

Synthesis and Identification of Pyromellitic diacids and Pyromellitdiimides derivatives.

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Abstract

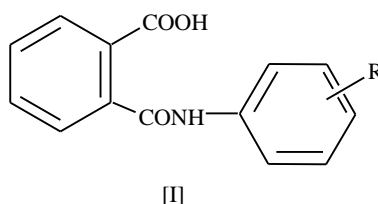
New derivatives of pyromellitic diacids and pyromellitdiimides have been prepared by the reaction of one mole of pyromellitic dianhydride with two moles of aromatic amines, these derivatives were characterized by elemental analysis, FT-IR and melting point.

الخلاصة

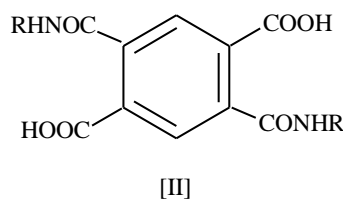
تم في هذا البحث تحضير وتشخيص بعض مركبات حامض البايرومليتاميك الثنائية والبايرومليت ايميد الثنائي من تفاعل (١) مول من البايرومليتاميك داي انهدريد مع (٢) مول من امينات اورماتية وشخصت هذه المركبات بالطرق الطيفية المتوفرة ، طيف الاشعة تحت الحمراء ، تحليل العناصر وقياس درجة الانصهار .

Introduction

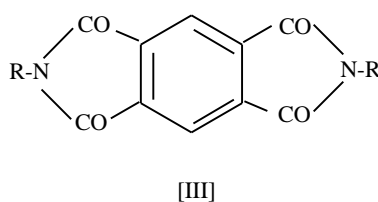
Phthalamic acids [I] were obtained from the reaction of arylamines with phthalic anhydride [Sherrill , 1928; Allen ,1955; Ponos, 1960; Subbarao ,1962].



Diamic acids synthesized from pyromellitic dianhydride (PMDA) have also prepared from the reaction of amines (2 moles) with (PMDA) (1 mole), Dine et al [dine – hart and Wright,1967] have given the structure [II] for such diamic acids.



Diamic acids on dehydration using acetic anhydride, sodium acetate system yielded, the corresponding diimides [III] [Awad , and Ali, 1977; Cotter *et al.*, 1961]



The synthesis of pyromellitic diacids and pyromellitdiimides have been steadily widening their application in different fields such as:

Excited doublet states of electrochemically [David Gosztola, *et al.*,2000], preparation new alkali-soluble polyimides and alternating multilayer nano-films therefrom [Kyung and follow,2004], neutral [2] Rotaxanes [Takahiro Iijima, Scott A. Vignon, and follow ,2004], formation sole products [Valdimir *et al.*,2008], switchable self-Assembly of Donor-Acceptor Metallo-[2] catenanes [Gayane and follow,2008], used in synthesized viaslippage a neutral rotaxane [Richie Kohman, 2005], using for high Mobility n-channel transistor [Qingdong and Follow,2008], as curing behaviour and thermal stability of DGEBA [Darshan and follow,2009], has proven to be a valuable architectural tool in the preparation of large macrocycles [Gondo and follow ,2009], photophysical Behavior of Heteroduplexes [ZHAO Shu-min And follow ,2009], has arisen because of their potential applications for supramolecular and new functional materials [C. Ge and follow ,2009], can be used as liquid-phase, homogeneous catalysts or can be supported on a solid carrier to provide a heterogeneous catalyst [Cheng *et al.*,2009], aqueous suspension prepregging [Liliana Burakowski Nohara and follow,2010].

Experimental Section:

A- Materials:

All chemicals used without further purification pyromellitic dianhydride (Fluka), acetone (Fluka), 2,3-dimethyl aniline (BDH), 4-Iodo aniline (BDH), O-Anisidine (BDH), M-Anisidine (BDH), O-Toluidine (BDH), Acetic anhydride (Fluka), sodium acetate anhydrous (Fluka).

B- Instrumentation:

Melting points were recorded using electro thermal melting point apparatus- Infrared spectra were recorded with (SHIMADZU-FT-IR-8400) in Ibn-Al-Haitham College of Education. Elemental analysis were done on EURO EA instrument in Al-Mustansiriya University.

Synthesis of N,N'-Pyromellitic diacid (II) [Mohammad J. Al-Azzawi and follow,1988]

A solution of pyromellitic dianhydride (PMAD) (1 mole) in (10 ml) acetone was stirred , then a solution of amine (2 moles) in (10 ml) acetone was added drop wise for 2hr. (Table 1). The mixture was left at room temperature for 12hr, with continuous stirring, then the coloured product was filtered, refluxed with (10 ml) ether, (10 ml) acetone, and (10 ml) benzene for 20min, each to remove the remaining starting materials and impurities present after which the product was dried by vacuum oven.

Synthesis of N,N'-pyromellitdiimide (III) [Mohammad J. Al-Azzawi and follow,1988]:

(1 mole) of diamic acid (II) obtained, was placed in (100 ml) round bottom flask fitted with mechanical stirrer, and a mixture of freshly fused sodium acetate (1 mole) in (10 ml) acetic anhydride, was added. The mixture was heated up to (90 °C) in a water-Bath with continuous stirring for 2hr. The mixture was stirred for another 2hr at room temperature, then poured on crushed ice (10 fold) before being filtered. The residue was then refluxed with (10 ml) benzene, (10 ml) chloroform, (10 ml) acetone, (10 ml) dichloromethane, (10 ml) ethanol and finally with (10 ml) ether for (10 min) each .

Results and Discussion

The dehydration of diamic acids was carried out using a mixture of acetic anhydride-sodium acetate system according to the following sequence [Robert Thornton Morrison and Robert Neilson Boyd,2007]:

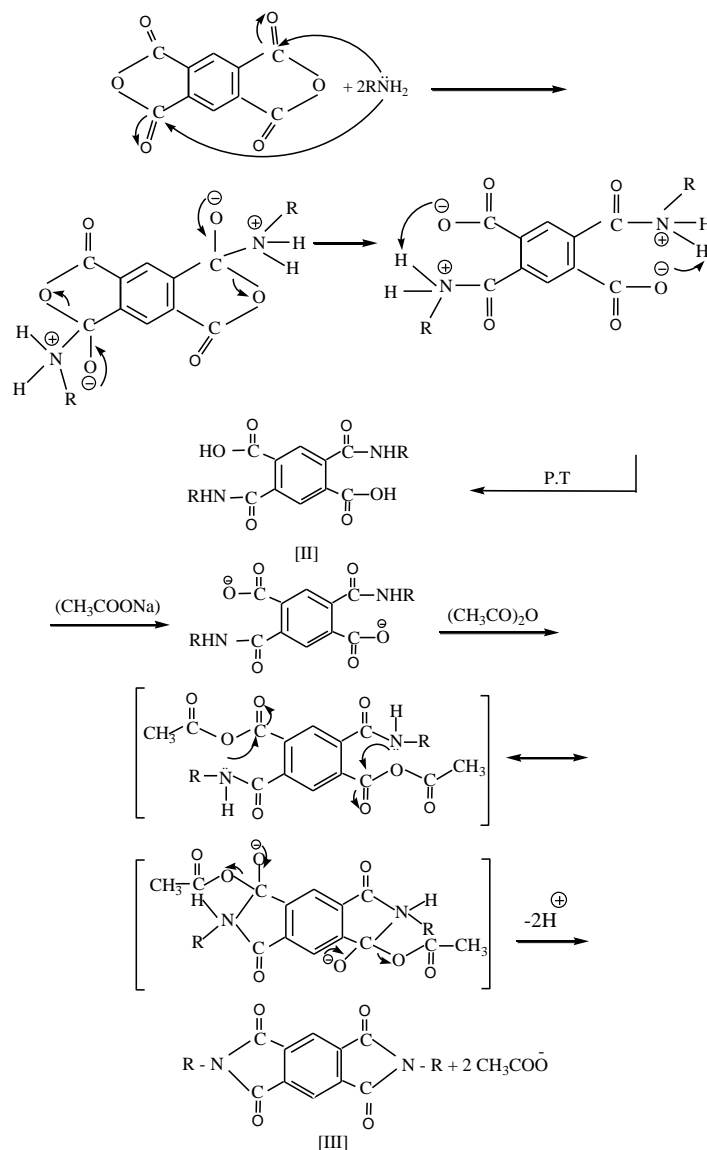


Table 1: The pyromellitimic diacids and pyromellitdiimides synthesized.

Comp. No.		Comp. No.	
1	R = o-xylene-	6	R = o-xylene-
2	R = p-Iodo phenyl-	7	R = p-Iodo phenyl-
3	R = m-Anisole-	8	R = m-Anisole-
4	R = o-Anisole-	9	R = o-Anisole-
5	R = o-Toluene-	10	R = o-Toluene-

The identification of the pyromellitic diacid and pyromellitdiimides was essentially based on C, H, N analysis, Melting point and their IR spectra (Tables 2 and 3).

Table 2: Structure confirmation of the synthesized compounds by M.P and C, H, N analysis.

Compounds	M.P °C	Yield	C% calculate (found)	H% calculate (found)	N% calculate (found)
C ₂₆ H ₂₄ N ₂ O ₆	> 300	89	67.82 (67.32)	5.21 (4.98)	6.08 (5.87)
C ₂₂ H ₁₄ N ₂ O ₆ I ₂	210 dec	77	40.36 (40.06)	2.14 (1.98)	4.28 (4.08)
C ₂₄ H ₂₀ N ₂ O ₈	> 300	78	62.06 (61.85)	4.31 (4.02)	6.03 (5.81)
C ₂₄ H ₂₀ N ₂ O ₈	> 300	88	62.06 (61.90)	4.31 (4.05)	6.03 (5.86)
C ₂₄ H ₂₀ N ₂ O ₆	220-222	92	66.66 (66.12)	4.62 (4.45)	6.48 (6.14)
C ₂₆ H ₂₀ N ₂ O ₄	> 250	89	73.58 (73.22)	4.71 (4.31)	6.60 (6.25)
C ₂₂ H ₁₀ N ₂ O ₄ I ₂	> 250	92	42.71 (42.23)	1.61 (1.33)	4.53 (4.29)
C ₂₄ H ₁₆ N ₂ O ₆	> 250	75	67.28 (66.90)	3.73 (3.26)	3.27 (3.06)
C ₂₄ H ₁₆ N ₂ O ₆	> 250	81	67.28 (66.94)	3.73 (3.33)	3.27 (3.10)
C ₂₄ H ₁₆ N ₂ O ₄	> 250	83	72.72 (72.22)	4.04 (3.75)	7.07 (6.68)

Spectra studies

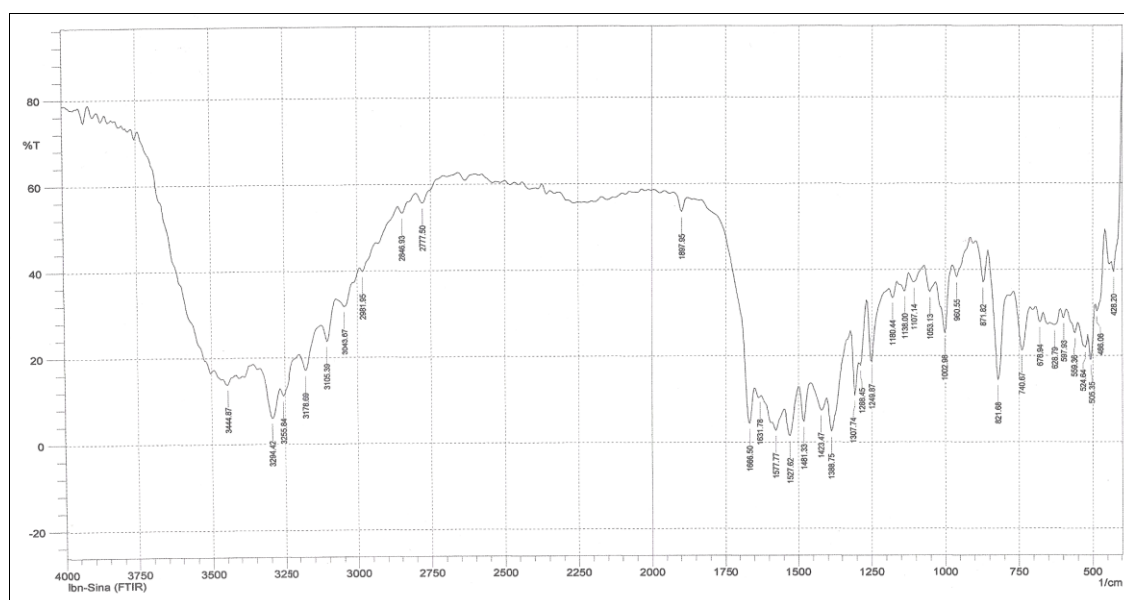
Infrared spectra

Figures (1, 2, 3, 4 and 5) show the absorption spectra of (P₁, P₂, P₃, P₄ and P₅) exhibited broad band near the region (2777 – 3444) cm⁻¹ due to stretching vibration of (O-H) carboxylic acid groups often interferes with (C-H) absorptions and (N-H) amide groups for all compounds. Bands near the region (1639-1720)cm⁻¹ were assigned the vibration modes of $\left(\overset{\text{O}}{\parallel} \text{C} - \right)$ acid groups [Silverstion, R.M., Bassler and C.G. Morril,1923,1981, Dyer. R. J.,1965, Dudley. H. Williams and Ian Fleming,1995, J. Michael Hollas,2008] for all compounds. Bands near the region (1558-1654)cm⁻¹ were assigned to the vibrational modes of $\left(\overset{\text{O}}{\parallel} \text{C} - \right)$ amide groups for all compounds (Table 3).

The bands related to acid and amide groups disappeared after dehydration [Mohammad J. Al-Azzawi and follow,1988], using acetic anhydride-sodium acetate. The characteristic absorption bands of Imides groups near (1612-1720)cm⁻¹ were present in the spectra figures (6, 7, 8, 9 and 10). These absorption bands confirm the presence of imide groups for all compounds (P₆, P₇, P₈, P₉ and P₁₀) (Table 3).

Table 3: Structure confirmation of the synthesized compounds by FTIR.

Compounds	$\nu(\text{N-H})$ amide cm^{-1}	$\nu(\text{O-H})$ acid cm^{-1}	$\nu(\text{C-H})$ arom cm^{-1}	$\nu(\text{C-H})$ aliph cm^{-1}	$\nu(\text{C=C})$ cm^{-1}	$\nu(\text{C=O})$ acid cm^{-1}	$\nu(\text{C=O})$ amide cm^{-1}	$\nu(\text{C=O})$ imide cm^{-1}
$\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_6$	3444	2777- 3444	3105	2981	1527	1666	1577	-
$\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_6\text{I}_2$	3444	3444	3290	-	1489	1639	1558	-
$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_8$	3444	3444	3305	2835	1550	1666	1639	-
$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6$	3444	3444	3286	2843	1558	1639	1639	-
$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6$	3406	3406	3200	2927	1566	1720	1654	-
$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_4$	-	-	3089	2924	1573	-	-	1685
$\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_4\text{I}_2$	-	-	3070	-	1542	-	-	1720
$\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_6$	-	-	3078	2839	1450	-	-	1612
$\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_6$	-	-	3078	2843	1504	-	-	1643
$\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_4$	-	-	3116	2900	1458	-	-	1573

**Fig.(1): FT-IR Spectrum of ($\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_6$).**

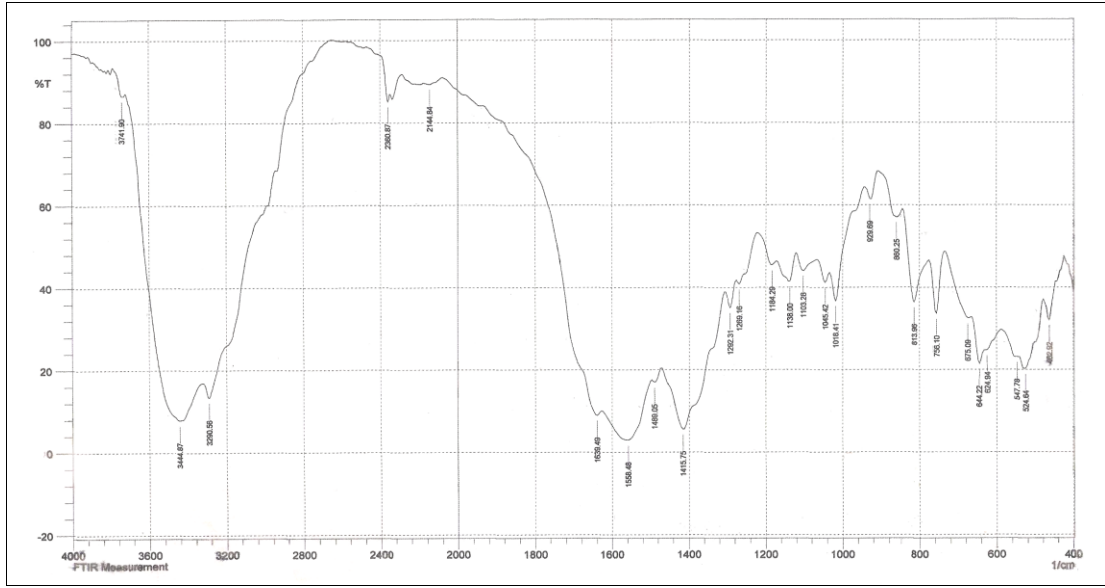


Fig.(2): FT.IR Spectrum of (C₂₂H₁₄N₂O₆I₂).

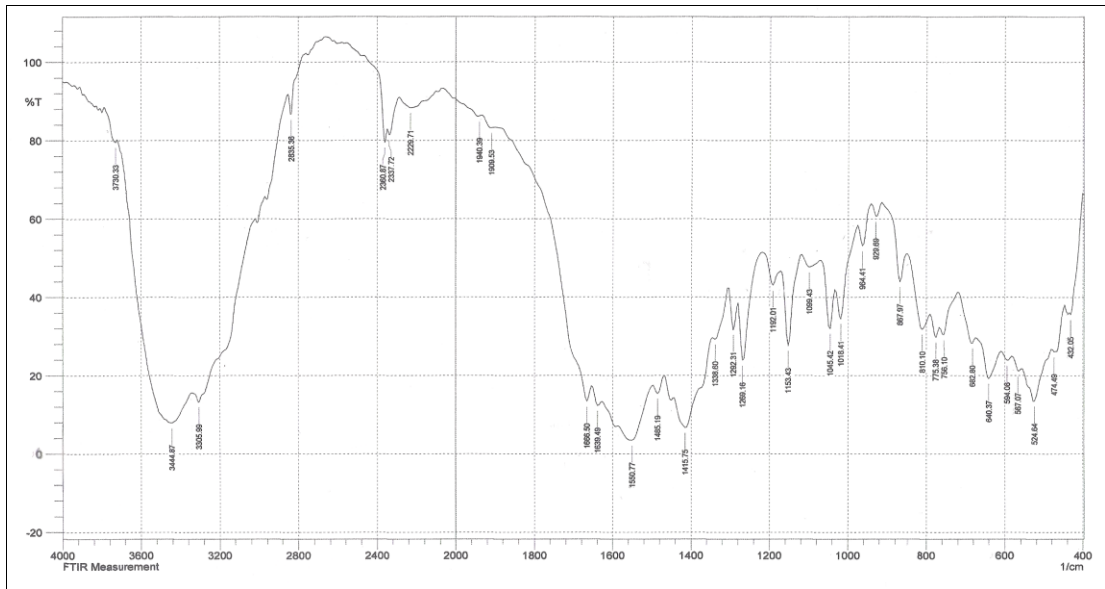


Fig.(3): FT.IR Spectrum of (C₂₄H₂₀N₂O₈).

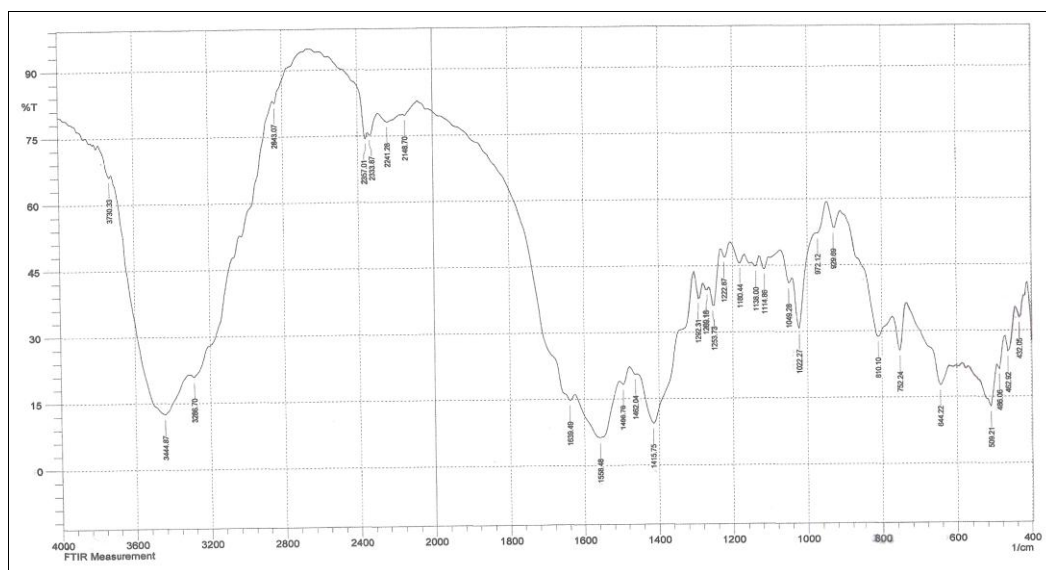


Fig.(4): FT-IR Spectrum of $(C_{24}H_{20}N_2O_8)$.

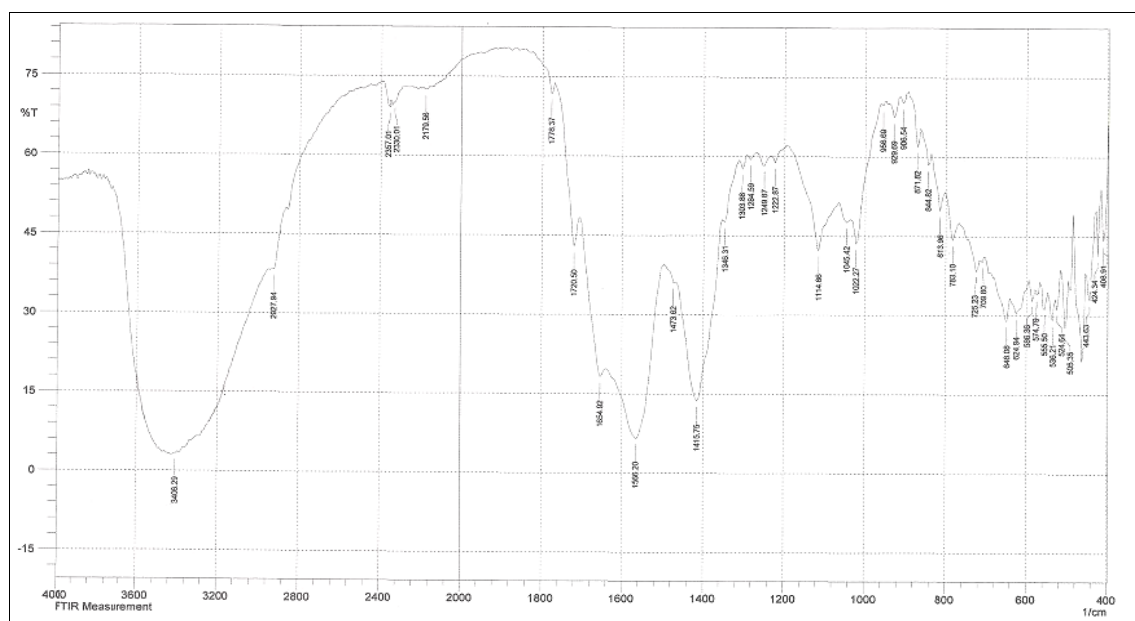


Fig.(5): FT-IR Spectrum of $(C_{24}H_{20}N_2O_6)$.

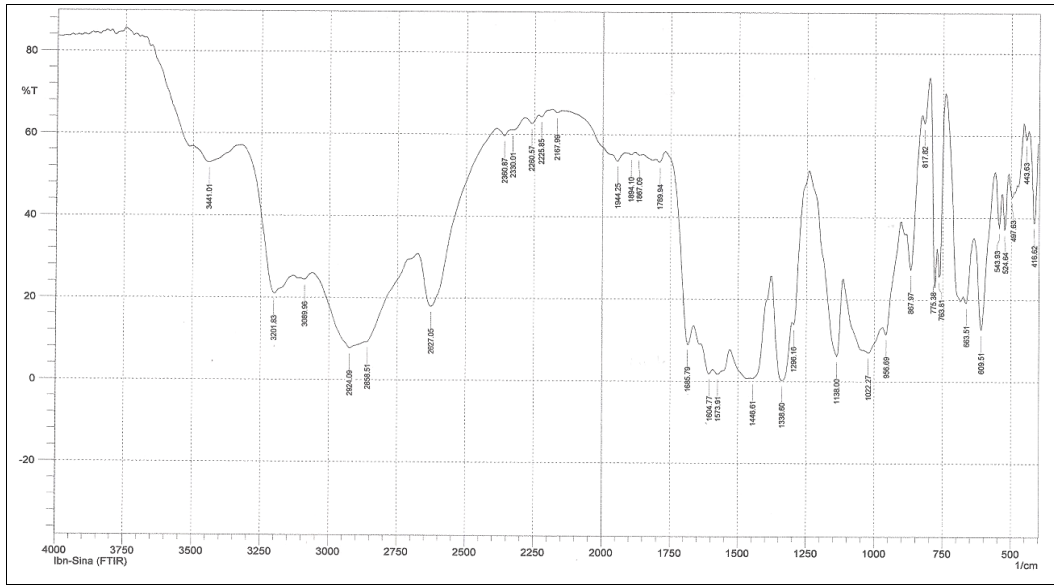


Fig.(6): FT-IR Spectrum of (C₂₆H₂₀N₂O₄).

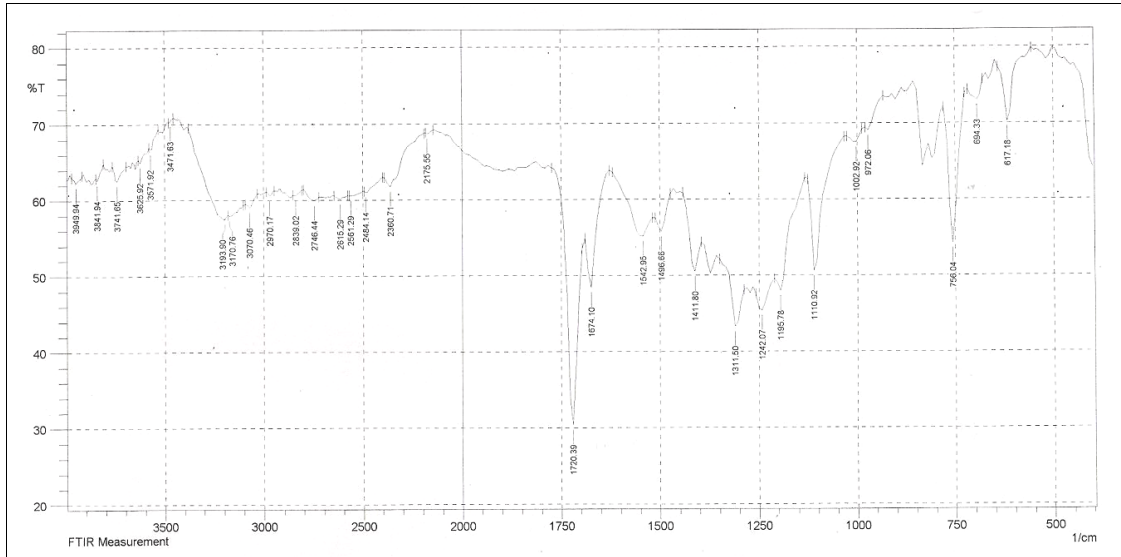


Fig.(7): FT-IR Spectrum of (C₂₂H₁₀N₂O₄I₂).

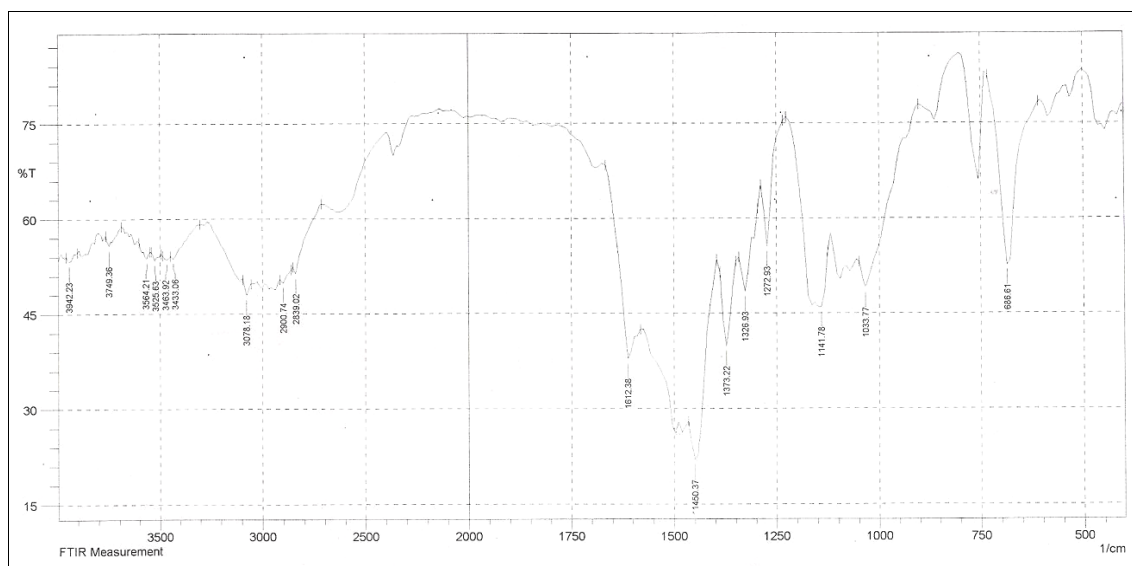


Fig.(8): FT.IR Spectrum of (C₂₄H₁₆N₂O₆).

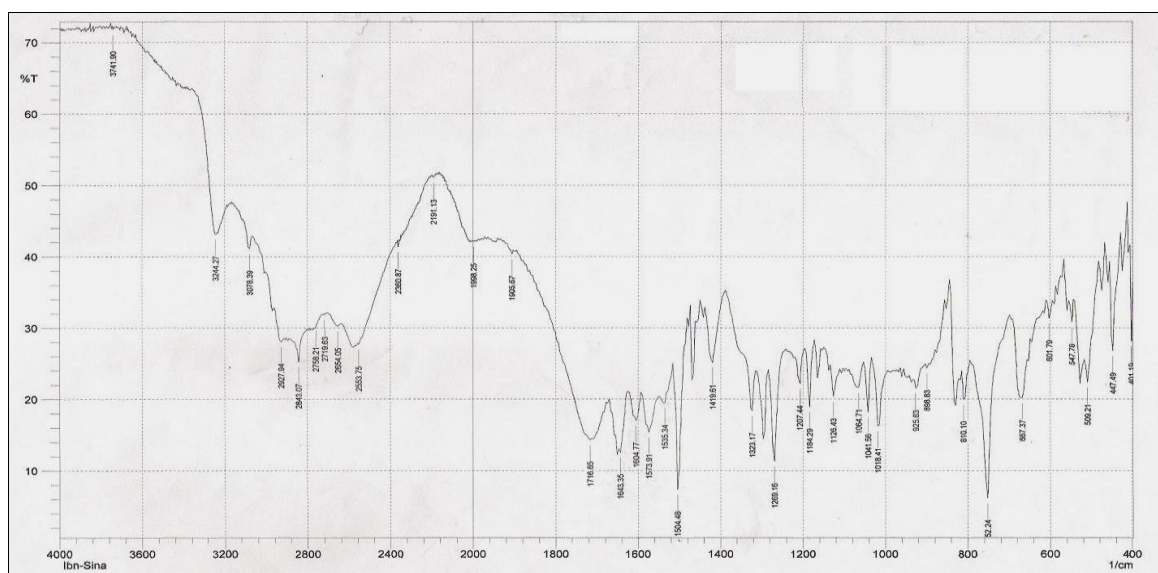


Fig.(9): FT.IR Spectrum of (C₂₄H₁₀N₂O₆).

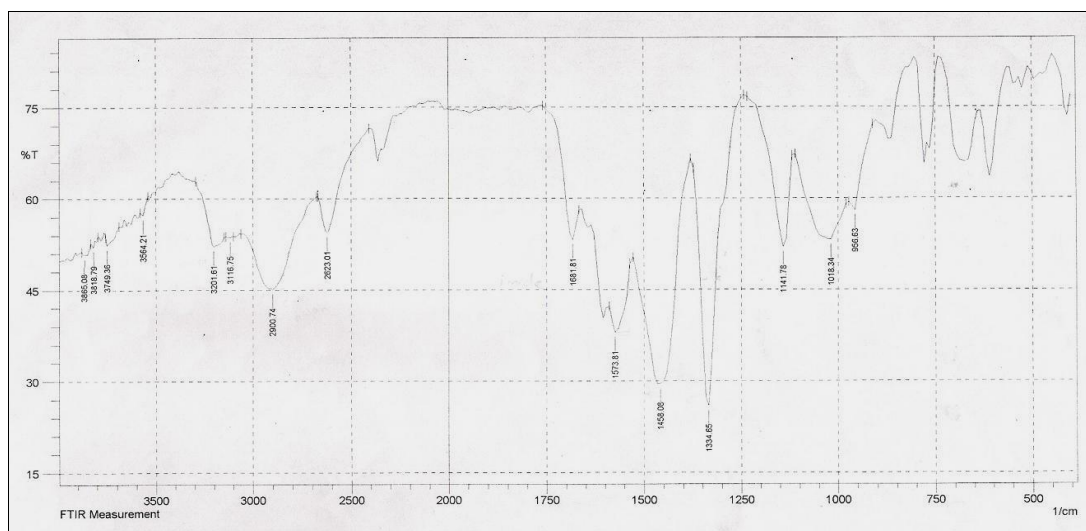


Fig.(10): FT-IR Spectrum of (C₂₄H₁₀N₂O₄).

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