[247] SEAT No.________ *No. of Printed pages: [3+7]*

**SARDAR PATEL UNIVERSITY**
M. Sc. Analytical Chemistry, 4th Semester **(NC)** Examination (CBCS)
**Paper:** PS04CANC21, **Subject:** Spectroscopy- II,
**Date:** Saturday, 16th November 2019, **Time:** 2:00 p.m. to 5:00 p.m.

*N.B.: i) Figure to the right indicate marks.*
*ii) Assume the suitable data if necessary and indicate clearly.* **[Total Marks: 70]**

**Q. 1. Answer highlighting the appropriate option :** **[8]**

**i.** In $^1$H estimation, naphthalene will give ______
(a) 2 signals (b) 8 signals
(c) 10 signals (d) 3 signals

**ii.** In UV, the highest energy transition ______
(a) $n - \pi^*$ (b) $\sigma - \sigma^*$
(c) $n - \sigma^*$ (d) $\pi - \pi^*$

**iii.** In $^{13}$C- NMR, 1,3-difluoro-2-propanone will give _____ signal.
(a) 3 (b) 1
(c) 2 (d) None

**iv.** ______ may the stable neutral molecule eliminated during fragmentation.
(a) carbon (b) acid
(c) polymer (d) water

**v.** The aliphatic -C≡N stretching absorption by IR is observed at _______
(a) 2240-2260 cm$^{-1}$ (b) 1650-1700 cm$^{-1}$
(c) 1150-1300 cm$^{-1}$ (d) 2750-2800 cm$^{-1}$

**vi.** In HETCOR spectra, the connectivity between $^1$H and $^{13}$C observed is
(a) $^2$J (b) $^1$J
(c) $^3$J (d) $^2$J and $^3$J

**vii.** In CI techniques for recording mass spectra, reagent gas used is generally____.
(a) argon (b) helium
(c) methane (d) nitrogen

**viii.** Styrene gives______ first order spectrum at 300MHz.
(a) AX (b) ABM
(c) AB (d) AMX

(P.T.O)

**Q. 2. Attempt any *Seven* :** **[14]**

**(i).** Give the full form and structure of TMS. Why it is used as internal reference in PMR spectroscopy?

**(ii).** Define chromophores and auxochromes with example.

**(iii).** Give full form of : (a) DEPT NMR, (b) HSQC

**(iv).** Define Lambert-Beers law.

**(v).** Calculate stretching frequency for C-H bond.

**(vi).** Why the $^{13}$C-NMR spectra are usually studied as proton decoupled spectra?

**(vii).** PMR analysis of cyclohexane gives one signal at room temperature while two signal at (-90°C), justify.

**(viii).** Do the mass fragmentation of Benzamide.

**(ix).** Calculate $\lambda_{max}$ for 2-hydroxycyclopent-2-en-1-one

**Q. 3. Answer the following :**

**[A].** Explain, as the number of conjugated $\pi$ - bond increases, the $\lambda_{max}$ increases as well, show the energy gap diagram by considering examples of ethane, butadiene and hexatriene. **[6]**

**[B]. Answer the following :** **[6]**

**(1).** Enlist the various factors affecting the >C=O stretching frequency. Discuss any two of them in detail.

**(2).** Arrange following compounds in increasing order of >C=O stretching frequency. Explain the order assigned by you.
(i) Cyclopropanone, (ii) Cyclohexanone, (iii) Cyclopentanone

**OR**

**[B]. Answer the following :** **[6]**

**(1).** Write note on Fermi resonance.

**(2).** Discuss characteristic absorptions observed in IR spectra of
(i) Aldehydes (ii) Esters

**Q. 4.**

**[A]. Answer the following :** **[6]**

**(1).** Draw the structures of all the possible isomers for the compound with molecular formula $C_3H_9N$. How many $^1$H-NMR signal(s) will be produced by each isomer?

**(2).** What is Nuclear Overhauser Effect (NOE)? How will you distinguish Vanilin and Isovanilin using NOE studies?

**[B]. Answer the following :** [6]

(1). What is pople notation? Give pople notation to the aromatic protons of furan-2-aldehyde. Draw PMR spectrum of the same in detail.
(2). Define coupling constant. Discuss geminal and vicinal coupling constants in detail.

**OR**

**[B]. Answer the following :** [6]

(1). Discuss "effect of electronegativity on chemical shift in $^1$H-NMR".
(2). "*N,N*-Dimethyl formamide (DMF) gives to signals in $^1$H-NMR at room temperature while only two signals above 123°C." Explain.

**Q. 5.**

**[A]. Answer the following :** [6]

(1). Discuss various DEPT-$^{13}$C NMR spectra and information obtained from them.
(2). Sketch **'broad band decoupled'** and **'off-resonance'** $^{13}$C-NMR spectra for 1-nitro propane by taking approximate δ-value for each signal.

**[B].** Calculate $^{13}$C NMR chemical shift for the following compounds. [6]
(i) 3-Methyl pentane, (ii) 3-Pentanol, (iii) Phenol

**OR**

**[B]. Answer the following :** [6]

(1). Draw $^1$H-$^1$H COSY and HETCOR spectra for **2-butanol** by taking approximate chemical shift value for each signal.
(2). Predict number of signals for following deutarated solvents in $^{13}$C NMR. Give multiplicity for each signal.
(i) Pyridine-$d_5$, (ii) Dimethyl sulfoxide-$d_6$ (iii) Chloroform-d

**Q. 6.**

**[A].** Enlist different ionization techniques used in mass spectrometry. Discuss any three of them in detail. [6]

**[B]. Answer the following :** [6]

(1). Discuss general rules for predicting prominent peaks in EI-Mass spectra.
(2). Write fragmentation pattern for following compounds.
(i) Hexanoic acid, (ii) Benzene, (iii) 2-Pentanone.

**OR**

**[B]. Attempt the following :** [6]

(1). What is nitrogen rule? Discuss in detail with examples.
(2). How will you distinguish following isomers using mass spectrometry?
(i) 2-Pentanol, (ii) 2-Methyl-2-butanol, (iii) 1-Pentanol

—x—

(3)

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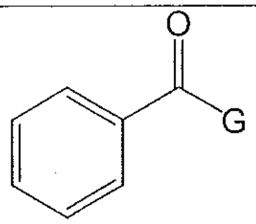
| Table 1. Characteristics absorptions for dienes | |
|---|---|
| Base value for homo-annular diene | 253 nm |
| Base value for hetero-annular diene | 214 nm |
| **Increment for:** | |
| Double bond extending conjugation | +30 nm |
| Alkyl substituent or ring residue | +5 nm |
| Exocyclic double bond | +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 |

| **Increment for each substituent on aromatic ring:** | | |
|---|---|---|
| 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 |

(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 |

## Characteristic Infrared Absorption Frequencies

| Bond | Compound type | Frequency range, cm$^{-1}$ |
|---|---|---|
| C-H | Alkanes | 2850-2960<br>1350-1470 |
| C-H | Alkenes | 3020-3080 (m)<br>675-1000 |
| C-H | Aromatic rings | 3000-3100 (m)<br>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<br>Hydrogen bonded alcohols, phenols<br>Carboxylic acids | 3610-3640 (v)<br>3200-3600 (broad)<br>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<br>1345-1385 |

## CHARACTERISTIC PROTON CHEMICAL SHIFTS

| Type of proton | | Chemical shift, ppm |
|---|---|---|
| | | $\delta$ |
| Cyclopropane | | 0.2 |
| Primary | $RCH_3$ | 0.9 |
| Secondary | $R_2CH_2$ | 1.3 |
| Tertiary | $R_3CH$ | 1.5 |
| Vinylic | $C{=}C{-}H$ | 4.6–5.9 |
| Acetylenic | $C{\equiv}C{-}H$ | 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)

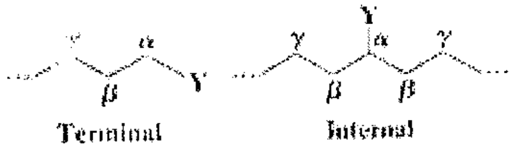
Table 5.1 The $^{13}C$ Shift Parameters in Some Linear and Branched Hydrocarbons

| $^{13}C$ Atoms | Shift (ppm) (A) |
|---|---|
| α | +9.1 |
| β | +9.4 |
| γ | −2.5 |
| δ | +0.3 |
| $1^\circ (3^\circ)^a$ | −1.1 |
| $1^\circ (4^\circ)^a$ | −3.4 |
| $2^\circ (3^\circ)^a$ | −2.5 |
| $2^\circ (4^\circ)$ | −7.2 |
| $3^\circ (2^\circ)$ | −3.7 |
| $3^\circ (3^\circ)$ | −9.5 |
| $4^\circ (1^\circ)$ | −1.5 |

Table 5.2 The $^{13}C$ 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)



| | α | | β | | γ |
|---|---|---|---|---|---|
| Y | Terminal | Internal | Terminal | Internal | |
| $CH_3$ | +9 | +6 | +10 | +8 | −2 |
| $CH{=}CH_2$ | +20 | | +6 | | −0.5 |
| $C{\equiv}CH$ | +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

Chemical shift (δ) = 72 + Σ(increments for carbon atoms)

$$C-C-C-C-C{\equiv}C-C-C-C-C$$

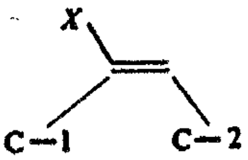
| | δ | γ | β | α | | α′ | β′ | γ′ | δ′ |
|---|---|---|---|---|---|---|---|---|---|
| increments | +0.5 | 0 | +5 | +7 | | −6 | +2 | −1 | +0.5 |

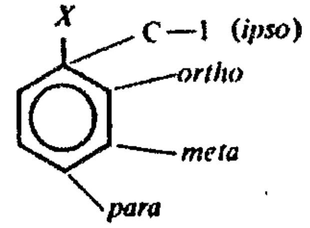
base value 72

④

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

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





| | 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 |
| $-CH{\equiv}CH$ | – | – | −6 | 4 | 0 | 0 |
| $-C_6H_5$, —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 |
| $-SO_3H$, $-SO_2N<$ | – | – | 16 | 0 | 0 | 4 |
| $-PMe_2$ | – | – | 14 | 1.6 | 0 | −1 |
| $-PAr_2$ | – | – | 9 | 5 | 0 | 0 |

(P.T.O)

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

$$X—\underset{\alpha}{C}—\underset{\beta}{C}—\underset{\gamma}{C}—C$$

| | α-shift | | | β-shift | γ-shift |
|---|---|---|---|---|---|
| X | $X—CH_2—$ | $X—\underset{R}{CH}—$ | $X—\overset{R}{\underset{R}{C}}—$ | | |
| | 1° or | 2° or | 3° | | |
| —$CH_3$ | 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 |
| —$C{\equiv}CH$ | 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 |

**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[a]

| 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 |
| $CH_2CH_3$ | 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 ($CH_2$) |
| $C{\equiv}CH$ | −5.8 | 6.9 | 0.1 | 0.4 | 84.0 (C), 77.8 (CH) |
| $C_6H_5$ | 12.1 | −1.8 | −0.1 | −1.6 | |
| $CH_2OH$ | 13.3 | −0.8 | −0.6 | −0.4 | 64.5 |
| $CH_2O(C{=}O)CH_3$ | 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 |
| $OC_6H_5$ | 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) |
| $(C{=}O)C_6H_5$ | 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 | |
| $C{\equiv}N$ | −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 |
| $SO_2NH_2$ | 15.3 | −2.9 | 0.4 | 3.3 | |
| $Si(CH_3)_3$ | 13.4 | 4.4 | −1.1 | −1.1 | |

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

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