

## Spectroscopic Study of New Schiff Bases Derived from Dibenzoylmethane and Benzoylacetone

N.A. ABOOD, Z.H. AIUBE, AND B.A. SAEED  
*Department of Chemistry, College of Education,  
University of Basrah, Basrah, Iraq*

(Received 27th November, 1989, revised 21st December, 1991)

**Summary:** UV,  $^1\text{H-NMR}$ , IR and Mass spectra of new Schiff bases derived from dibenzoylmethane and benzoylacetone are described. The strong absorption bands in the UV region between 350-380 nm have been attributed to the electronic transitions which arise from hydrogen bonded conjugate chelate rings. The other bands in the region 250-200 nm were attributed to aromatic and conjugated aromatic rings. The appearance of the signals due to the methylene protons adjacent to the nitrogen atom as a doublet centered at  $\delta = 4.5$  ppm in the NMR spectra and the ion  $\text{C}_6\text{H}_5\text{CO}^+$  at  $m/z$  105 in the mass spectra were taken as evidence that these compounds exist primarily in the keto-enamine form in solution.

### Introduction

The Schiff bases derived from  $\beta$ -diketones have attracted considerable attention, mainly in connection with investigations of the chelating abilities and analytical applications, and in the field of metal chelate catalysis [1-3]. In addition, metal chelates of  $\beta$ -diketone Schiff bases can act as reversible oxygen carriers [4,5]. However, this class of compounds is expected to show keto-enol tautomerism, and there has been controversy in the literature concerning the nature of the tautomeric species [6-8].

A recent UV study of Schiff bases derived from acetylacetone and benzoylacetone and aliphatic and aromatic amines has provided evidence for their existence in solution as equilibrium mixtures of hydrogen-chelating enol-imine and keto-enamine forms, while the former is the predominant species [6,9].

Ueno and Holtzclaw *et al* have studied the UV and IR spectra of bisacetylacetonate-ethylene diimine and bisbenzoylacetone-ethylene diimine and their metal chelates [10-12].

Moss and Robinson on the basis of  $^1\text{H-NMR}$  and IR data revealed that Schiff bases derived from 2-acetylcyclohexanone and 2-acetylcyclopentanone exist entirely in the keto-enamine form in solution and the equilibrium position is insensitive to the nature of the solvent [8,11].

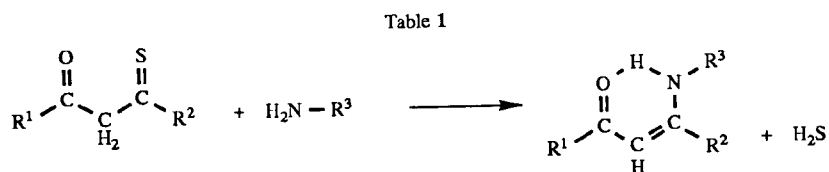
It is well known that replacement of one of the carbonyl groups by azomethine group ( $\text{C}=\text{N}$ ) in  $\beta$ -diketones results in a considerable bathochromic shift in the UV long wavelength absorption band in the spectra of  $\beta$ -diketones [9,11,13].



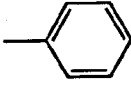
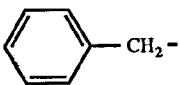
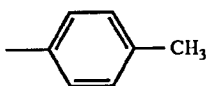
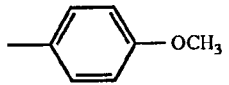
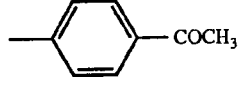
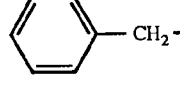
Acetylacetone and 4-(N-propylamino)-pent-3-ene-2-one show strong absorption bands at 271 and 307 nm respectively, which are attributed to the hydrogen bonded chelated rings of the enol form [9].

In previous work, it has been shown that introducing either phenyl or  $\text{CF}_3$  groups adjacent to one of the carbonyl groups in  $\beta$ -diketones or in the corresponding Schiff bases causes a bathochromic shift and increase in intensities of the UV bands [11,14-16]. Thus benzoylacetone and 1-phenyl-3-(N-propylamino)-but-2-ene-1-one absorb strongly at 308 and 340 nm respectively [9].

Recent studies on UV,  $^1\text{H-NMR}$  and IR data of Schiff bases derived from dimedon indicated the keto-enamine form [7,11].

The aim of the present work was to determine the structure of Schiff bases derived from dibenzoylmethane and benzoylacetone in solution in terms of their UV,  $^1\text{H-NMR}$ , IR and Mass spectra.



Compounds No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
1			
2	=	=	
3	=	=	
4	=	=	
5	=	=	
6	=	CH <sub>3</sub>	

## Results and Discussion

### UV spectra and structure

The absorption spectra of the studied Schiff bases in ethanol are illustrated in Fig. 1, and the spectral data are tabulated in Table 2.

The spectra appeared quite similar and are characterized by three strong absorption bands. Molecule 1 shows these bands; I, II and III at 375, 252 and 206 nm respectively. Previous work has shown that replacement of a carbonyl group in  $\beta$ -diketones by an azomethine group results in a bathochromic shift in band I. Introducing a phenyl group on the nitrogen atom of a  $\beta$ -diketone Schiff base causes further red shift.

This is in agreement with experimental data since molecule I and dibenzoylmethane have shown band I at 375 and 343 nm respectively.

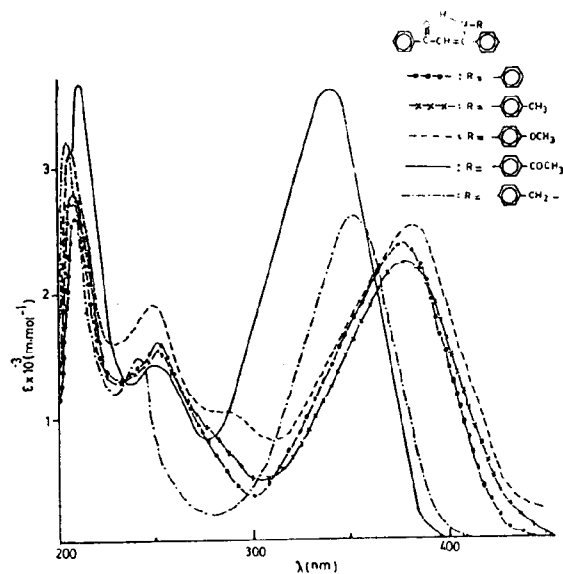


Fig.1: UV spectra of Schiff bases in ethanol.

Table 2: UV absorption data of Schiff bases in ethanol

Comp- No	$\lambda_{\max}$ , nm ( $\epsilon$ max, $\text{m}^2\text{mol}^{-1}$ )		
	Band I	Band II	Band III
1	375(2300)	252(1560)	206(2660)
2	352(2600)	244 (1760)	208 (3200)
3	376 (2220)	252 (1570)	208 (2800)
4	380 (2790)	248 (1900)	208(3100)
5	338(3720)	250(1720)	211(3800)
6	343(2800)	242(1200)	206(2400)
7	*360(1640)	246(1850)	
8	*324(2870)		266(1170)
9	312(2143)		

\* From reference [9]

(7) 1-phenyl-4-(N-phenylamino)-but-2-ene-1-one, (8) acetylacetone-amiline, (9) 4-(N-propylamino)-pent-3-ene-2-one

On the other hand, band I of molecule 1 corresponds to 4-(N-propylamino)-pent-3-ene-2-one has strong absorption band at 312 nm.

Comparison the band I in molecule 2 with that of molecule 1 assists in showing the extent of interaction of the benzene ring the electrons with the lone pair of electrons on the nitrogen atom and with the hydrogen bonded chelate ring system.

The blue shift of band I in molecule 2 can be understood, since the introduction of the methylene (-CH<sub>2</sub>-) between the benzene and the nitrogen atom would destroy the interaction.

However replacement of methyl group by phenyl in molecule 1 leads to a bathochromic shift of 12 nm in band I.

The introduction of electron donating groups in the para position in the aniline part of molecule 1 causes a small bathochromic shift in band I, whereas electron withdrawing groups cause a noticeable blue shift Table 2.

For instance molecule 5 absorbs strongly at 338 nm, while molecule 1 absorbs at 375 nm. All these observations lead to suggestion that these compounds possess the keto-enamine structure.

However band I bathochromically shifted when the solvent was changed from nonpolar to polar Table 3 which reveals the  $\pi \rightleftharpoons \pi^*$  nature of the transition of the band, while the insensitivity of

Table 3: Solvent effect on UV absorption bands of molecule 2

Solvent	$\lambda_{\max}$ , nm ( $\epsilon$ max, $\text{m}^2\text{mol}^{-1}$ )		
	Band I	Band II	Band III
n-hexane	344(200)	238(1460)	205(2600)
CHCl <sub>3</sub>	354(1970)	248(1400)	
Methanol	345(2580)	256(1900)	
THF	352(2060)	243(1960)	213(2040)
Dioxane	352(2040)	243(1320)	215(1200)
CCl <sub>4</sub>	352(1960)	260(1700)	
DMSO	356(2040)	260(1700)	

its intensity to various solvents indicated that molecule 1 exists only as keto-enamine and the other tautomers are either present in undetectable quantities or absent.

B and II and III are not observed in the spectrum of 4-(N-propylamino)-pent-3-ene-2-one, quite clearly they are associated with the phenyl groups. The bathochromic shift of band II with respect to the acetophenone band at 244 nm can be attributed to the effect of the presence of two phenyl groups attached to the hydrogen bonded chelated ring system in the keto-enamine structure. Therefore band II is related to the conjugation of the aromatic ring with unsaturated chelated ring system, whereas band III attributed to the aromatic ring.

#### NMR spectra and structure

The NMR studies are in agreement with that of UV in suggesting that all of the Schiff bases examined exist in solution as keto-enamine form as hydrogen bonded chelated tautomers.

No evidence has been observed which could be assigned to a keto-imine tautomer, i.e no signal was detected for the methylene protons.

The NMR data and the assignments are summarised in Table 4. The data were obtained at 250 MHz and the solvent was CDCl<sub>3</sub>.

The spectra were characterized by two singlet lines. The down field broad lines in the region 11.71 to 12.95 ppm were attributed to hydrogen bonded protons; i.e. N-H-O group, while the other ones between 5.76 and 6.18 ppm were assigned to the C=C-H protons Table 4.

Table 4: NMMR data of Schiff bases in CDCl<sub>3</sub> at 250 MHz

Mole-	Chemical Shift PPM			
	aromatic	aliphatic	-CH <sub>2</sub> -	N-H--O -C=C-H
1	7.98 <sup>d</sup> 7.72 <sup>m</sup> 7.19 <sup>t</sup> 7.0 <sup>t</sup> 6.97 <sup>d</sup>			12.90 <sup>s</sup> 6.09 <sup>s</sup>
2	7.90 <sup>d</sup> 7.30 <sup>m</sup>		4.42 <sup>d</sup> J = 6.7Hz	11.71 <sup>s</sup> 5.87 <sup>s</sup>
3	7.96 <sup>d</sup> 7.35 <sup>m</sup> 6.92 <sup>d</sup> 6.68 <sup>d</sup>	2.23 <sup>s</sup>		12.86 <sup>s</sup> 6.05 <sup>s</sup>
4	7.97 <sup>d</sup> 7.37 <sup>m</sup> 6.70 <sup>t</sup>	3.70 <sup>s</sup>		12.90 <sup>s</sup> 6.04 <sup>s</sup>
5	7.97 <sup>d</sup> 7.73 <sup>d</sup> 7.47 <sup>m</sup> 6.78 <sup>d</sup>	2.51 <sup>s</sup>		12.88 <sup>s</sup> 6.18 <sup>s</sup>
6	7.90 <sup>d</sup> 7.37 <sup>m</sup>	2.08 <sup>s</sup>	4.55 <sup>d</sup> J = 6.7Hz	11.77 <sup>s</sup> 5.76 <sup>s</sup>

s = singlet, d = doublet, t = triplet, q = quartet

This indicates that these bases exist primarily in the hydrogen bonded conjugated chelated keto-enamine.

Comparison of the spectra of molecules 2 and 6 with other molecules examined, shows clearly that the doublets in the region 4.41 to 4.58 ppm arose from methylene protons of the benzyl groups. The coupling of the methylene protons with the N-H--O proton splits the methyles signal into doublet with J = 6.7Hz. Similar results have been found in studying the NMR spectra of Schiff bases derived from 2-acetyl cyclic-ketones, these results support the above conclusion.

#### Infrared spectra and structure

Infrared spectra showed a very weak broad absorption band between 3400 to 2700 cm<sup>-1</sup> and a weak band at 3060 cm<sup>-1</sup>. These bands were attributed to hydrogen-bonded stretching vibration of N-H group.

Characteristic absorptions of the compounds are expected to appear in the region 1750 to 1500 cm<sup>-1</sup>. Since the double bonds C=O, C=C, C=N and phenyl ring show vibrational absorptions in this region as well as both C-O and C-N bonds which

have partial double bond character. Therefore the assignments of the bands must be considered as tentative [2,10,12].

In fact the compounds have shown a number of strong bands in this region, but there was no indication for the free carbonyl group, i.e. absorption around 1700 cm<sup>-1</sup>, and therefore the possibility of existence of the ket-imine was ruled out for these compounds.

A strong absorption band appeared in the spectra of all the compounds studied in the region 1600 to 1595 cm<sup>-1</sup>, was assigned to the hydrogen bonded conjugated chelated C=O group, while the next bands between 1585 to 1540 cm<sup>-1</sup> was attributed to C=C stretching vibration. The other bands in the region, at lower wave number, can be attributed to vibrations of functional groups such as phenyl rings. A similar conclusion was obtained by Holtzclaw *et al* and Khuhawar [2,10].

A number of strong bands were observed in the region 700 to 850 cm<sup>-1</sup>. These bands around 800 and 700 cm<sup>-1</sup> were assigned to bending vibrations of C=C-H of the keto-enamine form and aromatic protons of phenyl rings respectively.

#### Mass spectra and structure

The compounds studied showed quite characteristic behaviour upon electron impact. All the compounds exhibited parent peaks with relatively high intensities. The appearance of the ion [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> at m/z = 105, and the absence of the molecular ion at CH<sub>3</sub>CO<sup>+</sup> at m/e = 43 in the spectrum of molecule 6 can be taken as a strong evidence that the condensation of benzoylacetone and amines occurred on the acetyl group. On the other hand, the ion [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> appeared in all examined spectra.

On basis of this, one can conclude that these compounds are mainly existed in keto-enamine form, in agreement with the conclusion which was obtained from NMR and IR studies.

#### Experimental

##### Preparation of Schiff bases

The investigated Schiff bases in this work are summarized in Table 1.

The bases were prepared by condensation of equimolar quantities of the corresponding  $\beta$ -thioxo ketones and appropriate amines as reported elsewhere [17]. The compounds were identified by sharp melting points, microanalysis, IR,  $^1\text{H-NMR}$  and mass spectra.

#### Spectral measurements

UV absorption spectra were recorded in various spectral solvents on a Pye unicam SP8-200 spectrophotometer, using 1 cm quartz cells, at a concentration of  $5 \times 10^{-5}\text{M}$ , at room temperature. IR spectra were measured in KBr discs and in  $\text{CHCl}_3$  and  $\text{CCl}_4$  solutions, concentration range 1 to  $10^{-3}\text{M}$ , with NaCl cells 0.5 - 0.2 mm - pathlength, using a Pye Unicam SP 3300 spectrophotometer.  $^1\text{H-NMR}$  spectra were obtained with a Bruker WM 250 spectrometer at 250 MHz, in  $\text{CDCl}_3$  solutions, using TMS as internal standard. Mass spectra were obtained on a MAT 1125 Finnigan using an ionizing energy of 70 eV.

Microanalysis,  $^1\text{H-NMR}$  and mass spectra were performed at the Faculty of Chemistry, Konstanz University, West Germany.

#### References

1. A.E. Martell, *Pure and Appl. Chem.*, **12**, 129 (1968).
2. M.Y. Khuhawar, *J.Chem.Soc.Pk.*, **6**, 225 (1984).
3. K. Ueno and A.E. Martell, *J.Phys.Chem.*, **41**, 257 (1957)
4. K. Unco and A.E. Martell, *J.Am.Chem.Soc.*, **60**, 270 (1956)
5. A.E. Martell and M. Calvin 1952. "Chemistry of the Metal Chelate Compounds", Prentice-Hall New York, N.Y. P.337.
6. A.A. Saeed, A.W.A. Sultan, S.A. Selman and N.A. Abood, *Can. J. Spectrosc.*, **28**, 104 (1983).
7. J. Greenhill, *J.Chem.Soc. Perkin Trans I*, 207 (1976).
8. K.C. Moss and F.P. Robinson, *Can. J.Chem.*, **51**, 505 (1973).
9. A.A. Saeed, M.N. Al-Zagoum and M.H. Waton, *Can. J. Spectrosc.*, **25**, 137 (1980).
10. H.F. Holtzclaw, J.P. Collman and R.M. Alire, *J. Am.Chem.Soc.*, **80**, 1102 (1958).
11. N.A. Abood, N.A. Al-Mansoudi and A.A. Saeed, *J. Iraqi Chem.Soc.*, **2**, 149 (1986).
12. A.A. Saeed, N.A. Abood, N.A. Al-Mansoudi and G.Y. Matti, *Can. J.Chem.* **52**, 55 (1984).
13. A. Gillam and E.S. Stern, 1954. "An Introduction to Electron Absorption Spectroscopy in Organic Chemistry", Edward Arnold Ltd. London, P. 100.
14. G.O. Dudek and R.H. Holm, *J.Am.Chem.Soc.*, **83**, 2099 (1961).
15. P.J. McCarthy and A.E. Martell, *Inorganic Chem.*, **6**, 781 (1976).
16. L.N. Ferguson, 1973. "The Modern Structural Theory of Organic Chemistry", Prince-Hall of India Private Ltd., New Delhi.
17. N.A. Abood, Z.H. Aiube and B.A. Saeed, to be published).