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## A comparative study for the determination of pKa values of some new imines derived from N – formyl – pipyridine and other imines by potentiometric method

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### ABSTRACT

The project is concerned with the synthesis of a new five imines in a forms of syn or anti oxime and phenolic Schiff bases. They are derived from the mother compound the N-formyl pipyridine. Their structures are confirmed by the available physical means, namely UV, IR spectra and melting points. The pKa for these five imines with other eleven imines prepared from our earlier work using other 2–furfuryl aldehyde, 4- fluorobenzaldehyde, 4- hydroxylbenzaldehyde and benzil are evaluated by potentiometric method and compared together. The acid strengths of these sixteen acids at 293K are experimentally governed by two factors. First is the electro negativity of nitrogen atom of pipyridine ring, second the electron donation property of lone pair of electrons available on hetero nitrogen atom of ring mentioned.

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### INTRODUCTION

Schiff bases derived from aromatic amines and aromatic aldehyde had a wide variety of applications in many fields example biological, inorganic and analytical chemistry<sup>[1-5]</sup>. Oximes as another form of imines were used in industrial purposes as Lactam<sup>[6]</sup> formation as Nylon – 6 synthesis and analytical<sup>[7]</sup> reagent.

Experimentally and during the last few years, Azzouz<sup>[8-13]</sup> et al had compared a varieties of physical constants as kinetic and stability constants of 2-pyridine aldoxime<sup>[8]</sup> with some positive ions, the interactions of phenols with 2,3-butadione monoxims<sup>[9]</sup>, o-methoxy benzylidene-p-aminoaniline<sup>[10]</sup> and benzil mono benzylidene aniline<sup>[11]</sup>, the pKa values and thermodynamic kinetic stability<sup>[13]</sup> of benzaloximes. In all these studies, all physical constants mentioned and determined were found to depend on the structure of imines and

the temperature during measurements.

In our laboratory Al-Azzawi<sup>[12,14,15]</sup> and Al-Niemi<sup>[16-19]</sup> had used the potentiometric method for the determination of a pKa a varieties of weak acids imines as derived from benzaldehyde or its substituents and benzil. The same potentiometric method after doing some simplification for calculation of pKa was applied in this work for the determination of pKa for some acids imines from N-formyl pipyridine. Therefore, the lack of pKa values for a new five imines and their comparison with earlier l- Azzawi<sup>[12,14,15]</sup> and Al-Niemi<sup>[16-19]</sup> was prompted this work.

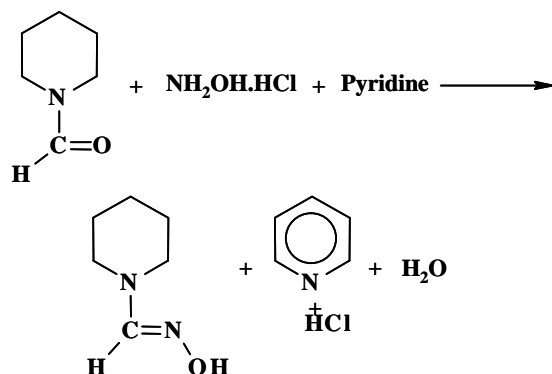
### EXPERIMENTAL

The following chemicals were of Fluka or BDH origin. They were used as supplied as, N-formyl pipyridine, 2-furfuryl aldehyde, 4-fluoro benzaldehyde,

4-hydroxy benzaldehyde, benzil, hydroxyl amine hydro-chloride, 2,3 or 4-aminophenols, sodium hydroxide and ethanol.

Syn N-formyl piperidine aldoxime (syn-NFPA) was prepared by standard method<sup>[20]</sup> as follows :-

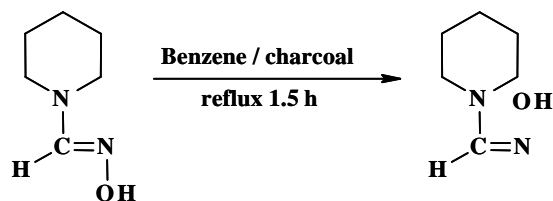
In 100ml round bottom flask attached to a reflux condenser, mix 3.4759 of hydroxyl amine hydrochloride with 5.45ml of N-formyl piperidine, 5ml of ethanol with 2ml of pyridine. The mixture was refluxed for 1.5 hour, cool the mixture. A white needle of oxime was separated and dried in air. The reaction of aldoxime is the following :-



Anti N-formyl piperidine aldoxime (anti-NFPA) was prepared by a standard method<sup>[21]</sup>.

In a 50ml round bottom flask attached with a reflux, add 20ml of dry benzene and about 1g of syn N-formyl piperidine aldoxime.

To the mixture about 0.5g of dry animal charcoal was added. The mixture was refluxed for about 1.5hour, cooled and filtered, A yellow powdered was collected and dried in air. The reaction of isomerisation of aldoxime is the following :-



### Preparation of Schiff bases

Piperidine N-formyl-p-amino phenol, piperidine N-formyl m-amino phenol, piperidine N-formyl-o-aminophenol were prepared according to a standard<sup>[21]</sup> procedure i.e by mixing equimolar amounts of aldehyde and the suitable aminophenol. Added about 5-10ml of ethanol to the mixture and cooled. A solid imi-

nes were separated and recrystallized from ethanol. TABLE 1 shows the compound number, abbreviation, nomenclature and structure of imine prepared.

TABLE 1

Comp. No.	Abbreviation	Nomenclature	Structure
1	syn NFPA	syn-N-formyl piperidine aldoxime	
2	anti NFPA	anti-N-formyl piperidine aldoxime	
3	PF <sub>4</sub> AP	Piperidine-N-formylpyridine-p-aminophenol	
4	PF <sub>3</sub> AP	Piperidine-N-formylpyridine-m-aminophenol	
5	PF <sub>2</sub> AP	Piperidine-N-formylpyridine-o-aminophenol	

For a sake of comparisons, other imines were taken from earlier works<sup>[12,17,18]</sup>.

There names and abbreviations were syn benzil monoxime (syn BMO), anti-benzil monoxime (anti BMO), syn furfural aldoxime (syn FAO), anti furfural aldoxime (anti FAO), syn 4-fluoro benzaloxime (syn 4FBAO) anti 4-fluoro-benzaloxime (anti 4FBAO) syn 4-hydroxy benzaloxime (syn 4HBAO), anti 4-hydroxy benzaloxime (anti 4-HBAO), benzil 2-hydroxy amino phenol (B<sub>2</sub>HAP), benzil 3-hydroxyamino phenol (B<sub>3</sub>HAP) and benzil 4-hydroxy amino phenol (B<sub>4</sub>HAP) 0.1M NaOH and HCl were prepared by standard<sup>[22]</sup> procedure. 0.01M of benzoic acid as a standard<sup>[23]</sup> for calibration of potentiometric method used in pKa determination of imines under study.

### Solution required

0.1M NaOH and HCl were prepared by standard<sup>[22]</sup> procedure. 0.01M of benzoic acid as standard<sup>[23]</sup> for calibration of potentiometric method used for pKa determination of imines under study.

## Full Paper

### Determination of pKa of imines

This required a calibration of pH meter used, by using a buffer solution of pH nine. For determination of pKa for any imine under study at any desired temperature, this needs the preparation of the following solutions :-

- 1  $10^{-2}$ M of imines.
- 2 0.1M NaOH.

Pipette 50ml of  $10^{-2}$ M of any acid imines and placed in a special titration cell containing double layers, for circulating water inside the cell. Water was pumped from any thermostat at any temperature range between (10-50)C. When the temperature of imine reached an equilibrium temperature, addition of 0.5ml successive quantities of 0.1M NaOH was done. The mixture was stirred with magnetic bar placed in side the cell after each addition, followed by measurement of pH after each addition. Titration was continued for about seven times, then followed by calculation of pKa from Handerson-Hasselbach equation of the form :-

$$pKa = pH + \log \frac{[HA]}{[A^-]}$$

### INSTRUMENTATION

- 1 Electrothermal melting point apparatus was used for measurement of melting points of imines.
- 2 FTIR spectrophotometer was used for measurement of IR spectra of solid imines by KBr disc method or in solution after dissolving imines in dry benzene.
- 3 A computerized double beam Shimadzu 1601 for measurement of UV spectra of imines solutions in solvent ethanol and dry benzene.
- 4 A memmert thermostat manufactured by Searle company model L200, for fixation the temperature of imines solution. Water is pumped out from thermostat to cell by using water pump.
- 5 A digital Philips pH meter model pw 9421 was used for measuring pH of solutions during potentiometric titration.

### RESULTS AND DISCUSSION

#### Identification of imines by physical method

TABLE 1 shows the compound No., nomenclature

abbreviation and structure of imines prepared in this work.

The following divisions of results are thought necessary

#### (A) Melting points

##### (a) Melting points of oximes

TABLE 2 showed that melting point of oxime syn NFPA was slightly greater from oxime anti NFPA. This comes in agreement with earlier work<sup>[21]</sup>. These were caused by the presence of intermolecular and intramolecular hydrogen bonding in oximes respectively and agreement with numerous studies<sup>[12,21]</sup>.

##### (b) Melting points of phenolic Schiff bases

TABLE 2 showed that melting points of these imines are increased in order of  $pF_4AP > pF_3AP > pF_2AP$  or their tendency for association followed the same increasing order.

#### (B) Chemical tests<sup>[24]</sup>

A ferric chloride test which is specific to oxime or phenol showed a positive test. This was in agreement with oximes or phenols shown in TABLE 2.

TABLE 2 : Chemical test and melting points of imines

Comp. No.	Ferric Chloride test	Melting Points C°
1	positive	251-249
2	positive	247-244
3	positive	181-180
4	positive	178-176
5	positive	122-121

#### (C) IR spectra<sup>[25]</sup>

TABLE 3 showed the IR spectra for solid imines and illustrate the following facts :-

- 1 The stretching vibration for OH group in oxime and phenol forms with different intensities and in a range (3340.85-3424.09) $cm^{-1}$ .
- 2 All imines showed the stretching azomethine linkage with different intensities in a range (1604.31-1670.37) $cm^{-1}$ .
- 3 A stretching absorption for CH group with different intensities and in a range (2919.08-2958.22) $cm^{-1}$ .
- 4 The stretching frequency for aromaticity was appeared with different intensities at wavenumber 1600 $cm^{-1}$ .

TABLE 3 : The IR spectra for solid imines

Comp. No.	Wavenumber $\text{cm}^{-1}$			
	OH	C=N	C-H	Ph
1	3424.09 (b)	1670.37 (m)	2949.1 (s)	-
2	3423.90 (m)	1635.97 (m)	2949.42 (m)	-
3	3340.85 (m)	1615.70 (s)	2919.08 (w)	1600 (w)
4	3362.50 (b)	1652.03 (vs)	2942.74 (m)	1600 (s)
5	3365.9 (s)	1604.31 (s)	2958.22 (w)	1600 (s)

In order to investigate the type of hydrogen bonding in imines under study, this encourage to repeat the IR spectra of imines in solution and in dry benzene. Accordingly a dilution method<sup>[25]</sup> was used in this respect with concentrations  $10^{-3}\text{M}$  and  $10^{-4}\text{M}$  of imines solutions. Typical example was the IR spectrum of syn NFPA before and after dilution to ratio 1:3 as in Figure 1.

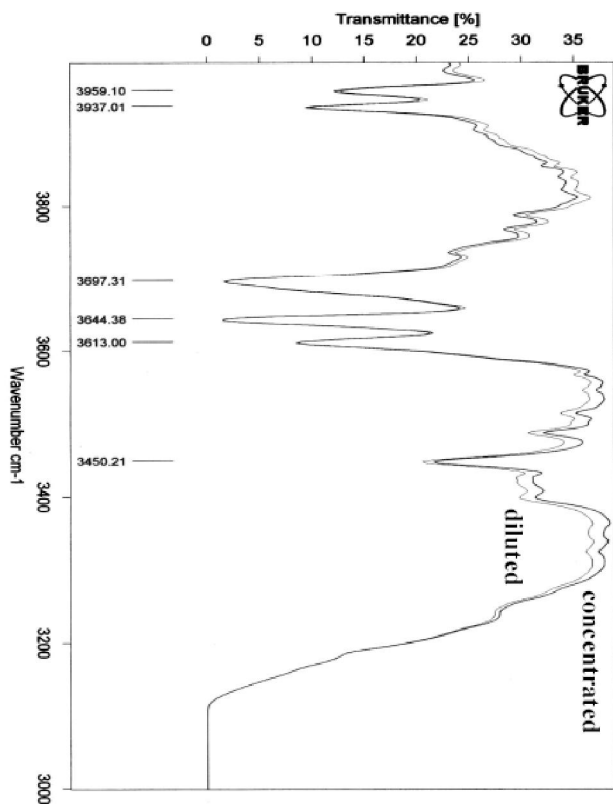


Figure 1 : IR spectrum of  $10^{-3}\text{M}$  and  $10^{-4}\text{M}$  of syn NFPA in benzene solvent

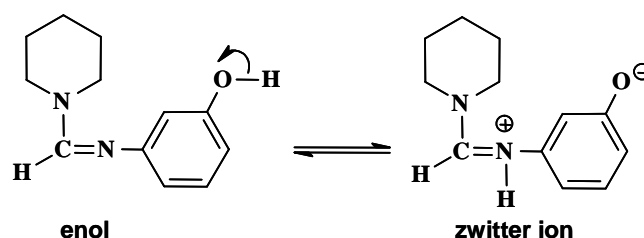
TABLE 4 showed the type of intra or inter molecu-

lar hydrogen bonding in imines.

TABLE 4 : The type of hydrogen bonding in imines

Comp. Abbrev.	Position of hydrogen bonding $\text{cm}^{-1}$	Type of H-bonding
Syn NFPA	3450.2	Inter
anti NFPA	3450.17	Intra
PF <sub>2</sub> AP	2450.32	Intra

Experimentally, it was difficult to determine the type of hydrogen bonding in imines PF<sub>4</sub>AP and PF<sub>3</sub>AP by IR method, due to the lack solubilities of imines mentioned in benzene. This was explained by their occurrence as zwitter ion forms as in the following chemical equation for PF<sub>3</sub>AP imines.



### Electronic spectra

This method<sup>[25]</sup> was used previously for the investigation of hydrogen bonding for imines in a forms of oximes and Schiff bases. Experimentally, the UV spectra of imines under study were measured in ethanol polar solvent and benzene non polar solvent. The type of transition for UV band is identified from the molar extension coefficient. The change in wavenumber  $\bar{\Delta\nu}$  for the hydrogen bond band was calculated from equation:-  $\bar{\Delta\nu} = \nu_{\text{ethanol}} - \nu_{\text{benzene}}$ . TABLE 5 shows a summary of electronic spectra for imines (1-5). This confirms the presences of hydrogen bonding of non specified type in imines 1, 2 and 5 with exclusions of imines 3 and 4 due to their lack of solubilities in benzene as mentioned before.

### A comparative pKa study for some acidic imines

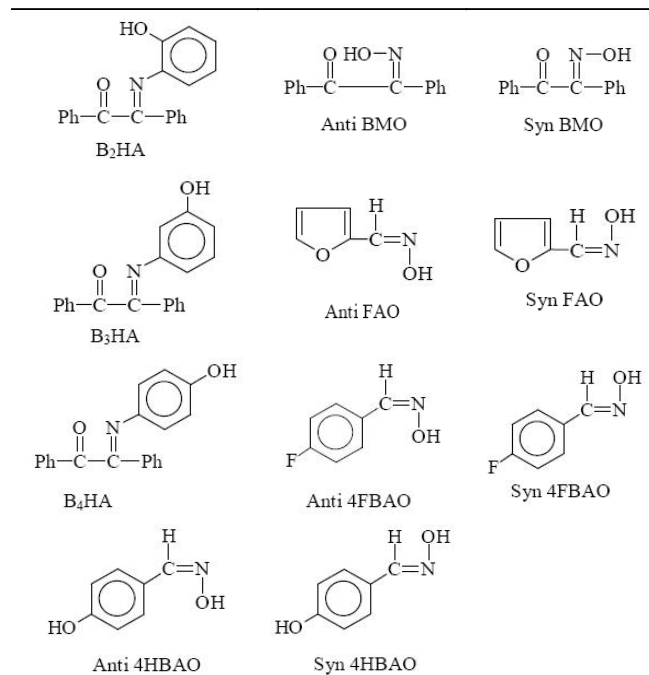
The study included a comparison of pKa of a five imines in this study in a forms of oximes and Schiff bases with other earlier studied<sup>[27,28]</sup>. The last had a similar structures to those given in our study. They were derived from benzil, fufuryl aldehyde, 4-hydroxy benzaldehyde and 4-fluoro benzaldehyde as in TABLE 6.

A potentiometric method was used for the evaluation of pKa for all acidic imines at 293K. Results obtained were collected in TABLE 7.

## Full Paper

TABLE 5 : The electronic spectra of imines in ethanol and benzene solvents

Comp. No.	Ethanol			Benzene			Type of transition	$\Delta\nu$ (cm)
	$\lambda_{\max}$ (nm)	A	$\epsilon_{\max}$ l.mol <sup>-1</sup> .cm <sup>-1</sup>	$\lambda_{\max}$ (nm)	A	$\epsilon_{\max}$ l.mol <sup>-1</sup> .cm <sup>-1</sup>		
1	282	0.061	61	316	0.027	27	n→π*	+3815.42
2	280	0.118	118	284	0.271	271	n→π*	+503.025
3	298	0.549	5490					
4	506	0.187	1870			Not soluble		
5	432	0.537	5370	416	0.686	6860	π→π*	-890.311

TABLE 6 : The structures and symbols of imines from earlier works<sup>[27,28]</sup>

In this paper all the azomethine linkage of imines were attached at nitrogen atoms of pipyridine rings, where as the other earlier works<sup>[27,28]</sup>, the stated linkages were attached to carbon atom. Actually the differences in electro negativities between nitrogen and carbon atoms at a position of attached of azomethine linkage, raised the curiosity of the worker to do such important comparison.

Nitrogen atom had two opposing effects, the first was the higher electro negativity when compared to carbon atom. The second was, the donor property of electrons. This was due to the presence of 2S lone pair of electrons in a non bonding orbital, which would increase the bond strength and order. According, the capability of ionization for acidic groups in acid was also decreased.

In determining the acidities of imines, this led to con-

TABLE 7 : A comparison of pKa for acidic imines at 293k

Compound Abbreviation	pKa
Syn NFPA	10.67
Syn BMO	10.71
Syn FAO	11.83
Syn 4FBAO	10.90
Syn 4HBAO	12.08
Anti NFPA	10.56
Anti BMO	11.60
Anti FAO	10.25
Anti 4FBAO	9.70
Anti 4HBAO	11.86
PF <sub>2</sub> AP	9.44
PF <sub>3</sub> AP	9.546
PF <sub>4</sub> AP	9.97
B <sub>2</sub> HA	11.73
B <sub>3</sub> HA	11.34
B <sub>4</sub> HA	11.90

sider pKa values of different imines as in TABLE 7. This Table showed the following observations:-

- 1 For the five syn oxime found in TABLE 7 the pKa of syn NFPA had a lower pKa value. This was due to the attachment of oxime group CH = N – OH of such molecule on the nitrogen of pipyridine ring. This was in contradiction with other four oxime attached to carbon atoms. The higher acidity of syn NFPA as compared with other oximes mean that the first effect is greater pronounced than second effect.
- 2 Oximes anti NFPA had higher acidity if compared with anti BMO and anti 4HBAO. This was in agreement last paragraph and in a disagreement with anti FAO and anti 4FBAO. Therefore, the net result in the latter oximes, the second effect was greater pronounced than first effect.
- 3 In the six phenolic Schiff bases, the acidities of PF<sub>2</sub>AP, PF<sub>3</sub>AP and PF<sub>4</sub>AP were greater than B<sub>2</sub>HA,

B<sub>3</sub>HA and B<sub>4</sub>HA. This was in a good agreement with paragraph (1).

### CONCLUSION

When an acidic oxime group or phenols groups attached on any carbon atoms of acids were exchanged by nitrogen atoms of another acids, there would be a clear effect either in a direction of increasing acidity or decreasing acidity of imines.

### REFERENCES

- [1] Z.Cimerman, S.Milijanic, N.Galic; *Croatia Chemica Acta*, **73**(1), 81 (2010).
- [2] P.Singh, R.L.Goel, B.P.Singh; *J.Indian Chem.Soc.*, **52**, 958 (1975).
- [3] B.F.Perry, A.E.Beezer, R.J.Miles, B.W.Smith, J.Miller, M.G.Nascimento; *Microbois.*, **45**, 181 (1988).
- [4] A.Elmali, M.Kabak, Y.Elerman; *J.Mol.Struct.*, **477**, 151 (2000).
- [5] P.R.Patel, B.T.Thaker, S.Zele; *Indian J.Chem.*, **38A**, 563 (1999).
- [6] Toyo Rayoo Co.; *Lactams, Japan Appli.*, **14**, (1966); *Chem.Abst.*, **76**, 59481e (1972).
- [7] Z.Hdzbecher, L.Divis, M.Kral, L.Sucha, F.Vlacil; *Hand Book of Organic Reagents in Inorganic Analysis*, Ellis, Horwood Ltd., Chichester, 691-94 (1976).
- [8] A.S.P.Azzouz, K.A.Abdullah, Kh.I.Neemi; *Microchemical J.*, **43**, 54 (1991).
- [9] A.S.P.Azzouz, A.A.Siddieq, N.B.Sharif; *J.Edu.Sci.*, **22**(1), 1 (2009).
- [10] A.S.P.Azzouz, S.S.Othman, A.N.Al-Dabagh; *Nat.J. Chem.*, **36**, 782 (2009).
- [11] A.S.P.Azzouz; *Z.Phys.Chem.*, **216**, 1053 (2002).
- [12] A.S.P.Azzouz, N.A.Al-Azzawi; *J.Edu.Sci.*, **14**(4), 90 (2002).
- [13] A.S.P.Azzouz, S.S.Othman; *J.Edu.Sci.*, **48**, 32 (2001).
- [14] A.S.P.Azzouz, N.A.El-Azzawi; *J.Edu.Sci.*, **14**, 20 (2002).
- [15] A.S.P.Azzouz, N.A.El-Azzawi; *J.Edu.Sci.*, **16**, 93 (2004).
- [16] A.S.P.Azzouz, M.S.Saeed, Kh.I.Al-Niemi; *J.Edu. Sci.*, **17**, 16 (2005).
- [17] *Ibid*; *J.Edu.Sci.*, **17**(3), 29 (2005).
- [18] *Ibid*; *J.Edu.Sci.*, **18**(2), 1 (2006).
- [19] *Ibid*; *J.Edu.Sci.*, **18**(4), 1 (2006).
- [20] A.F.Vogel; *Text Book of Practical Organic Chemistry*, 4<sup>th</sup> Edition, Longman, (1978).
- [21] J.R.Majer, A.S.P.Azzouz; *J.Chem.Soc., Farad. Trans.*, **1**(79), 675 (1983).
- [22] A.I.Vogel, D.S.Lond; *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrument Analysis*, 3<sup>rd</sup> Edition, Longman, London, (1972).
- [23] A.Albert, E.P.Serjeant; *The Determination of Ionization Constant*, 3<sup>rd</sup> Edition, Chapman and Hill, London, (1984).
- [24] N.D.Chronic; *Identification of Organic Compounds*, John Wiley, London, (1963).
- [25] R.M.Silverstein, G.C.Bassler; *Spectrophotometric Identification of Organic Compounds*, 2<sup>nd</sup> Edition, John Wiley New York.
- [26] A.S.P.Azzouz, A.Rahman, A.G.Taki; *J.Edu.Sci.*, **15**(2), 1 (2003).
- [27] N.Al-Azzawi; *Ph.D Thesis*, Mosul University, Iraq, (1988).
- [28] Kh.I.Al-Niemi; *Ph.D Thesis*, Mosul University, Iraq, (1999).