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Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-COM-08-2021-002731.R1
Article Type:	Communication
Date Submitted by the Author:	09-Sep-2021
Complete List of Authors:	Klapoetke, Thomas; LMU München, Chemistry Kofen, Moritz ; Ludwig Maximilians University Munich, Stierstorfer, Joerg; LMU Munich, Chemistry

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N-Functionalisation of 5,5'-bistetrazole providing 2,2'-di(azidomethyl)bistetrazole: A melt-castable metal-free green primary explosive

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

N-Hydroxymethylation of heterocyclic compounds offers a promising starting procedure to ultimately introduce nitratomethyl- as well as azidomethyl- moieties. Applied to 5,5'-bistetrazole, the resulting 2,2'-di(azidomethyl)bistetrazole (3) and 2,2'-di(nitratomethyl)bistetrazole (4) are high-performing melt-castable energetic materials. Sensitivities were predicted by Hirshfeld analysis and explored in detail by experimental analysis. Because of their increased values towards mechanical stimuli and a short deflagration to detonation transition (DDT), especially the diazidomethyl derivative shows promising as new melt-castable primary explosive.

For a long time, research on energetic materials focused on replacing RDX and HMX with even higher performing compounds to increase the performance of an explosive device. With respective detonation velocities of 9778 m s⁻¹ and 9698 m s⁻¹, CL-20¹ and TKX-50² are two of the best performing compounds resulting from extensive synthetic research. Especially ϵ -CL-20, having a theoretical maximum density of 2.04 g cm⁻³ at 298 K, reached the somewhat established threshold in crystal density of 2.0 g cm⁻³ for a compound consisting purely of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O).³ As high explosives are generally used within formulations such as Composition B, consisting of RDX (60%) and TNT (40%), the effect on the performance of an explosive device by solely replacing RDX is limited. Together with the challenge of surpassing the performance of RDX/HMX, one of the most promising strategies is the replacement of toxic melt-castable trinitrotoluene (TNT) which shows a rather low detonation velocity of 6800 m s⁻¹. Recently *Sabatini et al.*⁴ published bis(1,2,4-oxadiazole)bis(methylene) dinitrate (BODN), a very promising compound to replace TNT based on the bisoxadiazole scaffold. In a previous paper, we showed that the replacement of the nitratomethyl moieties in BODN by

azidomethyl moieties results in 3,3'-bis(azidomethyl)-5,5'-bis(1,2,4-oxadiazole) (DAMBO), which also shows a melting point around 80°C.⁵ Both compounds, BODN and DAMBO, possess methylene bridged azides or nitrates, a motive also found in 5-nitro-2-nitratomethyltetrazole (NNMT)⁶. While the -CH₂-N₃ (DAMBO) and CH₂-ONO₂ (BODN) substituents are C-bond, the CH₂-ONO₂ group in NNMT is N-bond. The introduction of a N-bonded methylene moiety is achieved by N-hydroxymethylation of the heterocycle with formaldehyde, but extensive adjustment of the reaction conditions are required.⁷ The goal of this work was to develop adequate reaction conditions as well as to apply this procedure to 5,5'-bistetrazole as it is the basic framework of several high-performing energetic materials such as TKX-50² and potassium 1,1'-dinitramino-5,5'-bistetrazole (K₂DNABT)⁸. Due to the high endothermic heat of formation of 5,5'-bistetrazole (+560.8 kJ mol⁻¹) a good performance of the synthesized compounds can be assumed.

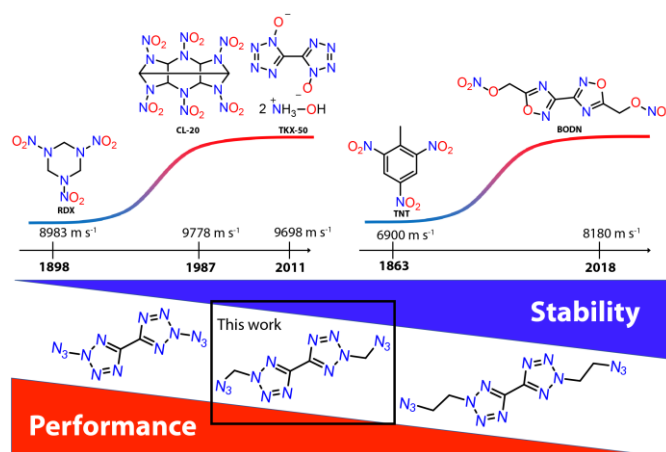


Figure 1. Evolution of high explosives as well as melt-castable explosives. N-methylene moiety balancing between stability. As such its performance and stability perfectly balances between unstable 2,2'-diazido-5,5'-bistetrazole (not described yet) and more stable 2,2'-bis(azidoethyl)-5,5'-bistetrazole (also not described yet).

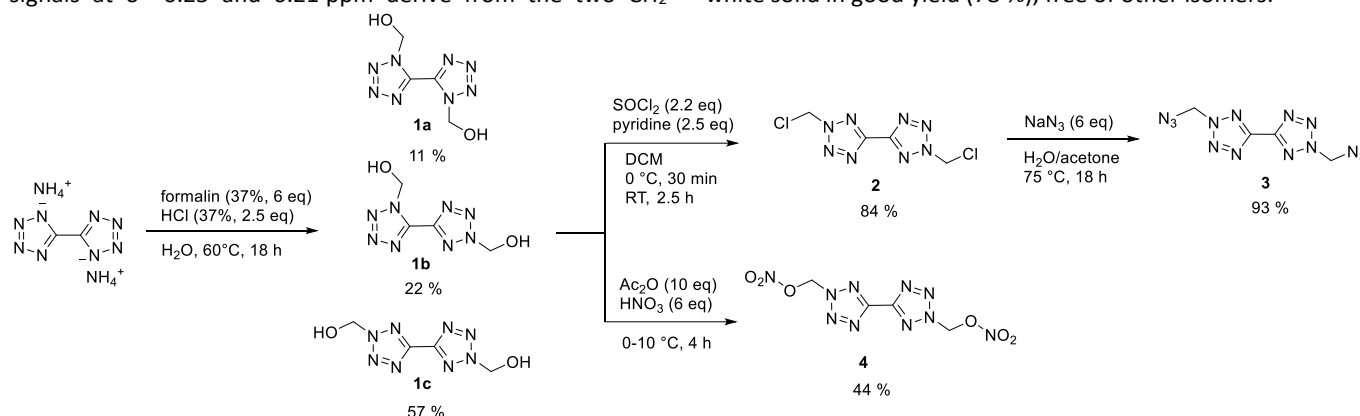
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Electronic Supplementary Information (ESI) available: [(1) Experimental, (2) Crystallographic Data, (3) Computations, (4) NMR data, (5) IR Spectroscopy, (6) DTA measurement. CCDC 2094642 (1c), 2094645 (2), 2094644 (3), and 2094643 (4)]. See DOI: 10.1039/x0xx00000x

Warning! The synthetic work described in this section involves the handling of highly sensitive products (3, and 4). Proper protective measurements and equipment must be used!

Diammonium 5,5'-bistetrazolate, synthesized according to literature⁹, is dissolved in water, and formalin (37 %) together with hydrochloric acid (37 %) is added in excess. After stirring at 60 °C overnight, the isomeric mixture of 1,1'- (**1a**), 1,2'- (**1b**), and 2,2'-di(hydroxymethyl)bistetrazole (**1c**) is extracted into DCM (Scheme 1). After drying the organic phase over MgSO₄ and removing the solvent *in vacuo*, isomeric mixture **1** is obtained as a white solid in moderate yield. The ¹H NMR of **1** in acetone-d₆ shows four signals at δ = 6.34, 6.25, 6.21, and 6.19 ppm (Figure 2). The signal at δ = 6.34 ppm attributes to the two equivalent CH₂-groups of the 1,1'-isomer (**1a**), while the signals at δ = 6.25 and 6.21 ppm derive from the two CH₂-

groups of the 1,2'-isomer (**1b**). The signal at δ = 6.19 ppm derives from the two equivalent CH₂-groups of the 2,2'-isomer (**1c**), also being the main product. Integration of the signals reveals a ratio of 1/2/5 between the three isomers. Mixture **1** is then dissolved in DCM and thionyl chloride and pyridine are added while keeping the temperature below 5 °C. The reaction solution is allowed to warm to room temperature over 2.5 h. When all solids are dissolved, the reaction solution is washed with water, hydrochloric acid (2 M), and water to remove excess thionyl chloride as well as pyridine. After removing the solvent, crude 2,2'-di(chloromethyl)bistetrazole (**2**) is obtained as an off-white solid in good yield (78 %), free of other isomers.



Scheme 1. Synthesis of 2,2'-di(hydroxymethyl)bistetrazole (**1c**) as well as further functionalisation towards 2,2'-di(azidomethyl)bistetrazole (**3**) and 2,2'-di(nitratomethyl)bistetrazole (**4**)

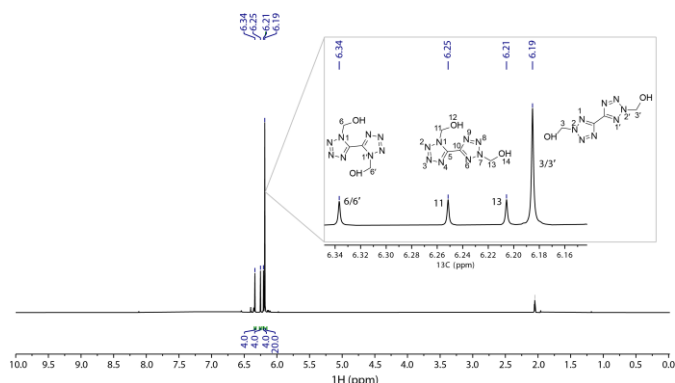


Figure 2 ¹H NMR spectrum and assignment of signals of isomeric mixture **1** in acetone-d₆.

Crude compound **2** is then added to a solution of sodium azide in water/acetone (1:4) and stirred at 75 °C overnight. The reaction solution is extracted into DCM, dried over MgSO₄ and the solvent is removed *in vacuo*, thus obtaining a colourless oil of 2,2'-di(azidomethyl)bistetrazole (**3**) in very good yield. The oil starts to solidify immediately after removing the flask from the water bath of the rotary evaporator, leaving **3** as a colourless, extremely sensitive (!) solid. Isomeric mixture **1** is also added to a large excess of acetic anhydride to which nitric acid (100%) was added at 0 °C. After the reaction is complete, it is quenched on ice and the precipitate is filtered off, and purified by column chromatography on silica gel with pure DCM as eluting solvent. By removing the solvent *in vacuo*, 2,2'-di(nitratomethyl)bistetrazole (**4**) is obtained as an off-white solid in moderate yield (44%), free of other isomers. The ¹H NMR of compound **3** in acetone-d₆ shows one signal at

δ = 6.39 ppm for the two CH₂-groups, while the ¹³C NMR of **3** shows two signals at δ = 155.6 and 65.7 ppm for the carbon atoms of the bistetrazole and the CH₂-groups, respectively. The ¹⁵N NMR of compound **3** (Figure 3) shows seven distinct signals. Due to the symmetry of the molecule, all nitrogen atoms appear in pairs. The resonances for the two azides at δ = -302.1 (N_α), -159.6 (N_γ), and -136.0 (N_β) ppm are in the same range as for comparable azido-methyl compounds.⁵ The resonances for the bistetrazole at δ = -90.6 (N_{2/2'}), -76.9 (N_{1/1'}), -46.9 (N_{4/4'}), and 3.0 (N_{3/3'}) are in the typical range for 2*N*-substituted tetrazoles¹⁰. The signals attributing N_{1/1'} as well as the signal for both N_β, split into triplets due to J³-coupling with the hydrogen atoms of the CH₂-groups. Crystals of compound **1c-4** suitable for single crystal X-Ray diffraction were obtained by recrystallization from ethyl acetate. The solid-state crystal structures of all of the compounds synthesized in this work were determined using low-temperature single-crystal X-ray diffraction. Obtained crystal densities are recalculated to their respective room temperature density (calculation method is given in the Supporting Information). All of the data and parameters of the measurements, as well as of the refinements and crystal structures of **1c** and **2** are given in the Supporting Information Table S1. Compound **3** crystallises in the tetragonal space group *I*4₁/*a* with a calculated density of 1.62 g cm⁻³ (298 K) and eight molecules in the unit cell (Figure 4). The bistetrazole moiety is perfectly planar with a torsion angle of 180 ° between N1-C1-C1'-N1'. Due to the sp³-hybridization of the methylene groups, both azides are protruding from the bistetrazole plane in opposite directions. Compound **4** (Figure 5) crystallizes in the tetragonal space group *P*-42₁*c* with four

loosely added **3** (Figure 7) while preliminary initiation testing with compound **4** was negative.

Table 1. Physicochemical properties of 2,2'-di(azidomethyl)bistetrazole (**3**) and 2,2'-di(nitratomethyl)bistetrazole (**4**), compared with the primary explosives K₂DNABT and lead azide

	3	4	K ₂ DNABT ⁸	LA ¹⁴
Formula	C ₄ H ₄ N ₁₄	C ₄ H ₄ N ₁₀ O ₆	C ₂ K ₂ N ₁₂ O ₄	N ₆ Pb
M [g mol ⁻¹]	248.17	288.14	334.30	291.3
IS [J] ^[a]	2	<1	1	2.5-4
FS [N] ^[b]	< 0.1	0.3	≤1	≤1
ρ [g cm ⁻³] ^[c]	1.62	1.69	2.11	4.8
N / O [%] ^[d]	79.0, 0.0	48.6, 33.3	50.3, 19.1	50.3 / 0
Ω _{CO} [%] ^[e]	-38.7	0.0	-4.8	-11.0
T _{endo} /T _{exo} ^[f] [°C]	102 / 177	100 / 150	- / 200	- / 315
Δ _r H ^o [kJ mol ⁻¹] ^[g]	1257.9	440.5	326.4	450.1
Explo5 V6.05.04				
-Δ _{Ex} U ^o [kJ kg ⁻¹] ^[h]	4928	5385	4948	1560
P _{C-J} [kbar] ^[i]	237	286	310	356
V _{det} [m s ⁻¹] ^[j]	8155	8377	8459	6187

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] From X-ray diffraction analysis recalculated to 298 K. [d] Nitrogen and oxygen content. [e] Oxygen balance towards CO formation. [f] Temperature of endothermic (melting) and exothermic event (DTA; β = 5 °C min⁻¹). [g] Calculated enthalpy of formation. [h] Energy of explosion. [i] Detonation pressure at Chapman-Jouguet point. [j] Detonation velocity.

We strongly want to point out the possibility of dripping molten **3** on a possible secondary charge, which to the best of our knowledge has not been described so far. Hence, compound **3** offers the possibility to replace the metal-containing lead azide with an all CHN-containing metal-free melt-castable green primary explosive in initiation devices.

Hydroxy methylation with further nitration or chlorination with subsequent chloride azide exchange proved to be a reliable procedure for the design of high energetic melt-castable explosives. The application of this procedure to the 5,5'-bistetrazole scaffold resulted in two high-performing but also highly sensitive compounds with melting points around 100°C. Starting from diammonium bistetrazolate, 2,2'-di(azidomethyl)- (**3**) and 2,2'-di(nitratomethyl)bistetrazole (**4**) were synthesized by a straight forward synthesis. Both compounds were analysed by multinuclear NMR spectroscopy, accompanied by elemental analysis confirming their purity. Hirshfeld analysis of their crystal structure indicated a very high mechanical sensitivity, which was confirmed by experimental measurement of friction and impact sensitivities. Both compounds are extremely sensitive (<1–2 J, <1 N), while showing explosive properties of a secondary high explosive (>8000 m s⁻¹). The fast DDT of compound **3** together with a melting point of 100 °C and thermal stability of up to 177 °C makes it an outstanding melt-castable, metal-free green primary explosive for initiation devices.

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. N00014-19-1-2078 as well as the Strategic Environmental Research and Development Program (SERDP) under grant no. WP19-1287 is gratefully acknowledged. The authors thank Prof. K. Karaghiosoff for ¹⁵N NMR measurement.

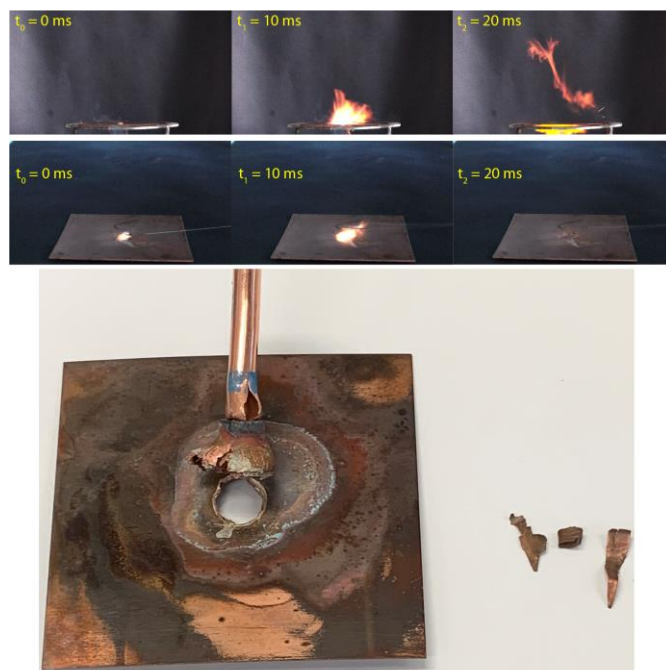


Figure 7. Top) Showing individual frames of detonation in the hot plate test. Middle) Showing individual frames of detonation upon touching with red-hot needle. Bottom) Positive initiation of PETN (200 mg) pressed into the copper tube, and loosely covered with **3**. The hole in the witness-plate confirms the positive initiation of the main charge.

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