*J. Chem. Sci.* (2021)133:13
https://doi.org/10.1007/s12039-020-01865-3

**REGULAR ARTICLE**

# Nitrogen-rich compounds: s-triazine and tri-s-triazine derivatives as high energy materials

MUDDAMARRI HANUMANTHA RAO[a], VIKAS D GHULE[b] and KRISHNAMURTHI MURALIDHARAN[a,c,*]
[a] Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad, Telangana 500 046, India
[b] Department of Chemistry, National Institute of Technology Kurukshetra, Kurukshetra, Haryana 136119, India
[c] School of Chemistry, University of Hyderabad, Hyderabad, Telangana 500 046, India
E-mail: murali@uohyd.ac.in

MS received 17 August 2020; revised 8 October 2020; accepted 22 October 2020

**Abstract.** This article describes the syntheses, characterization, and energetic properties of 4, 6-diazido-N, N-dimethyl-1, 3, 5-triazin-2-amine and 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine. Also, this paper emphasizes the insensitive and thermally stable energetic molecules like melem, melem-ammonium perchlorate mixture, and hydrazinium cyamelurate. All these compounds possess good energetic properties *viz.,* the heat of formation and heat of combustion.

**Keywords.** s-triazines; tri-s-triazines; 3+2 cyclo additions; high energy materials; nitrogen-rich compounds.

## 1. Introduction

In view of the hazards related to high energy materials (HEMs) research, the synthesis of innovative molecules for energetic application has been a challenging task. A significant focus of research in HEMs is on the synthesis of stable and better-performing compounds. An energetic material's performance depends on good oxidizer or fuel balance, density, amount of generated gas or working fluid, burning rate, and heat of formation.[1–9] It is well-known that their molecular structure directs the enthalpies of chemical systems. Therefore, considerable research efforts are focused on synthesizing molecules containing strained or caged structures[10] and nitrogen-rich compounds with N-N and C-N bonds in their molecular backbone.[11] These molecules are expected to derive their energy from the combustion of hydrocarbon skeleton, relief from molecular strain, and breakage of C-N and N-N bonds. Hence, the synthesis and properties of nitrogen-rich compounds with the high heat of formation, good thermal stability, and reduced sensitivity are desired.

Five-membered nitrogen-containing heterocycles such as imidazole, pyrazole, triazole, furazan, and tetrazole are promising frameworks for HEMs and hence widely used while designing energetic materials.[12] The main advantages of these compounds are better oxygen balance over their carbocyclic analogues, the high heat of formation, high propulsive power and a high specific impulse of the propellant.[13] Similarly, heterocyclic rings such as s-triazine ($C_3N_3H_3$) and tri-s-triazine (also known as heptazine, $C_6N_7H_3$) are also useful moieties in HEMs due to their high heats of formation, better stability and high nitrogen content.[14] The s-triazine derivatives are well-studied in literature for their possible applications in HEMs.[13,15] The heptazine and its derivatives also gained considerable attention because of their unusual conjugated structure and applications.[14] Considering the properties of the nitrogen-rich molecules, we have designed a few derivatives of s-triazine ($C_3N_3$) and heptazine ($C_6N_7$). Herein, we have discussed synthesis, characterization, and evaluation of their energetic

---

*For correspondence

*Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-020-01865-3) contains supplementary material, which is available to authorized users.*

properties of molecules with triazine and heptazine as the core structure.

## 2. Experimental

Caution: None of the compounds presented in this work detonated or exploded during the preparation and handling. Nevertheless, appropriate safety precautions, such as kevlar gloves, face shield, leather jacket, earplugs, Teflon spatulas safety goggles and earthed equipments must be used.

### 2.1 *Instruments*

IR spectra were recorded on JASCO 5300 FTIR with KBr pellet. $^1$H, $^{13}$C were recorded on Bruker Avance 400 M Hz in 5mm NMR tubes at room temperature. Chemical shifts are given with respect to tetramethylsilane ($^1$H, $^{13}$C). LCMS was recorded on 2010A, Shimadzu, Japan. Elemental analysis was recorded on EA1112, Thermo Finnigan, France. Single crystal X-ray diffraction data was recorded on Oxford CCD X-ray diffractometer (Yarnton, Oxford UK). Melting and decomposition points were obtained on DSC by using Nietzsche-DSC instrument. TGA was recorded on Mettler Toledo, Switzerland, and TA instrument. The heats of combustion were determined by using an isoperibolic bomb calorimeter (Parr 6300). The prepared target compounds were burned in the presence of oxygen (pressure of 2.9 Mpa). Benzoic acid (SRM 39i, NIST) was used for standardization of calorimeter and fuse wire correction (Parr 45C10 alloy fuse wire, 2.3 (IT) cal, 21 cm) has been applied in all measurements.

### 2.2 *Materials*

Cyanuric Chloride (Avra Synthesis laboratories), Sodium Azide (Loba chemicals), Ammonium Chloride (Merck), 4,5-dicyano-imidazole, hydrazinium bromide (Sigma-Aldrich) and dimethylformamide (Sisco Research Laboratory).

### 2.3 *Synthesis of 4, 6-diazido-N, N-dimethyl-1, 3, 5-triazin-2-amine ($C_5H_6N_{10}$)* (**3**)

$C_3N_{12}$ (1.53 g, 7.5 mmol) and $NH_4Cl$ (0.29 g, 6.5 mmol) were added to a solution of (4, 5-Dicyano)-imidazole (0.59 g, 5 mmol) in DMF (20 mL).[15] The resulting mixture was heated to 90 °C for 12 h until the starting material was fully consumed (with the help of TLC detection). The mixture was allowed to cool to room temperature and acidified to pH-2 with 1M aqueous hydrochloric acid. The resulting precipitate was collected and washed with a small amount of cold water and air-dried. Then compound was purified by GPC-HPLC column chromatography with chloroform as eluted solvent. After the solvent was evaporated, a colorless solid compound of (**2**) was obtained, which was crystallized from slow evaporation of acetonitrile and confirmed by the X-ray diffraction. The isolated yield was 64% (0.65 g, 3.19 mmol). IR(cm$^{-1}$): 2926 s, 2854 s, 2364 s, 2170 s, 2121 s, 1597 s, 1562 s, 1417 s, 1358 s, 1234 s, 1205 s, 1062 s, 970 s, 893.12 s, 796 s, 758 s, 582 s, 555 s. Elem. Anal. Calcd (found) for $C_5H_6N_{10}$: C, 29.13 (29.21); H, 2.93 (2.86); N, 67.94 (67.75). LCMS: M$^+$ 207. $^1$H NMR ($CDCl_3$): δ 3.19 (6H, s). $^{13}$C NMR: δ 169.8, 165.8, and 36.6.

### 2.4 *Synthesis of 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine* (**4**)

A mixture of 3, 5-dinitro benzonitrile (20 mmol, 3.86 g), triazine triazide (1.49 g, 7.33 mmol), and zinc bromide (4.50 g, 20 mmol) in 40 mL water was refluxed for 24 h with vigorous stirring. HCl (3N, 30 mL) and ethyl acetate (100 mL) were then added to the suspension and stirring was continued until the disappearance of solid. The organic layer was separated and the aqueous layer extracted with two portions of 100 mL of ethyl acetate. The organic layers were combined and concentrated; 200 mL of 0.25 N NaOH was added. The mixture was stirred until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension then filtered and solid washed with 20 mL of 1N NaOH. 40 mL of 3N HCl was added to the filtrate with stirring, resulted in the product of 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine to precipitated out. The compound (**4**) was filtered and washed with two portions of 20 mL of 3N HCl and dried by applying high vacuum to furnish the product of 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine as a yellow colored powder. The isolated yield was 69% (3.67g, 4.68 mmol).

IR(cm$^{-1}$): 3096 s, 1693 s, 1626 s, 1543 s, 1346 s, 1267 s, 1151 s, 1080 s, 918 s, 729 s. Elem. Anal. Calcd (found) for $C_{24}H_9N_{21}O_2$: C, 36.79 (36.78); H, 1.16 (1.18); N, 37.54 (37.56). LCMS: M$^+$ 784. $^1$H NMR ($CDCl_3$): δ 9.1(6H, s), 8.9 (2 H, s). $^{13}$C NMR: δ 120.6, 127.3, 128.3, 149.2, 154.9, 172.5.

### 2.5 *Preparation of silver cyanurate* (**9**)

3 mmol (1.01g) of potassium cyanurate was dissolved in deionised water and 9 mmol of (1.53 g) $AgNO_3$ was added and continued stirring for one hour. A voluminous precipitate was obtained immediately after the addition of silver nitrate; allow it to complete the precipitate. Then filter the solution followed by washing the residue with deionised water to remove starting materials. The compound was dried under reduced pressure to obtain the grey colored powdered compound in quantitative yield. It is insoluble in most of the solvents and it can be used in subsequent

reactions. IR(cm$^{-1}$): 1610 s, 1545 s, 1380 s, 1167 s, 778 s, 673 s. Elem. Anal. Calcd (found) for $C_6Ag_3N_7O_{32}$: C, 13.30 (13.33); N, 18.10 (18.11).

### 2.6 *Preparation of hydraziniumcyamelurate (**10**)*

4.5 mmol (0.50 g) of hydrazinium bromide was dissolved in deionised water and 1.5 mmol (0.80 g) of silver cyamelurate was added to the reaction mixture continue the stirring for 24 h. Then the solution was filtered and the filtrate was collected, followed by evaporation that lead to obtaining the product which was dried under reduced pressure. The isolated yield was 73%, as a colorless solid.

IR(cm$^{-1}$): 3452 s, 3321 s, 3047 s, 1668 s, 1520 s, 1402 s, 1309 s, 1097 s, 964 s, 796 s, 457 s. Elem. Anal. Calcd (found) for $C_6H_{15}N_{13}O_3$: C, 22.71 (22.72); H, 4.77 (4.79); N, 57.39 (57.41); LCMS: $M^+$ 318. $^1H$ NMR (DMSO-$d_6$): δ 7.0 (15 H, broad peak). $^{13}C$ NMR: δ 151.2 and 156.4.

## 3. Results and Discussion

### 3.1 *Amino and azido substituted triazine*

Numerous azide-containing organic compounds are produced for the application as HEM because azide group (-$N_3$) impacts their energy contents significantly.[16] However, most of them are sensitive to external stimuli that complicate their handling.[17] For example, triazine triazide (**2**) is a well-known nitrogen-rich HEM (82.35% of nitrogen content). Despite possessing very high heat of formation (∼961 kJ/mol), it has less practical applications due to its high sensitivity. However, over the last years, relatively stable carbon-nitrogen heterocycles with azide substitution have been reported.[18] The advantage of azide functional group is that it can be readily derivatized by [3+2]-cyclo addition reaction with unsaturated functionalities such as cyano group, olefins, and alkynes.[19]

The compound 5,5'-(1H-imidazole-4,5-diyl)bis(1H-tetrazole) reported in the literature was obtained by the reaction of 1H-imidazole-4,5-dicarbonitrile (4,5-dicyanoimidazole, **1**) with sodium azide and ammonium chloride in the presence of dimethylformamide.[15] Similarly, we were interested in reacting compound **1** with **2** to obtain a new molecule with high nitrogen content through simple click chemistry at both cyano groups of **1**. However, the reaction of compound **2** (7.5 mmol) with **1** (5 mmol) in the presence of $NH_4Cl$ (6.5 mmol) in DMF failed to yield the target molecule, but unexpectedly yielded 4, 6-diazido-N,N-dimethyl-1,3,5-triazin-2-amine (**3**) (67.94% of nitrogen content) with good yield. This may be due to the stabilization of $Me_2N^-$ generated from DMF, which might have produced through abstraction of acidic proton in DMF by compound **1**. This nucleophile was probably competing with compound **1** and reacted with **2** to yield compound **3**. The compound **3** was characterized spectroscopically. Further, the solid-state structure of **3** was obtained through the single-crystal X-ray diffraction technique. The ORTEP diagram showing the molecular structure of compound **3** is depicted in Figure 1. It was crystallized in the monoclinic crystal system with C2/c point group. The asymmetric unit contained half-molecule. In the crystal structure, all C-N bond distances were close to 1.33 Å.

The introduction of one or more amino group(s) was found to improve the stability of compounds containing azido groups.[15] For example, hexaazide substituted cyclo tri phosphazene was reported to be highly sensitive. At the same time, the replacement of two azido groups with amino groups reduced the sensitivity of corresponding molecules.[20,22] Similarly, compound **3** had lesser values of some energetic properties than **2**, but it was not sensitive and could be handled easily than **2** (Table 1).[21] However, the energetic parameters of **3** are comparable to other conventional energetic compounds, and therefore, it attracts interest since it can overcome the sensitivity issues of **2** (Scheme 1).

### 3.2 *Tetrazole derivative of triazine*

The high nitrogen content (∼80%) of tetrazole makes it interesting to incorporate in various HEMs to improve energetic properties.[23] Since it is possible to derivatize azide with organic cyano groups to form tetrazole, we were interested in using tetrazole scaffolds to build macromolecular nitrogen-rich

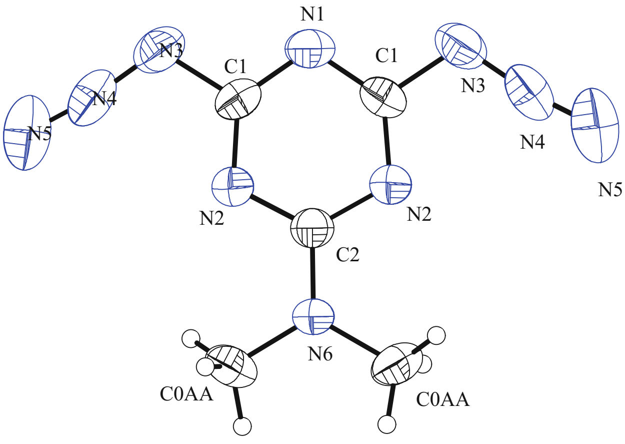
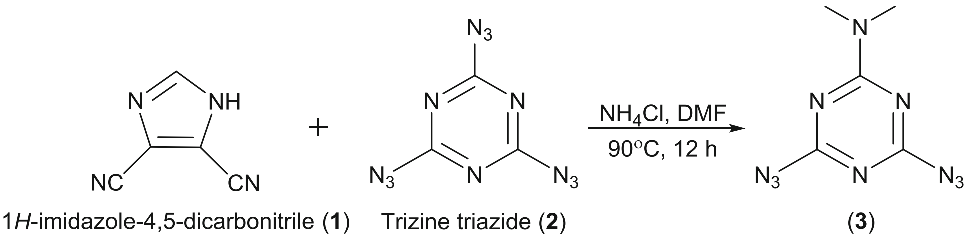


**Figure 1.** The ORTEP diagram of 4, 6-diazido-N, N-dimethyl-1, 3, 5-triazin-2-amine (**3**).

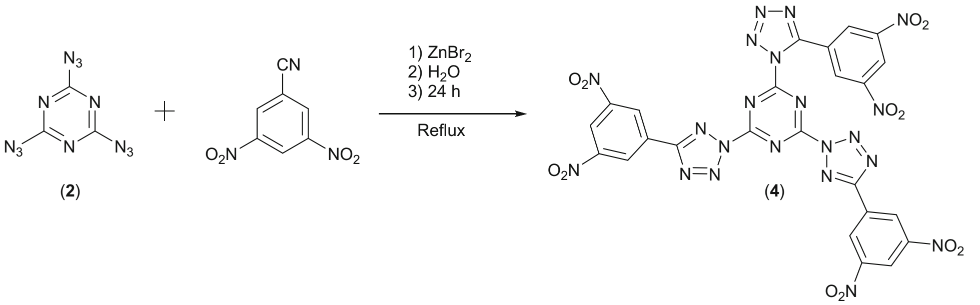
**Table 1.** Energetic properties of triazine and heptazine based molecules comparison with known Standard energetic materials.

| C | MP (°C) | Td (°C) | D (g/cm$^3$) | HOF (kJ/mol) | VOD (km/s) | DP (GPa) | Q (cal/g) | NC (%) | OB (%) | IS (J) | FS (N) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 94 | 150 | 1.59 | 961 | 6.93 | 19.29 | 1126 | 82.4 | −47.1 | 5[25] | 0.49[25] |
| **3** | 152 | 152 | 1.45 | 649 | 5.99 | 13.84 | 911 | 68.0 | −101.0 | 40 | 360 |
| **4** | ** | ** | 1.68 | 1511 | 6.85 | 19.93 | 1244 | 37.5 | −82.5 | 50 | 360 |
| **5** | – | 450 | 1.64 | 249 | 5.22 | 11.39 | 422 | 64.2 | −110.1 | 50 | 360 |
| **5+AP** | – | – | – | – | – | – | 1356.2* | – | 0.0 | 50 | 360 |
| **7** | – | 420 | 1.79 | −260 | 5.65 | 14.12 | 430 | 44.3 | −76.0 | 50 | 360 |
| **10** | 252 | 252 | 1.54 | 616.39 | 7.08 | 20.14 | 1165 | 57.4 | −83.3 | 50 | 360 |
| RDX[26] | 205 | – | 1.80 | 63 | 8.75 | 33.8 | 1202.8 | 37.8 | −21.6 | 7.5 | 120 |
| HMX[26] | 291 | – | 1.90 | 76 | 9.10 | 39.0 | 1196.6 | 37.8 | −21.6 | 7.4 | 120 |
| PETN[26] | 140 | 203 | 1.76 | −514.63 | 8.40 | 32.0 | 1383.8 | 25.4 | −40.5 | 3 | 60 |
| TNT[26] | 80 | 295 | 1.65 | −54.39 | 6.90 | 19.0 | 1014.3 | 18.5 | −74.0 | 15 | 353 |
| PA[26] | 121 | – | 1.76 | −214.35 | 7.35 | 23.2 | 776.0 | 18.3 | −45.4 | 7.4 | 353 |

C: Compound; PA: Picric Acid; MP: Melting point; Td: Temperature decomposition; HOF: the heat of formation; VOD: velocity of detonation; DP: detonation pressure; Q: heat of explosion; NC: nitrogen content; OB: oxygen balance; IS: Impact Sensitivity; FS: Friction Sensitivity; * Experimental value; ** The compound is spill out from the crucible while performing TGA studies.



**Scheme 1.** Synthesis of 4, 6-diazido-N,N-dimethyl-1,3,5-triazin-2-amine (**3**).



**Scheme 2.** Synthesis of 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine (**4**).

molecules. One such a designed compound, 2, 4, 6-tris (5-(3, 5-dinitrophenyl)-1H-tetrazol-1-yl)-1, 3, 5-triazine (**4**), was synthesized through a 3+2 cycloaddition.[18] For this purpose, triazine triazide was reacted with three equivalents of 3,5-dinitrobenzonitrile in the presence of zinc bromide as a catalyst in the water at reflux temperature for 24 h (Scheme 2). The compound **4** was obtained in good yield and characterized using spectral data and elemental analysis.

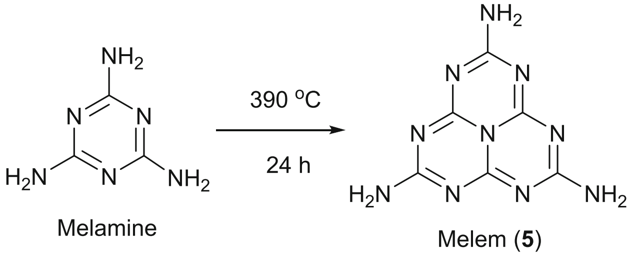
### 3.3 *Heptazine based energetic materials*

Heptazine containing compounds were found to be thermally stable and promising nitrogen-rich compounds having sp2-bonded carbon nitride materials. The heptazine derivatives were reported in literature earlier.[24] We have synthesized some of the heptazine based compounds like melem (**5**), cyameluric acid (**7**) and hydrazinium cyamelurate (**10**). We have synthesized melem (**5**) successfully on a 5 g scale from melamine using the reported procedure (Scheme 3). The energetic properties of these molecules have been studied.

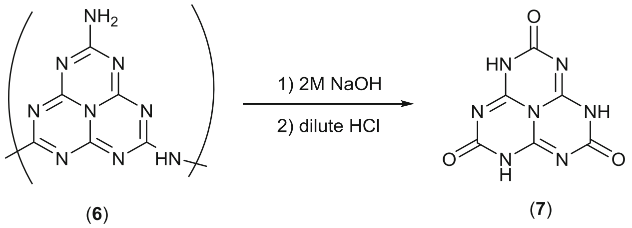
The oxygen balance of melem is -110%, which would yield more solid carbon waste in the combustion process and thus may reduce its overall detonation performance. Hence, melem needs external oxidizer to complete its combustion process. To overcome this problem, we used the mixture of ammonium perchlorate and melem (5+AP) in appropriate equivalents to make oxygen balance neutral and improve performance. The mixing of melem and ammonium perchlorate was achieved by using mechanical blending for three days. The energetic properties of melem and melem-perchlorate mixture are discussed in the later section. The hydrolysis of polymer melon (**6**) with sodium hydroxide at reflux temperature yielded the cyameluric acid (**7**) (Scheme 4). The resulting sodium cyamelurate was transformed into cyameluric acid by the acidification of dilute hydrochloric acid.[24] The synthesis of hydrazinium cyamelurate (**10**) was achieved in four steps according to the procedure starting from ammonium thiocyanate (Scheme 5).

### 3.4 *Energetic properties of the compounds 2, 3, 4, 5, 5+AP, 7 and 10*

The VOD, DP, and Q are the most critical properties of energetic materials, and they should be high as possible, however, while these parameters are improved the explosive sensitivity (IS and FS) of the materials increases, which make it unusable. More density would allow for packing materials in less volume, which indirectly influence DP. The new material should have high energy content with reduced sensitivity. Therefore, it is required to optimize all energetic properties along with sensitivity so that it can be useful in several other applications. The energetic parameters of compounds were evaluated by computational methods, and the results are summarized in Table 1. The evaluated properties are compared with the properties of known standard energetic materials currently in use in the propellant or explosive formulations.



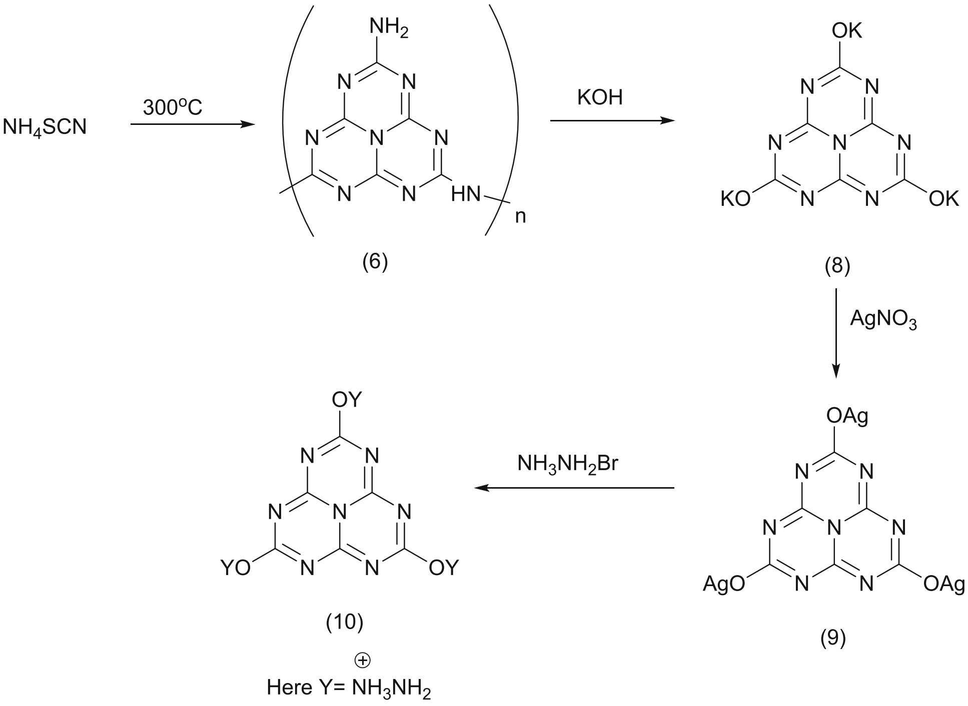
**Scheme 3.** Synthesis of Melem (**5**).



**Scheme 4.** Synthesis of cyameluric acid (**7**).

The newly synthesized triazine and heptazine based compounds have a density in the range of 1.45 to 1.79 g/cm$^3$. Whereas, the density of standard HEMs such as RDX, HMX, PETN, TNT, and picric acid was found to be in the range of 1.65 to 1.87 g/cm$^3$. In the case of the heat of formation of synthesized compounds, they have a higher positive heat of formation than the standard high explosives like RDX (63 kJ/mol) and HMX (76 kJ/mol).[27] For example, triazine triazide (**2**) has a high heat of formation (961 kJ/mol) and high nitrogen content (82.4%), but highly sensitive to external stimuli, which limit its usage in energetic applications. The compound **3** showed performance comparable to triazine triazide (**2**) despite having lesser density (1.45 g/cm$^3$) and negative oxygen balance (-100 %). However, in this case of compound (**3**), it can be used as an alternative as it possesses reasonable energy (649 kJ/mol) and nitrogen content (68%). The heat of formation of compound (**4**) is 1511 kJ/mol. Its detonation pressure (DP) and chemical energy (Q) values are 19.93 Gpa and 1244 cal/g.

The heptazine based compounds such as melem, melem-perchlorate mixture, cyameluric acid, and hydrazinium cyamelurate showed good energetic properties. The heat of formation of melem and hydrazinium cyamelurate are 249 kJ/mol and 616 kJ/mol, respectively. The heat of explosion of hydrazinium cyamelurate is 1244 cal/g. In terms of detonation velocity and pressure, none of these compounds surpasses RDX or HMX. However, the newly synthesized compounds are less sensitive than the standard high energetic materials. We have also calculated the heat of combustion of the melem-



**Scheme 5.** Synthesis of hydrazinium cyamelurate (**10**).

ammonium perchlorate mixture as 1356.2 cal/g. This value is approximately three times that of commonly used initiating explosives such as lead azide. Further, melem and ammonium perchlorates are individually possessed lesser values of heat of combustion than the mixture of components.

### 3.5 *Thermal stability and sensitivity*

The melting point of compound **2** was 94 °C and its decomposition started at 150 °C; whereas the melting point of compound **3** was 152 °C, but it decomposed after melting. Unfortunately, the TG-DTA of compound **4** was not possible to record because the sample was spilling out from the crucible even with very lesser amounts (<0.25 mg) in several trials. The compound **10** is stable up to 252 °C.

The performance and safety characteristics of molecules need to be evaluated for the safe handling of energetic materials. Impact and friction sensitivity are more important characteristics in the context of manufacturing. Therefore, the impact and friction sensitivities of all the compounds were measured using the standard BAM fall hammer, and BAM friction techniques. About 20 mg of compounds (**3**, **4**, and **10**) were subjected to a fall-hammer test using a 5 or 10 kg dropping weight. The impact sensitivity of all the compounds was above 50J except the compound (**3**), which was >40J. The friction sensitivity of the compounds was higher than 360N. The reduced sensitivity of compound (**3**) was attributed to the substitution of N, N-dimethyl group in the place of one of the azide groups in triazine triazide (**2**). This sensitivity data revealed that these compounds were much less sensitive than the other known energetic materials such as TNT, PETN, RDX, and HMX.

### 3.6 *Computational details*

In the present study, all quantum chemical calculations were performed using the Gaussian G03 program package.[28] The geometries of all the derivatives were fully optimized at the DFT (B3PW91) level with 6-31G(d,p) basis set. The computational methodology used in this work is similar to our previous reports.[29]

## 4. Conclusions

We have successfully synthesized and fully characterized two classes of compounds based on s-triazine and heptazine. All these compounds possess good energetic properties such as heat of combustion and heat of the explosion. We have studied the energetic properties of melem for the first time and found that it has the potential to use as high energy material in propellants and explosive formulations. Besides, the composition of the melem-ammonium perchlorate mixture contained the high heat of combustion than its components of ammonium perchlorate and melem. However, performance evaluation needs to be performed for all compounds to prove their usage in the propellants and explosive formulations.

## Supplementary Information (SI)

The crystal structure refinement parameters, bond lengths and angles are provided in supplementary information Tables S1 and S2. The CCDC number of compound **3** is CCDC2009397. TG-DTA plots of triazine and heptazine based molecules are provided at www.ias.ac.in/chemsci.

## Acknowledgements

Authors thank ACRHEM, the University of Hyderabad for financial support. Authors also thank the School of Chemistry, the University of Hyderabad for infrastructure facilities. Authors also thank K. Sathish Kumar for his help in single-crystal X-ray diffraction studies.

## References

1. Venugopalan S 2015 *Demystifying Explosives: Concepts in high energy materials* (Netherlands: Elsevier)
2. Klapötke T M and Sabate C M 2008 Bistetrazoles: Nitrogen-Rich, High-Performing, Insensitive Energetic Compounds *Chem. Mater.* **20** 3629
3. (a) Tao G, Guo Y, Parrish D and Shreeve J M 2010 Energetic 1,5-diamino-4H-tetrazolium nitro-substituted azolates *J. Mater. Chem.* **20** 2999; (b) Singh R P, Verma R D, Meshri D T and Shreeve J M 2006 Energetic Nitrogen-Rich Salts and Ionic Liquids *Angew. Chem. Int. Ed.* **45** 3584; (c) Steinhauser G and Klapötke T M 2008 "Green" Pyrotechnics: A Chemists Challenge *Angew. Chem. Int. Ed.* **47** 3330; (d) Chavez D E, Hiskey M A, Naud D L and Parish D 2008 Synthesis of an Energetic Nitrate Ester *Angew. Chem. Int. Ed.* **47** 8307
4. (a) Akhavan J 1998 *The Chemistry of Explosives* (Cambridge: The Royal Society of Chemistry); (b) Klapötke T M 2007 *High Energy materials: Structure and Bonding* (Berlin, Heidelberg: Springer) p. 125
5. (a) Nair U R, Asthana S N, Rao A S and Gandhe B R 2010 Advances in High Energy Materials *Def. Sci. J.* **60** 137; (b) Talawar M B, Sivabalan R, Mukundan T, Muthurajan H, Sikder A K, Gandhe B R and Rao A S 2009 Environmentally Compatible Next Generation Green Energetic Materials (GEMs) *J. Hazard. Mater.* **161** 589
6. Badgujar D M, Talawar M B, Asthana S N and Mahuli Kar P P 2008 Advances in Science and Technology of Modern Energetic Materials: An Overview *J. Hazard. Mater.* **151** 289
7. Petrie M A, Sheehy J A, Boatz J A, Rasul G, Prakash G K S, Olah G and Christe K O 1997 Novel High-Energy Density Materials. Synthesis and Characterization of Triazidocarbenium Dinitramide, -Perchlorate, and –Tetrafluoroborate *J. Am. Chem. Soc.* **119** 8802
8. (a) Joo Y H and Shreeve J M 2008 1-Substituted 5-Aminotetrazoles: Syntheses from $CNN_3$ with Primary Amines *Org. Lett.* **10** 4665; (b) Steinhauser G, Giester G, Wagner C, Weinberger P, Zachhuber B, Ramer G, Villa M and Lendl B 2012 Nitrogen-rich Compounds of the Actinoids: Dioxouranium(VI) 5,5′-Azobis[tetrazolide] Pentahydrate and Its Unusually Small Uranyl Angle *Inorg. Chem.* **51** 6739
9. Hiskey M A, Goldman N and Stine J R 1998 High-nitrogen energetic materials derived from azotetrazolate *J. Energ. Mater.* **16** 119
10. (a) Pagoria P F, Lee G S, Mitchell A R and Schmidt R D 2002 A review of energetic materials synthesis *Thermochim. Acta* **384** 187; (b) Talawar M B, Sivabalan R, Anniyappan M, Gore G M, Astana S N and Gandhe B R 2005 Novel Ultra high-Energy Materials *Combust. Expl. Shock Waves.* **41** 264
11. (a) Joo Y H and Shreeve J M 2010 Polynitramino compounds outperform PETN *Chem. Commun.* **46** 142; (b) Hammerl A and Klapötke T M 2002 Tetrazolylpentazoles: Nitrogen-Rich Compounds *Inorg. Chem.* **41** 906; (c) Srinivas D, Ghule V D and Muralidharan K 2014 Synthesis of nitrogen-rich imidazole, 1,2,4-triazole and tetrazole-based compounds *RSC Adv.* **4** 7041
12. (a) Chavez D E, Hiskey M A and Gilardi R D 2000 3,3′-Azobis(6-amino-1,2,4,5-tetrazine): A Novel High-Nitrogen Energetic Material *Angew. Chem. Int. Ed.* **39** 1791; (b) Gao H and Shreeve J M 2011 Azole-Based Energetic Salts *Chem. Rev.* **111** 7377; (c) Fried L E, Manaa M R, Pagoria P F and Simpson R L 2001 Design and Synthesis of Energetic Materials *Annu. Rev. Mater. Res.* **31** 291
13. Turker L, Atalar T, Gumus S and Camur Y 2009 A DFT study on nitrotriazines *J. Hazard. Mater.* 167 440
14. (a) Ghule V D, Radhakrishnan S, Jadhav P M and Tewari S P 2012 Computational Study on Substituted s-Triazine Derivatives as Energetic Materials *E-J. Chem.* **9** 583; (b) Klapötke T M and Sabate C M 2009 New energetic compounds based on the nitrogen-rich 5,5′-azotetrazolate anion *New J. Chem.* **33** 1605
15. Guo M 2009 4,5-Bis(1H-tetrazol-5-yl)-1H-imidazole monohydrate *Acta. Cryst.* **E65** o1403
16. (a) Rao M H, Ghule V D and Muralidharan K 2017 2, 4, 6-tris [bis (1H-tetrazol-5-yl) amino]-1, 3, 5-triazine as a nitrogen-rich material *J. Chem. Sci.* **129** 657; (b) Holfter H, Klapötke T M and Schulz A 1 1997 High energetic materials: Reaction of Azides with Dioxygenyl Salts *Propellants. Explos. Pyrotech.* **22** 51
17. (a) Abe T, Tao G H, Joo Y H, Huang Y, Twamley B and Shreeve J M 2008 Activation of the C-F Bond: Transformation of $CF_3N$=N- into 5-Azidotetrazoles *Angew. Chem. Int. Ed.* **47** 7087
18. (a) Christe K O, Haiges R, Wilson W W and Boatz J A 2010 Synthesis and Properties of $N_7O^+$ *Inorg. Chem.* **49** 1245; (b) Rao M H and Muralidharan K 2013 Syntheses, characterization and energetic properties of *closo*-$(B_{12}H_{12})^{2-}$ salts of imidazolium derivatives *Dalton. Trans.* **42** 8854; (c) Rao M H and Muralidharan K 2016 *closo*-Dodecaborate $(B_{12}H_{12})^{2-}$ salts with nitrogen based

cations and their energetic properties *Polyhedron* **115** 105; (d) Ghule V D, Sarangapani R, Jadhav P M and Pande R K 2011 Computational design and structure–property relationship studies on heptazines *J. Mol. Model.* **17** 2927

19. Kolb H C, Finn M G and Sharpless K B 2001 Click Chemistry: Diverse Chemical Function from a Few Good Reactions *Angew. Chem. Int. Ed.* **40** 2004
20. (a) Deokar P, Vasiliu M, Dixon D A, Christe K O and Haiges R 2016 The Binary Group 4 Azides $[PPh_4]_2[Zr(N_3)_6]$ and $[PPh_4]_2[Hf(N_3)_6]$ *Angew. Chem. Int. Ed.* **55** 14350; (b) Saal T, Blastik Z E, Haiges R, Nirmalchandar A, Baxter A F, Christe Karl O, Vasiliu M, Dixon D A, Beier P and Sutya Prakash G K 2020 Protonation of $CH_3N_3$ and $CF_3N_3$ in Superacids: Isolation and Structural Characterization of Long-Lived Methyl- and Trifluoromethylamino Diazonium Ions *Angew. Chem. Int. Ed.* **59** 2
21. Karaghiosoff K, Klapötke T M, Mayer P, Sabate C M, Penger A and Welch J M 2008 Salts of Methylated 5-Aminotetrazoles with Energetic Anions *Inorg. Chem.* **47** 1007
22. Muralidharan K, Omotowa B A, Twamley B, Piekarski C and Shreeve J M 2005 High energy density materials from azido cyclophosphazenes *Chem. Commun.* 5193
23. (a) Gao H and Shreeve J M 2011 Azole-Based Energetic Salts *Chem. Rev.* **111** 7377; (b) Srinivas D, Ghule V D, Muralidharan K and Jenkins H D B 2013 Tetraanionic Nitrogen-Rich Tetrazole-Based Energetic Salts *Chem. Asian J.* **8** 1023; (c) Huynh M H V, Hiskey M A, Chavez D E, Naud D L and Gilardi R D 2005 Synthesis, Characterization, and Energetic Properties of Diazido Heteroaromatic High-Nitrogen C−N Compound *J. Am. Chem. Soc.* **127** 12537; (d) Banert K, Joo Y H, Ruffer T, Walfort B and Lang H 2007 The Exciting Chemistry of Tetraazidomethane *Angew. Chem. Int. Ed.* **46** 1168; (e) Jenkins H D B, Tudela D and Glasser L 2002 Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements *Inorg. Chem.* **41** 2364; (f) Glasser L and Jenkins H D B 2000 Lattice Energies and Unit Cell Volumes of Complex Ionic Solids *J. Am. Chem. Soc.* **122** 632
24. (a) Sorescu D C, Rice B M and Thompson D L 1997 Intermolecular Potential for the Hexahydro-1,3,5-trinitro-1,3,5-s-triazine Crystal (RDX): A Crystal Packing, Monte Carlo, and Molecular Dynamics Study *J. Phys. Chem. B* **101** 798; (b) Kroke E, Schwarz M, Bordon E H, Kroll P, Noll B and Norman A D 2002 Tri-s-triazine derivatives. Part I. From trichloro-tri-s-triazine to graphitic $C_3N_4$ structures *New J. Chem.* **26** 508
25. Anniyappan M, Sonawane S H, Shee S K and Sikder A K 2015 Method of Producing Uniformly Shaped and Sized Particles of 2,4,6-Triazido-1,3,5-triazine by Emulsion Crystallization *Cent. Eur. J. Energ. Mat.* **12** 785
26. Agarwal J P 2010 *High Energy Materials* (Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA) p.19
27. Badgujar D M, Talawar M B, Asthana S N and Mahulikar P P 2008 Advances in science and technology of modern energetic materials: an overview *J. Hazard. Mater.* **161** 289
28. Frisch M J et al. 2003 *Gaussian 03*, Revision B.05, Gaussian, Inc., Pittsburgh PA
29. (a) Ghule V D 2012 Computational Studies on Energetic Properties of Trinitro-Substituted Imidazole–Triazole and Pyrazole–Triazole Derivatives *J. Phys. Chem. A* **116** 9391; (b) Deswal S, Ghule V D, Tittal R K and Radhakrishnan S 2015 Quantum-chemical design of tetrazolo [1, 5-b][1, 2, 4, 5] tetrazine based nitrogen-rich energetic materials *Comput. Theor. Chem.* **1054** 55; (c) Jadhav P M, Radhakrishnan S, Ghule V D and Pandey R K 2015 Energetic salts from nitroformate ion *J. Mol. Model* **21** 134