Tautomerism study for some macro bi imines derived from benzoin and acetyl acetone

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Abstract

Four new macro bi imines as derived from benzoin and acetyl acetone with succinyl dihydrazide (1) , phthaloyl dihydrazide (2) and 4-amino salicylic acid (3) or 5-amino salicylic acid (4) were prepared respectively by a standard method. The structures of these bi imines were confirmed by the measurements of their melting points , UVand IR spectra. The study deals with the tautomerism reactions for the synthesised compounds in ethanol and by the aid of UV spectroscopy. The thermodynamics of tautomerism reaction of these bi imines , showed that the tautomerism processes as evident from ΔG parameters were spontaneous and non spontaneous in compound (1,3,4) and (2) respectively. The enthalpies of tautomerism reactions ΔH were varied from exothermic to endothermic reactions and for the same previous compounds numbers . The entropies of reactions ΔS were also estimated and discussed. Finally, all thermodynamic parameters evaluated , support the tautomerism processes in these macro bi imines.

الخلاصة

اشتمل البحث على تحضير اربعة انواع جديدة من الجزيئات الكبيرة ثنائية الايمين المشتقة من البنزوين والأسيتايل اسيتون مع سكسنايل ثنائي هيدرازيد(1)، فثالويل ثنائي هيدرازيد(2)، و 4 - امينو حامض السلسليك(3) او 5- امينو حامض السلسليك(4) بطريقة قياسية. تم اثبات التراكيب الجزيئية لهذه الأيمينات الثنائية من خلال قياس درجات انصهارها واستخدام اطياف الأشعة فوق البنفسجية والأشعة تحت الحمراء تشمل الدراسة تفاعلات التوتومرية للمركبات المحضرة في الأيثانول بأستعمال مطيافية الأشعة فوق البنفسجية دلات دراسة ثرموديناميكية تفاعل التوتومرية لهذه الأيمينات الثنائية ومن المتغيرات ΔG ان عمليات التوتومرية للمركبات (1,3,4) هي تلقائية وغير تلقائية للمركب (2) .اما انثالبيات تفاعلات التوتومرية والمحددة ب ΔH هي متغيرة بين تفاعلات باعثة وماصة للحرارة ولنفس المركبات الواردة بالفقرة السابقة. ان انتروبيات التفاعلات والمحددة ب ΔS هي محسوبة ايضا في

البحث وتم مناقشتها، اخيرا فأن جميع المتغيرات الثرموديناميكية المحسوبة تدعم عمليات التوتومرية في جزيئات ثنائية الأيمين الكبيرة .

Introduction

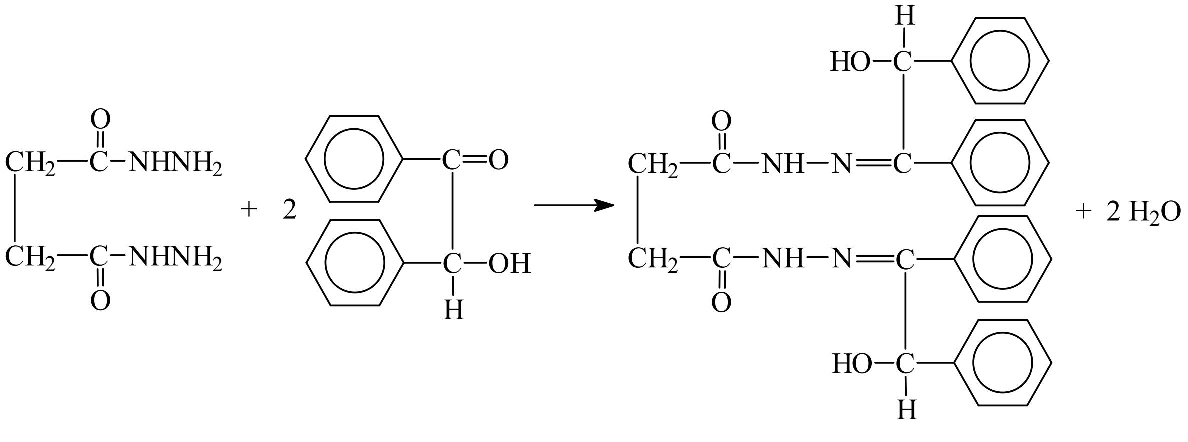
The chemistry[1] of imines had paid a great attentions by many workers during the last decade . This arised the curiosity of many workers[2] to increase their experimental works in such direction . A few workers had directed their works to the chemistry of bi imines[3,4] .Azomethines derived from various carbonyls , β –ketones , β –keto esters and amines are well known compounds and have previously studied extensively[1,5-8] . The keto-enol equilibria for a varities of Schiff bases[9-11] had studied by p.m.r. These studies confirmed the tautomerism study and the temperature dependence of spectra, yielded an information on tautomeric equilibria. Azzouz etal[8,12-13] had previonsly studied the tautomerisim reactions of deoxy benzoin[12] and some related compounds , imines[8] derived from 2-hydroxy-1-naphthaldehyde and mono and bi Schiff bases[13] derived from salicyilaldehyde .These studies show that the equilibrium constants for the tautomerised reactions were depend on the structure of compounds , the pH of the medium with temperature[8,13] and the solvent[14] used throughout the study .The present investigation was an extension of the last studies[12-14], it deals with tautomerisim of a new macro bi imines derived from benzoin and acetyl acetone with compounds having NH_2 group as succinyl dihydrazide , phthaloyl dihydrazide , 4-amino salicylic acid and 5-amino salicylic acid in ethanol . The influence of temperatures on equilibrium constants and the thermodynamic parameters of tautomerism were also considered .

Experimental

Synthesis of benzoin binylidene succinyl dihydrazide (1)

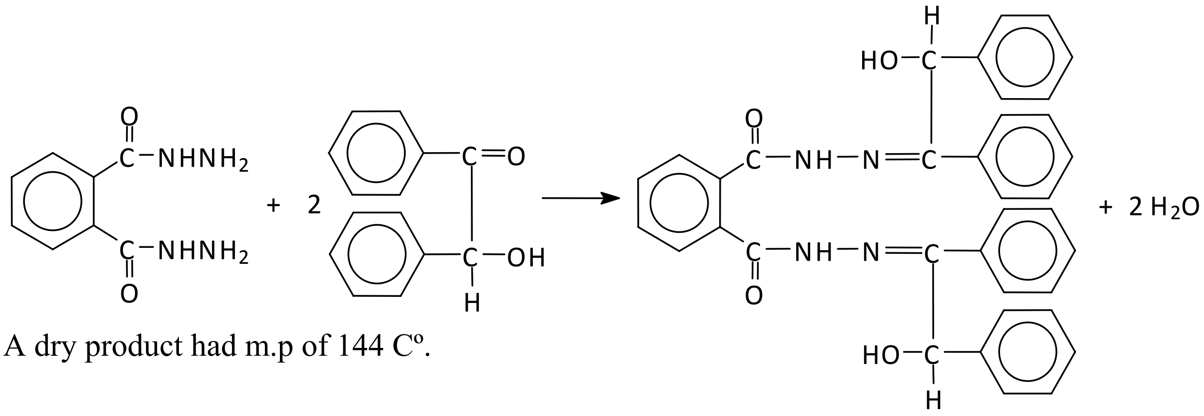
This compound was prepared[15] by mixing 0.08 mole (11.68 g) of succinyl dihydrazide with 0.16 mole (33.9 g) of benzoin . In 100 ml round bottom flask , mix the quantities of succinyl dihydrazide and the amounts of benzoin mentioned . Add to the mixture 150 ml of ethanol . The mixture was reflexed for 6 hours . The product was cooled in ice bath , following by washing the product with cold ethanol and dried.

Dry sample had a m.p of 190 C°.



Synthesis of benzoin binylidene phthaloyl dihydrazide (2)

A similar procedure was followed to that given for (1) , i.e by mixing 0.08 mole (15.5 g) of phthaloyl dihydrazide with 0.16 mole (33.9 g) of benzoin .

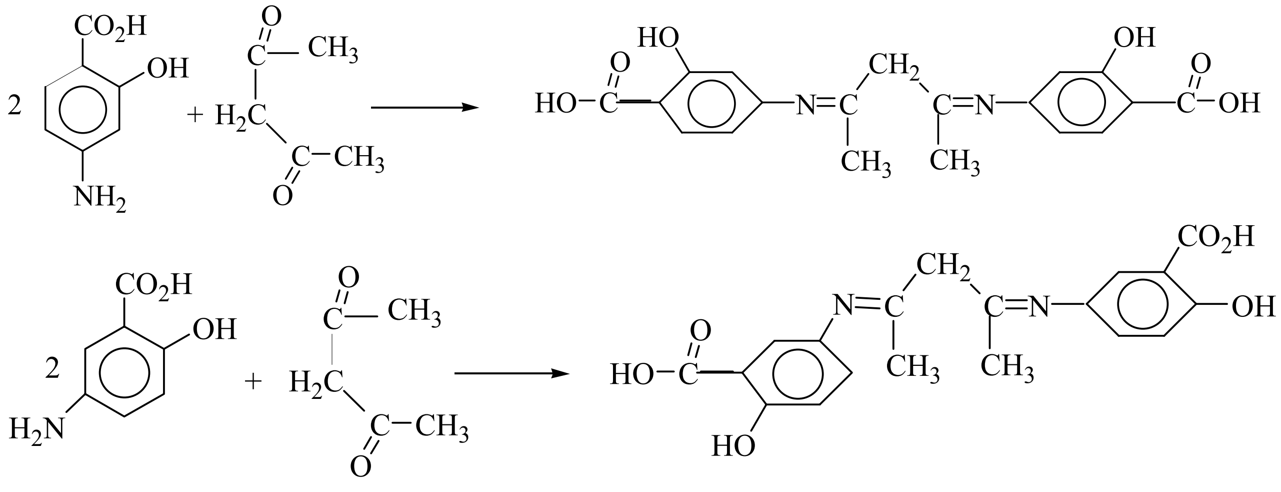


A dry product had m.p of 144 C^{o}.

Synthesis of acetyl acetone binylidine 4-amino salicylic acid (3) and acetyl acetonyl binylidine 5-amino salicylic acid (4)

A similar procedures were followed to that given for (1) , i.e by mixing 0.08 mole (8.0g) of acetyl acetone with 0.16 mole (24.48 g) of 4-amino salicylic acid and 5-amino salicylic acid respectively .

The reactions were as follows :



The effect of temperature on equilibrium constant value[8] of tautomerism in imines (1-4) were followed by measuring the UV spectrum of each 10^{-4} M imine in ethanol at a range of temperatures between (10-50) C^{o}. The thermodynamic parameters of tautomerism process are evaluated by a standard method[4] .

Instrumentation

The UV absorption spectra were measured by using UV-Visible 1650 PC Shimadzu having a computrized recording spectrophotometer. The absorption spectra of 10^{-4} M imines in ethanol were measured by using 1×1×3 cm^3 matached silica cells .The influence of temperatures on UV spectra of imines were measured by using cintra 5 UV–Visible spectrophotometer . The last is connected by water circulating thermostat of type HAAKE NK 22 . The IR spectra for solid imines (1-4) were measured by computerized Bruker Tensor 27 by KBr disc method. Electrothermal melting point apparatus was used for measurement of melting point of solid sample .

Results and Discussion

At the begginnig of this investigation , it was decided to confirm the structures of imines by UV and IR spectra , in addition to the melting points stated before. Originally , it was anticipated that the UV absorption spectra of 10^{-4} M (1-4) imines in ethanol were complex[16] . This was due to the presence of more than chromophore or auxochrome groups in each imine . Careful examination of Table (1) reveals that molecules (1,4) and (2,3) had appeared two and three UV bands respectively. All UV bands listed in Table (1) reveals that molecules (1,4) and (2,3) had appeared two and three UV bands respectively . all UV bands [4,8] listed in Table (1) , had a molar extension coefficient values of more than one thousand and were assigned to л-л* transitions , where as compound (2) slows one band with molar extension value of less than one thousand and was attributed to n-л transition. Figure (1) shows the UV absorption spectra for imines (1-4) in ethanol and at 20 C^o. Expermintally , it was observed that the first and second bands in all imines spectra are sensitive to the variation of temperature . Hence they are assigned[8,17] to keto and enol tautomers respectively in each imine and were used as a measure for equilibrium constant values for tautomerism reactions under study as we will see later.

The solid IR spectra for imines (1,4) show the following absorptions for a main five groups as shown in Figures (2-5) as follows :

1- A medium stretching absorptions in the range (3388.16 – 3443.10) cm^{-1}. These absorptions were either for the alcoholic groups in imines 1 and 2 or in the phenolic forms for imines 3 and 4.

2- A medium absorption stretching bands in the range (3200-3300)cm^{-1} were only for appeared the amide linkage in imines 1 and 2.

3- A sharp absorption bending bands were observed for the carbonyl groups in arrange (1670-1651.13) . The were assigned to the carbonyl groups in imines 3 and These values mentioned were lower than the expected values in imines under study . This was due to the possibility of association of carboxylic acids by hydrogen bonding .The last comes in full agreement with our previous work[18] with substituted benzoic acids .

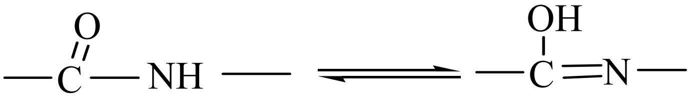
4- A strong stretghing absorption bonds were observed in a range (1616.73-1681.31) cm^{-1} . They were assigned for the double imine linkage i.e C=N in imines 1-4 .

5- A strong stretching bands were also seen at a wave number of about 1597 cm^{-1}.It was assingned for aromaticity in imines 1-4 .

These IR absorption bands were in full agreement[19] with the chemical structures of imines1-4.

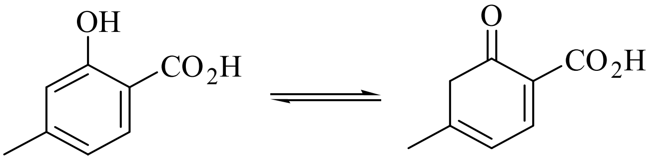
These UV and IR spectroscopic studies beside the melting points were a good confirmation[16,19] for the chemical structures of imines under study . This encourage the workers to increase expermentation in a direction of tautomerism study by the aid of UV spectra .

Several workers had observed a clear influence for tautomeric equilibria[8,13,20,2] for a number of organic compounds by changing the temperature .In this study the tautomerism process in compounds 1and 2 were achieved by measuring the UV spectra at arange of temperatures (283-323) K in ethanol . The phenomena of tautomerism reactions were expected in compounds (1-2) by the following equilibria as called : lactam – lactim tautomerism[22] .



$$-\overset{O}{\overset{\|}{C}}-NH- \rightleftharpoons -\overset{OH}{\overset{|}{C}}=N-$$

Similarly, compounds 3 and 4 show an enol-keto tautomerism[22] of the type:



Some workers[14,23-24] had observed that keto tautomer in Salicylidene 2- hydroxy napthylidine schiff bases absorbs at longer wave length as compared with enol tautomer . This faciliates the evaluation of equilibrium constant[8] K for the tautomerism reactions under study from the relation ship : $K = A_{keto} / K_{enol}$

$A_{\mathbf{keto}}$ and $A_{\mathbf{enol}}$ are absorbance of keto and enol tautomers from UV spectra shown in Table (1) . Table (2) shows lnK and the thermodynamic parameter for the tautomerism reactions in compounds (1-4) in ethanol . The plot of ln K versus the inverse of absolute temperature show a straight lines with R^2 values range between 0.8712- 0.9479 , as evident from statagraph computer programme as shown in Figure (6). Hence Vant Hoff equation were able to evaluate the enthalpies of tautomerism in compounds (1- 4) at five temperatures and their average value of $\overline{\Delta H}$ as in Table (2)

$$\mathbf{\ln K = constant - \Delta H / RT \quad .... (1)}$$

The $\overline{\Delta H}$ values had either negative signs or the tautomerism process were exothermic as in compounds 1,3 and 4 . On the contrary to that the ΔH value in compound 2 had a possitive sign or the tautomerism process was endothermic. These negative ΔH values were in agreement with similar tautomerism studies for imines[8] derived from 2-hydroxy napthaldehyde or and for deoxy benzoin[12] and some related compounds . Other tautomerism study as in phenolic mono and bi schiff[13] bases show both negative and possitive signs for ΔH parameter . The free energy of tatomerism values were estimated from an equation (2) of the form :

$$\mathbf{\overline{\Delta G} = - RT \ln K \; ....(2)}$$

The $\overline{\Delta G}$ values collected in table (2) were similarly varied from negative signs as in compouns 1,3 and 4 to positive signs in compound 2 . These negative and positive signs of ΔG thermodynamic parameters mean that the tautomerism processes were occured in spontanious and non spontaneous processes respectively . The entropies of tautomerism in compounds under study were evaluated from Gibbs equation of the form (3) :

$$\overline{\Delta G} = \overline{\Delta H} - T\,\overline{\Delta S} \quad \text{....(3)}$$

Compounds 1,3 and 4 show a negative signs of ΔS values or the tautomerism process were directed toward the less random . Compound (2) Shows an inverse result to the last . Finally all thermodynamic parameters collected in Table (2) were in full agreement[8,12,13] with other studies .

Table (1): UV and IR absorption spectra for imines (1-4)

Comp.NO.	**UV absorption in ethanol λnm (ε_{Max})**	**IR spectra (cm^{-1})**				
		OH^-	**$\overset{\overset{O}{\|}}{C}-NH$**	**C=O**	**C=N**	**C-H aromatic**
1	296 (7710) 248 (7140)	3400.00	3201.29		1681.31	1597.53
2	320 (800) 280 (3670) 246 (6910)	3421. 67	3300.00		1677.25	1597.88
3	317.7(20000) 284 (13520) 240 (16470)	3388.16		1670.00	1616.73	1597.88
4	296(9000) 245(3710)	3443.19		1651.13	1619.66	1597.20

Table (2) Thermodynamic of tautomerism reactions in compounds (1-4) in ethanol

No.of compound	Temp.	ln K	ΔH J.mol^{-1}	ΔG J.mol^{-1}	ΔS J.mol^{-1}. deg^{-1}	$\overline{\Delta H}$ J.mol^{-1}	$\overline{\Delta G}$ J.mol^{-1}	$\overline{\Delta S}$ J.mol^{-1}. deg^{-1}
1	328	0.076	-3003.0	-178.8	-10.0	-3048.8	-25.0	-10
	293	0.056	-3060.4	-136.4				
	303	0.036	-3114.4	-90.7				
	313	0.017	-3079.3	44.2				
	323	-0.088	-2987.0	236.3				
2	328	-0.539	2815.5	1268.2	5.5	2845.5	1188.8	5.5
	293	-0.524	2878.5	1276.5				
	303	-0.486	2881.0	1224.3				
	313	-0.421	2806.9	1095.6				
	323	-0.402	2845.5	1079.5				
3	328	0.391	-2933.3	-920.0	-7.1	-2979.9	-824.3	-7.1
	293	0.405	-3071.0	-986.6				
	303	0.321	-2964.3	-808.6				
	313	0.270	-2929.4	-702.6				
	323	0.262	-3001.5	-703.6				
4	283	0.886	-13091.5	-2084.6	-31.3	-10627.1	-1130.8	-31.3
	293	0.541	-1271.7	-1317.9				
	303	0.426	-12857.9	-1073.2				
	313	0.266	-12865.9	-692.2				
	323	0.181	-13048.7	-486.0				

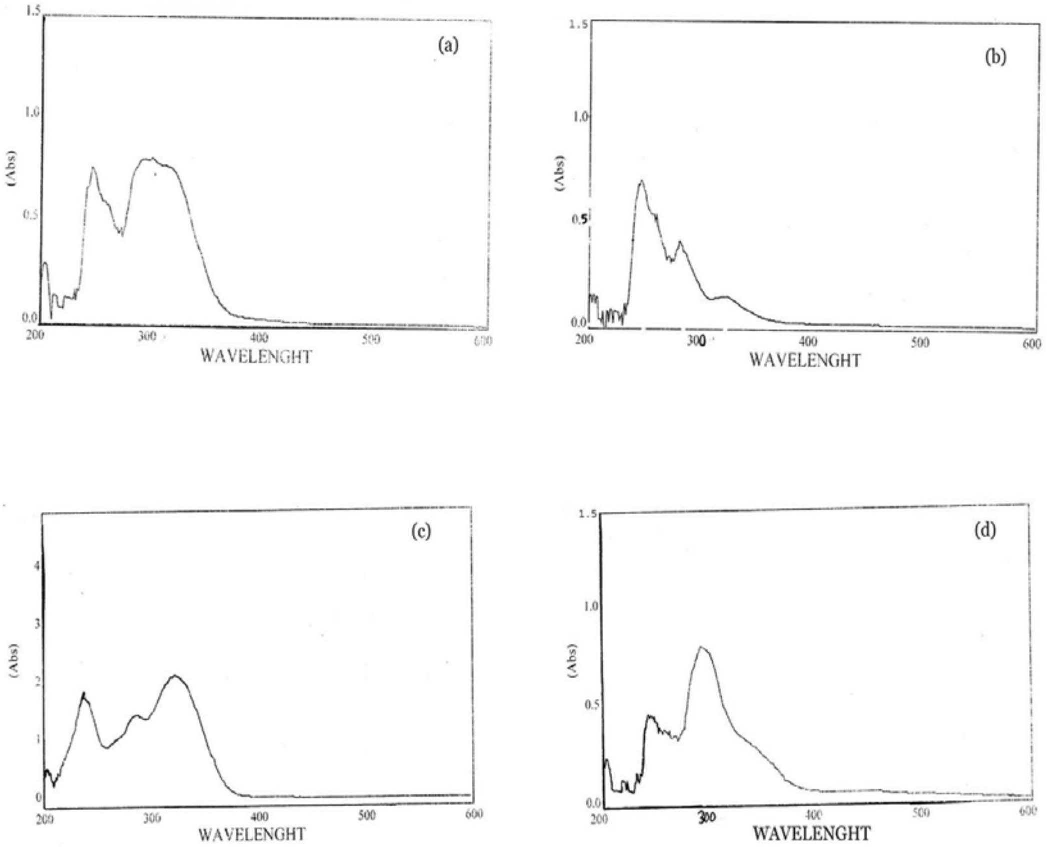


Figure (1) The UV absorption spectra for 10^{-4} M in ethanol for :

a) compound(1)

b) compound(2)

c) compound(3)

d) compound(4)

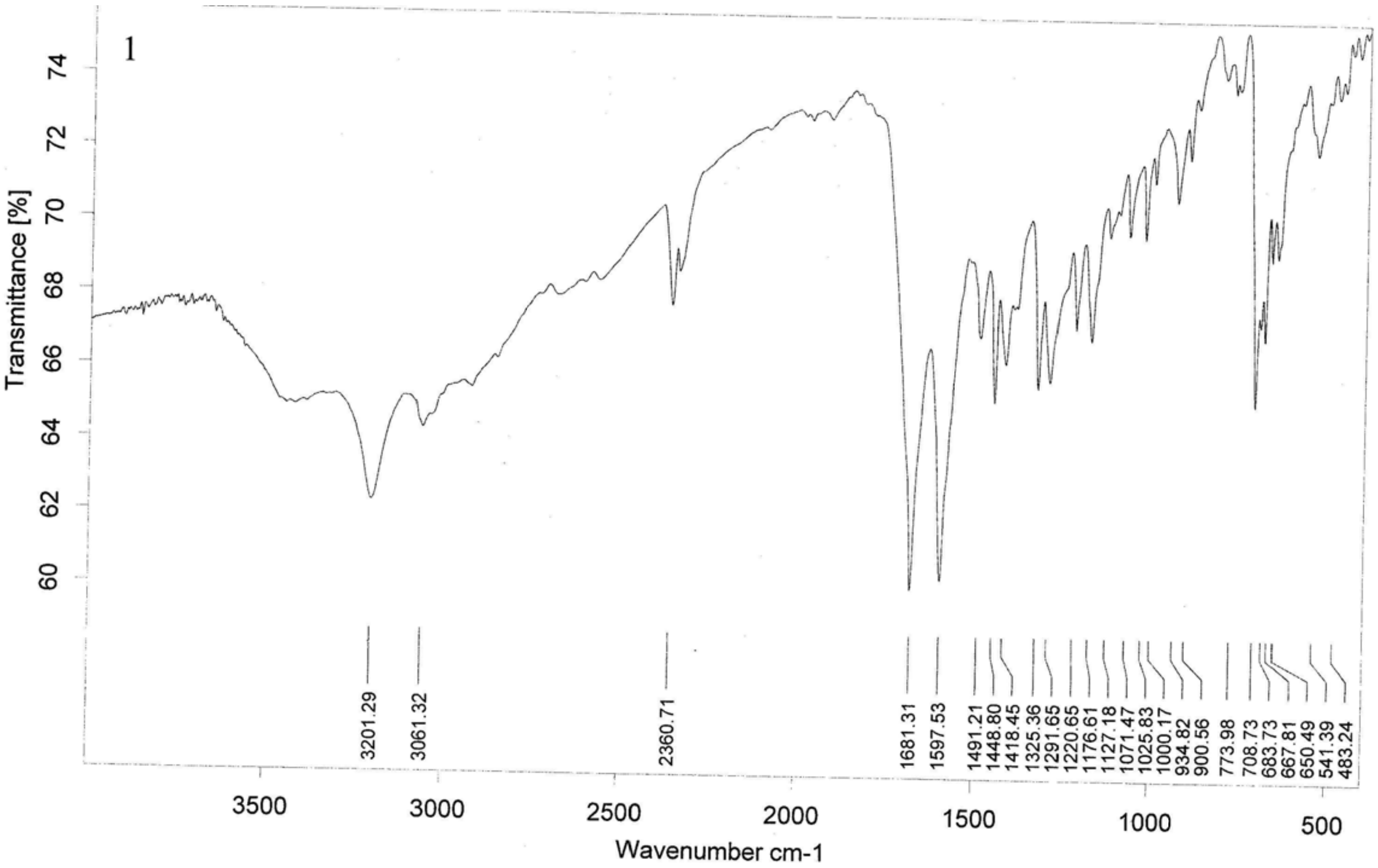


Figure (2) IR absorption spectra for compound 1

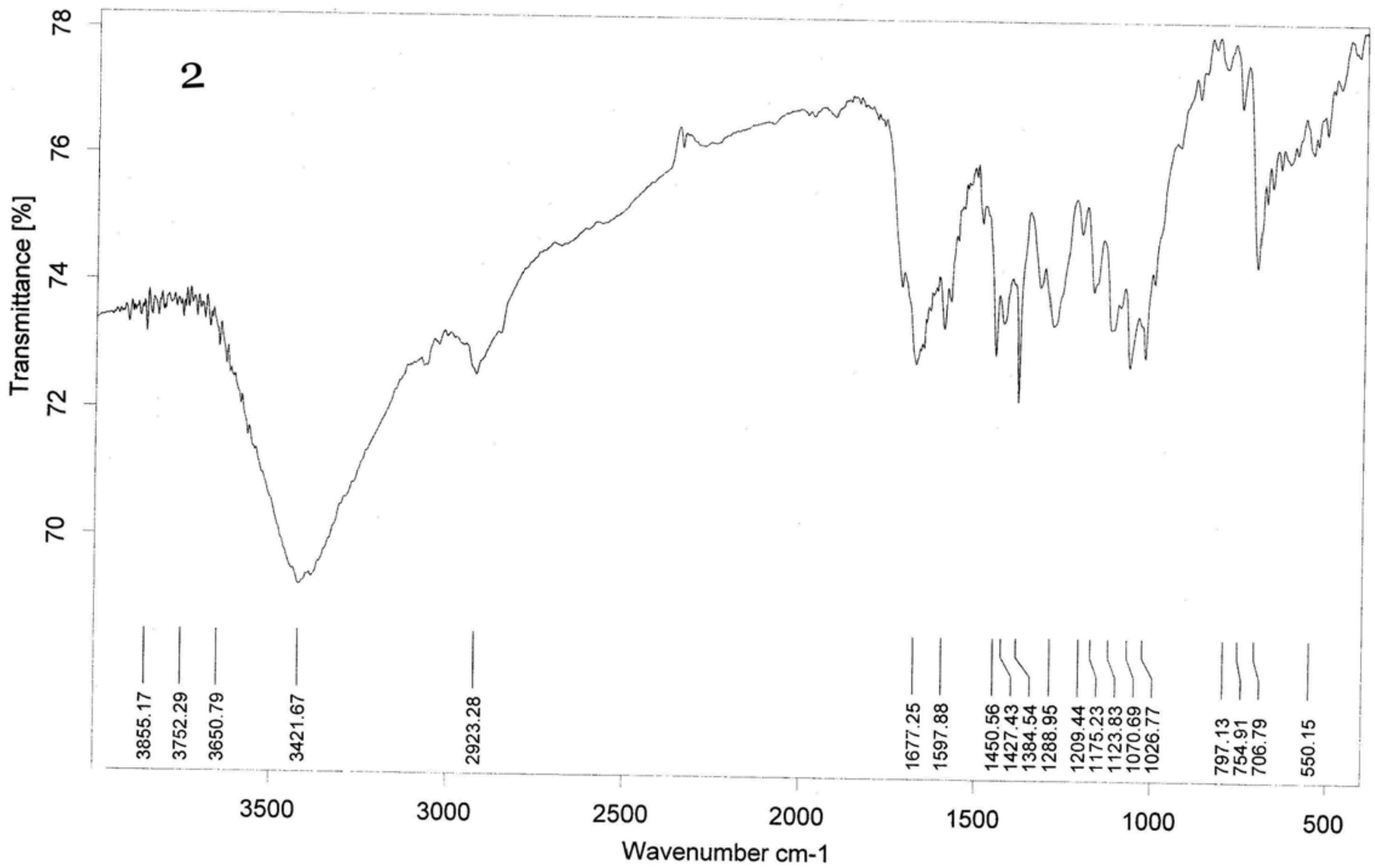


Figure (3) IR absorption spectra for compound 2

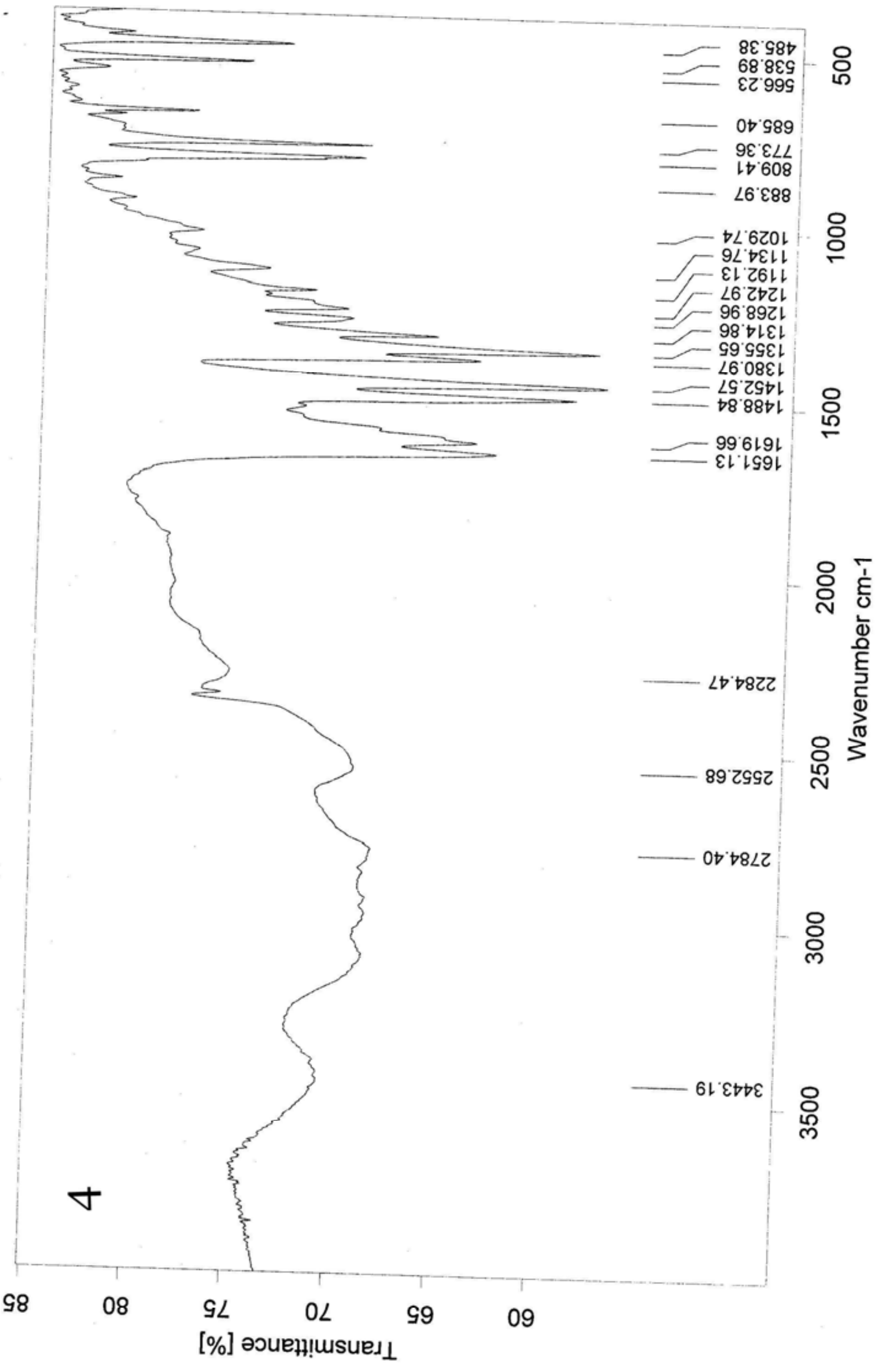
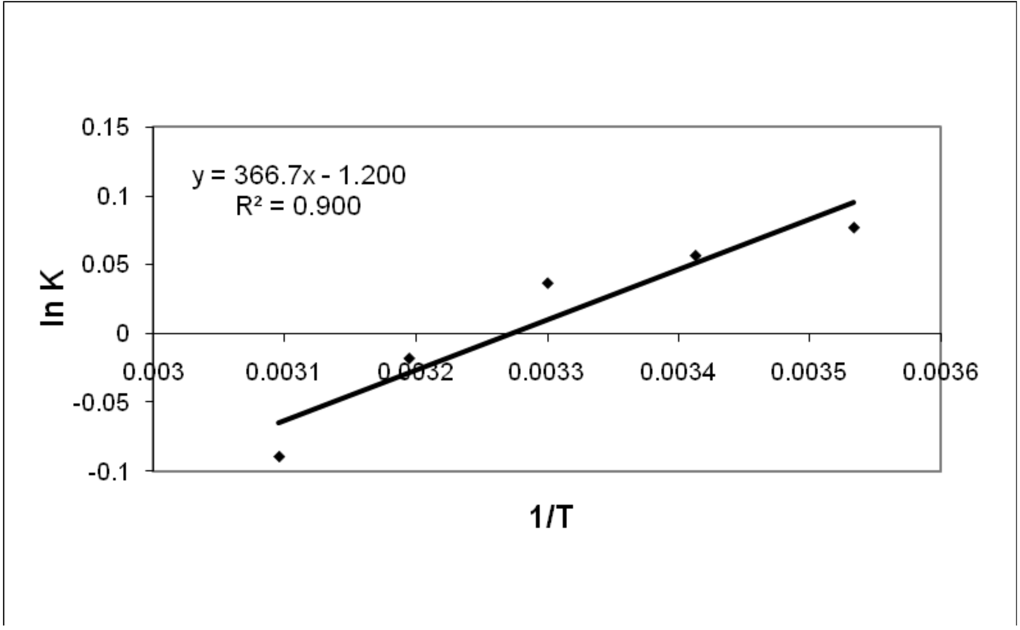
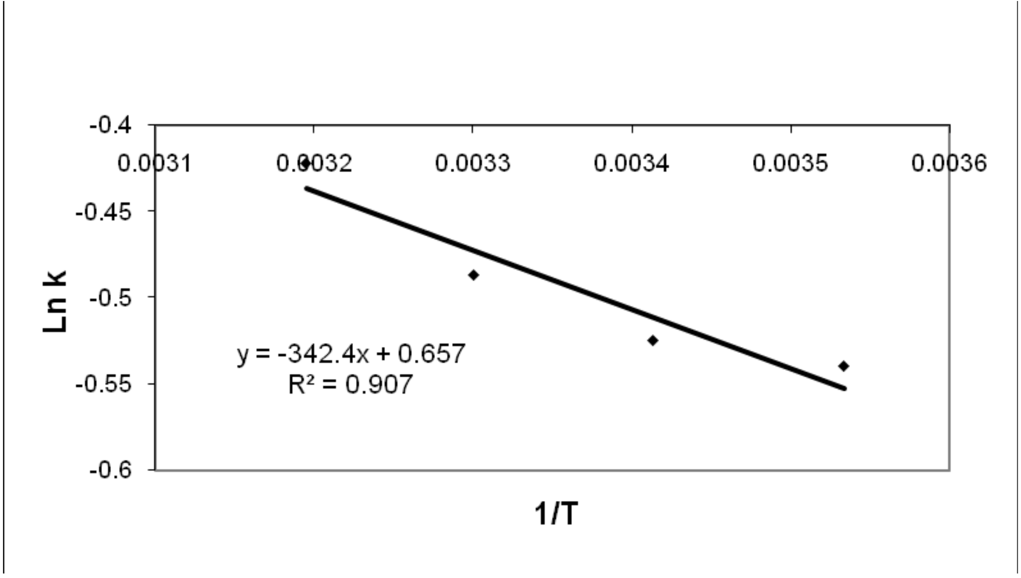


Figure (5) IR absorption spectra for compound 4

(a)

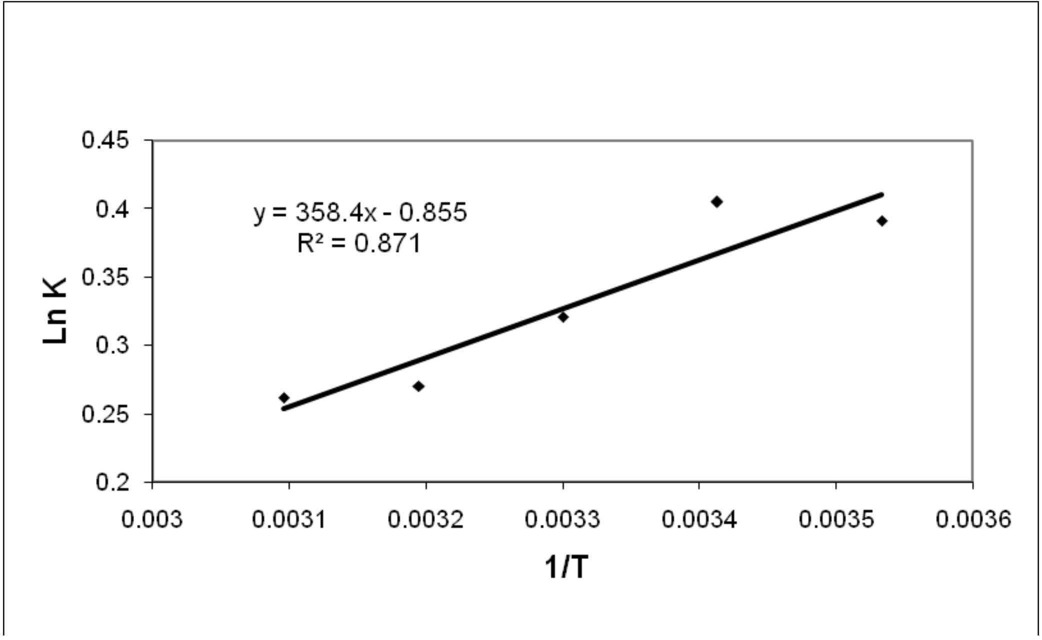

y = 366.7x - 1.200
R² = 0.900
ln K
1/T
0.15
0.1
0.05
0
-0.05
-0.1
0.003
0.0031
0.0032
0.0033
0.0034
0.0035
0.0036

(b)


y = -342.4x + 0.657
R² = 0.907
Ln k
1/T
-0.4
-0.45
-0.5
-0.55
-0.6
0.0031
0.0032
0.0033
0.0034
0.0035
0.0036

Cont .

(c)



(d)

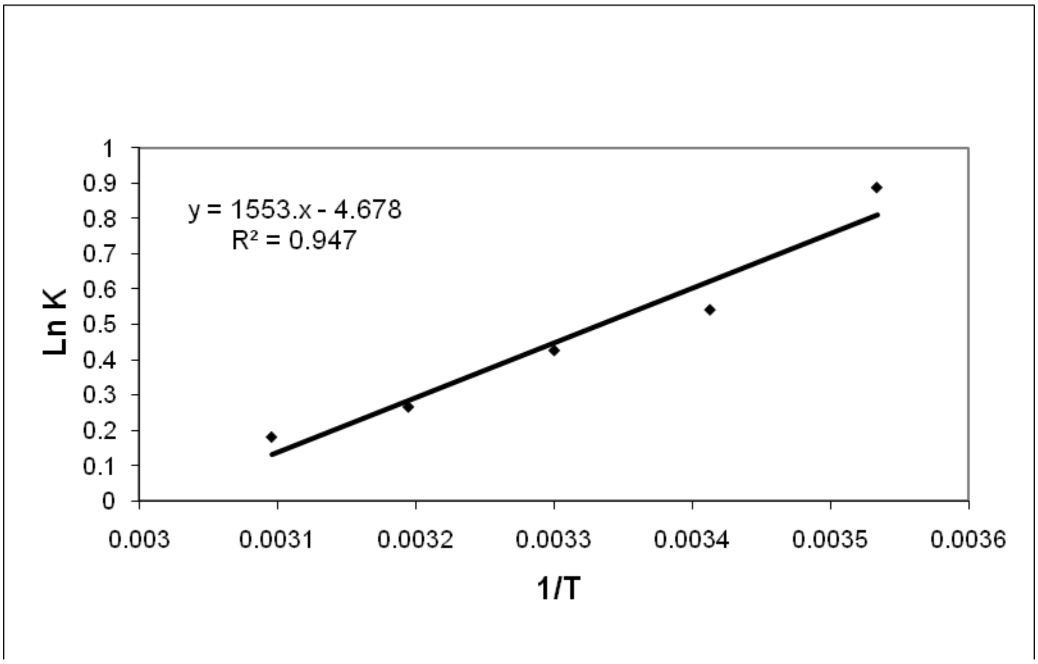


Figure (6) Vant Hoff plots for :

a- compound (1) b - compound (2)
c- compound (3) d- compound (4)

Conclusions

1- Four new bi imines were synthesised from benzoin and acetyl acetone with suitable amines having dihydrazide group and primary amino group.

2-The structures of bi imines under study had been confirmed by using physical methods , namely such as UV, IR spectra with melting points.

3-The process of tautomerism in bi imines (1-4) had been studied in ethanol by using UV spectra .

4-Imines (1-2) and (3-4) show a tautomerism[22] process of types lactam-lactim and enol-keto respectively .

5-The keto forms in imines (1-4) absorb[14,23,24] at longer wave –length as compared with enol forms .

6-The tautomerism in compounds (1-4) were varied from either exothermic process[8,12] as in compound 1,3 and 4 or endothermic[13] process as in compound 2. These show negative and possitive ΔH values respectively .

7-The processes of tautomerism in compounds (1-4) as evident from ΔG parameter were either spontaneous as in compounds 1,3 and 4 or nonspontaneous in compound (2).

8-The entropies of tautomerism in compounds under study had a negative or positive ΔS parameters in compounds (1,3,4) and (2) respectively. In otherwords that the tautomerism processes in compounds mentionted were directed toward the less and greater randoms respectively .

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