



Evidence Supports The Formation Of Isoimides Derived From Pyromellitic Dianhydride

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Abstract

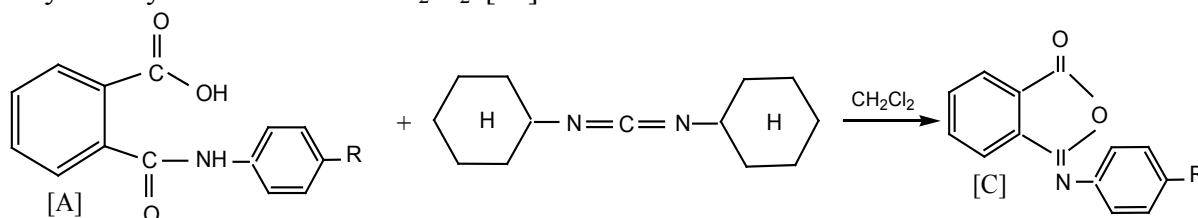
Some new mono isoimides of asymmetrical pyromellitdiimide derived from pyromellitic dianhydride were synthesized and studied by their melting points , FTIR , and ¹HNMR spectroscopy and C.H.N analysis (for some of them) and it was proved that the mechanism of the formation of these isoimides followed , the mechanism suggested by Cotter et al . by using N, N⁻ dicyclohexylcarbodiimide as dehydrating agent , in spite of the groups attached to the phenyl moiety as mentioned in literatures .

Keyword: pyromellitic dianhydride , pyromellit imide , isoimide

Introduction

substituted cyclic imides are heterocyclic compounds represent an important class of bioactive molecules that show a wide range of pharmacological activities [1] such as androgen receptor antagonistic [2], anti-inflammatory, anxiolytic [3], antiviral [4], antibacterial [5], and antitumor [6] properties. Moreover, they are synthetic precursors with application in organic synthesis, supermolecular chemistry, polymer synthesis, and for the development of new materials and molecular electronic device [7]. Aromatic polyimides that derived from pyromellitic dianhydride are widely used in advanced technology 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 [8,9]. Also they are used in microelectronics, as well as in nanotechnology as a matrix in the production of nanocomposite layers [10].

The new isoimide [C] was prepared by the reaction of amic acid [A] with N,N-dicyclohexyl carbodiimide in CH_2Cl_2 [11].



The aim of this work is synthesis and characterization of isoimide derivatives and to prove that these isoimides derived from Pyromellitic dianhydride follow the same mechanism if and only if there were attracting or repelling group attached to the phenyl moiety.

Experimental part

a) FTIR spectra were recorded by using potassium bromide disc on a shimadzu (8400S) spectrophotometer and Shimadzo (Ir prestige-21) spectrophotometer.

b) ^1H NMR spectra were carried out by company: Bruker, model: ultra shield 300 MHz, origin: Switzerland and are reported in ppm(S), DMSO was used as a solvent with TMS as an internal standard were made at chemistry department, AL-Bayt University, Jordan.

c) Melting Points Uncorrected melting points were determined by using Hot-stage, Gallen Kamp melting point apparatus.

Synthesis of Asymmetrical [N-(4-substituted phenyl) - N'-(4-substituted phenyl)-iso imino]-pyromellitimide :

Synthesis of N-substituted -pyromellitic monoacid [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 which has been added to the solution was filtered off from any precipitate and the clear solution was evaporated under reduced pressure and the product filtered [12], washed and recrystallized from chloroform. The physical data of N-substituted -pyromellitic monoacid [I]_{a-d} are listed in Table 1.

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

A (0.001 mole) of N-pyromellitic 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) °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,

recrystallized from acetone . The physical data of N- substituted- pyromellitimide [II]_{a-d} are listed in Table 1 .

Synthesis of (N- substituted-pyromellitimide)-N⁻- (substituted-pyromellitic monoacid) [III]_{a-d}- [VI]_{a-d}

To a solution of N- substituted- pyromellitimide [II]_{a-d} (0.001mol) in (30mL) acetone , an amine (0.001 mole) in (30mL) acetone was added dropwise during about 6 hrs. After all the amine has been added , the mixture was left for 24 hrs then it was filtered off and recrystallized from acetone . The physical data of (N- substituted - pyromellitimide)-N⁻- (substituted-pyromellitic acid) .

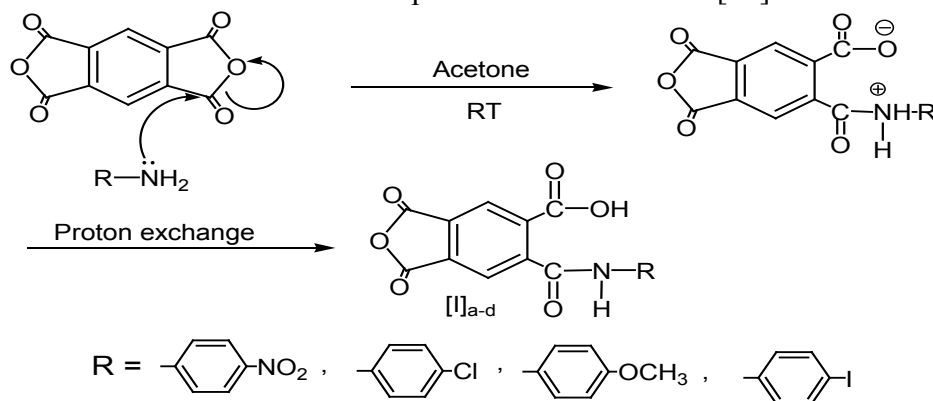
[III]_{a-d}- [VI]_{a-d} are listed in Table 1 .

Synthesis of [N-(4-substituted phenyl) -N⁻- (4-substituted phenyl)-iso imino]-pyromellitimide [VII]_{a-d}- [X]_{a-d}

Aslurry (N- substituted-pyromellitimide)- N⁻- (substituted-pyromellitic monoacid) [III]_{a-f} (0.001 mole) in (75 ml) di chloromethane was stirred at room temperature , and a solution of N, N⁻ - dicyclohexylcarbodiimide (0.01 mole) in dichloromethane was add dropwise during (30 min) the mixture was stirred for 24 hours then filtered of from the precipitated dicyclohexyl urea , the filtrate was evaporated under reduced pressure and the product worked out as described in each separate case . N- (4-substitutedphenyl) - N⁻- (4- substitutedphenyl) – isoimino - pyromellitimide [VII]_{a-d}- [X]_{a-d} are listed in table 1.

Results and Discussion

The amic acids [I]_{a-d} were synthesized by the reaction of one mole of pyromellitic dianhydride with one mole of different amines in the presence excess of dry acetone as a solvent . The mechanism involves nucleophilic addition reaction[13] as follows :



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

The FTIR absorption-spectra showed the disappearance of absorption bands due to NH₂ 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[14] which could be attributed to stretching vibration of C=O (anhydride) symmetry and asymmetry , in addition appearance of absorption band around (1040) cm⁻¹ for the C-O-C (cyclic) [15]. The FTIR absorption bands data of these compounds [I]_{a-d} are listed in Table 3.

¹HNMR spectrum of compound [I]_d , (Figure 3.5) showed the following characteristic chemical shift (DMSO as a solvent) : 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 at δ 7.0-7.3 ppm due to p-

disubstituted benzene ring , and finally, a proton of carboxylic moiety (O-H) appeared at δ 10.07 ppm .

N-substituted-pyromellitimonoimide [II]_{a-d} were obtained by the intramolecular cyclization reaction of N-substituted-pyromellitic monoacid [II]_{a-d} in acetic anhydride and sodium acetate at (80-90) °C .

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

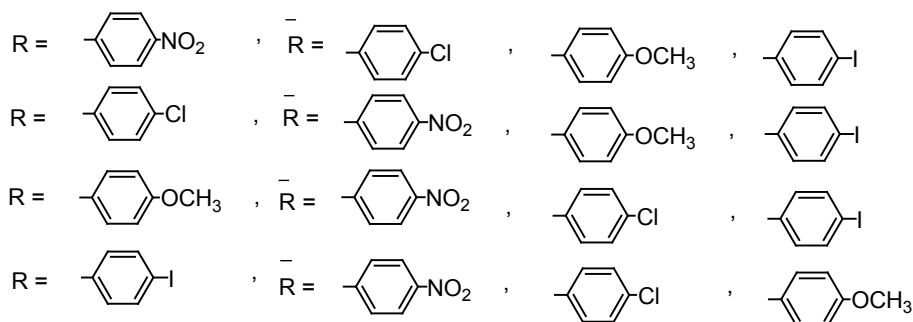
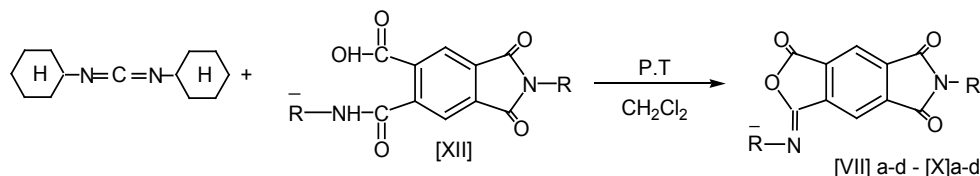
The FTIR spectra exhibited significant two peaks in the region (1675-1710) cm⁻¹ which could be attributed to stretching vibration of the carbonyl group (imide cyclic) and two absorption bands around 1170 cm⁻¹ and 755cm⁻¹ for asymmetry and symmetry of C-N-C (cyclic) [16]together with the appearance of two peaks in the region (1709-1800) cm⁻¹ which could be attributed to stretching vibration of C=O (cyclic anhydride) symmetry and asymmetry , appearance absorption band around (1040) 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 FTIR absorption bands data of these compounds [II]_{a-d} are listed in Table 3.

¹HNMR spectrum of compound [II]a showed the following characteristic chemical shift (DMSO as a solvent) : A singlet sharp signal at δ 7.9 ppm for the two protons of centre aromatic ring , and four aromatic protons appeared as multiplet bands at δ 7.8-7.88 ppm due to the p-disubstituted benzene ring .

The amic acids [III]_{a-d}- [VI]_{a-d} were synthesized by the reaction of one mole of N-substituted-pyromellitimonoimide [II]_{a-d} 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-d}- [VI]_{a-d} was studied by melting point , FTIR and ¹HNMR spectroscopy . The FTIR absorption-spectra showed the disappearance of absorption peaks characterized of cyclic anhydride of pyromellitimonoimides [III]_{a-d}- [VI]_{a-d} 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 asymmetry and symmetry of C-N-C (cyclic) . The FTIR absorption bands data of these compounds [III]_{a-d}- [VI]_{a-d} are listed in Table 4.

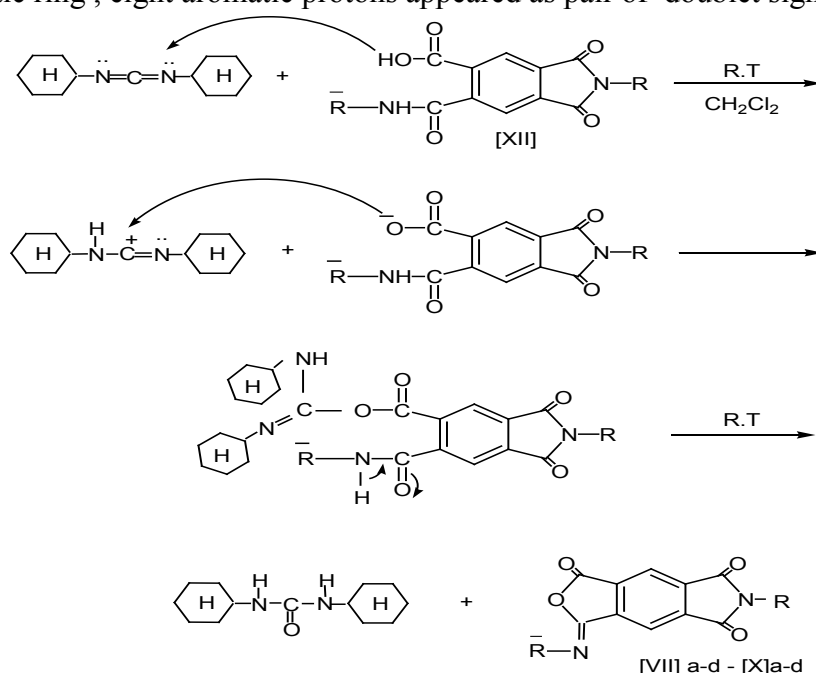
[N-(4-substituted phenyl) - N⁻ - (4-substituted phenyl)-iso imino]- pyromellitimide [VII]_{a-d} - [X]_{a-d} were obtained by the intramolecular cyclization reaction of amic acid [III]_{a-d}- [VI]_{a-d} in N, N⁻ - dicyclohexylcarbodiimide and CH₂Cl₂ .



The structure of these compounds [VII]_{a-d} - [X]_{a-d} was studied by melting point , FTIR and ¹HNMR 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 asymmetry and symmetry of C-N-C (cyclic) , in addition to ,a good peak around 1625 cm⁻¹ for C=N group and a stretching band around 1720 cm⁻¹ due to C=O group of lactone ring . 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-d}- [VI]_{a-d}. The FTIR absorption bands data of these compounds [VII]_{a-d} - [X]_{a-d} are listed in Table 5 .

¹HNMR spectrum of compound [VII]_a , showed the following characteristic chemical shift (DMSO as a solvent) : a singlet signal at δ 1.93 ppm due to the three protons of terminal CH₃ group , a good singlet signal at δ 7.94 ppm due to the two protons of centre aromatic ring , eight aromatic protons appeared as pair of doublet signal at δ (7.07-7.2) ppm.



Hence, the formation of the compound [VII]_a which contains the (-CH₃) group attached to the phenyl , and the formation of the compound [X]_c which contains (-NO₂) group attached to the phenyl ,will sport the above mechanism , which wasn't affected by the type of the group attached to the phenyl group which will be forbid the formation of isoimide due to cross hyper conjugation as mentioned previously .

And , upon this phenomena it is possible to synthesis any type of isoimide derived from any amic acid by using N, N' - dicyclohexylcarbodiimide as dehydrating agent .

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Table (1) :Physical properties of new synthesized compounds [I]_{a-d} - [X]_c.

Com. No.	Nomenclature	Structural formula	Molecular formula	M.P °C	Yield %	Color
[I] _a	N-(4-nitro phenyl)-pyromellitic monoacid		C ₁₆ H ₈ N ₂ O ₈	>300	96	Yellow
[I] _b	N-(4-chlorophenyl)-pyromellitic monoacid.		C ₁₆ H ₈ NO ₆ Cl	>300	95	Pale grey
[I] _d	N-(4-iodophenyl)-pyromellitic monoacid.		C ₁₆ H ₈ NO ₆ I	>300	86	Pale Brown
[II] _a	N-(4-nitro phenyl)-pyromellitimide.		C ₁₆ H ₆ N ₂ O ₇	198-200	91	Yellow
[II] _b	N-(4-chlorophenyl)-pyromellitimide.		C ₁₆ H ₆ NO ₅ Cl	174-176	83	Dark grey
[II] _d	N-(4-iodophenyl)-pyromellitimide		C ₁₆ H ₆ NO ₅ I	183-185	79	Pale Peggy
[III] _a	N-(4-nitro phenyl)-pyromellitimide, N ⁻ -(4-tolyl) -pyromellitic monoacid.		C ₂₃ H ₁₅ N ₃ O ₇	300 dec.	91	Pale Brown
[IV] _b	N-(4-chloro phenyl)-pyromellitimide, N ⁻ -(4-methoxy phenyl)-pyromellitic monoacid		C ₂₃ H ₁₅ N ₂ O ₆ Cl	>300	83	Pale Peggy
[VI] _c	N-(4-iodophenyl)-pyromellitimide, N ⁻ -(4-nitro phenyl) -pyromellitic monoacid.		C ₂₂ H ₁₂ N ₃ O ₇ I	208-210	81	Yellow
[VII] _a	[N-(4-nitro phenyl)- N ⁻ -(4-tolyl)-isoimino]-pyromellitimide .		C ₂₃ H ₁₃ N ₃ O ₆	213-215	95	White
[X] _c	[N-(4-iodo phenyl)- N ⁻ -(4-nitro phenyl)- isoimino]-pyromellitimide .		C ₂₂ H ₁₀ N ₃ O ₆ I	178-180	86	Dark Yellow

Table (2): Characteristic FTIR absorption bands of compounds [I]_{a,b,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	3643	050-24313	1760,1705	1690	1632	1570	1035
[I] _b	8532	4353350-2	1749,1732	1681	1665	1595	1042
[I] _d	3063	405-23753	1775, 1710	1688	1674	1580	1061

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

Com p.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	3094	1805,1740	1769,1682	1599	1037	1179,768	4-NO ₂ : 1504,1303
[II] _b	3076	1815,1769	1735,1667	1595	1050	1171,752	4-Cl : 970
[II] _d	3065	1835,1775	1745,1667	1597	1045	1180,765	VC-H aliphatic 2980-2837

Table(4): Characteristic FTIR absorption bands of compounds [III]_a, [IV]_b, [VI]_c

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	3308	3335-2420	1682,1649	1638	1618	1599	1180,750	4-NO ₂ : 1503,1303
[IV] _b	3304	3405-2435	1775,1701	1666	1647	1597	1171,754	4-Cl : 970
[VI] _c	3317	3415-2465	1775,1799	1668	1631	1598	1180,775	

Table (5): Characteristic FTIR absorption bands of compounds [VII]_a , [XI]_c

Comp. No.	Characteristic bands FTIR spectra (cm ⁻¹)						
	VC-H arom.	VC=O Imide, asym.,sym.	VC=O Ester	VC=N.	VC=C arom	VC-N-C cyclic asym., sym.	Other
[VII] _a	3098	1735,1715	1682	1626	1599	1179,750	4-NO ₂ : 1506,1306
[XI] _c	3279	1735,1668	1717	1626	1578	1180,750	

اثباتات على تكوين مركبات الايزو ايميد المشتقة من انهيدريد البايرومليتاميك

شيماء طه حسين

عماد تقي علي

خالد فهد علي

جمبد هرمز توما

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

استلم البحث في: 12 ايلول 2012 - قبل البحث في: 22 تشرين الأول 2012

الخلاصة

حضرت بعض مشتقات الايزو ايميدات الجديدة المشتقة من انهيدريد البايرومليتاميك (اللامائي) . درست خواصها من خلال درجات الانصهار، واطياف الاشعة تحت الحمراء ، وتحليل العناصر C.H.N ، وطيف الرنين النووي المغناطيسي (البعض منها) وتم التثبيت بان ميكانيكية التفاعل المعتمدة من Cotter وجماعته يمكن اعتمادها على جميع الامينات المستعملة وبصرف النظر عن نوع المجموعة الموجودة على مجموعة الفينيل الاروماتية سواء كانت مجموعة ساحبة او دافعة ، وذلك من خلال استعمال الـ N^- ، N - داي سايكلو هكسيل كاربودايميد مادة (ساحبة) نازعه للماء من دون سواها من المواد الاخرى المستعملة في الادبيات .

الكلمات المفتاحية : انهيدريد البايرومليتاميك ، بايرومليت احادي الايميد ، ايزو ايميد