Energetic Materials Hot Paper

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Potassium 1,1′-Dinitramino-5,5′-bistetrazolate: A Primary Explosive with Fast Detonation and High Initiation Power**

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Abstract: *Adequate primary explosives such as lead azide mostly contain toxic ingredients, which have to be replaced. A new candidate that shows high potential, potassium 1,1′-dinitramino-5,5′-bistetrazolate (K_2DNABT), was synthesized by a sophisticated synthetic procedure based on dimethylcarbonate and glyoxal. It was intensively characterized for its chemical (X-ray diffraction, EA, NMR and vibrational spectroscopy) and physico-chemical properties (sensitivity towards impact, friction, and electrostatic, DSC). The obtained primary explosive combines good thermal stability with the desired mechanical stability. Owing to its high heat of formation (326 kJ mol^{-1}) and density (2.11 g cm^{-3}), impressive values for its detonation velocity (8330 m s^{-1}) and pressure (311 kbar) were computed. Its superior calculated performance output was successfully confirmed and demonstrated by different convenient energetic test methods.*

Primary explosives are substances that show a very rapid transition from deflagration to detonation and generate a shock-wave that makes transfer of the detonation to a less sensitive secondary explosive possible.[1,2] Lead azide and lead styphnate are the most commonly used primary explosives today.[3,4] However, the long-term use of these compounds has caused considerable lead contamination in military training grounds and costly clean-up operations waste money that could better be spent improving the defense capability of our forces.[5] A recent article published on December 4, 2012 in the Washington Post entitled "Defense Dept. Standards On Lead Exposure Faulted"[6] stated: "*… it has found overwhelming evidence that 30-year-old federal standards governing lead exposure at Department of Defense firing ranges and other sites are inadequate to protect workers from ailments associated with high blood lead levels, including problems with the nervous system, kidney, heart, and reproductive system*."

The most prominent and most promising lead azide replacement today is copper(I) 5-nitrotetrazolate (DBX-1, Figure 1) which was developed by Fronabarger, Williams, et al. at PSEMC.[7–9] Despite its promise as a "greener" alternative for lead azide, DBX-1 has shown a tendency to decompose with periodate salts, thus inhibiting its explosive activity.[10] More research is needed to determine long-term storage and potential compatibility of the material with the chemicals it would come in contact with in an energetic formulation.

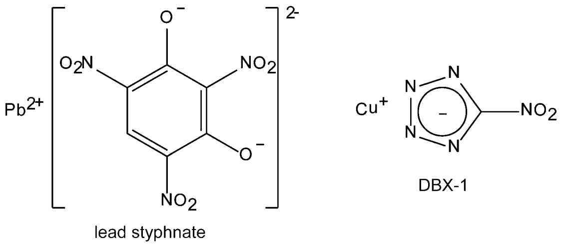

Figure 1. Structures of lead styphnate and copper(I) 5-nitrotetrazolate (DBX-1).

A "green" lead azide replacement needs to possess the following properties: a) insensitivity to light; b) sensitivity to detonation (but not too sensitive to handle and transport); c) stability to at least 180 °C; d) stability upon storage for long periods of time; e) being free of toxic metals; f) being free of toxic perchlorate; and g) ease and safety of synthesis.[3]

Herein, we report the synthesis and characterization of the new primary explosive potassium dinitraminobistetrazolate (K_2DNABT), which only contains potassium as the metal and is an alternative to lead azide. Many tetrazoles have been described as energetic materials.[11] While 5-nitriminotetrazoles are commonly known, 1-dinitramino-tetrazoles are very rare, which is due to their hard accessibility.[12] In theory, unprotected 1,1′-diamino-5,5′-bistetrazole[12] could be nitrated, but the amination of 5,5′-bistetrazole is a procedure with low yield and high effort, so an alternative route was developed. Looking for better starting materials, the bisnitrileimine seems to be a suitable precursor for this molecule. Unfortunately unprotected bisnitrilimine is only known as its diphenyl derivative,[13] so another more easily removable protecting group than a phenyl moiety was chosen. The following synthetic process describes the synthesis of K_2DNABT starting from commercially available dimethyl carbonate. The carbonate reacts with hydrazine hydrate to methyl carbazate **1**.[14] The condensation reaction with half an equivalent of glyoxal forms **2**,[15] which is subsequently oxidized with NCS (N-chlorosuccinimide) to the corresponding chloride. Substitution with sodium azide offers the diazide (in only 38 % yield), which is then cyclized with hydrochloric acid in a diethyl ether suspension. The N-methoxycarbonyl-protected 1,1′-diamino-5,5′-bistetrazole (**5**) is gently nitrated with N_2O_5. An alkaline aquatic work-up with KOH precipitates dipotassium K_2DNABT (Scheme 1).

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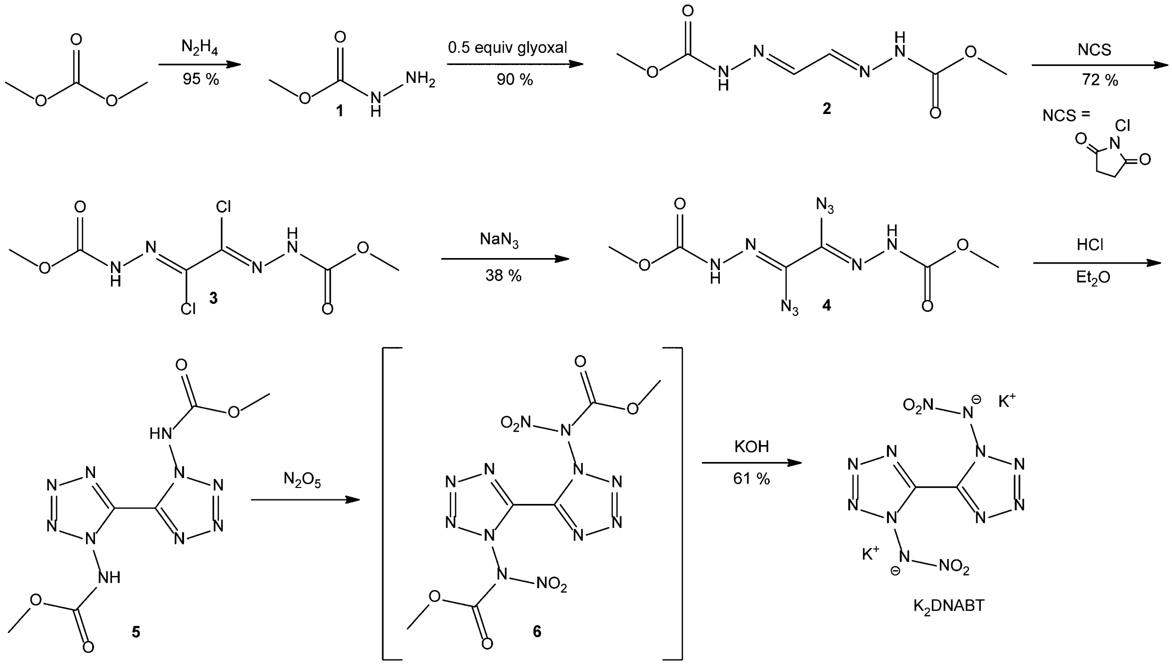

Scheme 1. Synthetic pathway towards K_2DNABT.

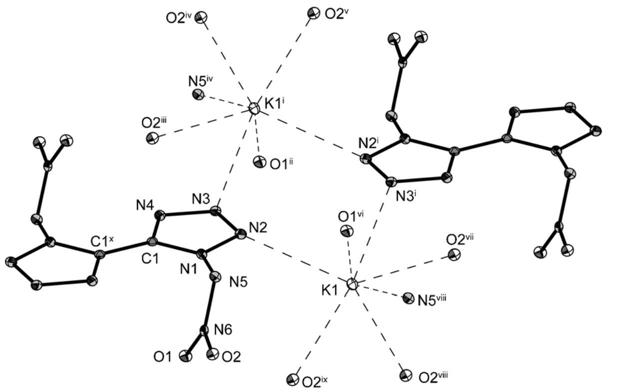

Figure 2. Molecular structure of K_2DNABT with cation coordination. Ellipsoids are set at 50% probability. Selected bond lengths [Å]: C1–C1^{i} 1.453(4), N1–C1 1.352(3), N4–C1 1.322(3), N1–N2 1.355(2), N1–N5 1.394(2), N5–N6 1.332(3), O1–N6 1.248(2), O2–N6 1.261(2); selected torsion angles [°]: C1-N1-N5-N6 75.3(3), N1-C1-C1^{i}-N4 −1.5(4), O1-N6-N5-N1 1.6(3). Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) $-x$, $1-y$, $1-z$; (iii) x, y, $1+z$; (iv) $1-x$, $-y$, $1-z$; 1; (v) $1+x$, y, $1+z$; (vi) $1+x$, y, z; (vii) $1-x$, $1-y$, $-z$; (viii) x, $1+y$, z; (ix) $-x$, $1-y$, $-z$; (x) $-x$, $-y$, $1-z$.

All of the intermediate products can be used as obtained; no column chromatography is required. Fortunately K_2DNABT shows low water solubility, which facilitates isolation and purification. The toxicity of K_2DNABT in water was determined using the known luminous bacteria method with *Vibrio fischeri* NRRL-B-11177.[16] The EC_{50} concentration of this compound after 30 min of incubation time is higher than 1.4 $\mathrm{g\,L^{-1}}$. With a value above 1 $\mathrm{g\,L^{-1}}$, a compound can basically be considered as nontoxic.

The molecular structure of K_2DNABT in the solid state (Figure 2) was determined by low-temperature single-crystal X-ray diffraction.[17] It crystallizes in the triclinic space group $P\bar{1}$ with a density of 2.172 $\mathrm{g\,cm^{-3}}$ at 100 K. The potassium atoms are coordinated irregularly by either the nitrogen atoms N2, N3, N5 or the nitro oxygen atoms O1 and O2. Both tetrazole rings as well as atom N5 are almost planar to each other. The nitro groups are twisted out of this plane by almost 75°.

Several energetic tests were performed ensuring the suitability of K_2DNABT as a primary explosive. The friction and impact sensitivity is comparable to $Pb(N_3)_2$. Along with the successful ignition of one gram of RDX by 40 mg of K_2DNABT, a flame test (Figure 3d) and a "hot needle test" (see the Supporting Information for videos) indicated the instant detonation of the material in contact with a flame or a hot metal needle.

Several detonation parameters were calculated using the EXPLO5 code[19] in its latest version 6.02 using a calculated heat of formation and density (recalculated from the X-ray structure 100 K value to room temperature). It can be seen from Table 1 that K_2DNABT easily outperforms lead azide in all critical detonation parameters, while the sensitivities (impact, friction, and electrostatic discharge) are in the same range. The experimental explosive work released was demonstrated by a detonation (Figure 3b) against an aluminum block in comparison with the commonly used lead azide. Owing to their good flowability, both compounds were simply poured into the steel block and ignited unpressed. The indentation is 1.4 mm, whereas lead azide reaches only 0.2 mm, using 500 mg of each compound (Figure 3c). Additionally, K_2DNABT shows excellent thermal stability. The compound was heated up to 100 °C and the temperature was held for 48 h. No loss of mass or any decomposition was observed (the TGA plot is shown in the Supporting Information). A violent decomposition was observed at 200 °C using a DSC experiment (heating rate of 5 deg min^{-1}). All tests point to the fact that this material is a suitable and non-toxic replacement for lead azide, with a straightforward synthesis from commonly available chemicals.

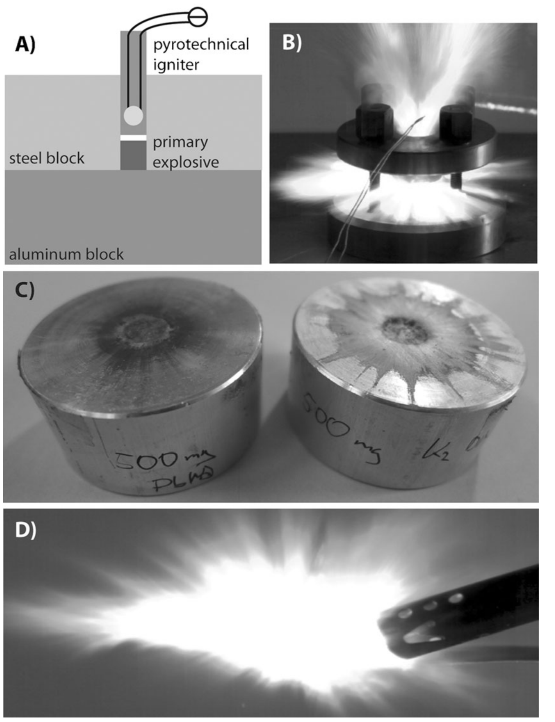

Figure 3. A) Setup of explosive work test; B) moment of detonation; C) result of explosive work test (left: $Pb(N_3)_2$, right: K2DNABT); D) flame test of K_2DNABT at the moment of detonation.

Table 1: Comparison of the energetic properties and calculated performance data of lead azide and K_2DNABT.

	$Pb(N_3)_2$	K_2DNABT
Formula	N_6Pb	$C_2K_2N_{12}O_4$
M [g mol^{-1}]	291.3	334.3
IS [J][a]	2.5–4	1
FS [N][b]	0.1–1	≤ 1
ESD [J][c]	<0.005	0.003
N [%][d]	28.9	50.3
Ω [%][e]	-11.0	-4.8
$T_{Dec.}$ [°C][f]	ca. 315	200
ρ [g cm^{-3}][g]	4.8	2.172 (100 K) 2.11 (298 K)[18]
$\Delta_fH_m°$ [kJ mol^{-1}][h]	450.1	326.4
$\Delta_fU°$ [kJ kg^{-1}][i]	1574.9	1036.1
EXPLO5 6.02 (BKWG-S)		
$-\Delta_{Ex}U°$ [kJ kg^{-1}][j]	1569	4959
T_{det} [K][k]	3401	3424
P_{CJ} [kbar][l]	338	317
V_{det} [m s][m]	5920	8330
V_0 [L kg][n]	252	489

[a] Impact sensitivity according to the BAM drop hammer (method 1 of 6). [b] Friction sensitivity according to the BAM friction tester (method 1 of 6). [c] Electrostatic discharge sensitivity (OZM ESD tester). [d] Nitrogen content. [e] Oxygen balance. [f] Temperature of decomposition according to DSC (onset temperatures at a heating rate of 5 deg min^{-1}). [g] Density at RT. [h] Heat of formation. [i] Energy of formation. [j] Heat of detonation. [k] Temperature of detonation. [l] Detonation pressure. [m] Detonation velocity; volume of gases after detonation. [n] Gas volume after detonation.

Experimental Section

The detailed experimental description of the whole synthetic procedure is shown in Scheme 1; the general methods are given in the Supporting Information.

Dipotassium dinitraminobistetrazolate (K_2DNABT): Compound **5** (1 g, 3.52 mmol) was suspended in 50 mL dry acetonitrile and cooled to 0–5 °C. N_2O_5 (1.5 g, 13.9 mmol) was added and the mixture was stirred at this temperature. After all of the starting material was dissolved (1–2 h), the solution was stirred for additional 30 min. Then 2 M KOH (14 mL) was added and the mixture was stirred vigorously at ice bath temperature. Additional KOH solution was added until the pH of the aqueous phase stayed constantly at 12 or above. The precipitated solid was filtered and suspended in 20 mL of ice water, stirred for 5 min, and filtered again, yielding 720 mg (61 %) of finely powdered colorless K_2DNABT.

DSC (5 °C min^{-1}): 200 °C (dec); IR (KBr): $\tilde{\nu} = 3450$ (m), 1635 (w), 1440 (s), 1382 (w), 1360 (w), 1300 (vs), 1256 (m), 1163 (w), 1124 (w), 1031 (w), 998 (w), 872 (w), 773 (w), 729 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu} = 1610$ (100), 1455 (9), 1270 (12), 1251 (19), 1142 (6), 1084 (14), 1016 (34), 992 (4), 889 (2), 750 (2), 732 (3), 512 (7), 301 cm^{-1} (4); EA ($C_2K_2N_{12}O_4$, 334.30): C 7.19, N 50.28 %; found: C 7.62, N 47.95 %; *m*/*z* (FAB^-): 257 ($C_2HN_{12}O_4^-$); BAM drop hammer: 1 J; friction tester: <5 N; ESD: 3 mJ.

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[17] Selected X-ray data: colorless plate, triclinic, $P\bar{1}$, $a = 5.0963(6)$, $b = 6.8248(8)$, $c = 8.4271(8)$ Å, $\alpha = 7.56(1)$, $\beta = 86.15(1)$, $\gamma = 71.02(1)°$, $V = 255.65(5)$ Å^3, $Z = 1$, 2.172 g cm^{-3}, wR_2 6.57 %, $S = 1.09$, CCDC 999474 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] The room-temperature value was calculated by the volume expansion equation $\rho_{298K} = \rho_T/(1+\alpha_v(298-T))$; $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}.

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