

Spectroscopic Investigations of High-Nitrogen Compounds for Near-Infrared Illuminants

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Abstract: Alkaline metal salts are widely used in pyrotechnic formulations. For NIR pyrotechnics, potassium, and cesium nitrate are mainly used as oxidizers and infrared emitters. Herein, new NIR illuminant formulations were tested using several potassium and cesium salts of high-nitrogen compounds such as tetrazole and triazole deriva-

tives. The research of new formulations comprises the evaluation of sensitivity data and radiometric measurements of new formulations. It was further investigated whether the IR emission can be improved using different nitrogen releasing agents like aminotetrazole or diethylene triamine trinitrate (DETT) as hexamethylenetetramine replacements.

Keywords: High-nitrogen compounds • NIR illuminants • Potassium and cesium salts • Hexamine replacements

1 Introduction

Since the development of night vision devices (NVD) pyrotechnic formulations emitting in the NIR (near infrared) region are of research interest. The mainly used spectral region for night vision detection is between 700 and 1000 nm, which can be explained by the spectral limit of night vision goggle detectors [1]. NIR pyrotechnics therefore find applications in mostly military clandestine night operations and are used for example as parachute flares (ground to air), to illuminate large (combat) areas [2].

The main charge of currently used NIR formulations are so called "Black Nite" formulations. They consist of: silicon powder (fuel, burning rate modifier), potassium and/or cesium nitrate (oxidizer, IR emitter), hexamine (fuel, nitrogen release), and a binder fuel [3,4]. Compared to cesium ions formed from the oxidizer, the NIR emission for rubidium nitrate is lower but the maximum IR output is blue shifted and therefore within a better region for night vision detectors. Due to higher costs and restricted availability, rubidium salts are not used regularly [5,6,7].


The main focus regarding new NIR illuminants is on high burning rates, a clean burning behavior, high NIR emission and low emission in the visible spectrum. In addition, non visible diffuse flames which disseminate condensed reaction products would be favored because solid reaction products which are close to the flame can alter or dim the radiant characteristics. Therefore compounds, which release large amounts of nitrogen, are desirable. They produce non-luminous flames and hence lead to a clear burning behavior. It is further assumed that certain potassium and cesium high-nitrogen compounds possess enough energy to achieve both exothermal decomposition and thermal ex-

citation but generate sufficient N₂ gas to remain dim in the visible range.

Several high nitrogen materials were synthesized and tested in new NIR formulations with respect to their safety, their emission between 600 and 1000 nm as well as in the visible. Possible candidates for NIR emitting compounds are potassium and cesium salts of e.g. 3-nitro-1,2,4-triazol-5-(1*H*,4*H*)-one (NTO), 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI), 5,5'-bistetrazolylamine (BTA), or 3,5-dinitro-1,2,4-triazole (DNT) (Figure 1).

Investigated hexamine replacements and nitrogen releasing agents are for example hexogen (RDX), octogen (HMX), 5-aminotetrazole (5AT), 3-amino-1*H*-1,2,4-triazole (3ATR), ethylene diamine dinitrate (EDD), diethylene triamine trinitrate (DETT), or ethylene diamine diperchlorate (EDP) (Figure 2). The latter three were selected due to their similar constitution.

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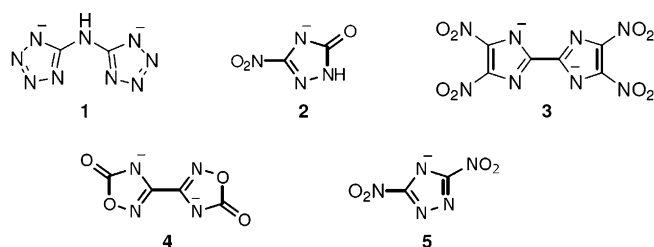


Figure 1. Overview of potassium and cesium salts: BTA (1), NTO (2), TNBI (3), BOX (4), DNT (5) anion.

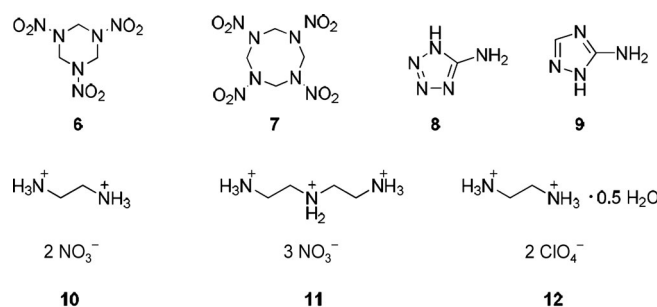


Figure 2. Overview of possible hexamine replacements: RDX (6), HMX (7), 5AT (8), 3ATR (9), EDD (10), DETT (11), EDP (12).

2 Results and Discussion

2.1 Sensitivity Data

The sensitivities of all new formulations were determined by BAM (Bundesanstalt für Materialforschung- und prüfung) methods [8,9] and are presented in Table 1 together with their mass, density, and burning time data.

Exclusively all investigated *Black Nite* formulations are insensitive against friction and electric discharge (360 N, 1.5 J).

Only several compositions are classified as “less sensitive” (35–25 J) against impact e.g. control 1, 3ATR, HMX, and EDP, whereas composition 5AT and RDX are classified as “sensitive” (25–7 J) against impact. The sensitivity data of DETT and EDD could not be determined due to the hygroscopicity of the pellets.

2.2 Pyrotechnic Formulations

The characterization of new pyrotechnic formulations includes sensitivity testing against external stimuli as well as performance measurements for the visible output between 400–600 nm and near-infrared output between 600–1050 nm. In addition, concealment indices, which specify the ratio between near infrared and visible light ($\chi = I_{\text{NIR}}/I_{\text{vis}}$) are listed in Table 5. The US Army in-service *Black Nite* formulation is given in Table 2. The results obtained for new formulations were compared with control charges containing either 70% potassium nitrate or 30% potassium and 40% cesium nitrate. The tested formulations containing high-nitrogen compounds and hexamine replacements respectively are listed in Table 3 and Table 4. Formulations containing 16% EDD, DETT, or EDP in place of hexamine were not ignitable due to their hygroscopic behavior. Therefore the total amount was reduced to 8% of the material (Table 4).

Table 2. *Black Nite* control formulation [wt-%].

Component	Control 1	Control 2
Silicon powder	10	10
Hexamine	16	16
KNO ₃	70	30
CsNO ₃		40
Binder	4	4

Table 1. Sensitivity data.

Formulation	FS [N]	IS [J]	ESD [J]	Mass [g]	Density [g cm ⁻³]	Burning time [s]
Control 1 ^{a)}	360	35	1.5	9.8	1.57	25
Control 2 ^{a)}	360	40	1.5	9.6	1.85	19
BTA ^{b)}	360	40	1.5	9.9	1.56	21
NTO ^{b)}	360	40	1.5	9.8	1.90	18
TNBI ^{b)}	360	40	1.5	9.9	1.74	22
BOX ^{b)}	360	40	1.5	9.8	1.97	11
DNT ^{b)}	360	40	1.5	9.9	1.98	17
RDX ^{c)}	360	7	1.5	9.8	1.69	> 35
HMX ^{c)}	360	35	1.5	9.8	1.63	> 35
5AT ^{c)}	360	10	1.5	9.6	1.66	36
3ATR ^{c)}	360	30	1.5	9.5	1.61	30
EDD ^{c)}	n.d.	n.d.	1.5	10.0	1.71	> 35
DETT ^{c)}	n.d.	n.d.	1.5	9.9	1.69	> 35
EDP ^{c)}	360	35	1.5	9.8	1.61	> 35

a) See Table 2. b) See Table 3. c) See Table 4.

Table 3. Investigated formulations of high-nitrogen compounds [wt-%].

Component	1	2	3	4	5
Silicon powder	10	10	10	10	10
Hexamine	16	16	16	8	12
KNO ₃	60	25	25	30	30
CsNO ₃		30	35	40	40
Binder		4	4	4	4
Potassium BTA	10				
Cesium NTO		15			
Cesium TNBI			10		
Potassium BOX				8	
K and Cs DNT ^{a)}					4

a) 2 wt-% potassium and 2 wt-% cesium salt.

Table 4. Investigated formulations of hexamine replacements [wt-%].

Component	6	7	8	9	10	11	12
Silicon	10	10	10	10	10	10	10
Hexamine		12.5			8	8	8
KNO ₃	70	70	70	70	70	70	70
Binder	4	4	4	4	4	4	4
RDX	16						
HMX		3.5					
5AT			16				
3ATR				16			
EDD					8		
DETT						8	
EDP							8

2.3 Intensity Measurements

The default intensities values for a payload larger than 10 g are $> 25 \text{ Wsr}^{-1}$. These values are stated for the maximum intensity. Because most flares tested therein consist of approximately 10 g, 25 Wsr^{-1} are normally not reached. As it can be seen from the compared 10/20 g charges nearly double the IR output was achieved for a 20 g pellet (Table 5). Surprisingly this was observed for all new formu-

lations but not for control 1. A single test with a 30 g charge of control 1 and 2 results in 25 Wsr^{-1} ($\chi = 27$, $I_{\text{vismax}} = 600 \text{ Cd}$) and 18 Wsr^{-1} ($\chi = 57$, $I_{\text{vismax}} = 215 \text{ Cd}$), respectively (not listed in Table 5). Tested formulations bearing possible hexamine replacements show a low visible as well as a low NIR output in a range of 1–6 Wsr^{-1} .

Similar NIR emission and concealment indices to both controls are obtained for the formulation containing 10%

Table 5. Radiant intensities of *Black Nite* formulations^{a)}.

Formulation	$I_{\text{vis}}^{\text{b)}}$ [Cd]	$I_{\text{NIR}}^{\text{c)}}$ [W sr^{-1}]	$I_{\text{NIR}}^{\text{d)}}$ [$\text{Ws sr}^{-1} \text{ g}^{-1}$]	$\chi^{\text{e)}}$
Control 1	281/264 ^{f)}	10.96/13.15 ^{f)}	27.96	27/34
Control 2	144	12.37	24.48	59
1	218	11.74	24.90	37
2	92	5.25	9.64	99
3	163	10.68	23.73	45
4	172/432 ^{f)}	11.80/26.15 ^{f)}	13.24	47/41 ^{f)}
5	178/398 ^{f)}	12.70/24.94 ^{f)}	21.80	49/43
6	40	1.15	4.11	20
7	184/527 ^{f)}	6.85/15.60 ^{f)}	24.46	25/20 ^{f)}
8	28	1.04	3.90	25
9	61	2.50	7.89	28
10	46	1.80	6.30	26
11	46	1.65	5.83	24
12	122	3.76	13.43	21

a) All values are mean values of 3–5 measurements. b) I_{vis} (maximum value) = 400–700 nm. c) I_{NIR} (maximum value) = 700–1000 nm. d) I_{NIR} (maximum value) calculated for 10 g charges. e) Concealment index. f) 10 g/20 g batch.

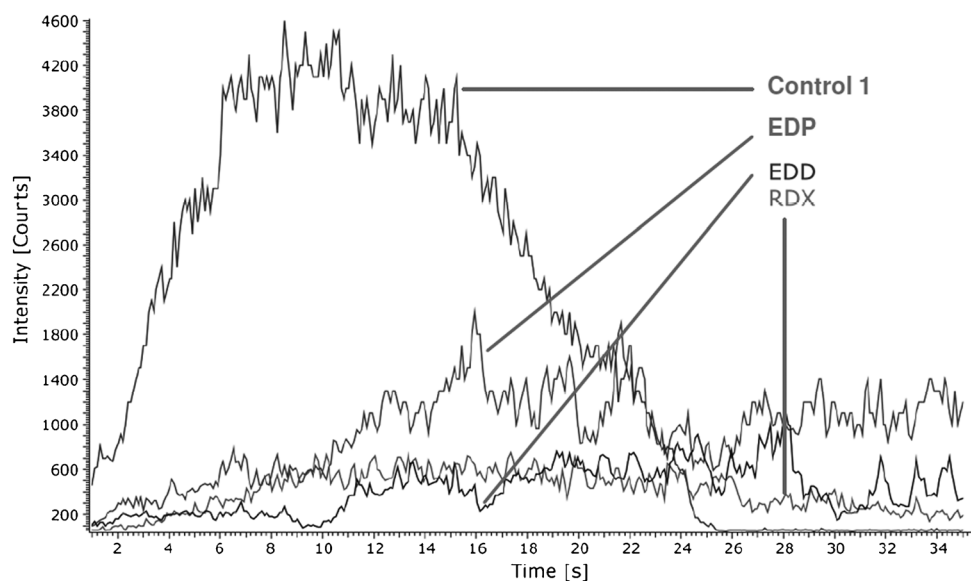


Figure 3. Intensity graph of Control 1, EDP, EDD, and RDX.

potassium BTA. Hence, this formulation would be a good candidate for further experiments.

Due to the large amount of cesium NTO, the concealment index of 99 is much higher than both control charges but the maximum intensity output is in the range of 5 Wsr^{-1} . Moderate emission values are obtained for TNBI, BOX, and DNT formulations. All results are with $10\text{--}13 \text{ Wsr}^{-1}$ in the range of the control charge.

The burning times for 5AT, 3ATR, EDD, DETT, DETP, RDX, and HMX are extended to 30 s or in most cases to over 35 s but all flares showed a marginal flame surface. The burning time for all other formulations lie between both control charges, except the BOX formulation burned much faster (11 s). To illustrate the burning nature, the intensity as a function of time plots of several selected formulations is illustrated in Figure 3.

2.4 X-ray Diffraction

Since the solid-state structures of EDD, DETT, and EDP were not determined yet, a short description is given in the following. Details of the single-crystal X-ray measurements and refinements are given in the Supporting Information. Figure 4 shows the molecular structures of EDD, DETT, and EDP. All structures show expected bond lengths and angles, as well as hydrogen bonds involving the anions and amine hydrogen atoms.

3 Experimental Section

3.1 Preparation of the Pyrotechnic Charge

Epon 828, Epikure 3140 (binder system) and silicon MIL-S-250 (grade 2, class C) were obtained from ARDEC. The

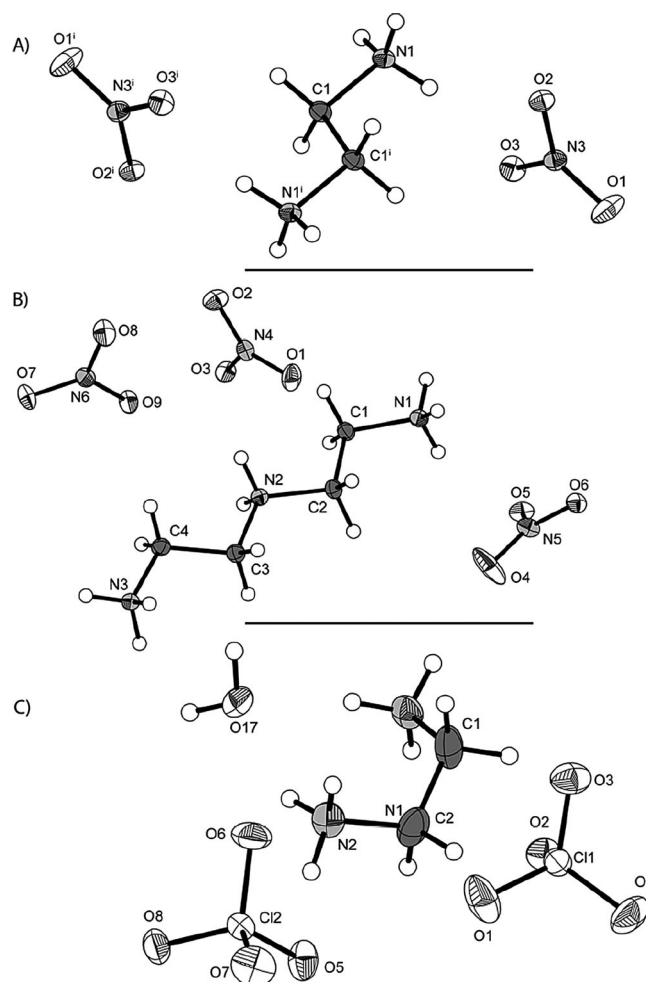


Figure 4. Depiction of the molecular structures of EDD (A), DETT (B), and EDP (C). Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $1-x$, $1-y$, $-z$. The asymmetric unit of EDP consists of two ethylene diammine dication, four perchlorate anions and one water molecule.

epoxy system was used as 70% Epon and 30% Epikure with a total amount of 4%. Hexamine, potassium nitrate, and cesium nitrate were received from Sigma-Aldrich, pulverized separately in a ball mill from Harbor Freight Tools for several hours, sieved, and dried at 60 °C for at least 12 h before use. *Black Nite* formulations were prepared as 50 g (5 × 10 g) batches according to their respective weight percentages in the formulations (Table 2, Table 3, and Table 4) and mixed in a mortar. 10 g of the formulation was pressed with 2–3 t in a 54PM250 hydraulic press and corresponding 20 mm die set from Maassen GmbH. The average weight of five 10 g pellets and their average densities are given in Table 1. First tests were carried out without a primer charge or a first fire.

3.2 Radiometric Measurements

Radiometric emissive properties of new *Black Nite* formulations were characterized using a HR2000 + ES spectrometer with an ILX511B linear silicon CCD-array detector, UV2/OFLV-5 filter, L2 lens, 10 μm slit and included software from Ocean Optics. The spectrometer was calibrated by Ocean Optics for radiometric measurements.

For intensity measurements the optical fiber was coupled with a CC-3-UV cosine corrector (= irradiance probe) with a diameter of 3900 μm. The intensity of light was measured normal to the probe surface. The performance data were calculated with an in-house Matlab program.

3.3 Synthesis

Caution! The herein described alkali and alkaline earth metal salts are energetic materials and show partly increased sensitivities towards shock and friction, especially if water free or dehydrated. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar® gloves and ear plugs) have to be applied while synthesizing and handling the described compounds.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ¹H and ¹³C NMR spectra were recorded with a JEOL Eclipse 270, JEOL EX 400, or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (¹H, ¹³C). To determine the melting and decomposition temperatures of the described compounds a Linseis PT 10 DSC (heating rate 5 k min⁻¹) was used with aluminum sample pans (1 μm hole on top for gas release) in a nitrogen flow of 20 mL min⁻¹. Infrared spectra were measured with a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr pellets. Raman spectra were recorded with a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector. Mass spectra of the described compounds were measured with a JEOL MStation JMS 700 using FAB technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

The low temperature determination of the crystal structures of **10**, **11**, and **12** was performed with an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and reduction was carried out using the CrysAlis-Pro software [10]. The structures were solved either with SIR-92 [11] or SHELXS-97 [12], refined with SHELXL-97 [13] and finally checked using the PLATON [14] software integrated in the WinGX [15] software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a Scale3 Abspack multi-scan method [16].

The impact sensitivity tests were carried out according to STANAG 4489 modified instruction using a BAM (Bundesanstalt für Materialforschung) drophammer. The friction sensitivity tests were carried out according to STANAG 4487 modified instruction using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods" [8]. Additionally, all compounds were tested upon the sensitivity towards electrical discharge using the OZM Small Scale Electrostatic Spark Tester ESD 2010 EN [9].

5-Aminotetrazole and 3-aminotriazole were used as received from Sigma-Aldrich. RDX and HMX were synthesized according to Bachman et al. [17,18]. The potassium and cesium salts of the corresponding anions of BTA, NTO, TNBI, BOX, and DNT were synthesized according to the literature [19].

Ethylene Diamine Dinitrate (**10**) and Diethylene Triamine Trinitrate (**11**)

10: Nitric acid (65%, 9 mL, 200 mmol) was stirred under ice-cooling and ethylene diamine (6.7 mL, 100 mmol) was added slowly via a dropping funnel. After the addition of methanol **10** precipitated, was filtered off and washed with small amounts of methanol (17.9 g, yield 96%).

11: Nitric acid (65%, 17.9 mL, 400 mmol) was stirred under ice-cooling and diethylene triamine (10.7 mL, 100 mmol) was added slowly via a dropping funnel. A yellow-brownish solid was obtained and the product precipitated after the addition of methanol. **11** was filtered off and washed with less amounts of methanol (26.6 g, yield 91%).

Both products were recrystallized from methanol/water.

10: DSC (5 k min⁻¹): 294 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3492 (m), 3190 (s), 3009 (s), 2927 (s), 2793 (m), 2587 (w), 2491 (w), 2396 (w), 1763 (w), 1590 (m), 1562 (m), 1511 (s), 1385 (vs), 1033 (s), 1006 (m), 825 (m), 782 (w), 724 (w) cm⁻¹. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3007 (9), 2984 (14), 2830 (1), 1647 (1), 1597 (3), 1514 (2), 1469 (6), 1436 (2), 1401 (2), 1330 (6), 1219 (3), 1057 (16), 1044 (100), 934 (3), 917 (4), 727 (9), 708 (5), 467 (5) cm⁻¹. ¹H NMR (DMSO-*d*₆, 25 °C, ppm): δ = 6.93 (br., -NH₃⁺, 6 H), 3.01 (s, CH₂, 4 H). ¹³C NMR (DMSO-*d*₆, 25 °C, ppm): δ = 37.5. MS (FAB⁺) *m/z* = 61.1

($C_2H_9N_2^+$). $C_2H_{10}N_4O_6$ (MW 186.12): calcd.: C 12.91, H 5.42, N 30.10%; found: C 13.14, H 5.31, N 29.84%. **BAM drophammer:** > 40 J; **friction tester:** 360 N; **ESD:** 1.0 J (grain size 100–500 μ m).

11: **DSC** (5 k min⁻¹): 151 °C (m.p.), 257 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3444 (s), 3022 (s), 2426 (w), 1766 (w), 1621 (m), 1385 (vs), 1178 (w), 1131 (w), 996 (w), 825 (w), 772 (w), 589 (w) cm⁻¹. **Raman** (1064 nm, 300 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 2995 (13), 2967 (20), 2921 (3), 2818 (2), 1592 (3), 1460 (5), 1407 (2), 1342 (4), 1272 (2), 1202 (3), 1045 (100), 1016 (4), 963 (2), 733 (4), 713 (8) cm⁻¹. **¹H NMR** (DMSO-*d*₆, 25 °C, ppm): δ = 8.76 (br., $CH_2-NH_2^+-CH_2$), 8.08 (br., NH_3^+ , 6 H), 3.23 (m, $-NH_2^+-CH_2-$, 4 H), 3.09 (m, $H_3N^+-CH_2-$, 4 H). **¹³C NMR** (DMSO-*d*₆, 25 °C, ppm): δ = 44.6, 35.7. $C_4H_{16}N_6O_9$ (MW 292.20): calcd.: C 16.44, H 5.52, N 28.76%; found: C 16.59, H 5.41, N 28.57%. **BAM drophammer:** > 40 J; **friction tester:** 360 N; **ESD:** 1.0 J (grain size 100–500 μ m).

Ethylene Diamine Dipchlorate-0.5H₂O (12)

HClO₄ (1 N, 60 mL, 60.3 g, 60 mmol) was stirred in a 250 mL flask and ethylene diamine (2.15 mL, 1.94 g, 32 mmol) was added. The mixture was stirred for 1 h at room temperature and afterwards the acid was removed in vacuo. The obtained oil was dried under high vacuum for several hours and a colorless solid was obtained (5.4 g, yield 63%).

DSC (5 k min⁻¹): 335 °C (dec.). $C_2H_{11}N_2O_{8.5}Cl_2$ (MW 269): calcd.: C 8.90, H 4.11, N 10.37%; found: C 8.86, H 4.14, N 10.07%. **BAM drophammer:** 3 J; **friction tester:** 48 N; **ESD:** 0.15 J (grain size 100–500 μ m).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-930969 (EDD), CCDC-930968 (DETT) and CCDC-930970 (EDP) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Supporting Information (see footnote on the first page of this article): Details on the X-ray diffraction of EDD, DETT, and DETP.

4 Conclusion

Several energetic materials like potassium and cesium 3,5-dinitro-1,2,4-triazolate or 3-nitro-1,2,4-triazol-5-one were synthesized and investigated as possible additives in near infrared pyrotechnic formulations, so called *Black Nite* formulations. Before executing radiometric measurements, all formulations were tested with respect to their sensitivity and combustion behavior. Exclusively all formulations are insensitive towards friction and electric discharge and only few are moderate or less sensitive towards impact e.g. those containing RDX. Most of the new investigated formulations show similar or lower maximum intensity values as

both control charges. Several additional tests are of further interest and will be carried out with 3,5-dinitrotriazole (DNT), 5,5'-bis(tetrazolyl)amine (BTA), 2,2',3,3'-tetranitrobisimidazole (TNBI), or bis(oxadiazolon) (BOX), which showed good burning behaviors and acceptable IR output and are therefore promising candidates.

Symbols and Abbreviations:

BAM	Bundesanstalt für Materialforschung und -prüfung
CCDC	Cambridge crystallographic data centre
DSC	Differential scanning calorimetry
FW	Formula weight [g mol ⁻¹]
IS	Impact sensitivity [J]
FS	Friction sensitivity [N]
ESD	Electrostatic discharge [J]
EN	Electronegativity
IR	Infrared
λ (Mo- <i>K</i> _α)	X-ray laser wavelength
MS	Mass spectrometry
N	Nitrogen content [%]
NIR	Near infrared
NMR	Nuclear magnetic resonance
ρ	Density [g cm ⁻³]
STANAG	Standardization agreement
<i>T</i> _{dec.}	Decomposition temperature [°C]
<i>T</i> _{dehydr.}	Dehydration temperature
χ	Concealment index
Z	Number of molecular units per unit cell

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