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Synthesis and spectroscopic characterization of some schiff bases derived from Dimedone

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Abstract
The synthesis, characterization of three Schiff bases 3,3- dimethyl-5(phenylimino) cyclohexan-1-one [L1], [(4-chlorophenyl) imino]-3,3- dimethyl-5(phenylimino) cyclohexan-1-one [L2], and 3,3- dimethyl-5-[(4-nitrophenyl) imino]-3,3- dimethyl-5(phenylimino) cyclohexan-1-one [L3], derived by condensation of an equimolar amounts of dimedone with different amine such as aniline, 4- Chloroaniline and 4-nitroaniline in ethanol were reported . Spectroscopic techniques, including NMR (^{1}H and ^{13}C), UV- vis spectroscopy, FT-IR, MS, and melting point were used to identify the products.

Keywords: schiff base, dimedone, condensation, amine

1. Introduction

Schiff bases were discovered by a German chemist and Nobel Prize winner, Hugo Schiff in 1864 [1, 2], and named after him (1834-1915), possess a functional group containing a carbon-nitrogen double bond with the nitrogen atom linked to an aryl or alkyl group, with the exception of hydrogen [3]. Schiff base compounds are condensation products of primary amines and carbonyl compounds (aldehydes and ketones). These compounds have been known by different names such as imines, azomethines and, anils (which is common for Schiff bases derived from aromatic amines, aldehydes, and ketones). In general, the Schiff bases which have been derived from aldehydes, are called aldimine and from ketones as ketamine [4].

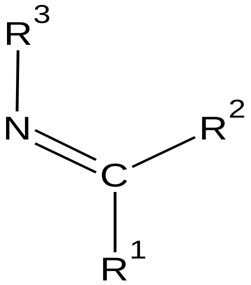


Fig 1: The general structure of the Schiff base

The presence of aryl substituents in Schiff bases usually eases the synthesis and stability of Schiff bases while Schiff bases containing alkyl are relatively unstable. Schiff-bases will decompose or polymerize rapidly unless there is at least one aryl group bonded to the nitrogen or the carbon atom of the C=N double bond [5]. The reactivity of aldehydes is generally faster than those of the ketones in a condensation reaction, thereby resulting in the formation of Schiff bases with a centre that is less steric than the ketones, relatively unstable and freely polymerizable [6]. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals [7], and acts as active ligands due to the presence of low electronegativity of nitrogen N of the azomethine group (>C=N), lone pair of electrons on the nitrogen atom, electron donating character of the double bond , and thus bring about stability in metals several oxidation states, regulating metal activities for variety of useful biological, catalytic conversions [3]. Schiff-base ligands have received much attention in recent years due to their wide use as dyes and pigments, catalysts, intermediates in organic synthesis, polymer stabilizers and due to their broad range of biological activities, including anti-fungal, anti-bacterial, anti-malarial, anti-proliferative, anti-inflammatory, anti-viral, and anti-pyretic properties [8, 9]. The exceptional qualities of Schiff bases such as facile syntheses, easily tunable steric, electronic properties and good solubility in common solvents have led to their extensive study. The objective of this study is to synthesize new Schiff bases namely 3, 3-dimethyl-5-(phenylimino) cyclohexan-1-one [1], [(4-chlorophenyl) imino]-3, 3-dimethylcyclohexan-1-one [2], 3, 3-dimethyl-5-[(4-nitrophenyl) imino] cyclohexan-1-one [3]. The resulting compounds will be characterized using different analytical technique.

2. Materials and Methods

2.1 Materials

Absolute ethanol (DuKSAN/ India), Absolute methanol (Lobachemie/india), Chloroform ($CDCl_3$) (Sigma / USA), Glacical acetic acid (Sigma/USA), Dimedone (Lobachemie/india), Aniline (Sigma/USA) , p-Chloroaniline (Sigma/USA), p- nitroaniline (Sigma/USA) and Dimetheylsulfoxide (DMSO), (Lobachemie/india).

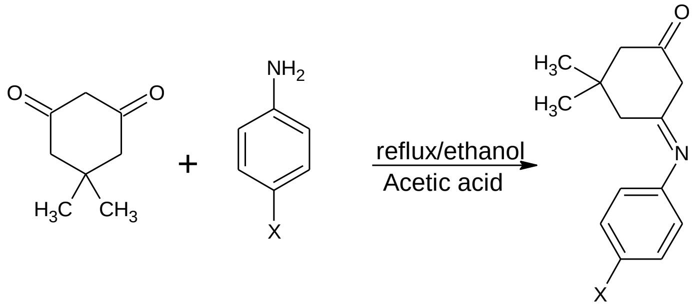
2.2 Instruments

FTIR-8400S SHIMADZU Spectrophotometer in the range (400-4000) cm^{-1} using KBr disc, Mass spectra Shimatzu, model Q.p-2010 plus, JENWAY 7205 UV/Visible spectrophotometer in methanol at 25◦C, For (c = 1.0×10^{-3}mol /cm^{-3}) of the compounds using a 1 cm quartz cell in the range 200-800 nm, ^{1}H NMR and ^{13}C NMR Bruker Avance III HD 700 MHz spectrometer (UK) equipped with 5 mm TCI H/C/N cryoprobe with $CDCl_3$ or DMSO-d6, the proton decoupled ^{13}C NMR experiment was run using composite pulse decoupling scheme operating at 176.08 MHz.^{1}H NMR data were processed with Top Spin 3.5 pl 6 software, Chemical shifts (δ) are reported in ppm, Melting pointelectrical, type (Gallenkamp, England), serial No. MFB, 600.100F. APP.NO2CO117.

2.3 Methods

2.3.1 Synthesis of Schiff base ligands

(1.4g, 0.01 mol) of dimedone dissolved in 25 ml of absolute ethanol. To this solution (0.90 ml, 0.01 mol) of aniline, (1.3g, 0.01 mol) of 4- chloroaniline and (1.4g, 0.01 mol) of 4- nitroaniline dissolved in 25 ml of hot absolute ethanol was added, followed by addition of few drops of glacial acetic acid. The mixture was refluxed for 6 h at 70 ◦C with constant stirring and then was cooled in ice. A yellow solid gradually appeared, it was filtered, washed thoroughly with cold distilled water and then dried in air and finally in a vacuum. The solid was recrystallized from ethanol.
The structures of ligands are given in scheme [1]



X=H, Cl, NO_2

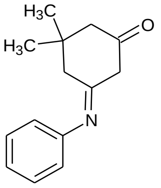
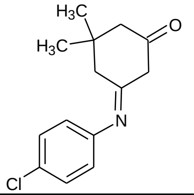
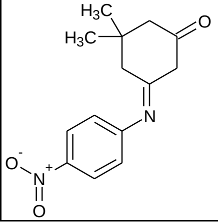
Fig 2: Synthesis of Schiff base ligands

3. Results and Discussion

3.1 Physiochemical data

The Schiff bases 3,3- dimethyl-5(phenylimino) cyclohexan-1-one [1], [(4-chlorophenyl) imino]-3,3- dimethyl-5(phenylimino) cyclohexan-1-one [2], and 3,3- dimethyl-5-[(4-nitrophenyl) imino]-3,3- dimethyl-5(phenylimino) cyclohexan-1-one [3], were prepared by reacting aniline, 4- Chloroaniline and 4- nitroaniline with an equimolar amount of dimedone in ethanol. All synthesized Schiff bases are air stable and high yield products. The physical properties of synthesized Schiff base ligands were listed in table (1)

Table 1: Physical properties for the synthesized Schiff bases

Ligand	Molecular formula	Structure	M.W	Color	M.P. (ºC)	Yield (%)
L1	$C_{14}H_{17}NO$		215	Yellow	184	88.4
L2	$C_{14}H_{16}CLNO$		249	Dark Yellow	198	80.3
L3	$C_{14}H_{16}N_2O_3$		260	Yellow	***140***	96.2

3.2 Electronic spectra

The electronic spectra of Schiff bases ligands [1, 2, 3] (Table 2 and Figure 1, 2, 3) were carried out in methanol (10^{-3} mol^{-1}) at room temperature. In the UV-visible spectra of all these synthesized ligands, the band appearing at lower energy is attributed to $n \rightarrow \pi^*$ transition of conjugation between the lone pair of electrons of p orbital of N atom in azomethine group and conjugated π bond of the benzene ring. The bands appearing at higher energy are attributed to $\pi \rightarrow \pi^*$ of the benzene ring and $\pi \rightarrow \pi^*$ transition of the azomethine group.

Table 2: UV-visible spectral data (nm) of synthesized ligands in methanol (10^{-3} mol l^{-1})

Ligand	λ_{max}(nm)	Band assignment
L1	230,255 295	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
L2	225,255 295	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
L3	230,275 360	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$

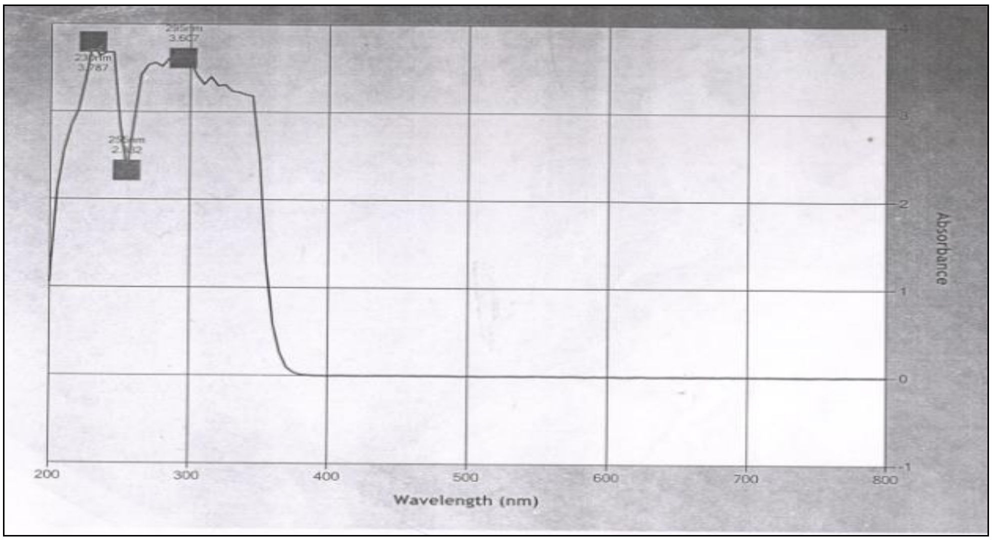


Fig 3: Ultra violet spectrum of L1

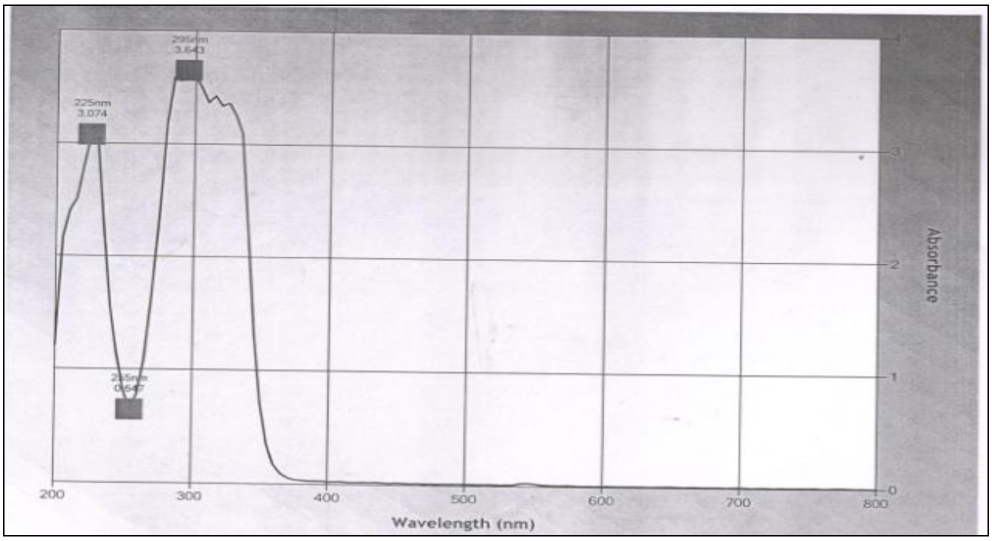


Fig 4: Ultra violet spectrum of L2

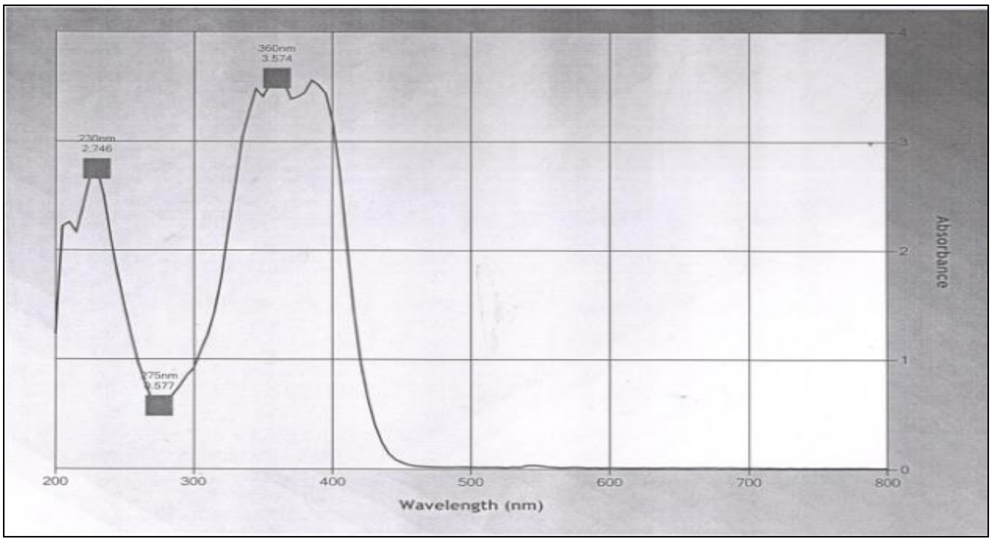


Fig 5: Ultra violet spectrum of L3

3.3 Infrared spectra

The infrared spectra of all the Schiff base ligands (Table 3 and Figure 4, 5, 6) showed a strong band in the Region 1531- 1593 cm^{-1} which were assigned to □C=N stretching mode of the azomethine function of the ligands, whereas the IR stretching vibration bands appear at 1569cm^{-1}, 1610cm^{-1}, 1631cm^{-1} corresponding to the C=O group in dimedone moiety of L1, L2, L3 respectively. The medium intensity bands observed in the range 1155-1110 cm^{-1} correspond to –C-N stretching vibration of an amine group. A group of bands observed in the range 1442-1446 cm^{-1} may be due to the stretching vibrations of the aromatic ring.

Table 3: infrared spectral bands (cm^{-1}) for the Schiff base ligands

nC-N	nC=C, Ar	nC=N	nC=O	Ligand
1151	1442	1531	1569	L1
1155	1446	1583	1610	L2
1110	1444	1593	1631	L3

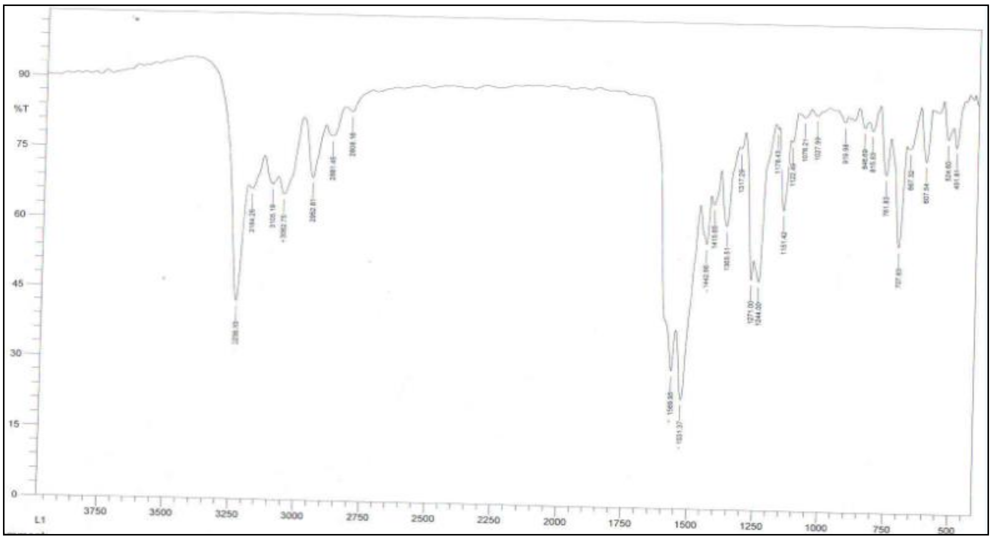


Fig 6: Infrared spectrum bands (KBr) cm^{-1} of L1

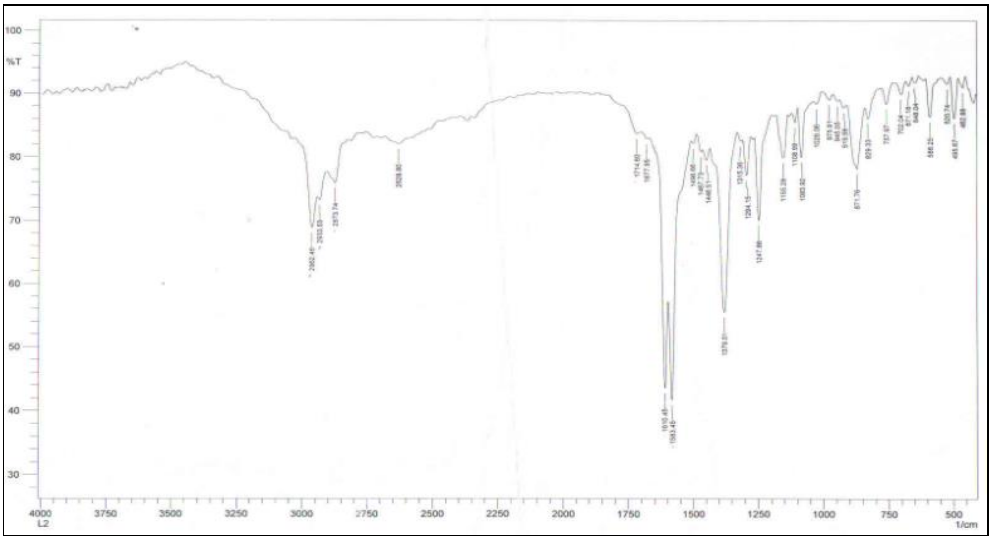


Fig 7: Infrared spectrum bands (KBr) cm^{-1} of L2

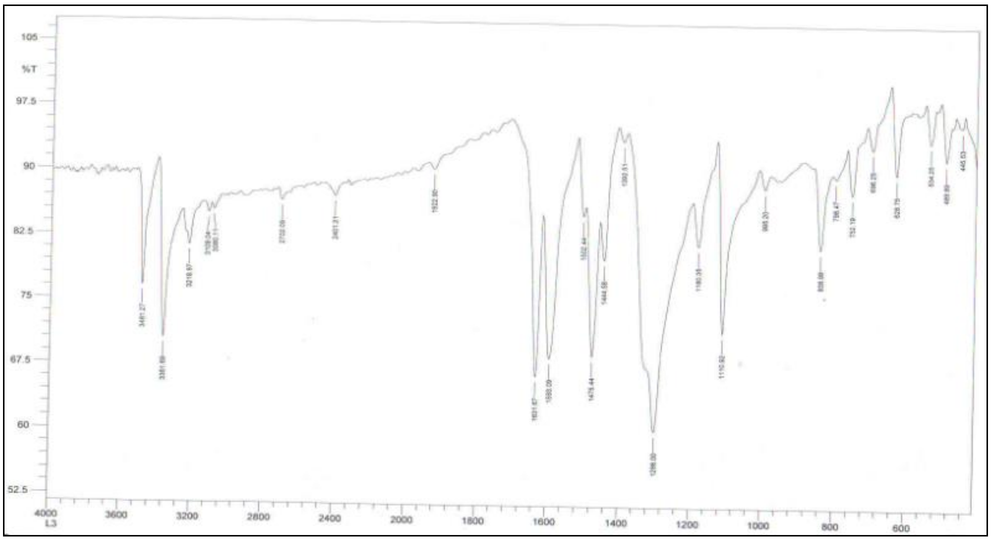


Fig 8: Infrared spectrum bands (KBr) cm^{-1} of L3

3.4 ^{1}H–NMR Spectra

The ^{1}H NMR spectrum of Schiff bases L1, L2 in $CDCl_3$ and L3 in DMSO exhibited proton signals in the range 1.06-1.1 ppm (S, 6H-CH_3) was assigned for the two methyl groups, while the singlet at 2.08 – 2.51 ppm (S, 2H-CH_2) corresponds to methylene proton neighboring of imine, and signals at 2.37-3.36 ppm (S, 2H-CH_2) corresponds to methylene proton neighboring carbonyl group of dimedone moiety. Triplet signals observed in the 6.64-7.30 ppm range are due to the aromatic protons of the Schiff bases.

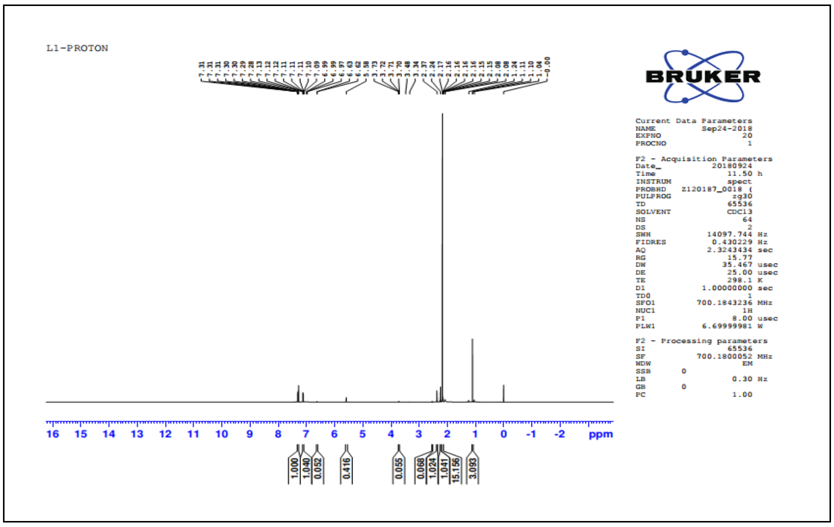


Fig 9: ^{1}HNMR of L1

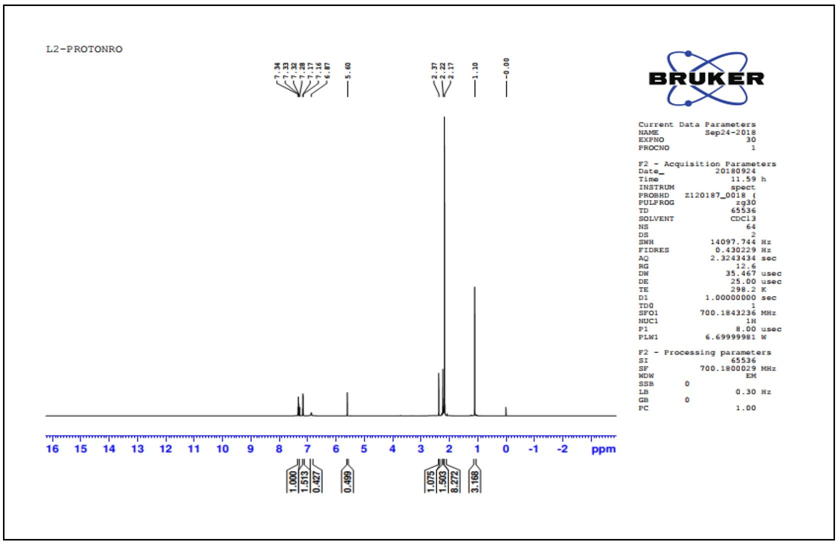


Fig 10: ^{1}HNMR of L2

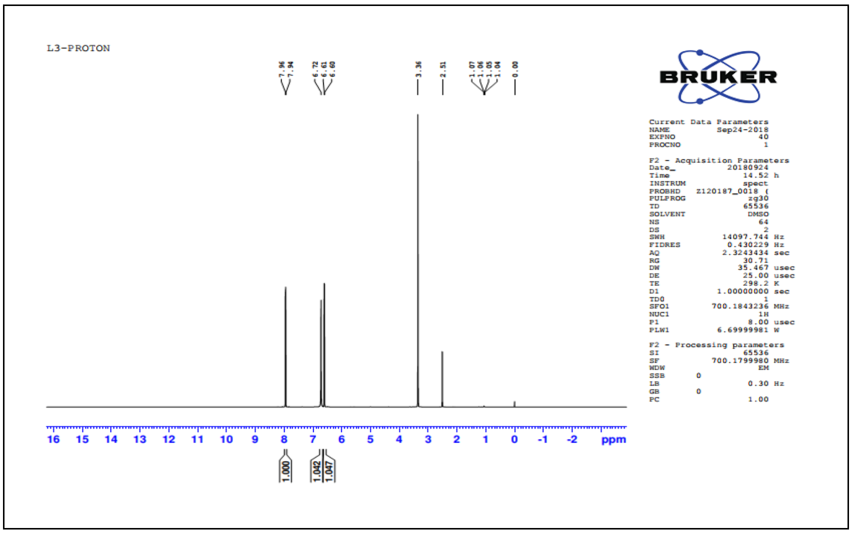


Fig 11: ^{1}HNMR of L3

3.5 ^{13}C NMR Spectra

The ^{13}C NMR spectrum of L1, L2 in $CDCl_3$ and L3 in DMSO showed signals at 19.02-30.20 ppm rang which were assigned for the two methyl groups, while the Signals Observed at 155.99-161.05 ppm were attributed to imine Group carbon. Signals observed at 156.32-207.07ppm due to a carbon atom of the carbonyl group. Aromatic Carbon exhibited signals at 124.18-128.39 ppm.

The ^{1}H NMR and ^{13}CNMR spectrum of Schiff bases is shown in Figure (7 -12) and the chemical shifts of various types of protons and carbons are summarized in Table 4.

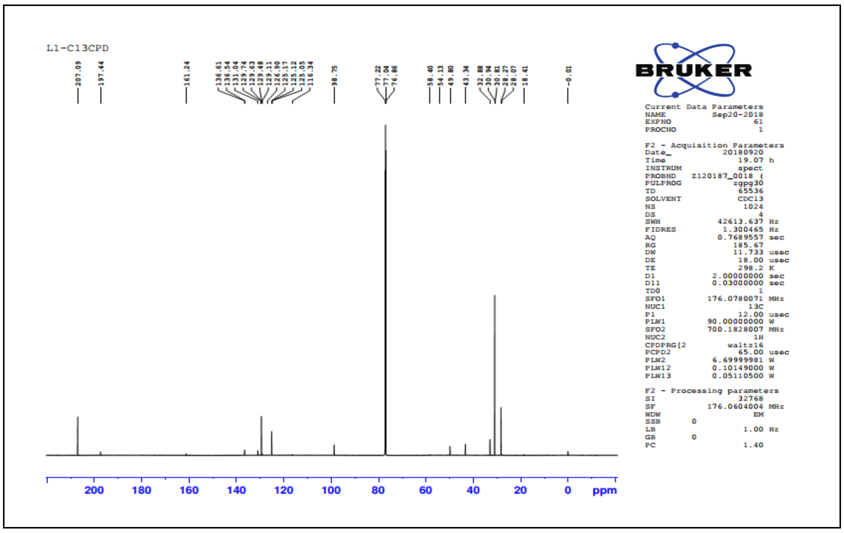


Fig 12: ^{13}CNMR of L1

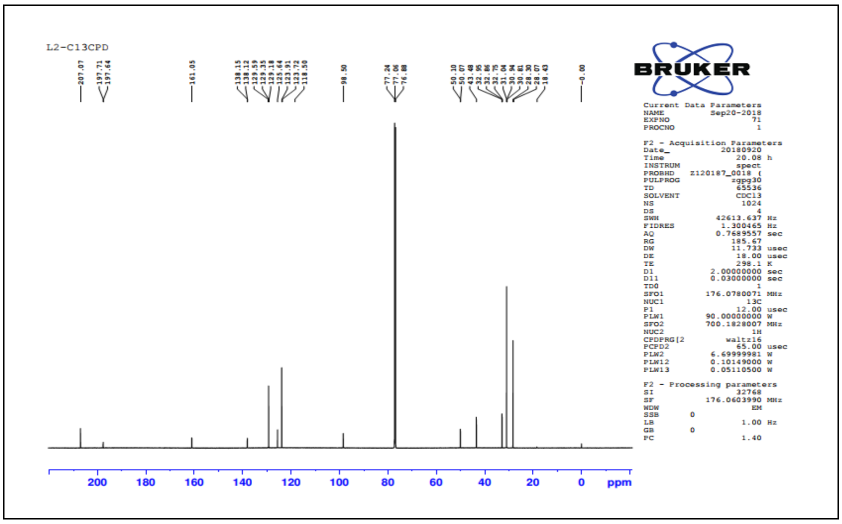


Fig 13: ^{13}CNMR of L2

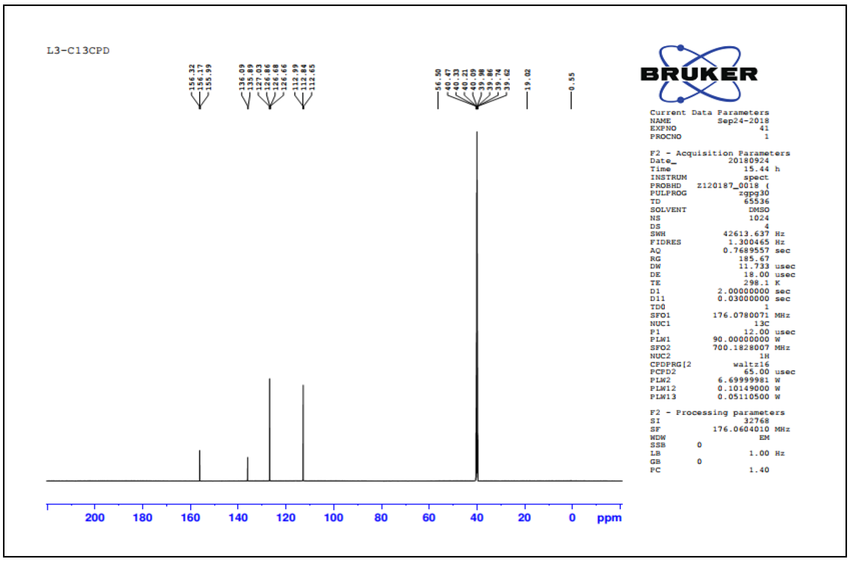
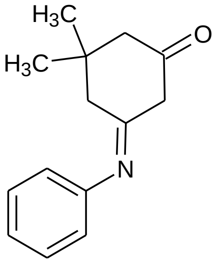
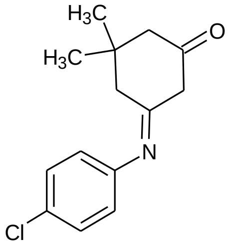
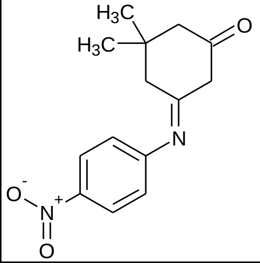


Fig 14: ^{13}CNMR of L3

Table 4: ^1H NMR and ^{13}CNMR data of the Schiff bases

Ligand	^1H NMR chemical shifts, ppm	^{13}CNMR chemical shifts, ppm
	1.1(S,6H-CH_3) 2.08(S,2H-CH_2) 2.37(S,2H-CH_2) 7.30 (t,5H arom)	30.20(2C,CH_3) 161.24(1C,C= N) 207.09(1C,C=O) 128.39(5C,arom)
	1.1(S,6H-CH_3) 2.17(S,2H-CH_2) 2.37(S,2H-CH_2) 7.33(t,4H arom)	30.97(2C,CH_3) 161.05(1C,C= N) 207.07(1C,C=O) 128.46(4C,arom)
	1.06(S,6H-CH_3) 2.51(S,2H-CH_2) 3.36(S,2H-CH_2) 6.64(t,4H arom)	19.02(2C,CH_3) 155.99(1C,C= N) 156.32(1C,C=O) 124.18(4C,arom)

3.6 Mass Spectra

The electronic impact mass spectra of 3, 3-dimethyl-5 (phenylimino)cyclohexan-1-one [1] , and [(4-chlorophenyl) imino]-3,3-dimethylcyclohexan-1-one [2] , Schiff base ligands show molecular ion(M^+) peaks at m/z = 215 a.m.u, m/z = 249 a.m.u, corresponding to the $[C_{14}H_{17}NO]^+$, $[C_{14}H_{16}CLNO]^+$ respectively, confirming the empirical formulae of the ligands. The spectra also show a series of peaks corresponding to various fragments in each compound Figures (13.14).The ligand 3, 3-dimethyl-5-[(4-nitrophenyl)imino]cyclohexan-1-one [3], molecular ion(M^+) peaks at m/z = 260 a.m.u, corresponding to the empirical formulae of the ligands is absent, but show a series of peaks confirming the empirical formulae of the ligand, Figure (15).

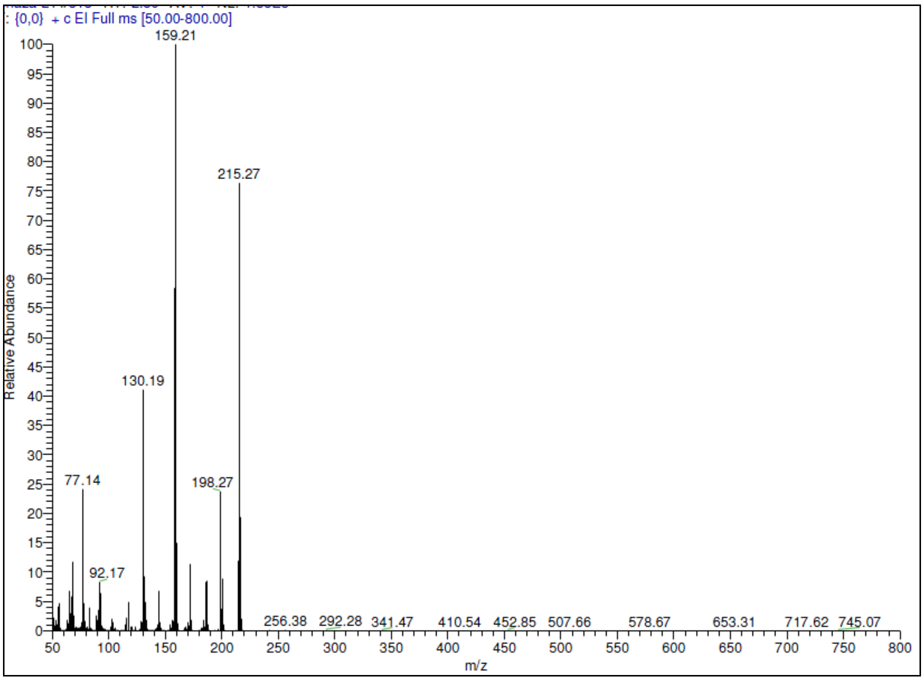


Fig 15: EI-mass spectrum for the ligand L1

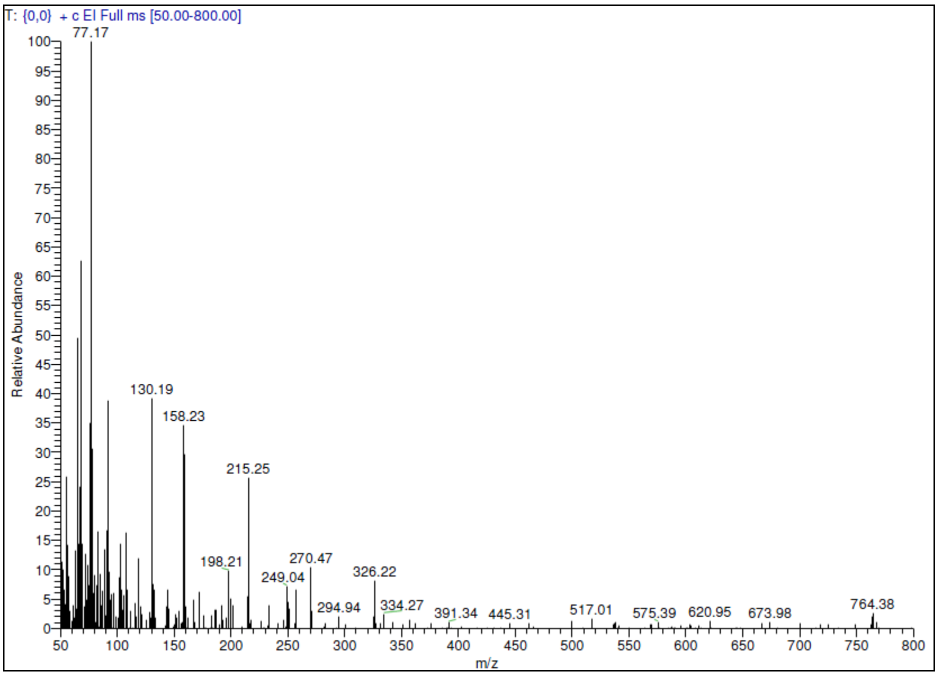


Fig 16: EI-mass spectrum for the ligand L2

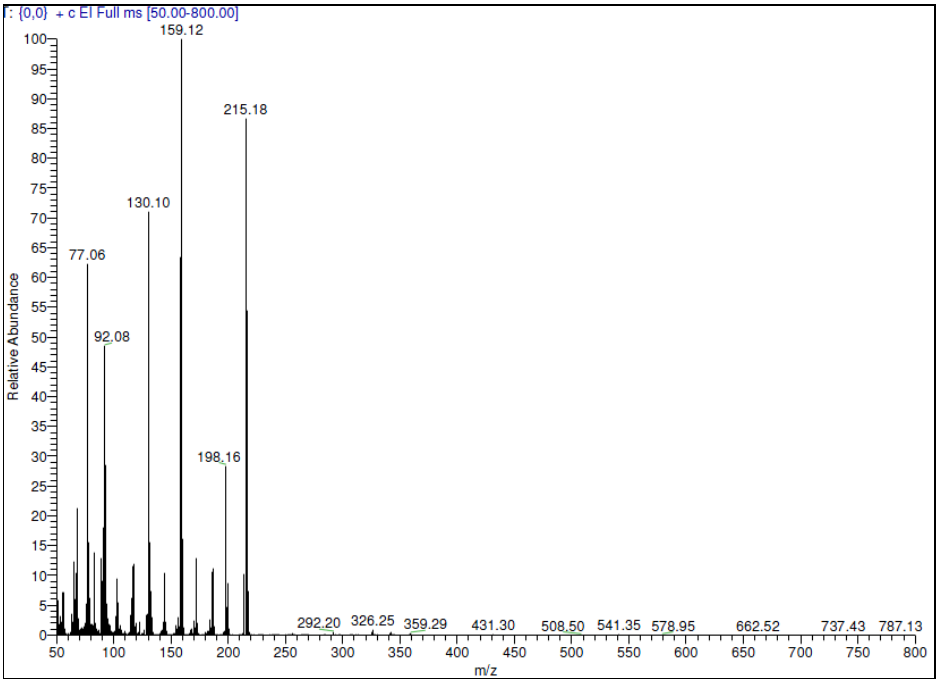


Fig 17: EI-mass spectrum for the ligand L3

4. Conclusion

In this study three Schiff bases 3, 3-dimethyl-5 (phenylimino)cyclohexan-1-one , [(4-chlorophenyl) imino]-3,3-dimethylcyclohexan-1-one ,and 3, 3-dimethyl-5-[(4-nitrophenyl)imino]cyclohexan-1-one have been successfully prepared and characterized , the Schiff bases are solid and having sharp melting point.

5. Reference

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