DOI: 10.1002/ejoc.200900389

Functionalized Tetrazoles from Cyanogen Azide with Secondary Amines

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Keywords: Tetrazole / Cyclization / Azides / Nitrogen heterocycles

Secondary amines react with cyanogen azide at ambient temperature in water/acetonitrile to provide tetrazole derivatives directly. The scope and limitations with regard to steric hindrance of the amine are discussed. Although reaction yields are moderate, 29–81 %, the cyanogen azide reactions provide a direct and versatile route to functionalized tetrazoles that may be especially useful considering the diversity of amines suitable for this transformation.

Introduction

Tetrazoles are five-membered aromatic heterocycles[1] that exhibit an unusually wide range of interesting applications, for example as the cores of high energy-density materials (HEDM).[2] Very recently, energetic nitrogen-rich salts and ionic liquids of 5-aminotetrazole were introduced as weak acids by our laboratory.[3] In the last decade elegant studies gave tetrazoles in water by click chemistry requiring stoichiometric amounts of a cyano compound, zinc salt and sodium azide.[4] The scope of the reaction is quite broad; a variety of aromatic nitriles,[4b] activated and nonactivated alkyl nitriles,[4b] substituted vinyl nitriles, thiocyanates,[4b] cyanamides,[4b] α-amino nitriles[4e] and *N*-cyano sulfoximines[4f] have all been shown to be viable substrates for this reaction. Additionally, the development of an efficient method for the synthesis of perfluoroalkylated tetrazoles is thus of growing interest due to the wide potential envisioned for these moieties based on their bioactivities and commercial applications.[5] The direct syntheses of 1-substituted 4-perfluoroalkyl tetrazol-5-ones were reported via the reaction of isocyanates with fluorinated alkyl azides in good to excellent yields.[5c] Although many different synthetic methods for preparation of substituted tetrazoles are known, there remains active interest in developing new and versatile conditions, given the considerable interest in tetrazoles for their wealth of biological properties.

Currently, the development of mono-, di-, and tri-substituted 5-aminotetrazole compounds by our research group has been extended by the utilization of an excellent in situ method which involves reactions of cyanogen azide[6] and primary amines[7a] or hydrazines.[7b] It has been postulated that an imidoyl azide[4b,4c,8] is the intermediate during the formation of aminotetrazole upon cyclization. Nitration of these aminotetrazoles using 100% nitric acid has been shown to form mono-, di- or trisubstituted nitroiminotetrazole derivatives and their salts which are energetic materials (HEDM).[9]

Results and Discussion

Now we report that a variety of secondary amines serve as versatile intermediates for the synthesis of substituted tetrazoles, in a transformation which can be viewed as a functionalized-tetrazole synthesis reaction. At ambient temperature, amines in water/acetonitrile in the presence of cyanogen azide,[6] which was synthesized at 0–5 °C from cyanogen bromide and dry sodium azide in dry acetonitrile, are cleanly converted into the tetrazoles **1**–**15** (Scheme 1). Pure cyanogen azide is extremely dangerous and toxic. Therefore, when utilizing the substance as a reactant, it must always be dissolved in a solvent to give a dilute solution. During the reaction, traces of moisture resulted in formation of the byproduct sodium 5-azidotetrazolate,[6b,10a,10b] which was subsequently isolated as a highly explosive and shock-sensitive solid (see safety precautions).

All reactions proceeded to completion in less than 24 h, and tetrazoles were isolated in moderate yields (29–81%) after washing with water or acetonitrile (Table 1). The attractiveness of this route stems from the ease with which the secondary amine precursors can be synthesized in one step to form tetrazole derivatives.

The case of tetrazole, **8**·H_2O, which was formed by double substitution of cyanogen azide, is not typical for a simple tetrazole. This compound was characterized by the usual spectroscopic methods and single-crystal X-ray diffraction analysis (Figure 1). A compound formed by coupling[13] of two nonsymmetric tetrazoles, **8**·H_2O, displays usual features with N2–C6 bond lengths at approximately 1.410(2) Å. The N3–N4 1.318(2) Å and N8–N9 1.312(2) Å bonds are typically the shortest in each tetrazole ring. There

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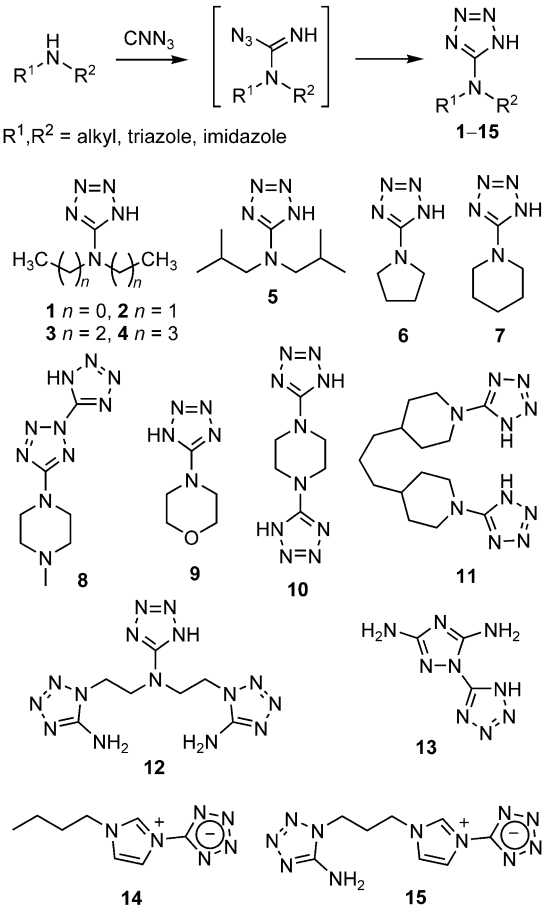
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900389.



Scheme 1. Reactions of secondary amines, triazoles and imidazoles with cyanogen azide.

Table 1. Yield of tetrazoles **1**–**15**.

	Yield [%]		Yield [%]		Yield [%]
1[a]	81	**6**[c]	56	**11**	68
2[b]	30	**7**[d]	50	**12**	29
3	60	**8**	45	**13**	63
4[c]	43	**9**[d]	44	**14**	42
5[c]	46	**10**	57	**15**	74

[a] Ref.[11]. [b] Ref.[4b,11,12a]. [c] Ref.[12b]. [d] Ref.[12a,12b]

are relatively few heterobicyclic (triazole-imidazole, triazole-triazole or triazole-tetrazole) systems in the literature.[13]

Attempts to prepare two different kinds of unsymmetrical mono- and disubstituted aminotetrazoles in the same molecule resulted in **12**. This structure is based on the appearance of $[M - H]^+$ using FAB mass spectroscopy (**12** dissolved in tetrabutyl ammonium hydroxide/methanol with glycerol as a matrix) as well as elemental analysis. Then the preparation of triazole-substituted tetrazoles was studied. We attempted the well-established reaction of aminotriazoles with reactive cyanogen azide, which is of considerable importance for the synthesis of energetic 1-substituted 3,5-diamino-1,2,4-triazoles (Scheme 1).

Earlier we reported that 3,5-damino-1,2,4-triazole reacted with cyanamide or cyanogen guanidine to give 1-substituted addition products.[14] The reaction of diaminotriazole with cyanogen azide proceeded analogously in acetonitrile/water at room temperature for 18 h to form the corresponding diaminotriazole-substituted energetic tetrazole **13** (63%) (Scheme 1).

In Figure 2, the ^{15}N NMR spectrum of tetrazole **13** was measured in [D$_6$]DMSO solution and chemical shifts are given with respect to CH_3NO_2 as external standard (Figure 1). The spectrum of **13** with 7 signals at –326.48, –315.26 (t, $^1J_{N,H}$ = 87 Hz), –221.78 (N3), –189.30 (N5), –160.37 (N4), –119.51 (N1) and –6.47 (N2) ppm is depicted in the Supporting Information. The signals of the amines formed from 1,2,4-triazole appear as expected at high field (N6 and N7). The assignments are given on the basis of the literature values of the chemical shift of the 1,2,4-triazole and tetrazole.[7,15]

Forty years ago it was shown that the alkylation reaction of sodium 5-(dimethylamino)tetrazolate and benzyl chloride in aqueous ethanol gave not only the expected 1- and 2-benzyl isomers but also a novel tetrazole ylide, based on IR, NMR and single-crystal X-ray analysis evidence.[16a,16b] We find that 1-substituted imidazoles react with CNN_3 to also give 3-substituted tetrazole ylides, 14 (42%) and 15 (74%). By using heteronuclear multiple-bond correlation (HMBC), heteronuclear single quantum correlation (HSQC) as well as elemental analysis, the imidazole-substituted tetrazole ylides[16c] were confirmed.

In particular, we were interested in utilizing our well-established tetrazole synthesis methodology with the highly hindered 4-amino-2,2,6,6-tetramethylpiperidine. However, substitution of the secondary amine in the piperidine ring did not occur. Rather the piperidinium azidotetrazolate salt, **16**, was obtained and confirmed by single-crystal X-ray diffraction analysis (Scheme 2, Figure 1).

Dimethyl sulfoxide was the only solvent found from which **16** could be successfully crystallized for structural analysis. The 5-azidotetrazolate anion apparently was formed as a by-product from the reaction of cyanogen azide with water.[6b] The geometry of the azidotetrazole anion[10a] structure of **16** is similar to that observed for neutral 5-azido-1*H*-tetrazole[10b] and mono-[10c] or di-substituted 5-azidotetrazole.[10d] In the azidotetrazole anion structures, the N17–N18 [1.340(3) Å] and the N22–N23 [1.239(3) Å] bond lengths are shorter than those in neutral 5-azidotetrazole, while the N18–N19 [1.308(3) Å] as well as the C21–N22 [1.402(3) Å] distances are found to be longer. For the N19–N20 [1.350(3) Å], N17–C21 [1.322(3) Å], N20–C21 [1.327(3) Å], and N23–N24 [1.116(3) Å] bond lengths, no special trend was observed. The angles at the nitrogen of the azide attached directly to the tetrazole ring are N17–C21–N22 119.8(2)° and N20–C21–N22 126.4(2)°. These are similar to those of other covalent carbon bonded 5-azidotetrazole groups.[10c,10d] The azide moiety is bent [N22–N23–N24 171.2(3)°], which is quite common for covalent azides[10e,10f] and can be explained by hyperconjugation effects.[10g] The N23–N24 bond length is clearly shorter than

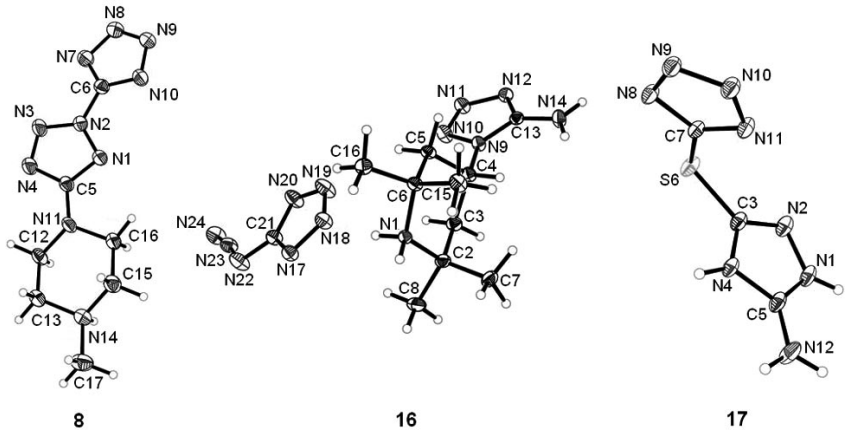


Figure 1. Single crystal X-ray structures of **8**, **16** and **17**. Solvent molecules in **8**, **16** and **17** have been omitted for clarity. 50% Thermal ellipsoids of the atoms are shown.

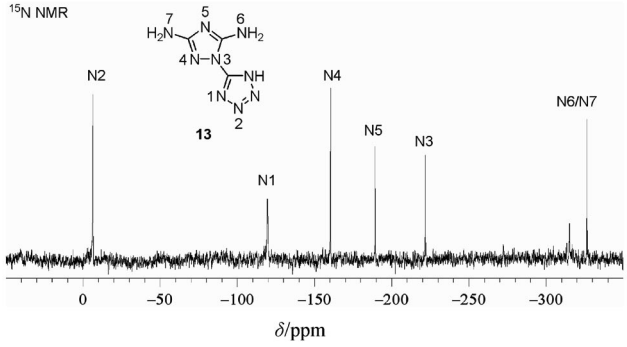
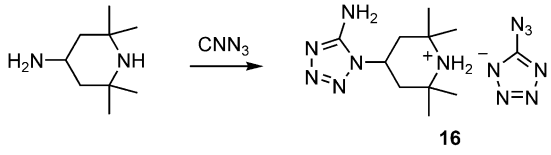


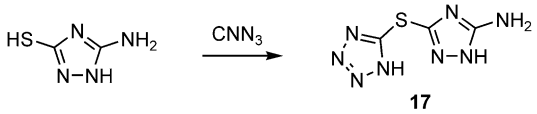
Figure 2. ^{15}N NMR spectrum of tetrazole **13**: delay of 10 s between pulses.



Scheme 2. Reaction of 4-amino-2,2,6,6-tetramethylpiperidine with cyanogen azide.

that of N22–N23. In the 5-aminotetrazole group of **16**, the bond lengths of N9–C13 1.348(3) Å, N9–N10 1.370(3) Å, N10–N11 1.289(3) Å, N11–N12 1.357(3) Å, N12–C13 1.335(3) Å, C13–N14 1.332(3) Å are comparable with those of found in other similar 5-aminotetrazoles.[7]

Interestingly, reaction of unsymmetric amine- and thiol-substituted 1,2,4-triazole resulted in zwitterionic tetrazole **17** (70%) which was characterized by spectroscopic methods and by single-crystal X-ray diffraction analysis (Scheme 3, Figure 1).



Scheme 3. Reaction of 3-amino-5-mercapto-1,2,4-triazole with cyanogen azide.

The C7–N8 bond [1.3325(16) Å] is approximately 0.007 Å shorter than the C7–N11 [1.3390(16) Å]. The ring N–N bonds also show considerable variation, e.g., the N8–N9 bond length is 1.3537(16) Å, whereas N10–N11 is 1.3506(16) Å. Since the bond length C3–S6 and S6–C7 of triazole-tetrazole are 1.7485(13) Å and 1.7581(13) Å, respectively, they are depicted as single bonds. The C3–S6–C7 angle is 98.07(6)°. The hydrogen bonding which results in intermolecular interaction is stronger than in **8** and **16**. The layers in **17** are held together by hydrogen bonding between **17** and dimethyl sulfoxide as a solvent [N1···N11_#1 2.8076(16) Å, N4···N9_#2 2.8081(16) Å, N12···N8_#3 2.9259(17) Å, N12···O1S_#4 2.741(2); symmetry transformation used to generate equivalent atoms, #1: x, $-y$ +1/2, z – 1/2; #2: $-x$ + 2, $-y$, $-z$ + 2; #3: $-x$ + 2, y + 1/2, $-z$ + 3/2; #4: x + 1, $-y$ + 1/2, z + 1/2].

Conclusions

In summary, cyanogen azide was found to be an efficient reagent for the synthesis of readily purified substituted tetrazoles from secondary amines under noncatalytic mild conditions. The general procedure described herein is applicable to secondary amines leading to the preparation of tetrazoles in good yields. The chemical efficiency, the low cost of reagents, and the water tolerance, in the absence of catalytic metal salts, make this process particularly attractive.

Experimental Section

Safety Precautions: Pure cyanogen azide is extremely dangerous and toxic. Therefore, when utilizing the substance as a reactant, it must always be dissolved in a solvent to give a dilute solution. Manipulations must be carried out in a hood behind a safety shield. Leather gloves must be worn. Any excess cyanogen azide in acetonitrile can be destroyed by adding to triphenylphosphane or norbornene.[6b,6d]

General Methods: ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) and 500 MHz (Bruker

AVANCE 500) Nuclear Magnetic Resonance spectrometer operating at 300.13, 75.48 and 50.69 MHz, respectively, by using [D$_6$]-DMSO as solvent and locking solvent. The melting and decomposition points were obtained on a Differential Scanning Calorimeter (TA Instruments Company, Model: Q10) at a scan rate of 10 °C/min, respectively. IR spectra were recorded using KBr pellets for solids on BIORAD model 3000 FTS spectrometer. Densities of aminotetrazole compounds were obtained at room temperature by employing a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were determined using an Exeter CE-440 elemental analyzer. Mass spectra were obtained on a GCMS-QP5050A spectrometer manufactured by SHIMADZU Company.

Crystal Structure Analysis: Data collection was performed and the unit cell was initially refined using APEX2 [v2.1-0].[17a] Data Reduction was performed using SAINT [v7.34A][17b] and XPREP [v2005/2].[17c] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].[17d] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[17e]

Crystal Data for 8: $C_{7.25}H_{14}N_{10}O_{1.25}$ (including H_2O and CH_3OH), M_w = 261.68, crystal size: 0.89 × 0.83 × 0.71 mm^3, tetragonal, $I4_1/a$, a = 13.8158(5) Å, b = 13.8158(5) Å, c = 25.5079(18) Å, α = 90°, β = 90°, γ = 90°, V = 4868.9(4) Å^3, Z = 16, $\rho_{calcd.}$ = 1.426 Mg m^{-3}, μ = 0.108 mm^{-1}, F(000) = 2200, R_1 = 0.0541 for 1619 observed [$I > 2\sigma(I)$] reflections and 0.0629 for all 1978 reflections, goodness-of-fit = 1.034, 174 parameters. **16**: $C_{13}H_{27}N_{13}OS$ (including DMSO), M_w = 413.54, crystal size: 0.24 × 0.19 × 0.14 mm^3, triclinic, $P\bar{1}$, a = 9.074 Å, b = 11.036 Å, c = 12.397 Å, α = 65.842(6)°, β = 89.834(6)°, γ = 70.135(6)°, V = 1051.9(7) Å^3, Z = 2, $\rho_{calcd.}$ = 1.306 Mg m^{-3}, μ = 0.187 mm^{-1}, F(000) = 440, R_1 = 0.0637 for 3619 observed [$I > 2\sigma(I)$] reflections and 0.0939 for all 5241 reflections, goodness-of-fit = 1.058, 259 parameters. **17**: $C_5H_{10}N_8O_1S_2$ (including DMSO), M_w = 262.32, crystal size: 0.73 × 0.64 × 0.35 mm^3, monoclinic, $P2_1/c$, a = 10.1191(10) Å, b = 16.6980(17) Å, c = 6.8583(7) Å, α = 90°, β = 104.145(2)°, γ = 90°, V = 1123.7(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.551 Mg m^{-3}, μ = 0.469 mm^{-1}, F(000) = 544, R_1 = 0.0338 for 2591 observed [$I > 2\sigma(I)$] reflections and 0.0367 for all 2818 reflections, goodness-of-fit = 1.053, 147 parameters.

CCDC-724960 (for **8**), -724961 (for **16**) and -724959 (for **17**) contain the supplementary crystallographic data for this paper; these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure: At 0 °C, 10 mmol cyanogen bromide was dissolved in 50 mL of dry acetonitrile to which was added 40 mmol dry sodium azide. The reaction mixture was stirred at 0–5 °C for 4 h. The inorganic salt was filtered off (***Caution!*** After filtering, the salt must be dissolved in cold water quickly). The cyanogen azide solution is added to a solution containing 5 mmol secondary amine (for diamine: 2.5 mmol) or amino ester (for ammonium hydrochloride 4.5 mmol NaOH was required.) in 20 mL of water at 0 °C. After stirring overnight at ambient temperature, the solvent was removed in air. The product was purified by washing with water and acetonitrile.

5-(Dimethylamino)-1*H*-tetrazole (1): Yield 0.49 g, 81%, colorless crystals, m.p. 248 °C. IR (KBr): $\tilde{\nu}$ = 3429, 2944, 2822, 2520, 2479, 1645, 1459, 1414, 1036, 945, 733 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, 25 °C): δ = 2.97 (s, 6 H, NMe$_2$), 14.81 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 38.8, 159.7 ppm. $C_3H_7N_5$ (113.12): calcd. C 31.85, H 6.24, N 61.91; found C 31.82, H 6.32, N 63.38.

5-(Diethylamino)-1*H*-tetrazole (2): Yield 0.23 g, 30%, white solid, m.p. 124 °C. IR (KBr): $\tilde{\nu}$ = 3426, 2974, 2936, 2813, 2760, 2676, 2550, 2488, 1626, 1454, 1409, 1383, 1328, 1195, 1079, 1042, 1007, 781, 735 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.1 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2-H), 3.4 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, 1-H), 14.6 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 12.6, 43.3, 157.5 ppm. $C_5H_{11}N_5$ (141.17): calcd. C 42.54, H 7.85, N 49.61; found C 42.54, H 7.86, N 49.74.

5-(Dipropylamino)-1*H*-tetrazole (3): Yield 1.0 g, 60%, white solid, m.p. 132 °C. IR (KBr): $\tilde{\nu}$ = 3428, 2968, 2878, 2802, 2658, 2535, 2481, 1620, 1411, 1034 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.9 (t, ^3J = 7.4 Hz, 6 H, 3-H), 1.5 (sext, $^3J_{H,H}$ = 7.4 Hz, 4 H, 2-H), 3.3 (t, $^3J_{H,H}$ = 7.4 Hz, 4 H, 1-H), 14.6 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 10.7, 20.3, 50.9, 157.9 ppm. $C_7H_{15}N_5$ (169.23): calcd. C 49.68, H 8.93, N 41.38; found C 49.87, H 9.01, N 41.65.

5-(Dibutylamino)-1*H*-tetrazole (4): Yield 0.53 g, 43%, white solid, m.p. 131 °C. IR (KBr): $\tilde{\nu}$ = 3430, 2962, 2933, 2870, 2803, 2755, 2660, 1619, 1408, 1042 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.9 (t, ^3J = 7.3 Hz, 6 H, 4-H), 1.3 (sext, $^3J_{H,H}$ = 7.5 Hz, 4 H, 3-H), 1.5 (quin, $^3J_{H,H}$ = 7.4 Hz, 4 H, 2-H), 3.3 (t, $^3J_{H,H}$ = 7.4 Hz, 4 H, 1-H), 14.5 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 13.7, 19.3, 29.1, 48.9, 157.9 ppm. $C_9H_{19}N_5$ (197.28): calcd. C 54.79, H 9.71, N 35.50; found C 54.79, H 9.77, N 35.81.

5-(Diisobutylamino)-1*H*-tetrazole (5): Yield 0.45 g, 46%, white solid, m.p. 187 °C. IR (KBr): $\tilde{\nu}$ = 3430, 2961, 2874, 2810, 2747, 2658, 2479, 1620, 1042 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.8 (d, ^3J = 6.7 Hz, 12 H, Me$_3$), 2.0 (sept, $^3J_{H,H}$ = 6.7 Hz, 2 H, 2-H), 3.2 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, 1-H), 14.5 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 19.6, 26.2, 57.1, 158.4 ppm. $C_9H_{19}N_5$ (197.28): calcd. C 54.79, H 9.71, N 35.50; found C 54.97, H 9.77, N 35.90.

5-(Pyrrolidin-1-yl)-1*H*-tetrazole (6): Yield 0.38 g, 56%, white solid, m.p. 235 °C. IR (KBr): $\tilde{\nu}$ = 3428, 3093, 2946, 2874, 2780, 2671, 2490, 1634, 1457, 1417, 1360, 1150, 1034, 957, 735 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.91–1.93 (m, 4 H), 3.33–3.35 (m, 4 H), 14.6 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]-DMSO, 25 °C): δ = 25.0, 48.1, 156.5 ppm. $C_5H_9N_5$ (139.16): calcd. C 43.15, H 6.52, N 50.33; found C 43.06, H 6.45, N 50.61.

5-(Piperidin-1-yl)-1*H*-tetrazole (7): Yield 0.39 g, 50%, white solid, m.p. 199 °C. IR (KBr): $\tilde{\nu}$ = 3430, 3085, 2941, 2857, 2806, 2713, 1623, 1448, 1408, 1227, 1039, 1016, 916, 735 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.6 (br. s, 6 H, 2-H and 3-H), 3.6 (br. s, 4 H, 1-H), 14.7 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 23.3, 24.3, 47.7, 159.0 ppm. $C_6H_{11}N_5$ (153.19): calcd. C 47.04, H 7.24, N 45.72; found C 47.12, H 7.22, N 45.85.

5-(4-Methylpiperazin-1-yl)-2,5′-bi(2*H*-tetrazole) (8)·H$_2$O: Yield 0.62 g, 45%, white crystal, m.p. 180 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3411, 3031, 2923, 2720, 2653, 2493, 1629, 1565, 1527, 1456, 1397, 1371, 1292, 1196, 992, 927 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 2.9 (s, 3 H, Me), 3.4 (t, $^3J_{H,H}$ = 4.9 Hz, 4 H), 3.7 (br. s, 4 H), 5.2 (br. s, 3 H, NH and H_2O) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 42.4, 43.8, 51.4, 157.8, 167.8 ppm. $C_7H_{12}N_{10}\cdot H_2O$ (254.25): calcd. C 33.07, H 5.55, N 55.09; found C 33.39, H 5.18, N 55.24.

5-(Morpholin-4-yl)-1*H*-tetrazole (9): Yield 0.39 g, 44%, white crystal, m.p. 177 °C. IR (KBr): $\tilde{\nu}$ = 3429, 3083, 2964, 2864, 2807, 2701, 1624, 1452, 1414, 1365, 1266, 1151, 1114, 1026, 928, 737 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 3.4 (m, 4 H), 3.7 (m, 4 H), 15.1 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO,

25 °C): δ = 46.9, 65.1, 159.8 ppm. $C_5H_9N_5O$ (155.16): calcd. C 38.70, H 5.85, N 45.14; found C 38.24, H 5.76, N 46.06.

1,4-Bis(1*H*-tetrazol-5-yl)piperazine (10)·2H$_2$O: Yield 0.86 g, 57%, white solid, m.p. 118 °C (H_2O), 308 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3417, 3239, 3103, 2975, 2803, 2683, 2541, 1608, 1448, 1272, 1081, 1013, 944, 741, 628 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 3.5 (s, 8 H), 4.62 (br. s, 6 H, NH and H_2O) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 45.9, 160.1 ppm. $C_6H_{10}N_{10}$·2H_2O (258.24): calcd. C 27.91, H 5.46, N 54.24; found C 27.73, H 5.67, N 52.99.

1,4-Bis(1*H*-tetrazol-5-yl)piperazine (10): Yield 0.74 g, 57%, white solid, m.p. 307 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3434, 3089, 2978, 2810, 2711, 1604, 1447, 1392, 1302, 1271, 1155, 1015, 941 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 3.5 (s, 8 H), 11.4 (br. s, 2 H, NH) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 45.9, 159.9 ppm. $C_6H_{10}N_{10}$ (222.21): calcd. C 32.43, H 4.54, N 63.03; found C 32.30, H 4.63, N 62.36.

1,3-Bis[1-(1*H*-tetrazol-5-yl)piperidin-4-yl]propane (11)·0.5H$_2$O: Yield 0.90 g, 68%, white solid, m.p. 228 °C. IR (KBr): $\tilde{\nu}$ = 3429, 2919, 2840, 2765, 2705, 1625, 1446, 1402, 1370, 1245, 1038, 729 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.06–1.43 (m, 12 H), 1.69–1.73 (m, 4 H), 2.90–2.94 (m, 4 H), 3.78–3.82 (m, 4 H), 14.8 (br. s, 2 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 22.9, 30.7, 34.6, 36.0, 47.2, 158.9 ppm. $C_{15}H_{26}N_{10}$·0.5H_2O (355.44): calcd. C 50.69, H 7.66, N 39.41; found C 50.33, H 7.58, N 39.70.

***N*,*N*-Bis[2-(5-amino-1*H*-tetrazol-1-yl)ethyl]-5-amino-1*H*-tetrazole (12):** Yield 0.87 g, 29%, white solid, m.p. 258 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3420, 3375, 3329, 3246, 3183, 2932, 1650, 1584 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 3.6 (t, $^3J_{H,H}$ = 5.8 Hz, 4 H), 4.3 (t, $^3J_{H,H}$ = 5.8 Hz, 4 H), 6.7 (s, 4 H), 14.1 (br. s, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 42.2, 48.0, 155.6, 158.6 ppm. MS (FAB$^-$): *m*/*z* (%) = 306.08 (100) [M – H]$^+$. $C_7H_{13}N_{15}$ (307.28): calcd. C 27.36, H 4.26, N 68.37; found C 27.66, H 4.42, N 67.01.

3,5-Diamino-1-(1*H*-tetrazol-5-yl)-1*H*-1,2,4-triazole (13): Yield 0.75 g, 63%, white solid, m.p. 248 °C. IR (KBr): $\tilde{\nu}$ = 3442, 3347, 3143, 2659, 1684, 1632, 1582 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, 25 °C): δ = 7.3 (s, 2 H), 7.8 (br. s, 3 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 151.5, 154.6, 162.7 ppm. ^{15}N NMR (50.7 MHz, [D$_6$]DMSO, 25 °C): δ = –326.5, –315.3 (t, $^1J_{N,H}$ = 87 Hz, NH_2), –221.8 (N3), –189.3 (N5), –160.4 (N4), –119.5 (N1), –6.5 (N2) ppm. $C_3H_5N_9$ (167.13): calcd. C 21.56, H 3.02, N 75.43; found C 21.29, H 3.11, N 73.43.

5-(1-Butyl-1*H*-imidazol-1-ium-3-yl) Tetrazolide (14): Yield 0.48 g, 42%, white solid, m.p. 163 °C. IR (KBr): $\tilde{\nu}$ = 3425, 3090, 3007, 2958, 2933, 2870, 1576, 1495, 1450, 1306, 1261, 1187, 1138, 1076, 791, 737, 637 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.9 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, Me), 1.3 (sext, $^3J_{H,H}$ = 7.5 Hz, 2 H), 1.9 (quin, $^3J_{H,H}$ = 7.3 Hz, 2 H), 4.3 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 8.0 (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 1.7 Hz, 1 H), 8.2 (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 1.7 Hz, 1 H), 9.9 (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 1.7 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 13.2, 18.8, 31.1, 49.0, 120.3, 123.2, 134.2, 155.9 ppm. $C_8H_{12}N_6$ (192.22): calcd. C 49.99, H 6.29, N 43.72; found C 49.89, H 6.50, N 44.28.

5-{1-[3-(5-Amino-1*H*-tetrazol-1-yl)propyl]-1*H*-imidazol-1-ium-3-yl} Tetrazolide (15): Yield 0.62 g, 74%, white solid, m.p. 288 °C. IR (KBr): $\tilde{\nu}$ = 3414, 3320, 3135, 3012, 1668, 1593, 1571 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.4 (quin, $^3J_{H,H}$ = 7.0 Hz, 2 H), 4.2 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 4.3 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 6.7 (s, 2 H, NH_2), 8.0 (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 1.7 Hz, 1 H), 8.2 (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 1.7 Hz, 1 H), 9.8 (dd, $^4J_{H,H}$ = 1.6, $^4J_{H,H}$ = 1.6 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 28.2, 41.5, 46.6, 120.2, 123.1, 134.5, 155.3, 157.0 ppm. $C_8H_{11}N_{11}$ (261.12): calcd. C 36.78, H 4.24, N 58.98; found C 36.43, H 4.37, N 57.25.

4-(5-Amino-1*H*-tetrazol-1-yl)-2,2,6,6-tetramethylpiperidinium 5-Azidotetrazolate (16)·0.5DMSO: Yield 0.55 g, 47%, white crystal (with DMSO), m.p. 148 °C, 169 (dec.). IR (KBr): $\tilde{\nu}$ = 3308, 3148, 2950, 2799, 2769, 2649, 2509, 2143 (N_3), 1659, 1586, 1466, 1400, 1344, 1231, 1024 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.4 (s, 6 H), 1.5 (s, 6 H), 1.91–2.07 (m, 4 H), 4.8 (m, 1 H), 6.9 (s, 2 H, NH_2) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ = 24.4, 30.2, 46.6, 56.0, 154.7, 157.4 ppm. $C_{11}H_{21}N_{13}$·0.5DMSO (372.44): C 40.31, H 6.50, N 48.89; found C 40.23, H 6.60, N 49.36.

3-Amino-5-(1*H*-tetrazol-5-ylthio)-2*H*-1,2,4-triazole (17)·H$_2$O: Yield 0.61 g, 70%, white solid, m.p. 136 °C (H_2O), 218 °C. IR (KBr): $\tilde{\nu}$ = 3602, 3287, 3200, 3139, 3016, 2891, 2757, 2666, 2585, 2500, 2455, 1690, 1634, 1614, 1524, 1469, 1341, 1237, 1214, 1128, 1063, 978, 896, 835, 719, 558 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.3 (br. s, 4 H), 7.7 (br. s, 2 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C: δ = 149.7, 150.2, 158.0 ppm. $C_3H_4N_8S$·H_2O (202.20): calcd. C 17.82, H 2.99, N 55.42; found C 17.73, H 2.91, N 55.62.

3-Amino-5-(1*H*-tetrazol-5-ylthio)-2*H*-1,2,4-triazole (17): Yield 0.56 g, 70%, white solid, m.p. 217 °C. IR (KBr): $\tilde{\nu}$ = 3255, 3152, 3083, 2774, 1686, 1543, 1451, 1341, 1090, 1045, 986, 801, 704, 606 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.3 (br. s, 2 H), 12.6 (br. s, 2 H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, 25 °C: δ = 149.7, 150.2, 158.0 ppm. $C_3H_4N_8S$ (184.18): calcd. C 19.56, H 2.19, N 60.84; found C 19.67, H 2.19, N 61.46.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C spectra of all the tetrazoles **1**–**17**.

Acknowledgments

We gratefully acknowledge the support of Defense Threat Reduction Agency (HDTRA1-07-1-0024), National Science Foundation (NSF) (CHE-0315275), and Office of Naval Research (N00014-06-1-1032).

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Received: April 8, 2009
Published Online: June 4, 2009

