第14章 芳香族化合物(Aromatic compounds)

1）芳香族化合物

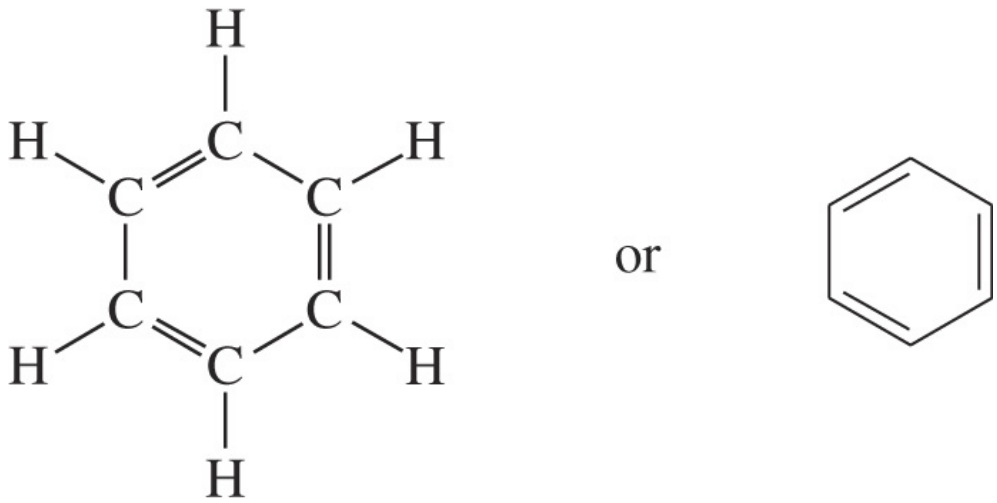
有機化合物被人為地分成兩大類；即:脂肪族 （aliphatic）和芳香族 （aromatic）

最簡單的aromatic 化合物:苯（benzene,C_6H_6）是由Michael Faraday在1825年所合成。

$$C_6H_5CO_2H + CaO \xrightarrow{heat} C_6H_6 + CaCO_3$$

其分子式是由Eilhardt Mitscherlich在1834年所確定.

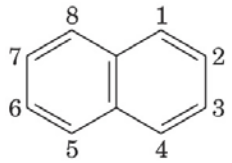
1865年， Kekulé將苯的結構定義為：



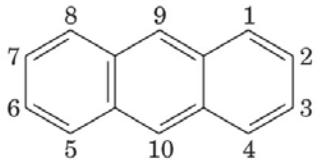
or

The Kekulé formula for benzene

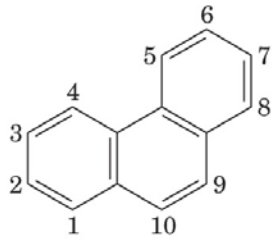
有別於其它有機化合物(aliphatic)，芳香族化合物有其特殊的性質。



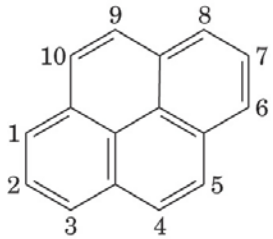
Naphthalene
$C_{10}H_8$



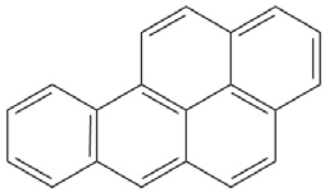
Anthracene
$C_{14}H_{10}$



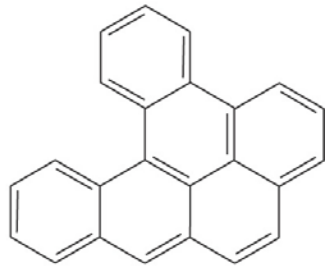
Phenanthrene
$C_{14}H_{10}$



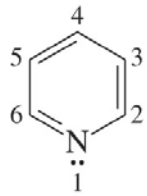
Pyrene
$C_{16}H_{10}$



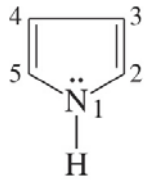
Benzo[*a*]pyrene
$C_{20}H_{12}$



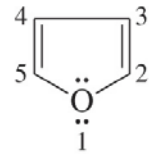
Dibenzo[*a*,*l*]pyrene
$C_{24}H_{14}$



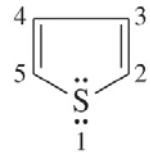
Pyridine



Pyrrole



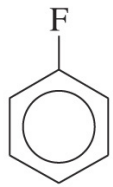
Furan



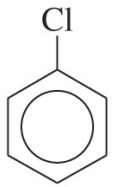
Thiophene

2）苯類衍生物的化學命名

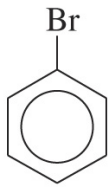
a）以苯環結構為母體



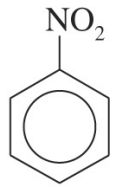
Fluorobenzene



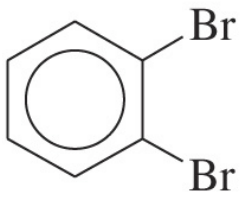
Chlorobenzene



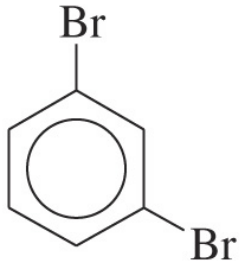
Bromobenzene



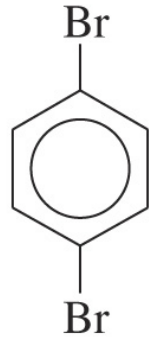
Nitrobenzene



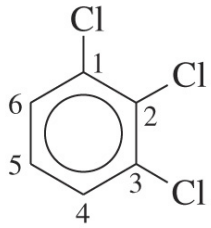
1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho



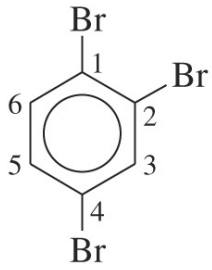
1,3-Dibromobenzene
(*m*-dibromobenzene)
meta



1,4-Dibromobenzene
(*p*-dibromobenzene)
para



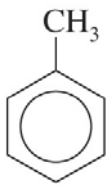
1,2,3-Trichlorobenzene



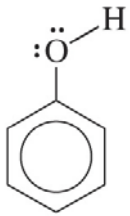
1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

若有三個以上取代基，則使編號總和為最小

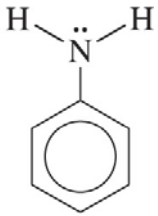
b）以苯環單取代物結構為母體



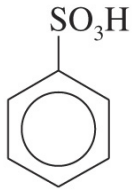
Toluene



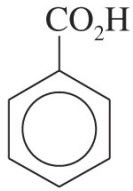
Phenol



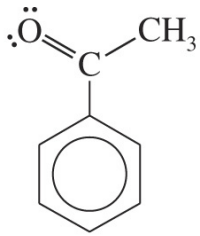
Aniline



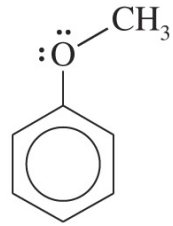
Benzenesulfonic acid



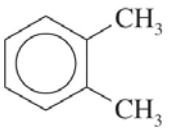
Benzoic acid



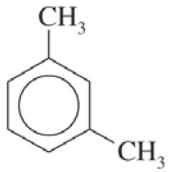
Acetophenone



Anisole

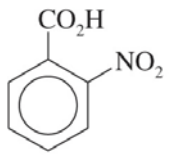


1,2-Dimethylbenzene
(*o*-xylene)

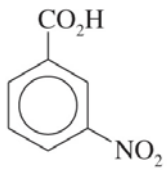


1,3-Dimethylbenzene
(*m*-xylene)

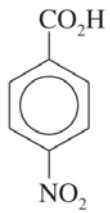
1,4-Dimethylbenzene
(*p*-xylene)



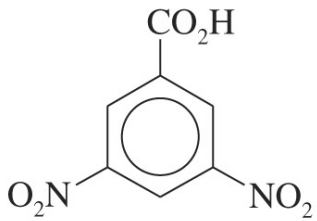
2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)



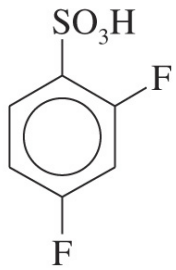
3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)



4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)



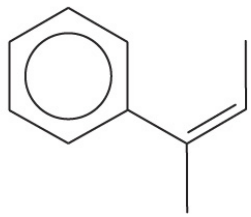
3,5-Dinitrobenzoic acid



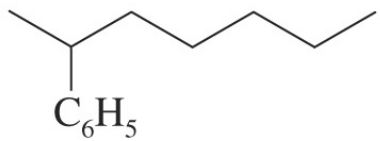
2,4-Difluorobenzenesulfonic acid

母體取代基的編號為1

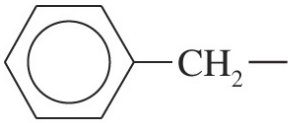
c) 以苯環為取代基



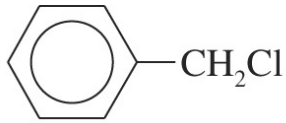
(*Z*)-2-Phenyl-2-butene



2-Phenylheptane

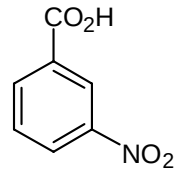


The benzyl group (the phenylmethyl group)

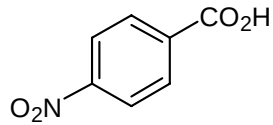


Benzyl chloride (phenylmethyl chloride or BzCl)

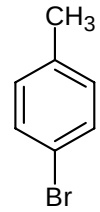
練習(page 655, 14.16)



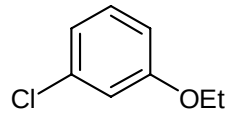
3-Nitrobenzoic acid



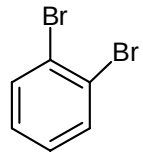
p-Nitrobenzoic acid



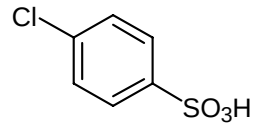
p-Bromotoluene



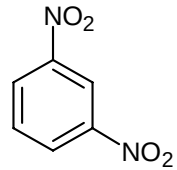
3-Chloro-1-ethoxybenzene



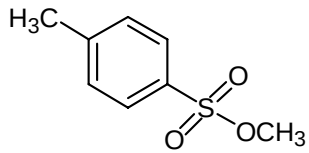
o-Dibromobenzene



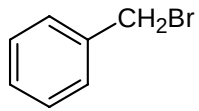
p-Chlorobenzenesulfonic acid



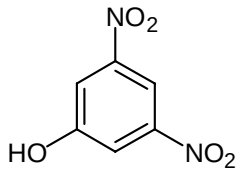
m-Dinitrobenzene



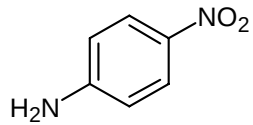
Methyl p-toluenesulfonate



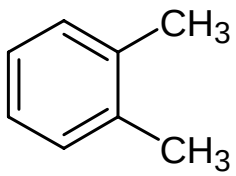
Benzyl bromide



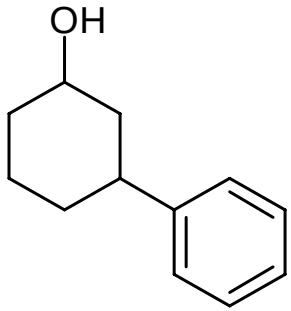
3,5-Dinitrophenol



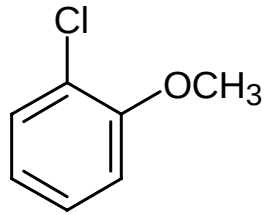
p-Nitroaniline



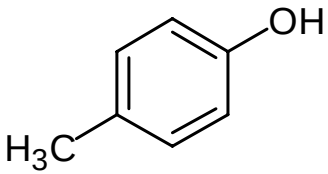
o-Xylene



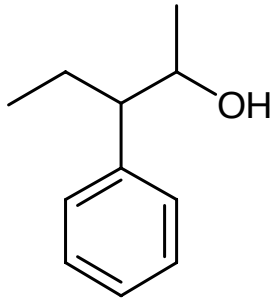
3-Phenylcyclohexanol



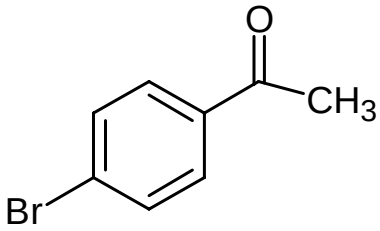
o-Chloroanisole



p-Cresol



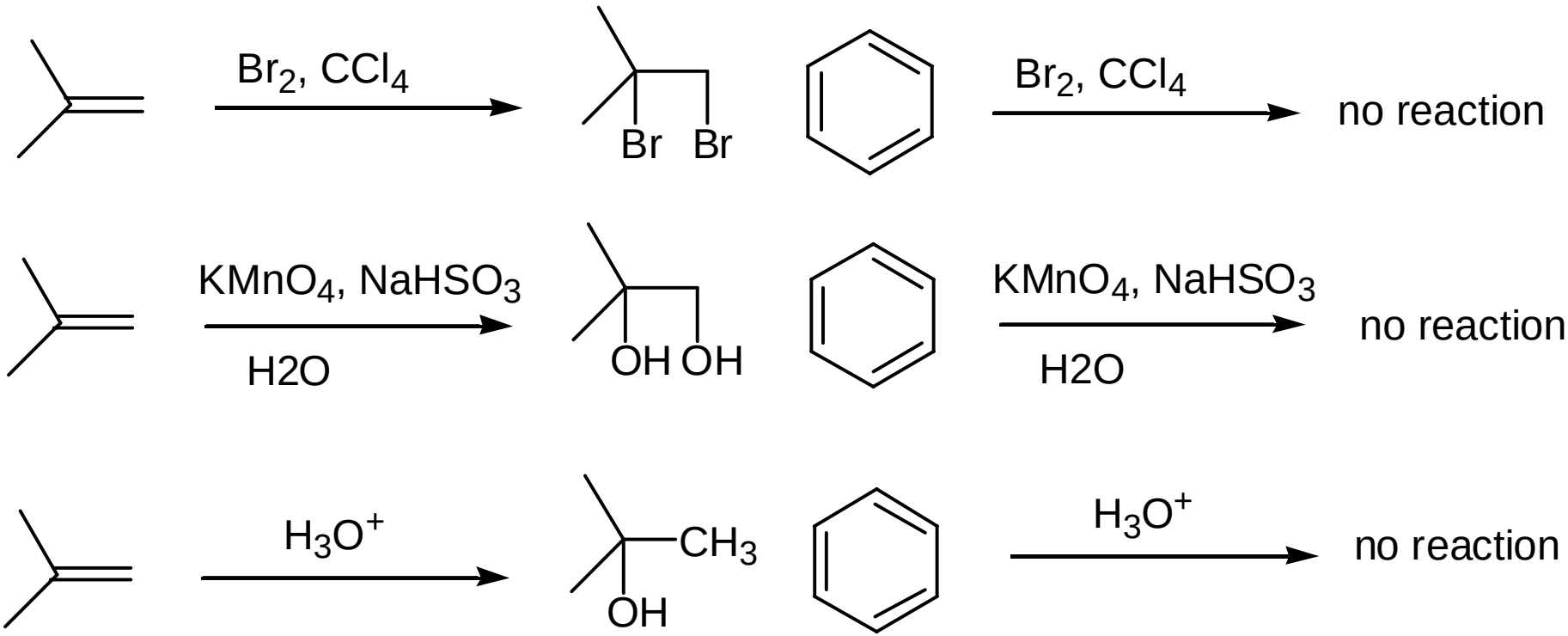
2-Methyl-3-phenyl-1-butanol



p-Bromoacetophenone

3）苯的特殊化學穩定性，及穩定性的解釋

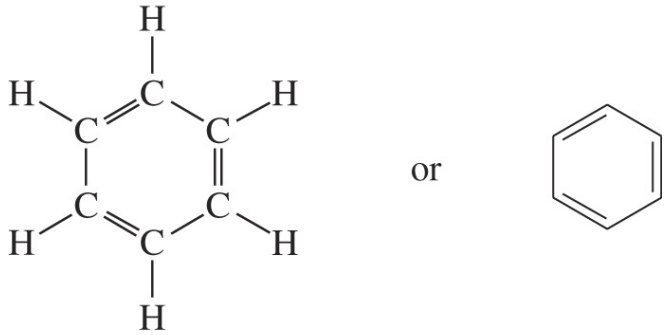
a）苯有別於烯烴的特殊穩定性：



苯在Lewis acid的催化作用下與Br_2發生取代反應而並非加成反應而且僅生成一種取代產物(implying苯環上的氫均為相等)：

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$ **Observed**

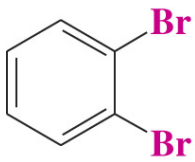
$$C_6H_6 + Br_2 \not\longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6$$ **Not observed**



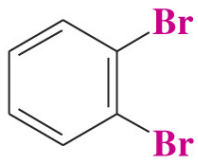
or

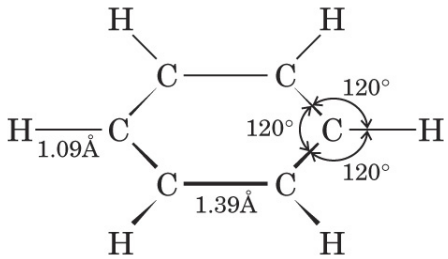
The Kekulé formula for benzene

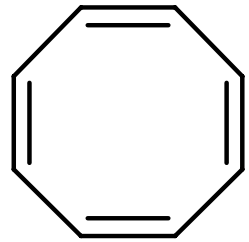
Kekule結構可以解釋在環上的六個氫均為相等的氫；但不能夠合理解釋 1）為什麼只有一種1，2-dibromobenzene存在而不是兩種，2）苯環的六個鍵長(1.39 Å; < 1.47 Å) 及鍵角(120°)都相等 3）為什麼cyclooctatraene則不具有苯的穩定性



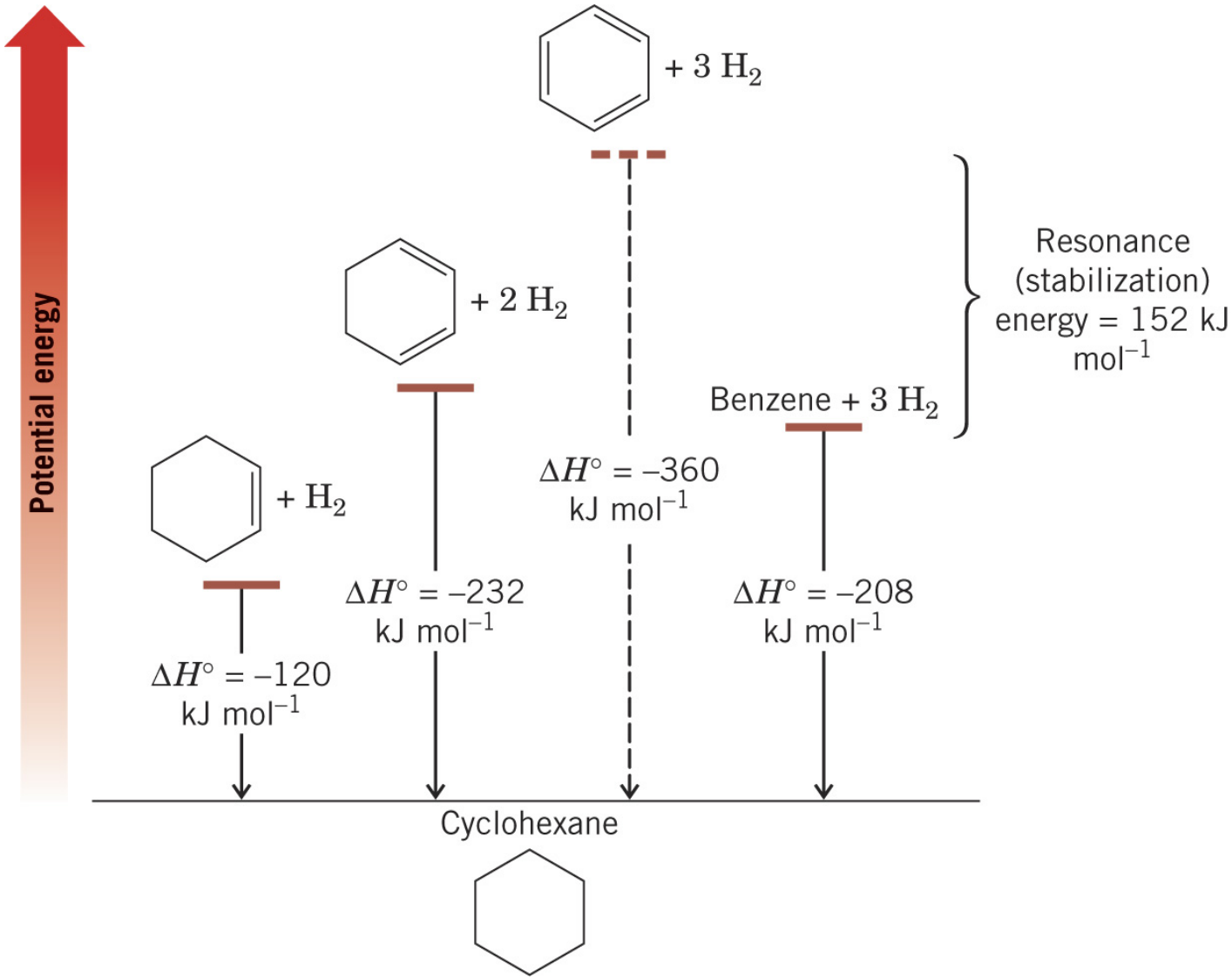
and



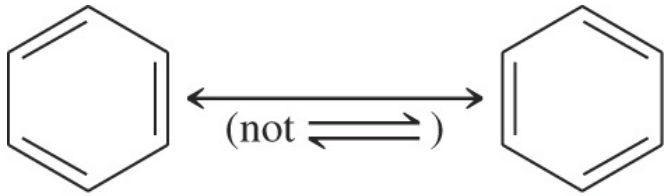




b)從能量的角度來觀察苯的穩定性：resonance energy

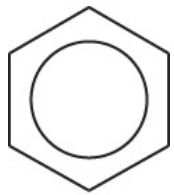


c)用共振(resonance)理論解釋苯的穩定性

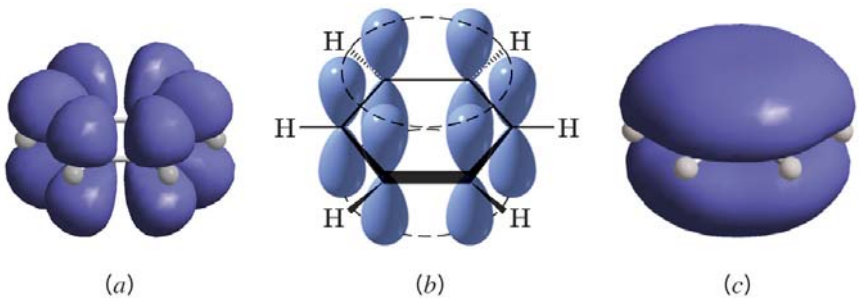


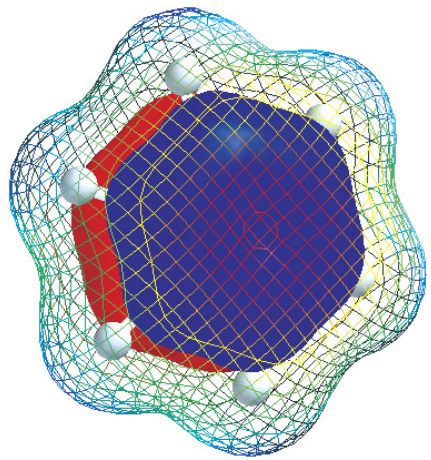
I　　II

I與II單獨均不能反應苯的真實結構。其真正的結構應為I和II的共振混合體(III):



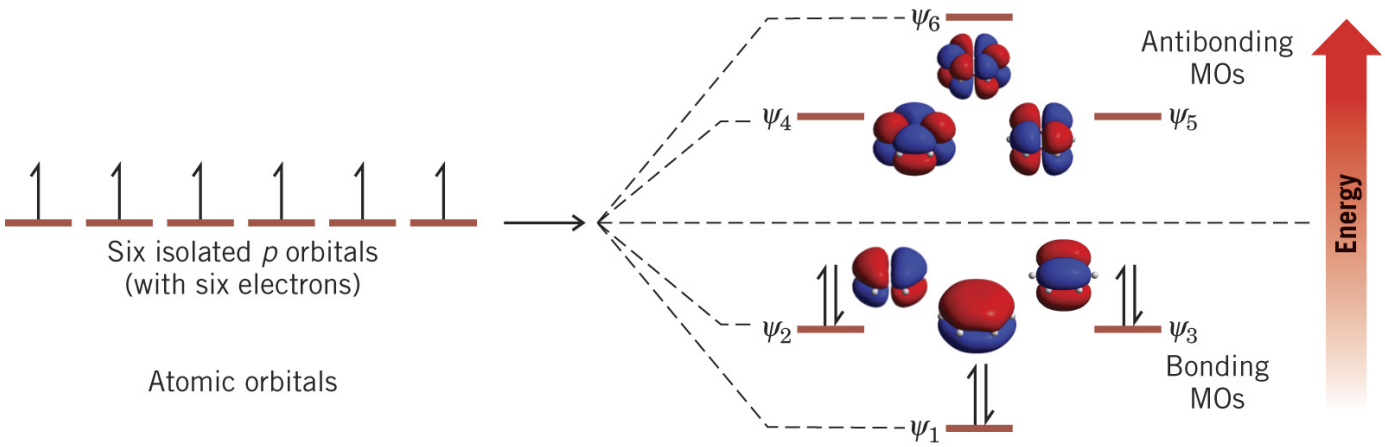
III





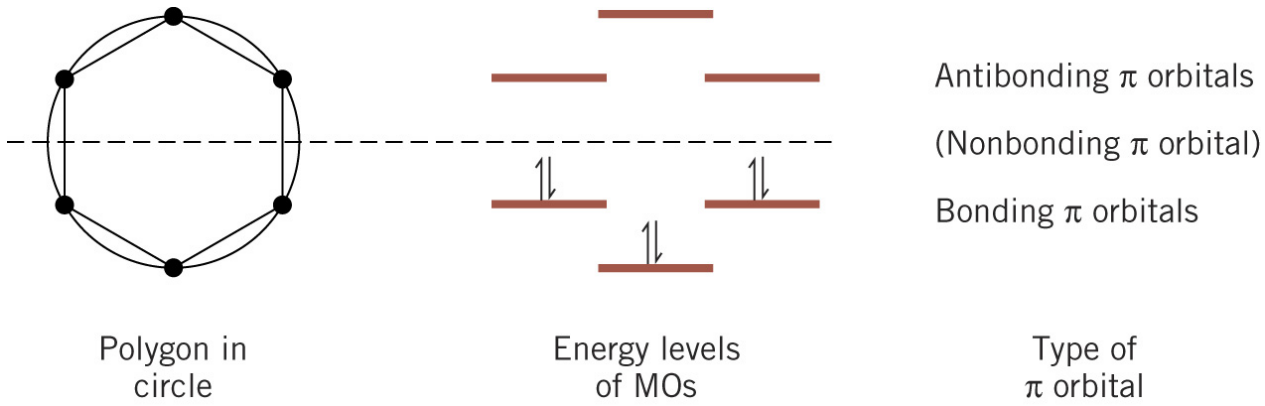
Delocalized

d)用近代分子軌道理論解釋苯的穩定性

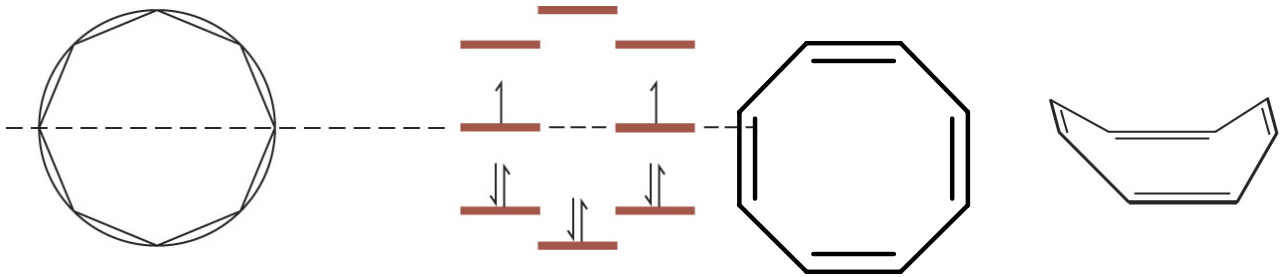


There are six π molecular orbitals for benzene

Huckel's rule:

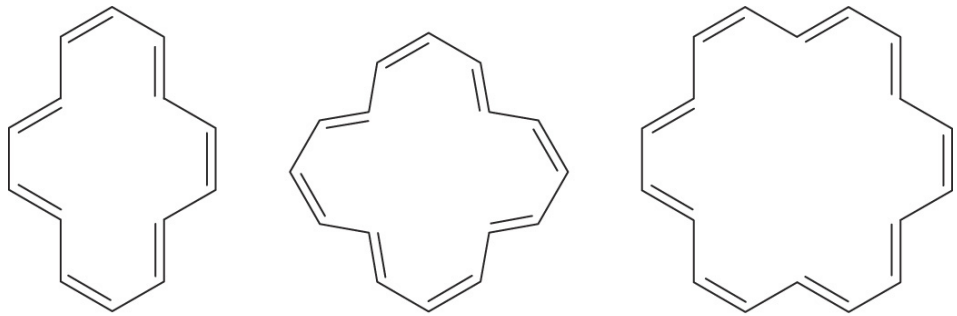


Polygon-and-circle method: 將polygon的一角置於圓圈的底部



Cyclooctatetraene has two nonbonding orbitals each with one electron

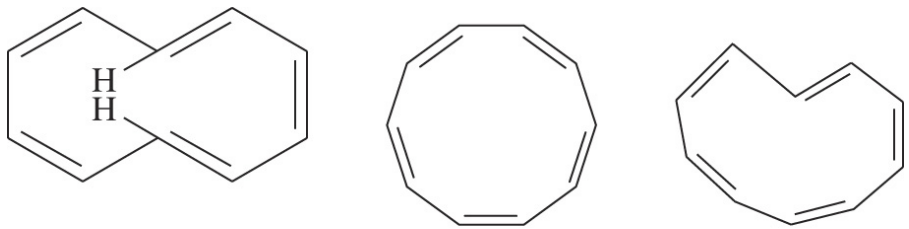
Huckel’s rule:若有一個成平面結構的環狀化合物，其delocalized的π電子數為4n + 2 (n = 0，1, 2, 3…),這一化合物則具有aromatic的性質



[14]Annulene (aromatic)　[16]Annulene (*not* aromatic)　[18]Annulene (aromatic)

The [14]and [18]annulenes are aromatic (4n+2, where n= 3,4)
The [16] annulene is not aromatic

The [10]annulenes below should be aromatic <u>but</u> none of them can be planar

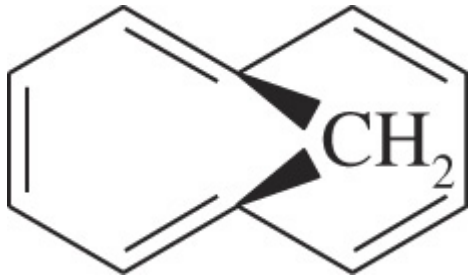


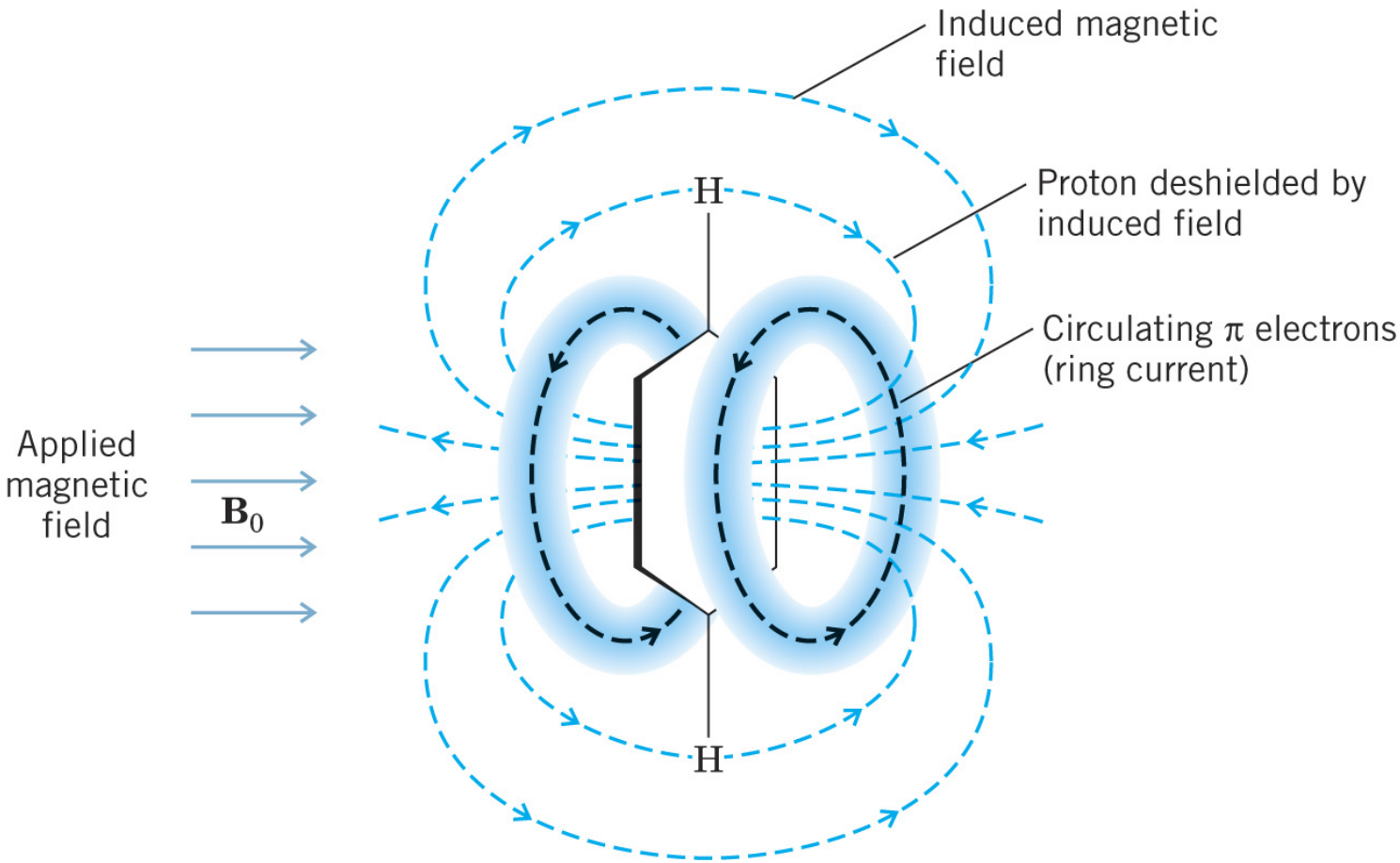
4　5　6

[10]Annulenes
None is aromatic because none is planar.

分別解釋

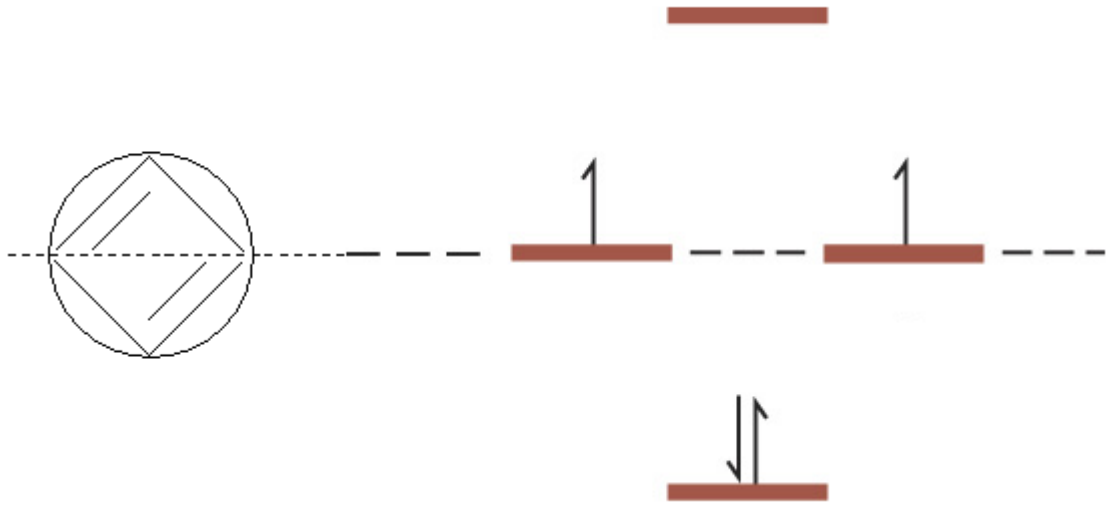
解釋為什麼此化合物屬於aromatic類




Induced magnetic field
Proton deshielded by induced field
Circulating π electrons (ring current)
Applied magnetic field
$\mathbf{B}_0$
H
H

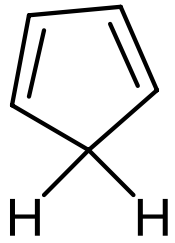
Exercise in page 635

Cyclobutadiene
or [4]annulene
(*not* aromatic)

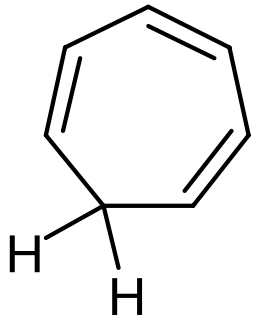


4）具有芳香性的離子(Aromatic ions)

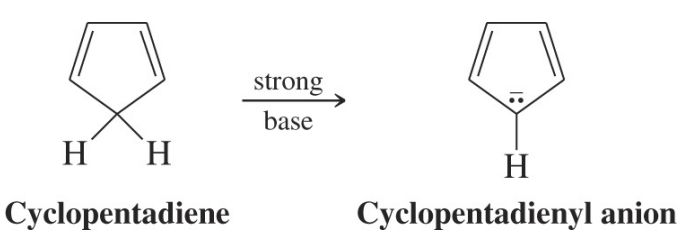
解釋：

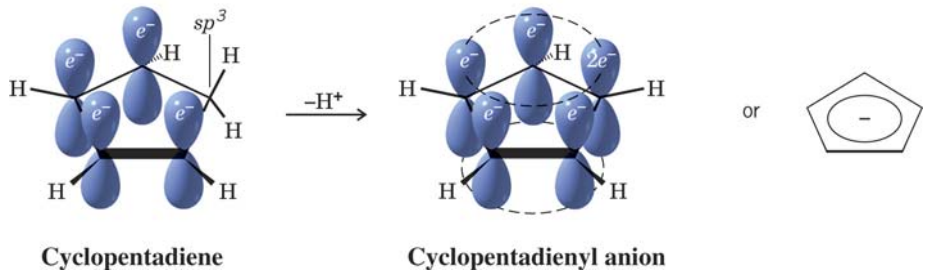


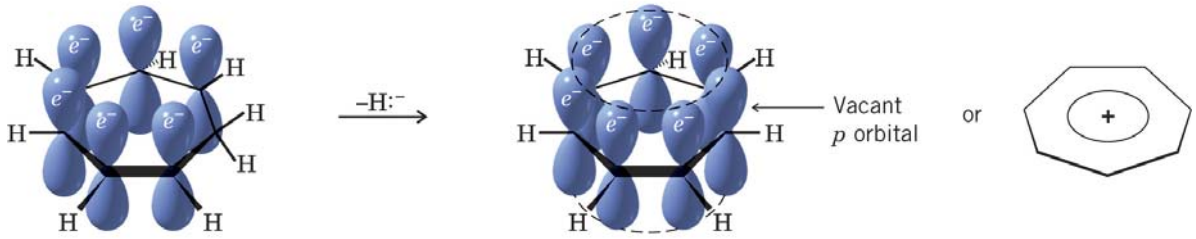
PKa = 16



PKa = 36



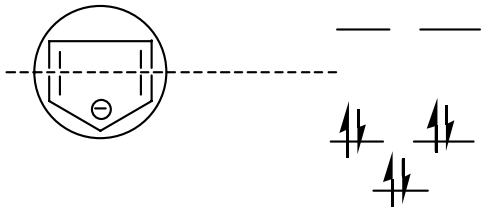


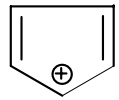


Cycloheptatriene　　Cycloheptatrienyl cation

課堂練習(page 638)

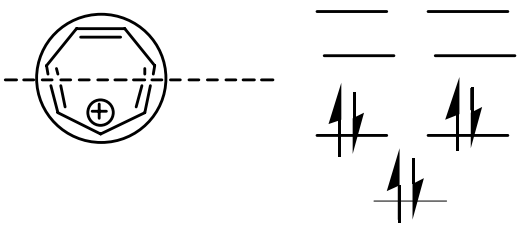
14.4





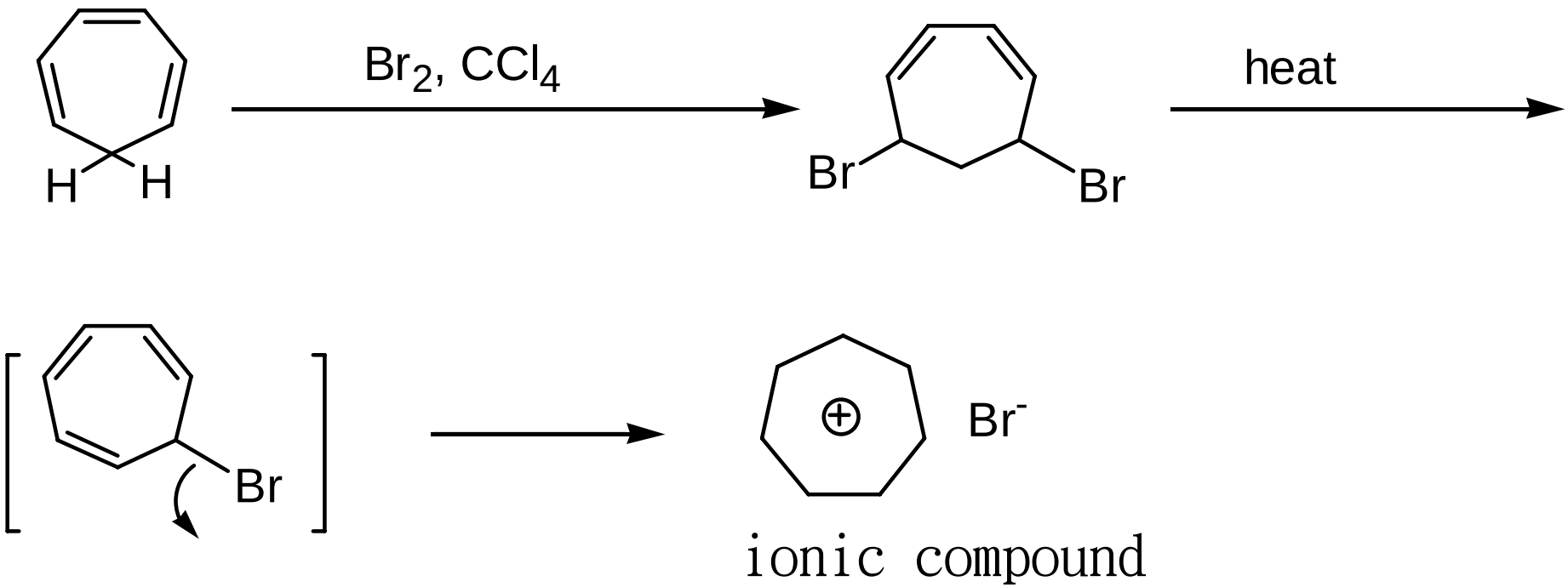
不是aromatic,　不符合4n + 2 rule.

14.5



不是aromatic,　不符合4n + 2 rule.

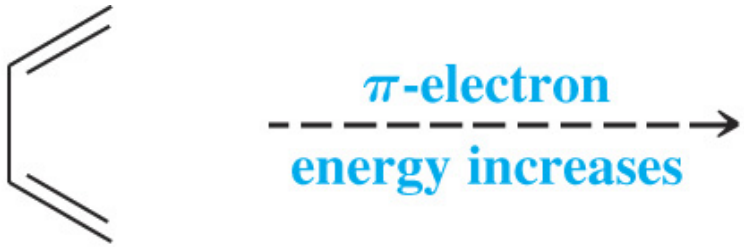
14.7



ionic compound

5）Aromatic, Antiaromatic, and nonaromatic之定義

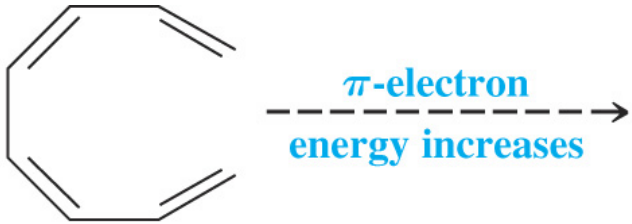
當我們說一個化合物為aromatic,即代表此化合物的π電子為delocalized.



+ H_2

1,3-Butadiene
4 π electrons

Cyclobutadiene
4 π electrons (antiaromatic)



+ H_2

8 π electrons

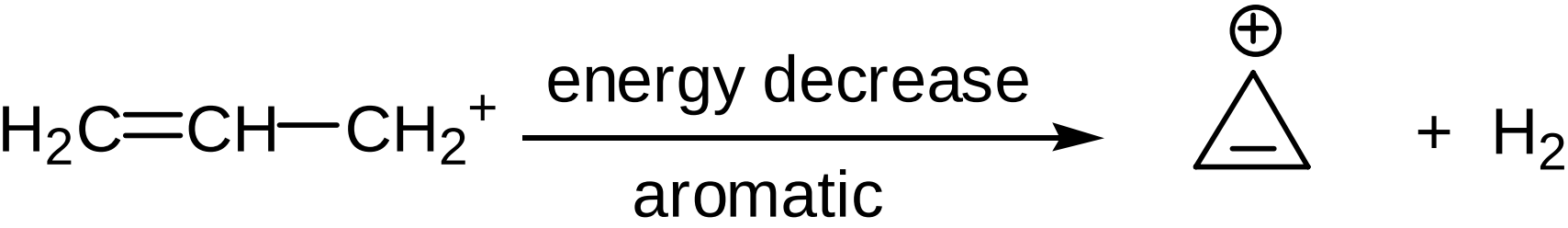
Hypothetical planar
cyclooctatetraene
8 π electrons (antiaromatic)

1,3,5-Hexatriene
6 π electrons

Benzene
6 π electrons (aromatic)

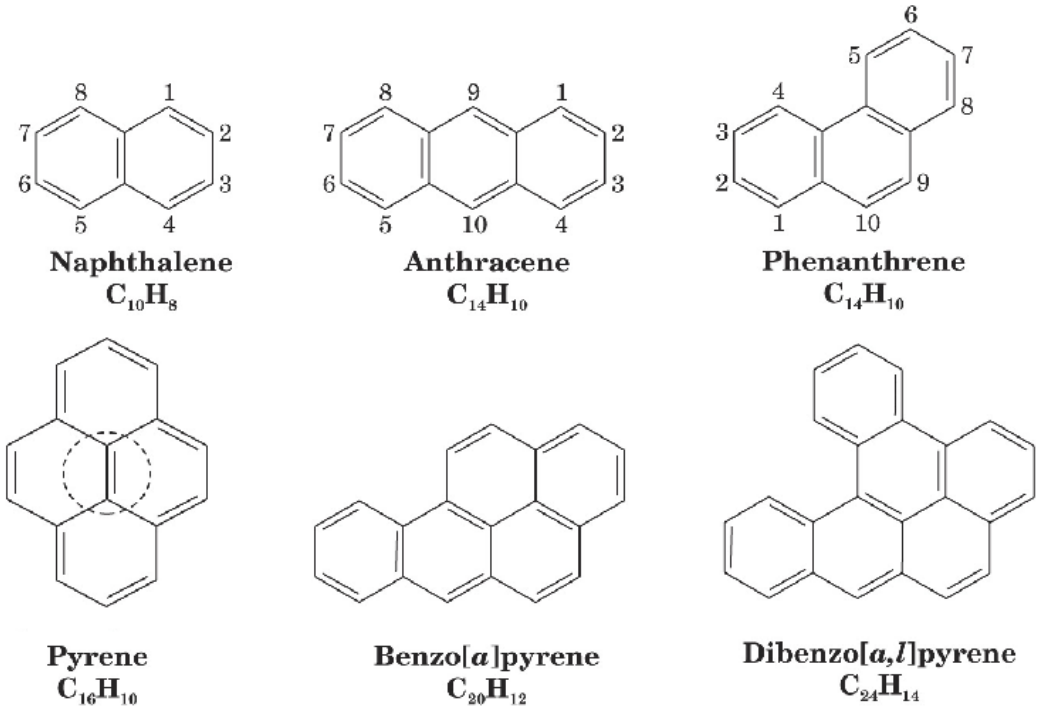
6 π electrons

Cyclopentadienyl anion
6 π electrons (aromatic)

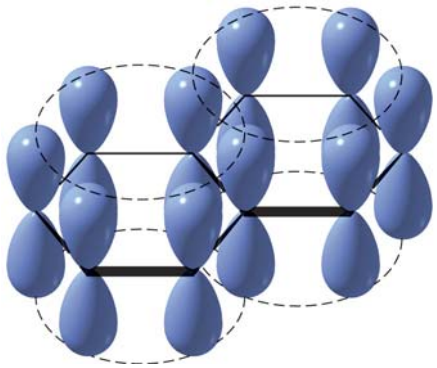


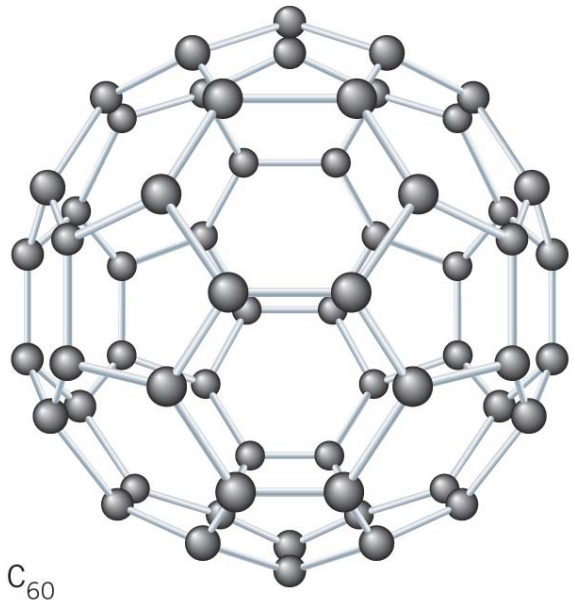
比較成環前後能量的大小

6）其它類型的aromatic化合物

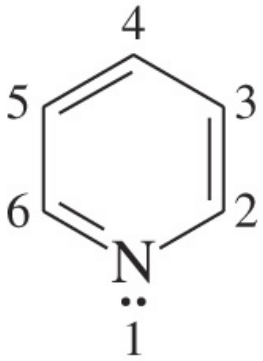


Polycyclic benzenoid aromatic compounds

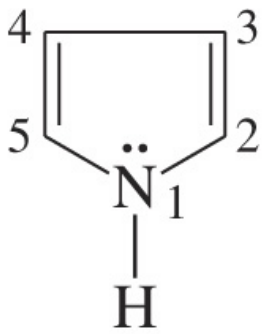




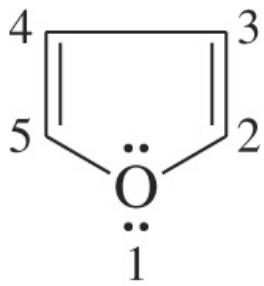
fullerene



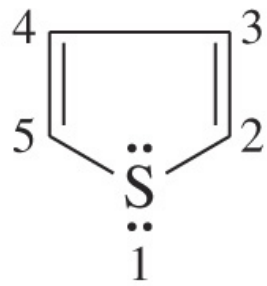
Pyridine



Pyrrole

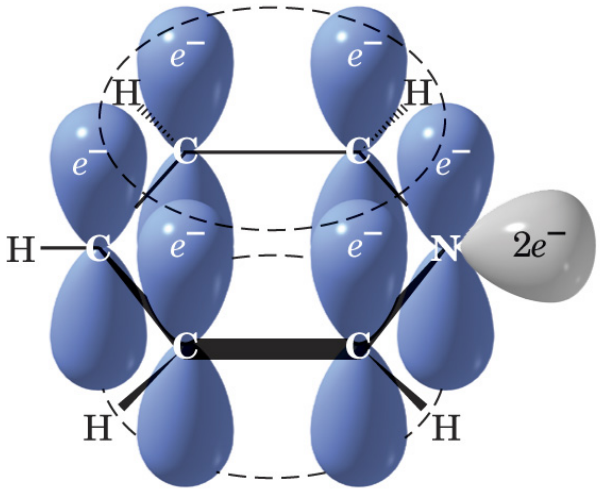


Furan



Thiophene

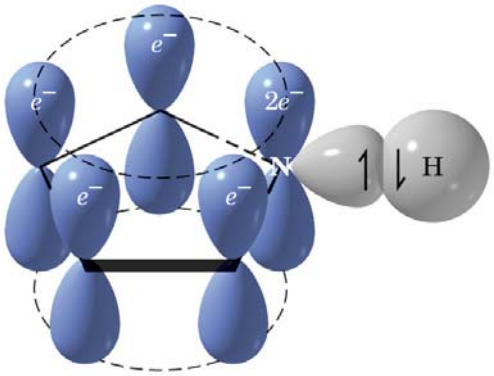
heteroaromatic compounds



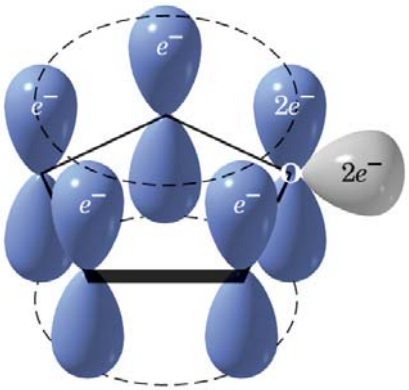
Pyridine has an *sp*2 hybridized nitrogen

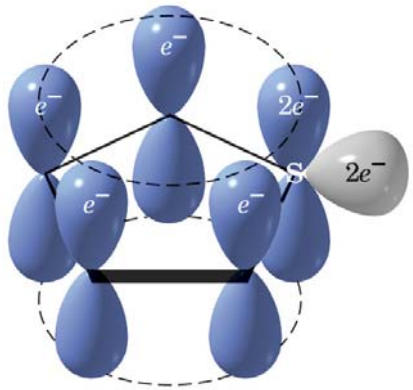
The *p* orbital on nitrogen is part of the aromatic π system of the ring

The nitrogen lone pair is in an *sp*2 orbital orthogonal to the *p* orbitals of the ring;

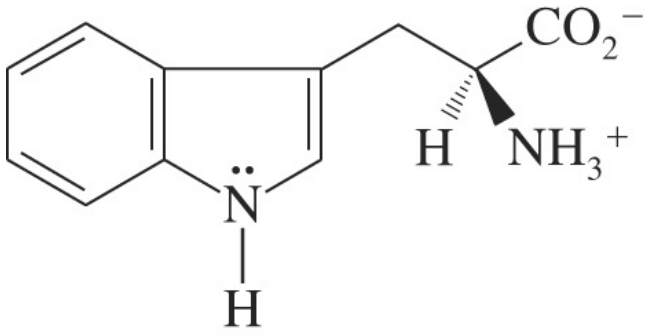


The nitrogen in pyrrole is *sp*2 hybridized and the lone pair resides in the p orbital

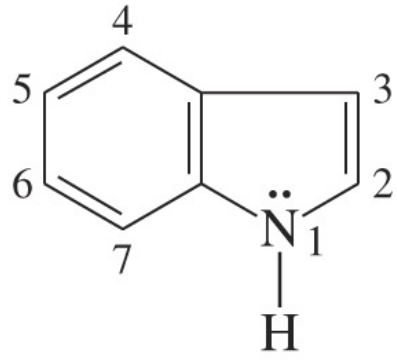




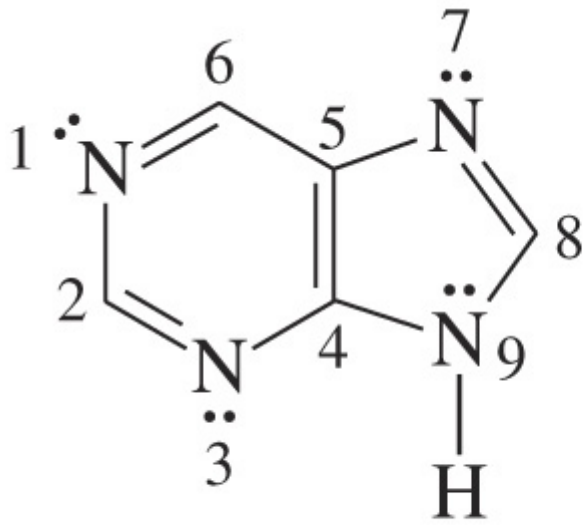
In furan and thiophene an electron pair on the heteroatom is also in a *p* orbital which is part of the aromatic system



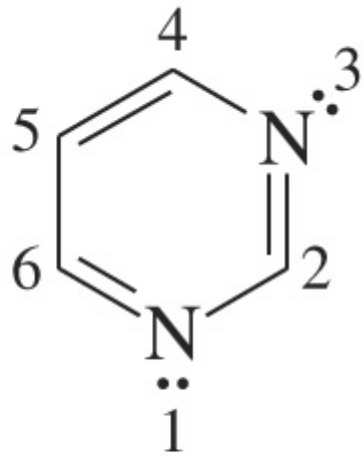
Tryptophan



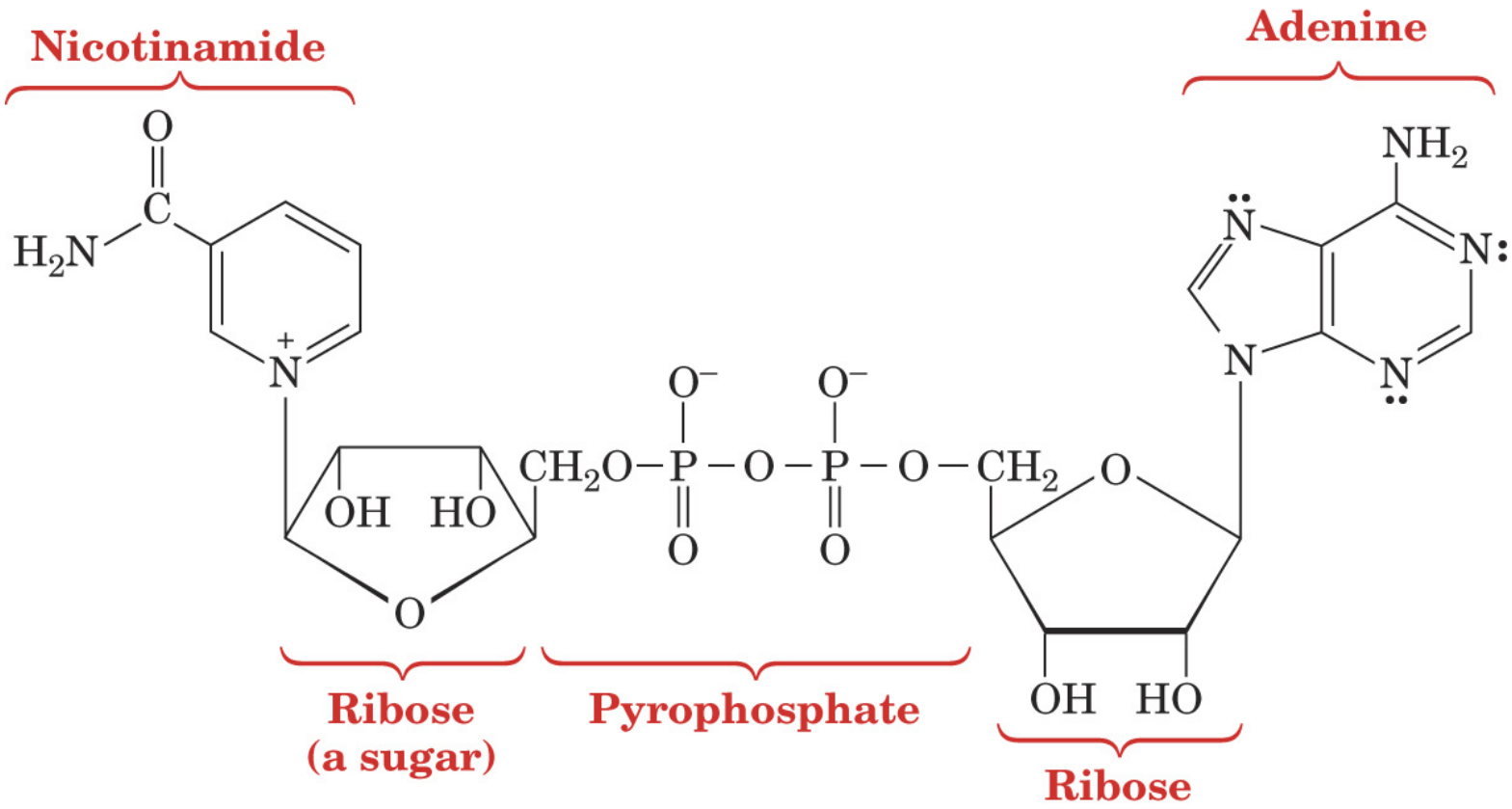
Indole

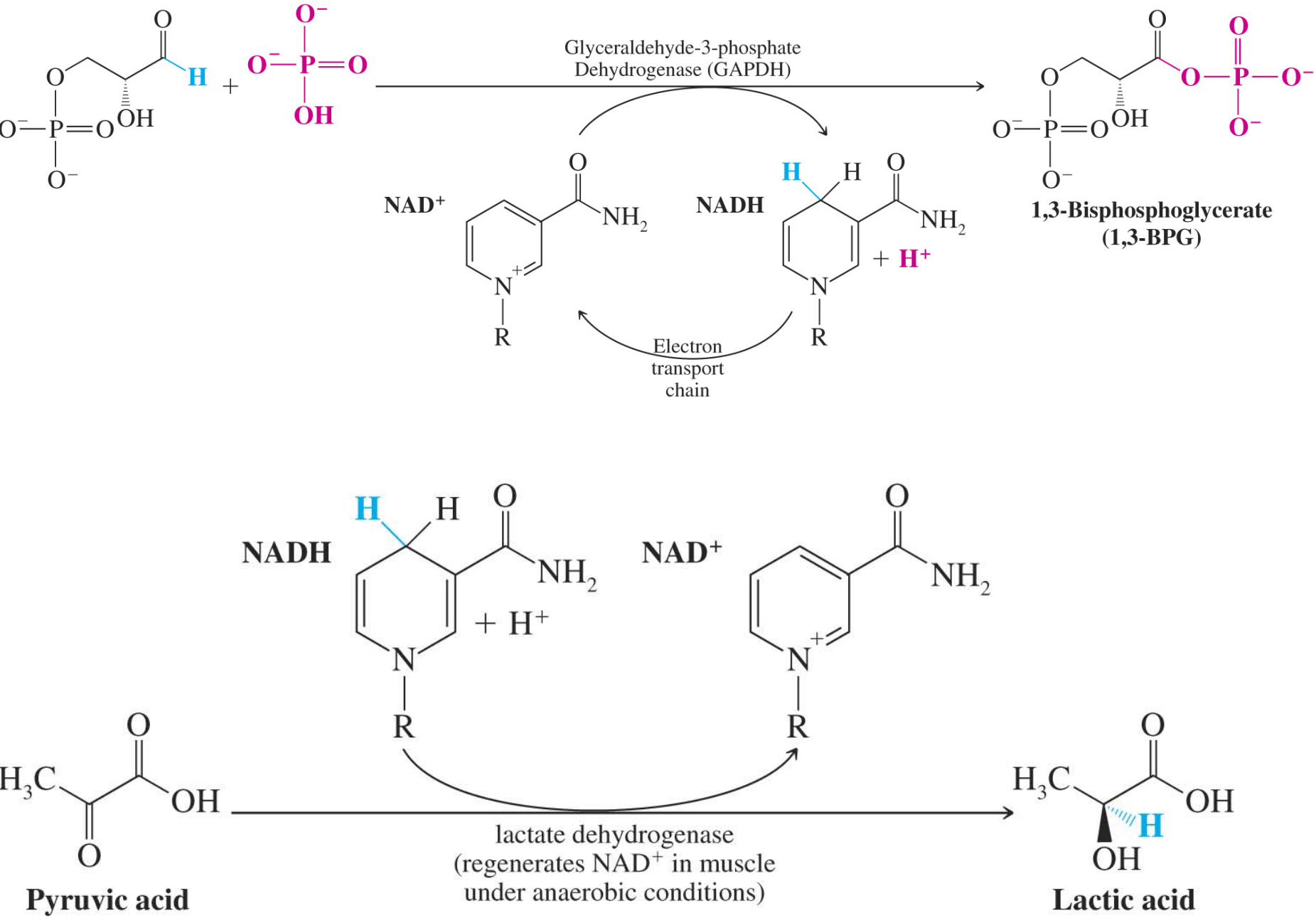


Purine

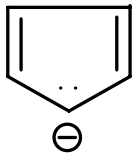


Pyrimidine

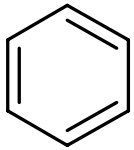

Nicotinamide
Adenine
Ribose
(a sugar)
Pyrophosphate
Ribose


Glyceraldehyde-3-phosphate
Dehydrogenase (GAPDH)
NAD+
NADH
+ H+
Electron
transport
chain
1,3-Bisphosphoglycerate
(1,3-BPG)
NADH
NAD+
+ H+
Pyruvic acid
lactate dehydrogenase
(regenerates NAD+ in muscle
under anaerobic conditions)
Lactic acid

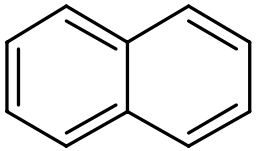
根據4n + 2 規則， 判斷下列化合物是否具有芳香性 (aromatic)



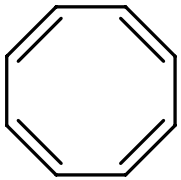
I



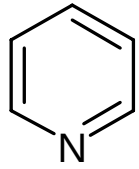
II



III



IV



V

VI