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Spectroscopic Study of some Schiff Bases Derived from Dibenzoylmethane

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Abstract

A series of Schiff bases **7-11** derived from dibenzoylmethane have been prepared. The UV, IR, ^{1}H NMR and mass spectra revealed theses compounds were existed mainly as the keto-enamine tautomer in the solution. The absorption bands which appeared in the range λ_{max} = 376-406 nm were assigned to the electronic transitions which arised from the central hydrogen bonded chelated unsaturated ring system in this tautomer. The appearance of the broad singlet near δ = 13 ppm due to the N-H proton and a singlet near δ = 6 ppm due to the –C=C-H proton inaddition to benzoyl fragment ion signal *m/z* = 105 in the mass spectra supported the above suggested products.

Keywords: Dibenzoylmethane; Keto-enamine Tautomer; Schiff Bases; Spectroscopic Study.

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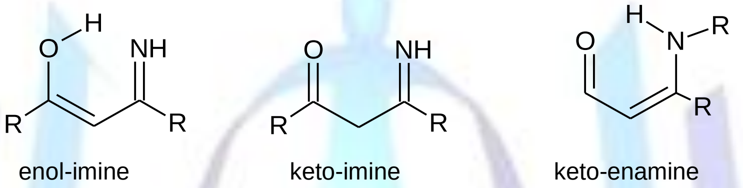
1. Introduction

The imines formation is a particularly important chemical reaction in some biological processes [1, 2]. For example, the covalent binding of carbonyl-containing compounds to an enzyme usually involves the formation of imine, meawhile Haung *et al.* [3] have reported that dibenzoyl-methane (DBM) itself showed that DBM had strong anti-inflammatory and anti-tumor promoting activities in mouse skin.

In recent years, the understanding of the tautomerism progresses due to the investigation of this phenomenon became one of the major topics in theoretical chemistry. For example, tautomerism in keto-enol [4,5] imine-enamine [6,7] purines [8], pyrimidines [9] and many other systems [10,11] have been studied during past two decades. Thereupon, compounds containing tautomers can be the subject of interest for the theoreticians. In title compounds, the tautomerism affects their chemical and biological activities, and any systematic publications on theoretical study of their tautomerisms have been not take place. In this connection, it seems to be important to study the complete scheme of tautomerism and the reaction pathways between different tautomers. In this line, effects of solvent on this tautomerism should also be worked out clearly [12]. Furthermore, the utility of Schiff bases that derived from β-diketones as models in the investigation of the keto-enol tautomerism, their application as metal chelate catalysts and their analytical importance [13, 14] in addition to the fact that their metal chelates have conjugated systems similar to those of the synthetic chelated oxygen carriers [15, 16] have drown an increasing interest to them. These compounds could be exist as a tautomeric mixture of the enol-imine, the keto-imine and the keto-enamine tautomers:



The most important intramolecular enol-imine and keto-enamine tautomerism in biological system exists in pyridoxal-5-phosphate (PLP) dependent enzymes. From the crystal structure data of PLP dependent enzymes, it is clear that the cofactor PLP forms a Schiff base with the amino group of a lysine residue or with the amino acid substrates which are going to be transferred [17-21].

Previous concerning studies showed such Schiff bases existed mainly as a tautomeric mixture of both the enol-imine and the keto-enamine forms [22, 23], whereas some studies supposed the predominance of the enol-imine in other systems [24, 25], in addition to the predominance of the keto-enamine [26, 27] in other studies. Furthermore, some interested studies have indicated the exsistence of the keto-enamine form for Schiff bases derived from demidone on the basis of their UV, ^{1}H NMR and IR data [26, 28]. Theoretical calculations by B3LYP/6-31G(d,p) level of theory showed that the enolic form was the most stable within the possible tautomeric forms of the compounds [29]. Metal complexes of Schiff bases occupy a central role in coordination chemistry for analytical, physical, and biochemical purposes [30].

This work is devoted to investigate the structures of some Schiff bases derived from dibenzoylmethane on the basis of their UV, IR, NMR, and mass spectra.

2. Experimental

Melting points were determined on a Gallenkamp melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded by a Brucker WM 250 spectrometer at 250 MHz in $CDCl_3$ using TMS as internal standard. The mass spectra were measured on a MAT 1125 Finnigam using an ionizing energy of 70 ev. The UV absorption spectra were obtained with LKB Biochrom ULTROSPEC II UV/VIS spectrophotometer, using 1 cm quartz cells, at a concentration of 5x10^{-5} M. The IR spectra were recorded by SP3-300 spectrophotometer as KBr discs. All the solvents which used for the spectral purposes are of spectroscopic grade and used with no further purification. The microanalyses, NMR and mass spectra were performed at konstanz University, Germany.

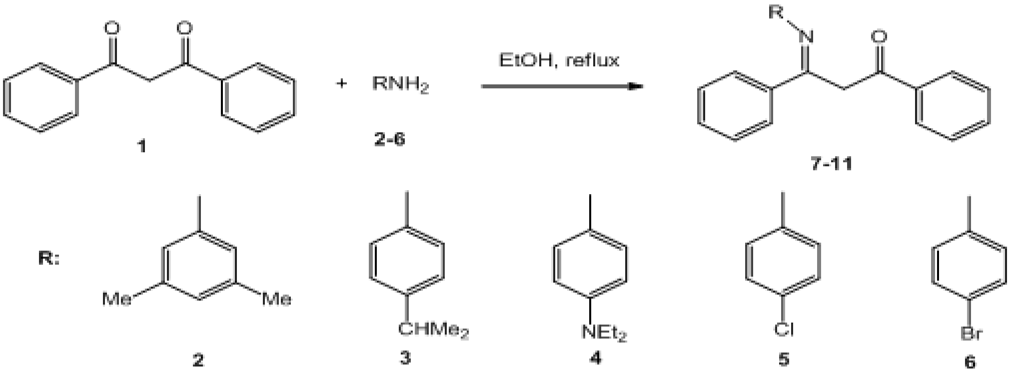
3-((4-Aryl)imino)1,3-diphenylpropan-1-one (**7-11**).

A mixture of dibenzoylmethane **1** (1.0 mmol) and arylamines **2-6** (1.0 mmol) in EtOH (15 mL) was heated under reflux for 2-3 h. After cooling, the products were filtered and recrystallized from EtOH to give the desired products.

3. Results and discussion

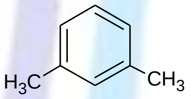
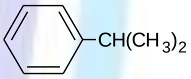
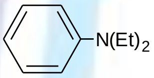
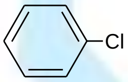
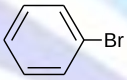
The Schiff bases of dibenzoylmethane **7-11** were prepared from treatment of equimolar of the dibenzoyl-methane **1** and the appropriate amines in refluxing EtOH (Scheme 1).

The molecular structures, the molecular formula, the melting points and the micro-analyses of the bases are gathered in Table 1.



Scheme 1. Synthesis of Schiff bases of dibenzoylmethane (7-11)

Table 1. Physical data of the synthesized Schiff bases of dibenzoylmethane.

Entry	R	m.p.(^{0}C)	molecular formula	Elemental analysis		
				C	H	N
7		105-107	$C_{23}H_{21}NO$ 327.4	(84.37) 83.98	(6.46) 6.38	(4.28) 4.32
8		110-112	$C_{24}H_{23}NO$ 341.4	(84.42) 84.31	(6.79) 6.69	(4.10) 4.02
9		118-117	$C_{25}H_{26}N_2O$ 370.5	(81.05 80.82	(7.07) 7.01	(7.56) 7.42
10		140-141	$C_{21}H_{16}NOCl$ 333.8	(75.54) 75.32	(4.83) 4.78	(4.19) 4.22
11		149-150	$C_{21}H_{16}NOBr$ 378.2	(66.68) 66.42	(4.26) 4.18	(3.70) 3.42

3.1. NMR spectra

The Schiff bases are displayed a typical ^{1}H NMR spectra (Table 2), characterized by two broad singlets within the region δ = 2.80-13.0 ppm, one assigned to the chelated proton of the group N-H…O [23, 26, 27], and the other singlet within the region δ = 5.98-6.11 ppm which assigned to C=C-H proton. The former signal suggested the existence of the keto-enamine tautomer, meanwhile the absence of the methylene protons signal ruled out the existence of the keto-imine form. This indicates that these bases are existed primarily as the keto-enamine tautomer in solution.

3.2. IR spectra

The important features of the IR spectra are tabulated in Table 2. The absence of the absorption around ν_{max} = 1700 cm^{-1} attributed to the free C=O group leave a negligible chance to the existence of the keto-imine tautomer, and this fact was also confirmed based on the data of the NMR spectra. In addition, the spectra showed number of strong bands within the region ν_{max} = 1606-1560 cm^{-1}, which contained the absorption of the stretching vibrations of the C=O, C=N, and the C=C bonds of the chelated unsaturated ring systems of the enolic forms, together with the stretching vibration of the C=C bonds of the phenyl groups and the C=O and the C=N bonds which have a partial double bond character in addition to the bending vibration of the N-H bond in the keto-enamine tautomer. This crowd of absorption frequencies would any effort to assign them only an a trivial attempt [26-28]. Therefore, the strong bands that appeared at this region might be attributed to the conjugated chelated C=O, C=N and the bending of the N-H group in the keto-inamine tautomer, or to the C=N and the C=O groups in the enol-imine tautomer in addition to the C=C groups in both of the tautomers and the phenyl rings.

3.3. Mass spectra

All the compounds exhibited parent peaks with relatively high intensity (Table 2). The appearance of the fragment ion $C_6H_5CO^+$ at *m/z* 105 in all of the spectra was an indicative for existence of the keto-inamine tautomer. In addition, the signal of the fragment ion [M^+-17] indicated the existence of the enol-imine tautomer as a partener in the tautomeric tautomeric equilibrium mixture at least in the gas phase.

Table 2. The IR, ^1H NMR and mass spectra of the Shiff bases

Entry	IR		^1H NMR (δ, $CDCl_3$)		Mass spectra		
	C=O	C=N	N-H	C=C-H	Molecular ion	*m/z*	Relative intensity
7	1606(s)	1591(s)	12.87	6.05	M^+	327	57.3
					M^+-17	310	17.1
					$C_6H_5CO^+$	105	16.5
8	1600(s)	1590(s)	12.93	6.04	M^+	341	100
					M^+-17	324	17.3
					$C_6H_5CO^+$	105	58.5
9	1600(s)	1590(s)	12.99	5.98	M^+	370	100
					M^+-17	355	41.8
					$C_6H_5CO^+$	105	20.3
10	1592(s)	1581(s)	12.84	6.11	M^{+a}	333	97.0
						335	32.8
					M^+-17^a	316	10.6
						318	3.5
					$C_6H_5CO^+$	105	58.5
11	1591(s)	1586(s)	12.83	6.11	M^{+a}	378	52.1
						380	50.8
					M^+-17^a	360	5.9
						362	5.6
					$C_6H_5CO^+$	105	54.8

(s): strong, a: two masses for each ion due to two different isotopes.

3.4. UV spectra

The UV spectra of the Schiff bases are tabulated in Table 3. The spectra were characterized by existence of three strong bands. The investigated bases showed three bands: I, II, and III at the ranges λ_{max} = 376-406, 253-266 and 205-208 nm, respectively. The effect of the substituents attached to the aniline part of the molecules is appeared clearly, especially at compound **9** which has the longest absorption band at λ_{max} = 406 nm due to the strong donating group NEt_2, while the corresponding band at compound **8** is centered at λ_{max} = 378 nm, is in agreement with the behavior of the π- π^* transition. Band I in the molecule **11** is bathochromically shifted by λ_{max} = 41 nm in comparison to the corresponding band of the parent molecule, the dibenzoylmethane, This shift, which appeared as a result of the replacement of the carbonyl group in the β-diketones by the azomethine group, is further enlarged on the introducing of an aryl group on the nitrogen atom of the Schiff base [24, 26, 27].

The correspondence of band I with the long wavelength band at λ_{max} = 343 nm in dibenzoyl methane, arised from the central hydrogen bonded chelated conjugated ring system may lead to the suggestion that band I is arose from a similar system in the Schiff bases which represented by either the keto-enamine or the enol-imine tautomer. The bathochromic shift of the band I upon changing from nonpolar solvents to polar solvents, Table 4, reveals the π-π* nature of the transitions responsible for the band.

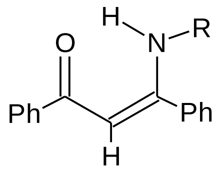


Table 3. The UV spectra data of compound 11 in different solvents

Solvent	λ max, nm (Σ max, m^2mol^{-1})		
	Band I	Band II	Band III
n-Hexane	374 (1701)	256 (1407)	208 (451)
CCl_4	374 (1653)	260 (1160)	
$CHCl_3$	376 (1618)	258(1106)	
Ethyl acetate	376 (1492)	259 (1122)	206 (893)
DMSO	384 (1800)	260 (1213)	

Table 3 shows no systematic order of the intensity of band I upon changing from nonpolar to polar solvents. This insensitivity of the band to the polarity of the solvent indicates that molecule **11** exist mainly in one of the enolic tautomers, the keto-enamine or the enol-imine in the solvent. This finding in addition to what have been concluded on the basis of the nmr spectra lead to suggest that the tasted Schiff bases exist mainly as the keto-enamine tautomer in solution with no rejection to the other tautomers which may present in much smaller concentrations in tautomeric mixtures. Band II is related to the aromatic ring conjugated with the unsaturated chelated ring system, whereas the band III is related to the local excitation of the aromatic rings.

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Dr. Wasfi Abboud Al-Masoudi, assistant professor and researcher in the Department of Physiology and Chemistry, Faculty of Vet. Medicine at the University of Basrah, born Basrha - Iraq in 1959, holds a bachelor's, master's and Ph.D. from the Department of Chemistry - Faculty of Education - University of Basrha,Specialization Organicmettalic Chemistry - professor of organic chemistry in the number of Libyan universities and the University of Basrha, published 14 research specialization in a number of international scientific journals also participated by more than a dozen scientific conferences in chemistry with a number of Arab and international countries - published a number of scientific articles and local educational magazines. Awarded several certificates of appreciation for his scientific them a certificate of appreciation from the Union Chemical Arab and African Conference of chemistry.

Asst. Prof. Dr- Wasfi A. Al-Masoudi