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Pushing the Limits of Energetic Materials - The synthesis and characterization of dihydroxylammonium 5,5´-bistetrazole-1,1´-diolate

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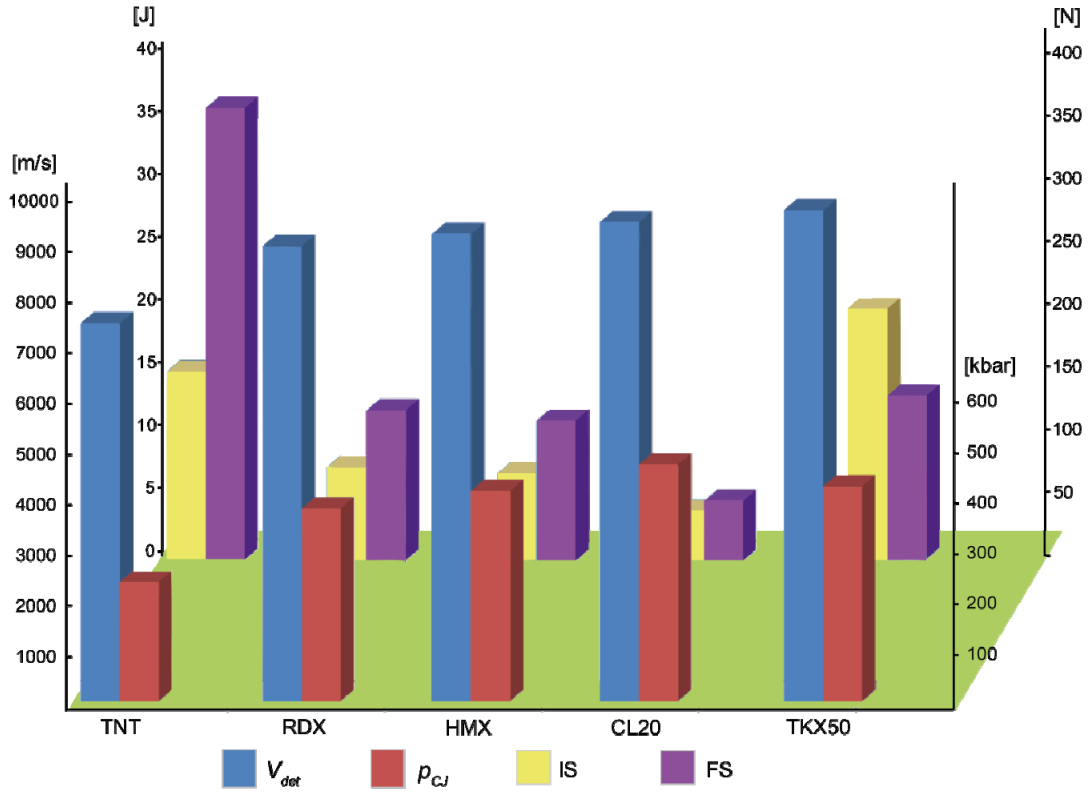

Graphical comparison of the energetic properties of TKX-50 with commonly used explosives (TNT, RDX, HMX, CL-20)

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1. Materials and Methods

Caution! 5,5′-Bistetrazole-1,1′-diol and its salts are energetic materials with increased sensitivities towards shock and friction. Therefore, proper security precautions (safety glass, face shield, earthened equipment and shoes, Kevlar gloves and ear plugs) have to be applied while synthesizing and handling the described compounds. Specifically, compounds described having the azido group are extremely sensitive and have to be handled very carefully.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros) without further purification unless otherwise stated.

1.1. NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to tetramethylsilane (^{1}H, ^{13}C).

1.2. Vibrational spectroscopy

Infrared spectra were measured using a Perkin Elmer Spectrum One FT-IR spectrometer as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector.

1.3. Mass spectrometry and elemental analysis

Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 using either DEI or FAB technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

1.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures of **2**–**9** (about 1.5 mg of each energetic material) were performed in covered Al-containers containing a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL per minute on a Linseis PT 10 DSC[1] calibrated with standard pure indium and zinc at a heating rate of 5°C min^{-1}.

1.5. Sensitivity testing

The impact sensitivity tests were carried out according to STANAG 4489[2] modified instruction[3] using a BAM (Bundesanstalt für Materialforschung) drophammer.[4] The friction sensitivity tests were carried out according to STANAG 4487[5] modified instruction[6] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[7] Additionally all compounds were tested upon the sensitivity towards electrical discharge using the Electric Spark Tester ESD 2010 EN.[8]

2. Experimental work

2.1. Synthesis of TKX-50 via oxidation of 5,5´-bistetrazole with potassium peroxymonosulfate

5,5´-Bistetrazole (3.00 g, 21.7 mmol) was dissolved in 200 mL of water. Oxone (80.0 g, 109 mmol, 5eq.) was added to the clear solution and the resulting solution was buffered with trisodium phosphate to pH 7. The mixture turned to a pink color, as soon as the pH exceeds a certain value. The mixture was stirred at room temperature for 5 h, was then acidified with conc. sulfuric acid and extracted into diethyl ether. Evaporation of the solvent gave the raw product as a slightly yellow solid, which can be recrystallized from methanol to remove remaining sulfates or phosphates. The reaction yielded a mixture of the 1,1´-isomer, the 2,2´-isomer and the 1,2´-isomer in overall 71% yield (2.60 g, 15.3 mmol) with the 2,2´-isomer being the main product. The isomer mixture (1.70 g, 10 mmol) was

dissolved in 20 mL of hot water. An aqueous solution of hydroxylamine (50% w/w, 1.32 g, 20 mmol) was added and a colorless precipitate formed instantly. The precipitate was redissolved by warming the mixture and the product, which is the dihydroxylammonium salt of the 1,1´-isomer started to precipitate again. It was filtered off and recrystallized from water to remove the salt of the remaining 2,2´-isomer, which showed better solubility in water. Due to the predominant formation of the 2,2´-isomer via the oxidation with oxone, the dihydroxylammonium salt of the 1,1´-isomer could only be obtained in minor yields (0.31 g, 1.3 mmol, 13%).

2.2. Synthesis of TKX-50 via isolation of diazidoglyoxime

Glyoxime

27.5 g (0.69 mol) of NaOH was dissolved in 75 mL of water and the solution was cooled to 0°C in a salt-ice bath. Hydroxylammonium chloride (69.5 g, 1.00 mol) was added while stirring. To the obtained solution glyoxal (72.5 g, 0.50 mol, 40% w/w in H_2O) was added, while the temperature is kept below 10 °C. After complete addition of the glyoxal the solution was further chilled in the salt-ice bath until glyoxime precipitated. The solid was removed by suction filtration and washed with only little ice-water to remove remaining sodium chloride.

^{1}H NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 7.73, 11.61; ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 145.9; EA (found, calc. for $C_2H_4N_2O_2$, MW = 88.07): C (27.07, 27.28), H (4.69, 4.58), N (31.45, 31.81) %.

Dichloroglyoxime

17.6 g (200 mmol) of glyoxime was suspended in 200 mL of ethanol. Chlorine was bubbled through the suspension at -20 °C until the green suspension turned into a yellowish solution. The solution was allowed to warm up slowly to room temperature meanwhile releasing dissolved chlorine. Then the solvent was removed under vacuum and the remaining solid was resuspended in 50 mL of chloroform, stirred for 15 min at room temperature and filtered yielding 26.6 g (85 %) of the colorless product.

^{1}H NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 13.10; ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 131.2; EA (found, calc. for $C_2H_2Cl_2N_2O_2$, MW = 156.96): C (15.65, 15.30), H (1.25, 1.28), N (17.49, 17.85) %.

Diazidoglyoxime

784 mg (5 mmol) of dichloroglyoxime was dissolved in 10 mL of dimethyl formamide. At 0 °C 841 mg (12.93 mmol) sodium azide was added. The suspension was stirred for 20 min at 0 °C and 100 mL of water was added. The precipitate was filtered, washed with 20 mL of water and air dried yielding 713 mg (84%) of the colorless product.

DSC (5 °C min^{-1}): 170 °C (dec.); IR (atr, cm^{-1}): $\tilde{\nu}$ = 3209 (w), 2170 (w), 2123 (w), 1622 (w), 1400 (w), 1361 (w), 1286 (m), 1013 (vs), 930 (m), 920 (s), 855 (s), 731 (s); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2166 (8), 2129 (5), 2091 (3), 1621 (100), 1457 (14), 1390 (12), 1216 (19), 1034 (3), 882 (20), 672 (3), 442 (6); ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 12.08; ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C, ppm) δ: 136.5; EA (found, calc. for $C_2H_2N_8O_2$, MW = 170.09): C (14.38, 14.12), H (1.46, 1.19), N (66.01, 65.88) %; BAM drophammer: 1.5 J; friction tester: <5 N; ESD: 7 mJ.

5,5´-Bistetrazole-1,1´-diol dihydrate

850 mg (5 mmol) of diazidoglyoxime was suspended in 40 mL of diethyl ether. Gaseous HCl was bubbled through the reaction mixture at 0 to 5 °C while stirring for 2 hours and then the flask was sealed and stirred at room temperature overnight. The solution was allowed to stand for crystallization yielding 760 mg (73 %) of 5,5´-bistetrazole-1,1´-diol dihydrate as pale yellow crystals.

DSC (5 °C min^{-1}): 214 °C (dec.); IR (atr, cm^{-1}): $\tilde{\nu}$ = 3229 (m), 1665 (m), 1411 (w), 1375 (w), 1302 (w), 1208 (w), 1144 (m), 995 (s), 714 (w), 662 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1608 (100), 1270 (26), 1157 (46), 1133 (38), 1019 (22), 766 (31), 738 (13), 693 (4), 597 (6), 402 (29); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ: 6.80; ^{13}C{^{1}H} NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ: 135.8; EA (found, calc. for $C_2H_6N_8O_4$, MW = 206.12): C (12.01, 11.65), H (2.81, 2.93), N (54.04, 54.36) %; BAM drophammer: >40 J; friction tester: 216 N; ESD: 0.5 J.

Dihydroxylammonium 5,5´-bistetrazole-1,1´-diolate (TKX-50)

5,5´-Bistetrazole-1,1´-diol dihydrate (2.06 g, 10 mmol) was dissolved in 50 mL of warm water. Hydroxylamine (1.32 g, 20 mmol, 50% w/w in H_2O) was added while stirring. Cooling down the solution to room temperature forced the dihydroxylammonium salt to crystallize. It was isolated by suction filtration and air dried. (Yield: 82%).

DSC (5 °C min^{-1}, °C): 221°C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3425 (m), 3219 (s), 3081 (s), 3050 (s), 2936 (s), 2689 (s), 2513 (m), 1599 (m), 1577 (m), 1527 (s), 1426 (s), 1413 (s), 1389 (m), 1352 (m), 1338 (m), 1316 (w), 1236 (vs), 1174 (m), 1145 (w), 1095 (w), 1046 (w), 1029 (w), 1011 (m), m997 (m), 800 (m), 723 (m), 676 (w), 612 (w), 579 (w), 539 (w), 498 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1616 (100), 1469 (3), 1278 (2), 1239 (25), 1173 (2), 1143 (6), 1116 (10), 1014 (7), 1004 (12), 763 (4), 612 (3), 409 (4), 335 (2), 257 (2), 199 (2); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ: 9.66 (s, 8H, NH_3OH); ^{13}C{^{1}H} NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ: 135.5 ((CN$_4$)$_2$); m/z (FAB^+): 34.0 [NH_3OH^+]; m/z (FAB^-): 169.1 [$C_2HN_8O_2^-$]; EA (found, calc. For $C_2H_8N_{10}O_4$, MW = 236.15): C (10.50, 10.17), H (3,63, 3.41), N (59.31, 59.31) %; BAM drophammer: 20 J; friction tester: 120 N; ESD: 0.11 J (at grain size <100 µm).

2.3. Safer synthesis including a multi-step one pot reaction

DMF-route:

Dichloroglyoxim (785 mg, 5 mmol) was dissolved in 10 mL of DMF at room temperature. The solution is cooled to 0°C and NaN_3 (715 mg, 11 mmol) was added. The mixture was stirred for 40 min at 0°C. NaCl precipitated, whereas diazidoglyoxim stayed in solution. The mixture was transferred to a flask containing 100 mL of diethyl ether, which was cooled to 0°C in a salt-ice bath. HCl was bubbled through the suspension maintaining the temperature below 20 °C, until saturation of the diethyl ether indicated by a drop of the temperature back to 0-5 °C was reached. A precipitate, which was formed during the reaction first agglomerates and then was resuspended, once the mixture was saturated with HCl. The flask was stoppered tightly and the reaction mixture was stirred overnight at room temperature under a slight overpressure of HCl, which formed upon warming the mixture to room temperature. The pressure was released and the mixture was poored into an open dish for evaporation either overnight at room temperature or in 1-2 h at 50°C. After most of the diethyl ether was evaporated, 50 mL of water was added resulting in a clear solution. The water was evaporated on a rotary evaporator and the remaining DMF was removed under high vacuum, yielding crude dimethylammonium 5,5´-bistetrazole-1,1´-diolate as a colorless solid. The solid was dissolved in the smallest possible volume of boiling water (app. 10 mL) and hydroxylammonium chloride (750 mg, 10.8 mmol, 2.16 eq.) as a concentrated aqueous solution was added. TKX-50 precipitated from the

solution in 74.6 % yield (882 mg, 3.73 mmol), which was isolated by suction filtration, washed with cold water and air dried.

NMP-route:

Dichloroglyoxime (785 mg, 5 mmol) was dissolved in 10 mL of NMP at room temperature. The solution was cooled to 0 °C and NaN_3 (715 mg, 11 mmol) was added. The mixture was stirred for 40 min at 0 °C. NaCl precipitated, whereas diazidoglyoxime stayed in solution. The mixture was transferred to a flask containing 150 mL of diethyl ether, which was then cooled to 0 °C in a salt-ice bath. HCl was bubbled through the suspension maintaining the temperature below 20 °C, until saturation of the diethyl ether, as indicated by a drop of the temperature back to 0-5 °C, was reached. A thick precipitate, which was formed during the reaction first agglomerated and then was resuspended, once the mixture was saturated with HCl. The flask was stoppered tightly and the reaction mixture was stirred overnight at room temperature under a slight overpressure of HCl, resultant form warming the mixture to room temperature. The pressure was released and the mixture was poored into an open dish for evaporation either overnight at room temperature or in 1-2 h at 50 °C. After evaporation of the diethyl ether and HCl, 50 mL H_2O was added and the mixture was evaporated on a rotary evaporator to completely remove HCl and diethyl ether. The thick, colorless residue containing 5,5´-bistetrazole-1,1'-diol in NMP was taken up in 20 mL of 2M NaOH, whereas the di-sodium salt of 5,5´-bistetrazole-1,1'-diol started to precipitate. The mixture was heated to reflux and upon cooling, the disodium salt precipitated almost quantitatively (90% yield starting from dichloroglyoxime). After isolation of the disodium salt, the solid was dissolved in minimal boiling water (ca. 10 mL) and hydroxylammonium chloride (750 mg, 10.8 mmol, 2.16 eq.) as a concentrated aqueous solution was added. TKX-50 precipitated from the solution in 85.1 % yield (1.00 g, 4.25 mmol), which was isolated by suction filtration, washed with cold water and air dried.

3. X-ray diffraction

3.1. Instrument and refinement software

Suitable single crystal of TKX-50 and its precursors were picked from the crystallization mixture and mounted in Kel-F oil, transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was performed using the CRYSALIS CCD software[9], the data reduction using the CRYSALIS RED software[10]. The structures were solved with SIR-92[11], refined with SHELXL-97[12] and finally checked using the PLATON software[13] integrated in the WINGX software suite.[14] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected using a SCALE3 ABSPACK multi-scan method.[15] Data and parameters of the X-ray measurements and solutions are gathered in Table S1.

3.2. Crystallographic data and refinement parameters

Table S1. Crystallographic data and refinement parameters

	TKX-50 (100K)	**TKX-50 (173K)**	**TKX-50 (298K)**	**1-BTO*2H_2O**	**1-BTO*2MeOH**	**Me_2H_2N_BTO**
Formula	$C_2H_8N_{10}O_4$	$C_2H_8N_{10}O_4$	$C_2H_8N_{10}O_4$	$C_2H_6N_8O_4$	$C_4H_{10}N_8O_4$	$C_4H_9N_9O_2$
Form. weight [g mol^{-1}]	236.18	236.18	236.18	206.12	234.20	215.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/m$ (No. 12)	*Pbca* (No. 61)	*Pbca* (No. 61)
Color / Habit	Colorless Blocks	Colorless Block	Colorless Block	Colorless Block	Colorless Block	Colorless Plate
Size, mm	0.25 x 0.30 x 0.40	0.17 x 0.21 x 0.27	0.10 x 0.25 x 0.40	0.13 x 0.18 x 0.20	0.31 x 0.35 x 0.43	0.12 x 0.20 x 0.20
a [Å]	5.4872(8)	5.4260(5)	5.4408(6)	7.7443(3)	7.6818(10)	11.660(2)
b [Å]	11.5472(15)	11.6597(12)	11.7514(13)	6.2459(3)	6.7692(12)	8.7050(17)
c [Å]	6.4833(9)	6.5013(7)	6.5612(9)	8.7000(3)	18.884(3)	18.028(3)
α [°]	90	90	90	90	90	90
β [°]	95.402(12)	95.256(9)	95.071(11)	116.052(2)	90	90
γ [°]	90	90	90	90	90	90
V [$Å^3$]	408.97(10)	409.58(7)	417.86(9)	378.06(3)	982.0(3)	1829.9(6)
Z	2	2	2	2	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.918	1.915	1.877	1.811	1.584	1.562
μ [mm^{-1}]	0.173	0.173	0.169	0.166	0.138	0.128
F(000)	244	244	244	212	488	896
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100	173	298	173	173	173
Theta Min-Max [°]	4.7, 27.2	4.7, 27.1	4.7, 27.0	4.4, 27.5	4.2, 26.0	4.2, 25.8
Dataset	-6:7; -11:14; -4:8	-5: 6; -9:14; -8:7	-5:6; -13:15; -8:8	-10:10; -8:8; -11:11	-9:8; -8:8; -14:23	-14:14; -10: 9; -22:16
Reflections collected	1773	2267	1798	1625	4803	8586
Independent reflections	910	901	911	472	968	1741
R_{int}	0.022	0.024	0.017	0.025	0.068	0.063
Observed reflections	769	681	729	460	555	1244
No. parameters	89	89	89	53	968	173
R_1 (obs)	0.0342	0.0334	0.0344	0.0458	0.0404	0.0437
wR_2 (all data)	0.0895	0.0856	0.0915	0.1431	0.0891	0.1201
GooF	1.06	0.97	1.02	1.22	0.84	1.08
Resd. Dens. [e/ $Å^3$]	-0.31, 0.24	-0.19, 0.23	-0.22, 0.23	-0.26, 0.47	-0.22, 0.29	-0.20, 0.24
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Bruker Kappa CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	872231	872230	872232	884561	884559	884560

3.3. Bond lengths, bond angles and hydrogen bonding of TKX-50

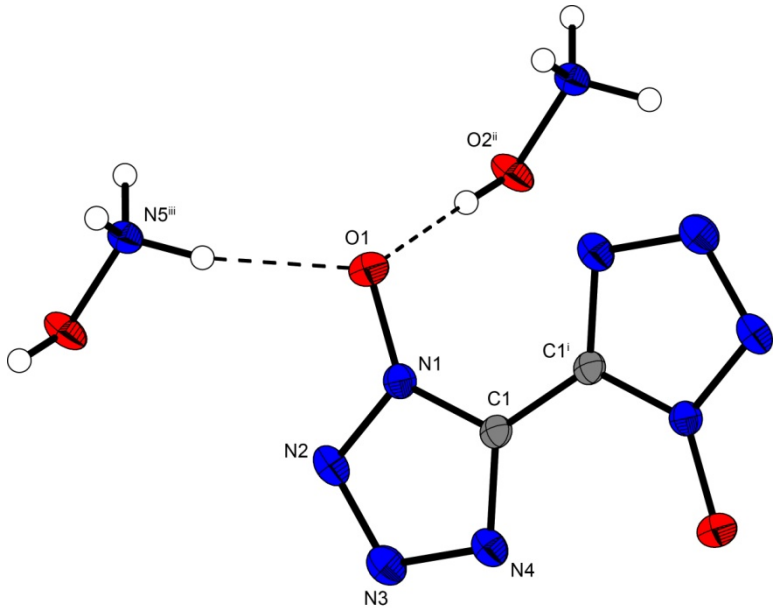

Figure S1. Representation of the solid state molecular structure of TKX-50 at 100 K. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): O1–N1 1.3280(15), N1–N2 1.3424(17), N1–C1 1.3451(18), N2–N3 1.3128(17), N3–N4 1.3513(18), N4–C1 1.3358(19), C1–C1^{i} 1.445(3), O2–N5 1.4152(15). Selected bond angles (°): O1–N1–N2 122.09(11), O1–N1–C1 129.25(12), N2–N1–C1 108.65(12), N3–N2–N1 106.16(12), N2–N3–N4 111.24(11), C1–N4–N3 105.43(11), N4–C1–N1 108.52(13), N4–C1–C1^{i} 127.46(16), N1–C1–C1^{i} 124.02(16); symmetry codes: (i) 2–x, –y, 2–z; (ii) x, 0.5–y, –0.5+z; (iii) –1+x, 0.5–y, –0.5+z. Hydrogen bonds (D–H···A: d(D–H) [Å], d(H···A) [Å], d(D···A) [Å], <(D–H···A) [°]): N5–H5B···O1^{i}: 0.91(2), 2.15(2), 2.9305(17), 144.1(16); N5–H5B···N4^{ii}: 0.91(2), 2.44(2), 3.0464(18), 124.5(16); N5–H5A···O1 0.93(2), 1.91(2), 2.8327(17), 170.8(18); N5–H5A···N1: 0.93(2), 2.67(2), 3.5481(18), 158.1(15); N5–H5C···O2 ^{iii}: 0.89(2), 2.21(2), 2.9913(18), 145.9(17); N5–H5C···N3^{iv}: 0.89(2), 2.429(19), 2.9187(17), 115.0(15); O2–H2···O1^{v}: 0.87(3), 1.74(3), 2.6000(16), 169(3); O2–H2···N1^{v}: 0.87(3), 2.47(3), 3.2032(16), 142(2); symmetry codes: (i) 1–x, –y, 1–z; (ii) 1+x, y, 1+z; (iii) x, 0.5–y, 0.5+z; (iv) x, y, 1+z; (v) 1+x, y, z.

3.4 Crystal structures of 5,5´-bistetrazole-1,1´-diol

Crystals of 5,5´bis(1-hydroxy)tetrazole dihydrate (**1,1´BTO·2H$_2$O**) can be obtained either from water, acetonitrile, glacial acetic acid, ethanol or diethylether. It crystallizes in the monoclinic space group *C*2/*m* with two molecular units in the unit cell. Its density of 1.811 gcm^{-3} is significantly lower than that of TKX-50 but higher than that of the methanol adduct (1.584 g cm^{-3}). The molecular unit is shown in figure S2.

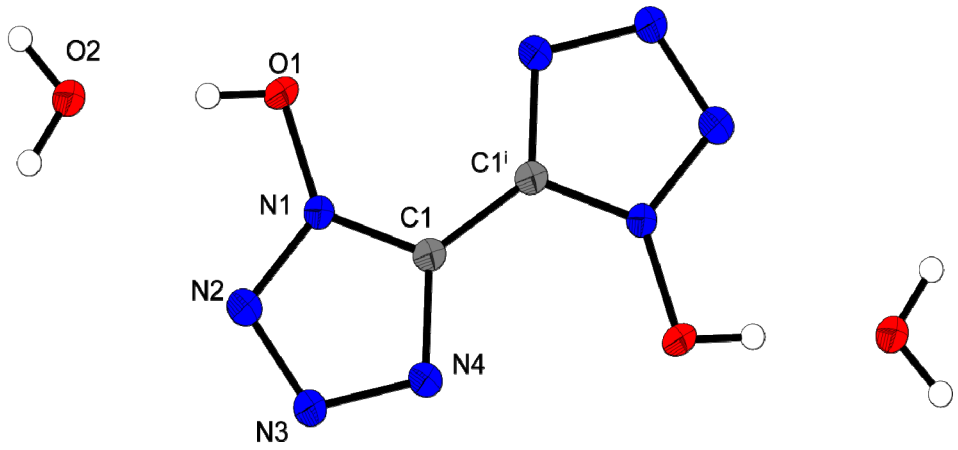

Figure S2 Molecular moiety of 5,5'-bis(1-hydroxy-tetrazole) dihydrate **(1,1´BTO·2H$_2$O)**. Ellipsoids are drawn at the 50 % probability level. (i) 1-x, y, -z. Selected bond lengths (Å): O1–N1 1.340(2),O1 H1 0.84(7) .N1–N2 1.332(3), N1–C1 1.338(3), N2–N3 1.304(3), N3–N4 1.353(3), N4–C1 1.334(3), C1–C1^{i} 1.434(4).

Within the structure layers within the ac-plane are formed by an intensive hydrogen bon network depiced Figure S3.

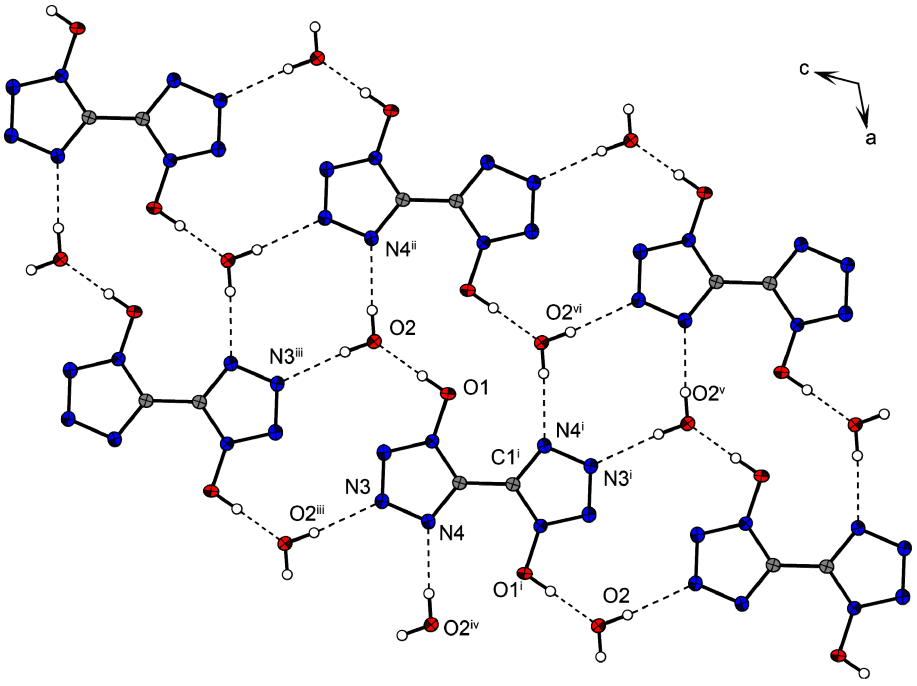

Figure S3 View on a layer within the *ac*-plane showing the intense hydrogen bond network. Hydrogen bonds (D–H···A: d(D–H) [Å], d(H···A) [Å], d(D···A) [Å], <(D–H···A) [°]):O1–H1···O2 0.84(7), 1.59(8), 2.430(2), 179(8); O2–H2···N4^{ii} 0.84(3), 1.94(3), 2.771(3), 176(5); O2–H3···N3^{iii} 0.830(14), 2.012(11), 2.839(3), 175(4).Symmetry codes: (i) 1-x, y, -z; (ii) -1+x, y, z; (iii) 1-x, y, 1-z; (iv) 1+x, y, z; (v) x, y, -1+z; (vi) -x, y, -z.

Recrystallization from methanol yielded single crystal of 5,5´bis(1-hydroxy)tetrazole dimethanolate (**1,1´BTO·2MeOH**). The structure of the tetrazolate backbone is similar to that of its dihydrate.

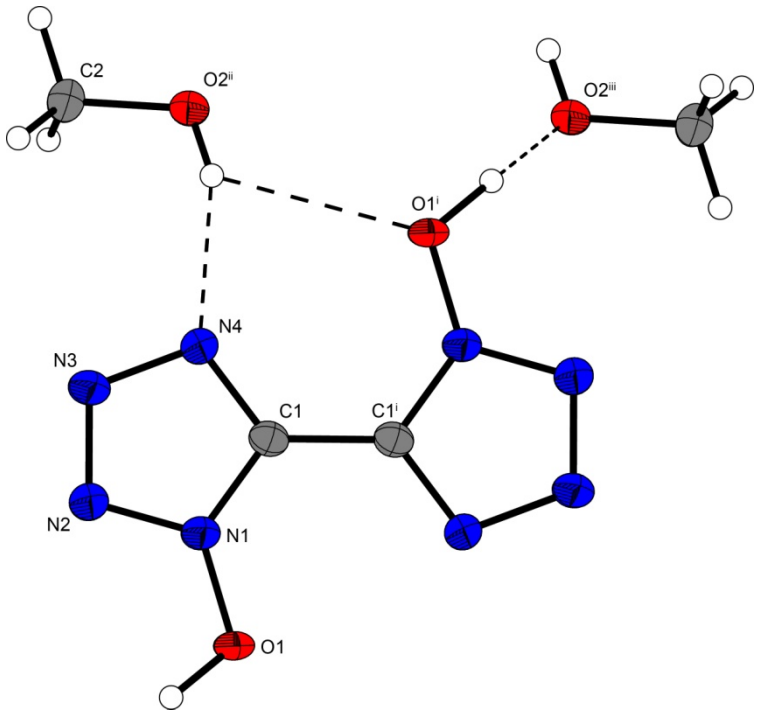

Figure S4 Molecular moiety of **1,1´BTO ·2MeOH**. Ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å): O1–N1 1.349(2), O2–C2 1.451(3), N4–C1 1.329(3), N4–N3 1.349(3), N1–N2 1.334(2), N1–C1 1.334(3), N3–N2 1.309(3), C1–C1^{i} 1.438(4). Symmetry codes: (i) 2-x, -y, 1-z, (ii) 1.5-x, 0.5+y, z; (iii) -0.5+x, -0.5-y, 1-z.

3.5. Crystal structure of dimethylammonium 5,5´-bistetrazole-1,1´-diolate

The dimethylammonium salt formed during the one-pot synthesis of TKX-50 was recrystallized from water. It crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell and a calculated density of 1.562 g cm^{-3}.

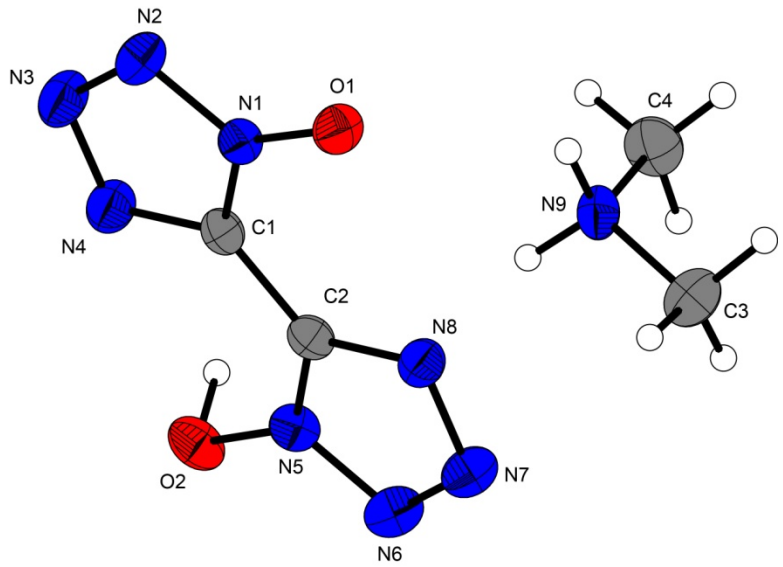

Figure S5 Molecular structure of dimethylammonium 5-(1-hydroxytetrazolyl)-5-(1-oxidotetrazolate. Selected bond lengths (Å): O2–N5 1.346(2), O1–N1 1.333(2), N9–C4 1.472(3), N9–C3 1.480(3), N7–N6 1.300(3), N7–N8 1.361(2), N2–N3 1.310(2), N2–N1 1.337(2), N1–C1 1.335(3), N3–N4 1.350(2), N8–C2 1.331(3), N5–C2 1.340(3), N5–N6 1.342(3), N4–C1 1.333(3), C2–C1 1.445(3)

4. Explosive performance

4.1. Heat of formation calculations

Electronic energies (CBS-4M method) were calculated with the Gaussian09 Revision A.02 software.[16] Gas phase enthalpies of formation were computed using the atomization method (equation 1) often described recently.[17]

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \qquad (1)$$

The gas phase enthalpy of formation of TKX-50 was converted into the solid state enthalpy of formation by substraction of lattice enthalpies ($\Delta_L H$ = 1515.6 kJ mol^{-1}) calculated according to Jenkins et al.[18,19] Detonation parameters were calculated with the EXPLO5.05 computer code.[20,21]

Table S2. CBS-4M calculation results and molecular volume taken from X-ray solution at 100 K.

M	$-H^{298}$ / a.u.	$\Delta_f H°$(g,M) / kJ mol^{-1}	V_M / nm^3
C	37.786156	716.7 (NIST value)	
H	0.500991	218.0 (NIST value)	
N	54.522462	472.7 (NIST value)	
O	74.991202	249.2 (NIST value)	
NH_4O^+	131.863217	687.2	
BTO^{2-}	663.687267	587.7	
TKX-50		131.2	0.204

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation (2) (Table S2).

$\Delta U_m = \Delta H_m - \Delta n\, RT$ (2) (Δn being the change of moles of gaseous components)

4.2. Small scale shock reactivity test

The Small-Scale Shock Reactivity Test (SSRT)[22,23] was introduced by researchers at IHDIV, DSWC (Indian Head Division, Naval Surface Warfare Center). The SSRT measures the shock reactivity (explosiveness) of energetic materials, often well-below critical diameter, without requiring a transition to detonation. The test setup combines the benefits from a lead block test[24] and a gap test.[25] In comparison to gap tests, the advantage is the use of a much smaller sample size of the tested explosive (ca. 500 mg). The sample volume V_s is recommended to be 0.284 mL (284 mm^3). For our test setup no possible attenuator (between detonator and sample) and air gap (between sample and aluminum block) was used. The used sample weight m_s was calculated using the formula V_s x ρ_{Xray} x 0.95. Several tests with commonly used explosives such as TNT, PETN, RDX, HMX and also CL-20 were performed in order to obtain different dents within the aluminum plate. The dent sizes were measured by filling them with powdered SiO_2 and measuring the resulting weight.

Table S3. Results from the Small Scale Shock Reactivity Test (SSRT).

Explosive	weight [mg]	dent [mg SiO_2]
RDX	504	589
CL-20	550	947
TKX-50	509	857

4.3 Flame test

The flame test is an essential and easy test within for our coworker in order to get first impression of the energetic behavior of a new compound. TKX-50 burns intensively without smoke and significantly residues when brought into an open flame.

Figure S6 TKX-50 held in the flame on a spatula burns without detonation.

4.4 Hot plate test

Typical secondary explosives deflagrate when heated and show no deflagration-to-detonation transition. Latter case can be heard by fulmination of the compound or deformation of the copper plate of the hot-plate test setup. In the hot-plate test the compound is placed on a 2 mm copper plate and heated with a Bunsen burner below.

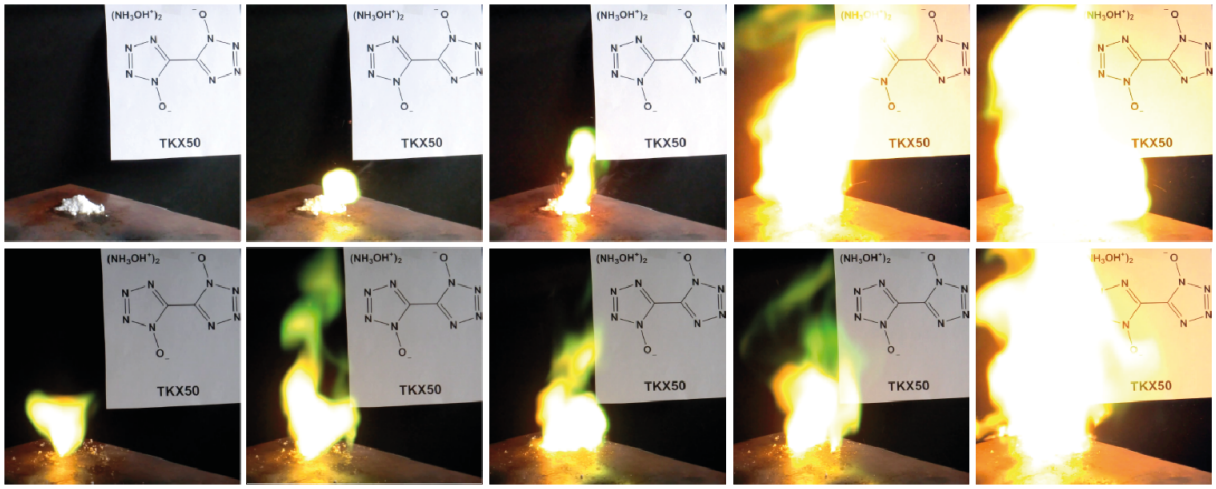

Figure S7 TKX-50 on a copper plate with a Bunsen burner underneath only burns without detonation.

5. Toxicity assessment

The sample dilution sequence corresponds to DIN 38412 L34, which ranges from 1:2 to 1:32 dilution of the compound in the test system. For better reproducability, all dilution steps were made in duplicate. The change of intensity of bacterial luminescence in the absence (controls) and in the presence (samples) of the tested substances after different incubation times (15 min, 30 min) were recorded. The controls (2% NaCl only) were measured for calculating the correction factor, which is necessary to consider the normal decrease of luminescence without any toxic effect per time. The EC_{50} value can be determined by plotting log Γ against log c, where Γ = inhibition (in %) / 100 – inhibition (in %) and c = concentration of the test sample. The EC_{50} value is identical with the intersection of the resulting graph with the X-axis (Γ = 0). For better comparison of the resulting toxicities we also determined the toxic effect of RDX to the bacterial strain under the same conditions applied for the toxicity assessment of TKX-50. To imitate the natural environment of the employed marine bacterium as good as possible, the samples need to be diluted with a 2% (w/v) sodium chloride solution. Since RDX is barely soluble in water, a stock solution in acetone was prepared, which was further diluted with the sodium chloride solution to a mixture containing 200 ppm RDX in water/acetone 99/1 (v/v). The poor water solubility of 5,5´-bistetrazole-1,1´-diolates also sets problems during the toxicity tests of TKX-50. Here, an aqueous solution containing 1467 ppm TKX-50 was prepared and sodium chloride was added to adjust the final sodium chloride concentration of the stock solution to 2 % (w/v). Since disodium 5,5´-bistetrazole-1,1´-diolate shows nearly as poor water solubility as TKX-50, no higher concentration of the investigated compound could be used without precipitating disodium 5,5´-bistetrazole-1,1´-diolate tetrahydrate from the stock solution.

6. Fast Cook-Off Test

In order to get an "Interim Hazard Classification" also a fast cook-off test[26] (FCO, UN test 3d) was performed in which TKX-50 deflagrated (no explosion occurred). The setup of the FCO is shown in Figure S7. 10 g TKX-50 were loaded in a plastic sample container (unconfined, without cap) and placed in sawdust soaked with kerosene. The kerosene was ignited and the reaction was recorded with a video camera. After ~80 s TKX-50 deflagrated controlled within ~9 s (see supplementary video).

Figure S8 Fast Cook-Off Test of TKX-50

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