

Théorie de Hückel et Applications

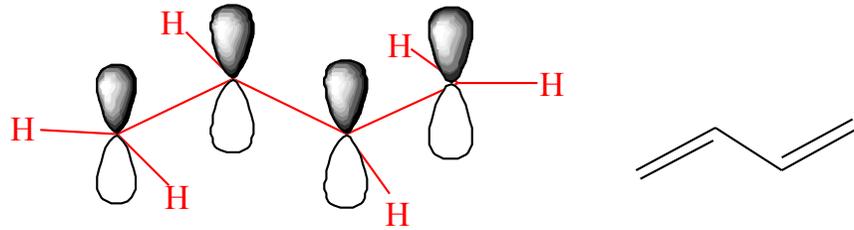
◆ *Hückel*

◆ *Formules de Coulson*

◆ *Aromaticité*

◆ *Application aux réactions électrocycliques*

Molécules « conjuguées »



Les électrons π se meuvent dans le potentiel créé par le **systeme σ**

Orbitales σ ignorées,
non pas négligées

$$\begin{vmatrix}
 \alpha - E & \beta & 0 & 0 \\
 \beta & \alpha - E & \beta & 0 \\
 0 & \beta & \alpha - E & \beta \\
 0 & 0 & \beta & \alpha - E
 \end{vmatrix} = 0$$

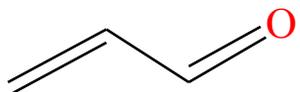
$$\alpha_{ij} = \alpha$$

$$\beta_{ij} = \beta \text{ (atomes voisins)}$$

$$\beta_{ij} = 0 \text{ (atomes non voisins)}$$

$$S_{ij} = 0$$

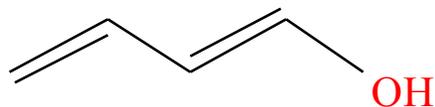
- Extension aux hétéroatomes



$$\alpha_{\text{O}} = \alpha + \beta$$

$$\beta_{\text{C-O}} = \beta$$

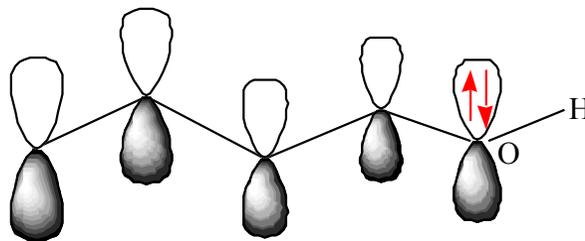
O apporte 1 électron

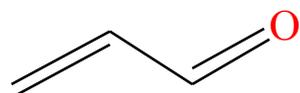


$$\alpha_{\text{O}} = \alpha + 2\beta$$

$$\beta_{\text{C-O}} = 0.8\beta$$

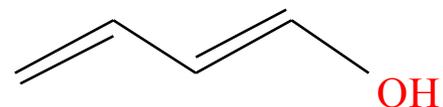
O apporte 2 électrons





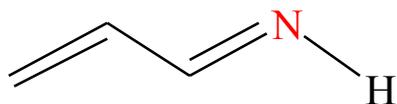
$$\alpha_{\text{O}} = \alpha + \beta$$
$$\beta_{\text{C-O}} = \beta$$

O apporte 1 électron



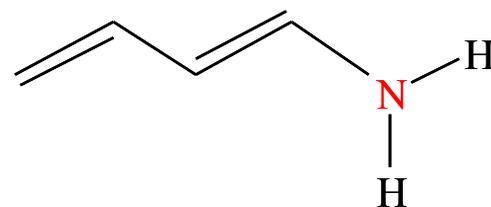
$$\alpha_{\text{O}} = \alpha + 2\beta$$
$$\beta_{\text{C-O}} = 0.8\beta$$

O apporte 2 électrons



$$\alpha_{\text{N}} = \alpha + 0.5\beta$$
$$\beta_{\text{C-N}} = \beta$$

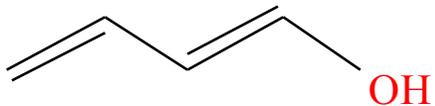
N apporte 1 électron



$$\alpha_{\text{N}} = \alpha + 1.5\beta$$
$$\beta_{\text{C-N}} = 0.8\beta$$

N apporte 2 électrons

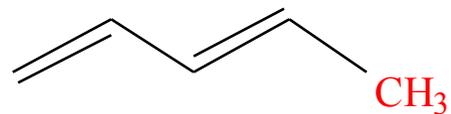
Groupe plan



$$\alpha_{\text{O}} = \alpha + 2\beta$$

$$\beta_{\text{C-O}} = 0.8\beta$$

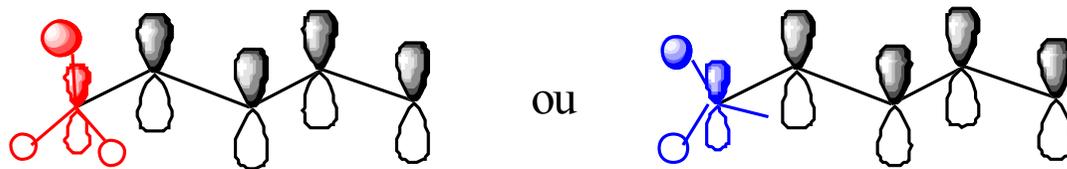
O apporte 2 électrons



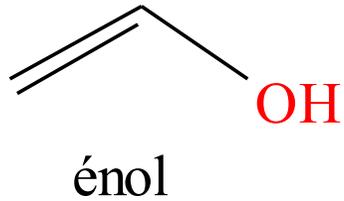
$$\alpha_{\text{CH}_3} = \alpha + 2\beta$$

$$\beta_{\text{C-CH}_3} = 0.7\beta$$

CH₃ apporte 2 électrons

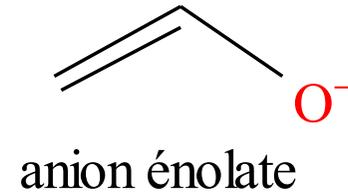


- Effets de charge, de complexation...



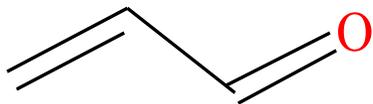
$$\alpha_{\text{O}} = \alpha + 2\beta$$

$$\beta_{\text{C-O}} = 0.8\beta$$



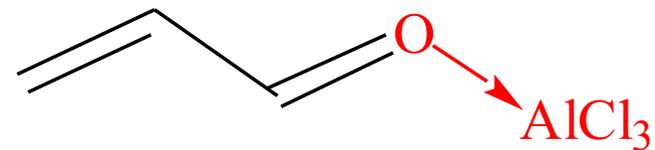
$$\alpha_{\text{O}} = \alpha + 1.75\beta$$

$$\beta_{\text{C-O}} = 0.8\beta$$



$$\alpha_{\text{O}} = \alpha + \beta$$

$$\beta_{\text{C-O}} = \beta$$



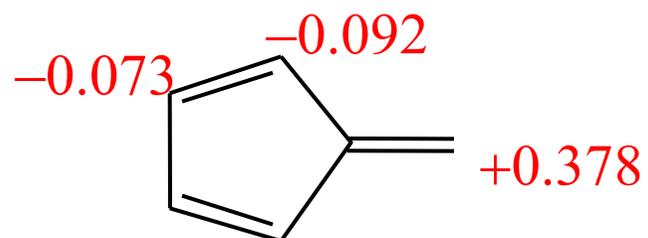
$$\alpha_{\text{O}} = \alpha + 1.5\beta$$

$$\beta_{\text{C-O}} = 0.7\beta$$

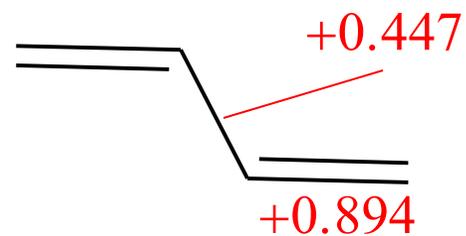
◆ *Energie totale*

Somme des énergies des électrons

◆ *Charges nettes*



◆ *Indices de liaison*



SHMO₂, téléchargeable sur le net

Attention aux points suivants:

- **Unité d'énergie: $|\beta|$** (au lieu de β habituellement)
- **Hétéroatomes:**
 - **paramètres \neq de Streitweiser**
 - **Définir α d'abord, β ensuite (cause bug)**

Formules de Coulson

Polyènes linéaires

Energies des OM

Coefficients des OM

Annulènes

Energies de OM

Coefficients des OM

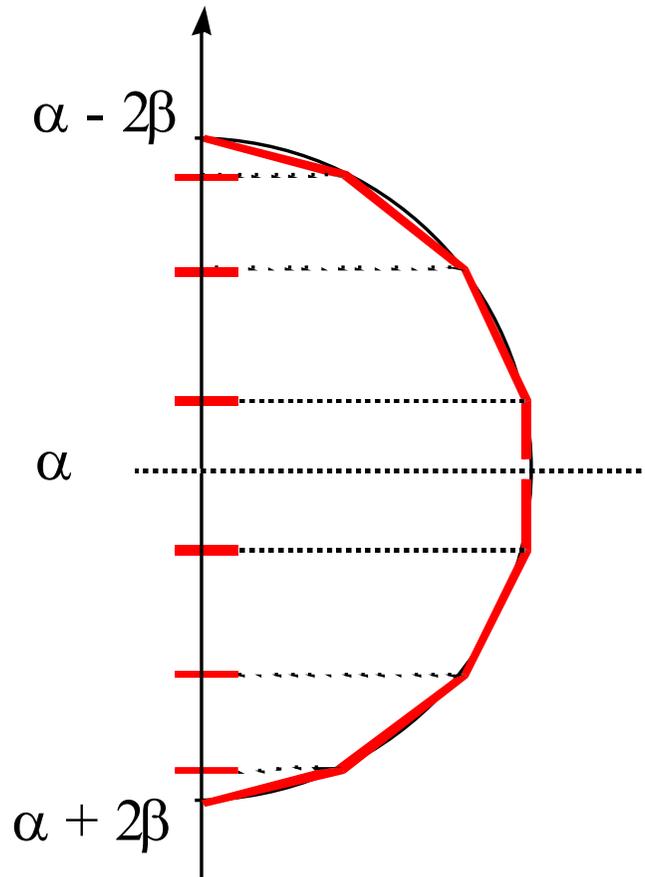
Expression:

Formules analytiques

Procédés graphiques

◆ *Polyènes linéaires*

◆ Energies des OM



Polyène à n atomes:

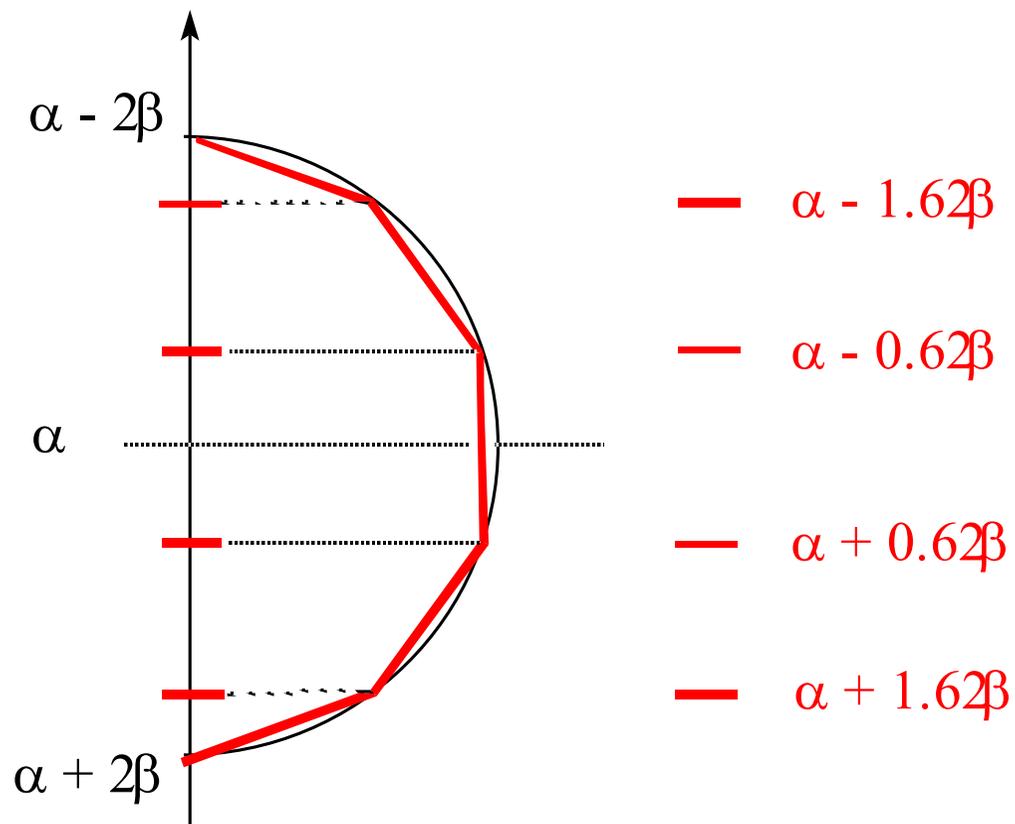
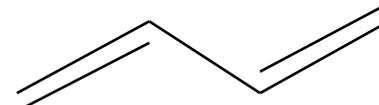
Tracer $(n+1)$ segments

- ⊗ Niveaux symétriques par rapport à α
- ⊗ de + en + resserrés quand n augmente

◆ *Exemple: le butadiène*

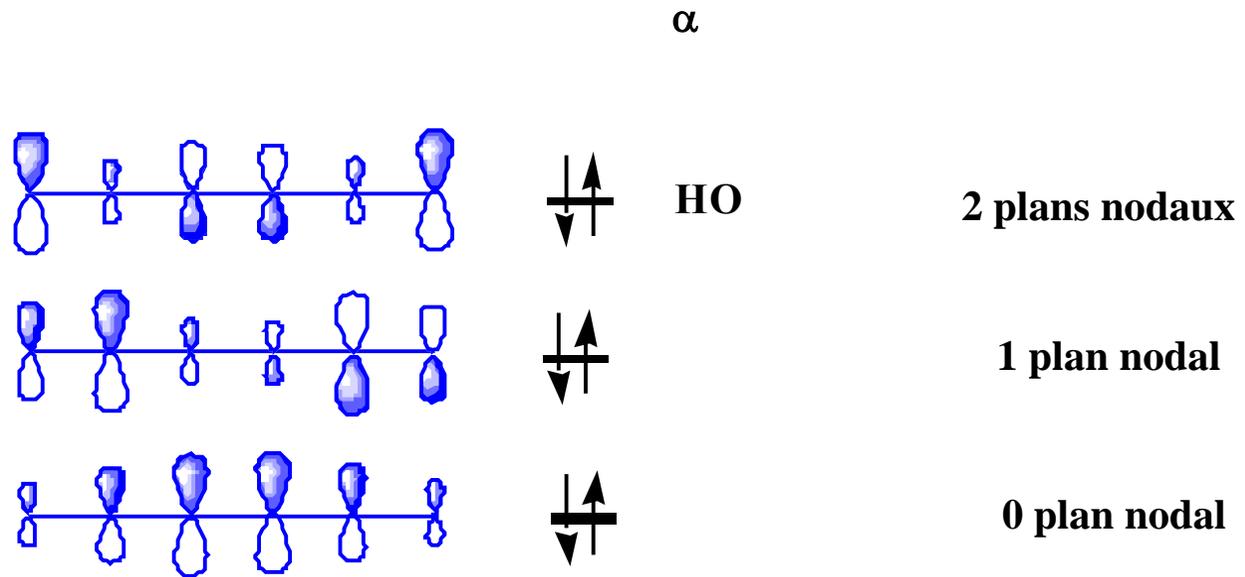
Polyène à 4 atomes:

Tracer 5 segments



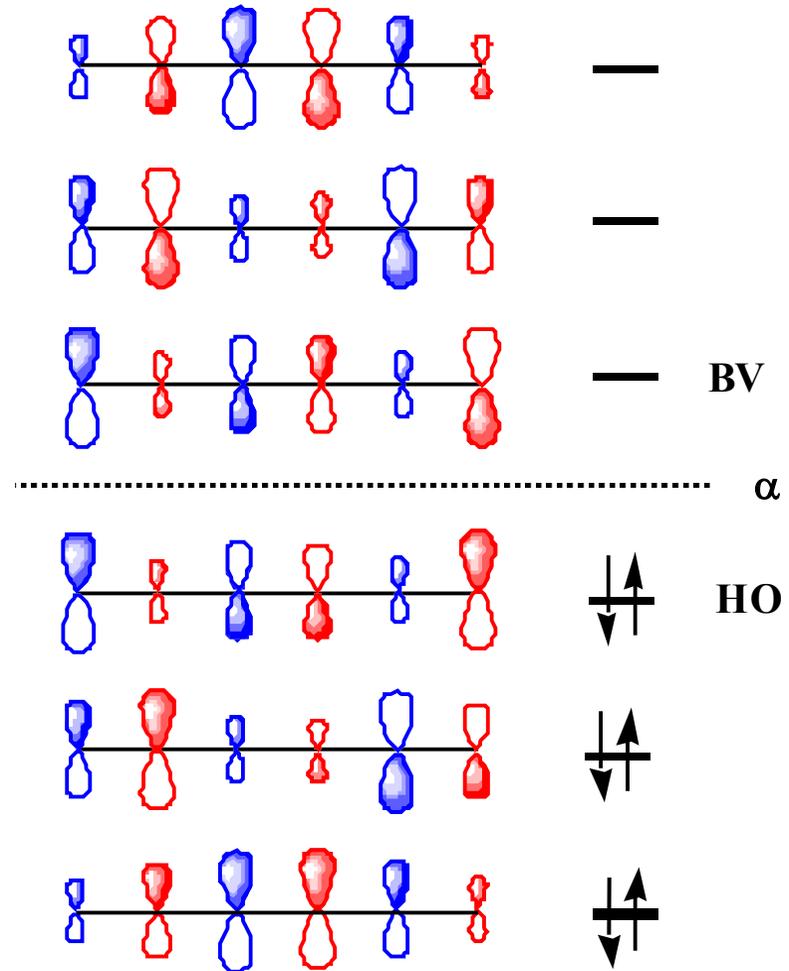
◆ *Polyènes linéaires*

◆ Allure des OM (Coeff. des OA)



Allure des OM (Coeff. des OA)

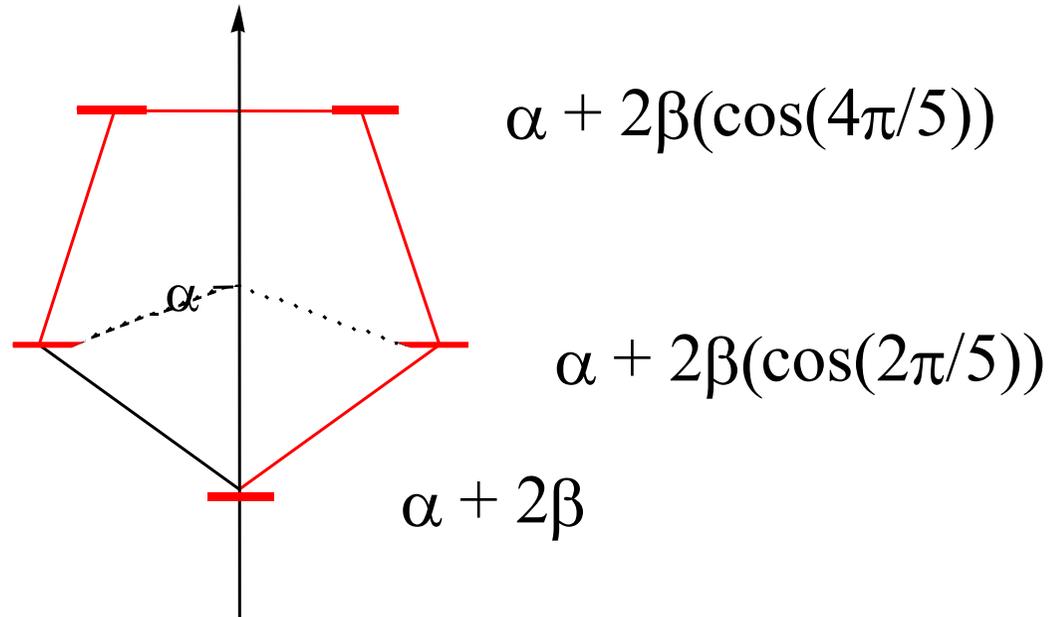
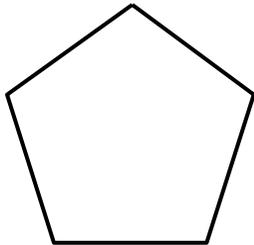
- De bas en haut, de + en + de plans nodaux
- Correspondance 2 à 2 des occupées et des virtuelles:
- Atomes impairs => coefficients égaux
- Atomes pairs => coefficients opposés



◆ *Annulènes*

◆ Energies des OM

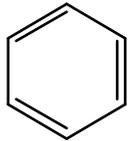
**Exemple:
le cyclopentadiényle**



- ◆ Dégénérescences
- ◆ Energies précises

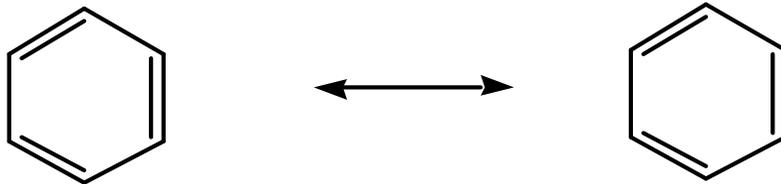
Aromaticité, antiaromaticité

- *Faits expérimentaux*



Très stable

Explication (?)



Stabilisé par « résonance » entre 2 structures de Kekulé

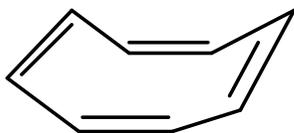
- Faits expérimentaux*



Très stable



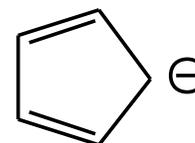
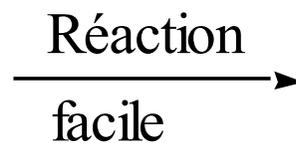
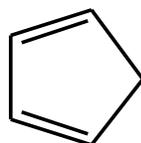
Très instable
rectangulaire



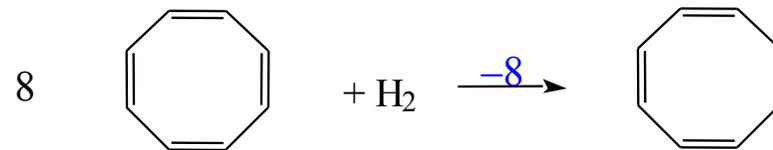
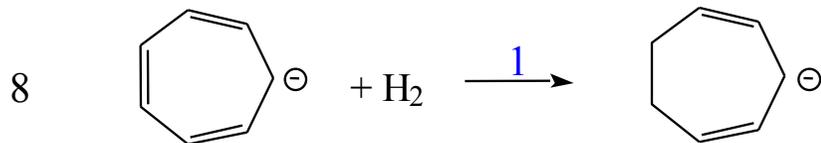
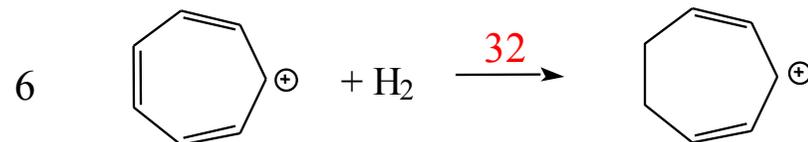
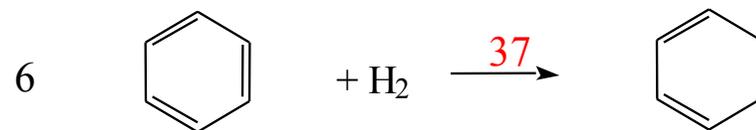
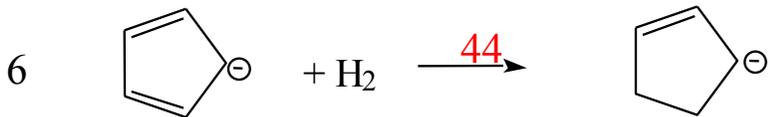
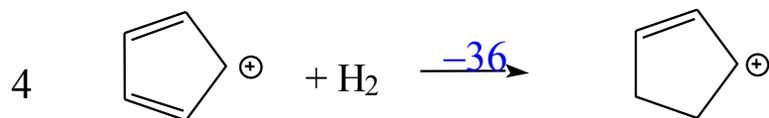
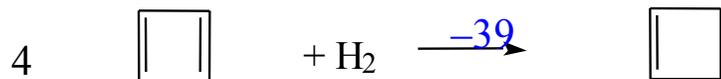
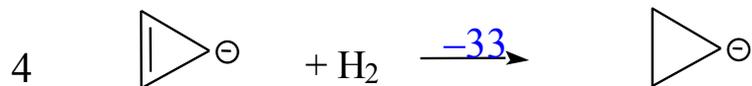
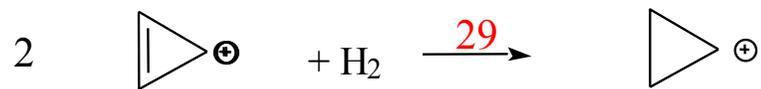
Non plan



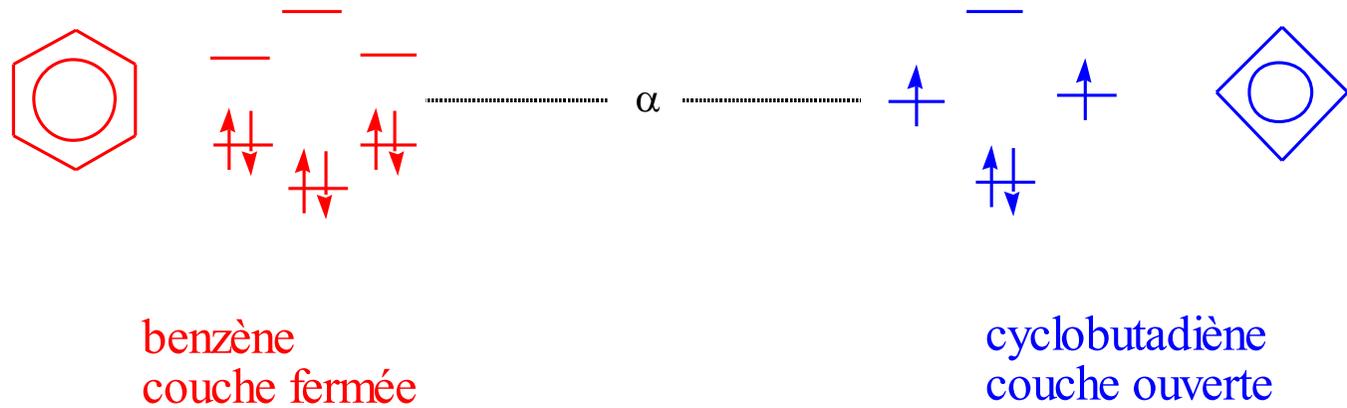
Acide



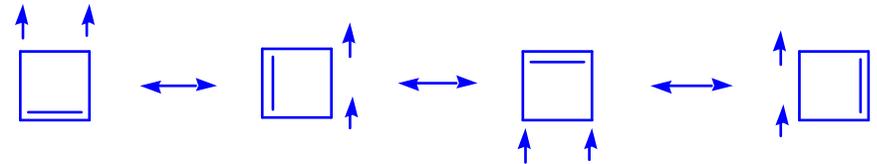
- Quantité corrélante: nombre d'électrons π*



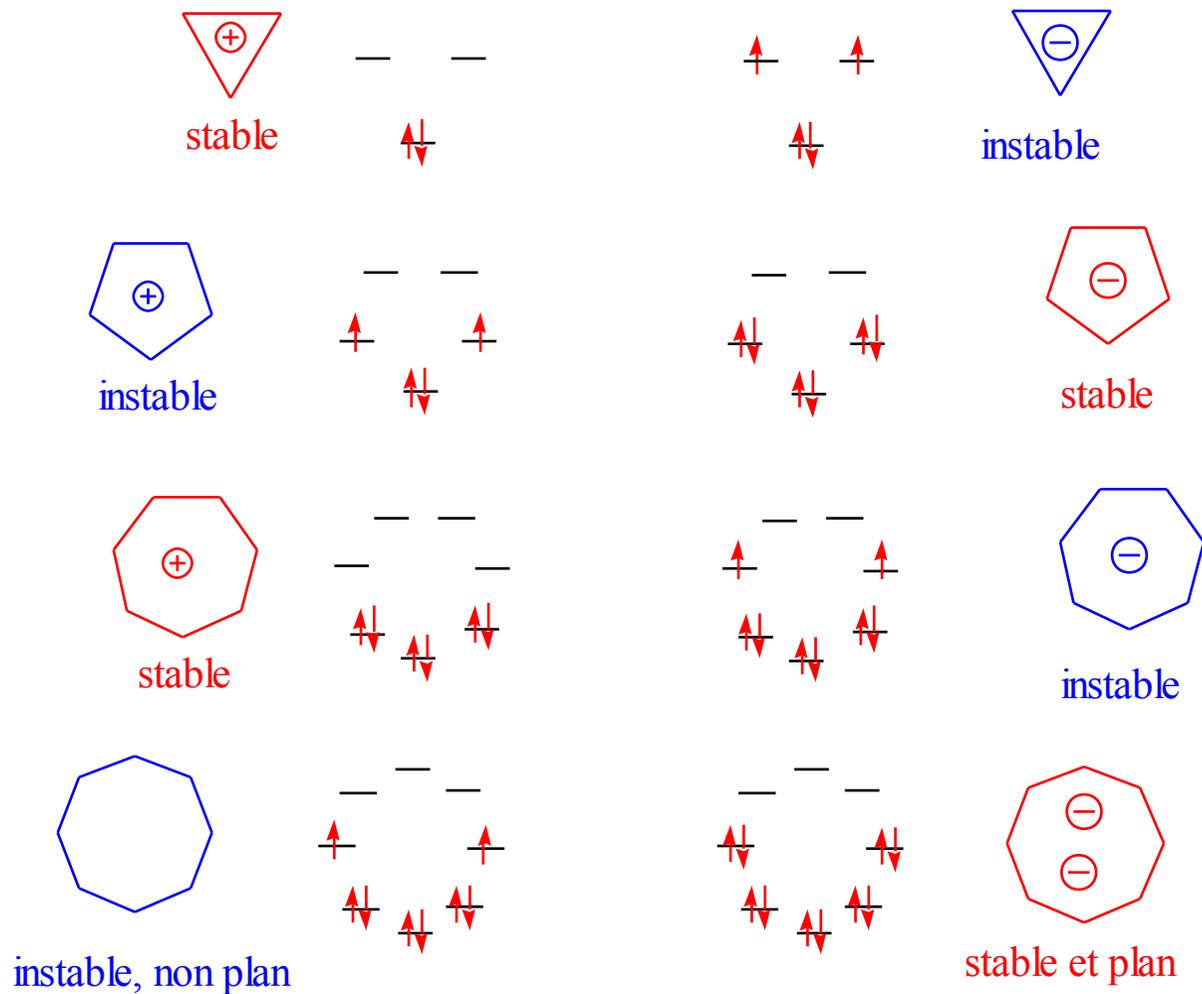
- Règle $4n+2/4n$ de Hückel



Caractère *diradicalaire*



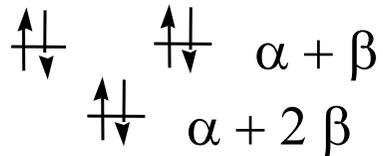
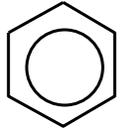
• Généralisation à tous les annulènes



$(4n+2)$ électrons : couche fermée, *stable*

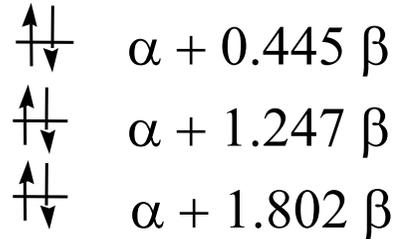
$4n$ électrons : couche ouverte, *instable*

- Energie de résonance



$$E_{\text{tot}} = 6\alpha + 8\beta$$

$$E_{\text{R}} = -2\beta$$



$$E_{\text{tot}} = 6\alpha + 6.988\beta$$

$$E_{\text{R}} = -0.988\beta$$

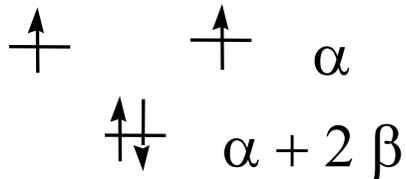
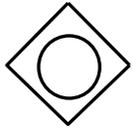
3 éthylènes:



$$E_{\text{tot}} = 6\alpha + 6\beta$$

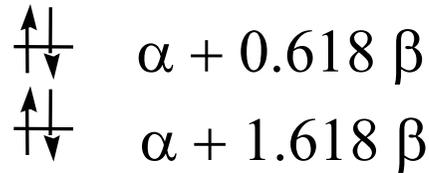
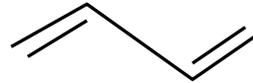
- Benzène « aromatique »

- Energie de résonance



$$E_{\text{tot}} = 4\alpha + 4\beta$$

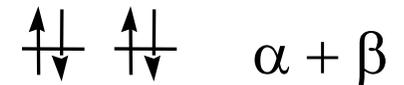
$$E_{\text{R}} = 0$$



$$E_{\text{tot}} = 4\alpha + 4.472\beta$$

$$E_{\text{R}} = -0.472\beta$$

2 éthylènes:



$$E_{\text{tot}} = 4\alpha + 4\beta$$

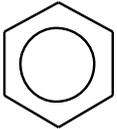
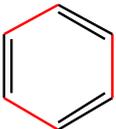
- Cyclobutadiène « antiaromatique »

Energie de résonance des polyènes linéaires

	E_R	
	0	$E_R \approx -0.5 \beta$ par contact entre doubles liaisons
	-0.47β	
	-0.99β	~ Mêmes énergies d'hydrogénation
	-1.52β	
	-2.05β	

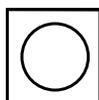
- Polyènes linéaires : **non aromatiques** par définition

• Critère élaboré d'aromaticité :

Comparer  à  non aromatique
 (même E_R que )

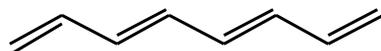


$$E_R = -0.99\beta$$

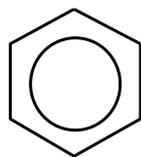


$$E_R = 0$$

antiaromatique



$$E_R = -1.52\beta$$

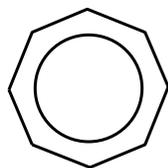


$$E_R = -2\beta$$

aromatique



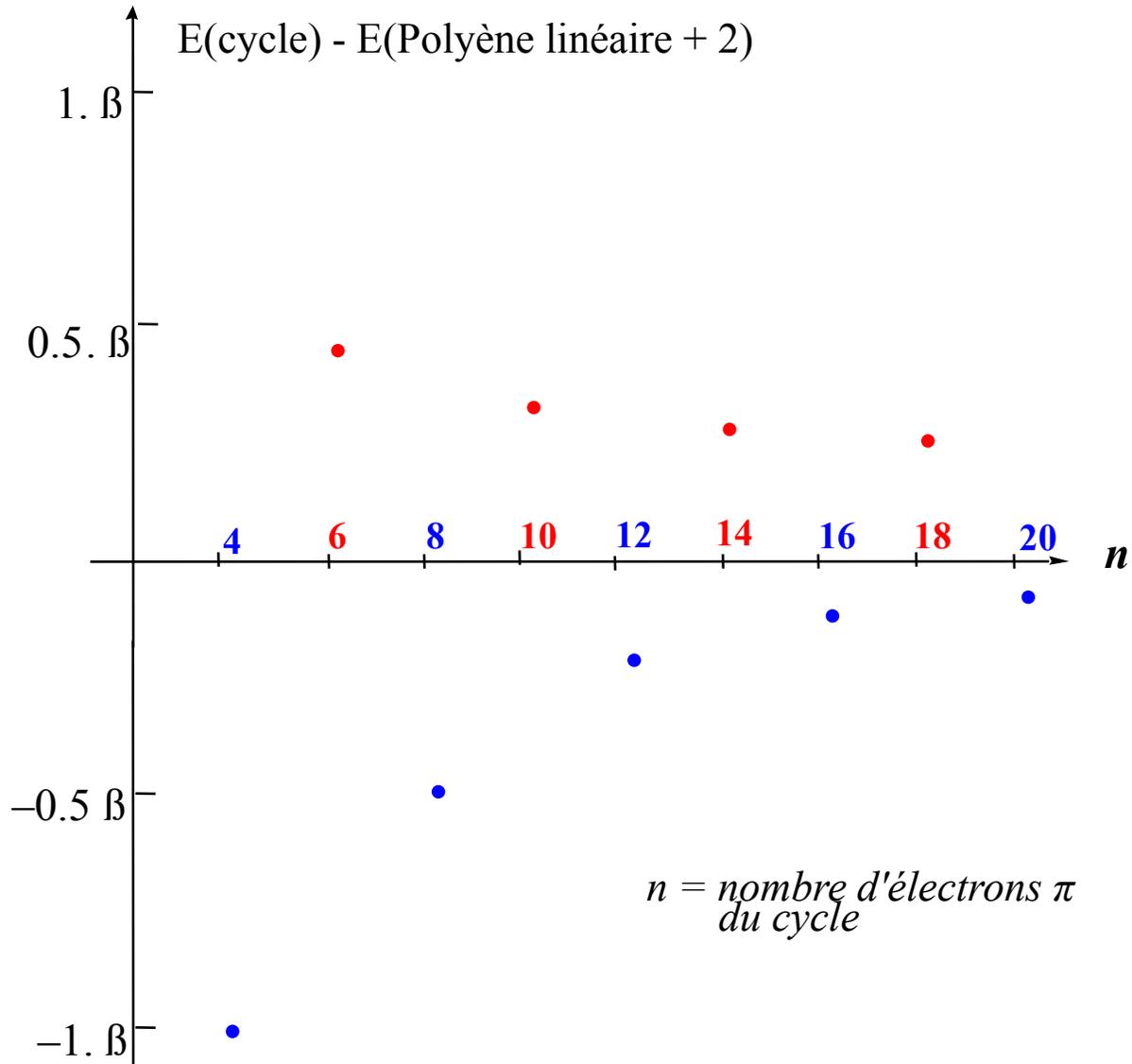
$$E_R = -2.05\beta$$



$$E_R = -1.66\beta$$

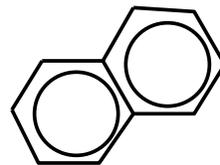
antiaromatique

Application: aromaticité des annulènes :



**Autres molécules
conjuguées :**

aromatique

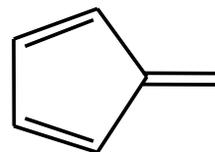


$$E_R = -3.68 \beta$$

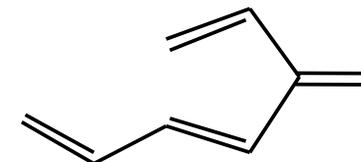
E_R (polyène linéaire +2)

$$E_R = -2.59\beta$$

non aromatique

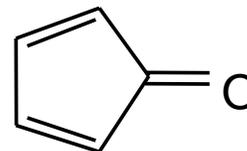


$$E_R = -1.47 \beta$$

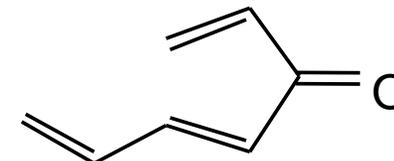


$$E_R = -1.41 \beta$$

antiaromatique

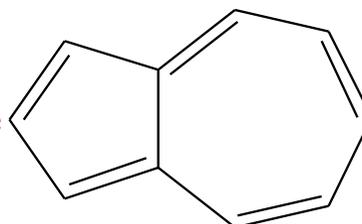


$$E_R = -1.18 \beta$$



$$E_R = -1.52 \beta$$

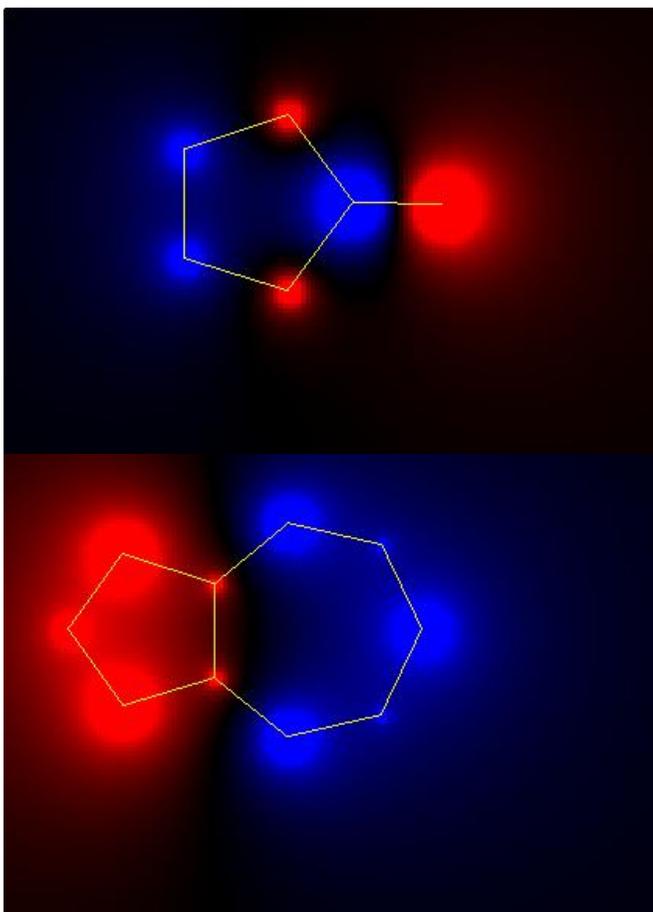
aromatique



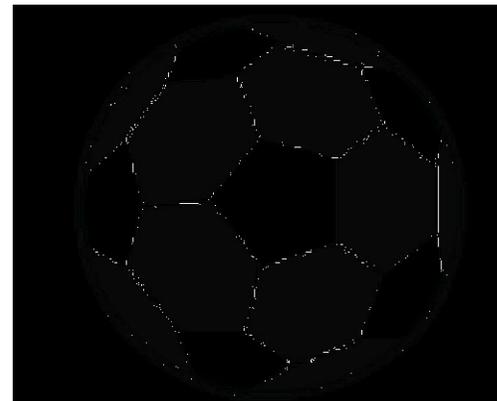
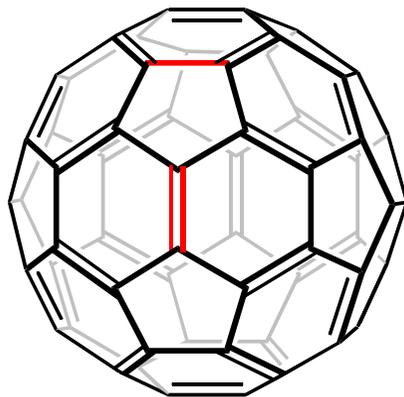
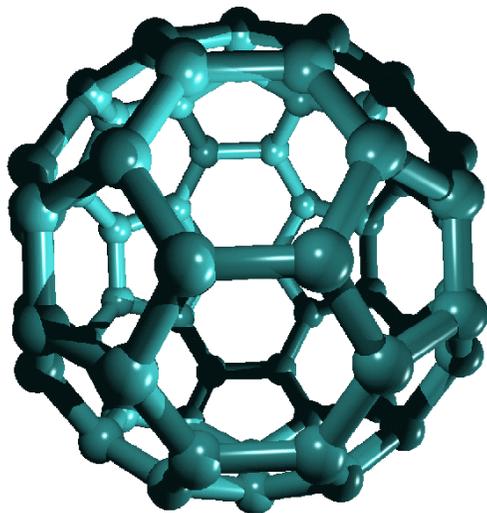
$$E_R = -3.36 \beta$$

E_R (polyène linéaire +2)

$$= -2.59 \beta$$

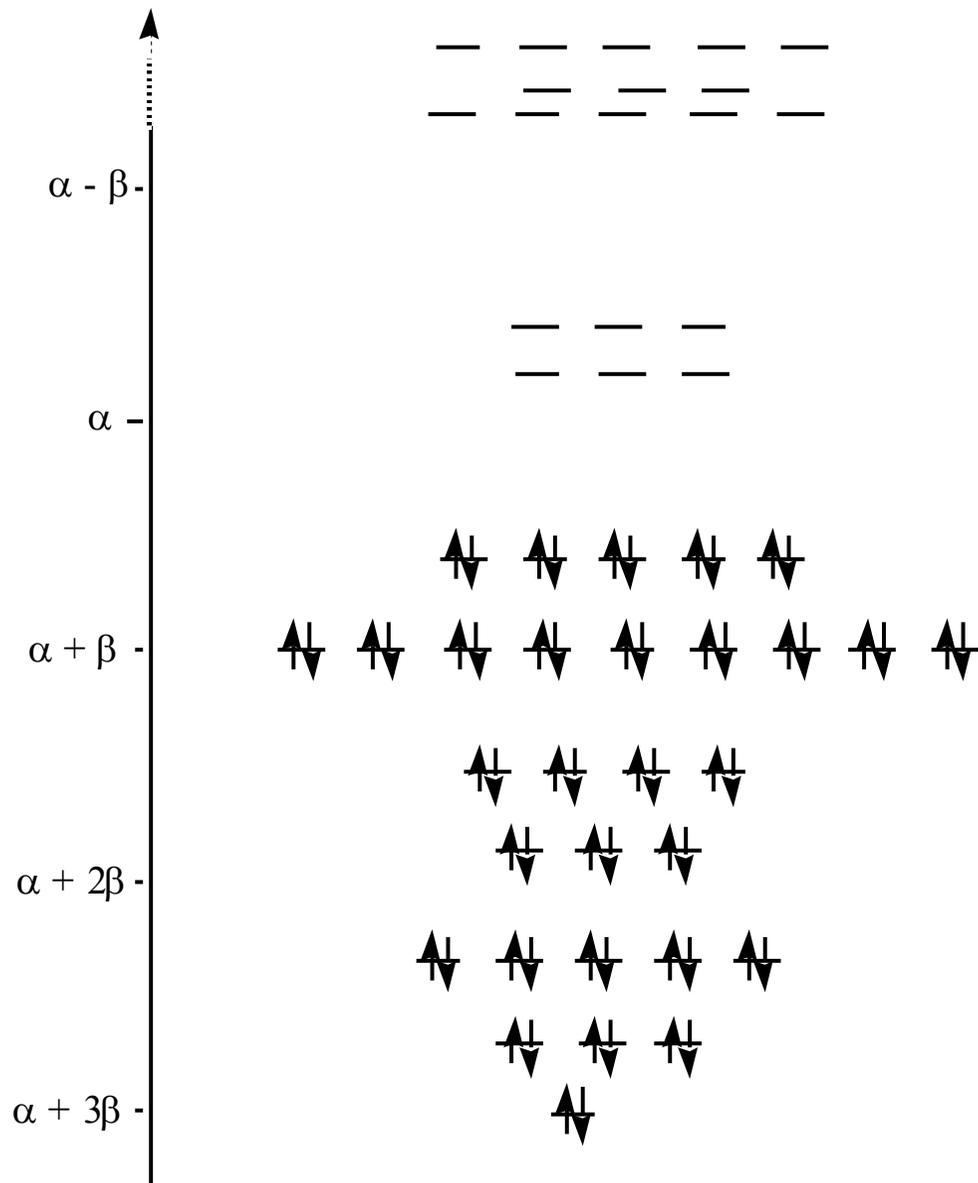


Aromaticité en 3D :



C₆₀ (footballene, sockerballene,...)

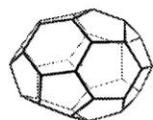
Famille des fullerenes (C₃₂, C₇₀, C₈₄, C₁₂₀, C₁₈₀, ...)



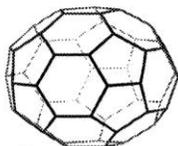
$E_R = -0.365 \beta/\text{électron}$
 (-0.333β dans C_6H_6)

Ions stables prévus:

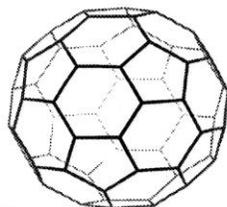




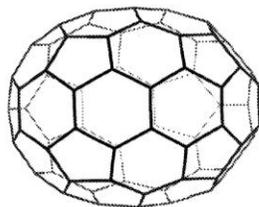
D_2-C_{32}



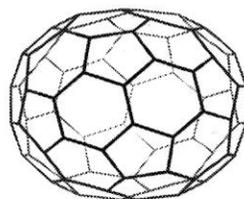
$D_{5h}-C_{50}$



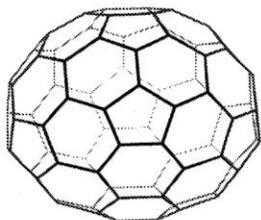
I_h-C_{60}



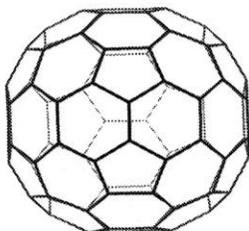
$D_{5h}-C_{70}$



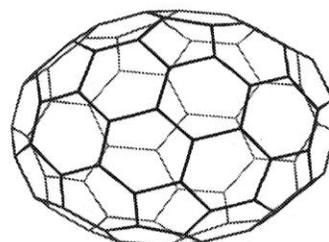
D_2-C_{76}



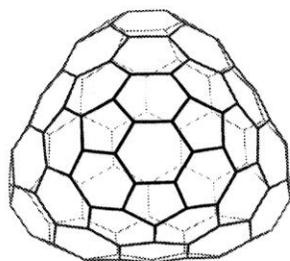
$C_{2v}(1)-C_{78}$



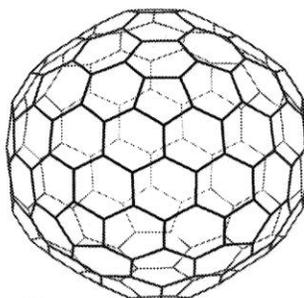
$D_{2d}(23)-C_{84}$



$D_{2d}(4)-C_{84}$

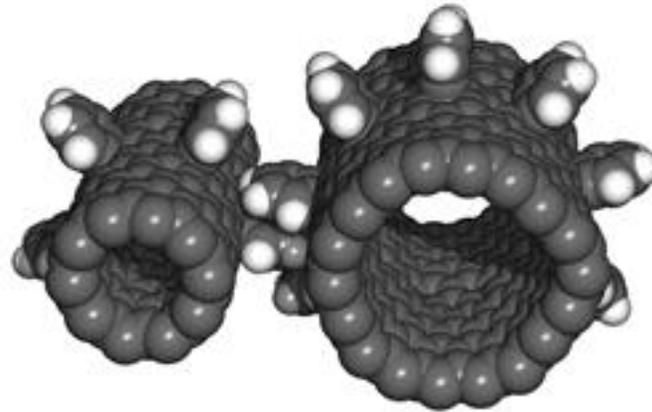
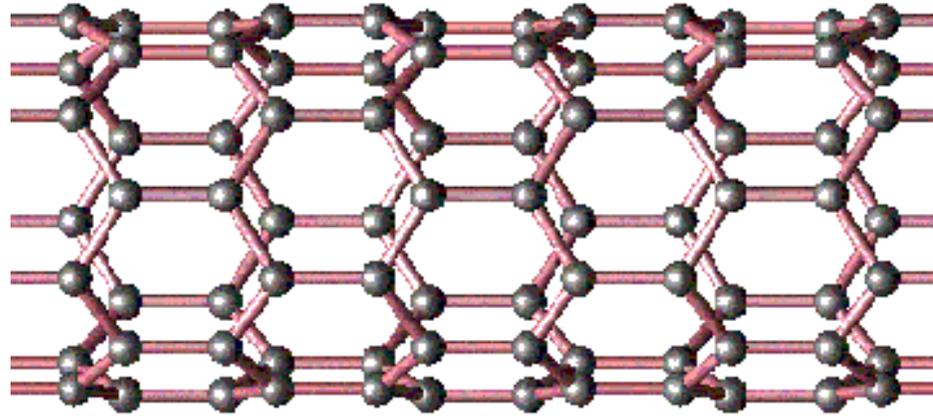


I_h-C_{120}



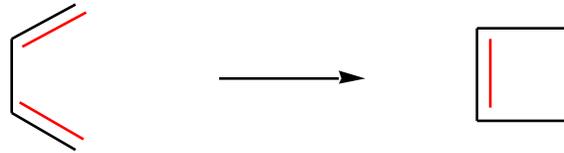
I_h-C_{180}

Nanotubes
(nanotechnologies,
...)



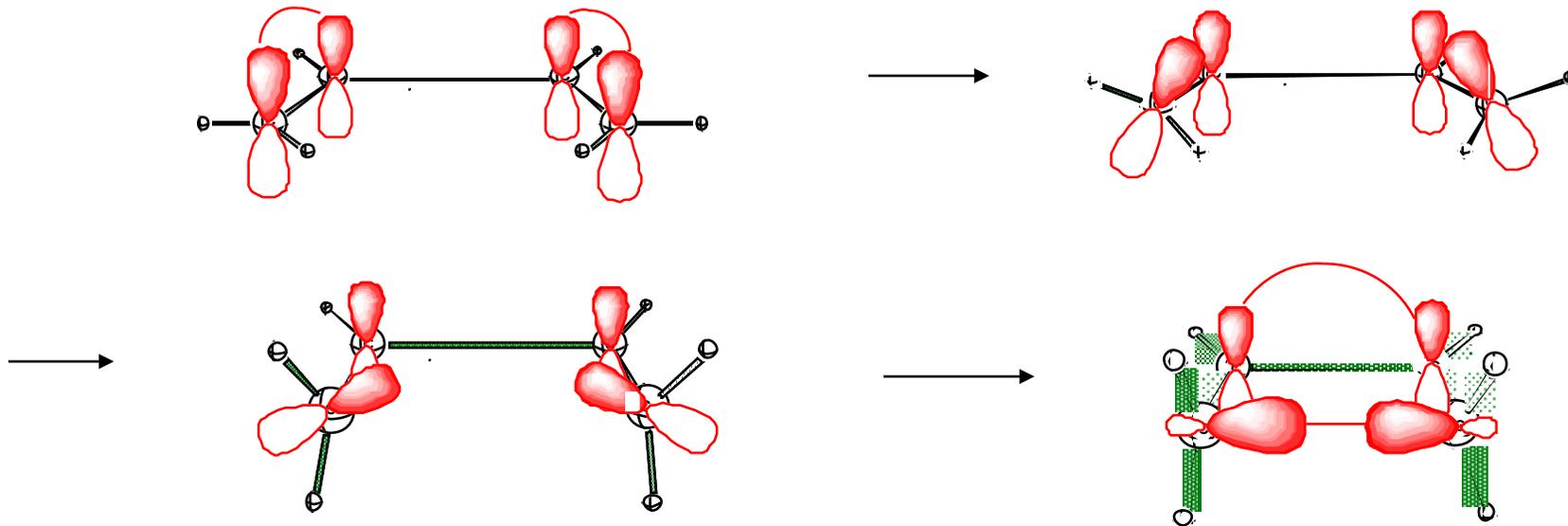
- Réactions électrocycliques

Exemple: cyclisation du butadiène

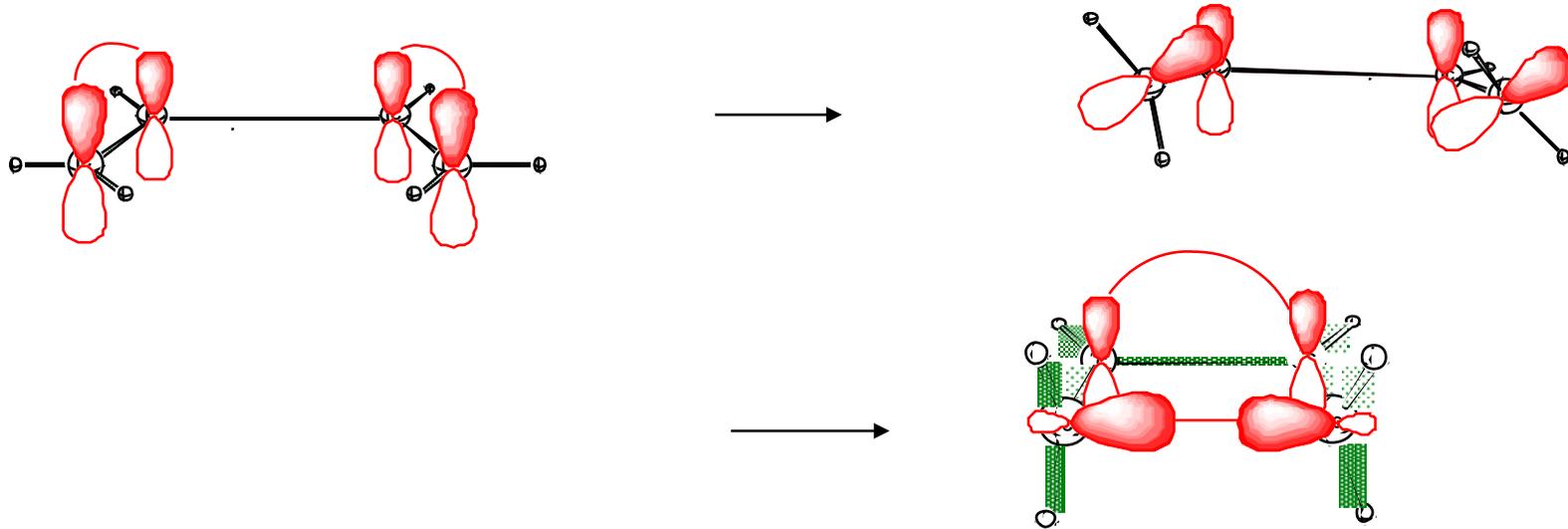


4 électrons
participent

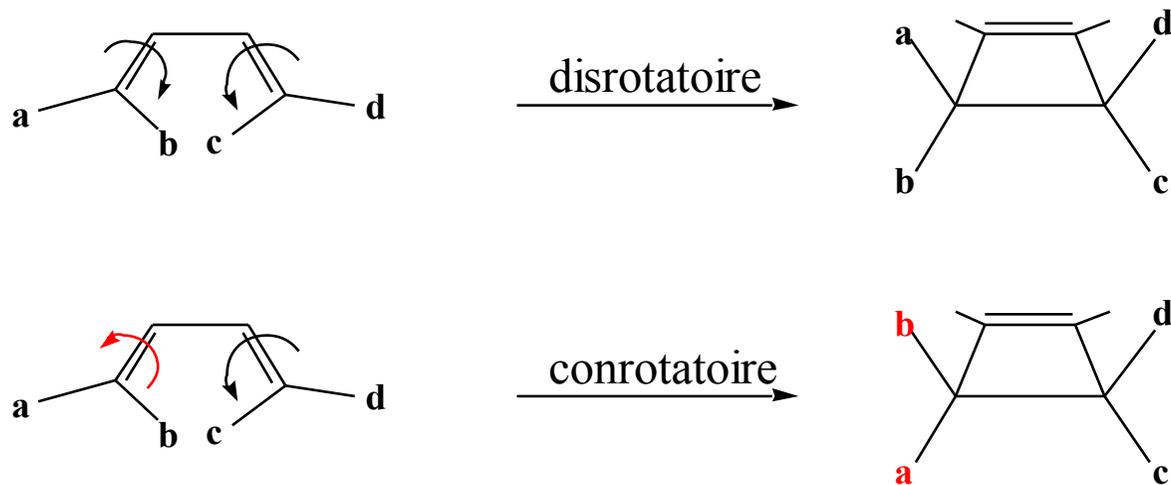
1) Mécanisme « disrotatoire »



1) Mécanisme « conrotatoire »

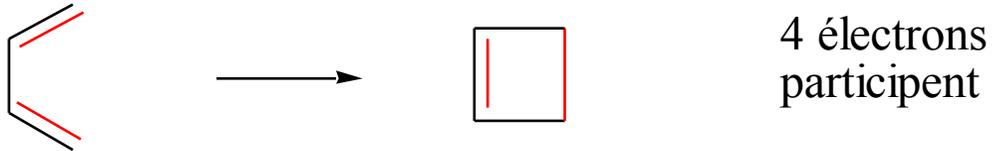


2 mécanismes => 2 produits différents:

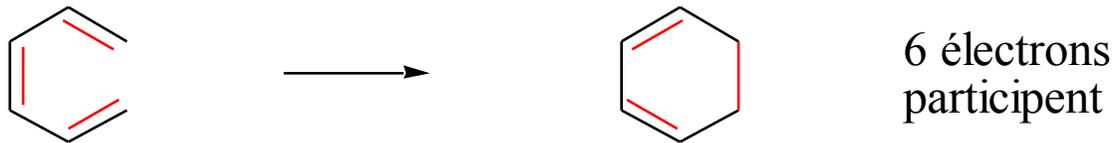


- Réactions électrocycliques

- Exemple: cyclisation du butadiène



- Autres réactions...



- Etc...

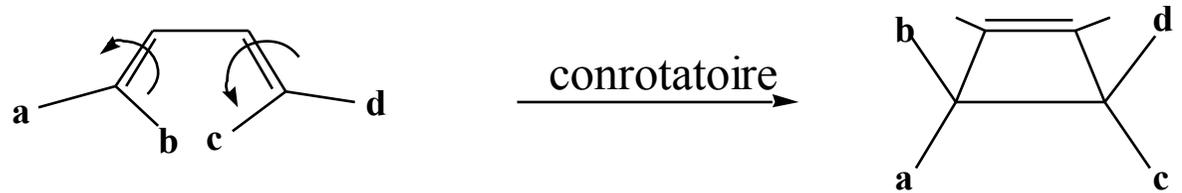
-

2, 8, 10, 12 électrons...

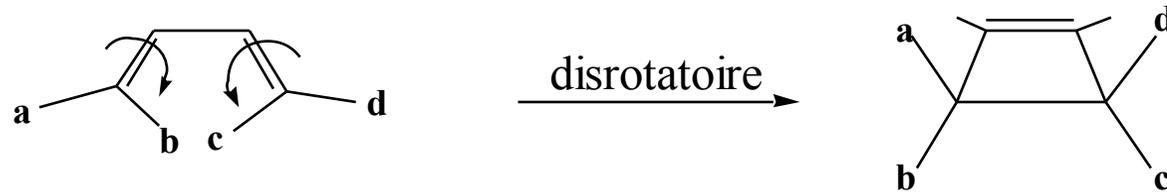
Faits expérimentaux:

◆ Cyclisation du butadiène:

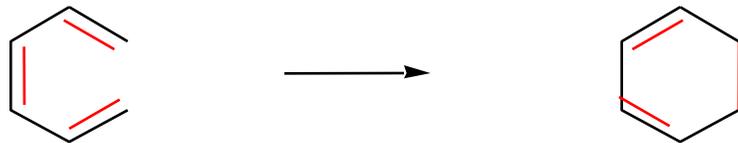
- Thermique



- Photochimique:



◆ Cyclisation de l'hexatriène.



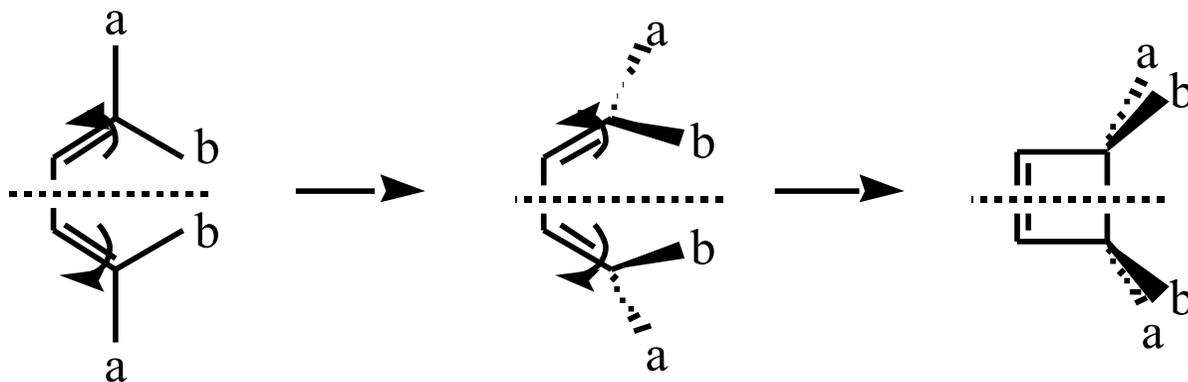
Thermique **Disrotatoire**

Photochimique **Conrotatoire**

◆ Etc... Forte sélectivité, aucune explication classique !

- **La Conservation de la Symétrie des Orbitales (Woodward et Hoffmann, 1965)**

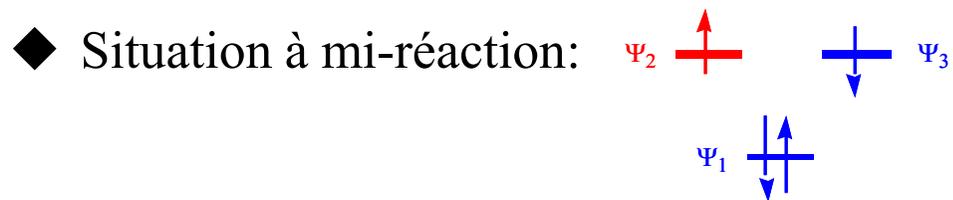
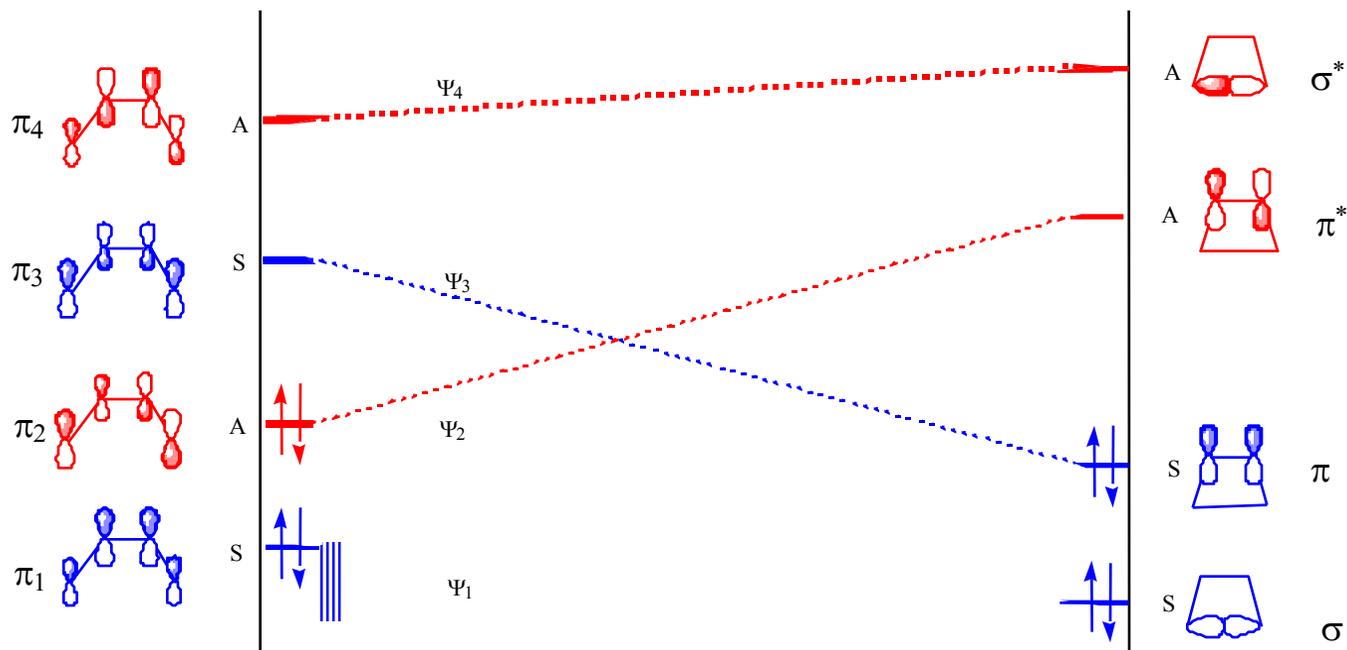
- ◆ On choisit un élément de symétrie qui se conserve au cours de la réaction:



Exemple: plan bissecteur pour réaction disrotatoire

- ◆ On classe les OM en symétriques (**S**) ou antisymétriques (**A**)
- ◆ On trace le diagramme de corrélation d'OM, des réactifs aux produits.

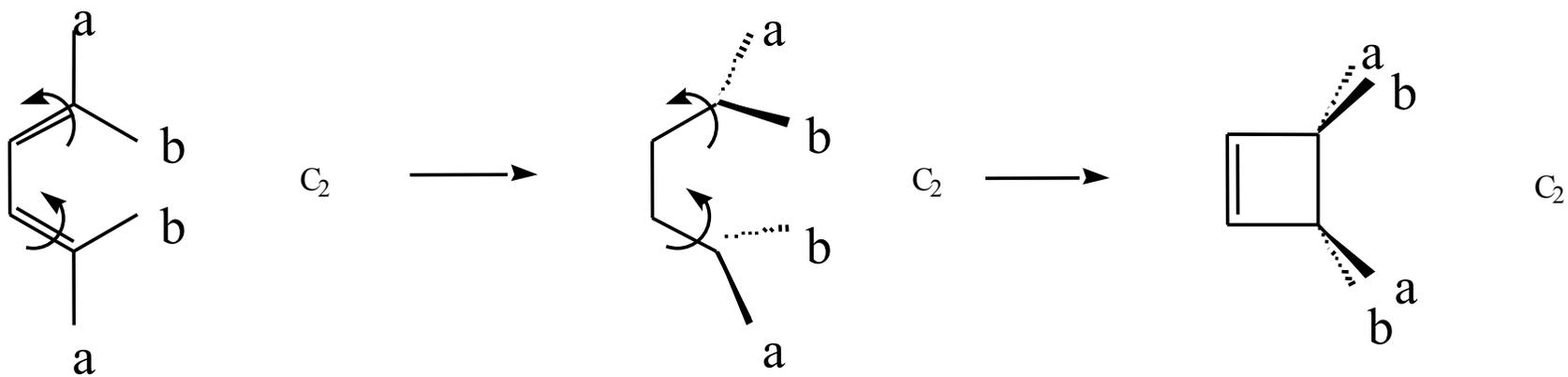
- Cyclisation thermique **disrotatoire** du butadiène



Antiaromatique: complexe activé haute énergie,

Réaction **interdite** thermiquement

Cyclisation thermique **conrotatoire** du butadiène



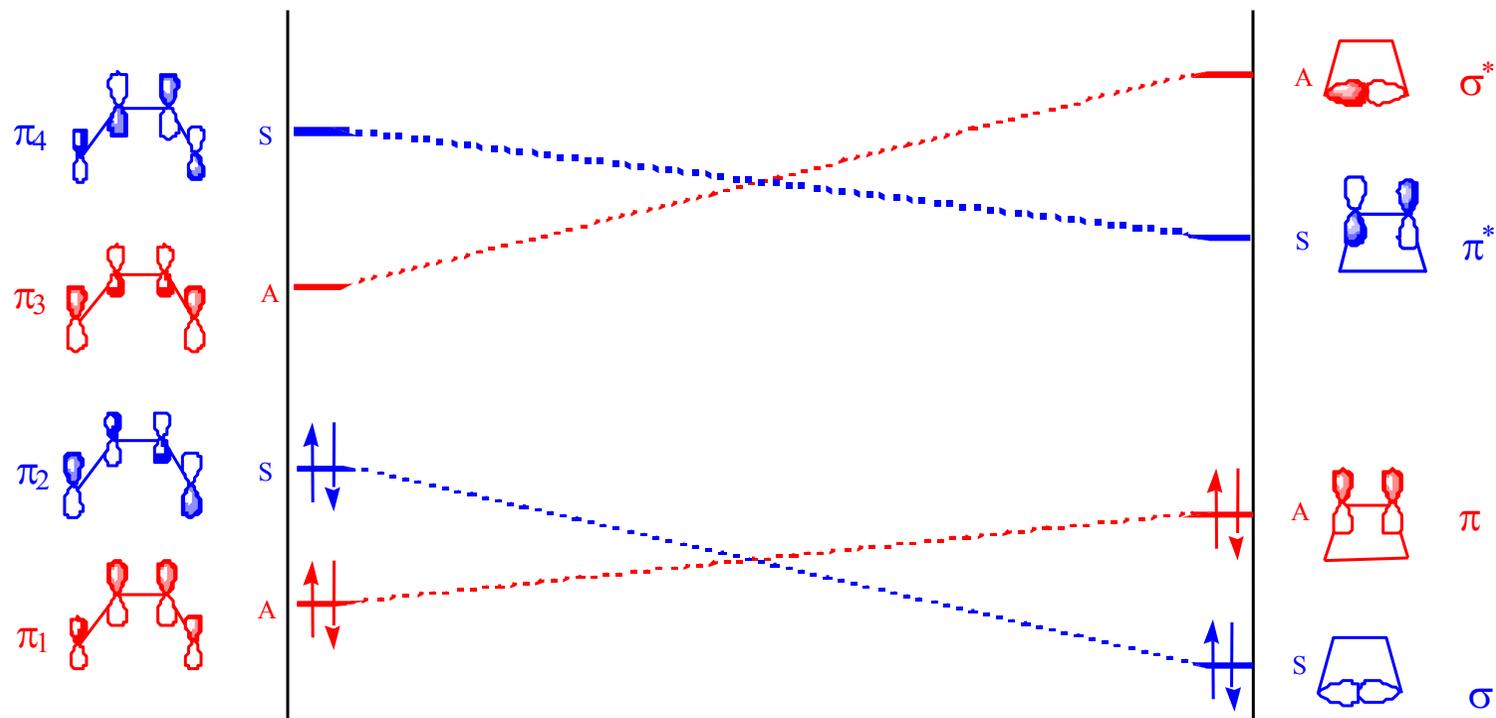
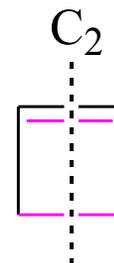
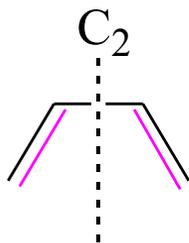
◆ Pas de plan de symétrie...

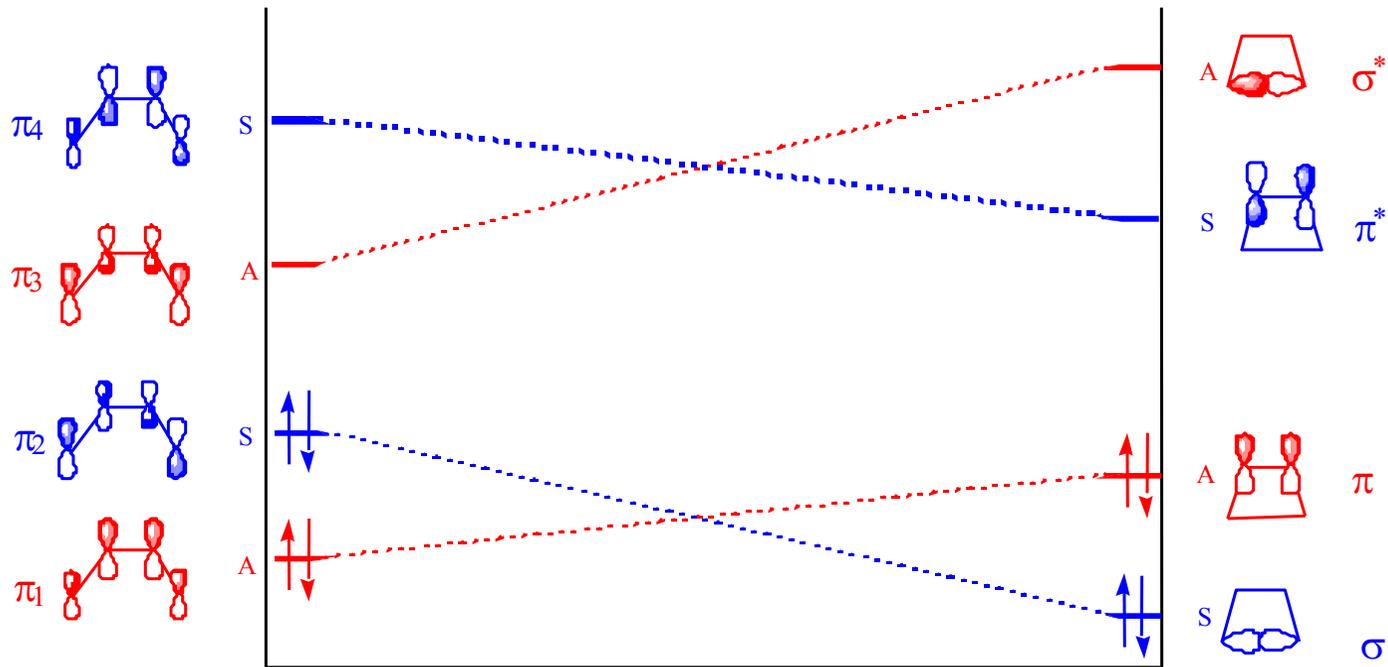
mais un axe de rotation (axe C_2)

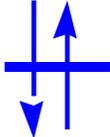
=> Nouvelle classification des orbitales

conrot

Cyclisation thermique **conrotatoire** du butadiène

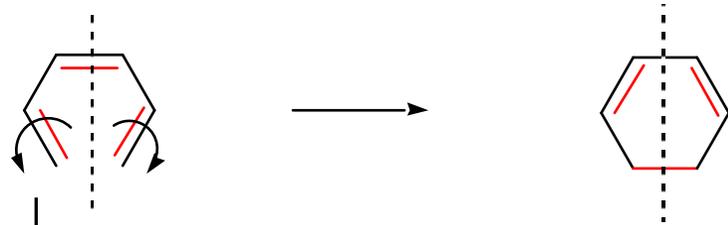




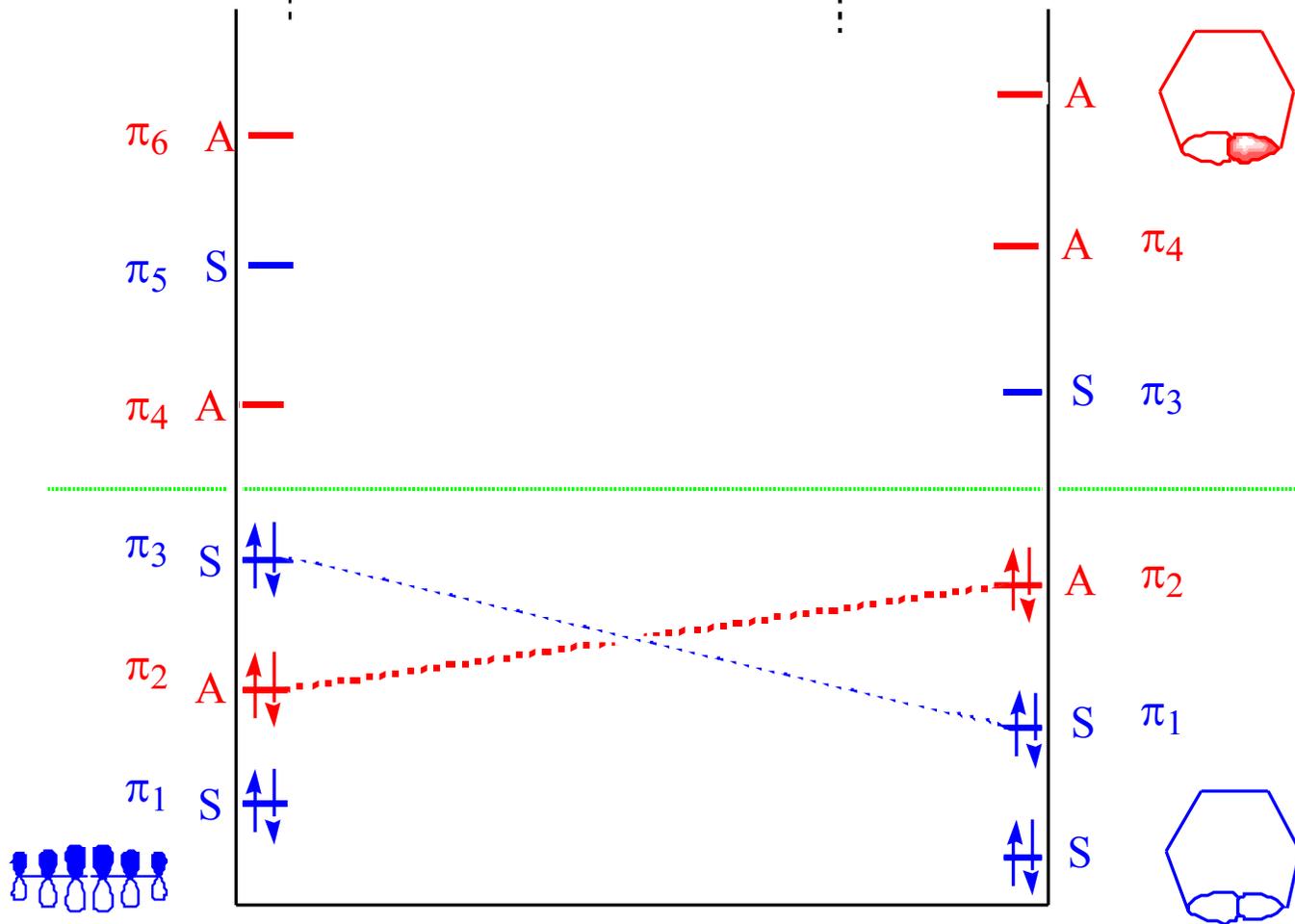
◆ Situation à mi-réaction: Ψ_1  Ψ_2 

Complexe activé « couche fermée », pas particulièrement instable, **Réaction permise thermiquement**

Réaction disrotatoire à 6 électrons

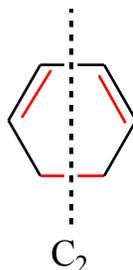
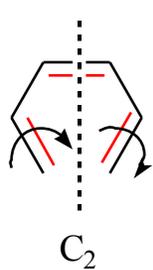


Plan de symétrie
conservé

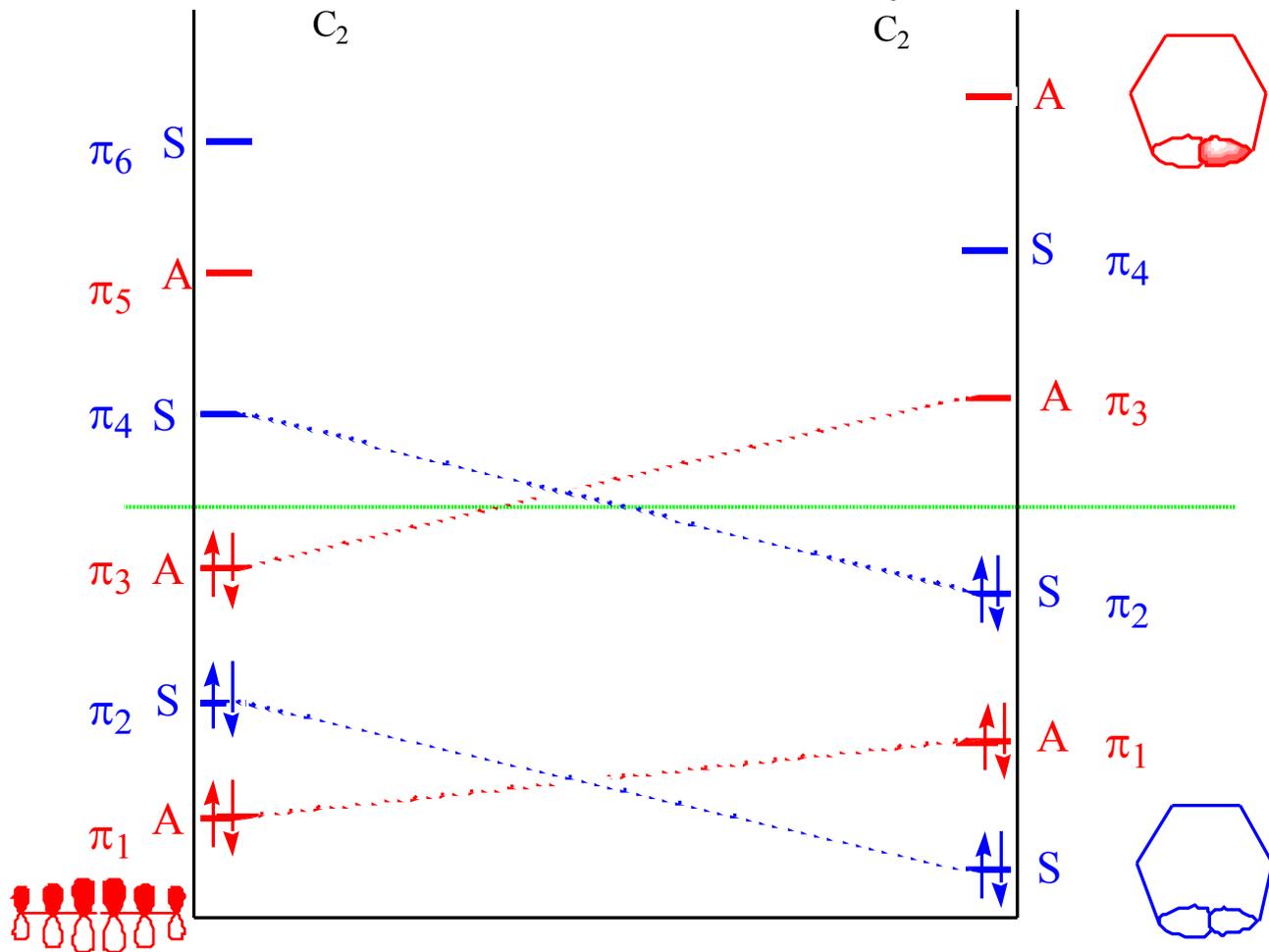


Réaction thermique
disrotatoire
permise

Réaction conrotatoire à 6 électrons



Axe C_2 conservé



Réaction thermique
conrotatoire

interdite thermiquement

Généralisation: Règles de sélection

Nombre
d'électrons

Réactions
thermiques

$4n$

Conrotatoire

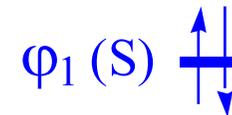
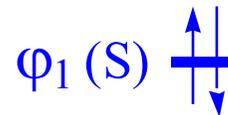
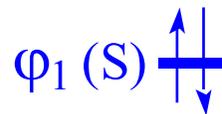
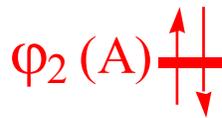
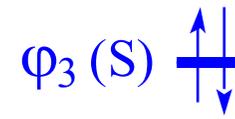
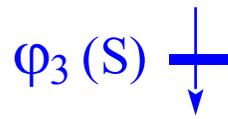
$4n + 2$

Disrotatoire

Diagrammes de corrélation d'états

◆ Notion d'état électronique

Exemple: Etat Fondamental $\Psi = (\varphi_1^2)(\varphi_2^2)$



Fondamental
(sym)

Monoexcité
(antisym)

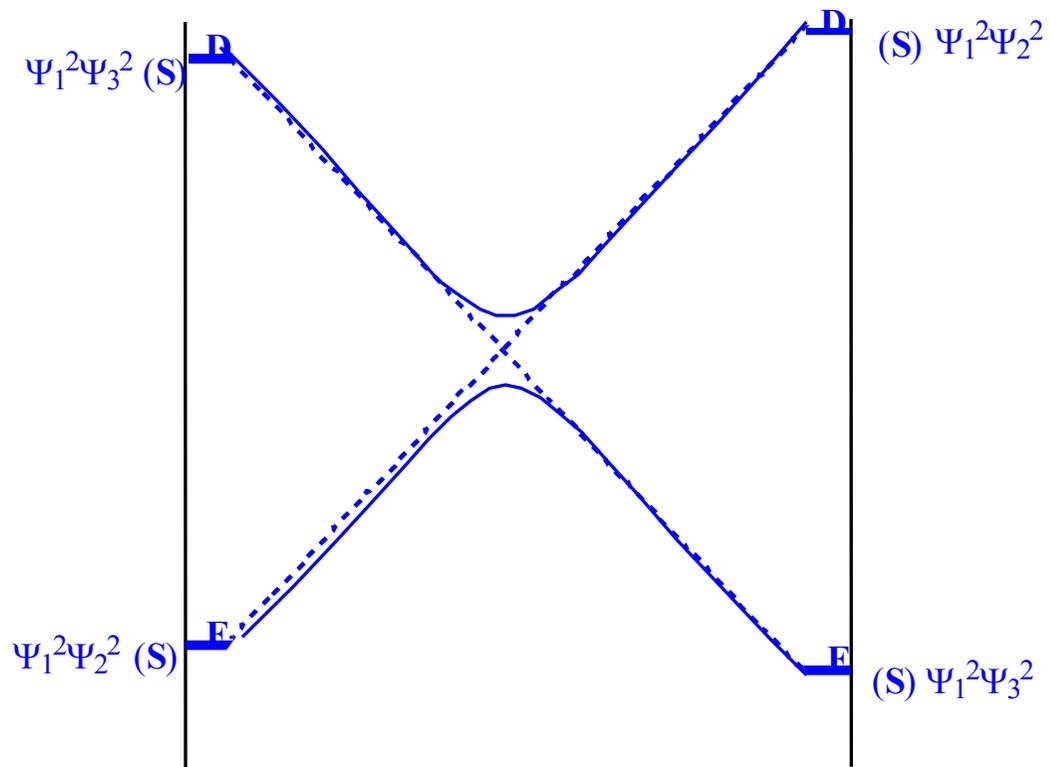
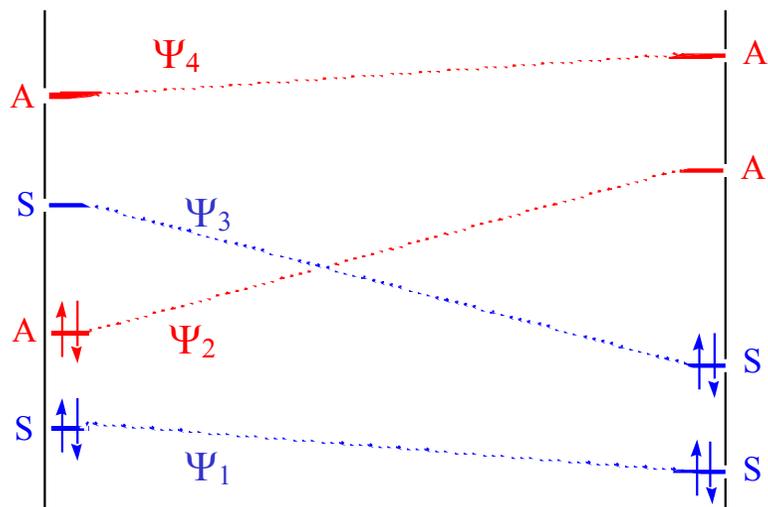
Diexcité
(sym)

Symétrie d'une fonction polyélectronique
= produit des symétries de ses orbitales

Cyclisation *disrotatoire* du butadiène

Diagramme de Corrélation d'états:

Rappel: Corrélation d'orbitales



« Croisement évité »

Réaction thermique **interdite**

Réaction photochimique

Rappel: Corrélation d'orbitales
(C_4H_6 , disrotatoire)

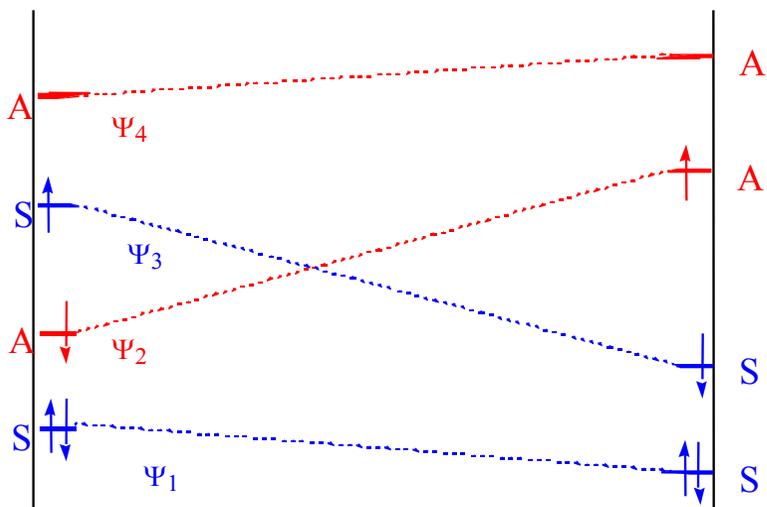
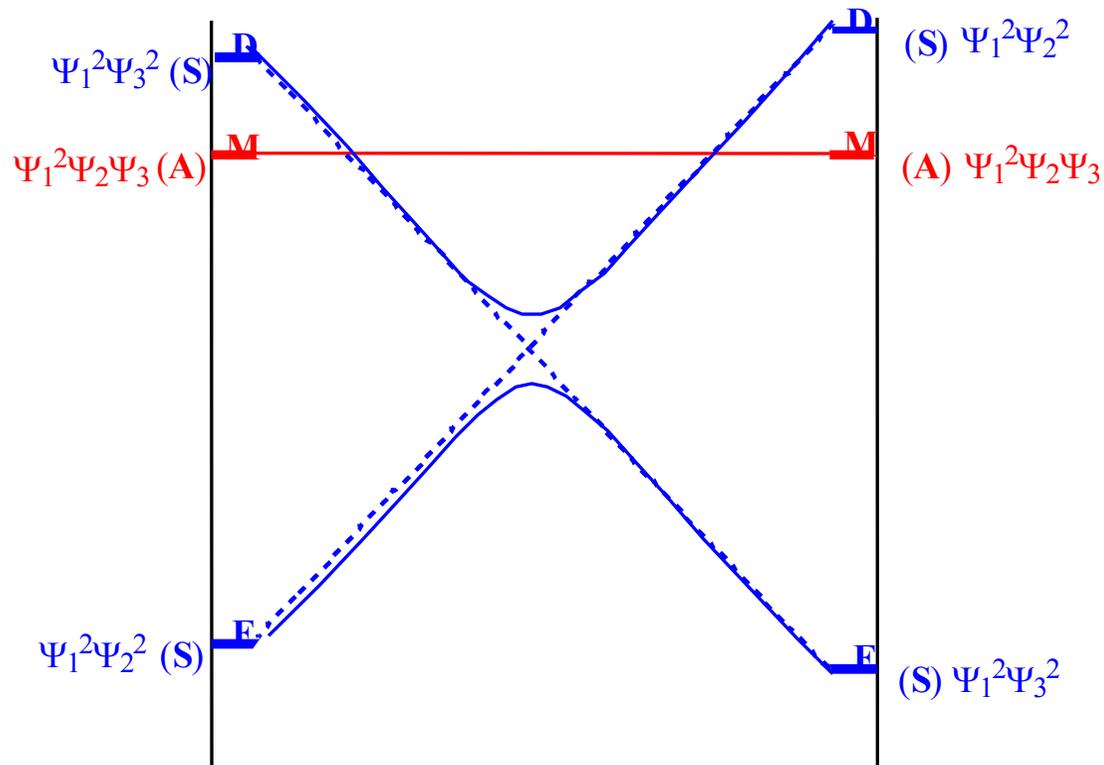
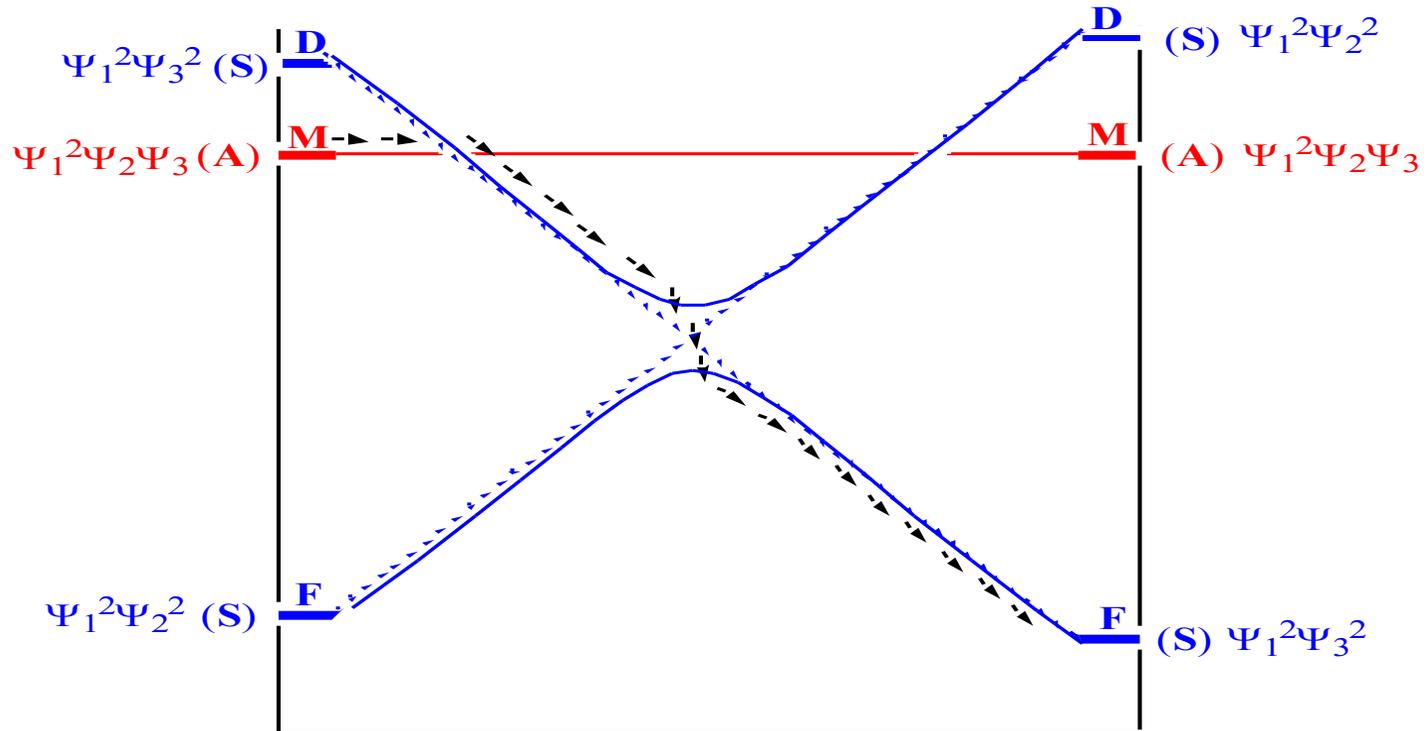


Diagramme de corrélation d'états



Pas de croisement évité pour le 1er état excité

Mécanisme de la réaction photochimique



Transition du 1er excité (réactifs) vers le
fondamental (produit): Toujours exothermique

Réaction disrotatoire **photochimique permise**

Réaction disrotatoire **thermique interdite**

Cyclisation *conrotatoire* du butadiène

◆ Rappel: Corrélation d'orbitales (C_4H_6 , disrotatoire)

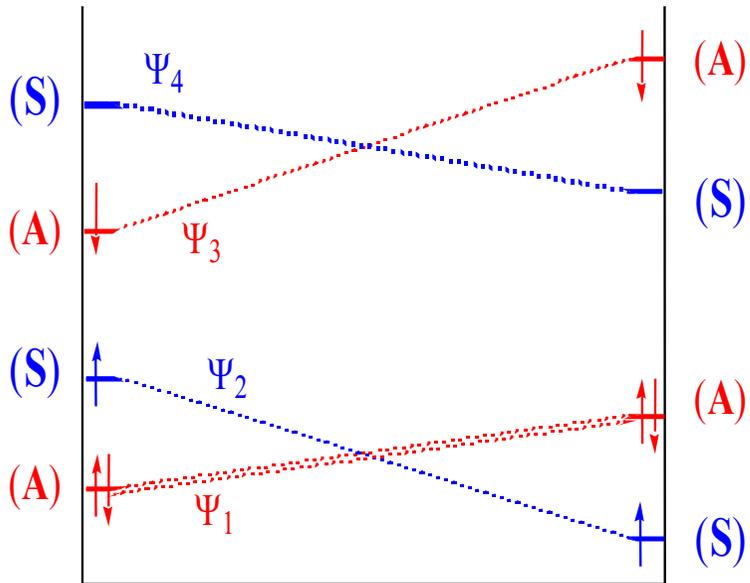
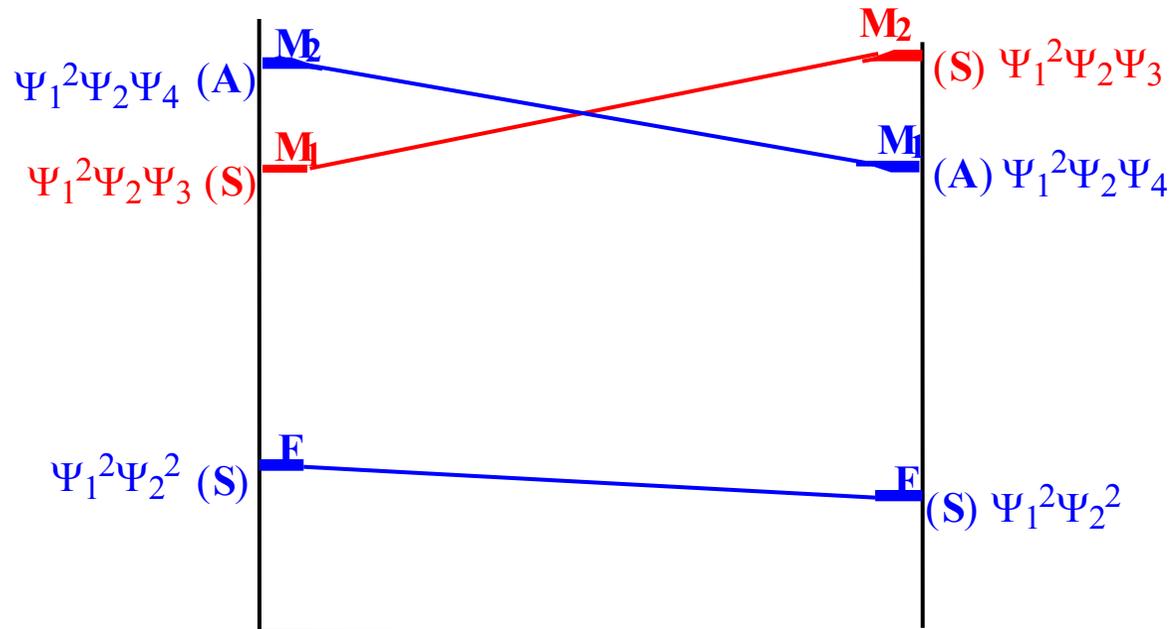


Diagramme de corrélation d'états



Réaction thermique **permise**, photochimique **interdite**

Généralisation: Règles de sélection

Nombre d'électrons	Réactions thermiques	Réactions photochimiques
$4n$	Conrotatoire	Disrotatoire
$4n + 2$	Disrotatoire	Conrotatoire

Thermiques (Δ) vs Photochimiques ($h\nu$):

Règles inversées