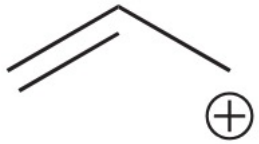
Tutorial 2

Introduction to Resonance

А.И.Соч

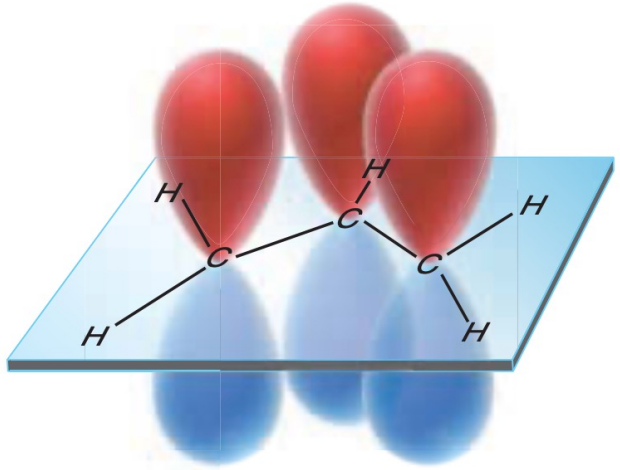
2021/12/2

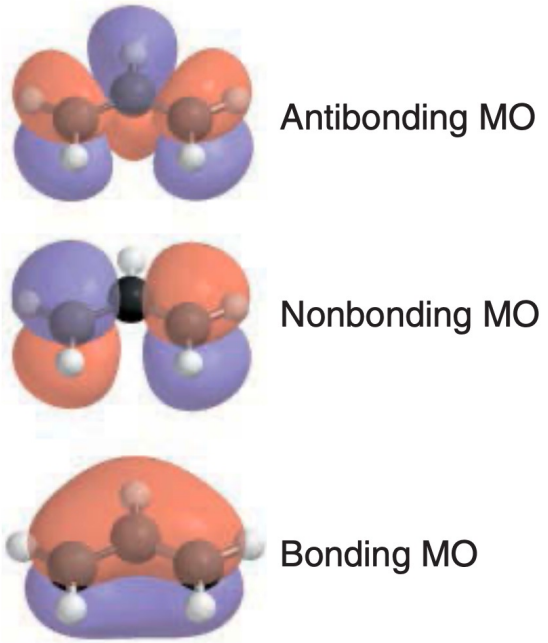
- 共振理论的提出



烯丙基碳正离子

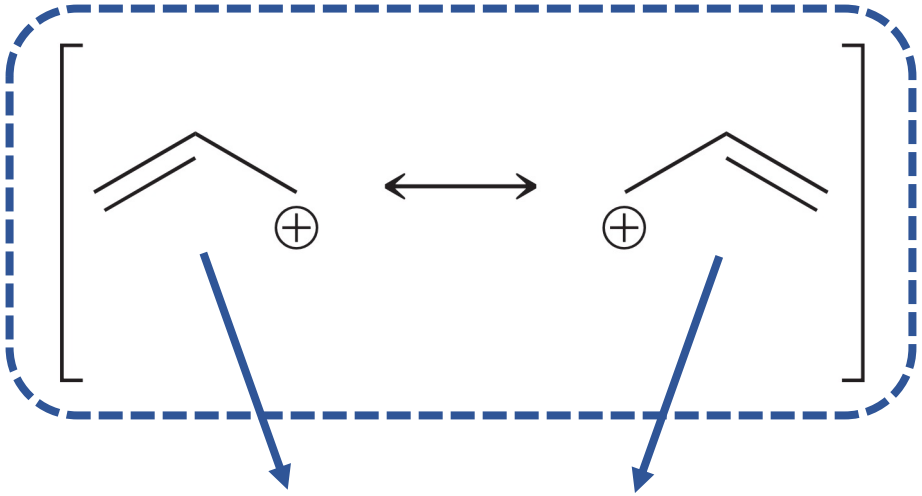
allyl carbocation





普通的结构式不能反映出该分子真实的结构

- Resonance



resonance hybrid

"one entity"

A resonance hybrid is not flipping back

and forth between the different resonance structures!

- Imagine a nectarine if you have never seen it…

Picture a *peach* in your mind, and now picture a *plum* in your mind. Well, a *nectarine* has features of both fruits: the inside tastes like a peach, the outside is smooth like a plum, and the color is somewhere in between the color of a peach and the color of a plum. So take your image of a peach together with your image of a plum and *meld them together* in your mind into one image. That's a nectarine.

The nectarine does not vibrate back and forth
every second between being a peach and being a plum!

…similarly, with resonance structures, no single drawing adequately
describes the nature of the electron density spread out over the molecule!

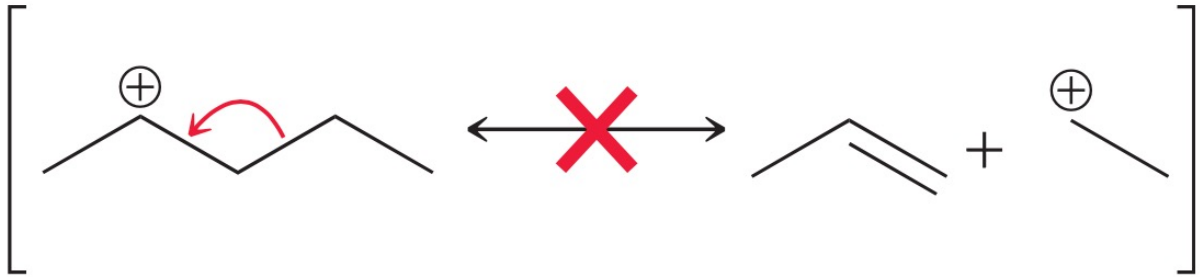
- Use curved arrows to represent resonance structures

a single arrow indicates the transfer of **a pair** of electrons

Rules

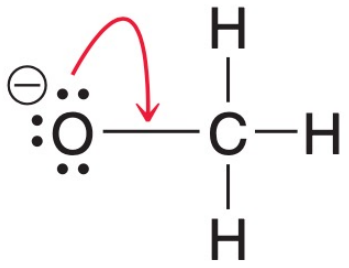
1. *Avoid breaking a single bond.*
2. *Never exceed an octet for second-row elements.*

- Avoid breaking a single bond when drawing resonance structures

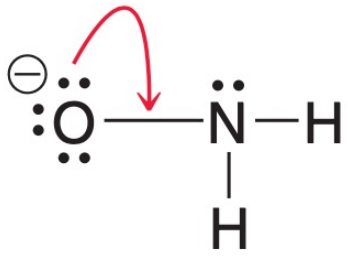


Don’t break a single bond

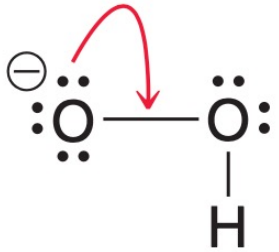
- Never exceed an octet for second-row elements



Bad arrow



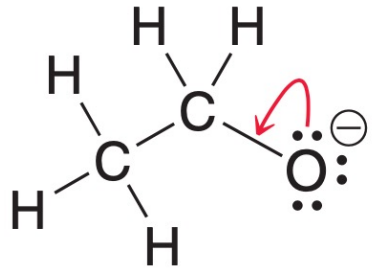
Bad arrow



Bad arrow

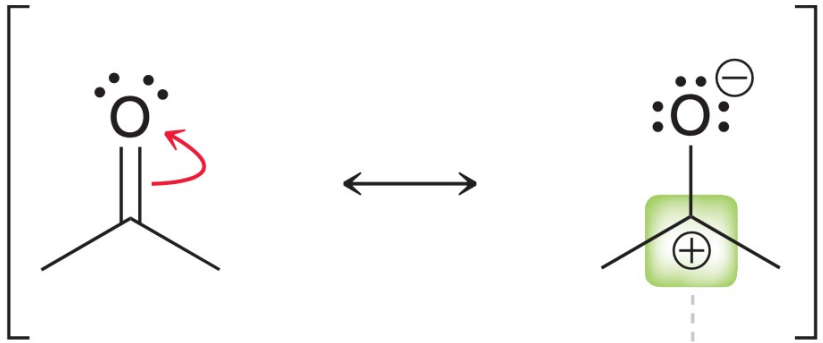
Bad arrow

is the same as



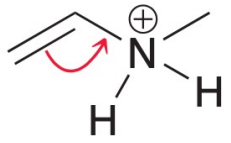
Bad arrow

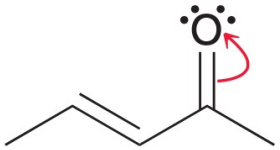
- Never exceed an octet for second-row elements

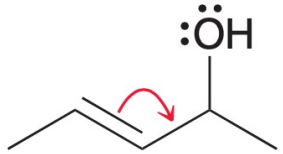


This carbon atom
does not have an octet

- Practice: in each of the following cases, determine whether the curved arrow violates either of the two rules and describe the violation, if any. (Don't forget to count all hydrogen atoms and all lone pairs.)

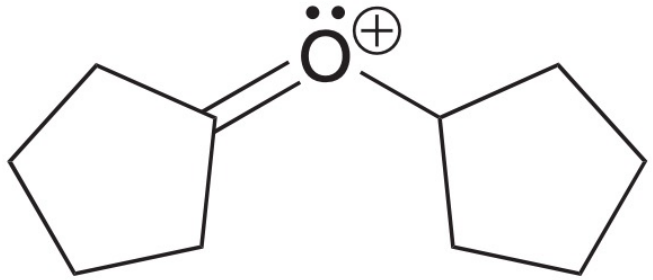
(a) 

(b) 

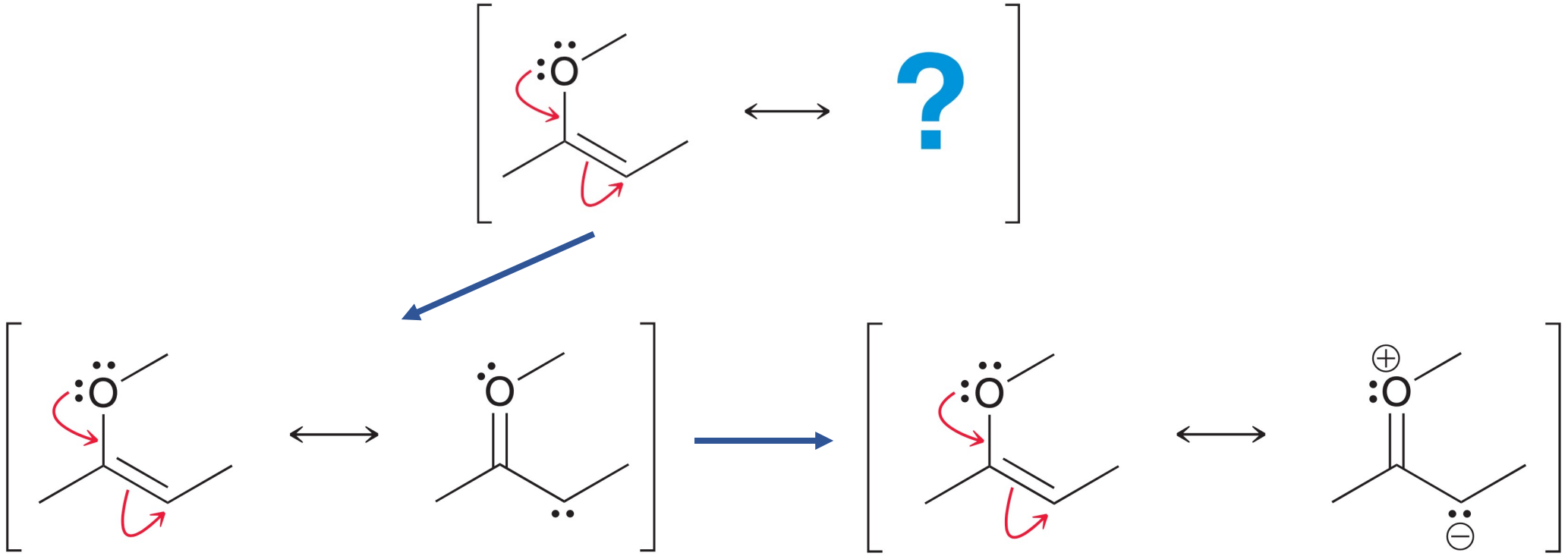
(c) 

(d) 

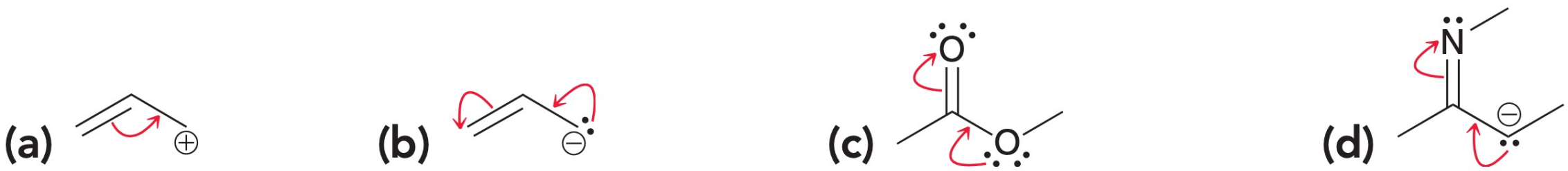
- Practice: drawing the resonance structure of the following compound requires one curved arrow.



- Formal Charges in Resonance Structures

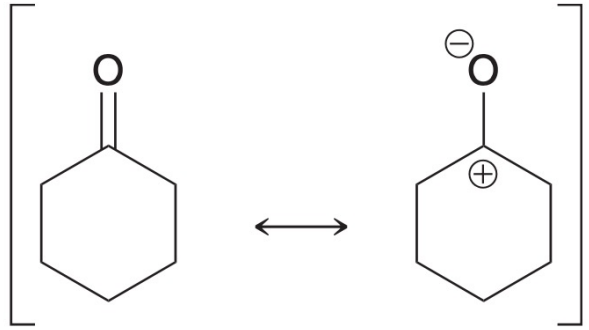


- Practice: for each of the structures below, draw the resonance structure that is indicated by the curved arrows. Be sure to include formal charges.

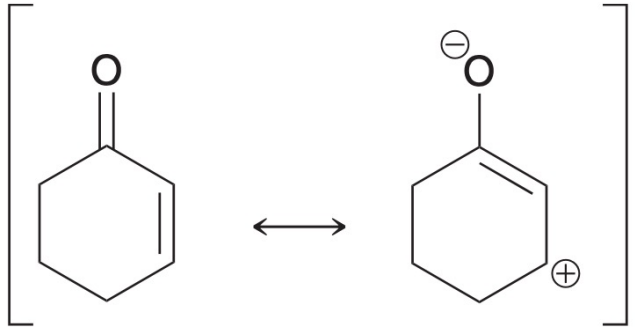


- Practice: in each case below, draw the curved arrow(s) required in order to convert the first resonance structure into the second resonance structure. In each case, begin by drawing all lone pairs and then use the formal charges to guide you.

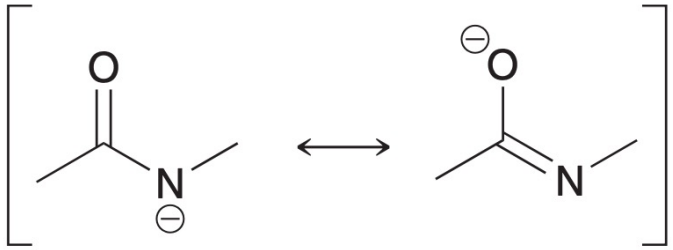
(a)



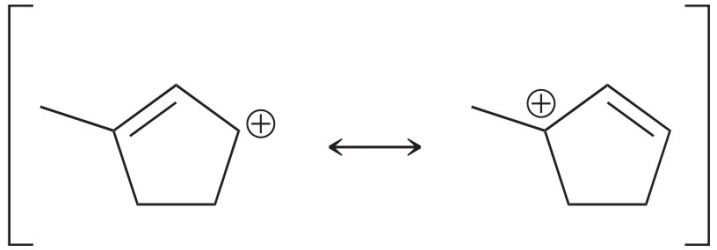
(b)



(c)

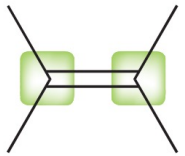


(d)



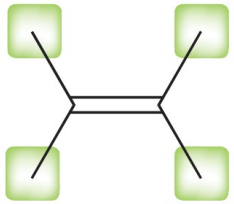
- 识别特定结构[pattern recognition]
  - 烯丙位的孤对
  - 烯丙位的C+
  - C+毗邻原子上的孤对
  - 不同电负性原子间的π键
  - 环内的共轭π键

- 烯丙位的孤对



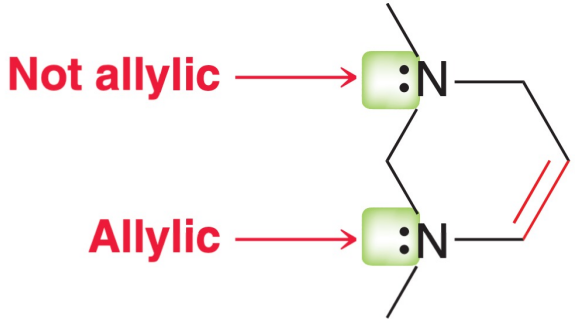
Vinylic positions

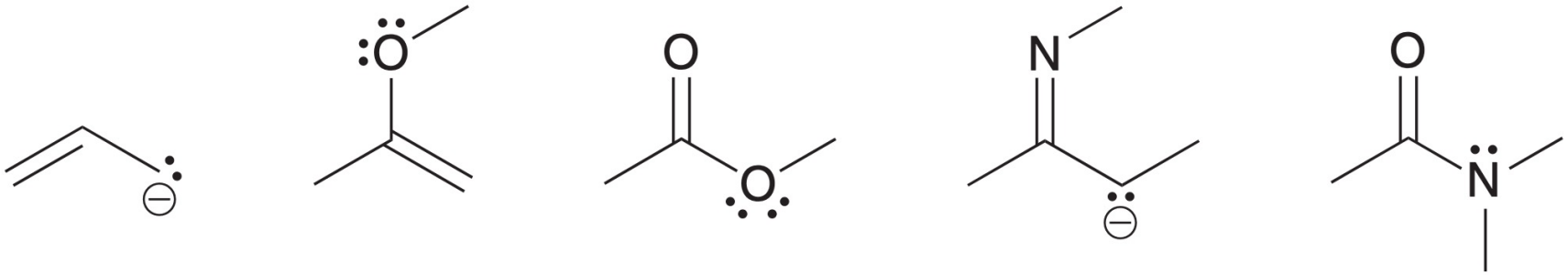
丙烯位



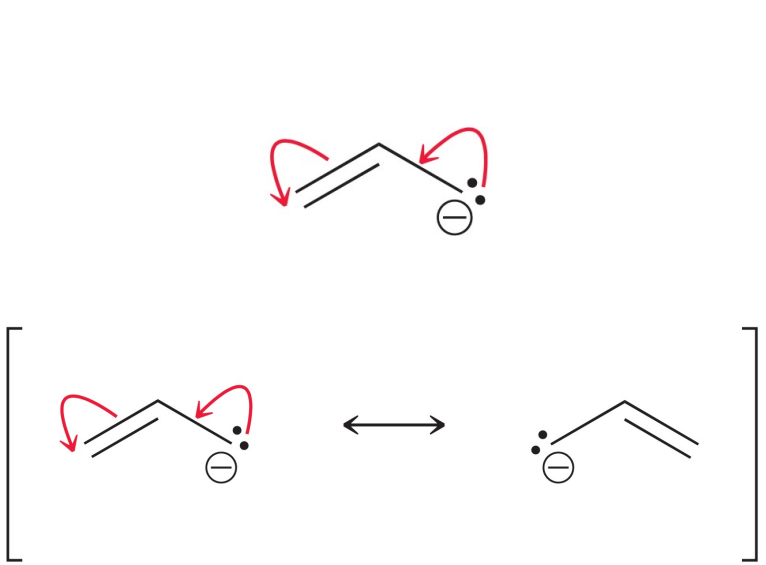
Allylic positions

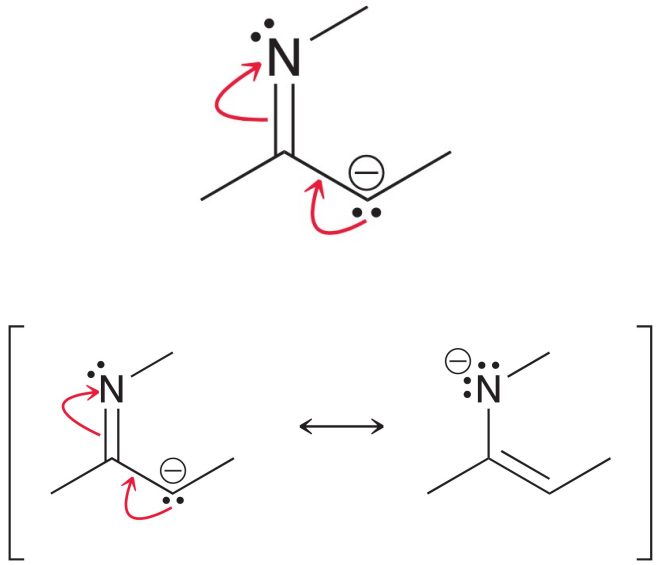
烯丙位





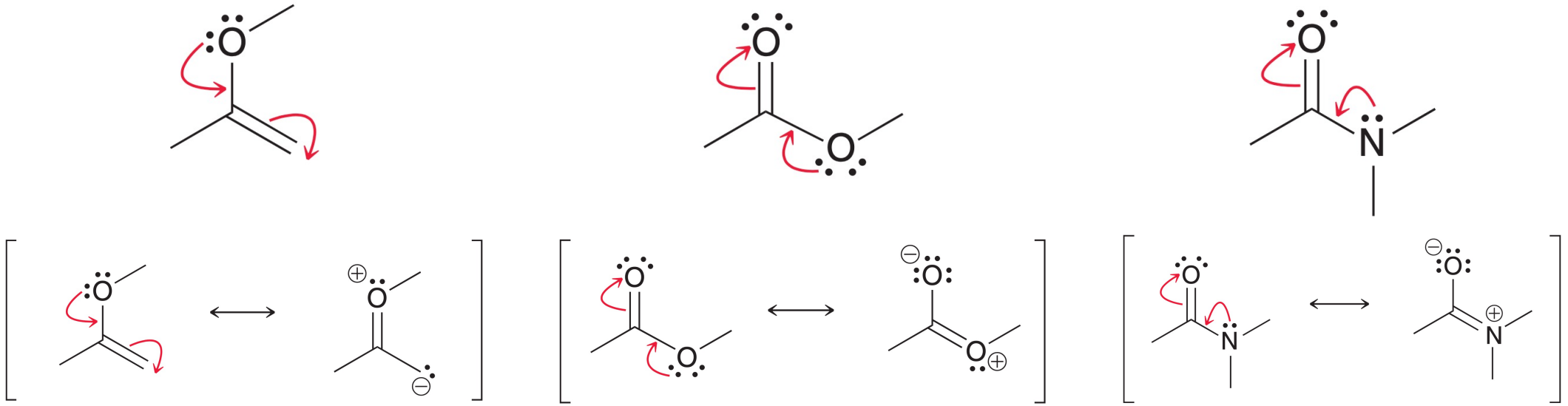
- 烯丙位的孤对





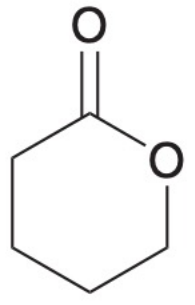
如带孤对的原子上有负电荷，负电荷最终转移至接受孤对的原子上

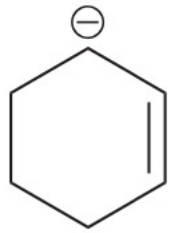
- 烯丙位的孤对

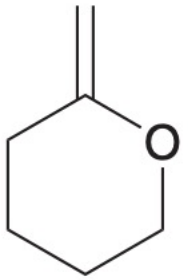


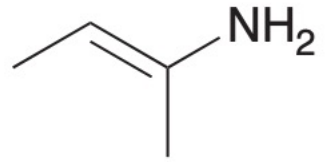
如带孤对的原子没有负电荷，该原子上会产生一个正电荷，接受孤对的原子上会产生一个负电荷

- Practice: for each of the compounds below, locate the pattern we just learned (lone pair next to a π bond) and draw the appropriate resonance structure:

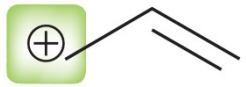
(a) 

(b) 

(c) 

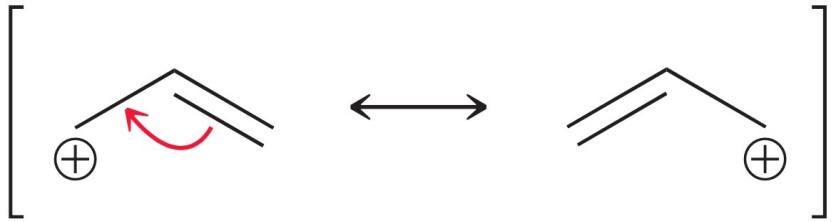
(d) 

- 烯丙位的C^+



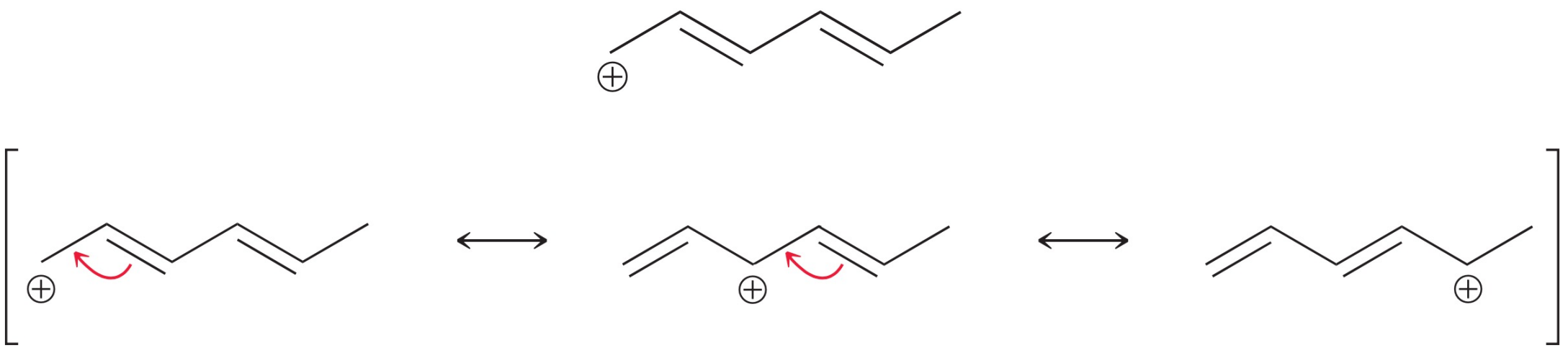
Allylic carbocation

烯丙基碳正离子



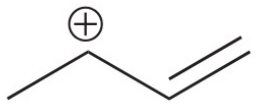
箭头从π键出发，指向新形成的π键

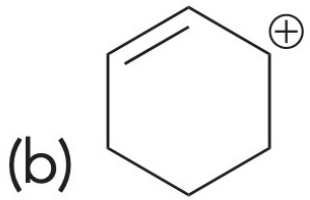
- 烯丙位的C^+
  - 共轭体系中的共振结构

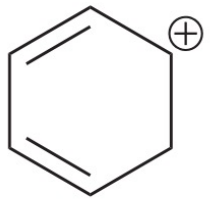


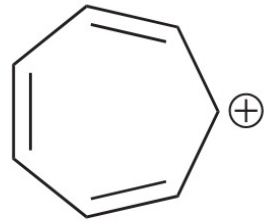
Attention! Never place the tail of a curved arrow on a positive charge!

- Practice: draw the resonance structure(s) for each of the compounds below:

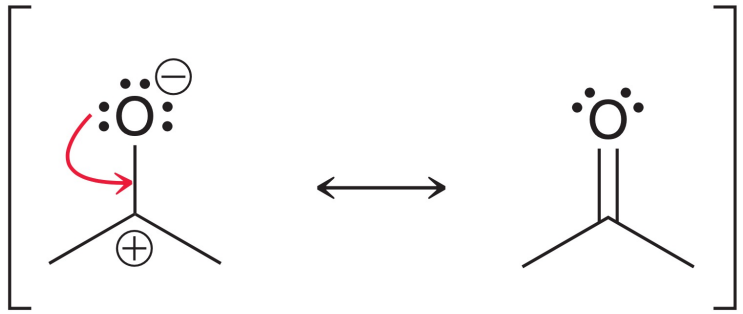
(a) 

(b) 

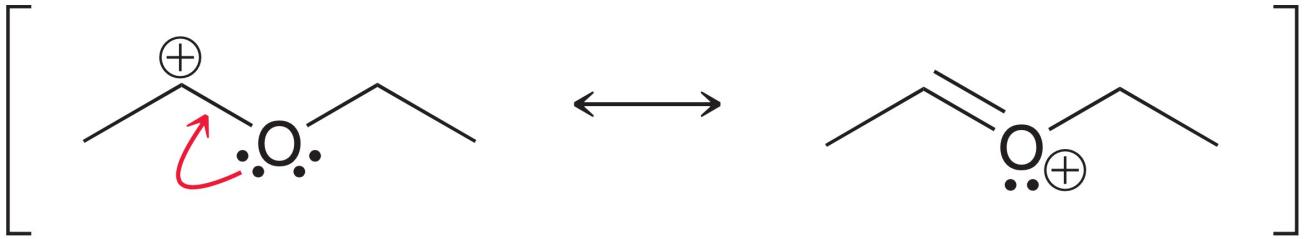
(c) 

(d) 

- C^+毗邻原子上的孤对

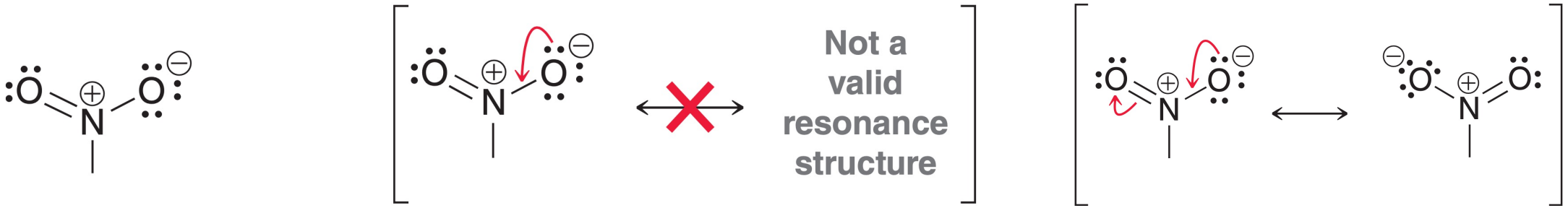


正负电荷可被中和



（无负电荷）不能中和

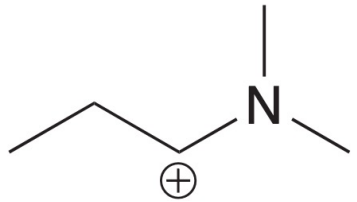
- C^+毗邻原子上的孤对

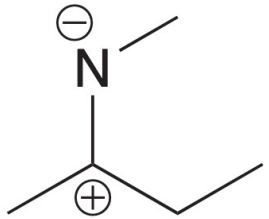


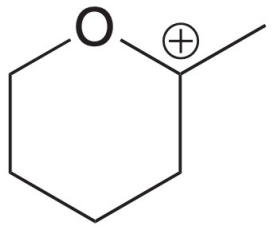
N违反了octet rule

这种情况电荷不能中和！

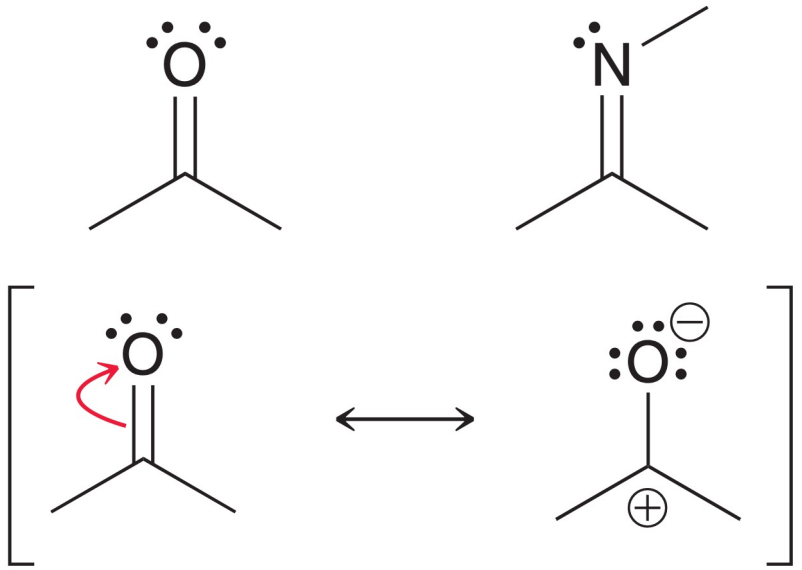
- Practice: for each of the compounds below, locate the lone pair adjacent to a positive charge and draw the resonance structure:

(a) 

(b) 

(c) 

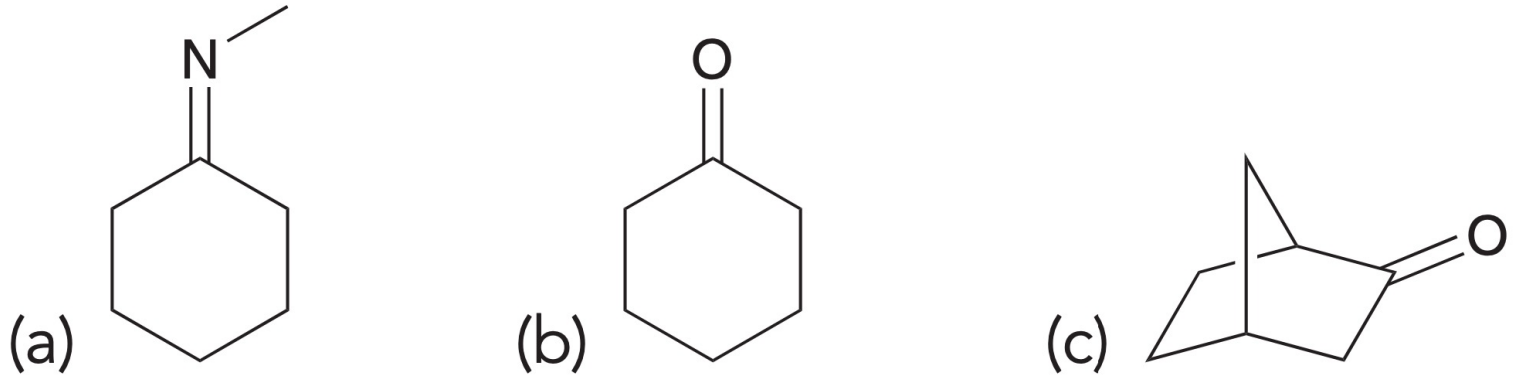
- 不同电负性原子间的π键



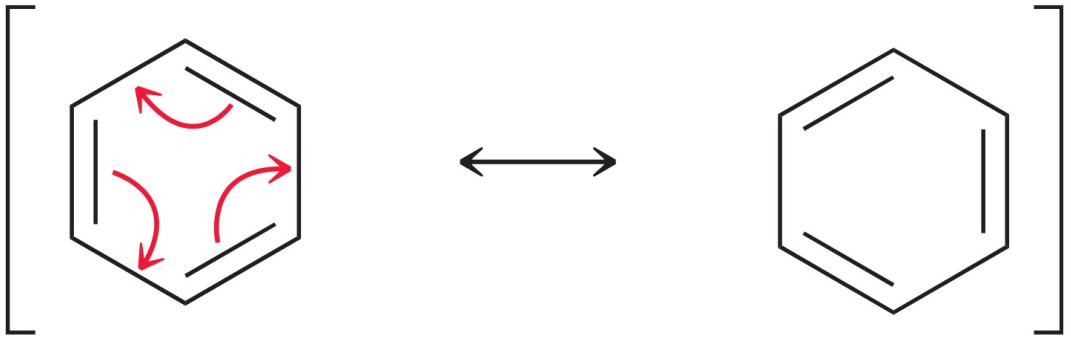
π键的电子倾向于往电负性较大的原子上转移

在此过程中产生形式电荷

- Practice: draw a resonance structure for each of the compounds below.



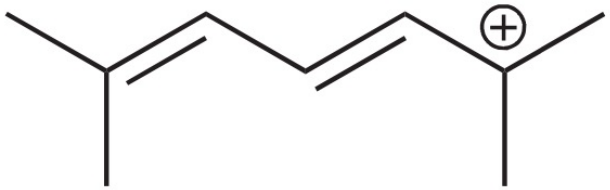
- 环内的共轭π键

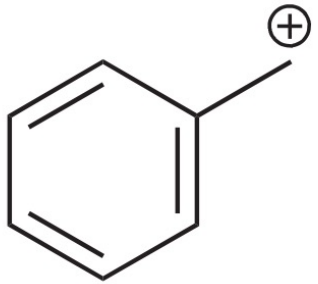


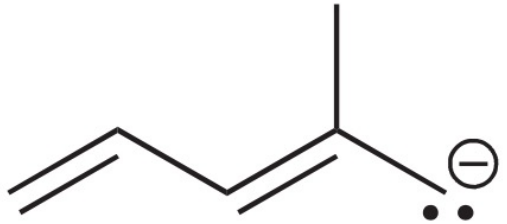
单双键交替的体系称为共轭体系(conjugated system)

共轭体系的电子在环内顺时针或逆时针转移

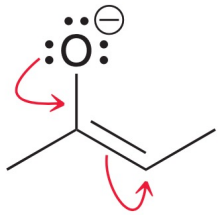
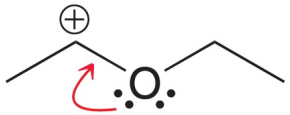
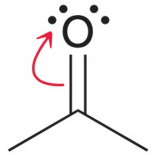
- Practice: for each of the following compounds, draw the resonance structures.







- Summary of specific patterns

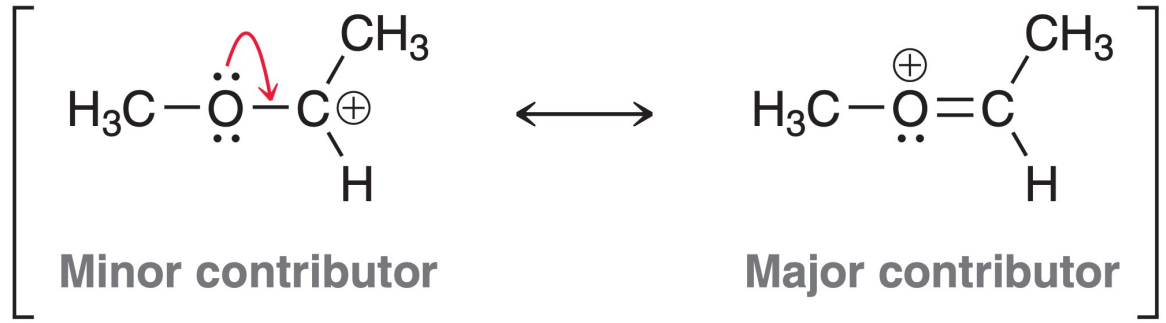
Allylic lone pair	Allylic carbocation	Lone pair adjacent to C+	π bond between two atoms of differing electronegativity	Conjugated π bonds enclosed in a ring
				
Two curved arrows	One curved arrow	One curved arrow	One curved arrow	Three curved arrows

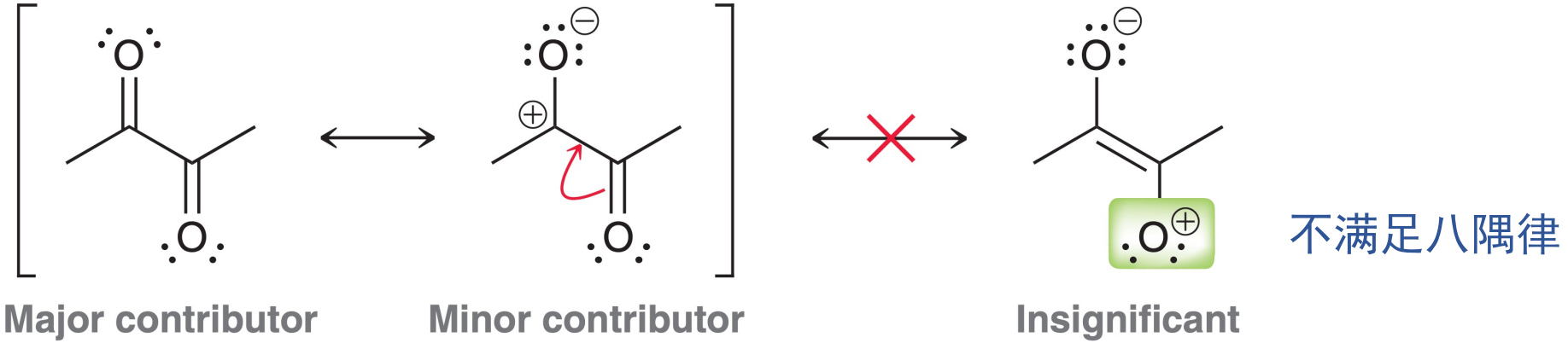
- 比较不同共振式的相对稳定程度

比较顺序

  - 相对最稳定的共振式电子尽可能满足八隅律（达到八电子稳定）
  - 形式电荷越少的共振式越稳定
  - 负电荷在电负性较大的原子上的共振式更稳定
  - 在上述因素上相同的共振式对共振杂化体的贡献相同

- 相对最稳定的共振式电子尽可能满足八隅律

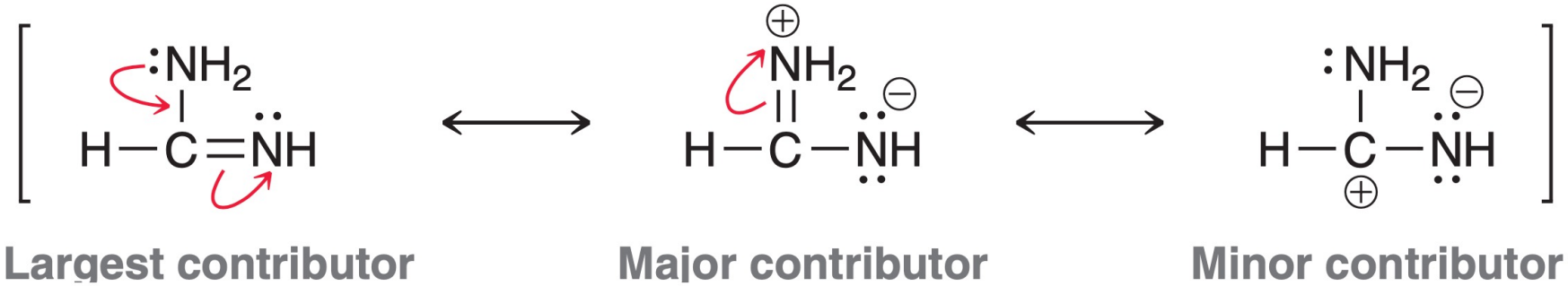


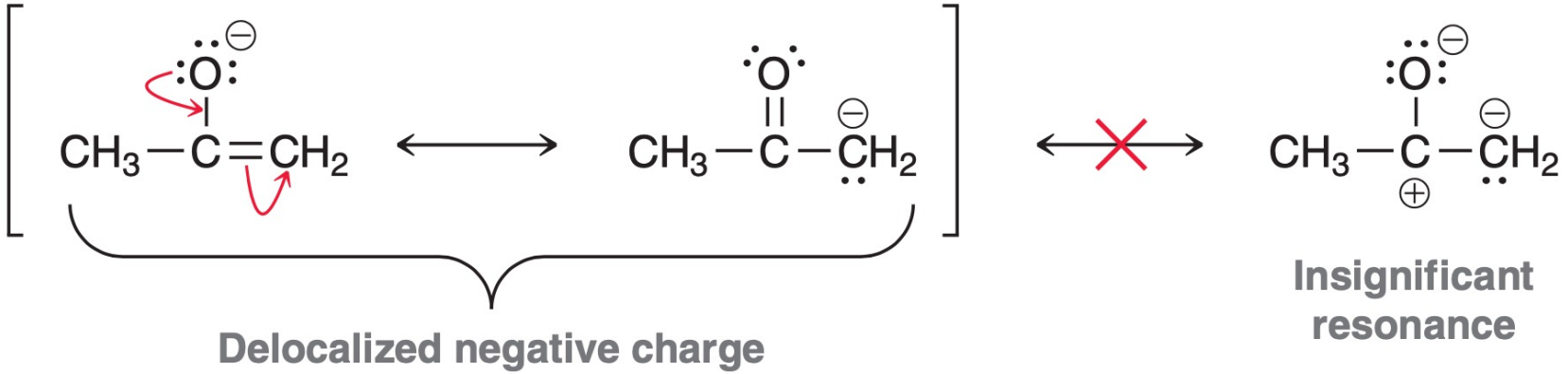


不满足八隅律

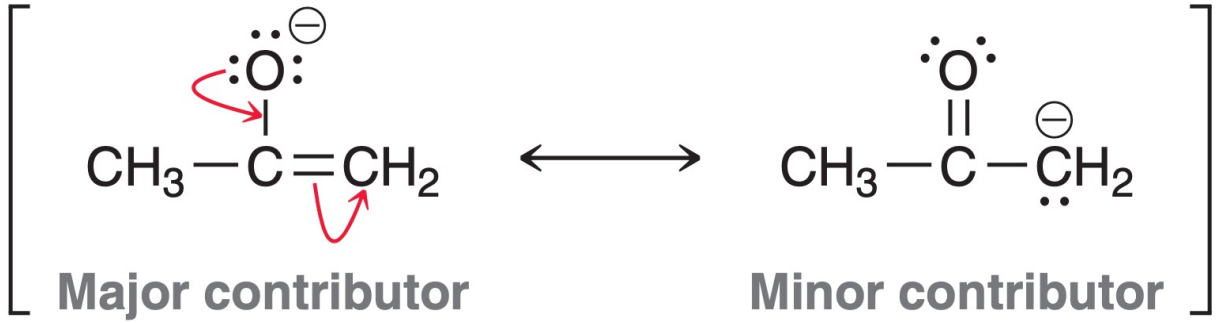
如某个<u>原子</u>携带有+2或-2的形式电荷
那么这个共振式将很不稳定
分子将极不易以这种形式存在

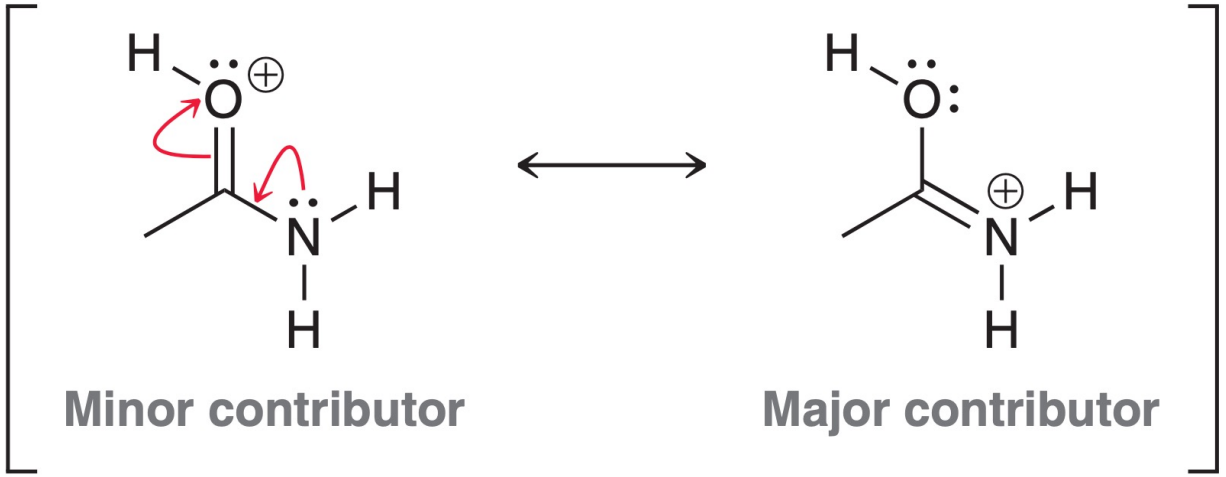
- 形式电荷越少的共振式越稳定





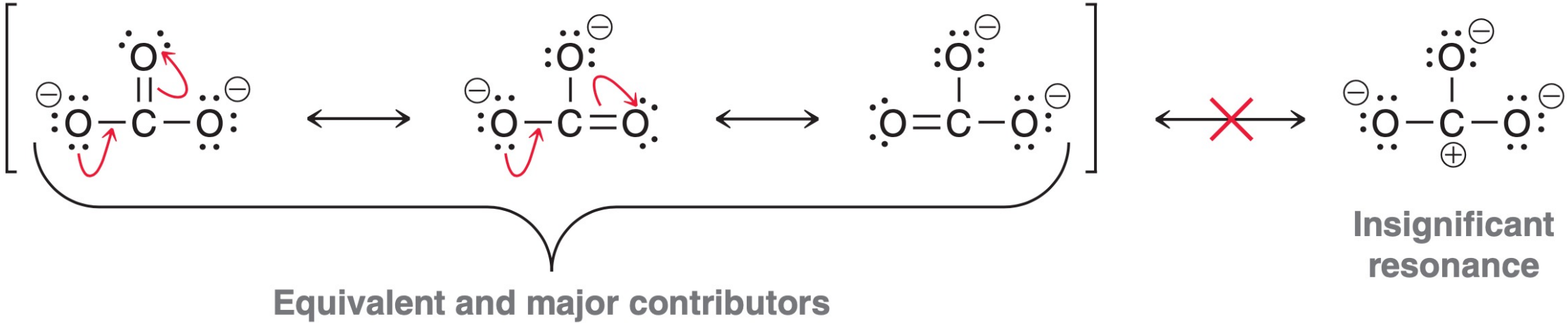
- 负电荷在电负性较大的原子上的共振式更稳定



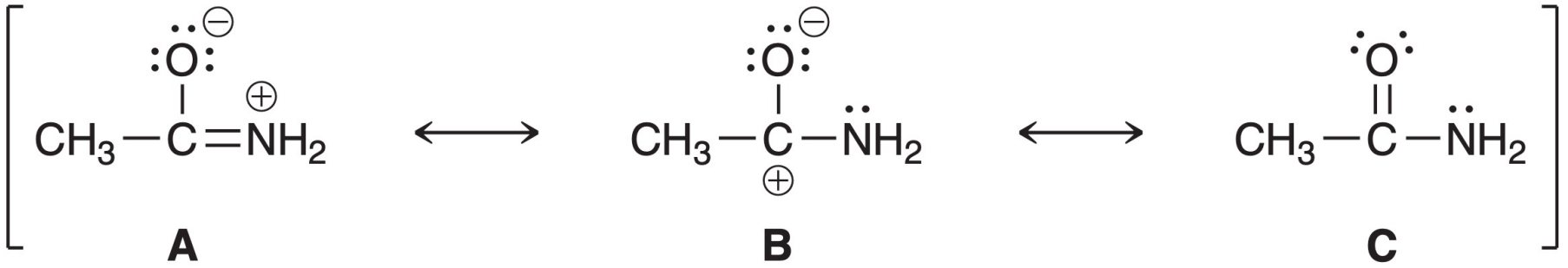


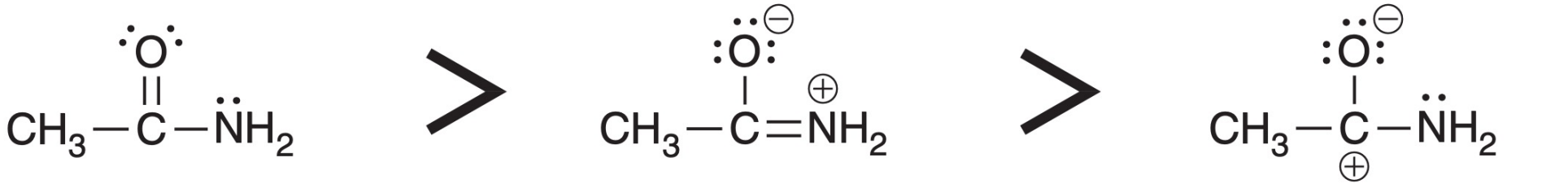
当然啦 正电荷在电负性相对较小的原子上
也会更稳定啦(´▽`)/

- 在上述因素上相同的共振式对共振杂化体的贡献相同



- Practice: rank the following resonance forms, from most significant to least significant, and briefly explain the rankings.





Largest contributor (#1)

满足八隅律
无形式电荷

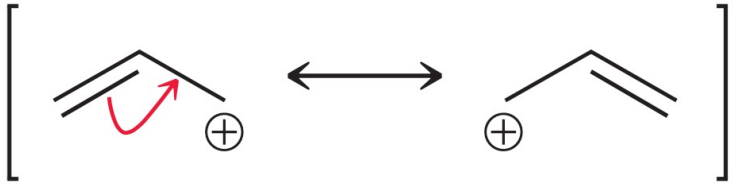
Major contributor (#2)

满足八隅律

Minor contributor (#3)

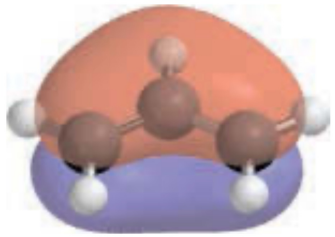
C^+不满足八隅律

- 共振杂化体(resonance hybrid)

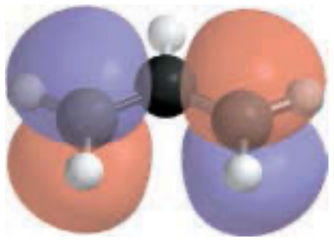


Resonance structures

Resonance hybrid

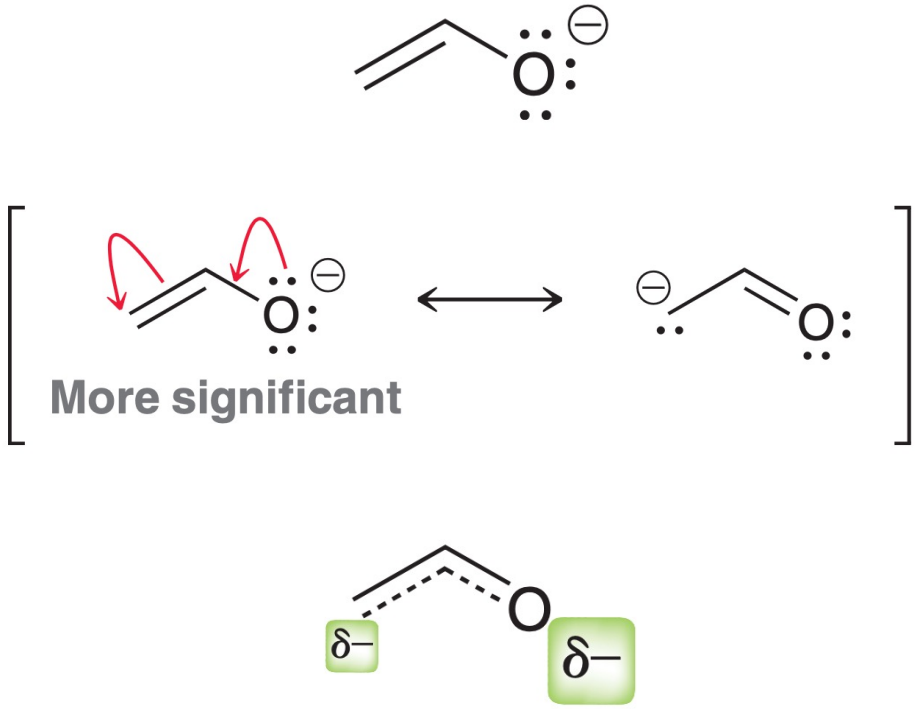


成键π轨道

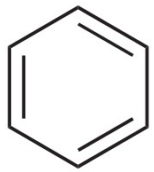


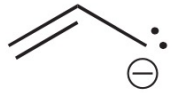
非键π轨道
反映电子密度低的部分
（正电荷所在部分）

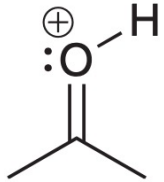
- How to draw a resonance hybrid

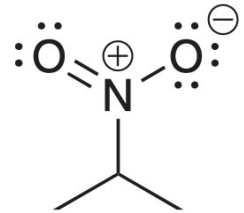


- Practice: draw a resonance hybrid for each of the following.

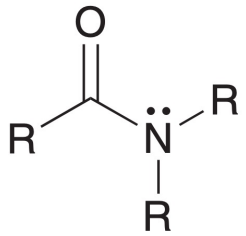
(a) 

(b) 

(c) 

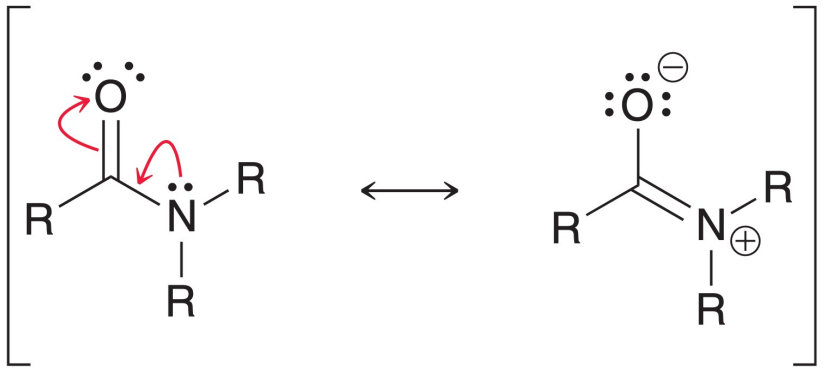
(d) 

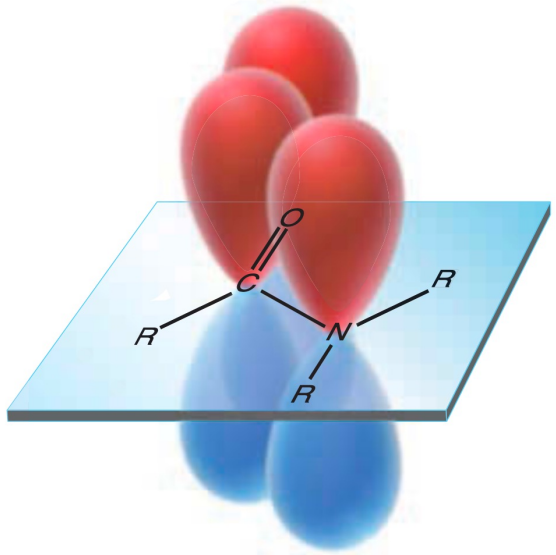
- 离域孤对电子(delocalized lone pairs)



An amide

酰胺

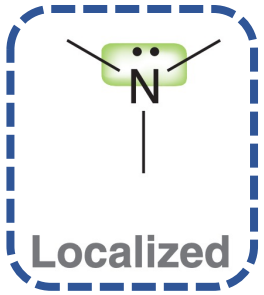


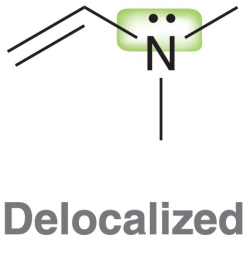


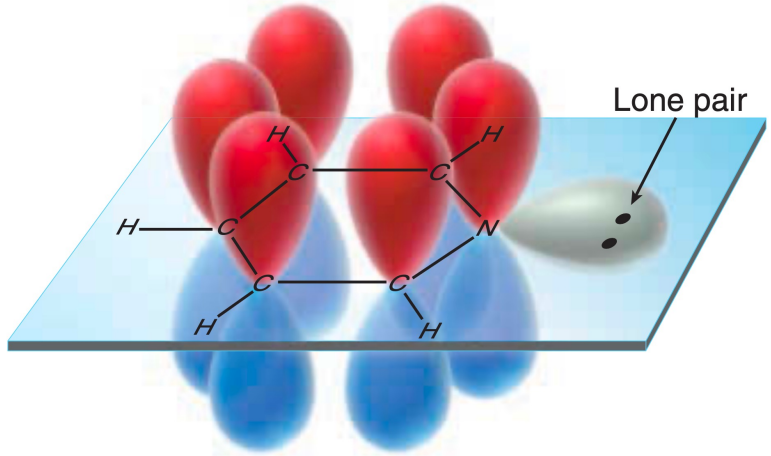
发生离域的孤对电子
必定在p轨道上

- 定域孤对电子(localized lone pairs)

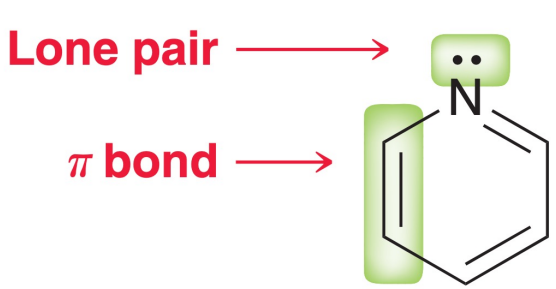
不处于烯丙位的孤对电子
必定为定域电子



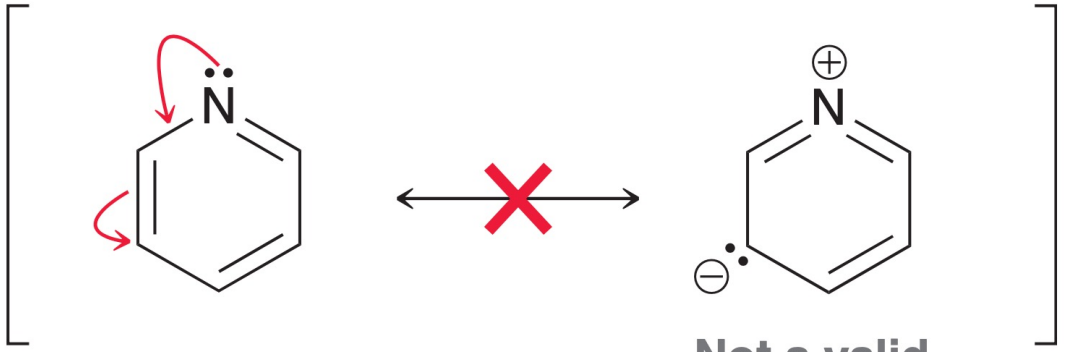




孤对电子在sp^2杂化轨道上
不能发生离域



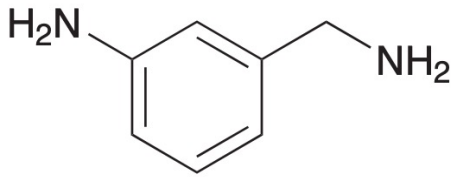
Pyridine
吡啶

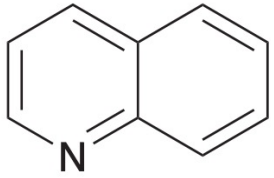


Not a valid
resonance structure

- 不变的原则：
  - 当一个原子同时拥有π键和孤对电子时，它们**不会全部参与**共振
  - **孤对电子占据**sp^2或sp**杂化轨道**（与π键上原子所在平面平行）
  - 原子的**p轨道**用于**形成π键**，此时**p轨道上的电子参与共振**

- Practice: for each compound below, identify all lone pairs and indicate whether each lone pair is localized or delocalized. Then, use that information to predict the geometry for each atom that exhibits a lone pair.

(a) 

(b) 

(c)