Supplementary Information

A Comprehensive Study of the Methyl Effect on the Solvolysis Rates of Bridgehead Derivatives

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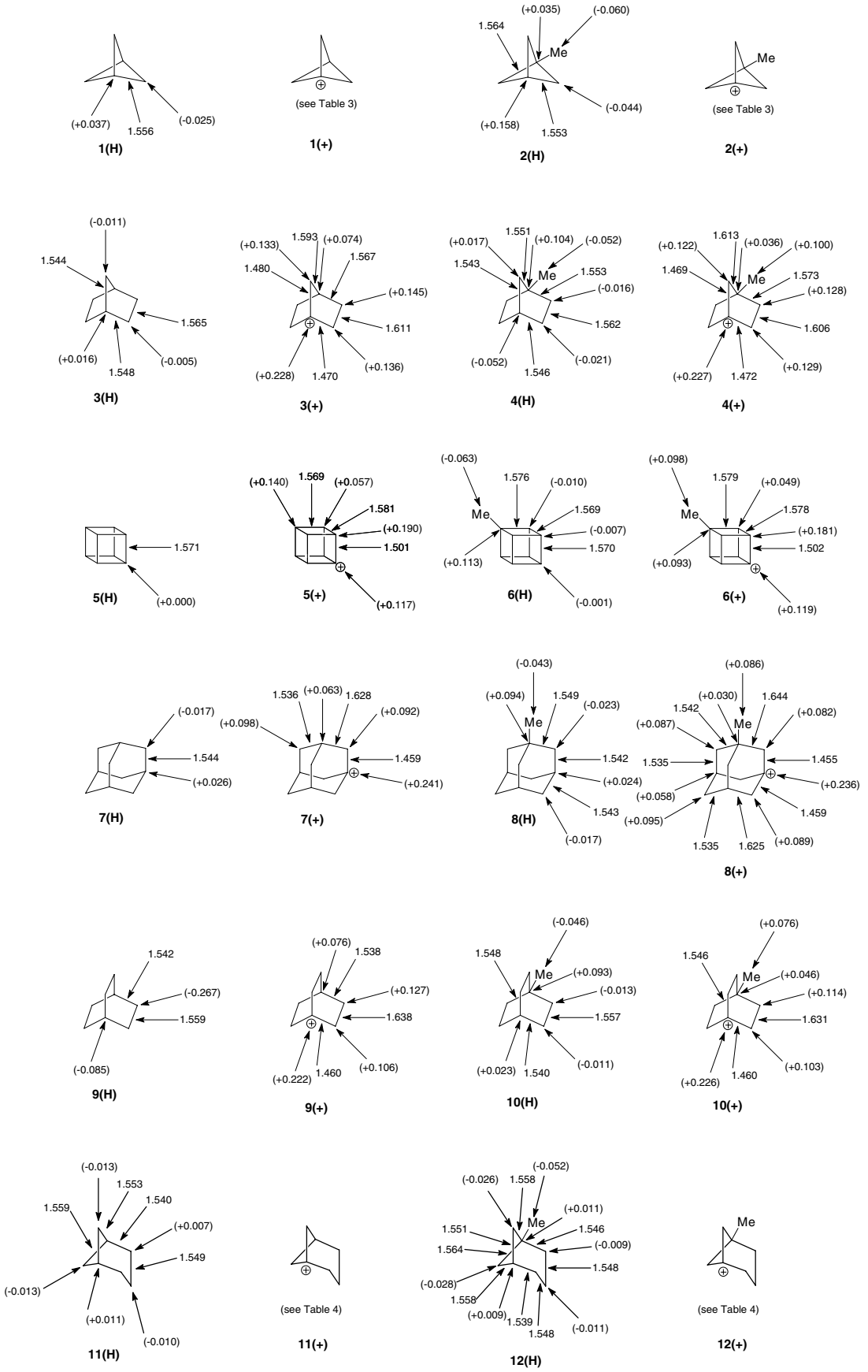


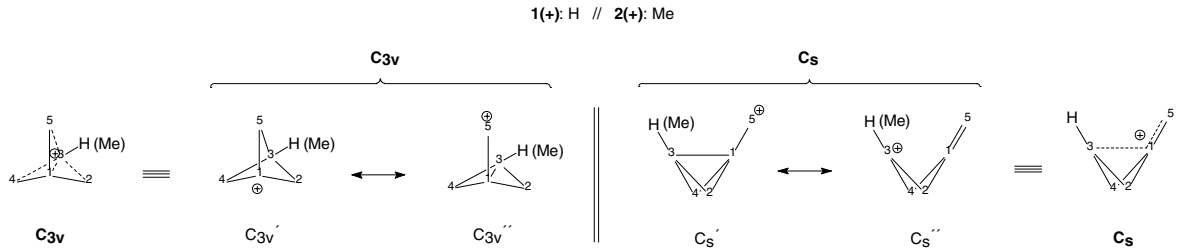
Figure 1. B3LYP/6-31G*-Computed Geometries (Lengths in Angstroms) and Atom Charges (Hydrogens Summed into Carbons) in a.u.

Table 1. B3LYP/6-31G*-, B3LYP/6-31+G**-, MP2(full)/6-31G*- and MP2(full)/6-311G**-Computed Total Energies (E) and Free Energies (G) (298 K, 1 atm) (all data in Hartrees).

Computed Structure	**B3LYP/6-31G***		**B3LYP/6-31+G**// B3LYP/6-31G***	**MP2(full)/6-31G***	**MP2(full)/6-311G****
	E	**G**	**E**	**E**	**E**
1(H)	-195.26054	-195.16929	-	-194.58233 [22]	-194.78406
1(+)	[a]	[a]	-	-193.70207 [22]	-193.88237
2(H)	-234.58140	-234.46439	-	-233.76212 [22]	-234.00682
2(+)	[a]	[a]	-	-232.88581 [22]	-233.10962
3(H)	-273.96849	-273.81954	-273.99140	-272.97591 [3]	-273.16434 [17a]
3(+)	-273.04078	-272.90554	-273.05838	-272.06593 [3]	-272.23517 [17a]
4(H)	-313.28523	-313.11038	-313.31182	-312.14813 [3]	-
4(+)	-312.36316	-312.20191	-312.38422	-311.24370 [3]	-
5(H)	-309.46037	-309.35440	-	-	-308.58061 [17a] [-308.47912 [b]]
5(+)	-308.54070	-398.44948	-	-	-307.66556 [17a] [-307.57142 [b]]
6(H)	-348.78166	-348.64978	-	-	-
6(+)	-347.86492	-347.74764	-	-	-
7(H)	-390.72542	-390.51152	-	-	-
7(+)	-389.83823	-389.63731	-	-	-
8(H)	-430.04159	-429.80170	-	-	-
8(+)	-429.15645	-428.92958	-	-	-
9(H)	-313.28991	-313.11356	-	-312.1477 [23]	-312.36649 [17a]
9(+)	-312.38879	-312.22501	-	-311.2642 [23]	-311.46450 [17a]
10(H)	-352.60594	-352.40420	-352.63564	-351.32259	-
10(+)	-351.70520	-351.51504	-351.72932	-350.43941	-
11(H)	-273.94298	-273.79480	-	-	-
11(+)	[c]	[c]	-	-	-
12(H)	-313.26104	-313.08700	-	-	-
12(+)	[c]	[c]	-	-	-

[a] Converges to a Cs structure. [b] Computed with the MP2/6-31G** method. [c] Converges to a C_1 structure.

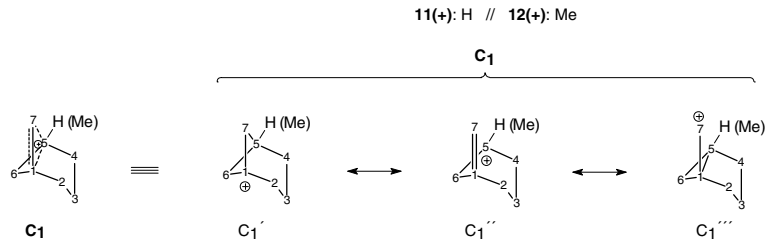
Table 2. B3LYP/6-31G*-, B3LYP/6-311G**- and MP2(full)/6-311G**-Computed Geometries for Cations **1(+)** and **2(+)** [Total Energies (E), in Hartrees, Lengths (R) in Angstroms], and Atom Charges (q) (Hydrogens Summed into Carbons) in a.u., and B3LYP/6-31G*-Computed Free Energies (G) (298 K, 1 atm) in Hartrees.



Optimised Geometry	Method	E	G	R(1,2) R(1,4)	R(2,3) R(3,4)	R(1,5)	R(3,5)	R(1,3)	q(1)	q(2) q(4)	q(3)	q(5)	q(Me)
1(+)[C_{3v}]	B3LYP/6-31G*	**converges to 1(+)[C_s]**	—	—	—	—	—	—	—	—	—	—	—
	B3LYP/6-311G**	-194.39530	—	1.469	1.609	1.469	1.609	1.535	+0.105	+0.251	+0.143	+0.251	—
	MP2(full)/6-31G*	-193.70207 [a]	—	1.472	1.598	1.472	1.598	1.525	+0.003	+0.216	+0.138	+0.216	—
	MP2(full)/6-311G**	-193.88237	—	1.468	1.592	1.468	1.592	1.529	+0.003	+0.310	+0.066	+0.310	—
1(+)[C_s]	B3LYP/6-31G*	-194.37219	-194.29649	1.550	1.464	1.353	2.776	1.642	+0.118	+0.167	+0.305	+0.242	—
	B3LYP/6-311G**	-194.41712	—	1.552	1.462	1.348	2.773	1.641	-0.172	+0.269	+0.255	+0.380	—
	MP2(full)/6-31G*	-193.71307 [b]	—	1.536	1.464	1.358	2.703	1.621	-0.061	+0.189	+0.002	+0.345	—
	MP2(full)/6-311G**	-193.89180	—	1.540	1.469	1.360	2.701	1.631	-0.306	+0.301	+0.239	+0.464	—
2(+)[C_{3v}]	B3LYP/6-31G*	**converges to 2(+)[C_s]**	—	—	—	—	—	—	—	—	—	—	—
	B3LYP/6-311G**	-233.73054	—	1.461	1.625	1.461	1.625	1.551	+0.073	+0.248	-0.175	+0.248	+0.350
	MP2(full)/6-31G*	-232.88521 [b]	—	1.461	1.603	1.461	1.603	1.539	+0.217	+0.190	-0.074	+0.190	+0.281
	MP2(full)/6-311G**	-233.10962	—	1.471	1.589	1.471	1.589	1.547	-0.040	+0.309	-0.262	+0.309	+0.369
2(+)[C_s]	B3LYP/6-31G*	-233.70709	-233.60550	1.543	1.475	1.347	2.876	1.722	+0.134	+0.129	+0.247	+0.072	+0.188
	B3LYP/6-311G**	-233.76244	—	1.544	1.473	1.341	2.887	1.730	-0.150	+0.266	-0.018	+0.314	+0.323
	MP2(full)/6-31G*	-232.90331	—	1.536	1.468	1.353	2.791	1.665	-0.054	+0.172	+0.216	+0.297	+0.199
	MP2(full)/6-311G**	-233.12505	—	1.540	1.472	1.354	2.797	1.670	-0.296	+0.312	-0.036	+0.405	+0.302

[a] Incorrectly described in lit. 22b as a **1(+)[C_s]**-like geometry. [b] Obtained geometry and corresponding E agree with previously reported data (see lit. 22b).

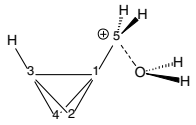
Table 3. B3LYP/6-31G*-Computed Geometries and Energies for Cations **11(+)** and **12(+)** [Total Energies (E) and Free Energies (G) (298 K, 1 atm) in Hartrees, Lengths (R) in Angstroms], and Atom Charges (q) (Hydrogens Summed into Carbons) in a.u.



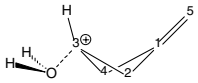
Optimised Geometry	E	G	R(1,2)	R(2,3)	R(3,4)	R(4,5)	R(5,6)	R(6,1)	R(1,7)	R(5,7)	R(1,5)
11(+)	-273.05643	-272.92314	1.515	1.553	1.545	1.495	1.446	1.564	1.359	2.595	1.855
12(+)	-312.38521	-312.22670	1.511	1.551	1.542	1.495	1.456	1.560	1.348	2.839	2.039

Optimised Geometry	q(1)	q(2)	q(3)	q(4)	q(5)	q(6)	q(7)	q(Me)
11(+)	+0.047	+0.112	+0.079	+0.157	+0.193	+0.174	+0.210	-
12(+)	+0.092	+0.100	+0.076	+0.134	+0.195	+0.112	+0.126	+0.165

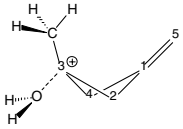
Table 4. MP2(full)/6-31G*- and B3LYP/6-311G**-Computed Water-Complexes of Cations **1(+)** and **2(+)** [Relative Total Energies (ΔE) in Hartrees, Lengths (R) in Angstroms and Atom Charges (q) (Hydrogens Summed into Carbons) in a.u.].



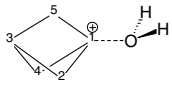
1(+)a.$H_2O[C_s]$



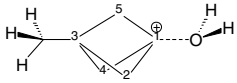
1(+)b.$H_2O[C_s]$



2(+)b.$H_2O[C_s]$



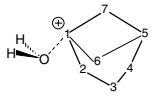
1(+).$H_2O[C_{3v}]$



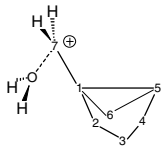
2(+).$H_2O[C_{3v}]$

Computed Structure	Method	E	E_{rel} (kcal/mol)	R(1,2) R(1,4)	R(1,3)	R(2,3) R(3,4)	R(1,5)	R(3,5)	R(C⁺,O)	q(1)	q(2) q(4)	q(3)	q(5)	q(Me)
1(+)a·$H_2O[C_s]$	MP2(Full)/6-31G*	-269.93152	10.3	1.518	1.602	1.479	1.370	2.517	1.614	-0.026	+0.150	+0.236	+0.454	—
	B3LYP/6-311G**	-270.88298	10.9	1.533	1.607	1.475	1.366	2.647	2.371	-0.147	-0.218	+0.193	+0.408	—
1(+)b·$H_2O[C_s]$	MP2(Full)/6-31G*	-269.94801	0.0	1.523	2.018	1.519	1.330	3.280	1.564	+0.055	+0.111	+0.347	+0.044	—
	B3LYP/6-311G**	-270.90034	0.0	1.531	2.056	1.526	1.322	3.333	1.594	-0.168	+0.206	-0.005	+0.160	—
1(+)·$H_2O[C_{3v}]$	MP2(Full)6-31G*	-269.93359	9.0	1.507	1.731	1.563	1.512	1.562	1.614	+0.262	+0.122	+0.118	+0.104	—
	B3LYP/6-311G**	-270.87257	17.4	1.509	1.721	1.577	1.514	1.575	1.691	+0.090	+0.178	+0.073	+0.172	—
2(+)b·$H_2O[C_s]$	MP2(Full)/6-31G*	-309.13335	0.0	1.522	2.043	1.526	1.330	3.316	1.591	+0.066	+0.110	+0.219	+0.032	+0.154
	B3LYP/6-311G**	-310.23736	0.0	1.529	2.081	1.534	1.322	3.369	1.653	-0.140	+0.222	-0.087	+0.148	+0.274
2(+)·$H_2O[C_{3v}]$	MP2(Full)6-31G*	-309.11559	11.4	1.503	1.740	1.570	1.508	1.570	1.618	+0.275	+0.111	+0.030	+0.102	+0.132
	B3LYP/6-311G**	-310.20600	19.7	1.504	1.733	1.586	1.733	1.587	1.694	+0.082	+0.179	-0.155	+0.171	+0.235

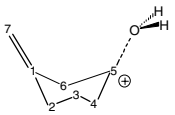
Table 5. B3LYP/6-31G*-Computed mono-Water-Complexes of Cations **11(+)** and **12(+)** [Relative Total Energies (ΔE) in Hartrees, Lengths (R) in Angstroms and Atom Charges (q) (Hydrogens Summed into Carbons) in a.u.].



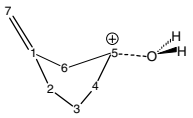
11(+).H$_2$O



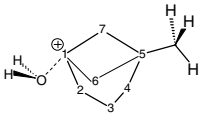
11(+)a.H$_2$O



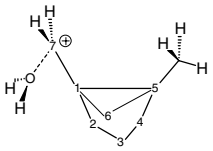
11(+)b.H$_2$O(a)



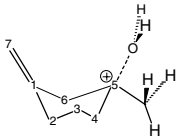
11(+)b.H$_2$O(pe)



12(+).H$_2$O



12(+)a.H$_2$O



12(+)b.H$_2$O(a)

Computed Structure	E	E_{rel} (kcal/mol)	R(1,2)	R(2,3)	R(3,4)	R(4,5)	R(5,6)	R(6,1)	R(1,7)	R(5,7)	R(1,5)	R(C*,O)
11(+)·H$_2$O	-349.48466	10.5	1.513	1.566	1.548	1.537	1.578	1.514	1.507	1.580	2.014	1.682
11(+)a·H$_2$O	-349.48173	12.3	1.540	1.548	1.546	1.523	1.519	1.518	1.371	2.680	1.511	2.428
11(+)b·H$_2$O(a)	-349.50133	0.0	1.512	1.548	1.542	1.516	1.528	1.518	1.345	3.425	2.444	1.591
11(+)b·H$_2$O(pe)	-349.48350	11.2	1.513	1.553	1.554	1.490	1.448	1.557	1.353	2.683	1.940	2.597
12(+)·H$_2$O	-388.80407	14.1	1.512	1.564	1.547	1.545	1.586	1.512	1.606	1.584	2.032	1.681
12(+)a·H$_2$O	-388.80636	12.7	1.513	1.550	1.541	1.502	1.452	1.559	1.353	2.749	1.961	2.749
12(+)b·H$_2$O(a)	-388.82662	0.0	1.511	1.545	1.542	1.525	1.533	1.517	1.344	2.482	2.482	1.630

Computed Structure	q(1)	q(2)	q(3)	q(4)	q(5)	q(6)	q(7)	q(Me)
11(+)·H$_2$O	+0.211	+0.049	+0.076	+0.099	+0.067	+0.087	+0.090	-
11(+)a·H$_2$O	+0.042	+0.053	+0.042	+0.091	+0.051	-0.011	+0.337	-
11(+)b·H$_2$O(a)	+0.145	+0.052	+0.057	+0.128	+0.255	+0.057	-0.025	-
11(+)b·H$_2$O(pe)	+0.078	+0.097	+0.066	+0.149	+0.262	+0.136	+0.149	-
12(+)·H$_2$O	+0.207	+0.047	+0.073	+0.077	+0.071	+0.071	+0.074	+0.061
12(+)a·H$_2$O	+0.065	+0.091	+0.066	+0.125	+0.168	+0.119	+0.191	+0.144
12(+)b·H$_2$O(a)	+0.136	+0.050	+0.045	+0.077	+0.209	+0.063	-0.018	+0.147