Synthesis of 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine

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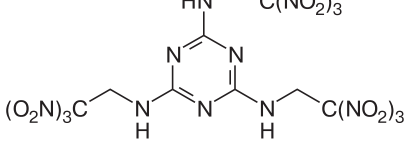
An alternative procedure for synthesizing 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine was developed. Nitration of this compound gave hitherto unknown 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine, which is of interest as potential component of solid rocket fuel compositions.

Key words: 1,3,5-triazine amino derivatives, *N*-trinitroethylation, *N*-nitration, 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine, 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine.

1,3,5-Triazines possess three positions suitable for varying the substituents thus favoring the synthesis of a wide range of their derivatives including compounds bearing the nitrogen-rich moieties. These heterocycles are used to widen the scope of high-energy compounds[1—6] that are of interest as the components of explosives, rocket fuels, and other energetic compositions. Thus, a series of publications was devoted to the synthesis of 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine[7—9] (TTET[9], **1**). The patent[7] claimed the synthesis of compound **1** by condensation of melamine (2,4,6-triamino-1,3,5-triazine, **2**) with trinitroethanol but details of the procedure are not given. Makhova and coworkers[8] failed to synthesize compound **1** by condensation of melamine with trinitroethanol in water at different temperatures, therefore they synthesized TTET **1** by condensation of melamine **2** with formaldehyde in water at 70 °C to generate *N*-methylol derivative **3** followed by its *in situ* reaction with trinitromethane. The procedure gives the product with melting point of 55—57 °C in 81% yield. The authors gave no other physical properties except for the IR and NMR spectral data. In 2014, Pang and coworkers[9] published the synthesis of TTET **1** by the reaction of melamine with trinitroethanol in water at 70 °C. The product with melting point of 160 °C was isolated from the reaction mixture by filtration in 80% yield. The authors reported good thermal stability of the synthesized compound (the decomposition point of 186 °C), reasonable impact sensitivity (21.5 J), and high density (1.88 g m^{-3}).[9] Additionally, they declare that the computed detonation properties of the obtained product identify it as a competitive energetic compound, which properties in some cases superior than that of hexahydro-1,3,5-trinitro-1,3,5-triazine (hexogen).[9]



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Results and Discussion

The aim of the present work is the improvement of energetic characteristics of TTET **1** by its *N*-nitration. However, our attempts to synthesize compound **1** for subsequent nitration using known procedures[8,9] gave unsatisfactory results. In our hands, the multiple attempts to synthesize TTET **1** as earlier described[8,9] using filtration of the solution of the product through a silica gel pad followed by recrystallization of the product from chloroalkanes provide pure TTET **1** in the isolated yields of about 15—20%. Product **1** melts at 159—160 °C and shows satisfactory spectral and microanalysis data. It should be emphasized that Makhova[8] and Pang[9] reported melting points of TTET **1** differing by 100 °C along with the acceptable elemental analysis and similar NMR data. Apparently, the low yield of pure compound **1** is attributable to the polymerization side reactions (like formulation of melamine-formaldehyde resins, which signals did not appear in the NMR spectra). To increase the yield of TTET **1**, we modified the method described by Makhova and coworkers.[8] The reaction was carried out in DMSO under basic catalysis conditions (Scheme 1). Namely, the synthesis of TTET **1** was based on the principles of trinitroethylation of low-basic amines described in our previous works[3,10] devoted to the synthesis of 4,6-diazido-2-(2,2,2-trinitroethylamino)-1,3,5-triazine and 6-azido-2,4-bis(2,2,2-trinitroethylamino)-1,3,5-triazine.

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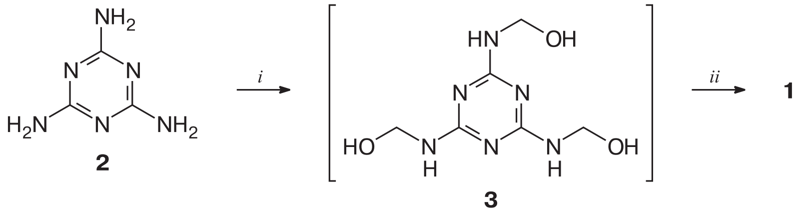
Scheme 1



Reagents: *i.* CH_2O, NaOH (cat.), DMSO; *ii.* $CH(NO_2)_3$, H_2O.

The crude product was purified by reprecipitation form isopropyl alcohol followed by recrystallization from chloroform. The suggested procedure is well reproducible and gives 65—66% yield of the target product **1** with m.p. 159—160 °C. The structure of compound **1** was confirmed by IR and NMR spectroscopy and elemental analysis.

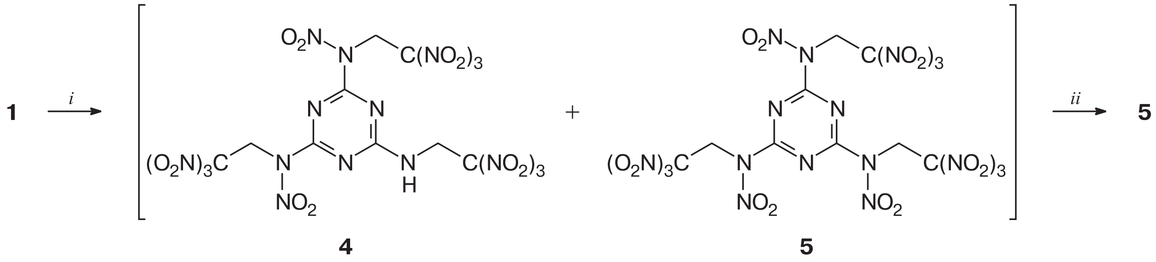
Nitration of TTET **1** was based on the results of our previous work[10] on nitration of 6-azido-2,4-bis(2,2,2-trinitroethylamino)-1,3,5-triazine. This compound was nitrated in good yield on both NH groups with HNO_3—$(CF_3CO)_2O$ using a molar ratio substrate : HNO_3 : : $(CF_3CO)_2O$ of 1 : 48 : 28.5. Taking into account the fact that compound **1** contains three NH groups instead of two NH groups of 6-azido-2,4-bis(2,2,2-trinitroethylamino)-1,3,5-triazine, a molar ratio **1** : HNO_3 : $(CF_3CO)_2O$ was 1 : 71.9 : 42.3. However, this reagent ratio did not ensure exhaustive nitration of TTET **1**. Therefore, the reaction was carried out in two steps (Scheme 2). The nitration products obtained on the first step by nitration of TTET **1** were isolated and subjected to the repeated nitration (see Experimental). The product of partial nitration, compound **4**, was not isolated in individual state. Its structure and content (~25%) in the product mixture obtained after first nitration step were determined by NMR spectroscopy. The yield of pure product **5** (NTTET) was 34% based on the starting TTET **1**. Compound **5** has melting point of 128—129 °C (decomp.), density of 1.92 g cm^{-3}, and the oxygen excess coefficient (α) of 1.14. The structure of NTTET **5** was established by IR and NMR spectroscopy and confirmed by elemental analysis.

In the ^1H, ^{13}C, and ^{14}N NMR spectra of compounds **1** and **5**, the NMR chemical shift values, the NMR signal shapes, and the integral intensity ratios of the signals are consistent with the expected values and the known data for the related compounds.[3,10]

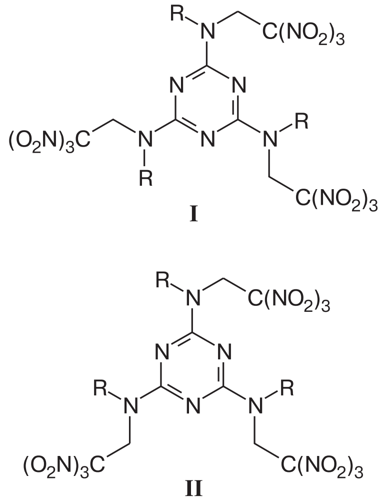
Due to the hindered rotation of the substituents around all three C—N bonds (ring—substituent bonds), the NMR spectra of TTET and NTTET are usually the superposition of the partially overlapping signals of several conformers. The NMR spectra of compound **1** synthesized by us exhibit the signals of comparable intensities attributable to two conformers (Fig. 1), *i.e.*, to symmetrical conformer **I** with a third order symmetry axis and unsymmetrical conformer **II**. This is most clearly seen in the ^1H NMR spectrum of compound **1** recorded in DMSO-d_6 showing for conformer **II** two doublets of the CH_2 group protons at δ 5.19 and 5.29 widened due to proton exchange with the neighboring NH group (see Experimental). Compound **5** also can exist in two conformations; however, owing to steric hindrance NMR spectra of **5** contains only signals of conformer **I**.

In summary, in the present work we developed new synthetic method to 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine, which is superior than other known methods. *N*-Nitration of 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine gave NTTET **5** having higher density and higher oxygen content than that of the starting compound. Additionally, the fact that NTTET **5** melts at lowered temperature with decomposition may indicate its lowered thermal stability.

Scheme 2



Reagents and conditions: *i.* HNO_3, $(CF_3CO)_2$, 0→20 °C, 5 h; *ii.* HNO_3, $(CF_3CO)_2O$, $ClCH_2CH_2Cl$, 1→20 °C, 4 h 40 min.



I

II

Fig. 1. Structures of symmetrical (**I**) and unsymmetrical (**II**) conformers of compounds **1** (R = H) and **5** (R = NO_2).

Experimental

IR spectra were recorded with a Bruker ALPHA FTIR spectrometer in KBr pellets. ^1H, ^{13}C, and ^{14}N NMR spectra were run on a Bruker AVANCE III 500 instrument (working frequencies of 500 (^1H), 127.75 (^{13}C), and 36.14 MHz (^{14}N)) in $(CD_3)_2CO$ (if not stated otherwise) using the same sample for recording NMR spectra for all nuclei. The ^1H and ^{13}C NMR shifts are given relative to Me_4Si (internal standard), the ^{14}N NMR shifts are given relative the signal of nitromethane. NMR signals were assigned based on the chemical shift values, shapes of the multiplets, a comparison of integral intensities of the signals, and the published data[3,10] for the related compounds. Elemental analysis was carried out with an Elementar vario EL cube CHNO analyzer (Germany). Melting points were measured using a Boetius apparatus heating near the melting point at a rate of 4 deg min^{-1}. Density of compound **5** was measured by a pycnometer method.[11]

Melamine **2** (99%) was purchased from Aldrich.

2,4,6-Tris(2,2,2-trinitroethylamino)-1,3,5-triazine (1). A mixture of melamine **2** (0.5 g, 4 mmol), DMSO (8 mL), and 25% aqueous formaldehyde (2 mL, 17 mmol) was stirred at room temperature for 30 min. Then the stirred mixture was treated dropwise with a solution of NaOH (0.02 g, 0.5 mmol) in water (3 mL). The obtained solution was stirred for 2 h, cooled to 10 °C, and a solution of H_2SO_4 (0.033 g, 0.34 mmol) in water (2 mL) was added dropwise. Cooling was removed and after warming up to 17 °C a solution of trinitromethane (3.6 g, 24 mmol) in water (12 mL) was added dropwise. Addition of trinitromethane was exothermic causing the rise of the reaction temperature up to 23—25 °C and turning the mixture cloudy. The mixture was stirred at 25 °C for 2 h and then at 60 °C for 5 h. After spontaneous cooling to room temperature, the precipitate formed was collected by filtration, washed with water, and dried in an air stream to give 2.42 g of the yellow product. The obtained product was dissolved in propan-2-ol (35 mL), the resulting solution was filtered, the filtrate was diluted with water (400 mL), and the obtained mixture was stirred for 2.5 h. The colorless precipitate formed was filtered off, washed with water (150 mL), and dried in an air stream to give 2.05 g (84%) of the product with m.p. 144—150 °C. Recrystallization from a mixture of CCl_4 (8 mL) and $CHCl_3$ (36 mL) (reflux, hot filtration, stepwise cooling to −15 °C for 4 days) afforded 1.6 g (66%) of compound **1** with m.p. 159—160 °C (decomp.). IR, ν/cm^{-1}: 1612 sh., 1591, 1584, 814 sh. (triazine ring); 1500, 1330, 806 (NO_2); 3415, 3426 (NH); 2958, 2894, 1437 (CH_2). ^1H NMR (DMSO-d_6), a mixture of two conformers (**I** : **II** ≈ 3 : 2), the signals partially overlap, δ: 5.19 and 5.29 (both br.d, 3.6 H and 2.4 H, $C\underline{H}_2NH$); 8.01 and 8.08 (both br.t, 3 H, $CH_2N\underline{H}$). ^1H NMR (acetone-d_6), a mixture of two conformers (**I** : **II** ≈ 1 : 1.2), the signals partially overlap, δ: 5.45 (br.s, 6 H, $C\underline{H}_2NH$); 7.49, 7.43, and 7.27 (all br.s, 3 H, $CH_2N\underline{H}$). $^{13}C\{^1H\}$ NMR, δ: 166.9 and 166.5 (ring, symm. and unsymm. $\underline{C}NHCH_2$); 125.5 (br.s, $C(NO_2)_3$); 44.5 (br.s, CH_2NH). ^{14}N NMR, δ: −31.9 ($C(NO_2)_3$). Found (%): C, 17.56; H, 1.46; O, 47.11. $C_9H_9N_{15}O_{18}$. Calculated (%): C, 17.57; H, 1.47; O, 46.81.

2,4,6-Tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine (5). To a stirred mixture of compound **3** (0.185 g, 0.3 mmol) and $(CF_3CO)_2O$ (1.8 mL, 12.7 mmol), HNO_3 (0.9 mL, 21.6 mmol) was added dropwise over 30 min at 1—2 °C (ice bath). The mixture was stirred for 5 h at room temperature (18—20 °C) and poured onto crashed ice. After 15 min, the precipitate formed was collected by filtration, washed with water, and dried under water-jet vacuum over P_2O_5. Recrystallization from $CHCl_3$ gave 0.18 g of colorless product with m.p. 121—123 °C (decomp.). According to NMR spectroscopy, this product is a ~1 : 3 mixture of 4-(2,2,2-trinitroethylamino)-2,6-bis(2,2,2-trinitroethylnitramino)-1,3,5-triazine (**4**) and 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine (**5**). NMR spectra of the mixture are superpositions of the spectra of compounds **4** and **5**. The signals of the individual compounds **4** and **5** were identified in the spectra. Both compounds exist as conformers **I** (NMR data).

<u>Compound 5.</u> ^1H NMR (acetone-d_6), δ: 6.57 (s, 6 H, $CH_2N(NO_2)$). $^{13}C\{^1H\}$ NMR, δ: 166.52 (ring); 123.92 (br., $C(NO_2)_3$); 50.53 (s, $CH_2N(NO_2)$). ^{14}N NMR, δ: −54.07 ($N(\underline{N}O_2)$).

<u>Compound 4</u>. ^1H NMR (acetone-d_6), δ: 5.64 (m, 2 H, $C\underline{H}_{ab}NH$); 6.50, 6.44 (both s, 2 H each, $C\underline{H}_2N(NO_2)$). $^{13}C\{^1H\}$ NMR, δ: 167.60 and 154.82 (ring); 123.92 (br., $C(NO_2)_3$); 44.26 (br., CH_2NH). ^{14}N NMR δ: −34.8 ($C(NO_2)_3$); −53.5 (br., $(N(\underline{N}O_2))$.

To a mixture of compounds **4** and **5** (0.22 g), dichloroethane (1 mL) was added followed by addition of HNO_3 (0.5 mL, 12.6 mmol) under stirring and cooling to 1—2 °C. The resulting solution was treated dropwise with $(CF_3CO)_2O$ (1 mL, 7.1 mmol) at 1—2 °C. The mixture was stirred at 18—20 °C for 4 h and 40 min, treated dropwise with CCl_4 (2 mL), and stirring was continued for 20 min. The mixture was poured onto crashed ice, the precipitate formed was collected by filtration, washed with water, and dried under water-jet vacuum over P_2O_5. Recrystallization from $CHCl_3$ afforded 0.095 g (34% based on the starting triazine **3**) of compound **5** with m.p. 128—129 °C (decomp.). IR, ν/cm^{-1}: 1613, 1608 sh., 1592 (triazine ring); 1640, 1259, 851 (NNO_2); 1560, 1337, 1296 (NO_2), 2972, 2888, 1424, 1386 (CH_2). ^1H NMR (acetone-d_6), δ: 6.57 (s, 6 H, $CH_2N(NO_2)$). $^{13}C\{^1H\}$ NMR, δ: 165.25 (ring); 123.91 (br., $C(NO_2)_3$); 50.53 (s, $CH_2N(NO_2)$). ^{14}N NMR, δ: −34.9 ($C(NO_2)_3$); −53.5 (br., $N(\underline{N}O_2)$. Found (%): C, 14.90; H, 0.83; O, 50.93. $C_9H_6N_{18}O_{24}$. Calculated (%): C, 14.41; H, 0.81; O, 51.18.

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