

Synthesis and Spectroscopic Studies of Some Novel 4-Substituted β -Diketo-Anils in Free and in Coordinated Forms

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Summary: The Schiff bases of activated anilines with β -diketone have been synthesized. The electron donating effects of methyl, methoxy and chloro groups, before and after coordination, were studied with the help of vibrational spectra and supported by UV-vis studies. In these β -diketo-anils and their complexes, instead of a band in the region 1590–1620 cm^{-1} for C=N group, bands in the regions 1100–1300 cm^{-1} and 3100–3300 cm^{-1} were observed and were assigned to C-N and N-H bonds. No significant band appeared for C=N in any of these ligands either in free or in coordinated forms. It was concluded that unlike other aldehydes and ketones, β -diketone upon reacting with anilines form C=C-N-H bonding instead of producing C=N functional group.

Introduction

Schiff base is a nitrogen analogue of an aldehyde or ketone in which the C=O group is replaced by a C=N-R group [1]. A large group of Schiff bases is utilized as metal ligands. They may be bi, tri, tetra or polydentate having NO, N₂O, N₂S, NO₂, NSO or N₂O₂ donor sets. In the case of mono dentate Schiff base the basic strength of the C=N group is not sufficient to obtain stable complexes by coordination of the imino-nitrogen atom to a metal ion. Hence, the presence of at least one other donor atom, suitably near the nitrogen atom, generally stabilizes the metal-nitrogen bond through formation of chelate ring. Some complexes of Schiff bases whose anions can act as bi, tri or tetra dentate ligands are shown in Figs. 1(a, b), 2 and 3.

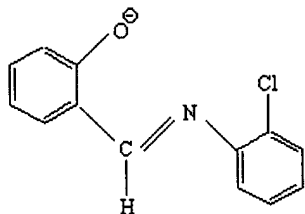


Fig. 1(a): Bidentate NO donor set.

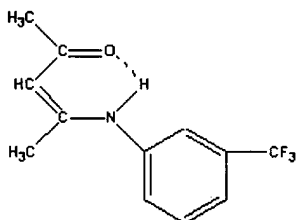


Fig. 1(b): Bidentate NO donor set.

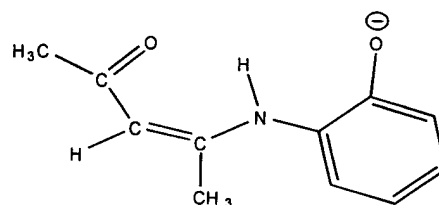


Fig. 2: Tridentate NO₂ donor set.

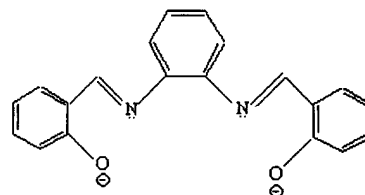


Fig. 3: Tetradentate N₂O₂ donor set.

The first reaction of a β -diketone with an amino compound was carried out in 1885 by Fisher and Bülow [2]. Simple substituted anilines and aryl amines condense readily with several β -diketones to give β -amino- α,β -unsaturated ketones [3], but the condensation of alkyl amines with β -diketones is difficult [4]. It is generally known that compounds having a Schiff base bonding, C=N, are affected by hydrogen ions in solution [5].

Ueno and Martell [6, 7] reported the preparation and IR spectra of some α,β -unsaturated- β -ketoamines and several corresponding metal chelates. They suggested three possible forms, A, B and C in Fig. 4, for the α,β -unsaturated- β -ketoamines in solutions.

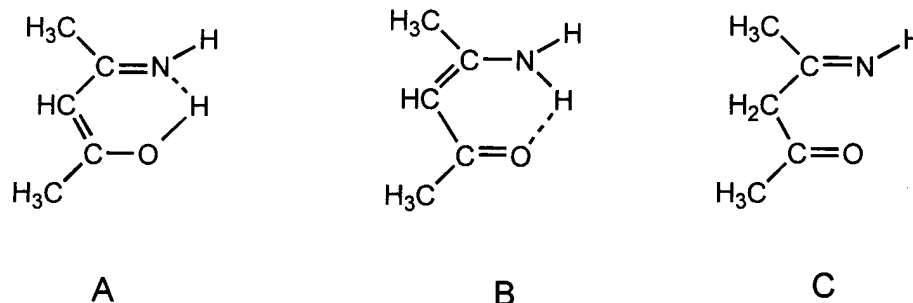


Fig. 4:

They concluded that a tautomeric equilibrium exists between the forms corresponding to A and B. Cromwell *et al.* [8] presented convincing evidence for structure B on the basis of their IR studies, which was supported by Holtzclaw and coworkers [9]. Dudek and associates [10-12] described NMR studies of 4-amino-3-pentene-2-ones, which established the validity of structure B in solution.

As these compounds contain two reactive functional groups *i.e.* C=N and C=O, which are also activating groups, so there are reactions which depend on the activated methylene hydrogen as well as the usual reactions of the keto and amino groups which are expected with such substances. In general the β -aminoketones are stable at elevated temperatures or in the presence of acids. The β -aminoketones, like β -amino acids, exhibit a tendency to reproduce the α,β -unsaturated carbonyl compound [13-15].

Most of the chelates of Schiff bases are synthesized by template reactions in which the carbonyl oxygen first combines with a metal ion to give an intermediate complex, which then reacts with a basic nitrogen donor, *i.e.* -NH₂ group to form Schiff base chelate. Utilized bidentate Schiff bases as metal ligands are usually characterized by having NO or N₂ donor set. Since the oxygen is often present as an OH group, these ligands generally function as mono anions [16].

Some Schiff base chelates were obtained with Co (II), Cu (II) and Ni (II) chloride salts. The proposed structure of the ligands and their complexes are based on IR, UV – visible, Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) [17-18].

Graph between Absorbance and Time

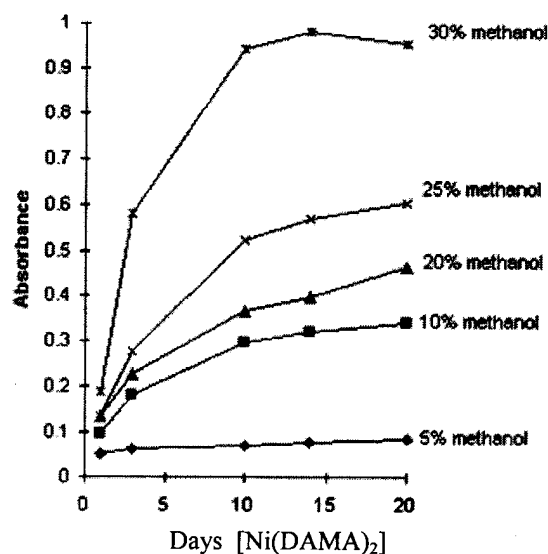


Fig. 5: Graph of DAMA Absorbance plotted against days in different Methanol/water concentrations.

Results and Discussion

All the compounds have been characterised by various techniques including melting points (Tables-3, 4), I.R. (Table-5) and U.V. Spectroscopies (Tables-3, 4 and Fig. 5). Abbreviations used and general information are given in Tables-1 and 2. Physical properties are given in Tables-3 and 4.

All the ligands gave stretches for C-N and N-H bonds instead of C=N which gives an idea that there is no C=N bond formation is taking place, instead peak for C=C bond was observed. All the ligands and their complexes gave peaks nearly in the

Table-1: General information of ligands.

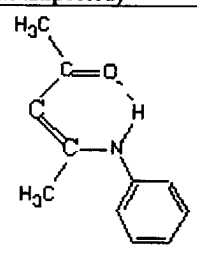
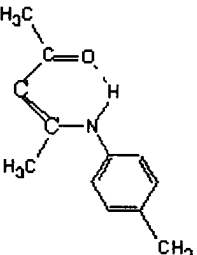
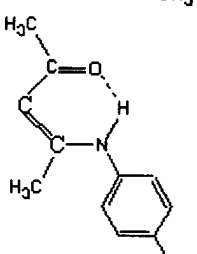
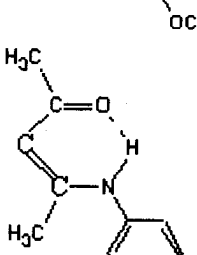
Structural Formula (as Expected)	Molecular Formula	Formula Weights (Calc.)	IUPAC Names	Abbreviations Used
	C ₁₁ H ₁₃ ON	175	Diacetyl Methane Anil	DAMA
	C ₁₂ H ₁₅ ON	189	Diacetyl methane-4- methyl Anil	DAM4(CH ₃)A
	C ₁₂ H ₁₅ O ₂ N	205	Diacetyl methane-4- methoxy Anil	DAM4(OCH ₃)A
	C ₁₁ H ₁₁ ONCl	209	Diacetyl methane-4- chloro Anil	DAMA4(Cl)A

Table-2: General information of complexes.

Compounds	Molecular Formula	Formula Weights (Calc.)	Abbreviations Used
Ni[diacetylmethane anil] ₂	Ni[C ₂₂ H ₂₆ O ₂ N ₂]	408	Ni[DAMA] ₂
Ni[Diacylmethane-4(methyl)Anil]	Ni[C ₂₄ H ₃₀ N ₂ O ₂]	436	Ni[DAM4(CH ₃)A] ₂
Ni[Diacylmethane-4-(methoxy)Anil] ₂	Ni[C ₂₄ H ₃₀ N ₂ O ₄]	468	Ni[DAM4(OCH ₃)A] ₂
Ni[Diacylmethane-4-chloro]Anil	Ni[C ₂₂ H ₂₄ O ₂ N ₂ Cl ₂]	477	Ni[DAM4(Cl)A] ₂

Table-3: Physical properties of ligands.

Ligands	MP °C	State	Color	% Yield	λ max
DAMA	48	Sticky Solid	Dark Brown	80.4	365.5
DAM4CH ₃ A	58	Rhombic Plates	Light Brown	73.8	380
DAM 4OCH ₃ A	40	Solid	Brown	68	360
DAM4ClA	42	Solid	Brown	72	330

Table-4: Physical properties of chelates.

Complexes	M. P °C	State	Color	λ max
Ni[DAMA] ₂	50	Platelets	Brown	380
Ni[DAM4(CH ₃)A] ₂	60	Flakes	Rust	370
Ni[DAM4(OCH ₃)A] ₂	106	Powder	Green	365
Ni[DAM4(Cl)A] ₂	48	Solid Granules	Brown	360

respective regions and no characteristic change in peaks were noticed before and after coordination except in C=O and C-N stretches, as expected *i.e.* they are coordination centers. Their peaks shifted to high field side. No variation of peaks appears in other bonds of both ligands and their complexes were noticed.

U.V. Scans

U.V. scans of the solutions of the ligands and complexes at different concentrations (10 %, 20 %, 25 %, 30 %) in methanol/water mixtures were recorded over a period of time. A graph of absorbance plotted against time gave an ascending curve, showing the solubilisation in progress. The plot straightened after a certain time indicating saturation of the solution. There was no change in

the wavelength of maximum absorption, and no new peak at any other wavelength appeared. Thus it was concluded that the compounds were stable in solution.

Experimental

Reagents and Chemicals

All chemicals used were of reagent grade and are obtained from Aldrich and used as such.

Synthesis of Chelating Agent

Schiff bases were prepared by the condensation reaction of diacetyl methane and some substituted aniline, as given in the literature [19]. 25 ml of 1 molar of an ethanolic solution of diacetyl methane (DAM), in 25 ml of ethanolic solution 1 molar of substituted aniline was added in small portions, (in one to one molar ratio). The reaction mixture was then stirred and refluxed for 6 hours. Precipitation began on cooling slowly. The resulting precipitates were washed with water and filtered off

Table-5: IR data for ligands.

Compound	Aromatics (Stretch + Bend)	Stretches cm ⁻¹					
		C=C	C=O	N-H	C-N	O-C	C-Cl
DAMA	3175m,3125m, 805s, 700s, 679s	1570m	1780m	3420m,3390m, 3350m,3215	1197m,1170m	-	-
DAM4(CH ₃)A	3135m,3100s,810m 798s, 700s, 630s	1600s	1745s	3340w,3310w, 3275m,3215m	1335m,1310m, 1215m,1175s, 1140m,1010s	-	-
DAM4(OCH ₃)A	3075w,2960s,918s, 830s,740s	1570m	1780w	3370m,3250w	1250s,1015s	1250s, 1197m	-
DAM4ClA	2940w,810s,630w	1565m	1810w	3370s,3230w	1280s,1100s,1005s	-	750s

Table-6: IR data of DAMA complexes:

Compound	Aromatic (Stretch + Bend)	Stretches cm ⁻¹					
		C=C	C=O	N-H	C-N	O-C	C-Cl
Ni[DAMA] ₂	3120m,3050s,865w,78 9s,730m,700s	1580w	1850s	3420m,3350m, 3280s	1315m,1270m, 1190s,1000w	-	-
Ni[DAM4(CH ₃)A] ₂	3100m,3000m,818s, 750s,660m	1580w	1840m	3370m,3350s, 3200m	1310w,1260m, 1185s,1000s	-	-
Ni[DAM4(OCH ₃)A] ₂	3210w,3000w,819s, 730m,650s	1560w	1820m	3350w,3170w	1239s,1010s	1300s,1239s	-
Ni[DAM4(Cl)A] ₂	3050s, 839m, 800m	1590m	1830m	3410s,3310m, 3220s	1315s,1272s, 1198s,1000m	-	759m,738m, 718m

Table-7: Comparison between ν cm⁻¹ chelates and their free ligands.

Substituent	C=O		C-N		N-H	
	Ligand	Chelate	Ligand	Chelate	Ligand	Chelate
-H	1780m	1850s	1170m	1190s	3420m	3420m
-CH ₃	1745s	1840m	1175s	1185s	3340w	3370m
-OCH ₃	1780m	1820m	1250s	1239s	3370m	3350m
-Cl	1810w	1830m	1280s	1272s	3370s	3410s

by suction and dried under vacuum desiccator. The dried precipitates were recrystallized for purification.

Synthesis of Ni(II) Chelates

A nickel chloride solution in 50 % ethanol/water was added to a hot ethanolic solution

of the respective ligand in 1:2 ratios, and on cooling a few drops of ethanolic NaOH solution were added. The precipitates were filtered, washed with a small amount of ethanol, and dried in a desiccator under vacuum.

Purification and Recrystallization

Crystals of these Schiff bases were grown using a number of purifying and crystallizing methods as described below.

(I) By Slow Cooling

The sample was refluxed in ethanol for half an hour and then allowed to cool, first within the heating mantle and then in cold water into which ice was added in small portions. When the temperature was in the range of 5-10°C crystals appeared. However, the crystals were very large and were stacked together and were not suitable for X-ray analysis.

(II) By Solvents Mixture

(a) By Slow Evaporation at Low Temperature

A number of solvent mixtures were tried, for example ethanol / n-hexane, CH₂Cl₂/n-hexane, and ether/n-hexane. The crystals were visible in ethanol / n-hexane, CH₂Cl₂/n-hexane mixtures on slow evaporation at 0-5°C were pure and well shaped and size.

(b) By Adding Cold Solvent into a Hot Ligand Solution

The sample was dissolved in a small volume of ethanol, in which it was very miscible. This solution was heated to reflux temperature, the other solvent (usually n-hexane) was added drop wise down the condenser until turbidity was seen, followed by a bit of first solvent to clear the turbidity. The solution was allowed to cool slowly. On cooling flaky crystals were apparent.

(III) By Slow Evaporation

The sample was dissolved either in CH₂Cl₂ or ethanol, in a small tube having three tiny holes in its top, and was left at 5°C for several weeks. As the solvent evaporated crystals appeared at the bottom of

the tube. The solvent was then drawn out with a fine pipette, leaving crystals of good geometrical shape and size.

Analytical Data

I.R spectra were recorded on a Hitachi 270-30 Infrared Spectrophotometer.

Conclusion

The preparation of these ligands was straightforward. Most of the compounds were isolated as crystals, and were easily recrystallised for purification.

IR studies revealed the fact that instead of C=N, -C=C-N-H linkage is formed. They are air and hydrolytically stable in solid and solution forms. No significant effect of electron donating groups on the properties of the ligands and their chelates was found.

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