EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202201073

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

VIP *Very Important Paper*

Nitrogen-Rich Oxetanes Based on the Combination of Azides and Tetrazoles

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Literature known energetic oxetane derivatives have a nitrogen content of up to 49.98%. Through the introduction of azide and tetrazole functionalities attached to an oxetane ring, energetic oxetanes with higher nitrogen contents than previously reported in the literature were obtained. The newly synthesized oxetane derivatives were extensively characterized via ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{14}N NMR, ^{15}N NMR, ^{1}H-^{15}N HMBC, FT-IR spectroscopy and/or DTA. Their crystal structures were elucidated using X-ray diffraction, their sensitivities towards impact, friction and electrostatic discharge were determined and their energetic properties were calculated using the EXPLO5 code.

Introduction

Oxetanes are generally strained four-membered heterocycles containing an oxygen atom. The ring tension is minimized by a nearly planar configuration of the ring itself, as shown by Luger.[1] Oxetanes offer many benefits to the pharmaceutical industry because of their chemical similarity to carbonyl and gem-dimethyl groups. For instance, these groups suffer from solubility and stability in the human body and can be easily substituted with an oxetane that has superior properties.[2–3] For this reason, the pharmaceutical sector has a legitimate strong interest in oxetanes, which has made them readily available, especially in the past few years, and they are no longer just specialty and laboratory chemicals. Another great property of oxetanes is that they can be opened by cationic ring-opening polymerization to obtain polyethers. The ring-opening occurs at one of the carbon atoms adjacent to the protonated oxygen atom.[4] Therefore, a mono- or di-substitution at the 3-position is beneficial to obtain a primary hydroxyl function after termination of the polymerization.[5–6] Thus it is possible through suitable substitution to obtain energetic polymers as binders. In 1962, BAMO (3,3-bis(azidomethyl)oxetane) was described and synthesized by Carpenter.[7] Since then, it has been the oxetane compound with the highest nitrogen content of 49.98%. In the following years, several other energetic oxetane motifs were synthesized and investigated for energetic polymers, but none of them were outstanding in terms of energetic performance and they were only partially applied due to the high price of the compounds.[8–12] In recent work by our group, we reported several energetic oxetanes, one of which came close to the high nitrogen content with 49.55% (Figure 1).[13]

A main strategy to obtain higher nitrogen content is the incorporation of azoles. Comparing different unsubstituted azoles, tetrazoles offer the best properties along the azole family.[14–18] Unsubstituted tetrazole has a density of 1.529 g cm^{-3} and an endothermic heat of formation of 237 kJ mol^{-1}, resulting in a detonation velocity of 7813 m s^{-1}.[14] These properties come along with a thermal stability of 188 °C which is sufficient for the unsubstituted species.[14] All properties can be maintained or enhanced by substitution in the 5-position. For example, 5-aminotetrazole has a higher thermal stability (melting at 202 °C) while 5-nitrotetrazole has a very high performance (9457 m s^{-1}).[19–20] Those compounds allow further functionalization in 1- and 2-position such as methylation, amination or hydroxylation to tune the properties even further.[21-23] Another strategy for higher nitrogen content is the use of azides which also give a positive heat of formation as well as a good energetic performance. However, herein we report on the combination of oxetanes with tetrazoles and azides to obtain energetic oxetane monomers with the highest nitrogen content reported to date.

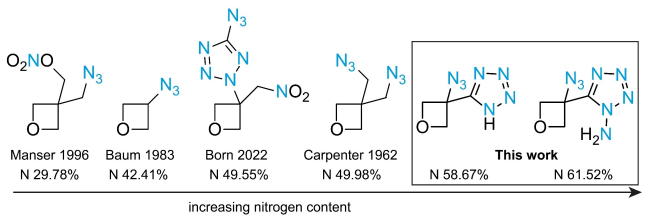

Figure 1. Different energetic oxetanes sorted according to their nitrogen content.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202201073

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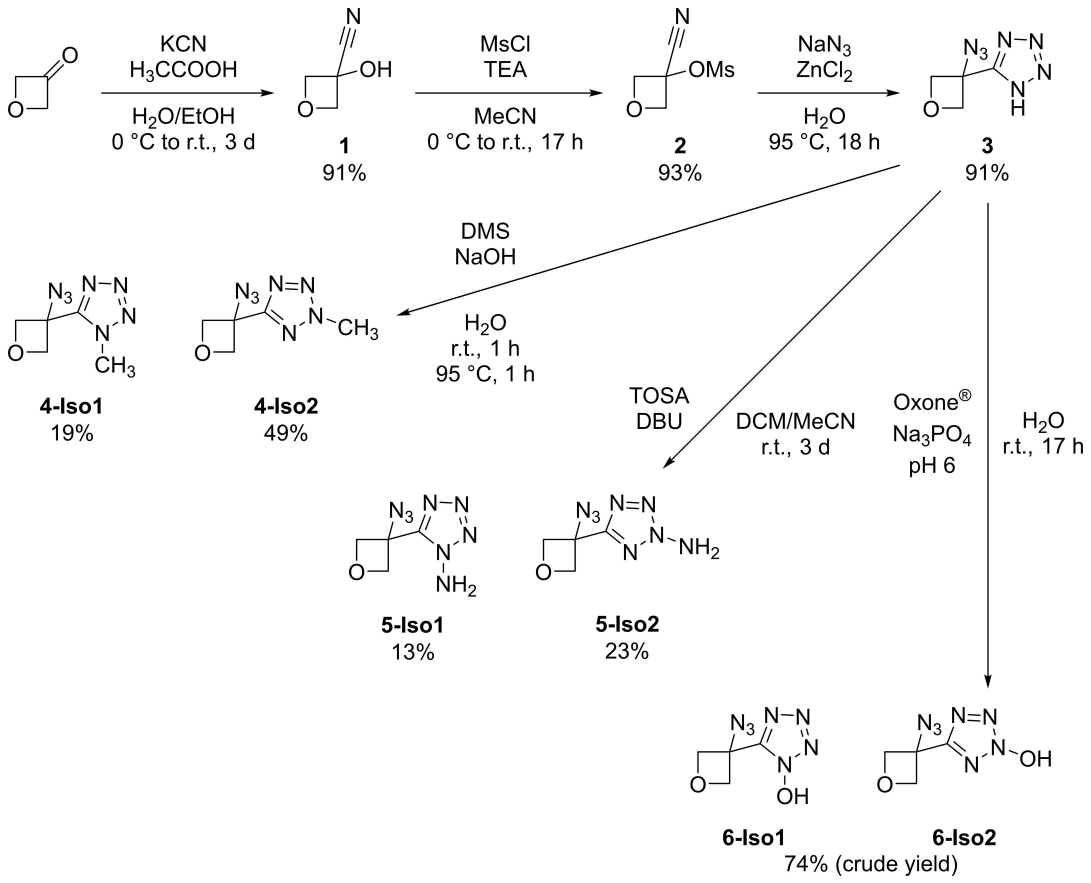
doi.org/10.1002/ejoc.202201073

Results and Discussion

Synthesis

The synthesis of 3-hydroxyoxetane-3-carbonitrile (**1**) was achieved by a 1,2-addition of HCN to the carbonyl group of oxetan-3-one (Scheme 1). Acetic acid was used for the *in situ* generation of HCN from the starting material KCN. **1** was obtained as a colorless to yellowish crystalline solid in excellent yield (91%). In the following mesylation reaction, **1** was converted to 3-cyanooxetan-3-yl methanesulfonate (**2**) with methanesulfonyl chloride and triethylamine as a base in order to replace the poor leaving group of the alcohol (OH^-) by a good leaving group (mesylate anion). This step is inevitable to enable the subsequent nucleophilic substitution. The mesylation reaction gave **2** as a yellow to orange oil in excellent yield (93%). Afterwards, **2** was treated with an excess of NaN_3, resulting in a nucleophilic substitution of the mesylate group by an azide group and a concomitant $ZnCl_2$ mediated azide nitrile [2+3]-cycloaddition, forming a tetrazole residue. The reaction product 5-(3-azidooxetan-3-yl)-1*H*-tetrazole (**3**) was obtained as a yellow oil in excellent yield (91%). Crystallization of the oil occurred upon standing overnight. **3** was further converted in a methylation, amination and hydroxylation reaction to yield the respective target molecules. For the methylation, **3** was treated with dimethyl sulfate. A mixture of the isomers 5-(3-azidooxetan-3-yl)-1-methyl-tetrazole (**4-Iso1**) and 5-(3-azidooxetan-3-yl)-2-methyl-tetrazole (**4-Iso2**) in a ratio of approximately 1:3 was obtained in the reaction. The methylation gave the crude product **4-Iso1**/**4-Iso2** in very good yield (79%) and without major impurities. After separation and purification of the isomers by column chromatography (SiO_2, Et_2O/*n*-pentane 1:1, R_f (**4-Iso1**) = 0.08, R_f (**4-Iso2**) = 0.40), **4-Iso1** (19%) and **4-Iso2** (49%) were obtained in high purity. **4-Iso2** is eluted first during column chromatography due to its lower polarity, while the more polar **4-Iso1** passes more slowly through the column. **4-Iso1** is a yellow oil which crystallized upon standing in the freezer and **4-Iso2** is a yellowish oil which froze upon standing in the freezer. Apart from this, **3** was aminated by the reaction with an organic base (1,8-diazabicyclo[5.4.0]undec-7-ene; DBU) and *O*-tosylhydroxylamine (TOSA). TOSA was freshly prepared from ethyl *N*-(tosyloxy)-acetimidate (**7**) and $HClO_4$ prior to each amination reaction (Scheme 2). A mixture of the isomers 5-(3-azidooxetan-3-yl)-1-amino-tetrazole (**5-Iso1**) and 5-(3-azidooxetan-3-yl)-2-amino-tetrazole (**5-Iso2**) in a ratio of approximately 2:3 was obtained in the reaction. Two column chromatographies were required to obtain the isomers in pure form. Major impurities (including by-products) were removed from the crude product by the first column chromatography (SiO_2, EtOAc, R_f (crude) = 0.85). The



Scheme 1. Overview of the synthesis routes towards the energetic oxetane derivatives **3**, **4-Iso1**, **4-Iso2**, **5-Iso1**, **5-Iso2**, **6-Iso1** and **6-Iso2** (DMS: dimethyl sulfate, TOSA: *O*-tosylhydroxylamine, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene).

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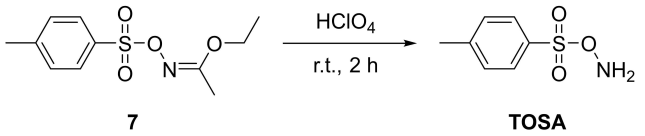

Scheme 2. Preparation of *O*-tosylhydroxylamine (TOSA) from ethyl *N*-(tosyloxy)acetimidate (**7**) and $HClO_4$.

isomers **5-Iso1** and **5-Iso2** were separated and purified by a second column chromatography (SiO_2, Et_2O/*n*-pentane 2:1, R_f (**5-Iso1**) = 0.23, R_f (**5-Iso2**) = 0.45). **5-Iso1** (13%) and **5-Iso2** (23%) were obtained in high purity but moderate yield. Due to their polarities, the isomers **5-Iso1** and **5-Iso2** elute in the same order as described above for the compounds **4-Iso1** and **4-Iso2**. **5-Iso1** is a colorless crystalline solid and **5-Iso2** is a yellow oil which crystallized upon standing in the freezer. An alternative reaction approach towards the products **5-Iso1** and **5-Iso2** with hydroxylamine-*O*-sulfonic acid (HOSA) instead of TOSA was investigated. Since the yields of these experiments were even lower than the ones with TOSA, no further research was performed in this regard. The TOSA precursor **7** was prepared according to a literature procedure.[24] Ethyl *N*-hydroxyacetimidate was converted with 4-methylbenzenesulfonyl chloride in a condensation reaction. The product **7** was obtained as a white crystalline solid in a very good yield (78%). **3** was also reacted with Oxone® to yield the hydroxylated product isomers 5-(3-azidooxetan-3-yl)-tetrazol-1-ol (**6-Iso1**) and 5-(3-azidooxetan-3-yl)-tetrazol-2-ol (**6-Iso2**). In the first reaction approach performed, a whitish solid was obtained which contained the product isomers **6-Iso1** and **6-Iso2** in a ratio of approximately 1:9. The crude yield of this approach proved to be good (74%) and it was possible to obtain the crystal structure of **6-Iso2** by X-ray diffraction. However, all further reaction approaches which were carried out in exactly the same way yielded a yellow oil as reaction product. ^{1}H NMR spectra showed that the ratios of the product isomers **6-Iso1** and **6-Iso2** in the yellow oils differed from the ratio in the whitish solid.

Crystal Structures

Crystal structures of the starting material oxetan-3-one and the synthesized compounds **1**, **3**, **4-Iso1**, **4-Iso2**, **5-Iso1**, **5-Iso2** and **6-Iso2** were obtained by X-ray diffraction. The respective crystals were obtained from EtOAc (**1**, **3**, **6-Iso2**), Et_2O/*n*-pentane 1:1 (**4-Iso1**, **4-Iso2**), Et_2O/*n*-pentane 2:1 (**5-Iso1**, **5-Iso2**) or used as received (oxetan-3-one). Oxetan-3-one and compound **1** both crystallize in the orthorhombic space group *Pnma* with densities of 1.478 g cm^{-3} at 109 K (oxetan-3-one) and 1.520 g cm^{-3} at 101 K (**1**).

Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with a density of 1.581 g cm^{-3} at 100 K (Figure 2a). The azide moiety is slightly bent with an angle of 173.0° at N5-N6-N7 and the molecule contains an almost planar tetrazole motif. The plane of the tetrazole ring is almost perpendicular to the plane formed by the carbon atoms of the oxetane ring.

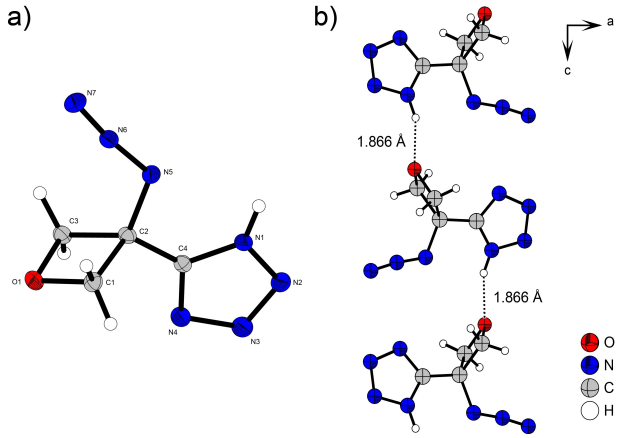

Figure 2. a) Crystal structure of 5-(3-azidooxetan-3-yl)-1*H*-tetrazole (**3**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules are stabilized by short intermolecular hydrogen bonds with distances of 1.866 Å.

Compound **3** is stabilized by short intermolecular hydrogen bonds with a distance of 1.866 Å (Figure 2b).

The methylated product isomer **4-Iso1** crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.512 g cm^{-3} at 173 K (Figure 3a). The azide moiety has an angle of 173.9° at N5-N6-N7 and the tetrazole motif is almost perfectly planar. In the crystal structure, heteroaromatic π-stacking interactions of the tetrazole rings with a mean distance of around 3.4 Å cause the molecules to arrange in layers. **4-Iso1** does not form classic intra- or intermolecular hydrogen bonds between the molecules (Figure 3b).

The second isomer of the methylated product **4-Iso2** crystallizes in the monoclinic space group $P2_1/m$ with a density of 1.548 g cm^{-3} at 102 K (Figure 4a). The molecule contains a slightly bent azide moiety with an angle of 172.4° at N5-N6-N7 and a planar tetrazole motif. All atoms of the azide group and the methyl tetrazole lie in one plane which is perpendicular to the plane formed by the carbon atoms of the oxetane ring. The azide group of compound **4-Iso2** points away from the tetrazole ring, while it points more towards the tetrazole ring in **4-Iso1**. In the crystal structure, the molecules arrange in sheets with the plane of the azide group and the methyl tetrazole being perpendicular to the plane formed by the carbon atoms of the

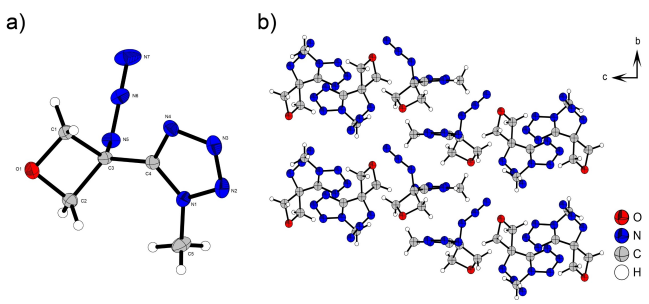

Figure 3. a) Crystal structure of 5-(3-azidooxetan-3-yl)-1-methyl-tetrazole (**4-Iso1**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules arrange in layers. View along the *a* axis.

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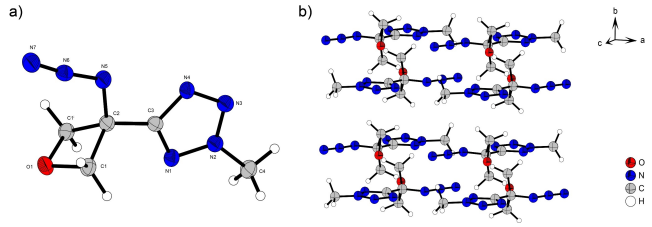

Figure 4. a) Crystal structure of 5-(3-azidooxetan-3-yl)-2-methyl-tetrazole (**4-Iso2**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules arrange in sheets.

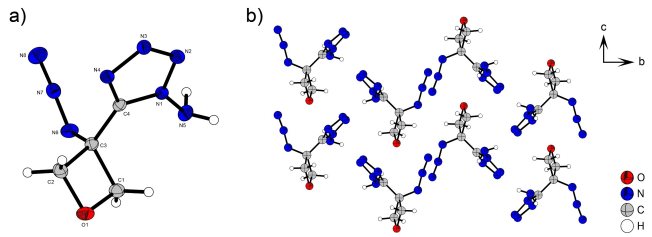

Figure 5. a) Crystal structure of 5-(3-azidooxetan-3-yl)-1-amino-tetrazole (**5-Iso1**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules arrange in a wave-like pattern. View along the *a* axis.

oxetane ring (Figure 4b). No classic intra- or intermolecular hydrogen bonds between the molecules can be observed.

Compound **5-Iso1** crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.593 g cm^{-3} at 102 K (Figure 5a). The azide moiety is slightly bent with an angle of 172.6° at N6-N7-N8 and the tetrazole motif is almost planar. In the crystal structure, the molecules arrange in a wave-like pattern with the azide groups facing each other. Intermolecular hydrogen bonds from the amino group of the tetrazole to nitrogen atoms of neighbored tetrazole rings and to oxygen atoms of neighbored oxetane rings can be observed (Figure 5b).

The second isomer of the aminated product **5-Iso2** crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.649 g cm^{-3} at 173 K (Figure 6a). The molecule contains a slightly bent azide moiety with an angle of 173.9° at N6-N7-N8 and an almost planar tetrazole motif. As observed for the methylated isomers **4-Iso1** and **4-Iso2**, the azide group of compound **5-Iso2** points away from the tetrazole ring, whereas in **5-Iso1** it points more towards the tetrazole ring. In the crystal structure, the molecules arrange in layers (Figure 6b). Intermolecular hydrogen bonds from the amino group of the tetrazole to oxygen atoms of neighbored oxetane rings and to nitrogen atoms of neighbored azide groups are found.

The hydroxylated product isomer **6-Iso2** crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.706 g cm^{-3} at 101 K (Figure 7a). The azide moiety has an angle of 171.7° at N5-N6-N7 and is oriented towards the tetrazole ring. The tetrazole motif is almost planar. In the crystal structure, the molecules arrange in pairs, having two short, symmetrical intermolecular hydrogen bonds from the hydroxy group H2 to the neighbored O1 of the oxetane ring with a distance of 1.518 Å (Figure 7b).

Further information regarding the crystal structures of all solid compounds can be found in the Supporting Information.

Spectroscopy

The obtained oxetane compounds were extensively characterized by NMR and FT-IR spectroscopic techniques.

The ^{1}H NMR spectrum of compound **3** showed two doublet of doublets at 5.04 and 4.90 ppm which arise from the protons of the oxetane ring, while the proton of the tetrazole ring was not observable. In the ^{13}C{^{1}H} NMR spectrum of compound **3**, three signals were observed at 157.3, 79.3 and 59.6 ppm. The signal at 157.3 ppm can be assigned to the carbon atom of the tetrazole ring. The peak at 59.6 ppm belongs to the sp^3-hybridized carbon atom which has the tetrazole and the azide group attached to it. The signal at 79.3 ppm arises from the other two remaining oxetane carbon atoms.

In the ^{1}H NMR spectrum, the two isomers **4-Iso1** and **4-Iso2** each show two doublet of doublets belonging to the protons of the oxetane ring and one singlet arising from the protons of the methyl group. Compared to the isomer **4-Iso1** (5.24 and 5.03 ppm), the signals of the oxetane ring of **4-Iso2** (5.03 and 4.89 ppm) are shifted upfield. The protons of the methyl group show the opposite effect, with their signal being shifted downfield for **4-Iso2** (4.43 ppm) in comparison with **4-Iso1** (4.04 ppm).

Two doublet of doublets of the oxetane protons and one singlet from the protons of the amino group are observed for each of the isomers **5-Iso1** and **5-Iso2** in the ^{1}H NMR spectrum.

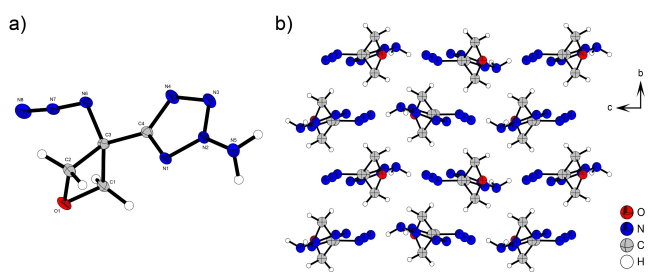

Figure 6. a) Crystal structure of 5-(3-azidooxetan-3-yl)-2-amino-tetrazole (**5-Iso2**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules arrange in layers. View along the *a* axis.

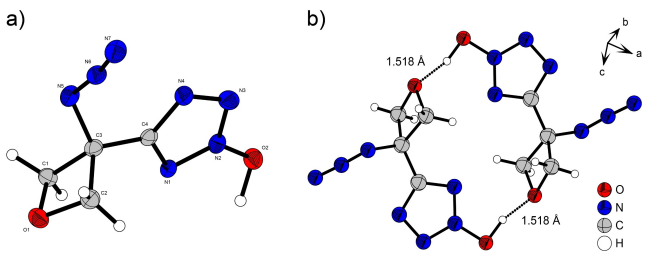

Figure 7. a) Crystal structure of 5-(3-azidooxetan-3-yl)-tetrazol-2-ol (**6-Iso2**). Thermal ellipsoids are drawn at the 50% probability level. **b)** The molecules arrange in pairs via two symmetrical hydrogen bonds with a distance of 1.518 Å.

Research Article
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The signals of the oxetane protons of **5-Iso2** (5.01 and 4.87 ppm) show an upfield shift compared to the corresponding peaks of **5-Iso1** (5.19 and 4.91 ppm). The reverse trend can again be observed for the protons of the amino group (**5-Iso1**: 7.15 ppm, **5-Iso2**: 8.29 ppm). The ^{14}N NMR spectra of the compounds **5-Iso1** and **5-Iso2** showed two resonance signals of the azide group at around −138 ppm for N7 and −160 ppm for N8. The N6 azide signal and the signal of the amino group were not observable in the ^{14}N NMR spectra.

In the ^{1}H NMR spectrum, compound **6-Iso2** shows two doublet of doublets at 5.00 and 4.83 ppm arising from the protons of the oxetane ring. The proton of the hydroxy group was not observable in the spectrum.

The ^{13}C{^{1}H} NMR shifts of **4-Iso1**, **4-Iso2**, **5-Iso1** and **5-Iso2** and their assignments to the respective carbon atoms are similar to those described above for compound **3**. Further details on the ^{13}C{^{1}H} NMR spectroscopy of these compounds are provided in the Supporting Information.

In addition, proton-coupled ^{15}N NMR spectroscopy was used to characterize the energetic oxetanes **4-Iso2** and **5-Iso2** in more detail. The assignment of the ^{15}N NMR signals to their respective nitrogen atoms was performed by means of ^{1}H-^{15}N HMBC spectra and calculation of the ^{15}N NMR shifts (see Supporting Information). In the ^{15}N NMR spectrum of **4-Iso2**, the signals of the tetrazole nitrogen atoms arise in the range of 2.6 ppm (N3) to −100.1 ppm (N2) (Figure 8a). Two distinct singlets for the nitrogen atoms of the azide group can be observed at −136.3 ppm (N6) and at −159.4 ppm (N7), while the shift of the third azide nitrogen atom at −293.0 ppm (N5) was derived from the peak in the ^{1}H-^{15}N HMBC spectrum (Figure 8b).

For compound **5-Iso2**, the signals of the tetrazole nitrogen atoms in the ^{15}N NMR spectrum are observed rather upfield in the range of −10.9 ppm (N3) to −86.0 ppm (N2) (Figure 9a). The shifts of the azide nitrogen atoms (−136.2 ppm (N7), −159.4 ppm (N8), −292.7 ppm (N6)) are virtually unchanged compared to the respective values of **4-Iso2**. The peak of the third azide nitrogen atom N6 was again derived from the corresponding ^{1}H-^{15}N HMBC spectrum (Figure 9b). A triplet with a large coupling constant (−284.0 ppm (t, J = 72.9 Hz, N5)) originates from the amino group of **5-Iso2**.

FT-IR spectroscopy further confirmed the presence of an azide group in the products **3**, **4-Iso1**, **4-Iso2**, **5-Iso1**, **5-Iso2** and **6-Iso2**. All of these FT-IR spectra showed very strong signals in the range of 2119–2108 cm^{-1}, which is in accordance with the expected value for an organic azide.

Physical and Energetic Properties

All of the new energetic oxetane derivatives presented in this work (**3**, **4-Iso1**, **4-Iso2**, **5-Iso1**, **5-Iso2** and **6-Iso2**) have higher

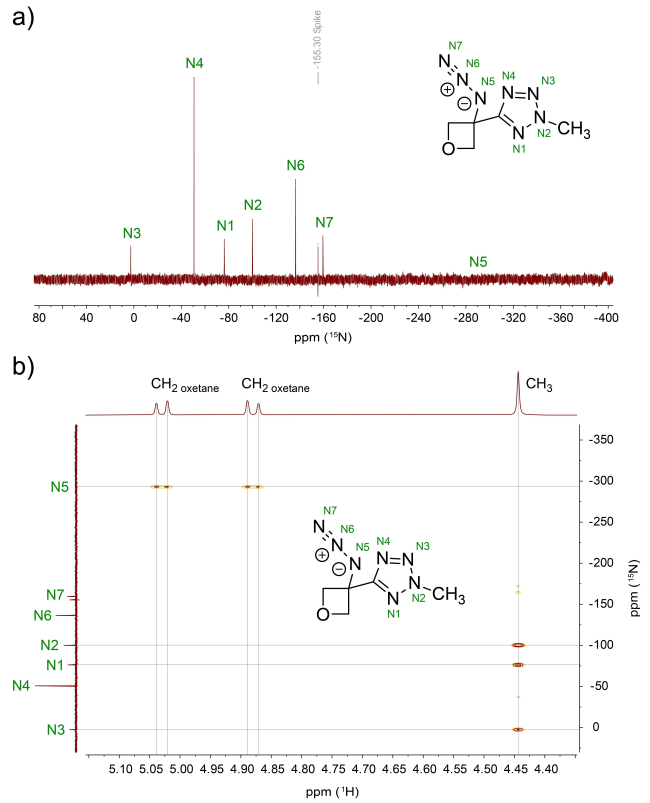

Figure 8. a) Proton-coupled ^{15}N NMR spectrum of compound **4-Iso2**. Chemical shifts are given in ppm and refer to nitromethane. **b)** ^{1}H-^{15}N HMBC spectrum of compound **4-Iso2**. DMSO-d$_6$ was used as a solvent in both NMR measurements.

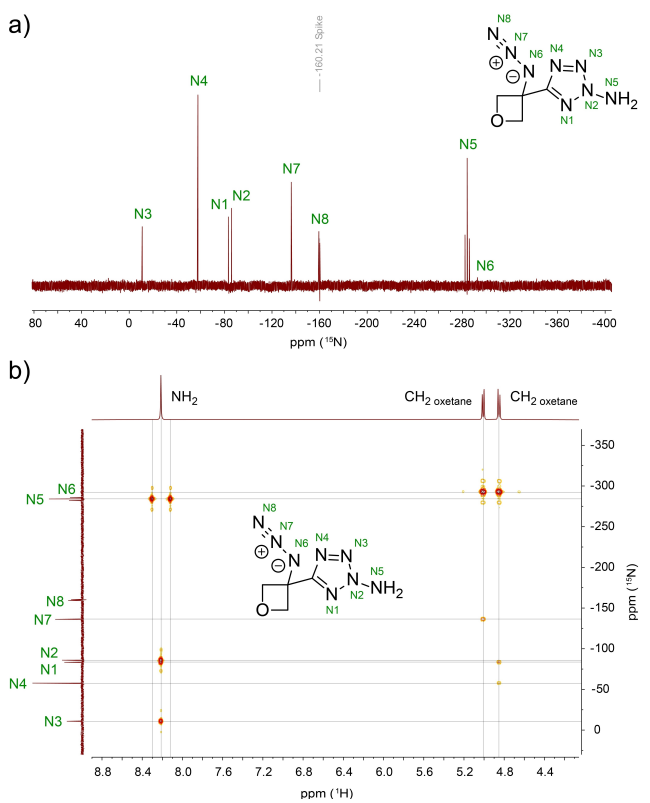

Figure 9. a) Proton-coupled ^{15}N NMR spectrum of compound **5-Iso2**. Chemical shifts are given in ppm and refer to nitromethane. **b)** ^{1}H-^{15}N HMBC spectrum of compound **5-Iso2**. DMSO-d$_6$ was used as a solvent in both NMR measurements.

nitrogen contents than BAMO, which is the most nitrogen-rich oxetane compound known so far in literature (Table 1).[7] The new energetic oxetanes are all very sensitive towards impact (IS = 1–3 J) and compounds **5-Iso1** and **5-Iso2** are also extremely sensitive towards friction (FS = 5–7 N). **3** is very sensitive towards friction (FS = 60 N) while the methylated compounds **4-Iso1** and **4-Iso2** both are insensitive towards friction (FS > 360 N). The new oxetanes show decomposition temperatures from 157 °C (**3**) to 187 °C (**4-Iso2**). Their densities are significantly higher than the value of BAMO (1.23 g cm^{-3}) with **5-Iso1** (1.548 g cm^{-3}), **5-Iso2** (1.619 g cm^{-3}) and **6-Iso2** (1.657 g cm^{-3}) having the highest densities of the newly synthesized oxetane derivatives. Consequently, all new oxetanes also show considerably better detonation parameters than BAMO. This is particularly evident for **5-Iso1** (7692 m s^{-1}), **5-Iso2** (8007 m s^{-1}) and **6-Iso2** (7840 m s^{-1}), whose detonation velocities clearly exceed the detonation velocity of BAMO (6548 m s^{-1}). The detonation pressures generated by these compounds are also significantly higher than that of BAMO, with the values of **5-Iso2** (22.7 GPa) and **6-Iso2** (22.9 GPa) being almost twice as high as the one of BAMO (12.4 GPa).

Based on its sensitivities towards external stimuli (IS = 1 J, FS = 5 N, ESD = 9 mJ), compound **5-Iso2** could be classified as a primary explosive.[25] On the contrary, however, its detonation velocity (8007 m s^{-1}) and detonation pressure (22.7 GPa) are within the range of typical secondary explosives.[25] The hot-plate test of **5-Iso2** did indeed show a violent detonation, but this does not necessarily indicate the presence of a primary explosive. However, the hot-needle test of **5-Iso2** was negative due to the lack of a deflagration to detonation transition, which indicates that **5-Iso2** is not a suitable primary explosive. Finally, **5-Iso2** was not able to initiate PETN, disqualifying it as a primary explosive. In conclusion, **5-Iso2** should be classified as a secondary explosive rather than a primary explosive. Further information regarding the hot-plate, hot-needle and initiation test of **5-Iso2** is available in the Supporting Information.

Conclusion

The new energetic oxetane derivative 5-(3-azidooxetan-3-yl)-1*H*-tetrazole and its methylation and amination products were synthesized in high purities and moderate to excellent yields. *N*-Oxidation products of 5-(3-azidooxetan-3-yl)-1*H*-tetrazole were obtained but the respective isomers could not be separated. The new energetic oxetanes can easily be monitored by ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{14}N NMR, ^{15}N NMR and FT-IR spectroscopy. DTA measurements show decomposition temperatures in the range of 157 °C (**3**) to 187 °C (**4-Iso2**). The sensitivities towards external stimuli (impact, friction and electrostatic discharge) show the following trend: The aminated oxetane derivatives **5-Iso1** (IS = 1 J, FS = 7 N, ESD = 16 mJ) and **5-Iso2** (IS = 1 J, FS = 5 N, ESD = 9 mJ) have the highest sensitivities. They are followed by **3** (IS = 1 J, FS = 60 N, ESD = 16 mJ), while the methylated compounds **4-Iso1** (IS = 3 J, FS > 360 N, ESD = 100 mJ) and **4-Iso2** (IS = 1 J, FS > 360 N, ESD not measurable because the compound was liquid) are insensitive towards friction but are also very sensitive towards impact. Crystal structures were elucidated using X-ray diffraction. The new oxetanes crystallize in the monoclinic space groups $P2_1/c$ (**4-Iso1**, **5-Iso1**, **5-Iso2** and **6-Iso2**), $P2_1/m$ (**4-Iso2**) and in the orthorhombic space group $P2_12_12_1$ (**3**). Their densities increase in the order: **4-Iso1** (1.512 g cm^{-3}), **4-Iso2** (1.548 g cm^{-3}), **3** (1.581 g cm^{-3}), **5-Iso1** (1.593 g cm^{-3}), **5-Iso2** (1.649 g cm^{-3}) and **6-Iso2** (1.706 g cm^{-3}). All of the newly synthesized energetic oxetanes have a higher nitrogen content than previously reported in the literature. The highest nitrogen content of 61.5 % was observed for the isomers **5-Iso1** and **5-Iso2**. In particular, **5-Iso1**, **5-Iso2** and **6-Iso2** outperform the well-known BAMO in terms of their energetic performance. Detonation velocities of up to 8007 m s^{-1} (**5-Iso2**) were calculated using the EXPLO5 code.[27] A violent detonation of **5-Iso2** occurred during a hot-plate test, which demonstrates its energetic performance. The compounds can definitely be used as sensitizers in

Table 1. Physicochemical properties of 5-(3-azidooxetan-3-yl)-1*H*-tetrazole (**3**), 5-(3-azidooxetan-3-yl)-1-methyl-tetrazole (**4-Iso1**), 5-(3-azidooxetan-3-yl)-2-methyl-tetrazole (**4-Iso2**), 5-(3-azidooxetan-3-yl)-1-amino-tetrazole (**5-Iso1**), 5-(3-azidooxetan-3-yl)-2-amino-tetrazole (**5-Iso2**), 5-(3-azidooxetan-3-yl)-tetrazol-2-ol (**6-Iso2**) and 3,3-bis(azidomethyl)oxetane (**BAMO**).

	3	4-Iso1	4-Iso2	5-Iso1	5-Iso2	6-Iso2	BAMO[26]
Formula	$C_4H_5N_7O$	$C_5H_7N_7O$	$C_5H_7N_7O$	$C_4H_6N_8O$	$C_4H_6N_8O$	$C_4H_5N_7O_2$	$C_5H_8N_6O$
FW [g mol^{-1}]	167.13	181.16	181.16	182.15	182.15	183.13	168.16
IS[a] [J]	1	3	1	1	1	n.d.	40
FS[b] [N]	60	> 360	> 360	7	5	n.d.	360
$N+O$[c] [%]	58.7 + 9.6	54.1 + 8.8	54.1 + 8.8	61.5 + 8.8	61.5 + 8.8	53.5 + 17.5	50.0 + 9.5
Ω[d] [%]	−52.7	−66.2	−66.2	−52.7	−52.7	−39.3	−76.12
T_m[e]/T_{dec}[f] [°C]	71/157	35/172	-/187	110/172	53/170	-/150*	-/207
ρ[g] [g cm^{-3}]	1.535	1.484	1.504	1.548	1.619	1.657	1.23
$\Delta_fH°$[h] [kJ mol^{-1}]	542.0	522.5	469.4	646.9	630.8	508.2	510.5
EXPLO5V6.05[27]							
$-\Delta_EU°$[i] [kJ kg^{-1}]	4362	4066	3752	4691	4615	4867	4479
$D_{C\text{-}J}$[j] [m s^{-1}]	7272	7126	7025	7692	8007	7840	6548
$p_{C\text{-}J}$[k] [GPa]	18.3	16.9	16.2	20.5	22.7	22.9	12.4

[a] Impact sensitivity (BAM drophammer, method 1 of 6); [b] Friction sensitivity (BAM friction tester, method 1 of 6); [c] Nitrogen and oxygen content; [d] Oxygen balance toward carbon monoxide ($\Omega_{CO} = (nO - xC - yH/2)(1600/FW)$); [e] Melting point (DTA, $\beta = 5$ °C min^{-1}); [f] Temperature of decomposition (DTA, $\beta = 5$ °C min^{-1}); [g] Density at 298 K; [h] Standard molar enthalpy of formation; [i] Detonation energy; [j] Detonation velocity; [k] Detonation pressure; n.d.: not determined; *estimated.

energetic mixtures. Preliminary initiation tests in blasting caps filled with PETN were negative so far. Nevertheless, the newly synthesized oxetane derivatives prove to be powerful energetic compounds that could find application in energetic polymers, to which they could be converted via cationic ring-opening polymerization (CROP). Furthermore, co-polymerization, for instance with glycidyl azide or other oxetanes, seems possible in order to adjust the energetic character of the final polymer.

Experimental Section

CAUTION! *All described compounds are powerful energetic materials with high sensitivities towards shock and friction. Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves and ear plugs) have to be applied all time while synthesizing and handling the described compounds.*

Chemicals and solvents were employed as received (Sigma-Aldrich, Acros, TCI). ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded using a Bruker AMX 400 instrument. The chemical shifts quoted in ppm refer to tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N, ^{15}N). Decomposition temperatures were determined on an OZM Research DTA 552-Ex instrument with a heating rate of 5 °C min^{-1}. Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Elemental analyses were performed with an Elementar Vario el by pyrolysis of the sample and subsequent analysis of formed gases. The sensitivity data were collected using a BAM (Bundesanstalt für Materialforschung) drophammer[28] according to STANAG 4489[29] modified instruction[30] and a BAM friction tester[28] according to STANAG 4487[31] modified instruction.[32] The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods'.[33]

3-Hydroxyoxetane-3-carbonitrile (1)

KCN (2.71 g, 41.62 mmol, 3.0 eq.) was dissolved in H_2O (10 mL) under ice-cooling. Oxetan-3-one (1.01 g, 14.02 mmol, 1.0 eq.) was dissolved in EtOH (10 mL) and the solution was added to the reaction mixture. Acetic acid (3.6 mL, 100 %) was added while still maintaining the reaction mixture at 0 °C with an ice bath. The reaction mixture was allowed to come to room temperature over 3 d. The obtained yellowish solution was neutralized by adding $NaHCO_3$ (6.58 g, 78.32 mmol, 5.6 eq.) and H_2O (ca. 30 mL). It was extracted with EtOAc (3×50 mL) and the organic phase was washed with brine (2×30 mL), dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo*. The product 3-hydroxyoxetane-3-carbonitrile (**1**) (1.26 g, 12.72 mmol, 91 %) was obtained as a colorless to yellowish crystalline solid.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.46 (br s, 1H, OH), 4.85–4.83 (m, 2H, $CH_{2\,oxetane}$), 4.57–4.55 (m, 2H, $CH_{2\,oxetane}$) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 120.2, 81.0, 64.7 ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3289 (m), 3210 (w), 3011 (w), 2965 (w), 2253 (vw), 1453 (w), 1434 (m), 1214 (s), 1149 (m), 1138 (w), 967 (s), 944 (s), 902 (vs), 843 (s), 660 (s), 629 (m), 605 (w), 544 (m), 410 (w) cm^{-1}; **EA** ($C_4H_5NO_2$) calcd.: C 48.49, H 5.09, N 14.14; found: C 48.33, H 4.89, N 13.99; **DTA** (T_{onset}, 5 °C min^{-1}): 97 °C (mp.), 129 °C (bp.).

3-Cyanooxetan-3-yl methanesulfonate (2)

3-Hydroxyoxetane-3-carbonitrile (**1**) (4.95 g, 49.96 mmol, 1.0 eq.) was dissolved in MeCN (80 mL). The solution was cooled to 0 °C with an ice bath. Methanesulfonyl chloride (6.29 g, 54.91 mmol, 1.1 eq.) and triethylamine (6.07 g, 59.98 mmol, 1.2 eq.) were simultaneously added dropwise to the reaction mixture. The addition of methanesulfonyl chloride was completed first. The reaction mixture was allowed to come to room temperature over 17 h. The obtained yellow suspension was poured into EtOAc (240 mL) and filtered through a kieselguhr plug. The solution was washed with H_2O (120 mL), HCl solution (120 mL, 2 M in H_2O), and H_2O (120 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*. The product 3-cyanooxetan-3-yl methanesulfonate (**2**) (8.21 g, 46.34 mmol, 93 %) was obtained as a yellow to orange oil.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 5.05–5.03 (m, 2H, $CH_{2\,oxetane}$), 4.96–4.94 (m, 2H, $CH_{2\,oxetane}$), 3.51 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 116.0, 78.0, 69.5, 40.1 ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3024 (vw), 2943 (vw), 2892 (vw), 1740 (vw), 1454 (vw), 1416 (vw), 1358 (s), 1336 (s), 1237 (w), 1179 (s), 1148 (m), 1122 (s), 981 (m), 948 (s), 904 (vs), 827 (m), 791 (s), 743 (m), 659 (m), 558 (m), 532 (s), 512 (s), 449 (vw), 414 (w) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 266 °C (dec.).

5-(3-Azidooxetan-3-yl)-1*H*-tetrazole (3)

3-Cyanooxetan-3-yl methanesulfonate (**2**) (3.01 g, 16.99 mmol, 1.0 eq.) was dissolved in H_2O (120 mL). NaN_3 (6.60 g, 101.52 mmol, 6.0 eq.) and $ZnCl_2$ (4.63 g, 33.97 mmol, 2.0 eq.) were added and the reaction mixture was stirred at 95 °C for 18 h. The obtained yellowish solution was allowed to come to room temperature and it was further cooled to 0 °C with an ice bath. HCl (60 mL, 37 % in H_2O) was added and the aqueous phase was saturated with $(NH_4)_2SO_4$. EtOAc (150 mL) was added and the reaction mixture was stirred at room temperature for approximately 1 h to remove gaseous HN_3 which is formed during the acidification of the solution. The reaction mixture was extracted with EtOAc (3× 150 mL) and the organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*. The product 5-(3-azidooxetan-3-yl)-1*H*-tetrazole (**3**) (2.59 g, 15.50 mmol, 91 %) was obtained as a yellow oil which crystallized upon standing.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 5.04 (dd, J = 7.4, 0.9 Hz, 2H, $CH_{2\,oxetane}$), 4.90 (dd, J = 7.4, 0.9 Hz, 2H, $CH_{2\,oxetane}$) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 157.3, 79.3, 59.6 ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3420 (w), 3385 (w), 3123 (w), 3107 (w), 2994 (m), 2954 (m), 2887 (m), 2782 (w), 2740 (m), 2618 (w), 2474 (w), 2139 (s), 2119 (vs), 1749 (vw), 1563 (m), 1498 (vw), 1454 (w), 1414 (w), 1384 (w), 1352 (w), 1293 (m), 1279 (s), 1245 (s), 1197 (m), 1154 (w), 1135 (w), 1117 (m), 1090 (m), 1054 (m), 1034 (s), 987 (vs), 946 (m), 933 (s), 877 (m), 833 (s), 747 (w), 709 (w), 673 (s), 552 (w), 535 (m), 465 (m), 420 (w) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 71 °C (mp.), 157 °C (dec.); **IS**: 1 J (> 500 μm); **FS**: 60 N (> 500 μm); **ESD**: 16 mJ (> 500 μm).

5-(3-Azidooxetan-3-yl)-1-methyl-tetrazole (4-Iso1) and 5-(3-azidooxetan-3-yl)-2-methyl-tetrazole (4-Iso2)

5-(3-Azidooxetan-3-yl)-1*H*-tetrazole (**3**) (2.56 g, 15.32 mmol, 1.0 eq.) was dissolved in H_2O (40 mL). The solution was cooled to 0 °C with an ice bath. NaOH (1.10 g, 27.50 mmol, 1.8 eq.) was added, followed by the dropwise addition of dimethyl sulfate (3.28 g, 26.01 mmol, 1.7 eq.). The reaction mixture was stirred at room temperature for 1 h and at 95 °C for 1 h. EtOAc (35 mL) was added and the yellowish solution was stirred at room temperature for 17 h. The reaction mixture was extracted with EtOAc (3×100 mL) and the organic phase was washed with H_2O (100 mL), $NaHCO_3$ solution (100 mL, saturated aqueous solution) and brine (100 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*. The crude product 5-(3-azidooxetan-3-yl)-1-methyl-tetrazole (**4-Iso1**)/5-(3-azidooxetan-3-yl)-2-methyl-tetrazole (**4-Iso2**) (2.19 g, 12.09 mmol, 79 %) was obtained as a yellowish oil. The isomers **4-Iso1** and **4-Iso2** were separated and purified by column chromatography (SiO_2, Et_2O/*n*-

pentane 1:1). **4-Iso1** (0.54 g, 2.98 mmol, 19%) was obtained as a yellow oil which crystallized upon standing in the freezer and **4-Iso2** (1.37 g, 7.56 mmol, 49%) was obtained as a yellowish oil which froze upon standing in the freezer.

4-Iso1

R_f (SiO_2, Et_2O/*n*-pentane 1:1) = 0.08; **^{1}H NMR** (400 MHz, DMSO-d_6, 25 °C): δ = 5.24 (dd, J = 7.6, 0.9 Hz, 2H, $CH_{2\,oxetane}$), 5.03 (dd, J = 7.6, 1.0 Hz, 2H, $CH_{2\,oxetane}$), 4.04 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 152.4, 77.5, 58.5, 34.7 ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3014 (w), 2956 (m), 2885 (m), 2417 (w), 2118 (vs), 2092 (s), 2048 (m), 1531 (m), 1522 (m), 1455 (s), 1423 (m), 1401 (m), 1286 (m), 1260 (m), 1237 (s), 1227 (vs), 1174 (m), 1128 (m), 1115 (m), 1062 (m), 1032 (m), 980 (vs), 944 (m), 930 (s), 870 (m), 849 (m), 827 (s), 807 (s), 745 (m), 706 (s), 696 (s), 661 (s), 644 (m), 555 (m), 506 (m), 468 (m), 455 (m), 417 (m) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 35 °C (mp.), 172 °C (dec.); **IS**: 3 J (> 500 μm); **FS**: > 360 N (> 500 μm); **ESD**: 100 mJ (> 500 μm).

4-Iso2

R_f (SiO_2, Et_2O/*n*-pentane 1:1) = 0.40; **^{1}H NMR** (400 MHz, DMSO-d_6, 25 °C): δ = 5.03 (dd, J = 7.2, 0.8 Hz, 2H, $CH_{2\,oxetane}$), 4.89 (dd, J = 7.2, 0.9 Hz, 2H, $CH_{2\,oxetane}$), 4.43 (s, 3H, CH_3) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 164.1, 79.1, 59.8, 39.9 ppm; **^{15}N NMR** (41 MHz, DMSO-d_6, 25 °C): δ = 2.6 (q, J = 1.6 Hz, N3), −50.7 (s, N4), −76.2 (q, J = 1.7 Hz, N1), −100.1 (q, J = 2.2 Hz, N2), −136.3 (s, N6), −159.4 (s, N7), −293.0 (s, N5) ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 2958 (w), 2885 (w), 2110 (vs), 1497 (w), 1456 (w), 1384 (w), 1338 (w), 1250 (s), 1203 (m), 1183 (w), 1141 (w), 1118 (w), 1053 (m), 1028 (w), 985 (vs), 936 (m), 857 (m), 827 (m), 760 (w), 719 (m), 688 (w), 661 (w), 555 (w), 511 (w), 466 (w), 419 (w) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 187 °C (dec.); **IS**: 1 J (liquid); **FS**: > 360 N (liquid).

5-(3-Azidooxetan-3-yl)-1-amino-tetrazole (5-Iso1) and 5-(3-azidooxetan-3-yl)-2-amino-tetrazole (5-Iso2)

Ethyl *N*-(tosyloxy)acetimidate (**7**) (4.63 g, 17.99 mmol, 1.2 eq.) was dissolved in $HClO_4$ (44 mL, 60% in H_2O) and the reaction mixture was stirred at room temperature for 2 h. The obtained white suspension was stirred into ice water (400 mL) and the solution was extracted with DCM (7 × 20 mL). The organic phase was dried over $MgSO_4$ and filtered. 5-(3-Azidooxetan-3-yl)-1*H*-tetrazole (**3**) (2.51 g, 15.02 mmol, 1.0 eq.) was dissolved in MeCN (400 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (2.73 g, 17.93 mmol, 1.2 eq.) and the DCM phase containing *O*-tosylhydroxylamine (TOSA) were added to this solution. The reaction mixture was stirred at room temperature for 3 d. The solvent of the yellowish solution was removed *in vacuo* and a yellowish oil was obtained. The oil was dissolved in small amounts of EtOAc and MeOH and filtered through a kieselguhr plug. The solvent was again removed *in vacuo* to yield the crude product as a yellow to orange oil. The crude product was purified by column chromatography (SiO_2, EtOAc, R_f = 0.85) which yielded a yellow oil. The isomers **5-Iso1** and **5-Iso2** were separated and purified by a second column chromatography (SiO_2, Et_2O/*n*-pentane 2:1). **5-Iso1** (0.35 g, 1.92 mmol, 13%) was obtained as a white crystalline solid and **5-Iso2** (0.62 g, 3.40 mmol, 23%) was obtained as a yellow oil which crystallized upon standing in the freezer.

5-Iso1

R_f (SiO_2, Et_2O/*n*-pentane 2:1) = 0.23; **^{1}H NMR** (400 MHz, DMSO-d_6, 25 °C): δ = 7.15 (s, 2H, NH_2), 5.19 (dd, J = 7.5, 0.9 Hz, 2H, $CH_{2\,oxetane}$), 4.91 (dd, J = 7.5, 0.9 Hz, 2H, $CH_{2\,oxetane}$) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 151.6, 77.4, 58.0 ppm; **^{14}N NMR** (29 MHz, DMSO-d_6, 25 °C): δ = −138, −160 ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3334 (m), 3268 (m), 3216 (w), 2996 (w), 2958 (w), 2889 (w), 2492 (vw), 2116 (vs), 2074 (s), 1621 (m), 1525 (w), 1517 (w), 1470 (w), 1452 (m), 1345 (w), 1299 (m), 1273 (m), 1251 (vs), 1180 (s), 1146 (m), 1125 (m), 1115 (m), 1075 (w), 1034 (w), 994 (m), 981 (vs), 950 (m), 923 (s), 848 (m), 828 (s), 759 (w), 728 (m), 703 (w), 650 (s), 552 (m), 532 (w), 466 (m), 423 (m) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 110 °C (mp.), 172 °C (dec.); **IS**: 1 J (> 500 μm); **FS**: 7 N (> 500 μm); **ESD**: 16 mJ (> 500 μm).

5-Iso2

R_f (SiO_2, Et_2O/*n*-pentane 2:1) = 0.45; **^{1}H NMR** (400 MHz, DMSO-d_6, 25 °C): δ = 8.29 (s, 2H, NH_2), 5.01 (dd, J = 7.1, 0.8 Hz, 2H, $CH_{2\,oxetane}$), 4.87 (dd, J = 7.1, 0.9 Hz, 2H, $CH_{2\,oxetane}$) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): δ = 161.8, 79.0, 59.9 ppm; **^{14}N NMR** (29 MHz, DMSO-d_6, 25 °C): δ = −137, −161 ppm; **^{15}N NMR** (41 MHz, DMSO-d_6, 25 °C): δ = −10.9 (t, J = 1.1 Hz, N3), −57.8 (s, N4), −83.4 (t, J = 1.0 Hz, N1), −86.0 (t, J = 1.8 Hz, N2), −136.2 (s, N7), −159.4 (s, N8), −284.0 (t, J = 72.9 Hz, N5), −292.7 (s, N6) ppm; **FT-IR** (ATR): $\tilde{\nu}$ = 3312 (w), 3280 (w), 3177 (w), 2958 (w), 2887 (w), 2110 (vs), 1615 (w), 1497 (vw), 1457 (w), 1391 (w), 1251 (s), 1204 (m), 1142 (w), 1117 (w), 1047 (m), 1026 (w), 978 (vs), 932 (s), 862 (m), 828 (m), 761 (w), 728 (w), 662 (w), 554 (w), 518 (w), 471 (w) cm^{-1}; **DTA** (T_{onset}, 5 °C min^{-1}): 53 °C (mp.), 170 °C (dec.); **IS**: 1 J (> 500 μm); **FS**: 5 N (> 500 μm); **ESD**: 9 mJ (> 500 μm).

5-(3-Azidooxetan-3-yl)-tetrazol-1-ol (6-Iso1) and 5-(3-azidooxetan-3-yl)-tetrazol-2-ol (6-Iso2)

5-(3-Azidooxetan-3-yl)-1*H*-tetrazole (**3**) (1.01 g, 6.04 mmol, 1.0 eq.) was dissolved in H_2O (50 mL) and Oxone® (10.00 g, 32.53 mmol, 5.4 eq.) was added to the solution. Na_3PO_4 was added to adjust the pH value of the solution from pH 1 to pH 6. The reaction mixture was stirred at room temperature for 17 h. The obtained colorless, turbid liquid was cooled to 0 °C with an ice bath. HCl (20 mL, 37% in H_2O) was added and the reaction mixture was extracted with EtOAc (3 × 60 mL). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*. The crude product 5-(3-azidooxetan-3-yl)-tetrazol-1-ol (**6-Iso1**)/5-(3-azidooxetan-3-yl)-tetrazol-2-ol (**6-Iso2**) (0.82 g, 4.48 mmol, 74%) was obtained as a whitish solid. The isomers could not be separated by column chromatography due to decomposition occurring upon contact with the column material SiO_2.

6-Iso2

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 5.00 (dd, J = 7.2, 0.9 Hz, 2H, $CH_{2\,oxetane}$), 4.83 (dd, J = 7.1, 0.9 Hz, 2H, $CH_{2\,oxetane}$) ppm (OH group was not observable in DMSO-d_6); **FT-IR** (ATR): $\tilde{\nu}$ = 2975 (w), 2963 (w), 2890 (w), 2457 (w), 2321 (w), 2108 (vs), 1834 (w), 1689 (w), 1642 (w), 1572 (w), 1484 (w), 1463 (w), 1449 (w), 1421 (w), 1371 (m), 1334 (m), 1256 (vs), 1226 (s), 1198 (s), 1172 (m), 1132 (w), 1120 (m), 1065 (w), 1044 (m), 1021 (s), 973 (s), 918 (s), 859 (s), 829 (s), 757 (m), 747 (m), 662 (s), 557 (m), 540 (m), 477 (m), 452 (m) cm^{-1}.

Ethyl *N*-(tosyloxy)acetimidate (7)

Ethyl *N*-(tosyloxy)acetimidate (**7**) was prepared according to a literature procedure.[24] Ethyl *N*-hydroxyacetimidate (4.51 g, 43.74 mmol, 1.0 eq.) was dissolved in DMF (30 mL) and triethylamine (4.50 g, 44.47 mmol, 1.0 eq.) was added. The solution was cooled to 0 °C with an ice bath and 4-methylbenzenesulfonyl chloride (8.30 g, 43.70 mmol, 1.0 eq.) was added in portions. The

reaction mixture was stirred at 0 °C for 10 min and at room temperature for 4 h. A yellow suspension was obtained. The by-product triethylammonium chloride was filtered off and washed with Et_2O. The solvent of the organic phase was partly removed *in vacuo* until all of the Et_2O was evaporated. The remaining organic phase was stirred into ice water (300 mL) and the precipitate was filtered off. The product ethyl *N*-(tosyloxy)acetimidate (**7**) (8.78 g, 34.12 mmol, 78 %) was obtained as a white crystalline solid.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): $\delta = 7.83–7.80$ (m, 2H, $CH_{2\ arene}$), 7.49–7.45 (m, 2H, $CH_{2\ arene}$), 3.93 (q, $J = 7.0$ Hz, 2H, $\mathbf{CH_2}CH_3$), 2.42 (s, 3H, $\mathbf{CH_3}C_{\ arene}$), 1.96 (s, 3H, $\mathbf{CH_3}CN$), 1.16 (t, $J = 7.0$ Hz, 3H, $\mathbf{CH_3}CH_2O$) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6, 25 °C): $\delta = 170.2$, 145.3, 131.7, 129.9, 128.5, 63.7, 21.1, 14.7, 13.8 ppm.

Deposition Numbers 2194730 (for oxetan-3-one), 2194734 (for **1**), 2194727 (for **3**), 2194728 (for **4-Iso1**), 2194731 (for **4-Iso2**), 2194733 (for **5-Iso1**), 2194732 (for **5-Iso2**) and 2194729 (for **6-Iso2**) contain 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 www.ccdc.cam.ac.uk/structures.

Acknowledgements

Financial support of this work by Ludwig Maximilian University (LMU), the Office of Naval Research (ONR) under Grant ONR N00014-19-1-2078, and the Strategic Environmental Research and Development Program (SERDP) under Contract W912HQ19C0033 is gratefully acknowledged. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

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.

Keywords: Energetic binder · Isomers · Oxetanes · Structure elucidation · Tetrazoles

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[33] Impact: insensitive >40 J, less sensitive 35–40 J, sensitive 4–35 J, very sensitive <4 J; Friction: insensitive >360 N, less sensitive $=360$ N, sensitive 80–360 N, very sensitive 10–80 N, extremely sensitive <10 N; According to the UN Recommendations on the Transport of Dangerous Goods.

Manuscript received: September 13, 2022
Revised manuscript received: November 3, 2022
Accepted manuscript online: November 4, 2022