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# Synthesis and characterization of a new family of energetic salts based on guanidinium cation containing picryl moiety

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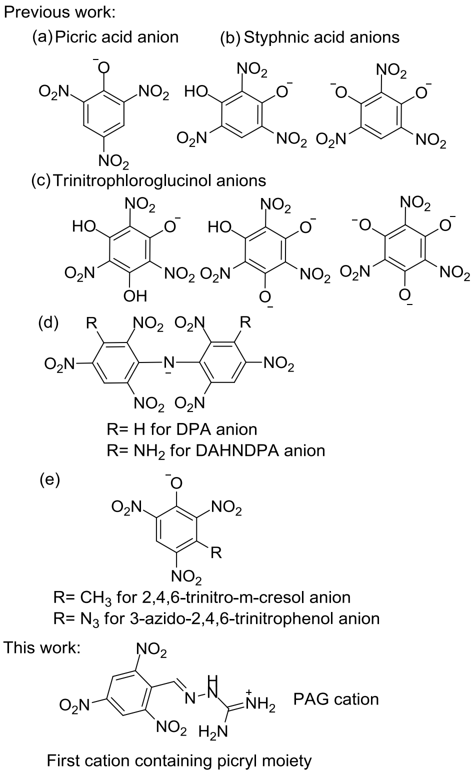
A new family of energetic salts based on a new guanidinium cation containing picryl moiety, *N*-(2,4,6-trinitrobenzylideneamino) guanidinium cation, were synthesized and well characterized by IR and multinuclear NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetry analysis (TG) and elemental analysis. The structures of *N*-(2,4,6-trinitrobenzylideneamino)guanidinium nitrate (**1**) and *N*-(2,4,6-trinitrobenzylideneamino)guanidinium 5-nitrotetrazolate (**5**) were confirmed by single crystal X-ray diffraction. Most of the salts decompose at temperatures over 180 °C. Furthermore, except for salts **1** and **9**, most energetic salts exhibit low impact sensitivities (20-40 J), friction sensitivities (220-340 N), and are insensitive to electrostatics. The detonation pressure values calculated for energetic salts **1** and **3-9** range from 23.7 to 30.3 GPa, and the detonation velocities range from 7842 to 8394 m $s^{-1}$. These values indicate that some energetic salts can be the candidate for energetic materials possessing good thermal stabilities and low sensitivities.

## Introduction

In the recent years, energetic materials acted as controllable storage systems for relatively large amounts of chemical energy have been widely studied for civilian and military applications.[1] To meet the requirements for improved energetic materials, the synthesis of energetic compounds with high performance or enhanced insensitivity to thermal or shock insults has attracted considerable interest. Energetic salts as a unique class of high energetic materials have been developed.[1e, 1f, 2] They often possess the advantages of lower vapor pressure (less toxic vapor in handling) and better thermal stability over nonionic analogues. In these ionic species, energetic salts based on high nitrogen content moiety are predominant. Generally, these energetic salts possess high heats of formation, which are directly attributed to the large number of energetic N–N and C–N bonds.[3] Nitrogen-containing heterocycles can act as cations or anions in energetic salts, depending on the substituents attached to them. In general, nitrogen-containing heterocycles containing energetic groups, such as nitro groups,[4] azo groups,[5] nitramines[6] and furazan[7] fragments, were used as energetic anions. Synthesis of energetic salts based on the combination of these anions with different cations, is of particular interest.

Polynitroarenes have been widely investigated and used in civil as well as military applications due to their remarkable properties.[8] Benzene compounds having three or more nitro groups exhibit distinctly marked explosive properties (e.g., TNT, picric acid, 2,4,6-trinitroanisole, and 1,3,5-triamino-2,4,6-trinitrobenzene(TATB)). The nitro-group is a powerful moiety in building high performance energetic compounds. The presence of nitro groups tends to decrease the heat of formation, but contributes markedly to the density and oxygen balance.[4b, 9] Overall, it is helpful to enhance the energetic performance (detonation pressure and velocity). In the aspect of energetic salts, as shown in Scheme 1, polynitroarene-based energetic salts have been reported: energetic salts of picric acid,[10] styphnic acid (2,4,6-trinitrobenzene-1,3-diol),[10f, 10g] trinitrophloroglucinol,[10f, 10g, 11] dipicrylamine (DPA),[12] 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenylamine (DAHNDPA),[12] 2,4,6-trinitro-m-cresol[10g] and 3-azido-2,4,6-trinitrophenol.[10g] Among them, compounds containing polynitroarene moiety only act as anions, inheriting the feature of electron-withdrawing inductive effect from nitro groups. On the other hand, few energetic salts based on the cations containing polynitro moieties have been reported.[13] In the present work, a new family of energetic salts based on the *N*-(2,4,6-trinitrobenzylideneamino)guanidinium cation (PAG cation), were designed and successfully synthesized. All new energetic salts were well characterized by IR and multinuclear NMR spectroscopy, differential scanning calorimetry, thermogravimetry analysis and elemental analysis. Their key detonation properties and the sensitivities towards impact, friction and electrical discharge were characterized by experimental and theoretical methods.

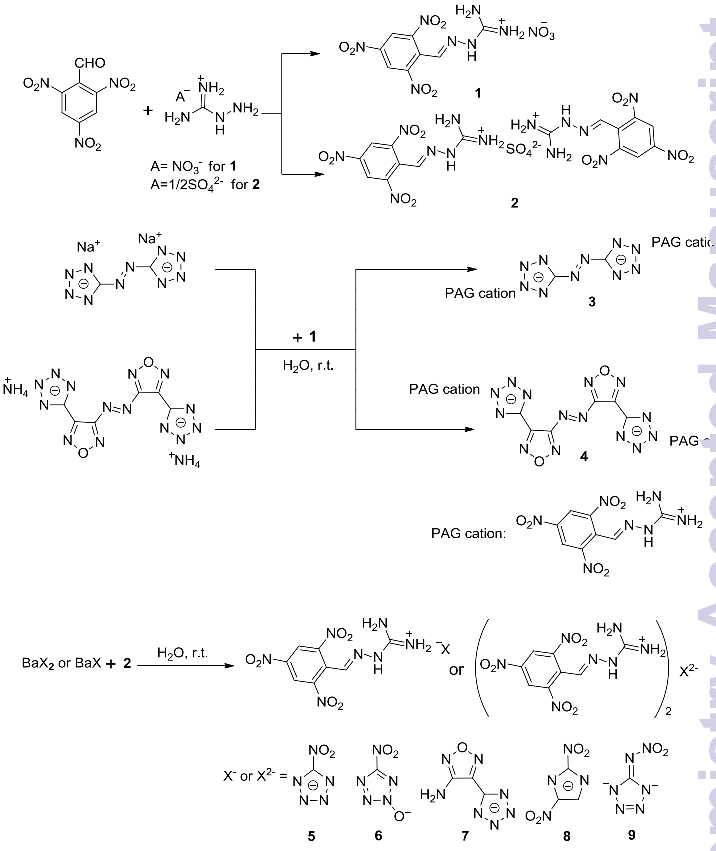


Scheme 1 Energetic anions and PAG cation based on polynitroarene

## Results and discussion

### Synthesis

As illustrated in Scheme 2, the synthetic pathway to all of the new energetic salts **3-9** is depicted. The starting compounds, *N*-(2,4,6-trinitrobenzylideneamino)guanidinium nitrate (**1**) and bis(*N*-(2,4,6-trinitrobenzylideneamino)guanidinium) sulphate (**2**) were prepared via the condensation reactions of aminoguanidium nitrate and bis(1-aminoguanidinium) sulphate with 2,4,6-trinitrobenzaldehyde in ethanol solution in yield of 90% and 92%, respectively. Direct reactions of *N*-(2,4,6-trinitrobenzylideneamino)guanidinium nitrate (**1**) with disodium 5,5'-azotetrazolate pentahydrate and diammonium (*E*)-1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene resulted in the formation of salts **3** and **4**, which deposited almost immediately in aqueous solution. As known, one of the widely used methods for synthesis of energetic salts is based on metathesis reactions of the barium salts with sulfates. In the present work, energetic salts **5-9** were prepared from anion exchange of barium 5-nitrotetrazolate, barium 5-nitrotetrazolate-2*N*-oxide, barium 4-amino-3-(5-tetrazolate)furazan, barium 2,4-dinitroimiazolate and barium 5-nitroiaminotetrazolate with bis(*N*-(2,4,6-trinitrobenzylideneamino)guanidinium) sulphate (**2**) in water.



Scheme 2 Synthesis of new energetic salts **3-9**

### Structure Analysis

The $^1H$ NMR and $^{13}C$ NMR spectra of salts **1-9** were measured in [$D_6$]DMSO. Additionally, the $^{15}N$ NMR spectra of salts **1** and **5** were measured in [$D_6$]DMSO and the chemical shifts are given with respect to $CH_3NO_2$ as external standard. The $^1H$ and $^{13}C$ NMR spectra of all compounds were given in the Supporting Information (Figures S1-S18). For salts **3-6** and **9**, in the $^1H$ NMR spectra, all the proton signals are assigned to the PAG cation. For salts **7** and **8**, the rest proton signals are assigned to $–NH_2$ group and imidazole ring, respectively. In the $^1H$ NMR spectra of **3-9**, the proton signals of picryl moiety range between $\delta$ = 8.58 and 9.14 ppm, which agrees with that of reported picryl derivatives.[14] The proton signals of the -C*H*=N- groups were observed ranging from $\delta$ = 8.39 to 8.59 ppm. For salts **3**, **5**, **7** and **9**, the proton signals of protonated guanidinium moiety were observed as a sharp singlet at $\delta$ = 7.55, 7.73, 7.75 and 7.08 ppm, respectively. In the case of salts **6** and **8**, the resonance of protonated guanidinium moieties split into three and two different signals, respectively. The proton signals of protonated guanidinium moiety appear as a broad singlet at $\delta$ = 6.45 ppm in the case of **4**. The difference can be attributed to the different hydrogen bonding interactions between cations and anions within their structures. In the $^{13}$C NMR spectra, for all salts, the carbon signals of picryl moiety are identified around $\delta$ = 150, 148, 130 and 125 ppm. The carbon signals of the -*C*=N- group bonded to the picryl moiety, and the protonated guanidinium moiety appear approximately between $\delta$ = 136 and 145 ppm and between $\delta$ = 155.5 and 163.7 ppm, respectively. The rest carbon signals of energetic salts are assigned to the anions, which are consistent with previously recorded shifts for such anions.[4a, 4d, 5a, 6h, 7a, 15]

The $^{15}$N NMR spectra of salts **1** and **5** are presented as examples in Figure 1. The assignments for all nitrogen signals are based on the literature values of the similar compounds.[16] For salt **1**, as shown in Figure 1, six nitrogen signals were observed. The nitrogen signals of nitrate anion were found at the lowest field appearing at $\delta$ = -4.32 (N8) ppm. The strong signals assigned to the nitro groups appeared at $\delta$ = -16.74 (N1/N3) and -19.97 (N2) ppm, respectively. The signal of the N4 atom of the -C=N- group, which is directly attached to the picryl moiety, can be assigned to the resonances at $\delta$ = -59.63 ppm due to the presence of three nitro groups in the benzene ring. The signals of nitrogen atoms in -*N*H- group appeared at $\delta$ = -231.62 (N5). The nitrogen signals of protonated guanidinium moiety were observed at the highest field with $\delta$ = -303.82 (N6/N7). For salt **5**, eight nitrogen signals were observed. Among them, five signals were assigned to the PAG cation and the remaining three signals were assigned to the 5-nitrotetrazolate anion. As depicted in Figure 1, for the PAG cation in salt **5**, two nitrogen signals for nitro groups of picryl moiety were found at $\delta$ = -17.11 (N1/N3) and -20.35 (N2) ppm. The nitrogen signals of the -C=N- group and -*N*H- group were found at $\delta$ = -60.22 (N4) and -231.93 (N5) ppm, respectively. The nitrogen signals of the protonated guanidinium moiety were observed at $\delta$ = -303.81 ppm. For 5-nitrotetazolated anion, three signals were observed at $\delta$ = 17.12 (N9/N10), -23.10 (N12), -63.33 (N8/N11) ppm, which were in good agreement with that of energetic slats based on 5-nitrotetrazolated anion.[4a]

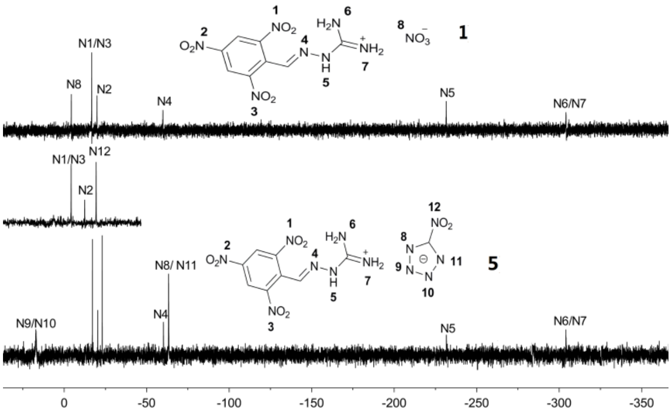


Figure 1 $^{15}$N NMR spectra of salts **1** and **5**.

Two salts described herein (**1** and **5**) were characterized by low-temperature single-crystal X-ray diffraction analysis. Selected data and parameters of the measurements and refinements are gathered in Table 1.

Table 1 Crystal data and structure refinement details of **1** and **5**.

| | **1** | **5** |
|---|---|---|
| Formula | $C_8H_8N_8O_9$ | $C_9H_8N_{12}O_8$ |
| Formula weight | 360.22 | 412.27 |
| Temperature | 173(2) K | 173(2) K |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ | $P$-1 |
| Volume/ Å$^3$ | 2722.8(3) | 790.11(14) |
| $Z$ | 8 | 2 |
| $\rho$ | 1.757 | 1.733 |
| F(000) | 1472 | 420 |
| $a$/ Å | 17.5820(10) | 8.0665(8) |
| $b$/ Å | 10.4936(6) | 8.3119(8) |
| $c$/ Å | 15.8405(10) | 13.9189(14) |
| $\alpha$/ ° | 90 | 90.693(3) |
| $\beta$/ ° | 111.304(2) | 104.018(3) |
| $\gamma$/ ° | 90 | 118.084(3) |
| $\theta$ min-max/ ° | 3.06, 25.35 | 3.05, 25.50 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0478, w$R_2$ = 0.0932 | $R_1$ = 0.0451, w$R_2$ = 0.0698 |
| R indices (all data) | $R_1$ = 0.1073, wR2 = 0.1143 | $R_1$ = 0.1080, w$R_2$ = 0.0795 |
| GooF | 1.016 | 1.009 |
| CCDC | 1031502 | 1024546 |

Salt **1**, *N*-(2,4,6-trinitrobenzylideneamino)guanidinium nitrate, crystallizes from acetonitrile in the monoclinic space group $P2_1/c$ as a twin. There are eight molecules in the unit cell and the density is 1.757 g cm$^{-3}$. The molecules are in an *E* configuration. In two independent *N*-(2,4,6-trinitrobenzylideneamino) guanidinium cations, the atoms in benzene ring are planar with mean deviations from their respective plane of 0.0048 and 0.0059 Å, respectively. And the atoms in the guanidinium moiety are planar with mean deviations from their respective plane of 0.0083 and 0.0589 Å, respectively. The benzene ring and guanidinium moiety are slightly twisted with the dihedral angles between them of 3.6 ° and 0.6 °, respectively. The C—N bond lengths of the protonated guanidinium moiety ranging from 1.308(3) to 1.351(3) Å, lie in the value range of C—N single bond and C—N double bond due to the presence of π-conjugation system.[17] As shown in Figure 2, in the structure of **1**, classical intramolecular hydrogen bonds N12—H12B•••N9, N4—H4B•••O4 and N4—H4B•••N2 were observed. In addition, due to the strong acidity of the protons of –CH=N– groups, non-classical intramolecular hydrogen bonds C7—H7•••O2 and C15—H15•••O7 were observed. As presented in Figure 3, rhombic units built the packing diagram of **1** along the *c* axis. Classical N—H•••O intermolecular hydrogen bonds were found between the protons in guanidinium fragment and the oxygen atoms of nitro groups, and between the protons in guanidinium fragment and nitrate anions. Nonclassical intermolecular hydrogen bonds C7—H7•••O17$^{i}$, C12—H12•••O4$^{i}$ and C15—H15•••O15$^{ii}$ (i: 1-x, 1-y, 1-z; ii: 1+x, y, z) are also observed within the structure of **1**. The details of hydrogen bonds were summarized in in Supporting Information (see Table S4).

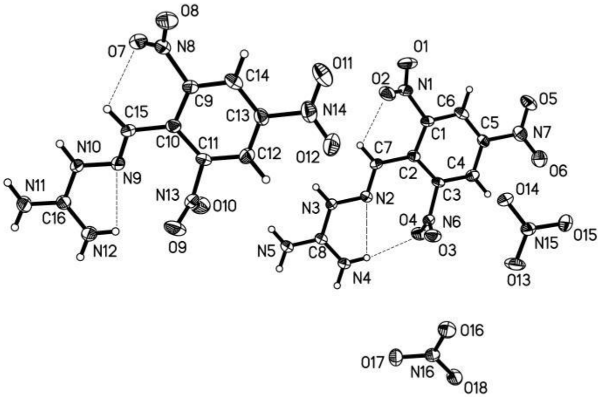


Figure 2 Molecular structure of **1**. Ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

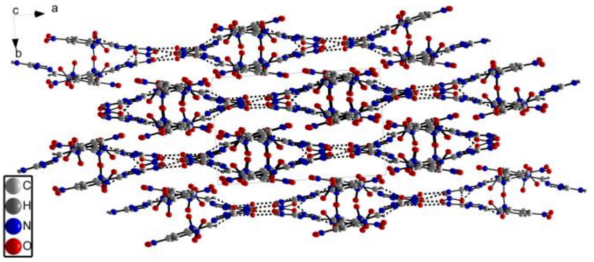


Figure 3 Ball and stick packing diagram of **1** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonds.

*N*-(2,4,6-trinitrobenzylideneamino)guanidinium 5-nitrotetrazolate (**5**) crystallizes from ethanol/toluene in the triclinic space group *P*-1 with four formula units per unit cell. A density of 1.733 g cm$^{-3}$ was determined. As illustrated in Figure 4, the molecules are in an *E* configuration. In the *N*-(2,4,6-trinitrobenzylideneamino) guanidinium cation of salt **5**, the atoms in either benzene ring or guanidinium moiety are also planar with mean deviations from their respective plane of 0.0238 and 0.0252 Å, respectively. But the dihedral angle between the benzene ring and guanidinium moiety is 56.3°, which is much higher than that of salt **1** due to the difference of interactions between the PAG cation and different anions. The bond geometries of the PAG cation in salt **5**, are nearly identical to those of salt **1**. The 5-nitrotetrazolate anions presented in salt **5** also have nearly identical geometries found in other energetic salts based on 5-nitrotetrazolate anions.[4a] As presented in Figure 4, classical intramolecular hydrogen bond N10—H10B•••N7 and non-classical intramolecular hydrogen bond C8—H8•••O5 were observed. In the packing diagram of **5**, as depicted in Figure 5, the benzene rings in the PAG cation pack in parallel along the *b* axis. Classical hydrogen bonds N8—H8A•••N2$^{i}$, N9—H9A•••N4$^{ii}$ and N10—H10A•••N3$^{ii}$ (i: 1-x, 1-y, -z; ii: 1-x, 2-y, -z) can be considered strong hydrogen bonds with the D•••A distances of 2.862(3), 2.916(3) and 3.068(3) Å, which are below the sum of van der Waals radii ($r_w$(N) + $r_w$(N) = 3.10 Å). The D•••A distances of N9—H9B •••O5$^{i}$ and N10—H10B•••O7$^{iii}$ (iii: 2-x, 2-y, 1-z) are below the sum of van der Waals radii ($r_w$(N) + $r_w$(O) = 3.07 Å) at 2.916(3) and 3.038(3) Å, respectively. In addition, due to the higher acidity of the protons of picryl moety, non-classical hydrogen bonds C—H•••O (C5—H5•••O4$^{iv}$ and C7—H7 •••O1$^{iii}$; iv: 1+x, y, z) were found between the protons in picryl moiety and the oxygen atoms of nitro groups. These extensive hydrogen-bonding interactions form a complex 3D network within the structure of salt **5**. The details of all hydrogen bonds are gathered in Supporting Information (see Table S7).

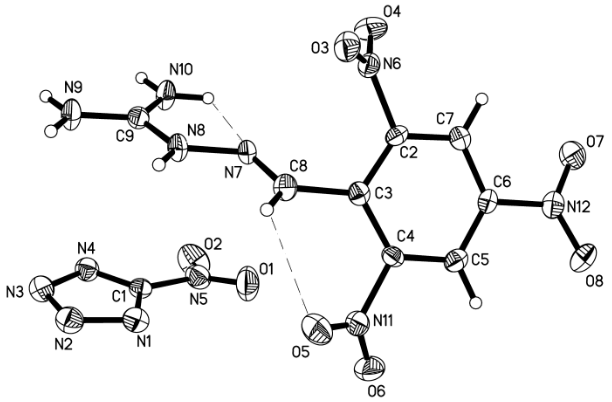


Figure 4 Molecular structure of **5**. Ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

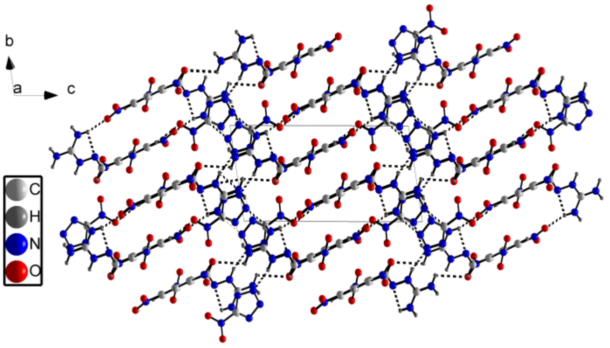


Figure 5 Ball and stick packing diagram of **5** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonds.

## Physicochemical Properties

The thermal behavior of the prepared energetic salts **1** and **3-9** was investigated by differential scanning calorimetry (DSC) and thermogravimetry analysis (TG) at a heating rate of 5 °C min$^{-1}$ (Electronic Supplementary Information, Figures S19-S26). Their decomposition temperatures are determined by the decomposition onset temperatures. As shown in Table 2, salts **6** and **8** have a melting process, whereas the other salts decompose directly. Except for the salts **1** ($T_{d,\ \mathrm{onset}}$ = 133.8 ℃), **3** ($T_{d,\ \mathrm{onset}}$ = 173.4 ℃), **7** ($T_{d,\ \mathrm{onset}}$ = 160.2 ℃) and **9** ($T_{d,\ \mathrm{onset}}$ = 171.1 ℃), the decomposition temperature ($T_{d,\ \mathrm{onset}}$) of all other energetic salts is higher than 180 ℃, which is a general temperature requirement for energetic materials prior to adaptation for practical use.[18] In particular, the decomposition process of salt **3** possesses two steps with the peak temperatures of 186.3 ℃ and 206.6 ℃. Meanwhile, the other energetic salts exhibit one exothermic process. Among these energetic salts, salt **8** has the highest thermal stability, $T_{\mathrm{d,\ onset}}$ = 207.3 ℃, which is comparable to that of RDX (205 ℃).[18a] For all salts, the exothermic temperature range agrees with that of weight loss. Among these energetic materials, the least mass loss with the value of 50% can be observed in the exothermic temperature range of salts **3**, **4** and **7**. It can be attributed to their low nitrogen and oxygen content. A mass loss of 60% can be observed in the exothermic range of salts **6** and **8**. Within the decomposing process of salts **1** and **9**, mass loss of 75% and 80% are observed, respectively. In particular, salt **5** decomposed with the most mass loss of 90% at the exothermic temperature range.

Table 2. Physicochemical properties of salts **1** and **3**–**9** compared with 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and triaminotrinitrobenzene (TATB).

| Salts | $T_d$ [a] [°C] | $\Delta H_c^o$ [b] [kJ mol$^{-1}$] | $\Delta H_a^o$ [c] [kJ mol$^{-1}$] | $\Delta H_L$ [d] [kJ mol$^{-1}$] | $\Delta H_f^o$ [e] [kJ mol$^{-1}$] | IS [f] [J] | FS [g] [N] | ESD [h] [J] | P [i] [m s$^{-1}$] | D [j] [GPa] |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 133.8 | 866 | -314 | 446 | 106 | 11 | 168 | 0.32 | 29.6 | 8256 |
| **3** | 173.4 | 866 | 788 | 932 | 722 | 40 | 340 | 0.82 | 23.7 | 7842 |
| **4** | 190.5 | 866 | 1200 | 880 | 1187 | 38 | 320 | 0.52 | 25.0 | 7980 |
| **5** | 196.7 | 866 | 112 | 431 | 547 | 30 | 300 | 0.36 | 29.0 | 8320 |
| **6** | 199.3 | 866 | 58 | 428 | 496 | 20 | 220 | 0.30 | 30.3 | 8394 |
| **7** | 160.2 | 866 | 332 | 420 | 777 | 40 | 340 | 0.78 | 26.1 | 8116 |
| **8** | 207.3 | 866 | -130 | 420 | 316 | 34 | 300 | 0.54 | 27.6 | 8107 |
| **9** | 171.1 | 866 | 402 | 955 | 313 | 8 | 140 | 0.2 | 25.1 | 7955 |
| RDX[18a] | 230 | - | - | - | - | 7.4 | 120 | 0.2 | 35.2[19] | 8977[19] |
| TATB[14h, 18b] | 350 | - | - | - | 76 | 50 | 350 | - | 31.15 | 8114 |

[a] Decomposition temperature. [b] Molar enthalpy of the formation of the cation. [c] Molar enthalpy of the formation of the anion. [d] Lattice enthalpy. [e] Molar enthalpy of the formation of the salt. [f] Impact sensitivity. [g] Friction sensitivity. [h] Electrostatic discharge sensitivity. [i] Detonation pressure. [j] Detonation velocity.

The sensitivities of the energetic salts **1** and **3-9** towards impact, friction, and electrostatic discharge were tested by using standard procedures.[20] As presented in Table 2, for the electrostatic sensitivities, salts **3** (0.82 J), **4** (0.52), **7** (0.78 J) and **8** (0.54 J) are significantly less sensitive than RDX (0.20 J).[18a] The electrostatic sensitivity values of salts **1**, **5** and **6** are 0.32 J, 0.36 J and 0.30 J, respectively, which are slightly greater than that of RDX (0.20 J). The electrostatic sensitivity of **9** is comparable to RDX (0.20 J) with the value of 0.2 J. For energetic salts **1** and **3-9**, their impact sensitivity values lie in the range between 8 (**9**) to 40 J (**3** and **7**). The friction sensitivity values are found in the range from 120 (**9**) to 340 N

(**3** and **7**). It indicates that all energetic salts are more sensitive than TATB (50 J, 350 N).[14h, 18b] But based on the classification standard of sensitivities,[21] salts **3** and **7** are classified as less sensitive due to their impact sensitivities of 40 J and friction sensitivity of 330 N, respectively. The impact sensitivities of salts **4**, **5** and **8** are 38, 30 and 34 J, respectively, which shows that they are significantly less sensitive than RDX (7.4 J). Salts **1**, **6** and **9** are less sensitive to impact and friction than RDX (7.4 J, 120 N) due to their impact sensitivities of 11, 20 and 8 J, and friction sensitivities of 168, 220 and 140 N, respectively.

To evaluate the performance of energetic salts, the heat of formation is an important parameter. It can be calculated with good accuracy through the results of the heats of formation of the cation and anions, and the lattice energy of salts. The details are presented in Supporting Information. The heats of formation of the PAG cation and presented anions were calculated by using the Gaussian 09 suite of programs:[22] geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-311+G** basis set[23] through designed isodesmic reactions (Supporting Information, Scheme S1). The calculated heats of formation are summarized in Table 2, and that of the PAG cation is 866 kJ mol$^{-1}$. All energetic salts possess positive heats of formation ranging from 106 to 1187 kJ mol$^{-1}$, of which salt **4** exhibits the highest value at 1187 kJ mol$^{-1}$.

The detonation velocity (*D*) and detonation pressure (*P*), which are used to characterize the performance of a high explosive, were calculated by using the EXPLO5 v6.01 program.[24] As shown in Table 2, the detonation pressures of salts **3-9** lie in the range between $P$ = 23.7 and P = 30.3 GPa (compared with TNT, 19.53 GPa; TATB, 30.5 GPa; RDX, 35.2 GPa). Their detonation velocities are found in the range between $D$ = 7842 and 8394 m s$^{-1}$ (compared with TNT, 6881m s$^{-1}$; TATB, 8176 m s$^{-1}$; RDX, 8997 m s$^{-1}$).

## Conclusions

A new family of energetic salts **3-9** based on guanidinium cation (PAG cation) containing picryl moiety, were synthesized and well characterized with NMR and IR spectra, differential scanning calorimetry (DSC), thermogravimetry analysis (TG), as well as elemental analysis. The structures of salts **1** and **5** were confirmed by single crystal X-ray measurements. According to the DSC results, except for the salts **1**, **3**, **7** and **9**, the decomposition onset temperatures ($T_{\mathrm{d,\ onset}}$) of the remaining energetic salts are higher than 180 ℃. In particular, the most stable salt was **8**, which decomposed at 207.3 ℃. Its decomposition onset temperature is comparable to that of RDX ($T_{\mathrm{d}}$ = 205 °C). Except for salts **1** (11 J, 168 N) and **9** (8 J, 140 N), the remaining energetic salts exhibit low impact sensitivities (20–40 J) and friction sensitivities (220–340 N). Salts **1** and **3-9** possess positive heats of formation, whose values lie in the range from 106 to 1187 kJ mol$^{-1}$. With the EXPLO5 v6.01 program, the detonation pressures and velocities were calculated. For energetic salts **1** and **3-9**, calculated detonation pressures and velocities ranged from 23.7 to 30.3 GPa and 7842 to 8394 m s$^{-1}$, respectively. Based on these results, some energetic salts are potential promising candidates for energetic materials.

## Experimental

*Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged.*

### General Methods

All chemical reagents and solvents were obtained by purchase and were used as supplied without further purification. The NMR spectra ($^{1}$H, $^{13}$C and $^{15}$N) were recorded on a Bruker Avance III 300 instrument at 25 ℃. The chemical shifts are given relative to dimethyl sulfoxide ($^{1}$H, $^{13}$C) or nitromethane ($^{15}$N) as external standards. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 ℃. DSC and TG studies were performed at a heating rate of 5 °C min$^{-1}$ in closed Al containers with a nitrogen flow of 30 mL min$^{-1}$ on an STD-Q600 instrument. Analyses of C/H/N were performed with a Vario EL III Analyzer. The electrostatic sensitivity tests were carried out with an Electric Spark Tester ESD JGY-50 III. The sensitivities towards impact and friction were determined by using a HGZ-1 drophammer and a BAM friction tester.

### X-ray Crystallography

The X-ray diffraction measurements for **1** and **5** were performed with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The data collection and the initial unit cell refinement was performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

**Starting materials**: 2,4,6-trinitrobenzaldehyde,[25] disodium 5,5'-azotetrazolate pentahydrate,[5a] diammonium (*E*)-1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene,[7a] ammonium 5-nitrotetrazolate,[4a] ammonium 5-nitrotetrazolate-2*N*-oxide,[4d] 4-amino-3-(5-tetrazolyl)furazan,[7e] 2,4-dinitro-1,3-imidazole[26] and 5-nitroiminotetrazole[6h, 15a] were synthesized according to literature procedures.

### Synthesis of *N*-(2,4,6-trinitrobenzylideneamino) guanidinium nitrate (1)

A solution of aminoguanidinium nitrate (5.0 mmol, 0.69 g) and 2,4,6-trinitrobenzaldehyde (6.0 mmol, 1.446 g) in 30 mL ethanol was stirred at 60 °C for 24 h. The reaction mixture was cooled to 0 °C and the precipitate was formed. Then the precipitated solid was filtered off, washed with cold ethanol and dried in vacuo to afford 1.62 g of **1** as gray powder in a yield of 90%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 12.34 (s, 1H, -N*H*-), 9.14 (s, 2H, C*H*), 8.58 (s, 1H, -C*H*=N-), 7.73 (s, 4H, -N$H_2$). $^{13}$C NMR (75 MHz, DMSO): $\delta$ = 156.5 (-*C*(NH$_2$)=NH$_2$), 150.5 (-*C*NO$_2$), 149.0 (-*C*NO$_2$), 141.3 (-*C*H=N-), 129.6 (-*C*(CH=N-)), 125.1 (*C*H) ppm. $^{15}$N NMR (30 MHz, [D$_6$]DMSO): $\delta$ = -4.37 ($NO_3^-$), -16.78 (-$NO_2$(N1/N3)), -20.00 (-$NO_2$(N2)), -59.91(-CH=*N*-), -231.65 (-*N*H-), -304.61 (-$NH_2$) ppm. IR (KBr): 3551, 3472, 3417, 3245, 3106, 1688, 1638, 1617, 1539, 1465, 1401, 1349, 1231, 1146, 1115, 1086, 917, 847, 827, 723, 628, 500 cm$^{-1}$. Elemental analysis calcd (%) for $C_8H_8N_8O_9$ (360.20): C 26.68, H 2.24, N 31.11; found: C 27.32, H 2.44, N 30.98.

**Synthesis of bis(*N*-(2,4,6-trinitrobenzylideneamino) guanidinium) sulphate (2)**

A solution of bis(1-aminoguanidinium) sulphate (2.5 mmol, 0.615 g) and 2,4,6-trinitrobenzaldehyde (6.0 mmol, 1.446 g) in 25 mL ethanol was stirred at 60 °C for 24 h. The reaction mixture was cooled to 0 °C and the gray precipitate was formed. Then the precipitated solid was filtered off, washed with cold acetone and dried in vacuo to afford 1.592 g of **2** as gray powder in a yield of 92%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 8.14 (s, 5H, -CH=N-, -NH$_2$), 2.35 (s, 3H, -CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 156.4 (-*C*(NH$_2$)=NH$_2$), 150.5 (-*C*NO$_2$), 149.0 (-*C*NO$_2$), 141.4 (-*C*H=N-), 129.6 (-*C*(CH=N-)), 125.1 (*C*H) ppm. IR (KBr): 3461, 3397, 3203, 3001, , 1691, 1631, 1462, 1402, 1381, 1325, 1196, 1161, 1088, 1041, 973, 925, 861 843, 827, 720, 629, 534 cm$^{-1}$. Elemental analysis calcd (%) for $C_{16}H_{16}N_{14}O_{16}S$ (692.06): C 27.75, H 2.33, N 28.32; found C 27.69, H 2.29, N 29.64.

**Synthesis of bis(*N*-(2,4,6-trinitrobenzylideneamino) guanidinium) 5,5'-azotetrazolate (3)**

To a solution of *N*-(2,4,6-trinitrobenzylideneamino) guanidinium nitrate (**1**) (0.2377 g, 0.66 mmol ) in 10 mL water, 10 mL solution of sodium 5,5'-azotetrazolate pentahydrate (0.100 g, 0.33 mmol ) in water was added at room temperature. The precipitate formed immediately. After 0.5 h later, the precipitate was filtered, washed with H$_2$O and dried in vacuo. 0.2264 g of **3** was afforded as orange solid in a yield of 90%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 9.12 (s, 2H, C*H*), 8.55 (s, 1H, -C*H*=N-), 7.55 (s, 4H, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 171.9 ($C_2N_{10}$), 157.9 (-*C*(NH$_2$)=NH$_2$), 150.2 (-*C*NO$_2$), 148.3 (-*C*NO$_2$), 139.5 (-*C*H=N-), 129.8 (-*C*(CH=N-)), 124.8 (*C*H) ppm. IR (KBr): 3460, 3399, 3287, 3091, 1692, 1623, 1600, 1555, 1539, 1481, 1347, 1242, 1201, 1181, 1148, 1081, 1022, 922, 846, 824, 775, 737, 723, 666, 566, 526 cm$^{-1}$. Elemental analysis calcd (%) for $C_{18}H_{18}N_{24}O_{12}$ (762.15): C 28.35, H 2.38, N 44.09; found C 28.23, H 2.29, N 45.67.

**Synthesis of bis(*N*-(2,4,6-trinitrobenzylideneamino) guanidinium) (*E*)-1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene (4)**

A similar procedure was followed as that described above for **3**. Diammonium (*E*)-1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene (0.111 g, 0.75 mmol) was subjected to the method to give 0.640 g of **4** as red powder in a yield of 95%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 8.92 (s, 2H, C*H*), 8.05 (s, 1H, -C*H*=N-), 6.45 (br, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 164.3 ($CN_4$), 163.7 (-*C*(NH$_2$)=NH$_2$), 149.7 (-*C*NO$_2$), 148.5 (-*C*NO$_2$), 146.4 (-*C*NO(CN$_4$)), 145.0 (-*C*NO(N$_2$)), 131.0 (-*C*H=N-), 130.6 (-*C*(CH=N-)), 123.8 (*C*H) ppm. IR (KBr): 3457, 3101, 3009, 1695, 1614, 1557, 1501, 1463, 1420, 1381, 1169, 1082, 1040, 1002, 863, 842, 556 cm$^{-1}$. Elemental analysis calcd (%) for $C_{22}H_{18}N_{28}O_{14}$ (898.16): C 29.41, H 2.02, N 43.65; found C 21.39, H 2.71, N 50.11.

**Synthesis of *N*-(2,4,6-trinitrobenzylideneamino) guanidinium 5-nitrotetrazolate (5)**

Barium hydroxide octahydrate (0.237 g, 0.75 mmol) was added to a stirring aqueous solution of ammonium 5-nitrotetrazolate (0.198 g, 1.5 mmol) in H$_2$O (15 mL) and the resulting mixture was stirred at 25 °C for 0.5 h. The volume was then reduced to ~5 mL on a rotary evaporator with heating to remove as much ammonia as possible. The pH was subsequently checked (7-8). Meanwhile, 0.519 g (0.75 mmol) of the sulfate salt (**2**) was dissolved in 10 mL of deionized water at room temperature. Then, the barium 5-nitrotetrazolate solution was added dropwise resulting in the formation of a white precipitate at room temperature. The solution was stirred for 1 h and then filtered. Water was removed by evaporating the filtrate and then 0.576 g of **5** was obtained as red solid in a yield of 93%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 9.14 (s, 2H, C*H*), 8.59 (s, 1H, -C*H*=N-), 7.73 (s, 4H, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 170.1 (NO$_2$*C*N$_4$), 156.6 (-*C*(NH$_2$)=NH$_2$), 150.5 (-*C*NO$_2$), 148.9 (-*C*NO$_2$), 141.3 (-*C*H=N-), 129.7 (-*C*(CH=N-)), 126.1 (*C*H) ppm. $^{15}$N NMR (30 MHz, [D$_6$]DMSO): $\delta$ = 17.12 (N9/N10), -17.11 (-$NO_2$(N1/N3)), -20.35 (-$NO_2$(N2)), -23.10 ($NO_2CN_4$), -60.22 (-CH=*N*-), -63.33 (N8/N11), -231.93 (-*N*H-), -303.81 (-$NH_2$) ppm. IR (KBr): 3439, 3352, 3081, 1696, 1632, 1608, 1538, 1438, 1416, 1351, 1314, 1231, 1181, 1156, 1081, 1016, 931, 834, 777, 742, 724, 671, 597, 567, 538 cm$^{-1}$. Elemental analysis calcd (%) for $C_9H_9N_{12}O_8$ (413.07): C 26.16, H 2.20, N 40.67; found C 26.02, H 2.15, N 41.32.

**Synthesis of *N*-(2,4,6-trinitrobenzylideneamino) guanidinium 5-nitrotetrazolate-2*N*-oxide (6)**

A similar procedure was followed as that described above for **5**. Ammonium 5-nitrotetrazolate-2*N*-oxide (0.222 g, 1.5 mmol) was subjected to the method to give 0.610 g of **6** as dark red solid in a yield of 95%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 9.01 (s, 2H, C*H*), 8.65 (br, -N*H*-), 8.23 (s, 1H, -C*H*=N-), 7.29 (br, -NH$_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 160.4 (NO$_2$*C*N$_4$O), 157.4 (-*C*(NH$_2$)=NH$_2$), 150.3 (-*C*NO$_2$), 148.5 (-*C*NO$_2$), 139.8 (-*C*H=N-), 129.8 (-*C*(CH=N-)), 124.9 (*C*H) ppm. IR (KBr): 3420, 3371, 3343, 3296, 1675, 1548, 1384, 1313, 1196, 1120, 984, 824, 783, 719, 618, 509 cm$^{-1}$. Elemental analysis calcd (%) for $C_9H_8N_{12}O_9$ (428.05): C 25.24, H 1.88, N 39.25; found C 25.17, H 1.80, N 40.12.

**General procedure for the preparation of energetic salts 7–9**

Barium hydroxide octahydrate (0.157 g, 0.5 mmol) was added to a stirring 10 mL aqueous solution of 4-amino-3-(5-tetrazolyl)furazan (0.153 g, 1.0 mmol), 2,4-dinitro-1,3-imidazole (0.158 g, 1.0 mmol) and 5-nitroiminotetrazole (0.065 g, 0.5 mmol), respectively. After the mixture was stirred for 0.5 h, the sulfate salt (**2**) (0.346 g, 0.5 mmol) was added resulting in the formation of precipitate at room temperature. The solution was stirred for 1 h and then filtered. After the removal of the solvent, the target product was obtained.

***N*-(2,4,6-trinitrobenzylideneamino) guanidinium 4-amino-3-(5-tetrazolate)furazan (7)**: 0.406 g of **7** was obtained as dark red solid in a yield of 90%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 9.13 (s, 2H, C*H*), 8.59 (s, 1H, -C*H*=N-), 7.75 (s, 4H, -N$H_2$), 6.57 (s, 2H, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 156.9 (-*C*(NH$_2$)=NH$_2$), 151.9 (*C*N$_4$), 150.4 (-*C*NO$_2$), 148.7 (-*C*NO$_2$), 141.1 (-*C*NO(CN$_4$)), 140.8 (-*C*H=N-), 129.7 (-*C*(CH=N-)), 125.0 (*C*H) ppm. IR (KBr): 3426, 3379, 3270, 1665, 1629, 1540, 1446, 1345, 1215, 1122, 987, 927, 905, 866, 776, 731, 617, 570, 518 cm$^{-1}$. Elemental analysis calcd (%) for $C_{11}H_{11}N_{14}O_7$ (451.09): C 29.28, H 2.46, N 43.45; found C 29.11, H 2.39, N 44.29.

***N*-(2,4,6-trinitrobenzylideneamino) guanidinium 2,4-dinitro-1,3-imidazolate (8)**: 0.422 g of **8** as dark red solid in a yield of 92%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 8.58(s, 2H, C*H*), 7.74 (s, 2H, C*H*), 7.27 (br, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D6]DMSO): $\delta$ = 160.3 (O$_2$N*C*N$_2$), 155.5 (-*C*(NH$_2$)=NH$_2$), 150.3 (-*C*NO$_2$), 148.3 (-*C*NO$_2$), 140.5 (-*C*H=N-), 137.4 (O$_2$N*C*(CH)N), 131.7 (-*C*(CH=N-)), 125.8 (*C*H, picryl moiety), 120.5 (*C*H, imidazole ring) ppm. IR (KBr): 3441, 3360, 3256, 3139, 3102, 1667, 1503, 1463, 1429, 1350, 1289, 1227, 1204, 1143, 1081, 998, 934, 869, 837, 779, 757, 656, 616, 572, 506 cm$^{-1}$. Elemental analysis calcd (%) for $C_{11}H_{13}N_{11}O_{10}$ (459.08): C 28.77, H 2.85, N 33.55; found C 28.70, H 2.82, N 34.90.

**Bis(*N*-(2,4,6-trinitrobenzylideneamino) guanidinium) 5-nitroiminotetrazolate (9)**: 0.334 g of **9** as dark red solid in a yield of 92%. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 9.03 (s, 4H, C*H*), 8.32 (s, 1H, -C*H*=N-), 7.08 (s, 4H, -N$H_2$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 160.5 (O$_2$NN=*C*N$_4$), 159.2 (-*C*(NH$_2$)=NH$_2$), 149.5 (-*C*NO$_2$), 146.9 (-*C*NO$_2$), 136.0 (-*C*H=N-), 130.2 (-*C*(CH=N-)), 124.4 (*C*H) ppm. IR (KBr): 3461, 3387, 3093, 1695, 1629, 1600, 1539, 1538, 1479, 1448, 1367, 1339, 1303, 1243, 1204, 1177, 1151, 1076, 1019, 919, 874, 822, 764, 720, 664, 575 cm$^{-1}$. Elemental analysis calcd (%) for $C_{17}H_{16}N_{20}O_{14}$ (724.12): C 28.19, H 2.23, N 38.67; found C 28.06, H 2.11, N 39.23.

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## Notes and references

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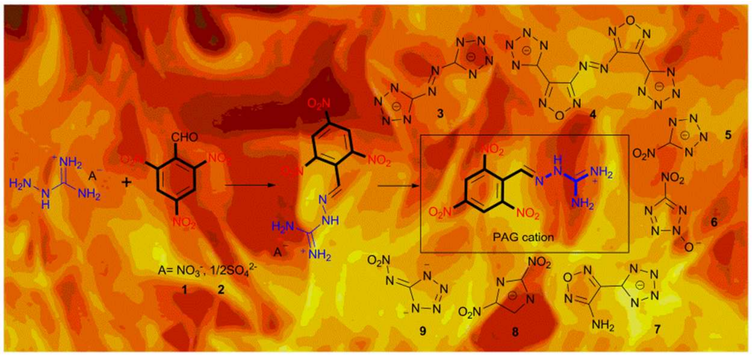

A series of energetic salts based on a guanidinium cation containing picryl moiety, were successfully synthesized and characterized.