Synthesis and Characterization of New Heterocyclic Derived from Pyromellitic Dianhydride

Sahar F. Abbas
Emad T. Ali
Jumbad H. Tomma

Dept. of Chemistry/College of Education for Pure Science (Ibn Al-Haitham)/University of Baghdad

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Abstract

In this work two moles of 2-amino benzothiazole were allowed to react with one mole of pyromellitic dianhydride to produce NN^-Bis-(benzathiazol-2-yl) pyromellitamic diacid [I] which was submitted to esterification via the reaction with dimethyl sulphate in sodium carbonate in acetone as a solvent to synthesize N,N^-bis-(benzothiazol-2-yl) pyromellitam diacetate [II]. This ester was used to produce novel compounds through two paths -:

Path one:-

Reaction of ester [II] with hydrazine in ethanol as a solvent to form the corresebonding N,N^-bis (benzothiazole-2-yl) –pyromellitamic acid hydrazide [III] which react with acetyl acetone in ethanol or with phthalic anhydride in dioxane to yield new pyrazole, N,N^-bis[(2-amidobenzothiazol) 3,5-dimethyl pyrazole] pyromellitic [IV] and new imide; N,N^-bis-[(2-amidobenzothiazol)-amido phthalimide] pyromellit [V] respectively.

Path two:-

Reaction of ester [II] with thiosemicarbazide to form bis [N,N^-(2-amidobenzothiazole) thiosemicarbazide] pyromellitamic acid [VI], which is converted to triazole. bis[N,N^- (2-amido benzothiazol) 1,2,4-triazole -3-yl] pyromellit [VII] under basic condition treatment of the last product with different alkyl halides to give new series of thioalkyl triazoles; bis [N,N-(2-amido benzothiazole)-5-thio alkyl 1,2,4-triazole-3-yl] pyromellit[VIII]n.

All the above compounds were characterized by their melting points, elemental analysis and by their spectral data, FTIR and ^1HNMR for (some of them).

Key word : pyromellitic dianhydride , pyrazol , imide ,1,2,4- triazole , hydrazide.
Introduction

The widespread applications of pyromellitic dianhydride (PMDA) in several fields, such as synthesis of an important monomer in the preparation of a variety of thermoplastic polymers such as polyimides, epoxy resins and metal carboxylate complexes. Moreover, it is also useful in the preparation of high performance coatings that have been widely employed in many fields in our daily life because of its excellent thermal, oxidative stability and excellent mechanical properties [1].

Pyrazoles played a crucial part in the development of theoretical studies and also useful building blocks in organic synthesis, with wide applications as dyestuff, analytical reagents and agrochemicals. The pyrazole ring system is a useful structural moiety found in numerous biologically active compounds. and in the field of the medicinal chemistry. They display various biological activities such as, analgesic, anti-inflammatory, anti-anxiety, antibacterial, antifungal, antitumour, antitubercular, and antiparasitic [2].

Imides possess excellent mechanical properties, thermal stability and important class of bioactive molecules that show a wide range of pharmacological activities such as androgen receptor antagonistic, anti-inflammatory, anxiolytic, antiviral, antibacterial, and antitumor properties. Moreover, they are synthetic precursors with application in organic synthesis, polymer synthesis, and for the development of new materials and molecular electronic devise [3].

A large number of 1,2,4-triazole-containing ring system have been incorporated into a wide variety of therapeutically interesting drug candidates including Anti-septic, analgesic, anti-convulsant, anti-biotic, anti-allergic, anti-inflammatory, diuretic, fungicidal, insecticidal, herbicidal, anti-bacterial, anti-viral, anti-depressant, anti-microbial, anti-tumor, and antihypertensive [4].

The aim of this work is the synthesis of a novel pyrazole, imides, 1,2,4-triazole derivatives from pyromellitic anhydride by many reaction steps which are given in scheme 1

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 Shimadzo (Ir prestige-21) FTIR spectroscopy. Uncorrected melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus, $^1$HNMR spectra were carried out by company: Ultra Shield 300 MHz, Bruker, Switzerland, at University of Al-albayt, Jordan, and are reported in ppm($\delta$), DMSO was used as a solvent with TMS as an internal standard. Elemental analyses of some compounds were performed on a (C.H.N.S) Company: Euro vector, model EA 3000A origin: Italy. University of Al-albayt, Jordan
Synthesis of asymmetrical diamic acid N,N'-Bis-(benzothiazol-2-yl) pyromellitimic diacid [I]

To a solution of pyromellitic dianhydride (0.218g, 0.001mole) in (15mL) acetone, a solution of the 2-amino benzothiazol (0.3 g,0.002 mole) in (15mL) acetone was added dropwise during one hour, the mixture was then left at room temperature with continuous stirring for 24 hrs, the white product was then filtered off and recrystallized from acetone to give the a corresponding N,N'-Bis-(benzothiazol-2-yl) pyromellitimic diacid [I] [5], yield 90%, mp >300 °C.
Synthesis of N,N′-bis-(benzothiazol-2-y1) pyromellitamic acid hydrazide [III]

A solution of N,N′-bis-(benzothiazol-2-y1) pyromellitamic acid hydrazide [II] (32.76 g, 0.06 mol) and hydrazine hydrate (15 mL) in 25 mL of ethanol was heated under reflux for 2 hrs. The mixture was then cooled at room temperature, and the obtained pale orange solid was filtered and recrystallized from ethanol. Yield 86%, mp 135-137°C.

Synthesis of N,N′bis-[2-amido benzothiazol)-3,5 dimethyl pyrazole] pyromellitic [IV]

A mixture of acid hydrazide [III] (1.09 g, 0.002 mol) and acetyl acetone (0.002 mol) in absolute ethanol 4 mL was heated under reflux for 4 hrs. The reaction mixture was cooled and the formed precipitate was filtered off and recrystallized to give yellow compound [IV], yield 71%, mp 162-164°C.

Synthesis of N,N′bis-[2-amidobenzothiazol)-amido phthalimide] pyromellite [V]

A mixture of acid hydrazide [III] (1.09 g, 0.002 mol) and phthalic anhydride (0.59 g, 0.002 mol) was refluxed in dry dioxane (20 mL) for 5 hrs. The reaction mixture was left overnight for slow evaporation. The brown product was recrystallized from dioxane to give new imide [V], yield 60%, mp >300°C.

Path two:

Synthesis of symmetrical bis [N,N′-(2-benzothiazol) thiosemicarbazide] pyromellitamic acid [VI]

To a solution of compound [II] (0.54 g, 0.01 mol) in absolute ethanol (20 mL) was added thiosemicarbazide (0.18 g, 0.01 mole), the mixture was refluxed for 4 hrs. And after cooling the white precipitate was filtered and recrystallized from ethanol [7], yield 93%, mp 150-152°C.

Synthesis of symmetrical bis[ N,N′-(2-benzothiazol) -1,2,4 -triazole-3-yl] pyromellit amide [VII]

A stirring solution of compound [VI] (6.64 g, 0.01 mol) and 10 mL 4% aqueous sodium hydroxide solution was refluxed for 4 hrs. After that, the mixture was filtered and the filtered was acidified with dilute hydrochloric acid. The pale brown precipitate was filtered and washed several times with water, yield 58%, mp (100-101) °C.

Synthesis of a new series of symmetrical bis [N,N′-(2-benzothiazol) -5-thio alkyl- 1,2,4 –triazole -3-yl] pyromellit amide [VIII]

Potassium hydroxide (6.72 g, 0.12 mole) dissolved in minimum volume of water, was added dropwise to a stirred solution of triazole (5.74 g, 0.01 mole) in (10 mL) of dioxane at 250°C. After heating, the mixture for (15 min.) and cooling, n-alkyl halide ((methyl
iodide, ethyl bromide, propyl bromide, butyl bromide or benzyl bromide) (0.01 mole) was added dropwise. The solution was refluxed for (3 hrs). Afterwards the solvent was evaporated on a rotator evaporator, ice-water (100 mL) was added, the resulting precipitate was collected, and recrystallized. The physical properties data of a new series [VIII], are given in table 1.

**Result and Discussion**

**N,N'-Bis-(benzothiazol-2-yl) pyromellitamic diacid** [I] was synthesized by the reaction of one mole of pyromellitic dianhydride with two moles of 2-amino benzothiazole in acetone as a solvent. The mechanism involves nucleophilic addition reaction, as follows scheme 2.[5]

![Scheme 2](image)

The structure of amic acid was studied by its melting point and FTIR. FTIR spectrum which shows the disappearance of absorption bands of NH2 group and other peaks characterized of cyclic anhydride of the starting materials together with the appearance of new absorption stretching bands due to O-H of carboxylic moiety at (3284-2450) cm⁻¹, C=O (carboxylic acid) stretching at (1685) cm⁻¹, C=O (amid) stretching at (1654) cm⁻¹ and C=N (endocyclic) stretching at (1627) cm⁻¹ of heterocyclic unite. The FTIR data support the proposed structure.

**N,N'-Bis-(benzothiazol-2-yl) pyromellitamic diacid** [I] was converted to ester by the common esterification process using dimethyl sulphate in the presence of anhydrous sodium carbonate in dry acetone. **N,N'-bis-(benzothiazol-2-yl) pyromellitam diacetate** [II] was characterized by melting point, C.H.N.S and FTIR spectrum. The FTIR spectrum shows absorption band at 1734 cm⁻¹ due to stretching vibration of the (C=O) for ester, also appearance band at 1188 cm⁻¹ was due to (C-O) bending of ester, besides to disappearance two bands of O-H and C=O of carboxylic moiety. The (C.H.N.S) analysis is consistent with their proposed structure.

The new **N,N'-bis-(benzothiazol-2-yl) pyromellitam diacetate** [II] was used to synthesize new compounds by using two paths as follows:

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272 | Chemistry
Path one: -

The acid hydrazide [III] was synthesized by the reaction of compound [II] with hydrazine hydrate and refluxing in ethanol to form compound [III] which was characterized by melting point, FTIR and 1HNMR spectra. FTIR spectrum shows absorption bands at (3278-3170) cm\(^{-1}\) due to the asymmetric and symmetric stretching vibration of the (-NH-NH\(_2\)) group and stretching vibration band at 1680 cm\(^{-1}\) due to (C=O) for amide.

1HNMR spectrum (in DMSO as a solvent) of acid hydrazide [III] showed broad signals at \(\delta 2.77\) ppm for two protons of CONH group, many signals at \(\delta (7.17 - 7.66)\) ppm that could be attributed to the ten aromatic protons. The spectrum also showed a doublet signal at \(\delta 1.2\) ppm for protons of NH\(_2\) group and a triplet signal at \(\delta (3.43 - 3.72)\) ppm due to NH protons of hydrazide moiety.

The pair of electrons on nitrogen atoms in compound [III] facilitate the reaction of this compound in two ways:

A) Acetyl acetone as shown in the following mechanism (scheme 3) to produce the pyrazole derivatives, which was identified by its melting point, FTIR, 1HNMR spectroscopy. FTIR spectrum of pyrazole compound showed the following: the disappearance of a stretching band at (1680 cm\(^{-1}\)) due to C=O amide groups of hydrazide moiety. Appearance of new absorption bands of NH at (3419) cm\(^{-1}\) and C=N group endocyclic of pyrazole at (1618 cm\(^{-1}\)) was shown.

1HNMR of pyrazole compound [IV] showed two sharp signals at \(\delta 1.74\) ppm and \(\delta 1.79\) ppm due to two CH\(_3\) groups of pyrazole ring [8], a singlet signal at \(\delta 3.15\) ppm could be attributed to two protons of NH group and many signals in the region \(\delta (6.76 - 7.28)\) ppm for aromatic protons.

B) Phthalic anhydride to form the imide as a final product as shown in (scheme 4) was studied by melting point, FTIR spectrum. The FTIR spectrum exhibited significant two peaks at 1735 cm\(^{-1}\) and 1720 cm\(^{-1}\) which could be attributed to asymmetry and symmetry.
stretching vibration of the carbonyl group (imide cyclic) [9] and two absorption bands around 1186 cm\(^{-1}\) and 750 cm\(^{-1}\) for asymmetrical and symmetrical of C-N-C (cyclic) [10-12]
The triazole compound [VII] was synthesized by oxidative cyclization of carboxylic thiosemicarbazide derivatives [VI] in the presence of (4%) aqueous NaOH. The mechanism of the reaction may be outlined as follows in scheme (6).

This compound was characterized by melting point and FTIR, $^1$HNMR spectroscopy. The FTIR spectrum showed disappearance of absorption bands due to $\nu$C=O.
(amide) and NH₂ group of compound [VI] together with the appearance of three characteristic stretching bands at 3248 cm⁻¹, 1645 cm⁻¹ and 1205 cm⁻¹, which are assigned to υN-H, υC=N and υC=S groups, respectively.

¹H NMR spectrum of triazole compound [VII] showed the following characteristic chemical shifts (in DMSO as a solvent) showed two singlet signals at δ8.63 ppm and δ8.16 ppm that could be attributed to protons of two NH groups of triazole (tautomerism stat between thion and thiol forms SH+NH), many signals (triplet, doublet and singlet) in the region δ6.94-8.54 ppm due to ten aromatic protons. The spectrum also showed a good sharp singlet signal SH group and a weak peak at δ 4.05 ppm due to protons of amide group (NHCO).

Thio alkyl derivatives [VIII]₁,₅ of triazole was obtained by the treatment of compound [VII] with selective alkyl halides and potassium hydroxide in dry dioxane as a solvent. These compounds were identified by melting points and FTIR,¹HNMR.

\[
\text{Scheme 7}
\]

The FTIR spectra show disappearance bands of S-H, C=S and NH together with the appearance of new bends at 2966-2854 cm⁻¹ due to υC-H aliphatic and 869-855 cm⁻¹ for C-S stretching group [13] the spectral data of new series [VIII]₁,₅ are listed in table 2.

¹H NMR spectrum of 5-thio methyl triazole compound [VIII]₁ showed the following signals (in DMSO as a solvent): as singlet signal at δ3.07 ppm for two protons of NH (amide) group, a good signal at δ8.17 ppm for two protons of NH (triazol) group. The spectrum also showed three doublet signals which could be assigned to the eight aromatic protons of para substitution benzene ring in the region δ6.97-7.67 ppm and a singlet signal at δ7.50 ppm due to two aromatic protons of central benzene ring and a singlet for six aliphatic protons at δ1.29 ppm of SCH₃ group.

References


### Table No. (1): The physical properties of compounds [VIII] 1-5

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Nomenclature</th>
<th>Structural formula</th>
<th>Molecular formula</th>
<th>M. P°C</th>
<th>Yield%</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>[VIII]₁</td>
<td>bis[N,N’-(2-benzothiazole)-5-thio methyl - 1,2,4- triazol-3yl] pyromellit amide</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>C₂₇H₁₇O₂N₁₀S₄</td>
<td>158-160</td>
<td>67</td>
<td>Pale orange</td>
</tr>
<tr>
<td>[VIII]₂</td>
<td>bis[N,N’-(2-benzothiazole)-5-thio ethyl - 1,2,4- triazol-3yl] pyromellit amide</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>C₂₈H₁₉O₂N₁₀S₄</td>
<td>130-132</td>
<td>92</td>
<td>Pale Brown</td>
</tr>
<tr>
<td>[VIII]₃</td>
<td>bis[N,N’-(2-benzothiazole)-5-thio propyl - 1,2,4- triazol-3yl] pyromellit amide</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>C₂₉H₂₁O₂N₁₀S₄</td>
<td>94-95</td>
<td>93</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>[VIII]₄</td>
<td>bis[N,N’-(2-benzothiazole)-5-thio butyl - 1,2,4- triazol-3yl] pyromellit amide</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>C₃₀H₂₅O₂N₁₀S₄</td>
<td>108-109</td>
<td>83</td>
<td>Pale Brown</td>
</tr>
<tr>
<td>[VIII]₅</td>
<td>bis[N,N’-(2-benzothiazole)-5-thio pentyl - 1,2,4- triazol-3yl] pyromellit amide</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>C₃₁H₂₉O₂N₁₀S₄</td>
<td>118-120</td>
<td>95</td>
<td>Pale Brown</td>
</tr>
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</table>
Table No.(2): Characteristic FTIR absorption band of compound [VIII]$_1$-$5$

<table>
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<tr>
<th>Comp. No.</th>
<th>$\sqrt{\text{NH of triazole}}$</th>
<th>$\sqrt{\text{C-H Aliph.}}$</th>
<th>$\sqrt{\text{C=O amid}}$</th>
<th>$\sqrt{\text{C=N Of triazole}}$</th>
<th>$\sqrt{\text{C=C arom.}}$</th>
<th>$\sqrt{\text{C=S}}$</th>
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</thead>
<tbody>
<tr>
<td>[VIII]$_1$</td>
<td>3248</td>
<td>2954-2854</td>
<td>1645</td>
<td>1636</td>
<td>1598</td>
<td>869</td>
</tr>
<tr>
<td>[VIII]$_2$</td>
<td>3246</td>
<td>2926-2854</td>
<td>1653</td>
<td>1642</td>
<td>1597</td>
<td>858</td>
</tr>
<tr>
<td>[VIII]$_3$</td>
<td>3248</td>
<td>2966-2864</td>
<td>1656</td>
<td>1645</td>
<td>1597</td>
<td>856</td>
</tr>
<tr>
<td>[VIII]$_4$</td>
<td>3248</td>
<td>2962-2856</td>
<td>1658</td>
<td>1645</td>
<td>1597</td>
<td>855</td>
</tr>
<tr>
<td>[VIII]$_5$</td>
<td>3248</td>
<td>2945-2854</td>
<td>1655</td>
<td>1640</td>
<td>1599</td>
<td>865</td>
</tr>
</tbody>
</table>
تحضير مركبات حلقية غير متجانسة مشتقة من انهيدريد البایروملتیک ودراستها

سحر فاضل عباس
عماد تقی علي
عميد هرمز تومن
قسم الكيمياء / كلية التربية للعلوم الصرفة (ابن الهيثم) / جامعة بغداد

استلم البحث في: 28 أيار 2013 ، قبل البحث في: 26 آب 2013

الخلاصة

تم في هذا البحث مفاعلة مولين من (2-امينو بيزوثيرازول ) مع مول واحد ( انهيدريد البایروملتیک) للحصول على N,N-بس- (بيزوثيرازول-2-يل) بایروملتیميك داي اسيد [I]. N,N- المقابله من خلال مفاعلة مع داي مثل سلفيت ووجود كاربوات الصوديوم واستعمال الاستون منيبا للحصول على N,N- (بيزوثيرازول-2-يل) بایروملتیميك داي اسيد [II].

استعمل هذا الا ستر لانتاج وتحضير مركبات جديدة من خلال عملية;

1- العملية الأولى:

تفاعل الاستر مع الهيدروازين في الابیتانول منيبا للحصول على N,N, N,N- (بيزوثيرازول-2-يل) بایروملتیميك اسيد هیدرازید [III]

الذي بدوره تفاعل استن في الابیتانول منيبا أو مع انهيدريد الفثالك في الابیتانول للحصول على مركبات حلقية غير متجانسة جديدة (البايرولزات) [IV]

والأيميدات المقابلة على التوالي;

N,N- (2-امينو بيزوثيرازول)-امیدو [بایروملتیك] [V]

2- العملية الثانية:


الكلمات المفتاحية: انهدريد البایروملتیک، البایروزول، الامیدات، 4,2,1-ترایژول، هیدرزايد