^{13}C NMR

Setup ^{13}C 1d NMR experiment : (See as well manual experiment setup)

- Load your sample

* Start by acquiring a ^{1}H spectrum (useful 1) to check your samples 2) to cross reference the spectrum)

- Command : **newnmr** (create a ^{1}H dataset)
- Command : **atma** (tuning) ; **rsh** (read standard shim file); **lock** (solvent); **topshim** (shim)
- Command : **zg** (start the experiment)

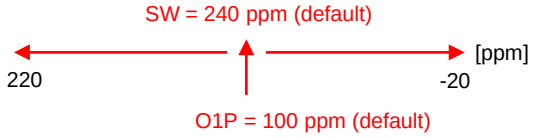
* Setup ^{13}C experiment

- Command : **edc** (create a new dataset); **rpar refe*** (read pre-set experiment) → choose **refe_13Ccpd** in user
- Command : **atma** (^{13}C tuning as it was not done before)
- Command : **zg** (start the experiment)

You can eventually change some parameters:

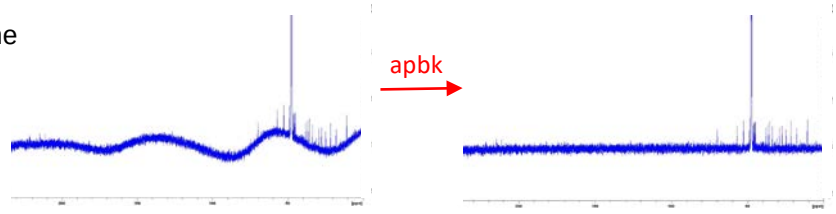
- **ns** : change number of scans.
  Rem : The signal to noise (SNR) accumulate proportionally to the square root of the number of scans (ns)
  Ex: if 1024 scans are needed to have a SNR of 5, 4096 scans will be needed to have a SNR of 10
  → Consider using cryoprobes if your SNR is still too small within a decent acquisition time

- **O1P** and **SW** : the centre and the width (in ppm) of the spectral window



Baseline correction : (using left shift and linear backward prediction)

In topspin 4: command **apbk** → correct the baseline



To open processed data in MestreNova:
- Do not drag and drop the entire exp
- Go in expname /expno/pdata/1/1r
  → drag and drop this file in MestreNova

Quantitative ^{13}C :

The **default** ^{13}C experiment is **NOT quantitative** (fast repetition time, NOE transfer)

It is possible to make ^{13}C quantitative for protonated carbons :
→ change pulse sequence to **zgig**, change **d1 for 60 s** (ask us if this sequence is needed)

If quantitative integration on quaternary carbons is needed
→ One can eventually add **relaxing agents** such as $Cr(acac)_3$ 0.1M or $MgCl_2$ 3M
→ change pulse sequence to **zgig**, change **d1 for 10 s** (ask us if this sequence is needed)

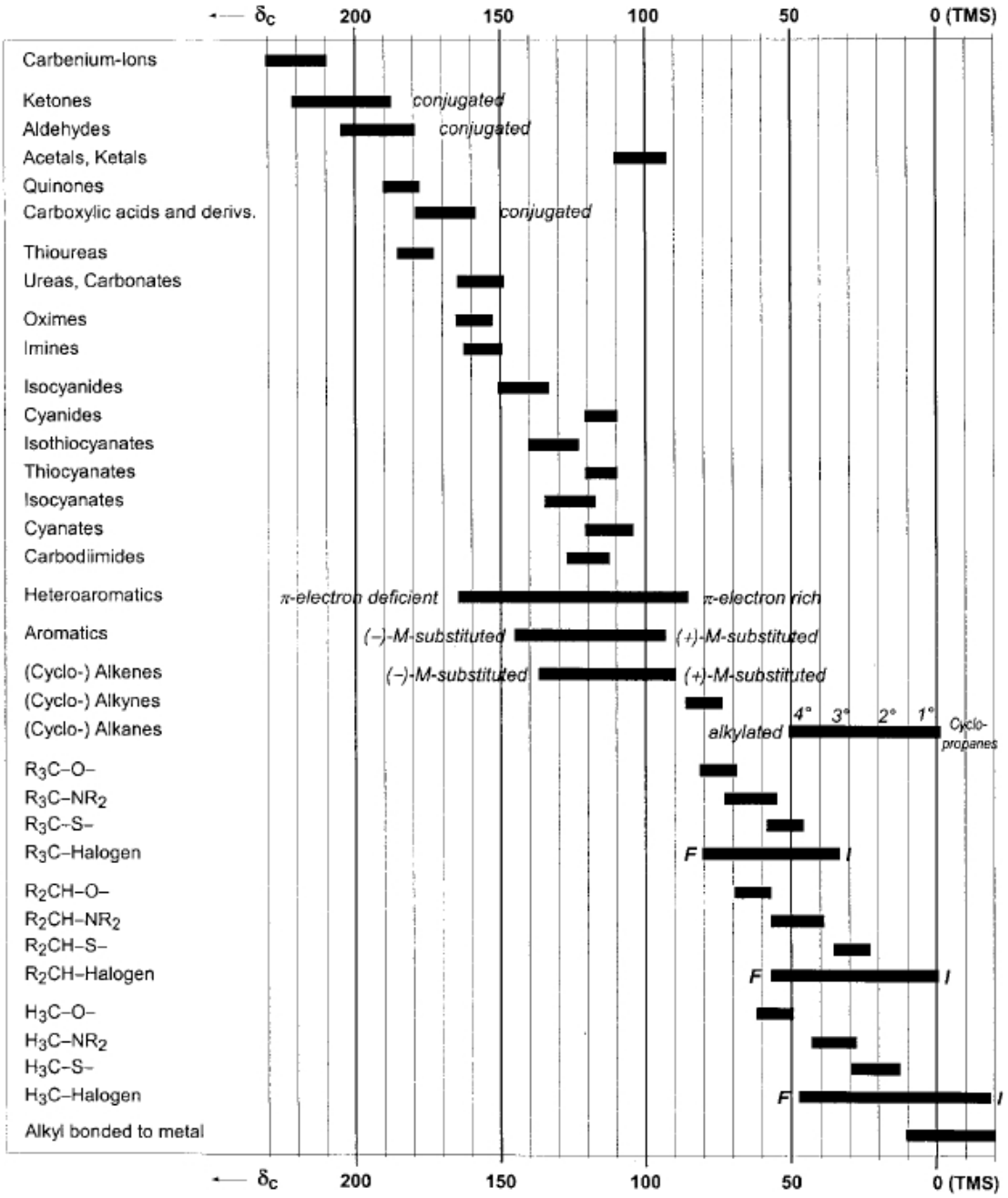
^{13}Cchemical shifts :

- See next table for general chemical shift
- See next tables for ^{13}C chemical shifts estimations

sources:
- Balci, M. (2005).
  13C Chemical Shifts of Organic Compounds. Basic 1H- and 13C-NMR Spectroscopy, 293–324.
  doi: http://dx.doi.org/10.1016/B978-044451811-8.50013-9
- Dr. Hans J. Reich. University of Wisconsin, Madison: page

^{13}C general chemical shifts table :

(source: …)



Estimating ^{13}C chemical shifts :

source: Balci, M. (2005).
13C Chemical Shifts of Organic Compounds. Basic 1H- and 13C-NMR Spectroscopy, 293–324.
doi: http://dx.doi.org/10.1016/B978-044451811-8.50013-9

A. Substituted Alkanes

^{13}C-NMR chemical shift values of some hydrocarbons

Compound	Chemical shifts of the carbon atoms				
	C_1	C_2	C_3	C_4	C_5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3			
n-Butane	13.4	25.2			
n-Pentane	13.9	22.8	34.7		
n-Hexane	14.1	23.1	32.2		
n-Heptane	14.1	23.2	32.6	29.7	
n-Octane	14.2	23.2	32.6	29.9	
n-Nonane	14.2	23.3	32.6	30.0	30.3
n-Decane	14.2	23.2	32.6	31.1	30.5
i-Butane	24.5	25.4			
2-Methylbutane	22.2	31.1	32.0	11.7	
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2-Methylpentane	22.7	28.0	42.0	20.9	14.3
3-Methylpentane	11.5	29.5	36.9	18.8 (C_6)	
3,3-Dimethylpentane	7.7	33.4	32.2	25.6 (C_6)	

Shift parameters of the substituents [87]

Substituent	Position of the substituent			
	α	β	γ	δ
–F	70.0	7.8	−6.8	0.0
–Cl	31.0	10.0	−5.1	−0.5
–Br	18.9	11.0	−3.8	−0.7
–I	−7.2	10.9	−1.5	0.9
–OH	49.0	10.1	−6.2	0.0
–OR	58.0	7.2	−5.8	0.0
–OCOR	54.0	6.5	−6.0	0.0
–COOH	20.1	2.0	−2.8	0.0
–COOR	22.6	2.0	−2.8	0.0
–COCl	33.1	2.3	−3.6	0.0
–CN	3.1	2.4	−3.3	−0.5
–CHO	29.9	−0.6	−2.7	0.0
–COR	22.5	3.0	−3.0	0.0
–CH=CHR	20.0	6.9	−2.1	0.4
–C≡C–	4.4	5.6	−3.4	−0.6
–Ph	22.1	9.3	−2.6	0.3
$–NH_2$	28.3	11.2	−5.1	0.1
$–NO_2$	61.6	3.1	−4.6	−1.0
–SH	10.6	11.4	−3.6	−0.4
$–SCH_3$	20.4	6.2	−2.7	0.0

Example:

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—OH$

	8	7	6	5	4	3	2	1
Octane	13.9	22.9	32.2	29.5	29.5	32.2	22.9	13.9
Subst. Effect	–	–	–	–	0.0	−6.2	10.1	49.0
Calculated	13.9	22.9	32.2	29.5	29.5	26.0	33.0	62.9
Experimental	13.9	22.8	32.1	29.6	29.7	26.1	32.9	61.9

B. Substituted Cycloalkanes

^{13}C-NMR chemical shifts of some cycloalkanes

Number of the ring carbon atoms *n*	δ
3	−3.8
4	22.10
5	26.30
6	27.60
7	28.20
8	26.60
9	25.80
10	25.00
11	25.40
12	23.20
13	25.20
14	24.60
15	26.60
16	26.50
17	26.70
18	27.50

Shift parameters of the substituents attached to cyclohexane ring

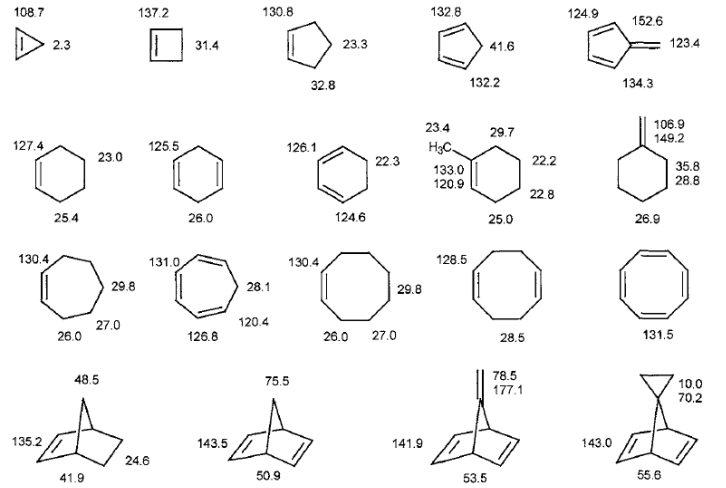
Substituent 	Shift parameters (cyclohexane δ_C = 27.6 ppm)			
	C_1	$C_{2,6}$	$C_{3,5}$	C_4
–F	62.9	5.5	−4.1	−1.6
–Cl	32.2	9.6	−2.4	−2.0
–Br	25.0	10.3	−1.5	−2.0
–I	4.2	12.2	−0.2	−2.1
–OH	42.4	8.4	−2.6	−1.2
$–OCH_3$	51.0	4.7	−3.3	−0.9
$–OCOCH_3$	44.7	4.6	−3.2	−1.5
–COOH	16.1	2.0	−1.4	−1.0
–CHO	19.6	−1.0	−2.4	−1.4
$–COCH_3$	15.8	2.0	−1.6	−1.2
–COCl	27.8	2.1	−2.1	−1.7
–CN	0.7	2.5	−3.0	−1.8
$–NH_2$	23.5	10.1	−1.8	−1.1
$–NH_3^+$	23.9	5.8	−2.0	−1.6
$–NO_2$	57.0	3.8	−2.9	−2.1
–SH	10.9	10.9	−0.8	−1.7
–Ph	17.5	7.3	−0.2	−0.9
$–CH_3$	5.8	8.4	−0.5	−0.6
$–C_2H_5$	12.6	6.1	−0.5	−0.2
$–C_4H_9$	10.8	6.5	−0.5	−0.3
$–C(CH_3)_3$	21.2	0.5	0.1	−0.5

C. Substituted Alkenes

^{13}C-NMR chemical shift in some selected alkenes

Compounds	Chemical shifts (ppm)					
	C_1	C_2	C_3	C_4	C_5	C_6
Ethene	123.5					
Propene	115.9	133.4	19.4			
1-Butene	113.5	140.5	27.4	13.4		
1-Pentene	114.5	139.0	36.2	22.4	13.6	
1-Hexene	114.2	139.2	33.8	31.5	22.5	14.0
cis-2-Butene	11.4	124.2				
trans-2-Butene	16.8	125.4				
trans-2-Pentene	17.3	123.5	133.2	25.8	13.6	
cis-3-Hexene	14.1	25.9	131.2			
1,3-Butadiene	116.6	137.2				
2,4-Hexadiene	12.9	124.9	125.3			
2,3-Dimethyl-1,3-butadiene	113.0	143.8				

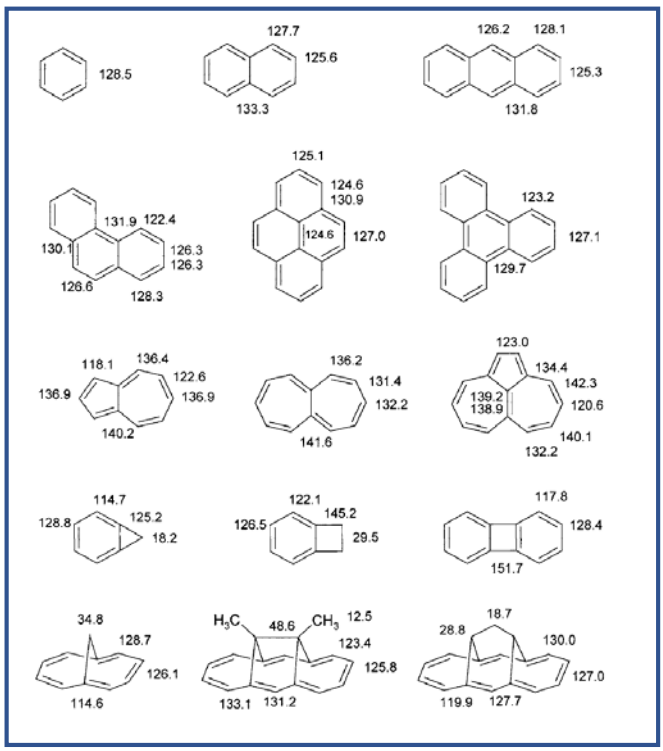
^{13}C-NMR chemical shift in some selected cyclic alkenes



Shift parameters in substituted alkenes

Substituent	Shift parameters Z_i	
$X-\overset{1}{C}H=\overset{2}{C}H_2$	C_1	C_2
$-H$	0.0	0.0
$-CH_3$	10.6	−8.0
$-C_2H_5$	15.5	−9.7
$-CH_2-CH_2-CH_3$	14.0	−8.2
$-CH(CH_3)_2$	20.3	−11.5
$-C(CH_3)_3$	25.3	−13.3
$-CH=CH_2$	13.6	−7.0
$-Ph$	12.5	−11.0
$-CH_2OR$	13.0	−8.6
$-CHO$	13.1	12.7
$-COCH_3$	15.0	5.9
$-COOH$	4.2	8.9
$-COOR$	6.0	7.0
$-CN$	−15.1	14.2
$-OR$	28.8	−39.5
$-OCOR$	18.0	−27.0
$-NR_2$	16.0	−29.0
$-NO_2$	22.3	−0.9
$-F$	24.9	−34.3
$-Cl$	2.6	−6.1
$-Br$	−7.9	−1.4
$-I$	−38.1	7.0

D. Substituted Aromatics



Shift parameters in substituted benzenes [87]

X =	Shift parameters (ppm)			
	ipso	*ortho*	*meta*	*para*
$-H$	0.0	0.0	0.0	0.0
$-CH_3$	9.3	−0.1	0.7	−3.0
$-CH(CH_3)_2$	20.3	−0.2	−0.1	−2.6
$-CH=CH_2$	9.1	−2.4	−0.2	−0.9
$-C\equiv CH$	−5.8	3.9	0.1	0.4
$-Ph$	13.0	−1.1	0.5	−1.0
$-F$	35.0	−14.4	0.9	−4.4
$-Cl$	6.4	0.2	1.0	−2.0
$-Br$	−5.9	3.0	1.5	−1.5
$-I$	−32.3	9.9	2.6	−0.4
$-OH$	26.6	−12.8	1.6	−7.1
$-OCH_3$	31.4	−14.4	1.0	−7.8
$-OCOCH_3$	23.0	−6.4	1.3	−2.3
$-SH$	2.0	0.6	0.2	−3.3
$-NH_2$	20.0	−14.1	0.6	−9.6
$-N(CH_3)_2$	22.2	−15.8	0.5	−11.8
$-NO_2$	20.6	−4.3	1.3	6.2
$-COCl$	4.8	2.9	0.6	6.9
$-COOH$	2.9	1.3	0.4	4.6
$-COOCH_3$	2.1	1.2	0.0	4.4
$-CHO$	8.2	0.5	0.5	5.8
$-COCH_3$	8.9	−0.1	−0.1	4.5
$-CN$	−15.5	1.4	1.4	5.0