

[175]

Seat No. _____

No. of printed pages: 04+07

SARDAR PATEL UNIVERSITY

M. Sc. SEMESTER – III (Organic Chemistry) Examination

Monday, 18th November 2019

Time: 02.00 p.m. to 05.00 p.m.

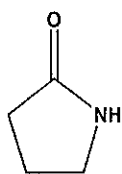
PS03CORC21: Organic Spectroscopy

Total Marks: 70

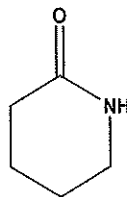
Q. 1 Select the correct answer from the alternatives given below to the each question [08]

- [1] $n \rightarrow \sigma^*$ transition will be present in which of the following compound(s) _____
 [a] Cyclohexane [b] Ethylamine [c] Acetone [d] Both b & c

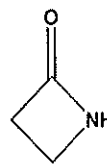
- [2] Decreasing " $>C=O$ " stretching frequency order for the following compounds is



(I)



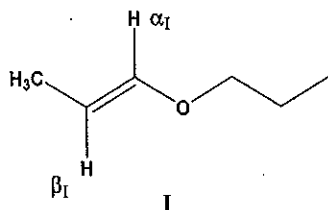
(II)



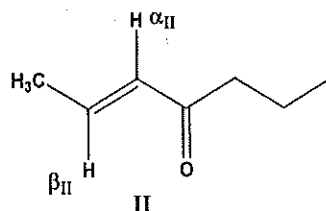
(III)

- [a] I > II > III [b] II > I > III [c] III > II > I [d] III > I > II

- [3] For vinyl ether (I) and α, β -unsaturated ketone (II), which is true for β_I and β_{II} protons?



I



II

- [a] β_I is shielded compared to α_I , while β_{II} is deshielded compared to α_{II}
 [b] β_I is shielded compared to α_I , and β_{II} is also shielded compared to α_{II}
 [c] β_I is deshielded compared to α_I , and β_{II} is also deshielded compared to α_{II}
 [d] β_I is deshielded compared to α_I , while β_{II} is shielded compared to α_{II}

- [4] Pople notation for the protons present in o-dichlorobenzene is _____
 [a] A_2B_2 [b] $AA'XX'$ [c] A_2X_2 [d] $AA'BB'$

- [5] Full form of HOHAHA is _____
 [a] Homonuclear Hannmann Hart [b] Homonuclear Hartmann Hann
 [c] Homonuclear Halo Hart [d] Heteronuclear Hartmann Hann

- [6] Which is correct statement?
 [a] Length of FID is more than sharp signal
 [b] FID is a frequency domain spectrum
 [c] Length of FID is short than broad signal
 [d] Both a & c

①

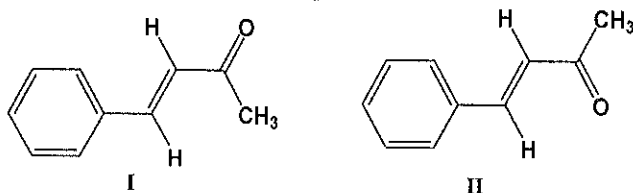
(PTO)

- [7] Which of the following isomer(s) will show McLafferty rearrangement in the mass spectra?
 I. 2-Methyl Butanal, II. 3-Pentanone, III. 2-Pentanone, IV. Pentanal
 [a] I and II [b] I, III and IV [c] I, II and III [d] All
- [8] If an organic compound contain two Cl atoms in its molecular formula than what will be relative abundance of $M : M+2 : M+4$ will be
 [a] 6 : 3 : 1 [b] 1 : 2 : 1 [c] 9 : 6 : 1 [d] 3 : 4 : 1

Q.2 Answer the following questions (ANY SEVEN)

[14]

- [1] Define : (i) Chromophore (ii) Bathochromic shift
 [2] Among *s-trans* (I) and *s-cis* (II) isomers of benzalacetone which one have higher $>C=O$ stretching frequency? Explain.

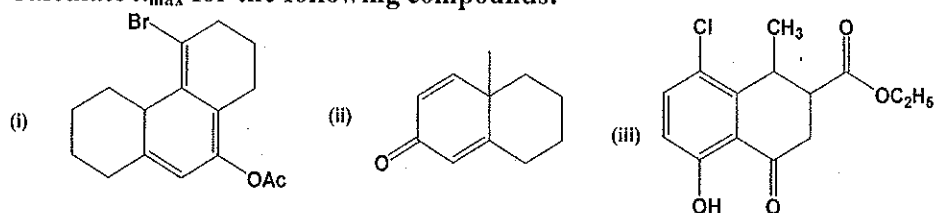


- [3] Discuss various stretching vibrations.
 [4] How to differentiate α -D-glucose and β -D-glucose by 1H NMR?
 [5] Sketch the 1H NMR spectrum of ethylacetate by taking approximate δ value for each signal and showing appropriate multiplicity.
 [6] Predict multiplicity of signals for (i) fluoro acetone in ^{19}F NMR and (ii) tetramethylsilane in ^{29}Si NMR.
 [7] How will you differentiate following pairs of isomers by ^{13}C NMR?
 (i) Catechol and Resorcinol
 (ii) Anthracene and Phenanthrene
 [8] Discuss about metastable ion peaks.
 [9] What is nitrogen rule? Which of the following compounds will follow it?
 (i) C_3H_9N (ii) C_9H_7N (iii) $C_5H_{11}N_2$

Q.3

- [a] Calculate λ_{max} for the following compounds:

[06]



- [b] Answer the following questions.

- [1] Discuss IR spectra of alcohols and phenols in details. [03]
 [2] Discuss the effect of conjugation and electronegativity of the substituent on the $>C=O$ stretching. [03]

OR

(2)

[b] Answer the following questions.

- [1] Write a note on effect of conjugation on λ_{\max} and ϵ_{\max} in UV-Visible spectra. [03]
- [2] How will you distinguish following pairs of compounds by IR? [03]
- Ethylamine and Triethylamine
 - Butanoic acid and Butanal
 - Propyne and Cyanomethane

Q. 4

[a] Answer the following questions.

- [1] What is popple notation? Give popple notation to the vinylic protons of styrene. Draw detailed PMR spectrum for the same. [03]
- [2] Define coupling constant. Discuss long range and vicinal coupling constants in detail. [03]

[b] Answer the following questions.

- [1] Define first order and second order ^1H NMR spectra? Discuss use of shift reagents in simplification of complex ^1H NMR spectra. [03]
- [2] Enlist the solvents used in NMR spectroscopy. What are the characteristics which NMR solvents must have? Discuss the effect of solvent on chemical shift. [03]

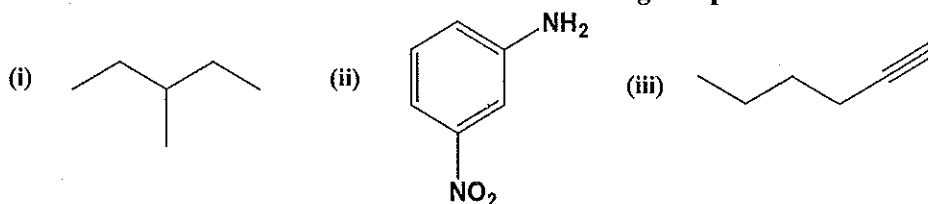
OR

[b] Answer the following questions.

- [1] Predict the number of PMR signals for the following compounds: [03]
- 2-Bromobutane
 - Ethylmethylether
 - Methyl cyclopropane
 - Propene
 - m-Xylene
 - 3-Hydroxy butanoic acid
- [2] Write note on "chemical equivalence by rapid rotation". [03]

Q. 5

[a] Calculate ^{13}C NMR chemical shift for the following compounds. [06]



[b] Answer the following questions.

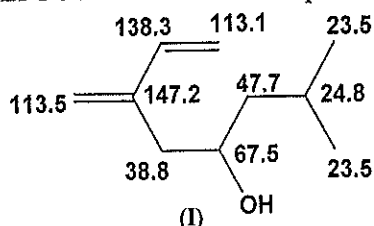
- [1] Draw DQF-COSY and HETCOR spectra for $\text{CH}_3\text{CH}_2\text{CHO}$ by taking approximate chemical shift value for each signal. [03]
- [2] What are the difficulties in recording ^{13}C NMR? What are the solutions for these difficulties? [03]

OR

③

(P.T.O)

- [b] Answer the following questions.
 [1] Draw ^{13}C NMR, DEPT 90° and DEPT 135° spectra for Ipsenol (I). [03]



- [2] Enlist various types of HOMCOR and HETCOR spectroscopy. What information each of them do provide? [03]

Q. 6

- [a] Answer the following questions.
 [1] Write note on mass spectra of:
 (i) Aromatic hydrocarbons (ii) Alkyl aryl hydrocarbons. [03]
 [2] Discuss following ionization techniques in mass spectrometry. [03]
 (i) CI (ii) ESI
- [b] Answer the following questions.
 [1] Write fragmentation pattern for following compounds. [03]
 (i) 2-Hexene (ii) 3,3-Dimethyl-2-butanamine (iii) 1-Pentanol
 [2] Discuss the general rules for predicting prominent peaks in EI-mass spectrometry. [03]

OR

- [b] Spectral data for the compound with molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$ is given below. Interpret the data and assign the structure for the compound. [06]

IR: 3028, 2940, 2824, 1724, 1603, 1500, 1375, 1210, 1100, 840 cm^{-1} .

^1H NMR			^{13}C NMR	
Signal (δ)	Multiplicity	Protons	^{13}C (δ)	DEPT 135°
3.66	Doublet ($J=7.2$ Hz)	2H	50.5	-Ve
3.81	Singlet	3H	55.8	+Ve
6.72	Doublet	2H	114.8	+Ve
7.14	Doublet	2H	124.2	-
9.72	Triplet ($J=7.2$ Hz)	1H	130.6	+Ve
			159.5	-
			200	+Ve

Mass (m/z): 150 (M^+), 149, 121, 119, 107, 90, 43.

- x -
 (4)

Table 3.16 Influence of functional group X on the chemical shift positions (δ) nearby carbons in alkene groups and benzene rings

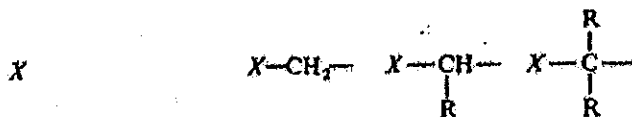
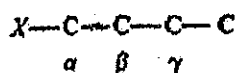
Base values: ethylene (δ 123) and benzene (δ 128)

Alkenes

Benzenes

	Alkenes		Benzenes			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
-CH ₃	10	-8	9	0	0	-2
R,	16	-8	15	0	0	-2
R,	23	-8	21	0	0	-2
-CH=CH ₂	15	-6	9	0	0	-2
-CH≡CH	-	-	-6	4	0	0
-C ₆ H ₅ , -Ar	13	-11	13	-1	1	-1
-F	25	-34	35	-14	1	-5
-Cl	3	-6	6	0	1	-2
-Br	-8	-1	-5	3	2	-2
-I	-38	7	-32	10	3	-1
-NH ₂	-	-	18	-13	1	-10
-NHR	-	-	20	-14	1	-10
-NR ₂	-	-	22	-16	1	-10
-NO ₂	22	-1	20	-5	1	6
-NHCOR, -NRCOR	-	-	10	-7	1	-4
-CN	-15	15	-16	4	1	6
-SH	-	-	4	1	1	-3
-OH	-	-	27	-13	1	-7
-OR	29	-39	30	-15	1	-8
-OCOR	18	-27	23	-6	1	-2
-COOH, -COOR, -CON<	4	9	2	2	0	5
-COR, -CHO	14	13	9	1	1	6
-SO ₂ H, -SO ₂ N<	-	-	16	0	0	4
-PMe ₂	-	-	14	1.6	0	-1
-PAr ₂	-	-	9	5	0	0

Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chain



1° or 2° or 3°

X	1°	or	2°	or	3°	β -shift	γ -shift
-CH ₃	9		6		3	9	-3
-R: see table 3.11							
axial-CH ₃	1		-		-	5	-6
equatorial-CH ₃	6		-		-	9	0
(in cyclohexanes)							
-CH=CH ₂	22		16		12	7	-2
-C≡CH	4		-		-	3	-3
-C ₆ H ₅ , -Ar	23		17		11	10	-3
-F	70		-		-	8	-7
-Cl	31		35		42	10	-5
-Br	19		28		37	11	-4
-I	-7 to 20		-		-	11	-2
-NH ₂ , -NHR, -NR ₂	29		24		18	11	-4
-NO ₂	62		-		-	3	-5
-NHCOR, -NRCOR	10		-		-	0	0
-NH ₃ ⁺	25		-		-	7	-3
-CN	3		4		-	2	-3
-SH	2		-		-	2	-2
-OH	50		45		40	9	-3
-OR	50		24		17	10	-6
-OCOR	52		50		45	7	-6
-COOH, -COOR, -CON<	20		16		13	2	-3
-COR, -CHO	30		24		17	2	-3
-SO ₃ H, -SO ₂ N<	50		-		-	3	0

TABLE 4.12 Incremental Shifts for the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from benzene at 128.5 ppm), ^{13}C Chemical Shifts of Substituents in ppm from TMS*

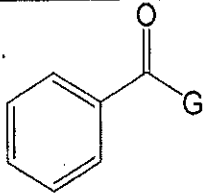
Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	9.3	0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	9.1	-2.4	0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C≡CH	-5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	12.1	-1.8	-0.1	-1.6	
CH ₂ OH	13.3	-0.8	-0.6	-0.4	64.5
CH ₃ O(C=O)CH ₃	7.7	~0.0	~0.0	~0.0	20.7 (CH ₃), 66.1 (CH ₂), 170.5 (C=O)
OH	26.6	-12.7	1.6	-7.3	
OCH ₃	31.4	-14.4	1.0	-7.7	54.1
OC ₆ H ₅	29.0	-9.4	1.6	-5.3	
O(C=O)CH ₃	22.4	-7.1	-0.4	-3.2	23.9 (CH ₃), 169.7 (C=O)
(C=O)H	8.2	1.2	0.6	5.8	192
(C=O)CH ₃	7.8	-0.4	-0.4	2.8	24.6 (CH ₃), 195.7 (C=O)
(C=O)C ₆ H ₅	9.1	1.5	-0.2	3.8	196.4 (C=O)
(C=O)F ₃	-5.6	1.8	0.7	6.7	
(C=O)OH	2.9	1.3	0.4	4.3	168
(C=O)OCH ₃	2.0	1.2	-0.1	4.8	51.0 (CH ₃), 166.8 (C=O)
(C=O)Cl	4.6	2.9	0.6	7.0	168.5
(C=O)NH ₂	5.0	-1.2	0.0	3.4	
C≡N	-16	3.6	0.6	4.3	119.5
NH ₂	19.2	-12.4	1.3	-9.5	
N(CH ₃) ₂	22.4	-15.7	0.8	-11.8	40.3
NH(C=O)CH ₃	11.1	-9.9	0.2	-5.6	
NO ₂	19.6	-5.3	0.9	6.0	
N=C=O	5.7	-3.6	1.2	-2.8	129.5
F	35.1	-14.3	0.9	-4.5	
Cl	6.4	-0.2	1.0	-2.0	
Br	-5.4	3.4	2.2	-1.0	
I	-32.2	9.9	2.6	-7.3	
CF ₃	2.6	-3.1	0.4	3.4	
SH	-2.3	0.6	0.2	-3.3	
SCH ₃	10.2	-1.8	0.4	-3.6	15.9
SO ₂ NH ₂	15.3	-2.9	0.4	3.3	
Si(CH ₃) ₃	13.4	4.4	-1.1	-1.1	

*See Ewing, D.E. (1979) *Org. Magn. Reson.* 12, 499, for 709 chemical shifts of monosubstituted benzenes.

— X —
7

Base value for homo-annular diene	253 nm
Base value for hetero-annular diene	214 nm
Increment for:	
Double bond extending conjugation	+30 nm
Alkyl substituent or ring residue	+5 nm
Exocyclic double bond	+5 nm
Polar groups (auxochrome):	
-OAc	+0 nm
-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
-NR ₂	+60 nm

Table 2. Characteristics absorptions for substituted benzene derivatives

	G	Base value
	Alkyl or ring residue (Ketone)	246 nm
	H (Aldehyde)	250 nm
	-OR / -OH (Ester/ Acid)	230 nm

Alkyl / ring residue	o, m	+ 3 nm
	p	+ 10 nm
-OCH ₃ / -OH / -OR	o, m	+ 7 nm
	p	+ 25 nm
-O ⁻ (Oxy anion)	o	+11 nm
	m	+20 nm
	p	+78 nm
-Cl	o, m	+ 0 nm
	p	+ 10 nm
-Br	o, m	+ 2 nm
	p	+ 15 nm
-NH ₂	o, m	+13 nm
	p	+58 nm
-NHCOCH ₃	o, m	+ 20 nm
	p	+ 45 nm
-NHCH ₃	o, m	+ 73 nm
-N(CH ₃) ₂	o, m	+ 20 nm
	p	+ 85 nm

①

(P.T.O)

Table 3. Characteristic absorption for α,β -unsaturated carbonyl compounds (enones)			
Base values:			
Acyclic α,β -unsaturated ketones	215 nm		
Six membered cyclic α,β -unsaturated ketones	215 nm		
Five membered cyclic α,β -unsaturated ketones	202 nm		
α,β -unsaturated aldehyde	210 nm		
α,β -unsaturated carboxylic acid/ester	195 nm		
Increment for:			
Double bond extending conjugation	+30 nm		
Homocyclic diene component	+39 nm		
Exocyclic double bond	+5 nm		
Alkyl substituent or ring residue			
	α	+10 nm	
	β	+12 nm	
	γ & higher	+18 nm	
Polar groups:			
	-OH	α	+35 nm
		β	+30 nm
		δ	+50 nm
	-OCOCH ₃	α, β, δ	+6 nm
	-OCH ₃	α	+35 nm
		β	+30 nm
		γ	+17 nm
		δ	+31 nm
	-SR	β	+85 nm
	-Cl	α	+15 nm
		β	+12 nm
	-Br	α	+25 nm
		β	+30 nm
	-NR ₂	β	+95 nm
Solvent correction:			
	Ethanol	+0 nm	
	Methanol	+0 nm	
	Chloroform	+1 nm	
	Ether	+7 nm	
	Water	-8 nm	
	Hexane	+11 nm	
	Cyclohexane	+11 nm	

(2)

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkanes	2850-2960
		1350-1470
C-H	Alkenes	3020-3080 (m)
		675-1000
C-H	Aromatic rings	3000-3100 (m)
		675-870
C-H	Alkynes	3300
C=C	Alkenes	1640-1680 (v)
C≡C	Alkynes	2100-2260 (v)
C=C	Aromatic rings	1500, 1600 (v)
C-O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O-H	Monomeric alcohols, phenols	3610-3640 (v)
	Hydrogen bonded alcohols, phenols	3200-3600 (broad)
	Carboxylic acids	2500-3000 (broad)
N-H	Amines	3300-3500 (m)
C-N	Amines	1180-1360
C≡N	Nitriles	2210-2260 (v)
-NO ₂	Nitro compounds	1515-1560
		1345-1385

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift, ppm
	δ
Cyclopropane	0.2
Primary	RCH ₃ 0.9
Secondary	R ₂ CH ₂ 1.3
Tertiary	R ₃ CH 1.5
Vinyllic	C=C-H 4.6-5.9
Acetylenic	C≡C-H 2-3
Aromatic	Ar-H 6-8.5
Benzylic	Ar-C-H 2.2-3
Allylic	C=C-CH ₃ 1.7
Fluorides	HC-F 4-4.5
Chlorides	HC-Cl 3-4
Bromides	HC-Br 2.5-4
Iodides	HC-I 2-4
Alcohols	HC-OH 3.4-4
Ethers	HC-OR 3.3-4
Esters	RCOO-CH 3.7-4.1
Esters	HC-COOR 2-2.2
Acids	HC-COOH 2-2.6
Carbonyl compounds	HC-C=O 2-2.7
Aldehydic	9-10
Hydroxylic	1-5.5
Phenolic	4-12
Enolic	C=C-OH 15-17
Carboxylic	RCOOH 10.5-12
Amino	RNH ₂ 1-5

(P.T.O.)

Table 5.1 The ¹³C Shift Parameters in Some Linear and Branched Hydrocarbons

¹³ C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
1° (3°) ^a	-1.1
1° (4°) ^b	-3.4
2° (3°) ^a	-2.5
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5

Table 5.2 The ¹³C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH ₃)	

Table 5.3 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal^a (+ left, - right)

Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+ 9	+ 6	+10	+ 8	-2
CH=CH ₂	+20		+ 6		-0.5
C≡CH	+ 4.5		+ 5.5		-3.5
COOH	+21	+16	+ 3	+ 2	-2
COO ⁻	+25	+20	+ 5	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH ₂	+22		+ 2.5		-0.5
COR	+30	+24	+ 1	+ 1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+ 9	+ 7	-2
OH	+48	+41	+10	+ 8	-5
OR	+58	+51	+ 8	+ 5	-4
OCOR	+51	+45	+ 6	+ 5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR ₂	+42		+ 6		-3
NR ₃	+31		+ 5		-7
NO ₂	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+ 7		-3
F	+68	+63	+ 9	+ 6	-4
Cl	+31	-32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	- 6	+ 4	+11	+12	-1

EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

$$\text{Chemical shift } (\delta) = 72 + \Sigma(\text{increments for carbon atoms})$$

	C	-	C	-	C	-	C	-	C	≡	C	-	C	-	C	-	C
	δ	γ	β	α		α'	β'	γ'	δ'								
increments	+0.5	0	+5	+7		-6	+2	-1	+0.5								

base value 72

(4)