

Synthesis and Properties of Tetranitro-Substituted Adamantane Derivatives

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Several new nitro-substituted adamantane compounds based on adamantane-1,3,5,7-tetrol were synthesized and the previously only briefly reported tetranitrate was reinvestigated. The materials were completely characterized by spectroscopic methods including some by X-ray diffraction. The energetic properties, thermal stabilities, and sensitivities of the nitrocarbamate, nitrocarbamate salt, and nitrate were determined and compared to current composites in terms of potential highenergy dense oxidizers (HEDOs). Furthermore, the enthalpies of all compounds were calculated, and their energetic performances investigated by using the EXPLO5 code.

Introduction

The investigation of new explosives is an important and broad field in both organic and inorganic chemistry. Some of the latest research in this area focuses on the potential application of polycarbocyclic cage compounds as a new class of energetic materials. Such systems, owing to their rigid, compact structures, generally pack efficiently in the solid state and therefore exhibit unusually high crystal densities. Furthermore, their carbocyclic frameworks often possess extraordinary strain energies, rendering them thermodynamically unstable in comparison to isomeric chain structures, which results in a better performance on detonation.^[1]

High performance data, for example, the detonation velocity, detonation pressure, and heat of explosion are essential characteristics of high explosives.^[2] Such compounds must satisfy a number of well-known requirements. In addition to the high energy content and crystal density, they should exhibit good stability, environmental compatibility, and low sensitivity to external stimuli.^[3] Adamantane derivatives, in particular polynitroadamantanes as a class of polynitrated cage compounds, are recognized as promising explosives and propellants with a high degree of thermal stability.^[4] Their calculated densities, sensitivities, and detonation properties are similar to those obtained for standard high explosives like RDX (hexogen), HMX (octogen), TNT (trinitrotoluene), and PETN (pentaerithrityltetranitrate).^[5] Most recently the novel high-energy-density compound 2,4,9-trinitro-2,4,9-triazaadamantane-7-yl nitrate was prepared and characterized, featuring high thermal stability and high density.^[6] According to the calculated energetic prop-

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erties, some of the polynitro derivatives of the simple adamantane, such as 1,3,5,7-adamantane tetranitrate and 1,3,5,7-tetrakis(trinitroxymethyl)adamantane, might even have better performance values than TNT.^[5] Motivated by this theoretical prediction, we synthesized some new potentially energetic adamantane derivatives starting from the relatively inexpensive adamantane. This contribution gives a detailed insight into the chemistry of adamantine-based energetic materials and their synthetic approaches.

Results and Discussion

Syntheses

Commercially available adamantane is the starting material for this study (Scheme 1). The activation of the four tertiary carbon atoms succeeds via an initial bromination to yield 1,3,5,7-tetrabromoadamantane (1) as a colorless crystalline solid in the presence of aluminum bromide;^[7] this was later improved by using the more economic chloride AlCI₃.^[8] This replacement had no influence on the overall yield of 1. Further reaction of 1 with fuming sulfuric acid, silver sulfate, and aqueous sodium hydroxide afforded the corresponding hydrolysis product, 1,3,5,7-tetrahydroxyadamantane (2), which is a suitable precursor for the synthesis of nitro esters and nitrocarbamates. Reaction of 2 with chlorosulfonyl isocyanate led to adamantane-1,3,5,7-tetracarbamate (3). Further treatment of 3 with mixed acid followed by aqueous workup resulted in formation and isolation of the nitrated compound, adamantane-1,3,5,7-tetranitrocarbamate (4), which was obtained as a tetrahydrate. Due to the acidic hydrogen in the nitrocarbamate moiety, it was possible to fourfold deprotonate 4 with aqueous base, such as guanidinium carbonate or ammonia, under formation of the corresponding tetraguanidinium (5) and tetraammonium (6) salts. The nitration of tetrol 2 with mixed acid was previously briefly reported in a patent; the obtained adamantane tetranitro ester 7 was only insufficiently characterized,



Scheme 1. Syntheses of the adamantane derivatives 1-7.

regarding its energetic properties.^[9] Nitrate **7** was isolated in 71% yield in high purity as a colorless crystalline solid, which was found to be stable towards moisture.

NMR Spectroscopy

All compounds reported herein were characterized by ¹H, ¹³C, and ¹⁴N/¹⁵N NMR spectroscopy. The spectra were recorded in either CDCl₃ (1 and 7) or [D₆]DMSO (2–6). The C₃ symmetry of the tetrasubstituted derivatives produces degeneracy of spectral frequencies resulting in a simple spin system. In the ¹H NMR spectra of all compounds, the CH₂ signals of the cage hydrogens appear as singlets ranging from 2.27 ppm for the negatively charged cage 5 to 2.64 ppm for the brominated species 1. In the spectrum of the tetracarbamate 3 the NH_2 resonance is located at 6.4 ppm and exhibits signal broadening which is explained by the restricted rotation around the C-N bond due to the partial double-bond character. For the nitrated compound 4 the corresponding resonance displays a narrower linewidth and is also shifted downfield to 11.18 ppm. This strong deshielding in the nitrocarbamate moiety depends on the presence of an adjacent nitro group, which causes a remarkable acidification of the NHNO₂ hydrogen.

In the ¹³C NMR spectra the CH_2 resonances appear within the range of 54.6–40.7 ppm. The carbon atoms of the carbamate group in **3** at 155.8 ppm are shifted significantly upfield

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upon nitration to the nitrocarbamate **4** (147.5 ppm) and prove the successful insertion of NO₂ groups. The strong inductive effect of the four nitro groups affects the electronic structure of all carbon atoms in the adamantane skeleton, resulting in the lowfield shift of the bridgehead carbons (76.5 ppm (**3**) and 79.6 ppm (**4**)). The resonance of the bridgehead carbons of **7** shifts yet further downfield at 83.3 ppm since the nitrate substituents are directly bound to the adamantane cage. In the ¹³C NMR spectra of the salts **5** and **6** the most significant change occurs for the signal of carbamate carbon atoms, which are shifted from 147.5 ppm (**4**) to 159.2 ppm (**5**) and 159.6 ppm (**6**). The signal of the tertiary cage carbon suffers a highfield shift depending on the cation present.

The ¹⁴N NMR spectrum of **4** exhibits a characteristic and relatively sharp signal for the NO_2 moiety at -42 ppm and proves the successful nitration of **3**.^[10] The nitrogen resonances of the NH_2 (**3**) and $NHNO_2$ groups (**4**) are too broad to be observed. These nitrogen atoms are visible in the ¹⁵N NMR spectrum, as observed for the ammonium salt **6**. Here, the nitro nitrogen atom is shifted significantly downfield to -7.8 ppm (from -42 ppm for the neutral molecule), the deprotonated nitrogen is at -130.9 ppm, and the ammonium resonance is detected at -358.6 ppm. All measured shifts are in good agreement with those of the analogous tetraammonium pentaerythritol tetranitrocarbamate and its comparison to the neutral molecule.^[10] The ¹⁴N nitrogen resonance of the ONO_2 substituent in the nitrate **7** appears as a relatively sharp signal at -48 ppm, typical for nitric esters.

Vibrational Spectroscopy

The IR and Raman spectra for compounds **3–7** show characteristic vibrations for the carbonyl and/or nitro moieties. The carbonyl stretching vibrations \tilde{v} (C=O) of **3–6** are located within the range of 1778 to 1653 cm⁻¹ in the IR and between 1765 and 1676 cm⁻¹ in the Raman spectra.^[11] The symmetric stretching vibrations of the nitro groups \tilde{v}_s (NO₂) are identified between 1343 and 1208 cm⁻¹, whereas the asymmetric vibrations \tilde{v}_{as} (NO₂) are assigned at 1589 cm⁻¹ (IR) and 1608 cm⁻¹ (Raman) for the tetranitrocarbamate **4**. For the nitrate **7** strong bands attributed to the stretching and deformation vibrations of the ONO₂ moiety are observed at 1630 cm⁻¹, 1280 cm⁻¹, and 865 cm⁻¹.^[9] The C–O stretching vibration is detected in the Raman spectrum at the characteristic wavenumber of 1067 cm⁻¹.

Single-Crystal X-ray Diffraction

Single crystals suitable for X-ray diffraction measurements were obtained for compounds **3–5** and **7** by recrystallization from water (**3** and **5**), ethanol (**4**), and *n*-butanol (**7**). The measurement and crystal data are shown in Table 1. Carbamate **3** crystallizes in the triclinic space group $\bar{P}1$ with two molecules per unit cell and a density of 1.397 g cm⁻³. The molecular structure of **3** is depicted in Figure 1, together with selected bond lengths and angles. The structure of **3** exhibits some very typical characteristics of carbamates. The C11–N1 bond length in



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Table 1. Crystal data and details of the structure determinations and refinement of 3–5 and 7.							
	3	4	5	7			
formula	C ₁₄ H ₂₀ N ₄ O ₈	C ₁₄ H ₁₆ N ₈ O ₁₆ ·4H ₂ O	C ₁₈ H ₃₆ N ₂₀ O ₁₆	C ₁₀ H ₁₂ N ₄ O ₁₂			
FW [g mol ⁻¹]	372.34	624.41	788.67	380.24			
T [K]	173(2)	123(2)	173(2)	123(2)			
λ [Å]	0.71069	0.71073	0.71073	0.71073			
crystal system	triclinic	tetragonal	monoclinic	monoclinic			
space group	<i>P</i> 1	14 ₁ /a	C2/c	P21/c			
crystal size [mm]	0.31×0.26×0.14	0.40×0.19×0.19	0.35×0.15×0.03	0.40×0.35×0.05			
crystal habit	colorless block	colorless block	colorless block	colorless platelet			
a [Å]	9.314(6)	18.0118(5)	7.8201(4)	8.4128(3)			
b [Å]	10.123(6)	18.0118(5)	25.8490(10)	9.1656(3)			
c [Å]	10.266(7)	7.4883(4)	16.5369(8)	19.2211(7)			
α [°]	88.832(5)	90	90	90			
β [°]	73.216(6)	90	95.234(4)	95.528(4)			
γ [°]	73.198(5)	90	90	90			
V [ų]	885.0(10)	2429.39(19)	3328.9(3)	1475.21(9)			
Z	2	4	4	4			
$ ho_{calc.} [gcm^{-3}]$	1.397	1.707	1.574	1.712			
μ [mm ⁻¹]	0.116	0.162	0.137	0.160			
F(000)	392	1296	1648	784			
Θ range [°]	4.43-32.06	4.34-28.27	4.41-26.40	4.26–26.37			
index ranges	$-11 \le h \le 11$	$-22 \le h \le 24$	$-9 \leq h \leq 9$	$-10 \le h \le 9$			
	$-11 \le k \le 12$	$-24 \le k \le 23$	$-31 \le k \le 32$	$-11 \le k \le 11$			
	$-12 \le l \le 12$	-9 <i>≤l≤</i> 9	$-20 \le l \le 19$	$-22 \le l \le 24$			
refl. collected	6952	8499	13147	12167			
refl. unique	3617	1469	3392	3012			
parameters	316	107	317	283			
GooF	1.031	1.046	1.035	1.032			
$R_1/wR_2 \ [l > 2 \ \sigma(l)]$	0.0343/0.0819	0.0419/0.1043	0.0495/0.1116	0.0330/0.0778			
R_1/wR_2 [all data]	0.0425/0.0879	0.0567/0.1167	0.0809/0.1285	0.0458/0.0857			
max/min residual	-0.191/0.289	-0.206/0.339	-0.219/0.345	-0.227/0.321			
electron density [Å ⁻³]							
CCDC	1587496	1587495	1587498	1587497			



Figure 1. X-ray molecular structure of adamantane-1,3,5,7-tetracarbamate (**3**). Selected bond lengths [Å] and angles [°]: N1-C11 1.329(7), N1-H1 0.87(3), O2-C11 1.219(9), O1-C11 1.351(2), O1-C1 1.460(1), N1-C11-O2 124.5(6), O2-C11-O1 124.8(0), C11-O1-C1 121.0(3), H1-N1-C11-O2 -2.8(0), H1-N1-C11-O1 177.5(3). the carbamoyl moiety equals 1.329(7) Å and is in good agreement with already reported carbamate compounds.^[12] The quite short C11–N1 bond and the almost perfect planarity of the carbamate moiety indicate the partial double-bond character between C11 and N1.

Another feature of the structure is the shortened N–H bond with a length of 0.87(3) Å. The rigid carbon backbone is influenced by the introduction of the carbamoyl substituents which is evident as a slight distortion of the cage. The C-C-C angles are in the range of 106.4(4)–112.2(5)° and deviate from the ideal of 109.5° for adamantane.^[13] The extended structure involves secondary interactions in terms of classical intermolecular N–H…O hydrogen bonds and unusual intramolecular nonclassical interactions of the type C–H…O. Both hydrogen atoms of the NH₂ group interact with the carbonyl oxygen of a neighboring molecule and form two moderate hydrogen bonds with lengths in the range of 2.10(7)–2.18(9) Å.^[14]

In contrast to carbamate **3**, nitrocarbamate **4** crystallizes as a tetrahydrate in the tetragonal space group $l_{1/a}$ with four formula units within the unit cell. One of the units is depicted in Figure 2. The asymmetric unit of **4** remarkably consists of only one nitrocarbamate moiety bound to the tertiary C3 and two secondary carbon atoms C1 and C1, respectively. This simplification is due to the tetragonal space group which causes a fourfold rotoinversion axis. Compared to the carbamate **3**, the



Figure 2. X-ray molecular structure of adamantane-1,3,5,7-tetranitrocarbamate (**4**) tetrahydrate. Selected bond lengths [Å] and angles [°]: N1-N2 1.372(2), N1-H1 0.91(7), N1-C4 1.384(8), O1-C4 1.338(2), O4-C4 1.198(7), O1-C3 1.458(4), C3-C1 1.532(2), O6-N2-N1-C4 -15.6(1), O7-N2-N1-C4 165.6(3), O4-C4-N1-H1 172.6(4), O4-C4-N1-N2 4.0(7).

nitrocarbamate moiety does not exhibit any planarity since the torsion angles O6-N2-N1-C4 $(-15.6(1)^{\circ})$ and O7-N2-N1-C4 $(165.6(3)^{\circ})$ deviate from 180° by about 15°. This specific feature was already observed in structures of nitrocarbamates.^[12] The short N1–N2 bond length of about 1.37 Å indicates significant double-bond character which is achieved by delocalization of the nitrogen lone pair on N1. Furthermore, the length of the C–O bond in the carbonyl groups in **4** is slight shorter than in **3**, which is a result of the electron-withdrawing nitro group. The latter is also a reason for the longer bond between C4 and N1 in **4** since there is lower electron density on N1 and therefore less ability for resonance stabilization. The extended structure involves moderate intermolecular N–H…O and O–H…O hydrogen bonds.

The tetraguanidinium salt **5** crystallizes in the monoclinic space group *C*2/*c* with four units in the unit cell. Selected bond lengths and angles are shown in Figure 3. The molecular structure of the salt is similar to the neutral compound **4**. The nitro groups are twisted about $17.6(8)^{\circ}$ out of the plane of the carbamate moiety. The C8-N3-N4 angle decreases in comparison to the neutral compound due to the increased negative charge at the N3 nitrogen. The guanidinium ions take a special position in the unit cell, and are linked with the chelating nitrocarbamate anion by hydrogen bonds. Each cation forms hydrogen bonds to the O5 and O7 oxygen atoms as well as the negatively charged N3 nitrogen. The lengths of the H-bonds are in the range of 2.146–2.579 Å with the N10–H3…O7 bond as the shortest.



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Figure 3. X-ray molecular structure of tetraguanidinium adamantane-1,3,5,7tetranitrocarbamate (5). Selected bond lengths [Å] and angles [°]: O7-N4 1.255(5), O8-N4 1.230(1), N3-N4 1.327(8), N3-C8 1.377(7), O6-C8 1.209(3), O5-C8 1.352(3), C3-O5 1.458(6), O7-N4-O8 119.8(2), N4-N3-C8 116.0(5), N3-C8-O5 105.9(9), O5-C8-O6 124.4(0), O7-N4-N3-C8 -17.6(8), N3-N4-C8-O6 13.4(8).

The tetranitrate derivative **7** crystallizes as colorless platelets in the monoclinic space group $P2_1/c$ with four molecule units per unit cell and a relatively high density of 1.712 g cm⁻³ at 123 K (Figure 4). The extended structure of **7** exhibits unusual intermolecular nonclassical, but weak secondary interactions of type C–H···O between the cage hydrogen atoms and the NO₂ oxygens of a neighboring molecule (e.g. H6A···O5 2.57 Å, H2B···O5 2.58 Å, H2A···O8 2.66 Å, H4A···O12 2.90 Å).

Thermal and Energetic Properties

All compounds reported herein are stable to air and moisture. The thermal stabilities of compounds **3–7** were tested by differential scanning calorimetry (DSC) with a heating rate of $5 \,^{\circ}$ C min⁻¹ and are listed in Table 2. Due to the low decomposition temperature of the tetraammonium salt **6** ($T_{dec} = 152 \,^{\circ}$ C) this salt is omitted from the following study of thermal and energetic properties. A remarkably high decomposition temperature of 215 °C was observed for the guanidinium salt **5**, likely owing to its extensive hydrogen bonds in the ionic structure. 1,3,5,7-Adamantane tetranitrate (**7**) is the only compound in this compilation to melt at 136 °C before decomposing at 173 °C. When heated on a spatula over a flame, **7** melted and flashed shortly thereafter (Figure 5). The observation that the decomposition point of the nitrocarbamate **4** ($T_{dec} = 180 \,^{\circ}$ C) is





Figure 4. X-ray molecular structure of adamantane-1,3,5,7-tetranitrate (7). Selected bond lengths [Å] and angles [°]: C1-O1 1.468(4), N1-O1 1.417(3), N1-O3 1.2024(22), N1-O2 1.1993(21), C1-O1-N1 118.715, C1-O1-N1-O2 -1.265.



Figure 5. Burning behavior of adamantane-1,3,5,7-tetranitrate (7) in timelapse photographs.

higher than that of compound ${\bf 7}$ is in good agreement with the already often observed stability trend. $^{[10]}$

For classification of the sensitivities, the impact (IS), friction (FS), and electrostatic discharge sensitivities (ESD) of compounds **4**, **5**, and **7** were tested.^[15] The impact sensitivity measurements were carried out using a BAM fall hammer according to STANAG 4489.^[16] For friction sensitivity measurements a BAM friction tester was used according to STANAG 4487.^[17] The tetranitrocarbamate **4** and its guanidinium salt **5** showed no sensitivities towards any of the tested stimuli ($FS \ge 360$ N, $IS \ge 40$ J, $ESD \ge 1.5$ J). The nitrate **7** is only sensitive to impact exhibiting a value of 10 J, which is still less than that of the well-known high explosive hexogen (RDX) with a value of 7.5 J.^[18,19]

For use of these compounds as energetic materials, the heat of explosion (Q_v) as well as the detonation pressure (P_{CJ}) and detonation velocity (V_{det}) are important parameters. These values were calculated using the EXPLO5 V6.02 and EXPLO V6.03 codes based on previously computed enthalpies and free energies of formation and are listed in Table 2.^[20–22] The energetic parameters of **4**, **5**, and **7** were calculated based on their respective densities at 25 °C, which were recalculated from the low-temperature crystal measurement data. The ni**Table 2.** Physical and chemical properties and calculated and predicted detonation and combustion parameters (EXPLO V6.02/V6.03 codes) of **4**, **5**, **7**, and AP.

	4	5	7	AP ^[10]
formula	C ₁₄ H ₁₆ N ₈ O ₁₆ ·4H ₂ O	C18H36N20O16	C ₁₀ H ₁₂ N ₄ O ₁₂	NH ₄ CIO ₄
MW $[gmol^{-1}]$	624.33	788.67	278.09	117.49
T _m [°C] (onset) ^[a]	-	-	136	-
T _{dec} [°C] (onset) ^[b]	180	215	173	240
<i>IS</i> [J] ^[c]	\geq 40	$\geq \! 40$	10	15
FS [N] ^[d]	\geq 360	\geq 360	\geq 360	\geq 360
ESD [J] ^[e]	\geq 1.5	\geq 1.5	0.15	\geq 1.5
N [%] ^[f]	18.0	35.5	14.7	11.9
O [%] ^[g]	51.3	32.5	50.5	54.5
N+O [%] ^[h]	69.3	68.0	65.2	66.4
$arOmega_{ m CO}$ [%] ^[i]	-15	-41	-17	+35
$arOmega_{ ext{CO2}}$ [%] ^[j]	-51	-77	-59	+35
density RT	1.67	1.54	1.67	1.95
[g cm ⁻³] ^[k]				
$\Delta H_{\rm f}^{\circ}$ [kJ mol ⁻¹] ^[I]	-1432	-1628	-581	-295.8
$\Delta U_{ m f}^{\circ}~[m kJkg^{-1}]^{[m m]}$	-2503	-1515	-1437	-2623.2
Q _v [kJ kg ⁻¹] ^[n]	-4534	-2762	-5008	-1422
T _{ex} [K] ^[0]	3172	2132	3172	1735
V ₀ [Lkg ⁻¹] ^[p]	445	511	445	885
P _{CJ} [kbar ^[q]	229	159	229	158
$V_{\rm det} \ [{ m m s^{-1}}]^{[r]}$	5392	6809	7282	6368
<i>I</i> _s [s] ^[s]	182	173	202	157
<i>I</i> _s [s] [15 % Al] ^[t]	221	225	251	235
<i>I</i> _s [s] [20% Al] ^[t]	230	222	237	244
<i>I</i> _s [s] [15 % Al,	217	219	239	261
14% binder] ^[u]				
<i>l</i> ₅/ [s] [20% Al, 14% binder] ^[u]	225	219	230	258

[a] Melting and [b] decomposition temperature determined by DSC measurements carried out at a heating rate of 5 °C min⁻¹. [c] Impact sensitivity. [d] Friction sensitivity. [e] Sensitivity towards electrostatic discharge. [f] Nitrogen content. [g] Oxygen content. [h] Sum of nitrogen and oxygen contents. [i] Oxygen balance assuming the formation of CO and the formation of [j] CO₂ upon combustion. [k] RT densities are recalculated from Xray densities. [I] Enthalpy and [m] energy of formation calculated by the CBS-4M method using Gaussian 09. [n] Heat of explosion, [o] explosion temperature, [p] volume of gaseous products, [q] detonation pressure, and [r] detonation velocity calculated by using the EXPLO5 V6.03 code.[21] [s] Specific impulse for the neat compound using the EXPLO5 V6.02 code (70.0 bar chamber pressure, isobaric combustion conditions (1 bar), initial temperature of 3300 K, equilibrium expansion).^[20] [t] Specific impulse for compositions with 85% or 80% oxidizer/compound and 15% or 20% aluminum (70.0 bar chamber pressure, isobaric combustion conditions (1 bar), initial temperature of 3300 K, equilibrium expansion). [u] Specific impulse for compositions with 71% or 66% oxidizer/compound, 15% or 20% aluminum and 14% binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenol A ether) (70.0 bar chamber pressure, isobaric combustion conditions (1 bar), initial temperature of 3300 K, equilibrium expansion).

trate **7** achieves the highest detonation velocity of all compounds reported here with a value of 7282 m s⁻¹ and it outperforms the well-known high explosive TNT ($V_{det} = 7073 \text{ m s}^{-1}$). The detonation velocity of **7** is comparable to that of the military explosive tetryl.

The specific impulse I_s represents the most relevant parameter for the utilization of energetic compounds as possible composite propellants. For a rough approximation of the performance it is important to know that the payload of a rocket can be doubled if the specific impulse is increased by 20 s.^[23]



Since the specific impulse is proportional to the square root of the ratio of the combustion chamber's temperature T_c and the average molecular mass of the combustion products, a high burning temperature is necessary. The addition of aluminum can achieve the latter. The benefits of aluminum are also its low price, the high heat of combustion, and the non-hazardous combustion product Al₂O₃, which is formed in the reaction between the metal and excess oxygen provided by the oxidizer. For application as composite propellants, compounds 4, 5, and 7 were calculated as neat samples (all wt.%), containing aluminum (15% and 20%), as well as in a binder/aluminum system (15% or 20% aluminum, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, and 2% bisphenol A). The calculation results are summarized in Table 2. Since the carbon backbones of the synthesized compounds can also be oxidized in composite propellants and therefore may act as fuel, the tetranitrate 7 obtains the highest specific impulse of 251 s in a mixture with 15% aluminum and outperforms ammonium perchlorate in an analogous mixture. All neat compounds show better I_s values than AP; nonetheless, the I_s value of 261 s displayed by the optimized AP composite could not be exceeded. When 14% binder is added to the composite propellants, the specific impulses are slightly lower than those for a similar mixture with ammonium perchlorate ($l_s = 261$ s) but still are in a satisfying range.

Conclusion

Several tetrasubstituted adamantane derivatives were synthesized starting from commercially available adamantane and comprehensively characterized by standard techniques such as multinuclear magnetic resonance spectroscopy, vibrational spectroscopy, and single-crystal X-ray diffraction. The materials were also investigated as potential high-energy dense oxidizers, that is, their physical and energetic properties were studied. Thermal stabilities were determined by DSC measurements, whereas all new compounds show satisfying decomposition temperatures of above 150 °C. Both the neutral nitrocarbamate 4 and the anionic nitrocarbamate salt 5 are completely insensitive to external stimuli like impact, electrostatic discharge, and/or friction. The nitro ester 7 is insensitive towards friction but is still sensitive to impact and electrostatic discharge. In a composite propellant consisting of 85% oxidizer and 15% aluminum 7 achieves a promising specific impulse of 251 s, which is higher than that of a comparable mixture of ammonium perchlorate and aluminum. When the specific impulse in an oxidizer/fuel/binder system was calculated, the specific impulse decreases slightly but is still within the range of a promising oxidizer.

Experimental Section

General Information

All chemicals were used as supplied. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation up to 1000 mW at 1064 nm in the range between 400 and 4000 cm⁻¹. Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature. NMR spectra were recorded with Bruker TR and JEOL Eclipse 400 MHz instruments and chemical shifts were determined with respect to external standards Me₄Si (¹H, 399.8 MHz; ¹³C, 100.5 MHz) and MeNO₂ (¹⁴N, 28.9 MHz; ¹⁵N, 40.6 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI +, DEI +). CHN analyses were performed with an Elemental VarioEL Analyzer. Melting and decomposition points were measured with a PerkinElmer Pyris6 DSC and an OZM Research DTA 552-Ex with a heating rate of 5 °Cmin⁻¹ in a temperature range of 15 to 400 °C and checked by a Büchi Melting Point B-540 apparatus (not corrected). The sensitivity data were recorded using a BAM drophammer and a BAM friction tester.^[16-17]

X-ray Crystallography

Crystals suitable for X-ray crystallography were mounted on the tip of a glass fiber and selected by means of a polarization microscope. All compounds were investigated with an Oxford XCalibur3 (3, 4, 5, and 7). The diffractometer was equipped with a generator (voltage 50 kV, current 40 mA) and a KappaCCD detector operating with Mo K α radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods (SIR97)^[24] and refined by full-matrix least-squares on F^2 (SHELXL)^[25] implemented in the WINGX software package^[26] and finally checked with the PLATON software.^[27] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned in a difference Fourier map. ORTEP plots are shown with thermal ellipsoids at the 50% probability level. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre CCDC (CCDC 1587495-1587498 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre).

Quantum Chemical Calculations

All ab initio calculations were carried out using the program package Gaussian 09 (Rev. A.02)^[28] and visualized by GaussView 5.08.^[29] Structure optimizations and frequency analyses were performed with Becke's B3 three-parameter hybrid functional using the LYP correlation functional (B3LYP). For C, H, N, and O the correlationconsistent polarized double-zeta basis set cc-pVDZ was used. The structures were optimized with symmetry constraints and the energy was corrected with the zero point vibrational energy.^[30] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method in order to obtain accurate values. The CBS models used the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4M starts with a HF/3-21G(d) geometry optimization, 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 CBS-4M method used additionally implements a MP4(SDQ)/6-31+(d,p) calculation to approximate higher order contributions and also includes some additional empirical corrections.[31] The enthalpies of the gas-phase species were estimated according to the atomization energy method.[32]



Calculation of Energetic Performance

All calculations regarding the detonation parameters were carried out using the program package EXPLO5 V6.03.^[21] The detonation parameters were calculated at the CJ point with the aid of the steady-state detonation model using a modified Becker–Kistiakowski–Wilson equation of state for modeling the system. The CJ point is found from the Hugoniot curve of the system by its first derivative. The specific impulses were calculated with the EXPLO5 V6.02^[20] program, assuming an isobaric combustion of a composition of 70% or 65% oxidizer, 15% or 20% aluminum as fuel, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile as binder and 2% bisphenol A ether as epoxy curing agent. A chamber pressure of 70.0 bar and an ambient pressure of 1.0 bar with frozen equilibrium expansion conditions were assumed for the calculations.

Synthesis

CAUTION! Some of the prepared compounds are energetic materials with sensitivity toward heat, impact, and friction. No hazards occurred during preparation and manipulation. However, additional proper protective precautions (face shield, leather coat, earthed equipment and shoes, Kevlar gloves, and ear plugs) should be used when undertaking work with these compounds.

1,3,5,7-Tetrabromoadamantane (1): Bromine (21 mL, 65.14 g, 408 mmol) and anhydrous aluminum chloride (4.95 g, 37 mmol) were added to a 100 mL three-necked round-bottomed flask equipped with a water condenser, magnetic stirrer, and a rubber septum connected to a nitrogen inlet. The mixture was cooled to $5\,^{\circ}C$ with an ice bath and adamantane (5.00 g, 37 mmol) was added over a period of 30 min with constant stirring. The suspension was refluxed at 70°C for 24 h leading to vigorous HBr evolution. Excess bromine was distilled off and the residue was treated with aqueous sodium sulfite and 50 mL of a 6 м HCl solution. The precipitate was filtered off, washed with water, and air dried. Recrystallization from glacial acetic acid yielded 1 as a light beige crystalline product (12.27 g, 74%). ¹H NMR (CDCl₃) δ = 2.64 ppm (s, 12 H, CH₂); ¹³C{¹H} NMR (CDCl₃) δ = 54.8 (CBr), 54.6 ppm (CH₂); elemental analysis C₁₀H₁₂Br₄ (451.82): calcd C 26.56, H 2.67%; found C 26.58, H 2.73 %; MS (DEI+) [m/z]: 452.7 [M+H⁺]; IR (ATR): $\tilde{\nu}$ = 2958 (vw), 2936 (vw), 2858 (vw), 1450 (vw), 1440 (w), 1315 (s), 1246 (vw), 1211 (m), 984 (w), 937 (vw), 900 (vw), 856 (vw), 842 (vs), 762 (vw), 738 (vw), 715 (vs) cm⁻¹; Raman (500 mW): $\nu = 2969$ (21), 2931 (8), 2860 (2), 1433 (11), 1319 (11), 1212 (17), 1039 (3), 1022 (29), 1013 (12), 986 (23), 844 (32), 717 (28), 488 (3), 267 (50), 229 (4), 215 $(100) \text{ cm}^{-1}$.

1,3,5,7-Tetrahydroxyadamantane (2):^[33] Silver sulfate (13.97 g, 44 mmol) and 1,3,5,7-tetrabromoadamantane (1) (9.07 g, 20 mmol) were finely crushed in a mortar under exclusion of moisture. The resulting mixture was suspended in concentrated sulfuric acid (18.90 mL) and heated to 80 °C for 30 min, followed by 1 h by 50 °C. The suspension was cooled to room temperature and the precipitated silver bromide was filtered off and washed with water. The filtrate was neutralized with potassium hydroxide and evaporated to dryness. The solid residue was extracted with boiling methanol (1 L) and filtered through silica gel, and the solvent was removed to yield **2** as a colorless solid product (1.14 g, 30%). ¹H NMR ([D₆]DMSO) δ = 69.4 (COH), 52.1 ppm (CH₂); MS (DEI +) [*m*/*z*]: 200.2 [*M*]⁺; IR (ATR): \tilde{v} = 3234 (m, br), 2944 (w), 2924 (vw), 2862 (vw), 2642 (vw), 1652 (vw), 1456 (w), 1434 (vw), 1413 (vw),

1331 (s), 1235 (m), 1204 (s), 1046 (vs), 996 (w), 967 (s), 943 (s), 840 (m), 814 (m), 762 (s) cm⁻¹; Raman (802 mW): $\nu = 2976$ (2), 2945 (100), 2900 (3), 2889 (7), 2869 (3), 2860 (10), 2271 (12), 2244 (13), 2222 (11), 2209 (10), 2197 (5), 2182 (16), 2172 (8), 2157 (14), 2148 (8), 2137 (4), 2125 (18), 2110 (6), 2092 (7), 2075 (9), 2059 (10), 2024 (10), 1437 (54), 1337 (10), 1240 (19), 1212 (3), 1200 (9), 1053 (69), 999 (20), 882 (19), 828 (6), 819 (12), 558 (66), 441 (25) cm⁻¹.

Adamantane-1,3,5,7-tetracarbamate (3): The alcohol 2 (200 mg, 1.0 mmol) was dissolved in dry acetonitrile (20 mL) and cooled to 0°C. After addition of chlorosulfonyl isocyanate (623 mg, 0.4 mL, 4.4 mmol), the ice bath was removed and stirring at room temperature was continued for 1 h. The reaction mixture was again cooled to $0\,^\circ\text{C}$ and water (10 mL) was added with caution. Once gas evolution was complete, the organic solvent was removed in vacuo and the formed precipitate was filtered and washed with water. Adamantane-1,3,5,7-tetracarbamate (3) was obtained as a colorless solid (289 mg, 78%). ¹H NMR ([D₆]DMSO) δ = 6.4 (br, 8H, NH₂), 2.34 ppm (s, 12 H, CH₂); ${}^{13}C{}^{1}H$ NMR ([D₆]DMSO) $\delta = 155.8$ (OC(O)NH₂), 76.5 (COC(O)), 44.4 ppm (CH₂); elemental analysis $C_{14}H_{20}N_4O_8$ (372.33): calcd C 45.17, H 5.41, N 15.05%; found C 44.88, H 5.42, N 14.94%; IR (ATR): $\tilde{\nu} =$ 3444 (vw), 3424 (w), 3350 (w), 3330 (w), 3267 (vw), 3205 (vw), 2966 (vw), 1734 (vw), 1679 (m), 1631 (m), 1607 (w), 1469 (vw), 1376 (s), 1321 (vs), 1288 (w), 1251 (m), 1124 (w), 1060 (vs), 1040 (s), 922 (vw), 904 (vw), 889 (vw), 832 (vw), 801 (vw), 785 (w), 728 (vw), 697 cm⁻¹ (vw); Raman (802 mW): $\tilde{v} =$ 3213 (11), 3032 (2), 3022 (8), 3006 (2), 3000 (7), 2988 (18), 2980 (8), 2967 (62), 2951 (9), 2933 (4), 2903 (16), 2878 (8), 2652 (11), 2379 (8), 2363 (8), 2331 (14), 2283 (12), 2269 (13), 2247 (14), 2218 (13), 2206 (14), 2196 (6), 2184 (19), 2167 (15), 2157 (20), 2145 (22), 2138 (5), 2126 (4), 2119 (10), 2111 (6), 2104 (4), 2098 (6), 2092 (14), 2076 (13), 2061 (21), 2043 (9), 2031 (16), 2023 (5), 2009 (8), 2002 (2), 1983 (3), 1676 (38), 1456 (12), 1444 (30), 1333 (15), 1253 (60), 1112 (23), 1070 (12), 1055 (20), 1017 (100), 1007 (3), 1000 (10), 922 (13), 889 (21), 718 (15), 614 (46), 593 (8), 400 (10), 339 (61), 299 (13), 242 (4), 236 (52) cm⁻¹; DSC (5 °Cmin⁻¹, onset): 245 °C (m.p.).

Adamantane-1,3,5,7-tetranitrocarbamate tetrahydrate (4): Nitric acid (100%, 8 mL) was added dropwise to concentrated sulfuric acid (96%, 8 mL) and the mixed acid was cooled to 0 $^\circ\text{C},$ before 3 (372 mg, 1.0 mmol) was added in small portions. The suspension was stirred for 10 min at 5 °C and 1.5 h at ambient temperature. The reaction mixture was poured onto ice water and the precipitate was filtered off, washed with small portions of cold water, and air dried. Adamantane-1,3,5,7-tetranitrocarbamate tetrahydrate (4) was obtained as a colorless solid (429 mg, 69%). ¹H NMR $([D_6]DMSO) \delta = 11.18$ (s, 4H, NH), 2.56 ppm (s, 12H, CH₂); ¹³C{¹H} NMR ([D₆]DMSO) $\delta = 147.5$ (OC(O)NH), 79.6 (COC(O)), 42.8 ppm (CH₂); ¹⁴N NMR ([D₆]DMSO) $\delta = -42$ ppm (NO₂); elemental analysis C₁₄H₁₆N₈O₁₆·4H₂O (624.39): calcd C 26.93, H 3.87, N 17.95%; found C 27.15, H 3.94, N 17.72%; IR (ATR): $\tilde{v} = 3625$ (vw), 3288 (vw), 3112 (vw), 2984 (vw), 2858 (vw), 2772 (vw), 2361 (vw), 2340 (vw), 1778 (w), 1626 (w), 1589 (vw), 1456 (vw), 1428 (vw), 1343 (w), 1327 (w), 1290 (vw), 1261 (vw), 1160 (vs), 1106 (w), 999 (m), 940 (m), 910 (vw), 838 (w), 805 (vw), 762 (w), 754 (w), 738 (w), 668 cm⁻¹ (w); Raman (802 mW): $\tilde{\nu}$ = 3002 (14), 2985 (20), 2963 (45), 2924 (6), 2908 (2), 2882 (11), 2268 (7), 2221 (7), 2186 (7), 2125 (7), 1765 (27), 1616 (3), 1608 (12), 1455 (56), 1446 (18), 1343 (100), 1335 (6), 1261 (30), 1250 (14), 1161 (5), 1145 (15), 1105 (12), 1074 (21), 1013 (85), 946 (10), 873 (44), 840 (12), 798 (8), 741 (11), 601 (20), 504 (21), 477 (13), 454 (31), 408 (11), 319 (21), 276 (9) cm⁻¹; IS: >40 J (grain size < 100 μ m); FS: 360 N (grain size < 100 μ m); ESD: 1.5 J (grain size < 100 μ m); DSC (5 °C min⁻¹, onset): 180 °C (dec.).

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Tetraguanidinium adamantane-1,3,5,7-tetranitrocarbamate (5): Tetranitrocarbamate 4 (372 mg, 1 mmol) was suspended in water (15 mL) and saturated aqueous solution of guanidinium carbonate was added slowly until the solid was completely dissolved. The solvent was evaporated under standard pressure at room temperature to obtain colorless, crystalline tetraguanidinium adamantane-1,3,5,7-tetranitrocarbamate (5) in quantitative yield. ¹H NMR ([D₆]DMSO) δ = 7.0 (br, 24 H, NH₂), 2.27 ppm (s, 12 H, CH₂); ¹³C{¹H} NMR ([D₆]DMSO) $\delta = 159.2$ (OC(O)N), 158.4 (C(NH₂)₃), 76.2 (COC(O)N), 44.5 ppm (CH₂); ¹⁴N NMR (D₂O) $\delta = -10$ (NO₂), $-302 \text{ ppm} (NH_2)$; elemental analysis $C_{18}H_{36}N_{20}O_{16}$ (788.61): calcd C 27.42, H 4.60, N 35.52 %; found C 27.20, H 4.64, N 35.27 %; IR (ATR): $\tilde{\nu}\!=\!3419$ (w), 3330 (w), 3184 (w), 1653 (s), 1563 (w), 1559 (w), 1507 (vw), 1457 (vw), 1396 (w), 1316 (w), 1262 (w), 1208 (s), 1074 (vs), 1004 (s), 952 (m), 801 (m), 782 (m), 740 (m) cm⁻¹; Raman (802 mW): $\nu = 3037$ (2), 2983 (2), 2972 (9), 2951 (3), 2878 (5), 1699 (16), 1569 (6), 1447 (11), 1398 (6), 1334 (7), 1255 (10), 1133 (4), 1090 (7), 1069 (5), 1011 (100), 979 (23), 875 (28), 841 (4), 805 (8), 771 (4), 620 (6), 528 (13), 400 (4), 335 (13) cm⁻¹; IS > 40 J (grain size 100–500 µm); FS: 360 N (grain size 100-500 µm); ESD: 1.5 J (grain size 100-500 μm); DSC (5 °C min⁻¹, onset): 215 °C (dec.).

Tetraammonium adamantane-1,3,5,7-tetranitrocarbamate trihydrate (6): The tetranitrocarbamate 4 (372 mg, 1 mmol) was suspended in water (15 mL) and aqueous ammonia (25%, 0.5 mL) was added slowly until no precipitate remained. After evaporation of the solvent, colorless tetraammonium salt 6 was obtained as a trihydrate in quantitative yield. ¹H NMR ([D₆]DMSO) δ = 7.13 (s, 16 H, NH₄⁺), 2.29 ppm (s, 12 H, CH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]DMSO) $\delta\!=\!159.6$ (OC(O)N), 78.3 (COC(O)N), 42.8 ppm (CH_2); ^{15}N NMR ([D_6]DMSO) $\delta\!=$ -7.8 (NO₂), -130.9 (NNO₂), -358.6 ppm (NH₄⁺); elemental analysis C₁₄H₂₈N₁₂O₁₆·3 H₂O (674.49): calcd C 24.93, H 5.08, N 24.92%; found C 25.16, H 5.00, N 24.28%; IR (ATR) $\tilde{\nu} = 3197$ (vw), 1715 (w), 1653 (vw), 1636 (vw), 1559 (vw), 1540 (vw), 1506 (vw), 1404 (m), 1349 (w), 1300 (w), 1252 (vw), 1189 (vs), 1081 (vs), 1007 (s), 971 (w), 918 (w), 840 (w), 787 (m), 765 (m), 747 (w) cm⁻¹; Raman (802 mW): $\nu =$ 3021 (7), 2977 (32), 2956 (5), 2914 (6), 2886 (15), 1699 (34), 1462 (30), 1450 (11), 1373 (7), 1341 (24), 1302 (27), 1261 (27), 1219 (7), 1196 (18), 1132 (19), 1091 (18), 1070 (30), 1013 (49), 972 (88), 877 (100), 844 (19), 815 (7), 794 (13), 622 (8), 590 (11), 523 (13), 490 (11), 407 (12), 323 (26), 230 (38) cm⁻¹; DSC (5°C min⁻¹, onset): 152 °C (dec.).

Adamantane-1,3,5,7-tetranitrate (7):^[9] 1,3,5,7-Tetrahydroxyadamantane (2) (200 mg, 1.0 mmol) was added to concentrated sulfuric acid (96%, 1.3 mL) at 0°C. Methylene chloride (6.7 mL) was added to the suspension, which was then cooled to -21 °C. Concentrated nitric acid (100%, 1.1 mL) was dropped to the mixture and agitated for 30 min while warming up to 0 °C. After the addition of ice water (2.0 mL), the organic layer was separated, washed with brine (2×10 mL), and dried over magnesium sulfate. After evaporation to dryness and recrystallization from *n*-butanol, adamantane-1,3,5,7-tetranitrate (7) (270 mg, 71%) was obtained as a colorless, crystalline product. ¹H NMR (CDCl₃) $\delta = 2.57$ ppm (s, 12 H, CH₂); ¹³C{¹H} NMR (CDCl₃) δ = 83.8 (CONO₂), 40.7 ppm (CH₂); ¹⁴N NMR (CDCl₃) $\delta = -48 \text{ ppm}$ (ONO₂); elemental analysis C₁₀H₁₂N₄O₁₂ (380.22): calcd C 31.59, H 3.18, N 14.74%; found C 31.63, H 3.18, N 14.62%; IR (ATR): $\tilde{\nu} = 2907$ (vw), 2360 (vw), 2327 (vw), 1622 (s), 1471 (vw), 1337 (w), 1278 (vs), 1243 (m), 1098 (vw), 1074 (vw), 1055 (vw), 1019 (vw), 1003 (w), 953 (w), 939 (m), 927 (m), 855 (vs), 818 (vs), 751 (m), 736 (m), 703 cm⁻¹ (m); Raman (502 mW): $\tilde{\nu} =$ 3015 (34), 2996 (10), 2965 (69), 2927 (4), 2903 (8), 2885 (2), 1663 (5), 1648 (26), 1621 (13), 1457 (33), 1448 (17), 1340 (19), 1301 (36), 1244 (43), 1097 (30), 1079 (6), 1067 (12), 1005 (33), 954 (4), 942 (6), 914 (3), 889 (100), 865 (13), 842 (16), 823 (3), 756 (3), 740 (21), 712 (12), 688 (10), 678 (18), 662 (11), 506 (2), 493 (7), 478 (3), 412 (13), 343 (36), 307 (11), 283 (9), 268 (14), 246 (34), 227 (79) cm⁻¹; *I*S: 10 J (grain size < 100 μ m); *FS*: 360 N (grain size < 100 μ m); *ESD*: 0.15 J (grain size < 100 μ m); DSC (5 °C min⁻¹, onset): 136 °C (m.p.), 173 °C (dec.).

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Conflict of interest

The authors declare no conflict of interest.

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