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Synthesis Of New Asymmetrical Pyromellitdiimides Derived From Pyromellitic Dianhydride

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Abstract

This work involves the synthesis and characterization of asymmetrical pyromellitdiimide derivatives $[IV]_{a-f}$ by four sequence steps selective reaction . One mole of pyromellitic dianhydride was reacted with one mole of various primary aromatic amines [4-nitro aniline , 4-chloro aniline , 4-toludine and 4-anisidine] in excess of dry acetone to produce six compounds (N-substituted-pyromellitamic monoacid) $[I]_{a-f}$. These new compounds $[I]_{a-d}$ were converted to the corresponding N- substituted- pyromellitmonoimide $[II]_{a-d}$ via their heating at (80-90) ^{0}C in sodium acetate-acetic anhydride mixture .

The compounds $[II]_{a-f}$ were allowed to react with one mole of another primary amines in excess of dry acetone to give new derivatives of amic acid $[II]_{a-d}$ followed by intramolecular cyclization reaction of these compounds $[IV]_{a-f}$ in sodium acetate-acetic anhydride system to yield the desired asymmetrical pyromellitdiimide derivatives $[IV]_{a-f}$, the above reactions can be summarized in Scheme 1.

All the synthesized compounds have been studied and charachterized by their melting points , FTIR , and ^{1}HNMR spectroscopy (for some of them).

Key words: pyromellitic dianhydride, pyromellitidiimides, pyromellitidiisoimides.

Introduction

Pyromellitdiimides are best known as segments of highly insulating polyimide dielectrics , it is though nevertheless quit surprising that no attempt has been made to fabricate transistor from pyromellitdiimide derivatives , which have the simple aromatic ring (benzene) in the center, and the tetracarboxylic 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 the pyromellitdiimide derivatives [1,2].

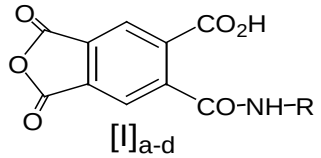
N-substituted cyclic imides are heterocyclic compounds represent an important class of bioactive molecules that show a wide range of pharmacological activities [3] such as androgen receptor antagonistic [4], anti-inflammatory , anxiolytic [5] , antiviral [6], antibacterial [7], and antitumor [8] properties . Morover , they are synthetic precursors with application in organic synthesis , supramolecular chemistry , polymer synthesis , and for the development of new materials and molecular electronic devise [9] . Aromatic polyimides that derived from pyromellitic dianhydride are widely used in advanced technological areas because of their excellent thermal stability , chemical resistance and they are extensively used in the electronics industry as insulators in complex devices , owing to their high thermal resistance and low dielectric constant , beside the electrical properties , their optical properties have been extensively investigated due to the potential applications in the field of optical communications [10,11]. Also they are used in microelectronics , as well as in nanotechnology as a matrix in the production of nanocomposite layers [12].

In addition , The effect of different concentrations of some pyromellitamic diacids and pyromellitdiimides on the activity of human serum cholinesterase have been investigated in vitro , the inhibitory effect increases with the increase of the concentration of such compounds [13] .

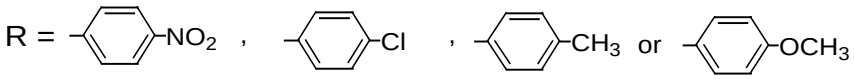
The aim of this work is the synthesis of a new asymmetrical pyromillitdiimide derivatives and proved the truth of the pathway which is used for synthesis of these compounds by using opposite pathway to give the same product.

Synthesis of Asymmetrical Pyromellitimide :

Synthesis of N-substituted -pyromellitamic monoacid[I]$_{a-d}$

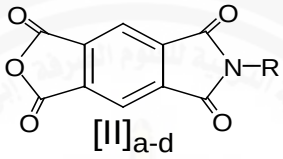


[I]$_{a-d}$

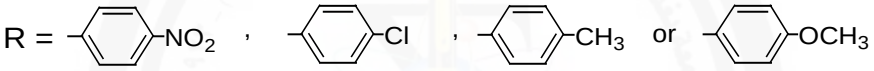


To a solution of pyromellitic dianhydride (0.218g, 0.001 mol) in (30mL) acetone , a very dilute solution of amine (0.001 mole) in (90mL) acetone was added dropwise during about 18 hrs . After all the amine has been added the solution was filtered off from any precipitate and the clear solution was evaporated under reduced pressure and the product filtered [14], washed and recrystalized from chloroform . The physical data of N-substituted –pyromellitamic monoacid [I]$_{a-d}$ are listed in Table 1 .

Synthesis of N- substituted- pyromellitmonoimide[II]$_{a-d}$

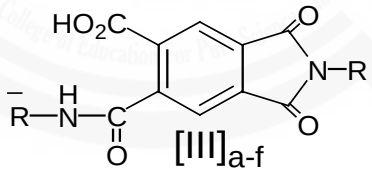


[II]$_{a-d}$

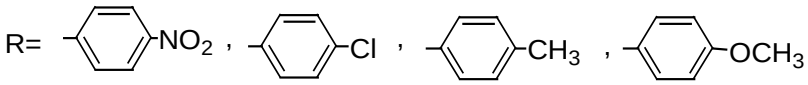


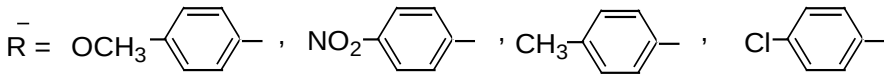
A (0.001 mole) of N-pyromellitamic monoacid was placed in (50 mL) round bottom flask fitted , a mixture of sodium acetate (0.082g , 0.001 mole) and acetic anhydride (1mL ,0.001mole) was added . The mixture was maintained between (80-90) ^{0}C by means of a water-bath and stirred for half hour . The mixture was allowed to stirring for one hour at room temperature . Then the mixture was poured on ice-water (400mL) and filtered off , recrystalized from acetone . The physical data of N- substituted- pyromellitmonoimide [II]$_{a-d}$ are listed in Table 1 .

Synthesis of (N- substituted-pyromellitmonoimide)-N^{-}- (substituted-pyromellitamic monoacid) [III]$_{a-f}$



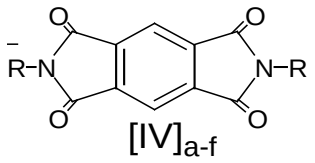
[III]$_{a-f}$



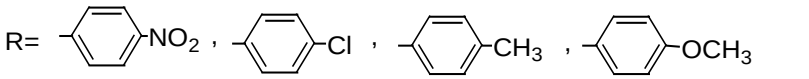


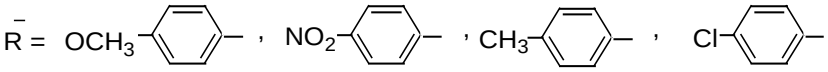
To a solution of N- substituted- pyromellitmonoimide [II]$_{d-f}$ (0.001mol) in (30mL) acetone , A very dilute solution of amine (0.001 mole) in (90mL) acetone was added dropwise during about 18 hrs. After all the amine has been added the solution was filtered off from any precipitate and the clear solution was evaporated under reduced pressure and the residue recrystalized from acetone . The physical data of (N- substituted - pyromellitmonoimide)-N^{-}- (substituted-pyromellitamic acid) [III]$_{a-f}$ are listed in Table 1 .

Synthesis of N,N^{-}- disubstituted pyromellitdiimide [IV]$_{a-f}$



$[IV]_{a-f}$

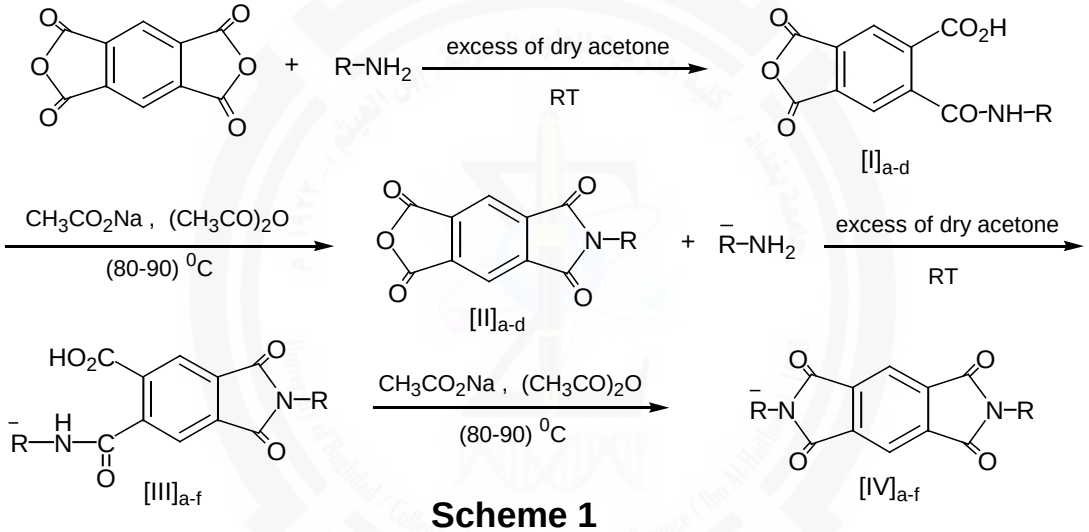




These novel compounds were prepared as described in procedure which is used for the synthesis of compounds [II]. All these compounds were recrystalized from diethylether . The physical data of N,N¯- disubstituted pyromellitdiimide [IV] are listed in table 1.

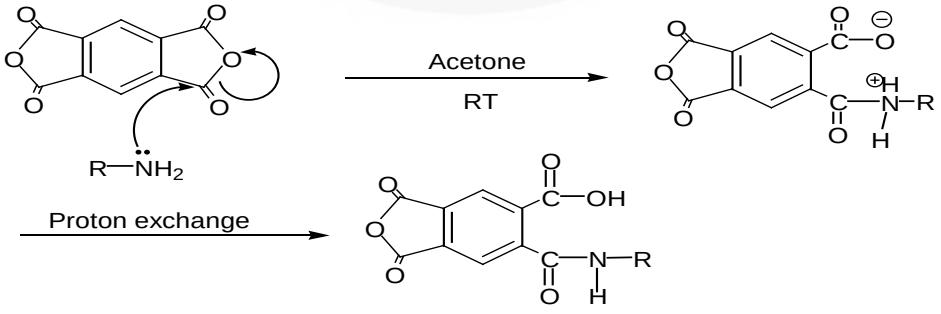
Results and Discussion

The reaction sequences leading to the formation of novel compounds of asymmetrical pyromellitdiimide $[IV]_{a-f}$ are outlined in the following scheme 1.



Scheme 1

The amic acids $[I]_{a-f}$ were synthesized by the reaction of one mole of pyromellitic dianhydride with one mole of different amines in the presence of excess of dry acetone as a solvent . The mechanism involves nucleophilic addition reaction [15] as follows , in scheme 2.



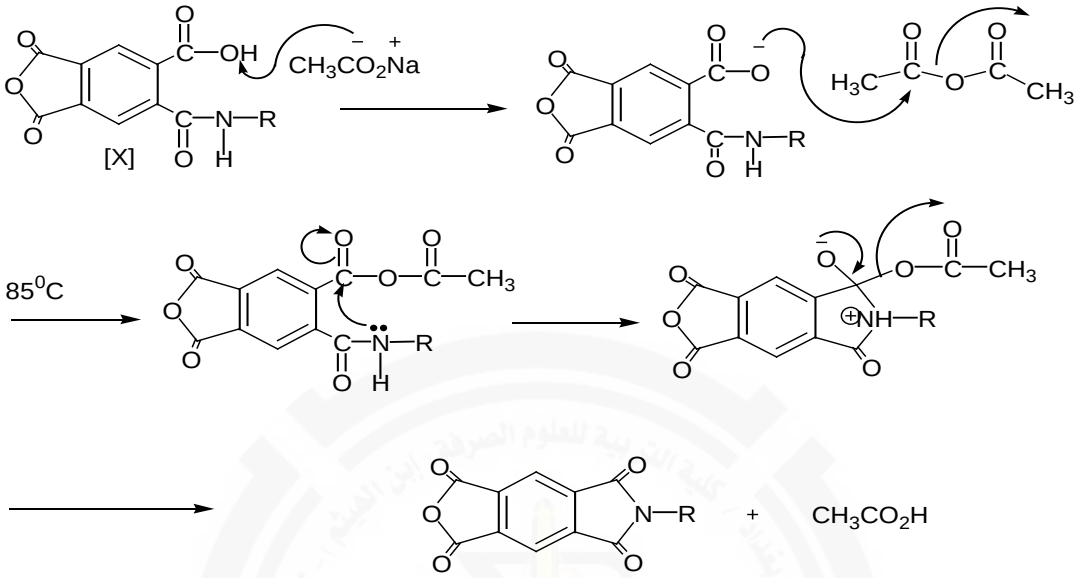
Scheme 2

The structure of these acids$[I]_{a-f}$ was studied by melting point , FTIR spectroscopy .

The FTIR absorption-spectra showed the disappearance of absorption bands due to NH_2 of the starting materials together with the appearance of new absorption stretching bands due to O-H of carboxylic moiety at (2410-3530) cm^{-1}, C=O (carboxylic acid) at (1680-1709) cm^{-1} and C=O (amid) at (1630-1655) cm^{-1} and NH group at (3217-3277) cm^{-1} . And appearance of two peaks in the region (1715-1840) cm [16] which could be attributed to stretching vibration of C=O (anhydride)

symmetry and asymmetry , in addition to the appearance of absorption band around at (1040) cm^{-1} for the C-O-C (cyclic) [17] . The FTIR absorption bands data of these compounds $[I]_{a-f}$ are listed in Table 3.

N-substituted-pyromellitmonoimide $[II]_{a-f}$ were obtained by the intramolecular cyclization reaction of N-substituted-pyromellitamic monoacid $[II]_{a-f}$ in acetic anhydride and sodium acetate at (80-90) ^0C . The mechanism involves nucleophilic substitution reaction [18] as follows , in scheme 3.



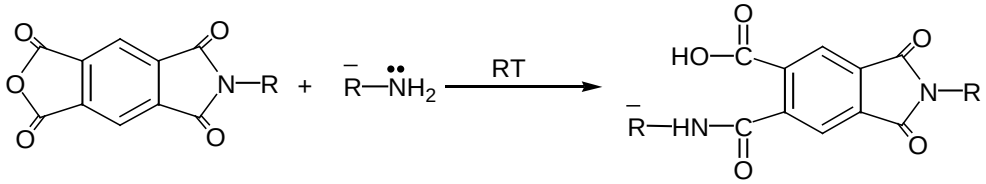
Scheme 3

The structure of these compounds $[II]_{a-f}$ was studied by melting point , FTIR , and ^{1}HNMR spectroscopy.

The FTIR spectra exhibited significant two peaks in the region (1675-1710) cm^{-1} which could be attributed to stretching vibration of the carbonyl group (imide cyclic) and two absorption bands around 1170 cm^{-1} and 755cm^{-1} for asymmetrical and symmetrical of C-N-C (cyclic) [19] together with the appearance of two peaks in the region (1709-1800) cm^{-1} which could be attributed to stretching vibration of C=O (cyclic anhydride) symmetry and asymmetry , also the appearance of absorption band around (1040) cm^{-1} due to C-O-C (cyclic) . They also show the disappearance of stretching absorption bands of N-H , O-H and C=O (carboxylic moiety) groups of amic acid . The FTIR absorption bands data of these compounds $[II]_{a-f}$ are listed in Table 3.

^{1}HNMR spectrum of compound $[II]_c$ showed the following characteristic chemical shift (DMSO as a solvent) : a pair of doublet band appear at δ (7.06-7.46) ppm due to the four aromatic protons , a singlet sharp signal at δ 8.73 ppm for the two protons of centre aromatic ring . A singlet sharp signal at δ 2.23 ppm could assigned to the three protons of termenal CH_3 group .

The amic acids $[III]_{a-f}$ were synthesized by the reaction of one mole of **N**-substituted-pyromellitmonoimide $[III]_{a-f}$ with one mole of another primary aromatic amine in the presence excess of dry acetone as a solvent.



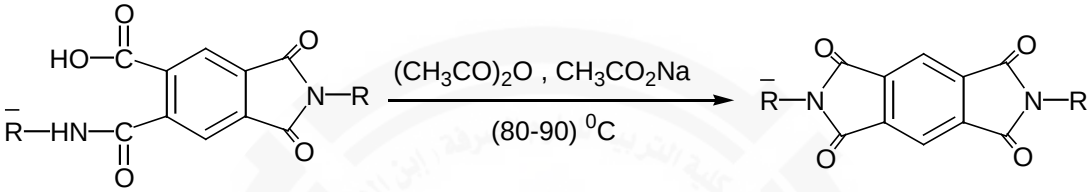
The structure of these compounds $[III]_{a-f}$ was studied by melting point , FTIR and ^{1}HNMR spectroscopy . The FTIR absorption-spectra showed the disappearance of absorption peaks characterized of cyclic anhydride of pyromellitmonoimides $[III]_{a-f}$ together with the appearance of new absorption stretching bands due to O-H of carboxylic moiety at (2420-3504) cm^{-1}, NH amide in the region (3273-3304) cm^{-1} , C=O (carboxylic acid) at (1663-1692) cm^{-1} , and C=O (amid) at (1632-1650) cm^{-1}. Two peaks in the region (1720-1780) cm^{-1} which could be attributed to

stretching vibration of the carbonyl group (imide cyclic) and two absorption bands around 1175cm^{-1} and 745cm^{-1} for asymmetrical and symmetrical of C-N-C (cyclic) . The FTIR absorption bands data of these compounds $[III]_{a-f}$ are listed in Table 4.

^{1}HNMR spectrum of compound $[III]_c$ showed the following characteristic chemical shift (DMSO as a solvent) : a singlet signal at δ 2.04 ppm due to the three protons of terminal CH_3 group , ten aromatic protons appeared at δ (7.34-7.94) ppm . Also showed a singlet signal at δ 4.34 ppm could be attributed to the one proton of NH amide group and a good signal at δ 10.05 ppm could be attributed to the one proton of carboxylic moiety (O-H) .

^{1}HNMR spectrum of compound $[III]_e$ showed the following characteristic chemical shift (DMSO as a solvent) : A singlet signal at δ 3.61 ppm could assigned to the three protons of termenal OCH_3 group , a singlet signal at δ 4.30 ppm could be attributed to the one proton of NH amide group . A singlet sharp signale at δ 8.19 ppm for two protons of centre aromatic ring , eight aromatic protons appeared as in the region at δ 6.57-8.60 ppm . Finally, a proton of carboxylic moiety (O-H) appeared at δ 10.54 ppm .

N,N¯- disubstituted pyromellitdiimide $[IV]_{a-f}$ were obtained by the intramolecular cyclization reaction of amic acid $[III]_{a-f}$ in acetic anhydride and sodium acetate at (80-90) ^{0}C .

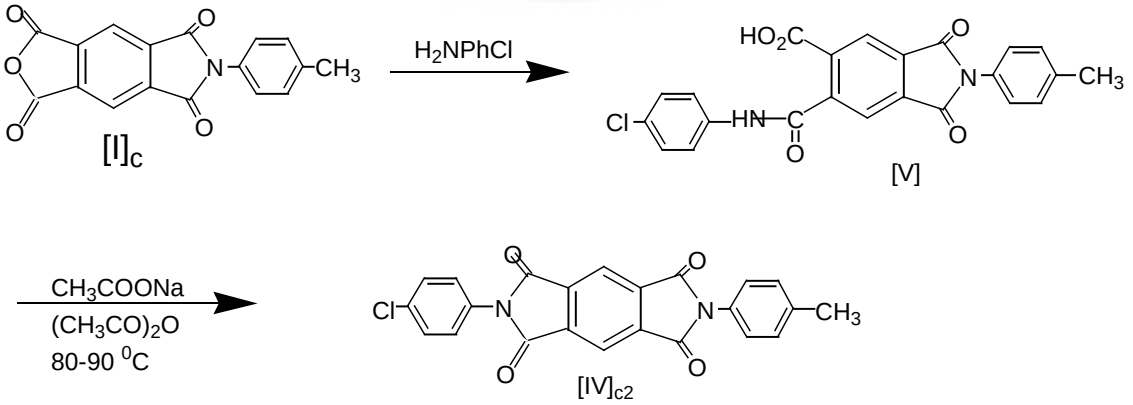


The structure of these compounds $[IV]_{a-f}$ was studied by melting point , FTIR and ^{1}HNMR spectroscopy.

The FTIR spectra exhibited significant two peaks in the region (1670-1786) cm^{-1} which could be attributed to stretching vibration of the carbonyl group (imide cyclic) and two absorption bands around 1175 cm^{-1} and 760 cm^{-1} for asymmetrical and symmetrical of C-N-C (cyclic) , in addition to two peaks of (imide cyclic) from another side in the region (1668-1734) cm^{-1} and two absorption bands around 1160 cm^{-1} and 740 cm^{-1} for asymmetrical and symmetrical of C-N-C (cyclic) . They also shows the disappearance of absorption stretching bands of N-H , O-H and C=O (carboxylic moiety) groups of amic acid $[III]_{a-f}$. The FTIR absorption bands data of these compounds $[IV]_{a-f}$ are listed in Table 5 .

^{1}HNMR spectrum of compound $[IV]_f$ showed the following characteristic chemical shift (DMSO as a solvent) : a singlet signal at δ 2.20 ppm due to the three protons of terminal CH_3 group , three protons of OCH_3 group appeared as a singlet signal at δ 4.77 ppm . A signal at δ 9.79 ppm due to the two protons of central aromatic ring , eight aromatic protons appeared as many signals at δ (6.85-7.71) ppm .

For comparision purpose the compound $[IV]_{c2}$ was also synthesized by as follows :



Scheme 4

The physical and spectral data of compound $[IV]c_{1,2}$ which is synthesized by two ways in Scheme 1 and Scheme 4 are the same in the two cases . These data give a good evidence for the

formation of these compounds and a prove the truth of the pathway which is used to synthesis the compounds by using opposite pathway to give the same product.

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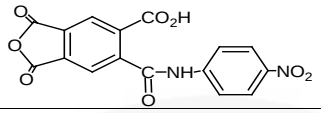
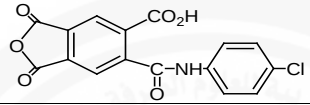
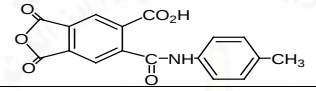
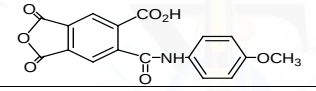
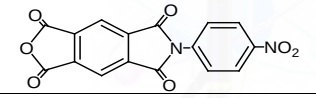
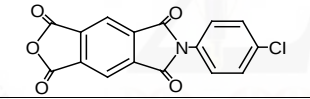
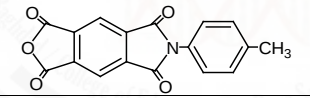
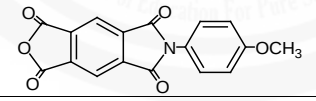
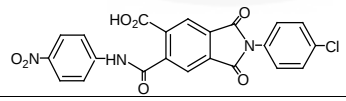
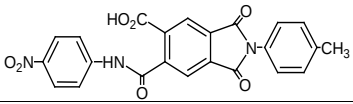
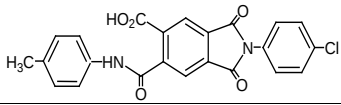
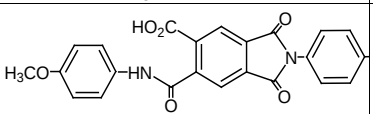
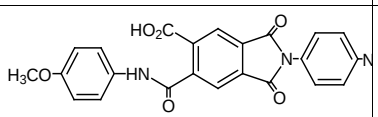
Table (1) : Physical properties of new synthesized compounds $[I]_{a-d}$ - $[IV]_{a-f}$

Com .No.	Nomenclature	Structural formula	Molecular formula	M.P ◦C	Yield %	Color
$[I]_a$	N-(4-nitro phenyl)-pyromellitamic monoacid		$C_{16}H_8N_2O_8$	>300	96	Yellow
$[I]_b$	N-(4-chlorophenyl)-pyromellitamic monoacid.		$C_{16}H_8NO_6Cl$	>300	95	Pale grey
$[I]_c$	N-(4-tolyl)-pyromellitamic monoacid.		$C_{17}H_{11}NO_6$	>300	98	Pale yellow
$[I]_d$	N-(4-methoxy phenyl)-pyromellitamic monoacid.		$C_{17}H_{11}NO_7$	>300	93	Pale Brown
$[II]_a$	N-(4-nitro phenyl)]-pyromellitmonoimide.		$C_{16}H_6N_2O_7$	198-200	91	Yellow
$[II]_b$	N-(4-chlorophenyl)-pyromellitmonoimide.		$C_{16}H_6NO_5Cl$	174-176	83	Dark grey
$[II]_c$	N-(4-tolyl)-pyromellitmonoimide.		$C_{17}H_9NO_5$	>300	60	Pale yellow
$[II]_d$	N-(4-methoxy phenyl)-pyromellitmonoimide		$C_{17}H_9NO_6$	210-212	82	Brown
$[III]_a$	N-(4-chloro phenyl)- pyro mellitmonoimide, N¯-(4-nitroph enyl)pyromellitamicmonoacid.		$C_{22}H_{12}N_3O_7Cl$	140-142	92	Grey
$[III]_b$	N-(4-tolyl)-pyromellitmonoimide ,N¯- (4-nitro phenyl) -pyromellitamic monoacid.		$C_{23}H_{15}N_3O_7$	200-202	90	Pale yellow
$[III]_c$	N-(4-chloro phenyl)-pyromellitmonoimide , N¯- (4-tolyl)-pyromellitamic monoacid.		$C_{23}H_{15}N_2O_5Cl$	158-160	88	Pale grey
$[III]_d$	N-(4-chloro phenyl)-pyromellitmonoimide , N¯- (4-methoxy phenyl)-pyromellitamic monoacid.		$C_{22}H_{15}N_2O_6Cl$	154-156	87	Brown
$[III]_e$	N-(4-nitro phenyl)-pyromellitmonoimide , N¯-(4-methoxy phenyl)-Pyromellitamic monoacid.		$C_{22}H_{12}N_3O_8$	198-200	85	Pale brown

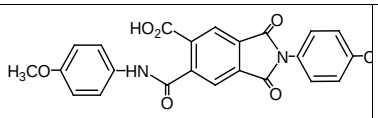
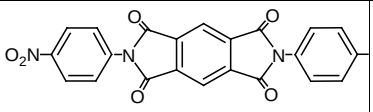
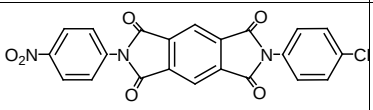
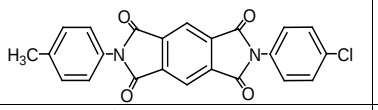
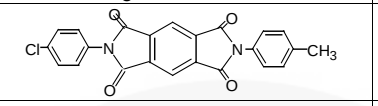
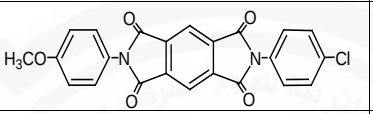
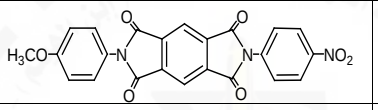
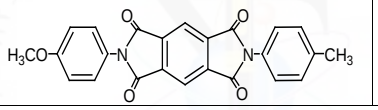
$[III]_f$	N-(4-tolyl)-pyromellitmonoimide , N¯-(4-methoxy phenyl)-pyromellitamic monoacid.		$C_{23}H_{15}N_2O_6$	>300	90	Pale Brown
$[IV]_a$	N-(4-chloro phenyl),N¯-(4-nitro phenyl) - pyromellitdiimide.		$C_{22}H_{10}N_3O_6Cl$	168-170	88	Brown
$[IV]_b$	N-(4-nitro phenyl), N¯- (4-nitro phenyl) - pyromellitdiimide.		$C_{23}H_{13}N_3O_6$	220-222	87	Yellow
$[IV]_{c1}$	N-(4-chloro phenyl) , N¯- (4-tolyl)-pyromellitdiimide.		$C_{23}H_{13}N_2O_4Cl$	198-200	81	Grey
$[IV]_{c2}$	N-(4-tolyl) , N¯- (4-chlorophenyl)-pyromellitdiimide.		$C_{23}H_{13}N_2O_4Cl$	198-200	81	Grey
$[IV]_d$	N-(4-chloro phenyl), N¯-(4-meth oxy phenyl)-pyromellitdiimide.		$C_{22}H_{13}N_2O_5Cl$	141-143	76	Dark brown
$[IV]_e$	N-(4-nito phenyl),N¯(4-methoxy phenyl)-pyromellitdiimide.		$C_{22}H_{10}N_3O_7$	178-180	77	Brown
$[IV]_f$	N-(4-tolyl), N¯(4-methoxy phenyl)-pyromellitdiimide.		$C_{23}H_{13}N_2O_5$	>300	68	Brown

Table (2): Characteristic FTIR absorption bands of compounds $[I]_{a-d}$

Comp. No	Characteristic bands FTIR spectra (cm^{-1})						
	VN-H amide	VO-H	VC=O cyclic anhyd. (asym, sym	VC=O carboxylic	VC=O amide	VC=C arom.	VC-O-C cyclic
$[I]_a$	3217	3540-2410	1836,1785	1705	1632	1597	1036
$[I]_b$	3220	3350-2500	1810,1770	1709	1640	1585	1042
$[I]_c$	3277	3400-2500	1790,1742	1684	1655	1589	1068
$[I]_d$	3433	3480-2550	1840, 1715	1630		1590	1031

Table (3): Characteristic FTIR absorption bands of compounds $[II]_{a-d}$

Comp. No.	Characteristic bands FTIR spectra (cm^{-1})						
	VC-H arom.	VC=O cyclic anhydride asym.,sym.	VC=O Imide, asym.,sym.	VC=C arom.	VC-O-C cyclic	VC-N-C cyclic asym., sym.	Other
$[II]_a$	3096	1780,1745	1755,1684	1599	1035	1178,750	4-NO_2: 1506,1304
$[II]_b$	3075	1847,1775	1735,1675	1603	1040	1171,752	4-Cl : 970
$[II]_c$	3060	1780,1709	1740,1680	1603	1045	1159,756	VC-H aliphatic 2954-2831
$[II]_d$	3067	1861,1796	1784,1726	1606	1032	1180,767	VC-H aliphatic 2980-2837

Table (4): Characteristic FTIR absorption bands of compounds $[III]_{a-f}$

Comp. No.	Characteristic bands FTIR spectra (cm^{-1})							
	VN-H amide	VO-H	VC=O Imide asym.,sym	VC=O carboxylic	VC=O amide	VC=C arom.	VC-N-C cyclic asym.,sym	Other
$[III]_a$	3304	3485-2650	1760,1720	1665	1632	1597	1182,754	4-NO_2 : 1506,1304
$[III]_b$	3279	3320,2700	1780,1735	1682	1650	1599	1179,751	VC-H aliphatic 2824 4-NO_2:1505,1304
$[III]_c$	3279	3310-2420	1775,1735	1682	1650	1599	1179,750	4-Cl : 968
$[III]_d$	3304	3500-2780	1780,1740	1667	1645	1595	1170,754	4-Cl : 970
$[III]_e$	3278	3320-2450	1765,1735	1682	1645	1599	1179,750	VC-H aliphatic 2924-2855
$[III]_f$	3273	3504-2550	1775,1738	1680	1647	1600	1175,756	VC-H aliphatic 2953-2868 ,VN-H: 3352,VC=S:1321

Table (5): Characteristic FTIR absorption bands of compounds $[IV]_{a-f}$

Comp.No.	Characteristic bands FTIR spectra (cm^{-1})				
	VC-H arom.	VC=O Imide asym., sym.	VC=C aroma.	VC-N-C cyclic asym., sym	Other
$[IV]_a$	3065	1740,1682 1730,1670	1599	1178,766 1155,760	4-NO_2 :1506 , 1304
$[IV]_b$	3100	1746,1695 1732,1682	1599	1179,754 1163,735	4-NO_2 :1506,1304, VN-H : 3337, VC=S:1330
$[IV]_c$	3061	1786,1696 1717,1674	1597	1171,760 1160,725	4-Cl: 935
$[IV]_d$	3100	1750,1695 1734,1668	1593	1178,752 1165,740	4-Cl:933, VN-H: 3337, VC=S:1315
$[IV]_e$	3060	1740,1697 1720,1670	1602	1170,768 1160,760	VC-H aliphatic 2970-2920
$[IV]_f$	3100	1745,1695 1734,1670	1593	1175,755 1170,735	VC-H aliphatic 2928-2855 ,VN-H at 3339,VC=S:1317

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تحضير البيروميليت ثنائية الاميد غير المتماثلة الجديدة المشتقة من البايروميليت ثنائي الانهيدريد

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قسم الكيمياء ، كلية التربية- ابن الهيثم للعلوم الصرفة ،جامعة بغداد
استلم البحث في :27 أيار 2012 قبل البحث في : 22 تشرين الأول 2012

الخلاصة

تضمن هذا البحث تحضير وتشخيص مشتقات البايروميلت ثنائية الايميد غير المتماثلة $[VI]_{a-f}$ بتفاعل انتقائي مكون من اربع خطوات متتابعة الاولى تبدأ بمفاعلة مول واحد من البايروميليتك ثنائي الانهدريد مع مول واحد من الامينات الاروماتية الاولية المتنوعة 4-نيتروانلين ،و4-كلورو انلين ،و 4-تولودين ،و4-انيسيدين وتكوين حوامض الاميك الاحادية $[I]_{a-d}$ باستعمال وفرة من الاسيتون الجاف مذيبا" وبدرجة حرارة الغرفة . والثانية تحويل المركبات المحضرة الى N- بايروميليت احادي الايميد $[II]_{a-d}$ وذلك بتسخينها بدرجة حرارة (80-90) ْم في مزيج من خلات الصوديوم وانهدريد الخليك . أما الخطوة الثالثة فتضمنت تفاعل مول واحد من مركبات البايروميليت احادية الايميد $[II]_{a-d}$ مع مول واحد من امينات اروماتية اولية متنوعة لتعطي مشتقات جديدة من حوامض الاميك $[III]_{a-f}$ باستعمال وفرة من الاسيتون الجاف مذيبا" وبدرجة حرارة الغرفة . واخيرا" الخطوة الرابعة تضمنت الغلق الحلقي الضمني لحوامض الاميك الاحادية $[III]_{a-f}$ لنحصل على ستة مركبات من البايروميلت ثنائي الايميد غير المتماثل $[IV]_{a-f}$ بوجود مزيج من خلات الصوديوم وانهدريد الخليك عوامل مساعدة وبدرجة حرارة (80-90) ْم .
درست وشخصت جميع المركبات المحضرة باستعمال قياس درجات انصهارها والطرائق الطيفية المتمثلة بطيف الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي البروتوني (لبعض منها) .

الكلمات المفتاحية: انهدريد البايروميليمتاميك ،بايروملیت ثنائي الاميد ،بايروملیت ثنائي الايزو اميد .