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New Azidotetrazoles: Structurally Interesting and Extremely Sensitive

Thomas M. Klapötke,* Burkhard Krumm, Franz A. Martin, and Jörg Stierstorfer[a]

Abstract: The treatment of triaminoguanidinium chloride with two equivalents of sodium nitrite under acidic conditions, followed by the cyclization with stoichiometric amounts of either sodium hydroxide solution or solid sodium carbonate yielded 1-amino-5-azidotetrazole (**1**), 5-azido-1-diazidocarbamoyltetrazole (**2**), and 1-(aminoazidocarbamoyl)-5-azidotetrazole (**3**). The three novel compounds could be isolated by short-column liquid chromatography by using chloroform in reasonable yields. The mechanism of the formation as well as the decomposition pathway of the materials was investigated and a full characterization of all three compounds is presented. Compounds **1**–**3** have been characterized by means of Raman and IR as well as multinuclear NMR spectroscopy, mass spectrometry, and X-ray diffraction studies. Thermal stabilities have been evaluated by differential scanning calorimetry. Theoretical calculations have been performed to ensure the assignment of the vibrational modes obtained from Raman and IR measurements. The sensitivity values obtained from our measurements reflect the behavior of the compounds, which show an extremely high sensitivity toward mechanical as well as thermal stimuli.

Keywords: azides · diazotation · heterocycles · sensitivity · tetrazoles

Introduction

Among the group of nitrogen-containing heterocycles, tetrazoles possess the second-highest amount of nitrogen at above 80%. The highest percentage is shown by pentazoles that are only stable with large electron-donating substituents.[1] Tetrazoles are more frequently the compounds of choice for the synthesis of new energetic nitrogen-rich compounds.[2] Together with their high thermal stability and the high heat of formation of $+237\ kJ\ mol^{-1}$ (5*H*-1,2,3,4-tetrazole),[3] they offer a good backbone for the development of energetic compounds. Recently, many examples of energetic compounds that contain a tetrazole moiety have been investigated and synthesized.[4] An increase in nitrogen content is useful in the formation of new C, H, N or binary C, N compounds, which can be used either as energetic materials to increase the N_2/CO ratio or as precursor for interesting materials such as C_3N_4 or C_3N_5.[5] The azido group is often used as a highly energetic ligand in energetic materials to increase the enthalpy of formation to about $+364\ kJ\ mol^{-1}$[6] along with an increase in nitrogen content. Whereas 5*H*-tetrazole itself offers a nitrogen content of 80%, 5-azidotetrazole shows a nitrogen content of 88.28%, and the anion of the compound shows a content of 89.09%. Both compounds were synthesized more than 70 years ago,[7] and many publications have dealt with the synthesis and characterization of these compounds since then.[8] As 5-azidotetrazoles are very sensitive towards shock and friction, attempts have been made to desensitize these materials by introduction of aryl[9] and alkyl groups[4a,10] or even the coupling of two azidotetrazole moieties with alkyl chains such as ethyl or butyl groups.[11]

The introduction of alkyl and aryl substituents is accompanied by a decrease in nitrogen content but also by slightly lower sensitivities towards friction and impact. The approach to introduce electron-donating substituents in either the 1- or 2-position on the tetrazole ring to increase the overall electron density within the aromatic ring system has proved promising in several examples. One of the highest positive mesomeric effects is provided by the amine substituent, which can be introduced at either the 1- or 2-position of the tetrazole backbone. At the same time, the $-NH_2$ substituent increases the overall nitrogen content. To the best of our knowledge, only theoretical calculations on aminoazidotetrazoles have been performed in the past,[12] either with the azide group located on the C5, N1, or N2 position. Here we present 1-amino-5-azidotetrazole (**1**) as the first tetrazole that carries only amino and azido substituents. In addition, two very interesting 1-substituted 5-azidotetrazoles—namely, 5-azido-1-(aminoazidocarbamoyl)tetrazole (**3**) and 5-azido-1-diazidocarbamoyltetrazole (**2**)—are presented. The latter one with the exciting sum formula C_2N_{14} was announced by us in a short communication earlier this year.[13]

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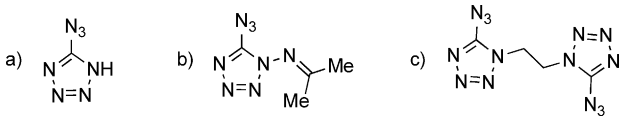
Results and Discussion

Synthesis

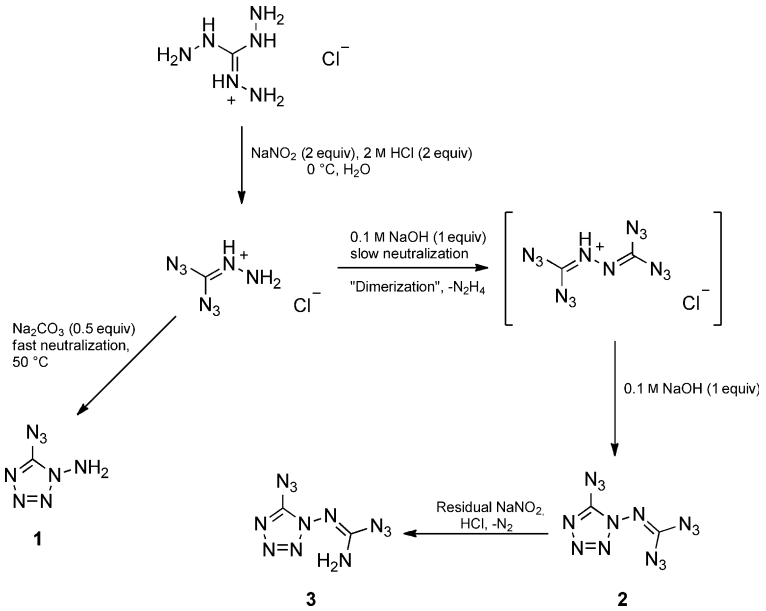
Initially, the direct formation of 1-amino-5-azidotetrazole (**1**) from 1,5-diaminotetrazole (DAT), first synthesized by Gaponik et al.,[14] was favored. A direct diazotation of the amino group in the 5-position with sodium nitrite and hydrochloric acid was not possible because the attack took place at the amino group on the 1-position, thereby resulting in a ring opening and destruction of the heterocyclic ring system. Selective protection of the 1-subsituted amino group followed by diazotation of the amino group at the 5-position and displacement with azide was omitted due to the harsh reaction conditions generally needed for deprotection of amine groups, which would have resulted in the destruction of the fragile azidotetrazole system. Therefore a different route was chosen. It is well known from the recent literature that tetrazole systems and especially DAT can be synthesized from diaminoguanidinium salts by diazotation of one hydrazine group and subsequent ring closure under basic conditions (Scheme 1).[15]



Scheme 1. Examples for known 5-azidotetrazole derivatives. a) 5-azidotetrazole, b) 1-(aminopropan-2-ylidene)-5-azidotetrazole, and c) 1,2-bis(5-azidotetrazol-1-yl)ethane. Impact sensitivity values are all below 1 J for (BAM measurements).[4a,11]

The treatment of triaminoguanidinium chloride with two equivalents of sodium nitrite instead of one, as used in the formation of DAT,[15] and subsequent ring closure should therefore result in the formation of desired **1**. The diazotation of triaminoguanidinium chloride was performed with two equivalents of sodium nitrite and the subsequent ring-closure reaction was initiated in two different ways afterwards. In one experiment, the ring closure was performed by adding slowly two equivalents of 0.1 M sodium hydroxide solution, whereas in a second experiment it was initiated quickly with one equivalent of solid sodium carbonate that was added in one portion at elevated temperatures (50 °C). The solutions were extracted with diethyl ether, dried with magnesium sulfate, and left for evaporation at room temperature. The raw products were examined by TLC, and three different compounds were identified. Whereas the reaction with 0.1 M sodium hydroxide solution yielded only two separable compounds, the neutralization with sodium carbonate showed three different reaction products, two of them with the same R_f values as the products from the neutralization reaction with 0.1 M sodium hydroxide solution. The compounds were found to be two "dimerization" products of the twice-diazotized triaminoguanidinium species—namely, 5-azido-1-diazidocarbamoyltetrazole (**2**) and 1-(aminoazidocarbamoyl)-5-azidotetrazole (**3**)—extracted from both reaction mixtures, whereas the third product, the desired 1-amino-5-azidotetrazole (**1**), was only isolated from the reaction neutralized with sodium carbonate. The reaction pathways and possible mechanism are shown in Scheme 2.

As **1** was only observed when the reaction was neutralized very quickly at elevated temperature, it is obvious that the coupled products are favored over the single ring closure. Compound **1** could not be identified from reactions that have been slowly neutralized. Therefore, it is rather a kinetically and not a thermodynamically controlled reaction pathway for the formation of **1**. Compound **2** was found to be the direct coupling product of two intermediate diazotation products, thus forming a binary carbon nitrogen compound with the sum formula C_2N_{14} under the cleavage of hydrazine and retaining three azide groups as substituents.[13] One azide group of the carbamoyldiazide group of **2** was then directly degraded with residual sodium nitrite under acidic conditions to result in the formation of **3**. The formation of **3** can be forced to higher yields if the reaction mixture is stirred at a pH value of 5–6 for a longer period of time during neutralization. Nevertheless, a complete degradation of **2** could not be observed. All three compounds are stable



Scheme 2. Reaction pathways and mechanism towards the formation of azidotetrazoles **1**–**3**.

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against hydrolysis in acidic media and can be easily isolated with short-column flash chromatography by using silica as the stationary phase and with chloroform as the eluent. Compounds **2** and **3** are recrystallized from diethyl ether in their anhydrous forms as colorless crystals with decomposition temperatures of 124 and 136 °C, respectively, whereas **1** can only be crystallized as the monohydrate in the form of light-yellow crystals; it shows the highest decomposition temperature of the three azidotetrazoles at 142 °C.

Caution: All three azidotetrazoles tend to explode under nearly every kind of physical stress, and therefore safety precautions have to be taken when handling or manipulating these materials, even in solution!

Spectroscopic Data

Vibrational Spectroscopy

IR and Raman spectra of all three azidotetrazoles were recorded with only very small amounts of material, and the frequencies have been assigned based on literature values[16] and on quantum mechanical calculations at the B3LYP/cc-pVDZ[17] level of theory as implemented in the Gaussian 09W program package.[18] The calculated frequencies have been fitted according to Witek et al.[19] with a scaling factor of 0.9704. The frequencies derived from Raman and IR measurements are compiled in Tables S1, S2, and S3 in the Supporting Information together with the calculated values and their possible assignment. As all compounds could only be measured with traces of solvent ($CHCl_3$) left, bands in the C–H region are observed at 3000–2800 cm^{-1} in the IR spectra of **2** and **3** and in the Raman spectra of **1** and **2**. Caution: Compound **2** detonated several times during the Raman measurement (laser energy <150 mW!). Measurements were therefore performed at 50 mW using a higher number of scans using one crystal.

The ν_s stretching modes of the amine group in **1** are observed at 3332 and 3228 cm^{-1} in the IR spectrum and at 3205 cm^{-1} in the Raman spectrum, whereas the ν_{as} stretching mode is observed at 3152 cm^{-1} for IR and at 3154 cm^{-1} for the Raman spectra, respectively. Although no N–H stretching mode was observed for **2**, only the ν_s stretching mode of the amine group was observed for **3** in the IR spectrum at 3278 cm^{-1} as a very weak band. The vibrations of interest for the characterization of the three compounds are the antisymmetric stretching modes of the azide substituents, all located in the region of 2200–2130 cm^{-1} in both IR and Raman spectra. Each single azide substituent can be assigned to one unique frequency. Hence **1** shows only one vibrational mode ν_{as} at 2150 (IR) and 2156 cm^{-1} (Raman), whereas the signals for the three chemically nonequivalent azide substituents in **2** are observed at 2175, 2155, and 2133 cm^{-1} (IR) and at 2179, 2165, and 2133 cm^{-1} (Raman). As expected, two unique frequencies characterize the two ν_{as} stretching modes at 2164 and 2152 cm^{-1} in the IR spectrum and at 2170 and 2157 cm^{-1} in the Raman spectrum of **3**, respectively. From the comparison of the IR and Raman spectra of the three compounds, the tetrazole-bound azide substituents were identified at 2150 (**1**), 2155 (**2**), and 2152 cm^{-1} (**3**) (IR). The remaining stretching modes in the case of **2** and **3** are hence assigned to the remaining one (**3**) or two (**2**) azide substituents bound to the carbamoyl group. Although calculations of the Raman and IR spectra were performed to assign these vibrational modes correctly, they cannot be distinguished clearly from these results because the difference in the wavenumber is too small and only coupled stretching modes of the azide substituents are calculated for **2** and **3**. The comparisons of the Raman as well as the IR spectra are presented in Figure 1 and Figure 2, respectively.

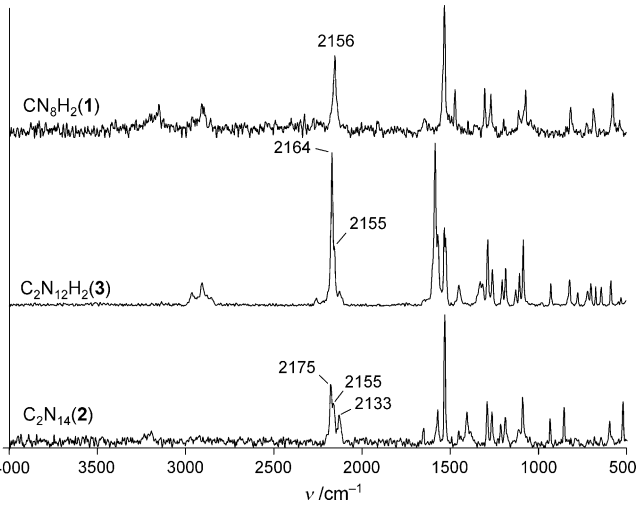

Figure 1. Direct comparison of the Raman spectra of CN_8H_2 (**1**), C_2N_{14} (**2**), and $C_2N_{12}H_2$ (**3**) presenting the unique frequencies of the azide substituents.

Deformation modes of the amine group are observed at 1639 cm^{-1} (IR) and 1648 cm^{-1} (Raman) for **1** and at lower frequencies at 1526 cm^{-1} (Raman) for compound **3**. The difference in the wavenumber can be explained by the different chemical surroundings: the nitrogen atom in the amine group of **1** is sp^3 hybridized, whereas the configuration of the amine group in **3** is planar and therefore the nitrogen atom is sp^2 hybridized. Compounds **2** and **3** both revealed stretching modes of the C2=N8 double bond at 1578 (**2**) and 1584 cm^{-1} (**3**) in the IR spectra and at 1573 (**2**) and 1586 cm^{-1} (**3**) in the Raman spectra. The stretching mode of the C1–N5 bond is visible for all three compounds at 1532 (**1**), 1530 (**2**), and 1522 cm^{-1} (**3**) in the IR spectra and at 1536 (**1**), 1534 (**2**), and 1534 cm^{-1} (**3**) in the corresponding Raman spectra. The ν_{as} stretching mode N1–C1–N4 of the tetrazole ring is observed for all three compounds in both Raman and IR spectra. In the IR spectra, the bands are observed at 1472 (**1**), 1456 (**2**), and 1448 cm^{-1} (**3**), whereas lines are observed in the Raman spectra at 1476 (**1**), 1454 (**2**), and 1451 cm^{-1} (**3**). The vibrational mode of the shortest bond length within the tetrazole ring between N2=N3 is observed at 1302 (**1**), 1291 (**2**), and 1329 cm^{-1} (**3**) in the IR

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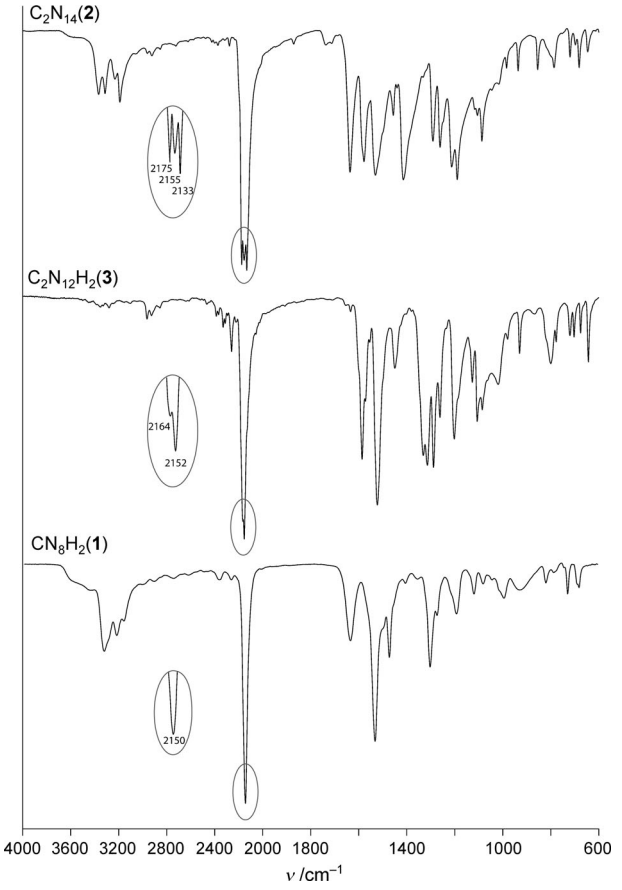

Figure 2. Direct comparison of the IR spectra of CN_8H_2 (**1**), C_2N_{14} (**2**), and $C_2N_{12}H_2$ (**3**) presenting the unique frequencies of the azide substituents.

spectra and at 1308 (**1**), 1293 (**2**), and 1331 cm^{-1} (**3**) in the corresponding Raman spectra. Stretching modes of the N_α=N_β nitrogen atoms can be observed for all three compounds: for **1** they are a combination of ν_{as} = N8–N1–N2 and ν = N5=N6 at 1191 cm^{-1} (IR) and 1200 cm^{-1} (Raman), whereas for **2** and **3** combinations of the stretching modes of the double bonds within the tetrazole ring (C1=N4 and N2=N3) and the corresponding N_α=N_β stretching modes are observed (N5=N6, N9=N10, and N12=N13 (**2**); N5=N6 and N9=N10 (**3**)). The vibrations are observed at 1261 (**2**) and 1287 cm^{-1} (**3**) in the IR spectra, whereas lines are observed in the Raman spectra at 1266 (**2**) and 1288 cm^{-1} (**3**). Antisymmetric and symmetric stretching modes of the N1–N2 and N3–N4 bonds are observed for all compounds in the region of 1120–1080 cm^{-1} and are assigned in detail in Tables S1, S2, and S3 in the Supporting Information. Between 1000 and 500 cm^{-1}, many strongly coupled stretching and deformation modes of the entire molecule and especially deformation (in-plane and out-of-plane) and torsion modes of the tetrazole rings are observed.

Multinuclear NMR Spectroscopy

The ^1H NMR spectrum of **1** showed, as expected, only one singlet at a chemical shift of $\delta = 5.45$ ppm that represented the NH_2 group in the 1-position. One resonance is also observed for compound **3** at a chemical shift of $\delta = 5.35$ ppm, which is assignable to the NH_2 group of the aminoazidocarbamoyl substituent.

^{13}C NMR spectroscopic studies reveal also clearly assignable resonances for each carbon atom. Whereas only one signal for the tetrazole carbon was observed at a chemical shift of $\delta = 151.4$ ppm for **1**, both **2** and **3** show two signals as expected. The resonances for **2** are observed at chemical shifts of $\delta = 160.4$ ppm that represent the carbon atom of the diazidocarbamoyl moiety and at $\delta = 148.4$ ppm for the tetrazole carbon atom. The same is observed for **3** at chemical shifts of $\delta = 157.9$ and 148.2 ppm, respectively.

Although ^{15}N NMR spectroscopic studies could not be performed due to the amount of material required of these highly energetic compounds, ^{14}N NMR spectroscopic studies in [D_6]DMSO and $CDCl_3$ revealed clearly assignable resonances for the nitrogen atoms of the azide groups. Compound **1** revealed only two signals in the NMR spectra. The signal of the N_β atom of the azide group is observed at a chemical shift of $\delta = -147$ ppm as a very intense resonance, whereas the N_γ atom showed a very broad singlet of low intensity, partially overlapped by the N_β resonance at a chemical shift of $\delta = -140$ ppm. Two signals are observed for the N_β nitrogen atoms of the three azide groups in **2** at chemical shifts of $\delta = -147$ and -149 ppm, thereby representing the tetrazole bound azide group and the two azide groups of the diazidocarbamoyl moiety (N6, N10, and N13). Since the diazidocarbamoyl moiety can rotate freely around the N1–N8 bond, only one signal is observed for the two azide groups located at the carbamoyl group. As observed in **1**, the three N_γ atoms are observed as a very broad singlet at a chemical shift of $\delta = -145$ ppm, again partially overlapped by the very intense signals for the N_β atoms. The three N_α atoms are observed as a very broad singlet at a chemical shift of $\delta \approx -305$ ppm. If the solvent is changed to [D_6]DMSO, only the N_β atoms are observed as one slightly broader singlet at $\delta = -147$ ppm, whereas N_α and N_γ atoms could not be observed at all. As observed for **2**, compound **3** exhibits two resonances for the chemically nonequivalent N_β nitrogen atoms (N6, N10) of the azide substituents at chemical shifts of $\delta = -148$ and -152 ppm. The N_γ nitrogen atoms are again observed as a very broad singlet at a chemical shift of $\delta = -138$ ppm, whereas the N_α nitrogen atoms are not observed.

Molecular Structures

Single crystals of 1-amino-5-azidotetrazole (**1**) have been obtained from chloroform at $-18\,^\circ C$ as light yellow blocks that contain one molecule of crystal water. Single crystals of 5-azido-1-diazidocarbamoyltetrazole (**2**) and 1-(aminoazidocarbamoyl)-5-azidotetrazole (**3**) suitable for X-ray diffraction measurements have been obtained from diethyl ether

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Table 1. Selected crystallographic data and parameters.

	CH_2N_8 (**1**)	C_2N_{14} (**2**)	$C_2H_2N_{12}$ (**3**)
formula	$CH_2N_8{\cdot}H_2O$	C_2N_{14}	$C_2H_2N_{12}$
M_r [g mol^{-1}]	144.10	220.16	194.12
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1$	*Pbcn*	$P\bar{1}$
color/habit	light yellow block	colorless needles	colorless rods
size [mm]	0.43×0.18×0.05	0.01×0.05×0.10	0.12×0.08×0.07
a [Å]	4.7942(3)	18.1289(1)	7.2321(3)
b [Å]	8.0012(5)	8.2128(7)	7.2828(4)
c [Å]	7.7650(6)	11.4021(9)	7.8104(5)
α [°]	90	90	108.408(5)
β [°]	99.566(7)	90	98.467(4)
γ [°]	90	90	91.593(4)
V [Å^3]	293.72(3)	1697.6(2)	384.86(4)
Z	2	8	2
ρ_{calcd} [g cm^{-3}]	1.629	1.723	1.675
μ [mm^{-1}]	0.138	0.140	0.135
$F(000)$	148	880	196
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073
T [K]	173	150	100
θ min/max [°]	4.31/26.50	3.74/25.50	3.93/30.12
reflns collected	1588	6862	5862
independent reflns	651	1563	2238
observed reflns	581	763	1765
no. parameters	103	145	122
R_{int}	0.0197	0.1423	0.0198
R_1, wR_2 ($I>2\sigma(I)$)	0.0239, 0.0502	0.0673, 0.0847	0.0307, 0.0774
R_1, wR_2 (all data)	0.0289, 0.0513	0.1660, 0.1177	0.0433, 0.0827
S	0.971	1.084	1.075

and chloroform, respectively, as colorless blocks. Crystallographic data of compounds **1**–**3** are shown in Table 1.

Compound **1** crystallizes in the monoclinic space group $P2_1$ with a cell volume of 293.72(3) Å^3 and only two molecular moieties in the unit cell. The density calculated from the measurement at 173 K is 1.629 g cm^{-3}, which is slightly lower than the densities calculated for **2** (1.723 g cm^{-3}) and **3** (1.675 g cm^{-3}). The asymmetric unit of **1** is displayed in Figure 3.

The bond lengths within the aromatic tetrazole ring are between bond lengths of single and double bonds, with the N2–N3 bond being the shortest (1.296(2) Å) and the N3< C-N4 bond being the longest (1.374(2) Å). The distance of atoms N1–N8 is slightly longer (1.397(2) Å) and more in the range of a formal N–N single bond (1.48 Å).[20] Hence, a look at the structure of the amine group shows an angled rather than a planar structure, which indicates an sp^3-hybridized nitrogen atom. The azide group lies nearly exactly in the plane of the tetrazole ring, which is in agreement with the literature;[8c] it displays a torsion angle of only 3.6(3)° (N6–N5–C1–N4) and shows an angle N5–N6–N7 of 171.7(2)°. The C1–N5 bond is shorter than the N1–N8 bond and displays a bond length of 1.378(3) Å but is closer to a formal C–N single than double bond (1.47, 1.22 Å).[20]

Five hydrogen bonds, illustrated in Figure 4, are observed in the structure of **1**, one of them being bifurcated. Rows

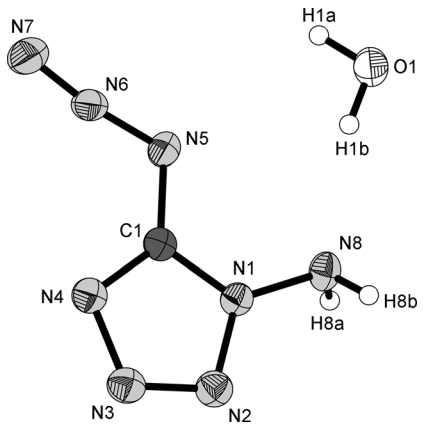

Figure 3. Asymmetric unit of **1**. Selected bond lengths [Å] and angles [°]: N1–C1 1.337(2), N1–N2 1.358(2), N1–N8 1.397(2), N2–N3 1.296(2), N3–N4 1.374(2), N4–C1 1.319(3), N8–H8A 0.91(2), N8–H8B 0.87(3), N5–N6 1.249(2), N5–C1 1.378(3), N6–N7 1.123(2), O1–H1A 0.86(3), O1–H1B 0.89(3); C1–N1–N2 108.30(2), C1–N1–N8 126.7(2), N2–N1–N8 125.0(2), N3–N2–N1 106.0(2), N2–N3–N4 111.3(2), C1–N4–N3 104.9(2), N6–N5–C1 113.4(2), N7–N6–N5 171.7(2), N4–C1–N1 109.6(2), N4–C1–N5 130.5(2), N1–C1–N5 120.0(2), H1a–O1–H1b 101(2). Selected torsion angles [°]: C1–N1–N2–N3 −0.9(2), N8–N1–N2–N3 −178.77(18), N1–N2–N3–N4 0.8(2), N2–N3–N4–C1 −0.5(2), C1–N5–N6–N7 179.3(15), N3–N4–C1–N1 −0.1(2), N3–N4–C1–N5 −179.5(2), N2–N1–C1–N5 −179.89(17), N6–N5–C1–N4 3.6(3).

are formed with molecules of **1** exactly opposite to one another. The rows are connected by the two hydrogen bonds: N8–H8a···O1 (D–H···A angle 139°) and O1(i)–H1a(i)···N4(iv) (D–H···A angle 169°). Both bonds show

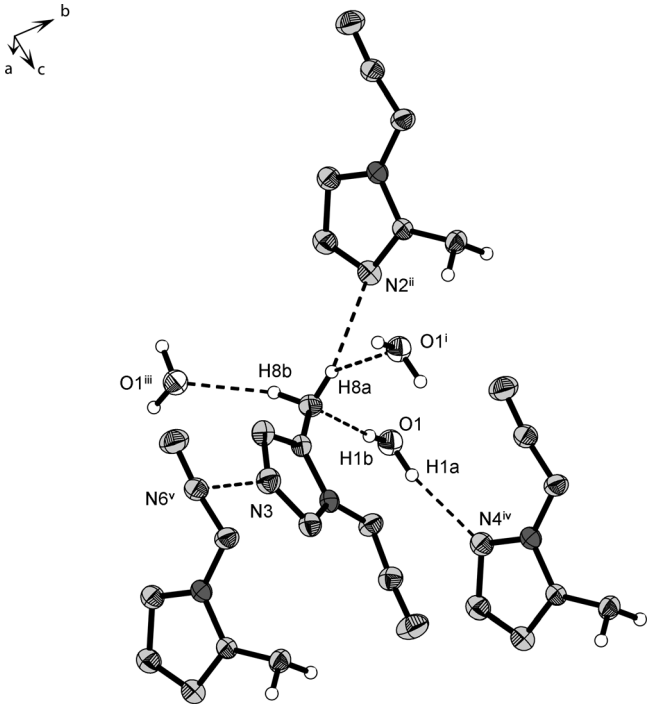

Figure 4. Hydrogen-bonding scheme present in **1**, displayed for clarity only for the asymmetric unit.

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D···A distances significantly below the sum of van der Waals radii (r_w(N)+r_w(O) = 3.07 Å)[21] at 2.981(2) and 2.940(2) Å, respectively, thus representing moderately strong hydrogen bonds. A short contact between the N3 nitrogen atom of the tetrazole ring and the partially positive-charged N_β atom (N6) of the azide group (2.998(3) Å) completes the connectivity pattern of the rows (symmetry operator: $-x$, $y-{}^1/_2$, $-z+1$). The remaining three hydrogen bonds connect the rows between one another, thereby building up a dense three-dimensional network. N8–H8b···O1(iii) connects to one row below, whereas the O1–H1b···N8 and N8–H8a···N2(ii) hydrogen bonds connect to two independent rows above. The two hydrogen bonds that involve an oxygen atom are both directed at an angle of 169°, whereas the N8–H8a···N2(ii) hydrogen bond exhibits a very small D–H···A angle of 129° and also shows a longer D···A distance than the sum of van der Waals radii (r_w(N)+r_w(N) = 3.10 Å)[21] at 3.217(2) Å. Hence this hydrogen bond is more of an electrostatic nature and not as strong as the other four bonds observed. The hydrogen bonds are compiled in Table 2.

Table 2. Hydrogen bonds and short contacts present in **1**.[a]

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D–H···A) [Å]	∢(D–**H**···A) [°]
N8–H8a···O1^{i}	0.91(2)	2.23(2)	2.981(2)	139(2)
N8–H8a···N2^{ii}	0.91(2)	2.57(2)	3.217(2)	128(2)
N8–H8b···O1^{iii}	0.87(3)	2.10(3)	2.940(2)	161(2)
O1–H1a···N4^{iv}	0.86(3)	2.13(3)	2.979(2)	169(3)
O1–H1b···N8	0.89(3)	2.15(3)	3.025(2)	169(2)
N3···N6^{v}			2.998(3)	

[a] Symmetry operators: i) $x-1$, y, z; ii) $-x$, $y+{}^1/_2$, $-z$; iii) $-x+1$, $y-{}^1/_2$, $-z$; iv) $-x+1$, $y+{}^1/_2$, $-z+1$; and v) $-x$, $y-{}^1/_2$, $-z+1$.

The rows show a zigzag motif and present an angle of 81.97° within the rows. The rows are stacked, as shown in Figure 5, and display a distance of 3.118 Å between the rows on top of each other.

Compound **2** crystallizes in the orthorhombic space group *Pbcn* with a cell volume of 1697.6(2) Å^3 and eight molecules in the unit cell. The asymmetric unit is presented in Figure 6. A detailed description was published earlier.[13]

Even though the compound has no ability to form hydrogen bonds, and is hence built up exclusively from nitrogen–nitrogen interactions, it displays a high density of 1.732 g cm^{-3}. That requires a very unequal charge distribution within the molecule, as it is observed from calculations of the electrostatic potential of **2** at the B3LYP/cc-pVDZ level of theory.[17] Short contacts are observed between the nearly uncharged N_γ atom (N7) of the tetrazole bound azide group with the N2 and N3 atoms of the tetrazole ring, thereby representing the region of the highest negative charge (N7···N3 = 3.047 Å, N7···N2 = 3.243 Å). A third contact is observed between N_γ (N11, slightly negative charge) and N_β (N13, most positive charge) at a distance of 3.125 Å.

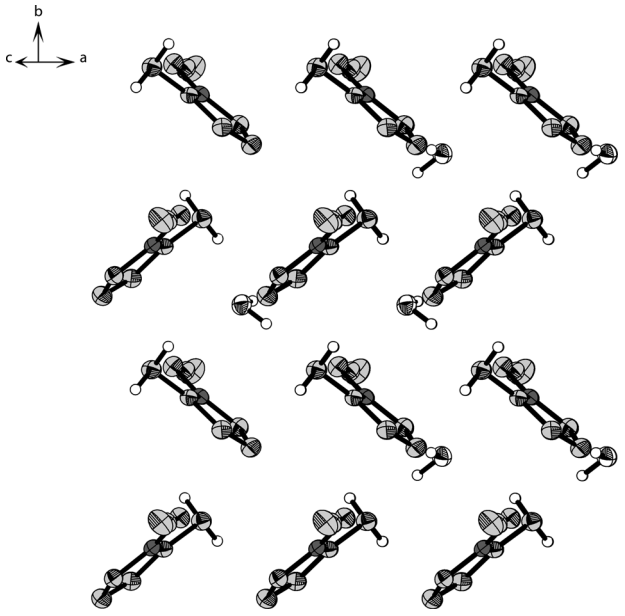

Figure 5. Presentation of the zigzag rows in **1**, enclosing an angle of 81.97°, together with their stacked packing.

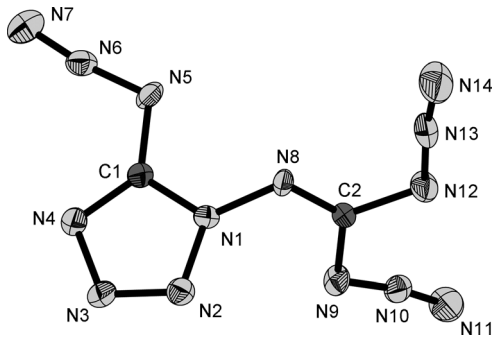

Figure 6. Asymmetric unit of **2**. Selected bond lengths [Å] and angles [°]: N1–C1 1.344(5), N1–N2 1.351(4), N1–N8 1.403(4), N4–C1 1.313(5), N4–N3 1.377(4), N10–N11 1.119(5), N10–N9 1.265(5), N8–C2 1.288(5), N–C2 1.388(5), N2–N3 1.298(4), N6–N7 1.121(5), N6–N5 1.263(5), N12–N13 1.279(5), N12–C2 1.395(5), N5–C1 1.384(5), N14–N13 1.121(5); C1-N1-N2 108.0(3), C1-N1-N8 126.2(3), N2-N1-N8 123.3(3), C1-N4-N3 104.5(3), N11-N10-N9 171.0(4), C2-N8-N1 113.8(3), N10-N9-C2 114.5(3), N3-N2-N1 106.1(3), N7-N6-N5 172.4(5), N13-N12-C2 111.1(4), N6-N5-C1 112.0(4), N2-N3-N4 111.4(3), N14-N13-N12 173.2(4), N8-C2-N9 124.6(4), N8-C2-N12 120.4(4), N9-C2-N12 115.0(4), N4-C1-N1 109.9(4), N4-C1-N5 130.4(4), N1-C1-N5 119.7(4). Selected torsion angles [°]: C1-N1-N8-C2 −123.8(5), C1-N1-N2-N3 2.1(5), N8-N1-N2-N3 165.1(3), N1-N8-C2-N9 −2.2(6), N1-N8-C2-N12 179.1(4), N13-N12-C2- N8 2.9(6), N3-N4-C1-N1 1.5(5), N8-N1-C1-N5 15.9(7), N6-N5-C1-N4 4.2(7).

The bond lengths and angles are in the normal range expected for azidotetrazoles and close to the ones presented for **1**. The N1–N8 bond (1.403(4) Å) is close to a formal single bond (1.48 Å), as already seen in **1**, whereas the N8–C2 bond towards the diazido moiety is much shorter at 1.288(5) Å and hence in the range of a formal C=N double bond (1.22 Å).[20] As observed for **1**, the tetrazole bound

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azide moiety is nearly in the plane with the tetrazole and shows only slight deviations (N4–C1–N5–N6 4.2(7)°). The diazido moiety is not in the plane of the tetrazole ring but twisted out of the plane by 66.12° relative to the plane formed by N12, C2, N9, and N8. The twist results in the formation of two-dimensional chains along the *c* axis and shows a zigzag conformation (113.22°). The rows are arranged next to one another and form layerlike structures, but every second row is oriented the opposite way (turned by 180°). The rows are stacked on top of each other along the *b* axis (Figure 7, only one set of rows is shown, the opposite rows are omitted for clarity).

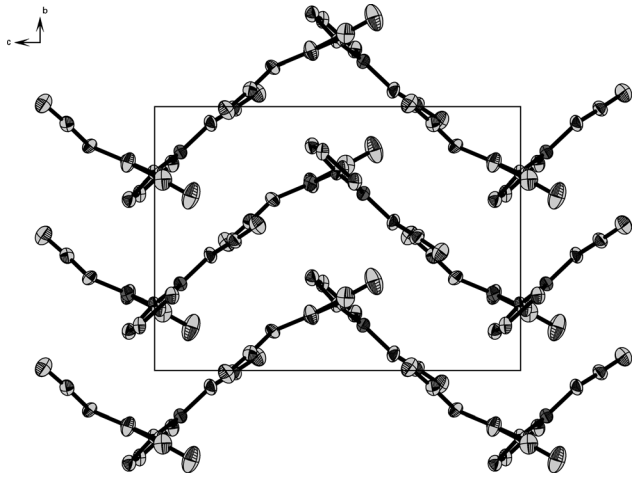

Figure 7. Stacking of the 2D chains along the *b* axis in **2**.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with a cell volume of 384.86(4) Å^3 and two molecular moieties in the unit cell. The density of 1.675 g cm^{-3} is in between compounds **1** and **2**. The asymmetric unit of **3** is displayed in Figure 8. Selected bond lengths and angles are given in the figure caption.

As observed for **1** and **2**, the bond lengths of both the C–N and N–N bonds in the tetrazole ring are right in between the formal bond lengths of single and double bonds; they range between 1.296(1) Å (N2–N3) and 1.267(1) Å (N3–N4). The bond angles in the tetrazole ring range between 104.72(7)° (C1–N4–N3) and 111.78(8)° (N2–N3–N4). The N1–N8 bond, which connects the aminoazidocarbamoyl moiety to the tetrazole ring, again displays a bond length of 1.397(1) Å as observed for **1** and is therefore close to a formal N–N single bond (1.48 Å),[20] whereas the N8–C2 bond is again closer to a formal C=N double bond (1.22 Å)[20] at 1.312(1) Å. Both, the N8 and N2 atoms showed planar sp^2 hybridization. The C2–N8 bond is 0.3 Å longer than the corresponding bond in **2**, as the C2–N12 bond is also shortened to 1.324(1) Å in **3**. The double-bond character of the C2–N12 bond is also indicated by the planar amine group (H12a–N12–H12b), which shows sp^2 hybridization for N12. The tetrazole-bound azide lies nearly in the plane of the tetrazole ring and shows a torsion angle N6–N5–C1–N1 of 176.86(9)°. The aminoazidocarbamoyl moiety is twisted out of the plane of the tetrazole ring by 85.0° relative to the plane formed by N8, C2, N9, and N12. The azide substituents show bond lengths as expected and bond angles of 172.8(1)° (N5–N6–N7) and 171.4(1)° (N9–N10–N11).

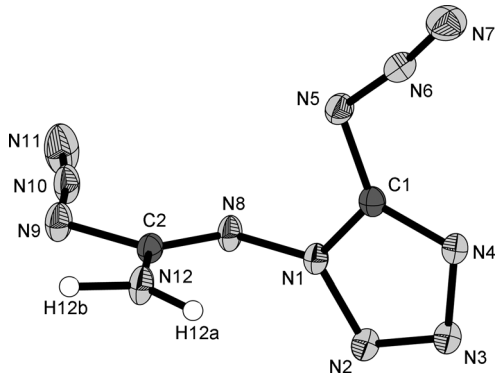

Figure 8. Asymmetric unit of **3**. Selected bond lengths [Å] and angles [°]: N1–C1 1.3390(1), N1–N2 1.356(1), N1–N8 1.397(1), N2–N3 1.296(1), N3–N4 1.367(1), N4–C1 1.322(1), N5–N6 1.265(1), N5–C1 1.383(1), N6–N7 1.116(1), N8–C2 1.312(1), N12–C2 1.324(1), N12–H12a 0.87(1), N12–H12b 0.88(1), N9–N10 1.259(1), N9–C2 1.403(1), N10–N11 1.117(1); C1-N1-N2 108.31(7), C1-N1-N8 128.27(8), N2-N1-N8 122.50(8), N3-N2-N1 105.75(8), N2-N3-N4 111.78(8), C1-N4-N3 104.72(7), N6-N5-C1 111.54(8), N7-N6-N5 172.8(1), C2-N8-N1 111.86(7), C2-N12-H12a 120.8(8), C2-N12-H12b 118.1(8), N10-N9-C2 113.09(8), N11-N10-N9 171.4(1), N4-C1-N1 109.41(8), N4-C1-N5 130.26(9), N1-C1-N5 120.31(8), N8-C2-N12 129.71(9), N8-C2-N9 117.49(8), N12-C2-N9 112.80(8). Selected torsion angles [°]: C1-N1-N2-N3 1.5(1), N8-N1-N2-N3 171.36(7), C1-N5-N6-N7 −175.2(8), C1-N1-N8-C2 −90.3(1), N3-N4-C1-N5 179.37(9), N2-N1-C1-N4 −1.5(1), N8-N1-C1-N4 −170.66(8), N2-N1-C1-N5 179.85(8), N6-N5-C1-N1 176.86(8), N10-N9-C2-N8 −1.9(1), N10-N9-C2-N12 177.79(9).

The structure of **3** is indeed built up rather simply. The structure consists of rows along the *c* axis connected through two short nitrogen–nitrogen interactions that favor the N_γ atom of the tetrazole-bound azide substituent and the N2 and N3 atoms of the tetrazole ring, thus presenting a planar arrangement. Both contacts, N3···N7(iii) and N2–N7(iii), are shorter than the sum of van der Waals radii (r_w(N)+r_w(N) = 3.10 Å) at 3.056(2) and 3.033(5) Å, respectively. The third nitrogen–nitrogen contact, N8···N6(iv), is in the same range as the latter two (3.032(6) Å). The interaction connects the rows that involve the two hydrogen bonds, N12–H12a···N4(i) and N12–H12b···N3(ii), and is responsible for the formation of the three-dimensional network. Both hydrogen bonds are shorter than the sum of van der Waals radii and display D···A distances of 3.032(1) and 3.026(1) Å, respectively, and D–H···A angles of 164(1) and 157(1)°, respectively. The two bonds are hence not only of electrostatic nature, but also directed, as can be seen in Figure 9. Due to the short H···A distances of 2.19(1) Å for both hydrogen bonds, they can be assigned as moderately strong.[22] The packing scheme within the unit cell is presented in Figure 10.

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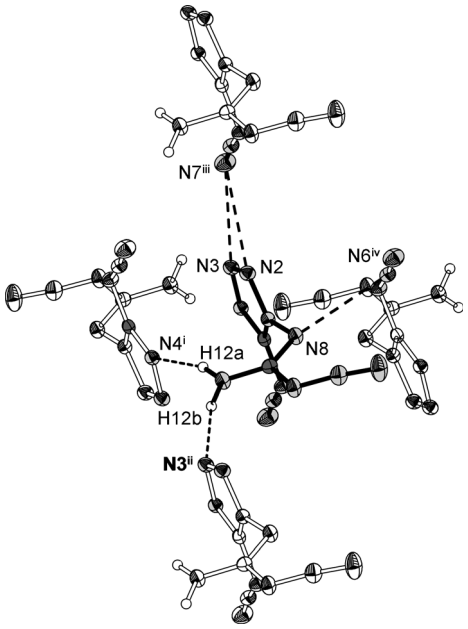

Figure 9. Hydrogen bonds and short contacts observed for **3**. Only the surrounding of the asymmetric unit is displayed; surrounding molecules are set transparent for clarity. Symmetry operators: i) $-x+1$, $-y+2$, $-z+1$; ii) x, $y-1$, z; iii) x, y, $z-1$; and iv) $-x$, $-y+2$, $-z+1$.

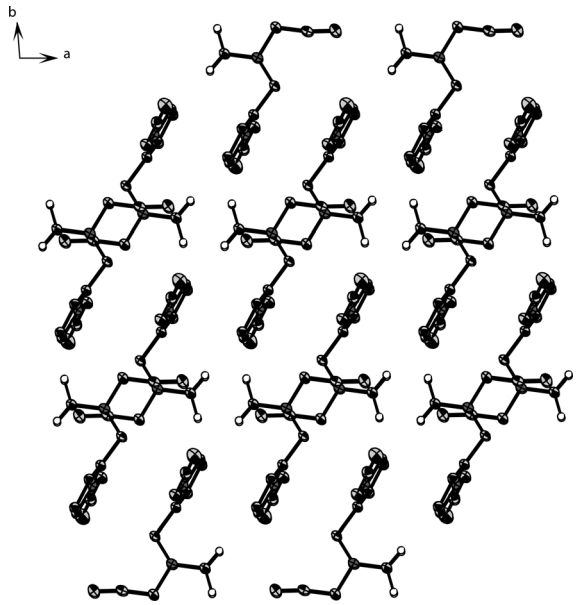

Figure 10. Presentation of the unit cell and the packing of **3** along the *c* axis. The aminoazidocarbamoyl moieties are coplanar to the *ab* plane.

Sensitivities and Thermal Stabilities

All three azidotetrazoles **1**–**3** have been investigated for their thermal stabilities and their sensitivities towards outer stimuli. Due to their behavior during the process of synthesis, it was obvious that the sensitivities will be not less than extreme, especially for compound **2**. The sensitivities have been measured using BAM (Bundesanstalt für Materialforschung und -prüfung) techniques,[23] as described in the Experimental Section. However, the sensitivity values of **1**–**3** were too high to be measured and hence are all smaller than 1 J in terms of impact and smaller than 5 N in terms of friction sensitivity (**1** and **3**). Compound **2** was initiated even without force being applied, only when touched with a spatula. Therefore the impact and friction sensitivities are assumed to be lower than 0.25 J and 1 N, respectively. All three compounds have to be considered extremely sensitive and proper safety precaution must be taken during synthesis and workup procedures!

Compound **2** is also sensitive towards laser irradiation. Several laser-induced explosions were observed during the RAMAN measurements of **2**. Compound **2** was initiated at a laser-energy impact of 150 mW after the first scan. Therefore, the spectra had to be recorded at minimum energies ($\approx$50 mW), thereby resulting in very bad signal-to-noise ratios. The decomposition temperatures of **1**–**3** increase with the loss of azide substituents: 124 °C for **2**, 136 °C for **3**, and 142 °C for **1**.

Additionally, theoretical calculations have been performed at the CBS-4M[24] level of theory to obtain heat of formation values of the compounds. These values have been used to calculate several detonation parameters of **1**–**3** with the EXPLO5 (version 5.04) code.[25] The calculated detonation parameters and also the sensitivities in comparison to those of the typical primary and secondary explosives 2,4,6-triazido-1,3,5-triazine (TAT) and hexogen (RDX) are listed in Table 3. Although the extremely high sensitivities of compound **2** probably will exclude any practical application, its calculated performance—for example, its calculated detonation velocity (V_{det}) of 8960 m s^{-1}—is much higher than that of the primary explosive TAT (V_{det} = 8288 m s^{-1}), which is currently under investigation as a "green" alternative to lead azide. Although compounds **1** and **3** exhibit slightly lower sensitivities than **2**, they are also extremely sensitive towards physical stimuli and together with their low thermal stability they seem to be unsuitable for most practical applications.

Table 3. Compiled sensitivity data and detonation parameters of **1**–**3** in comparison to RDX and TAT.[a]

Compd	IS [J]	FS [N]	ρ [g cm^{-3}]	ΔH_f^0(s) [kJ mol^{-1}]	Q_v [kJ kg^{-1}]	$P_{c\text{-}j}$ [kbar]	V_{det} [m s^{-1}]
1	<1	<5	1.70[b]	722	−5933	332	8983
2	<0.25	$\ll5$	1.723	1495	−6855	339	8960
3	<1	<5	1.675	1100	−5794	305	8655
RDX[c]	120	7	1.80	70	−6125	349	8748
TAT	<1	<5	1.736[d]	1053[e]	−5140	280	8288

[a] IS: Impact sensitivity; FS: friction sensitivity; ΔH_f^0: heat of formation; Q_v: heat of explosion; $P_{c\text{-}j}$: detonation pressure at the Chapman–Jouguet point; V_{det}: detonation velocity. [b] Estimated density for the anhydrous compound. [c] Values taken from Ref. [39]. [d] Values taken from Ref. [26]. [e] Values taken from Ref. [27].

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Conclusion

Three novel azidotetrazole compounds (**1**–**3**) have been prepared by diazotization reactions of triaminoguanidinium chloride, followed by ring-closure reactions with bases under various reaction conditions. All three compounds could only be synthesized in small yields, but were successfully separated by short-column chromatography with chloroform. The single-crystal X-ray structures of all three compounds were determined. Compounds **1**–**3** were also characterized by means of vibrational and multinuclear spectroscopy. A separation of the lines and bands in Raman and IR measurements, respectively, was observed for the azide stretching modes in **2** and **3**. Whereas two unique stretching modes were observed for **3**, three stretching modes were observed for compound **2** that represent azide groups with different chemical surroundings in the solid state. The same fact was also observed in the ^{14}N NMR spectra, in which a separation into two signals was observed for compounds **2** and **3** due to the possible free rotation of the carbamoyl moieties around the N1−N8 bond. Finally, the sensitivities of all three compounds have been measured. They are all extremely sensitive towards any form of manipulation such as friction and impact. Whereas **1** and **3** can be handled well with great care, compound **2** explodes under nearly any kind of conditions. Compound **2** exploded in solution as well as under radiation with a Nd:YAG laser (100–150 mW) when recording Raman spectra. The decomposition temperatures of **1**–**3** are in the range between 124 and 142 °C.

Experimental Section

Caution

All azidotetrazoles reported in this publication are sensitive towards friction, impact, and electrostatic discharge. Therefore proper safety precautions should be taken when handling these compounds. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs are recommended.

General

All chemical reagents and solvents were obtained from Sigma–Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied without further purification. ^{1}H, ^{13}C{^{1}H}, and ^{14}N NMR spectra were recorded with a JEOL Eclipse 400 instrument in [D$_6$]DMSO or $CDCl_3$ at 25 °C. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{14}N) as external standards. Infrared (IR) spectra were recorded with a Perkin–Elmer Spectrum BX FTIR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). Raman spectra were recorded with a Bruker RAM II spectrometer equipped with a Nd:YAG laser operating at 1064 nm and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum sample pans with a 1 μm hole in the top for gas release to avoid an unsafe increase in pressure under a nitrogen flow of 20 mL min^{-1} with an empty identical aluminum sample pan as a reference. Elemental analyses have not been performed due to the highly energetic nature of the compounds and in addition to avoid possible damage of the measurement equipment. The mass spectra were recorded with DEI and DCI methods on a JEOL MStation JMS 700 mass spectrometer. Silica was used for the short column chromatography as the stationary phase, whereas $CHCl_3$ was used as the eluent.

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489[28] modified according to WIWEB instruction 4-5.1.02[29] using a BAM[23] drop hammer. The friction sensitivity tests were carried out according to STANAG 4487[30] and modified according to WIWEB instruction 4-5.1.03[31] using the BAM friction tester. Electrostatic sensitivity tests were not performed due to the very high sensitivity and difficult handling of the compounds.

Crystallographic Measurements

The single-crystal X-ray diffraction data of **1**, **2**, and **3** were collected with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CRYSALIS CCD software,[32] whereas the data reduction was performed with the CRYSALIS RED software.[33] The structures were solved with SIR-92[34] or SHELXS-97[35] and refined with SHELXL-97[36] implemented in the program package WinGX[37] and finally checked using PLATON.[38] All structure figures are displayed with thermal ellipsoids at 50% probability.

CCDC-795273 (**1**), 693485 (**2**), and 693484 (**3**) 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.

*1-Amino-5-azidotetrazole (**1**)*

Triaminoguanidinium chloride (2 mmol, 0.282 g) was dissolved in water (30 mL) and hydrochloric acid (2 M, 2 mL) was added. The reaction was carried out at 0 °C (ice-bath cooling). A solution of sodium nitrite (4 mmol, 0.278 g) in water (30 mL) was added dropwise over a period of 20 min. After complete addition, the mixture was allowed to warm up and stirred for an additional 30 min. The temperature was raised to 50 °C and half an equivalent of sodium carbonate was added fast in one portion (caution: strong gas release!). The reaction mixture was stirred for an additional hour at ambient temperature and afterwards extracted three times with diethyl ether (50 mL). The combined organic extracts were allowed to evaporate until dryness to yield the raw product (51 mg). The raw material was cleaned with short-column chromatography by using chloroform as solvent to yield pure 1-amino-5-azidotetrazole monohydrate (32 mg, 11% yield) with compounds **2** (≈2.5%) and **3** (≈3%) as byproducts. R_f ($CHCl_3$) = 0.06; m.p. (decomp) 142 °C; ^{1}H NMR ($CDCl_3$): δ = 5.45 ppm (s, 2H; $-NH_2$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 151.4 ppm; ^{14}N NMR ($CDCl_3$): δ = −140 (br; N_γ), −147 ppm (N_β); IR: $\tilde{\nu}$ = 3332 (m), 3228 (m), 3162 (w), 2150 (vs), 1635 (m), 1531 (s), 1472 (m), 1404 (w), 1301 (m), 1272 (w), 1191 (m), 1118 (w), 1079 (w), 992 (w), 926 (w), 816 (w), 783 (w), 725 (w), 678 cm^{-1} (m); IR (Raman): $\tilde{\nu}$ = 3205 (18), 3154 (26), 2156 (63), 1648 (14), 1535 (100), 1475 (37), 1307 (38), 1272 (34), 1200 (14), 1115 (21), 1075 (37), 1045 (14), 820 (2), 730 (11), 691 (22), 581 (34), 543 (14), 400 (11), 314 cm^{-1} (37); MS (DEI+): *m*/*z* calcd (%): 127.08 (2) [M+H$^+$], 111.05 (2) [$M-NH_2^+$], 77.13 (2), 69.02 (100), 55.01 (72), 41.05 (100), 31.07 (48), 30.04 (79), 29.06 (100), 28.05 (75); sensitivities (anhydrous): IS: < 1 J; FS: < 5 N.

*5-Azido-1-diazidocarbamoyltetrazole (**2**)*

Triaminoguanidinium chloride (2 mmol, 0.282 g) was dissolved in water (30 mL) and hydrochloric acid (2 M, 2 mL) was added. The reaction was carried out at 0 °C (ice-bath cooling). A solution of sodium nitrite (4 mmol, 0.278 g) in water (30 mL) was added dropwise over a period of 20 min. After complete addition, the mixture was allowed to warm and was then stirred for an additional 30 min. Exactly one equivalent of a 0.1 M sodium hydroxide solution was added slowly (slightly orange color). Immediately afterwards, the reaction mixture was extracted three times with diethyl ether (50 mL). The combined organic fractions were allowed to evaporate until dryness to yield the raw product (0.058 g, 26%). The

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raw material was cleaned by short-column chromatography using chloroform as solvent yielding pure 5-azido-1-diazidocarbamoyltetrazole (0.036 g, 16%). R_f ($CHCl_3$) = 0.12; m.p. 78 °C; m.p. (decomp) 124 °C; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 160.4, 148.1 ppm (C_{Tet}); ^{14}N NMR ([D$_6$]DMSO): δ = −148 ppm (N_β); ^{14}N NMR ($CDCl_3$): δ = −145 (br; N_γ), −147 (N_β), −149 (N_β), −305 ppm (br; N_α); IR: $\tilde{\nu}$ = 3367 (m), 3314 (m), 3231 (m), 3190 (m), 2175 (vs), 2155 (vs), 2133 (vs), 1636 (s), 1578 (s), 1530 (s), 1456 (m), 1414 (s), 1290 (m), 1261 (m), 1213 (s), 1190 (s), 1106 (m), 1087 (m), 984 (w), 936 (w), 855 (w), 786 (w), 720 (w), 698 (w), 682 (w), 646 cm^{-1} (w); IR (Raman): $\tilde{\nu}$ = 3196 (12), 2179 (48), 2165 (33), 2133 (25), 1653 (15), 1573 (28), 1534 (100), 1454 (13), 1408 (27), 1386 (12), 1293 (34), 1266 (27), 1216 (18), 1189 (23), 1115 (13), 1092 (38), 936 (22), 857 (30), 598 (29), 522 (35), 395 (27), 297 cm^{-1} (37); MS (DEI+): *m/z* calcd (%): 221.1 [M+H$^+$]; sensitivities (anhydrous): IS: < 0.25 J; FS: ≪ 5 N.

*1-(Aminoazidocarbamoyl)-5-azidotetrazole (**3**)*

As in the preparation for C_2N_{14}, triaminoguanidinium chloride (2 mmol, 0.282 g) was dissolved in water (30 mL) and hydrochloric acid (2 M, 2 mL) was added. The reaction was carried out at 0 °C (ice-bath cooling). A solution of sodium nitrite (4 mmol, 0.278 g) in water (30 mL) was added dropwise over the course of 20 min. After the addition, the mixture was allowed to warm and stirred for an additional 30 min. Then a 0.1 M sodium hydroxide solution (1.0 equiv) was added slowly (slightly orange color) over 1.5 h, and the reaction mixture was extracted four times with diethyl ether (50 mL each time) afterwards. The combined organic extracts were allowed to evaporate to dryness to yield between 0.04 and 0.065 g as a raw product. Two products could be separated by short-column chromatography using chloroform. At an R_f value of 0.22, 1-(amino-azidocarbamoyl)-5-azidotetrazole was isolated with yields between 10% (0.02 g) and 23% (0.045 g), whereas at an R_f value of 0.12, 5-azido-1-diazidocarbamoyltetrazole was isolated in yields between 5% (0.012 g) and 14% (0.03 g). The product ratio could not be verified exactly. In successive attempts different ratios were obtained. R_f ($CHCl_3$) = 0.22; m.p. (decomp) 136 °C; ^1H NMR ($CDCl_3$): δ = 5.35 ppm (−NH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 157.9, 148.2 ppm (C_{Tet}); ^{14}N NMR ($CDCl_3$): δ = −138 (br; N_γ), −148 (N_β), −152 ppm (N_β); IR: $\tilde{\nu}$ = 3278 (vw), 2327 (vw), 2257 (w), 2164 (vs), 2152 (vs), 1584 (s), 1573 (m), 1559 (w), 1521 (s), 1448 (w), 1330 (s), 1313 (s), 127 (s), 1260 (m), 1201 (m), 1126 (w), 1105 (m), 1084 (m), 1018 (w), 978 (w), 928 (w), 799 (w), 776 (w), 719 (w), 702 (w), 674 (w), 642 cm^{-1} (w); Raman: $\tilde{\nu}$ = 2170 (94), 2157 (37), 2128 (12), 1585 (100), 1580 (44), 1534 (48), 1526 (42), 1451 (13), 133 (15), 1317 (14), 1288 (41), 1261 (23), 1206 (16), 1186 (24), 1129 (10), 1108 (16), 1086 (41), 930 (14), 823 (17), 778 (8), 722 (9), 703 (14), 676 (12), 644 (12), 590 (16), 533 (5), 494 (13), 452 (22), 394 (13), 359 (18), 305 cm^{-1} (26); MS (DEI+): *m/z* calcd (%): 195.2 [M+H$^+$]; sensitivities (anhydrous): IS: < 1 J; FS: < 5 N.

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