647510 **MSC4OrE1404A** **Seat No :_____**

M.Sc.(Chem.) Semester - 4 (*CBCS*) Examination
Oct/Nov -2020 [NEW COURSE]
Modern Spectroscopy (Elective)

Time: 2:00 Hours **Marks: 56**

Instructions:

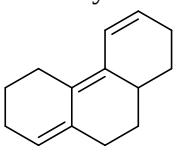
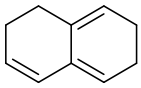
1. Figures to the right indicate marks.
2. There are five questions in the question paper.
3. Answer any four of the following questions.

Unit-1 [1(4)]

Answer **ALL** questions

Q.1 (a) 2 Questions of 2 Marks Each. **(4)**

1. What is spectroscopy? Classify spectroscopy based on their principles.
2. Identify the number of exocyclic double bonds in following compounds:

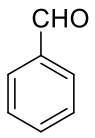
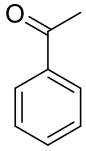
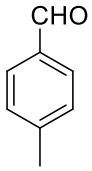
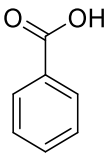
1.  2. 

Q.1 (b) Answer any two questions out of three. **(10)**

(1) Explain different types of absorption and intensity shift observed in UV spectroscopy. 5

(2) Discuss instrumentation of double beam UV spectrophotometer with schematic diagram. 5

(3) Arrange the following compounds in decreasing order in their wavelength (λmax) with λmax Value: 5

1.  2.  3.  4. 

Unit-2 [1(4)]

Answer **ALL** questions

Q.2 (a) 1 Question of (4) **(4)**

Calculate number of fundamental modes of vibration in following molecules:

(1) CO_2
(2) H_2O
(3) SO_2
(4) CS_2

Q.2 (b) Answer any two questions out of three. **(10)**

(1) Describe schematic diagram of FTIR and give its advantage. 5

(2) Explain fundamental modes of vibration in IR spectroscopy. 5

(3) Discuss solid sample handing techniques used in IR spectroscopy. 5

Unit-3 [1(4)]

Answer **ALL** questions

Q.3 (a) 1Question of (4). **(4)**

1. Explain Mclafferty rearrangement in Mass spectroscopy with example.

Q.3 (b) Answer any two questions out of three. **(10)**

(1) Discuss Homolytic and Heterolytic cleavage in mass spectroscopy. 5

(2) Analyze the Mass Fragmentation patterns of Pentane. 5

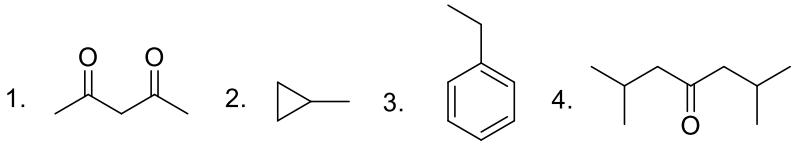
(3) Discuss any two ionization methods in Mass spectroscopy. 5

Unit-4 [1(4)]

Answer **ALL** questions

Q.4 (a) 1 Question of (4) **(4)**

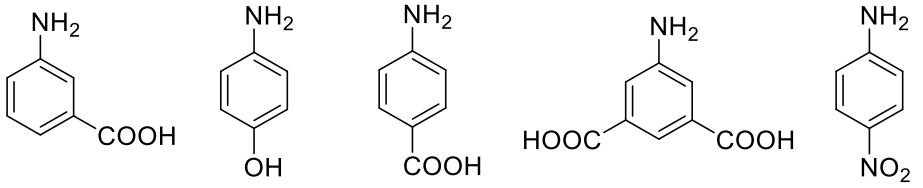
1. Identify the types of protons in following compounds:



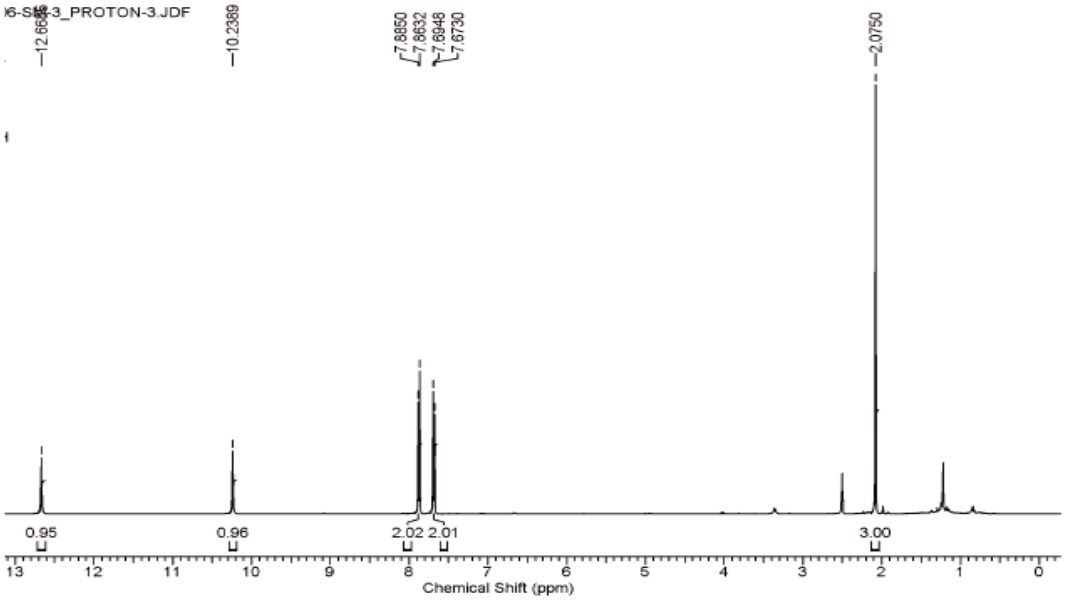
Q.4 (b) Answer any two questions out of three. **(10)**

(1) Predict Spin-Spin splitting in Chloroethane and illustrate Pascal's triangle. 5

(2) Acetylation of following compounds were carried out with acetic anhydride in the presence of catalytic amount of Con. H_2SO_4. 5



Among them one of the product ^{1}H NMR spectrum is given below. Identify the product and interpret it.



(^{1}H NMR 400 MHz)

(3) Which reference standard is used in NMR spectroscopy? And Why? 5

Unit-5 [1(4)]

Answer **ALL** questions

Q.5 (a) 2 Questions of 2 Marks Each. **(4)**

1. Give the principle of Fourier Transform technique in ^{13}C NMR.
2. Indicate the number of signals and multiplicity of Isopropyl benzene in off-resonance decoupled ^{13}C NMR spectra.

Q.5 (b) Answer any two questions out of three. **(10)**

(1) Calculate the chemical shift value of carbon of following compounds: 5
   1. 2-flouropentane 2. 3-bromotoluene 3. p-xylene

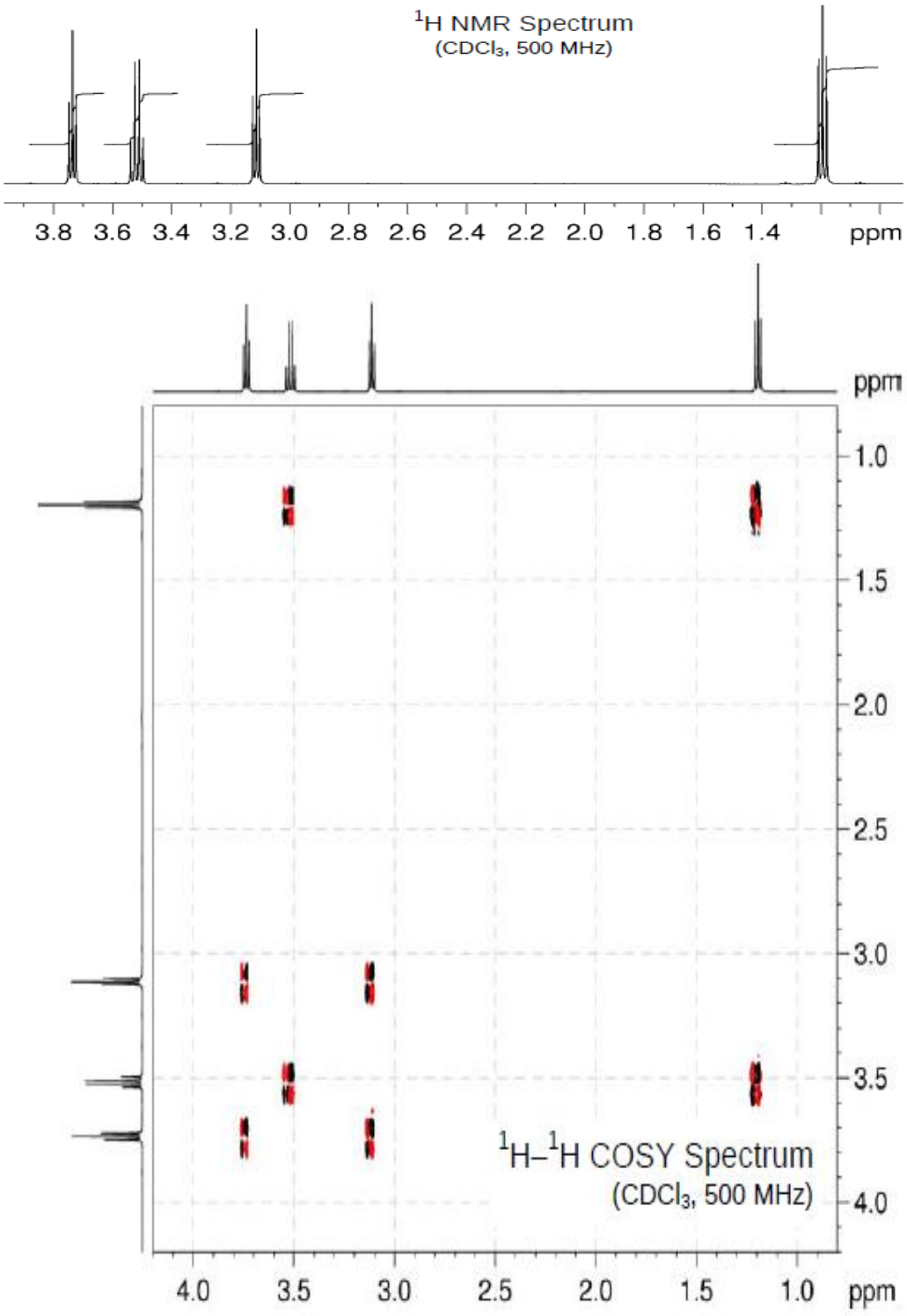
(2) An organic compound with MF: $C_6H_{10}O_4$ furnished the following spectral data: 5

UV: No significant absorption above 210 nm.
IR: 2950,1765 and 1050 cm^{-1}
PMR: δ 1.5 (3H, d), 2.2 (6H, s) and 6.9 (1H, q)
CMR (Off-resonance decoupled): One singlet at δ170, one doublet and two quartets
MS: Prominent peaks at m/e 146, 87 and 43.
Deduce the structure of the compound and explain the spectral data.

(3) Deduce the structure of compound from the given spectral data and interpret correlation peak in 2D NMR and assign protons. 5

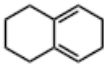
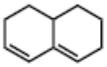
MF: $C_5H_9ClO_2$

PMR: δ 1.2 (3H, t), 3.1 (2H, t), 3.5 (2H, q), 3.7 (2H, t).



UV Spectroscopy

Woodward Fieser Rules for Dienes

			
	s-trans	**homoannular** (cisoid)	**heteroannular** (transoid)
base values:	**217 nm**	**253 nm**	**214 nm**

Increments:

For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each alkyl group or Ring Residue	+ 5 nm
For each of the following groups:	
- OR	+ 6 nm
- O(C=O)R	+ 0 nm
- Cl	+ 6 nm
- Br	+ 6 nm
- SR	+ 30 nm
- NR_2	+ 60 nm
- Ph	+ 60 nm

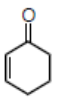
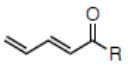
not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λmax is used.

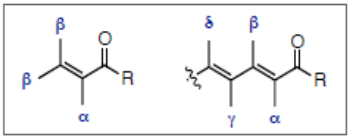
Solvent Correction	nm
H_2O	- 8
EtOH	0
$CHCl_3$	+ 1
Dioxane	+ 5
Et_2O	+ 7
Hydrocarbon	- 11

UV Spectroscopy

Woodward Fieser Rules for Enones

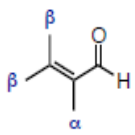
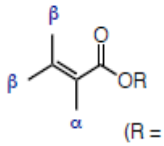
				
	acyclic enone	**6-membered ring enone**	**5-membered ring enone**	**acyclic dienone**
base values:	**215 nm**	**215 nm**	**202 nm**	**245 nm**

Increments:		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:	- OH	+ 35 nm	+ 30 nm		+ 50 nm
	- OR	+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
	- O(C=O)R	+ 6 nm	+ 6 nm		+ 6 nm
	- Cl	+ 15 nm	+ 12 nm		
	- Br	+ 25 nm	+ 30 nm		
	- SR	+ 30 nm	+ 85 nm		
	- NR_2	+ 60 nm	+ 95 nm		



UV Spectroscopy

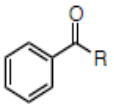
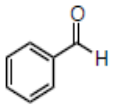
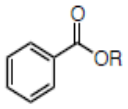
Woodward Fieser Rules for Other Conjugated Carbonyls

	 aldehydes	 (R = H or R') carboxylic acid or ester
Base Values		
unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm

as for enones, solvent correction is also relevant

UV Spectroscopy

Woodward Fieser Rules for Benzoyl Derivatives

	 aryl ketones (R = alkyl)	 benzaldehydes	 benzoic acids and esters
base values:	246 nm	250 nm	230 nm
Increments:	ortho	meta	para
For each alkyl group or RR	+ 3 nm	+ 3 nm	+ 10 nm for RR +7 nm
For each OH or OR (R = alkyl)	+ 7 nm	+ 7 nm	+ 25 nm
For each $O^{\ominus}$	+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:			
- Cl	+ 0 nm	+ 0 nm	+ 10 nm
- Br	+ 2 nm	+ 2 nm	+ 15 nm
- NH_2	+ 13 nm	+ 13 nm	+ 58 nm
- $NH(C{=}O)CH_3$	+ 20 nm	+ 20 nm	+ 45 nm
- $NHCH_3$			+ 73 nm
- $N(CH_3)_2$	+ 20 nm	+ 20 nm	+ 85 nm

Standard Data Sheet for IR spectroscopy

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Alkanes and Alkyls	2850-3000	s	C-H stretch
	1450-1470	s	C-H bend
	1370-1390	m	CH_3 C-H bend
	1365 + 1395 (two bands)	m	$-CH(CH_3)_2$ or $-(CH_3)_3$ bend
	715-725	w	$-(CH_2)_n$ bend
Alkenes	3020-3140	w-m	=C-H stretch
	1640-1670	vw-m	C=C stretch
$RCH=CH_2$	910 + 990 (two bands)	m + s	=C-H bend
$RR'C=CH_2$	885-895	s	=C-H bend
cis-RCH=CHR'	665-730	m-s, broad	=C-H bend
trans-RCH=CHR'	960-980	s	=C-H bend
RCH=CR'R"	790-840	s	=C-H bend
Alkynes			
R-C≡C-H	3265-3335	s, sharp	≡C-H stretch
	2100-2140	m	C≡C stretch
	610-700	s, broad	≡C-H bend
R-C≡C-R'	2190-2260	vw-w	C≡C stretch
Alkyl halides			
R-F	1000-1350	vs	C-F stretch
R-Cl	750-850	s	C-Cl stretch
R-Br	500-680	s	C-Br stretch
R-I	200-500	s	C-I stretch
Alcohols	3300-3400	s, broad	O-H stretch
$C=C-CH_2$-OH	1035-1050	m-s	C-O stretch
$R-CH_2$-OH (1^o) or C=C-CH(R)-OH	1050-1085	m-s	C-O stretch
RR'CH-OH (2^o) or C=C-CRR'-OH	1085-1125	m-s	C-O stretch
RR'R"C-OH (3^o)	1125-1205	m-s	C-O stretch
Ar-O-H	1180-1260	m-s	C-O stretch
Ethers			
R-O-R'	1085-1150	s	C-O-C stretch
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch
Aldehydes	2700-2725	m	H-C=O stretch
R-CH=O	1720-1740	s	C=O stretch
C=C-CH=O or Ar-CH=O	1685-1710	s	C=O stretch
Ketones			
RR'C=O	1710-1720	s	C=O stretch
C=C-C(O)-R	1665-1685	s	C=O stretch
Ar-C(O)-R	1675-1695	s	C=O stretch
four member cyclic	1770-1780	s	C=O stretch
five member cyclic	1740-1755	s	C=O stretch
six member cyclic	1710-1720	s	C=O stretch

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Carboxylic Acids	2500-3500	s, broad	O-H stretch
R-C(O)-OH	1710-1715	s, broad	C=O stretch
C=C-C(O)-OH or Ar-C(O)-OH	1680-1710	s	C=O stretch
Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310	s-vs	O=C-O-C stretch
R-C(O)-O-R	1735-1750	s	C=O stretch
C=C-C(O)-O-R or Ar-C(O)-O-R	1715-1730	s	C=O stretch
R-C(O)-O-Ar	1760-1790	s	C=O stretch
Acyl Chlorides			
R-C(O)-Cl	1785-1815	s	C=O stretch
Ar-C(O)-Cl	1770-1800	s	C=O stretch
Anhydrides			
R-C(O)-O-C(O)-R	~1750 + ~1815	s,s	C=O symmetric
Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
Nitriles			
R-C≡N	2240-2260	m-s	C≡N stretch
C=C-C≡N or Ar-C≡N	2220-2240	s	C≡N stretch
Amines			
$R-NH_2$	~3400 + ~3500 (two bands)	w	N-H symmetric & asym. stretch
	1580-1650	w-m	N-H bend
RR'N-H	3310-33350	w	N-H stretch
Amides			
$R-C(O)-NH_2$	3200-3400 and 3400-3500 (two bands)	w-m	N-H symmetric & asym. stretch
	1650-1690	s, broad	C=O stretch
	1590-1655	m-s	N-H bend
R-C(O)-NH-R	3400-3500	w-m	N-H stretch
	1640-1690	s, broad	C=O stretch
	1510-1560	m-s	N-H bend
R-C(O)-NR'R"	1630-1680	m-s	C=O stretch
Nitro Compounds			
$R-NO_2$	~1550 and	s	N-O symmetric
	~1370	s	& asym. stretch
$C=C-NO_2$ or $Ar-NO_2$	~1525 and	s	N-O symmetric
	~1335 (both two bands)	s	& asym. stretch
Aromatic Compounds	3010-3100	m	Ar C-H stretch
	1450-1600 (two to four bands)	m-s sharp	ring C=C stretch
monosubstituted	730-770 and	s	C-H bend
	690-710 (two bands)	s	C-H bend
o-disubstituted	735-770	s	C-H bend
m-disubstituted	750-810 and	s	C-H bend
	690-710	s	C-H bend
p-disubstituted	810-840	s	C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

^{13}C chemical shifts for some linear and branched-chain alkanes

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
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
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	

Olefinic carbons	
Substituent carbon C	**Correction**
α	+10.6
β	+7.2
γ	-1.5
α’	-7.9
B’	-1.8
γ’	-1.5
z *(cis)*	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+9	+6	+10	+8	−2
$HC{=}CH_2$	+20		+6		−0.5
$C{\equiv}CH$	+4.5		+5.5	+2	−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
NH_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

Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm)

Substituent	C-1	C-2 (*ortho*)	C-3 (*meta*)	C-4 (*para*)
H	0.0	0.0	0.0	0.0
CH_3	+9.3	+0.7	–0.1	–2.9
CH_3CH_2	+15.6	–0.5	0.0	–2.6
$CH(CH_3)_2$	+20.1	–2.0	0.0	–2.5
$HC=CH_2$	+9.1	–2.4	+0.2	–0.5
C_6H_5	+12.1	–1.8	–0.1	–1.6
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
OH	+26.6	–12.7	+1.6	–7.3
OCH_3	+31.4	–14.4	+1.0	–7.7
CHO	+8.2	+1.2	+0.6	+5.8
$COCH_3$	+7.8	–0.4	–0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	–16.0	+3.6	+0.6	+4.3
NO_2	+19.6	–5.3	+0.9	+6.0
NH_2	+19.2	–12.4	+1.3	–9.5
$NHCOCH_3$	+11.1	–9.9	+0.2	–5.6
$COOCH_3$	+2.0	+1.2	–0.1	+4.8

****