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The Nature of the 4th Bond in the Ground State of C$_2$:

The Quadruple Bond Conundrum

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A. External σ-Bond

A.1. VBSCF

Table S1. VBSCF weights of the structures and composition of the respective hybrids

1. Weights

	Mulliken	Renormalized
Covalent	0.969	0.996
Ionic	0.015	0.002
Ionic	0.015	0.002

2. Orbital Coefficients for the hybrids

	ϕ_{right}	ϕ_{left}
S	0.455151	0.455119
Pz	0.316669	-0.316577
S	0.460263	0.460328
Pz	0.232198	-0.232229
D	0.020412	0.020460

3. VBSCF Bond Energies of the 4th bond

Energy of 3st -75.46275753 au
Energy of cov st -75.46178082 au
Energy of QC determinant -75.445008 au

D^{4th} = 11.14 kcal/mol

A.2. BOVB

Table S2. BOVB weights of the structures and composition of the respective hybrids

1. Weights

	Mulliken	Renormalized
Covalent	0.745	0.849
Ionic	0.128	0.076
Ionic	0.128	0.076

2. Orbital Coefficients for the hybrids

	$\phi_{Right,cov}$	$\phi_{Left,cov}$	$\phi_{Right,ion}$	$\phi_{Left,ion}$
S	0.422827	0.422855	0.578141	0.578145
Pz	0.407220	-0.407301	0.220460	-0.220417
S	0.427536	0.427413	0.314152	0.314153
Pz	0.246752	-0.246806	0.358878	-0.358887
D	0.022277	0.022394	-0.040406	-0.040656

Right,cov   Left,cov   Right,ion   Left,ion

3. BOVB Bond Energies of the 4th bond

BOVB energy   -75.476888 au
D^{4th} = 20.0 kcal/mol

B. Internal π-bond(s)

B.1. VBSCF

Table S3. VBSCF weights of the structures and composition of the respective hybrids

1. Weights

	Mulliken	Renormalized
Covalent	0.744	0.838
Ionic	0.128	0.081
Ionic	0.128	0.081

2. Orbital Coefficients

	ϕ_{right}	ϕ_{left}
Px	0.714646	0.714646
Px	0.400685	0.400685
D$_{+1}$	-0.049351	0.049351
D$_{+2}$	-0.000001	0.000002

3. VBSCF Bond energies

Energy of 3st -75.406489 au
Energy of cov st -75.364040 au
Energy of determinant -75.285457 au

D_π = 75.95 kcal/mol

B.2. BOVB

Table S3. BOVB weights of the structures and composition of the respective hybrids

1. Weights

	Mulliken	Renormalized
Covalent	0.611	0.649
Ionic	0.194	0.175
Ionic	0.194	0.175

2. Orbital Coefficients

	$\phi_{Right,cov}$	$\phi_{Left,cov}$	$\phi_{Right,ion}$	$\phi_{Left,ion}$
2Px	0.745499	0.745500	0.709364	0.709364
3Px	0.364438	0.364438	0.407014	0.407014
D_{+1}	-0.042719	0.042717	-0.046292	0.046291
D_{+2}	-0.000066	-0.000015	-0.000022	-0.000123

3. BOVB Bond energies

BOVB energy   -75.439476 au

D_π = 96.65 kcal/mol

C. Calculations of 2 π-bonds together.

BOVB(20st) = -75.504590 au
VBSCF(20st) = -75.457627 au
Cov = -75.346988 au
Determinant1 = -75.217824 au
Determinant2 = -75.164197 au

$D_{2\pi}$ = 196.8 kcal/mol

The quasi classical state for the 4 π electrons is taken as average of the $\alpha\beta\alpha\beta$ and $\alpha\alpha\beta\beta$ spin arrangements. See explanation in, *J. Chem. Theor. Comput.* **2011**, *7*, 955-968.

II. New VBSCF/6-311G(d) and BOVB/6-311G(d) Calculations for the external σ-bond and Internal π-bonds of C_2

A. The external σ-bond

A.1. VBSCF

Table S4. Weights of the structures and bond energies

1. Weights

	Mulliken	Lowdin
Covalent	0.972	0.997
Ionic	0.014	0.002
Ionic	0.014	0.002

2. Bond energies

Energy of 3st -75.478070 au
Energy of cov st -75.477330 au
Energy of determinant -75.461193 au

D^{4th} = 10.59 kcal/mol

A.2. BOVB

Table S5. Weights of the structures

1. Weights

	Mulliken	Renormalized
Covalent	0.779	0.869
Ionic	0.111	0.065
Ionic	0.111	0.065

2. Bond energies

BOVB energy   -75.493348 au

D^{4th} = 20.18 kcal/mol

B. The Internal π-bond

B.1. VBSCF

Table S6. Weights of the structures and bond energies

1. Weights

	Mulliken	Renormalized
Covalent	0.748	0.843
Ionic	0.126	0.078
Ionic	0.126	0.078

2. Bond energies

Energy of 3st -75.421428 au
Energy of cov st -75.382734 au
Energy of determinant -75.301762 au

D_π = 75.09 kcal/mol

B.2. BOVB

Table S7. Weights of the structures and bond energies

1. Weights

	Mulliken	Renormalized
Covalent	0.610	0.648
Ionic	0.195	0.176
Ionic	0.195	0.176

2. Bond energies

BOVB energy   -75.454137 au

D_π = 95.62 kcal/mol

III. Bond Dissociation Energies (BDEs) of C_2

The BDEs are the bond dissociation energies relative to $2C(^3P)$ in their s^2p^2 configurations. The BDEs are different than the above D quantities, which are in situ bond interaction energies as described in Ref. 16 and in the methods section.

As shown in Ref. 15, with 92 VB structures VBSCF/6-31G(d) and the corresponding VBCIS yield BDEs close to experiment (BDE_{exp}) = 145.2 kcal/mol). We show these values again and compare them with the GVB/aug-cc-pVQZ value in Ref. 21

Table S8. BDE values with VBSCF/6-31G(d) and VBCI/6-31G(d) calculations with 92 structures.[a]

	1.256Å	5Å	10Å[b]	BDE (kcal/mol)
VBSCF	-.599656	-.391175	-.391248	130.77
VBCIS	-.630081	-.401860	-.401919	143.17
GVB				112.6[c]

[a] The VB energies are relative to E= -75.0 au. [b] Note that the energies at 5Å and 10Å are virtually the same. [c] GVB/aug-cc-pVQZ datum

Table S9. BDE values of the **quadruply-bonded structure** with VBSCF/6-31G(d), VBCIS/6-31G(d), and VBCISD/6-31G(d) with 21 structures (Group 1 in Ref. 15).[a]

	1.256Å (21 st Group1)	92st -5Å[b]	BDE (kcal/mol)

VBSCF	-.570000	-.391175	112.17
VBCIS	-.585220	-.401860	115.08
VBCISD	-.632810	-.439067	121.58
GVB-PP[c]			92.2[c]

[a] The VB energies are relative to E= -75.0 au. [b] To obtain the correct dissociation limit, the full VB set of 92 structures is calculated at 5Å. [c] This is the GVB/aug-cc-pVQZ datum.

IV. Estimation of D^{4th} from C-H BDEs of HC≡CH

Table S10. Energies of C_2 at its optimized geometry, at the R_{CC} of the HCC radical, and the corresponding reorganization energies (RE).

	E(C_2) at optimized R_{CC}		E(C_2) at R_{CC}(HCC)		
	R_{CC} (Å)	E_{tot} (-75. au)	R_{CC} (Å)	E_{tot} (-75. au)	RE(kcal/mol)[a]
aug-cc-pVQZ	1.24603	-.80214242			
aug-cc-pV5Z	1.24483	-.8067304	1.210461	-.80495163	1.116
CBS	1.24379	-.81079412	1.209508	-.80901742	1.115

[a] Reorganization energy in C_2 molecule due to change of R_{CC} distance from 1.24483Å (in C_2) to 1.210461Å (in HCC).

Table S11a. Energies of HCC• at its optimized geometry, at the R_{CC} of the C_2 molecule, and the corresponding reorganization energies (RE), and the BDE(CH_2) Datum.

	E(HC_2) at optimized R_{CC}		E(HC_2) at $R_{CC}(C_2)$		
	R_{CC} (Å)	E_{tot} (-76. au)	R_{CC} (Å)	E_{tot} (-76. au)	RE(kcal/mol)[a]
aug-cc-pVQZ	1.21155 1.06462	-.48986369			
aug-cc-pV5Z	1.210461 1.06429	-.49491532			BDE(CH_2)[b] =119.207
aug-cc-pV5Z	1.210461 25.0	-.30494642	1.244828 25.0	-.30672482	1.116[a]
CBS	1.209509 1.064027	-.49928331	1.24379 1.064027	-.49733188	1.225[a]
CBS	1.209509 25.0	-0.30901221	1.24379 25.0	-.31078891	1.115

[a] Reorganization energy for HCC due to change of R_{CC} distance from 1.210461Å (in HCC) to 1.24483Å (in C_2). [b] BDE(CH_2)[(CCSD(T)/aug-cc-pV5Z)] is the vertical energy difference between total energy of HCC molecule and that of C_2 + H and at R_{CH}= 25Å.

Table S11b. Total energies calculated by CCSD(T)/aug-cc-pV5Z and MRCI/aug-cc-pV5Z basis sets as well as CBS energies using aug-cc-pVQZ, aug-cc-pV5Z and aug-cc-pV6Z basis sets based on the energies calculated by CCSD(T) and MRCI methods. Optimized CCSD(T)/aug-cc-pV5Z geometries also presented. (In parenthesis results for MRCI/aug-cc-pV5Z optimization)

	HC≡CH	HC_2	C_2	H
E_t(CCSD(T))	-77.21648089	-76.49491532	-75.80673004	-0.49999478
ZPVE	-77.189970	-76.480770	-75.802498	-0.499995
CBS	-77.22172324	-76.49971646	-75.81109204 -75.809859 (HC_2)	-0.50002678
E_t(MRCI)		-76.48560176	-75.79977061	0.49999478

ZPVE		-76.471234	-75.795548	-0.499995
CBS		-76.49978340	-75.81345354	-0.50002678
Geometry (Å)	1.2058 1.0631	1.2105 (1.2114) 1.0643 (1.0639)	1.2448 (1.2459)	

Table S11c. Bond Dissociation Energies of the $H_2C_2 \rightarrow C_2H.+H.$ and $C_2H. \rightarrow C_2+H.$ reactions calculated with CCSD(T)/aug-cc-pV5Z and MRCI/aug-cc-pV5Z as well as complete basis set interpolations (CBS) using aug-cc-pVQZ, aug-cc-pV5Z and aug-cc-pV6Z basis sets based on the energies calculated by CCSD(T) and MRCI methods. (Second line corresponds to vaues with ZPVE correction)

process	CCSD(T)	CBS	MRCI	CBS
$H_2C_2 \rightarrow C_2H.+H.$	139.04 131.27	139.29	-	-
$C_2H. \rightarrow C_2+H.$	118.09 111.87	118.35	116.61 110.25	116.91

V. BDEs H_2 at different distances

Table S12. BDE (kcal/mol), R_{HH} (Å), calculated with FCI/6-31G** and ω_{cov} values calculated with BOVB/6-31G**.

R_{HH} (Å)	BDE (kcal/mol)	ω_{cov}-Mulliken	ω_{cov}-Lowdin	ω_{cov}-Inverse
0.74	105.85	0.761 0.807	0.510 0.538	0.869 0.917
1.0	88.17	0.792 0.818	0.597 0.620	0.905 0.927
1.25	61.35	0.831 0.852	0.681 0.705	0.937 0.950
1.5	38.22	0.875 0.893	0.767 0.790	0.962 0.971
1.75	21.80	0.917 0.931	0.846 0.866	0.979 0.984
2.0	11.55	0.950 0.959	0.908 0.923	0.989 0.991
2.5	2.79	0.985 0.989	0.974 0.980	0.997 0.998
3.0	0.63	0.996 0.997	0.994 0.996	0.999 0.999
5.0	0.0	1.0	1.0	1.0

Second line corresponds to VBSCF/6-31G(p)

VI. Force Constants and Other Data at Various Levels and for Various State Functions

Table S13. Equilibrium distance R(A), Force constant FC (N cm^{-1}), Harmonic Frequency ω (cm^{-1}) and Reciprocal compliance force constant RCFC (cm^{-1}) and BDEs calculated for C_2 at various levels[a] with 6-31G(d).

	HF	TCS(4bonds)[b]	CAS1(π)[c]	CAS2(σ)[d]	CAS3(π)[e]	CAS4(σ/π)[f]	FCI[h]

R	1.245	1.2042	1.291	1.2115	1.291	1.255	1.2603
FC	13.3395	17.345	9.310	16.525	9.271	12.562	
ω	1940.33	2212.53	1621.01	2159.59	1617.58	1882.95	
RCFC	13.333						
BDE	15.61	48.30	71.54	60.53	62.46	116.13	137.88

	CAS5(σ)[g]
R	1.210
FC	16.62
ω	2165.67
RCFC	
BDE	

[a] In all the MCSCF calculations the orbitals with non-active electrons were optimized and kept doubly occupied. [b] TCS(4 bonds) is CASSCF(2,2) calculations which include only the $2\sigma_u$ and $3\sigma_g$ orbitals and only two CSFs (20 and 02). [c] CAS1(π) is CASSCF(4,12) calculation which includes all π_u and π_g orbitals. [d] CAS2(σ) is CASSCF(4,14) calculation, which includes all σ type orbitals. [e] CAS3(π) is CASSCF(4,4) calculation which includes only $1\pi_u$ and $1\pi_g$ orbitals. [f] CAS4(σ/π) is CASSCF(6,6) calculation which includes only $2\sigma_u$, $3\sigma_g$, $1\pi_u$ and $1\pi_g$ orbitals. [g] CAS5(σ) is CASSCF(4/4) which includes all σ_u and σ_g orbitals. [h] FCI includes all orbitals (8,26).

Table S14. Equilibrium distance R(A), Force constant FC (N cm^{-1}), Harmonic Frequency ω (cm^{-1}) and Reciprocal compliance force constant RCFC (cm^{-1}) calculated for HC≡CH at various levels[a] with 6-31G(d).

	HF	TCS[b]	CAS1(π)[c]	CAS2(σ)[d]	CAS3(π)[e]	CAS4(π/σ)[f]	CAS5(π/σ)[g]
R	1.1858	1.1857	1.2086	1.1894	1.2093	1.2094	1.2140
FC	19.33	19.31	16.76	18.79	16.70	16.58	
ω	2243.55	2242.22	2089.31	2206.67	2085.00	2077.77	
RCFC	20.408						
BDE	185.34						

[a] In all the MCSCF calculations the orbitals with non-active electrons were optimized and kept doubly occupied. [b] TCS is CASSCF(2,2) which includes only $2\sigma_u$ and $3\sigma_g$ orbitals and only two CSF (20 and 02). [c] CAS1(π) is CASSCF(4,12) which includes all π_u and π_g orbitals. [d] CAS2(σ) is CASSCF(6,18), which includes all σ type orbitals. [e] CAS3(π) is CASSCF(4,4) which includes only $1\pi_u$ and $1\pi_g$ orbitals. [f] CAS4(π/σ) is CASSCF(6,6) calculations which includes only $2\sigma_u$, $3\sigma_g$, $1\pi_u$ and $1\pi_g$ orbitals. [g] CAS5(π/σ) is CASSCF(10,22) calculations which include all virtual orbitals below 2.0 eV.

Table S.15. Equilibrium distance R(A), Force constant FC (N cm^{-1}), Harmonic Frequency ω (cm^{-1}) and Reciprocal compliance force constant RCFC (cm^{-1}) calculated for CN$^+$ at various levels[a] with 6-31G(d).

	HF	TCS(4bonds)[b]	CAS1(π)[c]	CAS2(σ)[d]	CAS3(π)[e]	CAS4(π/σ)[f]	FCI[g]
R	1.1570	1.1331	1.2014	1.1395	1.1993	1.1828	1.1935
FC	18.4236	22.9448	13.0139	21.8287	13.2241	16.2078	
ω	2197.56	2452.43	1846.96	2392.04	1861.82	2061.18	
RCFC	18.519						

[a] In all the MCSCF calculations the orbitals with non-active electrons were optimized and kept doubly occupied. [b] TCS(4bonds) is CASSCF(2,2) which includes only $2\sigma_u$ and $3\sigma_g$ orbitals and only two CSF (20 and 02). [c] CAS1(π) is CASSCF(4,12) which includes all π_u and π_g orbitals. [d] CAS2(σ) is CASSCF(4,14) which includes all σ type orbitals. [e] CAS3(π) is CASSCF(4,4) which includes only $2\pi_u$

and $2\pi_g$ orbitals. [f] CAS4(π/σ) is CASSCF(6,6) which includes only $2\sigma_u$, $3\sigma_g$, $2\pi_u$ and $2\pi_g$ orbitals. [g] FCI is calculations that include all orbitals (8,26).

Table S.16. Equilibrium distance R(A), Force constant FC (N cm^{-1}), Harmonic Frequency ω (cm^{-1}) and Reciprocal compliance force constant RCFC (cm^{-1}) calculated for N_2^{2+} at various levels[a] with 6-31G(d).

	HF	TCS(4bonds)[b]	CAS1[c]	CAS2[c]	CAS3[c]	CAS4[c]	FCI[c]
R	1.1234	1.0712	1.2102	1.0779	1.2066	1.1360	1.1515
FC	20.5717	30.5078	7.7280	28.7040	7.8774	17.7379	
ω	2231.29	2717.23	1367.59	2635.68	1380.74	2071.92	
RCFC	20.408						

[a] In all the MCSCF calculations the orbitals with non-active electrons were optimized and kept doubly occupied. [b] TCS(4bonds) is CASSCF(2,2) which includes only $2\sigma_u$ and $3\sigma_g$ orbitals and only two CSF (20 and 02). [c]CAS1-CAS4 and FCI are identical to Table S15.

VII. GVB (CASVB) Calculations

A. Molpro input for the CASVB calculations of C_2 molecule

```
***,C2
memory,250,m
gprint,orbital,civector;
gthresh,energy=1.d-12;
r = 1.247 ang;
 geometry={C; C,1,r}
basis=aug-cc-pV5Z;
hf
{multi; occ,3,1,1,0,3,1,1,0; frozen,1,0,0,0,1,0,0,0;
natorb,,ci,save=3500.2}
{multi; occ,3,1,1,0,3,1,1,0; frozen,1,0,0,0,1,0,0,0;
{vb; start,3500.2;
guess
orb, 1,  0.97176980, -0.02317260,  0.00000000,  0.00000000,  0.16557690, \
        0.16646570,  0.00000000,  0.00000000,
orb, 2,  0.97176980, -0.02317260,  0.00000000,  0.00000000, -0.16557690, \
        -0.16646570,  0.00000000,  0.00000000,
orb, 3,  0.48957140, -0.51520430,  0.00000000,  0.00000000,  0.70345170, \
        -0.00633300,  0.00000000,  0.00000000,
orb, 4, -0.48957130,  0.51520430,  0.00000000,  0.00000000,  0.70345180, \
        -0.00633300,  0.00000000,  0.00000000,
orb, 5,  0.00000000,  0.00000000,  0.90866440,  0.00000000,  0.00000000, \
        0.00000000, -0.41752710,  0.00000000,
orb, 6,  0.00000000,  0.00000000,  0.90866450,  0.00000000,  0.00000000, \
        0.00000000,  0.41752710,  0.00000000,
orb, 7,  0.00000000,  0.00000000,  0.00000000,  0.90866440,  0.00000000, \
        0.00000000,  0.00000000,  0.41752710,
orb, 8,  0.00000000,  0.00000000,  0.00000000,  0.90866450,  0.00000000, \
        0.00000000,  0.00000000, -0.41752710,
scorr; vbweights,all}}
```

The data presented in the Tables S17a-S21a were obtained with SPINS program of David L. Cooper (http://www.liv.ac.uk/~dlc/dlc/SPINS.html). We are thankful to him for making his program available.

B. CASVB/6-31G(d) for C_2 (optimized R_{CC}=1.2545Å)

Table S17a. Renormalized input spin function coefficients (Kotani spin basis):

```
   k        Spin-Coupling pattern   Coefficient        Weightᵃ
  ----------------------------------------------------------------
   1:  ((1/2)1(3/2)2(3/2)1(1/2))     0.099344        0.009869
   2:  ((1/2)1(3/2)1(3/2)1(1/2))     0.139953        0.019587
   3:  ((1/2)1(1/2)1(3/2)1(1/2))    -0.098961        0.009793
   4:  ((1/2)0(1/2)1(3/2)1(1/2))    -0.247064        0.061040
   5:  ((1/2)1(3/2)1(1/2)1(1/2))    -0.098961        0.009793
   6:  ((1/2)1(1/2)1(1/2)1(1/2))     0.069976        0.004897
   7:  ((1/2)0(1/2)1(1/2)1(1/2))     0.174700        0.030520
   8:  ((1/2)1(1/2)0(1/2)1(1/2))     0.046279        0.002142
   9:  ((1/2)0(1/2)0(1/2)1(1/2))     0.230019        0.052909
  10:  ((1/2)1(3/2)1(1/2)0(1/2))    -0.171406        0.029380
  11:  ((1/2)1(1/2)1(1/2)0(1/2))     0.121202        0.014690
  12:  ((1/2)0(1/2)1(1/2)0(1/2))     0.302590        0.091561
  13:  ((1/2)1(1/2)0(1/2)0(1/2))    -0.011629        0.000135
  14:  ((1/2)0(1/2)0(1/2)0(1/2))     0.814668        0.663683
```
ᵃ· Structure 14 is GVB-PP

Table S17b. Transformed spin function coefficients (Rumer spin basis):

```
   k    Spin-Coupling pattern   Coefficient      Weightᵃ
  ----------------------------------------------------------
   1:    (1-2,3-4,5-6,7-8)       1.074656      0.875488
   2:    (1-4,2-3,5-6,7-8)       0.076662     -0.031999
   3:    (1-2,3-6,4-5,7-8)       0.482684     -0.070126
   4:    (1-6,2-3,4-5,7-8)       0.088856      0.014979
   5:    (1-6,2-5,3-4,7-8)      -0.197977      0.116636
   6:    (1-2,3-4,5-8,6-7)       0.355694     -0.074031
   7:    (1-4,2-3,5-8,6-7)       0.091324      0.013133
   8:    (1-2,3-8,4-5,6-7)       0.088856      0.009247
   9:    (1-8,2-3,4-5,6-7)       0.177712     -0.012778
  10:    (1-8,2-5,3-4,6-7)       0.088856      0.009247
  11:    (1-2,3-8,4-7,5-6)      -0.304973      0.204144
  12:    (1-8,2-3,4-7,5-6)       0.088856      0.022110
  13:    (1-8,2-7,3-4,5-6)       0.375689     -0.084729
  14:    (1-8,2-7,3-6,4-5)       0.177712      0.008680
```
ᵃ· Structure 1 is GVB-PP

C. CASVB/aug-cc-pV5Z for C_2 molecule (optimized R_{CC}=1.2453Å)

Table S18a. Renormalized input spin function coefficients (Kotani spin basis):

```
   k     Spin-Coupling pattern  Coefficient      Weight
  ----------------------------------------------------------------
   1: ((1/2)1(3/2)2(3/2)1(1/2))   0.097165    0.009441
   2: ((1/2)1(3/2)1(3/2)1(1/2))   0.137298    0.018851
```

```
 3: ((1/2)1(1/2)1(3/2)1(1/2))     -0.097085    0.009425
 4: ((1/2)0(1/2)1(3/2)1(1/2))     -0.246465    0.060745
 5: ((1/2)1(3/2)1(1/2)1(1/2))     -0.097085    0.009425
 6: ((1/2)1(1/2)1(1/2)1(1/2))      0.068649    0.004713
 7: ((1/2)0(1/2)1(1/2)1(1/2))      0.174277    0.030372
 8: ((1/2)1(1/2)0(1/2)1(1/2))      0.045914    0.002108
 9: ((1/2)0(1/2)0(1/2)1(1/2))      0.227390    0.051706
10: ((1/2)1(3/2)1(1/2)0(1/2))     -0.168155    0.028276
11: ((1/2)1(1/2)1(1/2)0(1/2))      0.118904    0.014138
12: ((1/2)0(1/2)1(1/2)0(1/2))      0.301856    0.091117
13: ((1/2)1(1/2)0(1/2)0(1/2))     -0.011178    0.000125
14: ((1/2)0(1/2)0(1/2)0(1/2))      0.818264    0.669557[a]
```
[a]Structure 14 is GVB-PP

Table S18b. Kotani to Rumer transformation
Transformed spin function coefficients (Rumer spin basis):

k	Spin-Coupling pattern	Coefficient	Weight
1:	(1-2,3-4,5-6,7-8)	1.074275	0.879041[a]
2:	(1-4,2-3,5-6,7-8)	0.075640	-0.031679
3:	(1-2,3-6,4-5,7-8)	0.478915	-0.070744
4:	(1-6,2-3,4-5,7-8)	0.086907	0.014590
5:	(1-6,2-5,3-4,7-8)	-0.194354	0.114181
6:	(1-2,3-4,5-8,6-7)	0.351115	-0.074509
7:	(1-4,2-3,5-8,6-7)	0.090188	0.013112
8:	(1-2,3-8,4-5,6-7)	0.086907	0.009221
9:	(1-8,2-3,4-5,6-7)	0.173815	-0.012635
10:	(1-8,2-5,3-4,6-7)	0.086907	0.009221
11:	(1-2,3-8,4-7,5-6)	-0.305100	0.204584
12:	(1-8,2-3,4-7,5-6)	0.086907	0.021808
13:	(1-8,2-7,3-4,5-6)	0.368169	-0.084965
14:	(1-8,2-7,3-6,4-5)	0.173815	0.008774

[a]Structure 1 is GVB-PP

D. CASVB/6-31G(d) for HC≡CH molecule (optimized R_{CC}=1.2187Å)

Table S19a. Renormalized input spin function coefficients (Kotani spin basis):

```
  k          Spin-Coupling pattern    Coefficient        Weight
--------------------------------------------------------------------
  1:  ((1/2)1(3/2)2(5/2)2(3/2)1(1/2))     0.022941       0.000526
  2:  ((1/2)1(3/2)2(3/2)2(3/2)1(1/2))    -0.018731       0.000351
  3:  ((1/2)1(3/2)1(3/2)2(3/2)1(1/2))    -0.043098       0.001857
  4:  ((1/2)1(1/2)1(3/2)2(3/2)1(1/2))     0.019783       0.000391
  5:  ((1/2)0(1/2)1(3/2)2(3/2)1(1/2))     0.046611       0.002173
  6:  ((1/2)1(3/2)2(3/2)1(3/2)1(1/2))    -0.002892       0.000008
  7:  ((1/2)1(3/2)1(3/2)1(3/2)1(1/2))    -0.072010       0.005185
  8:  ((1/2)1(1/2)1(3/2)1(3/2)1(1/2))     0.039169       0.001534
  9:  ((1/2)0(1/2)1(3/2)1(3/2)1(1/2))     0.097973       0.009599
 10:  ((1/2)1(3/2)1(1/2)1(3/2)1(1/2))     0.065263       0.004259
```

```
11:  ((1/2)1(1/2)1(1/2)1(3/2)1(1/2))    -0.037840    0.001432
12:  ((1/2)0(1/2)1(1/2)1(3/2)1(1/2))    -0.051709    0.002674
13:  ((1/2)1(1/2)0(1/2)1(3/2)1(1/2))     0.001772    0.000003
14:  ((1/2)0(1/2)0(1/2)1(3/2)1(1/2))    -0.198547    0.039421
15:  ((1/2)1(3/2)2(3/2)1(1/2)1(1/2))     0.002045    0.000004
16:  ((1/2)1(3/2)1(3/2)1(1/2)1(1/2))     0.050919    0.002593
17:  ((1/2)1(1/2)1(3/2)1(1/2)1(1/2))    -0.027697    0.000767
18:  ((1/2)0(1/2)1(3/2)1(1/2)1(1/2))    -0.069278    0.004799
19:  ((1/2)1(3/2)1(1/2)1(1/2)1(1/2))    -0.046148    0.002130
20:  ((1/2)1(1/2)1(1/2)1(1/2)1(1/2))     0.026757    0.000716
21:  ((1/2)0(1/2)1(1/2)1(1/2)1(1/2))     0.036564    0.001337
22:  ((1/2)1(1/2)0(1/2)1(1/2)1(1/2))    -0.001253    0.000002
23:  ((1/2)0(1/2)0(1/2)1(1/2)1(1/2))     0.140394    0.019711
24:  ((1/2)1(3/2)1(1/2)0(1/2)1(1/2))    -0.011764    0.000138
25:  ((1/2)1(1/2)1(1/2)0(1/2)1(1/2))     0.013743    0.000189
26:  ((1/2)0(1/2)1(1/2)0(1/2)1(1/2))     0.017539    0.000308
27:  ((1/2)1(1/2)0(1/2)0(1/2)1(1/2))     0.012690    0.000161
28:  ((1/2)0(1/2)0(1/2)0(1/2)1(1/2))     0.190202    0.036177
29:  ((1/2)1(3/2)2(3/2)1(1/2)0(1/2))     0.003542    0.000013
30:  ((1/2)1(3/2)1(3/2)1(1/2)0(1/2))     0.088194    0.007778
31:  ((1/2)1(1/2)1(3/2)1(1/2)0(1/2))    -0.047972    0.002301
32:  ((1/2)0(1/2)1(3/2)1(1/2)0(1/2))    -0.119992    0.014398
33:  ((1/2)1(3/2)1(1/2)1(1/2)0(1/2))    -0.079930    0.006389
34:  ((1/2)1(1/2)1(1/2)1(1/2)0(1/2))     0.046344    0.002148
35:  ((1/2)0(1/2)1(1/2)1(1/2)0(1/2))     0.063331    0.004011
36:  ((1/2)1(1/2)0(1/2)1(1/2)0(1/2))    -0.002171    0.000005
37:  ((1/2)0(1/2)0(1/2)1(1/2)0(1/2))     0.243170    0.059132
38:  ((1/2)1(3/2)1(1/2)0(1/2)0(1/2))     0.012222    0.000149
39:  ((1/2)1(1/2)1(1/2)0(1/2)0(1/2))     0.007061    0.000050
40:  ((1/2)0(1/2)1(1/2)0(1/2)0(1/2))    -0.005903    0.000035
41:  ((1/2)1(1/2)0(1/2)0(1/2)0(1/2))     0.011475    0.000132
42:  ((1/2)0(1/2)0(1/2)0(1/2)0(1/2))     0.874652    0.765015ᵃ
  ᵃ·This is the GVB-PP structure
```

Table S19b. Renormalized Transformed spin function coefficients (Rumer spin basis):

```
  k    Spin-Coupling pattern    Coefficient      Weight
  --------------------------------------------------------
  1:   (1-2,3-4,5-6,7-8,9-10)     1.028471     0.899554ᵃ
  2:   (1-4,2-3,5-6,7-8,9-10)     0.037202    -0.015900
  3:   (1-2,3-6,4-5,7-8,9-10)     0.041546    -0.018381
  4:   (1-6,2-3,4-5,7-8,9-10)     0.017751     0.003933
  5:   (1-6,2-5,3-4,7-8,9-10)    -0.023795     0.010284
  6:   (1-2,3-4,5-8,6-7,9-10)     0.236200    -0.053555
  7:   (1-4,2-3,5-8,6-7,9-10)    -0.018403    -0.001965
  8:   (1-2,3-8,4-5,6-7,9-10)     0.010648     0.001740
  9:   (1-8,2-3,4-5,6-7,9-10)    -0.004708     0.000240
 10:   (1-8,2-5,3-4,6-7,9-10)    -0.072733    -0.003040
 11:   (1-2,3-8,4-7,5-6,9-10)    -0.098543     0.054577
 12:   (1-8,2-3,4-7,5-6,9-10)     0.047635     0.010599
 13:   (1-8,2-7,3-4,5-6,9-10)     0.147146    -0.047206
 14:   (1-8,2-7,3-6,4-5,9-10)     0.006336     0.001042
 15:   (1-2,3-4,5-6,7-10,8-9)     0.242559    -0.066123
```

```
16:  (1-4,2-3,5-6,7-10,8-9)     0.022563   0.003178
17:  (1-2,3-6,4-5,7-10,8-9)     0.039618   0.006022
18:  (1-6,2-3,4-5,7-10,8-9)     0.004671  -0.000336
19:  (1-6,2-5,3-4,7-10,8-9)    -0.034947  -0.004214
20:  (1-2,3-4,5-10,6-7,8-9)    -0.011043  -0.001505
21:  (1-4,2-3,5-10,6-7,8-9)    -0.011043   0.000778
22:  (1-2,3-10,4-5,6-7,8-9)     0.072337  -0.005498
23:  (1-10,2-3,4-5,6-7,8-9)    -0.022086  -0.000795
24:  (1-10,2-5,3-4,6-7,8-9)    -0.094424   0.005693
25:  (1-2,3-10,4-7,5-6,8-9)     0.062658   0.008541
26:  (1-10,2-3,4-7,5-6,8-9)     0.041936  -0.002953
27:  (1-10,2-7,3-4,5-6,8-9)    -0.020722  -0.002825
28:  (1-10,2-7,3-6,4-5,8-9)     0.000000   0.000000
29:  (1-2,3-4,5-10,6-9,7-8)    -0.258286   0.167348
30:  (1-4,2-3,5-10,6-9,7-8)    -0.003683  -0.001181
31:  (1-2,3-10,4-5,6-9,7-8)     0.061690   0.017212
32:  (1-10,2-3,4-5,6-9,7-8)    -0.017379   0.002965
33:  (1-10,2-5,3-4,6-9,7-8)    -0.021691  -0.008468
34:  (1-2,3-10,4-9,5-6,7-8)     0.223859  -0.071817
35:  (1-10,2-3,4-9,5-6,7-8)    -0.016742  -0.003430
36:  (1-10,2-9,3-4,5-6,7-8)    -0.188591   0.104449
37:  (1-10,2-9,3-6,4-5,7-8)    -0.006336  -0.001762
38:  (1-2,3-10,4-9,5-8,6-7)     0.072337   0.006189
39:  (1-10,2-3,4-9,5-8,6-7)    -0.022086   0.001141
40:  (1-10,2-9,3-4,5-8,6-7)    -0.094424  -0.013331
41:  (1-10,2-9,3-8,4-5,6-7)     0.000000   0.000000
42:  (1-10,2-9,3-8,4-7,5-6)     0.052979   0.018802
```
[a] This is the PP structure

E. CASVB/aug-cc-pV5Z for HC≡CH molecule (optimized R_{CC}=1.2111Å)

Table S20a. Renormalized input spin function coefficients (Kotani spin basis):

k	Spin-Coupling pattern	Coefficient	Weight
1:	((1/2)1(3/2)2(5/2)2(3/2)1(1/2))	0.039874	0.001590
2:	((1/2)1(3/2)2(3/2)2(3/2)1(1/2))	-0.022906	0.000525
3:	((1/2)1(3/2)1(3/2)2(3/2)1(1/2))	-0.039539	0.001563
4:	((1/2)1(1/2)1(3/2)2(3/2)1(1/2))	0.022672	0.000514
5:	((1/2)0(1/2)1(3/2)2(3/2)1(1/2))	0.029429	0.000866
6:	((1/2)1(3/2)2(3/2)1(3/2)1(1/2))	0.000574	0.000000
7:	((1/2)1(3/2)1(3/2)1(3/2)1(1/2))	-0.143335	0.020545
8:	((1/2)1(1/2)1(3/2)1(3/2)1(1/2))	0.084741	0.007181
9:	((1/2)0(1/2)1(3/2)1(3/2)1(1/2))	0.096390	0.009291
10:	((1/2)1(3/2)1(1/2)1(3/2)1(1/2))	0.084741	0.007181
11:	((1/2)1(1/2)1(1/2)1(3/2)1(1/2))	-0.051942	0.002698
12:	((1/2)0(1/2)1(1/2)1(3/2)1(1/2))	-0.053881	0.002903
13:	((1/2)1(1/2)0(1/2)1(3/2)1(1/2))	-0.001534	0.000002
14:	((1/2)0(1/2)0(1/2)1(3/2)1(1/2))	-0.109810	0.012058
15:	((1/2)1(3/2)2(3/2)1(1/2)1(1/2))	-0.000406	0.000000
16:	((1/2)1(3/2)1(3/2)1(1/2)1(1/2))	0.101353	0.010272
17:	((1/2)1(1/2)1(3/2)1(1/2)1(1/2))	-0.059921	0.003590
18:	((1/2)0(1/2)1(3/2)1(1/2)1(1/2))	-0.068158	0.004645

```
19:  ((1/2)1(3/2)1(1/2)1(1/2)1(1/2))    -0.059921    0.003590
20:  ((1/2)1(1/2)1(1/2)1(1/2)1(1/2))     0.036729    0.001349
21:  ((1/2)0(1/2)1(1/2)1(1/2)1(1/2))     0.038100    0.001452
22:  ((1/2)1(1/2)0(1/2)1(1/2)1(1/2))     0.001085    0.000001
23:  ((1/2)0(1/2)0(1/2)1(1/2)1(1/2))     0.077648    0.006029
24:  ((1/2)1(3/2)1(1/2)0(1/2)1(1/2))    -0.016788    0.000282
25:  ((1/2)1(1/2)1(1/2)0(1/2)1(1/2))     0.006393    0.000041
26:  ((1/2)0(1/2)1(1/2)0(1/2)1(1/2))     0.012520    0.000157
27:  ((1/2)1(1/2)0(1/2)0(1/2)1(1/2))     0.017399    0.000303
28:  ((1/2)0(1/2)0(1/2)0(1/2)1(1/2))     0.187263    0.035068
29:  ((1/2)1(3/2)2(3/2)1(1/2)0(1/2))    -0.000703    0.000000
30:  ((1/2)1(3/2)1(3/2)1(1/2)0(1/2))     0.175549    0.030817
31:  ((1/2)1(1/2)1(3/2)1(1/2)0(1/2))    -0.103786    0.010771
32:  ((1/2)0(1/2)1(3/2)1(1/2)0(1/2))    -0.118053    0.013936
33:  ((1/2)1(3/2)1(1/2)1(1/2)0(1/2))    -0.103786    0.010771
34:  ((1/2)1(1/2)1(1/2)1(1/2)0(1/2))     0.063616    0.004047
35:  ((1/2)0(1/2)1(1/2)1(1/2)0(1/2))     0.065991    0.004355
36:  ((1/2)1(1/2)0(1/2)1(1/2)0(1/2))     0.001879    0.000004
37:  ((1/2)0(1/2)0(1/2)1(1/2)0(1/2))     0.134489    0.018087
38:  ((1/2)1(3/2)1(1/2)0(1/2)0(1/2))    -0.004508    0.000020
39:  ((1/2)1(1/2)1(1/2)0(1/2)0(1/2))    -0.013479    0.000182
40:  ((1/2)0(1/2)1(1/2)0(1/2)0(1/2))     0.010703    0.000115
41:  ((1/2)1(1/2)0(1/2)0(1/2)0(1/2))    -0.004101    0.000017
42:  ((1/2)0(1/2)0(1/2)0(1/2)0(1/2))     0.879306    0.773179[a]
```

[a.] This is the PP structure.

Table S20b. Permuted spin function coefficients (Kotani spin basis):

k	Spin-Coupling pattern	Coefficient	Weight
1:	((1/2)1(3/2)2(5/2)2(3/2)1(1/2))	0.039874	0.001590
2:	((1/2)1(3/2)2(3/2)2(3/2)1(1/2))	-0.022906	0.000525
3:	((1/2)1(3/2)1(3/2)2(3/2)1(1/2))	-0.039539	0.001563
4:	((1/2)1(1/2)1(3/2)2(3/2)1(1/2))	0.022672	0.000514
5:	((1/2)0(1/2)1(3/2)2(3/2)1(1/2))	0.029429	0.000866
6:	((1/2)1(3/2)2(3/2)1(3/2)1(1/2))	0.000574	0.000000
7:	((1/2)1(3/2)1(3/2)1(3/2)1(1/2))	-0.143335	0.020545
8:	((1/2)1(1/2)1(3/2)1(3/2)1(1/2))	0.084741	0.007181
9:	((1/2)0(1/2)1(3/2)1(3/2)1(1/2))	0.096390	0.009291
10:	((1/2)1(3/2)1(1/2)1(3/2)1(1/2))	0.084741	0.007181
11:	((1/2)1(1/2)1(1/2)1(3/2)1(1/2))	-0.051942	0.002698
12:	((1/2)0(1/2)1(1/2)1(3/2)1(1/2))	-0.053881	0.002903
13:	((1/2)1(1/2)0(1/2)1(3/2)1(1/2))	-0.001534	0.000002
14:	((1/2)0(1/2)0(1/2)1(3/2)1(1/2))	-0.109810	0.012058
15:	((1/2)1(3/2)2(3/2)1(1/2)1(1/2))	-0.000406	0.000000
16:	((1/2)1(3/2)1(3/2)1(1/2)1(1/2))	0.101353	0.010272
17:	((1/2)1(1/2)1(3/2)1(1/2)1(1/2))	-0.059921	0.003590
18:	((1/2)0(1/2)1(3/2)1(1/2)1(1/2))	-0.068158	0.004645
19:	((1/2)1(3/2)1(1/2)1(1/2)1(1/2))	-0.059921	0.003590
20:	((1/2)1(1/2)1(1/2)1(1/2)1(1/2))	0.036729	0.001349
21:	((1/2)0(1/2)1(1/2)1(1/2)1(1/2))	0.038100	0.001452
22:	((1/2)1(1/2)0(1/2)1(1/2)1(1/2))	0.001085	0.000001

```
23: ((1/2)0(1/2)0(1/2)1(1/2)1(1/2))     0.077648     0.006029
24: ((1/2)1(3/2)1(1/2)0(1/2)1(1/2))    -0.016788     0.000282
25: ((1/2)1(1/2)1(1/2)0(1/2)1(1/2))     0.006393     0.000041
26: ((1/2)0(1/2)1(1/2)0(1/2)1(1/2))     0.012520     0.000157
27: ((1/2)1(1/2)0(1/2)0(1/2)1(1/2))     0.017399     0.000303
28: ((1/2)0(1/2)0(1/2)0(1/2)1(1/2))     0.187263     0.035068
29: ((1/2)1(3/2)2(3/2)1(1/2)0(1/2))    -0.000703     0.000000
30: ((1/2)1(3/2)1(3/2)1(1/2)0(1/2))     0.175549     0.030817
31: ((1/2)1(1/2)1(3/2)1(1/2)0(1/2))    -0.103786     0.010771
32: ((1/2)0(1/2)1(3/2)1(1/2)0(1/2))    -0.118053     0.013936
33: ((1/2)1(3/2)1(1/2)1(1/2)0(1/2))    -0.103786     0.010771
34: ((1/2)1(1/2)1(1/2)1(1/2)0(1/2))     0.063616     0.004047
35: ((1/2)0(1/2)1(1/2)1(1/2)0(1/2))     0.065991     0.004355
36: ((1/2)1(1/2)0(1/2)1(1/2)0(1/2))     0.001879     0.000004
37: ((1/2)0(1/2)0(1/2)1(1/2)0(1/2))     0.134489     0.018087
38: ((1/2)1(3/2)1(1/2)0(1/2)0(1/2))    -0.004508     0.000020
39: ((1/2)1(1/2)1(1/2)0(1/2)0(1/2))    -0.013479     0.000182
40: ((1/2)0(1/2)1(1/2)0(1/2)0(1/2))     0.010703     0.000115
41: ((1/2)1(1/2)0(1/2)0(1/2)0(1/2))    -0.004101     0.000017
42: ((1/2)0(1/2)0(1/2)0(1/2)0(1/2))     0.879306     0.773179a
```
[a] This is the PP structure

Kotani to Rumer transformation

Table S21a Transformed spin function coefficients (Rumer spin basis):

```
 k   Spin-Coupling pattern   Coefficient     Weight
-----------------------------------------------------------------
 1: (1-2,3-4,5-6,7-8,9-10)     1.034210   0.909387a
 2: (1-4,2-3,5-6,7-8,9-10)     0.024339  -0.010787
 3: (1-2,3-6,4-5,7-8,9-10)     0.039592  -0.017040
 4: (1-6,2-3,4-5,7-8,9-10)    -0.019160  -0.003963
 5: (1-6,2-5,3-4,7-8,9-10)    -0.043499   0.018970
 6: (1-2,3-4,5-8,6-7,9-10)     0.149659  -0.048367
 7: (1-4,2-3,5-8,6-7,9-10)     0.005849   0.000964
 8: (1-2,3-8,4-5,6-7,9-10)     0.022311   0.004606
 9: (1-8,2-3,4-5,6-7,9-10)     0.016767  -0.000980
10: (1-8,2-5,3-4,6-7,9-10)    -0.002527  -0.000174
11: (1-2,3-8,4-7,5-6,9-10)    -0.068429   0.038055
12: (1-8,2-3,4-7,5-6,9-10)     0.078639   0.014842
13: (1-8,2-7,3-4,5-6,9-10)     0.308576  -0.072576
14: (1-8,2-7,3-6,4-5,9-10)     0.004203   0.000469
15: (1-2,3-4,5-6,7-10,8-9)     0.245190  -0.068035
16: (1-4,2-3,5-6,7-10,8-9)     0.034329   0.005272
17: (1-2,3-6,4-5,7-10,8-9)     0.028530   0.004094
18: (1-6,2-3,4-5,7-10,8-9)    -0.004795   0.000335
19: (1-6,2-5,3-4,7-10,8-9)    -0.039123  -0.004848
20: (1-2,3-4,5-10,6-7,8-9)    -0.008802  -0.001221
21: (1-4,2-3,5-10,6-7,8-9)     0.000000   0.000000
22: (1-2,3-10,4-5,6-7,8-9)     0.063563  -0.004560
23: (1-10,2-3,4-5,6-7,8-9)     0.021837   0.000764
24: (1-10,2-5,3-4,6-7,8-9)    -0.070248   0.004352
```

```
25:  (1-2,3-10,4-7,5-6,8-9)      0.072365   0.010040
26:  (1-10,2-3,4-7,5-6,8-9)      0.092085  -0.007070
27:  (1-10,2-7,3-4,5-6,8-9)      0.010919   0.001515
28:  (1-10,2-7,3-6,4-5,8-9)      0.010919  -0.000783
29:  (1-2,3-4,5-10,6-9,7-8)     -0.167262   0.093018
30:  (1-4,2-3,5-10,6-9,7-8)     -0.005849  -0.001628
31:  (1-2,3-10,4-5,6-9,7-8)      0.052171   0.011683
32:  (1-10,2-3,4-5,6-9,7-8)      0.005070  -0.000752
33:  (1-10,2-5,3-4,6-9,7-8)     -0.067720  -0.024880
34:  (1-2,3-10,4-9,5-6,7-8)      0.213158  -0.068889
35:  (1-10,2-3,4-9,5-6,7-8)      0.013446   0.003422
36:  (1-10,2-9,3-4,5-6,7-8)     -0.286739   0.184692
37:  (1-10,2-9,3-6,4-5,7-8)      0.017635   0.005620
38:  (1-2,3-10,4-9,5-8,6-7)      0.052645   0.006472
39:  (1-10,2-3,4-9,5-8,6-7)      0.000000   0.000000
40:  (1-10,2-9,3-4,5-8,6-7)     -0.070248  -0.016445
41:  (1-10,2-9,3-8,4-5,6-7)      0.021837  -0.003327
42:  (1-10,2-9,3-8,4-7,5-6)      0.092085   0.037755
```
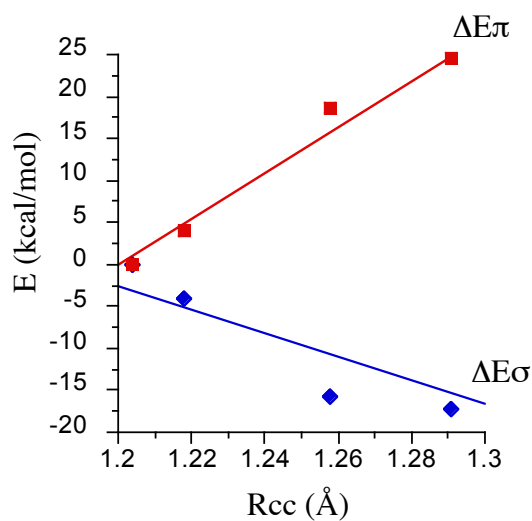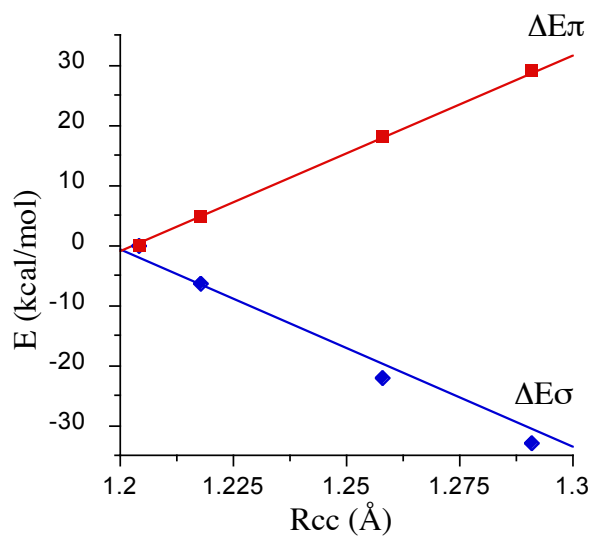a. This is the PP structure.

Note: The above weights of the Rumer structures conserve the same orbital ordering as used for obtaining the Kotani weights. Since the Rumer basis is not orthogonal, when one changes the ordering of the orbitals, the coefficients and weights for the Rumer calculations also change, e.g., for permuting orbitals 5 and 6 (both being p_x orbitals on atoms A and B), one gets $W_{PP}(C_2)=0.540$ and W_{PP} (HC≡CH)=0.351.

VIII. The Balance of σ- and π-Energies Upon Bond Stretching.

As discussed in *J. Chem. Theor. Comput.* **7**, 955-968 (2011), the quasiclassical state of HC≡CH and C_2 where the π-bonds are decoupled represents the σ-component of the molecule. This σ-component is represented by the filled σ-MOs of the molecule (hence for C_2 the σ–component does not involve the 4th bond). Calculating the full VB state and the quasicalssical state provides therefore the σ- and π-energies of the molecules, respectively. The two plots below show these energies along the stretching coordinate.

The last two figures show that the two molecules have π-bonds with different characters. In C_2 the bonds have significantly larger charge shift (CS) character than in HCCH. In fact, the C_2 bonds approach being CS-bonds (Ref. 52 for CS bonding). The 4th bond is a CS bond much like the inverted bond in [1.1.1]-propellane. The bonds of HCCH are more covalent.