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Energetic Salts from Phenolate Derivatives

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Several organic salts with 1:1, 2:1, and 3:1 charge ratio (cation: anion) based on various cations and phenolate anions have been prepared. Their structures were characterized and confirmed by ^{1}H, ^{13}C NMR, DEPT spectroscopy, IR spectroscopy, MS and elemental analysis. Picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid, 2,4,6-trinitro-1,3,5-benzenetriol, and their salts were synthesized by a straightforward and simple method. Thermal stabilities were determined from thermo gravimetric differential thermal analysis (TG-DTA) measurements. Molecular structures of nitrophenols and their salts were investigated at the B3PW91/6-31G(d,p) level, and isodesmic reactions were designed for calculating the gas phase heats of formation. The solid state heats of formation for nitrophenols and selective nitrogen-rich heterocyclic compounds were calculated by the Politzer approach using heats of sublimation. Lattice potential energies and lattice energies for salts were predicted using Jenkins approach. Finally, the influence of nitrophenols, nitrogen-rich heterocyclic compounds and their salts on the energetic properties has been discussed.

Introduction

The enormous growth in the literature related to energetic salts since the year 2000 reflects their versatility, performance, controllable storage of energy and environmentally friendly properties in comparison to their starting materials.[1] Adding cations and anions with various functionalities to form energetic salts typically alters the energetic properties of individual starting materials, which is a desired characteristic of most of the energetic materials. Energetic salts possess several advantages over their atomically similar non-ionic analogs as these salts tend to exhibit lower vapour pressures and higher densities.[2] In recent years, the synthesis of energetic materials composed of heterocyclic compounds
considerable interest due to their higher heats of formation, densities, and oxygen balance than their hydrocarbon analogs.[3] The high positive heats of formation of these compounds are directly attributed to the large number of energetic N-N and C-N bonds in their molecular skeleton.[4]

The chemistry of polynitroarenes have been widely studied and used in civil as well as military applications due to their remarkable properties.[3a,5] Benzene compounds having three or more nitro groups, exhibit distinctly marked explosive properties (e.g. 2-methyl-1,3,5-trinitrobenzene (TNT), 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitroaniline (picramide) 2,4,6-trinitroanisole, 1,3-diammino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), etc.). Nitro group is an important source of oxygen in nitroarenes and most of these compound release energy mainly from the oxidation of hydrocarbon backbone. Thus, the combination of these compounds with heterocyclic compounds were expected to modify energetic properties. Previously, few salts of phenolate have been reported.[6] Salts of picric acid with ammonium, guanadinium, or heavy metal cations represented promising properties for applications in military charges and in initiating mixtures.[7] Nitrophenols have limited applications in energetic materials as they are known to react with surrounding metals to yield very sensitive compounds. Nitrophenols are also well known for salt formation and to stabilize the materials through the formation of hydrogen-bonded networks.[8]

We have synthesized energetic salts based on picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid (2,4,6-trinitrobenzene-1,3-diol), and 2,4,6-trinitro-1,3,5-benzenetriol, with concomitant determination of structural and thermal properties. We have extended our studies to understand structure-performance relationship with various cations in combination with phenolate anions having 1:1, 2:1, and 3:1 charge ratio. While the typical cations used in these systems are for example, 4-amino-4H-1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3,4-diaminofurazan, and guanidine, until now their phenolate salts have not been synthesized. In the field of energetic materials, these compounds have received much attention since they combine higher nitrogen content, higher enthalpy, and lower sensitivity to external stimuli. Table 1 and 2 in Supporting Information summarizes the total energies, the zero-point energies, the values of the thermal correction, gas phase heat of formation, molecular surface properties, and calculated solid state heat of formation for the starting materials selected for salt preparation. They can form all kinds of salts with inorganic and organic acids due to the alkaline nature of these compounds. These salts have wide applications in propellants, secondary explosives and gas

generator compositions. Further, it is necessary to study the influence of hydroxyl and nitro groups on the physicochemical properties of its salts systematically and to understand what characteristics make salts suited to high energy materials applications.

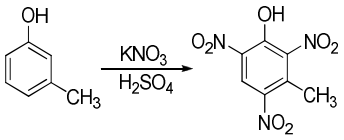
Results and Discussion

Synthesis

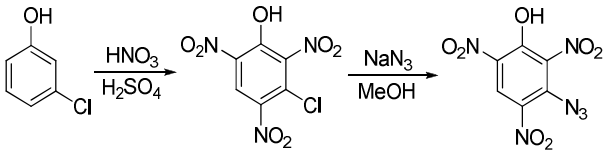
To meet the continuing need for high performance energetic materials with improved properties, the synthesis of materials containing heterocyclic compounds has gained considerable attention because of their high nitrogen content, large densities, good oxygen balances, and high heats of formation. Energetic salts of nitrophenols are interesting as a new class of ionic energetic materials since they have good thermal stabilities, high densities, good oxygen balances, and good performances. Their syntheses are feasible to scale-up through straightforward synthetic routes. The variations of nitro groups on phenol rings also have a significant influence on their microstructures and physicochemical properties.[9] We have mainly chosen trinitrophenols due to their stronger acidity than phenol and it is also necessary to study the influence of nitro groups on the structure-performance relationship of nitrophenol salts systematically. The acidity of nitrophenols arises from the greater resonance stabilization of phenoxide anion compared with phenol itself.

The synthesis of picric acid was achieved by nitration of 2,4-dinitrophenol using concentrated H_2SO_4 and HNO_3. The nitration of m-cresol using sulfuric acid and nitric acid resulted in vigorous reaction and hence, we attempted nitration using potassium nitrate and sulfuric acid to give 2,4,6-trinitro-m-cresol with excellent yield (scheme 1). We observed that nitration using KNO_3 was convenient and efficient for multiple nitrations in a single step. Generally, trinitrations needs more vigorous reaction conditions than mono- or dinitrations. However, in the case of picric acid the strong nitration mixture promoted oxidative decomposition of starting substrate, intermediates, and products which led to poor yields. It is worth mentioning here is that sulfuric acid solutions of nitrate salts like $NaNO_3$, KNO_3, and NH_4NO_3 were once widely used as nitrating agents but eventually lost popularity in favor nitration mixture.[10]

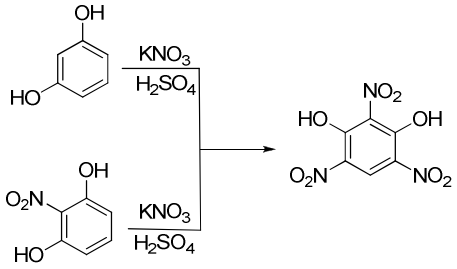
Nitration of 3-chlorophenol with nitrating agents (Scheme 2) gives 3-chloro-2,4,6-trinitrophenol. The displacement of the chlorine of 3-chloro-2,4,6-trinitrophenol by azide occurred to give 3-azido-2,4,6-trinitrophenol. The nitration of 3-chlorophenol with KNO_3 results in 3-chloro-2,4-dinitrophenol, however, we paid attention to trinitro derivatives of phenols. Next similar successful attempts were made to prepare styphnic acid and 2,4,6-trinitrophloroglucinol with good yields and their salts were obtained in high yield (Scheme 3 and 4). The choice of the nitrate salt ($NaNO_3$ and KNO_3) had minor effects on the yields of trinitrations of resorcinol and phloroglucinol. The new energetic salts (**1a**-**1e**) were easily obtained by reacting picric acid with an equivalent amount of heterocyclic cationic molecules in methanol (Scheme 5). All salts of nitrophenols prepared in methanol at room temperature, while the reaction of 3-azido-2,4,6-trinitrophenol (**3**) and styphnic acid (**4**) with 4-amino-4H-1,2,4-triazole (**a**) did not occur under similar conditions; hence, the corresponding salts (**3a** and **4a**) could not be prepared by this route. Scheme 5 represents the different anionic and cationic compounds selected in salt preparation. The structures of nitrophenols and their salts were characterized by ^1H, ^{13}C NMR, DEPT, IR, MS as well as elemental analysis.



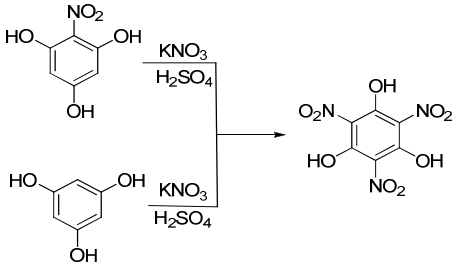
Scheme 1. Synthesis of 2,4,6-trinitro-m-cresol**.**



Scheme 2. Synthesis of 3-azido-2,4,6-trinitrophenol.



Scheme 3. Synthesis of styphnic acid.



Scheme 4. Synthesis of 2,4,6-trinitrophloroglucinol.

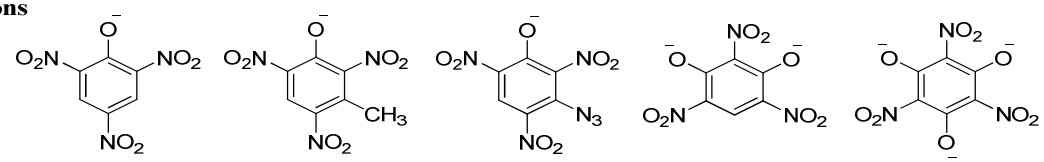
Energetic properties

The most fundamental performance properties of a potentially energetic compound are the heat of formation (HOF), density, chemical energy of detonation (Q), detonation velocity (D) and detonation pressure (P). The gas phase HOFs of molecules were obtained from the isodesmic reactions and the details are provided in Supporting Information.

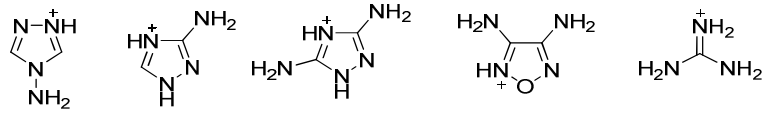
The enthalpies of formation of high energy materials depend on the molecular skeleton of that compound. As a result, nitrogen-rich heterocycles, especially triazole, showed

higher heats of formation (192 kJ/mol).[11] Increasing the number of nitrogen atoms in heterocycles resulted in considerable gain in the standard heat of formation in the resulting compounds. Comparing the heats of formation of phenol (-96 kJ/mol),[12] m-cresol (-133 kJ/mol),[12] resorcinol (-284 kJ/mol),[13] and phloroglucinol (-452 kJ/mol)[14] clearly reveal no significant energy contribution from these molecules and tend to reduce the overall HOF. In case of two –OH groups in phenol reduce the HOF of phloroglucinol by ~350 kJ/mol. Adding one methyl ($-CH_3$) group to picric acid slightly decreases the HOF of 2,4,6-trinitro-m-cresol, while insertion of two –OH groups in phenol reduce the HOF of phloroglucinol by ~350 kJ/mol. Adding one methyl ($-CH_3$) group to picric acid slightly decreases the HOF of 2,4,6-trinitro-m-cresol, while insertion of azido ($-N_3$) in picric acid group significantly improves the HOF of 3-azido-2,4,6-trinitrophenol to positive (Table 1).

Anions



Cations



Scheme 5. Synthesis of energetic salts from nitrophenolate derivatives.

Table 1. Energetic properties of nitrophenols.

Compd.	OB[a]	HOF_{Solid}[b]	D[c]	VOD[d]	DP[e]	Q[f]	T_{dec}[g]	Mp[h]
Picric acid	-45.4	-268.44 (-218)[19]	1.77 (1.77)[7]	7.50 (7.35)[7]	24.68 (23.2)[17]	1227 (1317)[22]	242	120
2,4,6-Trinitro-m-cresol	-62.6	-296.14	1.69 (1.68)[7]	7.08 (6.85)[7]	21.39	1174 (1325)[22]	212	106
3-Azido-2,4,6-trinitrophenol	-35.6	26.26	1.84	7.94	28.31	1282	254	86
Styphnic acid	-35.9	-485.42 (-468, -523)[20,21]	1.79 (1.83)[7]	7.51	24.90	1127 (1155)[22]	190	173
2,4,6-Trinitro-1,3,5-benzenetriol	-27.6	-654.07	1.81	7.58 (8.05)[19]	25.59 (27.56)[19]	1084	191	166

[a] Oxygen balance (%). [b] Heat of formation in solid state (kJ/mol). [c] Density (g/cm3). [d] Velocity of detonation (km/s). [e] Detonation pressure (GPa). [f] Chemical energy of detonation (cal/g). [g] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [h] Melting point (°C).

The calculated energetic properties of the nitrophenols are summarized in Table 1. As evident from Table 2, replacement of 3-amino-1,2,4-triazole with 3,5-diamino-1,2,4-triazole reduces the HOF of corresponding salts. However, we observed that 4-amino-4H-1,2,4-triazole significantly improves the HOF of its related salts. HOF of 4-amino-4H-1,2,4-triazole is the highest among a series of heterocyclic compounds selected (Table 1 in Supporting Information) and hence its salts possess highest HOFs in different series of compounds. Guanidine show negative HOF and hence, has very less impact on their energetic salts. Among the series of nitrophenol salts, the salts of 3-azido-2,4,6-trinitrophenol (**3b**-**3e**) possess highest HOFs attributed to the presence of azido group.

Density is one of the most important physical properties of energetic materials. The Hofmann approach[15] is used to predict the densities of ionic materials from its volume and the molecular mass. The densities of most of the new salts ranged between 1.58 and 1.76 g/cm^3 (Table **2-4**). The presence of nitro groups and N-H in the molecular framework increased the opportunity for hydrogen bonding and may responsible for the increased densities in the designed compounds. Introduction of $–CH_3$ group in parent picric acid reduced the density and

similar trend is observed in salts of picric acid (**1a**-**1e**) and 2,4,6-trinitro-m-cresol (**2a**-**2e**). However, introduction of $-N_3$ group in picric acid improves the density and similar can be seen in salts of picric acid (**1a**-**1e**) and 3-azido-2,4,6-trinitrophenol (**3b**-**3e**). Replacement of 3-amino-1,2,4-triazole with 3,5-diamino-1,2,4-triazole show marginal change in density. Among the energetic salts, guanidine containing salts possessed lower densities.

Table 2. Energetic properties of picric acid, 2,4,6-trinitro-m-cresol and 3-azido-2,4,6-trinitrophenol salts.

Compd.	OB[a]	HOFc[b]	HOFa[c]	U_{Pot}[d]	H_L[e]	HOF_{salt}[f]	D[g]	VOD[h]	DP[i]	Q[j]	T_{dec}[k]	Mp[l]
1a	-63.9	946.92	-458.31	465	471	18	1.68	7.21	22.08	1186	240	192
1b	-63.9	796.42	-458.31	465	471	-132	1.68	7.02	20.98	1071		231
1c	-63.4	753.78	-458.31	458	463	-168	1.67	6.96	20.54	1012	254	241
1d	-55.9	849.56	-458.31	460	465	-74	1.70	7.37	23.29	1204	238	112
1e	-61.1	567.16	-458.31	475	479	-371	1.66	6.94	20.32	984	291	120
2a	-75.8	946.92	-457.17	455	460	29	1.63	6.96	20.20	1176	225	175
2b	-75.8	796.42	-457.17	455	460	-121	1.63	6.79	19.23	1066	225	185
2c	-74.9	753.78	-457.17	449	454	-157	1.63	6.76	19.08	1009	235	206
2d	-67.6	849.56	-457.17	451	456	-63	1.65	7.13	21.35	1194	211	103
2e	-74.2	567.16	-457.17	464	468	-359	1.60	6.67	18.35	984	175	107
3b	-54.2	796.42	-143.59	453	458	194	1.74	7.43	24.02	1152	191	119
3c	-54.2	753.78	-143.59	447	452	158	1.73	7.37	23.52	1096	210	
3d	-47.6	849.56	-143.59	448	454	252	1.76	7.74	26.23	1267	198	78
3e	-51.1	567.16	-143.59	462	466	-43	1.72	7.38	23.49	1084	156	

[a] Oxygen balance (%).[b] Heat of formation of cation (kJ/mol). [c] Heat of formation of anion (kJ/mol). [d] Lattice potential energy (kJ/mol). [e] Lattice energy (kJ/mol). [f] Heat of formation of salt (kJ/mol). [g] Density (g/cm^3). [h] Velocity of detonation (km/s). [i] Detonation pressure (GPa).[j] Chemical energy of detonation (cal/g). [k] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [l] Melting point (°C)

Table 3. Energetic properties of styphnic acid salts.

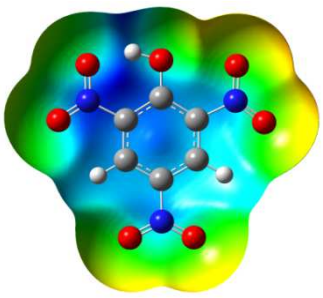
Compd.	OB[a]	HOFc[b]	HOFa[c]	U_{Pot}[d]	H_L[e]	HOF_{salt}[f]	d[g]	VOD[h]	DP[i]	Q[j]	T_{dec}[k]	Mp[l]
4b	-67.8	796.4	-523.4	1281	1289	-220	1.66	6.79	19.44	927	227	
4c	-66.8	753.8	-523.4	1253	1261	-277	1.65	6.71	18.95	858	248	
4d	-55.7	849.6	-523.4	1261	1268	-93	1.69	7.35	23.05	1140	219	146
4e	-63.9	567.2	-523.4	1320	1328	-717	1.61	6.49	17.43	757	199	

[a]Oxygen balance (%). [b]Heat of formation of cation (kJ/mol). [c]Heat of formation of anion (kJ/mol). [d]Lattice potential energy (kJ/mol). [e]Lattice energy (kJ/mol). [f]Heat of formation of salt (kJ/mol). [g]Density (g/cm^3). [h]Velocity of detonation (km/s). [i]Detonation pressure (GPa). [j]Chemical energy of detonation (cal/g). [k]Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [l]Melting point (°C).

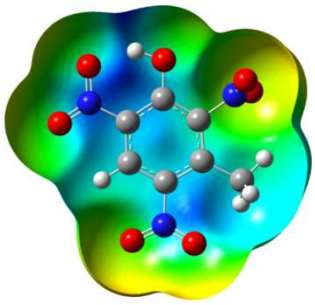
Table 4. Energetic properties of 2,4,6-trinitro-1,3,5-benzenetriol salts.

Compd.	OB[a]	HOFc[b]	HOFa[c]	U_{Pot}[d]	H_L[e]	HOF_{salt}[f]	D[g]	VOD[h]	DP[i]	Q[j]	T_{dec}[k]	Mp[l]
5a	-70.2	946.9	-203.5	2238	2247	389	1.64	7.17	21.50	1164	196	
5b	-70.2	796.4	-203.5	2238	2247	-62	1.64	6.82	19.46	954	223	147
5c	-68.8	753.8	-203.5	2176	2186	-128	1.63	6.74	18.97	877	202	
5d	-55.6	849.6	-203.5	2193	2203	143	1.68	7.49	23.87	1211	182	
5e	-65.8	567.2	-203.5	2325	2335	-837	1.58	6.43	16.89	731	170	

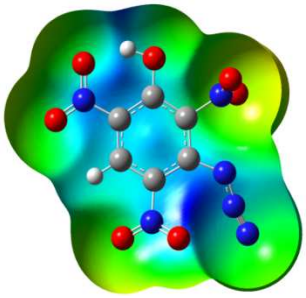
[a] Oxygen balance (%). [b] Heat of formation of cation (kJ/mol). [c] Heat of formation of anion (kJ/mol). [d] Lattice potential energy (kJ/mol). [e] Lattice energy (kJ/mol). [f] Heat of formation of salt (kJ/mol). [g] Density (g/cm^3). [h] Velocity of detonation (km/s). [i] Detonation pressure (GPa).[j] [1]Chemical energy of detonation (cal/g). [k] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [1]Melting point (°C).



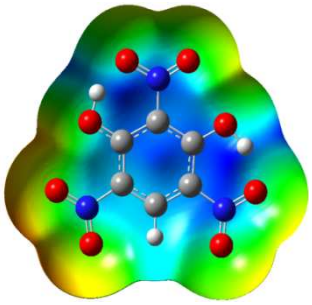
Picric acid



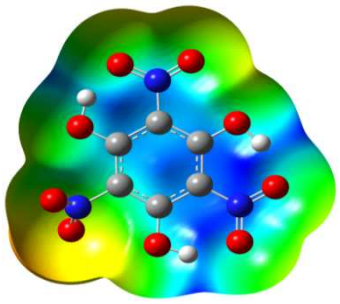
2,4,6-Trinitro-m-cresol



3-Azido-2,4,6-trinitrophenol



Styphnic acid



2,4,6-Trinitro-1,3,5-benzenetriol

Figure 1. Calculated molecular electrostatic potential on the 0.001 au molecular surface of the nitrophenols. The red regions represent electron-rich regions, the blue regions extremely electron-deficient regions. Gray=carbon; white=hydrogen; blue=nitrogen; red=oxygen.

The detonation performance of an energetic compound is basically depending on the density, the heat of formation, and the oxygen balance. By using the calculated values of the HOFs and densities of the energetic nitrophenols and their salts, the detonation velocities and detonation pressures were calculated based on Kamlet-Jacobs equations. In the present study, the designed compounds composed only of the atoms C, H, N, and O and hence, N_2(g), H_2O(g), CO_2(g), and C(s) are assumed as important detonation products, explained by Kamlet et al.[16] and Politzer and Murray.[17]

The predicted detonation characteristics of picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid, and 2,4,6-trinitrophloroglucinol listed in Table 1 and found close agreement with experimental data. The calculated detonation pressures of picric acid salts (**1a**-**1e**), styphnic acid (**4b**-**4e**) and 2,4,6-trinitrophloroglucinol (**5a**-**5e**) lie in the range between P=16.8 and P=24 GPa and detonation velocities lie between D=6.4 and D=8 km/s. Comparing the performance characteristics of 2,4,6-trinitro-m-cresol (**2a**-**2e**) and 3-azido-2,4,6-trinitrophenol (**3b**-**3e**) salts reveals that 3-azido-2,4,6-

trinitrophenol salts possess better performance due to their high densities. The formal replacement of 2,4,6-trinitro-m-cresol's methyl group by a hydroxyl group, as in the parent styphnic acid, results in detonation parameters better than those of 2,4,6-trinitro-m-cresol. Among the nitrophenol salts, 3,4-diaminofurazan salts show better detonation performance and these performance properties coupled with the better thermal stabilities make these salts attractive candidates for energetic materials.

For energetic materials, stability and physical properties are very important. The melting points and the decomposition temperatures of nitrophenol salts were obtained by using TG-DTA from a heating rate of 10 °C/min and corresponding values are listed in Table 2-4. As shown in Table 2, for salts **1a**-**1e** in which the picric acid anion is present, all salts appear to be sufficiently thermally stable, their decomposition temperatures found in the range 231-291 °C, while their melting points lie between 110-241 °C. Salt **1b** observed to decompose without melting above 230 °C. All the picric acid salts have melting points greater than 100 °C. Similar to picric acid salts, styphnic acid salts (**4b**-**4e**) and 2,4,6-trinitro-1,3,5-benzenetriol salts (**5a**-**5e**) exhibit better thermal stabilities. Styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol salts shows decomposition temperatures above 190 and 170 °C, respectively. Among the 2,4,6-trinitro-m-cresol salts, **2a**, **2b**, and **2c** have decomposition temperature above 220 °C with high melting points (>170 °C). 3-Azido-2,4,6-trinitrophenol salts possess decomposition temperature above 150 °C. The experimental results show that with the increase of nitro groups in the phenol rings, the amount of releasing heat increase, which are beneficial to improve the performance of energetic organic salts.

The objective of computing the molecular electrostatic potential (MESP) is to examine the insights into intermolecular association and to achieve a better understanding of the basic factors that determine the reactive properties of hydroxyl groups in these classes of high energy molecules. The MESP depends on the whole effect of al1 the charges in the molecule. The relative magnitudes of the positive and negative electrostatic potentials in various regions of anionic compounds are shown in Fig. 1. The surface is taken to be the 0.001 au (electrons/Bohr^3) contour of the electronic density, as proposed by Bader et al.[18] Regions (blue) in which the ESP is positive are electron deficient, while regions (red) which have negative potentials are electron rich. It is readily discernible that the negative potential has largely been localized near the nitro groups and strong positive potential on the H of the hydroxyl group of these compounds. This clearly represents the acidity of this proton and donation of H from hydroxyl group to form salts with nitrogen-rich heterocyclic compounds. The introduction of $–NO_2$ group has the consistent effect of weakening the negative potentials associated with the C–C bonds in aromatic ring; this reflects the electron-withdrawing power of the nitro group. With –OH and $–CH_3$ substituents, the situation is similar, however not as extreme.

Conclusions

In summary, we have synthesized and characterized different nitrophenolate salts with appropriate synthetic methods in high yields. The low cost and the availability of the starting materials, easy and clean work-up, and high yields make these salts attractive for their applications as energetic materials. Comparing energetic properties of picric acid, styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol reveals that –OH group tends to reduce heat of formation, while improving density, oxygen balance and thus, performance. All the phenolate salts exhibit good thermal stabilities, better densities, reasonable detonation pressures and detonation velocities.

Experimental section

Caution! *We have synthesized all compounds in millimolar amounts and have experienced no difficulties with temperature. However, appropriate safety precautions should be taken, especially when these compounds are prepared on a large scale. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory. All compounds should be stored in explosive cases. Ignoring safety precautions can lead to an accident or serious injury.*

Material and instruments: The reagents were available commercially and were used as purchased without further purification. Reactions were monitored by TLC analysis, by using precoated silica gel TLC plates obtained from Merck. ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard using [D_6]DMSO as the solvent. MS was performed on a LC-MS spectrometer. Melting points and decomposition temperatures were determined by DSC-TGA using TA instruments SDT Q 600 instrument. The IR spectra were recorded on a Perkin–Elmer IR spectrometer by using KBr pellets. Elemental analyses were performed on a flash EA 1112 full automatic trace element analyzer.

Picric acid: 2,4-Dinitrophenol (0.184 g, 0.001m) dissolved in Conc. H_2SO_4 (5 ml). Round bottom flask charged with Conc. H_2SO_4 (5ml) and fuming nitric acid (8 ml) and cooled to approximately 5 °C. The solution of 2,4-dinitrophenol added slowly for over 30 min with stirring. After complete addition, the reaction mixture stirred for additional 15 min and the cooling bath was removed. The reaction mixture subjected to heating (80 °C) for 2hrs. The reaction mixture was cooled and poured into crushed ice. Resulting precipitate was isolated by filtration and thoroughly washed with water to give yellow solid (0.155 g, 68%). IR (KBr): 3107, 3088, 1631, 1629, 1610, 1567, 1561, 1498, 1483, 1432, 1342, 1316, 1279, 1168, 1089, 938 cm^{-1}. ^{1}H N MR (400 MHz, DMSO): δ (ppm) 10.19 (s, 1H) 8.83 (s, 2H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 152.8, 138.8, 136.7, 125.4. LC-MS (EI, *m/z*): 228 [M^+]. C, H, N analysis (%): $C_6H_3N_3O_7$ (229.10), Calculated result: C, 31.45; H, 1.32; N, 18.34; Found: C, 31.34; H, 1.40; N, 18.41.

General procedure for the preparation of salts from picric acid: A solution of 4-amino-4*H*-1,2,4-triazole (0.168 g, 0.002m), 3-amino-1,2,4-triazole (0.168 g, 0.002m), 3,5-diamino-1,2,4-triazole (0.198 g, 0.002m), 3,4-diaminofurazan (0.200 g, 0.002m), or guanidine nitrate (0.244 g, 0.002m) was slowly added to a solution of picric acid (0.458 g, 0.002mol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product.

4H-1,2,4-Triazol-4-aminium 2,4,6-trinitrophenolate (1a): Yellow solid (0.591 g, 94%). IR (KBr): 3364, 3254, 3112, 3079, 1621, 1567, 1539, 1484, 1419, 1364, 1326, 1265, 1156, 1084, 942 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.511 (s, 2H) 8.587 (s, 2H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.282, 144.469, 142.269, 125.732, 124.833. LC-MS (EI, *m/z*): 313 [M^+]. C, H, N analysis (%): $C_8H_7N_7O_7$ (313.18), Calculated result: C, 30.68; H, 2.25; N, 31.31; Found: C, 30.54; H, 2.34; N, 31.42.

3-Amino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (1b): Yellow solid (0.583 g, 93%). IR (KBr): 3452, 3361, 3167, 3106, 1698, 1632, 1550, 1501, 1424, 1336, 1271, 1254, 1172, 1090, 953 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.601 (s, 2H) 8.329 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.3, 151.1, 142.2, 139.6, 125.7, 124.7. LC-MS (EI, *m/z*): 314 [M^+]. C, H, N analysis (%): $C_8H_7N_7O_7$ (313.18), Calculated result: C, 30.68; H, 2.25; N, 31.31; Found: C, 30.55; H, 2.31; N, 31.44.

3,5-Diamino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (1c): Yellow solid (0.592 g, 90%). IR (KBr): 3468, 3424, 3315, 3172, 3265, 1693, 1660, 1616, 1534, 1495, 1474, 1336, 1380, 1265, 1167, 1084, 1002, 909 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.583 (s, 2H) 7.026 (s, 4H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.375, 151.806, 142.220, 125.787, 124.897. LC-MS (EI, *m/z*): 328 [M^+]. C, H, N analysis (%): $C_8H_8N_8O_7$ (328.20), Calculated result: C, 29.28; H, 2.46; N, 34.14; Found: C, 29.34; H, 2.49; N, 34.28.

3,4-Diamino-1,2,5-oxadiazol-2-ium 2,4,6-trinitrophenolate (1d): White solid (0.625 g, 95%). IR (KBr): 3430, 3320, 3189, 3101, 1649, 1605, 1517, 1430, 1336, 1260, 1156, 1084, 942 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.597 (s, 2H) 6.882 (s, 5H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 160.5, 150.1, 142.0, 125.8, 125.6. LC-MS (EI, *m/z*): 330 [M^+]. C, H, N analysis (%): $C_8H_7N_7O_8$ (329.18), Calculated result: C, 29.19; H, 2.14; N, 29.78; Found: C, 29.27; H, 2.18; N, 29.64.

Diaminomethaniminium-2,4,6-trinitrophenolate (1e): Yellow solid (0.657 g, 94%). IR (KBr): 3468, 3430, 3254, 3194, 3095, 1660, 1605, 1556, 1424, 1342, 1260, 1145, 1073, 915 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.591 (s, 2H), 6.944 (s, 6H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.0, 158.3, 142.0, 125.8, 125.4. LC-MS (EI, *m/z*): 289 [M^+]. C, H, N analysis (%): $C_7H_8N_6O_7$ (288.17), Calculated result: C, 29.18; H, 2.80; N, 29.16; Found: C, 29.10; H, 2.76; N, 29.09.

2,4,6-Trinitro-m-cresol: The preparation of 2,4,6-trinitro-m-cresol is given in Scheme 1. A round-bottom flask was charged with sulfuric acid (98%, 20mL) and cooled to approximately 5 °C. Potassium nitrate (0.808 g, 0.008m) was added slowly with stirring to avoid rise in the temperature. After complete addition of potassium nitrate, the reaction mixture stirred for 15 min and m-cresol (0.208g, 0.002m) was added at a rate such that the temperature did not exceed 10 °C. Vigorous stirring was maintained to prevent concentrating the solid in the center. After complete m-cresol addition, the reaction mixture was stirred for 15 min and the cooling bath was removed. The reaction was stirred for an additional 30 min at room temperature. The reaction mixture poured into crushed ice and resulting precipitate was isolated by filtration, washed with cold 10% HCl and water. The resultant yellow solid was air dried to afford 2,4,6-trinitro-m-cresol (0.420 g, 86%). IR (KBr): 3326, 3210, 3106, 1643, 1594, 1545, 1463, 1424, 1342,1315, 1178, 1063, 1035, 920 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.739 (s, 1H) 2.340 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.567, 149.809, 135.690, 131.132, 128.544, 126.617, 16.170. LC-MS (EI, *m/z*): 244 [M^+]. C, H, N analysis (%): $C_7H_5N_3O_7$ (243.13), Calculated result: C, 34.58; H, 2.07; N, 17.28; Found: C, 34.44; H, 2.11; N, 17.38.

General procedure for the preparation of salts from 2,4,6-trinitro-m-cresol: A solution of 4-amino-4*H*-1,2,4-triazole (0.084 g, 0.001m), 3-amino-1,2,4-triazole (0.084 g, 0.001m), 3,5-diamino-1,2,4-triazole (0.099 g, 0.001m), 3,4-diaminofurazan (0.100 g, 0.001m), or guanidine nitrate (0.122 g, 0.001m) was slowly added to a solution of 2,4,6-trinitro-m-cresol (0.243 g, 0.001m) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product.

4H-1,2,4-Triazol-4-aminium 3-methyl-2,4,6-trinitrophenolate (2a): Yellow solid (0.307 g, 94%). IR (KBr): 3347, 3293, 3117, 1605, 1419, 1271, 1156, 1068 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.494 (s, 2H) 8.740(s, 1H) 2.328 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 160.100, 150.545, 144.478, 135.691, 130.834, 127.002, 126.905, 16.285. DEPT (100 MHz, DMSO): δ (ppm) 144.475, 126.907, 16.288. LC-MS (EI, *m/z*): 326 [M^+]. C, H, N analysis (%): $C_9H_9N_7O_7$ (327.21), Calculated result: C, 33.04; H, 2.77; N, 29.96; Found: C, 33.18; H, 2.71; N, 29.86.

3-Amino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (2b): Yellow solid (0.295 g, 90%). IR (KBr): 3452, 3331, 3161, 1682, 1632, 1575, 1532, 1435, 1347, 1320, 1249, 1161, 1052, 953 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.722 (s, 1H) 8.300 (s, 1H) 2.312 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 160.259, 151.199, 150.628, 139.685, 135.725, 130.776, 126.919, 16.274. LC-MS (EI, *m/z*): 328 [M^+]. C, H, N analysis (%): $C_9H_9N_7O_7$ (327.21), Calculated result: C, 33.04; H, 2.77; N, 29.96; Found: C, 33.11; H, 2.69; N, 29.89.

3,5-Diamino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (2c): Orange solid (0.319 g, 93%). IR (KBr): 3463, 3369, 3189, 1698, 1660, 1627, 1567, 1528, 1309, 1249, 1150, 1079, 1024, 920 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.744 (s, 1H) 2.334 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 160.289, 151.886, 150.610, 135.690, 130.823, 126.925, 126.883, 16.268. DEPT (100 MHz, DMSO): δ (ppm) 126.998, 16.268. LC-MS (EI, *m/z*): 343 [M^+]. C, H, N analysis

(%): $C_9H_{10}N_8O_7$ (342.23), Calculated result: C, 31.59; H, 2.95; N, 32.74; Found: C, 31.51; H, 2.87; N, 32.68.

3,4-Diamino-1,2,5-oxadiazol-2-ium 3-methyl-2,4,6-trinitrophenolate (2d): Brown solid (0.302 g, 88%). IR (KBr): 3424, 3320, 3260, 3106, 1638, 1594, 1545, 1452, 1353, 1315, 1161, 1068, 920 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.745 (s, 1H) 7.200(s, 4H) 2.346 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.659, 150.172, 149.851, 135.712, 131.142, 128.539, 126.594, 16.171. DEPT (100 MHz, DMSO): δ (ppm) 126.598, 16.174. LC-MS (EI, *m/z*): 344 [M^+]. C, H, N analysis (%): $C_9H_9N_7O_8$ (343.21), Calculated result: C, 33.04; H, 2.77; N, 29.96; Found: C, 33.11; H, 2.69; N, 29.89.

Diaminomethaniminium 3-methyl-2,4,6-trinitrophenolate (2e): Yellow solid (0.338 g, 93%). IR (KBr): 3408, 3205, 3106, 1665, 1638, 1594, 1539, 1463, 1419, 1347, 1172, 1063, 915 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.738 (s, 1H) 6.948(s, 6H) 2.336 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.849, 158.381, 149.882, 135.652, 131.183, 128.529, 126.613, 16.151. DEPT (100 MHz, DMSO): δ (ppm) 126.617, 16.154. LC-MS (EI, *m/z*): 303 [M^+]. C, H, N analysis (%): $C_8H_{10}N_6O_7$ (302.20), Calculated result: C, 31.80; H, 3.34; N, 27.81; Found: C, 31.70; H, 3.17; N, 27.76.

3-Azido-2,4,6-trinitrophenol: The preparation of 3-azido-2,4,6-trinitrophenol is given in Scheme 2. To a 100-ml round-bottomed flask, 10 ml of concentrated H_2SO_4 was transferred and 8 ml of fuming nitric acid was added drop wise at room temperature with stirring. After complete addition, nitrating mixture chilled to approximately 5 °C. To this nitrating mixture, 3-chlorophenol (0.645g, 0.005m) was added slowly over a period of 30 min to avoid a vigorous reaction. After complete addition, ice bath removed and the reaction mixture subjected to heating (70 °C) for 2hrs. The reaction mixture was cooled and poured into crushed ice. Resulting precipitate was isolated by filtration and thoroughly washed with water to give 3-chloro-2,4,6-trinitrophenol yellow solid (0.920g, 75%). This compound (0.396 g, 0.0015m) dissolved in methanol (10 mL) and sodium azide (0.117 g, 0.0018m) was added and the reaction continued for 2 h at room temperature. The resulting mixture was heated at reflux for an additional 2 h. After this, the solvent was removed and the residue was extracted with ethyl acetate and washed with water. The solvent was removed under reduced pressure to give pure product **3** (0.380 g, 94%). IR (KBr): 3495, 2920, 2849, 2136, 1660, 1578, 1528, 1484, 1347, 1260, 1117 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.76 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 159.4, 149.1, 136.5, 127.3, 124.3. DEPT (100 MHz, DMSO): δ (ppm) 127.3. LC-MS (EI, *m/z*): 271 [M^+]. C, H, N analysis (%): $C_6H_2N_6O_7$ (270.12), Calculated result: C, 26.68; H, 0.75; N, 31.11; Found: C, 26.54; H, 0.72; N, 31.02.

General procedure for the preparation of salts from 3-azido-2,4,6-trinitrophenol: A solution of 4-amino-4*H*-1,2,4-triazole (0.084 g, 0.001m), 3-amino-1,2,4-triazole (0.084 g, 0.001m), 3,5-diamino-1,2,4-triazole (0.099 g, 0.001m), 3,4-diaminofurazan (0.100 g, 0.001m), or guanidine nitrate (0.122 g, 0.001m) was slowly added to a solution of 3-azido-2,4,6-trinitrophenol (0.270 g, 0.001m) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product.

3-Amino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (3b): Brown solid (0.295 g, 83%). IR (KBr): 3048, 2164, 2054. 1660, 1578, 1550, 1534, 1501, 1457, 1353, 1260, 1123, 1057, 997, 750 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.054 (s, 1H) 7.405 (s, 1H) 5.833 (s, 2H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.7, 157.2, 149.4, 148.3, 135.2, 127.5, 115.2, 111.4. LC-MS (EI, *m/z*): 355 [M^+]. C, H, N analysis (%): $C_8H_6N_{10}O_7$ (354.20), Calculated result: C, 27.13; H, 1.71; N, 39.54; Found: C, 27.01; H, 1.74; N, 39.47.

3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (3c): Brown solid (0.319 g, 86%). IR (KBr): 3408, 2920, 2153, 2049, 1649, 1567, 1490, 1408, 1375, 1347, 1254, 1128, 1063 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.033 (s, 1H) 5.168 (s, 4H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.7, 148.3, 135.2, 127.5, 115.2, 111.4. LC-MS (EI, *m/z*): 368 [M^+]. C, H, N analysis (%): $C_8H_7N_{11}O_7$ (369.21), Calculated result: C, 26.02; H, 1.91; N, 41.73; Found: C, 25.84; H, 1.98; N, 41.85.

3,4-Diamino-1,2,5-oxadiazol-2-ium 3-azido-2,4,6-trinitrophenolate (3d): Brown solid (0.302 g, 82%). IR (KBr): 3441, 3309, 3260, 2926, 2147, 2054, 1649, 1572, 1528, 1473, 1347, 1260, 1128, 1002, 975 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.051 (s, 1H) 5.931 (s, 4H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.7, 150.2, 148.3, 135.2, 127.5, 115.1, 111.4. LC-MS (EI, *m/z*): 372 [M^+]. C, H, N analysis (%): $C_8H_6N_{10}O_8$ (370.20), Calculated result: C, 25.96; H, 1.63; N, 37.84; Found: C, 25.79; H, 1.74; N, 37.96.

Diaminomethaniminium 3-azido-2,4,6-trinitrophenolate (3e): Orange solid (0.338g, 86%). IR (KBr): 3589, 3402, 2147, 2049, 1650, 1567, 1528, 1479, 1347, 1123, 986 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 9.056 (s, 1H) 7.063 (s, 6H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 161.7, 158.5, 148.3, 135.2, 127.5, 115.2, 111.4. LC-MS (EI, *m/z*): 330 [M^+]. C, H, N analysis (%): $C_7H_7N_9O_7$ (329.19), Calculated result: C, 25.54; H, 2.14; N, 38.29; Found: C, 25.41; H, 2.10; N, 38.20.

Styphnic acid: The preparation of styphnic acid is given in Scheme 3. The compound was prepared from two different starting materials, 2-nitroresorcinol (0.620 g, 0.004m) and resorcinol (0.550 g, 0.005m) with the similar method for compound **2**, forming a yellow solid in 88% yield. IR (KBr): 3649, 3577, 3177, 1648, 1582, 1544, 1467, 1374, 1308, 1166, 1073, 919 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.608 (s, 1H) 6.744(s, 2H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 155.7, 135.4, 126.1, 126.0. LC-MS (EI, *m/z*): 246 [M^+]. C, H, N analysis (%): $C_6H_3N_3O_8$ (245.10), Calculated result: C, 29.40; H, 1.23; N, 17.14; Found: C, 29.54; H, 1.12; N, 17.03.

General procedure for the preparation of salts from styphnic acid: A solution of 4-amino-4*H*-1,2,4-triazole (0.084 g, 0.001m), 3-amino-1,2,4-triazole (0.084 g, 0.001m), 3,5-diamino-1,2,4-triazole (0.099 g, 0.001m), 3,4-diaminofurazan (0.100 g, 0.001m), or guanidine nitrate (0.122 g, 0.001m) was slowly added to a solution of styphnic acid (0.123 g, 0.0005m) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h

at room temperature, the solvent was removed in vacuo to leave the desired product.

Bis(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (4b): Yellow solid (0.184 g, 89%). IR (KBr): 3304, 3139, 1698, 1600, 1556, 1490, 1304, 1189, 1079, 958 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.628 (s, 1H) 7.883 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 156.3, 154.7, 143.9, 135.6, 126.2, 125.8. DEPT (100 MHz, DMSO): δ (ppm) 143.9, 126.6. LC-MS (EI, *m/z*): 414 [M^+]. C, H, N analysis (%): $C_{10}H_{11}N_{11}O_8$ (413.26), Calculated result: C, 29.06; H, 2.68; N, 37.28; Found: C, 29.17; H, 2.61; N, 37.12.

Bis(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (4c): Orange solid (0.21 g, 95%). IR (KBr): 3451, 3407, 3270, 3183, 1703, 1648, 1572, 1478, 1385, 1308, 1199, 1045, 1002, 936 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.66 (s, 1H) 7.25 (s, 8H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.0, 154.5, 136.3, 126.9, 126.1. DEPT (100 MHz, DMSO): δ (ppm) 126.9. LC-MS (EI, *m/z*): 444 [M^+]. C, H, N analysis (%): $C_{10}H_{13}N_{13}O_8$ (443.29), Calculated result: C, 27.09; H, 2.96; N, 41.08; Found: C, 27.17; H, 2.93; N, 40.95.

Bis(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3-diolate (4d): Gray solid (0.198 g, 89%). IR (KBr): 2915, 2849, 2706, 2597, 2010, 1747, 1594, 1528, 1473, 1331, 1249, 1210, 1123, 1057, 1008, 920 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.63 (s, 1H) 6.25 (s, 8H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 155.9, 150.1, 135.4, 126.1, 125.9. DEPT (100 MHz, DMSO): δ (ppm) 126.1. LC-MS (EI, *m/z*): 446 [M^+]. C, H, N analysis (%): $C_{10}H_{11}N_{11}O_{10}$ (445.26), Calculated result: C, 26.97; H, 2.49; N, 34.60; Found: C, 26.87; H, 2.54; N, 34.50.

Bis(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3-diolate (4e): Gray solid (0.234 g, 95%). IR (KBr): 3643, 3413, 3331, 3199, 1665, 1577, 1539, 1467, 1363, 1308, 1160, 1067, 919 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.63 (s, 1H) 6.96 (s, 12H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.3, 156.0, 135.4, 126.2, 125.8. DEPT (100 MHz, DMSO): δ (ppm) 126.2. LC-MS (EI, *m/z*): 362 [M^+]. C, H, N analysis (%): $C_8H_{13}N_9O_8$ (363.24), Calculated result: C, 26.45; H, 3.61; N, 34.70; Found: C, 26.56; H, 3.55; N, 34.78.

2,4,6-Trinitro-1,3,5-benzenetriol: The preparation of 2,4,6-trinitro-1,3,5-benzenetriol is given in Scheme 4. The compound was prepared from two different starting materials, 2-nitrophloroglucinol (0.684 g, 0.004m) and phloroglucinol (0.630 g, 0.005m) with the similar method for compound **2**, forming a yellow solid in 90% yield. IR (KBr): 3643, 3577, 1637, 1582, 1528, 1413, 1352, 1308, 1210, 1171, 1111, 908 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 6.633 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 154.2, 122.4. LC-MS (EI, *m/z*): 262 [M^+]. C, H, N analysis (%): $C_6H_3N_3O_9$ (261.10), Calculated result: C, 27.60; H, 1.16; N, 16.09; Found: C, 27.68; H, 1.12; N, 15.96.

General procedure for the preparation of salts from 2,4,6-trinitro-1,3,5-benzenetriol: A solution of 4-amino-4*H*-1,2,4-triazole (0.101 g, 0.0012m), 3-amino-1,2,4-triazole (0.101 g, 0.0012m), 3,5-diamino-1,2,4-triazole (0.119 g, 0.0012m), 3,4-diaminofurazan (0.120 g, 0.0012m), or guanidine nitrate (0.146 g, 0.0012m) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.0004mol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product.

Tris(4H-1,2,4-triazol-4-aminium) 2,4,6-trinitrobenzene-1,3,5-triolate (5a): Orange solid (0.185g, 90%). IR (KBr): 3429, 3287, 3122, 1615, 1506, 1374, 1254, 1193, 1067, 1023, 892 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 8.71 (s, 6H), 6.07 (s, 9H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 154.6, 144.5, 122.3. LC-MS (EI, *m/z*): 514 [M^+]. C, H, N analysis (%): $C_{12}H_{15}N_{15}O_9$ (513.34), Calculated result: C, 28.08; H, 2.95; N, 40.93; Found: C, 28.21; H, 3.05; N, 40.99.

Tris(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (5b): Yellow solid (0.176 g, 86%). IR (KBr): 3419, 3315, 3150, 3052, 1687, 1638, 1556, 1490, 1331, 1238, 1123, 1041, 944 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 7.724 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 156.1, 155.9, 145.5, 122.6. LC-MS (EI, *m/z*): 514 [M^+]. C, H, N analysis (%): $C_{12}H_{15}N_{15}O_9$ (513.34), Calculated result: C, 28.08; H, 2.95; N, 40.93; Found: C, 28.01; H, 3.07; N, 41.05.

Tris(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (5c): Orange solid (0.198 g, 89%). IR (KBr): 3446, 3402, 3309, 3188, 3122, 1703, 1654, 1621, 1572, 1489, 1413, 1368, 1254, 1056, 1002 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 7.493 (s, 12H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 159.4, 155.5, 123.6. LC-MS (EI, *m/z*): 559 [M^+]. C, H, N analysis (%): $C_{12}H_{18}N_{18}O_9$ (558.39), Calculated result: C, 25.81; H, 3.25; N, 45.15; Found: C, 25.96; H, 3.30; N, 45.02.

Tris(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (5d): Yellow solid (0.202 g, 90%). IR (KBr): 3616, 3528, 3424, 3320, 3254, 3265, 3117, 1632, 1182, 1511, 1478, 1347, 1193, 1171, 969 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 6.422 (s, 12H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 154.3, 150.1, 122.4. LC-MS (EI, *m/z*): 562 [M^+]. C, H, N analysis (%): $C_{12}H_{15}N_{15}O_{12}$ (561.34), Calculated result: C, 25.68; H, 2.69; N, 37.43; Found: C, 25.81; H, 2.74; N, 37.34.

Tris(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3,5-triolate (5e): Yellow solid (0.223 g, 89%). IR (KBr): 3435, 3336, 3259, 3199, 1522, 1462, 1369, 1314, 1193, 1139, 903 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ (ppm) 6.98 (s, 18H). ^{13}C NMR (100 MHz, DMSO): δ (ppm) 158.3, 154.5, 122.3. LC-MS (EI, *m/z*): 439 [M^+]. C, H, N analysis (%): $C_9H_{18}N_{12}O_9$ (438.31), Calculated result: C, 24.66; H, 4.14; N, 38.35; Found: C, 24.78; H, 4.10; N, 38.48.

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Table of Content

Energetic salts with 1:1, 2:1, and 3:1 charge ratio (cation: anion) based on various nitrogen-rich cations and phenolate anions have been synthesized by a straightforward and simple method.