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A new polymorph of HMTD

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ABSTRACT

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 conformation of the HMTD, only previously predicted by computational methods and through the use of specialized NMR reagents.

KEYWORDS

Hexamethylene triperoxide diamine (HMTD); polymorph; peroxide

1. Introduction

Hexamethylene triperoxide diamine (HMTD) is a peroxide-based explosive that was first synthesized in 1885 by German chemist Legler. Its structure was proposed in 1900, but not confirmed by X-ray analysis until 1985 (Baeyer and Villiger 1900; Legler 1885; Schaefer, Fourkas, and Tiemann 1985). 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 (Santora, Rashbaum, and Goldman 2018). Its simple synthesis from hexamine, hydrogen peroxide, and a weak acid such as citric acid, has made HMTD the focus of several research groups (DeGreeff, Cerreta, and Katilie 2017; Oxley et al. 2016; Simon and DeGreeff 2019; Steinkamp et al. 2016).

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) (Denekamp et al. 2005; Widmer et al. 2002). 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 (Denekamp et al. 2005; Haroune, Crowson, and Campbell 2011; Widmer et al. 2002).

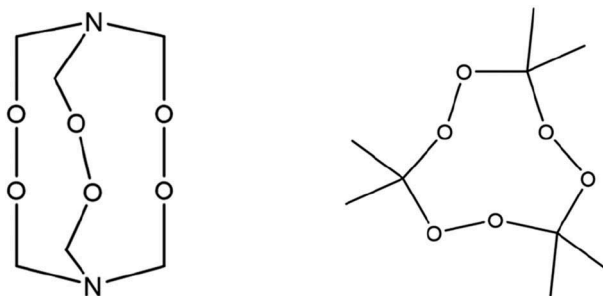


Figure 1. Hexamethylene triperoxide diamine (HMTD, left) and triacetone triperoxide (TATP, right).

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 (Peterson et al. 2013; Reany et al. 2009). HMTD has been isolated as only the D_3 conformer (Guo, Persons, and Harbison 2006). 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 (Schaefer, Fourkas, and Tiemann 1985). Shortly after, the infrared, Raman, and NMR spectra of HMTD were published (Sülzle et al. 1988). Assignments of IR and Raman peaks were in good agreement with HMTD having D_3 symmetry. The ^1H 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 (Wierzbicki and Cioffi 1999; Wierzbicki et al. 2001). 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 of chiral shift agents (Guo, Persons, and Harbison 2006). The authors were able to observe the C_2 conformer via ^1H and ^{13}C NMR.

Polymorphism in energetic materials is important; many common military explosives exhibit polymorphism which needs to be thoroughly characterized prior to use in the field (Dreger, Tao, and Gupta 2013; Liu et al. 2018; Miller and Garraway 2001). Some of the polymorphs are accessed by different crystallization methods; others through temperature and/or pressure changes. Changes in the crystal structure, as the result of a molecule adopting a new conformation, for example, can result in a change in volume and thus, density. Density changes can have significant impact on material performance. For homemade explosives, however, the concern lies less with effect on performance and more with detection methods. TATP polymorphs exhibit differences in x-ray diffraction and spectroscopic techniques (i.e. Raman spectroscopy) that have implications for detection, especially field methods that rely on library matches (Peterson et al. 2013; Reany et al. 2009). In this

work, the preparation and characterization of HMTD from a different synthesis route is studied and reported for the first time.

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 (Standard HMTD, Form I)

In a 50 mL round bottom flask, hexamine (2.43 g, 17.3 mmol) was slowly added to stirring chilled 50 wt% hydrogen peroxide (9.87 g, 145 mmol). Once hexamine dissolved, 3.61 g (18.8 mmol) of anhydrous citric acid was added portionwise. 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. 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 50 wt% 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). 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 $10^{\circ}\text{C}/\text{min}$. 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 (Reany et al. 2009). While studying the synthesis pathway of HMTD, an unexpected precipitate from a reaction mixture containing formaldehyde, hydrogen peroxide, and ammonium hydroxide was recovered. ^1H NMR analysis of a d_6 -DSMO solution of this material confirmed that it was HMTD (Figure 2) (Guo, Persons, and Harbison 2006). DSC analysis revealed that the two samples behave similarly; a single sharp peak for the exothermic decomposition of HMTD at 162°C and the absence of a melting point (Figure 3) (Oxley et al. 2016).

Structural analysis of the solid HMTDs suggested that there was a difference between the two samples. 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 $2\text{-}\theta$. Over multiple samples of suspected HMTD II, the peak locations matched, suggesting that the differences were not a factor of preferred orientation.

The Raman spectra of both forms of HMTD are relatively similar but differ in some key regions that allow Raman to be one of the main methods to differentiate between the two forms. Specifically, the use of an Ondax THz Raman system equipped with a notch filter that is able to attenuate the Rayleigh line in order to obtain spectra in the low wavenumber, or THz region (5 – 200 cm^{-1}). Modes in this region are related to whole molecule vibrations and movements and have been widely used to differentiate crystal forms in pharmaceutical and explosives applications, specifically in polymorph identification (Heyler, Carriere, and Havermeier 2013; Roy, Chamberlin, and Matzger 2013). Figure 5 compares the THz regions of both forms of HMTD. Leigh et al has reported the THz Raman region for HMTD (Leigh, Monson, and Kim 2016). Our HMTD I Raman spectrum is in good agreement with that previously reported, with three peaks in the THz region 64 , 110 , and 169 cm^{-1} , although the peak we observed at 42 cm^{-1} was not as prominent under our conditions as that reported (Leigh, Monson, and Kim 2016). The THz region for HMTD II has more peaks than HMTD I (Table 1).

In the fingerprint region of the HMTD spectra, assignments to vibrational modes have previously been made (Leigh, Monson, and Kim 2016; Oxley et al. 2008; Sülzle et al. 1988). Only slight differences are seen here between the two forms of HMTD (Figure 6). In the middle of the spectral window, in the 770 – 780 cm^{-1} region, 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 (Guo, Persons, and Harbison 2006). In the 1300 – 1500 cm^{-1} region, where CH_2

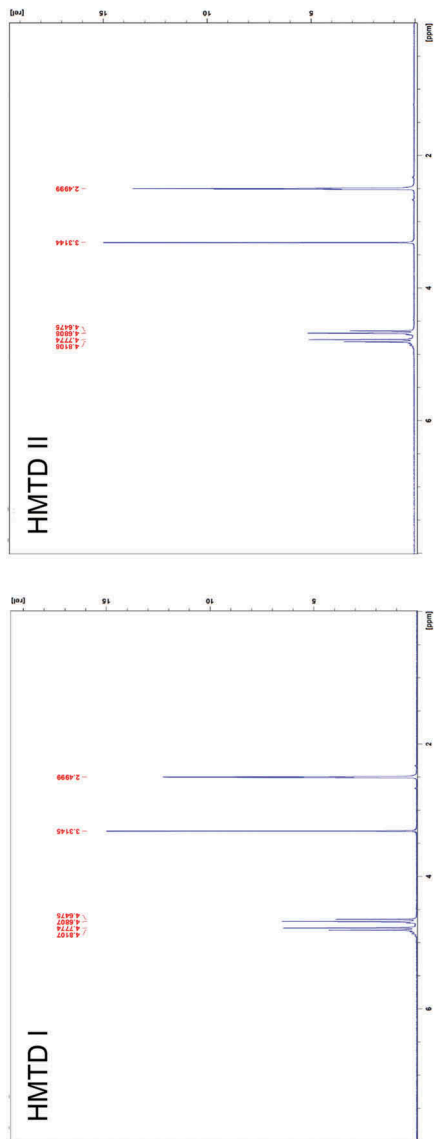


Figure 2. ¹H NMR of standard HMTD I (left) and HMTD II (right).

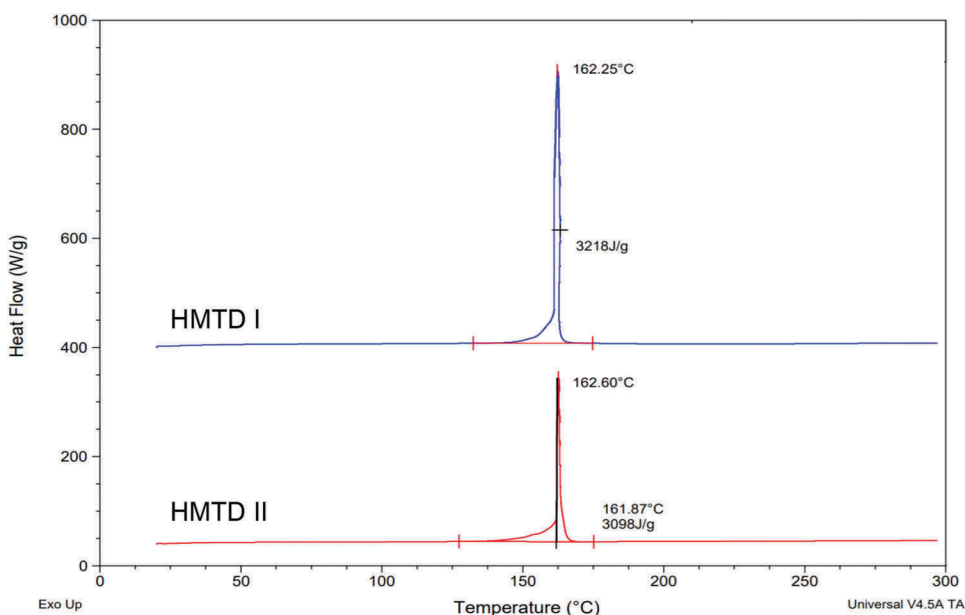


Figure 3. DSC of HMTD I (top) and HMTD II (bottom).

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.

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). Table 1 summarizes the different frequencies observed between the two structures.

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 as seen in the 1050 – 1250 cm^{-1} region (Oxley et al. 2008; Pena-Quevedo et al. 2006; Schulte-Ladbeck et al. 2006). The slight blue shift of these modes suggests that there are different, if not new, interactions in HMTD II. In the 1400 – 1500 cm^{-1} there are differences in the $-\text{CH}_2$ modes, as was seen in the Raman in Figure 6.

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 (Oxley et al. 2016). 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.

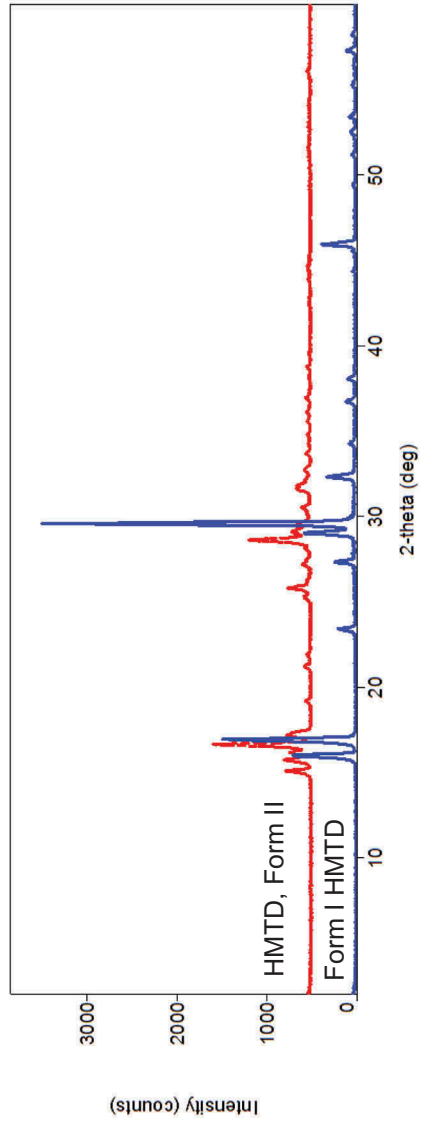


Figure 4. Powder XRD of HMTD I (solid line, bottom) and HMTD II (dashed line, top).

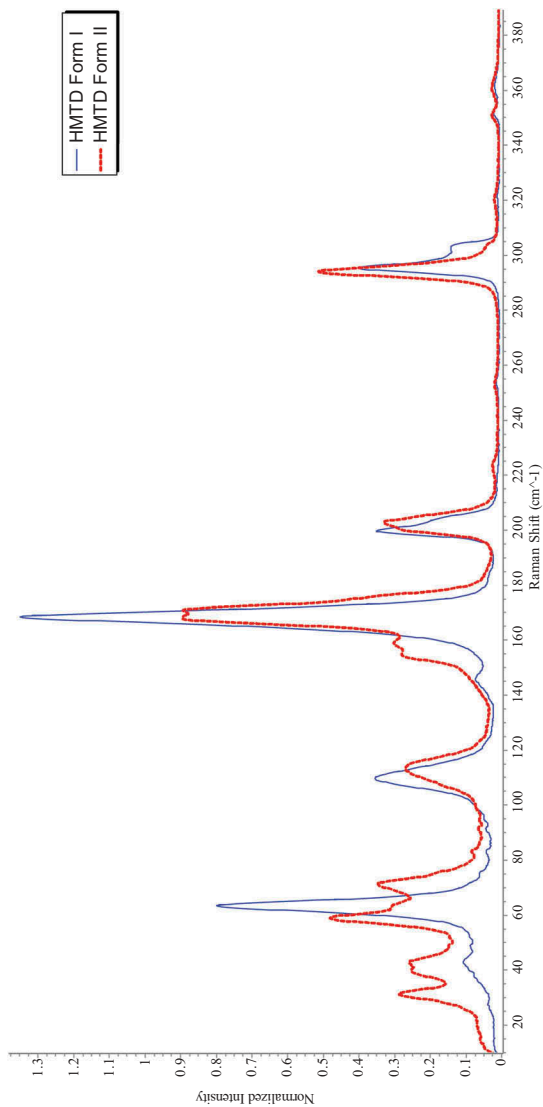


Figure 5. Low-wavenumber region (THz region) of HMTD I (solid line) and HMTD II (dashed line).

Table 1. Summary of Raman wavenumbers (cm^{-1}) for the two forms of HMTD.

HMTD I	HMTD II	HMTD I	HMTD II
42	31	899	870
	40	910	910
	43	949	948
	59	975	967
64	64	1039	1035
	72	1066	1062
110	114	1232	1229
146	155	1317	1315
169	159	1338	1343
	169	1367	1365
	171	1397	1391
200	203		1398
	224		1408
295	294	1418	1420
412	410		1427
439	440		1432
488	487	1439	1436
571	569	1470	1463
582	578	2918	2911
772	767	2929	2940
	776	2964	2974

When a precipitate was formed, it was analyzed by Raman and its form assessed by the spectral features in the THz region and around the peroxide bond (770 cm^{-1} region). The results are summarized in Table 2 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 anion of the ammonium salt is the conjugate base of a weak acid, 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 (Satterfield et al. 1954). 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 (Espinosa-Fuentes et al. 2016). A similar phenomenon may occur with preparing HMTD under basic conditions.

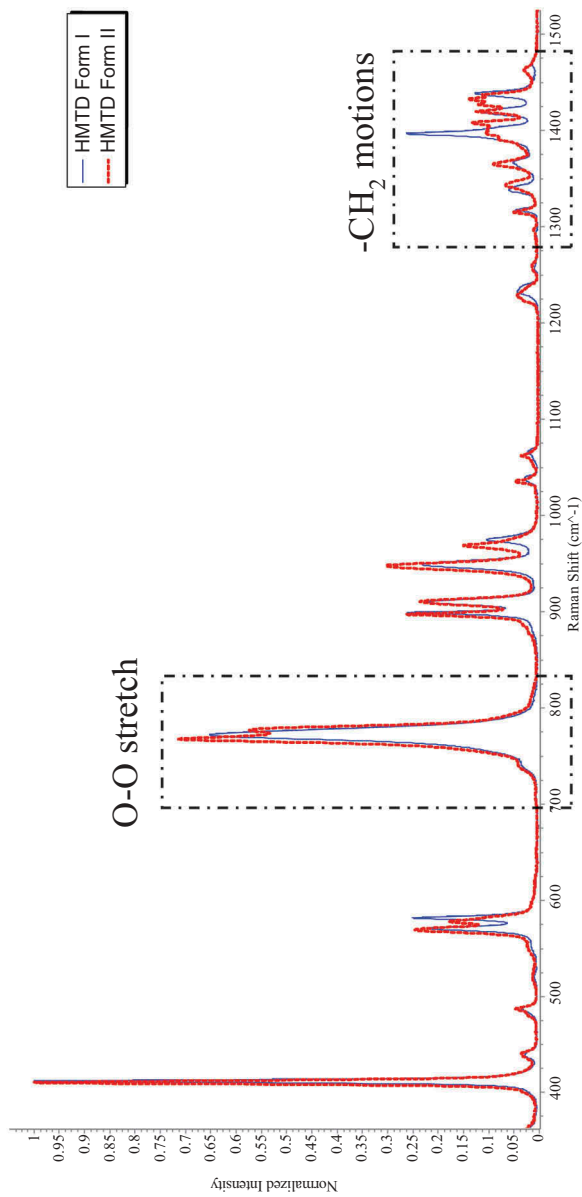


Figure 6. Mid-wavenumber region of HMTD I (solid line) and HMTD II (dashed line).

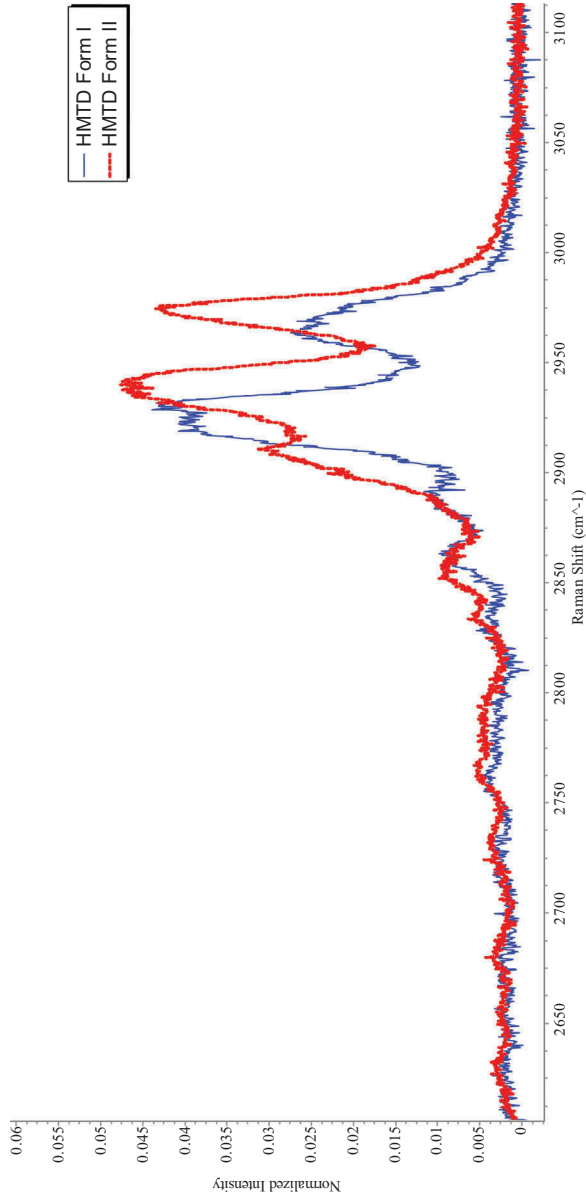


Figure 7. High-wavenumber region of HMTD I (solid line) and HMTD II (dashed line) showing differences in symmetric and asymmetric C-H modes.

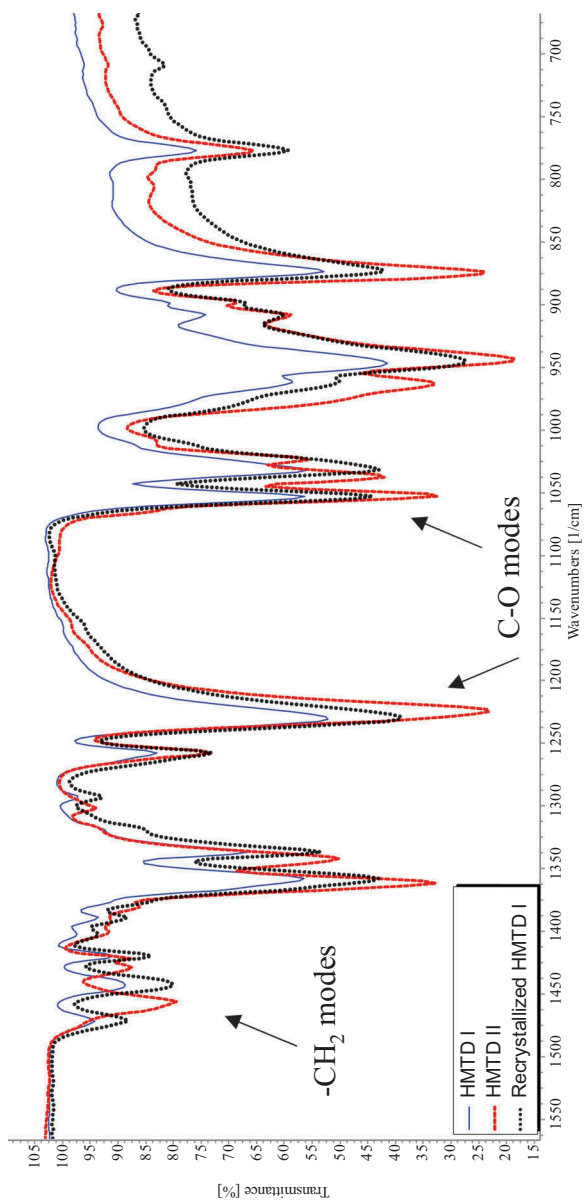


Figure 8. IR spectra of HMTD I (solid, dotted lines) and HMTD II (dashed).

Table 2. Summary of HMTD synthesis from hydrogen peroxide and formaldehyde using alternative nitrogen sources.

Ammonium Salt/Nitrogen Source		% Yield*	Comments/Observations
Ammonium chloride	NH ₄ Cl	0	No HMTD formed, pH ~1-2
Ammonium nitrate	NH ₄ NO ₃	0	No HMTD formed, pH ~1-2
Ammonium sulfate	(NH ₄) ₂ SO ₄	0	No HMTD formed, pH ~3
Monoammonium phosphate	(NH ₄)H ₂ PO ₄	0	No HMTD formed, pH ~1-2
Diammonium phosphate	(NH ₄) ₂ HPO ₄	10.3	HMTD I formed
Ammonium carbonate	(NH ₄) ₂ CO ₃	28.4	HMTD II formed
Ammonium bicarbonate	NH ₄ HCO ₃	43.2	HMTD II formed
Ammonium acetate	NH ₄ C ₂ H ₃ O ₂	34.6	HMTD I formed
Ammonium hydroxide (28%)	NH ₄ OH	44.0	HMTD II formed
Hexamine	C ₆ H ₁₂ N ₄	105**	HMTD I formed

*% yield based off 500 mg theoretical yield (assuming 2 N to 1 HMTD)

**Assumed a 1:1 hexamine to HMTD ratio

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 D₃ conformer. Despite being stored at -20°C, the HMTD polymorph will convert to normal HMTD on extended storage.

4. Conclusion

Though only predicted and observed through the use of chiral shift reagents in ¹H and ¹³C NMR, it was thought that HMTD had a C₂ conformer in addition to the easily prepared D₃ 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 C₂ form.

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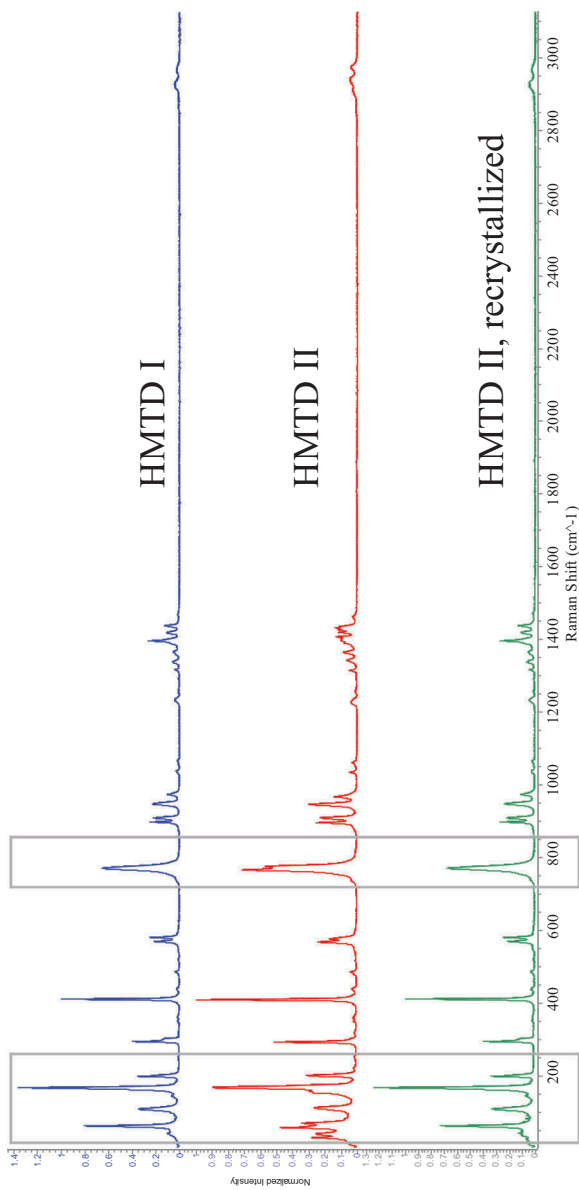


Figure 9. Comparison of form I HMTD, Form II HMTD, and recrystallized Form II HMTD.

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