

Supporting information for paper:

Synthesis and properties of 5-nitrotetrazole derivatives as new energetic materials

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Table S1. Comparison of the (corrected) calculated and experimentally determined IR and Raman frequencies with tentative assignment of the vibrational modes for the 5-(5-nitrotetrazole-2-ylmethyl)-tetrazolate anion.

	v (calc., cm ⁻¹) ^a	v (exp., cm ⁻¹) ^b (IR / Raman)	IR intensity ^c (Calc. / Exp.)	Raman activity ^d (Calc. / Exp.)	Vibration Assignment ^e
1	62	- / 89(4)	3.2 / -	0.6 / w	$\tau(\text{NO}_2 + \text{NT-ring})$
2	320	- / 309(6)	1.9 / -	2.3 / w	$\tau(\text{CH}_2)$
3	351	- / 348(8)	0.9 / -	1.4 / w	$\tau(\text{CH}_2)$
4	530	546(7) / 545(6)	2.2 / m	4.2 / m	$\omega(\text{NO}_2)$
5	646	656(3) / n.o.	17.2 / m	2.3 / n.o.	$\gamma(\text{NO}_2 + \text{NT-ring} + \text{Tz-ring})$
6	669	687(2) / 690(4)	6.9 / m	4.4 / w	$\gamma(\text{NO}_2 + \text{NT-ring} + \text{Tz-ring})$
7	696	704(3) / n.o.	2.0 / w	0.3 / n.o.	$\gamma(\text{NT-ring} + \text{Tz-ring})$
8	727	760(2) / n.o.	30.1 / m	0.6 / n.o.	$\gamma(\text{N6-N7-N8})$
9	765	n.o. / 771(5)	1.6 / n.o.	2.5 / m	$\gamma(\text{NO}_2 + \text{NT-ring})$
10	825	822(4) / 821(3)	92.5 / m	1.8 / m	$\delta(\text{NO}_2)$
11	1020	1035(6) / n.o.	3.9 / w	4.3 / n.o.	$\delta(\text{C3-N9-N8})_{\text{Tz-ring}}$
12	1048	1069(1) / 1032(2)	4.6 / w	14.1 / s	$\delta(\text{N4-N5-C1})_{\text{NT-ring}}$
13	1086	1097(7) / 1104(3)	2.1 / w	41.2 / s	$\nu_{as}(\text{N-N})_{\text{NT-ring}} + \omega(\text{CH}_2)$
14	1163	1137(7) / 1144(2)	9.6 / w	3.6 / m	$\nu(\text{N7-N8})_{\text{Tz-ring}} + \gamma_{sym}(\text{CH}_2)$
15	1220	1216(3) / 1220(1)	10.7 / w	49.1 / m	$\nu(\text{N4-N5}) + \omega(\text{CH}_2)$
16	1279	1277(1) / 1288(5)	28.6 / m	8.5 / m	$\gamma(\text{CH}_2)$
17	1313	1312(1) / n.o.	3.1 / w	26.9 / n.o.	$\nu(\text{N2-N3} + \text{C1-N2})$
18	1316	1323(3) / 1320(2)	106.0 / s	7.0 / s	$\nu_{sym}(\text{NO}_2) + \nu(\text{C1-N5})$
19	1374	1344(3) / 1348(8)	39.7 / m	33.9 / s	$\delta(\text{CH}_2)$
20	1400	1418(1) / n.o.	24.9 / s	2.1 / n.o.	$\nu(\text{N-C3})_{\text{Tz-ring}}$
21	1415	1435(3) / 1420(1)	1.2 / m	26.7 / s	$\nu(\text{C2-C3})_{\text{Tz-ring}}$
22	1451	1476(5) / 1463(3)	22.7 / s	58.5 / s	$\nu(\text{C-N} + \text{N-N})_{\text{NT-ring}}$
23	1590	1579(8) / 1559(3)	220.1 / m	7.1 / w	$\nu_{as}(\text{NO}_2)$
24	2961	n.o. / 2971(3)	20.0 / n.o.	132.0 / w	$\nu_{sym}(\text{CH}_2)$
25	3026	3021(6) / 3025(5)	2.6 / m	60.9 / w	$\nu_{as}(\text{CH}_2)$

^a Calculated frequencies corrected according to ref. 28; ^b Experimentally observed values for the IR and Raman frequencies calculated as an average for compounds **6a**, **6b**, **7** and **8** with standard deviations in curved brackets (n.o. = not observed); ^c Calculated and experimentally observed IR intensities; ^d Calculated and experimentally observed Raman activities; ^e Vibrational mode assignment: ν = stretching, δ = in-plane bending, γ = out-of-plane bending, ω = in plane rocking, τ = torsion, ν_{as} = asymmetric and ν_{sym} = symmetric.

Table S2. Selected bond lengths (\AA) and angles ($^\circ$) for the nitrogen-rich 5-nitrotetrazole derivatives.

Parameter	4	5a	6a (A)	6a (B)	7 (A)	7 (B)
N1–O1	1.225(1)	1.217(3)	1.223(2)	1.217(2)	1.225(3)	1.228(3)
N1–O2	1.220(1)	1.228(2)	1.222(2)	1.227(2)	1.220(3)	1.221(3)
N1–C1	1.448(1)	1.444(3)	1.444(2)	1.447(2)	1.455(3)	1.450(3)
N2–C1	1.319(1)	1.316(3)	1.315(2)	1.311(2)	1.315(3)	1.321(3)
N2–N3	1.325(1)	1.326(2)	1.320(2)	1.321(2)	1.328(3)	1.322(3)
N3–N4	1.332(1)	1.331(3)	1.324(2)	1.329(2)	1.330(3)	1.328(3)
N4–N5	1.317(1)	1.317(3)	1.323(2)	1.317(2)	1.323(3)	1.324(3)
N5–C1	1.336(1)	1.336(3)	1.330(2)	1.328(2)	1.328(3)	1.329(4)
N3–C2	1.462(1)	1.458(3)	1.467(2)	1.478(2)	1.486(4)	1.468(4)
C2–C3	1.471(2)	1.491(3)	1.484(2)	1.486(2)	1.475(4)	1.493(4)
C3–N6	1.138(2)	1.318(3)	1.331(2)	1.328(2)	1.324(3)	1.330(3)
N6–N7		1.362(3)	1.352(2)	1.339(2)	1.347(3)	1.362(3)
N8–N7		1.299(2)	1.308(2)	1.313(2)	1.323(3)	1.308(3)
N9–N8		1.345(3)	1.345(2)	1.342(2)	1.342(3)	1.359(3)
N9–C3		1.328(3)	1.324(2)	1.325(2)	1.326(3)	1.323(3)
O1–N1–O2	125.9(1)	125.7(2)	126.0(1)	125.4(1)	125.7(3)	125.2(3)
O1–N1–C1	116.7(1)	117.7(2)	117.0(1)	118.2(1)	117.3(3)	117.2(3)
O2–N1–C1	117.4(1)	116.6(2)	116.9(1)	116.3(1)	117.0(3)	117.7(3)
N2–C1–N1	122.2(1)	122.0(2)	121.0(1)	122.0(1)	122.2(3)	122.1(3)
C1–N2–N3	99.4(1)	99.7(2)	100.1(1)	99.7(1)	99.7(2)	99.7(2)
N2–N3–N4	114.7(1)	114.3(2)	114.1(1)	114.1(1)	114.2(2)	114.5(2)
N5–N4–N3	105.8(1)	106.0(2)	106.1(1)	106.1(1)	105.9(2)	105.9(2)
N4–N5–C1	104.6(1)	104.6(2)	104.3(1)	104.2(1)	104.5(2)	104.5(2)
N5–C1–N1	122.4(1)	122.6(2)	123.7(1)	122.2(1)	122.1(3)	122.5(3)
N2–N3–C2	123.1(1)	123.5(2)	123.1(1)	122.4(1)	121.8(2)	123.4(3)
N4–N3–C2	122.2(1)	121.8(2)	122.5(1)	123.5(1)	123.7(2)	122.1(3)
N3–C2–C3	110.0(1)	112.3(2)	112.2(1)	110.3(1)	111.9(3)	109.7(2)
N2–C1–N5	115.4(1)	115.3(2)	115.2(1)	115.8(1)	115.7(2)	115.4(2)
N6–C3–C2	177.8(1)	126.2(2)	124.3(1)	122.8(1)	123.8(3)	124.0(3)
C3–N6–N7		106.0(2)	104.4(1)	104.6(1)	104.5(2)	104.6(2)
N6–N7–N8		109.9(2)	109.4(1)	109.1(1)	109.3(2)	109.3(2)
N7–N8–N9		106.8(2)	109.2(1)	109.7(1)	108.9(2)	109.0(2)
C3–N9–N8		108.5(2)	105.0(1)	104.1(1)	105.0(2)	105.1(2)
N6–C3–N9		108.8(2)	111.9(1)	112.4(1)	112.4(2)	111.9(2)
N9–C3–C2		124.9(2)	123.7(1)	124.7(1)	123.7(3)	124.1(2)

Table S3. Hydrogen-bonding geometry in nitrogen-rich 5-nitrotetrazole derivatives.

D–H \cdots A	D–H (Å)	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (°)
4				
C2–H1 \cdots N6 ⁱ	0.98(1)	2.73(1)	3.314(2)	118(1)
5a				
O3–H5 \cdots N8 ⁱ	0.85(3)	2.26(3)	3.008(3)	147(3)
O3–H4 \cdots O3 ⁱⁱ	0.88(4)	1.93(4)	2.796(3)	170(3)
N9–H3 \cdots N6 ⁱⁱⁱ	0.89(3)	1.92(3)	2.771(3)	159(2)
C2–H3 \cdots O3 ⁱⁱⁱ	0.94(2)	2.69(2)	3.118(3)	109(2)
6a				
N21–H5 \cdots N17	0.95(2)	1.97(2)	2.911(2)	170(2)
N21–H5 \cdots N16	0.95(2)	2.52(2)	3.302(2)	139(1)
O5–H15 \cdots N7	0.91(2)	1.99(2)	2.882(2)	168(2)
N19–H12 \cdots O5	0.95(3)	1.91(3)	2.847(2)	167(2)
O6–H9 \cdots N15	0.91(2)	1.85(2)	2.7551(2)	173(2)
N21–H8 \cdots N18 ⁱ	0.96(2)	2.14(2)	2.987(2)	146(2)
N21–H8 \cdots O6 ⁱⁱ	0.96(2)	2.60(2)	3.151(2)	117(1)
N21–H6 \cdots N16 ⁱⁱ	0.91(2)	2.15(2)	3.016(2)	160(2)
N21–H7 \cdots O6 ⁱⁱⁱ	0.99(2)	1.84(2)	2.807(2)	167(2)
N19–H14 \cdots N2 ⁱⁱⁱ	0.87(2)	2.18(2)	3.020(2)	163(2)
N19–H14 \cdots O1 ⁱⁱⁱ	0.87(2)	2.62(2)	3.130(2)	119(2)
N19–H11 \cdots O5 ^{iv}	1.03(3)	1.86(3)	2.877(2)	167(2)
N19–H13 \cdots O4 ^v	0.89(3)	2.14(3)	2.946(2)	150(2)
O5–H16 \cdots N6 ^{vi}	0.90(2)	1.99(2)	2.884(2)	174(2)
O6–H10 \cdots N9 ^{vii}	0.88(2)	1.96(2)	2.831(2)	167(2)
8				
N22–H10 \cdots N9	0.93(3)	2.12(3)	3.023(4)	166(2)
N19–H5 \cdots N7 ⁱ	0.86(3)	2.24(3)	3.053(4)	158(3)
N21–H9 \cdots N7 ⁱ	0.84(2)	2.39(2)	3.166(4)	152(2)
N21–H9 \cdots O4 ⁱⁱ	0.84(2)	2.48(2)	3.030(3)	123(2)
N22–H11 \cdots N6 ⁱⁱ	0.88(3)	2.25(3)	3.046(4)	151(3)
N19–H6 \cdots N16 ⁱⁱⁱ	0.90(3)	2.07(3)	2.962(4)	171(2)
N20–H7 \cdots N15 ⁱⁱⁱ	0.88(3)	2.17(4)	3.007(4)	160(3)
N24–H15 \cdots N18 ^{iv}	0.91(4)	1.99(4)	2.882(4)	164(3)
N25–H16 \cdots N17 ^{iv}	0.88(3)	2.20(3)	3.051(4)	163(2)
N23–H13 \cdots N8 ^v	0.85(3)	2.29(3)	3.039(4)	147(2)
N24–H14 \cdots N8 ^v	0.87(3)	2.37(3)	3.046(4)	135(3)
N23–H12 \cdots N7 ^{vii}	0.87(4)	2.63(4)	3.099(4)	115(3)
N20–H8 \cdots N2 ^{viii}	0.84(3)	2.47(3)	3.238(4)	152(3)

Symmetry codes for **4**: (i) 0.5+x, -0.5-y, -z. **5a**: (i) -1+x, 1+y, z; (ii) -x, -0.5+y, -z; (iii) x, -1+y, z. **6a**: (i) 1-x, 2-y, -z; (ii) -x, 2-y, -z; (iii) x, 1+y, z; (iv) 1-x, 2-y, 1-z; (v) x, 1+y, 1+z; (vi) 2-x, 1-y, 1-z; (vii) 1-x, 1-y, -z; **8**: (i) -0.5+x, 0.5-y, -0.5+z; (ii) 0.5+x, 0.5-y, -0.5+z; (iii) -x, 1-y, 3-z; (iv) -1+x, y, z; (v) -1.5+x, 0.5-y, 0.5+z; (vii) -0.5+x, 0.5-y, 0.5+z; (viii) 1+x, y, z.

Combustion Equations (Section: Physico-chemical properties)

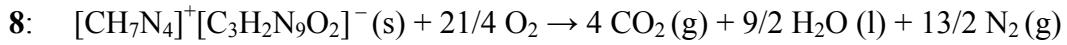
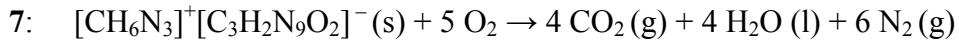
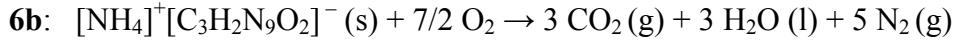
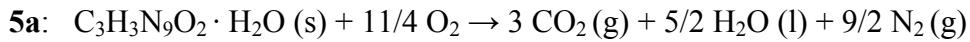
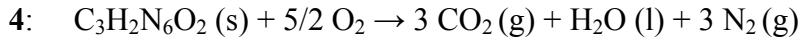
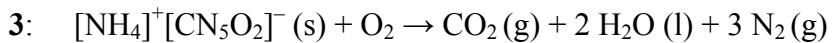


Table S4. Thermodynamic and explosive properties of ammonium nitrate (AN) and formulations of nitrogen-rich 5-nitrotetrazole derivatives with AN.

	AN	AN + 3 ^a	AN + 4 ^b	AN + 5a ^c	AN + 5b ^d	AN + 6a ^e	AN + 6b ^f	AN + 7 ^g	AN + 8 ^h
$\rho (\text{g cm}^{-3})^i$	1.722	1.684	1.729	1.747	1.747	1.685	1.688	1.703	1.701
$M (\text{g mol}^{-1})$	80.04	103.46	100.77	124.62	116.34	124.15	117.59	122.28	125.91
$\Omega (\%)^j$	20.0	0.1	-0.1	-0.1	0.0	0.2	-0.2	0.2	0.3
$\Delta U^\circ_f / \text{kJ kg}^{-1} k$	-4424	-2190	-2261	-2475	-2161	-2948	-2655	-2805	-2791
$\Delta H^\circ_f / \text{kJ kg}^{-1} l$	-4548	-2318	-2383	-2602	-2284	-3080	-2785	-2936	-2923
$T_{\text{ex}} / \text{K}^m$	1705	3183	3432	3207	3312	3023	3150	3111	3103
$V_0 / \text{L kg}^{-1} n$	979	921	890	907	897	934	927	933	938
P / GPa^o	15.1	25.4	28.1	27.2	27.5	24.3	25.6	25.9	26.0
$D / \text{m s}^{-1} p$	6602	8181	8440	8322	8356	8011	8196	8226	8246

^a 55% AN + 45% **3**; ^b 72% AN + 28% **4**; ^c 67% AN + 33% **5a**; ^d 69% AN + 31% **5b**; ^e 71% AN + 29% **6a**; ^f 72% AN + 28% **6b**; ^g 76% AN + 24% **7**; ^h 76% AN + 24% **8**; ⁱ Density from EXPLO5; ^j Oxygen balance

according to ref. 63; ^k Calculated energy of formation; ^l Calculated enthalpy of formation; ^m Temperature of the explosion gases; ⁿ Volume of the explosion gases; ^o Detonation pressure; ^p Detonation velocity.

Table S5. Thermodynamic and explosive properties of ammonium dinitramide (ADN) and formulations of nitrogen-rich 5-nitrotetrazole derivatives with ADN.

	ADN	ADN + 3 ^a	ADN + 4 ^b	ADN + 5a ^c	ADN + 5b ^d	ADN + 6a ^e	ADN + 6b ^f	ADN + 7 ^g	ADN + 8 ^h
ρ (g cm ⁻³) ⁱ	1.808	1.719	1.788	1.803	1.806	1.733	1.740	1.760	1.758
M (g mol ⁻¹)	124.06	128.23	133.97	159.57	151.09	161.87	153.79	162.36	166.72
Ω (%) ^j	25.8	-0.2	-0.1	-0.1	-0.3	-0.1	0.0	0.2	0.3
ΔU_f° / kJ kg ⁻¹ ^k	-1087	-241	-360	-85	380	-474	-104	-99	-82
ΔH_f° / kJ kg ⁻¹ ^l	-1207	-357	-242	-210	272	-604	-219	-229	-213
T_{ex} / K ^m	2596	3799	4343	4038	4252	3864	4000	4029	3982
V_0 / L kg ⁻¹ ⁿ	903	877	826	850	837	877	867	872	877
P / GPa ^o	22.7	28.6	33.5	33.4	34.9	30.1	30.8	32.5	31.7
D / m s ⁻¹ ^p	7650	8542	8943	8960	9095	8675	8752	8930	8825

^a 48% ADN + 52% **3**; ^b 67% ADN + 33% **4**; ^c 61% ADN + 39% **5a**; ^d 63% ADN + 37% **5b**; ^e 65% ADN + 35% **6a**; ^f 67% ADN + 33% **6b**; ^g 71% ADN + 29% **7**; ^h 71% ADN + 29% **8**; ⁱ Density from EXPLO5; ^j Oxygen balance according to ref. 63; ^k Calculated energy of formation; ^l Calculated enthalpy of formation; ^m Temperature of the explosion gases; ⁿ Volume of the explosion gases; ^o Detonation pressure; ^p Detonation velocity.

Experimental part

General procedure. All chemicals and solvents (analytical grade) were used as supplied by Sigma-Aldrich Inc. ¹H, ¹³C, ¹⁴N and ¹⁵N NMR spectra were recorded in a JEOL Eclipse 400 instrument at room temperature and using tetramethylsilane (¹H, ¹³C) and nitromethane (¹⁴N, ¹⁵N) as external standards for the chemical shifts. Differential scanning calorimetry (DSC) measurements were conducted using a Linseis DSC PT-10 instrument,⁷¹ which had previously been calibrated with standard pure indium and zinc. Closed aluminium sample pans with a 1 µm hole in the top for gas release were used for the measurements. A nitrogen flow of 20 mL min⁻¹ was continuously purged in the oven compartment containing the sample and an empty reference aluminium pan. A JEOL MStation JMS 700 machine⁷² was used for the mass spectrometry measurements and a Netsch Simultaneous Thermal Analyzer STA 429 was used to perform the elemental analyses. For the IR spectra KBr pellets were measured using a Perkin-Elmer Spectrum One FT-IR instrument⁷³ and Raman measurements were conducted with a

Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm).

Calorimetric measurements. Samples of ~200 mg were carefully mixed with ~800 mg analytical grade benzoic acid and pressed into pellets, which were burned in a 3.05 MPa atmosphere of pure oxygen in a Parr 1356 bomb calorimeter equipped with a Parr 207A oxygen bomb for the combustion of highly energetic materials.⁷⁴ The instrument had been previously calibrated with certified benzoic acid. Five single measurements were run for each compound and the values were averaged.

- 71 http://www.linseis.net/html_en/thermal/dsc/dsc_pt10.php.
- 72 <http://www.jeol.com/tabid/96/Default.aspx>;
<http://www.jeolusa.com/DesktopModules/Bring2mind/DMX/Download.aspx?EntryId=331&PortalId=2&DownloadMethod=attachment>; <http://www.jeoleuro.com/instr/mass/mass.htm>.
- 73 <http://www.perkinelmer.com>.
- 74 <http://www.parrinst.com>.