3-Nitro, 1-Amino Guanidine and 5-Hydrazino-1*H*-Tetrazole Derivatives as New Energetic Materials

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ABSTRACT: *The synthesis of 3-amino-1-nitroguanidine (3-ANQ) and 5-hydrazino tetrazole (5-HT) derivatives as new energetic materials are described. Reaction of 3-ANQ with triethyl orthoformate leads to the formation of 3-nitramino triazole while no reaction was observed whit 5-HT. Addition of NaN_3 to a mixture of 3-ANQ and triethyl orthoformate, afforded 1-nitroguanidyl tetrazole in excellent yield. On the other hand, these compounds showed different reactivity toward dicyandiamide. Cyclization of 5-HT with dicyandiamide in EtOH/Water reflux caused formation of 3,5-Diamino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole in good yield, nitration of which afforded 3,5-Dinitramino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole as a potentially new high energetic molecule. No reaction was observed between 3-ANQ and dicyandiamide. The reaction of 3-ANQ and 5-HT were exanimated with trichloro triazine (TCT). 5-HT gave mixture of products while no reaction between 3-ANQ and TCT was detected. Unusual hydrazone condensation was observed between 3-ANQ and acetone, when acetone/water mixture used as solvent at 0 °C.*

KEY WORDS: *Energetic materials, Nitrogen-rich compounds, Amino guanidine, Tetrazole, Triazine, Triazole.*

INTRODUCTION

In our modern life, nitrogen rich compounds are playing undeniable role. They have wide utility in drug development and biomedicine [1], fertilizers, materials [2], gas generators [3] and energetic materials in explosives, pyrotechnics and propellants [4]. During the recent years, many research groups have focused on synthesis and development of new nitrogen rich compounds as energetic materials [5, 6]. In the new energetic material area, the main challenge is to overcome some disadvantages of traditional explosives. For example, widely used RDX is toxic and it is harmful for humans and aquatic organism. On the other hand, new designed compounds must fulfill various factors to be introduced into technical applications. First of all, it should at least exceed the detonation power of TNT and be close to RDX. Low solubility in water, insensitivity, thermal and chemical stability, non-toxicity and low price are the characteristics that are also desired [7]. Among new designed energetic compounds, there is a great interest toward nitrogen rich heterocyclic molecules

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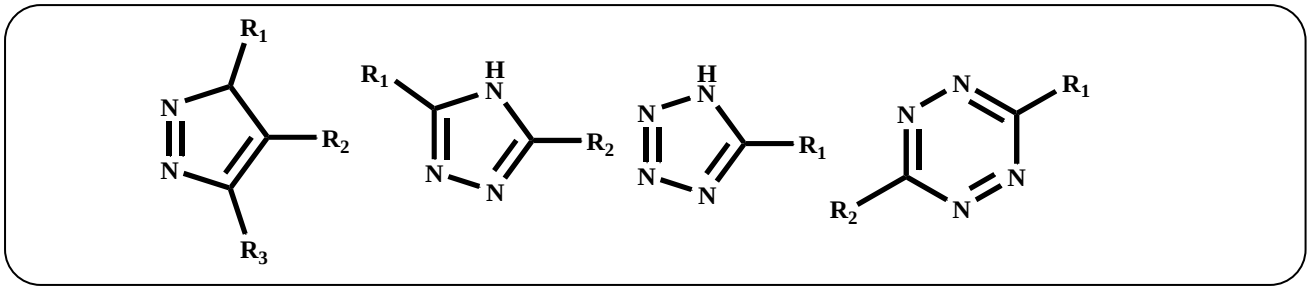


Fig. 1: Hydrazine based heterocyclics.

and their salts due to their rather large densities, good oxygen balance, insensitivity and high heats of reaction compared to non-heterocyclic explosives. Moreover, kinetic and thermodynamic stability beside easy modification have made *N*-Heterocycles, especially five and six membered rings as interesting candidate for design and synthesis of new energetic compounds. During last decade, plenty of energetic molecules with azole skeleton have been synthesized and studied. Incorporation of energetic moiety e.g. nitro, azido, hydrazino and *N*-oxide also has expanded diversity of azole energetic salts [8]. A number of methods for the synthesis of pyrazols, imidazoles, triazoles and tetrazole are known [9]. Hydrazine and hydrazine containing molecules are one of the most important tools for the synthesis of pyrazole, triazole, tetrazole and tetrazine (Fig. 1). 5-hydrazino 1*H*-tetrazole (5-HT) and 3-amino-1-nitroguandine (3-ANQ) are energetic nitrogen rich compounds both having hydrazine moiety in their structure. 3-ANQ which is synthesized from commercial available nitroguanidine has been known for a long time and in energetic compounds [10]. It has been used widely as cation moiety in nitrogen rich salts [11] and recently its transition metal complexes as laser ignitable primary explosive has been studied [12]. 5-HT which is prepared from 5-amino tetrazole; has been used as ligand for preparation of metal based primary explosives [13] and more recently its energetic salts with oxygen rich anion has been prepared where these salts show promising detonation parameters [14]. In this study we present new methods for synthesis of new energetic compounds through reaction of hydrazine moiety of 3-ANQ and 5-HT.

EXPERIMENTAL SECTION

Caution

Most compounds used and prepared herein are energetic compounds, sensitive towards impact, friction, and electric discharge. Although we had no problems working the compounds, extreme care and proper safety protection should be used.

General Methods

All chemical was purchased from Merck and Aldrich companies and used without purification. 3-Amino-1-nitroguandine was prepared from nitroguanidine according to literature [12]. ^{1}H, ^{13}C spectra were recorded on a 400 MHz (Bruker 400) NMR spectrometer by using DMSO-d6 as solvent. The melting and decomposition points were obtained on a Differential Scanning Calorimeter (1/700 Mettler Toledo) at a scan rate of 10 °C/ min, respectively. Mass spectra were recorded by Agilent Technology (HP). Elemental analysis was performed by Leco-Chns truspec. IR spectra were recorded using KBr pellets for solids by ABB Bomem mb-100 spectrometer.

3,5-Diamino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole (1)

5-Hydrazino tetrazole hydrochloride 138 mg (1mol) and 100mg (1.2 mmol) dicyandiamide was refluxed for 2 hours in 5 mL 1:1 EtOH and H_2O. The white solid was collected by filtration and washed by EtOH. Drying in the air yield 125 mg (75%) desired product. m.p = 340 °C (DSC) (Fig. 2). IR (KBr): 3460, 3381, 3135, 2312, 1681, 1644, 1581 cm^{-1}. ^{1}H NMR (400 MHz, (DMSO-d6)) (Fig. 3): δ = 7.28 (s, 1H), 5.61(broad, 2H), 4.81(broad, 2H), ^{13}C NMR (100 MHz, (DMSO-d6)) (Fig. 4): 163.1, 155.0, 151.5. MS m/z: 167 $(C_3H_5N_9)^+$, 99, 69 (Fig. 5). Elemental analysis for $C_3H_5N_9$ (MW= 167 g/mol) calculated.C, 21.86; H, 3.02; N, 75.34; found, C, 22.34; H, 3.12; N, 74.68.

3,5-Dinitramino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole (2)

In a 5 ml bottom round flask, 200 mg HNO_3 (99.8%) was poured in 2 mL sulfuric acid in ice bath and cooled to 0 °C. 3,5-Diamino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole

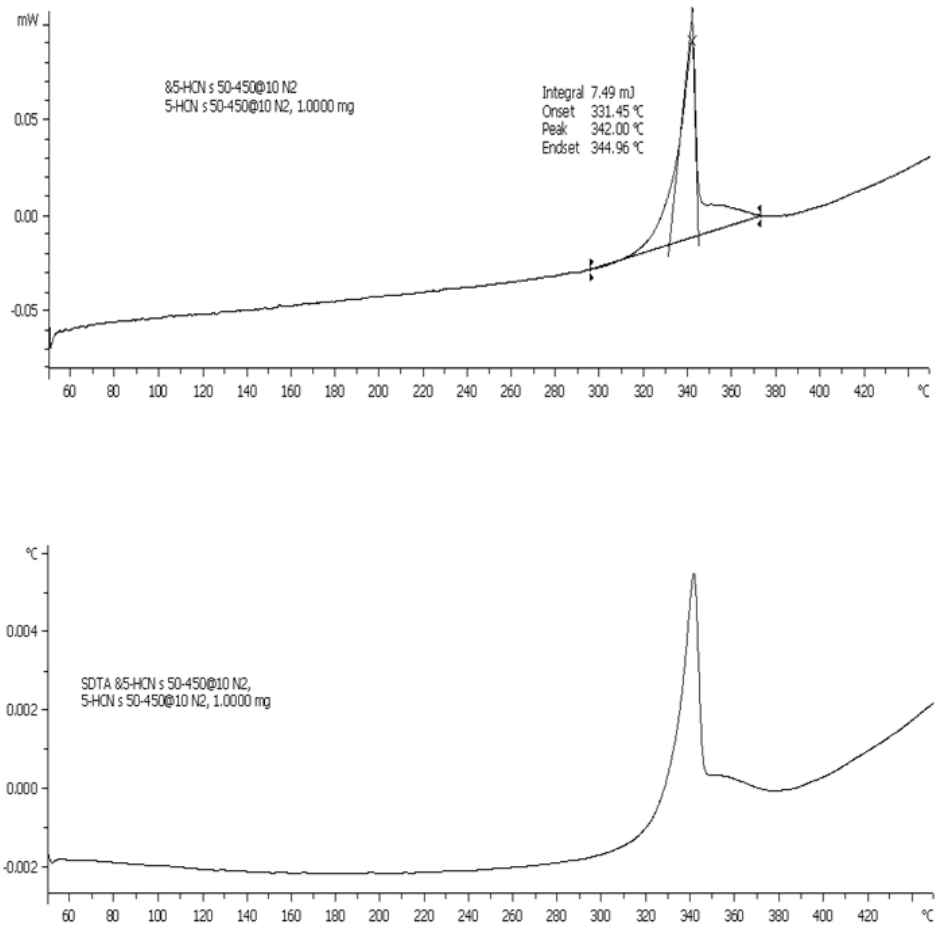


Fig. 2: DSC analysis of compound 1.

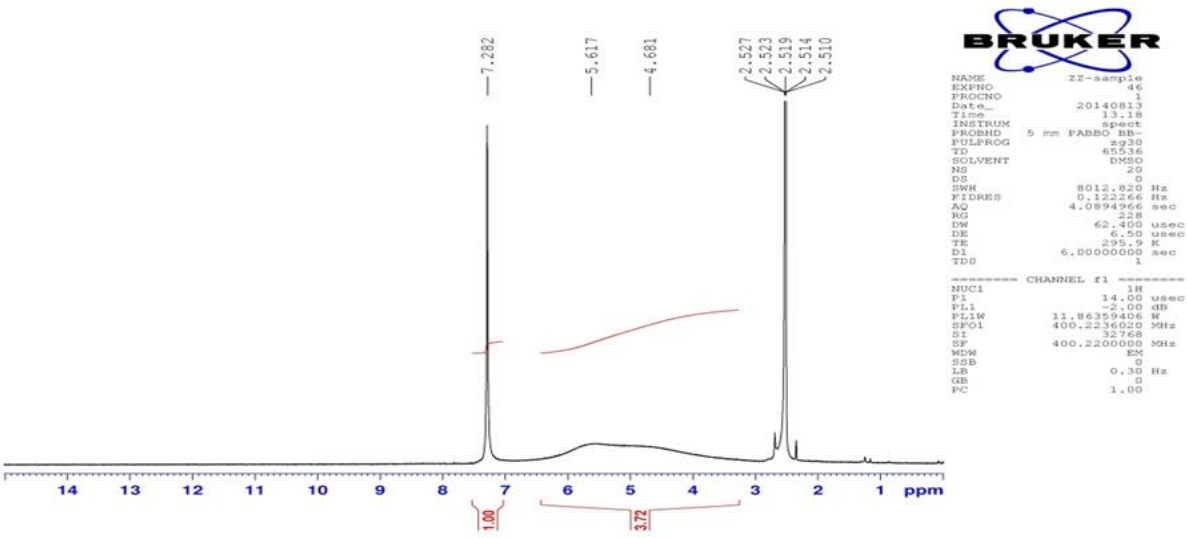


Fig. 3: ^{1}H NMR spectra of compound 1.

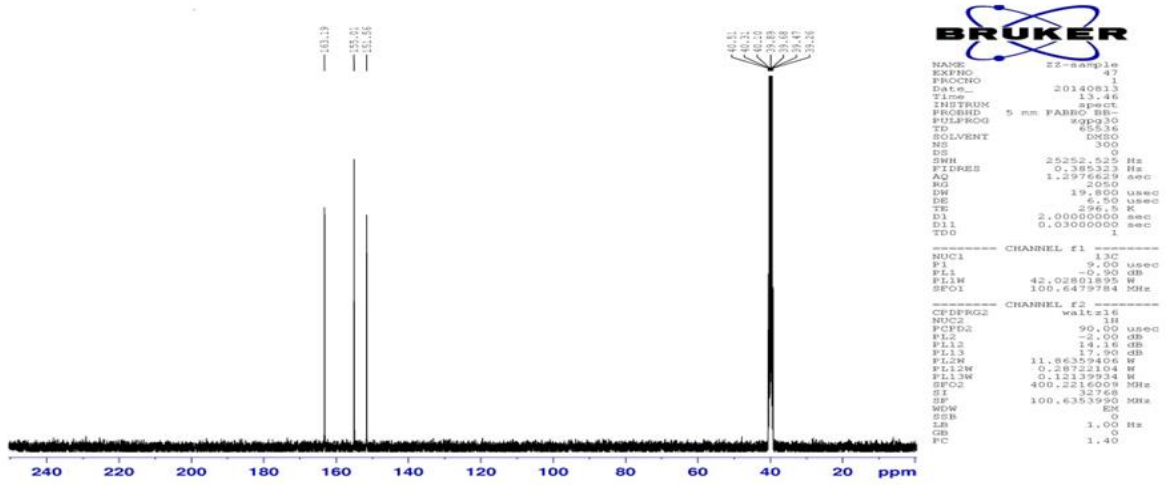


Fig. 4: ^{13}C NMR spectra of compound 1.

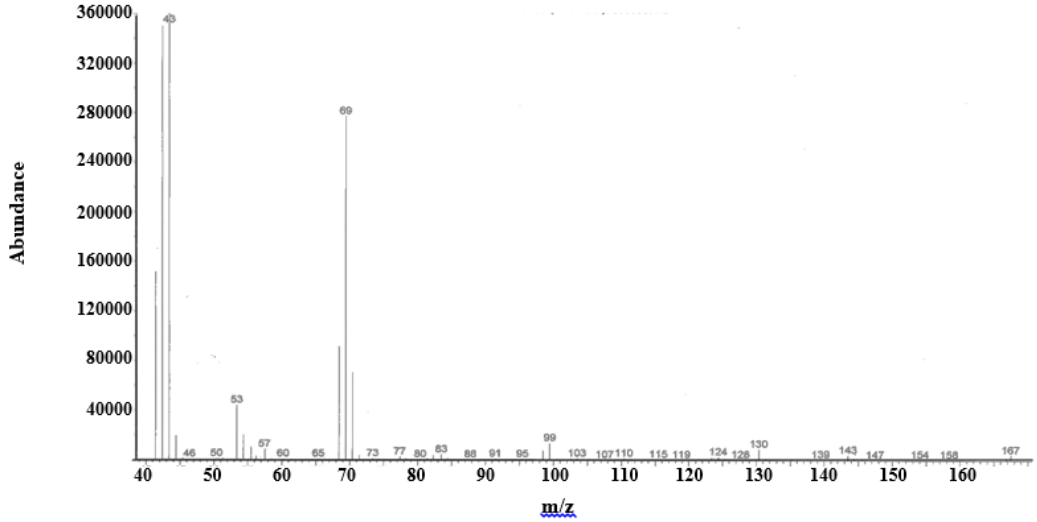


Fig. 5: Mass spectra of compound 1.

167 mg (1 mmol) was added in small portions to the acid mixture and was stirred for 1 h in 0 °C. The reaction mixture was warmed to room temperature slowly and stirred for additional 1 h. the homogeneous yellow solution was poured in 10 gr crashed ice. The yellow solid was collected by filtration and washed with cold ethanol and dried in air. Yield 208 mg, 81%, m.p 192 °C (DSC) (Fig. 6). IR (KBr): 3339, 3290, 3102, 2968, 1691, 1604, 1403 cm^{-1}. ^1H NMR (400 MHz, (DMSO-d6)) (Fig. 7): 6.8-10.5 (broad, 2 H), 7.68(s, 1H). ^{13}C NMR (100 MHz, (DMSO-d6)) (Fig. 8): 155.8, 154.1, 152.9. MS m/z: 257 $(C_3H_3N_{11}O_4)^+$ (Fig. 9). Elemental analysis for $C_3H_3N_{11}O_4$ (MW= 257 g/mol) C, 14.01; H, 1.18; N, 59.92; found C, 14.86; H, 1.31; N, 58.89.

3-Nitramino 1,2,4-triazole (3)

120 mg (1mmol), 3-amino-1-nitroguanidine and 1.4 mL (10 mmol), triethyl orthoformate was refluxed in 5 mL glacial acetic acid for 2 hours. The volume of the reaction was reduced to 1 ml by evaporation of solvent in vacuum. The reaction mixture cooled to room temperature. The light yellow crystals obtained, filtered and washed with cold ethanol and dried in air to yield a light yellow powder. (Yield 118 mg, 91%). m.p 201°C (DSC) (Fig. 10). MS m/z: $129(C_2H_3N_5O_2)^+$, $83(C_2H_3N_5)^+$, 54, 46,42. FT-IR (KBr): 3384, 3273, 3088, 1678, 1644, 1627, 1514, 1279, 1193 cm^{-1}. Elemental analysis for $C_2H_3N_5O_2$ (MW= 129 g/mol) C, 18.61; H, 2.34; N, 54.26; found C, 18.92; H, 2.43; N, 53.95.

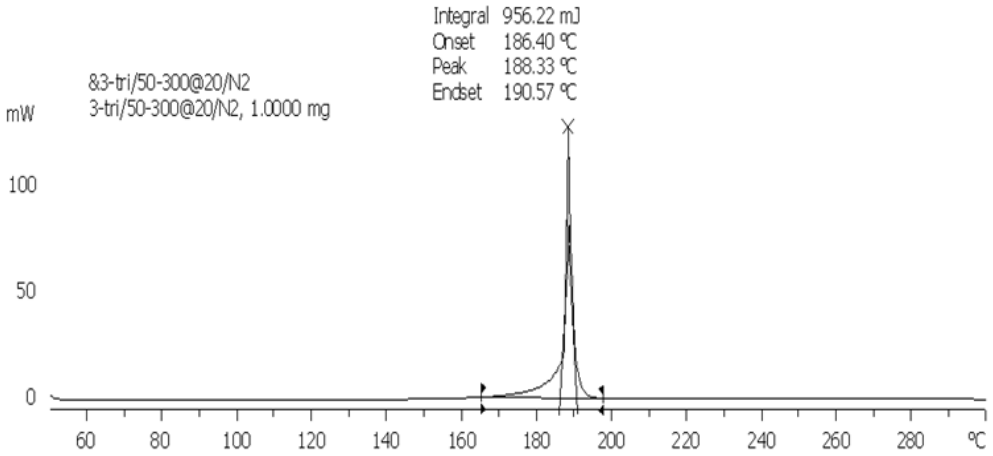


Fig. 6: DSC analysis of compound 2.

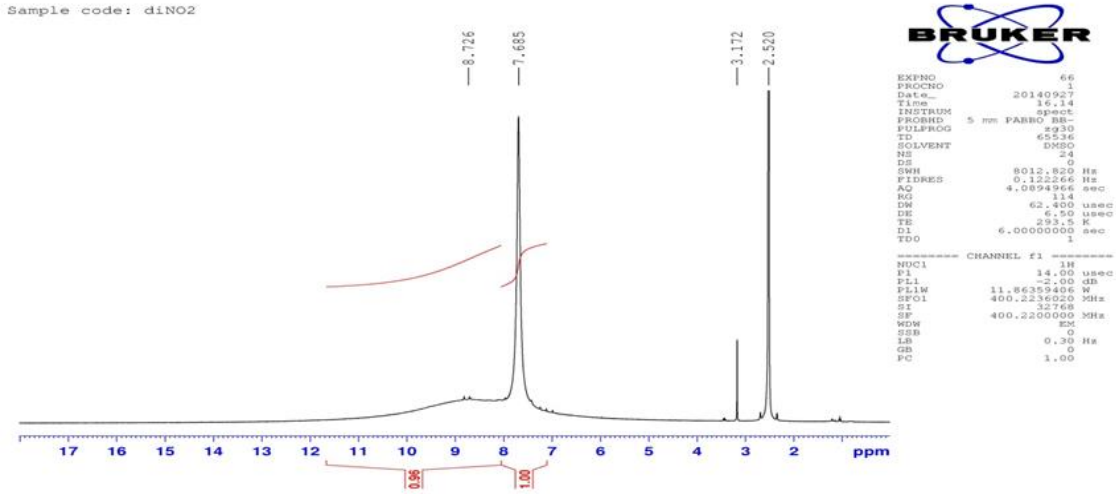


Fig. 7: ^{1}H NMR spectra of compound 2.

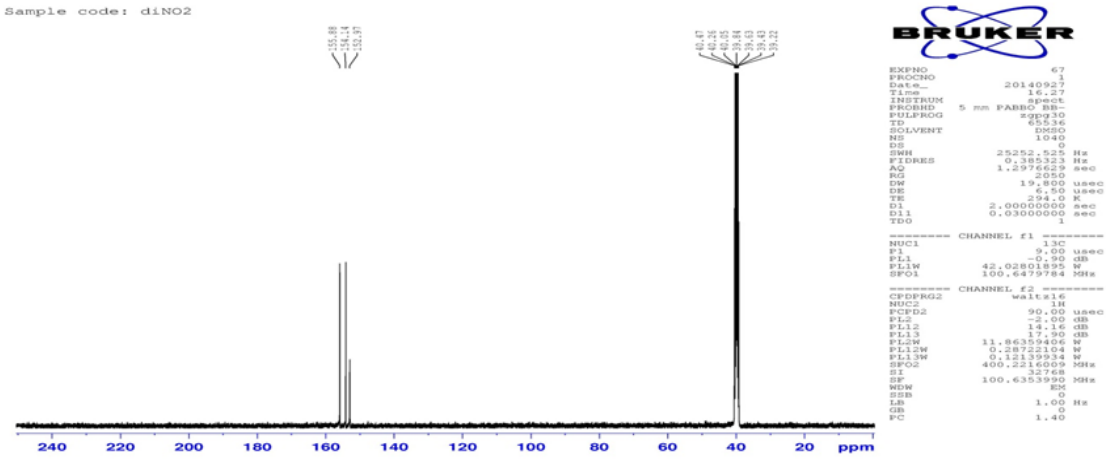


Fig. 8: ^{13}C NMR spectra of compound 2.

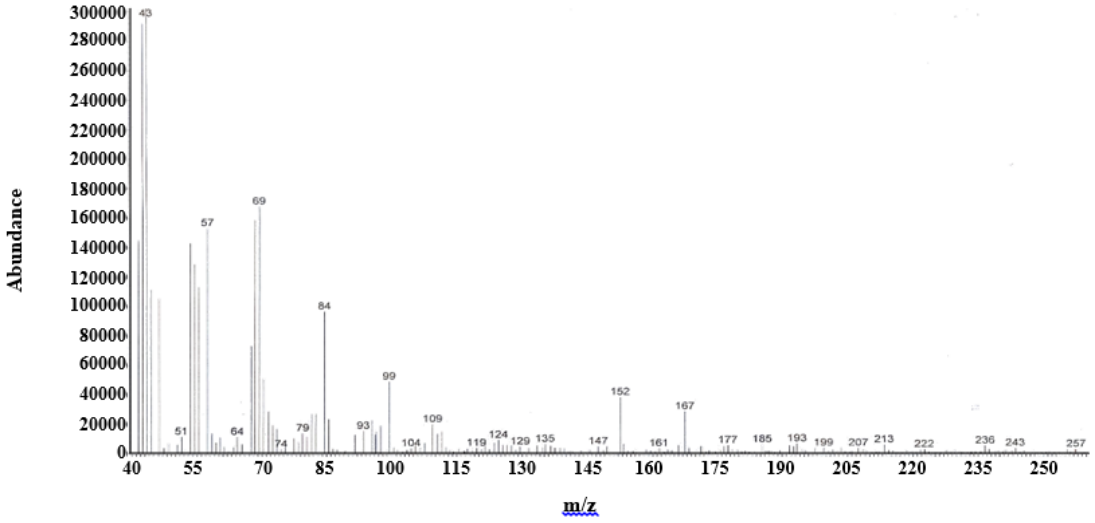


Fig. 9: Mass spectra of compound 2.

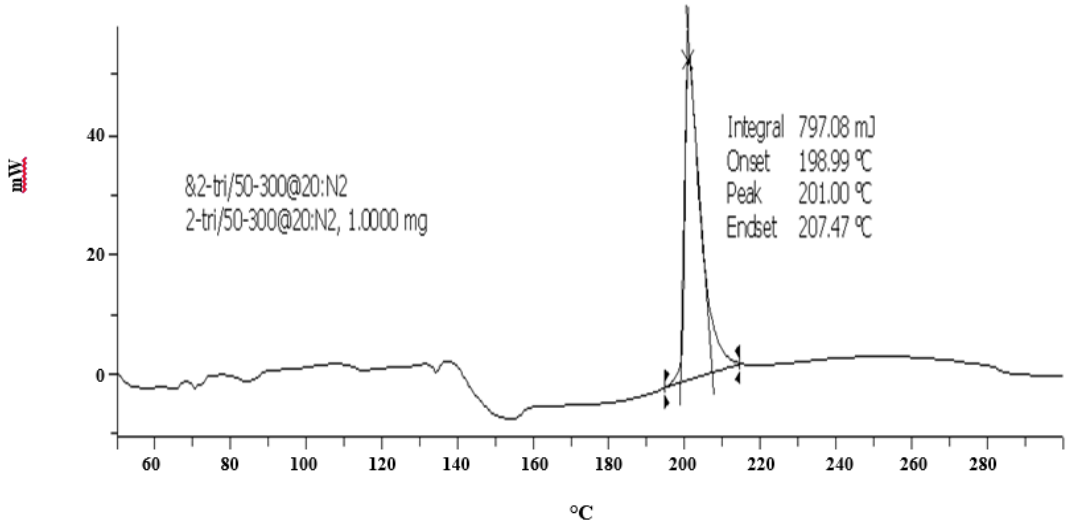


Fig. 10: DSC analysis of compound 3.

N-Acetyl-3-amino-1-nitroguandine (4)

3-Amino-1-nitroguanidine (2 mmol) was refluxed in glacial acetic acid for 1h. Evaporation of the solvent in vacuum yield compound 4 as white solid. m.p 169 °C. ^{1}H NMR (400 MHz, (DMSO-d6)) (Fig. 11): 9.89 (broad, 1H), 9.61 (broad, 1H), 8.63 (broad, 1H), 8.05 (broad, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, (DMSO-d6)) (Fig. 12): 170.0, 161.6, 22.3. Elemental analysis for $C_3H_7N_5O_3$ (MW= 161 gr/mol) calculated C, 22.36; H, 4.38; N, 43.47. Found C, 23.16; H, 4.18; N, 42.91.

1-Nitroguanidyltetrazole (5)

To the mixture of 5 mmol, 600 mg 3-amino-1-nitroguanidine, 6 mmol sodium azide and 8 mmol triethylorthofrmate was added 5 mL glacial acetic acid drop wise in 30 min and reaction mixture was refluxed for 2 h. After cooling to room temperature, the yellow solid was filtered, washed with EtOH and dried in air to yield 790 mg (92%) 1-nitroguanidyltetrazole. Recrystallization from water and ethanol gave very pure yellow crystals. Decomposition point = 221 °C (DSC) (Fig. 13).

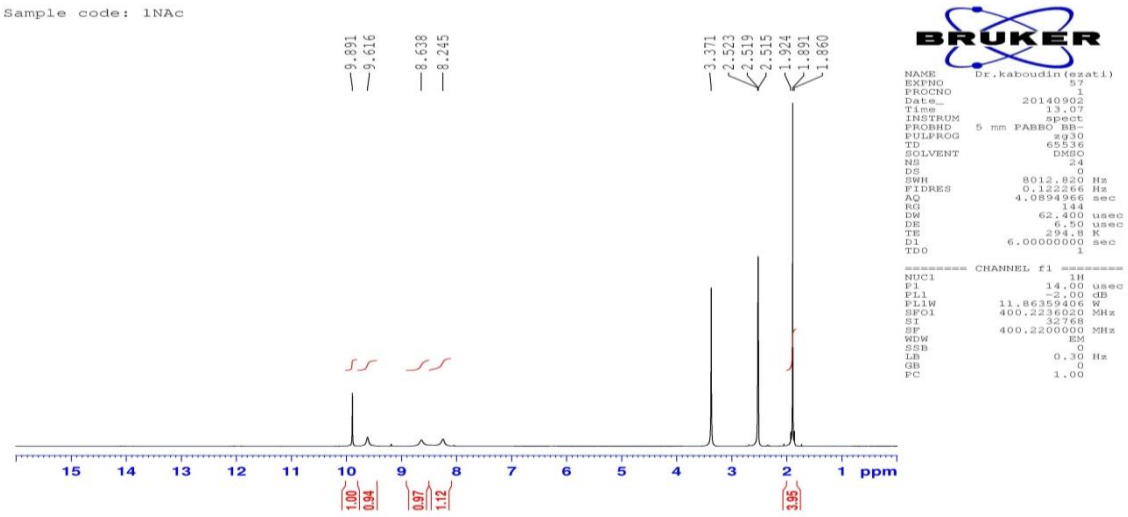


Fig. 11: A NMR spectra of compound 4.

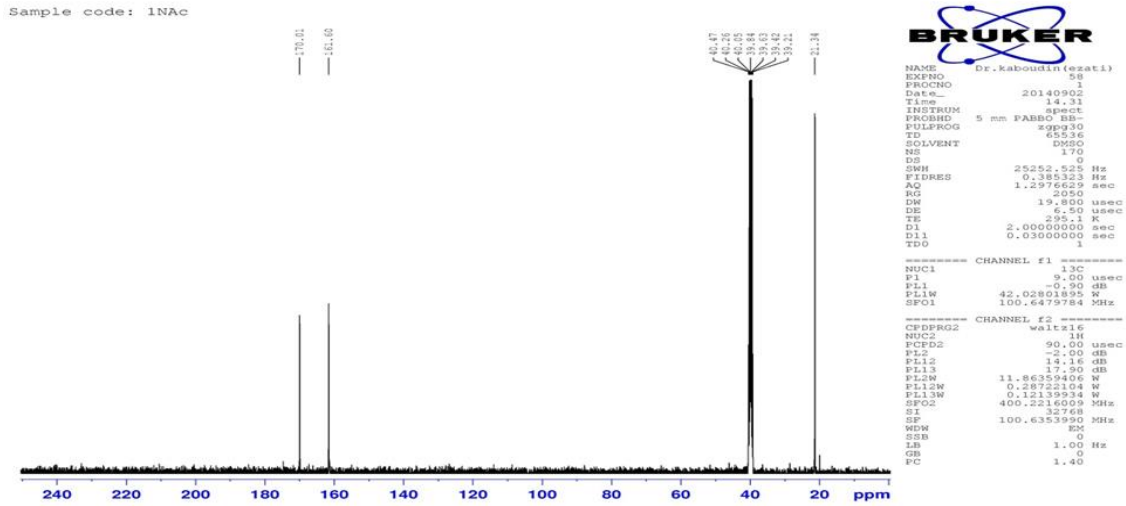


Fig. 12: ^{13}C NMR spectra of compound 4.

IR (KBr): 3266, 3153, 2064, 1562, 1542, 14466 cm^{-1}. ^{1}H NMR (400 MHz, (DMSO-d6)) (Fig. 14): 13.93(broad, 2H), 8.50 (s, 1H), 7.38 (broad, 1H). ^{13}C NMR (100 MHz, (DMSO-d6)) (Fig. 15): 152.5, 139. MS m/z (Fig. 16): 172 $(C_2H_5N_8O_2)^+$, 162, 100, 85. Elemental analysis for $C_2H_5N_8O_2$ (MW= 172 gr/mol) C, 13.96; H, 2.34; N, 65.11; found C, 14.12; H, 2.55; N, 64.77.

3-(Isopropylidene hydrazono) nitroguandine (6)

Trichlorotriazine 184 mg (1mmol) and 3-amino-1-nitroguandine 360 mg (3 mmol) was added to previously cool 1:1 mixture of acetone and water in ice bath. To this mixture, 250 mg $NaHCO_3$ was added in small portions. Large amount of bubbles was observed and reaction mixture turned to yellow. The reaction mixture was stirred in 0 °C for 1 h, then slowly warmed to r.t and stirred for additional 1h. The reaction flask was put in refrigerator overnight. Compound 6 was crystallized as light yellow crystals which was separated by filtration and washed with cold ethanol. Drying in air, yield 205 mg (65%) compound 6, m.p 181°C . ^{1}H NMR (400 MHz, (DMSO-d6)) (Fig. 17): 10.77 (broad, 1H), 8.65 (broad, 1H), 8.01 (broad, 1H), 2.02 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, (DMSO-d6)) (Fig. 18): 158.6, 57.3,

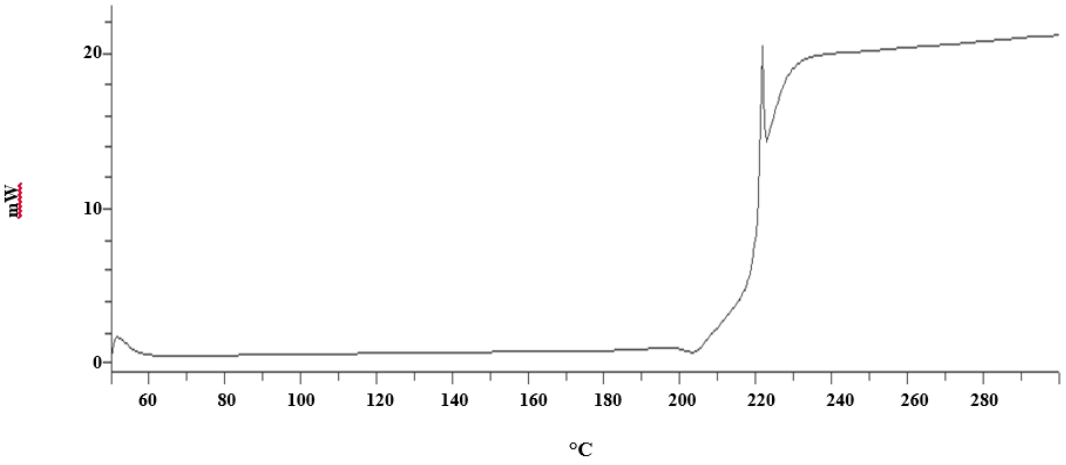


Fig. 13: DSC analysis of compound 5.

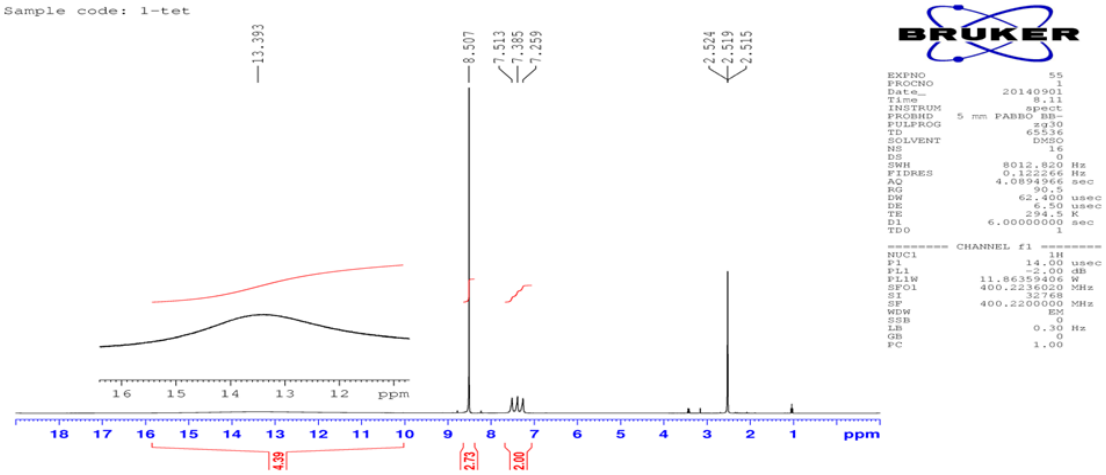


Fig. 14: ^{1}H NMR spectra of compound 5.

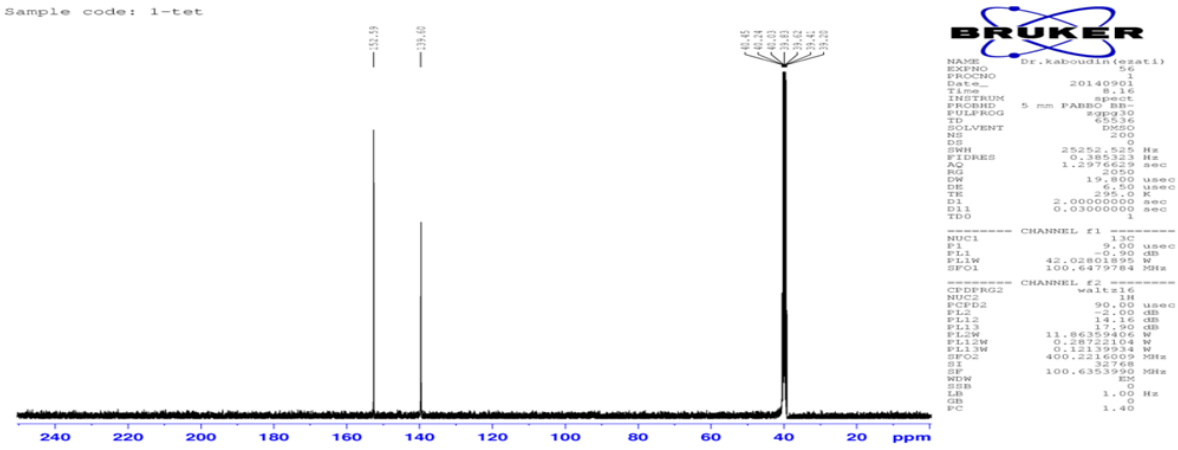


Fig. 15: ^{13}C NMR spectra of compound 5.

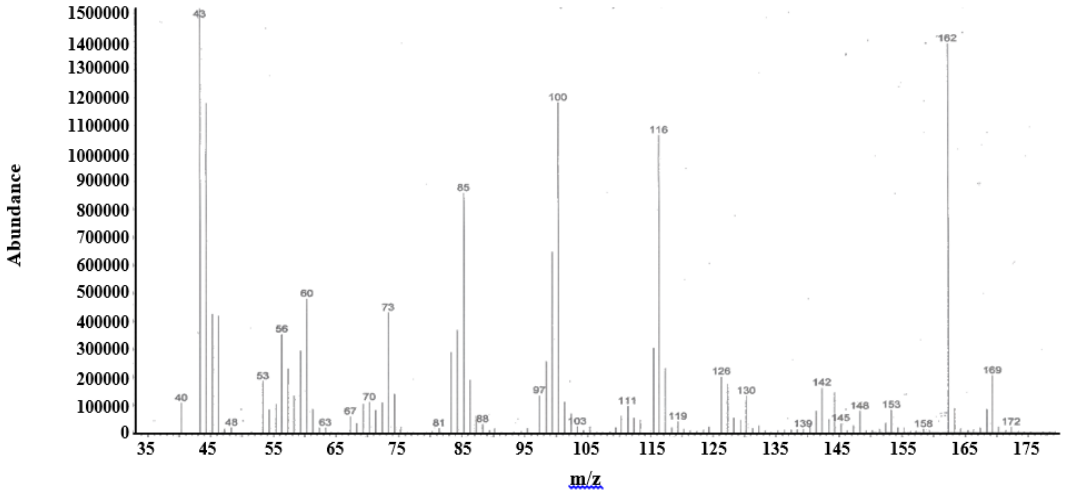


Fig. 16: Mass spectra of compound 5.

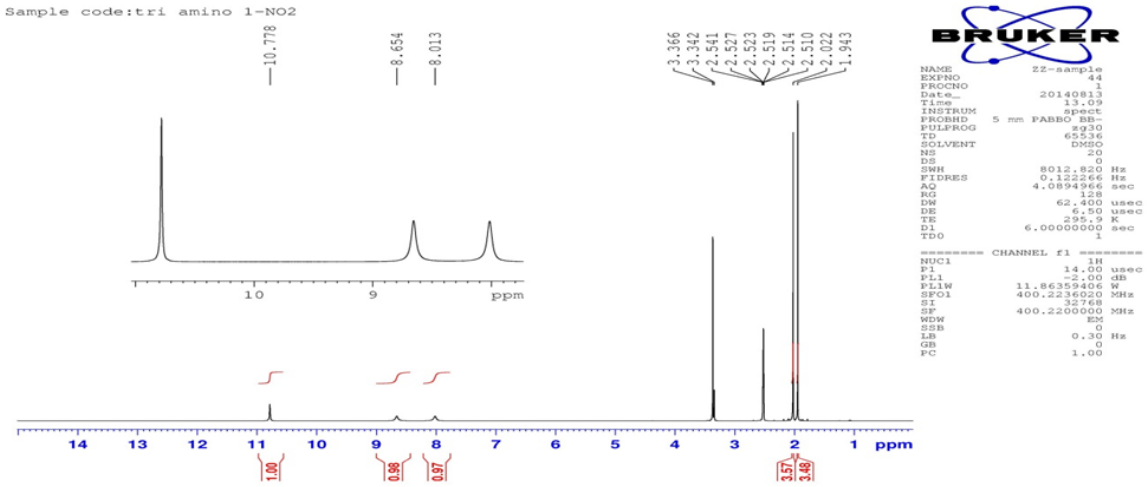


Fig. 17: ^{1}H NMR spectra of compound 6..

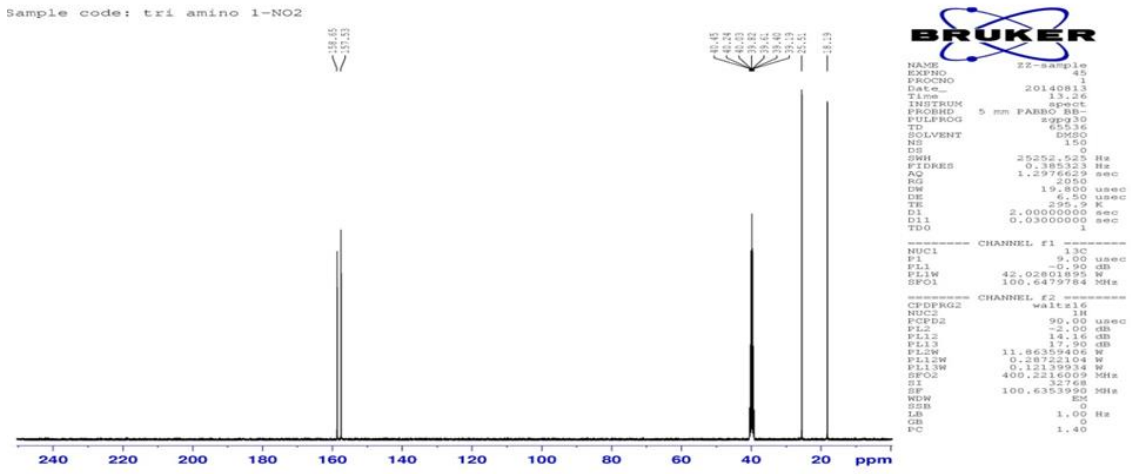


Fig. 18: ^{13}C NMR spectra of compound 6.

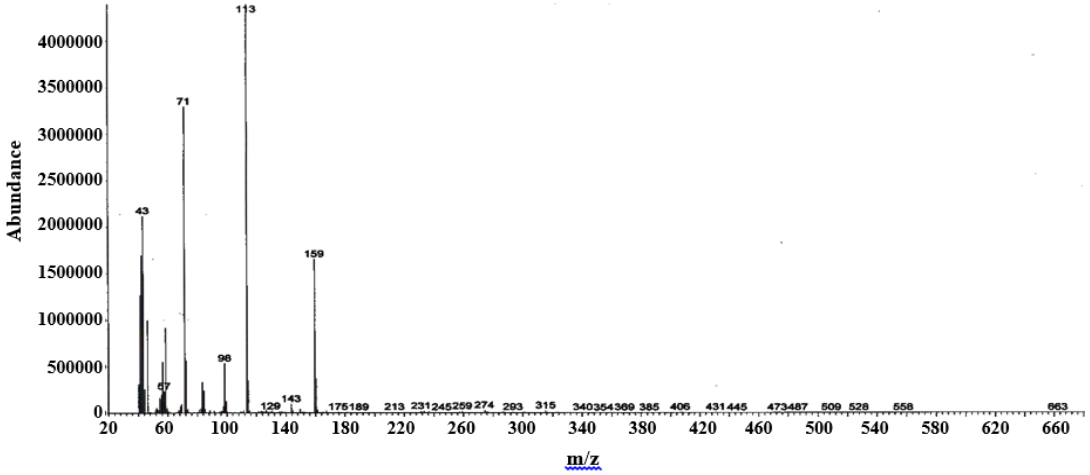


Fig. 19: Mass spectra of compound 6.

25.5, 18.1. MS m/z (Fig. 19): 159 $(C_4H_9N_5O_2)^+$, 113, 71. Elemental analysis for $C_4H_9N_5O_2$ (MW= 159 g/mol) calculated; C, 30.19; H, 5.70; N, 44.01; found C, 31.12; H, 5.92; N, 43.50.

RESULTS AND DISCUSSION

Reaction with dicyandiamide

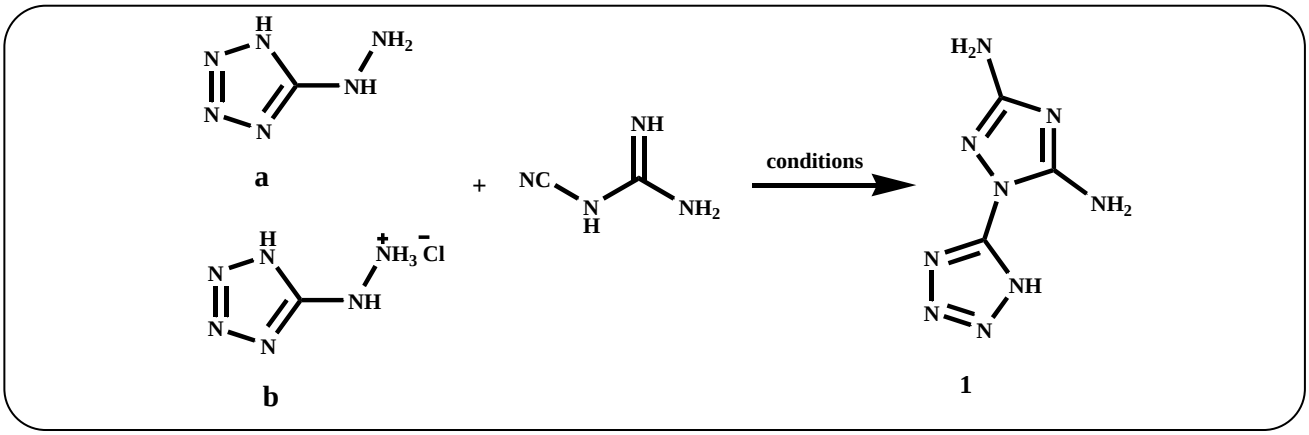
Reaction of hydrazine and dicyandiamide is a well-known process for preparation of 3,5-diamino-1,2,4-triazole which has wide application in medicinal chemistry [15] and energetic materials [16]. Dicyandiamide (DCDA) is a 1,3-bielectrophiles, so hydrazine containing compounds could react with DCDA to produce 3,5-diamino-1,2,4-triazole derivatives. So far, reaction of thiosemicarbazide and 2-hydrazino thiazole [17], semicarbazide and aminoguanidine [18] with DCDA has been reported. Although, 3-amino-1-nitroguanidine has been known for a long time and its reaction with DCDA could produce an interesting nitrogen-rich compound, but surprisingly, this reaction has not been reported in literature. To evaluate this reaction in details, in the first step, 3-ANQ and DCDA was refluxed in water according to similar literature method [17]. After 5 h, TLC analysis of the reaction mixture indicated no reaction. Repetition of the reaction in 5% HCl solution gave several products and changing the solvent to EtOH, MeOH and glacial acetic acid was useless and only starting material was recovered. In the second step, we changed 3-ANQ with 5-hydrazino-1-H-tetrazole to synthesize compound **1**. Nevertheless, this compound has been prepared by *Shreeve et al.* previously, but therein cyanogen azide has been used as a reagent which is extremely dangerous and toxic [19]. So finding an alternative way to synthesize compound **1** could be useful. This reaction was performed with 5-hydrazino tetrazole and its hydrochloride salt in different solvent (Scheme 1). The yield and progress of the reaction were strongly depended on the exerted condition. The results are summarized in Table 1. As shown in Table 1, 5-hydrazino tetrazole is quite inactive toward DCDA which may be due to electron withdrawing effect of the tetrazole ring. 5-HT.HCl, on the other hand, reacts readily with DCDA, 5-hydrazino tetrazole gave same results when the reaction was performed in dilute HCl solution.

The amino groups, decrease detonation performance of energetic molecules [15], but are powerful tools for incorporation of energetic group like azido, nitro and nitramino group which has been utilized in large number of modern energetic compounds. 1-(Tetrazole-5-yl)-3,5-diamino-1,2,4-triazole by having two amino groups and blocked 1-position seems to be a good candidate for synthesis of new energetic compounds and corresponding salts. Numerous Energetic salts based on nitramino, nitro and azido 1,2,4-triazole has been synthesized using commercially available 3,5-diamino1,2,4-triazole and their detonation properties have been studied [16]. To obtain new energetic derivative based on 1,2,4-triazole, transformation of amino group in compound **1** to nitro and nitramino groups were studied according to known literature methods.

Nitration of compound 2 was accomplished with slight modification as it is described for 3-amino-1*H*-1,2,4-triazole

Table 1: The yield of compound 1 in various conditions.

	EtOH	Water	H_2O/EtOH
1	0	0	0
2	0	55	75



Scheme 1: Preparing compound 1 from reactants.

in literature using a volume ratio H_2SO_4/HNO_3 of 6:1 and three equivalents of nitric acid per amino group [20]. A light yellow solid was precipitated, by pouring the nitration mixture on ice and the product was easily isolated by simple filtration (Scheme 2).

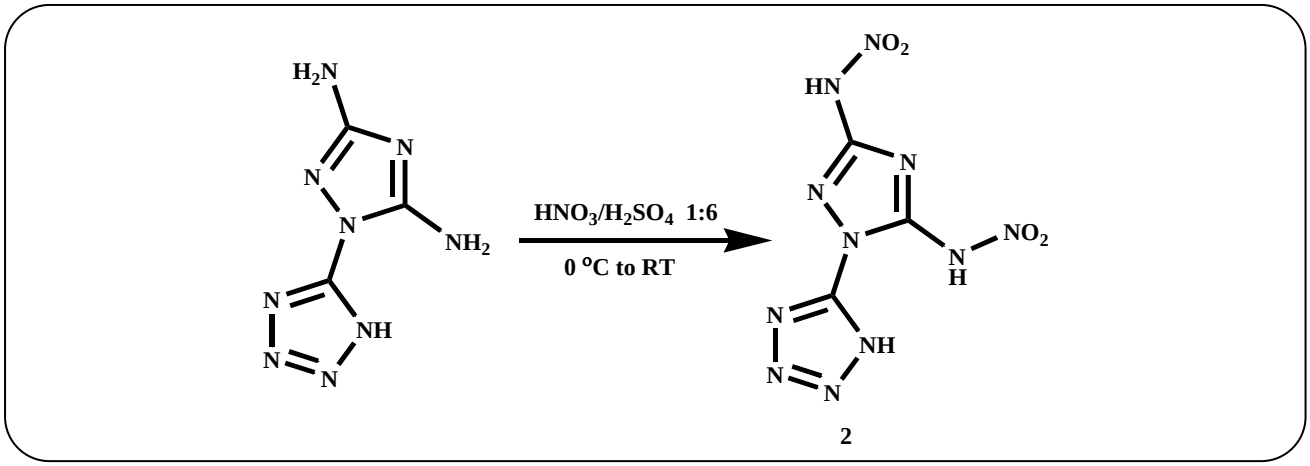
Multinuclear NMR and elemental analysis confirmed formation of desired product. By having three acidic protons, compound 4 is readily convertible to corresponding salts in reaction with mineral and organic bases.

Incorporation of nitro group on azole compound not only increase their oxygen balance and density but also has a positive effect on their detonation parameters. Due to poor activity of azole ring toward electrophilic substitution, nitroazoles are usually prepared from corresponding amines and via well-known diazotization reaction [8]. For the synthesis of dinitro derivative, compound **1** was put on in the same reaction condition for the preparation of 3,5-dinitro 1,2,4-triazole [21]. Two products were obtained in several reaction conditions, the work is in progress to optimize the reaction condition to obtain interesting dinitro derivative as the sole reaction product.

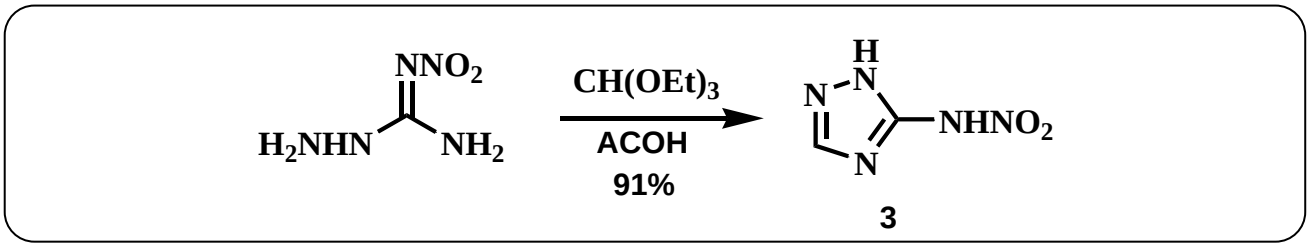
Reaction with triethylorthoformate

With three leaving group, triethyl orthoformate is a clean and active C-H group transfer and has been used extensively in organic synthesis. Reaction of triethylorthoformate with sodium azide and ammonium chloride lead to formation of tetrazole ring while condensation of amidrazone or amino guanidine derivatives with triethylorthoformate furnish corresponding triazole [22]. Reaction of aminoguanidine with triethylorthoformate is a facile way to synthesis 3-amino-1,2,4-triazole which could be converted to 3-nitrimino-1,2,4-triazole (3NAT) with reaction by HNO_3 (99.8%). This compound is one of the high density energetic materials and its salts have been synthesized and their detonation properties have been studied [23]. Condensation of triethylorthoformate and 3-nitro-1-amino guandine 3-ANQ; seems to be a practical alternative way to reach 3NAT without using very corrosive HNO_3 (99.8%). To testify this idea, reaction of ANQ with triethylorthoformate was investigated. When 3-ANQ was heated with excess of triethylorthoformate in 90 °C, no product was observed. The reaction was repeated in AcOH and triethylorthoformate 1:1 volume ratio. After 4 h heating in 90 °C and then cooling the reaction mixture to r.t, a slightly yellow crystal was precipitated from reaction solution (Scheme 3).

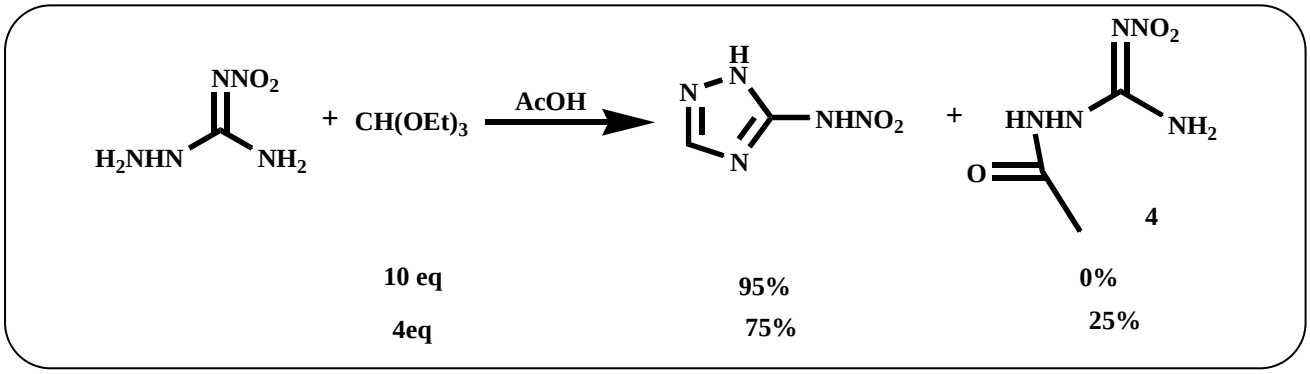
MS and DSC analysis confirmed formation of 3-NAT. The peak in 129 m/z clearly confirmed the formation of compound **3**, when losing a nitro group converts the M^+ ion to the stable 3-amino triazolium ion radical in 83 m/z (Fig. 20).



Scheme 2. Preparing route of compound 2.



Scheme 3: Preparing route of compound 3.



Scheme 4: Preparing route of compound 4.

W0hile optimization of orthoformate ratio to 3-ANQ, we noticed another product on TLC pattern when orthoformate amount is reduced to less than five eq. By omitting the orthoformate, the new compound was the sole product. Removing of AcOH gave a white crystal. Analysis of this new compound shows that 3-ANQ has been acylated in hydrazine moiety and compound **4** has been produced. It seems in low orthoformate ratio, acylation process plays a competitive reaction in elevated temperature (Scheme 4). It is worthy to note that compound **4** is unstable in refluxed AcOH and smoothly converts to another product.

Hydrazine group readily react with orthformate to produce an intermediate which can be reacted with second nucleophile [24]. In organic synthesis it is a known way to synthesize diazo furoxane from semicarbazide [25]. To evaluate reactivity of this intermediate toward an external nucleophile, we added sodium azide to a mixture of ANQ and triethyl orthoformate in glacial acetic acid (Scheme 5). Heating to 90 °C instantly precipitated yellow solid. After 1 h, the reaction mixture was cold to r.t and the solid was filtered. Elemental analysis and NMR spectroscopy

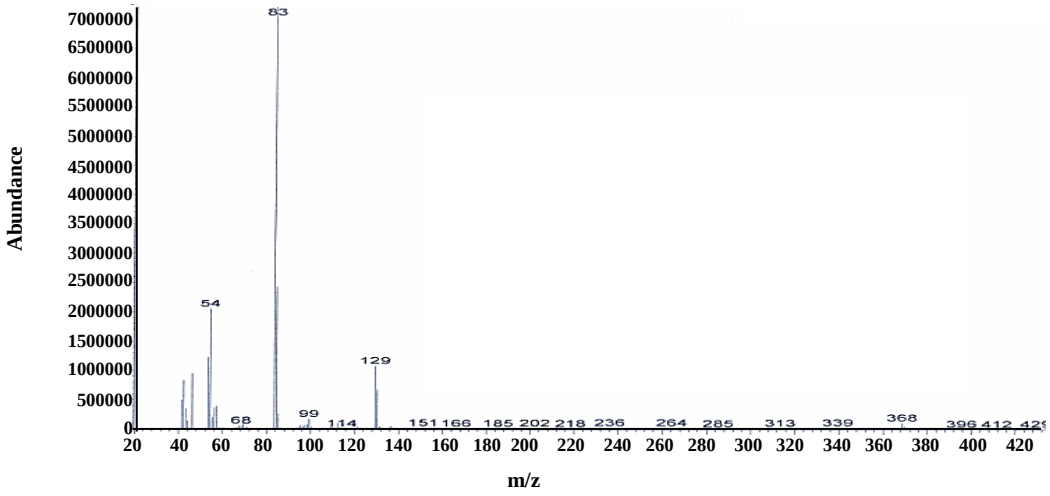


Fig. 20: Mass spectra of of 3-nitramino 1,2,4-triazole.

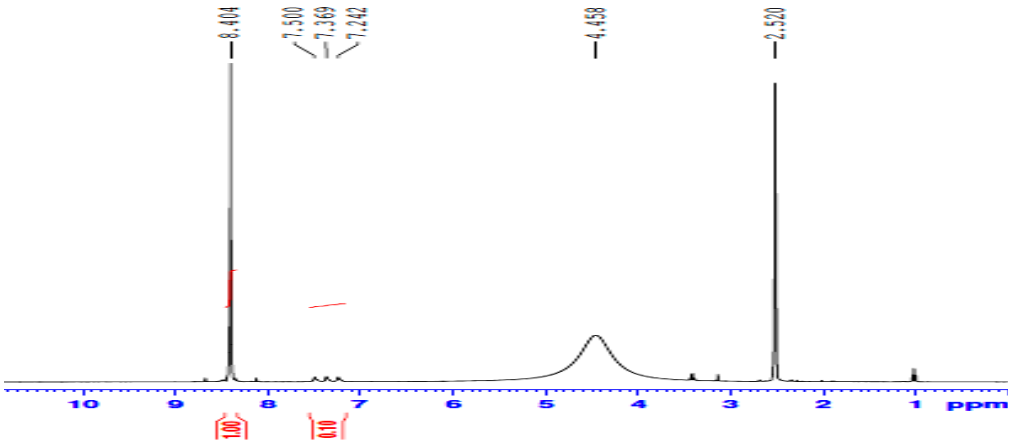


Fig. 21: ^{1}H NMR spectra of compound 5 in (D_2O/DMSO-d6).

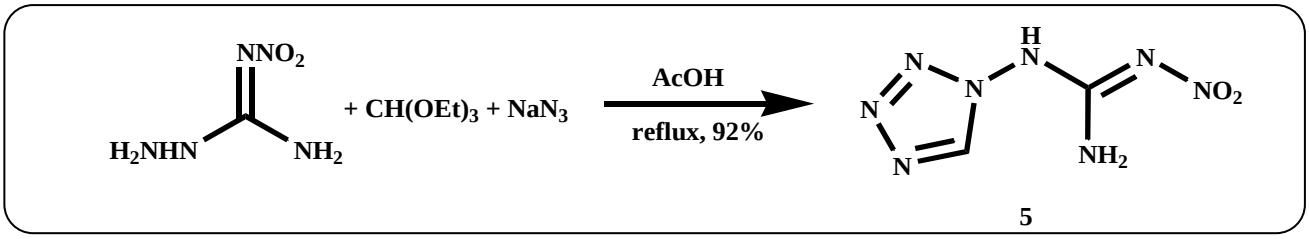
showed that compound **5** has been produced. A singlet peak in ^{1}H NMR (D_2O/DMSO-d6) is attributed to aromatic C-H bond which confirmed formation of tetrazole ring (Fig. 21).

This compound is readily soluble in water and insoluble in cold organic solvents. 5-Nitroguanidyltetrazole salts has been synthesized with interesting detonation performance and thermal stability, due to extensive intramolecular hydrogen bonds [26]; but synthesis of 1- Nitroguanidyltetrazole has not reported so far according to our best knowledge.

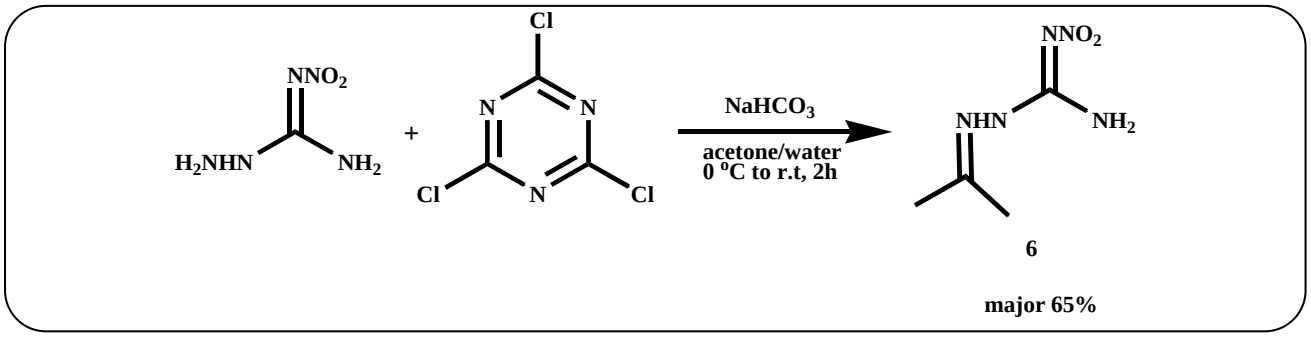
To synthesize new nitrogen rich compound, we replaced 5-hydrazino tetrazole with 3-ANQ in reaction with triethyl orthoformate and NaN_3. No reaction happened when 5-hydrazino tetrazole or its hydrochloride salt and triethyl orthoformate was heated to reflux in AcOH; no reaction with NaN_3 observed and only starting material was recovered. When glacial acetic acid was replaced with absolute ethanol as reaction solvent, mixture of products was obtained.

Reaction with trichlorotriazine

Triazine based compounds have been found growing application in agrochemicals especially herbicides. In energetic material area, tris(trinitromethyl) triazine is a powerful and well known explosive. Some polynuclear nitrogen-rich systems are synthesized by addition of tetrazole to trichlorotriazine [27]. To testify reactivity of 3-ANQ and 5HT toward triazine to prepare new triazine derivatives, we set up two reactions according to



Scheme 5: Preparing route of compound 5.



Scheme 6: Preparing route of compound 6.

literature procedure. When 3-ANQ was poured to sodium bicarbonate solution in 1:1 mixture of acetone and water in 0 °C, after a few minutes, reaction color turned to yellow immediately. The reaction mixture was warmed to r.t in the period of 2 h, then addition of water lead to crystallization of a yellow solid overnight which was separated by simple filtration. The mass and NMR results was quite surprising. There was no trizine ring in the new compound but with two methyl group and m/z 159, it was deduced that compound 6 has been formed via condensation of ANQ and acetone (Scheme 6).

In the absence of trichlorotriazine, no reaction was occurred between acetone and 3-ANQ. Condensation of 3-ANQ and ketone usually happens in high temperature and acidic media. This reaction shows that trichlorotrizine acts as catalyst for hydrazone condensation. Altering 3-ANQ with 5-HT gave mixture of product even at -10 °C. A detail study to optimize the reaction of 3-ANQ and 5HT reaction with trichloro triazine is under progress.

CONCLUSIONS

3-Nitramino-1,2,4-triazole is synthesized via a simple and safe mode by condensation of 3-ANQ and triethylorthoformate. 1-Nitroguanidine tetrazole is synthesized for the first time through formation of tetrazole ring on 3-ANQ. 3,5-Diamino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole is prepared via condensation of 5-HT and dicyandiamide in good yield. By nitration of this compound in HNO_3/H_2SO_4, 3,5-Dinitramino-1-(1H-tetrazol-5-yl)-1H-1,2,4-triazole was obtained as new energetic material.

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