INFRA RED SPECTROSCOPY

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by chemists. When infrared light is passed through a sample of an organic compound, some of the frequencies are absorbed, while other frequencies are transmitted through the sample without being absorbed. If we plot absorbance or transmittance against frequency, the result is an infrared spectrum.

The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of infrared radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

Infrared 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 infrared region has been subdivided into near, middle and far infrared region. The region of most interest for chemical analysis is the mid-infrared region (4,000 cm\(^{-1}\) to 400 cm\(^{-1}\)) which corresponds to changes in vibrational energies within molecules. The far infrared 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.

(A) Characteristic group frequencies of sydnones:
Infrared spectroscopy shows two distinct characteristics for sydnones. The most characteristic feature is the very strong carbonyl stretching band in the range 1770-1718 cm\(^{-1}\). Usually this consists of a single peak, but occasionally multiple peaks occur.\(^{200}\) This effect is due to Fermi resonance splitting. The carbonyl absorption of γ-lactones (i) is near 1740 cm\(^{-1}\) while that of tropone (ii) is at 1638 cm\(^{-1}\), and it has been suggested that this is evidence against the mesoionic structure [9] for sydnones.
On the other hand, Zaitsev and Sheinker\textsuperscript{201} have measured the integrated absorption of sydnone carbonyl bands for a number of the compounds. The values obtained (6-12 x 10\textsuperscript{4} mole\textsuperscript{-1} l/cm\textsuperscript{2}) are greater than those for other carbonyl compounds (1.5-5.7 x 10\textsuperscript{4} mole\textsuperscript{-1} l/cm\textsuperscript{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\textsuperscript{-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\textsuperscript{-1}. This makes this absorption useful in determining whether or not the C-4 position is substituted in a sydnone with an unresolved structure.\textsuperscript{64}

(B) Characteristic group frequencies of organic molecules:

This is concerned with a comprehensive look at these characteristic group frequencies and their relationship to molecular structure. No attempt has been made to present a detailed discussion of all the available information concerning the group frequencies or to discuss all of the compound classes. Much more extensive coverage may be found in the text of Colthup et al.\textsuperscript{202} and L. J. Bellamy.\textsuperscript{203} A through coverage of characteristic group frequencies is also presented in the treatise of Jones and Sandorfy,\textsuperscript{204} Nakanishi’s text,\textsuperscript{205} Silverstein et al.\textsuperscript{206} and Williams et al.\textsuperscript{207} is to be recommended for its concise presentation of group frequencies in tubular form along with illustrative spectra.
IR Spectrum of compound (1b)

IR (KBr, cm⁻¹): 3325 (N-H, SO₂NH), 1743 (C=O, sydnone), 1512 (NO₂), 1340 (NO₂), 1366 (S=O), 1177 (S=O), 1240 (C-O-C), 1028 (C-O-C).

Figure: 1
CHARACTERIZATION

IR Spectrum of compound (1f)

\[
\begin{array}{c}
\text{H}_3\text{CO}-\begin{array}{c}
\text{N} \\
\text{N}
\end{array}-\text{SO}_2-\begin{array}{c}
\text{NH} \\
\text{N}
\end{array}-\text{CH}_3
\end{array}
\]

Figure: 2

\textbf{IR (KBr, cm}^{-1}\text{): 3350 (N-H, SO}_2\text{NH), 2912 (C-H, CH}_3\text{), 2854 (C-H, CH}_3\text{),}
\text{1743 (C=O, sydnone), 1366 (S=O), 1166 (S=O), 1247 (C-O-C), 1025 (C-O-C).}
IR Spectrum of compound (2f)

\[
\begin{align*}
\text{IR (KBr, cm}^{-1} & \): 3344 (N-H, SO_2NH), 1741 (C=O, sydnone), 1520 (NO_2), \\
& 1327 (NO_2), 1380 (S=O), 1178 (S=O), 1242 (C-O-C), 1025 (C-O-C).
\end{align*}
\]
CHARACTERIZATION

IR Spectrum of compound (2j)

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{N} \quad \text{SO}_2\text{NH} \\
\text{N} & \quad \text{O} \quad \text{CN}
\end{align*}
\]

Figure: 4

**IR (KBr, cm}^{-1})**: 3320 (N-H, SO\textsubscript{2}NH), 2235 (C≡N), 1743 (C=O, sydnone), 1381 (S=O), 1165 (S=O), 1265 (C-O-C), 1018 (C-O-C).
IR Spectrum of compound (3c)

Figure: 5

IR (KBr, cm\(^{-1}\)): 1742 (C=O, sydnone), 1359 (S=O), 1165 (S=O), 1250 (C-O-C), 1019 (C-O-C), 791 (C-Cl).
CHARACTERIZATION

IR Spectrum of compound (3d)

\[
\begin{align*}
&\text{H}_3\text{CO}-\text{N} & \text{N} & \text{SO}_2 \\
&\text{H}_3\text{CO}-\text{N} & \text{N} & \text{O} & \text{CO}
\end{align*}
\]

**Figure: 6**

**IR (KBr, cm}^{-1}): 1743 (C=O, sydnone), 1370 (S=O), 1170 (S=O), 1259 (C-O-C), 1015 (C-O-C).
IR Spectrum of compound (4b)

IR (KBr, cm\(^{-1}\)): 3257 (N-H, \(\text{CH}_2\text{NH}\)), 2952 (C-H, \(\text{CH}_2\)), 2841 (C-H, \(\text{CH}_2\)), 1744 (C=O, sydnone), 1507 (NO\(_2\)), 1357 (NO\(_2\)), 1231 (C-O-C), 1025 (C-O-C).
CHARACTERIZATION

IR Spectrum of compound (4f)

![IR Spectrum Diagram]

Figure: 8

**IR (KBr, cm⁻¹):** 3286 (N-H, CH₂NH), 2987 (C-H, CH₃), 2942 (C-H, CH₂), 2850 (C-H, CH₂), 1752 (C=O, sydnone), 1236 (C-O-C), 1054 (C-O-C).
IR Spectrum of compound (5f)

IR (KBr, cm\(^{-1}\)): 3283 (N-H, CH\(_2\)NH), 2937 (C-H, CH\(_2\)), 2865 (C-H, CH\(_2\)), 1754 (C=O, sydnone), 1521 (NO\(_2\)), 1327 (NO\(_2\)), 1212 (C-O-C), 1048 (C-O-C).
IR Spectrum of compound (5j)

Figure: 10

IR (KBr, cm$^{-1}$): 3270 (N-H, CH$_2$NH), 2937 (C-H, CH$_2$), 2851 (C-H, CH$_2$), 2238 (C≡N), 1754 (C=O, sydnone), 1234 (C-O-C), 1034 (C-O-C).
CHARACTERIZATION

IR Spectrum of compound (6c)

Figure: 11

IR (KBr, cm\(^{-1}\)): 2925 (C-H, CH\(_2\)), 2857 (C-H, CH\(_2\)), 1753 (C=O, sydnone), 1225 (C-O-C), 1039 (C-O-C), 834 (C-Cl).
IR Spectrum of compound (6d)

\[
\begin{align*}
\text{H}_3\text{CO-} & \text{N} & \text{CH}_2 \\
\text{H}_3\text{CO-} & \text{N} & \text{O} \\
\text{N} & \text{H}_3\text{CO}
\end{align*}
\]

Figure: 12

IR (KBr, cm\(^{-1}\)): 2937 (C-H, CH\(_2\)), 2854 (C-H, CH\(_2\)), 1760 (C=O, sydnone), 1237 (C-O-C), 1021 (C-O-C).
NUCLEAR MAGNETIC RESONANCE SPECTRA

In 1946, two scientists in United States, independently of each other described a physicochemical phenomenon that was based upon the magnetic properties of certain nuclei in the periodic system. This was “Nuclear Magnetic Resonance”, in short “NMR”. The two scientists Felix Bloch and Edward M. Purcell were awarded the Nobel Prize in Physics in 1952 for this. As is implied in the name, Nuclear Magnetic Resonance (NMR) is concerned with the magnetic properties of certain atomic nuclei, notably the nucleus of the hydrogen atom - the proton and that of the carbon-13 isotope of carbon.

NMR is commonly used in organic chemistry to elucidate molecular structures and conformations by studying $^1$H and $^{13}$C nuclei. NMR is sensitive to many other nuclei, however, and is not restricted to these uses. The field of NMR continues to grow at a prodigious rate and applications of NMR can be found in virtually every field of chemistry. NMR has even lead to the development of Magnetic Resonance Imaging (MRI), an important medical imaging technique.

The most appropriate starting point for a study of NMR is the proton.

From NMR, 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.

Shoji Tanaka and Masatoki Yakoi studied molecular motion in neat 3-methyl sydnone and also studied molecular interaction in 3-methyl sydnone-water mixture by the multinuclear FT-NMR method. According to shift variation of the $^{13}$C, $^{14}$N and $^{17}$O nuclei of the sydnone molecule in sydnone-water mixture, the sydnone forms a hydrogen bond with water at the carbonyl oxygen and not at the ring oxygen site.

F. H. C. Stewart obtained NMR spectra of number of sydnones in an effort to throw more light on the electronic nature of the ring system, in particular to observe any indications of an aromatic ring current. Daeniker and Druey obtained a value for the ring proton resonance of 3-n-butylsydnone at 6.34 ppm. and considered that this value, in conjunction with those for several
sydnone imine derivatives at somewhat lower field, tended to support the mesoionic structure.

To aid in the identification of newly prepared compounds, $^1$H NMR spectroscopy was used.

**NMR spectra of sydnone:**

NMR spectra, the proton (when present) at the C-4 position of the sydnone ring is greatly deshielded in comparison to saturated congeners, usually shifted between 6.5-7.5 δ ppm (depending on solvent). This drastic shift indicates a polar nature and the presence of an aromatic ring current, further discrediting structure [18].

The resonance of 3-alkyl protons occurs at considerably lower field than that of 4-alkyl protons owing to the strong deshielding effect of the positively charged 3-nitrogen atom.

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 (1b)

$\text{H}_3\text{CO}-\begin{array}{c} \text{N} \\ \text{SO}_2-\text{NH} \end{array}$\(\text{NH})\begin{array}{c} \text{O} \\ \text{O} \end{array}-\begin{array}{c} \text{N} \\ \text{OH} \end{array}$\begin{array}{c} \text{NO}_2 \end{array}$

Figure: 13

$^1\text{H NMR (400 MHz, DMSO-d}_6$, $\delta$ ppm): 3.36 (s, 3H, -OCH$_3$), 6.89-7.96 (m, 8H, Ar-H), 8.96 (s, 1H, -SO$_2$NH).
PMR Spectrum of compound (1f)

\[
\begin{align*}
\text{H}_3\text{CO} & - \text{N} - \text{SO}_2 - \text{NH} - \text{C}_\text{H}_3 \\
\end{align*}
\]

Figure: 14

\[^1\text{H} \text{NMR (}400 \text{ MHz, DMSO-d}_6, \delta \text{ ppm):} \mathrm{2.10} \text{ (s, 3H, -CH}_3\text{), 3.88 (s, 3H, -OCH}_3\text{), 7.15-8.17 (m, 8H, Ar-H), 8.77 (s, 1H, -SO}_2\text{NH).}\]
PMR Spectrum of compound (2f)

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

Figure: 15

\(^1\text{H} \text{NMR (400 MHz, DMSO-}d_6, \delta \text{ ppm):} \) 3.89 (s, 3H, -OCH\textsubscript{3}), 7.03-8.48 (m, 7H, Ar-H), 9.80 (s, 1H, -SO\textsubscript{2}NH).
PMR Spectrum of compound (2j)

Figure: 16

$^1$H NMR (400 MHz, DMSO-$d_6$, δ ppm): 3.89 (s, 3H, -OCH$_3$), 7.11-8.95 (m, 7H, Ar-H), 9.85 (s, 1H, -SO$_2$NH).
CHARACTERIZATION

PMR Spectrum of compound (3c)

Figure: 17

$^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$ ppm): 3.89 (s, 3H, -OCH$_3$), 6.84-7.94 (m, 11H, Ar-H).
PMR Spectrum of compound (3d)

\[ \text{Figure: 18} \]

\( ^1\text{H NMR (400 MHz, DMSO-}d_6\text{, \(\delta\) ppm): 3.88 (s, 6H, -OCH}_3\text{), 7.13-7.85 (m, 12H, Ar-H).} \)
PMR Spectrum of compound (4b)

\[
\text{H}_3\text{CO-} \quad \text{N} \quad \text{CH}_2\text{-NH-} \quad \text{N} \quad \text{O-NO}_2
\]

\[\text{Figure: 19}\]

\(^1\text{H} \text{NMR (400 MHz, DMSO-}\text{d}_6, \delta \text{ ppm}):\]

3.28 (s, 2H, -CH\(_2\)-), 3.87 (s, 3H, -OCH\(_3\)), 4.84 (s, 1H, -NH-), 6.92-8.05 (m, 8H, Ar-H).
PMR Spectrum of compound (4f)

Figure: 20

$^1$H NMR (400 MHz, DMSO-d$_6$, δ ppm): 2.22 (s, 3H, -CH$_3$), 3.33 (s, 2H, -CH$_2$-), 3.89 (s, 3H, -OCH$_3$), 4.74 (s, 1H, -NH-), 6.94-8.05 (m, 8H, Ar-H).
PMR Spectrum of compound (5f)

\[
\text{CH}_2-\text{NH}\]

\[
\text{H}_3\text{CO}-\text{N}^+\text{O}^-\]

\[
\text{NO}_2
\]

\[
\text{N}\]

\[
\text{S}
\]

\[
\text{CH}_2-\text{NH}-\text{N}
\]

\[
\text{N}\]

\[
\text{O}
\]

\[
\text{O}
\]

\[
\text{S}
\]

\[
\text{N}
\]

\[
\text{NO}_2
\]

Figure: 21

\(^1\text{H NMR}\ (400 \text{ MHz, DMSO}-d_6, \delta \text{ ppm}): 3.32 (s, 2H, \text{-CH}_2\text{-}), 3.89 (s, 3H, \text{-OCH}_3), 4.89 (s, 1H, \text{-NH-}), 7.09-8.54 (m, 7H, \text{Ar-H}).\]
PMR Spectrum of compound (5j)

\[
\text{CH}_2-\text{NH} \quad \text{CN} \\
\text{H}_3\text{CO} - \text{N} \quad \text{CH}_2-\text{NH} \quad \text{S} \quad \text{N} \quad \text{CN}
\]

\[\text{H}_3\text{CO} - \text{N} \quad \text{CH}_2-\text{NH} \quad \text{S} \quad \text{N} \quad \text{CN}\]

\[\text{PMR} \quad \text{Spectrum} \quad \text{of} \quad \text{compound} \quad (5j)\]

\[\text{Figure: 22}\]

\[\text{\textsuperscript{1}H NMR (400 MHz, DMSO-}\text{d}_6, \delta \text{ ppm): 3.29 (s, 2H, -CH}_2-\text{), 3.89 (s, 3H, -OCH}_3\text{), 4.87 (s, 1H, -NH-), 7.10-7.96 (m, 7H, Ar-H).}\]

[104]
PMR Spectrum of compound (6c)

\[
\text{N} \quad \text{Cl} \\
\text{Cl} \quad \text{N} \quad \text{H}_3\text{CO} \\
\text{N} \quad \text{Cl}
\]

\[
\text{H}_3\text{CO} - \text{N} + \text{O}^{-}
\]

Figure: 23

\(^1\text{H} \text{NMR (400 MHz, DMSO-}d_6, \delta \text{ ppm)}: 2.13 \text{ (s, 2H, -CH}_2\text{-)}, \quad 3.89 \text{ (s, 3H, -OCH}_3\text{)}, \quad 7.11-7.95 \text{ (m, 11H, Ar-H).}
\]
PMR Spectrum of compound (6d)

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \begin{array}{c}
\text{N} \\
\text{O} \\
\text{CH}_2
\end{array} \\
\text{H}_3\text{CO} & \quad \begin{array}{c}
\text{N} \\
\text{O}
\end{array}
\end{align*}
\]

Figure: 24

\(^1\text{H} \text{ NMR (400 MHz, DMSO-}d_6, \delta \text{ ppm):} \) 2.11 (s, 2H, -CH\text{$_2$}-), 3.84 (s, 3H, -OCH$_3$), 3.88 (s, 3H, -OCH$_3$), 6.93-8.09 (m, 12H, Ar-H).