Full Paper

Energetic Derivatives of 2-Nitrimino-5,6-dinitro-benzimidazole

Thomas M. Klapötke,*[a] Andreas Preimesser,[a] and Jörg Stierstorfer[a]

Abstract: 2-Nitrimino-5,6-dinitrobenzimidazole (**1**) was synthesized by nitration of 2-aminobenzimidazole at ambient temperature in good yield. In order to explore new insensitive explosives four energetic nitrogen-rich 1:1 salts such as the guanidinium (**1a**), aminoguanidinium (**1b**), triaminoguanidinium (**1c**) and hydroxylammonium (**1d**) were synthesized either by facile acid/base or in situ metathesis reaction. In addition 2-nitrobenzimidazole (**2**) was synthesized by the reaction of 2-aminobenzimidazole using potassium hyperoxide in THF. Different nitration methods were tested to obtain a theoretically 2,4,5,6,7-pentanitrobenzimidazole but only the already known 4,5,6,7-tetranitrobenzimidazol-2-one (**3**) could be isolated. All synthesized compounds were characterized especially by low temperature X-ray diffraction, CHN elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. The heat of formation of all new synthesized compounds was calculated using CBS-4M electronic enthalpies in combination with the atomization method to calculate their detonation parameters with the EXPLO 5 V5.05 computer code.

Keywords: Explosives · Benzimidazole · Nitration · Sensitivities · Structure elucidation

1 Introduction

Most commercially secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are toxic for human and animal organisms [1]. Therefore it is a main goal to substitute these toxic compounds. Another goal is to enhance the performance of secondary explosives which is defined by parameters like the detonation velocity (V_{det}), detonation pressure (P_{CJ}), heat of detonation ($\Delta_{Ex}U^0$) and volume of detonation gases (V_0) generated during their detonation [2]. It is a recent task to investigate energetic materials and compositions [3] with higher performance and thermostability and lower sensitivity (towards impact (*IS*), friction (*FS*), electrostatic discharge (*ESD*)) and also lower toxicity than the current used ones. One approach is the use of azoles in combination with energetic substituents at the carbon atom(s) like nitro or azide groups [4]. Benzimidazole and especially 2-aminobenzimidazole are commercially available substances, which are poorly characterized with respect to their polynitro-derivatives. The probably most common derivative of this class of substances is 4,5,6,7-tetranitro-benzimidazol-2-one (**3**, Scheme 1), which was synthesized by Schindlbauer et al. in 1976 by direct nitration of benzimidazol-2-one [5]. Furthermore Sizov et al. forced the research of thermal rearrangement of *N*-nitrobenzimidazol-2-one in different organic solvents [6]. Investigations regarding enzymatic reactions and cytotoxicity of different nitrobenzimidazoles were made by Cenas et al. in 1997 [7]. All reported syntheses of **3** were carried out under thermodynamical conditions; this means the nitration mixtures were heated over a longer period of time. So far no one reported about 2-nitrimino-5,6-dinitrobenzimidazole (**1**), which is formed at
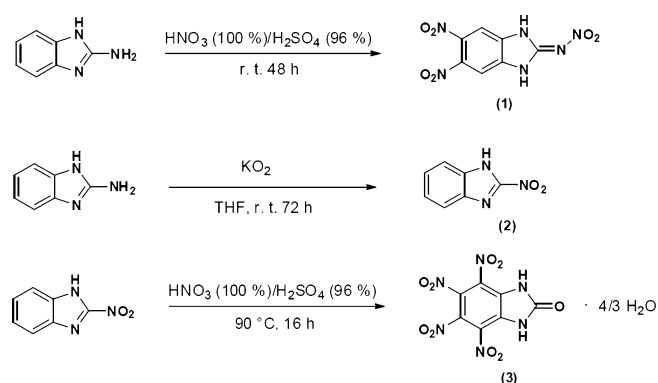
Scheme 1. Synthetic protocol towards compounds **1**, **2** and **3**.

ambient temperature using 2-aminobenzimidazole as starting material, and its high-nitrogen containing salts (**1a–1d**). Furthermore we report on the oxidation of 2-aminobenzimidazole yielding 2-nitrobenzimidazole (**2**) by using potassium hyperoxide in THF. This method was used by Schmitzer et al. for oxidation of 1,4-diaminobenzene, yielding the

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corresponding 1,1'-diamino-4,4'-azobenzene [8]. The nitration of **2** was also investigated by us.

2 Results and Discussion

2.1 Syntheses

2-Nitrimino-5,6-dinitrobenzimidazole (**1**) was synthesized by nitration, using 100% HNO_3 and concentrated sulfuric acid (96–98%) at ambient temperature. We have tested different reaction durations (12–48 h) and found that a reaction time of 48 h seems to be the optimum. Yields of **1** varied between 45 and 50%, depending on the amount of water, which was used to wash **1** free of acid after filtration. We think that firstly the nitrimino group is formed at 0 °C, because the amino group is kinetically favored to be nitrated first. In the second step the benzene ring is nitrated selectively at carbon atoms C5 and C6 at ambient temperature because the nitrimino group decreases the electron density at atoms C4 and C7. Afterwards we tried to chlorinate **1** in C4 and C7 position using either chlorine gas in different aprotic solvents or *N*-chloro-succinimide in acetonitrile but no reaction occurred. Since **1** is stable up to 250 °C it might become suitable for secondary explosive applications. We additionally synthesized four different nitrogen-rich salts, the guanidinium (**1a**), the aminoguanidinium (**1b**), the triaminoguanidinium (**1c**) and hydroxylammonium (**1d**) salt. The syntheses of these corresponding salts are depicted in Scheme 2. The oxidation reaction of 2-aminobenzimidazole with potassium hyperoxide (KO_2) yields 2-nitrobenzimidazole (**2**). Byproducts like different azo-coupled species, which could be detected in the mass spectra, were removed by recrystallization of the raw material from acetone. Various attempts to synthesize a pentanitro-benzimidazole using harsh nitration conditions were carried out.
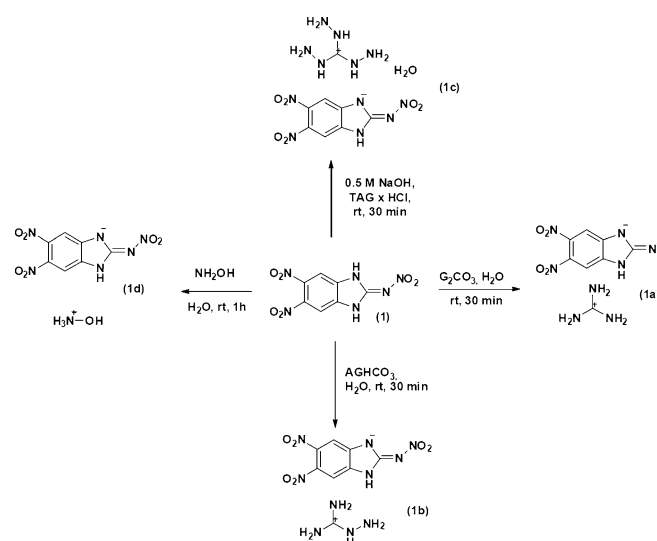
The amount of sulfuric acid was varied as well as additional SO_3 (10–65% weight). However, compound **2** seems to be incompatible with H_2SO_4/SO_3 mixtures. Use of concentrated sulfuric acid and 100% HNO_3 resulted in the formation of compound **3**. We conclude that firstly the benzene ring has been nitrated four times. The electron deficit was increased in that way that hydrolysis in C2 position specifically leading to the much more stable urea derivative **3**.

Scheme 2 shows typical deprotonation reactions in order to synthesize the high-nitrogen salts **1a–d**. In contrast to the syntheses of **1a**, **1b** and **1d**, which are typical acid/base reactions, the synthesis of **1c** represents an in situ salt metathesis, in which the sodium salt is formed and triaminoguanidinium chloride is added afterwards. All salts (**1a–d**) can be synthesized in high yields and their perfect purity was confirmed by CHN elemental analysis.

Crystal Structures

Single crystals for XRD of compounds **1**, **1a–d**, **2**, and **3·4/3H₂O** could be obtained during this work. Single crystals of **1** were obtained out of acetone, whereas all corresponding salts crystallized from EtOH/H₂O mixture. 2-Nitrobenzimidazole (**2**) and 4,5,6,7-tetranitrobenz-imidazole·4/3hydrate (**3**) crystallized from water/acetone. Crystallographic data and parameters are given in Table S1 in the Supporting Information. The cif files were deposited at the Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge by the numbers CCDC-986185 (**1**), -986187 (**1a**), -986186 (**1b**), -986189 (**1c**), -986190 (**1d**), -986191 (**2**), and -986188 (**3**).

2-Nitrimino-5,6-dinitrobenzimidazole (**1**) crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The molecular unit is shown in Figure 1. It is the first 2-nitramino-benzimidazole derivative which is characterized by XRD. Its calculated density of 1.850 g cm^{-3} (at 100 K) is higher than those of its salts **1a–1d**. Both acidic protons (located on the imidazole nitrogen atoms) participate in strong hydrogen bonds e.g. intramolecular: N2—H2···O1 840(30) ppm, 217(3), 264.2(2) 116(2)°; intermolecu-
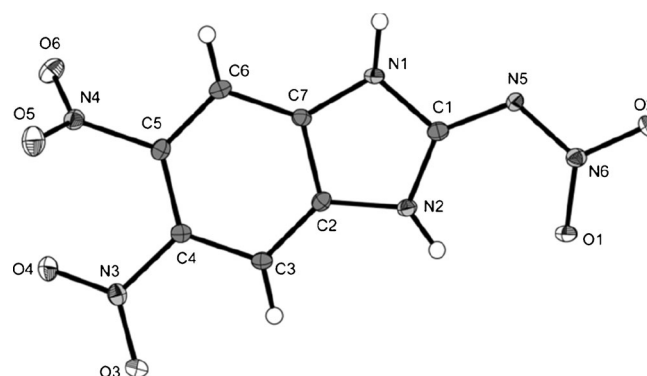

Scheme 2. Syntheses of nitrogen-rich salts (**1a–1d**).

Figure 1. Molecular unit of **1**. Thermal ellipsoids are drawn at the 50% probability level.

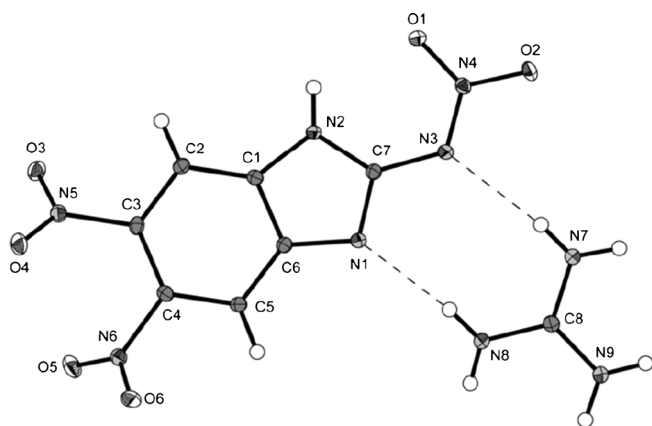*T. M. Klapötke, A. Preimesser, J. Stierstorfer*

Figure 2. Molecular unit of **1a**. Thermal ellipsoids are drawn at the 50% probability level.

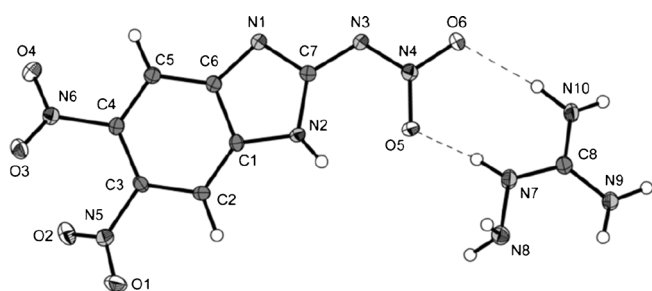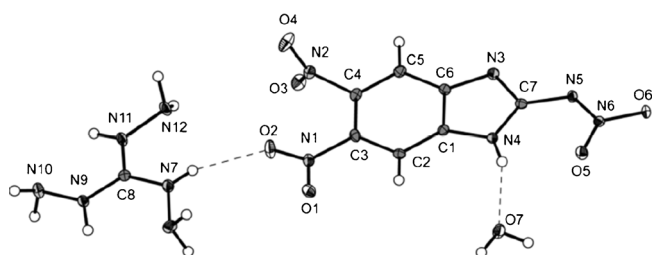**Figure 3.** Molecular unit of **1b**. Thermal ellipsoids are drawn at the 50% probability level.

Figure 4. Molecular unit of **1c**. Thermal ellipsoids are drawn at the 50% probability level.

lar: N2–H2···O2^i 840(30), 203(3), 284.4(2) ppm, 163(3)°, N1–H1···O2^{ii} 89(2) ppm, 208(3), 293.3(2), 162(2)° (symmetry codes: (i) 1.5−*x*, −0.5+*y*, 1.5−*z*; (ii) 1−*x*, 1−*y*, 1−*z*). Except for the oxygen atoms of the nitro group at carbon atom C5 all atoms are almost planar to each other.

The investigated salts of **1** crystallize in monoclinic (*P*2$_1$/*c:* **1a**, **1d**, *P*2$_1$/*n:* **1b**,) and triclinic (*P*1̄: **1c**) space groups. The densities decrease in the following (expected) order: 1.835 g cm^{-3} (**1d** at 173 K) > 1.743 g cm^{-3} (**1a** at 100 K) > 1.735 g cm^{-3} (**1c** at 123 K) > 1.706 g cm^{-3} (**1b** at 100 K).

It has often been observed that hydroxylammonium salts show higher densities than other corresponding ammonium, hydrazinium, and guanidinium salts. The triaminogua-
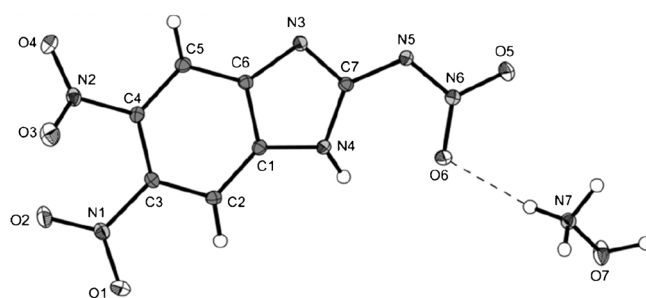

Figure 5. Molecular unit of **1d**. Thermal ellipsoids are drawn at the 50% probability level.

nidinium salt **1c** is the only salt synthesized that includes a molecule of crystal water. Views on the molecular units are given in Figure 2, Figure 3, Figure 4, and Figure 5. All structures are dominated by strong hydrogen bond interactions. As a general trend in all salts the intramolecular hydrogen bridge (graph set R6(1,1)) between the nitramine oxygen atom and the remaining imidazole N–H functionality can be observed.

2-Nitrobenzimidazole (**2**) crystallizes in the orthorhombic space group *Fdd*2 with 16 molecules in the unit cell. Interestingly its density of 1.593 g cm^{-3} (at 173 K) is significantly lower than that of **1** (1.85 g cm^{-3}) but still significantly higher than that of 2-aminobenzimidazole (1.347 g cm^{-3}) described in literature [9]. The nitro group is slightly twisted out from the benzimidazole plane (torsion angle: N1–C7–N3–O1 = − 7.9(3)°). It forms a wave-like layer structure, which is shown in Figure 6.

The 2-nitrobenzimdazole molecules are linked by the hydrogen bond N1–H1···N2^i 89(3) ppm, 207(3) 294.1(2) 169(3)°; (i) − 0.25 + *x*, 0.25 − *y*, − 0.25 + *z*.

4,5,6,7-Tetranitro-benzimidazol-2-one·4/3hydrate (**3**) crystallizes in the triclinic space group *P*1̄ and has a density of 1.825 g cm^{-3} (at 173 K). In addition to hexanitrobenzene [10] and pentanitroaminobenzene [11], it is the third example in the Cambridge crystallographic database (CCDC) which carries four vicinal nitro groups on one benzene ring. They all are twisted out of the ring plane due to steric reasons. The structure can be compared best with that published for 5-nitro-benzimidazol-2-one monohydrate [12]. The asymmetric unit consists of three 4,5,6,7-tetranitro-benzimidazole and four crystal water molecules. Figure 7 shows a selected hydrogen bond connection of one 4,5,6,7-tetranitro-benzimidazol-2-one and one crystal water. The complex 3-dimensional packing of **3**·4/3H$_2$O is dominated by many hydrogen bond interactions involving all water molecules.

Energetic and Thermal Properties

Compounds **1**–**3** were tested for their sensitivities towards impact (IS), friction (FS) and electrostatic discharge (ESD). Furthermore the decomposition temperatures (T_{dec}) of all
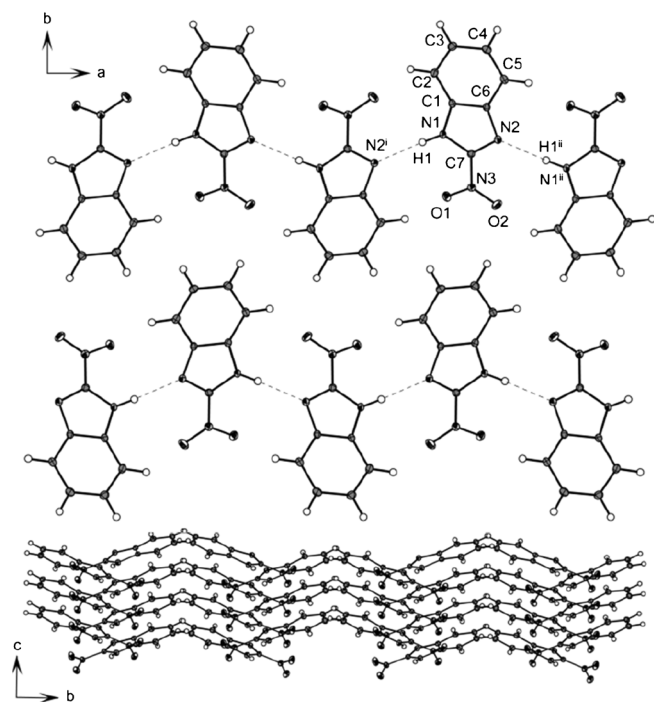
Figure 6. View on the packing of **2**. Top: View along the *c* axis and drawn H-bond interactions. Below: View along the *a* axis. Thermal ellipsoids are drawn at the 50% probability level.
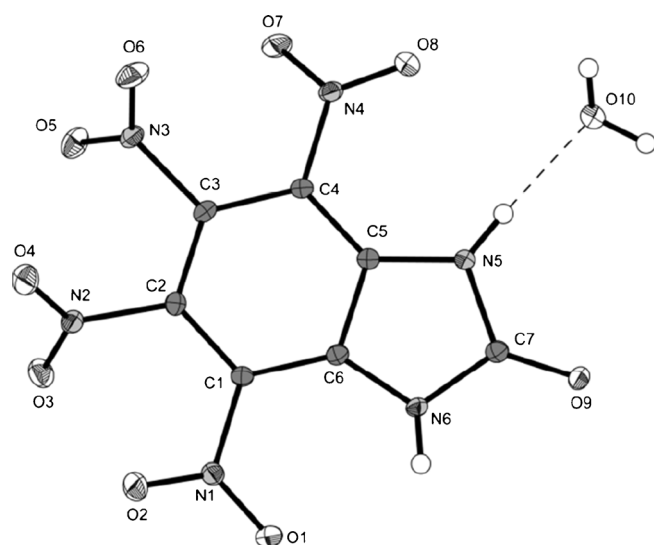

Figure 7. Molecular unit of **3**·4/3H$_2$O. Thermal ellipsoids are drawn at the 50% probability level. For clarity two tetranitrobenzimidazoles and three crystal waters have been neglected.

here presented compounds (**1–3**) were determined using differential scanning calorimetry (DSC) with a heating rate of 5 K min^{-1}. The corresponding DSC-curves of compounds **1–1d** are shown in Figure 8. As can be seen all these compounds have sharp decomposition points. The sensitivity data of compounds **1–3** and their thermal stability are shown in Table 1.
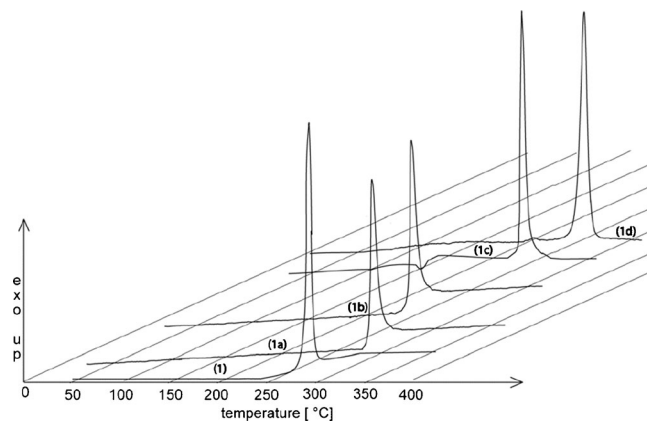

Figure 8. DSC plots of compounds **1–1d** measured with a heating rate of 5 K min^{-1} (*exo*-up).

Table 1. Sensitivity data and thermal stability of compounds **1**, **1a–1d**, **2**, and **3**.

	IS [J] [a]	FS [N] [b]	ESD [J] [c]	Grain Size [μm]	T$_{dec.}$ [°C] [d]
1	>3	>324	>0.1	<100	250
1a	>20	>360	>0.3	<100	275
1b	>5	>360	>0.2	<100	232
1c	>5	>360	>0.4	100–500	218
1d	>5	>360	>0.2	<100	242
2	>40	>360	>1.0	<100	180
3	>5	>360	>0.2	<100	255
RDX[16]	>7.5	>120	>0.1	<100	210

a) Impact sensitivity (BAM drophammer, 1 of 6); b) friction sensitivity (BAM friction tester 1 of 6); c) electrostatic discharge device; d) onset temperatures measured by DSC ($\beta = 5$ K min^{-1}).

Regarding compounds **1–1d** one can observe that the guanidinium salt (**1a**) is the thermally most stable. An increasing number of N—N single bonds in the corresponding cation is followed by lower thermostability. The detonation parameters were calculated with the EXPLO5.05 computer code [15] using calculated heats of formation (see Supporting Information). Compound **1d** has a similar density like **1** at 298 K but shows better detonation parameters due to its higher heat of formation ($\Delta_f H_m° = 80$ kJ mol^{-1}(**1**), 126 kJ mol^{-1} (**1d**)). Although **1b** has a slightly higher heat of formation its density with 1.657 g cm^{-3} is quite low. The advantage of these compounds (**1** and its salts **1a–1d**) is the very simple one-step nitration reaction which yields secondary explosives with better performance than TNT and varying sensitivities: very high sensitive (**1**), moderate sensitive (**1b**, **c**, **d**) and low sensitive (**1d**) towards impact. Except for **1**, which showed slightly charcoal formation at 324 N, all of the investigated compounds are insensitive towards friction. The energetic characteristics for the solvent-free compounds **1**, **1a**, **1b** and **1d** are summarized in Table 2.

Table 2. Energetic properties of compounds **1**, **1a**, **1b**, and **1d** in comparison to RDX.

	1	1a	1b	1d	RDX
Formula	$C_7H_3N_6O_6$	$C_8H_9N_9O_6$	$C_8H_{10}N_{10}O_6$	$C_7H_7N_7O_7$	$C_3H_6N_6O_6$
FW [g mol^{-1}]	268.14	327.21	342.23	301.17	222.12
N [%] [a]	31.34	38.53	40.93	32.55	37.84
Ω_{CO_2} [%] [b]	−59.7	−70.9	−70.1	−55.8	−21.61
ρ [g cm^{-3}] [c]	1.850 (100K), 1.80 (298K)	1.743 (100K), 1.69 (298K)	1.706 (100K), 1.657 (298K)	1.835 (173K), 1.80 (298K)	1.858 (90K) [13], 1.806 (298K) [14]
$\Delta_f H_m°$ [kJ mol^{-1}] [d]	80.0	27.4	134.6	125.7	86
$\Delta_f U°$ [kJ kg^{-1}] [e]	372.2	174.6	487.4	503.8	489
EXPLO5.05 values:					
$\Delta_{Ex}U°$ [kJ kg^{-1}] [f]	4911	4301	4497	5395	6190
T_{det} [K] [g]	3675	3117	3212	3767	4232
P_{CJ} [GPa] [h]	26.2	22.1	22.1	29.4	38.0
$V_{Det.}$ [m s^{-1}] [i]	7760	7526	7565	8177	8983
V_o [L kg^{-1}] [j]	584	670	690	643	734

a) Nitrogen content; b) oxygen balance; c) from X-ray diffraction; d) calculated (CBS-4 M) heat of formation; e) energy of formation; f) energy of explosion; g) explosion temperature; h) detonation pressure; i) detonation velocity; j) assuming only gaseous products.

3 Experimental Section

CAUTION! All high nitrogen and oxygen containing compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, and ear plugs).

2-Nitrimino-5,6-dinitro-benzimidazole (1)

2-Aminobenzimidazole (5.00 g, 37.58 mmol) was added to an ice-cooled (0 °C) solution of red fuming nitric acid (100%, 20 mL, 480 mmol) and concentrated sulfuric acid (96%, 35 mL, 630 mmol) while stirring. Afterwards, the mixture was stirred for 48 h at 25 °C before it was poured on crushed ice. The precipitate was filtered and washed with nitric acid (20%) and afterwards with a small amount of water. 4.4 g (15.38 mmol; 41%) of **1** was obtained as a pale yellow solid.

DSC (5 K min^{-1}): $T_{dec.} = 250$ °C; **EA** ($C_7H_4N_6O_6$ 268.02 g mol^{-1}) found (calc): C 31.11 (31.35), H 1.50 (1.50), N 30.77 (31.34). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 4.98$ (br. s, 2 H, NH), 8.08 (s, 2 H, CH). **^{13}C NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 109.7$ (2C, CH), 132.4, 139.3, 155.7. **^{14}N NMR** (DMSO-d_6, 25 °C, ppm): $\delta = -12$ (3N, NO$_2$); **Raman** [cm^{-1}]: $\tilde{\nu} = 3084$ (7), 1638 (26), 1582 (100), 1548 (9), 1478 (53), 1340 (69), 1264 (7), 1248 (26), 1226 (9), 1117 (6), 1080 (5), 1033 (5), 993 (78), 857 (20), 831 (5), 809 (11), 768 (17), 756 (6), 638 (4); **Sensitivities: IS:** > 3 J; **FS:** > 324 N; **ESD:** < 0.1 J

Syntheses of Compounds 1a–d (see Supporting Information)2-Nitro-benzimidazole (2)

2-Aminobenzimidazole (5.00 g, 37.55 mmol) was dissolved in THF (200 mL) at 25 °C. Potassium superoxide (18.00 g,

0.38 mol) was added and the suspension was stirred for 72 h and filtered from the inorganic compound, which was washed several times with THF. The filtrate was discarded and the permeate was solved in water. The solution was adjusted to pH-value 1 with sulfuric acid. The orange precipitate was filtered and washed with cold water yielding 3.0 g (18.40 mmol, 49%) 2-nitrobenzimidazole as an orange solid.

DSC (5 K min^{-1}): $T_{dec} = 180$ °C: **EA** ($C_7H_5N_3O_2$ 163.04 g mol^{-1}) found (calc): C 51.83 (51.54), H 3.19 (3.09), N 25.41 (25.76). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 4.98$ (br. s, 2 H, NH), (AA'BB'-spectra, $\delta_A = 7.71$ 2 H, CH, N=$|J_{AB} + J_{AB'}|$ = 9.45 Hz), AA'BB'-spectra, $\delta_B = 7.43$ 2 H, CH, N=$|J_{AB} + J_{AB'}|$ = 9.45 Hz) **^{13}C NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 109.0$, 118.0, 126.3, 149.6. **^{14}N NMR** (DMSO-d_6, 25 °C, ppm): $\delta = -19$ (NO$_2$); **Raman** [cm^{-1}]: $\tilde{\nu} = 3089$ (7), 3075 (3), 1585 (10), 1542 (5), 1503 (21), 1472 (11), 1407 (66), 1377 (3), 1331 (17), 1306 (9), 1267 (100), 1227 (38), 1209 (20), 1153 (25), 1141 (8), 1128 (13), 1018 (21), 995 (2), 784 (19), 615 (3). **IR (ATR)** [cm^{-1}]: $\tilde{\nu} = 3029$ (vw), 2958 (vw), 2859 (vw); 2763 (vw), 2594 (vw), 1584 (vw), 1549 (s); 1503 (vs), 1472 (s), 1408 (m), 1375 (vw), 1337 (s), 1306 (m), 1265 (m), 1227 (w), 1202 (vw), 1140 (m), 1018 (vw), 994 (vw), 943 (vw), 904 (vw), 850 (m), 774 (w), 750 (m), 738 (vs). **MS:** (DEI (+) m/z): 163.1 (100) [M$^+$]. **Sensitivities: IS:** > 40 J; **FS:** > 360 N; **ESD:** 1.0 J.

4,5,6,7-Tetranitro-benzimidazol-2-one (3)

2-Nitrobenzimidazole (2.80 g, 17.2 mmol) was added to an ice cooled solution (0 °C) of concentrated sulfuric acid (96%, 20 mL, 0.48 mol) and red fuming nitric acid (100%, 5.0 mL, 0.12 mol). The mixture was stirred for 16 h at 100 °C and poured on ice. The yellow suspension was extracted five times with ethyl acetate (50 mL each) and afterwards with water and brine. A yellow-orange precipitate of crude 4,5,6,7-tetranitro-benzimidazole-2-one (**3**) (3.14 g, 58%) was obtained. Single crystals obtained, contained 4/3 crystal

water, whereas the crude compound did not. Proper NMR spectroscopic data could be obtained by recrystallizing the crude compound out of toluene/EtOH. During this process **3** precipitates as adduct with one molecule of toluene. This was confirmed via CHN elemental analysis and ^{1}H and ^{13}C NMR spectroscopy using 4096 scans, a pulse delay of 2 s and a pulse width of 30°. This adduct was dissolved in THF (20 mL) and reprecipitated with an excess of ice-water. This results in the solvent-free compound **3**.

DSC (5 K min^{-1}): $T_{dec} = 255$ °C; **EA** (single crystals) (**3** $C_7H_4N_6O_9 \cdot 4H_2O$ 337.94 g mol^{-1}) found (calc): C 25.35 (25.31), H 1.45 (1.21), N 24.62 (25.30); **EA** (water-free compound **3**) ($C_7H_4N_6O_9$ 314.13 g mol^{-1}) found (calc): C 27.05 (26.76), H 0.92 (0.64), N 26.52 (26.75). **MS:** (DEI (+) *m/z*): 222.1 (8), 253.0 (2), 269.1 (6), 314.1 (100) [M$^+$]. **IR** (water-free compound) **(ATR)** [cm^{-1}]: $\tilde{v} = 3388$ (s), 3277 (s), 1763 (s), 1735 (s), 1618 (m), 1553 (vs), 1400 (m), 1332 (vs), 1312 (vs), 1197 (m), 1050 (m), 974 (m), 931 (m), 910 (s), 862 (m), 761 (m); **Sensitivities: IS:** > 5 J; **FS:** > 360 N; **ESD:** 0.2 J.

EA (toluene adduct) ($C_7H_2N_6O_9 \cdot C_7H_8$ 406.26 g mol^{-1}) found (calc): C 41.00 (41.39), H 2.75 (2.48), N 20.79 (20.69). ^{1}**H NMR** (acetone-d_6, 25 °C, ppm) toluene in adduct: $\delta = 7.16$ (m, 5 H, toluene), 2.30 (s, 3 H, toluene); signals from **3** $\delta = 12.14$ (s,br, 2 H, NH), ^{13}**C NMR** (acetone-d_6, 25 °C, ppm) toluene in adduct: $\delta = 21.4$ (1C,CH$_3$, toluene), 126.1 (2C, toluene), 129.0 (2C, toluene), 129.8 (2C, toluene), 138.5 (1C, toluene); Signals from **3**: $\delta = 123.7$ (2C, C$_q$), 132.8 (2C, C—NO$_2$), 133.8 (2C, C—NO$_2$), 154.6 (1C, C=O). ^{14}**N NMR** (acetone-d_6, 25 °C, ppm): $\delta = -22$.

Supporting Information (see footnote on the first page of this article): XRD data and parameters for compounds **1**–**3**; calculations of the heats of formations of compounds **1**–**3**; syntheses of compounds **1a**–**d**.

4 Conclusion

From this experimental study the following conclusions can be drawn:

It has been shown that 2-aminobenzimidazole is a valuable and cheap starting material for the synthesis of energetic materials. Its nitration at ambient temperature yield the 2-nitrimino-5,6-dinitrobenzimidazole (**1**) in good yields. Nitrogen-rich salts of **1** could be synthesized in good yield by facile acid/base reaction. Furthermore we managed the oxidation of 2-aminobenzimidazole to its corresponding 2-nitro-derivative using potassium hyperoxide. All attempts to synthesize a pentanitrobenzimidazole yielded 4,5,6,7-tetranitro-benzimidazol-2-one (**3**), which was characterized by X-ray diffraction. Purification of **3** was achieved by recrystallizing **3** as toluene adduct. Afterwards the toluene could be removed by resolving the material in THF and precipitation of **3** with an excess of ice-water. All here synthesized compounds were characterized by low temperature X-ray diffraction. For compounds **1**, **1a**, **1b** and **1c**, which can be

synthesized very easily, moderate detonation parameters were calculated.

Symbols and Abbreviations

BAM	Bundesanstalt für Materialforschung und -prüfung
CCDC	Cambridge Crystallographic Data Centre
DSC	differential scanning calorimetry
EA	elemental analysis
ESD	electrostatic discharge [J]
FS	friction sensitivity [N]
FW	formula weight [g mol^{-1}]
IR	infrared
IS	impact sensitivity [J]
$\lambda_{MoK\alpha}$	X-ray laser wavelength
MS	mass spectrometry
N	nitrogen content [%]
NMR	nuclear magnetic resonance
ρ	density [g cm^{-3}]
$T_{dec.}$	decomposition temperature [°C]

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