SUPPORTING INFROMATION FOR: ENERGETIC 1,2,4-TRIAZINES: 3,5-DIAMINO-6-NITRO-1,2,4-TRIAZINE AND ITS OXIDE

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Experimental Methods

General Safety Precautions

Caution! The materials prepared in this work are energetic with potential sensitivity to various stimuli. While no issues were encountered in the handling of these compounds, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) are recommended.

General Methods

All reagents and solvents were used as received unless otherwise stated. 3-Azido-5-amino-6-nitro-1,2,4-triazine was prepared according to literature.[1] ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-III-500-HD and Bruker Avance-III-800 (5mm QCI Z-gradient cryoprobe) NMR spectrometer. All chemical shifts are quoted in ppm relative to TMS (1H, 13C). Infrared spectra were recorded with a PerkinElmer Spectrum Two spectrometer with UATR (Universal Attenuated Total Reflectance) accessory. Transmittance values are described as "strong" (s), "medium" (m), "weak" (w), and "very weak" (vw). Melting and decomposition points were measured with a TA Instruments Q50 TGA using heating rates of 5 °Cmin^{-1}. Low resolution mass spectra were measured with an Agilent 1260 Infinity II Quaternary LC instrument. Sensitivity data were determined using a BAM friction tester and BAM Drophammer (OZM research). Elemental analysis was performed using an Elementar vario EL cube elemental analyzer.

3,5-diamino-6-nitro-1,2,4-triazine (DANT)

3-azido-5-amino-6-nitro-1,2,4-triazine (AANT) (2 g; 10.98 mmol) was dissolved in ethanol (175 mL) and heated to 60°C. Stirring vigorously triphenylphosphine (1 eqv.; 2.89 g; 11.02 mmol) was added in portions. Upon the formation of precipitates nitric acid was added in 1 mL portions until solids dissolved. After AANT fully reacted with triphenylphosphine (2 hr) water (100 ml, 500 eqv.) was added to the reaction solution and stirred overnight at 60°C. The solvent was then removed via vacuum and the remaining solid extracted with hot ether (5x; 25 mL) to give DANT a pale-yellow solid (1.171 g; 68% yield). Recrystallization from hot water gives shiny-yellow flakes. ^{1}H NMR (DMSO-d): δ 8.26 (s, 1H), 7.98 (s, 1H), 7.84 (s, 1H) 7.63 (s, 1H); ^{13}C NMR: δ 162.49, 151.12, 143.07; LRMS: 156m/z; IR: 3419 (w), 3392 (w), 3315 (w), 3315 (w), 3215(w), 3169 (w), 3053 (w), 2840 (w), 2688 (w), 2154 (w), 1947 (w), 1623 (m), 1546 (m), 1499 (m), 1464 (m), 1432 (m), 1350 (m), 1306 (m), 1266 (w), 1194 (m), 1163 (m), 1120 (m), 1020 (m), 971 (m), 852 (m), 788 (m), 768 (m), 736 (m), 689 (m), 668 (m), 559 (s), 472 (s); Elemental Analysis (%) for $C_3N_6H_4O_2$ (156.1029 gmol^{-1}): Calcd. C 23.08; H 2.58; N 53.85; O 20.50; Found C 22.56; H 2.55; N 52.66; TGA: $T_{dec.}$ 240°C; Impact Sensitivity: >40 J; Friction Sensitivity: 160-192 N.

3,5-diamino-6-nitro-1,2,4-triazine-2-oxide (DANTX)

DANT (200mg; 1.28mmol) and Oxone® (0.6 eqv.; 472.6 mg) were stirred in water (5 mL) at 40°C for 12 hr. Additional portions of Oxone® (3x; 0.2 eqv.; 157.5 mg) were added in 12hr intervals and the reaction stirred at 40°C until completed. The solution was then extracted with hexane (3x; 10 mL), filtered and washed with water giving a reddish-orange solid (60 mg; 27% yield). The solid crystallized out of nitromethane and a THF/water mixture. ^{1}H NMR (DMSO-d): δ 9.11 (s, 1H), 8.68 (s, 1H), 8.49 (s, 1H), 8.22 (s, 1H); ^{13}C NMR: δ 152.13, 146.42, 127.27; LRMS: 172m/z; IR: 3480 (w), 3455 (w), 3419 (w), 3386 (w), 3362 (w), 3297 (w), 3224 (w), 3176 (w), 2157 (vw), 1664 (m), 1645 (m), 1606 (m), 1566 (m), 1525 (w), 1463 (m), 1435 (m), 1348 (w), 1320 (w), 1277 (m), 1189 (m), 1127 (m), 1080 (m), 965 (m), 912 (m), 868 (m), 803 (m), 758 (m), 744 (m), 721 (m), 690 (m), 668 (m), 643 (m), 601 (m), 552 (s), 498 (s), 470 (s); Elemental Analysis (%) for $C_3N_6H_4O_3$ (172.1023gmol^{-1}): Calcd. C 20.94; H 2.34; N 48.83; O 27.89; Found: C 20.32; H 2.21; N 47.97; TGA: $T_{dec.}$ 200°C; Impact Sensitivity: >40 J; Friction Sensitivity: 144 N (Sensitivity reported for the low-density DANTX polymorph).

Crystallographic Data

Single crystal X-ray diffraction data for DANT were collected on a Bruker Quest diffractometer with a fixed chi angle, a Mo Kα wavelength (λ = 0.71073 Å) sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, and a Photon II area detector. Data for the DANTX samples were collected on a Bruker Quest diffractometer with kappa geometry, a Cu Kα wavelength (λ = 1.54178 Å) I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror for monochromatization, and a Photon III C14 area detector. Both instruments were equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3[2] and SADABS[3]. The space groups were assigned using XPREP within the SHELXTL suite of programs[4, 5] and solved by direct methods using ShelXS[5] and refined by full matrix least squares against F^2 with all reflections using Shelxl2018[6, 7] using the graphical interface Shelxle[8]. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.98 Å for aliphatic CH_3 moieties and were allowed to rotate but not to tip to best fit the experimental electron density. The solvate molecule in the DANTX acetonitrile solvate is located on a two-fold axis and the methyl H-atoms are thus 1:1 disordered. N-H bond distances were either constrained to 0.88 Å and NH_2 groups were constrained to be planar (sp^2 hybridized) (for DANT, DANTX-DMSO solvate) or amine H atom positions were freely refined (DANTX low and high density polymorphs, DANTX-ACN solvate). $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3 and 1.2 or 1.5 for NH_2 units, respectively.

Additional data collection and refinement details are given in the table below. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2057283-2057287 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic Data

	DANT	DANTX			
Name	DANT	Low density polymorph	High-density polymorph	Dimethyl sulfoxide solvate	Acetonitrile solvate
Crystallization Solvent	Water	Nitromethane	Tetrahydrofuran	Dimethyl Sulfoxide	Acetonitrile
Formula	$C_3H_4N_6O_2$	$C_3H_4N_6O_3$	$C_3H_4N_6O_3$	$C_3H_4N_6O_3 \bullet C_2H_6OS$	$2(C_3H_4N_6O_3) \bullet C_2H_3N$
Formula Weight [g mol^{-1}]	156.12	172.12	172.12	250.25	385.30
Temperature [K]	150	150	150	150	150
Crystal System	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space Group	$P\,2_1/c$	$P\bar{1}$	$P\,2_1/c$	$P\bar{1}$	$C2/c$
a [Å]	4.6115 (11)	6.6850 (5)	5.0535 (3)	5.4545 (2)	16.754 (4)
b [Å]	16.953 (4)	8.7556 (6)	5.3907 (3)	9.4042 (3)	12.645 (2)
c [Å]	7.4329 (19)	11.9207 (8)	22.3375 (11)	10.8334 (5)	7.1381 (15)
α [°]	90	79.812 (3)	90	98.907 (2)	90
β [°]	100.679 (10)	81.840 (3)	93.131 (4)	102.005 (2)	95.214 (11)
γ [°]	90	69.876 (3)	90	99.824 (1)	90
V [Å3]	571.0 (2)	642.32 (8)	607.61 (6)	525.03 (4)	1506.0 (5)
Z	4	4	4	2	4
ρ [g cm^{-3}] [150 K]	1.816	1.780	1.882	1.583	1.699
R1 /wR2 (all data)	0.1265/0.1858	0.0463/0.1373	0.0376/0.1043	0.0476/0.1215	0.0383/0.1019
R2/wR2 (I>2σ)	0.0707/0.1612	0.0430/0.1337	0.0359/0.1024	0.0442/0.1181	0.0355/0.0990
S	1.01	1.12	1.14	1.07	1.04
No. of reflec.	1408	2587	1308	2140	1455
Restraints	0	0	0	0	0
CCDC[a]	2057283	2057287	2057284	2057286	2057285

[a]These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

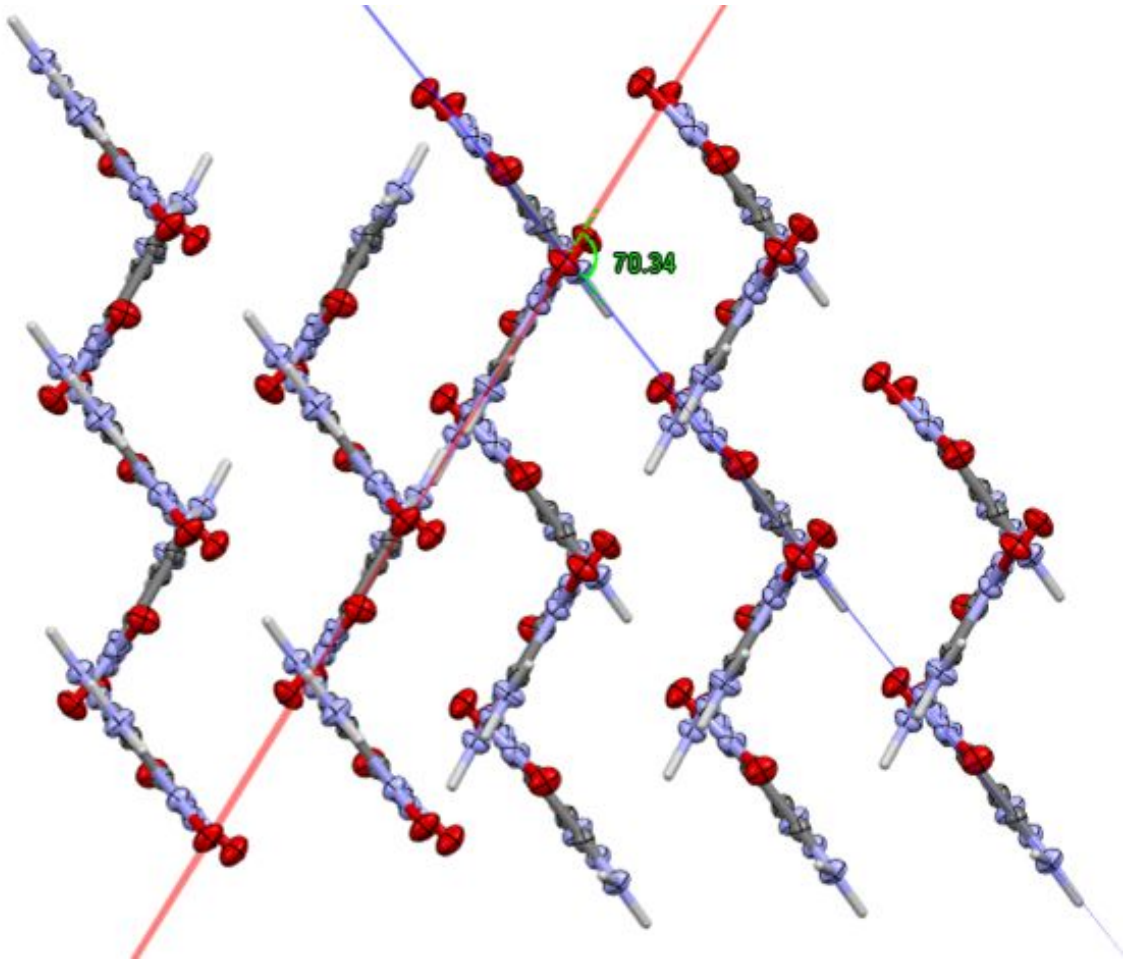

Figure 1. Ribbon rotation for mixed crystal structure of high-density DANTX.

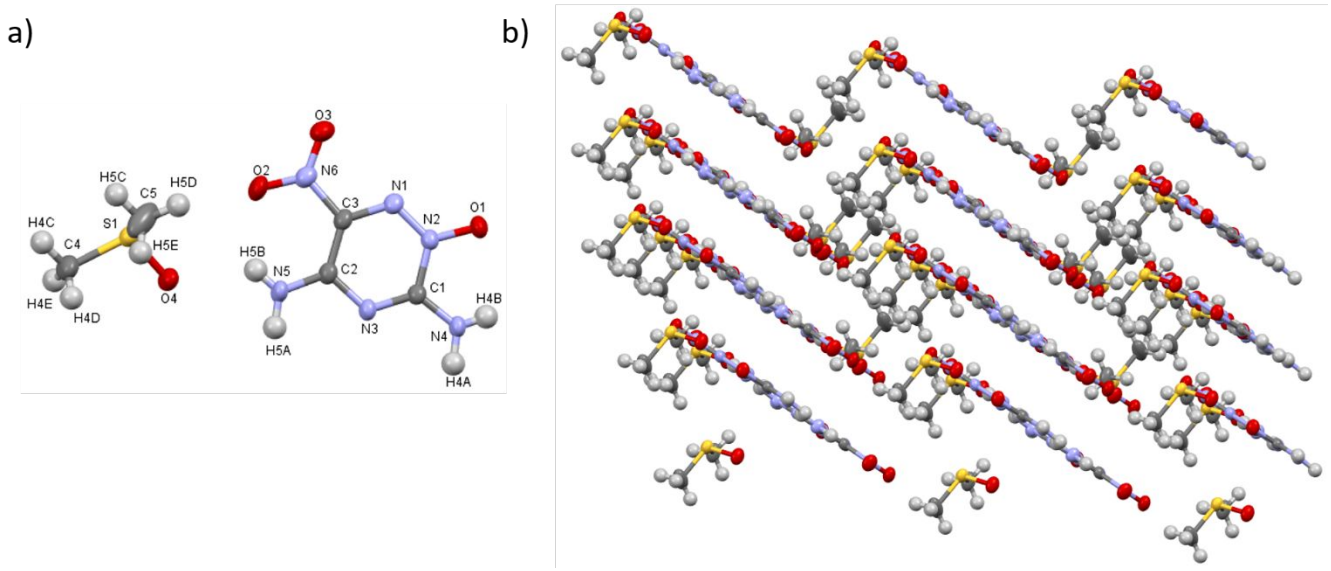

Figure 2. a) DMSO solvated-crystal X-ray structure of DANTX; b) Packing diagram of DANTX●DMSO solvated crystal

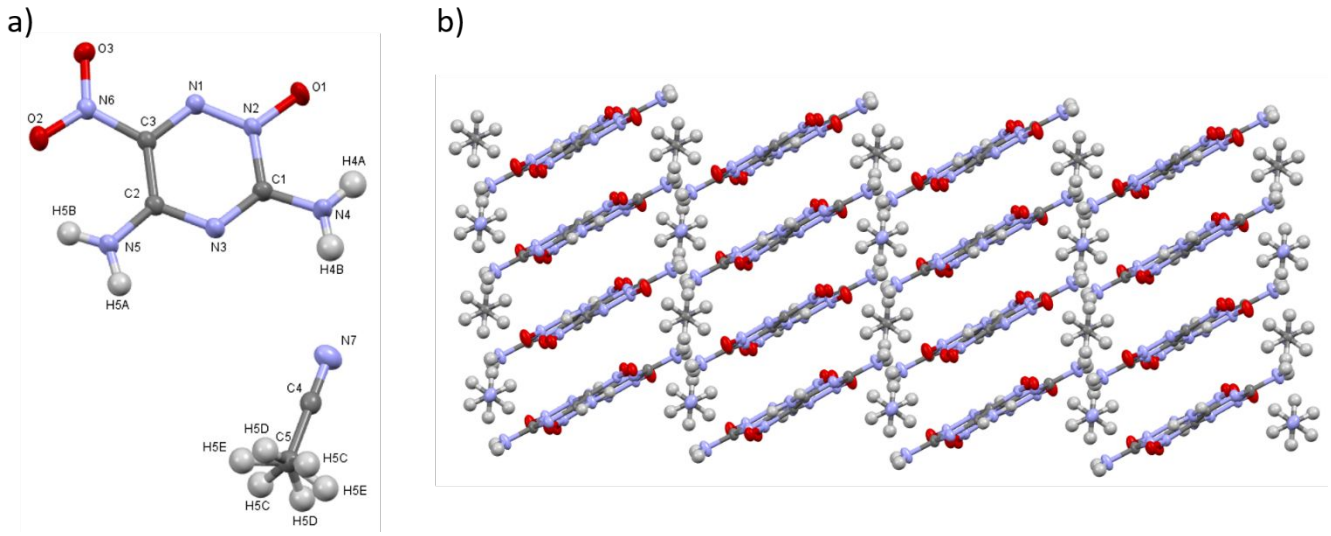

Figure 3. a) MeCN solvated-crystal X-ray structure of DANTX; b) Packing diagram of DANTX●1/2MeCN solvated crystal

Heats of Formation and Sublimation

Table 2. Heats of formation and sublimation for DANT and DANTX

	Solid-State $\Delta_f H_m$ [kJ mol^{-1}]	Gas-phase $\Delta_f H$ [kJ mol^{-1}]	ΔH_{sub} [kJ mol^{-1}]
DANT	134.1	236.04	101.95
DANTX	102.1	205.66	103.55

Thermal Stability

Thermal stabilities were measured by TGA in platinum pans with a heating rate of 5°C per minute; onset of decomposition temperatures were determined as the temperature at which 5% mass loss occurred.

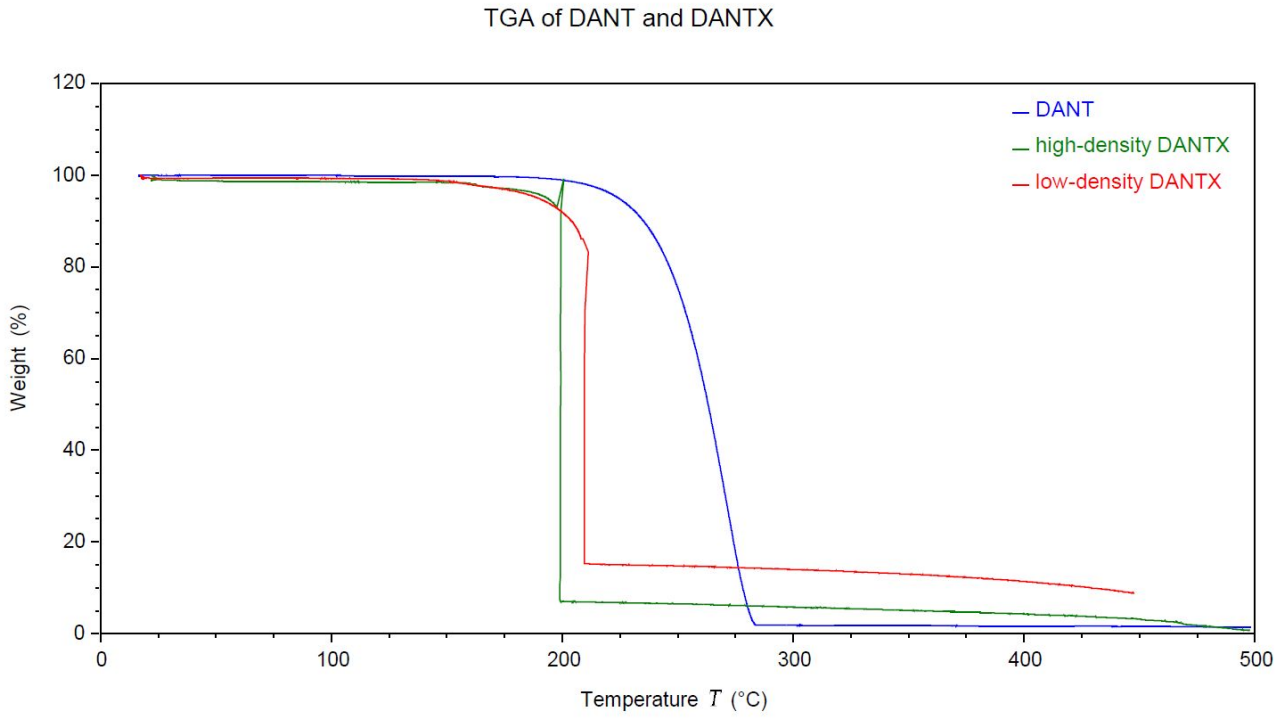

Figure 4. Graph of DANT and DANTX TGA curves generated by TA Instruments Trios V4.4.0.40883

Mechanical Sensitivity

For initial safety testing, impact and friction sensitivities were determined for DANT and DANTX. Impact sensitivity was carried out according to STANAG 4489[9] and modified according to instruction[10] on an OZM drophammer by the BAM method[11]. Friction sensitivity was carried out in accordance with STANAG 4487[12] and modified according to instruction[13] using a BAM friction tester. The determination of DANT decomposition was made based on color-change from yellow to orange.

Energetic Properties

With the Gaussian09 program package[14], the molecular geometries of DANT and DANTX were optimized using the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT)[15-18] with the 6-31G** Pople Gaussian basis set[19-21]. Using the Byrd and Rice method[22-24] for neutral molecules, computational enthalpies of formation and densities were calculated. The computational densities were obtained by dividing the mass of the molecule by the volume calculated from the volume contained within the B3LYP/6-31G** 0.001 electron/bohr3 isosurface of the electron density, and subsequently modified by electrostatic parameters generated from charge distributions of said isosurface. For the computational heat of formation, the B3LYP/6-311++G(2df,2p) energy was computed from the B3LYP/6-31G* optimized geometry to obtain the gas phase heat of formation.

The detonation parameters, for the compounds, at the CJ point were calculated with the EXPLO6.05 software package[25, 26] using the computational heat of formation and the density measured by single-crystal X-ray at room temperature. For solid carbon the software uses the Becker-Kistiakowsky-Wilson's equation of state (CFEOS) [27]. The equilibrium composition of detonation products was calculated utilizing the modified White, Johnson, and Dantzig's free energy minimization technique. BKWN parameters (α, β, κ, θ) were used in the following BKW equation, with X_i representing the mol fraction of the i^{th} gaseous product and k_i being the molar co-volume of said i^{th} gaseous product: [26, 28-30]

$$\frac{pV}{RT} = 1 + xe^{\beta x}\, x = \frac{(\kappa \Sigma X_i k_i)}{[V(T + \theta)]^a}$$

α = 0.5, β = 0.38, κ = 9.41, θ = 4250

Table 3. Energetic properties and detonation parameters of DANT and DANTX polymorphs

	DANT	DANTX		DPX-26[31]	DPX-27[31]	ICM-102[32]	TATB[32]	RDX
Formula	$C_3H_4N_6O_2$	$C_3H_4N_6O_3$		$C_4H_2N_8O_4$	$C_4H_2N_8O_5$	$C_4H_6N_6O_4$	$C_6H_6N_6O_6$	$C_3H_6N_6O_6$
FW [g mol^{-1}]	156.10	172.10		226.11	242.12	202.13	258.15	222.12
IS [J] [a]	>40	>40[m]		29	10.3	>60	>60	7.5
FS [N] [b]	160-192	144[m]		>360	258	>360	>360	120
N [%][c]	52.7	47.97		46.30	46.3.0	-	-	37.84
Ω [%][d]	-61.49	-46.48		-	-	-55.45	-55.81	-21.61
T_{dec} [°C][e]	225	190[m]/196[n]		232	138	284	360	205
$\Delta_f H_m^o$ [kJ mol^{-1}] [f]	134.1	102.1		387	378	-8.1	-139.5	86.3
ρ [g·cm^{-3}]^{calc}	1.742	1.814		-	1.904	-	-	-
		Low-Density	High-Density					
ρ [g·cm^{-3}][g]	1.778	1.747	1.852	1.86	-	1.95[o]	1.94[o]	1.80[p]
EXPLO6								
$-\Delta_{Ex}U°$ [kJ kg^{-1}][h]	-3445	-4046	-4065	-	-	-	-	-5740
T_{det} [K][i]	2584	2973	2915	-	-	-	-	3745
P_{CJ} [GPa][j]	22.91	24.20	27.82	32	35.4	34.3	32.4	33.63
$V_{Det.}$ [m s^{-1}][k]	7896	7938	8407	8700	8970	9169	8114	8801
V_o [cm^3 g^{-1}][l]	774	772	761	-	-	-	-	784

[a] impact sensitivity (BAM drophammer (1 of 6)); [b] friction sensitivity (BAM friction tester (1 of 6)); [c] nitrogen content; [d] oxygen balance (Ω = (xO–2yC–1/2zH)M/1600); [e] onset decomposition temperature from DSC or TGA (β = 5 °C); [f] calculated solid-state heat of formation; [g] room temperature density by X-ray diffraction; [h] energy of explosion; [i] detonation temperature; [j] detonation pressure; [k] detonation velocity; [l] volume of detonation gases (assuming only gaseous products); [m] value determined for low-density DANTX polymorph; [n] value determined for high-density DANTX; [o] density measured by gas pycnometry; [p] density referenced from [33]

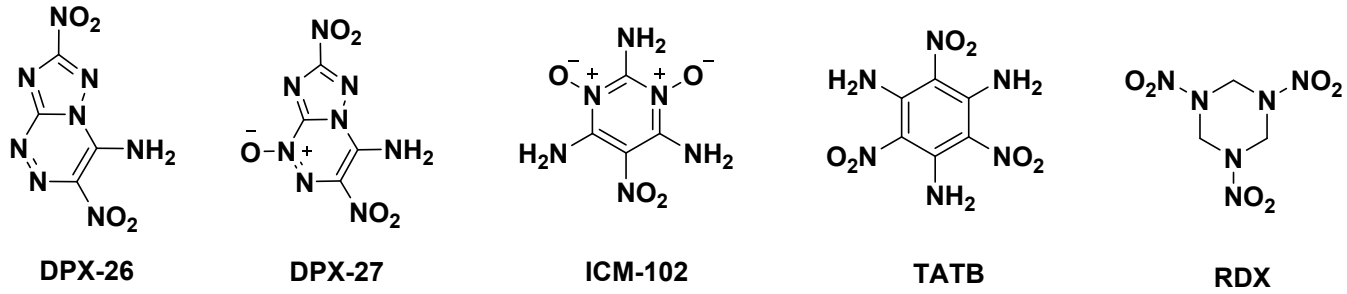

Figure 5. Structures for compounds referenced in Table 2.

References for Supporting Information

1. Creegan, S. E.; Zeller, M.; Byrd, E. F. C.; Piercey, D. G., Synthesis and Characterization of the Energetic 3-Azido-5-amino-6-nitro-1,2,4-triazine. *Propellants Explos. Pyrotech.* **2021,** *46* (2), 214-221.
2. Bruker *Apex3 v2019.1-0, Saint V8.40A, Bruker AXS Inc.:* , Madison (WI), USA, 2019.
3. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D., Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015,** *48* (1), 3-10.
4. *SHELXTL suite of programs, Version 6.14*, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA 2000-2003.
5. Sheldrick, G., A short history of SHELX. *Acta Crystallographica Section A* **2008,** *64* (1), 112-122.
6. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015,** *71* (1), 3-8.
7. Sheldrick, G. M., *University of Göttingen, Germany* **2018**.
8. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B., ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011,** *44* (Pt 6), 1281-1284.
9. *NATO Standardization Agreement (STANAG) on Explosives*; Impact Sensitivity Test, no. 4489; Brussels, September 17, 1999.
10. *WIWEB-Standardarbeitsanweisung 4-5.1.02*; Ermittlung der Explosions- gefährlichkeit, hier: der Schlagempfindlichkeit mit demFallhammer: Erding, November 8, 2002.
11. BAM BAM. https://www.bam.de/.
12. *NATO Standardization Agreement (STANAG) on Explosives*; Friction Sensitivity Tests, no. 4487; Brussels, August 22, 2002.
13. *WIWEB-Standardarbeitsanweisung 4-5.1.03*; Ermittlung der Explosions gerfährlichkeit oder der Reibeempfindlichkeir mit dem Reibeapparat: Erding, November 8, 2002.
14. M. J. Frisch. G. W. Trucks, H. B.; Schlegel, G. E. S., M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,; B. Mennucci, G. A. P. *Guassian 09, Wallingford CT*, n.d.
15. Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993,** *98* (7), 5648-5652.
16. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988,** *37* (2), 785-789.
17. Vosko, S. H.; Wilk, L.; Nusair, M., Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980,** *58* (8), 1200-1211.
18. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994,** *98* (45), 11623-11627.
19. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980,** *72* (1), 650-654.
20. Frisch, M. J.; Pople, J. A.; Binkley, J. S., Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984,** *80* (7), 3265-3269.
21. Schleyer, P. V. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G., Structures and stabilities of α-hetero-substituted organolithium and organosodium compounds. Energetic unimportance of d-orbital effects. *J. Am. Chem. Soc.* **1984,** *106* (22), 6467-6475.
22. Byrd, E. F. C.; Rice, B. M., A Comparison of Methods To Predict Solid Phase Heats of Formation of Molecular Energetic Salts. *J. Phys. Chem. A* **2009,** *113* (1), 345-352.
23. Rice, B. M.; Byrd, E. F. C., Evaluation of electrostatic descriptors for predicting crystalline density. *J. Comput. Chem.* **2013,** *34* (25), 2146-2151.
24. Rice, B. M.; Hare, J. J.; Byrd, E. F. C., Accurate Predictions of Crystal Densities Using Quantum Mechanical Molecular Volumes. *J. Phys. Chem. A* **2007,** *111* (42), 10874-10879.
25. Sućeska, M., Zagreb. Croat., 2018.
26. Sućeska, M., *Mater. Sci. Forum*, 2009; Vol. 465-466, p 325.
27. Sućeska, M., EXPLO6.04 Program. Zagreb, Coatia, 2017.
28. Sućeska, M., Calculation of the Detonation Properties of C-H-N-O explosives. *Propellants Explos. Pyrotech.* **1991,** *16* (4), 197-202.
29. Sućeska, M., Evaluation of Detonation Energy from EXPLO5 Computer Code Results. *Propellants Explos. Pyrotech.* **1999,** *24* (5), 280-285.
30. Hobbs, M. L.; Baer, M. R., Proc. Of the 10th Symp. (International) on Detonation, ONR 33395-12. Boston, MA,, July 12-16, 1993; p 409.

31. Piercey, D. G.; Chavez, D. E.; Scott, B. L.; Imler, G. H.; Parrish, D. A., An Energetic Triazolo-1,2,4-Triazine and its N-Oxide. *Angew. Chem. Int. Ed.* **2016,** 55 (49), 15315-15318.
32. Wang, Y.; Liu, Y.; Song, S.; Yang, Z.; Qi, X.; Wang, K.; Liu, Y.; Zhang, Q.; Tian, Y., Accelerating the discovery of insensitive high-energy-density materials by a materials genome approach. *Nature Communications* **2018,** *9* (1), 2444.
33. Kettner, M. A.; Klapötke, T. M., Synthesis of New Oxidizers for Potential Use in Chemical Rocket Propulsion. In *Chemical Rocket Propulsion: A Comprehensive Survey of Energetic Materials*, De Luca, L. T.; Shimada, T.; Sinditskii, V. P.; Calabro, M., Eds. Springer International Publishing: Cham, 2017; pp 63-88.