SUPPLEMENTARY INFORMATION

Enthalpy of Formation of the Nitrogen-Rich Salt Guanidinium 5,5'-Azotetrazolate (GZT) and a Simple Approach for Estimating the Enthalpy of Formation of Energetic C, H, N, O Salts

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This supplementary information includes:

- Data of all the combustion calorimetry experiments of guanidinium 5,5'-azotetrazolate (Table S1).
- Data of computational results on 1:1 salts at CBS-4M level of theory (Table S2)
- Data of computational results on 1:1 salts at CBS-QB3 level of theory (Table S3)
- Data of computational results on 1:1 adducts at CBS-4M level of theory (Table S4)
- Data of computational results on 1:1 adducts at CBS-QB3 level of theory (Table S5)
- Data of computational results on 2:1 salts at CBS-4M level of theory (Table S6)
- Data of computational results on 2:1 salts at CBS-QB3 level of theory (Table S7)
- Data of computational results on 2:1 adducts at CBS-4M level of theory (Table S8)
- Data of computational results on 2:1 adducts at CBS-QB3 level of theory (Table S9)

Acronym used throughout this supplementary data:

- GZT for guanidinium 5,5'-azotetrazolate.

Combustion calorimetry

- The calibration experiments were development in an oxygen atmosphere at $p = 3.04$ MPa, with 1.00 cm^3 of deionized water added to the bomb; the energy equivalent of the calorimeter, ε_{cal}, was determined from the combustion of benzoic acid (NIST SRM 39j) having a mass energy of combustion, under standard bomb conditions, of $-(26434 \pm 3)$ J·g^{-1}. From six calibration experiments $\varepsilon_{cal} = -(16002.6 \pm 1.7)$ J·g^{-1}, for an average mass of water added to the calorimeter of 3119.6 g; the uncertainty associated is the standard deviation of the mean.
- The samples of compound were ignited in pellet form under the same conditions of the calibration experiments.
- The cotton thread fuse (empirical formula is $CH_{1.686}O_{0.843}$) has a standard massic energy of combustion of -16240 J g^{-1} [S1].
- n-Hexadecane (Aldrich, mass fraction > 0.999), stored under nitrogen, was added to each pellet of studied compound to prevent incomplete combustions; the massic energy of combustion of the sample used, was determined in our laboratory as $\Delta_c u^{\circ} = -(47136.7 \pm 2.3)$ J·g^{-1}.
- The ignition energy was determined from the change in potential difference on discharge of a 1400 F condenser across a platinum wire.
- The calorimeter temperature was measured to $\pm(1 \times 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett-Packard HP 2804 A), interfaced to a computer; the ignition occurs at $T = (298.150 \pm 0.001)$ K.
- Pressure coefficient of specific energy $(\partial u / \partial p)_T = -0.2$ J·g^{-1}·MPa^{-1} (typical value for organic compounds [S2])
- The energetic correction for the nitric acid formation, $\Delta U(HNO_3)$ was based on -59.7 kJ·mol^{-1} for the molar energy of formation of 0.1 mol·dm^{-3} HNO$_3$(aq) from N$_2$(g), O$_2$(g), and H$_2$O(l) [S3].
- Corrections for carbon formation relied on the standard massic energy of combustion of carbon, $\Delta_c u^{\circ} = -32.76$ kJ·g^{-1} [S4].
- Specific density of the studied compound and the cotton thread, at $T = 298.15$ K: $\rho = 1.538$ g·cm^{-3} for GZT [S5] and $\rho = 1.50$ g·cm^{-3} for cotton fuse [S6].
- The value of the massic heat capacity, at $T = 298.15$ K, was calculated as 1.527 J·K^{-1}g^{-1} for GZT using Kopp's rule [S7].

S1. Coops, J.; Jessup, R.S.; van Nes, K. Calibration of calorimeters for reactions in a bomb at constant volume. In *Experimental Thermochemistry. Measurement of Heats of Reaction*, 1st ed.; Rossini F.D., ed.; Interscience Publishers, Inc., New York, 1956; Volumen 1, pp. 27-58.

S2. Washburn, E.W. Standard states for bomb calorimetry, *J. Res. Nat. Bur. Stand.*, **1933**, 10, 525.

S3. Wagman, D.D.; Evans, W.H.; Parker, V.B.; Schumm, R.H.; Halow, I.; Bailey, S.M.; Churney, K.L.; Nuttall, R.L. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. *J. Phys. Chem. Ref. Data* **1982**, 11, (Suppl.2).

S4. Cox, J.D.; Wagman, D.D.; Medvedev, V.A. *CODATA key values for thermodynamics,* Hemisphere, New York, 1979.

S5. Hiskey, M.A.; Goldman, N.; Stine, J. R. High-nitrogen energetic materials derived from azotetrazolate, *J. Energ. Mater.* **1998**, *16*, 119–127.

S6. Hubbard, W.N.; Scott D.W.; Waddington, G. Standard states and corrections for combustions in a bomb at constant volume. In *Experimental Thermochemistry. Measurement of Heats of Reaction*, 1st ed.; Rossini F.D., ed.; Interscience Publishers, Inc., New York, 1956; Volumen 1, pp. 75–128.

S7. Hurst, J.E.; Harrison, B.K. Estimation of liquid and solid heat capacities using a modified Kopps'rule, *Chem. Eng. Comm.*, **1992**, 112, 21-30.

Table S1. Standard ($p° = 0.1$ MPa) mass energy of combustion of solid guanidinium 5,5′-azotetrazolate, at $T = 298.15$ K [a]

m(cpd)/g	0.35343	0.38225	0.30214	0.24884	0.25331	0.25140
m(fuse)/g	0.00249	0.00233	0.00212	0.00479	0.00238	0.00252
m(n-hexadec.)/g	0.28255	0.30748	0.30046	0.30752	0.25240	0.25210
T_i/K	298.1513	298.1507	298.1507	298.1504	298.1505	298.1508
T_f/K	299.3575	299.4507	299.3662	299.3474	299.1921	299.1933
ΔT_{ad}/K	1.13020	1.22766	1.13986	1.11941	0.95747	0.95580
ε_i /J·K^{-1}	16.81	16.91	16.77	16.71	16.31	16.31
ε_f /J·K^{-1}	17.79	17.99	17.79	17.73	17.16	17.15
$-\Delta U$(IBP)/J	18105.17	19667.02	18260.02	17932.17	15337.42	15310.98
ΔU(HNO$_3$)/J	72.43	72.57	66.63	62.34	55.41	60.36
ΔU(ign)/J	1.06	0.81	0.97	1.14	1.01	0.69
ΔU_Σ/J	6.59	7.24	6.25	5.79	5.17	5.11
$-\Delta U$(n-hexadec.)/J	13318.52	14493.81	14162.46	14495.69	11897.32	11883.16
$-\Delta U$(fuse)/J	40.44	37.84	34.43	77.79	38.65	40.92
$-\Delta_c u°$/(J·g^{-1})	13205.42	13225.79	13206.63	13223.60	13188.86	13211.73

$$\langle \Delta_c u° \rangle = -(13210.34 \pm 5.53) \text{ J·g}^{-1} \text{ [b]}$$

m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(n-hexadec.) is the mass of n-hexadecane used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalents of contents in the initial and final state, respetively; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(HNO$_3$) is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; ΔU(n-hexadec.) is the energy of combustion of the n-hexadecane; ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u°$ is the standard massic energy of combustion.
[a] All masses were adjusted for buoyancy. [b] Mean value and standard deviation of the mean.

Table S2. Computational results on 1:1 salts at CBS-4M level of theory.

Compound	$\Delta_f H^\circ$ base (kJ·mol⁻¹)	$\Delta_f H^\circ$ acid (kJ·mol⁻¹)	$\Delta_r H$ (kJ·mol⁻¹)	$\Delta_f H^\circ$ (s) salt (kJ·mol⁻¹)
$NH_4^+C(NO_2)_3^-$	NH_3 (g) = -46.11[2]	$HC(NO_2)_3$ (s) = -48.2[4]	-145.35	-239.70
$NH_4^+N_3^-$	NH_3 (g) = -46.11[2]	HN_3 (l) = +264.0[2]	-145.35	+72.54
$NH_4^+HCO_2^-$	NH_3 (g) = -46.11[2]	H_2CO_2 (l) = -424.72[2]	-145.35	-616.18
$NH_4^+HCO_3^-$	NH_3 (g) = -46.11[2]	H_2CO_3 equivalent to CO_2(ao) + H_2O (l) = -699.65[2]	-145.35	-891.1
$NH_4^+CH_3COO^-$	NH_3 (g) = -46.11[2]	CH_3COOH (l) = -484.5[2]	-145.35	-675.96
$NH_4^+picrate^-$	NH_3 (g) = -46.11[2]	picric acid (s) = -217.9[6]	-145.35	-409.36
NH_4^+3,5-dinitrobenzoate⁻	NH_3 (g) = -46.11[2]	3,5-dinitrobenzoic acid (s) = -432.6[7]	-145.35	-624.06
$NH_4^+N(NO_2)_2^-$	NH_3 (g) = -46.11[2]	$HN(NO_2)_2$ (l) = +54.4[1]	-145.35	-137.06
$NH_4^+H_2NCOO^-$	NH_3 (g) = -46.11[2]	H_2NCOOH (s) = -547[1,5]	-145.35	-738.46
$NH_4^+H_2NCOO^-$	NH_3 (g) = -46.11[2]	H_2NCOOH (s) = -437.7[9]	-145.35	-626.16
$(H_2N)_3C^+picrate^-$	guanidine (s) = -56.1[2]	picric acid (s) = -217.9[6]	-156.8	-430.8
$(H_2N)_3C^+N(NO_2)_2^-$	guanidine (s) = -56.1[2]	$HN(NO_2)_2$ (l) = +54.4[1]	-156.8	-158.5
$(H_2N)_3C^+$3,5-dinitrobenzoate⁻	guanidine (s) = -56.1[2]	3,5-dinitrobenzoic acid (s) = -432.6[7]	-156.8	-645.5
$AG^+N(NO_2)_2^-$	AG (s) = +58.5[3]	$HN(NO_2)_2$ (l) = +54.4[1]	-163.1	-50.9
$TAG^+N(NO_2)_2^-$	TAG (s) = +287.7[3]	$HN(NO_2)_2$ (l) = +54.4[1]	-163.8	+178.3
$N_2H_5^+C(NO_2)_3^-$	N_2H_4 (l) = +50.63[2]	$HC(NO_2)_3$ (s) = -48.2[4]	-128.1	-125.67
$N_2H_5^+NTO^-$	N_2H_4 (l) = +50.63[2]	HNTO (s) = -129.4[8]	-128.1	-206.87
$N_2H_5^+N(NO_2)_2^-$	N_2H_4 (l) = +50.63[2]	$HN(NO_2)_2$ (l) = +54.4[1]	-128.1	-23.07
$N_2H_5^+CH_3NNO_2^-$	N_2H_4 (l) = +50.63[2]	CH_3NHNO_2 (l) = -51.29[1]	-128.1	-128.76
$NH_3OH^+N(NO_2)_2^-$	NH_2OH (s) = -114.8[2]	$HN(NO_2)_2$ (l) = +54.4[1]	-78.2	-138.6

[1]Value for $\Delta_{sub,vap}H_m^\circ$ obtained from RoseBoom©. [2]Value taken from NBS tables. [3]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [4]Value taken from NIST webbook https://webbook.nist.gov/chemistry/. [5]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M. [6]Value taken from Byrd, E.F.C.; Rice, B.M. Improved prediction of heats for formation of energetic materials using quantum mechanical calculations. *J. Phys. Chem. A* **2006**, *110*, 1005-1013. [7]Value for $\Delta_{sub}H_m^\circ$ unknown, therefore value of $\Delta_{sub}H_m^\circ$ for 2,4-DNBA used from Vecchio, S.; Brunetti, B. Vapor pressures and standard molar enthalpies, entropies, and Gibbs free energies of sublimation of 2,4- and 3,4-dinitrobenzoic acid. *J. Chem. Thermodyn.* **2009**, *41*, 880-887. [8]Value taken from Sinditskii, V. P.; Smirnov, S. P.; Egorshev, V. Y. *Thermal decomposition of NTO: explanation of high activation energy,* Proc. 37th Int. Ann. Conf. ICT Karlsruhe, Germany, 2006, pp. 40-1 – 40-16. [9]Value for $\Delta_f H_m^\circ$(g) calculated at CBS-4M; value for $\Delta_{sub,vap}H_m^\circ$ = 0 since at T > -23°C decomposition occurs forming NH_3(g) and CO_2 (g).

Table S3. Computational results on 1:1 salts at CBS-QB3 level of theory.

Compound	$\Delta_f H^\circ$ base (kJ·mol⁻¹)	$\Delta_f H^\circ$ acid (kJ·mol⁻¹)	$\Delta_r H$ (kJ·mol⁻¹)	$\Delta_f H^\circ$ (s) salt (kJ·mol⁻¹)
$NH_4^+C(NO_2)_3^-$	NH_3 (g) = -46.11[1]	$HC(NO_2)_3$ (s) = -48.4[4]	-145.35	-239.66
$NH_4^+N_3^-$	NH_3 (g) = -46.11[1]	HN_3 (l) = +273.84[5]	-145.35	+82.38
$NH_4^+HCO_2^-$	NH_3 (g) = -46.11[1]	H_2CO_2 (l) = -424.72[1]	-145.35	-616.18
$NH_4^+HCO_3^-$	NH_3 (g) = -46.11[1]	H_2CO_3 equivalent to CO_2(ao) + H_2O (l) = -699.65[1]	-145.35	-891.11
$NH_4^+CH_3COO^-$	NH_3 (g) = -46.11[1]	CH_3COOH (l) = -484.5[1]	-145.35	-675.96
NH_4^+picrate⁻	NH_3 (g) = -46.11[1]	picric acid (s) = -217.9[1,11]	-145.35	-409.36
NH_4^+3,5-dinitrobenzoate⁻	NH_3 (g) = -46.11[1]	3,5-dinitrobenzoic acid (s) = -432.6[1]	-145.35	-623.52
$NH_4^+N(NO_2)_2^-$	NH_3 (g) = -46.11[1]	$HN(NO_2)_2$ (l) = +34.13[3]	-145.35	-157.33
$NH_4^+H_2NCOO^-$	NH_3 (g) = -46.11[1]	H_2NCOOH (s) = -550.75[9]	-145.35	-742.21
$NH_4^+H_2NCOO^-$	NH_3 (g) = -46.11[1]	H_2NCOOH (s) = -438.75[10]	-145.35	-629.91
$(H_2N)_3C^+$picrate⁻	guanidine (s) = -56.1[1]	picric acid (s) = -217.9[11]	-156.8	-430.8
$(H_2N)_3C^+N(NO_2)_2^-$	guanidine (s) = -56.1[1]	$HN(NO_2)_2$ (l) = +34.13[3]	-156.8	-178.77
$(H_2N)_3C^+$3,5-dinitrobenzoate⁻	guanidine (s) = -56.1[1]	3,5-dinitrobenzoic acid (s) = -432.06[1]	-156.8	-644.96
$AG^+N(NO_2)_2^-$	AG (s) = +58.5[2]	$HN(NO_2)_2$ (l) = +34.13[3]	-163.1	-70.47
$TAG^+N(NO_2)_2^-$	TAG (s) = +287.7[2]	$HN(NO_2)_2$ (l) = +34.13[3]	-163.8	+158.03
$N_2H_5^+C(NO_2)_3^-$	N_2H_4 (l) = +50.63[1]	$HC(NO_2)_3$ (s) = -48.2[4]	-128.1	-125.67
$N_2H_5^+NTO^-$	N_2H_4 (l) = +50.63[1]	HNTO (s) = -129.4[7]	-128.1	-206.87
$N_2H_5^+N(NO_2)_2^-$	N_2H_4 (l) = +50.63[1]	$HN(NO_2)_2$ (l) = +34.13[3]	-128.1	-43.34
$N_2H_5^+CH_3NNO_2^-$	N_2H_4 (l) = +50.63[1]	CH_3NHNO_2 (l) = -61.0[8]	-128.1	-138.47
$NH_3OH^+N(NO_2)_2^-$	NH_2OH (s) = -114.8[1]	$HN(NO_2)_2$ (l) = +34.13[3]	-78.2	-158.87

[1]Value taken from NBS tables. [2]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [3]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3; value for $\Delta_{vap} H_m^\circ$ obtained from RoseBoom©. [4]Value taken from NIST webbook https://webbook.nist.gov/chemistry/. [5]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3; value for $\Delta_{vap} H_m^\circ$ obtained from RoseBoom©. [6]Stated in NBS tables as being equivalent to CO_2 (g) and H_2O (l). [7]Value taken from Sinditskii, V. P.; Smirnov, S. P.; Egorshev, V. Y. *Thermal decomposition of NTO: explanation of high activation energy,* Proc. 37th Int. Ann. Conf. ICT Karlsruhe, Germany, 2006, pp. 40-1 – 40-16. [8]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3 (-9.9 kJ·mol⁻¹); value for $\Delta_{vap} H_m^\circ$ (51.0 kJ·mol⁻¹) obtained from RoseBoom©. [9]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3 (-438.45 kJ·mol⁻¹); value for $\Delta_{sub} H_m^\circ$ (112.3 kJ·mol⁻¹) obtained from RoseBoom©. [10]H_2NCOOH is unstable above -23°C with respect to the formation of NH_3 and CO_2, both NH_3 and CO_2 are gases under ambient conditions. [11]Value taken from Byrd, E.F.C.; Rice, B.M. Improved prediction of heats for formation of energetic materials using quantum mechanical calculations. *J. Phys. Chem. A* **2006**, *110*, 1005-1013.

Table S4. Computational results on 1:1 adducts at CBS-4M level of theory.

Compound	$\Delta_{trs}H^{\circ}$ base (kJ·mol⁻¹)	$\Delta_{trs}H^{\circ}$ acid (kJ·mol⁻¹)	$\Delta_f H^{\circ}$(g) Adduct (kJ·mol⁻¹)	$\Delta_f H^{\circ}$(s) Adduct (kJ·mol⁻¹)
$NH_3 \bullet HC(NO_2)_3$	0	$\Delta_{sub}H^{\circ} = 45.8$[2]	-67.9	-113.7
$NH_3 \bullet HN_3$	0	$\Delta_{vap}H^{\circ} = 30$[10]	+232.56	+202.56
$NH_3 \bullet H_2CO_2$	0	$\Delta_{vap}H^{\circ} = 36.0$[2]	-459.3	-495.3
$NH_3 \bullet H_2CO_3$	0	$\Delta_{vap}H^{\circ}$ H₂O = 43.99[11]	-696.3	-740.29
$NH_3 \bullet CH_3COOH$	0	$\Delta_{vap}H^{\circ} = 42.0$[2]	-516.97	-558.97
$NH_3 \bullet$ picric acid	0	$\Delta_{sub}H^{\circ} = 105.1$[5]	-182.91	-288.01
$NH_3 \bullet$ 3,5-dinitrobenzoic acid	0	$\Delta_{sub}H^{\circ} = 134$[6]	-437.44	-571.44
$NH_3 \bullet HN(NO_2)_2$	0	$\Delta_{vap}H^{\circ} = 63.4$[4]	+64.69	+1.09
$NH_3 \bullet H_2NCOOH$	0	0[8]	-518.3	-518.3
$NH_3 \bullet H_2NCOOH$	0	$\Delta_{sub}H^{\circ} = 112.3$[9]	-518.3	-630.6
$(H_2N)_2CNH \bullet$ picric acid	$\Delta_{sub}H^{\circ} = 78.3$[1]	$\Delta_{sub}H^{\circ} = 105.1$[5]	-201.4	-384.8
$(H_2N)_2CNH \bullet HN(NO_2)_2$	$\Delta_{sub}H^{\circ} = 78.3$[1]	$\Delta_{sub}H^{\circ} = 63.4$[4]	+51.62	-90.08
$(H_2N)_2CNH \bullet$ 3,5-dinitrobenzoic acid	$\Delta_{sub}H^{\circ} = 78.3$[1]	$\Delta_{sub}H^{\circ} = 134$[6]	-376.2	-588.5
$AG \bullet HN(NO_2)_2$	$\Delta_{sub}H^{\circ} = 65.4$[1]	$\Delta_{vap}H^{\circ} = 63.4$[4]	+146.61	+17.81
$TAG \bullet HN(NO_2)_2$	$\Delta_{sub}H^{\circ} = 65.4$[1]	$\Delta_{vap}H^{\circ} = 63.4$[4]	+405.30	+263.7
$N_2H_4 \bullet HC(NO_2)_3$	$\Delta_{vap}H^{\circ} = 44.5$[2]	$\Delta_{sub}H^{\circ} = 45.8$[2]	+83.10	-7.2
$N_2H_4 \bullet HNTO$	$\Delta_{vap}H^{\circ} = 44.5$[2]	$\Delta_{sub}H^{\circ} = 110.5$[7]	+29.8	-125.2
$N_2H_4 \bullet HN(NO_2)_2$	$\Delta_{vap}H^{\circ} = 44.5$[2]	$\Delta_{vap}H^{\circ} = 63.4$[4]	+191.37	+83.47
$N_2H_4 \bullet CH_3NHNO_2$	$\Delta_{vap}H^{\circ} = 44.5$[2]	$\Delta_{vap}H^{\circ} = 51.0$[4]	+61.32	-34.18
$NH_2OH \bullet HN(NO_2)_2$	$\Delta_{sub}H^{\circ} = 64.2$[2]	$\Delta_{vap}H^{\circ} = 63.4$[4]	+62.93	-64.67

[1]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [2]Value taken from Acree Jr., W.; Chickos, J.S. Enthalpies of Sublimation of Organic an Organometallic Compounds. 1910 - 2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537–698. [3]Value taken from NIST webbook https://webbook.nist.gov/chemistry/. [4]Value for $\Delta_{vap}H^{\circ}_m$ estimated using RoseBoom©. [5]Value taken from Keshavarz, M.H. Improved prediction of heats of sublimation of energetic compounds using their molecular structure. *J. Haz. Mater.* **2010**, 177, 648-659. [6]Value of $\Delta_{sub}H^{\circ}_m$ for the 2,4-dinitrobenzoic acid isomer used from Vecchio, S.; Brunetti, B. Vapor pressures and standard molar enthalpies, entropies, and Gibbs free energies of sublimation of 2,4- and 3,4-dinitrobenzoic acid. *J. Chem. Thermodyn.* **2009**, *41*, 880-887. [7]Value taken from Sinditskii, V. P.; Smirnov, S. P.; Egorshev, V. Y. *Thermal decomposition of NTO: explanation of high activation energy,* Proc. 37th Int. Ann. Conf. ICT Karlsruhe, Germany, 2006, pp. 40-1 – 40-16. [8]Using a value of $\Delta_{sub}H^{\circ}_m = 0$ for H₂NCOOH since it is unstable above -23°C and both NH₃ and CO₂ are gases at room temperature. [9]Value for $\Delta_{sub}H^{\circ}_m$ estimated using RoseBoom©. [10]Argonne National Laboratory Active Thermochemical Tables. [11]Values take from Chickos, J.S.; Acree Jr., W. Enthalpies of Vaporization of Organic and Organometallic Compounds. 1880 - 2002. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519–878.

Table S5. Computational results on 1:1 adducts at CBS-QB3 level of theory.

Compound	$\Delta_{trs}H^{\circ}$ base (kJ·mol^{-1})	$\Delta_{trs}H^{\circ}$ acid (kJ·mol^{-1})	$\Delta_f H^{\circ}$(g) Adduct (kJ·mol^{-1})	$\Delta_f H^{\circ}$(s) Adduct (kJ·mol^{-1})
NH$_3$•HC(NO$_2$)$_3$	0	$\Delta_{sub}H^{\circ}$ = 45.8[2]	-99.15	-144.95
NH$_3$•HN$_3$	0	$\Delta_{vap}H^{\circ}$ = 30[10]	+223.7	+193.7
NH$_3$•H$_2$CO$_2$	0	$\Delta_{vap}H^{\circ}$ = 36.0[2]	-469	-505
NH$_3$•H$_2$CO$_3$	0	$\Delta_{vap}H^{\circ}$ H$_2$O = 43.99[2]	-699.58	-743.57
NH$_3$•CH$_3$COOH	0	$\Delta_{vap}H^{\circ}$ = 42.0[2]	-518.12	-560.12
NH$_3$•picric acid	0	$\Delta_{sub}H^{\circ}$ = 105.1[5]	-219.81	-324.91
NH$_3$•HN(NO$_2$)$_2$	0	$\Delta_{vap}H^{\circ}$ = 63.4[4]	+4.13	-59.27
NH$_3$•H$_2$NCOOH	0	0[8]	-524.89	-524.89
NH$_3$•H$_2$NCOOH	0	$\Delta_{sub}H^{\circ}$ = 112.3[9]	-524.89	-637.19
(H$_2$N)$_2$CNH•HN(NO$_2$)$_2$	$\Delta_{sub}H^{\circ}$ = 78.3[1]	$\Delta_{sub}H^{\circ}$ = 63.4[4]	+18.31	-123.39
(H$_2$N)$_2$CNH•3,5-dinitrobenzoic acid	$\Delta_{sub}H^{\circ}$ = 78.3[1]	$\Delta_{sub}H^{\circ}$ = 134[6]	-407.34	-619.64
AG•HN(NO$_2$)$_2$	$\Delta_{sub}H^{\circ}$ = 65.4[1]	$\Delta_{vap}H^{\circ}$ = 63.4[4]	+111.53	-17.27
TAG•HN(NO$_2$)$_2$	$\Delta_{sub}H^{\circ}$ = 65.40[1]	$\Delta_{vap}H^{\circ}$ = 63.4[4]	+372.76	+231.16
N$_2$H$_4$•HC(NO$_2$)$_3$	$\Delta_{vap}H^{\circ}$ = 44.5[2]	$\Delta_{sub}H^{\circ}$ = 45.8[2]	+39.03	-51
N$_2$H$_4$•HNTO	$\Delta_{vap}H^{\circ}$ = 44.5[2]	$\Delta_{sub}H^{\circ}$ = 110.5[7]	+19.99	-135.01
N$_2$H$_4$•HN(NO$_2$)$_2$	$\Delta_{vap}H^{\circ}$ = 44.5[2]	$\Delta_{vap}H^{\circ}$ = 63.4[4]	+141.70	+33.8
N$_2$H$_4$•CH$_3$NHNO$_2$	$\Delta_{vap}H^{\circ}$ = 44.5[2]	$\Delta_{vap}H^{\circ}$ = 51.0[4]	+47.79	-47.71
NH$_2$OH•HN(NO$_2$)$_2$	$\Delta_{sub}H^{\circ}$ = 64.2[2]	$\Delta_{vap}H^{\circ}$ = 63.4[4]	+23.41	-104.19

[1]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [2]Value taken from Acree Jr., W.; Chickos, J.S. Enthalpies of Sublimation of Organic an Organometallic Compounds. 1910 - 2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537–698. [3]Value taken from NIST webbook https://webbook.nist.gov/chemistry/. [4]Value for $\Delta_{vap}H_m^{\circ}$ estimated using RoseBoom©. [5]Value taken from Keshavarz, M.H. Improved prediction of heats of sublimation of energetic compounds using their molecular structure. *J. Haz. Mater.* **2010**, 177, 648-659. [6]Value of $\Delta_{sub}H_m^{\circ}$ for the 2,4-dinitrobenzoic acid isomer used from Vecchio, S.; Brunetti, B. Vapor pressures and standard molar enthalpies, entropies, and Gibbs free energies of sublimation of 2,4- and 3,4-dinitrobenzoic acid. *J. Chem. Thermodyn.* **2009**, *41*, 880-887. [7]Value taken from Sinditskii, V. P.; Smirnov, S. P.; Egorshev, V. Y. *Thermal decomposition of NTO: explanation of high activation energy*, Proc. 37th Int. Ann. Conf. ICT Karlsruhe, Germany, 2006, pp. 40-1 – 40-16. [8]Using a value of $\Delta_{sub}H_m^{\circ}$ = 0 for H$_2$NCOOH since it is unstable above -23°C and both NH$_3$ and CO$_2$ are gases at room temperature. [9]Value for $\Delta_{sub}H_m^{\circ}$ estimated using RoseBoom©. [10]Argonne National Laboratory Active Thermochemical Tables.

Table S6. Computational results on 2:1 salts at CBS-4M level of theory.

Compound	$\Delta_f H^\circ$ base (kJ·mol⁻¹)	$\Delta_f H^\circ$ acid (kJ·mol⁻¹)	$\Delta_r H$ (kJ·mol⁻¹)	$\Delta_f H^\circ$ (s) salt (kJ·mol⁻¹)
TKX-50	2 x NH₂OH (s) 2 x -114.8[1]	+542.2[6]	2 x -78.2	+156.2
TKX-50	2 x NH₂OH (s) 2 x -114.8[1]	+554.1[5]	2 x -78.2	+168.1
GZT	2 x G (s) 2 x -56.1[1]	+806.4[2]	2 x -156.8	+380.6
(AG)₂AzT	2 x AG (s) 2 x +58.5[3]	+806.4[2]	2 x -163.1	+597.2
(DAG)₂AzT	2 x DAG (s) 2 x +167.4[3]	+806.4[2]	2 x 150.6	+840
(TAG)₂AzT	2 x TAG (s) 2 x +287.7[3]	+806.4[2]	2 x -163.8	+1054.2
(NH₄)₂AzT	2 x NH₃ (g) 2 x -46.11[1]	+806.4[2]	2 x -145.35	+423.48
(N₂H₅)₂AzT	2 x N₂H₄ (l) 2 x +50.63[1]	+806.4[2]	2 x -128.1	+651.5
(G)₂CO₃	2 x G (s) 2 x -56.1[1]	-607.78[4]	2 x -156.8	-1033.58
(NH₄)₂SO₄	2 x NH₃ (g) 2 x -46.11[1]	-813.989[1]	2 x -145.35	-1196.9
(NH₃OH)₂SO₄	2 x NH₂OH (s) 2 x -114.8[1]	-813.989[1]	2 x -78.20	-1200.0
(NH₄)₂C₂O₄	2 x NH₃ (g) 2 x -46.11[1]	-827.2[1]	2 x -145.35	-1210.12

[1]Value taken from NBS tables. [2]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M; $\Delta_{sub} H_m^\circ$ estimated based on value for the acid of TKX-50 estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 (129 kJ·mol⁻¹). [3]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [4]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M. [5]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M; $\Delta_{sub} H_m^\circ$ estimated using RoseBoom© (117.1 kJ·mol⁻¹). [6]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M; $\Delta_{sub} H_m^\circ$ estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 (129 kJ·mol⁻¹).
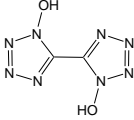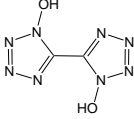
Table S7. Computational results on 2:1 salts at CBS-QB3 level of theory.

Compound	$\Delta_f H^\circ$ base (kJ·mol⁻¹)	$\Delta_f H^\circ$ acid (kJ·mol⁻¹)	$\Delta_r H$ (kJ·mol⁻¹)	$\Delta_f H^\circ$ (s) salt (kJ·mol⁻¹)
TKX-50	2 x NH₂OH (s) 2 x -114.8[1]	+542.5[2]	2 x -78.2	+156.5
TKX-50	2 x NH₂OH (s) 2 x -114.8[1]	+554.3[3]	2 x -78.2	+168.3
GZT	2 x G (s) 2 x -56.1[1]	+800[5]	2 x -156.8	+374.2
(AG)₂AzT	2 x AG (s) 2 x +58.5[4]	+800[5]	2 x -163.1	+590.8
(DAG)₂AzT	2 x DAG (s) 2 x +167.4[4]	+800[5]	2 x 150.6	+833.6
(TAG)₂AzT	2 x TAG (s) 2 x +287.7[4]	+800[5]	2 x -163.8	+1047.8
(NH₄)₂AzT	2 x NH₃ (g) 2 x -46.11[1]	+800[5]	2 x -145.35	+417.08
(N₂H₅)₂AzT	2 x N₂H₄ (l) 2 x +50.63[1]	+800[5]	2 x -128.1	+645.06
(G)₂CO₃	2 x G (s) 2 x -56.1[1]	-618.83[2]	2 x -156.8	-1044.6
(NH₄)₂SO₄	2 x NH₃ (g) 2 x -46.11[1]	-813.989[1]	2 x -145.35	-1196.9
(NH₃OH)₂SO₄	2 x NH₂OH (s) 2 x -114.8[1]	-813.989[1]	2 x -78.2	-1200.0
(NH₄)₂C₂O₄	2 x NH₃ (g) 2 x -46.11[1]	-827.2[1]	2 x -145.35	-1210.2

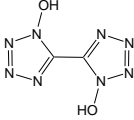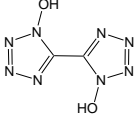[1]Value taken from NBS tables. [2]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3; $\Delta_{sub} H_m^\circ$ for TKX-50 estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 (129 kJ·mol⁻¹). [3]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M; $\Delta_{sub} H_m^\circ$ estimated using RoseBoom© (117.1 kJ·mol⁻¹). [4]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [4]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-4M. [5]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3; $\Delta_{sub} H_m^\circ$ estimated based on value for the acid of TKX-50 estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 (129 kJ·mol⁻¹). [6]Value for $\Delta_f H_m^\circ$(g) calculated using CBS-QB3.

Table S8. Computational results on 2:1 adducts at CBS-4M level theory.

Compound	$\Delta_{trs}H^\circ$ base (kJ·mol^{-1})	$\Delta_{trs}H^\circ$ acid (kJ·mol^{-1})	$\Delta_f H^\circ$(g) Adduct (kJ·mol^{-1})	$\Delta_f H^\circ$(s) Adduct (kJ·mol^{-1})
NH$_2$OH• •NH$_2$OH	2 x $\Delta_{sub}H^\circ$ = 64.2[1]	129[3]	+547.8	+290.4
NH$_2$OH• •NH$_2$OH	2 x $\Delta_{sub}H^\circ$ = 64.2[1]	117.1[5]	+547.8	+302.3
G•H$_2$AzT•G	2 x $\Delta_{sub}H^\circ$ = 78.3[2]	129[4]	+806.82	+521.2
AG•H$_2$AzT•AG	2 x $\Delta_{sub}H^\circ$ = 65.4[2]	129[4]	+999.7	+739.9
DAG•H$_2$AzT•DAG	2 x $\Delta_{sub}H^\circ$ = 74.0[2]	129[4]	+1298.23	+1021.23
TAG•H$_2$AzT•	2 x $\Delta_{sub}H^\circ$ = 78.2[2]	129[4]	+1485.20	+1199.6
NH$_3$•H$_2$AzT•NH$_3$	0	129[4]	+739.83	+610.8
N$_2$H$_4$•H$_2$AzT•N$_2$H$_4$	2 x $\Delta_{vap}H^\circ$ = 44.5[1]	129[4]	+1012.40	+794.4
G•H$_2$CO$_3$•G	2 x $\Delta_{sub}H^\circ$ = 78.3[2]	43.99[1]	-688.51	-889.1
NH$_3$•H$_2$SO$_4$•NH$_3$	0	56[6]	-892.97	-948.97
NH$_2$OH•H$_2$SO$_4$•NH$_2$OH	2 x $\Delta_{sub}H^\circ$ = 64.2[1]	56[6]	-891.69	-1076.09
NH$_3$•H$_2$C$_2$O$_4$•NH$_3$	0	93[1]	-888.43	-981.43

[1]Value taken from Acree Jr., W.; Chickos, J.S. Enthalpies of Sublimation of Organic an Organometallic Compounds. 1910 - 2001. Part 1. C1–C10. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537–698. [2]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [3]Value for $\Delta_{sub}H^\circ_m$ estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0. [4]Value for $\Delta_{sub}H^\circ_m$ estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 for acid of TKX-50 was used. [5]Value for $\Delta_{sub}H^\circ_m$ estimated using RoseBoom©. [6]Value taken from https://www.chemicalbook.com/ProductMSDSDetailCB9675634_EN.htm.

Table S9. Computational results on 2:1 adducts at CBS-QB3 level of theory.

Compound	$\Delta_{trs}H_m^\circ$ base (kJ·mol⁻¹)	$\Delta_{trs}H_m^\circ$ acid (kJ·mol⁻¹)	$\Delta_f H^\circ$(g) Adduct (kJ·mol⁻¹)	$\Delta_f H^\circ$(s) Adduct (kJ·mol⁻¹)
NH₂OH• •NH₂OH	$2 \times \Delta_{sub}H^\circ = 64.2$[1]	129[3]	+547.8	+290.40
NH₂OH• •NH₂OH	$2 \times \Delta_{sub}H^\circ = 64.2$[1]	117.1[5]	+547.8	+302.3
G•H₂AzT•G	$2 \times \Delta_{sub}H^\circ = 78.3$[2]	129[4]	+806.82	+521.2
AG•H₂AzT•AG	$2 \times \Delta_{sub}H^\circ = 65.4$[2]	129[4]	+999.7	+739.9
DAG•H₂AzT•DAG	$2 \times \Delta_{sub}H^\circ = 74.0$[2]	129[4]	+1298.23	+1021.23
TAG•H₂AzT•	$2 \times \Delta_{sub}H^\circ = 78.2$[2]	129[4]	+1485.2	+1199.6
NH₃•H₂AzT•NH₃	0	129[4]	+739.83	+610.8
N₂H₄•H₂AzT•N₂H₄	$2 \times \Delta_{vap}H^\circ = 44.5$[1]	129[4]	+1012.4	+794.4
G•H₂CO₃•G	$2 \times \Delta_{sub}H^\circ = 78.3$[2]	43.99[1]	-688.51	-889.1
NH₃•H₂SO₄•NH₃	0	56[6]	-892.97	-948.97
NH₂OH•H₂SO₄•NH₂OH	$2 \times \Delta_{sub}H^\circ = 64.2$[1]	56[6]	-891.69	-1076.09
NH₃•H₂C₂O₄•NH₃	0	93[1]	-888.43	-981.43

[1]Value taken from Acree Jr., W.; Chickos, J.S. Enthalpies of Sublimation of Organic an Organometallic Compounds. 1910 - 2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537–698. [2]Value taken from Dorofeeva, O.V.; Ryzhova, O.N.; Sinditskii, V.P. Enthalpy of formation of guanidine and its amino and nitro derivatives. *Struct. Chem.* **2015**, *26*, 1629-1640. [3]Value for $\Delta_{sub}H_m^\circ$ estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0. [4]Value for $\Delta_{sub}H_m^\circ$ estimated using Keshavarz, M.H. (**2021**). Energetic Materials Designing Bench (EMDB), Version 2.0 for acid of TKX-50 was used. [5]Value for $\Delta_{sub}H_m^\circ$ estimated using RoseBoom©. [6]Value taken from https://www.chemicalbook.com/ProductMSDSDetailCB9675634_EN.htm.