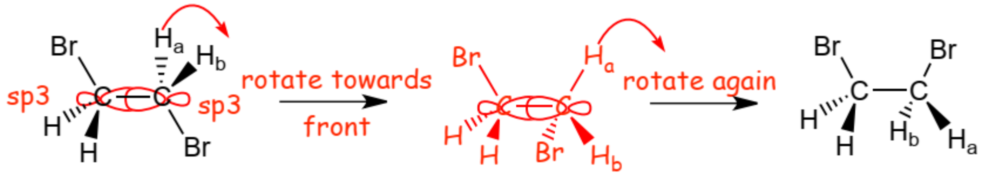
Bonding and Structure Part 2 Organic Molecular Structure

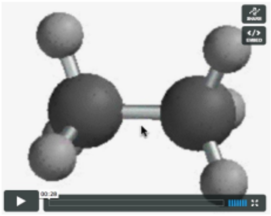
Now that we have a good understanding of how molecules are constructed, and have been introduced to the main **models** that describe bonding, specifically Lewis Structures and Molecular Orbital theory, we are in a position to understand more details of molecular structure and the properties of molecules.

1 Revisit Isomers: Stereoisomers

- We have already seen that isomers are different compounds with the same molecular formula.
- Structural isomers differ in the order in which the atoms are connected (connectivity of the atoms), the order in which the atoms are bonded together are different: Discussed above.
- Another form of isomer, **stereoisomers**, are associated with C=C bonds arise as a consequence of TWO structural features of C=C bonds.

Structural Feature #1: Bond rotation around C-C single σ-bonds is relatively easy because rotating around a σ-bond does **not** change the overlap of the sp3 AOs that are used to make the MOs.

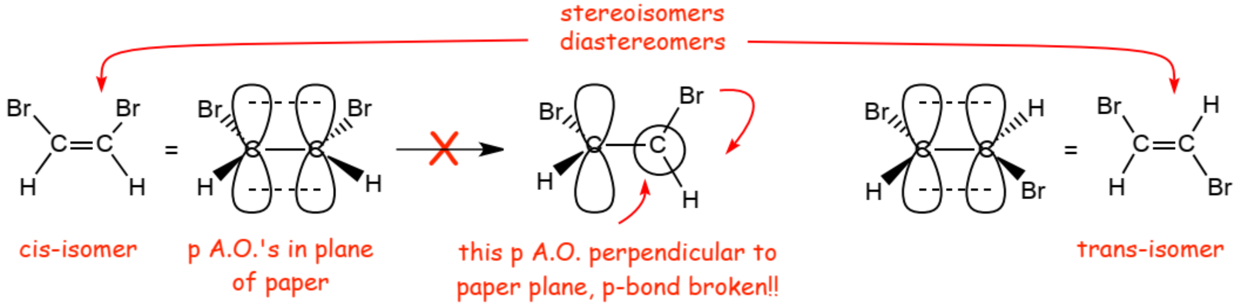


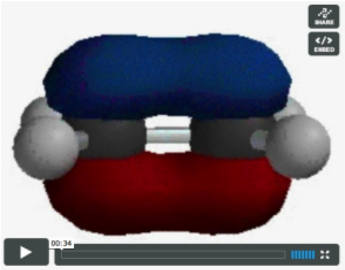


Visualize Rotation Around a Single Bond

- **Remember**, we said that the direction that bonds "point" doesn't matter when drawing structures, which is true for those that contain only single bonds, because rotation around single bonds is allowed and is easy.

However: Compare a C=C double bond, rotation around a π-bond **would destroy** the p A.O./p A.O. overlap, breaking the π-bond, the same kind of rotation is NOT possible in this case.



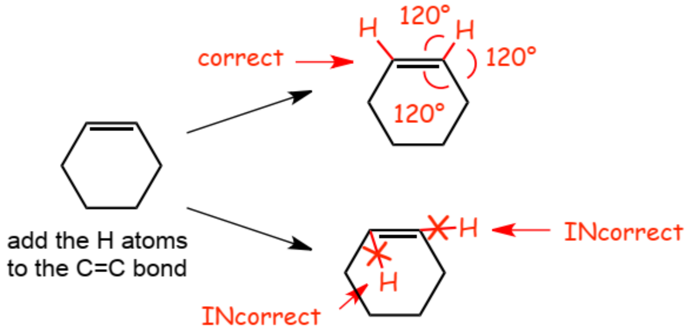


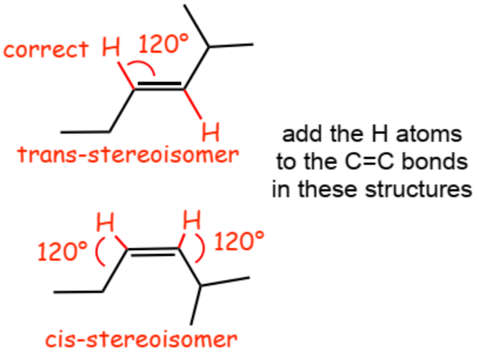
Visualize Rotation Around a Double Bond

- Rotation around a double bond is thus **restricted** (essentially, we can assume that it does not occur under normal conditions), **STEREOISOMERS CAN thus form in suitable structures that have C=C double bonds** (although not all structures with C=C double bonds will have isomers)

Structural Feature #2: The bond angles at atoms that are part of double bond are well-defined and fixed.

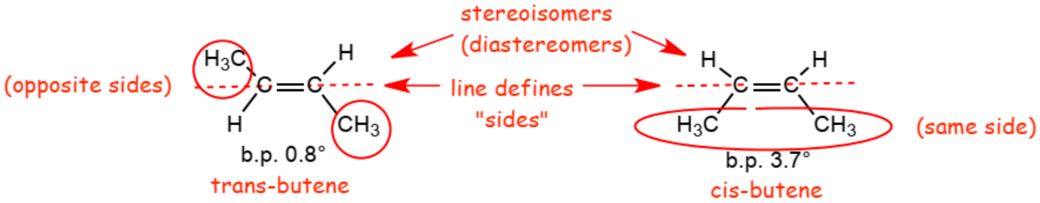
- **VSEPR** defines the bond angles as ca. 120°

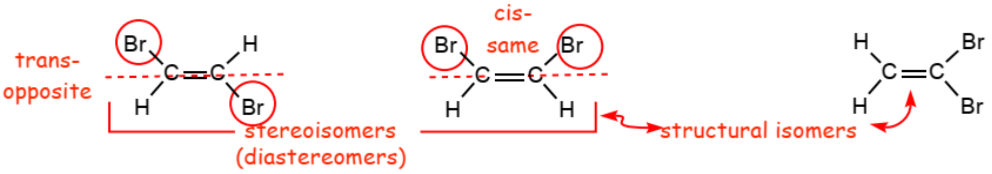




- Stereoisomers have the **same** atom connectivity (the atoms are connected together in the same order), but they differ in the orientation of at least some atoms in space (the direction in which the bonds point)
- Their physical and chemical properties are **different**, they are different structures, different molecules
- There are **different names for stereoisomers**! This can be confusing but we use the simplest terminology
- The stereoisomers that we discuss in this section are called geometrical isomers, but that is an older term, they are also sometimes called configurational isomers, but the term *cis-/trans-* isomers is probably most commonly used and is very explicit (it is easy to understand), this is the term that we will mainly use
- The term **diastereomer** also applies to **this kind of stereoisomer**, and we will use it to distinguish from another kind of stereoisomer that we will meet later in the course although we will probably mainly use *cis-/trans-* isomers.

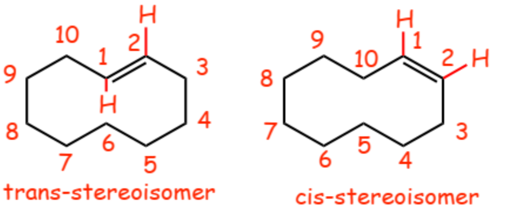
Example: Are the following structures the same or are they isomers and what kind of isomers?





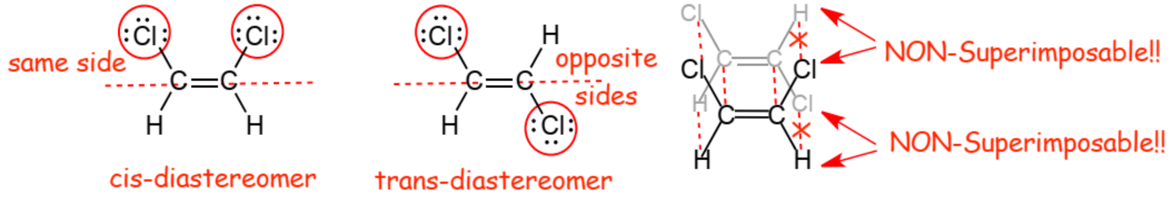
- Although the direction in which the bonds "point" doesn't matter for structures with only single bonds, **the direction in which the bonds point around the C=C bond DOES matter, they** are not arbitrary and are important and if we don't get the bonds angles correct we will not be able to identify stereoisomers

Example: Are the following structures the same or are they isomers and what kind of isomers?



the ORDER in which the atoms are connected together are the SAME: **NOT structural isomers**

Example: Are the following two structures the same or are they isomers?

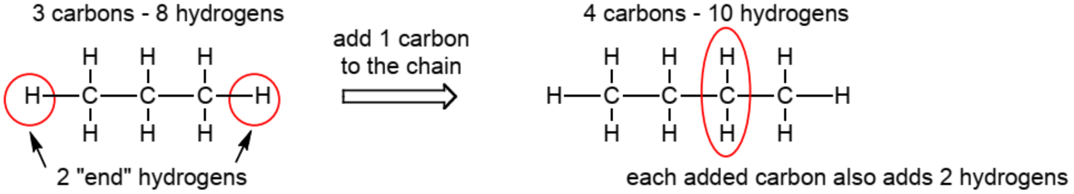


- trying to superimpose the *cis*-structure on top of the *trans*-structure fails, the structures are non-superimposable, because they are stereoisomers, the atoms point in different directions in space
- **It is NOT NECESSARY to confirm lack of superimposability** since these structures are clearly different, however, superimposability is the most critical test for isomers and although not really needed here, we have now introduced it for when we really WILL need it later in the course.

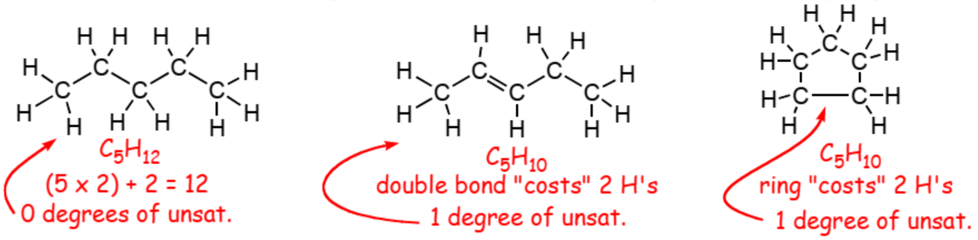
1.1 Generating Isomers Using Degrees of Unsaturation

- The degrees (ALSO KNOWN AS ELEMENTS) of unsaturation is an important piece of information about a molecule/structure that is obtained from the molecular formula

Consider structures consisting of linear chains of carbon atoms joined by single bonds. How many hydrogen atoms can be attached to these chains of carbon atoms?



- every time **ONE CARBON** is added to a chain, **TWO HYDROGEN ATOMS** are also added
- that maximum # of H's any organic molecule can have is (2 x # of carbons) **+** 2 (the "end" H atoms)
- a molecule that has the **maximum number of hydrogen atoms** is referred to as **SATURATED**
- a molecule that does **not** have the maximum number of hydrogen atoms is **UNSATURATED**
- a molecule can be unsaturated by having double or triple bonds and rings, each "cost" hydrogen atoms



Calculating Degrees (Elements) of Unsaturation

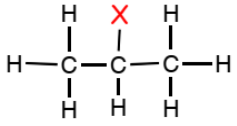
$$\text{degrees (elements) of unsaturation} = \frac{(\text{Max \# of H atoms}) - (\text{Actual \# of H atoms})}{2}$$

Where

Where: the Max # of H atoms = (# carbons x 2) + 2

What if the molecule contains other elements?

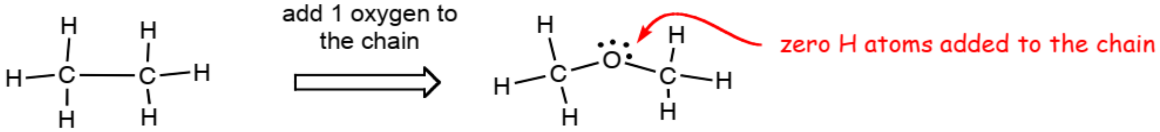
Halogens are monovalent, they take the place a hydrogen and are counted as a hydrogen



X = F, Cl, Br, I

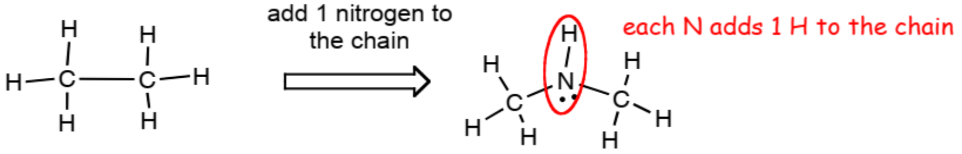
Oxygen is divalent, when an oxygen atom is added to a chain zero hydrogens are added, oxygen is IGNORED

2 carbons - 6 hydrogens 2 carbons and 1 oxygen - STILL 6 hydrogens



Nitrogen is trivalent, when a nitrogen atom is added to a chain, one hydrogen atom is also added. Thus, one nitrogen atom is equivalent to half a carbon atom as far as adding hydrogen atoms to the chain is concerned, N is counted as HALF a carbon atom

2 carbons - 6 hydrogens 2 carbons and 1 nitrogen - 7 hydrogens



Example 1 C_5H_9OCl

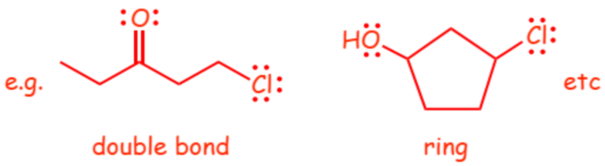
Max # of H atoms = (5 x 2) + 2 = 12

Actual # of H atoms = 9 + 1 = 10 (Cl counted as H)

degrees of unsaturation = (12 - 10) / 2 = 1 degree

C_5H_9OCl MUST have

one ring or one double bond but NOT both



(Two POSSIBLE structures are shown above, other isomers are also possible for this molecular formula)

Example 2 C_4H_7NO

C_4H_7NO

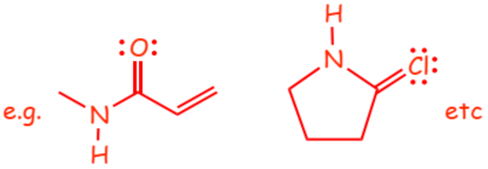
Max # of H atoms = (4 x 2) + 1 + 2 = 11

Actual # of H atoms = 7

degrees of unsaturation = (11 - 7) / 2 = 2 degrees

C_4H_7NO MUST have

2 rings or 2 double bonds or 1 ring and 1 double bond



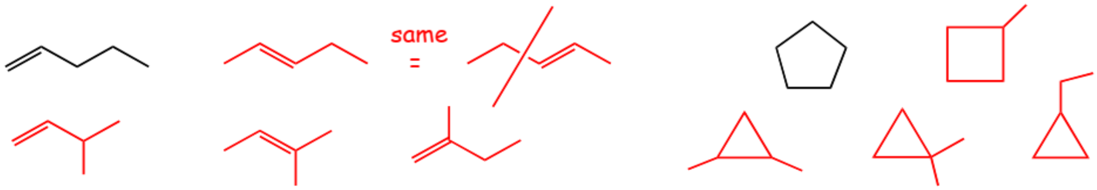
(Two POSSIBLE structures are shown above, other isomers are also possible for this molecular formula)

Knowing the degrees (elements) of unsaturation helps in drawing Lewis structures, from the molecular formula you can determine the number of double bonds, rings etc.

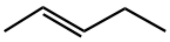
Example: Generate as many line-angle structures as you can that have the molecular formula C_5H_{10}

$$\text{degrees (elements) of unsaturation} = \frac{(5 \times 2) + 2) - (10)}{2} = 1 \text{ degree}$$

- THEREFORE, all structures must have ONE double bond or a ring, but not both….
- RECOMMENDED APPROACH: start with the longest chain and progressively and systematically branch
- where rings are possible, start with the largest ring and progressively get smaller



- **A maximum of TEN possible STRUCTURAL ISOMERS can be drawn, AND one PAIR OF STEREOISOMERS**



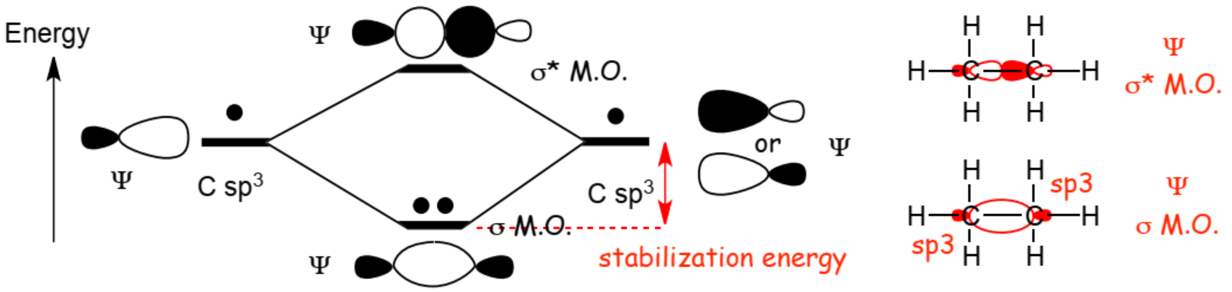
trans-isomer (from above)

cis-isomer

2 Polar Bonds

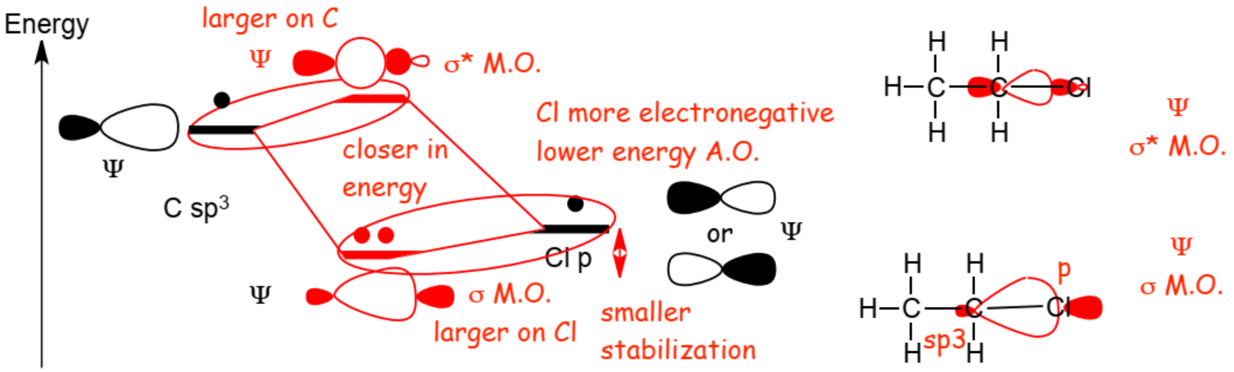
- Understanding unequal distribution of electrons in bonds is crucial to understanding reactivity

Carbon-Carbon Bond in Ethane: C_2H_6

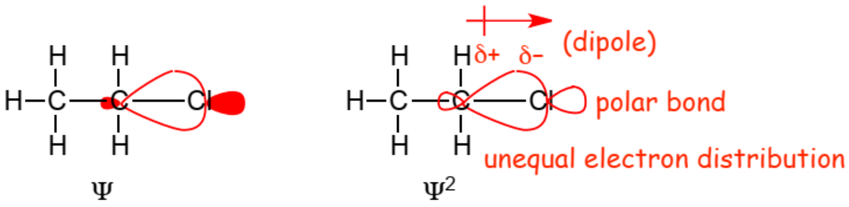


- equal contribution from each carbon A.O., electrons **equally** distributed between the two carbons in the localized σ-orbital, both electrons stabilized to same extent, **this is a NON-POLAR BOND**

Carbon-Chlorine Bond in Chloroethane: C_2H_5Cl



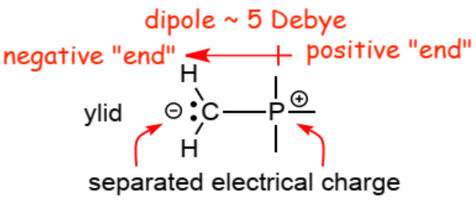
- much higher contribution from lower energy Chlorine A.O. to the localized bonding M.O.
- the electrons in the bonding M.O. are **unequally** distributed (they are closer to Chlorine since this LOWERS THEIR ENERGY), AND, there is less stabilization of the electron that was formally associated with the Cl atom
- The localized bonding σ M.O. "looks" more like Chlorine A.O., it is CLOSER IN ENERGY to the chlorine p A.O., **THIS IS A POLAR BOND**
- The localized ANTIBonding MO, "looks" more like the Carbon AO. If we use more of the Chlorine A.O. to make the bonding MO then we have a lot of the carbon A.O. "left over" that we must use to make the Anti-bonding MO, it is CLOSER IN ENERGY to the carbon sp3 hybrid AO
- The polarization of electrons via σ-bonds is called the **INDUCTIVE EFFECT**
- The wavefunction squared for the bonding electrons shows how they are not equally shared by the atoms

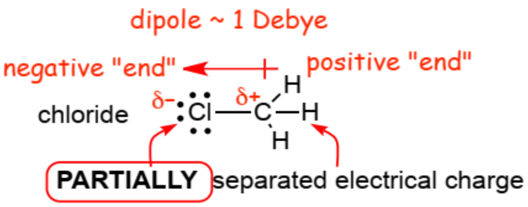


2.1 Bond Dipole Moments

- A DIPOLE MOMENT measures a separation of positive and negative charges

Example: The structure below is an ylid (ylids appear later in organic chemistry), it has opposite formal charges on adjacent C and P atoms that represents a SUBSTANTIAL separation of charges – a DIPOLE



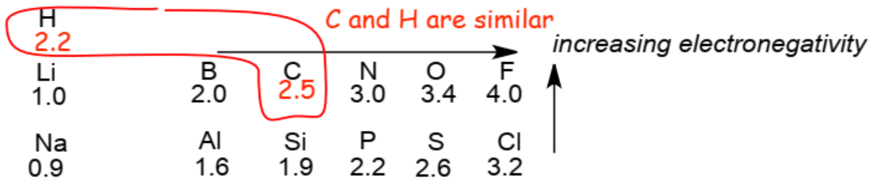


- the **extent** pf charge separation can be measured in units of Debye (D)
- Compare to the chloride above. There are no ACTUAL charges, but there are PARTIAL charges as a result of the electronegativity difference between carbon and chlorine.
- There is STILL a separation of charges in the C-Cl bond, but smaller than in the case where there are REAL CHARGES, roughly 1D versus roughly 5 D for the charged ylid

Even though the dipole moment is smaller in the uncharged molecule, it is still enough to influence chemistry, and we need to understand these

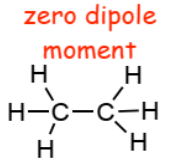
The Inductive Effect

- The unequal distribution of electrons in polar bonds is called the **INDUCTIVE EFFECT**
- The **INDUCTIVE EFFECT** occurs as a consequence of differences in electronegativity between atoms

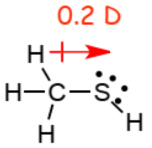


- Electronegativity increases with increasing nuclear charge (left to right)
- Electronegativity increases with decreased electron shielding (bottom to top)
- Dipole Moment measured in units of Debye (D), more polar bonds, larger D!

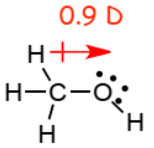
Examples



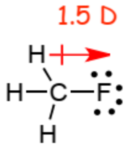
C–C bond
pure covalent



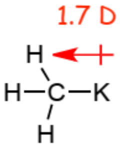
C–S bond



C–O bond

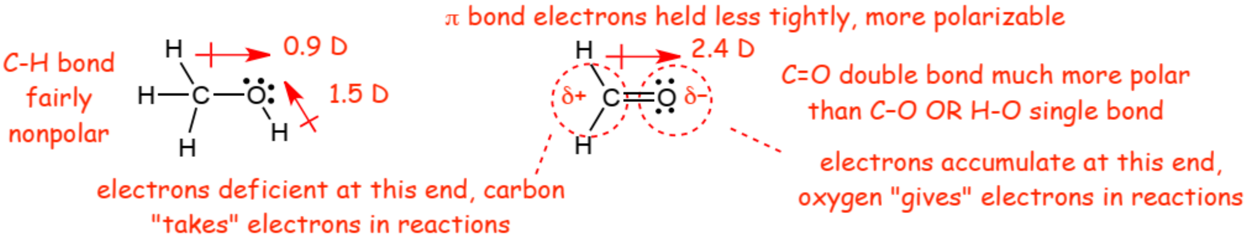


C–F bond



C–K bond
highly ionic

- Bonds have a **RANGE** of polarities and properties, **FROM** nonpolar and pure covalent **TO** highly polar almost pure ionic. You will not be asked to decide whether a bond is ionic or covalent, but you will be expected to predict relative bond polarities, which is almost the same thing as asking how ionic a bond is.
- Bond dipole moments are not something that we can measure (they are not a physical property of a molecule, but they are very useful in determining how we think about molecules and in particular, their chemical reactivity. We will use bond dipole moments a great deal when we discuss chemical reactions later.

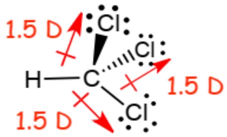


2.2 Molecular Dipole Moments

- Bond dipole moments are the property of an individual CHEMICAL BOND: They are important in determining the chemistry of specific bonds
- Molecular dipole moments are the property of an entire molecule: These can be measured by experiment, and they are important in determining the physical properties of molecules since they are important contributors to **I**nter**M**olecular **F**orces (**IMF**), that control properties such as melting point, boiling point, solubility etc.

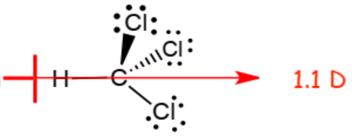
For Example

chloroform



3 C–Cl bonds have **bond** dipole moments (indicated)

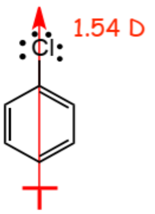
chloroform



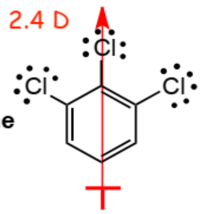
Molecular dipole moment, given by the **vector sum** of the **bond** dipoles

- Molecular dipole moments are determined as the **VECTOR SUM** of the individual bond dipole moments
- However, **it is not necessary to do vector math to solve almost all molecular dipole moment problems in organic chemistry**, you can use "common sense" to see how the individual bond dipoles reinforce or oppose each other
- Although, having said that, in reality there are some tricky cases where you really would need to at least think about the vectors, for example, the 3 vectors in trichlorobenzene below, right, add up to a LARGE molecular dipole than in chloroform, above.

chlorobenzene



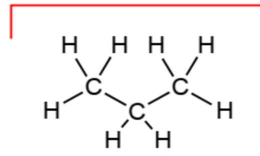
trichlorobenzene



- This is because there is "cancellation" in all vector planes in chloroform, since none of the three C-Cl bonds are in the same plane. However, the three C-Cl bonds are in the same plane when attached to the benzene ring, which results in less overall cancellation of dipole moment in trichlorobenzene compared to chloroform.
- Usually you will not be asked to compare between examples such as chloroform and trichlorobenzene, you will be asked to compare structures that are more similar.

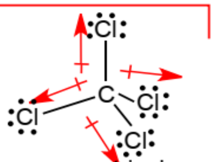
Some More Examples

NONPOLAR MOLECULES



C–H bonds essentially nonpolar

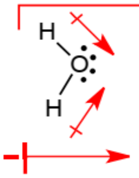
dipole moment ignored



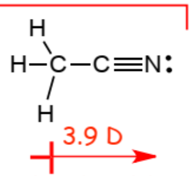
symmetrical bond dipoles cancel

zero molecular dipole moment

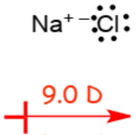
POLAR MOLECULES



1.9 D

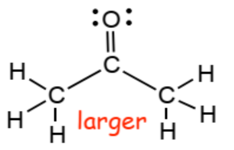


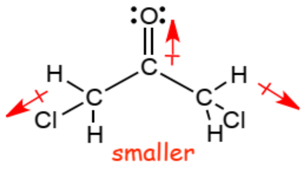
(2 π bonds)



(ionic)

Example Problem: which has larger dipole moment and why?

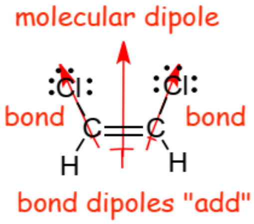


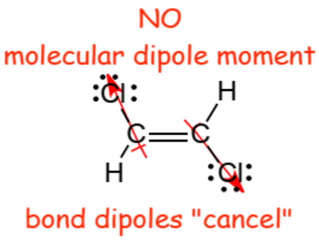


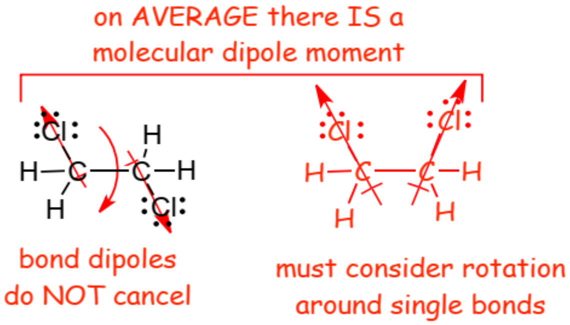
- the C–Cl bond dipoles **oppose** the C=O dipole, **BUT, the large bond dipole moment associated with the C=O DOUBLE BOND will always be larger and will "win" over opposing dipoles in single bonds**

Unlike bond dipole moments, which we can think about but not measure, molecular dipole moments are a real physical property of a molecule (like molecular weight, density etc.), that can be measured, and which influences other physical properties such as melting point, boiling point etc.

We Must Consider ALL Conformations (rotations around single bonds)



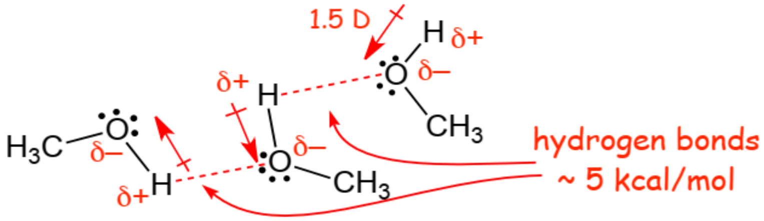




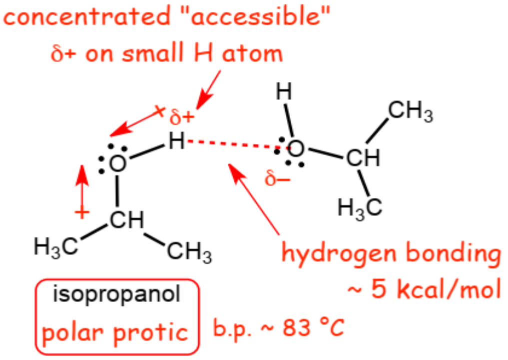
- need to consider ALL possible orientations of the bond dipole moments
- because rotation around a C=C bond is not allowed, the bond dipoles for the two alkenes have fixed directions
- because of allowed bond rotation around the single bond, on AVERAGE, the bond dipoles do NOT cancel for the structure on the right

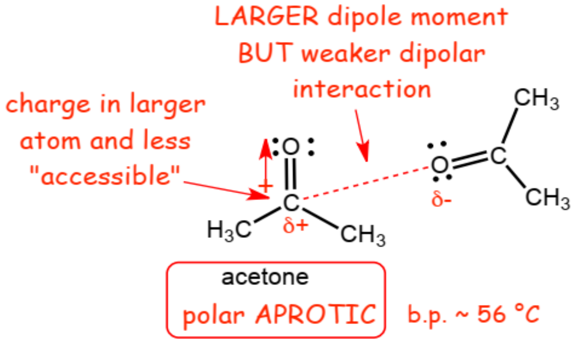
2.3 Hydrogen Bonds: A Special Kind of Dipolar Interaction

- Polarization of electrons away from a hydrogen atom is different from any other atoms, because hydrogen has no CORE ELECTRONS, and so removing electron density reveals an UNSHIELDED PROTON and a **CONCENTRATED** and **LARGE** partial positive charge



- The O-H bond dipole moment is large for a single bond, as large as a C-F bond dipole moment, AND, the partial positive charge on hydrogen is concentrated and large, which results in a strong dipolar interaction
- Hydrogen-bonding almost certainly involves more than just a dipole-dipole interaction, there is evidence for at least some covalent bonding, but that is a detail that we don't need to go into here
- H-bonding is observed for molecules with –OH and N–H bonds





- Even though the C-O and O-H bond dipole moments in isopropanol above are smaller than the C=O bond dipole moment in acetone above, the INTERMOLECULAR (between molecules) dipolar interaction for isopropanol is larger because the partial positive charge in isopropanol is concentrated on the small hydrogen atom that is also very accessible (nothing around it), whereas the partial positive charge in acetone is less "concentrated" on a larger C atom, and it is much less accessible, the carbon is surrounded by the two -CH3 groups, and so the INTERMOLECULAR dipolar interaction is much weaker, despite the fact that the bond dipole moment is larger.

- Solvents that can hydrogen bond are called **POLAR PROTIC** and have some important properties that we will return to later, polar molecules such as acetone that can't hydrogen bond are called **polar APROTIC**, but we will return to give a more detailed description of these terms later.

3 Strengths of Bonds

- Organic reactions involve breaking bonds and making new bonds
- The most important factor to consider is that the energy of electrons DECREASE when they form a bond
- the **LOWER THE ENERGY OF THE ELECTRONS** in the bond, the **STRONGER THE BOND** (but see below)

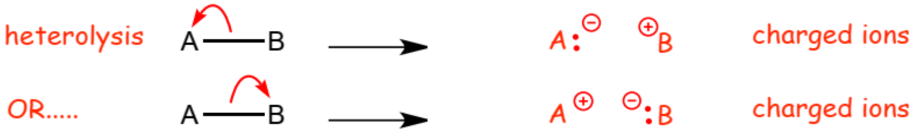
3.1 Homolytic and Heterolytic Cleavage of bonds : Measuring bond dissociation energies

- In organic chemical reactions, bonds are broken by either **homolysis** or **heterolysis** (-lysis means breaking)

HOMOLYTICALLY, i.e. breaking the bond so that each atom in the bond gains ONE of the shared pair

- Singleheaded (fishhook) curved arrow shows the movement of ONE electron
- Homolysis usually forms two RADICALS

HETEROLYTICALLY, i.e. breaking the bond so that ONE of the atoms gains BOTH of the shared pair

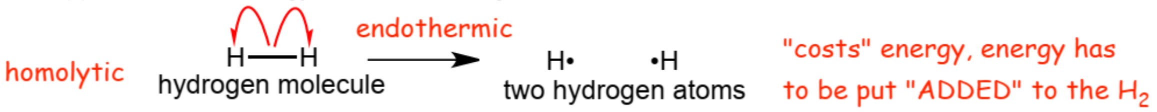


- A doubleheaded curved arrow shows the movement of a PAIR of electrons
- Homolysis usually forms two IONS

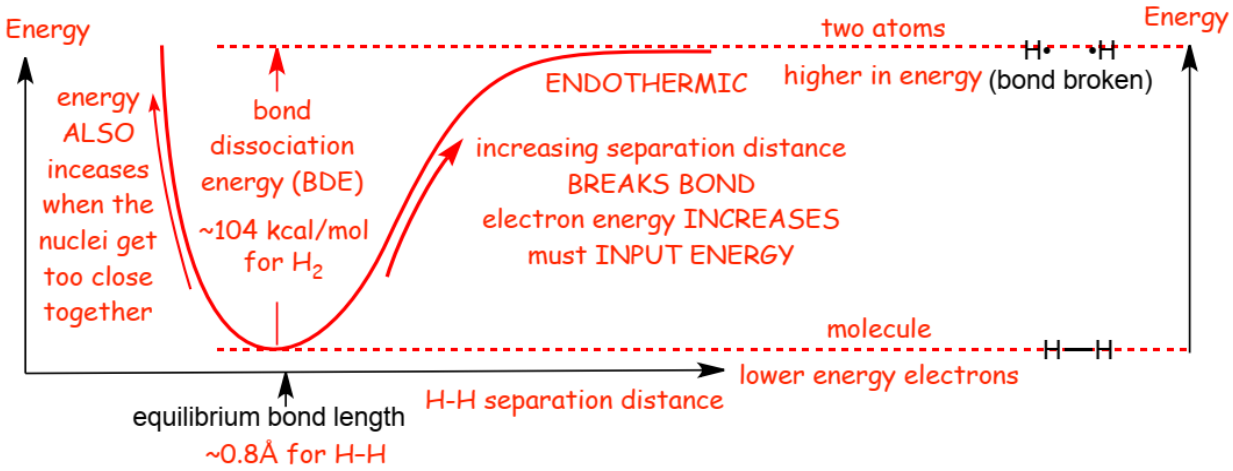
Whether homolytically or heterolytically, IT COSTS ENERGY TO BREAK A BOND!

3.2 Bond Making/Breaking in H2 as the simplest chemical reaction : Energy Diagrams

- Consider **homolytic** cleavage the H-H bond in H_2 as a simple chemical reaction
- **Bond breaking** means **separation of two atoms**, when this happens the overlap of the A.O.s decreases, the M.O. disappears and the energy of the electrons goes UP



- the energy required to break a bond has to be "added" to the H2, usually this comes from the environment/solvent in the form of thermal energy, (RT)



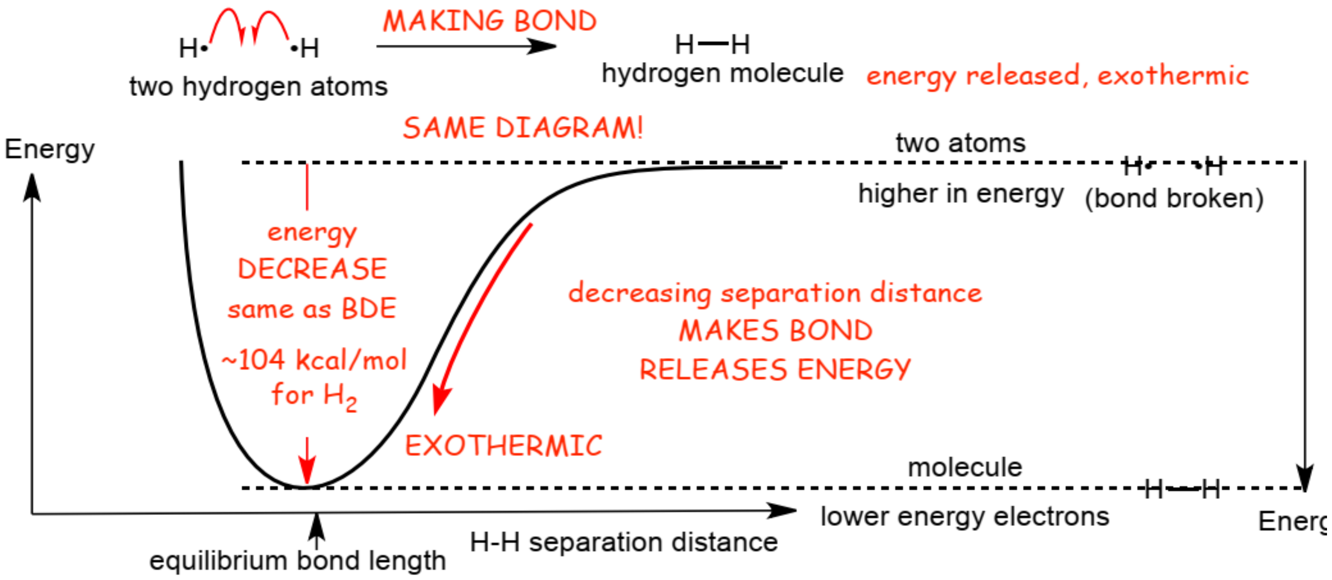
- The electrons in the bond in the molecule are low in energy (they are in a bond) and have low chemical reactivity, the electrons in the atoms are high in energy, they are chemically reactive
- The ENERGY DIAGRAM shows how the energy changes as the atoms separate, which is what has to happen

for this simple reaction to occur

- The energy also increases if the atoms get too close together, the lowest energy is at the optimum separation distance, the equilibrium bond length, which is ~0.8Å for the hydrogen molecule
- The **Bond Dissociation Energy (BDE)** is defined as the energy required to break the bond **homolytically**, no heterolytically
- This is because the energy required to heterolyze a bond will be very different in different solvents (because charged ions are solvated very differently in solvents of different polarity), whereas the homolytic bond dissociation energy is essentially the same in all solvents since the neutral radicals and/or atoms are solvated similarly in solvent of different polarity. Nevertheless, the **relative** energies required for the two different processes are often related, since they both depend upon the energies of the electrons in the bonds and the relevant atomic orbitals.

Consider bond formation by reaction of 2 H atoms to make H_2 as a simple chemical reaction

- Bond formation can occur when two atoms approach each other.
- When they get close enough to overlap AOs, MOs form and the energy of the electrons goes down.
- Energy released upon bond formation goes into the solvent in the form of heat (i.e. kinetic energy).



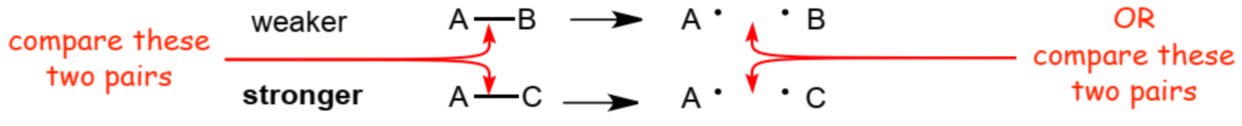
- Two H atoms make a **bond** because doing so **lowers the energies of the electrons**
- When heat is **released** in a reaction, the reaction is **EXOTHERMIC**

3.3 Factors That Determine Homolytic Bond Dissociation Energies

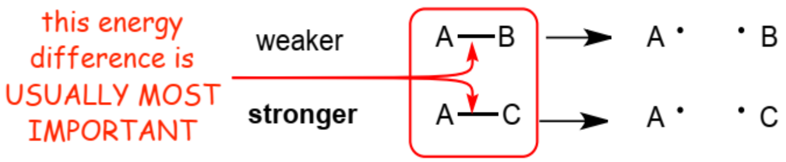
When comparing the BDEs of two different bonds, which pairs of electrons do we compare?

- How do we COMPARE TWO Bond Dissociation Energies - **Which electron energies do we compare**?
- There is no SINGLE ELECTRON ENERGY TO CONSIDER NOW, we need to think about the energies of the electrons IN THE BONDS, and also AFTER THE BONDS ARE BROKEN.

Example: Compare the following two generic bonds, to understand their relative BDEs, do we compare the energies of the two pairs of electrons IN THE BONDS, or do we compare the energies of the two pairs of electrons AFTER THE BONDS ARE BROKEN?



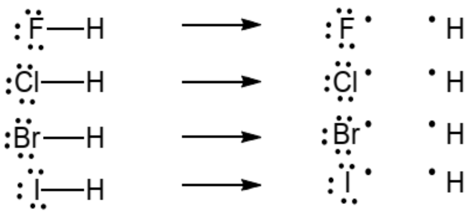
- Most of the variations in bond energies and bond strengths we meet are understood by **comparing the energies of the electrons in the bonds!**



- Do not memorize the values of any BDEs, but be able to **recognize and explain the trends.**

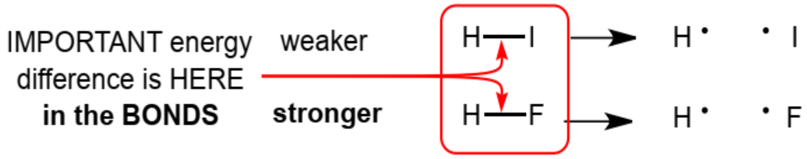
Down the periodic table: Effect of atomic size

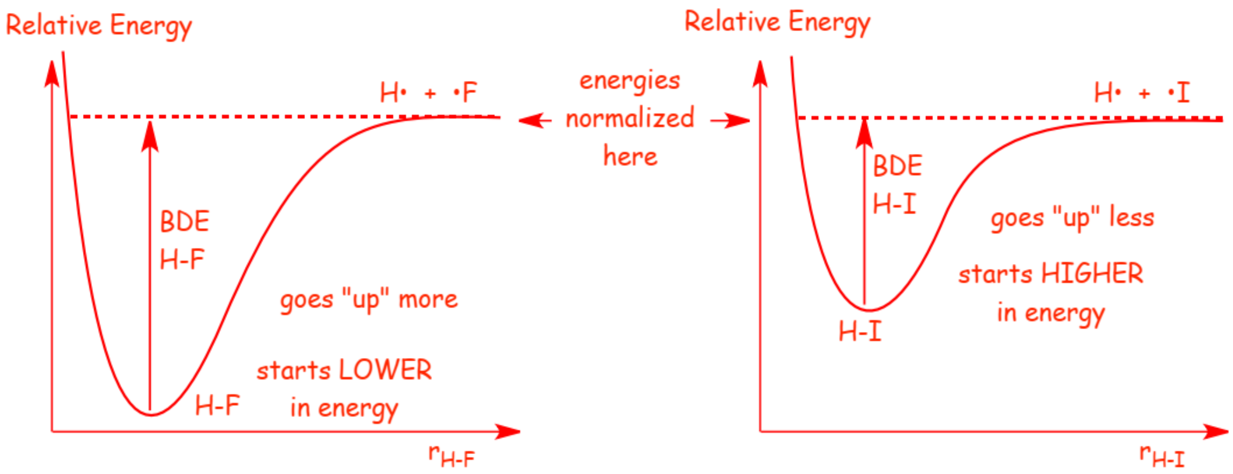
- In most cases this is the **most influential factor**, atomic **size** has a **large influence** on **BDE**.
- Comparing different bond dissociation energies **down the periodic table**, largest energy differences are **in the bonds**.

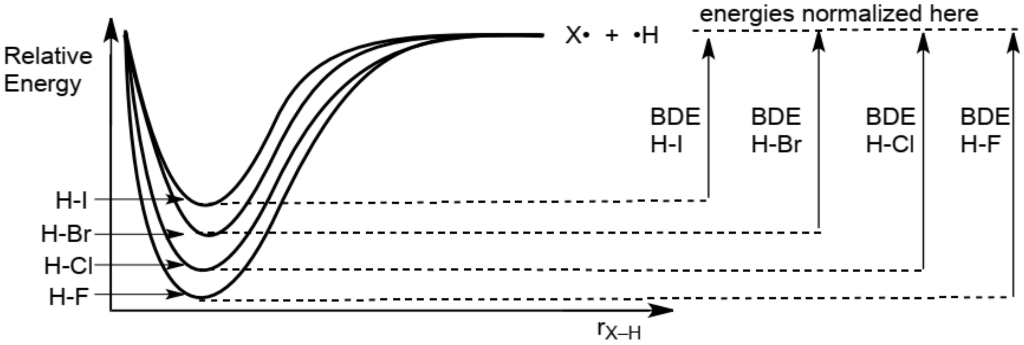


	B.D.E. (kcal/mol)	Length (Å)
F—H	134	0.92
Cl—H	103	1.27
Br—H	88	1.41
I—H	71	1.61

- The **energies of the electrons** in the **bonds to smaller atoms are lower** because of smaller atoms have smaller atomic orbitals that overlap strongly when they are combined to make the molecular orbitals
- The energies of electrons in bonds to **larger** atoms are **higher**, because larger atoms have larger atomic orbitals that overlap much less when they are combined to make the molecular orbitals
- Bonds to **smaller** atoms thus tend to be **stronger** and **shorter**.
- Bonds to **larger** atoms thus tend to be **weaker** and **longer.**
- Fluorine is very electronegative and small, the electrons in the H-F bond are very low in energy, this is a strong short bond. With increasing atomic size and decreasing electronegativity, there is poorer A.O. overlap in bond, larger orbitals, less electrostatic stabilization, the energy of the electrons in the bonds goes up, the bonds get weaker and longer *(a fluorine atom is roughly twice as large as a hydrogen atom and an iodine atom is roughly four times as large as a hydrogen atom).*
- This effect is shown in the energy diagrams below, note, these are **relative energy** diagrams, the absolute energies of H-F and H-I are very different, they are **normalized** at the energies of the H atom and the halogen atom so that they can be compared.



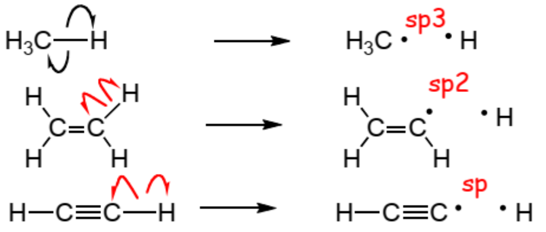




- The energies of the electrons on the halogen atoms formed **after** cleavage are also lower in energy on the smaller and more electronegative elements, however, the energies of the electrons in the bonds went up MORE in these cases.

Carbon-Hydrogen Bonds: Effect of Carbon Hybridization

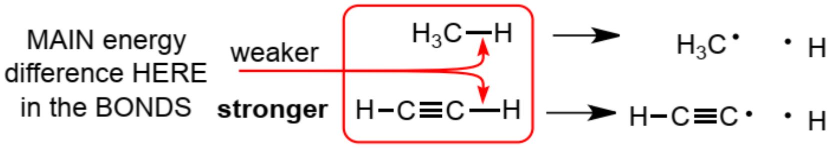
- In most cases, this is the second most influential factor influencing bond energies
- **Comparing** different bond dissociation energies **with different hybridizations**, largest energy differences are **in the bonds**, because they are **different bonds!**

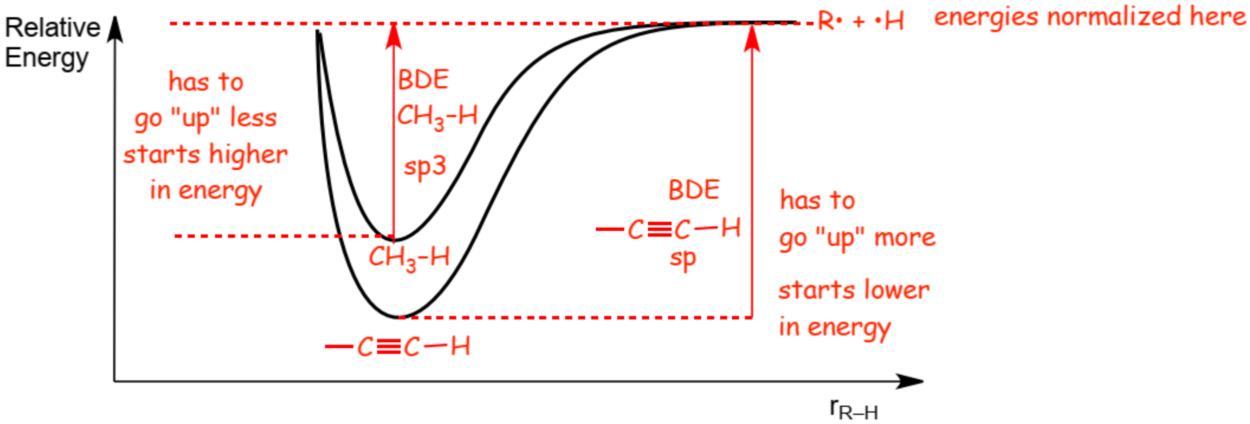


B.D.E. kcal/mol	Length Å
104	1.09
108	~1.08
133	~1.055

The energies of the electrons in bonds to carbon atoms are lower the less p character there is in the A.O. used to make the bond. Hybrid AOs with less p character are smaller and lower in energy and therefore make stronger more bonding MOS, i.e. sp3 is higher in energy than sp2 is higher in energy than sp.

- The energies of the electrons in the radicals formed **after** cleavage are also lower in energy in sp2 and sp, however, the energies of the electrons on the H atoms went up **more** in these cases, again, it is the energies of the electrons **in the bonds** that is critical here.

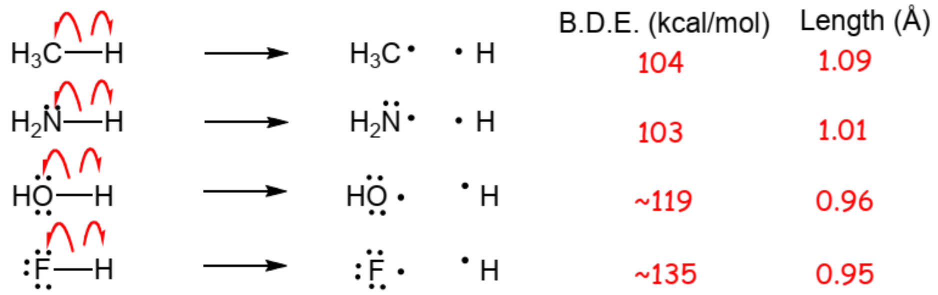




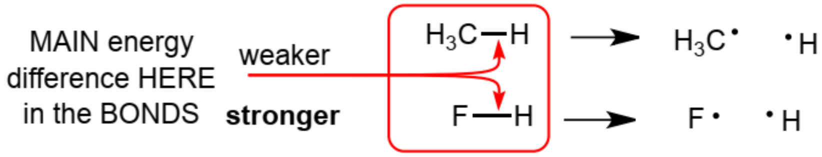
- **Note** that again the energies are normalized to the energy after bond cleavage to make it clear that it is the differences in the energies of the electrons **in the bonds** that is responsible for the differences in the BDEs.

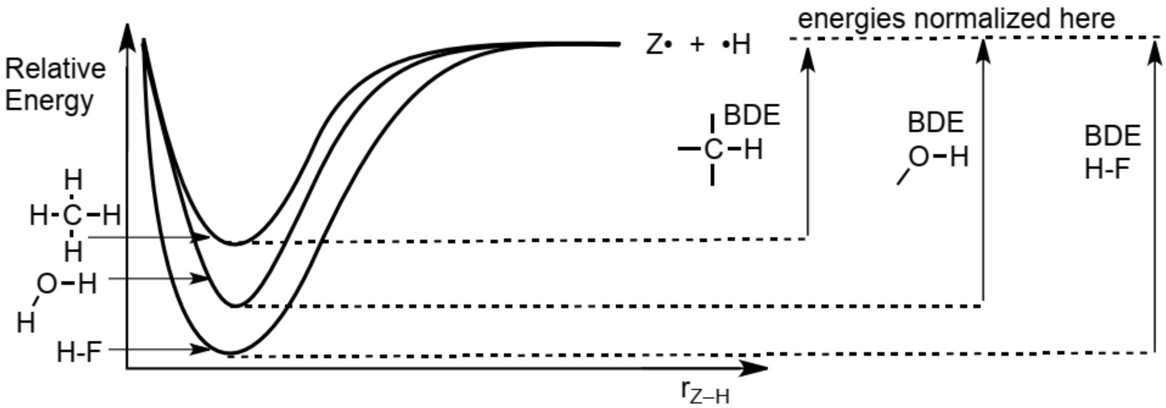
4. Across the periodic table: Effect of electronegativity

- This is often the third most influential factor influencing bond energies **for bonds to Carbon and Hydrogen**
- **Comparing** different bond dissociation energies **with different electronegativity**, largest energy differences are **in the bonds**, because they are **different bonds!**



		B.D.E. (kcal/mol)	Length (Å)
H_3C-H	$\longrightarrow H_3C\cdot \ \cdot H$	104	1.09
H_2N-H	$\longrightarrow H_2N\cdot \ \cdot H$	103	1.01
$HO-H$	$\longrightarrow HO\cdot \ \cdot H$	~119	0.96
$F-H$	$\longrightarrow F\cdot \ \cdot H$	~135	0.95

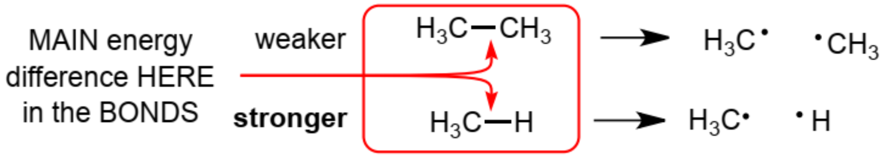




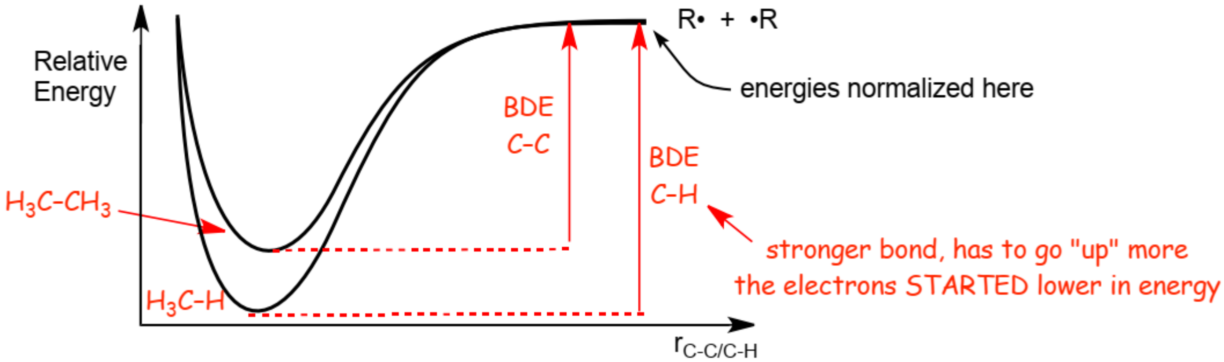
- bonds from carbon to more electronegative elements are generally stronger and shorter, the energies of the electrons in bonds from CARBON and HYDROGEN to more electronegative elements are lower *(bonds involving other combinations of electronegative elements are a bit more complicated and beyond the scope of this course*)

5. Carbon-Carbon Bonds versus Carbon-Hydrogen bonds

- **Comparing** different bond dissociation energies **for C-H versus C-C bonds**, largest energy differences are **in the bonds**, because they are **different bonds!**

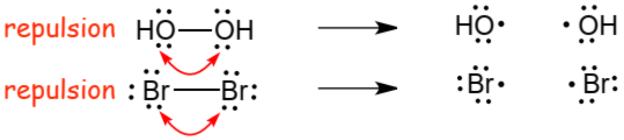


		B.D.E. (kcal/mol)	Length (Å)
H_3C-H	$\longrightarrow H_3C\cdot \ \cdot H$	104	1.09
H_3C-CH_3	$\longrightarrow H_3C\cdot \ \cdot CH_3$	~88	~1.54



- Carbon-carbon bonds are "built" by combining an sp3 A.O. from carbon with another sp3 A.O. from the other carbon
- Carbon-hydrogen bonds are "built" by combining an sp3 A.O. from carbon with a 1s A.O. from hydrogen
- sp3/sp3 A.O. overlap in a C-C bond is poorer than sp3/1s A.O. overlap in a C-H bond, AND, an electron in a 1s A.O. is lower in energy than one in a carbon sp3 A.O., and this character "transmits" to the bonding molecular orbital *(a carbon atom is roughly twice as large as a hydrogen atom)*
- Thus, the electrons in a C-H bond are (slightly) lower in energy than those in a C-C bond, it costs more energy to break a C-H bond, the C-H bond has a larger BDE.

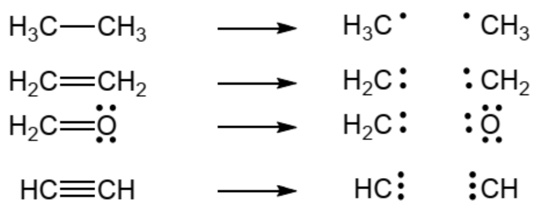
6. Weaker Bonds



	B.D.E. (kcal/mol)	Length (Å)
$HO{-}OH \rightarrow HO\cdot \;\; \cdot OH$	~51	1.48
$Br{-}Br \rightarrow Br\cdot \;\; \cdot Br$	46	2.28

- Oxygen lone pairs repel each other in the peroxide, electrons are higher in energy in the bonded state, thus a weak and long bond, even more so for the larger bromine atoms

7. Multiple Bonds



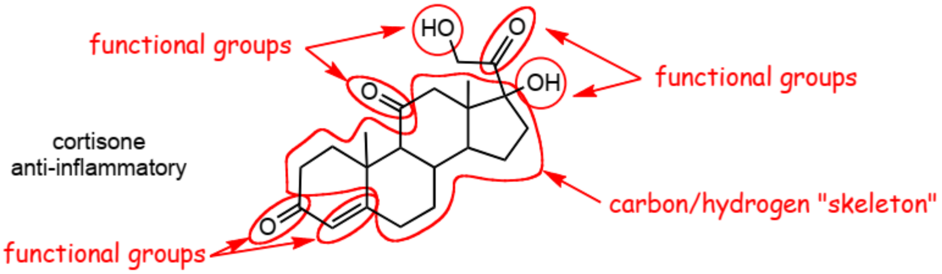
	B.D.E. (kcal/mol)	Length (Å)
$H_3C{-}CH_3 \rightarrow H_3C\cdot \;\; \cdot CH_3$	~88	~1.54
$H_2C{=}CH_2 \rightarrow H_2C\colon \;\; \colon CH_2$	~160	~1.33
$H_2C{=}O \rightarrow H_2C\colon \;\; \colon O$	~175	~1.21
$HC{\equiv}CH \rightarrow HC\vdots \;\; \vdots CH$	~230	~1.20

- Multiple bonds are obviously stronger (and shorter) than single bonds.
- π-bonds are essentially always weaker than corresponding σ-bonds, of course, but breaking multiple bonds requires π- **and** σ-bonds (breaking more than one bond).
- Electronegativity effects are still important, compare the C=C and C=O double bonds.

4 Functional Groups

- Organic molecules consist, in general, of a carbon/hydrogen (hydrocarbon) "skeleton", that mainly determines the size and shape of the molecule, and……
- The **functional groups**, generally involving atoms that are more electronegative than carbon (so that polar bonds result), such as O, N, S etc.
- Chemistry takes place at the **functional groups**. When we start to discuss reactions, we will divide them into those characteristic of the various functional groups.

The Main Structural Features of a typical organic molecule:

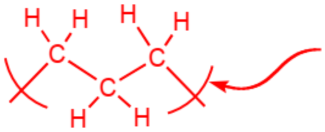


cortisone
anti-inflammatory

Alkane (hydrocarbon)

The alkane part of a molecule is not really a functional group, but the important "backbone" or "skeleton" of many organic molecules.

C-C and C-H bonds tend to be strong and relatively unreactive.

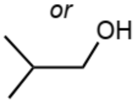


means "the rest of the molecule is attached here"

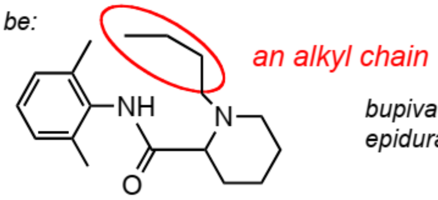
R *stands for any alkyl chain, e.g. R–OH could be:*

$H_3C–OH$ *or* CH_3CH_2OH

or



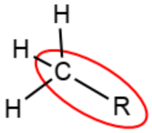
etc.



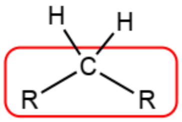
bupivacaine, an epidural anesthetic

- CARBON or NITROGEN atoms can be characterized by the number of SUBSTITUENTS attached to them
- The **substituent** is usually an **alkyl chain** (-R) or an **aryl (aromatic)** group (-Ar)
- Atoms with **ONE** substituent are **PRIMARY (1°)**
- Atoms with **TWO** substituents are **SECONDARY (2°)**
- Atoms with **THREE** substituents are **TERTIARY (3°)**
- Atoms with **FOUR** substituents are **QUARTERNARY (4°)**

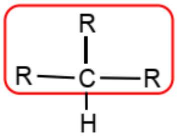
For the case of carbon atoms…



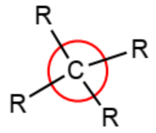
Primary or 1° carbon



Secondary or 2° carbon



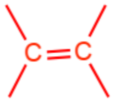
Tertiary or 3° carbon

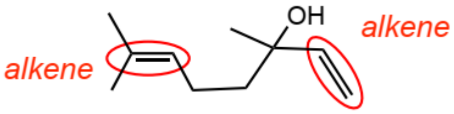


Quaternary or 4° carbon

Alkene Functional Group

- Carbon-carbon double bond



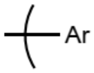


linalool, used in the perfume industry

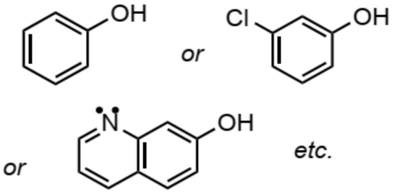
NOT aromatic (see next section)
does not have alternating double/single bonds

Aromatic Functional Group

- Alternating C-C and C=C bonds in a ring - **be careful to distinguish from Alkene**

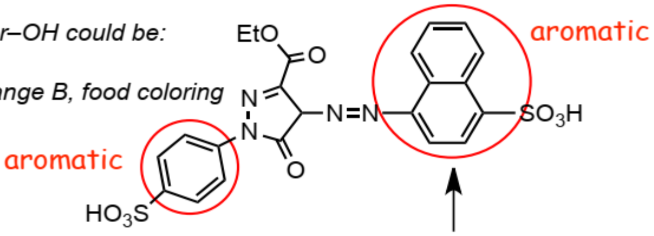


stands for any aromatic ring system, e.g. Ar–OH could be:



etc.

orange B, food coloring

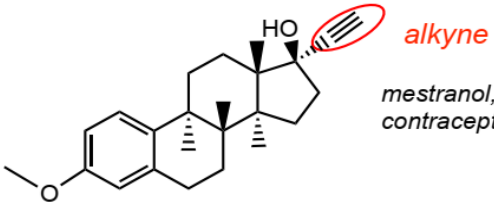


this is aromatic because it has alternating single/double bonds in a (large) ring, an aromatic ring can have more than 6 carbon atoms!

Alkyne Functional Group

- Carbon-carbon triple bond

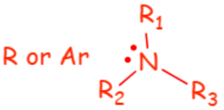
$-C\equiv C-$



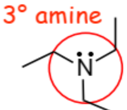
mestranol, the estrogen used in many oral contraceptives

Amine Functional Group

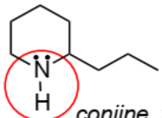
- Contain a nitrogen with at least one alkyl or aryl group, here R_1, R_2 etc. stands for any alkyl chain that may or may not be the same



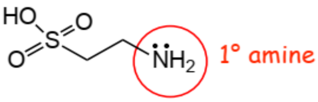
tertiary (3°) amine



triethylamine fishy smell!



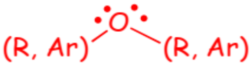
2° amine *coniine, the poison in hemlock*

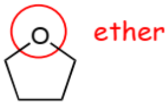


taurine, supposedly active ingredient in energy drinks e.g. Red Bull

Ether Functional Group

- Oxygen between 2 alkyl or aryl groups

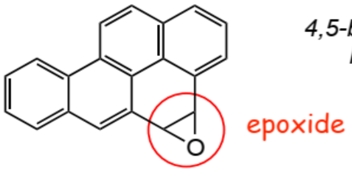




tetrahydrofuran, THF, common organic solvent

Epoxide Functional Group

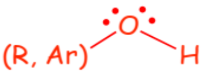
- 3-membered ring containing oxygen

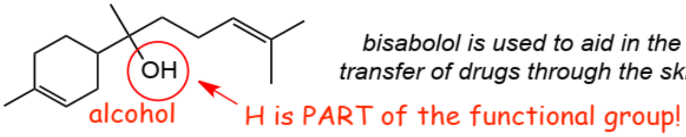


4,5-benzo[a]pyrene oxide, highly carcinognic

Alcohol Functional Group

- Oxygen with 1 R or Ar group and 1 hydrogen
- Hydrogen atoms are not included in line-angle structures UNLESS they are part of a functional group, the alcohol functional group provides an example of this





bisabolol is used to aid in the transfer of drugs through the skin

Halide Functional Group

- Aryl or alkyl group with fluoride, chloride, bromide, iodide...

R or Ar

R—F

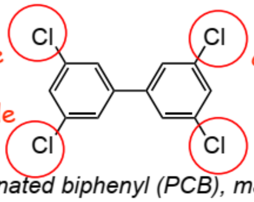
R—Cl

R—Br

R—I

chloride

chloride

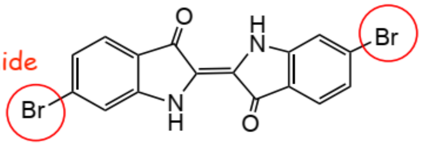


chloride

chloride

a polychlorinated biphenyl (PCB), many industrial uses but toxic, bioaccumulates in animals

bromide

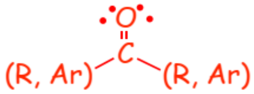


bromide

6,6'-dibromoindigo, a component of a natural purple dye

Ketone Functional Group

- C=O double bond with 2 akyl or aryl groups

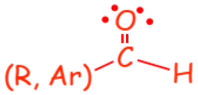


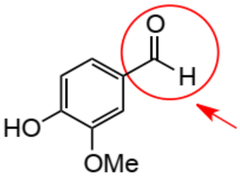
ketone

acetone, the simplest ketone, common organic solvent, nail-polish remover

Aldehyde Functional Group

- C=O double bond with 1 R or Ar group and 1 H
- **Hydrogen atoms are not included in line-angle structures UNLESS they are part of a functional group**, the aldehyde functional group provides another example of this





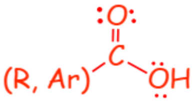
aldehyde

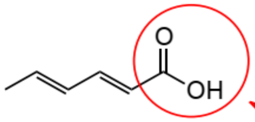
vanillin, main extract fron vanilla bean

H is PART of the functional group!

Carboxylic Acid Functional Group

- C=O with 1 R or Ar group and 1 –OH
- **Hydrogen atoms are not included in line-angle structures UNLESS they are part of a functional group**, the carboxylic acid functional group provides another example of this





carboxylic acid

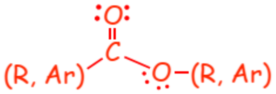
sorbic acid, food preservative

NOT ketone, NOT alcohol!

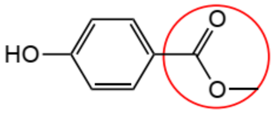
H is PART of the functional group!

Ester Functional Group

C=O double bond with –OR or -OAr group



ester

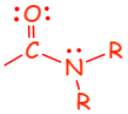


methyl paraben, food preservative, cosmetics additive, anibacterial/fungal

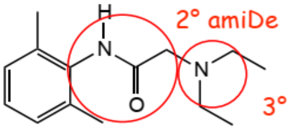
NOT ketone, NOT ether!

Amide Functional Group

C=O with -NR₂ (R or Ar)



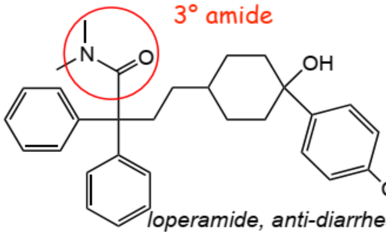
3° amide



2° amiDe

3° amiNe

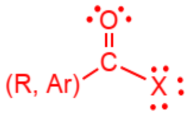
3° amide



loperamide, anti-diarrhea drug

Acid Halide Functional Group

C=O double bond with a halide, X means any halide, Cl, Br etc.



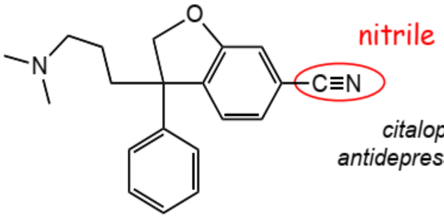
acetyl chloride, many useful reactions

Nitrile Functional Group

Aryl or alkyl group with carbon nitrogen triple bond

$(Ar, R){-}C{\equiv}N{:}$

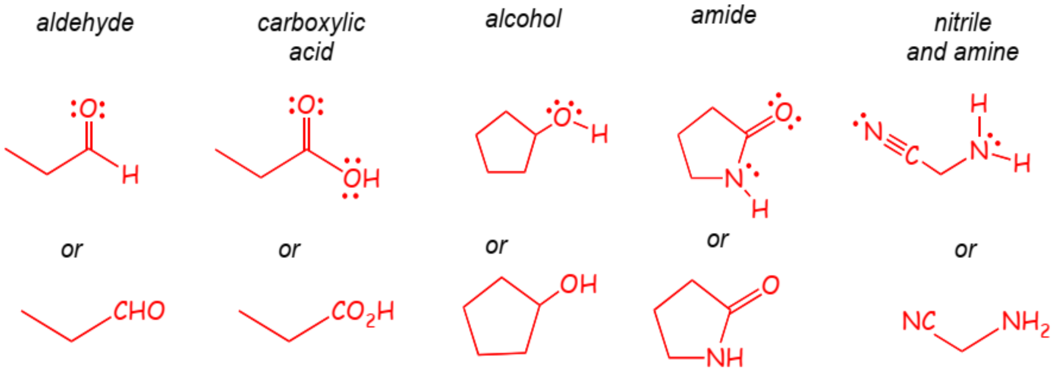
(Ar,R) means aryl or alkyl



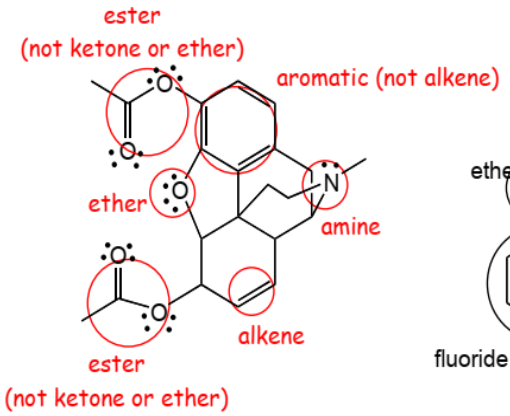
citalopram, antidepressant drug

How Functional Groups are Represented

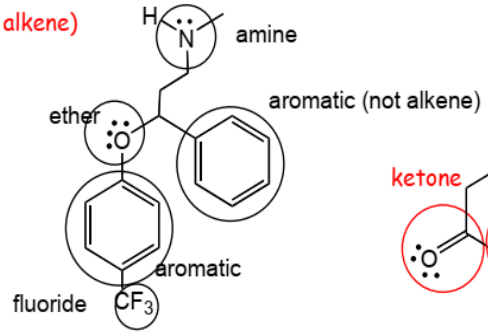
Here are some functional groups incorporated into line-angle and condensed structures that you will see and need to understand



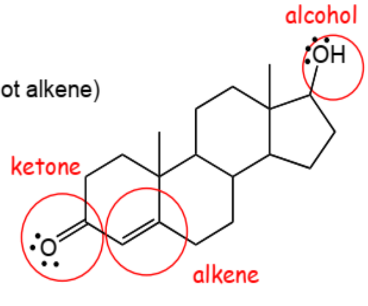
Example problems: Indicate all functional groups, do not include alkanes



Heroin



Fluoxetine (Prozac)



testosterone

You cannot work out the names and structures of the functional groups, this is something that you will just have to know….