

CHEMISTRY HONOURS EXAMINATION: JUNE 2018

MODULE: CEM 8X04- INSTRUMENTAL ANALYSIS



Examiners: Prof R. Meijboom, Dr E.M. Mmutlane and Dr N.S. Bingwa

Moderator: Dr R. Mampa (University of Limpopo)

INSTRUCTIONS

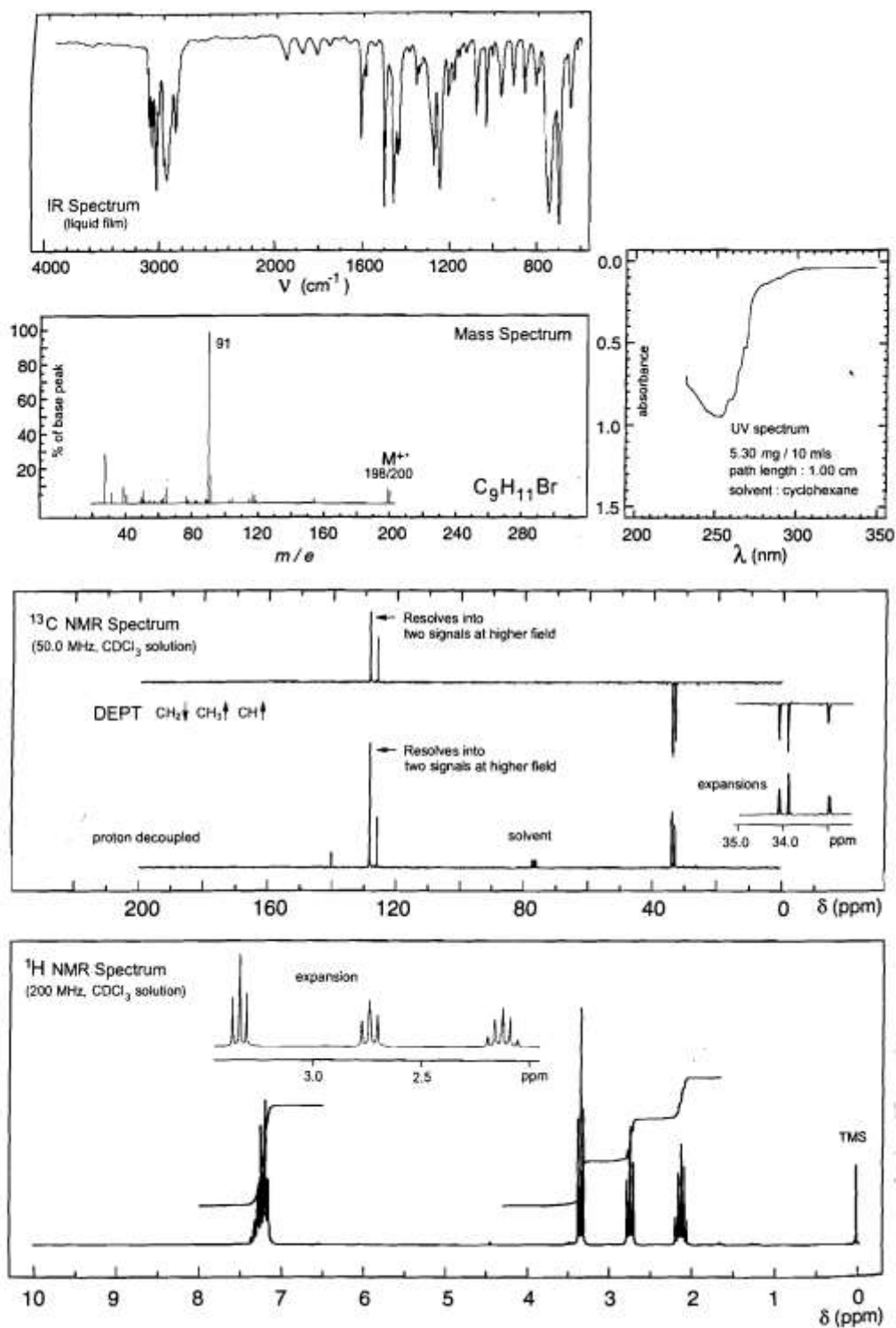
- (i) This examination is out of a Total of 100 Marks and you have 3 Hours (180 Minutes) to complete it. No extra time will be allowed for any reason.
- (ii) The Exam comprises 2 Sections. PLEASE ANSWER EACH SECTION IN A SEPARATE BOOK.
- (iii) The use of cell phones and other electronic communication devices is forbidden and they must be switched off. No data/image storing devices, including calculators capable of such, are permitted in this examination.
- (iv) This is a closed book examination. You are NOT allowed to have any book, memorandum, notes, paper, photographs, document or written/printed material other than the question paper and the answer books provided by the examiner/invigilator. If you need paper for rough work, an additional exam answer sheet will be given to you, which must be clearly labelled as rough work: not for marking, and handed in together with the question paper and all your answer books.

SECTION 1: NMR, IR, MS and UV-VIS SPECTROSCOPY

QUESTION 1

[38]

Consider the following spectra:



- a) Determine the degree of unsaturation (2)
- b) Identify the structural elements based on the Mass Spectrum. (4)
- c) Calculate the extinction coefficient (2)
- d) What structural elements does the UV-vis spectrum suggest? (2)
- e) Identify the structural elements based on the IR spectrum. (4)
- f) Estimate the integrals for each proton and tabulate them (4)

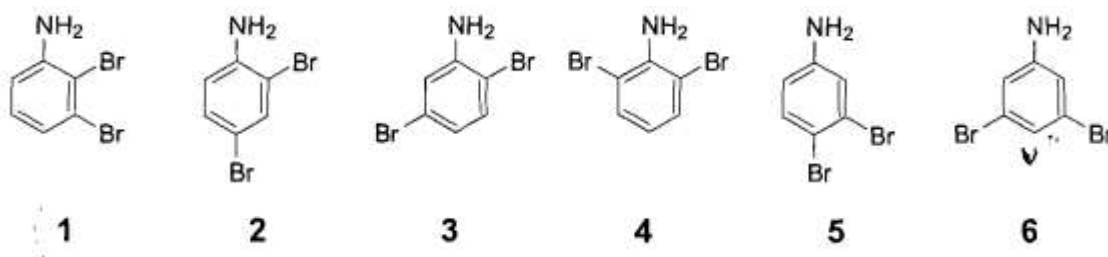
δ ^1H (ppm)	integral	Relative No of H	Rounded No of H

- g) What structural elements do the ^1H NMR spectra suggest? (8)
- h) What structural elements does the ^{13}C NMR suggest? (6)
- i) Draw and name the structure which is consistent with the above analysis. (6)

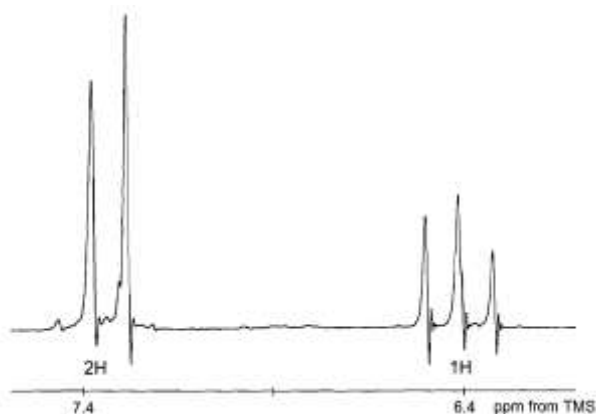
QUESTION 2

[4]

A portion of the 90 MHz ^1H NMR spectrum (5% in CDCl_3) of one of the six possible isomeric dibromoanilines is given below. Only the resonances of the aromatic protons are shown.



Determine which is the correct structure for this compound using arguments based on symmetry and the magnitudes of spin-spin coupling constants.



QUESTION 3**[20]**

An organic compound has the molecular formula $C_{12}H_{17}NO$. Identify the compound using the spectroscopic data given below.

ν_{\max} (KBr disc): 3296 m, 1642 s cm^{-1} .

1H NMR ($CDCl_3$ solution): δ 7.23-7.42, m, 5H; 5.74, br s, exch. D_2O , 1H; 5.14, *q*, *J* 6.7 Hz, 1H; 2.15, *t*, *J* 7.1 Hz, 2H; 1.66, m, 2H; 1.48, *d*, *J* 6.7 Hz, 3H; 0.93, *t*, *J* 7.3 Hz, 3H ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$ solution): δ 172.0 (C), 143.3 (C), 128.6, 127.3, 126.1, 48.5 (CH), 38.8 (CH_2), 21.7 (CH_3), 19.1 (CH_2), 13.7 (CH_3) ppm.

Mass spectrum: *m/e* 191 (M^+ , 40), 120 (33), 105 (58), 104 (100), 77 (18), 43 (46).

Question 4**[8]**

How do DEPT experiments differ from normal NMR experiments? Distinguish between the various (3) DEPT techniques.

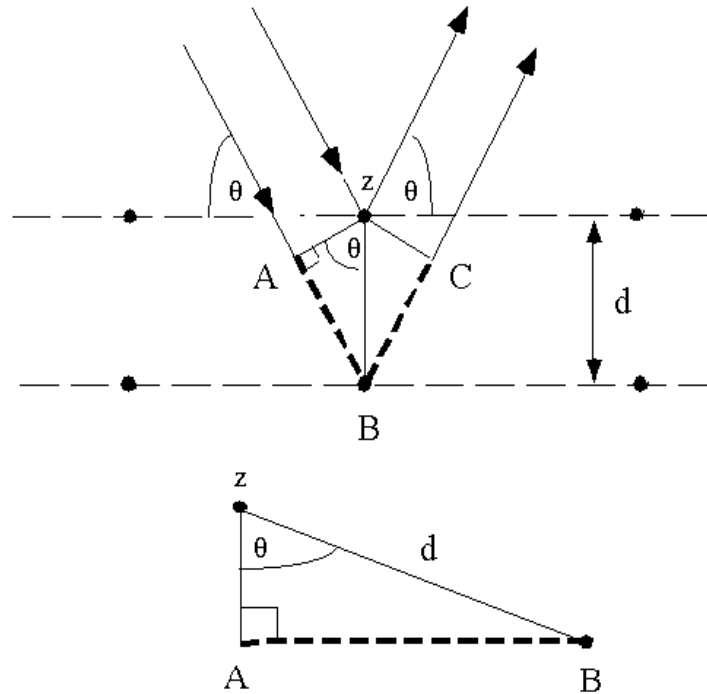
SECTION 2: SURFACE CHARACTERIZATION TECHNIQUES

QUESTION 5

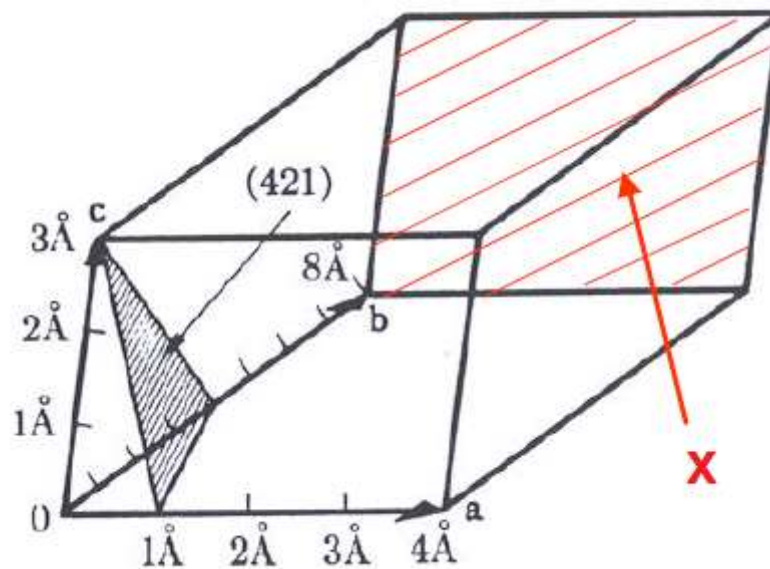
[10]

- a) From the diagrams below, if $n\lambda = AB + BC$, derive Bragg's equation.

(5)



- b) If you are given the unit cell below with a triangle-like plane and plane X,



Complete the table below

(5)

	Triangle-like plane			Plane X		
	a	b	c	A	B	C
Axial length (Å)						
Intercept length (Å)						
Fractional indices						
Miller indices						

QUESTION 6

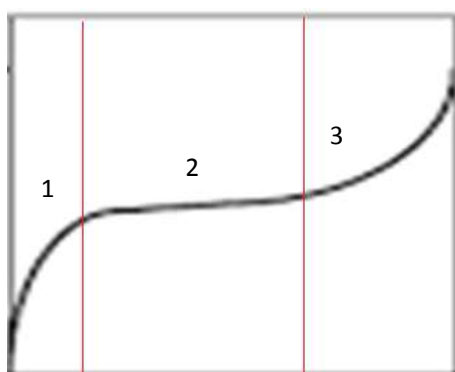
[10]

- What is an Auger electron? (1)
- If a peak in an XPS spectrum is identified as $2p_{3/2}$. What is the electron's (i) orbital momentum (l), (ii) spin momentum (s), and the total momentum (j)? (3)
- Differentiate between the two photoelectron peaks of Pt, $4f_{7/2}$ and $4f_{5/2}$ (3)
- Explain the increase in binding energy as the oxidation state of an atom increases. (2)
- How can you eliminate Auger electron peaks from an XPS spectrum? (1)

QUESTION 7

[10]

- Explain the formation of hysteresis loop in the type IV isotherm. Use diagram(s) where necessary. (2)
- Derive the BET equation from first principles. (5)
- Explain regions 1, 2 and 3 in the type II isotherm shown below in terms of adsorption. Determine and briefly explain where you are most likely to get reliable surface area information in this isotherm. (3)



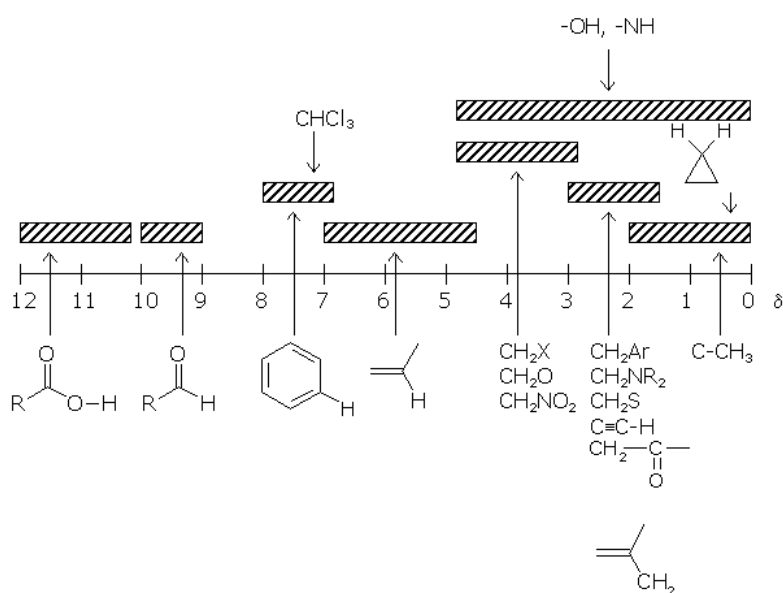
REFERENCE TABLES

Table of Characteristic IR Absorptions

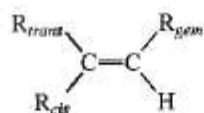
<i>frequency, cm⁻¹</i>	<i>bond</i>	<i>functional group</i>
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH ₂ X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

¹H NMR Correlation Chart



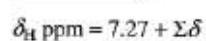
¹H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED ALKENES



$$\delta_H \text{ ppm} = 5.25 + \delta_{gem} + \delta_{cis} + \delta_{trans}$$

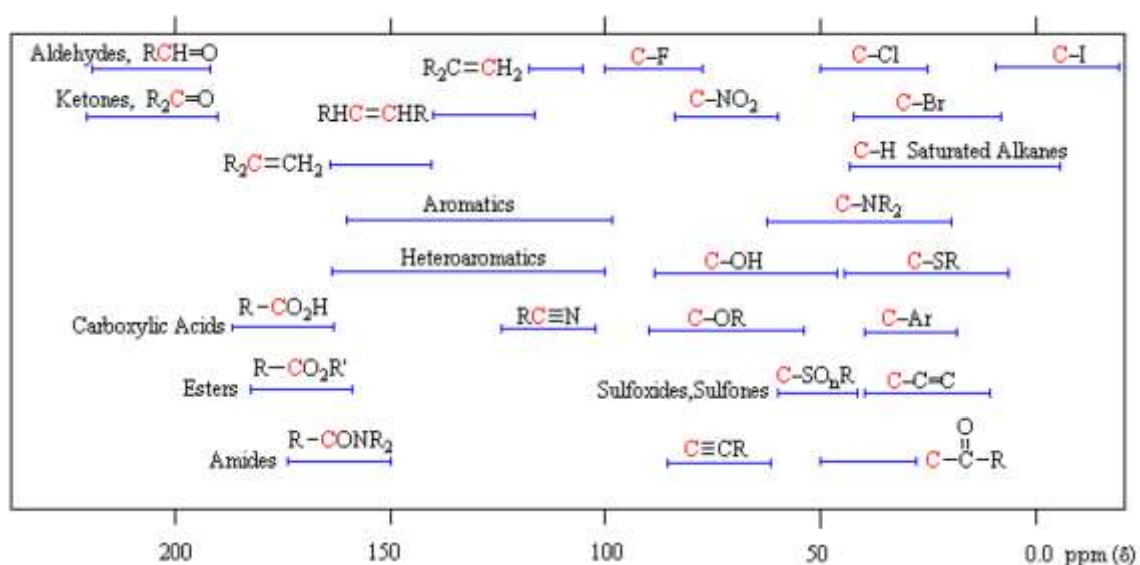
Substituents (-R)	δ_{gem}	δ_{cis}	δ_{trans}
Saturated carbon groups			
Alkyl	0.44	-0.26	-0.29
$-CH_2-O-$	0.67	-0.02	-0.07
Aromatic groups			
$-C_6H_5$	1.35	0.37	-0.10
Carbonyl, acid derivatives, and nitrile			
COR	1.10	1.13	0.81
$-COOH$	1.00	1.35	0.74
$-COOR$	0.84	1.15	0.56
$-C\equiv N$	0.23	0.78	0.58
Oxygen groups			
$-OR$	1.18	-1.06	-1.28
$-OCOR$	2.09	-0.40	-0.67
Nitrogen groups			
$-NR_2$	0.80	-1.26	-1.21
$-NO_2$	1.87	1.30	0.62
Halogen groups			
$-F$	1.54	-0.40	-1.02
$-Cl$	1.08	0.19	0.13
$-Br$	1.04	0.40	0.55
$-I$	1.14	0.81	0.88

¹H CHEMICAL-SHIFT CALCULATIONS FOR SUBSTITUTED BENZENE RINGS



Substituents (-R)	δ_{ortho}	δ_{meta}	δ_{para}
Saturated carbon groups			
Alkyl	-0.14	-0.06	-0.17
-CH ₂ OH	-0.07	-0.07	-0.07
Aldehydes and ketones			
-CHO	0.61	0.25	0.35
-COR	0.62	0.14	0.21
Carboxylic acids and derivatives			
-COOH	0.85	0.18	0.34
-COOR	0.71	0.10	0.21
-C≡N	0.25	0.18	0.30
Oxygen groups			
-OH	-0.53	-0.17	-0.45
-OCH ₃	-0.48	-0.09	-0.44
-OCOCH ₃	-0.19	-0.03	-0.19
Nitrogen groups			
-NH ₂	-0.80	-0.25	-0.65
-NO ₂	0.95	0.26	0.38
Halogen groups			
-F	-0.29	-0.02	-0.23
-Cl	0.03	-0.02	-0.09
-Br	0.18	-0.08	-0.04
-I	0.38	-0.23	-0.01

¹³C NMR Correlation Chart



¹³C SUBSTITUENT INCREMENTS FOR ALKENE (VINYL) CARBONS^{a,b}

$\begin{array}{c} \gamma-\beta-\alpha \\ \quad \diagdown \quad \diagup \\ \quad \text{C}=\text{C} \\ \quad \diagup \quad \diagdown \\ \alpha' \quad \beta'-\gamma' \end{array}$						
Substituent	α	β	γ	α'	β'	γ'
Carbon	10.6	7.2	-1.5	-7.9	-1.8	-1.5
-C ₆ H ₅	12			-11		
-OR	29	2		-39	-1	
-OCOR	18			-27		
-COR	15			6		
-COOH	4			9		
-CN	-16			15		
-Cl	3	-1		-6	2	
-Br	-8	0		-1	2	
-I	-38			7		

^aIn the upper chains, if a group is in the β or γ position, the preceding atoms (α and/or β) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3 ppm).

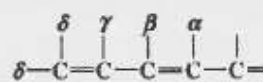
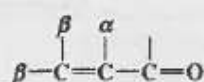
^bCalculate C1 as shown in the diagram. Redefine C2 as C1 when estimating values for C2.

¹³C SUBSTITUENT INCREMENTS FOR BENZENE RINGS (PPM)^a

Substituent Y	α (ipso)	o (ortho)	m (meta)	p (para)
-CH ₃	9.3	0.7	-0.1	-2.9
-CH ₂ CH ₃	11.7	-0.5	0	-2.6
-CH(CH ₂) ₂	20.1	-2.0	-0.3	-2.5
-C(CH ₃) ₃	18.6	-3.4	-0.4	-3.1
-CH=CH ₂	9.1	-2.4	0.2	-0.5
-C=CH	-6.2	3.6	-0.4	-0.3
-C ₆ H ₅	8.1	-1.1	-0.5	-1.1
-CHO	8.2	1.2	0.6	5.8
-COCH ₃	8.9	-0.1	-0.1	4.4
-COC ₆ H ₅	9.1	1.5	-0.2	3.8
-COOH	2.1	1.6	-0.1	5.2
-COOCH ₃	2.0	1.2	-0.1	4.3
-CN	-16.0	3.6	0.6	4.3
-NH ₂	18.2	-13.4	0.8	-10.0
-N(CH ₃) ₂	16.0	-15.7	0.8	-10.5
-NHCOCH ₃	9.7	-8.1	0.2	-4.4
-NO ₂	19.6	-4.9	0.9	6.0
-OH	28.8	-12.7	1.6	-7.3
-OCH ₃	33.5	-14.4	1.0	-7.7
-OCOCH ₃	22.4	-7.1	-0.4	-3.2
-F	33.6	-13.0	1.6	-4.5
-Cl	5.3	0.4	1.4	-1.9
-Br	-5.4	3.4	2.2	-1.0
-I	-31.2	8.9	1.6	-1.1

^aAdd these increments to the base value for benzene-ring carbons (128.5 ppm).

EMPIRICAL RULES FOR ENONES



Base values:

Six-membered ring or acyclic parent enone	= 215 nm
Five-membered ring parent enone	= 202 nm
Acyclic dienone	= 245 nm

Increments for:

Double-bond-extending conjugation	30
Alkyl group or ring residue	α 10
	β 12
	γ and higher 18

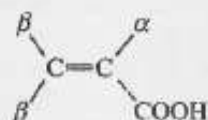
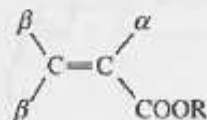
Polar groupings:

-OH	α 35
	β 30
	δ 50
-OCOCH ₃	α, β, δ 6
-OCH ₃	α 35
	β 30
	γ 17
	δ 31
-Cl	α 15
	β 12
-Br	α 25
	β 30
-NR ₂	β 95
Exocyclic double bond	5
Homocyclic diene component	39
Solvent correction	Variable

$$\lambda_{\text{max}}^{\text{Em}} (\text{calc}) = \text{Total}$$

EMPIRICAL RULES FOR UNSATURATED ACIDS AND ESTERS

Base values for:



With α or β alkyl group	208 nm
With α, β or β, β alkyl groups	217
With α, β, β alkyl groups	225
For an exocyclic α, β double bond	Add 5 nm
For an endocyclic α, β double bond in a five- or seven-membered ring	Add 5 nm