Lecture IV: Structure

01-21-2020

What is structure? Crystallography defines it as precise geometric positions of every atom in the molecule. We can talk about absolute positions, but they are largely irrelevant - relative positions are more important.

A–B is fully described by a bond length

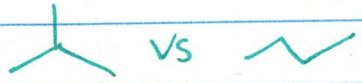
A–B–C " " " " 2 bond lengths and one angle.

A–B–C–D: 3 bond lengths, 2 angles, 1 torsional angle

For any linear molecule, we need $3n-6$ coordinates: $n-1$ bond length, $n-2$ angles and $n-3$ torsional angles. For branched molecules, this gets even more complicated, and rarely use it. Instead, we subdivide the concept of structure:

Composition – $C_x H_y O_z \ldots$

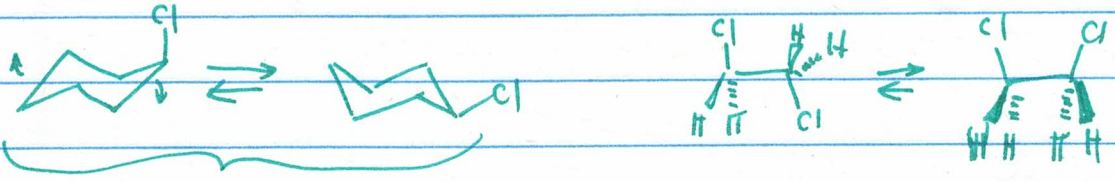
Constitution (connectivity)



Configuration } sometimes hard to distinguish, these two
Conformation } together represent the stereochemistry

Molecules with the same formula and molecular mass are called ISOMERS. They can be constitutional and stereo-isomers.

In the solid state, molecular geometries are fixed. But in solution they are not! Torsional angles change readily:

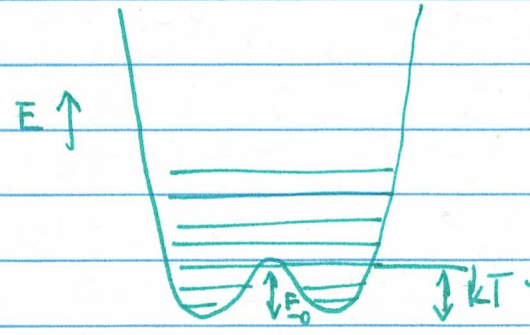


are these isomers of each other?

In IR, two signatures are observed.

In NMR, distillation, chromatography — only one molecule observed.

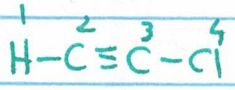
What is a molecule? What does "stable" mean?



If molecules at temp T. have enough E to jump over this barrier then it's one molecule. Otherwise it is two species — somewhat arbitrary.

Constitution

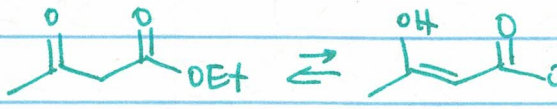
Can be described by an n^2 connectivity matrix, which atoms are connected by 0, 1, 2 or 3 bonds:



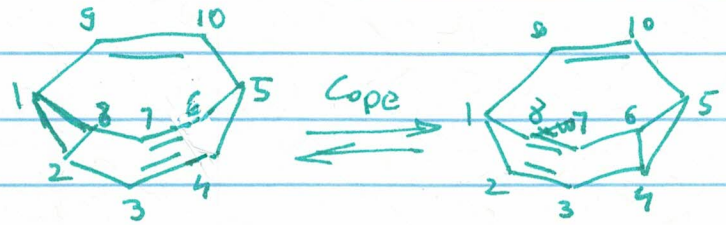
	1	2	3	4
1		1	0	0
2	1		3	0
3	0	3		1
4	0	0	1	

Bond lengths could only recently be observed experimentally by low temperature STM. So we assign them based on chemical logic.

Constitution is generally fixed, but not always:



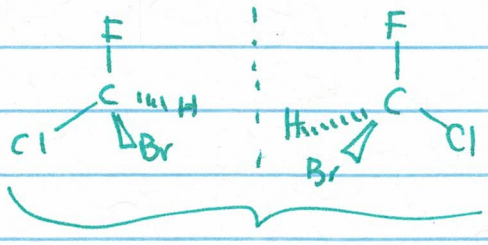
can be separated by vacuum distillation in quartz equipment



exists as 1,209,600 interconverting isomers! Call are degenerate, but ^{13}C NMR signals can be distinguished

Configuration

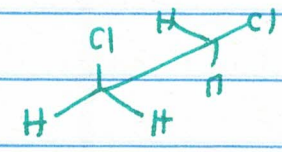
Same connectivity matrix, same constitution, but still different bc of different 3D orientation = configuration

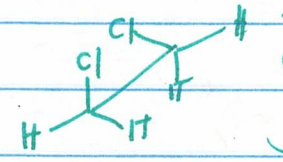


Can be isolated. Their bond angles are the same size, but differ in sign!

enantiomers = not superimposable mirror images

Are these enantiomers?



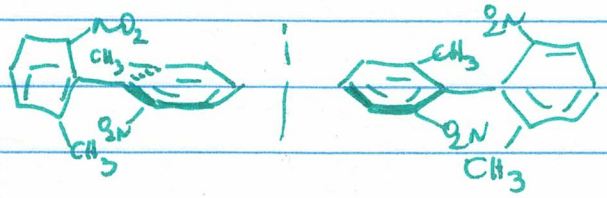


} isomers, cannot be isolated but again, T is critical!

they now differ in torsional angles, not bond angles!

CONFORMERS

The distinction gets murky in compounds with hindered rotation (atropisomers):

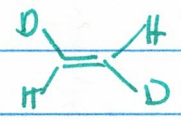


the two forms can be isolated — CONFIGURATION

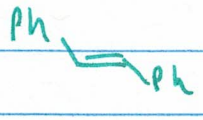
But they differ only in torsional angle — CONFORMATION

CONFORMATION

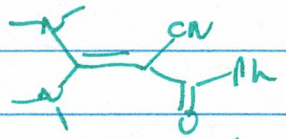
Rotational arrangement around all bonds in a molecule of a given constitution and configuration. Again, this definition would have cis/trans isomers of alkenes classified as conformers, which is weird. They are commonly considered to be configurational isomers, but energy differences vary:



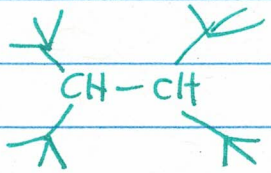
rotation barrier
55 kcal mol^{-1}



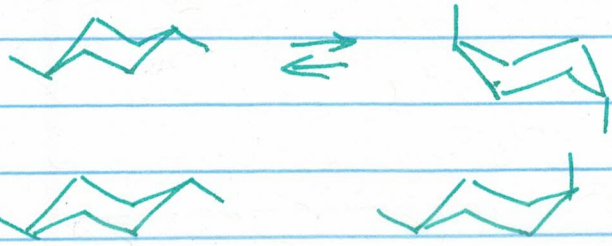
42.8 kcal/mol



15.3 kcal/mol

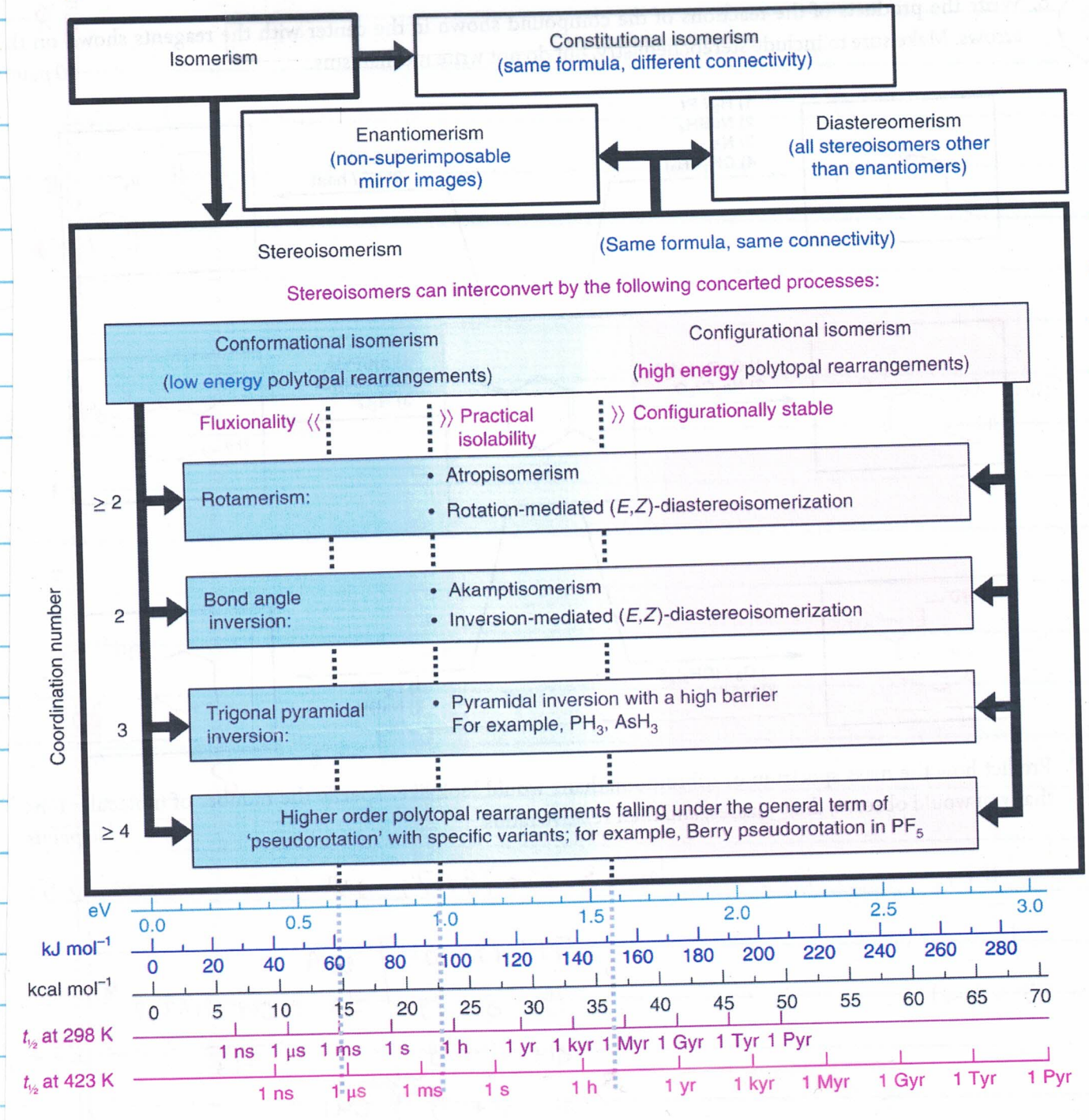


22.5 kcal/mol



Conformers

configurational isomers



From: Reimers / Crossley: Nature Chem 2018, 10, 615-624.