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Synthesis of new *bis* 1– and 5–substituted 1*H*-tetrazoles via Huisgen-type 1,3-dipolar cycloadditions[†]

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Abstract: The synthesis and characterization of one symmetrical *bis*-1-substituted-1*H*-tetrazole (69%) via a Huisgen-type 1,3-dipolar cycloaddition, as well as, one symmetrical *aza*-linked *bis*-5-substituted-1*H*-tetrazole (57%) via a classic Huisgen 1,3-dipolar cycloaddition followed by a reductive *aza*-coupling under greener reaction conditions are described. The main reason behind these tetrazole-based ligands is to construct novel Metal-Organic Framework (MOF) architectures to evaluate their CO_2 capture properties under relative humidity conditions. It is worthy to note that both herein reported products have not been synthesized nor isolated, anywhere. Besides, the synthesis of new ligands to fabricate novel MOFs with potential application in environmental remediation has become in a high valued field of opportunity for synthetic chemists and materials engineers.

Keywords: Symmetrical *bis*-tetrazole-based ligands; Huisgen 1,3-dipolar cycloadditions; MOFs chemistry; CO_2 capture properties.

1. Introduction

Metal-Organic Frameworks (MOFs) [1], also known as Porous Coordination Polymers (PCPs) [2] are crystalline hybrid materials built from metal ions (discrete or clusters) linked coordinately by organic polydentate ligands (L^{-n}), resulting in 1D, 2D or 3D infinite architectures. These materials have found a wide range of interesting applications, among it is worth of highlighting their use as catalysts for organic transformations [3], chemosensors [4], proton-conducting materials [5], magnetic materials [6], as well as platforms for gas-storage [7], for example, hydrogen [8], oxygen [9] and methane [10]. However, their use for carbon dioxide capture has become in a very attractive field of opportunity for environmental, synthetic, inorganic and materials/polymers researchers [11]. Most of the known metals have been used successfully to fabricate MOFs [12]. However, the ligands are responsible of conferring their structural properties such as flexibility, porosity, thermal and solvent resistance, pH susceptibility, as well as, their topology [13]. Thus, the most used anionic linkers to synthesize MOFs for carbon dioxide capture contain carboxylate groups ($RCOO^-$), for example, there are many reports using *di-*, *tri-*, *tetra-* and *hexa*-carboxylated ligands [14].

Besides, during the last two decades, the number of publications describing the use of non-carboxylate-based ligands have increased rapidly. Among them, tetrazole-based ligands have gained much attention due mainly to a relative ease in their lab-handling and synthesis in comparison to other polydentate ligands, just such as carboxylated. Thus, the synthesis, characterization and use of polytetrazole-based ligands as precursors of novel and complex porous coordination polymers was reviewed masterfully by Gámez (up to 2011) [15] and Galli (up to 2018) [16].

Tetrazoles are 6π-aromatic *tetra*-nitrogen containing azoles of high interest in various fields of science and technology [17]. From the substitution patterns in their aromatic ring systems, tetrazoles are classified into 1-, 2- and 5-monosubstituted, as well as, 1,5- and 2,5-disubstituted tetrazoles [18], **figure 1a**. Among them, the 5-monosubstituted-1*H*-tetrazoles (5-S-1*H*-T) are the most important because are isosters and bioisosters of carboxylic acids as result of the similarities in their physicochemical properties such as the acidity and the ability to present tautomeric forms toward 5-monosubstituted-2*H* -tetrazoles (5-S-2*H*-Ts). In the same context, their conjugate bases (RCN_4^-, tetrazolates) are considered as excellent carboxylate ($RCOO^-$) surrogates [19]. To coordinate metal-ions, Xiong and co-workers reported that tetrazoles have seven modes (I–VII) through the four-nitrogen electron-donating atoms that allow it to serve as multidentate or bridging building blocks in supramolecular assemblies [20], **figure 1b**.

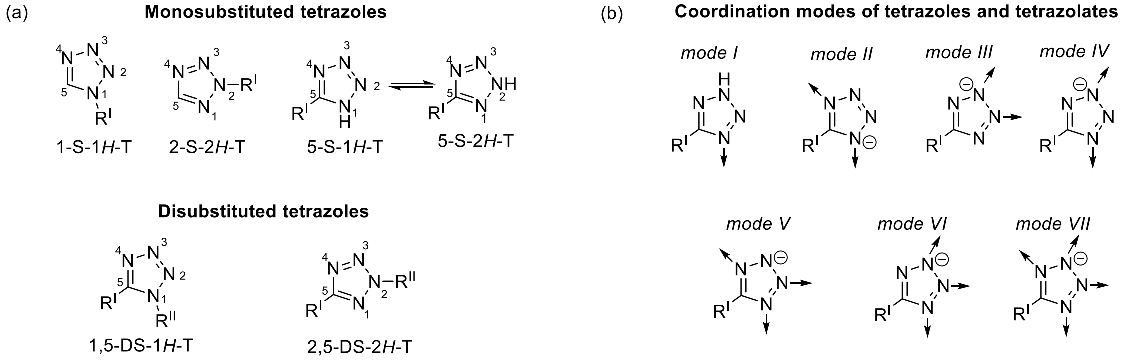


Figure 1. (a) Substitution patterns of tetrazoles. (b) Coordination modes of tetrazoles and tetrazolates

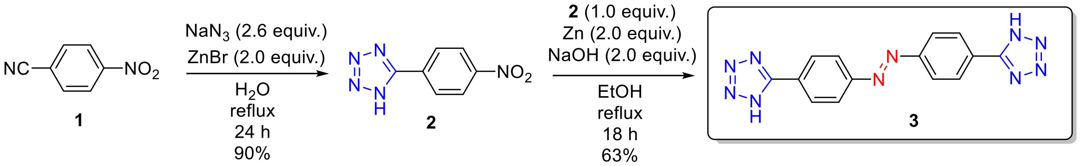
The classic method to synthesize efficiently monosubstituted-1*H*-tetrazoles is through Huisgen-type [3+2] dipolar cycloadditions between organic nitriles and a source of the azide anion [21]. For example, Finnegan and co-workers reported the synthesis of 5-substituted-1*H*-tetrazoles (5-S-1*H*-T) by combining nitriles with sodium azide and ammonium chloride in DMF at reflux, giving good to excellent yields [22]. Despite this methodology was reported in 1958, it is still the most used strategy toward monosubstituted-tetrazoles, and most of reported methods since then to date are considered variants of the Finnegan´s method, for example, the greener synthesis reported by Demko and Sharpless in 2001, in which various organic nitriles reacted with sodium azide and zinc bromide in water as solvent at reflux to give 5-substituted-1*H*-tetrazoles in excellent yields [23].

The stock of commercially available ligands to assemble new MOF architectures is limited. Thus, the aim of this communication is to describe the synthesis and characterization of two new ligands (MOF precursors), one symmetrical *bis*-1-substituted-1*H*-tetrazole and one symmetrical *aza*-linked *bis*-5-substituted-1*H*-tetrazole *via* efficient synthetic strategies involving Huisgen-type 1,3-dipolar cycloadditions. It is worth of highlighting that both herein reported ligands have not been synthesized nor isolated, anywhere. Besides, the synthesis of new ligands to fabricate novel MOFs with potential application in environmental remediation like for carbon dioxide capture has become in a high valued field of opportunity.

2. Results and Discussion

2.1 Synthesis of the (E)-1,2-bis(4-(1H-tetrazol-5-yl)phenyl)diazene (**3**)

The 4-nitrobenzonitrile (**1**) reacted with sodium azide and zinc bromide in water as solvent at reflux for 24 hours to give the 5-(4-nitrophenyl)-1*H*-tetrazole (**2**) in 90% yield via a Huisgen [3+2] cycloaddition taking the protocol described by Demko and Sharpless as the synthetic methodology [23]. Then, two equivalents of the tetrazole **2** reacted themselves in ethanol as solvent at reflux for 18 hours to synthesize the symmetrical *bis*-5-substituted-1*H*-tetrazole (**3**) in 63% yield via a Zn(0)-assisted reductive *aza*-coupling, **scheme 1**. As it can be seen, the yield for the two steps was 57%, which is excellent considering the complexity of the symmetrical bidentate ligand, that the linker functional group is an *aza*-bond, and that only two experimental steps were required for its total synthesis. In the same context, it is important to highlight the use of green conditions because ecofriendly solvents (water and ethanol) were used in both processes.



Scheme 1. Huisgen / *aza*-coupling strategy towards the new symmetrical *bis*-5-S-1*H*-Tetrazole **3**.

The tetrazole **2** and *bis*-tetrazole **3** were characterized by their physicochemical properties, as well as by spectroscopic techniques (*See the experimental part for further details*). The **figure 2** shows the ^{1}H and ^{13}C NMR spectra of the product **2**, and **figure 3** shows the ^{1}H and ^{13}C NMR spectra of the product **3**. For the tetrazole **2**, it is worthy to note the $A^{2}B^{2}$ system for the phenyl ring at 8.32 ppm (**figure 2a**), and the peak at 156.8 ppm typical for the C-5 of the tetrazole ring (**figure 2b**). Moreover, for the *bis*-tetrazole **3** (bidentate ligand for MOFs), it has a double $A^{2}B^{2}$ system for their symmetrical aromatic phenyl rings at 8.08 ppm (**figure 3a**). In the same way, there is a peak at 160.6 ppm, which can be attributed to both, C-5 and C-20 of their symmetrical tetrazole rings (**figure 3b**).

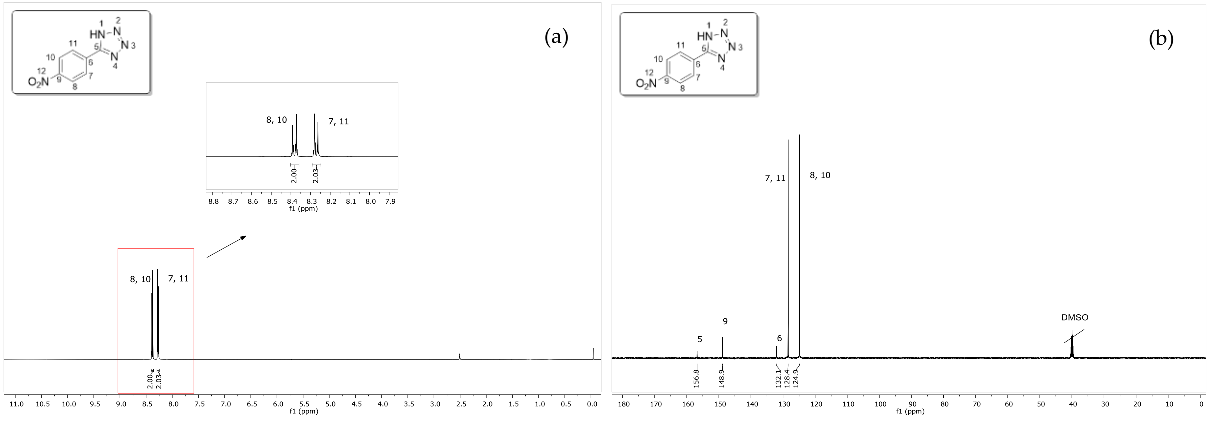


Figure 2. (a) ^{1}H NMR spectrum of the tetrazole **2**. (b) ^{13}C NMR spectrum of the tetrazole **2**.

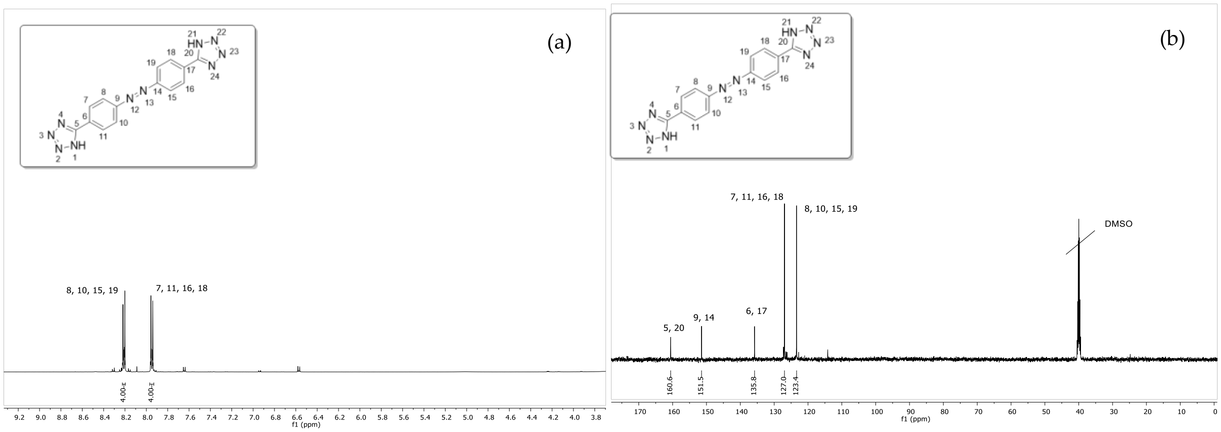
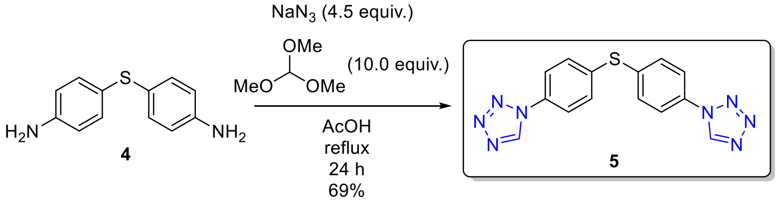


Figure 3. (a) ^{1}H NMR spectrum of the *bis*-tetrazole **3**. (b) ^{13}C NMR spectrum of the *bis*-tetrazole **3**.

2.2 *Synthesis of the bis(4-(1H-tetrazol-1-yl)phenyl)sulfane* (**5**)

The 4,4′-thiodianiline (**4**) reacted with sodium azide and trimethyl orthoformate in acetic acid as solvent at reflux for 24 hours to give the new thioether-bridged *bis*-tetrazole (**5**) in 69% yield via a Huisgen-type [3+2] cycloaddition, **scheme 2**. It is worthy to note that in 2010, Chen and co-workers synthesized some *bis*-1-substituted-1*H*-tetrazole based ligands to fabricate new 1D and 2D coordination polymers [24]. In this context, the use of anilines instead of benzonitriles to generate tetrazole rings result in a different connectivity, 5-S-1*H*-T (for the compound **2** and the ligand **3**), and 1-S-1*H*-T (for the ligand **5**).



Scheme 2. A Huisgen-type cycloaddition towards the symmetrical thioether-linked *bis*-1-S-1*H*-Tetrazole **5**.

The *bis*-tetrazole **5** was characterized by its physicochemical properties, as well as by spectroscopic techniques. The **figure 4** shows the ^{1}H and ^{13}C NMR spectra of the product **5**. As seen, there is a key symmetrical A^{2}B^2 system for their phenyl rings at 7.82 ppm, as well as a key singlet at 10.10 ppm, which is attributed to the H-16 and H-18 from the tetrazole rings (**figure 4a**). In the same way, there is a key peak at 142.7 ppm corresponding to the C-16 and C-18 of its tetrazole rings (**figure 4b**).

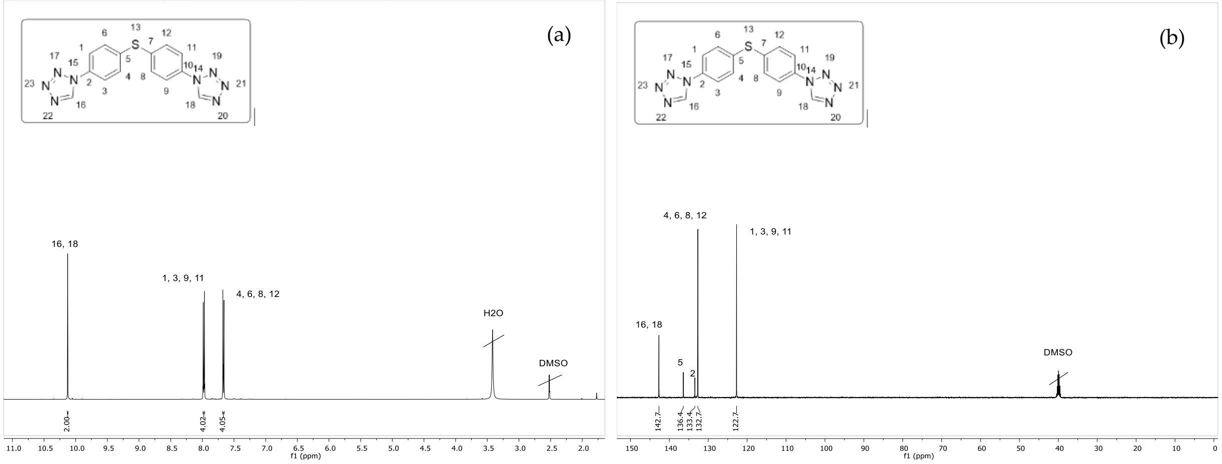


Figure 4. (a) ^{1}H NMR spectrum of the thioether-linked *bis*-tetrazole **5**. (b) ^{13}C NMR spectrum of **5**.

3. Conclusions

Two new symmetrical tetrazole-containing ligands with potential application as precursors of new MOFs were synthesized successfully via short and efficient strategies based on Huisgen-type [3+2] cycloadditions. The use of solvents like water, EtOH or AcOH make greener both synthetic methodologies resulting in low costs, ecofriendly conditions and in high yields. The first attempts to synthesize new porous coordination polymers are being performed and the results will be communicated soon.

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 (δ/ppm). Internal reference for NMR spectra is respect to 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 was treated using the MestReNova software (12.0.0-20080). IR spectra were acquired on a Bruker Tensor 27 spectrophotometer. The absorbance peaks are reported in reciprocal centimeters (cm^{-1}). Reaction progress was monitored by TLC on precoated Kieselgel 60 F$_{254}$ 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. Structure 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 the 5-(4-nitrophenyl)-1H-tetrazole (**2**)

In a round-bottomed flask of 100 mL equipped with a magnetic stirring bar, 1.48 g (1.0 equiv.) of the 4-aminobenzonitrile, 0.84 g (2.6 equiv.) of sodium azide and 2.25 g (2.0 equiv.) of zinc bromide were added sequentially into 40 mL of water. The reaction mixture was stirred at room temperature for 10 minutes and then, the temperature was raised to reflux using an oil bath as a heating system. The reaction progress was monitored by TLC. At the time the starting reagent disappeared, the reaction was stopped (24 hours). After the reaction system reached room temperature, 15 mL of a HCl solution [2 M] were added, and it was stirred vigorously for 15 minutes. When the agitation was stopped, a crystalline precipitate was formed, which was filtered and washed with hot water (70 ° C), methanol, ethyl acetate and acetone (2 x 10 mL per solvent). The compound **3** was dried for 14 hours obtaining 1.72 g of a white crystalline solid in 90% yield; R$_{f}$ = 0.28 (AcOEt–EtOH, 3:2 *v*/*v*); mp = 207–209 °C; ^{1}H NMR (500 MHz, d^{6}-DMSO): δ 8.38 (d, *J* = 9.0 Hz, H-8, H-10, 2H), 8.27 (d, *J* = 9.0 Hz, H-7, H-11, 2H) ppm; ^{13}C NMR (125 MHz, d^{6}-DMSO): δ 156.8 (C-5), 148.9 (C-9), 132.1 (C-6), 128.4 (C-7, C-11), 124.9 (C-8, C-10) ppm; HRMS [M+H]$^{+}$ Calculated for $C_7H_6N_5O_2^+$ = 192.0521, found = 192.0516.

4.3 Synthesis of the (E)-1,2-bis(4-(1H-tetrazol-5-yl)phenyl)diazene (**3**)

In a 100 mL round-bottomed flask equipped with a magnetic stirring bar, 0.5 g (1.0 equiv.) of the 5-(4-nitrophenyl)-1*H*-tetrazole, 0.34 g (2.0 equiv.) of zinc and 0.20 g (2.0 equiv.) of sodium hydroxide in 12.5 mL of ethanol and 5 mL of water were sequentially added. The reaction mixture was refluxed for 24 hours. At the end of this time, the presence of an orange spot by TLC indicated that the azo-coupling finished successfully. Once the reaction mixture reached room temperature, the zinc was filtered, and to new crude, 20 mL and 15 mL of water and ethyl acetate were added, respectively. Then, the extraction was carried out using 8 mL of ethyl acetate, then the organic phase was concentrated to dryness under reduced pressure, and the reaction crude was purified by a silica column using a mixture of DMC with MeOH (3:2 *v*/*v*) as eluent. The product was collected and concentrated to a vacuum obtained an orange solid, which was recrystallized using ethyl acetate. Finally, 0.57 g of an orange crystalline solid (**5**) was obtained in 63% yield; $R_f = 0.11$ (AcOEt–EtOH, 3:2 *v*/*v*); mp = 224–226 °C; ^{1}H NMR (500 MHz, d^6-DMSO): δ 8.21 (d, *J* = 8.7 Hz, H-8, H-10, H-15, H-19, 4H), 7.95 (d, *J* = 8.7 Hz, H-7, H-11, H-16, H-18, 4H) ppm; ^{13}C NMR (125 MHz, d^6-DMSO): δ 160.6 (C-5, C-20), 151.5 (C-9, C-14), 135.8 (C-6, C-17), 127.0 (C-7, C-11, C-16, C-18), 123.4 (C-8, C-10, C-15, C-19) ppm; HRMS $[M+Na]^+$ Calculated for $C_{14}H_{10}N_{10}Na^+ = 341.0988$, found = 341.0982.

4.4 *Synthesis of the bis(4-(1H-tetrazol-1-yl)phenyl)sulfane* (**5**)

In a round bottomed flask of 50 mL equipped with a magnetic stirring bar, 1.08 g of 4,4′-thiodianiline (1.0 equiv.), 1.5 g of sodium azide (4.5 equiv.) and 5.5 mL of trimethyl orthoformate (10 equiv.) were added sequentially into 10 mL of acetic acid. The reaction mixture was placed on an oil bath and the temperature was raised to 90 °C (reflux). The reaction progress was monitored by TLC and was stopped after being stirred for 24 h. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration, washed with cold distilled water and let dried at room temperature. Then, 1.11 g of a gray powder were obtained in 69% yield; $R_f = 0.23$ (Hex–AcOEt, 2:3 *v*/*v*); mp > 250 °C; ^{1}H NMR (500 MHz, d^6-DMSO): δ 10.1 (s, H-16, H-18, 2H), 7.98 (d, *J* = 8.8 Hz, H-1, H-3, H-9, H-11, 4H), 7.67 (d, *J* = 8.8 Hz, H-4, H-6, H-8, H-12, 4H) ppm, ^{13}C NMR (125 MHz, d^6-DMSO): δ 142.7 (C-16, C-18), 136.4 (C-5), 133.4 (C-2), 132.7 (C-4, C-6, C-8, C-12), 122.7 (C-1, C-3, C-9, C-11) ppm; HRMS $[M+H]^+$ Calculated for $C_{14}H_{11}N_8S^+ = 323.0827$, found = 323.0812.

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