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Synthetic Transformations of 1-Cyanomethylbenzotriazole

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ABSTRACT

*Lithiation of 1-cyanomethylbenzotriazole (**4**) with LDA and subsequent reactions with alkyl halides or carbonyl compounds afforded the corresponding 1-(α-cyanoalkyl)- and 1-(α-cyanoalkenyl)-benzotriazoles. Bromination of **4** with NBS formed 1-(bromocyanomethyl)benzotriazole. 1-Cyanoalkylbenzotriazoles condensed with hydrazine hydrate to give 4-amino-3,5-bis(benzotriazol-1-yl)triazoles which underwent deamination with sodium nitrite to yield 3,5-bis(benzotriazol-1-yl)triazoles.*

INTRODUCTION

Benzotriazole has been demonstrated to activate α-proton loss from an *N*-substituent [1]. This property, together with the well-established leaving ability of benzotriazolate anion [2], greatly extends its applications in organic synthesis. In particular, benzotriazole activated methane systems of the type $BtCH_2X$ (such as X = carbazol-9-yl, OMe) have been shown to be versatile formyl-, acyl-, and methylal-anion equivalents for the synthesis of aldehydes, ketones, and dimethyl acetals [3–6]. 1-Trimethylsilylmethylbenzotriazole (X = $SiMe_3$) has been used for the synthesis of 1-alkenylbenzotriazoles in an adaptation of the Peterson transformation [7].

Benzotriazole derivatives are themselves of considerable interest synthetically and industrially. 1-Alkenylbenzotriazoles are precursors of indoles [8,9] and undergo interesting thermal and photochemical transformations [10]. More recently, Johnson and coworkers reported a total synthesis of gelsemine utilizing 1-(methoxyalkenyl)benzotriazoles [11]. Some 1-alkylbenzotriazoles are biologically active as herbicides [12–14], insecticides [15], and acaricides [12].

We now report some synthetic transformations of 1-cyanomethylbenzotriazole (X = CN), which lead to 1-(α-cyanoalkyl)-, 1-(α-cyanoalkenyl), 1-(bromocyanomethyl)-, and 1-(triazolylalkyl)-benzotriazoles. These compounds are potentially useful synthetic intermediates due to the possible further elaboration of the cyano and benzotriazolyl groups.

RESULTS AND DISCUSSION

Lithiation of 1-Cyanomethylbenzotriazole and Subsequent Reactions with Electrophiles

1-Cyanomethylbenzotriazole (**4**) was prepared by reacting 1-chloromethylbenzotriazole (**1**) with sodium cyanide in DMSO [16]. Treatment of **4** with LDA at −78°C for 1 hour gave the anion **5**, which was quenched with a number of electrophiles (Scheme 1). Methyl iodide, benzyl bromide, and butyl bromide all gave mixtures of mono- (**8a–c**) and dialkylated products (**9a–c**), due to the further deprotonation of **8a–c** under these conditions. The use of 2 equivalents of LDA and of benzyl bromide provided the disubstituted product **9b** in a yield of 72%. Reaction of the anion **5** with benzaldehyde and *p*-tolualdehyde produced the acrylonitrile derivatives **6a**, **b** directly without detection of initial addition products. This is probably due to the acidity of the hydrogen α to the benzotriazolyl group and to the stability of the final products. This trend appeared to be general as even aliphatic aldehydes

Dedicated with affection and admiration to our friend Sig Oae.
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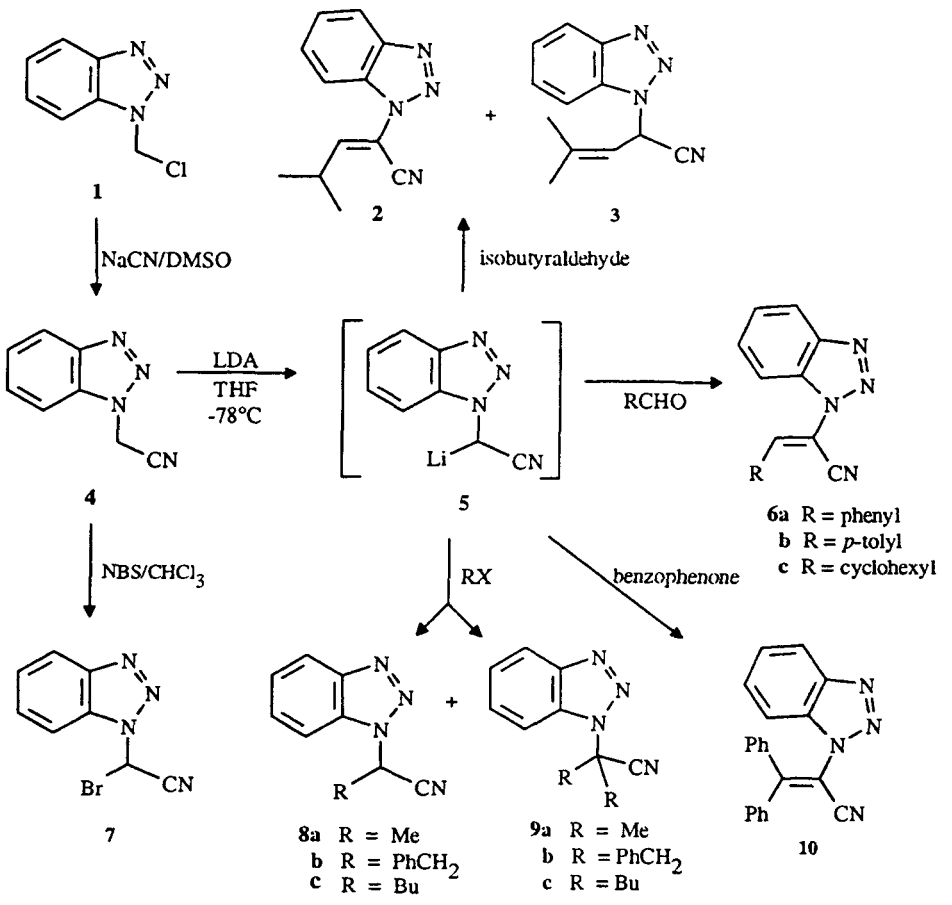
SCHEME 1



such as isobutyraldehyde afforded the corresponding acrylonitrile derivative **2** along with its alkene isomer **3** in yields of 46 and 8%, respectively. Cyclohexanecarboxaldehyde , on the other hand, gave the acrylonitrile derivative **6c** exclusively in 64% yield. Reaction of anion **5** with benzophenone afforded the adduct **10** in 82% yield. The structures of compounds **2**, **3**, **6a–c**, **8a–c**, **9a–c**, and **10** were confirmed by NMR spectroscopy and elemental analyses.

Compared with other α-benzotriazolyl carbanions [1], (benzotriazol-1-yl)cyanomethyl anion (**5**) showed relatively lower reactivity toward electrophiles due to the strong stabilizing effects of both the benzotriazolyl and the cyano group. Thus, reaction of anion **5** with equimolar amounts of alkyl halides uniformly gave the dialkylated derivatives **9a–c** as by-products. Ethyl benzoate, a commonly used electrophile in other systems, did not react with **5**.

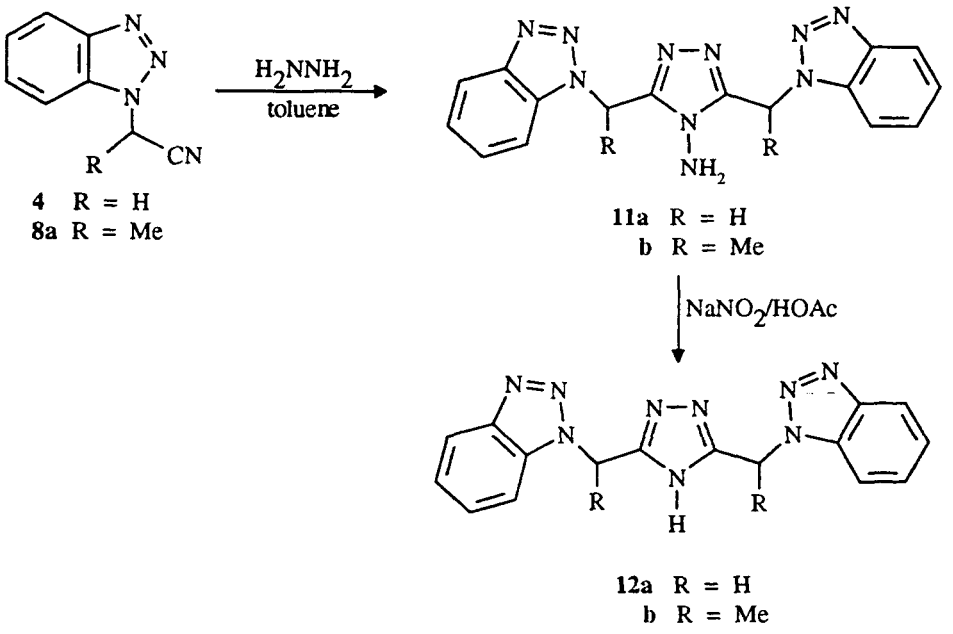
Bromination of 1-Cyanomethylbenzotriazole (**4**)

Bromination of **4** with *N*-bromosuccinimide (NBS) in chloroform afforded in a yield of 38% 1-(bromocyanomethyl)benzotriazole (**7**) (Scheme 1), which could be a useful synthetic intermediate since its bromine atom should be displaceable by nucleophiles [17].

Preparation of 3,5-Bis(benzotriazol-1-ylalkyl)triazoles

Condensations of nitriles with hydrazine are reported [18] to give either 3,6-disubstituted 1,2,4,5-tetrazines or 3,5-disubstituted 4-aminotriazoles, depending on the starting materials and reaction conditions used. 1,2,4,5-Tetrazines, generally products of aromatic nitriles, are converted thermally or by acid into 4-aminotriazoles, which are often formed from aliphatic nitriles.

In our hands, reaction of 1-(cyanoalkyl)-benzotriazoles **4** and **8a** with an excess of hydrazine hydrate in refluxing toluene produced the 4-aminotriazole derivatives **11a** and **11b** exclusively (Scheme 2). The signals for the two amino hydrogens in each of these compounds appeared at δ 5.6–6.3 in the ^{1}H NMR spectra compared with 8.9–9.1 generally observed for the two NH protons of tetrazines [19], thus confirming the structures as **11a** and **11b**. 4-Aminotriazoles **11a** and **11b** underwent normal deamination with sodium nitrite in acetic



SCHEME 2

4 R = H
8a R = Me

11a R = H
b R = Me

12a R = H
b R = Me

acid to give the corresponding triazoles **12a** and **12b** (Scheme 2).

In summary, we have investigated some synthetic transformations of 1-cyanomethylbenzotriazole (**4**). Lithiation and subsequent reaction with alkyl halides or carbonyl compounds afforded the corresponding 1-(α-cyanoalkyl)- and 1-(α-cyanoalkenyl)-benzotriazoles. Compared with other α-benzotriazolyl carbanions, (benzotriazol-1-yl)cyanomethyl anion (**5**) was more stable and less reactive toward electrophiles. Bromination of **4** with NBS gave 1-(bromocyanomethyl)benzotriazole, a potentially useful synthetic intermediate. Condensation of 1-cyanoalkylbenzotriazoles with hydrazine produced 4-amino-3,5-bis(benzotriazol-1-ylalkyl)triazoles, which underwent deamination with sodium nitrite to give 3,5-bis(benzotriazol-1-ylalkyl)triazoles.

EXPERIMENTAL

Melting points were determined on a Bristoline hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer with tetramethylsilane (TMS) as the internal reference. ^{13}C NMR spectra were recorded at 75 MHz on the same instrument using the solvent peak ($CDCl_3$, δ = 77.0; DMSO-d_6, δ = 39.5) as reference. Microanalyses were carried out using a Carlo Erba 1106 elemental analyzer. Flash column chromatography was run on EM Science silica gel (230–400 mesh).

1-Cyanomethylbenzotriazole (**4**) was prepared according to the literature procedure, mp 86–88°C (Ref. [16], mp 85–86°C).

Preparation of 1-(α-Cyanoalkyl)- (**8a–c, 9a–c**) *and 1-(α-Cyanoalkenyl)-benzotriazoles* (**2, 3, 6a–c, 10**)

General Procedure. LDA (5.5 mL, 11 mmol, 2 M in cyclohexane) was added at −78°C to a solution of 1-cyanomethylbenzotriazole (**4**) (1.58 g, 10 mmol) in THF (50 mL). The solution was stirred at this temperature for 1 hour and the appropriate electrophile (11 mmol) added. The mixture was stirred at −78°C for 2 hours, then at room temperature overnight. Water (50 mL) was added and the resulting mixture extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (2 × 50 mL), dried over $MgSO_4$, and evaporated at reduced pressure to give the crude product.

1-(Benzotriazol-1-yl)-1-cyanoethane (**8a**) *and 2-(benzotriazol-1-yl)-2-cyanopropane* (**9a**). Obtained as a mixture from methyl iodide and separated by column chromatography (hexane/ethyl acetate: 4/1). **8a**: yellow oil, yield 59%. Anal. found: C, 62.59; H, 4.71; N, 32.88. $C_9H_8N_4$ requires C, 62.78; H, 4.68; N, 32.54. ^{1}H NMR, δ 8.11 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 8.4 Hz), 7.60 (t, 1H, J = 7.3 Hz), 7.46 (t, 1H, J = 7.4 Hz), 6.09 (q, 1H, J = 7.4 Hz), and 2.13 (d, 3H, J = 7.3 Hz). ^{13}C NMR, δ 146.2, 131.2, 128.4, 124.6, 120.3, 115.9, 109.1, 44.8, and 19.3. **9a**: yellow oil, yield 16%. Anal found: C, 64.47; H, 5.45; N, 30.26. $C_{10}H_{10}N_4$ requires C, 64.54; H, 5.41; N, 30.09. ^{1}H NMR, δ 8.12 (d, 1H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.59 (t, 1H, J = 7.3 Hz), 7.45 (t, 1H, J = 7.4 Hz), and 2.27 (s, 6H). ^{13}C NMR, δ 146.7, 131.2, 128.0, 124.4, 120.4, 118.6, 110.4, 54.5, and 27.5.

1-(Benzotriazol-1-yl)-1-cyano-2-phenylethane (**8b**) *and 2-(benzotriazol-1-yl)-2-cyano-1,3-diphenylpropane* (**9b**). Obtained as a mixture from benzyl bromide and separated by column chromatography (hexane/ethyl acetate: 4/1). **8b**: yellow oil, yield 40%. Anal. found: C, 72.89; H, 4.92; N, 22.71. $C_{15}H_{12}N_4$ requires C, 72.56; H, 4.87; N, 22.57. ^{1}H NMR, δ 8.07 (d, 1H, J = 8.2 Hz), 7.51–7.43 (m, 2H), 7.42–7.36 (m, 1H), 7.28–7.18 (m, 3H), 7.13–7.04 (m, 2H), 6.06 (t, 1H, J = 7.6 Hz), 3.68 (dd, 1H, J_1 = 13.8 and J_2 = 7.4 Hz), and 3.61 (dd, 1H, J_1 = 13.8 and J_2 = 7.4 Hz). ^{13}C NMR, δ 146.1, 132.9, 131.8, 129.1, 128.9, 128.4, 128.2, 124.6, 120.4, 114.9, 109.1, 51.1, and 39.8. **9b**: yellow oil, yield 23%. Anal. found: C, 78.30; H, 5.45; N, 16.43. $C_{22}H_{18}N_4$ requires C, 78.08; H, 5.36; N, 16.56. ^{1}H NMR, δ 7.98 (d, 1H, J = 8.3 Hz), 7.30 (d, 1H, J = 8.4 Hz), 7.27–7.00 (m, 12H), 4.01 (d, 2H, J = 13.8 Hz), and 3.71 (d, 2H, J = 13.9 Hz). ^{13}C NMR, δ 145.8, 133.7, 132.6, 130.2, 128.4, 128.0, 127.7, 123.9, 119.7, 116.5, 110.6, 65.8, and 46.2.

1-(Benzotriazol-1-yl)-1-cyanopentane (**8c**) *and 5-(benzotriazol-1-yl)-5-cyanononane* (**9c**). Obtained as a mixture from butyl bromide and separated by column chromatography (hexane/ethyl acetate: 4/1). **8c**: yellow oil, yield 57%. Anal. found: C, 67.33; H, 6.62; N, 26.34. $C_{12}H_{14}N_4$ requires C, 67.27; H, 6.59; N, 26.15. ^{1}H NMR, δ 8.13 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 8.4 Hz), 7.60 (t, 1H, J = 8.3 Hz), 7.46 (t, 1H, J = 8.2 Hz), 5.92 (t, 1H, J = 8.0 Hz), 2.53–2.31 (m, 2H), 1.56–1.30 (m, 4H), and 0.89 (t, 3H, J = 7.1 Hz). ^{13}C NMR, δ 146.2, 131.4, 128.4, 124.6, 120.5, 115.3, 109.2, 49.6, 33.1, 27.3, 21.5, and 13.4. **9c**: yellow oil, yield 33%. Anal. found: C, 71.42; H, 8.40; N, 20.37. $C_{16}H_{22}N_4$ requires C, 71.08; H, 8.20; N, 20.72. ^{1}H NMR, δ 8.12 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 8.4 Hz), 7.56 (t, 1H, J = 7.3 Hz), 7.44 (t, 1H, J = 7.2 Hz), 2.69–2.56 (m, 2H), 2.42–2.29 (m, 2H), 1.53–1.19 (m, 8H), and 0.86 (t, 6H, J = 7.2 Hz). ^{13}C NMR, δ 146.4, 132.2, 128.1, 124.3, 120.4, 117.6, 110.7, 63.9, 39.0, 26.2, 22.0, and 13.5.

1-(Benzotriazol-1-yl)-1-cyano-3-methylbut-1-ene (**2**) *and 1-(benzotriazol-1-yl)-1-cyano-3-methylbut-2-ene* (**3**). Obtained as a mixture from isobutyraldehyde and separated by column chromatography (hexane/ethyl acetate: 4/1). **2**: orange oil, yield 46%. Anal. found: C, 68.08; H, 5.83; N, 26.23. $C_{12}H_{12}N_4$ requires C, 67.91; H, 5.70; N, 26.40. ^{1}H NMR, δ 8.10 (d, 1H, J = 8.4 Hz), 7.80 (d, 1H, J = 8.4 Hz), 7.60 (t, 1H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.7 Hz), 7.03 (d, 1H, J = 10.7 Hz), 3.23–3.08 (m, 1H), and 1.31 (d, 6H, J = 6.6 Hz). ^{13}C NMR, δ 150.8, 146.0, 131.4, 128.9, 124.8, 120.4, 111.8, 109.8, 109.4, 30.2, and 21.9. **3**: orange oil, yield 8%. Anal. found: C, 68.07; H, 5.84; N, 26.53. $C_{12}H_{12}N_4$ requires C, 67.91; H, 5.70; N, 26.40. ^{1}H NMR, δ 8.11 (d, 1H, J = 8.5 Hz), 7.74 (d, 1H, J = 7.4 Hz), 7.58 (t, 1H, J = 8.2 Hz), 7.44 (t, 1H, J = 8.2 Hz), 6.71 (d, 1H, J = 8.7 Hz), 5.77 (d, 1H, J = 8.7 Hz), 1.88 (s, 3H), and 1.83 (s, 3H). ^{13}C NMR, δ 146.4, 144.4, 131.1, 128.4, 124.6, 120.5, 114.9, 114.3, 109.5, 47.6, 25.5, and 18.4.

1-(Benzotriazol-1-yl)-2-phenylacrylonitrile (**6a**). Obtained as white needles from benzaldehyde and purified by column chromatography (hexane/ethyl acetate: 5/1), yield 34%, mp 119–120°C. Anal. found: C, 73.07; H, 4.06; N, 22.97. $C_{15}H_{10}N_4$ requires C, 73.16; H, 4.09; N, 22.75. ^{1}H NMR, δ 8.16–8.09 (m, 1H), 7.99–7.87 (m, 4H), 7.66–7.58 (m, 1H), and 7.57–7.43 (m, 4H). ^{13}C NMR, δ 146.2, 140.4, 131.9, 131.6, 130.4, 129.6, 129.3, 129.1, 125.0, 120.6, 113.5, 110.2, and 106.4.

1-(Benzotriazol-1-yl)-2-(4-tolyl)acrylonitrile (**6b**). Obtained as microcrystals from *p*-tolualdehyde and purified by column chromatography (hexane/ethyl acetate: 8/1), yield 55%, mp 100–101°C. Anal. found: C, 73.70; H, 4.58; N, 21.38. $C_{16}H_{12}N_4$ requires C, 73.83; H, 4.65; N, 21.52. ^{1}H NMR, δ 8.10 (d, 1H, J = 8.3 Hz), 7.89–7.80 (m, 4H), 7.60 (t, 1H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.7 Hz), 7.31 (d, 2H, J = 8.2 Hz), and 2.43 (s, 3H). ^{13}C NMR, δ 146.1, 142.8, 140.7, 131.5, 129.9, 129.5, 128.9, 127.5, 124.9, 120.4, 113.7, 110.1, 105.2, and 21.6.

1-(Benzotriazol-1-yl)-2-cyclohexylacrylonitrile (**6c**). Obtained as red crystals (*E* and *Z* isomers, *E*/*Z*: 2/1) from cyclohexanecarboxaldehyde and purified by column chromatography (hexane/chloroform: 2/1), yield 64%, mp 76–77°C. Anal. found: C, 71.59; H, 6.51; N, 22.29. $C_{15}H_{16}N_4$ requires C, 71.40; H, 6.39; N, 22.20. *E* isomer: ^{1}H NMR, δ 8.06 (d, 1H, J = 8.4 Hz), 7.79 (d, 1H, J = 8.4 Hz), 7.59 (t, 1H, J = 7.3 Hz), 7.44 (t, 1H, J = 7.2 Hz), 7.04 (d, 1H, J = 10.5 Hz), 2.92–2.77 (m, 1H), and 2.00–1.06 (m, 10H). ^{13}C NMR, δ 149.4, 145.9, 131.3, 128.7, 124.7, 120.2, 111.9, 109.7, 108.9, 39.4, 31.7, 25.1, and 24.8. *Z* isomer: ^{1}H NMR, δ 8.13 (d, 1H, J = 8.4 Hz), 7.67 (t, 1H, J = 7.2 Hz), 7.61 (d, 1H, J = 7.2 Hz), 6.82 (d, 1H, J = 10.6 Hz), 2.48–2.32 (m, 1H), and 2.00–1.06 (m, 10H). ^{13}C NMR, δ 154.7, 145.2, 132.2, 128.8, 120.1, 113.9, 110.9, 109.3, 107.5, 37.8, 31.3, 25.0, and 24.5.

1-(Benzotriazol-1-yl)-2,2-diphenylacrylonitrile (**10**). Obtained as white needles from benzophenone and purified by column chromatography (hexane/ethyl acetate: 4/1), yield 81%, mp 159–160°C. Anal. found: C, 78.12; H, 4.35; N, 17.41. $C_{21}H_{14}N_4$ requires C, 78.24; H, 4.38; N, 17.38. ^{1}H NMR, δ 8.04 (d, 1H, J = 8.2 Hz), 7.65–7.33 (m, 8H), 7.21–7.14 (m, 1H), 7.07 (t, 2H, J = 7.3 Hz), and 6.86 (d, 2H, J = 7.1 Hz). ^{13}C NMR, δ 158.9, 145.4, 136.2, 135.8, 132.2, 131.4, 130.4, 130.3, 129.2, 128.8, 128.7, 128.4, 124.6, 120.3, 115.1, 109.5, and 104.2.

Preparation of 1-Bromocyanomethylbenzotriazole (**7**)

A solution of 1-cyanomethylbenzotriazole (**4**) (0.79 g, 5 mmol) and NBS (1.78 g, 10 mmol) in chloroform (15 mL) was heated at reflux for 24 hours. Additional chloroform (30 mL) was added and the mixture washed with water (2 × 20 mL), dried over $MgSO_4$, and evaporated at reduced pressure to give the crude product. Purification by column chromatography (hexane/ethyl acetate: 15/1) gave compound **7** as a brown oil in 38% yield. Anal. found: C, 40.64; H, 2.15; N, 23.31. $C_8H_5BrN_4$ requires C, 40.53; H, 2.13; N, 23.63. ^1H NMR, δ 8.18 (d, 1H, J = 8.4 Hz), 7.94 (d, 1H, J = 8.4 Hz), 7.73 (t, 1H, J = 7.3 Hz), 7.69 (s, 1H), and 7.56 (t, 1H, J = 7.3 Hz). ^{13}C NMR, δ 146.9, 130.5, 129.7, 125.9, 121.1, 111.6, 110.4, and 34.7.

Preparation of 4-Amino-3,5-bis(benzotriazol-1-ylalkyl)triazoles **11a** *and* **11b**

General Procedure. A mixture of the appropriate 1-cyanoalkylbenzotriazole (**4** or **8a**) (10 mmol), hydrazine hydrate (2.5 g, 50 mmol), and toluene (25 mL) was heated at reflux for 5 days. The precipitate formed was collected by filtration and recrystallized from chloroform to give **11a** or **11b**.

4-Amino-3,5-bis(benzotriazol-1-ylmethyl)triazole (**11a**). Obtained as a white solid, yield 72%, mp 184–185°C. Anal. found: C, 55.31; H, 4.03; N, 40.94. $C_{16}H_{14}N_{10}$ requires C, 55.47; H, 4.08; N, 40.45. ^1H NMR, δ 8.08 (d, 2H, J = 8.3 Hz), 7.86 (d, 2H, J = 8.3 Hz), 7.56 (t, 2H, J = 7.3 Hz), 7.42 (t, 2H, J = 7.5 Hz), 6.25 (s, 2H), and 6.19 (s, 4H). ^{13}C NMR, δ 150.8, 145.2, 133.1, 127.5, 124.1, 119.1, 110.9, and 41.4.

4-Amino-3,5-bis(1-benzotriazol-1-ylethyl)triazole (**11b**). Obtained as a white solid, yield 76%, mp 99–101°C. Anal. found: $[M + H]^+$, m/z, 375.1797; $C_{18}H_{18}N_{10}$ requires $[M + H]^+$, m/z, 375.1794. ^1H NMR, δ 7.62 (d, 2H, J = 8.3 Hz), 7.37 (d, 2H, J = 8.4 Hz), 7.24 (t, 2H, J = 7.7 Hz), 7.06 (t, 2H, J = 7.6 Hz), 6.66 (q, 2H, J = 7.4 Hz), 5.77 (s, 2H), 2.14 (d, 6H, J = 7.4 Hz). ^{13}C NMR, δ 153.4, 145.6, 131.3, 127.5, 123.9, 119.3, 110.3, 50.1, 17.6.

Preparation of 3,5-Bis(benzotriazol-1-ylalkyl)triazoles **12a** *and* **12b**

General Procedure. The appropriate 4-amino-3,5-bis(benzotriazol-1-ylalkyl)triazole (**11a** or **11b**) (2 mmol) was dissolved in glacial acetic acid (10 mL) and the solution cooled in an ice-water bath. Sodium nitrite (0.21 g, 3 mmol) in water (2 mL) was added dropwise and the mixture allowed to stir at room temperature for 2 days. Water (20 mL) was added and the mixture extracted with chloroform (3 × 25 mL). The combined organic layers were washed with water (2 × 20 mL), dried over $MgSO_4$, and evaporated at reduced pressure to give the crude product, which was recrystallized from chloroform to give pure **12a** or **12b**.

3,5-Bis(benzotriazol-1-ylmethyl)triazole (**12a**). Obtained as a white powder, yield 37%, mp 218–220°C. Anal. found: C, 57.84; H, 3.99; N, 37.69. $C_{16}H_{13}N_9$ requires C, 58.00; H, 3.95; N, 38.05. ^1H NMR, δ 11.48 (s, br, 1H), 8.05 (d, 2H, J = 8.3 Hz), 7.77 (d, 2H, J = 8.3 Hz), 7.50 (t, 2H, J = 8.0 Hz), 7.39 (t, 2H, J = 7.8 Hz), and 6.08 (s, 4H). ^{13}C NMR, δ 155.3, 145.4, 133.0, 127.4, 124.1, 119.2, 110.8, and 44.2.

3,5-Bis(1-benzotriazol-1-ylethyl)triazole (**12b**). Obtained as a white powder, yield 74%, mp 83–85°C. Anal. found: $[M + H]^+$, m/z, 360.1752; $C_{18}H_{17}N_9$ requires $[M + H]^+$, m/z, 360.1685. ^1H NMR, δ 7.85 (d, 2H, J = 8.0 Hz), 7.50–7.41 (m, 2H), 7.34–7.20 (m, 4H), 6.40 (q, 2H, J = 7.2 Hz), and 2.14 (d, 6H, J = 7.2 Hz). ^{13}C NMR, δ 158.3, 145.8, 132.0, 127.4, 124.2, 119.4, 110.4, 52.9, 18.8.

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