

# Supporting Information for:

## The Quadruple Bonding in $C_2$ Reproduces The Properties of The Molecule

Sason Shaik<sup>1\*</sup>, David Danovich<sup>1</sup>, Benoit Braida<sup>2</sup>, Philippe C. Hiberty<sup>3\*</sup>

1. Institute of Chemistry and The Lise Meitner-Minerva Center for Computational Quantum Chemistry,  
Hebrew University of Jerusalem, 91904, Jerusalem, Israel

2. UPMC Université Paris 06, CNRS UMR 7616, Laboratoire de Chimie Théorique, C. 137, 4 Place  
Jussieu, 75252 Paris Cedex 05, France

3. Laboratoire de Chimie Physique, UMR CNRS 8000, Université de Paris Sud, 91405 Orsay Cédex,  
France

### Contents

(I)	<b>Methods</b>	S2
(II)	<b>Valence Bond Structures</b>	S2
(III)	<b>Force Constants</b>	S4
(IV)	<b>VB Structures and their weights along the <math>R_{CC}</math> distance</b>	S6
(V)	<b>Bonding-Crossover Pattern of the VB Structures</b>	S16
(VI)	<b>Convergence Properties of the VB Energies</b>	S19
(VII)	<b>VB Optimization of <math>R_{CC}</math> and Force Constant Values (<math>k_{CC}</math>)</b>	S21
(VIII)	<b>Determination of <math>D_{in-situ}</math> values for <math>C_2</math> and HCCH using corresponding quasi-classical states</b>	S23
(IX)	<b>Calculations of Overlap Populations for some orbitals of <math>C_2</math></b>	S25
(X)	<b>Transformation of Orbitals for the CASSCF Wave function</b>	S25
(XI)	<b>Assessments of the Bonding Model in Ref. 21a</b>	S26
(XII)	<b>Triplet State Calculations</b>	S29

## I. Methods

### Valence Bond Calculations

The VB calculations were done for  $C_2$  generally at the VBSCF/6-31G\* level using the XMVB package.<sup>[1]</sup> In one case, we used also VBCISD,<sup>[2]</sup> which performs singles and doubles CI for the local AOs and HAOs, and endows the VB wave function by dynamic correlation. In the calculations described in Figure 5 (text), we used semi-localized Coulson Fischer orbitals to allow for the dative bonds. The VBSCF-QMC calculations (QMC = Quantum Monte Carlo) used a Jastro factor (serving much the same as the  $F_{12}$  factor in explicitly correlated methods) and were carried out using a quadruple zeta basis set, with core pseudo potential, and especially designed for QMC calculations.<sup>[3]</sup>

### II. Valence Bond Structures

According to the Weyl formula,<sup>[4]</sup> the full valence shell of  $C_2$  involves 1764 structures, which are produced automatically by XMVB. The VBSCF(1764) calculations reproduced the same BDE value as the full CI (FCI) method at the same basis set. From the complete set, we systematically devised a truncated structure-set of 88 VB structures that reproduced closely the BDE in agreement with FCI and VBSCF(1764). The 88 structures are detailed below in Scheme S1).

In brief, we start with the 14 covalent structures in Scheme S1a,b based on Rumer's rules.<sup>[5]</sup> Scheme S1a shows the most-highly bonded structures: one with a quadruple bond ( $\Phi_{A,cov}$ ), one with a double  $\pi$ -bond ( $\Phi_{B,cov}$ ), two with ethylenic  $\sigma+\pi$  bonds ( $\Phi_{C,cov}$ ). Scheme S1b shows the other 10 structures (D5-14,cov), which have less covalent bonds. Each covalent structure generates in turn ionic structures (two per each covalent pair).

**Generating a Truncated VB-Set:** Schemes S1c-e show the truncated set of 88 structures. Thus, starting from each covalent structure, we generate all the remaining

ionic structures, corresponding to the respective Lewis structure. For example,  $\Phi_{A,\text{cov}}$  has 4 covalent bonds, and since each such Lewis bond contains also 2 ionic structures, then each bond function (Lewis bond) has 3 structures, one covalent and two ionics. The total set that describes all the Lewis bonds is the product wave function of the 4 bonds, which corresponds to 81 ( $3^4$ ) VB structures, one covalent and 80 ionics (mono-ionic, di-ionic, tri-ionic, etc). As we show in Table S6, the energy of the quadruply bonded structure A, with a truncated set of only 21 structures is practically identical to the energy of A with 81 structures. We therefore have an effective way of truncating the huge VB set into a compact one, based on the following logic:

The truncated VB set, for the first four covalent structures ( $\Phi_{A,\text{cov}}-\Phi_{C1,2,\text{cov}}$ ), is generated by using all the *low-lying ionic structures*, in the following manner:

(a) Since there are four electrons pairs in any covalent structure, each pair can generate a pair of mono-ionic structures with opposite sense of the ionicity (+/-)/(-/+ ) by shifting one electron from one atomic orbital (AO) or hybrid atomic orbital (HAO) to the other. This leads to 8 mono-ionic structures.

(b) Di-ionic structures are generated from two electron pairs, by shifting two electrons, one from each singlet-pair. Our selection avoids generation of  $C_2^{+2}$  and  $C_2^{-2}$  centers, ensures that the di-ionic structures are overall neutral or at most mono-ionic and avoids structures having two doubly occupied orbitals on the same atom, leading to 12 di-ionic structures in each group.

In this manner, the lowest energy four covalent structures generate four groups A, B, C1 and C2, each containing 21 VB structures, such that all covalent bonds in all structures are treated on equal footing. This set of 84 structures, VBSCF(84), is very good (compared with VBSCF(1764)) near the equilibrium distance of the molecules up to 2.5 Å.

The VBSCF(84) set misses however structures which describe the dissociation limit of  $C_2$  (taken at an internuclear distance of 10.0Å). The VB structures with the electronic configurations necessary for describing two carbon atoms in their  $^3P$  ground states are six structures shown in Scheme S1f. It is seen that two of them already exist in the set B (two of the di-ionic structures in that set, B16 and B21), and the other four belong to di-ionic structures made from the covalent structure 13 in the Set D.

We therefore add the four structures generated from covalent structure D13 (we label them here as D13-10, D13-11, D13-12 and D13-13 [while in Scheme 3d on the text, simply as D(1-4)]) to the VB(84) and obtain VB(88), which correlates at the dissociation limit to two carbon atoms in their  $^3P$  ground states. The dissociation limit of VB(88) structure differs from VB(1764) by only 0.004 kcal mol<sup>-1</sup>.

If we want however, to generate a Structure A (4-bonds) that correlates all the way to the dissociation limit, we have to add the 6 structures in Scheme S1f.

### III. Force Constants

Force constants  $k_{CC}$  ( $N\text{ cm}^{-1}$ ) for CCSD(T) and MRCI methods for both singlet  $C_2$  and as well for  $HC\equiv CH$ , were calculated using the following equation:

$$k_{cc} = 4\pi^2 c^2 \nu^2 \mu \quad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

where the frequency values  $\nu$  (in  $\text{cm}^{-1}$ ) were obtained from the corresponding frequency calculations using MOLPRO program.<sup>[6]</sup> The force constants for the different types of VB calculations of the singlet  $C_2$  molecule, and the one for the triplet state, were obtained from harmonic approximation as a second derivative of energy  $k_{CC} = d^2E/d^2x$ .

### References

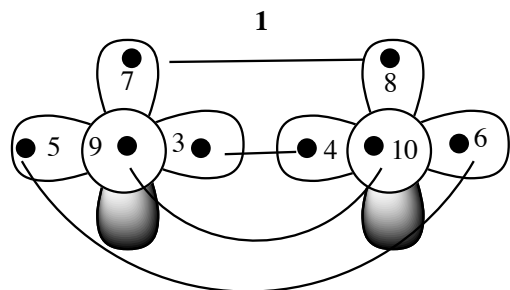
[1] Song L., Mo Y., Zhang Q., Wu W. *J. Comput. Chem.* 2005, 26, 514; Song L., Mo Y., Zhang Q., Wu W. XMVB, version 1.0; Xiamen University: Xiamen, China, 2003.

- [2] Song L., Wu W., Zhang Q.; Shaik S. *J. Comput. Chem.* 2004, 25, 472; Wu W., Song L., Cao Z., Zhang Q., Shaik S. *J. Phys. Chem. A* 2002, 106, 2721.
- [3] Burkatzki, M.; Filippi, C.; Dolg, M. *J. Chem. Phys.* 2007, 126, 234105; Basis sets and corresponding pseudopotentials are available online: <http://burkatzki.com/pseudos/index.2.html>, 2008; Umrigar C.J., Filippi C., Toulouse J. CHAMP, a Quantum Monte Carlo ab initio program, 2012. <http://pages.physics.comell.edu/~cyrus/champ.html>
- [4] Weyl H. In *The Theory of Groups and Quantum Mechanics*; Dover Publications: New York, 1956.
- [5] Rumer G. *Gottinger Nachr.*, 1932, 3, 337. Pauncz R. *Spin eigenfunctions*, Plenum Press, New York, 1979.
- [6] MOLPRO, version 2010.1, a package of ab initio programs written by H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schutz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. K ppel, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nickla , D. P. O'Neill, P. Palmieri, D. Peng, K. Pfl ger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang. (see [www.molpro.net](http://www.molpro.net)).

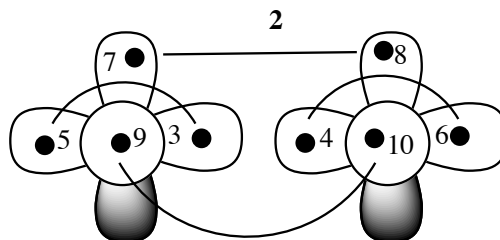
#### IV. VB Structures and their weights along the $R_{CC}$ distance

##### Scheme S1: The Truncated VB Structure-Set

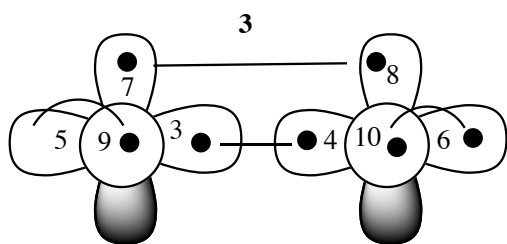
(a) Covalent Structures, A-C (Structures 1-4)



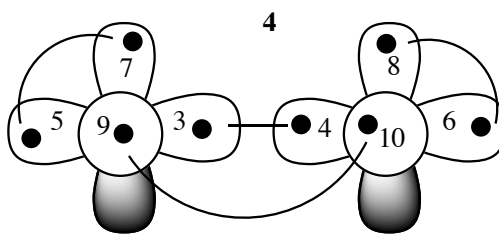
$\Phi_{A,cov}$  (4 bonds)



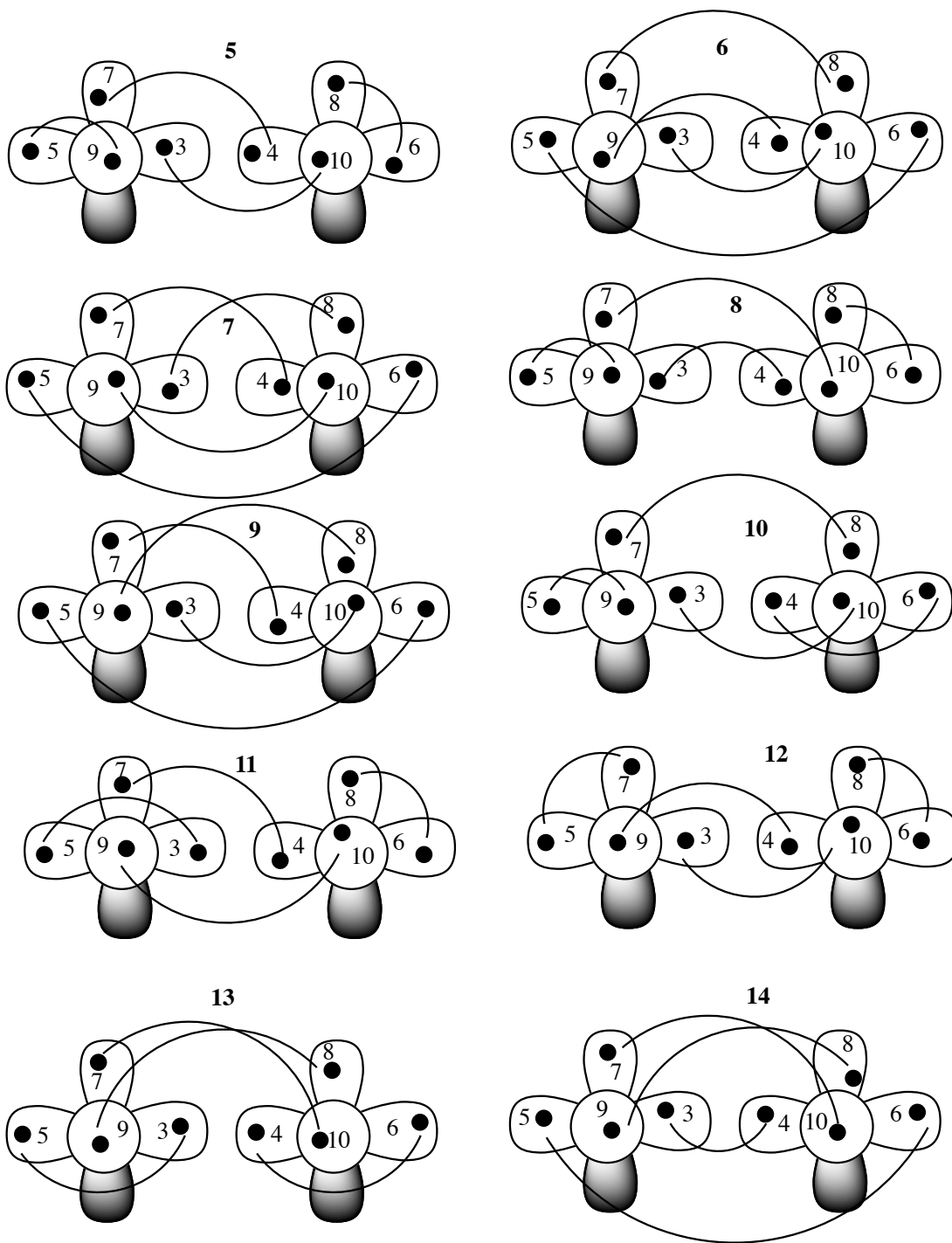
$\Phi_{B,cov}$  (2  $\pi$  bonds)



$\Phi_{C1,2,cov}$  (ethylenic double bond)

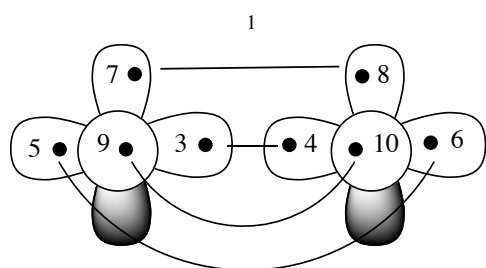


(b) Covalent Structures, D (Structures D5-14, cov)

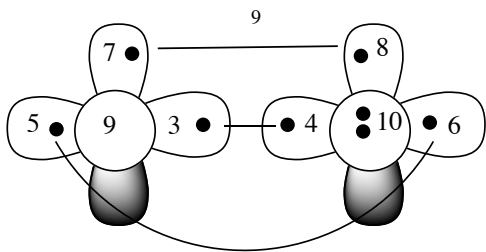
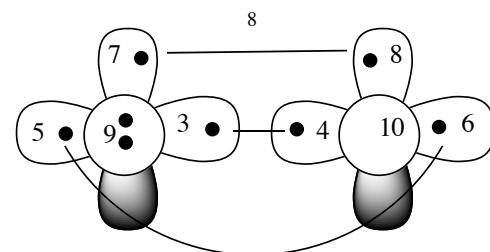
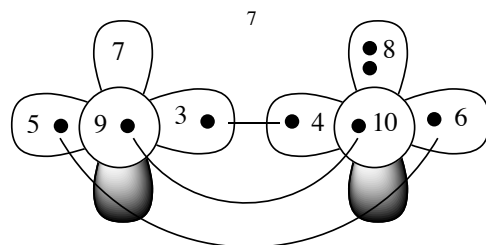
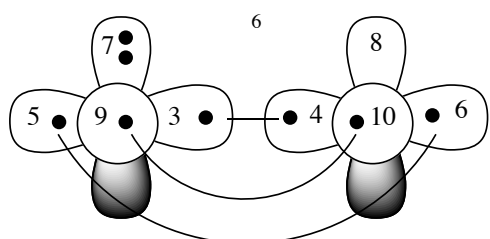
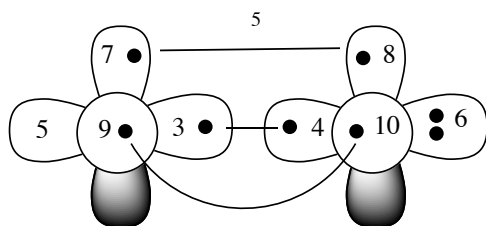
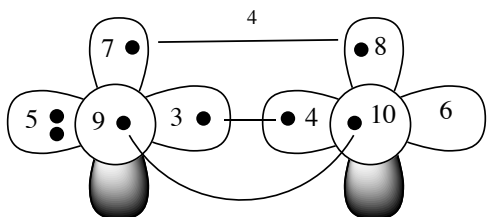
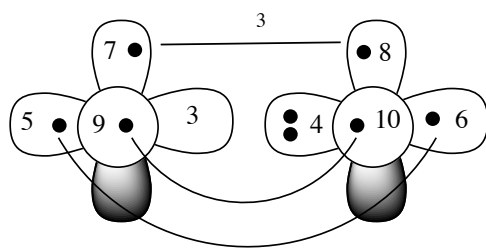
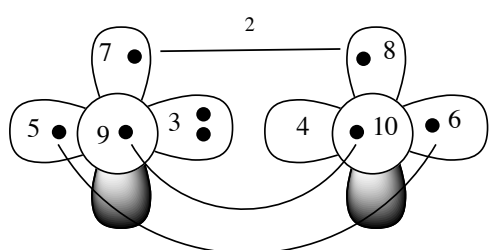


(c) The Set A of 21 VB Structures Generated from  $\Phi_{A,\text{cov}}$  (structure 1 in scheme S1a)

Covalent Structure for Set A

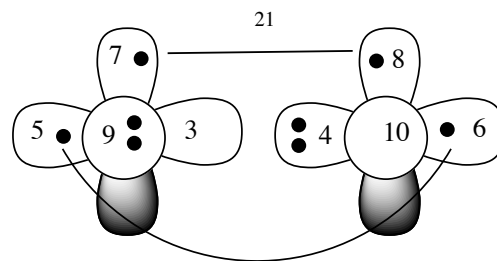
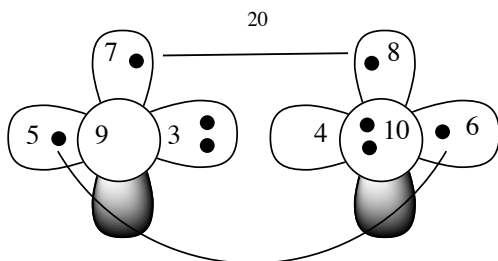
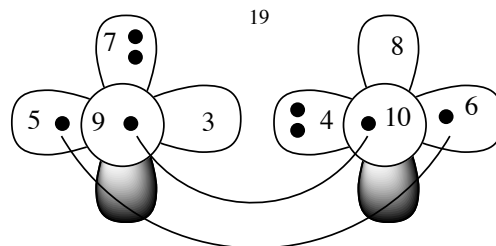
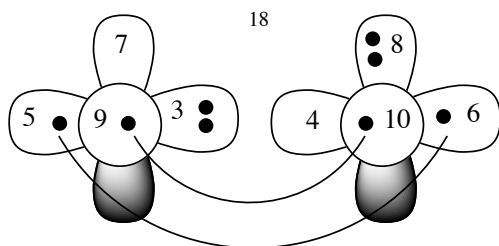
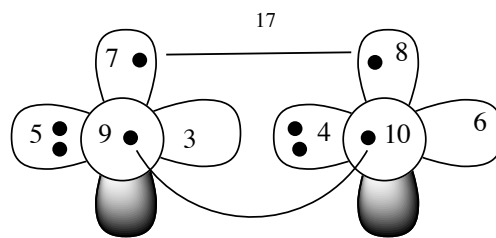
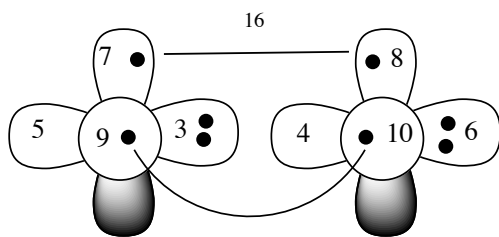
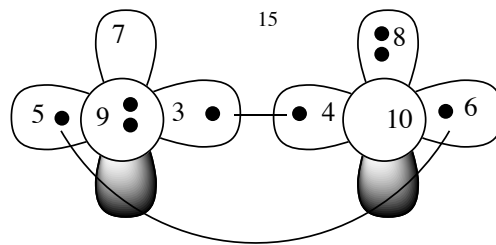
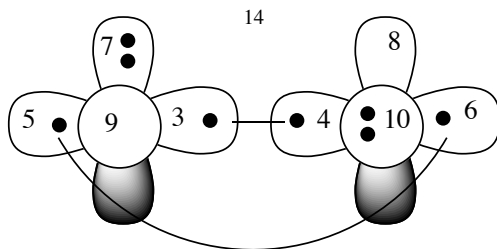
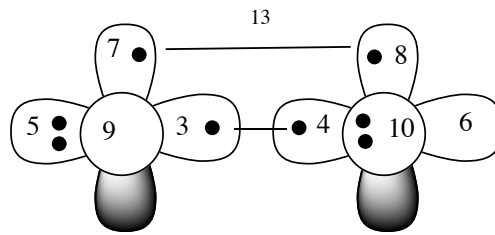
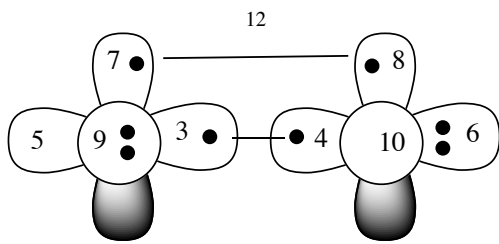
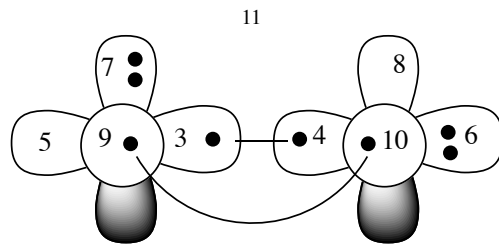
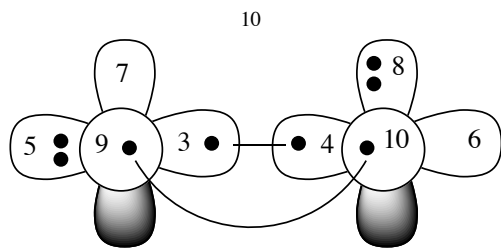


Mono-ionic Structures for Set A



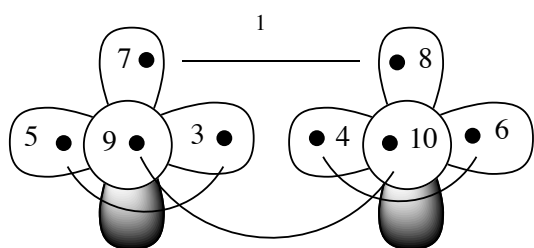


Di-ionic Structures for Set A

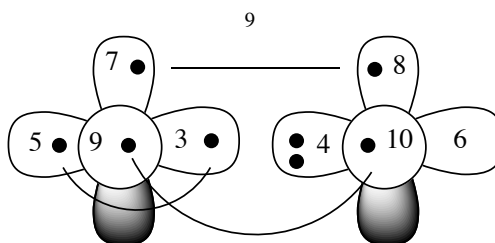
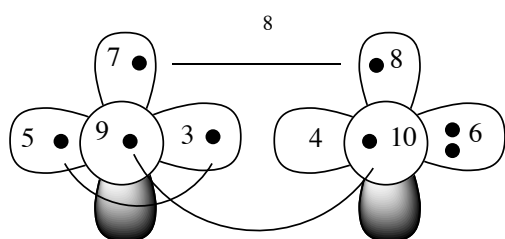
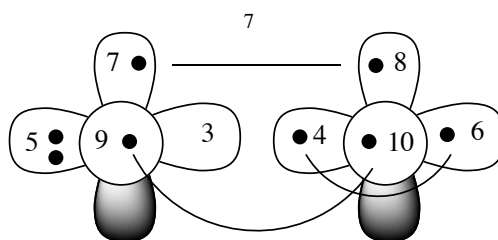
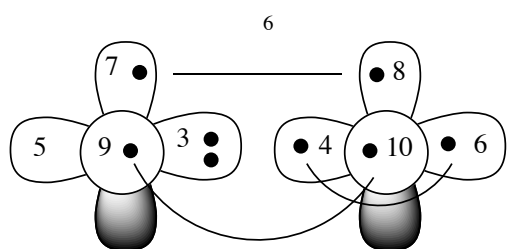
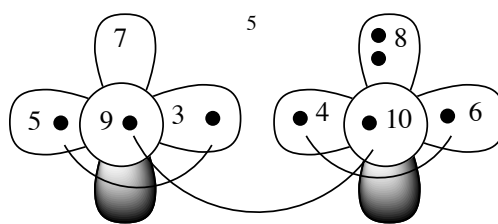
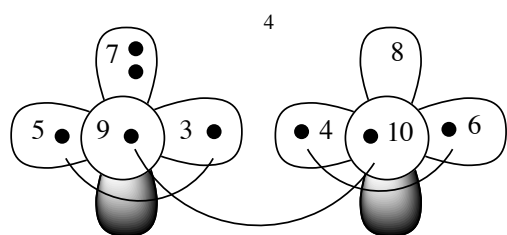
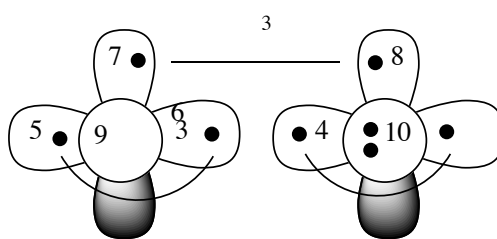
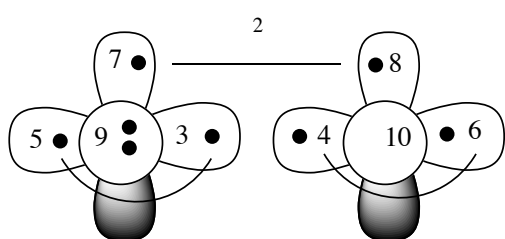


(d) The Set B of 21 VB Structures Generated from  $\Phi_{B,cov}$  (structure 2 in scheme S1a)

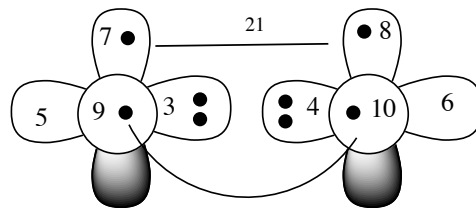
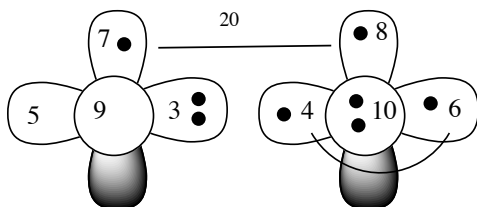
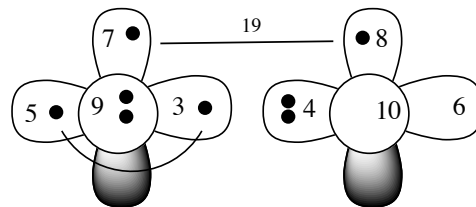
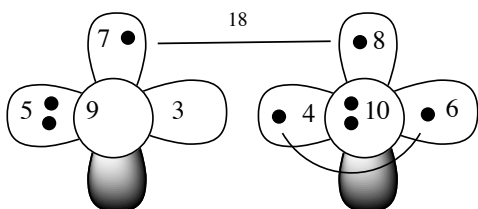
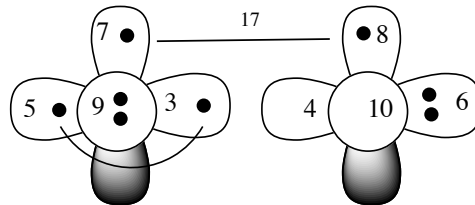
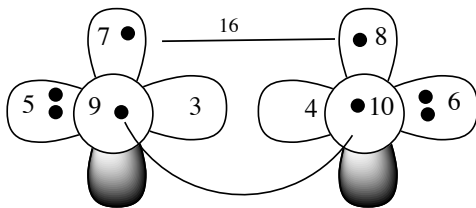
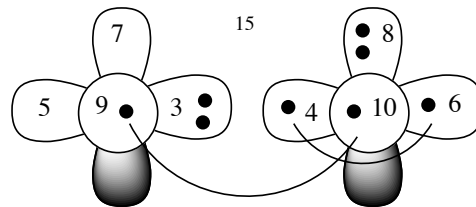
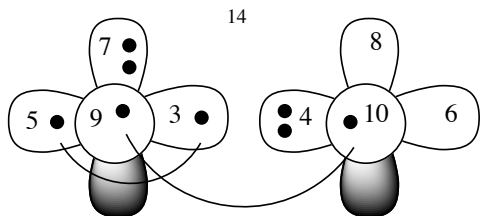
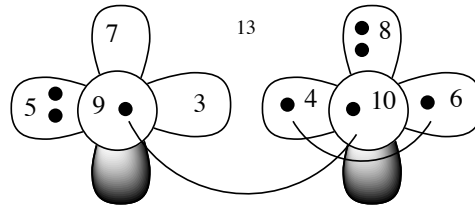
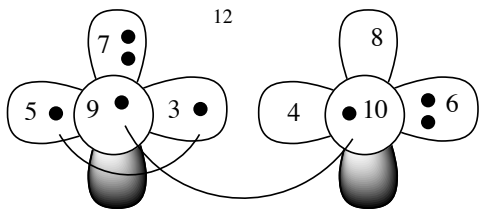
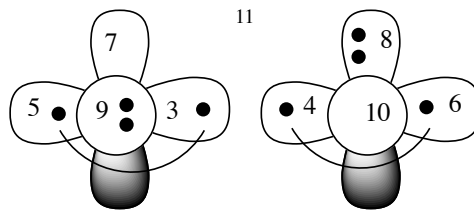
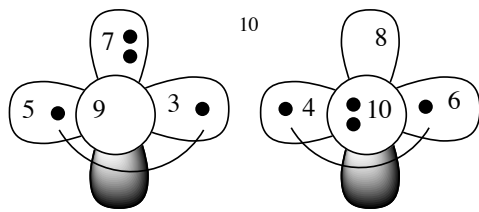
Covalent Structure for Set B



Mono-ionic Structures for Set B

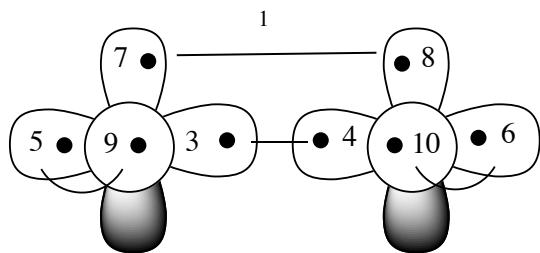


Di-ionic Structures for Set B

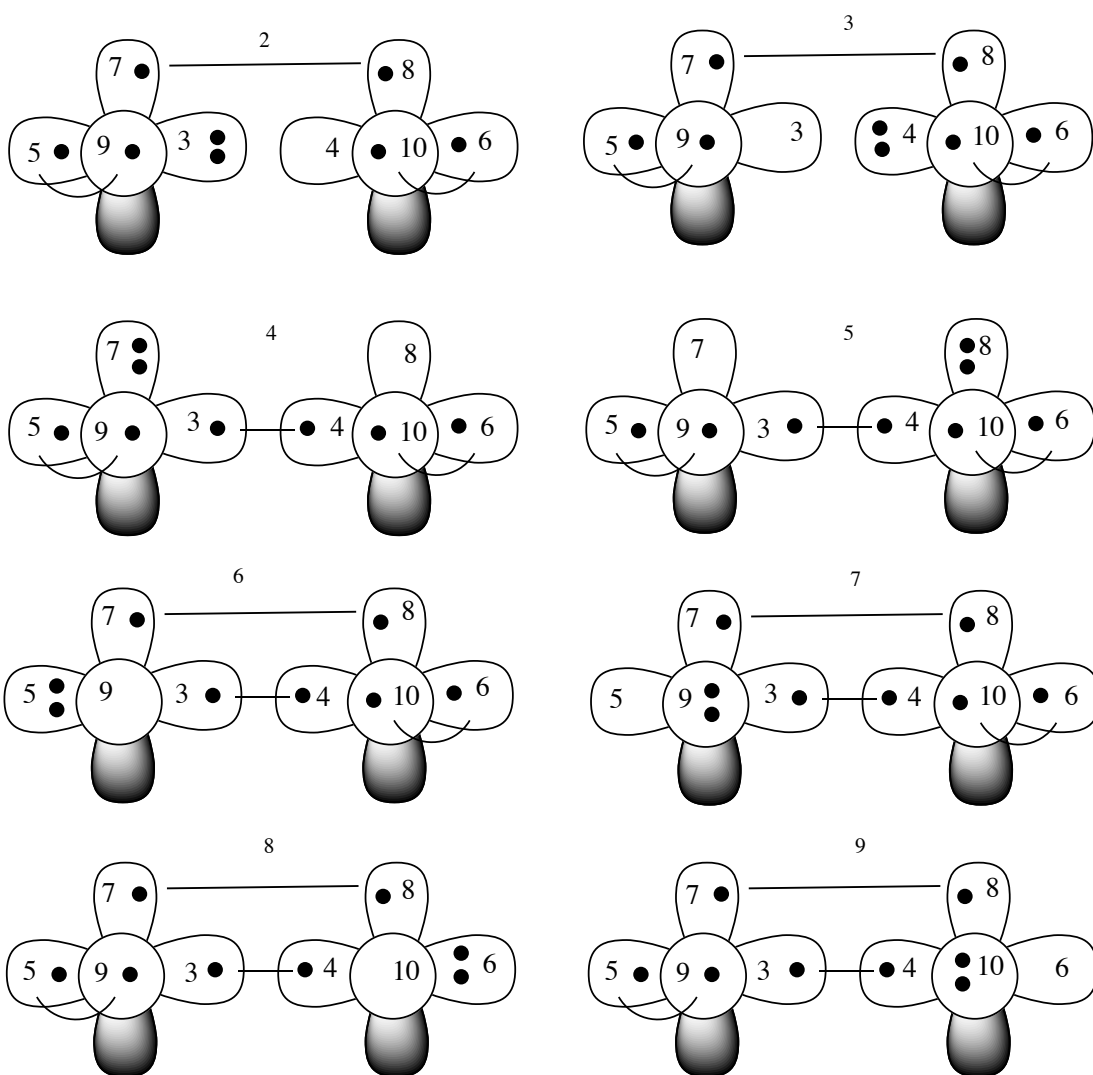


(e) The C Set of 42 VB Structures Generated from  $\Phi_{C1,2,cov}$

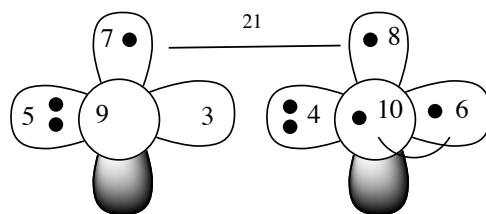
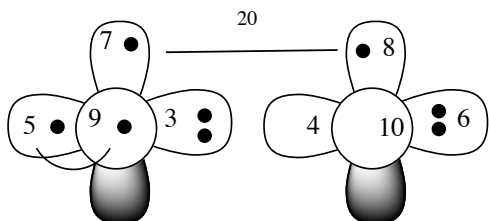
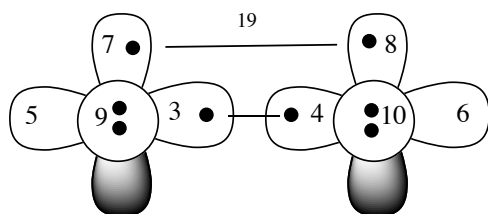
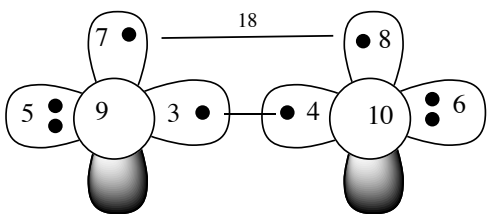
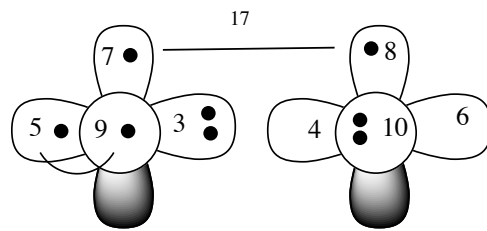
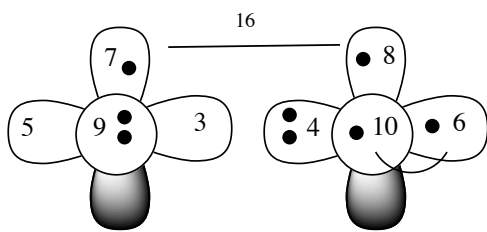
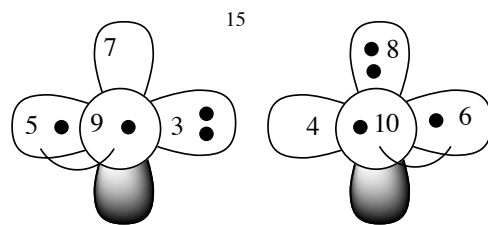
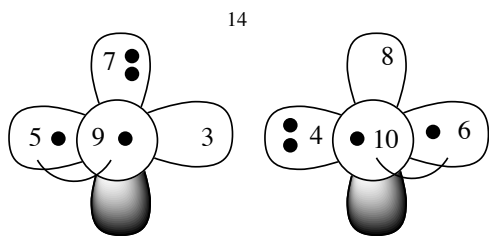
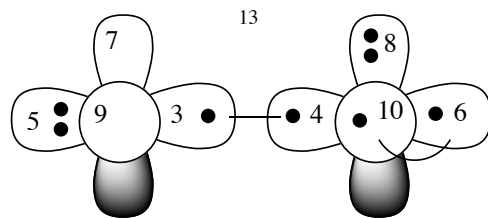
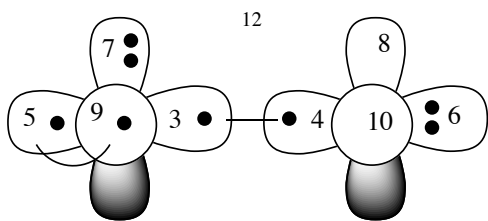
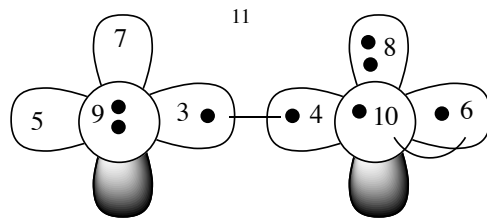
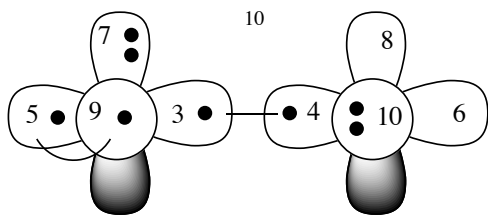
Covalent Structure C1 for Set C



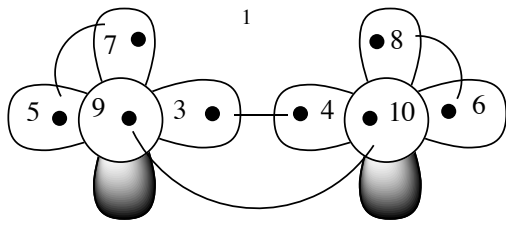
Mono-ionic Structures made form C1 for Set C



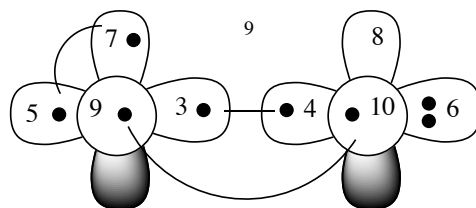
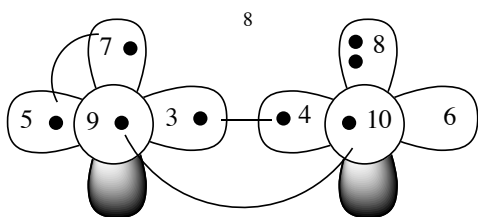
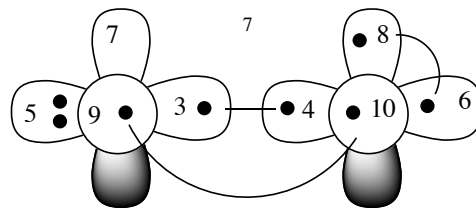
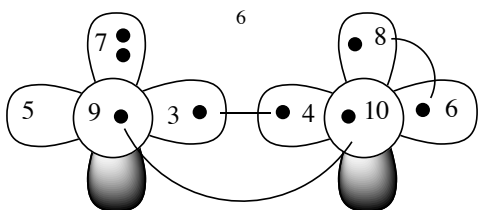
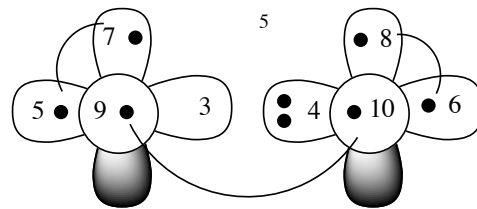
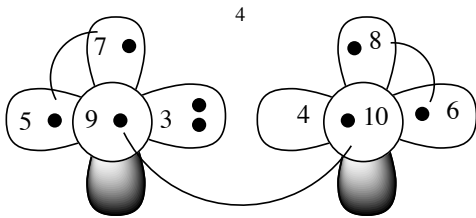
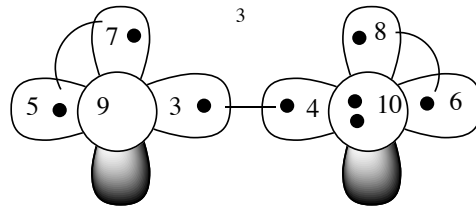
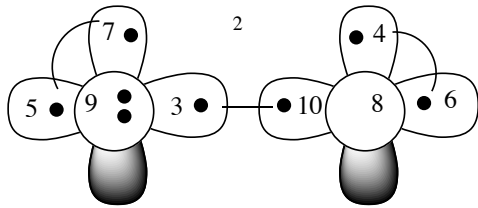
Di-ionic Structures made form C1 for Set C



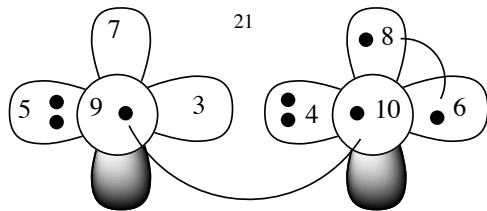
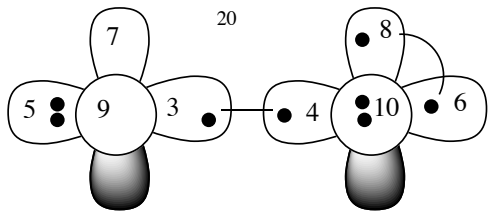
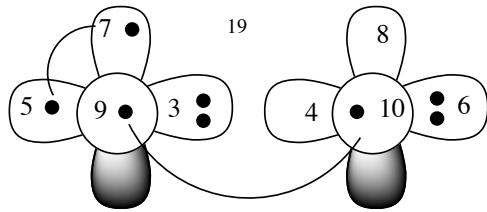
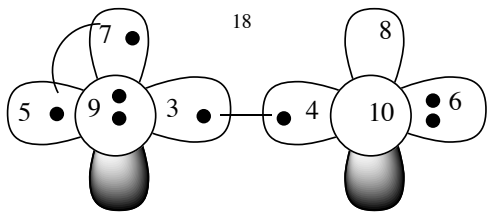
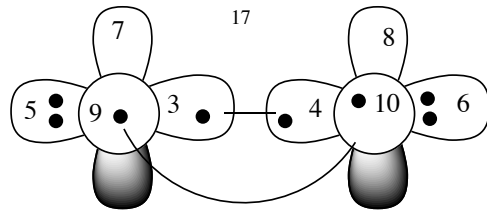
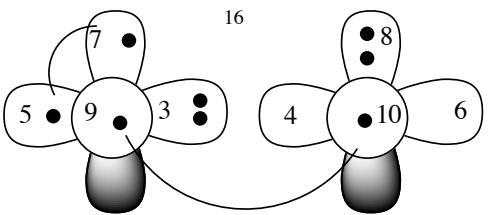
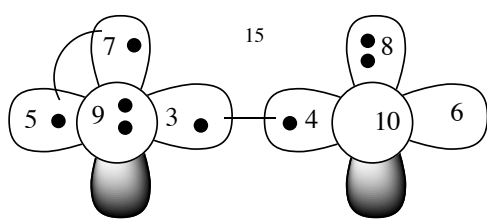
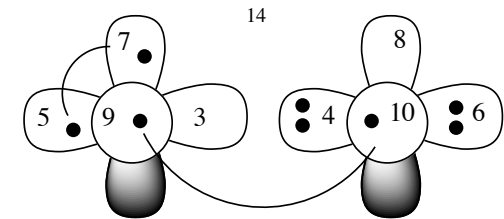
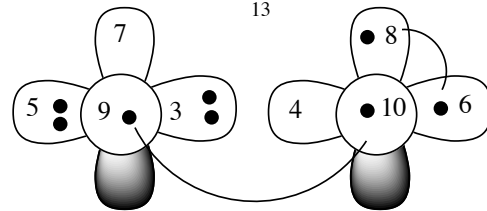
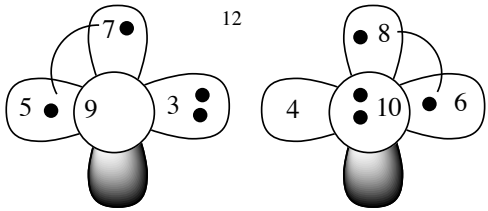
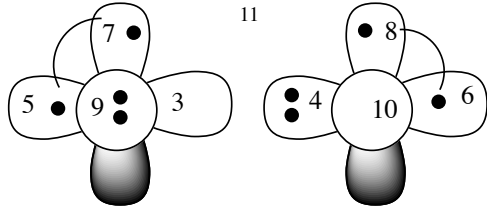
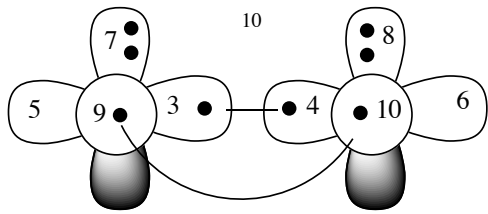
Covalent Structure C2 for Set C



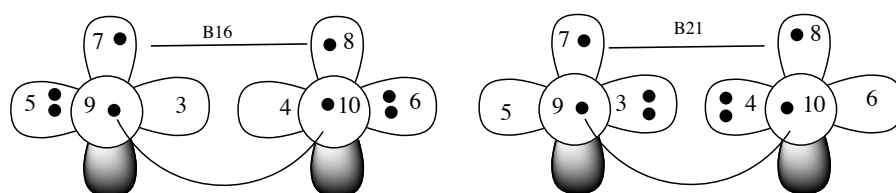
Mono-ionic Structures made form C2 for Set C



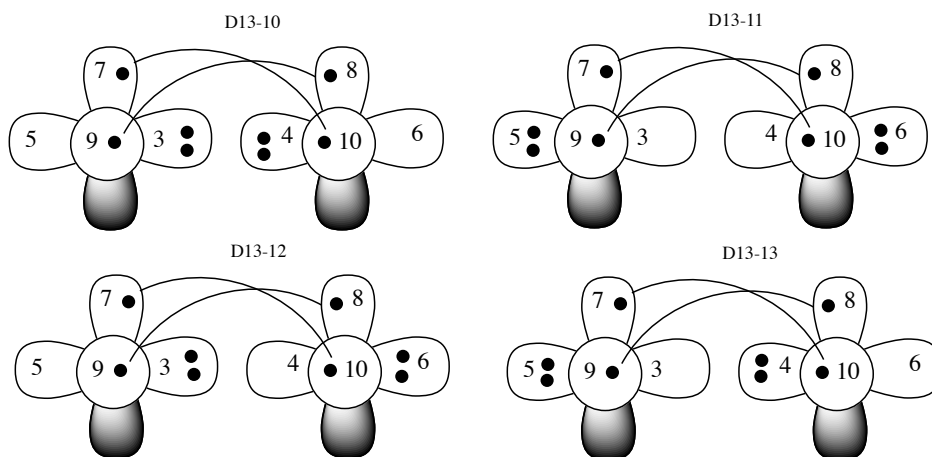
Di-ionic Structures made form C2 for Set C



(f) VB Structures Important at the Dissociation Limit



Structures made form covalent structure 13 in Set D in Scheme 1Sb



**V. Bonding-Crossover Pattern of the VB Structures:**

**Table S1.** Total energies  $E_t$  (au), Löwdin and Inverse weights (renormalized weights) calculated by VBSCF/6-31G\* of  $C_2$  molecule with only the four covalent structures A, B, C1,2.

R, Å	Covalent Structures, A+B+C1,2		
	$E_t$	Lowdin Weights	Inverse Weights
1.2	-75.461745	0.805 (A) 0.192 (B) 0.003 (C)	0.795 (A) 0.000 (B) 0.205 (C)
1.26	-75.465642	0.814 (A) 0.185 (B) 0.001 (C)	0.784 (A) 0.000 (B) 0.215 (C)
1.3	-75.462834	0.817 (A) 0.182 (B) 0.000 (C)	0.778 (A) 0.000 (B) 0.222 (C)
1.4	-75.444430	0.814 (A) 0.186 (B) 0.000 (C)	0.762 (A) 0.001 (B) 0.237 (C)
1.5	-75.418371	0.792 (A) 0.208 (B) 0.000 (C)	0.747 (A) 0.003 (B) 0.250 (C)
1.6	-75.392979	0.746 (A)	0.729 (A)

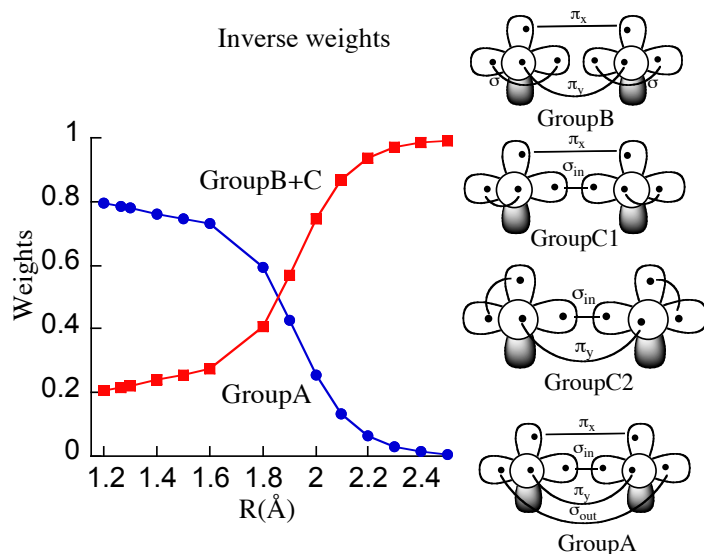


		0.254 (B) 0.000 (C)	0.015 (B) 0.258 (C)
1.8	-75.360884	0.576 (A) 0.414 (B) 0.010 (C)	0.593 (A) 0.175 (B) 0.232 (C)
1.9	-75.354922	0.485 (A) 0.492 (B) 0.023 (C)	0.429 (A) 0.391 (B) 0.180 (C)
2.0	-75.352930	0.412 (A) 0.552 (B) 0.036 (C)	0.256 (A) 0.628 (B) 0.117 (C)
2.1	-75.352990	0.357 (A) 0.595 (B) 0.048 (C)	0.132 (A) 0.803 (B) 0.065 (C)
2.2	-75.353942	0.317 (A) 0.625 (B) 0.058 (C)	0.063 (A) 0.904 (B) 0.034 (C)
2.3	-75.355165	0.290 (A) 0.644 (B) 0.066 (C)	0.029 (A) 0.954 (B) 0.016 (C)
2.4	-75.356350	0.271 (A) 0.657 (B) 0.072 (C)	0.014 (A) 0.978 (B) 0.008 (C)
2.5	-75.357378	0.258 (A) 0.665 (B) 0.076 (C)	0.007 (A) 0.989 (B) 0.002 (C)

**Table S2. Covalent Structures:** Relative total energies (au) of the covalent structures A, B and C1,2 at 1.244Å.<sup>a</sup>

		R=1.244Å
	# bonds	E <sub>t</sub> , au
Group A	4 bonds	-75.425141
Group B	2 π-bonds	-75.217432
Group C1,2	(π+ σ)bonds	-75.205424

a) 1.244Å is the energy minimum of Group A (all 21 structures)

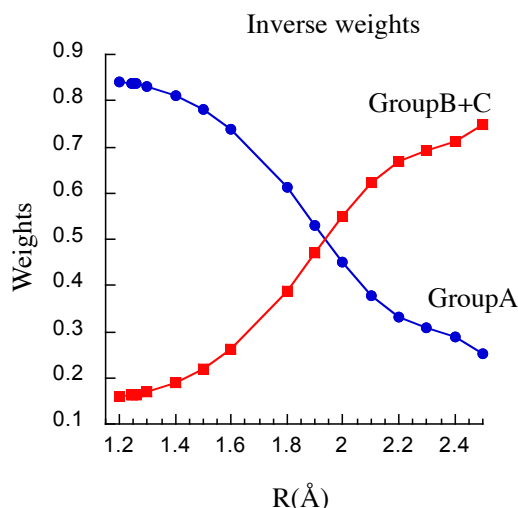


**Figure S1:** Bond-Crossover Patterns of the 4 Covalent Structures. The Combined weights of B+C1,2 cross the weight of A at  $R \approx 1.9 \text{ \AA}$ . At the right we show the covalent VB structures near the respective curves.

**Table S3.** Inverse weights ( $\omega$ ) for groups A and B+C and total energies  $E_t$  (au) for A+B+C using the full set of 84 structures.

$R(\text{\AA})$	$\omega(\text{A})$	$\omega(\text{B+C})$	$E_t^a$
1.2	0.840	0.159	-.592913
1.24	0.839	0.161	-.597120
1.244	0.838	0.162	-.597233
1.25	0.837	0.163	-.597308
1.26	0.836	0.164	-.597191
1.3	0.832	0.168	-.594037
1.4	0.811	0.189	-.572554
1.5	0.780	0.220	-.540641
1.6	0.737	0.263	-.505780
1.8	0.611	0.389	-.443074
1.9	0.530	0.470	-.418920
2.0	0.449	0.551	-.400233
2.1	0.378	0.622	-.386597
2.2	0.331	0.669	-.377186
2.3	0.308	0.692	-.371011
2.4	0.288	0.712	-.367124
2.5	0.252	0.748	-.364747

a) -75. au.



**Figure S3.** Dependence of the weights of the full sets A and B+C on the C-C distance. The calculations were done with 84 structures with VBSCF/6-31G(d) level of theory.

**Table S4.** Relative total energies (au) of the VB Sets (VB Set A is quadruply bonded, VB Set B is two  $\pi$  bonded, VB Set C is  $\pi$  and  $\sigma$  bonded) at 1.244Å

	$E_t$ , au (full sets) <sup>a</sup>	$E_t$ , au (covalent-only) <sup>b</sup>
Group A	-75.5703698	-75.425141
Group B	-75.3640544	-75.217432
Group C	-75.4012283	-75.205424

a) Total energy of the calculation involves all structures of the respective sets (21 structures – Sets A and B and 42 structures for Set C). b) Total energy of the main covalent structure only. For the set C there are 2 covalent structures.

## VI. Convergence Properties of the VB Energies

Table S5 shows that VBSCF(1764) is as good as FCI and MRCI. Full CASSCF artificially overestimates the BDE, since the dissociation limit is not accurate. Using state averaged CASSCF gives a reasonable BDE, slightly lower than FCI, MRCI, and VBSCF(1764).

**Table S5.** Total energies  $E_t$  (au) at 1.244Å and 10.0 calculated with 6-31G\* basis sets by different computational method and bond dissociation energies (BDE, kcal mol<sup>-1</sup>) for these method (-75.0 au should be added to energy).

	$E_t(1.244\text{Å})$	$E_t(10.0\text{Å})$	BDE
VBSCF(1764)	-.611790	-.391973	137.94
CAS	-.616766	-.391520	141.34 <sup>a</sup>
SA-CAS <sup>b</sup>	-.606261	-.389212	136.20
FCI	-.723072	-.503026	138.08
MRCI	-.719683	-.500000	137.85

a) The CAS curve is not parallel to the FCI curve. Their gaps are 66.71 kcal mol<sup>-1</sup> at 1.244Å and 69.97 at 10.0Å. Thus the indicated BDE is not meaningful. b) State-Average CASSCF with equal weights for each state. X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, B<sup>1</sup>Δ<sub>g</sub> and B'<sup>1</sup>Σ<sub>g</sub><sup>+</sup> states were averaged.

Table S6 shows the effectiveness of the truncated structure sets. Thus, the truncated set A(21) in entry 1 is as good as the full A(81) set in entry 2. Entries 5 and 6 show the effect of mixing groups B and C into A(21). C is much more important than B. Entry 7 shows that adding the proper dissociation limit to A(21) leads to a BDE value of 113. Using the A(21) without the dissociation limit structures hardly changes the BDE (which is calculated relative to the dissociation limit for the VBSCF(1764)). Using the untruncated A(81) set does not make much of a difference (entry 8) relative to the truncated one A(21). Adding the proper dissociation limit to A+B+C(84) gives a BDE value (entry 11) only 9 kcal mol<sup>-1</sup> short of VB(1764). Augmenting VB(88) with more and more structures converges at 168 structures to within 2.5 kcal/mol less than the full VBCF(174) set.

**Table S6.** VBSCF/6-31G\* total energies (au) at 1.244Å, 10Å and BDE Values (kcal mol<sup>-1</sup>)

Entry	Structures	Total energies at 1.244Å	Total energies at 10.0Å	BDE
1	A(21) <sup>a</sup>	-75.5703698		
2	A(81) <sup>b</sup>	-75.5727311	---	-----
3	B(21) <sup>a</sup>	-75.3640544	----	
4	C(42) <sup>c</sup>	-75.4012283	----	
5	A+B(42) <sup>d</sup>	-75.5726717	----	
6	A+C(63) <sup>e</sup>	-75.5958450	----	
7	A (21)+ 6 Dissoc. Limit Structures (Scheme S1f) <sup>f</sup>	-75.5719453	-75.3919662	112.94/111.95
8	A(81)+ 6 Dissoc. Limit Structures (Scheme S1f) <sup>g</sup>	-75.5742780	-75.3919662	114.40
9	VBCISD: A (21) + 6 Dissoc. Limit Structures (Scheme S1f) <sup>f</sup>	-75.6334658	-75.4274293	129.29
10	A+B+C (84) <sup>h</sup>	-75.5972329		
11	A+B+C+4 Dissoc. Lim. Structures in Scheme S1f (88) <sup>i</sup>	-75.5976613	-75.3919662	129.08
12	A+B+C (84) +D13(21) [105] <sup>j</sup>	-75.5987516	-75.3919662	129.76

13	A+B+C (84) +D1,14(42) [126] <sup>k</sup>	-75.6013394	-75.3919662	131.38
14	A+B+C (84) +D13,14,6,7 (84) [168] <sup>l</sup>	-75.6075730	-75.3919662	135.30
15	92 structure (JCTC paper)	-75.6036155	-75.3919662	132.81
16	1764 structures	-75.6117903	-75.391973	137.94

a) 21 structures, b) 81 structures represent all possible structures in set A, c) 42 structures, d) 42 structures, e) 63 structures, f) 27 structures. The second BDE datum in entry 7 uses A(21) and the energy of the dissociation limit of VB(1764), g) 87 structures, h) 84 structures, i) 88 structures. To groups A, B and C four di-ionic structures (D13-10, D13-11, D13-12, D13-13 scheme S1f) were added, j) the A+B+C(84) set plus 21 structures derived from the covalent structure D13 were added, k) 105 plus 21 structures derived from the covalent structure D14 were added, l) 126 plus 21 structures derived from the covalent structure D6 and 21 structures derived from the covalent structure D7 were added.

## VII. VB Optimization of $R_{CC}$ and Force Constant Values ( $k_{CC}$ )

Table S7 shows that the optimized  $R_{CC}$  and force constant ( $k_{CC}$ ) values for different VB levels do not change much beyond A(1) or A(21) [e.g.  $R_{CC}$  varies by 0.016Å from VB(21) to VB(1764)].

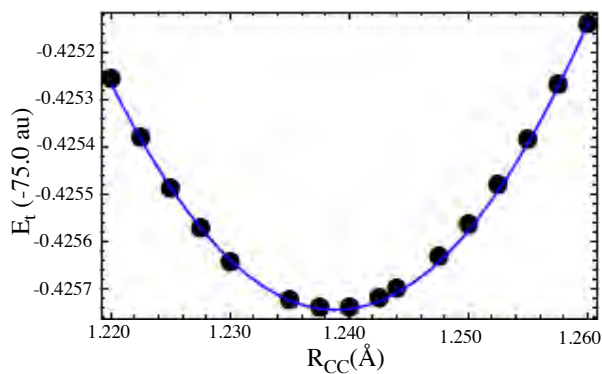
**Table S7.** Total energies  $E_t$  (au) for the calculations with 1 (only the covalent structure from Set A), 21 (only Set A), A(27), A+B+C(84), A+B+C+DissocLim.(88) and VB(1764).<sup>a</sup>

	VBSCF-1	VBSCF-21	VBSCF-27	VBSCF-84	VBSCF-88	VBSCF-1764
1.22	-.425255	-.569397	-.570879	-.595749	-.596140	-.609689
1.2225	-.425382	-.569591	-.571082	-.595997	-.596392	-.610001
1.225	-.425489	-.569762	-.571263	-.596222	-.596621	-.610290
1.2275	-.425576	-.569912	-.571422	-.596425	-.596828	-.610557
1.23	-.425645	-.570039	-.571560	-.596607	-.597013	-.610802
1.235	-.425729	-.570231	-.571771	-.596905	-.597319	-.611229
1.2375	<b>-.425744</b>	-.570296	-.571845	-.597023	-.597441	-.611412
1.24	-.425742	-.570340	-.571900	-.597120	-.597542	-.611573
1.2425	-.425723	-.570365	-.571934	-.597196	-.597622	-.611715
1.244	-.425704	<b>-.570370</b>	<b>-.571945</b>	-.597233	-.597661	-.611790
1.2475	-.425635	-.570355	-.571944	-.597290	-.597725	-.611939
1.25	-.425567	-.570321	-.571921	<b>-.597308</b>	-.597746	-.612022
1.2525	-.425483	-.570268	-.571878	-.597307	<b>-.597749</b>	-.612086
1.255	-.425384	-.570196	-.571817	-.597287	-.597734	-.612131
1.2575	-.425270	-.570107	-.571738	-.597248	-.597699	-.612158
1.26	-.425141	-.569999	-.571642	-.597191	-.597647	<b>-.612167</b>
1.2625	-.424997	-.569874	-.571527	-.597117	-.597577	-.612158
1.265	-.424840	-.569731	-.571396	-.597025	-.597489	-.612132
1.2675	-.424668	-.569571	-.571247	-.596916	-.597384	-.612088

1.27	-.424483	-.569395	-.571081	-.596789	-.597262	-.612028
1.2725	-.424284	-.569201	-.570900	-.596646	-.597123	-.611950
1.275	-.424073	-.568992	-.570702	-.596486	-.596968	-.611857
1.2775	-.423849	-.568766	-.570488	-.596310	-.596796	-.611747
1.28	-.423612	-.568525	-.570258	-.596118	-.596609	-.611621
1.2825	-.423363	-.568268	-.570013	-.595910	-.596406	-.611479
1.285	-.423102	-.567996	-.569753	-.595687	-.596187	-.611322
1.2875	-.422829	-.567709	-.569478	-.595449	-.595954	-.611150
1.29	-.422545	-.567407	-.569188	-.595195	-.595705	-.610963
1.3		-.566058	-.567889	-.594037	-.594566	-.610071
1.4		-.542879	-.545341	-.572554	-.573331	-.591230
1.5		-.509743	-.513136	-.540641	-.541797	-.561769
1.6		-.474195	-.478938	-.505780	-.507515	-.529074
1.8		-.411435	-.421216	-.443074	-.446933	-.480925
2.0				-.400233	-.408397	-.447751
2.5						-.401711
3.0						-.394327
10.0		-.343245	-.391966	-.362140	-.391966	-.391973
$k_{CC}^b$	11.8401	13.5909	13.4864	13.2837	13.2397	12.5588

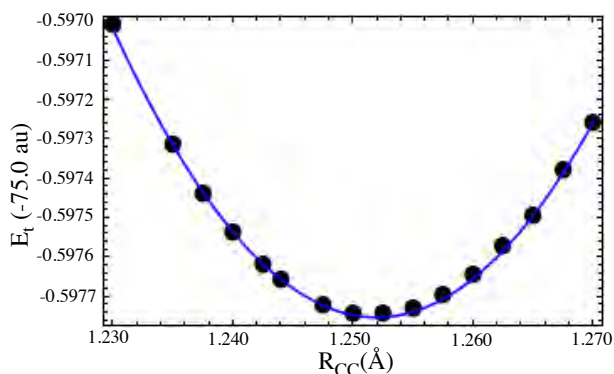
a) -75. au, b)  $k$  is a Force Constants ( $N\ cm^{-1}$ ) for different type of VB calculations obtained from harmonic approximation as a second derivative of energy  $k=d^2E/d^2x$ ,  $k=2E/x^2$

1 structures ( $k=11.84$ )



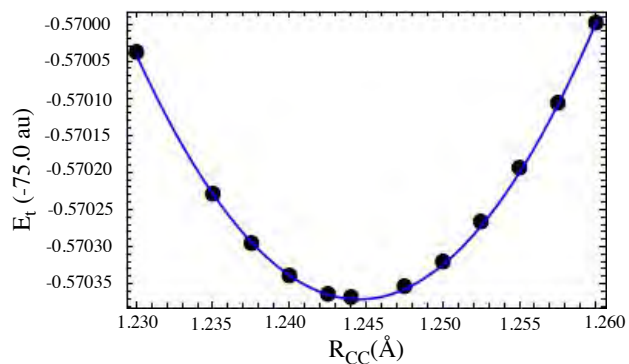
88 structures ( $k=13.24$ )

84 structures ( $k=13.28$ )



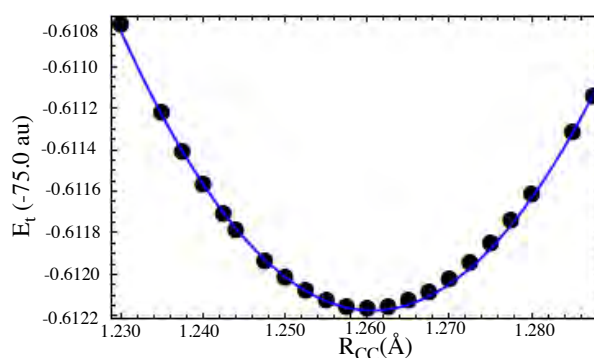
21 structures ( $k=13.59$ )

27 structures ( $k=13.49$ )



1764 structures ( $k=12.56$ )

MRCI/6-31G\* ( $k=12.29$ )



**Figure S4.** Graphs showing that energy well described by  $E=kx^2/2$  (blue line is a fit, point is a calculated datum).  $k=12.29 \text{ N cm}^{-1}$  for MRCI/6-31G\* calculation.

### VIII. Determination of $D_{\text{in-situ}}$ values for $\text{C}_2$ and HCCH using corresponding quasi-classical states.

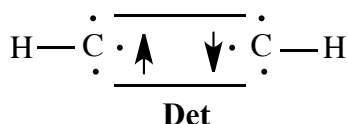
Calculations of  $D_{\text{in-situ}}$  show that the  $\sigma$ -system of  $\text{C}_2$  prefers CC distance of  $\sim 1.4\text{\AA}$ , s-acetylene refers a distance of  $\sim 1.3\text{\AA}$ . In both molecules the  $\pi$ -system prefer very short CC distance if not a zero distance.

#### QCS for Calculating $D_{\text{in-situ}}$

The following quasi-classical states (determinants) were used in the calculations of  $2\sigma$ -bonds in  $\text{C}_2$  molecule, and their averaged energies were used as the reference state.



The following quasi-classical state (determinant) was used in the calculations of  $\sigma_{\text{CC}}$  bond in HCCH molecule



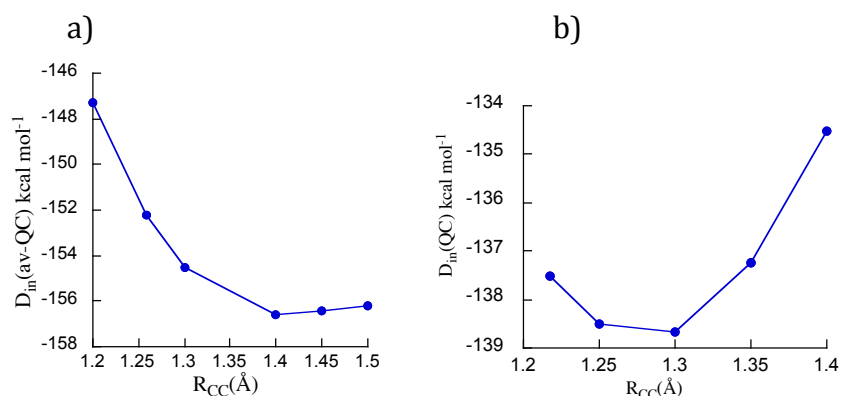
**Table S8.**  $D_{\text{in}}(\text{QC})$  values ( $\text{kcal mol}^{-1}$ ) for the  $2\sigma$ -bonds of  $\text{C}_2$  molecule (only  $\sigma$ -bonds are calculated by VB while the  $\pi$  bonds are being treated as delocalized MOs). Energies (au) of determinants ( $E_{\text{DET}}$ ), covalent structure ( $E_{\text{COV}}$ ) and VBSCF ( $E_{\text{VBSCF}}$ ) wave function with 20 structures<sup>a</sup> for  $4\sigma$  electrons ( $-75.0$  au should be added to energy).

$R_{\text{CC}}(\text{\AA})$	1.2	1.258	1.3	1.4	1.45	1.5
$2\sigma$ -bonds						
$E_{\text{DET}}(\text{av})$	-0.241221	-0.229385	-0.216676	-0.178418	-0.156993	-0.134724
$E_{\text{COV}}$	-0.462901	-0.454684	-0.442485	-0.400710	-0.376365	-0.351280
$E_{\text{VBSCF}}$	-0.475934	-0.471966	-0.462886	-0.427982	-0.406463	-0.383633
$D_{\text{in}}(\text{av-QC})$	-147.28	-152.22	-154.50	<b>-156.60</b>	-156.54	-156.19

a) For 4 electrons in 4  $\sigma$ -HOAs there are 20 VB structures.

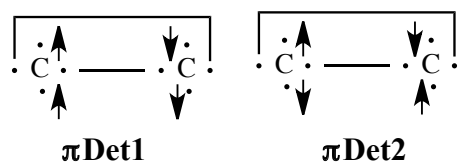
**Table S9.**  $D_{in}(QC)$  values ( $\text{kcal mol}^{-1}$ ) of for the  $\sigma$  bond of  $C_2H_2$  molecule (only the  $\sigma$ -bond is calculated by VB, while  $\pi$ - and C-H  $\sigma$ -bonds as delocalized MOs). Energies (au) of determinants ( $E_{DET}$ ), covalent structure ( $E_{COV}$ ) and VBSCF wave function ( $E_{VBSCF}$ ). (-76.0 au should be added to energy).

$R_{CC}(\text{\AA})$	1.218	1.25	1.3	1.35	1.4
$E_{DET}$	-.601570	-.594313	-.578746	-.559552	-.537980
$E_{COV}$	-.811474	-.804283	-.788681	-.762894	-.734959
$E_{VBSCF}$	-.820708	-.815049	-.799712	-.778263	-.752360
$D_{in}(QC)$	-137.51	-138.51	<b>-138.66</b>	-137.24	-134.53



**Figure S5.** Dependence of the  $D_{in}(QC)$  of  $C_2$  and HCCH molecule on the C-C interatomic distance where  $\pi$ -bonds were treated as MOs, and  $\sigma$  were treated as VB for a)  $2\sigma$  bonds in  $C_2$ , a) the  $\sigma$  bond in HCCH.

$D_{in-situ}(QC)$  for the  $2\pi$  bonds of  $C_2$  as a function of  $R_{CC}$ , using the corresponding quasi-classical determinants.



**Table S10.**  $D_{in}(QC)$  values ( $\text{kcal mol}^{-1}$ ) for the  $2\pi$ -bonds and a single  $\pi$ -bond of  $C_2$  calculated at VBSCF/6-31G\* level taking all bonds as VB.<sup>a</sup>

$R_{CC}(\text{\AA})$	1.0	1.1	1.2	1.258
$2\pi$ bonds				
$E_{DET}(av)$	-.003392	-.163659	-.251139	-.280814
$E_{COV}$	-.285308	-.393821	-.434931	-.440597
$E_{VBSCF}$	-.411712	-.525906	-.566810	-.569925
$D_{in}(av-QC), \pi$	271.28	227.31	198.09	181.42
$\pi$ -bond				
$E_{DET}$		-.339308	-.403731	-.420318
$E_{COV}$		-.453394	-.494819	-.499504
$E_{VBSCF}$		-.525906	-.566810	-.569925



$D_{in}(QC)$	>117.09	117.09	101.71	93.88
--------------	---------	--------	--------	-------

a) Energies in au, -75.0 au

## IX. Calculations of Overlap Populations for some orbitals of $C_2$

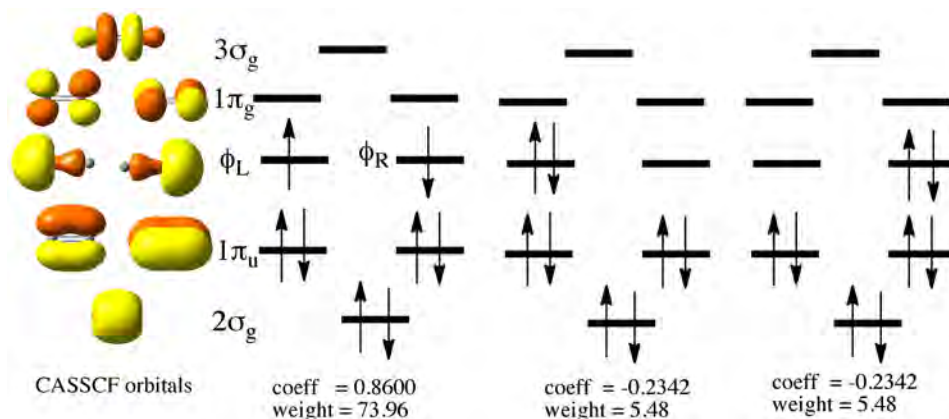
**Table S11.** Orbital overlap population calculations using CASSCF(8,8) method with different basis sets.

	6-31G*	6-311G*	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z
$2\sigma_u$	-0.009244	-0.123004	-0.107460	-0.076436	-0.144459	-0.024913	0.0138537
$2\sigma_g$	0.4096890	0.4152156	0.4153799	0.4145983	0.421948	0.428672	0.4260038

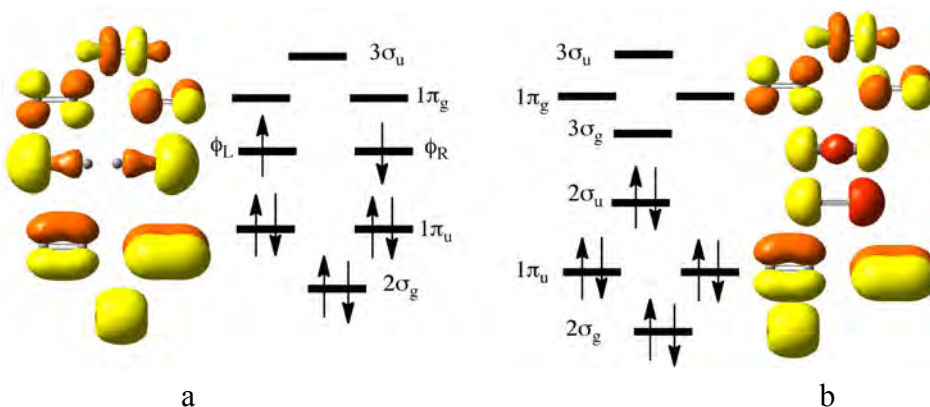
## X. Transformation of Orbitals for the CASSCF Wave function

We reproduced Zhang's transformation [Ref. 43 in the text] of the CASSCF wave function.

The transformation does not change the energy of the wave function, but changes the conclusion about the number of bonds.



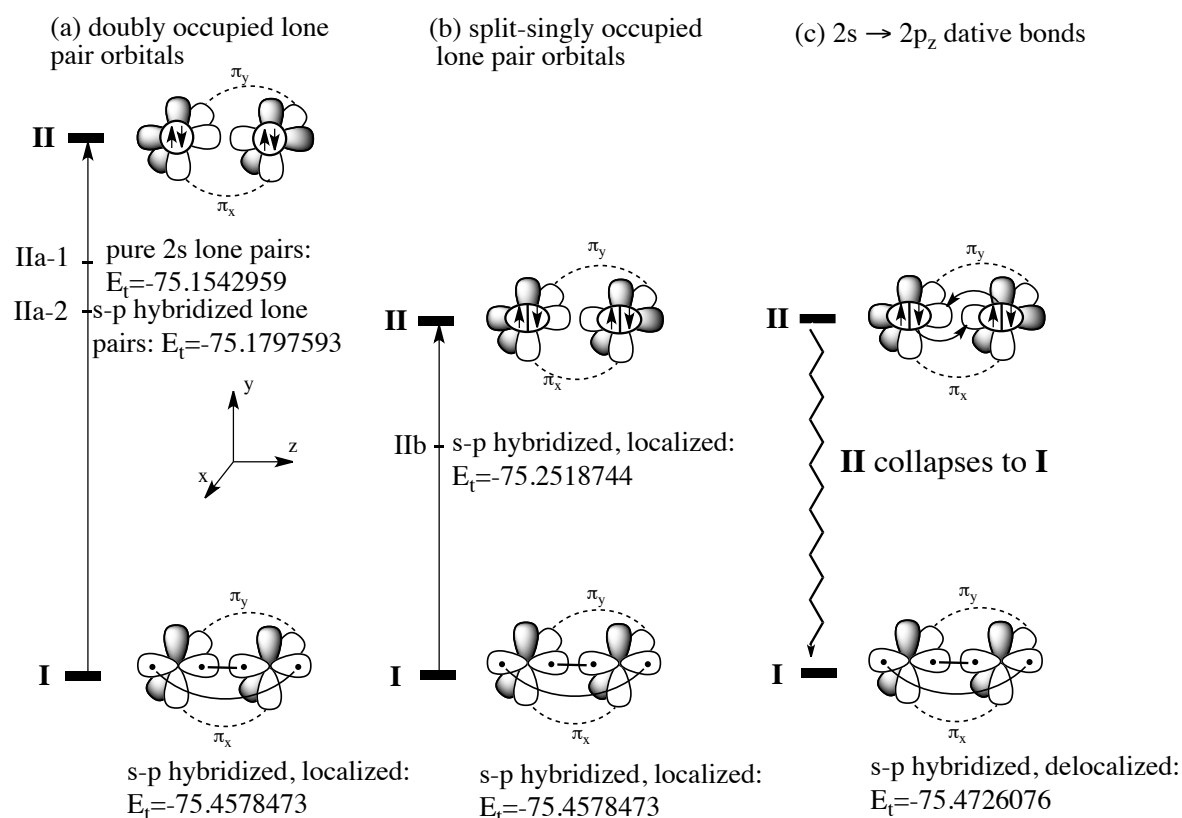
**Figure S6.** Transformed Orbitals (M. Zhang et al) and the three most important configurations of a CASSCF(8,8)/aug-cc-pVTZ calculations of  $C_2$  with coefficients and weights of the configurations at 1.244Å.



**Figure S7.** CASSCF(8,8)/6-31G\* calculation of C<sub>2</sub> at 1.244Å: (a) After orbital transformation as in M. Zhang et al, and (b) standard canonical orbitals of CASSCF(8,8)/6-31G\* calculations.

### XI. Assessments of the Bonding Model in Ref. 21a

The authors of Ref. 20b and 21a in the main article text suggested a bonding model with two  $\pi$  bonds and dative sigma bonds from a filled 2s orbital on one C to a vacant 2p<sub>z</sub> on the other and vice versa. This doubly-bonded model (State II) is calculated in the text (Fig. 5, text) relative to the quadruply bonded structure, State I, at different levels. In all the calculations of the states I and II, the  $\pi$ -bonds were taken as doubly occupied MOs, while the  $\sigma$ -frame was treated by VB.

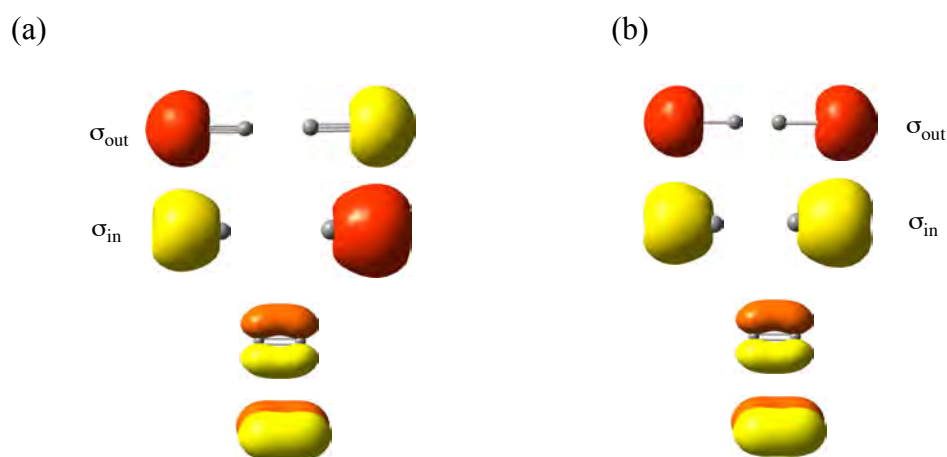


**Figure S8:** VBSCF/6-31G\* energies of the doubly bonded structure (State II) and the quadruply bonded one (State I) at different levels.  $E_t$  is au.

The total energies of States I and II are shown in Figure S8, which is a copy of Figure 5 (text). Thus, Figure S8 shows the following: (i) Part a shows that when the doubly bonded

model involves two localized lone pairs, it resides well above the quadruply bonded State I, by 190.5 kcal/mol (usage of cc-pVTZ instead of 6-31G\* raises this value by 0.7 kcal mol<sup>-1</sup>), when State II is described by pure 2s lone pairs, and 174.5 kcal mol<sup>-1</sup> when the 2s lone-pair orbitals are allowed to hybridize with the local 2p<sub>z</sub> AOs. (ii) Part b shows that the energy gap is lowered to 129.3 kcal mol<sup>-1</sup>, when the lone pairs of State II are described by split orbitals, which are 2s-2p<sub>z</sub> hybridized and localized. (iii) Part c shows that when we allow the lone pairs of State II (which are each split into two singlet paired hybrids) to delocalize (by usage of Coulson-Fischer orbitals) to the vacant 2s-2p<sub>z</sub> orbitals on the other side(s), *state II collapses to the quadruply-bonded structure, State I*, in which the four bonds are described also by Coulson-Fisher orbitals.

Figure S9 shows side by side, the orbitals of collapsed “State II + dative  $\sigma$ -bonds” (a), and those of the quadruply bonded structure (b). The two orbital sets are identical. Dative bonding at this short distance is not meaningful. The “dative  $\sigma$ -bonds” are simply the two  $\sigma$ -bonds of the quadruply bonded structure.



**Figure S9.** a) Left-side are VBSCF/6-31G\* orbitals after the collapse of the wave function in which we attempted to model C<sub>2</sub> as a molecule having two  $\pi$  bonds and two dative sigma bonds from a filled hybrid 2s-2p<sub>z</sub> orbital on one C to a vacant hybrid-2s-2p<sub>z</sub> in the other and vice versa (see **5** in Scheme 2 in the text). (b) The wave function of the quadruple bonded of C<sub>2</sub> calculated independently. The calculations were done at 1.244Å and involved two  $\pi$  bonds as MOs, and the  $\sigma$ -electrons were treated by VB.

**Additional Attempts to Assess the Dative  $\sigma$ -Bonding:** We have made four other attempts to generate the structure with the dative  $\sigma$ -bonds (**5** in Scheme 2) on top of the  $\pi$ -bonds (these are always treated as doubly occupied MOs). These were done as follows:

(a) The lone pairs on each carbon were allowed to undergo local hybridization (2s with  $2p_z$ ) and to delocalize onto the 2s and  $2p_z$  orbitals of the other carbon. This procedure generated a wave function having precisely the same energy as the simple Hartree-Fock (HF) solution ( $E(a) = -75.3790275$  au, i.e.  $58.7$  kcal mol<sup>-1</sup> above the quadruply bonded structure).

(b) The lone pairs on each carbon were kept as 2s but were allowed to delocalize into the  $2p_z$  AO of the other carbon. This procedure generates a wave function as close as possible to the dative bonding picture in **5**, and its energy is higher than the HF solution in (a) ( $E(b) = -75.3460860$  au) by  $20.7$  kcal mol<sup>-1</sup>. When the lone-pair was given a variational freedom, solution (b) simply collapsed the HF solution in (a).

(c) The lone pairs on each carbon were allowed to undergo local hybridization (2s with  $2p_z$ ) and to delocalize onto the  $2p_z$  orbitals of the other carbon. This procedure generates too, a wave function close to the dative bonding picture in **5**, and its energy is higher than the HF solution in (a) ( $E(c) = -75.3743747$  au) by  $2.9$  kcal mol<sup>-1</sup>. When the delocalization of the hybridized lone-pairs was given a variational freedom, solution (c) simply collapsed the HF solution in (a).

(d) The lone pairs on each carbon were allowed to undergo local hybridization (2s with  $2p_z$ ) and split into two singlet-paired hybrids, to lower repulsive interactions, and to delocalize onto  $2p_z$  orbital of the other carbon. This procedure generates a wave function which has two polarized  $\nu$ -bonds involving  $2s(C1)-2p_z(C2)$  and  $2p_z(C1)-2s(C2)$  overlaps, and each one of them is occupied by a single electron, thus forming two half  $\sigma$ -bonds. In addition, each of the carbons has a singly occupied AO which is closely a 2s-type and is singlet paired to one of the  $\nu$ -hemibonds. This solution has in fact a triple bond and a singlet diradical, unlike **5**. Its energy is higher than the quadruply bonded structure ( $E(d) = -75.4297246$  au) by  $26.9$  kcal/mol, and when it is allowed a variational freedom it collapses to the quadruply bonded structure.

(e) Starting from State **II** in Figure S8a, we delocalized the 2s lone pairs into the vacant  $2p_z$  orbitals, by allowing transfer of the electrons in pairs (as may be implied by the arrows in State **II** in Figure S8c). In so doing, we generated a wave function with a double  $\pi$ -bond

and three structures in resonance, such that the  $\sigma$ -electrons are in  $2s^2-2s^2$ ,  $2s^2 2p_z^2$  and  $2p_z^2 2s^2$  situations. The energy of this wave function -75.213895 au, namely it is 135.4 kcal mol<sup>-1</sup> higher than the quadruply bonded structure.

Thus, all our attempts to simulate the dative bonding as in structure **5**, yield high energy wave functions *which collapse either to the quadruply bonded wave function or to the Hartree-Fock solution*. Dative bonding at this short distance is not meaningful.

## XII. Triplet state ( $^3\Sigma_u^+$ ) calculations.

(a) Optimized bond length and force constant:

VB calculations were done for C<sub>2</sub> in the triplet state  $^3\Sigma_u^+$  state where the triplet electrons occupy the outer sigma hybrids. Changing the C-C distance we determined the energy minimum as shown in bold in Table S12.

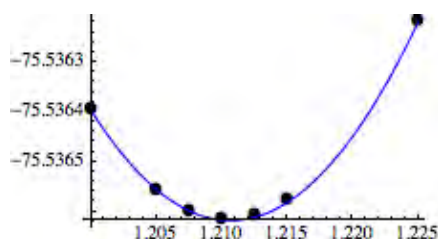
**Table S12.** Total E<sub>SCF</sub> (in au) energies of the  $^3\Sigma_u^+$  triplet state of C<sub>2</sub> molecules (using VBSCF calculations with 13 structures where all bonds were treated as spin paired VB, except for the triplet pair in the outer hybrids). The minimum is indicated in bold font.<sup>a</sup>

R (Å)	Triplet
1.1	-.506663
1.2	-.536396
1.205	-.536558
1.2075	-.536601
<b>1.21</b>	<b>-.536618</b>
1.2125	-.536611
1.215	-.536580
1.225	-.536219
1.24	-.535007
1.245	-.534435
1.25	-.533782
1.26	-.532246
1.275	-.529400
1.3	-.523354
1.4	-.487084

a) -75.0 au

The force constant (N cm<sup>-1</sup>) for the triplet state was obtained from the harmonic approximation, as a second derivative of energy. Figure S9 below shows that the energy is well described by  $E=kx^2/2$  (blue line is a fit).

$$k=16.9698$$



**Figure S9.** Force constant for the  $^3\Sigma_u^+$  triplet state (using VBSCF calculations with 13 structures). The points of the plot correspond to calculated energy values while the line is the fitted curve.

(b) In-situ bond interaction energy in the triplet state

To calculate the in situ bond interaction energy of the  $\sigma$ -bond in the triplet state, we used the requisite QCS:



To be compatible with the same calculation for the singlet state of  $\text{C}_2$  and acetylene (Table S8, S9), the two  $\pi$ -bonds were kept as MOs, and only the  $\sigma$ -bond was treated by VB. The data is given in the following table:

**Table S12a.**  $E_{\text{SCF}}$  (in au) corresponds to the triplet calculations where triplet electrons occupied outer sigma bond. For the QCS determinant the inner  $\sigma$ -bond was unpaired (only  $\sigma$ -bonds are calculated by VB while the  $\pi$  bonds are being treated as delocalized MOs).<sup>a</sup>

$R_{\text{CC}}(\text{\AA})$	1.2	1.25	1.3	1.4
$\sigma_{\text{in-bond}}$				
$E_{\text{det}}$	-.231602	-.220168	-.203609	-.161739
$E_{\text{SCF}}$	-.448922	-.426677	-.423763	-.374510
$D_{\text{in}}(\text{QC})^{\text{b}}$	-136.37	<b>-138.17</b>	-138.15	-133.52

a) -75.0 au, b) in kcal mol<sup>-1</sup>

It is seen that the  $\sigma$ -bond prefers a length shorter than the one in acetylene, and the in-situ interaction energy of this bond is very similar to the one in acetylene (see Table S9), both being smaller than the corresponding interaction energy in the ground state of  $\text{C}_2$  (Table S8).