

Lecture B5

Valence Bond Theory

Covalent Bond Theories

1. VSEPR (valence shell electron pair repulsion model).

A set of *empirical* rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

2. Valence Bond theory.

A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals.
Works especially well for organic molecules.

3. Molecular Orbital theory.

The most modern and powerful theory of bonding. Based upon QM.

Covalent Bond Theories

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Valence Bond Theory and Hybridization

Remember Linus Pauling?

A practical man.

Ionic Radius Scale

($O^{2-} = 140 \text{ pm}$)

Electronegativity Scale

($Li = 1, F = 4$)



Linus Pauling
1901-1994

Valence Bond Theory and Hybridization

Remember Linus Pauling?

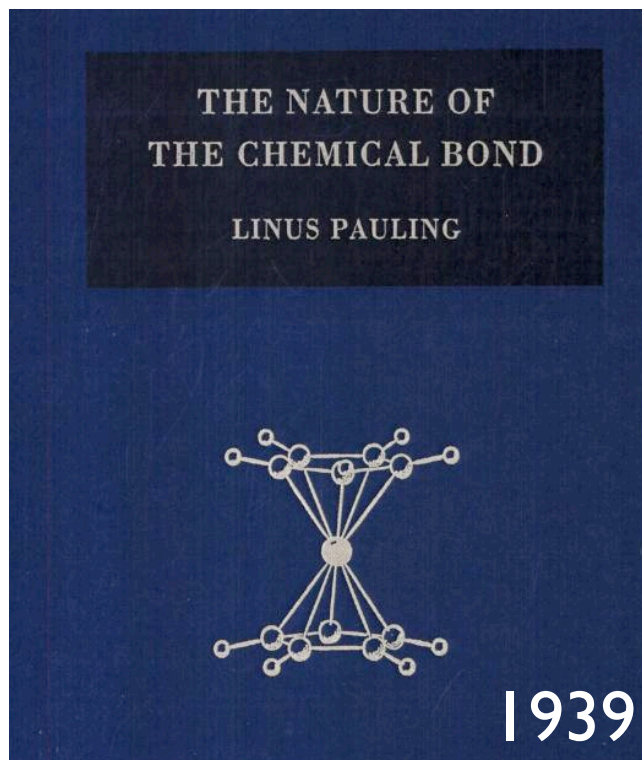
A practical man.

Comes up with an answer to the question: "How can we form tetrahedrally bonded molecules from s, p and d orbitals?"



Linus Pauling
1901-1994

Valence Bond Theory and Hybridization



The Nobel Prize in Chemistry 1954

"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"



Linus Pauling
1901-1994

Pauling wanted to understand how it is possible for s, p and d orbitals to give us all of the bonding geometries observed in molecules?

No single atomic orbital has...

linear symmetry about the central atom.

trigonal symmetry

trigonal bipyramidal symmetry

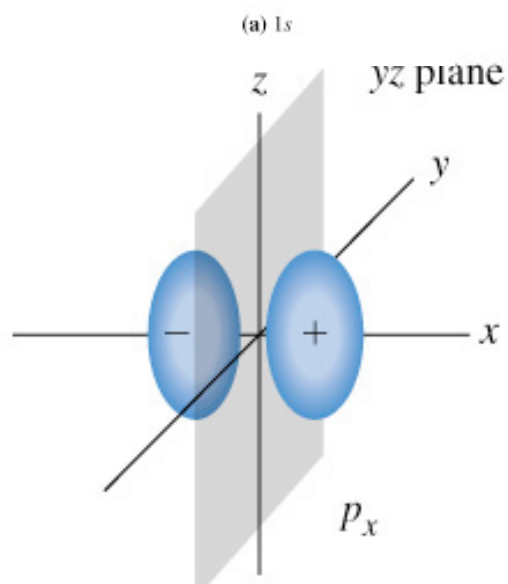
tetrahedral symmetry

etc.

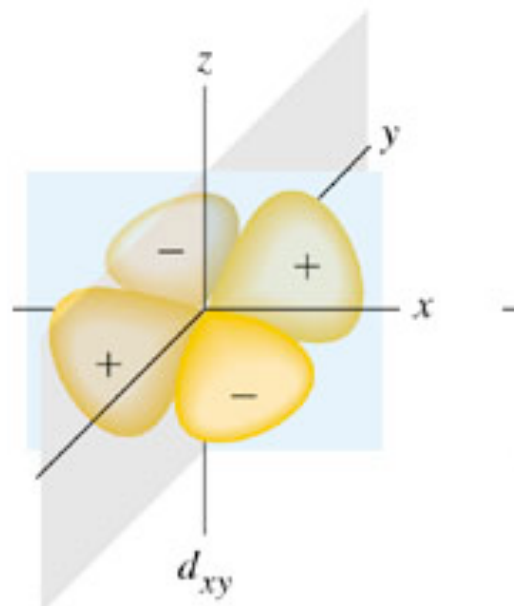
an s-orbital



How it is possible
for s, p and d orbitals
to give us all of the
bonding geometries
observed in nature?



a p-orbital



a d-orbital

Pauling's answer: a linear combination of orbitals.

sp orbitals

$$h_1 = s + p$$

$$h_2 = s - p$$

sp^2 orbitals

$$h_1 = s + (2)^{1/2}p_y$$

$$h_2 = s + (1.5)^{1/2}p_x - (0.5)^{1/2}p_y$$

$$h_3 = s - (1.5)^{1/2}p_x - (0.5)^{1/2}p_y$$

sp^3 orbitals

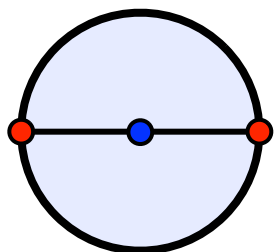
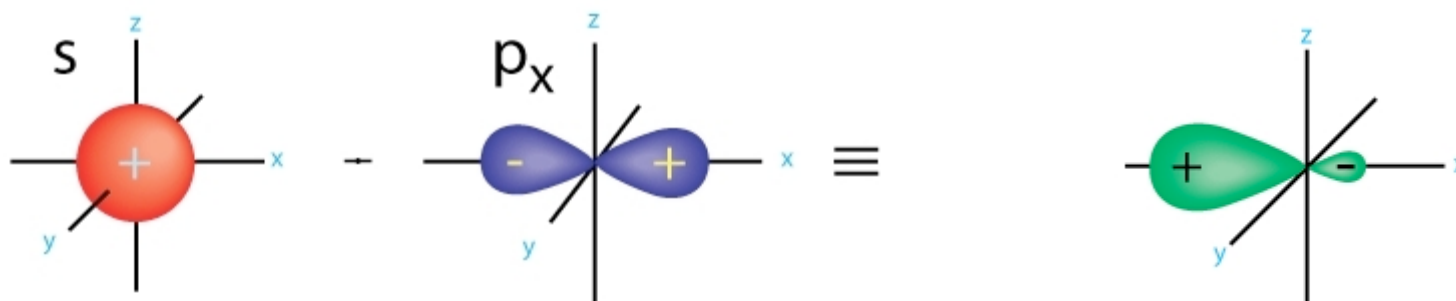
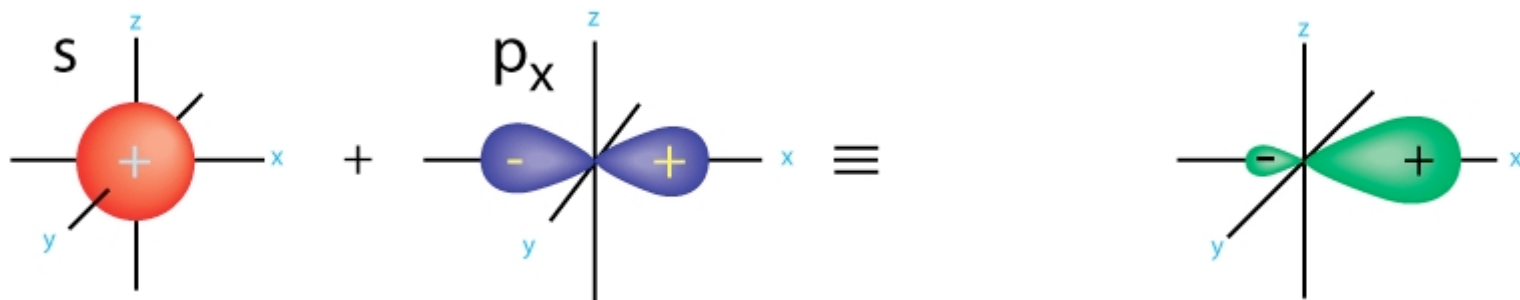
$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

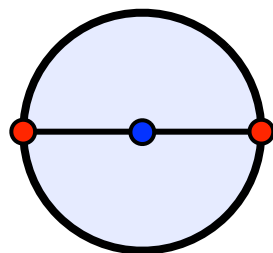
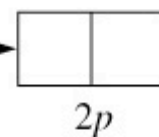
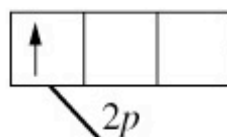
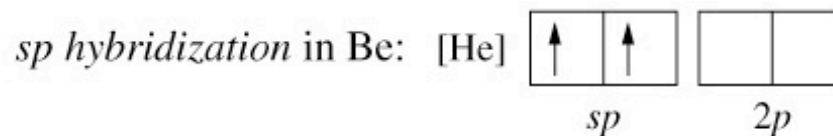
$$h_4 = s + p_x - p_y - p_z$$

Let's mix an s orbital together with a p orbital:
we create two "hybrid orbitals":



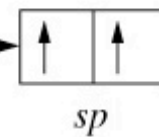
These orbitals are called "sp hybrid orbitals".

Beryllium needs a linear orbital for use with 2 valence electrons.



linear geometry

e.g., BeCl₂



two

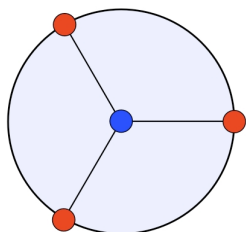
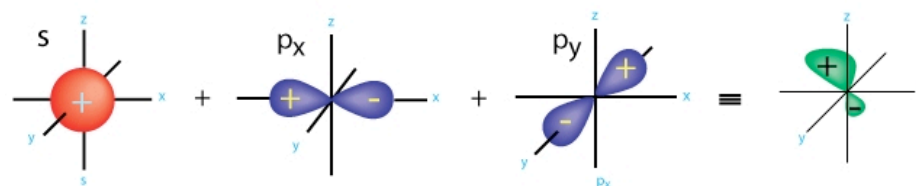
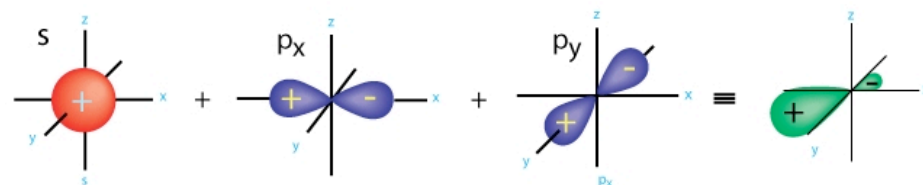
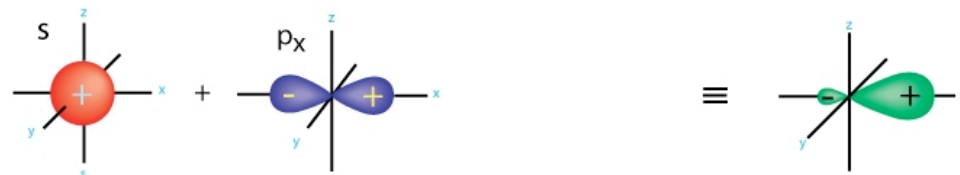
sp hybrid orbitals
capacity: **4 electrons.**

If we mix an s orbital together with **two** p orbitals, we create three "hybrid orbitals":

$$h_1 = s + (2)^{1/2}p_y$$

$$h_2 = s + (1.5)^{1/2}p_x - (0.5)^{1/2}p_y$$

$$h_3 = s - (1.5)^{1/2}p_x - (0.5)^{1/2}p_y$$

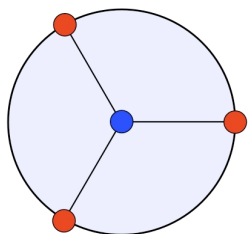


These orbitals are called "sp² hybrid orbitals".

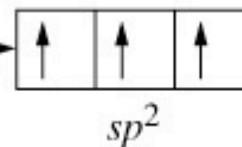
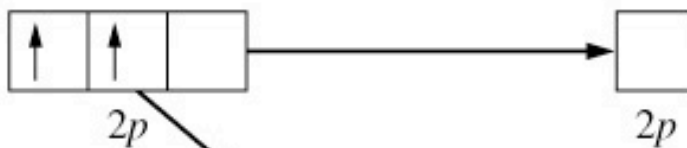
Boron has 3 valence electrons, and can use a trigonal planar orbital geometry.



two 2p-orbitals
capacity: 2 electron ea.
total: **4 electrons.**



trigonal planar
geometry

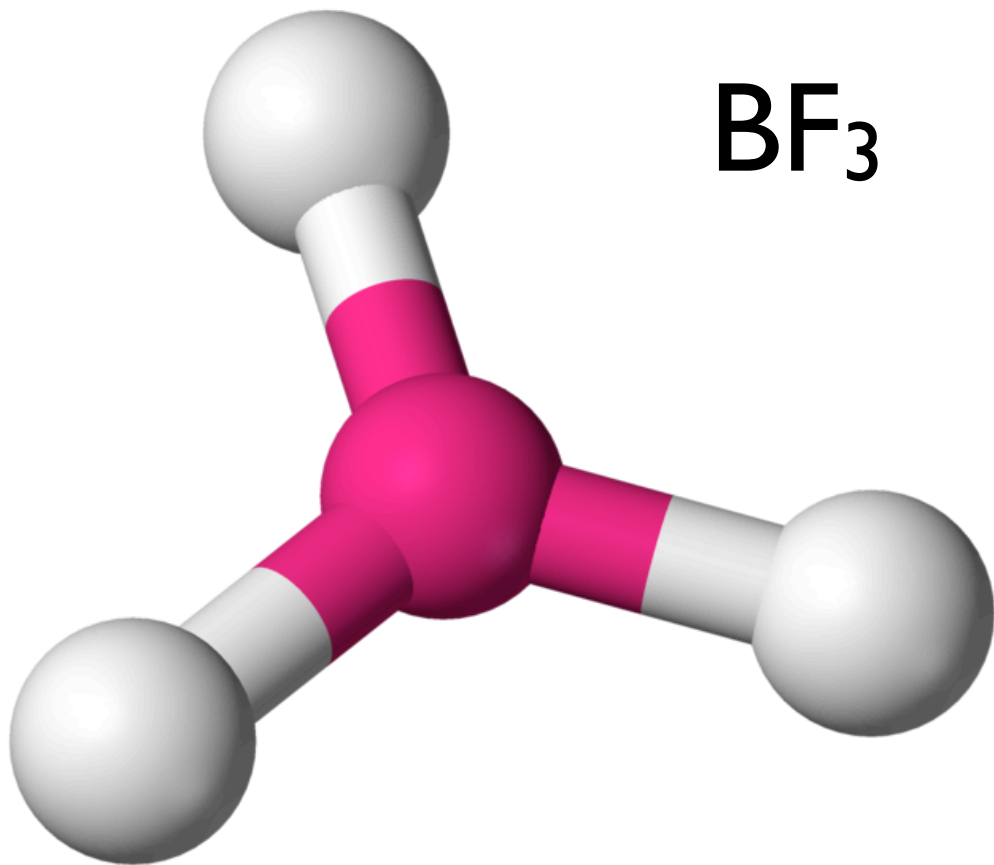


three
sp² hybrid orbitals
capacity: **6 electrons.**

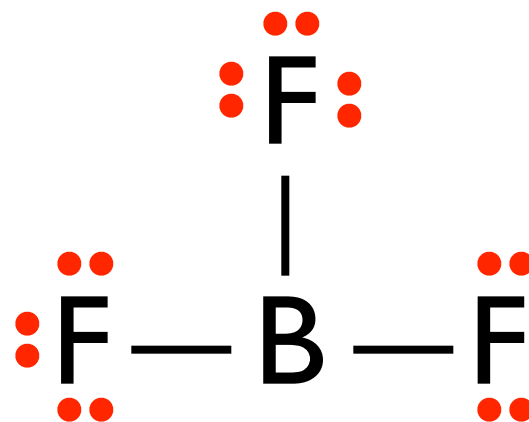


one 2s-orbital
capacity: 2 electron
total: **2 electrons.**

e.g., BF₃



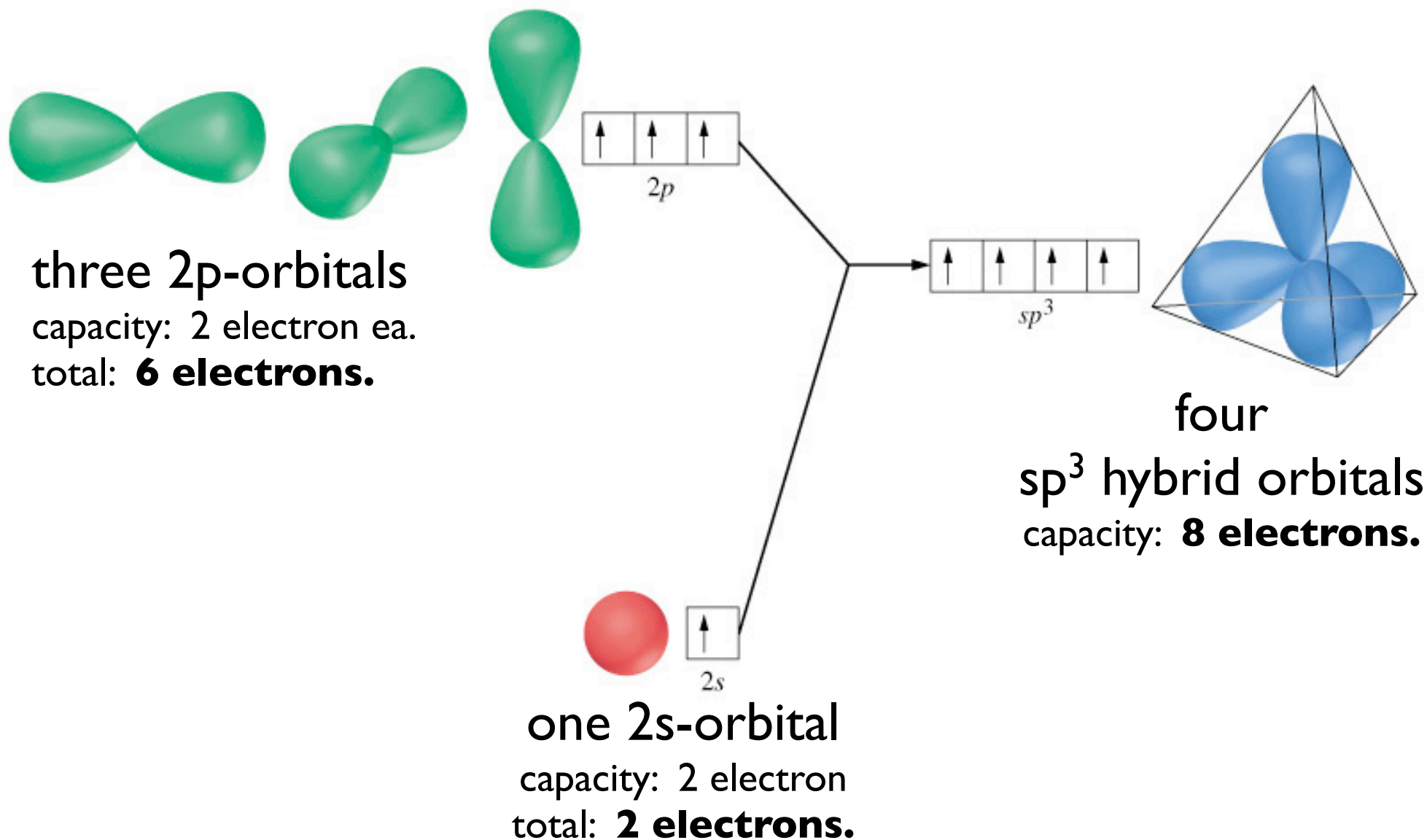
24 electrons



F-B-F angle: 120°

Trigonal Planar Geometry

And finally, to make hybrid orbitals with the right symmetry for methane, we'll mix one s orbital with **three** p orbitals:



Et voilà!

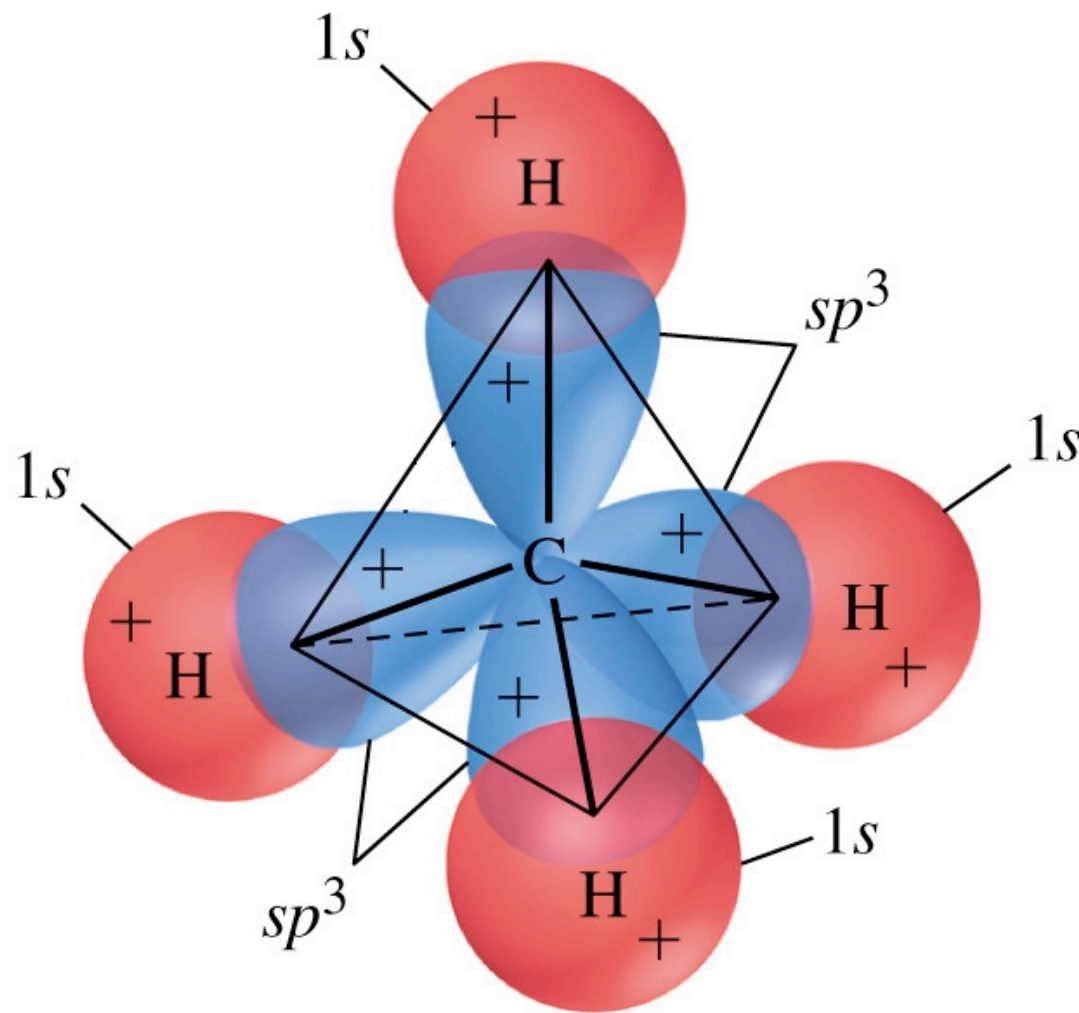
four
 sp^3 orbitals

$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$



Et voilà!

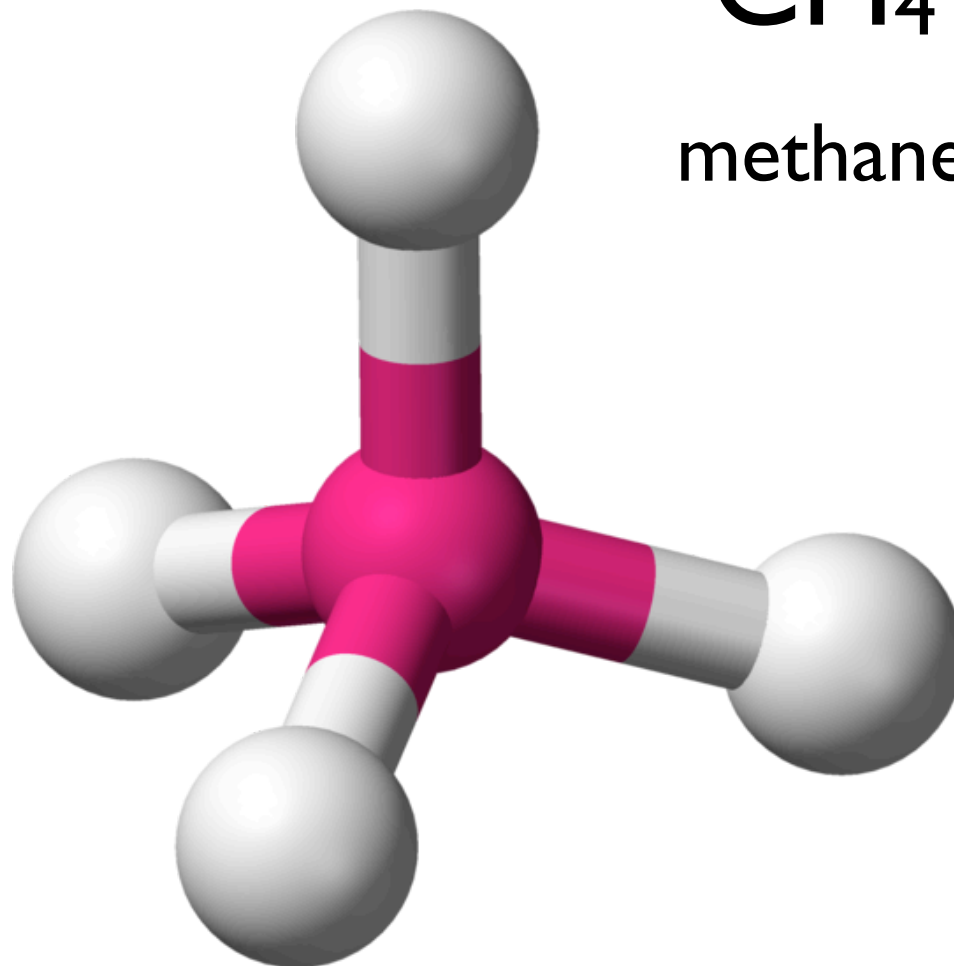
four
 sp^3 orbitals

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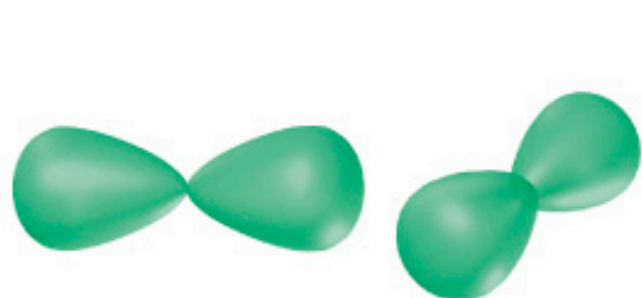
$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$

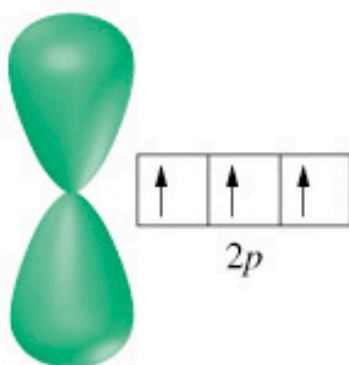


H-C-H angle: 109.47°

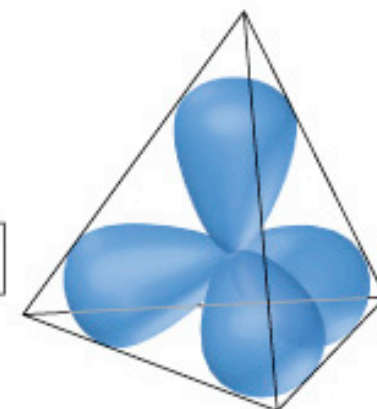
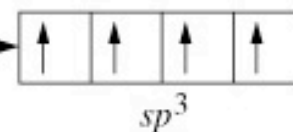
What about five (our favorite number)?
Can we mix one s orbital with **four** p orbitals???



three 2p-orbitals
capacity: 2 electron ea.
total: **6 electrons.**



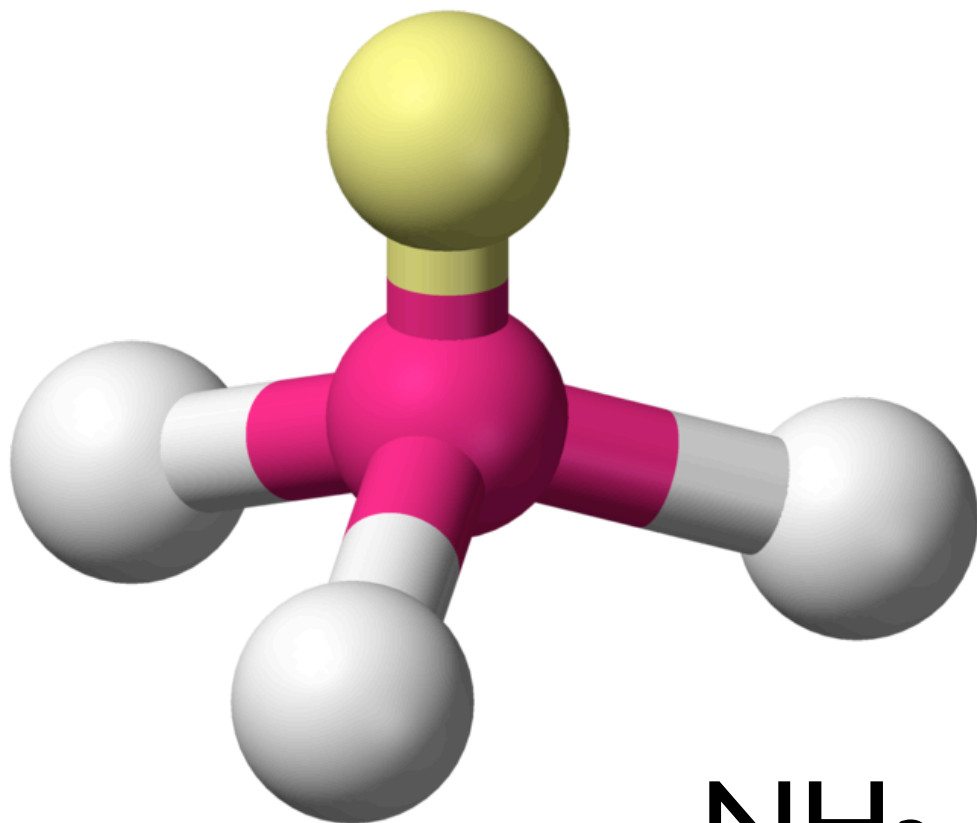
one 2s-orbital
capacity: 2 electron
total: **2 electrons.**



four
sp³ hybrid orbitals
capacity: **8 electrons.**

What about five (our favorite number)?

Can we mix one s orbital with **four** p orbitals???

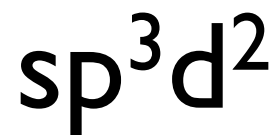
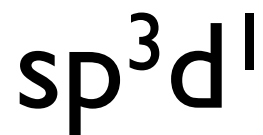


NH_3

Not really.

We just start filling up the sp^3 orbitals with lone pairs.

To get trigonal bipyramidal or octahedral symmetry,
Pauling had to employ d-orbitals in the hybrids:



These are NOT as useful (as predictors of electronic structure), so I will only mention them here briefly.

Okay, so hybridization explains the many, varied VSEPR bonding geometries.

But wait, there's more!

VB theory describes multiple bonds as the overlap between non-hybridized atomic orbitals...

...and it gives us information about molecular geometry that was missing in the Lewis Dot structures.

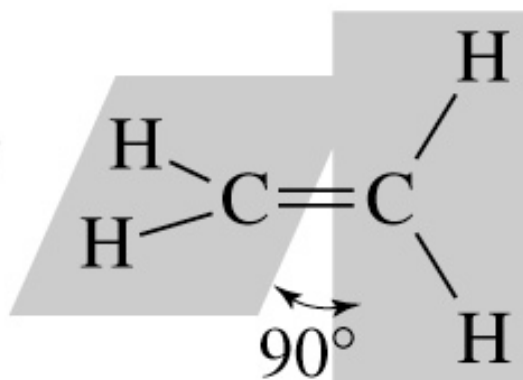
The Lewis Dot representation of ethylene tells us nothing about the relative orientation of the hydrogens, located in trigonal orbitals about each carbon. For example:

is ethylene flat?

...or twisted?



(a)

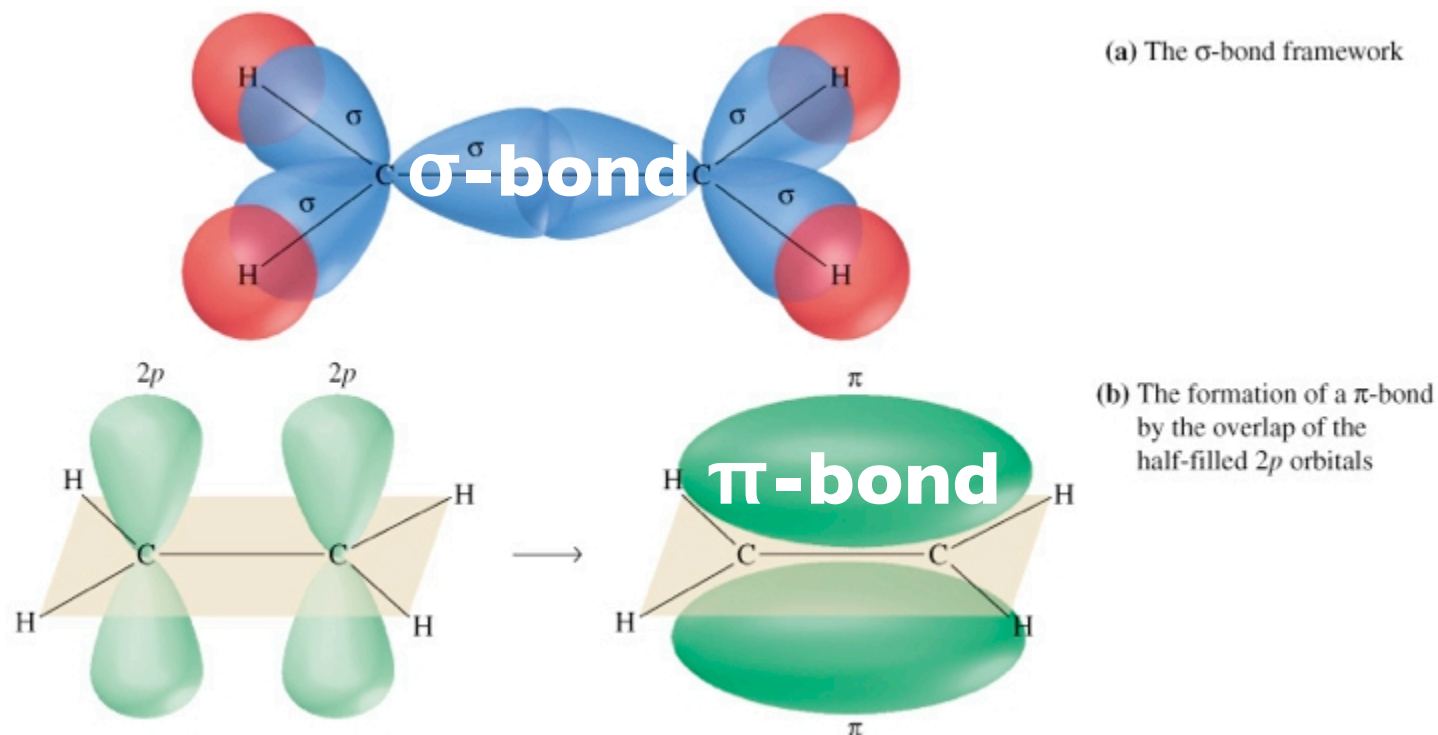


(b)



(c)

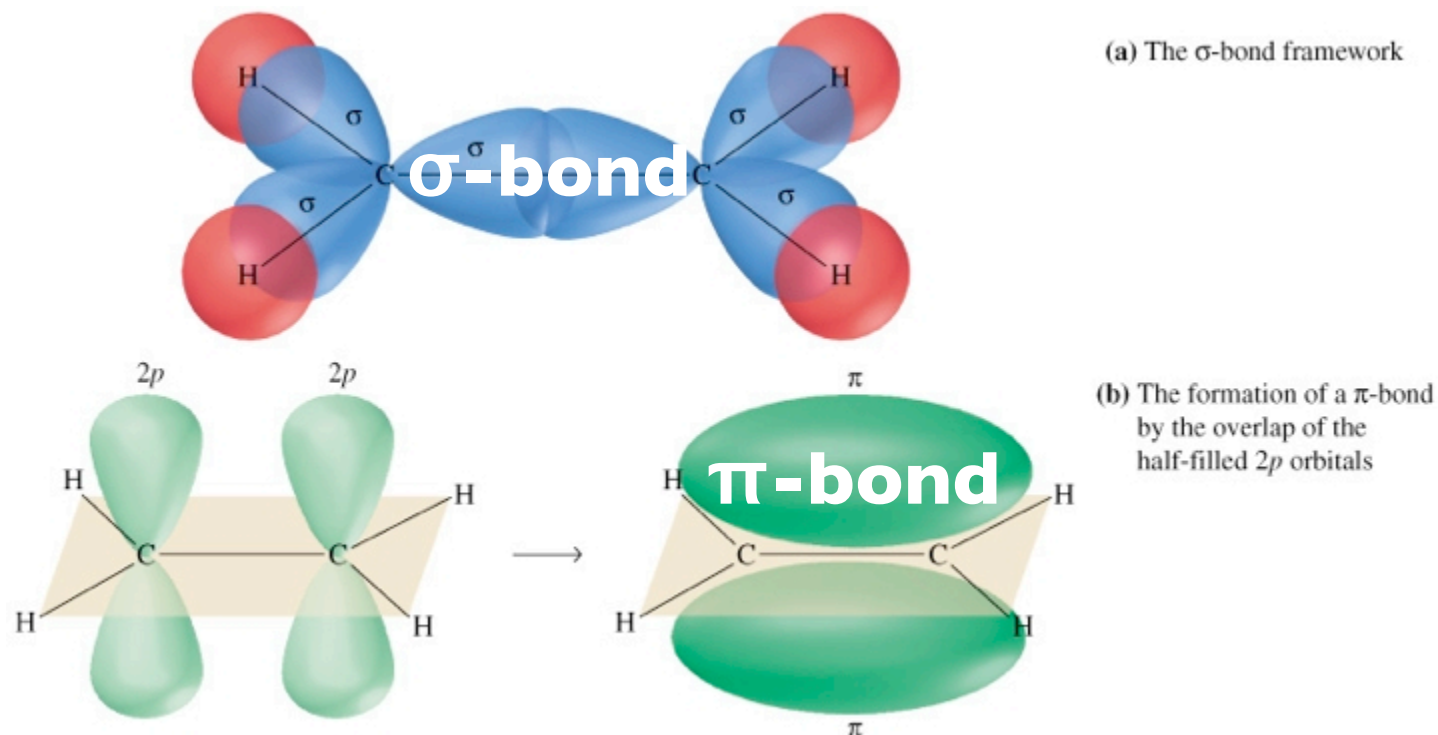
Ethylene is flat. And here's why:



On each carbon in ethylene, the four carbon valence electrons form **three** sp^2 hybrid orbitals and **one** $2p_z$ orbital.

The three sp^2 hybrid orbitals on the two carbons form three **σ bonds**.

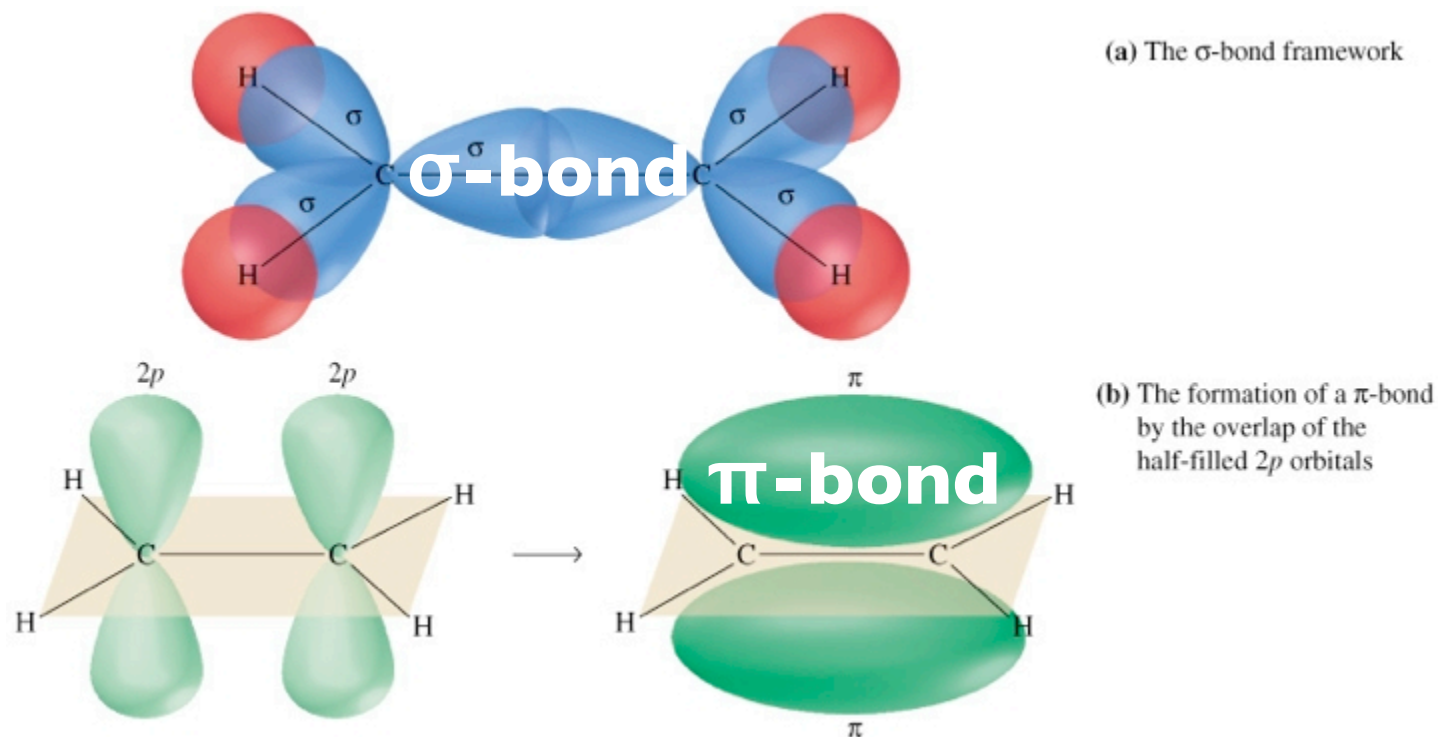
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On each carbon in ethylene, the four carbon valence electrons form **three** sp^2 hybrid orbitals and **one** $2p_z$ orbital.

The two $2p_z$ orbitals carbons overlap and form a **π -bond**.

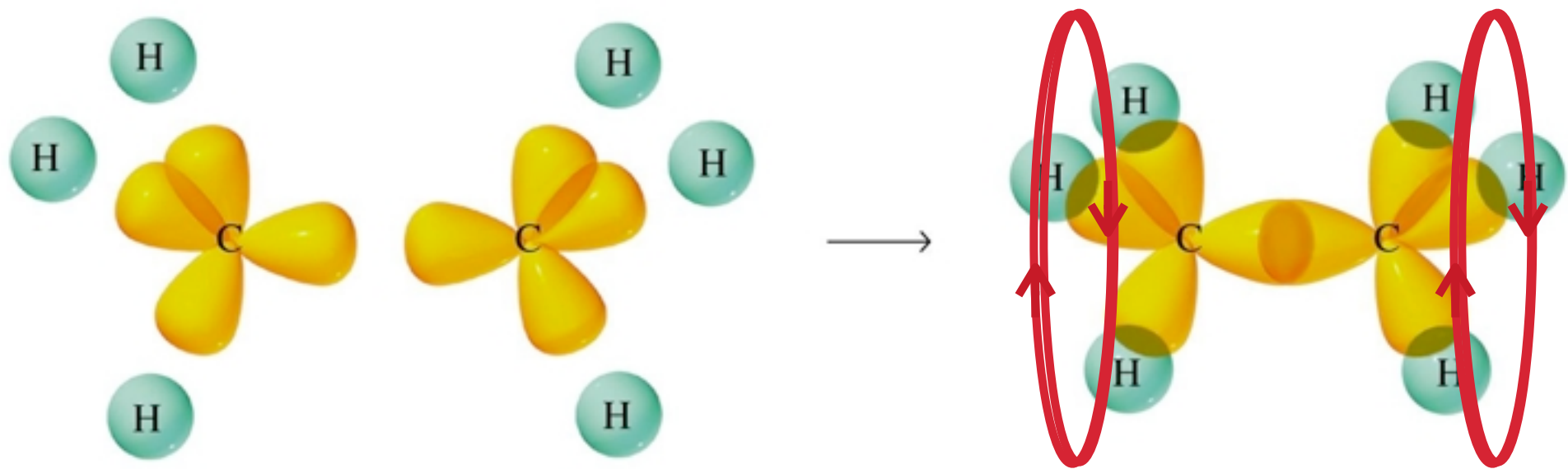
Ethylene is flat. And here's why:



The two $2p_z$ orbitals carbons overlap and form a **π -bond**.

This π -bond “locks” the CH_2 groups into a coplanar orientation with respect to one another.

In the molecule ethane (C_2H_6), on the other hand, which has no π -bonds, the two CH_3 groups are free to rotate:



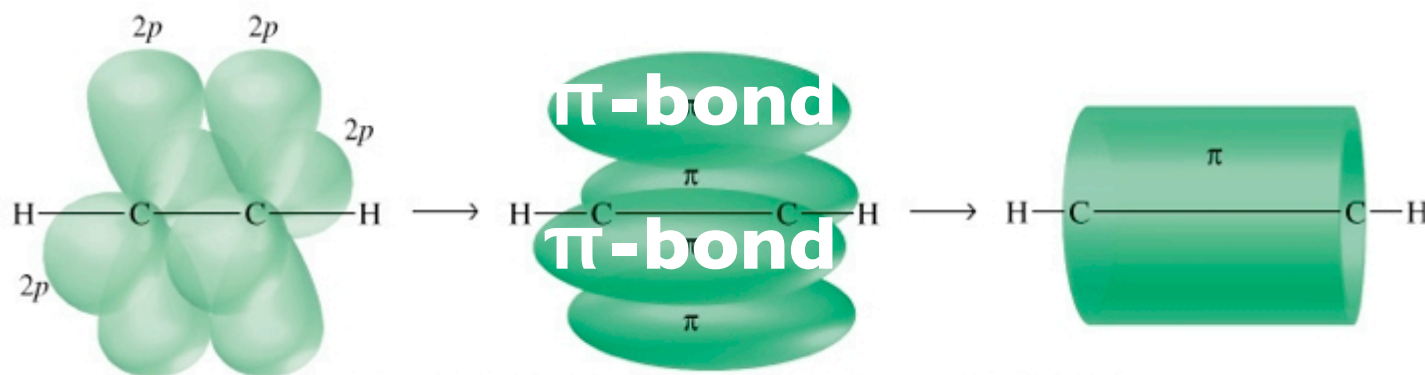
Carbon valence electrons are in sp^3 hybrid orbitals.

What about acetylene ($\text{HC}\equiv\text{CH}$)?

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Acetylene has two π -bonds, and one σ -bond:



(a) The σ -bond framework



(b) Formation of π -bonds by the overlap of half-filled $2p$ orbitals

acetylene

A Triple Bond!

And of course, there's N_2 :

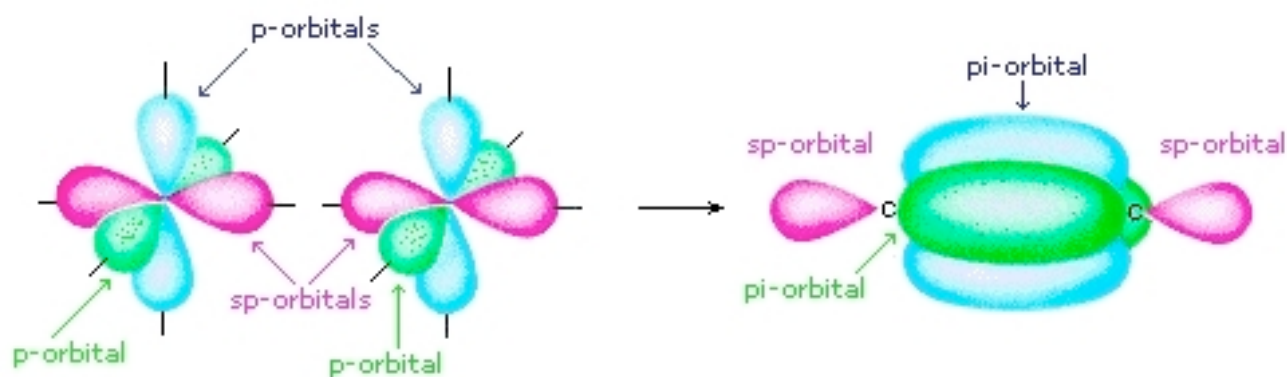
How about Double 07 (Nitrogen)?



How about Double 07 (Nitrogen)?

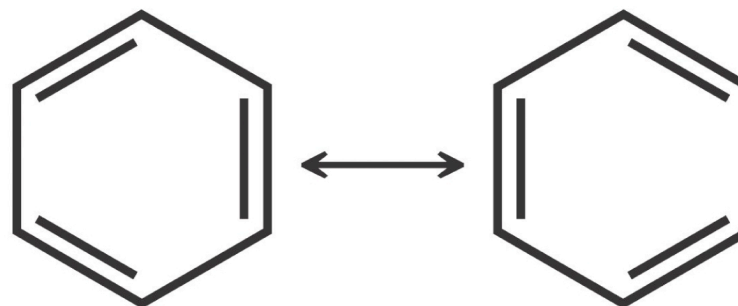
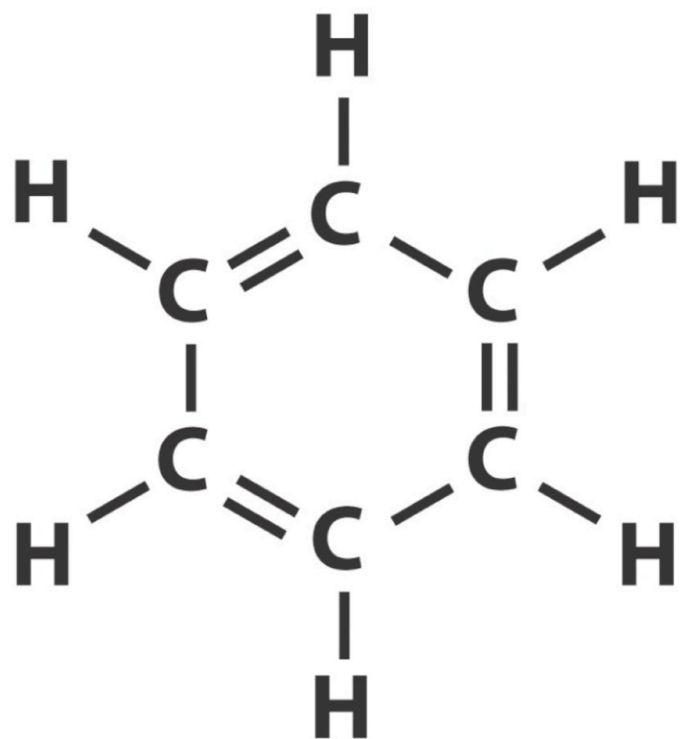


A Triple Bond!



each N atom has two sp hybrid orbitals plus two p -orbitals.

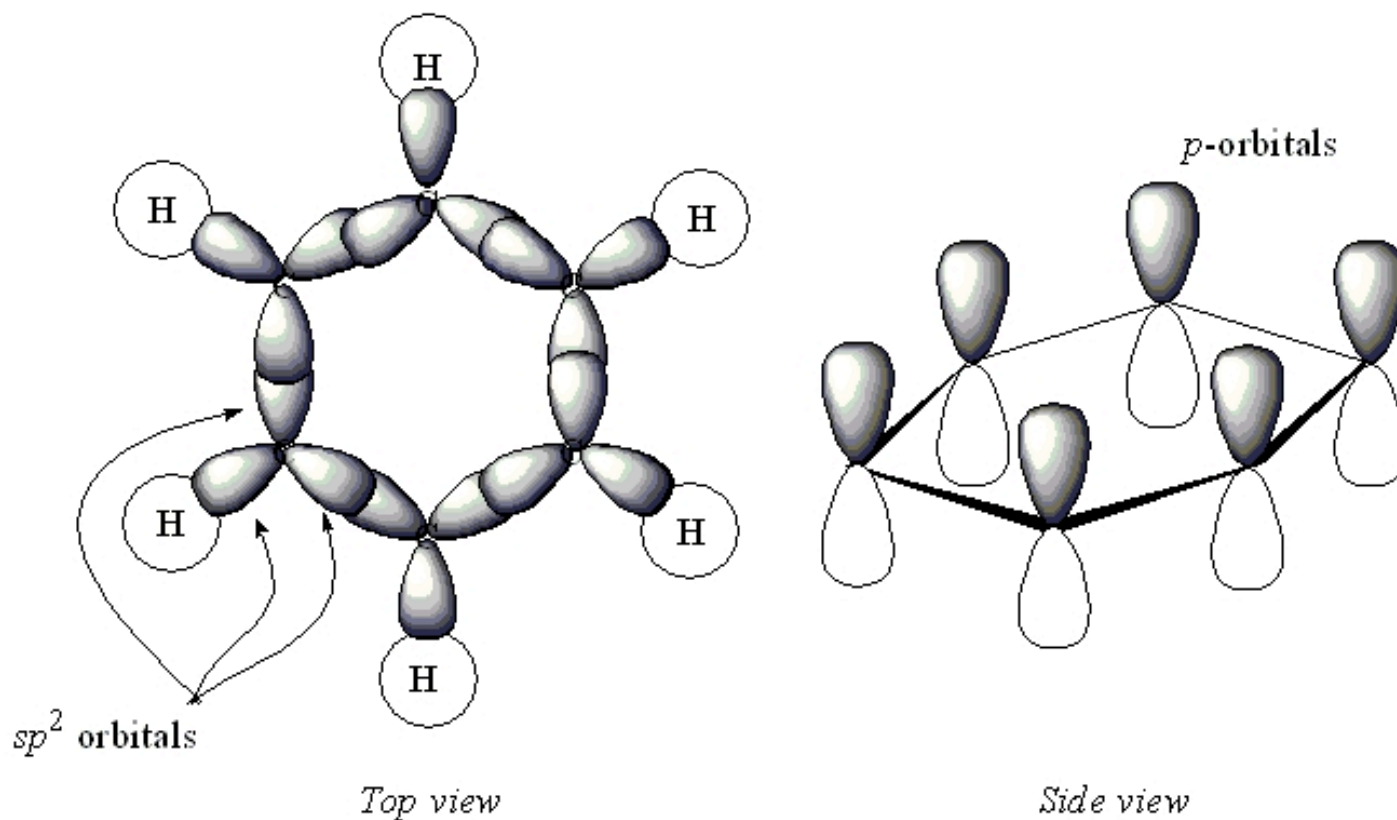
One more example: Benzene (C_6H_6)



resonance structures

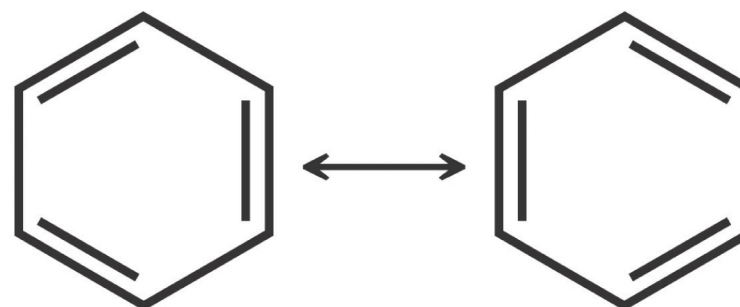
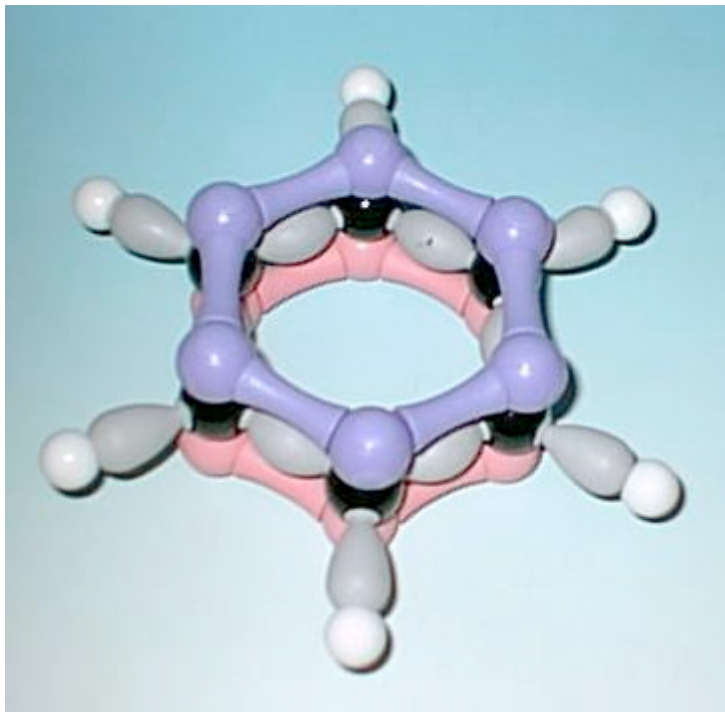
What do the carbon orbitals look like?

One more example: Benzene (C_6H_6)



Three sp^2 hybrid orbitals and one p-orbital.

One more example: Benzene (C_6H_6)



resonance structures

Resonant double bond network. We will use **Molecular Orbital Theory** to get this right.

Isomers and Conformers

The hindered rotation about π -bonds is one basis for **geometric isomerism**.

So what's an "isomer"?

i•so•mer |'isəmər|

noun

1 Chemistry each of two or more compounds with the same formula but a different arrangement of atoms in the molecule and different properties.

Isomers and Conformers

The hindered rotation about π -bonds is the basis for **geometric isomerism**.

So what's an "isomer"?

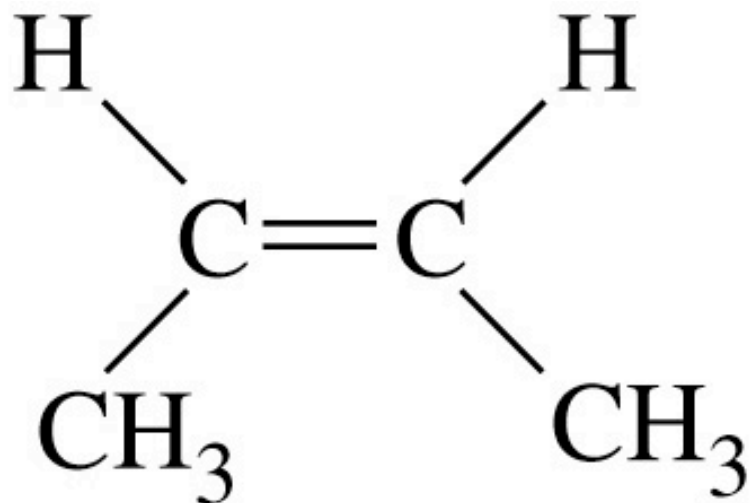
i•so•mer |'isəmər|

noun

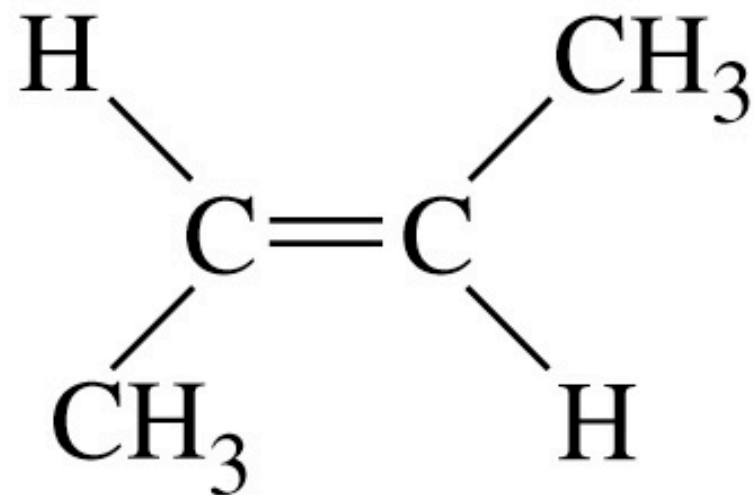
1 Chemistry each of two or more compounds with the same formula but a different arrangement of atoms in the molecule and different properties.

Isomers that can only be interconverted by breaking one or more covalent bonds.

First example: 2-butene (C_4H_8):

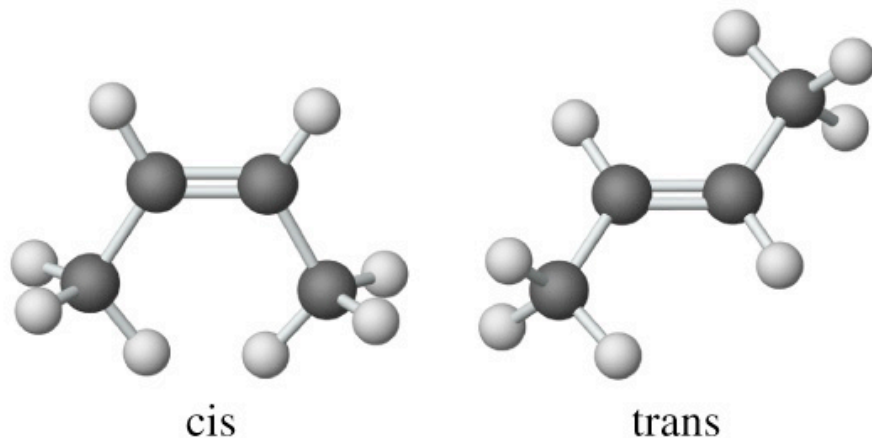


cis-2-Butene



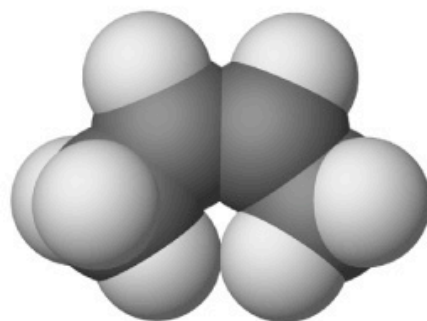
trans-2-Butene

First example: 2-butene (C_4H_8):

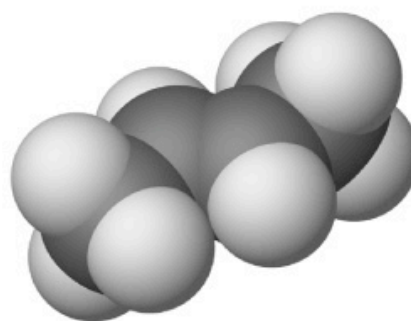


(a)

$T_b = 4^\circ C$



cis



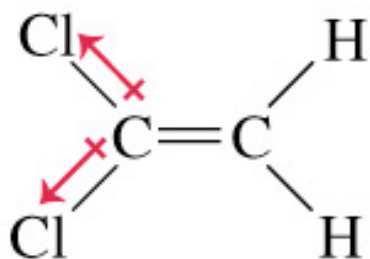
trans

$T_b = 1^\circ C$

(b)

These are different molecules, with different (but similar) physical properties.

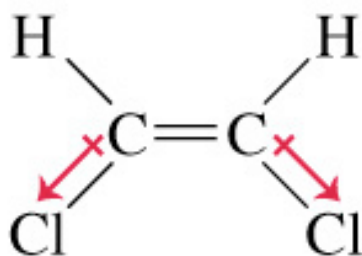
Second example: The 3 isomers of dichloroethene.



(I)

1,1-Dichloroethene

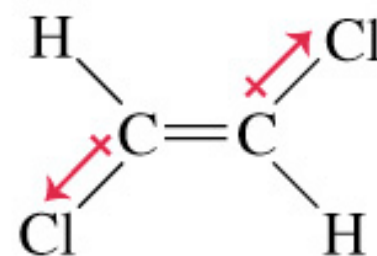
$$\mu = 2.3\text{D}$$



(II)

cis-1,2-Dichloroethene

$$\mu = 1.9\text{D}$$

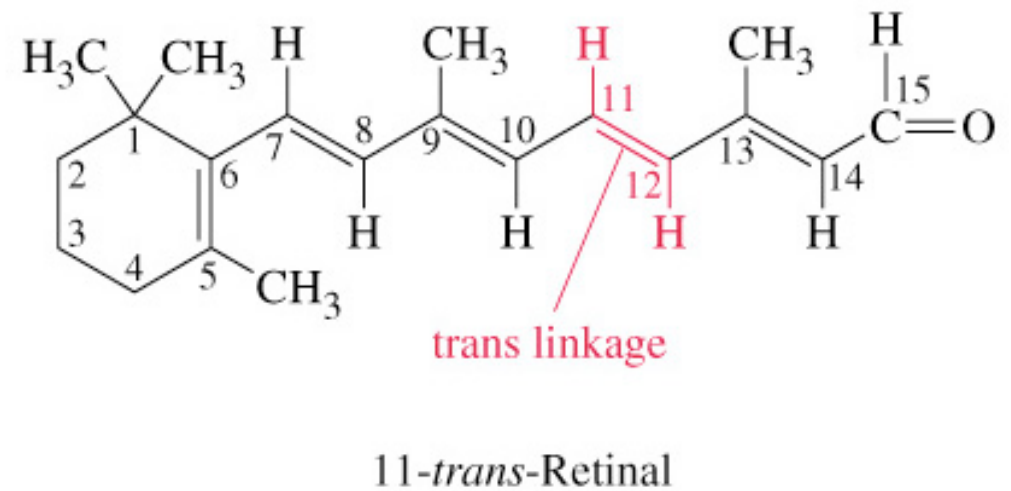
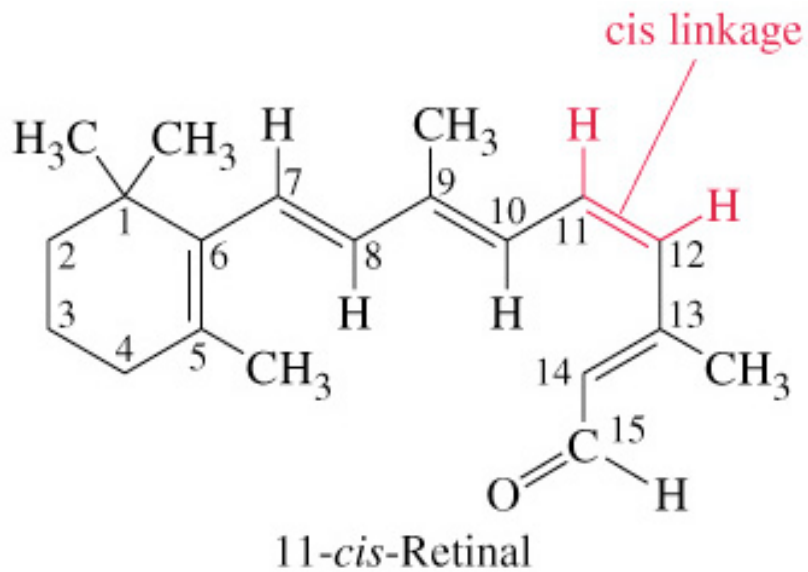


(III)

trans-1,2-Dichloroethene

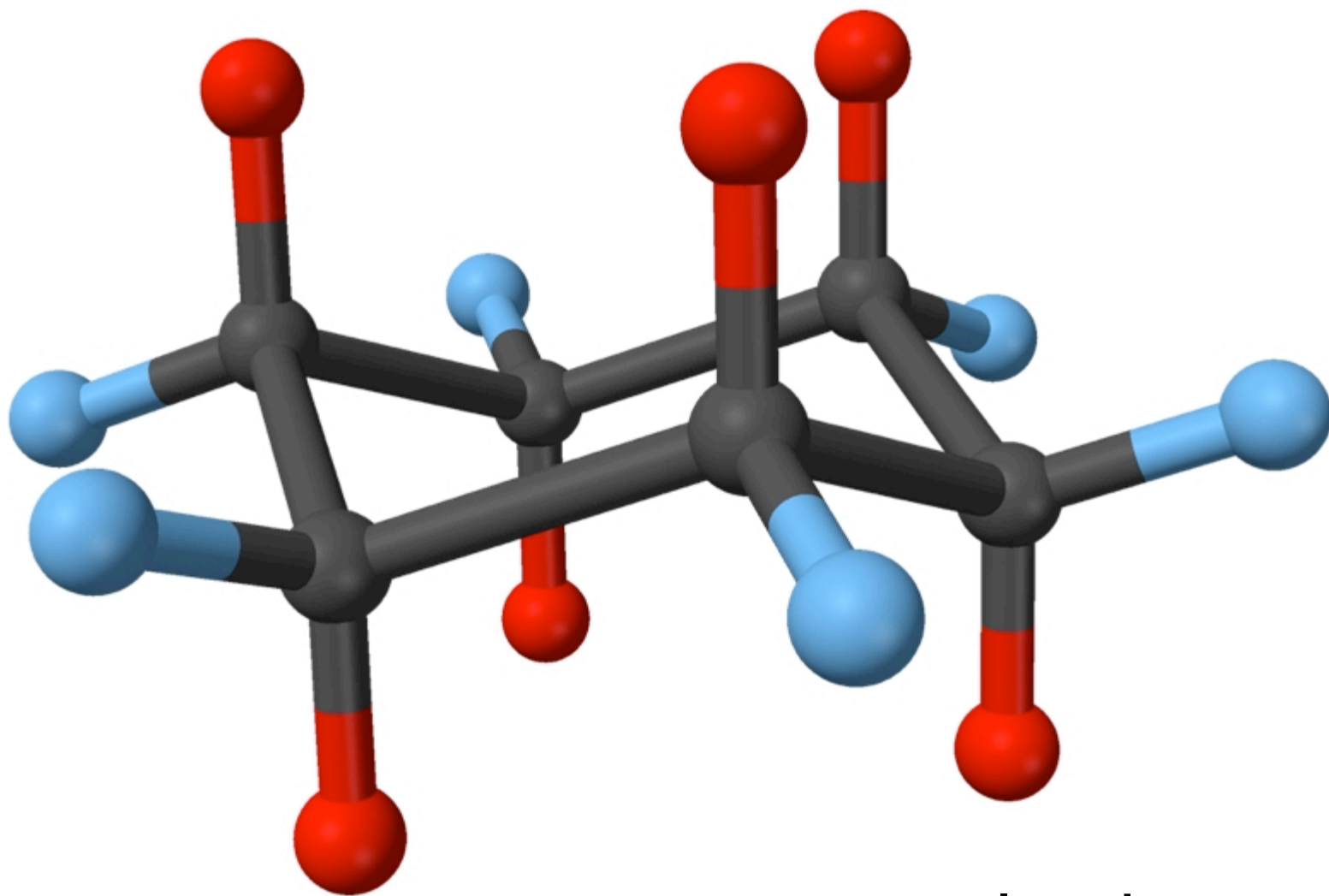
$$\mu = 0\text{D}$$

Third example: 11-cis, and 11-trans retinal



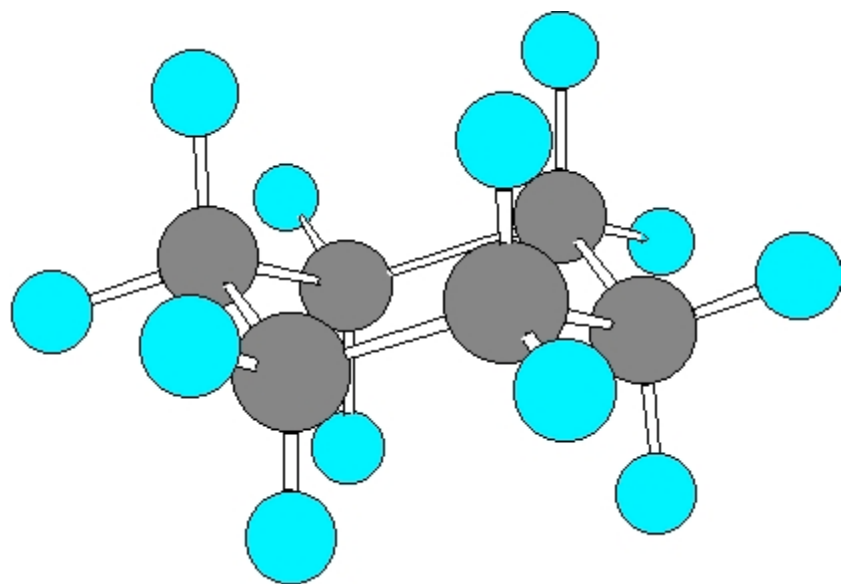
Many double bond isomers can be interconverted with light!

Cyclohexane, chair conformation:
Isomer or conformer?

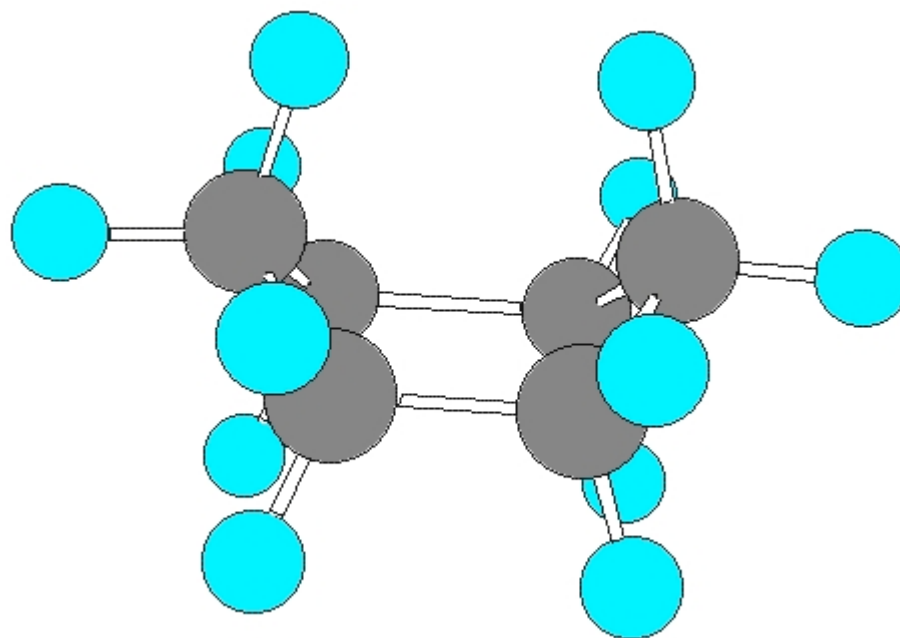


axial and equatorial
hydrogens

Conformers are more interchangeable -- no bonds need to be broken in order to switch between them.



chair



boat

two conformations
of cyclohexane