مجلة إبن الهيثم للعلوم الصرفة و التطبيقية المجلد 29 العدد (1) عام 2016
Ibn Al-Haitham Jour. for Pure & Appl. Sci. *Vol. 29 (1) 2016*

" New Schiff – Bases Prepared From Pyromellitic Dianhydride Via Its Hydrazide 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

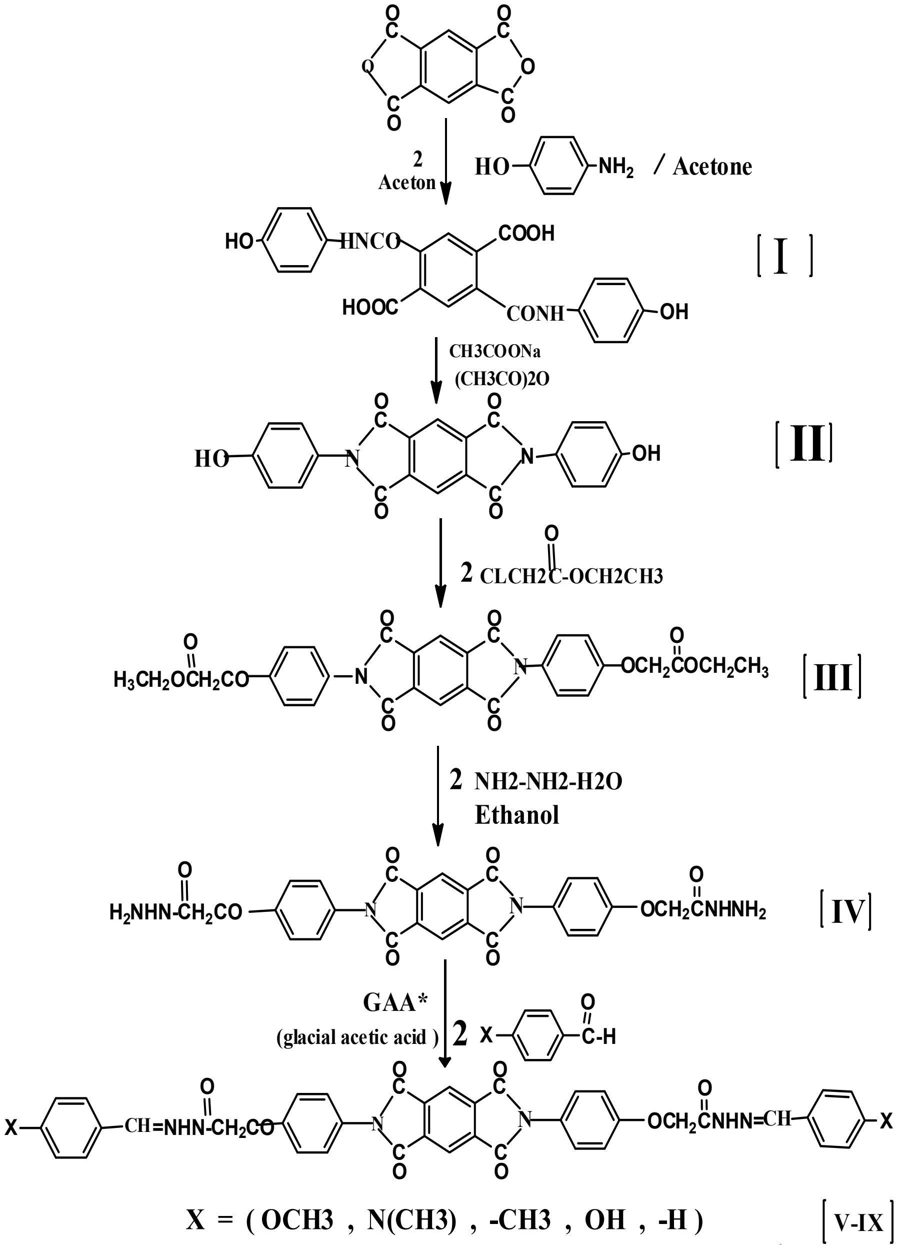
Received in:6/September/2015,Accepted in:12/October/2015

Abstract

N, N′- bis[4-hydroxy phenyl] pyromillitdiimide [II] was prepared from the corresponding diamic acid , which was transfered to its new ester by the reaction with chloroethyl acetate [III], [III] was used to prepare the novel hydrazide 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 ^{1}HNMR for some of them.

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


2
Aceton
HO–C6H4–NH2 / Acetone
[I]
CH3COONa
(CH3CO)2O
[II]
2 CLCH2C(=O)-OCH2CH3
[III]
2 NH2-NH2-H2O
Ethanol
[IV]
GAA*
(glacial acetic acid)
2 X–C6H4–C(=O)-H
X = (OCH3 , N(CH3) , -CH3 , OH , -H)
[V-IX]

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 quit surprising that no attempt have been made to fabricate transistor from pyromellitdiimide derivatives , which have the simple aromaticring(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 pyromellitdiimide derivatives [1,2] , inetermediate 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] , HIVinhibitors [5] Pesticidal [6] , antifangal [7] . These hydrazides can be prepared by different methods [8,9] ; the most popular method is through their correspounding 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 ^{1}HNMR 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 centeral lab at college of Education for ure science Ibn / Al-haitham . ^{1}HNMR 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 (stmart melting point [spm 10]) melting point apparatus.

Synthetic methods

Synthesis of N ,N′-Bis(4-hydroxyphenyl) pyromellitamic 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 recrystalized from acetone to give the corresponding N ,N′-Bis(4-hydroxyphenyl) pyromellitamic diacid [I] [19] .
Yeild 90% , m.p >300^o 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)pyromellitamic 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 ^{o}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 , recrystalized 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)pryromellitdiimide (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 recystalized from ethanol . the physical properties of the new ester are listed in table(1) (yeild70%).

Synthessis of the hydrazide(IV) [9]

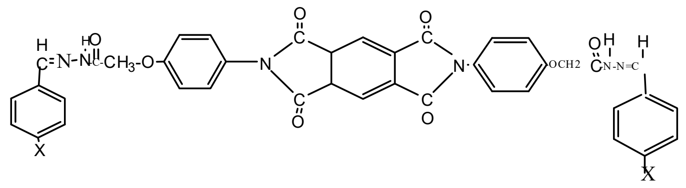
A mixture of (0.572 gm , 0.001 mole) of compound(III) and (0.072 gm , 0.002 mole) hydrazine hydrate was placed in 100 ml round bottom flask , 10 ml of absolute ethanol was added , the mixture was refluxed for 5hrs , then the solution was filtered off and the filterate was concentrated , allowed to cool 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]

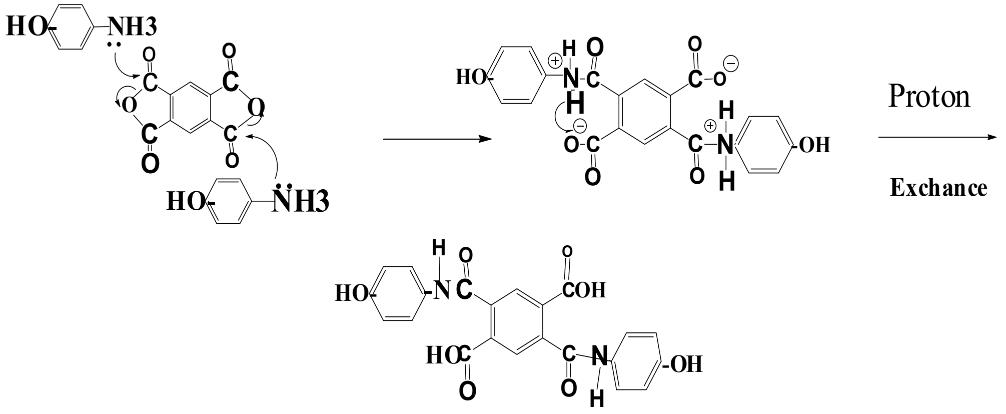
A solution of (0.002 mole) of certain aldehydes with three drops of glacial acetic acid in 10ml absolute ethanol was placed in 100 ml round bottom flask , (0.4 gm 0.001 mole) of hydrazid in 10 ml absolute ethanol was added . the mixture was allowed to reflux for 3-5 hrs , then the mixture was cooled 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	-CH3	-OCH3	-OH	-N(CH3)2
	V	VI	VII	VIII	IX

Results and discussion:

N, N′ - Bis(4-hydroxy phenyl) pyromellitamic diacid (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 nucloophilic addition , as follows scheme (2) .



[I]

Scheme 2

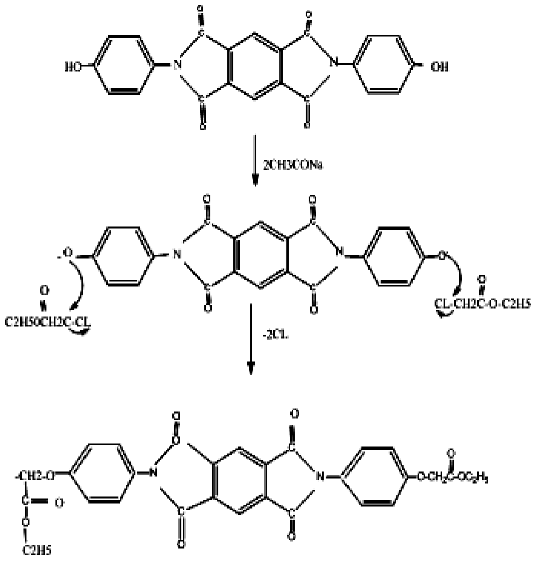
The characterization of N,N′ - Bis(4- hydroxyphenyl) pyromellitamic diacid was by its melting point . and FTIR , FTIR spectra show the disappearance of absorption bands due to NH_2 group and other characterizing peaks due to anhydride ring of 4-hydroxyl aniline and PMDA respecivly , with appearance of 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^o C) . The mechanism of the cyclization involves neucleophilic 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 subsititution reactions ,the etheylcholoroacetate 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 .

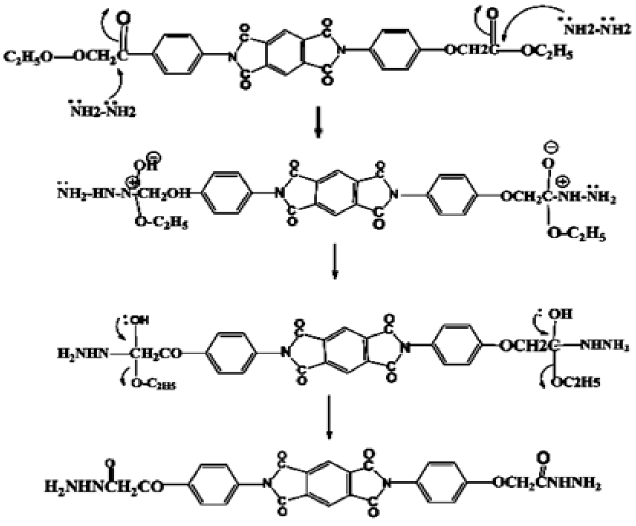

HO
OH
2CH3CONa
C2H5OCH2C-CL
CL-CH2C-O-C2H5
-2CL
-CH2-O
C2H5
O-CH$_2$C-OC$_2$H$_5$

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 prerpared ester was converted to the correspounding 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 subsititution reaction mehanism 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) .



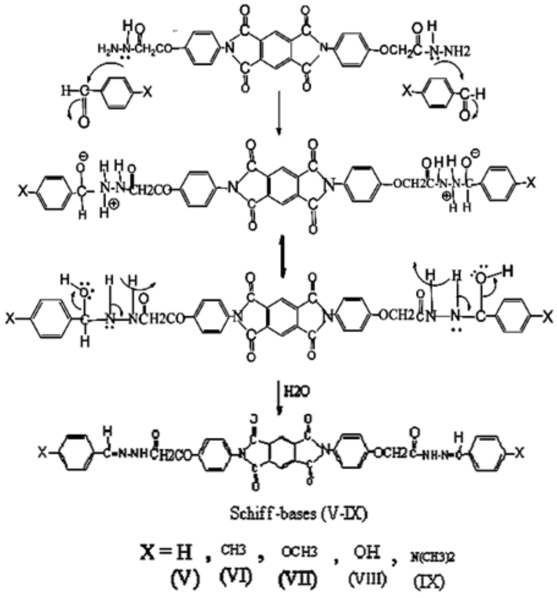
Scheme 4

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 setrtching freqancy , and at (3282 cm^{-1}) and (3340 cm^{-1}) due to NH_2 group,and a band at (1697cm^{-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 CH_2 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 NH_2 (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 certai aromatic aldehydes to form the new Schiff – bases in the acidic medium and follows the following mechanism . Schem (5) .



Scheme (5)

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

The FTIR spectra , show the diappearnace 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 OCH_3 (groups) at δ 3.8
Two protons of NH (groups) at δ 2.5
Four protons of CH_2 (groups) at δ 8.515
Eighteen protons of aromaticring 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 aldehdes 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 Aligining 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-Fluorobenzioe 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′ - hydroxyalky 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 – oxxa-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 Antifangal 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 Kuckgzel , 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 Sceince , (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.

Table (1):The physical properties of the prepared compounds

Compound No.	The name of the compound	Color	Melting Point °C	yield	Recrystalization solvent
I	[2,5-bis(4-hydroxy phenyl carbomoyl)terphthalic acid]	yellow	300>	90%	acetone
II	[2,6-bis(4-hydroxy phenyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone	deep yellow	300>	80%	acetone
III	[Ethyl 2-(4-(6-4-((ethoxy carbonyloxy))methyl)phenyl)-1,3,5,7,tetraoxo-6,7-dihydro pyrrolo[3,4-f]isoindole(-2(1H,3H,5H)-yl)phenoxy acetate]	Pale light	300>	70%	ethanol
IV	[4-(6-(4-(2-hydrazinyl-2-oxoethoxy phenyl)-1,3,5,7-tetraoxo-6,7-dihydro pyrrolo[3,4-f]isoindole 2(H,3H,5H)-yl)benzo hydrazide]	orange	(187-189)	75%	ethanol
V	[2,2'-(4,4'-(1,3,5,7-tetreoxo pyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl)bis(4,1-phenylene)bis(oxy)bis(N'-benzylideneaceto hydrazide]	grey	(190-192)	76%	ethanol
VI	[2,2'-(4,4'-(1,3,5,7-tetreoxo pyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl)bis(4,1-phenylene)bis(oxy)bis(N'-(4-methyl)benzylideneaceto hydrazide]	yellowish-grey	(207-209)	76%	benzene
VII	[2,2'-(4,4'-(1,3,5,7-tetreoxo pyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl)bis(4,1-phenylene)bis(oxy)bis(N'-(4-methoxy)benzylideneaceto hydrazide]	deep yellow	(238-240)	76%	benzene
VIII	[2,2'-(4,4'-(1,3,5,7-tetreoxo pyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl)bis(4,1-phenylene)bis(oxy)bis(N'-(4-hydroxy)benzylideneaceto hydrazide]	yellowish-red	>>300	70%	ethanol
IX	[2,2'-(4,4'-(1,3,5,7-tetreoxo pyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl)bis(4,1-phenylene)bis(oxy)bis(N'-(4-amino di methy)benzylideneaceto hydrazide]	deep orange	250	70%	ethanol

Table (2): The C, H, N analysis of the prepared Schiff - bases

Compound No.	Molecular formula	C %		H %	N %
(V) R =H	$C_{40}H_{28}N_6O_8$	Cal. found	66.66 66.18	3.88 3.90	11.66 11.56
(VI) R = CH3	$C_{42}H_{32}N_6O_8$	Cal. found	67.37 67.03	4.27 4.22	11.22 11.10
(VII) R= OCH3	$C_{42}H_{32}N_6O_{10}$	Cal. found	64.61 64.33	4.10 4.59	10.76 10.61
(VIII) R= OH	$C_{40}H_{28}N_6O_{10}$	Cal. found	63.82 63.69	3.72 3.77	11.17 10.98
IX) R = (N(CH3)2	$C_{44}H_{38}N_8O_8$	Cal. found	65.50 66.08	4.71 4.67	13.89 13.78

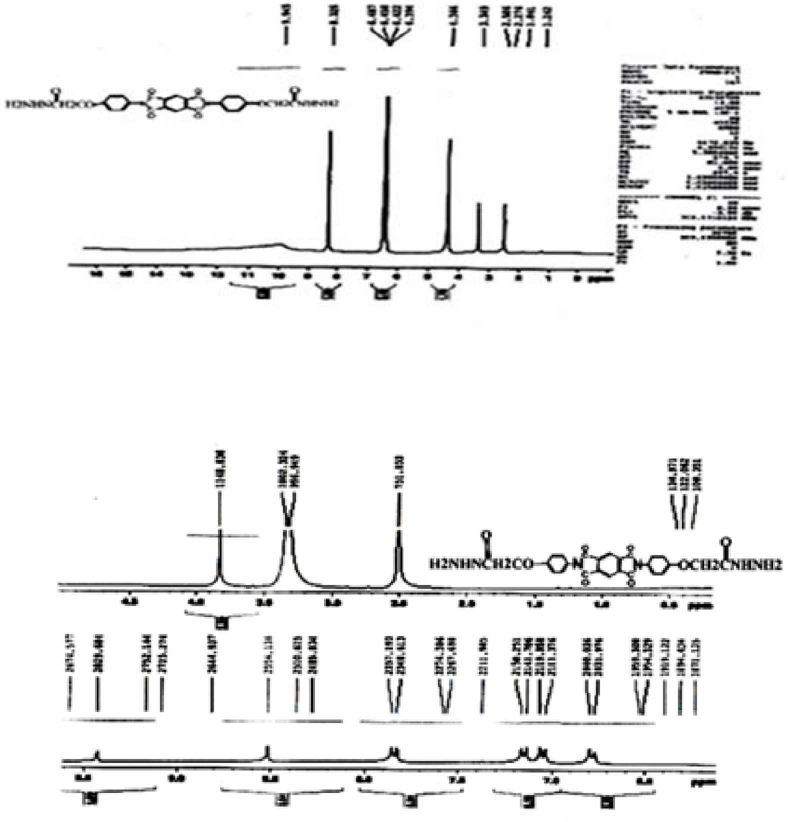


Figure (1)

HNMR for the hydrazide compound[IV]

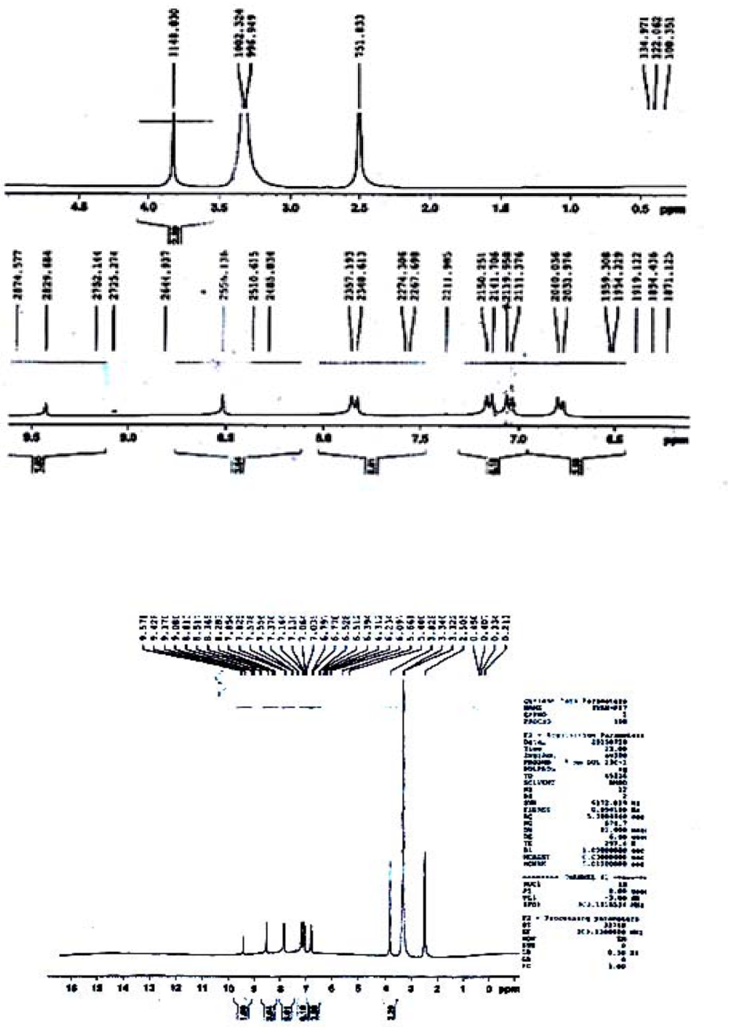


Figure (2)

HNMR for the compound [VII]

تحضير قواعد شف جديدة مشتقة من انهدريد البايروملتيك ومن خلال مشتقات الهيدرازايد

جنان محسن عبدالرسول
عماد تقي علي
جمبد هرمز توما

قسم الكيمياء / كلية التربية للعلوم الصرفة (ابن الهيثم) / جامعة بغداد

استلم في: 6/أيلول/2015 ،قبل في:12/تشرين الأول/2015

الخلاصة

تم تحضير N′,N - ثنائي [4- هيدروكسي فينيل] بايروملتيا داي ايميد (II) من الحوامض المقابله له (ثنائي اميك) , اذ تم تحويله الى الاستر الجديد من خلال تفاعله مع اثيل كلوروسيتيت (III) . وهذا الاستر الاخير(III) استعمل تحضير الهيدرازيد الجديد (IV) بمفاعلته مع الهايدرازين المائي بوجود الكحول كمذيب , تم مفاعله مجموعة من الديهايدات اوروماتية مع الهيدرازيد المحضر لتحضير قواعد شف الجديدة (V-IX).
شخصت جميع المركبات المحضرة الجديدة من خلال درجات الانصهار , والاشعة تحت الحمراء وتحليل العناصر الدقيق والرنين النووي المغناطيسي للبعض منها اذ وجد من نتائج التحليل تطابق التراكيب المقترحة.

الكلمات المفتاحية: الهيدرازايد , انهدريد البايروملتياميك , الاسترات , وقواعد شف.