



" New Schiff – Bases Prepared From Pyromellitic Dianhydride Via Its Hydrazone Derivative"

Jinan M. Abdulrasool

Emad T. Ali

Jumbad H. Tomma

Dept. of Chemistry / College of Education for pure science (Ibn Al- Haitham) /
University of Baghdad

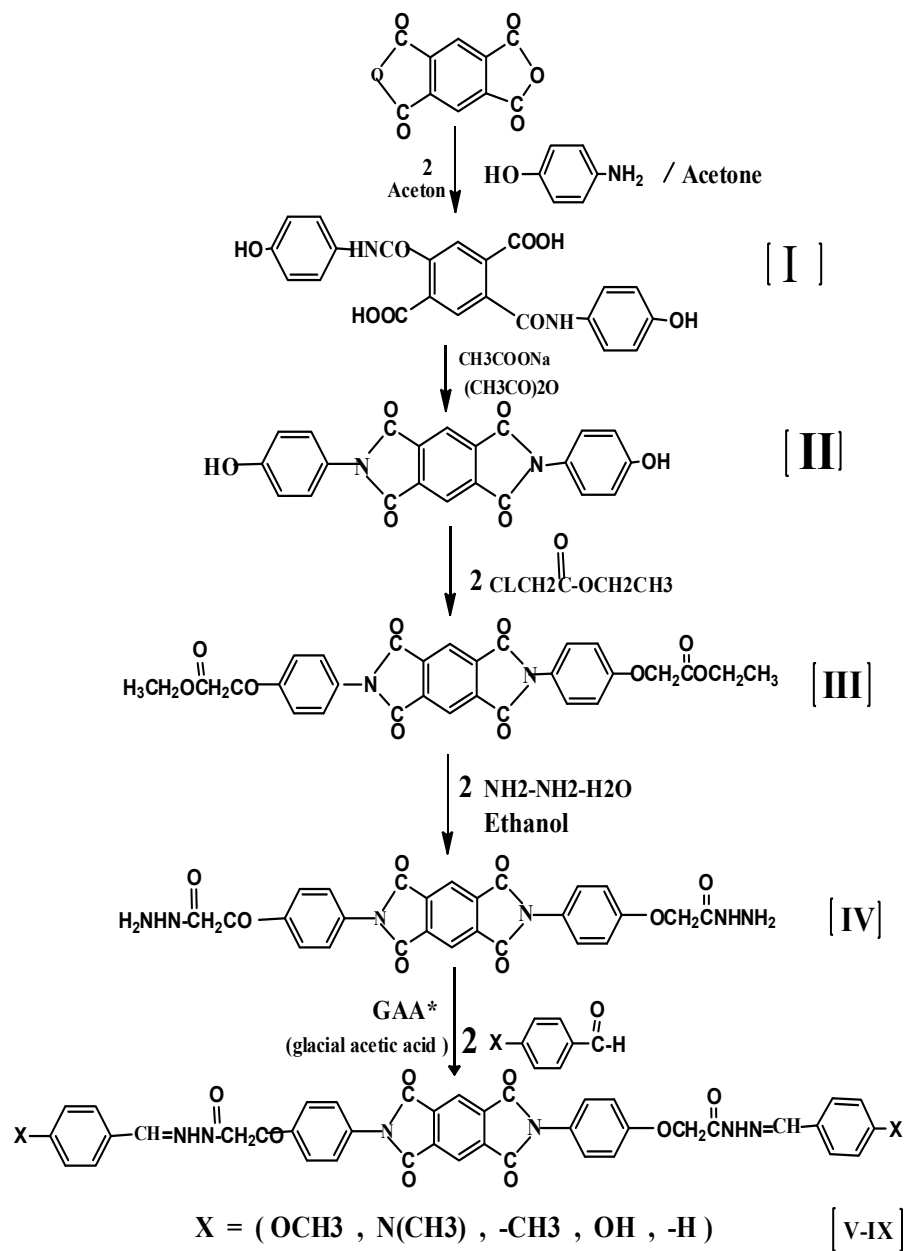
Received in:6/September/2015,Accepted in:12/October/2015

Abstract

N, N'- bis[4-hydroxy phenyl] pyromellitdiimide [II] was prepared from the corresponding diamic acid , which was transferred to its new ester by the reaction with chloroethyl acetate [III], [III] was used to prepare the novel hydrazone derivative [IV] , which was allowed to react with several aldehydes to yield the hydrazones [V – IX].

All the new compounds were synthesized , and characterized by their melting points ,FTIR,C,H,N analysis and ¹HNMR for some of them.

Key words: hydrazone , pyromellitic dianhydride , ester , Schiff – bases.



Scheme 1

Introduction

Pyromellitic diamic acids, imides are known to include an essential category in a wide range of applications such as, polymers, and are best known as segments of highly insulating polyimide dielectrics, they are though quite surprising that no attempt has been made to fabricate transistor from pyromellitimide derivatives, which have the simple aromatic ring (benzene) in the center and the tetra carboxylic diimides on both sides of the benzene ring. Thus, it is possible to screen a large number of imide side chains and investigate the impact of side chains on the mobility and environmental stability of pyromellitimide derivatives [1,2], intermediate compounds to a several reactions, biological activity ... etc.

On other hand, hydrazides, are known to have a great deal of their biological active organic compounds [3- 7] these hydrazide and their condensation products were state to possess a wide range of biological activities as well as antibacterial activity [3], HIV inhibitors [5] Pesticidal [6], antifungal [7]. These hydrazides can be prepared by different methods [8,9]; the most popular method is through their corresponding esters, by simple reaction between these esters and hydrazine hydrate [8].

Hydrazide and their different products show a wide range of biological activities, as well as, antibacterial activity [3], HIV inhibitors [5], pesticidal [6], and antifungal [7]. Some of them and their corresponding hydrazones are psychopharmacological agent such as monoamine oxidase inhibitor and serotonin antagonists [10].

Hydrazide – hydrazones compounds are not only intermediates but they are also very effective organic compounds in their own right. When they are used as intermediates, a very high number of derivatives can be synthesized and formed, that is because of the presence of the active hydrogen component of [- CONHN=CH-] azomethine (imine) group [11 – 14]. Hydrozone compounds as it was mentioned above, due to their azo methane group activities have taken an important role of many researchers in synthesizing a great numerous compounds of hydrazones by well – known hydrazinolysis method [15,16]. These compounds as well as their corresponding hydrazides found to have a wide applications in both health and medicine [17,18].

The aim of the following work is to synthesize, and characterize new hydrazide and their corresponding Schiff – bases, their characterization was done via melting points, FTIR, elemental analysis and ¹HNMR for some of them, Their biological activity was translated for further works.

Experimental

Material :- All the chemicals were supplied from fluka, Gcc, Merck and Aldrich Chemicals Co., and were used as received.

Techniques:- FTIR spectra were recorded on a FTIR – 600 FTIR spectrometer

Elemental microanalysis (C.H.N) were carried out by a (C.H.N) in the central lab at college of Education for ure science Ibn / Al-haitham. ¹HNMR spectra were carried out by company : bruker, model : ultra shield 300MHZ, origin : Switzerland and are reported in ppm(s), DMSO was used as a solvent with TMS as an internal standard uncorrected melting points were determined using Hot-stage (smart melting point [spm 10]) melting point apparatus.

Synthetic methods

Synthesis of N ,N'-Bis(4-hydroxyphenyl) pyromellitic diacid [I]

To a solution of pyromellitic dianhydride (0.218 gm , 0.001 mole) in (15 ml) acetone , a solution of 4-hydroxy aniline (0.218 gm , 0.002 mole) in (15 ml)acetone was added dropwise during one hour , the mixture was then left at room temperature with continuous stirring for 24 hrs , the yellowish product was then obtained and filtered off , washed and recrystallized from acetone to give the corresponding N ,N'-Bis(4-hydroxyphenyl) pyromellitic diacid [I] [19].

Yeild 90% , m.p >300° C. all physical properties are shown in table(1).

Synthesis of N, ,N'-Bis(4-hydroxyphenyl) pyromellitdiimide (II) [19]

A (0.436 gm 0.001 mole) of N, ,N'-Bis(4-hydroxyphenyl)pyromellitic diacid was placed in (50 ml) round bottom flask fitted with a condenser , a mixture of sodium acetate (0.164 gm , 0.002 mole) and acetic anhydride (3 ml) was added . The mixture was maintained between (80- 90 °C) by means of water – bath and stirred for one hour.The mixture was allowed to stirr for 24 hrs at room temperature. Then the mixture was poured on ice-water (400ml) and filtered off , recrystallized from acetone.

The physical data of N, ,N'-Bis(4-hydroxy phenyl) pyromellitdiimide are listed in table(1).

Synthesis of N,N'-Bis(4-methoxy acetate phenyl)pyromellitdiimide (III) [9]

[Ester]

In 100 ml round bottom flask , a (0.4 gm 0.001 mole) of compound (II) , (0.006mole) soduim acetate and (0.88 gm , 0.002 mole) chloro ethyl acetate were added , 10 ml of absolute ethanol was added , then the mixture was refluxed for 5 hrs , then the selvent was removed and the ester was washed with ethanol and recystallized from ethanol . the physical properties of the new ester are listed in table(1) (yeild70%).

Synthesis of the hydrazide(IV) [9]

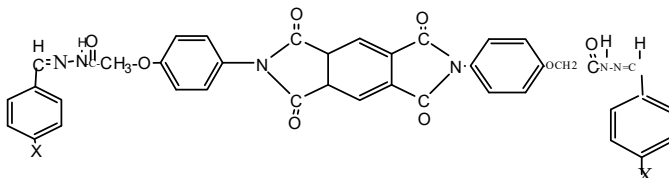
A mixture of (0.572 gm , 0.001 mole) of compound(III) and (0.072 gm , 0.002 mole) hydrazine hydrate was placed in 100 ml round bottom flask , 10 ml of absolute ethanol was added , the mixture was refluxed for 5hrs , then the solution was filtered off and the filtrate was concentrated , allowed to cool at room temperature , the precipitate was filter off , recrystallized from ethanol . (yield 68%) of the hydrazide . All physical propertie are listed in table(1).

The C,H,N analysis for prepared hydrazide are listed below

	C	H	N
Calculated%	57.35	3.67	15.44
Found	57.73	3.84	15.39

Synthesis of Schiff – bases: [V – IX]

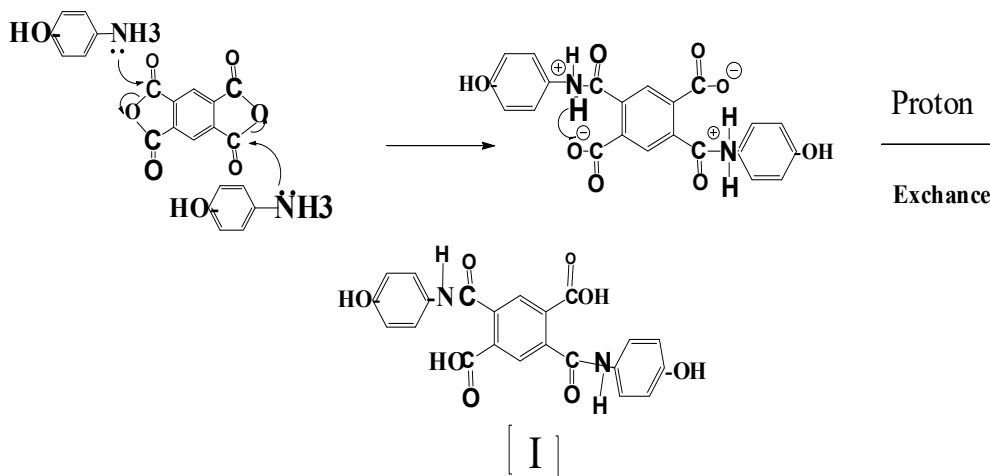
A solution of (0.002 mole) of certain aldehydes with three drops of glacial acetic acid in 10ml absolute ethanol was placed in 100 ml round bottom flask , (0.4 gm 0.001 mole) of hydrazid in 10 ml absolute ethanol was added . the mixture was allowed to reflux for 3-5 hrs , then the mixture was cooled to room temperature , filtered off and recrystallized from ethanol to get Schiff – bases [V – IX] . All physical properties are listed in table (1).



X=	-H	-CH ₃	-OCH ₃	-OH	-N(CH ₃) ₂
	V	VI	VII	VIII	IX

Results and discussion:

N, N' - Bis(4-hydroxy phenyl) pyromellitic acid (I) was synthesized by the reaction of one mole of PMDA. With two moles of 4 – hydroxyl aniline in acetone as a solvent [20]. The reaction mechanism involves nucleophilic addition , as follows scheme (2) .



Scheme 2

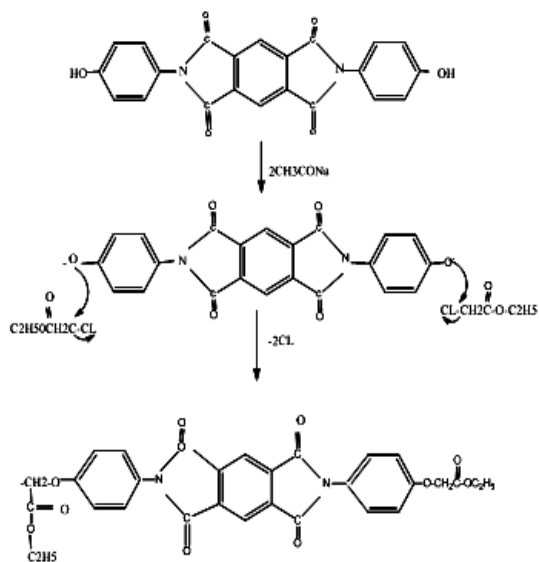
The characterization of N,N' - Bis(4- hydroxyphenyl) pyromellitic diacid was by its melting point . and FTIR , FTIR spectra show the disappearance of absorption bands due to NH₂ group and other characterizing peaks due to anhydride ring of 4-hydroxyl aniline and PMDA respectively , with appearance of new absorption stretching bands due to OH of carboxylic and phenolic groups at (3217 -3248) cm⁻¹ , C=O (carboxylic acid) stretching at(1705) cm⁻¹ , C=O (amid) stretching at (1643) cm⁻¹ . the FTIR data obtained support the proposed structure.

N,N' - Bis(4-hydroxy phenyl) pyromellitdiimide (II) was synthesized by the intra molecular cyclization reaction of the prepared diamic acid (I) using acetic anhydride – sodium acetate system [20] as a dehydrating agent at (80-90° C) . The mechanism of the cyclization involves nucleophilic substitution reaction This compound (II) was characterized by its melting point , FTIR spectroscopy [21].

The FTIR spectrum shows the disappearance of stretching absorption bands of NH , OH and C=O (amide and carboxylic acid moiety) groups of compound (I) , and the appearance of two peaks in the region (1718 - 1770) cm⁻¹ , which due to the stretching vibration of the C=O (cyclic imide) and , also two absorption bands at about (1132 cm⁻¹)and (713 cm⁻¹)symmetrical and asymmetrical C- N-C (cyclic) [21] , also the phenolic (OH) group appeared at (3323 cm⁻¹) , these FTIR data fit with the proposed compound (II).

N,N'-Bis -(4- ethyl acetoxy phenyl) pyromillidiimide (III) [9].

The phenolic group attached to the prepared diimide was converted to new ester by the reaction of compound (II) with ethylchloroacetate in a basic medium , by nucleophilic substitution reactions ,the ethylchloroacetate and the diimidic phenol form the new ester (III) , in which the phenoxide ion replaced the halogen of the ethyl chloro acetate to form the etheric ester , according to the following scheme .

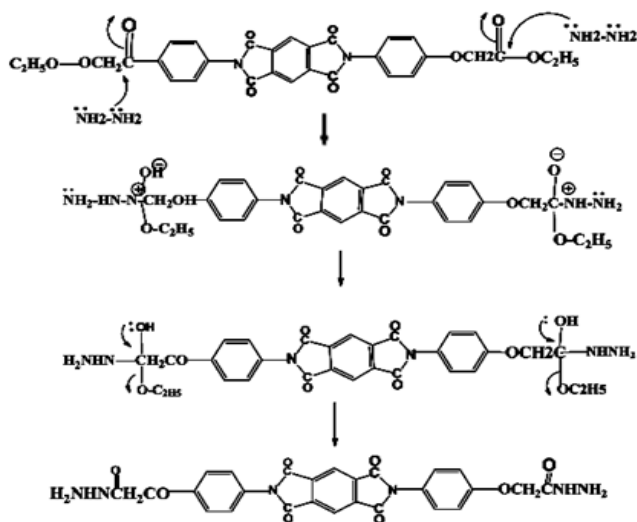


Scheme 3

The prepared ester was identified by its melting point, FTIR spectrum, which shows the disappearance of phenolic hydrogen (-OH) and the appearance of [-COO-] ester group at (1442 cm^{-1}), and the peak at (2927 cm^{-1}) due to (C-H) aliph. moiety. The following structure was proposed to the prepared ester.

Preparation of the hydrazide (IV) . [9]

The prepared ester was converted to the corresponding hydrazide by the reaction with hydrazine hydrate (80%) in ethanol as a solvent. The reaction between the hydrazine and the ester is a simple nucleophilic substitution reaction mechanism at the carbon of the carbonyl group, by which an unstable intermediate will be formed, which lose a good leaving group (ethoxide group) to form the hydrazide as a final product. as shown in the following mechanism. (schem 4).



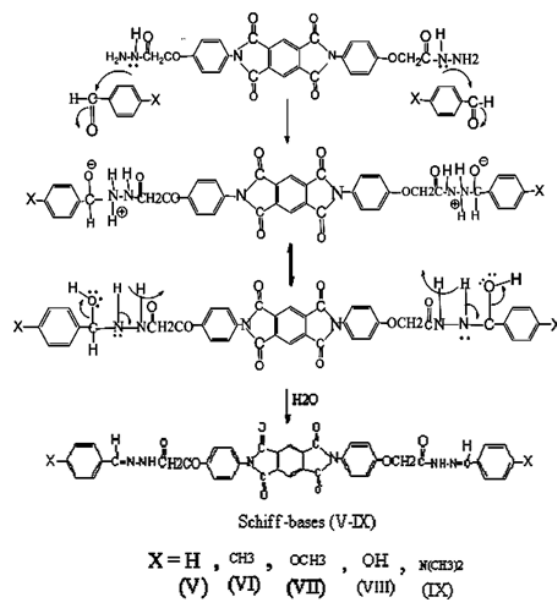
Scheme 4

The final product was identified by its crystal shape and its melting point, FTIR, C,H,N analysis and HNMR spectrum.

The FTIR results show a sharp peak at (3172 cm^{-1}) due the N-H stretching frequency, and at (3282 cm^{-1}) and (3340 cm^{-1}) due to NH_2 group, and a band at (1697 cm^{-1}) due to the C=O group, this band was observed to be in lower frequency compared to that found in C=O group of the ester due to the resonance phenomena in the hydrazide moiety which lead to reduce the double bond order of (C=O) group and then to reduce the force constant of the bond, so that its frequency will be, then, reduced too [21].

The HNMR data Figure (1) for the hydrazide (IV) shows the following signals:-
 Four protons of CH₂ groups at δ 8.425
 Ten protons of (aromatic ring protons) at δ 6.39 – 6.48
 Two protons of NH (group) at δ 2.5
 Four protons of NH₂ (groups) at δ 2.2
 These results (m.p , FTIR , C,H,N and HNMR) are fit with the proposed structure (IV).

Finally the formation of Schiff bases (V-IX) which were prepared by the reaction of one mole of the prepared hydrazide with two moles of certain aromatic aldehydes to form the new Schiff – bases in the acidic medium and follows the following mechanism . Schem (5) .



Scheme (5)

Schiff – bases were identified by their melting points FTIR ,C,H,N – analysis and HNMR for some of them.

The FTIR spectra , show the disappearance of C=O group of the aldehydes used , and the formation of C=N at frequencies ranges (1606 -1658) cm⁻¹ , also the C-N-C bond of the hydrazone moiety at (735 - 1130) cm⁻¹ , and finally the C=C aromatic bonds which appeared at (1435 - 1618) cm⁻¹ which may interfere with C=C groups.

The C,H,N- analysis shows the following results in the (table2).

The HNMR shows the following data [21] Figure (2).

Two protons of CH= N (imin protons) at δ 9.4
 Six proton of OCH₃ (groups) at δ 3.8
 Two protons of NH (groups) at δ 2.5
 Four protons of CH₂ (groups) at δ 8.515
 Eighteen protons of aromatic ring protons at δ 6.2 – 7.85

From the above data we can conclude that all the structure of the prepared Schiff – bases fit with the proposed one .

The formation of the new Schiff – bases derivatives which was affected by the presence of attracting or repulling groups attached to the phenyl moiety of the aldehydes was translated for further research works[22].

References

- 1-Sharma , P. ; Kukreja , P. ; Choudhary , V. and Narula , A . (2005) Curing and Thermal Behavior of Epoxy Resin in the Presence of Aromatic Imides – Amines , *Ind. J. of engine . and Mat. Sci.* , 12 : 259 – 264.
- 2-lee , S. ; Shin , G. ; Chi, J. ; Zin , W. ; Jung, J. ; Hahm , S. ; Ree , M. and Chang , T. (2006) Synthesis , Characterization and liquid – crystal Aligning properties of Novel aromatic polypyromellitimides bearing (n – alkyloxy) biphenyloxy side chains , *Polymer* , 47(19) : 6606 – 6621.
- 3-Rollas , S. ; Gulerman , N. and Erdeniz , H. (2000) Synthesis and Antimicrobial activity of some new hydrazones of 4-Fluorobenzoic acid hydrazide and 3-acetyl – 2 , 5 – disubstituted – 1,2,3 – oxadiazolines. *Farma Co* , 57 ; (2) : 171 – 174
- 4-Pavan , F. ; Maia , R. ; and Leite , S.(2010) , Thiosemi Carbazones , Semicarbazones , dithiocarbazate , and hydrazide / hydrazones : Anti – Mycobacterium tuberculosis activity and cytotoxicity . *Eur.J. Med Chem.* , 45 ; (5) : 1898 – 1905.
- 5-Marastoni , M. ; Baldisserotto , A. ; Trapelle , C. ; McDonald , J. ; Bortolotti , F. and Tomatis R. (2005) HIV protease inhibitor : synthesis and activity of N-aryl - N' - hydroxyalkyl hydrazide Pseudopeptides . *Eur – J. Med. Chem.* , 40 (5) ; 445 – 451.
- 6-Tabanca , N. ; Ali , A. and Bernier , UR.(2013) Biting deterrence and insecticidal activity of hydrazide – hydrazones and their corresponding 3- acetyl – b3 , 5-disubstituted – 2, 3 – dihydro – 1,3,4 – oxa-diozoles against *Aedes aegypti*. *Pest Manag Sci.* , 69 ;(6) 703 – 708.
- 7-Turan – Zitounti , G. ; Altintop , MD. ; Ozdemir , A. ; Demirci , F. ; Mohsen , UA. And Kaplancikli , ZA. (2012) Synthesis and Antifungal activity of new hydrazide derivatives. *J. Enzym Inhib. Med. chem.* ; 55 ; (3).
- 8-Aymen Nabeel Yaseen.(2005) ; M.Sc. Thesis submitted to College of Education for Pure Science , University of Mosul.
- 9-Karam , N. ; Tomma , J. and Al-dujalli , A. (2013) " Synthesis and Characterization of Heterocyclic compounds Derived from 4-hydrox and 4-amino Acetophenone . *Ibn Al-Haithum J. for pure and applied Sci – (36) 3* , 28 - 34.
- 10-Ashish , K. ; and JKM. (2012) A Highly Efficient Solvent free synthesis of hydrazides Using Grinding Technique , *An Int. Q.J. Heterocycles.* , 2 ; (4) :401 -404.
- 11-Rollas , S. ; and Kuckgzal , SG . (2007) Biological activities of hydrazone derivates. *Molecules.* , 12;(8) :1910 – 1939.
- 12-Kobayashi , M. ; Goda , M. ; and shimizu , S. (1999) Hydrazide synthesis : novel substrate specificity of amidase. *Biochem Biophys Res comman.* , 256 ; (2):415 – 418.

- 13-Hanumanagoud , H. ; and Basavaraja K.M. (2013) Synthesis and evaluation of some new oxadiazole and pyrazole derivatives incorporating benzofuran moiety . *Der pharma Chem.* , 5 ;(4) :87 – 98.
- 14-Mohammad , S. ; and Aymen , N. (2015) Synthesis and characterization of some new Hydrazides and their Derivatives . *Ibn Al-Haitham Journal for Pure and Applied Science* , (in press).
- 15-Zabivky , J. (1970) "the chemistry of Amides" John wiley and sons ltd.
- 16-Govindasami T. (2011) Synthesis , characterization and Antibacterial Activity of Biologically Important Vanillin related to hydrazone derivatives. *Int. J. Org . chem.* , 1 ; (9): 71-77.
- 17-Bernardino AMR. ; Gomes , AO. ; and charred Ks. (2006) Synthesis and Leishmanicidal Activities of 1-(4-X-phenyl)-N'-[(4-Y-phenyl)methelen]-1H-Parazole-4-Carbohyrazides. *Chem. Inform.* , 37 ; (27)
- 18-Turan-Zitouni G. ; Altintop , MD. ; Ozdemir A. ; Demirci F. ; Mohsen UA. ; and Kaplancikli ZA. (2013) Synthesis and Antifungal activity of new hydrazide derivatives. *J. Enzym Inhib.Med. chem.* , 28 ; (6) , 1211-1216 .
- 19-Ali , E. ; Aliawy , K. and Tomma , J. (2011) " Synthesis and Characterization of New Symmetrical pyromellitdiimide Derivatives and their Amic Acids " *Ibn Al-Haithum J. for Pure and Applied Science* , 24(3) :1-11.
- 20-Awad , W. ; and Ali , E. (1976) Synthesis of Some Pyromellillitic Acids , Pyromellitdiimides and Iso – imides" . *Iraqi J. of Chem.* (2), 88-94.
- 21-Silverstein , R.M. ; Webster , F. X. ; and Kiemle, D.J. (2005) ("Identification of Organic compounds") John Wiley and Sons , Inc. 7th , Eddition.
- 22-Zahmathesh , S. and Vakili , M. R. (2010) " Synthesis and Characterization of New Optically Active Poly(ethyl –L-lysinamides and poly(ethyl – L-(ysinimide)s , *J of Amino acids* , 1-6.