

REGULAR ARTICLE

2,4,6-tris[bis(1H-tetrazol-5-yl)amino]-1,3,5-triazine as a nitrogen-rich material

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Abstract. This paper describes the synthesis, characterization and energetic properties of tetrazole and triazine-based thermally stable, insensitive nitrogen-rich high energy density materials of N, N', N''-(1,3,5-triazine-2,4,6-triyl) tris(N-cyanocyanamide) [1] and 2,4,6-tris[bis(1H-tetrazol-5-yl)amino]-1,3,5-triazine [2]. The compound 2 is the first example for compounds having six tetrazole units on a triazine ring.

Keywords. Nitrogen rich compounds; high energy materials; density functional theory.

1. Introduction

Synthesizing more potent energetic compounds is an exciting task for the synthetic chemists due to their unknown hazardous nature. Besides, combining high positive heat of formation (HOF) and better density in the same molecule to achieve high detonation performance with the straightforward synthetic route is challenging. Hence, research on developing new strategies and methodologies to synthesize nitrogen-rich energetic compounds are getting tremendous importance due to their numerous applications in gas generators, propellants, and explosives.^{1–5} Nitrogen-rich compounds help to achieve high densities, high HOFs and stability due to nitrogen content, C-N and N-N bonds, and aromaticity. On decomposition, the nitrogen-rich molecules would produce a large quantity of eco-friendly nitrogen gas and large amounts of energy.^{6–8} The low molecular weight nitrogen compounds are known to give more thrust to a rocket motor because of their high kinetic energy.

Designing molecules with more number of tetrazole groups is an attractive strategy to produce nitrogen-rich molecules. Our group reported⁹ several tetra anionic nitrogen rich tetrazole-based energetic salts synthesized from simple starting materials in good yields. In this context, we have synthesized nitrogen-rich containing

triazine and tetrazole rings based on reference methods.^{10–13} Herein, we report the synthesis of nitrogen-rich molecules, N, N', N''-(1,3,5-triazine-2,4,6-triyl) tris(N-cyanocyanamide) (1) and 2,4,6-tris[bis(1H-tetrazol-5-yl)amino]-1,3,5-triazine (2) (Figure 1). Two newly synthesized molecules 1 and 2 were thermally stable up to 300°C, not sensitive to impact and friction, and possess higher density and HOF. To the best of our knowledge, the compound 2 is the first example of a compound having six tetrazole moieties in a single molecule constructed on triazine ring.

2. Experimental

Caution: The compounds 1 and 2 were not sensitive to moisture and stable until ignited inside the bomb calorimeter. However, the molecules with high nitrogen content and energy are expected to be sensitive towards shock, friction and heat. Hence, appropriate safety precautions, such as kevlar gloves, face shield, leather jacket, earplugs, Teflon spatulas, safety goggles and earthened equipment must be employed.

2.1 Materials and Instruments

Cyanuric Chloride (Sigma-Aldrich), Sodium dicyanamide (Sigma-Aldrich), Sodium Azide (Merck), Zinc bromide (Alfa-Aesar) were commercially available. IR spectra were recorded on JASCO 5300 FTIR with KBr pellet. ¹H and ¹³C NMR were recorded on Bruker Avance 500 MHz in 5 mm NMR tubes at room temperature. The isotropic solid state

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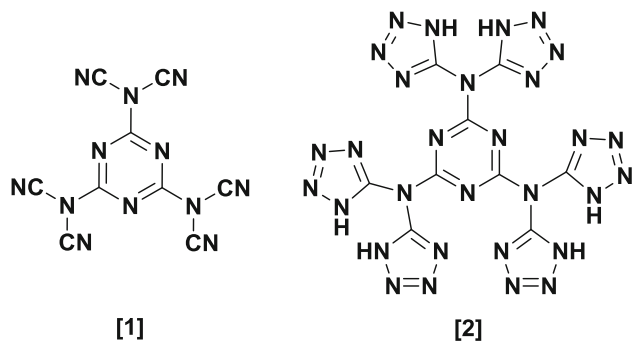


Figure 1. Molecular structures of compounds **1** and **2**.

spectra were recorded by MAS speed of 4 kHz in a zirconia rotor using Bruker Avance 400 spectrometer. Chemical shifts were recorded based on tetramethylsilane as reference. LCMS was recorded on 2010A, Shimadzu, Japan. The HRMS were recorded on a Bruker Maxis instrument. Elemental analysis was recorded on EA1112. Thermal decomposition experiments were performed under UHP nitrogen atmosphere in a TA instrument (SDT Q600). The samples (~1 mg) were analysed from room temperature to 800°C with a heating rate 10°C/min.

2.2 Synthesis of *N,N',N''*-(1,3,5-triazine-2,4,6-triyl)tris(*N*-cyanocyanamide) (**1**)

An aqueous solution of sodium dicyanamide (0.80 g, 9 mmol) (in 15 mL of deionized water) was added dropwise to the slurry of cyanuric chloride (0.18 g, 1 mmol) in acetone (50 mL) at 55°C. The reaction mixture was stirred continuously for 2 h. After cooling to room temperature, the reaction mixture was cooled by the addition of crushed ice and continued the stirring for 30 min. Then, the mixture was filtered and washed with water to obtain a white solid product of *N,N',N''*-(1,3,5-triazine-2,4,6-triyl)tris(*N*-cyanocyanamide). The isolated yield was 79% (0.22 g, 0.79 mmol). IR (ν/cm^{-1}): 3172 w, 2186 s [(N – (CN)₂], 1616 s [triazine ring], 1391 s. Elem. Anal. Calcd. % (Found %) for C₉N₁₂: C, 39.14 (39.26); N, 60.86 (60.75). LCMS: M⁺ 277. HRMS: Calculated mass (observed mass), 276.0369 (277.1790). ¹³C NMR (solid): δ 119.34, 162.13.

2.3 Synthesis of 2,4,6-tris[bis(1*H*-tetrazol-5-yl)amino]-1,3,5-triazine (**2**)

An aqueous solution [40 mL of deionized water] of **1** (0.91 g, 3.3 mmol), sodium azide (1.43 g, 22 mmol) and zinc bromide (4.50 g, 20 mmol) was refluxed (at 140°C of oil bath) for 24 h with vigorous stirring. After cooling to room temperature, the reaction mixture was cooled further by adding crushed ice. Then, the stirring was continued for another 30 min and the reaction mixture was filtered and washed with cold water. After that, the resultant product was air-dried to obtain a white,

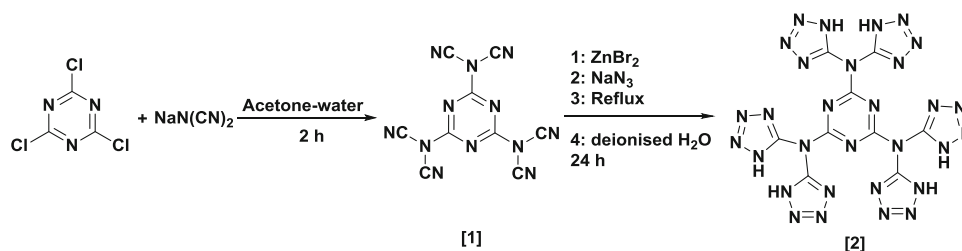
powdered sample (**2**). The isolated yield was 73% (1.29 g, 2.4 mmol). IR (ν/cm^{-1}): 3413 s, 3095 m, 1610 s, 1468 s, 1084 s, 794 s. Elem. Anal. Calcd. % (Found %) for C₉H₆N₃₀: C, 20.23 (20.15); H, 1.13 (1.21); N, 78.64 (78.52). LCMS: M⁺ 535. HRMS: Calculated mass (observed mass), 534.1392 (534.2941). ¹H NMR (DMSO-*d*₆): δ 7.308 (6H, s). ¹³C NMR (DMSO-*d*₆): δ 165.0, 154.8.

3. Results and Discussion

Cyanuric chloride was used as the starting material for the synthesis of compounds **1** and **2**. The synthesis of **1** was carried out by the reaction of cyanuric chloride with sodium dicyanamide (1:3 ratio) in acetone-water (80:20 ratio) mixture at 50 to 60°C for one hour (Scheme 1). The compound **1** was obtained in 79% yield as a white powder that was insoluble in water and common organic solvents. The mid-IR spectrum of the compound **1** showed a band at 2190 cm⁻¹ corresponding to the stretching vibration of the CN groups. The peaks at 1630–1650, 1380 and 1460 cm⁻¹ were related to the triazine ring stretching frequencies (Figure S1 in Supplementary Information). Further, the structure of **1** was confirmed by solid-state ¹³C NMR, elemental analysis, LCMS, and HRMS. The dried, powdered **1** was used in the reaction to synthesize compound **2**.

The attractive syntheses of novel energetic products include a broad range of neutral molecules and salts of tetrazole due to their high nitrogen content (~80%), the high positive heat of formation (320 kJ/mol), low sensitivity towards impact and excellent thermal stability that results from the aromatic ring system. The introduction of multiple heterocyclic rings within a single cation has been proved to possess promising energetic properties.⁹ The reaction of **1** with sodium azide and zinc bromide in deionized water at the reflux (oil bath temperature of 140°C) for 24 h resulted in the formation of compound **2** (Scheme 1).^{14,15} The crude product **2** was obtained as a precipitate, which was isolated by filtration. The compound **2** was characterized using FTIR and NMR spectral data.

In the FTIR spectrum, the stretching vibration of dicyanamide ion disappeared, and new peaks related to tetrazole was observed at 795, 1081, 1460, 1617, 3103, 3277, and 3423 cm⁻¹ (Figure S2 in Supplementary Information). The ¹³C NMR spectrum (Figure S3 in SI) showed two peaks at 156.34 ppm and 165.82 ppm corresponding to tetrazole and triazine rings; in ¹H NMR signal (Figure S4 in SI) at the 7.31 ppm indicates the presence of N-H of tetrazole. Also, the product was characterized by the elemental analysis, LCMS, and HRMS. Though many compounds were known with tetrazole groups, this is the first example of a compound having



Scheme 1. Synthesis of compounds **1** and **2**.

Table 1. Energetic properties of compounds **1** and **2**.

Compound	MF	NC %	OB %	D	HOF	VOD	DP	IS	FS
1	C ₉ N ₁₂	61	-104	1.62	1314.4	6.18	15.87	>50	>360
2	C ₉ H ₆ N ₃₀	79	-63	1.88	1833.0	7.43	25.11	>50	>360
RDX	C ₃ H ₆ N ₆ O ₆	38	-21.6	1.80	83.82	8.75	33.8	7.4	>120
HMX	C ₄ H ₈ N ₈ O ₈	38	-21.6	1.90	104.77	9.10	39.0	7.4	>112
TNT	C ₇ H ₅ N ₃ O ₆	19	-74.0	1.65	-54.39	6.90	19.0	15	>353

MF: Molecular Formula, NC: Nitrogen Content. OB: Oxygen Balance, D: Density in (g cm^{-3}), HOF: Heat of formation in the solid phase (kJ mol^{-1}), VOD: Velocity of Detonation (km s^{-1}), DP: Detonation Pressure (Gpa), IS: Impact Sensitivity (J), FS: Friction Sensitivity (N). (Data for RDX, HMX and TNT are taken from the literature).^{22c,d,e}

six tetrazole rings in a single molecule constructed on triazine ring.

All the DFT calculations were performed using Gaussian 09 program package.¹⁶ The geometries of **1** and **2** were optimized at the B3PW91 level with 6-31G(d,p) basis set. The computational methods used were similar to our previous reports.¹⁷ The gas phase HOF was predicted using isodesmic reactions while Politzer approach¹⁸ was used to compute heat of sublimation. The resultant heat of sublimation was deducted from the gas phase HOF to obtain solid phase HOF of **1** and **2**. The solid phase HOFs of **1** and **2** were 1314 and 1833 kJ mol^{-1} , respectively. These high positive HOFs attributed to more number of C–N and N–N bonds present in their structures. The compound **2** could be used as enthalpy enhancer due to the high HOF. The molecular surface properties were calculated via the Multiwfn program¹⁹ and used to predict the densities.²⁰ Compound **2** showed superior density (1.88 g cm^{-3}) to RDX (1.80 g cm^{-3}) while **1** showed density of 1.62 g cm^{-3} . The detonation velocity (VOD in km s^{-1}) and detonation pressure (DP in GPa) were computed using Kamlet-Jacobs empirical equations.²¹ The VOD (7.43 km s^{-1}) and DP (25.11 GPa) of **2** are found to be higher than those of TNT (VOD = 6.90 km s^{-1} , DP = 19.0 GPa).

The performance and safety characteristics of molecules need to be evaluated for safe handling of compounds. Impact and friction sensitivity are more important characteristics in the manufacturing context. Therefore, the impact and friction sensitivities of the

compound **2** were measured using the standard BAM fall hammer, and BAM friction techniques (Table 1).²² The impact sensitivity of compounds **1** and **2** was above 50 J while the friction sensitivity of compounds **1** and **2** was >360 N. This sensitivity data revealed that the compound **2** was an insensitive material and much less sensitive than TNT, RDX and HMX. Thermal stability is an essential parameter for any explosive in processing and storage, which need explosives that can withstand high temperatures. For common usage, a component explosive must be stable above 200°C . As observed in the thermogravimetric analyses (Figures S5 and S6 in Supplementary Information), the compounds **1** and **2** with a decomposition onset of 300°C certainly exceed this requirement.

4. Conclusions

In summary, the molecule, 2,4,6-tris[bis(1H-tetrazol-5-yl)amino]-1,3,5-triazine (**2**) having 79% nitrogen content was synthesized from cyanuric chloride in a two-step process with a 58% yield. Its structure was confirmed using spectroscopic methods, including FTIR and NMR spectroscopy (^1H and ^{13}C), elemental analysis, and HRMS. The high positive HOF values of **1** and **2** showed that these compounds could be potential enthalpy enhancers in energetic formulations. The high nitrogen content associated with high positive heat of formation of the compound **2** underlines the structural importance of six tetrazole groups in a molecule.

According to the data, these compounds are possible energetic materials; however, an extensive performance evaluation needs to be carried out to prove their usage in the Science and Technology of Propellants.

Supplementary Information (SI)

Electronic Supplementary Information (ESI) available are FT-IR, NMR spectra, TGDTA curves and computational details of compounds [1] and [2]. Supplementary Information is available at www.ias.ac.in/chemsci.

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