

82
10
86
A87 & A88

SARDAR PATEL UNIVERSITY
M.Sc. Semester – IV
(Organic/Analytical/Inorganic/Physical/Industrial Polymer Chemistry)
Examination
Tuesday, 5th April 2016
(PS04CORC01/PS04CANC01/PS04CINC01/PS04CPHC01/PS04CIPC01)

Spectroscopy-II

Time: 02:30 pm to 05:30 pm

Total Marks: 70

Note: Right hand figures indicate marks.

- Q. 1 Select the correct answer in the following. 08
- The number of fundamental vibrations for CO₂ is
 - Two
 - Three
 - Four
 - One
 - In UV, the highest energy electronic transition is
 - $n \rightarrow \sigma^*$
 - $n \rightarrow \pi^*$
 - $\pi \rightarrow \pi^*$
 - $\sigma \rightarrow \sigma^*$
 - The Pople notation for the protons present in p-chloro nitro benzene is
 - A₂X₂
 - AA'XX'
 - A₄
 - A₂B₂
 - In PMR, vicinal coupling is
 - ³J coupling
 - ²J coupling
 - ¹J coupling
 - ⁴J coupling
 - In ¹³C NMR, Phenanthrene will give
 - 14 signals
 - 4 signals
 - 7 signals
 - 10 signals
 - In proton coupled ¹³C NMR, the methylene group will give
 - Singlet
 - Triplet
 - Doublet
 - Quartet
 - In the molecular ion peak region, the mass spectrum of a compound containing two bromine atoms 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
 - The DEPT-135° spectrum will not show signal for
 - CH₃ carbon
 - CH₂ carbon
 - CH carbon
 - quaternary carbon

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

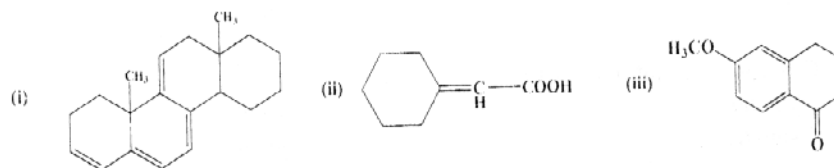
1. Explain Fermi resonance observed in IR spectroscopy.
2. In IR, the C=C stretching band is observed in 1-propyne but it is absent in acetylene. Explain.
3. With suitable example explain the terms chromophore and auxochrome.
4. Sketch the PMR spectrum for 1-nitro propane by taking approximate δ value for each signal and showing appropriate multiplicity.
5. Draw the structure of three isomeric difluoroethylenes. Show that protons present in each isomer are chemically equivalent but magnetically not equivalent.
6. Sketch the proton coupled and decoupled ^{13}C NMR spectra for n-pentane.
7. Indicate the number of signals along with approximate position and multiplicity observed in ^{13}C NMR spectra for acetone- d_6 and dimethylsulfoxide (DMSO)- d_6 .
8. Do the mass fragmentation of benzamide.
9. Sketch the ^1H - ^1H COSY spectrum for ethyl chloride by taking approximate δ value for each signal.

Q. 3 A. Answer the following.

(i) With suitable examples explain the effect of conjugation and H-bonding on C=O stretching absorptions of ketones in IR.

(ii) State and explain the Beer-Lambert law.

B. Calculate λ_{max} for the following molecules.



OR

B. Discuss the important characteristic vibrations observed in the IR spectra of acids and amides.

Q. 4 A. (i) Explain spin-spin coupling in PMR and discuss germinal and long range couplings in detail.

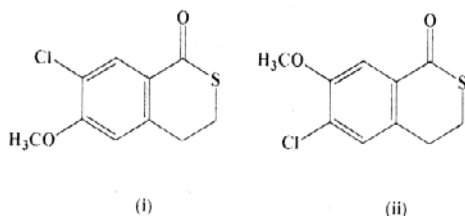
(ii) List the methods used for simplification of PMR spectra. Discuss the use of shift reagents in detail.

OR

- A. (i) A compound has a molecular formula C_8H_9Cl . It gives the following signals in PMR spectrum. Assign the structure of the compound by interpreting PMR data. 03

| Signal position(δ) | Multiplicity | Protons |
|-----------------------------|--------------|---------|
| 2.30 | Singlet | 3H |
| 4.50 | Singlet | 2H |
| 7.20 | Multiplet | 4H |

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

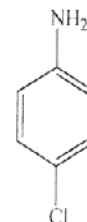


- B. (i) What is chemical shift equivalence? Dimethylformamide, in its PMR spectrum shows two separate signals for two methyl groups at room temperature but it shows only one signal for two methyl groups at 123 °C. Explain. 03

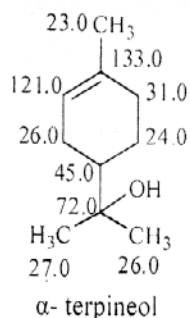
- (ii) Sketch the expected PMR spectrum for pure ethanol and show that it is an AMX system with two different coupling constants. 03

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

- (i) $H_2C=CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CN$ (ii) $H_2C=CH-O-C(=O)-CH_2-CH_3$ (iii)



- B. (i) Sketch proton decoupled ^{13}C NMR, DEPT 45°, DEPT 90° and DEPT 135° spectra for α -terpineol. (δ values for each carbon is assigned in the structure) 03



- (ii) Calculate the chemical shift values for carbon signals and sketch the proton coupled and decoupled ^{13}C NMR spectra for p-methoxy benzaldehyde. 03

OR

- B. (i) Sketch the HMBC spectrum for 3-heptanone by taking approximate δ value for each signal. 03

- (ii) A compound with molecular formula $\text{C}_5\text{H}_{10}\text{O}_2$ shows following signals in its proton coupled ^{13}C NMR. Interpret the data and assign the structure to the compound. 03

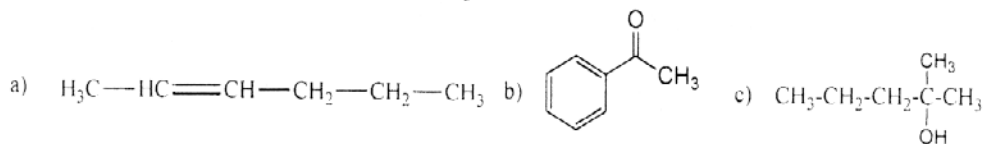
20.4 δ (quartet)

21.4 δ (quartet)

66.8 δ (doublet)

170 δ (singlet)

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



- B. (i) Discuss Chemical Ionization (CI) and MALDI techniques used in mass spectroscopy. 03

- (ii) Discuss McLafferty rearrangement in detail with suitable examples. 03

OR

- B. A compound has molecular formula $\text{C}_8\text{H}_8\text{O}_2$. It gives the following spectral data. Interpret the spectral data and determine the structure of the compound. 06

IR: 3100, 1765, 1594, 1493, 1371, 1193, 1031, 925, 749 and 692 cm^{-1}

^1H NMR:

| Signal (δ) | Multiplicity | Protons |
|---------------------|--------------|---------|
| 2.30 | Singlet | 3H |
| 7.1-7.4 | Multiplet | 5H |

^{13}C NMR: 23.9, 121.7, 125.3, 128.1, 151.1 and 169.7 δ

Mass(m/z): 136, 95, 94, 77, 66, 65, 63, 52, 50, 43

CHARACTERISTIC PROTON CHEMICAL SHIFTS

| Type of proton | Chemical shift, ppm |
|--------------------|----------------------|
| Cyclopropane | δ 0.2 |
| Primary | RCH_3 0.9 |
| Secondary | R_2CH_2 1.3 |
| Tertiary | R_3CH 1.5 |
| Vinyllic | $C=C-H$ 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 | $C=C-CH_2$ 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 | $R-CHO$ 9-10 |
| Hydroxylic | $R-OH$ 1-5.5 |
| Phenolic | $Ar-OH$ 4-12 |
| Enolic | $C=C-OH$ 15-17 |
| Carboxylic | $RCOOH$ 10.5-12 |
| Amino | RNH_2 1-5 |

Characteristic Infrared Absorption Frequencies

| Bond | Compound type | Frequency range, cm^{-1} |
|------------------|--|----------------------------|
| 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 ₂ | Nitro compounds | 1515-1560 1345-1385 |

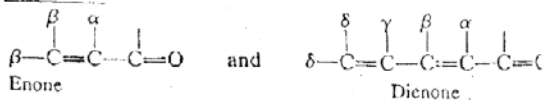
Characteristic absorption for dienes

| | |
|------------------------------------|-----|
| 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 |
| SAlk | +30 |
| Cl, Br | +5 |
| N(Alk) ₂ | +60 |
| Solvent correction ^a | +0 |
| $\lambda_{calc} = \text{Total}$ | |

Characteristic absorption for substituted benzene derivatives

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

Characteristic absorption for α, β -unsaturated carbonyl compounds



| Base values | (nm) |
|---|------|
| Acyclic α, β -unsaturated ketones | 215 |
| Six-membered cyclic α, β -unsaturated ketones | 215 |
| Five-membered cyclic α, β -unsaturated ketones | 202 |
| α, β -Unsaturated aldehydes | 210 |
| α, β -Unsaturated carboxylic acids and esters | 195 |

| Increments for | | |
|-----------------------------------|-------------------------|-----|
| Double bond extending conjugation | | +30 |
| Alkyl group, ring residue | α | +10 |
| | β | +12 |
| | γ and higher | +18 |
| Polar groupings: —OH | α | +35 |
| | β | +30 |
| | δ | +50 |
| —OAc | α, β, δ | +6 |
| —OMe | α | +35 |
| | β | +30 |
| | γ | +17 |
| | δ | +31 |
| —SAlk | β | +85 |
| —Cl | α | +15 |
| | β | +12 |
| —Br | α | +25 |
| | β | +30 |
| —NR ₂ | β | +95 |
| Exocyclic double bond | | +5 |
| Homodiene component ^a | | +39 |

¹³C shifts for terminal and internal systems

| Y | α | | β | | γ |
|------------------------------|----------|----------|----------|----------|------|
| | Terminal | Internal | Terminal | Internal | |
| CH ₃ | + 9 | + 6 | +10 | + 8 | -2 |
| CH=CH ₂ | +20 | | + 6 | | -0.5 |
| C≡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 |
| CO ₂ R | +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 |

¹³C 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 | 11.5 | 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) | |

¹³C shifts for substituted benzenes
Base value for benzene is 128.5 ppm

| 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 ₂ CH 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≡CH | -5.8 | +6.9 | +0.1 | +0.4 | 84.0 (C), 77.8 (CH) |
| C ₆ H ₅ | +12.1 | -1.8 | -0.1 | -1.6 | |
| CH ₂ OH | +13.3 | -0.8 | -0.6 | -0.4 | 64.5 |
| CH ₂ OOCH ₃ | +7.7 | -0.0 | -0.0 | -0.0 | 20.7 (CH ₂), 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 ₂ H ₅ | +29.0 | -9.4 | +1.6 | -5.3 | |
| OOCH ₃ | +22.4 | -7.1 | -0.4 | -3.2 | 23.9 (CH ₂), 169.7 (C=O) |
| OCH | +8.2 | +1.2 | +0.6 | +5.8 | 192.0 |
| OCH ₂ | +7.8 | -0.4 | -0.4 | +2.8 | 24.6 (CH ₂), 195.7 (C=O) |
| OC ₂ H ₅ | +9.1 | +1.5 | -0.2 | +3.8 | 196.4 (C=O) |
| OCF ₃ | -5.6 | +1.8 | +0.7 | +6.7 | |
| COH | +2.9 | +1.3 | +0.4 | +4.3 | 168.0 |
| COCH ₃ | +2.0 | +1.2 | -0.1 | +4.8 | 51.0 (CH ₃), 166.8 (C=O), 168.5 |
| CCl | +4.6 | +2.9 | +0.6 | +7.0 | |
| CNH ₂ | +5.0 | -1.2 | 0.0 | +3.4 | |
| C≡N | -16.0 | +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 |
| NHCOCH 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 ₂ NH ₂ | +15.3 | -2.9 | +0.4 | +3.3 | |
| Si(CH ₃) ₃ | +13.4 | +4.4 | -1.1 | -1.1 | |

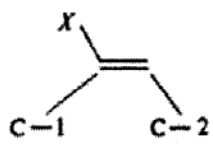
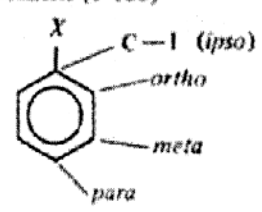
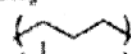

Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X-C-C-C-C$$

$$\alpha \quad \beta \quad \gamma$$

| X | α -shift | | | β -shift | γ -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 | | | | | |
| 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 ₆ H 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 ₃ H, -SO ₂ N< | 50 | - | - | 3 | 0 |

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≡CH | - | - | -6 | 4 | 0 | 0 |
| -C ₆ H 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 ₃ H, -SO ₂ N< | - | - | 16 | 0 | 0 | 4 |
| -PMe ₂ | - | - | 14 | 1.6 | 0 | -1 |
| -PAr ₂ | - | - | 9 | 5 | 0 | 0 |