

Energetic Materials

New Energetic Polynitrotetrazoles

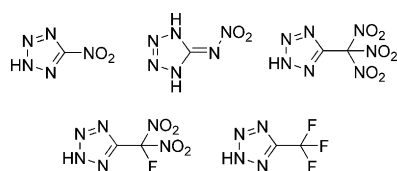
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Abstract: This combined experimental, theoretical and comparative study details the syntheses and chemical characterisation of two new energetic polynitromethyl tetrazole derivatives, namely, 2-(2-nitro-2-azapropyl)-5-(trinitromethyl)-2*H*-tetrazole and its fluorine-containing analogue 2-(2-nitro-2-azapropyl)-5-(fluorodinitromethyl)-2*H*-tetrazole.

Their crystal structures and energetic behaviour are compared to those of their starting materials, the ammonium salts of the corresponding 5-(polynitromethyl)-2*H*-tetrazoles. Additionally, the crystal structures of two further related polynitrotetrazoles are presented.

Introduction

Polynitroazoles are important and common compounds in energetic materials research.^[1] The design of new materials includes strategies based on tetrazoles,^[2] triazoles,^[3] furazanes,^[4] N-oxides,^[5] furoxanes^[6] and tetrazines.^[7] Their high nitrogen contents lead to large amounts of N₂ during combustion causing high detonation velocities and pressures.^[1] Tetrazole derivatives are of special interest owing to the highest nitrogen content of these five-membered heterocycles (Scheme 1). 5-substituted tetrazoles are easily accessible



Scheme 1. Some examples of five-substituted polynitromethyl- and polyfluoromethyl-tetrazole derivatives.

through treatment of organic nitriles with sodium azide.^[8] Several derivatives with oxygen-containing moieties such as nitro groups, nitrate esters or nitramines at the 5-position were investigated within our group and are suitable for various energetic applications. For instance, derivatives of 5-nitro-^[9] and 5-nitriminotetrazoles^[10] for gas-generating applications, or ener-

getic polymers based on tetrazoles.^[11] Moreover tetrazole derivatives with perfluorinated alkyl groups were investigated as ingredients in MTV (magnesium, teflon, viton) decoy flares.^[12]

The trinitromethyl and fluorodinitromethyl functionalities have proven to be useful functional groups in the synthesis of high-performing explosives as well as novel oxidisers for high-tech propellants.^[13] The combined high nitrogen and oxygen contents of this group allow full oxidation of fuels within the molecule leading to high performances. Additionally, the large dipole moment within the nitro and fluorine groups gives rise to extensive inter- and intramolecular interactions resulting in high densities, which also affect the performance advantageously.^[14]

The syntheses of 5-trinitromethyl- and 5-fluorodinitromethyl-2*H*-tetrazole and some of their salts were first published in 1981 by Grakauskas et al.^[15] and Fokin et al.,^[16] respectively. They used the corresponding polynitroacetonitriles^[17] for the 1,3-dipolar ring-closure reaction with trimethylsilyl azide or sodium azide. However, all starting materials are hazardous chemicals. A more convenient and "greener" route to the trinitromethyl derivative was introduced by Christe and Haiges in 2013 by decarboxylative nitration of the corresponding methyl carboxylic acid furnishing high yields.^[18] Owing to their high oxygen content these compounds can be considered as solid oxygen carriers in solid rocket propellants, replacing or partially replacing currently used ammonium perchlorate (AP).^[11] AP has been identified as toxic to humans thyroid gland^[19] and amphibians.^[20] Additionally, the decomposition product hydrogen chloride, which is produced in large amounts during a rocket launch, is environmentally critical.^[21] This visible and detectable expulsion affects guidance systems adversely, and is also unfavourable for tactical missiles.^[22]

However, the very high mechanical sensitivities of 5-trinitromethyl- and 5-fluorodinitromethyl-2*H*-tetrazole and their salts make these compounds inoperable concerning agitation and processing of propellant formulations. The alkylation described in this work was carried out to overcome some problematic issues of the known polynitromethyl tetrazole derivatives:

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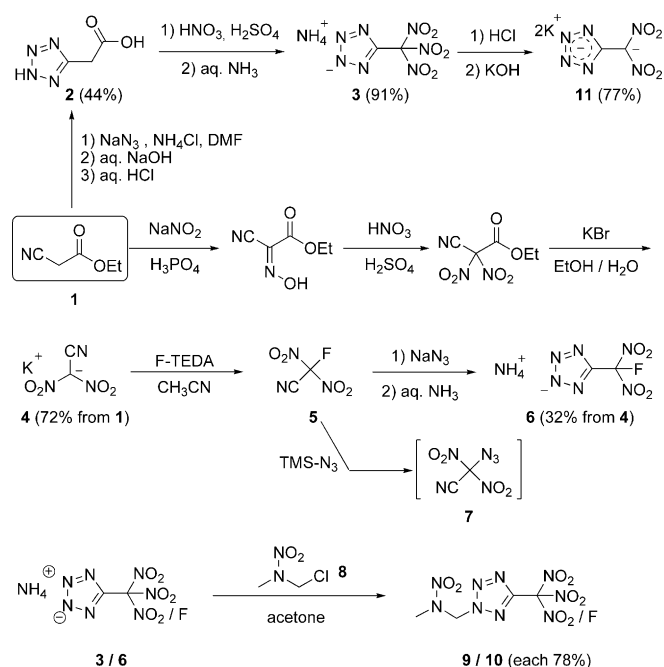
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1) the acidities associated with cyclic nitroazoles, 2) their low thermal stabilities and 3) their very high sensitivities towards impact and friction. As known from other 5-substituted tetrazole derivatives the methylation can significantly lower the sensitivities.^[9,10] However, to maintain the energetic character and by trying to keep the oxygen balance as high as possible, the secondary nitramine moiety was chosen to be incorporated to these tetrazoles.^[23]

Results and Discussion

Syntheses

All syntheses described in this work start from commercially available ethyl 2-cyanoacetate (**1**) (Scheme 2). Ammonium 5-(trinitromethyl)-2*H*-tetrazolate (**3**) was synthesised according to the literature-known procedure by decarboxylative nitration of ethyl 2-(1*H*-tetrazol-5-yl)acetate (**2**) furnishing high yields.^[18,24,25]



Scheme 2. All syntheses described in this work started from ethyl 2-cyanoacetate (**1**). 1,3-Dipolar ring-closure and saponification yielding compound **2** were carried out according to references [24] and [25]. The nitration yielding compound **3** was performed according to reference [18]. The synthesis of compound **4** from compound **1** was carried out according to references [26]–[28]. Synthesis of compound **5** was performed with Selectfluor (F-TEDA) in acetonitrile without isolation, and subsequent 1,3-dipolar ring closure yielding compound **6** was carried out according to reference [16]. Syntheses of compounds **9** and **10** were performed in anhydrous acetone. TMS = trimethylsilyl.

Ammonium 5-(fluorodinitromethyl)-2*H*-tetrazolate (**6**) was synthesised according to a slightly modified literature procedure from potassium dinitroacetone (**4**).^[16,26–28] Differing from the literature the fluorination of potassium dinitroacetone (**4**) was performed with Selectfluor (instead of 25% F₂ in

He) in anhydrous acetonitrile at ambient temperature in a closed vessel. Fluorodinitroacetone (**5**)^[17] was not isolated due to its high volatility. When the reaction mixture turned colourless, the solution containing compound **5** was distilled into a cooling trap (−78 °C) and compound **5** was identified by multinuclear NMR measurements from the acetonitrile solution. Subsequently, sodium azide was added to the solution and the reaction mixture was stirred at ambient temperature in a closed vessel.^[16] The progress of the 1,3-dipolar ring-closure reaction was monitored by ¹⁹F NMR spectroscopy. After an acidic workup and treatment with aqueous ammonia (25%) ammonium 5-(fluorodinitromethyl)-2*H*-tetrazolate (**6**) was isolated in acceptable yields of 32% (two steps from compound **4**). If trimethylsilyl azide is used instead of sodium azide as known from the literature,^[15] with heating the risk of the formation of undesired side products including azidodinitroacetone (**7**) is given. In fact, ¹⁹F NMR experiments out of this reaction mixture confirmed the generation of more than three species even without heating, and ring closing reactions were continued with sodium azide. The alkylation reactions of compounds **3** and **6** were performed with 2-nitro-2-azapropyl chloride (**8**)^[29] in anhydrous acetone, furnishing the according 2-(2-nitro-2-azapropyl)-5-(polynitromethyl)-2*H*-tetrazoles **9** and **10** as colourless crystalline solids in good yields of 78% each. Compounds **3** and **6** were alkylated exclusively in the β-position of the tetrazole ring. During the work with compound **3** also crystals of dipotassium 5-(dinitromethylidene)-tetrazolate (**11**)^[30] were isolated from the reaction of compound **3** with concentrated aqueous potassium hydroxide solution. The conversion of compound **3** with aqueous hydroxylamine and hydrazine to the corresponding dinitromethylidene salts has been reported previously.^[18]

NMR spectroscopy

Compounds **6** and **9–11** were investigated by multinuclear NMR spectroscopy in [D₆]acetone (Table 1). The chemical shifts of the methyl and methylene groups in compounds **9** and **10** are observed in the expected ranges of δ = 3.69 and 6.98 ppm in the ¹H NMR spectrum, and at δ = 38.6 and 67.5 ppm in the ¹³C NMR spectrum. The ¹³C signals of the tetrazole carbon atoms are shifted to δ = 152.3 ppm for compound **9**, to δ = 150.8 ppm for compound **6** with a ²J(C,F) coupling constant of

Table 1. Chemical shifts δ [ppm] of compounds **6** and **9–11**.

Nucleus	Assignment	6	9	10	11
¹ H	CH ₃	–	3.70	3.68	–
	CH ₂	–	7.00	6.96	–
¹³ C	CH ₃	–	38.6	38.6	–
	CH ₂	–	67.6	67.3	–
	C(NO ₂) _n F _m ^[a]	119.9 (d) ^[b]	121.2	115.4 (d)	128.5
	C _{Tz}	150.8 (d)	152.3	153.7 (d)	155.2
¹⁴ N	NNO ₂	–	–33	–32	–
	CNO ₂	–20.6(d) ^[c]	–37	–27 (d)	–23
¹⁹ F	CF	–95.5	–	–99.6	–

[a] n = 2, 3; m = 0, 1. [b] d = doublet. [c] * = ¹⁵N NMR spectroscopy.

23.0 Hz and to $\delta = 153.7$ ppm for compound **10** with a $^2J(\text{C},\text{F})$ coupling constant of 25.4 Hz. The signals of the polynitro carbon atoms are shifted to $\delta = 121.2$ ppm for compound **9**, to $\delta = 119.9$ ppm for compound **6** with a $^1J(\text{C},\text{F})$ coupling constant of 284.7 Hz and to 115.4 ppm for compound **10** with a $^1J(\text{C},\text{F})$ coupling constant of 282.9 Hz.^[31] Compound **11** was identified on the basis of the literature-known ^{13}C NMR chemical shifts.^[30] In the ^{14}N NMR spectra the signals of the nitro groups at the nitramine moiety are observed at $\delta = -33$ ppm for compound **9** and at $\delta = -32$ ppm for compound **10**. The signals of the polynitro groups are shifted to $\delta = -37$ ppm for compound **9** and to $\delta = -27$ ppm for compound **10** with a $^2J(\text{C},\text{F})$ coupling constant of 10 Hz.^[32]

For compound **6** a ^{15}N NMR spectrum was recorded. It shows the signal for the fluorodinitro group shifted to $\delta = -20.6$ ppm as a doublet ($^2J(^{15}\text{N},\text{F}) = 16.5$ Hz), and additionally the signals for the nitrogen atoms of the tetrazole ring ($\delta(\text{N}_\alpha) = 9.6$, $\delta(\text{N}_\beta) = -57.5$ ppm). The nitrogen NMR signal of the ammonium cation is found at $\delta = -362.2$ ppm. In the ^{19}F NMR spectrum the fluorine signal of compound **6** is observed at $\delta = -95.5$ and the signal of compound **10** is found at $\delta = -99.6$ ppm, both as broad singlets indicating multiplets.

The intermediate fluorodinitroacetonitrile (**5**), which was not isolated, was identified by ^{14}N and ^{19}F NMR spectroscopy from the acetonitrile solution (Figure 1). The ^{14}N NMR spectrum

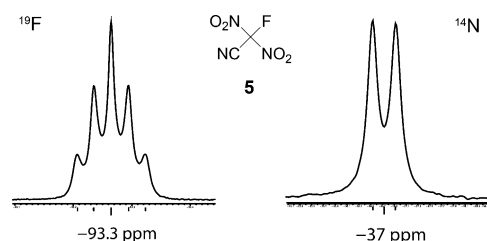


Figure 1. NMR spectra of compound **5**. Left) ^{19}F NMR spectrum, $^2J(\text{F},^{14}\text{N}) = 11$ Hz. Right) ^{14}N NMR spectrum, $^2J(^{14}\text{N},\text{F}) = 11$ Hz.

shows the signal of the two nitro groups at $\delta = -37$ ppm as a doublet due to a $^2J(^{14}\text{N},\text{F})$ coupling of 11 Hz. In the ^{19}F NMR spectrum the signal is observed at $\delta = -93.3$ ppm, splitted into a quintet due to coupling with two ^{14}N nuclei ($^2J(\text{F},^{14}\text{N}) = 11$ Hz).

Vibrational spectroscopy

Compounds **9** and **10** were also investigated by IR and Raman spectroscopy (Table 2).^[33] The IR spectrum of compound **9** shows the stretching vibrations of the CH_2/CH_3 groups in the range of $\tilde{\nu} = 3068\text{--}2883$ cm^{-1} . The absorption bands in the range of $\tilde{\nu} = 1468\text{--}1420$ cm^{-1} can be attributed to the deformation vibrations of the CH_2/CH_3 groups. At $\tilde{\nu} = 1540$ and 1258 cm^{-1} the asymmetric and symmetric stretching vibrations of the trinitromethyl moiety are observed. The nitramine unit shows the asymmetric stretching vibration at $\tilde{\nu} = 1598$ cm^{-1} and the symmetric stretching vibration at $\tilde{\nu} = 1299$ cm^{-1} . The

Vibration	9		10	
	IR	Raman	IR	Raman
$\nu(\text{CH}_2/\text{CH}_3)$	3068	3069	3050	3051
	3007	3008	3004	3004
	2883	2890	2966	2970
$\delta(\text{CH}_2)$	1468	1421	1460	1466
	1447		1427	1436
	1420			
$\nu_{\text{as}}(\text{NO}_2)$	1540	1540	1536	1552
$\nu_{\text{s}}(\text{NO}_2)$	1258	1260	1260	1276
$\nu_{\text{as}}(\text{N}\text{--}\text{NO}_2)$	1598	1607	1595	1590
$\nu_{\text{s}}(\text{N}\text{--}\text{NO}_2)$	1299	1304	1304	1304
$\nu(\text{C}\text{--}\text{F})$	–	–	1260	1276
$\nu(\text{C}=\text{N})$	–	1487	–	1503

Raman spectrum additionally shows the stretching vibration of the $\text{C}=\text{N}$ bond at $\tilde{\nu} = 1487$ cm^{-1} .

The IR spectrum of compound **10** displays the stretching vibrations of the CH_2/CH_3 groups in the range of $\tilde{\nu} = 3050\text{--}2966$ cm^{-1} . The absorption bands in the range of $\tilde{\nu} = 1460\text{--}1427$ cm^{-1} can be assigned to the deformation vibrations of the CH_2/CH_3 groups. At $\tilde{\nu} = 1536$ and 1260 cm^{-1} the asymmetric and symmetric stretching vibrations of the nitro groups in the fluorodinitromethyl moiety can be observed. The nitramine moiety shows the asymmetric stretching vibration at $\tilde{\nu} = 1595$ cm^{-1} and the symmetric stretching vibration at $\tilde{\nu} = 1304$ cm^{-1} . The $\text{C}\text{--}\text{F}$ stretching vibration is observed at $\tilde{\nu} = 1260$ cm^{-1} . The Raman spectrum additionally shows the stretching vibration of the $\text{C}=\text{N}$ bond at $\tilde{\nu} = 1503$ cm^{-1} .

X-ray diffraction

Single crystals suitable for low-temperature X-ray diffraction measurements were obtained from a toluene/ethyl acetate (1:1) mixture for compound **6**, and from a methanol/dichloromethane (1:1) mixture for compounds **9** and **10**. Compound **11** crystallised from an aqueous KOH solution. All relevant crystallographic and structural refinement data are listed in Table 3.

Ammonium 5-(fluorodinitromethyl)-2H-tetrazolate (**6**) crystallises in the monoclinic space group $P2_1/c$ with eight formulas per unit cell and a calculated maximum density of 1.747 g cm^{-3} at 113 K (Figure 2). The structure displays two crystallographically independent 5-(fluorodinitromethyl)-2H-tetrazolate anions and ammonium cations in the asymmetric unit. In the anions the $\text{C}\text{--}\text{F}$ bond lengths are slightly shorter than the common single $\text{C}\text{--}\text{F}$ bond length (1.36 Å). The $\text{C}\text{--}\text{NO}_2$ bond lengths are elongated as compared to the average value of a single $\text{C}\text{--}\text{N}$ bond length (1.47 Å).^[34]

The average $\text{N}\text{--}\text{O}$ bond lengths and $\text{O}\text{--}\text{N}\text{--}\text{O}$ angles are in the range of common nitro groups.^[34] The $\text{C}\text{--}\text{C}$ bond lengths are in between the common single (1.54 Å) and double bond (1.33 Å).^[34] The bond lengths and angles within the five-membered rings are in the expected range.^[18] It is remarkable that the $\text{C}\text{--}\text{C}\text{--}\text{N}\text{--}\text{O}$ torsion angles of both molecules ($\text{C}2\text{--}\text{C}1\text{--}\text{N}1\text{--}\text{O}3$ $-72.4(1)^\circ$, $\text{C}2\text{--}\text{C}1\text{--}\text{N}2\text{--}\text{O}1$ $3.3(1)^\circ$, $\text{C}4\text{--}\text{C}3\text{--}\text{N}8\text{--}\text{O}7$ $71.8(2)^\circ$, $\text{C}4\text{--}\text{C}3\text{--}$

Table 3. Crystallographic data of compounds **6** and **9–11**.

Compound	6	9	10	11
sum formula	C ₂ H ₄ N ₇ O ₄ F	C ₄ H ₅ N ₉ O ₈	C ₄ H ₅ N ₉ O ₆ F	K ₂ C ₂ N ₆ O ₄
formula weight [g cm ⁻³]	209.10	307.17	280.13	250.28
crystal dimensions [mm ³]	0.30×0.10×0.05	0.40×0.19×0.08	0.30×0.16×0.09	0.40×0.06×0.05
crystal description	colourless needles	colourless plates	colourless needles	yellow rods
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	<i>P2₁/n</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>Pbcn</i>
<i>a</i> [Å]	14.0080(7)	5.9400(5)	5.8497(3)	9.1698(3)
<i>b</i> [Å]	8.9900(7)	18.6730(13)	15.2996(8)	9.0743(3)
<i>c</i> [Å]	13.9790(4)	20.4840(13)	11.1992(5)	9.2617(4)
α and γ [°]	90.0	90.0	90.0	90.0
β [°]	115.397(8)	90.0	97.003(4)	90.0
<i>V</i> [Å ³]	1590.27(15)	2272.0(3)	994.83(8)	770.66(5)
<i>Z</i>	8	8	4	4
ρ_{calcd} [g cm ⁻³]	1.747	1.796	1.870	2.157
μ [mm ⁻¹]	0.173	0.171	0.182	1.230
<i>F</i> (000)	848	1248	568	496
temperature [K]	113(2)	100(2)	100(2)	100(2)
θ range [°]	4.12–25.50	4.11–26.00	4.15–26.00	4.40–25.98
index ranges	–16 ≤ <i>h</i> ≤ 16 –10 ≤ <i>k</i> ≤ 10 –16 ≤ <i>l</i> ≤ 16	–7 ≤ <i>h</i> ≤ 6 –23 ≤ <i>k</i> ≤ 23 –25 ≤ <i>l</i> ≤ 25	–7 ≤ <i>h</i> ≤ 7 –18 ≤ <i>k</i> ≤ 18 –13 ≤ <i>l</i> ≤ 12	–7 ≤ <i>h</i> ≤ 11 –11 ≤ <i>k</i> ≤ 11 –11 ≤ <i>l</i> ≤ 11
reflections measured	13 072	16 301	7 248	3 577
reflections independent	2 915	2 205	1 933	749
reflections unique	2 485	1 762	1 658	651
<i>R</i> _{int}	0.0325	0.0510	0.0231	0.0271
<i>R</i> ₁ , <i>wR</i> ₂ (2 σ data)	0.0280, 0.0600	0.0368, 0.0857	0.0270, 0.0613	0.0218, 0.0486
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0359, 0.0639	0.0502, 0.0938	0.0338, 0.0651	0.0284, 0.0517
data/restraints/parameters	2 915/0/285	2 205/0/210	1 933/0/192	749/0/65
GoF on <i>F</i> ²	1.026	1.038	1.035	1.098
residual electron density	–0.179/0.271	–0.160/0.239	–0.215/0.314	–0.239/0.351
weighting scheme ^[a]	0.0312, 0.5670	0.0460, 0.6430	0.0282, 0.3097	0.0195, 0.3762

[a] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2))]^{1/2}$ where $w = [(\sigma_c(F_o^2) + (\chi P)^2 + \gamma P)]$ and $P = (F_o^2 + 2F_c^2) / 3$.

N7–O6 –15.6(2)°) are not in the typical range for the propeller-like conformation of polynitromethyl moieties (23–67°) described by Brill et al.,^[35] but the nitro groups are rotated *syn*. However, this orientation results in intramolecular interactions with N...O, F...O and F...N distances well below the sum of the van der Waals radii as depicted in Figure 3.^[36]

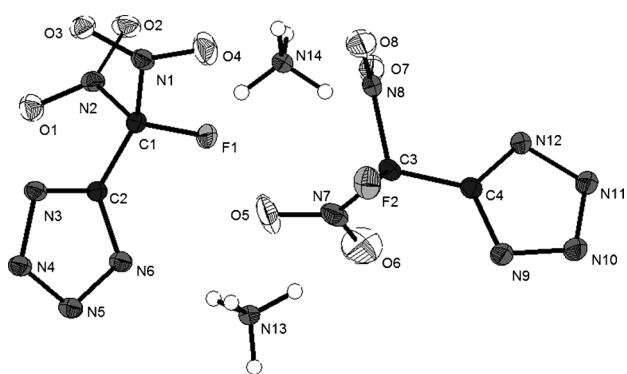


Figure 2. Asymmetric unit in the crystal structure of compound **6**. Selected bond lengths [Å] and angles [°]: N1–O3 1.219 (2), N1–O4 1.210 (2), N2–O1 1.208(2), N2–O2 1.227(2), C1–C2 1.481(3), C3–C4 1.478(2), C1–F1 1.337(2), C3–F2 1.328(3), C1–N1 1.539(2), C1–N2 1.544(2), C2–N3 1.334(2), C2–N6 1.335(2), N3–N4 1.343(2), N4–N5 1.323(1), N5–N6 1.342(2); O1–N2–O2 127.7(1), O3–N1–O4 127.5(1), O1–N2–C1 117.4(1), O2–N2–C1 115.1(1), N1–C1–F1 108.0(1), N2–C1–F1 105.6(1), N1–C1–N2 103.6(1), F1–C1–C2 113.3(1), N3–C2–C1 124.7(1), N4–N5–N6–C2 0.0(1).

The solid state structure of compound **6** consists of ammonium cations and 5-(fluorodinitromethyl)-2*H*-tetrazolate anions that are associated through classical hydrogen bonds (Figure 4). They are observed between N13 and N3 (N13–H3 0.93(2) Å, H3...N3 2.02(2) Å, N13...N3 2.918(3) Å, N13–H3...N3 164.1(1)°), and between N14 and O2 (N14–H8 0.89(2) Å, H8...O2 2.82(2) Å, N14...O2 3.189(3) Å, N14–H8...O2 106.8(1)°). In addition typical electrostatic interactions between the nitro groups are observed (Figure 4). The N2...O1(i) short contact (3.029(2) Å) between the nitro groups is slightly under the sum of the van der Waals radii ($\Sigma(\text{van der Waals radii})$: O...N 3.07 Å).^[36] The fluorine atoms also form intermolecular short contacts with distances below the van der Waals radii (F1...O5 2.870(2) Å, F2...O2ⁱ 2.853(3) Å; symmetry operator ⁱ = *x*, 1/2–*y*, –1/2+*z*; $\Sigma(\text{van der Waals radii})$: O...F 2.99 Å).^[36]

2-(2-Nitro-2-azapropyl)-5-(trinitromethyl)-2*H*-tetrazole (**9**) crystallises in the orthorhombic space group *Pbca* with eight molecules in the unit cell and a calculated maximum density of 1.796 g cm⁻³ at 100 K (Figure 5).

The C1–C2 bond length with 1.488(2) Å is shorter than a common C–C single bond (1.54 Å).^[34] The C2–N bonds to the nitro groups are slightly elongated (1.523–1.544 Å). The N–O bond lengths of all nitro groups are in the expected range (1.208–1.227 Å). The trinitromethyl group arranges into the typical propeller-like orientation as found in many trinitromethyl-containing compounds with intramolecular short contacts

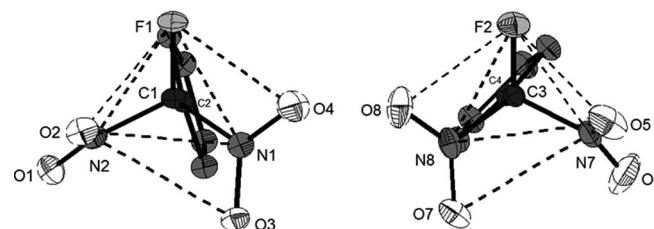


Figure 3. Views along the C1–C2 (left) and C3–C4 (right) bonds of compound **6** illustrating the geometry of the fluorodinitromethyl groups with its intramolecular interactions (dashed lines): F1...O2 2.637(2), F1...O4 2.544(2), F2...O5 2.567(2), F2...O8 2.517 Å, F1...N1 2.329(2), F1...N2 2.298(2) Å, F2...N7 2.301(2), F2...N8 2.320(2) Å, N1...O2 2.796(2), N2...O3 2.683(2), N7...O7 2.694(3), N8...O5 2.901(3) Å. $\Sigma(\text{van der Waals radii})$: F...O 2.99 Å, N...O 3.07 Å, F...N 3.02 Å.^[36]

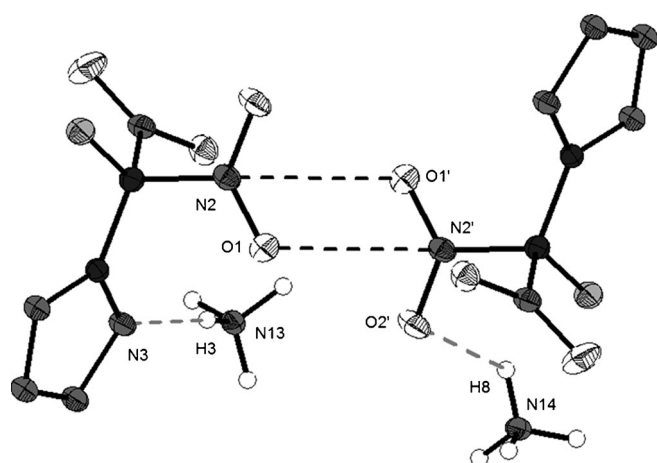


Figure 4. Hydrogen bonds (gray dashed lines) and electrostatic interactions (black dashed lines) in the crystal structure of compound **6**. Symmetry operator: $' = x, 1 - y, 1 - z$.

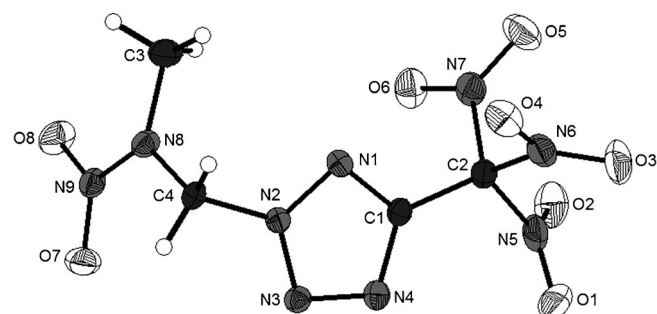


Figure 5. Molecular structure of compound **9** in the crystal. Selected bond lengths [Å] and angles [°]: C1–C2 1.488(2), N5–C2 1.523(2), N6–C2 1.538(2), N7–C2 1.544(2), O1–N5 1.208(1), O3–N6 1.213(2), O6–N7 1.210(2), N3–N4 1.316(2) N8–N9 1.366(2), O7–N9 1.227(2); N2–C4 1.471(2); O4–N6–O3 127.7(2), C4–N8–C3 122.5(2), C4–N8–N9–O7 -6.9(2), O1–N5–C2–C1 62.4(2), O4–N6–C2–C1 40.8(2), O6–N7–C2–C1 39.2(2).

well below the sum of the van der Waals radii.^[37,38] This is also reflected in the torsion angles (O1–N5–C2–C1 62.4(2)°, O4–N6–C2–C1 40.8(2)°, O6–N7–C2–C1 39.2(2)°), which are in the range for this propeller-like structure of polynitromethyl moieties described by Brill et al. (23–67°).^[35,37,38] The structure is mainly build up by multiple hydrogen bonds, whereby all hydrogen atoms participate and connect one molecule to six of its neighbours (Table 4, Figure 6).

Table 4. Structural parameters of the hydrogen bonds in the crystal of compound **9** presented in Figure 6.^[a]

D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D–H...A) [Å]	\angle (D–H...A) [°]
C3–H31...O8'	0.95(2)	2.54(2)	3.479(3)	167.3(9)
C4–H41...O7'	0.95(2)	2.50(2)	3.348(2)	149.5(5)
C3–H33...O8''	0.94(2)	2.58(2)	3.307(3)	133.6(8)
C3–H32...O6'''	0.95(3)	2.57(2)	3.501(2)	167.1(1)
C4–H42...O7''''	0.94(2)	2.39(2)	3.084(3)	130.7(5)

[a] Symmetry operators: $' = -1 + x, y, z$; $'' = -\frac{1}{2} + x, \frac{1}{2} - y, -z$; $''' = 1 - x, -y, -z$; $'''' = -\frac{1}{2} + x, y, \frac{1}{2} - z$.

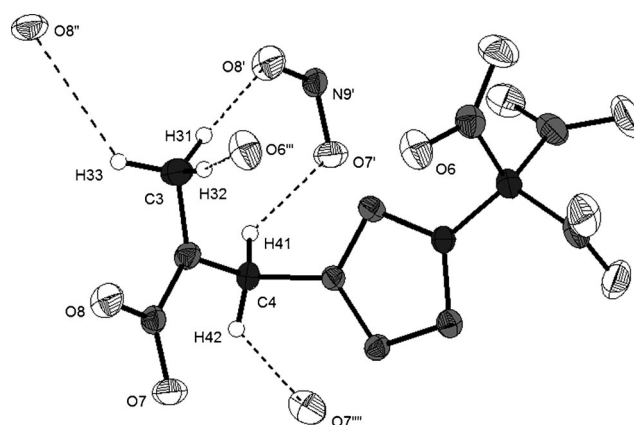


Figure 6. Strong hydrogen bonds presented by dashed lines in the crystal structure of compound **9** for the structural parameters given in Table 4.

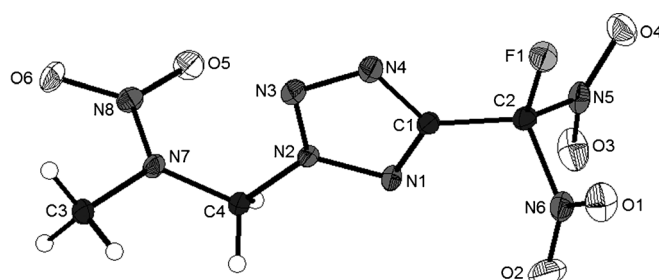


Figure 7. Molecular structure of compound **10** in the crystal. Selected bond lengths [Å] and angles [°]: C1–C2 1.492(2), F1–C2 1.313(2), N6–C2 1.557(2), N5–C2 1.551(2), N7–N8 1.363(1), N3–N4 1.321(2), O3–N5 1.208(2), O2–N6 1.210(2), O5–N8 1.234(1), N7–C3 1.461(2), N2–C4 1.486(2); O4–N5–O3 127.7(1), C4–N7–C3 123.0(1), C4–N7–N8 116.6(1), N4–C1–C2–F1 0.4(1), C1–C2–N6–O2 53.6(2), O3–N5–C2–C1 59.9(1).

2-(2-Nitro-2-azapropyl)-5-(fluorodinitromethyl)-2*H*-tetrazole (**10**) crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell and a calculated maximum density of 1.870 g cm⁻³ at 100 K (Figure 7).

The C1–C2 bond is shorter than a common C–C single bond (1.54 Å)^[34] but with 1.492(2) Å it is slightly elongated in comparison to the corresponding bond in the analogous compound **9**. The C2–F1 bond is slightly shorter (1.313(2) Å) than common C–F bonds (1.36 Å).^[34] The C2–N bonds to the nitro groups are elongated (1.551(2) and 1.557(2) Å). The N–O bond lengths of the nitro groups (1.208–1.212 Å) are between those of common single and double N–O bonds (1.45 and 1.17 Å, respectively).^[34] Differing from the starting material **6** the orientation of the fluorodinitromethyl moiety shows the propeller-like conformation, here with C1–C2–N–O torsion angles (C1–C2–N5–O3 -59.9(2)°, C1–C2–N6–O2 53.6(1)°) in the typical range for the propeller-like structure (23–67°) as described by Brill et al.^[35] The fluorine atom strongly stabilises this orientation by interacting with the oxygen and the nitrogen atoms of the nitro groups. Also the N...O distances between the nitro groups are clearly under the Σ (van der Waals radii) (dashed lines in Figure 8).^[36]

The structure of compound **10** is build up by extensive hydrogen bonding. Similar to compound **9** all hydrogen

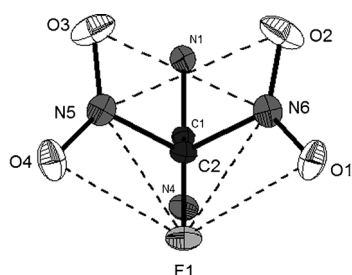


Figure 8. View along the C2–C1 bond of compound **10** illustrating the geometry of the fluorodinitromethyl group with its intramolecular interactions: F1...O4 2.480(1), F1...O1 2.481(1) Å, F1...N5 2.315(1), F1...N6 2.315(2) Å, N5...O2 2.941(1), N6...O3 2.883(1) Å. Σ (van der Waals radii): F...O 2.99, F...N 3.02, N...O 3.07 Å.^[36]

atoms participate in those hydrogen bonds and connect one molecule to eight of its neighbours (Table 5, Figure 9). Differing from compound **9** the tetrazole rings are arranged parallel to each other.

Dipotassium 5-(dinitromethylide)-tetrazolate (**11**) crystallises as yellow rods in the orthorhombic space group *Pbcn* with four formulas per unit cell and a calculated maximum density of 2.157 g cm⁻³ at 100 K (Figure 10). To the best of our knowledge, only the structure of the monopotassium salt is known so far,^[18] which mainly differs in the orientation of the dinitromethyl group relative to the five-membered ring. Whereas in the monopotassium salt the anion is almost planar with a C1–

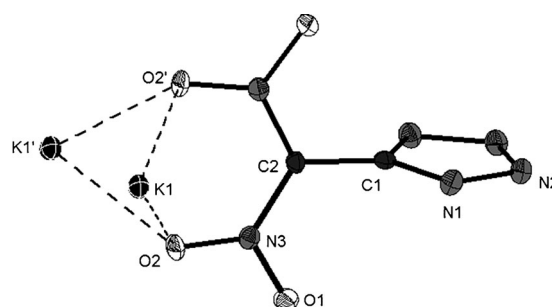


Figure 10. Molecular structure of compound **11** in the crystal. Selected atom distances [Å], bond lengths [Å] and angles [°]: K1...O2 2.997(2), K1...O2' 2.903(2); C1–C2 1.463(4), C1–N1 1.337(2), N1–N2 1.344(3), C2–N3 1.384(1), N3–O1 1.264(2), N3–O2 1.250(1); O2–K1–O2' 52.08(2), K1–O2–K1' 100.98(3), O1–N3–O2 120.2(1), O2–N3–C2 123.4(1), O1–N3–C2 116.4(2), N3–C2–N3' 120.8(1), O1–N3–C2 116.4(1), N1–C1–N1' 111.9(1), N1–C1–C2–N3' 93.5(2), N1–C1–C2–N3 –86.5(2). Symmetry operator ' = 1/2–x, –1/2+y, z.

C2 bond length of 1.449(1) Å,^[18] in the structure of compound **11** the dinitromethyl moiety is rotated out of the tetrazole plane with a torsion angle of N1–C1–C2–N3' = 93.5(2)° and a C1–C2 bond length of 1.463(4) Å. This indicates, that the negative charge of the dinitromethyl group is not delocalised into the tetrazole ring. The C1–C2 bond length in the structure of the free acid dihydro-(dinitromethylene)-tetrazole is even shorter with 1.418(2) Å and the molecule is completely planar.^[39]

The crystal structure is mainly build up by one repetitive motif illustrated in Figure 11. It forms chains along the *b* axis that run in both directions and in which the molecules are rotated by 90° with respect to each other. Every nitrogen atom of the ring and all oxygen atoms of the nitro groups are involved in ionic contacts to the potassium cations with distances ranging between 2.750(1) and 2.830(2) Å.

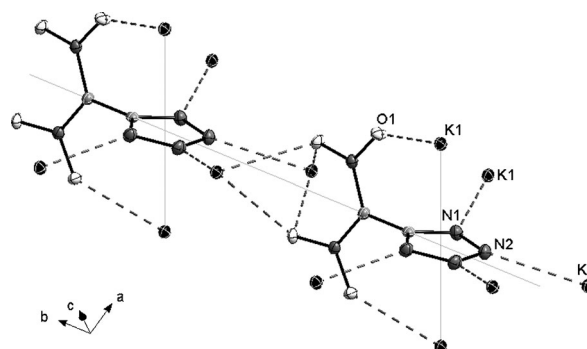


Figure 11. Arrangement of the molecules to form chains along the *b* axis in the crystal structure of compound **11**. Selected atom distances [Å]: O1...K1 2.750(1), N1...K1 2.774(2), N2...K1 2.830(2).

Physical, chemical and energetic properties

Owing to the energetic nature of all described compounds **3**, **6**, **9** and **10** and for initial safety testing their sensitivities and energetic behaviour were determined. Their investigated physical and thermodynamic properties are summarised in Table 6. The sensitivities towards impact and friction were determined

D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D–H...A) [Å]	\angle (D–H...A) [°]
C4–H42...O5'	0.98(2)	2.50(2)	3.287(1)	137.5(4)
C4–H42...O6'	0.98(2)	2.57(2)	3.479(2)	155.0(3)
C3–H33...O6'	0.97(2)	2.47(2)	3.382(2)	157.9(5)
C4–H41...O5''	0.95(1)	2.41(2)	3.270(2)	150.4(1)
C4–H41...O2'''	0.95(1)	2.64(1)	3.239(1)	122.0(1)
C3–H31...F1''''	0.94(2)	2.69(2)	3.460(1)	139.8(2)
C3–H32...F1°	0.98(2)	2.70(2)	3.264(2)	117.3(2)
C3–H32...N4°	0.98(2)	2.66(2)	3.623(2)	170.4(4)

[a] Symmetry operators: ' = 1+x, y, z; '' = –x, –y, 1–z; ''' = 1–x, –y, 1–z; '''' = –1/2+x, 1/2–y, 1/2+z; ° = 1/2–x, –1/2+y, 1/2–z.

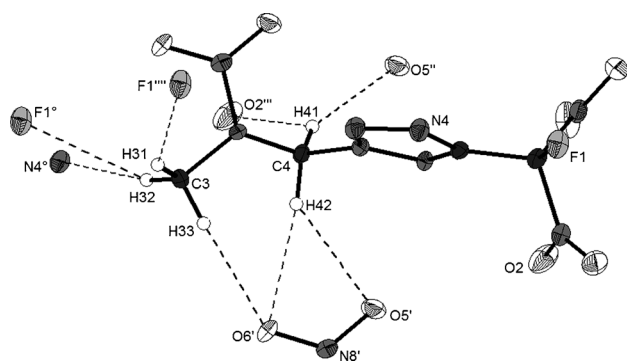


Figure 9. Strong hydrogen bonds represented by dashed lines in the crystal structure of compound **10** for the structural parameters listed in Table 5.

Table 6. Physical and thermodynamic properties of the alkylated compounds **9** and **10** in comparison to their starting materials **3** and **6**.

Compound	3	9	6	10
formula	C ₂ H ₄ N ₈ O ₆	C ₄ H ₅ N ₉ O ₈	C ₂ H ₄ N ₇ O ₄ F	C ₄ H ₅ N ₈ O ₆ F
weight [g mol ⁻¹]	236.10	307.17	209.10	280.13
impact [J] ^[a]	2	3	1	2
friction [N] ^[a]	8	40	16	36
ESD [mJ] ^[b]	50	100	100	100
grain size [μm] ^[c]	<100	100–500	<100	100–500
T _m [°C] ^[d]	–	87	–	46
T _{dec} [°C] ^[e]	128	134	166	184
N [%] ^[f]	47.46	41.04	46.89	40.00
N+O [%] ^[f]	88.12	82.71	77.50	74.27
Ω _{CO} [%] ^[g]	13.5	7.8	0.0	–2.9
Ω _{CO₂} [%] ^[h]	0.0	–13.0	–15.3	–25.7
ρ _{RT} [g cm ⁻³] ^[i]	1.78	1.75	1.70	1.83
Δ _f U [kJ kg ⁻¹] ^[j]	1074.7	1110.8	126.9	439.4
Δ _f H° [kJ mol ⁻¹] ^[k]	231.4	313.9	6.7	98.3

[a] Impact and friction sensitivities according to standard BAM methods.^[40] [b] Sensitivity towards electrostatic discharge according to standard BAM methods.^[42] [c] Grain size of the samples used for sensitivity tests. [d] Melting onset point from DSC measurements carried out at a heating rate of 5 °C min⁻¹. [e] Decomposition onset point from DSC measurements carried out at a heating rate of 5 °C min⁻¹. [f] Nitrogen and combined nitrogen and oxygen contents. [g] Absolute oxygen balance assuming to the formation of CO and HF. [h] Absolute oxygen balance assuming to the formation of CO₂ and HF. The oxygen balance of ammonium perchlorate is 34.0%. [i] Experimentally determined density from pycnometer experiments (average value from three measurements). [j] Energy of formation calculated at the CBS-4M level of theory.^[46] [k] Heat of formation calculated at the CBS-4M level of theory.^[46]

experimentally according to the standards of the German Federal Institute for Materials Research and Testing (BAM).^[40] According to the UN recommendations for the transport of dangerous goods,^[41] all compounds shall be classified as “very sensitive” towards impact, compounds **6**, **9** and **10** as “very sensitive” and compound **3** as “extremely sensitive” towards friction at the specified grain sizes. The electrostatic discharge (ESD) test was carried out in order to determine whether the compounds are ignitable by the human body, which can generate up to 0.025 J of static energy.^[42] It was measured on a small scale electric spark tester ESD 2010EN (OZM Research) operating with the Winspark 1.15 software package.^[43] All measured compounds are insensitive towards this energy.

Whereas the ammonium salts **3** and **6** decompose (128 and 166 °C) without melting, their alkylated derivatives **9** and **10** show improved decomposition points (134 and 184 °C), and melting points well below 100 °C. This fact might be explained by more hydrogen bonding within the structure and is observed for many compounds containing this secondary nitramine moiety.^[23,44] Thus, compounds **9** and **10** show large melting ranges of 47 and 138 °C, respectively. The very high combined nitrogen and oxygen contents ranging from 74.46 to 88.12% might make these compounds interesting for gas-generating applications. The trinitromethyl derivatives **3** and **9** show positive oxygen balances assuming the formation of carbon monoxide, as required for oxygen carriers in solid rocket propellants. The densities as obtained from ambient temperature pycnometer measurements range between 1.70

and 1.83 g cm⁻³. The heats of formation were computed by ab initio calculations by using the Gaussian 09 program package^[45] at the CBS-4M level of theory.^[46] All compounds are formed endothermically with the highest value of 313.9 kJ mol⁻¹ calculated for compound **9**.

The detonation and combustion parameters of compounds **3**, **6**, **9** and **10** were computed with the Expo5 computer code (Version 6.02),^[47] based on the calculated heats of formation and attributed to the corresponding densities at ambient temperature. The results are listed in Table 7. The detonation velocities and pressures of all the tetrazole derivatives **3**, **6**, **9**

Table 7. Calculated detonation and combustion parameters (EXPLOS, V6.02)^[47] of compounds **3**, **6**, **9** and **10**.

Detonation parameters	3	9	6	10
Δ _{ex} U° [kJ kg ⁻¹] ^[a]	–6190	–6016	–5540	–5394
T _{ex} [K] ^[b]	4356	4291	3734	3783
D _v [m s ⁻¹] ^[c]	9058	8704	8476	8773
P _{CJ} [kbar] ^[d]	341	334	299	342
V ₀ [L ⁻¹ kg ⁻¹] ^[e]	826	774	801	728
combustion parameters: oxidiser/aluminium/PBAN [%] ^[f]				
I _s (neat) [s] ^[g]	270	273	259	259
I _s (80:20:0) [s] ^[h]	275	274	263	253
I _s (70:16:14) [s] ^[i]	258	253	244	244
I _s (76:10:14) [s] ^[h]	260	256	246	246
I _s (80:13:7) [s] ^[j]	275	269	256	254

[a] Heat of detonation. [b] Temperature of the explosion gases. [c] Detonation velocity. [d] Detonation pressure. [e] Volume of gaseous detonation products (assuming only gaseous products). [f] Using isobaric combustion conditions at a chamber pressure of 70.0 bar versus ambient pressure with equilibrium expansion conditions at the nozzle throat. [g] Specific impulse of the neat compound. [h] Specific impulse of mixtures with aluminium and/or PBAN binder. Binder composition 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, 2% bisphenol A ether. [i] Original NASA composition (70:16:14) for the space shuttle solid rocket boosters.^[48] This mixture with AP as oxidiser exhibits a I_s of 260 s. [j] Specific impulse for a composition with 7% PBAN binder.

and **10** are comparable with those calculated for HMX (1,3,5,7-tetranitro-1,3,5,7-tetraoctane, 9235 m s⁻¹, 388 kbar), RDX (1,3,5-trinitroperhydro-1,3,5-triazine, 8838 m s⁻¹, 343 kbar) and PETN (pentaerythrityltetranitrate, 8404 m s⁻¹, 309 kbar).^[47] Hence, they are all useful high-performing and oxygen-rich explosives.

Regarding the combustion in a chamber with 70 bar pressure against atmosphere the trinitromethyl-containing derivatives **3** and **9** show the highest specific impulses as neat compounds as well as in their mixtures with aluminium and/or polybutadiene acrylonitrile binder (PBAN). Due to their higher oxygen balances (Ω) and heats of formation, the I_s values are about 10 s higher than those of the corresponding fluorine-containing analogues **6** and **10**. The I_s value of compound **3** in the original NASA mixture (70:16:14) almost achieves the maximum value of AP (260 s).^[48] The oxidiser/aluminium ratio can be varied from 70:16 to 76:10, whereas maintaining the PBAN binder at 14%. With this mixtures (76:10:14) the specific impulses I_s values of the trinitromethyl-containing compounds **3** and **9** are in the range of AP; the fluorine-containing materials **6** and **10** improve their I_s values only slightly.

When reducing the PBAN binder from 14 to 7%, the trinitromethyl-containing compounds **3** and **9** achieve considerably higher specific impulses I_s values than 260 s (Table 7). As a rule of thumb an increase of the value for I_s by 20 s leads empirically to a doubling of the usual carried payload (satellite or warhead) of a rocket.^[1] The I_s values of the fluorine-containing materials **6** and **10** in these mixtures are only about 5 s under the maximum value of AP of 260 s. However, these compounds might also be useful for application in agent defeat weapons owing the assumed toxic fluorine-containing combustion products.^[1]

The dipotassium salt **11** reveals a rather high detonation velocity of about 9100 ms⁻¹ while being thermally stable until 280 °C. With sensitivities (impact: 4 J, friction: 144 N, ESD: 100 mJ) in the range of PETN (impact: 4 J, friction: 80 N, ESD: 100 mJ) it might also be a good detonator material with improved performance and thermal stability compared to PETN (see the Supporting Information).^[49]

Conclusion

From this combined experimental, theoretical and comparative study the following conclusions can be drawn:

The alkylation of the 5-substituted tetrazoles is very selective at the N2 position of the ring.

The alkylation barely affects the impact sensitivity, but the friction sensitivity gets improved.

The target alkylated compounds have a large melting area and higher decomposition points than the starting materials, which have no melting point.

Comparing the trinitromethyl compounds with the fluorodinitromethyl compounds, the latter show slightly lower sensitivities, higher decomposition points and the alkylated fluorine-containing compound shows a much larger melting area than the alkylated trinitromethyl-containing compound.

The calculated heats of formation for the trinitromethyl-containing compounds are more endothermic than those of the fluorine-containing compounds. Moreover, they are higher endothermic for the corresponding alkylated compounds.

The calculated detonation velocities (D_v) are in the range of RDX and PETN.

The calculated specific impulses (I_s) of the trinitromethyl-containing compounds are in the range of the maximum value of aluminised mixtures of AP, and are considerably higher than those of the fluorodinitromethyl-containing compounds.

The dipotassium 5-(dinitromethylide)-tetrazolate reveals desirable detonation parameters while being thermally stable up to 280 °C and shows sensitivities in the range of PETN.

Experimental Section

General procedures

Melting points (T_m) and decomposition points (T_{dec}) were measured with a Perkin–Elmer Pyris6 DSC (T_{onset}), by using a heating rate of 5 °C min⁻¹ and checked by a Büchi Melting Point B-540 apparatus. Infrared spectra were measured with a Perkin–Elmer Spectrum BX-

FTIR spectrometer equipped with a Smiths DuraSAMPLR II ATR device, Raman spectra were recorded with a Perkin–Elmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser ($\lambda = 1064$ nm). All NMR spectra were recorded at ambient temperature in [D₆]acetone with a JEOL Eclipse 400 instrument and chemical shifts were determined with respect to external Me₄Si (¹H: 399.8 MHz, ¹³C: 100.5 MHz), MeNO₂ (¹⁴N: 28.9 MHz, ¹⁵N: 40.6 MHz) and CCl₃F (¹⁹F: 376.5 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (FAB⁺). Analyses of C/H/N were performed with an elemental Vario EL analyser.

X-ray diffraction

For compounds **6** and **9–11**, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection by using Mo_{K α} radiation ($\lambda = 0.71073$ Å). The data collection was performed by using the CrysAlispro software.^[50] The structures were solved by direct methods (SIR2004)^[51] and refined by full-matrix least-squares on F^2 (SHELXL-97).^[52] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located in a difference Fourier map and then refined freely. DIAMOND plots are shown with thermal ellipsoids at the 50% probability level.^[53] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers. CCDC 956909 (**6**), 974783 (**9**), 974784 (**10**) and 1026523 (**11**) 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.

Computational details

All quantum chemical calculations were carried out by using the program package Gaussian 09, revision C.01,^[45a] and visualised by Gaussview 5, V5.0.8.^[45b] The enthalpies (H) and free energies (G) were calculated by using the complete basis set (CBS) method in order to obtain accurate values.^[46,54] The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations by using a finite basis set to the estimated complete basis set limit. CBS-4 starts with a HF/3-21G(d) geometry optimisation, which is the initial guess for the following SCF calculation as a base energy and a final MP2/6-31 + G** calculation with a CBS extrapolation to correct the energy in second order. The used re-parameterised CBS-4M method additionally implements a MP4(SDQ)/6-31G calculation to approximate higher order contributions and also includes some additional empirical corrections.^[45] Solid-state enthalpies and energies of formation were calculated from the corresponding enthalpy derived from these quantum chemical CBS-4M calculations (H_{CBS-4M}). Therefore, the enthalpies of formation of the gas-phase species were computed according to the atomisation energy method.^[55] The solid-state enthalpies of formation ($\Delta_f H^\circ$) were estimated by subtracting the gas-phase enthalpies with the corresponding enthalpy of sublimation obtained by the rule of Trouton^[56] for the neutral compounds **9** and **10**.

The solid-state enthalpies of formation for the ionic compounds are derived from the calculation of the corresponding lattice energies (U_L) and lattice enthalpies (H_L), calculated from the corresponding molecular volumes, by the equations provided by Jenkins et al.^[57] The derived molar standard enthalpies of formation for the solid state ($\Delta_f H_m^\circ$) were used to calculate the solid-state energies of formation (ΔU_m°) according to Equation (1), with Δn being the change in the number of mol of gaseous components.^[1]

$$\Delta U_m = \Delta H_m - \Delta nRT \quad (1)$$

The calculations affecting the detonation parameters were carried out by using the program package EXPLO5, V6.02,^[47] with CBS-4M-calculated enthalpies of formation, and densities obtained from ambient temperature X-ray diffraction measurements. The detonation parameters were calculated at the C–J point (Chapman–Jouguet point) with the aid of the steady-state detonation model by using a modified Becker–Kistiakowski–Wilson equation of state for modelling the system. The C–J point was found from the Hugoniot curve of the system by its first derivative.^[58] Also the specific impulses I_s were calculated with the EXPLO5, V6.02 program,^[47] assuming an isobaric combustion, and a chamber pressure of 70.0 bar against an ambient pressure of 1.0 bar with equilibrium expansion conditions at the nozzle throat.

Syntheses

CAUTION! All of the described compounds are energetic materials with high sensitivities towards heat, impact, friction and electrostatic discharge. Although no incidents occurred during preparation and manipulation, additional proper protective precautions like face shield, leather coat, earthed equipment and shoes, Kevlar gloves and ear plugs should be used when undertaking work with these compounds.

Ammonium 5-(fluorodinitromethyl)-tetrazolate (**3**),^[18] potassium dinitroacetone nitrile (**4**)^[16,26–28] and 2-nitro-azapropyl chloride (**8**)^[29a] were synthesised according to the literature-known procedures and purified by re-crystallisation (compounds **3** and **4**) and distillation (compound **8**).

Ammonium 5-(fluorodinitromethyl)-tetrazolate (6): Selectfluor (10.00 g, 28.4 mmol) was added to a yellow solution of potassium dinitroacetone nitrile (**4**) (3.00 g, 17.7 mmol) in anhydrous acetonitrile (100 mL) and the mixture was stirred until the reaction mixture turned colourless (2–3 h). The reaction mixture was distilled (82 °C) by means of an additional argon flow and a cooling trap (–78 °C) and fluorodinitroacetone nitrile (**5**) was detected by multinuclear NMR spectroscopy in the resulting acetonitrile solution. ¹⁴N NMR ([D₆]acetone, 28.9 MHz): $\delta = -37$ ppm (d, ²J(¹⁴N,F) = 11 Hz, NO₂); ¹⁹F NMR ([D₆]acetone, 376.5 MHz): $\delta = -93.3$ ppm (q, ²J(F,¹⁴N) = 11 Hz, C(NO₂)₂F).

Sodium azide (1.48 g, 22.8 mmol or 3 mL trimethylsilyl azide) was added to the acetonitrile solution containing compound **5**. The reaction mixture was stirred in a barred flask at ambient temperature overnight and additional 12 h at 50 °C. The solvent was evaporated under reduced pressure and the remaining yellow oil was treated with water for 2 h. The solution was filtered off and the water was evaporated again under reduced pressure. The resulting brownish oil was stirred with aqueous ammonia (4 mL, 25 %) for 30 min. The solvent was evaporated and the resulting tan solid was re-crystallised in a 1:1 mixture of ethyl acetate and toluene (10 mL) yielding ammonium 5-(fluorodinitromethyl)-2H-tetrazolate (**6**) (1.18 g, 5.7 mmol, two steps yield from compound **4**: 32 %) as colourless crystals. DSC (5 °C min⁻¹, *T*_{onset}): *T*_{dec} = 166 °C; ¹H NMR ([D₆]acetone, 399.8 MHz): $\delta = 8.42$ ppm (brs, 4H; NH₄); ¹³C NMR ([D₆]acetone, 100.5 MHz): $\delta = 150.8$ (d, ²J(C,F) = 23.0 Hz, C_{TZ}), 119.9 ppm (d, ¹J(C,F) = 284.7 Hz, C(NO₂)₂F); ¹⁵N NMR ([D₆]acetone, 40.6 MHz): $\delta = 9.6$ (N_d), –20.6 (d, ²J₁₅(N,F) = 16.5 Hz, NO₂), –57.5 (N_g), –362.2 ppm (NH₄⁺); ¹⁹F NMR ([D₆]acetone, 376.5 MHz) $\delta = -95.5$ ppm (brs, CF); IR: $\tilde{\nu} = 3192$ (m), 3026 (vs), 2873 (m), 2806 (m), 1924 (vw), 1685 (vw), 1605 (vs), 1595 (vs), 1457 (vs), 1424 (s), 1408 (m), 1361 (w), 1310 (m), 1238 (s), 1190 (s), 1160 (w), 1152 (w), 1099 (s), 1066 (vw), 1046 (w), 982 (vs), 947 (w), 836 (vs), 798 (vs), 740 (w), 704 cm⁻¹ (w);

Raman (200 mW): $\tilde{\nu} = 3033$ (52), 2902 (38), 1683 (10), 1607 (32), 1471 (100), 1362 (43), 1317 (15), 1213 (10), 1190 (50), 1160 (17), 1101 (39), 1068 (20), 984 (53), 949 (60), 838 (70), 803 (10), 651 (8), 530 (7), 444 cm⁻¹ (16); MS (high res., FAB⁺): *m/z*: 190.99 [C₂N₆O₄F]⁺; elemental analysis calcd (%) for C₂H₄N₆O₄F: C 11.49, H 1.93, N 46.89; found: C 11.90, H 1.99, N 46.49; drophammer: 1 J; friction tester: 16 N; ESD: 100 mJ; grain size: < 100 μm.

2-(2-Nitro-2-azapropyl)-5-(trinitromethyl)tetrazole (9): 2-Nitro-2-azapropyl chloride (**3**) (130 mg, 1.04 mmol) was added to a solution of ammonium 5-(trinitromethyl)tetrazolate (**3**) (250 mg, 1.06 mmol) in anhydrous acetone (10 mL). The solution was stirred overnight at ambient temperature. Precipitated ammonium chloride was filtered off and washed with dichloromethane. Water (10 mL) was added to the filtrate and the mixture was extracted with dichloromethane (4 × 10 mL). The combined organic phases were dried over MgSO₄ and the solvent was concentrated to 2 mL under reduced pressure. Methanol (2 mL) was added to the residue and the 1:1 mixture was kept at 8 °C overnight whereas the desired compound **9** crystallised as colourless crystals (250 mg, 0.81 mmol, 78 %). DSC (5 °C min⁻¹): *T*_m = 87 °C, *T*_{dec} = 134 °C; ¹H NMR ([D₆]acetone, 399.8 MHz): $\delta = 7.00$ (s, 2H; CH₂), 3.70 ppm (s, 3H; CH₃); ¹³C NMR ([D₆]acetone, 100.5 MHz): $\delta = 152.3$ (C_{TZ}), 121.2 (C(NO₂)₃), 67.6 (CH₂), 38.6 ppm (CH₃); ¹⁴N NMR ([D₆]acetone, 28.9 MHz): $\delta = -33$ (NNO₂), –37 ppm (C(NO₂)₃); IR: $\tilde{\nu} = 3068$ (w), 3007 (w), 2883 (w), 1623 (m), 1598 (s), 1540 (s), 1468 (m), 1447 (m), 1420 (m), 1384 (w), 1331 (m), 1299 (s), 1258 (s), 1198 (m), 1132 (m), 1101 (w), 1044 (m), 1010 (s), 987 (m), 961 (w), 943 (m), 857 (w), 843 (s), 821 (w), 798 (s), 760 (s), 734 (m), 690 (m), 654 cm⁻¹ (w); Raman (300 mW): $\tilde{\nu} = 3069$ (34), 3038 (34), 3008 (100), 2963 (72), 2890 (20), 2859 (12), 1627 (20), 1608 (26), 1541 (9), 1487 (60), 1422 (18), 1398 (30), 1347 (12), 1305 (21), 1261 (42), 1134 (8), 1046 (27), 989 (29), 962 (30), 946 (40), 859 (86), 845 (61), 803 (7), 770 (10), 691 (8), 656 (10), 604 cm⁻¹ (17); MS (FAB⁻): *m/z*: 306.4 [M–H]⁻; elemental analysis calcd (%) for C₄H₅N₉O₈: C 15.64, H 1.64, N 41.04; found: C 18.43, H 2.08, N 25.09; drophammer: 3 J; friction tester: 40 N; ESD: 100 mJ; grain size: 100–500 μm.

2-(2-Nitro-2-azapropyl)-5-(fluorodinitromethyl)-tetrazole (10): 2-Nitro-2-azapropyl chloride (**3**) (150 mg, 1.20 mmol) was added to a solution of ammonium 5-(fluorodinitromethyl)-tetrazolate (**6**) (250 mg, 1.20 mmol) in anhydrous acetone (10 mL). The solution was stirred overnight at ambient temperature. Precipitated ammonium chloride was filtered off and washed with dichloromethane. Water (10 mL) was added to the filtrate and the mixture was extracted with dichloromethane (4 × 10 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was concentrated to 2 mL under reduced pressure. Methanol (2 mL) was added to the residue and the 1:1 mixture was kept at 8 °C overnight whereas the desired compound **10** crystallised as colourless crystals (260 mg, 0.93 mmol, 78 %). DSC (*T*_{onset}): *T*_m = 46 °C, *T*_{dec} = 184 °C; ¹H NMR ([D₆]acetone, 399.8 MHz): $\delta = 6.96$ (s, 2H; CH₂), 3.69 ppm (s, 3H; CH₃); ¹³C NMR ([D₆]acetone, 100.5 MHz): $\delta = 153.7$ (d, ²J(C,F) = 25.4 Hz, C_{TZ}), 115.4 (d, ¹J(C,F) = 282.9 Hz, C(NO₂)₂F), 67.3 (CH₂), 38.6 ppm (CH₃); ¹⁴N NMR ([D₆]acetone, 28.9 MHz): $\delta = -27$ (d, ²J(N,F) = 10 Hz, C(NO₂)₂F), –32 ppm (s, NNO₂); ¹⁹F NMR ([D₆]acetone, 376.5 MHz): $\delta = -99.6$ ppm (brs, CF); IR: $\tilde{\nu} = 3050$ (w), 3005 (w), 2967 (w), 1626 (s), 1595 (m), 1537 (s), 1461 (m), 1427 (w), 1409 (w), 1349 (m), 1325 (w), 1305 (m), 1260 (s), 1164 (m), 1084 (m), 1054 (w), 1039 (s), 963 (s), 871 (w), 835 (s), 804 (s), 765 (s), 722 (s), 684 (s), 664 cm⁻¹ (m); Raman (300 mW): $\tilde{\nu} = 3069$ (34), 3038 (34), 3008 (100), 2963 (72), 2890 (20), 2859 (12), 1627 (20), 1608 (26), 1541 (9), 1487 (60), 1422 (18), 1398 (30), 1347 (12), 1305 (21), 1261 (42), 1134 (8), 1046 (27), 989 (29), 962 (30), 946 (40), 859 (86), 845 (61), 803 (7), 770 (10), 691 (8), 656 (10), 604 cm⁻¹ (17); MS (FAB⁻): *m/z*: 306.4

$[M-H]^-$; elemental analysis calcd (%) for $C_4H_5N_6O_6F$: C 17.15, H 1.80, N 40.00; found: C 18.43, H 2.08, N 25.09; drophammer: 2 J; friction tester: 36 N; ESD: 100 mJ; grain size: 100–500 μm .

Dipotassium 5-(dinitromethylidene)-tetrazolate (11): A solution of compound **3** (0.5 g, 2.12 mmol) in water (20 mL) was acidified with HCl until pH 2 was reached and the solution was extracted with dichloromethane (4 × 40 mL). The organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was treated with an aqueous solution of KOH (10 M) overnight, the solvent was evaporated under reduced pressure and the residue was re-crystallised in a 1:1 mixture of ethyl acetate and toluene (20 mL) yielding the dipotassium salt **11** (410 mg, 1.64 mmol, 77%) as colourless crystals. DSC (T_{onset}): $T_m = 284^\circ\text{C}$, $T_{\text{dec}} = 291^\circ\text{C}$; ^{13}C NMR ($[\text{D}_6]$ acetone, 100.5 MHz): $\delta = 155.2$ (C_{12}), 128.5 ppm ($\text{C}(\text{NO}_2)_2$); ^{14}N NMR ($[\text{D}_6]$ acetone, 28.9 MHz) $\delta = -23$ ppm (NO_2); drophammer: 4 J; friction tester: 160 N; ESD: 100 mJ; grain size: 100–500 μm .

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