Supplementary material (ESI) for Journal of Materials Chemistry

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.

	ν (calc., cm^{-1}) [a]	ν (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	$\tau(NO_2 + NT\text{-ring})$
2	320	- / 309(6)	1.9 / -	2.3 / w	$\tau(CH_2)$
3	351	- / 348(8)	0.9 / -	1.4 / w	$\tau(CH_2)$
4	530	546(7) / 545(6)	2.2 / m	4.2 / m	$\omega(NO_2)$
5	646	656(3) / n.o.	17.2 / m	2.3 / n.o.	$\gamma(NO_2 + NT\text{-ring} + Tz\text{-ring})$
6	669	687(2) / 690(4)	6.9 / m	4.4 / w	$\gamma(NO_2 + NT\text{-ring} + Tz\text{-ring})$
7	696	704(3) / n.o.	2.0 / w	0.3 / n.o.	$\gamma(NT\text{-ring} + Tz\text{-ring})$
8	727	760(2) / n.o.	30.1 / m	0.6 / n.o.	γ(N6–N7–N8)
9	765	n.o. / 771(5)	1.6 / n.o.	2.5 / m	$\gamma(NO_2 + NT\text{-ring})$
10	825	822(4) / 821(3)	92.5 / m	1.8 / m	$\delta(NO_2)$
11	1020	1035(6) / n.o.	3.9 / w	4.3 / n.o.	δ(C3–N9–N8)$_{Tz\text{-ring}}$
12	1048	1069(1) / 1032(2)	4.6 / w	14.1 / s	δ(N4–N5–C1)$_{NT\text{-ring}}$
13	1086	1097(7) / 1104(3)	2.1 / w	41.2 / s	ν_{as}(N–N)$_{NT\text{-ring}}$ + $\omega(CH_2)$
14	1163	1137(7) / 1144(2)	9.6 / w	3.6 / m	ν(N7–N8)$_{Tz\text{-ring}}$ + $\gamma_{sym}(CH_2)$
15	1220	1216(3) / 1220(1)	10.7 / w	49.1 / m	ν(N4–N5) + $\omega(CH_2)$
16	1279	1277(1) / 1288(5)	28.6 / m	8.5 / m	$\gamma(CH_2)$
17	1313	1312(1) / n.o.	3.1 / w	26.9 / n.o.	ν(N2–N3 + C1–N2)
18	1316	1323(3) / 1320(2)	106.0 / s	7.0 / s	$\nu_{sym}(NO_2)$ + ν(C1–N5)
19	1374	1344(3) / 1348(8)	39.7 / m	33.9 / s	$\delta(CH_2)$
20	1400	1418(1) / n.o.	24.9 / s	2.1 / n.o.	ν(N–C3)$_{Tz\text{-ring}}$
21	1415	1435(3) / 1420(1)	1.2 / m	26.7 / s	ν(C2–C3)$_{Tz\text{-ring}}$
22	1451	1476(5) / 1463(3)	22.7 / s	58.5 / s	ν(C–N + N–N)$_{NT\text{-ring}}$
23	1590	1579(8) / 1559(3)	220.1 / m	7.1 / w	$\nu_{as}(NO_2)$
24	2961	n.o. / 2971(3)	20.0 / n.o.	132.0 / w	$\nu_{sym}(CH_2)$
25	3026	3021(6) / 3025(5)	2.6 / m	60.9 / w	$\nu_{as}(CH_2)$

[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, as = asymmetric and sym = symmetric.

Table S2. Selected bond lengths (Å) and angles (°) 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•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (º)
		4		
C2–H1•••N6^{i}	0.98(1)	2.73(1)	3.314(2)	118(1)
		5a		
O3–H5•••N8^{i}	0.85(3)	2.26(3)	3.008(3)	147(3)
O3–H4•••O3^{ii}	0.88(4)	1.93(4)	2.796(3)	170(3)
N9–H3•••N6^{iii}	0.89(3)	1.92(3)	2.771(3)	159(2)
C2–H3•••O3^{iii}	0.94(2)	2.69(2)	3.118(3)	109(2)
		6a		
N21–H5•••N17	0.95(2)	1.97(2)	2.911(2)	170(2)
N21–H5•••N16	0.95(2)	2.52(2)	3.302(2)	139(1)
O5–H15•••N7	0.91(2)	1.99(2)	2.882(2)	168(2)
N19–H12•••O5	0.95(3)	1.91(3)	2.847(2)	167(2)
O6–H9•••N15	0.91(2)	1.85(2)	2.7551(2)	173(2)
N21–H8•••N18^{i}	0.96(2)	2.14(2)	2.987(2)	146(2)
N21–H8•••O6^{ii}	0.96(2)	2.60(2)	3.151(2)	117(1)
N21–H6•••N16^{ii}	0.91(2)	2.15(2)	3.016(2)	160(2)
N21–H7•••O6^{iii}	0.99(2)	1.84(2)	2.807(2)	167(2)
N19–H14•••N2^{iii}	0.87(2)	2.18(2)	3.020(2)	163(2)
N19–H14•••O1^{iii}	0.87(2)	2.62(2)	3.130(2)	119(2)
N19–H11•••O5^{iv}	1.03(3)	1.86(3)	2.877(2)	167(2)
N19–H13•••O4^{v}	0.89(3)	2.14(3)	2.946(2)	150(2)
O5–H16•••N6^{vi}	0.90(2)	1.99(2)	2.884(2)	174(2)
O6–H10•••N9^{vii}	0.88(2)	1.96(2)	2.831(2)	167(2)
		8		
N22–H10•••N9	0.93(3)	2.12(3)	3.023(4)	166(2)
N19–H5•••N7^{i}	0.86(3)	2.24(3)	3.053(4)	158(3)
N21–H9•••N7^{i}	0.84(2)	2.39(2)	3.166(4)	152(2)
N21–H9•••O4^{ii}	0.84(2)	2.48(2)	3.030(3)	123(2)
N22–H11•••N6^{ii}	0.88(3)	2.25(3)	3.046(4)	151(3)
N19–H6•••N16^{iii}	0.90(3)	2.07(3)	2.962(4)	171(2)
N20–H7•••N15^{iii}	0.88(3)	2.17(4)	3.007(4)	160(3)
N24–H15•••N18^{iv}	0.91(4)	1.99(4)	2.882(4)	164(3)
N25–H16•••N17^{iv}	0.88(3)	2.20(3)	3.051(4)	163(2)
N23–H13•••N8^{v}	0.85(3)	2.29(3)	3.039(4)	147(2)
N24–H14•••N8^{v}	0.87(3)	2.37(3)	3.046(4)	135(3)
N23–H12•••N7^{vii}	0.87(4)	2.63(4)	3.099(4)	115(3)
N20–H8•••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)

3: $[NH_4]^+[CN_5O_2]^-$ (s) + O_2 → CO_2 (g) + 2 H_2O (l) + 3 N_2 (g)

4: $C_3H_2N_6O_2$ (s) + 5/2 O_2 → 3 CO_2 (g) + H_2O (l) + 3 N_2 (g)

5a: $C_3H_3N_9O_2 \cdot H_2O$ (s) + 11/4 O_2 → 3 CO_2 (g) + 5/2 H_2O (l) + 9/2 N_2 (g)

5b: $C_3H_3N_9O_2$ (s) + 11/4 O_2 → 3 CO_2 (g) + 3/2 H_2O (l) + 9/2 N_2 (g)

6a: $[NH_4]^+[C_3H_2N_9O_2]^- \cdot H_2O$ (s) + 7/2 O_2 → 3 CO_2 (g) + 4 H_2O (l) + 5 N_2 (g)

6b: $[NH_4]^+[C_3H_2N_9O_2]^-$ (s) + 7/2 O_2 → 3 CO_2 (g) + 3 H_2O (l) + 5 N_2 (g)

7: $[CH_6N_3]^+[C_3H_2N_9O_2]^-$ (s) + 5 O_2 → 4 CO_2 (g) + 4 H_2O (l) + 6 N_2 (g)

8: $[CH_7N_4]^+[C_3H_2N_9O_2]^-$ (s) + 21/4 O_2 → 4 CO_2 (g) + 9/2 H_2O (l) + 13/2 N_2 (g)

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]
ρ (g cm^{-3}) [i]	1.722	1.684	1.729	1.747	1.747	1.685	1.688	1.703	1.701
M (g mol^{-1})	80.04	103.46	100.77	124.62	116.34	124.15	117.59	122.28	125.91
Ω (%) [j]	20.0	0.1	–0.1	–0.1	0.0	0.2	–0.2	0.2	0.3
$\Delta U°_f$ / kJ kg^{-1} [k]	–4424	–2190	–2261	–2475	–2161	–2948	–2655	–2805	–2791
$\Delta H°_f$ / kJ kg^{-1} [l]	–4548	–2318	–2383	–2602	–2284	–3080	–2785	–2936	–2923
T_{ex} / K [m]	1705	3183	3432	3207	3312	3023	3150	3111	3103
V_0 / 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 / 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
$\Delta U°_f$ / kJ kg^{-1} [k]	–1087	–241	–360	–85	380	–474	–104	–99	–82
$\Delta H°_f$ / 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. ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded in a JEOL Eclipse 400 instrument at room temperature and using tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N, ^{15}N) 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 machine[72] was used for the mass spectrometry measurements and a Netsch Simultanous 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 instrument[73] 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.