SECTION-III

CHARACTERIZATION
INFRA RED SPECTROSCOPY

Infrared Spectroscopy is widely employed for research in organic chemistry, such as in the quantitative analysis of structural units in unknown compounds. In the hands of theoretical physicists, the spectra can be used to obtain fundamental data on the mechanics of simple molecules. These studies are extremely useful to the analysis, in that the particular motion associated with various characteristic frequencies are determined. So that it is possible to assess to some extent the frequency shifts occurring with changes in the local environment of the group.

Infra red radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. The infrared region of the electromagnetic spectrum extends from 14,000 cm\(^{-1}\) to 10 cm\(^{-1}\). From application and instrumentation point of view, the infra red region has been subdivided into near, middle and far infra red region. The region of most interest for chemical analysis is the mid-infra red region (4,000 cm\(^{-1}\) to 400 cm\(^{-1}\)) which corresponds to changes in vibrational energies within molecules. The far infra red region (400 cm\(^{-1}\) to 10 cm\(^{-1}\)) is useful for molecules containing heavy atoms such as inorganic compounds but requires rather specialized experimental techniques.

Infrared spectra (\(v_{\text{max}}\) in cm\(^{-1}\)) of synthesized derivatives have been scanned in KBr pellets by using Thermo Scientific Nicolet iS10 FT-IR Spectrophotometer instrument at Department of Chemistry, Veer Narmad South Gujarat University, Surat. In this instrument highly purified and desiccated 100 mg of KBr and 4 to 5 mg of sample was mixed thoroughly and grounded in a mortar. The finely grounded mixture was then transferred to the mould and the pellets of high transparency were prepared by pressing on the hydraulic press. The pellets prepared in this manner were used to scan Infrared spectra of the sample.

Infrared spectroscopy shows two distinct characteristics for sydnones. The most characteristic feature is the very strong carbonyl stretching band in
the range 1718-1770 cm\(^{-1}\). Usually this consists of a single peak, but occasionally multiple peaks occur.\(^{403}\) This effect is due to Fermi resonance splitting. The carbonyl absorption of γ–lactones is near 1740 cm\(^{-1}\) while that of tropone is at 1638 cm\(^{-1}\), and it has been suggested that this is evidence against the mesoionic structure for sydnones.

On the other hand, Zaitsev and Sheinker\(^{404}\) have measured the integrated absorption of sydnone carbonyl bands for a number of the compounds. The values obtained (6-12×10\(^4\) mol/cm\(^2\)) are greater than those for other carbonyl compounds (1.5-5.7×10\(^4\) mol/cm\(^2\)) and were taken to indicate that the bond is highly polarized as a result of the electron drift required by the mesoionic formula.

Another characteristic band C-H stretch absorption with medium intensity at ~3150 cm\(^{-1}\) for the C-4 ring position (when present). The C-H absorption for the C-4 position (when present) is different from what is normally expected for an alkyl or aryl substituent or from an epoxide with similar ring strain, which shows the absorption around 2900-3050 cm\(^{-1}\). This makes this absorption useful in determining whether or not the C-4 position is substituted in a sydnone with an unresolved structure.

The characteristic group frequencies were showed by Silverstein \textit{et al.}\(^{405}\) Workman and Weyer,\(^{406}\) Stuart.\(^{407}\) A thorough coverage of characteristic group frequencies is also presented in the treatise of Jones and Sandorfy,\(^ {408}\) Smith’s text,\(^ {409}\) and Socrates\(^ {410}\) is to be recommended for its concise presentation of group frequencies in tubular form along with illustrative spectra.
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IR Spectrum of compound (YA₁)

IR (KBr, cm⁻¹): 3312 (N-H, SO₂NH), 3010 (C-H, Ar.), 2912 (C-H, CH₃), 2854 (C-H, CH₃), 1753 (C=O, sydnone), 1605 (C=O, chalcone), 1545 (CH=CH), 1320 (S=O), 1175 (S=O).

Figure: 1
CHARACTERIZATION

IR Spectrum of compound (YA₆)

Figure: 2

IR (KBr, cm⁻¹): 3352 (N-H, SO₂NH), 3018 (C-H, Ar.), 2916 (C-H, CH₃), 2857 (C-H, CH₃), 1756 (C=O, sydnone), 1605 (C=O, chalcone), 1554 (CH=CH), 1298 (S=O), 1132 (S=O) 1542 (N=O), 1346 (N=O).
IR Spectrum of compound (YB₁)

Figure: 3

IR (KBr, cm⁻¹): 3386 (N-H, SO₂NH), 3059 (C-H, Ar.), 2922 (C-H, CH₃), 2874 (C-H, CH₃), 1753 (C=O, sydnone), 1653 (C=N, isoxazole), 1317 (S=O), 1176 (S=O).
IR Spectrum of compound (YB₆)

Figure: 4

IR (KBr, cm⁻¹): 3387 (N–H, SO₂NH), 3008 (C–H, Ar.), 2921 (C–H, CH₃), 2848 (C–H, CH₃), 1750 (C=O, sydnone), 1654 (C=N, isoxazole), 1312 (S=O), 1177 (S=O) 1518 (N=O), 1346 (N=O).
IR Spectrum of compound (YC₁)

IR (KBr, cm⁻¹): 3378 (N-H, SO₂NH), 3026 (C-H, Ar.), 2921 (C-H, CH₃), 2853 (C-H, CH₃), 1753 (C=O, sydnone), 1688 (C=N, benzodiazepines), 1337 (S=O), 1142 (S=O) 1542 (N=O), 1346 (N=O).

Figure: 5
IR Spectrum of compound (YC6)

IR (KBr, cm\(^{-1}\)): 3358 (N=H, SO\(_2\)NH), 3009 (C-H, Ar.), 2932 (C-H, CH\(_3\)), 2846 (C-H, CH\(_3\)), 1748 (C=O, sydnone), 1687 (C=N, benzodiazepines), 1352 (S=O), 1179 (S=O), 1522 (N=O), 1346 (N=O).
IR Spectrum of compound (YD₁)

![Chemical Structure](image)

**Figure: 7**

**IR (KBr, cm⁻¹):**
- 3342 (N-H, SO₂NH),
- 3068 (C-H, Ar.),
- 2923 (C-H, CH₃),
- 2852 (C-H, CH₃),
- 1757 (C=O, sydnone),
- 1598 (C=N, pyrazoline),
- 1174 (C=N, pyrazoline),
- 1320 (S=O),
- 1132 (S=O).
IR Spectrum of compound (YD₆)

IR (KBr, cm⁻¹): 3314 (N-H, SO₂NH), 3060 (C-H, Ar.), 2910 (C-H, CH₃), 2850 (C-H, CH₃), 1752 (C=O, sydnone), 1598 (C=N, pyrazoline), 1178 (C-N, pyrazoline), 1321 (S=O), 1109 (S=O), 1518 (N=O), 1197 (N=O).
**IR Spectrum of compound (YE₁)**

![IR Spectrum of compound (YE₁)](image)

**Figure: 9**

**IR (KBr, cm⁻¹):** 3420 (NH₂), 3316 (N-H, SO₂NH), 3048 (C-H, Ar.), 2909 (C-H, CH₃), 2852 (C-H, CH₃), 1750 (C=O, sydnone), 2194 (C=N, cyanopyran), 1545 (C-N, cyanopyran), 1320 (S=O), 1178 (S=O).
IR Spectrum of compound (YE₆)

IR (KBr, cm⁻¹): 3422 (NH₂), 3342 (N-H, SO₂NH), 3080 (C-H, Ar.), 2912 (C-H, CH₃), 2835 (C-H, CH₃), 1750 (C=O, sydnone), 2194 (C=N, cyanopyran), 1597 (C-N, cyanopyran), 1352 (S=O), 1129 (S=O) 1518 (N=O), 1196 (N=O).
IR Spectrum of compound (YF₁)

**Figure: 11**

**IR (KBr, cm⁻¹):** 3378 (N-H, SO₂NH), 3078 (C-H, Ar.), 2922 (C-H, CH₃), 2857 (C-H, CH₃), 1746 (C=O, sydnone), 2217 (C=N, cyanopyridine), 1341 (S=O), 1152 (S=O), 1176 (C-O-C).
IR Spectrum of compound (YF₆)

IR (KBr, cm⁻¹): 3382 (N-H, SO₂NH), 3073 (C-H, Ar.), 2926 (C-H, CH₃), 2868 (C-H, CH₃), 1752 (C=O, sydnone), 2209 (C=N, cyanopyridine), 1352 (S=O), 1152 (S=O), 1137 (C-O-C), 1516 (N=O), 1197 (N=O).

Figure: 12
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The phenomenon of nuclear magnetic resonance was first reported independently in 1946 by two groups of physicists: Block, Hansen and Packard at Stanford University detected a signal from the protons of water, and Purcell, Torrey and Pound at Harvard University observed a signal from the protons in paraffin wax. Block and Purcell were jointly awarded the Nobel Prize for physics in 1952 for this discovery. Since that time, the advances in the NMR techniques leading to wide spread applications in various branches of science resulted in the Nobel Prize in chemistry in 1991. The applications of NMR in clinical, solid state and biophysical sciences are really excellent.411

Nuclear magnetic resonance (NMR) is one of the latest physical methods of investigating organic compounds. The practical application of NMR spectroscopy to the study of the complex organic compounds became possible only after the discovery in 1951 that the spectrum of ethyl alcohol consists of three individual signals corresponding to the resonance of methyl, methylene and hydroxyl protons. Further these signals of different groups of magnetic nuclei in liquid molecules give rise to further fine splitting, which depends on the number and character of the nuclei contained in the molecule.

The most appropriate starting point for a study of PMR is the proton. From PMR, one can get information about (a) How many types of hydrogen? (b) How many of each type? (c) What types of hydrogen? (d) How are they connected? etc.

The scale of the spectrum is usually marked in parts per million (ppm) of the applied field or in frequency units (Hz). High resolution $^1$H NMR is considered another powerful technique and has been used in the investigation of organic structure.412

The NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer using DMSO d$_6$ as a solvent and Tetramethylsilane (TMS) as an internal reference (chemical shifts in δ, ppm) at SAIF (Sophisticated Analytical Instrument Facilities), Chandigarh.
PMR spectrum of compound (YA₁)

Figure: 13

$^1$H NMR (400 MHz, DMSO-d₆, δ ppm): 2.36 (s, 3H, -CH₃), 6.64-6.67 (d, 1H, -CO-CH, chalcone), 7.42-7.46 (d, 1H, =CH-Ar, chalcone), 7.72-8.92 (m, 13H, Ar-H), 9.64 (s, 1H, -SO₂NH).
CHARACTERIZATION

PMR spectrum of compound (YA₆)

Figure: 14

¹H NMR (400 MHz, DMSO-d₆, δ ppm): 2.36 (s, 3H, -CH₃), 6.46-6.48 (d, 1H, -CO-CH, chalcone), 7.42-7.45 (d, 1H, =CH-Ar, chalcone), 7.70-8.64 (m, 12H, Ar-H), 9.64 (s, 1H, -SO₂NH).
**PMR spectrum of compound (YB₁)**

![PMR spectrum](image)

**Figure: 15**

**¹H NMR (400 MHz, DMSO-d₆, δ ppm):** 2.78 (s, 3H, -CH₃), 6.82 (s, 1H, -CH, isoxazole), 7.10-8.12 (m, 13H, Ar-H), 9.67 (s, 1H, -SO₂NH).
PMR spectrum of compound (YB₆)

\[
\begin{align*}
\text{H}_3\text{C} &- \text{N}^- \text{SO} - \text{NH} - \text{N}^- \text{SO} - \text{NO}_2 \\
\end{align*}
\]

Figure: 16

\[^1\text{H NMR (400 MHz, DMSO-}d_6, \delta \text{ ppm}): \] 2.43 (s, 3H, -CH₃), 6.78 (s, 1H, -CH, isoxazole), 7.03-8.04 (m, 12H, Ar-H), 9.68 (s, 1H, -SO₂NH).
PMR spectrum of compound (YC₁)

Figure: 17

¹H NMR (400 MHz, DMSO-d₆, δ ppm): 2.24 (s, 3H, -CH₃), 7.24 (s, 1H, -NH, benzodiazepine), 8.35 (s, 1H, -CH, benzodiazepine), 6.73-8.46 (m, 17H, Ar-H), 9.28 (s, 1H, -SO₂NH).
PMR spectrum of compound (YC₆)

Figure: 18

¹H NMR (400 MHz, DMSO-d₆, δ ppm): 2.52 (s, 3H, -CH₃), 7.12 (s, 1H, -NH, benzodiazepine), 8.30 (s, 1H, -CH, benzodiazepine), 6.92-8.89 (m, 16H, Ar-H), 9.60 (s, 1H, -SO₂NH).
PMR spectrum of compound (YD₁)

\[
\begin{align*}
\text{PMR spectrum of compound (YD₁)}
\end{align*}
\]

Figure: 19

\(^1\text{H NMR (400 MHz, DMSO-}d_6, \delta \text{ ppm):} \ 2.46 \ (s, \ 3\text{H, } -\text{CH}_3), \ 2.18-2.28 \ (dd, \ 1\text{H, } -\text{CH}_2, \text{ pyrazoline}), \ 2.74-2.86 \ (dd, \ 1\text{H, } -\text{CH}_2, \text{ pyrazoline}), \ 5.47-5.55 \ (dd, \ 1\text{H, } -\text{CH}, \text{ pyrazoline}), \ 6.70 \ (s, \ 1\text{H, } -\text{NH}, \text{ pyrazoline}), \ 6.86-8.00 \ (m, \ 13\text{H, } \text{Ar-H}), \ 9.58 \ (s, \ 1\text{H, } -\text{SO}_2\text{NH}).
\]
PMR spectrum of compound (YD₆)

Figure: 20

¹H NMR (400 MHz, DMSO-d₆, δ ppm): 2.36 (s, 3H, -CH₃), 2.23-2.32 (dd, 1H, -CH, pyrazoline), 2.78-2.82 (dd, 1H, -CH, pyrazoline), 5.47-5.54 (dd, 1H, -CH, pyrazoline), 6.56 (s, 1H, -NH, pyrazoline), 7.21-8.30 (m, 12H, Ar-H), 9.51 (s, 1H, -SO₂NH).
PMR spectrum of compound (YE₁)

**Figure: 21**

¹H NMR (400 MHz, DMSO-odka, δ ppm): 2.18 (s, 3H, -CH₃), 7.28 (s, 2H, -NH₂), 7.03-8.69 (m, 14H, Ar-H), 9.32 (s, 1H, -SO₂NH).
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PMR spectrum of compound \((\text{YE}_6)\)

![PMR spectrum image]

Figure: 22

\(^1\text{H} \text{NMR} \ (400 \text{ MHz}, \text{DMSO-d}_6, \delta \text{ ppm})\): 2.32 (s, 3H, -CH\(_3\)), 7.18 (s, 2H, -NH\(_2\)), 6.66-8.42 (m, 13 H, Ar-H), 9.64 (s, 1H, -SO\(_2\)NH).
PMR spectrum of compound (YF₁)

\[
\text{H NMR (400 MHz, DMSO-d\textsubscript{6}, } \delta \text{ ppm): 2.54 (s, 3H, -CH\textsubscript{3}), 3.36 (s, 3H, -OCH\textsubscript{3}), 7.14-8.21 (m, 14H, Ar-H), 9.51 (s, 1H, -SO\textsubscript{2}NH).}
\]
PMR spectrum of compound (YF₆)

Figure: 24

$^1$H NMR (400 MHz, DMSO-d₆, δ ppm): 2.24 (s, 3H, -CH₃), 3.57 (s, 3H, -OCH₃), 7.09-8.28 (m, 13H, Ar-H), 9.52 (s, 1H, -SO₂NH).