

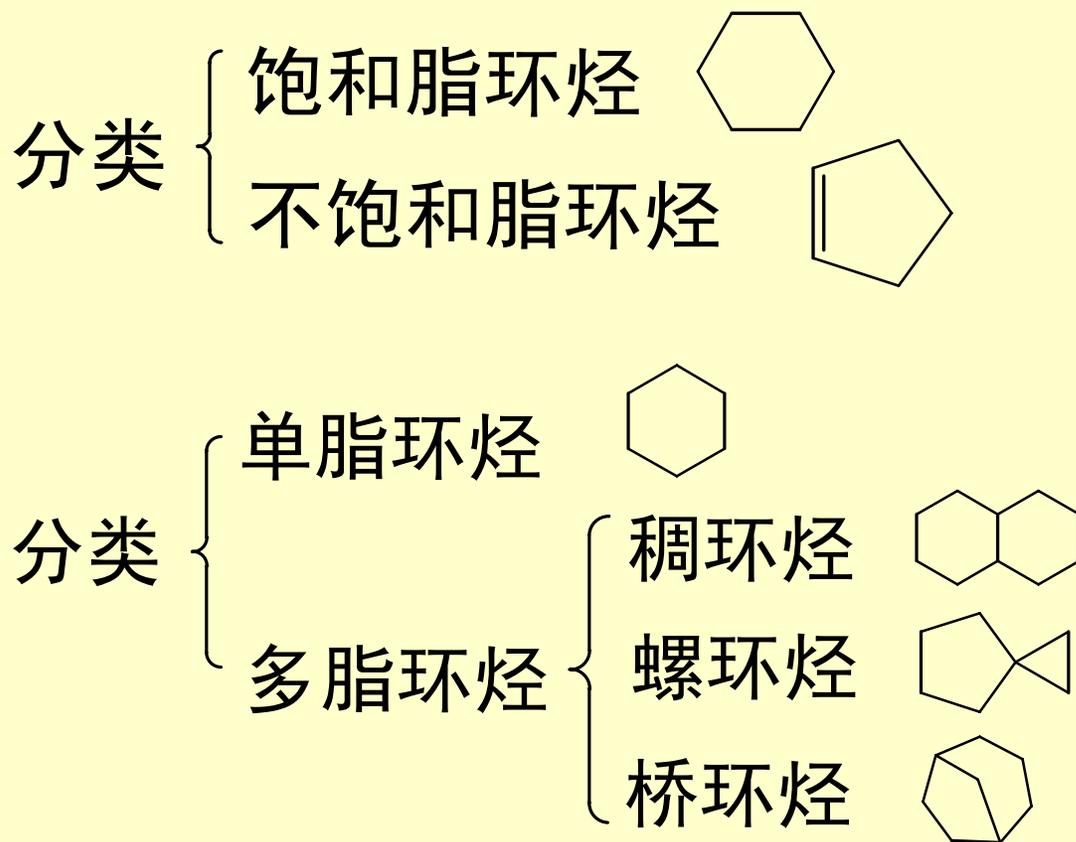
第五章

脂环烃

alicyclic hydrocarbons

第一节 脂环烃的分类和命名

一、分类及命名



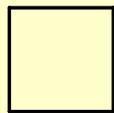
环烷烃的命名

单环:



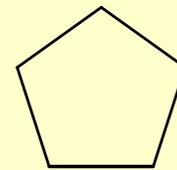
环丙烷

cyclopropane



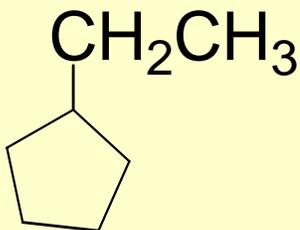
环丁烷

cyclobutane

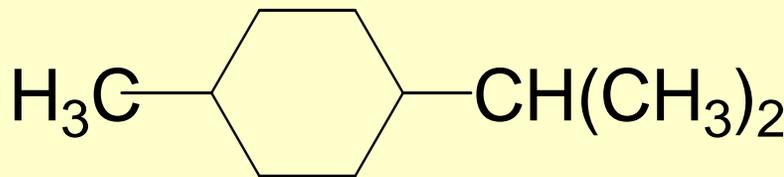


环戊烷

cyclopentane

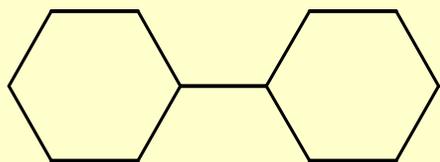


乙基环戊烷

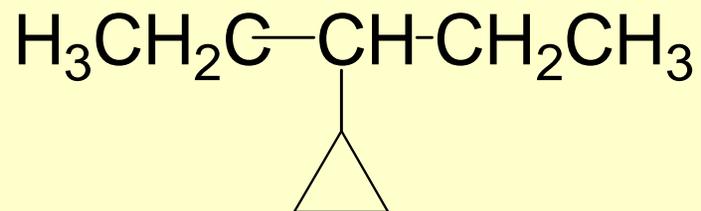


1-甲基-4-异丙基环己烷

环烷烃的命名



环己基环己烷



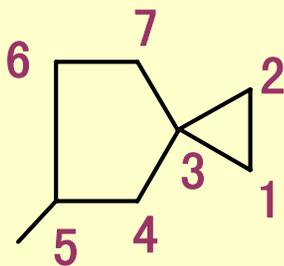
3-环丙基戊烷

多环的命名:

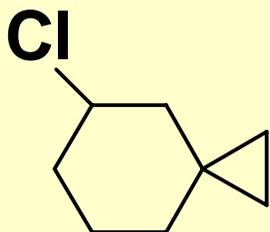
螺环:

- 根据成环的碳总数，叫螺[]某烷
- 两环除开共用C外的C数，由小到大，放于[]内，并用下角原点隔开
- 编号：从小环—共用C—大环（并尽可能使取代基为此小）

eg.



5-甲基螺[2.4]庚烷



5-氯螺[2.5]辛烷

桥环烃（包括稠环烃）：

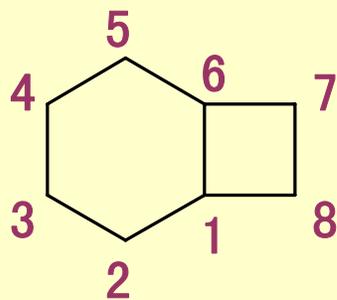
a. 判断环数及总碳数，称几环[]某烷

*环数：将桥环烃变为开链化合物需要断开的C-C键的最小数

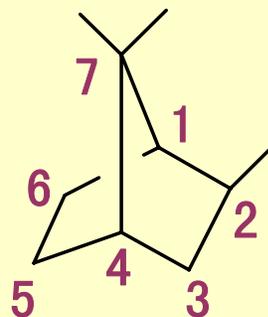
b. 将桥上碳原子数（不包括桥头碳）由多到少顺序列在[]内，并用下角原点隔开（有几个桥就有几个数字）。

c. 编号：从第一个桥头碳开始，从最长的桥编到第二个桥头碳，再沿次长的桥回到第一个桥头碳，即按桥渐短的次序将其余的桥依次编号。（若有取代基，则尽量使其位次较小）

eg.

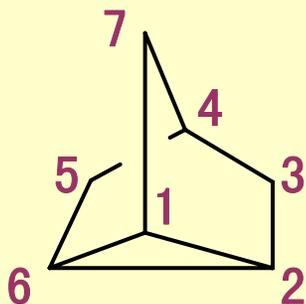


二环[4.2.0]辛烷

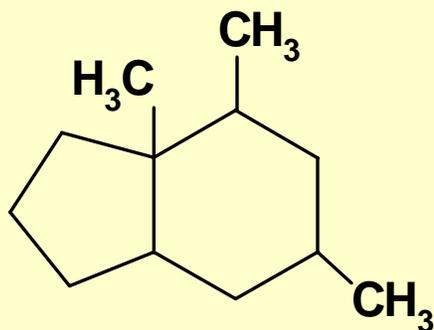


2,7,7-三甲基二环[2.2.1]庚烷

桥环烃（包括稠环烃）：



三环[2.2.1.0^{2,6}]庚烷

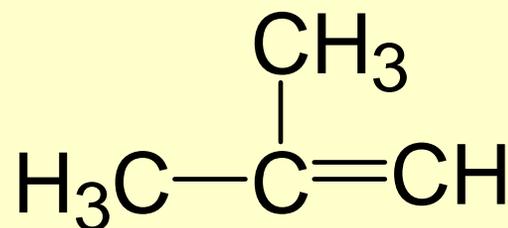
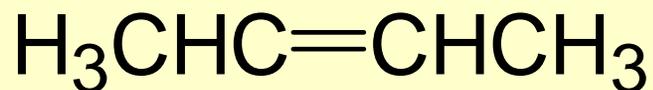
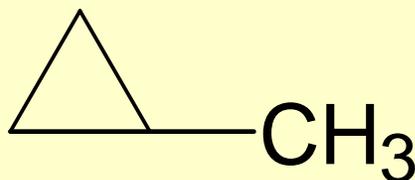
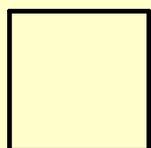


1,2,4-三甲基二环[4.3.0]壬烷

二、同分异构

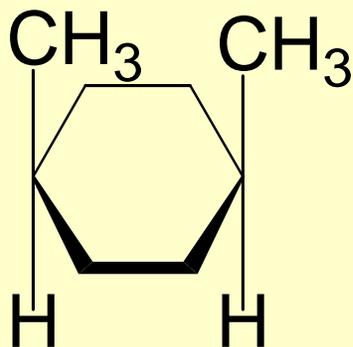
(一) 构造异构

饱和环烷烃的通式： C_nH_{2n}

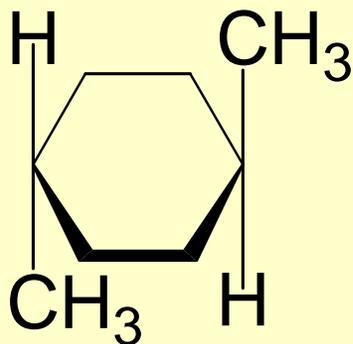


(二) 顺反异构

定义： 由于分子中存在不能旋转的因素，而使原子在空间的排列方式不同的现象。

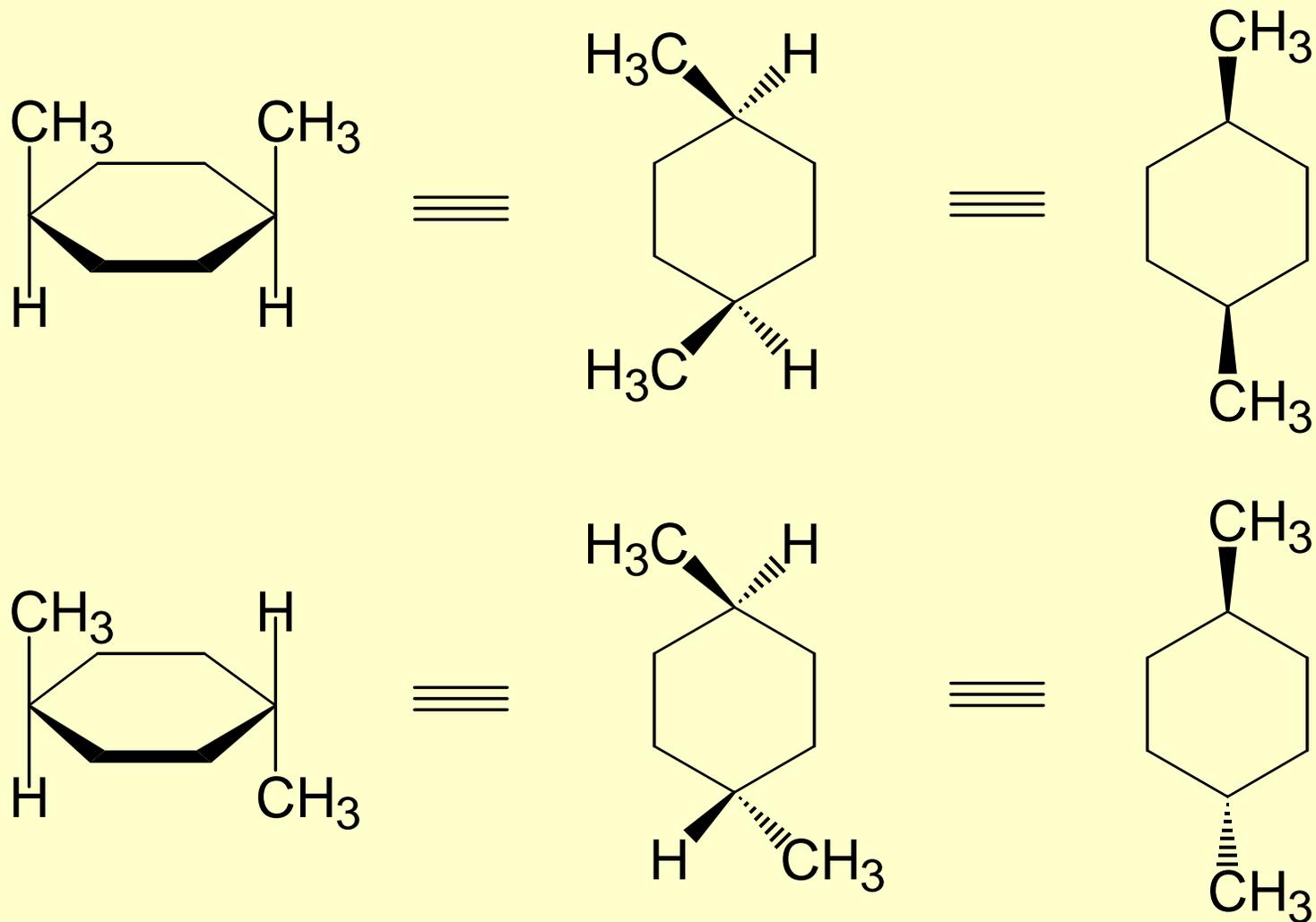


顺-1, 4-二甲基环己烷



反-1, 4-二甲基环己烷

(二) 顺反异构



第二节 环烷烃的性质

一、物理性质

环烷烃的bp. mp和相对密度比同碳原子数的直链烷烃高

例题：将下列化合物按沸点降低的顺序排列：

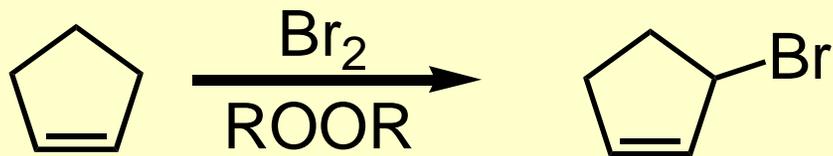
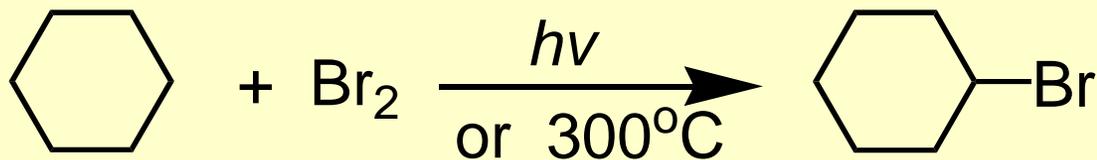
- (1) 丁烷 (2) 己烷 (3) 3-甲基戊烷
(4) 2-甲基丁烷 (5) 2, 3-二甲基丁烷
(6) 环己烷

解：(6) (2) (3) (5) (4) (1)

二、化学性质

饱和环烷烃对强酸、强碱、强氧化剂稳定

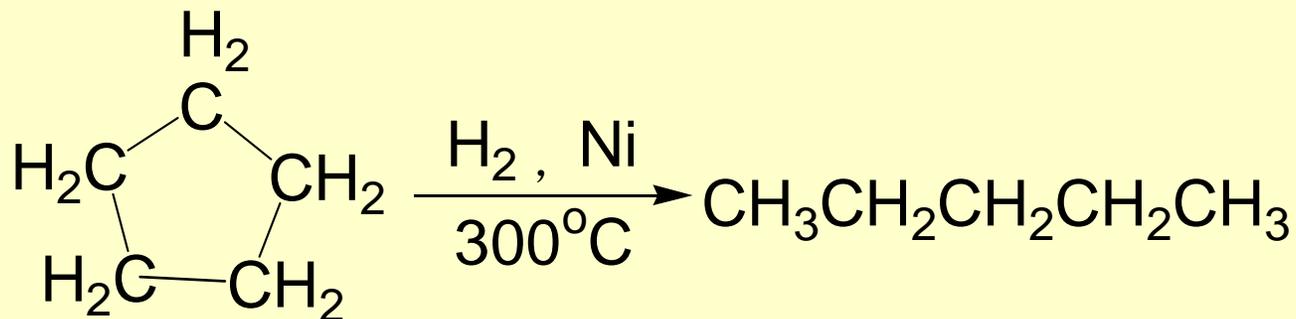
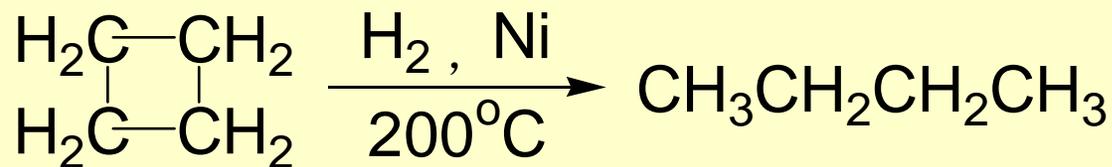
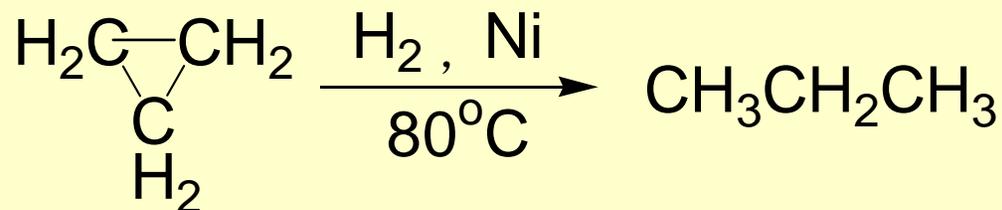
1、自由基取代反应



二、化学性质

2、加成反应

(1) 加氢



例题与讨论

例题：如何将丙烷、丙烯、环丙烷区别开？

解：1、各取少许上述三种溶液，分别加入高锰酸钾的酸性溶液，使其褪色的是丙烯。

2、另取剩余两种溶液，分别加入溴水，使其褪色的是环丙烷。余下的是丙烷。

例题：如何将环丙烷、环丁烷和环戊烷区别开？

解：各取少许上述三种溶液，分别加入溴水，使其褪色的是环丙烷，加热后退色的是环丁烷，不退色的是环戊烷。

第三节 环烷烃的结构与稳定性

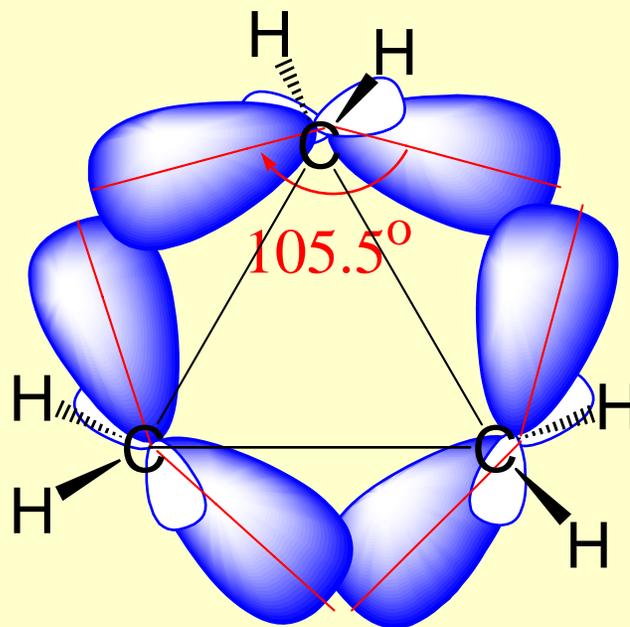
一、结构

以环丙烷为例：

C: sp^3 键角为： $109^{\circ}28'$

每个键的弯曲角度为：

$$(109^{\circ}28' - 60^{\circ}) \div 2 = 24^{\circ}44'$$



$24^{\circ}44'$



$9^{\circ}44'$



$44'$

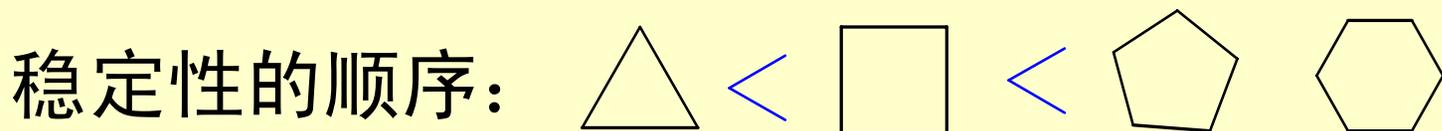


$-5^{\circ}16'$

第三节 环烷烃的结构与稳定性

二、化学键的观点

- 1、电子云并非沿对称轴重叠，所以形成弯曲键。
- 2、电子云重叠程度小，所以键不稳定，易断裂。
- 3、成键的电子云分布在两原子的外侧，易受亲电试剂的进攻，而发生亲电加成。



第三节 环烷烃的结构与稳定性

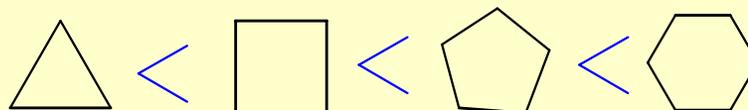
三、燃烧热(heat of combustion)的观点



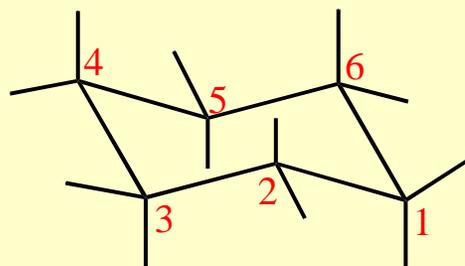
表 2-3 环烷烃的燃烧热(kJ·mol⁻¹)

名称	每个 CH ₂ 的燃烧热	名称	每个 CH ₂ 的燃烧热
环丙烷	697.0	环癸烷	663.6
环丁烷	686.2	环十一烷	662.3
环戊烷	664.0	环十二烷	658.8
环己烷	658.6	环十三烷	659.6
环庚烷	662.3	环十四烷	657.9
环辛烷	664.2	环十五烷	659.0
环壬烷	664.4	环十七烷	657.1

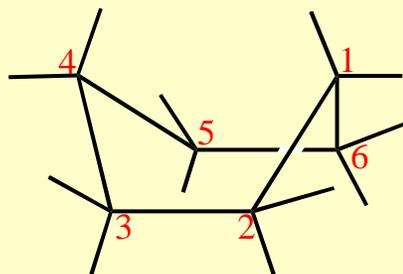
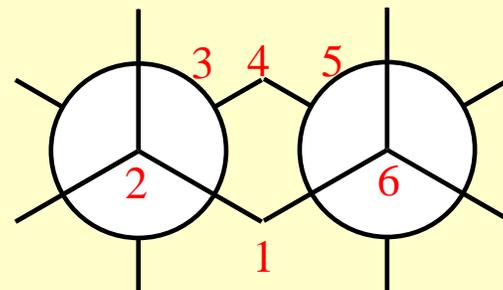
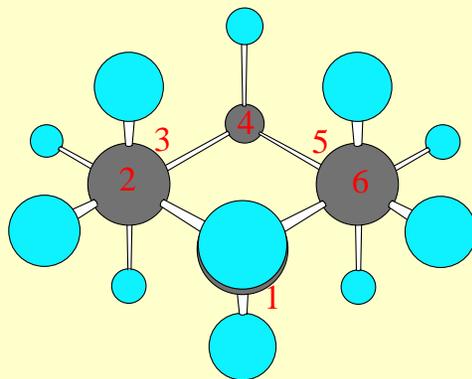
稳定性的顺序:



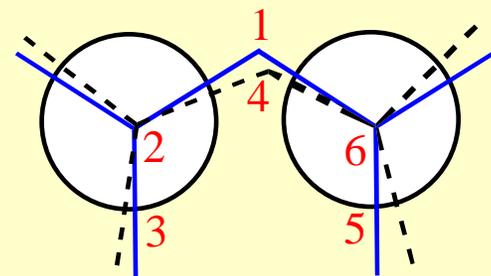
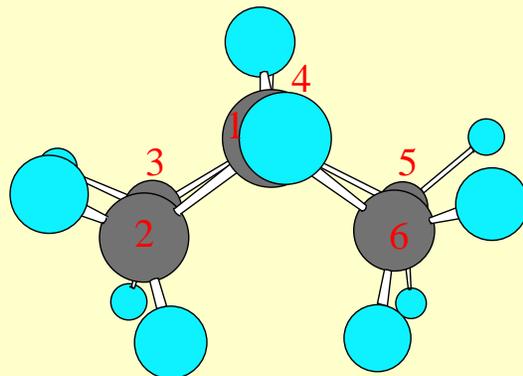
第四节 环己烷的构象



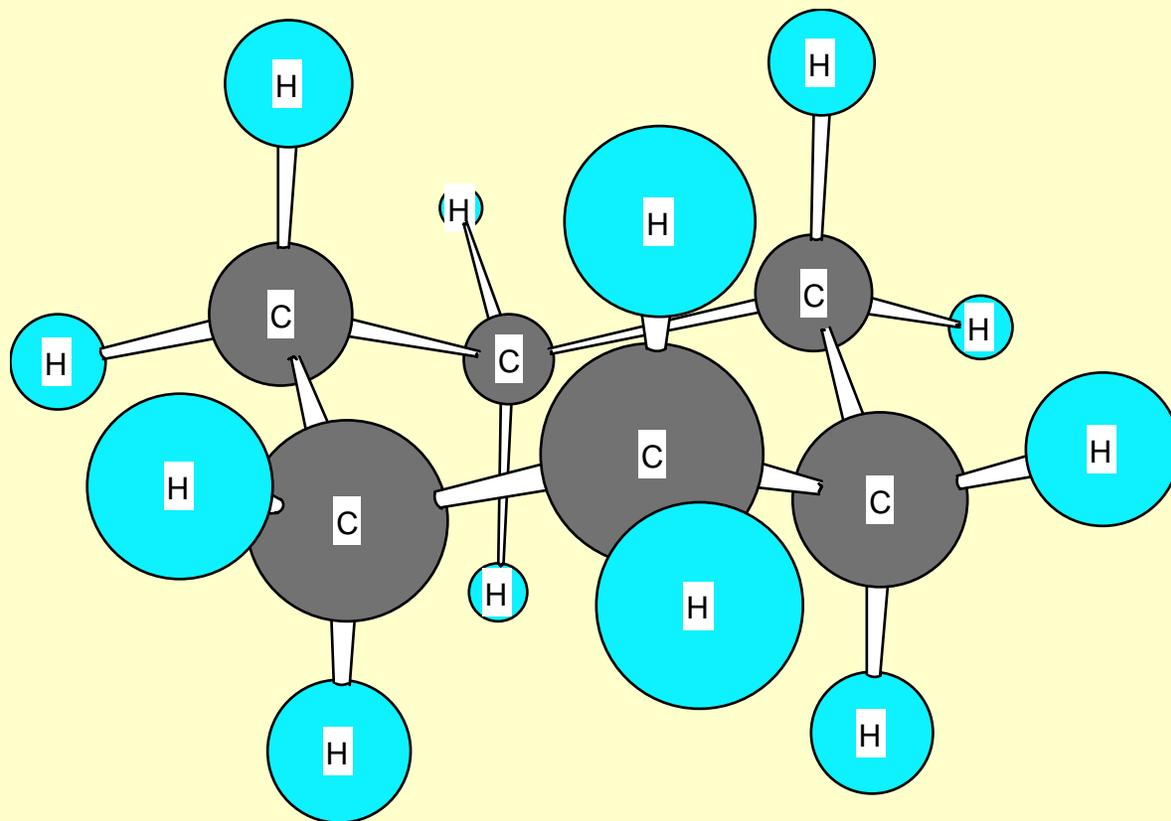
椅式



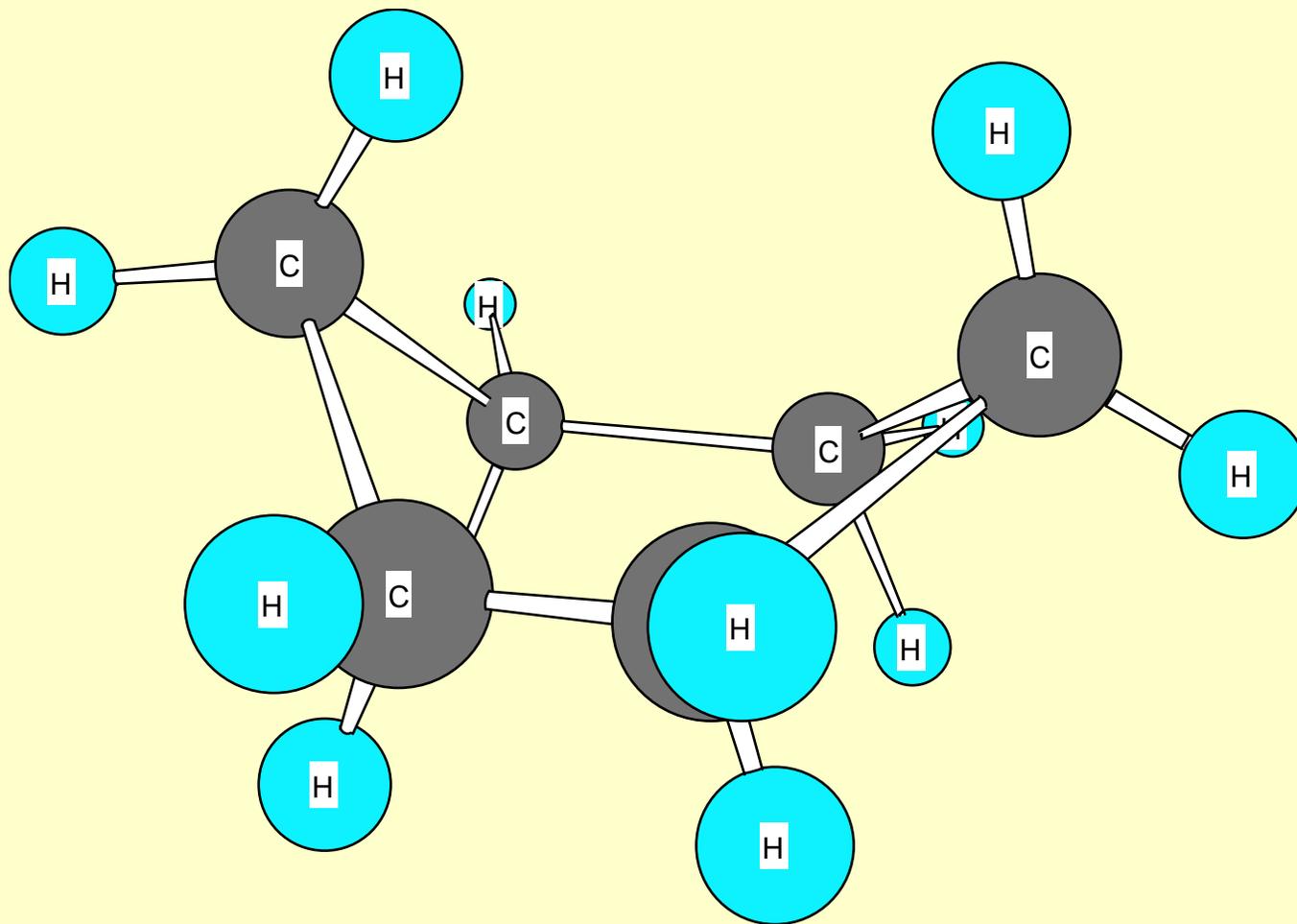
船式



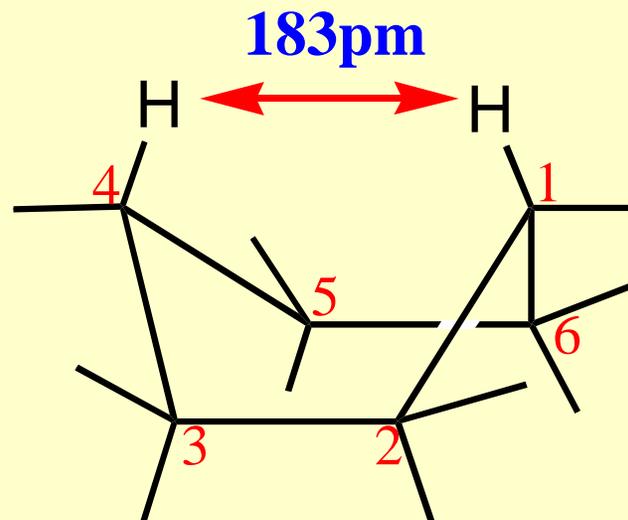
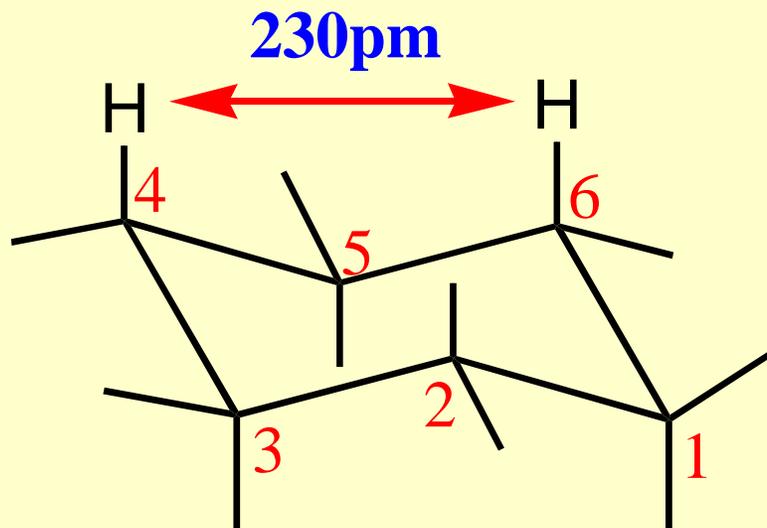
环己烷的椅式构象



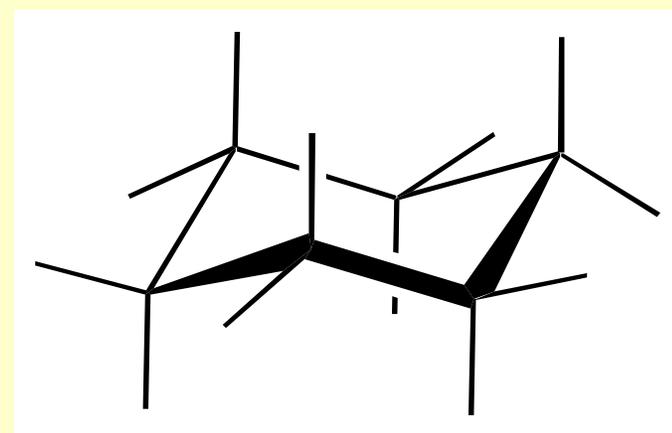
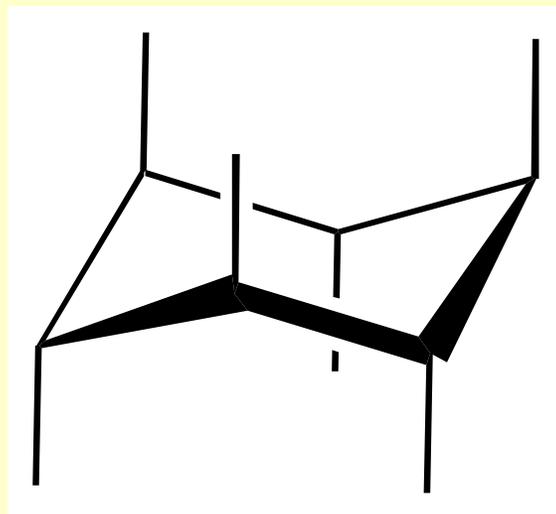
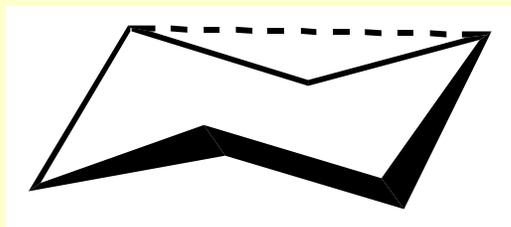
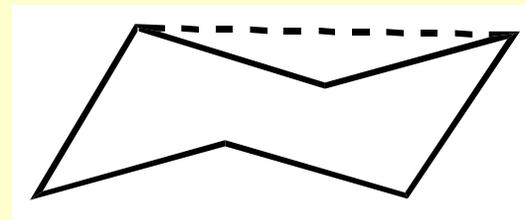
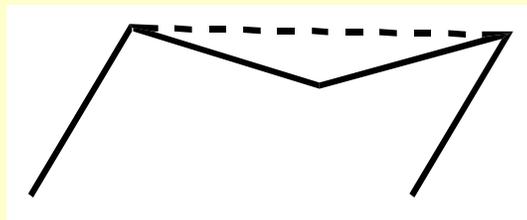
环己烷的船式构象



第四节 环己烷的构象

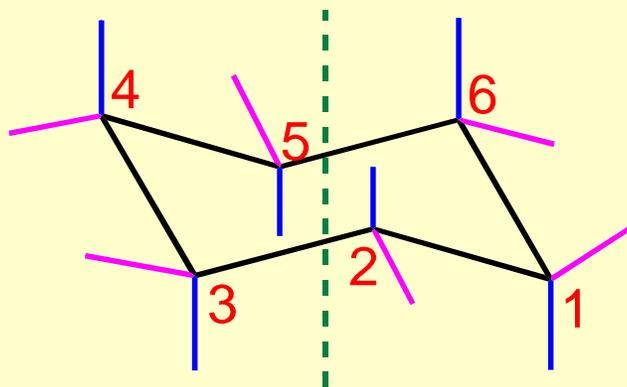
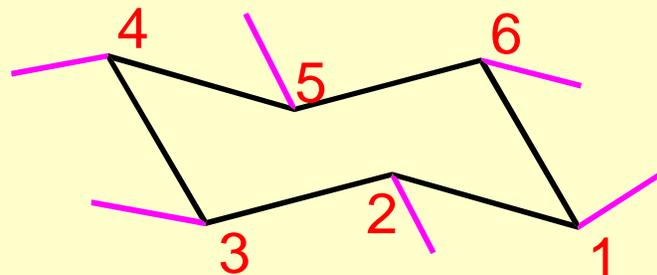
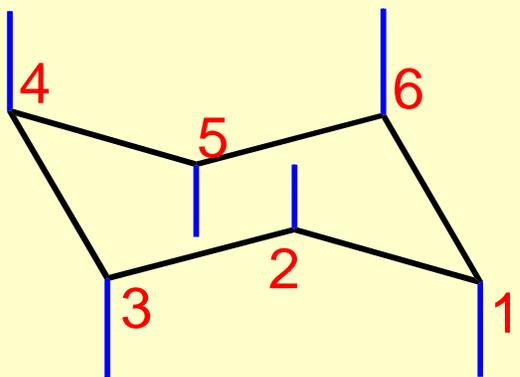


环己烷的构象画法



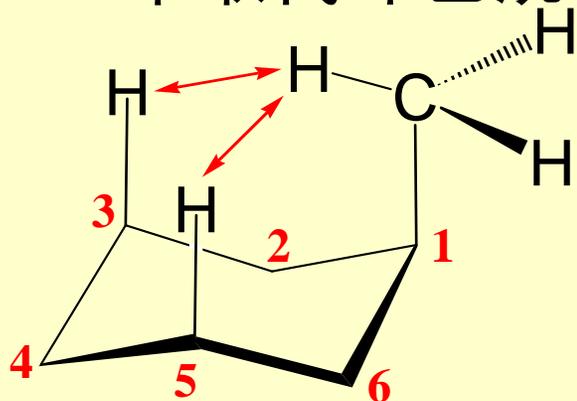
环己烷椅式构象中的竖键与横键

竖键 (a) 和横键 (e)

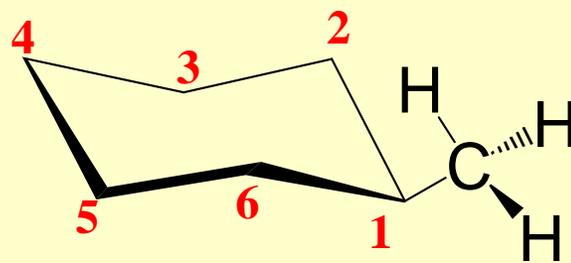
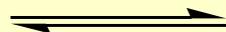


取代环己烷的构象分析

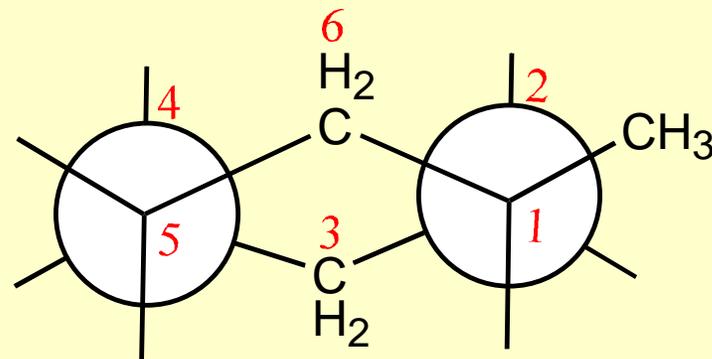
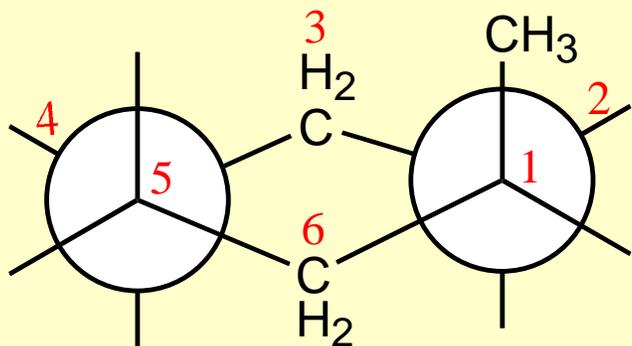
1、单取代环己烷



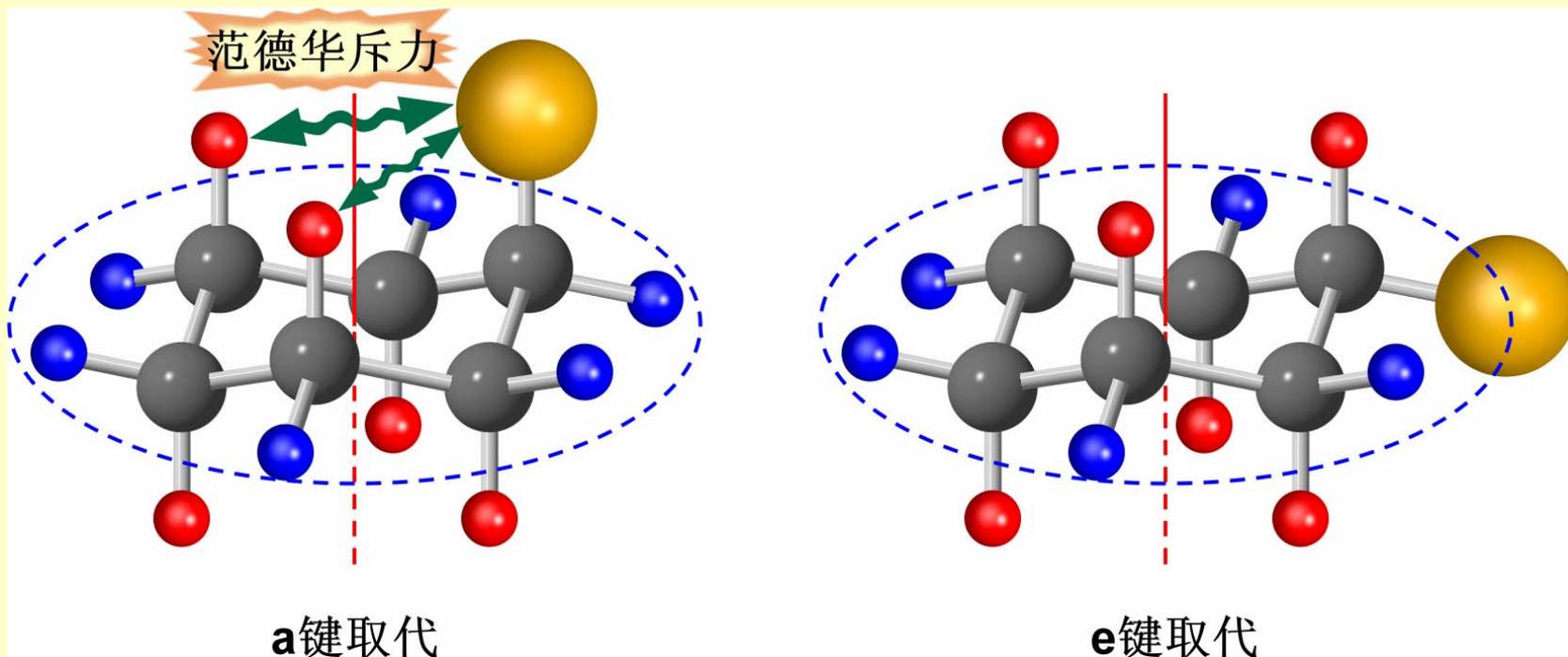
5%



95%

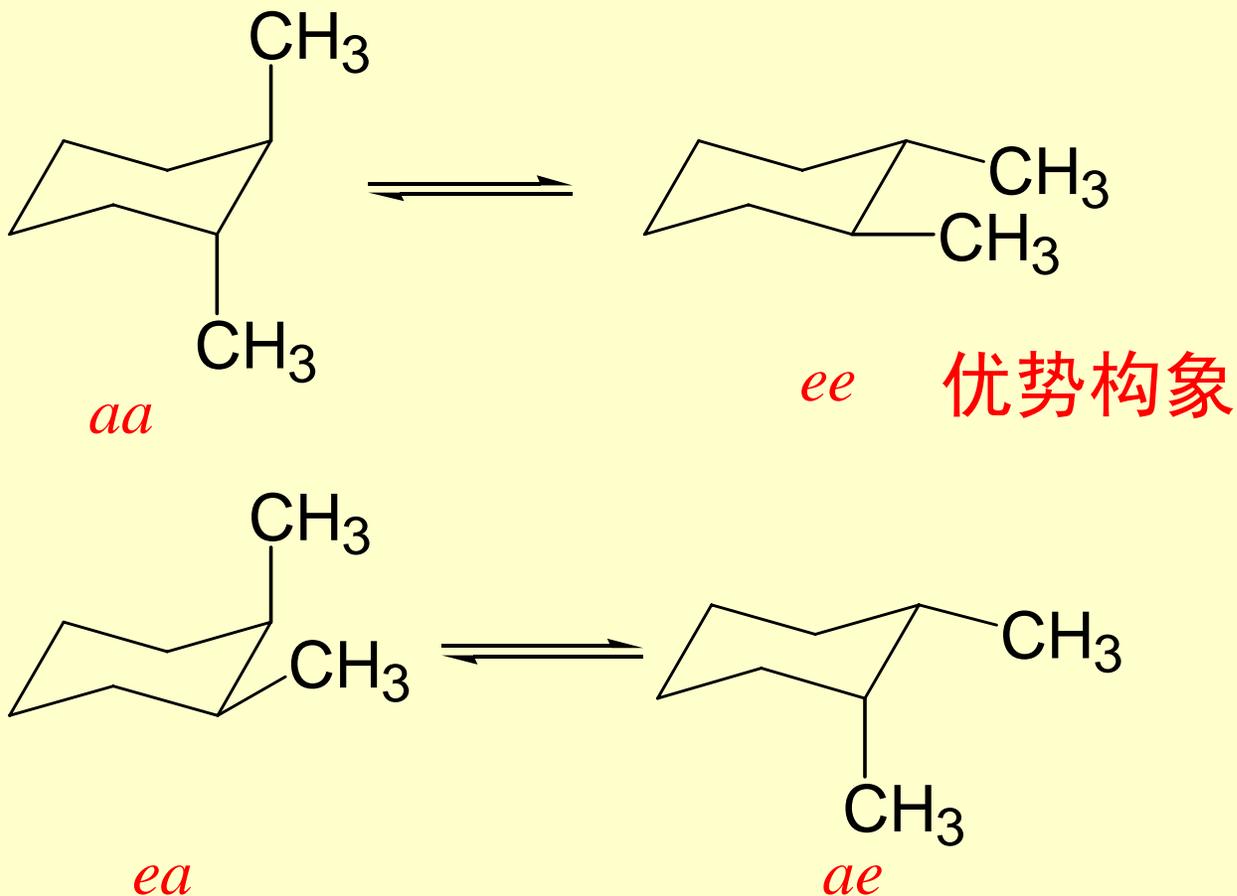


1、单取代环己烷



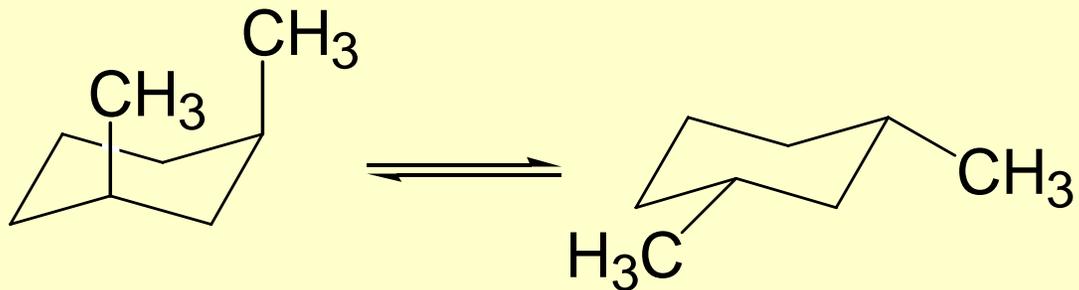
2、二取代环烷烃

1, 2-二甲基环己烷



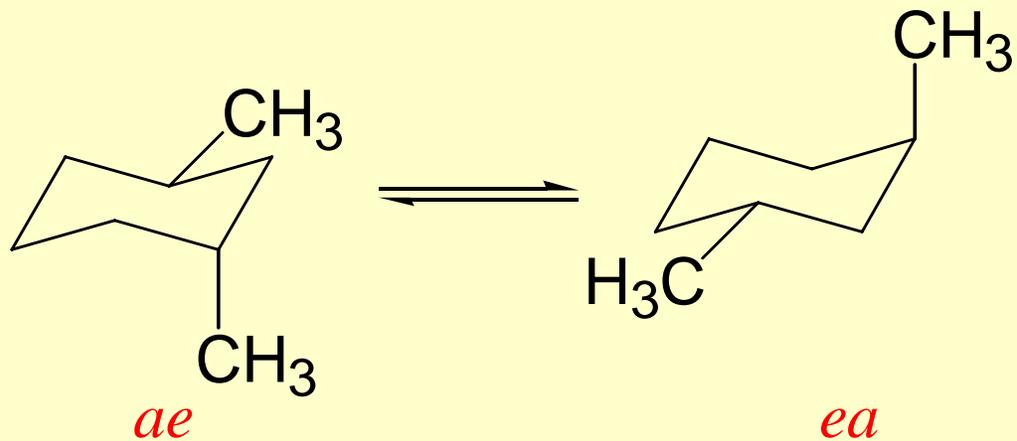
2、二取代环烷烃

1, 3-二甲基环己烷



aa

ee 优势构象

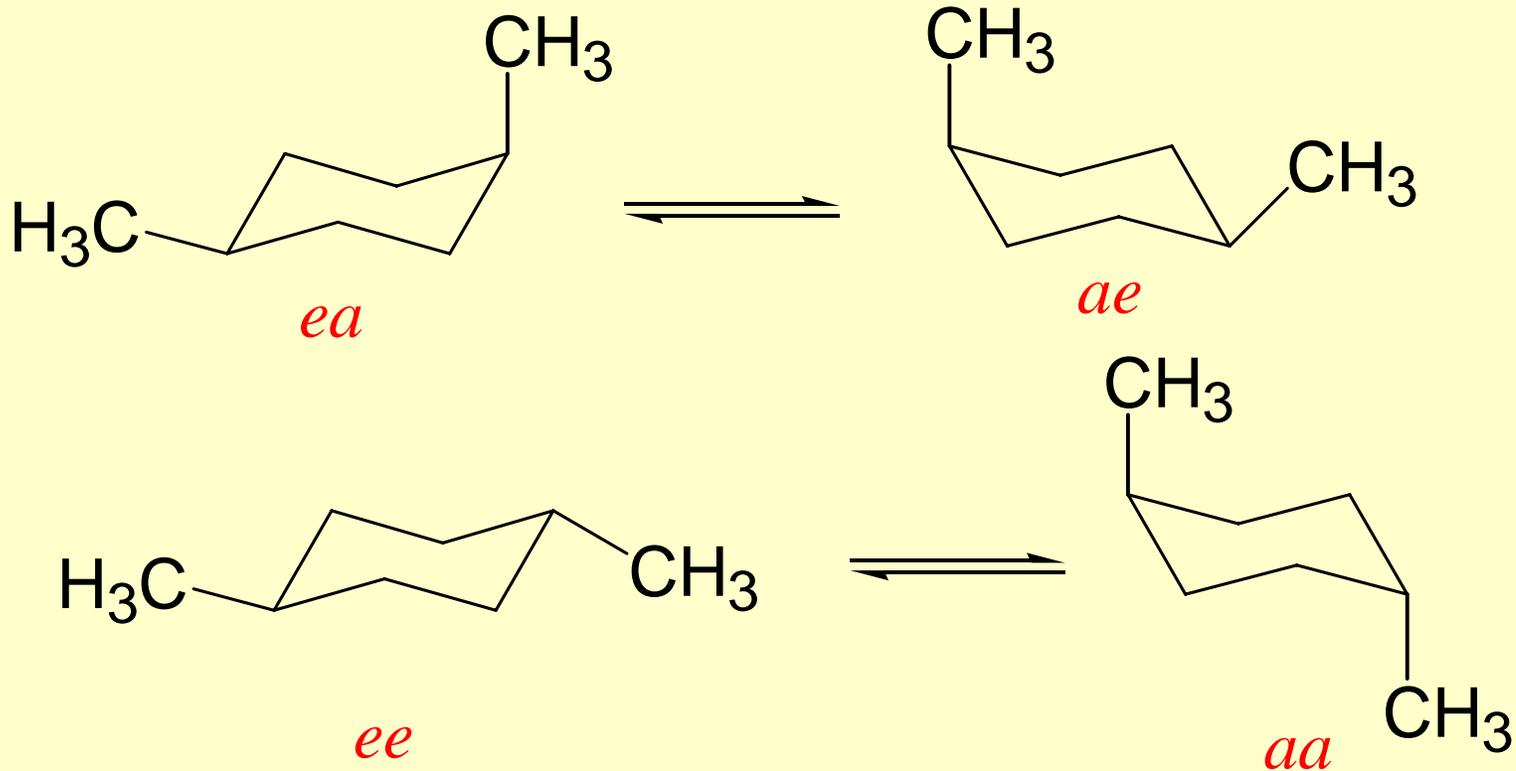


ae

ea

2、二取代环烷烃

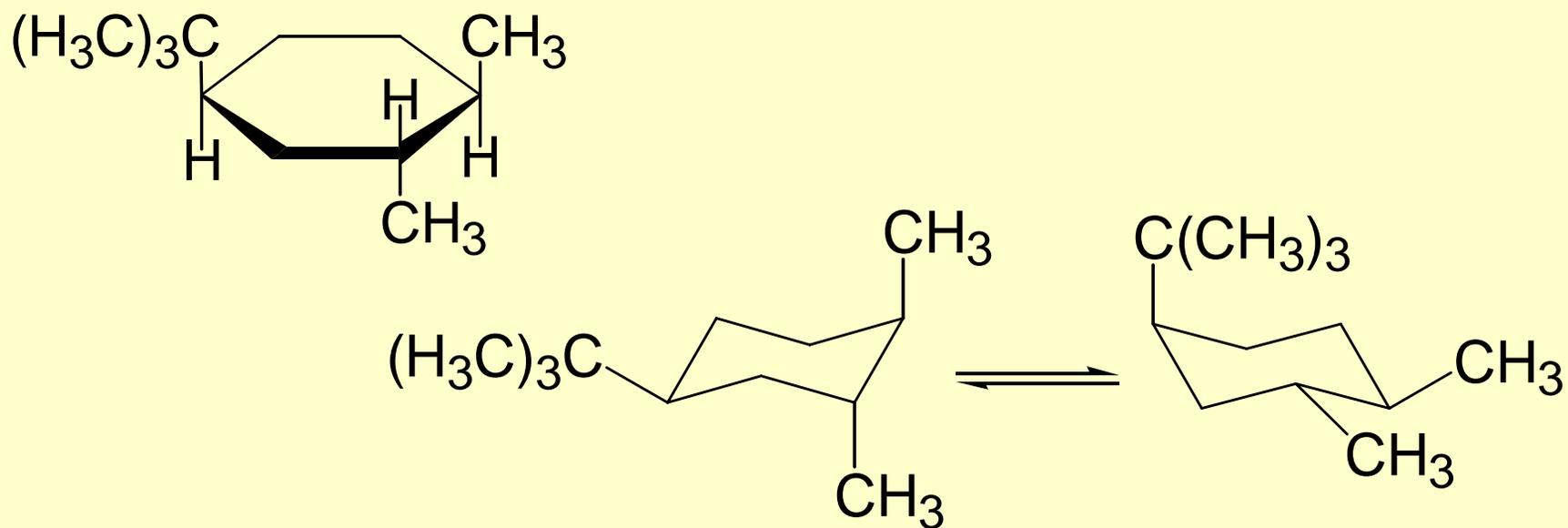
1, 4-二甲基环己烷



优势构象

取代烷烃的优势构象

- ① 椅式构象为稳定构象。
- ② 取代基占横键多得为优势构象。
- ③ 体积大的基团处于横键是为优势构象。



例题

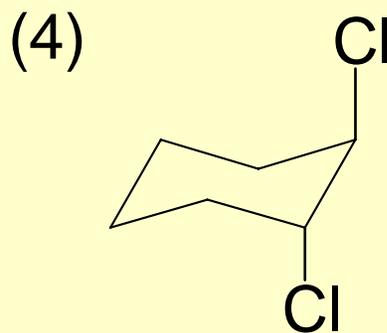
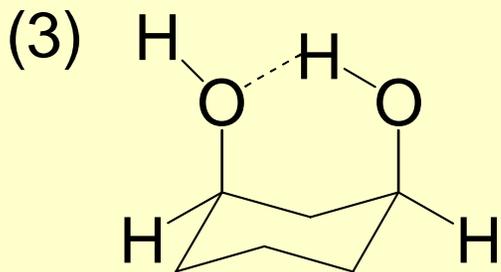
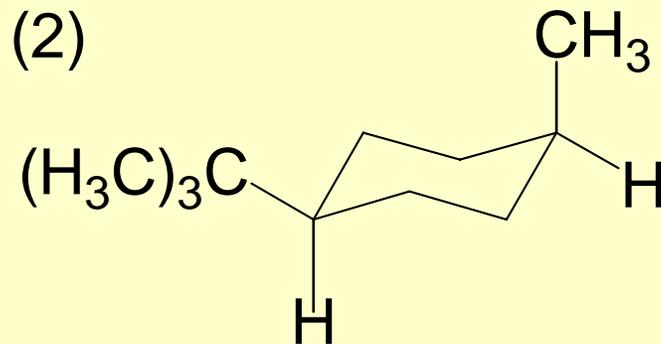
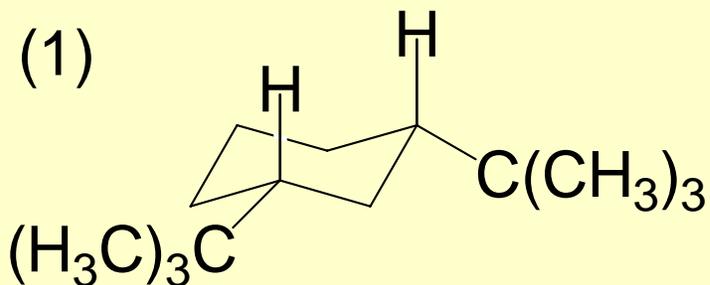
写出下列化合物最稳定的构象:

(1) 顺-1, 3-二叔丁基环己烷

(3) 顺-1, 3环己二醇

(2) 顺-1-甲基-4-叔丁基环己烷

(4) 反-1, 2-二氯环己烷



第五节 多环烃

十氢化萘:

