867359	2.776723	0.921762
H	1.867359	2.776723	-0.921762
H	0.706502	3.785603	0.000000
C	-1.386908	0.077822	0.000000
C	1.057380	-0.504389	0.000000
C	-1.685632	-1.274940	0.000000
C	0.704316	-1.843826	0.000000
C	-0.654025	-2.243718	0.000000
H	-2.168216	0.846742	0.000000
H	2.104296	-0.179085	0.000000
H	-2.736416	-1.592838	0.000000
H	1.499679	-2.601808	0.000000
H	-0.906795	-3.311782	0.000000

3^{+}‡

E(BPW91/cc-pVDZ) = -325.934 11 h
SM5.4/A NOPOL solvation free energy (DFT-ESP charges/DFT geometry)
= -28.5 kcal/mol (*n*-heptane) and -52.9 kcal/mol (acetonitrile)
SM5.4/A NOPOL solvation free energy (CM1A charges/AM1 geometry)
= -30.9 kcal/mol (*n*-heptane) and -57.8 kcal/mol (acetonitrile)
SM5.4/A solvation free energy (relaxed CM1A charges/SM5.4/A geometry)
= -32.0 kcal/mol (*n*-heptane) and -63.7 kcal/mol (acetonitrile)

BPW91/cc-pVDZ geometry:

N	-1.822529	-0.557460	-0.105780
C	-0.483079	-0.204799	-0.018329
C	-2.903466	0.303754	0.003786
H	-3.876245	-0.132439	-0.254658
H	-2.601432	-0.636317	0.953632
H	-2.811934	1.392460	0.099079
C	0.424985	-1.307788	-0.009299
C	0.011531	1.134179	-0.008867
C	1.799004	-1.074946	0.008529
C	1.384468	1.351471	0.002094
C	2.278593	0.250717	0.015765
H	0.014045	-2.317497	-0.028266
H	-0.668233	1.987048	-0.028079
H	2.497892	-1.911243	0.011485
H	1.777316	2.368529	-0.002143
H	3.354075	0.436156	0.027339