JOC Article

Synthesis of Functionalized Tetrazenes as Energetic Compounds

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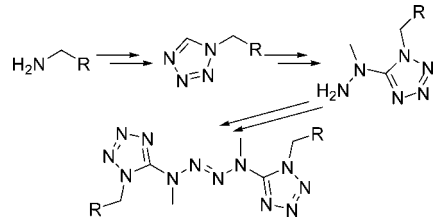

1,4-Bis[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**12a**), 1,4-bis[1-isopropoxycarbonylmethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**12b**), and 1,4-bis[1-carboxymethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**13**) have been synthesized as new nitrogen-rich compounds. The tetrazenes were obtained by oxidation of the corresponding tetrazolylhydrazines using bromine. Moreover, a new method to prepare tetrazolylhydrazines in high yield using 5-bromotetrazoles has been developed. **12a**, **12b**, and **13** were characterized using vibrational spectroscopy (IR, Raman), mass spectrometry, and multinuclear NMR spectroscopy. The crystal structures of **12a**, **12b**, and **13** were determined using single crystal X-ray diffraction. Furthermore, the energetic properties of **12a**, **12b**, and **13** have been investigated using DSC and bomb calorimetric measurements. The sensitivity data toward impact and friction has been determined using BAM methods.

Introduction

Tetrazoles are nitrogen-rich compounds, covering a wide range of applications. They are used as pharmaceuticals,[1] for biomedical applications,[2] as membranes,[3] as antifoggants in photographic materials,[4] or as energetic materials.[5] The advantages of tetrazoles include their high nitrogen content along with a sufficiently high thermal stability,[3] rendering them as unique nitrogen building blocks. Beside the usage for military devices, energetic materials based on nitrogen-rich compounds like tetrazoles can be used as gas generating agents for civil applications.[6] To obtain even higher contents of nitrogen, tetrazoles were used as anions to form salts with nitrogen-containing cations of guanidine, aminoguanidine, diaminoguanidine, or triaminoguanidine.[7]

Another method to build nitrogen-rich tetrazole-containing molecules is the usage of moieties like tetrazine,[8] nitramine,[9] or azide.[10] The disadvantages of these compounds lie in their low physical and thermal stability and high explosion temperature. In particular, with regard for possible application as air bags in vehicles, a low heat of explosion is desired to protect the person from burns. Moreover, a reduced heat of explosion lessens the erosion of guns. Therefore, the investigation and

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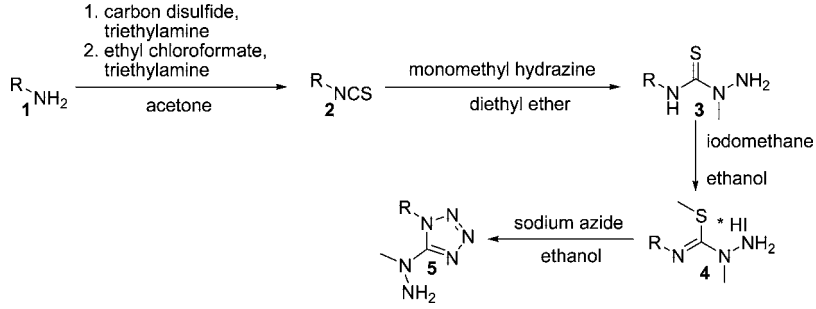
SCHEME 1. Synthesis of Tetrazolylhydrazines from Thiosemicarbazides



development of new nitrogen-rich compounds with a low heat of explosion is of great interest.

A suitable class of nitrogen-rich compounds are 1,4-bistetrazolyltetrazenes. 1,4-Bis[1-methyltetrazol-5-yl]-1,4-dimethyl-2-tetrazene was first prepared in 2004 by nitrosylation of *N*,1-dimethyl-1*H*-tetrazol-5-amine and reduction to the corresponding 1-methyl-1-(1-methyl-1*H*-tetrazol-5-yl)hydrazine. The tetrazolylhydrazine was then oxidized to form the 1,4-bis[1-methyltetrazol-5-yl]-1,4-dimethyl-2-tetrazene using bromine.[11] In this work, we present a general route for the preparation of tetrazenes in high yields. The synthesis of bromotetrazoles[12] was generalized and used to establish a new route to form the corresponding methyltetrazolylhydrazines in high yields.

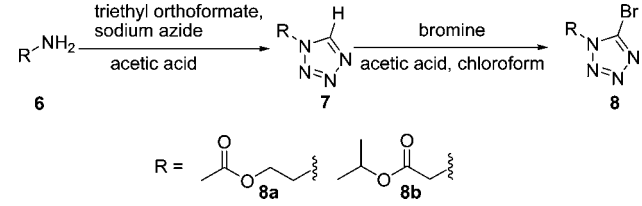
Results and Discussion

Tetrazenes can be prepared by oxidation of hydrazines.[13] As a consequence, the tetrazolyltetrazenes presented in this work have been obtained via the corresponding tetrazolylhydrazines. Therefore, efficient routes for the synthesis of tetrazolylhydrazines were necessary. A possible pathway reported in literature starts from thiosemicarbazides, which are converted to the corresponding *S*-methylthiosemicarbazides. The methylated sulfur atom is subsequently substituted by sodium azide, followed by an electrocyclic ring closure yielding the tetrazolylhydrazine[14] (Scheme 1).

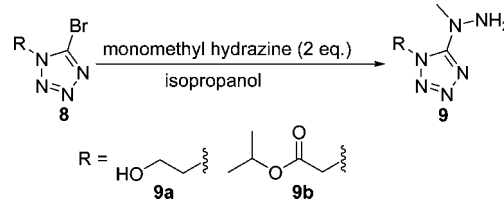
Taking into account that a purification of tetrazole **5** by column chromatography is necessary, the reaction proves not to be efficient for upscaling.

To improve the synthesis, a new route using 5-bromotetrazoles as intermediates has been developed. Despite being useful starting materials for 5-substituted tetrazoles, only a small number of 5-bromotetrazoles have been reported in the literature.[15] The synthesis of 2-(5-bromo-tetrazol-1-yl)-ethanol (**8a**) reported as a patent by Bayes[16] was generalized and used to prepare the (5-bromo-tetrazol-1-yl)-acetic acid isopropyl ester (**8b**), with 2-aminoethyl acetate and isopropyl 2-aminoacetate as suitable starting materials. The experiments showed that in case of the aminoacetate derivative (to form **8b**) only the isopropyl ester proved to be a stable protecting group against an intramolecular attack of the monomethylhydrazine moiety later inserted, in contrast to the ethyl or methyl ester. To form the tetrazoles, the amine group was converted into the 5*H*-tetrazole using standard reactions of triethyl orthoformate and sodium azide in acetic acid.[17] In the following step, the 5-position of the tetrazole was brominated using elemental bromine (Scheme 2).

SCHEME 2. Synthesis of 5-Bromotetrazoles



SCHEME 3. Synthesis of the Tetrazolylhydrazines



In the case of **8a**, the resulting 5-bromotetrazole was deprotected by hydrochloric acid. A purification by column chromatography was not possible because of decomposition during the process. Crude **8a** and **8b** were converted into the corresponding tetrazolylhydrazines by substitution of the bromine atom by monomethylhydrazine. The experiments showed that isopropanol was a suitable solvent, whereas the yields dropped using alcohols, acetonitrile, or other organic solvents. When the reaction was carried out, neither the 2-methyl isomer nor side products arising from a hydrolysis of the bromotetrazole were observed (Scheme 3). The tetrazolylhydrazines were obtained as slightly impure oil. The crude products were used for further reactions.

A deprotection of **9b** using potassium hydroxide in water yielded the bicycle **11** as crystalline solid along with several other compounds, which were not identified. The formed carbon acid undergoes immediately an intra- or intermolecular condensation with the hydrazine moiety, even in alkaline medium, yielding either **11** or polymeric side products (Scheme 4).

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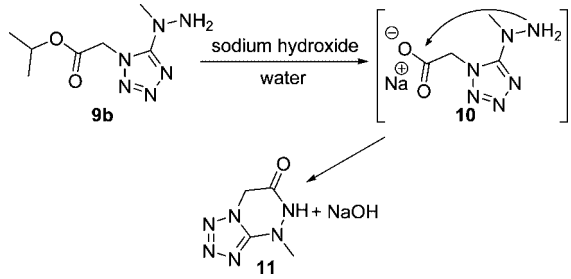
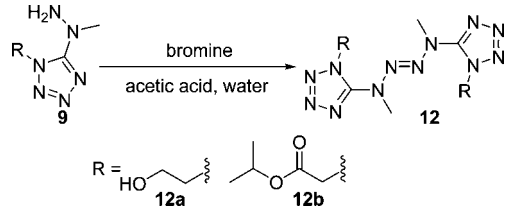
SCHEME 4. Formation of 11



SCHEME 5. Synthesis of the Tetrazolyltetrazenes



Bicycle **11** crystallizes in the orthorhombic space group *Pcnn* with eight molecular formulas per unit cell. Two hydrogen bonds are present in the crystal structure. The donor atom N6 forms one intermolecular hydrogen bond to O1, leading to dimers.

The tetrazolylhydrazines **9a** and **9b** were converted into the corresponding tetrazenes using saturated bromine water at 0 °C. The product precipitates from the clear reaction mixture and was filtered off. The yields varied between 50% and 60% (Scheme 5).

Compound **12b** was deprotected using boiling concentrated sodium hydroxide solution. The corresponding carbon acid **13** was recovered by neutralizing the alkaline solution using hydrochloric acid.

Compound **12a** crystallizes in the orthorhombic space group *Pbca* with four molecular formulas per unit cell. The bond distances and angles of the tetrazole moiety and the alkyl substituent are in accordance with values reported in the literature.[18] The bond distance between N6 and N7 (125.5 pm) equates to common values of double bonds (125 pm).[19] The bond distance of N5−N6 (136.6 pm) lies between a N−N single bond (146 pm) and a double bond (125 pm). Furthermore the C1−N5 bond (136.6 pm) is shortened by 12.6 pm, compared to C−N single bonds (147 pm) commonly observed. The crystal structure is stabilized by an intermolecular hydrogen bond between the donor atom O1 and the acceptor atom N4. Thereby, the tetrazole moieties are connected by two hydrogen bonds between each other. As a result, three molecules are connected by four hydrogen bonds.

Compound **12b** crystallizes in the triclinic space group *P*-1 with one molecular formula per unit cell. The bond distances and angles are in correspondence with **12a**. As a result of the protected carbon acid no inter- or intramolecular interactions are observed.

Compound **13** crystallizes in the monoclinic spacegroup $P2_1/c$ with four molecular formulas per unit cell (Figure 1). The bond distances and angles are in accordance with those of compounds

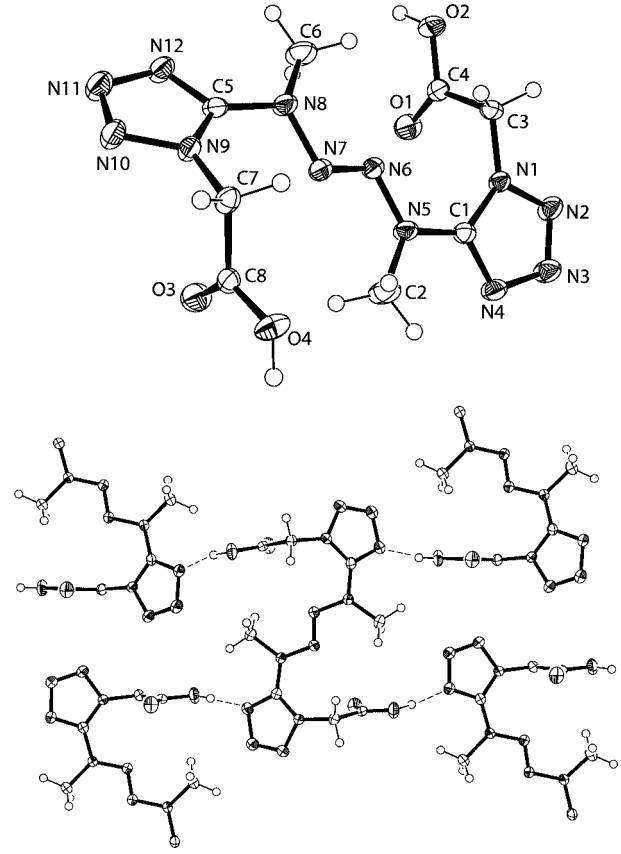


FIGURE 1. Molecular structure and intermolecular hydrogen bonds of **13**. Thermal ellipsoids are drawn at the 50% probability level.

TABLE 1. Hydrogen Bonds of 12a and 13

	donor atom	acceptor atom	D−H [pm]	H···A [pm]	D···A [pm]	(D−H···A)
12a	O1	N4	88.8	201.0	289.5	173.8
13	O2	N4	94.1	181.0	273.7	167.8
	O4	N12	93.9	179.1	271.4	166.8

12a and **12b**. The crystal structure is stabilized by four intermolecular hydrogen bonds, one between the donor atom O2 and the acceptor atom N4 and the other between the donor atom O4 and the acceptor atom N12. In contrast to the structure of **12a**, five molecules are connected to each other by the four hydrogen bonds.

A comparison between the hydrogen bonds of **12a** and **13** is given in Table 1.

Compounds **12a**, **12b**, and **13** were identified using vibrational IR spectroscopy. Selected values are given in Table 2. The calculated values given in Table 2 were used to assign the frequencies.

A comparison between the ^{15}N spectra of **13** and **12a** is given in Figure 2. The assignment of the nitrogen atoms was carried out in analogy to values reported in literature.[20] In the case of **12a**, N2 shows a clear triplet, resulting of a ^3J-coupling (^3J = 2.0 Hz) with the CH_2 group. N1 forms a muliplet by the ^2J- and ^3J-coupling with the hydroxyethyl group. In contrast, **13** only shows the triplet of N2 (^3J = 1.7 Hz). N1 forms a broad signal without showing any clear ^2J-coupling with the CH_2-group. An explanation for the missing ^2J-coupling could be the much lower concentration, due to the low solubility of **13** in

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TABLE 2. Comparison between Selected Vibrations of 12a, 12b, and 13 with the Calculated Values of 13 using DFT BLYP/6-31G*

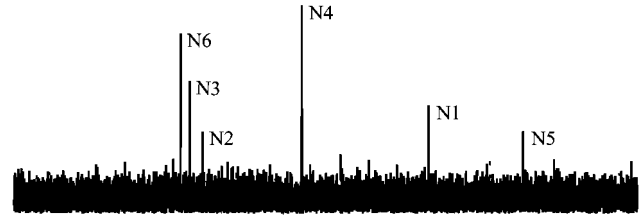
12a exptl	**12b** exptl	**13** exptl	theory × 0.9940	theory	vibration
3347		3436	3502	3524	ν_s/ν_{as}(OH)
2972	2999	3012	3036	3055	$\nu_{as}(CH_3)$
2944	2984	2972	3007	3026	$\nu_s(CH_2)$
2885	2944	2945	2977	2995	$\nu_s(CH_3)$
	1754	1747	1778	1789	ν_{as}(COOH)
		1738	1777	1788	ν_{as}(COOH)
1572	1569	1565	1527	1537	ν_{as}(tetrazol)
1470	1470	1478	1479	1488	$\delta_s(CH_3)$
1444	1450	1447	1436	1445	ν_s(tetrazene)/$\delta_s(CH_3)$
1417		1433	1421	1430	$\delta_s(CH_3)/\delta_s(CH_2)$
		1423	1417	1426	ν_s(tetrazene)/$\delta_s(CH_3)$
	1414	1413	1416	1425	$\delta_s(CH_3)/\delta_s(CH_2)$
	1394	1400	1397	1406	ν_s(tetrazole)/$\delta_s(CH_3)/\delta_s(CH_2)$
1360	1348	1351	1360	1369	$\nu_s(CH_2COOH)$
1337		1332	1312	1320	ν_s(tetrazene)/$\delta_{as}(CH_2)$
1295	1278	1295	1282	1290	$\nu_s(CH_2COOH)$
1261		1262	1250	1258	ν_s(tetrazol)
1224	1218	1207	1190	1198	ν_s(tetrazole)/δ_{as}(tetrazole)/$\delta_{as}(CH_2)$
1106	1106	1100	1100	1107	ν_{as}(COOH)/ν_{as}(tetrazole)/ ν_{as}(tetrazene)/ν_s(*N*-CH_3)
1098	1083	1075	1060	1067	ν_{as}(tetrazole)/δ_{as}(tetrazole)/ν_{as}(tetrazene)
1015	1007	1020	1023	1030	$\nu_{as}(CH_2COOH)/\nu_{as}$(tetrazole)/ ν_{as}(tetrazene)/δ_s(*N*-CH_3)
978		993	980	986	ν_s(tetrazole)/δ_s(*N*-CH_3)/ν_{as}(tetrazene)
	959	965	972	978	ν_{as}(tetrazole)/δ_s(N-CH_3)/ν_{as}(tetrazene)/ $\gamma(COCH_2)$
857	848	854	866	872	ν_{as}(tetrazole)/$\gamma(COCH_2)$
		798	778	783	$\nu_s(CH_2COOH)/\nu_{as}$(tetrazole)/ ν_{as}(tetrazene)/δ_s(N-CH_3)
	658	656	654	658	γ_s(COOH)

DMSO. In both cases neither the ^2J- nor the ^3J-coupling with the methyl moiety was obvious.

Since **12a**, **12b**, and **13** are energetic materials, determination of the energetic properties was or interest of us. Therefore, the thermal behavior was investigated by DSC measurements, the heats of combustion by bomb calorimetric measurements, and the sensitivity toward impact and friction by BAM methods.[21,22]

The tetrazenes show no melting points but sharp decomposition points. Comparing the DSC data of the tetrazenes, compound **12a** and **12b** possess similar points of decomposition of 167 and 160 °C. In contrast, the point of decomposition of **13** (207 °C) is about 40 °C higher than those of **12a** and **12b**. This effect can be rationalized by strong intermolecular interactions of the molecules in the crystal structure, as already shown in Figure 1, resulting in a stabilization of the molecule. Taking the crystallographic data of **12a**, **12b**, and **13** into account, the points of decomposition can be correlated with the amount of intermolecular interactions. Compound **12b** shows no intermolecular interactions at all and possesses a decomposition point of 160 °C. Compound **12b** forms four hydrogen bonds between a hydroxyl group and the tetrazole moiety connecting three molecules (decomposition point 167 °C). The structure of **13** stabilized most by four hydrogen bonds between the carboxylic acid and the tetrazole moiety shows the highest decomposition point (207 °C). Electronic effects of the different moieties of the tetrazoles **12b** and **13** can be neglected. The difference between **12b** and **13** is the esterfication of the carbon acid.

bis(1,1'-methyl-1,1'-(2-(1*H*-tetrazolyl)acetic acid))tetrazene **13**



bis(1,1'-methyl-1,1'-(2-hydroxyethyl)-1*H*-tetrazolyl))tetrazene **12a**

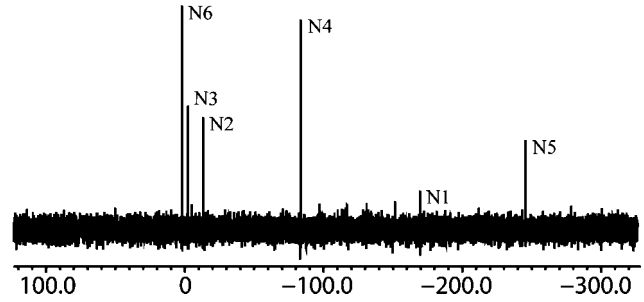


FIGURE 2. ^{15}N-spectra of **13** and **12a** in d_6-DMSO.

12 a $C_8H_{16}N_{12}O_2 + 11\ O_2 \longrightarrow 8\ CO_2 + 8\ H_2O + 6\ N_2$

12 b $C_{14}H_{24}N_{12}O_4 + 18\ O_2 \longrightarrow 14\ CO_2 + 12\ H_2O + 6\ N_2$

13 $C_8H_{12}N_{12}O_4 + 9\ O_2 \longrightarrow 8\ CO_2 + 6\ H_2O + 6\ N_2$

FIGURE 3. Combustion reactions of **12a**, **12b**, and **13**.

The isopropyl ester should lead to a reduction of the electron-withdrawing effect of the carbon acid. Electron-rich tetrazole moieties are known to be much more stable than tetrazoles bearing electron-withdrawing groups.[23] As a result, compound **12b** should be more stable than **13**. Since the experimental data proves **13** as being more stable than **12b**, this effect can be ascribed to the crystal structure and not to electronic effects of the substituents.

To analyze the energetic properties of the compounds, the energies of combustion (ΔU_c) were measured using bomb calorimetry. Using these values, the enthalpy of formation was calculated by applying the Hess thermochemical cycle, as reported in the literature.[24] The heats of formation of H_2O (l) and CO_2 (g), −286 and −394 kJ mol^{-1}, were obtained from the literature,[25] and the combustion reactions of **12a**, **12b**, and **13** are given in Figure 3.

The energetic values of the energy of explosion, the explosion temperature, the detonation pressure, the detonation velocity, and the gas volume have been calculated using the enthalpies of formation and the EXPLO5 programm[26] (Table 3).

(21) (a) Suceska, M. *Test Methods for Explosives*; Springer: New York, 1995; pp 21 (impact); 27 (friction). (b) http://www.bam.de/.

(22) 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, extreme sensitive <1 0 N. According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates not safe for transport.

(23) Gao, A.; Rheingold, A. L.; Brill, T. B. *Propellants, Explos., Pyrotech.* **1991**, *16*, 97.

(24) Klapötke, T. M.; Stein, M.; Stierstorfer, J. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1711.

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TABLE 3. Energetic Properties of 12a, 12b, and 13

	12a	12b	13	TNT[k]	RDX[k]	nitrocellulose[k]
formula	$C_8H_{16}N_{12}O_2$	$C_{14}H_{24}N_{12}O_4$	$C_8H_{12}N_{12}O_4$	$C_3H_6N_6O_6$	$C_3H_6N_6O_6$	$C_6H_{7.26}N_{2.74}O_{10.48}$
molecular mass	312.33	424.45	340.26	227.1	222.1	285
density (g cm^{-1})[a]	1.539	1.401	1.614	1.65	1.82	1.3−1.7 (1.5 for calculation)
$-\Delta U_{comb}$ (cal g^{-1})[b]	4528	4976	3528			
$-\Delta H_{comb}$ (kJ mol^{-1})[c]	473	−101	153			
$\Delta_f H_m$ (kJ mol^{-1})[d]	435	−151	119			
Values Calculated by EXPLO5 V5.02						
$-\Delta_E U_m°$ (kJ kg^{-1})[e]	3586	2560	3363	5099	6052	4479
T_E (K)[f]	2441	1914	2588	3737	4358	3736
$p_{C\text{-}J}$ (kbar)[g]	197	121	179	205	356	167
D (m s^{-1})[h]	7662	6355	7073	7176	9055	6673
gas vol (L kg^{-1})[i]	773	730	721	620	793	711
I_s (s)[l]	160		163	200	252	227
I_s (s)[m] (70% AND)	238	216	240	240	232	230

[a] Estimated from a structure determination. [b] Experimental (constant volume) combustion energy. [c] Experimental molar enthalpy of combustion. [d] Molar enthalpy of formation. [e] Energy of explosion. [f] Explosion temperature. [g] Detonation pressure. [h] Detonation velocity. [i] Assuming only gaseous products. [k] Obtained from the database of EXPLO5 V5.02. [l] Specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion). [m] Specific impulse of a mixture containing 70% ammonium dinitramide as oxidizer.

Compared to RDX (a common high explosive) and nitrocellulose (a common propellant), the values of **12a** and **13** lie between those of RDX and nitrocellulose. The temperature of explosion is about 1300 K (nitrocellulose) and 2000 K (RDX) lower. Compared to nitrocellulose, a common propellant, the detonation pressure is comparable, whereas the temperature of explosion is significantly lower.

The sensitivity toward impact and friction was determined according to BAM standard. The sensitivity toward friction of **12a** and **13** is lower than 240 N, and the sensitivity toward impact is lower than 5 J. In the case of **12b**, the sensitivity toward friction is lower than 160 N, and the sensitivity toward impact lower than 7 J. The lower sensitivity toward friction of **12b** compared to **12a** and **13** can be rationalized by the lack of intermolecular interactions and the resulting lower stabilization in the crystal structure.

Conclusions

1,4-Bis[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**12a**), 1,4-bis[1-isopropoxycarbonylmethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**12b**), and 1,4-bis[1-carboxymethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (**13**) were prepared as nitrogen-rich compounds. The evaluation of the energetic properties points out that these compounds are suitable as propellants or gas-generating agents. The advantage lies in the high thermal stability and the low temperature of explosion, along with average detonation velocities and pressures. Moreover, a new synthesis of tetrazolylhydrazines via bromotetrazoles has been developed that results in high yields.

Experimental Section

CAUTION! Tetrazoles and tetrazolyltetrazenes are energetic compounds with sensitivity toward heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, grounded equipment and shoes, Kevlar gloves, and ear plugs) should be used when undertaking work involving tetrazoles or tetrazenes on larger scales.

Isopropyl-2-aminoacetate hydrochloride was synthesized according to the literature,[27] 2-(5-bromo-1*H*-tetrazol-1-yl)ethanol (**8a**) according to Bayes,[16] and isopropyl 2-(1*H*-tetrazol-1-yl)acetate (**7b**) according to the literature.[28]

Synthesis of (5-Bromo-1*H*-tetrazol-1-yl)-Acetic Acid Isopropyl Ester (8b). Crude 1*H*-tetrazol-1-yl-acetic acid isopropyl ester (**7b**) (33.4 g, 214 mmol) and bromine (81.1 g, 508 mmol) were dissolved in a mixture of 350 mL of chloroform and 175 mL of acetic acid. The solution was stirred at 80 °C under reflux for 48 h. Afterward the bromine and the acetic acid were removed under reduced pressure. The residue was neutralized with saturated sodium carbonate solution, extracted with ethyl acetate, and washed with 2 M HCl and saturated sodium carbonate solution. The organic phase was dried over $MgSO_4$, and solvent was removed under reduced pressure. The product was obtained as slightly impure orange oil (26.3 g, 106 mmol, yield 50%). IR (KBr) (cm^{-1}): $\tilde{\nu}$ 3390 (w), 3141 (w), 2986 (m), 2941 (w), 2881 (w), 2160 (w), 1749 (vs),1630 (w), 1542 (w), 1455 (m), 1419 (m), 1377 (s), 1344 (w), 1300 (w), 1272 (m), 1233 (vs),1184 (m), 1147 (w), 1058 (w), 1021 (w), 978 (w), 957 (w), 901 (w), 843 (w), 776 (w), 702(w), 584 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.20 (d, 6H, ^3J = 6.3 Hz, CH_3), 5.03 (sept, 1H, ^3J = 6.2 Hz, CH), 5.08 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 14.0 (*C*H$_3$), 21.3 (*C*H$_3$), 48.9 (*C*H), 70.3 (*C*H$_2$),135.6 (C_q), 165.0 (*C*O). *m*/*z* (DEI+): 249.0 [M + H] (8), 248.0 [M] (2), 235.0 (11), 233.0 (9), 191.0 (42), 189.0 (43), 164.0 (45), 163.0 (8), 162.0 (43), 134.9 (42), 132.9 (43), 107.9 (22), 105.9 (22), 92.9 (10), 90.9 (10), 55.0 (47), 54.0 (20), 53.0 (23), 43.0 (100), 42.0 (11), 41.0 (31). $C_6H_9BrN_4O_2$ (247.9909 found M 247.9890).

Synthesis of *N*-[5-(*N*-Methyl-hydrazino)-1*H*-tetrazol-1-yl]-acetic Acid Isopropyl Ester (9b). Crude (5-bromo-1*H*-tetrazol-1-yl)-acetic acid isopropyl ester (**8b**) (6.50 g, 26.1 mmol) and monomethylhydrazine (2.40 g, 52.0 mmol) were dissolved in 50 mL of propan-2-ol and heated under reflux for 6 h. Afterward the solution was evaporated to dryness, and 50 mL of dichloromethane was added. The precipitate was filtered off, and the filtrate was concentrated under reduced pressure. The product was obtained as slightly impure orange oil (5.30 g, 24.7 mmol, yield 95%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3337 (m), 3202 (w), 2982 (m), 2938 (m), 2879 (w), 1747 (vs), 1661 (s), 1574 (s), 1450 (m), 1412 (m), 1379 (m), 1281 (m), 1223 (vs), 1147 (m), 1103 (s),

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1047 (m), 958 (m), 915 (m), 903 (m), 845 (w), 779 (w), 737 (w), 627 (vw), 589 (vw). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 1.13 (d, 6H, ^3J = 6.3 Hz, CH_3), 3.09 (s, 3H, NCH_3), 4.90 (sept, 1H, ^3J = 6.2 Hz, CH), 4.73 (s, 2H, NH_2), 5.18 (s, 2H, CH_2). ^{13}C NMR (d_6-DMSO, 100 MHz, 25 °C): δ 21.4 (CH_3), 29.5 (CH_3), 43.1 (NCH_3), 49.8 (CH_2), 68.8 (CH), 158.3 (C_q), 166.9 (CO). ^{15}N NMR (d_6-DMSO) δ: 1.6 (N3), −18.0 (N2), −91.3 (N4), −180.9 (N1), −300.4 (N6), −309.7 (N5). *m/z* (DEI+): 214.1 (5) [M], 172.1 (7), 156.1 (10), 155.1 (16), 141.1 (10), 127.1 (5), 101.0 (32), 85.1 (6), 73.1 (26), 56.0 (12), 55.0 (48), 46.0 (6), 45.0 (29), 44.0 (11), 43.0 (100), 42.0 (8), 41.0 (20). $C_7H_{14}N_6O_2$ (214.1178 found M 214.1166).

Synthesis of *N*-[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (9a). 2-(5,2-(5-Bromo-tetrazol-1-yl)-ethanol (**8a**) (4.70 g, 20.0 mmol) and monomethylhydrazine (1.90 g, 41.2 mmol) were dissolved in 50 mL of propan-2-ol and heated under reflux for 6 h. Afterward the solution was evaporated to dryness, and 50 mL of DCM was added. The precipitate was filtered off, and the filtrate was concentrated under reduced pressure. The product was obtained as colorless solid (5.30 g, 24.7 mmol, yield 95%). Mp 111.0−117.8 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3350 (s), 3266 (s), 2967 (w), 2926 (w), 2878 (w), 1656 (vs), 1563 (vs), 1455 (m), 1415 (m), 1373 (m), 1340 (w), 1325 (w), 1282 (m), 1233 (m), 1122 (m), 1104 (m), 1069 (vs), 1039 (m), 983 (m), 948 (w), 903 (m), 864 (m), 745 (m), 707 (m), 684 (m), 493 (m). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ 3351 (40), 3232 (38), 3193 (34), 3028 (32), 2976 (100), 2928 (37), 2882 (38), 2809 (24), 1654 (41), 1566 (35), 1466 (56), 1418 (47), 1378 (32), 1352 (34), 1284 (66), 1268 (59), 1231 (30), 1105 (55), 1071 (29), 987 (19), 950 (23), 864 (52), 692 (91), 633 (54), 523 (28), 498 (27). ^{1}H NMR (d_6-DMSO) δ: 3.09 (s, 3H, NCH_3), 3.72 (t, 2H, OCH_2), 4.49 (t, 2H, NCH_2), 4.82 (s, 2H, NH_2), 4.96 (br. t, 1H, OH). ^{13}C NMR (d_6-DMSO) δ: 44.4 (CH_3), 50.8 (OCH_2), 59.5 (NCH_2), 159.2 (C_q). ^{15}N NMR (d_6-DMSO) δ: −11.0 (N3), −21.9 (N2), −100.1 (N4), −174.5 (N1), −301.6 (N6), 313.3 (N5). *m/z* (DEI+): 158.1 [M], 143.1, 127.1, 113.1, 87.1, 69.1, 55.1, 43.1, 31.1, 28.1. $C_4H_{10}N_6O$ (158.1 found M 158.1). $C_4H_{10}N_6O$ calcd: C 30.77, H 5.16, N 53.82. Found: C 30.63, H 5.13, N 53.29.

Synthesis of 1,4-Bis[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (12a). To a solution of *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**9a**) (0.25 g, 1.70 mmol) in a mixture of 2 mL of water and 0.5 mL of acetic acid was added dropwise 25 mL of a saturated solution of bromine in water at 0 °C. The precipitate was filtered off and evaporated to dryness. The product was obtained as a colorless solid (0.13 g, 0.45 mmol, yield 53%). IR (KBr) (cm^{-1}): $\tilde{\nu}$ 3347 (m), 2972 (w), 2944 (w), 2885 (w), 1717 (w), 1636 (w), 1572 (vs), 1470 (m), 1444 (m), 1417 (m), 1381 (w), 1360 (w), 1337 (w), 1295 (w), 1274 (w), 1261 (w), 1224 (m), 1149 (m), 1106 (m), 1098 (m), 1059 (m), 1036 (w), 1015 (m), 978 (w), 945 (w), 857 (w), 802 (w), 728 (m), 696 (m), 668 (m), 639 (w), 551 (w); 497 (w), 459 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ 3022 (3), 2973 (5), 2944 (5), 1611 (23), 1502 (100), 1463 (21), 1447 (18), 1410 (32), 1382 (9), 1360 (7), 1308 (4), 1278 (4), 1240 (15), 1125 (5), 1105 (10), 1057 (3), 973 (3), 856 (6), 672 (9), 537 (4), 362 (5), 331 (7), 257 (3). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 3.61 (s, 3H, CH_3), 3.76 (t, 2H, ^3J = 5.82 Hz, OCH_2), 4.58 (t, 2H, ^3J = 5.82 Hz, CH_2), 5.14 (broad s, 1H, OH). ^{13}C NMR (d_6-DMSO, 100 MHz, 25 °C): δ 35.5 (NCH_3), 51.3 (OCH_2), 59.1 (NCH_2), 154.2 (C_q). ^{15}N NMR (d_6-DMSO) δ: 2.0 (N6), −2.4 (N3), −13.2 (N2), −83.5 (N4), −169.5 (N1), −245.4 (N5). *m/z* (DEI+): 312.3 [M] (7.6), 284.3 (8.5), 225.3 (1.7), 198.3 (3.8), 172.3 (16.9), 142.3 (75.1), 113.2 (90.7), 100.2 (61.6), 45.2 (100), 28.2 (59.4). $C_8H_{16}N_{12}O_2$ calcd: C, 30.77; H, 5.16; N, 53.58. Found: C, 30.59; H, 5.40; N, 53.67. Impact sensitivity: 5 J. Friction sensitivity: 240 N.

Synthesis of 1,4-Bis[1-isopropoxycarbonylmethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (12b). To a solution *N*-[5-(*N*-methyl-hydrazino)-1*H*-tetrazol-1-yl]-acetic acid isopropyl ester (**9b**) (6.30 g, 29.4 mmol) in a mixture of 20 mL of water and 5 mL of acetic acid was added dropwise 400 mL of a saturated solution of bromine in water at 0 °C. The precipitate was filtered off and evaporated to dryness. The product was obtained as colorless solid (5.65 g, 13.3 mmol, yield 60%). IR (KBr) (cm^{-1}): $\tilde{\nu}$ 3487 (w), 3395 (w), 2999 (m), 2984 (m), 2965 (w), 2944 (w), 2884 (w), 1754 (s), 1627 (w), 1569 (vs), 1470 (m), 1450 (m), 1414 (m), 1383 (m), 1348 (w), 1329 (w), 1278 (w), 1218 (s), 1181 (w), 1144 (m), 1106 (s), 1083 (m), 1007 (m), 959 (m), 944 (w), 903 (w), 848 (m), 732 (w), 711 (w), 658 (m), 586 (w), 476 (w), 458 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ 2999 (26), 2963 (32), 2945 (24), 1753 (11), 1601 (44), 1500 (100), 1471 (24), 1445 (24), 1408 (34), 1351 (17), 1328 (11), 1226 (23), 1188 (10), 1149 (8), 1104 (23), 1010 (6), 971 (6), 904 (9), 866 (20), 835 (10), 770 (7), 723 (9), 683 (7), 593 (5), 537 (7), 417 (13), 381 (19), 290 (19), 227 (13). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 1.13 (d, 6H, ^3J = 6.32 Hz, CCH_3), 3.58 (s, 3H, NCH_3), 4.91 (sept, 1H, ^3J = 6.32 Hz, CH), 5.53 (s, 2H, CH_2). ^{13}C NMR (d_6-DMSO, 100 Hz, 5 °C): δ 21.9 (CCH_3), 35.3 (NCH_3), 50.4 (CH), 70.5 (CH_2), 154.6 (C_q), 166.9 (CO). *m/z* (DEI+): 424.3 [M] (89.1), 410.3 (6.6), 337.3 (8.7), 282.3 (1.9), 226.3 (42.0), 199.3 (47.8), 156.3 (26.3), 127.2 (25.7), 113.2 (15.9), 101.2 (6.7), 84.2 (8.4), 73.2 (13.5), 55.2 (20.1), 43.2 (17.8). Impact sensitivity: 7 J. Friction sensitivity: 160 N.

Synthesis of 1,4-Bis[1-carboxymethyl-1*H*-tetrazol-5-yl]-1,4-dimethyl-2-tetrazene (13). A suspension of bis(1,1′-methyl-1,1′-(iso-propyl-2-(1*H*-tetrazolyl) acetate))tetrazene (0.10 g, 0.24 mmol) in a 10 M solution of NaOH in water was heated until the solid was dissolved. Afterward concentrated hydrochloric acid was added to the cooled solution, and the precipitate was filtered off. The product was obtained as colorless solid (0.07 g, 0.19 mmol, yield 78%). IR (KBr) (cm^{-1}): $\tilde{\nu}$ 3436 (m), 3012(m), 2972 (m), 2945 (w), 2718 (w), 2592 (w), 2515 (w), 1786 (w), 1747 (s), 1738 (s), 1607 (m), 1565 (vs), 1478 (m), 1433 (w), 1423 (w), 1413 (w), 1400 (m), 1351 (vw), 1332 (vw), 1262 (vw), 1207 (s), 1140 (m), 1100 (m), 1075 (m), 1020 (w), 1009 (m), 993 (m), 965 (vw), 942 (vw), 893 (vw), 854 (vw), 818 (m), 798 (m), 733 (vw), 728 (vw), 693 (w), 689 (w), 565 (m), 648 (m), 463 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ 3044 (7), 3014 (19), 2973 (37), 2947 (16), 1739 (15), 1603 (94), 1492 (92), 1467 (100), 1446 (41), 1404 (61), 1354 (35), 1330 (18), 1312 (16), 1271 (11), 1235 (27), 1185 (16), 1117 (19), 1103 (27), 964 (9), 943 (8), 898 (14), 855 (24), 795 (12), 733 (13), 694 (9), 651 (9), 583 (13), 528 (9), 428 (26), 380 (15), 327 (20), 291 (20), 249 (15). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 3.62 (s, 6H, CH_3), 5.46 (s, 2H, CH_2), 13.68 (br.s, 1H, COOH). ^{13}C NMR (d_6-DMSO, 100 MHz, 25 °C): δ 35.3 (CH_3), 50.8 (CH_2), 154.7 (C_q), 169.0 (CO). ^{15}N NMR (d_6-DMSO) δ: 3.1 (N6), −3.6 (N3), −12.7 (N2), −84.3 (N4), −175.6 (N1), −243.7 (N5). *m/z* (DEI+): 340.4 [M] (6), 322.2 (16), 256.3 (13), 212.2 (14), 211.2 (13), 191.1 (10), 189.1 (9), 177.3 (11), 167.2 (9), 164.1 (13), 162.2 (10), 161.2 (9), 152.2 (9), 149.2 (32), 137.3 (8), 135.2 (37), 133.1 (10), 129.2 (12), 127.2 (21), 125.3 (10), 121.2 (8), 113.2 (9), 112.2 (14), 111.2 (23), 109.2 (10), 105.2 (11), 99.2 (9), 98.2 (13), 97.2 (36), 96.2 (9), 95.2 (16), 91.2 (10), 85.2 (19), 84.2 (18), 83.2 (42), 82.1 (27), 81.2 (29), 80.0 (11), 79.1 (8), 77.1 (10), 71.2 (31), 70.2 (21), 69.2 (58), 68.2 (11), 67.2 (12), 60.1 (9), 57.1 (52), 56.1 (19), 55.1 (53), 54.1 (11), 45.1 (9), 44.1 (43), 43.1 (100), 41.1 (34); $C_8H_{12}N_{12}O_4$ (340.3 found M 340.4). $C_8H_{12}N_{12}O_4$ calcd: C, 28.24; H, 3.55; N, 49.40. Found: C, 28.25; H, 3.95; N, 49.09. Impact sensitivity: 5 J. Friction sensitivity: 240 N.

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Supporting Information Available: General experimental methods; ^{1}H and ^{13}C NMR spectra for **12a**, **12b**, and **13**; and X-ray crystallographic data (CIF files) for **11**, **12a**, **12b**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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