Benoît BRAÏDA

How VB theory can help to understand multicenter bonding

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Purpose

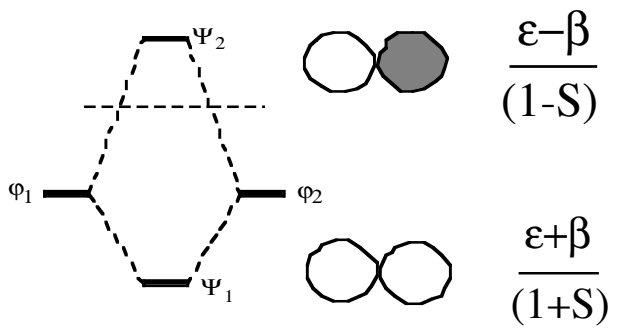
How VB theory can elucidate electronic structure of large & complex systems

- VB description of elementary interactions
- Qualitative VB & MO analysis of «Pancake bonding»
- Quantitative VB results, and conclusion

Qualitative VB

Effective Hamiltonian : $\mathbf{H^{eff} = (h(1) + h(2) + h(3) + \ldots.)}$

Parameters: β, **S**, ε (same as in the MO framework)



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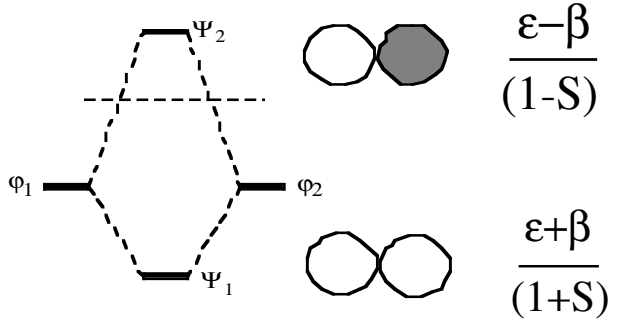

1) Energy of a determinant :

$$\langle D_i | H | D_i \rangle = \frac{-2n\beta S}{1 - S^2}$$

n **= N# of neighboring (↑↑) pairs**

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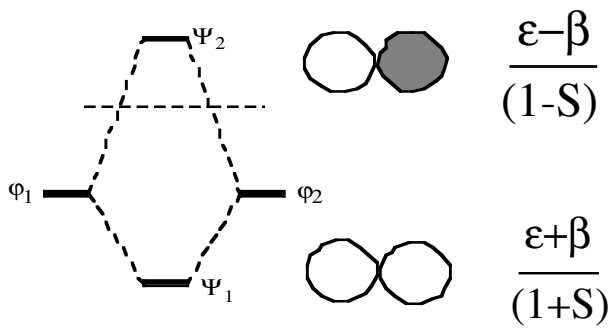


1) Energy of a determinant :

$$\langle D_i | H | D_i \rangle = \frac{-2n\beta S}{1 - S^2}$$

n **= N# of neighboring (↑↑) pairs**

2) Off diagonal terms :

- Determinants differ by 2 spinorbitals:

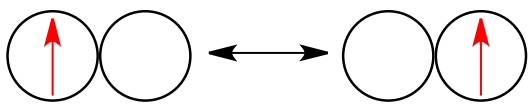
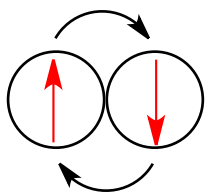
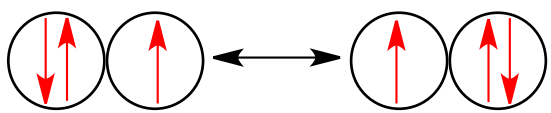
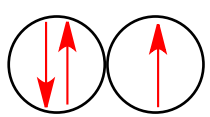
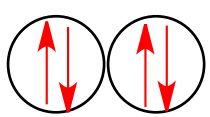
$$\langle (|a\bar{b}|) | H | (|b\bar{a}|) \rangle = 2\beta_{ab} S_{ab}$$

- Determinants differ by + than 2 spinorbitals :

$$\langle D_i | H | D_j \rangle = 0$$

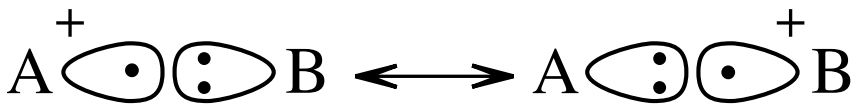
Qualitative VB

- Elementary interactions :

		VB	MO
1-e bond (A↑ B) =		$\frac{ß}{1+S}$	$\frac{ß}{1+S}$
2-e bond (A–B) =		$\frac{2ßS}{1+S^2}$	$\frac{2ß}{1+S}$
3-e bond(A ∴ B) =		$\frac{ß(1-3S)}{1-S^2}$	$\frac{ß(1-3S)}{1-S^2}$
3-e repulsion (A↑↓ ↑B) =		$\frac{-2ßS}{1-S^2}$	$\frac{-2ßS}{1-S^2}$
4-e repulsion (A↑↓ ↓↑B) =		$\frac{-4ßS}{1-S^2}$	$\frac{-4ßS}{1-S^2}$

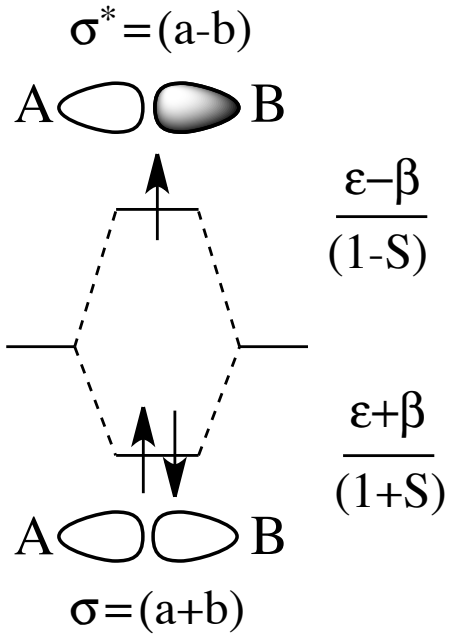
The three-electron bond*

- VB vs. MO qualitative descriptions :



$$\Psi_{MO} = \left|\sigma\bar{\sigma}\sigma^{*}\right| = \left|(a+b)\overline{(a+b)}(a-b)^{*}\right|$$

$$= \ldots = -\left|a\bar{a}b\right| - \left|b\bar{b}a\right| = \Psi_{VB}$$



** Pauling, L. J. Am. Chem. Soc.* ***1931****, 53, 3225*

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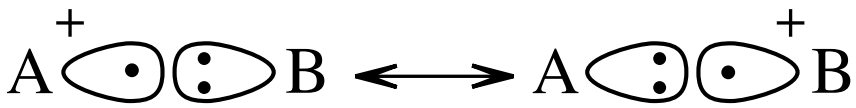

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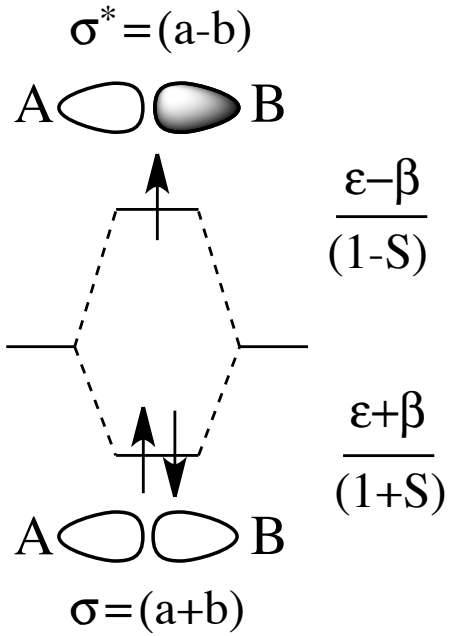
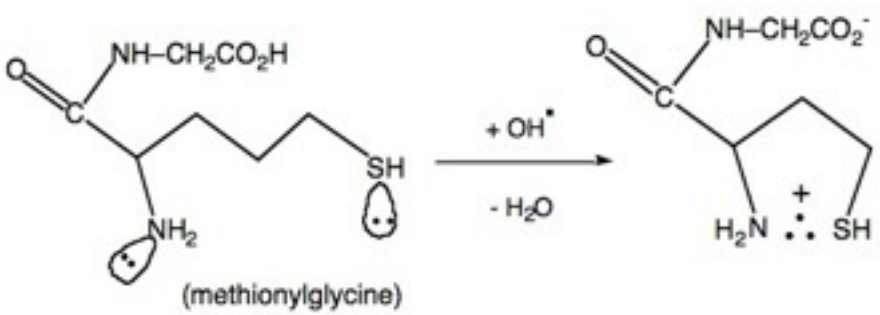
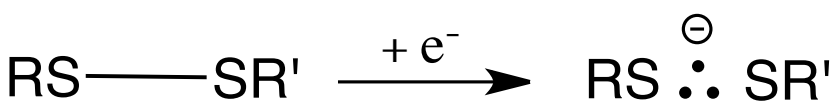


- Examples :





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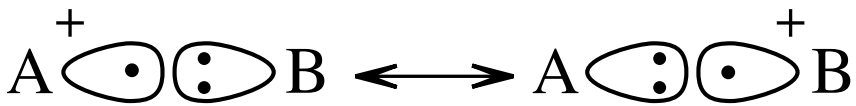
The three-electron bond*

- VB vs. MO qualitative descriptions :



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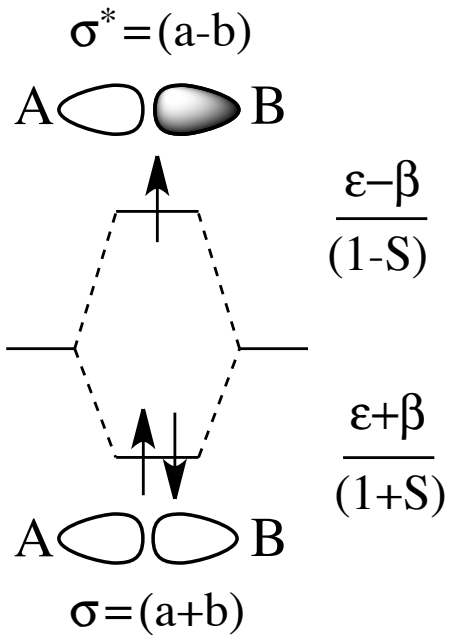


- Some features :
  - Long bonds : $R_{eq}\,S\!-\!S(2e) \approx 2\text{Å}$ $R_{eq}\,S\therefore S(2e) \approx 2.8\text{Å}$
  - Small S_{ab} overlaps : $E = \dfrac{\beta(1-3S)}{(1-S^2)} \Rightarrow S_{opt} \approx 0.17$
  - Correlation purely dynamical : $D_e\,F_2^{-}$: *UHF* ≈ 0. ; *MP2* ≈ 30. *kcal/mol*

* *Pauling, L. J. Am. Chem. Soc.* ***1931****, 53, 3225*

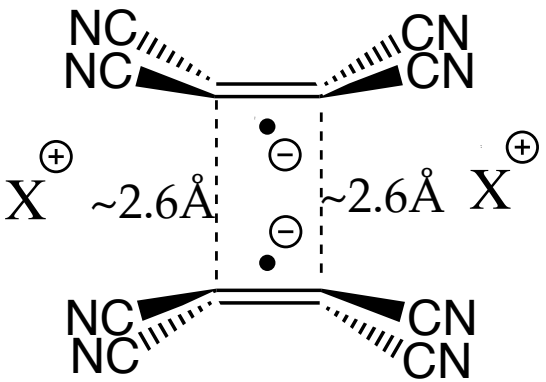
«Pancake bonding»

- Prototype : $TCNE_2^{2-}$

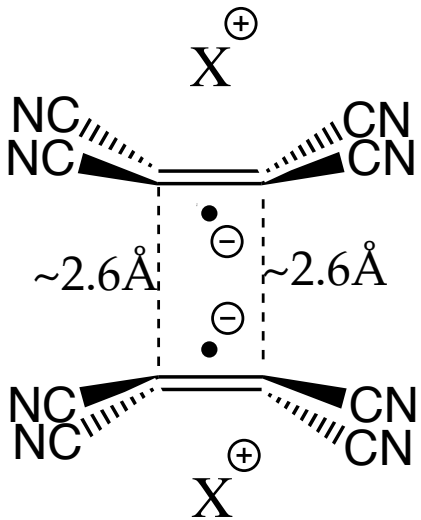
- R_{C-C} < vdW radii (3.4Å)

- Strongly bonded :

not only electrostatic & dispersion

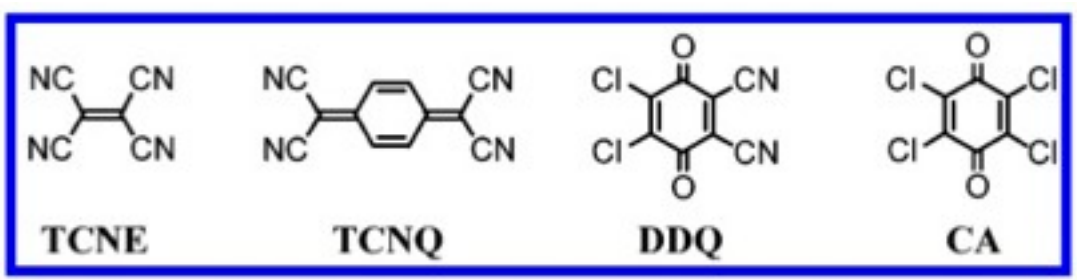


$D_e \approx 80.\ kcal/mol$

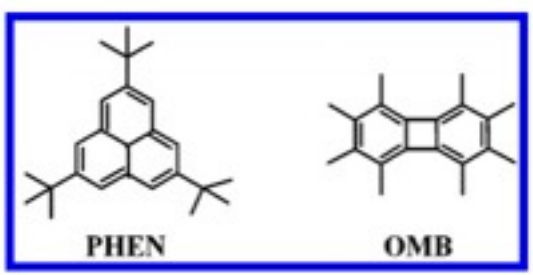


$D_e \approx 11.\ kcal/mol$

- Others :



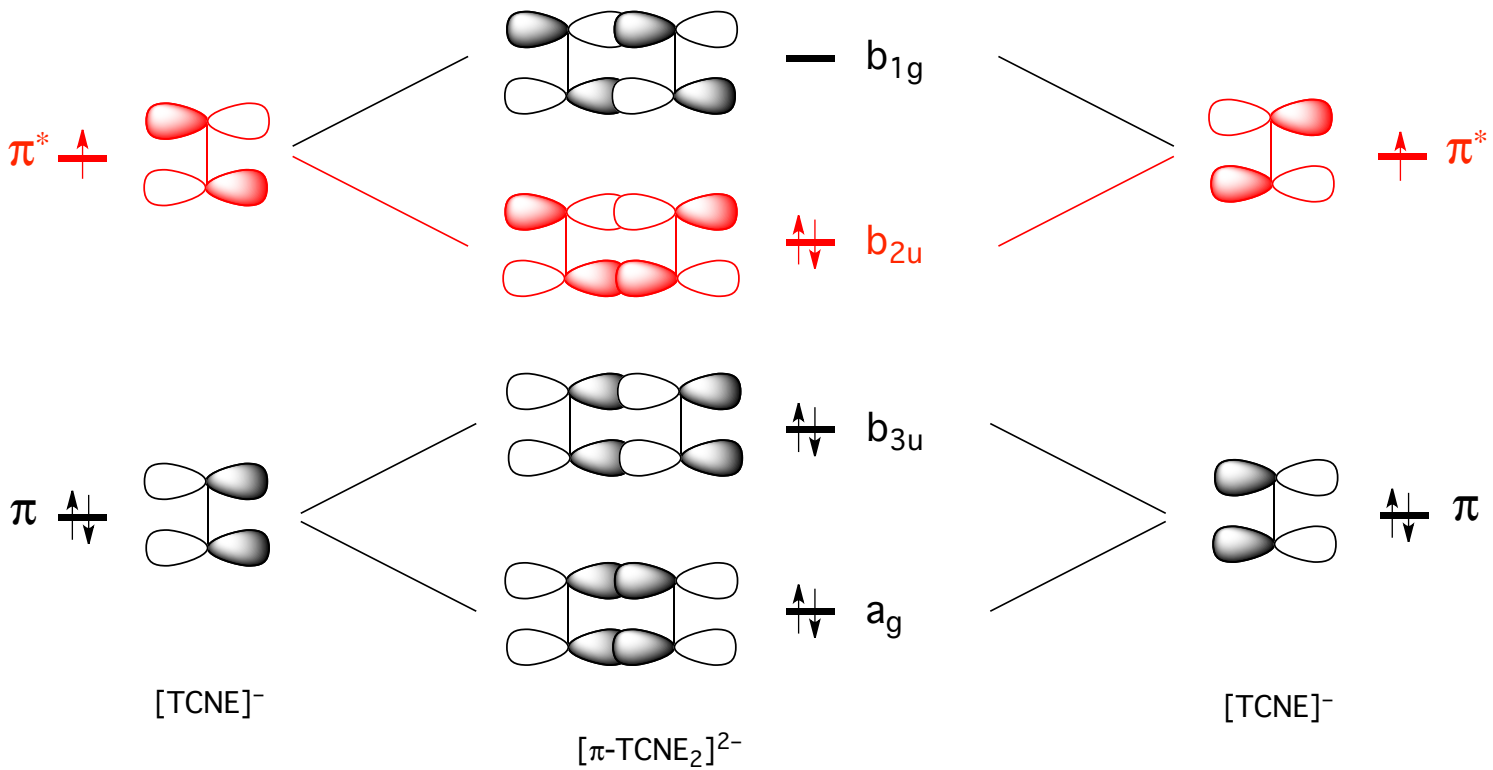
$TCNE_2^{2-}$ $TCNQ_2^{2-}$ DDQ_2^{2-} CA_2^{2-}



$PHEN_2$ OMB_2^{2+}

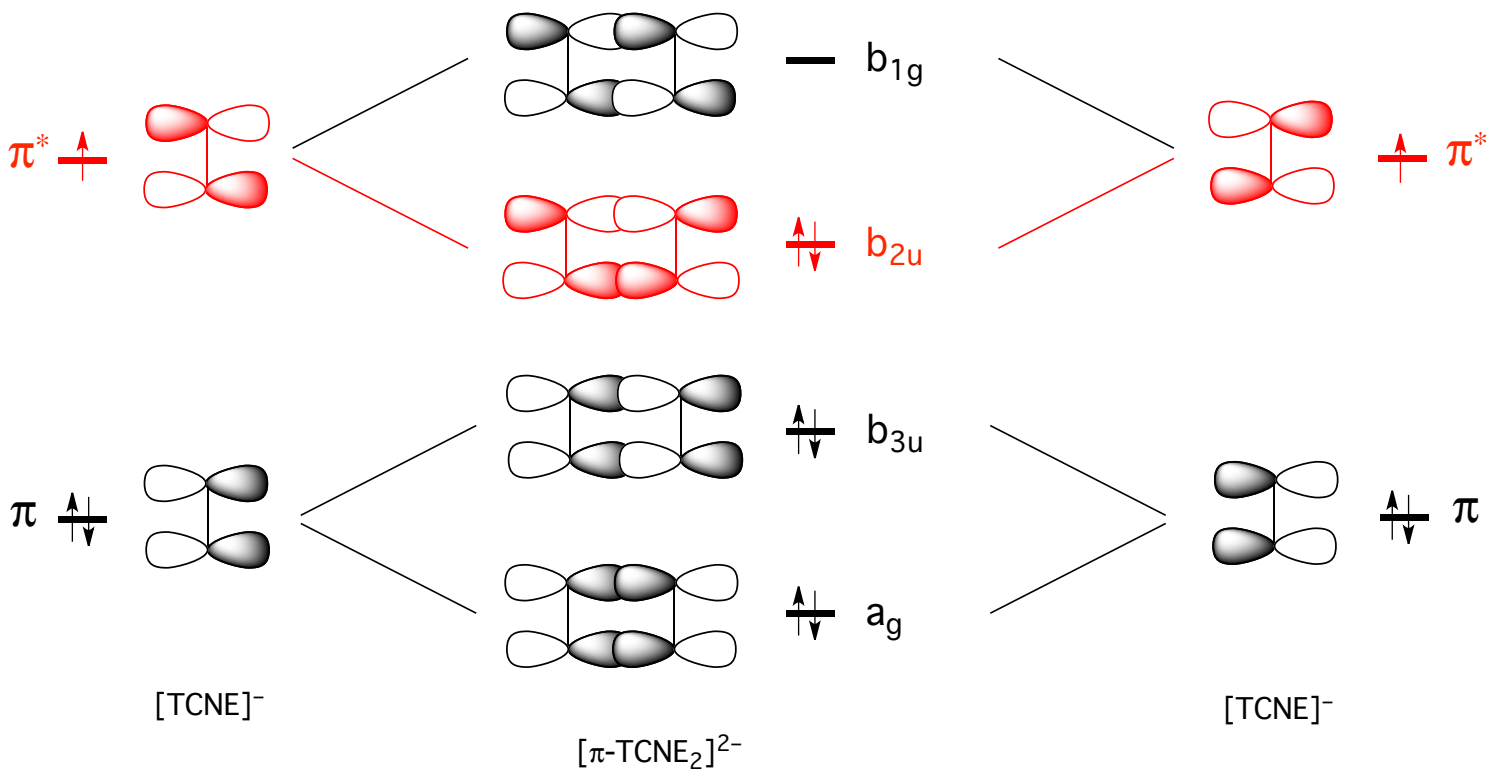
«First sight» MO analysis

- A multicenter 2e$^-$ bond ?



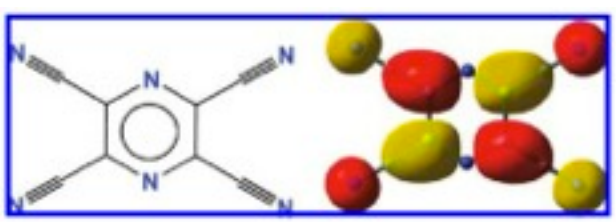
«First sight» MO analysis

- A multicenter 2e⁻ bond ?

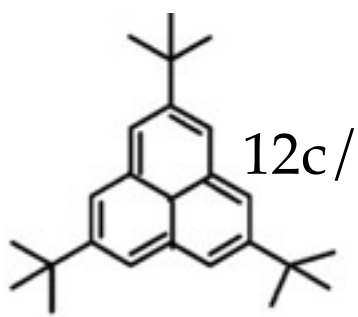


=> a **4c/2e⁻ bond**

extension : **nc/me⁻ bond** :



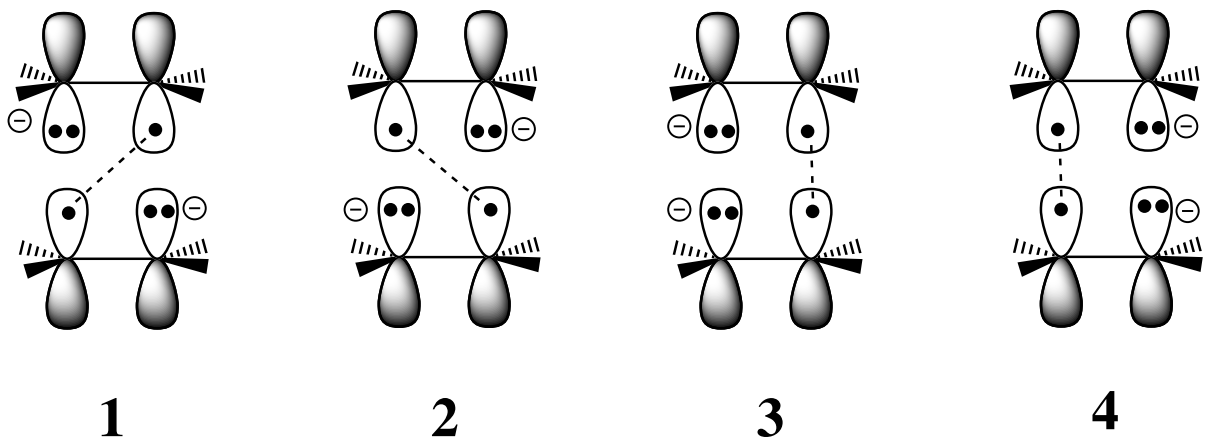
8c/2e⁻

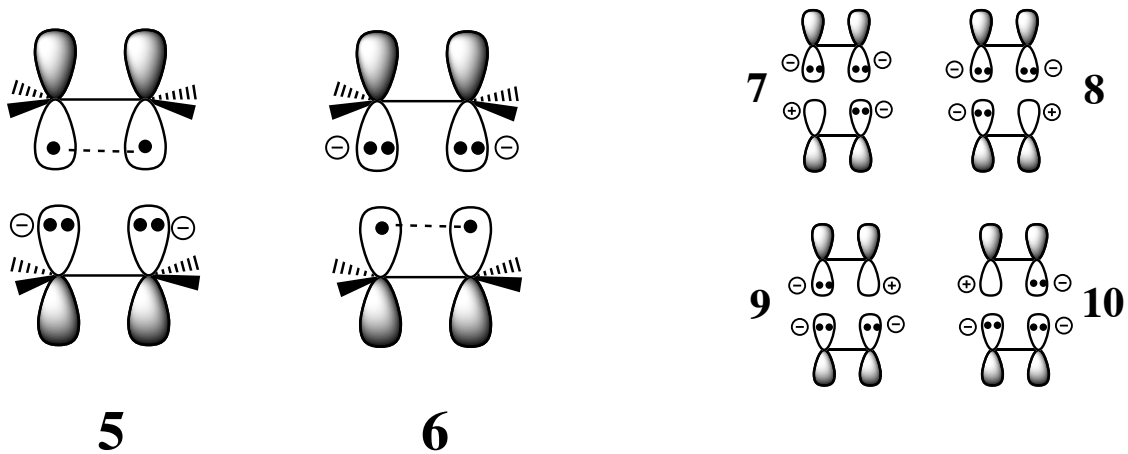


12c/2e⁻

VB analysis

- VB set of structures :





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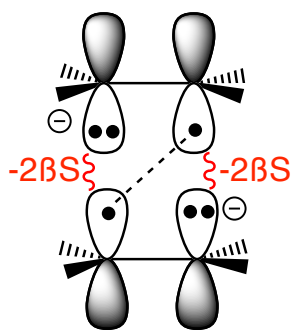
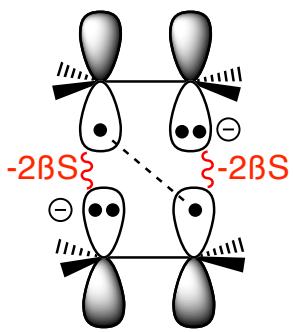
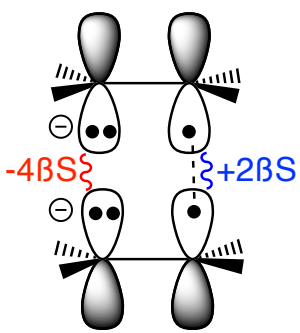


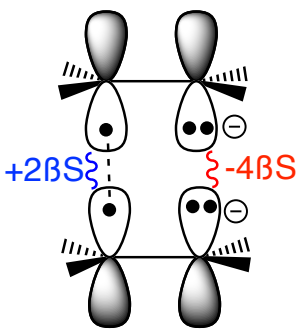
1



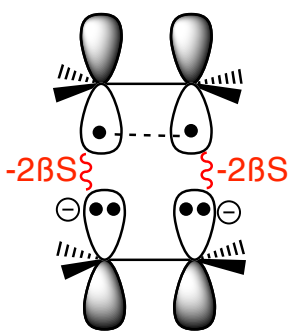
2



3



4



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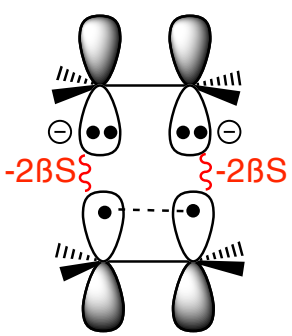
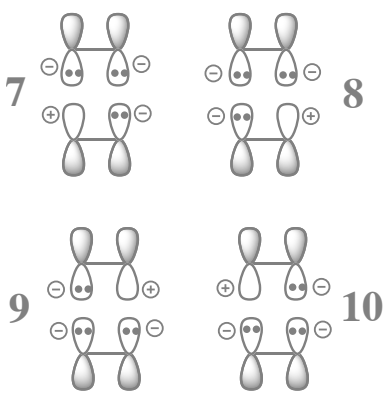


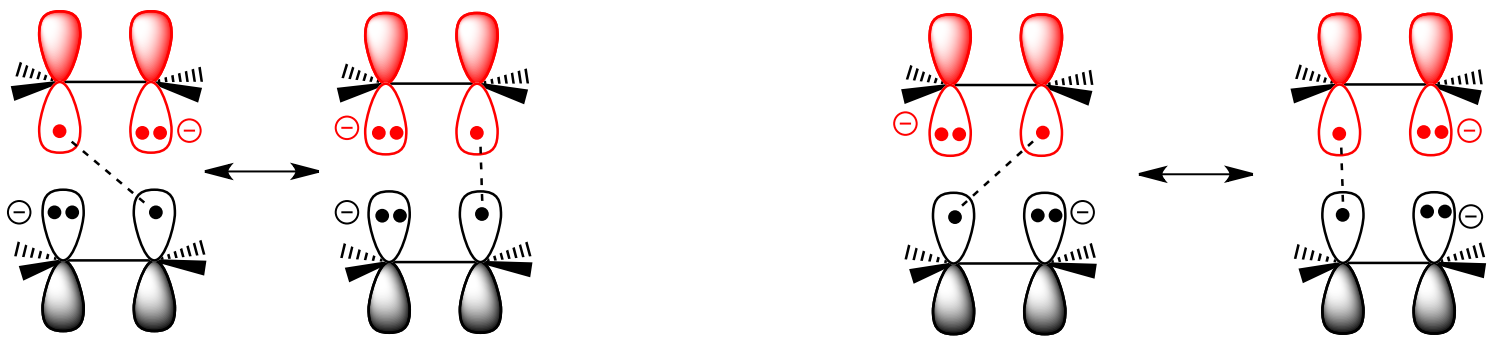
6



=> No structure is bonding by itself, **all the bonding comes from the resonance**

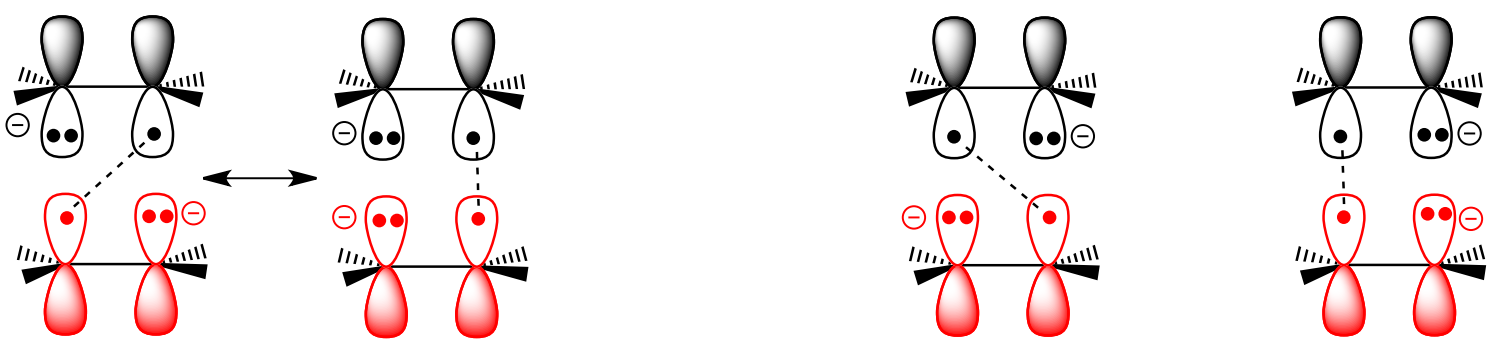
VB analysis

- 2↔3 and 1↔4 : **intra-fragment 3e⁻ π bond** (upper part) :



2 **3** **1** **4**

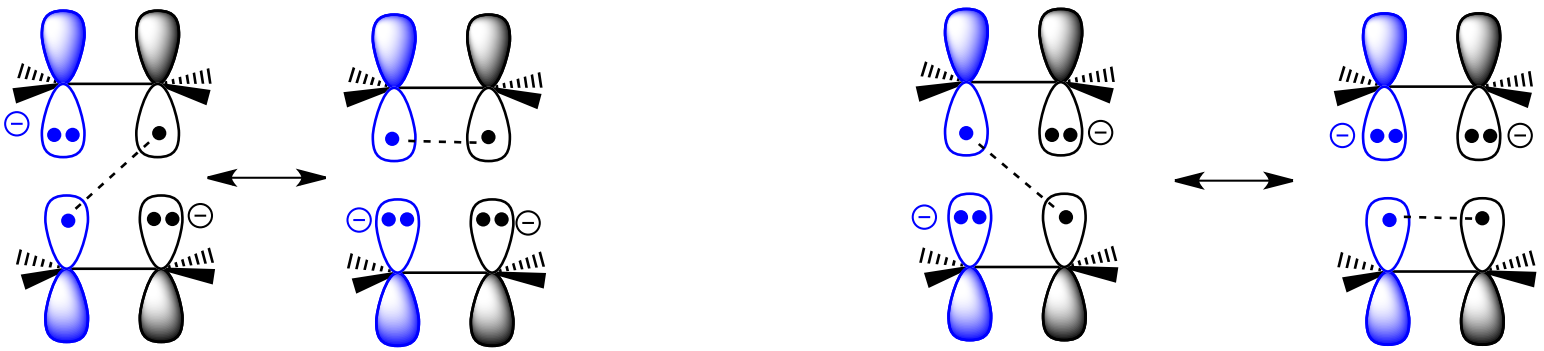
- 1↔3 and 2↔4 : **intra-fragment 3e⁻ π bond** (lower part) :



1 **3** **2** **4**

VB analysis

- 1↔5 and 2↔6 : **inter-fragment 3e⁻ π bond** (left-hand side) :



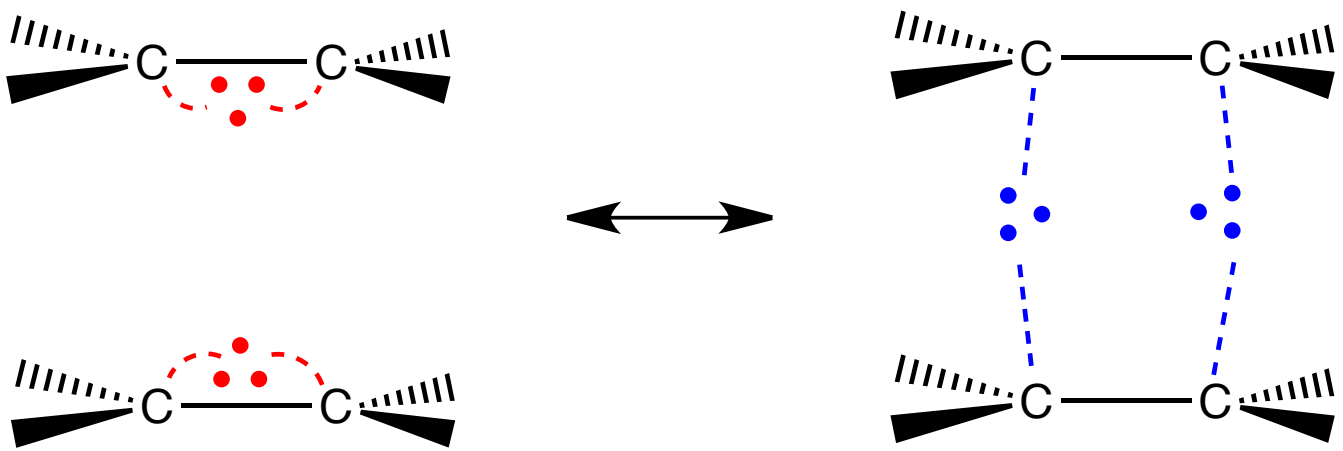
1 **5** **2** **6**

- 2↔5 and 1↔6 : **inter-fragment 3e⁻ π bond** (right-hand side) :

1 **6** **2** **5**

VB analysis

- Conclusion of the qualitative VB analysis :

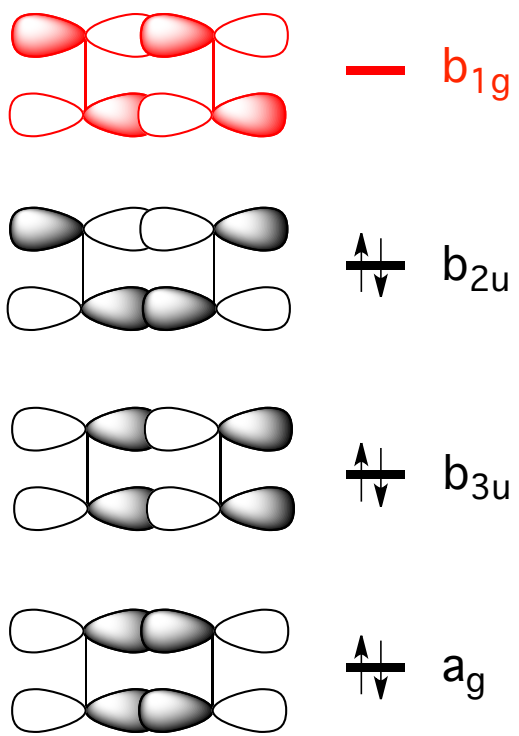


1↔2↔3↔4 1↔2↔**5**↔**6**

=> $3e^-$ bonding nature of TCNE anion dimer

MO/VB mapping

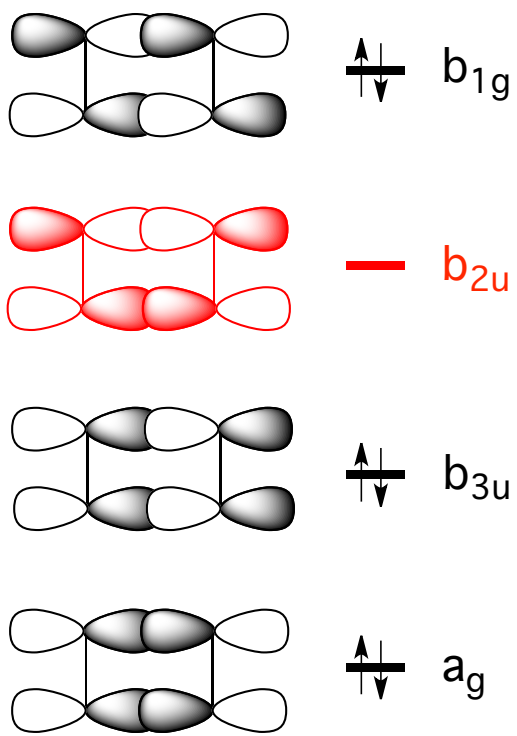
- HF determinant - development in VB basis of structures :



$$\Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB}$$

MO/VB mapping

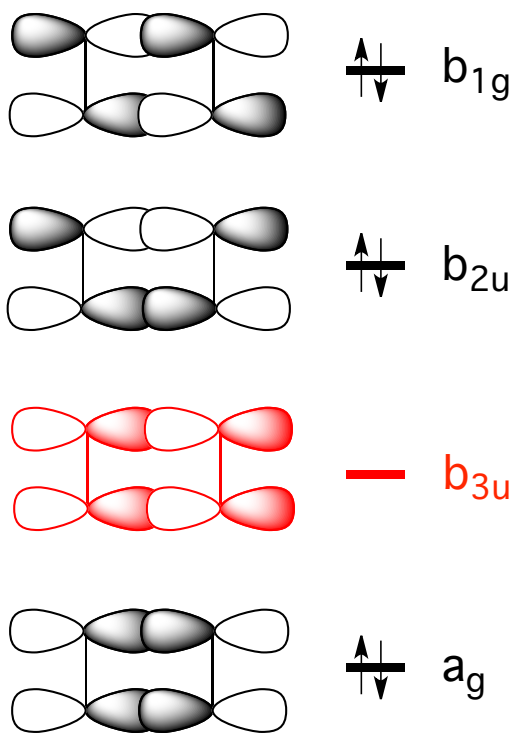
- 1st excited det. - development in VB basis of structures :



$$\Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

MO/VB mapping

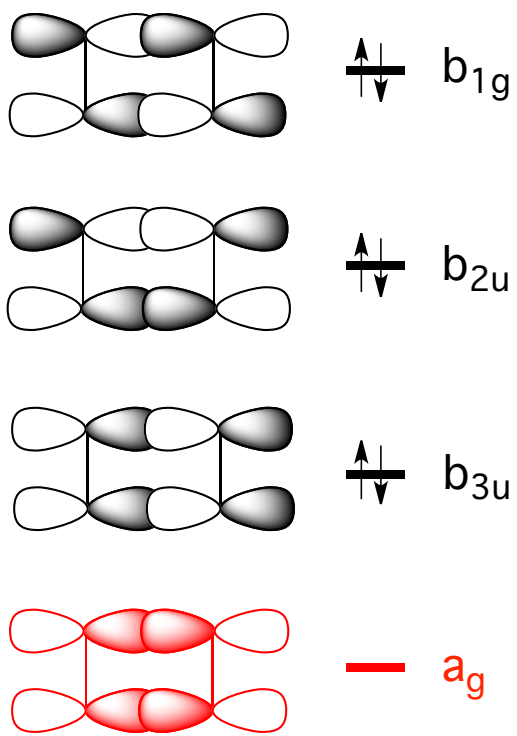
- 2nd excited det. - development in VB basis of structures :



$$\Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB}$$

MO/VB mapping

- 3rd excited det. - development in VB basis of structures :



$$\Psi_{3-ext} = \left| b_{3u}\bar{b}_{3u}b_{2u}\bar{b}_{2u}b_{1g}\bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

MO/VB mapping

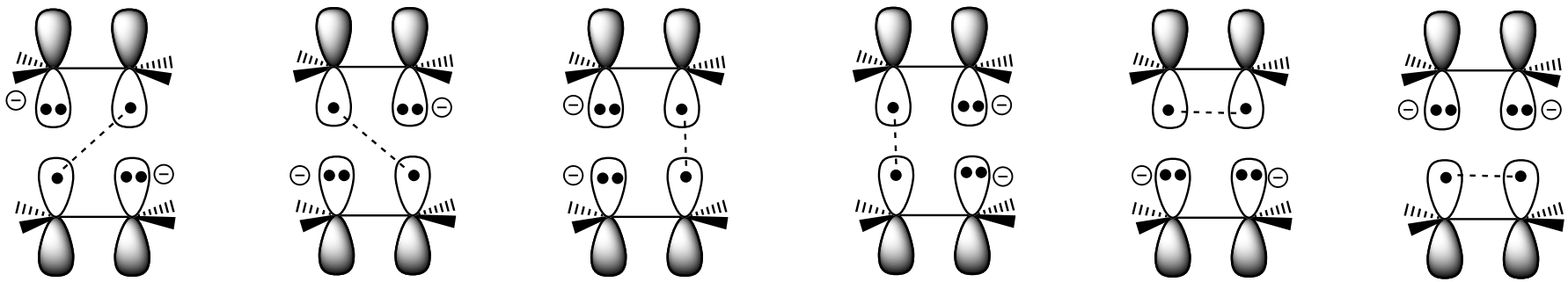
- CAS(4,4) ⇔ 6 VB structures mixing :

$$\begin{cases} \Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB} \\ \Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{3-ext} = \left| b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB} \end{cases}$$

- MO description = VB description
- VB analysis reveals the 3e-bond nature

Quantitative proof (1)

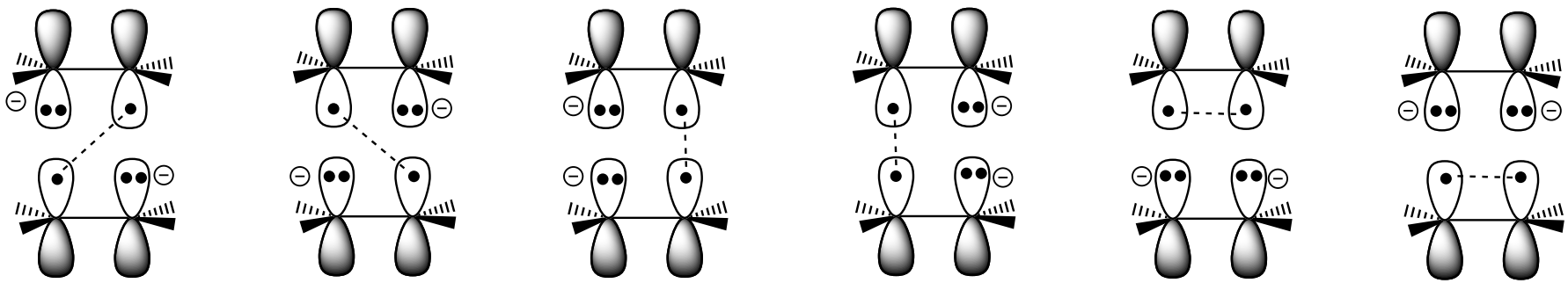
- DTCNE computed weights :



1	2	3	4	5	6
20.2%	20.2%	16.1%	16.1%	**10.1%**	**10.1%**

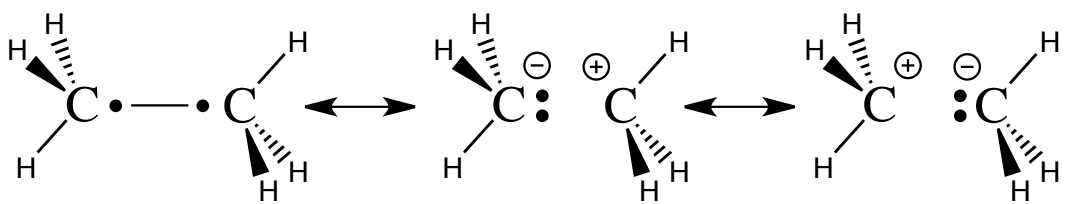
Quantitative proof (1)

- DTCNE computed weights :



1	2	3	4	5	6
20.2%	20.2%	16.1%	16.1%	**10.1%**	**10.1%**

- Stretched ethane :

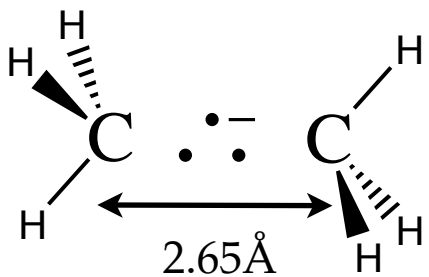


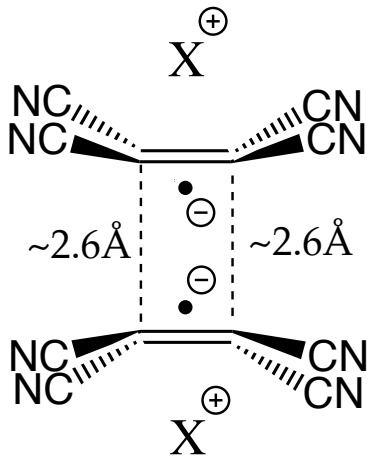
92.8% 3.6% 3.6%

⇒ Str. 5-6 weights are not compatible with a 2c2e bond

Quantitative proof (2)

1) DTCNE bond length close to $3e^-$ bonded ethane anion :





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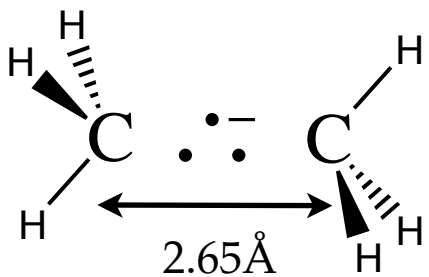
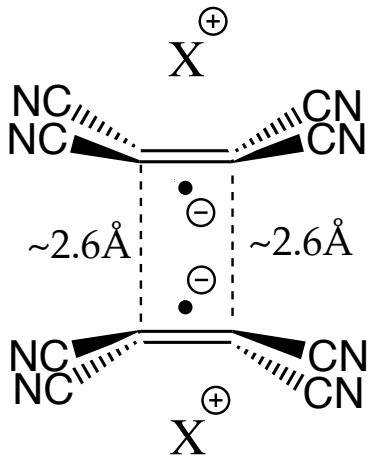
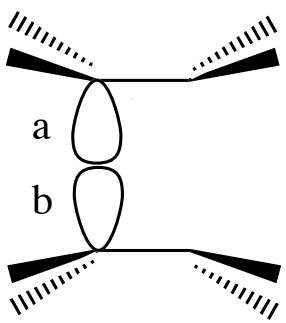




2) DTCNE active orb. overlaps close to optimal $3e^-$ bond value :

$S_{ab} = 0.15$

(computed)

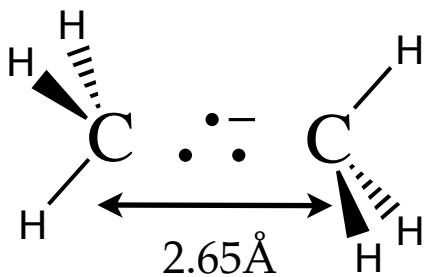


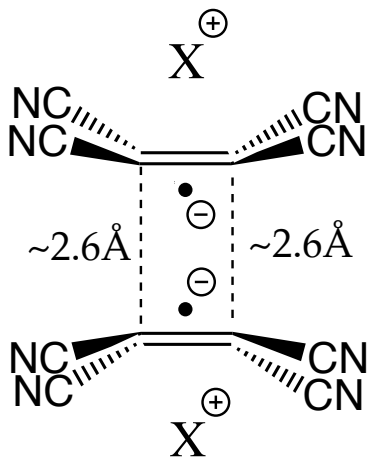
$S_{opt} \approx 0.17$

(from qualitative MO andVB)

Quantitative proof (2)

1) DTCNE bond length close to $3e^-$ bonded ethane anion :





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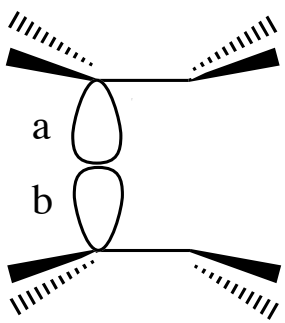
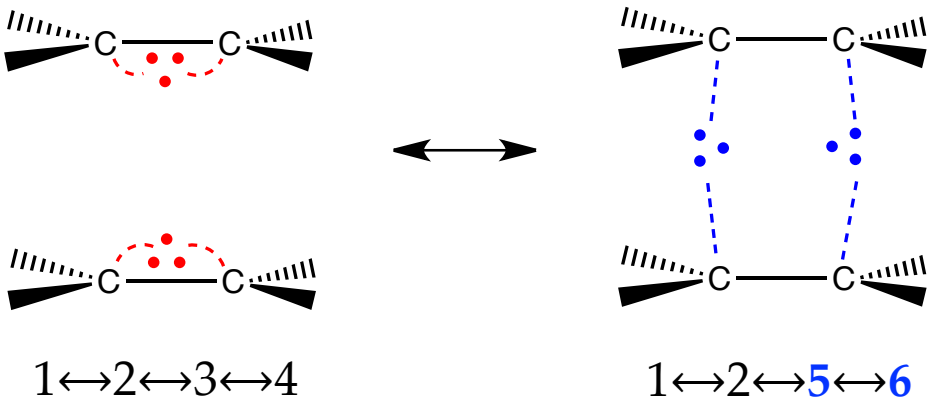


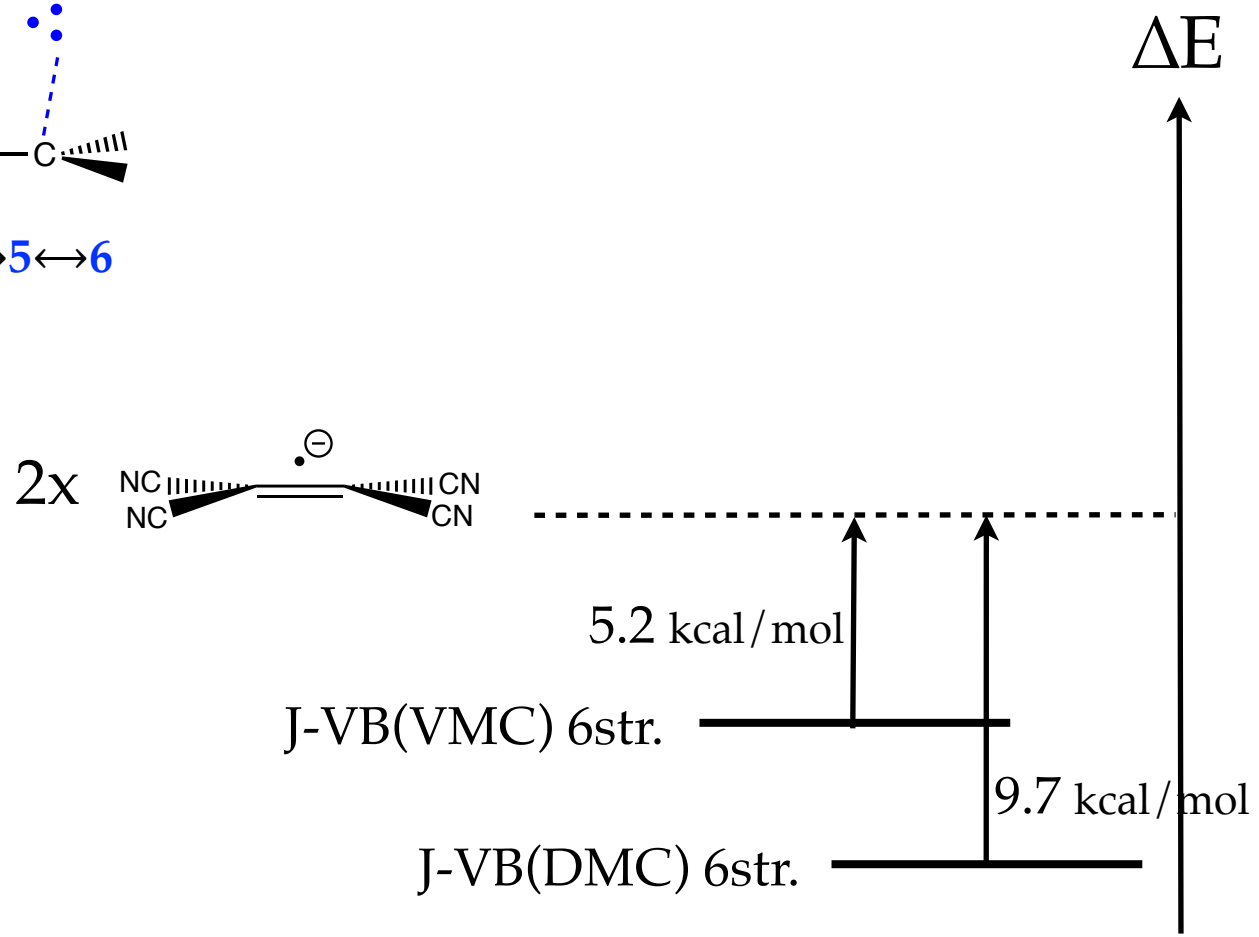
$S_{opt} \approx 0.17$

(from qualitative MO andVB)

3) Dynamical Correlation Energy important for DTCNE

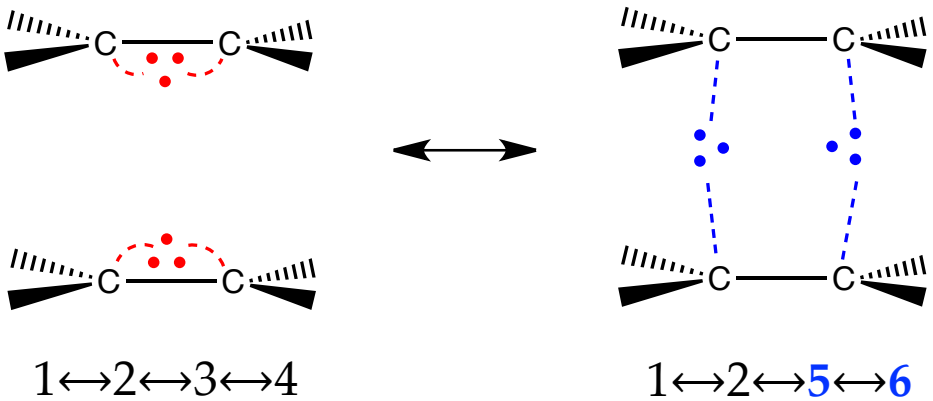
Quantitative proof (3)

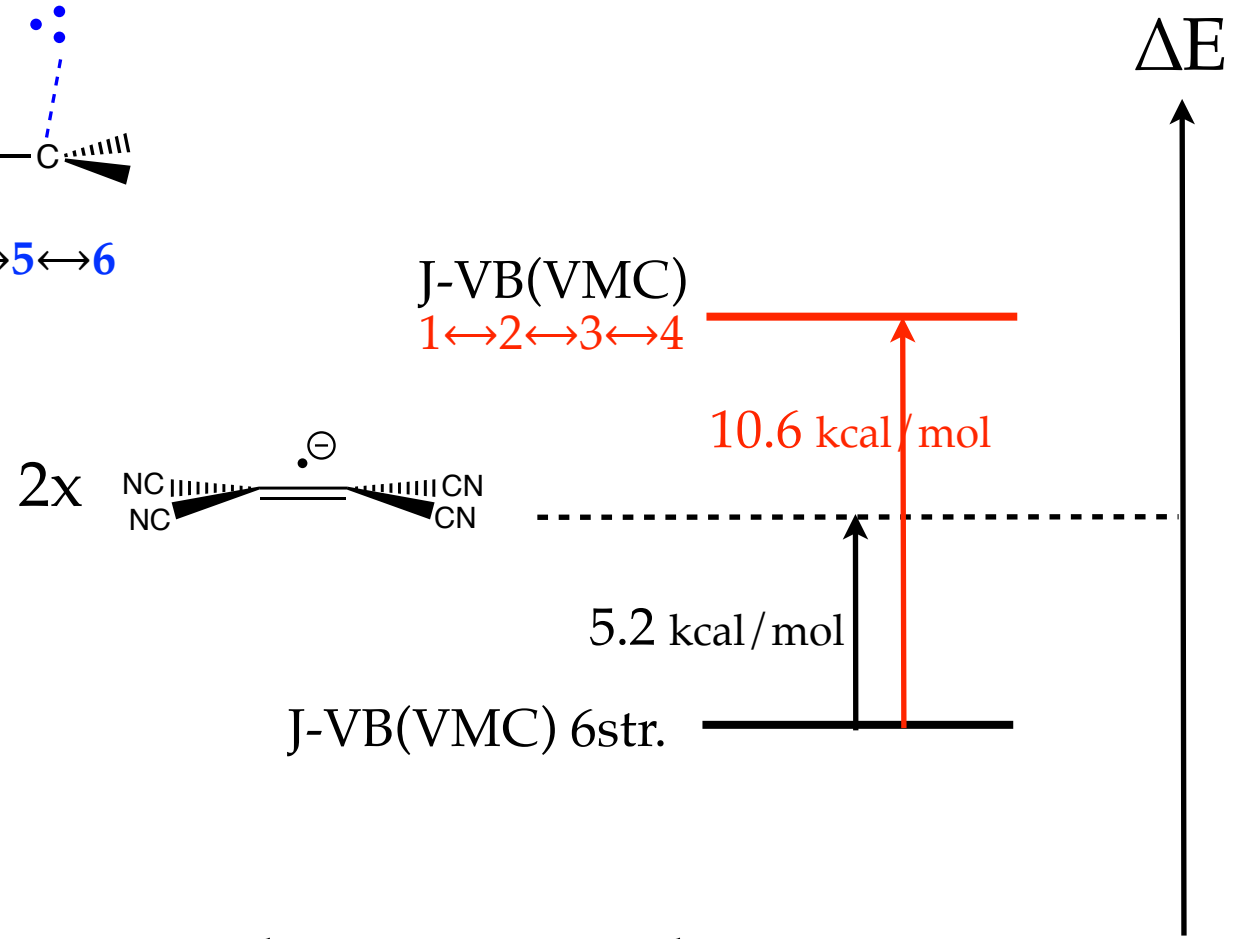




ΔE(«exact») ≈ 11. kcal/mol

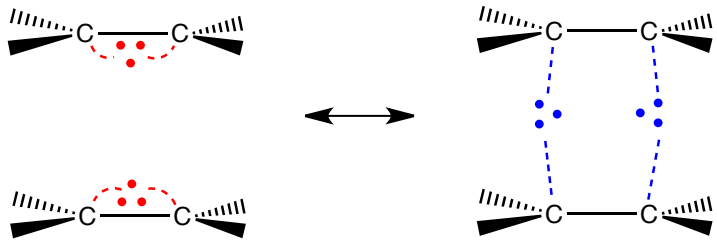
Quantitative proof (3)





⇒ Without str. 5-6, DTCNE becomes repulsive !

Conclusion



- Qualitative VB analysis reveals the 3e-bonding nature in multicenter «pancake» bonding systems
- Confirmed by quantitative VB/QMC calculations (resonance energies) - size limit : ~30 atoms / ~100 electrons
- Importance of interpretative models in chemistry :

«I know that the computer has understood,

but I would like to understand too» (E. Wigner)

VB workshop in Paris !

- plenary lectures on Valence Bond theory, methods, and related models,
- short talks given by participants on a topic relevant to VB theory,
- ample space dedicated to free discussions,
- "hands-on" lab : basic initiation to the XMVB and BLW programs (limited to 30 participants)

Paris, July 2012

The name is Bond, Valence Bond !

XMVB

An Ab Initio Non-orthogonal Valence Bond Program

➟ http://wiki.lct.jussieu.fr/workshop

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