# Two Outstanding Explosives Based on 1,2-Dinitroguanidine: Ammoniumdinitroguanidine and 1,7-Diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6triazaheptane

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**Abstract.** Ammonium-dinitroguanidine (**ADNQ**) and 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (**APX**) have been synthesized in high yield and purity. Both compounds were characterized by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N) and vibrational spectroscopy. The molecular structures were elucidated by single-crystal X-ray diffraction. **ADNQ** crystallizes in the monoclinic space group  $P2_1/c$  with a crystal density of  $\rho = 1.735$  g·cm<sup>-3</sup>, **APX** in the orthorhombic space group *Pbnc* with a crystal density of  $\rho = 1.911$  g·cm<sup>-3</sup>. **ADNQ** decomposes at 197 °C, **APX** at 174 °C. Impact (IS), friction (FS) and electrostatic discharge (ESD) sensitivities were determined experimentally for both compounds. (**ADNQ**: IS  $\geq 10$  J, FS  $\geq 252$  N and ESD  $\geq 0.4$  J,

# Introduction

Exceeding the detonation performance of known explosives like RDX (1,3,5-trinitro-1,3,5-hexahydrotriazine) is a long term goal in the research of new energetic compounds. The development of strained cages like CL-20 (HNIW: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaiso-wurzitane) [1a] or ONC (octanitrocubane) [1b] has attracted lots of interest, however both materials bear several drawbacks. The presence of polymorphs as well as a costly preparation makes both compounds unlikely to find contemporary application. These caged, highly nitrated compounds like HNB (hexanitrobenzene) showed most promising properties, but often the chemical stability towards acids or bases is insufficient. As the material density is the key for good performing high explosives a different approach was started with the concept of zwitterionic structures. A model capable for these requirements is 1,2-dinitroguanidine (DNQ), which was previously reported in literature and well described [2a-f]. The crystallographic characterization of DNQ illustrates different nitro group surroundings, contrary to dissolved DNQ which shows rapid prototropic tautomerism. The presence of an acidic nitramine ( $pK_a = 1.11$ )

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Energetic Materials Research Ludwig-Maximilian University Butenandtstr. 5–13 (D) 81377 Munich, Germany **APX:** IS  $\geq$  3 J, FS  $\geq$  80 N and ESD  $\geq$  0.1 J). Polymer bonded mixtures of **APX** with 5 % PVAA resin proved to be less sensitive towards mechanical stimuli (IS  $\geq$  5J, FS = 160 N). The detonation parameters (EXPLO5 code) were calculated using combined quantum chemical (CBS-4M) methods and a chemical equilibrium calculation based on the steady-state model of detonation: **ADNQ** ( $V_{det} = 9066 \text{ m}\cdot\text{s}^{-1}$ ,  $p_{C-J} =$ 332 kbar,  $Q_v = -5193 \text{ kJ}\cdot\text{kg}^{-1}$ ), **APX** ( $V_{det} = 9540 \text{ m}\cdot\text{s}^{-1}$ ,  $p_{C-J} = 395$ kbar,  $Q_v = -5935 \text{ kJ}\cdot\text{kg}^{-1}$ ). The experimentally determined detonation velocity (fibre optic technique) agrees well with the theoretical values, indicating that **APX** shows better detonation performance than HMX (1,3,5,7-Tetranitro-1,3,5,7-tetraazoctane).

[2a] in DNQ makes it possible to produce monoanionic dinitroguanidine salts. Furthermore nucleophilic substitution reactions with the dinitroguanidine anion are reported in literature.

# **Results and Discussion**

# Synthesis

1,2-Dinitroguanidine (1) was synthesized as reported by *As*trafyev [2a]. As it is known that strong nucleophiles like hydrazine or ammonia can substitute nitramine groups at elevated temperatures, **ADNQ** was produced from a stoichiometric amount of ammonium carbonate to avoid free base. 1,7-Diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triaza-heptane (**APX**) was synthesized according to the method of *Astrafyev* [2a], starting from 1,3-bis(chloromethyl)nitramine (2) and potassium dinitroguanidine (3). The former compound is readily available starting from the nitrolysis of hexamine with subsequent chlorination [3] (Scheme 1).

## X-ray Diffraction Structures

To obtain suitable crystals for X-ray diffraction, **APX** was recrystallized from an acetone chloroform mixture by slow evaporation of the solvent at room temperature. In the case of **ADNQ** recrystallization from an ethanol water mixture yielded crystalline material. Data sets were collected with an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector using the Crys-Alis CCD software [4]. The data re-



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Scheme 1. Synthesis of ADNQ and APX.

duction was performed with Crys-Alis RED software [5]. Structures were solved using the software packages implanted in WinGX [6–9] and finally checked by using PLATON [10]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were located from difference Fourier elec-

Table 1. Crystallographic data and parameters.

	ADNQ	APX
Formula	CH <sub>6</sub> N <sub>6</sub> O <sub>4</sub>	C <sub>4</sub> H <sub>8</sub> N <sub>12</sub> O <sub>10</sub>
Formula Mass /g•mol <sup>-1</sup>	166.09	384.18
Crystal system	Monoclinic	Orthorhombic
Space Group	$P2_1/c$ (No. 14)	Pbcn (No. 60)
Color / Habit	colorless cubic	colorless platelet
Size /mm	$0.4 \times 0.3 \times 0.28$	$0.11 \times 0.08 \times 0.02$
a /Å	10.7925	8.9909(18)
b /Å	6.2994	6.3392(13)
c /Å	10.6651	23.4311(47)
$\beta$ /°	118.679	90
$V/Å^3$	636.13(8)	1335.5(5)
Ζ	4	4
$\rho_{\rm calcd.}/{\rm g}\cdot{\rm cm}^{-3}$	1.735	1.911
$\mu / \text{mm}^{-1}$	0.17	0.183
F(000)	344	784
$\lambda \operatorname{Mo} K_{\alpha} / \operatorname{\AA}$	0.71073	0.71073
T/K	173	200
$q_{\min-\max}$ /°	4.30-26.00	3.48-25.34
Dataset $h$ ; $k$ ; $l$	-13:11; -5:7; -10:13	-10:10; -7:7; -28:28
Reflect. coll.	3026	7353
Independ. refl.	1240	1221
Reflection obs.	839	1038
No. parameters	124	135
$R_1 / R_1 \ (I > 2 \ \sigma)$	0.0331 / 0.0589	0.0389/ 0.0472
$wR_2 / wR_2 \ (I > 2 \ \sigma)$	0.0676 / 0.0724	0.1024/ 0.1077
S	0.891	1.157
Resd. Dens /e•Å <sup>-3</sup>	0.19 / -019	0.214/ -0.266
CCCD	757221	757222

Table 2.	Bond	lengths	and	bond	angles	of Al	PX.
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atoms	bond length	atoms	bond length
O3–N3	1.234(2) Å	O4-N3	1.242(2) Å
O5-N7	1.229(2) Å	N6-N7	1.375(4) Å
N6-C1	1.447(2) Å	O1-N2	1.220(2) Å
N7-O5	1.229(2) Å	N4-C2	1.335(3) Å
N4-N3	1.362(2) Å	O2-N2	1.220(2) Å
N1-N2	1.396(3) Å	N1-C2	1.419(3) Å
N1C1	1.470(3) Å	N5-C2	1.297(3) Å
N5–H5B	0.85(3) Å	N5–H5A	0.93(3) Å
C1–H1A	0.95(3) Å	C1–H1B	0.95(3) Å
atoms	bond angle	atoms	bond angle
N7-N6-C1	118.0(1)°	C1-N6-C1	124.0(3)°
O5-N7-O5	126.4(3)°	O5-N7-N6	116.8(1)°
C2-N4-N3	117.4(2)°	N2-N1-C2	121.4(2)°
N2-N1-C1	115.0 (2)°	C2-N1-C1	121.3(2)°
C2-N5-H5B	118.0 (2)°	C2-N5-H5A	113.5(2)°
H5B-N5-H5A	128.0 (3)°	O1-N2-O2	125.5 (2)°
O1-N2-N1	115.9(2)°	O2-N2-N1	118.5 (2)°
N6-C1-N1	111.5(2)°	N6-C1-H1A	109.2(1)°
N1-C1-H1A	106.2(1)°	N6-C1-H1B	108.9(1)°
N1-C1-H1B	109.1(1)°	H1A-C1-H1B	112.0 (2)°
N5-C2-N4	129.9(2)°	N5-C2-N1	119.4 (2)°
N4-C2-N1	110.7(2)°	O3-N3-O4	121.9(2)°
O3-N3-N4	115.0 (2)°	O4-N3-N4	123.1 (2)°

Table 3. Bond lengths and bond angles of ADNQ.

atoms	bond length	atoms	bond length
O1-N4	1.247(2) Å	O4-N5	1.253(2) Å
O2-N4	1.246 (2) Å	O3-N5	1.253(2) Å
N2-H2B	0.94(2) Å	N2-H2A	0.99(2) Å
N2-H2C	0.90(2) Å	N2-H2D	0.88(3) Å
N4-N6	1.348 (2) Å	N6-C1	1.360(2) Å
N3-N5	1.325(2) Å	N3-C1	1.377(2) Å
N1-H1A	0.82(2) Å	N1C1	1.306(2) Å
N1-H1B	0.87(2) Å		
atoms	bond angle	atoms	bond angle
H2B-N2-H2A	114.0(2)°	H2B-N2-H2D	112.0 (2)°
H2A-N2-H2D	109.2(2)°	H2B-N2-H2C	106.8(2)°
H2A-N2-H2C	109.1(2)°	H2D-N2-H2C	105(2)°
O2-N4-O1	120.2(1)°	O2-N4-N6	124.70(1)°
O1-N4-N6	115.1(1)°	N4-N6-C1	118.20(1)°
N5-N3-C1	118.9(1)°	O3-N5-O4	118.96(2)°
O3-N5-N3	125.0(1)°	O4-N5-N3	115.98(1)°
C1-N1-H1A	115.3(1)°	C1-N1-H1B	119.2(1)°
H1A–N1–H1b	125.3(2)°	N1-C1-N6	127.52(2)°
N1C1N3	125.85(2)°	N6-C1-N3	106.61(2)°

tron density maps and refined isotropically. The structure solution and refinement are tabulated in Table 1. Bond lengths and angles are given in Table 2 and Table 3, whereas the hydrogen bonding system is shown in Table 4 and Table 5. Further information concerning the crystal structure determinations in CIF formal are deposited at the Cambridge Crystallographic Data Centre [11] and are available free of charge (**ADNQ**: CCDC-757221, **APX**: CCDC-757222).

**APX** crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell and a density of  $1.911 \text{ g} \cdot \text{cm}^{-3}$ . The molecular structure is shown in Figure 1,

Table 4. Hydrogen bonds present in APX.

D–H···A	d(H–A)	<i>d</i> (H···A)	<dha< th=""><th><math>d(D \cdots A)</math></th></dha<>	$d(D \cdots A)$
N5–H5B…O2	0.853 Å	2.076 Å	119.03°	2.599 Å
N5-H5A…O4	0.934 Å	1.827 Å	130.97°	2.540 Å
N5–H5B…O4 <sup>a)</sup>	0.853 Å	2.350 Å	118.83°	2.861 Å
N5-H5A····O3 <sup>b)</sup>	0.934 Å	2.564 Å	125.26°	3.196 Å
N5–H5B…O2 <sup>c)</sup>	0.853 Å	2.367 Å	134.01°	3.023 Å

Symmetry code: a) [x-1/2, -y+3/2, -z]; b) [x-1/2, -y+3/2, -z]; c) [x+3/2, y+1/2, z].

Table 5. Hydrogen bonds present in ADNQ.

D–H…A	d(H–A)	<i>d</i> (H···A)	<dha< th=""><th><math>d(D \cdots A)</math></th></dha<>	$d(D \cdots A)$
N1–H1A…N6 <sup>a)</sup>	0.816 Å	2.567 Å	127.60°	3.132 Å
N1–H1B…O1 <sup>a)</sup>	0.866 Å	2.315 Å	122.76°	2.877 Å
N2-H2B····O1 <sup>b)</sup>	0.936 Å	1.974 Å	171.71°	2.903 Å
N2-H2B…O2 <sup>b)</sup>	0.936 Å	2.466 Å	129.11°	3.141 Å
N2–H2A…O4 <sup>c)</sup>	0.986 Å	1.897 Å	174.68°	2.881 Å
N2-H2D····O3 d)	0.883 Å	2.132 Å	151.22°	2.937 Å
N2–H2D…O4 <sup>d)</sup>	0.883 Å	2.436 Å	135.07°	3.125 Å
N1-H1A…O3	0.816 Å	1.942 Å	133.49°	2.572 Å
N1-H1B…O2	0.866 Å	1.951 Å	126.58°	2.563 Å
N2-H2C…N6	0.902 Å	2.486 Å	132.72°	3.168 Å
N2-H2C···N3	0.902 Å	2.095 Å	164.84°	2.975 Å

Symmetry codes: a) [x, -y+1/2, z-1/2]; b) [-x+1, y+1/2, -z+1/2]; c) [-x, -y+1, -z]; d) [-x, y+1/2, -z-1/2].

bond lengths and angles are given in Table 2. The zwitterionic bonding situation agrees well with the crystallographic observed bond lengths. The typical bond length for conjugated guanidine systems (1.328 Å) [12] agree perfectly with the C2–N4 bond length (1.335(3) Å), valuating this bond in between a single and a double bond. The C2–N5 bond length is shortened to 1.297(3) Å, which is in accordance with the reported value for  $C_{sp}^2$  = N-double bonded systems (1.279 Å) [12]. The C2–N1 bond length (1.419(3) Å) can be evaluated as a typical single bond, as the reported value for  $C_{sp}^2$ –N systems is 1.416 Å in literature [12]. The bond lengths for C1–N1 (1.470(3) Å) and C1–N6 (1.447(2) Å) fit for  $C_{sp}^3$ –N systems quite well [12].



Figure 1. Molecular Structure of APX, ellipsoids of non-hydrogen atoms are displaced with 50 % probability level.

N–N bond lengths are in the known magnitude for nitramines as reported [13] ranging from 1.3624(2) Å to



1.3956(2) Å. The hyperconjugative effect, which is well known for nitramines is most significant for the N3-N4 bond. The shortening of the bond is a consequence of the favored zwitterionic form in the crystalline state. The description of the crystal structure is strongly connected to the presence of hydrogen bonds, which are shown in Figure 2 and listed in Table 4. Besides the intramolecular hydrogen bonds in a dinitroguanidine unit, there are three different kinds of hydrogen bonding present. The intermolecular hydrogen bonds N5-H5B···O4 and N5-H5A···O3 are highly directional and due to the zwitterionic character. This results in dimer formation of two APX units as basic building block (see Figure 2), which is elongated in the crystal to wavelike strings. In between this layers the N5-H5B...O2 hydrogen bond works like a cross linker, see Figure 3. A consequence of this interaction is the twisting of one nitro group out of the dinitroguanidine unit by a torsion angle of 13.5°.



Figure 2. Selected hydrogen bonds of APX: Dimer formation.



Figure 3. Wavelike arrangement of **APX** with all hydrogen bonds present (view along *a* axis).

Besides the described hydrogen bond interactions, additional ionic interactions can be discussed. As the inner nitramine (N6–N7) is not capable to hydrogen bonding it arranges in a way to be surrounded by electropositive charged parts of the molecule.

**ADNQ** crystallizes in the monoclinic space group  $P_{1/c}$  with four molecules in the unit cell and a crystal density of 1.735 g·cm<sup>-3</sup> (Figure 4). The C–N bond length for C1–N1 (1.306(2) Å) is significantly shorter as for C1–N3 (1.377(2) Å) and C1–N6 (1.360(2) Å). This evidences that a zwitterionic description with charge separation is probably the best way to describe the bonding situation inside the dinitroguanidine anion. The N–N bond lengths for the deprotonated nitramines are 1.3484(19) Å and 1.3250(19) Å, which stands for a slight hyperconjugative effect. Interestingly, the dinitroguanidine anion loses its planarity, as one nitro group is twisted out of the plane by 11.8°. Reasonable for this phenomenon is a competition of hydrogen bonds: Intramolecular vs. intermolecular to the ammonium cation.



Figure 4. Molecular Structure of ADNQ, ellipsoids of non-hydrogen atoms are displaced with 50 % probability level.

The crystal structure of **ADNQ** can be described best as wavelike formation of layers (see Figure 5). In between these layers the N2–H2C–N6 and N2–H2C–N3 hydrogen bonds are crosslinking (Figure 6).



Figure 5. Wavelike arrangement of ADNQ with N–H…N interaction between the layers.



Figure 6. Hydrogen bonds present in ADNQ, light dashes are inside the wave layer, thick ones in between the layers.

### Thermal and Energetic Properties

Differential scanning calorimetry (DSC) measurements to determine the decomposition temperatures of **APX** and **ADNQ** were performed in covered aluminum containers containing a hole in the lid with a nitrogen flow of 20 mL·min<sup>-1</sup> on a Linseis PT10 DSC [14] calibrated by standard pure indium and

zinc at a heating rate of 5 °C·min<sup>-1</sup>. The DSC plot shown in Figure 7 indicates that decomposition of **APX** is starting at an onset temperature of 174 °C. In contrast to this behavior the decomposition temperature of the ionic compound **ADNQ** is raised to 197 °C. Both compounds were tested according to UN3c standard in a Systag, FlexyTSC Radex Oven at 75 °C for 48 hours with the result, that no weight loss or decomposition products were detected.



**Figure 7.** DSC thermogram for **APX** and **ADNQ** with a heating rate of  $\beta = 5$  °C·min<sup>-1</sup>.

### **Theoretical Calculations**

All calculations were carried out using the Gaussian G03W (revision B.03) program package [15]. The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models use 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-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of minimal population localization) which is a reparametrized version of the original CBS-4 method and also includes some additional empirical corrections [16a,b]. The enthalpies of the gas-phase species M were computed according to the atomization energy method [Equation (1)] (Table 6, Table 7, and Table 8) [17a-c].

$$\Delta_{\rm f} H^{\rm o}_{\rm (g, M, 298)} = H_{\rm (Molecule, 298)} - \sum H^{\rm o}_{\rm (Atoms, 298)} + \sum \Delta_{\rm f} H^{\rm o}_{\rm (Atoms, 298)}$$
(1)

The solid state energy of formation (Table 9) of **APX** was calculated by subtracting the gas-phase enthalpy with the heat of sublimation (19.2 kcal·mol<sup>-1</sup>) obtained by the *Troutman* rule  $(\Delta H_{sub} = 188 \cdot T_m)$  [19a,b]. In the case of **ADNQ**, the lattice energy  $(U_L)$  and lattice enthalpy  $(\Delta H_L)$  were calculated from the corresponding molecular volumes (Table 10) according to the equations provided by *Jenkins* [20a,b]. With the calculated lattice enthalpy (Table 11) the gas-phase enthalpy of formation (Table 8) was converted into the solid state (standard conditions) enthalpy of formation (Table 6). These molar standard enthalpies of formation  $(\Delta H_m)$  were used to calculate the molar solid state energies of formation  $(\Delta U_m)$  according to Equation (2) (Table 9).

Table 6. CBS-4M results.

	point group	el. state	-H <sup>298</sup> /a.u.	NIMAG
APX	Cs		1564.066859	0
$NH_4^+$	$T_{\rm d}$	${}^{1}A_{1}$	56.796608	0
DNQ <sup>-</sup>	$\tilde{C_s}$	$^{1}A$	613,123370	0
Н	-	$^{2}A_{1\sigma}$	0.500991	0
С		-6	37.786156	0
Ν		${}^{4}A_{1\sigma}$	54.522462	0
0		-8	74.991202	0

**Table 7.** Literature values for atomic  $\Delta H^{\circ}_{f}^{298}$  /kcal·mol<sup>-1</sup>.

	NIST [18]	
Н	52.1	
С	171.3	
Ν	113.0	
0	59.6	

Table 8. Enthalpies of the gas-phase species M.

М	М	$\Delta_{\rm f} H^{\circ}({\rm g,~M}) / {\rm kcal \cdot mol}^{-1}$
APX	C <sub>4</sub> H <sub>8</sub> N <sub>12</sub> O <sub>10</sub>	+392.6
$\mathrm{NH_4}^+$	$\mathrm{NH_4}^+$	+151.8
DNQ <sup>-</sup>	$CH_2N_5O_4^-$	-24.3
NH4 <sup>+</sup> DNQ <sup>-</sup>	CH <sub>6</sub> N <sub>6</sub> O <sub>4</sub>	+127.5

 $\Delta U_{\rm m} = \varDelta H_{\rm m} - \Delta n \ {\rm R}T \tag{2}$ 

 $(\Delta n$  being the change of moles of gaseous components)

### **Detonation Parameters**

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.03) [21]. The program is based on the chemical equilibrium, steady-state model of detonation. It uses the *Becker-Kistiakowsky-Wilson*'s equation of state (BKW EOS) for gaseous detonation products and *Cowan-Fickett's* equation of state for solid carbon [22]. The calculation of the equilibrium composition of the detonation products is done by applying modified *White, Johnson* and *Dantzig's* free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters ( $\alpha$ ,  $\beta$ ,  $\kappa$ ,  $\theta$ ) as stated below the equations and  $X_i$  being the mol fraction of *i*-th gaseous product,  $k_i$  is the molar covolume of the *i*-th gaseous product [22]:

$$pV / RT = 1 + xe^{\beta x} x = (\kappa \Sigma X_i k_i) / [V (T + \theta)]^{\alpha}$$

 $\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620.$ 

The detonation parameters calculated with the EXPLO5 program using the experimentally determined densities (X-ray) are summarized in Table 12.

Table 10. Molecular volumes.

	$V_{\rm M}$ /Å <sup>3</sup>	$V_{\rm M}$ /nm <sup>3</sup>
NH4 <sup>+</sup>	21.0 [20]	0.021
DNQ <sup>-</sup>	138.0 <sup>a)</sup>	0.138
ADNQ	159.0	0.159

a) From X-ray data (**ADNQ**) V = 636.1, Z = 4; NH<sub>4</sub><sup>+</sup> from literature [20].

### Table 11. Lattice energies and lattice enthalpies.

	$V_{\rm M}$ /nm <sup>3</sup>	$U_{\rm L}$ /kJ·mol <sup>-1</sup>	$\Delta H_{\rm L} / \rm kJ \cdot \rm mol^{-1}$	$\Delta H_{\rm L} / \rm kcal \cdot mol^{-1}$
ADNQ	0.159	536.8	540.3	129.0

### Table 12. Detonation parameters.

	APX	<b>APX</b> + 5 % PVAA	ADNQ
$\rho / \text{g-cm}^{-3}$	1.911	1.875	1.735
$\Omega'/\%$	-8.33	-16.28	-9.63
$Q_{\rm v}'/{\rm kJ}\cdot{\rm kg}^{-1}$	-5935	-5878	-5193
$T_{\rm ex}/{\rm K}$	4489	4377	3828
$p_{C-I}$ /kbar	398	373	327
$V_{\rm det} / \rm m \cdot s^{-1}$	9540	9211	9066
$V_0/L \cdot kg^{-1}$	816	784	934

### **Electrostatic Potential**

The electrostatic potential of **APX** is illustrated using Gauss-View 4.1 [23]. Figure 8 (grayscale) as well as the cover picture of this issue (color) show the 0.001 electron bohr<sup>-3</sup> 3D isosur-

**Table 9.** Solid state energies of formation  $(\Delta_f U^\circ)$ .

	$\Delta_{\rm f} H^{\circ}({\rm s}) / {\rm kcal} \cdot {\rm mol}^{-1}$	$\Delta_{\rm f} H^{\circ}({\rm s}) / {\rm kJ} \cdot {\rm mol}^{-1}$	$\Delta n$	$\Delta_{\rm f} U^{\circ}({\rm s}) / {\rm kJ} \cdot {\rm mol}^{-1}$	$M/g\cdot mol^{-1}$	$\Delta_{\rm f} U^{\circ}({\rm s}) / {\rm kJ} \cdot {\rm kg}^{-1}$
APX	65.0	272.1	-15	309.3	384.24	805.0
ADNQ	-1.5	-6.4	-8	13.5	166.13	81.0

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**Figure 8.** Calculated (CBS-4M) electrostatic potential of **APX** showing two different orientations. The dark grey regions represent electron rich regions, the black regions extremely electron-deficient regions.

face of electron density for **APX** with an electrostatic potential contour value of 0.05 hartree. The red regions represent extremely electron-rich regions ( $V(\mathbf{r}) < 0.05$  hartree) and the blue regions extremely electron-deficient regions ( $V(\mathbf{r}) > 0.05$  hartree). In general, the patterns of the calculated electrostatic potentials of the surface of molecules can be related to the impact sensitivities [24, 25a,b]. In contrary to non energetic organic molecules, where the positive potential is larger but weaker in strength, in nitro and azo compounds usually more extensive regions with larger and stronger positive potentials are observed which can be related to the increased impact sensitivities (see below).

### Sensitivities

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined [26]. The impact sensitivity tests were carried out according to STANAG 4489 [27] modified according to instruction [28] using a BAM (Bundesanstalt für Materialforschung) [29] drophammer [30]. The friction sensitivity tests were carried out according to STANAG 4487 [31] modified according to instruction [32] using the BAM friction tester. The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package" [33]. According to the UN recommendations [34] **ADNQ** is classified as *sensitive* towards impact and friction (IS: 10 J, FS: 252 N). Electrostatic sensitivity towards discharge (ESD) was determined to be 0.4 J. **APX** should be handled like primary explosive, as the compound is *very sensitive* towards impact (3 J) or friction (80 N) and a ESD of 0.1 J. Desensitizing of high explosives by coating or mixing with binder systems is common. Therefore we tested a mixture containing 95 % of **APX** and 5 weight% of **PVAA** (polyvinyl alcohol acetate) resin towards mechanical stimuli. Impact sensitivity was reduced to 5 J (*sensitive*) and friction to 160 N (*sensitive*). Optimization of the plastic bonded explosives with curing agents and for example HTPB (hydroxyl terminated polybutadien binder) should be an effective way for desensitizing the material.

## **Detonation Parameters**

Especially the detonation parameters of **APX** show to be very promising exceeding those of TNT and RDX and in part even those of HMX. The most important criteria of high explosives are detonation velocity ( $V_{det.} = APX$ : 9540, **ADNQ**: 9066, TNT: ~7178, RDX: 8906, HMX: 9324 m·s<sup>-1</sup>), detonation pressure ( $p_{C-J.} = APX$ : 398, **ADNQ**: 327, TNT: 205, RDX: 346, HMX: 393 kbar) and energy of explosion ( $\Delta_E U^\circ =$ **APX**: ~5943, **ADNQ**: ~5193, TNT: 5112, RDX: ~6043, HMX: ~6049 kJ·kg<sup>-1</sup>) [21]. Due to these great values, we tried to determine the detonation velocity of **APX** experimentally.

### **Detonation Velocity Measurement of APX**

The measurement of the detonation velocity of APX was performed using the OZM detonating velocity measuring system EXPLOMET-FO-2000. The use of the fiber optic technique insures excellent electrical noise immunity (Figure 9). The system used had two independent timers measuring the time intervals (in µs) between the illumination of two adjacent optical probes and calculated the velocity of detonation  $(m \cdot s^{-1})$ . The WinExplomet software package was used to transfer the results to a PC via a serial interface. For the detonation velocity measurement a 14 mm PE tube was equipped with two optical fibers in a distance of 2.0 cm. The amount of APX used for the test was 8.5 g. APX was loaded into the PE tube and manually compressed with 80 N. As a booster charge 0.5 g of nitropenta (PETN) were added on top and carefully compressed manually. Initiation was achieved with an electrically ignited (40 V, 5 A) PETN-Pb(N<sub>3</sub>)<sub>2</sub> detonator (0.8 g PETN, 0.2 g lead azide). The experimentally determined detonation velocity of 4853 m·s<sup>-1</sup> with an explosive density of  $0.63 \text{ g} \cdot \text{cm}^{-3}$  deviates less than 1 % to the theoretical value  $(4900 \text{ m} \cdot \text{s}^{-1}).$ 

### Koenen Steel Sleeve Test

**APX** was investigated according to its explosion performance under confinement using a "*Koenen test*" steel sleeve apparatus [35, 36a,b]. Also the shipping classification of the substance can be determined and the degree of venting required to avoid an explosion during processing operations can be evaluated. The explosion is initiated via thermal ignition using







**Figure 9.** Picture series showing the detonation velocity test: A) moment of initiation; B) start of detonation; C) shockwave expansion (time gap: 0.25 s).

four *Bunsen* burners, which are started simultaneously. The test is completed when either rupture of the tube or no reaction is observed, after heating the tube for a minimal time period of at least 5 min. In case of the tube's rupture the fragments are collected and weighed. The reaction is evaluated as an explosion if the tube is destroyed into three or more pieces. The *Koenen* test was performed with 19.0 g **APX** using a closing plate with an orifice of 10 mm. The first trial was successful indicated by the rupture of the steel tube into part powder (<100  $\mu$ m) like pieces, which are depicted in Figure 10. TNT destroys the steel sleeve up to an orifice width of 6 mm, RDX and HMX even up to 8 mm [37]. Compared to these applied explosives the performance of **APX** is obviously better, which

was also computed to the higher detonation parameters than RDX and HMX.



Figure 10. Main picture: Collected fragments of the Koenen test. Left: Steel Sleeve with closing plate; right: Koenen test setup showing the four Bunsen burner.

# Conclusions

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

(i) 1,7-Diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (**APX**) and ammonium dinitroguanidine (**ADNQ**) were prepared in high yield and purity. Both compounds were fully characterized spectroscopically and structurally.

(ii) The theoretical calculations indicate that both materials, especially **APX**, have excellent properties as energetic fillers in high explosive formulations.

(iii) An experimental detonation test revealed that the detonation performance of **APX** is in agreement with the theoretical determined values.

(iv) Sensitivities for both compounds were investigated experimentally. A calculation of the electrostatic potential of **APX** fits well to the experimental determined values for the impact sensitivities. A plastic bonded mixture with PVAA resin was tested and found to be less sensitive to impact and friction.

(v) The crystal structures of **APX** and **ADNQ** were determined by X-ray diffraction and analysis of the structure parameters clearly proved the presence of a zwitterionic structure.

# **Experimental Section**

**General Procedure:** All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics). Melting points were measured with a Perkin–Elmer Pyris6 DSC, using heating rates of 5 °C·min<sup>-1</sup>. <sup>1</sup>H, <sup>13</sup>C and <sup>14</sup>N spectra were recorded with a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS (<sup>1</sup>H, <sup>13</sup>C). Infrared (IR) spectra were recorded using a Perkin–Elmer Spektrum One FT-IR instrument. Raman spectra were measured using a Bruker MULTI-RAM with a Nd:YAG laser (1064 nm). Elemental analyses were per-

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formed with a Netsch STA 429 simultaneous thermal analyzer. Mass spectra were measured on a JEOL Mstation TM MS-700 with a high-performance double focusing magnetic sector.

**CAUTION!** The prepared compounds **ADNQ** and **APX** are highly explosive compounds. Although we had no problems during synthesis and investigation, the materials should be treated with proper safety measures such as safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs.

Ammonium dinitroguanidine (ADNO): 1,2-Dinitroguandine (5.0 g, 33.6 mmol) was dissolved in warm ethanol (50 mL). To this solution, ammonium carbonate (1.61 g, 16.8 mmol) was added in small portions. Afterwards, water (10 mL) was added and the mixture was stirred until gas evolution stopped. The reaction mixture was allowed to cool to room temperature and the product precipitated as colorless crystals. ADNQ was filtered off and washed with diethyl ether (5.02 g, 90 %). <sup>1</sup>**H NMR** (d<sub>6</sub>-DMSO):  $\delta$  = 7.46 (br., 2 H, C=NH<sub>2</sub>). <sup>13</sup>**C NMR**  $(d_6$ -DMSO):  $\delta = 161.4$  (C=NH<sub>2</sub>). <sup>14</sup>N NMR  $(d_6$ -DMSO):  $\delta = -9$  $(NO_2)$ , -130  $(NNO_2)$ , -284  $(NH_2)$ , -359  $(NH_4)$ . **IR**: v = 3602 (w), 3503 (w), 3450 (s), 3415 (vs), 3392 (vs), 3316 (s), 3283 (vs), 3241 (vs), 3198 (vs), 3073 (s), 2806 (s), 1717 (w), 1659 (m), 1605 (vs), 1529 (m), 1514 (m), 1501 (m), 1409 (s), 1344 (vw), 1417 (vs), 1129 (s), 1103 (s), 1103 (s), 1070 (m), 1040 (s), 945 (m), 783 (m), 771 (w), 750 (vw), 729 (w), 668 (w), 639 (w) cm<sup>-1</sup>. **Raman** (300 mW): v =3133 (2), 1596 (24), 1346 (7), 1267 (6), 1207 (24), 1131 (100), 1052 (10), 966 (61), 792 (11), 684 (4), 549 (9), 426 (5), 361 (14), 240 (3), 199 (3), 136 (2), 113 (74), 94 (18), 80 (10) cm<sup>-1</sup>. MS (FAB+): m/z =18 (100). **MS** (FAB-): m/z = 148 (100). **EA**: C<sub>4</sub>H<sub>8</sub>N<sub>12</sub>O<sub>10</sub>. Calculated (%): C 7.23; H 3.64; N 50.60; Found (%): C 7.18, H 3.68, N 50.15. **DSC:**  $T_{dec} = 197 \text{ °C}$  (onset). Sensitivities: IS = 10 J (100–500µm), FS = 252 N (100-500µm), ESD = 0.4 J (100-500µm).

1,7-Diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (APX): Potassium 1,2-dinitroguanidine (4.22 g, 23 mmol) was suspended in acetone (30 mL) and 1,3-bis(choromethyl)nitramine (1.79 g, 11 mmol) dissolved in acetone (5 mL) was added. Afterwards, sodium iodide (150 mg) and 18-crown-6 (100 mg) was added and the colorless solution turned slightly yellow. The reaction mixture was heated under reflux for 2 hours and cooled to room temperature. The inorganic salts were filtered off and the filter cake was washed with additional acetone till colorless. The acetone solutions were evaporated to dryness and a brownish oily solid remained. This solid was treated with hot 70 % ethanol for approximately 20 minutes and the colorless fine precipitate was filtered and washed with additional ethanol (50 mL) to yield 3.69 g of 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (APX), which corresponds to a yield of 85 %. The finely powdered material can be crystallized from an acetone chloroform solution, when slow evaporation of acetone is ensured. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  = 9.93 (br., 4 H, NH<sub>2</sub>), 6.68 (s, 4 H, CH<sub>2</sub>). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO):  $\delta = 156.9$  (C=NH<sub>2</sub>), 64.5 (CH<sub>2</sub>). <sup>14</sup>N NMR (d<sub>6</sub>-DMSO):  $\delta = -17, -100$ 35, -41 (NO<sub>2</sub>), -272 (NH<sub>2</sub>). **IR**: v = 3427 (s), 3294 (s), 3053 (w), 3002(w), 2978 (w), 2899 (w), 1656 (m), 1631 (s), 1604 (s), 1564 (m), 1518 (m), 1465 (m), 1448 (m), 1399 (m), 1358 (m), 1328 (m), 1266 (s), 1243 (s), 1220 (vs), 1150 (m), 1105(m), 1028 (m), 952 (w), 920 (s), 909 (s), 869 (w), 796 (w), 776 (w), 764 (w), 748 (w), 724 (w), 676 (w), 623 (w) cm<sup>-1</sup>. **Raman** (300 mW): v = 3283 (3), 3055(5), 3007(14), 2924 (3), 1653 (11), 1588 (10), 1510 (11), 1450 (9), 1408 (21), 1377 (22), 1329 (15), 1271 (24), 1242 (23), 1200 (18), 1151 (7), 1105 (10), 1042 (14), 953 (24), 915 (7), 870 (45), 797 (16), 751 (5), 670 (8), 653 (8), 636 (12), 533 (18), 468 (8), 430 (13), 415 (11), 306 (38), 270 (9), 245 (10), 120 (100) cm<sup>-1</sup>. MS (DCI+): m/z = 385.3(0.4), 265 (33), 177(6), 168 (6), 150 (40), 105 (31), 75 (42). EA: C<sub>4</sub>H<sub>8</sub>N<sub>12</sub>O<sub>10</sub>. Calculated (%): C 12.51; H 2.10; N 43.75; Found (%): C 12.64, H 2.28, N 43.66. **Bomb Calorimetry:**  $\Delta U_c = 1783 \text{ cal} \cdot \text{g}^{-1}$ . **DSC:**  $T_{dec} = 174 \text{ °C}$  (onset). Sensitivities: IS = 3 J (< 100 µm), FS = 80 N (< 100 µm), ESD = 0.1 J (< 100 µm).

1,3-Dichloro-2-nitrazapropane (2): A two liter 3-necked flask was charged with acetic anhydride (384 mL, 4.07 mol) and cooled to 0-10 °C, while 99 % nitric acid (144 mL, 3.43 mol) was added. To this nitrating mixture a solution of hexamine (94.9 g, 0.66 mol) in acetic acid (176 mL) was added within one hour. The reaction mixture was left standing for 12 h at room temperature. The solid 1,7-diacetoxy-2,4,6-trinitrazaheprane was filtered off and the acid filtrate was diluted with dichloromethane (150 mL). The organic layer was washed with water, 16 % sodium hydroxide solution and water. After evaporation, the crude reaction product 1,3-diacetoxy-2-nitrazapropane remained and was distilled yielding 34.7 g of sufficient purity for chlorination. After dissolving this material in dioxane (60 mL), gaseous hydrogen chloride was bubbled at a temperature range of 5-15 °C through the solution for 1.5 hours. The solution was stored for 80 hours in the refrigerator and concentrated with a rotary evaporator. After distillation (b.p. 51 °C at 4  $\cdot 10^{-2}$  mbar), 20.4 g of 1,3-dichloro-2-nitrazapropane remained as a colorless liquid, which corresponds a total yield of 28 % with respect to the hexamine and 76 % with respect to the 1,3diacetoxy-2-nitrazapropane.

Potassium dinitroguanidine (3): Dinitroguanidine (1) (5.00 g, 33.5 mmol) was dissolved in warm ethanol (30 mL). To this solution potassium hydrogen carbonate (3.36 g, 33.5 mmol) dissolved in water was added dropwise whilst stirring. After the addition was completed, the solution was cooled to room temperature and stirred for additional 20 minutes, until no gas evolution appeared. The colorless solid was filtered, washed with cold ethanol (10 mL) and dried in air vielding 6.6 g of potassium dinitroguanidine, which corresponds a yield of 95 %. IR: v = 3334 (vs), 3242 (vs), 1585 (m), 1486 (m), 1455 (m), 1359 (s), 1314 (m), 1220 (s), 1130 (s), 1036 (m), 944 (w), 787 (m), 724 (vs), 677 (w), 635 (w) cm<sup>-1</sup>. **Raman** (300 mW): v = 3249 (3), 1575 (10), 1460 (30), 1386 (31), 1270 (4), 1210 (35), 1132 (100), 1042 (12), 962 (56), 795 (26), 680 (4), 544 (22), 442 (7), 367 (35), 258 (8), 221 (17), 108 (57), 87 (83), 74 (92) cm<sup>-1</sup>. EA: KCH<sub>2</sub>N<sub>5</sub>O<sub>4</sub>. Calculated (%): C 6.42; H 1.08; N 37.42; Found (%): C 6.37; H 1.10; N 36.65. **DSC:**  $T_{dec} = 174$  °C (onset). Sensitivities: IS = 9 J (100–500 $\mu$ m), FS = 160 N (100-500µm).

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# References

- a) S. V. Sysolyatin, A. A. Lobanova, Y. T. Chernikova, G. V. Sakovich, *Russ. Chem. Rev.* **2005**, *74*, 757; b) P. E. Eaton, R. L. Gilardi, M. X. Zhang, *Adv. Mater.* **2000**, *12*, 1143.
- [2] a) A. A. Astratýev, D. V. Dashko, L. L. Kuznetsov, *Russ. J. Org. Chem.* 2003, 39, 501; b) A. D. Vasiliev, A. M. Astachov, M. S. Molokeev, L. A. Kruglyakova, R. S. Stepanov, *Acta Crystallogr., Sect. C* 2003, 59, o550; c) A. M. Astachov, V. A. Sokolenko, P. V. Brovchenko, A. L. Rubailo, *Kyimiya Khimicheskaya Tekhnologiya* 2005, 48, 36; d) N. V. Latypov, M. Johansson, L. N. Yudina-Wahlstroem, S. Ek, C. Eldsaeter, P. Goede, *New Trends*

in Research of Energetic Materials, Proceedings of Seminar, 9th, Pardubice, 2006, (Pt. 1), 160; e) A. M. Astachov, V. A. Revenko, A. D. Vasiliev, A. A. Nefedov, L. A. Kruglyakova, K. P. Konstantin, R. S. Stepanov, Internation Annual Conference of ICT 2006, 173/1; f) N. V. Latypov, M. Johannson, L. N. Yudina Wahlstroem, S. Ek, C. Eldsaeter, P. Goede, Cent. Eur. J. Energetic Mater. 2007, 4, 3.

- [3] J. E. Flanagan, M. B. Frankel, US 4085123.
- [4] CrysAlis CCD, Version 1.171.27p5 beta; Oxford Diffraction Ltd.
- [5] CrysAlis RED, Version 1.171.27p5 beta; Oxford Diffraction Ltd.
- [6] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. *Appl. Crystallogr.* **1993**, *26*, 343.
- [7] SHELXS-97, Program for Crystal Structure Solution, G. M. Sheldrick, Institut f
  ür Anorganische Chemie der Universit
  ät, Tammanstrasse 4, 3400 G
  öttingen, Germany, 1994.
- [8] SHELXS-97, Program for Crystal Structure Solution, G. M. Sheldrick, Institut f
  ür Anorganische Chemie der Universit
  ät, Tammanstrasse 4, 3400 G
  öttingen, Germany, 1997.
- [9] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837.
- [10] *PLATON*, A Multipurpose Crystallographic Tool. A. L. Spek, Utrecht, The Netherlands, **1999**.
- [11] A copy of the cif files for compound APX and ADNQ can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033. E-mail for inquiry: fileserv@ccdc.cam.ac.uk. E-mail for deposition: deposit-@ccdc.cam.ac.uk).
- [12] F. H. Allen, O. Kennard, D. G. Watson, J. Chem. Soc., Perkin Trans. 1, 1987, S1.
- [13] Y. Kohno, U. A. Imamura, J. Phys. Chem. 1996, 100, 4701.
- [14] http://www.linseis.com.
- [15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision B04, Gaussian Inc., Wallingford, CT, 2004.
- [16] a) J. W. Ochterski, G. A. Petersson, J. A. Montgomery Jr., J. Chem. Phys. **1996**, 104, 2598; b) J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, J. Chem. Phys. **2000**, 112, 6532.
- [17] a) L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, J. Chem. Phys. 1997, 106, 1063; b) E. F. C. Byrd, B. M. Rice, J. Phys. Chem. A 2006, 110, 1005; c) B. M. Rice, S. V. Pai, J. Hare, Comb. Flame 1999, 118, 445.

- [18] NIST Chemistry WebBook (Eds.: P. J. Linstrom, W. G. Mallard), NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).
- [19] a) M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, J. Am. Chem. Soc. 1995, 117, 5013; b) F. Trouton, Philos. Mag. 1884, 18, 54.
- [20] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609; b) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364.
- [21] M. Sućeska, EXPLO5.3, Zagreb, Croatia, 2009.
- [22] a) M. Sućeska, *Materials Science Forum*, 2004, 465–466, 325;
  b) M. Sućeska, *Propellants Explos. Pyrotech.* 1991, 16, 197;
  c) M. Sućeska, *Propellants Explos. Pyrotech.* 1999, 24, 280;
  d) M. L. Hobbs, M. R. Baer, *Proc. of the 10th Symp. (International) on Detonation*, ONR 33395–12, Boston, MA, July 12–16, 1993, p. 409.
- [23] Gaussview 4.1.2, Gaussian, Inc.: Wallingford, CT, 2006.
- [24] B. M. Rice, J. J. Hare, J. Phys. Chem. A 2002, 106, 1770.
- [25] a) P. Politzer, J. S. Murray, J. M. Seminario, P. Lane, M. E. Grice, M. C. Concha, *J. Mol. Struct.* **2001**, *573*, 1; b) J. S. Murray, P. Lane, P. Politzer, *Mol. Phys.* **1995**, *85*, 1.
- [26] M. Suceska, *Test Methods for Explosives*, Springer, New York 1995, p. 21 (impact), p. 27 (friction).
- [27] NATO Standardization Agreement (STANAG) on explosives, impact sensitivity tests, no. 4489, Ed. 1, Sept. 17, 1999.
- [28] WIWEB-Standardarbeitsanweisung 4–5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, 2002.
- [29] http://www.bam.de.
- [30] http://www.reichel-partner.de.
- [31] NATO Standardization Agreement (STANAG) on explosive, friction sensitivity tests, no. 4487, Ed. 1, Aug. 22, 2002.
- [32] WIWEB-Standardarbeitsanweisung 4–5.1.03, Ermittlung der Explosionsgefährlichkeit or der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, 2002.
- [33] a) S. Zeman, V. Pelikán, J. Majzlík, Centr. Eur. J. Energy Mater. 2006, 3, 45; b) D. Skinner, D. Olson, A. Block-Bolten, Propellants Explos. Pyrotechn. 1997, 23, 34; c) OZM research, Czech Republic, http://www.ozm.cz/testing-instruments/pdf/TI-SmallSpark.pdf.
- [34] impact: insensitive > 40 J, less sensitive  $\ge 35$  J, sensitive  $\ge 4$  J, very sensitive  $\le 3$  J; friction insensitive > 360 N, less sensitive =360 N, sensitive < 360 N; > 80 N, very sensitive  $\le 80$  N, extreme sensitive  $\le 10$  N; According to the UN recommendations on the transport of dangerous goods (+) indicates: not safe for transport.
- [35] J. Köhler, R. Meyer, A. Homburg, *Explosives*, 6th Ed., Wiley-VCH, Weinheim, **2007**, pp. 162.
- [36] a) T. M. Klapötke, J. Stierstorfer, *Phys. Chem. Chem. Phys.* 2008, 10, 4340; b) T. M. Klapötke, J. Stierstorfer, *Dalton Trans.* 2008, 4, 643.
- [37] J. Köhler, R. Meyer, A. Homburg, *Explosives*, 6th Ed., Wiley-VCH, Weinheim, 2007, pp. 174.

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