The Non-local Contribution to the Magnetic Shielding Constant

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

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

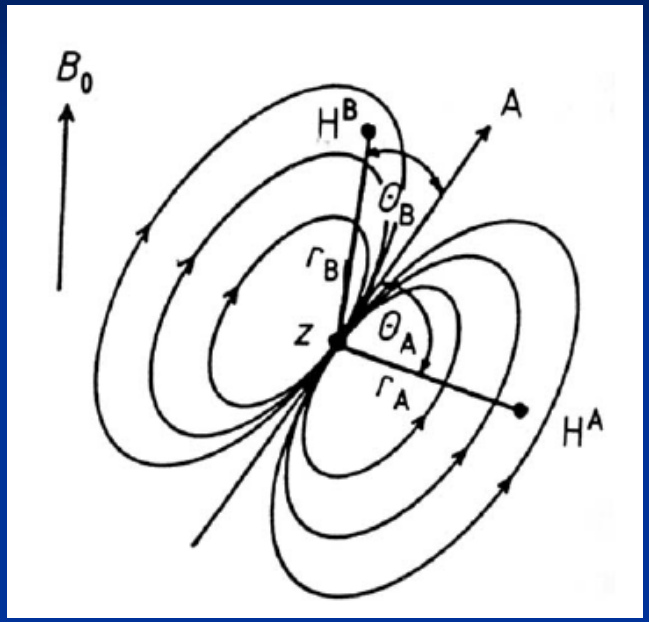
McConnell formula (cylindrical symmetry)

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

$\chi_{\parallel}$, $\chi_{\perp} < 0$

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

Magnetic Anisotropy



H = measured nucleus

Z = anisotropic neighboring groups

McConnel formula

(cylindrical symmetry, group Z approximated as a magnetic dipole

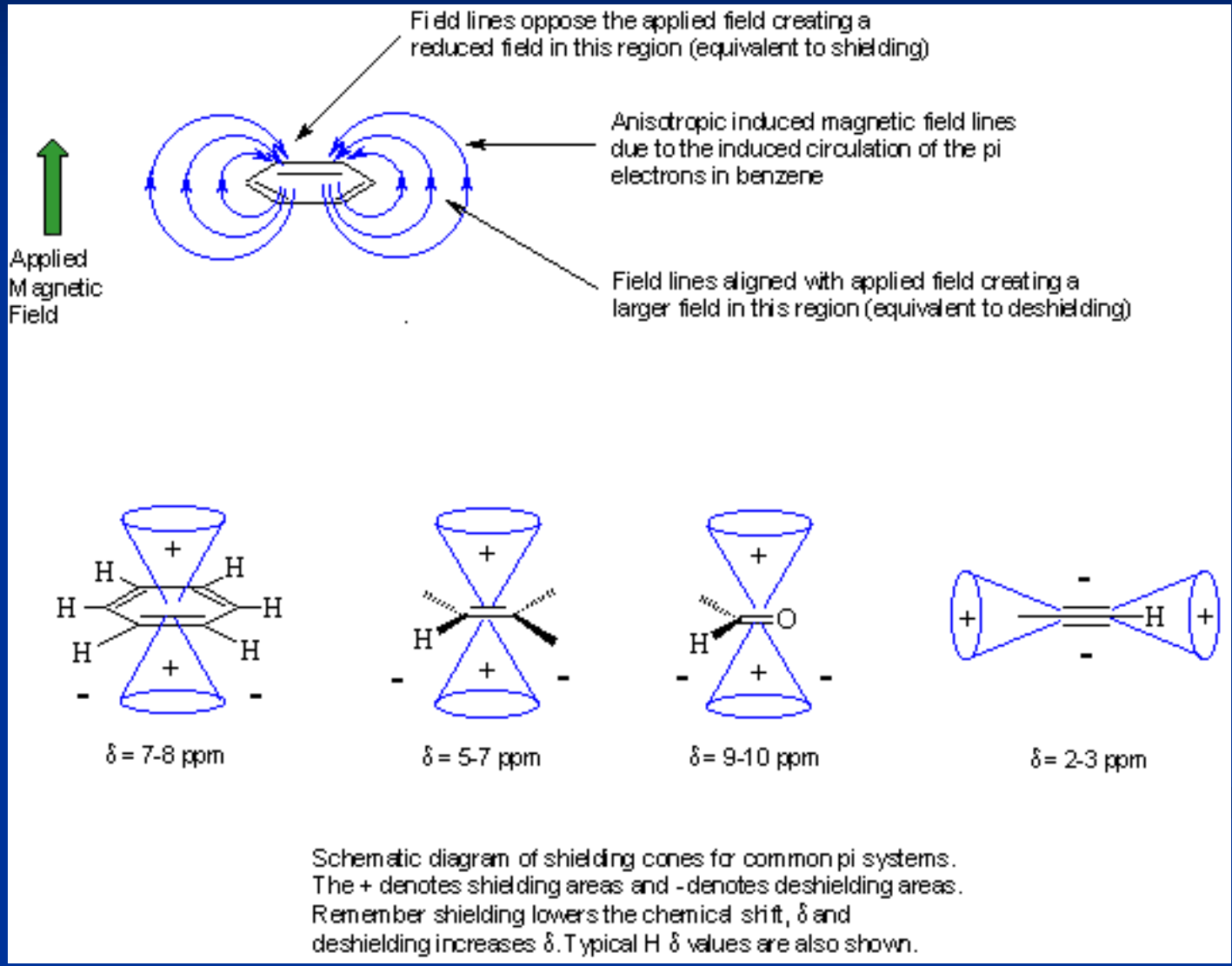
$$\sigma_{group} = (\chi_{\parallel} - \chi_{\perp})\,(1 - 3\cos^2\theta)/(3r^3)$$

θ is the angle between the vector **r** and the symmetry axis

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

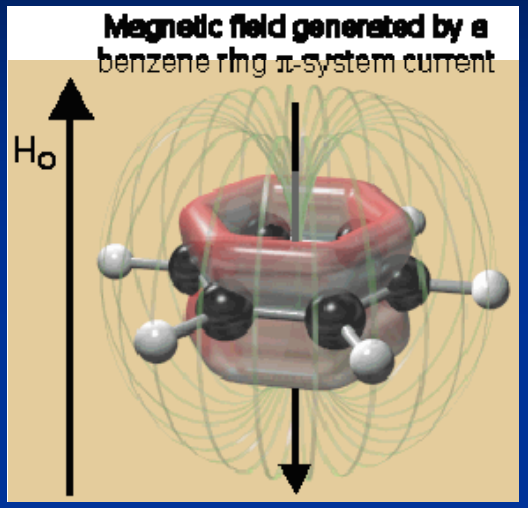
$\chi_{\parallel} - \chi_{\perp}$ the susceptibilities parallel and perpendicular to the symmetry axis

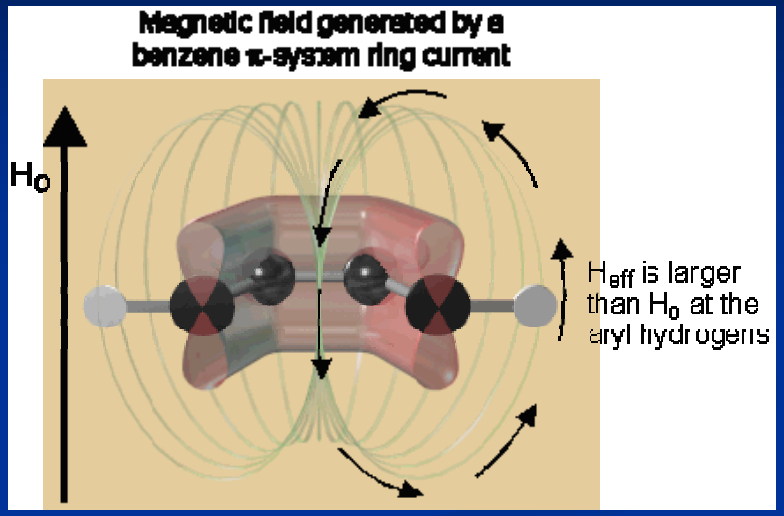
Groups with Magnetic Anisotropy



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





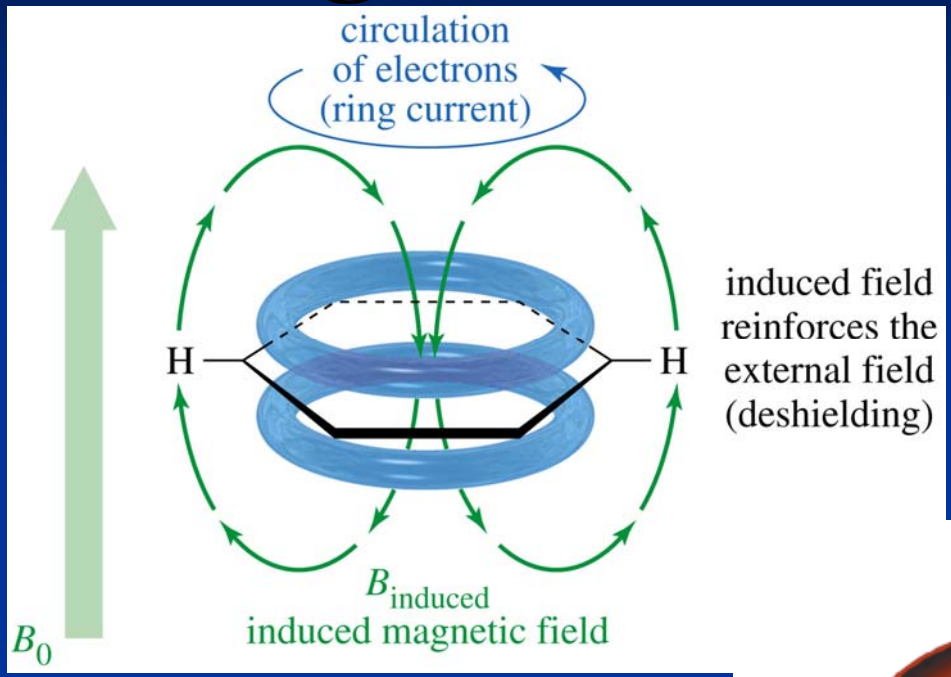
π electrons in aromatic rings are induced to circulate in a magnetic field

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)

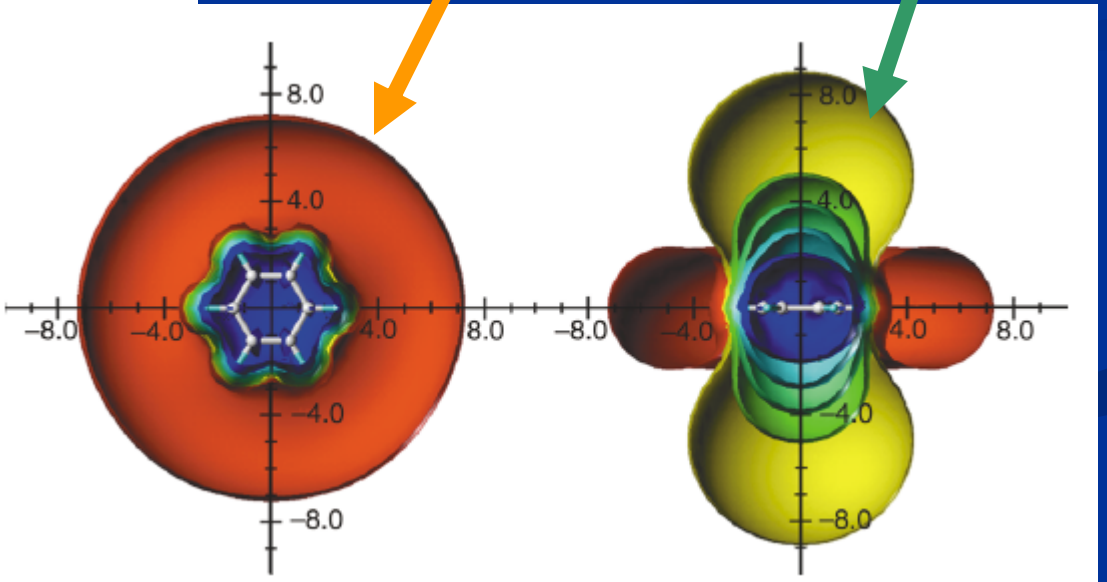
Ring Current in Aromatic Rings



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

Deshielding weak

Shielding strong



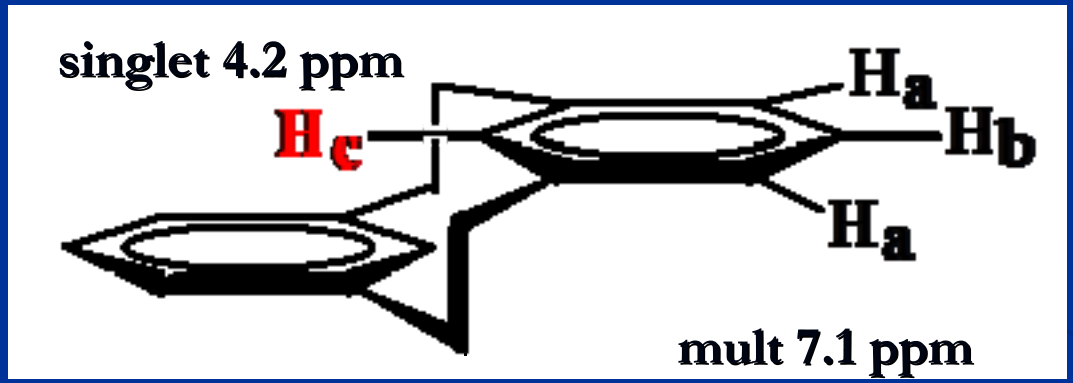
shielding surfaces
0.1 ppm in yellow, at 0.5 ppm in green, at 1 ppm in green-blue, at 2 ppm in cyan, and 5 ppm in blue

deshielding surface at 0.1 ppm in red

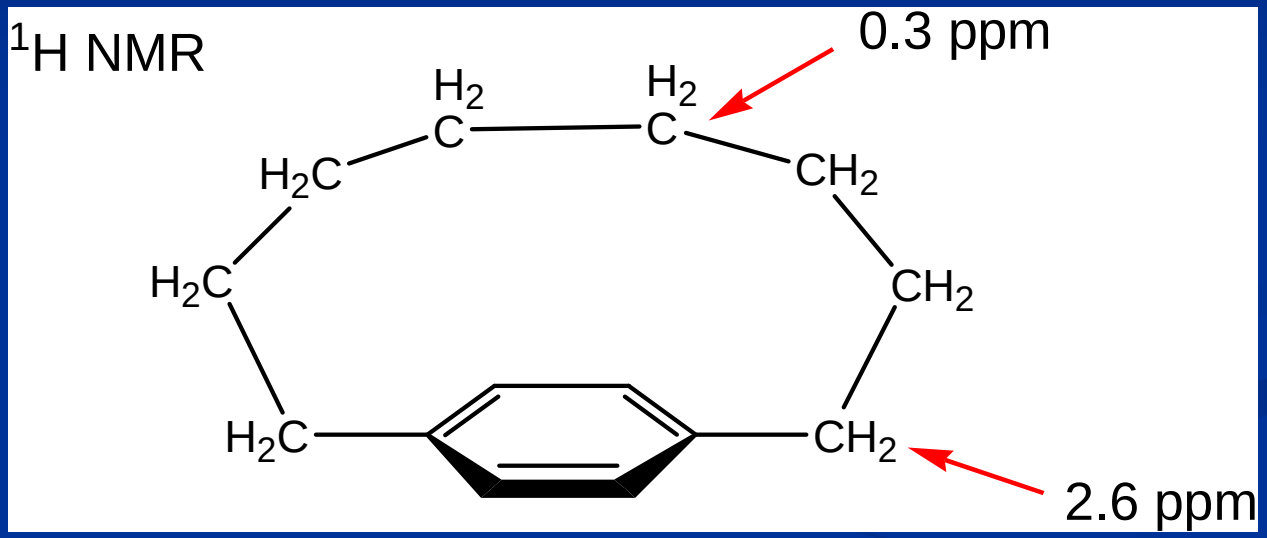
Magnetic Anisotropy

Octamethyl-[2, 2]-metacyclophane

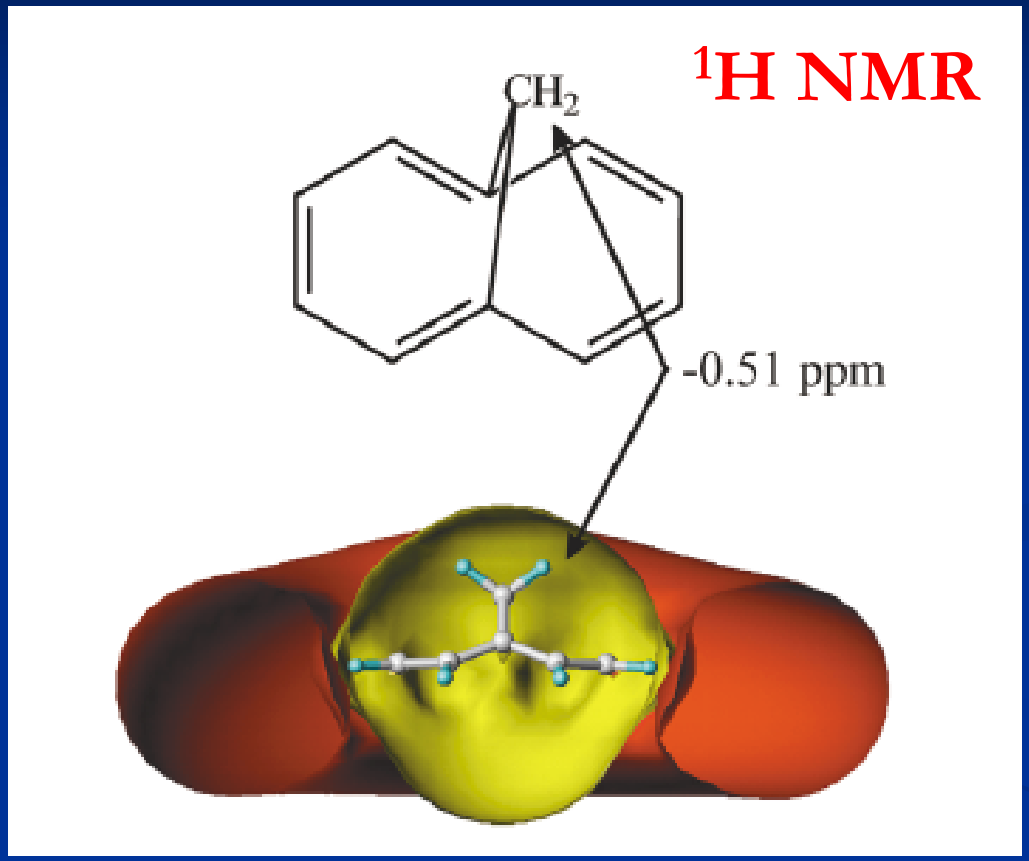
8 Me groups on C-C bridges not shown



Ring Current in Aromatic Rings

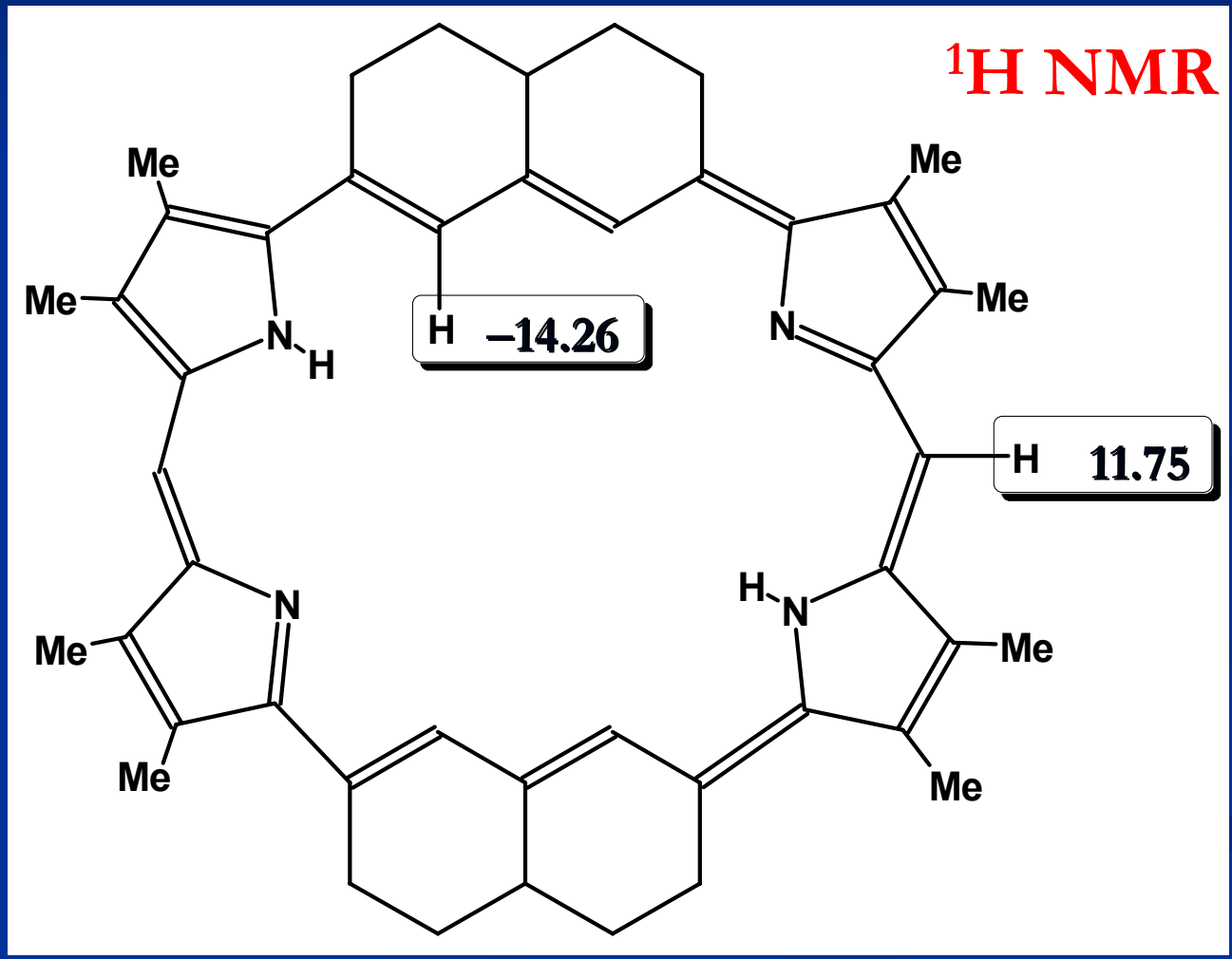


Ring Current in Aromatic Rings

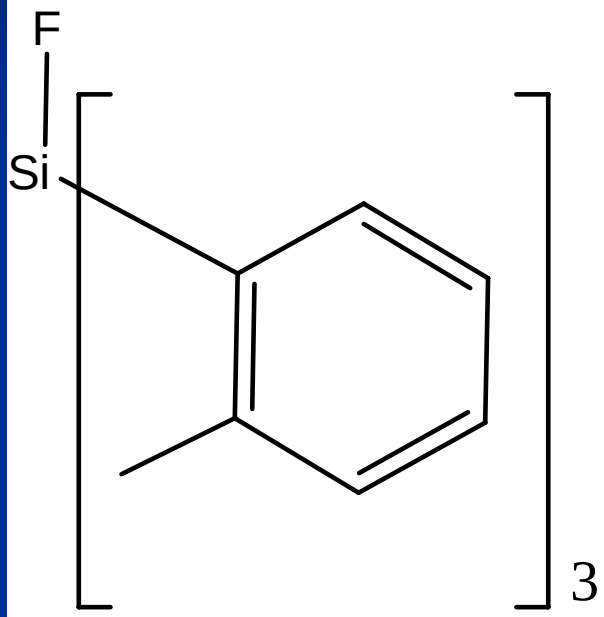


1,6-methano[10]annulene

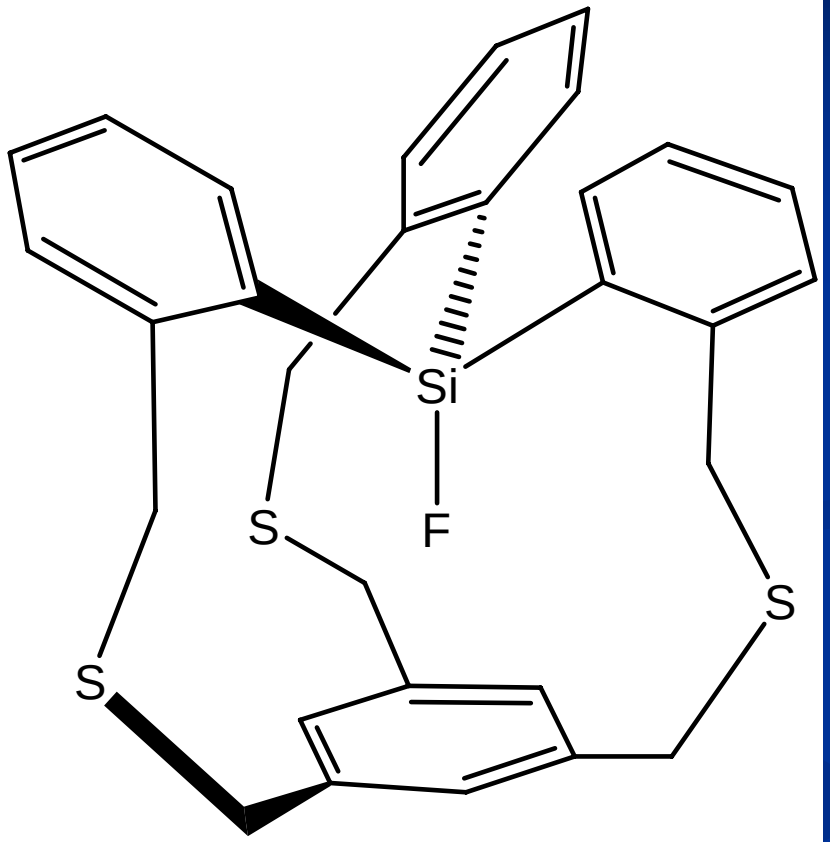
Magnetic Anisotropy



Magnetic Anisotropy



δ (^{19}F) 160.6



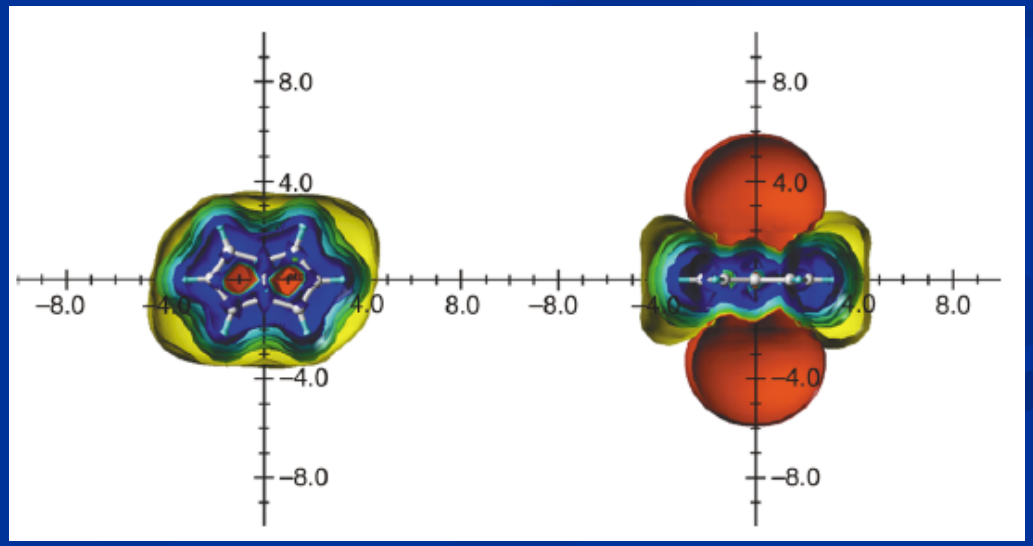
δ (^{19}F) 5.3

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

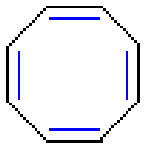
- a deshielding area above and below the plane of the ring system
- a shielding area in the plane of the ring system

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



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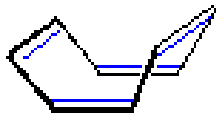
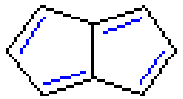
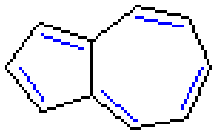


tub conformer
(non-planar)

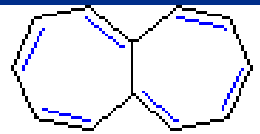
cyclooctatetraene stable b.p. 142 °C
gives alkene-like reactions
8 π-electrons



pentalene (planar)
very unstable
8 π-electrons



azulene (planar)
aromatic stability
10 π-electrons



heptalene (planar)
very unstable
12 π-electrons

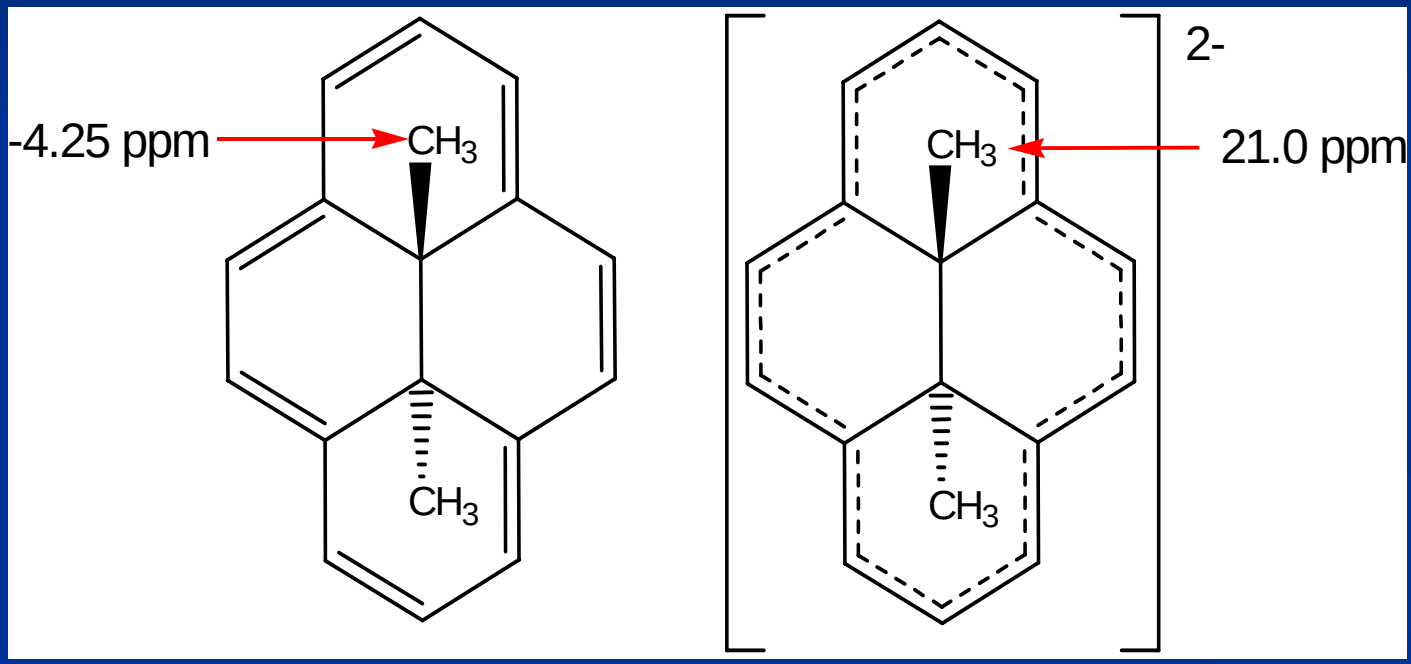
NICS Nucleus independent chemical shift

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

Negative NICS = aromatic
Positive NICS = antiaromatic

Aromatic/Antiaromatic Rings

^{1}H NMR



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

aromatic

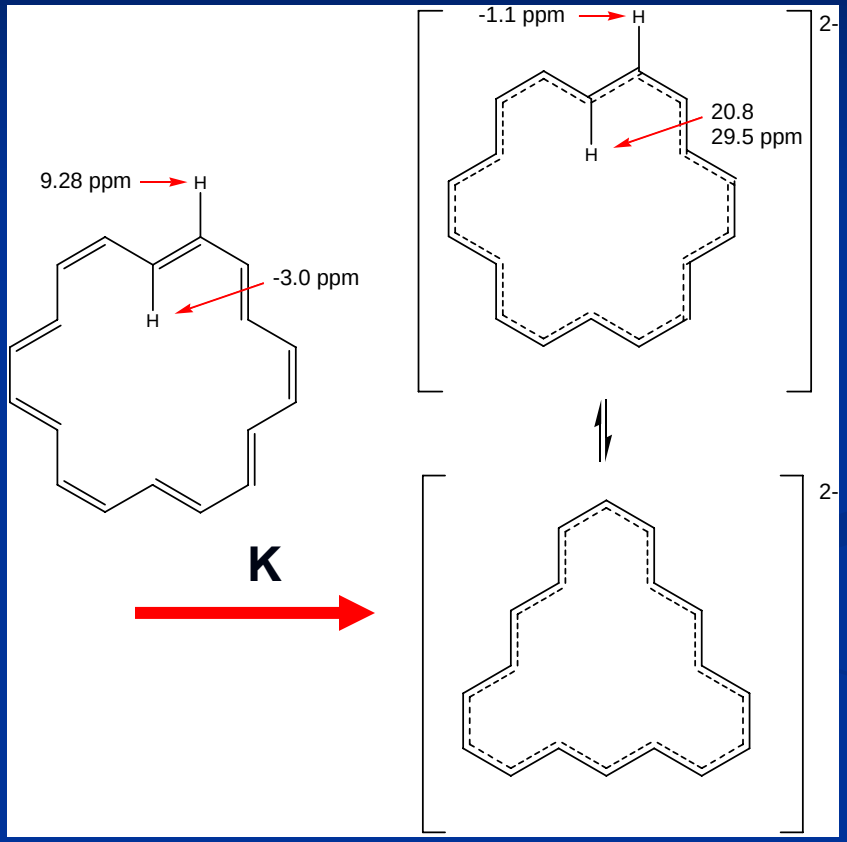
[4n+2] π-electrons

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

antiaromatic

[4n] π-electrons

Aromatic/Antiaromatic Rings



Low temp. ^{1}H NMR

[18] annulene dianions

antiaromatic

[4n] π-electrons

Paratropic ring current

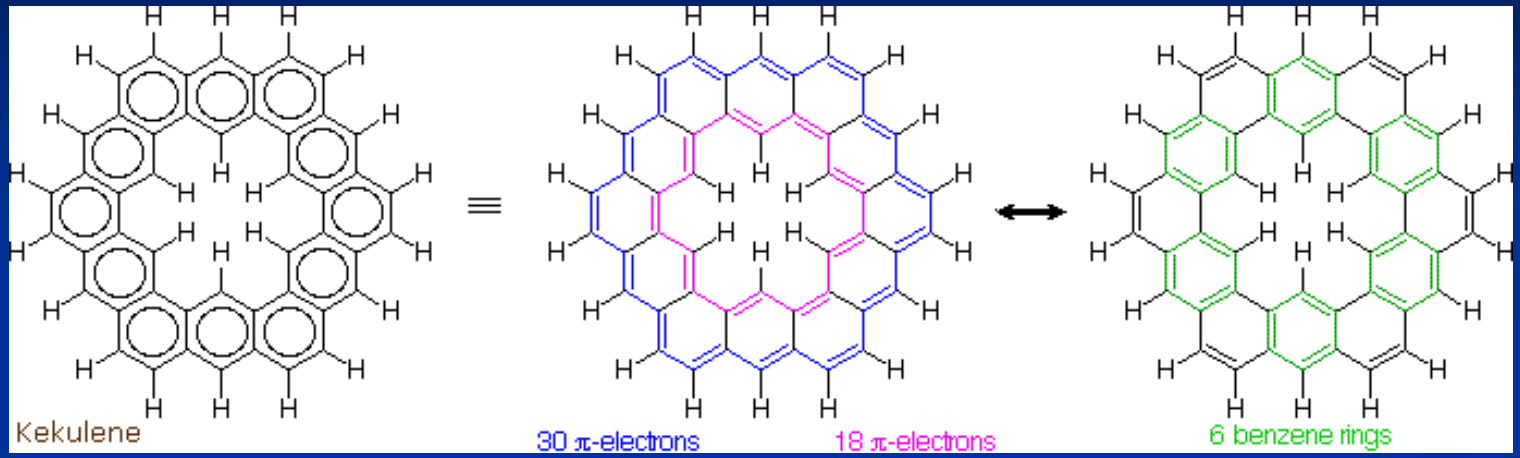
[18] annulene

aromatic

[4n+2] π-electrons

Diatropic ring current

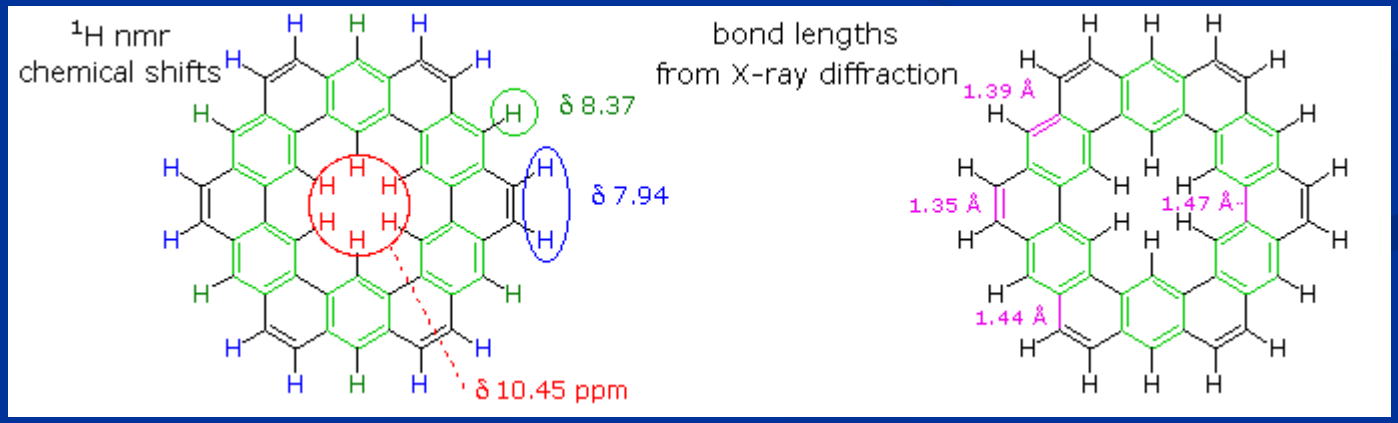
Kekulene



[4n+2] π-electrons

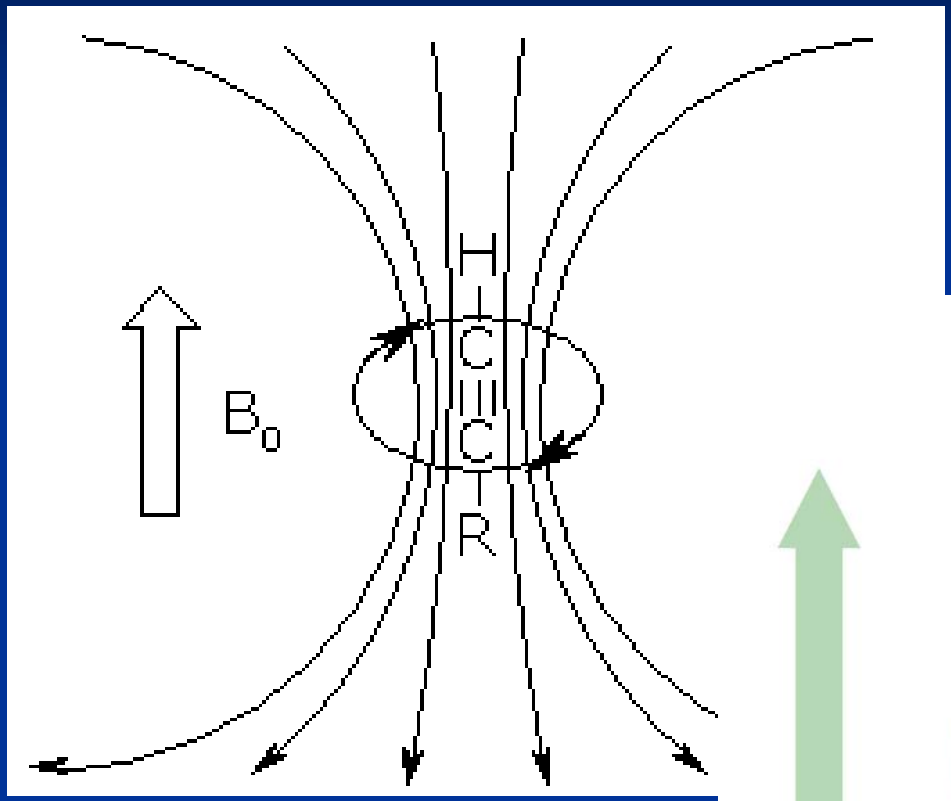
2 annulenes or 6 benzene rings

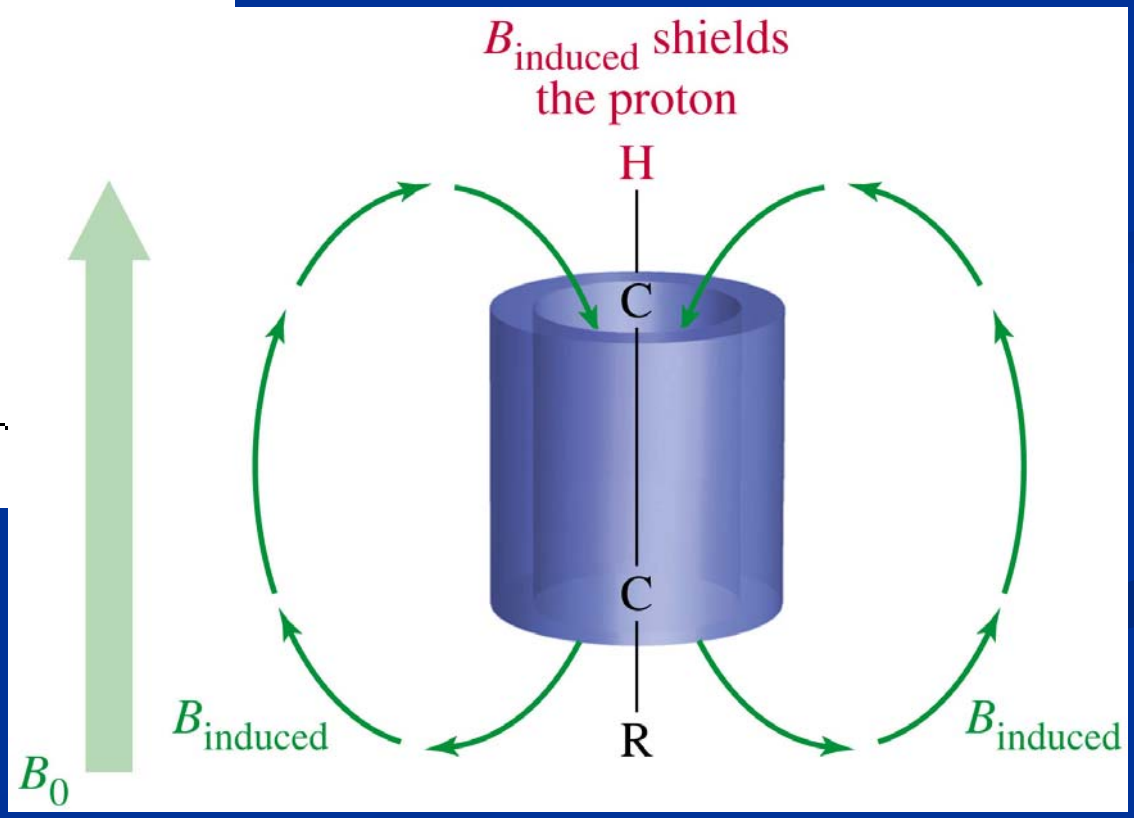
Kekulene is extremely insoluble. ^{1}H NMR spectrum taken at 200° C in deuterated tetrachlorobenzene



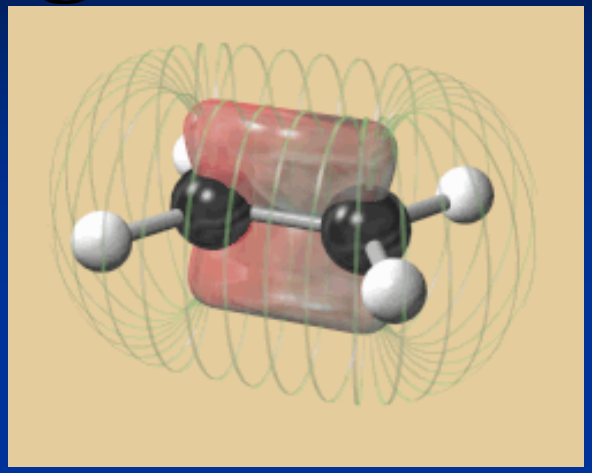
Magnetic Anisotropy

Acetylenic H

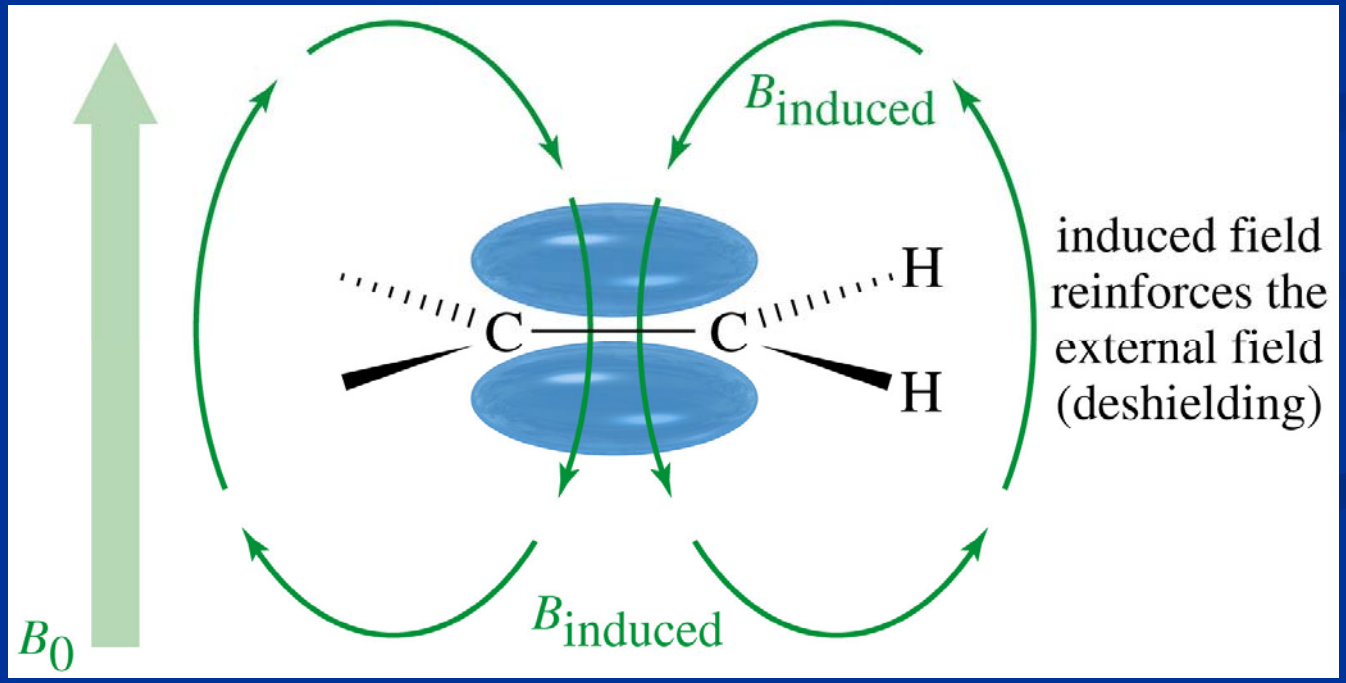




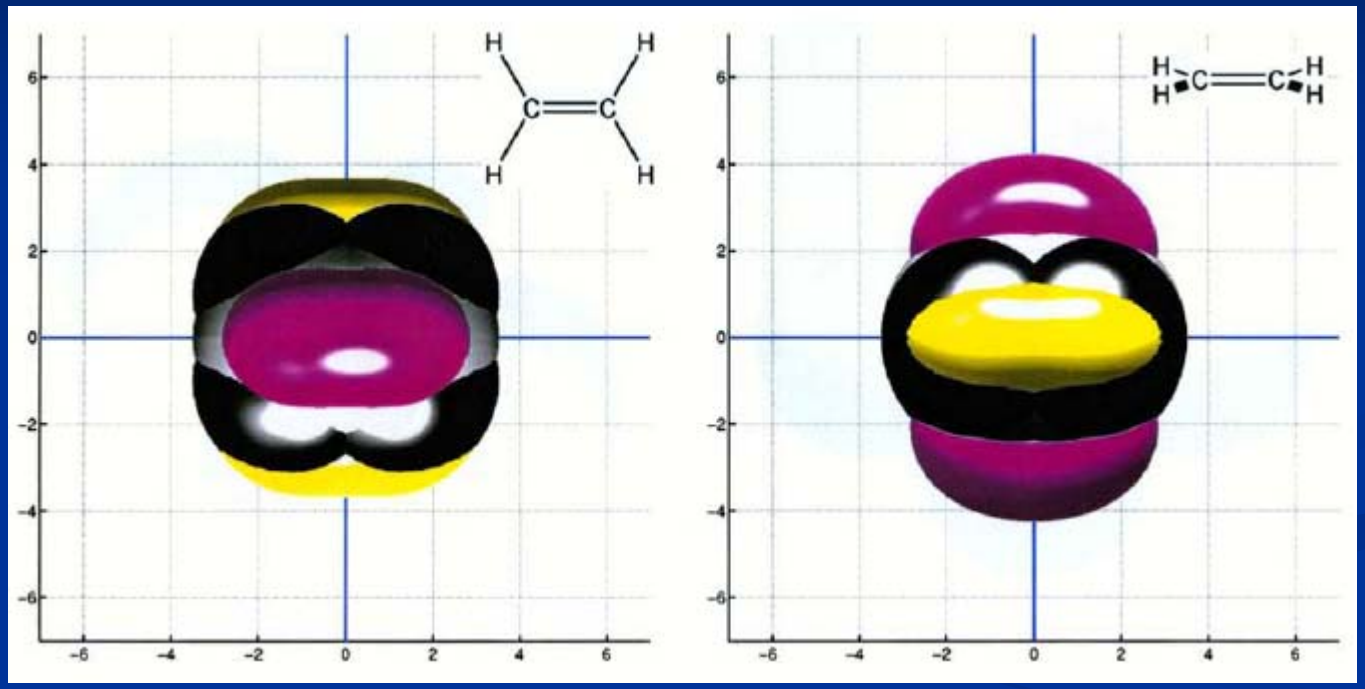
Magnetic Anisotropy of Ethylene



Ethylenic H



Magnetic Anisotropy of Ethylene



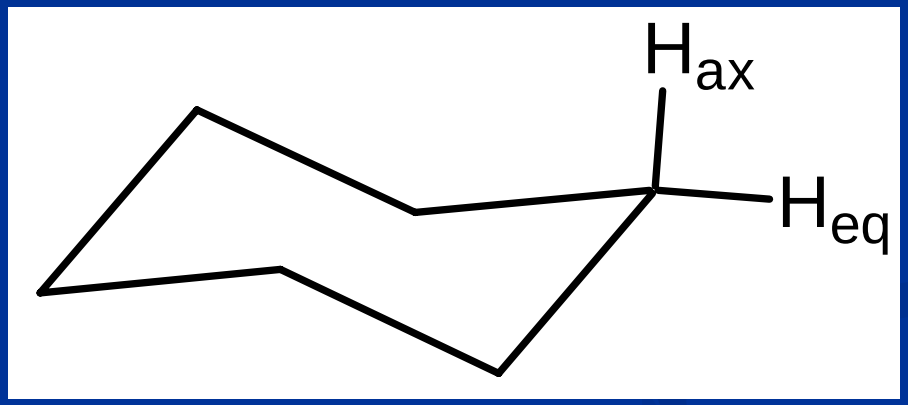
C = grey, H = black)

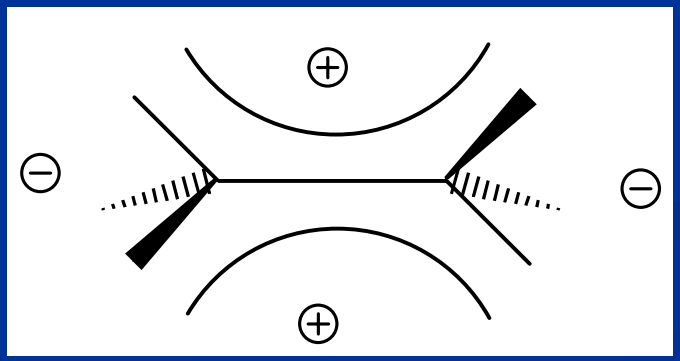
0.1 ppm deshielding isosurface = yellow

0.1 ppm shielding isosurface = magenta

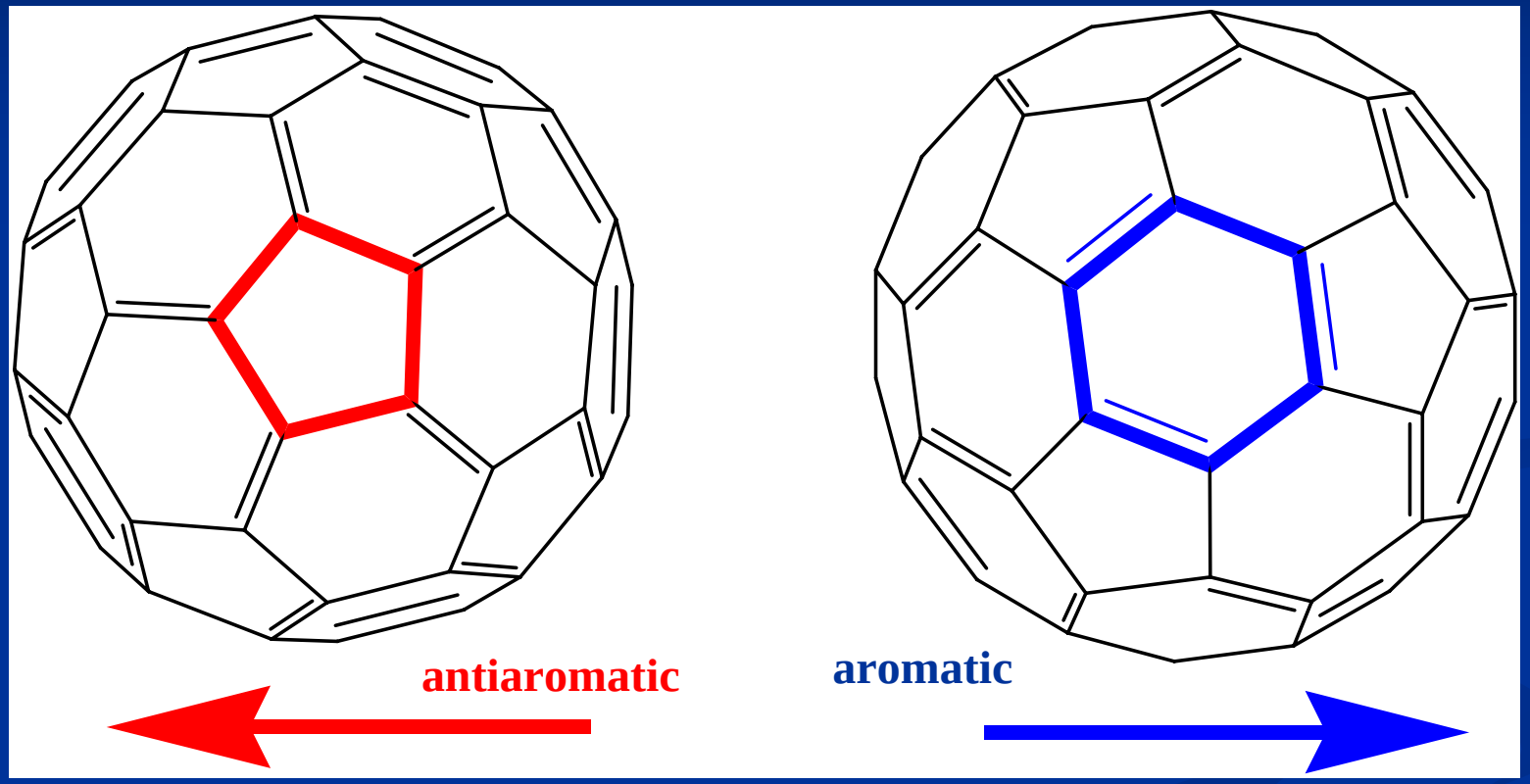
Magnetic Anisotropy

The equatorial protons are deshielded by 0.48 ppm wrt the axial





Magnetic Anisotropy of C_{60}



Paratropic ring current
+4.5 ppm

Diatropic ring current
–7.0 ppm

Magnetic Anisotropy

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

650 °C
3000 bar

^3He @ C_{60}

^3He @ C_{70}

δ (^3He) –6.3 ppm

δ (^3He) –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

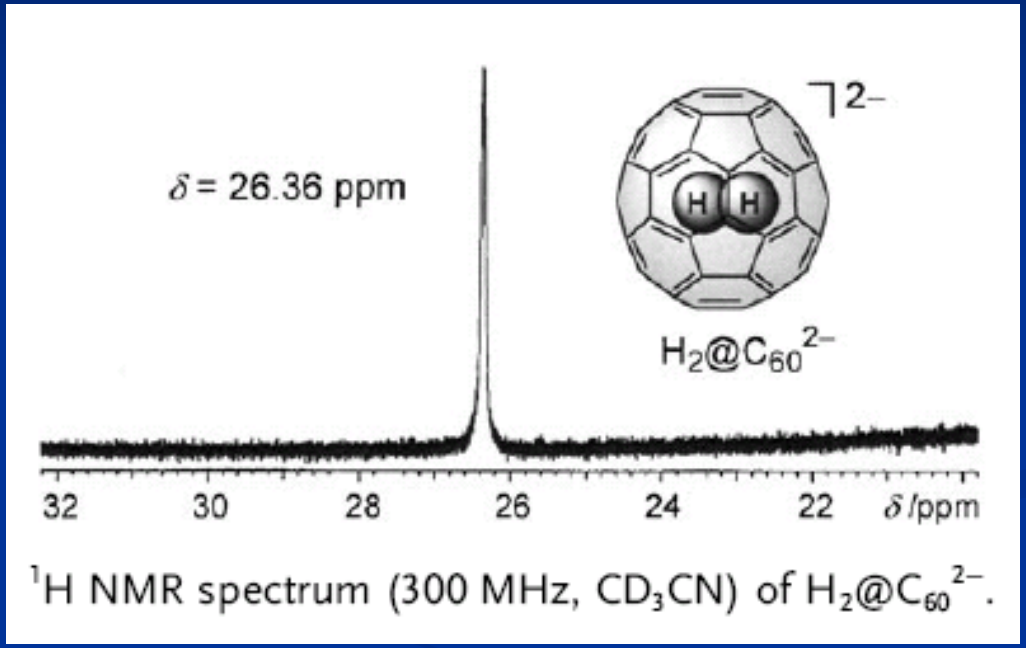
	Neutral[a]	Anion	Δ[d]
$He@C_{60}$	−6.40	−49.27 [b], (−49.17)[c]	−42.87
$He@C_{70}$	−28.82, (−28.81)	+8.20[b], (+8.04)[c]	+37.02
$He@C_{76}$	−18.75, (−18.61)	−20.62, (−20.55)	−1.87
$He@C_{78}$-C_{2v}	−16.91, (−16.79)	−10.02	+6.89
$He@C_{78}$-D_3	−11.94	−32.39, (−32.54)	−20.45
$He@C_{78}$-C'_{2v}	−17.60, (−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

^3He @ C_{70} ⟶ ^3He @ 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



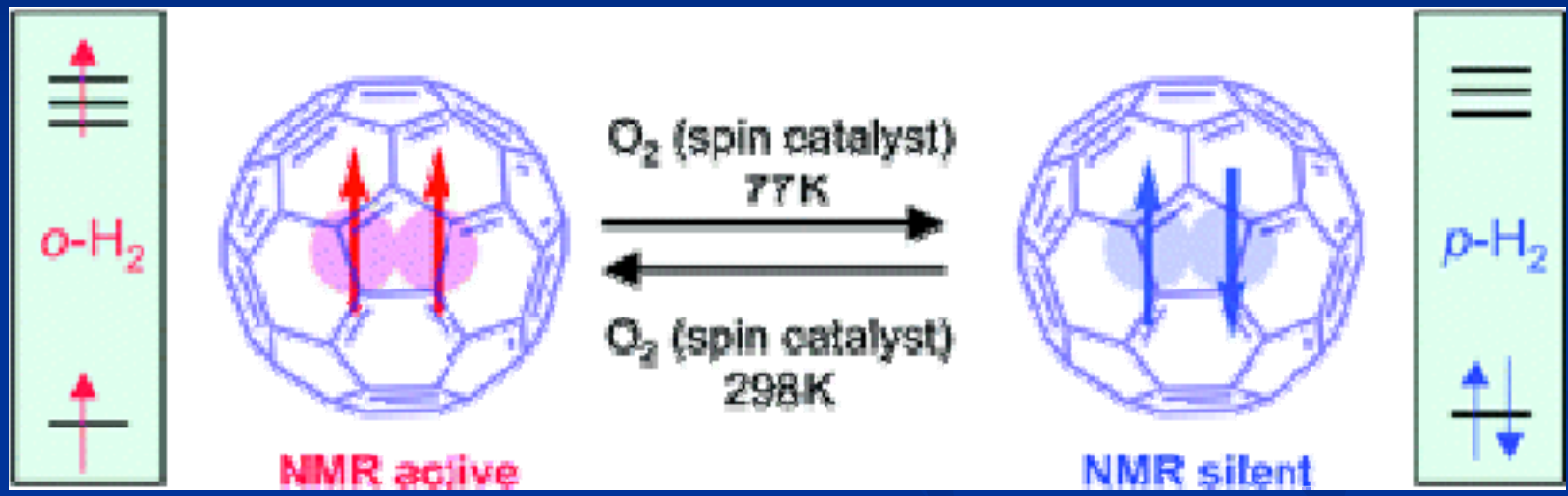
^{1}H NMR spectrum (300 MHz, CD_3CN) of $H_2@C_{60}^{2-}$.

^{1}H NMR spectra

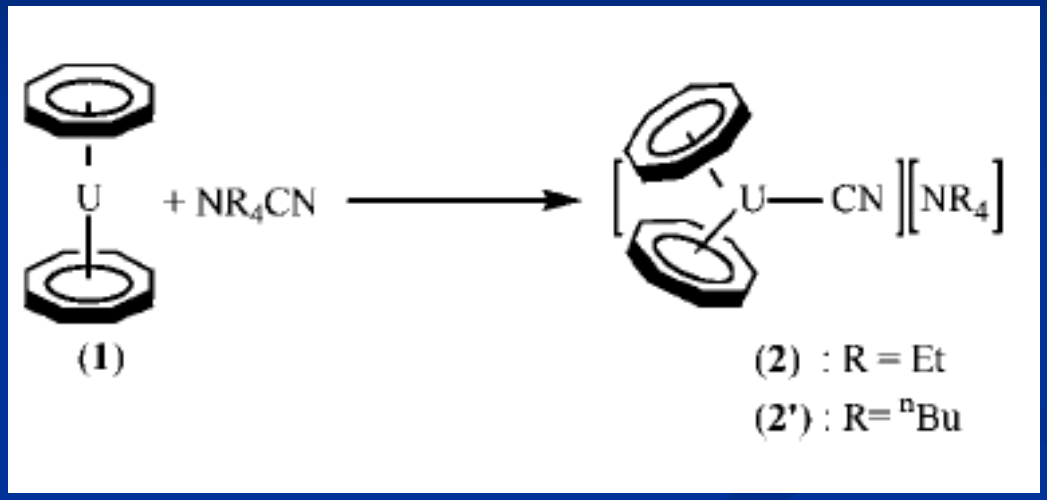
H_2 in liquids ~4 ppm

$H_2@C_{60}$ 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

Paramagnetic compounds

- Organic radicals, transition metal complexes
- Unpaired electron = large fluctuating magnetic field
- Chemical shift – ^{1}H NMR range 200 ppm
- Relaxation – unpaired electron reduces T_1 and T_2 = broad lines
- Coupling of nuclear and electron spins

Isotropic shift (diamagnetic vs. paramagnetic)

$$\Delta\nu_{iso} = \Delta\nu_{diamag} - \Delta\nu_{paramag}$$

Contact shift – delocalized e = through bond

Pseudocontact – dipolar = through space

$$\Delta\nu_{iso} = \Delta\nu_{cont} + \Delta\nu_{pseudocont}$$

Pseudocontact Shift

The anisotropic magnetic susceptibility affects the Larmor frequencies of nearby nuclei
the throughspace “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.

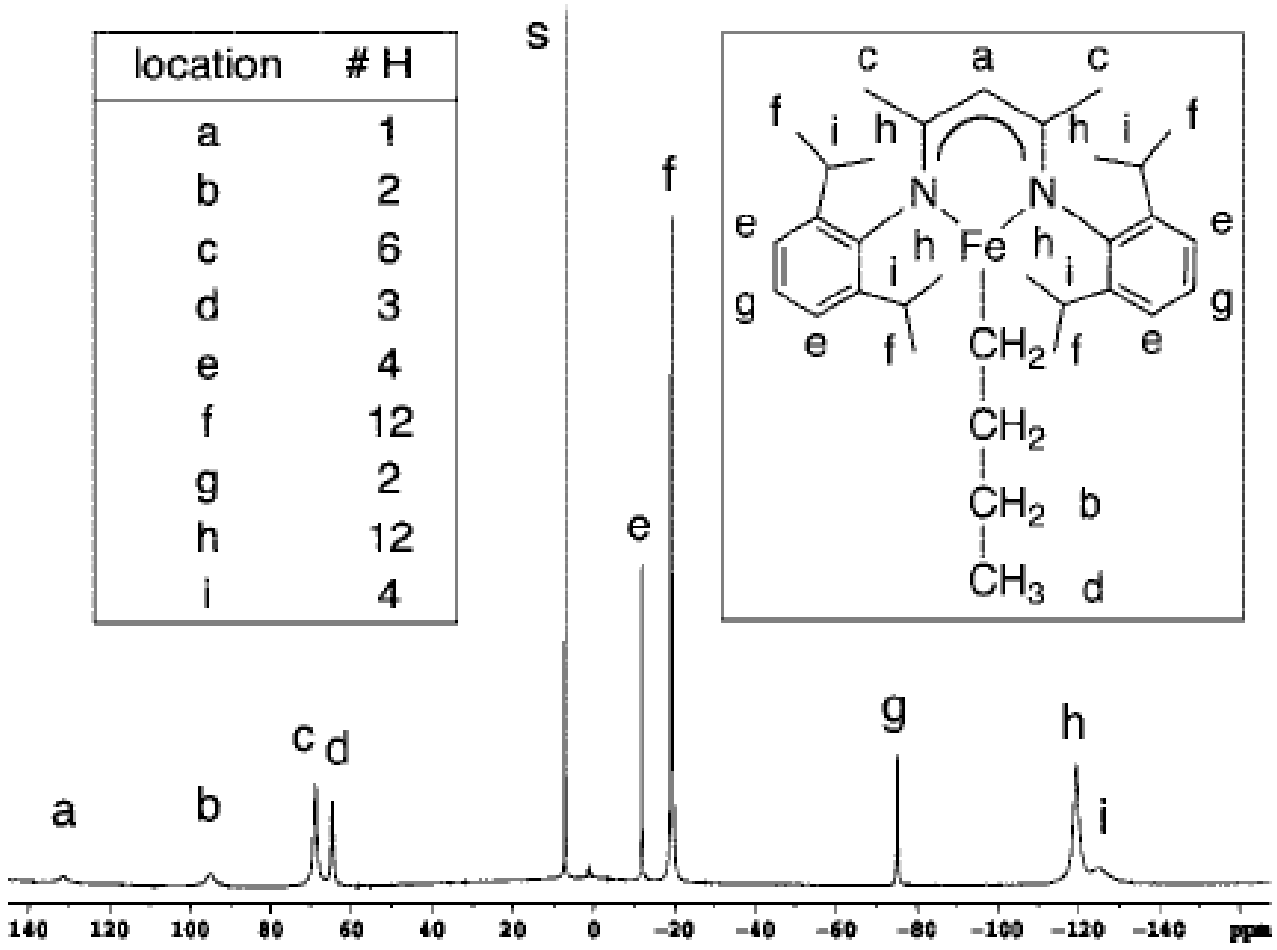
Pseudocontact Shift

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

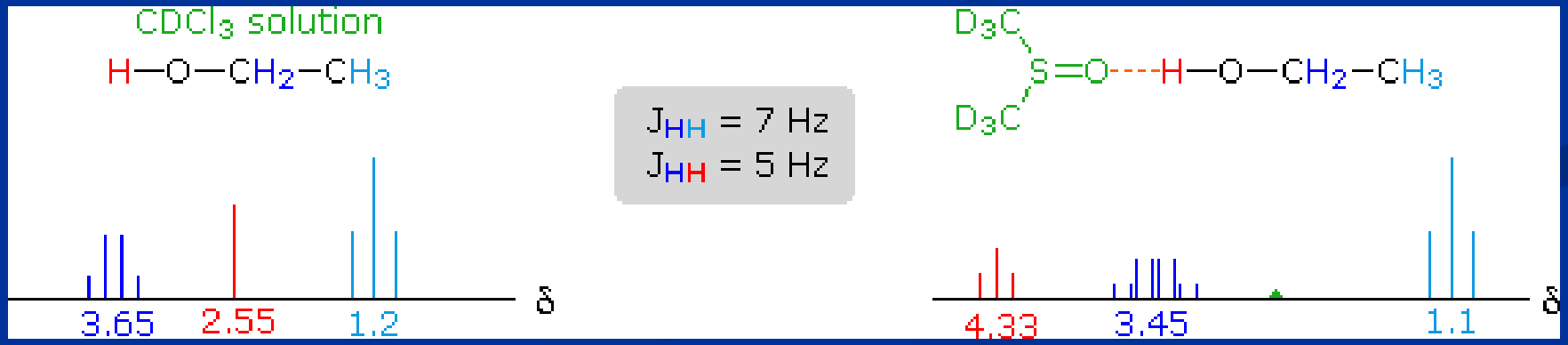
location	# H
a	1
b	2
c	6
d	3
e	4
f	12
g	2
h	12
i	4



Solvent Effects

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

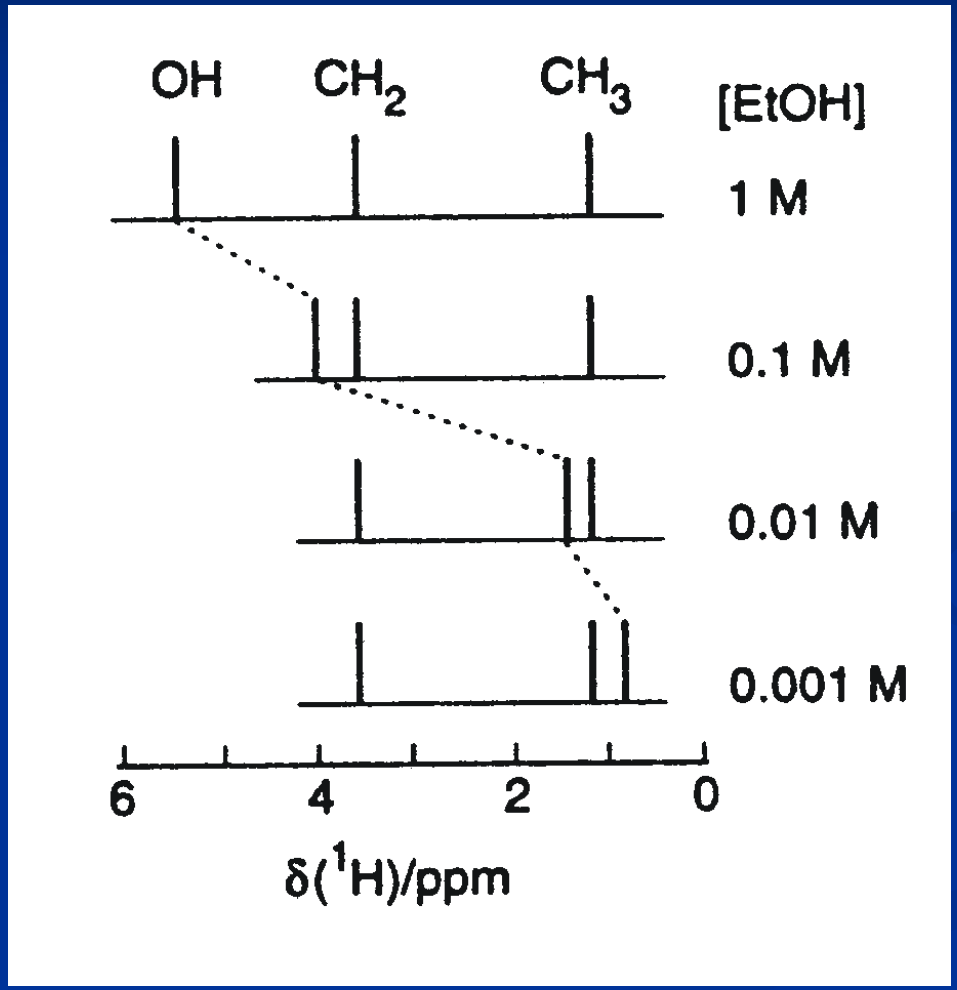
Van der Waals forces 0.1 – 0.2 ppm in ^{1}H NMR
Magnetic anisotropy of solvent – benzene, aromatics (solvent/solute orientation not averaged to zero)
Hydrogen bonding



^{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

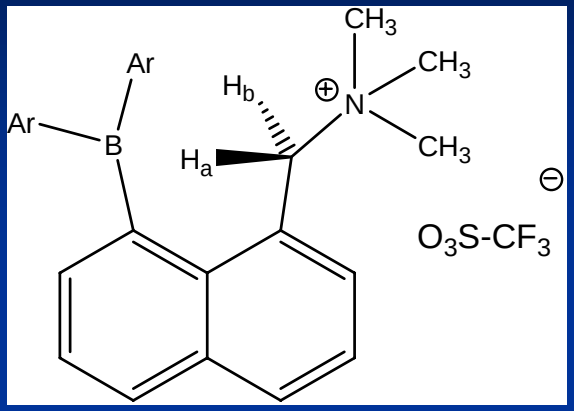
More extensive H-bonding

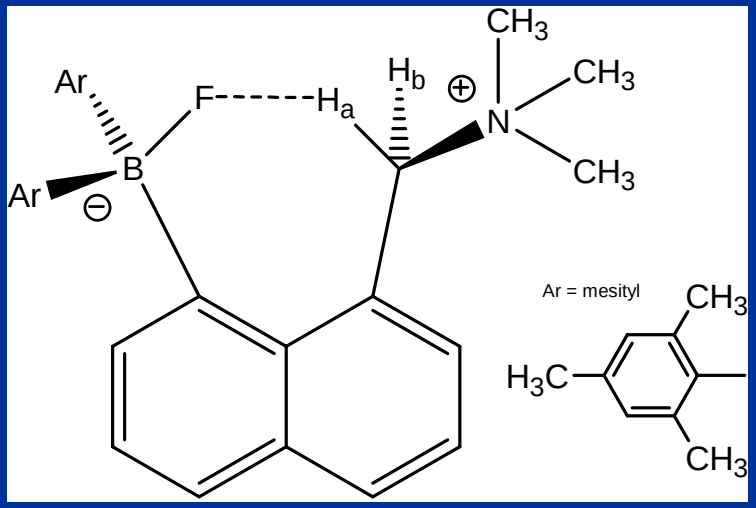
Deshielding of OH signal

Hydrogen Bonding

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

Hydrogen Bonding



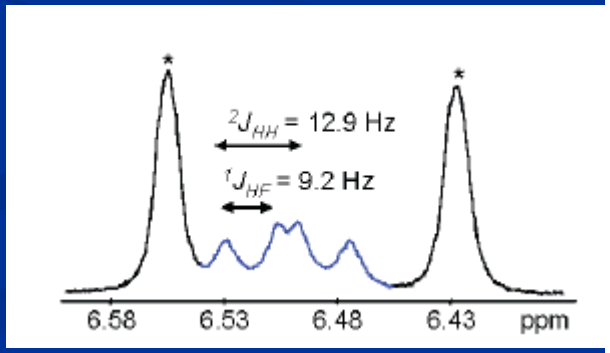


The methylene hydrogens are diastereotopic – steric congestion

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
$^1J_{H\text{-}F}$ = 9.2 Hz
$^2J_{H\text{-}H}$ = 12.9 Hz



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

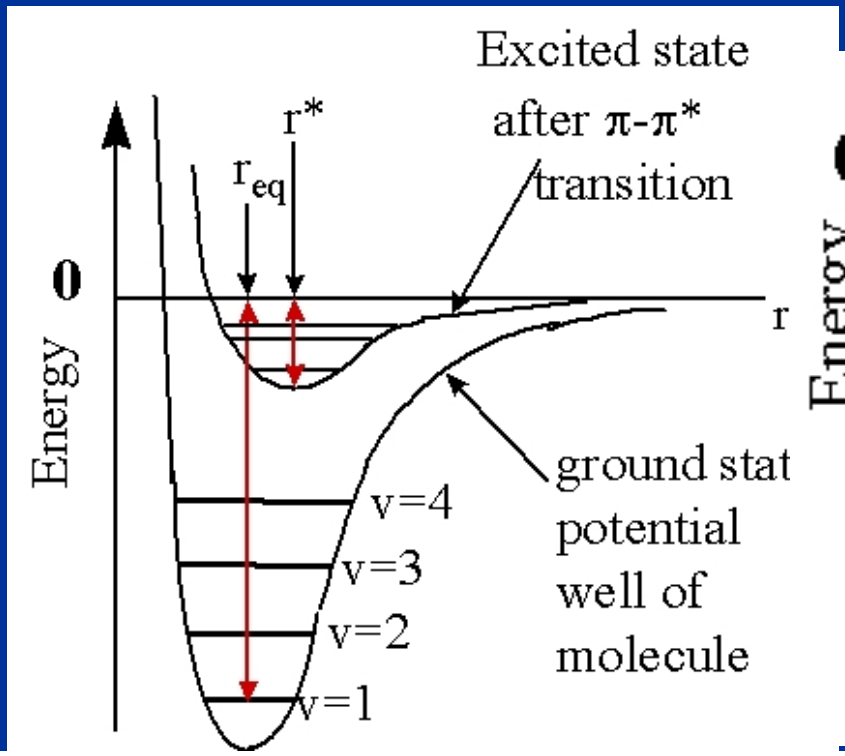
Temperature Effects

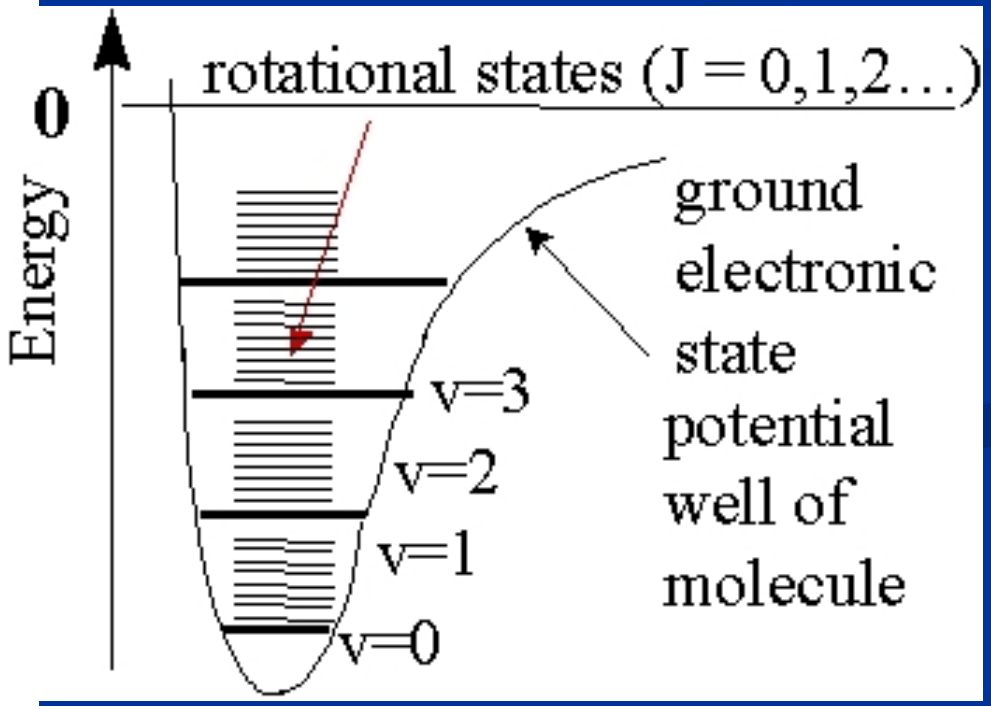
Anharmonic potential

Occupation of vibrational levels changes with temperature

Changes in effective distance between atoms

Chemical shift is a weighted average of the individual vibrational states





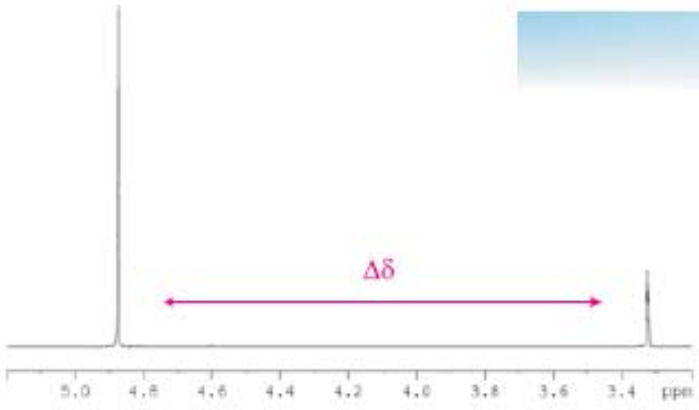
Temperature in NMR

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

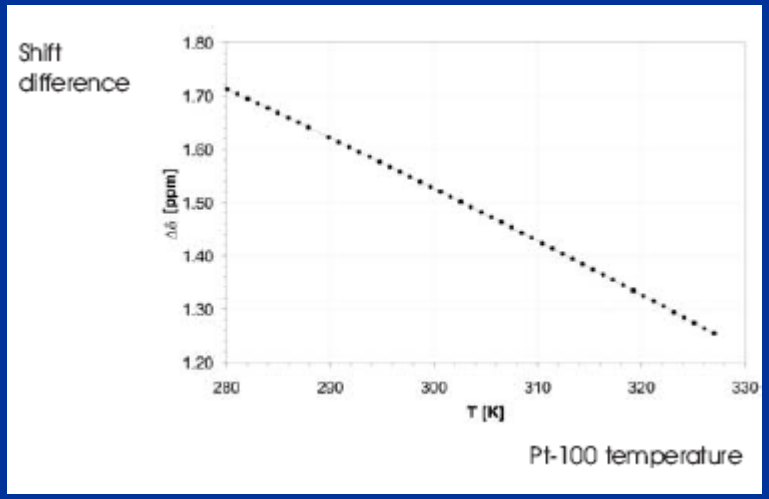
Methanol Thermometer



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

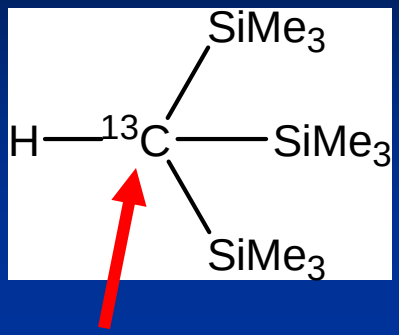
Wide range of temperatures

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