Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

Towards improved explosives with a high performance: *N*-(3,5-dinitro-1*H*-pyrazol-4-yl)-1*H*-tetrazol-5-amine and its salts

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Section 1. Theoretical study

Calculations were performed using the Gaussian 03 (Revision E.01) suite of programs.[S1] The geometric optimization of the structures and frequency analyses were conducted using the B3LYP functional with the 6–31+G** basis set,[S2] and single-point energies were calculated at the MP2(full)/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on the Born-Haber energy cycle (**Figure S1**), the heat of formation of a salt can be simplified according to Equation. (1), where ΔH_L is the lattice energy of the salt.

ΔH_f^o(ionic salt, 298K)=ΔH_f^o(cation, 298K)+ΔH_f^o(anion, 298K)-ΔH_L (1)

The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Eq. 2],[S2] in which U_{POT} is the lattice potential energy and n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_L = U_{POT} + [p(n_M/2-2) + q(n_X/2-2)]RT \quad (2)$$

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[S3]

$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma\ (\rho_m/M_m)^{1/3} + \delta \quad (3)$$

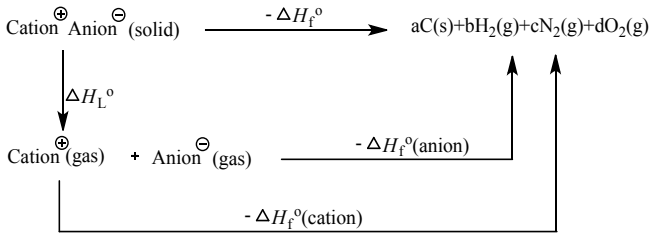
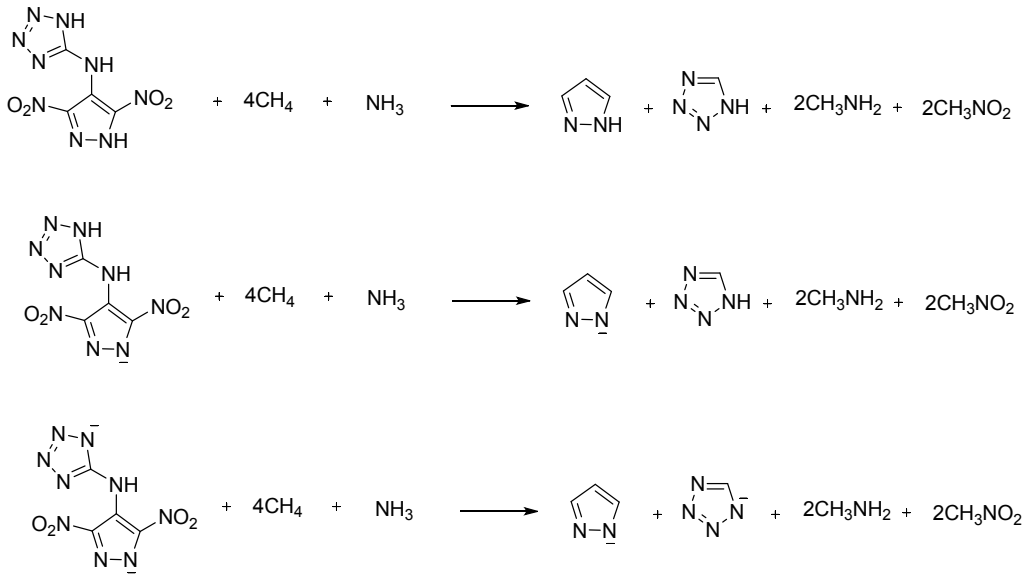


Figure S1. Born-Haber cycle for the formation for energetic salts.

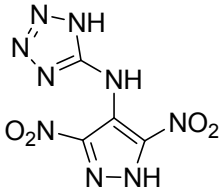
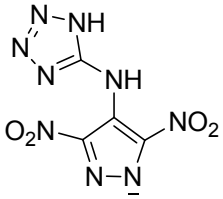
The remaining task was the determination of the heats of formation of the compound, which were computed by using the method of isodesmic reactions (**Scheme S1**). The enthalpy

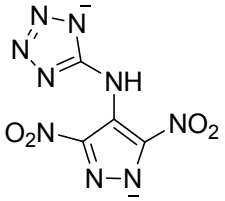
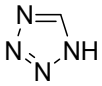
of an isodesmic reaction (ΔH_f^o 298) was obtained by combining the MP2(full)/6–311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6–31+G**). The heats of formation of the cations and anions being investigated could then be extracted readily.



Scheme S1. Isodesmic reactions for the calculations of heats of formation.

Table S1. Ab Initio computional data, Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E_0), Zero Point Energy (ZPE), Values of Thermal correction (HT), and Heats of Formation (HOF) [kJ mol^{-1}] of the compounds.

	E_0	ZPE	H_T	HOF
	-945.83964	0.120742	0.120742	856.4
	-945.35448	0.107113	0.120891	532.7

	-944.726997	0.093843	0.107601	674.4
	-257.7256749	0.046855	0.00443	333.2
	-257.218829	0.033827	0.004225	170.0
	-225.7180621	0.071265	0.004690	179.4
	-225.1444688	0.056627	0.004552	124.2
CH_4	-40.39849	0.044791	0.003812	-74.6
NH_3	-56.43462	0.034377	0.003818	-45.9
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0
CH_3NO_2	-244.5543604	0.049857	0.005272	-74.3

Section 2. X-ray crystallography

Crystals of **6·H$_2$O** and **10** was removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **6·H$_2$O** was collected at 153 K while for 10 were collected at 102.1 K, using a Rigaku Saturn724 CCD (AFC10/Saturn724+ for 7) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear-SM Expert 2.0 r2 software.[S4] The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F2 using the SHELXTL-97 system of programs.[S5] Structure were solved in the space group P2$_1$/c for **6**·H$_2$O, Pī for **10**,

by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. Band lengths, angles and dihedral angles of the data collection and refinement are given in **Table S2, S3, S4, S5, S6, S7.**

Table S2. Selected bond lengths for salt **6·H_2O.**

	Length/ Å		Length/ Å
O1-N3	1.247(3)	N13-C5	1.319(4)
O4-N4	1.252(3)	N13-H13A	0.8800
O2-N3	1.229(3)	N13-H13B	0.8800
O3-N4	1.234(3)	N12-C5	1.323(4)
N10-N11	1.418(3)	N12-H12A	A 0.8800
N10-H10A	0.8801	N12-H12B	0.8800
N10-H10B	0.8798	C1-C2	1.403(4)
N3-C1	1.417(4)	C2-C3	1.409(4)
N7-N8	1.317(4)	O5-H5A	0.8399
N7- N6	1.347(3)	O5-H5B	0.8401
N2-N1	1.332(4)	N14-N15	1.411(4)
N2-C3	1.373(4)	N14-H14A	0.8667
N1-C1	1.356(4)	N14-H14B	0.8662
N9-C4	1.329(4)	N17-C6	1.324(4)
N9-N8	1.351(4)	N17-H17A	0.8800
N4-C3	1.400(4)	N17-H17B	0.8800
N6-C4	1.333(4)	N16-C6	1.319(4)
N11-C5	1.342(4)	N16-H16A	0.8800
N11-H11	0.8800	N16-H16B	0.8800

N5-C2	1.360(4)	N15-C6	1.339(4)
N5-C4	1.394(4)	N15-H15	0.8800
N5-H5	0.8800		

Table S3. Bond angles for salt **6·H_2O.**

	Angle/°		Angle/°
N11-N10-H10A	103.7	C2-C1-N3	127.5(3)
N11-N10-H10B	103.1	N5-C2-C1	127.3(3)
H10A-N10-H10B	117.7	N5-C2-C3	132.3(3)
O2-N3-O1	123.3(3)	C1-C2-C3	100.4(2)
O2-N3-C1	119.2(2)	N9-C4-N6	113.1(3)
O1-N3-C1	117.4(2)	N9-C4-N5	122.5(3)
N8-N7-N6	109.3(2)	N6-C4-N5	124.4(3)
N1-N2-C3	107.6(2)	N13-C5-N12	121.0(3)
N2-N1-C1	107.7(2)	N13-C5-N11	120.9(3)
C4-N9-N8	103.7(2)	N12-C5-N11	118.1(3)
N7-N8-N9	109.8(2)	N2-C3-N4	117.9(2)
O3-N4-O4	121.6(2)	N2-C3-C2	111.6(2)
O3-N4-C3	120.5(2)	N4-C3-C2	130.1(3)
O4-N4-C3	117.9(2)	H5A-O5-H5B	98.8
C4-N6-N7	104.1(2)	N15-N14-H14A	110.2
C5-N11-N10	119.1(2)	N15 -N14- H14B	109.9
C5-N11-H11	120.4	H14A -N14 -H14B	108.8
N10-N11-H11	120.4	C6 -N17- H17A	120.0
C2-N5-C4	125.1(2)	C6 -N17- H17B	120.0

C2-N5-H5	118.2	H17A- N17 -H17B	120.0
C4-N5-H5	114.4	C6- N16- H16A	120.0
C5-N13-H13A	120.0	C6- N16 -H16B	120.0
C5-N13-H13B	120.0	H16A- N16- H16B	120.0
H13A-N13-H13B	120.0	C6- N15- N14	118.7(2)
C5-N12-H12A	120.0	C6- N15 -H15	120.6
C5-N12-H12B	120.0	N14 -N15 -H15	120.6
H12A-N12-H12B	120.0	N16 -C6 -N17	121.4(3)
N1-C1-C2	112.6	N16 -C6- N15	119.4(3)
N1-C1-N3	119.9	N17- C6 -N15	119.1(3)

Table S4. Torsion angles for salt **6·H_2O.**

	Angle/°		Angle/°
C3- N2 -N1 -C1	0.5(3)	N7- N6 -C4 -N9	-0.2(3)
N6 -N7 -N8- N9	-1.4(3)	N7- N6 -C4 -N5	-176.9(3)
C4- N9- N8 -N7	1.2(3)	C2 -N5 -C4- N9	154.9(3)
N8-N7- N6- C4	1.0(3)	C2- N5 -C4 -N6	-28.7(5)
N2-N1- C1 -C2	-0.2(4)	N10- N11- C5- N13	1.5(5)
N2-N1 -C1- N3	179.4(3	N10- N11- C5 -N12	-178.8(3)
O2- N3 -C1 -N1	11.1(4	N1 -N2- C3- N4	-174.4(3)
O1 -N3 -C1-N1	-168.7(3	N1 -N2- C3 -C2	-0.7(3)
O2-N3 -C1- C2	-169.4(3	O3- N4 -C3- N2	168.8(3)
O1 -N3 -C1- C2	10.8(4)	O4-N4- C3 -N2	-11.2(4)
C4- N5 -C2- C1	147.2(3	O3-N4 -C3 -C2	-3.6(5)
C4 -N5- C2 -C3	-32.5(5)	O4-N4- C3- C2	176.5(3)

N1 -C1- C2- N5	-180.0(3)	N5- C2 -C3- N2	-179.7(3)
N3- C1-C2- N5	0.5(5)	C1 -C2- C3 -N2	0.5(3)
N1- C1 -C2 -C3	-0.2(3)	N5- C2 -C3 -N4	-7.0(6)
N3- C1- C2 -C3	-179.7(3	C1-C2- C3 -N4	173.2(3)
N8-N9- C4 -N6	-0.6(3)	N14 -N15- C6 N16	10.8(4)
N8-N9 -C4-N5	176.2(3)	N14 -N15- C6 N17	-169.7(3)

Table S5. Bond lengths for salt **10**

	Length/ Å		Length/ Å
N5-C4	1.338(2)	N6-C3	1.355(3)
N5-N4	1.351(2)	N3-N4	1.294(2)
O4-N9	1.241(2)	C2-C1	1.387(3)
N1-C4	1.367(3)	C2-C3	1.400(3)
N1-C2	1.397(3)	N9-C3	1.424(3)
O3-N9	1.237(2)	N10-N13	1.403(2)
O1-N8	1.226(2)	N10-C5	1.395(2)
O2-N8	1.237(2)	N10-C6	1.352(3)
N8-C1	1.431(3)	N15-C5	1.336(3)
N7-N6	1.335(2)	N11-N12	1.405(2)
N7-C1	1.347(3)	N11-C6	1.321(2)
N2-C4	1.321(3)	N12-C5	1.308(3)
N2-N3	1.361(2)	N14-C6	1.318(3)

Table S6. Bond angles for salt **10**

	Angle/°		Angle/°

C4-N5-N4	108.11(17)	N3-N4-N5	106.41(16)
C4-N1-C2	123.34(16)	N7-C1-N8	119.51(19)
O1-N8-O2	123.29(18)	N7-C1-C2	113.06(18)
O1-N8-C1	119.42(18)	C2-C1-N8	127.42(19)
O2-N8-C1	117.30(18)	N6-C3-C2	111.81(19)
N6-N7-C1	107.07(18)	N6-C3-N9	119.30(18)
C4-N2-N3	105.32(15)	C2-C3-N9	128.9(2)
N5-C4-N1	128.0(2)	C5-N10-N13	128.07(18)
N2-C4-N5	109.06(18)	C6-N10-N13	124.20(15)
N2-C4-N1	122.95(17)	C6-N10-C5	107.64(17)
N7-N6-C3	107.63(16)	C6-N11-N12	112.39(18)
N4-N3-N2	111.08(18)	C5-N12-N11	103.65(15)
N1-C2-C3	130.5(2)	N15-C5-N10	121.25(19)
C1-C2-N1	129.15(18)	N12-C5-N10	110.59(18)
C1-C2-C3	100.39(19)	N12-C5-N15	127.98(17)
O4-N9-C3	118.11(17)	N11-C6-N10	105.71(17)
O3-N9-O4	123.89(18)	N14-C6-N10	126.43(19)
O3-N9-C3	118.00(19)	N14-C6-N11	127.9(2)

Table S7. Torsion angles for salt **10**

	Angle/°		Angle/°
O4-N9-C3-N6	178.52(15)	C2-N1-C4-N5	-5.0(3)
O4-N9-C3-C2	-3.6(3)	C2-N1-C4-N2	173.87(18)
N1-C2-C1-N8	-0.1(3)	N4-N5-C4-N1	179.21(19)
N1-C2-C1-N7	178.73(16)	N4-N5-C4-N2	0.2(2)

N1-C2-C3-N6	-178.74(17)	C1-N7-N6-C3	0.05(18)
N1-C2-C3-N9	3.3(3)	C1-C2-C3-N6	1.9(2)
O3-N9-C3-N6	-1.7(2)	C1-C2-C3-N9	-176.11(17)
O3-N9-C3-C2	176.13(17)	C3-C2-C1-N8	179.31(17)
O1-N8-C1-N7	-7.4(3)	C3-C2-C1-N7	-1.9(2)
O1-N8-C1-C2	171.42(18)	N11-N12-C5-N10	0.4(2)
O2-N8-C1-N7	172.27(15)	N11-N12-C5-N15	-174.70(19)
O2-N8-C1-C2	-9.0(3)	N12-N11-C6-N10	-0.9(2)
N7-N6-C3-C2	-1.3(2)	N12-N11-C6-N14	178.30(19)
N7-N6-C3-N9	176.91(15)	N13-N10-C5-N15	-8.7(3)
N2-N3-N4-N5	1.6(2)	N13-N10-C5-N12	175.81(17)
C4-N5-N4-N3	-1.1(2)	N13-N10-C6-N11	-175.82(16)
C4-N1-C2-C1	-115.9(2)	N13-N10-C6-N14	4.9(3)
C4-N1-C2-C3	64.8(3)	C5-N10-C6-N11	1.1(2)
C4-N2-N3-N4	-1.5(2)	C5-N10-C6-N14	-178.11(19)
N6-N7-C1-N8	-179.85(15)	C6-N10-C5-N15	174.50(18)
N6-N7-C1-C2	1.2(2)	C6-N10-C5-N12	-1.0(2)
N3-N2-C4-N5	0.8(2)	C6-N11-N12-C5	0.3(2)
N3-N2-C4-N1	-178.31(17)		

Section 3 Refernces

[S1] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P.

Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

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