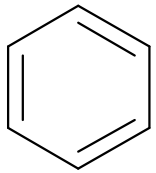
台灣大學開放式課程

有機化學乙

蔡蘊明　教授

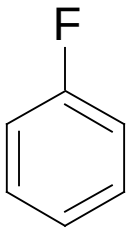
Chapter 14
Aromatic compounds (芳香族化合物)

※ Benzene  C_6H_6

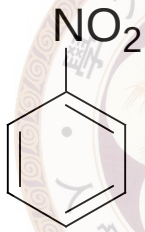
used as parent name

Special property: aromatic (芳香的)

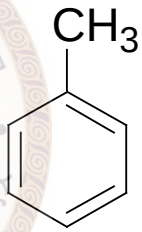
class name



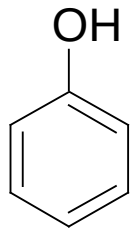
fluorobenzene



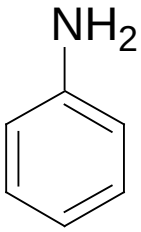
nitrobenzene



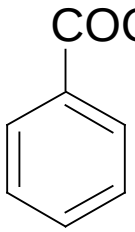
toluene
甲苯



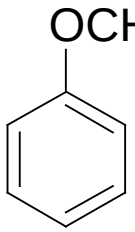
phenol
酚



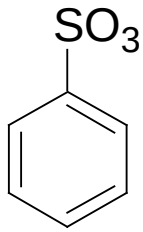
aniline
苯胺



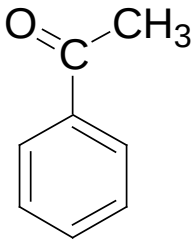
benzoic acid
苯甲酸



anisole

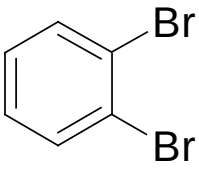


benzenesulfonic acid
苯磺酸



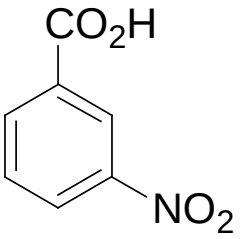
acetophenone (苯乙酮)
or methyl phenyl ketone (甲基乙基酮)

✓ Disubstituted benzene



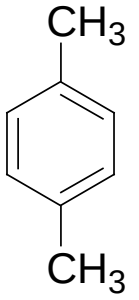
1,2-dibromobenzene
(*o*-dibromobenzene)

**o* = *ortho* (鄰)



3-nitrobenzoic acid
(*m*-nitrobenzoic acid)

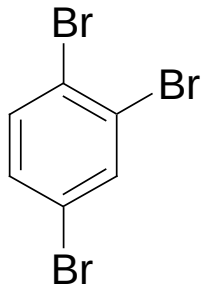
**m* = *meta* (間)



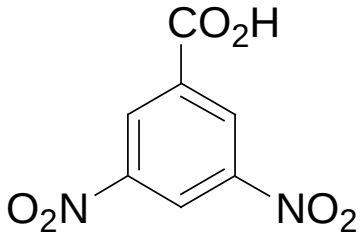
1,4-dimethylbenzene
(*p*-xylene)

**p* = *para* (對)

✓ Trisubstituted benzene

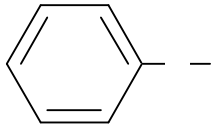


1,2,4-tribromobenzene

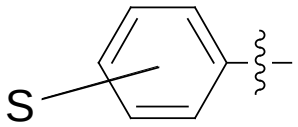


3,5-dinitrobenzoic acid

✓ As a substituent

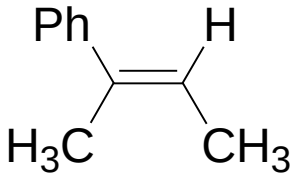


phenyl abbreviated as: Ph-, C_6H_5- or ϕ-

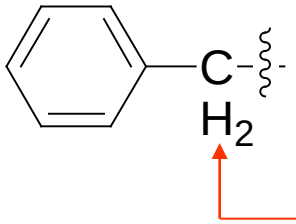


aryl (Ar-)

例



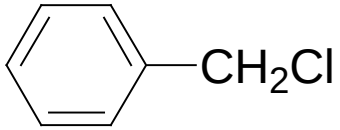
(*E*)-2-phenyl-2-butene



benzyl (Bn-) or phenylmethyl

苄基

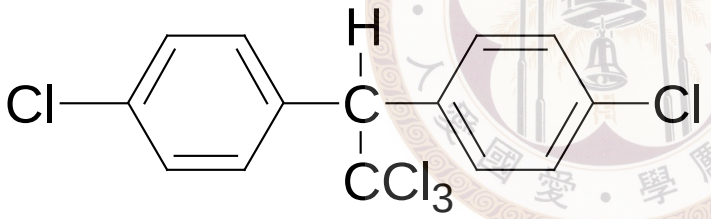
benzylic hydrogen



benzyl chloride (BnCl)

A poem by Dr. D. D. Perrin
(http://poetry.poetryx.com/poems/6091/)

A mosquito was heard to complain
That a chemist had poisoned his brain
The cause of his sorrow
Was *para*-dichloro-
diphenyltrichloroethane



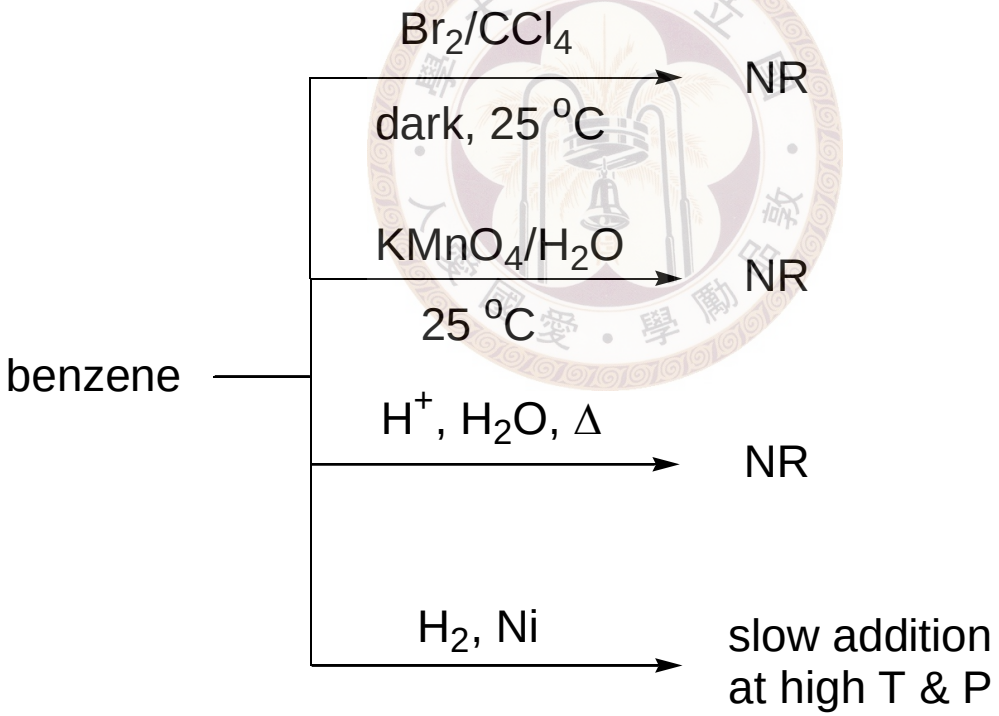
DDT

※ Structure and bonding of benzene

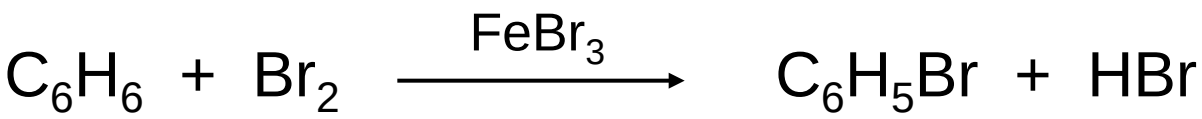
1825 Faraday: discovery

1834 C_6H_6 highly unsaturated

does not undergo typical alkene chemistry



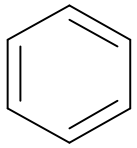
Undergoes substitution in the presence of a Lewis acid



only one compound

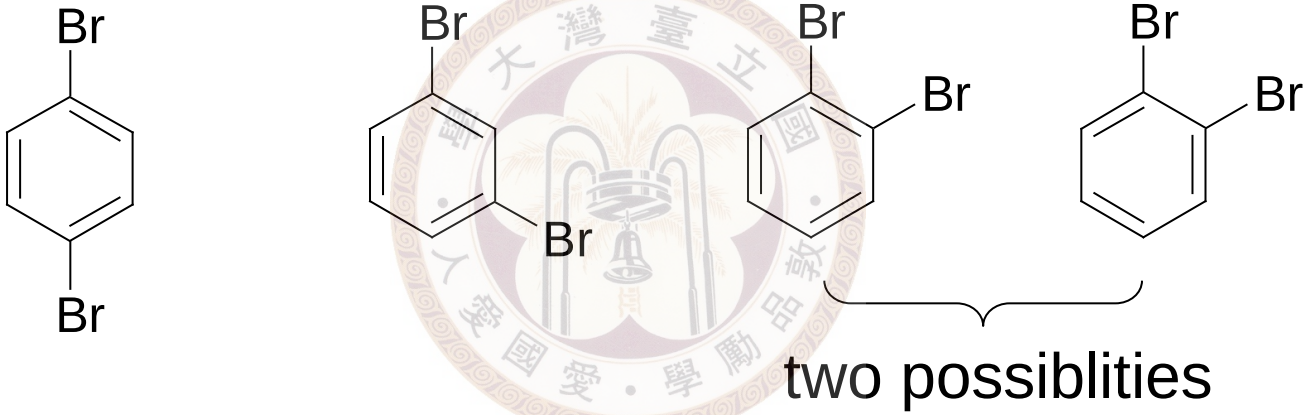
Disubstitution: three isomeric dibromobenzene

Q: What is the structure?

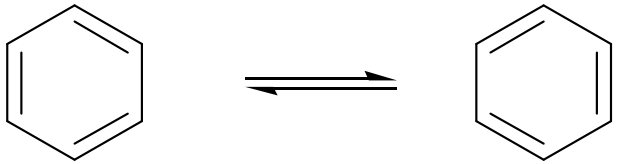
1865 August Kekulé: 

One possible bromobenzene: yes

Three possible dibromobenzene:

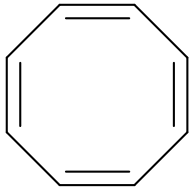


Kekulé's proposal:



in rapid equilibrium

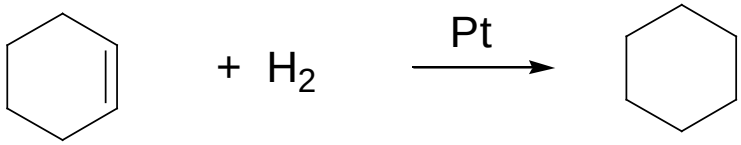
1911 Willstäter



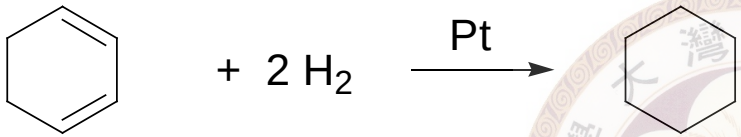
cyclooctatetraene

behaves like a typical alkene

※ The special stability of benzene

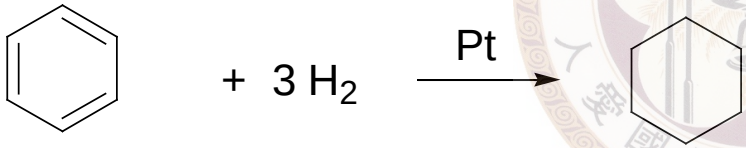


ΔH^o = –120 kJ/mol



ΔH^o = –232 kJ/mol
(cf. –120 x 2 = –240)

difference: 8



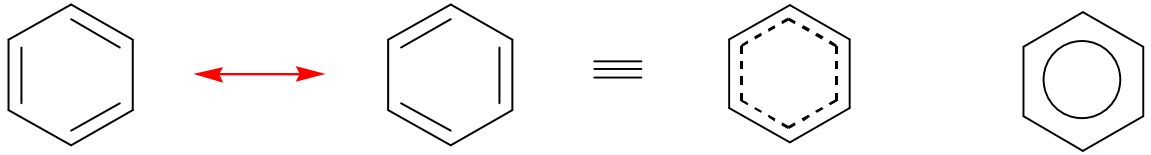
ΔH^o = –208 kJ/mol
(cf. –120 x 3 = –360)

difference: 152

the unusual extra stability

✓ VB view

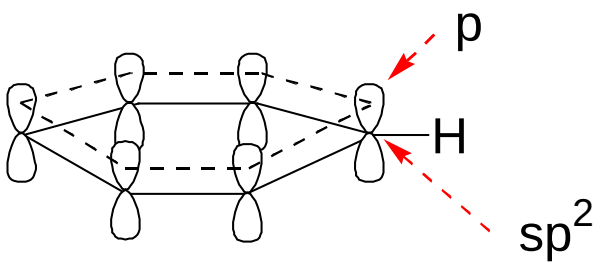
Resonance stabilization:



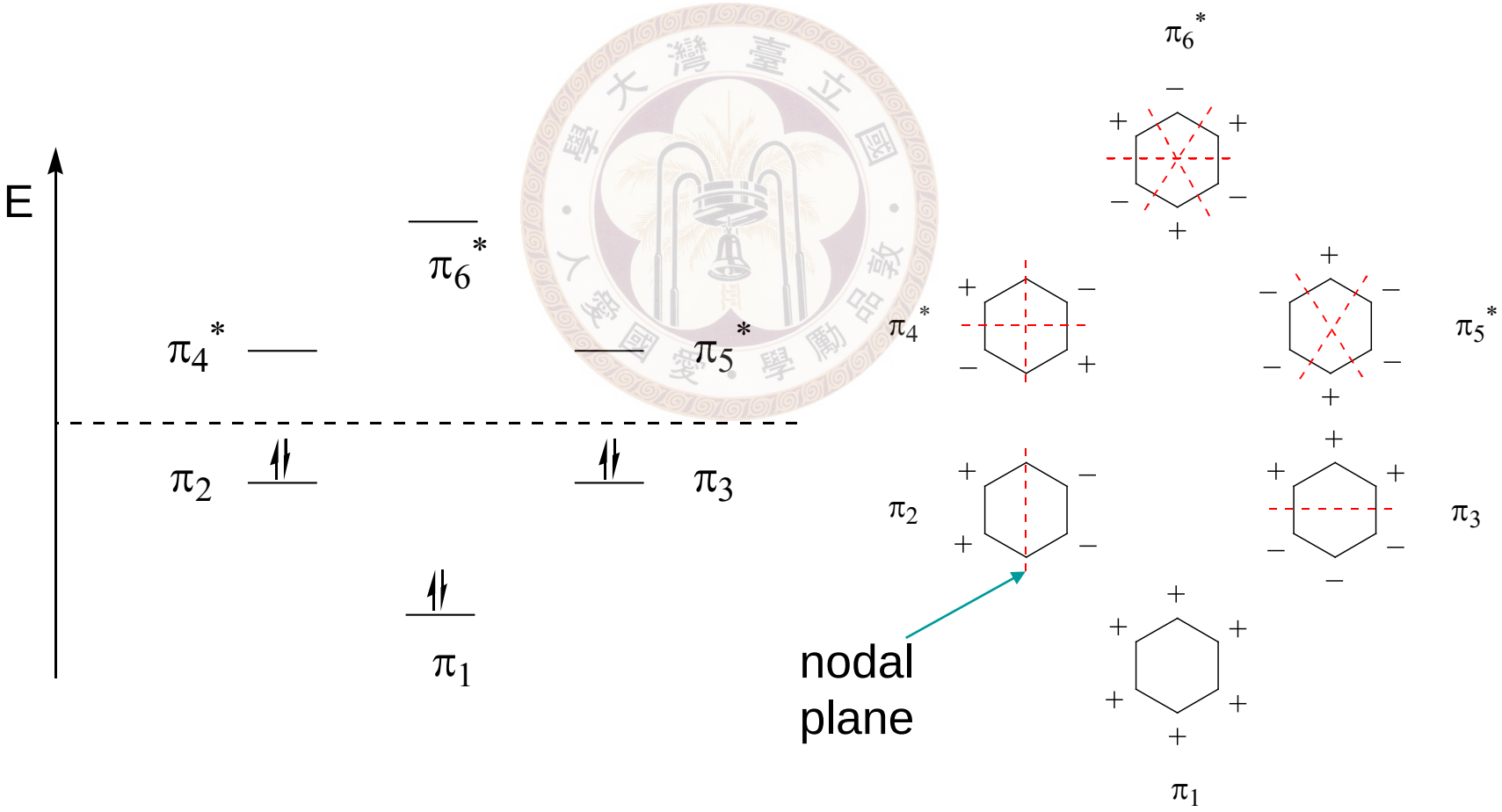
cf. H_3C-CH_3 1.54 Å $H_2C=CH_2$ 1.34 Å 1.39 Å

The extra stability is called resonance energy

✓ MO view



A closed shell delocalization of 6 π e⁻ over 6 p orbitals

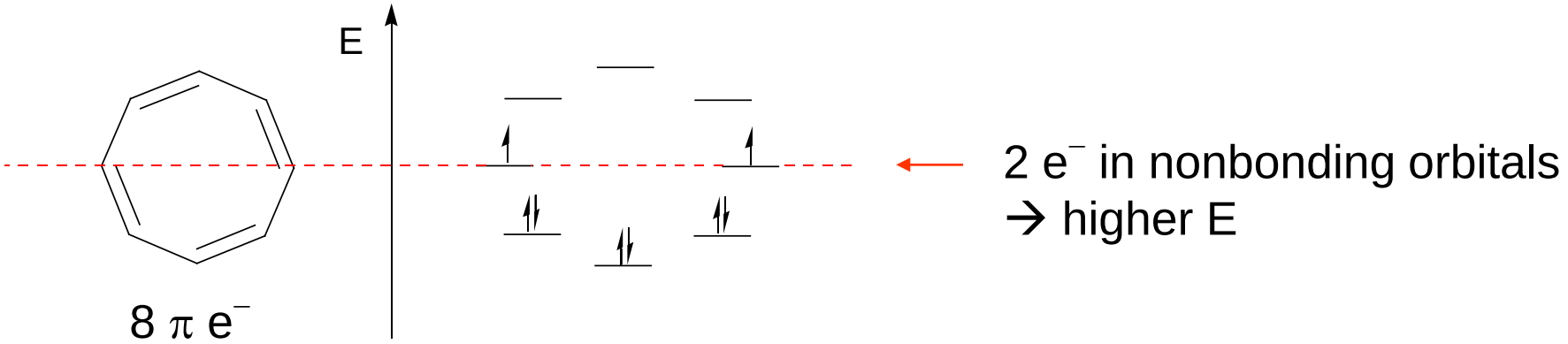


◎ Hückel's [4n + 2] rule

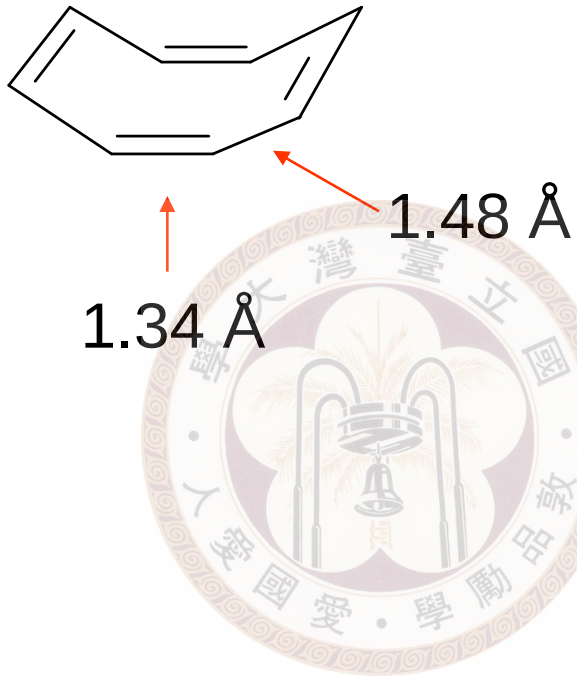
1931 Hückel

Planar monocyclic rings
with overlapping π (p) orbitals
closed shell as in benzene
containing (4n + 2) π electrons
should be aromatic

✓ With 4n π electrons
→ antiaromatic
highly unstable

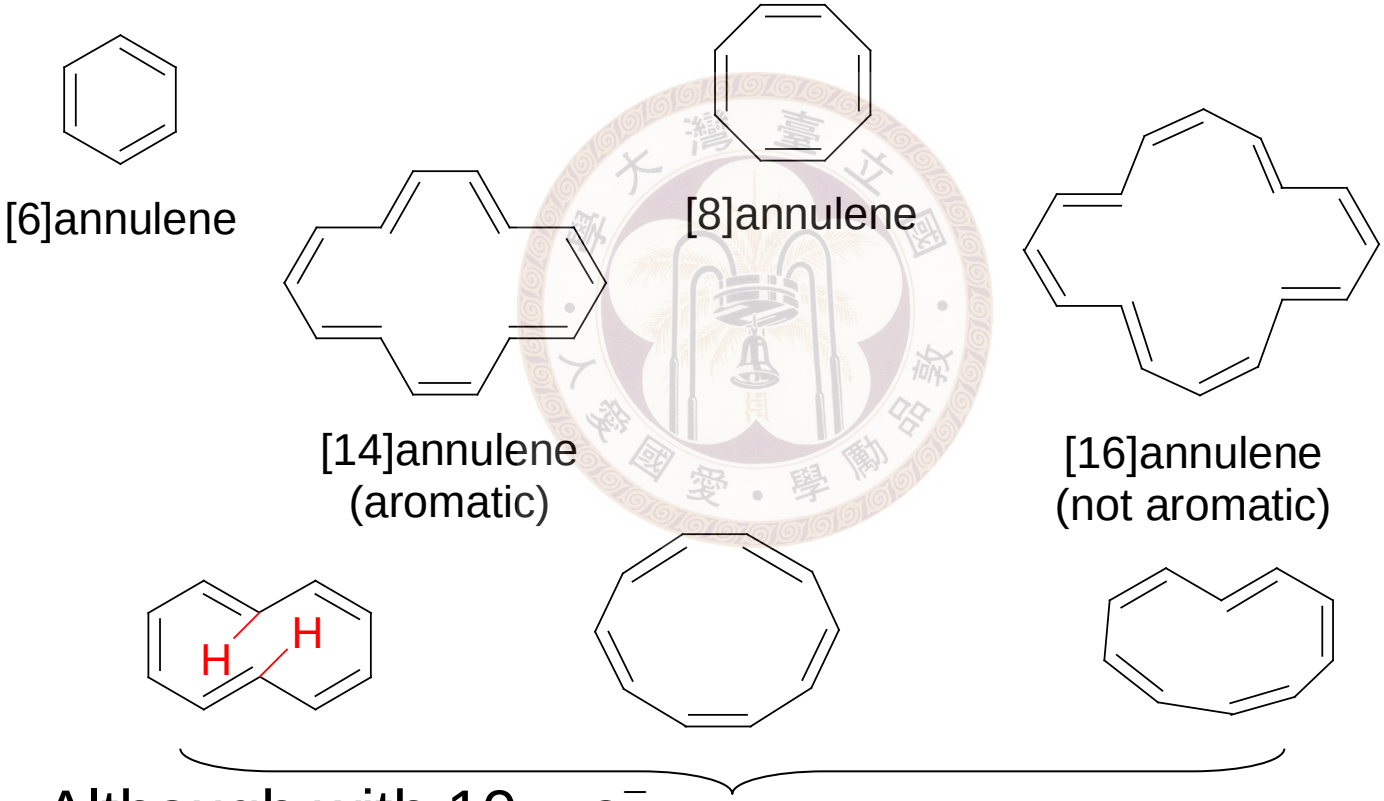


In fact cyclooctatetraene is not planar to avoid to be antiaromatic



※ The annulenes

Monocyclic compounds
with alternating single and double bonds

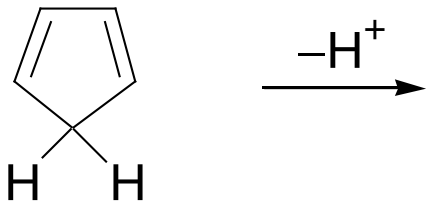


Although with 10 π e^-

→ can not be planar due to geometric constraint

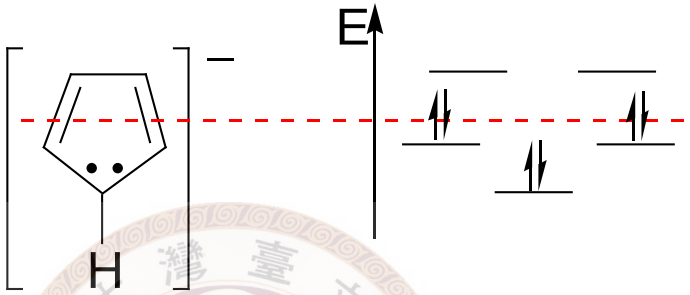
→ not aromatic

※ Aromatic ions



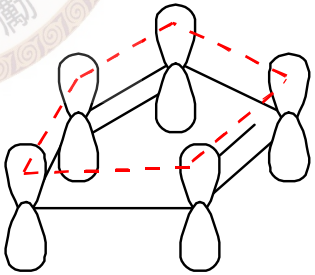
cyclopentadiene

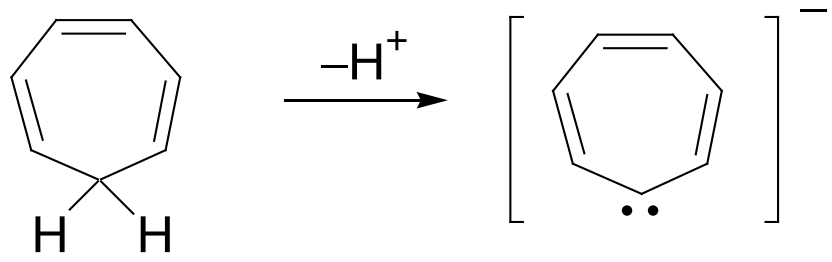
$pK_a = 15$



6 π e^- delocalized over 5-carbons

→ aromatic





cycloheptatriene

$pK_a = 36$

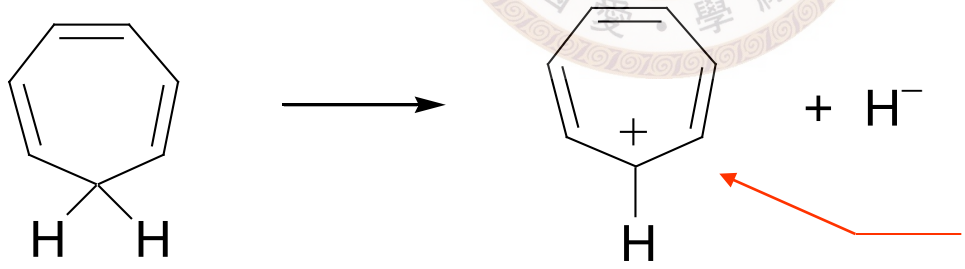
8 π e^-

→ nonaromatic

If planar

→ antiaromatic

Instead, cycloheptatriene looses H^- (hydride) very easily



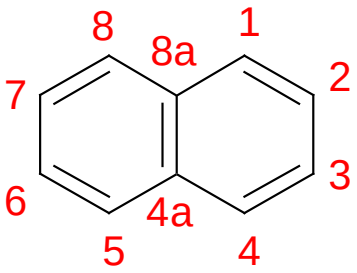
also known as tropylium ion

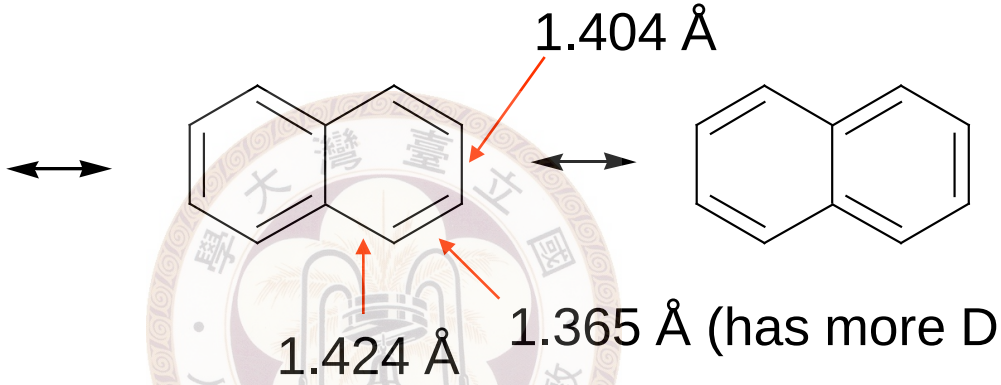
6 π e^-

delocalized over 7-carbons

※ Other aromatic compounds

◎ Benzenoid aromatic compounds



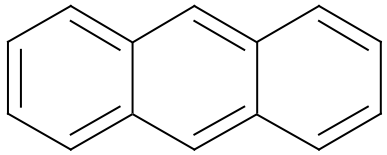


naphthalene

萘

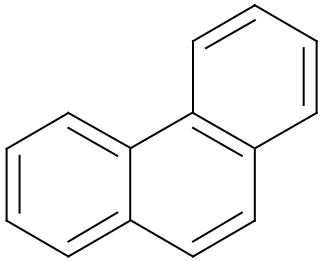
10 π e^-

RE = 255 kJ/mol



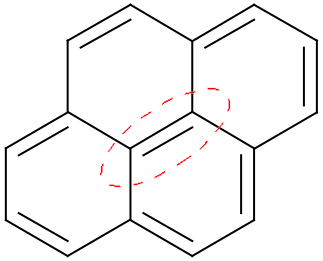
anthracene

蒽

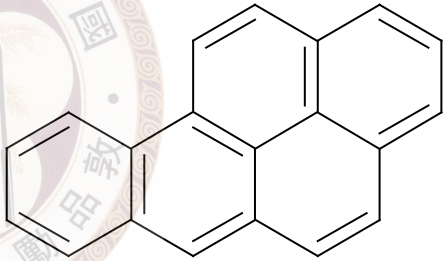


phenanthrene

菲



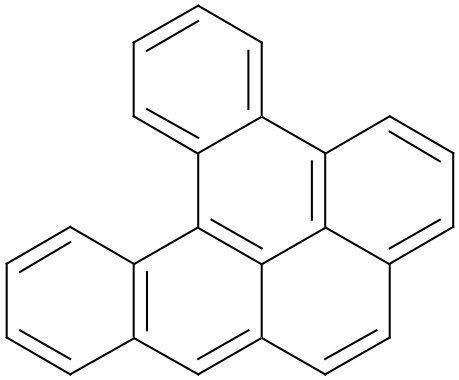
pyrene



benzo[a]pyrene

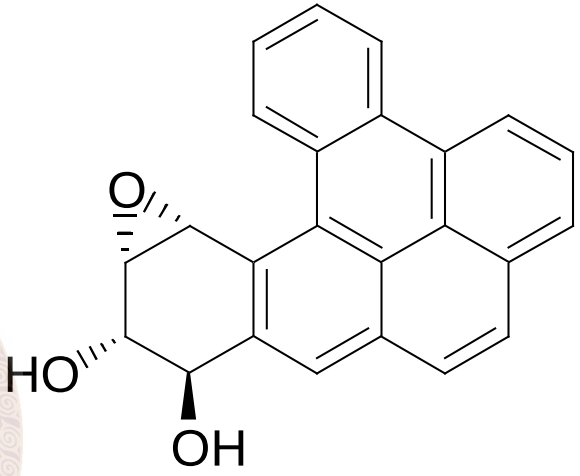
14 π e^- [14]annulene at the periphery

✓ Metabolism of aromatic compounds



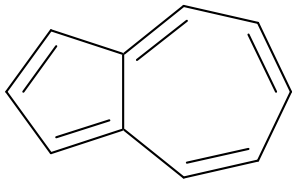
dibenzo[*a,l*]pyrene

enzymatic
epoxidation



carcinogenic

◎ Nonbenzenoid aromatic compounds



azulene
deep blue color

high dipole moment (1.0 D)
cf. naphthalene
dipole moment = 0

Reason for this special polarity:
it has a special resonance structure

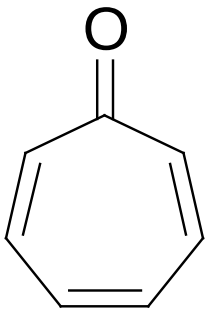
cyclopentadienyl anion

cycloheptatrienyl cation

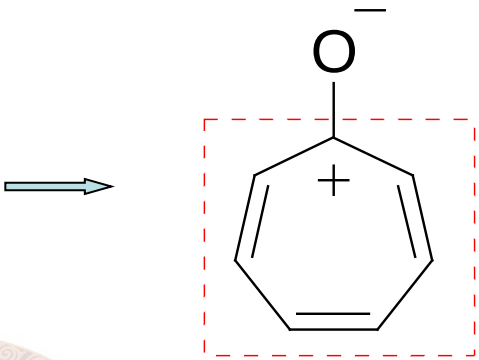
both are aromatic

⇩

This dipolar form has appreciable contribution to the overall hybrid

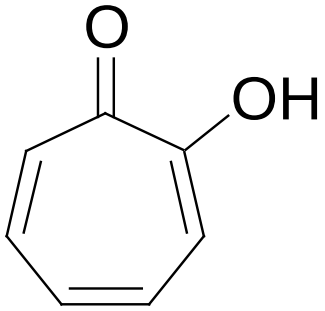


unusually polar



aromatic

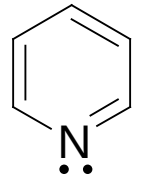
tropone



tropolone

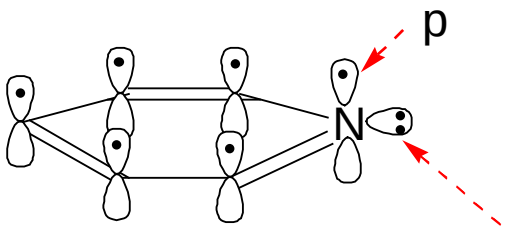
Basic skeleton of *hinokitiol* isolated (1936) in Taiwan by Nozoe (野副鐵男)

◎ Heterocyclic (雜環) aromatic compounds

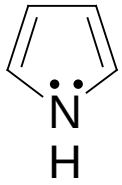


pyridine

≡

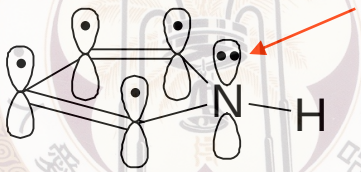


sp^2 : not participated in aromatic resonance
→ basic

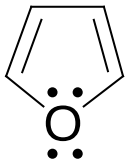


pyrrole

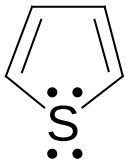
≡



This lone pair is participated in aromatic resonance
→ nonbasic

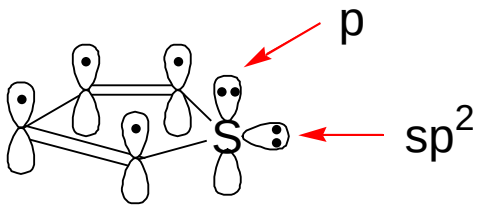


furan



thiophene

≡



※ Spectroscopy

✓^{1}H NMR

δ ~6.5–8 (protons are deshielded)

✓^{13}C NMR

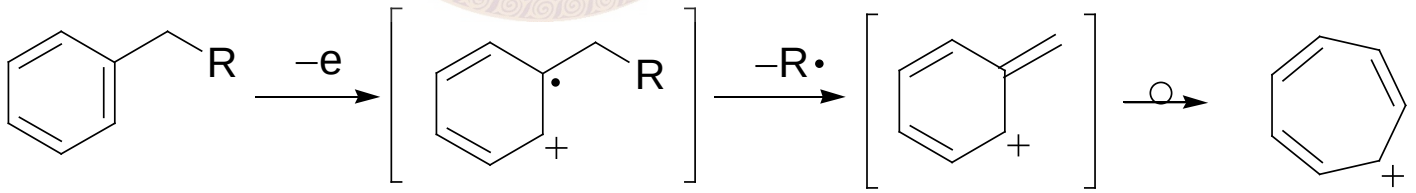
δ ~120–140 (carbons are deshielded)

✓IR

C-H stretch: near but larger than 3000 cm^{-1}

✓UV

✓ Mass



R may be H

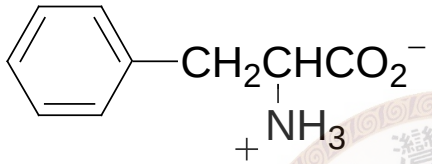
tropylium ion

strong ---------→ m/z = 91

※ Biological system

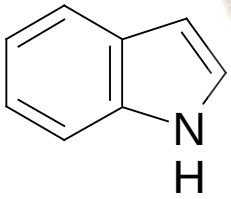
Compounds with aromatic rings occur in human body

例

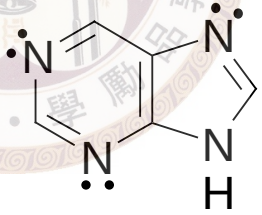


phenylalanine

Other important heterocyclic aromatics



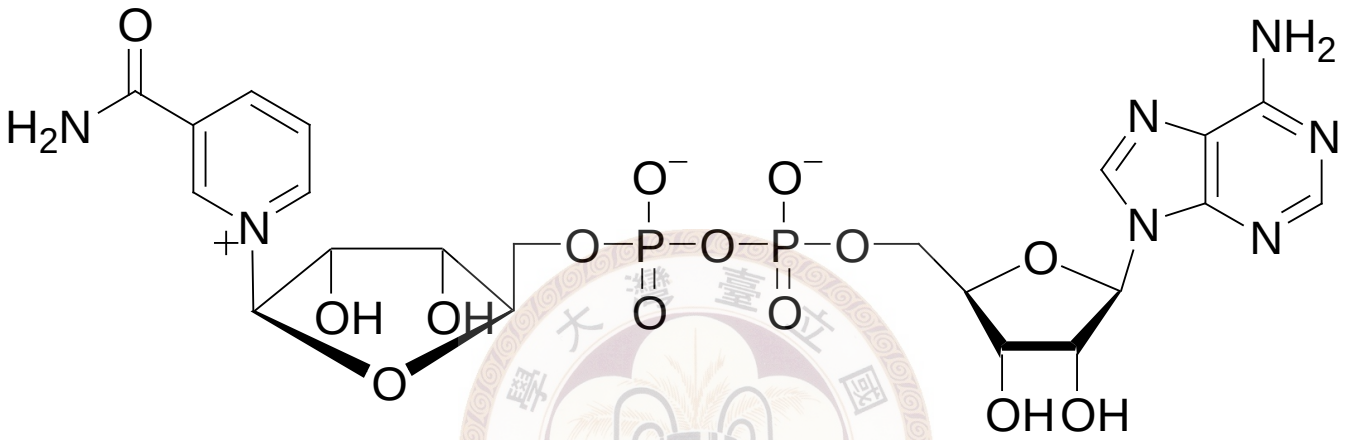
indole



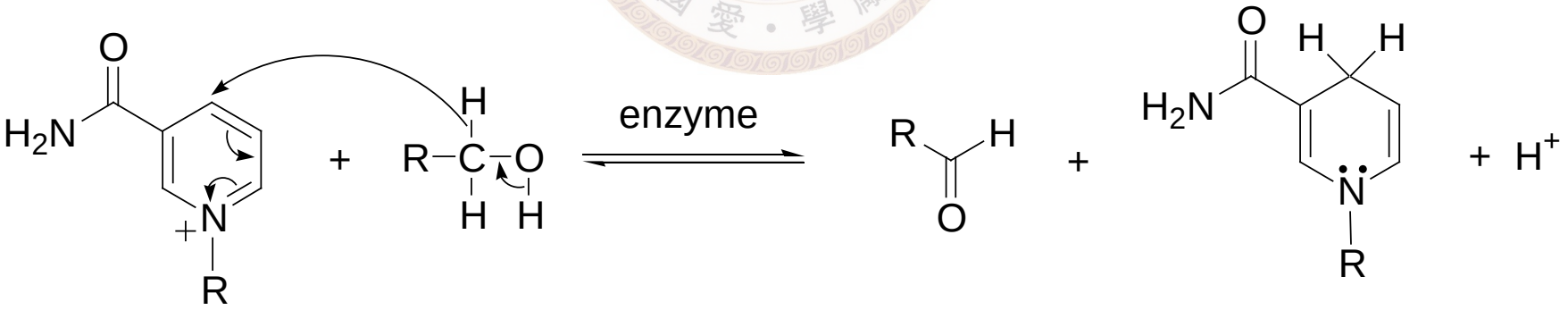
purine

✓ A biological redox system

NAD$^+$ (nicotinamide adenine dinucleotide)

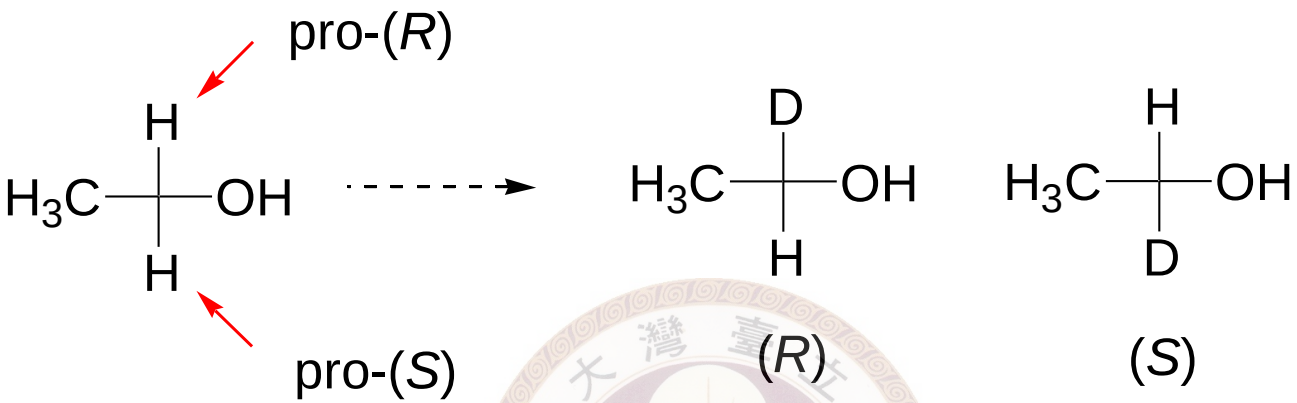


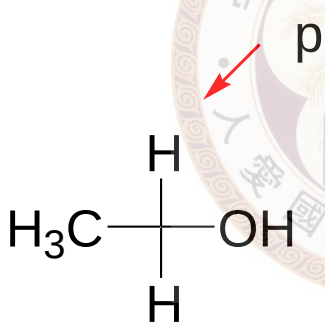
A coenzyme (輔酶)

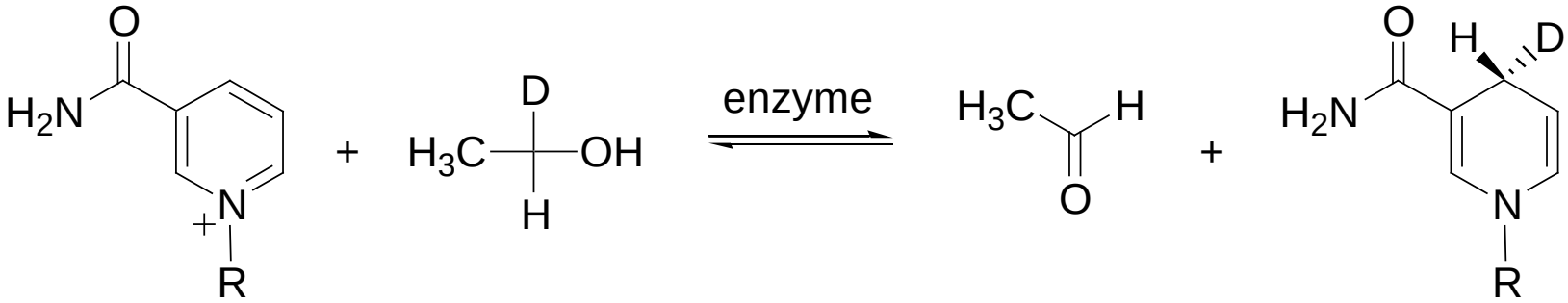


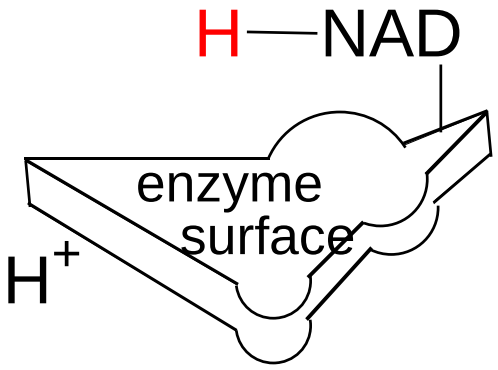
NADH
(reduced form)

✓ The enzyme reaction is stereospecific

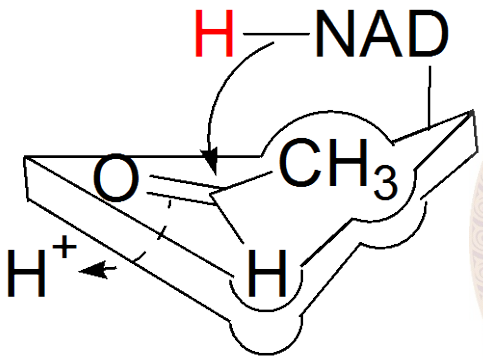


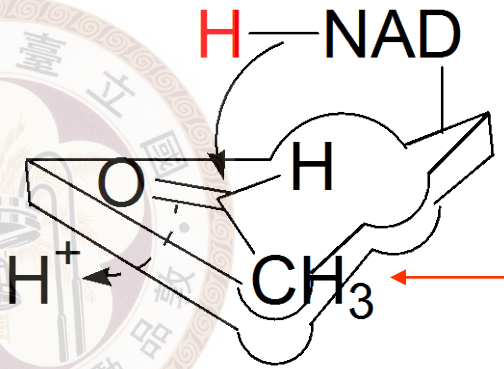






Enzyme NADH complex





Does not fit