

[104]

SEAT No. \_\_\_\_\_

No of Printed Pages: 03 + 04

**SARDAR PATEL UNIVERSITY**  
**M.Sc. Organic Chemistry**  
**Semester – IV, External Examination**  
**18<sup>th</sup> March , 2019, Monday**  
**Time: 02:00 am - 05:00 pm**  
**Spectroscopy-II [PS04CORC01]**

[Total Marks – 70]

N.B. Figures to the right indicate full marks

**Q.1 Answer the following multiple choice questions. [08]**

- 1 Number of Br atoms are \_\_\_\_\_ in a compound showing abundance of M: M+2:M+4:M+6 as 1:4:6:4:1 in mass spectrum.  
(a) 1 (b) 2 (c) 4 (d) 3
- 2 Carbonyl stretching of saturated aliphatic ketons falls in region \_\_\_\_\_  $\text{Cm}^{-1}$ .  
(a) 1600-1700 (b) 1220-1250 (c) 1700-1800 (d) 1400-1450
- 3 In PMR spectrum of benzene \_\_\_\_\_ signals are obtained.  
(a) 1 (b) 4 (c) 3 (d) 2
- 4 The HMBC spectra show \_\_\_\_\_.  
(a)  $^1\text{J}$  and  $^3\text{J}$  connectivity (b)  $^2\text{J}$  and  $^2\text{J}$  connectivity  
(c)  $^2\text{J}$  and  $^3\text{J}$  connectivity (d)  $^3\text{J}$  and  $^3\text{J}$  connectivity
- 5 In UV, the highest energy electronic transition is \_\_\_\_\_.  
(a)  $n \rightarrow \pi^*$  (b)  $n \rightarrow \sigma^*$  (c)  $\pi \rightarrow \pi^*$  (d)  $\sigma \rightarrow \sigma^*$
- 6 In CI techniques for recording mass spectra, reagent gas used is generally \_\_\_\_\_.  
(a) Argon (b) methane (c) helium (d) nitrogen
- 7 In  $^{13}\text{C}$ -NMR , p-benzoquinone will give \_\_\_\_\_ signals.  
(a) 1 (b) 4 (c) 3 (d) 2
- 8 At 300 MHz styrene gives \_\_\_\_\_ first order spectrum.  
(a) AMX (b) AX (c) AX (d) ABM

**Q.2 Answer the following questions. (ANY SEVEN) [14]**

- 1 Sketch the PMR spectrum for 1- nitropropane by taking approximate  $\delta$  value for each signal and showing appropriate multiplicity.
- 2 Explain long range coupling with suitable example.
- 3 Write structures of shift reagents.

①

(P.T.O.)

- 4 Explain McLafferty rearrangement takes place in alcohols.
- 5 Explain effect of conjugation on absorption of  $\lambda_{\max}$  in UV spectroscopy.
- 6 Explain Fermi resonance in IR spectroscopy.
- 7 Sketch the  $^1\text{H} - ^{13}\text{C}$  HETCOR spectrum for ethyl chloride by taking approximate  $\delta$  value for each signal.
- 8 Do the fragmentation of 2-pentanone based on McLafferty rearrangement.
- 9 Predict fragmentation pattern of diphenyl ether having molecular ion at  $m/z - 170$ .

**Q.3**

[A] Answer the following questions. [06]

- I A compound gives following data in its mass spectrum, deduce structure of the compound.

m/z -	129	130	131	132	133	134	135	136	137
Relative Abundance	30	100	31	98	12	32	1.7	3.5	0.07

- II Explain chemical ionization method used in mass spectroscopy.

[B] Explain fragmentation pattern for aldehydes and acids using McLafferty rearrangement. [06]

OR

[B] Answer the following questions.

- I Explain homolytic and heterolytic cleavage of single bond in mass spectroscopy.

II Derive,  $m/z = B^2 r^2 / 2V$ .

**Q.4**

[A] Answer the following questions. [06]

- I Write short note on  $\text{D}_2\text{O}$  exchange in PMR.

II Define NOE, explain with suitable example of distinction of isomers using NOE-PMR spectra.

[B] A compound with molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  shows following signals in its proton coupled  $^{13}\text{C}$ -Spectra, interpret the data and assign the structure. [06]

$\delta - 18$  (quartet, 6H),  $\delta - 28$  (quartet, 3H)

$\delta - 42$  (doublet, 1H),  $\delta - 212$  (singlet)

OR

[B] Discuss the use of symmetry operations for checking the chemical shift equivalence between protons in PMR spectroscopy.

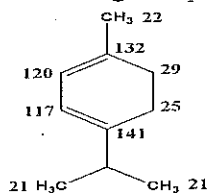
**Q.5**

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

i) n-butanol

ii) 3-me-pentane      iii) P-Amino toluene

- [B] Sketch proton decoupled  $^{13}\text{C-NMR}$ , DEPT-45, and DEPT-90 spectra for the following compound. (use  $\delta$  value assigned in the structure) [06]



OR

- [B] An organic compound with molecular formula  $\text{C}_9\text{H}_{10}\text{O}_2$  exhibits the following spectral data. Interpret and deduce the structure of the compound.

IR:  $1745, 1225, 749, 697 \text{ cm}^{-1}$

UV:  $\lambda_{\text{max}} 268, 264, 262, 257 \text{ nm}$

$^1\text{H-NMR}$ :  $\delta - 1.96(3\text{H}, \text{S}), 5.00(2\text{H}, \text{S}), 7.22(5\text{H}, \text{S})$

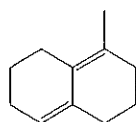
Q.6

- [A] Answer the following questions. [06]

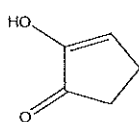
- I Write a short note on Fermi resonance.
- II Explain short range couplings.

- [B] Calculate  $\lambda_{\text{max}}$  for the following compounds [06]

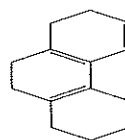
[1]



[2]



[3]



OR

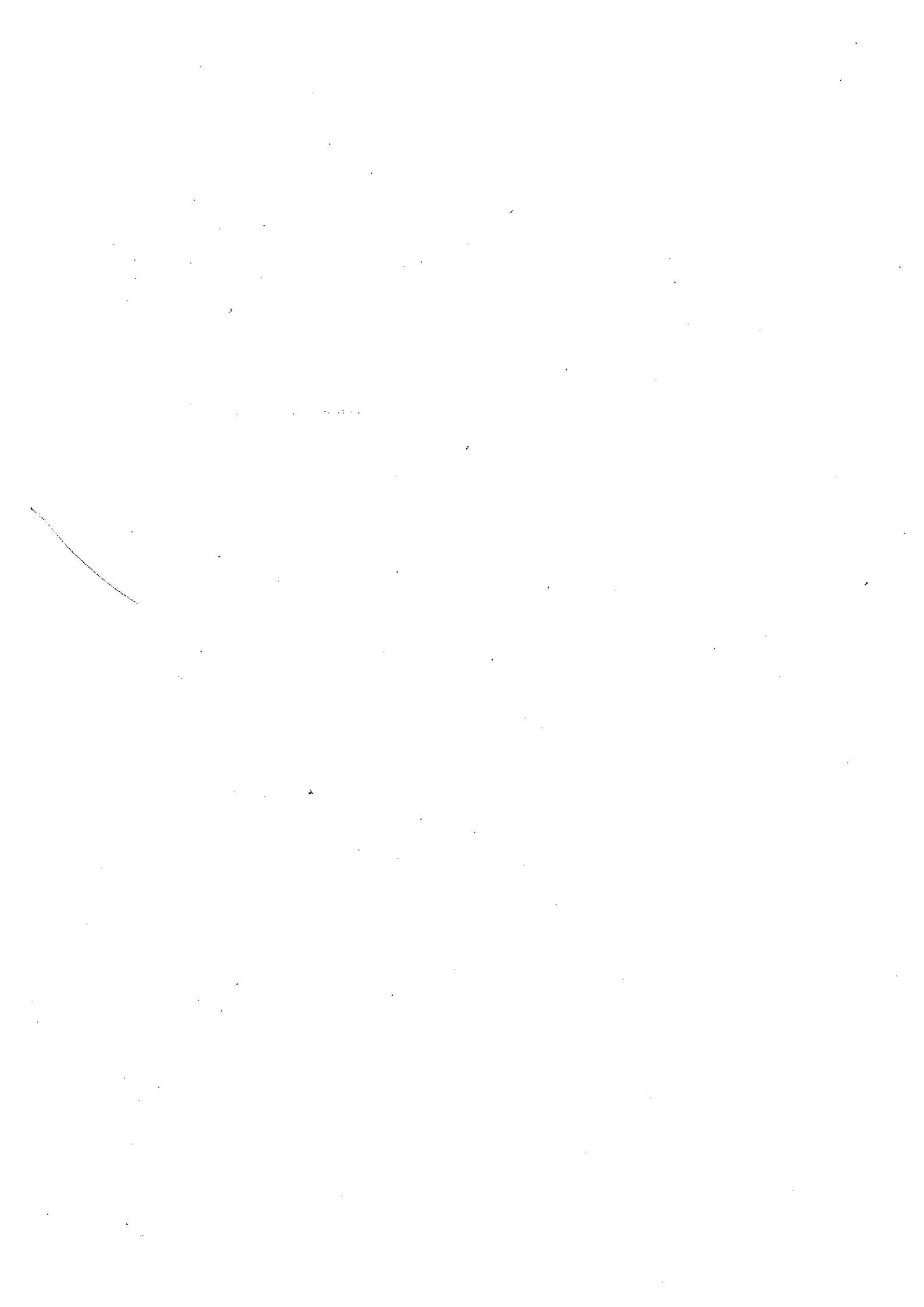
[B]

- I Discuss important characteristic vibrations observed in nitriles.
- II Calculate stretching frequency for C-C bond.

Ans

→ X ←

(3)



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PS04CORCO1

CHARACTERISTIC PROTON CHEMICAL SHIFTS

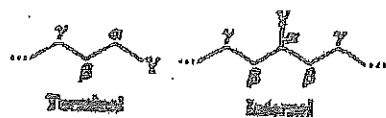
Type of proton	Chemical shift, ppm
Cyclopropane	δ
Primary	0.2
Secondary	0.9
Tertiary	1.3
Vinyl	1.5
Acetylenic	4.6-3.9
Aromatic	7-3
Benzylic	6-3.5
Allylic	2-2.3
Fluorides	1.7
Chlorides	HC-F
Bromides	4-6.5
Iodides	HC-Cl
Alcohols	3-4
Ethers	HC-Br
Esters	2.5-4
Acids	HC-I
Carbonyl compounds	3.4-4
Aldehydic	HC-OH
Hydroxylic	2-2.7
Phenolic	HC-OR
Enolic	3.3-4
Carboxylic	RCOO-CH
Amino	HC-COOR
	HC-COOH
	HC-C=O
	R-CHO
	R-OH
	Ar-OH
	C=C-OH
	RCOOH
	RNH <sub>2</sub>

Characteristic Infrared Absorption Frequencies

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



<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	+ 5	+ 3	-1
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	+38	+31	+ 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	+29	+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	-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	
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	11.3	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> )	

(P.T.O)

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

Substituent	C1 (Arbitrary)	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	29.1 (CH <sub>2</sub> ), 19.3 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.3	34.8 (CH), 24.1 (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	157.1 (CH), 119.3 (CH <sub>2</sub> )
C≡CH	-5.8	+6.9	+0.1	+0.4	84.9 (C), 77.3 (CH)
CH <sub>2</sub> OH	+12.1	-1.3	-0.1	-1.6	
CH(OH) <sub>2</sub>	+13.3	-0.2	-0.6	-0.4	64.5
CH <sub>2</sub> OOCCH <sub>3</sub>	+7.7	-0.0	-0.0	-0.0	20.7 (CH <sub>2</sub> ), 66.1 (CH <sub>3</sub> ), 171.5 (C=O)
OH	+25.6	-12.7	+1.6	-7.3	
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1
OCH <sub>2</sub> CH <sub>3</sub>	+29.7	-9.4	+1.6	-3.3	
OOCCH <sub>3</sub>	+22.6	-7.1	-0.4	-3.2	21.9 (CH <sub>3</sub> ), 169.7 (C=O)
CH=O	+8.3	+1.2	+0.6	+5.8	182.0
COCH <sub>3</sub>	+7.8	-0.4	-0.4	+2.8	24.6 (CH <sub>3</sub> ), 193.7 (C=O)
OCH <sub>2</sub> COCH <sub>3</sub>	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
COF <sub>3</sub>	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	169.0
COOCH <sub>3</sub>	+2.0	+1.2	-0.1	+4.8	51.0 (CH <sub>3</sub> ), 166.8 (C=O), 168.3
COCl	+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	+0.9	-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	+1.2	-2.8	129.5
F	+39.1	-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>	+18.2	-1.8	+0.4	-3.6	15.9
SO <sub>2</sub> NH <sub>2</sub>	+15.3	-2.9	+0.4	+3.3	
S(CH <sub>3</sub> ) <sub>2</sub>	+13.4	+4.4	-1.1	-1.1	