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No. of Printed Pages: 4+6

(A-31 to A-35)

SARDAR PATEL UNIVERSITY

M.Sc. Semester – IV

(Organic/Analytical/Inorganic/Physical/Industrial Polymer Chemistry)

Examination

Tuesday, 21<sup>st</sup> April 2015

(PS04CORC01/PS04CANC01/PS04CINC01/PS04CPHC01/PS04CIPC01)

Spectroscopy-II

Time: 10:30 am to 01:30 pm

Total Marks: 70

Note: Right hand figures indicate marks.

Q. 1 Select the correct answer in the following.

08

- In IR, the C=O stretching band (amide-I band) of primary amide in solid state is observed at
  - $\sim 3100 \text{ cm}^{-1}$
  - $\sim 1650 \text{ cm}^{-1}$
  - $\sim 2250 \text{ cm}^{-1}$
  - $\sim 3400 \text{ cm}^{-1}$
- In UV, the electronic transition shown by ethyl chloride is
  - $n \rightarrow \sigma^*$
  - $n \rightarrow \pi^*$
  - $\pi \rightarrow \pi^*$
  - $\sigma \rightarrow \pi^*$
- The Pople notation for the protons present in p-dichloro benzene is
  - $A_2X_2$
  - $A_2B_2$
  - $A_4$
  - $AA'XX'$
- The protons of two methyl groups in acetone are
  - Homotopic
  - Enantiotopic
  - Mesomeric
  - Diastereotopic
- In  $^{13}\text{C}$  NMR, naphthalene will give
  - 4 signals
  - 5 signals
  - 10 signals
  - 3 signals
- In  $^{13}\text{C}$  NMR, the solvent Benzene- $d_6$  will give signal as
  - Singlet at  $128.5 \delta$
  - Triplet at  $128.0 \delta$
  - Doublet at  $128.5 \delta$
  - Triplet at  $77.0 \delta$
- In the molecular ion peak region, the mass spectrum of a compound containing one bromine atom will show
  - Two peaks with almost 1:1 intensities
  - Two peaks with 3:1 intensities
  - Three peaks with 1:2:1 intensities
  - Four peaks with 1:3:3:1 intensities
- In HETCOR spectra, the connectivity observed between  $^1\text{H}$  and  $^{13}\text{C}$  is
  - $^2J$
  - $^3J$
  - $^2J$  and  $^3J$
  - $^1J$

**Q. 2** Answer the following (Any Seven).

14

1. Discuss the O-H stretching vibrations observed in the IR spectra of o-hydroxy acetophenone and p-hydroxy acetophenone.
2. Drawing figure, show scissoring, wagging, rocking and twisting bending vibrations observed in H<sub>2</sub>O.
3. Draw energy diagram for various electronic transitions observed in UV.
4. Sketch the PMR spectrum for isopropyl acetate by taking approximate  $\delta$  value for each signal and showing appropriate multiplicity.
5. In PMR, at room temperature cyclohexane gives one signal while at -70°C it gives two signals. Explain.
6. Sketch the proton coupled and decoupled <sup>13</sup>C NMR spectra for n-hexane.
7. Write the important characteristic properties of DEPT-90° and DEPT-135° spectra.
8. Do the mass fragmentation of n-butanal.
9. Sketch the <sup>1</sup>H-<sup>13</sup>C HETCOR spectrum for ethyl iodide by taking approximate  $\delta$  value for each signal.

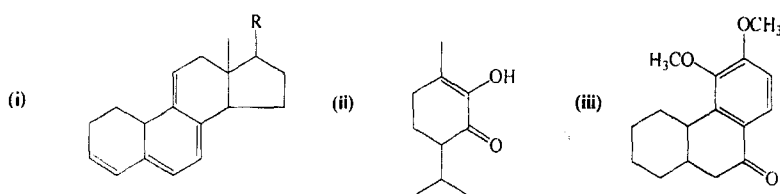
**Q. 3** A. Answer the following.

06

- (i) Discuss the important IR absorptions shown by saturated aliphatic carboxylic acid.
- (ii) Write a short note on chromophores and auxochromes.

B. Calculate  $\lambda_{\text{max}}$  for the following molecules.

06



OR

B. Discuss the important characteristic vibrations observed in the IR spectra of ketones and esters.

06

**Q. 4 A.** (i) What is coupling constant in PMR? Discuss vicinal and long range couplings in detail.

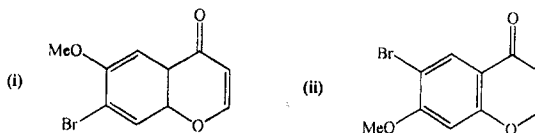
03

(ii) List the methods used for simplification of PMR spectra. Discuss the use of increasing field strength and double resonance (spin decoupling) in detail.

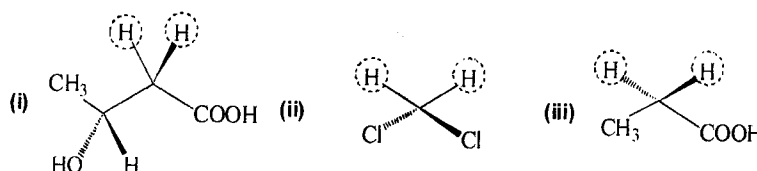
03

OR

- A. (i) Explain nuclear overhauser effect in PMR. How will you distinguish following isomers using NOE-PMR spectra? 03



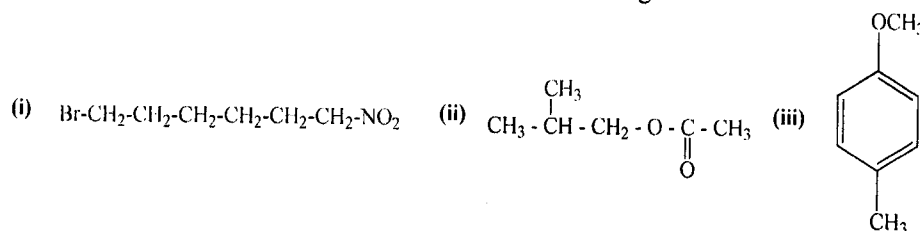
- (ii) Indicate whether the circled protons are homotopic, enantiotopic or diastereotopic in each of the following compounds. Give explanation of your answer. 03



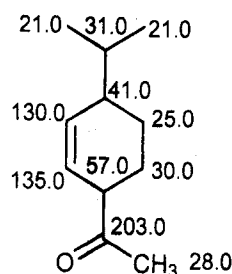
- B. (i) Sketch the expected PMR spectrum for styrene by taking approximate  $\delta$  value for each signal and show that styryl group is an AMX system with three coupling constants. 03

- (ii) In PMR, the acetylene protons give signal at 1.80  $\delta$  which is shielded compared to ethylene protons (5.5  $\delta$ ). Similarly benzene protons give signal at 7.7  $\delta$  which is deshielded signal compared to ethylene protons. Explain this on the basis of circulation of  $\pi$  electrons and ring current effect. 03

- Q. 5 A. Do the  $^{13}\text{C}$  NMR chemical shift calculations for the following molecules. 06



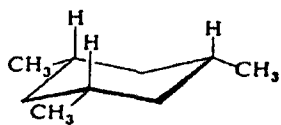
- B. (i) Sketch proton decoupled  $^{13}\text{C}$  NMR, DEPT 45°, DEPT 90° and DEPT 135° spectra for the following compound. ( $\delta$  values for each carbon is assigned in the structure) 03



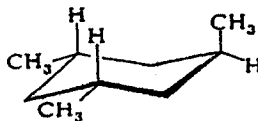
- (ii) Sketch the  $^1\text{H}-^1\text{H}$  COSY spectrum for 3-heptanone by taking approximate  $\delta$  value for each signal. 03

OR

B. (i) Show how will you differentiate the following stereoisomers (A and B) using proton decoupled  $^{13}\text{C}$  NMR spectra. 03



(A)

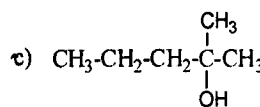
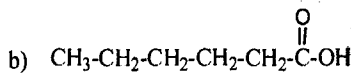
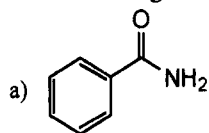


(B)

(ii) A compound with molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  shows following signals in its proton coupled  $^{13}\text{C}$  NMR. Interpret the data and assign the structure to the compound. 03

18  $\delta$  (quartet)  
28  $\delta$  (quartet)  
42  $\delta$  (doublet)  
212  $\delta$  (singlet)

Q. 6 A. Do the mass fragmentation for the following molecules. 06



B. (i) Discuss Fast Atomic Bombardment (FAB) and Electrospray Ionization techniques used in mass spectroscopy. 03

(ii) Answer the following 03

- Explain Nitrogen rule.
- Explain McLafferty rearrangement

OR

B. A compound has molecular formula  $\text{C}_7\text{H}_{12}\text{O}_3$ . It gives the following spectral data. Interpret the spectral data and determine the structure of the compound. 06

IR: 2960, 1725, 1160 and 1030  $\text{cm}^{-1}$

$^{13}\text{C}$  NMR:

$^1\text{H}$  NMR:

Signal ( $\delta$ )	Multiplicity	Protons
1.25	Triplet	3H
2.20	Singlet	3H
2.55	Triplet	2H
2.75	Triplet	2H
4.10	Quartet	2H

$^{13}\text{C}$ ( $\delta$ )	DEPT 135
14	+Ve
28	-Ve
29	+Ve
37	-Ve
60	-Ve
172	-
208	-

Mass(m/z), (% r.a) : 144(5%), 129(20%), 116(2%), 101(20%), 99(50%), 74(20%), 55(15%), 43(100%)

— X —

## CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift, ppm	
	δ	
Cyclopropane	0.2	
Primary	0.9	
Secondary	1.3	
Tertiary	1.5	
Vinyl	4.5-5.9	
Acetylenic	2-3	
Aromatic	6-8.5	
Benzylic	2.2-3	
Allylic	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	R <sub>2</sub> COO-CH	3.7-4.1
Esters	HC-COOR	2-2.2
Acids	HC-COOH	2-2.8
Carbonyl compounds	HC-C=O	2-2.7
Aldehydic	R-CHO	9-10
Hydroxylic	R-OH	1-5.5
Phenolic	Ar-OH	4-12
Enolic	C=C-OH	15-17
Carboxylic	R <sub>2</sub> COOH	10.5-12
Amino	RNE <sub>2</sub>	1-5

## Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm <sup>-1</sup>
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 <sub>2</sub>	Nitro compounds	1515-1560
		1345-1385

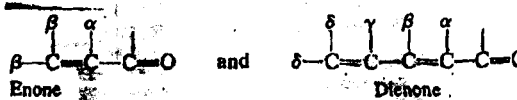
**Characteristic absorption for dienes**

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAIk	+30
Cl, Br	+5
N(Alk) <sub>2</sub>	+60
Solvent correction*	+0
$\lambda_{calc} = \text{Total}$	

**Characteristic absorption for substituted benzene derivatives**

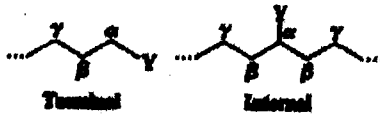
ArCOR/ArCHO/ArCO <sub>2</sub> H/ArCO <sub>2</sub> R	$\lambda_{max}^{obs}$ (nm)
Parent chromophore: Ar = C <sub>6</sub> H <sub>5</sub>	
G = Alkyl or ring residue, (e.g., ArCOR)	246
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO <sub>2</sub> H and ArCO <sub>2</sub> R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10
—OH, —OCH <sub>3</sub> , —OAlk	o-, m- +7 p- +25
—O <sup>-</sup> (oxyanion)	o- +11 m- +20 p- +78*
—Cl	o-, m- +0 p- +10
—Br	o-, m- +2 p- +15
—NH <sub>2</sub>	o-, m- +13 p- +58
—NHCOCH <sub>3</sub>	o-, m- +20 p- +45
—NHCH <sub>3</sub>	p- +73
—N(CH <sub>3</sub> ) <sub>2</sub>	o-, m- +20 p- +85

**Characteristic absorption for  $\alpha, \beta$ -unsaturated carbonyl compounds**



Base values	(nm)
Acyclic $\alpha, \beta$ -unsaturated ketones	215
Six-membered cyclic $\alpha, \beta$ -unsaturated ketones	215
Five-membered cyclic $\alpha, \beta$ -unsaturated ketones	202
$\alpha, \beta$ -Unsaturated aldehydes	210
$\alpha, \beta$ -Unsaturated carboxylic acids and esters	195
Increments for	
Double bond extending conjugation	+30
Alkyl group, ring residue	$\alpha$ +10 $\beta$ +12 $\gamma$ and higher +18
Polar groupings: —OH	$\alpha$ +35 $\beta$ +30 $\delta$ +50
—OAc	$\alpha, \beta, \delta$ +6
—OMe	$\alpha$ +35 $\beta$ +30 $\gamma$ +17 $\delta$ +31
—SAIk	$\beta$ +85
—Cl	$\alpha$ +15 $\beta$ +12
—Br	$\alpha$ +25 $\beta$ +30
—NR <sub>2</sub>	$\beta$ +95
Exocyclic double bond	+5
Homodiene component*	+39

<sup>13</sup>C shifts for terminal and internal systems



Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH <sub>3</sub>	+ 9	+ 6	+10	+ 8	-2
CH=CH <sub>2</sub>	+20		+ 6		-0.5
C≡CH	+ 4.5		+ 5.5		-3.5
COOH	+21	+16	+ 3	+ 2	-2
COO <sup>-</sup>	+25	+20	+ 3	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH <sub>2</sub>	+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 <sub>2</sub>	+29	+24	+11	+10	-5
NH <sub>3</sub> <sup>+</sup>	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR <sub>2</sub>	+42		+ 6		-3
NR <sub>3</sub> <sup>+</sup>	+31		+ 5		-7
NO <sub>2</sub>	+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

<sup>13</sup>C Shifts for some linear and branched chain alkanes

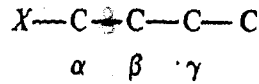
Compound	C-1	C-2	C-3	C-4	C-5
Methane	-23				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isobutane	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 <sub>3</sub> )	
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 <sub>3</sub> )	

<sup>13</sup>C shifts for substituted benzenes  
Base value for benzene is 128.5 ppm

Substituent	C1 (Attachment)	C2	C3	C4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH <sub>3</sub>	+9.3	+0.7	-0.1	-2.9	21.3
CH <sub>2</sub> CH <sub>3</sub>	+15.6	-0.5	0.0	-2.6	29.2 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.5	34.4 (CH), 34.1 (CH <sub>3</sub> )
C(CH <sub>3</sub> ) <sub>3</sub>	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH <sub>3</sub> )
CH=CH <sub>2</sub>	+9.1	-2.4	+0.2	-0.3	127.1 (CH), 113.3 (CH <sub>2</sub> )
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C <sub>6</sub> H <sub>5</sub>	+12.1	-1.8	-0.1	-1.6	
CH <sub>2</sub> OH	+13.3	-0.8	-0.6	-0.4	64.5
CH <sub>2</sub> OCCH <sub>3</sub>	+7.7	-0.0	-0.0	-0.0	20.7 (CH <sub>2</sub> ), 66.1 (CH <sub>3</sub> ), 178.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1
OC <sub>2</sub> H <sub>5</sub>	+29.0	-9.4	+1.6	-5.3	
OCCH <sub>3</sub>	+22.4	-7.1	-0.4	-3.2	23.9 (CH <sub>3</sub> ), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
OCH <sub>3</sub>	+7.8	-0.4	-0.4	+2.8	24.6 (CH <sub>3</sub> ), 195.7 (C=O)
OC <sub>2</sub> H <sub>5</sub>	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
OCF <sub>3</sub>	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH <sub>3</sub>	+2.0	+1.2	-0.1	+4.8	51.0 (CH <sub>3</sub> ), 166.8 (C=O) 168.5
CCl	+4.6	+2.9	+0.6	+7.0	
CNH <sub>2</sub>	+5.0	-1.2	0.0	+3.4	
C≡N	-16.0	+3.6	+0.6	+4.3	119.5
NH <sub>2</sub>	+19.2	-12.4	+1.3	-9.5	
N(CH <sub>3</sub> ) <sub>2</sub>	+22.4	-15.7	+0.8	-11.8	40.3
NHCOCH <sub>3</sub>	+11.1	-9.9	+0.2	-5.6	
NO <sub>2</sub>	+19.6	-5.3	+0.9	+6.0	
N=C=O	+5.7	-3.6	+1.3	-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 <sub>3</sub>	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH <sub>3</sub>	+10.2	-1.8	+0.4	-3.6	15.9
SO <sub>2</sub> NH <sub>2</sub>	+15.3	-2.9	+0.4	+3.3	
Si(CH <sub>3</sub> ) <sub>3</sub>	+13.4	+4.4	-1.1	-1.1	

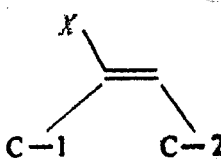
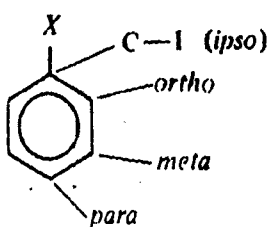




Influence of functional group X on the chemical shift position ( $\delta$ ) of nearby carbons in alkane chain



X	$\alpha$ -shift			$\beta$ -shift	$\gamma$ -shift
	$X-CH_2-$	$X-\underset{\substack{  \\ R}}{CH}-$	$X-\overset{\substack{R \\   \\ R}}{C}-$		
	1°	or 2°	or 3°		
$-CH_3$	9	6	3	9	-3
$-R$ : see table 3.11					
(in cyclohexanes)	axial $-CH_3$	1	-	5	-6
	equatorial $-CH_3$	6	-	9	0
$-CH=CH_2$	22	16	12	7	-2
$-C\equiv CH$	4	-	-	3	-3
$-C_6H_5, -Ar$	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
$-SO_3H, -SO_2N<$	50	-	-	3	0

Influence of functional group X on the chemical shift positions ( $\delta$ ) of nearby carbons in alkene groups and benzene rings

Base values:		ethylene ( $\delta$ 123)		and		benzene ( $\delta$ 128)			
									
		Alkenes				Benzenes			
		C-1	C-2	C-1	ortho	meta	para		
				(ipso)					
-CH <sub>3</sub>		10	-8	9	0	0	-2		
R, 		16	-8	15	0	0	-2		
R, 		23	-8	21	0	0	-2		
-CH=CH <sub>2</sub>		15	-6	9	0	0	-2		
-CH≡CH		-	-	-6	4	0	0		
-C <sub>6</sub> H <sub>5</sub> , -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 <sub>2</sub>		-	-	18	-13	1	-10		
-NHR		-	-	20	-14	1	-10		
-NR <sub>2</sub>		-	-	22	-16	1	-10		
-NO <sub>2</sub>		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 <sub>3</sub> H, -SO <sub>2</sub> N<		-	-	16	0	0	4		
-PMe <sub>2</sub>		-	-	14	1.6	0	-1		
-PAr <sub>2</sub>		-	-	9	5	0	0		