

SUPPLEMENTARY INFORMATION

REGULAR ARTICLE

Computational assessment of energetic salts containing

7H-[1,2,4]triazolo[4,3-b][1,2,4]triazole

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Table S1. Reported synthetic routes for the preparation of cations, studied in the present work.

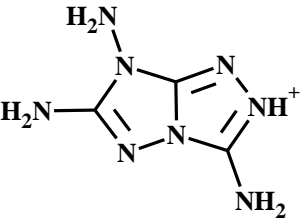
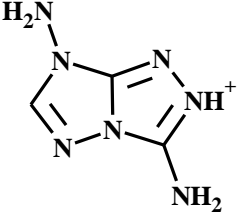
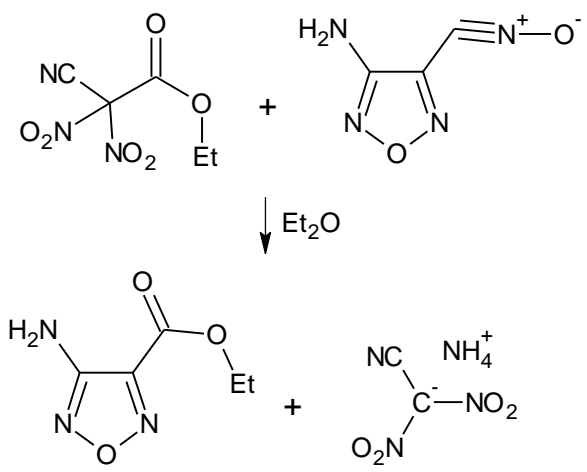
Sr. No.	Cation	Reference for the reported synthetic scheme for cations
1		<p>Reference:</p> <ol style="list-style-type: none"> 1. T M Klapotke, P C Schmid, S Schnell and J Stierstorfer 2015 <i>Chem. Eur. J.</i> 21 9219 2. P. Yin, C. He, J. M. Shreeve, <i>J. Mater. Chem. A</i>, 2016, 4, 1514. 3. S. Dharavath, J. Zhang, G. H. Imler, D. A. Parrish, J. M. Shreeve, <i>J. Mater. Chem. A</i>, 2017, 5, 4785. 4. Y. Tang, C. He, J. M. Shreeve, <i>J. Mater. Chem. A</i>, 2017, 5, 4314. 5. P. Yin, C. He, J. M. Shreeve, <i>Chem. Eur. J.</i> 2016, 22, 2108. 6. T. M. Klapotke, M. Leroux, P. C. Schmid, J. Stierstorfer, <i>Chem. Asian J.</i> 2016, 11, 844. 7. P. Yin, J. Zhang, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, <i>Angew. Chem. Int. Ed.</i> 2016, 55, 12895.
2		<p>Reference:</p> <ol style="list-style-type: none"> 1. Y. Tang, C. He, J. M. Shreeve, <i>J. Mater. Chem. A</i>, 2017, 5, 4314.

Table S2. Reported synthetic routes for the preparation of anions, studied in the present work.

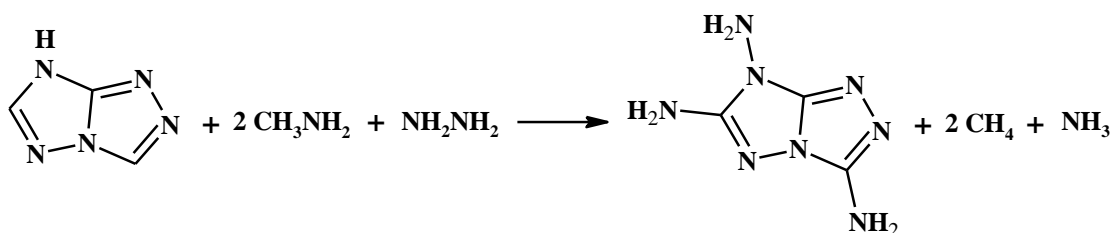
Sr. No.	Anion	Available raw material/Reported synthetic scheme for anions/References
1	NO_3^-	<p>AgNO_3</p> <p>Reference:</p> <p>1. C. M. Sabate, H. Delalu, E. Jeanneau, <i>Chem. Asian J.</i> 2012, 7, 2080.</p> <p>2. Q. H. Lin, Y. C. Li, C. Qi, W. Liu, Y. Wang, S. P. Pang, <i>J. Mater. Chem. A</i>, 2013, 1, 6776.</p>
2	N_3^-	<p>AgN_3</p> <p>Reference:</p> <p>1. C. M. Sabate, H. Delalu, E. Jeanneau, <i>Chem. Asian J.</i> 2012, 7, 2080.</p>
3	$\text{N}(\text{NO}_2)_2^-$	<p>$\text{AgN}(\text{NO}_2)_2$ and $(\text{NH}_4)\text{N}(\text{NO}_2)_2$</p> <p>Reference:</p> <p>1. Q. H. Lin, Y. C. Li, C. Qi, W. Liu, Y. Wang, S. P. Pang, <i>J. Mater. Chem. A</i>, 2013, 1, 6776.</p> <p>2. T. N. Manh, K. J. Kim, <i>Propellants, Explosives, Pyrotechnics</i>, 2016, 41, 709.</p> <p>3. H. Ostmark, U. Bemm, H. Bergman, A. Langlet, <i>Thermochimica Acta</i> 2002, 384, 253.</p> <p>4. N. N. Perreault, A. Halasz, S. Thiboutot, G. Ampleman, J. Hawari, <i>Environ. Sci. Technol.</i> 2013, 47, 5193.</p> <p>5. D. M. Badgujar, R. M. Wagh, S. J. Pawar, A. K. Sikder, <i>Propellants, Explosives, Pyrotechnics</i>, 2014, 39, 658.</p>
4	$\text{C}(\text{NO}_2)_3^-$	<p>$\text{AgC}(\text{NO}_2)_3$</p>

		<p>Reference:</p> <ol style="list-style-type: none"> 1. Q. H. Lin, Y. C. Li, C. Qi, W. Liu, Y. Wang, S. P. Pang, <i>J. Mater. Chem. A</i>, 2013, 1, 6776. 2. M. Göbel, T. M. Klapötke, <i>Z. Anorg. Allg. Chem.</i> 2007, 633, 1006.
5	$\text{N}(\text{CN})_2^-$	<p>$\text{AgN}(\text{CN})_2$</p> <p>Reference:</p> <ol style="list-style-type: none"> 1. Q. H. Lin, Y. C. Li, C. Qi, W. Liu, Y. Wang, S. P. Pang, <i>J. Mater. Chem. A</i>, 2013, 1, 6776.
6	$\text{C}(\text{NO}_2)_2(\text{CN})^-$	<p>$\text{AgC}(\text{NO}_2)_2(\text{CN})$ and</p>  <p>Reference:</p> <ol style="list-style-type: none"> 1. R. Wang, Y. Guo, R. Sa, J. M. Shreeve, <i>Chem. Eur. J.</i> 2010, 16, 8522. 2. A. G. Tyrkov, A. B. Sheremetev, O. I. Serebryakov, <i>Russian Journal of Organic Chemistry</i>, 2012, 48, 475. 3. A. G. Tyrkov, E. A. Yurtaeva, <i>Russian Journal of Organic Chemistry</i>, 2014, 50, 902. 4. Ralf Haiges, K. O. Christe, <i>Dalton Trans.</i> 2015, 44, 10166.
7	$\text{C}(\text{NO}_2)(\text{CN})_2^-$	$\text{AgC}(\text{NO}_2)(\text{CN})_2$

		<p>Reference:</p> <p>1. R. Wang, Y. Guo, R. Sa, J. M. Shreeve, <i>Chem. Eur. J.</i> 2010, 16, 8522.</p>
8	$\text{CH}(\text{NO}_2)(\text{CN})^-$	<p>Reference:</p> <p>1. H. Brand, J. F. Liebman, A. Schulz, P. Mayer, A. Villinger, <i>Eur. J. Inorg. Chem.</i> 2006, 4294.</p>
9	$\text{C}(\text{NO}_2)(\text{CN})(\text{NO})^-$	<p>Reference:</p> <p>1. H. Brand, J. F. Liebman, A. Schulz, P. Mayer, A. Villinger, <i>Eur. J. Inorg. Chem.</i> 2006, 4294.</p>
10	$\text{CH}(\text{NO}_2)_2^-$	<p>Reference:</p> <p>1. Ralf Haiges, K. O. Christe, <i>Dalton Trans.</i> 2015, 44, 10166.</p>
11	$\text{C}(\text{CN})_3^-$	<p>Reference:</p> <p>1. H. Brand, J. F. Liebman, A. Schulz, P. Mayer, A. Villinger, <i>Eur. J. Inorg. Chem.</i> 2006, 4294.</p>

Computational Details

Computations were carried out using the Gaussian 09 program suite.¹ The structure optimizations are performed with B3PW91 functional with 6-31G(d,p) basis set and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were found. *Heat of formation (HOF)* is a measure of energy content of an energetic material that can decompose, ignite and explode by heat or impact. It enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure, heat of detonation and specific impulse. However, it is impractical to determine the HOF of novel energetic materials because of their unstable intermediates and unknown combustion mechanism. The enthalpy criteria of energetic materials is governed by their molecular structure, and therefore, the move to heterocycles with a higher nitrogen content e.g. from benzene to tetrazine (Table S3) and from pyrrole to tetrazole (Table S4) the trend in the heats of formation is obvious. The calculated total energies (E_0), zero point energies (ZPE), and thermal corrections (ΔH_T) at the B3PW91/6-31G(d,p) level for the neutral compounds and cations are listed in Table S5 and S6. The gas phase heats of formation (HOF_{Gas}) of cations A and B are predicted using G3 method and isodesmic reactions (summarized in Figure S1). The usage of the HOF_{Gas} in the calculation of detonation properties slightly overestimates the values of detonation velocity and detonation pressure, and hence, the solid phase HOF (HOF_{Solid}) have been calculated which can efficiently reduce the errors.



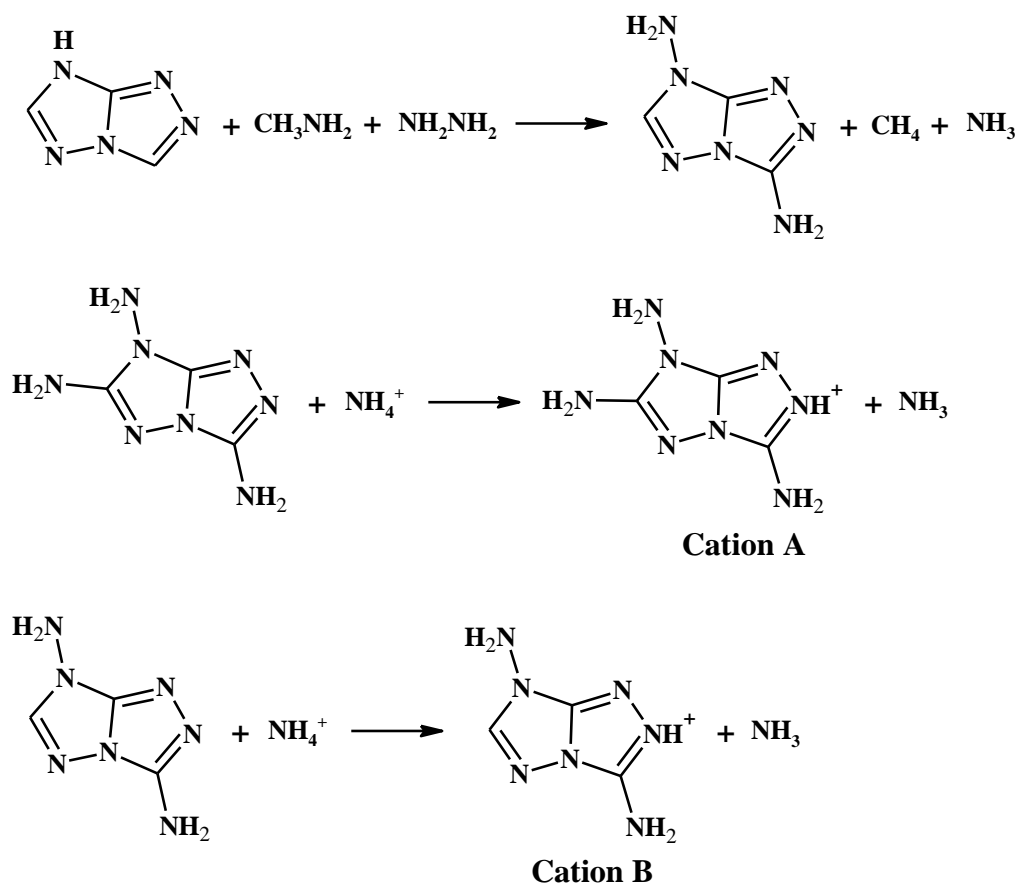


Figure S1. Designed isodesmic reactions for the cation A, B, and their neutral analogs.

The $\text{HOF}_{\text{Solid}}$ is calculated as the difference between HOF_{Gas} and heat of sublimation (HOF_{Sub}) as,

$$\text{HOF}_{\text{Solid}} = \text{HOF}_{\text{Gas}} - \text{HOF}_{\text{Sub}} \quad (1)$$

The heat of sublimation (HOF_{Sub}), which is required to convert the HOF_{Gas} to the $\text{HOF}_{\text{Solid}}$, was calculated from Equation (2),²

$$\text{HOF}_{\text{Sub}} = 4.4307 \times 10^{-4} A^2 + 2.0599 (\nu \sigma_{\text{tot}}^2)^{0.5} - 2.4825 \quad (2)$$

where A represent the surface area of the 0.001 electrons/bohr³ isosurface of electronic density, ν denotes the degree of balance between the positive and negative surface potentials, and σ_{tot}^2 is the electrostatic potential variance. These molecular surface properties were

obtained using the Multiwfn program³ and listed in Table S7-9. The heats of formation of energetic salts were predicted using Born–Haber cycle (Figure S2) and can be simplified by the equation (3),

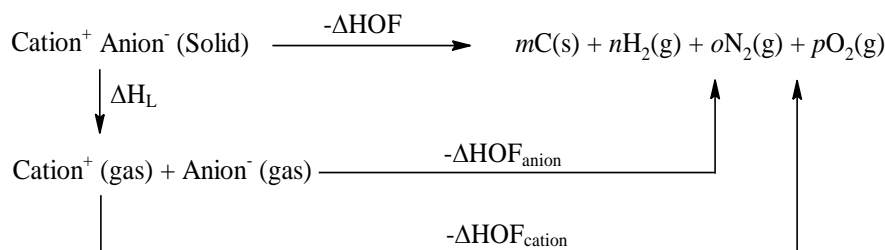


Figure S2. Born-Haber cycle for the formation of energetic salts.

$$\text{HOF} (\text{salt}, 298 \text{ K}) = \text{HOF} (\text{cation}, 298 \text{ K}) + \text{HOF} (\text{anion}, 298 \text{ K}) - \text{H}_\text{L} \quad (3)$$

in above equation, H_L is the lattice energy of the salts, which can be predicted by using the formula proposed by Jenkins et al.⁴

$$\text{H}_\text{L} = U_{\text{POT}} + [p(\frac{n_M}{2} - 2) + q(\frac{n_X}{2} - 2)]RT \quad (4)$$

The nature of the cation M_p^+ and anion X_q^- decide n_M and n_X values, respectively and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. U_{POT} is the lattice potential energy, calculated using the density (ρ in g/cm^3) and the chemical formula mass (M in g/mol) of the ionic salt by the formula given in the following equation:

$$U_{\text{POT}} = 1981.2(\frac{\rho}{M})^{1/3} + 103.8 \quad (5)$$

The calculated U_{POT} and H_L are given in Table S10. The density has been referred to as “the primary physical parameter in detonation performance” of explosives.⁵⁻¹¹ For example, the important performance attribute of detonation velocity is proportional to density, while the

detonation pressure is proportional to the square of the initial density.¹² An increase in density is also desirable in terms of the amount of material that can be packed into volume-limited warhead or propulsion configurations. For salt compounds, Politzer et al.¹³ approach has been used which involves an electrostatic interaction correction. The equation for density (ρ) prediction of ionic salts is,

$$\rho \text{ (g/cm}^3\text{)} = 1.0260 \left(\frac{M}{V_m} \right) + 0.0514 \left(\frac{V_s^+}{A_s^+} \right) + 0.0419 \left(\frac{V_s^-}{A_s^-} \right) + 0.0227 \quad (6)$$

Where V_m is the sum of the volumes of cation and anion in an ionic compound, M is the chemical formula mass of the ionic compound. A_s^+ and A_s^- are the positive and negative electrostatic potential portions of a cation and anion, while V_s^+ and V_s^- are the average values of these potentials, respectively. The calculated molecular surface properties for neutral compounds, cations and anions are listed in Table S7-9. Oxygen balance (OB) is one of the parameter of quantifying how well an explosive provides its own oxidant.¹⁴ Most of the energy released comes from oxidation (reaction with oxygen), the amount of oxygen available is a critical factor. If excess oxygen molecules are remaining after the oxidation reaction, the oxidizer is said to have a ‘positive’ OB. If the oxygen molecules are completely consumed and excess fuel molecules remain, the oxidizer is said to have a ‘negative’ OB. If neutral OB (OB = 0%), means that there is exactly enough oxygen for the complete oxidation. It is reported that the heat of detonation (Q) reaches a maximum for an OB of zero, since this corresponds to the stoichiometric oxidation of carbon to carbon dioxide and hydrogen to water. The OB can therefore be used to optimize the composition of the explosive to give an OB as close to zero as possible. In addition, knowledge of OB in explosives can be applied in the processing of mixtures of explosives. OB (%) for an explosive containing the general formula $C_aH_bN_cO_d$ with molecular mass M can be calculated as,

$$OB(\%) = \frac{(d - 2a - 0.5b)}{M} \times 1600 \quad (7)$$

The driving force behind the development of any new materials for the defence use is, and almost certainly will be, **performance**. For secondary explosives, the power of an explosive is often described by the **detonation velocity (D)** and the **detonation pressure (P)**. *D* reflects the velocity of the shockwave propagated by the explosive during detonation, while *P* is the peak dynamic pressure in the shock front. Detonation performance depends on the energy release that accompanies the decomposition and combustion processes occurring. The detonation velocity (*D* in km/s) and detonation pressure (*P* in GPa) are the performance parameters, computed using the empirical Kamlet–Jacobs equations:¹²

$$N = \frac{2c+2d+b}{48a+4b+56c+64d} \quad (8)$$

$$M = \frac{56c+88d-8b}{2c+2d+b} \quad (9)$$

$$Q = \frac{28.9b+47\left(d-\frac{b}{2}\right)+HOF_{Explosive}}{12a+b+14c+16d} \quad (10)$$

$$D = 1.01(NM^{0.5}Q^{0.5})^{0.5}(1+1.30\rho) \quad (11)$$

$$P = 1.55\rho^2NM^{0.5}Q^{0.5} \quad (12)$$

in which, *N* represents the moles of detonation gases per gram explosive, *M* is the average molecular weight of these gases(g/mol), *Q* denotes the heat of detonation (cal/g), and ρ is the predicted density of salts (g/cm³). The methodology proposed by Akhavan¹⁵ has been used to predict explosive power and power index using the heat of detonation (*Q*) and volume (*V*) of gaseous explosion products. Power index is a comparative numerical value used to rank the relative power of an explosive based on the heat and volume of gases produced by detonation of 1.0 gram of explosive.

$$\text{Explosive Power} = QV \quad (13)$$

$$\text{Power Index} = \frac{QV}{Q_{\text{Picric acid}}V_{\text{(Picric acid)}}} \times 100 \quad (14)$$

In the present work, decomposition products of salts are predicted by using the ‘Kistiakowsky-Wilson’ rules (K-W rules). These rules should only be used for moderately oxygen deficient explosives with an oxygen balance greater than – 40 %. Under these circumstances, the modified Kistiakowsky-Wilson rules are employed.

Kistiakowsky-Wilson Rules

1. Carbon atoms are converted to carbon monoxide.
2. If any oxygen remains then hydrogen is then oxidized to water.
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide.
4. All the nitrogen is converted to nitrogen gas, N₂.

Modified Kistiakowsky-Wilson Rules

1. Hydrogen atoms are converted to water.
2. If any oxygen remains then carbon is converted to carbon monoxide.
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide.
4. All the nitrogen is converted to nitrogen gas, N₂.

Gurney¹⁶ developed a simple model that permits the estimation of the velocity of metal driven by a detonating explosive. This model assumes that a given explosive liberates a fixed amount of specific energy (E) on detonation that is converted to kinetic energy partitioned between the driven metal and gaseous products. The specific energy determines the amount of mechanical work for the acceleration of the surrounding metal that can be done by the explosive. The Gurney velocity ($\sqrt{2E}$) provides a more relevant absolute indicator of the ability of an explosive to accelerate material under a wide variety of initial densities and geometries of interest. The Gurney velocity is predicted using Kamlet and Finger (K-F)

method,¹⁷ equation (13) and validated with Hardesty and Kennedy (H-K) method,¹⁸ equation (14).

$$\sqrt{\Delta E} = 0.887\Phi^{0.5}\rho^{0.4} \quad (15)$$

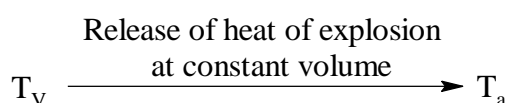
$$\sqrt{\Delta E} = 0.6 + 0.54\sqrt{1.44\Phi\rho} \quad (16)$$

Where in above equations, ρ is the density in g/cm^3 and Φ is the quantity used by Kamlet and Jacobs¹² to calculate detonation properties, depends on: 1. the number of moles of gaseous detonation products per gram of explosive, 2. the average molecular weight of these gases, and 3. the heat of detonation in calories per gram. Most of the explosives contain C, H, N, and O atoms. During an explosive reaction, the molecule uses the oxygen atoms available within it and does not depend on the external, atmospheric oxygen; it probably has no time for that because of the fast nature of the explosive process. It must be noted that all oxidation reactions are exothermic.¹⁹ The heat of combustion (ΔH_c) is defined as the heat evolved when 1 mole of a compound is completely burnt in excess of oxygen. It means that all C atoms and H atoms in the molecule are converted into carbon dioxide (CO_2) and water (H_2O) combustion products, respectively (see Table S11). A fuel burning in air gives out heat of combustion. Heat of combustion is often referred to as the “calorific value.” The HOFs of CO_2 and H_2O are -94.05 and -67.42 kcal/mol, respectively.

$$\Delta H_c = HOF_{\text{combustion products}} - HOF_{\text{explosive}} \quad (17)$$

Flame temperature of the gas products on firing explosives/propellants is of considerable importance in the study of ballistics and to understand the power of those explosives.¹⁹ When a certain amount of explosive is initiated in a thermally insulated container, the total heat evolved is called as heat of explosion which is used to increase the internal energy of the gases. Because the temperature is effectively a measure of the internal energy of a system, the

heat of explosion increases the temperature of the products of explosion. The maximum temperature to which the decomposition products are raised is called the isochoric flame temperature (T_v). Let us assume that during an explosive reaction, n_1 and n_2 moles of H_2O and CO_2 are produced, respectively, and the flame temperature is T_v . After the heat of explosion (ΔH_e) is released, the gases cool to ambient temperature (T_a). This can be represented as:



If $(C_v)_{H_2O}$ and $(C_v)_{CO_2}$ are the molar heat capacities of H_2O and CO_2 , respectively, then the heat of explosion (ΔH_e) can be calculated as,

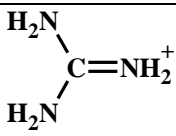
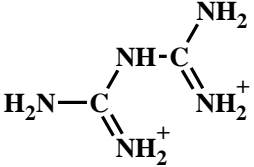
$$\Delta H_e = n_1(C_v)_{H_2O}[T_v - T_a] + n_2(C_v)_{CO_2}[T_v - T_a] \quad (18)$$

The above equation can be written as,

$$\Delta H_e = \sum C_v [T_v - T_a] \quad (19)$$

where $\sum C_v$ is the mean molar heat capacity of the product gases.

Table S3. HOF_{Gas} (kJ/mol) of various cations computed using G3, G4 and G4(MP2) methods.

No.	Cation	Calculated HOF_{Gas} (kJ/mol)			Reported HOF_{Gas} (kJ/mol)
		G3	G4	G4(MP2)	
1.		574.10	572.35	579.97	575.9 ²⁰
2.		1616.88	1614.45	1627.42	1618.0 ²¹

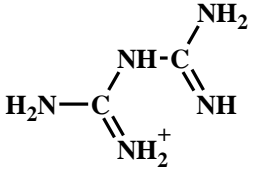
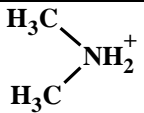
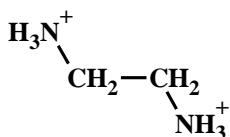
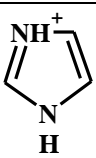
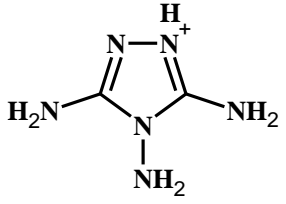
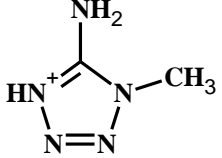
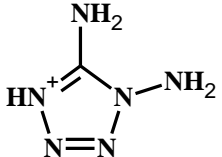
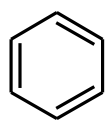
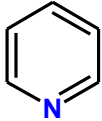
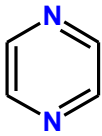
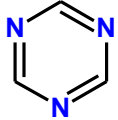
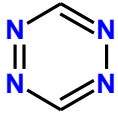
3.		619.34	612.31	622.50	621.0 ²²
4.	NH_4^+	634.85	636.86	638.91	635.5 ²³
5.	$\text{H}_3\text{N}^+\text{—NH}_2$	771.19	769.51	771.69	770.0 ²⁴
6.		586.20	587.29	590.84	579.5 ²⁵
7.		1635.20	1636.04	1640.11	1630.5 ²⁶
8.		724.52	719.33	722.45	720.2 ²⁶
9.		882.45	874.06	886.15	877.6 ²¹
10.		944.88	933.46	941.73	937.2 ²⁷
11.		1062.25	1048.83	1057.72	1055.2 ²⁷

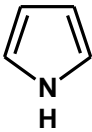
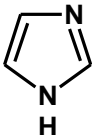
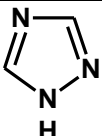
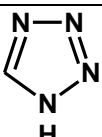
Table S4. Importance of nitrogen-rich backbone in increasing the heat of formation.

Compd.	Structure	HOF (kJ/mol)
Benzene		82.9 ²⁸

Pyridine		140.2 ²⁹
Pyrazine		196.1 ³⁰
1,3,5-Triazine		225.8 ³¹
1,2,4,5-Tetrazine		487.2 ³²

* HOFs are given in gas phase.

Table S5. Importance of nitrogen-rich backbone in increasing the heat of formation.

Compd.	Structure	HOF (kJ/mol)
Pyrrole		108.3 ³³
1 <i>H</i> -Imidazole		129.5 ³⁴
1 <i>H</i> -1,2,4-Triazole		192.7 ³⁵
1 <i>H</i> -Tetrazole		320.0 ³⁶

* HOFs are given in gas phase.

Table S6. Nitrogen content (NC), Total energy (E_0), zero point energy (ZPE), and thermal correction (H_T) at the B3PW91/6-31G(d,p) level for neutral compounds.

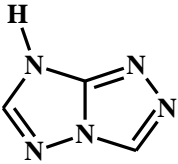
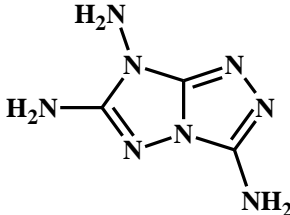
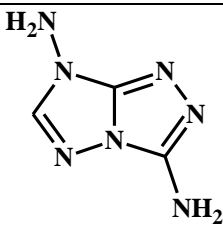
Compd.	NC (%)	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)
	64.20	-389.586300	0.0770	0.0061
	72.70	-555.511482	0.1277	0.0106
	70.48	-500.190476	0.1112	0.0091

Table S7. Total energy (E_0), zero point energy (ZPE), and thermal correction (H_T) at the B3PW91/6-31G(d,p) level for cations.

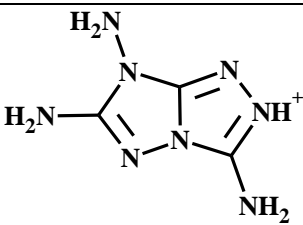
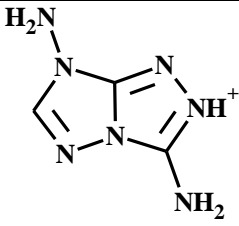
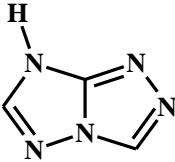
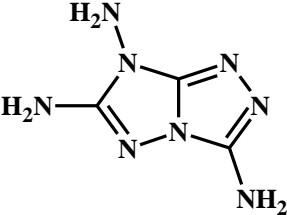
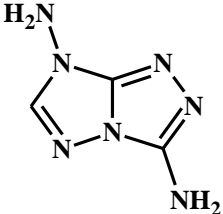
Compd.	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)
	-555.906618	0.1397	0.0115
	-500.570109	0.1240	0.0094

Table S8. Calculated molecular surface properties for the neutral compounds.

Compd.	Volume (Å ³)	Surface area (Å ²)	σ_{tot}^2 (kcal/mol) ²	ν
	115.71	127.31	488.06	0.2453
	163.60	171.91	515.86	0.2495
	148.33	158.55	321.13	0.2418

ν is unit less.

Table S9. Calculated molecular surface properties for the selected cations.

Cation	Volume (Å ³)	V_s^+ (kcal/mol)	A_s^+ (kcal/mol) ²
A	158.88	92.61	168.38
B	143.96	97.55	155.42

Table S10. Calculated molecular surface properties for the selected anions.

Anion	Volume (Å ³)	V_s^- (kcal/mol)	A_s^- (kcal/mol) ²
1	57.62	-134.25	77.02
2	54.16	-136.35	72.74
3	93.42	-111.42	111.4
4	126.83	-99.26	140.32
5	83.53	-113.07	103.16
6	122.27	-99.65	137.12
7	118.52	-99.42	135.69
8	94.87	-110.08	112.72
9	113.44	-102.48	129.83
10	99.05	-108.77	115.83
11	114.47	-98.96	133.41

Table S11. Calculated nitrogen content (NC), lattice energy (U_{POT}) and lattice enthalpy (H_L) for the designed salts.

Salt	Mol. Formula	Mol. Weight	NC (%)	U_{POT} (kJ/mol)	H_L (kJ/mol)
A1	$\text{C}_3\text{H}_7\text{N}_9\text{O}_3$	217.50	58.05	496	501
A2	$\text{C}_3\text{H}_7\text{N}_{11}$	197.16	78.15	497	503
A3	$\text{C}_3\text{H}_7\text{N}_{11}\text{O}_4$	261.15	59.00	478	484
A4	$\text{C}_4\text{H}_7\text{N}_{11}\text{O}_6$	305.17	50.49	464	469
A5	$\text{C}_5\text{H}_7\text{N}_{11}$	221.18	69.66	483	489
A6	$\text{C}_5\text{H}_7\text{N}_{11}\text{O}_4$	285.18	54.03	467	471
A7	$\text{C}_6\text{H}_7\text{N}_{11}\text{O}_2$	265.19	58.10	468	473
A8	$\text{C}_5\text{H}_8\text{N}_{10}\text{O}_2$	240.18	58.32	478	483
A9	$\text{C}_5\text{H}_7\text{N}_{11}\text{O}_3$	269.18	57.24	470	475
A10	$\text{C}_4\text{H}_8\text{N}_{10}\text{O}_4$	260.17	53.84	476	481
A11	$\text{C}_7\text{H}_7\text{N}_{11}$	245.20	62.83	470	475
B1	$\text{C}_3\text{H}_6\text{N}_8\text{O}_3$	202.13	55.44	506	511
B2	$\text{C}_3\text{H}_6\text{N}_{10}$	182.15	76.90	507	512
B3	$\text{C}_3\text{H}_6\text{N}_{10}\text{O}_4$	246.14	56.90	487	492
B4	$\text{C}_4\text{H}_6\text{N}_{10}\text{O}_6$	290.15	48.27	471	476
B5	$\text{C}_5\text{H}_6\text{N}_{10}$	206.17	67.94	492	497
B6	$\text{C}_5\text{H}_6\text{N}_{10}\text{O}_4$	270.16	51.84	473	478
B7	$\text{C}_6\text{H}_6\text{N}_{10}\text{O}_2$	250.18	55.99	475	480
B8	$\text{C}_5\text{H}_7\text{N}_9\text{O}_2$	225.17	55.98	486	491
B9	$\text{C}_5\text{H}_6\text{N}_{10}\text{O}_3$	254.17	55.11	477	482
B10	$\text{C}_4\text{H}_7\text{N}_9\text{O}_4$	245.15	51.42	484	489
B11	$\text{C}_7\text{H}_6\text{N}_{10}$	230.19	60.85	477	482

Table S12. Predicted combustion reactions used in the calculation of the heat of combustion (ΔH_C).

Salt	Combustion reactions
A1	$C_3H_7N_9O_3 + 3.25O_2 \rightarrow 3CO_2 + 3.5H_2O + 4.5N_2$
A2	$C_3H_7N_{11} + 4.75O_2 \rightarrow 3CO_2 + 3.5H_2O + 5.5N_2$
A3	$C_3H_7N_{11}O_4 + 2.75O_2 \rightarrow 3CO_2 + 3.5H_2O + 5.5N_2$
A4	$C_4H_7N_{11}O_6 + 2.75O_2 \rightarrow 4CO_2 + 3.5H_2O + 5.5N_2$
A5	$C_5H_7N_{11} + 6.75O_2 \rightarrow 5CO_2 + 3.5H_2O + 5.5N_2$
A6	$C_5H_7N_{11}O_4 + 5.75O_2 \rightarrow 6CO_2 + 3.5H_2O + 5.5N_2$
A7	$C_6H_7N_{11}O_2 + 6.75O_2 \rightarrow 6CO_2 + 3.5H_2O + 5.5N_2$
A8	$C_5H_8N_{10}O_2 + 6O_2 \rightarrow 5CO_2 + 4H_2O + 5N_2$
A9	$C_5H_7N_{11}O_3 + 5.25O_2 \rightarrow 5CO_2 + 3.5H_2O + 5.5N_2$
A10	$C_4H_8N_{10}O_4 + 4O_2 \rightarrow 4CO_2 + 4H_2O + 5N_2$
A11	$C_7H_7N_{11} + 8.75O_2 \rightarrow 7CO_2 + 3.5H_2O + 5.5N_2$
B1	$C_3H_6N_8O_3 + 3O_2 \rightarrow 3CO_2 + 3H_2O + 4N_2$
B2	$C_3H_6N_{10} + 4.5O_2 \rightarrow 3CO_2 + 3H_2O + 5N_2$
B3	$C_3H_6N_{10}O_4 + 2.5O_2 \rightarrow 3CO_2 + 3H_2O + 5N_2$
B4	$C_4H_6N_{10}O_6 + 2.5O_2 \rightarrow 4CO_2 + 3H_2O + 5N_2$
B5	$C_5H_6N_{10} + 6.5O_2 \rightarrow 5CO_2 + 3H_2O + 5N_2$
B6	$C_5H_6N_{10}O_4 + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + 5N_2$
B7	$C_6H_6N_{10}O_2 + 6.5O_2 \rightarrow 6CO_2 + 3H_2O + 5N_2$
B8	$C_5H_7N_9O_2 + 5.75O_2 \rightarrow 5CO_2 + 3.5H_2O + 4.5N_2$
B9	$C_5H_6N_{10}O_3 + 5O_2 \rightarrow 5CO_2 + 3H_2O + 5N_2$
B10	$C_4H_7N_9O_4 + 3.75O_2 \rightarrow 4CO_2 + 3.5H_2O + 4.5N_2$
B11	$C_7H_6N_{10} + 8.5O_2 \rightarrow 7CO_2 + 3H_2O + 5N_2$

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