The Non-local Contribution to the Magnetic Shielding Constant

$$\sigma = \underbrace{\sigma_{\text{dia}} + \sigma_{\text{para}}}_{\text{local}} + \sum \sigma_{\text{nonloc}}$$

magnetic anisotropy of neighboring groups

temperature

isotope shift

solvent effects ASIS, SIIS

H-bonding

concentration effects

Magnetic Anisotropy of Neighboring Groups

Magnetic anisotropy of neighboring groups
Remote shielding effects by electrons of non-spherically symmetric groups – (nearly all groups, but some strong)

In a magnetic field, valence electrons are induced to circulate.
This generates a secondary magnetic field that opposes/enhances the applied field near the nucleus

A higher/lower field is needed to achieve resonance =
shielding/deshielding effect

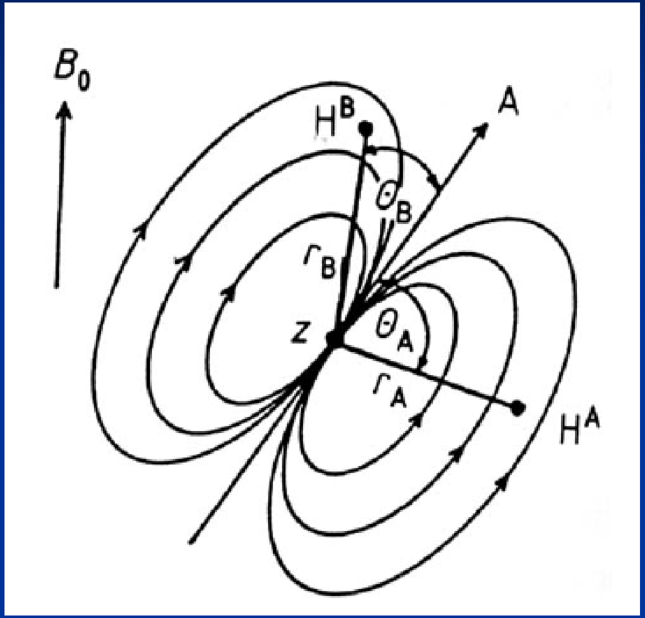
McConnell formula (cylindrical symmetry)

$$\sigma_{group} = (\chi_{\|} - \chi_{\perp})\,(1 - 3\cos^2\theta)/(3r^3)$$

$\chi_{\|}$, $\chi_{\perp} < 0$ magnetic susceptibility

$1 - 3\cos^2\theta = 0$
for $\theta = 54.7^{o}$

Magnetic Anisotropy



H = measured nucleus

Z = anisotropic neighboring groups

McConnel formula

For cylindrical symmetry, group Z approximated as a magnetic dipole

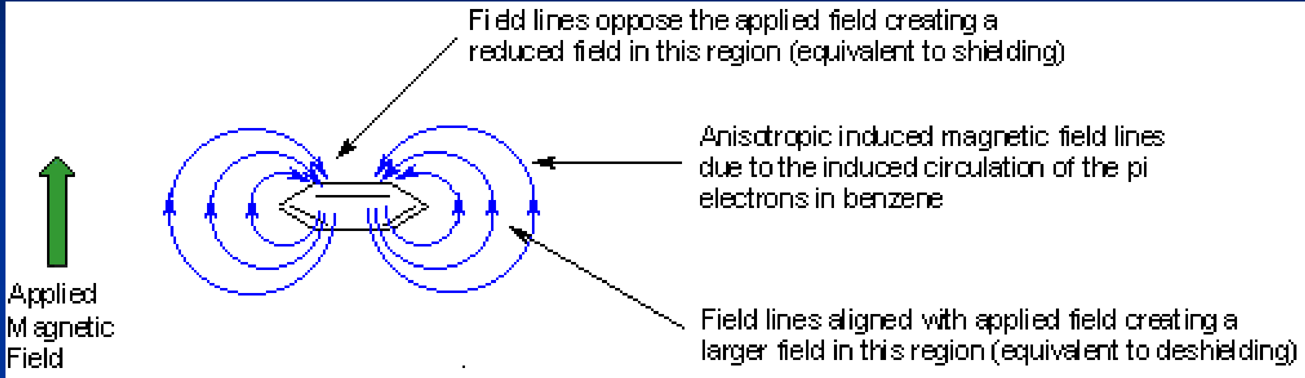
$$\sigma_{group} = (\chi_{\|} - \chi_{\perp})\,(1 - 3\cos^2\theta)/(3r^3)$$

θ is the angle between the vector $\mathbf{r}$ and the symmetry axis A

$(\chi_{\|} - \chi_{\perp})$ the molar anisotropy of the bond

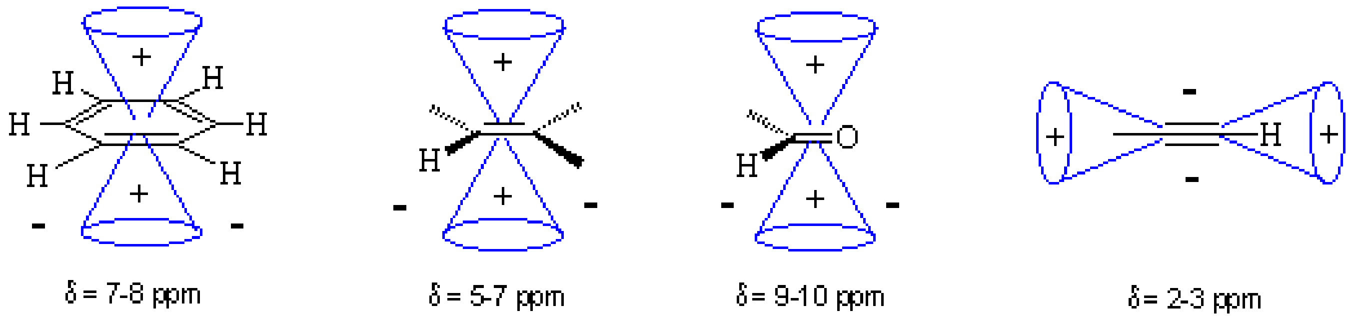
$\chi_{\|}$ - $\chi_{\perp}$ the susceptibilities parallel and perpendicular to the symmetry axis

Groups with Magnetic Anisotropy


Field lines oppose the applied field creating a reduced field in this region (equivalent to shielding)

Anisotropic induced magnetic field lines due to the induced circulation of the pi electrons in benzene

Field lines aligned with applied field creating a larger field in this region (equivalent to deshielding)

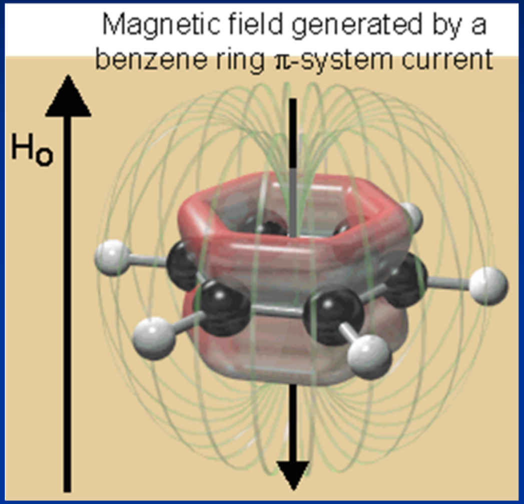


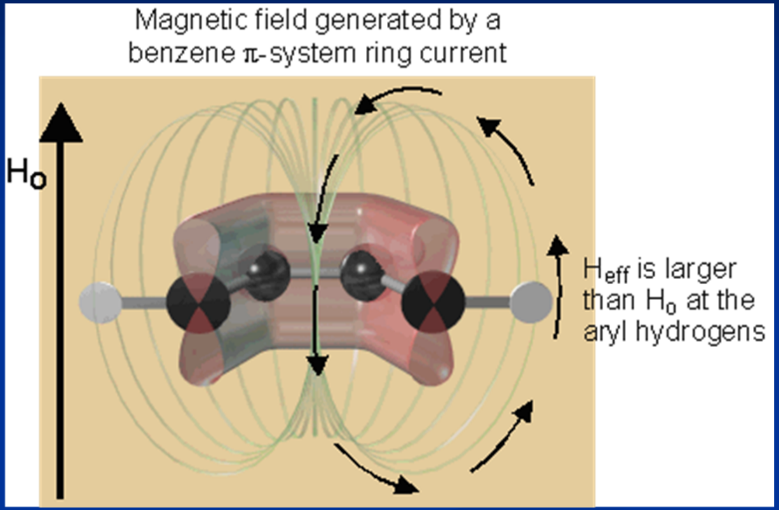
+ shielding

– deshielding

Schematic diagram of shielding cones for common pi systems. The + denotes shielding areas and - denotes deshielding areas. Remember shielding lowers the chemical shift, δ and deshielding increases δ. Typical H δ values are also shown.

Ring Current in Aromatic Rings





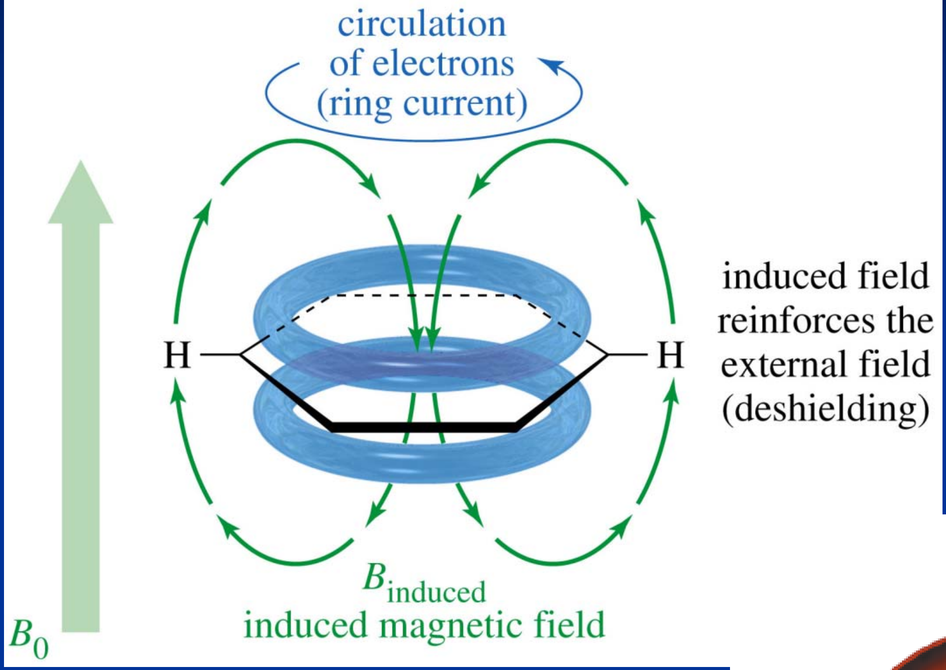
π electrons in aromatic rings are induced to circulate in a magnetic field

Diatropic ring current

•induces magnetic field aligned with the applied field in the vicinity of the aryl protons (causing deshielding = downfield shift)

•opposes the applied field at protons above and below the ring (causing shielding = upfield shift)

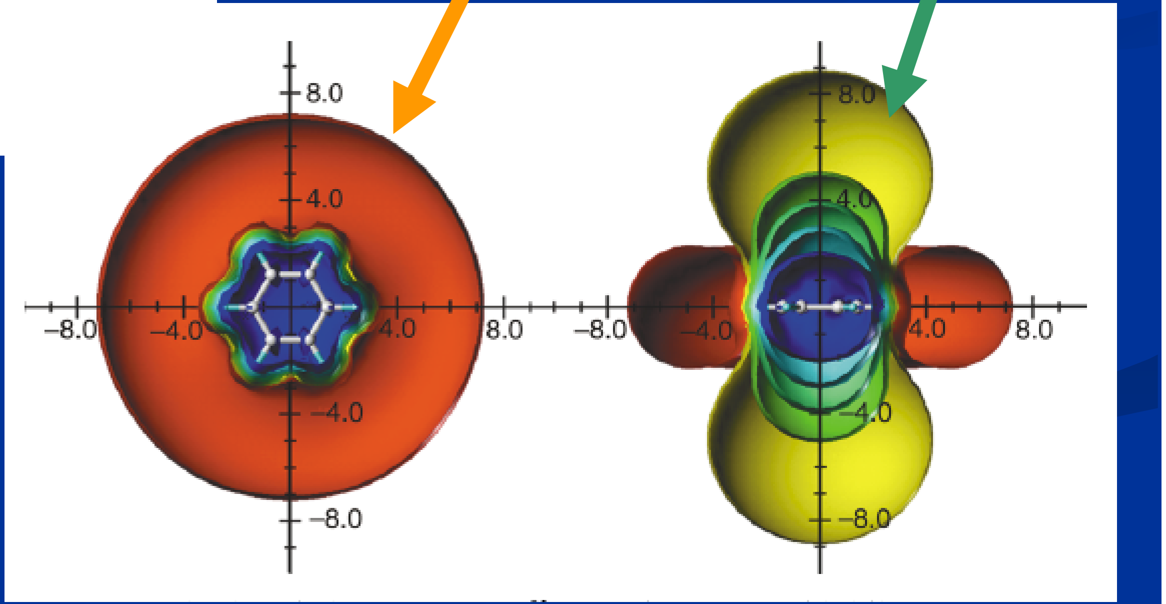
Ring Current in Aromatic Rings



Ring current = measure of cyclic delocalization of π electrons in aromatic rings

Deshielding
weak

Shielding
strong



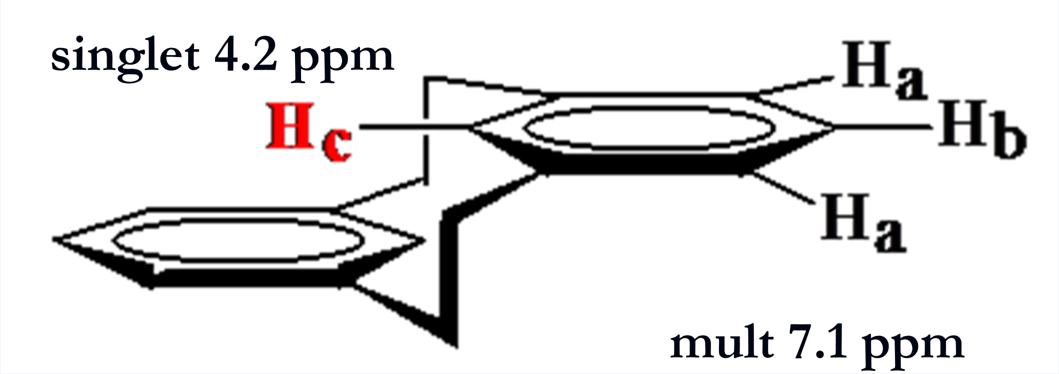
shielding surfaces
0.1 ppm in yellow, at 0.5 ppm in green,
at 1 ppm in green-blue, at 2 ppm
in cyan, and 5 ppm in blue

deshielding surface at 0.1 ppm in red

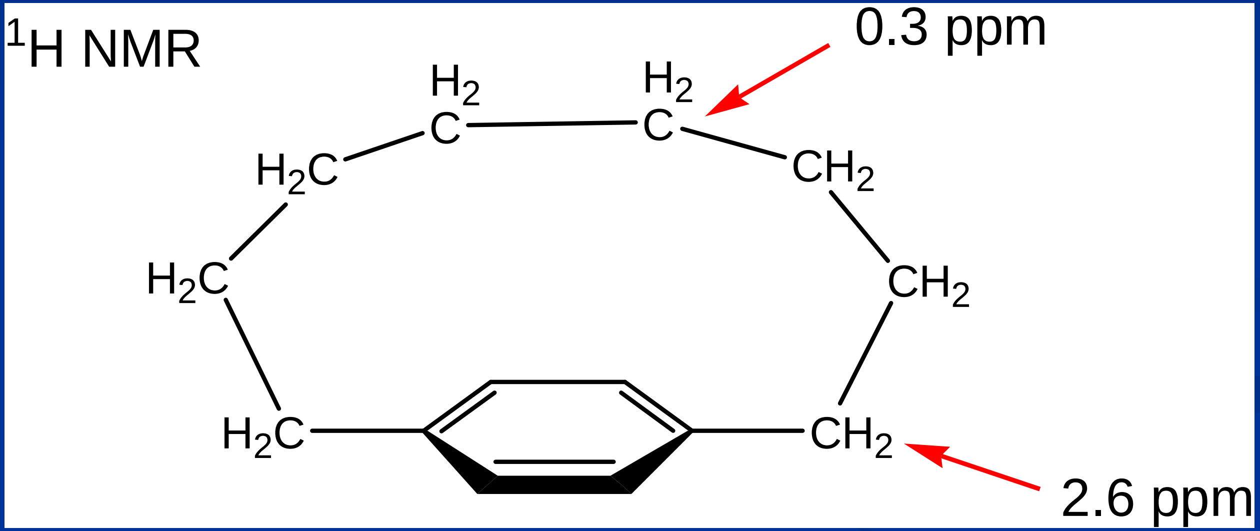
Magnetic Anisotropy

Octamethyl-[2, 2]-metacyclophane

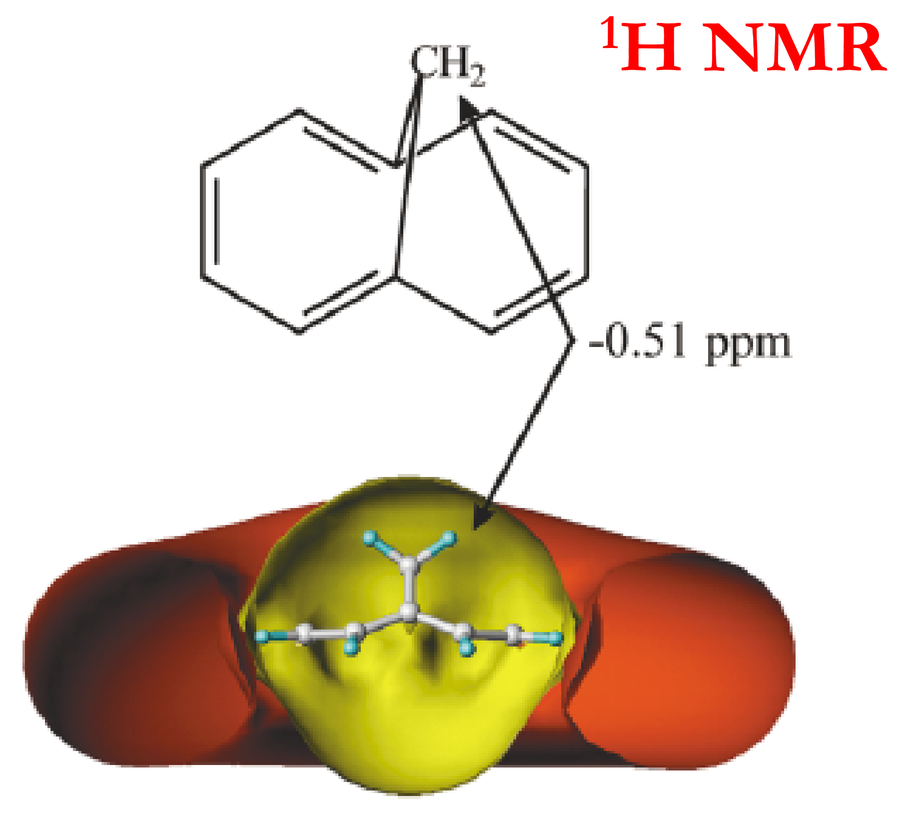
8 Me groups on C-C bridges not shown



Ring Current in Aromatic Rings

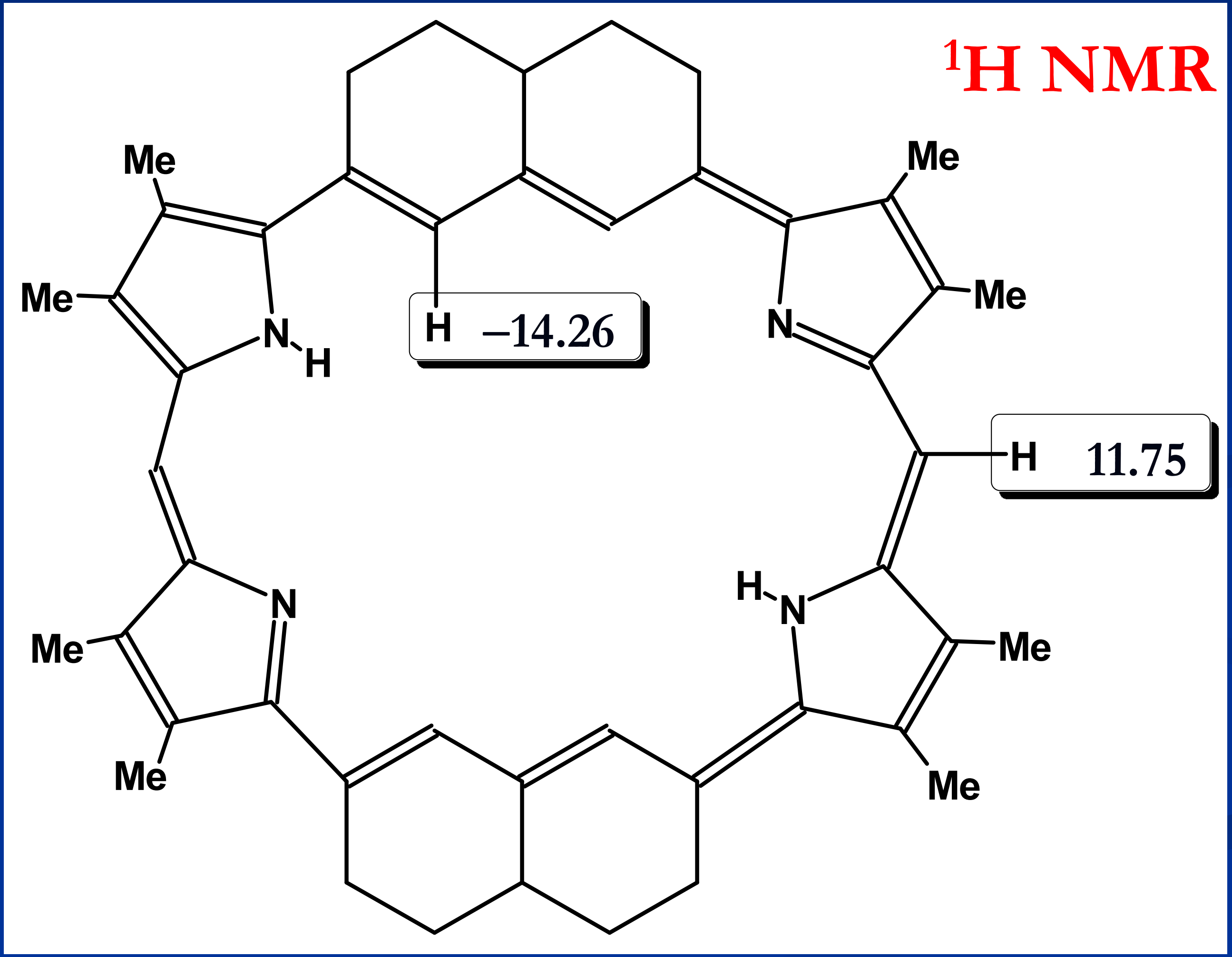


Ring Current in Aromatic Rings



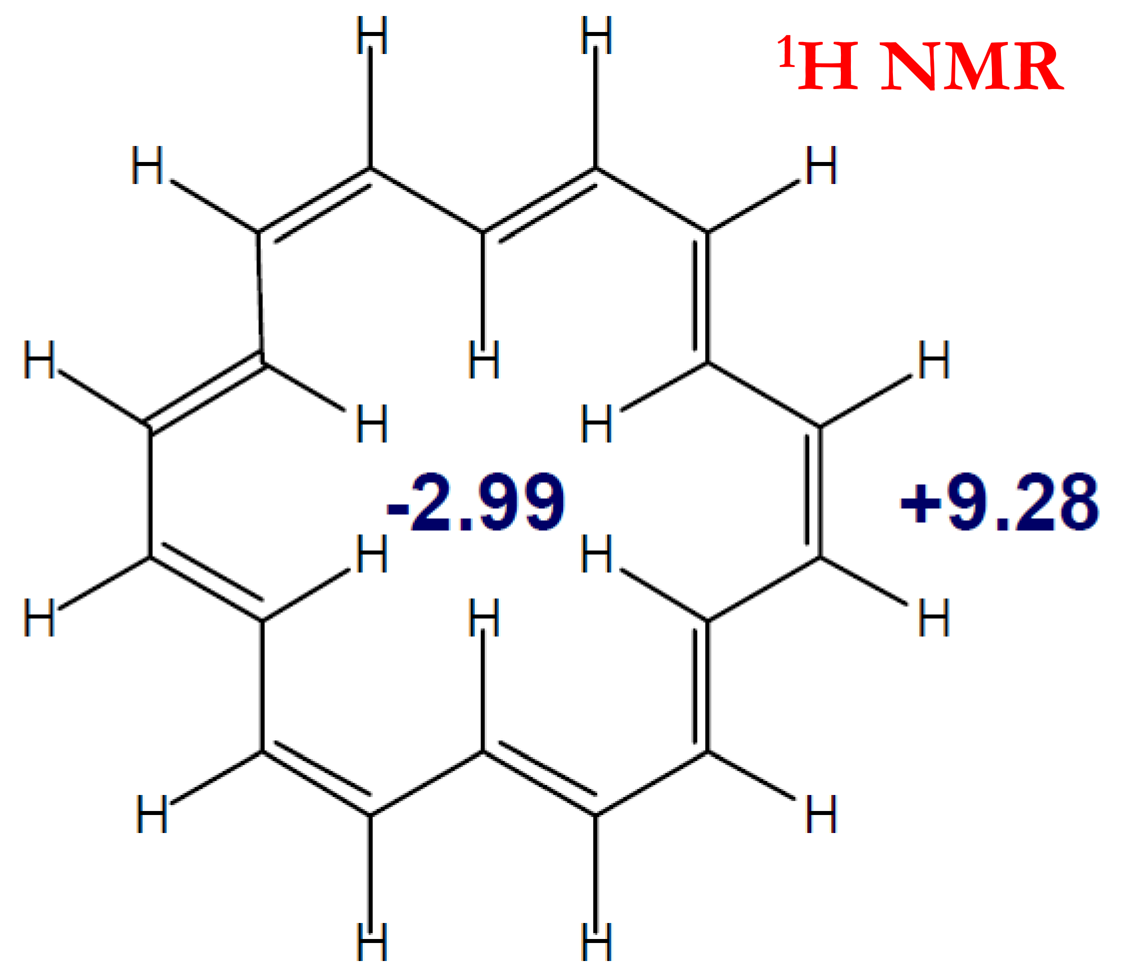
1,6-methano[10]annulene

Magnetic Anisotropy

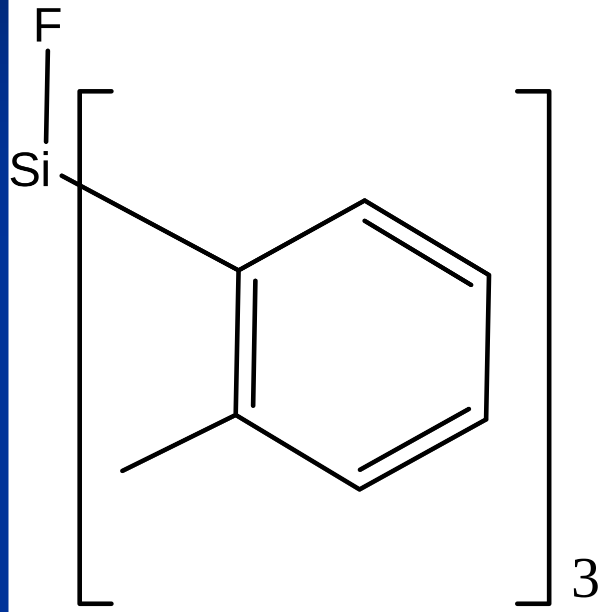


Magnetic Anisotropy

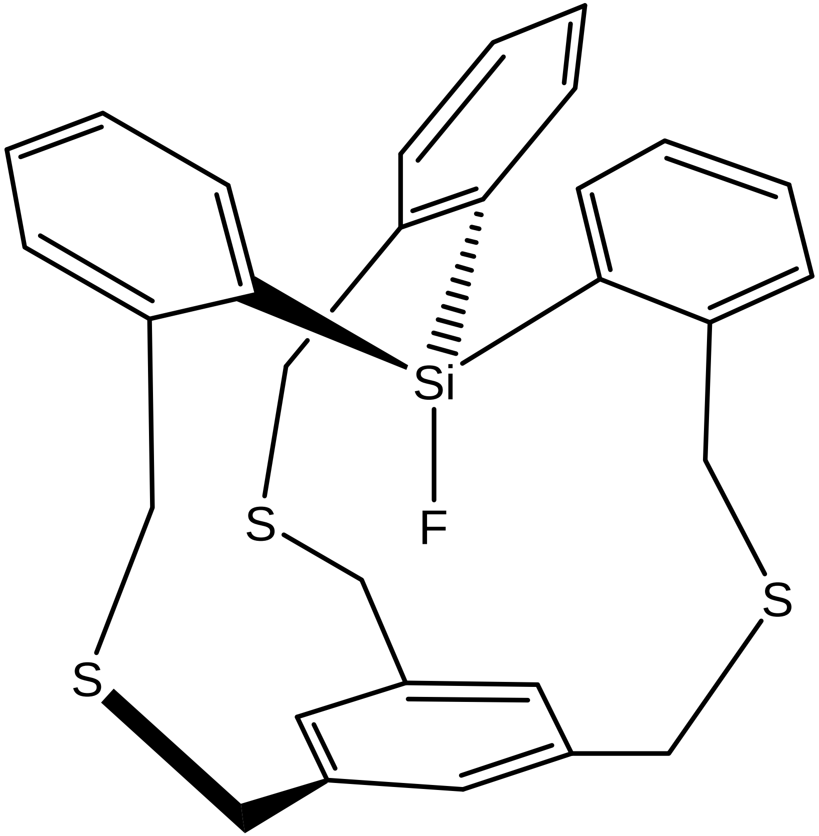
[18]annulene



Magnetic Anisotropy



δ (^{19}F) 160.6



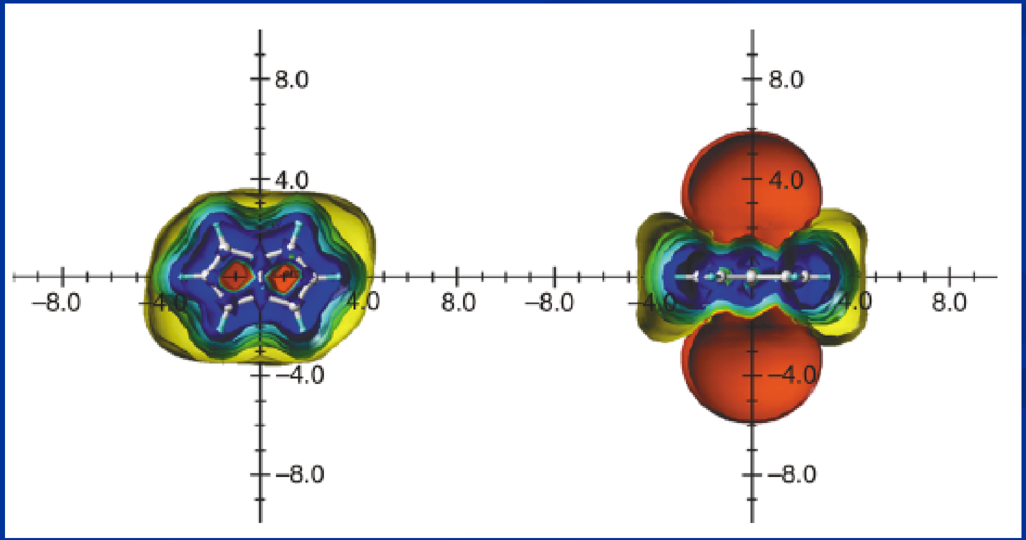
δ (^{19}F) 5.3

Ring Current in Antiaromatic Rings

Ring systems of antiaromatic character with [4n] π-electrons exhibit a reversed anisotropy effect of decreased intensity – paratropic ring current

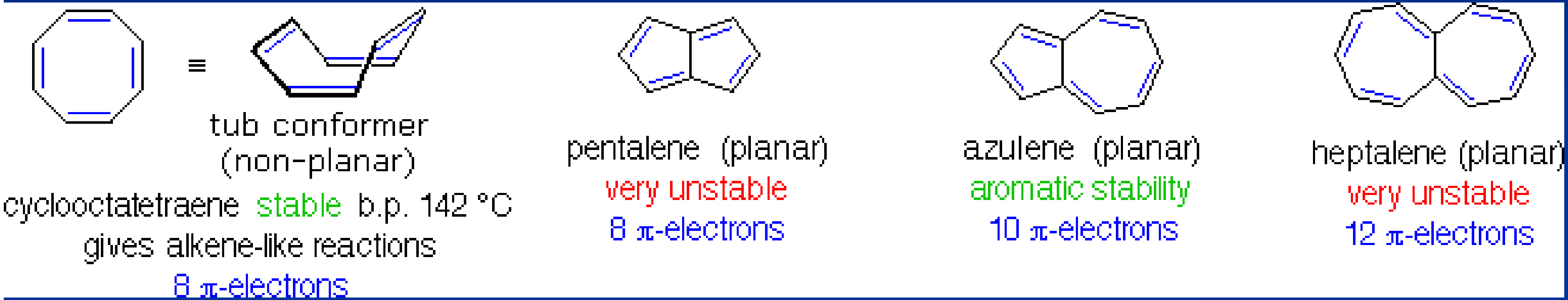
- a deshielding area above and below the plane of the ring system
- a shielding area in the plane of the ring system

pentalene



shielding surfaces
0.1 ppm in yellow
0.5 ppm in green
1 ppm in green-blue
2 ppm in cyan
5 ppm in blue
deshielding surface at 0.1 ppm in red

Ring Current in Aromatic/Antiaromatic Rings



≡ tub conformer (non-planar)

cyclooctatetraene stable b.p. 142 °C

gives alkene-like reactions

8 π-electrons

pentalene (planar)

very unstable

8 π-electrons

azulene (planar)

aromatic stability

10 π-electrons

heptalene (planar)

very unstable

12 π-electrons

NICS Nucleus independent chemical shift

- absolute shielding calculated in the center of a molecule
- measures aromaticity / antiaromaticity

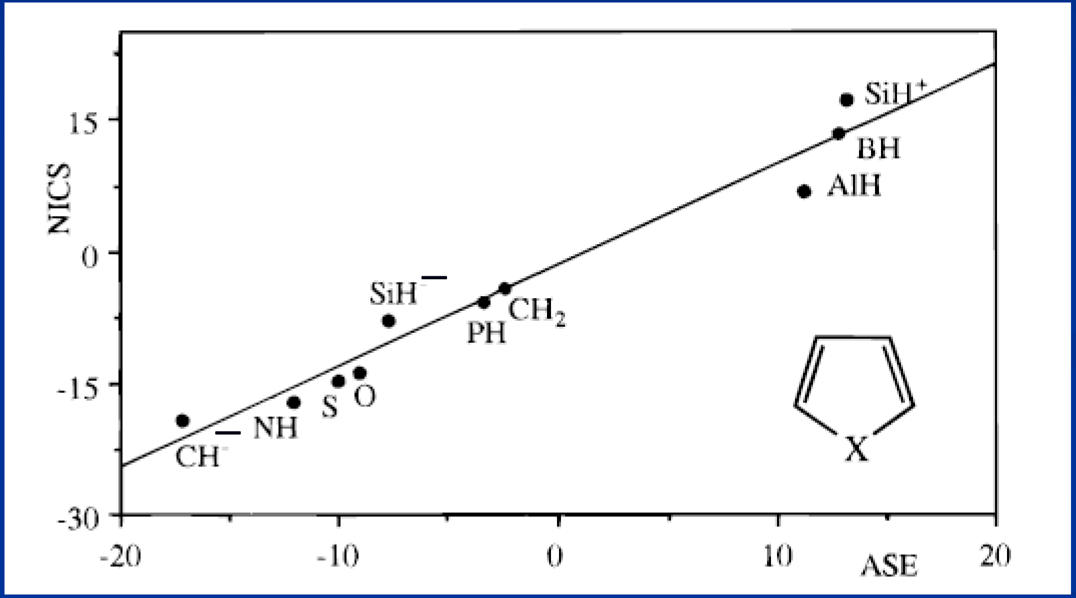
Negative NICS = shielded = diatropic = aromatic

Positive NICS = deshileded = paratropic = antiaromatic

NICS Nucleus independent chemical shift

Negative NICS = aromatic   Positive NICS = antiaromatic

NICSs (ppm)

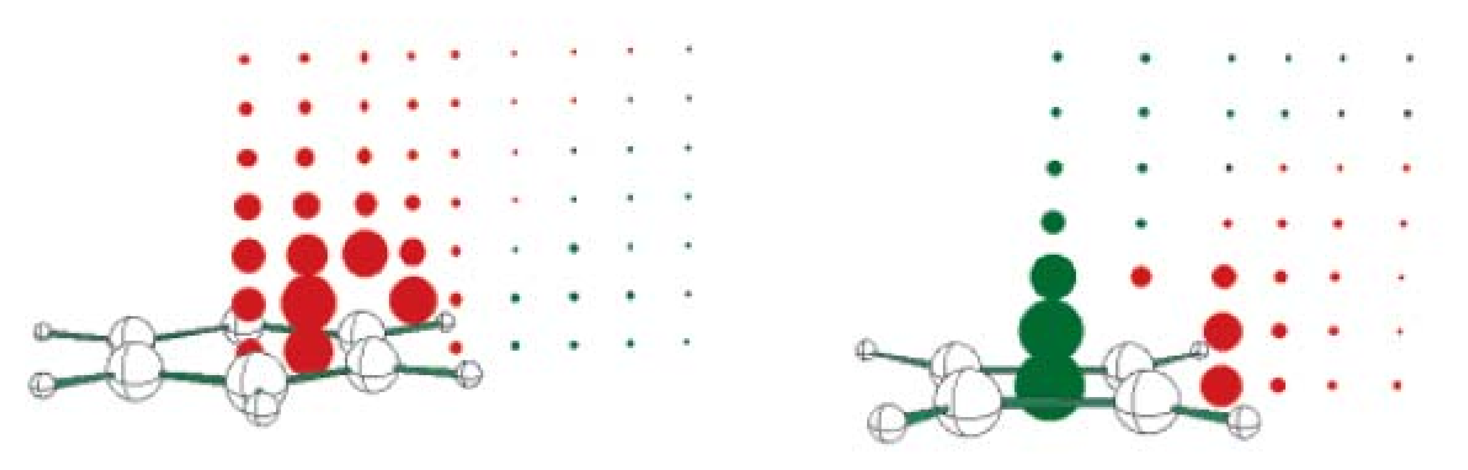


aromatic stabilization energies (ASEs, kcal/mol)

Spherical aromaticity: *closo*-$B_{12}H_{12}^{2-}$ (NICS = –34.4 ppm)

NICS Nucleus independent chemical shift

π-aromatic (benzene) and antiaromatic (cyclobutadiene)



Negative NICS = aromatic

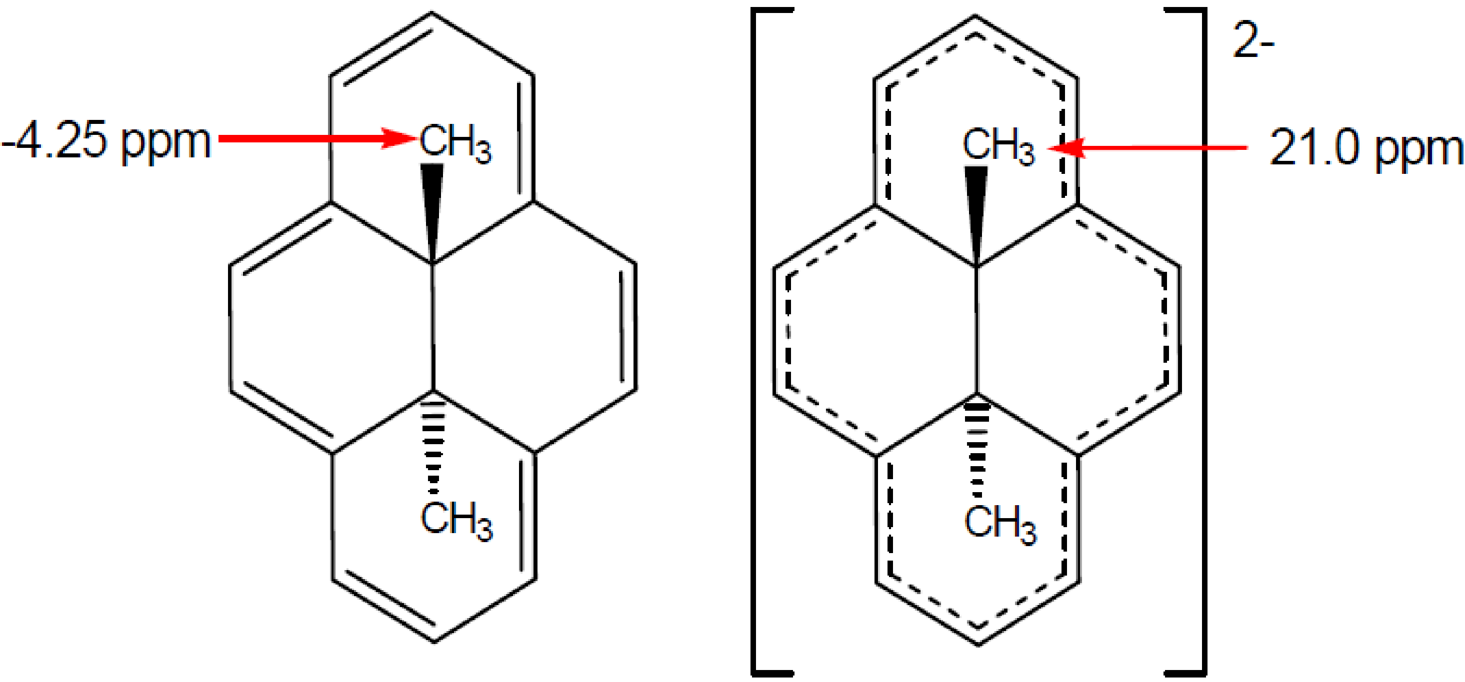
Positive NICS = antiaromatic

NICS(0) (computed in the ring center)
nonzero NICS for nonaromatic, saturated, and unsaturated hydrocarbon rings

NICS(1) (1 Å above the ring center)
the local contributions are diminished relative to the ring current effects

Aromatic/Antiaromatic Rings

^{1}H NMR



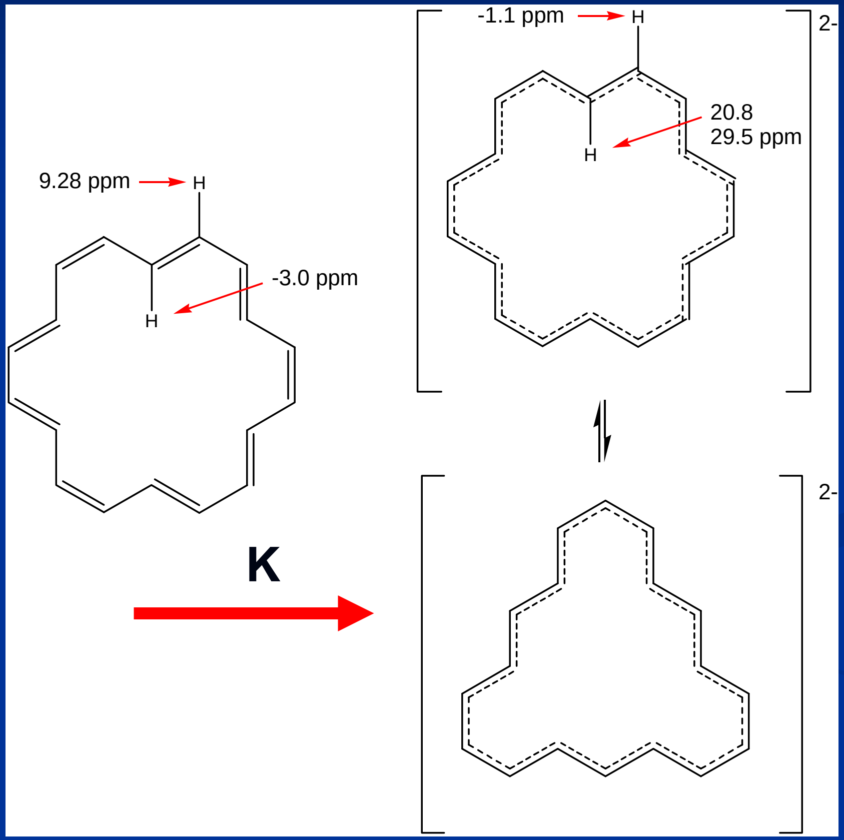
Trans-15,16-dimethyl-15,16-dihydropyrene

Trans-15,16-dimethyl-15,16-dihydropyrene dianion

aromatic
[4n+2] π-electrons

antiaromatic
[4n] π-electrons

Aromatic/Antiaromatic Rings



Low temp. ^{1}H NMR

[18] annulene dianions

antiaromatic

[4n] π-electrons

Paratropic ring current

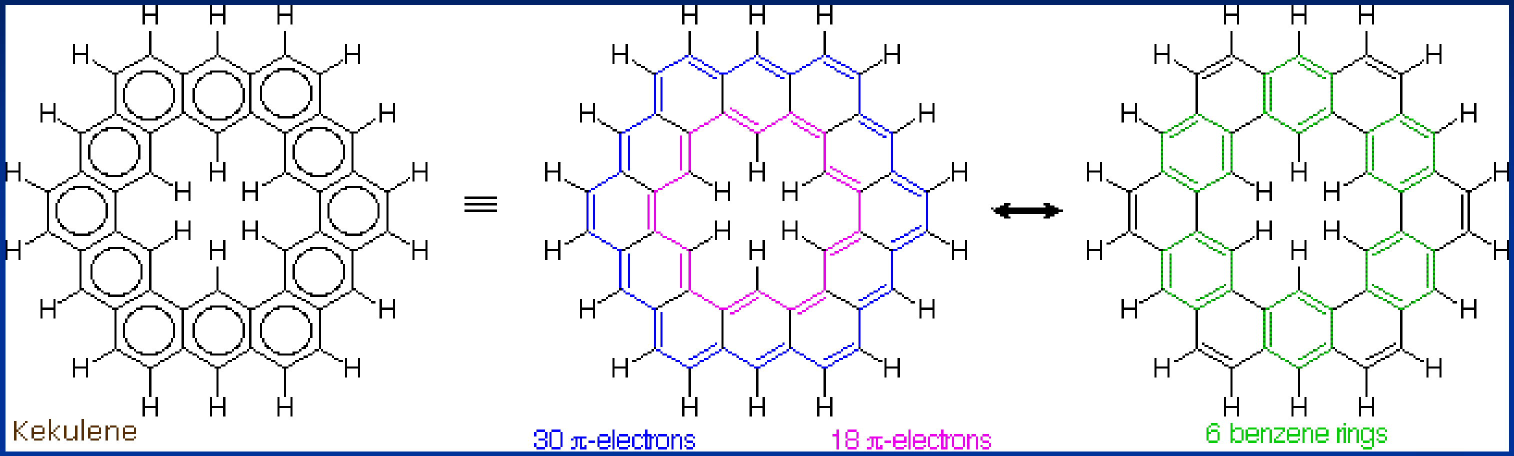
[18] annulene

aromatic

[4n+2] π-electrons

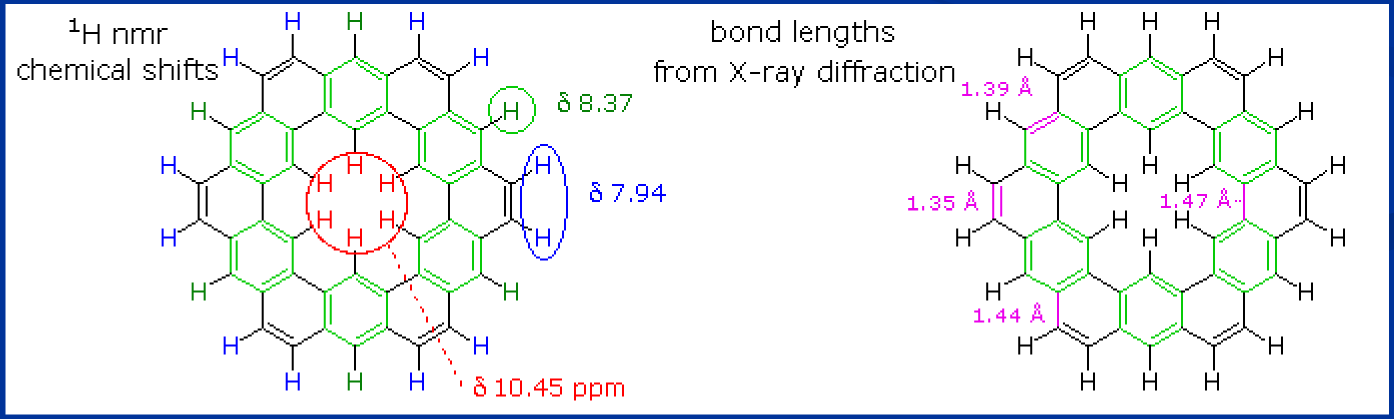
Diatropic ring current

Kekulene

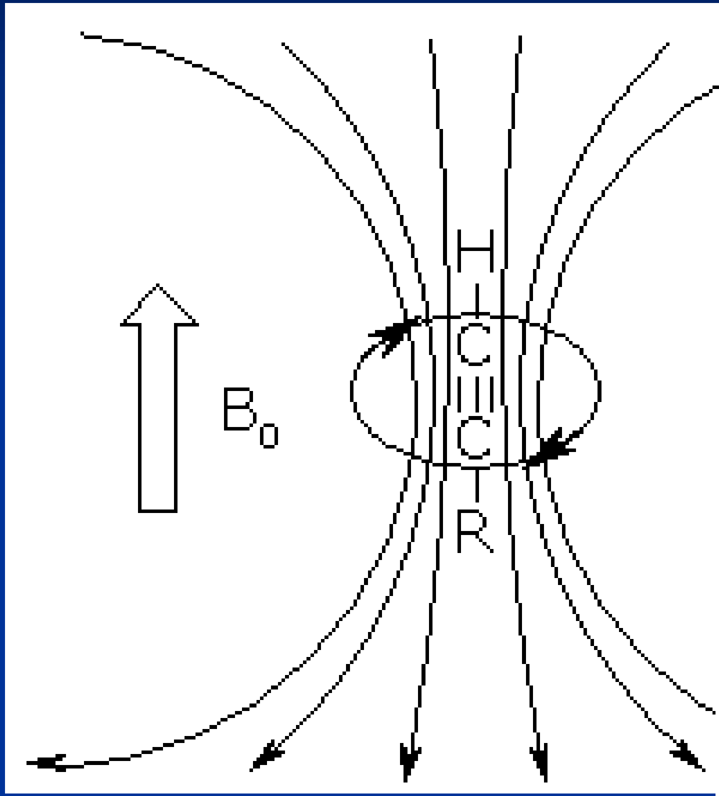


[4n+2] π-electrons 2 annulenes or 6 benzene rings

Kekulene is extremely insoluble. ^{1}H NMR spectrum taken at 200° C in deuterated tetrachlorobenzene

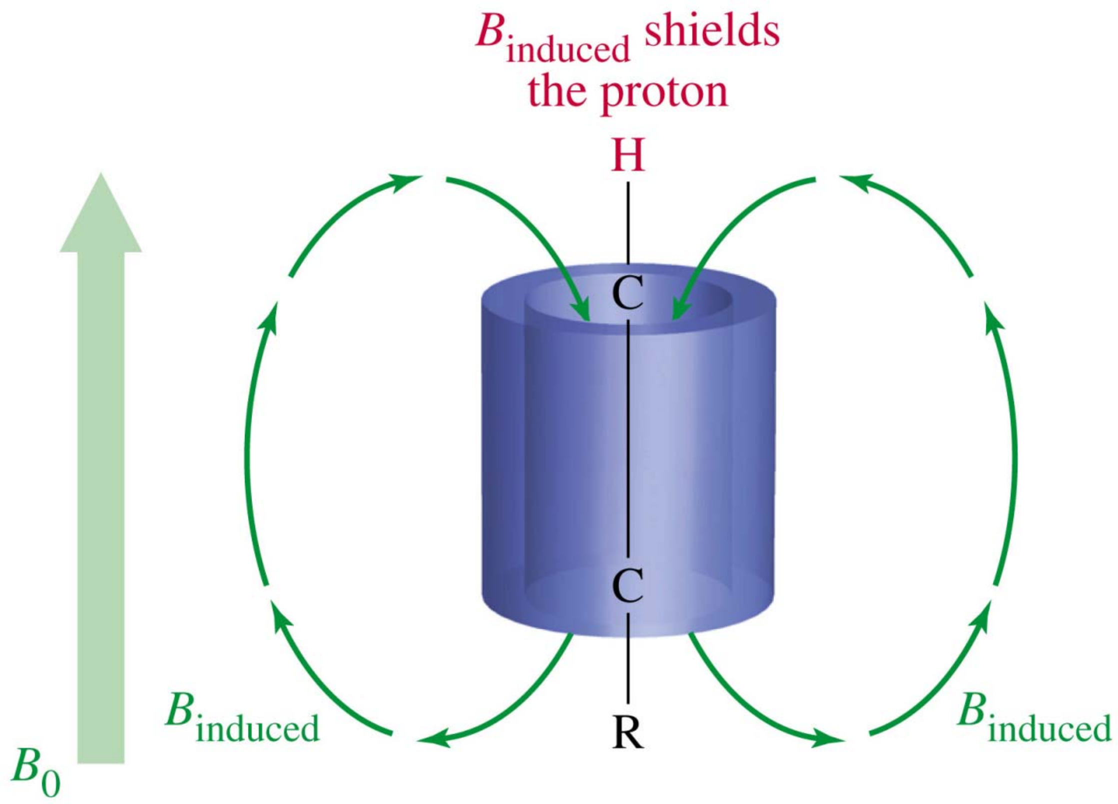


Magnetic Anisotropy

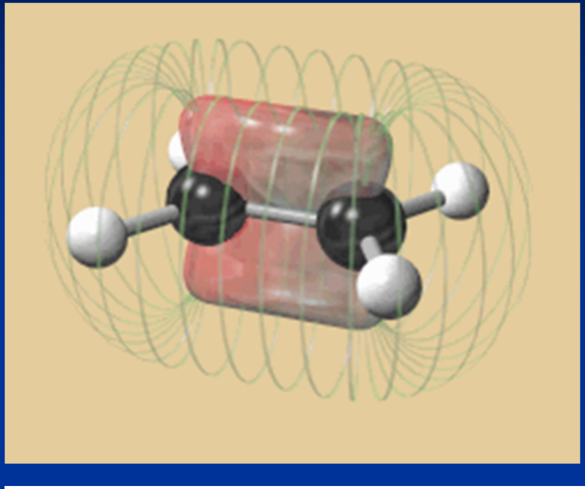


Acetylenic H

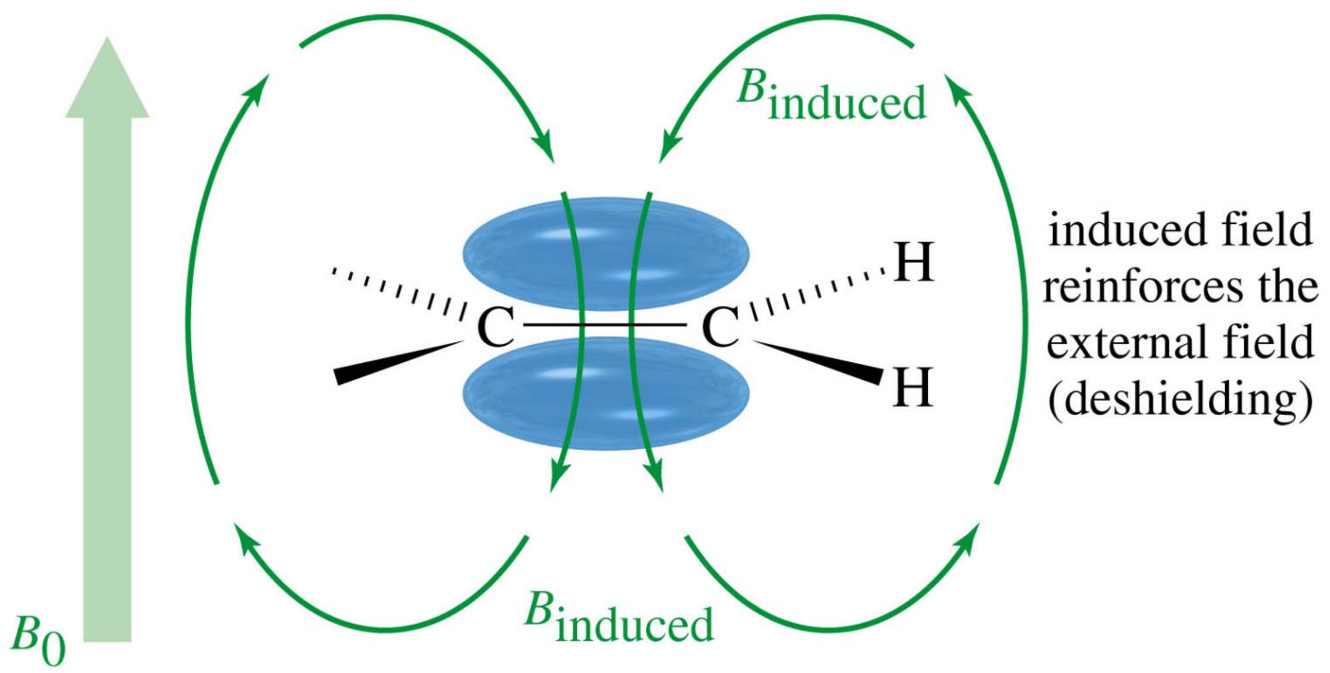
Acidic but shielded



Magnetic Anisotropy

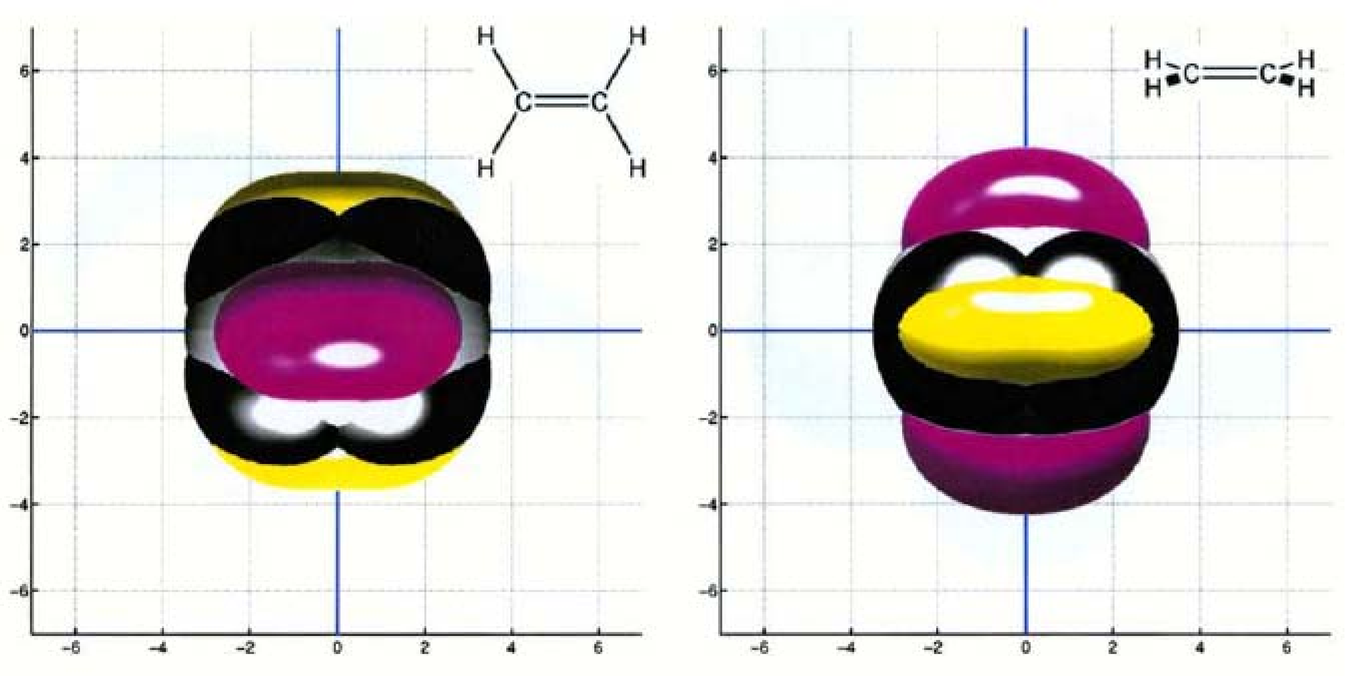


Ethylenic H



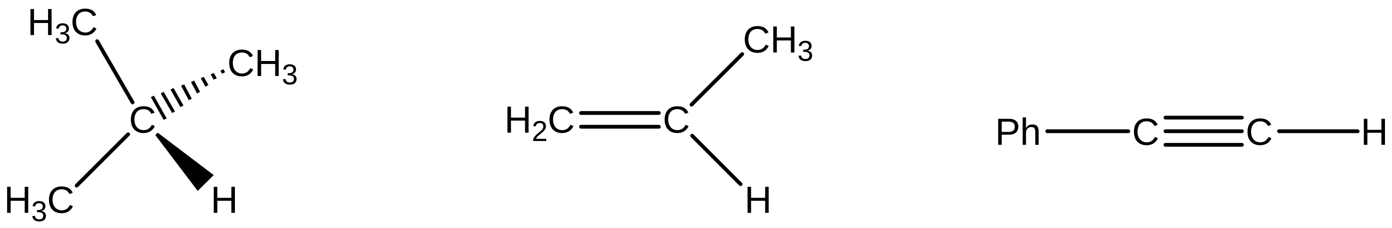
induced field reinforces the external field (deshielding)

Magnetic Anisotropy of Ethylene



C = grey, H = black)
0.1 ppm deshielding isosurface = yellow
0.1 ppm shielding isosurface = magenta

Magnetic Anisotropy

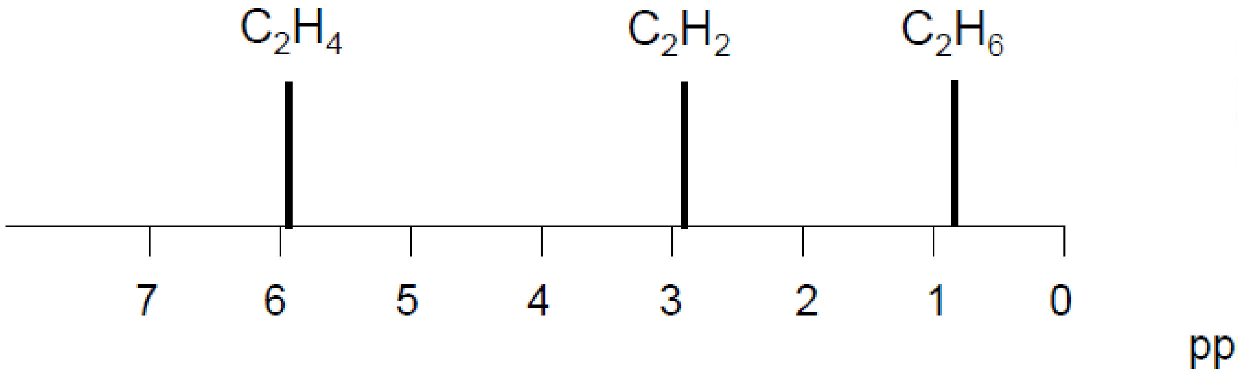


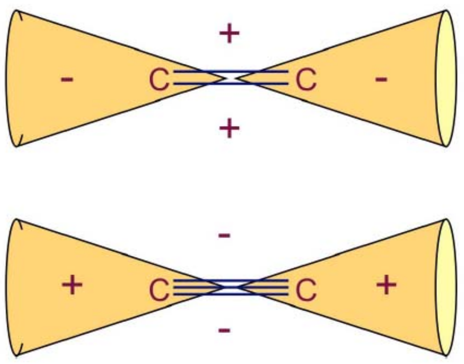
pK$_a$ (in DMSO) ~55 44 28.8

acidity of C increases →

% C-H s-character 25 33 50

electronegativity of C increases →

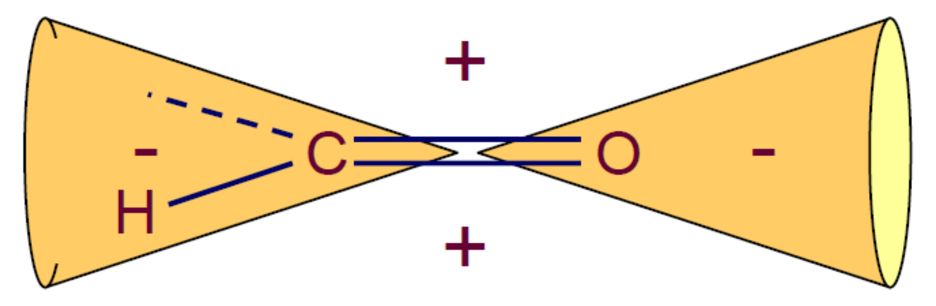




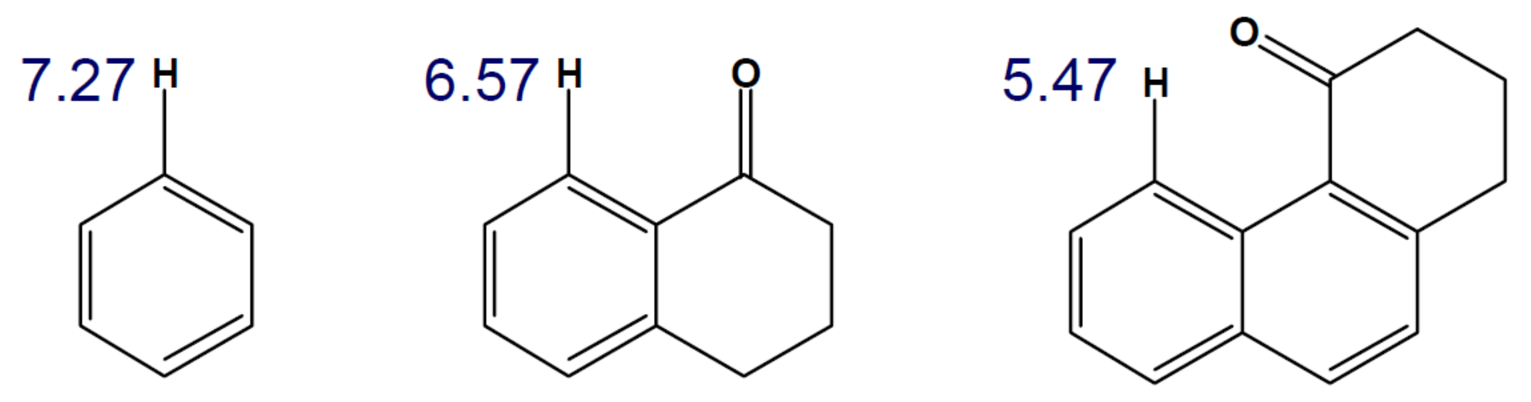
+ shielding

– deshielding

Magnetic Anisotropy

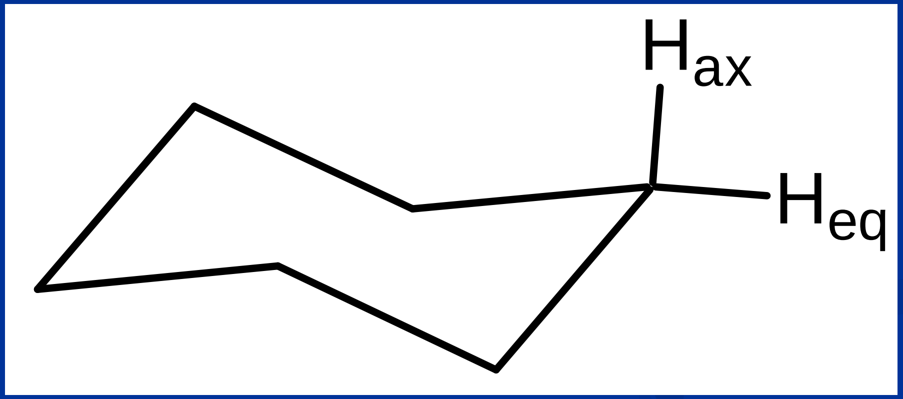


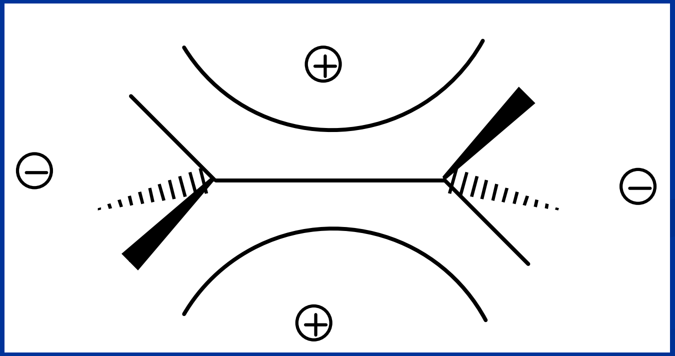
+ shielding
– deshielding



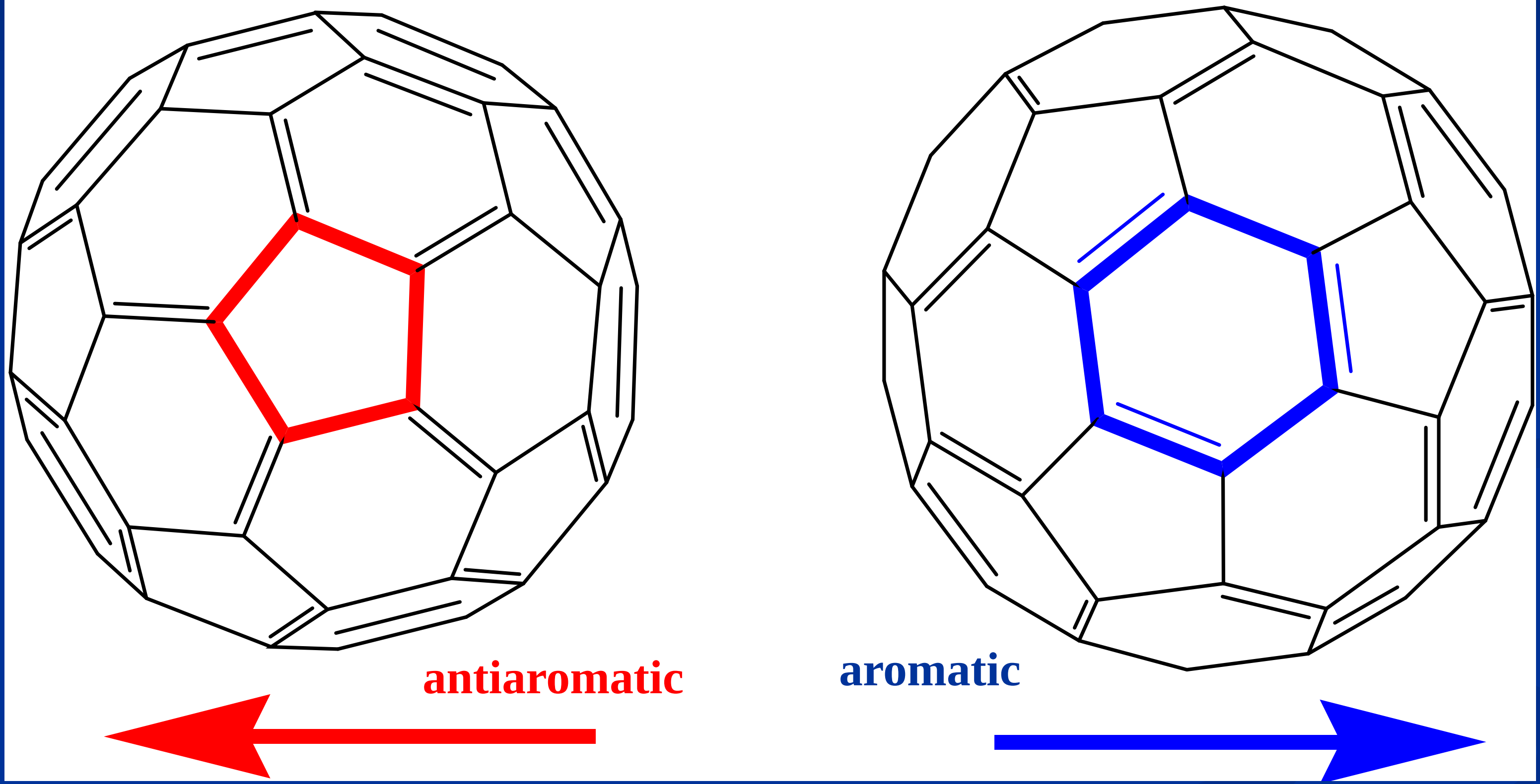
Magnetic Anisotropy

The equatorial protons are deshielded by 0.48 ppm wrt the axial





Magnetic Anisotropy of C_{60}



Paratropic ring current
+5.4 ppm

Diatropic ring current
–7.0 ppm

Magnetic Anisotropy

$^{3}He + C_{60}/ C_{70}$

650 ºC
3000 bar

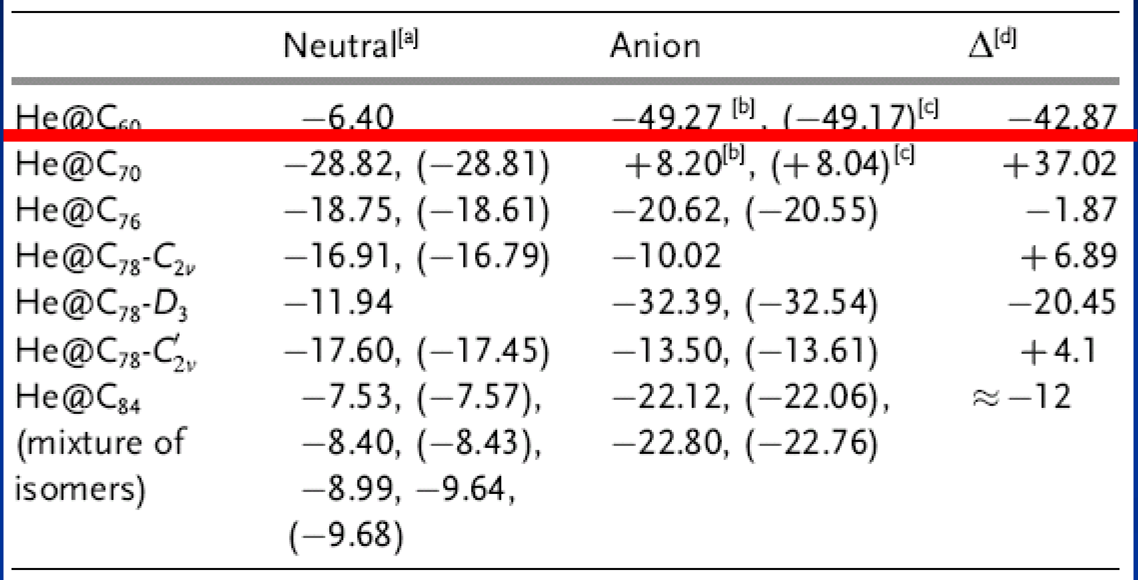
$^{3}He @ C_{60}$

$^{3}He @ C_{70}$

δ (^{3}He) –6.3 ppm

δ (^{3}He) –28.8 ppm

Magnetic Anisotropy



	Neutral[a]	Anion	Δ[d]
He@C_{60}	-6.40	-49.27 [b], (-49.17)[c]	-42.87
He@C_{70}	-28.82, (-28.81)	$+8.20$[b], $(+8.04)$[c]	$+37.02$
He@C_{76}	-18.75, (-18.61)	-20.62, (-20.55)	-1.87
He@C_{78}-C_{2v}	-16.91, (-16.79)	-10.02	$+6.89$
He@C_{78}-D_3	-11.94	-32.39, (-32.54)	-20.45
He@C_{78}-C'_{2v}	-17.60, (-17.45)	-13.50, (-13.61)	$+4.1$
He@C_{84} (mixture of isomers)	-7.53, (-7.57), -8.40, (-8.43), -8.99, -9.64, (-9.68)	-22.12, (-22.06), -22.80, (-22.76)	≈ -12

^{3}He @ C_{60} → ^{3}He @ C_{60}^{6-}

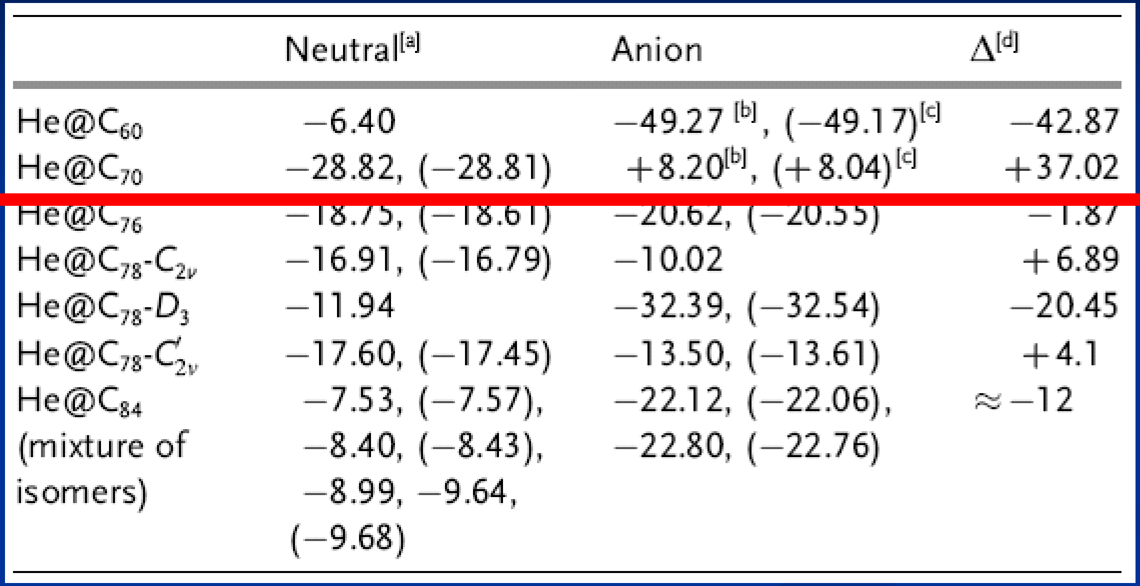
δ (^{3}He) –6.3 ppm

δ (^{3}He) –49.2 ppm

shifted to high field = higher aromatic character

6-MRs and 5-MRs of the fullerene cage of C_{60}^{6-} show diamagnetic ring currents

Magnetic Anisotropy



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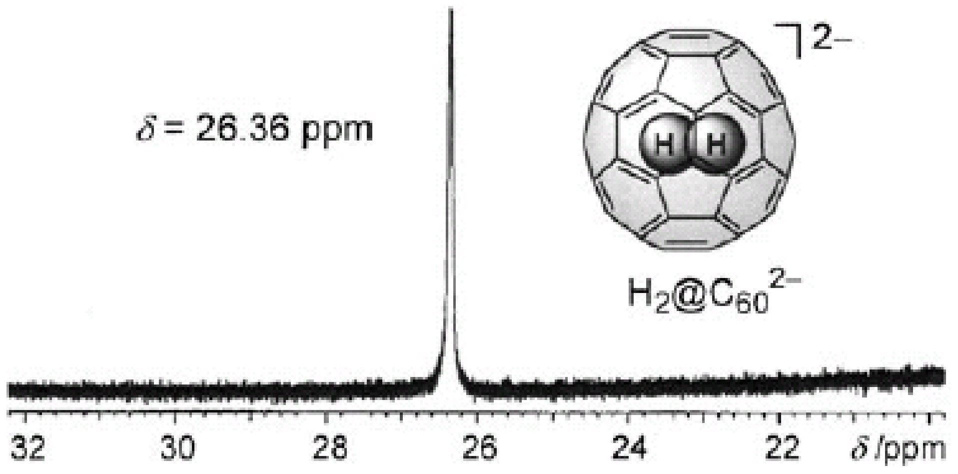
He@C_{76}	−18.75, (−18.61)	−20.62, (−20.55)	−1.87
He@C_{78}-C_{2v}	−16.91, (−16.79)	−10.02	+6.89
He@C_{78}-D_3	−11.94	−32.39, (−32.54)	−20.45
He@C_{78}-C'_{2v}	−17.60, (−17.45)	−13.50, (−13.61)	+4.1
He@C_{84} (mixture of isomers)	−7.53, (−7.57), −8.40, (−8.43), −8.99, −9.64, (−9.68)	−22.12, (−22.06), −22.80, (−22.76)	≈ −12

^{3}He @ C_{70} → ^{3}He @ C_{70}^{6-}

δ (^{3}He) –28.8 ppm δ (^{3}He) +8.2 ppm

shifted to low field = a reduction in aromaticity

Magnetic Anisotropy



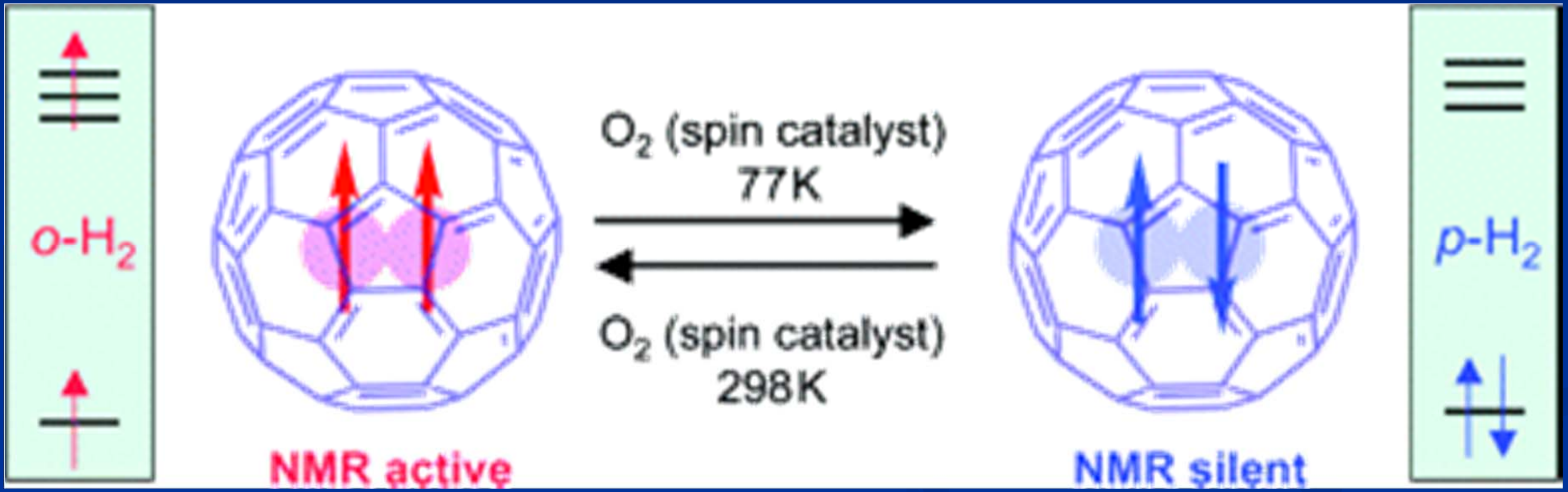
^1H NMR spectrum (300 MHz, CD_3CN) of $H_2@C_{60}^{2-}$.

^1H NMR spectra

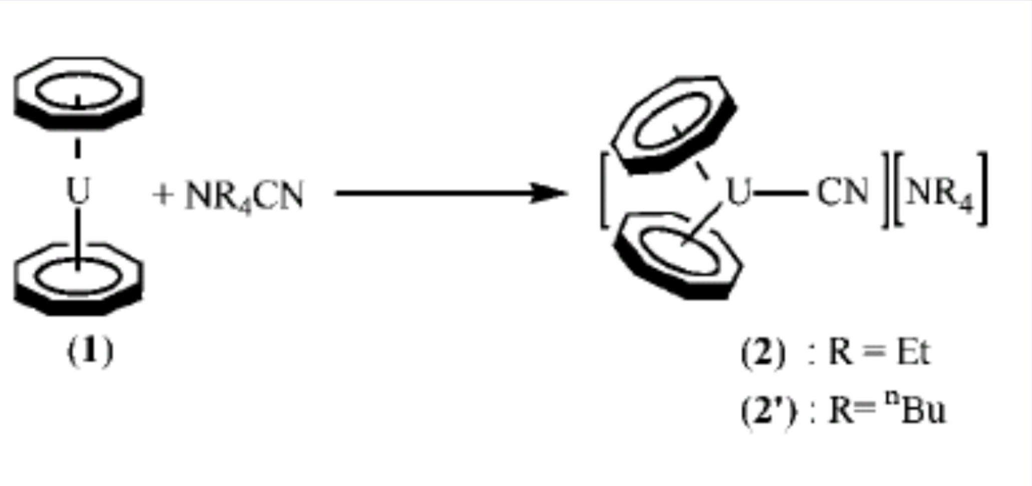
H_2 in liquids ~4 ppm

$H_2@C_{60}$ in 1,2-dichlorobenzene-d_4 –1.5 ppm

Ortho- and Parahydrogen



Magnetic Anisotropy

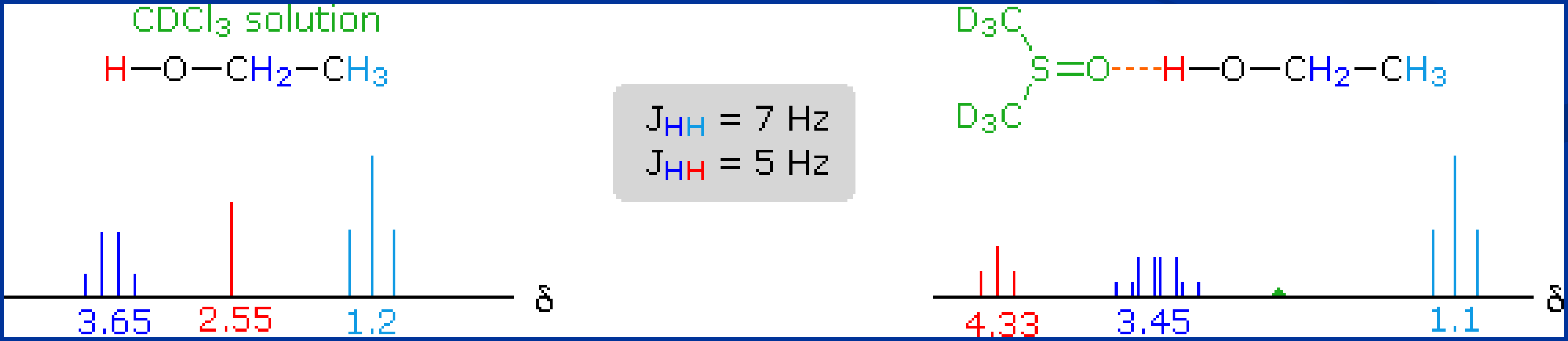


The ^{1}H NMR spectrum of 2 in pyridine-d_5
- A singlet at δ –32.18 (16 H) characteristic of a C_8H_8 ligand bound to uranium(IV)
- Two signals at δ +4.49 (8 H) and +1.96 (12 H) due to a single NEt_4^+ group

Solvent Effects

- Chemical shift – considerable influence
- Coupling constants – very small changes
- Relaxation – higher viscosity reduces T_1 and T_2 of small molecules

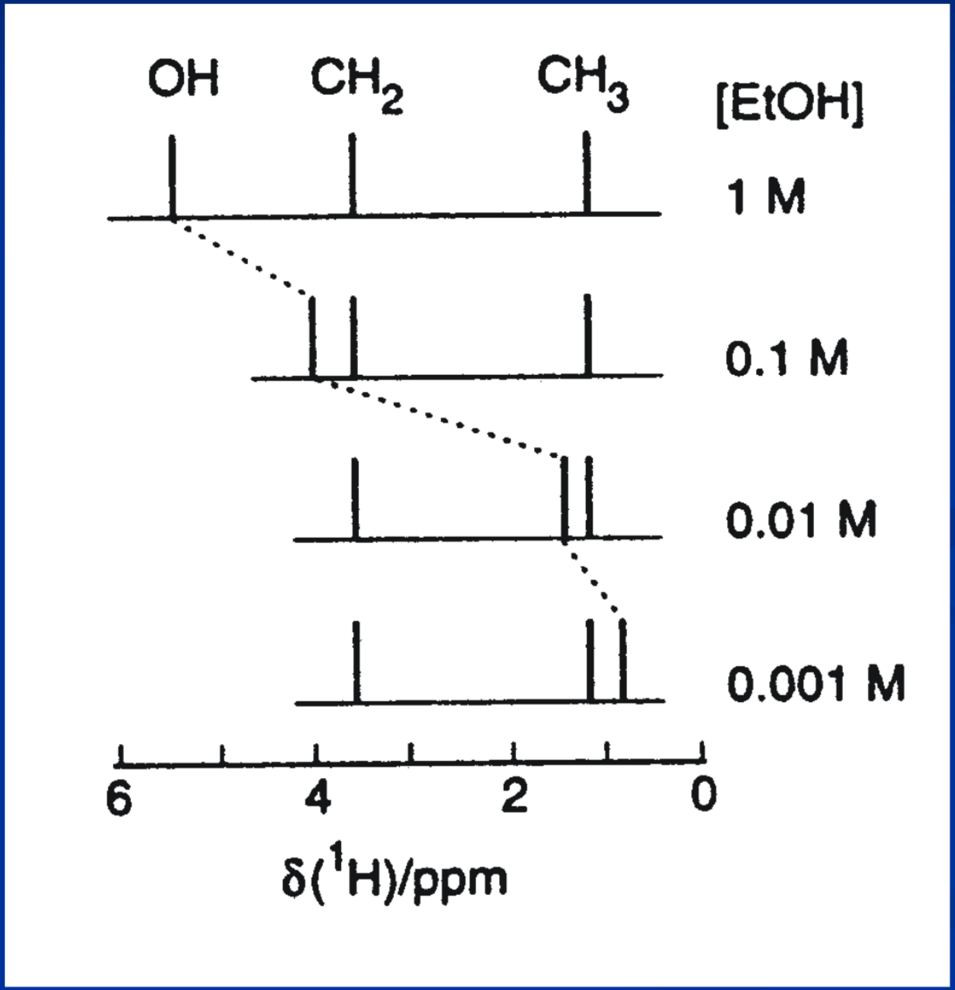
Van der Waals forces 0.1 – 0.2 ppm in ^{1}H NMR
Magnetic anisotropy of solvent – benzene, aromatics (solvent/solute orientation not averaged to zero)
Hydrogen bonding



^{1}H Chemical Shifts of Methanol in Selected Solvents

Solvent	$CDCl_3$	CD_3COCD_3	CD_3SOCD_3	$CD_3C\equiv N$
CH_3	3.40	3.31	3.16	3.28
O–H	1.10	3.12	4.01	2.16

Hydrogen Bonding



Increasing concentration

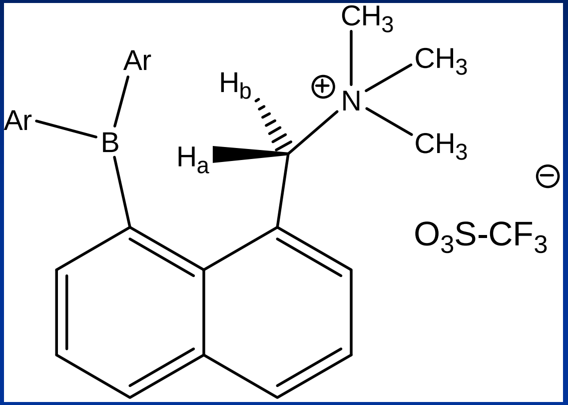
More extensive H-bonding

Deshielding of OH signal

Hydrogen Bonding

δ (^{17}O) water	liquid	0.0 ppm
	gas	–36.1 ppm

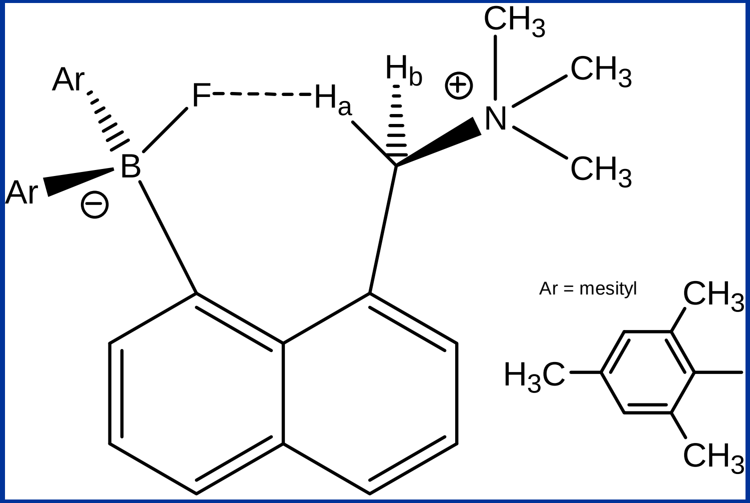
Hydrogen Bonding



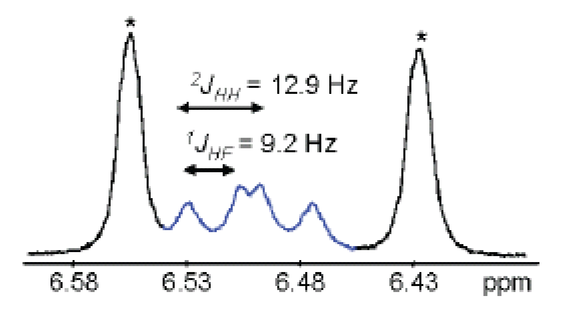
The methylene hydrogens are diastereotopic – steric congestion

two H signals at 3.69 and 4.81 ppm

H-F hydrogen bonding
H_a 6.50 ppm – deshielding
coupling to F nucleus



doublet of doublets
$^1J_{H-F}$ = 9.2 Hz
$^2J_{H-H}$ = 12.9 Hz



The peaks marked by *correspond to mesityl C*H* resonances

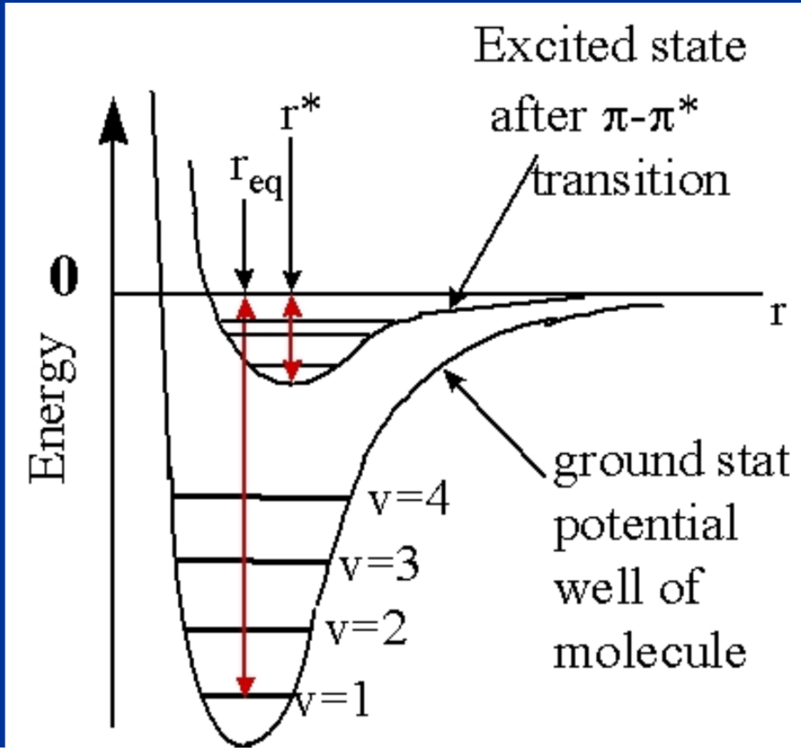
Temperature Effects

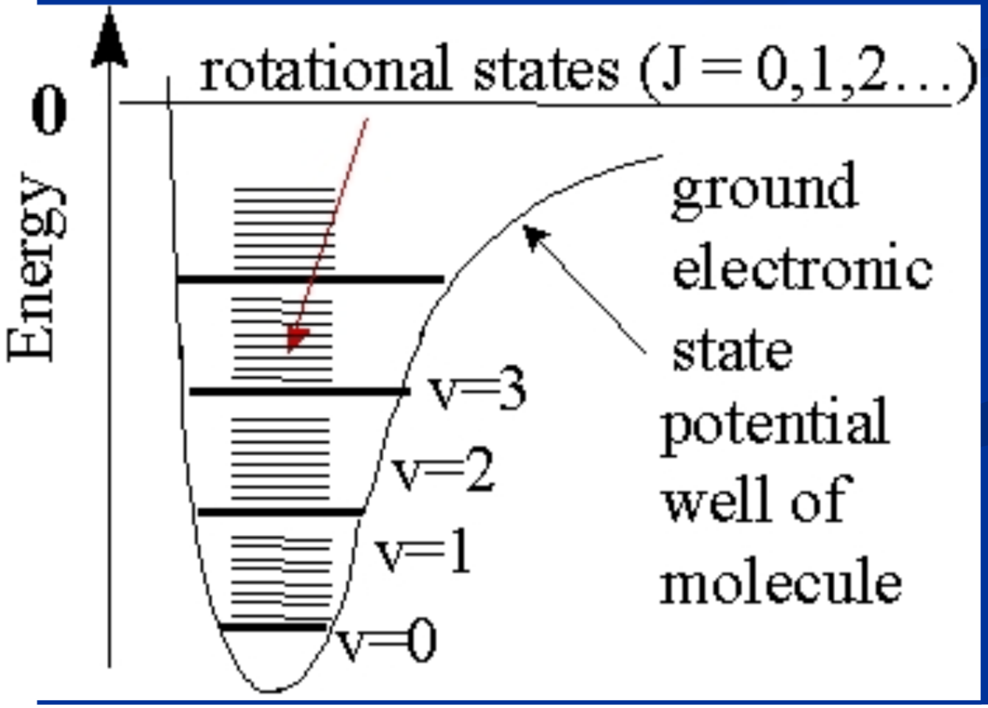
Anharmonic potential

Occupation of vibrational levels changes with temperature

Changes in effective distance between atoms

Chemical shift is a weighted average of the individual vibrational states





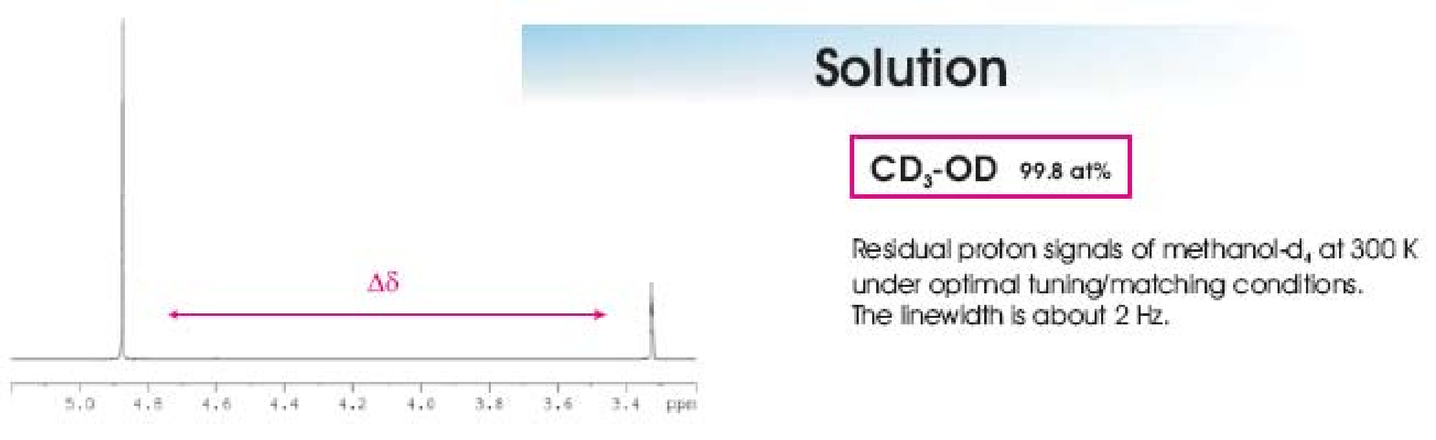
Temperature in NMR

Temperature dependent NMR parameters

- Chemical shift
- Number of signals – dynamic NMR spectroscopy
- Kinetics of exchange processes
- Equilibrium – reaction, tautomers, conformers
- Relaxation – T_1 and T_2 depend on molecular tumbling
- Dipolar and scalar coupling – exchange
- Molecular diffusion coefficient D – Stokes-Einstein
- Equilibrium magnetization M_0

Thermocouple position wrt sample
Temperature gradients within the sample
Sample heating by decoupling power

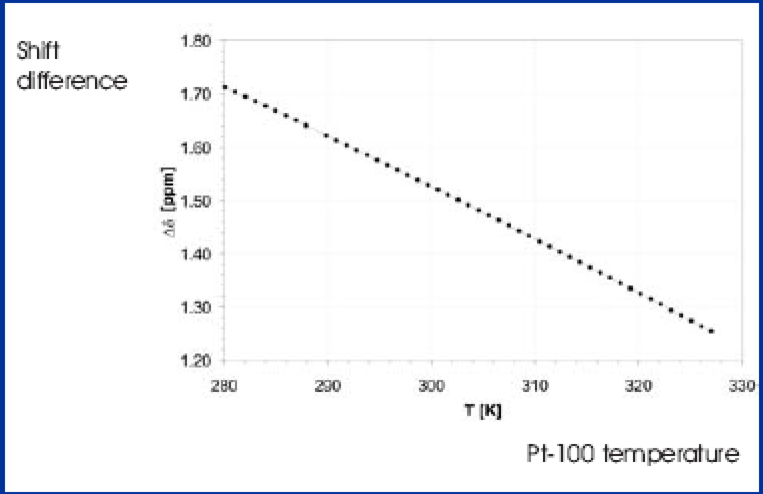
Methanol Thermometer



Solution

CD_3-OD 99.8 at%

Residual proton signals of methanol-d_4 at 300 K under optimal tuning/matching conditions. The linewidth is about 2 Hz.



$$\Delta\delta = -1.5243 \cdot 10^{-5} \times T^2 - 5.1576 \cdot 10^{-4} \times T + 3.0528$$

$\Delta\delta$ is the chemical shift difference (in ppm) and
T represents the temperature (between 280 and 328 K)
measured by the Pt-100 resistor within the sample.

Methanol (neat)

Temperature range: 178 – 330 K
Peaks used: -CH_3 and -OH
Equation: T [K] = 409.0 - 36.54 $\Delta\delta$ - 21.85 $(\Delta\delta)^2$
C. Amman, P. Meier and A. E. Merbach, *J. Magn. Reson.* **1982**, *46*, 319-321.

Ethylene glycol (neat)

Temperature range: 273 – 416 K
Peaks used: -CH_2- and -OH
Equation: T [K] = 466.5 - 102.00 $\Delta\delta$
C. Amman, P. Meier and A. E. Merbach, *J. Magn. Reson.* **1982**, *46*, 319-321.

CCl_4 and $(CD_3)_2CO$ (50/50 vol% mixture)

Temperature range: 190 – 360 K
Peaks used: CD_3-CO-CD_3 and CCl_4
Equation: T [K] = 5802.3 - 50.73 $\Delta\delta$
J. J. Led, S. B. Petersen, *J. Magn. Reson.* **1978**, *32*, 1-17.

$TeMe_2$ (neat)

Temperature range:
Peaks used: ^{125}Te
high field shift **0.128 ppm K^{-1}**

Ideal Thermometer

Nonreactive and stable/ internal thermometer

Intramolecular effect / one compound added, no concentration, solvent dependency

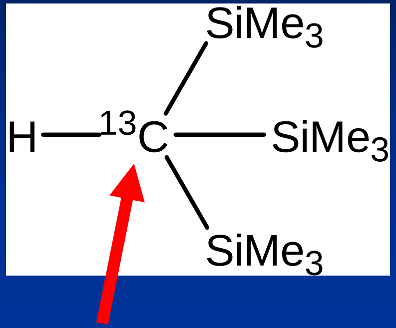
Wide range of temperatures

Linear response

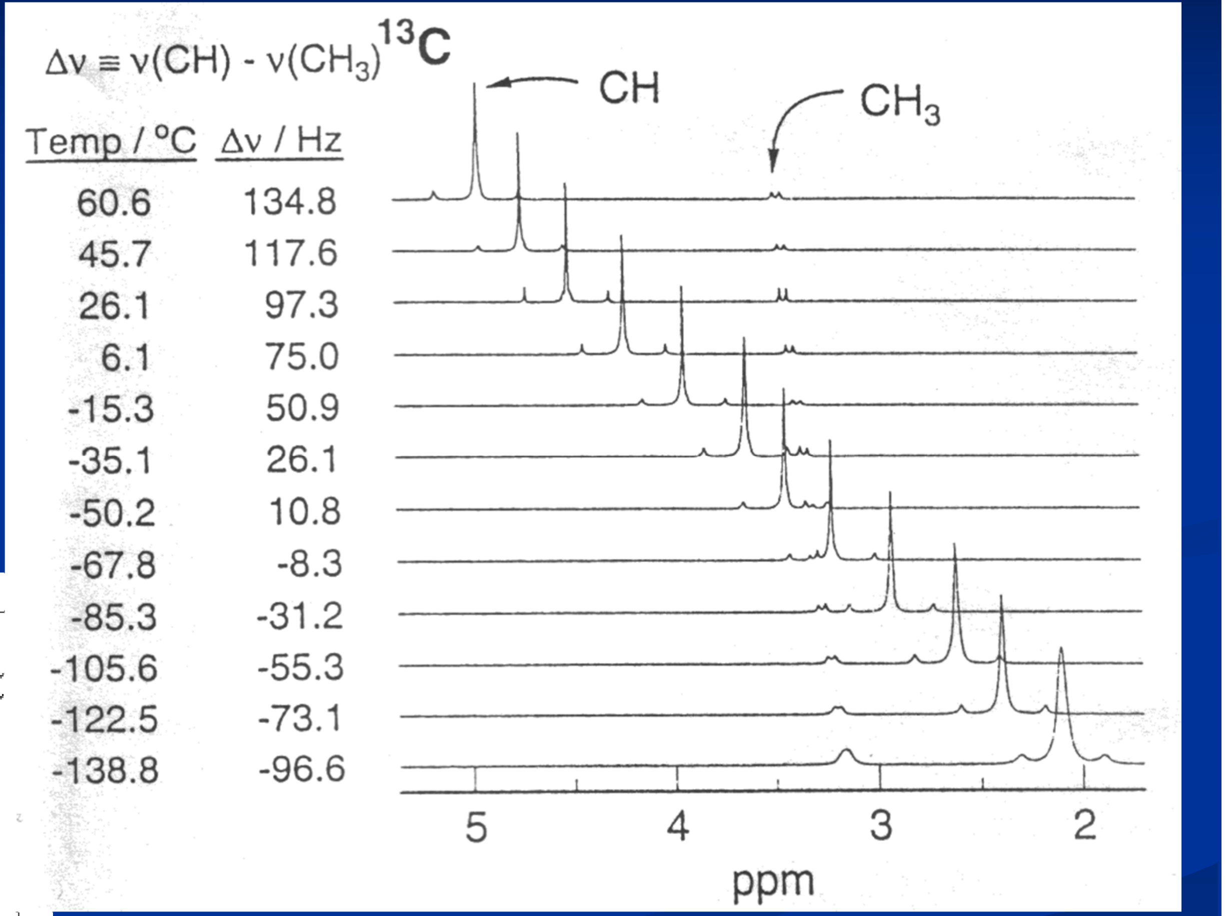
Strong response $\Delta\delta / \Delta T$

Solvent independent

Chemical Shift Thermometer

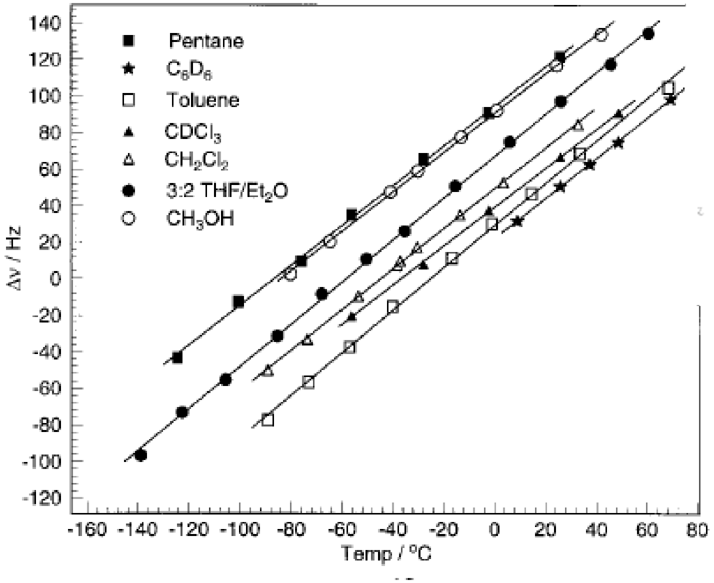


^{13}C Enriched



$\Delta\nu \equiv \nu(CH) - \nu(CH_3)$ ^{13}C

Temp / °C	Δν / Hz
60.6	134.8
45.7	117.6
26.1	97.3
6.1	75.0
-15.3	50.9
-35.1	26.1
-50.2	10.8
-67.8	-8.3
-85.3	-31.2
-105.6	-55.3
-122.5	-73.1
-138.8	-96.6



Paramagnetic Compounds

- Organic radicals, transition metal complexes
- Unpaired electron = large fluctuating magnetic field
- Magnetic moment of an electron
- $\mu_p = -9.285 \times 10^{-24}\,\text{J T}^{-1}$
- Magnetic moment of a proton
- $\mu_p = 1.411 \times 10^{-26}\,\text{J T}^{-1}$
- Relaxation – unpaired electron reduces T_1 and T_2
  = extremely broad lines
- Coupling of nuclear and electron spins
- The paramagnetic center induces additional
  paramagnetic shift
- Chemical shift
  ^{1}H NMR very large range 200 ppm
  ^{13}C NMR range 1000 ppm

Paramagnetic Compounds

δ_{iso} Isotropic shift (isotropic part of the tensor)

$$\delta_{iso} = \delta_{orbital} + \delta^{FC} + \delta^{PC}$$

$\delta_{orbital}$ Ramsay (diamagnetic + paramagnetic), the difference between the chemical shielding of a reference compound and the orbital contribution to the shielding tensor of the investigated paramagnetic molecule, temperature independent, approximated by the NMR shift of a diamagnetic analogue or experimentally the temperature-(in)-dependent parts can be separated by a least-squares fit (1/T dependence) of NMR spectra measured at different temperatures

δ^{FC} Fermi contact shift – delocalized e = through bond, vanishes relatively quickly as the number of bonds from the paramagnetic metal center increases (the spin density localized in the metal d-orbitals)

δ^{PC} Pseudocontact – dipolar = through space, an inverse distance dependence ($1/r^3$), temperature-dependent, obeys the Curie law (in the absence of zero-field splitting (ZFS) and when the (2S + 1) degenerate ground state is well-separated from excited energy levels)

Paramagnetic Compounds

$$\delta^{FC} = \frac{\mu_e S(S+1)}{3kT\gamma} g^{iso} A^{iso}$$

δ^{FC} Fermi contact shift – μ_e = the Bohr magneton, γ = the gyromagnetic ratio of nucleus , kT = the thermal energy, (2S + 1) = the multiplicity of the ground state, g^{iso} is the isotropic part of the g tensor, A^{iso} is the isotropic part of the hyperfine coupling tensor

$$m = g\frac{\mu_B}{\hbar} I$$

$$\delta^{PC} = \frac{\mu_e S(S+1)}{9kT\gamma} Tr(g^{ani} A^{dipolar})$$

δ^{PC} Pseudocontact – where g^{ani} = the g-tensor anisotropy, $A^{dipolar}$ = the dipolar part of the hyperfine coupling tensor
the dipolar interaction between an averaged electron magnetic moment (typically centered on the metal center) and the magnetic moment of the nucleus

Paramagnetic Compounds

$$\delta_{iso} = \delta_{orbital} + \delta_{paramag} = \delta_{orbital} + \delta^{FC} + \delta^{PC}$$

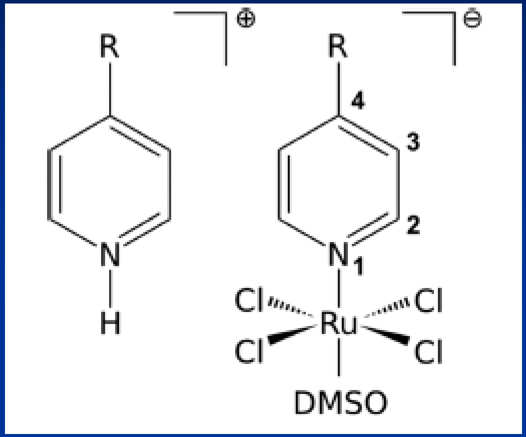
For small molecules, 1D NMR spectra measured at various temperatures, the temperature-independent (orbital) and temperature-dependent (paramagnetic) contributions are determined from a Curie plot:
NMR chemical shifts versus reciprocal absolute temperature (1/T)

the monotonic dependence in the Curie plots is obtained only for systems obeying the Curie law, i.e., for doublet or higher multiplets when the zero-field splitting effects are negligible

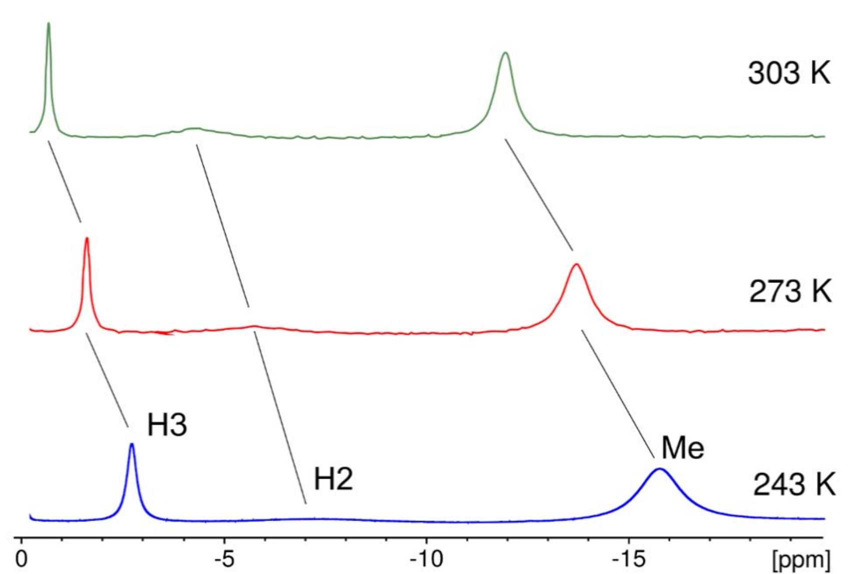
for systems with non-negligible zero-field splitting the NMR temperature dependence becomes more complicated

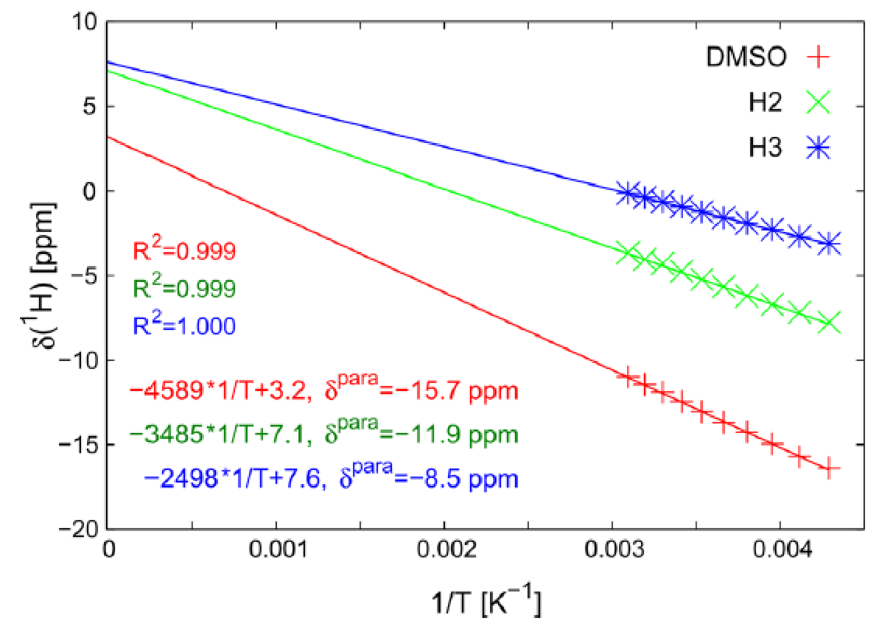
Paramagnetic Compounds

$$\delta_{iso} = \delta_{orbital} + \delta_{paramag}$$



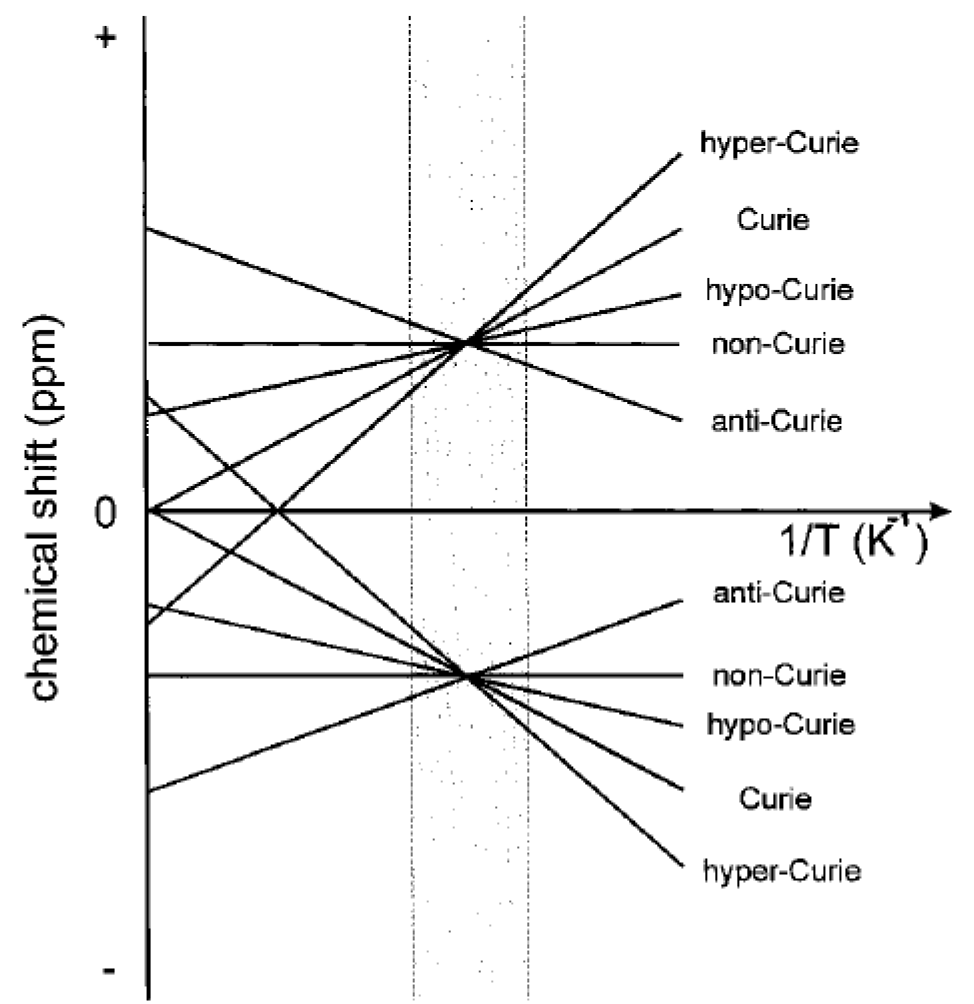
R = CN





Paramagnetic Compounds

$$\delta_{iso} = \delta_{orbital} + \delta^{FC} + \delta^{PC}$$



Pseudocontact Shift

The anisotropic magnetic susceptibility affects the Larmor frequencies of nearby nuclei

the through-space “dipolar” or “pseudocontact” shift

9 H along the Fe-C bond vector are shifted downfield (the addition of the internal field to the applied field causes them to resonate at a low applied field)

H along the yz plane (perpendicular to the Fe-C bond vector) are shifted upfield

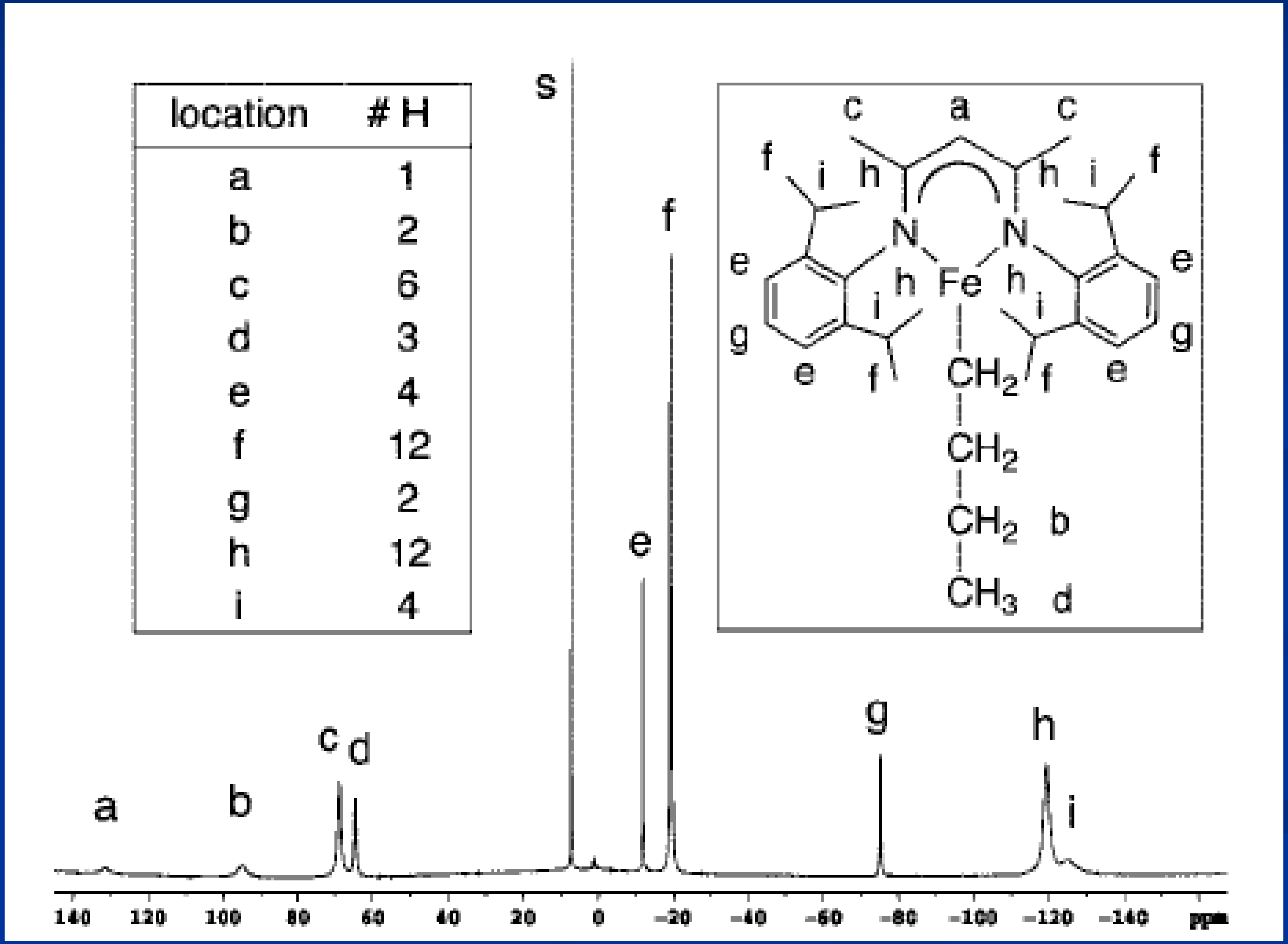
An analogy is the diamagnetic “ring current” in aromatics, which gives downfield shifts of protons in the plane of the electron circulation and upfield shifts of protons normal to the plane of the electron circulation

Pseudocontact Shift

The paramagnetic current in the iron compounds shifts H in the yz plane upfield those normal to the yz plane downfield

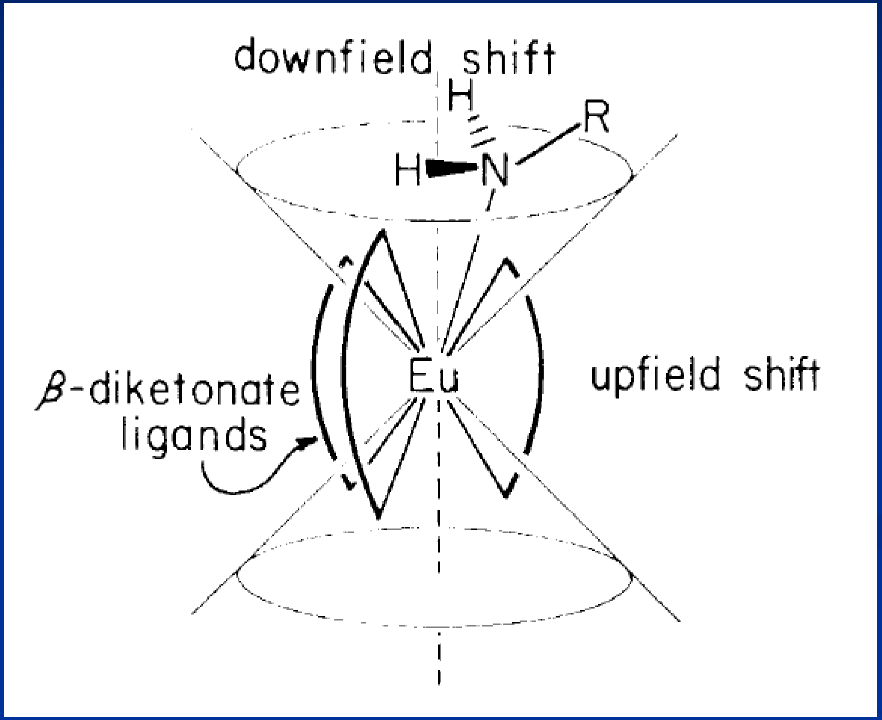
The dominance of the pseudocontact shift is anomalous for paramagnetic complexes, for which the chemical shifts typically are dominated by the through-bond “contact” shift.

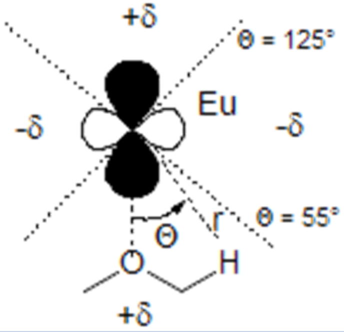
Pseudocontact Shift



location	# H
a	1
b	2
c	6
d	3
e	4
f	12
g	2
h	12
i	4

Lanthanide-Induced Shifts (LIS)

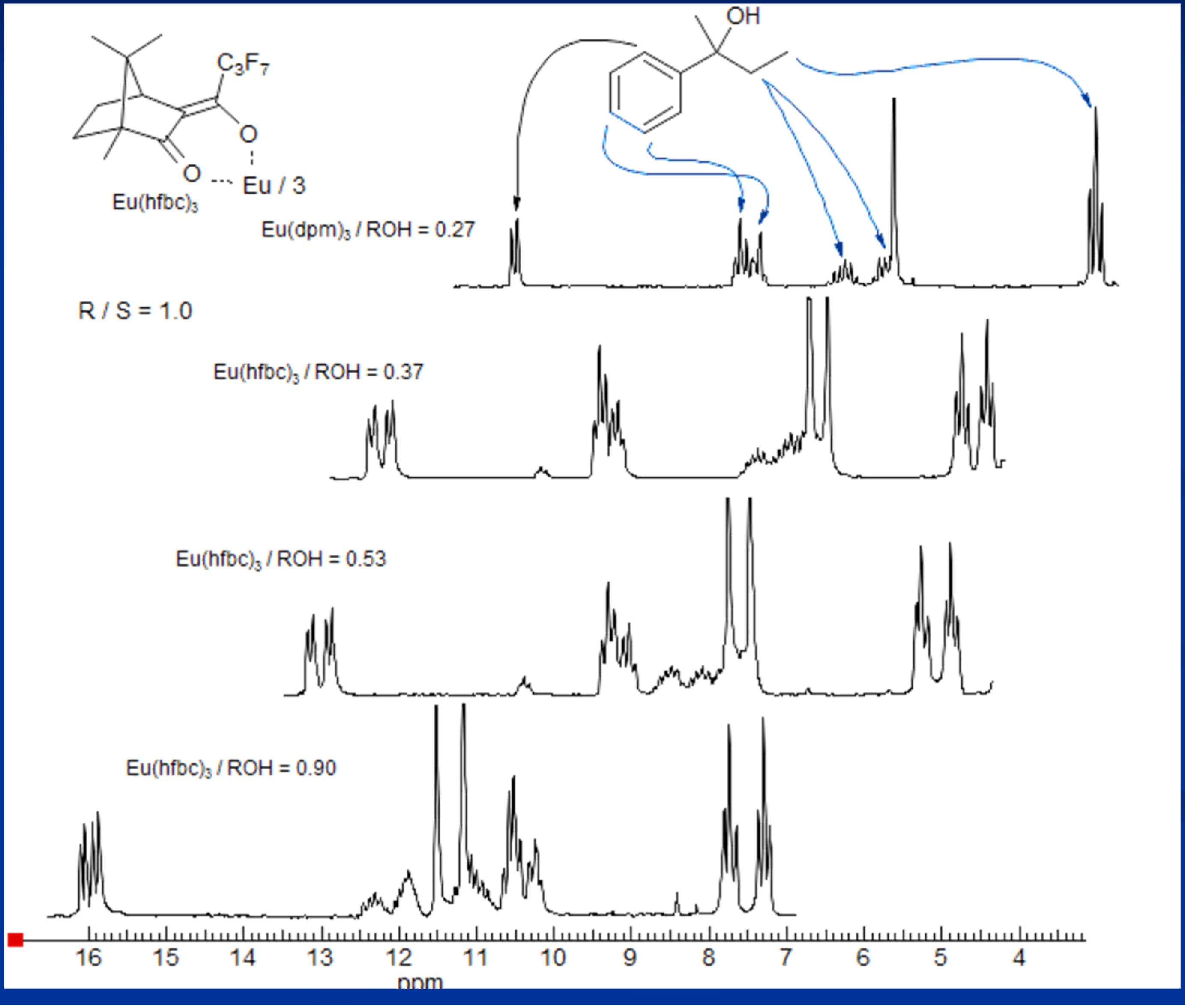




$$\Delta M = \frac{D}{r^3}(3\cos^2 \Theta - 1)$$

for Eu, ΔM is downfield for
Θ between +55° -55°

Lanthanide-Induced Shifts (LIS)



Lanthanide-Induced Shifts (LIS)