CHAPTER 3 CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

Nowadays, chemists use variety of spectroscopic methods to characterized and study their compounds, to follow reactions and understand bondings. A variety of new sensitive techniques have now been developed in order to examine formerly intractable samples. In our present work, newly synthesized compounds were characterized by IR and NMR spectroscopy.

**Infrared 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.

Infrared radiation refers broadly to that part of the electromagnetic spectrum between the electromagnetic and microwave regions. The portion between 400 and 4000 cm\(^{-1}\) is extremely important for organic chemist. Infrared radiation in this range is absorbed and converted by an organic molecule into energy of molecular vibration. The frequency of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms. There has been some interest in the near-IR (14290-4000 cm\(^{-1}\)) and far-IR region, 700-200 cm\(^{-1}\). Today, infrared technology has many exciting and useful applications. This technique is based on vibrations of the atoms of a molecule.

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 [233]. This effect is due to Fermi resonance splitting. The carbonyl absorption of \(\gamma\)-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 [234] have measured the integrated absorption of sydnone carbonyl bands for a number of the compounds. The values obtained (6-12×10^4 mol^−1/cm^2) are greater than those for other carbonyl compounds (1.5-5.7×10^4 mol^−1/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.

It is difficult to attribute the individual absorption bands to specific groups in many molecules. In the case of quinazolines, three bands are generally found which occur between ~1650 to 1700 cm\(^{-1}\) for >C=O stretching, ~1600 cm\(^{-1}\) for >C=N of quinazoline [235].

The characteristic group frequencies were found in the Silverstein et al [236], Workman and Weyer [237], Stuart [238]. A through coverage of characteristic group frequencies is also presented in the treatise of Jones and Sandorfy [239], Smith’s text [240], and Socrates [241] is to be recommended for its concise presentation of group frequencies in tubular form along with illustrative spectra.
IR spectrum of 3-(4-chlorophenyl)-4-[N-[2-phenyl-4-oxoquinazoline-3(4H)-yl] sulfamoyl] sydnone (SA₁)

**IR (KBr, cm⁻¹):** 3319 (N-H), 1730 (C=O, sydnone), 1660 (C=O, quinazoline), 1598 (C=N, quinazoline), 1589 (C=C, Ar.), 1512 (C=C, Ar), 1332 (S=O), 1160 (S=O), 754 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[2-(4-methoxyphenyl)-4-oxoquinazoline-3(4H)-yl] sulfamoyl] sydnone (SA₃)

IR (KBr, cm⁻¹): 3300 (N-H), 2950 (C-H), 2820 (C-H), 1760 (C=O sydnone), 1647 (C=O quinazoline), 1601 (C=N, quinazoline), 1585(C=C, Ar.), 1510 (C=C, Ar.), 1321 (S=O), 1175 (S=O), 1250 (C-O-C), 1030 (C-O-C), 752 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-(3-phenyl-4-methyl-2-oxo-2H-chromen-7-yl)sulfamoyl] sydnone (SB₁)

IR (KBr, cm⁻¹): 3325 (N-H), 2980 (C-H, -CH₃ gr.), 2870 (C-H, -CH₃ gr.), 1771 (C=O, coumarine), 1750 (C=O, sydnone), 1595 (C=C, Ar.), 1490 (C=C, Ar.), 1315 (S=O), 1180 (S=O), 820 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[3-(4-fluorophenyl)-4-methyl-2-oxo-2H-chromen-7-yl]sulfamoyl] sydnone (SB₂)

**IR (KBr, cm⁻¹):** 3320 (N-H), 2920 (C-H, -CH₃ gr.), 2860 (C-H, -CH₃ gr.), 1747 (C=O coumarine), 1710 (C=O sydnone), 1593 (C=C, Ar.), 1499 (C=C, Ar.) 1300 (S=O), 1190 (S=O), 1094 (C-F), 835 (C-Cl).
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IR spectrum of 3-(4-chlorophenyl)-4-[N-(2-fluoro acridine-9-yl)sulfamoyl] sydnone (SC₁)

IR (KBr, cm⁻¹): 3311 (N-H), 1750 (C=O sydnone), 1600 (C=C, Ar.), 1489 (C=C, Ar.), 1340 (C=N), 1320 (S=O), 1152 (S=O), 1095 (C-F), 824 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-{N-(2-methyl acridine-9-yl)sulfamoyl} sydnone (SC₄)

IR (KBr, cm⁻¹): 3301 (N-H), 2920 (C-H, -CH₃ gr.), 2860 (C-H, -CH₃ gr.), 1747 (C=O sydnone), 1600 (C=C, Ar.), 1489 (C=C, Ar.), 1330 (C-N), 1358 (S=O), 1150 (S=O), 823 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(4-methyl-2-phenylpiperazin-1-yl)quinazoline-6-yl]sulfamoyl] sydnone (SD₃)

IR (KBr, cm⁻¹): 3356 (N-H), 3030 (-CH₂⁻), 2920 (-CH₂⁻), 2800 (C-H, -CH₃ gr.), 1747 (C=O sydnone), 1616 (C=C, Ar.), 1489 (C=C, Ar.), 1319 (C-N), 1339 (S=O), 1170 (S=O), 833 (C-Cl).
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IR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(4-acetylpiperazin-1-yl)quinazoline-6-yl]sulfamoyl] sydnone (SD₄)

IR (KBr, cm⁻¹): 3313 (N-H), 2930 (C-H, -CH₃ gr.), 2840 (C-H, -CH₃ gr.), 1720 (C=O sydnone), 1602 (C=C, Ar.), 1493 (C=C, Ar.), 1373 (S=O), 1177 (S=O), 1320 (C-N), 1690 (C=O), 831 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[3-(4-chlorophenyl)-2-methyl-4-oxo-3,4-dihydroquinazoline-6-yl]sulfamoyl] sydnone (SE₂)

IR (KBr, cm⁻¹): 3310 (N-H), 2920 (C-H, -CH₃ gr.), 2830 (C-H, -CH₃ gr.), 1735 (C=O sydnone), 1655 (C=O quinazoline), 1614 (C=C, Ar.), 1493 (C=C, Ar.), 1300 (C-N), 1340 (S=O), 1181 (S=O), 833 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[3-(4-methoxyphenyl)-2-methyl-4-oxo-3,4-dihydroquinazoline-6-yl]sulfamoyl] sydnone (SE₈)

**IR (KBr, cm⁻¹):** 3300 (N-H), 2980 (C-H, -CH₃ gr.), 2840 (C-H, -CH₃ gr.), 1751 (C=O sydnone), 1660 (C=O quinazoline), 1591 (C=C, Ar.), 1493 (C=C, Ar.), 1342 (C-N), 1358 (S=O), 1178 (S=O), 1234 (C-O-C), 1011 (C-O-C), 833 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-{2-(4-chlorophenyl)-1H-benzo[d]imidazol-1-ylsulfonyl} sydnone (SF₁)

IR (KBr, cm⁻¹): 1734 (C=O sydnone), 1610 (C=C, Ar.), 1501 (C=C, Ar.), 1310 (C-N), 1350 (S=O), 1172 (S=O), 833 (C-Cl).
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IR spectrum of 3-(4-chlorophenyl)-4-[2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-ylsulfonyl] sydnone (SF₂)

IR (KBr, cm⁻¹): 1760 (C=O sydnone), 1320 (C-N), 1371 (S=O), 1180 (S=O), 1252 (C-O-C), 1009 (C-O-C), 833 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-(4-phenoxyphenyl)sulfamoyl] sydnone (SG₁)

IR (KBr, cm⁻¹): 3310 (N-H), 1747 (C=O sydnone), 1371 (S=O), 1150 (S=O), 1229 (C-O-C), 1090 (C-O-C), 829 (C-Cl).
IR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(p-tolyloxy)phenyl]sulfamoyl]sydnone (SG₂)

IR (KBr, cm⁻¹): 3317 (N-H), 2920 (C-H, -CH₃ gr.), 2870 (C-H, -CH₃ gr.), 1744 (C=O sydnone), 1350 (S=O), 1160 (S=O), 1227 (C-O-C), 1090 (C-O-C), 831 (C-Cl).
**NMR Spectroscopy:**

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, for short “NMR”. The two scientists Felix Bloch [242] and Edward M. Purcell [243] were awarded the Nobel Prize in Physics in 1952 for this invention.

NMR is commonly used in organic chemistry to elucidate molecular structures and conformations by studying $^1\text{H}$ and $^{13}\text{C}$ 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.

Tanaka and Yakoi [244] 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 $^{13}\text{C}$, $^{14}\text{N}$ and $^{17}\text{O}$ 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 [245] obtained PMR 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 [246] obtained a value for the ring proton resonance of 3-N-butyldyne 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.

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 ppm (depending on solvent). This drastic shift indicates a polar nature and the presence of an aromatic ring current.
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 of the compounds described in the present work have been carried out in CDCl₃. TMS (Tetra Methyl Silane) has taken as internal standard. The spectral pattern are shown as under.
NMR spectrum of 3-(4-chlorophenyl)-4-{N-[2-phenyl-4-oxoquinazoline-3(4H)-yl]sulfamoyl} sydnone (SA₁)

$^1$H NMR (400 MHz, CDCl₃, δ): 7.11-8.03 (m, 13H, Ar-H), 9.15 (s, 1H, -SO₂NH-).
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[2-(4-methoxyphenyl)-4-oxoquinazoline-3(4H)-yl] sulfamoyl] sydnone (SA₃)

\[\text{SA-3}\]

$^1\text{H NMR (400 MHz, CDCl}_3, \delta): 3.87 \text{ (s, 3H, -OCH}_3\text{), 6.69-7.95 (m, 12H, Ar-H), 9.22 (s, 1H, -SO}_2\text{NH-).} \]
NMR spectrum of 3-(4-chlorophenyl)-4-\{N-(3-phenyl-4-methyl-2-oxo-2H-chromen-7-yl)sulfamoyl\} sydnone (SB₁)

\[
{^1}H \text{ NMR (400 MHz, CDCl}_3, \delta): 2.25 (s, 3H, -CH}_3, \\
6.77-7.72 (m, 12H, Ar-H), 9.40 (s, 1H, -SO}_2NH-).
\]
NMR spectrum of 3-(4-chlorophenyl)-4-\{N-[3-(4-fluorophenyl)-4-methyl-2-oxo-2H-chromen-7-yl]sulfamoyl\} sydnone (SB₂)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl} \text{\textsubscript{3}}, \delta): 2.17 \text{ (s, 3H, } -\text{CH}_3), \]
6.74-7.62 (m, 11H, Ar-H), 9.30 (s, 1H, -SO\textsubscript{2}NH-).
NMR spectrum of 3-(4-chlorophenyl)-4-[N-(2-fluoroacridine-9-yl) sulfamoyl] sydnone (SC₁)

$\text{^1}{H}$ NMR (400 MHz, CDCl₃, $\delta$): 7.31-8.08 (m, 11H, Ar-H), 9.40 (s, 1H, -SO₂NH-).
NMR spectrum of 3-(4-chlorophenyl)-4-[N-(2-methylacridine-9-yl) sulfamoyl] sydnone (SC₄)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3, \delta): & \quad 2.54 \text{ (s, 3H, -CH}_3), \\
& \quad 7.27-8.15 \text{ (m, 11H, Ar-H), 9.46 (s, 1H, -SO}_2\text{NH-).}
\end{align*}
\]
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(4-methyl-2-phenyl piperazin-1-yl)quinazoline-6-yl]sulfamoyl] sydnone (SD₃)

\[ \text{SD-3} \]

**1H NMR (400 MHz, CDCl₃, } \delta): \]
2.56 (s, 3H, -CH₃), 2.95 (t, 2H, -N-CH₂-CH₂-N-), 3.20 (t, 2H, -N-CH₂-CH₂-N-), 3.36 (d, 2H, -N-CH₂-CH-N-), 5.30 (s, 1H, -N-CH₂-CH-N-), 6.72-8.02 (m, 12H, Ar-H), 9.50 (s, 1H, -SO₂NH-).
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(4-acetylpiperazin-1-yl)quinazoline-6-yl]sulfamoyl] sydnone (SD₄)

\[
\begin{align*}
^1H \text{ NMR (400 MHz, CDCl}_3, \delta): & \quad 2.58 \text{ (s, 3H, -CH}_3), \\
& \quad 3.15 \text{ (t, 4H, -N-CH}_2\text{-CH}_2\text{-N-)}, \\
& \quad 3.40 \text{ (t, 4H, -N-CH}_2\text{-CH}_2\text{-N-)}, \\
& \quad 6.85\text{-8.25 (m, 7H, Ar-H),} \\
& \quad 9.51 \text{ (s, 1H, -SO}_2\text{NH-).}
\end{align*}
\]
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[3-(4-chlorophenyl)-2-methyl-4-oxo-3,4-dihydroquinazoline-6-yl]sulfamoyl] sydnone (SE₂)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3, \delta): \ 2.20 \text{ (s, 3H, -CH}_3\text{)}, \ 6.75-7.70 \text{ (m, 11H, Ar-H)}, \ 9.51 \text{ (s, 1H, -SO}_2\text{NH-)}. \]
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[3-(4-methoxyphenyl)-2-methyl-4-oxo-3,4-dihydroquinazoline-6-yl]sulfamoyl] sydnone (SE\textsubscript{8})

\[\begin{array}{c}
\text{SE-8} \\
\end{array}\]

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3, \delta): \] 2.14 (s, 3H, -CH\textsubscript{3}), 3.79 (s, 3H, -OCH\textsubscript{3}), 7.03-7.92 (m, 11H, Ar-H), 9.60 (s, 1H, -SO\textsubscript{2}NH-).
NMR spectrum of 3-(4-chlorophenyl)-4-{2-(4-chlorophenyl)-1H-benzo[d]imidazol-1-ylsulfonyl} sydnone (SF₁)

\textsuperscript{1}H NMR (400 MHz, CDCl₃, δ): 7.19-8.19 (m, 12H, Ar-H).
NMR spectrum of 3-(4-chlorophenyl)-4-{2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-ylsulfonyl} sydnone (SF$_2$)

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 3.91 (s, 3H, -OCH$_3$), 7.30-7.99 (m, 12H, Ar-H).
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NMR spectrum of 3-(4-chlorophenyl)-4-[N-(4-phenoxyphenyl)sulfamoyl] sydnone (SG₁)

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3, \delta): 6.50-7.68 \text{ (m, 13H, Ar-H)}, 9.51 \text{ (s, 1H, } -\text{SO}_2\text{NH-)}.\]
NMR spectrum of 3-(4-chlorophenyl)-4-[N-[4-(p-tolyloxy)phenyl]sulfamoyl] sydnone (SG₂)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl₃, } & \delta \text{): 2.29 (s, 3H, } -\text{CH}_3, \\
& 6.67 \text{-} 7.69 \text{ (m, 12H, Ar-H), 9.50 (s, 1H, } -\text{SO}_2\text{NH-).}
\end{align*}
\]