

Synthesis of Bridged Tetrazoles with Promising Properties and Potential Applications by a One-Step Finkelstein Reaction

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Numerous nitramine bridged compounds which show promising combinations of properties have already been identified in the area of energetic materials. In this work, four new nitrazapropane bridged tetrazoles, as well as four new trinitrazaheptane tetrazoles and three oxapropane bridged tetrazoles were synthesized and fully characterized. These new compounds can all be synthesized by a simple, one-step synthesis using Finkelstein conditions. All of these new energetic materials were characterized using NMR spectroscopy, single crystal X-ray diffraction, vibrational analysis and elemental analysis. The thermal behaviour of these compounds

was studied by differential thermal analysis (DTA) and partly by thermogravimetric analysis (TGA). The BAM standard method was used to determine the sensitivities towards impact (IS) and friction (FS). The enthalpies of formation were calculated at the CBS-4M level, and the energetic performances were calculated using the EXPLO5 (V6.06.01) computer code. The properties of the new compounds were compared to each other as well as to the known energetic material RDX. Moreover, the iron(II) and copper(II) perchlorate complexes with 1,3-bis-1,1-tetrazolyl nitrazapropane as ligand were prepared and investigated.

Introduction

The demands on new energetic materials are diverse and difficult to reconcile. There are not only demands on the synthetic process – which should be cost-efficient and environmentally friendly – there are also demands on the properties of new compounds, such as reconciling a high performance with low sensitivity.^[1–4] Therefore, to obtain a compound which can be more easily handled, the right compromise between energy and stability has to be found.

Various synthetic strategies have been described for creating new energetic materials, such as the introduction of ring and cage strain, or aiming to reach the highest possible nitrogen content.^[5–8] In order to achieve these properties in a compound, the same energetic building blocks are often used.^[1–2] Well-known examples are functionalization with nitro,

nitrate, nitrimino and nitramino groups, or the addition of covalent azides.^[1,9–14] However, not only incorporation of the functional groups described above is used for the design of energetic materials. The inclusion of different building blocks like arenes or different heterocycles can increase the energy content in a molecule as well.^[1,15–20] Azoles such as pyrazoles, triazoles or tetrazoles are often used due to their positive enthalpies of formation. Examples of such novel energetic materials are TKX-50 (dihydroxylammonium-5,5-bistetrazolyl-1,1-diolate) or the primary explosive DBX-1 (copper(I) 5-nitrotetrazolate).^[21–22]

The nitramine functional group is also widely used as an energetic building block in energetic materials, and many compounds which incorporate this building block are known and show promise for use in applications. Examples of cyclic nitramines are the two secondary explosives hexogen (1,3,5-trinitro-1,3,5-triazinane, RDX) and octogen (1,3,5,7-tetranitro-1,3,5,7-tetrazocane, HMX), both of which are mainly used in the military sector in warheads or propellant formulations.^[23–25] In addition, there are also open-chain nitramine energetic compounds such as the nitroxyethyl nitramines (NENAs). Important examples of NENAs are BuNENA (*n*-butyl nitroxyethyl nitramine) or DINA (dioxyethyl nitramine dinitrate), both of which are used as plasticizers in propellant formulations.^[26–27]

In the literature it is reported that bridged energetic materials show a higher stability.^[28–30] In the previously reported compounds, simple saturated carbon chains have usually been used to act as bridging units, but also oxa, azo or nitramine bridged compounds have been reported.^[30–32] As is shown on the left side of Figure 1, many compounds with nitrazapropane or trinitrazaheptane as the bridging unit have been reported. Open-chain nitramine compounds such as the bridged *bis*-

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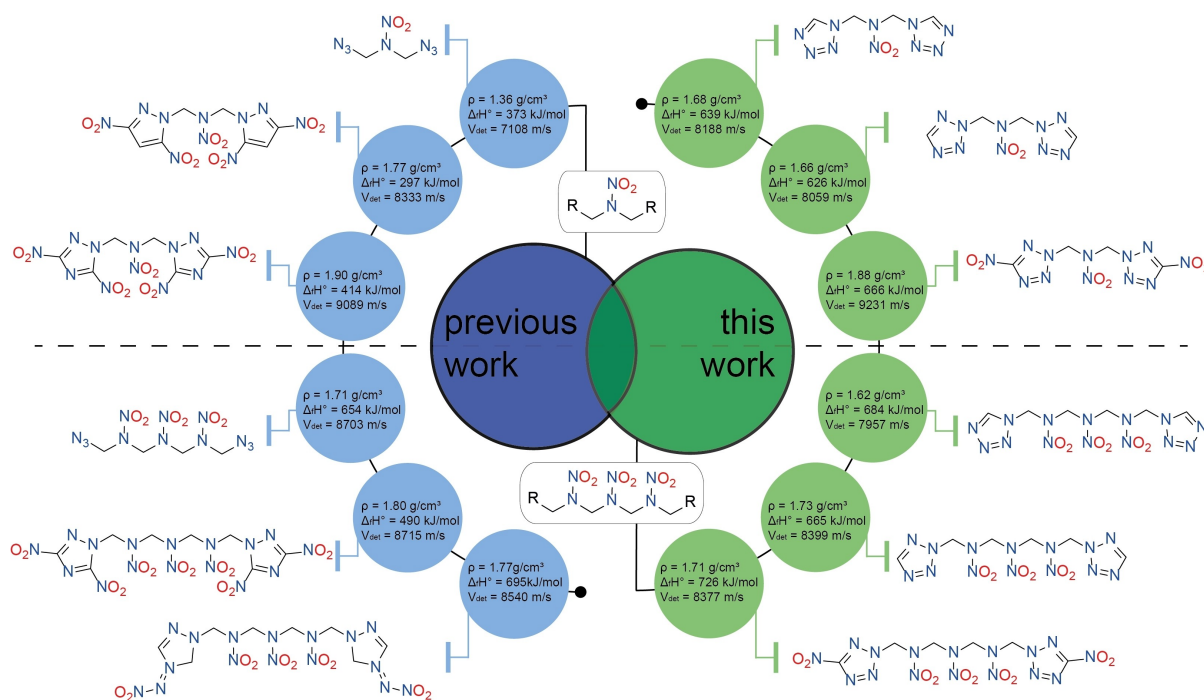


Figure 1. New nitramine-bridged compounds as well as those previously reported in the literature with their density, solid-state heat of formation (HoF) and detonation velocity (V_{det}).^[33–36]

azides or bridged azoles are already known in literature (Figure 1).^[33–36]

A closer look at the density, solid-state enthalpy of formations (HoF) and detonation velocities (V_{det}) of the compounds in shown Figure 1 shows that most exhibit promising properties. The 1,3-bis(3,5-dinitro-1,2,4-triazol-1-yl)-2-nitrazopropane stands out in this respect, because of its remarkable high density of 1.90 g cm^{-3} , which results in a calculated detonation velocity of 9089 m s^{-1} .^[34] However, the corresponding trinitraheptane-bridged compound 1,7-bis(3,5-dinitro-1,2,4-triazol-1-yl)-2,4,6-trinitraheptane also shows promising properties with a HoF of 490 kJ mol^{-1} and a detonation velocity of 8715 m s^{-1} .^[35]

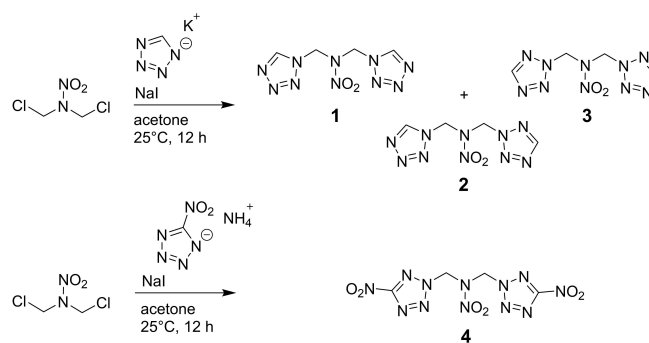
So far, only nitramine-bridged pyrazoles and triazoles are known in the literature, while the corresponding tetrazole compounds remain elusive.^[34–37] Therefore, in this work, the corresponding nitramine bridged tetrazole isomers and 5-nitrotetrazoles were synthesized, characterized, and their properties compared with those of known secondary explosives. In addition, 1,3-bis-1,1'-tetrazolynitrazopropane was used to act as a ligand in energetic coordination compounds (ECCs), and the properties of the new complex compounds were investigated.^[38]

Since the literature suggests that oxapropane-bridged compounds are more stable than nitrazopropane-bridged compounds, the three isomers of oxapropane-bridged tetrazole were also synthesized and compared with the nitramine-bridged compounds.^[30] The 1,1'-isomer **9** has been mentioned once before in the literature, however, in this work it was prepared via an alternative route and fully characterized for the first time in terms of its energetic properties.^[39]

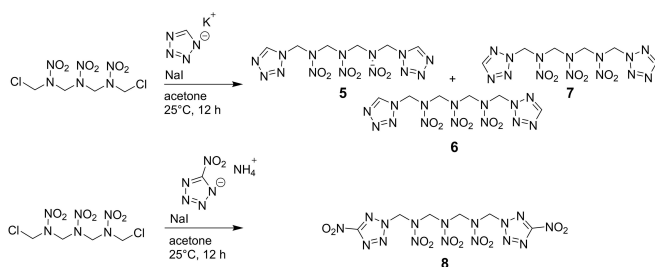
Results and Discussion

Synthesis

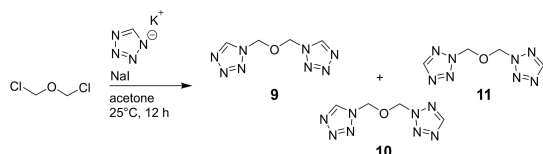
The syntheses of compounds **1** to **11** were all performed using a Finkelstein reaction, as shown in Scheme 1–3.^[40–42] Starting from the chloride, first a chloride-iodide exchange (S_N2 mechanism) is carried out by adding sodium iodide. This halide exchange is carried out to exploit the solubility differences of the halide salts in the corresponding solvent, which is in most cases acetone. While sodium iodide dissolves well in acetone, sodium chloride is almost insoluble. Therefore, the equilibrium of the nucleophilic substitution reaction is shifted, and the reaction to attach the tetrazole rings on the nitramine bridge is favored. In general, it is known that the Finkelstein reaction



Scheme 1. Synthetic route of 1,3-bis-1,1'-tetrazolynitrazopropane (**1**), 1,3-bis-1,2-tetrazolynitrazopropane (**2**), 1,3-bis-2,2'-tetrazolynitrazopropane (**3**) and 1,3-bis-2,2'-nitrotetrazolynitrazopropane (**4**).



Scheme 2. Synthetic route of 1,7-*bis*-1,1'-tetrazolylnitrazapropene (**5**), 1,7-*bis*-1,2-tetrazolylnitrazapropene (**6**), 1,7-*bis*-2,2'-tetrazolylnitrazapropene (**7**) and 1,7-*bis*-2,2'-nitrotetrazolylnitrazapropene (**8**).



Scheme 3. Synthetic route of 1,3-*bis*-1,1'-tetrazolyloxapropene (**9**), 1,3-*bis*-1,2-tetrazolyloxapropene (**10**) and 1,3-*bis*-2,2'-tetrazolyloxapropene (**11**).

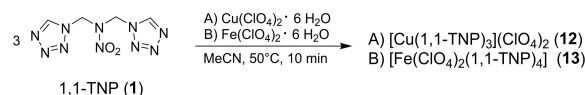
proceeds best for primary halides. In our work primary halides were used, therefore reaction times of no longer than 12 h were required and no increased temperatures were necessary.^[40–42]

All three possible isomers are formed from the reaction of 1,3-dichloro-2-nitrazapropene with potassium tetrazolate under Finkelstein conditions (Scheme 1). The 1,2-isomer (**2**) was obtained as the main component (60%), followed by the 2,2'-isomer (**3**, 25%) and the 1,1'-isomer (**1**, 15%). The isomers were obtained with a moderate overall yield of 62% and can be easily separated by column chromatography. In contrast, only one isomer was formed in the reaction with ammonium nitrotetrazolate. Due to the electron withdrawing effect of the nitro group on the tetrazole ring, only the 2,2'-isomer (**4**) is formed, leading to an almost quantitative conversion with a yield of 98%.

Similar results were observed for the reaction of 1,7-dichloro-2,4,6-trinitrazaheptane with potassium tetrazolate under Finkelstein conditions as shown in Scheme 2. All three isomers were again formed, with a ratio of 27% of 1,1'-isomer (**5**), 43% of 1,2-isomer (**6**) and 30% of 2,2'-isomer (**7**). The isomers can again be separated using column chromatography and are obtained with a moderate overall yield of 60%. For the nitrotetrazole derivative **8**, again only one isomer is obtained with a very good yield of 92%.

Scheme 3 shows the reaction of 1,3-dichloro-2-oxapropene with potassium tetrazolate under Finkelstein conditions. Here, again, all three isomers are formed with a total yield of 78%. The isomers can be separated using column chromatography, and are formed in the ratio of 14% of 1,1'-isomer (**9**), 50% of 1,2-isomer (**10**) and 36% of 2,2'-isomer (**11**).

In addition, 1,3-*bis*-1,1'-tetrazolylnitrazapropene (**1**) was used as a ligand in ECCs. In order to synthesize the ECCs shown in Scheme 4, three equivalents of **1** were reacted with one equivalent of the corresponding copper(II) or iron(II)



Scheme 4. Synthesis of energetic coordination compounds (ECCs) **12** and **13** using 1,3-*bis*-1,1'-tetrazolylnitrazapropene (**1**) as the energetic ligand.

perchlorate, which resulted in the formation of the energetic complexes **12** and **13**.

NMR spectroscopy

Compounds **1** to **11** were characterized by ¹H, ¹³C{¹H} and ¹⁴N NMR spectroscopy in acetone-*D*₆. Moreover, ¹⁵N NMR spectra of compounds **4** and **8** were obtained, which are discussed in more detail in the following section. All other spectra and assignments can be found in the Experimental Section or in the Supporting Information.

In Figure 2, the ¹⁵N NMR spectrum of **4** is shown. The resonance at −191.6 ppm can be assigned to the nitramine nitrogen (N1). The quintet (³J_{N,H} = 2.7 Hz) at −41.1 ppm corresponds to the nitro group (N2) of the nitramine moiety, while the signal at −35.1 ppm can be assigned to the nitro group (N7) which is attached to the tetrazole ring. The resonances corresponding to the remaining four tetrazole nitrogen atoms were assigned based on the assignments made for similar previously reported compounds: N3 at −78.8 ppm, N4 at −95.0 ppm, N5 at 8.6 ppm and N6 at −52.2 ppm.^[38]

The ¹⁵N spectrum of **8** is shown in Figure 3. The resonances corresponding to the two nitramine N atoms were assigned to −191.6 ppm (N1) and −195.5 ppm (N2), because of the integrals of 1:2. The nitro groups of the nitramine moieties are observed at −34.0 ppm (N3, quintet, ³J_{N,H} = 2.5 Hz) and at −36.8 ppm (N4, quintet, ³J_{N,H} = 2.5 Hz). Here, as well, the assignments were made based on the integrals. The resonance at −34.8 ppm is assigned to the nitrogen group (N9) attached to the tetrazole ring. The assignment of the resonances corresponding to the N atoms within the tetrazole ring is similar to

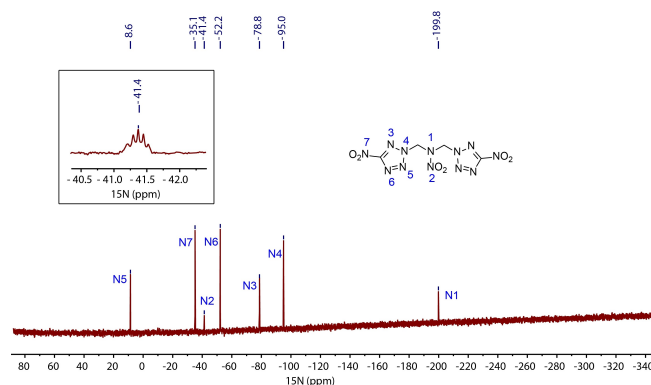


Figure 2. ¹⁵N NMR spectrum of 1,3-*bis*-2,2'-nitrotetrazolylnitrazapropene (**4**) in acetone-*D*₆.

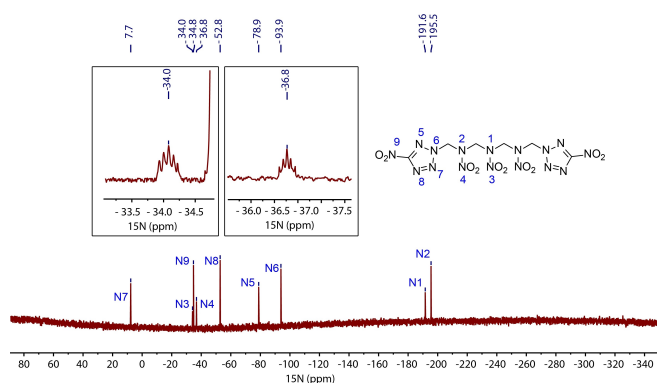


Figure 3. ^{15}N NMR spectrum of 1,7-*bis*-2,2'-nitrotetrazolylnitrazapropene (**8**) in acetone- D_6 .

that of **4**: N5 at -78.9 ppm, N6 at -93.9 ppm, N7 at 7.7 ppm and N8 at -52.8 ppm.^[38]

Single crystal analysis

The single crystal structures of compounds **1**, **3**, **4**, **7** and **9** were determined using low temperature X-ray diffraction. The individual crystal structures are shown and discussed in the following section. However, additional information about the measurements and refinements can be found in the Supporting Information.

The crystal structures of 1,3-*bis*-1,1'-tetrazolylnitrazapropene (**1**, left) and 1,3-*bis*-2,2'-tetrazolylnitrazapropene (**3**, right) are shown in Figure 4.

The nitrazapropene **1** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell and a re-calculated density of 1.68 g cm^{-3} at room temperature (25°C). The corresponding 2,2'-isomer **3** has similar structural parameters, also crystallizing in the monoclinic space group $P2_1/c$ with four molecules per unit cell. 1,3-*Bis*-2,2'-tetrazolylnitrazapropene, however, has a slightly lower recalculated density of 1.66 g cm^{-3} at room temperature. The spatial arrangement of the two isomers shows clear differences. While the tetrazole rings in the 1,1'-isomer are aligned as far away from each other as possible, in the 2,2'-isomer (**3**) they are arranged in such a way that they align themselves parallel to each other in a pincer-like manner.

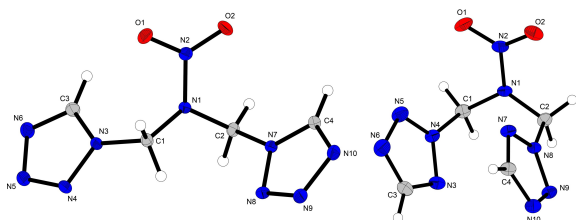


Figure 4. Crystal structures of **1** (left) and **3** (right) with selected bond lengths (\AA) and selected angles ($^\circ$): **1** N1-N2 1.3857 (14), N3-C1 1.4748 (15), N7-C2 1.4596 (15), C3-N3-C1-N1 -28.99 (17), C4-N7-C2-N1 -98.52 (14); **3** N1-N2 1.392 (2), N4-C1 1.463 (2), N8-C2 1.482 (2), N3-N4-C1-N1 -91.0 (2), N7-N8-C2-N1 -37.1 (2).

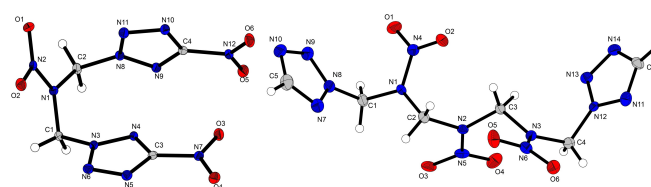


Figure 5. Crystal structures of **4** (left) and **7** (right) with selected bond lengths (\AA) and selected angles ($^\circ$): **4** N2-N1 1.404 (2), N3-C1 1.476 (3), N8-C2 1.482 (3), N4-N3-C1-N1 -62.9 (3), N9-N8-C2-N1 121.7(2); **7** N8-C1 1.450 (7), N12-C4 1.464 (7), N7-N8-C1-N1 -77.7 (6), N13-N12-C4-N3 -78.0 (6).

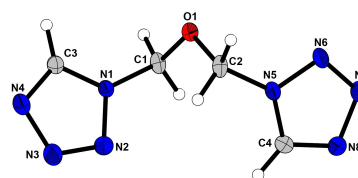


Figure 6. Crystal structure of **9** with selected bond lengths (\AA) and selected angles ($^\circ$): N1-C1 1.464 (2), N5-C2 1.466 (2), N2-N1-C1-O1 -102.1 (2), N6-N5-C2-O1 76.3 (2).

In Figure 5, the crystal structures of 1,3-*bis*-2,2'-nitrotetrazolylnitrazapropene (**4**, left) and 1,7-*bis*-2,2'-tetrazolylnitrazapropene (**7**, right) are shown.

1,3-*Bis*-2,2'-nitrotetrazolylnitrazapropene (**4**) crystallizes in the monoclinic space group Cc , with four molecules per unit cell. However, (**4**) shows a relatively high density of 1.88 g cm^{-3} at room temperature. In **4** the tetrazole rings are twisted towards each other in a pincer-like manner, similar to that observed in **3**.

Due to the longer trinitrazapropene bridge in **7**, the tetrazole rings are no longer twisted towards each other. 1,7-*Bis*-2,2'-tetrazolylnitrazapropene (**7**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell and a re-calculated density of 1.73 g cm^{-3} at room temperature.

Figure 6 shows the crystal structure of 1,3-*bis*-1,1'-tetrazolylnitrazapropene (**9**), which crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell and has a re-calculated density of 1.53 g cm^{-3} at room temperature.

The 1,1'-oxa-bridged bistetrazole **9** shows a similar spatial arrangement to that of the 1,1'-nitrazapropene-bridged **1**. The tetrazole rings are arranged in such a way that they are as far away from each other as possible.

Thermal analysis

In order to investigate the thermal behavior of the compounds prepared in this work, **1** to **13** were all analyzed by differential thermal analysis (DTA). DTA measurements were carried out in the range from 25 to 400°C with a heating rate of 5°C min^{-1} . The results of these measurements are shown in Table 1. Figure 7 shows the DTA plots of **4** and **8**, while the plots of the DTA measurements of the other compounds can be found in the Supporting Information (Figures S33–S36).

	T _{endo} ^[a] [°C]	T _{exo} ^[b] [°C]
1	167	171
2	99	154
3	72	173
4	157	213
5	–	187
6	–	194
7	193	212
8	210	217
9	98	168
10	–	180
11	–	185
12	–	246
13	–	220
RDX ^[43]	188	209

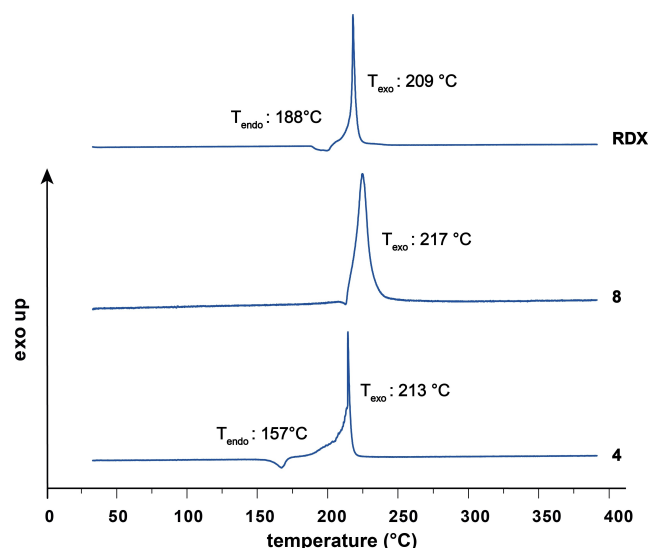


Figure 7. DTA measurements of 4 (bottom) and 8 (center), as well as of RDX^[43] for comparison, with a heating rate of 5 °C min⁻¹.

All compounds (1–13) were found to decompose above 150 °C. In general, the *bis*-nitrotetrazolyl derivatives (4, 8) are thermally more stable than the *bis*-tetrazolyl compounds (1–3, 5–7). Moreover, the trinitrazaheptane-bridged compounds (5–8) are more thermally stable than the nitrazapropane-bridged compounds (1–4). The trend that oxapropane bridged compounds are more thermally stable compared to the corresponding nitrazapropane bridged compounds is shown for the 1,2'-isomer (2 vs. 10) and 2,2'-isomer (3 vs. 11), but not for the 1,1'-isomer (1 vs. 9).

Furthermore, all of the compounds which showed an endothermic signal in the DTA (1–4 and 7–9) were additionally examined using thermogravimetric analysis (TGA). The TGA measurements confirmed that all of the endothermic signals in the DTA measurements correspond to melting points. The TGA

plots are shown in the Supporting Information (Figures S37–S41).

Based on the thermal stability of the two ECCs (12 and 13), it can be concluded that the decomposition temperature of the ligand can be significantly increased by coordination to the metals copper and iron.

Sensitivities and energetic properties

The sensitivities of 1–13 towards impact (IS) and friction (FS) were determined according to BAM standard methods^[44–48] and all values are shown in Table 2.

It is notable that the *bis*-nitrotetrazolyl derivatives (4, 8) are significantly more sensitive towards impact and friction than the *bis*-tetrazolyl derivatives (1–3, 5–7). According to the UN Recommendations on the Transport of Dangerous Goods,^[49] 4 and 8 are classified as being very sensitive towards impact. With respect to friction, 8 is classified as sensitive, and 4 even as very sensitive.

Comparing the sensitivities of the oxa-bridged compounds with those of the nitrazapropane-bridged compounds confirms the results in the literature:^[30] 9 to 11 are clearly less sensitive than 1 to 3. The sensitivities of the two ECCs (12 and 13) stand out showing very low values, both of which are in the range of primary explosives, with sensitivities towards impact being classified as very sensitive and towards friction as extremely sensitive.

Furthermore, hot needle and hot plate tests were performed on 12 and 13 to investigate their possible application as primary explosives. Both the copper and iron complexes showed deflagration in both tests, as is shown in Figure 8.

In addition, the energetic properties 1–11 were calculated using the EXPLO5 code version 6.06.01.^[50] These values were

Table 2. Sensitivities towards friction and impact of compounds 1–13 compared to that of RDX.^[43]

	IS [J] ^[a]	FS [N] ^[b]
1	30	> 360
2	20	120
3	30	72
4	3	60
5	30	> 360
6	25	288
7	30	> 360
8	3	160
9	40	> 360
10	40	> 360
11	40	288
12	< 1	10
13	< 1	9
RDX ^[43]	7.5	120

[a] impact sensitivity according to the BAM drophammer (method 1 of 6);
[b] friction sensitivity according to the BAM friction tester (method 1 of 6).

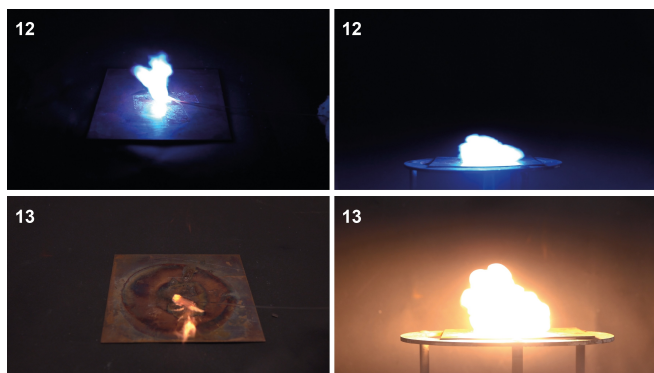


Figure 8. Hot needle (left) and hot plate (right) tests of the energetic coordination compounds (ECCs) 12 and 13.

calculated based on the density of the compounds, as well as on their enthalpy of formation which was calculated at the CBS-4M level. The results are shown in Table 3 and further details about the calculations can be found in the Supporting Information.

With a nitrogen plus oxygen content of over 70 percent in all compounds, all look promising at first glance. However, upon a closer look at the values, the oxapropane-bridged 9–11 have a significantly lower density and heat of formation (HoF), and thus give significantly lower performance parameters compared to the nitramine-bridged 1–8. The *bis*-nitrotetrazolyl derivatives 4 and 8 show higher HoFs compared to the corresponding *bis*-tetrazolyl derivatives. Due to the rather low densities of the latter (densities between 1.65 g cm^{-3} and 1.68 g cm^{-3}), this results in calculated detonation velocities for the nitrazapropane-bridged 1–3 of between 8000 – 8200 m s^{-1} . In the case of the trinitrazaheptane bridged compounds, larger differences between the isomers are obvious. While the 1,1'-isomer 5 has a density of only 1.62 g cm^{-3} , the 2,2'-isomer 7 has a considerably higher density of 1.73 g cm^{-3} . Thus, for the trinitrazaheptane-bridged compounds, the best values are obtained for the 2,2'-isomer (7) which has a calculated detonation velocity of almost 8400 m s^{-1} . The compound which shows the highest HoF in this work is the trinitrazaheptane bridged *bis*-nitrotetrazolate 8, with a value of $725.8 \text{ kJ mol}^{-1}$. However, since 8 shows only a moderate density of 1.71 g cm^{-3} , a detonation velocity of 8377 m s^{-1} is obtained, which is somewhat lower compared to that of 7 which has been described previously. Overall, the best detonation parameters in this work were obtained for 4. Due to its high density of 1.88 g cm^{-3} and good solid-state enthalpy of formation of $665.7 \text{ kJ mol}^{-1}$, an outstanding detonation velocity of 9231 m s^{-1} was predicted for 4.

It was also found that $[\text{Fe}(\text{ClO}_4)_2(1,1'\text{-TNP})_4]$ shows a thermochromic effect due to spin crossover, when cooled with liquid nitrogen. Therefore, magnetic properties of 13 were investigated and can be found in Figure S42 and S43 in the Supporting Information.

Conclusions

In this work, 11 new nitramine and oxa bridged energetic materials as well as two new energetic coordination compounds were synthesized and fully characterized. 1 to 11 can be prepared from the corresponding dichloro compounds by a one-step Finkelstein reaction. While the reaction to yield the corresponding *bis*-tetrazolyl derivatives 1–3, 5–7 and 9–11 always forms all three possible isomers, the reaction to yield the *bis*-nitrotetrazolyl derivatives 4 and 8 only forms the preferred 2,2'-isomer.

Figure 9 shows the two best compounds of this work, 1,3-*bis*-2,2'-nitrotetrazolyl nitrazapropane (4) and 1,7-*bis*-2,2'-tetrazolyl trinitrazaheptane (7), compared to the commonly used secondary explosive RDX. As described in the introduction, it is difficult to achieve the right balance between performance and stability when designing new energetic materials. Compound 4, for example, shows a higher detonation velocity than RDX ($4: V_{\text{det}} = 9231 \text{ m s}^{-1}$ vs. RDX: $V_{\text{det}} = 8794 \text{ m s}^{-1}$) with comparable thermal stability ($4: T_{\text{dec}} = 213 \text{ }^\circ\text{C}$ vs. RDX: $T_{\text{dec}} = 209 \text{ }^\circ\text{C}$) as can be seen in Figure 9. However, 4 is more sensitive towards impact and friction than RDX. Compound 7, on the other hand, has a lower sensitivity compared to RDX and is therefore safer to handle, but has a 400 m s^{-1} lower detonation velocity compared to RDX due to its lower density.

Nevertheless, both compounds show promising properties and are of interest as replacements for RDX, especially due to their easy synthesis.

Furthermore, 1,3-*bis*-1,1'-tetrazolyl nitrazapropane (1) was used as ligand in energetic coordination compounds (ECCs) to investigate its possible application in detonators. Both the sensitivities and thermal stabilities of 12 and 13 are in a good range. However, the hot needle and hot plate tests showed that the compounds deflagrate and do not detonate, which makes their use as ignition agents more promising.

Experimental Section

CAUTION! All investigated compounds are potentially explosive energetic materials, which show partly increased sensitivities towards various stimuli (e.g. elevated temperatures, impact or friction). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves,

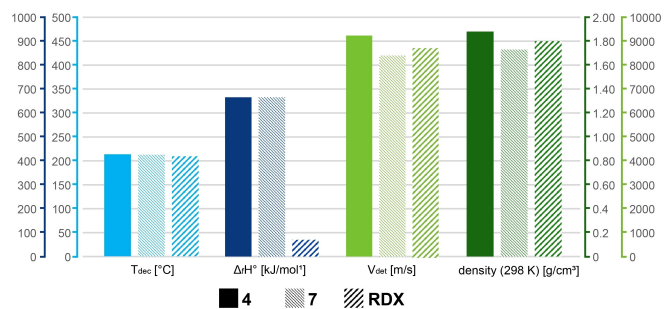


Figure 9. Bar chart comparing important properties of compounds 4 and 7 with RDX.

Table 3. Energetic properties of compounds 1–11 and RDX.^[a,3]

	1	2	3	4	5	6	7	8	9	10	11	RDX ^[a3,50]
Formula	C ₄ H ₆ N ₁₀ O ₂	C ₄ H ₆ N ₁₀ O ₂	C ₄ H ₆ N ₁₀ O ₂	C ₄ H ₄ N ₁₂ O ₆	C ₆ H ₁₀ N ₁₄ O ₆	C ₆ H ₁₀ N ₁₄ O ₆	C ₆ H ₁₀ N ₁₄ O ₆	C ₆ H ₈ N ₁₆ O ₁₀	C ₄ H ₆ N ₈ O	C ₄ H ₆ N ₈ O	C ₄ H ₆ N ₈ O	C ₃ H ₆ N ₆ O ₆
FW [g mol ⁻¹]	226.07	226.07	226.07	316.04	374.24	374.24	374.24	464.23	182.15	182.15	182.15	236.15
ρ_{calc} (298 K) [g cm ⁻³]	1.68 ^[a]	1.65 ^[b]	1.66 ^[a]	1.88 ^[b]	1.62 ^[b]	1.72 ^[b]	1.73 ^[a]	1.71 ^[b]	1.53 ^[a]	1.50 ^[c]	1.51 ^[c]	1.80
N + O [%] ^[d]	76.1	76.1	76.1	83.5	78.1	78.1	78.1	82.7	70.3	70.3	70.3	81.1
Ω_{CO_2} [%] ^[e]	-64	-64	-64	-20	-47	-47	-47	-21	-88	-88	-88	-22
T_{dec} [°C] ^[f]	171	154	173	213	187	194	212	217	168	180	185	209
ΔH° (s/l) [kJ mol ⁻¹] ^[g]	638.7 (s)	634.9 (s)	625.7 (s)	665.7 (s)	684.2 (s)	680.1 (s)	665.1 (s)	725.8 (s)	446.8 (s)	442.7 (l)	439.5 (l)	70.3 (s)
EXPLOS V6.06.01 ^[44]												
P_{co} [GPa] ^[h]	24.4	23.6	23.7	38.2	24.2	27.3	27.5	28.4	17.4	16.5	16.7	33.6
V_{det} [m s ⁻¹] ^[i]	8188	8027	8059	9231	7957	8368	8399	8377	7216	7068	7108	8794
$-\Delta_{\text{ox}}U^{\circ}$ [kJ kg ⁻¹] ^[j]	4621	4596	4560	5692	5021	5055	5020	5224	3618	3595	3579	5717
T_{det} [K] ^[k]	3178	3195	3168	4051	3503	3443	3418	3766	2582	2579	2567	3734
V_0 [dm ³ kg ⁻¹] ^[l]	804	806	805	762	822	810	809	795	789	791	790	784

[a] re-calculated from X-ray density; [b] determined by gas-pycnometer; [c] liquid at room temperature, therefore determined experimentally through the formula $\rho = m/V$; [d] Combined nitrogen and oxygen content; [e] oxygen balance assuming the formation of CO₂; [f] onset temperature of decomposition (at a heating rate of 5 °C min⁻¹); [g] calculated (CBS-4 M) heat of formation; [h] detonation pressure; [i] detonation velocity; [j] energy of explosion; [k] explosion temperature; [l] volume of detonation gases at standard temperature and pressure condition.

Kevlar sleeves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

Nitrazapropene-bridged tetrazoles (1–3)

1,3-Dichloro-2-nitrazapropene (1.00 g, 6.29 mmol, 1.0 equiv.) was dissolved in acetone (80 mL). Potassium tetrazolate (1.36 g, 12.58 mmol, 2.0 equiv.) and sodium iodide (1.89 g, 12.58 mmol, 2.0 equiv.) were added and the reaction was stirred for 12 h at 25 °C. The suspension was filtered and the filtrate was evaporated *in vacuo*. The residue was extracted with ethyl acetate (100 mL) and washed with water (3×100 mL). The organic phase was dried over magnesium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (80/20→90/10 ethyl acetate/isohexane) to yield **1** (226 mg, 16%), **2** (509 mg, 36%), **3** (124 mg, 9%) as off-white/yellowish solids.

1,3-Bis-1,1'-tetrazolylnitrazapropene (1)

TLC (90/10 ethyl acetate/isohexane): $R_f = 0.24$.

^1H NMR (400 MHz, acetone- D_6 , ppm): $\delta = 9.39$ (s, 1H), 6.85 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, acetone- D_6 , ppm): $\delta = 145.1$, 61.3; ^{14}N NMR (29 MHz, acetone- D_6 , ppm): $\delta = -37$, -152; IR (ATR, cm^{-1}): 3127 (m), 3109 (m), 3054 (w), 3027 (w), 2989 (w), 2922 (w), 2853 (vw), 2168 (vw), 1812 (vw), 1765 (vw), 1748 (vw), 1704 (vw), 1572 (s), 1478 (m), 1446 (m), 1434 (m), 1418 (m), 1389 (w), 1354 (m), 1340 (m), 1320 (w), 1283 (vs), 1261 (m), 1261 (m), 1248 (m), 1208 (m), 1170 (s), 1152 (s), 1116 (m), 1104 (s), 1085 (s), 1042 (w), 1015 (m), 969 (m), 951 (m), 937 (s), 906 (m), 885 (m), 767 (s), 727 (m), 717 (m), 661 (vs), 634 (s), 569 (w), 550 (w), 530 (w), 453 (m), 439 (m); elemental analysis calcd. (%) for $\text{C}_4\text{H}_6\text{N}_{10}\text{O}_2$ (226.07 g mol^{-1}): C 21.24, H 2.67, N 61.93; found: C 21.64, H 2.89, N 61.36; DTA (5 °C min^{-1}): onset: 166.7 °C (endo.), 170.5 °C (dec.); BAM drophammer: 30 J; Friction tester: > 360 N.

1,3-Bis-1,2-tetrazolylnitrazapropene (2)

TLC (90/10 ethyl acetate/isohexane): $R_f = 0.44$.

^1H NMR (400 MHz, acetone- D_6 , ppm): $\delta = 9.39$ (s, 1H), 8.82 (s, 1H), 7.01 (s, 2H), 6.88 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, acetone- D_6 , ppm): $\delta = 154.3$, 145.0, 65.3, 61.2; ^{14}N NMR (29 MHz, acetone- D_6 , ppm): $\delta = -37$, -98, -149; IR (ATR, cm^{-1}): 3151 (w), 3122 (w), 3049 (w), 3033 (w), 2986 (w), 2847 (vw), 1818 (vw), 1717 (vw), 1566 (s), 1476 (m), 1444 (s), 1415 (m), 1374 (w), 1357 (w), 1327 (m), 1279 (vs), 1232 (m), 1189 (m), 1173 (s), 1163 (s), 1146 (m), 1121 (m), 1100 (s), 1089 (s), 1070 (s), 1033 (m), 1020 (s), 1000 (w), 963 (s), 93 (s), 900 (s), 892 (m), 869 (w), 761 (vs), 741 (m), 717 (m), 704 (m), 678 (s), 665 (s), 645 (s), 632 (s), 550 (w), 502 (vw), 451 (m), 436 (w); elemental analysis calcd. (%) for $\text{C}_4\text{H}_6\text{N}_{10}\text{O}_2$ (226.07 g mol^{-1}): C 21.24, H 2.67, N 61.93; found: C 22.40, H 3.01, N 60.28; DTA (5 °C min^{-1}): onset: 98.6 °C (endo.), 154.3 °C/162.1 °C (exo.); BAM drophammer: 20 J; Friction tester: 120 N.

1,3-Bis-2,2'-tetrazolylnitrazapropene (3)

TLC (90/10 ethyl acetate/isohexane): $R_f = 0.77$.

^1H NMR (400 MHz, acetone- D_6 , ppm): $\delta = 8.78$ (s, 1H), 7.04 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, acetone- D_6 , ppm): $\delta = 154.3$, 65.0; ^{14}N NMR (29 MHz, acetone- D_6 , ppm): $\delta = -39$, -99; IR (ATR, cm^{-1}): 3147 (w), 3055 (w), 3041 (w), 3003 (w), 2994 (w), 2920 (vw), 2852 (vw), 2168 (vw), 2005 (vw), 1808 (vw), 1719 (vw), 1574 (s), 1458 (w), 1437 (s), 1421 (m), 1400 (w), 1367 (m), 1339 (m), 1327 (m), 1272 (vs), 1237 (m), 1193 (m), 1181 (s), 1181 (s), 1144 (m), 1130 (m), 1081 (s), 1022

(s), 1008 (s), 953 (m), 932 (vs), 903 (s), 879 (w), 765. (vs), 741 (m), 705 (s), 680 (m), 673 (m), 651 (s), 620 (s), 550 (w), 448 (m); elemental analysis calcd. (%) for $\text{C}_4\text{H}_6\text{N}_{10}\text{O}_2$ (226.07 g mol^{-1}): C 21.24, H 2.67, N 61.93; found: C 21.57, H 2.76, N 61.12; DTA (5 °C min^{-1}): onset: 71.6 °C (endo.), 173.1 °C (dec.); BAM drophammer: 30 J; Friction tester: 80 N.

1,3-Bis-2,2'-nitrotetrazolylnitrazapropene (4)

1,2-Dichloro-2-nitrazapropene (1.0 g, 6.29 mmol, 1.0 equiv.) was dissolved in acetone (80 mL). Ammonium-5-nitrotetrazolate hemihydrate (1.78 g, 12.58 mmol, 2.0 equiv.) and sodium iodide (1.89 g, 12.58 mmol, 2.0 equiv.) were added and the reaction was stirred for 12 h at 25 °C. The suspension was filtered and the filtrate was evaporated *in vacuo*. The residue was extracted with ethyl acetate (100 mL) and washed with water (1×100 mL). The organic phase was dried over magnesium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel (50/50 ethyl acetate/isohexane) to obtain **4** (1.87 g, 95%) as a yellowish solid.

TLC (50/50 ethyl acetate/isohexane): $R_f = 0.39$.

^1H NMR (400 MHz, acetone- D_6 , ppm): $\delta = 7.30$ (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, acetone- D_6 , ppm): $\delta = 66.8$; ^{15}N NMR (41 MHz, acetone- D_6 , ppm): $\delta = 8.6$, -35.1, -41.4, -54.9, -78.8, -95.0, -199.8; IR (ATR, cm^{-1}): 3148 (vw), 3067 (w), 3054 (w), 3047 (w), 2992 (w), 2925 (vw), 2877 (vw), 2736 (vw), 2168 (vw), 1729 (w), 1589 (s), 1566 (vs), 1492 (m), 1479 (m), 1439 (m), 1424 (m), 1413 (m), 1400 (m), 1369 (w), 1350 (w), 1326 (s), 1276 (vs), 1250 (s), 1250 (s), 1209 (m), 1197 (m), 1181 (w), 1139 (w), 1130 (w), 1085 (m), 1073 (w), 1058 (m), 1019 (m), 1009 (w), 948 (m), 925 (s), 904 (w), 881 (vw), 843 (m), 779 (m), 769 (s), 755 (s), 741 (m), 705 (w), 687 (m), 663 (m), 645 (m), 628 (s), 548 (w), 542 (w), 474 (w), 450 (m), 423 (w); elemental analysis calcd. (%) for $\text{C}_4\text{H}_6\text{N}_{12}\text{O}_6$ (316.04 g mol^{-1}): C 15.20, H 1.28, N 53.17; found: C 15.75, H 1.27, N 51.17; DTA (5 °C min^{-1}): onset: 157.2 °C (endo.), 212.6 °C (dec.); BAM drophammer: 3 J; Friction tester: 60 N.

Trinitrazapropene-bridged tetrazoles (5–7)

1,7-Dichloro-2,4,6-trinitrazaheptane (1.0 g, 3.26 mmol, 1.0 equiv.) was dissolved in acetone (80 mL). Potassium tetrazolate (705 mg, 6.25 mmol, 2.0 equiv.) and sodium iodide (977 mg, 6.25 mmol, 2.0 equiv.) were added and the reaction was stirred for 12 h at 25 °C. The suspension was filtered and the filtrate was evaporated *in vacuo*. The yellowish solid was washed with water and ethanol. The crude product was purified by column chromatography on silica gel (50/50→70/30 ethyl acetate/isohexane) to obtain **5** (223 mg, 19%), **6** (315 mg, 26%) and **7** (200 mg, 17%) as off-white/yellowish solids.

1,7-Bis-1,1'-tetrazolylnitrazapropene (5)

TLC (70/30 ethyl acetate/isohexane): $R_f = 0.39$.

^1H NMR (400 MHz, acetone- D_6 , ppm): $\delta = 9.32$ (s, 1H), 6.72 (s, 2H), 6.22 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, acetone- D_6 , ppm): $\delta = 145.0$, 66.2, 61.7; ^{14}N NMR (29 MHz, acetone- D_6 , ppm): $\delta = -35$; IR (ATR, cm^{-1}): 3146 (w), 3044 (w), 2995 (vw), 2926 (w), 2854 (vw), 1741 (vw), 1591 (m), 1571 (s), 1543 (s), 1467 (w), 1435 (s), 1414 (m), 1370 (w), 1353 (w), 1327 (w), 1269 (vs), 1229 (m), 1211 (s), 1190 (m), 1154 (s), 1121 (m), 1094 (s), 1073 (s), 1073 (s), 1021 (m), 966 (m), 928 (vs), 892 (m), 876 (m), 856 (m), 763 (s), 755 (s), 716 (m), 708 (m), 700 (m), 679 (w), 659 (m), 640 (m), 610 (s), 532 (vw), 479 (w), 447 (w); elemental analysis calcd. (%) for $\text{C}_6\text{H}_{10}\text{N}_{14}\text{O}_6$ (374.24 g mol^{-1}): C 19.26, H 2.69, N

52.40; found: C 19.41, H 2.88, N 52.67; DTA (5 °C min⁻¹): onset: 187.0 °C (dec.); BAM drophammer: 40 J; Friction tester: > 360 N.

1,7-Bis-1,2-tetrazolyltrinitrazaheptane (6)

TLC (70/30 ethyl acetate/isohexane): $R_f = 0.61$.

¹H NMR (400 MHz, acetone-*D*₆, ppm): $\delta = 9.32$ (s, 1H), 8.82 (s, 1H), 6.89 (s, 2H), 6.73 (s, 2H), 6.26 (d, 4H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm): $\delta = 154.2$, 145.0, 66.2, 65.9, 65.7, 61.8; ¹⁴N NMR (29 MHz, acetone-*D*₆, ppm): $\delta = -34$; IR (ATR, cm⁻¹): 3147 (w), 3044 (w), 2994 (vw), 2925 (w), 2854 (vw), 2168 (vw), 1790 (vw), 1729 (vw), 1590 (m), 1571 (s), 1541 (m), 1468 (w), 1436 (s), 1412 (m), 1370 (w), 1342 (w), 1270 (vs), 1212 (s), 1190 (m), 1153 (m), 1118 (m), 1103 (m), 1094 (s), 1094 (s), 1073 (s), 1063 (m), 1020 (m), 1001 (w), 966 (m), 927 (vs), 906 (m), 892 (m), 877 (m), 855 (m), 763 (s), 755 (s), 717 (w), 708 (m), 700 (m), 678 (m), 660 (m), 641 (m), 634 (m), 609 (s), 480 (w), 447 (w); elemental analysis calcd. (%) for C₆H₁₀N₁₄O₆ (374.24 g mol⁻¹): C 19.26, H 2.69, N 52.40; found: C 19.92, H 2.87, N 52.12; DTA (5 °C min⁻¹): onset: 194.2 °C (dec.); BAM drophammer: 25 J; Friction tester: 288 N.

1,7-Bis-2,2'-tetrazolyltrinitrazaheptane (7)

TLC (70/30 ethyl acetate/isohexane): $R_f = 0.78$.

¹H NMR (400 MHz, acetone-*D*₆, ppm): $\delta = 8.83$ (s, 1H), 6.89 (s, 2H), 6.29 (s, 2H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm): $\delta = 154.2$, 65.9, 65.7; ¹⁴N NMR (29 MHz, acetone-*D*₆, ppm): $\delta = -35$; IR (ATR, cm⁻¹): 3156 (vw), 3149 (vw), 3067 (w), 3016 (vw), 2213 (vw), 2174 (vw), 2168 (vw), 1732 (w), 1574 (m), 1557 (s), 1539 (s), 1463 (w), 1452 (w), 1436 (m), 1427 (m), 1412 (m), 1404 (m), 1394 (m), 1380 (w), 1368 (w), 1354 (w), 1337 (w), 1274 (vs), 1274 (vs), 1247 (m), 1232 (s), 1194 (m), 1185 (m), 1152 (m), 1122 (w), 1099 (s), 1072 (m), 1021 (m), 1005 (m), 921 (vs), 888 (m), 880 (m), 868 (m), 854 (m), 769 (s), 758 (s), 706 (m), 693 (w), 683 (m), 676 (m), 659 (w), 643 (m), 638 (m), 629 (w), 603 (s), 540 (vw), 503 (vw), 486 (w), 449 (m), 429 (vw), 424 (vw), 415 (w), 403 (vw); elemental analysis calcd. (%) for (C₆H₁₀N₁₄O₆) (374.24 g mol⁻¹): C 19.26, H 2.69, N 52.40; found: C 20.18, H 2.83, N 51.57; DTA (5 °C min⁻¹): onset: 193.1 °C (endo.), 211.5 °C (dec.); BAM drophammer: 30 J; Friction tester: 360 N.

1,7-Bis-2,2'-nitrotetrazolyltrinitrazaheptane (8)

1,7-Dichloro-2,4,6-trinitrazaheptane (1.0 g, 3.26 mmol, 1.0 equiv.) was dissolved in acetone (80 mL). Ammonium-5-nitrotetrazolate hemihydrate (920 mg, 6.25 mmol, 2.0 equiv.) and sodium iodide (977 mg, 6.25 mmol, 2.0 equiv.) were added and the reaction was stirred overnight at room temperature. The suspension was filtered and the filtrate was evaporated *in vacuo*. The residue was extracted with ethyl acetate (100 mL) and washed with water (1 × 100 mL). The organic phase was dried over magnesium sulfate. The dried solution was filtered and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (40/60 → 50/50 ethyl acetate/isohexane) to obtain **8** (1.32 g, 87%) as a colorless solid.

TLC (50/50 ethyl acetate/isohexane): $R_f = 0.63$.

¹H NMR (400 MHz, acetone-*D*₆, ppm): $\delta = 7.08$ (s, 1H), 6.30 (s, 1H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm): $\delta = 67.4$, 65.9; ¹⁵N NMR (41 MHz, acetone-*D*₆, ppm): $\delta = 4.5$, -34.1, -34.8, -36.8, -51.4, -72.0, -93.9, -186.7, -195.1; IR (ATR, cm⁻¹): 3048.00 (vw), 3005.00 (vw), 2962.00 (vw), 2927.00 (vw), 2865.00 (vw), 2168.00 (vw), 1728 (w), 1563 (s), 1558 (vs), 1504 (vw), 1488 (w), 1455 (w), 1439 (m), 1436 (m), 1409 (m), 1385 (w), 1373 (w), 1315 (m), 1276 (vs), 1243

(m), 1231 (m), 1211 (w), 1195 (m), 1195 (m), 1154 (w), 1109 (m), 1078 (m), 1059 (m), 1018 (w), 925 (s), 875 (w), 837 (s), 764 (s), 703 (w), 692 (w), 664 (w), 644 (m), 610 (s), 542 (w), 502 (vw), 478 (w), 466 (w), 446 (w), 427 (vw); elemental analysis calcd. (%) for C₆H₈N₁₆O₁₀ (464.23 g mol⁻¹): C 15.52, H 1.74, N 48.28; found: C 15.78, H 1.78, N 45.82; DTA (5 °C min⁻¹): onset: 210.3 °C (endo.), 217.1 °C (dec.); BAM drophammer: 3 J; Friction tester: 160 N.

Oxapropene-bridged tetrazoles (9–11)

Sodium iodide (2.61 g, 17.4 mmol, 2.0 equiv.) and potassium tetrazolate (1.88 g, 17.4 mmol, 2.0 equiv.) were added to 1,3-dichloro-2-oxapropene (1.0 g, 8.70 mmol, 1.0 equiv.) in acetone (80 mL). The suspension was stirred for 12 h at 25 °C with the exclusion of light. The resulting precipitate was filtered and the filtrate was concentrated *in vacuo*. The crude product was dissolved in ethyl acetate (50 mL) and washed with saturated sodium thiosulfate solution (3 × 50 mL). The organic phase was dried over MgSO₄ and filtered afterwards. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CHCl₃: MeOH, 9:1) to separate the different isomers. Compounds **10** (180 mg, 11%) and **11** (620 mg, 39%) were obtained as colorless liquids and **9** was obtained as a colorless solid (0.45 g, 28%).

1,3-Bis-1,1'-tetrazolyloxapropene (9)

¹H NMR (400 MHz, acetone-*D*₆, ppm) $\delta = 9.37$ (s, 2H), 6.19 (s, 4H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm) $\delta = 144.9$, 75.7; IR (ATR, cm⁻¹): 3122 (w), 3101 (m), 1484 (m), 1451 (w), 1429 (m), 1373 (m), 1319 (w), 1300 (w), 1281 (w), 1224 (w), 1199 (m), 1178 (s), 1171 (s), 1117 (m), 1106 (m), 1083 (vs), 1054 (m), 1028 (m), 1008 (m), 983 (s), 962 (s), 931 (s), 888 (m), 753 (vs), 715 (s), 652 (vs), 480 (w); elemental analysis calcd. (%) for C₄H₆N₈O (182.15 g mol⁻¹): C 21.24, H 2.67, N 61.93; found: C 22.64, H 2.89, N 60.06; DTA (5 °C min⁻¹): onset: 97.5 °C (endo.), 168.0 °C (dec.); BAM drophammer: 40 J; Friction tester: > 360 N.

1,3-Bis-1,2-tetrazolyloxapropene (10)

¹H NMR (400 MHz, acetone-*D*₆, ppm) $\delta = 9.35$ (s, 1H), 8.84 (s, 1H), 6.31 (s, 2H), 6.21 (s, 2H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm) $\delta = 154.4$, 144.88, 79.6, 76.0; IR (ATR, cm⁻¹): 3140 (w), 1483 (m), 1457 (w), 1428 (w), 1385 (w), 1338 (m), 1312 (w), 1283 (m), 1203 (w), 1166 (s), 1112 (s), 1085 (vs), 1049 (m), 1023 (s), 1002 (s), 953 (m), 934 (m), 886 (m), 766 (s), 755 (s), 715 (w), 707 (m), 677 (m), 653 (s), 492 (w), 479 (w); elemental analysis calcd. (%) for C₄H₆N₈O (182.15 g mol⁻¹): C 26.38, H 3.32, N 61.52; found: C 26.31, H 3.28, N 61.36; DTA (5 °C min⁻¹): onset: 180.0 °C (dec.); BAM drophammer: 40 J; Friction tester: > 360 N.

1,3-Bis-2,2'-tetrazolyloxapropene (11)

¹H NMR (400 MHz, acetone-*D*₆, ppm) $\delta = 8.84$ (s, 2H), 6.31 (s, 2H); ¹³C{¹H} NMR (101 MHz, acetone-*D*₆, ppm) $\delta = 154.6$, 79.6; IR (ATR, cm⁻¹): 3141 (vw), 1715 (s), 1463 (m), 1422 (w), 1394 (m), 1368 (s), 1284 (w), 1252 (w), 1234 (w), 1183 (m), 1169 (m), 1096 (vs), 1021 (m), 1002 (w), 972 (w), 956 (w), 940 (w), 875 (w), 772 (m), 751 (w), 708 (w), 682 (m), 654 (w), 631 (w), 580 (m), 549 (w), 500 (w), 483 (w), 473 (w), 455 (w); elemental analysis calcd. (%) for C₄H₆N₈O (182.15 g mol⁻¹): C 26.38, H 3.32, N 61.52; found: C 26.21, H 3.23, N 61.28; DTA (5 °C min⁻¹): onset: 185.0 °C (dec.); BAM drophammer: 40 J; Friction tester: 288 N.

General Procedure for the synthesis of the ECCs [Cu(1,1'-TNP)₃](ClO₄)₂ (12) and [Fe(ClO₄)₂(1,1'-TNP)₄] (13)

1,1'-TNP (169.6 mg, 0.75 mmol, 3 equiv.) was suspended in 4 mL of MeCN and heated to 50 °C until a clear solution was obtained. The respective perchlorate (Cu(ClO₄)₂·6H₂O: 92.6 mg, 0.25 mmol, 1 equiv.; Fe(ClO₄)₂·6H₂O: 90.7 mg, 0.25 mmol, 1 equiv.) was dissolved in 1 mL of MeCN at room temperature and added dropwise. The solution which was obtained was stirred at 50 °C for 10 min and then allowed to cool down to room temperature. On cooling down, precipitation was observed in both cases. The precipitates were filtered, washed with cold MeCN and dried in air.

[Cu(1,1'-TNP)₃](ClO₄)₂ (12)

Compound 12 was obtained as a light blue solid in a yield of 70% (165.8 mg, 0.18 mmol). IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3134 (w), 3047 (w), 2996 (vw), 1598 (m), 1496 (m), 1443 (m), 1420 (m), 1403 (w), 1335 (m), 1295 (s), 1256 (w), 1215 (m), 1180 (s), 1110 (m), 1079 (vs), 1018 (s), 995 (m), 979 (m), 937 (s), 904 (m), 872 (w), 761 (m), 749 (s), 714 (m), 672 (m), 662 (m), 639 (m), 621 (vs), 439 (m), 426 (w), 415 (w); elemental analysis calcd. (%) for C₁₂H₁₈Cl₂CuN₃₀O₁₄ (940.92 g mol⁻¹): C 15.32 H 1.93 N 44.66, found C 15.60 H 2.05 N 44.37; DTA (5 °C min⁻¹) onset: 246.1 °C (dec.); BAM drop hammer: < 1 J; Friction tester: 10 N.

[Fe(ClO₄)₂(1,1'-TNP)₄] (13)

The compound was obtained as a colorless solid i53% yield (152.6 mg, 0.13 mmol). IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3130 (w), 3045 (w), 2996 (w), 1600 (m), 1497 (m), 1443 (m), 1422 (w), 1403 (w), 1335 (w), 1295 (m), 1256 (w), 1215 (m), 1181 (m), 1110 (m), 1091 (vs), 1018 (m), 984 (m), 939 (m), 907 (w), 871 (w), 761 (m), 750 (s), 715 (m), 672 (m), 663 (m), 641 (w), 622 (s), 513 (w), 476 (vw), 437 (m), 419 (w). elemental analysis calcd. (%) for C₁₆H₂₄Cl₂FeN₄₀O₁₆ (1159.38 g mol⁻¹): C 16.58 H 2.09 N 48.33, found C 16.29 H 2.35 N 48.03; DTA (5 °C min⁻¹) onset: 220.0 °C (dec.); BAM drophammer: < 1 J; Friction tester: 9 N.

Supporting Information

The authors have cited additional references within the Supporting Information.^[51–62] The Supporting Information includes General Experimental Information, NMR Spectroscopy, IR Spectroscopy, DTA Measurements, TGA Measurements, X-ray Diffraction, Heat of Formation Calculations and Calculation of Energetic Performance Parameters, Magnetic Properties.

CCDC numbers

Deposition Number(s) 2290727 (for 1), 2290728 (for 3), 2290729 (for 4), 2290730 (for 7), 2290731 (for 9) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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