

## Organic Molecules ~ Structure, Chemistry and Nomenclature (cont.)- ~ Energy Structure~

- Cyclic compounds
- Aromatic hydrocarbons - Benzene
  
- Determining the structure of organic compounds  
(IR spectroscopy, Mass Spectroscopy, NMR)
  
- Energy Structure of a Diatomic Molecule

*Acknowledgement:*

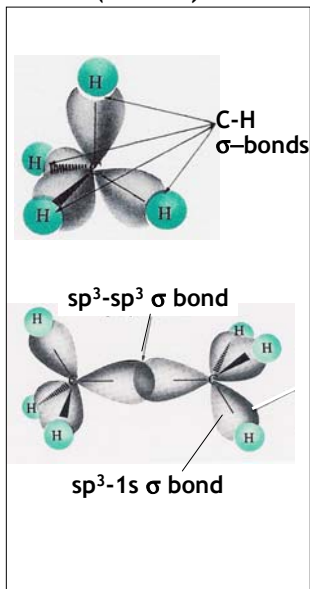


figures in slides 1-14,16 are from *Organic Chemistry* by G.M. Loudo,  
figures in slide 15 are from *Electronic Processes in Organic Crystals and Polymers*  
by M. Pope and C.E. Swenberg

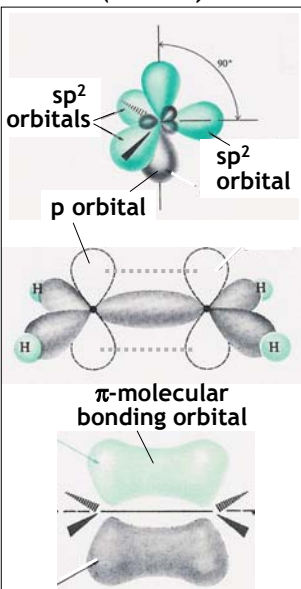
February 12, 2002 - Organic Optoelectronics - Lecture 3

### Bonding in Aliphatic Hydrocarbons

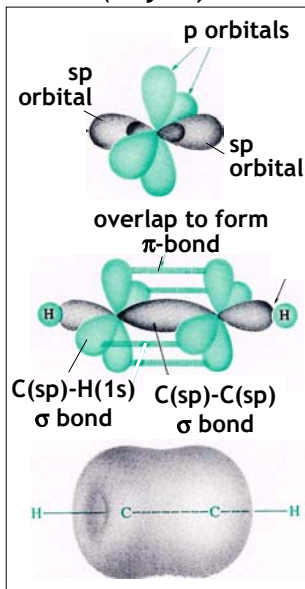
*single bonds  
(alkanes)*



*double bonds  
(alkenes)*



*triple bonds  
(alkynes)*

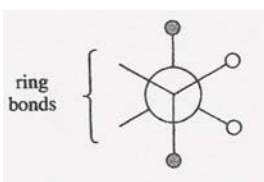


**TABLE 3.1 The n-Alkanes**

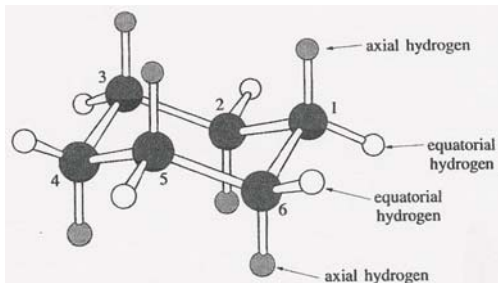
Compound name	Molecular formula	Condensed structural formula	Melting point, °C	Boiling point, °C	Density,* g/mL
methane	CH <sub>4</sub>	CH <sub>4</sub>	-182.5	-161.7	—
ethane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	-183.3	-88.6	—
propane	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-187.7	-42.1	0.5005
butane	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	-138.3	-0.5	0.5788
pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-129.8	36.1	0.6262
hexane	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	-95.3	68.7	0.6603
heptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	-90.6	98.4	0.6837
octane	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	-56.8	125.7	0.7026
nonane	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	-53.5	150.8	0.7177
decane	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	-29.7	174.0	0.7299
undecane	C <sub>11</sub> H <sub>24</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	-25.6	195.8	0.7402
dodecane	C <sub>12</sub> H <sub>26</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	-9.6	216.3	0.7487
eicosane	C <sub>20</sub> H <sub>42</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>	+36.8	343.0	0.7886

\*The densities tabulated in this text are at 20° unless otherwise noted.

## Cyclic Compounds

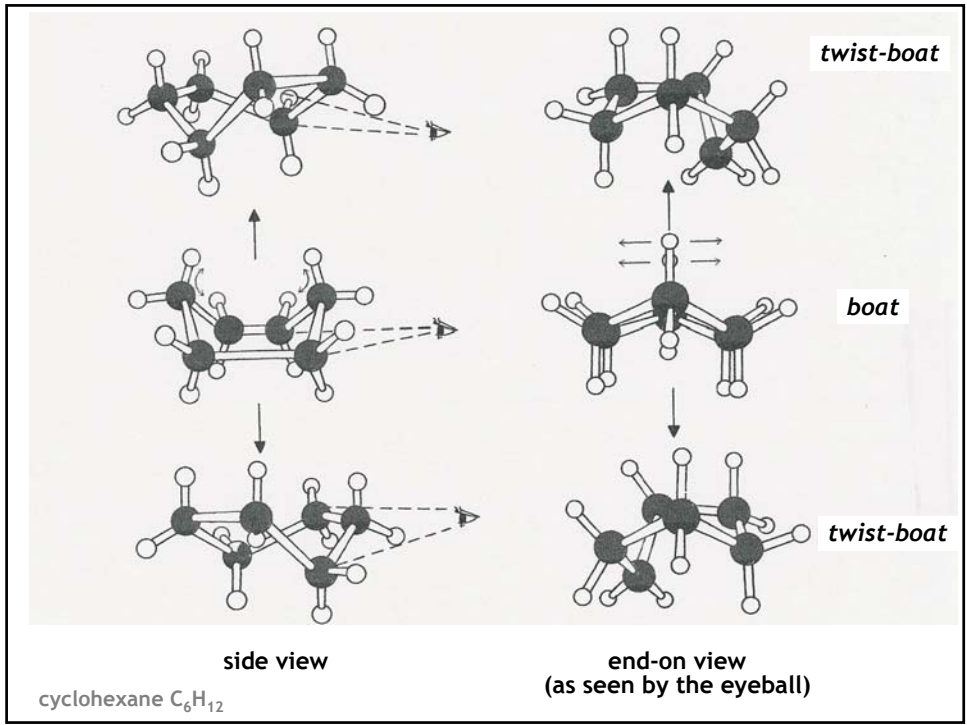
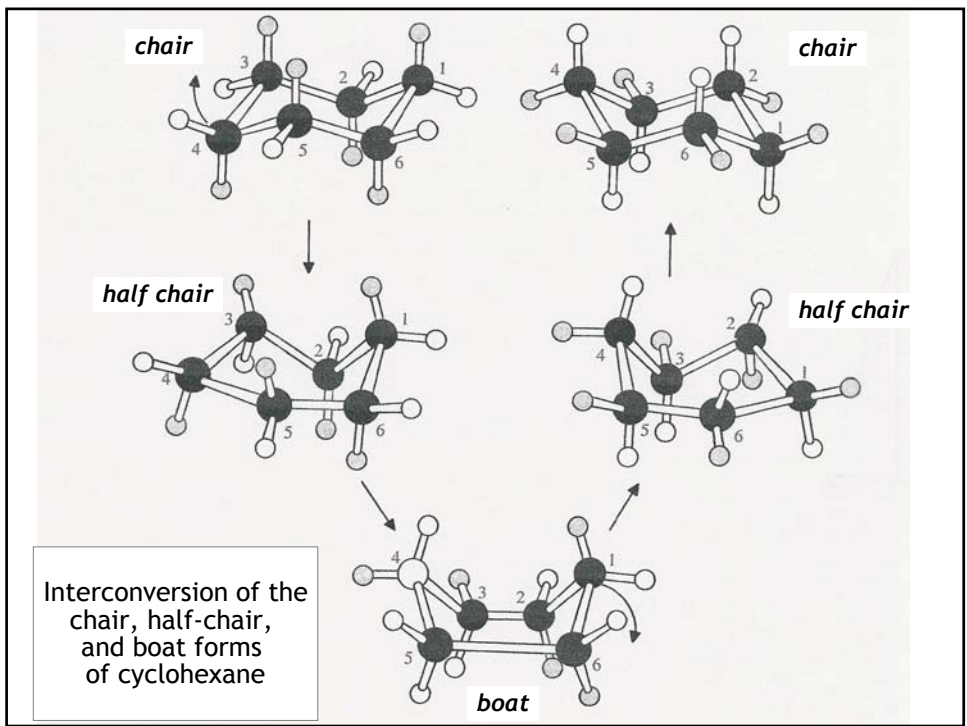


cyclohexane C<sub>6</sub>H<sub>12</sub>

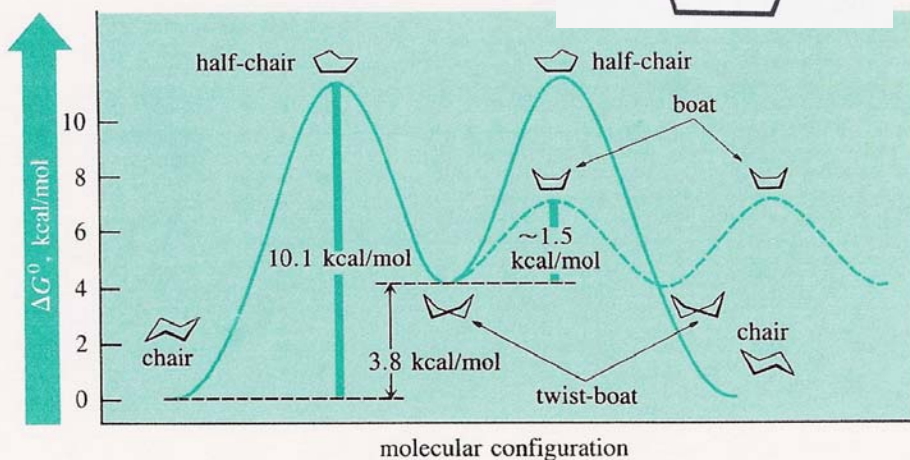


**TABLE 7.1 Heats of Formation Per —CH<sub>2</sub>— for Some Cycloalkanes (n = number of carbon atoms)**

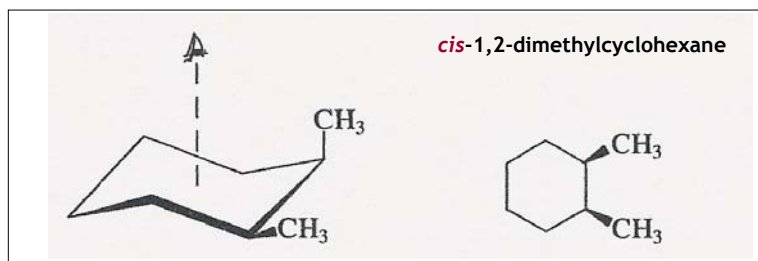
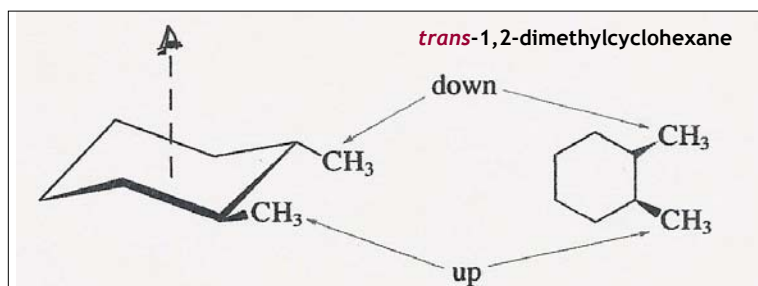
n	Compound	$\Delta H_f^\circ/n$ , kcal/mol	n	Compound	$\Delta H_f^\circ/n$ , kcal/mol
3	cyclopropane	+4.25	9	cyclononane	-3.95
4	cyclobutane	+1.65	10	cyclodecane	-3.75
5	cyclopentane	-3.65	11	cycloundecane	-4.95
6	cyclohexane	-4.95	12	cyclododecane	-4.65
7	cycloheptane	-4.05	13	cyclotridecane	-4.55
8	cyclooctane	-3.75	14	cyclotetradecane	-4.95



## Relative free energies of cyclohexane conformations



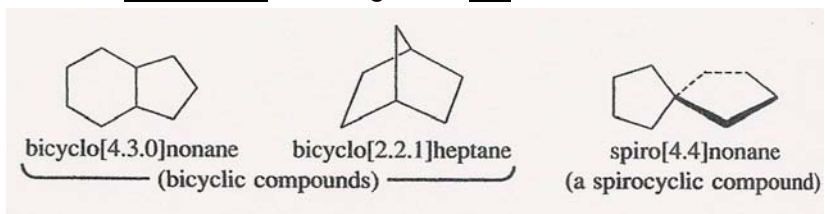
## Planar representation of cyclic compounds



## Bicyclic Compounds

**BICYCLIC** - two rings share two common atoms

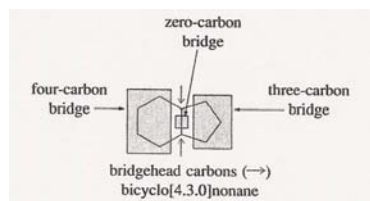
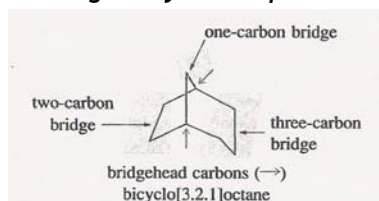
**SPIROCYCLIC** - two rings share one common atom



**FUSED** - when the two rings are joined at adjacent carbons

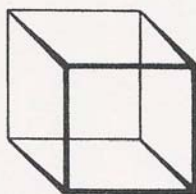
**BRIDGED** - when the two rings are joined at nonadjacent carbons

### Naming a bicyclic compounds

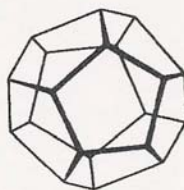


## Polycyclic Compounds

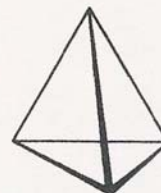
Compounds that contain many rings joined at common atoms



cubane

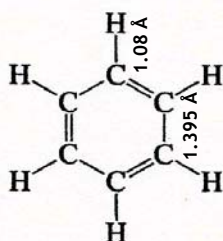


dodecahedrane

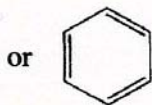


tetrahedrane

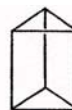
## Aromatic Hydrocarbons



... the simplest of which is Benzene  
(a puzzling "conjugated alkene")

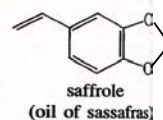
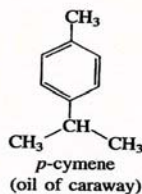
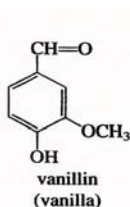


Ladenburg benzene,  
or prismane



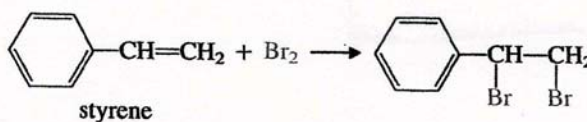
(the way benzene was  
imagined in the 19<sup>th</sup>  
century - no double bonds)

Name AROMATIC is historical as many fragrant compounds are derivatives of benzene



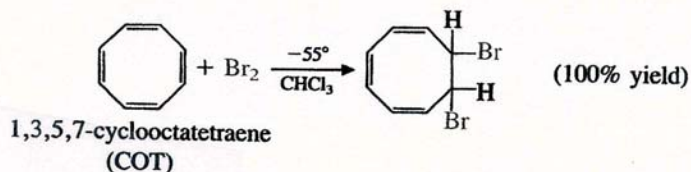
How does benzene differ from alkenes and other cyclic compounds ?

It is Very Stable !

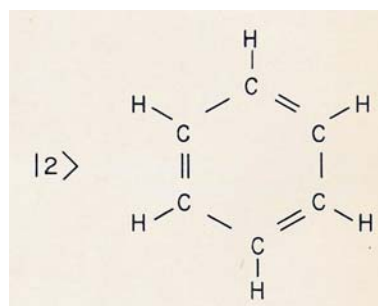
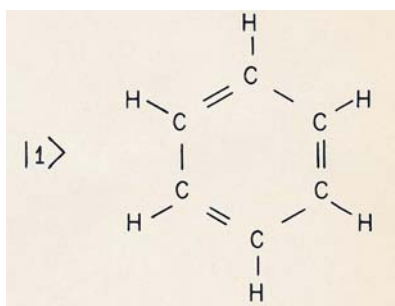


The noncyclic double bond in styrene rapidly adds bromine, but the benzene ring remains unaffected.

We might speculate that benzene's lack of reactivity has something to do with its cyclic structure; yet cyclohexene also brominates readily. Perhaps, then, it is the cyclic structure and the conjugated double bonds that *together* account for the unusual behavior of benzene. However, 1,3,5,7-cyclooctatetraene (which we shall abbreviate as COT) brominates smoothly even at low temperature.



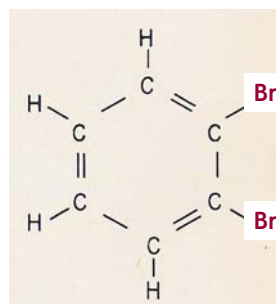
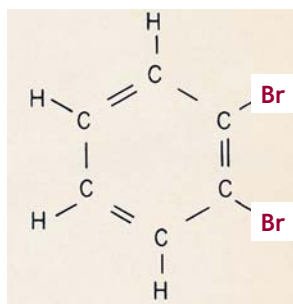
A set of base states for benzene molecule



Heat of formation of benzene is 19.82 kcal/mol or 3.3 kcal/mol per CH group  
 COT is 71.23 kcal/mol or 8.9 kcal/mol per CH group

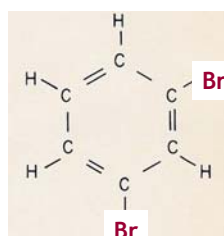
→ per CH group benzene is  $8.9 - 3.3 = 5.6$  kcal/mol more stable  
 this energy difference is known as the empirical resonance energy

RESONANCE STRUCTURE ENHANCES STABILITY

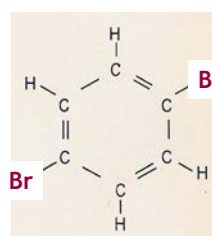


BASE STATES of ortho-dibromobenzene

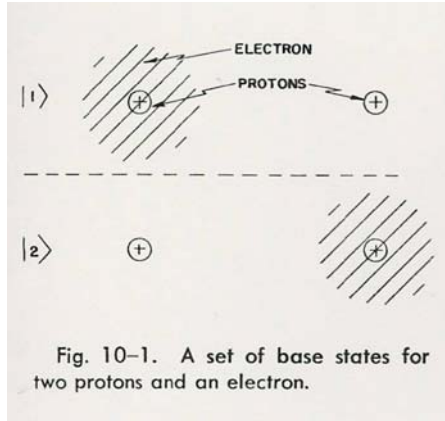
meta-dibromobenzene



para-dibromobenzene



## H<sub>2</sub><sup>+</sup> ion - a Two-Level System



$$|I\rangle = \frac{1}{\sqrt{2}} [ |1\rangle - |2\rangle ], \quad |II\rangle = \frac{1}{\sqrt{2}} [ |1\rangle + |2\rangle ]$$

$$E_I = \frac{H_{11} + H_{22}}{2} + \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}H_{21}}$$

$$E_{II} = \frac{H_{11} + H_{22}}{2} - \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}H_{21}}$$

where  $H_{12} = H_{21} = A$

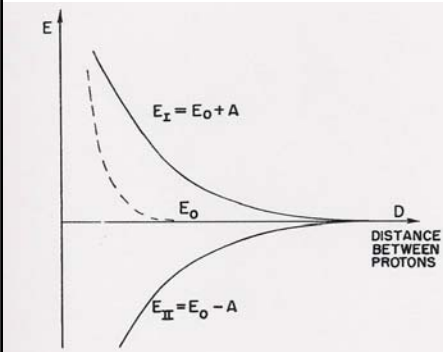


Fig. 10-2. The energies of the two stationary states of the H<sub>2</sub><sup>+</sup> ion as a function of the distance between the two protons.

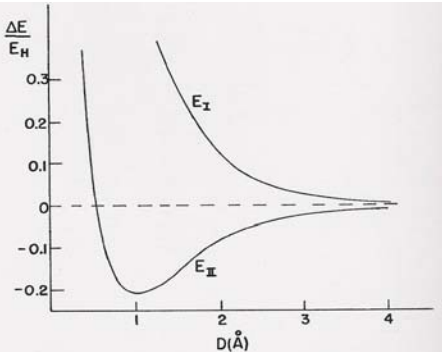


Fig. 10-3. The energy levels of the H<sub>2</sub><sup>+</sup> ion as a function of the interproton distance D. (E<sub>h</sub> = 13.6 eV.)

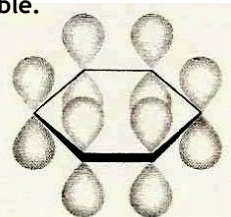


## Aromaticity

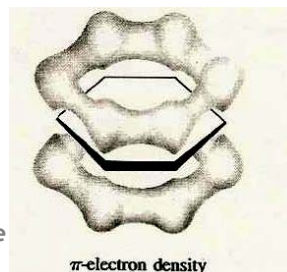
Compounds that conform to the Huckel's  $4n+2$  Rule are comparably to benzene in chemically stable. These are known as aromatic compounds

Aromatic compounds have:

1. cyclic arrangement of p-orbitals
2. p-orbital on every atom of the ring
3. aromatic rings that are planar
4. cyclic arrangement of the p-orbitals that contain  $4n+2$   $\pi$ -electrons (i.e. aromatic compounds have 2, 6, 10, ...  $\pi$ -electrons)



p orbitals

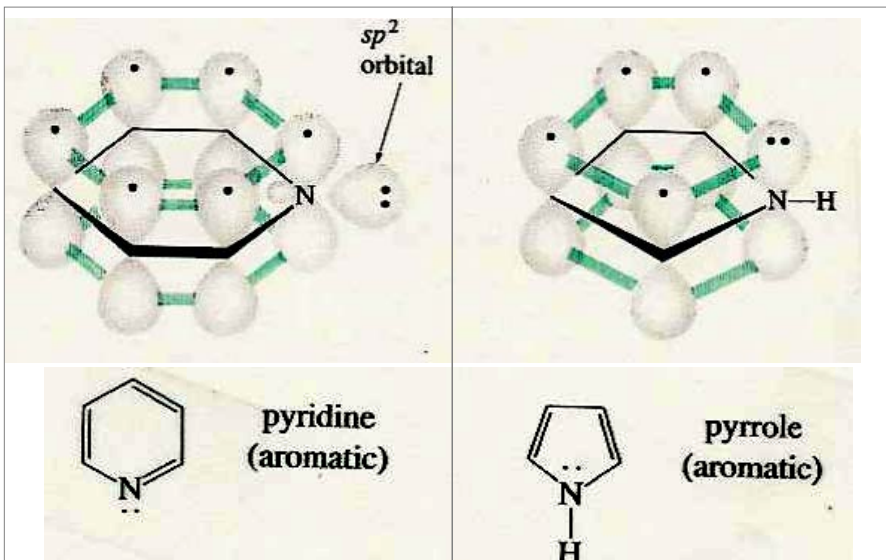


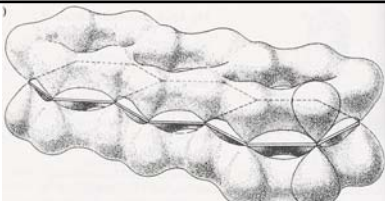
benzene

$\pi$ -electron density

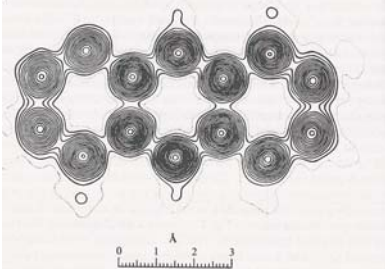
## Examples of Aromatic Compounds

(these are not pure hydrocarbons yet they are aromatic)



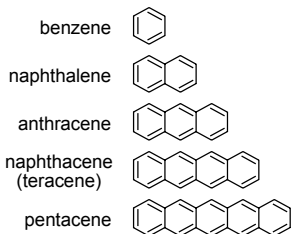


The lowest bonding MO of anthracene



### Examples of Aromatic Compounds (cont.)

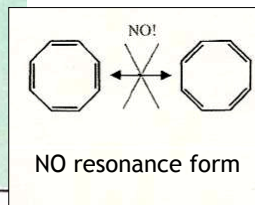
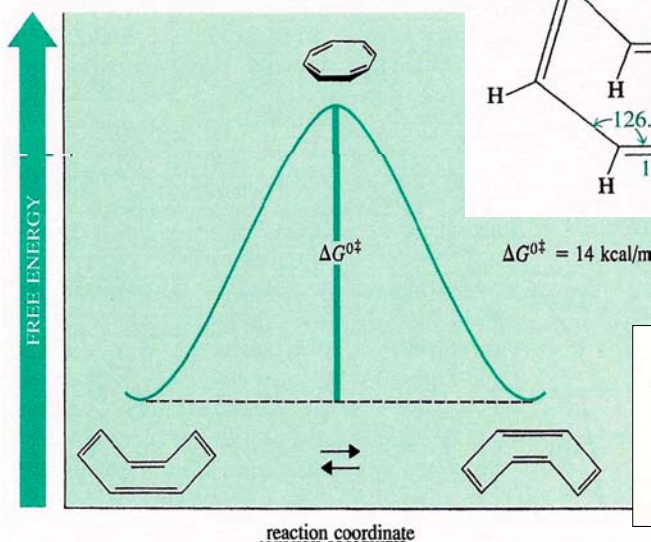
Class of materials known as polyacenes or acenes

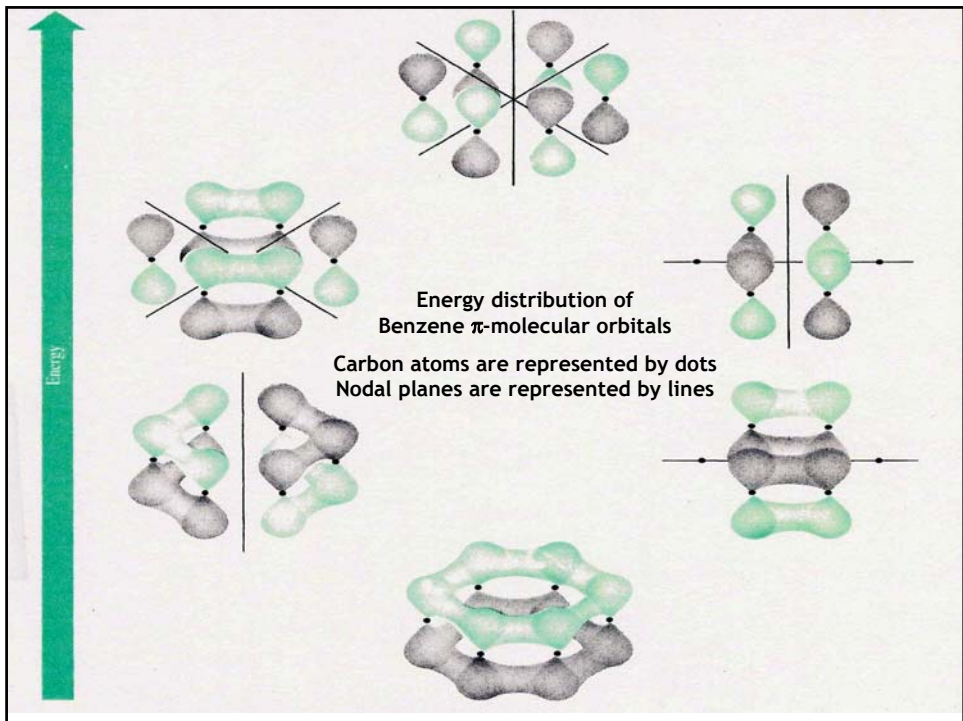
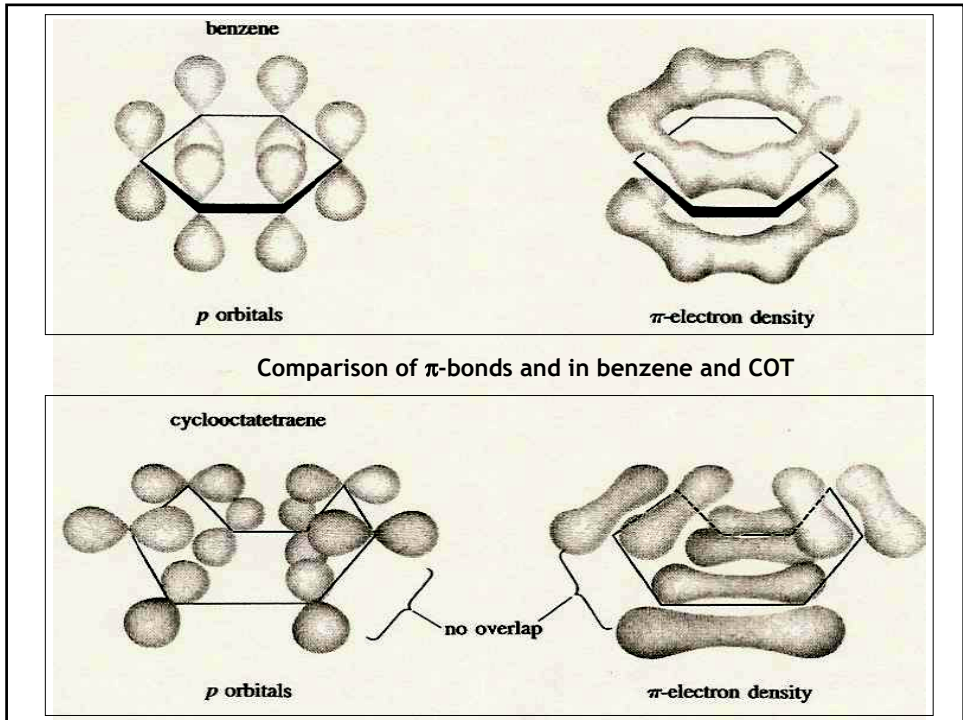


Chemical stability of these molecules decreases as the size of the molecule increases. (e.x. pentacene and hexacene oxidize readily in air, while benzene, naphthalene, and anthracene are stable in absence of light).

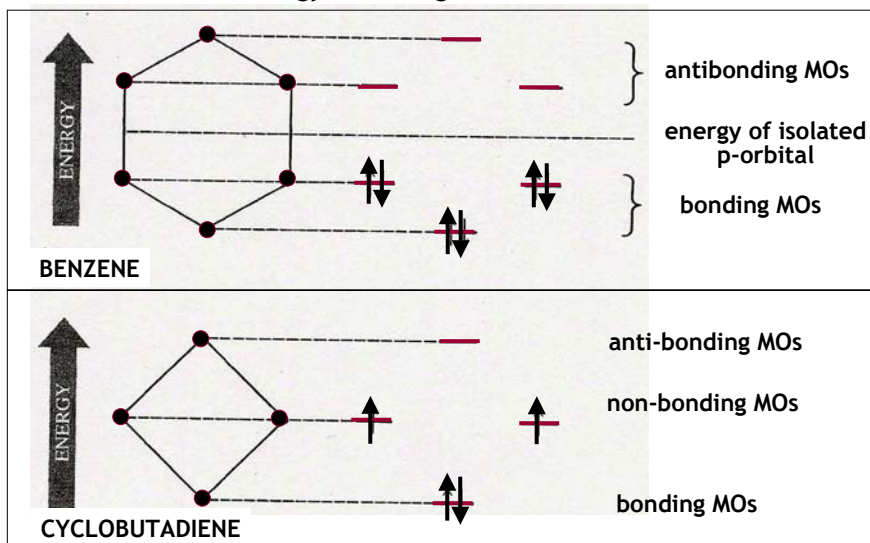
In studying the properties of polyacenes it will be sufficient to focus on the properties of the  $\pi$ -electrons

### COT is not aromatic





### Construction of energy-level diagrams for $\pi$ -molecular orbitals



Just as filled atomic orbitals are associated with stability of atoms (such as noble gases), filled *bonding molecular orbitals* are associated with stability in conjugated molecules → Aromatic compounds are stable !

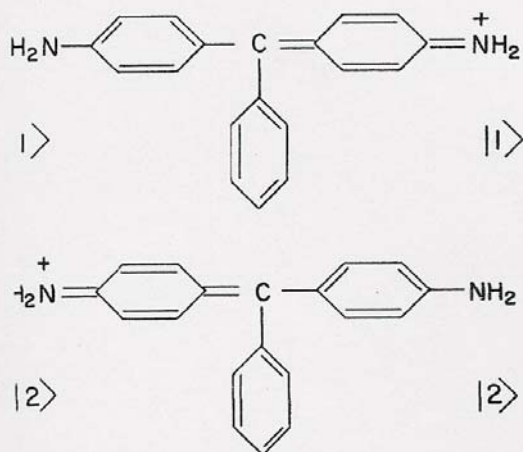


Fig. 10-9. Two base states for the molecule of the dye magenta.

## Common Organic Solvents

**Protic solvents** consist of molecules that can act as hydrogen-bond donors

**Polar solvents** have relatively high dielectric constant

**Donor Solvents** are capable of donating electron pairs

To dissolve a covalent compound in a solvent follow the rule of thumb: "Like dissolves like"

TABLE 8.2 Properties of Some Common Organic Solvents (Listed in order of increasing dielectric constant)

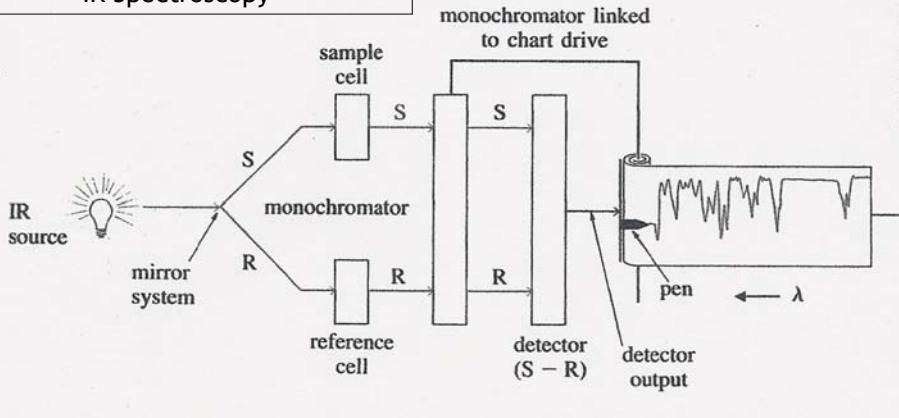
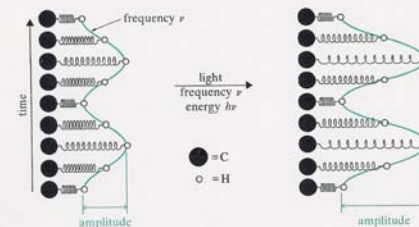
Solvent	Structure	Common abbreviation	Boiling point, °C	Dielectric constant, $\epsilon^*$	Class		
					Polar	Protic	Donor
hexane	<chem>CH3(CH2)4CH3</chem>	—	68.7	1.9			
1,4-dioxane**		—	101.3	2.2			x
carbon tetrachloride	<chem>CCl4</chem>	—	76.8	2.2			
benzene**		—	80.1	2.3			
diethyl ether	<chem>(C2H5)2O</chem>	<chem>Et2O</chem>	34.6	4.3			x
chloroform	<chem>CHCl3</chem>	—	61.2	4.8			
ethyl acetate	<chem>CH3CO2C2H5</chem>	<chem>EtOAc</chem>	77.1	6.0			x
acetic acid	<chem>CH3CO2H</chem>	<chem>HOAc</chem>	117.9	6.1		x	x
tetrahydrofuran		<chem>THF</chem>	66	7.6			x
methylene chloride	<chem>CH2Cl2</chem>	—	39.8	8.9			
acetone	<chem>CH3COCH3</chem>	<chem>Me2CO</chem> , <chem>DMK</chem>	56.3	21	x		x
ethanol	<chem>C2H5OH</chem>	<chem>EtOH</chem>	78.3	25	x	x	x
hexamethylphosphoric triamide**	<chem>[(CH3)3N]3P=O</chem>	<chem>HMPA</chem> , <chem>HMPPT</chem>	235	30	x		x
methanol	<chem>CH3OH</chem>	<chem>MeOH</chem>	64.7	33	x	x	x
nitromethane	<chem>CH3NO2</chem>	<chem>MeNO2</chem>	101.2	36	x		
<i>N,N</i> -dimethylformamide	<chem>H2C=N(CH3)2</chem>	<chem>DMF</chem>	153.0	37	x		x
acetonitrile	<chem>CH3C#N</chem>	<chem>MeCN</chem>	81.6	38	x		
sulfolane		—	287 (dec)	43	x		x
dimethylsulfoxide	<chem>CH3SCH3</chem>	<chem>DMSO</chem>	189	47	x		x
formic acid	<chem>HCOOH</chem>	—	100.6	59	x	x	x
water	<chem>H2O</chem>	—	100.0	78	x	x	x
formamide	<chem>HCNH2</chem>	—	211 (dec)	111	x	x	x

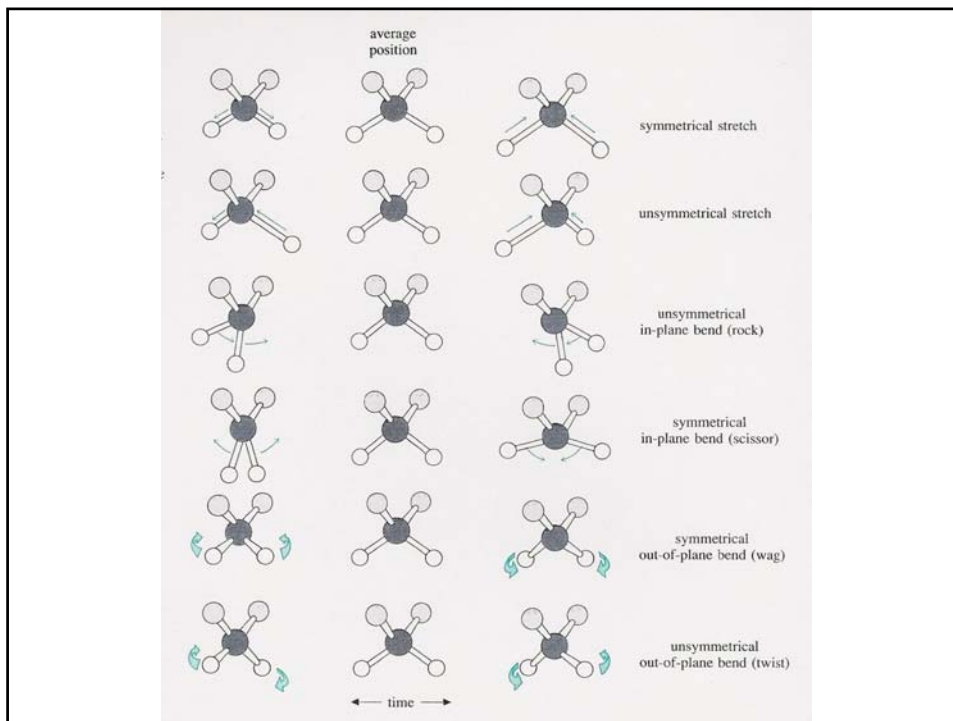
\*list values are at or near 25° \*\*Known carcinogen

## Common Spectroscopic Techniques

Infra-Red Spect.  
Mass Spect.  
UV-Visible Spect.  
NMR

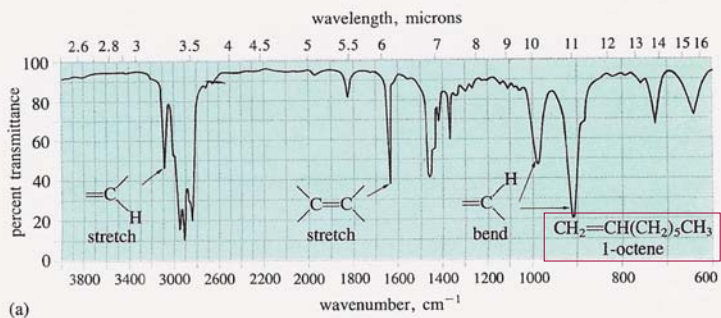
### IR Spectroscopy



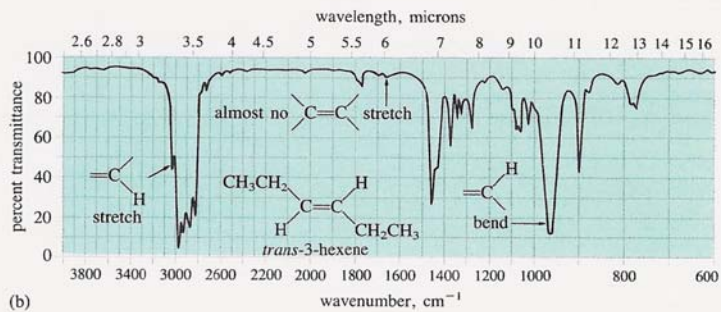


**TABLE 12.1 Important Infrared Absorptions of Alkenes**

Functional group	Absorption
stretching absorption	
$-\text{CH}=\text{CH}_2$ (terminal vinyl)	$1640\text{ cm}^{-1}$ (m)
$\text{C}=\text{CH}_2$ (terminal methylene)	$1655\text{ cm}^{-1}$ (m)
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">   <math>\text{H}-\text{C}=\text{C}-\text{H}</math>  <i>(cis-alkene)</i> </div> <div style="text-align: center;">   <math>\text{H}-\text{C}=\text{C}-\text{H}</math>  <i>(trans-alkene)</i> </div> </div>	$1660\text{--}1675\text{ cm}^{-1}$ (w) (absent in some compounds)
$\text{C}=\text{C}-\text{H}$	
<b>=C—H stretching absorption</b>	
$=\text{C}-\text{H}$	$3020\text{ cm}^{-1}$ (m)
$=\text{CH}_2$	$3080\text{ cm}^{-1}$ (m)
<b>=C—H bending absorption</b>	
$-\text{CH}=\text{CH}_2$ (terminal vinyl)	$910, 990\text{ cm}^{-1}$ (s) two absorptions
$\text{C}=\text{CH}_2$ (terminal methylene)	$890\text{ cm}^{-1}$ (s)
$\text{H}-\text{C}=\text{C}-\text{H}$ ( <i>trans</i> -alkene)	$960\text{--}980\text{ cm}^{-1}$ (s)
$\text{H}-\text{C}=\text{C}-\text{H}$ ( <i>cis</i> -alkene)	$675\text{--}730\text{ cm}^{-1}$ (br) (ambiguous and variable for different compounds)
$\text{C}=\text{C}-\text{H}$ (trisubstituted)	$800\text{--}840\text{ cm}^{-1}$ (s)

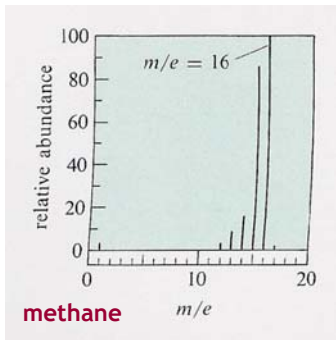


(a)



(b)

### Mass Spectroscopy



methane

$m/e$	relative abundance
1	3.36
12	2.80
13	8.09
14	16.10
15	85.90
16	100.00
17	1.11

