Supplementary information for
"Association mechanisms of unsaturated C2 hydrocarbons with their cations: Acetylene and ehthylene"

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Cartesian co-ordinates (Angstroms)

$[HCCH]_2^+$

Puckered cyclic cyclobutadiene cation CCSD(T)/cc-pVTZ

1	H	0.0000000000	1.8107499875	-0.6978009521
2	H	-2.1431366515	0.0000000000	0.1289555462
3	H	2.1431366515	0.0000000000	0.1289555462
4	H	0.0000000000	-1.8107499875	-0.6978009521
5	C	0.0000000000	0.9077362287	-0.0927468575
6	C	-1.0680655240	0.0000000000	0.2015922638
7	C	1.0680655240	0.0000000000	0.2015922638
8	C	0.0000000000	-0.9077362287	-0.0927468575

Bond Angles

1-5-6	129.8	1-5-7	129.8	1-5-8	146.1	2-6-5	136.9
2-6-7	176.1	2-6-8	136.9	3-7-5	136.9	3-7-6	176.1
3-7-8	136.9	4-8-5	146.1	4-8-6	129.8	4-8-7	129.8
5-6-7	41.5	5-6-8	78.6	5-7-6	41.7	5-7-8	78.6
5-8-6	50.6	5-8-7	50.6	6-5-7	96.4	6-5-8	50.6
6-7-8	41.7	6-8-7	96.4	7-5-8	50.6	7-6-8	41.7

Dihedral Angles

1-5-6-2	15.5	1-5-7-3	23.5	5-6-8-7	23.5	6-8-7-5	23.5
2-6-8-7	174.6						

Bridge CCSD(T)/cc-pVTZ

1	H	-1.2261721176	-1.6664480921	-0.2105285044
2	H	-1.2261721176	1.6664480921	-0.2105285044
3	H	0.4727843431	0.0000000000	1.6343641840
4	H	1.7223008510	0.0000000000	-1.3087994959
5	C	-0.9592281268	-0.6262251783	-0.1464208286
6	C	-0.9592281268	0.6262251783	-0.1464208286
7	C	0.4301656774	0.0000000000	0.5533377730
8	C	1.4966696174	0.0000000000	-0.2492537949

Bond Angles

1-5-6	165.2	1-5-7	126.2	2-6-5	165.2	2-6-7	126.2

3-7-5 116.7 3-7-6 116.7 3-7-8 124.7 4-8-7 138.9
5-6-7 68.1 5-7-6 43.8 5-7-8 114.2 6-5-7 68.0
6-7-8 114.2

Dihedral Angles
1-5-7-3 74.2 2-6-7-3 74.2 4-8-7-5 24.2 1-5-7-8 83.7 2-6-7-8 83.7

Linear connectivity isomer CCSD(T)/cc-pVTZ

1	H	-2.0791184442	-1.1256742607	0.6960880244
2	H	-0.7252632754	1.1118053924	-1.2358360182
3	H	0.7252946450	1.1122157825	1.2354271547
4	H	2.0790167353	-1.1259932266	-0.6957720014
5	C	-1.5484958586	-0.3936917376	0.1142914176
6	C	-0.7210651414	0.3984446378	-0.4239946394
7	C	0.7210863270	0.3985842136	0.4238248285
8	C	1.5484640117	-0.3937818020	-0.1142007674

Bond angles

1-5-6 168.2 2-6-5 136.8 2-6-7 112.5 3-7-6 112.5
3-7-8 136.8 4-8-7 168.2 5-6-7 110.3 6-7-8 110.3

Dihedral Angles
4-8-7-6 8.0 8-7-6-5 96.2 7-6-5-1 8.0 2-6-7-3 88.7

$[H2CCH2]_2^+$ Ethylene + Ethylene cation

Puckered cyclic cyclobutyl cation

1	C	-0.8068632968	-0.1822103237	0.1351697873
2	C	0.6964440866	0.0011924935	-0.1070820723
3	C	-0.6429454939	1.4247974402	0.1266979750
4	C	0.8604596629	1.6185937637	-0.1531289831
5	H	-1.3885697218	-0.5690635058	-0.6943118981
6	H	-1.1033140581	-0.5906464069	1.0951159833
7	H	0.9811959085	-0.3377327173	-1.1039903588
8	H	1.2786265886	-0.3190258750	0.7567537779
9	H	-1.2176699681	1.7987272895	-0.7234499427
10	H	-0.8727869374	1.7745811142	1.1342424675
11	H	1.1263781818	2.0057630472	-1.1309389277
12	H	1.4590450472	2.0250236804	0.6549221917

Bond Angles
1-2-3 53.1 1-2-4 102.8 1-2-7 111.2 1-2-8 111.3
1- 3- 2 49.4 1- 3- 4 103.0 1- 3- 9 106.9 1- 3-10 107.0

2-1-3 77.3 2-1-5 116.5 2-1-6 116.9 2-3-4 53.5
2- 3- 9 120.8 2- 3-10 119.0 2- 4- 3 76.7 2- 4-11 113.9
2- 4-12 114.0 3- 1- 5 113.9 3- 1- 6 114.0 3- 2- 4 49.6
3- 2- 7 120.7 3- 2- 8 118.8 3- 4-11 116.5 3- 4-12 116.7
4- 2- 7 104.8 4- 2- 8 105.1 4- 3- 9 109.2 4- 3-10 109.4
5- 1- 6 113.3 7- 2- 8 119.5 9- 3-10 119.8 11- 4-12 113.7

Dihedral Angles
1-2-4-3 1.3 2-1-3-4 1.4 6-1-2-4 112.1 6-1-2-7 136.1

Bridge CCSD(T)/cc-pVTZ

1	C	1.5495004709	0.1055478229	0.5187740667
2	C	0.5029424884	0.5267195033	-0.3872049659
3	C	-0.9175012196	-0.8404340326	-0.4680142430
4	C	-1.2679556574	0.1669246864	0.4051024586
5	H	1.7027156306	0.6238981388	1.4548489796
6	H	2.1770682645	-0.7395410861	0.2730538571
7	H	0.1708551457	1.5622353130	-0.3138583470
8	H	0.6222335154	0.2647499167	-1.4384442251
9	H	-0.3754583709	-1.7127356034	-0.1232328488
10	H	-1.2944372163	-0.8477137166	-1.4835583101
11	H	-1.0091160960	0.1086490313	1.4554357970
12	H	-1.9259789553	0.9676010259	0.0898467805

Bond angles

1-2-3 110.1 1-2-4 110.1 1-2-7 117.0 1-2-8 117.0
2-1-5 120.3 2-1-6 120.3 2-3-4 69.5 2-3-9 100.6
2- 3-10 107.0 2- 4- 3 69.5 2- 4-11 100.6 2- 4-12 107.0
3- 2- 4 40.8 3- 2- 7 116.2 3- 2- 8 82.6 3- 4-11 120.9
3- 4-12 120.6 4- 2- 7 82.6 4- 2- 8 116.2 4- 3- 9 120.9
4- 3-10 120.6 5- 1- 6 119.3 7- 2- 8 109.0 9- 3-10 117.8
11- 4-12 117.8

Dihedral Angles
1-2-3-4 97.9 1-2-3-10 145.1 5-1-2-7 111.4 6-1-2-7 24.2

C2 CCSD(T)/cc-pVTZ

1	C	1.8575052783	-0.2390034750	0.0000000000
2	C	-1.8575052783	0.2390034750	0.0000000000
3	C	0.5638949692	0.5164940706	0.0000000000
4	C	-0.5638949692	-0.5164940706	0.0000000000
5	H	2.3664881054	-0.4665274206	0.9314354471
6	H	2.3664881054	-0.4665274206	-0.9314354471
7	H	-2.3664881054	0.4665274206	0.9314354471

8	H	-2.3664881054	0.4665274206	-0.9314354471
9	H	0.4986423893	1.1439226900	0.8963954755
10	H	0.4986423893	1.1439226900	-0.8963954755
11	H	-0.4986423893	-1.1439226900	0.8963954755
12	H	-0.4986423893	-1.1439226900	-0.8963954755

Bond Angles

1- 3- 4 109.1 1- 3- 9 110.5 1- 3-10 110.5 2- 4- 3 109.1
2- 4-11 110.5 2- 4-12 110.5 3- 1- 5 120.6 3- 1- 6 120.6
3- 4-11 108.8 3- 4-12 108.8 4- 2- 7 120.6 4- 2- 8 120.6
4- 3- 9 108.8 4- 3-10 108.8 5- 1- 6 118.4 7- 2- 8 118.4
9- 3-10 108.7 11- 4-12 108.7

Dihedral Angles

1-3-4-2 180.0 8-2-4-3 93.7 9-3-1-5 25.9 5-1-3-10 146.7

$[HCCH\text{-}H2CCH2]_2^+$ Acetylene + Ethylene cation

Boat Cyclobutene cation CCSD(T)/cc-pVTZ

1	C	-0.6240947133	-0.0342318645	0.0432251091
2	C	0.7869971272	-0.0125795010	-0.1775879625
3	C	-0.7089548534	1.4538333101	0.1069932208
4	C	0.8426791063	1.4776408522	-0.1357742962
5	H	-1.3433803660	-0.8423454732	0.1287625695
6	H	1.5218983496	-0.7983786587	-0.3196301441
7	H	-1.3394558494	1.8920163261	-0.6742246610
9	H	-1.0655426725	1.8328869038	1.0708382455
0	H	1.1911127226	1.9308931699	-1.0701136781
10	H	1.4650271494	1.8716629361	0.6749455962

Bond angles

1-2-3 44.8 1-2-4 92.7 1-2-6 132.7 1-3-2 42.4
1-3-4 87.2 1-3-7 113.62 1-3-8 113.6 1-4-2 42.4
1- 4- 3 44.8 1- 4- 9 126.0 1- 4-10 126.0 2- 1- 3 92.7
2-1-4 44.8 2-1-5 132.7 2-3-4 44.8 2-3-7 126.0
2- 3- 8 126.0 2- 4- 3 87.2 2- 4- 9 113.6 2- 4-10 113.6
3-1-4 47.9 3-1-5 134.5 3-2-4 47.9 3-2-6 177.5
3- 4- 9 116.8 3- 4-10 116.8 4- 1- 5 177.5 4- 2- 6 134.5
4- 3- 7 116.8 4- 3- 8 116.8 7- 3- 8 107.5 9- 4-10 107.5

Dihedral Angles

5-1-2-4 180.0 5-1-3-8 61.7 1-3-4-10 115.2 1-2-4-3 0.0

Bridge CCSD(T)/cc-pVTZ

1	C	-0.7546475683	-0.0005148561	0.5926092443
2	C	0.2218620443	-0.0006077823	-0.3164595151
3	C	1.6506725071	0.7088089131	0.1687357839
4	C	1.6501012063	-0.7114351341	0.1686548563
5	H	-1.8364101681	-0.0003100111	0.6551890240
6	H	0.0431572702	-0.0004289834	-1.3877093362
7	H	1.5405965340	1.2503507045	1.0982799214
8	H	2.0231342022	1.2561821092	-0.6886223982
9	H	1.5395253925	-1.2530077728	1.0981223096
10	H	2.0220085803	-1.2590371866	-0.6887998895

Bond angles

1-2-3 115.3 1-2-4 115.3 1-2-6 123.4 2-1-5 140.3
2-3-4 64.7 2-3-7 112.0 2-3-8 106.2 2-4-3 64.7
2- 4- 9 112.0 2- 4-10 106.2 3- 2- 4 50.4 3- 2- 6 115.3
3- 4- 9 120.0 3- 4-10 120.3 4- 2- 6 115.3 4- 3- 7 120.0
4- 3- 8 120.3 7- 3- 8 117.5 9- 4-10 117.5

Dihedral Angles

5-1-2-4 151.9 1-2-3-4 102.9 1-2-4-3 102.9 10-4-3-7 163.3
6-2-4-10 13.5

Pi-complex CCSD(T)/cc-pVTZ

1	C	-1.8371226110	0.0000000000	0.2235509252
2	C	-0.9680217466	0.0000000000	-0.8774225359
3	C	1.0219762922	0.6126678503	0.1013382354
4	C	1.0219762922	-0.6126678503	0.1013382354
5	H	-2.1675669516	-0.9308801555	0.6676061232
6	H	-2.1675669516	0.9308801555	0.6676061232
7	H	-0.7748869730	-0.9160666629	-1.4246208649
8	H	-0.7748869730	0.9160666629	-1.4246208649
9	H	1.0980498108	1.6807236507	0.1376123118
10	H	1.0980498108	-1.6807236507	0.1376123118

Bond angles

1-2-7 120.4 1-2-8 120.4 2-1-5 120.7 2-1-6 120.7
3- 4-10 175.4 4- 3- 9 175.4 5- 1- 6 118.5 7- 2- 8 115.2

Dihedral Angle

6-1-2-7 169.4 1-2-3-4 93.3 1-2-4-3 93.3 1-4-3-9 0.0 5-1-2-8 169.4

B3LYP/cc-pVTZ, wB97x/cc-pVTZ and EOM-CCSD/cc-pVTZ excitation energies of the ten lowest doublet-doublet excitation of Pi complex of the acetylene-ethylene complex shown in figure 4h.

B3LYP/cc-pVTZ	wB97x/cc-pVTZ	EOM/cc-pVTZ
2.76	3.22	2.70
4.08 (0.06)	4.17	3.47
4.39	4.66	4.58
4.92	5.00	5.25
5.11 (0.26)	5.12	5.70
5.44	5.73	5.77
5.51	5.78	5.99
5.79	6.01	6.24
6.17	6.27	6.79
6.51 (0.05)	6.88	6.89