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Energetic but insensitive *spiro*-tetrahydrotetrazines based on oxetane-3-one

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Abstract

Energetic oxetanes were first described in the 1970s, such as 3,3-bis (azidomethyl)oxetanes (BAMO) and 3-(nitratomethyl)-3-(methyl)oxetanes (NIMMO). Over the past few years, oxetanes were hardly available only as special-purpose chemicals for the pharmaceutical industry. Oxetan-3-one is condensed with energetic compounds with a hydrazino function such as amino-nitroguanidine and picryl hydrazine to form energetic Schiff bases. Hydrazinolysis of the guanidine derivatives lead to energetic *spiro*-tetrahydrotetrazines which are quite rare in literature. All products were characterized by their crystal structure using single-crystal X-ray diffraction. Furthermore, the new compounds were analyzed using IR, EA, DTA, and multinuclear NMR spectroscopy (^{1}H and ^{13}C). The sensitivities towards external stimuli such as friction and impact were determined according to BAM standards and the energetic performances were calculated using the EXPLO5 code.

1 | INTRODUCTION

In 1878, *Reboul* discovered and described oxetanes as small strained four-membered heterocycles [1]. Since then, the availability of different oxetanes greatly increased, especially due to better and new synthetic approaches [2–4]. The pharmaceutical industry has an enormous interest in oxetanes because of the chemical similarity and stability of gem-dimethyl and carbonyl groups, resulting in better commercial availability [4]. Oxetanes are often used as substitutes for these gem-dimethyl and also carbonyl groups in pharmaceuticals, due to their nontoxic degradation in the human body and better solubility [4]. Some work has focused mainly on substitution in the 3-position of oxetanes, as these units are achiral and incorporation into a drug for medical use does not add a stereocenter [5]. In 1984, *Luger* successfully characterized the unsubstituted parent compound oxetane and showed that the planar structure minimizes the ring strain [6]. Nearly at the same time, several energetic oxetanes were synthesized such as 3,3-bis (azidomethyl)oxetane (BAMO) or 3-(nitratomethyl)-3-(methyl)oxetane (NIMMO) [7–10]. These energetic oxetanes can be polymerized via cationic ring-opening polymerization (CROP) which offered the development of further energetic polymers [11]. A good starting point for new energetic monomers is the commonly available oxetan-3-one which offers the carbonyl function as reactive site [5]. Carbonyl functions in general are very versatile chemical functional groups (Figure 1) and are able to react, for example with hydrogen peroxide under acidic conditions to form peroxo-compounds [12, 13]. Various

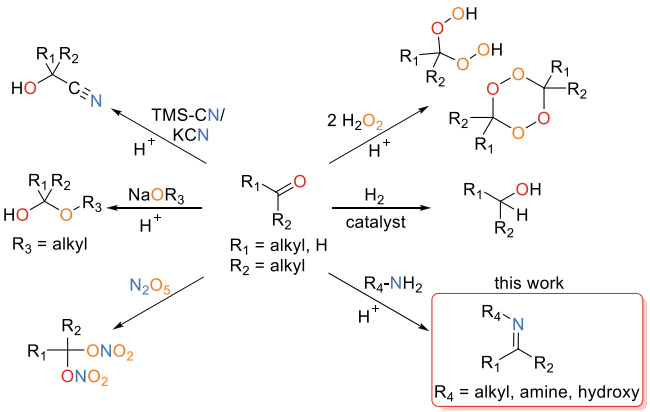
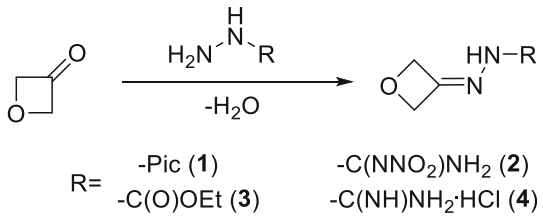


FIGURE 1 General reactions of carbonyl compounds with the focus on the condensation reaction to form a Schiff base in this work.

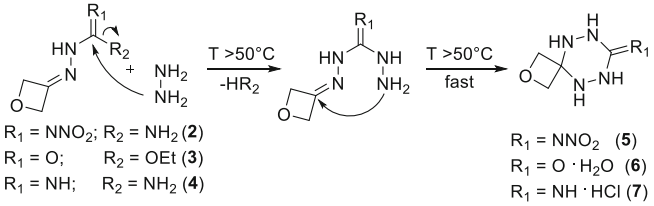
addition reactions such as the addition of dinitrogen pentoxide to the carbonyl function to obtain unstable dinitrates [14, 15] and the addition of trimethylsilyl cyanide or a cyanide salt to synthesize hydroxy-carbonitriles are also well reported in the literature [16–18]. However, oxetan-3-one is an extremely versatile building block for 3-monosubstituted and 3,3-disubstituted oxetanes as shown for the 3,3-dinitratooxetane by our group [14]. Another type of reaction is the addition of metal alkoxides to obtain hemiacetals [19, 20]. The C═O double bond can also be reduced with elemental compounds [21, 22]. Furthermore, carbonyl compounds can hydrogen to synthesize simple hydroxy condense easily and fast to form Schiff bases under acid catalysis [23–25]. Herein, we report several condensation reactions of oxetan-3-one with different energetic compounds having a hydrazino function such as aminoguanidine (AQ), amino-nitroguanidine (ANQ) and picryl hydrazine (PicHy). The guanidine derivatives can be further functionalized with hydrazine.

2 | RESULTS AND DISCUSSION

Commercially available oxetan-3-one (SpiroChemAG), aminoguanidine hydrochloride (Sigma-Aldrich), and 1,3-diaminoguanidine hydrochloride (Sigma-Aldrich) were used as received. Amino-nitroguanidine [26], picryl hydrazine [27], ethyl hydrazine carboxylate [28] were synthesized according to literature procedures. Oxetan-3-one was heated with picryl hydrazine in ethanol and a catalytical amount of concentrated hydrochloric acid to nearly boiling. After a short period of 5–10 min at 90°C, the mixture was cooled to room temperature and the pure orange precipitate **1** was collected in 92% yield. The same protocol can be applied for the reaction with



SCHEME 1 Reaction of oxetan-3-one with different compounds with a hydrazino function to obtain oxetane-hydrazone compounds (**1**–**4**).



SCHEME 2 Hydrazinolysis reaction of compounds **2**–**4**. Hydrazine cleaves R_2 to form the open intermediate, which then cyclizes rapidly intramolecularly to form the *spiro*-tetrahydrotetrazine derivatives (**5**–**7**).

amino-nitroguanidine, ethyl hydrazine carboxylate, and aminoguanidine to obtain the corresponding colorless compounds **2**–**4** (Scheme 1). The hydrazinolysis of compounds **2**–**4** did not lead to the open form compound but instead gave interesting *spiro*-1,2,4,5-tetrahydro-1,2,4,5-tetrazine derivatives (**5**–**7**). It is assumed, that first hydrazine cleaves the respective residue R_2 (Scheme 2) and the open form product is formed. In a second reaction step, the reactive hydrazine function attacks rapidly at the C═N double bond to form the thermodynamically favorable tetrazine derivative. Probably the *spiro*-tetrahydrotetrazine formation proceeds in a concerted manner. Such derivatives are neither well present in the literature nor structurally well characterized [29, 30]. However, the reaction of oxetan-3-one with 1,3-diaminoguanidine also lead to compound **7**, probably in the same manner as the hydrazinolysis reaction of **4**.

2.1 | Crystallography

A detailed crystallographic discussion can be found in Supporting Information. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. The single crystals suitable for X-ray diffraction were obtained by recrystallization from ethyl acetate (**1**, **2**), water (**4**, **6**, **7**), or methanol (**5**). Structures were deposited with the CCDC database under the following numbers: 2157490 (**1**),

2157477 (**2**), 2157480 (**4**), 2157481 (**5**), 2157478 (**6**), 2157482 (**7**).

1-(Oxetan-3-ylidene)-2-(2,4,6-trinitrophenyl)-hydrazine (**1**) crystallizes in the triclinic space group *P*–1 with 4 molecules in the unit cell and a density of 1.703 g cm^{-3} at 101 K (Figure 2). The bond length of C2–N1 (1.276(6) Å) is slightly shorter than typical C═N double bond (∼1.30 Å) [31]. N1–N2 (1.380(5)Å) is only slightly shorter than a N–N single bond (∼1.41 Å) and but much larger than a N–N double bond (∼1.24 Å) [31]. One nitro group at the *ortho*-position (O2–N3–O3) stands perpendicular (91.0(5)°) to the aromatic ring. The other nitro group is twisted only 22.9(5)° due to an intramolecular hydrogen bond of the hydrogen of N2 to O7 with a distance of 2.019 Å.

N-nitro-2-(oxetan-3-ylidene)hydrazine-1-carboximidamide (**2**) crystallizes in the orthorhombic space group $Pna2_1$ with 4 molecules in the unit cell and a density of 1.567 g cm^{-3} at 119 K (Figure 3). The electrons in the nitroguanidine moiety indicate a delocalization with bond lengths of 1.307(4) Å (C4–N3), 1.366(4) Å (C4–N4), and 1.351 Å (C4–N2). The oxetane ring has a puckering angle of 7.07° which is in the range of the reported puckering angle of Luger for unsubstituted oxetane (8.7°at 140 K) [6].

Compound **4** crystallizes monoclinic ($P2_1/n$) with 8 formula units in the unit cell and a density 1.465 g cm^{-3} at 119 K (Figure 4). The bond lengths are in the same range, as discussed for compound **2**, suggesting delocalization of electrons in the guanidine moiety. The molecule is essentially planar except the oxetane ring which is 15.66° off the planarity of the guanidine fragment. The molecules arrange themselves in the crystal as a light zig–zag pattern with an interlayer distance of 3.422 Å.

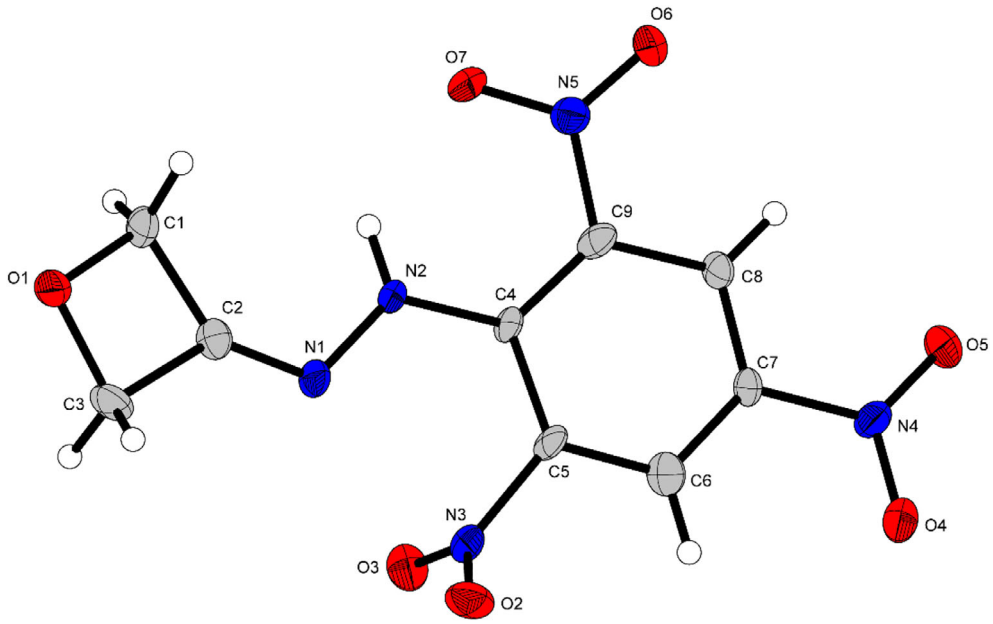


FIGURE 2 Crystal structure of 1-(oxetan-3-ylidene)-2-(2,4,6-trinitrophenyl)-hydrazine (**1**)

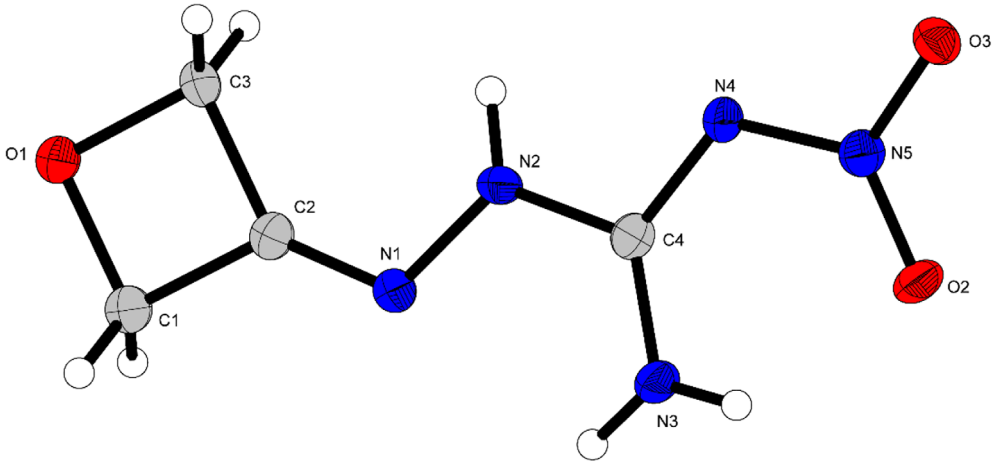


FIGURE 3 Molecular moiety of *N*-nitro-2-(oxetan-3-ylidene)hydrazine-1-carboximidamide (**2**)

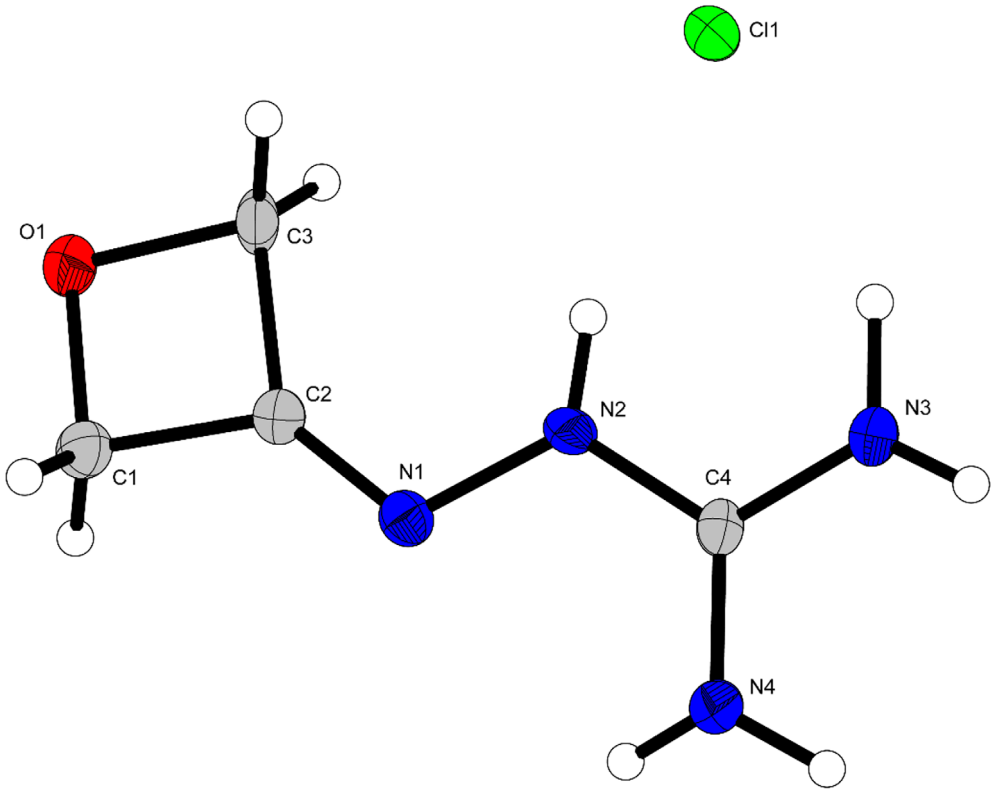


FIGURE 4 Crystal structure of amino(2-(oxetan-3-ylidene)hydrazineyl)-methaniminium chloride (**4**)

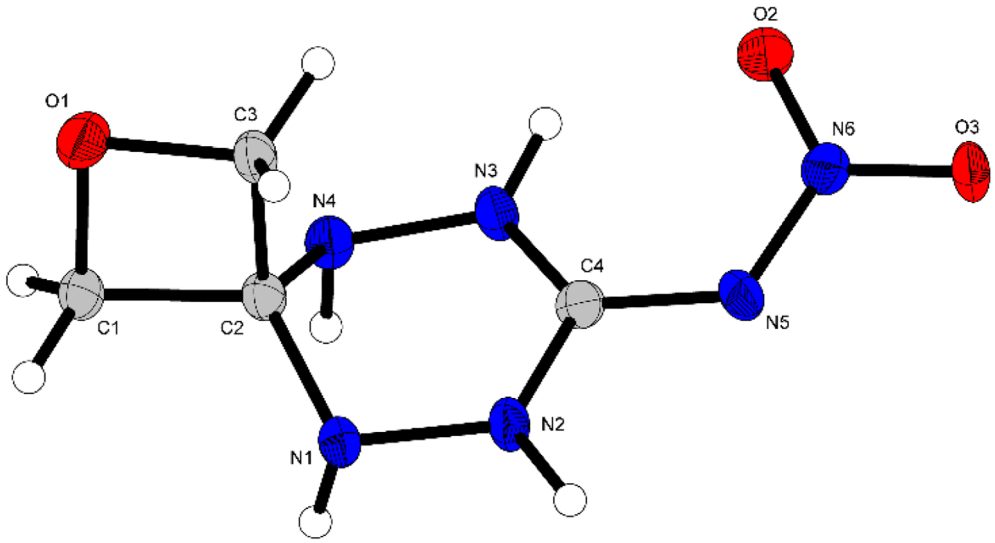


FIGURE 5 Crystal structure of *N*-(2-oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-ylidene)nitramide (**5**)

N-(2-oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-ylidene)-nitramide (**5**) crystallizes in the monoclinic space group *I*2/*a* with a density of 1.685 g cm^{-3} at 102 K which is significantly higher than the parent compound **2** with 1.567 g cm^{-3} (Figure 5). Furthermore, the bond lengths at C4 is very similar to the carbon atom of the guanidine derivatives. The tetrahydrotetrazine ring has a half-chair or envelope-like conformation being planar in N2–C4–N3–N4. The oxetane has a puckering of 16.38° which is larger than the reported puckering angle of 8.7° (140 K) for unsubstituted oxetane [6]. Furthermore, the oxetane ring stands nearly perpendicular to the tetrahydrotetrazine ring (81.24°).

2-Oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-one (**6**) crystallizes as monohydrate in the monoclinic space group *P*21/*n* with 4 molecules in the unit cell and a density of 1.547 g cm^{-3} at 103 K (Figure 6). The bond lengths are in the same range of the lengths for **5**, except the C4–O2 which has a length of a standard C=O double bond [31]. The tetrahydrotetrazine ring features an envelope-like conformation as compound **5**. Only C2 is out of the tetrazine plane. As discussed beforehand, the oxetane

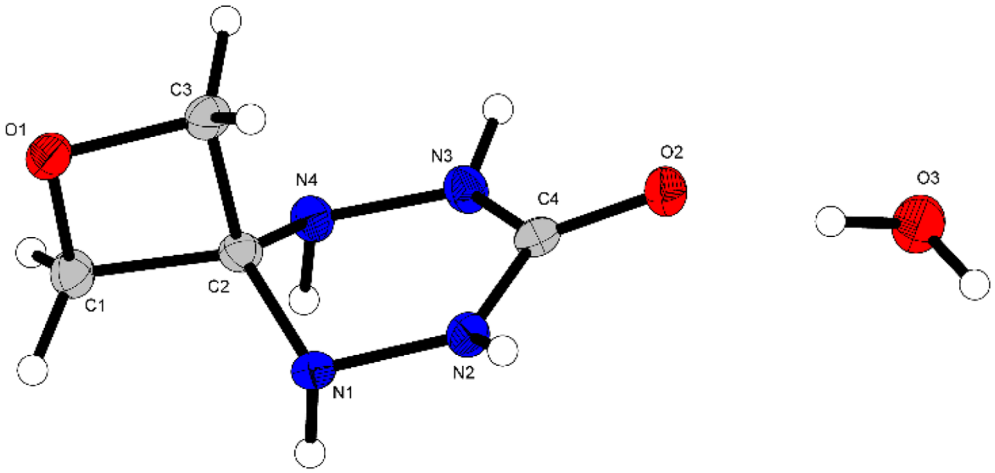


FIGURE 6 Crystal structure of 2-oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-one monohydrate (**6**)

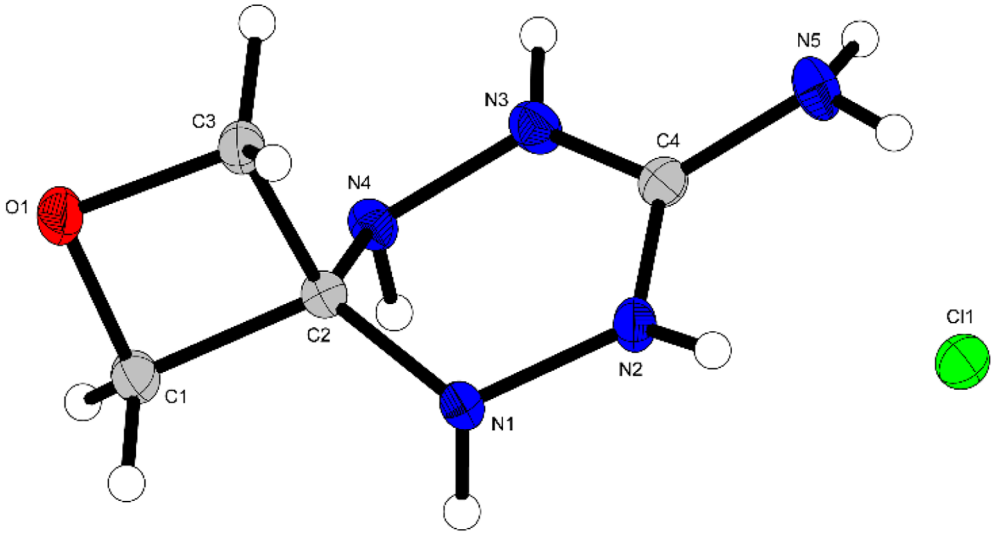


FIGURE 7 Crystal structure of 2-oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-imine hydrochloride (**7**)

ring stands approximately perpendicular to the tetrahydrotetrazine ring with an angle of 84.65°. The water molecule bridges three molecules via a hydrogen bond, forming a three-dimensional network.

2-Oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-iminium chloride (**7**) crystallizes also monoclinic ($P2_1/c$) with 4 molecules in the unit cell and a density of 1.617 g cm^{-3} at 102 K (Figure 7). The conformation of the tetrazine moiety is also a half-chair conformation with C2–N1–N2–C4 in a plane. The oxetane ring has an angle of 65.64° toward the tetrazine ring. Furthermore, the oxetane itself has a puckering angle of 14.77° which is near the puckering angle of compound **5**.

2.2 | Spectroscopic analysis

For better comparison, all NMR spectra were recorded using DMSO-d_6 as solvent. A detailed NMR discussion can be found in Supporting Information. The chemical shifts of the relevant positions (^{1}H and ^{13}C) are summarized in Table 1 and quoted in ppm. The methylene groups of the oxetane ring can be found around 5.20 ppm as multiplets for compounds **1**–**4**. The tetrahydrotetrazines **5**–**7** have only singlets for the oxetane CH_2 groups at around 4.30 ppm. In ^{13}C NMR, the methylene signals of the oxetane ring are found at about 80 ppm, but two signals are found for **1**–**4** due to the E/Z isomerism of the C=N bond, compared to only one signal for **5**–**7**. Furthermore, the C2 signal is found at 150 ppm except for the *spiro*-tetrahydrotetrazines which have a significant shift upfield to 67 ppm. The C4 signal is essentially unchanged for all compounds at about 153 ppm. Compounds **1**–**4** exhibit NH signals at around 10–11 ppm. Compounds **5**–**7** also have additional NH signals but now shifted upfield compared to the parent compounds.

2.3 | Physicochemical properties

All compounds were investigated for their physiochemical properties. The sensitivities towards

TABLE 1 Comparison of the relevant NMR shifts all quoted in ppm (^{1}H, ^{13}C)

	CH_2 (oxetane)		NH	NH_2	C2	C4
	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{1}H	δ ^{13}C	δ ^{13}C
1	5.44 (m) 5.28 (m)	80.0 79.8	10.87	—	157.1	—
2	5.27 (m)	80.4 80.0	11.34	8.78 (s) 8.41 (s)	158.3	153.4
3	5.17 (m)	80.4 80.1	10.49	—	148.2	153.7
4	5.29 (s)	80.1 79.7	11.75	7.64	155.6	153.1
5	4.33 (s)	77.2	9.73 7.08	—	67.8	152.4
6	4.29 (s)	76.9	7.78 5.03	—	67.7	154.6
7	4.33 (s)	77.1	9.76 7.09	5.86	67.8	152.4

impact and friction as well as their thermal decomposition temperature were determined experimentally. The enthalpies of formation for **1**, **2**, **4–7** were calculated using the atomization method on the CBS-4M level of theory in the Gaussian software suite [35]. The detonation parameters were calculated with the program EXPLO5 V6.05 using the calculated enthalpies of formation accompanied by the densities according to the crystal structures, or in case of compound **6**, determined pycnometrically for the anhydrous compound [33]. The calculated as well as the experimentally determined values are summarized in Table 2 and compared to the values of BAMO [32]. All investigated compounds are insensitive towards mechanical stimuli such as friction or impact which is also BAMO. Furthermore, all compounds exhibit a negative oxygen balance between −29.6% for **4** to −73.0% for **7** with respect to the formation of CO. Also, compound **4** has the lowest density with 1.423 g cm^{-3} and the picryl derivative **1** as well as nitriminotetrahydro-tetrazine **5** have the highest densities

TABLE 2 Physiochemical properties of compounds 1, 2, and 4–7 compared to BAMO [32]

	1	**2**	**4**	**5**	**6**	**7**	**BAMO [32]**
Formula	$C_9H_7N_5O_7$	$C_4H_7N_5O_3$	$C_4H_9N_4OCl$	$C_4H_8N_6O_3$	$C_4H_8N_4O_2$	$C_4H_{10}N_5OCl$	$C_5H_8N_6O$
FW (g mol^{-1})	297.2	173.1	164.4	188.2	162.1	179.6	168.2
IS[a] (J)	>40	>40	>40	>40	>40	>40	40
FS[b] (N)	>360	>360	>360	>360	>360	>360	360
$N + O$[c] (%)	61.3	68.2	43.8	70.2	64.2	47.9	59.5
Ω_{CO}[d] (%)	−29.6	−41.6	−73.0	−42.5	−59.2	−71.3	−76.1
T_m[e]/T_{dec}[f] (°C)	170/177	−/191	−/200	−/151	−/192	−/168	−/207
ρ[g] (g cm^{-3})	1.654	1.526	1.423	1.637	1.57*	1.571	1.23
$\Delta_f H$[h] (kJ mol^{-1})	238.1	107.8	323.8	223.1	−71.3	−17.4	510.5
EXPLO5 V6.05 [33]							
$-\Delta_E U$[i] (kJ kg^{-1})	4919	4234	4100	4650	2745	2084	4479
T_{C-J}[j] (K)	3424	2848	2773	2952	1930	1712	2786
p_{C-J}[k] (GPa)	20.2	18.1	17.3	23.2	17.3	15.2	12.4
D_{C-J}[l] (m s^{-1})	7062	7146	6798	7989	7279	6821	6548
V_0[m] (dm^3 kg^{-1})	658	814	795	834	817	810	797

[a]Impact sensitivity (BAM drophammer, method 1 of 6).
[b]Friction sensitivity (BAM friction tester, method 1 of 6).
[c]Combined nitrogen and oxygen content.
[d]Oxygen balance towards carbon monoxide ($\Omega_{CO} = (nO - xC - yH/2)(1600/FW)$).
[e]Melting point (DTA, $\beta = 5°C \cdot min^{-1}$).
[f]Temperature of decomposition (DTA, $\beta = 5°C \cdot min^{-1}$).
[g]Density recalculated to 298 K with the formula: $\rho_{298K} = \rho_T/[1 + \alpha_V(298\,K - T)]$ where $\alpha_V = 1.6 \times 10^{-4}\,K^{-1}$ [34].
[h]Standard molar enthalpy of formation.
[i]Detonation energy.
[j]Detonation temperature.
[k]Detonation velocity.
[l]Detonation pressure.
[m]Volume of detonation gases at standard temperature and pressure conditions.
*Pycnometrically determined.

with 1.654 g cm^{-3} and 1.637 g cm^{-3}, respectively. All compounds exceed the energetic performance of BAMO especially compound **5**, which has a detonation velocity of nearly 8000 m s^{-1}. The other compounds have detonation velocities in the range of 6798 m s^{-1} (**4**) to 7279 m s^{-1} (**6**). Furthermore, the detonation pressures are in between 15.2 GPa for compound **7** and 23.2 GPa for compound **5** which is an increase of at least 23%–87% compared to BAMO. The synthesized molecules decompose between 151°C (**5**) to 200°C (**4**). Along the tetrahydrotetrazines, compound **6** is the most thermally stable one with a decomposition temperature of 192°C. Only compounds **1** and **3** have melting points of 170°C shortly before decomposition at 177°C and 113°C with a decomposition point of 198°C. With respect to BAMO, all compounds are almost similar in thermal stability, but do not succeed in surpassing it.

3 | CONCLUSION

In this work, oxetan-3-one is utilized by the versatility of the keto function to obtain various energetic monomers suitable for ring-opening polymerization. The condensation reactions to form the Schiff base compounds **1**–**4** are fast and work in high yield and purity. Further reaction with hydrazine of compounds **2**–**4** lead to unexpected but energetic *spiro*-tetrahydrotetrazines which were intensively characterized. The crystal structures of the *spiro*-tetrahydrotetrazines give more insight into the reactivity and stability among these poorly described compounds. The energetic properties of the synthesized and insensitive compounds were calculated and it was shown that the nitrimino-derivatives **2** and **5** have good detonation performances, especially **5** which has a detonation velocity of nearly 8000 m s^{-1}. The major drawback is the poor thermal stability of all compounds with decomposition points below 200°C. In summary, all compounds are promising in the search for new energetic oxetane monomers.

4 | EXPERIMENTAL SECTION

General Methods Chemicals and solvents were employed as received (SpiroChemAG, Sigma-Aldrich, TCI). ^{1}H and ^{13}C and spectra were recorded using a Bruker AMX 400 instrument. The chemical shifts quoted in ppm refer to tetramethylsilane (^{1}H, ^{13}C). 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 [36] according to STANAG 4489 [37] modified instruction [38] and a BAM friction tester [36] according to STANAG 4487 [39] modified instruction [40]. The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods' [41].

1-(Oxetan-3-ylidene)-2-(2,4,6-trinitrophenyl)-hydrazine (1): Picrylhydrazine (0.675 g 2.78 mmol, 1.0 eq.) was dissolved in ethanol (10 ml) at 40°C and 4 drops of concentrated HCl were added. Oxetan-3-one (0.200 g, 2.78 mmol, 1.0 eq.) was added dropwise and the solution was heated to 90°C and subsequently cooled to room temperature. The precipitated bright orange solid was filtered and dried to give 1 (0.761 g, 2.57 mmol, 92%). DTA (T_{onset}, 5°C min^{-1}): 170°C (mp.), 177°C (dec.); FT-IR (ATR): ν = 3281 (w), 3039 (m), 1614 (s), 1590 (m), 1539 (m), 1429 (w), 1307 (w), 1177 (w), 1103 (m), 942 (s), 844 (w), 739 (m), 715 (m), 686 (m), 514 (s), 436 (m) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$, 25°C): δ = 10.87 (br s, 1H, NH), 8.90 (s, 2H, 2 × $C_{Harom.}$), 5.45–5.43 (m, 2H, CH_2 $_{oxetane}$), 5.29–5.27 (m, 2H, CH_2 $_{oxetane}$) ppm; ^{13}C NMR{^{1}H} (101 MHz, DMSO-d$_6$, 25°C): δ = 157.1, 137.0, 136.4, 135.8, 125.6, 80.0, 79.8 ppm; EA ($C_9H_7N_5O_7$) calcd.: C 36.37, H 2.37, N 23.57; found: C 36.51 H 2.40 N 23.33; BAM drophammer >40 J (>500 μm); Friction test >360 N (>500 μm).

N-nitro-2-(oxetan-3-ylidene)hydrazine-1-carboximidamide (2): Amino-nitroguanidine (0.496 g, 4.16 mmol, 1.0 eq.) was suspended in ethanol (10 ml) and 5 drops of concentrated HCl were added. Oxetan-3-one (0.300 g, 4.16 mmol, 1.0 eq.) dissolved in ethanol (5 ml) was added and the mixture was refluxed for 3 hours. After cooling to room temperature, the colorless precipitate was collected, washed with a small amount of ethanol and dried to give 2 (0.560 g, 3.24 mmol, 78%). DTA (T_{onset}, 5°C min^{-1}): 191°C (dec.); IR (ATR): $\tilde{\nu}$ = 3253 (w), 3090 (m), 1622 (m), 1573 (s), 1388 (m), 1218 (m), 1138 (m), 1048 (s), 944 (s), 856 (m), 792 (m), 714 (w), 579 (m), 540 (s), 462 (s) 416 (m) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$, 25°C): δ = 11.34 (s, 1H, NH), 8.78 (br s, 1H, NH), 8.41 (br s, 1H, NH), 5.29–5.24 (m, 4H, 2 x CH_2 $_{oxetane}$) ppm; ^{13}C NMR {^{1}H} (101 MHz, DMSO-d$_6$, 25°C): δ = 158.3, 153.4, 80.4, 80.0 ppm; EA ($C_4H_7N_5O_3$) calcd.: C 27.75, H 4.08, N 40.19; found: C 27.90 H 4.01 N 40.22; BAM drophammer >40 J (>500 μm); Friction test >360 N (>500 μm).

Ethyl 2-(oxetan-3-ylidene)hydrazine-1-carboxylate (3): Ethyl hydrazinecarboxylate (0.722 g, 6.94 mmol, 1.0 eq.) and oxetan-3-one (0.500 g, 6.94 mmol, 1.0 eq.)

were mixed in ethanol (20 ml) and refluxed for 3 hours. After cooling to room temperature, the colorless precipitate was collected and dried to give 3 (0.703 g, 4.43 mmol, 67%). DTA (T_{onset}, 5°C min^{-1}): 113°C (mp.), 198°C (dec.); IR (ATR): $\tilde{\nu}$ = 3121 (w), 1693 (s), 1500 (w), 1431 (m), 1384 (m), 1338 (m), 1310 (w), 1270 (w), 1182 (m), 1047 (m), 972 (m), 947 (s), 853 (m), 766 (m), 673 (w), 574 (m) cm^{-1} ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 10.49 (br s, 1H, NH), 5.19–5.15 (m, 4H, 2 × $CH_{2o\text{-}xetane}$), 4.12–4.07 (q, 2H, CH_2), 1.22–1.18 (t, 3H, CH_3) ppm; ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6, 25°C): δ = 153.7, 148.2, 80.4, 80.1, 60.5, 14.5 ppm; EA ($C_6H_{10}N_2O_3$) calcd.: C 45.57, H 6.37, N 17.71; found: C 45.95 H 6.02 N 17.91; BAM drophammer >40 J (>500 µm); Friction test >360 N (>500 µm).

Amino(2-(oxetan-3-ylidene)hydrazineyl) methaniminium chloride (4): Aminoguanidine hydrochloride (0.460 g, 4.16 mmol, 1.0 eq.) was suspended in ethanol (15 ml) and heated to 55°C, then oxetan-3-one (0.300 g, 4.16 mmol, 1.0 eq.) was added and the mixture heated to 85°C for 1.5 h. The solution was cooled and the colorless precipitate was collected and washed with a small amount of ethanol and dried to give 4 (0.589 g, 3.58 mmol, 86%). DTA (T_{onset}, 5°C min^{-1}): 200°C (dec.); IR (ATR): $\tilde{\nu}$ = 3254 (m), 2939 (w), 1669 (s), 1625 (s), 1429 (w), 1265 (w), 1124 (m), 985 (m), 965 (m), 944 (s), 858 (m), 755 (w), 698 (w), 537 (s) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6, 25°C): δ = 11.75 (s, 1H, NH), 7.64 (br s, 4H, 2 x NH_2), 5.29 (s, 4H, 2 × $CH_{2\ oxetane}$) ppm; ^{13}C NMR {^{1}H} (101 MHz, DMSO-d_6, 25°C): δ = 155.6, 153.1, 80.1, 79.7 ppm; EA ($C_4H_9N_4OCl$) calcd.: C 29.19, H 5.51, N 34.03; found: C 28.91 H 5.23 N 33.88; BAM drophammer >40 J (>500 µm); Friction test >360 N (>500 µm).

N-(2-oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-ylidene)nitramide (5): Compound 2 (0.210 g, 1.21 mmol, 1.0 eq.) was dissolved in water (10 ml) and heated to 55°C. Hydrazine hydrate (0.073 g, 1.46 mmol, 1.2 eq.) was added and the mixture stirred until a yellow solution was formed. The solvent was removed, yielding 0.174 g (0.93 mmol, 77%) of 5 as yellow solid. DTA (T_{onset}, 5°C min^{-1}): 151°C (dec.); IR (ATR): $\tilde{\nu}$ = 3203 (m), 3125 (m), 1645 (s), 1615 (s), 1408 (m), 1223 (m), 963 (s), 941 (s), 851 (s), 813 (s), 793 (m), 712 (m), 559 (s). 508 (s), 451 (s) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 9.73 (s, 2H, 2 x NH), 7.08 (s, 2H, 2 × NH), 4.33 (s, 4H, 2 × $CH_{2\ oxetane}$) ppm; ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6, 25°C): δ = 152.4, 77.2, 67.8 ppm; EA ($C_4H_8N_6O_3$) calcd.: C 25.54, H 4.29, N 44.67; found: C 25.77 H 4.53 N 44.28; BAM drophammer >40 J (>500 µm); Friction test >360 N (>500 µm).

2-Oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-one (6): Compound 4 (0.300 g, 1.90 mmol, 1.0 eq.) was mixed with hydrazine hydrate (6 ml) in ethanol/water (5 ml/5 ml) and heated to 80°C for 1.5 hours. The solvent was removed to give the colorless product 6 which was purified by washing with methanol and diethyl ether (0.170 g, 1.18 mmol, 62%). DTA (T_{onset}, 5°C min^{-1}): 192°C (dec.); IR (ATR): $\tilde{\nu}$ = 3254 (m), 3205 (m), 1646 (s), 1614 (m), 1466 (m), 1394 (s), 1288 (w), 1247 (m), 1213 (m), 1148 (m), 1123 (w), 1034 (w), 1013 (w), 947 (s), 912 (m), 840 (s), 708 (s), 665 (s), 642 (s), 523 (s). 477 (s) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 7.78 (s, 2H, 2 × NH), 5.06 (s, 2H, 2 × NH), 4.29 (s, 4H, 2 × $CH_{2\ oxetane}$) ppm; ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6, 25°C): δ = 154.6, 76.9, 67.7 ppm; EA ($C_4H_8N_4O_2$) calcd.: C 33.33, H 5.59, N 38.87; found: C 33.60 H 5.81 N 38.75; BAM drophammer >40 J (>500 µm); Friction test >360 N (>500 µm).

2-Oxa-5,6,8,9-tetraazaspiro[3.5]nonan-7-imine hydrochloride (7): *Procedure I*: Diamino guanidine hydrochloride (1.57 g, 12.48 mmol, 3.0 eq.) was suspended in water/ethanol (10 ml/10 ml) and heated to 70°C. Oxetan-3-one (0.300 g, 4.16 mmol, 1.0 eq.) dissolved in ethanol (2 ml) was added and the mixture heated at 70°C for 2 h. The solvent was removed and the residue dissolved in hot ethanol and filtrated hot. The solvent is removed to give 0.486 g (2.71 mmol, 65%) of 7 as a colorless solid.

Procedure II: Compound 4 (0.200 g, 1.22 mmol, 1.0 eq.) was mixed with hydrazine hydrate (4 ml) in ethanol/water (5 ml/5 ml) and heated to 80°C for 1.5 h. The solvent was removed, the mixture was mixed with methanol and filtered. The residue was collected and dried to give 0.143 g (0,0.796 mmol, 65%) of 7 as colorless solid. DTA (T_{onset}, 5°C min^{-1}): 168°C (dec.); IR (ATR): $\tilde{\nu}$ = 3200 (m), 3123 (m), 1645 (s), 1613 (s), 1419 (m), 1356 (w), 1223 (w), 1048 (m), 963 (s), 941 (s), 852 (s), 812 (s), 793 (s), 711 (m), 670 (m), 555 (s). 507 (s), 444 (s) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ = 9.76 (s, 2H, 2 x NH), 7.09 (s, 2H, 2 × NH), 5.86 (s, 2H, NH_2), 4.33 (s, 4H, 2 × $CH_{2\ oxetane}$) ppm; ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6, 25°C): δ = 152.4, 77.1, 67.8 ppm; EA ($C_4H_{10}N_5OCl$) calcd.: C 26.75, H 5.61, N 38.99; found: C 26.54 H 5.72 N 38.42; BAM drophammer >40 J (>500 µm); Friction test >360 N (>500 µm).

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DATA AVAILABILITY STATEMENT

Research data are not shared.

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