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1. Single crystal X-ray diffraction

1.1 4,4,4-Trinitrobutanamide (1)

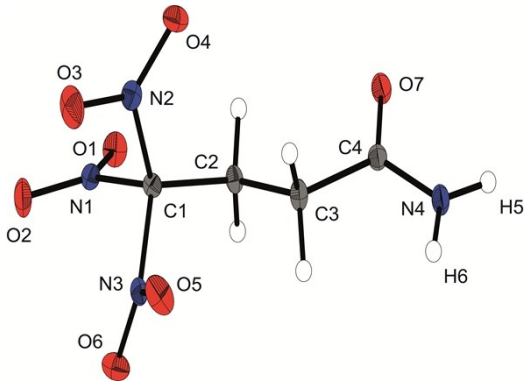

Figure S1. Molecular structure of 4,4,4-trinitrobutanamide (**1**).

Table S1. Hydrogen bonds of compound **1**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
C3	H3	O5	1−*x*, 1−*y*, −*z*	2.702	0.96	3.600	155.6
C2	H2	O4	1−*x*, 1−*y*, 1−*z*	2.434	0.95	3.276	145.7
N4	H6	O7	2−*x*, −*y*, 1−*z*	2.073	0.89	2.933	170.9
N4	H5	O6	2−*x*, 1−*y*, −*z*	2.440	0.86	3.314	168.3
C2	H1	O7	2−*x*, 1−*y*, 1−*z*	2.640	0.95	3.531	156.2

1.2 4,4,4-Trinitrobutanoic acid (2)

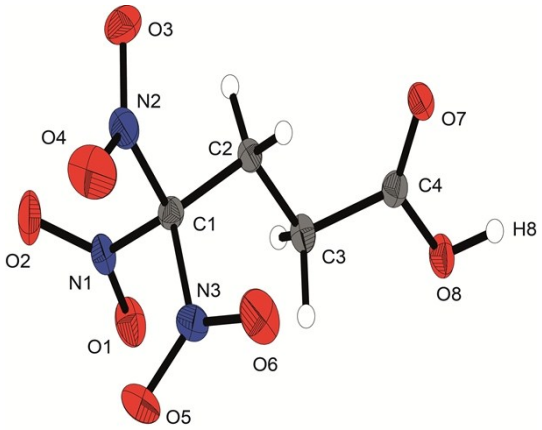

Figure S2. Molecular structure of 4,4,4-trinitrobutanoic acid (**2**).

Table S2. Hydrogen bonds of compound **2**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
C2	H1	O1	−1+*x*, *y*, *z*	2.628	0.96	3.565	166.3
O8	H8	O7	1−*x*, −*y*, −*z*	1.769	0.86	2.632	176.5
C2	H2	O4	−0.5+*x*, 0.5−*y*, −0.5+*z*	2.547	0.94	3.253	136.1
C2	H2	O2	−0.5+*x*, 0.5−*y*, 0.5+*z*	2.653	0.94	3.389	132.5

1.3 4,4,4-Trinitrobutanoyl azide (4)

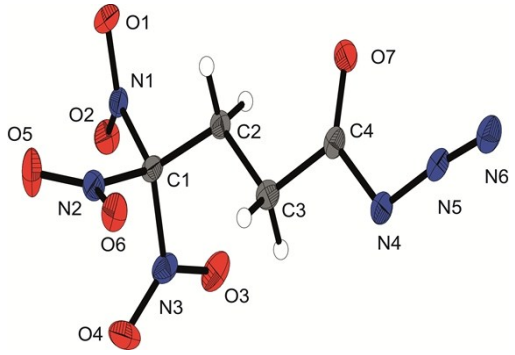

Figure S3. Molecular structure of 4,4,4-trinitrobutanoyl azide (**4**).

Table S3. Hydrogen bonds of compound **4**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
C2	H2	O1	−*x*, 1−*y*, −*z*	2.535	0.96	3.373	144.7
C2	H1	O7	1−*x*, 1−*y*, −*z*	2.386	1.00	3.221	141.3

1.4 3,3,3-Trinitropropyl-1-ammonium chloride (6a)

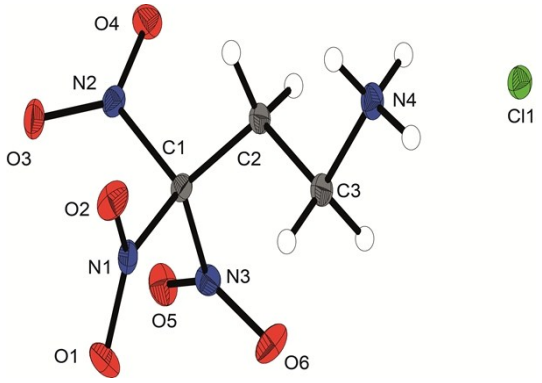

Figure S4. Molecular structure of 3,3,3-trinitropropyl-1-ammonium chloride (**6a**).

Table S4. Hydrogen bonds of compound **6a**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
N4	H6	O7		1.909	0.88	2.779	168.7
N4	H7	Cl1	−*x*+1, −*y*+2, −*z*+1	2.549	0.88	3.254	137.6
N4	H7	O5	*x*+1, *y*+1, *z*	2.574	0.88	3.206	129.3
N4	H8	Cl1		2.273	0.88	3.146	169.6
O7	H9	Cl1	*x*+1, *y*, *z*	2.469	0.82	3.235	155.2
O7	H10	Cl1	−*x*+1, −*y*+1, −*z*+1	2.380	0.82	3.184	169.0

1.5 3,3,3-Trinitropropyl-1-ammonium nitrate (6b)

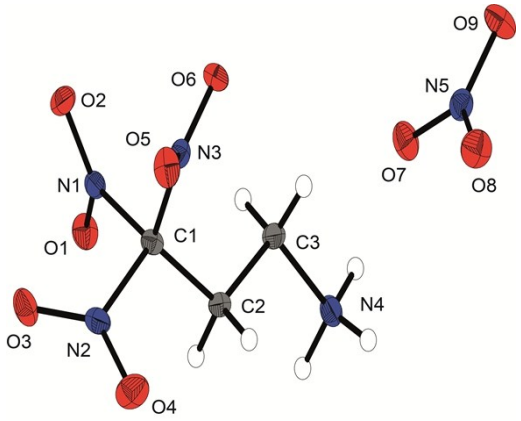

Figure S5. Molecular structure of 3,3,3-trinitropropyl-1-ammonium nitrate (**6b**).

Table S5. Hydrogen bonds of compound **6b**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
N4	H5	O9	−*x*+1, *y*−0.5, −*z*+½	1.948	0.91	2.859	173.6
N4	H6	O7		1.957	0.90	2.818	160.0
N4	H6	N5		2.667	0.90	3.391	138.3
N4	H7	O7	−*x*+2, *y*−0.5, −*z*+0.5	2.080	0.92	2.954	158.0
N4	H7	O9	−*x*+2, *y*−0.5, −*z*+0.5	2.361	0.92	3.094	136.5
N4	H7	N5	−*x*+2, *y*−0.5, −*z*+0.5	2.570	0.92	3.465	164.4
C2	H2	O7	−*x*+2, *y*−0.5, −*z*+0.5	2.546	0.91	3.286	138.4

1.6 3,3,3-Trinitropropyl-1-ammonium dinitramide (6d)

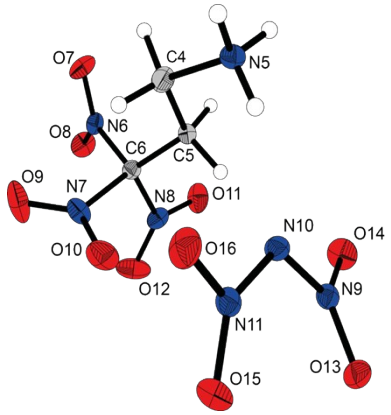

Figure S6. Molecular structure of 3,3,3-trinitropropyl-1-ammonium dinitramide (**6d**).

Table S6. Hydrogen bonds of compound **6d**.

D–H···A			sym. of A	H···A	D–H	D···A	angle, DHA
C1	H4	O3		2.398	0.990	3.027	120.79
C1	H5	O4	−1+*x*, *y*, *z*	2.828	0.990	3.446	121.23
C2	H7	O4	−1+*x*, *y*, *z*	2.930	0.990	3.608	126.54
C1	H5	O2	−*x*, −*y*, 1−*z*	2.485	0.990	3.439	161.87
N1	H1	O7	−1+*x*, −1+*y*, *z*	2.425	0.892	3.281	161.01
C4	H12	O6	−1+*x*, *y*, *z*	2.935	0.990	3.887	161.55
C2	H7	O10	−1+*x*, *y*, *z*	2.709	0.990	3.673	164.62
C1	H4	O11	*x*, −1+*y*, *z*	2.487	0.990	3.146	123.74
N1	H2	O15	−1+*x*, *y*, *z*	2.056	0.904	2.960	178.00
N1	H2	O16	−1+*x*, *y*, *z*	2.600	0.904	3.221	126.51
C2	H6	O13		2.574	0.990	3.460	148.97
N1	H3	O19		2.000	0.898	2.845	156.46
C2	H6	O19		2.579	0.990	3.460	134.42
N5	H9	O16		2.790	0.893	3.422	128.91
C5	H14	O14		2.641	0.990	3.605	164.55
N5	H10	O14	1+*x*, *y*, *z*	2.256	0.921	2.966	133.51
N5	H10	O16	2−*x*, 1−*y*, −*z*	2.356	0.921	3.089	136.31
C5	H13	O20	*x*, 1+*y*, *z*	2.508	0.990	3.334	140.81
N5	H8	O19	1−*x*, 1−*y*, −*z*	2.147	0.875	2.990	161.70
C4	H11	O17	2−*x*, 1−*y*, −*z*	2.408	0.990	3.335	155.71

1.7 2,2,2-Trinitroethyl-4,4,4-trinitrobutanoate (8)

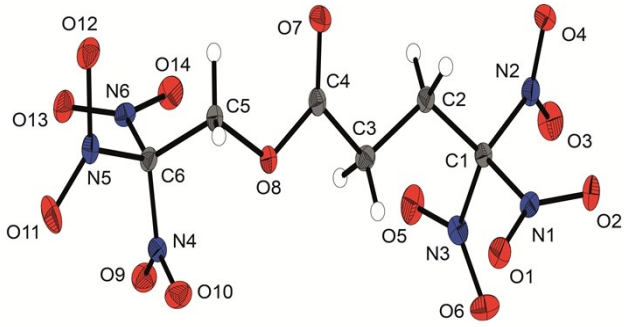

Figure S7. Molecular structure of 2,2,2-trinitroethyl-4,4,4-trinitrobutanoate (**8**).

Table S7. Hydrogen bonds of compound **8**.

D–H···A			sym. of A	H···A	D–H	D···A	∠, DHA
C2	H3	O6	−1+*x*, *y*, *z*	2.673	0.95	3.556	155.5
C5	H6	O10	−1+*x*, *y*, *z*	2.612	0.94	3.388	140.4
C2	H4	O7	−*x*, 1−*y*, 1−*z*	2.509	0.96	3.391	152.1
C3	H1	O12	−0.5+*x*, 0.5−*y*, 0.5+*z*	2.618	0.95	3.419	142.1

1.7 Crystallographic Data and Structure refinements

Table S8. Crystallographic data and structure refinements of **1**, **2**, **4**, and **6a**.

	1	**2**	**4**	**6a**
formula	$C_4H_6N_4O_7$	$C_4H_5N_3O_8$	$C_4H_4N_6O_7$	$C_3H_7N_4O_6Cl \times H_2O$
formula weight [g mol^{-1}]	222.11	223.11	248.13	248.58
temperature [K]	100(2)	100(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	triclinic	triclinic
space group (No.)	*P−1*(2)	$P2_1/n$ (14)	*P−1*(2)	*P−1*(2)
a [Å]	6.1081(5)	6.1307(7)	7.4160(5)	6.7434(6)
b [Å]	7.5366(6)	16.7082(6)	7.5385(6)	7.8045(8)
c [Å]	8.8543(7)	8.5025(4)	9.0347(8)	10.0663(10)
α [°]	80.728(7)	90	70.713(8)	90.393(8)
β [°]	87.505(7)	98.296(4)	80.100(7)	98.800(8)
γ [°]	88.355(6)	90	81.601(7)	114.135(9)
V [Å^3]	401.80(6)	861.82(7)	467.47(6)	476.36(8)
Z	2	4	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.836	1.720	1.763	1.733
μ [mm^{-1}]	0.177	0.171	0.168	0.430
F(000)	228	456	252	256
crystal habit	colorless plate	colorless block	colorless block	colorless plate
crystal size [mm]	0.35 × 0.21 × 0.05	0.25 × 0.22 × 0.18	0.35 × 0.27 × 0.25	0.32 × 0.27 × 0.08
q range [°]	4.27 – 28.27	4.15 – 26.37	4.20 – 26.36	4.23 – 28.28
index ranges	$-8 \le h \le 8$	$-7 \le h \le 5$	$-9 \le h \le 9$	$-7 \le h \le 8$
	$-10 \le k \le 10$	$-18 \le k \le 20$	$-9 \le k \le 9$	$-10 \le k \le 8$
	$-11 \le l \le 11$	$-8 \le l \le 10$	$-11 \le l \le 11$	$-13 \le l \le 13$
reflections measured	3448	3513	4352	4182
reflections independent	1971	1750	1909	2345
reflections unique	1685	1484	1653	2050
R_{int}	0.019	0.019	0.021	0.021
R_1, wR_2 (2σ data)	0.0308, 0.0735	0.0306, 0.0708	0.0309, 0.0726	0.0287, 0.0641
R_1, wR_2 (all data)	0.0380, 0.0794	0.0384, 0.0764	0.0384, 0.0782	0.0355, 0.0680
data/restraints/parameters	1971/0/154	1750/0/156	1909/0/170	2345/0/172
GOOF on F^2	1.060	1.040	1.040	1.083
residual el. density [e Å^{-3}]	−0.228/0.388	−0.198/0.228	−0.215/0.302	−0.292/0.336
CCDC	1506284	1506285	1506286	1506287

Table S9. Crystallographic data and structure refinements of **6b**, **6d**, and **8**.

	6b	**6d**	**8**
formula	$C_3H_7N_4O_6 \times NO_3$	$C_3H_7N_4O_6 \times N_3O_4$	$C_6H_6N_6O_{14}$
formula weight [g mol^{-1}]	257.14	301.16	386.14
temperature [K]	173(2)	123(2)	173(2)
crystal system	orthorhombic	triclinic	monoclinic
space group (No.)	$P2_12_12_1$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a [Å]	5.6622(4)	6.7087(5)	5.7264(3)
b [Å]	10.2826(7)	11.2547(7)	21.6530(11)
c [Å]	16.2582(18)	15.2144(9)	11.0910(6)
α [°]	90	75.527(5)	90
β [°]	90	79.280(5)	93.555(4)
γ [°]	90	75.733(6)	90
V [Å^3]	946.59(14)	1068.48(13)	1372.57(12)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.804	1.872	1.869
μ [mm^{-1}]	0.181	0.188	0.188
F(000)	528	616	784
crystal habit	colorless plate	colorless block	colorless plate
crystal size [mm]	0.32 × 0.28 × 0.08	0.36 × 0.13 ×0.04	0.12 × 0.11 × 0.04
q range [°]	4.11 – 31.44	4.19 – 26.00	4.14 – 27.09
index ranges	$-8 \le h \le 7$	$-8 \le h \le 6$	$-3 \le h \le 7$
	$-15 \le k \le 7$	$-13 \le k \le 13$	$-21 \le k \le 27$
	$-11 \le l \le 23$	$-18 \le l \le 18$	$-14 \le l \le 14$
reflections measured	5194	8204	6223
reflections independent	3069	4176	3023
reflections unique	2567	3456	2572
R_{int}	0.029	0.021	0.021
R_1, wR_2 (2σ data)	0.0424, 0.0793	0.0336, 0.0436	0.0301, 0.0652
R_1, wR_2 (all data)	0.0584, 0.0883	0.1020, 0.1144	0.0390, 0.0700
data/restraints/parameters	3069/0/175	4176/0/361	3023/0/259
GOOF on F^2	1.058	0.826	1.025
residual el. density [e Å^{-3}]	−0.229/0.418	−0.288/0.278	−0.240/0.379
CCDC	1506288	1506289	1506290

2. Theoretical studies

2.1 Theoretical aspects of thermodynamic calculations

The energy of all the compounds were calculated with the quantum chemical composite method CBS-4M. The *ab initio* calculations were carried out using the program package Gaussian 09 (Revision A.03). The geometric structure optimizations and the frequency analyses were performed with Becke's B3 parameter hybrid functional using the B3LYP correlation functional with 6-31G** basis set. All of the optimized structures were verified to be a local energy minimum on the potential energy surface without imaginary frequencies. The structures were optimized with symmetry constraints and the energy is corrected with the zero point vibrational energy (ZPEV). The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method in order to obtain accurate values.

The CBS-4M method starts with a HF/3-21G(d) geometry optimization, which is the initial guess for the following SCF calculation as a base energy and a final MP2/6-31+G calculation with a CBS extrapolation to correct the energy in second order. The used reparametrized CBS-4M method additionally implements a MP4(SDQ)/6-31+(d,p) calculation to approximate higher order contributions and also includes some additional empirical corrections.

The quantum chemical calculation results in an absolute value for $H°_{QC}$ of the compound. The gas phase enthalpies of formation $\Delta_f H°_{(g)}$ can be determined using the atomization method (Equation 1) with the number n_i of atoms A_i in the calculated substance. The values for $\Delta_f H°(A_i)$ are taken from the NIST database.

$$\Delta_f H^\circ_{(g)}(M) = H^\circ_{QC}(M) - \sum_i^{atoms\ A} n_i H^\circ_{QC}(A_i) + \sum_i^{atoms\ A} n_i\, \Delta_f H^\circ(A_i) \qquad \text{Eq. 1}$$

Using the approximation of the Trouton's rule the enthalpy of sublimation $\Delta_{sub}H°$ or enthalpy of vaporization $\Delta_{vap}H°$ can be determined (Equations 2 and 3).

$$\Delta_{sub}H = C_{sub} \cdot T_{melt} \approx 188\frac{J}{mol \cdot K} \cdot T_{melt} \qquad \text{Eq. 2}$$

$$\Delta_{vap}H = \Delta S_{vap} \cdot T_{boil} \approx 90\frac{J}{mol \cdot K} \cdot T_{boil} \qquad \text{Eq. 3}$$

The enthalpy of formation $\Delta_f H°_{(s,l)}$ for the solid (*s*) or liquid (*l*) state can be calculated by Equation 4.

$$\Delta_f H^{\circ}_{(s,l)} = \Delta_f H^{\circ}_{(g)} - \Delta_{sub/vap} H \qquad \text{Eq. 4}$$

The molar standard enthalpies of formation $\Delta_f H°$ were used to calculate the molar solid state energies of formation $\Delta_f U°_{(s,l)}$ according to Equation 5, where Δn is the change of moles of gaseous components:

$$\Delta_f U^{\circ}_{(s,l)} = \Delta_f H^{\circ}_{s,l} - \Delta n_g RT \qquad \text{Eq. 5}$$

2.2 Further predicted detonation and combustion parameters

Table S10. Calculated detonation and combustion parameters (using EXPLO5 V6.02).

	1	**2**	**4**	**6a**	**6b**	**6c**	**6d**	**6e**	**7**	**8**	**AP**
formula	$C_4H_6N_4O_7$	$C_4H_5N_3O_8$	$C_4H_4N_6O_7$	$C_3H_7N_4O_6Cl$	$C_3H_7N_5O_9$	$C_3H_7N_4O_{10}Cl$	$C_3H_7N_7O_{10}$	$C_8H_{14}N_{18}O_{12}$	$C_6H_7N_7O_{13}$	$C_6H_6N_6O_{14}$	NH_4ClO_4
density RT	1.78	1.67	1.71	1.76	1.77	1.97	1.84	1.67	1.84	1.83	1.95
$\Delta H°_f$ /kJ mol^{-1}	−326	−506	54	−96	−169	−119	32	972	−330	−466	−296
$\Delta U°_f$ /kJ kg^{-1}	−1374	−2178	301	−318	−554	−312	205	1851	−770	−1124	−2433
Q_v /kJ kg^{-1}	−4956	−4786	−5607	−5281	−6697	−6250	−6671	−6212	−5820	−6121	−1422
T_{ex} /K	3383	3505	4071	3793	4319	4309	4382	4141	4009	4277	1735
V_0 /L kg^{-1}	733	731	759	744	821	787	828	814	718	719	885
P_{CJ} /kbar	292	246	291	282	335	390	372	299	335	324	158
V_{Det} /m s^{-1}	8187	7624	8259	8019	8913	9096	9282	8541	8628	8616	6368
I_s /s	238	241	261	255	274	265	274	271	262	258	157
I_s /s (5 % Al)	248	248	266	261	276	268	276	278	264	261	198
I_s /s (10 % Al)	256	253	269	267	277	270	277	282	266	262	224
I_s /s (15 % Al)	261	256	270	269	278	270	278	276	267	263	235
I_s /s (20 % Al)	262	258	265	267	276	270	277	270	267	263	244
I_s /s (25 % Al)	251	256	252	265	275	269	276	258	264	262	247
I_s /s (5 % Al, 14 % binder)	216	215	237	230	258	264	266	249	239	242	250
I_s /s (10 % Al, 14 % binder)	232	229	248	243	264	269	272	256	248	251	257
I_s /s (15 % Al, 14 % binder)	244	241	247	247	270	272	275	254	253	255	261