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Synthesis of DNMT: A New Energetic Melt-Pour Ingredient

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Introduction

For the family of high performance melt-cast explosives that includes formulations such as Composition B, Octol, etc., TNT has been the primary binder. In recent years, 2,4-dinitroanisole (DNAN) has found widespread use as a binder to replace TNT. Although DNAN has lower explosive performance than TNT, it has melt characteristics, which allow its use in existing LAP facilities without requiring any modification, does not exhibit the shrinkage or long solidification time, and is considerably less sensitive to external stimuli.

Even though DNAN offers many advantages as a melt cast binder, relative to TNT, ideal “next generation” candidates would offer significantly improved performance and insensitivity over existing melt cast binders, and be amenable to the existing LAP infrastructure. As such, OSI and ARDEC have recently collaborated to evaluate new “next generation” melt cast binders, which have inherent performance characteristics equivalent to, or exceeding those of Composition B. A large number of nitrated pyrazoles, imidazoles, triazoles and furazan derivatives were modelled using melting point and density criteria. This list was then parsed for ease of preparation, and several candidates were identified for additional characterization and scalability.

One candidate for further investigation was selected based on melting point, calculated density and perceived ease of preparation; 1-methyl-3,5-dinitro-1,2,4-triazole (DNMT).

The first phase of the investigation involved preparation of <25 grams of each of the compounds for characterization and small scale safety evaluation. Based upon those results, the next phase envisioned scale-up to 250 grams of material, with an eye toward optimization of the syntheses, IHC and EX classification and somewhat larger scale safety and performance testing. Again, based upon those results, the final phase would involve preparation of 2.5 kilograms of each of the compounds for use in a melt cast formulation.

Cost was not a consideration in the early stages of investigation since market conditions and availability of starting materials, as well as synthetic methodologies, may improve in time. However, early identification of undesirable sensitivity or performance behavior was sufficient to eliminate a candidate from scale-up to larger quantities.

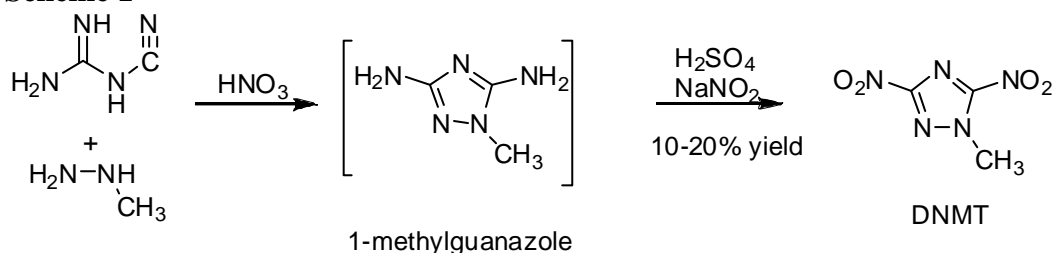
Synthesis of 1-Methyl-3,5-dinitro-1,2,4-triazole (DNMT)

The synthesis of the melt-pour candidate was based on literature procedures available in the public domain or from communication with university professors such as Alan Katritzky. Where possible, procedures were optimized or otherwise changed to improve yields, costs, or amenability to scale-up.

The synthetic methodology originally adopted for DNMT was a pseudo-one pot preparation developed by Prof. Alan Katritzky’s group at the University of Florida, wherein all of the reaction mixture from the first step is added to a second

set of diazotization/substitution reagents. The overall transformation is depicted in Scheme 1 below.

Scheme 1

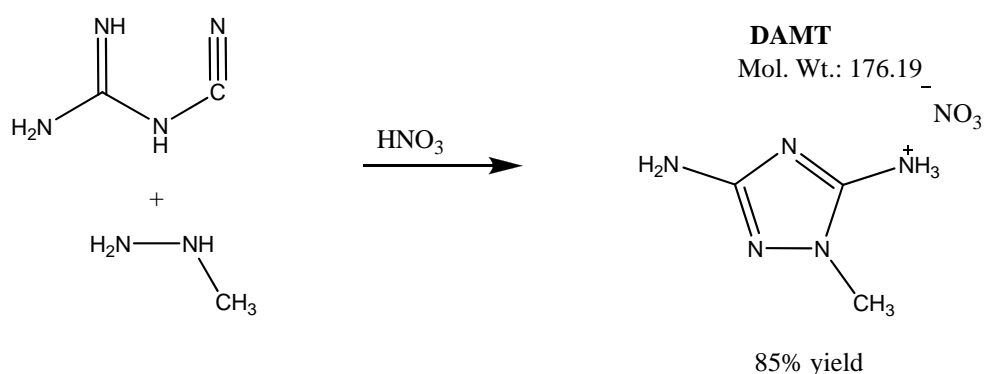


The first step is the condensation of cyanoguanidine with methyl hydrazine to give 3,5-diamino-1-methyl-1,2,4-triazole (1-methylguanazole) as shown in Scheme 1. The reaction mixture containing 1-methylguanazole is then added to a sodium nitrite solution, along with additional sulfuric acid to give the target compound, DNMT.

DNMT is surprisingly water soluble, given the N-alkylation. As such, overall reaction yields were ca. 10% without extraction with an organic solvent. Overall yields of up to 43% were obtained with an extraction step. Thus far, no attempts have been made to optimize the reaction conditions or isolation procedure.

The continued effort report by OSI scientists began by attempting to understand and optimize the first step of the reaction to make DAMT. In the first attempt, the reaction time was reduced from 5 hrs and, upon cooling, obtained a white solid which was believed to be the nitrate salt of 1-methylguanazole (DAMT). Many experiments were performed in an effort to understand and optimize the synthesis of DAMT (Scheme 2).

Scheme 2



Yields have fluctuated from 62% to 98%. The lower yields were thought to result from insufficient time at ambient or subambient post-reaction temperatures; i.e., the reaction mixture needs to be cooled and held for at least 2 hrs to ensure all the product precipitates from the solution. The reaction time has been shortened to to speed up the process. With the use of NMR and DSC, an impurity has been observed when higher mass yields are obtained. It is unclear what the impurity is or just how much is present, however, its presence does not seem to significantly

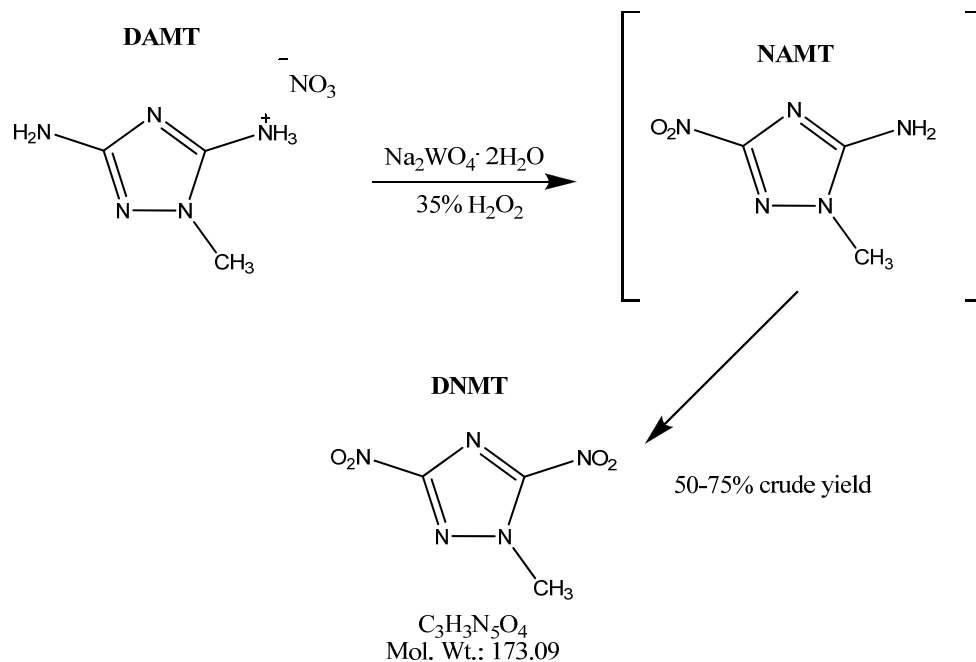
affect the subsequent oxidation or purity of DNMT, only a slightly reduced yield of DNMT. However, attempts were made to optimize the process and eliminate the unknown impurity. Two experiments were performed with this in mind. In one case, the reaction was performed as usual by allowing the final mixture to exotherm and holding at that temperature. A 62% yield of pure DAMT was obtained. Second, the reaction was performed while only allowing the reaction to exotherm to a lower temperature and holding for a period of time before heating. In this case, a 74% yield of pure DAMT was obtained.



Due to the hazards and toxicity of methylhydrazine, the possibility of purchasing methylhydrazine as an aqueous solution was considered. Ultimately this was not pursued although is still a viable option to mitigate safety concerns. This could potentially alleviate shipping and handling issues as well as potentially reducing the price of the raw material.

Being that the first step afforded good product in good yields, it was determined that the second step must be the cause of the low product yields in the original process. Therefore, a new synthetic approach was developed and investigated (Scheme 3). An oxidation of DAMT using sodium tungstate and hydrogen peroxide was performed initially on a 1 gram scale. By TLC, DSC, and IR analyses, it appears that the mono-oxidized material (NAMT) is formed first, followed by formation of DNMT. Some experiments were performed to generate NAMT in an effort to understand the process and to evaluate NAMT as a material of interest. Yields have typically been low (30-50%) for this process. NAMT shows good thermal stability (mp = 260°C) and, based on the presence of both a nitro group and an amino group, could be extremely insensitive, similar to TATB and DADNE. However, under this program, no further activities were performed to evaluate NAMT.

Scheme 3



Many experiments have been performed in an effort to understand and optimize these oxidation conditions to afford DNMT. The highest yield of crude DNMT to date is 75%. Lower yields were obtained when using less peroxide and less sodium tungstate. A major advantage of this methodology is that the crude DNMT precipitates from the reaction medium, enabling isolation of the product by simple filtration and washing, eliminating the need for solvent-based extractions which are not easily scalable. It was found that less sodium tungstate and a longer reaction time afforded no higher yield (~50% in both cases).

During attempts to recrystallize the DNMT, it has been found that there is an alcohol insoluble impurity that accounts for, at most, 50% of the mass of the material. At this time, it appears that the impurity is most likely an inorganic compound. This assumption is made due to the featureless profiles on HPLC, NMR and DSC.

A few modified oxidations were performed in a continued effort to optimize the process. In one case, the sodium tungstate was reduced and the hydrogen peroxide was increased. The mixture was incrementally and slowly heated to 80°C and held. The reaction was cooled to 10°C and filtered (no neutralization of acid or peroxide). A 10% yield of crude DNMT was obtained. In a second case, the same aforementioned amounts of tungstate and peroxide were used; however, the peroxide / tungstate solution was heated to 80°C and the DAMT was added slowly. The reaction was held at 80°C, cooled to 10°C and filtered (as before). In this case, a 5% yield was obtained. Although not yet confirmed, it is believed these materials should contain no insoluble byproducts because no neutralization procedure was used. The lack of a neutralization step may have also led to the reduced yields of the reactions.



Further modified oxidations were performed to determine if improvements in process and yields could be achieved. DAMT was oxidized using a sulfuric acid/hydrogen peroxide/ammonium persulfate mixture. This mixture afforded little product and required an extraction and/or neutralization steps. A mixture of just hydrogen peroxide and ammonium persulfate was also attempted with only a 16% crude yield of DNMT obtained. In a separate experiment using less peroxide and persulfate, an approximate 50% yield was obtained of an as yet unidentified substance that was not DNMT (determined by Mp). Going back to using peroxide and sodium tungstate (an increase from previous reactions) resulted in a difficult to control exotherm that resulted in a short duration of 96°C reaction temperature (desired temp was 80°C). This resulted in a yellow sticky semi-solid that was difficult to isolate. It was often found that if the reaction temperature exceeded 90°C, the precipitated product would melt slightly and result in a sticky solid which was difficult to isolate.

OSI scientists believe, and it should be noted, that this synthetic route to DNMT shows promise as an affordable and scalable process and warrants further investigations and evaluations.



Characterization

Initially, 25 grams of DNMT from the original process was delivered to Army partners at Picatinny Arsenal for further evaluations. Characterization of the DNMT at HSAAP consisted of determination of relative purity through HPLC, and confirmation of chemical identity by comparing NMR chemical shifts and melting points and / or exothermic decomposition onset / peak values with those reported in the literature, if known. Small scale safety and performance testing were performed at Picatinny. Table 1 shows impact sensitivity, friction sensitivity and ESD test results of DNMT and RDX. It is clear that DNMT is much less sensitive than RDX in these tests.

Table 1

	ERL Impact (cm)	BAM Friction (N)	ESD (J)
DNMT	>100	>252	>0.25
RDX	25.4	>144	>0.25

In an effort to determine if there were any polymorphs of DNMT, as exist with DNAN, a brief study was conducted to examine the thermal characteristics of DNMT before and after melting (Table 2). Although no polymorphs, or changes in melting point, were observed, the impact sensitivity of the DNMT improved dramatically after melting. It is hypothesized that this change could be due to the DNMT having amorphous character, instead of crystalline, after melting. Also, this change could be due to the removal of voids or hotspots upon melting and resolidifying.

Table 2

Impact Sensitivity (cm), Navy method		
	Pre-melt	Post-melt
DNMT	92.7	171.0

Table 3 shows comparative data (calculated and experimental) for the performance of DNMT and Comp B. While the experimental P_{cj} is only approximately 85% of Comp B, the experimental value for VOD is nearly 99% that of Comp B. This data suggests that DNMT, by itself, could be an effective and insensitive Comp B replacement.

Table 3

	P_{cj} , calc. (GPa)	P_{cj} , exp (GPa)	Energy out, calc. (cal/cc)	VOD, exp (Km/s)
DNMT	25.4	23.3	1739	7.850
Comp B	27.7	~27.6	1837	~7.960



In order to boost the performance to surpass Comp B, DNMT would need to have other energetic ingredients incorporated into a formulation. Initial compatibility tests were performed by conducting simple DSC measurements to determine if there were any significant changes in the exotherms of the tested materials. Table 4 suggests that DNMT would be compatible with RDX, DNAN, DNP (dinitropyrazole), and DNTF. TATB, HMX, NTO, and NQ showed significant shifts in the exotherms which suggests that actual VTS compatibility tests should be performed to accurately determine true compatibility.

Table 4

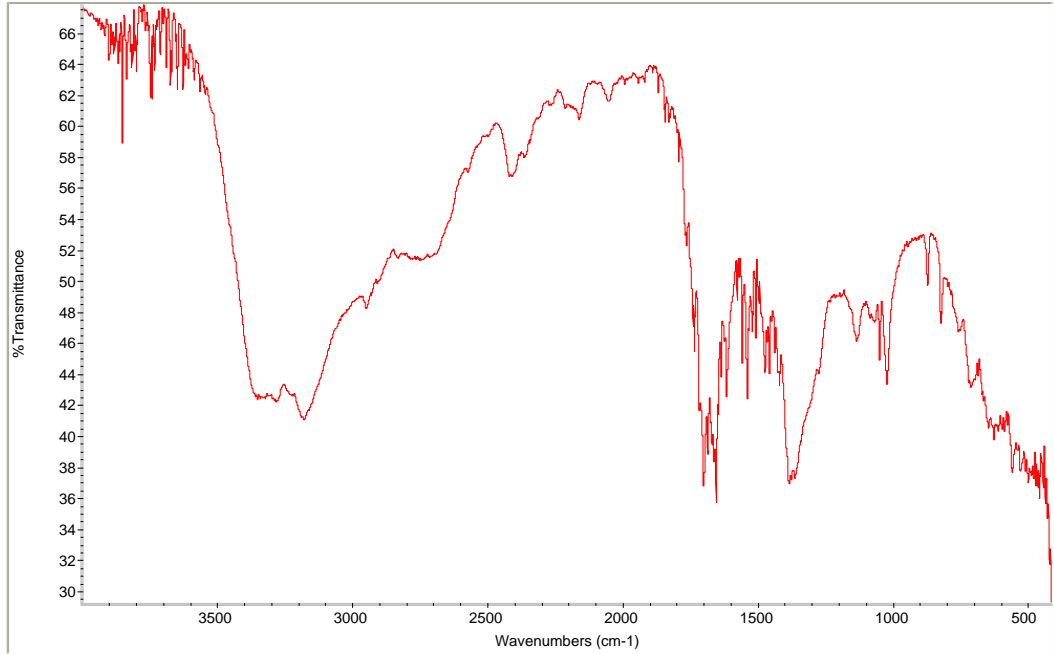
				DNMT		
				MP	Exo Onset	Exo Max
NEAT DNMT				95.7	260.6	280
RDX				88.2	204.3	230.9
MP	Exo Onset	Exo Max				
203.6	205.8	227.9				
HMX				93.7	223.4	252.8
MP	Exo Onset	Exo Max				
187.2	276.3	284.2				
NTO				97.7	176.9	231.4
MP	Exo Onset	Exo Max				
N/A	262.3	273.4				
TATB				97.6	227.1	243.5
MP	Exo Onset	Exo Max				
N/A	366.56	373.8				
DNAN				54.8	301.6	322.3
MP	Exo Onset	Exo Max				
94.2	326.9	342.9				
NQ				95.3	182.7	222.8
MP	Exo Onset	Exo Max				
N/A	195.2	202.8				
DNP				46.25	285.4	345.6
MP	Exo Onset	Exo Max				
86.5	275.8	296.9				
DNTF				81.1/92.5	233.8	268.7
MP	Exo Onset	Exo Max				
107.5	230.2	270.7				

Conclusions and Future Work

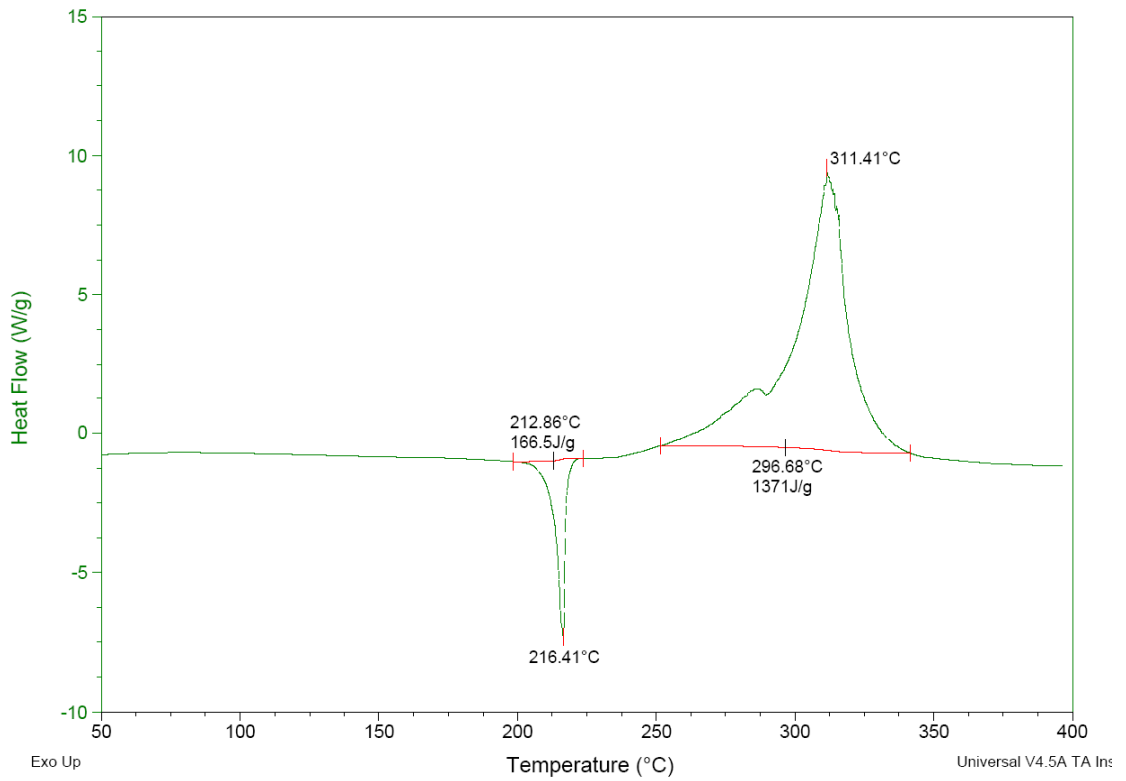
The synthetic work on DNMT shows great promise as a potentially scalable and affordable energetic melt-pour candidate. The synthesis of the DAMT precursor was considered optimized while the oxidation to DNMT still needs work. Future activities should include scale up of DNMT so that formulation activities could be pursued as well as further explosive performance testing.

Supplemental Data

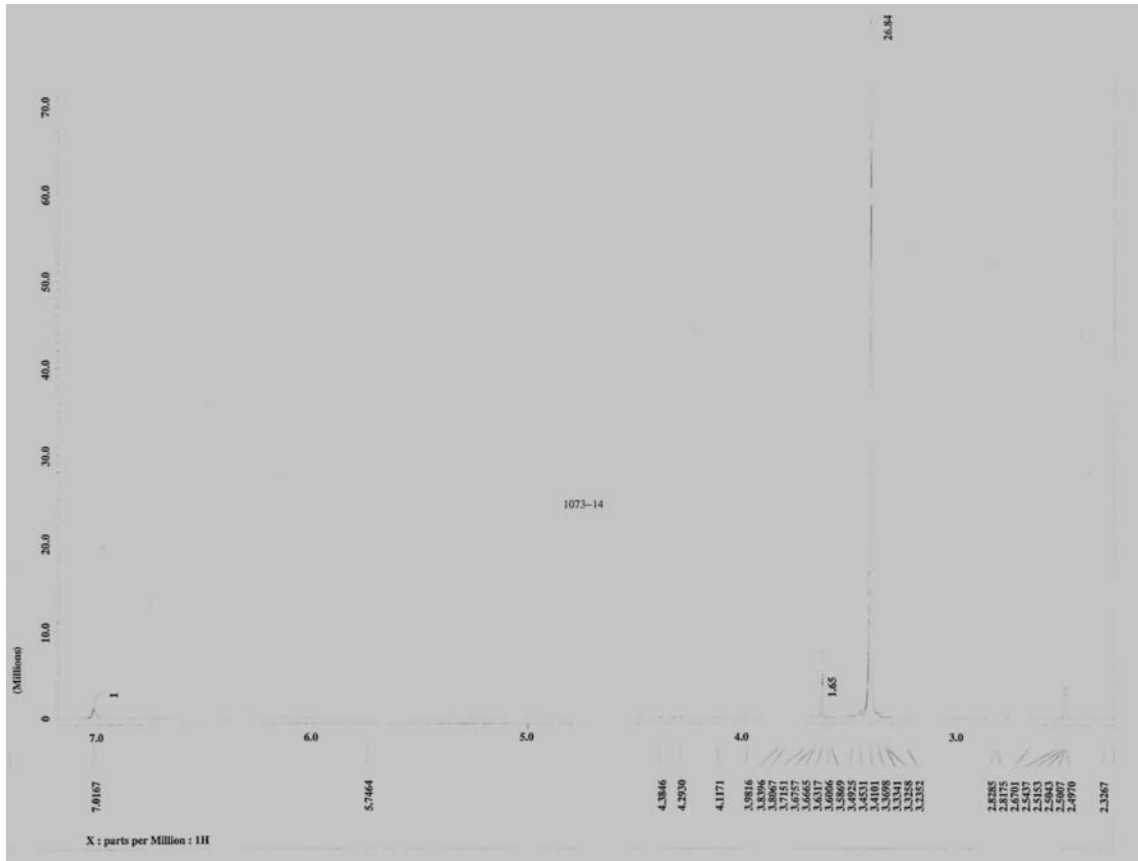
IR SPECTRUM OF DAMT



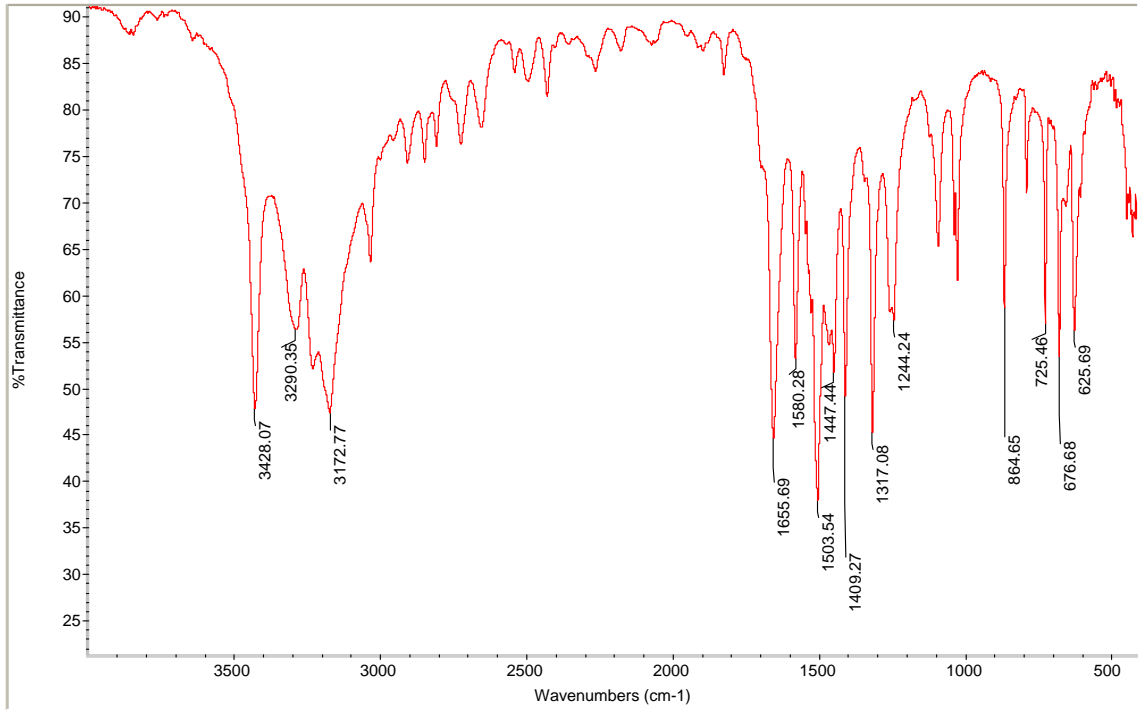
DSC OF DAMT



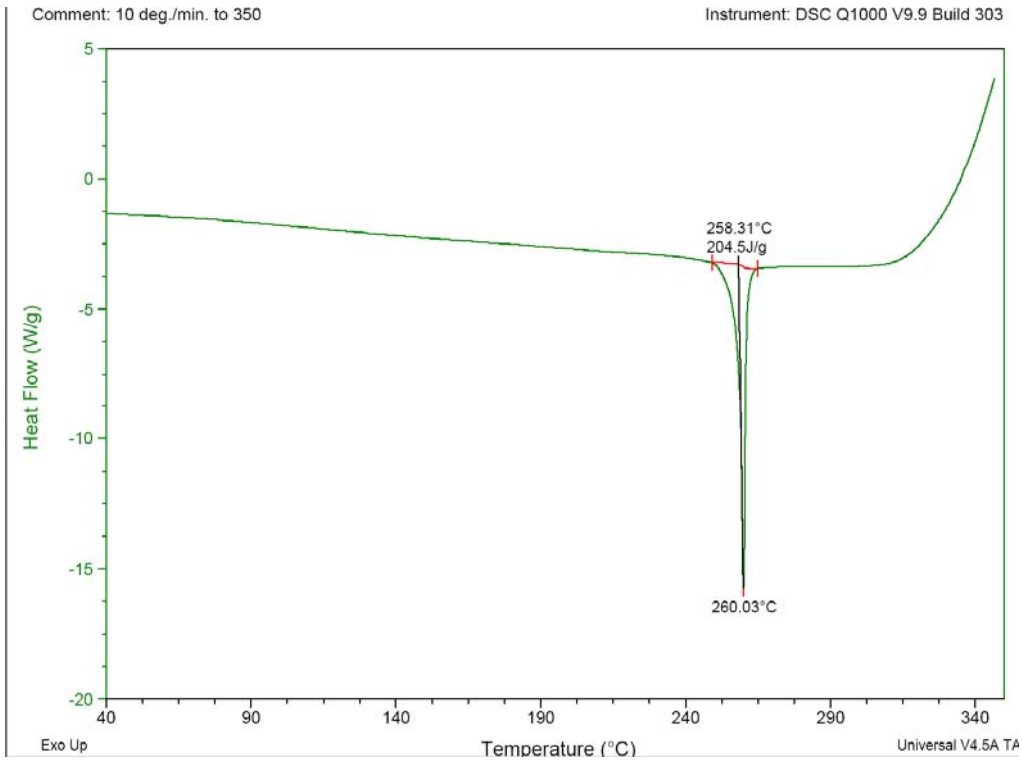
¹H-NMR SPECTRUM OF NAMT



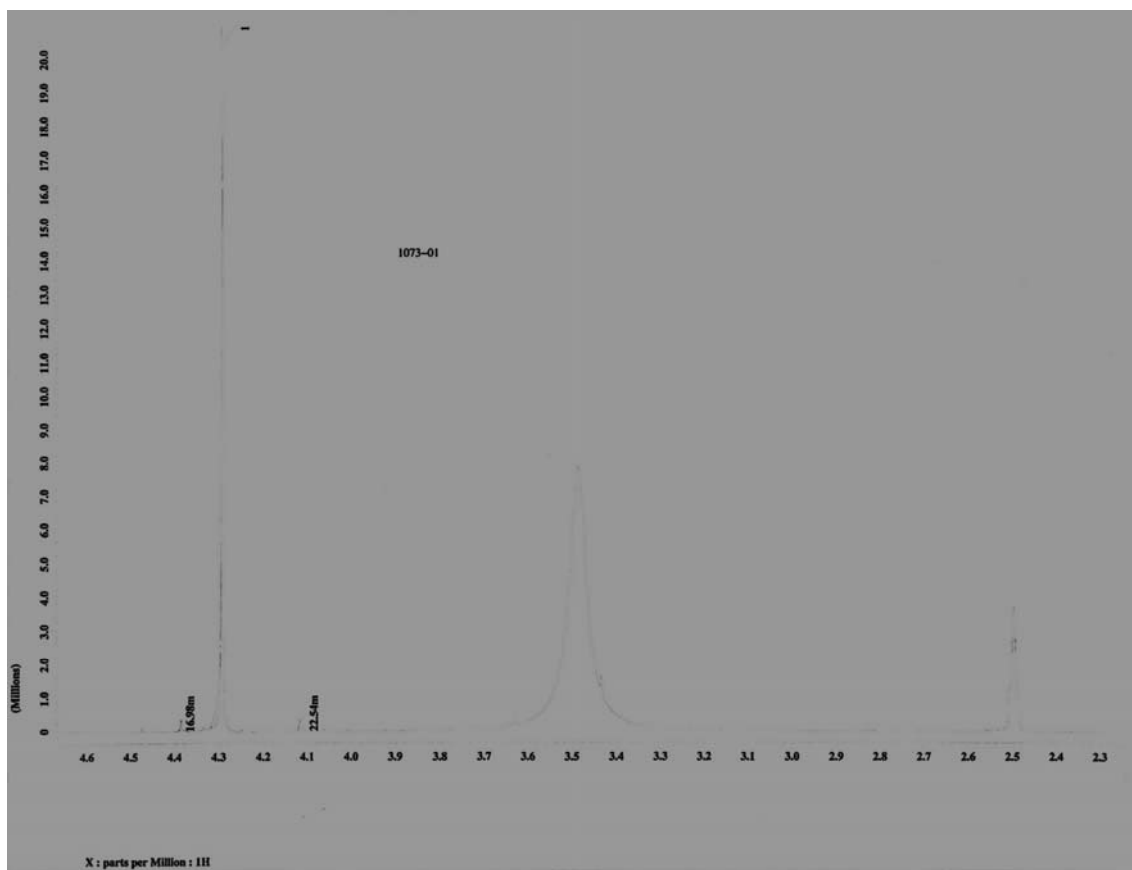
IR SPECTRUM OF NAMT



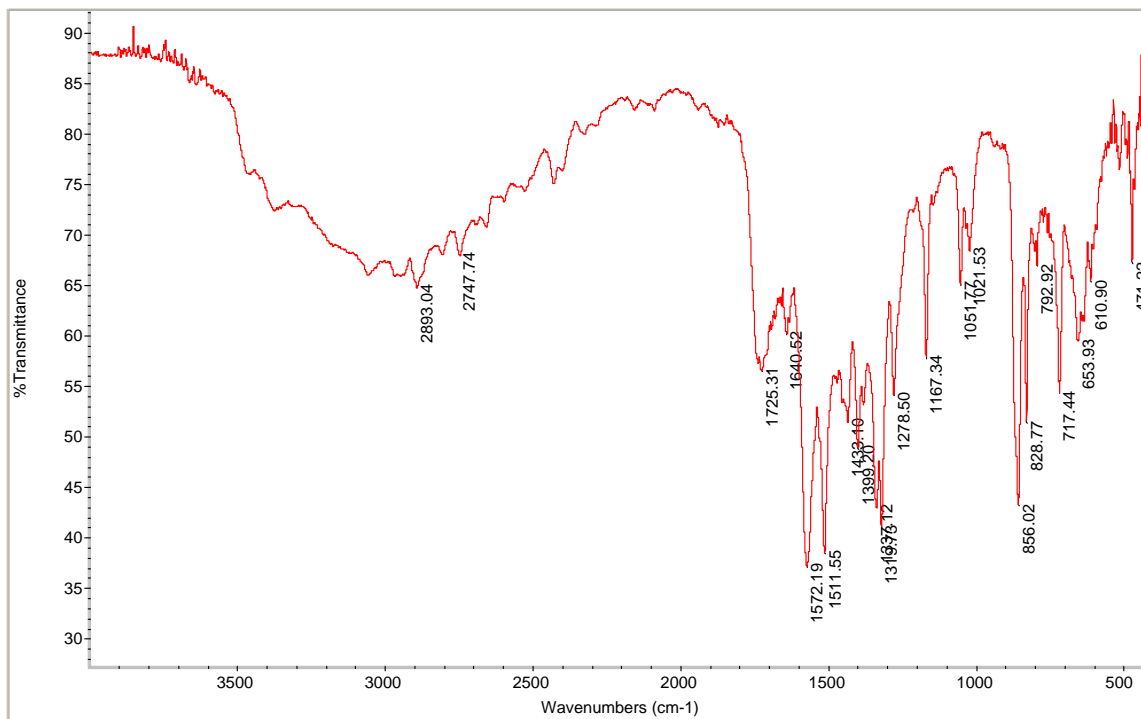
DSC OF NAMT



^1H -NMR SPECTRUM OF DNMT



IR SPECTRUM OF DNMT



DSC OF DNMT

Method: Ramp
Comment: 10C/min to 400C

Run Date: 18-Apr-2008 17:11
Instrument: DSC Q1000 V9.9 Build 303

