Synthesis of New *bis* 1-Substituted 1*H*-Tetrazoles via Efficient Heterocyclizations from Symmetric Dianilines, Methyl Orthoester, and Sodium Azide †

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Abstract: The synthesis and characterization of three new *bis* 1-substituted 1*H*-tetrazoles are described. Two products were synthesized in a single step via a direct heterocyclization of primary amines, methyl orthoester (trymethyl orthoformate), and sodium azide in 30% and 91% yields, respectively. Besides, another one was prepared via a three-step synthetic strategy: S_NAr (32%), nitro-group reduction (66%), and primary amine heterocyclization (83%), yielding 18%, overall. The aim behind the synthesis of new tetrazole-containing products is to construct novel MOF-like structures to evaluate their gas capture properties (CO_2, CO, and SO_2) under relative humidity conditions.

Keywords: *bis* tetrazoles; ligands; MOFs; symmetric dianilines; methyl orthoester; azides

1. Introduction

Metal organic frameworks (MOFs) are hybrid structures consisting in metal cations (nodes) connected through organic moieties (ligands) with different lengths that propagate into extended networks, which produce crystalline porous materials in 1-, 2-, or 3-dimensions [1]. The use of MOFs has been reported in a wide variety of fields of science and technology, for instance, as catalysts [2], luminescent materials [3], drug carriers/delivers [4], and as chemosensors [5]. However, their use as materials for gas capture, separation, and storage remains one of their most sought-after applications [6]. One of the two key components to fabricate MOFs is the metal cation. This component acts as a node and usually belongs to transition metals group [7]; although there are some reports of MOFs constructed with lanthanoid elements [8]. The other key component is the ligand, since it is responsible for most of the material's structural properties such as the flexibility, porosity, and topology [9]. Regarding the ligands used to assemble MOFs, most of them contain carboxylates as the electron-donating functional groups due to the increased stability that these 'teeth' offers when coordinating to the metal cation, since they do it in a charge-compensating way [10]. However, there

are some advantages when ligands containing azole-based donating groups are used. Tetrazoles are basic in their nature due to the four electron-withdrawing *N*-atoms in their structures. This property increases directly with the number of *N*-atoms present. Furthermore, the coordination between a transition metal cation (soft Lewis acid) and the azole (soft Lewis base) is expected to result in a stable bond, since their covalent nature grow up [11]. Furthermore, tetrazoles are an important class of heterocyclic compounds with many applications, for example, in medicinal chemistry [12], materials and polymer sciences [13], and as corrosion inhibitors [14]. In the same context, their salts have been used as energetic materials [15], among other interesting applications. The use of tetrazoles as ligands to fabricate complex MOFs was documented first by Franke et al. [16]. It has been reported that tetrazoles can act as a monodentate ligands through the N-4 donor sites [17]. In addition to the previously mentioned properties of tetrazoles, the ligands presented in this work may exhibit angular and flexible conformations, which could give rise to diverse types of MOF topologies. Also, the aromatic rings of the ligands could affect the packing of crystal structures through non-covalent interactions [18].

There are two main methods to synthesize 1-substituted 1*H*-tetrazoles: (i) through a Huisgen-type [3+2] acid-catalyzed cycloadditions between an azide ion source and isocyanides [19], and (ii) via heterocyclizations of primary amines, an orthoester, and the sodium azide [20] (Scheme 1). The second method has some advantages over the first one, since primary amines are inexpensive and readily available reagents, as well as the orthoesters. This reaction has a wide scope and can be used with numerous substrates to effectively introduce the 1-substituted 1*H*-tetrazole moiety into polyfunctional molecules [21]. As an example, Muttenthaler and co-workers [22] synthesized a series of *bis* 1-substitued 1*H*-tetrazoles from primary amines making use of this methodology obtaining good to excellent yields. Even to present days, this remains the most used methodology towards the synthesis of 1-substituted 1*H*-tetrazoles, despite it was first reported in a patent in 1973 [23].
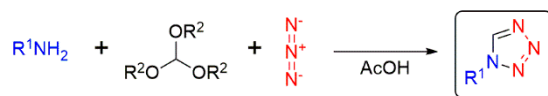

Scheme 1. Synthesis of 1-substituted 1*H*-tetrazoles from primary amines, orthoesters, and the azide anion.

The aim of this work is to increase the reserve of ligands with donor groups (different to carboxylates), which can be used to fabricate new MOFs. Thus, for the present work, the synthesis and characterization of three new *bis* 1-substituted 1*H*-tetrazoles with potential application to construct new MOFs is described. One of them is linked by a disulfane-bridge and the other by a biphenyl moiety, both synthesized in a single step via a direct heterocyclization of primary amines. The third one is linked by an aromatic secondary amine group. This one was obtained via a three-step synthetic strategy. It is noteworthy that these ligands have not previously been synthesized nor isolated.

2. Results and Discussion

2.1. Synthesis of 1,2-bis(4-(1H-tetrazol-1-yl)phenyl)disulfane (2)

The 4,4′-disulfanediyldianiline (**1**) reacted with an excess of both, sodium azide (3.0 equiv.) and trimethyl orthoformate (22.8 equiv.) in acetic acid as the solvent for 24 h to give the target molecule 1,2-*bis*(4-(1*H*-tetrazol-1-yl)phenyl)disulfane (**2**) in 30% yield via a primary amine heterocyclization (Scheme 2).
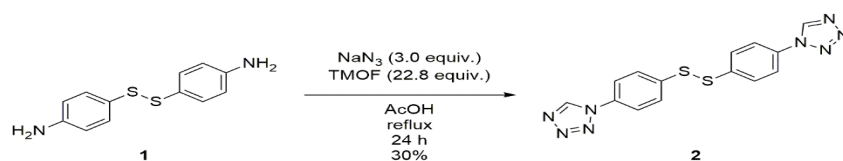
Scheme 2. Synthesis of the new disulfane-bridged *bis*-tetrazole ligand 2.
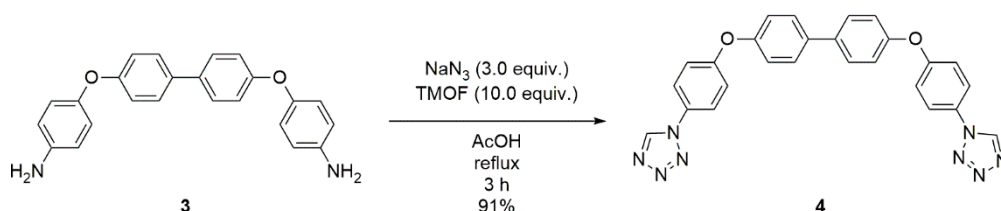
The *bis*-tetrazole compound **2** was characterized by its physicochemical properties, as well as by classic spectroscopic techniques. Figure 1 shows the ^{1}H and ^{13}C-NMR spectra of compound **2**. There is a characteristic singlet at 10.05 ppm (Figure 1), which is attributed to the H-atom from the tetrazole, as well as a couple of doublets for the A^2B^2 system from their aromatic rings. Figure 1b shows a key peak at 168.4 ppm corresponding to the C-atom from the tetrazole (C-5).
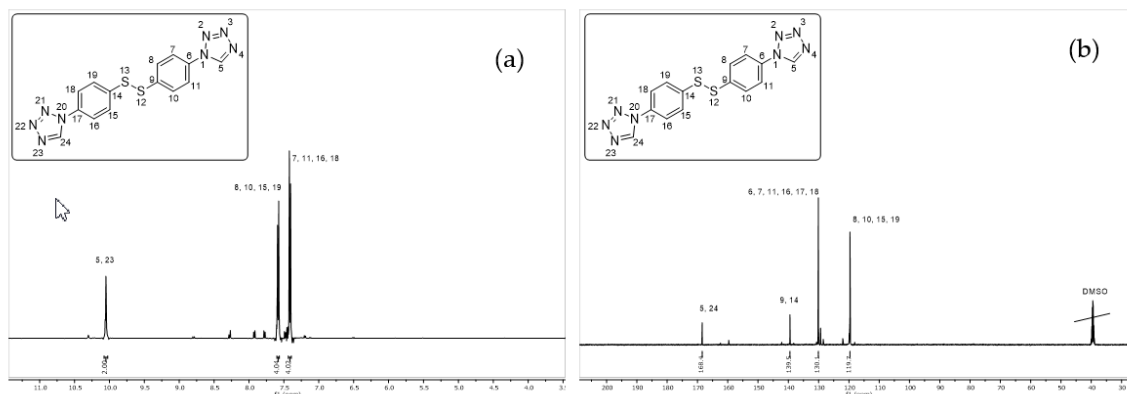
Figure 1. (**a**) ^{1}H-NMR spectrum of the disulfane-bridged *bis*-tetrazole **2**. (**b**) ^{13}C-NMR spectrum of the disulfane-bridged *bis*-tetrazole **2**.
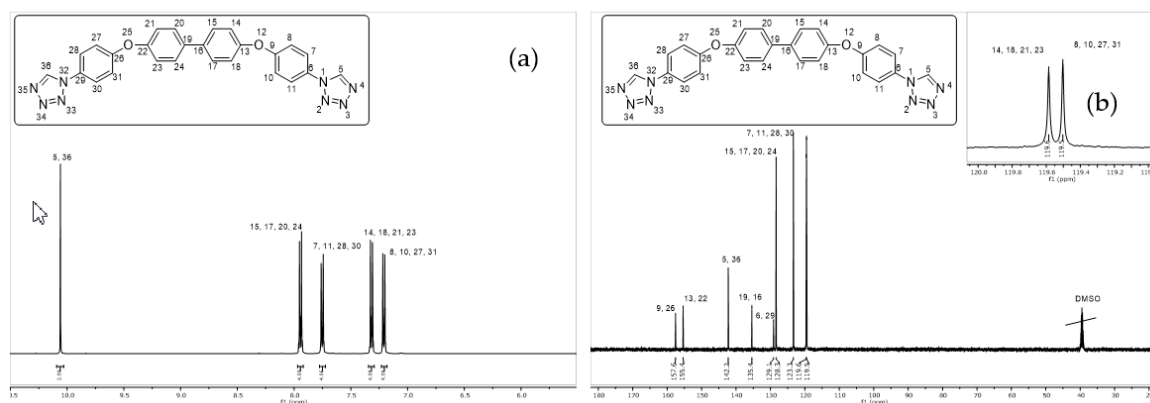
2.2. Synthesis of 4,4′-bis(4-(1H-tetrazol-1-yl)phenoxy)-1,1′-biphenyl (**4**)

The 4,4′-(1,1′-biphenyl-4,4′-diyldioxy)dianiline (**3**) was combined sequentially with sodium azide and trimethyl orthoformate in acetic acid as the solvent to furnish the target compound 4,4′-*bis*(4-(1H-tetrazol-1-yl)phenoxy)-1,1′-biphenyl (**4**) in 91% yield via a primary amine heterocyclization. The yield for this reaction is remarkably good considering the structural complexity of the ligand **4** (Scheme 3). It is noteworthy also that this yield (91%) is considerable higher than that one for the product **2** (30%) probably because the disulfane bridge is sensitive to higher temperatures and the acidic conditions as a result of the AcOH media.

**Scheme 3**. Synthesis of new biphenyldioxy-bridged *bis*-tetrazole ligand.

The *bis*-tetrazole **4** was characterized by its physicochemical properties, as well as by spectroscopic techniques. Figure 2 shows the ^{1}H and ^{13}C-NMR spectra of the compound **4**. The ^{1}H-NMR spectrum (Figure 2a) shows the typical singlet at 10.06 ppm, which is attributed to the H-atom from the tetrazole ring. The structure of **4** contains four symmetric para-substituted aromatic rings, so four doublets corresponding to non-equivalent A^2B^2 systems are expected. The ^{13}C-NMR spectrum (Figure 2b) shows the expected nine signals for the ligand, the key one being the peak at 142.2 ppm, which is characteristic for the C-atom of the 1-substituted tetrazole ring.

Figure 2. (**a**) ¹H-NMR spectrum of the biphenyldioxy-bridged *bis*-tetrazole **4**. (**b**) ¹³C-NMR spectrum of the biphenyldioxy-bridged *bis*-tetrazole **4**.

2.3. Synthesis of bis(4-(1H-tetrazol-1-yl)phenyl)amine (**9**)

The first step to synthesize the *bis*(4-(1*H*-tetrazol-1-yl)phenyl)amine (**9**) was a S$_N$Ar reaction between the para-nitroaniline (**5**) and the 1-chloro-4-nitrobenzene (**6**) to furnish the precursor *bis*(4-nitrophenyl)amine (**7**) in 32% yield. This reaction proceeded due to the strong activation of C-1 from **6** by the nitro group (Scheme 4).
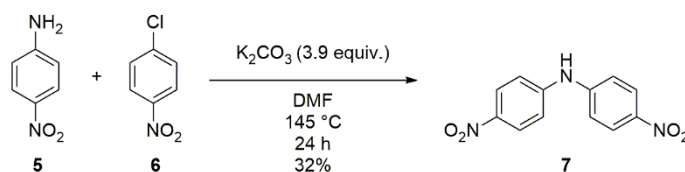
**Scheme 4**. Synthesis of the precursor *bis*(4-nitrophenyl)amine **7**.

The precursor **7** was characterized successfully by its physicochemical properties, as well as by spectroscopic techniques. Figure 3 shows the ¹H and ¹³C-NMR spectra of precursor **7**. The ¹H-NMR spectrum (Figure 3a) shows a key singlet at 9.96 ppm, corresponding to the NH-proton, as well as a pair of doublets for A²B² systems from both aromatic rings. The ¹³C-NMR spectrum (Figure 3b) shows the expected four signals for the compound with a key peak at 147.5 ppm, corresponding to the more unshielded C-1 and C-8 due to bonds to the amine group, as well as to the electron-withdrawing effect coming from the nitro groups.
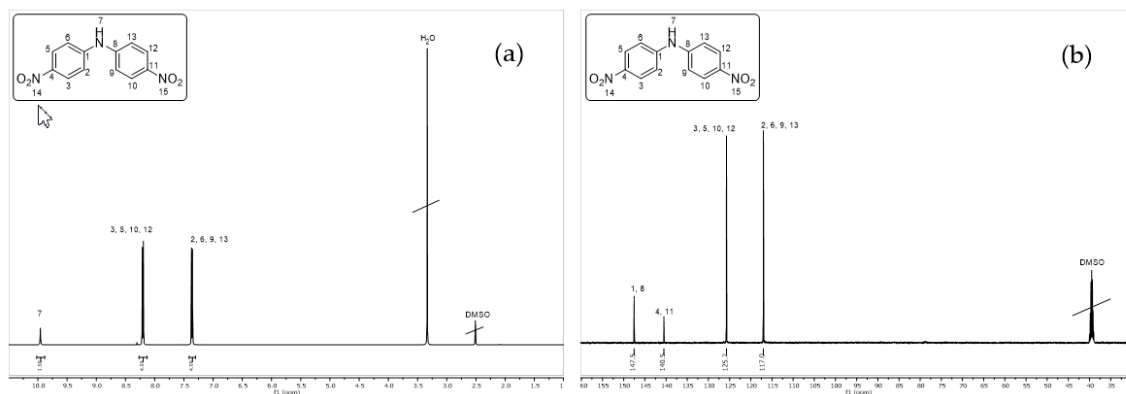
Figure 3. (**a**) ¹H-NMR spectrum of the *bis*(4-nitrophenyl)amine **7**. (**b**) ¹³C-NMR spectrum of the *bis*(4-nitrophenyl)amine **7**.

Having the *bis*(4-nitrophenyl)amine (**7**) in hand, the next step was to hydrogenate both nitro groups using the metallic iron/iron(II) sulfate heptahydrate reductive system in water as the solvent

to furnish the N^1-(4-aminophenyl)benzene-1,4-diamine (**8**) in 66% yield (Scheme 5). Unfortunately, the precursor **8** underwent a quick carbonatation with CO_2 from air, which did not allow its characterization by spectroscopic techniques. Thus, the compound **8** was used as soon as prepared (detected by TLC) for the next step, a heterocyclization with trimethyl orthoformate and sodium azide in acetic acid as the solvent, affording the new *bis*(4-(1*H*-tetrazol-1-yl)phenyl)amine (**9**) in 83% yield.
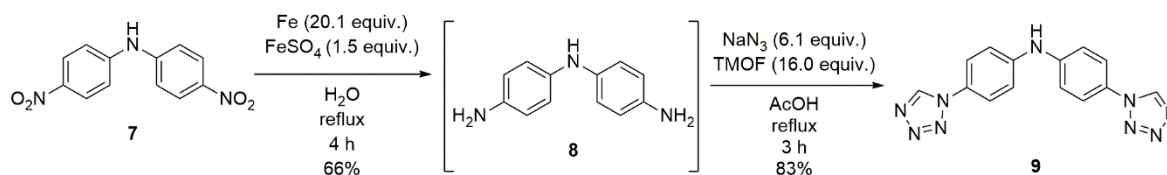
Scheme 5. Nitro groups reduction and primary amine heterocyclization toward the new *bis*-tetrazole **9**.

Figure 4 shows the ^{1}H and ^{13}C-NMR spectra of the compound **9**. The ^{1}H-NMR spectrum (Figure 4a) shows two key singlets, one at 9.96 ppm, corresponding to the H-atom from the tetrazole ring and the other at 8.99 ppm, which belongs to the NH-proton. Two doublets for the A^2B^2 systems is present as well. For the ^{13}C-NMR spectrum (Figure 4b), the expected five signals are present, with a characteristic peak at 141.9 ppm, which corresponds to the C-atom of the 1-substituted 1*H*-tetrazole moiety (C-5).
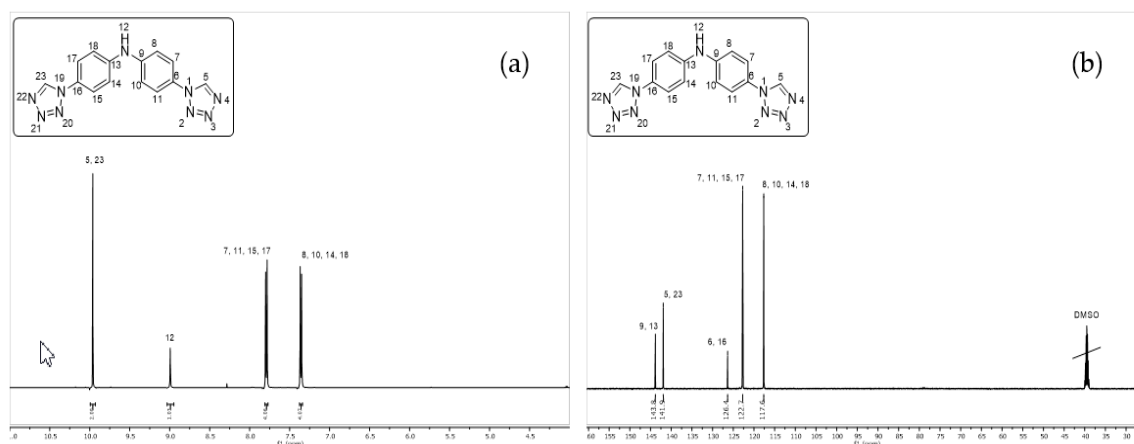
Figure 4. (**a**) ^{1}H-NMR spectrum of the *bis*(4-(1*H*-tetrazol-1-yl)phenyl)amine **9**. (**b**) ^{13}C-NMR spectrum of the *bis*(4-(1*H*-tetrazol-1-yl)phenyl)amine **9**.

3. Conclusions

The heterocyclization towards the disulfane-bridged ligand occurred with low yields because this functional group is very sensitive to high temperatures. The dioxy-biphenyl-bridged analogue was prepared in excellent yields considering its structural complexity. The amino-linked ligand required three steps for its synthesis. However, it would be interesting to prepare MOFs with an additional coordinating group. First attempts using these new ligands to try constructing novel porous coordination polymers are being conducted.

4. Experimental Section

4.1. General Information, Instrumentation, and Chemicals

^{1}H and ^{13}C NMR spectra were acquired on a Bruker Advance III (500 MHz) spectrometer. The solvent was deuterated dimethyl sulfoxide (d^6-DMSO). Chemical shifts are reported in parts per million (/ppm). The internal reference for NMR spectra is with respect to tetramethyl silane (TMS) at 0.0 ppm. Coupling constants are reported in Hertz (J/Hz). Multiplicities of the signals are reported

using the standard abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). NMR data were treated using the MestReNova software (12.0.0–20080). Reaction progress was monitored by thin layer chromatography (TLC) on precoated kieselgel 60 F254 plates and the spots were visualized under UV light (254 or 365 nm). Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Structural drawings were created using the ChemDraw professional software (15.0.0.106). All starting materials were purchased from Sigma-Aldrich and were used without further purification. The solvents were distilled and dried according to standard procedures.

4.2. Synthesis of 1,2-bis(4-(1H-tetrazol-1-yl)phenyl)disulfane (**2**)

In a 50-mL round-bottomed flask equipped with a magnetic stirring bar, were added 1.0 g (1.0 equiv.) of 4,4′-disulfanediyldianiline (**1**) and 0.78 g (3.0 equiv.) of sodium azide. The mixture was dissolved in 5 mL of acetic acid and then 10 mL of trimethyl orthoformate (22.0 equiv.) was added dropwise at RT. The reaction vessel was flushed with argon, it was placed in an oil bath at 100 °C and kept at reflux for 24 h. After this time, the crude of the reaction was filtered, washed with an acetone/ethanol (1:1, *v/v*) mixture, and dried under vacuum to afford 0.43 g of a grey solid with a 30% yield; R_f = 0.13 (Hex-AcOEt = 2:3, *v/v*); mp = 168–170 °C; ^{1}H NMR (500 MHz, d^6-DMSO): δ 10.05 (s, 2H), 7.58 (d, *J* = 8.7 Hz, 4H, H-8, H-10, H-15, H-19), 7.41 (d, *J* = 8.7 Hz, 4H, H-7, H-11, H-16, H-18); ^{13}C NMR (126 MHz, d^6-DMSO): δ 168.4 (C-5, C-24), 139.5 (C-9, C-14), 130.1 (C-6, C-7, C-11, C-16, C-17, C-18), 119.7 (C-8, C-10, C-15, C-19); HRMS [M+H]$^+$ calculated for $C_{14}H_{11}N_8S_2^+$ = 355.0503, found = 355.0517.

4.3. Synthesis of 4,4′-bis(4-(1H-tetrazol-1-yl)phenoxy)-1,1′-biphenyl (**4**)

A total of 1.08 g (1.0 equiv.) of 4,4′-(1,1′-biphenyl-4,4′-diyldioxy)dianiline (**3**), 1.5 g (3.0 equiv.) of sodium azide, and 5.5 mL (10.0 equiv.) of trimethyl orthoformate were sequentially added to a 50-mL round-bottomed flask equipped with a magnetic stirring bar. The flask was placed on an oil bath at 90 °C and 10 mL of acetic acid was added to the mixture. The reaction progress was monitored by TLC and was stopped after 3 h stirring. Then, the reaction mixture was poured into 200 mL of distilled water. The formed precipitate was collected by filtration. The solid was washed with cold distilled water and ethanol. Then, it was let to dry at RT, furnishing 2.10 g of a white powder with 91% yield; R_f = 0.61 (Hex-AcOEt = 1:3, *v/v*); mp = 219–221 °C; ^{1}H-NMR (500 MHz, d^6-DMSO): δ 10.06 (s, 2H, H-5, H-36), 7.94 (d, *J* = 9.0 Hz, 4H, H-15, H-17, H-20, H-24), 7.75 (d, *J* = 8.8 Hz, 4H, H-7, H-11, H-28, H-30), 7.32 (d, *J* = 9.0 Hz, 4H, H-14, H-18, H-21, H-23), 8.21 (d, *J* = 8.7 Hz, 4H, H-8, H-10, H-27, H-31); ^{13}C NMR (126 MHz, d^6-DMSO): δ 157.6 (C-9, C-26), 155.4 (C-13, C-22), 142.3 (C-5, C-36), 135.4 (C-16, C-19), 129.1 (C-6, C-29), 128.3 (C-15, C-17, C-20, C-24), 123.3 (C-7, C-11, C-28, C-30), 119.6 (C-14, C-18, C-21, C-23), 119.5 (C-8, C-10, C-27, C-31). HRMS [M+H]$^+$ calculated for $C_{26}H_{19}N_8O_2^+$ = 475.1586, found = 475.1598.

4.4. Synthesis of bis(4-nitrophenyl)amine (**7**)

In a 50-mL round-bottomed flask equipped with a magnetic stirring bar, were dissolved 2.06 g (2.5 equiv.) of *p*-nitroaniline (**5**), 0.96 (1.0 equiv.) of 1-chloro-4-nitrobenzene (**6**), and 3.35 g (3.9 equiv.) of potassium carbonate in 18 mL of *N,N*-dimethylformamide. The flask was connected to a reflux condenser and placed in an oil bath at 145 °C. The reaction progress was monitored by TLC and was stopped after 24 h stirring. After this time, the mixture was poured into 500 mL of distilled water, and then, concentrated hydrochloric acid was added until an acidic pH reached (pH = 2) and then, the mixture was filtered and washed with distilled water. The filtrate was crystallized from acetonitrile to furnish 0.55 g of a bright orange needles with 32% yield; R_f = 0.61 (Hex-AcOEt = 1:1, *v/v*); mp = 166–168 °C; ^{1}H-NMR (500 MHz, d^6-DMSO): δ 9.96 (s, 1H, H-7), 8.20 (d, *J* = 9.3 Hz, 4H, H-3, H-5, H-10, H-12), 7.36 (d, *J* = 9.3 Hz, 4H, H-2, H-6, H-9, H-13). ^{13}C NMR (126 MHz, d^6-DMSO): 147.5 (C-1, C-8), 140.5 (C-4, C-11), 125.7 (C-3, C-5, C-10, C-12), 117.0 (C-2, C-6, C-9, C-13). HRMS [M+H]$^+$ calculated for $C_{12}H_{10}N_3O_4^+$ = 260.0627, found = 260.0669.

*4.5. Synthesis of N¹-(4-aminophenyl)benzene-1,4-diamine (**8**)*

In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, were added 0.26 g (1.0 equiv.) of *bis*(4-nitrophenyl)amine (**7**), 1.12 g (20.1 equiv.) of metallic iron, and 0.41 g (1.5 equiv.) of iron(II) sulfate heptahydrate. The flask was connected to a reflux condenser, flushed with argon and then 10 mL of distilled water was added. The flask was placed in an oil bath and was refluxed for 4 h. After this time, the reaction mixture was cooled to RT, filtered, and extracted with 3 × 15 mL of ethyl acetate, the organic layer was dried with anhydrous sodium sulfate and evaporated to dryness furnishing 0.13 g of a light brown solid in 66% yield. This product undergoes a rapid carbonatation. Thus, it was used immediately for the subsequent step without spectrometric characterization; R_f = 0.48 (Hex-AcOEt = 1:3, *v/v*); mp = 172–174 °C.

*4.6. Synthesis of bis(4-(1H-tetrazol-1-yl)phenyl)amine (**9**)*

In a 50-mL round-bottomed flask equipped with a magnetic stirring bar, were added 0.11 g (1.0 equiv.) of N^1-(4-aminophenyl)benzene-1,4-diamine (**8**), 0.23 g (6.1 equiv.) of sodium azide, and 1.0 mL (16.0 equiv.) of trimethyl orthoformate. The flask was placed on an oil bath at 90 °C and 2 mL of acetic acid were added to the mixture. The reaction progress was monitored by TLC and was stopped after 3 h stirring. Then, the reaction mixture was poured into 100 mL of distilled water. The formed precipitate was collected by filtration. The solid was washed with cold distilled water and ethanol and purified by column chromatography with ethyl acetate furnishing 0.14 g of a light brown crystalline solid with 83% yield; R_f = 0.40 (Hex-AcOEt = 1:3, *v/v*); mp = 224–226 °C; ¹H-NMR (500 MHz, d^6-DMSO): δ 9.96 (s, 2H, H-5, H-23), 8.99 (s, 1H, H-12), 7.79 (d, *J* = 8.9 Hz, 4H, H-7, H-11, H-15, H-17), 7.36 (d, *J* = 8.9 Hz, 4H, H-8, H-10, H-14, H-18). ¹³C NMR (126 MHz, d^6-DMSO): δ 143.8 (C-9, C-13), 141.9 (C-5, C-23), 126.4 (C-6, C-16), 122.7 (C-7, C-11, C-15, C-17), 117.6 (C-8, C-10, C-14, C-18). HRMS [M+H]⁺ calculated for $C_{14}H_{12}N_9^+$ = 306.1171, found = 306.1187.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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