Novel Schiff Bases Derived From Pyromellitic Dianhydride

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Abstract

The new Schiff bases derived from pyromellitic dianhydride were synthesized by several steps reaction . A symmetrical diamic acide [I $]_{a-c}$ were synthesized by the reaction of pyromellitic dianhydride with some aromatic amines (containing electron withdrawing , repulling groups) in dry acetone.

In the second step the diacids were converted to their corresponding diimide [II]a-c using acetic anhydride and sodium acetate system as a dehydrating agent, via the intra molecular cyclization steps of amic acids.

The third step was to synthesize the hydrazone derivatives from the reaction of diimides , with 80 % hydrazine hydrate at (50-60)C° .

These hydrazone derivatives were allowed to react with several aromatic aldehydes to form new Schiff bases via step four at a temperature near by (50)C° .

All the novel compounds and their structures have been ascertained by their melting points , mixed melting points , C .H . N analysis , FTIR spectroscopy and HNMR for some of them .

Key Words : pyromellitic dianhydride , imides , Schiff Bases

Introduction

Due to the two anhydride functional groups present on pyromellitic dianhydride molecule, and due to its high reactivity towards many nucleophiles molecule, pyromellitic dianhydride has wide importance in many fields of synthesis and applications . Also because of the highest stability of whole derivatives that derived from it . It takes an attention to many chemists to work with it ,especially in the synthesis of monomers and preparation of a variety of thermoplastic polymers as polyimides , epoxy resin etc ….. .

Moreover , it is useful in preparation of high preformance coating ,that have been widely used in many fields in our life, since it has an excellent thermal stability and good mechanical properties [I].

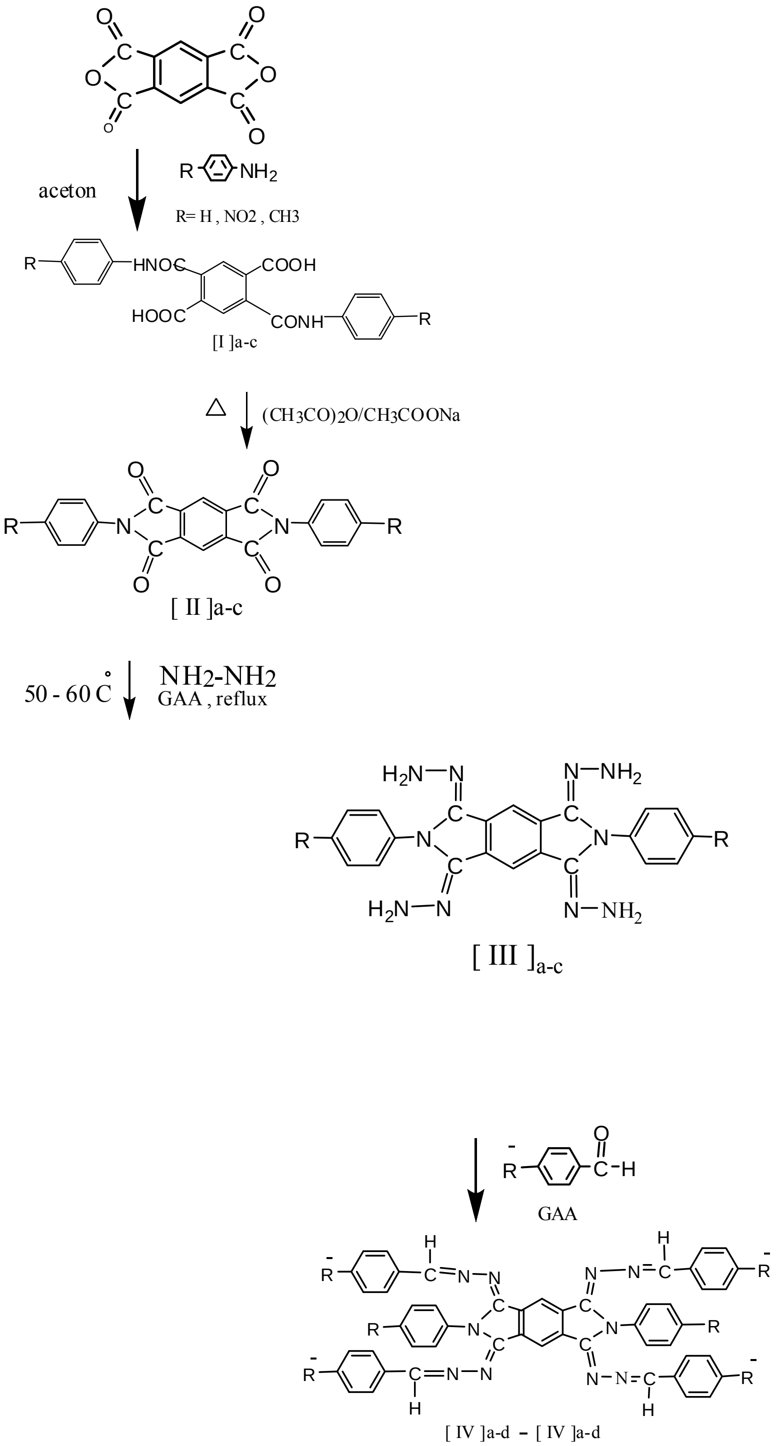
Imides show a very good mechanical properties , thermal stability and they are used as class of bioactive molecules that possess a wide range of pharmacological activity such as androgen receptor antagonistic ,anti-inflammatory, anxioulytic , antiviral , antibacterial , and antitumor properties. Besides that , they can be considered as a precursors with application in organic synthesis , polymer synthesis ,and development of the new materials and molecular electronic devises [2 ,3] .

One of the important functional groups present on imide molecules is the carbonyl groups , which can be readily reacted with hydrazine, to form the hydrazone derivatives (imine) , which have also a wide applications in organic synthesis to produce a very large types of reaction due to its high neucleophility due to the pair of electron on nitrogen atoms. [4 ,5] .

Schiff bases containing ring system have been used in to a wide variety of their apeutically interesting drugs condiclates ineluding anti-septic analysis , anti-biotic, anti-allergic, anti- depresent , anti- microbial, anti-tumor , and anti-hypertensive [3] .

Schiff bases also take an important roll and attraction at the both organic and inorganic chemists ,due to their importance in a variety of applications and studies . [6 ,7] .

The aim of the present work is to synthesize of a novel pyromellitic imides containing a hydrazone moiety and to synthesis of novel Schiff bases derived from them as shown in the following scheme (scheme 1).



$R = H , 4 - NO_2 , 4 - CH_3$

$\bar{R} = Cl , Br , OH , NO_2$

Scheme No.(1)

Experimental

Materials

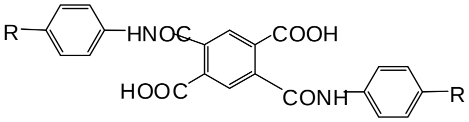
All chemical were supplied from Fulka ,Merch ,and Aldrich Chemicals Co .and were used as received .

Techniques

FT IR spectra were recorded by using KBr discs on a schimadzu IR prestige – 21 FT IR spectroscopy . uncorrected melting points were determined using (Stuart/melting point /smp30/) , C . H . N analysis were carried out by (Elemental Analyzer CHNS/O Euro EA) at the central lab. at College of Education for Pure Science –Ibn -Alhaitham- University of Baghdad .IRAQ

^{1}HNMR data were carried out by Company Bruker ,Model :Ultra Shield 300HZ .University of Jordan .

Synthesis of N ,N- (diaryl) pyromellitamic diacids [I]$_{a-c}$ [8]

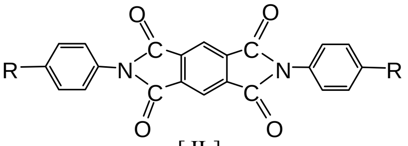


[I]$_{a-c}$

R = (a) H , (b) 4 - NO_2 , (c) 4 - CH_3

To a solution of pyromellitic dianhydride (0 .218g , 0 .001mole) in (15mL) acetone , a solution of amine (0 .002mole) in (15mL) acetone was added dropwise during one hour , the mixture was then left at room temperature with continues stirring for (24hours) ,the product was then filtered off and recrystallized from acetone or chloroform , the physical properties of the diamic acids are listed in Table (1) .

Synthesis of N,N- (diaryl) Pyromellitdiimide [II]$_{a-c}$ [8]



[II]$_{a-c}$

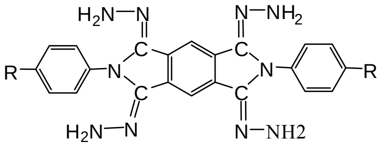
R = (a) H , (b) 4 - NO_2 , (c) 4 - CH_3

(0.01mole) of N,N-pyromellitamic diacid was placed in (100mL) round bottom flask , a mixture of anhydrous sodium acetate (0 .02mole) and acetic anhydride (5mL) was added . the mixture was maintained between (80 - 90)C° by means of water-bath and stirred for ½hour. The mixture was then allowed to stir for one hour at room temperature .The mixture was poured on to ice water (400mL) , filtered , washed with distilled water. The physical properties of these compounds are listed in (Table 1) .

Reaction of pyromellit diimide with hydrazine to form the hydrazone derivatives (imines)) (III)$_{a-c}$ [9]

A(0 .01mole) of the pyromellitdiimide was placed in a (100mL) round bottom flask , 5 drops of glacial acetic acid was added , and (0.04mole) of 80% hydrazine was added during ½ hour with continuous stirring , the mixture was allowed to react for further 6 hour at (50-60)C° using water bath .Then the mixture was dropped in to (100mL) water . A coloured precipitate was filtered, recrystallized from a suitable solvents .

All physical properties of the prepared hydrazones $(III)_{a-c}$ are listed in (Table 1).



$[III]_{a-c}$

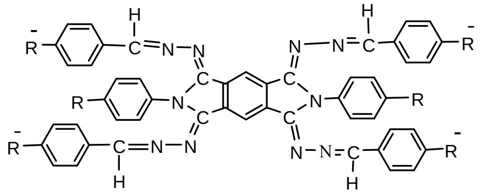
R = (a) H , (b) 4 - NO_2 , (c) 4 - CH_3

1- Elemental Analysis

Elemental analysis of compound $[III]_{a-c}$ are listed in Table No. (2) .

Synthesis of Schiff bases $[IV - VI]_{a-d}$ [9]

A mixture of (0 .04mole) of a selective aromatic aldehydes in 10mL ethanol ,and 5 drops of glacial acid acetic acid was added to(0 .01mole) of compound $(III)_{a-c}$ hydrazone with continuous stirring during ½ hour ,the mixture was left with stirring at 80C° for 4-5 hours , after the reaction has been completed , the yellowish to orange precipitated was filtered off , washed with ethanol and the physical data were given in Table (1) .



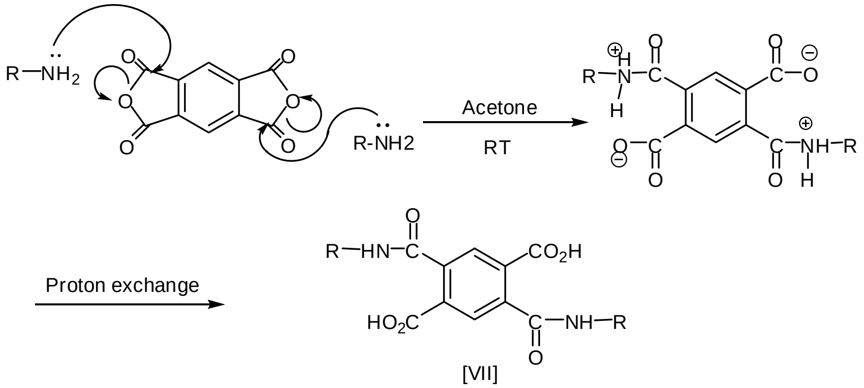
[IV]a-d – [IV]a-d

R = H , 4 - NO_2 , 4 - CH_3

$\bar{R}$ = Cl , Br , OH , NO_2

Results and Discussion

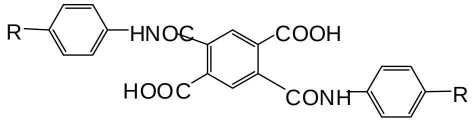
The diamic acid [1]were synthesized by the reaction of (one mole) pyromellitic dianhydried with two moles of certain aromatic amine in the presence of dry acetone as a solvent at room temperature, the mechanism involved neucleophilic addition reaction [7] as follows : in scheme (2)



[VII]

Scheme No.(2)

The structures of the prepared diamic acids were detected from their melting points, FTIR spectroscopy , which showed the disappearance of the absorption band due to NH_2 of the aromatic amines ,with the appearance of new bands due to O-H of the carboxylic acid between (3377 – 3359)cm^{-1} , C=O (carboxylic acid) at (1712 – 1697)cm^{-1} and C=O(amid) at (1666 – 1647)cm^{-1} beside the NH group at (3182 – 3132)cm^{-1} [7 ,10]



[I]$_{a-c}$

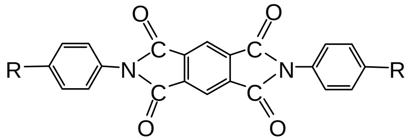
R = (a) H , (b) 4 - NO_2 , (c) 4 - CH_3

The FTIR absorption bands data of these compound [I]a-c are listed in Table (3).

N ,N-disubsititeted - pyromellitiimide [II]$_{a-c}$, were obtained by the intra molecular cyclization reaction of the prepared diamic acid [1]a-c using acetic anhydride-sadium acetate system [3 ,7] as a dehydrating agent at (80-90)C°. the mechanism of the cyclization involves neucleophilic substitution reaction [3]

These compounds [II]$_{a-c}$ were characterized by their melting points, FTIR spectroscopy . [7 ,10]

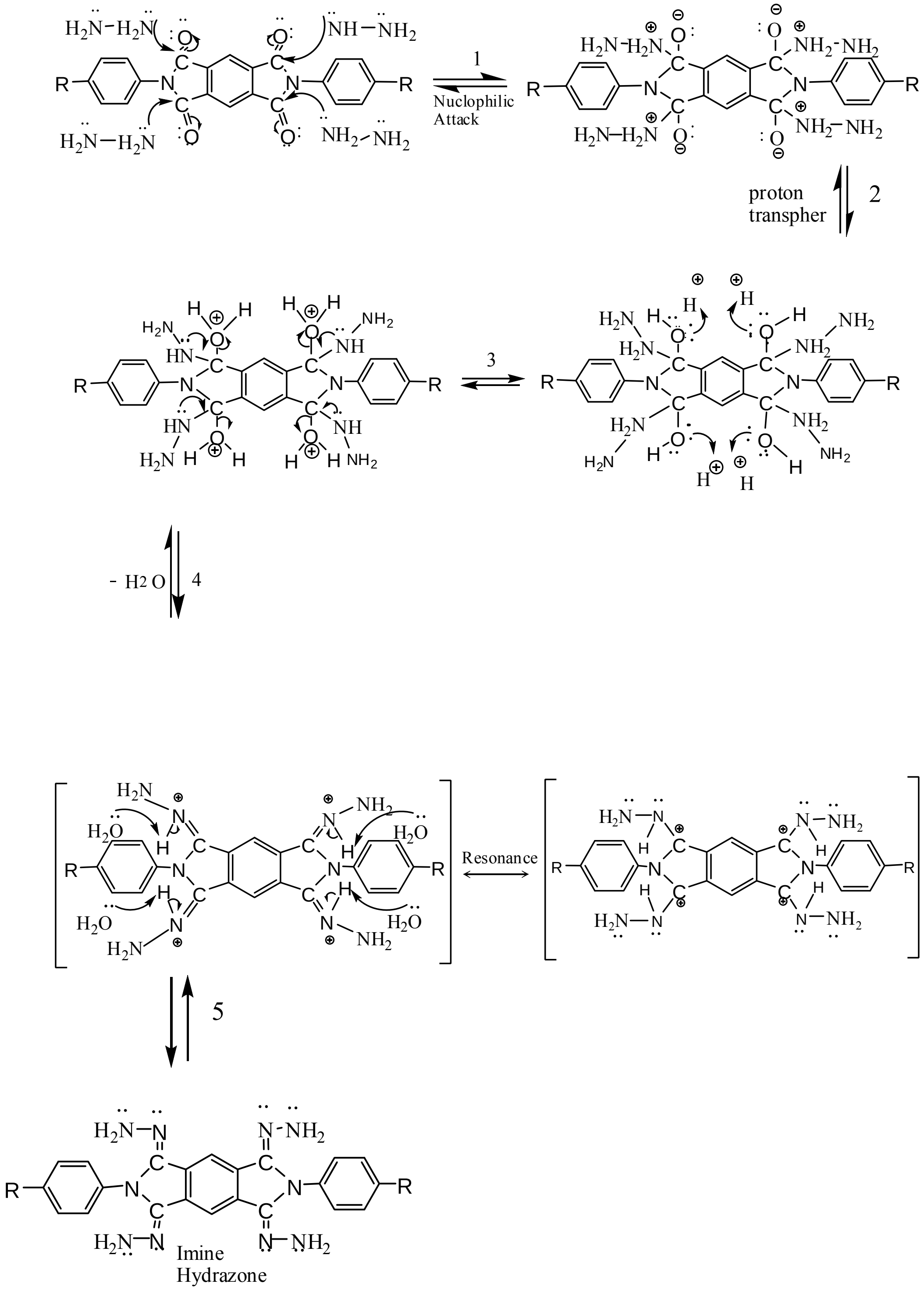
The FTIR spectra show the disappearance of the stretching absorption bands of N-H ,O-H and C=O(amid and carboxylic acid moiety) groups of the diamic acid , and the appearance of two peaks in the region (1724 - 1708)cm^{-1} which due to the stretching vibration of the C=O (imide cyclic) and two absorption bonds at about 1130cm^{-1} and 721cm^{-1} for symmetrical and asymmetrical C-N-C (cyclic) [10].The FTIR absorption bands data of these compounds [II] a-c are given in Table (4)



[II]$_{a-c}$

R = (a) H , (b) 4 - NO_2 , (c) 4 - CH_3

Due to the presence four carbonyl groups attached to diimide the authors try to treat these compounds with hydrazine hydrate 80% to form the novel hydrazone derivatives (imine) (III)a-c ,which were formed by the reaction involves the loss of water molecules according to the following mechanism . [4 ,5 ,12]



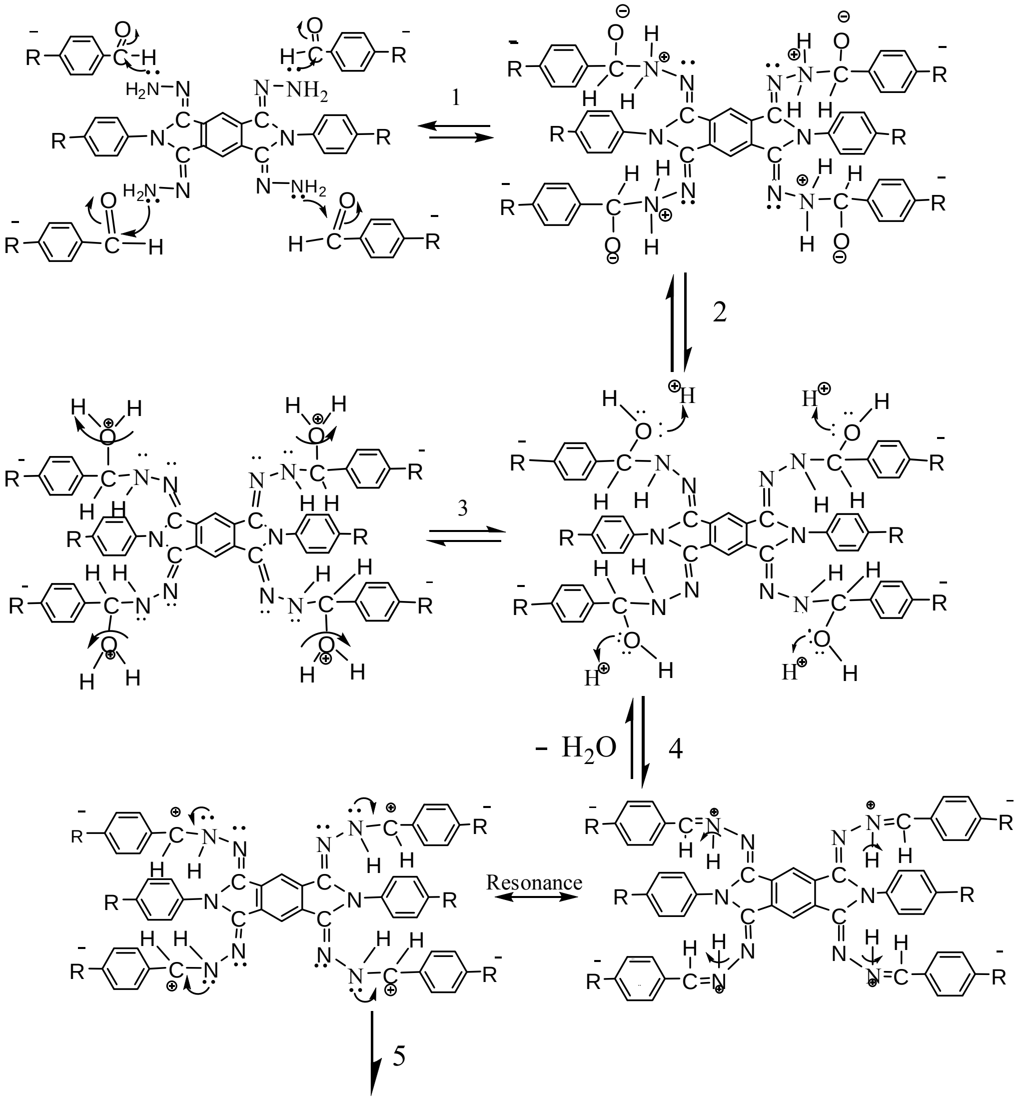
(III)a-c

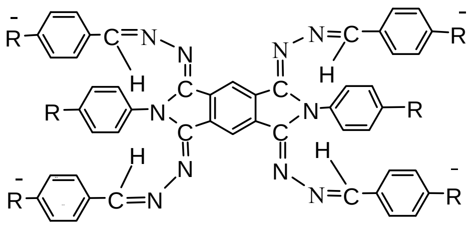
Adding 5 drops of glacial acetic acid will be needed for protonation of hydroxyl group in step [3] to form good leaving group.(water molecules) that step will let to form the hydrazone derivatives **,** these hydrazone derivatives were characterized by their melting points . C . H . N analysis ,FTIR

Elemental analysis for compound (III $)_{a-c}$ Table (2) .

The FTIR for the compounds (III)a-c show the appearance of stretching bands due to C=N in the region (1643-1639) cm^{-1} , and NH_2 stretching bands at (3394 - 3217) cm^{-1} with the disappearance of C=O (carbonyl group) for imide group at (1732-1778) cm^{-1} [10 ,11] , these are given in Table (**5**) .

Finally the formation of Schiff bases (IV - VI)(a-d) Which were prepared by the reaction of one mole of the last products (III)a-c with (four moles) of aromatic aldhydes to from Schiff bases derivatives in acidic medium that follows the following mechanism.





R = H , NO_2 , 4 - CH_3
$\bar{R}$ = Cl , Br , OH , NO_2

A series of Schiff bases were obtained from the above reaction mechanism . The detection of these Schiff bases was obtained by their m.p . C . H . N. anlysis and FTIR , HNMR spectra which show the following data .

FTIR show the disappearance of C=O (aldehydic) of the C=O (1690-1700)cm-^{1} stertching compounds and the formation of C=N at frequencies Ranges between (1643-1662)cm-^{1} also the C-N-C bond (hydrazone) derivatives at (742-1130)cm-^{1} Table (7) .

^{1}HNMR show the following data . [10 ,11]
1- Compound No. VI_d in which $\bar{R}$ = NO_2 Show
a- Six protons of two groups of CH_3 at δ 2 .53 ppm as a singlet .
b-Four protons of CH=N (imin protons) at δ 8 .43 ppm as a singlet .
c-26 protons of aromatic ring protons at δ (8 .24 – 8 .78) ppm
2-Compound No . VI_b in which $\bar{R}$ = Br shows
a- Four protons of CH=N (imin protons) at δ 8 .71 ppm as a singlet .
b-26 proton of aromatic ring protons at δ (7 .74 – 8 .76) ppm .
3-Compound No. IV_a in which $\bar{R}$ = CL shows
a- Four protons of CH=N (imin protons) at δ 8 .70 ppm as a singlet .
b- 28 protons of aromatic ring protons at δ (7 .57 – 8 .70)ppm .

The ease of the formation of hydrazone derivatives and Schiff bases derivatives which was effected by the presence of attracting or repulling groups attached to the phenyl at imide moiety was translated for further research works . [7 ,13]

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Table No.(1) : Physical properties of the compounds [I] - [VI] .

Comp. No.				Color	Melting Points˚c	Yield %	Recrystallization Solvent
[I]	[I]a			White	>300	88%	Acetone
	[I]b			White	>300	69%	Acetone
	[I]c			White	>300	90%	Acetone
[II]	[II]a			Off white	>300	72%	Ethanol
	[II]b			Off white	>300	66%	Ethanol
	[II]c			Off white	>300	75%	Ethanol
[III]	[III]a			Glow yellow	>300	79%	Ethanol
	[III]b			Glow yellow	>300	75%	Ethanol
	[III]c			Glow yellow	>300	79%	Ethanol
[IV]		R	R^{-}				
	[IV]$_a$	H	CL	Pale grey	>300	65%	Ethanol
	[IV]$_b$	H	Br	Pale yellow	>300	67%	Ethanol
	[IV]$_c$	H	OH	Deep yellow	>300	67%	Ethanol
	[IV]$_d$	H	NO_2	Yellow	>300	62%	Ethanol
[V]	[V]$_a$	NO_2	CL	Pale grey	>300	70%	Ethanol
	[V]$_b$	NO_2	Br	Pale yellow	>300	71%	Ethanol
	[V]$_c$	NO_2	OH	Deep yellow	>300	78%	Ethanol
	[V]$_d$	NO_2	NO_2	Yellow	>300	73%	Ethanol
[VI]	[VI]$_a$	CH_3	CL	Pale grey	>300	80%	Ethanol
	[VI]$_b$	CH_3	Br	Pale yellow	>300	83%	Ethanol
	[VI]$_c$	CH_3	OH	Deep yellow	>300	85%	Ethanol
	[VI]$_d$	CH_3	NO_2	Yellow	>300	72%	Ethanol

Table No(2):C . H . N . analysis data of compounds [III]$_{a-c}$.

Number of Compound	Molecular Formula	C		H		N	
[III]$_a$	$C_{22}H_{20}N_{10}$	C	62 .26	C	4 .11	C	33 .01
		F	61 .98	F	4 .09	F	33 .21
[III]$_b$	$C_{22}H_{18}N_{12}O_4$	C	51 .36	C	3 .50	C	32 .68
		F	52 .09	F	3 .42	F	32 .53
[III]$_c$	$C_{24}H_{24}N_{10}$	C	63 .71	C	5 .30	C	30 .97
		F	63 .11	F	5 .2	F	30 .25

Table No.(3) : FTIR absorption bands of compounds [I]$_{a-c}$.

Comp. No.	υ (O-H) cm^{-1}	υ (C=O) cm^{-1} Acid	υ (C=O) cm^{-1} Amid	υ (N-H) cm^{-1}	υ (C-H) cm^{-1} Aromatic	υ (C=C) cm^{-1} Aromatic
[I]a	3375	1712	1651	3132	3062	1597
[I]b	3359	1697	1666	3155	3089	1597
[I]c	3377	1701	1647	3182	3039	1600

Table No.(4):The FT IR data of compounds [II]$_{a-c}$.

Comp. No.	υ (C=O) cm^{-1} imide	υ (C-N-C) cm^{-1} cyclic asym.sym.	υ (C-H) cm^{-1} Aromatic	υ (C=C) cm^{-1} Aromatic
[II]a	1724 , 1708	1126 ,744	3059	1597
[II]b	1732	1114 ,748	3093	1597
[II]c	1724 , 1708	1130 , 721	3035	1585

Table No.(5) : The FTIR data for compound (III)$_{a-c}$.

Comp. No.	υ(C=N) cm^{-1}	υ (N-H) cm^{-1}	υ (C=C) cm^{-1} Aromatic	υ (C-H) cm^{-1} Aromatic
[III]a	1643	3321 , 3271	1568	3059
[III]b	1643	3360 , 3217	1550	3074
[III]c	1639	3394 , 3240	1566	3082

Table No(6):C . H . N . anaylsis of compounds (IV) – (VI) .

Com. No.	R	- R	C	H	N	Molecular Formula
[IV]a	H	Cl	C 65.64	C 3.50	C 15.31	C_{50} H_{32} N_{10} Cl_4
			F 65.19	F 3.44	F 15.08	
[IV]$_b$	H	Br	C 54.94	C 2.93	C 12.82	C_{50} H_{32} N_{10} Br_4
			F 55.16	F 3.18	F 12.29	
[IV]$_c$	H	OH	C	C	C	C_{50} H_{36} N_{10} O_4
			F	F	F	
[IV]$_d$	H	NO_2	C 62.76	C 3.34	C 20.50	C_{50} H_{32} N_{14} O_8
			F 62.01	F 3.24	F 21.01	
[V]$_a$	NO2	Cl	C	C	C	C50 H_{30} N_{12} O4 Cl_4
			F	F	F	
[V]$_b$	NO2	Br	C 50.76	C 2.53	C 14.21	C50 H30 N_{12} O4 Br_4
			F 51.02	F 2.59	F 13.98	
[V]$_c$	NO2	OH	C 64.51	C 3.65	C 18.06	C_{50} H_{34} N_{12} O_8
			F 63.99	F 3.61	F 18.28	
[V]$_d$	NO2	NO_2	C 57.36	C 2.86	C 21.41	C_{50} H_{30} N_{16} O_{12}
			F 56.99	F 2.81	F 20.91	
[VI]$_a$	CH3	Cl	C 66.24	C 3.82	C 14.86	C_{52} H_{36} N_{10} Cl_4
			F 65.89	F 3.48	F 14.19	
[VI]$_b$	CH3	Br	C	C	C	C_{52} H_{36} $N10_{10}$ Br_4
			F	F	F	
[VI]$_c$	CH3	OH	C 71.88	C 4.60	C 16.12	C_{52} H_{40} N_{10} O_4
			F 71.35	F 4.44	F 16.08	
[VI]$_d$	CH3	NO_2	C 63.41	C 3.65	C 19.91	C_{52} H_{36} N_{14} O_8
			F 64.08	F 3.19	F 20.11	

Table No.(7): FTIR data of compounds (IV) – (VI) (a-d) .

Comp. No.	R	– R	υ (C=N) cm^{-1}	υ (C-N-C) cm^1 asym.sym.	υ (C=C) cm^{-1} Aromatic	υ (C-H) cm^{-1} Aromatic	Other (υ) cm^{-1}
[IV]a	H	Cl	1658	1138 ,744	1608	3047	C-Cl 786
[IV]$_b$	H	Br	1658	1141 ,748	1585	3043	C-Br 648
[IV]$_c$	H	OH	1654	1141 ,725	1562	3012	OH 3336
[IV]$_d$	H	NO_2	1658	1138 ,744	1597	3043	N-O 1519 , 1346
[V]$_a$	NO_2	Cl	1658	1338 ,744	1593	3047	C-Cl 762
[V]$_b$	NO_2	Br	1658	1141 , 740	1562	3028	C-Br 678
[V]$_c$	NO_2	OH	1654	1141 , 736	1562	3016	OH 3325
[V]$_d$	NO_2	NO_2	1658	1138 , 744	1597	3043	N-O 1519 , 1346
[VI]$_a$	CH_3	Cl	1658	1138 , 744	1593	3047	C-Cl 750
[VI]$_b$	CH_3	Br	1658	1141 , 740	1585	3043	C-Br 675
[VI]$_c$	CH_3	OH	1654	1141 , 736	1562	3016	OH 3330
[VI]$_d$	CH_3	NO_2	1658	1149 ,740	1566	3039	N-O 1516 , 1342

تصنيع قواعد شف جديدة مشتقة من انـهدريد البايرومليتاميك

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استلم البحث في:19 حزيران 2014,قبل البحث في:20 تشرين الاول 2014

الخلاصة

تم تصنيع قواعد جديده مشتقة من انهدريد ثنائي البايروملیتامیك بخطوات عدة . اذ حضرت مشتقات حامض البايروملیتامیك المتناظره $[\text{ I }]_{a-c}$ من تفاعل انهدريد ثنائي البايروملیتامیك مع مولين من بعض الامينا ت الاورماتية الحاوية على (مجاميع ساحبة واخرى دافعة) في الاسيتون الجاف بوصفه مذيبا.

واشتملت الخطوة الثانية تحويل مشتقات حامض البايرومبليتاميك الى الايميدات المقابلة باستعمال نظام انهدريد الخليك – خلات الصوديوم عاملا نازعا للماء ومن خلال عملية التحولق الداخلي لهذه الاحماض . $[\text{II}]_{a-c}$

في الخطوه الثالثه صنعت مركبات الهيدرازون $[\text{III}]_{a-b}$ من خلال تفاعل الايميدات $[\text{ II }]_{a-c}$ مع 80% هايدرازين المائي وعند درجة حراره تتراوح بين 50-60 م°.

وفي الخطوه الرابعه صنعت قواعد شف الـــجديده من تفاعل الـــــهيدرازونات $[\text{III}]_{a-c}$ مع الديهايدات اوروماتيه مختاره بدرجة حراره تتراوح بين (80- 85) م °. جميع المركبات المحضرة والمصنعة تم الكشف عنها وتشخيصها من خلال درجات الانصهار . ومزيج لدرجات الانصهار (مع المواد المتفاعله) ،تحليل العناصر [N,H,C] واطياف الاشعه تحت الحمراء وطيف الرنين النووي المغناطيسي للبعض منها , اذ دلت الى تطابق التحاليل مع النتائج المحضرة.

الكلمات المفتاحية : انهدريد حامض البايرميليتاميك , ايميد , قواعد شيف