R1-A.1: Characterization of Explosives & Precursors

I. PARTICIPANTS INVOLVED FROM JULY 1, 2019 TO JUNE 30, 2020

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II. PROJECT DESCRIPTION

A. Project Overview

This project sought to determine the physical properties, synthesis, and destruction mechanisms of improvised explosives, often called homemade explosives (HMEs). In Year 7, we performed further characterization on erythritol tetranitrate (ETN) and on the nitro-sugars mannitol and sorbitol hexanitrate and HMTD. For ETN, we examined its synthesis and sought stable isotope signatures that might allow attribution to particular groups. For the sugars we are attempting to establish basic properties and observing different polymorphs. The existence of polymorphs was also found with HMTD.

B. State of the Art and Technical Approach

Stable isotope analysis is a technique capable of determining the subtle differences between the stable isotope ratios of hydrogen ($^2H/^1H$), carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), oxygen ($^{18}O/^{16}O$), and, with special modifications, sulfur ($^{34}S/^{32}S$). Stable isotope analyses are important for provenance studies, where minute differences in isotope ratios can determine production location. Stable isotope ratio mass spectrometry (IRMS) has been considered as a forensic science technique for attribution that has been applied to illicit drugs, chemical weapon agents, and recently to explosives. Now we have used IRMS to examine the signatures indicative of the method by which the homemade explosive erythritol tetranitrate (ETN) is synthesized. In an exhaustive study conducted by our lab at URI and the Netherlands Forensic Institute, we found only IRMS provided the unique signatures necessary for attribution to a particular synthetic route.[1,2] (Paper accepted in *International Journal of Forensic Science*)

The hexanitrates of the sugars mannitol and sorbitol were studied to resolve issues regarding their relative stability. During the course of preparing and characterizing these materials, a new polymorph of each was

discovered. Mannitol hexanitrate (MHN) that had been exposed to elevated temperatures exhibited a different crystal structure seen by X-ray diffraction and Raman spectroscopy, but no differences in the thermal behavior were observed. Sorbitol hexanitrate (SHN) has two distinct structures that are visibly different and that differ in structural spectra and thermal behavior. The thermal stability of these nitrate esters was also examined; despite being isomers, SHN and MHN differ in their long-term thermal stability. (Manuscript in preparation)

While exploring the synthesis pathway of HMTD, an unexpected new route for preparing HMTD was found through the reaction of formaldehyde, hydrogen peroxide, and ammonium hydroxide. The recovered HMTD was characterized by Raman spectroscopy and powder X-ray diffraction and found to be a different crystal structure. This HMTD is believed to be the result of a different confirmation of the HMTD, only previously predicted by computational methods and through the use of specialized NMR reagents. (Paper submitted, see R1-A.1 Appendix)

C. Major Contributions

- Extensive TATP characterization—safe-scent aids, gentle destruction (Years 1–4)

- The limitations of certain oxidizers in terms of terrorist use (Years 1–6)

- Baseline information about HMTD chemical properties and reactivity (Years 1–7)

- Identifying the hazards of humidity to HMTD (Years 2–3)

- Formation mechanism of HMTD initiated (Years 2–3)

- Gentle destruction methods for HMTD (Years 3–4)

- Safe-scent aids for HMTD (Years 3–4)

- Revealing modes by which peroxide explosive signature can be masked by solvent (Years 3–4)

- Canine training aids for TATP and HMTD (Years 3–4)

- Determining best practices in analyzing peroxide explosives (Years 5–6)

- An extremely reliable standard for HMTD quantification work has been developed (Year 5)

- Examination of ETN, tracking synthesis routes, and attribution (Years 6–7)

- Creating new method of "neutralizing" any small-scale (1-lb. scale) hazard SCHMOO & SCHMOO 2 (Years 6–7)

- Examination of toxicity issues for canines (Year 5) and humans (Years 6–7)

- Development of a new method for "injecting" nonvolatile explosives (e.g., chlorate) into IMS (Year 7)

D. Milestones

A major milestone was the examination of the six-carbon sugars. This study is close to complete. We expect to submit a paper by the end of the summer.

HMTD transformations required laboratory study, and that student has not been able to come into the lab due to COVID-19.

The book chapter(s) are still in progress. Cover and foreword have been submitted.

E. Final Results at Project Completion (Year 7)

Thirty-five papers on HME (TATP, HMTD, ETN, AN, UN), one full patent (safe-scent training aids), two full patents in process (SCHMOO and ADI), and one provisional patent (sheet pyrotechnics) in process.

Nine PhD, three MS, and numerous BS students have graduated, and many have entered the homeland security enterprise.

Safe-scent explosive training aids are on the market and have recently been suggested for authentication aids for TSA.

SCHMOO (Safe Control of Hazardous Materials or Others Onsite) has received a great deal of free publicity, and we expect to find a vendor for it shortly.

Ambient desorption ionization (ADI) with an additional task order from DHS S&T is being integrated into the Smiths 6000 ETD.

Explosive database has over a thousand subscribers.

It is difficult to separate these projects by project number. The basic chemical characteristic had to be established in R1-A.1 before any work could progress on other projects.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

Characterization of HMEs is an ongoing research effort within DHS, involving vendors and associated researchers. It impacts the entire HSE. In many cases, our methods of analysis have led the way for other members of the HSE. Our studies on the extreme sensitivity of HMTD to moisture and acidity may have prevented mishandling in a number of laboratories. Many vendors of explosives detection instrumentation have requested access to the explosives database, or have asked for help in working with various materials characterized in this project. The characterization of these materials is published on our database (URI Explosives Database), which is subscribed to by over a thousand people, about a quarter of which are from US government agencies. Furthermore, our work is cited in the DHS HME Safety Protocols Handbook, and we were invited to participate in the DHS Chemical Security Analysis Center & Explosives Division 1st Inter-agency Explosives Terrorism Risk Assessment Working Group. We have worked directly with ten vendors of explosive detection instrumentation.

B. Status of Transition at Project End

Safe-scent aids have been licensed to Detectachem. ADI is moving forward with Smiths Detection. Many papers on HME are available in the open literature.

C. Transition Pathway and Future Opportunities

The ADI-Smiths project is ongoing with a task order through Northeastern.

D. Customer Connections

The connections to DHS (central), TSL, and TSA are strong. To date the FBI is the major agency outside of DHS that is aware of the details of this project.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. *Education and Workforce Development Activities*

1. Course, Seminar, and/or Workshop Development

   a. Since June 2019, we have held seven classes with 105 attendees. The new class was CTH.

   b. Dr. Oxley gave an invited lecture at the International Pyrotechnic Symposium in Tours, FR, summer 2019.

2. Student Internship, Job, and/or Research Opportunities

   a. Five graduate students who were supported by ALERT and graduated are now at Signature Science supporting TSL (two students), the Navy Research Lab (two students), and Los Alamos National Laboratory (one student).

3. Interactions and Outreach to K–12, Community College, and/or Minority-Serving Institution Students or Faculty

   a. We ran two two-week workshops introducing high school students to chemical analysis. This program will end with the end of ALERT.

4. Training to Professionals or Others

   a. Since June 2019 we have held seven classes with 105 attendees. The new class was CTH.

B. *Peer Reviewed Journal Articles*

1. Bezemer, K., McLennan, L., van Duin, L., Kuijpers, C.-J., Koeberg, M., van den Elshout, J., van der Heijden, A., Busby, T., Yevdokimov, A., Schoenmakers, P., Smith, J., Oxley, J., & van Asten, A. "Chemical Attribution of the Home-Made Explosive ETN—Part I: Liquid Chromatography–Mass Spectrometry Analysis of Partially Nitrated Erythritol Impurities." *Forensic Science International*, *307*(110102), December 2019. https://doi.org/10.1016/j.forsciint.2019.110102.

2. Rettinger, R.C., Porter, M., Canaria, J., Smith, J.L., & Oxley, J.C. "Fuel-Oxidizer Mixtures: A Lab and Field Study." *Journal of Energetic Materials*, *38*(2), 23 October 2019, pp. 170–190. https://doi.org/10.1080/07370652.2019.1679282.

Pending –

1. Bezemer, K., McLennan, L., van Duin, L., Kuijpers, C.-J., Koeberg, M., van den Elshout, J., van der Heijden, A., Busby, T., Yevdokimov, A., Schoenmakers, P., Smith, J., Oxley, J., & van Asten, A. "Chemical Attribution of the Home-made Explosive ETN—Part II: Use of Isotopic Ratio." *Forensic Science International*, in preparation.

2. Gonsalves, M.D., Colizza, K., Smith, J., & Oxley, J.C. "In Vitro Metabolism and Enzyme Phenotyping of Triacetone Triperoxide (TATP) in Humans." *Forensic Toxicology*, submitted June 2020.

3. McLennan, L., Smith, J., & Oxley, J. "A New Polymorph of HMTD." Manuscript in preparation.

C. *Peer Reviewed Conference Proceedings*

1. Oxley, J.C., Smith, J.L., Colizza, K., & Gonsalves, M. "In Vitro Metabolism of TATP." *NTREM*, April 2020, meeting proceedings, meeting canceled.

D. *Seminars*

1. Oxley, J. "Evaluation of Explosive Characteristics via Energy-Resolved MS." *ISADE*, April 2020 canceled.

2. Yevdokimov, A. "A Novel Approach to IMS Sampling and Analysis." Student Award Winner, *ISADE*, April 2020 canceled.

E. *Poster Sessions*

1. Gonsalves, M. "Metabolism of TATP." *ISADE*, April 2020 canceled.

F. *Interviews and/or News Articles*

1. CBS News. "'Innovative Checkpoint' and 'digital dog nose': TSA tests new security technology." *CBS News*, 25 November 2019. https://www.cbsnews.com/news/tsa-testing-advanced-airport-security-technology-digital-dog-nose-innovation-checkpoint/.

2. Interview by Scripps the NOW November 2019.

G. *Other*

1. Consulted with American Chemical Society on July 2019 script for Gunpowder & Moon Smell; January 2020 advice on Explosive Vapor Detection.

H. *New and Existing Courses Developed and Student Enrollment*

New or Existing	Type	Title	Description	Enrollment
Existing	Short course	Explosive Stability	Analysis & safety of explosives	3
Existing	Short course	Propellants	Propellants	12
Existing	Short course	Fundamentals of Explosives	Fundamentals of explosives	26
Existing	Short course	Explosive Components	Device design	17
Existing	Short course	Explosive Components	Device design	17
Existing	Short course	Dynamic Diagnostics	Instrumentation & analysis	17
New	Short course	CTH for China Lake	Sandia computer code	13

I. *Technology Transfer/Patents*

1. Patent Applications Filed (Including Provisional Patents)

   a. Oxley, J.C., Smith, J.L., Yevdokimav, A.V., & Colizza, K. "Apparatus and Methods for Explosive Trace Detection Sample Preparation and Introduction into an Ionizing Detection System." Provisional Patent 62/816,253, 11 March, 2019.

   b. Oxley, J.C., Smith, J.L, Ichiyama, R., & Kagan, G. "Safe Control of Hazardous Materials or Others Onsite." US 62/837,520, April 2019

   c. Oxley, J.C., Smith, J.L., Kominia, A., Busby, T., & Stubbs, V. "Plasticized Flexible Pyrotechnic Material and Methods of Using the Same." Provisional Patent 62/993,992, 24 April 2020.

J. Requests for Assistance/Advice

1. From DHS

   a. Oxley is part of the DHS-formed Inter-Agency Explosive Terrorism Risk Assessment Working Group (IExTRAWG).

   b. On call for a variety of TSA TSS-E personnel.

2. From Federal/State/Local Government

   a. The URI bomb dog and his trainer rely on our lab for advice and explosives.

R1-A.1. APPENDIX

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A New Polymorph of HMTD

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ABSTRACT

While exploring the synthesis pathway of HMTD, an unexpected new polymorph of HMTD was found. Both Raman spectroscopy and powder x-ray diffraction support a different crystal structure. This HMTD is believed to be the result of a different confirmation of the HMTD, only previously predicted by computational methods and through the use of specialized NMR reagents.

1 INTRODUCTION

Hexamethylene triperoxide diamine (HMTD) is a peroxide-based explosive that was first synthesized in 1885 by the German chemist Legler. Its structure was proposed in 1900, but not confirmed by X-ray analysis until 1985 [1-3]. HMTD is an amine peroxide compound with bridgehead nitrogens that lie nearly planar. Combined with ring strain, planar nitrogens may contribute to the overall sensitivity of HMTD. Yet, even though it is considered one of the more sensitive peroxide molecules, it still is used by terrorists; most recently in the 2016 NY/NY pipe bomb incident [4]. Its simple synthesis from hexamine, hydrogen peroxide, and a weak acid such as citric acid, has made HMTD the focus of several research groups [5-8].

Like HMTD, triacetone triperoxide (TATP) is a cyclic organic that contains three peroxide functionalities. Both have been studied due to their use as a homemade explosive (Figure 1). In TATP the peroxide bonds in the cage compound can adopt two conformations, the "twist-boat-chair" confirmation (D_3) and "twist-chair-chair" confirmation (C_2) [9,10]. The barrier for the conversion from C_2 to the stable D_3 conformer is reported at 24 kcal/mol, supporting that the two conformers coexist in solution and are separable by chromatography methods [9-11]. Additionally, TATP is found to exhibit polymorphism beyond the crystal structures of the D_3 and C_2 conformers through the use of different acid catalysts or recrystallization solvents [12,13]. HMTD has been isolated as only the D_3 conformer [14]. The first crystal structure of HMTD was proposed by Schaefer et al. in 1985, where they found that the bridgehead nitrogens adopted a relatively planar geometry [1]. Shortly after, the infrared, Raman, and NMR spectra of HMTD were published [15]. Assignments of IR and Raman peaks were in good agreement with HMTD having D_3 symmetry. The ^{1}H NMR of HMTD in the same work showed that HMTD retains D_3 molecular symmetry in solution, and no other conformers were observed. Wierbizcki et al. sought to explain the interesting geometry of HMTD through density functional theory studies and additional X-ray techniques [16,17]. Initially, they performed their calculations without symmetry constraints but imposed the D_3 symmetry after additional X-ray analysis. In 2006, Guo et al. examined the helical chirality in HMTD via the use chiral shift agents [14]. The authors were able to observe the C_2 conformer via ^{1}H and ^{13}C NMR.
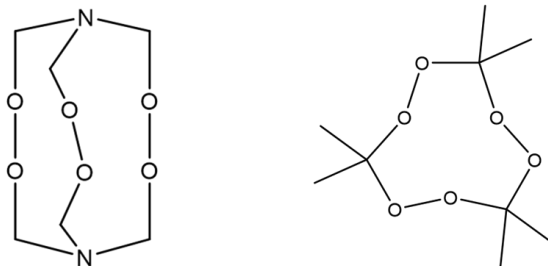
Figure 1. Hexamethylene triperoxide diamine (HMTD, left) and triacetone triperoxide (TATP, right)

2 EXPERIMENTAL SECTION

Warning: HMTD is a sensitive peroxide explosive and should only be synthesized and handled by trained personnel.

2.1 Synthesis of Hexamethylene triperoxide diamine (HMTD, Form I)

In a 50 mL round bottom flask, hexamine (2.43 g, 17.3 mmol) was slowly added to stirring chilled 50wt% hydrogen peroxide (9.87 g, 145 mmol). Once hexamine dissolved, 3.61 g (18.8 mmol) of anhydrous citric acid was added portion-wise. The reaction flask was covered with Parafilm and left in the ice bath to warm overnight. After 14 to 18 hours, the white precipitate was collected by filtration and rinsed with 600 mL of deionized water, followed by 200 mL of room temperature methanol [1]. Clumps were gently broken on the filter paper to prevent caking and allowed to dry under vacuum for at least 30 minutes (2.3 grams, 64% yield). The final powder was stored at -20°C until use.

2.2 Synthesis of HMTD polymorph (Form II)

In a 25 mL round bottom flask, 37% formaldehyde (5 mL, 67.1 mmol) was mixed with 50wt% hydrogen peroxide (2.48 g, 36.5 mmol) for 1 hr. The reaction mixture was then cooled via ice bath and concentrated ammonium hydroxide was added dropwise to slow the temperature increase (0.5 mL, 7.4 mmol) [2,3]. The reaction was left to warm overnight. The white precipitate was collected by vacuum filtration, rinsed with 300 mL deionized water and 100 mL room temperature methanol. The white solid was dried under vacuum for a minimum of 30 minutes and stored at -20°C until use (0.15 g, 20% yield).

2.3 Instrumentation

Raman spectra were obtained with an Ondax 785 nm laser and an Andor Shamrock 500i-D2-R spectrometer using a 1200 lines/mm grating. Unless noted, spectra were obtained five 5-second accumulations over the full range. Infrared (IR) spectra were collected on a Nicolet 6700 FT-IR at 4 cm^{-1} resolution and an average of 32 scans. Powder X-ray diffraction (XRD) spectra were collected on a Rigaku MiniFlex600 benchtop powder x-ray diffractometer. Differential scanning calorimetry (DSC) was done on a TA Q100 DSC (New Castle, DE, USA). Samples (150-250 μg) were sealed in aluminum hermetic pans and run in duplicate at 10 °C/min. NMR spectra were collected on a Bruker Ascend 400 MHz spectrometer.

3 Results and Discussion

TATP has two common conformers (C_2 and D_3); D_3 is the most stable conformer, but depending on reaction conditions (acid strength, recrystallization solvent, etc.) the ratio of the two conformers may vary in a given sample [12]. While studying the synthesis pathway of HMTD, an unexpected precipitate from a reaction mixture containing formaldehyde, hydrogen peroxide, and ammonium hydroxide was observed. ^{1}H NMR analysis of a d6-DSMO solution of this material confirmed that it was HMTD (Figure 2) [14]. DSC analysis

revealed that the two forms behave similarly; a single sharp peak for the exothermic decomposition of HMTD at 162°C and the absence of a melting point (Figure 3).
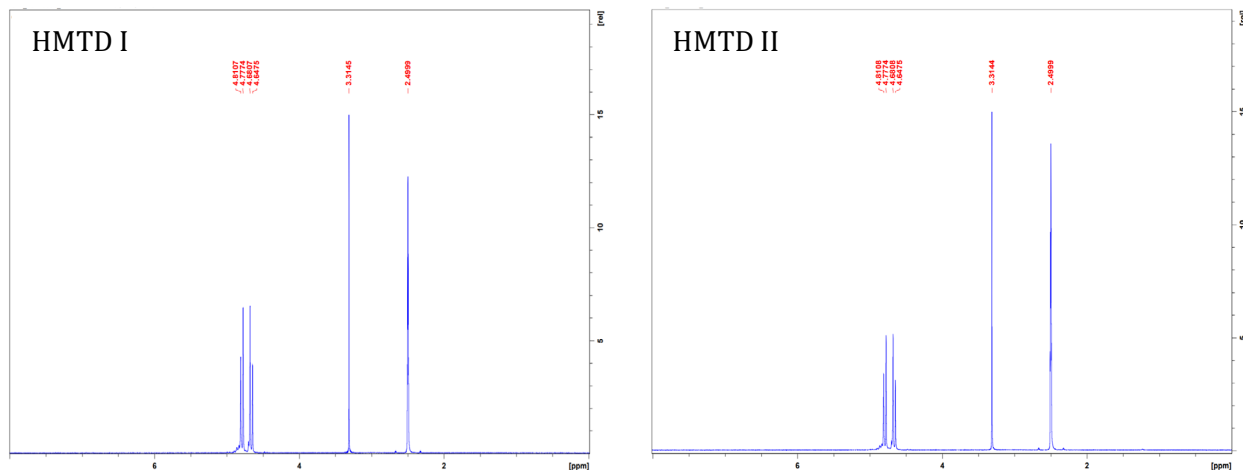

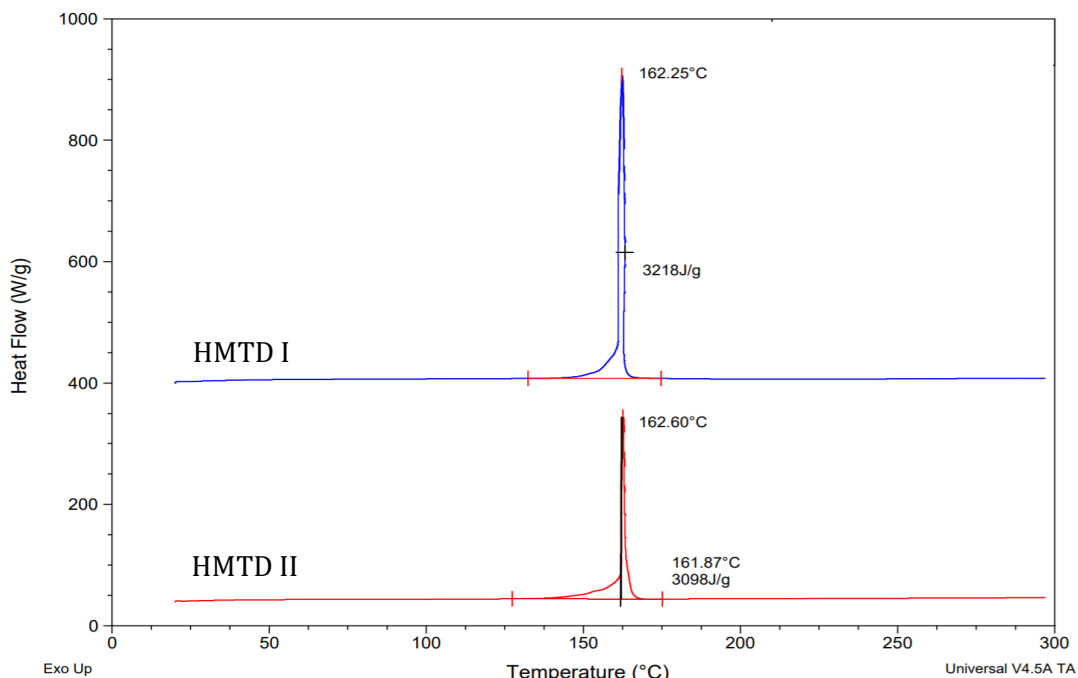**Figure 2.** ^{1}H NMR of standard HMTD I (left) and HMTD II (right)

Figure 3. DSC of HMTD I (top) and HMTD II (bottom)

Structural analysis of the solid HMTDs suggested that there was a difference between the two solids. Powder XRD analysis (Figure 4) showed differences in the structure between the two solids. A major difference between the two patterns is the more complex spectra in the 10-20 degree 2-θ. Over multiple samples of suspected HMTD II, the peak locations matched, suggesting that the differences were not a factor of preferred orientation.
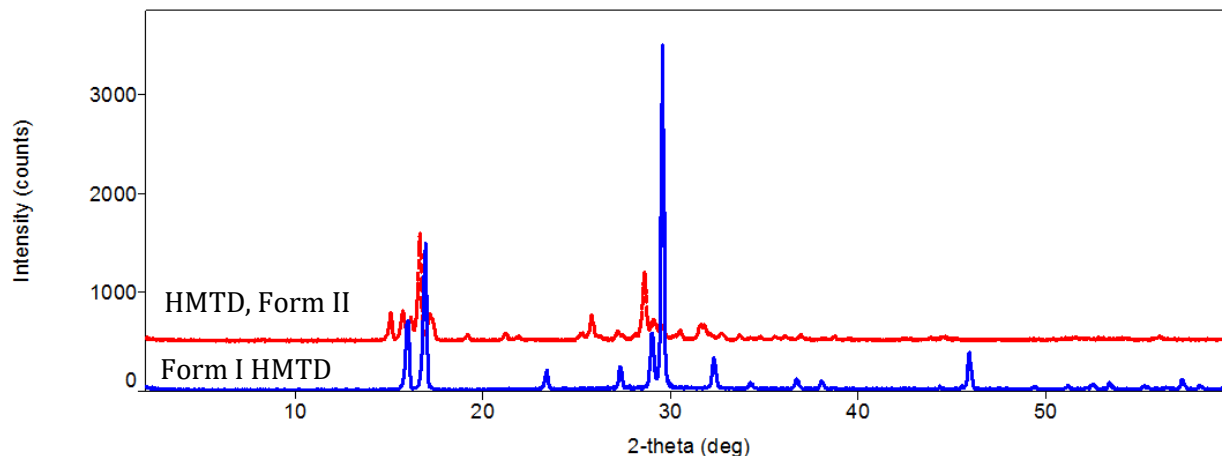
Figure 4. Powder XRD of HMTD I (solid line, bottom) and HMTD II (dashed line, top)

The Raman spectra of both forms of HMTD are relatively similar but differ in some key regions. The low wavenumber region of the Raman spectrum (often referred to as the THz Raman region) often contains vibrations that correspond to the movement of the entire molecular structure. Differences in Raman spectra in this region may be used to discriminate between different polymorphs of materials [18] and Figure 4 indicates several distinguishable differences. The THz region of Form II HMTD contains additional peaks, as well as some apparent shifting of peaks from those in HMTD I. Additional peaks in this region may indicate that there are different crystal structure interactions occurring in HMTD II.
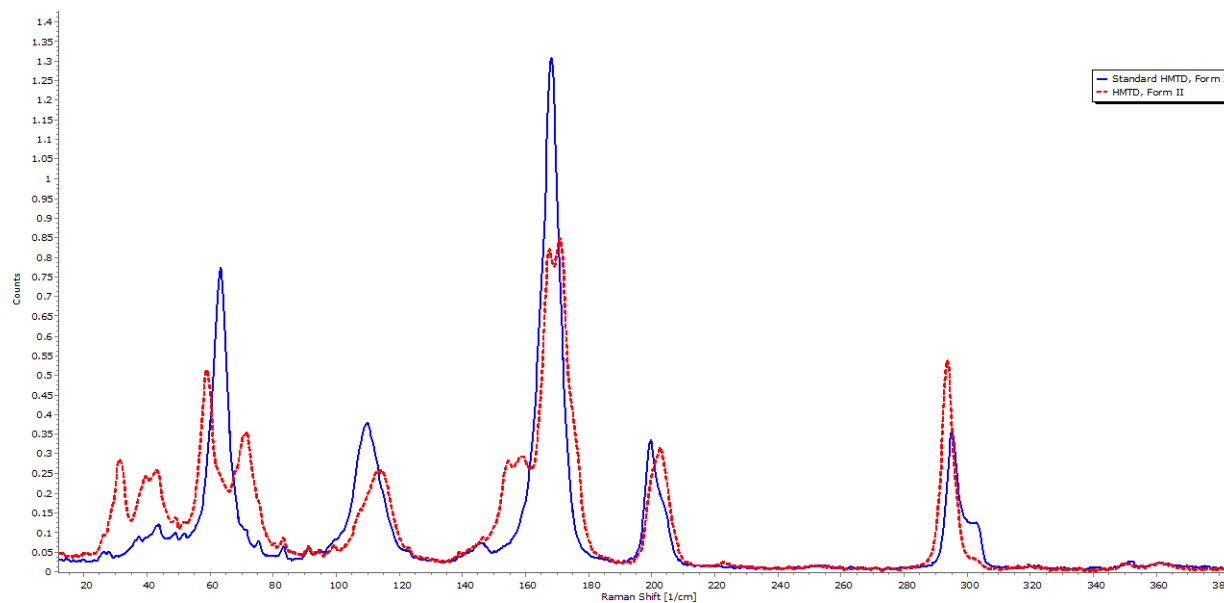

Figure 5. Low-wavenumber region of HMTD I (solid line) and HMTD II (dashed line)

In the fingerprint region of the HMTD spectra, assignments to vibrational modes have previously been made [15,19,20]. Only slight differences are seen here between the two forms of HMTD (Figure 6). In the middle of the spectral window, around 770 cm^{-1}, is the characteristic O-O stretch. The splitting of this peak may be attributed one of the three peroxide bonds having a different orientation, as is suggested by calculations for the C_2 conformer [14]. In the 1300-1500 cm^{-1} region, where CH_2 motions, e.g. CH_2 twist, wag, and scissor are observed, there are changes which support the theory that at least one of the peroxide arms in the HMTD molecule is in a different orientation.
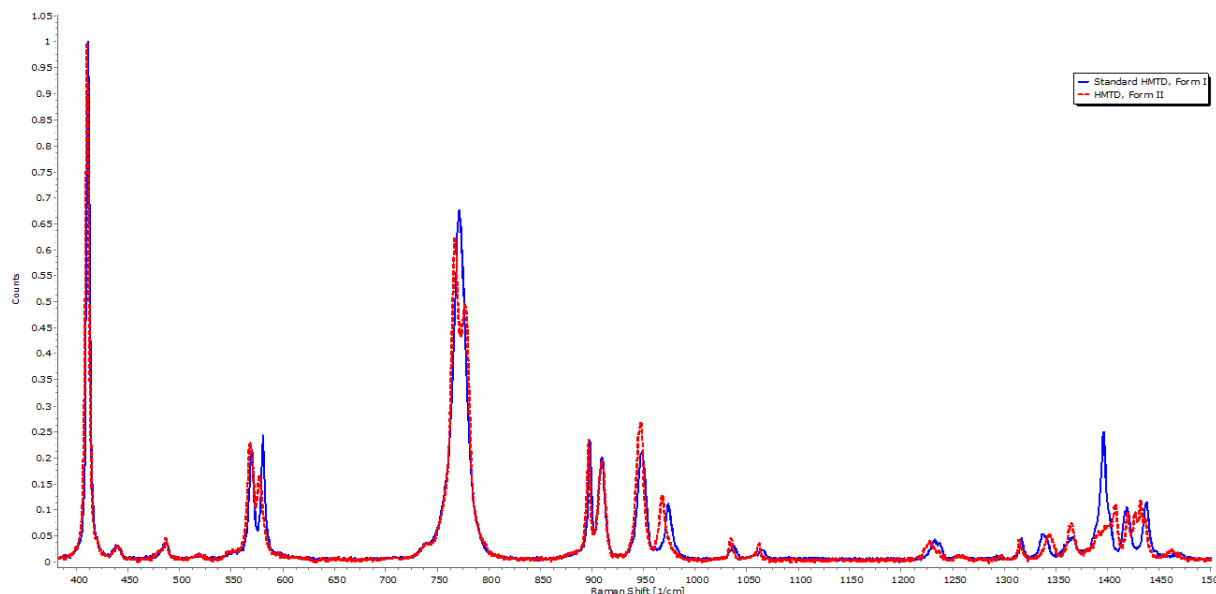
Figure 6. Mid-wavenumber region of HMTD I (solid line) and HMTD II (dashed line)

There are also differences in the high-wavenumber region of the HMTD spectra. Normal HMTD has symmetric (2917 and 2930 cm^{-1}) and asymmetric (2963 and 2976 cm^{-1}) C – H stretches. Though hardly resolved under these conditions, it is still clear that there are changes to both the symmetric and asymmetric C – H stretches in the new HMTD polymorph (Figure 7).
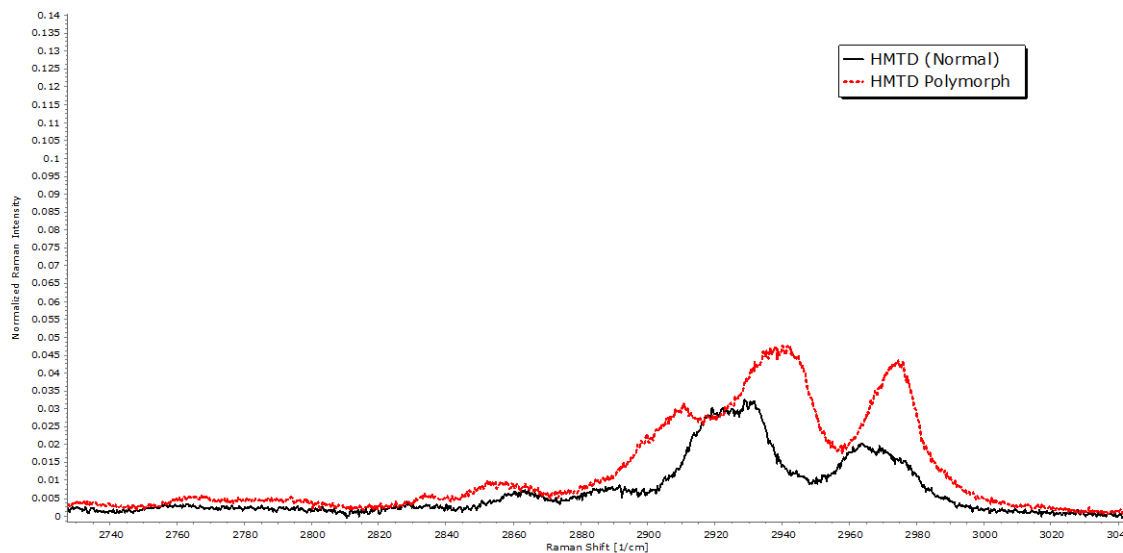

Figure 7. High-wavenumber region of HMTD I (solid line) and HMTD II (dashed line)

The infrared spectra of HMTD I and HMTD II also supports structural differences (Figure 8). There are shifts in the fingerprint region of HMTD II to higher frequencies, specifically in the transitions that correspond to C-O stretching modes [19,21,22]. The slight blue shift of these modes suggests that there are different, if not new, interactions in HMTD II.
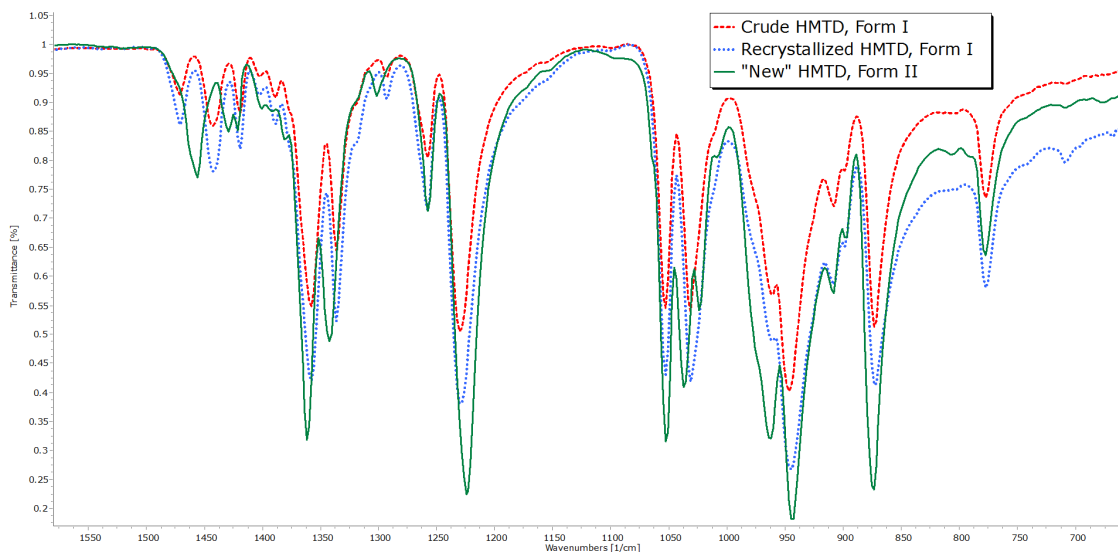
Figure 8. IR spectra of HMTD I (dotted, dashed lines) and HMTD II (solid)

HMTD synthesis requires an acid catalyst (often citric acid) for the reaction to optimally proceed, however, HMTD will form in the absence of acid after 5-7 days [8]. Ammonium hydroxide was used as the source of the nitrogen in the reaction. Several sources of ammonium were tested with hydrogen peroxide and formaldehyde to determine if any HMTD formed. The results are summarized in Table 1 below. Under the reaction conditions, even hexamine was able to form HMTD in appreciable amounts without the addition of acid. The greater than 100% yield is a factor of assuming a 1:1 ratio of hexamine to HMTD; the addition of formaldehyde provides extra carbon into the system to generate more product. When the ammonium salt anion is a weak acid/weak base, no HMTD formation was observed. The reaction mixtures were tested with pH paper prior to disposal; in cases where HMTD was not formed, the reaction mixture was very acidic. This is likely due to the formation of formic acid from the decomposition reaction of hydrogen peroxide and formaldehyde [23]. When the ammonium counterion was more basic, HMTD formation was seen, and as with the ammonium hydroxide, the recovered HMTD was HMTD II.

That these basic ammonium salts can form HMTD at all is surprising. The reaction has an increased danger during synthesis due to the incompatibility of bases and peroxides. The temperature of the reaction must be monitored; the decomposition reaction can generate enough heat to rapidly boil the reactants. Espinosa-Fuentes et al. found that the use of strong acids to prepare TATP led to the C_2 conformer and postulated that the energy release associated with strong acids in the system may give way to products of higher energy [24]. A similar phenomenon may occur with preparing HMTD under basic conditions.

Table 1. Summary of HMTD synthesis from hydrogen peroxide and formaldehyde using alternative nitrogen sources

Ammonium Salt/Nitrogen Source		% Yield*	Comments/Observations
Hexamine	$C_6H_{12}N_4$	105**	HMTD I formed
Ammonium acetate	$NH_4C_2H_3O_2$	34.6	HMTD I formed
Ammonium sulfate	$(NH_4)_2SO_4$	0	No HMTD formed, pH ~3
Ammonium chloride	NH_4Cl	0	No HMTD formed, pH ~1-2
Ammonium nitrate	NH_4NO_3	0	No HMTD formed, pH ~1-2
Ammonium hydroxide (28%)	NH_4OH	44.0	HMTD II formed
Ammonium carbonate	$(NH_4)_2CO_3$	28.4	HMTD II formed
Ammonium bicarbonate	NH_4HCO_3	43.2	HMTD II formed
Monoammonium phosphate	$(NH_4)H_2PO_4$	0	No HMTD formed
Diammonium phosphate	$(NH_4)_2HPO_4$	10.3	HMTD I formed

*% yield based off 500 mg theoretical yield (assuming 2 N to 1 HMTD)
**Assumed a 1:1 hexamine to HMTD ratio
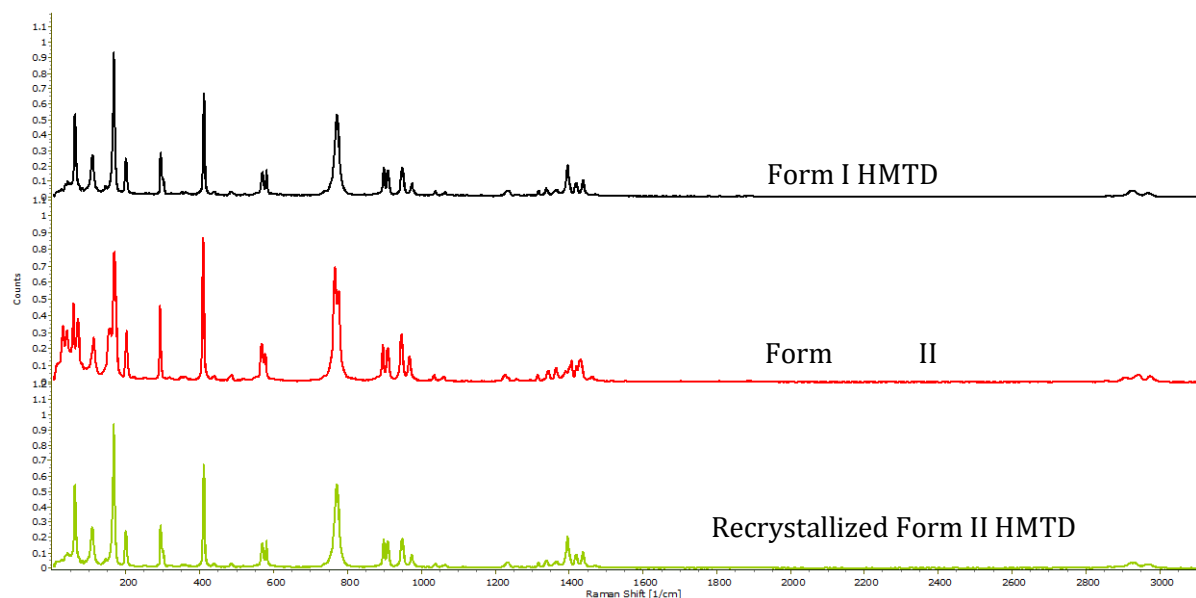
Figure 9. Comparison of Form I HMTD, Form II HMTD, and recrystallized Form II HMTD

Obtaining a crystal suitable in size for single crystal x-ray analysis was difficult. Altering the synthetic procedure to promote larger particle size only resulted in the normal HMTD structure. Different recrystallization solvents were also tried, to no success. In Figure 9, the Raman spectrum of a recrystallization of HMTD with acetonitrile is shown. After dissolving and reprecipitating out, the HMTD recovered was the standard Form I HMTD. Apparently, in solution, HMTD reverts to the stable D_3 conformer. Despite being stored at -20°C, the HTMD polymorph will convert to normal HMTD on extended storage.

4 CONCLUSION

Though only predicted and observed through the use of chiral shift reagents in ^{1}H and ^{13}C NMR, it was thought that HMTD had a C_2 conformer in addition to the easily prepared D_3 conformer. While studying a reaction mixture of formaldehyde, hydrogen peroxide, and ammonium hydroxide, a precipitate was

collected. The precipitate was determined to be HMTD, and subsequent structural analysis through XRD and Raman techniques suggested a new crystal structure of HMTD. Without single crystal XRD it can only be hypothesized that the new crystal structure is the result of HMTD adopting a higher energy confirmation in the C_2 form.

5 ACKNOWLEDGMENTS

REFERENCES

[1]   Schaefer, W. P.; Fourkas, J. T.; Tiemann, B. G., Structure of hexamethylene triperoxide diamine. *J. Am. Chem. Soc.* **1985,** *107* (8), 2461-2463.

[2]   Legler, L., Ueber Producte der langsamen Verbrennung des Aethyläthers. *Ber. Dtsch. Chem. Ges.* **1885,** *18* (2), 3343-3351.

[3]   Baeyer, A.; Villiger, V., Ueber die Nomenclatur der Superoxyde und die Superoxyde der Aldehyde. *Ber. Dtsch. Chem. Ges.* **1900,** *33* (2), 2479-2487.

[4]   Santora, M.; Rashbaum, W. K.; Goldman, A. Ahmad Khan Rahami Is Arrested in Manhattan and New Jersey Bombings. (accessed 14 February 2018).

[5]   Simon, A. G.; DeGreeff, L. E., Variation in the headspace of bulk hexamethylene triperoxide diamine (HMTD): Part II. Analysis of non-detonable canine training aids. *Forensic Chem.* **2019,** *13*, 100155.

[6]   DeGreeff, L. E.; Cerreta, M. M.; Katilie, C. J., Variation in the headspace of bulk hexamethylene triperoxide diamine (HMTD) with time, environment, and formulation. *Forensic Chem.* **2017,** *4*, 41-50.

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