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Computational DFT/CI spectroscopic structural studies of some complexes of benzalbarbituric acid

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ABSTRACT

Via Gaussian 98, calculations have been carried out as B3LYP/6-31G^{**} basis sets and the predominant tautomers of benzalbarbituric acid (BenzalBA) have been defined taking in consideration the energy of the density functional theory. The electronic transition energies have been calculated for the possible tautomers by the configuration interaction between the ground configuration Eigenfunction and the excited configuration Eigenfunctions explaining the absence of the relative intensity change in the UV spectrum by the heat effect as a result of the coincidence of the transition energies of the possible tautomers. The electronic spectra (UV–visible) were scanned for BenzalBA in different solvents of different polarities to determine the Einstein transition probabilities, dipole strengths, oscillator strengths, lifetime of the excited states and extinction coefficients. The hydrogen bonding and the orientation energy of the polar solvent molecules toward BenzalBA molecule were determined from the spectral studies in mixtures of polar and non-polar solvents. Some complexes were prepared from BenzalBA with some divalent metal ions, i.e. Fe⁺⁺, Zn⁺⁺ or Cu⁺⁺. Their structures have been confirmed by elemental analysis, mass spectra, ¹H NMR spectra, atomic absorption spectra and UV–visible spectra. It has been concluded that the structures of the complexes have the C_{2h} point group symmetry in which two BenzalBA moieties are chelated to any one of the metal ions Fe⁺⁺, Zn⁺⁺ and Cu⁺⁺.

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1. Introduction

The *n*-heterocyclic compounds containing amide linkages are widely used in medicine, principally as hypnotic drugs and produce depressive effects on the central nervous system [1]. The barbiturates possess effects on the motor and sensory functions [2].

Barbituric acid displays keto–enol tautomerism, the most important tautomer being the triketo-form and 4-hydroxy tautomer obtained from the methylene hydrogen to the adjacent keto oxygen [3].

The attention is directed to barbituric acid derivatives having inhibitory activity for matrix maetalloproteases comprised of formula (I): ##STR1## pharmaceutical compositions thereof, processes for preparing the derivatives, and methods for treating diseases associated with elevated or uncontrolled levels of matrix metalloprotease activity, e.g., cancer, specifically tumor progression and tumor metastasis, inflammation, or as a method of contraception. This invention has been reported in the literature [4].

A conformational study on barbituric acid and thiobarbituric acid was studied at ab initio MP2/6-31G level on the molecular, protonated, mono and di-anionic forms. More over the electronic transitions were obtained through ZINDO approaches [5].

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Ab initio and density functional theory (DFT) methods were used to study the tautomers of barbituric acid in the gas phase and in a polar medium. In the gas phase, the tautomers were optimized at HF/6-31G MP2/6-31G* and B3LYP/6-31G*, B3PW91/ 6-31G* levels of the theory. The self-consistent reaction field theory (SCRF) at HF/6-31G* level has been used to optimized the tautomers in a polar medium [6].

Benzalbarbituric acid was prepared by condensation reaction between barbituric acid and benzaldehyde; UV–visible spectra of BenzalBA have been scanned in pure and mixed solvents to calculate some parameters, and Gaussian 98 program had been used to study the structure of BenzalBA via the DFT.

Some of BenzalBA complexes were prepared from using divalent ions such as Fe⁺⁺, Zn⁺⁺ or Cu⁺⁺ therefore the structures of these complexes have been confirmed by some analyses such elemental analysis, mass spectra, atomic absorption spectra and UV-visible spectra.

2. Experimental work

2.1. Materials

The solvents were purified according to literature [7,8]; Benzal-BA was prepared according to literature [9] and its melting point has been detected to be 258 °C. The materials that were used to





prepare the complexes in addition to BenzalBA are copper acetate monohydrate Cu $(CH_3COO)_2 \cdot H_2O$, ferrous sulphate heptahydrate FeSO₄·7H₂O and zinc acetate dihydrate Zn $(CH_3COO)_2 \cdot 2H_2O$ which were obtained from Analar grade salts (BDH). All materials employed in the present preparations were chemically pure.

2.2. Preparation of BenzalBA

Preparation of the BenzalBA was done by mixing of (1 mol) barbituric acid (BA) and (1 mol) from benzaldehyde, in methanol then the mixture was refluxed for about 3 h, cooling, then filtered off the precipitate and recrystallized with appropriate solvent so the melting point of the prepared compound is 258 °C.

2.3. Preparation of complexes

Preparation of complexes was done using pure solvents and the materials which have been previously mentioned before. Preparation of complexes [10] between BenzalBA and Cu⁺⁺, Fe⁺⁺ or Zn⁺⁺ had been done by refluxing them in ethanolic solution in ratio 2:1 ligand to metal ion (M⁺⁺) for about 2 h then the complex was precipitated and washed firstly by ethanol.

All Melting points of the studied complexes have been mentioned in Table 1 and were determined on a SMP 10 melting point apparatus.

2.4. Instrumentations

The carbon, hydrogen and nitrogen contents were determined using Elementer Analyses System (GmbH, Donaustr-7, D-63452) Hanau, (Germany). Chemistry Department, Faculty of Science, Assiut University.

The electronic absorption spectra had been scanned by UV-2011 PC, UV–Vis Scanning Spectrophotometer (Shimadzu) using 1 cm matched silica cells, Chemistry Department, Faculty of Science, Assiut University.

The mass spectra of studied compound were performed by JEOL JMS 600 Spectrometer at ionizing potential of 70 eV using the direct inlet system, at Central Lab. Assiut University, Assiut.

The Atomic Absorption Spectra of the complexes were studied by using an Atomic Absorption (GBC Scientific Equipment Pityltd Model GBC 906 AA), Soils Laboratory for Analyses and Technical Consultation Department, Faculty of Agriculture, Assiut University.

¹H NMR spectra were recorded in deutrated dimethylsulphoxide (DMSO) with a Varian Instrument Division 90 MHz EM 390 NMR Spectrometry. All chemical shifts (δ) are given in ppm versus tetra-methylsilinate (TMS), American Company, Chemistry Department, Faculty of Science, Assiut University.

3. Method of calculations

3.1. Computational studies

Computational calculations on the isolated molecules in the gas phase were performed within GAUSSIAN 98 package. Minimum energy structures have been achieved by AM1 semi-empirical method. Calculations were performed on the minimum energy

Table 1Melting points of the complexes.

Compound	Melting point (°C)
(BenzalBA) ₂ -Cu ⁺⁺	300
(BenzalBA) ₂ -Fe ⁺⁺	320
(BenzalBA) ₂ -Zn ⁺⁺	296

structures using the closed shell Hartree–Fock, Becke's three parameters density functional theory (DFT) [11] in combination with the Lee, Yang and Parr correlation functional B3LYP [12] with basis sets 6-31G**. The differentiation between the different probable structures of BenzalBA was based on the total energy difference which has been achieved by the total energy which has been calculated via SCF using RHF for these types of molecules.

3.2. Spectroscopic parameters

The Einstein transition probability coefficients of emission, A_{if} , and absorption, B_{if} , between two initial (*i*) and final (*f*) electronic states are given as follows:

$$A_{if} = \frac{64\pi v^{-3} e^2}{3h} G_f D_{if} \tag{1}$$

$$B_{if} = \frac{8\pi^3 e^3}{3h^2 C} G_j D_{if} \tag{2}$$

where *e* is the electron charge, *h* the Planck's constant, *c* the light velocity, 3×10^{10} cm s⁻¹, $\tilde{\nu}$ the frequency of radiation in cm⁻¹, *G*_f *the* degeneracy of the final state, and *D*_{if} is the dipole strength.

Substituting the numerical values and assuming the singlet degeneracy state, then:

$$A_{if} = 7.211 \times 10^{10} \, v^{-3} \, \boldsymbol{D}_{if} \tag{3}$$

$$B_{if} = 14.50 \times 10^{24} D_{if} \tag{4}$$

The quantity B_{if} can be related to the oscillator strength, f_{ij} , which is the measure of the intensity.

$$\boldsymbol{f}_{ij} = \frac{8\pi^2 \boldsymbol{m} \boldsymbol{C}}{3\boldsymbol{h}} \boldsymbol{G}_f \tilde{\boldsymbol{\nu}} \boldsymbol{D}_{if} = 1.096 \times 10^{11} \boldsymbol{G}_f \tilde{\boldsymbol{\nu}} \boldsymbol{D}_{if}$$
(5)

Also the oscillator strength can be related to the absolute intensity as follows:

$$\boldsymbol{f}_{ij} = 0.102 \left(\frac{\boldsymbol{m} \boldsymbol{C}^2}{\boldsymbol{N} \boldsymbol{\pi} \boldsymbol{e}^2} \right) \int \boldsymbol{\varepsilon} \boldsymbol{d} \tilde{\boldsymbol{v}} = 4.315 \times 10^{-9} \int \boldsymbol{\varepsilon} \boldsymbol{d} \tilde{\boldsymbol{v}}$$
(6)

where *m* is the electron mass, *N* the Avogadro's number, and ε is the molar extinction coefficient.

If a molecule is in an excited state then, in the absence of an external electromagnetic field, on the average, after a time τ it will emit a photon. τ is called the mean lifetime of the excited state.

$$\tau = \frac{1}{A_{\rm if}} \tag{7}$$

Generally *D_{if}* can be calculated numerically as follows:

$$D_{if} = 4.23671 \times 10^{-20} \times \frac{h}{v} \varepsilon_{\text{max}}.$$
 (8)

where \hbar is the half width of the absorption band in cm⁻¹. Hence, the oscillator strength can be calculated directly as follows:

$$f_{ij} = 4.6 \times 10^{-9} \varepsilon_{\max} \times \hbar \tag{9}$$

4. Results and discussion

4.1. Structural studies of BenzalBA

From DFT calculations point of view as B3LYP/6-31G** basis sets using Gaussian 98 program to study the structure of BenzalBA, it has been concluded that the tautomer I has the lowest energy -759.0024 a.u. so it is considered the most predominant tautomer but when the energy difference was applied with all tautomers

(Scheme 1) it has been found that the three tautomers (I–II) are possible, Table 2. The energy difference between tautomers (I and II) is 0.6380 eV and the energy difference between tautomers (I and III) is 2.0468 eV. Also the energies difference between tautomers I, IV and V are 1.0314 and 1.9642 eV respectively. Therefore the high values of the energy difference between tautomer I with tautomers III–V do not permit their presence in equilibrium with tautomers I and II.



Table 2

B3LYP/6-31G** parameters of Possible minimum energy structures of BenzalBA molecule.

<i>E</i> (a.u.)	Dipole moment (Debye)
-759.0024	3.0954
-758.9789	7.1427
-758.2713	10.5433
-758.9645	8.4678
-758.9302	6.6454
	E (a.u.) -759.0024 -758.9789 -758.2713 -758.9645 -758.9302

The DFT(B3LYP/6-31G^{**}) energies and the dipole moments of the possible tautomers of BenzalBA have been tabulated in Table 2 after minimization by AM1 valence electron system. It can be noticed that the tautomer of the lowest energy has the minimum value of the dipole moment, 3.0954D. The second possible tautomer has the higher value, 7.1427D, therefore the dipole moment value of BenzalBA should be between them. The tautomer IV has a very poor existence with respect to the first tautomer as it appears in Table 3 and can be neglected. Hence its contribution to the dipole moment of BenzalBA is very poor.

 n/n_o is the ratio between the numbers of molecules of the higher energy tautomer, with respect to the number of the molecules of the lowest energy tautomer, n_o . This ratio has been calculated taking in consideration the DFT (B3LYP/6-31G^{**}) energy differences between the first tautomer of the lowest energy and the other tautomers of the higher energies, Table 3. The number of molecules *N*, of the tautomer of the higher energy per mole was calculated at 27 °C. All the other tautomers, III–V are absent due to the big energy differences in contrary to tautomer II which has more closer energy to that of tautomer I therefore BenzalBA has two possible tautomers of them in equilibrium with each other at 27 °C.

The configuration interaction between the ground configuration Eigenfunction Φ_0 with the excited singlet configuration Eigenfunctions Φ_1 ($\psi_{40\rightarrow41}$), Φ_2 ($\psi_{39\rightarrow41}$), Φ_3 ($\psi_{39\rightarrow42}$), Φ_4 ($\psi_{39\rightarrow43}$), Φ_5 ($\psi_{39\rightarrow44}$), Φ_6 ($\psi_{39\rightarrow45}$), Φ_7 ($\psi_{39\rightarrow48}$), Φ_8 ($\psi_{39\rightarrow49}$), Φ_9 ($\psi_{38\rightarrow41}$), Φ_{10} ($\psi_{38\rightarrow42}$), Φ_{11} ($\psi_{38\rightarrow44}$), Φ_{12} ($\psi_{38\rightarrow45}$), Φ_{13} ($\psi_{38\rightarrow47}$), Φ_{14} ($\psi_{37\rightarrow41}$), Φ_{15} ($\psi_{37\rightarrow42}$), Φ_{16} ($\psi_{37\rightarrow44}$), Φ_{17} ($\psi_{37\rightarrow45}$), Φ_{18} ($\psi_{36\rightarrow41}$), Φ_{19} ($\psi_{36\rightarrow42}$), Φ_{20} ($\psi_{36\rightarrow43}$), Φ_{21} ($\psi_{36\rightarrow44}$), Φ_{22} ($\psi_{36\rightarrow45}$), Φ_{23} ($\psi_{36\rightarrow47}$), Φ_{24} ($\psi_{35\rightarrow41}$), Φ_{25} ($\psi_{35\rightarrow42}$), Φ_{26} ($\psi_{35\rightarrow44}$), Φ_{27} ($\psi_{35\rightarrow45}$), Φ_{28} ($\psi_{35\rightarrow47}$), Φ_{29} ($\psi_{34\rightarrow41}$), Φ_{30} ($\psi_{34\rightarrow42}$), Φ_{31} ($\psi_{33\rightarrow41}$), Φ_{32} ($\psi_{33\rightarrow42}$) and Φ_{33} ($\psi_{33\rightarrow44}$) has been calculated by ZINDO program taking in consideration the eight HOMO's and eight LUMO's of the valence electron system molecular orbitals of the possible tautomers of BenzalBA. The following Tables 4, 6, 8, 10 and 12 show the singlet state Eigenfunctions of the five possible tautomers and the Tables 5, 7, 9, 11 and 13 show the singlet transition energies between the

Table 3		
B3LYP/6-31G**	energy difference of BenzalBA tautomers.	

Structures	$\Delta E (eV)$	n/n _o at 27 °C	<i>N</i> at 27 °C
I and II	0.6380	1.89764×10^{-11} 4.0077×10^{-35}	1.1424×10^{13}
I and IV	1.0314	4.6452×10^{-18}	2796415
I and V	1.9642	$9.7952 imes 10^{-34}$	0.0000

Singlet state Eigenfunctions of tautomer I.

 $\Psi_g = \Phi_0$

Table 4

 $\Psi_{ex1}^{'} = -0.22904\phi_{18} - 0.23576\phi_{19} + 0.28432\phi_{21} + 0.14195\phi_{23} + 0.41450\phi_{9}$

 $\begin{array}{l} - \ 0.29982 \phi_{11} + 0.13241 \phi_{12} \\ \Psi_{ex2} = - 0.33518 \phi_{18} + 0.22378 \phi_{21} - 0.18271 \phi_{22} - 0.24662 \phi_9 + 0.34583 \phi_{10} \end{array}$

 $-0.25370 \Phi_{12} - 0.18765 \Phi_{13}$ $\Psi_{ex3} = 0.68803 \Phi_1$

Scheme 1. Minimized energy tautomers of BenzalBA.

Table 5

Singlet excitation energies of tautomer I.

Transition	$\Delta E (eV)$	$\Delta E (nm)$	$\Delta E (nm exp)$	f
$\begin{array}{l} \Psi_g \rightarrow \Psi_{ex1} \\ \Psi_g \rightarrow \Psi_{ex2} \\ \Psi_g \rightarrow \Psi_{ex3} \end{array}$	3.3209 3.5865 3.6731	373.34 345.70 337.55	329	0.0002 0.0006 1.0165

Table 6

Singlet state Eigenfunctions of tautomer II.

 $\Psi_g = \Phi_0$

 $\tilde{\Psi_{ex1}} = -0.22904\phi_{18} - 0.23576\phi_{19} + 0.28432\phi_{21} + 0.14195\phi_{23} + 0.41450\phi_{9}$

 $-0.29982\phi_{11}+0.13241\phi_{12}$

$$\begin{split} \Psi_{ex2} = & -0.33518 \Phi_{18} + 0.22378 \Phi_{21} - 0.18271 \Phi_{22} - 0.24662 \Phi_{9} + 0.34583 \Phi_{10} \\ & -0.25370 \Phi_{12} - 0.18765 \Phi_{13} \end{split}$$

 $\Psi_{ex3} = 0.68803 \Phi_1$

Table 7

Singlet excitation energies of tautomer II.

Transition	$\Delta E (eV)$	$\Delta E (nm)$	ΔE (nm exp)	f
$\begin{array}{l} \Psi_g \to \Psi_{ex1} \\ \Psi_g \to \Psi_{ex2} \\ \Psi_g \to \Psi_{ex3} \end{array}$	3.3209 3.5865 3.6731	373.34 345.70 337.55	329	0.0002 0.0006 1.0165

Table 8

Singlet state Eigenfunctions of tautomer III.

 $\Psi_{\sigma} = \Phi_{\Omega}$

```
\tilde{\Psi_{ex1}} = 0.54599\Phi_2 - 0.23676\Phi_4 + 0.26954\Phi_6 + 0.11807\Phi_7 + 0.15687\Phi_8
```

 $\Psi_{ex2} = 0.10973 \Phi_{31} + 0.17418 \Phi_{18} + 0.11750 \Phi_{21} - 0.11135 \Phi_{14} + 0.11304 \Phi_{51} + 0.11304 \Phi_{$

+ $0.59984\phi_1$ $\Psi_{ex3} = 0.17929\phi_{33} - 0.24383\phi_{24} + 0.43836\phi_{18} - 0.15255\phi_{20} + 0.11111\phi_{22}$

 $+0.14727\phi_2 - 0.11974\phi_6 - 0.12765\phi_7 - 0.18498\phi_8 - 0.23917\phi_1$

Га	bl	le	9	

Singlet excitation energies of tautomer III.

Transition	$\Delta E (eV)$	$\Delta E (nm)$	ΔE (nm exp)	f
$\begin{array}{l} \Psi_g \rightarrow \Psi_{ex1} \\ \Psi_g \rightarrow \Psi_{ex2} \\ \Psi_g \rightarrow \Psi_{ex3} \end{array}$	3.0939 3.7764 3.9516	400.74 328.31 313.76		0.0002 0.6414 0.1305

Table 10

Singlet state Eigenfunction of tautomer IV.

$\Psi_g = \Phi_0$
$\Psi_{ex1} = 0.18159\Phi_{24} + 0.14831\Phi_{25} - 0.26353\Phi_{26} - 0.11710\Phi_{28} - 0.14147\Phi_{21}$
+ $0.41280\Phi_9 - 0.24890\Phi_{11}$ + $0.21239\Phi_{12}$
$\Psi_{ex2} = 0.26288 \Phi_{24} - 0.15601 \Phi_{26} + 0.13655 \Phi_{27} + 0.17783 \Phi_{18} + 0.10660 \Phi_{22}$
$+ 0.20381 \Phi_{14} - 0.10010 \Phi_{15} + 0.13611 \Phi_{17} - 0.18477 \Phi_9 + 0.29085 \Phi_{10}$
$-0.13146 \Phi_{11} - 0.21831 \Phi_{12} - 0.20888 \Phi_{13}$
$\Psi_{ex3} = -0.16084\Phi_{29} + 0.11034\Phi_{30} + 0.64329\Phi_1$

Singlet excitation energies of tautomer IV.

Transition	ΔE (eV)	$\Delta E (nm)$	$\Delta E (nm exp)$	f
$\begin{array}{l} \Psi_g \rightarrow \Psi_{ex1} \\ \Psi_g \rightarrow \Psi_{ex2} \\ \Psi_g \rightarrow \Psi_{ex3} \end{array}$	3.3834 3.5792 3.8413	366.45 346.40 322.76		0.0026 0.0089 0.5837

ground singlet state Eigenfunction, Ψ_g and the other singlet excited states Eigenfunctions, Ψ_{ex} .

From the heat effect on the UV spectrum [13] of BenzalBA in ethanol as a solvent it has been noticed that there is not change

nglet state Eigenfunctions of tautomer V	1.
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$\Psi_g = \Phi_0$	
$\Psi_{ex1} = -0.17126\Phi_{14} + 0.11962\Phi_{16} + 0.51843\Phi_2 - 0.30024\Phi_5 + 0.10569\Phi_6$	
$-0.14667 \Phi_7 - 0.10107 \Phi_1$	
$\Psi_{ex2} = -0.10474 \Phi_{18} + 0.17378 \Phi_2 + 0.63914 \Phi_1$	
Ψ_{ex3} = 0.10800 Φ_{33} - 0.19826 Φ_{24} + 0.45330 Φ_{18} - 0.18517 Φ_{19} - 0.10339 Φ_{22}	
$-0.15270 \Phi_2$ + $0.12067 \Phi_3$ - $0.16030 \Phi_5$ + $0.15800 \Phi_6$ - $0.12094 \Phi_7$	
$+0.20398\Phi_1$	
	•

Table 13	
Singlet excitation	energies of tautomer V.

Transition	ΔE (eV)	$\Delta E(nm)$	ΔE (nm exp)	f
$\begin{array}{l} \Psi_g \rightarrow \Psi_{ex1} \\ \Psi_g \rightarrow \Psi_{ex2} \\ \Psi_g \rightarrow \Psi_{ex3} \end{array}$	2.9789 3.7091 3.9595	416.21 334.27 313.13		0.0004 0.4807 0.0474

in the relative intensities in the absorption band at $\lambda = 325$ nm indicating to the existence of tautomers I and II since the allowed excitation energies $\Psi_g \rightarrow \Psi_{ex3}$ ($\pi \rightarrow \pi^*$) for them lie at the same value 3.6731 eV (337.55 nm), (Fig. 1) which is not far from the experimental value, 329 nm in chloroform as much lower solvent. Therefore there is not splitting at this band position 325 nm in ethanol, by the heat effect due to the presence of the two possible tautomers I and II since they have the same value of the excitation energies, 3.6731 Tables 5 and 7.

4.2. UV-spectral studies in pure solvents

The UV-spectra of BenzalBA have been scanned in different solvents of different polarities such as ethanol, methanol, isopropanol, chloroform, dimethylformamide (DMF), and *n*-hexane, Fig. 2; it has been noticed that the lifetime τ of the excitation has its maximum value in case of *n*-hexane solvent, 34.20 ns and the electronic transition energies in electronic spectra of BenzalBA have been blue shifted with increasing the solvent polarity from 329.1 nm in CHCl₃ as a solvent to 322.0 nm in *n*-hexane as a solvent, Table 14. The Einstein transition probabilities A_{if} (spontaneous transition probability) and B_{if} (induced transition probability) have their maximum values in the case of CHCl₃ as a solvent 2.2951 × 10⁸ s⁻¹ and





Fig. 2. Electronic absorption spectra of BenzalBA in organic solvents (conc, = 8×10^{-5} mol L⁻¹). (1) CHCl₃; (2) Isopropanol; (3) EtOH; (4) DMF; (5) MeOH; (6) *n*-hexane.

 16.382×10^8 s g⁻¹, respectively as well as the dipole strength D_{if} having its maximum value in the same solvent, 11.298×10^{-17} , Table 14.

4.3. UV-spectral studies in mixed solvents

The data of mixed solvents studies [14] have been tabulated in Table 15. The maximum wavelength λ_{max} of BenzalBA in the UVspectra has been blue shifted with increasing the mole fraction of the more polar solvent in the mixed solvents with respect to the other of lower polarity (e.g. from 329 nm in case of 100% CHCl₃ to 325.0 nm in case of 100% MeOH), Fig. 3. On plotting the excitation energy ΔE in kJ mol⁻¹, against the mole fraction of the MeOH with respect to CHCl₃ solvent, a broken line with three segments is obtained, Fig. 3; the first segment indicates to the orientation en-



Fig. 3. Hydrogen bonding and orientation energies of $\mathsf{BenzalBA}$ in $(\mathsf{MeOH-CHCl}_3)$ mixtures.

Table 14

The Einstein transition probabilities (A_{if} and B_{if}), dipole strength (D_{if}), oscillator strength (f_{if}), lifetime (τ) and extinction coefficient (ϵ) of the electronic transition bands of BenzalBA in different solvents.

Solvent	λ_{\max} (nm)	$\epsilon \times 10^{-4} (L M^{-1} cm^{-1})$	$A_{if} \times 10^{-8} (s^{-1})$	$B_{if} imes 10^{-8} \ ({ m s g}^{-1})$	$D_{if} imes 10^{17}$	$f_{ m if}$	τ (ns)
EtOH	325	1.0799	1.8001	12.928	8.9156	0.298	5.319
MeOH	325	0.885	1.6041	11.016	7.5974	0.254	6.234
Isopropanol	327	1.3356	2.1339	14.868	10.254	0.341	4.686
CHCl ₃	329	1.3963	2.2951	16.382	11.298	0.373	4.357
D.M.F	324	0.9652	1.7381	11.847	8.1706	0.274	5.753
n-Hexane	322	0.1625	0.2923	1.9551	1.3483	0.045	34.20

Table 15Electronic spectral data of BenzalBA in (MeOH–CHCl3) mixtures at λ_{max} = 329 nm.

MeOH (%)	λ_{\max} (nm)	Molarity		Mole fraction	ΔE (kJ mol ⁻¹)	
		MeOH	CHCl ₃	MeOH	CHCl ₃	
100	325	23.4535	0.00000	1.00000	0.0000	368.31
79.6	326	18.5159	2.49958	0.88106	0.1189	367.52
69.6	327	16.0471	3.74937	0.81060	0.1894	366.17
49.6	328	11.1096	6.24895	0.64001	0.3600	364.60
29.6	329	6.17197	8.74853	0.41365	0.5863	363.72
9.6	329	1.23439	11.2481	0.09888	0.9011	363.72
0.0	329	0.00000	11.8730	0.00000	1.0000	363.72

Table 16				
Data of BenzalBA	in	mixed	organic	solvents.

System	Orientation energy (K J mol ⁻¹)	H-bonding energy (K J mol ⁻¹)	п	K_{f}	$-\Delta G^{a}$ (K J mol ⁻¹)	
MeOH–CHCl ₃	1	2	2	10.7152	5.88976	
K _f is formation constant.						

^a ΔG is free energy.

Table 17

The nitrogen elemental analyses of the complexes.

Complex	% Theoretical	% Experimental
(BenzalBA) ₂ -Cu ⁺⁺	11.34	11.296
(BenzalBA) ₂ -Fe ⁺⁺	11.52	11.57
(BenzalBA) ₂ -Zn ⁺⁺	11.3	11.6

Table 18

The atomic absorption spectral data of the complexes.

Complex	% Theoretical	% Experimental
(BenzalBA) ₂ -Cu ⁺⁺	12.9	12.94
(BenzalBA) ₂ -Fe ⁺⁺	11.5	11.57
(BenzalBA) ₂ -Zn ⁺⁺	13.2	13.5

ergy which is equal to 1 kJ mol⁻¹ with respect to the orientation of MeOH molecules towards BenzalBA molecule in the ground and

excited states. The second segment corresponds to the hydrogen bonding between MeOH molecules with BenzalBA molecule. The hydrogen bonding energy in this case is equal to 2 kJ mol⁻¹, Table 16. The third segment represents the steady state of energy attained after complex formation of the MeOH-BenzalBA complex which is equal to 3 kJ mol⁻¹. The free energy change $\Delta G^{\#}$ of formation of MeOH-BenzalBA complex in case of MeOH/CHCl₃ mixed solvents equals to 5.8898 kJ mol⁻¹, Table 16. A support of bond formation between BenzalBA and solvent molecules may be obtained by determining the stability formation constant of the complex, K_{f} . The utilized method for determination of stability constant K_f of solvent-BenzalBA complex depends on the fact that absorbance variation when adding different proportions of the proton donor and it is the measure of formation tendency of the solute-solvent complex. The stability constant K_f of the solute–solvent complex has its value in case MeOH/CHCl₃ mixed solvents with BenzalBA molecule, 10.7152 kJ mol⁻¹, Table 16, as well as the free energy change $\Delta G^{\#}$ of the formation of MeOH/BenzalBA complex having the maximum value 5.889 kJ mol⁻¹. Generally the number of



Fig. 4. ¹H NMR spectrum of BenzalBA.



Fig. 5. ¹H NMR spectrum of [(BenzalBA)₂-Zn] complex.



Fig. 8. Mass spectrum of [(BenzalBA)₂-Cu] complex.

MeOH molecules oriented towards BenzalBA molecule being equal to 2, Table 16.

4.4. Structural spectral studies of complexes

The complexes of BenzalBA with one of the cations Cu⁺⁺, Fe⁺⁺ and Zn⁺⁺ have been prepared as has been mentioned previously in the experimental work and their melting points have been mentioned in Table 1. From the nitrogen elemental analyses, Table 17,

the theoretical percentages of nitrogen element have good coincidence with the experimental percentages of nitrogen element in the studied complexes confirming the ratio 2:1 (BenzalBA) to M(II) in the complex.

Dealing with the atomic absorption spectra, Table 18, it has been found that the theoretical percentage of the metal ions e.g., Cu^{++} is nearly coincident with the experimental percentage 12.9 and 12.94, respectively. Generally, the theoretical percentage of metal ion M⁺⁺ in the atomic absorption spectra has a good



Fig. 9. Mass spectrum of [(BenzalBA)₂-Zn] complex.



Fig. 10. Electronic absorption spectra of EtOH solutions of 8×10^{-5} mol L⁻¹ (1–4) as (1) BenzalBA, (2) (BenzalBA)₂–Cu, (3) (BenzalBA)₂–Fe, and (4) (BenzalBA)₂–Zn complexes.



Fig. 11. Electronic absorption spectra of DMF (dimethylformamide) solutions of 8×10^{-5} mol L⁻¹ (1–4) as (1) BenzalBA, (2) (BenzalBA)₂–Zn, (3) (BenzalBA)₂–Fe and (4) (BenzalBA)₂–Cu complexes.

coincidence with the experimental metal ion percentage in accordance with the ratio 2:1 (BenzalBA) to M⁺⁺ in the complex. Generally from the elemental analyses of nitrogen element of the complexes, Table 17, and from the data of the atomic absorption spectra, Table 18, it can be conclude that the complex molecule has been formed by the chelation of two molecules of BenzalBA with a metal ion M⁺⁺.

The ¹H NMR spectrum of BenzalBA (Fig. 4) has two signals at 11.71, 11.86 ppm, which are due to the protons of the two asymmetric amide groups in the barbituric acid moiety. The disappearance of one of the two signals of the amide hydrogen atoms in the ¹H NMR spectrum of (BenzalBA)₂–Zn(II) complex as an example, Fig. 5, confirms the consumption of one of the amide hydrogen atoms in the complexation between BenzalBA and metal ion (M⁺⁺), and the N–H bonds in the complex of BenzalBA molecule

have been replaced by $N-M^{++}-N$ bonds in the complex in the two moieties of BenzalBA of the complex.

Therefore, the complexation between two molecules of Benzal-BA with a metal ion M^{++} has been formed by the chelation of the metal ion with the more negative carbonyl oxygen atoms and one the amide nitrogen atoms consuming one of the amide hydrogen atoms to form the complex (BenzalBA)₂–M(II) including the nitrogen–metal bond.

The suggested complexes have been confirmed by EI–MS spectra (Figs. 6–9). These MS spectra show the m/z which is corresponding to the molecular weight of the complexes confirming the ratio between the ligand and the cation is 2:1 respectively. Therefore, the complexation between two molecules of BenzalBA with a metal M has been formed by the chelation of the metal ion with the more negative carbonyl oxygen atoms and one of

Table 19

The Einstein transition probabilities (A_{if} and B_{if}), dipole strength (D_{if}), oscillator strength (f_{if}) and lifetime (τ) and extinction coefficient (ε) of the electronic transition bands of [(BenzalBA)₂–M] complexes in EtOH solvent.

Compound	λ_{\max} (nm)	$\epsilon \times 10^{-4}~(LM^{-1}cm^{-1})$	$A_{if} imes 10^{-8} (s^{-1})$	$B_{if} imes 10^{-9} (s g^{-1})$	$D_{if} imes 10^{16}$	f_{if}	τ (ns)
[(BBA) ₂ Fe]	317	0.613	14.289	9.116	6.287	2.153	1
[(BBA) ₂ Cu]	467	0.044	0.020	0.042	0.029	0.007	489
[(BBA) ₂ Zn]	336	0.089	0.025	0.019	0.131	0.043	40

Table 20

The Einstein transition probabilities (A_{if} and B_{if}), dipole strength (D_{if}), oscillator strength (f_{if}), life time (τ) and extinction coefficient (ε) of the electronic transition bands of [(BenzalBA)₂–M] complexes in DMF solvent.

Compound	λ_{\max} (nm)	$\epsilon \times 10^{-4}~(L~M^{-1}~cm^{-1})$	$A_{if} \times 10^{-8} (s^{-1})$	$B_{if} imes 10^{-9} (s g^{-1})$	$D_{\it if} imes 10^{16}$	f_{if}	τ (ns)
[(BBA) ₂ -Fe]	410	0.0660	0.0524	0.0723	0.0499	0.0132	191
$[(BBA)_2-Cu]$	324	0.1117	0.5651	0.3849	0.2654	0.0889	18
	471	0.0429	0.0266	0.0555	0.0383	0.0088	376
[(BBA) ₂ –Zn]	318	0.4750	2.0222	1.2963	0.8939	0.3056	5

the amide nitrogen atom consuming one of the amide hydrogen atom to form the complex (BenzalBA)₂–M(II) including the nitrogen-metal bond and the complex structure which has been suggested to be C_{2h} point group symmetry, but the BenzalBA molecule itself has the suggested C_s point group symmetry in which the two amide group are not symmetric.

The UV-spectra of BenzalBA complexes have been scanned in ethanol as a solvent Fig. 10, and it has been noticed that the lifetime τ of the excitation has its maximum value in case of [(BenzalBA)₂–Cu] complex, 489 ns at λ_{max} = 467 nm Table 19. The Einstein transition probabilities A_{if} (spontaneous transition probability) and B_{if} (induced transition probability) have their maximum values in the case of [(BBA)₂–Fe] complex 14.2889 × 10⁸ s⁻¹ and 9.1160 × 10⁹ s g⁻¹, respectively as well as the dipole strength D_{if} has its maximum value in the same solvent, 6.2869 × 10⁻¹⁶, Table 19.

The UV-spectra of BenzalBA complexes have been scanned in DMF (dimethylformamide) solvent Fig. 11, and it has been noticed that the lifetime τ of the excitation has its maximum value in case of [(BBA)₂–Cu] complex, 376 ns at $\lambda_{max} = 471$ nm. Table 20. The Einstein transition probabilities A_{if} (spontaneous transition probability) and B_{if} (induced transition probability) have their maximum values in the case of (BBA)₂ Zn 2.0222 × 10⁸ s⁻¹ and 1.2963 × 10⁹ s g⁻¹, respectively as well as the dipole strength (D_{if}) has its maximum value in the same solvent, 0.8939 × 10⁻¹⁶ for the same complex, Table 20 at $\lambda_{max} = .318$ nm.

5. Conclusion

The structure of BenzalBA molecule has been confirmed by B3LYP/6-31G^{**} calculations and finally it has two conformers whose calculated transition energies are the same. Some complexes of BenzalBA with some divalent metal ions, i.e. Cu⁺⁺, Fe⁺⁺

and Zn^{++} were prepared. The structures of these complexes may have C_{2h} point group symmetry which has been confirmed by spectral studies.

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