Electronic Supplementary Information (ESI)

On the nature of bonding in the photochemical addition of two ethylenes. CC bond formation in the excited state?

Cristian Guerra,*[a] Leandro Ayarde-Henríquez,[a] Mario Duque-Noreña,[a] Carlos Cárdenas*,[b] Patricia Pérez,[a] and E. Chamorro*[a]

[a] Universidad Andrés Bello. Facultad de Ciencias Exactas. Departamento de Ciencias Químicas.

Avenida-República 275, 8370146, Santiago. Chile.

This file include:

1. Optimized Cartesian coordinates for the minimum energy structures which exhibit bifurcation catastrophes. The reaction pathway was initially generated by Nudged elastic band calculations at CASSCF(4,4)/def2-SVPD level and re-optimized using the NEVPT2/def2-TZVP level.

Point **A** (S_0)			
E = -156.78702985035702			
C	-1.7625192294	0.1118104295	0.9687635096
C	-1.3045657721	1.3496653441	0.7332868292
C	1.7615610114	-0.1117931097	-0.9705341929
H	-0.6609957450	1.8598973486	1.4379879024
H	-1.5568315909	1.8848840403	-0.1728391022
C	1.3054874077	-1.3496877577	-0.7316360538
H	2.4207396053	0.3934377652	-0.2767021813
H	1.4845757113	0.4320675870	-1.8641742391
H	1.5787781217	-1.8916715402	0.1643249683
H	0.6425774466	-1.8531855833	-1.4231141972
H	-2.4023255853	-0.4002027095	0.2619041012
H	-1.5064813814	-0.4252218145	1.8727326558
Point **B** (S_1)			
E = -156.45385470207671			
C	-1.7625192294	0.1118104295	0.9687635096
C	-1.3045657721	1.3496653441	0.7332868292
C	1.7615610114	-0.1117931097	-0.9705341929
H	-0.6609957450	1.8598973486	1.4379879024
H	-1.5568315909	1.8848840403	-0.1728391022
C	1.3054874077	-1.3496877577	-0.7316360538
H	2.4207396053	0.3934377652	-0.2767021813
H	1.4845757113	0.4320675870	-1.8641742391
H	1.5787781217	-1.8916715402	0.1643249683
H	0.6425774466	-1.8531855833	-1.4231141972
H	-2.4023255853	-0.4002027095	0.2619041012
H	-1.5064813814	-0.4252218145	1.8727326558
Point **C** (S_1)			
E= -156.57640644723085			
C	-1.7625192294	0.1118104295	0.9687635096
C	-1.3045657721	1.3496653441	0.7332868292
C	1.7615610114	-0.1117931097	-0.9705341929
H	-0.6609957450	1.8598973486	1.4379879024
H	-1.5568315909	1.8848840403	-0.1728391022
C	1.3054874077	-1.3496877577	-0.7316360538
H	2.4207396053	0.3934377652	-0.2767021813
H	1.4845757113	0.4320675870	-1.8641742391
H	1.5787781217	-1.8916715402	0.1643249683
H	0.6425774466	-1.8531855833	-1.4231141972
H	-2.4023255853	-0.4002027095	0.2619041012
H	-1.5064813814	-0.4252218145	1.8727326558
Point **D** (Minimum energy conical intersection point S_1/S_0)			
E=-156.646150797201			

C	1.4951526042	0.0402486755	0.0173113856
C	0.4107899332	0.9844738453	-0.0213836441
C	-1.4974473636	-0.0434017228	0.0270063466
H	0.1980399198	1.4881916872	-0.9508945177
H	0.1748990273	1.5572423362	0.8610755998
C	-0.4101623162	-0.9847755612	-0.0147346543
H	-2.0296264753	0.1968642425	-0.8799800402
H	-1.9691329754	0.1875140192	0.9695200099
H	-0.2055637908	-1.4951952831	-0.9427271347
H	-0.1722084346	-1.5562208078	0.8682697351
H	1.9773376917	-0.1796486622	0.9574845387
H	2.0279221797	-0.1952927688	-0.8909476246
Point **E**			
E = -156.702236734511			
C	1.3739214671	-0.2982883005	0.0277609702
C	0.4725195166	0.9430225195	-0.0165140465
C	-1.3745526149	0.2978614092	0.0275393710
H	0.5385709441	1.5205847666	-0.9365673387
H	0.5586510642	1.6108725056	0.8395363455
C	-0.4749808011	-0.9442226190	-0.0170746393
H	-1.8712421358	0.5952493771	-0.8843454092
H	-1.8335194683	0.5577096231	0.9700945984
H	-0.5390479221	-1.5210615240	-0.9376002311
H	-0.5576529435	-1.6112746832	0.8396078696
H	1.8339798902	-0.5559325137	0.9706943230
H	1.8733530036	-0.5945205609	-0.8831318130
Point **G**			
E = -156.726825006334			
C	1.3221872101	-0.3123548995	0.0263743902
C	0.4456973753	0.9541015309	-0.0155762677
C	-1.3220458939	0.3126012335	0.0259220022
H	0.5451168040	1.5391566926	-0.9294418050
H	0.5647043649	1.6241543279	0.8364969229
C	-0.4478488966	-0.9562844694	-0.0158499664
H	-1.8456980915	0.5836285150	-0.8801719511
H	-1.8073381485	0.5509033812	0.9621028586
H	-0.5458048463	-1.5405062963	-0.9302407726
H	-0.5650686061	-1.6253232700	0.8370325906
H	1.8080337679	-0.5489865258	0.9627024171
H	1.8480649607	-0.5810902200	-0.8793504188
Point **H** (Cyclobutane)			
E= -156.821555072179			

C	1.0383535922	-0.3421980076	0.0001529315
C	0.3422362039	1.0434754773	0.0001345624
C	-1.0386120775	0.3415789111	-0.0002218525
H	0.5426105732	1.6522273995	-0.8809506972
H	0.5422770603	1.6521174023	0.8813694927
C	-0.3420534259	-1.0427553094	-0.0000557476
H	-1.6470049034	0.5412466522	-0.8819001314
H	-1.6474926398	0.5412298507	0.8811232555
H	-0.5420511842	-1.6516169380	-0.8811787972
H	-0.5423349209	-1.6515066678	0.8810785917
H	1.6469131451	-0.5419609155	0.8816976772
H	1.6471585769	-0.5418378548	-0.8812492852

Table 1. Vertical excitation energies for ethylene molecule calculated at different theory levels. In this work was used the NEVPT2(4,4)/def2-TZVPD level.

Level	Excitation	Excitation energy
CIS/MP2/6-3lC*[1]	$\pi \rightarrow \pi^*$	8.39eV
MR-CISD1Q /TZ[2]	$\pi \rightarrow \pi^*$	8.25eV
MR-CISD/1aux/d-aug-cc-pVD[3]	$\pi \rightarrow \pi^*$	7.91eV
CASSCF (2,2)/1aux/d-aug-cc-pVD[3]	$\pi \rightarrow \pi^*$	8.63eV
Exp[4]	$\pi \rightarrow \pi^*$	7.66eV
NEVPT2(4,4)/def2-TZVPD	$\pi \rightarrow \pi^*$	7.76eV

(1) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. Electronically Excited States of Ethylene. *J. Phys. Chem.* **1992**, *96* (26), 10756–10768.

(2) Müller, T.; Dallos, M.; Lischka, H. The Ethylene 1 1B1u V State Revisited. *J. Chem. Phys.* **1999**, *110* (15), 7176–7184.

(3) Barbatti, M.; Paier, J.; Lischka, H. Photochemistry of Ethylene: A Multireference Configuration Interaction Investigation of the Excited-State Energy Surfaces. *J. Chem. Phys.* **2004**, *121* (23), 11614–11624.

(4) Sension, R. J.; Hudson, B. S. Vacuum Ultraviolet Resonance Raman Studies of the Excited Electronic States of Ethylene. *J. Chem. Phys.* **1989**, *90* (3), 1377–1389.

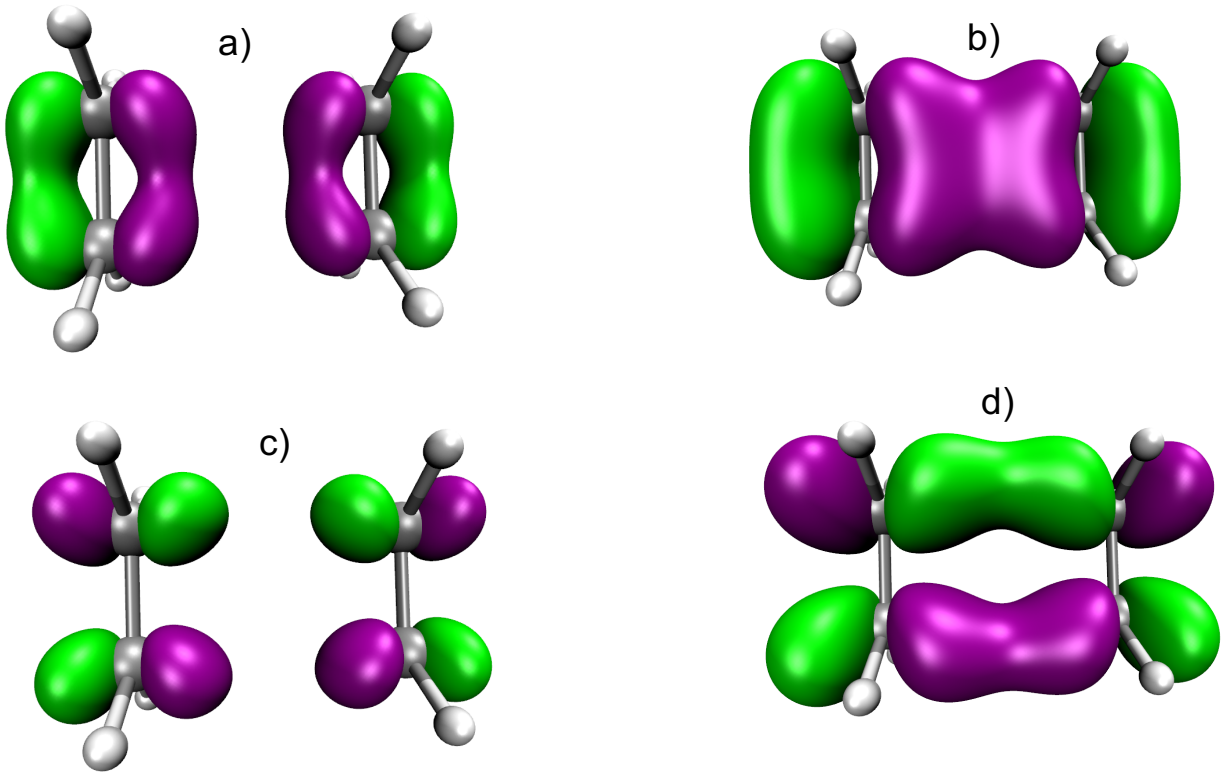

Figure 1. Molecular orbitals composing the active space used for the CASSCF (4, 4)/def2-SVPD calculations (isosurface = 0.05). *a* and *b* represent the HOMO and HOMO-1, whereas *c* and *d* depict the LUMO and LUMO+1 respectively (green and purple are associated with the negative and positive values of the wavefunction, respectively)

Derivative coupling (**g**) (Hartree borh^{-1})

0.0712193833	0.0633681205	0.0000141569
0.0319322269	-0.0517706280	0.0000045312
-0.0705314293	-0.0635645782	-0.0000126848
-0.0018977196	0.0009916254	-0.0008740180
-0.0018982381	0.0009919517	0.0008731568
-0.0325379722	0.0518918908	-0.0000052156
0.0105049505	-0.0066560493	-0.0009560796
0.0105062019	-0.0066568951	0.0009595201
0.0019178676	-0.0009984917	-0.0008694171
0.0019176205	-0.0009987486	0.0008697719
-0.0105671546	0.0067011597	0.0009678227
-0.0105657370	0.0067006426	-0.0009715445

Gradient difference (**h**) (borh^{-1})

-0.1605011952	0.0120393433	-0.0000278977
-0.0247244846	0.0978492460	-0.0000041134
0.1605005871	-0.0120176756	0.0000280042
0.0056151293	-0.0065304939	0.0004628745
0.0056149415	-0.0065304258	-0.0004598228
0.0249204170	-0.0978841936	0.0000014793
-0.0086931924	0.0080090378	0.0040804805
-0.0086942072	0.0080114514	-0.0040834902
-0.0056740839	0.0065422669	0.0004602529
-0.0056731978	0.0065419155	-0.0004606240
0.0086564223	-0.0080161619	-0.0040862132
0.0086528640	-0.0080143102	0.0040890700

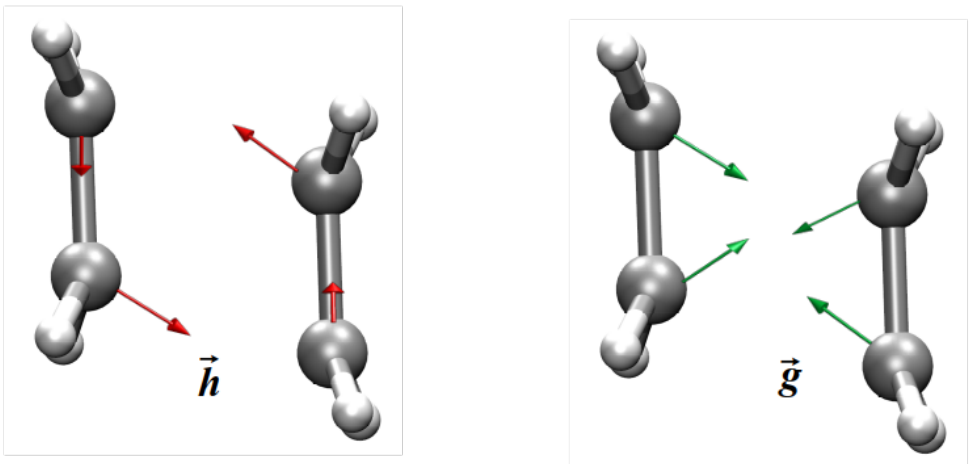

Figure 2. Derivative coupling (**h)** and gradient difference (**g**) vectors calculated for the rhomboidal conical intersection (S_1/S_0).

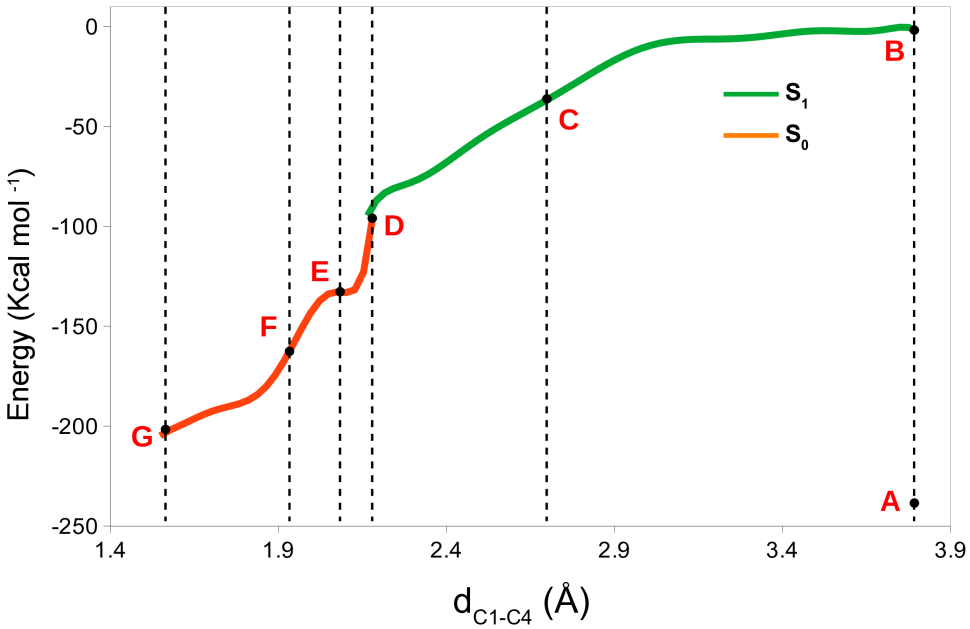

Figure 3. Minimum energy path (MEP) optimized at NEVPT2(4,4)/def2-TZVPD level. The S_1 excited state reaction path is depicted in green color and the S_0 path in orange color. Dashed lines indicate the bifurcations points reported above (A, B, C, D, E, F and G).

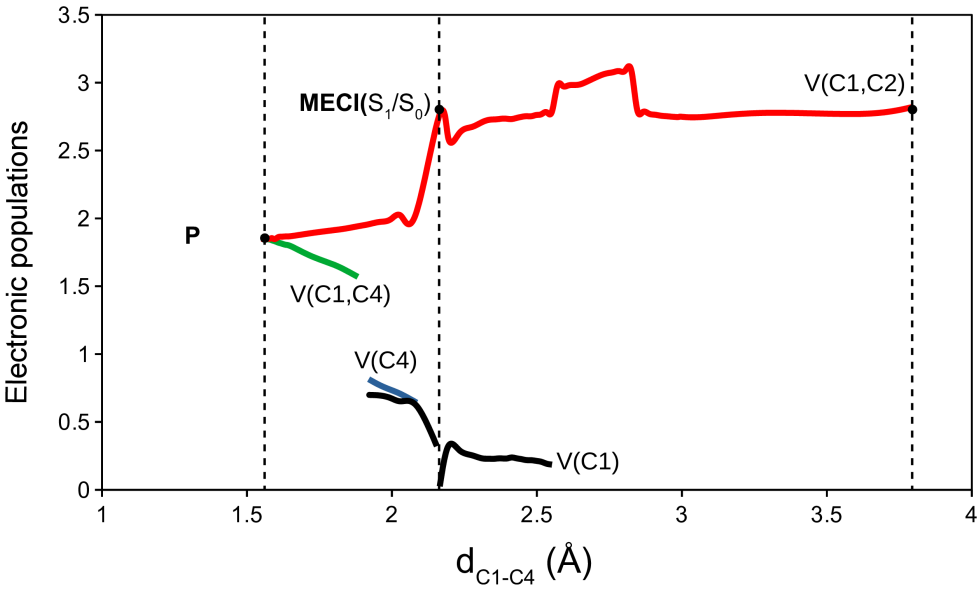

Figure 4. Electronic populations calculated for valence basins found from ELF topologic analysis. The V(C3, C4), V(C2, C3) V(C2), and V(C3) valence basins are omitted by simplicity. Dashed lines indicate the main stationary points; Reactants (B), minimum conical intersection point (D), and product (G).

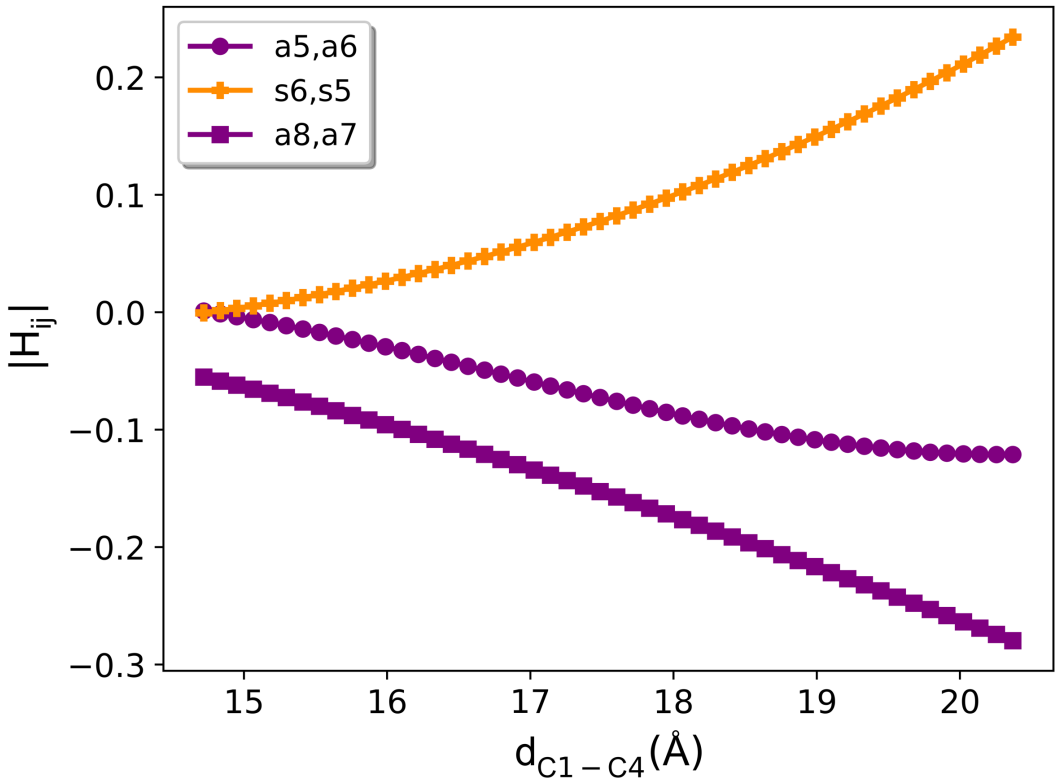

Figure 5. Determinant of hessian matrix characterizing the F: *a5* + s6 -> *wp* and F: *a6* + *s5* bifurcations associated with the C-C bond formation in the ground state.