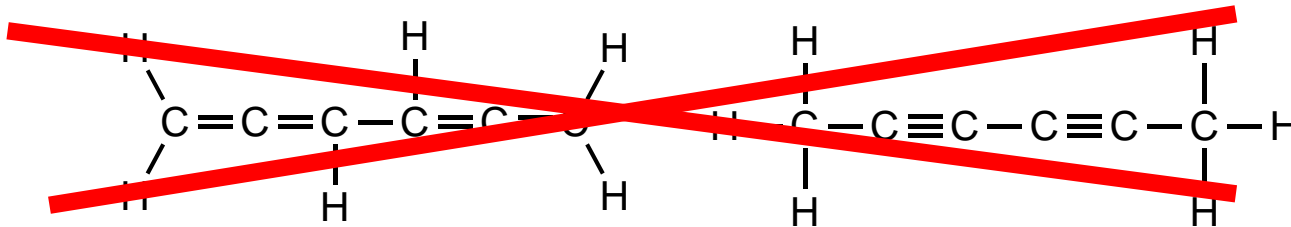


8 Aromatische Kohlenwasserstoffe

Das Rätsel um's Benzol

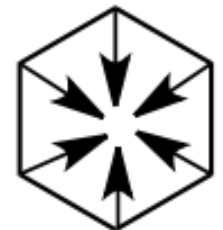
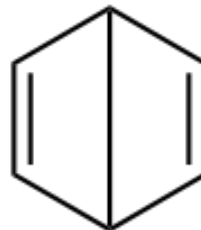
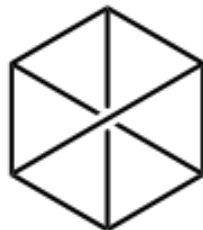
Empirische Formel: C_6H_6

- Beobachtungen:**
- keine Additionen von Brom, Chlor oder Halogenwasserstoffen
 - Reaktion mit Brom und Chlor nur mit Katalysator ($FeBr_3$, $FeCl_3$)
Substitution eines Wasserstoffs statt Addition
 - Monohalogenierung gibt nur ein Produkt, Dihalogenierung gibt drei Produkte

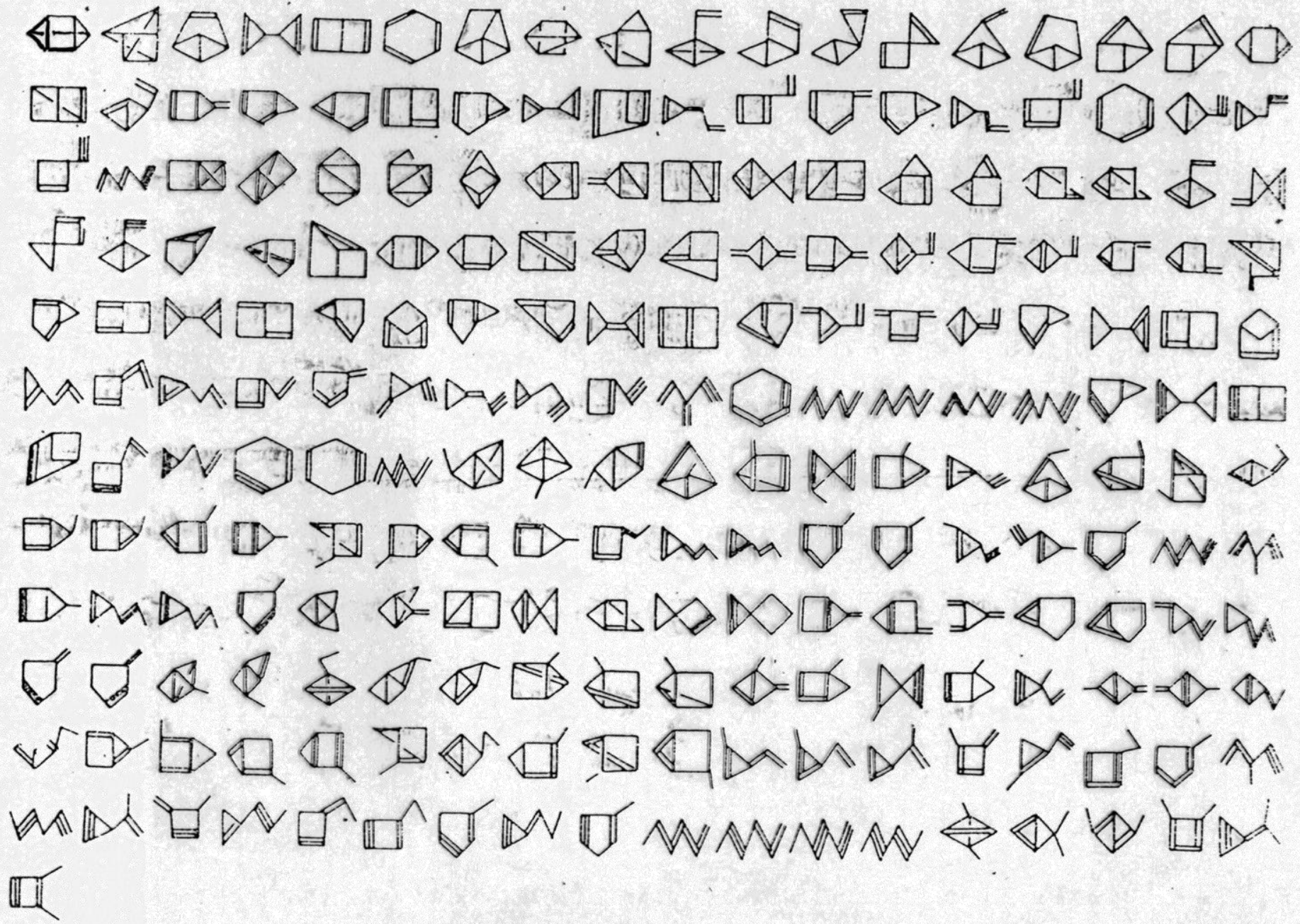


Lineare Strukturen enthalten Mehrfachbindungen, die mit Br_2 reagieren würden.

Vorschläge:

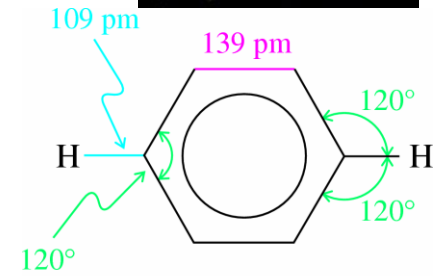
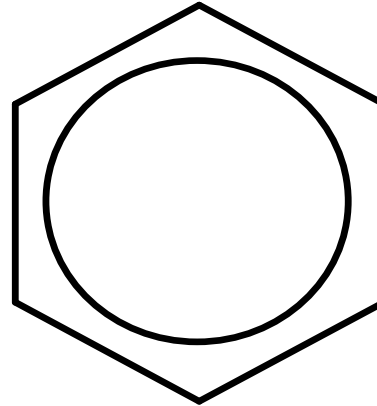


217 Isomere aus C₆H₆



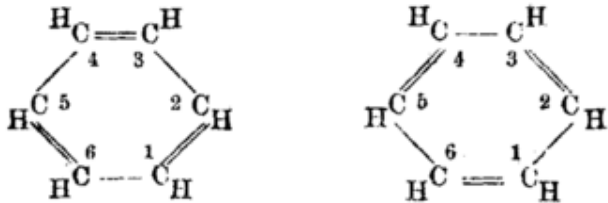
5 Aromatische Kohlenwasserstoffe

Struktur des Benzols



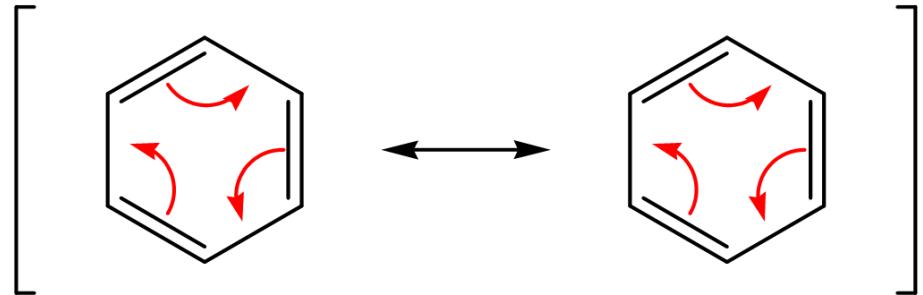
© 2012 Wiley-VCH Verlag GmbH & Co. KGaA
Vollhardt - Organische Chemie
ISBN: 9783527327546 Abb. 16-001

Kekulé's Strukturmodell (1865)



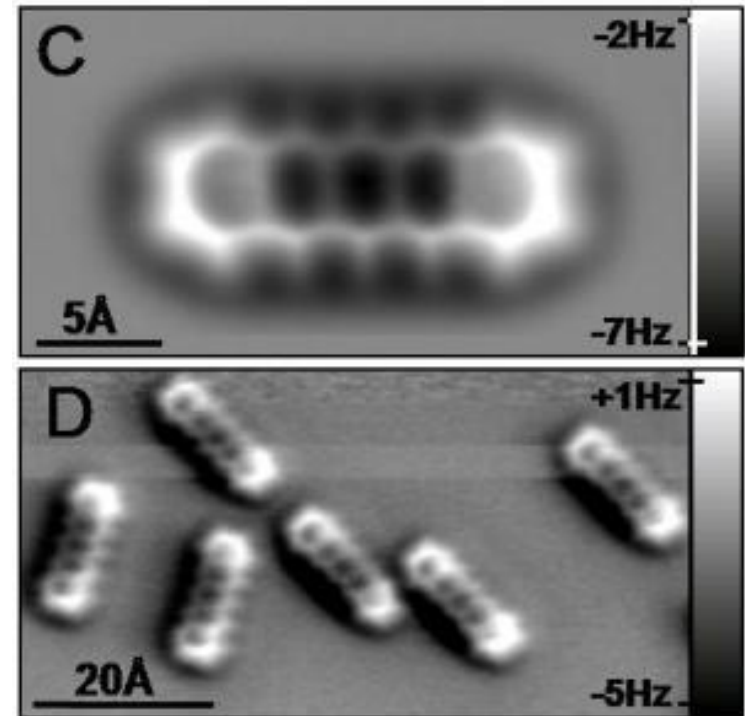
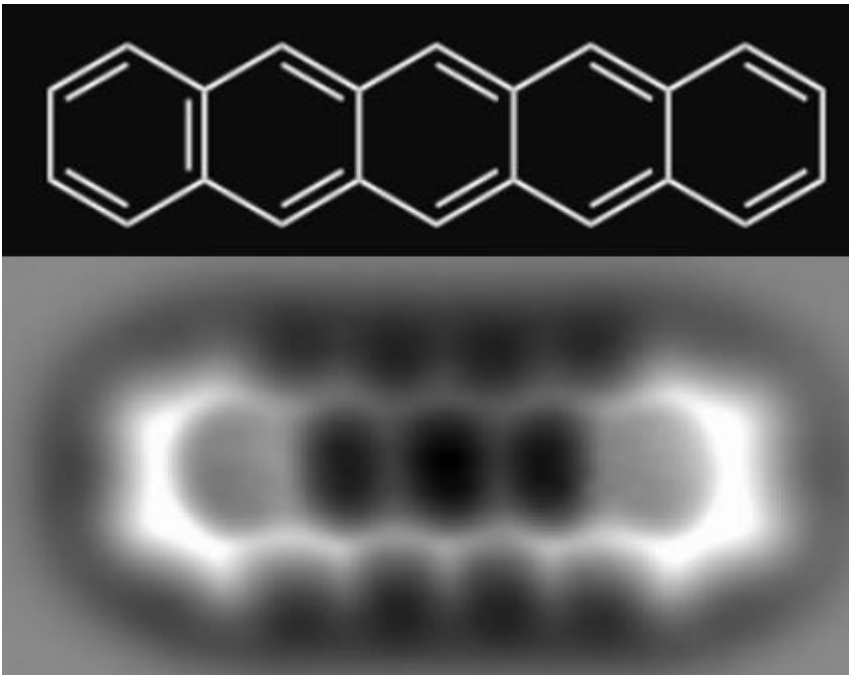
https://de.wikipedia.org/wiki/August_Kekul%C3%A9

Mesomere Grenzformeln



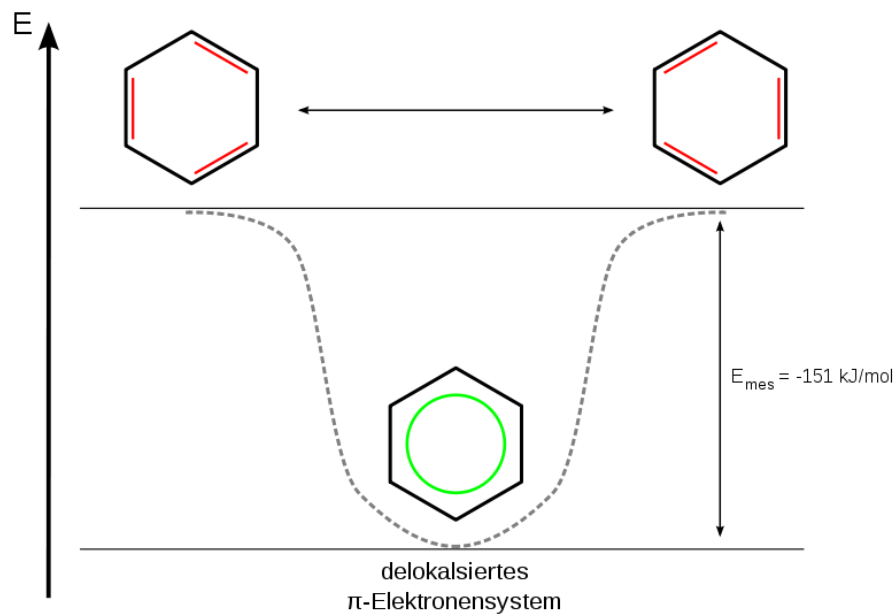
Erst seit 1929 ist zyklische Struktur zweifelsfrei gesichert

Rasterkraftaufnahme Pentacen



Zeigt die reale Struktur von aromatischen Systemen – Kekule's Struktur war korrekt!

Mesomere Grenzformeln: Benzol



Mesomere Grenzformeln werden durch „Umklappen“ von Elektronenpaaren ineinander überführt. Realität liegt dazwischen.

Bei konjugierten C=C, **delokalisieren** alle beteiligten **π -Elektronen** über das Molekül und bilden eine gemeinsame Elektronenwolke; dadurch wird Energie gewonnen (= **Resonanzenergie**)



Einhorn:
Mesomere Grenzformel

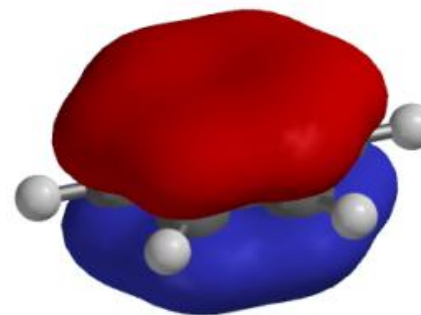


Drache:
Mesomere Grenzformel



Nashorn:
Mesomerer Zustand

Elektronenwolke im Benzol:

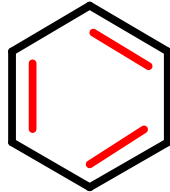


Aromatische Kohlenwasserstoffe

Cyclische Polyene/ Annulene: Die Hückel-Regel

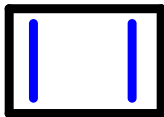
aromatisch:

planarer Monocyclus mit $4n+2$ π -Elektronen



$$(4 \times 1) + 2$$

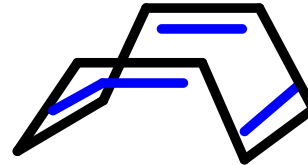
Antiaromatisch: $4n$ π -Elektronen



$$(4 \times 1)$$

alternierende Bindungen

nicht-aromatisch



$$(4 \times 2)$$

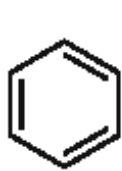
Nicht planar!

alternierende Bindungen

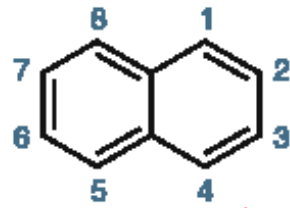
$4n+2$ π -Elektronen

Arene (Aromaten) 1

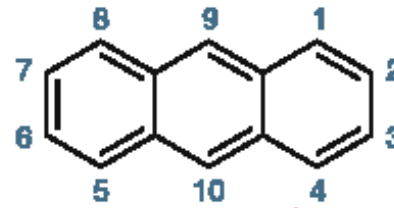
!: biologisch relevant



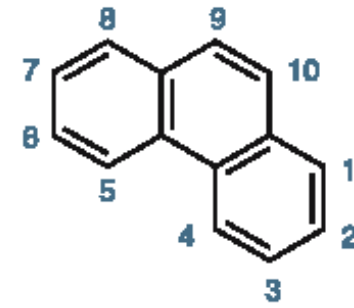
Benzol !



Naphthalin !



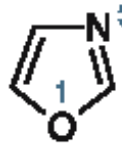
Anthracen !



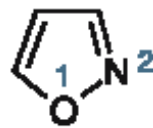
Phenanthren



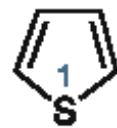
Furan !



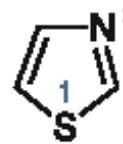
Oxazol !



Isoxazol



Thiophen



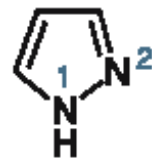
Thiazol !



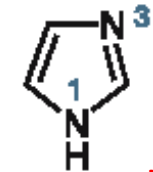
Isothiazol



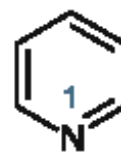
Pyrrol !



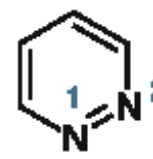
Pyrazol



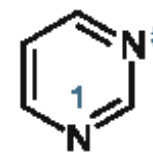
Imidazol !



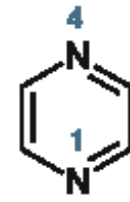
Pyridin !



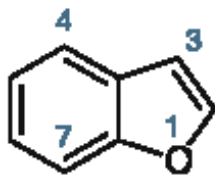
Pyridazin



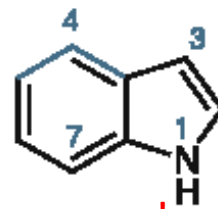
Pyrimidin !



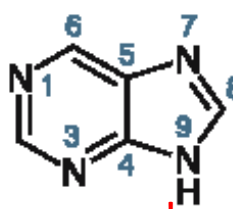
Pyrazin !



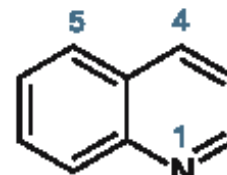
Benzofuran



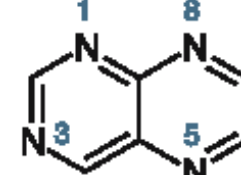
Indol !



Purin !

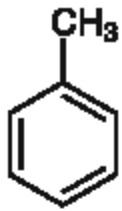


Chinolin !

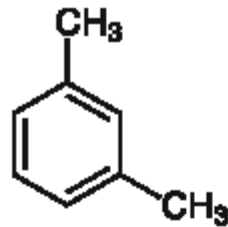


Pteridin !

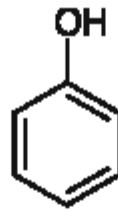
Arene (Aromaten) 2



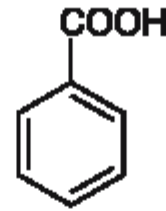
Toluol



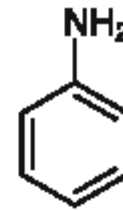
m-Xylol



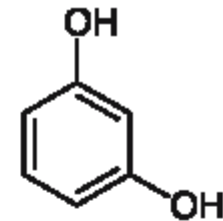
Phenol



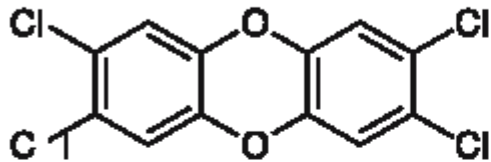
Benzoessäure



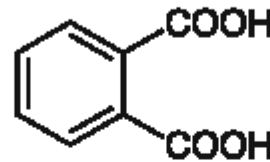
Anilin



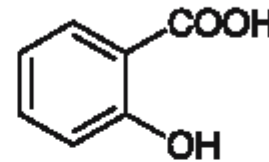
Resorcin



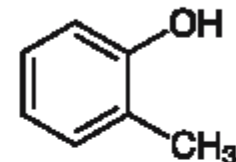
2,3,7,8-Tetrachlordibenzo-*p*-dioxin
(Dioxin)



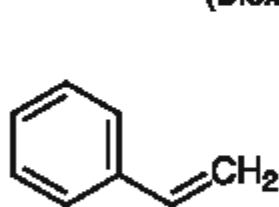
Phthalsäure



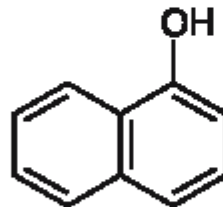
Salicylsäure



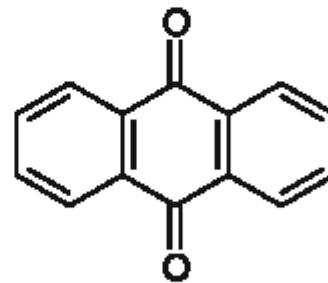
o-Kresol



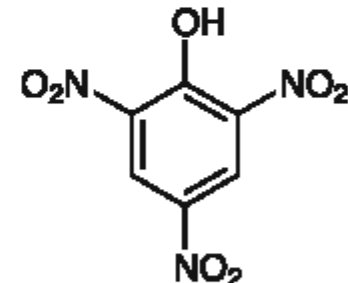
Styrol



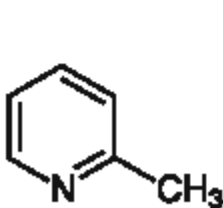
1-Naphthol



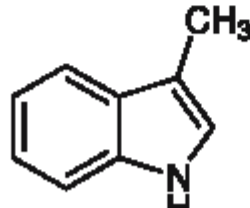
Anthrachinon



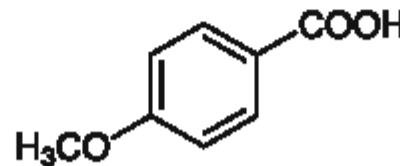
Pikrinsäure



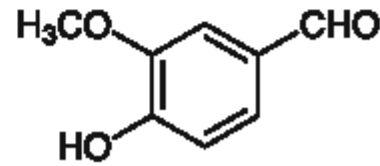
2-Methylpyridin
(α -Picolin)



3-Methylindol
(Skatol)

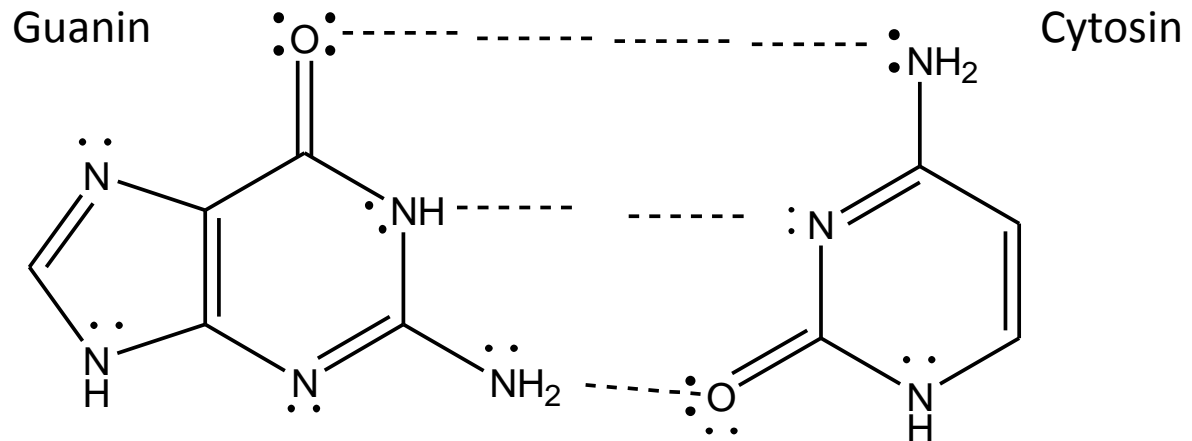
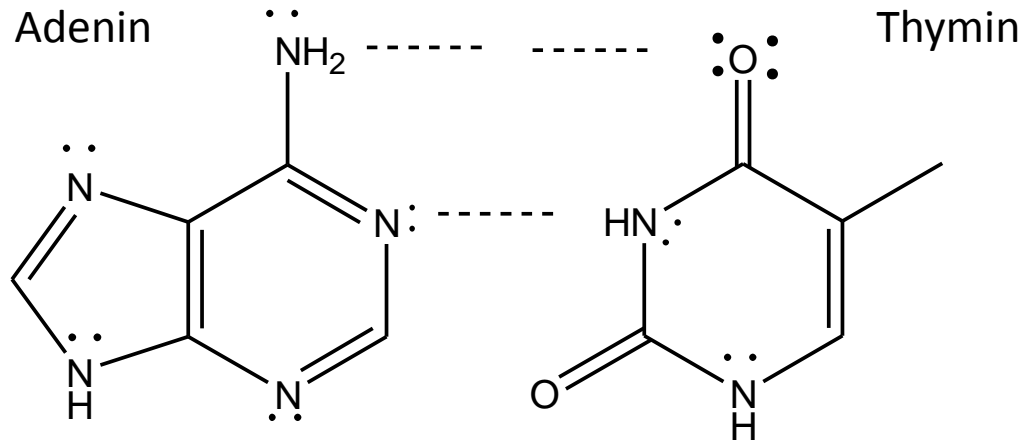


Anissäure



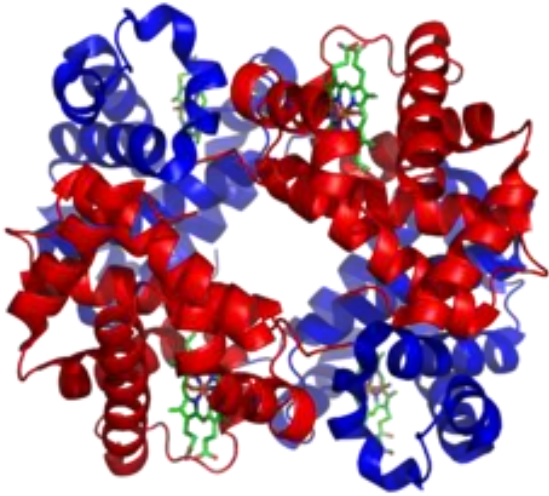
Vanillin

Heterocyclen des Lebens:

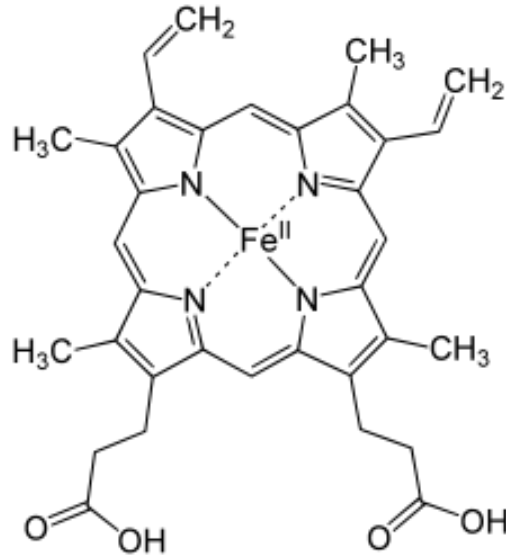


Aromatische Kohlenwasserstoffe

Einschub: Aromatizität und Hämoglobin



Hämoglobin



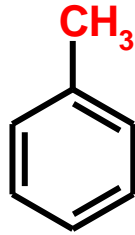
Häm b

(Substanzklasse: Porphyrine)

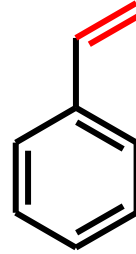
- 18 π -Elektronen; aromatisch nach Hückel-Regel
- Folge 1: besonders stabil
- Folge 2: flache Struktur; wichtig für Funktion (O₂ Transport)
- Folge 3: Farbigeit (auch: Chlorophyll!)

Aromatische Kohlenwasserstoffe

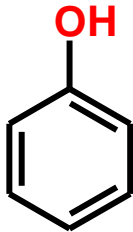
Nomenklatur einfach substituierter Benzole



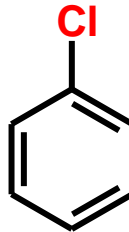
Methylbenzol
Toluol



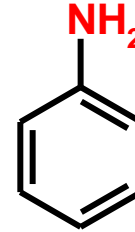
Ethenylbenzol
(**Vinyl**benzol)
Styrol



Hydroxybenzol
Phenol



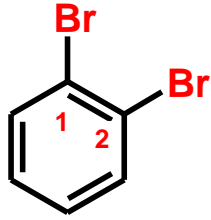
Chlorbenzol



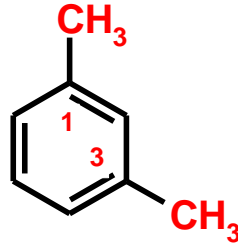
Aminobenzol
Anilin

Aromatische Kohlenwasserstoffe

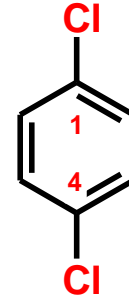
Nomenklatur doppelt substituierter Benzole



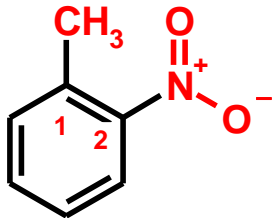
1,2-Dibrom benzol
ortho- Dibrombenzol



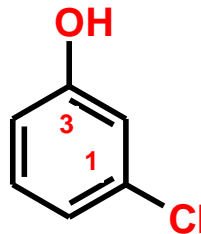
1,3-Dimethyl benzol
meta-Xylol



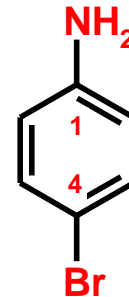
1,4-Dichlor benzol
para- Dichlor benzol



2-Methyl-1-nitrobenzol
ortho-Nitrotoluol



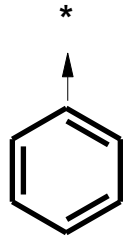
Chlor-3-hydroxy benzol
meta-Chlorphenol



1-Amino-4-brom benzol
para-Bromanilin

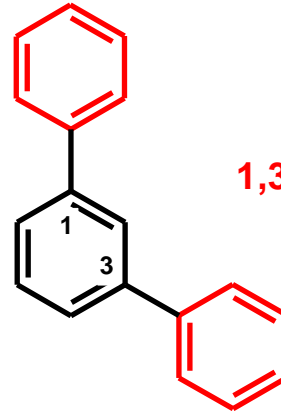
Aromatische Kohlenwasserstoffe

Nomenklatur von Phenylresten

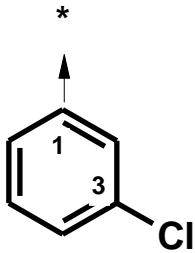


Phenyl

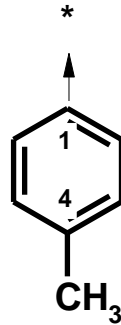
Beispiel:



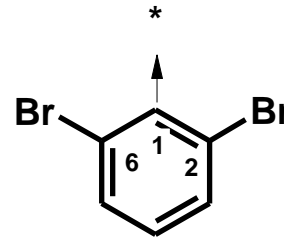
1,3-Diphenyl benzol



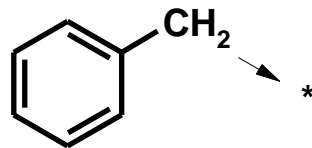
3-Chlorphenyl



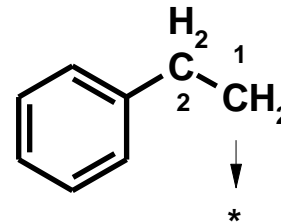
4-Methylphenyl



2,6-Dibromphenyl



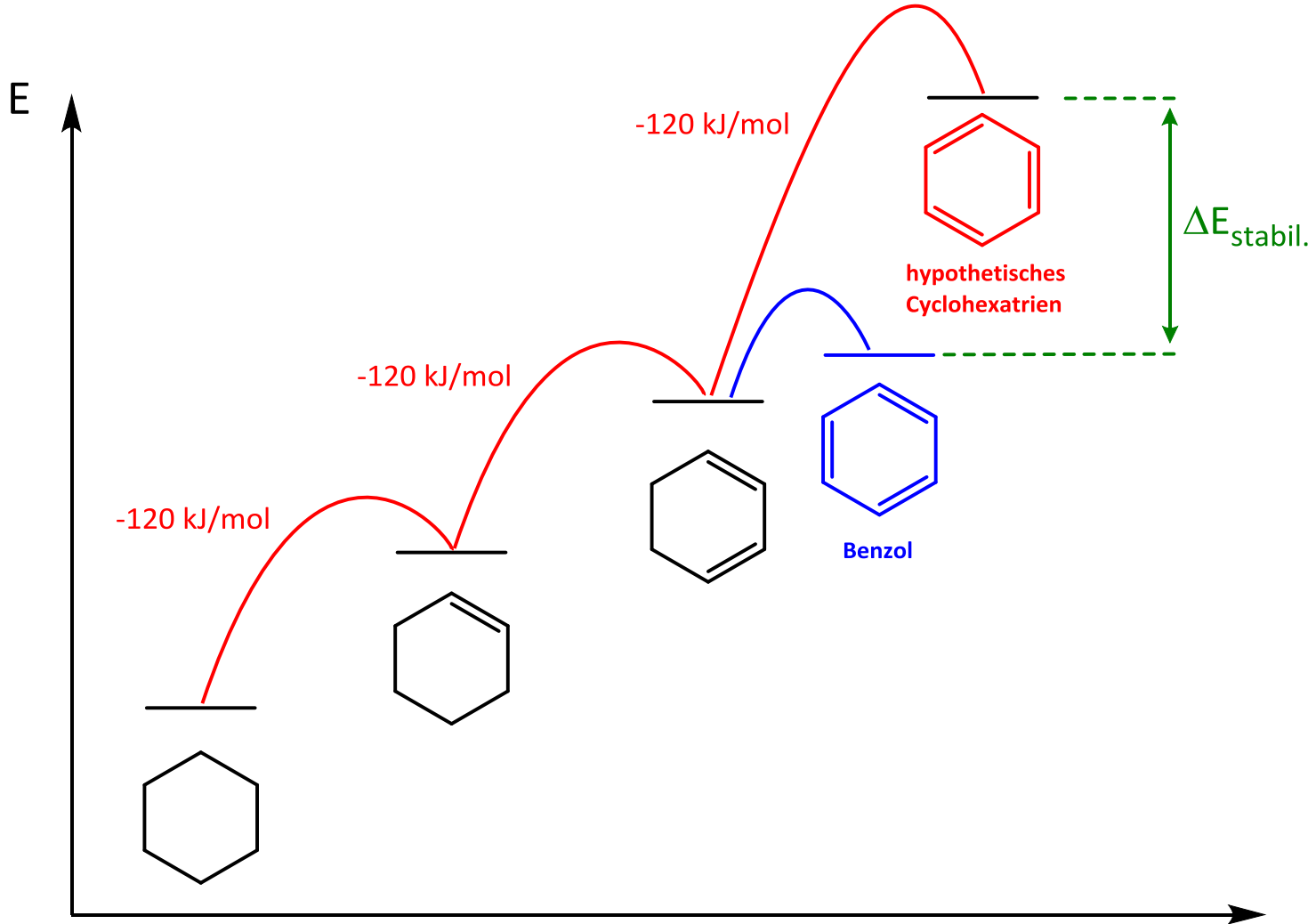
Benzyl



2-Phenylethyl

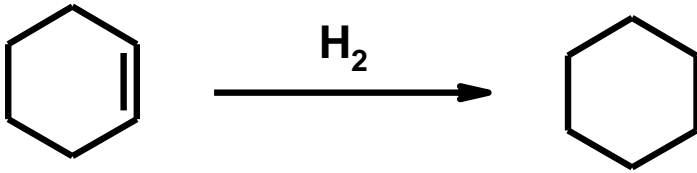
Aromatische Kohlenwasserstoffe

Resonanzenergie im Benzol: Beispiel Hydrierung

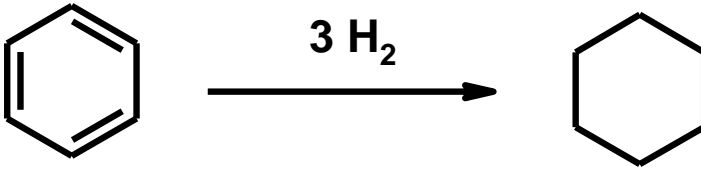


Aromatische Kohlenwasserstoffe

Resonanzenergie im Benzol: Hydrierungen



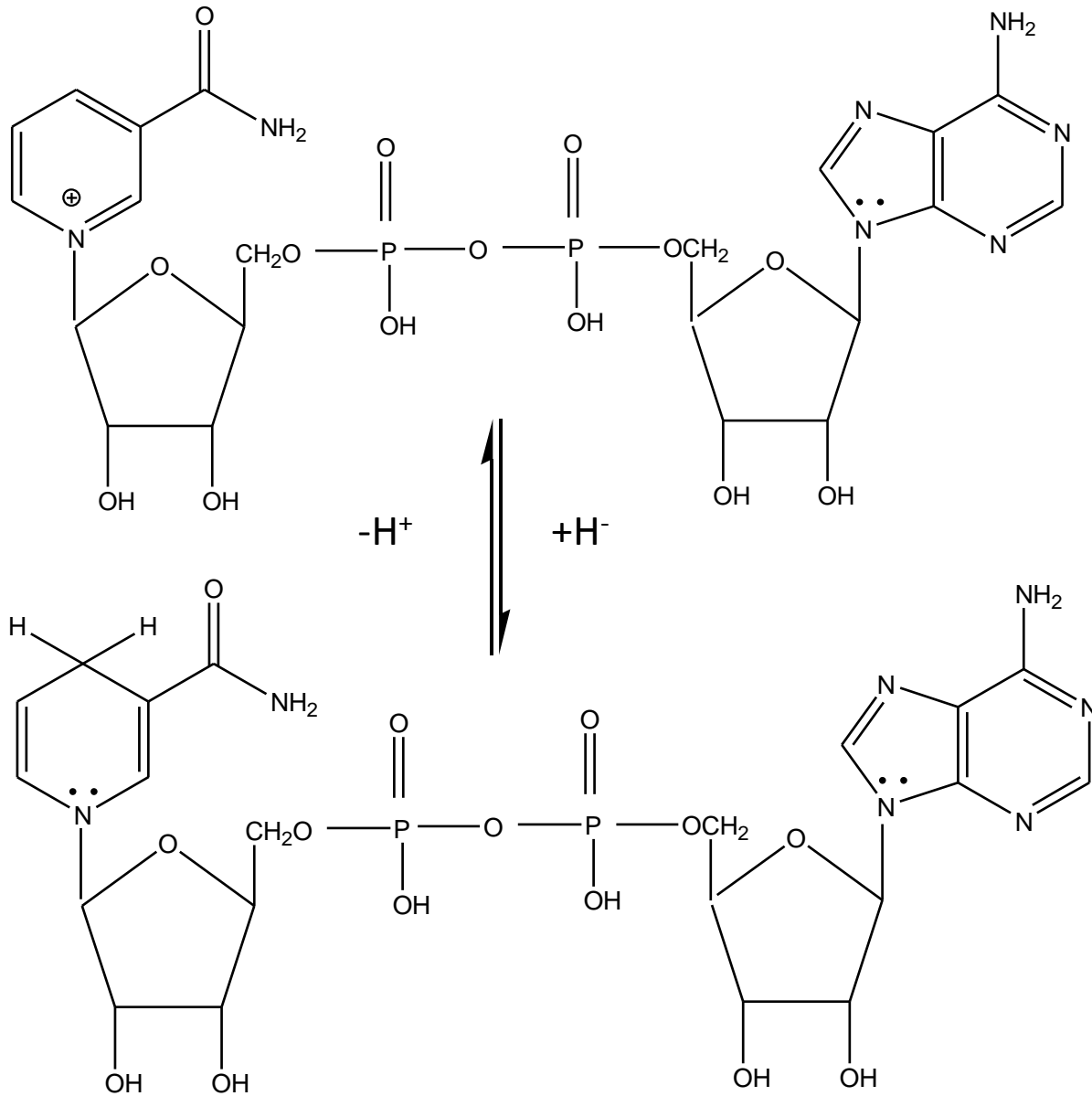
$$- 120 \text{ kJ / mol} \times 3 = -360 \text{ kJ / mol}$$



$$\underline{- 208 \text{ kJ / mol}}$$

$$\text{Resonanzenergie} \quad - 152 \text{ kJ / mol}$$

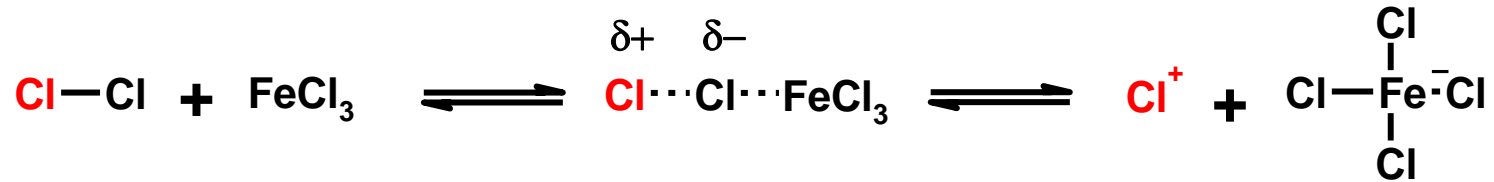
Heterocyclen des Lebens1: NAD⁺/NADH + H⁺



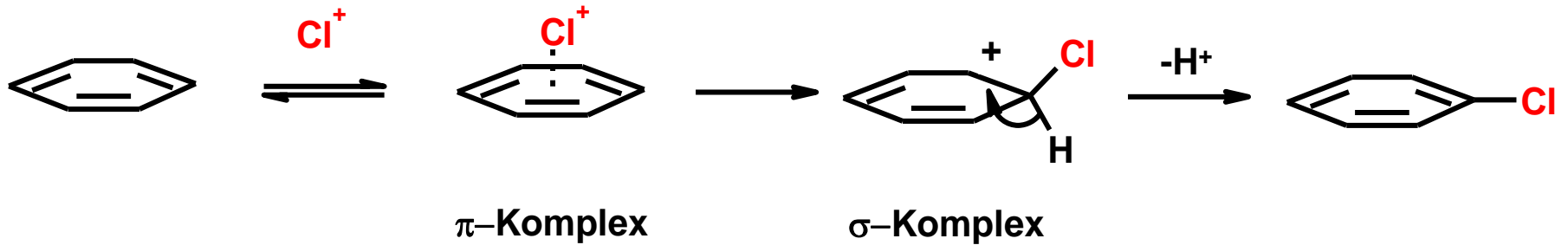
Aromatische Kohlenwasserstoffe

Halogenierung von Benzol

Erzeugung des Elektrophils

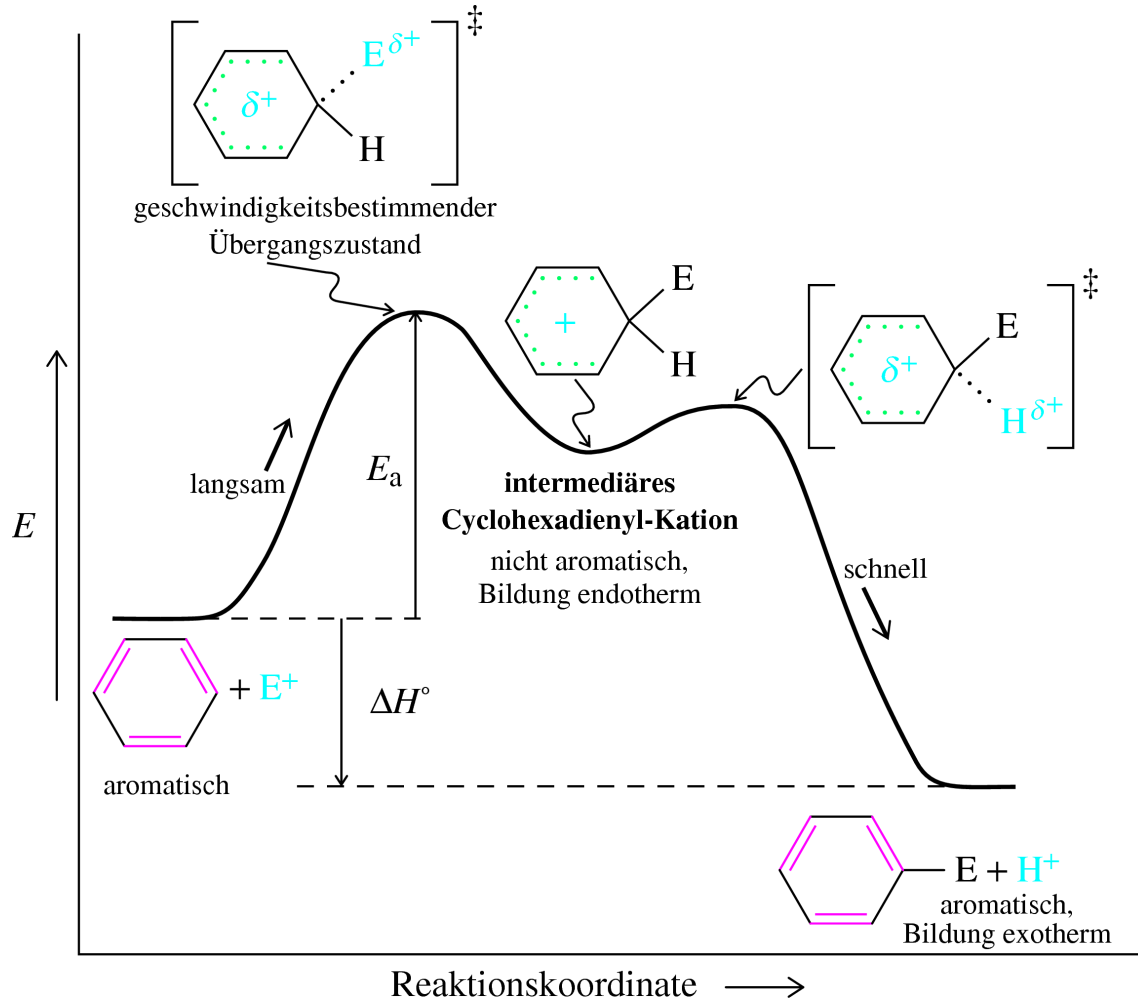


Substitution



Aromatische Kohlenwasserstoffe

Elektrophile aromatische Substitution: Energiediagramm



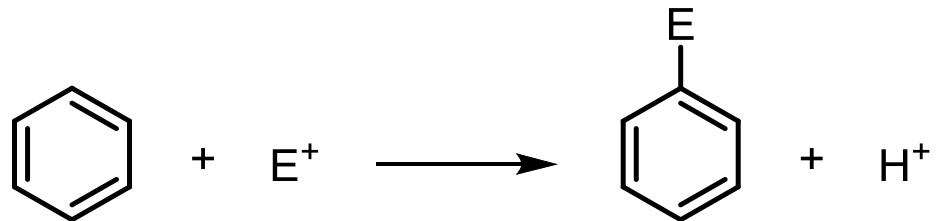
Aromatische Kohlenwasserstoffe

Einschub: Standardrezept S_EAr

- **Bildung des Elektrophils E^+** durch geeigneten Katalysator/Aktivator
- **Addition von E^+** an aromatischen Ring
→ Aromatizität „kaputt“ (schlecht), aber Mesomeriestabilisierung (gut)
Beachte: Der Aromat reagiert hier als Nukleophil!

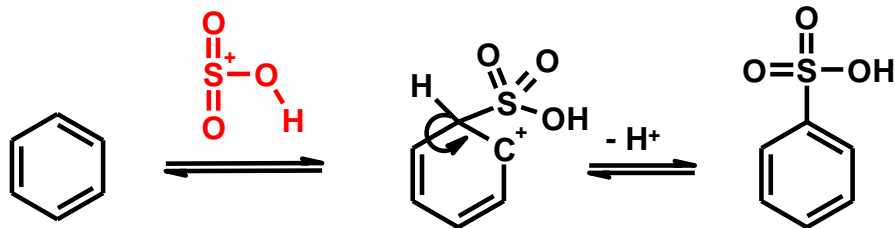
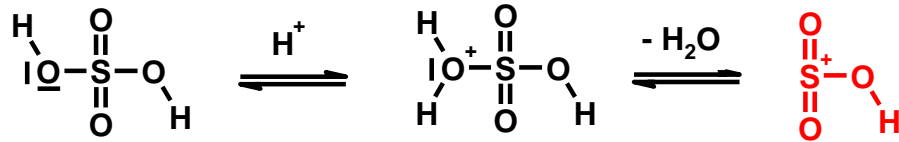
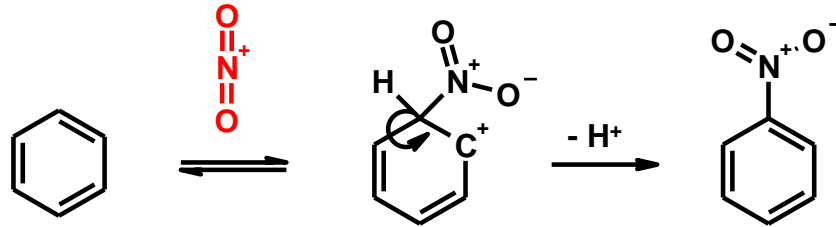
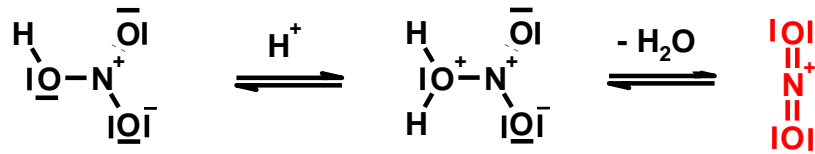
- **Eliminierung von H^+** von aromatischem Ring
→ Aromatizität wiederhergestellt (sehr gut)

- **Ergebnis:** E hat H ersetzt



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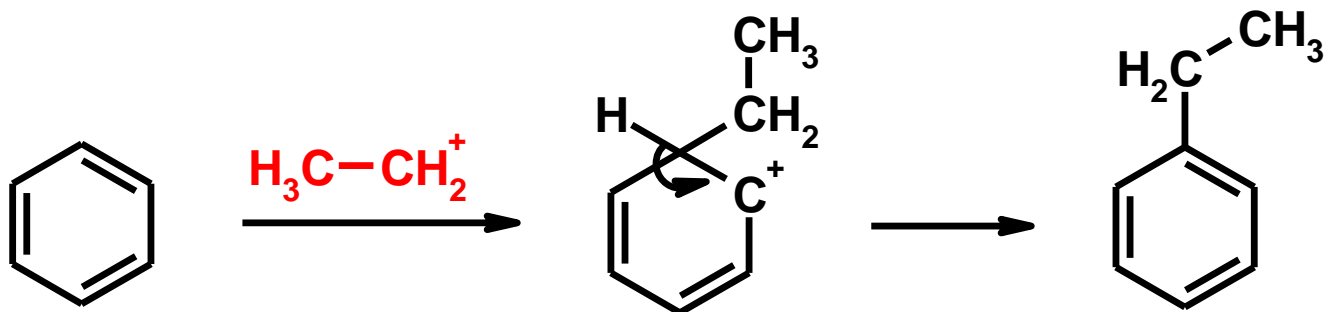
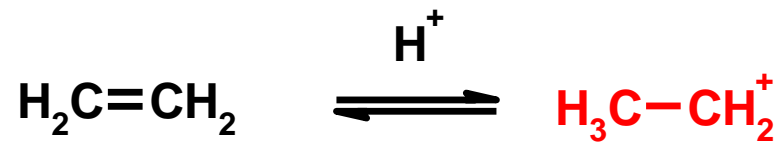
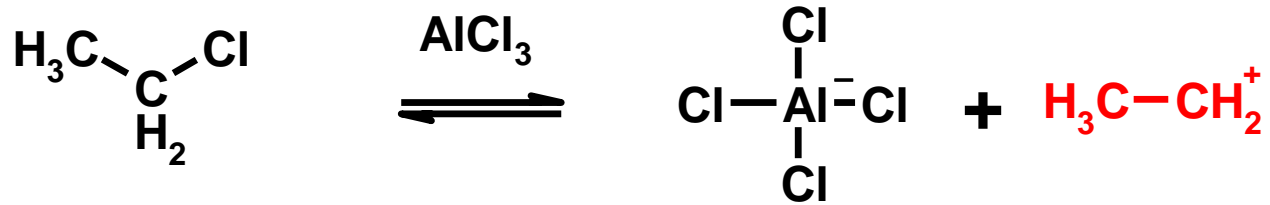
Nitrierung und Sulfonierung



Benzolsulfonsäure

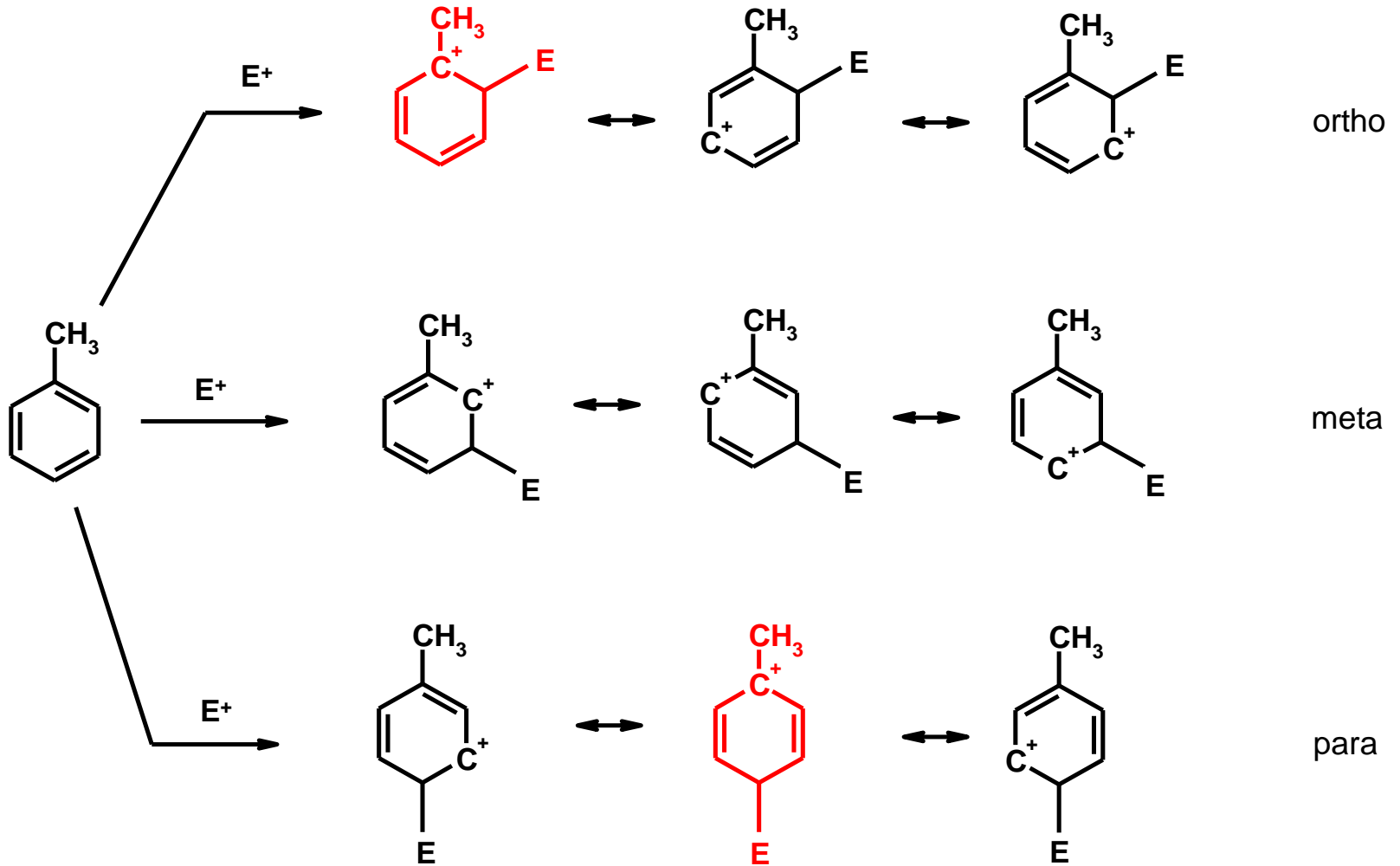
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C-Elektrophile: Friedel-Crafts-Alkylierung



Aromatische Kohlenwasserstoffe

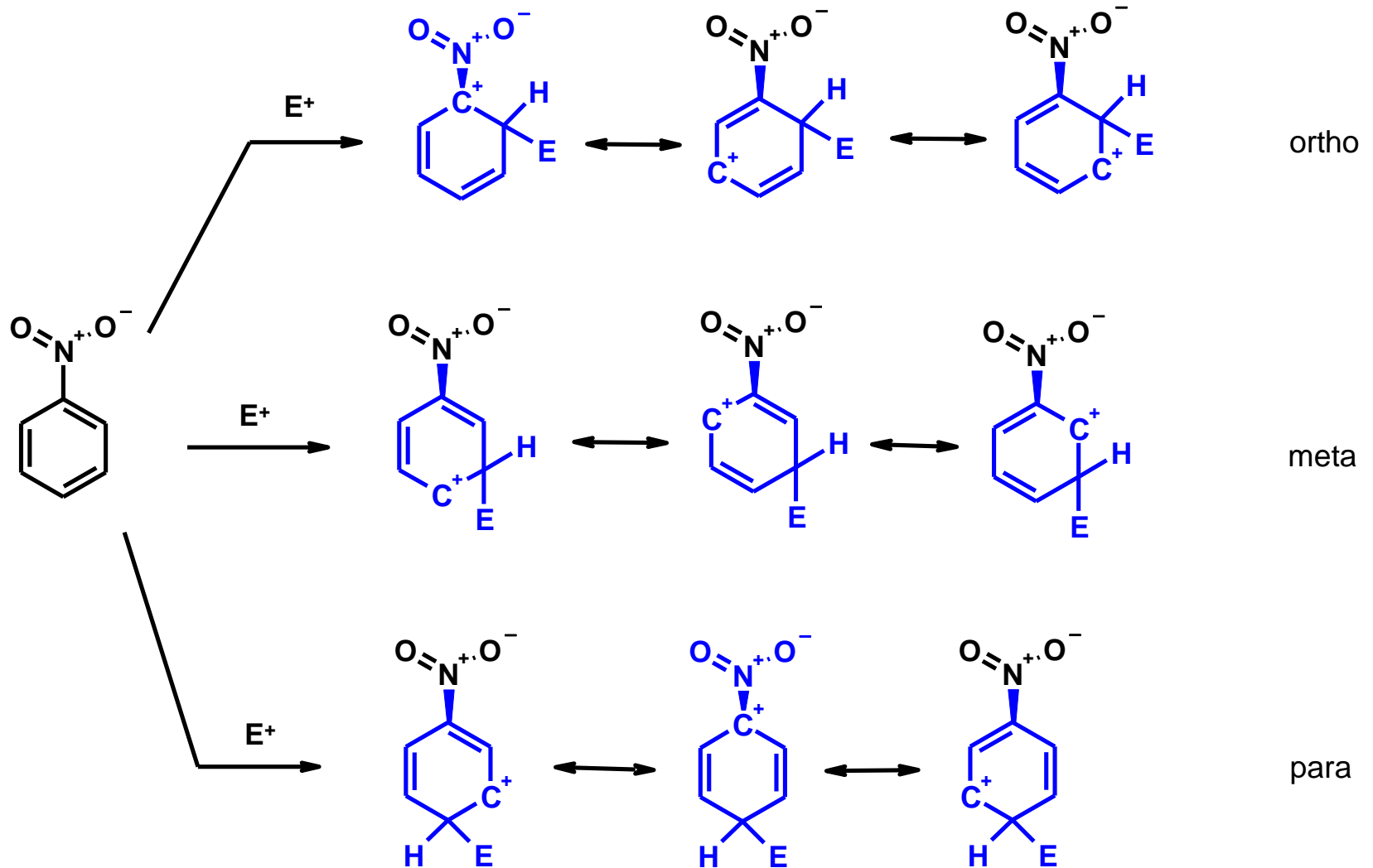
Mehrfachsubstitutionen: Regioselektivität bei Toluol



rote Strukturen: induktiv stabilisiert

Aromatische Kohlenwasserstoffe

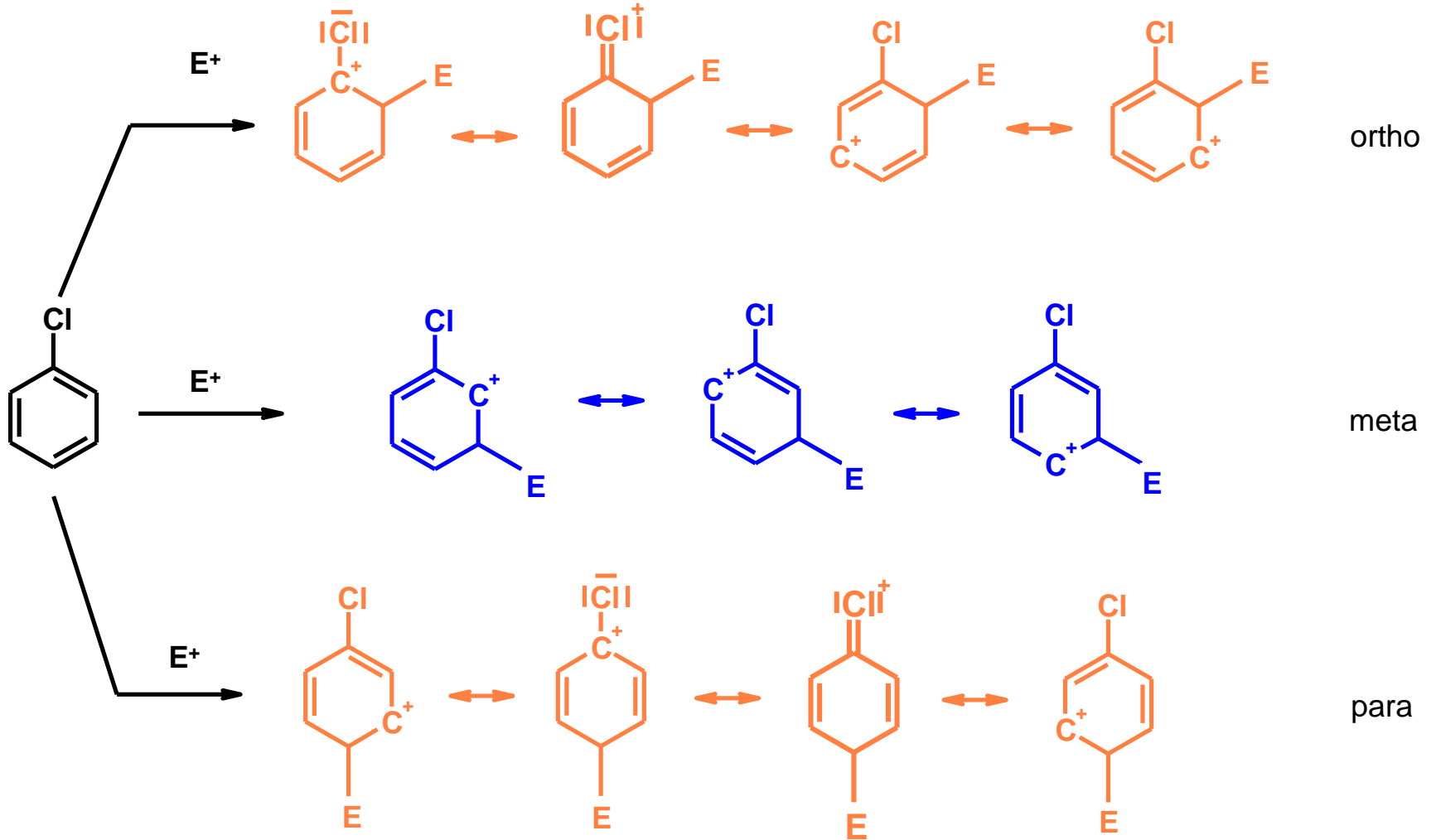
Mehrfachsubstitutionen: Regioselektivität bei Nitrobenzol



Strukturen mit blauer Nitrogruppe : mesomer destabilisiert

Aromatische Kohlenwasserstoffe

Mehrfachsubstitutionen: Regioselektivität bei Chlorbenzol



orange Strukturen : induktiv destabilisiert, mesomer stabilisiert

blaue Strukturen : induktiv destabilisiert

Aromatische Kohlenwasserstoffe

Elektronischer Einfluss von Substituenten

ortho & para	Donor:	$-\bar{\text{O}}\text{I}^{\ominus}$	$+\text{M}, +\text{I}$	
		$-\text{NR}_2, -\text{NH}_2$	$+\text{M}, -\text{I}$	
		$-\text{OR}, -\text{OH}, -\text{NHC}(=\text{O})\text{R}$		
		$-\text{OC}(=\text{O})\text{R}, -\text{SR}$		
		$-\text{Ph}$		
		$-\text{Alkyl}, -\text{CO}_2^{\ominus}$	$+\text{I}$	
	meta	Standard:	$-\text{H}$	$-$
			$-\text{CH}_2\text{Cl}$	$-\text{I} \rightarrow +\text{I}$
			$-\text{Cl}, -\text{Br}$	$-\text{I} \rightarrow +\text{M}$
			EWG:	$-\text{NR}_3^{\oplus}, -\text{NH}_3^{\oplus}$
			$-\text{C}(=\text{O})\text{R}, -\text{C}(=\text{O})\text{Het}$	$-\text{M}, -\text{I}$
			$-\text{C}\equiv\text{N}, -\text{SO}_3\text{H}$	
		$-\text{NO}_2$		

Induktive und mesomere Substituenteneffekte verschiedener funktioneller Gruppen.