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ARTICLE

Preparation and characterization of 3,5-dinitro-1*H*-1,2,4-triazole

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Neat 3,5-dinitro-1*H*-1,2,4-triazole was obtained in quantitative yield from potassium 3,5-dinitro-1,2,4-triazolate and sulfuric acid. The compound was purified by sublimation *in vacuo* at 110 °C. Pure HDNT is a hygroscopic white solid that is impact and friction sensitive and decomposes explosively upon heating to 170 °C. However, the presence of impurities might lower the decomposition temperature and increase the sensitivity of the material. Potassium 3,5-dinitro-1,2,4-triazolate was prepared from commercially available 3,5-diamino-4*H*-1,2,4-triazole with sodium nitrite and sulfuric acid. The synthesis of HDNT from 2-cyanoguanidine and hydrazine hydrate without isolation and purification of the 3,5-diamino-4*H*-1,2,4-triazole intermediate can result in the formation of azidotriazole impurities. A triclinic and a monoclinic polymorph of 3,5-dinitro-1*H*-1,2,4-triazole were found by X-ray structure determination. In addition, the crystal structure of the hydrate (HDNT)₃·4 H₂O, as well as those of several HDNT impurities and decomposition products were obtained.

Introduction

In recent years, much effort has been devoted to the development of environmentally friendly, green energetic materials (GEM).¹ Important building blocks for energetic materials are nitrogen-rich cyclic compounds, such as triazoles and tetrazoles, which can be further functionalized with explosophore groups, such as nitro, *N*-nitro, azo, or azido. 3-nitro-1*H*-1,2,4-triazole²⁻⁵ and especially 3,5-dinitro-1*H*-1,2,4-triazole (HDNT)^{6, 7} have attracted considerable interest for energetic material and high oxygen carrier applications. A significant number of compounds containing the 3,5-dinitro-1,2,4-triazolate anion have been prepared and characterized.^{5, 8-16} The synthesis of HDNT was first described in the 1960s^{8, 9} but the neat compound has not been isolated. Instead, the compound has been handled in solution only and subsequently been converted into salts containing the 3,5-dinitro-1,2,4-triazolate anion. Although related compounds, such as 3-amino-5-nitro-1*H*-1,2,4-triazole,¹⁷ 5-azido-3-nitro-1,2,4-1*H*-triazole¹⁸ and 3-nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine¹⁹ have been structurally characterized, to the best of our knowledge, the crystal structure of HDNT has not been reported so far.

As part of our research on energetic materials, we investigated the preparation of neat HDNT. Herein we report the synthesis and purification of HDNT together with the structural characterization of two of its polymorphs, as well as of a HDNT hydrate. We also identified and structurally

characterized several impurities that were found in HDNT, which was prepared according to literature methods.

Experimental Part

Caution! The compounds of this work are energetic materials that might explode under certain conditions (e.g., elevated temperature, impact, friction or electric discharge). Appropriate safety precautions,²⁰ such as the use of shields or barricades in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves and suits made from leather and/or Kevlar) should be taken at all the time when handling these materials. Pure HDNT decomposes explosively when heated above 160 °C, and certain impurities might further lower the decomposition temperature. The sublimation of HDNT should be carried-out behind a blast shield and only on a small scale. **Ignoring safety precautions may lead to serious injuries!**

Materials and apparatus

All chemicals and solvents were obtained from Sigma-Aldrich or Alfa-Aesar and were used as supplied. NMR spectra were recorded at 298 K on Bruker AMX500 or Varian VNMR5-600s spectrometers using (CD₃)₂CO or D₂O solutions in standard 5 mm o.d. glass tubes. Chemical shifts are given relative to neat tetramethylsilane (¹H, ¹³C) or neat CH₃NO₂ (¹⁴N, ¹⁵N). Raman spectra were recorded at ambient temperatures in Pyrex glass tubes in the range of 4000–80 cm⁻¹ on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm or a Cary 83 spectrometer using an Ar laser at 488 nm. Infrared spectra

were recorded in the range 4000-400 cm^{-1} on a Midac, M Series spectrometer using KBr pellets or on a Bruker Optics Alpha FT-IR ATR spectrometer. KBr pellets were prepared very carefully using an Econo mini-press (Barnes Engineering Co.). Differential thermal analysis (DTA) curves were recorded with a purge of dry nitrogen gas and a heating rate of 5 $^{\circ}\text{C}/\text{min}$ on an OZM Research DTA552-Ex instrument with the Meavy 2.2.0 software. The sample sizes were 3-15 mg. The impact and friction sensitivity data were determined with an OZM Research BAM Fall Hammer BFH-10 and an OZM Research BAM Friction apparatus FSKM-10, respectively, through five individual measurements that were averaged. Both instruments were calibrated using RDX. The samples were finely powdered materials that were not sifted.

X-ray Crystal Structure Determination

The single crystal X-ray diffraction data for **HDNT-1**, **HDNT-2**, **3**, **3·4** (co-crystals), and **5·H₂O** were collected on a Bruker SMART diffractometer, equipped with an APEX CCD detector, using Mo K_{α} radiation (graphite monochromator) from a fine-focus tube. The single crystal X-ray diffraction data for the remaining structures were collected on a Bruker SMART APEX DUO diffractometer, equipped with an APEX II CCD detector, using Mo K_{α} radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube or Cu K_{α} from a μS micro-source. The frames were integrated using the SAINT algorithm to give the hkl files corrected for L_p/decay .²¹ The absorption correction was performed using the SADABS program. The structures were solved and refined on F^2 using the Bruker SHELXTL Software Package.²²⁻²⁵ Non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-III for Windows V2.02 program.²⁶ Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1009538, 1013935-1013938 and 1045452, and from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD 427861-427864.

Synthesis of potassium 3,5-dinitro-1,2,4-triazolate (method 1)²⁷

In a 2000 mL three-necked round-bottom flask, equipped with a reflux condenser, an addition funnel and a mechanical stirrer, a mixture of sodium nitrite (220 g, 3.28 mol) in water (350 mL) was heated to 50 $^{\circ}\text{C}$ using a water bath until all sodium nitrite had dissolved. A solution of 3,5-diamino-1,2,4-triazole (DAT) (40.0 g, 0.404 mol) in water (500 mL) and concentrated sulfuric acid (36 mL) was added slowly and carefully through the addition funnel while the reaction mixture was stirred vigorously. Immediately, the reaction mixture turned red, foamed and formed some dark red precipitate. In addition, brown-orange fumes of nitric oxide were produced. After about one to two hours, the addition was completed and 80% sulfuric

acid (220 mL) was added carefully while the reaction mixture was stirred vigorously in order to avoid excessive foam formation. The reaction mixture was then refluxed for about 60 minutes and then allowed to cool to 40-50 $^{\circ}\text{C}$. Activated decolorizing charcoal (10 g) was added and the mixture stirred at ambient temperature for eight hours. The reaction mixture was then filtered over Celite 545 and the filtrate extracted six times with ethyl acetate (150 mL each). The combined organic phases were dried over magnesium sulphate and the solvent removed immediately using a rotary evaporator without (!) heating of the sample. The obtained yellow to orange oil or paste was dissolved immediately in acetone (200 mL) and the yellow solution poured onto potassium carbonate (60 g). Immediately, a gas was evolved and the mixture was stirred at ambient temperature. After about two hours, the mixture was filtered and the orange solid residue was washed extensively with acetone. The combined yellow filtrates were taken to dryness on a rotary evaporator leaving behind a yellow solid. Recrystallization from water resulted in the isolation of yellow crystals of KDNT·2H₂O that were dried *in vacuo* at 50 $^{\circ}\text{C}$ for eight hours, resulting in colourless to pale yellow KDNT¹⁶ (yield: 52.5 g, 65.9 %). DTA: 265 $^{\circ}\text{C}$ decomposition; NMR (CD₃CN) δ (ppm): ¹³C (125.76 MHz) 164.3 (C-NO₂); ¹⁴N (36.14 MHz) -20.3 (s, $\nu_{1/2}$ = 65Hz, 2N, C-NO₂), -52 (s, $\nu_{1/2}$ = 500 Hz, DNT¹⁶).

Synthesis of potassium 3,5-dinitro-1,2,4-triazolate (method 2)²⁷

In a 1000 mL three-necked round-bottom flask that was cooled by a water bath, concentrated nitric acid (80 mL) was slowly added to hydrazine hydrate (20.0 g, 0.40 mol). Water (140 mL) and 2-cyanoguanidine (33.6 g, 0.40 mol) was added and the reaction mixture heated to 50 $^{\circ}\text{C}$ for one hour. A solution of concentrated sulfuric acid (35 mL) in water (300 mL) was added, and the resulting DAT solution transferred into an addition funnel from which it was added carefully to a vigorously stirred solution of sodium nitrite (220 g, 3.28 mol) in water (350 mL) at 50 $^{\circ}\text{C}$. The procedure was continued as described above for method 1. A yellow-orange solid was obtained. Recrystallization from water resulted in the isolation of yellow crystals that were dried *in vacuo* at 50 $^{\circ}\text{C}$ for eight hours, resulting in yellow KDNT containing various impurities (yield: 54.3 g, 69% based on KDNT).

Synthesis of 3,5-dinitro-1H-1,2,4-triazole (HDNT)

A solution of KDNT (5.937 g, 30.11 mmol) in water (20 mL) was acidified with 20% sulfuric acid (50 mL) and the resulting yellow solution extracted four times with ethyl acetate (50 mL each). The combined organic phases were washed with water (50 mL), dried over magnesium sulphate and the solvent removed using a rotary evaporator. The resulting yellow oil was further dried in a high vacuum at 50-60 $^{\circ}\text{C}$ for eight hour, resulting in light-yellow, solid HDNT (yield: 4.502 g, 93.0%). HDNT of high-purity was obtained as a white solid through careful sublimation of the crude HDNT at 100-105 $^{\circ}\text{C}$ in a vacuum of less than 0.1 mTorr. The temperature was carefully

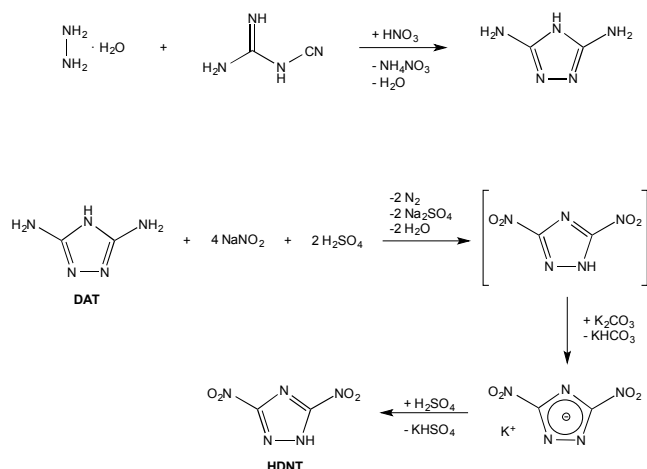
monitored in order to avoid a potentially explosive decomposition of the HDNT.

DTA: 170 °C (onset) explosive decomposition; Friction sensitivity: 144 N; Impact sensitivity: 35 J; NMR (CD₃CN) δ (ppm): ¹H (500.13 MHz) 13.6 ($\nu_{1/2}$ = 100 Hz); ¹³C (125.76 MHz) 157.1 (C-NO₂); ¹⁴N (36.14 MHz) -32.4 (s, $\nu_{1/2}$ = 20 Hz C-NO₂).

Results and discussion

Synthesis of HDNT

The synthetic route for the preparation of HDNT is shown in Scheme 1.



Scheme 1: Synthesis of HDNT

Potassium 3,5-dinitro-1,2,4-triazolate (KDNT) was prepared from 3,5-diamino-1,2,4-triazole (DAT, guanazole) through a Sandmeyer reaction²⁸ according to a modified literature procedure.²⁷ While the DAT starting material required for the synthesis of HDNT is commercially available, it can be prepared in high yield from 2-cyanoguanidine (dicyandiamide) and hydrazine hydrate.²⁹ The addition of a sulfuric acid solution of DAT to a vigorously stirred aqueous solution of excess sodium nitrite at 50-60 °C results in nitration of the triazole. It was found that the yield of the synthesis and the purity of the resulting KDNT were highly dependent on the addition rate of the DAT solution as well as the speed at which the solution was stirred. Low addition rates coupled with vigorous stirring with a mechanical stirrer instead of a magnetic stirrer resulted in higher yields and higher purity of the resulting KDNT and, subsequently, HDNT.

Extraction of the reaction mixture with ethyl acetate, followed by the immediate evaporation of the solvent using a rotary evaporator at ambient temperature resulted in the isolation of crude HDNT as yellow to dark orange oil or paste. This crude product contained various acidic impurities, which rendered it prone to decomposition. On several occasions, samples of crude HDNT started to decompose exothermically within minutes once the solvent had been removed. These samples started to heat up very fast, reaching temperature in excess of 60 °C and

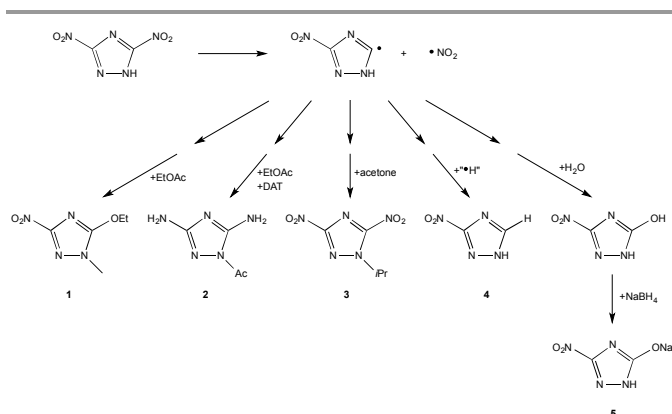
released large quantities of brown NO₂ gas. It was possible to quench this potentially dangerous decomposition reaction through the addition of large amounts of water. The resulting aqueous HDNT solutions contained various amounts of decomposition products and were discarded. The decomposition of the crude HDNT was avoided by immediately re-dissolving the dark orange evaporation residue in acetone. When the resulting yellow acetone solution was treated with an excess of potassium carbonate, carbon dioxide was evolved and the mixture turned orange. After filtration and evaporation of the solvent a yellow to orange solid was obtained. Recrystallization of the solid from water resulted in the isolation of the dihydrate KDNT·2H₂O as a crystalline solid which could be dried at 50 °C *in vacuo*.¹⁶

Potassium 3,5-dinitro-1,2,4-triazolate was dissolved in 5 M sulfuric acid and the solution extracted with ethyl acetate. The solvent was removed using a rotary evaporator, leaving behind yellow, very hygroscopic and deliquescent HDNT. According to its ¹H and ¹³C NMR spectra, the HDNT prepared in this way contains various amounts of impurities. As already described before, it was possible to minimize the amount of impurities through careful control of the reaction condition in the KDNT synthesis. In addition, it was also noted that the amount of impurities increases the longer HDNT remains dissolved in ethyl acetate. HDNT is strongly acidic and catalyses the cleavage of ethyl acetate, resulting in the formation of acetic acid which in turn appears to promote the decomposition of HDNT. It is therefore recommended to remove the ethyl acetate solvent immediately after each extraction step.

The crude yellow HDNT was further purified by sublimation *in vacuo* at 100-110 °C. Very pure 3,5-dinitro-1H-1,2,4-triazole was obtained as an off-white amorphous or colourless crystalline solid that is hygroscopic and deliquescent. The sublimation of HDNT should only be attempted on a small scale and behind blast shields. In addition, it is necessary to carefully monitor and control the temperature during the sublimation in order to avoid a possible explosion as pure HDNT decomposes explosively upon heating to 170 °C (DTA onset). The friction and impact sensitivity of HDNT was determined as 144 N and 35 J, respectively. However, it was found that certain impurities might increase the sensitivity of the material and also lower its explosion temperature. For example, one sample of crude HDNT showed an explosion temperature of 150 °C with friction and impact sensitivities of 130 N and 30 J, respectively.

The isolation of DAT prepared from 2-cyanoguanidine and hydrazine hydrate is complicated and labour intensive.²⁹ Chernyshev *et al.* developed a procedure for the synthesis of HDNT from 2-cyanoguanidine and hydrazine hydrate without isolation of the DAT intermediate.²⁷ Following this procedure, we found it very difficult to obtain pure HDNT. Even after repeated sublimation, the resulting HDNT always had a greenish to light yellow-orange colour and contained various unidentified impurities. A major concern is that HDNT prepared according to this procedure showed significantly lower explosion temperatures and higher impact sensitivities

than HDNT that was prepared from commercial DAT. The ^{14}N NMR and vibrational spectra of these samples indicated the presence of azido compounds and single crystals of 5-azido-3-nitro-1*H*-1,2,4-triazolate were obtained from such an HDNT sample.



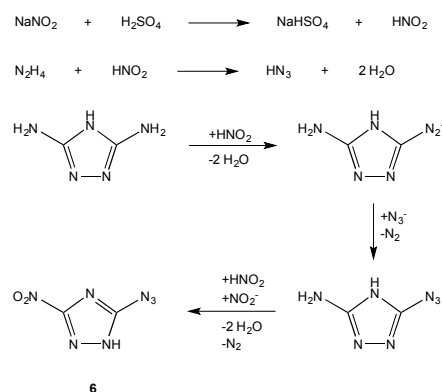
Scheme 2: Possible pathways for the formation of the HDNT impurities 1-5.

Impurities and decomposition products of HDNT

During the course of this work, several HDNT impurities and/or decomposition products have been identified by their X-ray crystal structures. However, no efforts were made to purify and further characterize these compounds other than by their X-ray crystal structure. From various batches of HDNT that have been prepared by nitration of DAT, crystals of 5-ethoxy-1-methyl-3-nitro-1*H*-1,2,4-triazole **1**, 1-acetyl-3,5-diamino-1*H*-1,2,4-triazole **2**, 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and a co-crystal of 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and 3-nitro-1*H*-1,2,4-triazole **4** were obtained. The crystals of these compounds were generally obtained through recrystallization of crude HDNT from acetonitrile, ethanol, ethyl acetate, or acetone. A small amount of crystals of sodium 3-nitro-1,2,4-triazol-5-olate **5** were obtained when a batch of crude HDNT was treated with NaBH_4 ,¹⁰ and the resulting product was recrystallized from acetonitrile. The formation of compounds **1-5** can be rationalized through a radical decomposition of HDNT under the formation of NO_2 , followed by reaction of the resulting radical with the solvents ethyl acetate, water or acetone (Scheme 2). This is consistent with the observation that the exothermic decomposition of crude HDNT involves the release of large quantities of brown $\text{NO}_2/\text{N}_2\text{O}_4$ gas.

Batches of HDNT that had been prepared directly from 2-cyanoguanidine and hydrazine hydrate generally contained more impurities than HDNT that had been prepared by nitration of commercial DAT. It is troublesome that not even through repeated sublimation it was possible to obtain pure HDNT from these batches. It is important to note that HDNT that had been prepared from 2-cyanoguanidine and hydrazine hydrate consistently showed significantly lower explosion temperatures and higher impact sensitivities than the one prepared from commercial DAT. The ^{14}N NMR spectra of HDNT prepared from 2-cyanoguanidine showed weak resonances at -146 ppm

and -232 ppm and the vibrational spectra of this HDNT showed bands at around 2100 cm^{-1} . These spectroscopic data indicate the presence of azido compounds, which would explain the increased sensitivity of the material. Conclusive evidence for the presence of an azido impurity was found when an aqueous solution of HDNT, which had been prepared from 2-cyanoguanidine was treated with PPN^+Cl^- ,¹⁰ and the resulting precipitate was recrystallized from acetone ($\text{PPN}^+ = \text{bis}(\text{triphenylphosphine})\text{iminium}$, $((\text{Ph}_3\text{P})_2\text{N}^+)$). The X-ray structure determination of a resulting single crystal resulted in the structure of PPN^+ 3,5-dinitro-1*H*-1,2,4-triazolate in which the anion showed a 25 % substitution disorder with 5-azido-3-nitro-1,2,4-triazolate (AzNT). In another instance, the structure of a crystal containing equal amounts of 5-azido-3-nitro-1*H*-1,2,4-triazole (HAzNT) and PPN^+ 5-azido-3-nitro-1,2,4-triazolate (PPNAzNT) was obtained. The formation of the azido compounds can be rationalized according to Scheme 3.



Scheme 3: Formation of azidotriazoles

DAT, prepared through the reaction of 2-cyanoguanidine and hydrazine hydrate (Scheme 1), which has not been isolated and purified, contains small amounts of unreacted hydrazine hydrate. The reaction of nitrous acid, formed from sodium nitrite and sulfuric acid, with hydrazine hydrate results in the formation of hydrazoic acid,³⁰ which in turn will form azidotriazoles in the Sandmeyer reaction.

X-ray Crystal Structures

Single crystals suitable for X-ray crystal structure determination were obtained for two polymorphs of neat HDNT and the hydrate (HDNT)·4 H_2O . In addition, crystal structures were obtained of the HDNT impurities or decomposition products 5-ethoxy-1-methyl-3-nitro-1*H*-1,2,4-triazole **1**, 1-acetyl-3,5-diamino-1*H*-1,2,4-triazole **2**, 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3**, a co-crystal of 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and 3-nitro-1*H*-1,2,4-triazole **4**, sodium 3-nitro-1,2,4-triazol-5-olate **5**, as well as $\text{PPN}^+[\text{H}(\text{AzNT})_2]^-$ **6** (AzNT = 5-azido-3-nitro-1,2,4-triazolate). The relevant data and parameters for the X-ray structure determinations and refinements of the investigated compounds are summarized in Tables 1-3. Further crystallographic data and representations of the unit cells for all crystal structures can be found in the Electronic Supplementary Information.

Table 1: Crystallographic data for the three HDNT crystal structures.

	HDNT-1	HDNT-2	(HDNT) ₃ ·4 H ₂ O
formula	C ₂ HN ₃ O ₄	C ₂ HN ₃ O ₄	C ₆ H ₁₁ N ₁₅ O ₁₆
mol wt [g/mol]	159.08	159.08	549.30
temp [K]	140(2)	140(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 1
a [Å]	6.1585(14)	8.7465(15)	6.1906(2)
b [Å]	9.083(2)	8.9684(16)	9.5492(3)
c [Å]	9.858(2)	11.942(2)	9.5656(3)
α [deg]	90	111.927(2)	111.377(2)
β [deg]	93.892(3)	96.726(3)	93.467(2)
γ [deg]	90	93.853(2)	90.765(3) ^a
V [Å ³]	550.2(2)	856.7(3)	525.22(4)
Z	4	6	1
ρ_{calc} [g/cm ³]	1.920	1.850	1.737
μ [mm ⁻¹]	0.183	0.176	0.169
F(000)	320	480	280
reflns collected	11484	5462	16510
ind reflns	1470	3826	5371
<i>R</i> _{int}	0.0308	0.0196	0.0241
no. of parameters	103	302	343
<i>R</i> ₁ [I > 2 σ (I)]	0.0327	0.0499	0.0251
w <i>R</i> ₂ [I > 2 σ (I)]	0.0831	0.1170	0.0554
GOF	1.050	1.036	1.015

Colourless crystals of 3,5-dinitro-1*H*-1,2,4-triazole that were obtained by sublimation *in vacuo* belong to space group *P*2₁/*c* (HDNT-1). The unit cell of this monoclinic modification contains four molecules per unit cell (*Z* = 4). A triclinic modification with six HDNT molecules per unit cell (space group *P* $\bar{1}$) was obtained by recrystallization from anhydrous acetonitrile (HDNT-2). The density of the triclinic modification (1.850 g/cm³) is lower than the one of the monoclinic modification (1.920 g/cm³). Crystals of the hydrate (HDNT)₃·4 H₂O were obtained by recrystallization of neat HDNT from moist acetone. The hydrate crystallizes in the triclinic space group *P*1 with one formula unit per unit cell. Its density of 1.737 g/cm³ is lower than the one of the two polymorphs of pure HDNT.

The geometry of the HDNT molecule remains virtually unchanged between the three different crystal structures. Selected bond lengths and bond angles of the molecule are listed in Table 2. The observed N-N bond distances range from 1.343(4) to 1.3471(13) Å and are shorter than the ones found for the 3,5-dinitro-1,2,4-triazolate (DNT) anion (1.350(2) to 1.368(5) Å).¹⁶ The five-membered ring contains two shorter C-N distances (C1-N2 and C2-N3) of 1.309(5) to 1.325(5) and two longer C-N distances (C1-N3 and C2-N1) of 1.3267(13) to 1.3479(13) Å. This is consistent with the common description of the 1*H*-1,2,4-triazole ring having double bonds between the 2-3 and 4-5 positions.

Table 2: Selected bond lengths [Å] and angles [°] for HDNT in the crystal structures.

	HDNT-1	HDNT-2 ^a	(HDNT) ₃ ·4H ₂ O ^a
N1-N2	1.3471(13)	1.346(3)	1.343(4)
N1-C2	1.3267(13)	1.330(3)	1.329(5)
N2-C1	1.3169(13)	1.313(3)	1.325(5)
N3-C1	1.3479(13)	1.346(3)	1.336(5)
N3-C2	1.3118(13)	1.312(3)	1.309(5)
C1-N4	1.4544(14)	1.451(3)	1.451(5)
C2-N5	1.4520(14)	1.445(3)	1.452(5)
N4-O1	1.2191(13)	1.218(3)	1.225(4)
N4-O2	1.2260(12)	1.221(3)	1.221(4)
N5-O3	1.2221(12)	1.213(3)	1.216(4)
N5-O4	1.2204(13)	1.223(3)	1.228(4)
N1-N2-C1	100.97(8)	101.1(2)	101.6(3)
N2-C1-N3	117.43(9)	118.0(2)	117.3(3)
C1-N3-C2	99.66(8)	99.0(2)	99.3(3)
N3-C2-N1	112.82(9)	113.3(2)	117.3(3)
C2-N1-N2	109.11(8)	108.6(2)	107.9(3)
O1-N4-O2	125.87(10)	125.7(2)	125.8(3)
O3-N5-O4	126.99(10)	126.2(2)	125.9(3)

^a Values given for one of the independent molecules in the asymmetric unit.

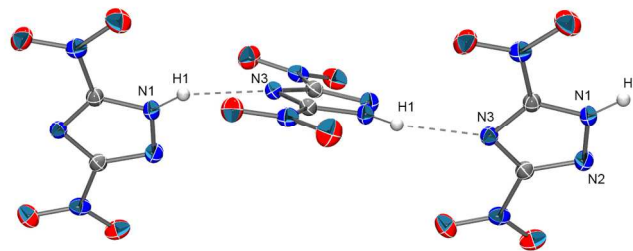


Figure 1: Part of a chain made through hydrogen bonding in the monoclinic crystal structure HDNT-1. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. The N1-N3 distance is 2.837(1) Å.

In the solid-state structure of the monoclinic modification HDNT-1, individual HDNT molecules are linked through single N1-H1...N3 hydrogen bonds, resulting in chains in which the individual HDNT molecules are rotated by 61° from each other (Figure 1). The chains are oriented along the *c*-axis of the crystal.

The hydrogen bonding of the triclinic polymorph HDNT-2 is more complex than the one of monoclinic HDNT-1. The molecules form chains along the (011) direction of the crystal in which units of two coplanar HDNT molecules are linked through hydrogen bonds to other units that are rotated by 75°. In addition, every HDNT molecule of a chain is linked to a single HDNT molecule through a hydrogen bond at the nitrogen atom in the 4-position of the triazole ring (N3 and

N13). A part of the hydrogen bonding in the triclinic HDNT polymorph is depicted in Figure 2.

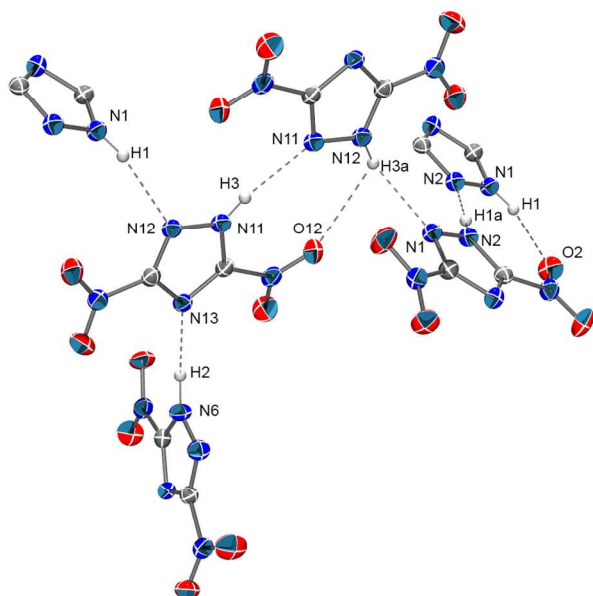


Figure 2: Hydrogen bonding in the crystal structure of triclinic HDNT-2. Thermal ellipsoids are shown at the 50% probability level. Some nitro groups have been omitted for clarity. Hydrogen atoms are depicted as spheres of arbitrary radius. The hydrogen atoms H1/H1a and H3/H3a show a 1:1 positional disorder, only one of the disordered atoms is shown per molecule. Selected distances (Å): N1-N12 2.959(2), N2-N2 2.975(3), N6-N13 2.858(3), N11-N11 2.971(3).

As expected, the solid-state structure of the hydrate (HDNT)₃·4 H₂O is dominated by hydrogen bonding. It is interesting to note that all hydrogen bonds involve water molecules and that no direct bonds between HDNT molecules can be observed. A part of the hydrogen bonding in (HDNT)₃·4 H₂O is shown in Figure 3.

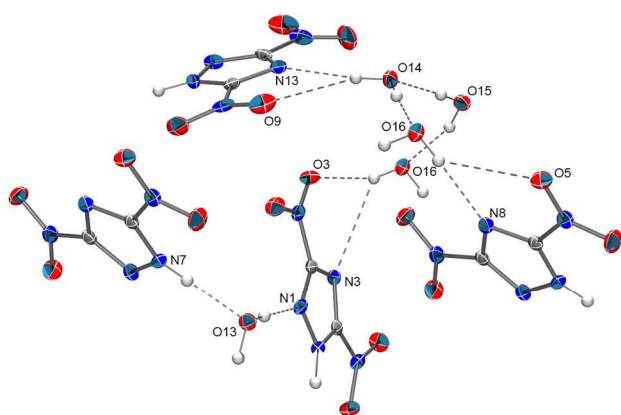


Figure 3: Hydrogen bonding in the crystal structure of (HDNT)₃·4 H₂O. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected distances (Å): N1-O13 2.849(4), N7-O13 2.587(4), N8-O16 2.882(3), N13-O14 2.984(5), O3-O16 2.927(4).

The crystallographic data for 5-ethoxy-1-methyl-3-nitro-1*H*-1,2,4-triazole **1**, 1-acetyl-3,5-diamino-1*H*-1,2,4-triazole **2**, 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3**, sodium 3-nitro-1,2,4-triazol-5-olate **5**, as well as the co-crystals of 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and 3-nitro-1*H*-1,2,4-triazole **4**, and 5-azido-3-nitro-1,2,4-triazole **6** and PPN⁺ 5-azido-3-nitro-1,2,4-triazolate **7** are listed in Table 3. The crystallographic data for the structure of PPN⁺ 3,5-dinitro-1*H*-1,2,4-triazolate that is disordered with 5-azido-3-nitro-1,2,4-triazolate is given in the ESI.

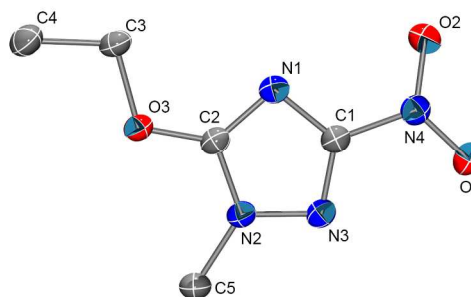


Figure 4: Crystal structure of 5-ethoxy-1-methyl-3-nitro-1*H*-1,2,4-triazole **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): C1-N1 1.351(2), C2-N1 1.326(2), N2-C2 1.346(2), N3-C1 1.311(2), C1-N4 1.455(2), N2-N3 1.364(2), N2-C5 1.461(2), N4-O2 1.223(2), N4-O3 1.227(2), C2-O1 1.321(2), C3-O1 1.467(2), C1-N1-C2 100.1(1), N1-C2-N2 117.7(1), C2-N2-N3 109.1(1), N2-N3-C1 100.9(1), N3-C1-N1 118.2(1), O2-N4-O3 125.4(1).

5-Ethoxy-1-methyl-3-nitro-1*H*-1,2,4-triazole **1** crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules per unit cell. In the solid-state structure, the molecules are aligned along parallel planes. The shortest distances between molecules of neighbouring planes are 3.007(2) Å (O2-O2') and 3.299(2) Å (C1-C2').

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Table 3: Crystallographic data for the crystal structures of the identified HDNT impurities and decomposition products.

	1	2	3	3·4	5·H ₂ O	6
formula	C ₅ H ₈ N ₄ O ₃	C ₄ H ₇ N ₅ O	C ₅ H ₇ N ₅ O ₄	C ₇ H ₈ N ₉ O ₆	C ₂ H ₃ N ₄ NaO ₄	C ₄₀ H ₃₁ N ₁₅ O ₄ P ₂
mol wt [g/mol]	172.15	141.15	201.16	314.22	170.07	847.74
temp [K]	100(2)	100(2)	130(2)	130(2)	140(2)	100(2)
λ [Å]	1.54178	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/c</i>	<i>P</i> $\bar{1}$
a [Å]	6.6336(8)	5.25150(10)	9.4402(19)	9.467(2)	10.7152(18)	11.1121(11)
b [Å]	7.6993(8)	7.69060(10)	10.611(2)	11.270(3)	8.3768(14)	12.5247(12)
c [Å]	8.5129(9)	8.49150(10)	17.296(4)	23.865(6)	6.7473(11)	16.0476(16)
α [deg]	83.636(5)	67.2290(10)	90	90	90	70.424(2)
β [deg]	73.035(5)	85.4460(10)	90	90	97.084(2)	72.600(2)
γ [deg]	65.784(7)	70.1300(10)	90	90	90	83.653(2)
V [Å ³]	379.25(7)	296.854(8)	1732.5(6)	2546.2(10)	601.01(17)	2007.9(3)
Z	2	2	8	8	4	2
ρ _{calc} [g/cm ³]	1.508	1.579	1.542	1.639	1.880	1.402
μ [mm ⁻¹]	1.086	0.122	0.134	0.144	0.232	0.172
F(000)	180	148	832	1288	344	876
reflns collected	8069	35219	13391	15158	6577	48323
ind reflns	1315	2865	2124	3102	1444	12028
R _{int}	0.0241	0.0256	0.0393	0.0323	0.0417	0.0605
no. of parameters	141	109	129	201	112	550
R ₁ [I > 2σ(I)]	0.0300	0.0288	0.0435	0.0551	0.0433	0.0692
wR ₂ [I > 2σ(I)]	0.0823	0.0807	0.0943	0.1588	0.1008	0.1441
GOF	1.055	1.123	1.024	1.052	1.055	1.026

In the solid-state structure of 1-acetyl 3,5-diamino-1*H*-1,2,4-triazole **2**, the molecules are associated by N-H...N and N-H...O hydrogen bonds, forming planar layers (Figure 5). The shortest distances between molecules of neighbouring planes are 3.1592(8) Å (C3-N4') and 3.3351(2) Å (N3-N4').

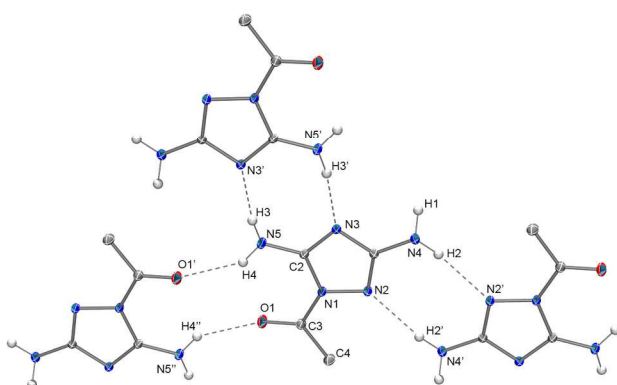


Figure 5: Intermolecular hydrogen bonding in the crystal structure of 1-acetyl 3,5-diamino-1*H*-1,2,4-triazole **2**. Thermal ellipsoids are shown at the 50% probability level. Some hydrogen atoms have been omitted for clarity. Selected distances (Å): N2-N4' 3.0771(5), N3-N5' 3.0160(5), N5-O1' 3.0174(6).

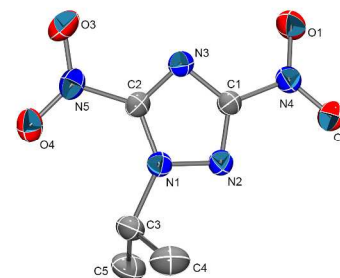


Figure 6: Crystal structure of 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): C2-N3 1.311(2), C1-N3 1.334(2), C2-N1 1.345(2), C1-N2 1.318(2), N1-N2 1.349(2), C2-N5 1.456(2), C1-N4 1.451(2), N4-O1 1.219(2), N4-O2 1.218 (2), N5-O3 1.2147(19), N5-O4 1.221 (2), N1-C3 1.491(2), N1-N2-C1 101.75(13), N2-N1-C2 107.67(12), C2-N3-C1 99.91(13), N3-C2-N1 113.05(14), N3-C1-N2 117.62(14), O1-N4-O2 124.94(14), O3-N5-O4 125.38(15).

1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** crystallizes in the orthorhombic space group *Pbca* with eight symmetry related molecules in the unit cell (*Z* = 8). The molecule is depicted in Figure 6. The five-membered ring is almost co-planar with both

nitro-groups (dihedral angles of 5.7° and 14.0°) and is perpendicular to the plane of the isopropyl group.

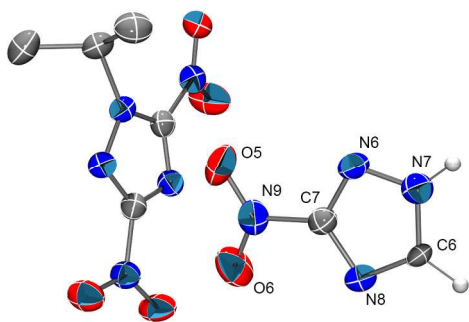


Figure 7: Asymmetric unit of the co-crystal of 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and 3-nitro-1*H*-1,2,4-triazole **4**. Thermal ellipsoids are shown at the 50% probability level. Some hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles ($^\circ$):

Similar to pure 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3**, the compounds 1-(*i*-propyl)-3,5-dinitro-1*H*-1,2,4-triazole **3** and 3-nitro-1*H*-1,2,4-triazole **4** co-crystallizes in the orthorhombic space group *Pbca* with eight symmetry related formula units per unit cell ($Z = 8$). However, the unit cell of the co-crystal **3·4** ($V = 2546.2(10) \text{ \AA}^3$) is almost 50% larger than that of the neat **3** ($V = 1732.5(6) \text{ \AA}^3$). The asymmetric unit of the crystal structure **3·4** is depicted in Figure 7. The closest distances between molecules **3** and **4** in the crystal structure are 2.820(3) and 2.854(3) Å. The geometry of compound **3** remains virtually unchanged going from the structure of the neat compound **3** to the co-crystal **3·4**.

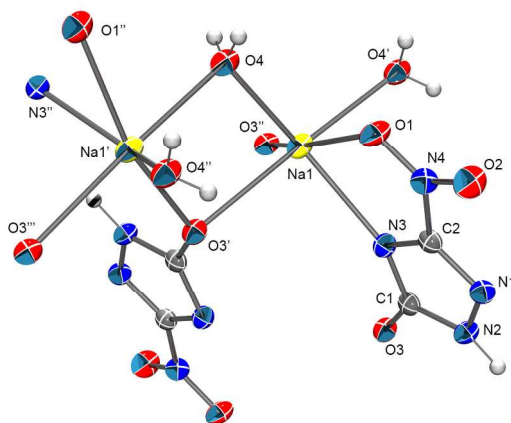


Figure 8: Crystal structure of sodium 3-nitro-1,2,4-triazol-5-olate **5·H₂O**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are depicted as spheres of arbitrary radius. Selected distances (Å) and angles ($^\circ$):

Sodium 3-nitro-1,2,4-triazol-5-olate **5** crystallizes as monohydrate in space group $P2_1/c$ with four symmetry related formula units in the unit cell ($Z = 4$). Not surprisingly, the crystal structure does not consist of isolated ions but is dominated by interactions between the sodium cation and the triazol-5-olate anion as well as the water molecule. The solid-state structure of **5·H₂O** is depicted in Figure 8.

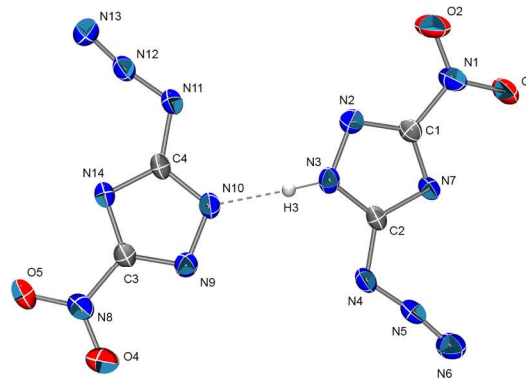


Figure 9: The anion part of the crystal structure **6**. The hydrogen atom is depicted as sphere of arbitrary radius and shows a 1:1 positional disorder located at N3 and N10. Only one of the disordered positions is shown. Selected distances (Å) and angles ($^\circ$): C1-N1 1.445(3), C3-N8 1.451(3), C2-N4 1.395(3), C4-N11 1.400(3), N3-N10 2.655(3), N4-N5 1.247(3), N5-N6 1.123(3), N11-N12 1.245(3), N12-N13 1.127(3), N4-N5-N6 171.4(3), N11-N12-N13 171.5(3).

When a sample of HDNT, which had been prepared from hydrazine hydrate, was reacted with PPN^+Cl^- and the resulting PPN^+DNT^- was recrystallized from acetone, single crystals of $\text{PPN}^+[\text{H}(\text{AzNT})_2]^-$ ($\text{AzNT} = 5\text{-azido-3-nitro-1,2,4-triazolate}$) were obtained. The solid-state structure of **6** contains isolated PPN^+ cations and anions in which two AzNT^- parts that are associated through a hydrogen bond between the N atoms in the 1-position of both triazole moieties (N-N distance: 2.655(3) Å). Both 5-azido-3-nitro-1,2,4-triazolate moieties have essentially identical geometries and are depicted in Figure 9. The H-atom shows in a 1:1 positional disorder between both triazolate moieties, occupying positions near N3 and N10.

Conclusions

The important energetic building block 3,5-dinitro-1*H*-1,2,4-triazole (HDNT) was structurally characterized for the first time. Neat HDNT was obtained in quantitative yield from potassium 3,5-dinitro-1,2,4-triazolate and sulfuric acid, followed by extraction with ethyl acetate. The compound was isolated as a pale yellow solid, which can be further purified by sublimation to give colourless crystals. Pure HDNT is a hygroscopic white solid that decomposes explosively upon heating to 170°C . However, the presence of impurities might lower the decomposition temperature and increase the sensitivity of the material.

Potassium 3,5-dinitro-1,2,4-triazolate was prepared from commercially available 3,5-diamino-1,2,4-triazole through a Sandmeyer reaction with sodium nitrite and sulfuric acid. The synthesis of HDNT from 2-cyanoguanidine and hydrazine hydrate in one step without isolation and purification of the 3,5-diamino-1,2,4-triazole intermediate is not recommended as it might lead to the formation of very sensitive azidotriazole impurities.

3,5-dinitro-1*H*-1,2,4-triazole was characterized by its multi-nuclear NMR and vibrational spectra, as well as its X-ray

crystal structure. The crystal structures of several HDNT impurities and decomposition products were obtained.

Acknowledgements

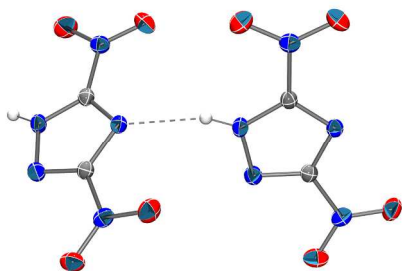
The Office of Naval Research (ONR) and the Defence Threat Reduction Agency (DTRA) financially supported this work. We acknowledge NSF CRIF grant 1048807 for an X-ray diffractometer. We thank Profs. G. K. S. Prakash and G. A. Olah for their help and stimulating discussions.

Notes and references

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Electronic Supplementary Information (ESI) available: Vibrational data and crystallographic reports including packing diagrams. See DOI: 10.1039/b000000x/

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Neat 3,5-dinitro-1*H*-1,2,4-triazole was obtained in quantitative yield from potassium 3,5-dinitro-1,2,4-triazolate and sulfuric acid. The compound was purified by sublimation *in vacuo* at 110 °C. Pure HDNT is a hygroscopic white solid that is impact and friction sensitive and decomposes explosively upon heating to 170 °C. However, the presence of impurities might lower the decomposition temperature and increase the sensitivity of the material. Potassium 3,5-dinitro-1,2,4-triazolate was prepared from commercially available 3,5-diamino-4*H*-1,2,4-triazole with sodium nitrite and sulfuric acid. The synthesis of HDNT from 2-cyanoguanidine and hydrazine hydrate without isolation and purification of the 3,5-diamino-4*H*-1,2,4-triazole intermediate can result in the formation of azidotriazole impurities. A triclinic and a monoclinic polymorph of 3,5-dinitro-1*H*-1,2,4-triazole were found by X-ray structure determination. In addition, the crystal structure of the hydrate (HDNT)₃·4 H₂O, as well as those of several HDNT impurities and decomposition products were obtained.