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Alkyl-Bridged Bis-5-azidotetrazoles: A Safe Way of Preparation

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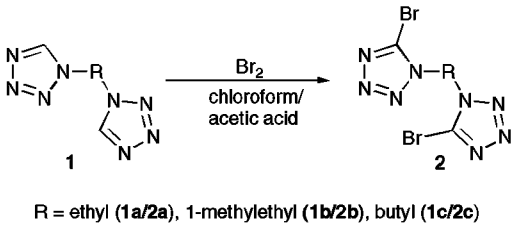
The general, high-yielding synthesis of extremely dangerous alkylated bis-5-azidotetrazoles is presented. The preparation using 5-bromotetrazoles for the generation of tetrazolyl hydrazines, which are then converted into the corresponding bis-5-azidotetrazoles, presents a safe, large-scale preparation of alkylated bis-5-azidotetrazoles. In this work, 1,2-bis(5-azido-1*H*-tetrazol-1-yl)ethane, 1,2-bis(5-azido-1*H*-tetrazol-1-yl)-1-methylethane, and 1,4-bis(5-azido-1*H*-tetrazol-1-yl)butane were synthesized and characterized by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy, vibrational spectroscopy (IR), and mass spectrometry. The crystal structure of 1,2-bis(5-azido-1*H*-tetrazol-1-yl)ethane was determined by single-crystal X-ray diffraction. In addition, the thermal behavior of the bis-5-azidotetrazoles was investigated by differential scanning calorimetry and their sensitivity towards friction and impact were determined.

Introduction

Among nitrogen-containing heterocycles, tetrazoles possess one of the highest contents of nitrogen. Among the organic, nitrogen-rich compounds, the tetrazole moiety peaks out with its unique thermal stability along with a nitrogen content of 80%. For this reason, the tetrazole moiety was applied to generate new nitrogen-rich compounds like hydrazinium azidotetrazolate, nearly reaching a nitrogen content of 90%.[1] Whereas 5-azidotetrazole and its salts were thoroughly investigated,[2] organic azidotetrazoles are rarely known.[3] The azidotetrazoles known in the literature have in common that they are stabilized by an aromatic substituent, like phenyl and its derivatives.[4] Therefore, the investigation of alkylated azidotetrazoles could lead to valuable, new nitrogen-rich building blocks. The problem while working with azidotetrazoles is their high sensitivity towards friction or impact. Some alkali salts of azidotetrazole even detonate spontaneously out of solution.[2] As a consequence, alkylation of ionic 5-azidotetrazolate in a manner analogous to known alkylations of 5-amino- or 5-nitrotetrazolates[5] was avoided. Taking these risks into account, it was necessary to develop a secure route for the preparation of alkylated bis-5-azidotetrazoles. Common syntheses for 1*H*-5-azidotetrazole use either diaminoguanidine[6] or the reaction of sodium nitrite in hydrochloric acid and tetrazolylhydrazine.[7] Because only a rare number of alkylated tetrazolylhydrazines are known in the literature, a general pathway for the preparation of tetrazolylhydrazines had to be developed. In order to introduce the hydrazine moiety into alkylated tetrazoles, 5-bromotetrazoles proved to be suitable starting materials. The advantage of this synthesis is that the first hazardous compounds appear in the last step as the desired bis-5-azidotetrazoles and can thereby be performed with a minimum of risk for the operating chemist.

Results and Discussion

The problem of the synthesis of bis-5-azidotetrazoles is their extremely high sensitivity towards friction and impact, making the handling of these compounds very dangerous. Therefore, a secure, high-yield synthesis of alkyl-bridged bisazidotetrazoles was developed. The synthesis starts with bistetrazolyl alkanes that are converted into the corresponding dibromotetrazolyl alkanes by bromination of the tetrazoles with elemental bromine[8] (Scheme 1).



Scheme 1. Synthesis of bromotetrazoles.

Experiments involving the use other reagents like *N*-bromosuccinimide for the bromination, yielded only mixtures of product and starting material. A complete conversion of the tetrazole into the corresponding 5-bromotetrazole was not possible, even after applying a large excess of *N*-bromosuccinimide and a reaction time of 3 d. Using elemental bromine for the bromination, a reaction time of 2 d is man-

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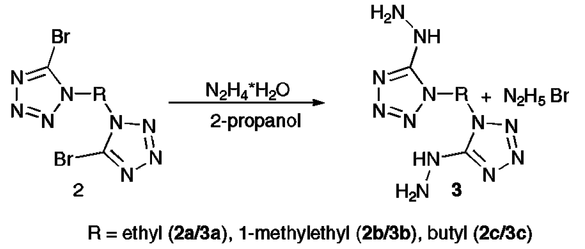
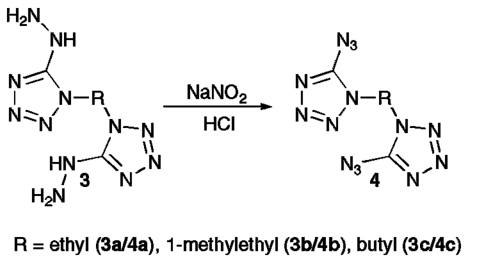
datory for complete conversion of the starting material. The next step is the substitution of the bromine atom by hydrazine. Carrying out the reaction, only 2-propanol turned out to be suitable as solvent. To obtain complete conversion into the bis(hydrazinyltetrazolyl) alkanes, an excess amount of hydrazine had to be applied (Scheme 2).



Scheme 2. Synthesis of bis(hydrazinyltetrazolyl) alkanes.

The formed hydrogen bromide precipitates as hydrazine hydrobromide and can be removed by hot filtration. Compound **3a** was purified by recrystallization from water and was obtained as a crystalline monohydrate, whereas recrystallized **3c** was obtained as a colorless amorphous powder. Compound **3b** was used as the crude material for further reactions, because recrystallization from any solvent was not possible as a result of hindered crystallization. An explanation gives the asymmetric character of the 1-methylethyl bridge disturbing the packing in the crystal. This effect becomes obvious by comparison of the melting points of **4a**, **4b**, and **4c**. The impurities of **3b** contain trace amounts of hydrazine and hydrogen bromide bound to the hydrazine moieties of the tetrazole. Purification by column chromatography (low solubility in organic solvents) was also not possible. Tetrazolylhydrazines **3** were then converted into the corresponding bis-5-azidotetrazoles **4** by reaction of sodium nitrite in hydrochloric acid. Therefore, the tetrazolylhydrazines were dissolved in 2 N hydrochloric acid and an excess amount of sodium nitrite in water was added dropwise until gaseous nitrogen dioxide was formed (Scheme 3).



Scheme 3. Synthesis of azidotetrazole.

In the cases of **4a** and **4c**, the product precipitated from solution and could be obtained by filtration. Compound **4b** was recovered by extraction of the aqueous solution with dichloromethane. The solvent was then removed under reduced pressure at 40 °C.

Compound **3a** crystallizes in the triclinic space group $P\bar{1}$ with one molecular formula per unit cell (Figure 1). The molecular structure is stabilized by several hydrogen-bonding interactions. Thereby, the outstanding significance of the water molecule becomes obvious. The structure is stabilized by three hydrogen bonds to the water molecule: one between the proton of N5 and the oxygen atom as acceptor and two with the oxygen atom as donor and N2 and N6 as acceptor. Another hydrogen bond is formed between the proton of N6 and N4 of a neighboring molecule of **3a** (Figure 2).

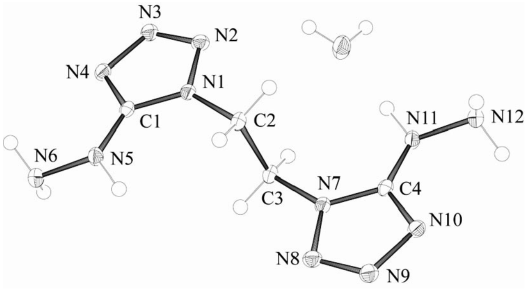


Figure 1. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level.

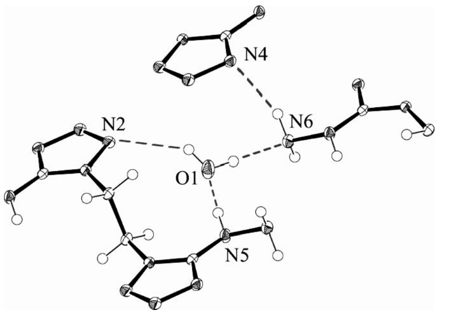


Figure 2. Hydrogen bonds formed between **3a** and the crystal water. Thermal ellipsoids are drawn at the 50% probability level.

Compound **4a** crystallizes in the triclinic space group $P\bar{1}$ with one molecular formula per unit cell (Figure 3). In contrast to compound **3a** there is no crystal water present. The high density of **4a** with 1.66 $g\,cm^{-3}$ is a result of the dense packing of the molecules. Thereby, the azidotetrazole moiety of one molecule lies above the azidotetrazole moiety of the next molecule, forming chains. The distance between two tetrazole moieties equates with 3.2 Å, which is two times the van der Waals radius of a nitrogen atom (1.54 Å).

The bis-5-azidotetrazoles can be easily analyzed by IR spectroscopy.[9] In the case of **4a**, the strong azide vibration lies at 2172 cm^{-1}, and in the cases of **4b** and **4c** it lies at 2168 cm^{-1}.

Figure 4 shows a comparison between the ^{15}N NMR spectroscopic data of **4a**, **4b**, and **4c**. The chemical shifts are in accordance with common values reported in the literature.[10] In the case of **4b**, N2, N3, and N6 are split due to the asymmetry of the molecule. The difference between the nitrogen atoms ($N3_a/N3_b$ and $N6_a/N6_b$) of 0.2 ppm and 0.3 ppm does not allow further assignments. The difference of 3.6 ppm of $N2_a/N2_b$ offers the assumption that $N2_b$ (–17.5 ppm) is part of the azidotetrazole moiety next to the methyl group.

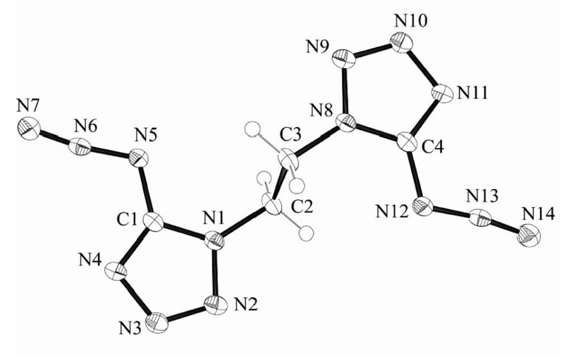


Figure 3. Molecular structure of **4a**. Thermal ellipsoids are drawn at the 50% probability level.

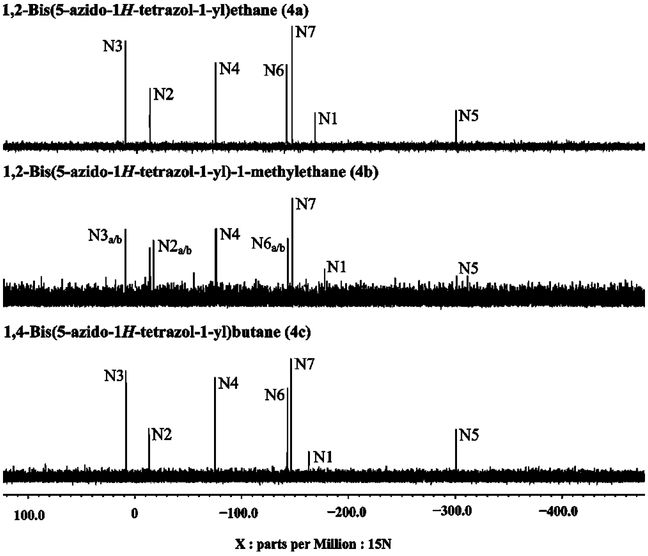


Figure 4. ^{15}N NMR spectra of **4a**, **4b**, and **4c**.

Despite their thermal stability up to 170 °C, the alkylated bis-5-azidotetrazoles presented are highly dangerous materials as a result of their high sensitivity towards friction or impact. The sensitivity of compounds **4a**–**c** towards impact was determined in each case to be lower than 0.15 J, and the sensitivity towards friction was lower than 5 N[11] (Table 1). The sensitivity of 5-bromotetrazoles **2a**–**c** towards friction was lower than 200 N and the sensitivity towards impact was lower than 15 J. Compared to the 5-azido- and 5-bromotetrazoles, hydrazine derivatives **3a** and **3b** were the most stable compounds towards impact and friction (impact > 50 J, friction > 360 N).

Table 1. Energetic properties of **4a**, **4b** and **4c**.

	4a	4b	4c
Formula	$C_4H_4N_{14}$	$C_5H_6N_{14}$	$C_6H_9N_{14}$
Molecular mass	248.0743	262.0895	276.1056
Density [$\mathrm{g\,cm^{-1}}$]	1.663	–	1.401
Melting point [°C]	110	77	94
Decomposition point [°C]	169	170	164
Impact sensitivity [J]	>0.15	>0.15	>0.15
Friction sensitivity [N]	<5	<5	<5
Ω [%]	–64.5	–	–92.7
$\Delta_f H$(g,M) [$\mathrm{kcal\,mol^{-1}}$][a]	322.0	–[g]	302.4
Q_v [$\mathrm{kJ\,kg^{-1}}$][b]	–5476	–	–4887
T_E [K][c]	4127	–	3487
p [kbar][d]	277	–	183
D [$\mathrm{m\,s^{-1}}$][e]	8429	–	7431
Gas vol. [$\mathrm{L\,kg^{-1}}$][f]	716	–	724

[a] Calculated using CBS-4M;[12] values obtained by calculation using the EXPLO5-software.[13] [b] Energy of explosion. [c] Explosion temperature. [d] Detonation pressure. [e] Detonation velocity. [f] Assuming only gaseous products. [g] Calculations did not lead to any results.

Conclusions

A general, high-yielding synthesis of alkylated bis-5-azidotetrazoles was developed. In contrast to common methods, the preparation presented is safe and with minimum risk for the operating chemist. By optimizing the synthesis of bis-5-azidotetrazoles, these nitrogen-rich compounds can evolve into useful building blocks for nitrogen chemistry by using the azide moiety for further reactions. The tetrazoles presented were all characterized by vibrational and NMR spectroscopy, mass spectrometry, and in cases of 1,2-bis(5-hydrazinyl-1*H*-tetrazol-1-yl)ethane (**3a**) and 1,2-bis(5-azido-1*H*-tetrazol-1-yl)ethane (**4a**), the crystal structure was determined by single-crystal X-ray diffraction.

Experimental Section

CAUTION! Tetrazoles, bromotetrazoles, tetrazolylhydrazines, and azidotetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves, and ear plugs) should be used when undertaking work involving these compounds.

General: All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded using a JEOL Eclipse 400 instrument. The spectra were measured in [D$_6$]-DMSO, $CDCl_3$, or D_2O. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N) as external standards. Coupling constants (*J*) are given in Hertz. Infrared (IR) spectra were recorded using a Perkin–Elmer Spectrum One FTIR instrument and KBr pellets or NaCl plates at room temperature. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Melting points were determined using differential scanning calorimetry (Linseis DSC PT-10 instrument). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum containers with a hole (1 µm) on the top for gas release with a nitrogen flow of 5 mL min^{-1}. The reference sample was a closed aluminum container. The sensitivity data were performed using a BAM drophammer and a BAM friction tester.

1,2-Bis(1-tetrazolyl)ethane,[14] 1-methyl-1,2-bis(1-tetrazolyl)ethane,[15] and 1,2-bis(1-tetrazolyl)butane[16] were prepared by using literature procedures.

General Procedure for the Synthesis of Bis(5-bromo-1*H*-tetrazolyl)-alkanes: Bis-1*H*-tetrazolylalkane (31 mmol) was dissolved in a mixture of acetic acid (20 mL) and chloroform (40 mL). The mixture was heated to 60 °C and bromine (20.0 g, 124 mmol) was added. The mixture was heated at reflux for 48 h, and the solvent was removed. The residue was neutralized by a saturated sodium carbonate solution. The aqueous phase was extracted with ethyl acetate. After removing the solvent, the bromotetrazole was obtained as a slightly yellow powder.

1,2-Bis(5-bromo-1*H*-tetrazolyl)ethane (2a): Yield: 3.8 g, 11.8 mmol, 38%. M.p. 159 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3443 (m), 3024 (w), 2974 (w), 2157 (w), 2126 (w), 1639 (w), 1571 (w), 1443 (s), 1419 (vs), 1396 (s), 1301 (w), 1290 (m), 1241 (s), 1172 (s), 1142 (s), 1098 (m), 1059 (w), 976 (m), 941 (w), 669 (m), 652 (m), 503 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 4.95 (s, 2 H, CH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 47.46 (CH_2), 135.70 (C_q) ppm. $C_4H_4Br_2N_8$ (323.93): calcd. C 14.83, H 1.24, N 34.59; found C 14.94, H 1.33, N 34.93.

1,2-Bis(5-bromo-1*H*-tetrazolyl)-1-methylethane (2b): Yield: 8.6 g, 25.7 mmol, 83%. M.p. 92 °C (decomp. 164 °C). IR (KBr): $\tilde{\nu}$ = 3013 (w), 2985 (w), 2924 (w), 1709 (m), 1636 (m), 1532 (w), 1454 (m), 1426 (vs), 1416 (vs), 1399 (vs), 1389 (vs), 1362 (m), 1356 (m), 1307 (w), 1297 (w), 1242 (m), 1201 (m), 1187 (m), 1157 (m), 1123 (m), 1095 (m), 1082 (w), 1058 (w), 1024 (w), 975 (w), 924 (vw), 912 (vw), 760 (w), 696 (vw), 687 (vw), 680 (vw), 644 (vw), 635 (vw), 538 (vw), 509 (vw), 485 (vw) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.75 (d, 3 H, CH_3), 4.92 (m, 2 H, CH_2), 5.20 (m, 1 H, CH) ppm. ^{13}C NMR ([D_6]-DMSO): δ = 17.8 (CH_3), 52.0 (CH_2), 55.3 (CH), 135.6 (C_q) ppm. MS (DEI): *m*/*z* (%) = 339 (1) [M + H], 259 (17), 179 (100), 149 (10), 99 (18), 83 (8), 69 (39), 68 (30), 67 (16), 56 (21), 55 (43), 54 (18), 53 (21), 42 (39), 41 (47), 39 (13), 28 (39), 27 (12). $C_5H_6Br_2N_8$ (337.96): calcd. C 17.77, H 1.79, N 33.16; found C 17.95, H 1.98, N 33.42.

1,4-Bis(5-bromo-1*H*-tetrazolyl)butane (2c): Yield: 3.9 g, 11.2 mmol, 36%. M.p. 140 °C (decomp. 196 °C). IR (KBr): $\tilde{\nu}$ = 2962 (w), 2926 (w), 2855 (w), 1699 (w), 1558 (w), 1540 (w), 1465 (m), 1456 (m), 1430 (m), 1416 (m), 1395 (s), 1281 (w), 1233 (m), 1175 (s), 1100 (m), 981 (m), 790 (vs), 656 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.88 (s, 1 H, CH_2), 4.44 (s, 1 H, CH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 25.8 (CH_2), 47.9 (CH_2), 134.8 (C_q) ppm. MS (DEI): *m*/*z* (%) = 348 (10) [M – H], 346 (10), 284 (19), 282 (19), 198 (6), 155 (34), 139 (4), 92 (10), 91 (100), 65 (25), 63 (6), 55 (4), 54 (4), 53 (4), 51 (4), 45 (5), 39 (8), 31 (10), 29 (5). $C_6H_8Br_2N_8$ (351.99): calcd. C 20.47, H 2.29, N 31.83; found C 20.96, H 2.30, N 32.68.

General Procedure for the Synthesis of Bis(5-hydrazinyl-1*H*-tetrazolyl)alkanes: To a slurry of bis(5-bromo-1*H*-tetrazolyl)alkane (2.9 mmol) in 2-propanol (30 mL) was added hydrazine hydrate (0.9 g, 18.0 mmol), and the reaction mixture was heated at reflux for 10 h, whilst the product precipitated as a colorless solid. The hot suspension was filtered, and the colorless product was washed with hot 2-propanol (30 mL). In cases of **3a** and **3b**, the residue was recrystallized from hot water (10 mL).

1,2-Bis(5-hydrazinyl-1*H*-tetrazol-1-yl)ethane (3a): Yield: 429 mg, 1.9 mmol, 65%. M.p. 155 °C (decomp. 206 °C). IR (KBr): $\tilde{\nu}$ = 3559 (m), 3306 (s), 3204 (s), 3163 (m), 3049 (m), 1639 (m), 1599 (vs), 1544 (m), 1459 (m), 1434 (w), 1331 (w), 1269 (w), 1167 (w), 1107 (m), 1078 (m), 975 (w), 843 (vw), 704 (w), 638 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.43 (s, 2 H, NCH_2), 4.62 (s, 2 H, NH_2), 8.11 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 44.9 (NCH_2), 158.6 (C_q) ppm. MS (DEI): *m*/*z* (%) = 226 (1) [M], 169 (14), 168 (6), 153 (4), 126 (4), 114 (10), 113 (8), 112 (10), 111 (37), 101 (3), 99 (3), 98 (6), 97 (5), 96 (4), 86 (23), 85 (35), 84 (13), 71 (9), 70 (14), 69 (100), 68 (8), 67 (5), 58 (8), 57 (28), 56 (25), 55 (35), 54 (8), 53 (12), 45 (4). $C_4H_{10}N_{12}\cdot H_2O\cdot 0.2HBr$ (226.20): calcd. C 18.45, H 4.72, N 64.55; found C 18.92, H 4.78, N 64.85.

1,4-Bis(5-hydrazinyl-1*H*-tetrazol-1-yl)butane (3c): Yield: 1.0 g, 2.4 mmol, 82%. M.p. 186 °C (decomp. 191 °C). IR (KBr): $\tilde{\nu}$ = 3329 (m), 3292 (m), 3023 (w), 1588 (vs), 1559 (s), 1521 (m), 1474 (m), 1457 (m), 1410 (m), 1377 (m), 1338 (m), 1294 (m), 1252 (m), 1227 (w), 1155 (w), 1109 (s), 1082 (vs), 1020 (w), 991 (w), 924 (m), 819 (s), 740 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.66 (br. m, 2 H, CCH_2), 4.18 (br. t, 2 H, NCH_2), 4.41 (s, 2 H, NH_2), 8.01 (s, 1 H, NH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 26.0 (CCH_2), 45.1 (NCH_2), 158.7 (C_q) ppm. $C_6H_{14}N_{12}\cdot 0.17HBr$ (254.25): calcd. C 26.92, H 5.33, N 62.78; found C 27.40, H 5.18, N 62.55.

General Procedure for the Synthesis of Bis(5-azido-1*H*-tetrazolyl)alkanes: Bis(5-hydrazinyl-1*H*-tetrazolyl)alkane (3.0 mmol) was dissolved in 2 N hydrochloric acid (30 mL). An excess amount of saturated sodium nitrite solution in water was added dropwise at 0 °C until the formation of gaseous NO_2 was observed. In cases of **4a** and **4c**, the product precipitated as a colorless solid, which was filtered off and washed with cold water (100 mL). In case of **4b**, the clear brownish solution was extracted with dichloromethane (3×). The organic phase was dried with sodium sulfate, and the solvent was removed under reduced pressure. The product was obtained as a slightly brownish oil, which solidified after 2–3 d.

1,2-Bis(5-azido-1*H*-tetrazol-1-yl)ethane (4a): Yield: 550 mg, 2.2 mmol, 74%. M.p. 110 °C (decomp. 169 °C). IR (KBr): $\tilde{\nu}$ = 3431 (w), 2172 (vs), 1629 (vw), 1539 (vs), 1474 (m), 1446 (vw), 1384 (vw), 1330 (w), 1265 (w), 1183 (w), 1095 (w), 1073 (vw), 723 (vw), 684 (w), 527 (vw) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 4.60 (s, 1 H, CH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 45.2 (CH_2), 153.2 (C_q) ppm. ^{15}N NMR ([D_6]DMSO): δ = 9.1 (N3), –14.1 (N2), –75.8 (N4), –142.2 (N6), –147.0 (N7), –168.6 (N1), –300.7 (N5) ppm. MS (DEI+): *m*/*z* (%) = 249.0772 (6) [M + H], 248.0743 (77) [M], 138.0530 (13), 124.0378 (55), 109.0405 (11), 82.0023 (4), 80.9947 (8), 68.9947 (10), 68.0000 (22), 67.0056 (12), 56.0261 (9), 55.0197 (41), 54.0256 (13), 54.0128 (51), 54.0006 (100), 53.0059 (43), 44.0343 (15), 43.0745 (33), 42.1062 (63). 41.0973 (19). HRMS: calcd. for $C_4H_4N_{14}$ $[M]^+$ 248.0743; found 248.0743.

1,2-Bis(5-azido-1*H*-tetrazol-1-yl)-1-methylethane (4b): Yield: 460 mg, 2.0 mmol, 66%. M.p. 77 °C (decomp. 170 °C). IR (KBr): $\tilde{\nu}$ = 2997 (vw), 2959 (vw), 2926 (vw), 2168 (vs), 1709 (w), 1622 (w), 1530 (vs), 1467 (m), 1383 (w), 1356 (w), 1315 (w), 1280 (vw), 1261 (m), 1191 (m), 1060 (w), 1028 (w), 976 (vw), 914 (vw), 876 (vw), 802 (vw), 721 (vw), 667 (w), 585 (vw), 526 (vw) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.60 (d, ^3J = 6.83 Hz, 3 H, CH_3), 4.60 (d, ^3J = 6.23 Hz, 2 H, CH_2), 4.86 (sext., ^3J = 6.23, 6.83 Hz, 1 H, CH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 17.1 (CH_3), 49.7 (CH), 53.4 (CH_2), 152.7 (C_q), 153.2 (C_q) ppm. ^{15}N NMR ([D_6]DMSO): δ = 9.1 ($N3_a$), 8.9 ($N3_b$), –13.9 ($N2_a$), –17.5 ($N2_b$), –75.8 ($N4_a$), –76.1 ($N4_b$), –143.0 ($N6_a$), –143.1 ($N6_b$), –147.4 (N7), –177.8 (N1), –301.4 (N5) ppm. MS (DEI+): *m*/*z* (%) = 232.0895 (42) [M], 138.0515 (11), 124.0372 (115), 95.0149 (9), 68.9947 (11), 68.0149 (19), 56.0472 (16), 54.0065 (100), 53.0104 (22), 43.9258 (14), 42.9305 (29), 41.9316 (19), 40.8796 (68). HRMS: calcd. for $C_5H_6N_{14}$ $[M]^+$ 262.0895; found 262.0900.

1,4-Bis(5-azido-1*H*-tetrazol-1-yl)butane (4c): Yield: 656 mg, 2.4 mmol, 79%. M.p. 94 °C (decomp. 164 °C). IR (KBr): $\tilde{\nu}$ = 2952 (vw), 2922 (vw), 2849 (vw), 2168 (vs), 1628 (w), 1533 (vs), 1473 (m), 1451 (m), 1482 (w), 1355 (w), 1331 (w), 1307 (w), 1258 (w), 1243 (m), 1219 (m), 1172 (w), 1097 (m), 1079 (w), 1008 (vw), 985 (vw), 787 (vw), 778 (vw), 723 (vw), 697 (vw), 643 (vw), 527 (vw) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.78 (s, 1 H, CH_2), 4.16 (s, 1 H, CH_2) ppm. ^{13}C NMR ([D_6]DMSO): δ = 25.6 (CCH_2), 46.0 (NCH_2), 152.7 (C_q) ppm. ^{15}N NMR ([D_6]DMSO): δ = 8.4 (N3), –13.1 (N2), –75.0 (N4), –142.9 (N6), –146.0 (N7), –163.0 (N1), –300.6 (N5) ppm. MS (DEI+): *m*/*z* (%) = 277.3 (1) [M + H], 276.3 (1), 245.2 (2), 206.3 (25), 165.3 (8), 124.3 (6), 109.3 (9), 95.2 (37), 81.2 (5), 68 (15), 56.2 (22), 55.2 (100), 54.2 (18), 53.2 (10), 43.2 (7), 42.2 (25), 40.2 (10), 39.2 (17), 29.2 (18), 28.2 (28), 27.2 (18). HRMS: calcd. for $C_6H_9N_{15}$ [M + H] 277.1135; found 277.1134.

Crystal Structure Analysis: The crystallographic data were collected with an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[17] and refined using SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. ORTEP plots showing thermal ellipsoids with 50% probability for the non-hydrogen atoms. CCDC-724763 (for **3a**) and -724764 (for **4a**) 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. Selected crystal data for **3a** and **4a** are summarized in Table 2.

Table 2. Selected crystal data for **3a** and **4a**.

	3a	**4a**
Formula	$C_4H_{14}N_{12}O_2$	$C_4H_4N_{14}$
M_r [g mol^{-1}]	262.27	248.21
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	6.536(3)	6.2749(4)
b [Å]	6.5993(18)	6.5994(5)
c [Å]	6.777(4)	6.7695(5)
α [°]	83.04(3)	108.840(6)
β [°]	72.78(4)	106.017(6)
γ [°]	84.22(3)	97.143(6)
V [Å^3]	276.5(2)	247.89(3)
Z	1	1
F(000)	138	126
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.575	1.663
μ [mm^{-1}]	0.128	0.130
2θ [°]	55.99	53.97
Index range	$-8 \leq h \leq 8$ $-8 \leq k \leq 8$ $-8 \leq l \leq 8$	$-8 \leq h \leq 8$ $-8 \leq k \leq 8$ $-8 \leq l \leq 8$
λ	0.71073	0.71073
T [K]	200(2)	200(2)
Reflections collected	3162	5540
Unique reflections	1331	1078
Parameter	110	90
S	1.131	1.039
R_{int}	0.0354	0.0285
R_1/wR_2 [$I > 2\sigma(I)$]	0.0299/0.0785	0.0285/0.0778
R_1/wR_2	0.0354/0.0809	0.0351/0.0806

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[11] Impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive >360 N, less sensitive = 360 N, > 80 N sensitive < 360 N, very sensitive < 80 N, extremely sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

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