



4,6-Diazo-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) and Its Silver Salt – Synthesis and Characterization

Tomáš Musil, Robert Matyáš,* Svatopluk Zeman, Aleš Růžička, Antonín Lyčka, Jiří Majzlík, Roman Vala, Petr Knotek

Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice,

Studentska 95, 532 10 Pardubice, Czech Republic

**E-mail: Robert.Matyas@upce.cz*

Abstract: 4,6-Diazo-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) and its silver salt (AgTNADAzT) were prepared and characterized. Elemental analysis, FTIR, NMR, DSC, AAS and X-ray diffraction were used for analytical characterization. The sensitivities of TNADAzT and AgTNADAzT were determined and compared with common explosives and MTX-1.

The crystal density of TNADAzT is 1.794 g·cm⁻³ and its heat of formation 899 kJ·mol⁻¹. The sensitivity of TNADAzT to impact and friction slightly exceeds PETN; the sensitivity to electrostatic discharge is lower than RDX. The sensitivity of AgTNADAzT is on the level of a primary explosives (between mercury fulminate and PETN). The initiation efficiency of AgTNADAzT is higher than 200 mg (acceptor PETN compressed by 64-70 MPa) and therefore excludes it from practical use as a primary explosive in detonators.

Keywords: azido derivative of triazine, silver salt, sensitivity, MTX-1, X-ray

1 Introduction

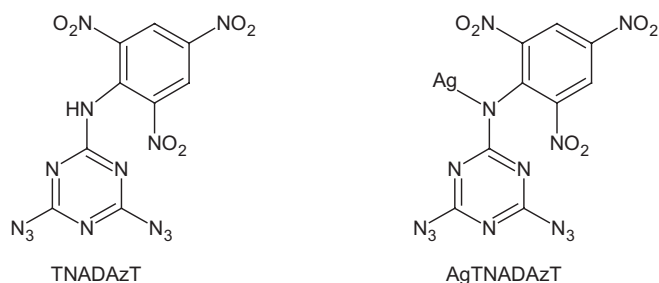
Molecules based on the triazine ring and containing two or three azido groups are among the powerful explosives that have, surprisingly, only been published a short time ago (an exception being cyanuric triazide). Cyanuric triazide has been known for more than one hundred years (probably first reported by Finger

in 1907 [1]). This compound is a powerful primary explosive with a high ignition efficiency. It would be good candidate as a lead azide replacement, except for its volatility and low thermal stability (m.p. is 94 °C) [2-6]. Despite this, it has recently been reconsidered as a constituent in initiator mixtures (LA replacement in stab detonators) [7].

A similar molecule, containing two azido groups and one nitramine group, 4,6-diazido-*N*-nitro-1,3,5-triazin-2-amine (DANT) was first reported by Fronabarger *et al.* in 2008 [8]. They published the synthesis and analytical data for DANT. A further study of this molecule that focused on its structure and sensitivity was published later [9].

Two other interesting molecules, 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine (TAHT) and 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT), were first described by Huynh *et al.* in 2004 [10, 11]. Both of these molecules, especially TAAT, are highly sensitive to mechanical stimuli. These compounds were not suggested as explosives, but TAAT was patented for the preparation of carbon nitrides, more specifically C₂N₃ and C₃N₅ [12].

4,6-Diazido-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) is, until the present, an almost unexplored triazine compound; only its thermal behaviour was published recently [13]. The present study is focused on determining the structure, and explosive properties of TNADAzT and its silver salt (Scheme 1).



Scheme 1. 4,6-Diazido-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) and its silver salt (AgTNADAzT)

2 Experimental

2.1 Synthesis

2.1.1 Synthesis of TNADAzT

4,6-Dichloro-*N*-phenyl-1,3,5-triazin-2-amine was synthesized according to the

Pirkl and Fisar procedure [14]. The yield was 94% with m.p. 135-136 °C (136-137 °C [14]). The product was not recrystallized. Elemental analysis: Calc. for $C_9H_6N_4Cl_2$: C 44.84, H 2.51, N 23.24, Cl 29.41%. Found: C 44.61, H 2.41, N 23.08, Cl 29.30%. IR (ATR, cm^{-1}): 3367m (NH), 1603m, 1567w, 1533s, 1514vs, 1495vs, 1484vs, 1454s, 1385s, 1334m, 1316m, 1242s, 1216vs, 1169s, 1157w, 1108w, 1082w, 1037w, 1014s, 996w, 961m, 907m, 886w, 869m, 836w, 823m, 789vs (triazine ring), 752vs, 708m, 689s, 650m, 631w, 619m, 602s, 551w.

4,6-Diazido-*N*-phenyl-1,3,5-triazin-2-amine was synthesized according to the procedure of Azev *et al.* [15]. The yield was 10.1 g (95%). The resulting white precipitate changed colour to brown when exposed to air and light. Elemental analysis: Calc. for $C_9H_6N_{10}$: C 42.52, H 2.38, N 55.10%. Found: C 42.18, H 2.53, N 54.98%. IR (ATR, cm^{-1}): 3327m (NH), 2169m (N_3^{as}), 2127m (N_3^{as}), 1622s, 1582s, 1558s, 1500s, 1411s, 1373s, 1348vs, 1264m, 1182w, 1166m, 1161m, 1054w, 973w, 922w, 895w, 796s (triazine ring), 744s, 704w, 688m, 617w.

TNADAzT was synthesized according to Yan *et al.* [13]. The yield of the raw product was 3.5 g (47%). Elemental analysis: Calc. for $C_9H_3N_{13}O_6$: C 27.77, H 0.78, N 46.78%. Found: C 27.74, H 0.73, N 46.69%. IR (ATR, cm^{-1}): 3311m (NH), 3108w (CH), 2180m (N_3^{as}), 2131m (N_3^{as}), 1623vs, 1605w, 1586m, 1525s, 1496s, 1421m, 1377m, 1328vs, 1300vs, 1239w, 1198s, 1176m, 1088m, 1068m, 926m, 912m, 810m (triazine ring), 769m, 754w, 734s, 718s, 700m. DSC ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$): m.p. 170 °C, decomposition during melting.

2.1.2 Synthesis of AgTNADAzT

Sodium hydroxide (0.04 g, 1.0 mmol) was dissolved in hot methanol and this solution was added to a suspension of TNADAzT (0.39 g, 1.0 mmol) in methanol (30 mL). The reaction mixture was stirred for 10 min when TNADAzT became completely dissolved to form a clear orange coloured solution. An aqueous solution of silver(I) nitrate(V) (0.19 g, 1.1 mmol) was then added to the reaction mixture and a yellow precipitate formed. The reaction mixture was stirred for an additional 45 min. The methanol was evaporated and the dark yellow product was filtered off, washed with water and dried at room temperature. The yield of the product was 0.44 g (89% theoret.). Elemental analysis for $C_9H_2AgN_{13}O_6$: Calcd. C 21.79, H 0.41, N 36.71, Ag 21.74%. Found: C 21.67, H 0.87, N 33.95, Ag 20.93%. IR (ATR, cm^{-1}): 3095w (CH), 2144m (N_3^{as}), 1633s, 1604s, 1592s, 1533vs, 1513vs, 1452w, 1432s, 1377m, 1341vs, 1317w, 1307w, 1201m, 1168w, 1101m, 1086m, 1006m, 938w, 916m, 840w, 824w, 768s, 719s, 698w. DSC ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$): it does not melt, decomposition commences at 154 °C, maximum at 208 °C.

2.2 Characterization of comparable explosives

Mercury fulminate (MF), pentrit (PETN) and hexogen (RDX) were used as standard explosives for comparison with the sensitivities of TNADAzT and AgTNADAzT. The sensitivities of TNADAzT and AgTNADAzT were also compared with those of MTX-1 (1-[(2E)-3-(1H-tetrazol-5-yl)triazin-2-en-1-ylidene]methanediamine), a recently synthesized primary explosive, which was suggested as a tetrazene replacement, possessing higher thermal and hydrolytic stability than tetrazene [16, 17].

The brown modification of MF was prepared according to a common procedure [18], PETN with the trade name "Pentrit NS" (with particles less than 200 μm) was provided by Explosia a.s. and RDX was provided by Chemko Strazke. MTX-1 was prepared in 62% yield according to the Fronabarger procedure [16, 17]. Elemental analysis: Calc. for $\text{C}_2\text{H}_5\text{N}_9$: C 15.49, H 3.25, N 81.27%. Found: C 15.26, H 3.33, N 80.13%. IR (ATR, cm^{-1}): 3316m, 3130m, 1698w, 1671s, 1620w, 1581m, 1552w, 1518w, 1503w, 1457m, 1425m, 1408w, 1350s, 1239vs, 1184s, 1152w, 1119s, 1099m, 1081w, 1052m, 1032m, 1014w, 981m, 831m, 750m.

2.3 Chemical analysis

Elemental analysis was measured using a FLASH 2000 apparatus from Thermo Scientific with an HCNS Analyzer. Nicotinamide (for samples having a nitrogen content up to 25%) and melamine (for substance having a nitrogen content up to 66%) were used as standards.

The shape and size of the crystals was visualized by scanning electron microscopy (Jeol JSM 5500 LV). A histogram was determined using optical microscopy (Olympus BX 60) after spin-coating of a water-colloidal solution onto an HCl-etched microscope slide. The diameter of the crystals was determined according to the procedure described in [19] for the number of particles $>200 \mu\text{m}$, employing SW Gwyddion version 2.25 [20].

Differential scanning calorimetry was performed using DSC Netzsch 200F3. Aluminum pans, with a pin-hole cover, in a dynamic nitrogen atmosphere (flow rate 40 mL/min) at a pressure of 0.1 MPa, were used. The heating rate was $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and the sample mass was 2 mg.

The heat of combustion was measured with an MS-10A (OZM Research s.r.o.) calorimeter calibrated using benzoic acid. The barrel was filled with oxygen at 20 bar. The measurement was repeated three times. The weight of each sample for analysis was about 0.3 g. The internal surface of the calorimeter bomb was washed with distilled water after the combustion of each sample for the determination of nitric acid in the combustion products. The washing water was

then titrated with a 0.03 M aqueous solution of sodium carbonate, with indicator phenolphthalein. The heat of formation was calculated according to Hess' law.

The infrared spectra were obtained using a Protégé 460 apparatus. OMNIC software (Thermo Electron Corporation) was used for both data acquisition and evaluation. ATR crystal was used for measuring of all samples.

The ^1H (500.13 MHz) and ^{15}N (50.69 MHz) NMR spectra were recorded on a Bruker Avance 500 spectrometer at room temperature. TNADAzT was dissolved in DMSO- D_6 . The ^1H chemical shifts were referenced to internal TMS and ^{15}N chemical shifts were referred to external neat $\text{CH}_3^{15}\text{NO}_2$ in a co-axial capillary ($\delta(^{15}\text{N}) = 0.0$). Two-dimensional experiments (gradient-selected (gs)- ^1H , ^{15}N -HMBC) were performed using the manufacturer's software (TOPSPIN 2.1).

Crystals of TNADAzT suitable for X-ray crystallographic analysis were obtained *via* solvent evaporation from two solvent systems (acetonitrile/water (1:1) and acetone). The X-ray data for the colourless crystals of TNADAzT were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo/ K_α radiation ($\lambda = 0.071073$ nm), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [21]. Absorption was corrected by integration methods [22]. The structures were solved by direct methods (Sir92) [23] and refined by full matrix least-square based on F^2 (SHELXL97) [24]. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure the uniformity of the treatment of the crystal, all hydrogens were recalculated into idealized positions (riding model) and temperature factors $\text{H}_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (pivot atom) were assigned with C–H bonds = 0.93 Å for aromatic hydrogen atoms, and 0.86 Å for N–H bonds. Crystallographic data for the structural analysis have been deposited with the Cambridge Structural Database CCDC. Deposition number: CCDC 1526313.

Crystallographic data for TNADAzT: $\text{C}_9\text{H}_3\text{N}_{13}\text{O}_6$, $M = 389.24$, monoclinic, $P 2_1/c$, $a = 11.1759(5)$, $b = 8.5390(5)$, $c = 17.7670(9)$ Å, $\beta = 121.787(4)^\circ$, $Z = 4$, $V = 1441.22(14)$ Å 3 , $D_c = 1.794$ g·cm $^{-3}$, $\mu = 0.154$ mm $^{-1}$, $T_{\text{min}}/T_{\text{max}} = 0.970/0.982$; $-14 \leq h \leq 14$, $-11 \leq k \leq 10$, $-22 \leq l \leq 22$; 12646 reflections measured ($\theta_{\text{max}} = 27.5^\circ$), 3278 independent ($R_{\text{int}} = 0.0477$), 2391 with $I > 2\sigma(I)$, 253 parameters, $S = 1.174$, $R_I(\text{obs. data}) = 0.0466$, $wR_2(\text{all data}) = 0.0921$; max., min. residual electron density = 0.271, -0.328 eÅ $^{-3}$. $R_{\text{int}} = \Sigma |F_o^2 - F_{o,\text{mean}}^2| / \Sigma F_o^2$, $\text{GOF} = [\Sigma (w(F_o^2 - F_c^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$ for all data, $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for observed data, $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2) / (\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

2.4 Explosive properties

A Kast fall hammer (produced by Reichel and Partner) was used for determining the impact sensitivity with a 0.5 kg hammer for AgTNADAzT, MTX-1 and MF, a 1 kg hammer for PETN and TNADAzT and a 2 kg hammer for RDX. Both cylinders (BFH-SR) and guide rings (BFH-SC) were produced by OZM Research. Five levels of impact energy and 15 trials at each level were used for each measured explosive. Probit analysis was used for measuring and construction of the sensitivity curves for all samples.

Sensitivity to friction was determined using a BAM type friction apparatus FSKM-08 (OZM Research) for TNADAzT, PETN and RDX samples. AgTNADAzT, MTX-1 and MF were measured on the small BAM friction apparatus FSKM-PEX (OZM Research). Porcelain plates (BFST-Pt) and porcelain pegs (BFST-Pn) were produced by OZM Research. Five levels of friction force and 15 trials at each level were used for each measured sample. Measuring details were the same as in a previous study [18].

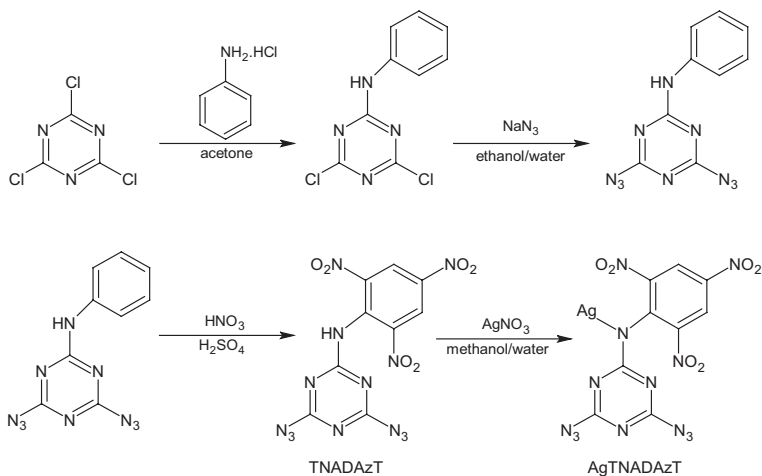
The apparatus ESZ KTTV 2001 (developed by the Institute of Energetic Materials, Czech Republic) was used for determining the sensitivity to electrostatic discharge of all compounds [25]. The oscillating discharge mode was used for the measurements. The sample volume was 8 mm³ and the distance between the steel electrodes 1 mm. For measuring and calculation of the sensitivity of all samples, the up and down method (30 repetitions on each sample) was used.

The initiation efficiency of AgTNADAzT was determined using the commonly constructed electric detonators that are produced by Austin Detonator s.r.o. A single detonator arrangement was used for all tests. AgTNADAzT was separately loaded into the instantaneous element using three quantities (50 mg, 100 mg and 200 mg) and each was covered by PETN (30-35 mg). Both were pressed down with 56-69 MPa. A secondary charge was created by using PETN (0.36-0.38 g) pressed down with 64-70 MPa into the aluminum shell, followed by a similar quantity of PETN pressed down in the same way on top of the original amount. Electric instantaneous detonators were coupled together with an electric fuse. The same procedure was used for fabrication of detonators with dextrinated lead azide (10 mg), used as a primary explosive. Detonators with dextrinated lead azide were used for comparing the initiation efficiency of AgTNADAzT. Correct functioning of the electric instantaneous detonators containing AgTNADAzT and dextrinated lead azide was verified by a witness lead plate. Each detonator was clamped vertically to the lead plate (40 × 40 mm and 5 mm thick) and initiated.

3 Results and Discussion

3.1 Synthesis and characterization of TNADAzT and AgTNADAzT

4,6-Diazido-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) was prepared by a three step synthesis from cyanuric chloride. The overall yield of 4,6-diazido-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine was 42%. A summary of the TNADAzT synthesis is shown in Scheme 2.



Scheme 2. Synthesis of TNADAzT

TNADAzT forms free-flowing crystals with an elongated hexagonal shape. The two major crystal characteristics were measured *i.e.* length and width of each particle (Figure 1). The typical width of the analyzed particles was 25–40 μm , with an aspect ratio (length-to-width ratio) of 1.4–1.8 (see black and gray columns on histogram in Figure 2 for width and length to width ratio).

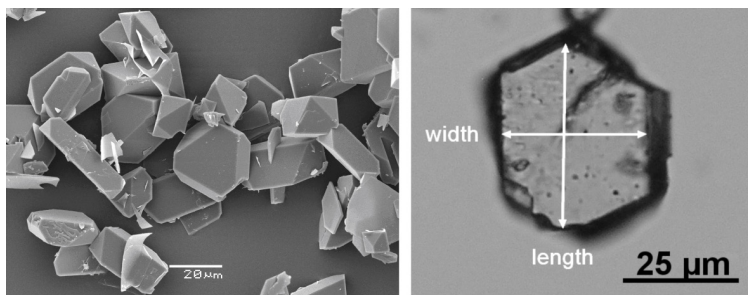


Figure 1. SEM image of the TNADAzT crystals (left) and measurement of crystal length and width (right)

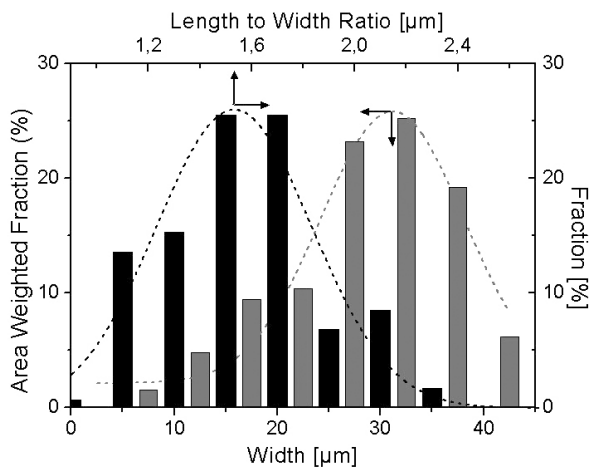


Figure 2. Histogram of the sizes of agglomerated particles

The purity of the samples was determined using elemental analysis. The results of C, H, N, Cl and Ag analysis of the intermediates and of the final product agreed satisfactorily with the calculated values. The presence of typical functional groups in the TNADAzT molecule was confirmed by infrared analysis. One medium strength band at 3311 cm^{-1} is typical for N–H stretching of secondary amines; a medium band at 3108 cm^{-1} belongs to aromatic C–H stretching and two strong bands at 2180 cm^{-1} and 2131 cm^{-1} belong to the asymmetric vibration of azido groups. The strong bands between 1525 cm^{-1} and 1239 cm^{-1} may belong to asymmetric and symmetric stretching of the nitro groups and the triazine ring stretching, but it is difficult to decide which belongs to the triazine ring and which to the nitro groups. The medium strength band at 810 cm^{-1} belongs to the out-of-plane bending vibration of the triazine ring. The structure of the TNADAzT molecule was unambiguously confirmed by the X-ray crystallographic study (Section 3.2). TNADAzT's heat of combustion was calculated as $4891\text{ kJ}\cdot\text{mol}^{-1}$ and the heat of formation as $899\text{ kJ}\cdot\text{mol}^{-1}$.

The silver salt of 4,6-diazido-*N*-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (AgTNADAzT) was prepared by reaction of TNADAzT with silver nitrate in aqueous methanol (Scheme 2). AgTNADAzT was formed in high yield (89%) due to its low solubility in methanol/water. The composition and structure of the product was determined using elemental analysis, AAS and infrared spectroscopy. The IR spectrum of AgTNADAzT confirmed the loss of the acidic hydrogen on the nitramine group at 3311 cm^{-1} , thus indicating the formation of the TNADAzT salt.

3.2 X-ray crystallographic study of TNADAzT

The details of the crystal structure determination and refinement for the compound studied are given below. The unit cell parameters for all of the types of crystal were determined and gave the same values, which indicated that no polymorphism or inclusion of solvent inside the crystals occurred. The molecular structure is displayed in Figure 3. The TNADAzT molecule crystallizes in the monoclinic space group $P2_1/c$. There is a high number of weak short contacts within this structure, including those of delocalized electron clouds of the azido and nitro groups and both rings, while the standard H-bond for N1-H1...O1 is really strong (N...O distance 2.644 Å) and the only one present here. The planes of both rings are mutually inclined at 38.34°, the rotation of the nitro groups from the phenyl ring are 39.29°, 19.27° and 3.94° for the pivot atoms N2, N4 and N3, respectively. The azide groups are in so-called open conformation and are perfectly coplanar with their parent ring. A direct comparison of the TNADAzT molecule was made with other molecules bearing similar structural arrangements, as for example cyanuric triazide [26, 27], 4,6-diaziido-2-hydrizo or -azo bridged 1,3,5-triazines [28], 2,6-diaziido-4-amino-1,3,5-triazine [29] or independently published structures of 4,6-diaziido-*N*-nitro-1,3,5-triazin-2-amine [9, 30]. The structural parameters in all of these compounds are close to those of TNADAzT, with one major difference, that all types of open, closed or alternating conformations of the azide groups were found within the series.

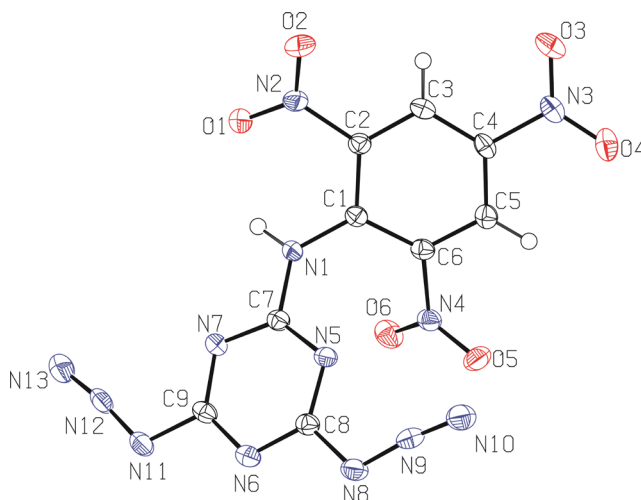


Figure 3. Molecular structure of TNADAzT (ORTEP 50% probability level)

The interplanar angle between the phenyl and triazine rings was 37.98°. All

distances and other parameters are in line with literature observed parameters [31]. Selected interatomic distances and angles are summarized in Tables 1 and 2.

Table 1. Interatomic distances (standard uncertainties) in the TNADAzT molecule

| Distances [pm] | | | Distances [pm] | | |
|----------------|----|----------|----------------|-----|----------|
| O6 | N4 | 122.4(2) | N6 | C8 | 133.4(3) |
| N5 | C8 | 132.9(3) | N12 | N13 | 111.6(3) |
| N5 | C7 | 133.4(3) | N12 | N11 | 126.3(3) |
| N1 | C7 | 137.1(2) | N4 | C6 | 147.7(3) |
| N1 | C1 | 138.0(3) | N2 | C2 | 146.6(3) |
| | | | N9 | N10 | 111.2(3) |
| O5 | N4 | 122.4(2) | N9 | N8 | 127.2(3) |
| O1 | N2 | 122.9(2) | N8 | C8 | 139.1(3) |
| O2 | N2 | 122.7(2) | N11 | C9 | 139.8(3) |
| O4 | N3 | 122.3(2) | C5 | C6 | 137.9(3) |
| O3 | N3 | 122.5(2) | C5 | C4 | 138.0(3) |
| N7 | C9 | 132.7(3) | | | |
| N7 | C7 | 133.5(3) | C4 | C3 | 136.8(3) |
| N3 | C4 | 147.3(3) | C3 | C2 | 138.5(3) |
| N6 | C9 | 133.4(3) | | | |
| C2 | C1 | 140.9(3) | C1 | C6 | 141.0(3) |

Table 2. Dihedral angles of groups in the TNADAzT molecule

| Azido and amino group angles [°] | | | Nitro group angles [°] | | |
|----------------------------------|----------|--|--------------------------------|----------|--|
| N13 N12 N11 | 173.1(2) | | O1 N2 C2 | 118.7(3) | |
| N12 N11 C9 | 112.2(3) | | O2 N2 C2 | 117.6(3) | |
| N10 N9 N8 | 172.7(2) | | O2 N2 O1 | 123.7(3) | |
| N9 N8 C8 | 112.6(3) | | O6 N4 C6 | 117.5(3) | |
| C7 N1 C1 | 126.8(3) | | O5 N4 C6 | 117.7(3) | |
| | | | O5 N4 O6 | 124.6(3) | |
| | | | O4 N3 O3 | 124.6(3) | |
| | | | O3 N3 C4 | 117.9(3) | |
| | | | O4 N3 C4 | 117.5(3) | |
| Angle within phenyl ring [°] | | | Angle within triazine ring [°] | | |
| N1 C1 C2 | 121.8(3) | | C8N5C7 | 113.5(3) | |
| C2 C1 C6 | 114.6(3) | | C9N6C8 | 112.4(3) | |
| N1 C1 C6 | 123.7(3) | | C9N7C7 | 113.4(3) | |

| | | | |
|----------|----------|-----------|----------|
| C3 C2 C1 | 122.9(3) | N5 C8 N6 | 127.2(3) |
| C3 C2 N2 | 115.5(3) | N5 C8 N8 | 119.4(3) |
| C1 C2 N2 | 121.6(3) | N6 C8 N8 | 113.4(3) |
| C4 C3 C2 | 118.8(3) | N5 C7 N7 | 126.1(3) |
| | | N5 C7 N1 | 118.9(3) |
| | | N7 C7 N1 | 115.0(3) |
| C3 C4 C5 | 122.0(3) | N7 C9 N6 | 127.4(3) |
| C5 C4 N3 | 118.8(3) | N6 C9 N11 | 113.6(3) |
| C3 C4 N3 | 119.2(3) | N7 C9 N11 | 119.0(3) |
| C6 C5 C4 | 118.0(3) | | |
| C5 C6 C1 | 123.6(3) | | |
| C5 C6 N4 | 114.7(3) | | |
| C1 C6 N4 | 121.4(3) | | |

H-bond N2 H2 N4' 3.017(2) 167.7, i is $-1/2+x$, $1/2-y$, $3/2-z$ and $-1/2+x$, y , $3/2-z$.

3.3 NMR

There are two ^1H chemical shifts in TNADAzT: $\delta = 11.70$ (s, 1H, NH) and $\delta = 9.11$ ppm (s, 2H, =CH-). The following ^{15}N chemical shifts were observed in the one-dimensional ^{15}N NMR spectrum: -17.2 ppm, -19.9 ppm, -137.8 ppm, -146.0 ppm, -169.8 ppm, -174.5 ppm, -181.6 ppm, -262.2 ppm and -276.2 ppm. The only signal resonating at -276.2 ppm had a negative phase in the one dimensional proton-noise decoupled ^{15}N NMR spectrum (due to the Overhauser effect and negative gyromagnetic ratio of ^{15}N isotope) and, thus, it belongs to the NH nitrogen. The signals of the nitro groups were assigned using g_s - ^1H , ^{15}N -HMBC spectrum where two cross-peaks corresponding to correlation of the appropriate nitro group/s with aromatic protons were observed ($\delta = -17.2$ ppm (2NO_2), -19.9 ppm (NO_2)). The other signals cannot be assigned unequivocally without ^{15}N selective labelling.

However, we can conclude that the above-mentioned ^{15}N chemical shifts can be unequivocally ascribed to a diazido derivative after comparison of the experimental data with those observed for 4,6-diazido-*N*-nitro-1,3,5-triazine-2-amine [9], where very similar ^{15}N chemical shifts were found for the appropriate nitrogen atoms (-137.1 ppm, -146.5 ppm, -164.7 ppm, -173.2 ppm, -176.7 ppm, and -261.3 ppm). No signals of a tetrazolo derivative, possibly existing in

a cyclization equilibrium, were detected, contrary to 4,6-diazido-*N*-nitro-1,3,5-triazine-2-amine, where the ratio of the symmetrical diazido derivative to the non-symmetrical one (as a consequence of cyclization of one azido group and one nitrogen of the triazine) was ca. 7:3. The ^{15}N chemical shifts indicate that the structure of TNADAzT in DMSO solution is the same as that shown in Figure 3 in the solid state, except that free rotation around N1-C7 bond must exist in solution, allowing the existence of only three nitrogen resonances for the three nitrogen atoms in the two azide fragments and the equivalency on the NMR time scale of the two nitro groups in the *ortho* positions, as well as the nitrogen atoms N5 and N7.

3.4 Sensitivity of TNADAzT and AgTNADAzT to impact

The sensitivities of TNADAzT and AgTNADAzT to impact was determined on a fall hammer apparatus. MF, MTX-1, PETN and RDX were also measured for comparison with the sensitivity of TNADAzT. The sensitivity curves are presented in Figure 4; values for 50% probability of initiation are summarized in Table 3. The impact sensitivity of TNADAzT slightly exceeds that of PETN, while the sensitivity of its silver salt is on the level of those of MF and MTX-1.

The results for PETN, RDX and MF were comparable with literature values. For example, the sensitivity of MF is mostly reported as being from 0.4 J to 1.2 J [3]; we obtained 0.62 J. PETN is mostly reported as being between 3 J and 4.1 J [3]; 50% probability of initiation determined in the present study was 3.93 J.

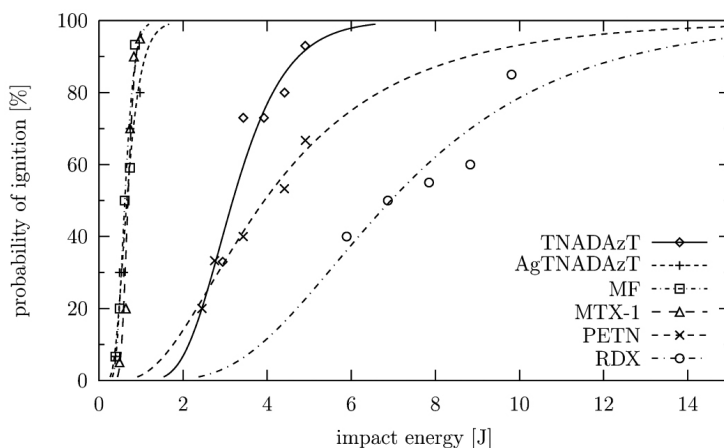


Figure 4. The impact sensitivity curves for TNADAzT, AgTNADAzT, MF, MTX-1, PETN and RDX

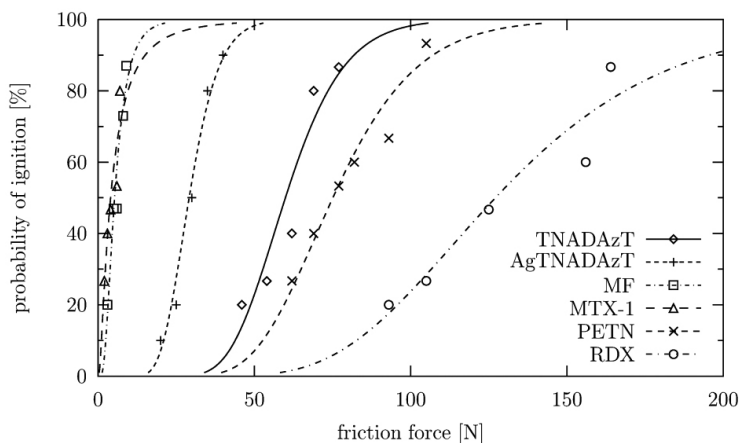
Table 3. Sensitivity of TNADAzT and AgTNADAzT to impact and friction compared with the sensitivities of MF, MTX-1, PETN, RDX (friction sensitivity compared with Meyer values [32])

| | Impact energy for 50% probability of initiation [J] | Friction force for 50% probability of initiation [N] | Friction force for 17% probability of initiation [N] | Friction sensitivity reported by Meyer ^a [N] |
|-----------|---|--|--|---|
| MF | 0.62 | 5.3 | 2.9 | 3 |
| MTX-1 | 0.69 | 1.5 | 4.0 | - |
| AgTNADAzT | 0.67 | 29.1 | 22.8 | - |
| PETN | 3.93 | 75.5 | 57.5 | 60 |
| TNADAzT | 3.18 | 59.9 | 47.5 | - |
| RDX | 6.94 | 127 | 95.5 | 120 |

^a The smallest load of the peg initiating at least once in six consecutive trials.

3.5 Sensitivity of TNADAzT and AgTNADAzT to friction

The sensitivity of TNADAzT and AgTNADAzT to friction was determined on a BAM friction apparatus and compared with MF, MTX-1, PETN and RDX. The sensitivity curves are presented in Figure 5; values for 50% probability of initiation are summarized in Table 3. The sensitivity of TNADAzT is higher than the sensitivity of PETN; the sensitivity of AgTNADAzT is between those of MF and PETN.

**Figure 5.** The friction sensitivity curves for TNADAzT, AgTNADAzT, MF, MTX-1, PETN, and RDX

We compared our results for the friction sensitivity of MF, PETN and RDX with the values reported by Meyer *et al.* [32], who used the same type of apparatus. However the methodology of measurement and evaluation was different; we used probit analysis while the values reported by Meyer *et al.* are values for the smallest load of the peg initiating at least once in six consecutive trials. Therefore we also evaluated the friction force for 17% probability of initiation from the sensitivity curves for all of the measured explosives. This probability of initiation is the closest to the Meyer values (but not exactly the same – the methodology of measuring and evaluation was different). The comparison is presented in Table 3.

Our values for 17% probability of initiation for MF and PETN correspond with the Meyer values; the result for RDX exhibits a significant divergence.

3.6 Sensitivity to electric discharge

The sensitivity of TNADAzT and AgTNADAzT was measured and compared with that of MF, PETN and RDX. The results of the electric spark sensitivity tests are presented in Table 4. TNADAzT is significantly less sensitive to electric discharge than PETN and RDX; the sensitivity of its silver salt is lower than that of MF and comparable with that of lead azide [3].

Table 4. Sensitivity to electric discharge

| | Energy of spark for 50% probability of initiation [mJ] |
|-----------|--|
| MF | 0.51-0.62 |
| AgTNADAzT | 9.9 |
| PETN | 26.8 |
| RDX | 59.4 |
| TNADAzT | 234.0 |

3.7 Initiation efficiency of AgTNADAzT

The initiation efficiency of AgTNADAzT was measured in electric detonators. None of the AgTNADAzT samples, 50 mg, 100 mg and 200 mg pressed at 56-69 MPa, was able to initiate the secondary PETN charge. The weight of 200 mg is the maximal load weight for the instantaneous element. For the comparison we obtained a full-sized hole in the lead witness plate for detonators contained 10 mg of dextrinated lead azide as the primary charge under the same test conditions (Figure 6). The initiation efficiency of the silver salt of TNADAzT is higher than 200 mg, which excludes it from practical use as a primary explosive in detonators.



Figure 6. Witness lead plate test: 200 mg AgTNADAzT (left), 10 mg dextrinated lead azide (right)

4 Conclusions

TNADAzT was synthesized from cyanuric chloride in a three-step process in a 42% overall yield; AgTNADAzT was prepared from TNADAzT in 89% yield. These compounds were identified by elemental analysis, AAS and FTIR methods. The structure of TNADAzT was examined using single crystal X-ray diffraction.

The sensitivity of TNADAzT to mechanical stimuli was examined and compared with well known standard explosives (MF, PETN and RDX), and with the new promising primary explosive MTX-1. TNADAzT was found to be impact and friction sensitive; its impact and friction sensitivity were higher than those of PETN. The sensitivity of AgTNADAzT is on the level of primary explosives. The initiation efficiency of the silver salt of TNADAzT is higher than 200 mg (acceptor PETN compressed by 64-70 MPa), which precludes it as a lead azide replacement.

Acknowledgments

Financial support of this work by the Technology Agency of the Czech Republic (project TA03010760) is gratefully acknowledged.

References

- [1] Finger, H. Derivatives of Tricyanogen. *J. Prakt. Chem.* **1907**, 75: 103-104.
- [2] Bagal, L. I. *Chemistry and Technology of Primary Explosives*. Mashinostrojenije, Moskva **1975**.
- [3] Matyáš, R.; Pachman, J. *Primary Explosives*. Springer, Heidelberg **2013**, pp. 32, 111-115; ISBN 978-3-642-28435-9.
- [4] Fedoroff, B. T.; Sheffield, O. E. *Encyclopedia of Explosives and Related Items*. Vol. 3, Picatinny Arsenal, New Jersey **1966**, pp. C590-C591.

- [5] Huynh, M. V.; Coburn, M. D.; Meyer, T. J.; Wetzer, M. Green Primaries: Environmentally Friendly Energetic Complexes. *PNAS* **2006**, *103*: 5409-5412.
- [6] Huynh, M. V.; Coburn, M. D.; Meyer, T. J.; Wetzer, M. Green Primary Explosives: 5-Nitrotetrazolato-*N*²-ferrate Hierarchies. *PNAS* **2006**, *103*: 10322-10327.
- [7] Mehta, N.; Cheng, G.; Cordaro, E.; Naik, N.; Lateer, B.; Hu, C.; Stec, D.; Yang, K. Performance Testing of Lead-free Stab Detonator. *NDIA 50th Annual Fuze Conference*, Norfolk, USA **2006**.
- [8] Fronabarger, J.; Sitzmann, M. E.; Williams, M. D. *Method for Azidotriazole, Nitrosoguanazine, and Related Compounds*. Patent US 7375221 B1, **2008**.
- [9] Musil, T.; Matyáš, R.; Růžička, A. 4,6-Diazido-*N*-nitro-1,3,5-triazin-2-amine (DANT) – Synthesis and Characterization. *Propellants Explos. Pyrotech.* **2012**, *37*: 275-281.
- [10] Huynh, M. H. V.; Hiskey, M. A.; Hartline, E. L.; Montoya, D. P.; Gilardi, R. Polyazido High-nitrogen Compounds: Hydrazo- and Azo-1,3,5-triazine. *Angew. Chem., Int. Ed.* **2004**, *43*: 4924-4928.
- [11] Huynh, M. H. V.; Hiskey, M. A.; Pollarod, C. J.; Montoya, D. P.; Hartline, E. L.; Gilardi, R. 4,4',6,6'-Tetrasubstituted Hydrazo- and Azo-1,3,5-triazines. *J. Energ. Mater.* **2004**, *22*: 217-229.
- [12] Huynh, M. H. V.; Hiskey, M. A. *Preparation of High Nitrogen Compound and Materials Therefrom*. Patent US 2006/0211565, **2006**.
- [13] Yan, Q. L.; Musil, T.; Zeman, S.; Matyáš, R.; Shi, X. B.; Vlček, M.; Pelikán, V. Preparation, Morphologies and Thermal Behavior of High Nitrogen Compound 2-Amino-4,6-diazido-*s*-triazine and Its Derivatives. *Thermochim. Acta* **2015**, *604*: 106-114.
- [14] Pirkli, J.; Fisar, C. *2-Anilino-4,6-dichlorotriazine and Derivatives*. Patent CS 171995, **1978**.
- [15] Azev, Yu. A.; Guselnikova, O. L.; Klyuev, N. A.; Shorshnev, C. V.; Rusinov, V. L.; Khupakhin, O. N. Products of Reactions of Azido Derivatives of *s*-Triazine with some *O*- and *N*-Nucleophiles. *Zh. Org. Khim.* **1995**, *31*: 1566-1572.
- [16] Fronabarger, J. W.; Williams, M. D.; Stern, A. G.; Parrish, D. A. MTX-1 – A Potential Replacement for Tetrazene in Primers. *Cent. Eur. J. Energ. Mater.* **2016**, *13*: 33-52.
- [17] Fronabarger, J. W.; Williams, M. D. *Alternative to Tetrazene*. Patent WO 2012/003031, **2012**.
- [18] Matyáš, R.; Šelešovský, J.; Musil, T. Sensitivity to Friction for Primary Explosives. *J. Hazard. Mater.* **2012**, *213-214*: 236-241.
- [19] Kucerova, J.; Svobodova, Z.; Knotek, P.; Palarcik, J.; Vlcek, M.; Kincl, M.; Horak, D.; Autebert, J.; Viovy, J.-L.; Bilkova, Z. PEGylation of Magnetic Poly(glycidyl methacrylate) Microparticles for Microfluidic Bioassays. *Mater. Sci. Eng. C* **2014**, *40*: 308-315.
- [20] Klapetek, P.; Nečas, D.; Anderson, C. Gwyddion – Free SPM Data Analysis Software; v. 2.25, **2011**.
- [21] Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in

- Oscillation Mode. *Meth. Enzymol.* **1997**, 276: 307-326.
- [22] Coppens, P. Evaluation of Absorption and Extinction in Single-crystal Structure Analysis. In: *Crystallographic Computing* (Ahmed, F. R.; Hall, S. R.; Huber, C. P., Eds.), Munksgaard, Copenhagen **1970**, pp. 255-263.
- [23] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. Completion and Refinement of Crystal Structures with SIR92. *J. Appl. Crystal.* **1993**, 26: 343-350.
- [24] Sheldrick, G. M. *SHELXL-97*. University of Göttingen, Göttingen **1997**.
- [25] Strnad, J.; Majzlík, J. Determination of Electrostatic Spark Sensitivity of Energetic Materials. *New Trends Res. Energ. Mater., Proc. Semin., 4th*, Pardubice, Czech Republic **2001**, 303-307.
- [26] Knaggs, I. E. The Crystal Structure of Cyanuric Triazide. *Proc. R. Soc. London, Ser. A* **1935**, 15: 576-302.
- [27] Kessenich, E.; Klapötke, T. M.; Knizek, J.; Noth, H.; Schulz, A. Characterization, Crystals Structure of 2,4-Bis(triphenylphosphanimino)tetrazolo[5,1-*a*]-[1,3,5] triazine, and Improved Crystal Structure of 2,4,6-Triazido-1,3,5-triazine. *Eur. J. Inorg. Chem.* **1998**, 12: 2013-2016.
- [28] Huynh, M. H. V.; Hiskey, M. A.; Hartline, E. L.; Montoya, D. P.; Gilardi, R. Polyazido High-nitrogen Compounds: Hydrazo- and Azo-1,3,5-triazine. *Angew. Chem., Int. Ed.* **2004**, 43: 4924-4928.
- [29] Chapyshev, S. V.; Lavitsky, V. F.; Akimov, A. V.; Misochko, E. Ya.; Shastin, A. V.; Korchagin, D. V.; Shilov, G. V.; Aldoshin, S. M. Photochemical Generation of Triplet-triplet Nitrene Pairs in Aromatic Diazide Crystals. *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ. Chem. Bull.)* **2008**, 57: 524-531.
- [30] Huang, Y.; Zhang, Y.; Shreeve, J. M. Nitrogen-rich Salts Based on Energetic Nitroaminodiazido[1,3,5]triazine and Guanazine. *Chem. Eur. J.* **2011**, 17: 1538-1546.
- [31] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of Bond Lengths Determined by X-ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1-S19.
- [32] Meyer, R.; Köhler, J.; Homburg, A. *Explosives*. 6th ed., Wiley-VCH, Weinheim **2007**, p. 141; ISBN 978-3-527-31656-4.