Electronic Supplementary Information

A quantum mechanical explanation of the structure of vinyl cation based on a CASSCF/CASMP2 study.

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S1. Theoretical methods and Computational details

Optimizations, Vibrational analysis and general considerations

For the CASSCF and CASMP2 [1-4] computations the procedure is as follows. According to this methodology we must first select an initial active space which contains a number of electrons (all valence electrons) and orbitals. Taking first an initial geometry for the classical form of the vinyl cation, we optimized it using Hartree-Fock (HF) theory and the STO-3G basis set.

1. #P HF/STO-3G Opt Freq nosymm geom=connectivity
   1,1 ← **Charge, Multiplicity**

Then in order to get a clear picture of the orbitals to be included in the active space, we used the method of localized Natural Bonding Orbitals (NBOs). [5, 6] Therefore, we take the previously found (HF) geometry and run a single point energy calculation using the NBO method,

2. #P HF/STO-3G nosymm Pop=(NBO,SaveNBO) nosymm guess=read geom=check

The localized orbitals are shown in Figure S1 below

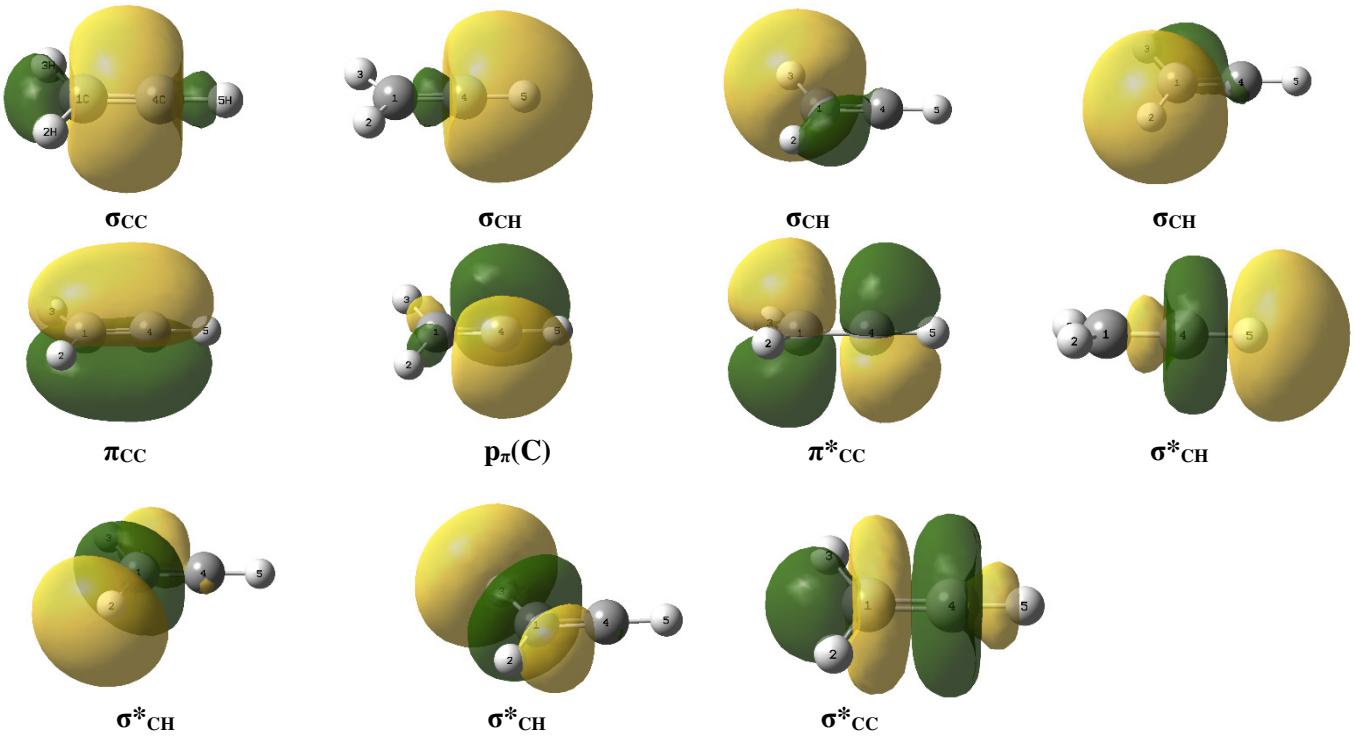


Figure S1. Initial localized NBOs to be used in the active space

Next, we shall include the aforementioned orbitals in a CASSCF/STO-3G exploratory calculation. Since we use 10 electrons and 11 orbitals, this calculation is denoted as CASSCF(10,11) or CAS(10,11). This calculation produces 106,953 Configuration State Functions (CSFs) or 213,444 Slater determinants (Slater Dets)

3. #P CAS(10,11)/STO-3G nosymm guess=read geom=check scfcon=6

The energy converges smoothly and an examination of the density matrix shows that all electron occupancies (diagonal elements) are correct:

```
             1             2             3             4             5
 1  0.198241D+01
 2 -0.145935D-05  0.197414D+01
 3  0.258803D-04 -0.112053D-03  0.196243D+01
 4 -0.258735D-04  0.112074D-03 -0.132040D-01  0.196243D+01
 5 -0.315386D-11 -0.199540D-10 -0.336695D-09  0.808285D-10  0.190221D+01
 6 -0.104119D-08 -0.207645D-08 -0.532269D-05 -0.532479D-05  0.646700D-08
 7 -0.895371D-10 -0.167002D-09 -0.394196D-10 -0.184536D-09 -0.141501D-05
 8 -0.765139D-06 -0.141566D-05  0.122833D-05 -0.122836D-05  0.182766D-09
 9 -0.953203D-06 -0.463014D-06 -0.569226D-07 -0.735166D-06  0.698161D-09
10 -0.952843D-06 -0.462389D-06  0.734640D-06  0.564283D-07 -0.435554D-09
11 -0.440199D-06 -0.143550D-05  0.155516D-06 -0.155709D-06  0.136358D-11
             6             7             8             9            10
 6  0.371664D-01
 7 -0.398965D-09  0.974106D-01
 8 -0.466774D-10 -0.139167D-10  0.271734D-01
 9  0.211592D-06 -0.694768D-10 -0.827052D-05  0.202150D-01
10 -0.211462D-06  0.854687D-10 -0.827087D-05  0.428953D-02  0.202147D-01
11 -0.250387D-10 -0.456795D-11  0.155053D-06 -0.213722D-04 -0.213612D-04
             11
11  0.141955D-01
```

A final check of the active space shows that all orbitals are included properly.

4. We then optimize the above structure using again the STO-3G basis set and afterwards we run a frequency calculation in order to verify the nature of the point.

a) #P CAS(10,11)/STO-3G Opt nosymm guess=read geom=check scfcon=6
b) #P CAS(10,11)/STO-3G Freq=Numer nosymm guess=read geom=check scfcon=6

The optimization is successful and all frequencies are positive, which means that we have found a minimum on the Potential Energy Surface (PES).

5. We continue with a Single Point Energy (SPE) calculation using the 3-21G basis

#P CAS(10,11)/3-21G nosymm guess=read geom=check scfcon=6

6. Next we optimize the structure by using the 6-31G(d), 6-311G(d,p) and cc-pVTZ basis sets in the following way

#P CAS(10,11)/6-31G(d), 6-311G(d,p), cc-pVTZ Opt nosymm guess=read geom=check scfcon=7

7. At the corresponding structures optimized with the above basis sets, we run frequency calculations to verify the nature of the point for each case

#P CAS(10,11)/6-31G(d) Freq=Numer nosymm guess=read geom=check scfcon=7

8. CASMP2 calculations were carried out on all optimized geometries with all basis sets

#P CAS(10,11)/6-31G(d), 6-311G(d,p), cc-pVTZ MP2 nosymm guess=read geom=check scfcon=7 IOP(5/42=7)

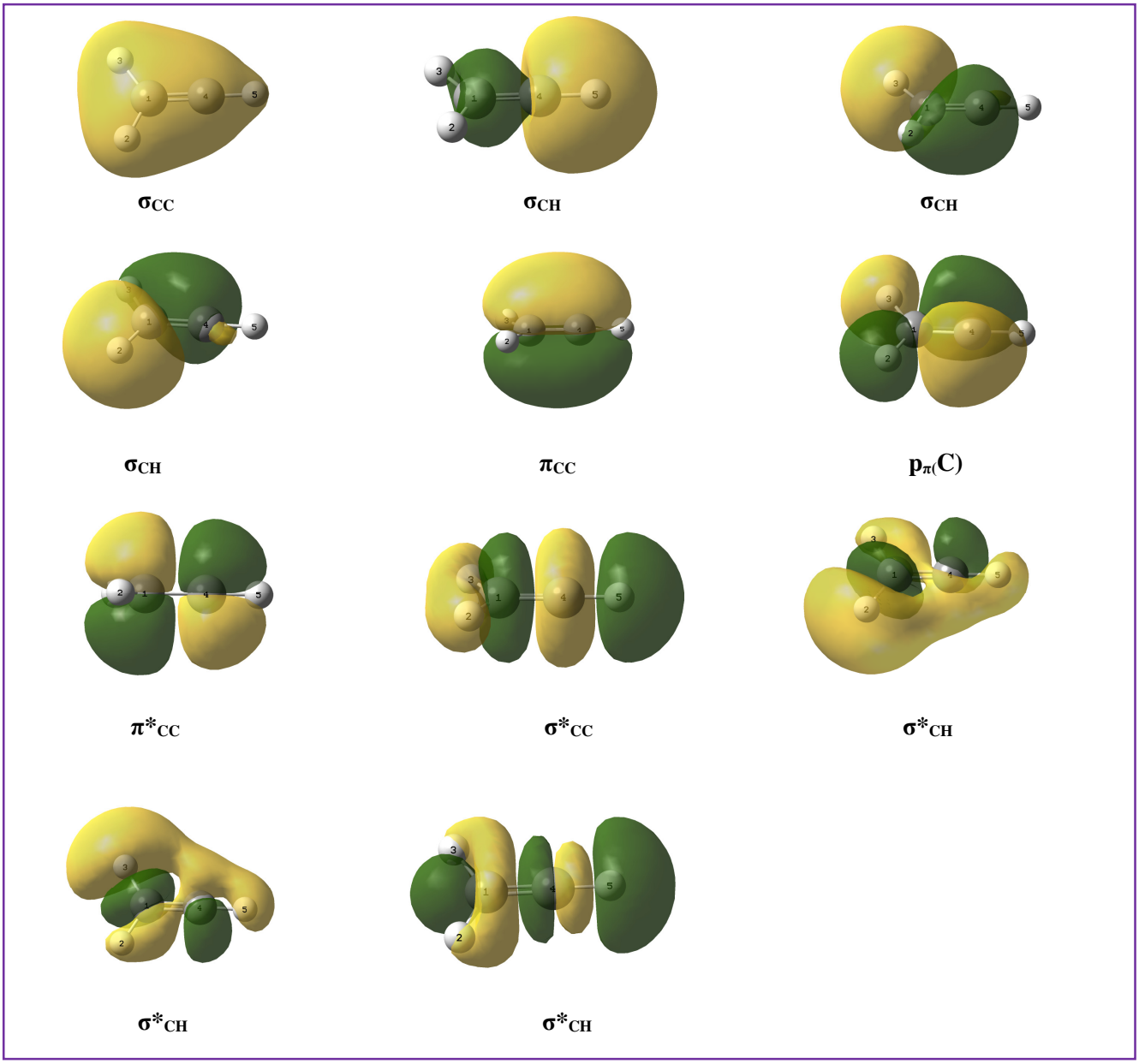
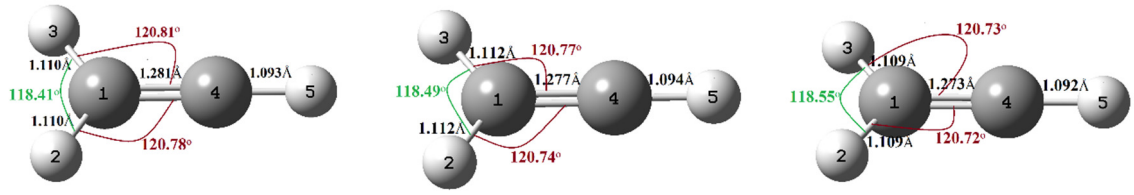


Figure S2. The final (canonical or diffuse) MOs of the optimized classical vinyl cation (Calculation method: CASSCF(10,11)/cc-pVTZ)



(a) (b) (c)

Figure S3. CASSCF(10,11) optimized structures for the classical vinyl cation with (a) 6-31G(d), (b) 6-311G(d,p) and (c) cc-pVTZ basis sets.

Transition state (TS) optimization

For the TS optimization we begin optimizing a deformed structure shown in Figure S4(a), and using the active space for the classical vinyl cation and the STO-3G basis. When the optimization is completed, we find an imaginary frequency which is equal to 523*i* cm^{-1}, Figure S4(b).

(a) (b)

Figure S4. (a) initial structure for optimization, (b) the normal mode corresponding to the imaginary frequency of 523*i* cm^{-1} found at the STO-3G level

We then continue our TS optimization process using the 3-21G basis set,

1) a) #p casscf(10,11)/3-21G Opt=(ReadFC,ts,noeigentest) nosymm guess=read geom=check scfcon=7
b) #p casscf(10,11)/3-21G Freq=Numer nosymm guess=read geom=check scfcon=7.

We check again the active space and all required orbitals are within the space. We note here that the 3-21G optimized TS geometry is similar to the one shown on Figure S3(b). We continue the optimization process using the 6-31g(d), 6-311g(d,p) and cc-pVTZ basis sets.

2) a) #P casscf(10,11)/6-31G(d) Opt=(ReadFC,ts,noeigentest) nosymm guess=read geom=check scfcon=7
b) #P casscf(10,11)/6-31G(d) Freq=Numer nosymm guess=read geom=check scfcon=7

Using the previous chk file containing the vibrational frequencies analysis, we then proceed to reoptimization using the 6-311G(d,p) basis, and similarly for the cc-pVTZ basis.

3) a) #P casscf(10,11)/6-311G(d,p) Opt=(ReadFC,ts,noeigentest) nosymm guess=read geom=check scfcon=7
b) #P casscf(10,11)/6-311G(d,p) Freq=Numer nosymm guess=read geom=check scfcon=7

4) a) #P casscf(10,11)/cc-pVTZ Opt=(ReadFC,ts,noeigentest) nosymm guess=read geom=check scfcon=7
b) #P casscf(10,11)/cc-pVTZ Freq=Numer nosymm guess=read geom=check scfcon=7

Corresponding CASMP2 calculations can be performed in an analogous way as described previously, by using the MP2 keyword.

In all the above cases there is an imaginary frequency. The normal mode of vibration in each case corresponds to that connecting the transition state and the two minima (Figure S5). An IRC calculation (Figure 3 of the paper) shows that this is actually the case. We also note that the optimized TS geometry found with the higher basis sets (Figure S5) is similar in each case, but different from that found using the lower size basis STO-3G and 3-21G.

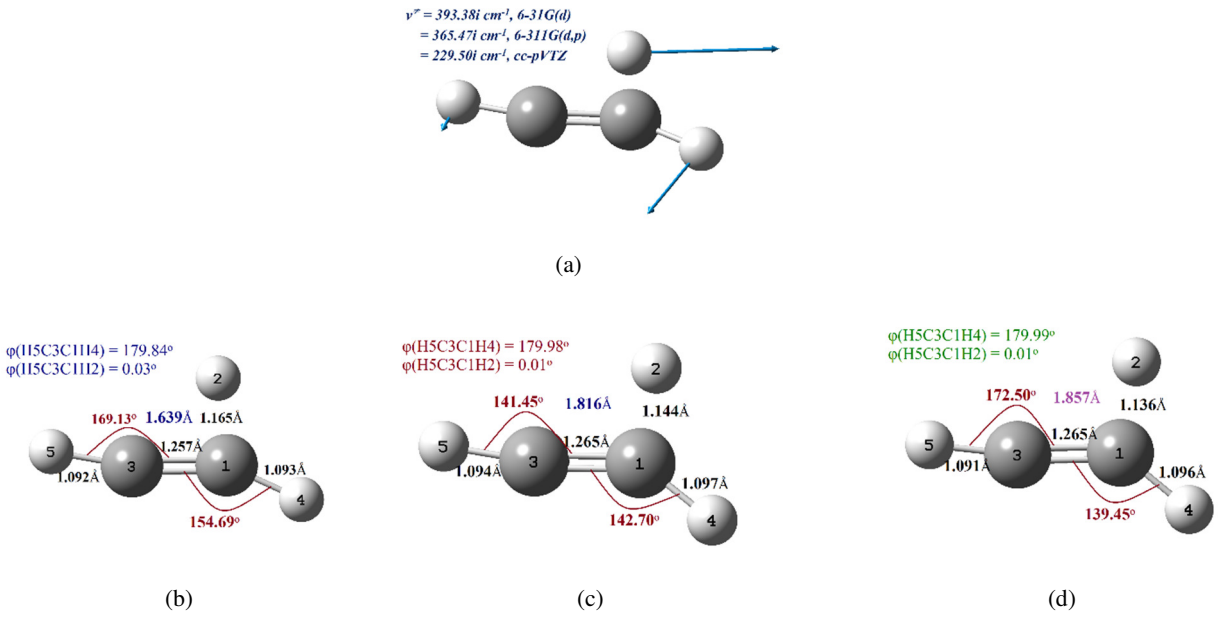


Figure S5. CASSCF(10,11) normal modes (a) and geometrical data of optimized TS structures with the 6-31G(d) (b), 6-311G(d,p) (c) and cc-pVTZ (d) basis sets.

Optimization of the bridged (non-classical) vinyl cation

The optimization method involves drawing an initial structure by taking a starting geometry representing the acetylene molecule and placing a hydrogen atom at a certain distance above the triple bond lying approximately equidistant from the two carbon atoms. We can then start optimizing this structure using the desired basis set.

a) optimization and frequency calculation using the 6-31G(d) basis set.
 i) #P CAS(10,11)/6-31G(d) Opt=tight nosymm guess=read geom=check scfcon=7
 ii) #P CAS(10,11)/6-31G(d) Freq=Numer nosymm guess=read geom=connectivity scfcon=7

Using the last chk file containing the frequency data we start reoptimizing again using the 6-311G(d,p) basis

b) i) #P CAS(10,11)/6-311G(d,p) Opt nosymm guess=read geom=check scfcon=7
 ii) #P CAS(10,11)/6-311G(d,p) Freq=Numer nosymm guess=read geom=check scfcon=7

c) i) #P CAS(10,11)/cc-pVTZ Opt=ReadFC nosymm guess=read geom=check scfcon=7

ii) #P #P CAS(10,11)/cc-pVTZ Freq=Numer nosymm guess=read geom=check scfcon=7

3) CASMP2 calculations.
i) CAS(10,11)/6-31G(d) MP2 nosymm guess=read geom=check scfcon=7 IOP(5/42=7)
ii) CAS(10,11)/6-311G(d,p) MP2 nosymm guess=read geom=check scfcon=7 IOP(5/42=7)
iii) CAS(10,11)/cc-pVTZ MP2 nosymm guess=read geom=check scfcon=7 IOP(5/42=7)

The geometries of the bridged structure as obtained with all basis sets are given in Figure S6.

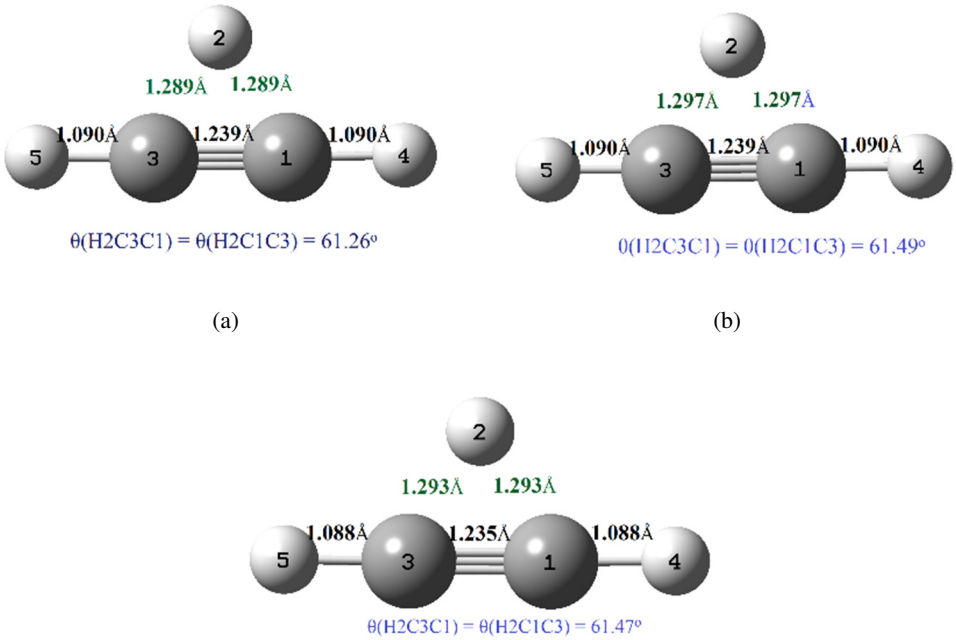


Figure S6. CASSCF(10,11) optimized structures of bridged vinyl cation with the (a) 6-31G(d), (b) 6-311G(d,p) and (c) cc-pVTZ basis sets.

The IRC calculation method represented at Figure 3, was performed at the CASSCF(10,11) / cc-pVTZ level of theory as follows:

We take the CAS(10,11)/cc-pVTZ optimized TS structure involving the frequency analysis and run the IRC computation using the LQA [7, 8] algorithm.

b) #p irc=(rcfc,recorrect=never,maxpoints=200,LQA,stepsize=6) casscf(10,11,nocpmcscf)/6-31g(d) nosymm guess=read geom=check scfcon=7

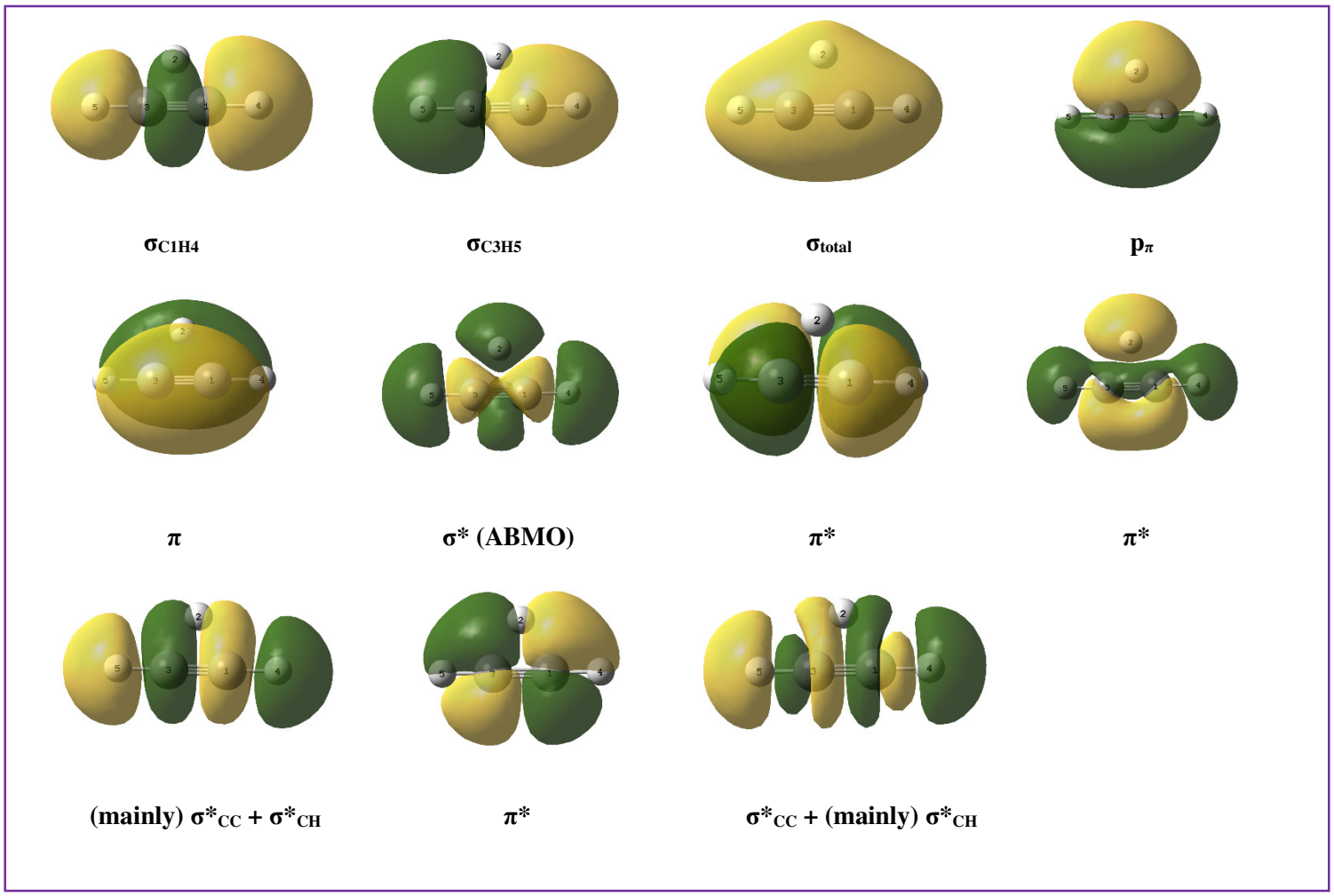


Figure S7. The canonical MOs for the optimized bridged vinyl cation (calculation method: CASSCF(10,11)/cc-pVTZ)

Boltzmann's distribution equation: $$\frac{N_1}{N_2} = \exp\left[-\left(E_1 - E_2\right)/k_B T\right]$$

Table S1 Calculated DFT activation energies ($E_{0,a}$), and energy differences (ΔE_0) between the classical and the bridged vinyl cations. All units in kcal/mol. ZPEs included

Method	Basis set	$E_{0,a}$	ΔE_0 [a]
APFD	6-311+G(2d,p)	- 0.004	1.88
APFD	cc-pVTZ	- 0.09	2.30
wB97XD	6-311+G(2d,p)	0.18	1.39
wB97XD	cc-pVTZ	0.031	1.87
M062X	6-311+G(2d,p)	- 0.324	3.66
M062X	cc-pVTZ	- 0.318	4.03

[a] $\Delta E_0 = E_0$(classical) – E_0(bridged)

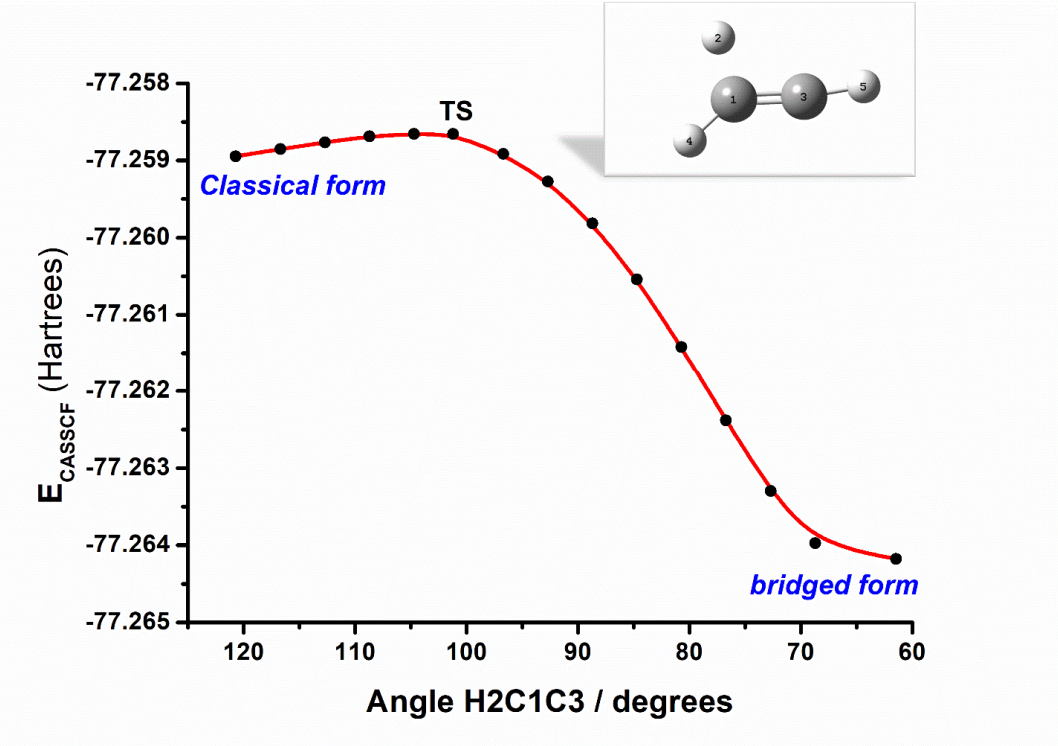


Figure S8. PES scan with respect to the H2C1C3 angle variation. Calculation method, CASSCF(10,11)/cc-pVTZ. E_{CASSCF} represent electronic energies.

Table S2 CASMP2 electron correlation energies, $E^{(2)}$. Units in Hartrees (ε_h)

Basis set	$E^{(2)}$ **(classical)**	$E^{(2)}$ **(bridged)**
6-31G(d)	- 0.1282862	- 0.1382459
6-311G(d,p)	- 0.1814978	- 0.1955255
cc-pVTZ	- 0.2101131	- 0.2272249

Table S3 Calculated CASSCF/CASMP2activation energies ($E_{0,a}$), and energy differences (ΔE_0) between the classical and the bridged vinyl cations. All units in kcal/mol. ZPEs included

Method	**Basis set**	$E_{0,a}$	ΔE_0 [a]
CASSCF	6-31G(d)	0.89	0.013
CASMP2	6-31G(d)	-1.34	6.26

S2. Cartesian coordinates

CASSCF Cartesian coordinates.

a) Classical vinyl cation

i) 6-31G(d) basis set

Tag	Symbol	X	Y	Z
1	C	-2.9656140	-0.3617030	-0.0306840
2	H	-2.2139250	-1.1786210	-0.0223370
3	H	-4.0416860	-0.6342920	-0.0437580
4	C	-2.5996250	0.8660860	-0.0252270
5	H	-2.2873520	1.9136630	-0.0206880

ii) 6-311G(d,p) basis set

Tag	Symbol	X	Y	Z
1	C	-2.9650920	-0.3600340	-0.0306490
2	H	-2.2115660	-1.1778100	-0.0223190
3	H	-4.0431840	-0.6322460	-0.0437850
4	C	-2.6004560	0.8633130	-0.0252410
5	H	-2.2879040	1.9119100	-0.0206990

iii) cc-pVTZ basis set

Tag	Symbol	X	Y	Z
1	C	-2.9647030	-0.3589110	-0.0306480
2	H	-2.2123160	-1.1747600	-0.0223160
3	H	-4.0408500	-0.6299810	-0.0437460
4	C	-2.6010870	0.8612020	-0.0252880
5	H	-2.2892460	1.9075830	-0.0206950

b) Transition state (TS)

i) 631-G(d) basis set

Tag	Symbol	X	Y	Z
1	C	0.9177330	-0.1272220	0.0074960
2	H	0.5676500	0.9801080	-0.0847650
3	C	-0.3087500	-0.4017130	0.0243620
4	H	1.9837270	-0.3659110	0.0308530
5	H	-1.3998840	-0.4357300	0.0220550

ii) 6-311G(d,p) basis set

Tag	Symbol	X	Y	Z
1	C	0.8836170	-0.0431670	0.0000880
2	H	0.7073750	1.0832600	-0.0924890
3	C	-0.3286590	-0.4042130	0.0242860
4	H	1.9096930	-0.4288630	0.0359610
5	H	-1.4115500	-0.5574860	0.0321540

iii) cc-pVTZ basis set

Tag	Symbol	X	Y	Z
1	C	0.8726080	-0.0192120	-0.0019110
2	H	0.7462960	1.1059210	-0.0941740
3	C	-0.3327710	-0.4006470	0.0239860
4	H	1.8816210	-0.4447830	0.0371390
5	H	-1.4072780	-0.5917470	0.0349610

c) Non-classical or bridged vinyl cation

i) 6-31G(d) basis set

Tag	Symbol	X	Y	Z
1	C	0.6205370	0.0282210	0.0004330
2	H	-0.1240690	1.0767770	-0.0884130
3	C	-0.6111520	-0.1130220	0.0065260
4	H	1.7021260	0.1666780	-0.0060970
5	H	-1.6960230	-0.2229580	0.0107090

ii) 6-311G(d,p) basis set

Tag	Symbol	X	Y	Z
1	C	0.6199020	0.0280360	-0.0001960
2	H	-0.1251630	1.0862070	-0.0891930
3	C	-0.6105000	-0.1129460	0.0071870
4	H	1.7020090	0.1619600	-0.0054850
5	H	-1.6948300	-0.2275610	0.0108450

iii) cc-pVTZ basis set

Tag	Symbol	X	Y	Z
1	C	0.6181070	0.0285420	0.0003910
2	H	-0.1248080	1.0830430	-0.0889330
3	C	-0.6088510	-0.1121460	0.0064680
4	H	1.6979040	0.1624090	-0.0057620
5	H	-1.6909330	-0.2261520	0.0109940

DFT Cartesian coordinates.

APFD/6-311+G(2d,p)

Classical vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.485818	0.519851	0.000000
2	1	0	-1.198239	-0.545132	0.000000
3	1	0	-2.564240	0.752000	0.000000
4	6	0	-0.624556	1.426837	0.000000
5	1	0	0.121837	2.212804	0.000000

Bridged vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.488566	0.585305	0.006485
2	1	0	-2.520494	0.263116	0.006525
3	6	0	-0.327414	0.953542	0.007075
4	1	0	0.702434	1.282341	0.007770
5	1	0	-0.570212	-0.303052	-0.114181

TS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.882850	-0.072154	0.002449
2	1	0	0.664566	1.043137	-0.089407
3	6	0	-0.313579	-0.391218	0.023300
4	1	0	1.915789	-0.407973	0.034284
5	1	0	-1.389149	-0.522260	0.029374

APFD/ cc-pVTZ

Classical vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.485660	0.519965	0.000000
2	1	0	-1.199210	-0.544169	0.000000
3	1	0	-2.563151	0.751165	0.000000
4	6	0	-0.624261	1.427108	0.000000
5	1	0	0.121265	2.212292	0.000000

Bridged vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.489357	0.585922	0.006532
2	1	0	-2.519488	0.261882	0.006348
3	6	0	-0.327297	0.953363	0.007006
4	1	0	0.701910	1.280328	0.007540
5	1	0	-0.570017	-0.300244	-0.113752

TS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.876029	-0.056757	0.001161
2	1	0	0.692211	1.059098	-0.090588
3	6	0	-0.318228	-0.391795	0.023321
4	1	0	1.900310	-0.416762	0.034938
5	1	0	-1.389846	-0.544252	0.031168

M06-2X/6-311+G(2d,p)

Classical vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.488916	0.516670	0.000000
2	1	0	-1.189136	-0.543088	0.000000
3	1	0	-2.562776	0.761091	0.000000
4	6	0	-0.628102	1.423031	0.000000
5	1	0	0.117914	2.208656	0.000000

Bridged vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.487809	0.585645	0.006501
2	1	0	-2.519147	0.262852	0.006467
3	6	0	-0.328414	0.952094	0.006923
4	1	0	0.701027	1.280837	0.007685
5	1	0	-0.569908	-0.300176	-0.113901

TS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.871988	-0.040832	-0.000125
2	1	0	0.707202	1.074814	-0.091823
3	6	0	-0.317669	-0.388936	0.023218
4	1	0	1.885386	-0.432393	0.036099
5	1	0	-1.386432	-0.563120	0.032633

M06-2X / cc-pVTZ

Classical vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.489257	0.517458	0.000001
2	1	0	-1.189622	-0.540971	-0.000001
3	1	0	-2.562223	0.759095	-0.000001
4	6	0	-0.627878	1.423604	0.000005
5	1	0	0.117964	2.207174	-0.000003

Bridged vinyl cation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.488252	0.585890	0.006525
2	1	0	-2.517289	0.261104	0.006184

3	6	0	-0.328242	0.952664	0.006954
4	1	0	0.700508	1.278318	0.007379
5	1	0	-0.570975	-0.296725	-0.113370

TS

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.866588	-0.027648	-0.001452
2	1	0	0.729562	1.086983	-0.092647
3	6	0	-0.321323	-0.388213	0.023071
4	1	0	1.870822	-0.440091	0.036798
5	1	0	-1.385173	-0.581500	0.034231

S3. References

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