Chemistry II (Organic): Introduction to Stereoelectronics

STRUCTURE: Conformational analysis and ground state stereoelectronics of hydrocarbons

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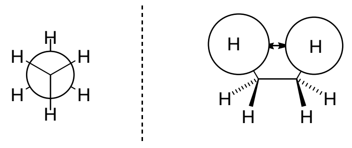
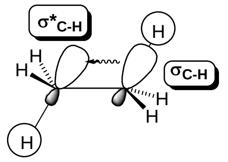
SATURATED HYDROCARBONS:

Saturated hydrocarbons prefer to exist in the staggered conformation. The eclipsed conformers suffer from unfavorable eclipsing interactions (i.e. non-bonded, van der Waals repulsions between the atoms concerned) which are minimised in the staggered conformation. Additionally, there is a stereoelectronic preferrence for adopting a staggered conformation because this arrangement has all the bonds on ajacent carbons anti periplanar to each other thereby allowing six ***σ->σ* stabilising interactions***. For a recent theoretical discussion of the relative importance of these effects see: L. Goodman *Nature*, **2001**, *411*, 539 and 565.



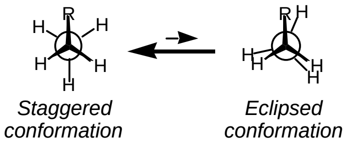
van der Waals repulsion is at maximum when eclipsed (shown) and minimum when staggered



σ_{C-H}->σ^*_{C-H} 'Cieplak' stabilising effects are at maximised when staggered (all six interacting bonds are anti periplanar)

The sum of these two factors is referred to as ***torsional-*** or ***Pitzer strain***. For hydrocarbons, the stereoelectronic component of this term is roughly constant irrespective of whether C-H or C-C bonds are involved since both types of bond have roughly similar σ-donor and σ*-acceptor characteristics. In contrast, the van der Waals, non-bonded component is strongly dependent on the groups (substituents) concerned: i.e. a Me group is clearly 'bigger' than a H group! Having said this, the difference in 'apparent size' between these two groups is not as large as might be expected and this is because a C-C bond is also longer than a C-H bond (1.54Å *cf*. 1.09Å).

We can roughly estimate barriers to rotation around hydrocarbon bonds by simple calculations. An eclipsing interaction between two H groups is roughly worth 4.2 kJ/mol, whereas that between a Me and a H group raises the energy by about 5.9 kJ/mol. Thus, the barrier to rotation around a C-C bond is about 12.6 kJ/mol in ethane but 14.3 kJ/mol in propane.



Barrier to Rotation:

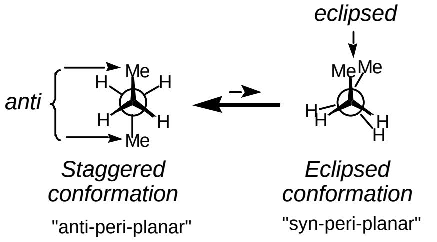
$\Delta H^{\#}$ = +12.6 kJ/mol, when R = H

$\Delta H^{\#}$ = +14.3 kJ/mol, when R = Me

Incremental Contributions to the Barrier

Structure	Eclipsed Atoms	$\Delta H^{\#}$ (kJ/mol)
Ethane	3 (H↔H)	+12.6
Propane	2 (H↔H)	+8.4
	1(H↔Me)	+5.9

As one would expect, the eclipsing interaction between two Me groups is more costly, about 13 kJ/mol. The values for the interactions discussed above, interactions between two H groups, an H and a Me group, and two Me groups can be used to approximate the rotational barrier for butane (see below).

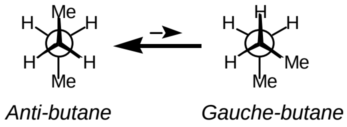


Incremental Contributions to the Barrier

Eclipsed Atoms	ΔH# (kJ/mol)
2 (H↔H)	+8.4
1(Me↔Me)	+13.0

Barrier to Rotation:
ΔH# = +21.4 kJ/mol

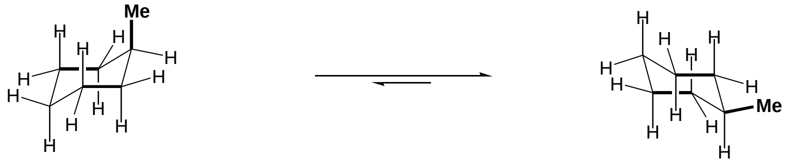
A third possible conformer is the gauche form. The difference in energy between anti butane and a gauche butane is 3.7 kJ/mole. That is, the torsional interaction between two Me groups gauche to each other costs ca. 3.7 kJ/mol (widely known as the ***gauche-butane interaction***).



For n-Butane Energy Profile see previous handout

Barrier to Rotation:
ΔH# = +3.7 kJ/mol

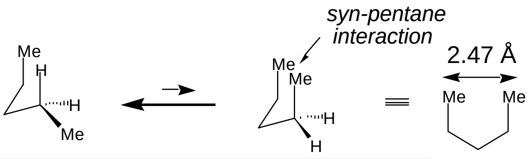
An axial Me group in cyclohexane suffers from two ***gauche butane interactions***; the ‘A value’ (i.e. the free energy corresponding to the value between the axial and equatorial Me-cyclohexane, see textbook) is therefore 7.4 (2 x 3.7 kJ/mol).



2 gauche-butanes in axial methylcyclohexane;
2 x 3.7 = 7.4 kJ/mol. (The A value of Me is 7.4 kJ/mol)

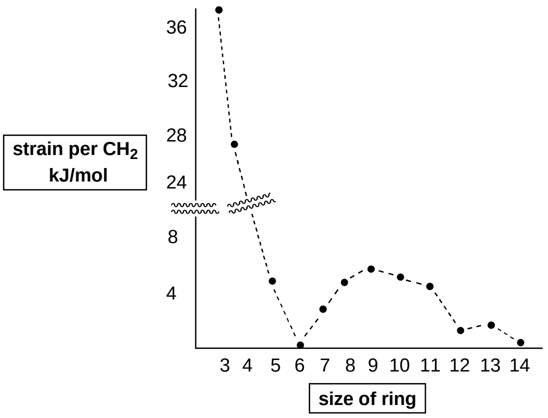
In addition to ***Pitzer strain*** there are a number of other important interactions (strains) which are important in determining the conformation of certain hydrocarbons. These include:

Syn pentane interactions: When two Me groups five atoms apart from each other adopt a syn conformation, as shown below, the two Me units are within about 2.5 Å of one another, and due to resulting van der Waals repulsion, such an orientation becomes rather costly (ca. 15.4 kJ/mol). This interaction is commonly referred to as the ***syn-pentane*** (or ***1,3-flagpole***) ***interaction*** and is encounterd between axial Me groups in cyclohexane chair-type structures.



Enthalpy diffference between conformers
ΔH° = +15.4 kJ/mol

Bond angle- or ***Baeyer strain*** : An sp^3 hybridised carbon ideally has a tetrahedral geometry with all bond angles ~109°. Deviation from this ideal incurrs an energetic penalty known as ***Baeyer strain*** both in a compressive (<109°) and tensile (>109°) sense. The *total* strain per CH_2 group for cyclanes (i.e. saturated cyclic hydrocarbons) are tabulated below. Of course the *total* strain energy includes unavoidable ***Pitzer- and Prelog strain***. The former is particularly significant in small and medium rings (n=3-5 & 8-11) and the latter (see below) in medium rings (8-11).



Size of ring	Strain per CH_2 (kJ/mol)	Total Strain (kJ/mol)
3	38.4	115
4	27.5	110
5	5.19	26
6	0.09	0.54
7	3.74	26
8	5.06	40.5
9	5.86	52.7
10	5.18	51.8
11	4.30	47.3
12	1.43	17.2
13	1.66	21.6
14	0.57	8
15	0.51	7.6
16	0.50	8

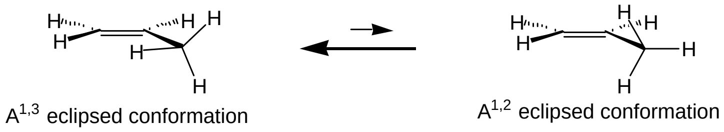
Ring strain in cyclanes

Transannular- or ***Prelog strain*** : One might question why medium rings are so strained, even though it is easy to construct puckered models for them that are free of ***Baeyer strain***. However, models of medium rings that are free of ***Baeyer strain*** tend to have large numbers of pairs of eclipsed hydrogen atoms on adjacent CH_2 groups (i.e. significant ***Pitzer strain***); moreover, with rings in the C_8-C_{11} range, such H atoms will tend to "bump" each other across the ring, leading to so-called ***transannular***- or ***Prelog strain***. Like Pitzer strain this strain arises from the van der Waals repulsions, but not between groups on adjacent carbon atoms.

The lowest energy conformation adopted by a given hydrocarbon will be that in which the most effective compromise between all these factors is attained.

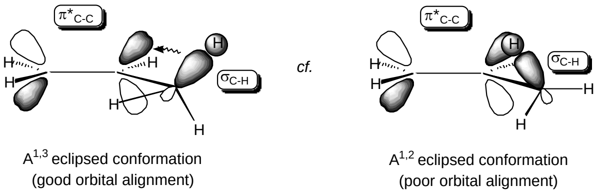
UNSATURATED HYDROCARBONS:

Sp^3 hybrid groups bonded to C-C double bonds (i.e. sp^3-sp^2 systems) prefer to exist in an ***A^{1,3} eclipsed*** conformation rather than an A^{1,2} eclipsed conformation. These conformations can be compared with those of eclipsed and staggered as analysed above for sp^3-sp^3 systems. For propene the barrier to rotation is 8.0 kJ/mol (*cf.* propane 14.8kJ/mol).

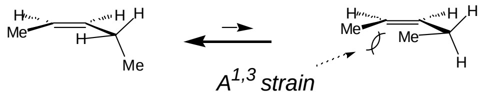


Enthalpy diffference between conformers
ΔH° = +8.0 kJ/mol

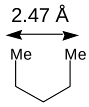
This preference is stereoelectronic in origin. The ***A^{1,3} eclipsed*** conformation allows for better overlap of the orbitals for a $\sigma_{C\text{-}H}$->$\pi^*_{C\text{-}C}$ stabilising interaction relative to the corresponding interaction in the ***A^{1,2} eclipsed*** conformation. This better overlap is a consequence of the ~109° angle subtended by the 'lobes' of the $\pi^*_{C\text{-}C}$ orbital relative to the C=C axis. This is also of course why more substituted double bonds are more stable than less substituted ones.



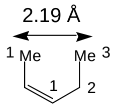
However, van der Waals interactions dominate affairs when groups other than H are involved. C-C double bonds are shorter than C-C single bonds; the two Me groups in alkene **B** are therefore brought in closer to one another than they are in the corresponding alkane **A** which suffers a ***syn pentane*** interaction in the conformation drawn. The resulting eclipsing interaction is consequently more costly (16.3 kJ/mol) and is referred to as ***$A^{1,3}$ allylic strain***.



Enthalpy diffference between conformers
$\Delta H° = +16.3$ kJ/mol

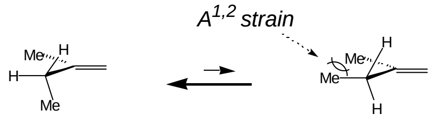


A
+15.4 kJ/mol

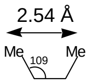


B
+16.3 kJ/mol

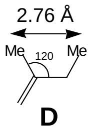
The C-C-C angle in an alkane (~109°) is smaller than a C-C-C angle in an alkene (~120°). As a result, in comparison to an eclipsed butane interaction (**C**), in the related alkene (**D**) the Me groups are more distant and the torsional strain is lower. This type of eclipsing interaction in olefins is referred to as ***$A^{1,2}$ allylic strain***.



Enthalpy diffference between conformers
$\Delta H° = +12.6$ kJ/mol



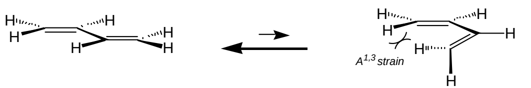
C
+13.0 kJ/mol



D
+12.6 kJ/mol

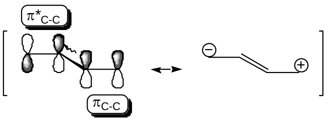
From this analysis we can see that the lowest energy conformation of an alkene will be a compromise between minimising ***$A^{1,3}$ allylic strain*** and ***$A^{1,2}$ allylic strain***. The former is the more significant interaction and consequently the conformation adopted by a more complex alkene is typically that in which the smallest group is $A^{1,3}$ eclipsed.

Dienes contain sp^2 hybrid groups bonded to C-C double bonds (i.e. they are sp^2-sp^2 systems) and prefer to exist in conformations in which both double bonds are co-planar. This preference is stereoelectronic in origin. A co-planar orientation of double bonds allows for optimal overlap of the orbitals for a π_{C-C}->π^*_{C-C} stabilising interaction. Additionally, the ***s-trans*** conformation is preferred over the ***s-cis*** conformation. This is so as to minimise ***$A^{1,3}$ allylic strain***. The case of butadiene is shown below.



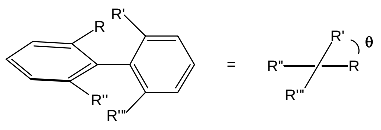
s-trans **conformation** ***s-cis*** **conformation**

Enthalpy diffference between conformers
$\Delta H° = +25$ kJ/mol

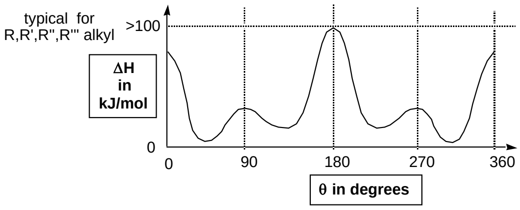


Maximum π_{C-C} -> π^*_{C-C} stabilisation for co-planar alkenes (i.e. best overlap)

Bi-aryls are interesting sp^2-sp^2 systems. These compounds suffer from extreme ***$A^{1,3}$ allylic strain*** between adjacent *ortho* aromatic substituents. These van der Waals repulsions force these compounds to adopt conformations in which the rings are not co-planar but have a dihedral angle of ~45°. This is a compromise between a stereoelectronic preference to be co-planar (π_{C-C}->π^*_{C-C}, as above) and the aforementioned unfavourable ***$A^{1,3}$ allylic*** interactions between *ortho* substituents. If at least three *ortho* substituents are large then the co-operative ***$A^{1,3}$ allylic*** interactions restrict C-C bond rotation to such an extent that the two conformers become configurationally stable and can be isolated as enantiomers known as ***atropisomers***.



Lowest energy conformation has dihedral angle *ca.* 45°



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