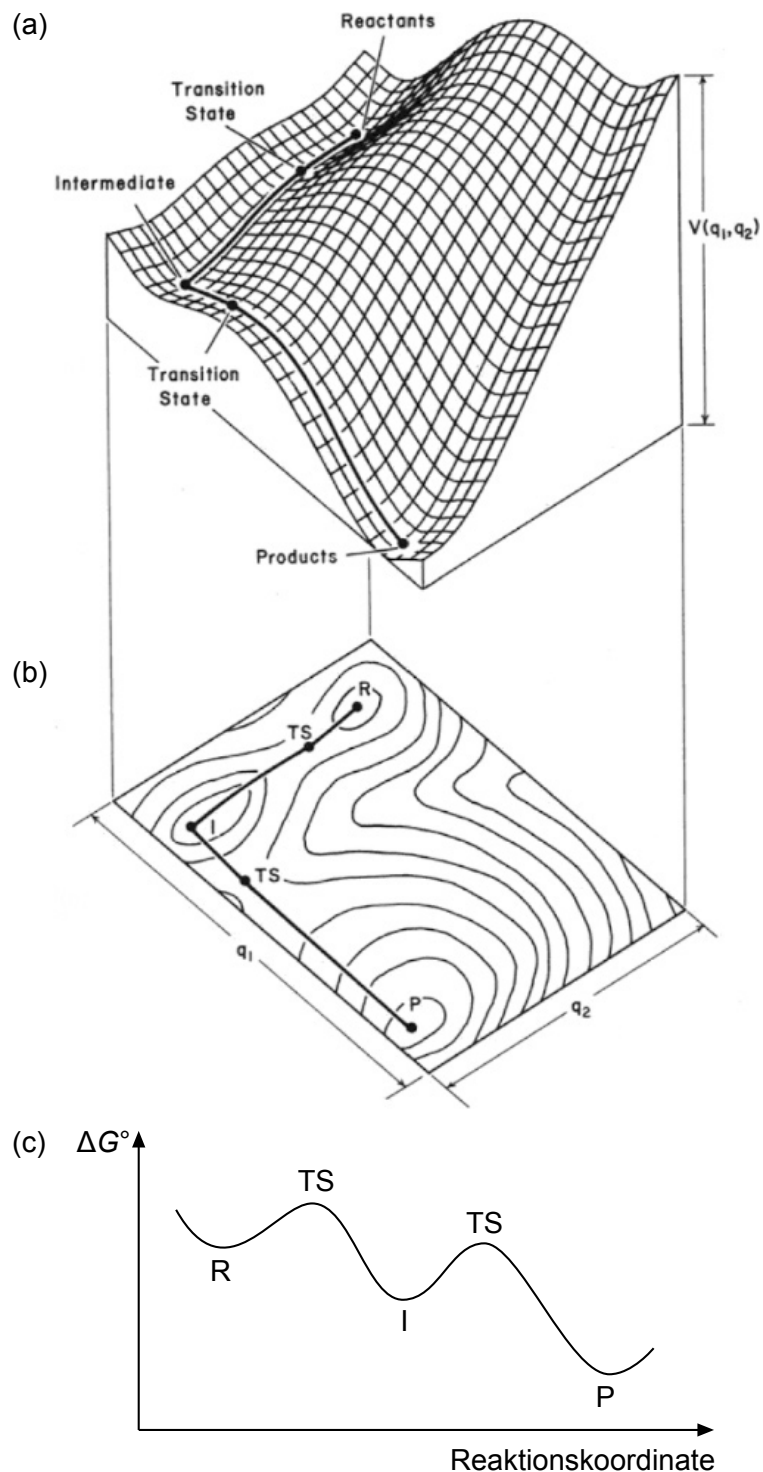


Potentialhyperfläche



(a) Potentialhyperfläche für eine allgemeine Reaktion $R \rightarrow I \rightarrow P$; (b) Konturplot, der zu der Hyperfläche korrespondiert; (c) Zweidimensionales Energieprofil, das die Veränderung der freien Enthalpie entlang der Reaktionskoordinate von R nach P beschreibt.

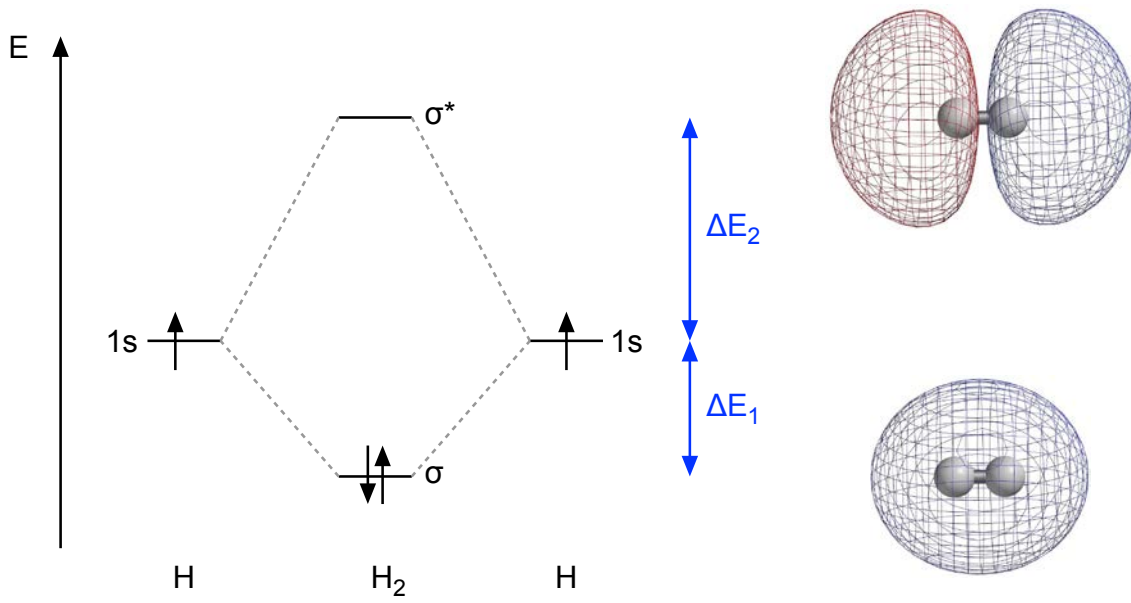
Hammett Substituentenkonstanten

Substituent	σ_m	σ_p	σ^+	σ^-
$-\text{O}^-$	-0,71	-1,00		
$-\text{OH}$	+0,13	-0,38	-0,92	
$-\text{OCH}_3$	+0,10	-0,12	-0,78	
$-\text{NH}_2$	-0,09	-0,30	-1,30	
$-\text{CH}_3$	-0,06	-0,14	-0,31	
$-\text{Ph}$	+0,05	+0,05	-0,18	+0,08
$-\text{H}$	0	0		
$-\text{SH}$	+0,25	+0,15		
$-\text{F}$	+0,34	+0,15	-0,07	
$-\text{Cl}$	+0,37	+0,24	+0,11	
$-\text{COOH}$	+0,35	+0,44		+0,73
$-\text{COCH}_3$	+0,36	+0,47		+0,82
$-\text{NO}_2$	+0,71	+0,81		+1,23
$-\text{NMe}_3^+$	+0,99	+0,96		
$-\text{N}_2^+$	+1,76	+1,91		

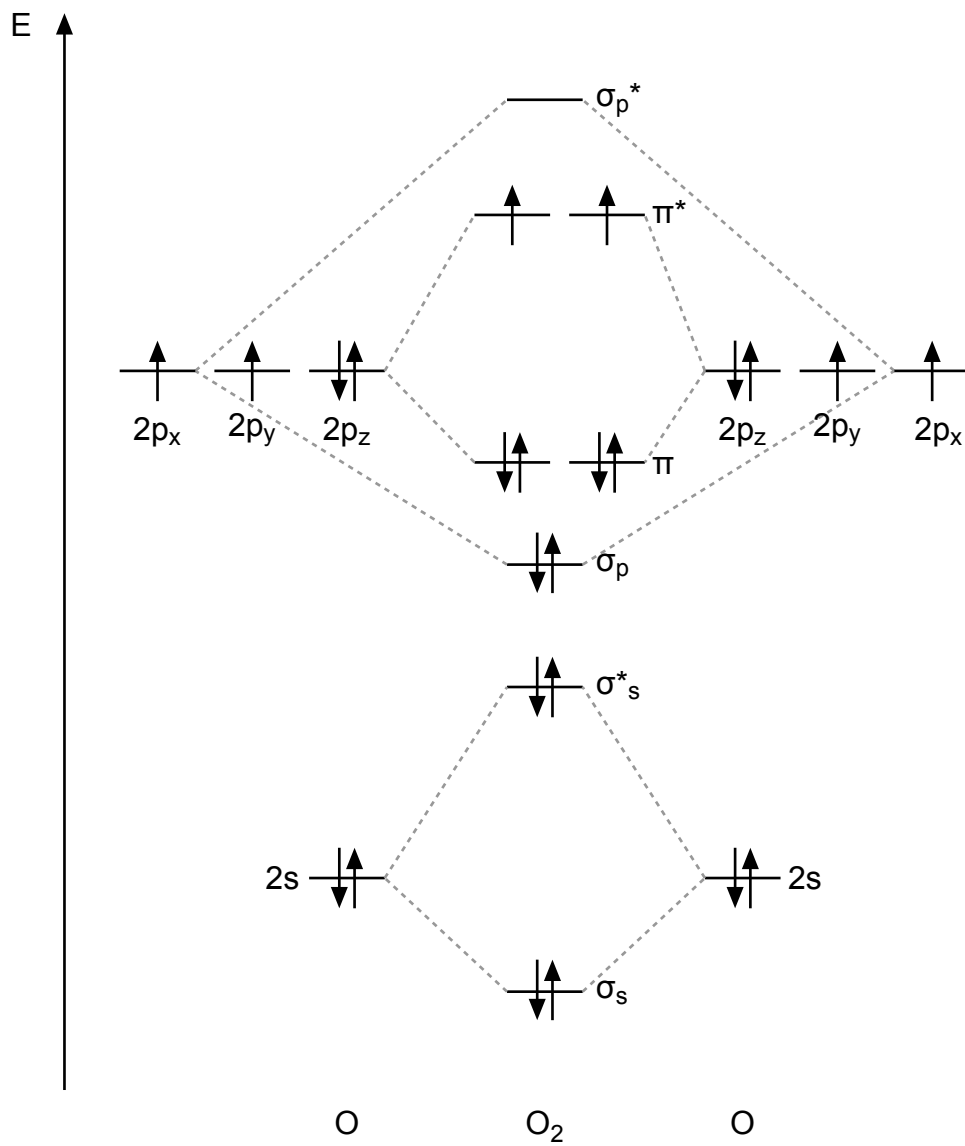
Taft Konstanten

Substituent	E_s	σ^*
$-\text{H}$	1,24	0,49
$-\text{Et}$	-0,07	-0,10
$-\text{iso-Pr}$	-0,47	-0,19
$-\text{tert-Bu}$	-1,54	-0,30
$-\text{CH}_2\text{Ph}$	-0,38	0,22
$-\text{Ph}$	-2,55	0,60

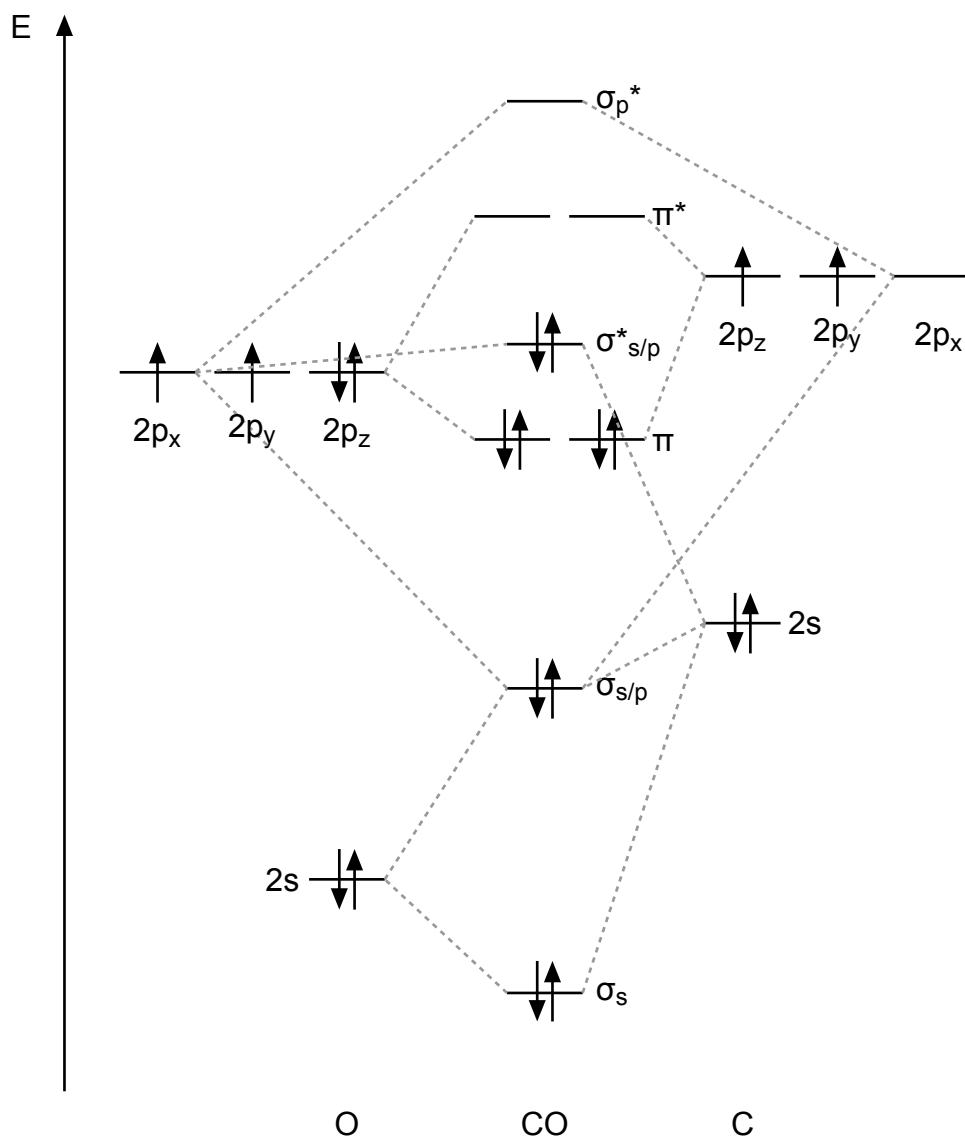
Termschema von Wasserstoff



Termschema von Sauerstoff



Termschema von Kohlenmonoxid



HMO Betrachtung von Ethen

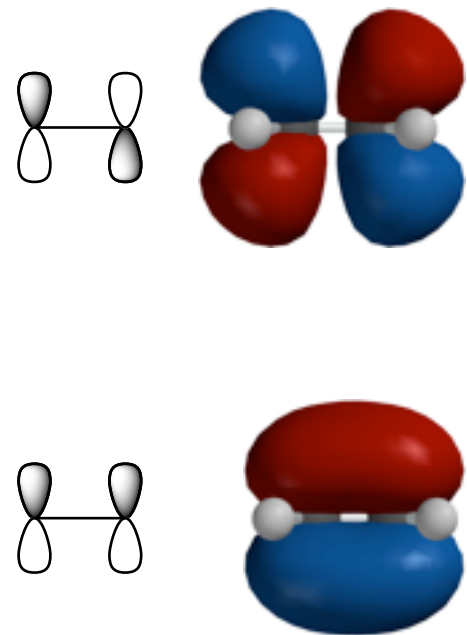
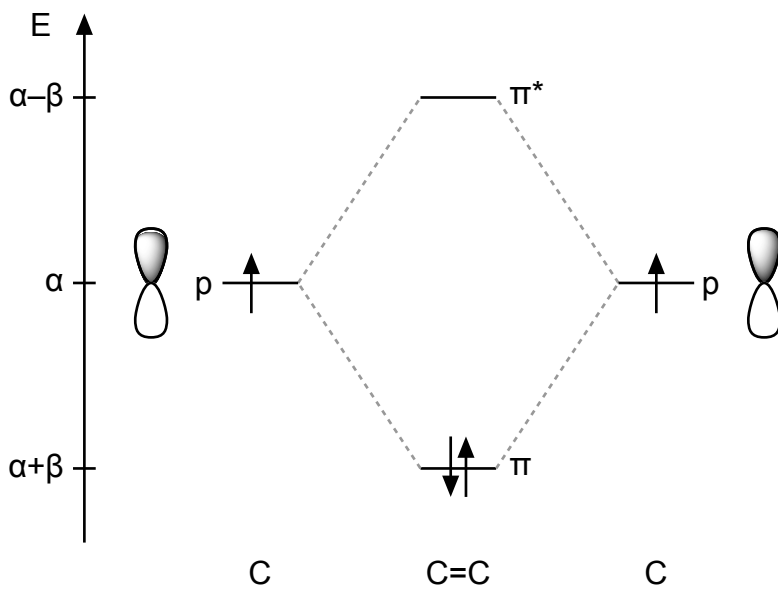
Säkulardeterminante

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

Lösungen

$$\begin{aligned} E_1 &= \alpha + \beta \\ E_2 &= \alpha - \beta \end{aligned}$$

Termschema



Säkulargleichungen

$$\begin{aligned} c_A(\alpha - E) + c_B\beta &= 0 \\ c_A\beta + c_B(\alpha - E) &= 0 \end{aligned}$$

Lösungen

$$\begin{aligned} c_A &= c_B \\ c_A &= -c_B \end{aligned}$$

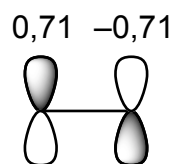
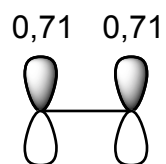
Wellenfunktionen

$$\begin{aligned} \psi_1 &= c_A\Phi_A + c_A\Phi_B \\ \psi_2 &= c'_A\Phi_A - c'_A\Phi_B \end{aligned}$$

Orbitalkoeffizienten

$$c_A = \sqrt{0,5}$$

$$c'_A = \sqrt{0,5}$$



HMO Betrachtung von Benzol

Säkulardeterminante

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

Lösungen

$$E_1 = \alpha + 2\beta$$

$$E_{2/3} = \alpha + \beta$$

$$E_{4/5} = \alpha - \beta$$

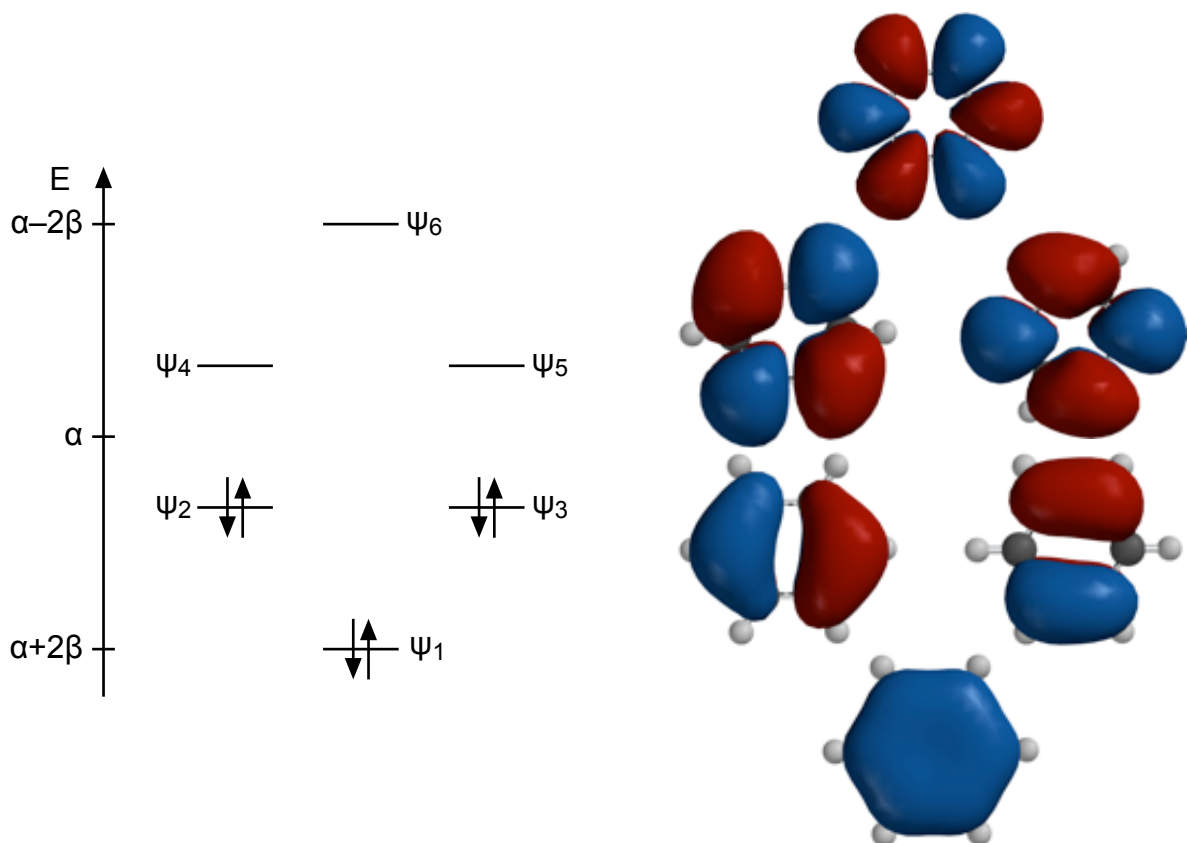
$$E_6 = \alpha - 2\beta$$

Berechnung der Energieniveaus cyclischer konjugierter Polyene beliebiger Ringgröße:

$$E = \alpha + 2\beta \cos \frac{360^\circ r}{n}$$

$$n = \text{Ringgröße}, r = 0, 1, 2 \dots n - 1$$

Termschema



Säkulargleichungen

$$c_A(\alpha - E) + c_B\beta + c_F\beta = 0$$

$$c_A\beta + c_B(\alpha - E) + c_C\beta = 0$$

$$c_B\beta + c_C(\alpha - E) + c_D\beta = 0$$

$$c_C\beta + c_D(\alpha - E) + c_E\beta = 0$$

$$c_D\beta + c_E(\alpha - E) + c_F\beta = 0$$

$$c_A\beta + c_E\beta + c_F(\alpha - E) = 0$$

Wellenfunktionen

$$\psi_1 = c_A\Phi_A + c_A\Phi_B + c_A\Phi_C + c_A\Phi_D + c_A\Phi_E + c_A\Phi_F$$

$$\psi_2 = 2c'_A\Phi_A + c'_A\Phi_B - c'_A\Phi_C - 2c'_A\Phi_D - c'_A\Phi_E + c'_A\Phi_F$$

$$\psi_3 = c''_A\Phi_B + c''_A\Phi_C - c''_A\Phi_E - c''_A\Phi_F$$

$$\psi_4 = c''_A\Phi_B - c''_A\Phi_C + c''_A\Phi_E - c''_A\Phi_F$$

$$\psi_5 = 2c'_A\Phi_A - c'_A\Phi_B - c'_A\Phi_C + 2c'_A\Phi_D - c'_A\Phi_E - c'_A\Phi_F$$

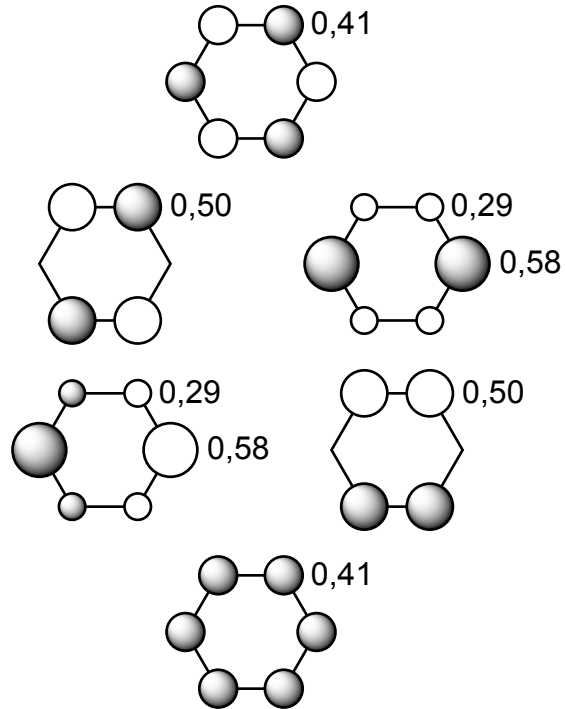
$$\psi_6 = c_A\Phi_A - c_A\Phi_B + c_A\Phi_C - c_A\Phi_D + c_A\Phi_E - c_A\Phi_F$$

Orbitalkoeffizienten

$$c_A = \sqrt{\frac{1}{6}}$$

$$c'_A = \sqrt{\frac{1}{12}}$$

$$c''_A = 0,5$$



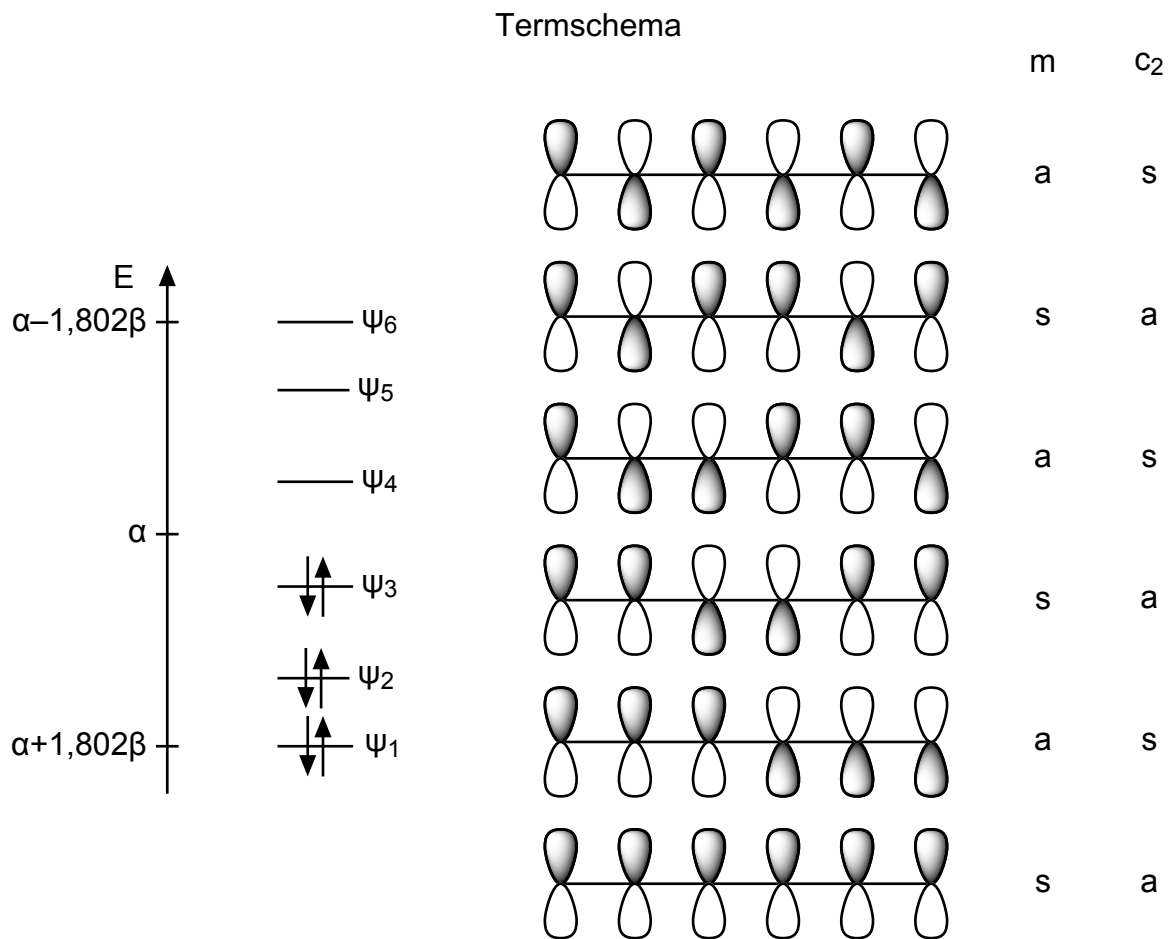
HMO Betrachtung von 1,3,5-Hexatrien

Säkulardeterminante	Lösungen
$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$	$\begin{aligned} E_1 &= \alpha + 1,802\beta \\ E_2 &= \alpha + 1,247\beta \\ E_3 &= \alpha + 0,445\beta \\ E_4 &= \alpha - 0,445\beta \\ E_5 &= \alpha - 1,247\beta \\ E_6 &= \alpha - 1,802\beta \end{aligned}$

Berechnung der Energieniveaus linearer konjugierter Polyene beliebiger Länge:

$$E = \alpha + 2\beta \cos \frac{180 r}{n + 1}$$

n = Länge der konjugierten Kette, $r = 1, 2, 3 \dots n$



vereinfachte Darstellung mit Atomorbitalen

Säkulargleichungen

$$\begin{aligned} c_A(\alpha - E) + c_B\beta &= 0 \\ c_A\beta + c_B(\alpha - E) + c_C\beta &= 0 \\ c_B\beta + c_C(\alpha - E) + c_D\beta &= 0 \\ c_C\beta + c_D(\alpha - E) + c_E\beta &= 0 \\ c_D\beta + c_E(\alpha - E) + c_F\beta &= 0 \\ c_E\beta + c_F(\alpha - E) &= 0 \end{aligned}$$

Wellenfunktionen

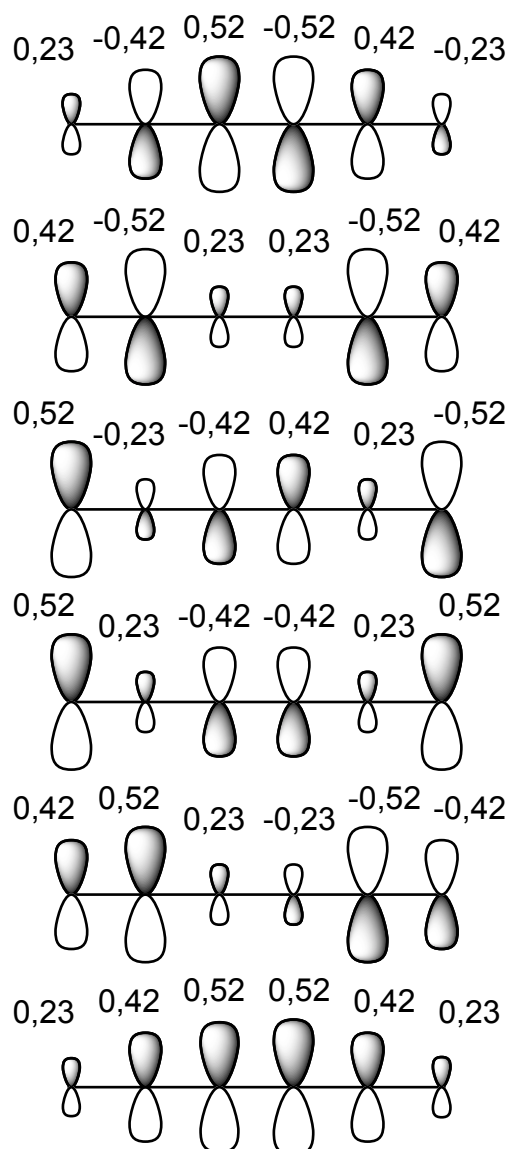
$$\begin{aligned}\psi_1 &= c_A \Phi_A + 1,802 c_A \Phi_B + 2,247 c_A \Phi_C + 2,247 c_A \Phi_D + 1,802 c_A \Phi_E + c_A \Phi_F \\ \psi_2 &= c'_A \Phi_A + 1,247 c'_A \Phi_B + 0,555 c'_A \Phi_C - 0,555 c'_A \Phi_D - 1,247 c'_A \Phi_E - c'_A \Phi_F \\ \psi_3 &= c''_A \Phi_A + 0,445 c''_A \Phi_B - 0,802 c''_A \Phi_C - 0,802 c''_A \Phi_D + 0,445 c''_A \Phi_E + c''_A \Phi_F \\ \psi_4 &= c''_A \Phi_A - 0,445 c''_A \Phi_B - 0,802 c''_A \Phi_C + 0,802 c''_A \Phi_D + 0,445 c''_A \Phi_E - c''_A \Phi_F \\ \psi_5 &= c'_A \Phi_A - 1,247 c'_A \Phi_B + 0,555 c'_A \Phi_C + 0,555 c'_A \Phi_D - 1,247 c'_A \Phi_E + c'_A \Phi_F \\ \psi_6 &= c_A \Phi_A - 1,802 c_A \Phi_B + 2,247 c_A \Phi_C - 2,247 c_A \Phi_D + 1,802 c_A \Phi_E - c_A \Phi_F\end{aligned}$$

Orbitalkoeffizienten

$$c_A = 0,232$$

$$c'_A = 0,418$$

$$c''_A = 0,521$$

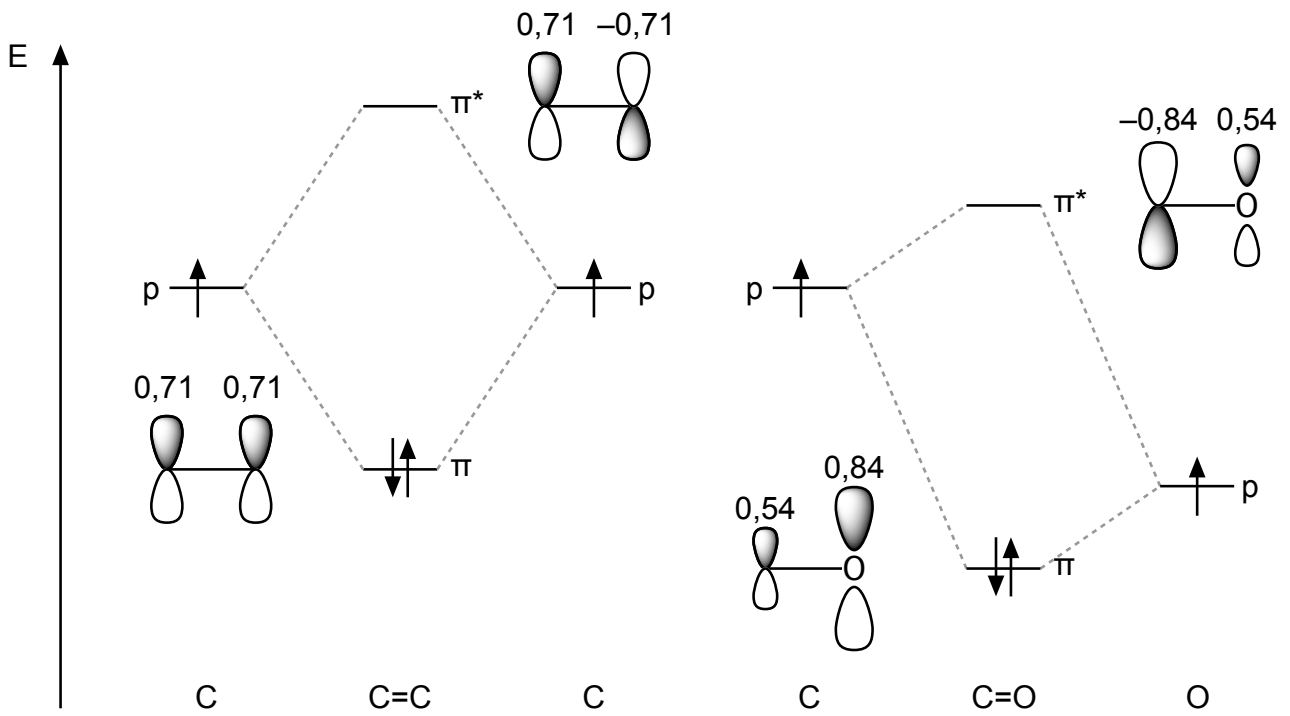


Berechnung der Orbitalkoeffizienten linearer konjugierter Polyene beliebiger Länge:

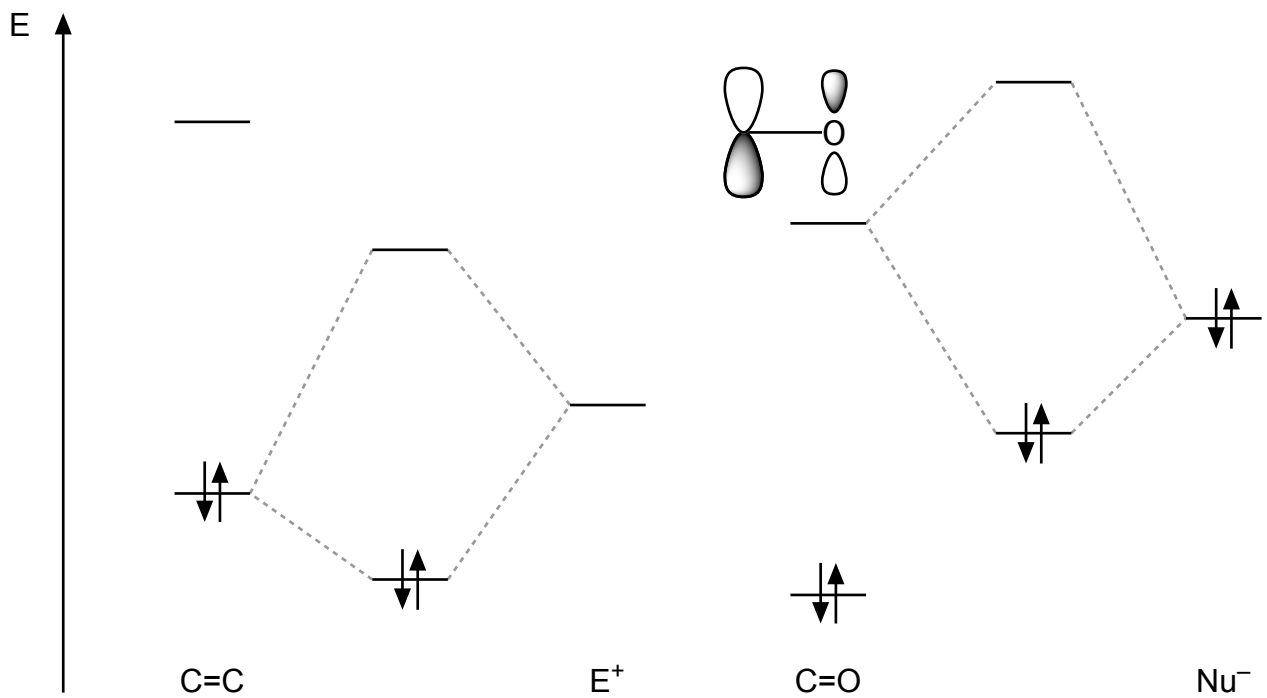
$$c_{jr} = \sqrt{\frac{2}{n+1}} \sin \frac{180 r j}{n+1}$$

j = Position des Kohlenstoffatoms in der Kette, r = Nummer des Molekülorbitals, n = Länge des konjugierten Systems

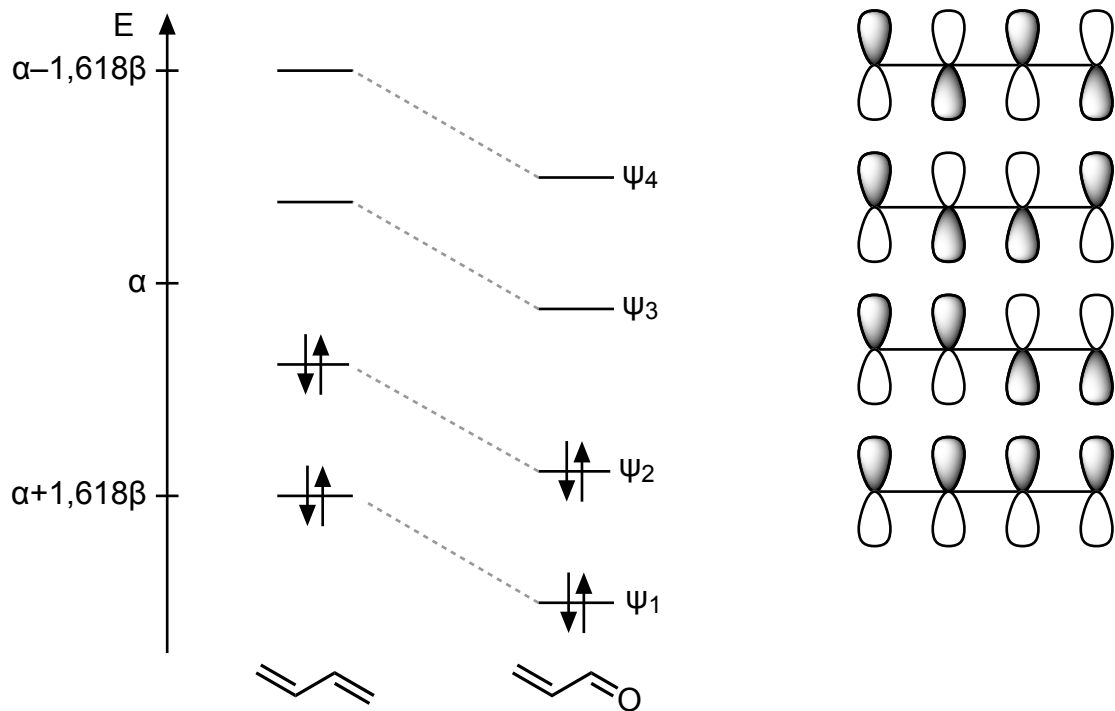
Vergleich der Termschemata einer C,C- und einer C,O-Doppelbindung



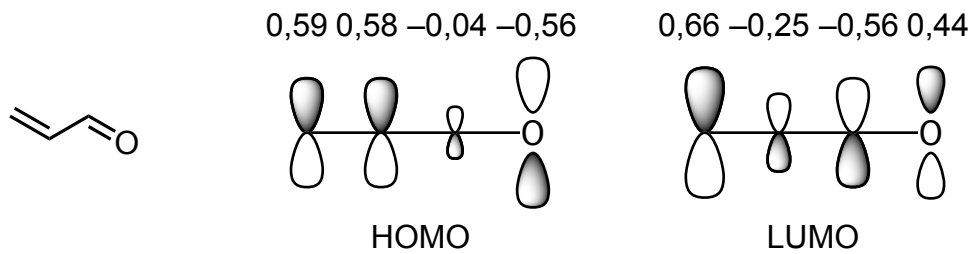
MO Betrachtungen zur Reaktion von C,C- und C,O-Doppelbindungen mit Elektrophilen bzw. Nucleophilen



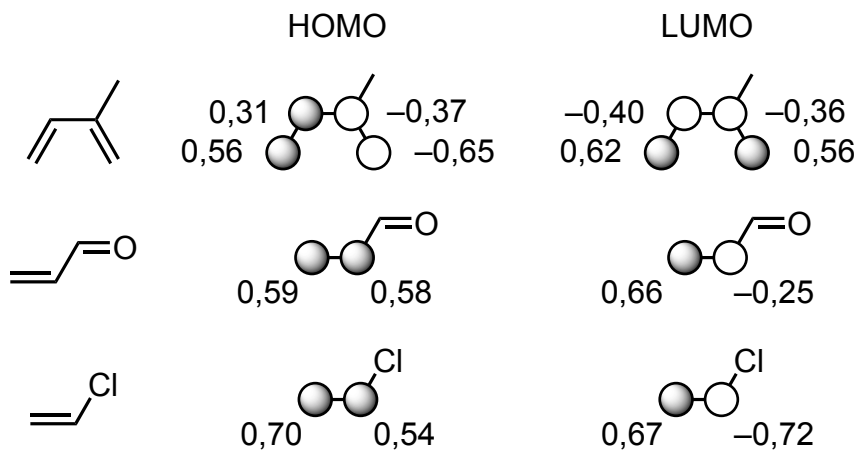
Vergleich der Termschemata von 1,3-Butadien und Acrolein



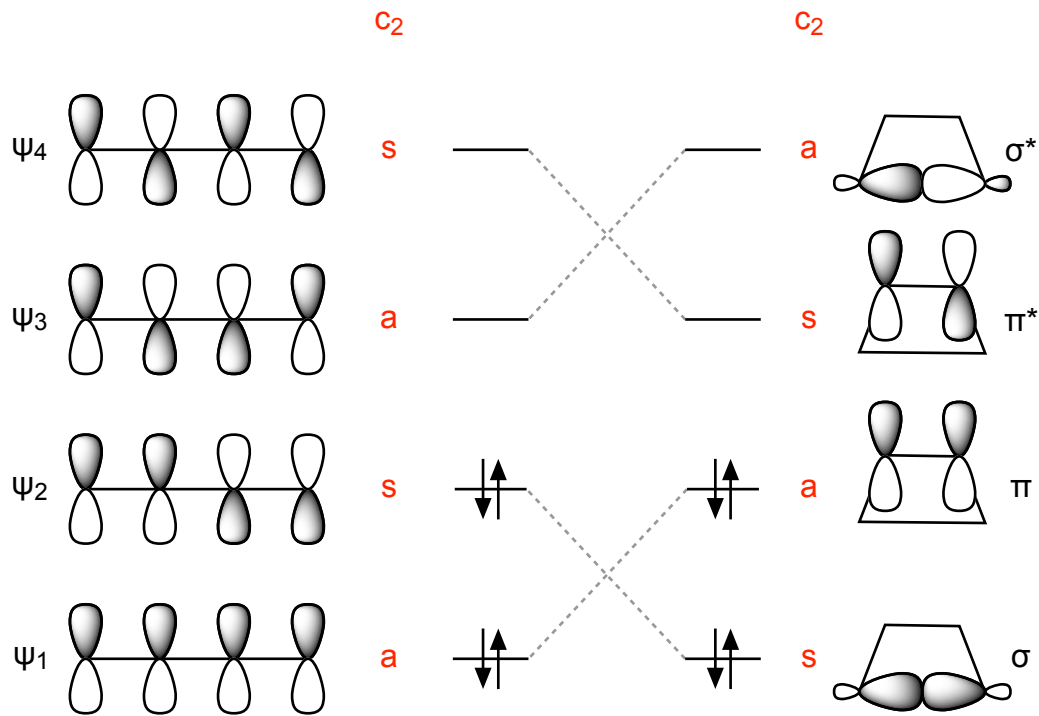
Orbitalkoeffizienten von Acrolein



Orbitalkoeffizienten ausgewählter Diene und Dienophile

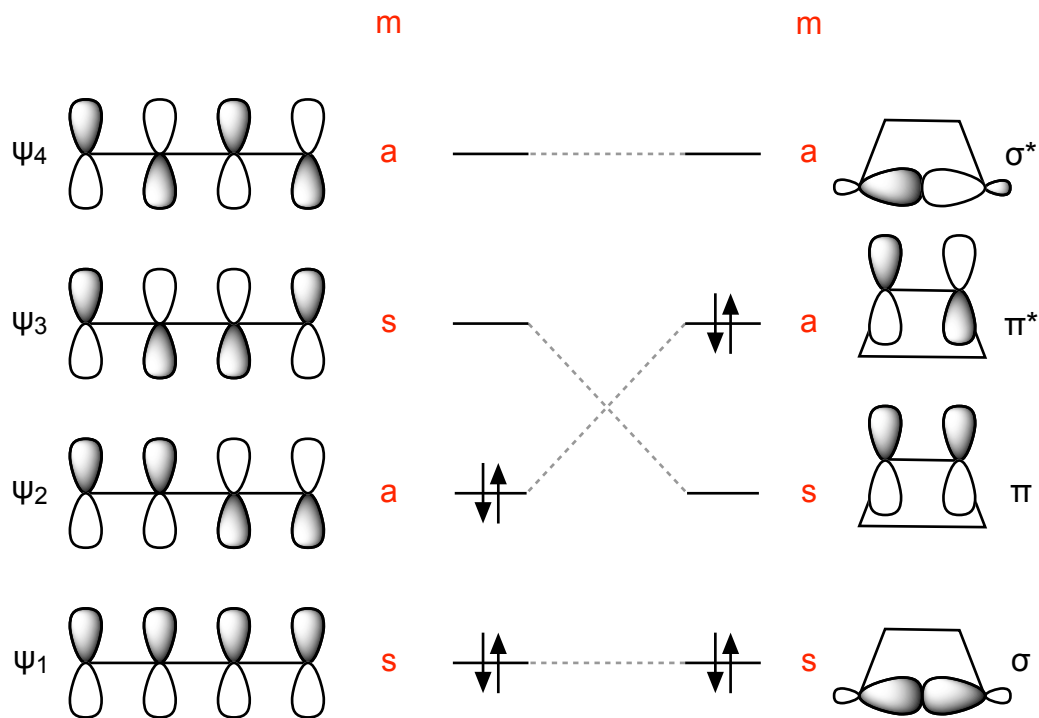


Orbitalkorrelationsdiagramm für den konrotatorischen electrocyclischen Ringschluss von 1,3-Butadien



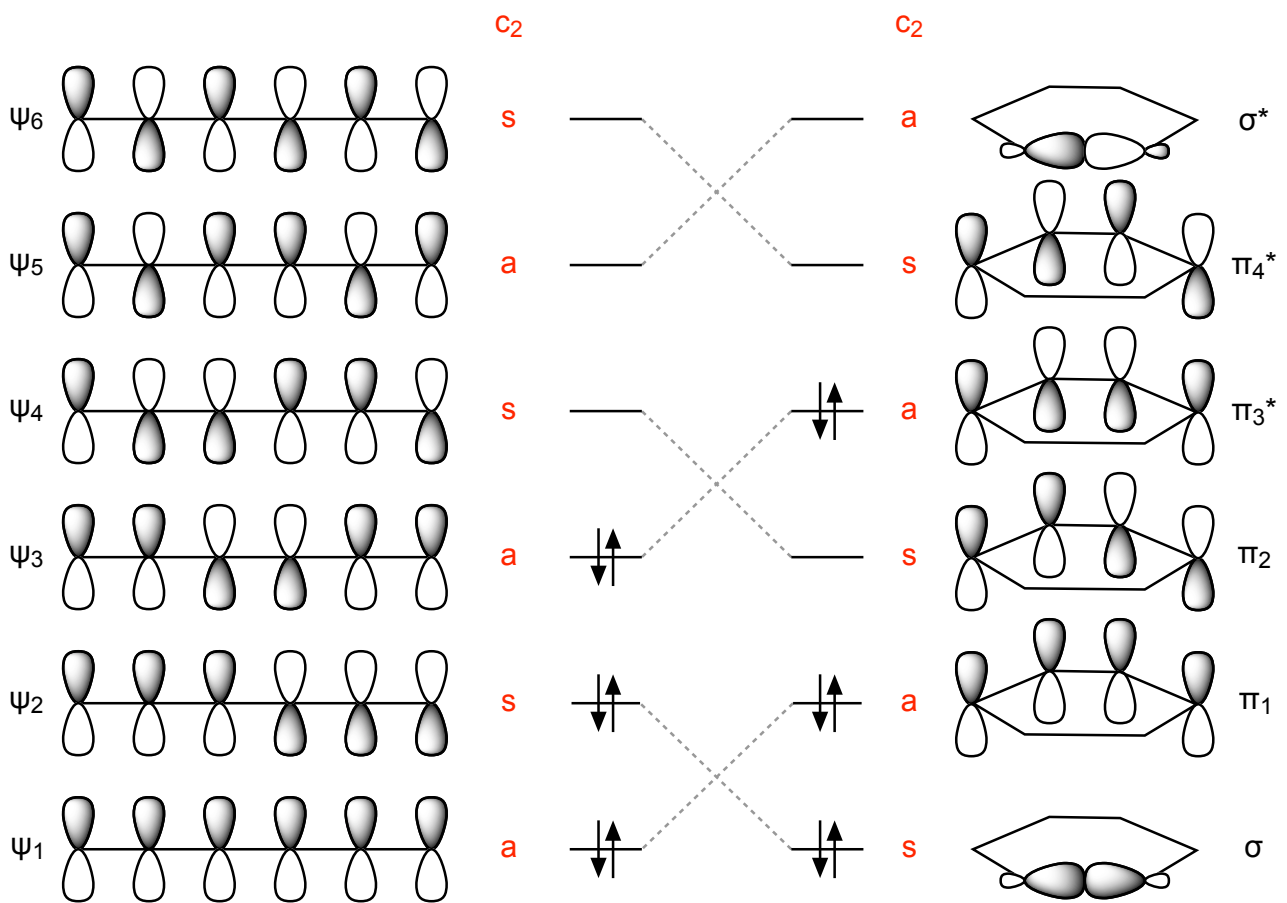
Der photochemische Ringschluss führt vom $\psi_1^2\psi_2^1\psi_3^1$ Zustand zum $\sigma^1\pi^2\sigma^{*1}$ Zustand.

Orbitalkorrelationsdiagramm für den disrotatorischen electrocyclischen Ringschluss von 1,3-Butadien



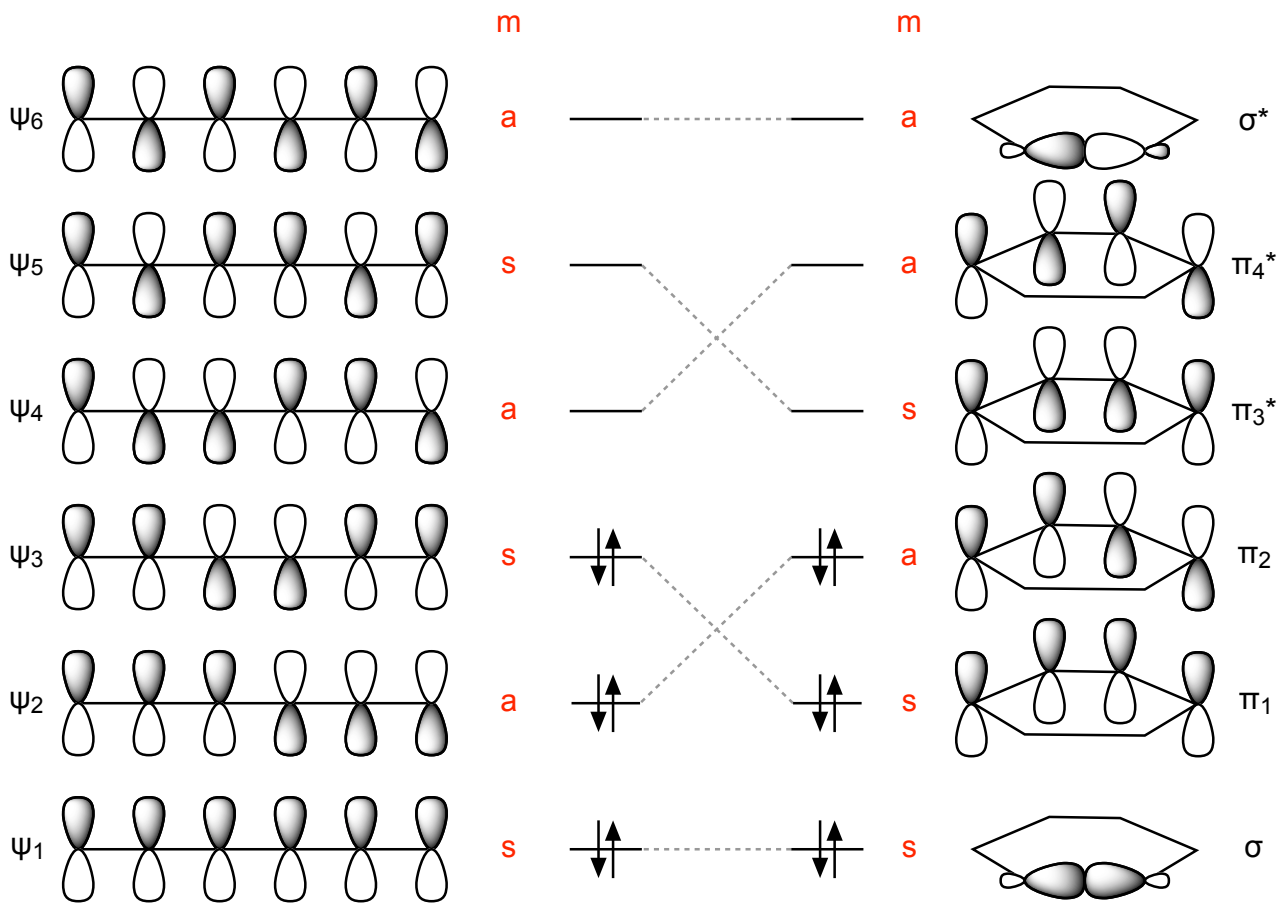
Der photochemische Ringschluss führt vom $\psi_1^2\psi_2^1\psi_3^1$ Zustand zum $\sigma^2\pi^1\pi^{*1}$ Zustand.

Orbitalkorrelationsdiagramm für den konrotatorischen electrocyclischen Ringschluss von 1,3,5-Hexatrien



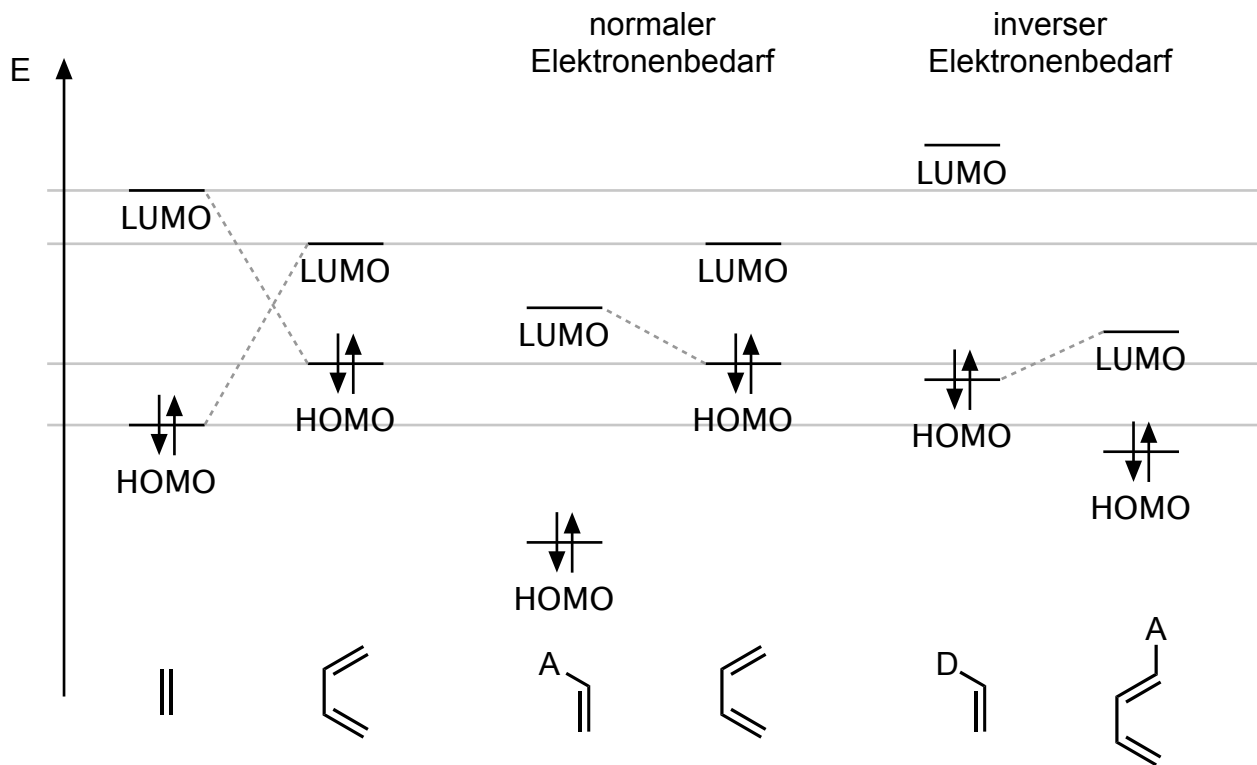
Der photochemische Ringschluss führt vom $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$ Zustand zum $\sigma^2\pi_1^2\pi_2^1\pi_3^{*1}$ stand.

**Orbitalkorrelationsdiagramm für den disrotatorischen
elektrocyclischen Ringschluss von 1,3,5-Hexatrien**



Der photochemische Ringschluss führt vom $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$ Zustand zum $\sigma^2\pi_1^1\pi_2^2\pi_4^{*1}$ Zustand.







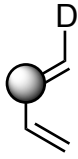
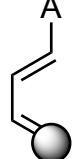
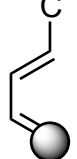
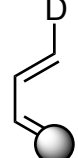
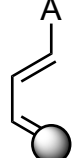
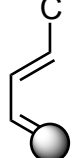
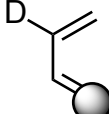
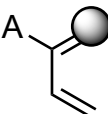
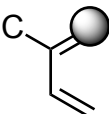
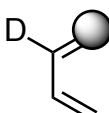
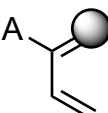
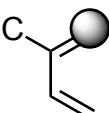
Elektronenbedarf von Diels-Alder Reaktionen

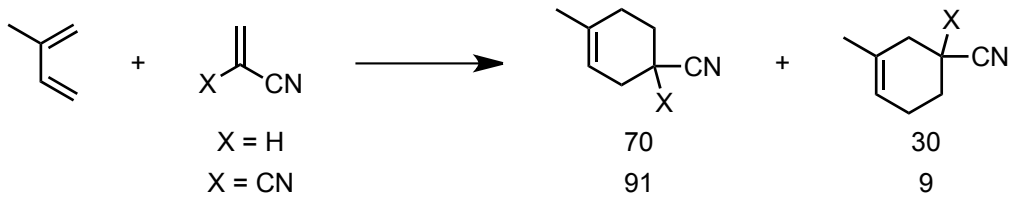


Substituenteneinfluss auf Orientierungselektivität

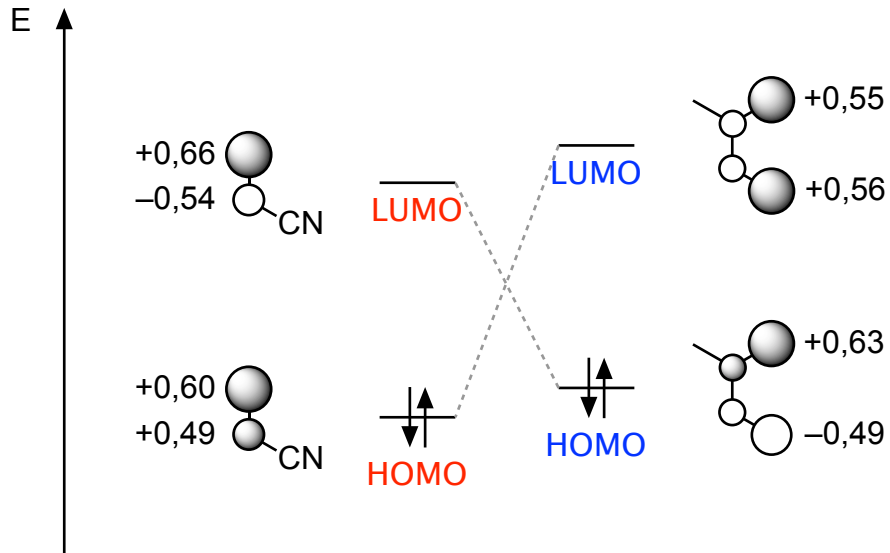
- A Akzeptoren (z.B. $-\text{CO}_2\text{R}$, $-\text{CN}$, $-\text{NO}_2$); erniedrigen die Energien von HOMO und LUMO.
- D Donoren (z.B. $-\text{OR}$, $-\text{NR}_2$, $-\text{CH}_3$); erhöhen die Energien von HOMO und LUMO.
- C in Konjugation stehende Substituenten (z.B. $-\text{Phenyl}$, $-\text{Vinyl}$); erhöhen die Energie von HOMO und erniedrigen die Energie von LUMO.

Position des größten Orbitalkoeffizienten

	D	A	C	
Dienophil				LUMO
				HOMO
1-substituiertes Dien				LUMO
				HOMO
2-substituiertes Dien				LUMO
				HOMO



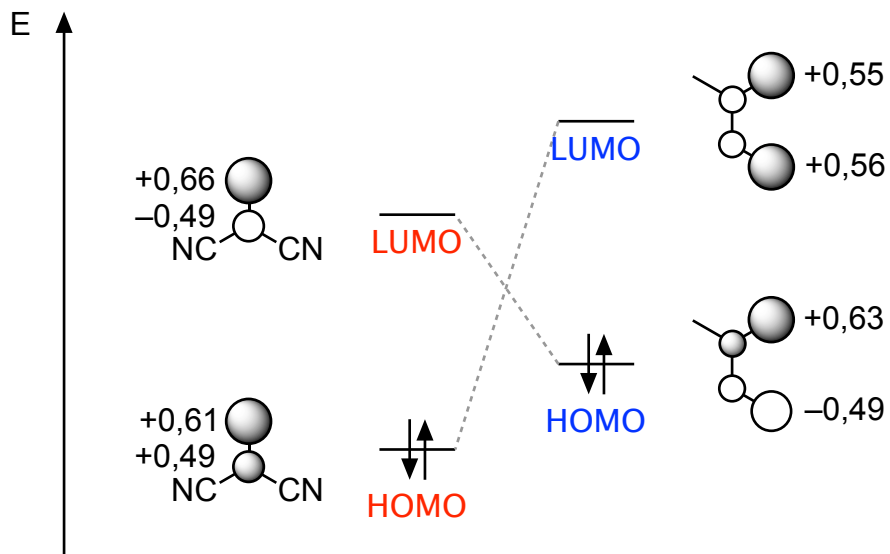
1. Fall: X = H



$$|E_{\text{HOMO}} - E_{\text{LUMO}}| = 11,7 \text{ eV}$$

$$|E_{\text{LUMO}} - E_{\text{HOMO}}| = 8,9 \text{ eV}$$

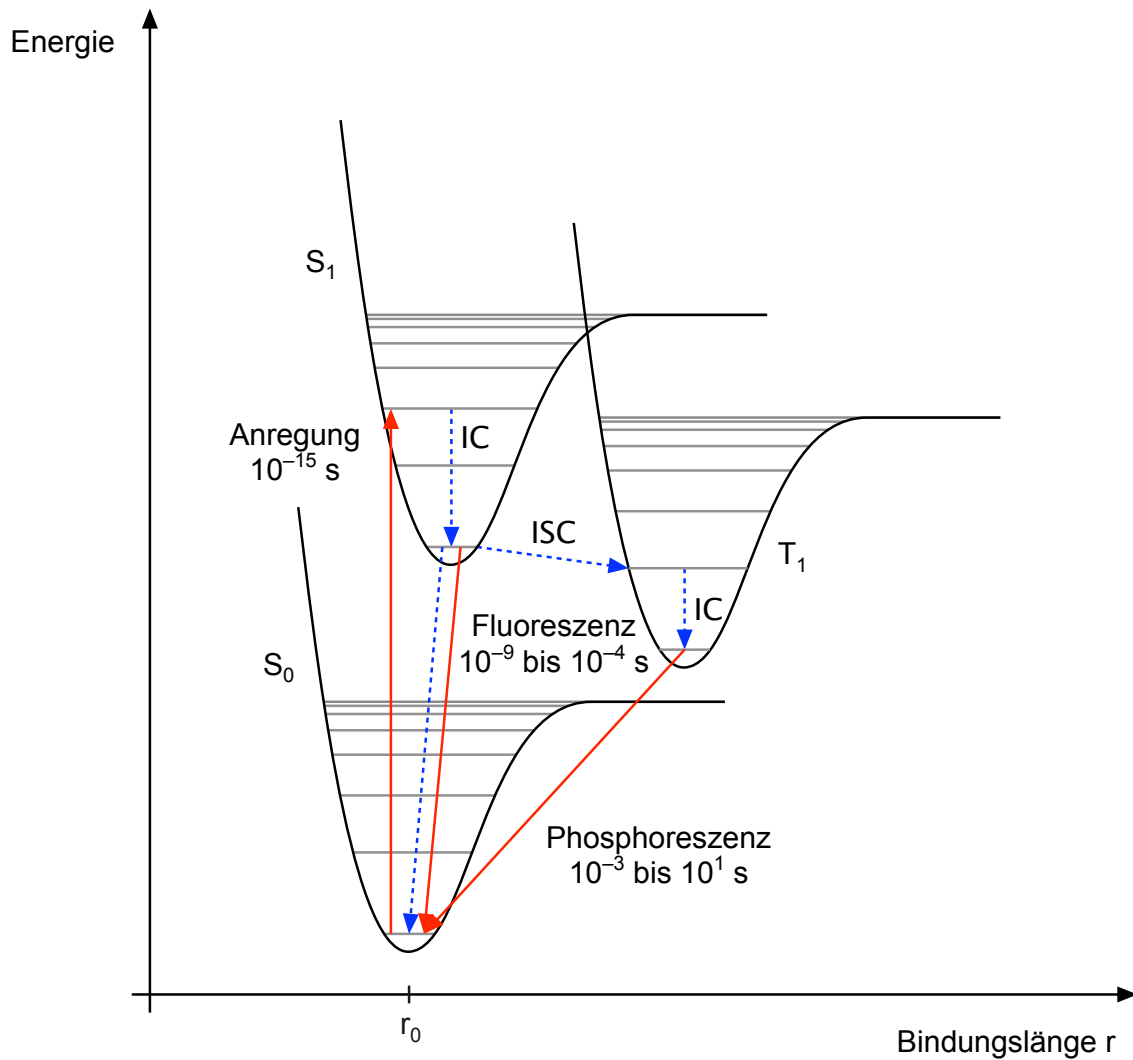
2. Fall: X = CN



$$|E_{\text{HOMO}} - E_{\text{LUMO}}| = 12,2 \text{ eV}$$

$$|E_{\text{LUMO}} - E_{\text{HOMO}}| = 7,3 \text{ eV}$$

Jablonski Termschema



- Emission/Absorption
- - -> strahlungslose Übergänge
- ISC intersystem crossing (Spinumkehr)
- IC internal conversion (10^{-13} bis 10^{-11} s)