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Full Paper

Normal coordinate analyses and spectroscopic studies of benzalbarbituric acid complexes

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Abstract

From DFT calculations, it has been carried out as B3LYP/6-31G** for the optimized structures and the predominant tautomer of benzalbarbituric acid (Benzal-BA) has been defined taking in consideration the total energy of the density functional theory. The structures of the possible tautomers of Benzal-BA have the C_1 symmetry point group. Also the normal coordinate analyses via B3LYP/6-31G** have been calculated for the tri-ketonic Benzal-BA and compared with the scanned infrared spectrum. The hydrogen bonding, the orientation energy of the polar solvent and the free energy of formation of the solute-polar solvent complex (Benzal-BA/MeOH) were determined from the studies of the mixed solvents spectra. Structural DFT studies of some complexes have been carried out for the Benzal-BA with divalent Cu^{++} and with the optimized structure of Zn^{++} complex. From the optimized structures, it has been concluded that the structure of $Cu(Benzal-BA)_2$ complex has C_{2h} point group symmetry but $Zn(Benzal-BA)_2$ complex has C_1 point group symmetry. The structure of the Benzal-BA metal ion complex has been verified by comparative infrared spectra studies.

Keywords: Benzalbarbituric acid, Cu^{++}, Zn^{++}, B3LYP/6-31G**, Normal coordinate analyses, IR, Mixed solvents.

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 (BA) reacts with chloral hydrate in alkaline medium after reflux for one minute at 100 °C to give an orange's yellow solution having maximum absorbance at 450 nm [3]. The acid dissociation constants

of some barbiturates in water-ethanol medium and the constants of some barbituraes of their equilibrium with benzoic acid have been determined [4]. The shifts in peak locations in the electronic spectra of barbituric and thiobarbituric acids were correlated with different solvent polarity parameters. An absorption band position for the gas phase spectra was compared with PPP-method calculated values [5]. The mass spectrometric behavior of barbituric acid and 1, 3-dimethyl barbituric acid was compared with that of the corresponding 5,5- difluoro derivatives and of some 5-fluoro-5-alkyl derivatives; this investigation performed using both electron impact ionization and positive and negative ions bombardment demonstrating the role of fluorine in barbiturate ring bond cleavages [6].

2. Materials and methods

2.1 Materials

Barbituric acid, benzaldehyde, copper acetate dehydrate, $(CH_3COO)_2Cu$ and zinc acetate dehydrate, $(CH_3COO)_2Zn$ obtained from Sigma- Aldrich and were used without any further purification. The solvents were purified according to literature [4, 5]. Preparation of the benzal barbituric acid (BBA) was obtained by mixing (0.1mol L^{-1}) of barbituric acid with (0.1mol L^{-1}) of benzaldehyde in methanol and refluxed for about three hours, cooling, then filtered off and recrystallized with appropriate solvent so the melting points of the prepared compound is 258°C. preparation of the complexes between benzalbarbituric acid (BBA) and Cu (II) and Zn (II) ions had been obtained by mixing of a solution of appropriate metal salt (10 mmol L^{-1}) with a solution of benzalbarbituric acid, (20 mmol L^{-1}) in ethanol and the resulting mixture was stirred under reflux for about two hours. Where upon the complex precipitated, they where removed by filtration, washed with ethanol and dried at 80° C [7].

2.2 Apparatus

The infrared spectra were measured as KBr disc from 4000 to 400 cm^{-1} using IR-470, IR Spectrophotometer-Shimadzu, Chemistry Department, Faculty of Science, Assiut University-Egypt.

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

3. Results and discussion

From scheme 1 of different possible structures, it has been concluded that tautomer I possesses the lowest energy, –759.22548 a.u., therefore it is the most predominant and the low energy difference between tautomers I and II, 0.75974 eV, permits the existence of tautomer II spontaneously together with tautomer I according to Maxwell Boltzmann distribution law at normal temperature. Also the energy difference between tautomer I and V permits the spontaneous existence of tautomer V together with tautomers I and II. The high relative energy barriers between tautomer I with tautomers III and IV don't permit the existence both of them. From general point of view, Benzal-BA has three tautomers (I, II and V) in its solutions at normal temperature. It can be noticed that there is a good resemblance between tautomer II and tautomer V and the energy difference between them is equal to 0.07783 eV therefore it is expected that there is a free rotation of the phenyl moiety with the ethylene bond with respect to BA moiety and in reality it is impossible the rotation around the double bond. Therefore there is a static rotation of the phenyl moiety around the ethylene bond in Benzal-BA molecule due to the commutative enolization of $C_1=O_8$ and $C_5=O_9$ in the BA moiety to realize the presence of the two tautomers II and V. Hence it seems that there is a fake rotation of the phenyl moiety around the ethylenic double bond. Finally tautomers III and IV exist in a very few negligible amount with respect to the other tautomers as shown from table 1., where N is the number of higher energy tautomer per mole., and n/ n_o is the ratio between the number of molecules of the higher energy tautomer n with respect to the number of molecules of lower energy tautomer (I) n_o.
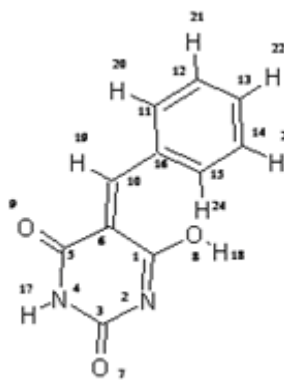
Table 1: B3LYP / 6-31G** Energy Differences of Benzal-BA Structures.

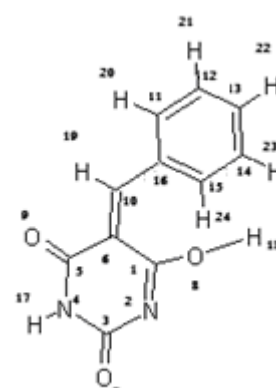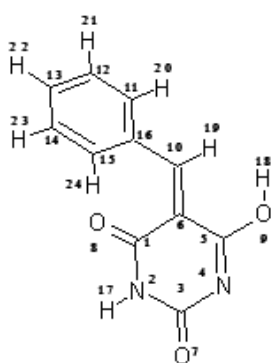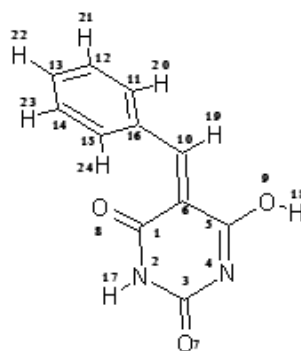| Structures	ΔE a.u.	ΔE eV	n/n_o at 27°C	N at 27°C
I,II	0.02792	0.75974	1.70740×10^{-13}	1.02837×10^{11}
I,III	0.03706	1.00845	1.12898×10^{-17}	6799846 ~0
I,IV	0.00870	1.12130	2.04321×10^{-19}	1230620 ~0
I,V	0. 2524	0.68682	2.86932×10^{-12}	1.72819×10^{12}
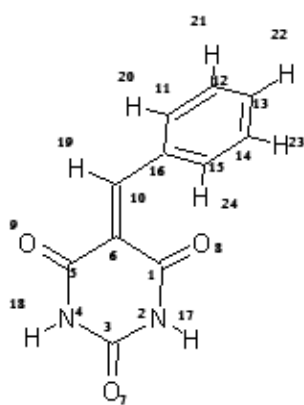
I

−759.22548 a.u.

II

−759.19756 a.u.

III

−759.18842 a.u.

IV

−759.18461 a.u.

V

−759.20024 a.u.

Scheme1: Total energies of some possible optimized structures of Benzal-BA.

Table 2: DFT Mulliken Charge Densities of Benzal-BA (Tautomer I).

NO.	Atom	Charge density	NO.	Atom	Charge density
1	C (BA)	0.595725	13	C (benzene)	−0.069539
2	N (BA)	−0.599625	14	C (benzene)	−0.095900
3	C (BA)	0.743733	15	C (benzene)	−0.100368
4	N (BA)	−0.608109	16	C (benzene)	0.115447
5	C (BA)	0.599511	17	H (NH)	0.294777
6	C (BA)	−0.058123	18	H (NH)	0.293888
7	O (C=O)	−0.478683	19	H (CH)	0.147659
8	O (C=O)	−0.496383	20	H (benzene)	0.105349
9	O (C=O)	−0.498645	21	H (benzene)	0.099527
10	C (CH)	−0.137491	22	H (benzene)	0.100608
11	C (benzene)	−0.116792	23	H (benzene)	0.101412
12	C (benzene)	−0.092269	24	H (benzene)	0.154289

From the charge density data of tautomer I in table 2, it is clear that the oxygen atoms of the two adjacent carbonyl groups to the phenyl group in the barbituric acid moiety have higher negative charges than that of the oxygen atom of the carbonyl group in the para-position, $C_3=O_7$. It is obvious that all the carbon atoms in the barbituric moiety have positive charges due to their attachment to the oxygen atoms of higher electron affinities. But carbon atom at position 6 has negative charge since it has conjugation with the phenyl group via double bond bridge with carbon atom at position 10. All the carbon atoms in the phenyl moiety acquire negative charges except carbon atom at position 16 with the barbituric acid moiety. All hydrogen atoms have positive charges especially H_{24} has the higher positive charge in the phenyl moiety. The two hydrogen atoms in the barbituric moiety have the highest positive charges in the barbituric acid moiety since they are attached with the nitrogen atoms of higher electron affinities. From the data of tautomer II in table 3, it can be concluded that the general feature of the charge distribution in tautomer II is the same as in tautomer I. The hydroxyl oxygen atom, O_8 in the barbituric moiety has the highest negative charge rendering its hydrogen atom, H_{18} in the barbituric moiety having the highest positive charge and can be easily ionized.

Table 3: DFT Mulliken Charge Densities of Benzal-BA (Tautomer II) .

NO.	Atom	Charge density	NO.	Atom	Charge density
1	C (BA)	0.517555	13	C (benzene)	-0.071558
2	N (BA)	-0.553487	14	C (benzene)	-0.096915
3	C (BA)	0.691930	15	C (benzene)	-0.072893
4	N (BA)	-0.595139	16	C (benzene)	0.116039
5	C (BA)	0.599189	17	H (NH)	0.285888
6	C (BA)	0.008329	18	H (OH)	0.336584
7	O (C=O)	-0.466125	19	H (CH)	0.154227
8	O (OH)	-0.508442	20	H (benzene)	0.105416
9	O (C=O)	-0.503624	21	H (benzene)	0.101319
10	C (CH)	-0.155875	22	H (benzene)	0.101300
11	C (benzene)	-0.110628	23	H (benzene)	0.099688
12	C (benzene)	-0.090773	24	H (benzene)	0.107997

Table 4: DFT Mulliken Charge Densities of Benzal-BA (Tautomer V).

NO.	Atom	Charge density	NO.	Atom	Charge density
1	C(benz.BA).	0.595452	13	C (benzene)	-0.069731
2	N(benz.BA).	-0.586269	14	C(benzene)	-0.095677
3	C(benz.BA).	0.693710	15	C(benzene)	-0.101339
4	N(benz.BA).	-0.560113	16	C(benzene)	0.122565
5	C(benz.BA).	0.536967	17	H(NH)	0.286403
6	C(benz.BA).	-0.002194	18	H(OH)	0.337803
7	O(C=O)	-0.469705	19	H(CH)	0.142277
8	O(C=O)	-0.504678	20	H(benzene)	0.099499
9	O(OH)	-0.520524	21	H(benzene)	0.099384
10	C(CH)	-0.156903	22	H(benzene)	0.101509
11	C(benzene)	-0.118665	23	H(benzene)	0.103122
12	C(benzene)	-0.092017	24	H(benzene)	0.159125

From the charge density data of tautomer V in table 4, it is clear that the change of phenyl moiety position doesn't alter the general feature of the charge distribution with tautomers II. The hydroxyl oxygen atom, O_9, has the highest negative charge and the hydroxyl hydrogen atom, H_{18}, has the highest positive charge as the same situation in the tautomer II.

Mixed Solvent Studies

The mixed solvents studies have been tabulated in table 5. The maximum wavelength λ_{max} of Benzal-BA UV-Spectra has been blue shifted with increasing the mole fraction of the higher polarity solvent in the mixed solvents with respect to the other of lower polarity (e.g from 329 nm in case of 100% $CHCl_3$ to 324.4 nm in case of 100% MeOH) Fig.1. On plotting the excitation energy ΔE in kJ mol^{-1}, against the mole fraction of the MeOH with respect to $CHCl_3$ solvent, a broken line with three segments is obtained Fig. 2; the first segment indicates to the orientation energy which is equal to 1 kJ mol^{-1} for the MeOH molecules towards Benzal-BA molecule in the ground and excited states. The second segment corresponds to the molecular complex formation between MeOH molecules with Benzal-BA molecule which is the hydrogen

bonding energy between them. The hydrogen bonding energy in this case is equal to 2 kJ mol^{-1}. The third segment represents the steady state of energy attained after complex formation of the MeOH-Benzal-BA complex being equal to 3 kJ mol^{-1}. The free energy $\Delta G^{\#}$ of formation of MeOH /Benzal-BA complex in case of MeOH / $CHCl_3$ mixed solvents equals to - 5.88976 kJmol^{-1}, table 6. A support of hydrogen bond formation between Benzal-BA and solvent molecules may be obtained by determining the stability constant of the complex formed, K_f. The utilized method for determination of stability constant K_f of solvent-Benzal-BA complex depends on the fact that absorbance variation when adding the 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/ $CHCl_3$ mixed solvents and is equal to 10.71519 kJ mol^{-1}, table 6. Generally the obtained number of solvent molecules oriented towards Benzal-BA molecule have been found equal to 2, table 6. The assignments of the vibrational infrared bands of Benzal-BA were carried out by the aid of GaussView 98 using basis sets B3LYP/6-31G** in DFT calculations as shown in Table 7.

Table 5: Electronic Spectral Data of Benzal-BA in (MeOH- $CHCl_3$) Mixtures at λ_{max}=329nm.

Mole Fraction (MeOH)	λ_{max} (nm.)	Ab	ΔE,kJ mol^{-1}
1.000	324	0.870	38.880
0.881	326	0.959	367.52
0.810	327	1.017	366.17
0.640	328	1.141	364.60
0.413	329	1.228	363.72
0.098	329	1.296	363.72
0.000	329	1.334	363.72

Table 6 : Data of Benzal-BA in mixed organic solvent (MeOH- $CHCl_3$) .

System	Orientation energy kJ.mol^{-1}	H-bonding energy kJ.mol^{-1}	n	K_f	$\Delta G^{\#}$ kJ.mol^{-1}
MeOH-$CHCl_3$	1	2	2	10.7152	-5.88976

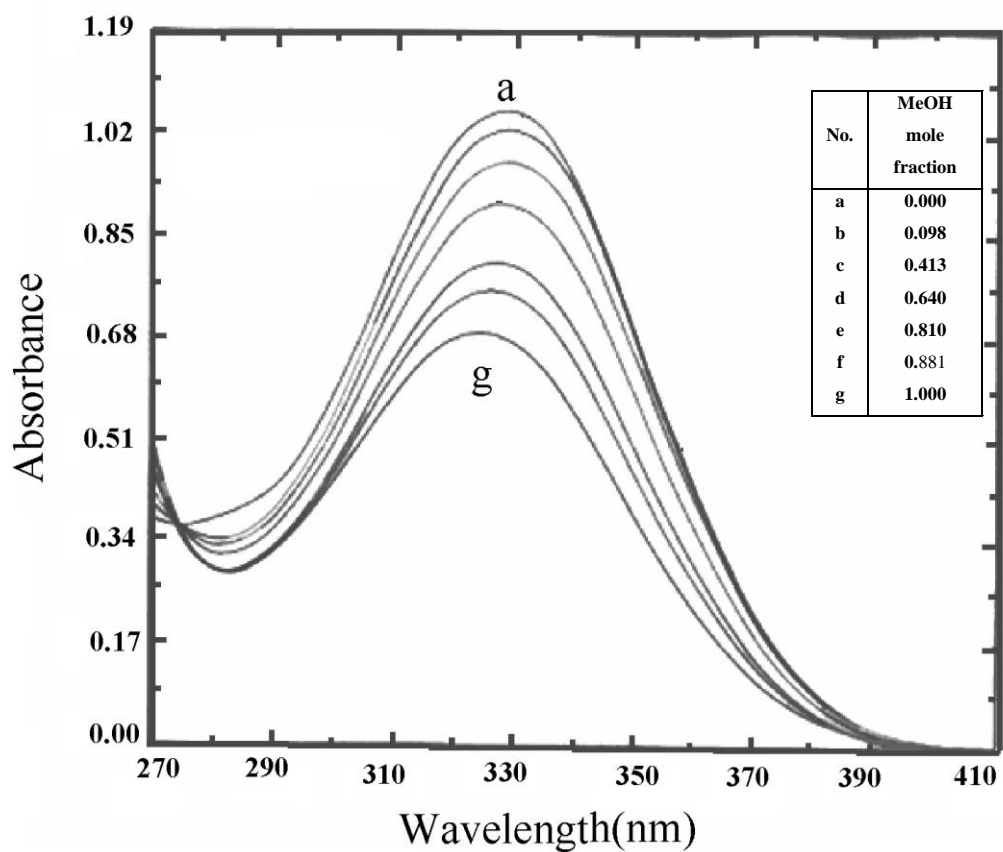K_f is the formation constant; $\Delta G^{\#}$ is free energy.

Fig. 1 : Electronic absorption spectra of BBA (80 µmolL^{-1}) in (MeOH - CHCl$_3$) mixtures.
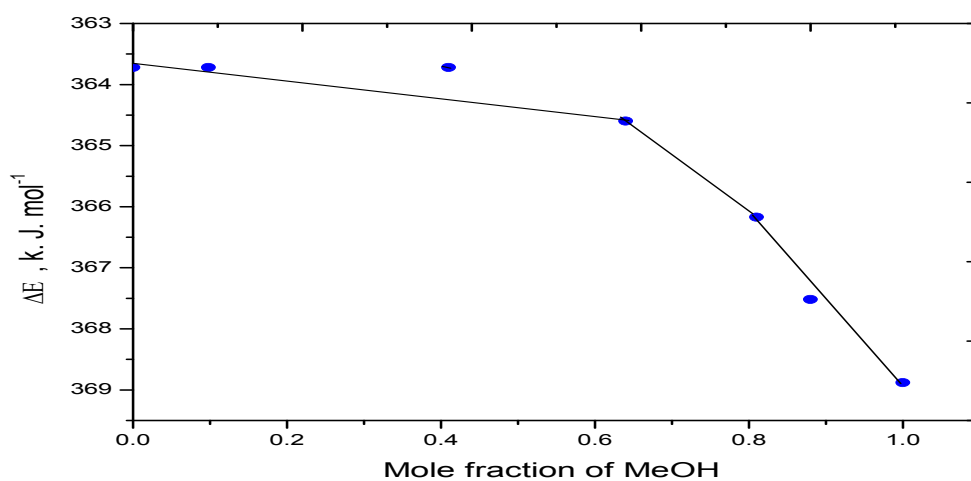

Fig. 2: Hydrogen bonding and orientation energy of Benzal-BA in (MeOH-CHCl$_3$) mixtures**.**

Table 7 : B3LYP/6-31G** Normal Coordinate Analyses of Benzal-BA acid (Tautomer I).

Vibration	ν(Cal.)	ν(Exp.)	Assignments	Relative intensity
1	379.7		γ (H C=C)	0.00
2	389.3		δ (C=O) in BA	0.05
3	422.2	420	δ (C=O) in BA	0.00
	422.8	425	Bzene deformation	0.00
5	509.5	430	Deformation of BA	0.03
6	515.7		γ (C=C-H) ethylene	0.01
7	517.2	520	Deformation of BA Sym.	0.13
8	602.7	590	Deformation of benzene ring	0.00
9	629.1	618	γ (N-H) sym. In BA	0.00
10	633.6	625	Deformation of benzene ring	0.00
11	640.2	645	Deformation of benzene ring, BA	0.00
12	690.2	680	γ (N-H) Asym. In BA	0.21
13	698.5	685	Benzene deformation	0.03
14	698.9		Benzene deformation	0.00
15	724.8		γ (N-C-N) in BA	0.00
16	742.8		γ (N-C-N) in BA	0.13
17	785.7	760	γ (C-H) in benzene	0.06
18	790.0		γ(C-H) in benzene	0.01
19	793.7		Breathing of benzene	0.02
20	866.5	800	δ(C-H) in benzene	0.00
21	892	860	γ(C-H) in benzene	0.00
22	955	924	δ(C-H) in benzene	0.00
23	994.7	966	γ (C-H) in benzene	0.00
24	105.7		Benzene deformation	0.00
25	1020.3	980	γ (C-H) in benzene	0.00
26	1028.9	1024	δ (C-H) in benzene	0.01
27	1031.9		δ (N-H), δ C-H in benzene	0.00
28	1058.7		δ(C-H) sym in BA	0.01
29	1083.4	1064	δ(C-H) in benzene	0.01

N.B. γ is out-of-plane bending, δ is in-plane bending and ν is stretching vibration.

Table 7 : B3LYP/6-31G** Normal Coordinate Analyses of Benzal-BA acid (Tautomer I) (Continued).

Vibration	V Cal.)	V(Ex.)	Assignments	Relative intensity
30	1122.5		γ C-H) in BA	0.01
31	1191.8		γ(C-H) in BA	0.01
32	1213.4	1200	ν (C-N) in BA	0.08
33	1219.1		δ (C-H) sym. in BA	0.16
34	1233.4		ν (C-CH) benzene	0.15
35	1333.5	1295	ν (C-N) in BA, ν (C-C) benzene	0.34
36	1362.4		δ (C-H), δ (N-H)	0.07
37	1375.4		δ (C-H) in benzene ring	0.02
38	1390.6	1320	ν (C-N), δ (N-H)	0.02
39	1430.4	1400	δ (N-H), δ (C-H)	0.25
40	1444.3	1440	ν (C-N), δ (N-H)	0.45
41	1460.7		ν (C-C), ν (C-N) in BA	0.24
42	1493.6		ν (C-CH) in benzene, δ (C-H)	0.18
43	1533.8		ν (C-CH) in benzene, δ (C-H)	0.01
44	1605.8		ν (C-CH) in BA	0.65
45	1627.5	1560	ν (C-C) in benzene	0.23
46	1656.6	1580	ν (C-C) in benzene	0.00
47	1762.0	1680	sym. ν (C=O)	0.60
48	1799.4	1700	Asym. ν (C=O)	0.36
49	1846.2	1740	ν (C=O)	1.00
50	3148.8	2666	BA-ν (C-H)- benzene	0.00
51	3183.3		ν (C-H) benzene	0.00
52	3189.4	2830	ν (C-H) benzene	0.00
53	3201.1	3066	ν (C-H) benzene	0.03
54	3211.2	3100	ν (N-H) in BA	0.03
55	3265.2	3200	ν (C-H) benzene	0.06
56	3624.2		ν(N-H)	0.14
57	3627.3		ν(N-H)	0.13

Benzal-BA molecule of tautomer I has C_1 point group symmetry but the local symmetry, C_{2v} of the mono substituted benzene ring controls the selection rule of the vibrations in the infrared spectra. Also the local symmetry point group C_{2v} of the BA moiety controls the infrared selection rule of the tri-ketonic BA moiety. Therefore the absorption stretching bands of the carbonyl groups $C_1=O_8$ and $C_5=O_9$ in the BA moiety lie at υ_{asym} 1700 cm^{-1}(1799cm^{-1}calc) and υ_{sym} 1680 cm^{-1} (1762cm^{-1} calc). The symmetry species of υsym is A_1 and the symmetry species of υ_{asym} is B_1, therefore the symmetrical stretching band at 1680 cm^{-1} is more intense than the asymmetric stretching at 1700 cm^{-1}, table7. The stretching absorption band of the carbonyl group $C_3=O_7$ in the BA moiety lies at 1740 cm^{-1} (1864 cm^{-1}calc) and its intensity is high due to its totally symmetric vibration of A_1 symmetry species, table 7. The in-plane pending of N-H, in-plane bending of C-H and the stretching bands of N-C in the BA moiety lie at 1320 cm^{-1} (1391 cm^{-1}calc) ,

1400 cm^{-1}(1430 cm^{-1} calc) and 1440 cm^{-1} (1444 cm^{-1} calc). The out of plane bending deformation of N-H in the BA moiety lies at υ_{sym} 618 cm^{-1} (629 cm^{-1} calc) and its υ_{asym} lies at 680 cm^{-1}(690 cm^{-1} calc). The stretching infrared absorption vibration of N-H in the BA moiety lies at 3100 cm^{-1}, Fig. 3. In the Phenyl moiety the in-plane bending deformation bands of C-H lie at, 800 cm^{-1} (867 cm^{-1} cal), 924 cm^{-1} (955 cm^{-1} calc), 966 cm^{-1} (994 cm^{-1} cal), 1024 cm^{-1} (1029 cm^{-1}calc) and 1064 cm^{-1} (1083 cm^{-1} calc). The out of plane bending deformation in phenyl moiety lies at 760 cm^{-1} (786 cm^{-1} calc), (790 cm^{-1} calc), 860cm^{-1}(892 cm^{-1}calc), 966 cm^{-1} (995 cm^{-1} calc) and 980 cm^{-1} (1020 cm^{-1}calc). It can be noticed that some of the γ_{C-H} are inactive in the infrared spectrum due to the inactive A_2 symmetry species in the infrared spectra, Fig. 3. The assignments of phenyl group vibrations have been performed by the aid of Gaufres and El-Shahawy [8] who studied the Raman spectrum of azidobenzene by He-Ne laser at 632.8 nm.
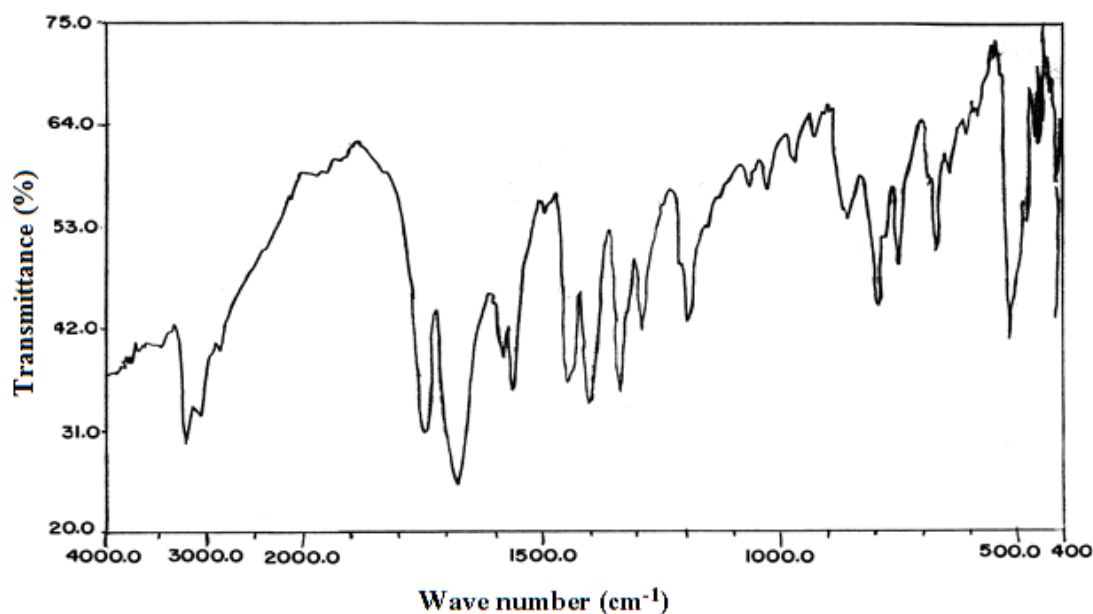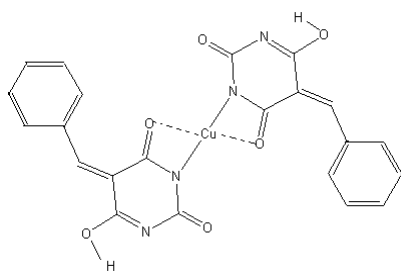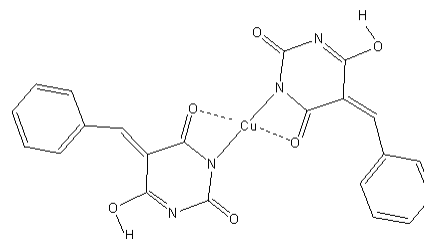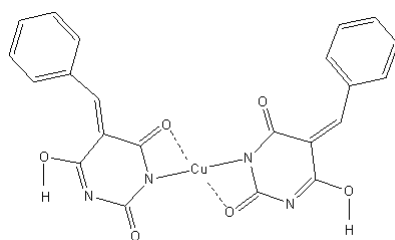

Fig.3. Infrared Spectrum of BBA
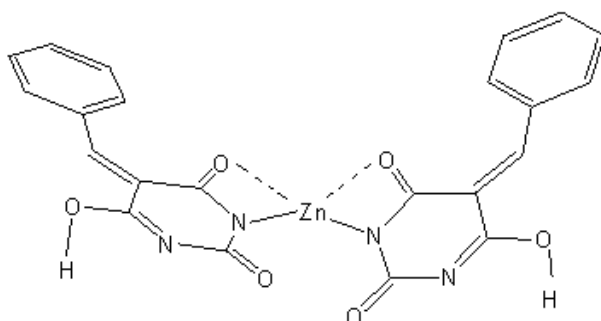
E = −3157.03286253   a.u.
I

E = −3157.02813316 a.u.
II

E= −3157.02674573 a.u.
III

Scheme2 a: Possible Structures of (Benzal-BA)$_2$-Cu^{++} Complex.

Scheme2 b : Optimized Structure of (Benzal-BA)$_2$-Zn^{++} Complex

From DFT structure point of view to study Benzal-BA complexes [7], it has been found that the Cu-complex I has the lowest energy − 3157.03286253 a.u., so it is considered as the most stable structure among three possible structures, scheme 2a, and from these calculations it has been found that the predominant structure of complex of copper is planar. The optimized structure of complex of Benzal-BA/zinc is non-planar, scheme 2b. It has been concluded that the carbonyl group of band at 1690 cm^{-1}, Fig 4, table 8, with blue shift from that of Benzal-BA at 1680 cm^{-1}, Fig. 3, due to the chelation of the carbonyl oxygen atom of BA moiety with the copper ion in the complex. The stretching absorption band at 1740 cm^{-1}, table 8, is due to the carbonyl group C$_3$=O$_7$ in which the O$_7$ attached with carbon atom between the two nitrogen atoms in the BA moiety indicating that this carbonyl group doesn't suffer from chelation with copper ion in the complex.

BA moiety in the complex has an absorption (Benzal-BA)$_2$Cu complex, it has been noticed the disappearance of the υ_{N-H} frequency due to the replacement of the bond υ_{Cu-N} instead of the bond υ_{N-H} in the BA moiety. The appearance of the OH stretching vibration band in the infrared of the complex verify that the Benzal-BA has tautomer II or V   which suffer from the commutative enolization of the carbonyl groups of the BA moiety in the complex since copper complex prepared at high temperature enhancing the presence of the enolic forms (II and V) at high temperature according to Maxwell-Boltzmann distribution law [9].

Table 8: Comparative infrared studies of Benzal-BA complexes.

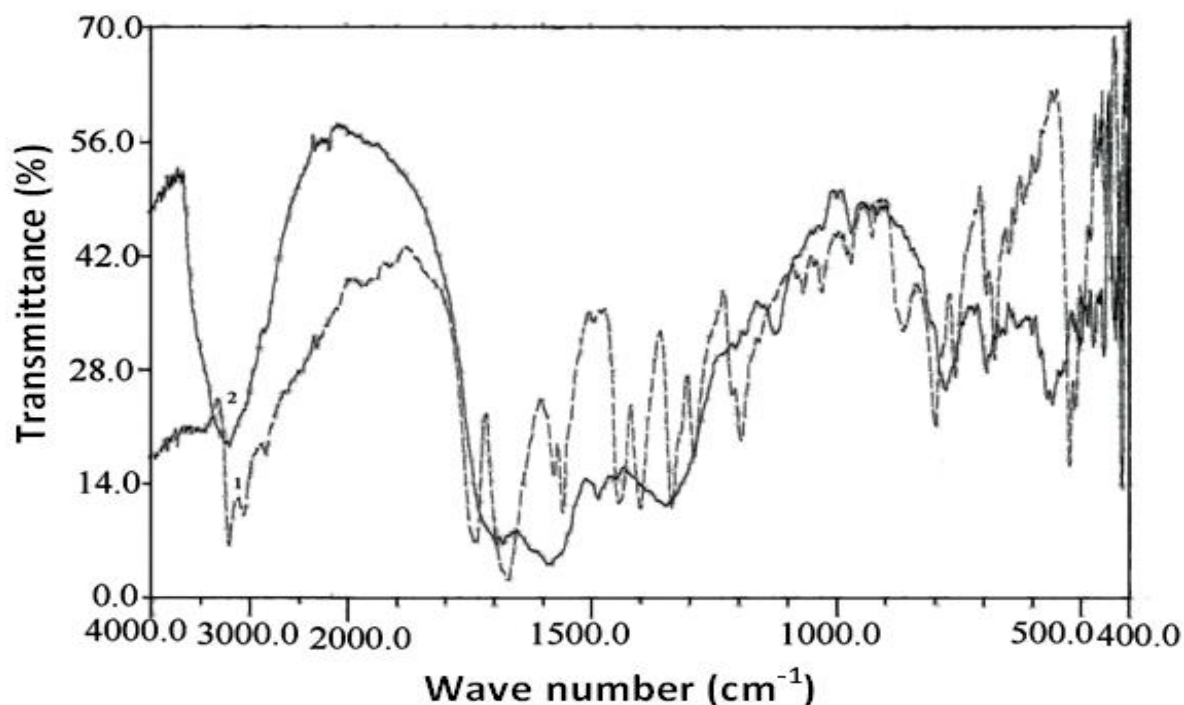| Compound	Stretching Functional group	Wave number cm^{-1}
Benzal-BA	NH	3100
	OH	3200
	CH	2850
	C=O	1680, 1740
(Benzal-BA)$_2$Zn^{++}	NH	--------
	OH	3200
	CH	2850(vw)
	C=O	1690, 1740
(Benzal-BA)$_2$Cu^{++}	NH	------
	OH	3200
	CH	2850
	C=O	1690-1740

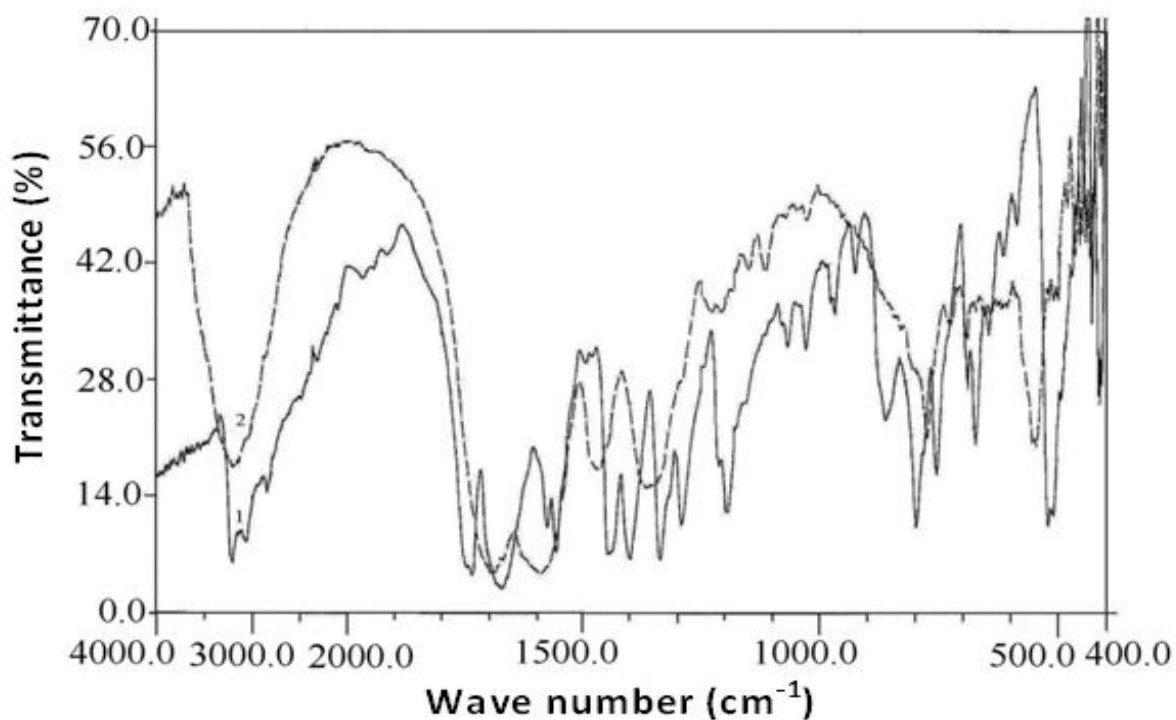**Fig. 4 :** Infrared spectra of BBA (1) and (Benzal-BA)$_2$ Cu complex (2).

Fig. 5 : Infrared spectra of BBA (1) and (Benzal-BA)$_2$ Zn complex (2).
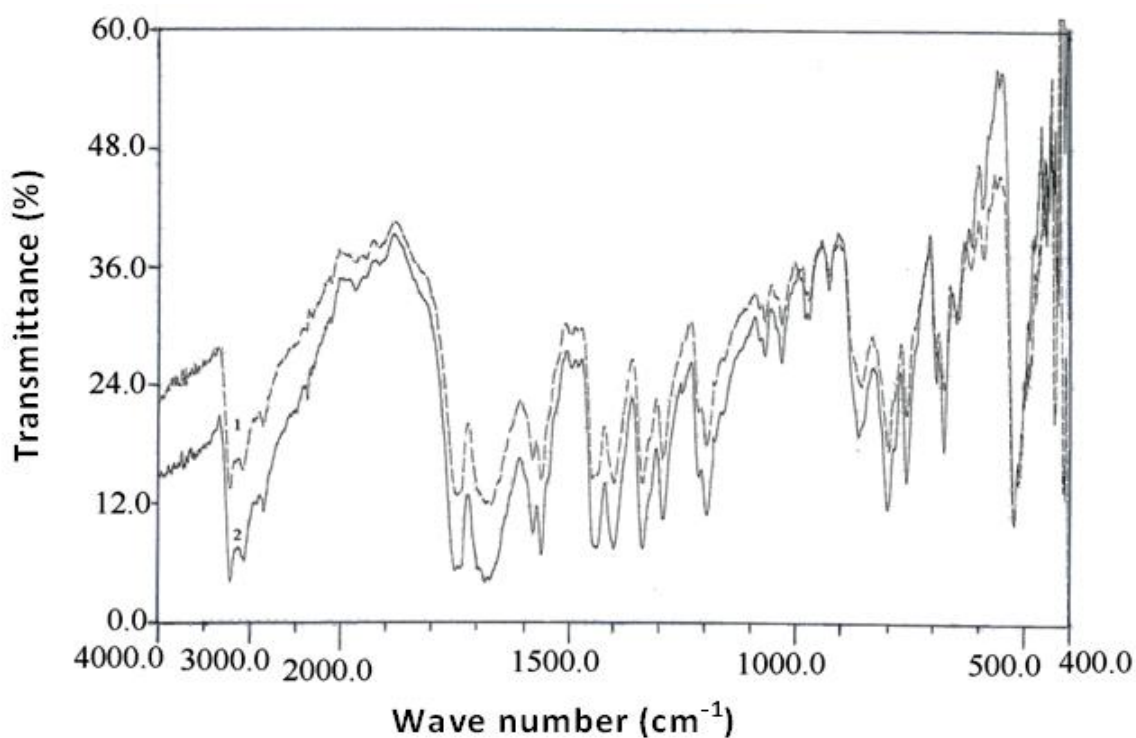

Fig. 6: Qualitative temperature effect of Benzal-BA infrared spectrum.

The qualitative temperature effect, Fig. 6, shows obvious changes in the relative intensities at the bottom of the infrared bands confirming the presence of other enolic tautomers II and V in addition to the tri-ketonic tautomer I. The elevation of the temperature increase the ratios of the enolic tautomers of higher enegies.

4. Conclusion

Benzal-BA molecule has two different conformers in addition to the predominant triketonic form having C_1 point group symmetry. Copper complex of Benzal-BA has Cs point group symmetry but the optimized zinc-Benzal-BA complex has C_1 point group symmetry. The calculated normal modes of vibration of Benzal-BA (tautomer I) have good coincidence with the experimental Infrared data between 400-4000 cm^{-1}.

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