USE OF DIFFERENTIAL SCANNING CALORIMETRY (DSC) FOR ANALYSIS OF ENRGETIC HETEROCYCLES

A M.Sc. Dissertation report by:

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USE OF DIFFERENTIAL SCANNING CALORIMETRY (DSC) FOR ANALYSIS OF ENRGETIC HETEROCYCLES

A DISSERTATION REPORT

Submitted in the partial fulfilment of
The M.Sc. Degree (Analytical Chemistry)

By
Ms. VANISHA DIAS
20P0490018

Under the supervision of
Dr. Hari Kadam

To
School of Chemical Sciences
Goa University 403206
April 2022

CERTIFICATE

This is to certify that the dissertation entitled **“Use of Differential Scanning Calorimetry (DSC) for the analysis of Energetic Heterocycles”** is bonafide work carried out by Ms. Vanisha Dias under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Dr. Hari Kadam

Guiding Teacher
Assistant Professor

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Dean of School of Chemical Sciences
Goa University

STATEMENT

I hereby declare that the literature review and the matter presented in this dissertation entitled, '**Use of Differential Scanning Calorimetry (DSC) for the analysis of Energetic Heterocycles**' has been carried out by me in School of Chemical Sciences, Goa University. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

Vanisha Dias

ACKNOWLEDGEMENT

I would like to express my special thanks and gratitude to my Project guide Dr Hari K. Kadam, who suggested this project titled “Use of Differential Scanning Calorimetry for analysis of Energetic Heterocycles”, which has motivated us for research, and encouraged us to learn new concepts and develop new skills.

Secondly, I would like to thank Dr. Vidhyadatta M. Shet Vernekar, Dean of School of Chemical Sciences for the encouragement and support. I would also like to thank the faculty of School of Chemical Sciences for their steadfast co-operation throughout the course of this dissertation.

I am extremely grateful to my parents for their immense love and support. I would like to thank each and everyone who have helped me directly or indirectly. Last but not the least I would like to thank God for his blessings.

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INTRODUCTION

Differential Scanning Calorimetry (DSC) is the thermal analysis technique in which the heat flows into or out of the sample is measured as a function of temperature or time while the sample is exposed to a controlled program. It is a very powerful technique to evaluate material properties such as gas transition temperature, melting, crystallization, specific heat capacity, cure process, purity, oxidation behaviour, and thermal stability. The basic principle underlying this technique undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature.

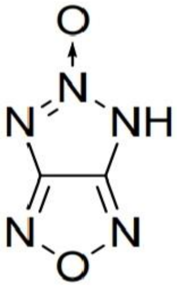
DSC analysis provides test data for a wide range of materials, including polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceutical, organic materials, rubber, petroleum, chemicals, explosives, biological, samples and more. DSC also measures the rate of heat flow and compares difference between the heart flow rate of the test sample and known reference material. The difference determines variations in material composition, crystallinity and oxidation.

Heterocyclic compounds possess a cyclic structure with 2 or more different kind of stoms in the ring (Oxygen, Nitrogen, Sulphur). Fused cyclic energetic materials, a unique class of large conjugate structures which contain two or more rings that share two atoms and the bond between the rings, have been identified as promising contenders to traditional energetic materials. With a coplanar polycyclic structure, fused heterocyclic ring-based energetic materials feature considerably higher heats of formation (HOF) and ring-strain energy stored in the molecules. These result in attractive features of good energetic performance, enhanced thermal stability and low sensitivity toward destructive mechanical stimuli, which increases the safety of the synthesis, transfer, and storage of high-energy density compounds.

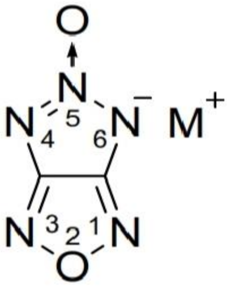
Thermal behaviour is an important parameter for evaluating the actual application and long-term storage. To assess the thermal stabilities of these salts, differential scanning calorimetric (DSC) was carried out to test the thermal properties. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase_diagrams for various chemical systems

LITERATURE REVIEW

4H-[1,2,3]Triazolo[4,5-c][1,2,5]oxadiazole 5-oxide and its salts: promising multipurpose energetic material[1]

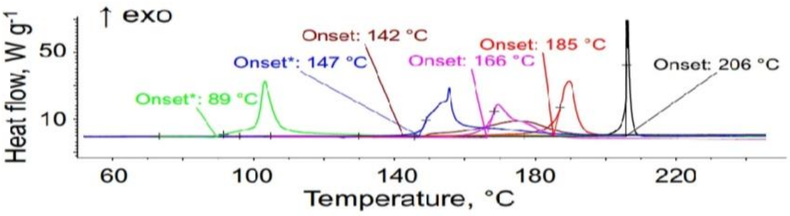


1



2

M^+ = K^+ (**2a**), Ag^+ (**2b**), NH_4^+ (**2c**),
$N_2H_5^+$ (**2d**), NH_3OH^+ (**2e**), $CH_9N_6^+$ (**2f**)



DSC for studied substances upon linear heating at 5 K･min-1.

1(green) hydroxylammonium 2e(blue) triaminoguanidium 2f(brown) hydrazinium
2d(purple) ammonium 2c(red) potassium 2a(black) salts

Differential scanning calorimetry (DSC) was used to assess the thermal safety of the compounds synthesized.TODO 1 had the lowest stability whereas K salt 2a revealed the highest decomposition onset among the analyzed sample. Ammonium salt 2c was the second in terms of thermal stability with the extrapolated decomposition onset of 185 °C. No endothermic effects of phase transition were observed for this salt. Hydroxyl ammonium salt 2e revealed a phase transition (possibly melting) at 123 °C with a decomposition upon further heating to 147 °C. Triaminoguanidinium salt 2f showed the decomposition behaviour just after endothermic event at 142 °C that was assumed to be melting. Since the K salt 2a was the only compound that did not contain hydrogen atoms, its decomposition onset as high as 206 °C was suggested as a measure of thermal stability of the furazanotriazole oxide moiety.

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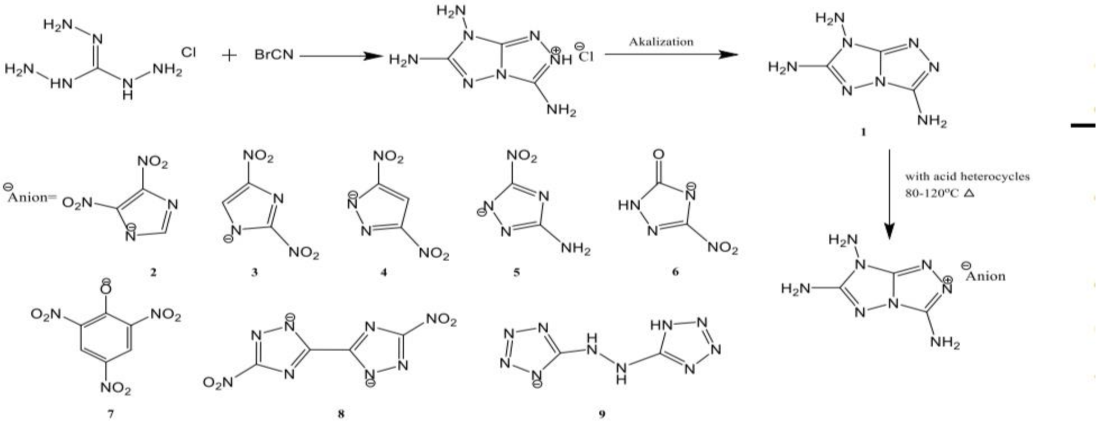
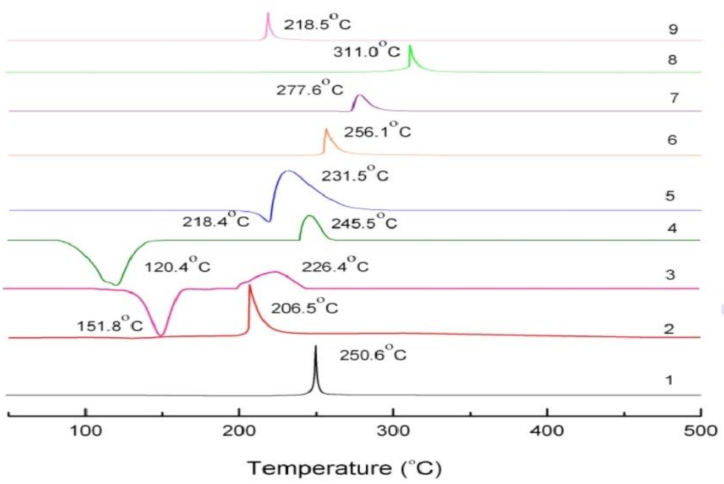
Thermally stable energetic salts based on 3,6,7-triamino-7H-striazolo[5,1-c]-s-triazole composed of heterocyclic cation and anion: synthesis and intermolecular interaction study[2]





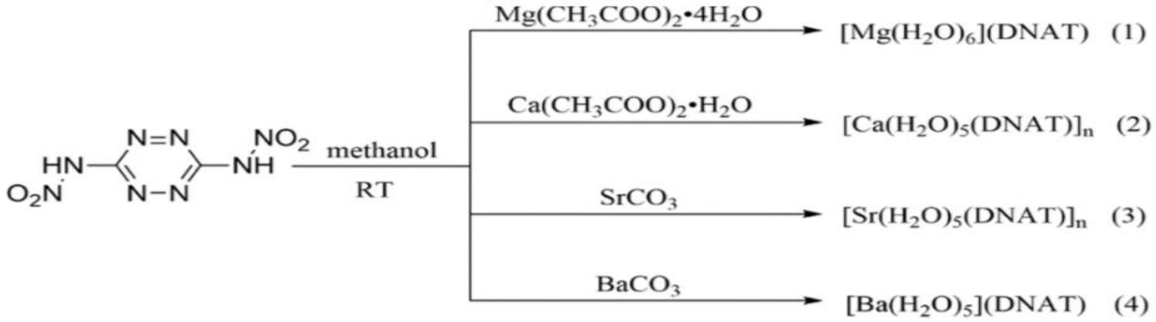
DSC curves for TATT and its energetic salts

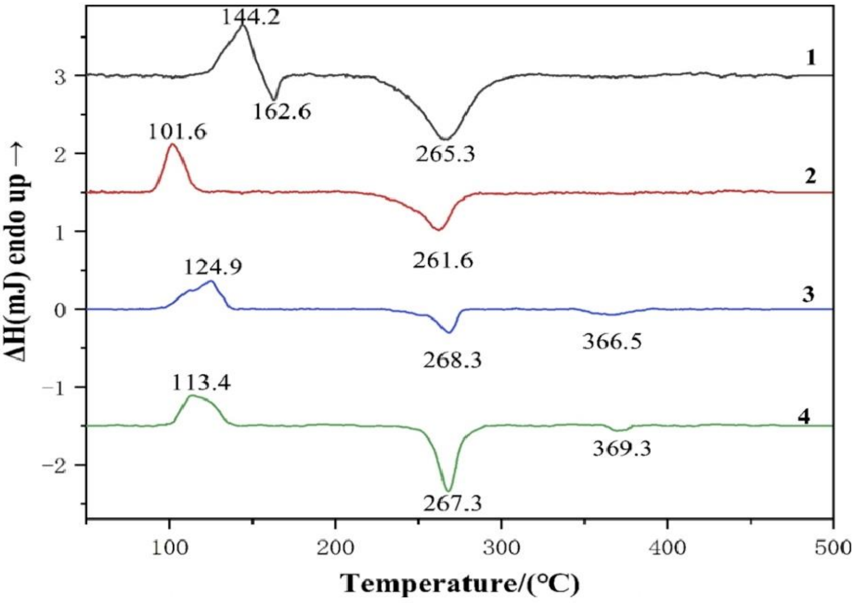
Thermal behaviour is an important parameter for evaluating the actual application and long-term storage. To assess the thermal stabilities of these salts, differential scanning calorimetric (DSC) was carried out to test the thermal properties. The DSC testing results show that all the salts have decomposition temperature ranging from 200 ˚C to 311˚C, suggesting these salts are thermally stable. It is evident that most of salts decompose directly without melting points expect salts 3, 4 and 5. The salts 6, 7, 8 possess higher decomposition temperature than the starting material 1.

Alkaline earth metal salts of 3,6-dinitramino-1,2,4,5-tetrazine: Prospective candidates for environmentally friendly energetic applications[3]

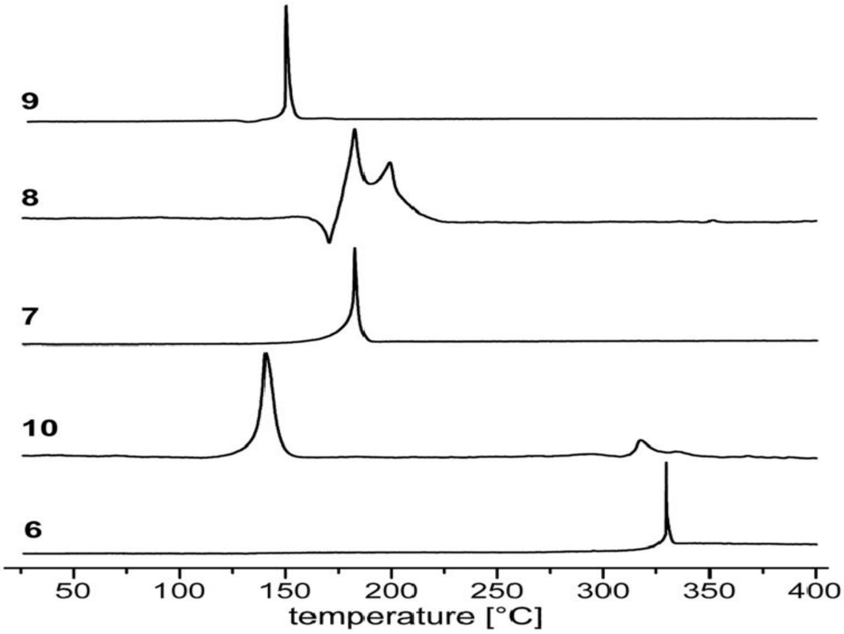
The thermal decomposition processes of compounds 1 to 4 were determined by differential scanning calorimetry (DSC) and thermos gravimetric analysis (TGA) methods. The similar dehydration processes of all compounds are came up within a range of 101.6℃-144℃. The DSC curves show strength with which the water molecules coordinate to the metal centre increase is of the order 2 < 4 < 3 < 1. These curves also reveal the relationship between the decomposition temperature of these compounds is of order 1 < 2 < 4 < 3.

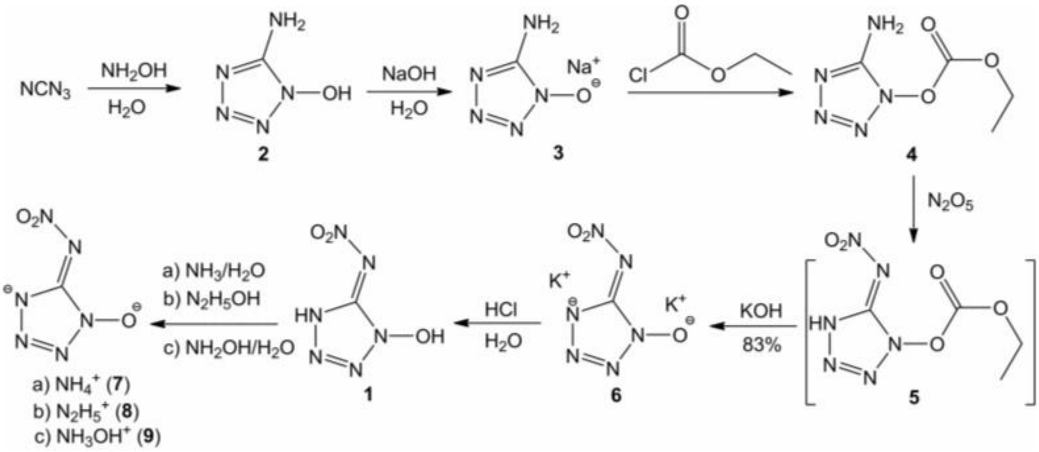
Comparison with others, magnesium salt (1) decomposes promptly after the dehydration process at 162.6 ℃. The DSC curve of 1 shows one endothermic and two exothermic processes: the first process takes place at 144 ℃. The second process occurs immediately at 162.6 ℃. The third process happens at 265.3 ℃. The distinct difference in decomposition temperature of magnesium salt (1) may affected by the non-coordination between metal cation and DNAT anion, which determines whether exists a relatively stable structure after dehydration.





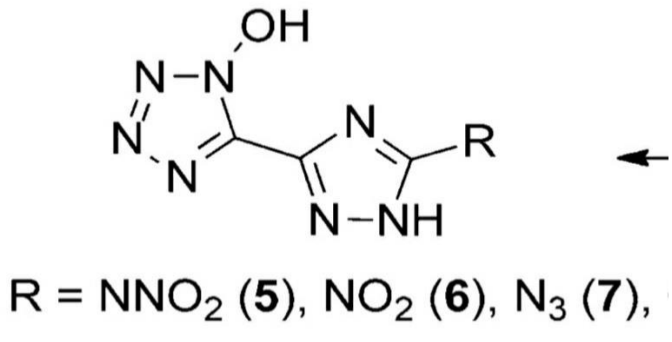
5-Nitriminotetrazole 1-Oxide: An Exciting Oxygen- and Nitrogen[4]

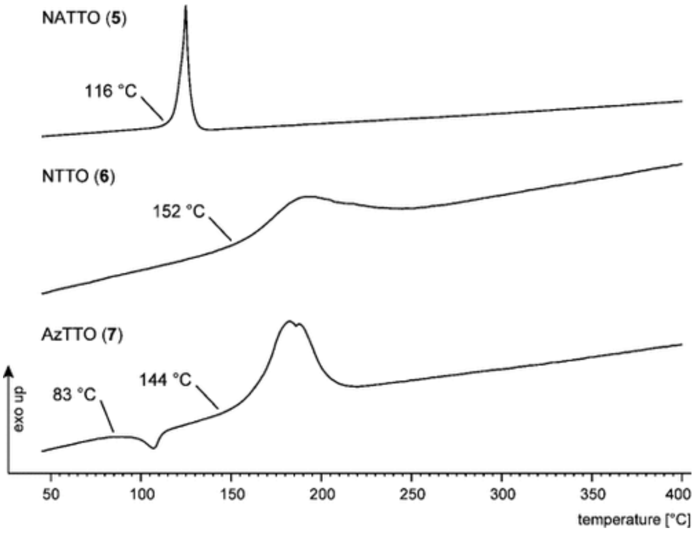




Differential scanning calorimetry (DSC) measurements for compounds 6–10 were performed at a heating rate of 5°min–1. Compound 6 possesses a remarkably high decomposition temperature of 320 °C, whereas high-nitrogen-content salts 7, 8, and 9 decompose. DSC plots of 6–10 at 5 °C min–1 (exotherm up).at 150, 160, and 130 °C, respectively. Mono-deprotonated potassium salt 10 decomposes at 125 °C, which is almost200 °C lower than the decomposition temperature of 6. For the DSC measurements, anhydrous 6–10 were used, which were obtained by precipitation from methanol.

A Study of 5-(1,2,4-Triazol-*C*-yl)tetrazol-1-ols: Combining the Benefits of Different Heterocycles for the Design of Energetic Materials[5]

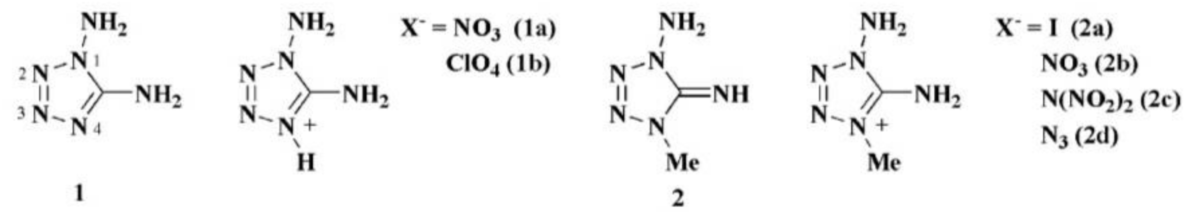




DSC plots for NATTO (**5**), NTTO (**6**) and AzTTO (**7**) with a heating rate of 5 °C min^{-1}.

The thermal stabilities of the title compounds **5**–**7** were analyzed by differential scanning calorimetry with a heating rate of 5 °C min^{-1}. The compounds were dried at 60 (**5**, **7**) or 110 °C (**6**), respectively, prior to sample preparation to remove moisture and crystal water. The thermal stabilities determined are rather low with decomposition beginning at 116 (**5**), 144 (**7**) and 152 °C (**6**). The azide derivative **7** is the only compound to feature a melting point, starting at 83 °C. The decomposition point of **7** is almost identical to the derivative lacking the nitrogen bound hydroxyl group.

A study on the thermal decomposition behaviour of derivatives of 1,5-diamino-1H-tetrazole (DAT): A new family of energetic heterocyclic-based salts[6]



1

$X^- = NO_3$ (1a)
ClO_4 (1b)

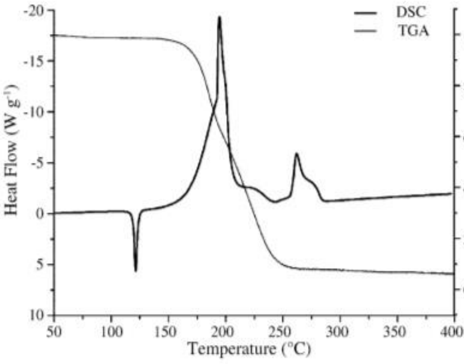
2

$X^- = I$ (2a)
NO_3 (2b)
$N(NO_2)_2$ (2c)
N_3 (2d)

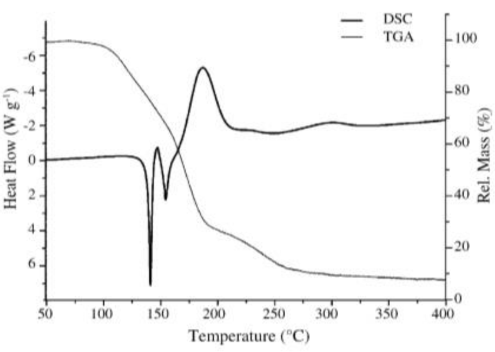
DSC and TGA were used to evaluate the relative thermal stabilities of 2b, 2c and 2d and are measured under comparable condition (Al-containers with a hole (1 m) on the top for gas release for DSC measurements. Show the obtained DSC and TGA thermographs of these salts. All three compounds have relatively low melting points (2b,mp 121 ◦C (onset); 2d, 135 ◦C , with the lowest for the dinitramide salt (2c, 85 ◦C)) and start to decompose in the range of 175–250 ◦C (2b), 150–230 ◦C (2c) and137–310 ◦C (2d). The enthalpy of melting, mH, were found to be 122 (2b), 118 (2c) and 181 (2d).

2b shows three main signals which can be related to the melting, first endothermic signal, the main decomposition reaction (second exothermic signal) and third exothermic signal, which corresponds to condensation reaction of the residual fragments of the exothermic step.

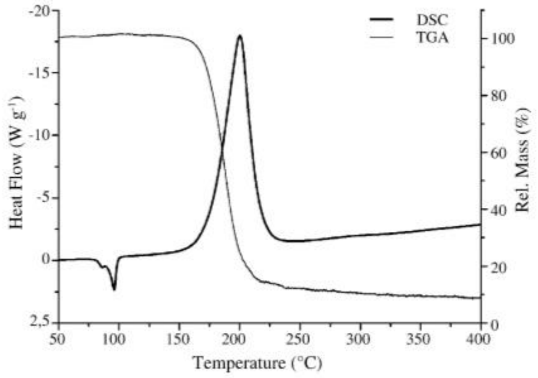
In the case of the azide 2d, two endothermic steps indicate a marked degree of sublimation around the melting temperature together with the start of the decomposition. Repeating the experiment with a closed Al-container with the same heating rate resulted in the coalescence of the two endothermic signals into one signal. The main decomposition step of 2d is found in the region of 160–220 ◦C and, comparable to 2b, the weak exothermic region (275–325 ◦C) also corresponds to condensation reactions of residual fragments of the decomposition step. The DSC curves of the investigated 2c is divided into three parts, the first one corresponds to a phase transition region which appears as one small endothermic reaction (Tg = 82 ◦C), the second part shortly after, is related to the melting region of2c as a endothermic peak. The third exothermic peak corresponds to the decomposition reaction



2b

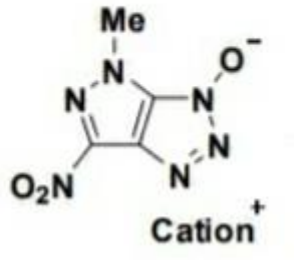


2d

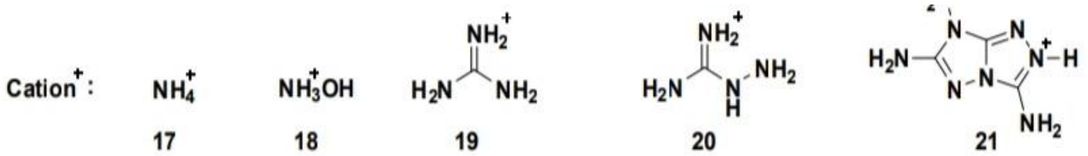


2c

Fused heterocycle-based energetic salts: alliance of pyrazole and 1,2,3-triazole[7]

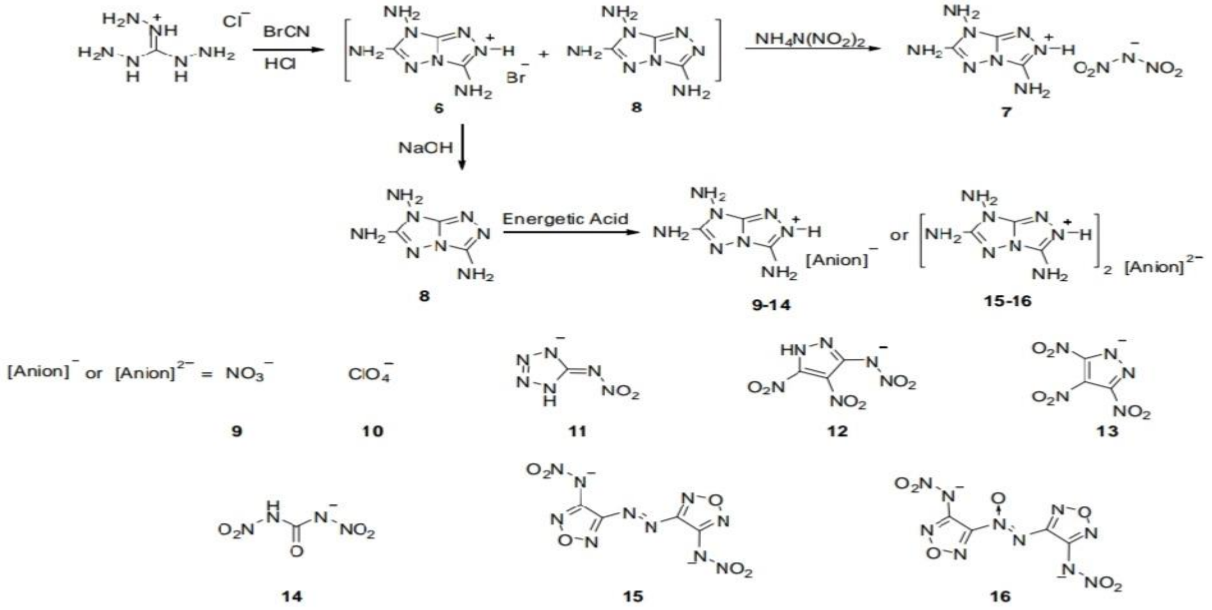


17-21



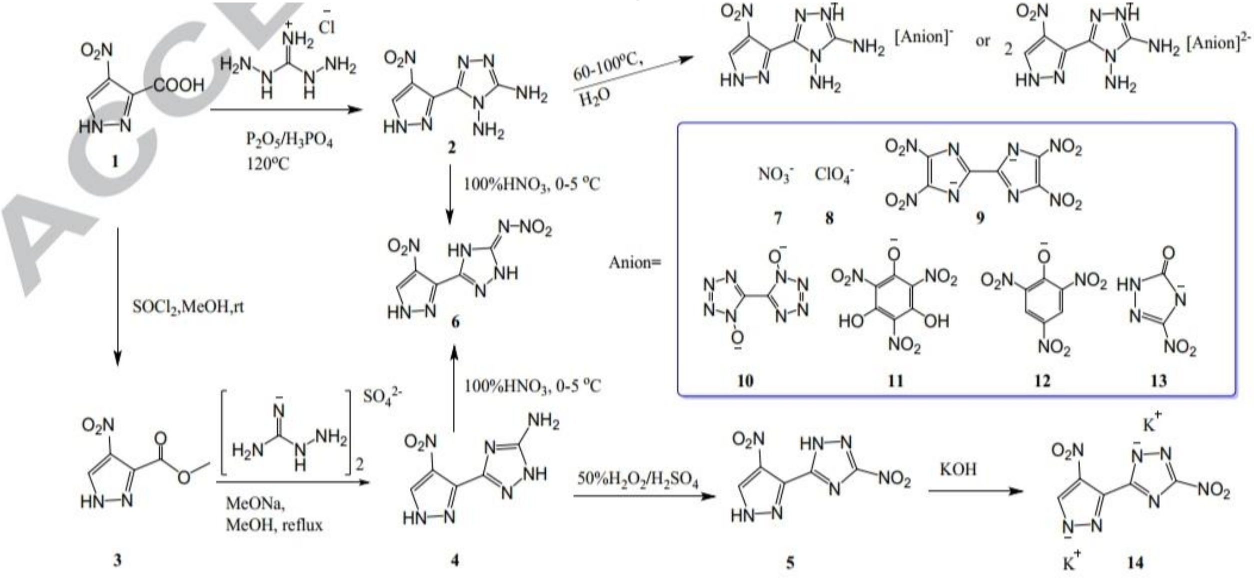
The thermal stabilities of these new energetic salts were determined by differential scanning calorimetric (DSC) measurements. All compounds decompose between 85 and 192 °C (on-set temperature) without melting. With extensive hydrogen bonding, the guanidinium salt **19** shows the best thermal stability.

Energetic fused triazoles – a promising C–N fused heterocyclic cation[8]



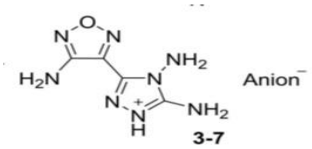
Thermal stability is a key criterion to evaluate the application potential of energetic materials. All new compounds were examined using differential scanning calorimetry (DSC) at a heating rate of 5 °C/minute, and decomposed between 167-279 °C. Salt 9 has a high decomposition temperature of 279 °C, which is superior to RDX (205 °C) and comparable to TNT (295°C) (Table 1). Compared to the reported decomposition temperature of dinitramide salts, e.g. ammonium dinitramide (ADN, 147 °C),11 guanidinium dinitramide (GDN, 149 °C),12 1,5-diamino-tetrazolium dinitramide (135 °C),134,4’,5,5’tetraamino-3,3’-bi-1,2,4-triazolium dinitramide (200 °C),14 and N-guanylurea dinitramide (201°C),15 7 decomposes at 199 °C, which ranks it with the highest in thermal stability of the dinitramide family.

Energetic Pyrazol-triazole hybrid with high thermal stability and decreased sensitivity: facile synthesis, characterization and promising performance[9]

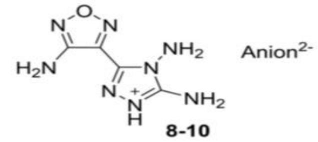


The thermal behaviour was determined with DSC at a heating rate of 5 ^{o} C min-^{1}. Compound 2 has a remarkably high thermal stability with an onset decomposition temperature of 331^{o}C and a peak temperature of 346^{o}C which exceed that of heat resistant explosive hexanitrostilbene (HNS, Td: 318^{o}C), recently reported 5,6-fused bicyclic energetic molecule (Td: 315^{o}C) and 4,4’,5,5’-tetranitro-2H,2’H-3,3’- 18 bipyrazole (TNBP, Td: 252^{o}C) based on pyrazole. This material can be also comparable to those of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB, Td: 330^{o}C) and 5,5’-bis(2,4,6-trinitrophenyl)-2,2’-bi(1,3,4-oxadiazole) (TKX-55, Td: 335^{o}C).

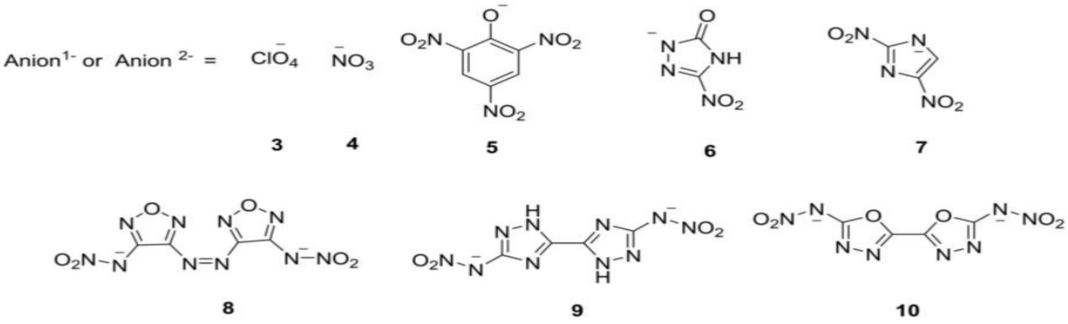
Energetic Furazan and Triazole Moieties: A Promising Heterocyclic Cation[10]



3-7

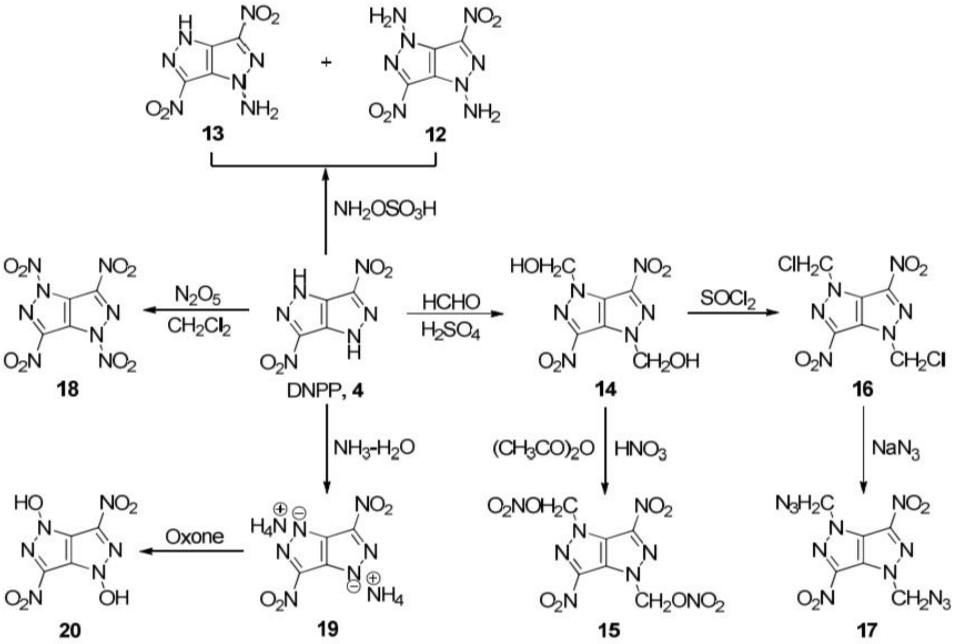


8-10



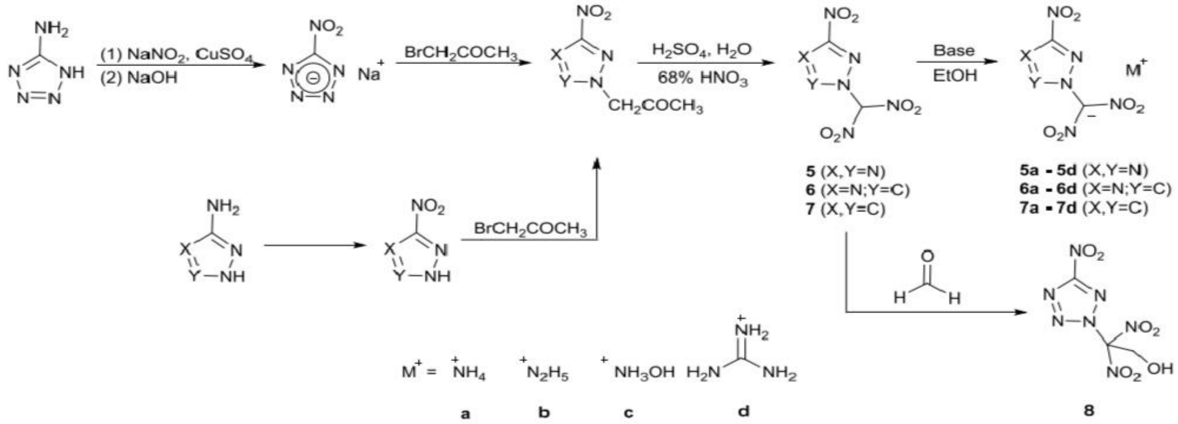
The thermal stabilities of all compounds were determined using differential scanning calorimetry (DSC) at a heating rate of 5°C min 1 using dry nitrogen. The decomposition temperatures are given as onset temperatures. It should be noted that all the samples were placed in an oven at 60°C for 24 h to ensure that no crystal water remained. 3-(3-amino-1,2,5-oxadiazol)-4,5-diamino-1,2,4-tirazole possesses highest thermal stability (272°C), whereas the combination of different anions leads to a reduced but still satisfactory thermal stability. The decomposition temperatures of the salts (3-10) range from 197 to 254°C. The nitrate salt 4 has the highest decomposition temperature (254 °C) in these salts. The decomposition temperatures of salts 3 (197°C), 7 (201 °C) and 10 (201°C) are slightly lower than that of RDX (204 °C), the others are higher than that of RDX. Compounds 2, 4–5 behave melting characteristics at 238°C, 202°C and 226°C, respectively. However, all of them meet the benchmark temperature (180 °C) of energetic materials.

Synthesis, structure and properties of neutral energetic materials based on *N*-functionalization of 3,6-dinitropyrazolo[4,3-*c*]pyrazole[11]



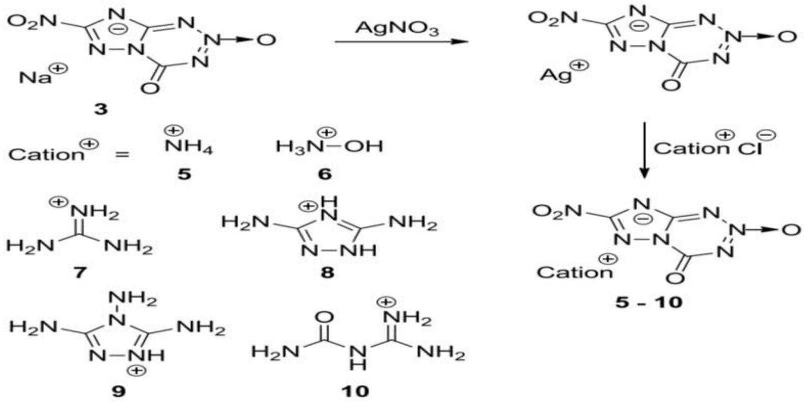
The thermal stabilities of all these compounds were determined by differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C min^{-1}. With the exception of **18**, the decomposition temperatures of DNPP and its energetic derivatives lie in the range between 178 (**13**) and 336 °C (**4**), compared with RDX (230 °C). Compound **18** easily decomposed in the solid state at room temperature after a few hours, which could produce DNPP and 1,3,4-tetranitropyrazolo[4,3-*c*]pyrazole with losing two or one nitro group, but it was stable in the solution at lower temperature for several weeks.

Design and Synthesis Energetic Materials towards High Density and Positive Oxygen Balance by N-dinitromethyl Functionalization of Nitroazoles[12]



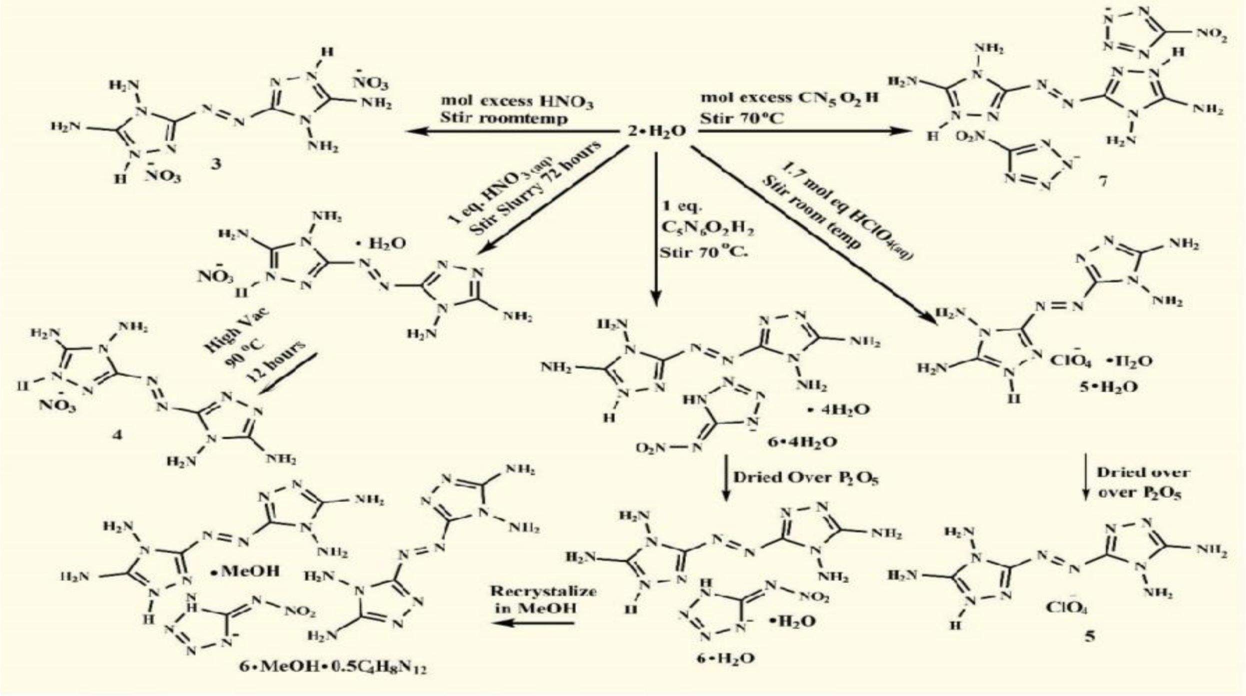
Thermal stability is the first concern because an unacceptably low decomposition temperature will strictly limit the application of energetic materials. In this work, the thermal stabilities of all compounds were determined by differential scanning calorimetric measurements scanning at 10 °C min^{-1}. All molecules are stable when exposed to air and or moisture. The decomposition temperature (T_d) of these new compounds is in the range of 109.3–196.4 °C. Compounds **6c** (T_d = 182.0 °C), **6d** (T_d = 188.8 °C), **7a** (T_d = 196.4 °C), **7b** (T_d = 191.2 °C), and **7d** (T_d = 194.2 °C) have better thermal stabilities than 180 °C. The introduction of hydroxyl methyl causes compound **8** (T_d = 123.9 °C) to be a little more stable than **5,** whereas **5d** is stable up to 174.2 °C. It therefore seems that making salts is a more effective way to improve the thermal stability. The thermal stability of all energetic salts greatly exceeds those of their parent compounds. Among these energetic salts, guanidinium salts are more stable than other salts. The formation of salts gives decomposition points that are 35–60 °C higher than those of the corresponding neutral molecules. This indicates that the formation of salts contributes more to improving thermal stabilities than introducing hydroxymethyl. Therefore, more salts were synthesized other than neutral hydroxymethyl derivatives of *N*-dinitromethyl nitroazoles.

The unique synthesis and energetic properties of a novel fused heterocycle: 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazine 2-oxide and its energetic salts [13]



The melting points (T_m, onset) and decomposition temperatures (T_d, onset) of the energetic salts were determined by DSC at a heating rate of 5 °C min^{-1}.The guanidinium (**7**), 3,4,5-triamino-1,2,4-triazolium (**9**), and *N*-carbamoyl guanidinium (**10**) salts melt prior to decomposition, having T_m = 266, 213, and 208 °C, respectively. With the exception of hydroxylammonium salt (**6**), the decomposition temperatures of most salts are higher than 237 °C, which are superior to that of 1,3,5-trinitro-1,3,5-triazinane (RDX, T_d = 230 °C).

4,4′,5,5′-Tetraamino-3,3′-azo-bis-1,2,4-triazole and the electrosynthesis of high-performing insensitive energetic materials[14]

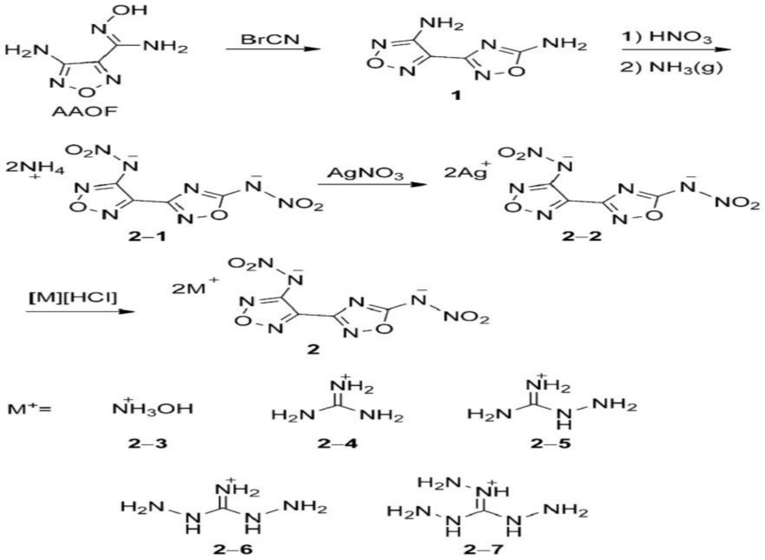


The thermal behaviours of compounds **2**, **2·H2O**, **3**, **4**, **5**, **6·H2O**, and **7** were investigated by combination differential scanning calorimetry-thermogravimetric analysis (DSC/TGA). All measurements were conducted with a heating rate of 10 K min^{-1}. Decomposition temperatures for **2·H2O** and **2** were both near 300 °C, while the remaining compounds decomposed below 250 °C. The waters of hydration for **2·H2O** and energetic salts were lost prior to decomposition. Temperatures of decomposition were determined from the onset of the exothermic detonation peak as seen on the DSC. Onset of decomposition was based on deviation from the baseline and not peak values which can overestimate thermal stabilities. This demonstrates a high degree of thermal stability beyond conventional energetics of similar performance.

An Energetic *N*-Oxide and *N*-Amino Heterocycle and its Transformation to 1,2,3,4Tetrazine1-oxide[15]

For determination of the decomposition temperature of DPX2, a differential scanning calorimetry (DSC) experiment was run at a heating rate of 5 °C min^{-1}. Exothermic decomposition occurred beginning at 210 °C. This implies the ability of the new energetic moiety *N*-amino *N*-oxides to be capable of forming thermally stable energetic materials.

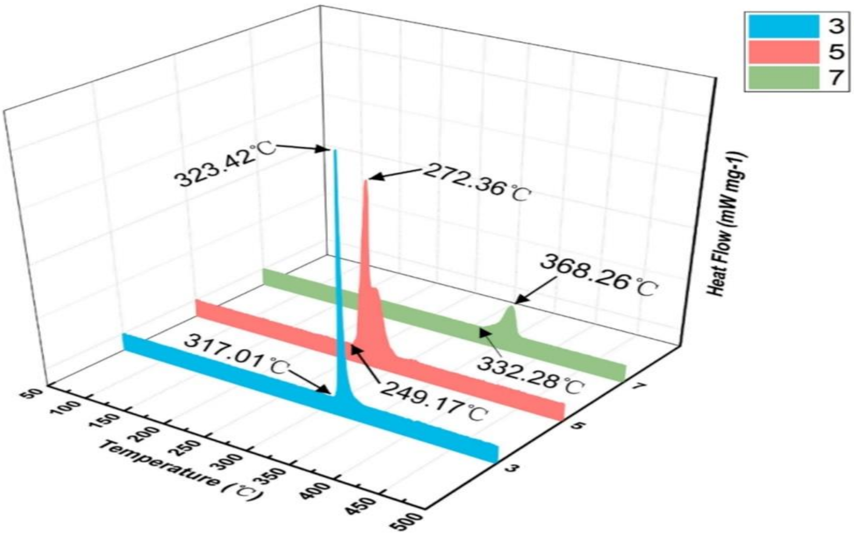
Combination of 1,2,4-Oxadiazole and 1,2,5-Oxadiazole Moieties for the Generation of High-Performance Energetic Materials[16]



The phase-transition temperature and thermal stability of the salts were determined by DSC measurements with scanning at 5 °C min^{-1} (Table 1). All salts showed good thermal stability with decomposition temperatures ranging from 172 (**2**–**6**) to 269 °C (**2**–**4**). Salts **2**–**5**, **2**–**6**, and **2**–**7** melted between 142 and 179 °C and then decomposed. The decomposition temperature of all compounds, except **2**–**3** and **2**–**6**, was above 200 °C, which indicates their thermal stability.

Combining 5,6-fused triazolo-triazine with pyrazole: A novel energetic framework for heat-resistant explosive[17]

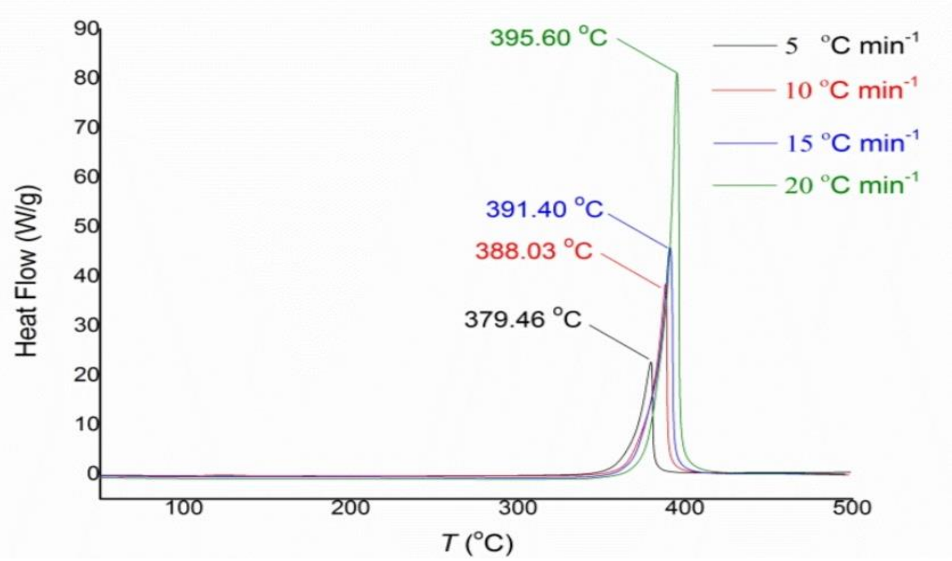
Thermodynamic stability, as an essential factor to evaluate the application of energetic materials, cannot be ignored. Differential scanning calorimetry (DSC) is increasingly used as evidence to support a favourable thermodynamic stability of energetic materials. The thermal stabilities of compound 3, 5 and 7 were determined by DSC measurements at heating rate of 5 ◦C min− 1 under a nitrogen atmosphere. All compounds are directly decomposed without melting point which is desirable for heat-resistant explosives because the solid state is conducive to reducing the decomposition rate of the substance. Compound 3 has an obvious exothermic peak with an onset decomposition temperature of 317.01 ◦C and a peak temperature of 323.42 ◦C,



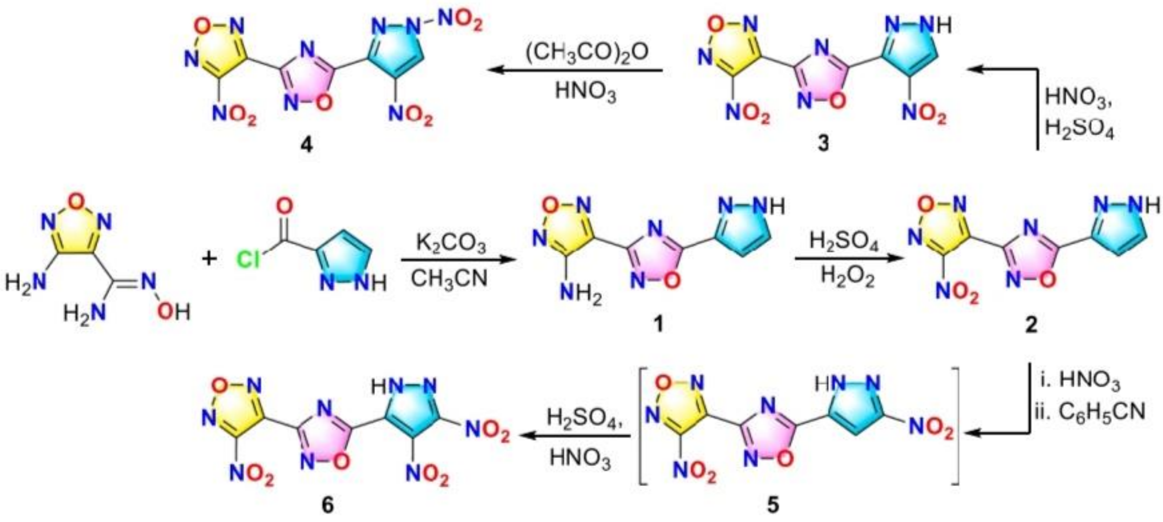
Aminonitro Groups Surrounding a Fused Pyrazolotriazine Ring: A Superior Thermally Stable and Insensitive Energetic Material[18]

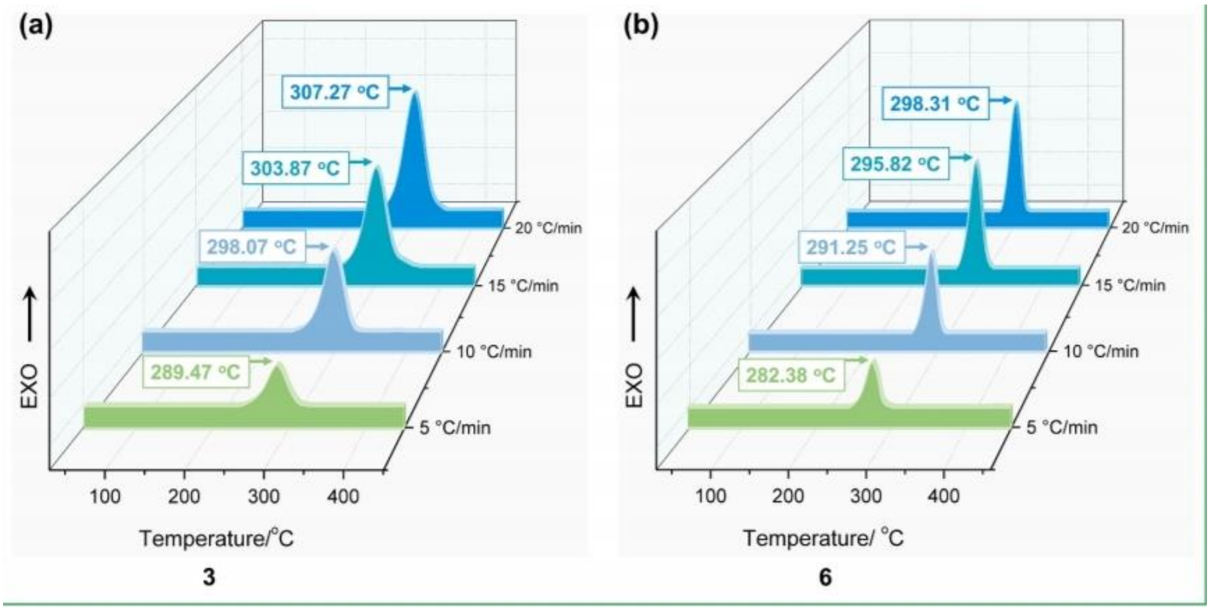
The thermal behaviour was determined with DSC at a heating rate of 5 oC min-1. Compound 5 has a remarkably high thermal stability with an onset decomposition temperature of 355 oC. This is a little higher than that of traditional heat-resistant energetic compounds, TATB or LLM-105 The heat of formation for 5 is higher than that of either TATB or LLM-105.

Since compound 5 shows superior thermal stability, the Kissinger50 and Ozawa51 methods were employed to investigate the thermodynamic properties in comparison with traditional heatresistant explosives, TATB. Both the activation energy and extrapolated peak temperature (Tp0) of 5 showing that 5 has a better heat resistance than TATB, probably because 5 has a larger conjugate system.



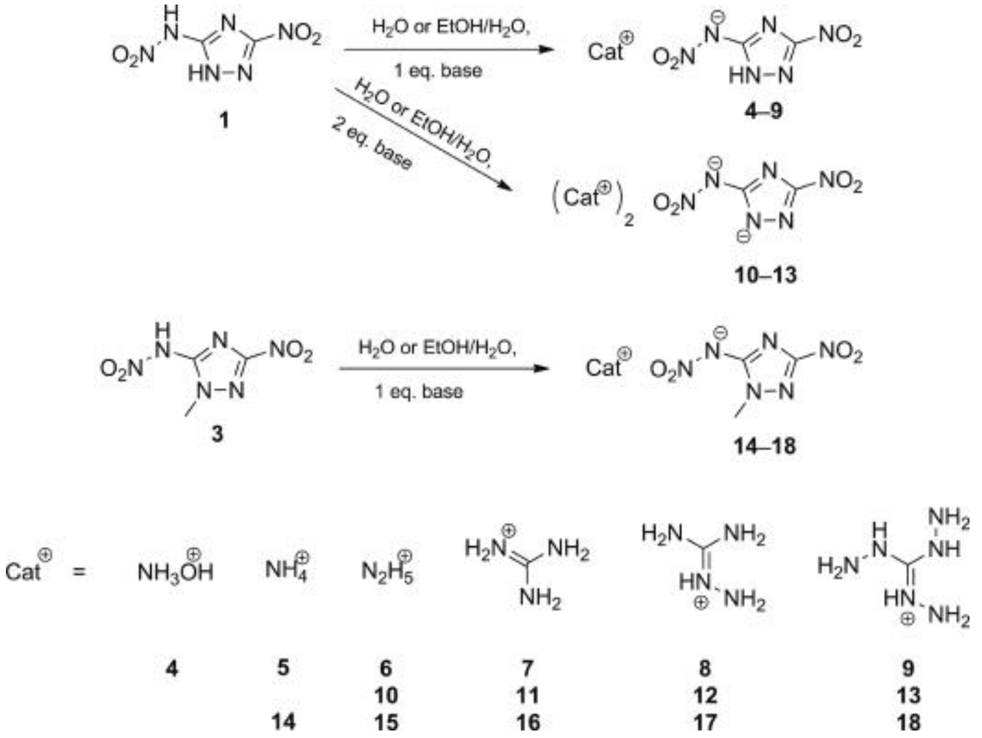
Intramolecular integration of multiple heterocyclic skeletons for energetic materials with enhanced energy & safety[19]

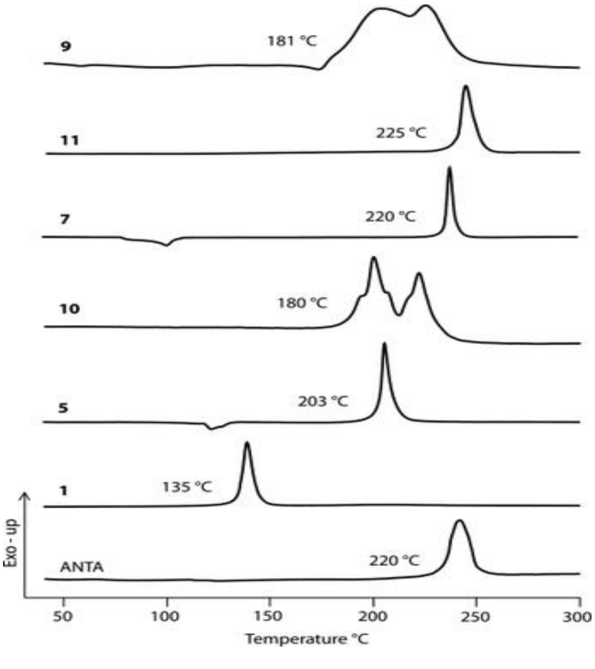




The thermal stability is often a reflection of the difficulty level of the accidental explosions or decompositions of EMs under the severe thermal environment such as deep-well mining and space exploration areas .In this study, the differential scanning calorimetry (DSC) was performed to evaluate the thermostability of 3, 4 and 6–10 with the temperature rate of 10 ◦C min− 1 under N2 flow. The thermal decomposition temperatures (onset, Tdec) of 3, 6 and 7 were determined to be higher than that of RDX (3: 272 ◦C; 6: 265 ◦C; 7: 215 ◦C; RDX: 204 ◦C). By contrasting the structure of 3 with that of 6, we found that the introduction of another one nitro group did not cause an obvious decrease of thermal stability for compound 6. Compound 6 not only possesses a high energy level (Dv = 9094 m s− 1, P = 36.67 GPa) but also shows a high thermal stability (265 ◦C) and low sensitivities (IS = 24 J, FS = 300 N).

Nitraminoazoles Based on ANTA – A Comprehensive Study of Structural and Energetic Properties[20]





DSC plots of ANTA, NANTA (**1**), NH_4^+ $NANTA^-$ (**5**), G^+ $NANTA^-$ (**7**), TAG^+ $NANTA^-$ (**9**), $(N_2H_5^+)_2$ $NANTA^{2-}$ (**10**) and $(G^+)_2$ $NANTA^{2-}$ (**11**). DSC plots were recorded with a heating rate of 5 °C min^{-1}.

Both neutral nitramino compounds **1** and **3** display low decomposition temperature values of 135 and 108 °C, respectively. In contrast, all of the corresponding ionic compounds decompose at much higher temperatures between 180 °C for the hydrazinium salt **10** and 225 °C for the guanidinium salt **11**, which is well above the decomposition temperature of the 3,5-bis(nitramino)-1,2,4-triazolate salts.

The double deprotonation of **1** does not yield a higher stability with regard to the thermal properties, but leads to increased sensitivity values towards impact and friction.
Compound **11** and **12** are both insensitive with regard to impact and friction.

CONCLUSION

Thermal behaviour is an important parameter for evaluating the actual application and long-term storage. To assess the thermal stabilities of these salts, differential scanning calorimetric (DSC) was carried out to test the thermal properties. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase_diagrams for various chemical systems.

In the research, Differential Scanning Calorimetry is used as a technique to find the thermal stabilities of energetic heterocycles.

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