

The UV and IR spectra of Some Schiff bases derived from salicylaldehyde and O-methoxybenzaldehyde. Study the influence of concentration of Schiff base on tautomerism reaction process

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Abstract

The paper includes the preparation of eight Schiff bases , derived for salicylaldehyde and o-methoxybenzaldehyde with aromatic amines such as o,m,p-amino aniline and o,m,p-phenylene diamine by standard method. The ratio of aldehyde to amine during synthesis of imines are either 1:1 or 2:1 respectively .The last ratio gives a new class of di-salicylidene anilines of limited publications is known on them till now.

The presence of hydrogen bondings in imines , are identified by using UV and IR spectra.

The study led to a conclusion that imines under investigation , are exist as an equilibrium mixtures of enol and keto forms in 1,2- dichloro ethane. The mechanisms of tautomerism reactions of imines are included. Finally , the influence of concentrations of Schiff bases on tautomerism process , namely on equilibrium constants values and ΔG thermodynamic parameter are given.

1:2 1:1

-2,1

ΔG

Introduction

During the last few years, a considerable attention has been focused on the spectroscopical studies of imines by U.V¹⁻⁴, I.R⁵⁻⁶, N.M.R⁶ and mass spectra^{2,6-7}. This is because of their wide application in various fields^{8,9}.

Several studies were reported^{1,10-11} regarding hydrogen bond formation and proton transfer in certain Schiff bases. The authors speculated that bathochromic shift in visual pigments might be caused by this process.

Azzouz¹² had studied the U.V absorption of 3 and 4 substituted benzaldoximes, the study shows either one or two absorptions in the range 225-290 nm. Others 2-substituted benzaldoximes as 2-F, 2-NH₂, 2-OH and 2,4-di-OH show three absorptions one of them is led to a bathochromic absorption band or shoulder in the range 305-327nm. The cause of the last new assignment was given and discussed in terms of polar resonance structures of oximes intermediates.

The lack of informations about the U.V and IR spectra of some Schiff bases derived from salicylaldehyde and o-methoxy-benzaldehyde with aromatic amines are reported here. An evidences supporting the hydrogen bonding and tautomerism reactions in imines under investigation are discussed. A suggested mechanisms for the tautomerism reaction of the disalicylidene anilines are given. Finally, the influence of concentrations of solute on the values of equilibrium constant of tautomerism reactions in Schiff bases in solvents of different polarities are also included.

Experimental

Apparatus:

All absorption measurements were made on Pye Unicam SP 8000 spectrophotometer using a matched 1 cm silica cells. The IR spectra were recorded on Pye Unicam SP 1110 spectrophotometer, in solid (KBr disk) and liquid states. 1,2-dichloro ethane (1,2-DCE) is the proper solvent used to prepare 10⁻³M of Schiff bases used in IR studies.

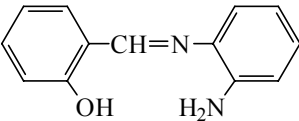
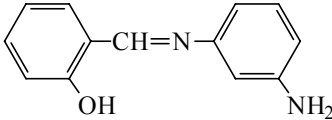
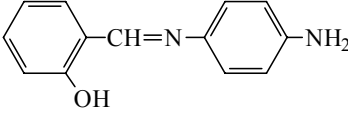
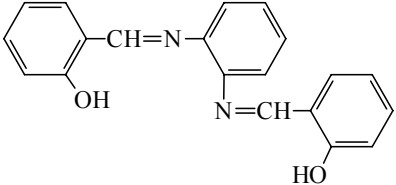
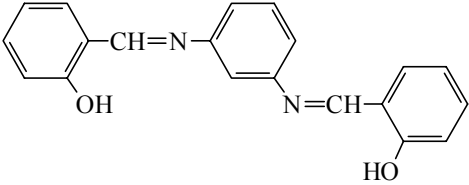
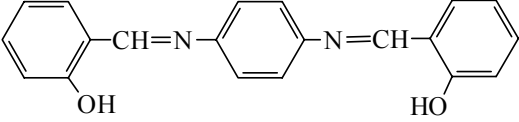
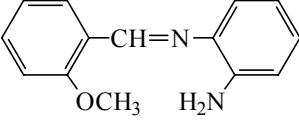
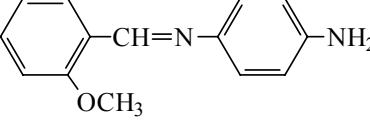
Materials and methods:

All aldehydes and amines used throughout this work were of Fluka origin. They were converted to their corresponding Schiff bases¹³ by mixing 1:1 or 2:1 mole ratio of the suitable aldehyde / amine.

To the mixture, a few ml's of absolute ethanol is added, followed by reflux for about one hour. Recrystallization of the crude sample is done by using absolute ethanol. Tabel (1-3) summarises the melting points the UV and IR spectra of the Schiff bases prepared.

U.V spectra of Schiff bases were measured in acetone and dichloro methane (DCM) while the IR spectra of the same compounds are measured either in solids by KBr disc or for 10⁻³M solutions in 1,2-DCE. The influence of concentration of Schiff baese on tautomerism reactions are studied in four solvents having a different polarities.

Tabel (1) Nomenclatures , structures and melting points of imines

No.	Nomenclature	Structure	Melting point (°C)
1	Salicylidene-o-aminoaniline		62-63
2	Salicylidene-m-aminoaniline		84-85
3	Salicylidene-p-aminoaniline		199-200
4	Disalicylidene-o-aminoaniline		165-166
5	Disalicylidene-m-aminoaniline		208-209
6	Disalicylidene-p-aminoaniline		218-219
7	o-Methoxybenzylidene-o-aminoaniline		90-92
8	o-Methoxybenzylidene-p-aminoaniline		105-107

Results and Discussion

1. The UV spectra

At the beginning of this investigation, the UV spectra had measured to prove the existence of hydrogen bonding in Schiff bases under study.

Accordingly the UV spectra of any molecule are measured in two solvents having a high and low polarities. Such specification are fulfilled with acetone and 1,2-DCE respectively. This is in accordance with hydrogen bonding^{6,14} study in any molecule. Tabel (2) shows two main absorption bands for Schiff bases (1-5) and 8 with their wavelengths and molar extinction coefficients in two solvents stated above. Meanwhile, Schiff bases 6-7 show one main absorption.

A $\pi \rightarrow \pi^*$ transitions have identified for all Schiff bases from their \sum_{\max} values of greater than one thousand. Finally the change of wavenumber $\Delta\bar{U}$ for any absorption band is calculated from the relationship :-

$$\Delta\bar{U} = \bar{U}_{\text{Acetone}} - \bar{U}_{\text{DCE}}$$

It was observed that $\Delta\bar{U}$ calculated for the bands shown in Tabel (1) have a negative signs. This support^{6,14,15} the idea of existing hydrogen bonding in Schiff bases under study. Schiff bases 1,3,5,8 for one band with longer wavelength show an exclusion to the last result i.e with positive $\Delta\bar{U}$ signs are observed. This does not agree with hydrogen bond formation. The last can be interpreted to the greater polarity of DCE solvent that overcome on solubility problem of Schiff base compared to nonpolar CCl_4 solvent used in routine study.

Tabel (2) shows that Schiff base (1) contains OH and NH_2 groups in ortho positions on the aromatic ring. Possibly such compound is able to form two folds intramolecular hydrogen bondings, having five and six membered rings.

This assumption does not agree with EL-Bayoumi¹⁶ finding of unplaner benzylidene aniline molecule. In other words the intramolecular hydrogen bonding in Schiff bases (1) is responsible on its coplaner structure.

Molecules (2) and (3) are prepared from salicylaldehyde with m and p-amino anilines, are able to form both an intramolecular hydrogen bonding with OH group of aldehyde and nitrogen azomethine and the intermolecular hydrogen bond with NH_2 group of the amine part. An exclusion to the last case of the capability of molecules (7) and (8) to form the only intermolecular hydrogen bonding with the NH_2 group, due to the presence of methoxy groups on the aldehyde part of the molecules.

Tabel 2: The UV spectra of Schiff bases at wavelength λ_{nm} , molar extinction coefficient $\sum_{mole^{-1}. m^2}$ and their wavenumber $\nu_{m^{-1}}$

Comp.No	1,2-DCM		Aceton		1,2-DCM $\nu \times 10^{-9}$	Aceton $\nu \times 10^{-9}$	$\Delta\nu \times 10^{-9}$
	λ	\sum	λ	\sum			
1	301	1992	343.5	2190	0.00332	0.00291	-0.00041
	395	2122	388.5	2166	0.00253	0.00257	0.00004
2	301	1870	343.5	2185	0.00332	0.00291	-0.00041
	382	1954	393.5	2273	0.00261	0.00254	-0.00007
3	326	1949	343.5	2262	0.00306	0.00291	-0.00015
	410.5	3260	409	2451	0.00243	0.00244	0.00001
4	301	1860	343.5	1879	0.00332	0.00291	-0.00041
	350.5	1380	396	2176	0.00285	0.00252	-0.00033
5	301	1886	343.5	1841	0.00332	0.00291	-0.00041
	382	1882	384.5	1928	0.00361	0.00260	-0.00001
6	410	2495	450	2330	0.00243	0.00221	-0.00173
7	301	2046	342.5	1819	0.00332	0.00291	-0.00041
8	301	2233	343	1886	0.00332	0.00291	-0.00041
	409.5	2404	406	2342	0.00244	0.00246	0.00002

Tabel 3: IR spectra of Schiff bases in 1,2-DCE

Comp.No	Wavenumber cm^{-1}					
	1	1600(s)	1725(m)	3150(vs)	3440(w)	3520(w)
2	1605(s)	1680-1710(m)	3140(vs)	3280(w)	3420(w)	3660(s)
3	1610(s)	1680-1720(m)	3150(vs)	3380(w)	3400(w)	3650(s)
4	1605(s)	1710(m)	3180(vs)	3420(w)	3520(w)	3560(w)
5	1600-1620(s)	1700-1720(w)	3160(vs)	3420(vw)	3520(w)	3560(w)
6	1600(m)	1700-1720(m)	3120(vs)	3520(w)	3650(w)	3560(w)

w=weak
m=medium
vw=very weak
vs=very sharp
s=sharp

2. The IR spectra

This method¹⁴⁻¹⁵ is widely used for the investigation of hydrogen bonding type. Preliminary study is conducted on compound (2) in the following states:

- 1- Solid state shows a spectrum of (2) with a broad band of 3050(m) cm^{-1} for the unspecified hydrogen bonding, that encourage to perform more experimental works.
- 2- At liquid state, two experiments are done to Schiff bases under the study, the first one by dissolving any Schiff base in carbon tetrachloride. This gives unfortunately a poor IR spectrum¹⁴ due to the limited solubility of solute in such unpolar solvent. This encourage to replace the solvent to another one of greater polarity as

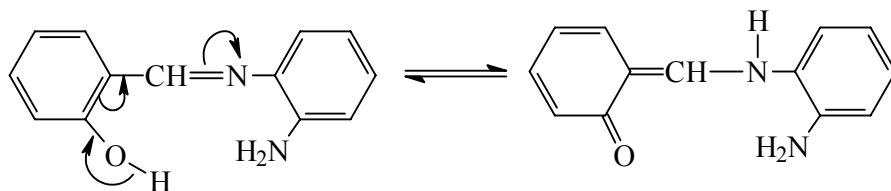
1,2-dichloro ethane (1,2-DCE).

Tabel (3) summarizes the IR spectra of $10^{-3}M$ Schiff bases (1-6) in 1,2-DCE. These spectra show bands ranges at values^{6,15,17}, (1600-1620)s cm^{-1} , (1680-1725)m or w cm^{-1} , (3120-3180) vs cm^{-1} , (3280-3520) w or vw cm^{-1} , (3400-3650) w cm^{-1} and (3560-3600) s or w cm^{-1} . They are assigned to aromaticity, the carbonyl group of tautomerised Schiff base, the asymmetrical and symmetrical intramolecular stretching N...H bonding and the free phenol group respectively.

Schiff base (1) is able to form an intramolecular hydrogen bonding either from the phenol group with nitrogen atom -O-H...N, forming a six membered ring or from the amine

group with nitrogen atom N-H...N of a five membered ring. This results to produce a two folds intramolecular hydrogen bondings in Schiff base (1). This may result to an increase in the stability of enol form. Similar behavior can be expected for Schiff bases (4-6), but of hydrogen bonding type of -O-H...N only.

Now the question which can be raised, how carbonyl bands in the IR spectra of Schiff base are appeared in the range (1680-1825) cm^{-1} or w cm^{-1} . This can be interpreted by assuming the tautomerism^{18,19} reaction in any molecule, with typical example of Schiff base (1) as in Scheme (1):-



Scheme (1) Tautomerism reaction in Schiff base (1)

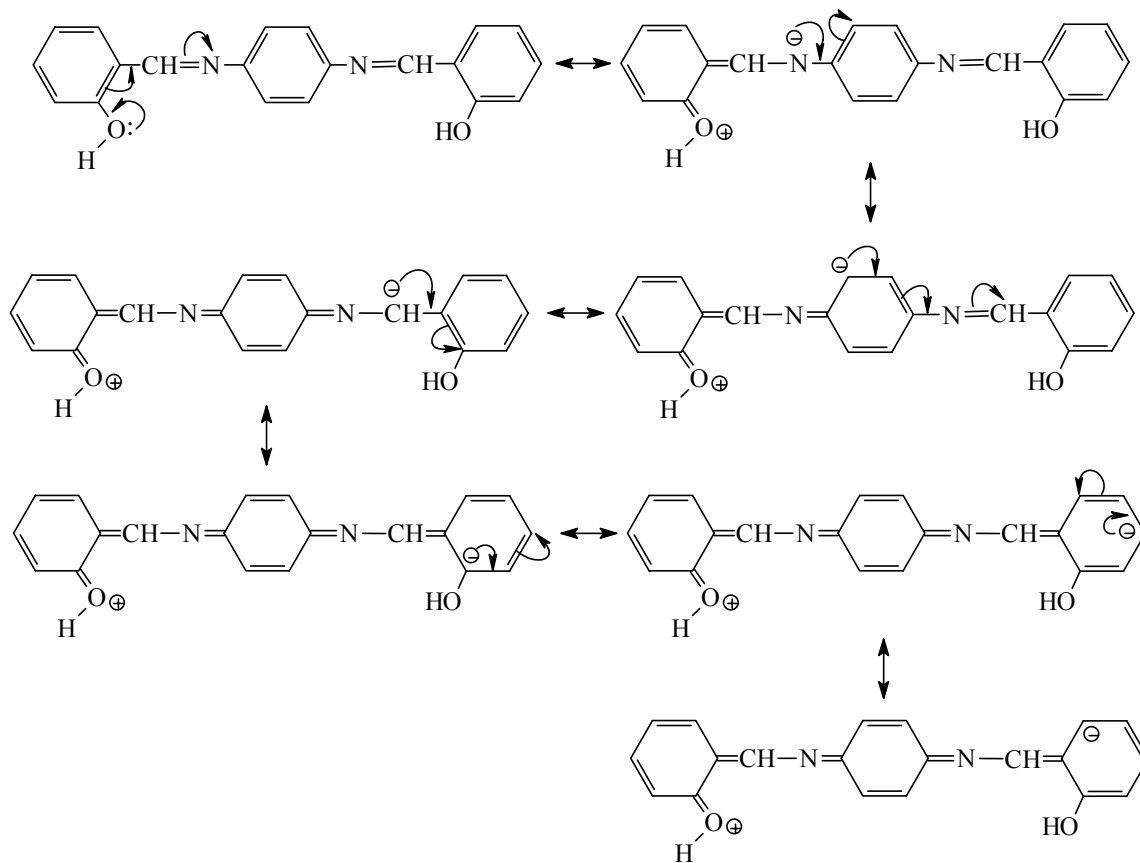
Schiff bases (4-6) are prepared from two moles of aldehydes with one mole of phenylene diamine, so they contain a double imine linkages in each molecule. Schiff bases (4) and (6) show a medium intensity bands for the carbonyl groups at wavenumbers $1710(\text{m}) \text{ cm}^{-1}$ and $1700-1720(\text{m}) \text{ cm}^{-1}$ respectively of tautomerism reactions. Mean while, Schiff base (5) shows a similar and weak band at $(1700-1720) \text{ cm}^{-1}$. Actually, the enol \rightleftharpoons Keto tautomerism reaction in Schiff bases (4-6) are resemble those of Schiff bases (1-3), with the appearance of stretching vibrations at $3420(\text{w}) \text{ cm}^{-1}$, $3520(\text{w}) \text{ cm}^{-1}$ and $3560(\text{w}) \text{ cm}^{-1}$. They are referred²⁰ to the symmetrical, asymmetrical and free N-H vibrations in Schiff base (4). Similar bands are observed for Schiff bases (5) and (6).

The intensity of carbonyl in Schiff bases (4-6) show a medium intensities in molecules (4) and (6) and weak intensity in molecule (5). It is believed that the intensity of carbonyl band is reflected to the ease of tautomerism process in any Schiff base.

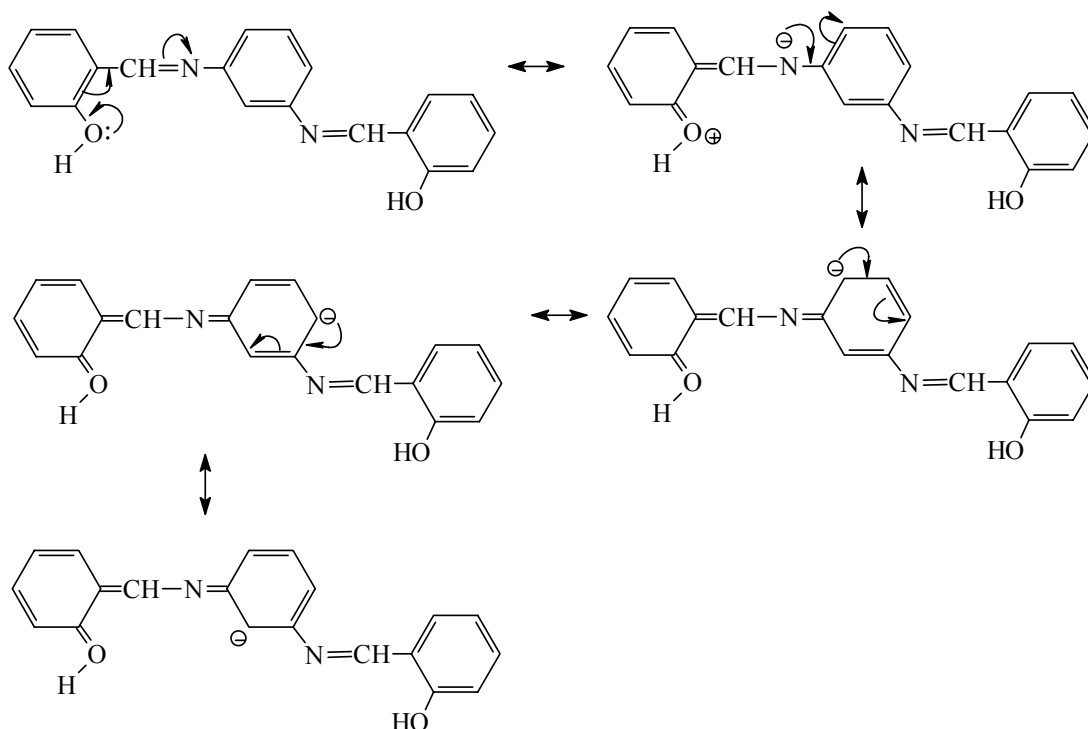
Accordingly, the speed of tautomerism process as expected to the in order of Schiff bases (4),(6) > Schiff base (5). The last is originated by the inductive and mesomeric effects of phenol group as known²¹ in any Schiff base. Now when the last effect is considered, the mechanisms of tautomerism in Schiff base under study are suggested in the scheme (2) :-

a- Mechanism of tautomerism in Schiff bases (4) and (6)

Similar mechanisms are suggested, typical example is given for Schiff base (6) as in Scheme (2)



Scheme (2) Tautomerism reaction in Schiff base (6)
b- Mechanism of tautomerism in Schiff base (5) as in Scheme (3)



Scheme (3) Tautomerism reaction in Schiff base (5)

Scheme (2) shows that delocalization of electrons in Schiff base (4) and (6) are extended over the whole molecules i.e. three aromatic rings, resulting to seven resonance hybrids. This facilitates the tautomerism processes in molecules (4) and (6). By contrast, Schiff base (5) produces five resonance hybrids by partial electrons delocalization in two aromatic rings. This is a good answer of a medium and weak carbonyl intensities are obtained in molecules (4-6) and (5) respectively. The foregoing discussion encourage the workers to deal with studying the influence of three concentrations of Schiff bases having a values $(0.2, 0.5, 1.0) \times 10^{-4} \text{M}$ on values of equilibrium constants, as well as the change of Gibbs free energy ΔG of tautomerized reactions in Schiff bases. Two types of tautomerism reactions can be expected in Schiff bases under as:- enol \rightleftharpoons keto(I)

amine-imine \rightleftharpoons imine-enamine... (II)

Tautomeric categories I and II are occurred in Schiff bases (1-6) and (7-8) respectively as a well known tautomerism⁶ reactions in Schiff bases. Equilibrium constants K for the tautomerism reactions are evaluated by using ethanol and acetone as a strongly polar solvents and dichloro methane (DCM) and dichloro ethane (1,2-DCE) as a weakly polar solvents. Table (4) summarizes the results that are collected from UV spectra measured on Schiff bases. This shows absorbances of reactant (A_1), product (A_2), K and ΔG values estimated. Actually, K is evaluated²³ from a relationship of type:- $K = A_{\text{product}}/A_{\text{reactant}}$. Also the ΔG thermodynamic parameter is calculated from a standard equation of the type, $\Delta G = -RT \ln K$. A careful examination of Table (4) reveals that changing the concentrations of Schiff base in ethanol, acetone, DCM and 1,2-DCE solvents are accompanied by changing both the values of equilibrium constants and ΔG of the tautomerism reactions in Schiff bases.

This means that increasing the concentrations of Schiff bases resulted to a noticeable variation in the values of equilibrium constants, and is highly expected. This can be interpreted by the following explanation, as the concentration of solute increases, the intermolecular distances between Schiff bases are decreased. Hence the intermolecular attractions or repulsions between similar solute molecules are varied. The last are accompanied by a greater increasing the stability of either enol or keto tautomer and the equilibrium constant values are shifted in the directions of positive and negative sense. The last are agreed well with experimental findings collected in Table(4), which shows an equilibrium constant values of either lower than unity or greater than one's. The former values are accompanied by the appearance of positive values of ΔG thermodynamic parameters or it is a nonspontaneous thermodynamic tautomerism process. On the contrary to that, the negative sign of ΔG thermodynamic function means a spontaneous tautomerism process. The influence of concentrations on tautomerism process are agreed strongly with keto \rightleftharpoons enol of acetyl acetone²² in solvents CCl_4 , CHCl_3 , CH_2Cl_2 and $\text{HCON}(\text{CH}_3)_2$. Finally, Schiff base (6) shows a difficult tautomerism reactions in acetone, DCM and 1,2-DCE and an ease tautomerism reaction in ethanol, probably for its high polarity of the latter. In other word, this enol is highly stable in the first three solvents mentioned and has only one stable tautomer. Meanwhile, Schiff base (7) shows a tautomerism reaction in 1,2-DCE. This is only happen from the amine part of the molecule and resulted to the conversion¹⁸ of amine-imine to imine-enamine. Similar behavior can be adopted to Schiff base (8).

Tabel (4) Influenc of concentration on equilibrium constants K and ΔG of tautomerism reactions in Schiff bases and in different solvents at 298 K

Schiff Base No.	Conc. $\times 10^4$	Ethanol				Acetone				DCM				DCE			
		A ₁	A ₂	$K = \frac{A_2}{A_1}$	ΔG J.mole ⁻¹	A ₁	A ₂	$K = \frac{A_2}{A_1}$	ΔG J.mole ⁻¹	A ₁	A ₂	$K = \frac{A_2}{A_1}$	ΔG J.mole ⁻¹	A ₁	A ₂	$K = \frac{A_2}{A_1}$	ΔG J.mole ⁻¹
1	0.25	0.2	0.12	0.600	1265.6	0.43	0.32	0.744	732.6	0.39	0.42	1.065	-183.6	0.40	0.12	0.300	2982.9
	0.5	0.26	0.20	0.769	650.0	0.82	0.62	0.756	693.0	0.72	0.76	1.055	-133.9	0.52	0.16	0.285	3103.8
	1.0	0.34	0.22	0.647	1078.5	1.06	1.46	1.377	-792.6	1.33	1.47	1.103	-247.9	0.96	0.65	0.677	966.2
2	0.25	0.10	0.20	0.693	1717.3	0.22	0.19	0.863	363.2	0.25	0.40	1.60	-1164.5	0.10	0.15	1.500	-1004.5
	0.50	0.17	0.50	2.941	-2672.0	0.45	0.38	0.844	418.9	0.61	0.72	1.18	-410.8	0.20	0.12	0.600	1265.6
	1.0	1.09	0.87	0.798	558.5	1.04	0.85	0.817	499.8	1.12	1.20	1.07	-167.6	0.92	0.52	0.565	1413.6
3	0.25	0.048	0.096	2.000	-1717.3	0.29	0.32	1.103	-243.8	0.28	0.17	0.625	1263.3	0.42	0.44	1.047	-115.3
	0.50	0.544	0.217	0.398	2277.0	0.43	0.47	1.093	-220.4	0.77	0.65	0.844	419.7	0.84	0.64	0.761	673.7
	1.0	0.840	0.352	0.419	2154.9	0.89	1.04	1.168	-385.9	1.18	1.14	0.966	85.4	1.36	1.34	0.985	36.7
4	0.25	0.37	0.150	0.405	2236.9	0.32	0.40	1.250	-552.9	0.62	0.54	0.870	342.3	0.11	0.14	1.272	-597.5
	0.50	1.13	0.336	0.297	3004.9	0.67	0.75	1.119	-279.5	0.96	0.66	0.687	928.3	0.16	0.69	4.312	-3621.0
	1.0	1.144	0.470	0.410	2203.9	1.5	1.4	0.933	170.9	1.16	1.78	1.534	-1060.8	0.12	0.56	4.666	-3816.5
5	0.25	0.68	0.28	0.411	2198.3	0.29	0.25	0.862	367.9	0.75	0.46	0.613	1211.2	0.14	0.158	1.071	-170.9
	0.50	1.24	1.0	0.806	532.9	0.55	0.45	0.818	497.7	0.41	0.65	1.586	-1141.7	0.16	1.020	0.879	318.7
	1.0	1.72	1.08	0.627	1152.9	1.07	0.70	0.654	1052.0	0.94	1.10	1.170	-389.4	0.18	0.19	1.055	-134.0
6	0.25	0.58	0.94	1.62	-1196.3	0.368	-	-	-	0.80	-	-	-	0.50	-	-	-
	1.0	1.42	1.62	1.14	-326.5	0.787	-	-	-	1.36	-	-	-	0.80	-	-	-
	0.5	1.60	1.64	1.03	-61.2	0.897	-	-	-	2.0	-	-	-	1.10	-	-	-
7	0.25	-	-	-	-	1.012	-	-	-	0.36	-	-	-	0.80	0.52	0.65	1067.3
	0.50	-	-	-	-	1.12	-	-	-	0.96	-	-	-	0.20	0.12	0.60	1265.6
	1.0	-	-	-	-	1.28	-	-	-	1.39	-	-	-	0.11	0.60	5.45	-4208.0
8	0.25	0.15	0.192	1.28	-611.6	0.38	0.48	1.26	-578.8	0.82	0.8	0.925	61.17	0.38	0.24	0.631	1138.5
	0.50	0.236	1.096	4.64	-3804.5	0.84	1.16	1.38	-799.7	0.90	1.5	1.666	-1265.6	0.48	0.37	0.770	644.8
	1.0	0.512	0.22	0.43	2092.0	1.38	2.0	1.44	-919.3	1.9	0.9	0.473	1851.3	1.15	0.98	0.852	396.3

References

- 1-A.S.P. Azzouz , *Z . phys. Chem.*, 2002 ,**216** , 1053 .
- 2-A.A.Saeed A.W.A. Sultan , S.A.Selman and N.A.Abood, *Can.J.Spectrosc.* , 1983, **28** , 104 .
- 3- A.A.Saeed , M.N.Al-Zagoum and M.H. Watton , *Can.J.Spectrosc.* , 1980 ,**25** ,137.
- 4- A.A.Saeed , S.A.W.Othman , K.A.Al-Jhalil and A.T.Atto , *Can.J.Spectrosc.* , 1981 ,**26**, 138.
- 5- A.A.Saeed , N.A.Abood , N.A.Al-Mosoudi and G.T.Matti , *Can.J.Spectrosc.* , 1985 ,**30** ,142.
- 6- Ed.S.Patai , “ **The Chemistry of Carbon-Nitrogen Double Bond** ” 1970 ,John Wiley and Sons , New york ,149-180 .
- 7- A.A.Saeed , *J.Chem .Eng. Data* , 1984, **29** , 358 .
- 8-S.S.Othman , M.Sc Thesis , Mosul University , 1994.
- 9-A.S.P. Azzouz , K.A.Abdallah and Kh.I.Niemi , *Microchem.J.* 1991,**43** , 45.
- 10-M.Bissonette, H.Lrthanh and D.Vocelle , *Can.J.Chem.*,1984 ,**62**, 1459.
- 11-T.Takemura , P.K.Das , G.Hug and R.S.Becker , *J.Am.Chem.Soc.* , 1978 , **100** , 2626.
- 12-A.S.P.Azzouz and S.S.Othman , *J.Edu.Sci* , 2000 ,**45**,3.
- 13-S.K.Al-Dilami , J.C.Aumiller , R.H.Johnson and P.E.Blat2 , *Photo Chem. Photobiol.* , 1987 , **46**, 403.
- 14- A.S.P.Azzouz, A.A.A.Rahman and A.G.Taki , *J.Edu.Sci.* , 2003 ,**15**,1.
- 15- A.S.P.Azzouz, and S.M.Saleh , *J.Edu.Sci.* , 2000 ,**46**,51.
- 16-M.A.El-Bayoumi , M.El-Aassar and F.Anbdul-Halim , *J.Amer. Chem. Soc.* , 1971,**39**,586.
- 17-G.C.Pimental and A.L.Mcelellan, *The hydrogen bond* , 1960 , Freeman , W.H.San Francisco , P.169-195.
- 18-Ed.J.Zabicky , **The chemistry of carbonyl group** , 1970 , vol.2 , interscience , London
- 19-R.H.Tomsan , *Quart. Rev.* , 1956 ,**10**,27.
- 20-R.M.Silverstein and G.C.Bassler , **Spectrophotometric identification of Organic compounds** ,1967 2nd.ed. , John Wiley , New york , P.68.
- 21-P.sykes , **Aguidebook to mechanism in organic Chemistry** , 1963 , Longmans , London , P. 41-44.
- 22- C.Reichardt , **Solvents and Solvent Effect in Organic Chemistry** , 1988 , VCh.F.R. Germany , pp.92-93 , 407.
- 23- A.S.P. Azzouz and A.B.N.Al-Dabagh, *National J.Chem.* , 2007, **26** , pp. 295-304