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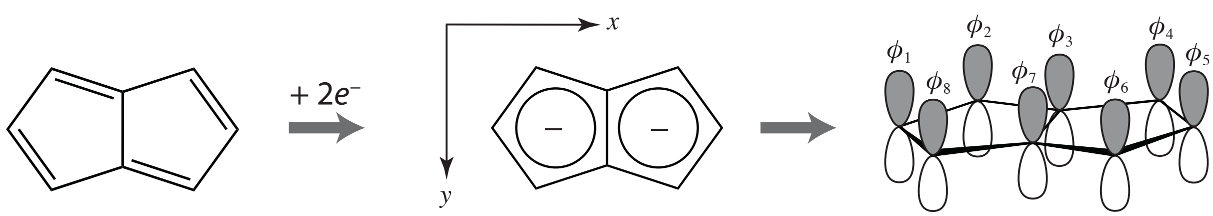
Molecular Orbital Theory for Organometallic Complexes: $[Ti(\eta^8\text{-}C_8H_8)_2]$

Pentalene (Pn = C_8H_6, shown below) is an unsaturated hydrocarbon that is related to the cyclopentadienyl (Cp) fragment by the edge-sharing ring-fusion of two C_5H_5 groups. In its doubly charged form, $C_8H_6^{2-}$, the pentalene dianion is capable of coordination to transition metals via its π system. Using the Hückel approach, we will first generate the MO diagram for the π system of planar $C_8H_6^{2-}$ in D_{2h} symmetry. We will then consider how the orbitals change upon bending of the fragment about the central C-C bond (C_{2v}). Finally, we will develop the qualitative MO diagram for the sandwich complex, $[Ti(\eta^8\text{-}C_8H_6)_2]$.

To begin, let us consider the pentalene dianion in D_{2h} symmetry with the following coordinate system:



(C_{2h}) (D_{2h})

Generating a representation for the 8 p_π orbitals in D_{2h} symmetry gives:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_π	8	0	-2	-2	0	-8	2	2

$$\text{Decomposing gives: } \Gamma_\pi = 2b_{2g} + 2b_{3g} + a_u + 3b_{1u}$$

Descending to the pure rotational subgroup, D_2 gives:

$$\Gamma_\pi = 2b_2 + 2b_3 + a + 3b_1$$

Applying the projection operator to each unique orbital (ϕ_1, ϕ_2, and ϕ_3) generates the SALCs:

$$P^a(\phi_1) = (1)\phi_1 + (1)\phi_5 + (1)(-\phi_5) + (1)(-\phi_1) \Rightarrow 0$$
$$P^a(\phi_2) = (1)\phi_2 + (1)\phi_6 + (1)(-\phi_4) + (1)(-\phi_8) \Rightarrow \boldsymbol{\xi_1 = {}^1/_2(\phi_2 - \phi_4 + \phi_6 - \phi_8)}$$
$$P^a(\phi_3) = (1)\phi_3 + (1)\phi_7 + (1)(-\phi_3) + (1)(-\phi_7) \Rightarrow 0$$
$$P^{b_1}(\phi_1) = (1)\phi_1 + (1)\phi_5 + (-1)(-\phi_5) + (-1)(-\phi_1) \Rightarrow \boldsymbol{\xi_2 = {}^1/_{\sqrt{2}}(\phi_1 + \phi_5)}$$
$$P^{b_1}(\phi_2) = (1)\phi_2 + (1)\phi_6 + (-1)(-\phi_4) + (-1)(-\phi_8) \Rightarrow \boldsymbol{\xi_3 = {}^1/_2(\phi_2 + \phi_4 + \phi_6 + \phi_8)}$$
$$P^{b_1}(\phi_3) = (1)\phi_3 + (1)\phi_7 + (-1)(-\phi_3) + (-1)(-\phi_7) \Rightarrow \boldsymbol{\xi_4 = {}^1/_{\sqrt{2}}(\phi_3 + \phi_7)}$$
$$P^{b_2}(\phi_1) = (1)\phi_1 + (-1)\phi_5 + (1)(-\phi_5) + (-1)(-\phi_1) \Rightarrow \boldsymbol{\xi_5 = {}^1/_{\sqrt{2}}(\phi_1 - \phi_5)}$$
$$P^{b_2}(\phi_2) = (1)\phi_2 + (-1)\phi_6 + (1)(-\phi_4) + (-1)(-\phi_8) \Rightarrow \boldsymbol{\xi_6 = {}^1/_2(\phi_2 - \phi_4 - \phi_6 + \phi_8)}$$
$$P^{b_2}(\phi_3) = (1)\phi_3 + (-1)\phi_7 + (1)(-\phi_3) + (-1)(-\phi_7) \Rightarrow 0$$
$$P^{b_3}(\phi_1) = (1)\phi_1 + (-1)\phi_5 + (-1)(-\phi_5) + (1)(-\phi_1) \Rightarrow 0$$
$$P^{b_3}(\phi_2) = (1)\phi_2 + (-1)\phi_6 + (-1)(-\phi_4) + (1)(-\phi_8) \Rightarrow \boldsymbol{\xi_7 = {}^1/_2(\phi_2 + \phi_4 - \phi_6 - \phi_8)}$$
$$P^{b_3}(\phi_3) = (1)\phi_3 + (-1)\phi_7 + (-1)(-\phi_3) + (1)(-\phi_7) \Rightarrow \boldsymbol{\xi_8 = {}^1/_{\sqrt{2}}(\phi_3 - \phi_7)}$$

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To determine the energies for each MO, we must solve the symmetry-factored secular determinant.

		a	$\boldsymbol{b_1}$			$\boldsymbol{b_2}$		$\boldsymbol{b_3}$	
		ξ_1	ξ_2	ξ_3	ξ_4	ξ_5	ξ_6	ξ_7	ξ_8
a	ξ_1	$H_{11} - ES_{11}$							
	ξ_2		$H_{22} - ES_{22}$	$H_{23} - ES_{23}$	$H_{24} - ES_{24}$				
$\boldsymbol{b_1}$	ξ_3		$H_{32} - ES_{32}$	$H_{33} - ES_{33}$	$H_{34} - ES_{34}$				
	ξ_4		$H_{42} - ES_{42}$	$H_{43} - ES_{43}$	$H_{44} - ES_{44}$				
$\boldsymbol{b_2}$	ξ_5					$H_{55} - ES_{55}$	$H_{56} - ES_{56}$		
	ξ_6					$H_{65} - ES_{65}$	$H_{66} - ES_{66}$		
$\boldsymbol{b_3}$	ξ_7							$H_{77} - ES_{77}$	$H_{78} - ES_{78}$
	ξ_8							$H_{87} - ES_{87}$	$H_{88} - ES_{88}$

Solving for the Coulomb/resonance integrals and using the Hückel approximation ($H_{ij} = \alpha, \beta, or\ 0$; $S_{ij} = \delta_{ij}$) yields the following:

$$
\begin{aligned}
H_{11} &= \langle \xi_1|\hat{H}|\xi_1\rangle = \tfrac{1}{4}(H_{22} - H_{24} + H_{26} - H_{28} - H_{42} + \cdots - H_{86} + H_{88}) = \tfrac{1}{4}(4\alpha) = \alpha \\
H_{22} &= \langle \xi_2|\hat{H}|\xi_2\rangle = \tfrac{1}{2}(H_{11} + H_{15} + H_{51} + H_{55}) = \tfrac{1}{2}(2\alpha) = \alpha \\
H_{23} &= \langle \xi_2|\hat{H}|\xi_3\rangle = (\tfrac{1}{2\sqrt{2}})(H_{12} + H_{14} + H_{16} + H_{18} + H_{52} + H_{54} + H_{56} + H_{58}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{24} &= \langle \xi_2|\hat{H}|\xi_4\rangle = \tfrac{1}{2}(H_{13} + H_{17} + H_{53} + H_{57}) = 0 \\
H_{32} &= \langle \xi_3|\hat{H}|\xi_2\rangle = (\tfrac{1}{2\sqrt{2}})(H_{21} + H_{25} + H_{41} + H_{45} + H_{61} + H_{65} + H_{81} + H_{85}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{33} &= \langle \xi_3|\hat{H}|\xi_3\rangle = \tfrac{1}{4}(H_{22} + H_{24} + H_{26} + H_{28} + H_{42} + \cdots + H_{86} + H_{88}) = \tfrac{1}{4}(4\alpha) = \alpha \\
H_{34} &= \langle \xi_3|\hat{H}|\xi_4\rangle = (\tfrac{1}{2\sqrt{2}})(H_{23} + H_{27} + H_{43} + H_{47} + H_{63} + H_{67} + H_{83} + H_{87}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{42} &= \langle \xi_4|\hat{H}|\xi_2\rangle = \tfrac{1}{2}(H_{31} + H_{35} + H_{71} + H_{75}) = 0 \\
H_{43} &= \langle \xi_4|\hat{H}|\xi_3\rangle = (\tfrac{1}{2\sqrt{2}})(H_{32} + H_{34} + H_{36} + H_{38} + H_{72} + H_{74} + H_{76} + H_{78}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{44} &= \langle \xi_4|\hat{H}|\xi_4\rangle = \tfrac{1}{2}(H_{33} + H_{37} + H_{73} + H_{77}) = \tfrac{1}{2}(\alpha + \beta + \beta + \alpha) = \alpha + \beta \\
H_{55} &= \langle \xi_5|\hat{H}|\xi_5\rangle = \tfrac{1}{2}(H_{11} - H_{15} - H_{51} + H_{55}) = \alpha \\
H_{56} &= \langle \xi_5|\hat{H}|\xi_6\rangle = (\tfrac{1}{2\sqrt{2}})(H_{12} - H_{14} - H_{16} + H_{18} - H_{52} + H_{54} + H_{56} - H_{58}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{65} &= \langle \xi_6|\hat{H}|\xi_5\rangle = (\tfrac{1}{2\sqrt{2}})(H_{12} - H_{14} - H_{16} + H_{18} - H_{52} + H_{54} + H_{56} - H_{58}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{66} &= \langle \xi_6|\hat{H}|\xi_6\rangle = \tfrac{1}{4}(H_{22} - H_{24} - H_{26} + H_{28} - H_{42} + \cdots - H_{86} + H_{88}) = \tfrac{1}{4}(4\alpha) = \alpha \\
H_{77} &= \langle \xi_7|\hat{H}|\xi_7\rangle = \tfrac{1}{4}(H_{22} + H_{24} - H_{26} - H_{28} + H_{42} + \cdots + H_{86} + H_{88}) = \tfrac{1}{4}(4\alpha) = \alpha \\
H_{78} &= \langle \xi_7|\hat{H}|\xi_8\rangle = (\tfrac{1}{2\sqrt{2}})(H_{23} - H_{27} + H_{43} - H_{47} - H_{63} + H_{67} - H_{83} + H_{87}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{87} &= \langle \xi_8|\hat{H}|\xi_7\rangle = (\tfrac{1}{2\sqrt{2}})(H_{32} + H_{34} - H_{36} - H_{38} - H_{72} - H_{74} + H_{76} + H_{78}) = (\tfrac{1}{2\sqrt{2}})(4\beta) = (\tfrac{2}{\sqrt{2}})\beta \\
H_{88} &= \langle \xi_8|\hat{H}|\xi_8\rangle = \tfrac{1}{2}(H_{33} - H_{37} - H_{73} + H_{77}) = \tfrac{1}{2}(\alpha - \beta - \beta + \alpha) = \alpha - \beta
\end{aligned}
$$

	$\xi_1(\boldsymbol{a})$	$\xi_2(\boldsymbol{b_1})$	$\xi_3(\boldsymbol{b_1})$	$\xi_4(\boldsymbol{b_1})$	$\xi_5(\boldsymbol{b_2})$	$\xi_6(\boldsymbol{b_2})$	$\xi_7(\boldsymbol{b_3})$	$\xi_8(\boldsymbol{b_3})$
$\xi_1(\boldsymbol{a})$	$\alpha - E$							
$\xi_2(\boldsymbol{b_1})$		$\alpha - E$	$(\sqrt{2})\beta$	0				
$\xi_3(\boldsymbol{b_1})$		$(\sqrt{2})\beta$	$\alpha - E$	$(\sqrt{2})\beta$				
$\xi_4(\boldsymbol{b_1})$		0	$(\sqrt{2})\beta$	$\alpha + \beta - E$				
$\xi_5(\boldsymbol{b_2})$					$\alpha - E$	$(\sqrt{2})\beta$		
$\xi_6(\boldsymbol{b_2})$					$(\sqrt{2})\beta$	$\alpha - E$		
$\xi_7(\boldsymbol{b_3})$							$\alpha - E$	$(\sqrt{2})\beta$
$\xi_8(\boldsymbol{b_3})$							$(\sqrt{2})\beta$	$\alpha - \beta - E$

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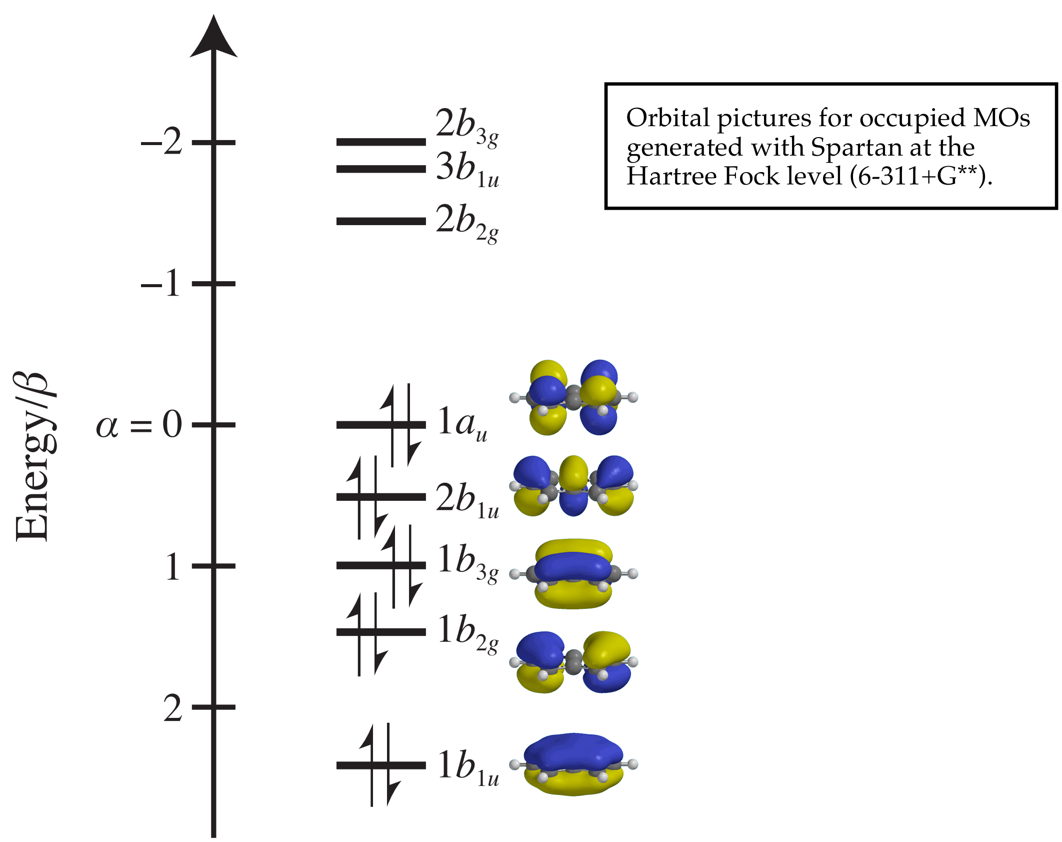
Solving each square determinant gives the energies of each molecular orbital. Take note that we have one 3 × 3 determinant, which is more difficult to solve than our normal 2 × 2 determinant (cannot use the simple quadratic equation). Using any one of a variety of solver programs on the Internet, the roots to the 3rd order polynomial can be easily determined. The final energies in units of β are:

$$a_u\!: E(\psi_1) = \alpha \Rightarrow \mathbf{0}$$
$$b_{1u}\!: E(\psi_2, \psi_3, \psi_4) \Rightarrow \mathbf{2.343\beta, 0.471\beta, -1.814\beta}$$
$$b_{2g}\!: E(\psi_5, \psi_6) \Rightarrow \mathbf{1.414\beta, -1.414\beta}$$
$$b_{3g}\!: E(\psi_7, \psi_8) \Rightarrow \mathbf{\beta, -2\beta}$$

Using these energies, the orbital coefficients are determined from the simultaneous equations that give rise to the secular determinant (see appendix). Combining gives the forms of the MOs (colored coded for phase):

$$1a_u(\psi_1) = 0.5\phi_2 - 0.5\phi_4 + 0.5\phi_6 - 0.5\phi_8$$
$$1b_{1u}(\psi_2) = 0.272\phi_1 + 0.318\phi_2 + 0.474\phi_3 + 0.318\phi_4 + 0.272\phi_5 + 0.318\phi_6 + 0.474\phi_7 + 0.318\phi_8$$
$$2b_{1u}(\psi_3) = 0.512\phi_1 + 0.121\phi_2 - 0.457\phi_3 + 0.121\phi_4 + 0.512\phi_5 + 0.121\phi_6 - 0.457\phi_7 + 0.121\phi_8$$
$$3b_{1u}(\psi_4) = 0.404\phi_1 - 0.367\phi_2 + 0.260\phi_3 - 0.367\phi_4 + 0.404\phi_5 - 0.367\phi_6 + 0.260\phi_7 - 0.367\phi_8$$
$$1b_{2g}(\psi_5) = 0.5\phi_1 + 0.354\phi_2 - 0.354\phi_4 - 0.5\phi_5 - 0.354\phi_6 + 0.354\phi_8$$
$$2b_{2g}(\psi_6) = 0.5\phi_1 - 0.354\phi_2 + 0.354\phi_4 - 0.5\phi_5 + 0.354\phi_6 - 0.354\phi_8$$
$$1b_{3g}(\psi_7) = 0.408\phi_2 + 0.408\phi_3 + 0.408\phi_4 - 0.408\phi_6 - 0.408\phi_7 - 0.408\phi_8$$
$$2b_{3g}(\psi_8) = 0.288\phi_2 - 0.577\phi_3 + 0.288\phi_4 - 0.288\phi_6 + 0.577\phi_7 - 0.288\phi_8$$

We can now generate the MO diagram for the π system of the pentalene dianion within the Hückel approximation:



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Now let us consider folding of the C_8 ring to give the bent pentalene dianion, which is the form that binds to a single metal center. Within the Hückel approximation, I will roughly estimate the effect of this folding by changing the value of certain resonance integrals (H_{ij}) from β to $\beta\cos\omega$, where ω represents the new angle between adjacent p_π orbitals (see Appendix). If we assume a bending angle of 140° (estimated from X-ray data for other Ti pentalene compounds), the secular determinant will change with new values for the resonance integrals describing interactions with orbitals ϕ_3 and ϕ_7:

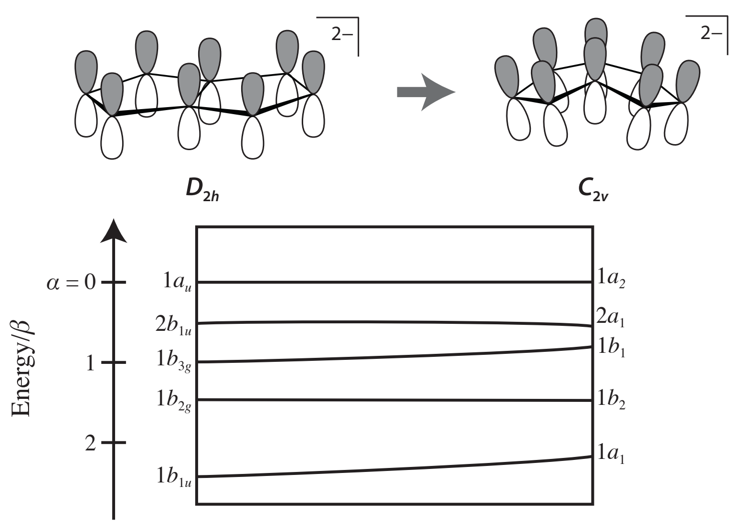
$$H_{34} = \langle \xi_3|\hat{H}|\xi_4\rangle = (\tfrac{1}{2\sqrt{2}})(H_{23} + H_{27} + H_{43} + H_{47} + H_{63} + H_{67} + H_{83} + H_{87}) = (\tfrac{1}{2\sqrt{2}})(4\beta\cos\omega) = (\tfrac{2}{\sqrt{2}})\beta\cos\omega$$
$$H_{43} = \langle \xi_4|\hat{H}|\xi_3\rangle = (\tfrac{1}{2\sqrt{2}})(H_{32} + H_{34} + H_{36} + H_{38} + H_{72} + H_{74} + H_{76} + H_{78}) = (\tfrac{1}{2\sqrt{2}})(4\beta\cos\omega) = (\tfrac{2}{\sqrt{2}})\beta\cos\omega$$
$$H_{78} = \langle \xi_7|\hat{H}|\xi_8\rangle = (\tfrac{1}{2\sqrt{2}})(H_{23} - H_{27} + H_{43} - H_{47} - H_{63} + H_{67} - H_{83} + H_{87}) = (\tfrac{1}{2\sqrt{2}})(4\beta\cos\omega) = (\tfrac{2}{\sqrt{2}})\beta\cos\omega$$
$$H_{87} = \langle \xi_8|\hat{H}|\xi_7\rangle = (\tfrac{1}{2\sqrt{2}})(H_{32} + H_{34} - H_{36} - H_{38} - H_{72} - H_{74} + H_{76} + H_{78}) = (\tfrac{1}{2\sqrt{2}})(4\beta\cos\omega) = (\tfrac{2}{\sqrt{2}})\beta\cos\omega$$

	$\xi_1(\boldsymbol{a})$	$\xi_2(\boldsymbol{b_1})$	$\xi_3(\boldsymbol{b_1})$	$\xi_4(\boldsymbol{b_1})$	$\xi_5(\boldsymbol{b_2})$	$\xi_6(\boldsymbol{b_2})$	$\xi_7(\boldsymbol{b_3})$	$\xi_8(\boldsymbol{b_3})$
$\xi_1(\boldsymbol{a})$	$\alpha - E$							
$\xi_2(\boldsymbol{b_1})$		$\alpha - E$	$(\sqrt{2})\beta$	0				
$\xi_3(\boldsymbol{b_1})$		$(\sqrt{2})\beta$	$\alpha - E$	$(\sqrt{2})\beta\cos\omega$				
$\xi_4(\boldsymbol{b_1})$		0	$(\sqrt{2})\beta\cos\omega$	$\alpha + \beta - E$				
$\xi_5(\boldsymbol{b_2})$					$\alpha - E$	$(\sqrt{2})\beta$		
$\xi_6(\boldsymbol{b_2})$					$(\sqrt{2})\beta$	$\alpha - E$		
$\xi_7(\boldsymbol{b_3})$							$\alpha - E$	$(\sqrt{2})\beta\cos\omega$
$\xi_8(\boldsymbol{b_3})$							$(\sqrt{2})\beta\cos\omega$	$\alpha - \beta - E$

Re-solving the determinants provides a new set of energies for the $a_1(b_{1u})$ and $b_1(b_{3g})$ symmetry MOs:

$$a_1(b_{1u}): E(\psi_2, \psi_3, \psi_4) \Rightarrow \mathbf{2.271\boldsymbol{\beta}, 0.498\boldsymbol{\beta}, -1.769\boldsymbol{\beta}}$$
$$b_1(b_{3g}): E(\psi_7, \psi_8) \Rightarrow \mathbf{0.920\boldsymbol{\beta}, -1.920\boldsymbol{\beta}}$$

Are these energies conceptually reasonable? Yes, orbital $1a_1(b_{1u})$ is destabilized upon bending because it is fully bonding whereas orbitals $2a_1$ and $3a_1$ are stabilized because they possess antibonding interactions between $\phi_{2,4,6,8}$ and $\phi_{3,7}$. The same logic holds for MOs $1b_1$ and $2b_1$. Incorporating these results into a Walsh diagram (occupied MOs only) gives us the MO diagram for bent $C_8H_6^{2-}$. Keep in mind that the symmetry labels change as we move from D_{2h} to C_{2v} symmetry.



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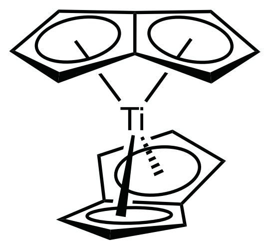
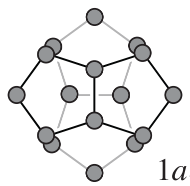
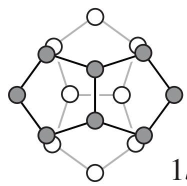
Although no crystal structure exists, one proposed geometry of $[Ti(C_8H_6)_2]$ possesses staggered pentalene ligands giving rise to overall D_{2d} symmetry.



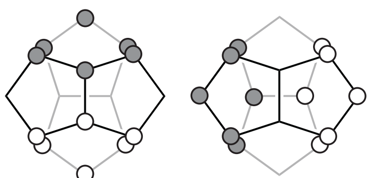
To determine the ligand group orbitals for a set of two bent pentalene dianions we take + and – linear combinations of each of the filled Hückel type orbitals shown above and consider their resulting symmetries [note that in moving from C_{2v} to D_{2d} symmetry, the b_1 and b_2 orbitals must combine to give an *e* set; use a correlation table!]. The resulting ligand group orbitals are shown below in an overhead view along with their symmetries and matches to metal *s*, *p*, and *d* orbitals:



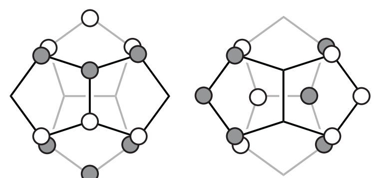
$1a_1$ (s, d_{z^2})



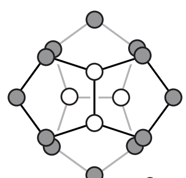
$1b_2$ (p_z, d_{xy})



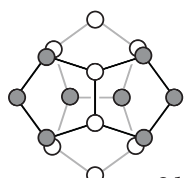
$1e$ ($p_{x,y}$)



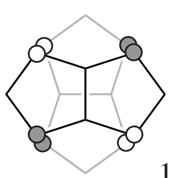
$2e$ ($d_{xz,yz}$)



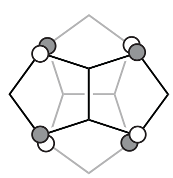
$2a_1$ (s, d_{z^2})



$2b_2$ (p_z, d_{xy})



$1b_1$ ($d_{x^2-y^2}$)



$1a_2$

We are now ready to construct our MO diagram for $[Ti(C_8H_6)_2]$. Since the two $C_8H_6^{2-}$ ligands are separated by several Angstroms, I will assume there is negligible interaction between the two ring orbitals when giving rise to the ligand group orbitals (in other words, the MO of the form $\psi_{1a_1} + \psi_{1a_1}$ is of the same energy as $\psi_{1a_1} - \psi_{1a_1}$). We shall also convert from the Hückel energy scale (α and β) to eV. To do so, I will use a value of ~2.6 eV for β, and a value of ~7 eV for α. The energies of the titanium orbitals (3*d*, 4*s*, and 4*p*) can be approximated from the valence orbital ionization energies (VOIEs).

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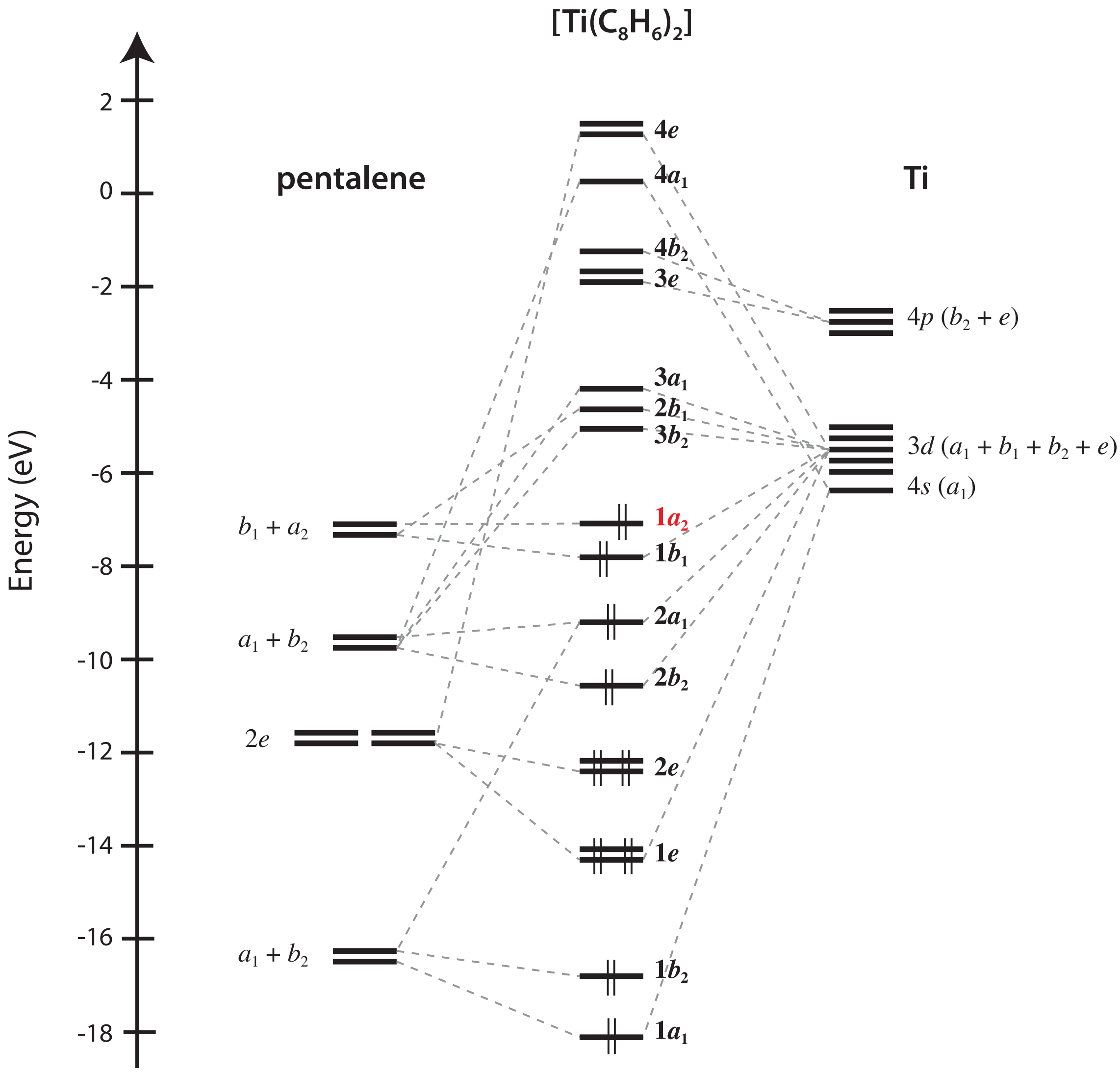

Our diagram predicts a complex with 18 electrons occupying M-L bonding orbitals and a purely ligand based non-bonding orbital ($1a_2$). This diagram is reasonably consistent with both experimental PES data, and calculations using much higher levels of theory (although the true geometry of $[Ti(\eta^8\text{-}C_8H_6)_2]$ is believed to be other than purely D_{2d})!

Further Reading

1. Costuas, K.; Saillard, J.-Y. Is Ti(η^8-pentalene)$_2$ a 20-electron complex? A theoretical investigation of a pseudo electron-rich molecule. *Chem. Commun.* **1998**, 2047-2048.

2. Gleiter, R.; Bethke, S.; Okubo, J.; Jonas, K. Electronic structure of bispentalene complexes of titanium, zirconium, and hafnium: A photoelectron spectroscopic study. *Organometallics* **2001,** *20*, 4274-4278.

3. King, R. B. Chemical applications of topology and group theory: 37. Pentalene as a ligand in transition metal sandwich complexes. *Appl. Organomet. Chem.* **2003**, *17*, 393-397.

4. Li, H.; Feng, H.; Sun, W.; Xie, Y.; King, R. B.; Schaefer, H. F. Mononuclear bis(pentalene) sandwich compounds of the first-row transition metals: variable hapticity of the pentalene rings and intramolecular coupling reactions. *New J. Chem.* **2011**, *35*, 1718-1729.

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Appendix

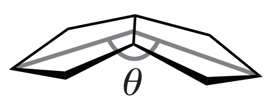
Example orbital coefficient calculation for b_{1u} MOs (ψ_2, ψ_3, ψ_4):

The MOs will have the form: $\psi = c_1\xi_2 + c_2\xi_3 + c_3\xi_4$
Secular equations describing theses MOs are: $c_1(\alpha - E) + c_2(\sqrt{2})\beta = 0$ AND $c_2(\sqrt{2})\beta + c_3(\alpha + \beta - E) = 0$

Assigning the lowest of the three energies, $E = \alpha + 2.343\beta$, to ψ_2 gives:
$c_1(\alpha - \alpha - 2.343\beta) + c_2(1.414\beta) = 0 \Rightarrow c_1 = -(1.414\beta c_2)/(-2.343\beta) = 0.603c_2$
$c_2(1.414\beta) + c_3(\alpha + \beta - \alpha - 2.343\beta) = 0 \Rightarrow c_3 = -(1.414\beta c_2)/(-1.343\beta) = 1.053c_2$
Applying the normalization condition: $(0.603c_2)^2 + c_2^2 + (1.053c_2)^2 = 1 \Rightarrow c_2 = 0.636$; $c_1 = 0.383$; $c_3 = 0.670$

So we have: $\psi_2 = (0.383)\xi_2 + (0.636)\xi_3 + (0.670)\xi_4 = (0.271)(\phi_1 + \phi_5) + (0.318)(\phi_2 + \phi_4 + \phi_6 + \phi_8) + (0.474)(\phi_3 + \phi_7)$
Employing the other two energies for b_{1u} will give coefficients for MOs ψ_3 and ψ_4. Similar logic can be applied for MOs of other symmetry using the appropriate energies.

Description of ω from pentalene bending angle:



$$\omega = \tfrac{1}{2}(\pi - \theta)$$