

Onepot Synthesis and Characterization of 2-Amino-5 (Substituted Phenyl) 1,3,4-Thiadiazole Based Tridentate Imines

S. N. Ibatte

Department of Chemistry

Dayanand Science College, Latur, Maharashtra, India

ibateshyam@gmail.com

Abstract: 2-amino-5(substituted phenyl)1,3,4-thiadiazole is a heterocyclic nucleus was prepared in laboratory for synthesis of the novel ligands 3-sub.benzylidene-4(5-sub.aryl-[1, 3, 4] thiadiazole-2-ylimino) pentan-2-one, were synthesized by Knoevenagel condensation. The derived heterocyclic nucleus condensed with substituted aromatic/heterocyclic aldehyde and acetoacetone using solid supported catalyst. Synthesized Schiff base ligands were characterized by IR, ¹H NMR and Mass spectroscopy for their structural identification.

Keywords: Thiadiazole, Ligand, Synthesis, Characterization

I. INTRODUCTION

The imines containing substituted 2-amino-5(substituted phenyl)1, 3, 4-thiadiazole moiety have wide range of applications such as anticonvulsant activity¹⁻², anticancer agents³, antifungal and antibacterial⁴ activity screened by various researchers. Imines of heterocyclic ligands have vital role in coordination chemistry due to presence of one or more hetero atoms in it. The ligands of substituted 1, 3, 4-thiadiazole have potential sites for metal complexation. Wide range of imines based on 1, 3, 4-thiadiazole were synthesized by extending with some active organic molecules and synthesized their metal complexes with transition metals as well as with rare earth metals.

In recent years, sulfur containing ligands such as thiosemicarbazones and their transition metal complexes have received more attention in the area of medicinal chemistry, due to their pharmacological properties, such as antiviral, antibacterial, antifungal, antiprastic, antitumor, anticancer and anti HIV activities.

1,3,4-Thiadiazole derivatives possess interesting biological activity probably conferred to them by the strong aromaticity of this ring system, which leads to great in vivo stability and generally, a lack of toxicity for higher vertebrates, including humans. When diverse functional groups that interact with biological receptors are attached to this ring, compounds possessing outstanding properties are obtained

In fact, Schiff bases are able to stabilize many different metals in various oxidation states controlling the performance of metals in a large variety of useful catalytic transformations. Most commonly Schiff bases have NO or N₂O₂-donor groups but the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms.

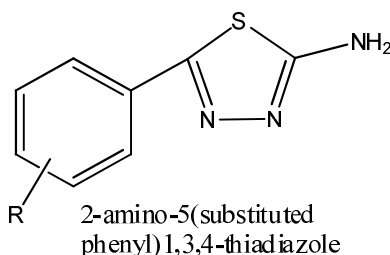
With this interest study of new imines synthesis is carryout. The novel imines were synthesized by condensation of functionalized aromatic and heterocyclic aldehydes, acetoacetone and substituted 1, 3, 4-thiadiazole. In the synthetic route of complexes recent convenient reversible catalyst can be employed. The catalyst in Free State is not much effective, so catalyst supported on solid silica will be more efficient. The catalyst can be reused five to six times after the completion of the reaction. Synthesized ligands were screened by physical and spectroscopic analysis for elucidation of structures.

II. EXPERIMENTAL

2.1. Preparation of 2-amino-5(substituted phenyl) 1, 3, 4- thiadiazole:

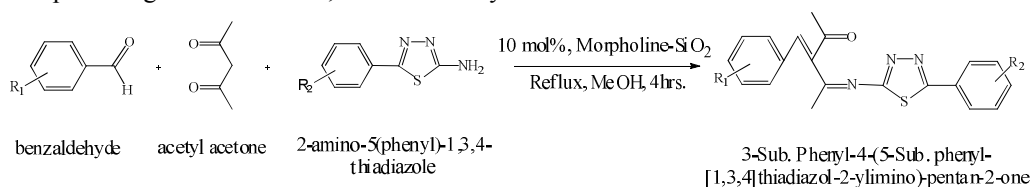
The commercially purchased all reagents and solvents of analytical grade were used without any purification. 2-amino-5(substituted phenyl) 1, 3, 4-thiadiazole was prepared⁵⁻⁷ in laboratory by alkanoylation of thiosemicarbazide

followed by dehydration. The reaction progress was screened by thin layer chromatography (TLC). Molecular structure of derived moiety is as shown in figure 1.


Figure 1

2.2. Preparation of novel Schiff base 3-sub.benzylidene-4(5-sub.aryl-[1, 3, 4] thiadiazole-2-ylimino) pentan-2-one:

A round bottom flask charged with substituted aromatic aldehyde, acetoacetone (10mmol) each and along with 10 mole % solid supported Morpholine in methanol (20ml) are refluxed at 70 °C by for 3 hours. The progress of reaction was monitored by using pet ether and ethyl acetate system (7:3 v/v). After that 2-amino-5-(substituted aryl) thiadiazole (10mmol) added and continued further refluxing for 1 hour. The progress of reaction was monitored by benzene, acetone system (7:3 v/v). The reaction mixture was poured on flaks of ice. The obtained solid yellow precipitate of expected ligand was filtered, dried and recrystallized in methanol.


Figure-2

Obtained ligands were characterized by various analytical techniques. The melting point of synthesized Schiff base ligand was recorded on Cotech digital melting point apparatus. Elemental C, H, N, and S analysis was carried out on a Fison EA1108 analyzer. The Infrared (FTIR) spectra were recorded by using FITR 8300 shimadzu spectrometer by using CsI disk in the frequency range of 4000 to 400cm⁻¹. The ¹H NMR spectra were recorded on Brunner 400 MHz spectrometer using CDCl₃ as a solvent and TMS as internal standard. Mass spectra were recorded by mass wiff (turbo spray) spectrometer.

III. RESULT AND DISCUSSION

3.1. Physical Characterization of Synthesized Ligands

For purity and structural elucidation synthesized ligand were screened by physical and spectroscopic techniques. Synthesized ligands and their physical characterizations are depicted in Table-1. The elemental analysis was performed with respect to C, H, N, O and S, the m/z values of Schiff bases are in good arrangement with the calculated values. The melting point of all Schiff bases was recorded which were 107 °C and above up to 145 °C, the color of Schiff base ligands were found to be yellow/ Buff.

Table-1: Melting Points, Elemental Analytical data (%) and m/z values of ligands.

Compounds	Symbol	Physical appearance	M.P. (°C)	Elements (%)					m/z
				C	H	N	O	S	
C ₁₉ H ₁₇ N ₃ O ₂ S	L ₁	Yellow	107	63.70	5.05	12.38	9.43	9.45	351
C ₂₁ H ₁₈ N ₃ OSF	L ₂	Yellow	145	65.37	4.94	11.44	4.35	8.73	379
C ₂₂ H ₂₁ N ₃ O ₂ S	L ₃	Buff	136	66.47	5.58	11.07	8.43	8.45	391
C ₂₁ H ₁₈ N ₄ O ₃ S	L ₄	Yellow	138	60.90	4.60	14.20	12.17	8.13	406
C ₂₁ H ₁₉ N ₃ O ₂ S	L ₅	Yellow	132	66.20	5.29	11.02	12.59	8.41	381



C ₂₁ H ₁₈ N ₃ O SCl	L ₆	Yellow	142	63.85	4.85	10.63	8.10	8.11	395
C ₂₂ H ₂₁ N ₃ OS	L ₇	Buff	139	70.46	5.91	11.20	8.53	8.55	375
C ₂₂ H ₂₁ N ₃ O ₃ S	L ₈	Buff	144	64.92	5.45	10.32	15.72	7.88	407

The infrared spectrum data used to assign the formation of imines. The stretching bands obtained at 1693- 1708 assigned characteristic¹¹ of ν(C=O) and at 1606-1660 for ν(C=N) for L₁-L₈. (Table-2)

Table-2: Key Infrared Data of Ligands

Compounds	Frequency (cm ⁻¹)			
	ν(C=O)	ν(C=N)	ν(C-S-C)	ν(N-N)
C ₁₉ H ₁₇ N ₃ O ₂ S	1708	1633	634	1020
C ₂₁ H ₁₈ N ₃ OSF	1693	1620	632	1018
C ₂₂ H ₂₁ N ₃ O ₂ S	1693	1606	634	1031
C ₂₁ H ₁₈ N ₄ O ₃ S	1726	1662	603	1012
C ₂₁ H ₁₉ N ₃ O ₂ S	1704	1635	634	1062
C ₂₁ H ₁₈ N ₃ O SCl	1707	1660	632	1012
C ₂₂ H ₂₁ N ₃ OS	1707	1656	634	1022
C ₂₂ H ₂₁ N ₃ O ₃ S	1691	1633	634	1033

The ¹H NMR spectra of ligands L₁-L₈ gave additional information of imine formation. The structure and spectra of L₁ shown in figure-3, sharp peaks obtained are similar to the literature data. ¹H NMR (400 M Hz, CDCl₃) δ 1.79 (S, 3H, N=C-CH₃), 2.10 (S, 3H, O=C-CH₃), 5.30 (S, 1H, HC=C), 2.41 (S, 3H, Ar-CH₃), 6.20-7.80 (M, 8H, Ar-H).

A1

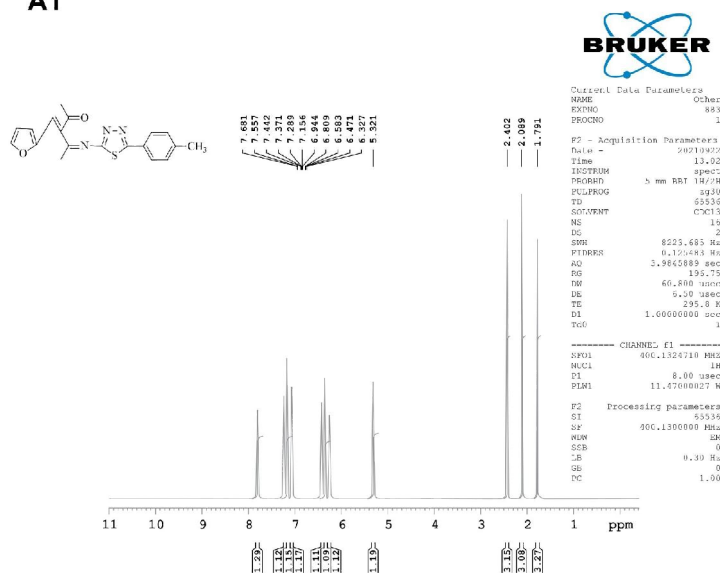


Figure-3

Synthesized ligands also screened by mass spectroscopic analysis. Mass spectra levels confirmation of molecular structure. For ligand L₁ m/z is 351, spectra obtained at same mass is shown in figure-4. Furthermore spectra obtained of loss in mass with respect to temperature.

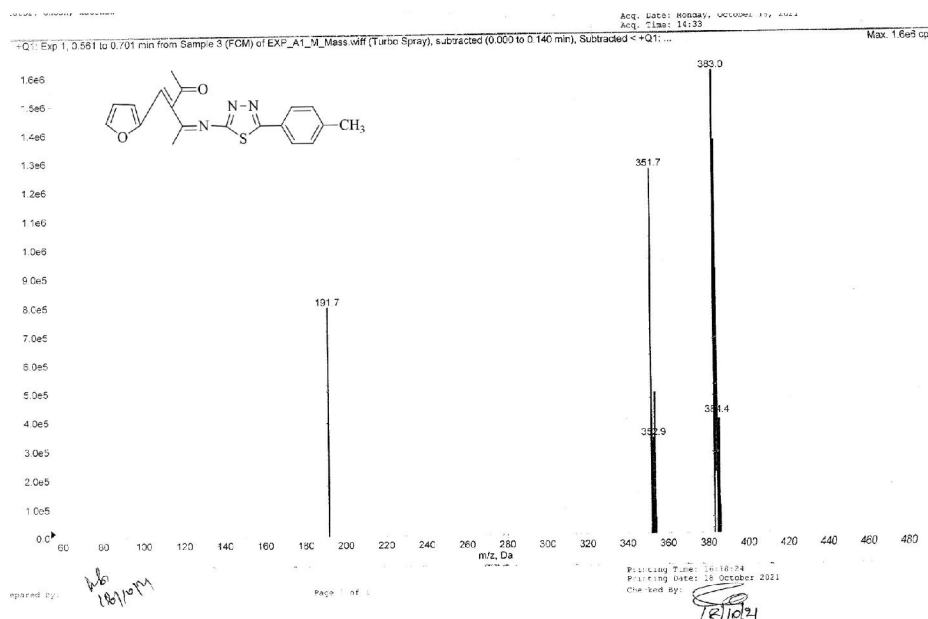


Figure-4

IV. CONCLUSION

The structure of synthesized ligands matches with their physical and spectroscopic data. L_1 - L_8 tridentate ligands are confirmed on their analytical data. Synthesized ligands were three (ONS/ONN) coordinated atoms, analyzed by various analytical techniques.

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