EPR Course

NTU Fall 2001

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Lecture 6

Nuclear Hyperfine Interaction

Spin polarization (continue)

Recall Hydrogen atom

$^2S_{1/2}$,

$\mathcal{H}_C$ = Fermi-contact Interaction between unpaired electron spin and proton spin

$= a\,\vec{I}\cdot\vec{S}$

where $a = \frac{8\pi}{3} g_S g_N \beta \beta_N |1s(0)|^2$

$1s(0)$ = value of 1s orbital at proton i.e., $(\vec{r}=\vec{r}_N)$.

α-state for s-electron

electron $= \int_V \rho(\vec{r})d\vec{r} = \boxed{\int_V 1s^*(0)\,1s(0)\,d\vec{r} = 1}$

$\langle 2S_z \rangle = \int_V 1s^*(\vec{r})\alpha^* \cdot 2S_z \cdot 1s(\vec{r})\alpha \, d\vec{r}\, d\tau_s$

$= \int_V 1s^*(\vec{r})1s(\vec{r})\,d\vec{r} \cdot \int \alpha^* 2S_z \alpha \, d\tau_s$

$= \int_V \rho(\vec{r})d\vec{r} \cdot (1)$ = spin along z-axis

So define $\boxed{\text{spin density } \rho_s}$

$\rho_s^{\uparrow}$ = electron density with spin ↑

$$= \psi^*(\vec r)\,\psi(\vec r)\int \alpha^*\, 2S_z\, \alpha\, d\tau_s \quad = \quad \psi^*(\vec r)\,\psi(\vec r)\cdot(+1)$$

$\rho_s^{\downarrow} = \psi^*(\vec r)\,\psi(\vec r)\int \beta\, 2S_z\, \beta\, d\tau_s$ = electron density with spin ↓

$$= \psi^*(r)\,\psi(\vec r)\quad(-1)$$

and $\rho_s(\vec r_N) = \int \psi^*(\vec r)\,\psi(\vec r)\,\delta(\vec r-\vec r_N)\,d\vec r \cdot \left.\begin{matrix} \overset{(+1)}{\int \alpha^*\, 2S_z\, \alpha\, d\tau_s} \\ \underset{(-1)}{\int \beta^*\, 2S_z\, \beta\, d\tau_s} \end{matrix}\right\}$

spin density at nucleus N

$$= \pm\,\psi^*(\vec r_N)\,\psi(\vec r_N)$$

+ for α-spin
− for β-spin

$\rho_s(\vec r_N)$
unpaired electr
density at
nucleus is
a probability
density measured
in electrons/Å^3
Carries a sign!!

$\psi(\vec r_N) \neq 0$ only for s-electrons

1s, 2s, 3s, . . .

So, in general, write

$$\mathcal{H}_c = a\,\vec I\cdot\vec S$$

where $a = \frac{4\pi}{3}\, g_s\, g_N\, \beta\, \beta_N \int_V \psi^*\, 2\hat S_z\, \delta(\vec r-\vec r_N)\,\psi\, d\vec r\, d\tau_s$

for 1-electron system!

For example, if electron (& hence unpaired electron spin) is localized in a MO

$\sum_n c_n \phi_n$ & one of the atoms is a hydrogen atom

$$\psi_{MO} = \cdots + \cdots \quad + C_H \Phi_H = \cdots + \cdots C_H 1s_H$$

Then

$$a = \frac{4\pi}{3} g_S g_N \beta \beta_N \rho_S(\vec{r}_N)$$

and $\rho_S(\vec{r}_N) = \rho_S(H) = C_H^* C_H |1s(0)|^2$ probability density measured in electrons/$Å^3$

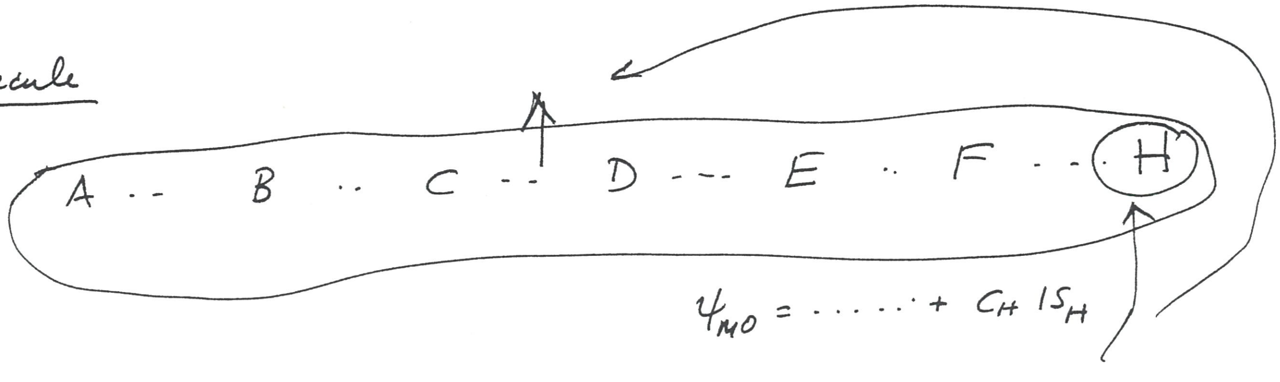
Another definition

Unpaired electron density or spin density in an orbital (ao or mo) on an atom

= fractional population of unpaired electrons on an atom

$\rho_H = C_H^* C_H (+1)$ a number!

Molecule



$$\psi_{MO} = \cdots\cdots + C_H 1s_H$$

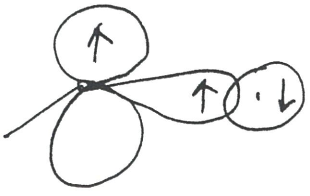
$$\rho_H = |C_H|^2 (+1)$$

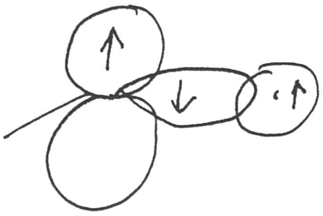
Spin density at hydrogen atom $= +|C_H|^2 > 0$

positive

Negative spin density

e.g. π-radical


Ⓐ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Unpaired electron is in p_z-orbital, which has a node in xy plane. So expect $\rho_H = 0$

But experimentally, $\frac{a}{h} \sim 23$ gauss in $\cdot CH_3$

McConnell proposed $\boxed{\text{spin polarization}}$

Normally, assume "perfect pairing", meaning ψ_{MO} the same whether electron spin is α or β in molecular orbital theory. In valence bond theory, valence structures Ⓐ and Ⓑ are in equal proportions!

But "perfect pairing" is only an approximation. Electrons occupying different orbitals prefer to have their spins in the same direction because of more favorable exchange (electron repulsion) energies!

So, within MO theory

$\psi_{MO}(1)\,\alpha(1)$

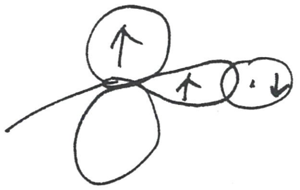
$\psi'_{MO}(2)\,\beta(2)$

$\psi_{MO} \neq \psi'_{MO}$!

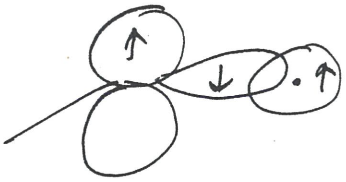
split orbitals

Lead to spin density at hydrogen.

Within valence-bond theory, we say that



Ⓐ



Ⓑ

Valence structure Ⓐ preferred slightly over

Valence structure Ⓑ

<u>Now</u> the two structures have different proton spin densities! In fact, they have the opposite sign.

$\rho_H^{(A)} = |C^A|^2(-1)$

$\rho_H^{(B)} = |C^B|^2(+1)$

Valence-bond function $= C^A \phi_C(1)\alpha(1)\,\phi_H(2)\beta(2)$

$+ C^B \phi_C(1)\beta(1)\,\phi_H(2)\alpha(2) + \cdots$

Net spin density at in-plane hydrogen atom

$$= \rho_H^{(A)} + \rho_H^{(B)} = -|C^A|^2 + |C^B|^2 < 0$$

$$|C^A| > |C^B|$$

negative spin density!

McConnell's Relation

For π-radicals, expect $a_H = Q \rho_c$

where a_H = proton hyperfine interaction of C–H bond in π-radical through indirect coupling

ρ_c = π-spin density at carbon of the C–H bond

and $Q \cong -23$ gauss

Spin distributions in Alternant Hydrocarbon Ions

Even alternant hydrocarbons

≡ hydrocarbons that have an even number of carbon atoms linked to form even-membered rings

e.g. benzene, anthracene, tetracene, and perylene.

Many of these aromatic hydrocarbons form positive or negative radical ions that are quite stable in solution and there are hundreds of these molecules known.

$$HC + \begin{matrix} Na \\ K \end{matrix} \longrightarrow HC^{\ominus}\cdot + \begin{matrix} Na^+ \\ K^+ \end{matrix}$$

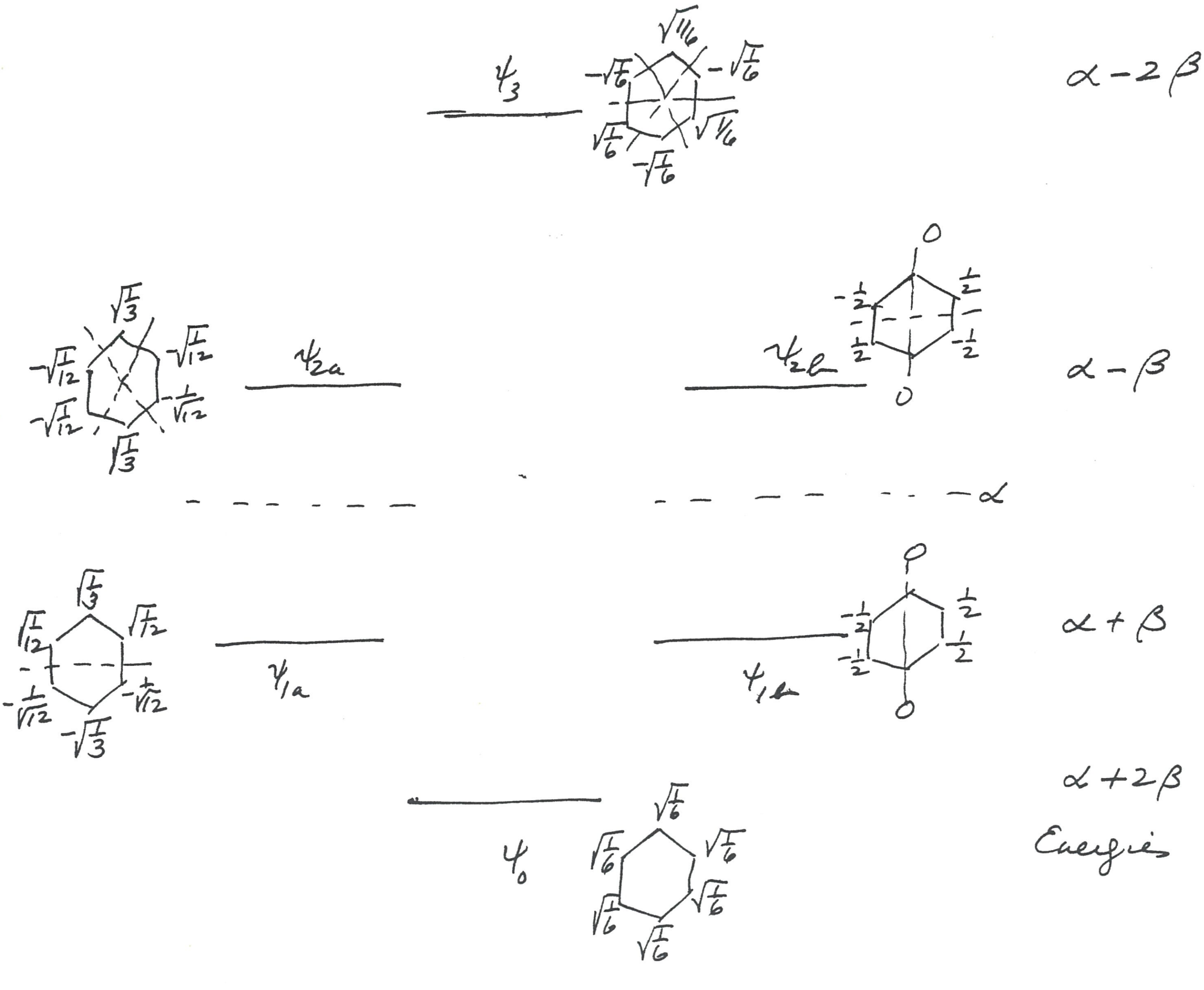
$$HC + \text{concentrated } H_2SO_4 \longrightarrow HC^{\oplus}\cdot$$

i's

A typical example is benzene, whose $\overline{\pi\text{-MO's}}$ may be written as a linear combination of C $\underline{2p_z \text{ atomic}}$ orbitals ϕ_r's

$$\psi_i = \sum_r c_{ri}\,\phi_r$$

The Huckel MO's are given by

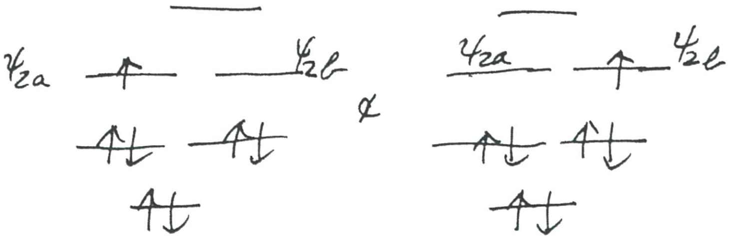


where $\alpha = \int \phi_r^* \mathcal{H}\, \phi_r\, d\tau$ for all r's

$\beta = \int \phi_r^* \mathcal{H}\, \phi_s\, d\tau$ and r, s are adjacent carbons

$= 0$ for r + s not adjacent

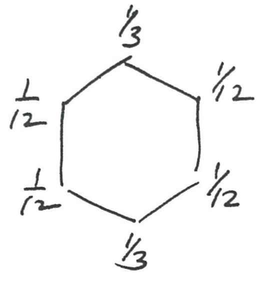
Benzene negative ion



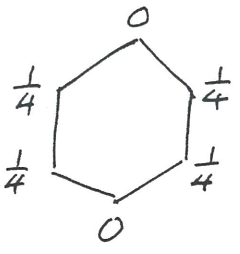
a linear combination of ψ_{2a} and ψ_{2b} for unpaired electron

ρ_C

$= |C_{ri}|^2$



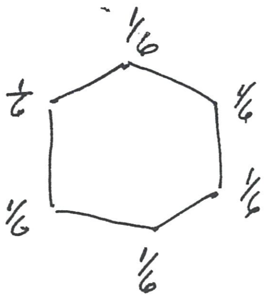
ψ_{2a}



ψ_{2b}

Note that $\sum_i \rho_{C_i} = \sum |C_{ri}|^2 = 1$ for both ψ_{2a} + ψ_{2b}

Average



Predicts $a_H \sim -23 \times \frac{1}{6} = -3.9$ gauss

$|a_H \text{ observed}| = 3.75$ gauss

Substituted benzene anions

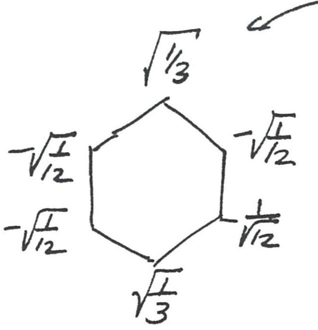
ψ_{2a}, ψ_{2b} degenerate in benzene anion.

Therefore spectrum of $C_6H_6^-$ itself does not provide a test of molecular orbital predictions, since the extra electron is equally distribution in the two MO's ψ_{2a} & ψ_{2b}.

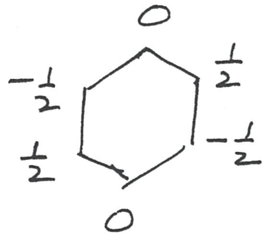
Can lift degeneracy of ψ_{2a} & ψ_{2b} via substituents.

e.g. CH_3 - substituent.

Methyl group is an electron - repelling substituent, so a methyl group



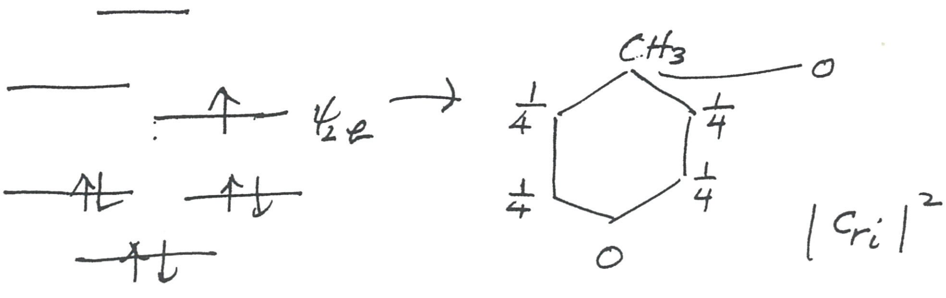
ψ_{2a}



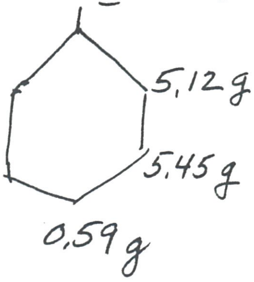
ψ_{2b}

in toluene would raise the orbital energy of ψ_{2a}, namely, destabilize ψ_{2a} relative to ψ_{2b}.

So in toluene,

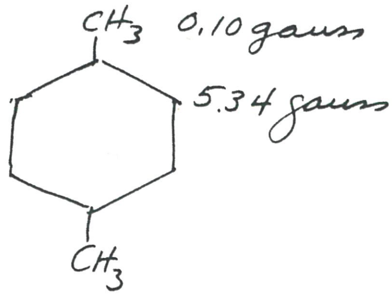


Expect	ortho	meta	methyl	para
ρ_c	$\sim\frac{1}{4}$	$\sim\frac{1}{4}$	~ 0	~ 0
	−5 to −6 gauss		0 or small	

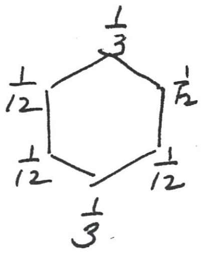


Observed

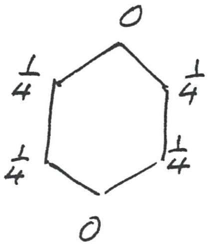
Expect same for p-xylene anion radical



However, if methyls appear on either side of symmetry plane, as they would in <u>meta</u> and ortho-xylene, unpaired electron will occupy ψ_2



ψ_{2a}

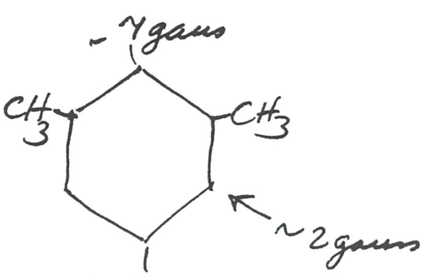


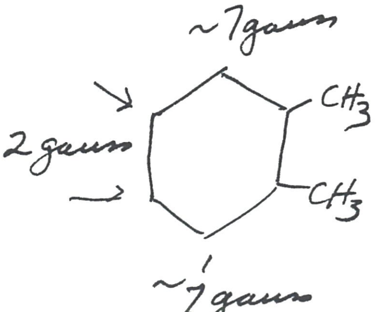
ψ_{2b}

$$\underline{\underline{|C_{ri}|^2}}$$

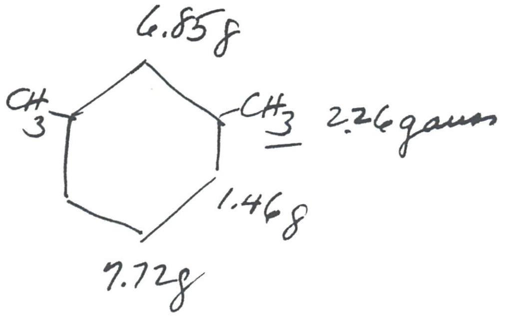
ψ_{2b} is destabilized and unpaired electron occupies ψ_{2a}

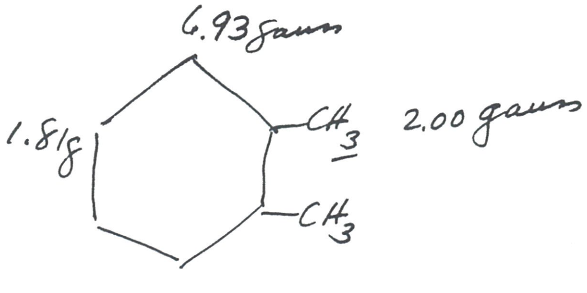
Expects





<u>Observed</u>



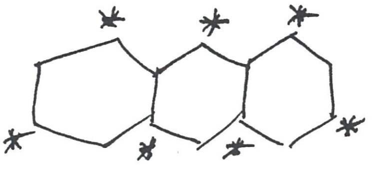


Pairing of electronic states

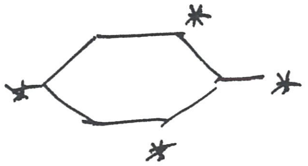
In alternant hydrocarbons, Huckel MO's always appear in pairs. If a π-MO, bonding ψ_i exists with energy $\alpha + \epsilon_i \beta$ (ϵ_i a positive #), then there is a "mirror image" antibonding orbital $\psi_{i'}$ with energy $\alpha - \epsilon_i \beta$. This pairing relation depends on the fact that all the rings of carbon atoms are even-membered, so that it is possible to divide the carbon atoms into two sets, "starred atoms" and "unstarred atoms".

e.g. anthracene

even alternant

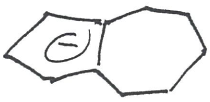


benzyl



odd alternant

NA possible for azulene negative anion



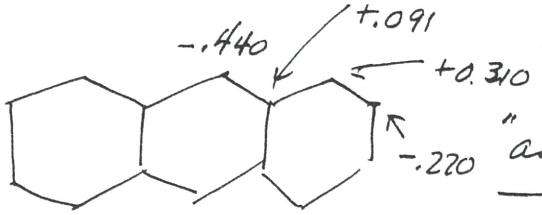
odd-membered rings

So for even alternant HC's

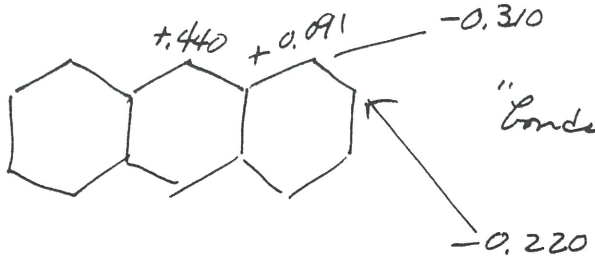
$$|c_{ri}|^2 = |c_{ri'}|^2$$

$$\text{and } \rho_r^{\oplus} = \rho_r^{\ominus}$$

i.e., radical anions and cations (singly charged) should have common spin distribution.

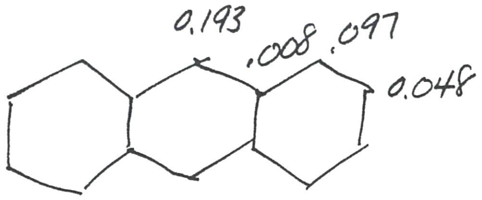


"antibonding"



"bonding"

coefficient c_{ri}



predicted spin distribution

Hyperfine splittings in Anthracene Ions (gauss)

	a_1	a_2	a_9
Positive	3.11	1.40	6.65
Negative	2.74	1.57	5.56

$a_9 : a_1 : a_2 \longrightarrow 4 : 2 : 1$

Odd alternant radicals

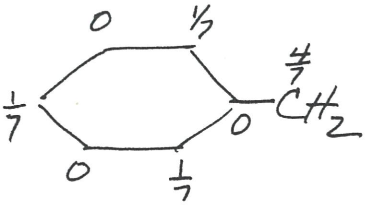
Alternant hydrocarbons that possess an odd number of carbon atoms are called "odd alternant"

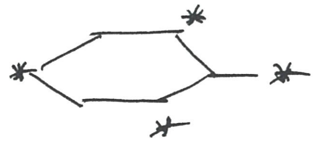
1) Pairing theorem relating to "bonding" and "antibonding" molecular orbitals still holds.

2) However, such molecules possess a non-bonding

orbital of energy $E = \alpha$, which is occupied by unpaired e^- in anion radical. This orbital is confined to the starred atoms, and has a node at all the "unstarred" atoms.

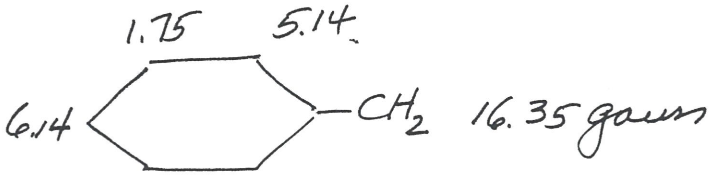
Best example





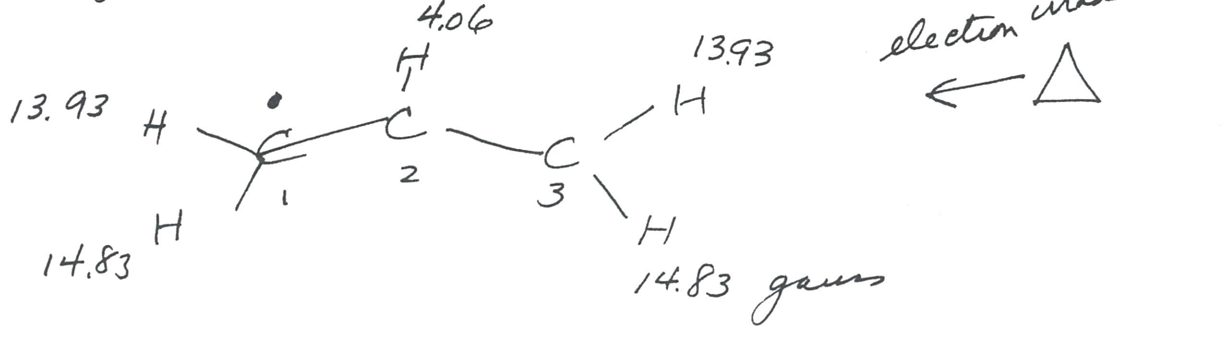
$|c_{ri}|^2$ in non-bonding orbital

Observed

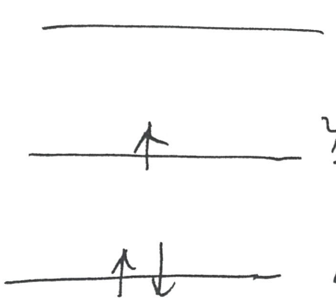


Another example (simpler)

Allyl radical



Huckel MO's



$\psi_3 = \frac{1}{2}(\phi_1 - \sqrt{2}\phi_2 + \phi_3)$ $E = \alpha - \sqrt{2}\beta$

$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$ $E = \alpha$

$\psi_1 = \frac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3)$ $E = \alpha + \sqrt{2}\beta$

predicts

$\rho_{c_1} = \frac{1}{2}$

$\rho_{c_2} = 0$ ← 4.06 gauss observed

$\rho_{c_3} = \frac{1}{2}$

So finite ρ_{c_2} must come from spin-polarization of ψ_1 (split orbitals) and spin density at C_2 proton must be negative!

also

$\rho_{c_1} = \frac{14}{23}$

$\rho_{c_2} = \frac{4}{23}$

$\rho_{c_3} = \frac{14}{23}$

If $\rho_{c_1}, \rho_{c_2}, \rho_{c_3}$ all have the same sign

$\sum_r \rho_{cr} = \frac{32}{23} > 1$

$\sum_r |\rho^s_{cr}|$

Therefore

$\rho^s_{c_1} = +\frac{14}{23}$

$\rho^s_{c_2} = -\frac{4}{23}$

$\rho^s_{c_3} = +\frac{14}{23}$

$\sum_r \rho^s_{cr} = \frac{24}{23} \sim 1$