Synthesis of New Asymmetrical Pyromellitdiimide and Their Amic Acids Containing Heterocyclic Unit

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Abstract

This work involves the synthesis and characterization of asymmetrical pyromellitdiimide derivatives $[VII]_{a-f}$ by four sequences steps reaction . One mole of pyromellitic dianhydride was reacted with one mole of various primary aromatic amines [2-aminothiazole , 2-aminobenzothiazole , 5-(4-amino phenyl)-1,3,4-oxadiazole-2-thiol , 4-nitro aniline , 4-chloro aniline , 4-toludine] in excess of dry acetone to produce six compounds (N-substituted-pyromellitamic monoacid) $[IV]_{a-f}$. These new compounds $[IV]_{a-f}$ were converted to the corresponding N- substituted- pyromellitmonoimide $[V]_{a-f}$ when heating then at (80-90) ^{0}C in sodium acetate-acetic anhydride system .The compounds $[V]_{d-f}$ were allowed to react with one mole of another primary amines (containing benzothiazole or 1,3,4-oxadiazole unit) in dry acetone to give new derivatives of amic acid $[VI]_{a-f}$ followed by intramolecular cyclization reaction of these compounds in sodium acetate-acetic anhydride system to yield the desired asymmetrical pyromellitdiimide derivatives $[VII]_{a-f}$, the above reactions can be summarized in Scheme 1.

Structures of the synthesized compounds have been ascertained by their melting points , C.H.N analysis , UV-Vis, FTIR and ^{1}HNMR spectroscopy.

Key words : Asymmetrical pyromellitdiimide, Pyromellitic dianhydride, pyromellitamic monoacid , pyromellitmonoimide.

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 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 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 . Moreover , 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 are 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]. Also they are used in microelectronics, as well as in nanotechnology as a matrix in the production of nanocomposite layers [11]. 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 [12] .

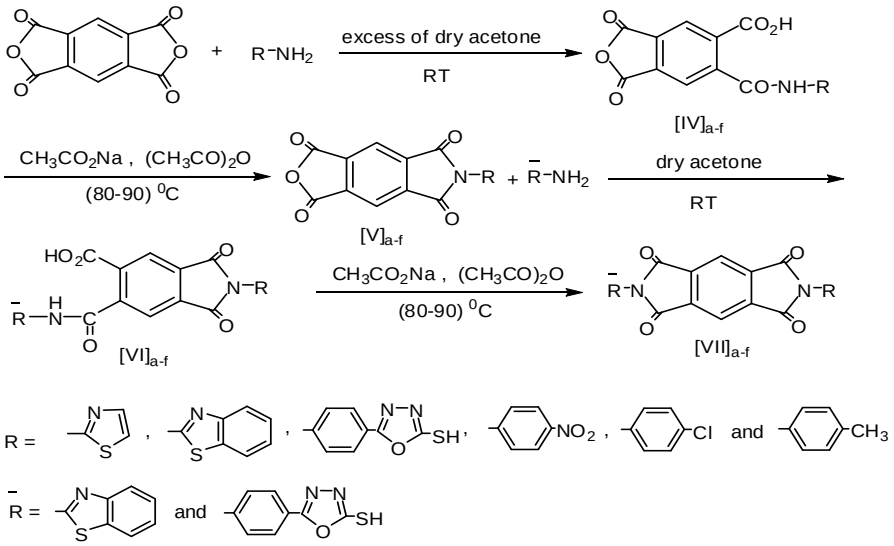
The aim of this work is the synthesis of novel asymmetrical pyromillitdiimide derivatives containing heterocyclic unit such as benzothiazole or 1,3,4-oxadiazole.

Experimental

Materials: All the chemicals were supplied from Merck , Fluka ,GCC and Aldrich chemicals Co. and used as received.

Techniques : FTIR spectra were recorded using potassium bromide discs on a shimadzu (8400S) and shimadzu (IR Prestige-21).^{1}HNMR spectra were carried out by company : Bruker , model: ultra shield 300 MHz , origin : Switzerland and are reported in ppm(S), DMSO was used as solvent with TMS as an internal standard. Measurements were made at Chemistry Department, AL-Albyat University, Elemental microanalysis (C.H.N) were carried out by a (C.H.N) company : Euro vector , model EA3000A origin : Italy . AL-Albayt University, Jordan . Uncorrected melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus .UV-Vis spectra of solution were performed on CEC1 7200 England Spectrophotometer using $CHCl_3$ as a solvent.

Synthesis methods



scheme (1)

Ethyl-4-Amino benzoate [I]: was prepared following the procedure by Vogel [13] .
4-amino phenyl hydrazide[II]: This compound was prepared according to the let.[14].
5-(4-amino phenyl)-1,3,4-Oxadiazole-2-thiol [III]: This compound was prepared according to the let. [15].

N-substituted -pyromellitamic monoacid[IV]$_{a-f}$:

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

Synthesis of N- substituted- pyromellitmonoimide[V]$_{a-f}$:

A (0.001 mole) of N-pyromellitamic monoacid was placed in (50 mL) round bottom flask with a condenser , 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 an 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 [V]$_{a-f}$ are listed in Table 2.

Synthesis of (N- substituted pyromellitmonoimide)-N¯- (substituted-pyromellitamic monoacid) [VI]$_{a-f}$:

These compounds were synthesized as described in procedure which is used for synthesized of monoimide[IV]$_{a-f}$. The physical data of (N- substituted -pyromellitmonoimide)-N¯- (substituted-pyromellitamic acid) [VI]$_{a-f}$ are listed in Table 3.

Synthesis of N,N''- disubstituted pyromellitdiimide [VII]$_{a-f}$:

These novel compounds were synthesized as described in procedure which is used for the synthesis of compounds [V]$_{a-f}$ .All these compounds were recrystalized from diethyl ether . The physical data of N,N''- disubstituted pyromellitdiimide [VII]$_{a-f}$ are listed in Table 4 .

Elemental analysis of compound [VII]$_a$:

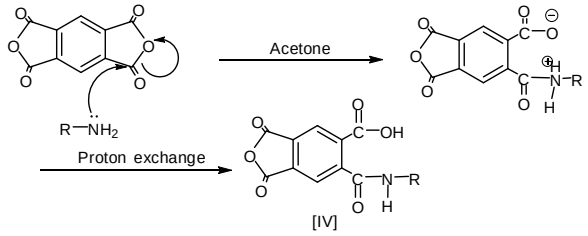
Theoretical : C% = 58.71 , H% = 2.14 , N% = 11.19

Found : C% = 57.83 , H% = 3.03 , N% = 11.98

Results and discussion

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

The amic acids [IV]$_{a-f}$ 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 [16] as follows , scheme 2.

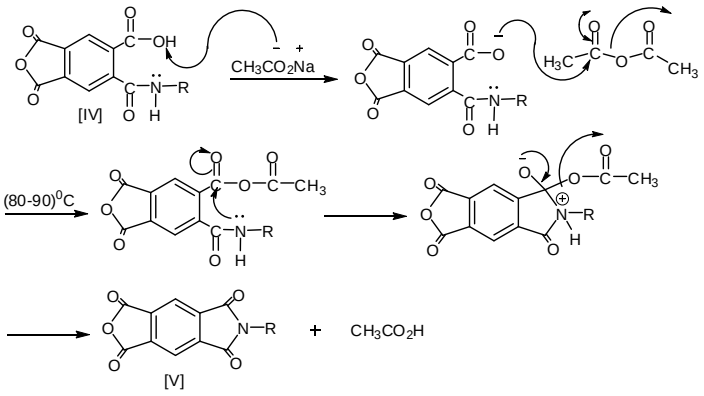


Scheme (2)

The structure of these acids[IV]$_{a-f}$ was studied by melting points , FTIR and UV-Vis 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 (2350-3530) cm^{-1}, C=O (carboxylic acid) at (1684-1709) cm^{-1} , C=O (amid) at (1632-1674) cm^{-1} and C=N (endocyclic) for [IV]$_{a-c}$ at (1609-1628) cm^{-1} of heterocyclic unit . And there is an appearance of two peaks in the region (1720-1838) cm^{-1} which could be attributed to stretching vibration of C=O (anhydride) symmetrical and asymmetrical , in addition to the appearance of absorption band around (1060) cm^{-1} for the C-O-C (cyclic) [17].

The UV-Vis spectroscopy of these compounds [IV]$_{a-f}$ exhibited the characteristic bands due to π-π* and n-π* transitions. The FTIR data of functional groups which are characteristic of the these new amic acids[IV]$_{a-f}$ and the UV-Vis data (λ_{max}) are listed in Table 5.

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



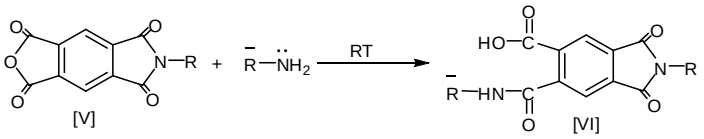
Scheme(3)

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

The FTIR spectra exhibited significant two peaks in the region (1674-1765) 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) together with the appearance of two peaks in the region (1709-1857) cm^{-1} which could be attributed to stretching vibration of C=O (cyclic anhydride) symmetrical and asymmetrical , the appearance of absorption band around (1050) cm^{-1} for the C-O-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 . The UV-Vis spectroscopy of these compounds $[V]_{a-f}$ exhibited the characteristic bands due to π-π* and n-π* transitions . The FTIR absorption bands data and the (λ_{max}) data of these compounds $[V]_{a-f}$ are listed in Table (6).

^{1}HNMR spectrum of compound $[V]_a$,showed the following characteristic chemical shift (DMSO as a solvent) : A doublet band at δ (7.85-7.87) ppm due to the two protons of thiazole aromatic ring , a singlet sharp signal at δ 8.48 ppm for the two protons of centre aromatic ring .

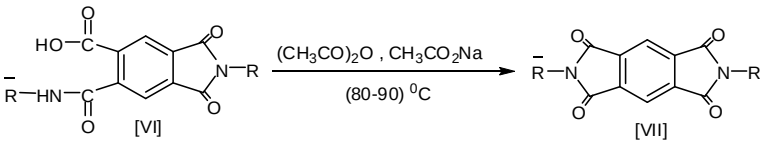
The amic acids $[VI]_{a-f}$ were synthesized by the reaction of one mole of N-substituted-pyromellitmonoimides $[V]_{d-f}$ with one mole of 2-amino benzothiazole or 5-(4-amino phenyl)-1,3,4-Oxadiazole-2-thiol in the presence of excess dry acetone as a solvent.



The structure of these compounds $[VI]_{a-f}$ was studied by melting point , FTIR , UV-Vis and ^{1}HNMR spectroscopy. The FTIR absorption-spectra, showed the disappearance of absorption peaks characterized of cyclic anhydride of pyromellitmonoimides $[V]_{d-f}$ together with the appearance of new absorption stretching bands due to O-H of carboxylic moiety at (2450-3520) cm^{-1}, C=O (carboxylic acid) at (1663-1692) cm^{-1} , C=O (amid) at (1635-1645) cm^{-1} and C=N (endocyclic) at (1609-1630) cm^{-1} of heterocyclic unit . Two peaks in the region (1695-1790) 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 UV-Vis spectrum data showed the characteristic (λ_{max}) in the region (254-320) nm . The FTIR absorption bands data and the UV-Vis spectrum data of these compounds $[VI]_{a-f}$ are listed in Table 7.

^{1}HNMR spectrum of compound $[VI]_e$, showed the following characteristic chemical shift (DMSO as a solvent) : A singlet sharp signal at δ 1.97 ppm could be assigned to the three protons of terminal CH_3 group , a singlet signal at δ 4.78 ppm could be attributed to the one proton of NH amide group . A singlet sharp signal at δ 7.46 ppm for two protons of centre aromatic ring , four aromatic protons appeared as mulitiplet bands at δ 7.0-7.3 ppm and a doublet signal at δ 7.59-7.62 ppm due to four aromatic protons of p-disubstituted benzene ring . Finally, a proton of carboxylic moiety (O-H) appeared at δ 10.07 ppm .

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



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

The FTIR spectra , exhibited significant two peaks in the region (1682-1786) 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 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 $[VI]_{a-f}$. The UV-Vis spectroscopy of these compounds $[VII]_{a-f}$ exhibited the characteristic bands due to π-π* and n-π* transitions. The FTIR absorption bands data and the (λ_{max}) data of these compounds $[VII]_{a-f}$ are listed in Table 8 .

^{1}HNMR spectrum of compound $[VII]_f$, showed the following characteristic chemical shift (DMSO as a solvent) : A singlet signal at δ 1.93 ppm is due to the three protons of terminal CH_3 group , one proton of S-H group appeared as a sharp signal at δ 2.2 ppm . A good singlet signal at δ 7.94 ppm is due to the two protons of centre aromatic ring , eight aromatic protons appeared as a pair of doublet signal at δ (7.07-7.2) ppm . Also, the ^{1}HNMR spectrum showed a sharp signal at δ 12.3 ppm which is due to the one proton of N-H group of oxadiazole ring[19] .

The elemental analysis (C.H.N) of compound $[VII]_a$ are consistent with their proposed structure .

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Table (1): The physical properties of N-substituted-pyromellitamic monoacid[IV]$_{a-f}$

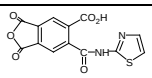
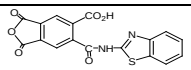
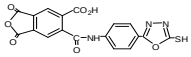
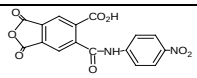
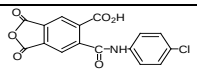
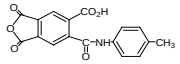
Com. No.	Nomenclature	Structural formula	Molecular formula	M.P ◦C	Yield %	Color
[IV]$_a$	N-(2-thiazole)-pyromellitamic monoacid.		$C_{13}H_6N_2O_6S$	>300	95	Pale yellow
[IV]$_b$	N-(2-benzothiazole)-pyromellitamic monoacid.		$C_{17}H_8N_2O_6S$	>300	99	White
[IV]$_c$	N-[4-(2-thiol-1,3,4-oxadiazole-5-yl)- phenyl]-pyromellitamic monoacid.		$C_{18}H_9N_3O_7S$	270 dec.	89	Orange
[IV]$_d$	N-(4-nitro phenyl)-pyromellitamic monoacid		$C_{16}H_8N_2O_8$	>300	96	Yellow
[IV]$_e$	N-(4-chlorophenyl)-pyromellitamic monoacid.		$C_{16}H_8NO_6CI$	>300	95	Pale grey
[IV]$_f$	N-(4-tolyl)-pyromellitamic monoacid.		$C_{17}H_{11}NO_6$	>300	98	Pale yellow

Table (2): The physical properties of N- substituted- pyromellitmonoimide[V]$_{a-f}$

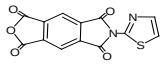
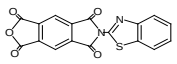
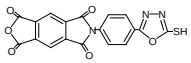
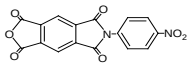
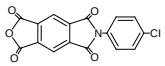
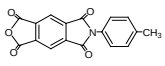
Com. No.	Nomenclature	Structural formula	Molecular formula	M.P ◦C	Yield %	Color
[V]$_a$	N-(2-thiazole)-pyromellitmonoimide.		$C_{13}H_4N_2O_5S$	>300	90	Yellow
[V]$_b$	N-(2-benzothiazole)-pyromellitmonoimide.		$C_{17}H_6N_2O_5S$	>300	78	Yellow
[V]$_c$	N-[4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitmonoimide.		$C_{18}H_7N_3O_6S$	150-52	84	Yellow
[V]$_d$	N-(4-nitro phenyl)]-pyromellitmonoimide.		$C_{16}H_6N_2O_7$	198-200	91	Yellow
[V]$_e$	N-(4-chlorophenyl)-pyromellitmonoimide.		$C_{16}H_6NO_5CI$	174-76	83	Dark grey
[V]$_f$	N-(4-tolyl)-pyromellitmonoimide.		$C_{17}H_9NO_5$	>300	60	Pale yellow

Table (3): The physical properties of (N- substituted-pyromellitmonoimide)-N¯-(substitutedpyromellitamic monoacid) $[VI]_{a-f}$

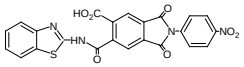
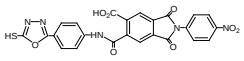
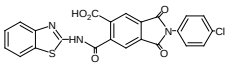
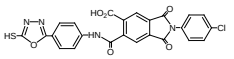
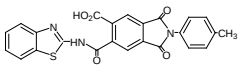
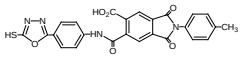
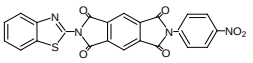
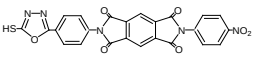
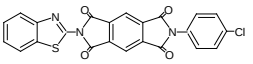
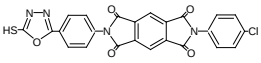
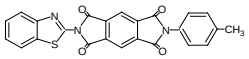
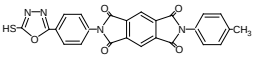
Com.No.	Nomenclature	Structural formula	Molecular formula	M.P ◦C	Yield %	Color
$[VI]_a$	N-(4-nitro phenyl)-pyromellitmonoimide, N¯-(2-benzothiozole)]-pyromellitamic monoacid.		$C_{23}H_{12}N_4O_7S$	164-66	98	Yellow
$[VI]_b$	N-(4-nitro phenyl)-pyromellitmonoimide ,N¯-[4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitamic monoacid.		$C_{24}H_{13}N_5O_8S$	192-94	96	Pale yellow
$[VI]_c$	N-(4-chloro phenyl)-pyromellitmonoimide , N¯-(2-benzothiazole) -pyromellitamic monoacid.		$C_{23}H_{12}N_3O_5SCl$	138-40	96	Pale grey
$[VI]_d$	N- (4-chloro phenyl)-pyromellitmonoimide , N¯- [4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitamic monoacid.		$C_{24}H_{13}N_4O_6SCl$	204-06	93	Orange
$[VI]_e$	N- (4-tolyl)-pyromellitmonoimide , N¯-(2-benzothiazole)-Pyromellitamic monoacid.		$C_{24}H_{15}N_3O_5S$	84-86	93	Pale yellow
$[VI]_f$	N-(4-tolyl)-pyromellitmonoimide , N¯-[4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitamic monoacid.		$C_{25}H_{16}N_4O_6S$	182-83	90	Orange

Table (4): The physical properties of N,N¯- disubstituted pyromellitdiimide[VII]$_{a-f}$

Com. No.	Nomenclature	Structural formula	Molecular formula	M.P ◦C	Yield %	Color
[VII]$_a$	N-(4-nito phenyl), N¯-(2-benzothiazole)-pyromellitdiimide		$C_{23}H_{10}N_4O_6S$	170-72	90	Yellow
[VII]$_b$	N-(4-nitro phenyl) N¯-[4-(2-thiol-1,3,4-ox-adiazole-5-yl)-phenyl]-pyromellitdiimide.		$C_{24}H_{11}N_5O_7S$	150-52	87	Yellow
[VII]$_c$	N-(4-chloro phenyl) N¯-(2-benzothiazole)-pyromellitdiimide.		$C_{23}H_{10}N_3O_4SCl$	178-80	90	Yellow
[VII]$_d$	N-(4-chloro phenyl) N¯-[4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitdiimide.		$C_{24}H_{11}N_4O_5SCl$	118-20	90	Yellow
[VII]$_e$	N-(4-tolyl) N¯-(2-benzothiazole)]-pyromellitdiimide.		$C_{24}H_{13}N_3O_4S$	129-31	90	Yellow
[VII]$_f$	N-(4-tolyl) N¯-[4-(2-thiol-1,3,4-oxadiazole-5-yl)-phenyl]-pyromellitdiimide.		$C_{25}H_{14}N_4O_5S$	148-50	85	Pale yellow

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

Comp. No.	λ_{ma} (nm)	VN-H	VO-H	VC=O cyclic anhydride asym.,sym	VC=O carboxylic	VC=O amid	VC=N endocyc.	VC=C arom.	VC-O-C cyclic
[IV]$_a$	274	3302	3390-2350	1830,1720	1690	1655	1625	1580	1055
[IV]$_b$	248	3285	3350-2350	1815,1780	1686	1659	1628	1591	1051
[IV]$_c$	307	3399	3530-2380	1838,1750	1704	1674	1609	1580	1072
[IV]$_d$	353	3217	3540-2410	1836,1785	1705	1632		1597	1036
[IV]$_e$	253	3220	3350-2500	1810,1770	1709	1640		1585	1042
[IV]$_f$	248	3277	3400-2500	1790,1742	1684	1655		1589	1068

Table(6): Characteristic FTIR absorption bands and UV data (λ_{max}) of compounds $[V]_{a-f}$

Comp.No.	λ_{max} (nm)	VC-H arom.	VC=O cyclic anhydride asym., sym.	VC=O Imide asym., sym.	VC=N endocyc.	VC=C arom.	VC-O-C cyclic	VC-N-C cyclic Asym., Sym.	Other
$[V]_a$	296	3107	1857,1782	1732,1685	1640	1605	1066	1171,736	
[V] b	276	3048	1790,1710	1744,1674	1639	1597	1038	1161,768	
$[V]_c$	302	3101	1820,1730	1765,1695	1624	1593	1083	1151,756	VN-H:3339 VC=S:1306 VS-H: 2522
$[V]_d$	317	3096	1780,1745	1755,1684		1599	1035	1178,750	4-NO_2: 1506,1304
$[V]_e$	263	3075	1847,1775	1735,1675		1603	1040	1171,752	4-Cl:970
$[V]_f$	259	3060	1780,1709	1740,1680		1603	1045	1159,756	VC-H aliphatic 2954-2831

Table(7): Characteristic FTIR absorption bands and UV data (λ_{max}) of compounds$[VI]_{a-f}$

Comp.No.	λ_{max} (nm)	VN-H arom.	VO-H	VC=O Imide asym.,sym	VC=O carboxyl	VC=O amide	VC=N endocyc.	VC=C arom.	VC-N-C cyclic asym.,sym	Other
$[VI]_a$	320	3277	3500-2480	1790,1740	1682	1641	1620	1597	1182,746	4- NO_2 : 1503, 1304
[VI] b	316	3279	3480-2515	1736,1700	1682	1635	1616	1600	1173,748	4- NO_2: 1503,1304 VN-H: 3352 VC=S:1334
$[VI]_c$	268	3194	3500-2500	1755,1715	1670	1645	1609	1595	1180,745	4-Cl : 905
$[VI]_d$	318	3352	3520-2400	1745,1720	1692	1665	1618	1600	1171,745	4-Cl: 935, VN-H : 3336, VC=S:1308
$[VI]_e$	254	3302	3400-2500	1738,1715	1667	1645	1630	1604	1175,743	aliphatic: 2924-2855
$[VI]_f$	306	3292	3400-2450	1740,1695	1663	1640	1612	1595	1171,752	VC-H aliphatic 2953-2868, VN-H:3352 VC=S:1321

Table(8): Characteristic FTIR absorption bands and UV data(λ_{max}) ofcompounds[VII]$_{a-f}$

Comp. No	λ_{ma} (nm)	VC-H arom	VC=O Imide asym.,sym	VC=N endocyc.	VC=C arom.	VC-N-C cyclic Asym., Sym.	Other
[VII] $_a$	300	3065	1740,1682 1730,1670	1640	1599	1178,766 1155,760	4- NO_2:1506, 1304
[VII] $_b$	308	3100	1746,1695 1732,1682	1616	1599	1179,754 1163,735	4- NO_2:1503, 1304, VN-H : 3337 ,VC=S:1330
[VII] $_c$	276	3061	1786,1696 1717,1674	1640	1597	1171,760 1160,725	4-Cl : 935
[VII]$_d$	302	3100	1750,1695 1734,1668	1618	1593	1178,752 1165,740	4-Cl : 933 , VN-H : 3337 ,VC=S:1315
[VII]$_e$	280	3060	1740,1697 1720,1670	1635	1602	1170,768 1160,760	aliphatic: 2970-2920
[VII]$_f$	302	3100	1745,1695 1734,1670	1622	1593	1175,755 1170,735	aliphatic: 2928-2855, VN-H : 3339 ,VC=S:1317

تحضير مركبات البايروميلت ثنائية الايميد غير المتماثلة وحوامض الاميك لها الجديدة التي تحتوي على حلقة غير متجانسة

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استلم البحث في : 10 أيلول 2013 ، قبل البحث في: 4 كانون الأول 2013

الخلاصة

تضمن هذا البحث تحضير وتشخيص مشتقات البايروميلت ثنائية الايميد غير المتماثلة $[VII]_{a-f}$ بتفاعل انتقائي مكون من أربع خطوات متتابعة الأولى تبدأ بمفاعلة مول واحد من البايروميليتك ثنائي الانهدريد مع مول واحد من الأمينات الأولية الاروماتية المتنوعة (2-امينو ثايازول و 2-امينو بنزوثايازول و 2-الكيل ثايو-5-(4-امينوفنيل)-1، 3، 4– اوكسادايازول و 4-نايتروأنيلين و 4-كلورو أنيلين ، 4-تولويدين) وتكوين حوامض الاميك الأحادية $[IV]_{a-f}$ باستعمال وفرة من الأسيتون الجاف مذيباً. والثانية تحويل المركبات المحضرة $[IV]_{a-f}$ إلى N- بايروميليت أحادي الايميد $[V]_{a-f}$ وذلك بتسخينها بدرجة حرارة (80-90) °م في مزيج من خلات الصوديوم وانهدريد الخليك. أما الخطوة الثالثة فتضمنت تفاعل مول واحد من مركبات البايروميليت أحادية الايميد $[V]_{d-f}$ مع مول واحد من أمينات أولية تحتوي حلقة غير متجانسة (بنزوثايازول و 1، 3، 4-اوكسادايازول) لتعطي مشتقات جديدة من حوامض الاميك $[VI]_{a-f}$ باستعمال وفرة من الأسيتون الجاف مذيبا .

وأخيراً الخطوة الرابعة تضمنت الغلق الحلقي الضمني لحوامض الاميك الأحادية $[VI]_{a-f}$ لنحصل على ستة مركبات من البايروميلت ثنائي الايميد غير المتماثل $[VII]_{a-f}$ بوجود مزيج من خلات الصوديوم وانهدريد الخليك عوامل مساعدة وبدرجة حرارة (80-90) °م .

درست وشخصت جميع المركبات المحضرة باستعمال قياس درجات انصهارها والتحليل الدقيق للعناصر والطرائق الطيفية المتمثلة بطيف الأشعة فوق البنفسجية، وطيف الأشعة تحت الحمراء، وطيف الرنين النووي البروتوني للبعض منها .

الكلمات المفتاحية : بايروميليت ثنائي الايميد الغير متماثل, بايروميليتيك ثنائي الانهدريد , حامض البايرميلتاميك الأحادي ، بايروميليت أحادي الايميد .