Chemical Bonding and Structure

Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σ and π bonds

Chemical Bonding and Structure

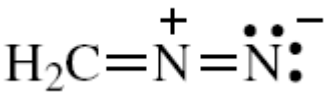
Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σ and π bonds
- **formal charge**

Formal Charge

formal charge = (valence electrons of element)
− (number of π and σ bonds)
− (number of unshared valence electrons)

Formal Charge



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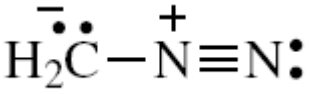

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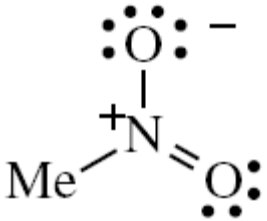

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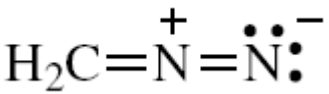
Formal Charge



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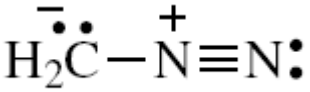

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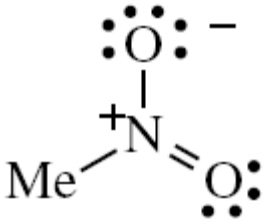

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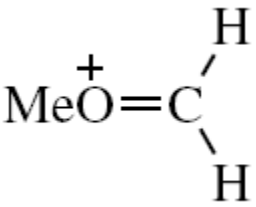

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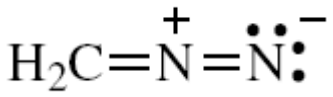
Formal Charge



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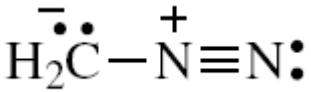

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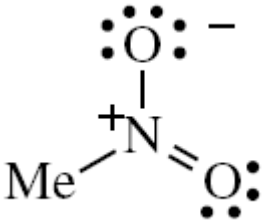

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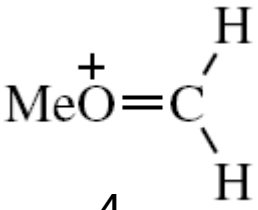

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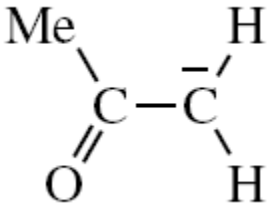

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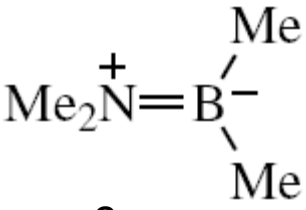

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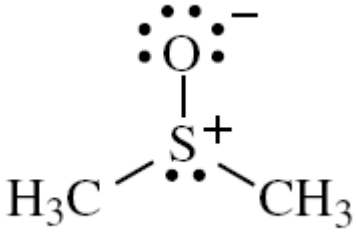

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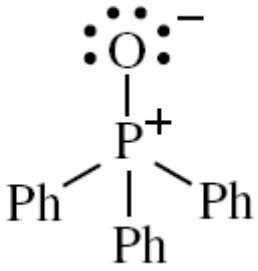

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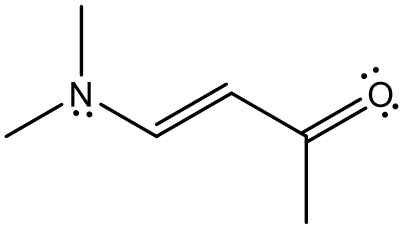
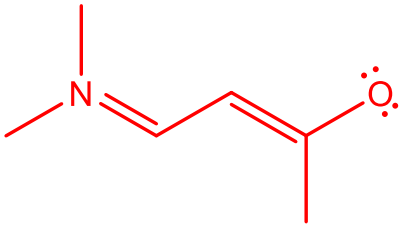
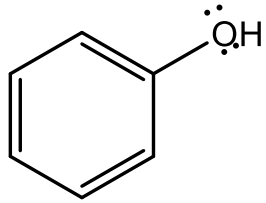
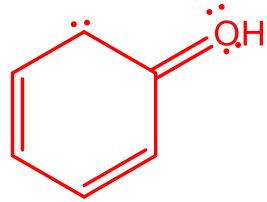
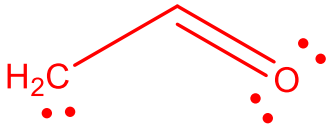
Exercise 1

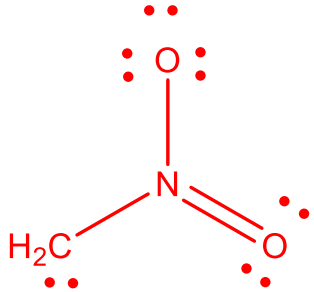


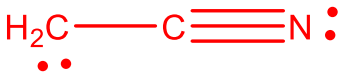


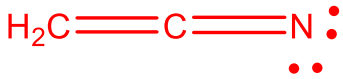


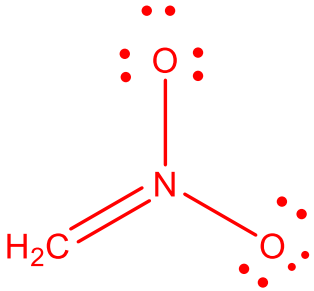












Formal Charge

The properties of formal positive charge, electropositivity, electron-deficiency and electrophilicity are independent of one another --- **DO NOT CONFUSE!!!**

in NH_4^+, N has formal positive charge but it is electroneutral

BF_3 , B has no formal positive charge but it is electron-deficient

BH_4^-, B has formal negative charge but is not electron-rich

Chemical Bonding and Structure

Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σand π bonds
- formal charge, **electronegativity**

Electronegativity of atoms

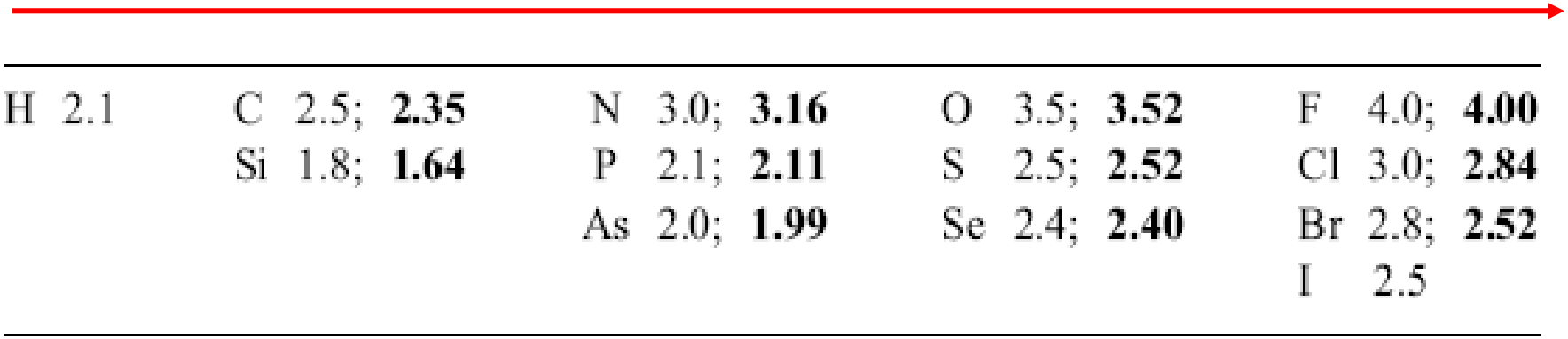
- The tendency of an atom to attract electrons
- Electronegativity correlates strongly with position in the periodic table
- A number of different approaches to assigning electronegativity, most are numerically scaled to a definition originally proposed by Pauling

Electronegativity of atoms

H	2.1	C	2.5;	**2.35**	N	3.0;	**3.16**	O	3.5;	**3.52**	F	4.0;	**4.00**
		Si	1.8;	**1.64**	P	2.1;	**2.11**	S	2.5;	**2.52**	Cl	3.0;	**2.84**
					As	2.0;	**1.99**	Se	2.4;	**2.40**	Br	2.8;	**2.52**
											I	2.5	

From L. Pauling, *The Nature of the Chemical Bond*, 3rd edition, Cornell University Press, Ithaca, New York, 1960. Boldface values from G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.* **98:**7869 (1976).

Electronegativity of atoms



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Electronegativity of functional groups

CH_3	2.3;	**2.55**	H	2.28;	**1.20**	F	3.95;	**4.00**
CH_2Cl	2.75;	**2.61**	NH_2	3.35;	**3.12**	Cl	3.03;	**3.05**
$CHCl_2$	2.8;	**2.66**	$^+NH_3$	3.8;	**3.21**	Br	2.80;	**2.75**
CCl_3	3.0;	**2.70**	NO_2	3.4;	**3.22**	I	2.28;	
CF_3	3.35;	**2.71**	OH	3.7;	**3.55**			
Ph	3.0;	**2.58**						
$CH{=}CH_2$	3.0;	**2.58**						
$C{\equiv}CH$	3.3;	**2.66**						
$C{\equiv}N$	3.3;	**2.69**						

From P. R. Wells, *Prog. Phys. Org. Chem.* **6:**111 (1968). Boldface values from R. J. Boyd and S. L. Boyd, *J. Am. Chem. Soc.* **114:**1652 (1992).

- Values scaled to be numerically consistent with elemental electronegativities
- A **qualitative** impression of the electron attracting capacity of the groups

Chemical Bonding and Structure

Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σand π bonds
- formal charge, electronegativity, **polarity**

Polarity of covalent bonds

In organic chemistry , the polarity of covalent bonds between **carbon** and **substituents** is the basis of important **structure-reactivity relationships**.

Polarity of covalent bonds

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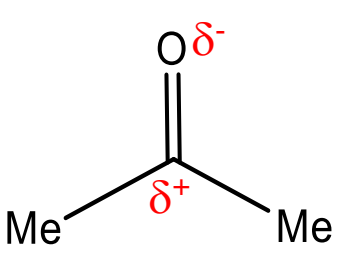
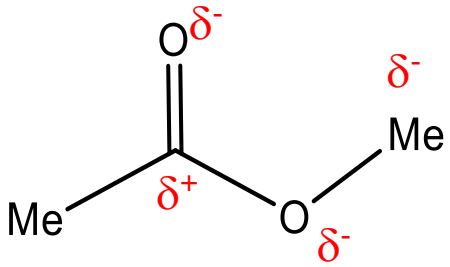
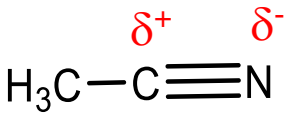






Polarity of covalent bonds

Effects for bond polarization

- **Inductive effects**
- **Conjugation effects**
- **Field effect**

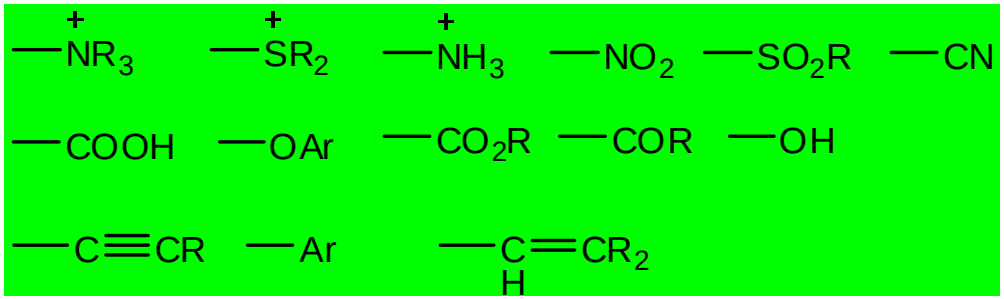
Inductive effects

Effects for bond polarization

- **Inductive effects**

electron withdrawing through σ bonds to the more electronegative atom or group

Groups with -I



Groups with +I

Conjugation effects

Effects for bond polarization

- **Conjugation effects**

electron effect induced by conjugated π system

Groups with - C

$-NO_2$ $-CN$ $-COOH$ $-CO_2R$ $-CONH_2$ $-CONHR$ $-CONR_2$

$-CHO$ $-COR$ $-SO_3R$ $-SO_2R$ $-NO$

Groups with + C

$-\bar{O}$ $-\bar{S}$ $-NR_2$ $-NHR$ $-NH_2$ $-NHCOR$ $-OR$

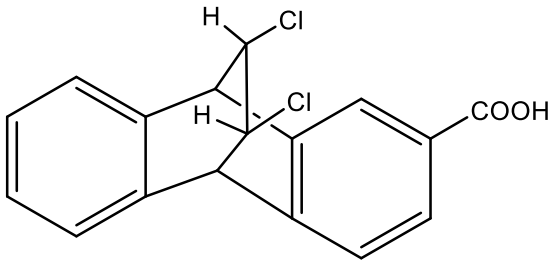
$-OCOR$ $-SR$ $-SH$ $-Br$ $-I$ $-Cl$ $-F$ $-Ar$

Polarity of covalent bonds

Effects for bond polarization

Field effect:

polarization in a molecule resulted from charges interacting through space



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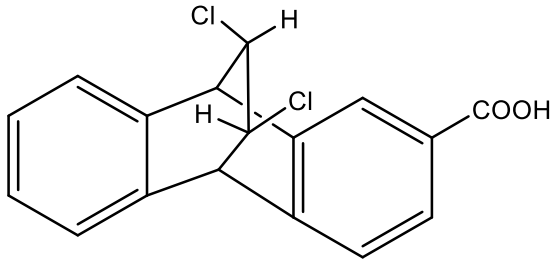

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Chemical Bonding and Structure

Basic concepts:

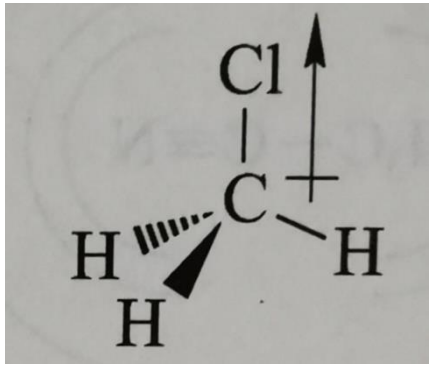
- atomic orbitals, electron configurations
- hybridization, σand π bonds
- formal charge, electronegativity, polarity, **bond dipoles, molecular dipole**

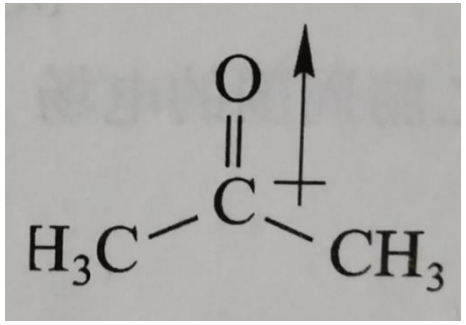
Bond dipoles

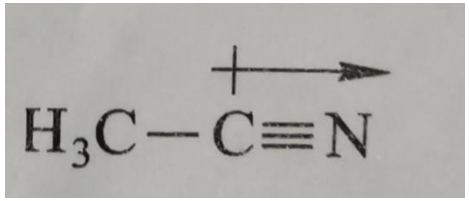
Bond dipole: produced by the unequal distribution of electron density in covalent bonds

Dipole moment (μ) is the expression of the magnitude of bond dipole.

$\mu = q \times r$, in units of Debye (D), $1D = 10^{-18}$ esu.cm







Bond & group dipoles

C–H	0.4	C–N	0.22	MeO	1.3
C–F	1.41	C–O	0.74	NH_2	1.2
C–Cl	1.46	C=O	2.3	CO_2H	1.7
C–Br	1.38	C≡N	3.5	COMe	2.7
C–I	1.19			NO_2	3.1
				CN	4.0

From C. P. Smyth, *Dielectric Behavior and Structure*, McGraw-Hill Book Company, New York, 1955, pp. 244, 253.
In e.s. units $\times 10^{18}$.

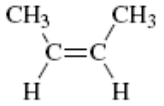
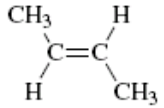
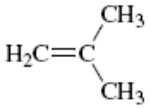
Covalent bonds with significant bond dipoles are described as being polar.

Molecular dipole moments

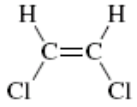
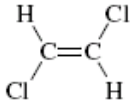
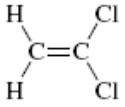
A sum of bond dipoles

Dipole Moments for Some Organic Compounds[a]

A. Hydrocarbons

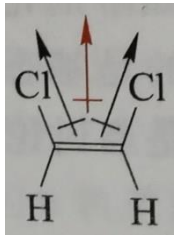
$H_2C{=}CHCH_2CH_3$	$HC{\equiv}CCH_2CH_3$		
0.34	0.800	0.253	0 (symmetry)
	$CH_3C{\equiv}CCH_3$	$H_2C{=}CHCH_3$	$HC{\equiv}CCH_3$
0.503	0 (symmetry)	0.366	0.781

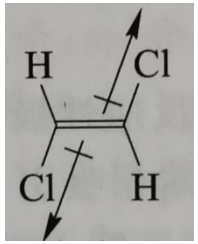
B. Substituted molecules

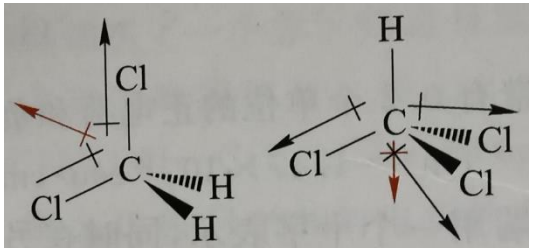
			
1.90	0 (symmetry)	1.34	1.63

CH_3CN	CH_3NO_2	CH_3OCH_3	CH_3OH	CH_3CO_2H	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	$CH_3\overset{O}{\overset{\|}{S}}CH_3$
3.92	3.46	1.30	1.70	1.74	2.88	3.96

a. Units are in debye. Data are from *Handbook of Chemistry and Physics*, 78th edition, CRC Press, Inc., Boca Raton, Florida, 1997.







Chemical Bonding and Structure

Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σand π bonds
- formal charge, electronegativity, polarity, bond dipoles, molecular dipole moments
- **resonance**

Resonance

- **Resonance theory** is the second concept that makes valence bond theory useful for the structural description of complex molecules.
- **Resonance theory** recognizes that, for many molecules, more than one Lewis structure can be written.
- A convenient way of depicting electron delocalization.
- Particularly useful in describing conjugated compounds and reactive intermediates.
- Arguments based on resonance theory are usually made in a qualitative way.

Resonance

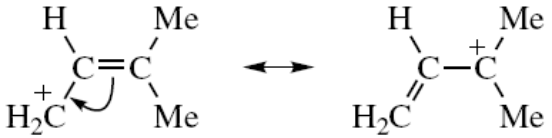
How to generate a resonance structure of a given Lewis structure?

- Look for an <u>electron-deficient atom</u> next to a lone-pair-bearing atom.

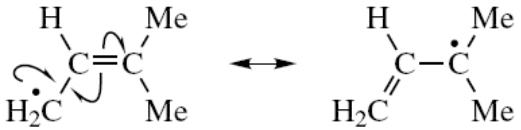
Resonance

How to generate a resonance structure of a given Lewis structure?

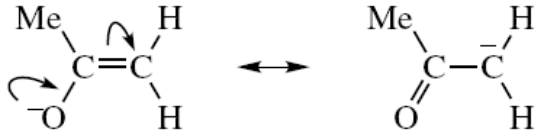
- Look for an electron-deficient atom adjacent to a π bond.



- Look for a radical adjacent to a π bond.



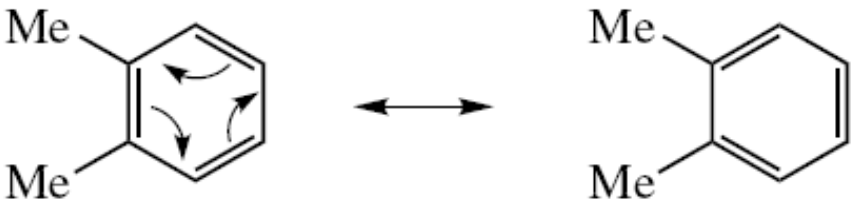
- Look for a lone pair adjacent to a π bond.



Resonance

How to generate a resonance structure of a given Lewis structure?

- π Bonds move around in aromatic compounds.



Resonance

How to generate a resonance structure of a given Lewis structure?

- The two electrons of a π bond can be divided evenly or unevenly between the two atoms making up the bond.

Resonance

How to generate a resonance structure of a given Lewis structure?

- Look for an electron-deficient atom next to a lone-pair-bearing atom.
- Look for an electron-deficient atom adjacent to a π bond.
- Look for a radical adjacent to a π bond.
- Look for a lone pair adjacent to a π bond.
- π Bonds move around in aromatic compounds.
- The two electrons of a π bond can be divided evenly or unevenly between the two atoms making up the bond.

Resonance

Appropriate Resonance Structure

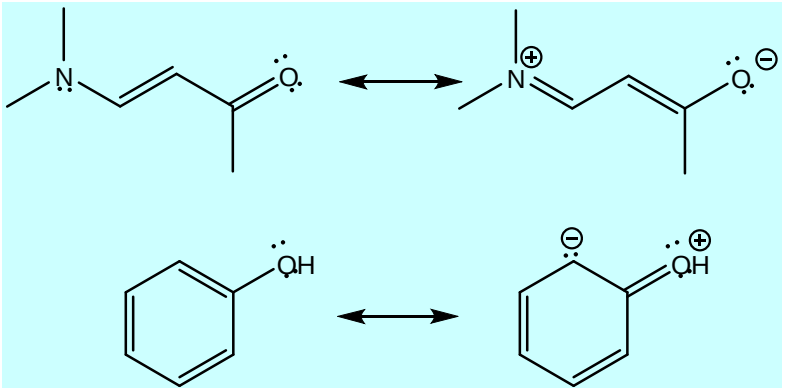
- Having a noble gas configuration for the atoms
- A maximum number of covalent bonds
- A minimum number of like charges
- Close proximity of unlike charges
- Placement of negative charges on electronegative atoms

Resonance

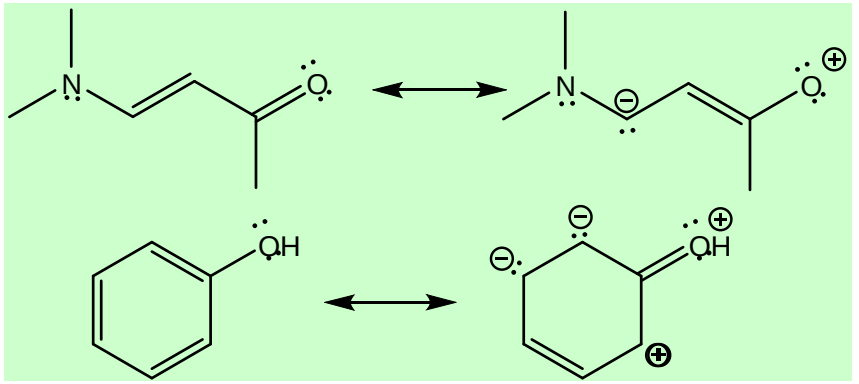
Important rules to remember:

- A lone pair or empty orbital cannot interact with a π bond to which it is orthogonal
- Two resonance structures must have the same number of electrons and atoms

Exercises 2

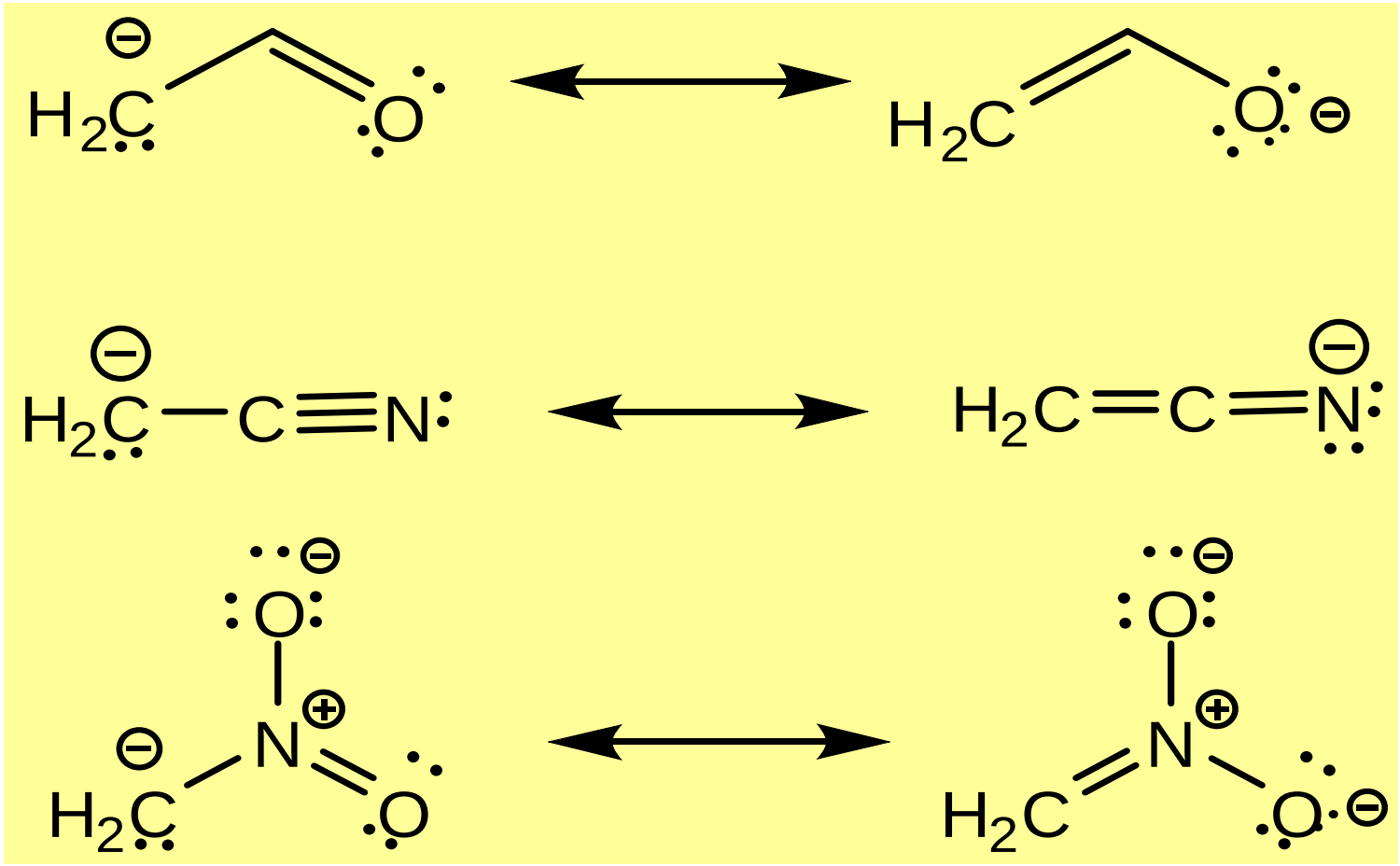


Reasonable



Unreasonable

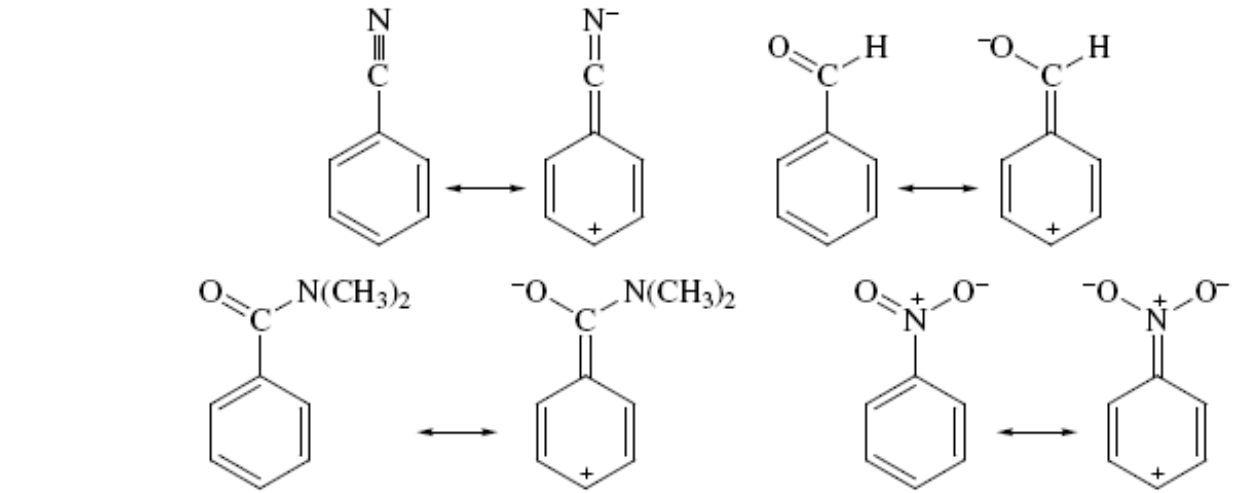
Exercises 2



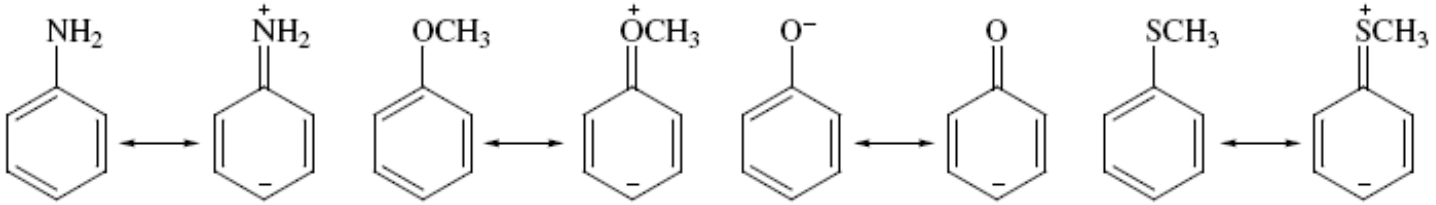
Stabilized carboanions

Resonance related to charge density

Electron-withdrawing substituents



Electron-releasing substituents



Alerts in writing resonance structures

- Tetravalent C or N atoms do not participate in resonance
- Electronegative atoms like N and O must have their octet
- If you donate one or two electrons to an atom that already has an octet, regardless of whether it has a formal positive charge, another bond to that must break
- In bridged bicyclic compounds with less than 7 atoms in a ring, a bond between a bridgehead atom and its neighbor is forbidden due to ring strain

Chemical Bonding and Structure

Basic concepts:

- atomic orbitals, electron configurations
- hybridization, σand π bonds
- formal charge, electronegativity, polarity, inductive effects bond dipoles, molecular dipole moments
- resonance
- **polarizability**

Polarizability

- Polarizability measures the response of an ion or molecule to an electric field
- Polarizability is expressed in units of volume, typically in 10^{-24} cm^3
- Polarizability depends on the effectiveness of nuclear screening and increases as each valence shell is filled.
- Polarizability increases with atomic or ionic radius

Polarizability of Some Atoms, Ions, and Molecules

Atoms		Ions		Molecules		Hydrocarbons	
H	0.67			H_2O	1.45	CH_4	2.59
Li	24.3			N_2	1.74	C_2H_6	4.47
Be	5.6			CO	1.95	$CH_2{=}CH_2$	4.25
B	3.0			NH_3	2.81	$HC{\equiv}CH$	3.93
C	1.8			CO_2	2.91	C_3H_8	6.29
N	1.1			BF_3	3.31	$CH_3CH{=}CH_2$	6.26
O	0.8					$CH_3C{\equiv}CH$	6.18
F	0.06	F^-	1.2			*n*-C_4H_{10}	8.20
Ne	1.4	Na^+	0.9			*i*-C_4H_{10}	8.14
Cl	2.2	Cl^-	3			*n*-C_5H_{12}	9.99
Ar	3.6	K^+	2.3			Neopentane	10.20
Br	3.1	Br^-	4.5			*n*-C_6H_{14}	11.9
Kr	4.8					Cyclohexane	10.9
I	5.3	I^-	7			C_6H_6	10.3
Xe	6.9						

a. T. M. Miller, in *Handbook of Chemistry and Physics*, 83rd Edition, pp. 10-163–10-177, 2002.

b. A. Dalgano, *Adv. Phys.*, **11**, 281 (1962), as quoted by R. J. W. Le Fevre, *Adv. Phys. Org. Chem.*, **3**, 1 (1965).

Polarizability --- Hardness and Softness

Numerical measures of hardness:

$\eta = (I-A)/2$

I: ionization potential

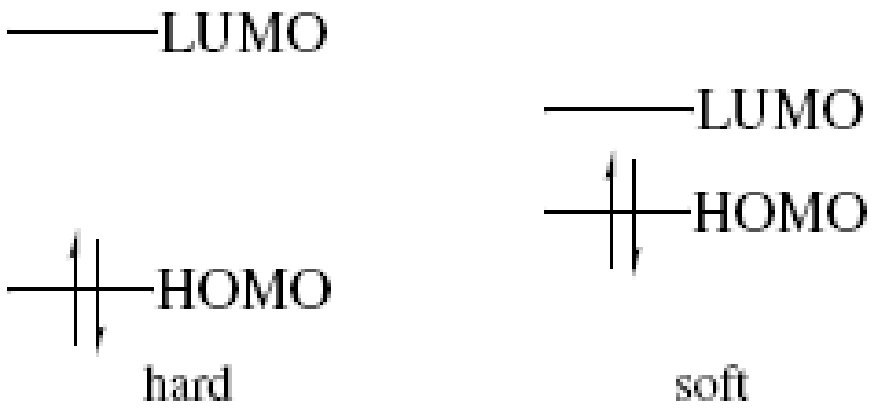
A: electron affinity

Atom	η	Acid	η_A	Base	η_B
H	6.4	H^+	∞	H^-	6.8
Li	2.4	Li^+	35.1	F^-	7.0
C	5.0	Mg^{2+}	32.5	Cl^-	4.7
N	7.3	Na^+	21.1	Br^-	4.2
O	6.1	Ca^{2+}	19.7	I^-	3.7
F	7.0	Al^{3+}	45.8	CH_3^-	4.0
Na	2.3	Cu^+	6.3	NH_2^-	5.3
Si	3.4	Cu^{2+}	8.3	OH^-	5.6
P	4.9	Fe^{2+}	7.3	SH^-	4.1
S	4.1	Fe^{3+}	13.1	CN^-	5.3
Cl	4.7	Hg^{2+}	7.7		
		Pb^{2+}	8.5		
		Pd^{2+}	6.8		

J. Am. Chem. Soc. **1983**, 7512

Polarizability --- Hardness and Softness

- Polarizability is also related to the LUMO- HOMO energy gap



- Polarizability has applications to explain some reactivity

Concepts you get to know now

- Hybridization (consistent sets of hybrid atomic orbitals contributed bonding)
- σ and π bonds (both in VBT and in MOT)
- Resonance (can be used to suggest subtle features of the electronic structure of functional groups)
- Electronegativity and bond polarization (introduce polarity into bonds and result in bond dipoles and molecular dipoles)
- Induction
- Polarizability (important in understanding solvent properties and many reactivity patterns)

Thermochemistry of stable molecules

Type of energies & energy changes

- Gibbs free energy (ΔG°), Enthalpy (ΔH°), Entropy (ΔS°)

Thermochemistry of stable molecules

Type of energies & energy changes

- Gibbs free energy (ΔG°), Enthalpy (ΔH°), Entropy (ΔS°)
- Bond Dissociation Energy (BDE), Strain Energy

Gibbs free energy (ΔG°)

$A \rightarrow B$

$\Delta G^\circ = G_B - G_A$

$\Delta G^\circ < 0$ --- transformation of A to B is exergonic

$\Delta G^\circ > 0$ --- transformation of A to B is endergonic

$\ln K_{eq} = -\Delta G^\circ / RT \quad K_{eq} = [B]/[A]$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ （Gibbs-Helmholtz equation）

$\ln K_{eq} = -\Delta H^\circ / RT + \Delta S^\circ / R$

Enthalpy (ΔH°)

- Enthalpy (ΔH°): heat of reaction, including heat of formation, heat of combustion, heat of hydrogenation, etc.

- $\Delta H^\circ < 0$ reaction is exothermic
- $\Delta H^\circ > 0$ reaction is endothermic

Entropy (ΔS°)

- Entropy (ΔS°): a measure of molecular disorder
- Degrees of freedom: translational (bond stretches), rotational (bond rotations), vibrational (bond angle vibrations)
- In general, the more kinds of motions and the more unconstrained those motions are, the more favorable the entropy.

Bond dissociation energies (BDE)

- R-H→R·+H· (gas phase, homolytic bond cleavage) ΔH° = BDE
- Thermodynamic BDE can be used to predict the reactivity of a molecule
- Use BDE to predict exothermicity and endothermicity

CH_3-H + H-OH → CH_3-OH + H-H

BDE 105.1 119 92.3 104.2

ΔH°= (105.1+119) – (92.3+104.2)= 27.6

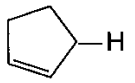
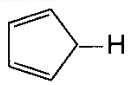
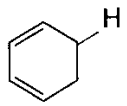
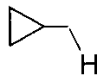
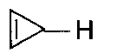
**Use BDE values from the same data set

Thermodynamic parameters for stable molecules

- Basic thermodynamic parameters for stable molecules (Δ G, Δ H, Δ S)
- Thermodynamic data available for comparison of relative stabilities of reactive intermediates: BDEs for radicals, HIAs for cations, pKa for anions.
- Molecular structures are dynamic --- conformational analysis, strain energy…

BDE of different Bond

Some Specific Bond Dissociation Energies (in kcal/mol)*

Bond	BDE	Bond	BDE	Bond	BDE
H–H	104.2 (104.2)	CH_2=CH–H	110 (110.7)	CH_3–CH_3	90.4 (90.1)
CH_3–H	105.1 (105.0)	C_6H_5–H	110.9 (112.9)	CH_3–F	109.9 (115)
CH_3CH_2–H	98.2 (101.1)	HC≡C–H	132 (131.9)	CH_3–Cl	84.6 (83.7)
$(CH_3)_2$CH–H	95.1 (98.6)	$C_6H_5CH_2$–H	88 (89.7)	CH_3–Br	70.9 (72.1)
$(CH_3)_3$C–H	93.2 (96.5)	CH_2=$CHCH_2$–H	86.3 (88.8)	CH_3–I	57.2 (57.6)
c$(CH_2)_3$–H	106.3	$CH_3C(O)$–H	86 (88.1)	CH_3–OH	92.3 (92.1)
c$(CH_2)_4$–H	96.5	HO–H	119 (118.8)	CH_3–NH_2	84.9 (85.2)
c$(CH_2)_5$–H	94.5	CH_3O–H	104.4 (104.6)	CH_3–SH	74
c$(CH_2)_6$–H	95.5	NH_2–H	107.4 (107.6)	CH_3–SiH_3	88.2
	82.3	CH_3S–H	90.7 (87.4)	CH_3–$SiMe_3$	89.4
		HO–OH	51	CH_3–$GeMe_3$	83
	71.1	CH_3O–OCH_3	37.6 (38)	CH_3–$SnMe_3$	71
		$HOCH_2$–H	94 (96.1)	CH_3–$PbMe_3$	57
	73	H_2C=CH_2	(174.1)	CH_3–OCH_3	(83.2)
	97.4	HC≡CH	(230.7)	CH_3–C_2H_5	(89.0)
	90.6	H_2C=O	(178.8)	CH_3–$CH(CH_3)_2$	(88.6)
CH_3–CH=CH_2	(101.4)	CH_3–C_6H_5	(103.5)	CH_3–$C(CH_3)_3$	(87.5)
C_6H_5–C_6H_5	(118)	CH_3–$CH_2C_6H_5$	(77.6)	CH_3–CH_2CH=CH_2	(76.5)

*The bond of interest is shown in color. Values are from two sources. Numbers not in parentheses are from McMillen, D. F., and Golden, D. M. "Hydrocarbon Bond Dissociation Energies." *Ann. Rev. Phys. Chem.*, **33**, 493 (1982). Numbers in parentheses are from a recent attempt to provide the most current estimates, reconciling variations among results obtained from different methods. Blanksby, S. J., and Ellison, G. B. "Bond Dissociation Energies of Organic Molecules." *Acc. Chem. Res.*, **36**, 255–263 (2003).

Group increment

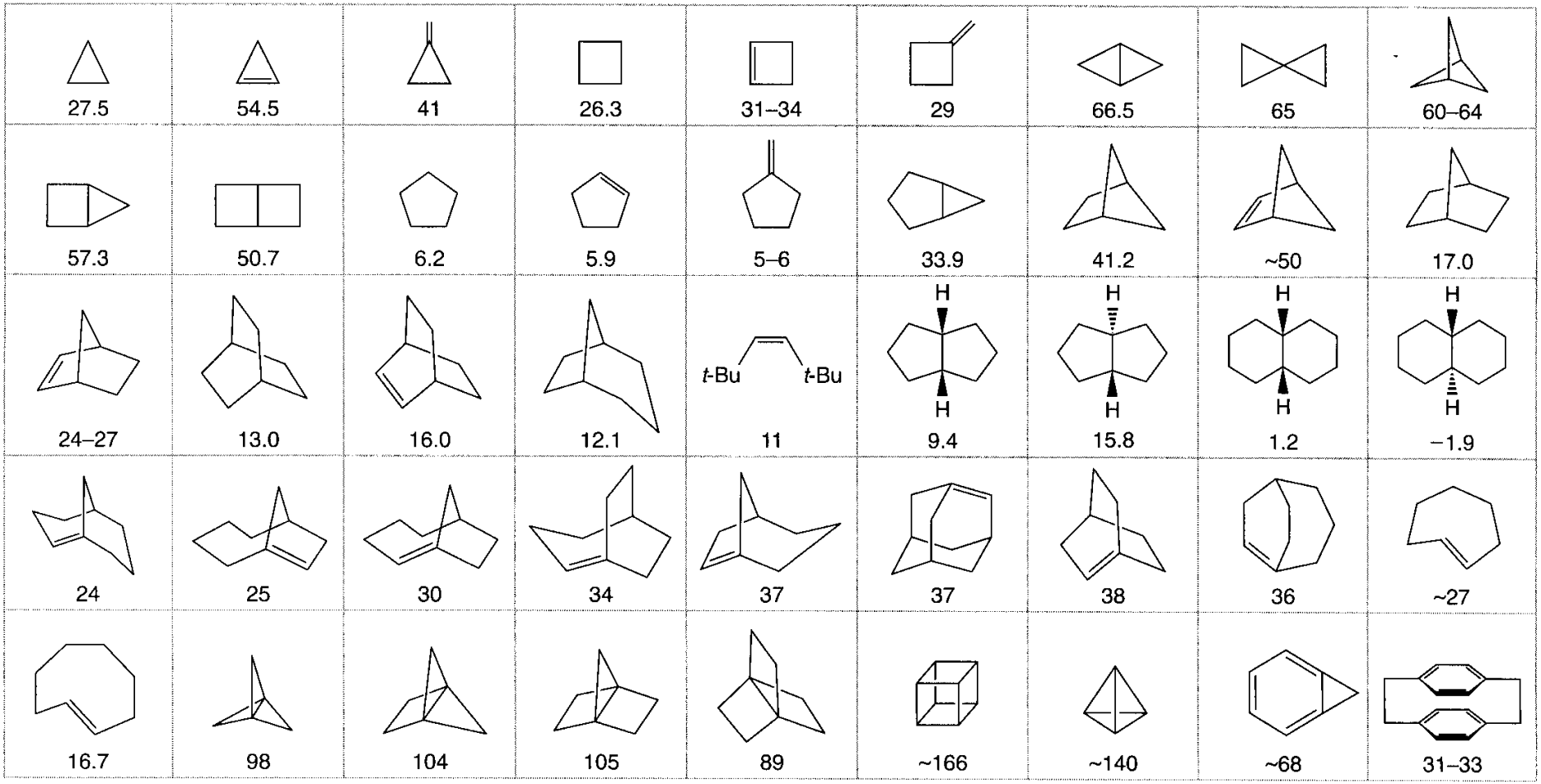
Group Increments (in kcal/mol) for Fundamental Groupings*

Group	ΔH_f°	Group	ΔH_f°	Group	ΔH_f°
$C-(H)_3(C)$	−10.20	$C-(O)(C_d)(H)_2$	−6.5	$C-(O)_2(C)_2$	−18.6
$C-(H)_2(C)_2$	−4.93	$C_B-(O)$	−0.9	$C-(O)_2(C)(H)$	−16.3
$C-(H)(C)_3$	−1.90	$O-(C)_2$	−23.2	$C-(O)_2(H)_2$	−16.1
$C-(C)_4$	0.50	$O-(C)(H)$	−37.9	$C-(N)(H)_3$	−10.08
$C_d-(H)_2$	6.26	$O-(C_d)_2$	−33.0	$C-(N)(C)(H)_2$	−6.6
$C_d-(H)(C)$	8.59	$O-(C_d)(C)$	−30.5	$C-(N)(C)_2(H)$	−5.2
$C_d-(C)_2$	10.34	$O-(C_B)_2$	−21.1	$C-(N)(C)_3$	−3.2
$C_d-(C_d)(H)$	6.78	$O-(C_B)(C)$	−23.0	$C_B-(N)$	−0.5
$C_d-(C_d)(C)$	8.88	$O-(C_B)(H)$	−37.9	$N-(C)(H)_2$	4.8
$C_d-(C_B)(H)$	6.78	$C-(CO)(C)_3$	1.58	$N-(C)_2(H)$	15.4
$C_d-(C_B)(C)$	8.64	$C-(CO)(C)_2(H)$	−1.83	$N-(C)_3$	24.4
$C_d-(C_d)_2$	4.6	$C-(CO)(C)(H)_2$	−5.0	$N-(C_B)(H)_2$	4.8
$C_B-(H)$	3.30	$C-(CO)(H)_3$	−10.08	$N-(C_B)(C)(H)$	14.9
$C_B-(C)$	5.51	$C_B-(CO)$	9.7	$N-(C_B)(C)_2$	26.2
$C_B-(C_d)$	5.68	$CO-(C)_2$	−31.4	$N-(C_B)_2(H)$	16.3
$C_B-(C_B)$	4.96	$CO-(C)(H)$	−29.1	$N_I-(H)$	16.3
$C-(C_d)(C)(H)_2$	−4.76	$CO-(H)_2$	−26.0	$N_I-(C)$	21.3
$C-(C_d)_2(H)_2$	−4.29	$CO-(C_B)_2$	−25.8	$N_I-(C_B)$	16.7
$C-(C_d)(C_B)(H)_2$	−4.29	$CO-(C_B)(C)$	−30.9	$CO-(N)(H)$	−29.6
$C-(C_B)(C)(H)_2$	−4.86	$CO-(C_B)(H)$	−29.1	$CO-(N)(C)$	−32.8
$C-(C_d)(C)_2(H)$	−1.48	$CO-(O)(C)$	−35.1	$N-(CO)(H)_2$	−14.9
$C-(C_B)(C)_2(H)$	−0.98	$CO-(O)(H)$	−32.1	$N-(CO)(C)(H)$	−4.4
$C-(C_d)(C)_3$	1.68	$CO-(O)(C_d)$	−32.0	$N-(CO)(C)_2$	—
$C-(C_B)(C)_3$	2.81	$CO-(O)(C_B)$	−36.6	$N-(CO)(C_B)(H)$	0.4
$C-(O)(C)_3$	−6.6	$CO-(C_d)(H)$	−29.1	$N-(CO)_2(H)$	−18.5
$C-(O)(C)_2(H)$	−7.2	$O-(CO)(C)$	−43.1	$N-(CO)_2(C)$	−5.9
$C-(O)(C)(H)_2$	−8.1	$O-(CO)(H)$	−58.1	$N-(CO)_2(C_B)$	−0.5
$C-(O)(H)_3$	−10.08	$C_d(CO)(C)$	7.5		
$C-(O)(C_B)(H)_2$	−8.1	$C_d-(CO)(H)$	5.0		

C_d = double bond; C_B = benzene carbon; N_I = imine nitrogen.

*Data are from Benson, S. W. (1976). *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2d ed., John Wiley & Sons, New York.

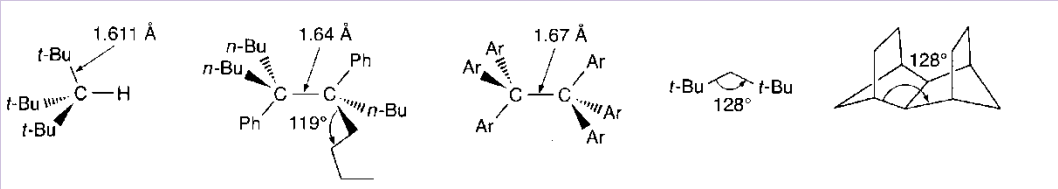
Strain energy



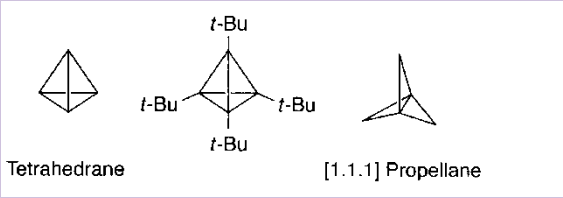
A potpourri of strained molecules and their associated strain energies (in kcal/mol).

Highly strained molecules

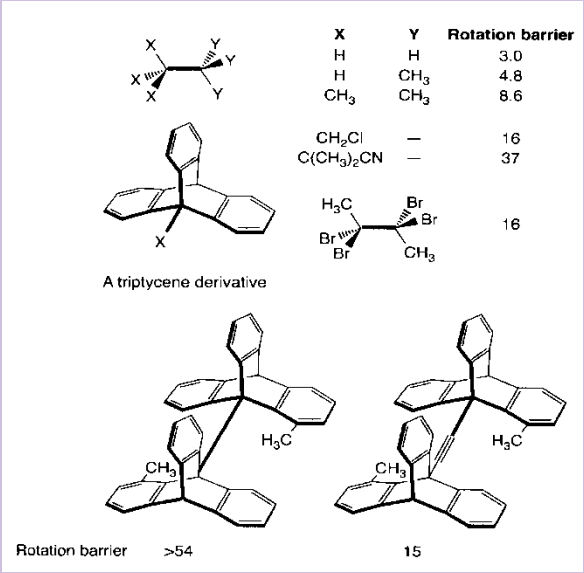
- Long Bonds and large angles resulted from excessive steric crowding



- Small rings (some are unstable but persistent)



- Very large rotation Barriers



Electronic effects

- **Interactions involving π systems**

Substitution on alkenes

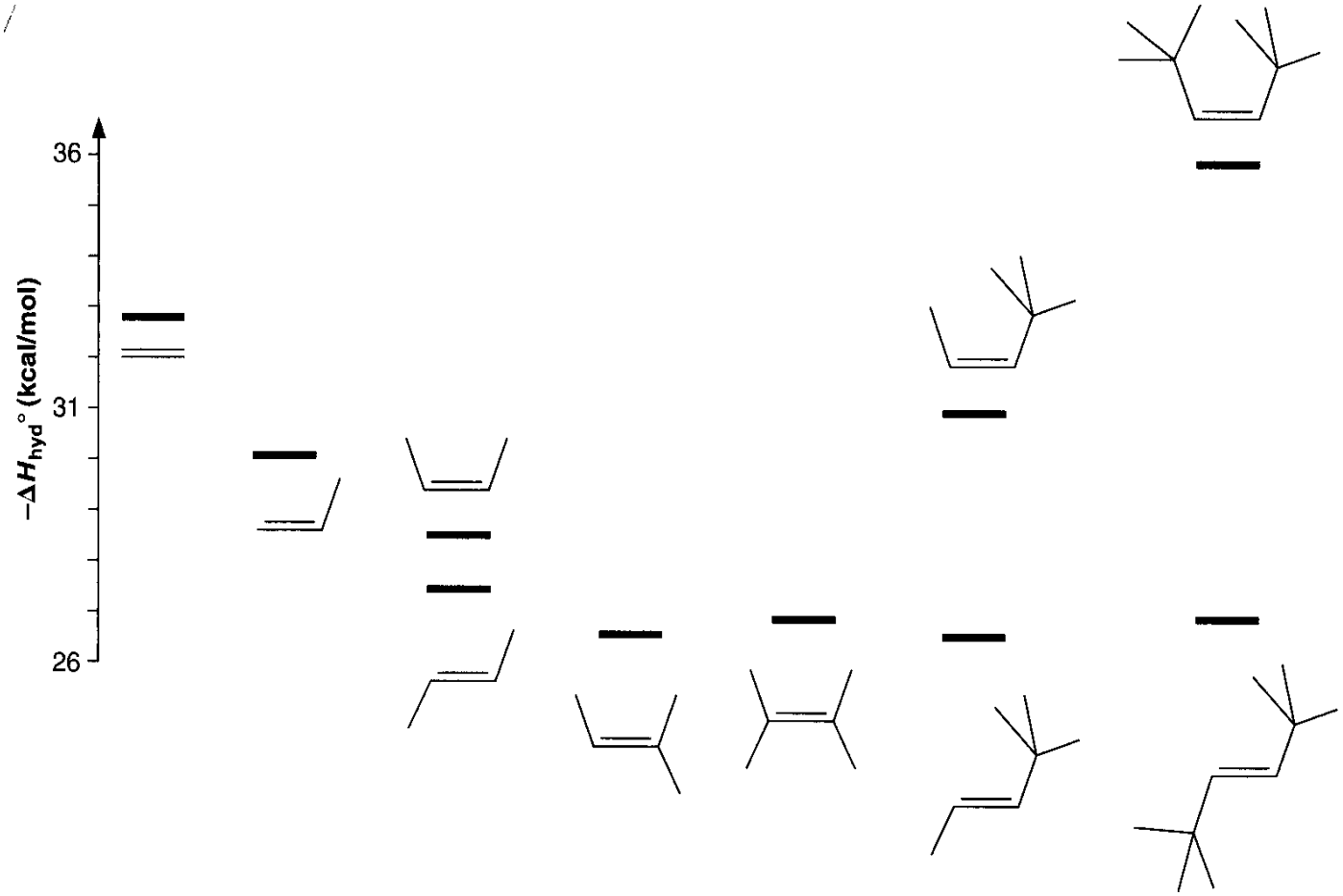
Conjugation

Aromaticity and antiaromaticity

Polycyclic aromatic hydrocarbons and large annulenes

- **Effects of heteroatoms**

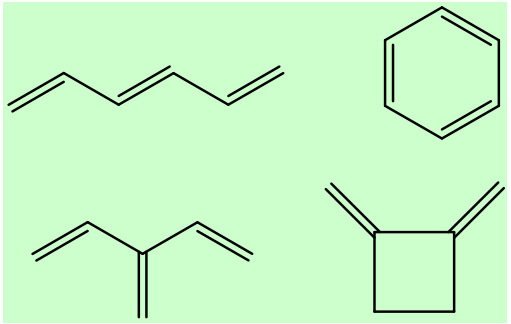
Substitution on alkenes



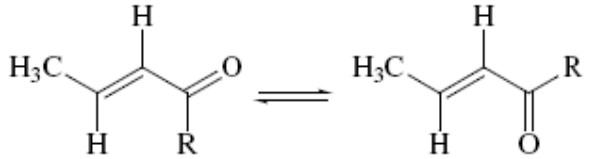
Heat of hydrogenation values ($\Delta H°$) for several alkenes. The effect of alkyl substitution is evident. Also, the stability of trans double bonds remains relatively constant, but significant destabilization of the cis alkenes is seen as the R group size increases. Derived from data in Turner, R. B., Jarrett, A. D., Goebel, P., and Mallon, B. J. "Heats of Hydrogenation. IX. Cyclic Acetylenes and Some Miscellaneous Olefins." *J. Am. Chem. Soc.* **95**, 790 (1973).

Conjugation

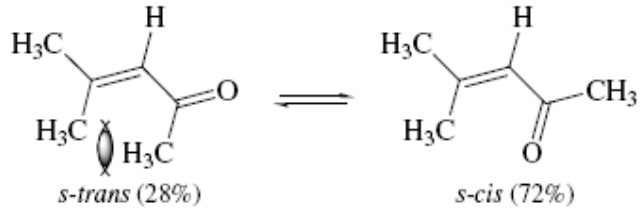
Conjugation and cross-conjugation



Conformation of conjugated dienes and α,β-unsaturated ketones

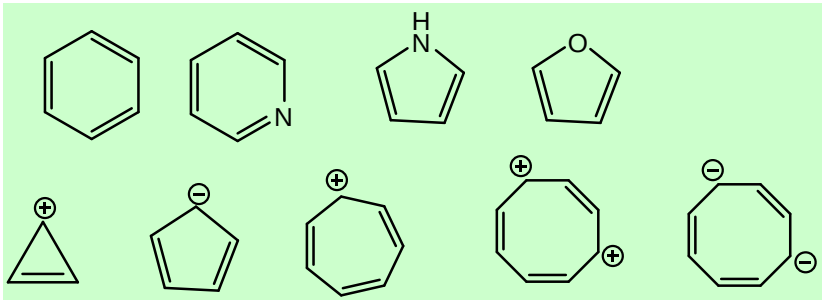


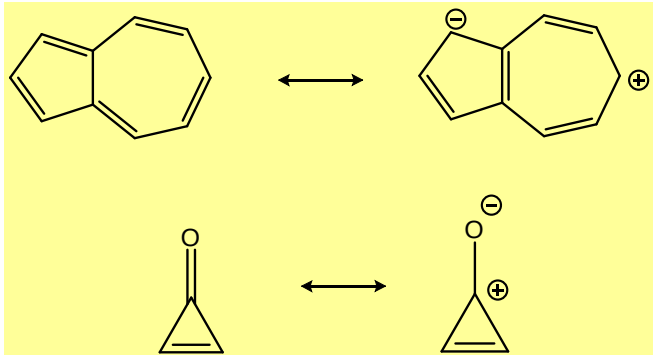
	s-trans	*s-cis*
R = CH_3	0.7	0.3
CH_3CH_2	0.55	0.45
$(CH_3)_2CH$	0.3	0.7
$(CH_3)_3C$	0.0	1.0



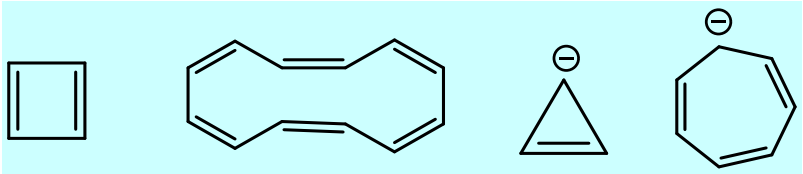
Aromaticity and antiaromaticity

- Aromaticity --- Hückel 4n+2 rule

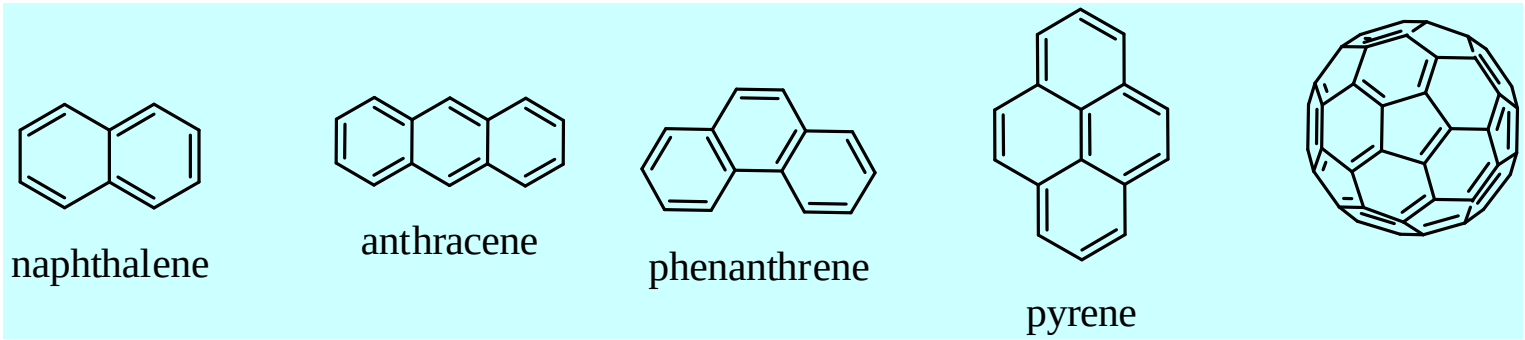


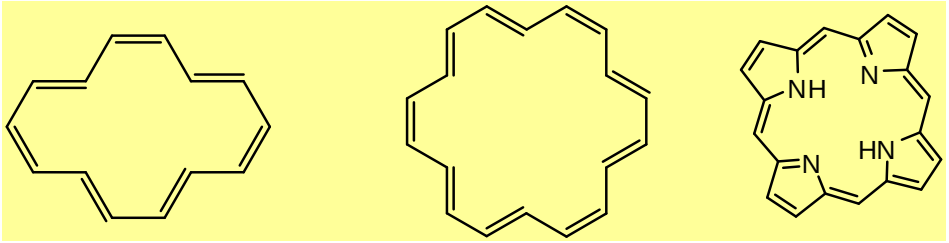


- Antiaromaticity



Polycyclic aromatic hydrocarbons and large annulenes

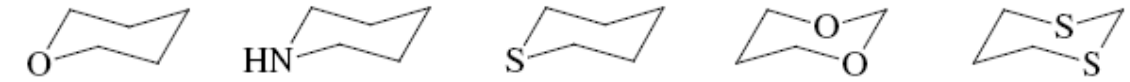




Effects of heteroatoms

- Bond length and angles

Bond length: C-O **1.43** Å, C-N **1.47** Å, C-C **1.54** Å, C-S **1.82** Å



tetrahydropyran piperidine thiane 1,3-dioxane 1,3-dithiane

Comparison of Conformational Free-Energy Values for Substituents on Tetrahydropyran, 1,3-Dioxane, and 1,3-Dithiane Rings with Those for Cyclohexane

	$-\Delta G^\circ$ (kcal/mol)					
		Tetrahydro-pyran[a]	1,3-Dioxane[b]		1,3-Dithiane[c]	
Group	Cyclohexane	2-Position	2-Position	5-Position	2-Position	5-Position
CH_3-	1.8	2.9	4.0	0.8	1.8	1.0
CH_3CH_2-	1.8		4.0	0.7	1.5	0.8
$(CH_3)_2CH-$	2.1		4.2	1.0	1.5	0.8
$(CH_3)_3C-$	>4.5			1.4	> 2.7	
$CH_2=CH-$	1.7	2.3				
$CH\equiv C-$	0.5	0.3				

a. E. L. Eliel, K. D. Hargrave, K. M. Pietrusiewicz, and M. Manoharan, *J. Am. Chem. Soc.* **104:**3635 (1982).
b. E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.* **90:**3444 (1968); F. W. Nader and E. L. Eliel, *J. Am. Chem. Soc.* **92:**3050 (1970).
c. E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc.* **91:**2703 (1969).