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Eric C Johnson, and Joseph E Banning**

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14. ABSTRACT Two new hypergolic systems have been discovered based on 3-amino-1,2,4-triazine as the fuel source. The compound was synthesized and found to be hypergolic with 100% nitric acid under ambient conditions and with solution of hydroxyl ammonium nitrate at elevated temperatures. Based on the exothermicity of these reactions, the material was selected as a candidate for further study as a possible base for a hybrid hypergolic system. The ignition delay of the nitric acid system and its predicted performance is discussed. The ignition temperature of the hydroxylamine nitrate system was determined through the use of differential scanning calorimetry at both a standard heating rate of 10 °C/min and a maximum heating rate of 40 °C/min.					
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1. Introduction

Materials that when mixed together generate enough heat to spontaneously ignite are known as hypergolic materials. These mixtures are useful in a variety of aviation applications such as space travel, where they are used to ignite rocket motors, or used as the propellant in the motors themselves, and in aviation where they have been used to ignite jet engines. While there are a number of materials that are known to be hypergolic, for these materials to be useful, it is important that they have short ignition times and be controllable. Interest has been developing in the Army for hypergolic materials that are solid/liquid or solid/gel type systems.^{1,2}

Recently, it was discovered that 3-amino-1,2,4-triazine (also referred to in this report as **1**), (see Fig. 1) a solid material, is hypergolic when mixed with 100% nitric acid (HNO₃) and in solution of hydroxylamine nitrate (HAN) when dropped onto a preheated plate. The hypergolic reaction between **1** and HNO₃ varies rapidly under ambient temperature and pressure, and is highly exothermic while the reaction of the solution of HAN requires heating. Based on observance of this phenomenon, it was determined this system should be examined to determine its properties and performance.

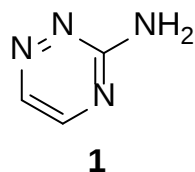


Fig. 1 Structure of 3-amino-1,2,4-triazine

2. Theoretical Property Measurements

The predicted performance characteristics of the system were obtained through first using quantum mechanical modeling to determine the heat of formation (ΔH_f) and the density of **1**. From these data, it is possible to use the CHEETAH 7.0³ code to obtain calculated performance values. The ΔH_f and density measurements were obtained using the methods detailed by Rice and Byrd.⁴⁻⁸ Using their methodology, **1** is predicted to have a density of 1.439 g/cm³ and a ΔH_f of 53.851 kilocalorie per mole (kcal/mol). The calculated density is in good agreement with the experimentally determined 1.473 g/cm³ measured through X-ray diffraction.⁹ Using CHEETAH 7.0, a formulation of 100% HNO₃ and **1** were optimized to generate the highest specific impulse (ISP). Using the formulation optimization tool, CHEETAH predicts the formulation should consist of 33.82% of **1** and

66.18% HNO_3 by weight. This optimized formulation is predicted to generate an ISP of 259.82 s.

CHEETAH was also used to optimize formulation of compound **1** and HAN. From these calculations, it was determined the optimum ratio of HAN to **1** would be 79.72% to 20.28% by weight. From the optimized formulation, CHEETAH predicts the performance of this system to be 243.7 s.

3. Ignition Delay of 3-amino-1,2,4-triazine and HNO_3

The ignition delay of the system was determined both through the analysis of a standard video camera shooting 24 frames per second (fps) and through analysis of high-speed video obtained from a photron camera system. Based on the analysis of the standard definition video, the ignition time of the system was calculated to be 294 ms. Photron analysis of the event filmed at 500 fps gave an average ignition time over 5 runs of 588 ms (Fig. 2).

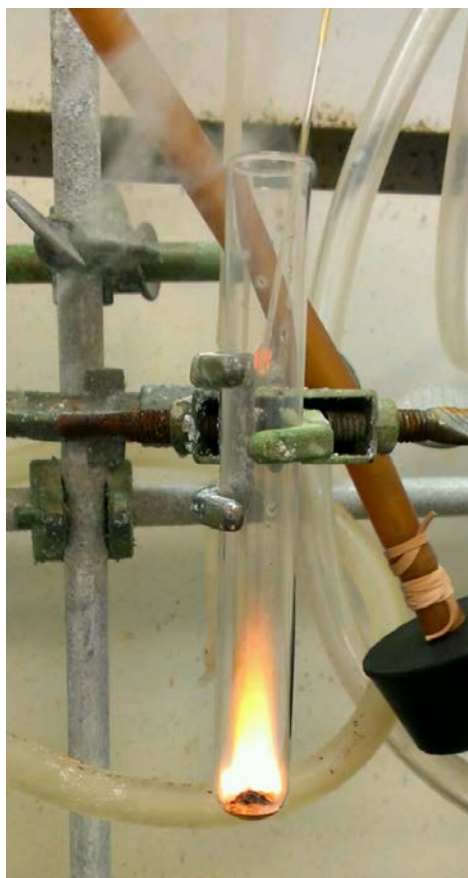


Fig. 2 Hypergolic reaction between 3-amino-1,2,4-triazine and HNO_3

4. Propellant Mixture with HAN

Compound **1** was investigated as a potential hypergol with HAN. A solution of HAN was prepared and mixed with **1**. Under ambient conditions, no reaction occurred. Slight heating was required for all of the **1** to dissolve in the HAN solution. No bubbles or other signs of decomposition were observed in the mixture. When the mixture is slowly heated in a test tube to approximately 300 °C, after all of the water has boiled out of the mixture, there is a large volume of nitrogen oxide (NO_2) gas that is liberated. This is accompanied with charring of the residual sample. However, when the solution is dropped on a plate that has been preheated to approximately 300 °C, large flames appear from the mixture and very little residue is left on the plate after the event has completed (Fig. 3). Both a solution of HAN and solid **1** were dropped onto the same preheated plate, and neither sample exhibited the same decomposition behavior as was seen with the solution of HAN and **1**.



Fig. 3 HAN and 3-amino-1,2,4-triazine dropped onto preheated plate

The differential scanning calorimetry (DSC) analysis of the solution in a hermetic pan at the maximum heating rate of the instrument shows an ignition temperature of 190 °C (Fig. 4).

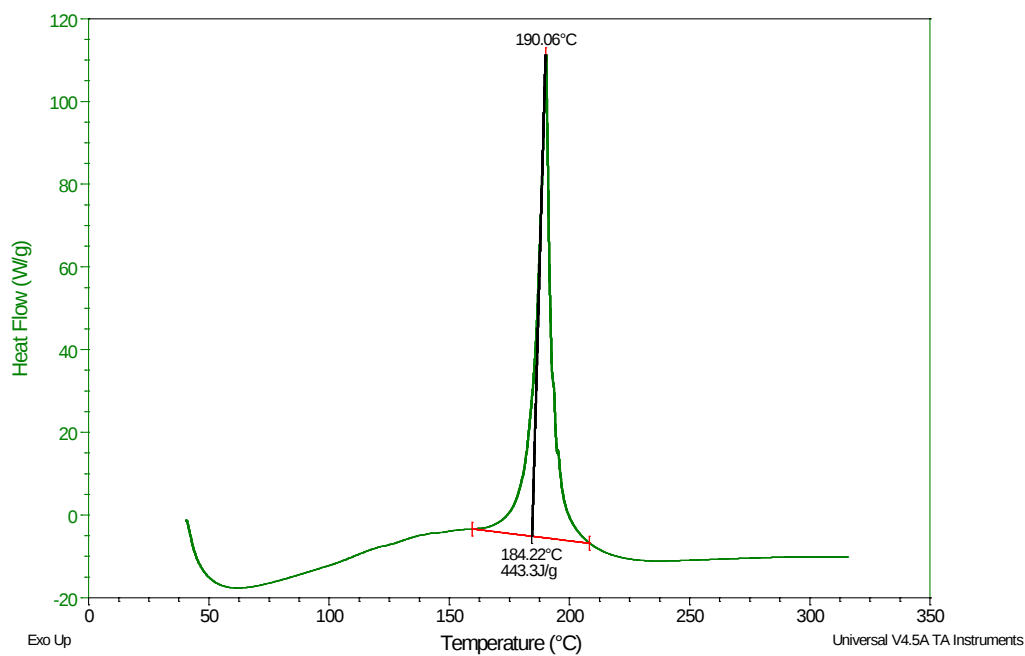


Fig. 4 DSC of HAN and 3-amino-1,2,4-triazine at maximum heating rate

Running the DSC on the solution at a heating rate of 10 °C gives a slightly different ignition temperature of 156 °C (Fig. 5).

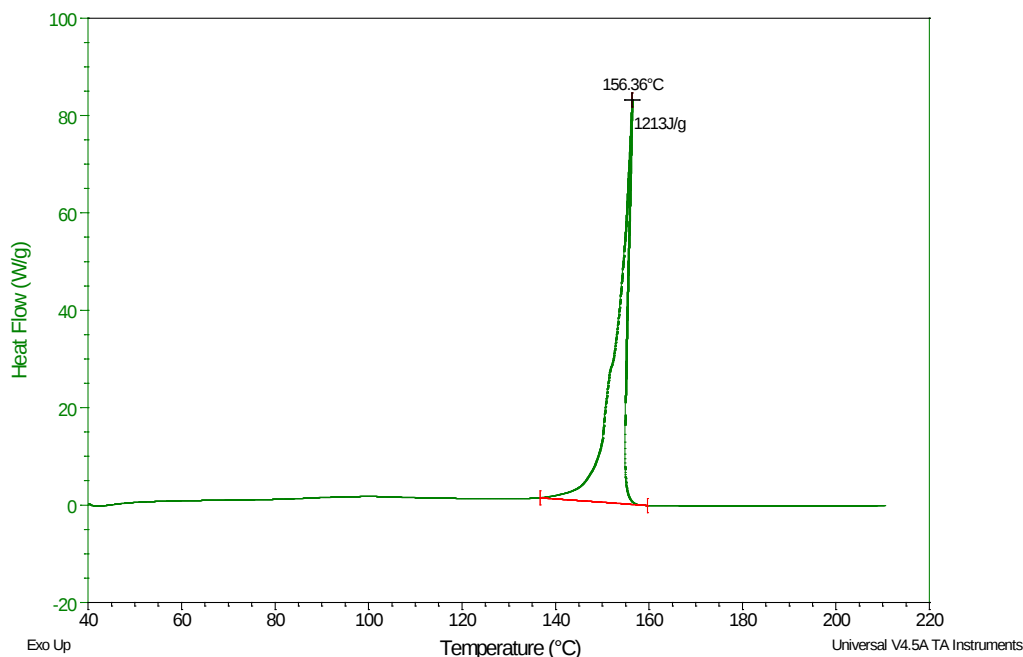


Fig. 5 DSC of HAN and 3-amino-1,2,4-triazine at 10 °C/min

Standard definition video of the event recorded at 24 fps gives an ignition delay of the system of between 500 and 1,000 ms.

A brief optimization of the fuel to oxidizer ratio was run starting at the CHEETAH-defined optimum 80% HAN to 20% **1**. At the 80% HAN mixture, the material was unable to be ignited even when the plate was heated to near 400 °C. However, by decreasing the amount of HAN to 76% the material was readily ignited. The material was still capable of being ignited until the amount of HAN dropped below 65% at which point there was not enough oxidizer present to allow for any combustion and the mixtures simply charred on the heated plate. The results are summarized in the following Table.

Table Summarized results of optimization screening

HAN^a (wt %)	1^b (wt %)	Result	Predicted ISP^c (s)^d
80	20	No ignition	250.94
76	24	Ignited	247.74
70	30	Ignited	239.63
67	33	Ignited	235.01
65	35	No ignition charring	231.73

^a Hydroxylamine nitrate. ^b Reference to 3-amino-1,2,4-triazine. ^c Specific impulse.

^d Chamber pressure held to 70 atm.

5. Experimental

5.1 General Information

Nuclear magnetic resonance (NMR) spectra were recorded on an Anasazi Instruments 90 MHz NMR. Dimethyl sulfoxide (DMSO)-D₆ was obtained from Sigma-Aldrich and used as received. All NMR chemical shifts are reported in ppm and are relative to a ¹H (which is the proton designation referring to NMR) shift of 2.50 ppm and ¹³C (which is the carbon designation referring to NMR) shift of 39.54 ppm for DMSO-D₆. All NMR spectra are available in the appendix to this report. Gas chromatograph mass spectrometer (GC/MS) analyses were performed on a Shimadzu GC-2010 gas chromatograph interfaced with a Shimadzu QP-2010S mass spectrometer, and equipped with an AOC-20i auto-injector with either a 6 or 12 sample rack. The column was a 25 m × 0.25 mm × 0.25 μm Shimadzu designated SHR5XLB polydimethylsiloxane, 5% Ph capillary column. Helium (99.96%) was the carrier gas and it was pretreated by passing it through a VICI Metronics oxygen/moisture trap (P100-1). Fourier transform infrared (FTIR) spectra were recorded on a Brüker Alpha-T equipped with a platinum attenuated total reflectance (ATR) diamond cell and were sampled neat. DSC was conducted on a TA instruments Q10 or Q20 calorimeter and is available in the appendix of this report. High-speed videography was conducted using a Photron model SA-5 camera system shooting at 500 fps. Aminoguanidine bicarbonate and 40% aqueous glyoxal were obtained from Sigma-Aldrich and were used as received.

5.2 Synthesis of 3-amino-1,2,4-triazine

Compound **1** was prepared via a slight modification of the method described by Erickson in his patent¹⁰. Amino guanidine bicarbonate (29.2 g, 215 mmol) was suspended in 60 mL of water. To this was added 22.8 g (157 mmol) of 40% aqueous glyoxal and the mixture was allowed to stir for 18 h at 20–25 °C. The suspended solid was then filtered and the mother liquor was evaporated to dryness. The resulting residue was extracted with ice-cold methanol (3 × 50 mL) and the combined methanol rinses were then re-cooled, filtered, and the mother liquor was concentrated. The resulting solid was recrystallized from acetonitrile to yield 11.23 g (117 mmol, 75%) of a slightly yellow solid, 3-amino-1,2,4-triazine.

DSC 10 °C/min melt at 177 °C is in good agreement with literature values. NMR data are in agreement with what has been previously published in the literature¹¹. **¹H NMR** DMSO-*d*₆ (90.420 MHz) δ 8.52 (d, *J* = 2.4 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.16 (br. s. 2H); **¹³C NMR** DMSO-*d*₆ (22.605 MHz) δ 163.4, 150.0, 140.7; **FTIR** (DATR), $\tilde{\nu}$ = 3292, 3098, 1557, 1532, 1516, 1489, 1113, 1076, 1044, 865, 848, 794, 633, 593, 460; **MS (EI)** = 42, 68, 96 (*M*⁺).

5.3 3-amino-1,2,4-triazine and HNO₃ Determination of Ignition Delay

Fifty milligrams of **1** was placed into a test tube. Using a 9-inch glass pipette, a single drop of 100% HNO₃ was dropped onto **1**, and the event was filmed at 24 fps. The resulting video footage was placed into video editing software, and 7 frames were counted from the time the drop of HNO₃ touched **1** until the first emission of light. With each one of the frames equating to 24 ms, the ignition delay of the system under ambient conditions was determined to be 294 ms.

To determine the ignition delay of the HAN solution of **1**, a metal plate was heated to 350 °C using a heat gun. The temperature of the plate was measured using a thermocouple. Once the temperature of the plate had stabilized, a 9-inch pipette was used to drop a single drop of the HAN solution onto the heated plate. The event was filmed using a camera shooting at 24 fps. Using video editing software, 12 to 35 frames were counted from the time the drop first hit the plate until the first emission of light. The large variability in these measurements can be attributed to inconsistent drop size as well as inconsistencies in the heating of the plate.

5.4 Preparation of HAN

Using a volumetric pipette, 1 mL of a commercially available 50% by weight solution of hydroxylamine was added to a test tube and cooled to 0 °C in an ice bath. To this was slowly added 953 mg of 100% HNO₃ and the mixture was stirred for 5 min and then allowed to warm to ambient temperature. This resulted in a solution that was 74% HAN by weight.

5.5 Preparation of HAN and 3-amino-1,2,4-triazine Mixture

A sample of 340 mg of **1** was dissolved with slight heating into the 1-mL HAN solution prepared according to the method previously described.

6. Conclusions

The compound **1** has been found to exhibit hypergolic properties with both HNO₃ and HAN. In the case of HNO₃, the hypergolic reaction takes place at ambient temperature and pressure; it has a measured ignition delay of 588 ms, and a predicted ISP of 259.82 s. With HAN, the reaction takes place at elevated temperatures with an ignition point between 150 and 190 °C depending on heating rate. The predicted ISP for this system is 243.7 s. The reaction between HAN and **1** is promising based on the fact that the solution would behave as a monopropellant using water as the solvent. The solution of the **2** is nonviscous, making it possible to be pumped easily and ignites readily on exposure to a preheated surface.

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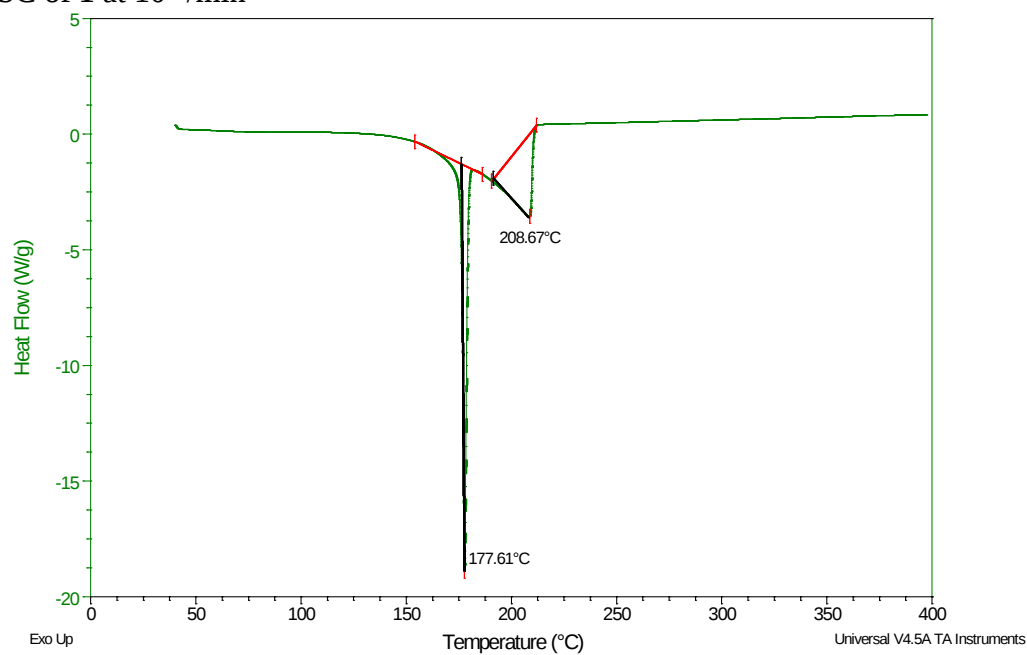
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Appendix. Spectral Data

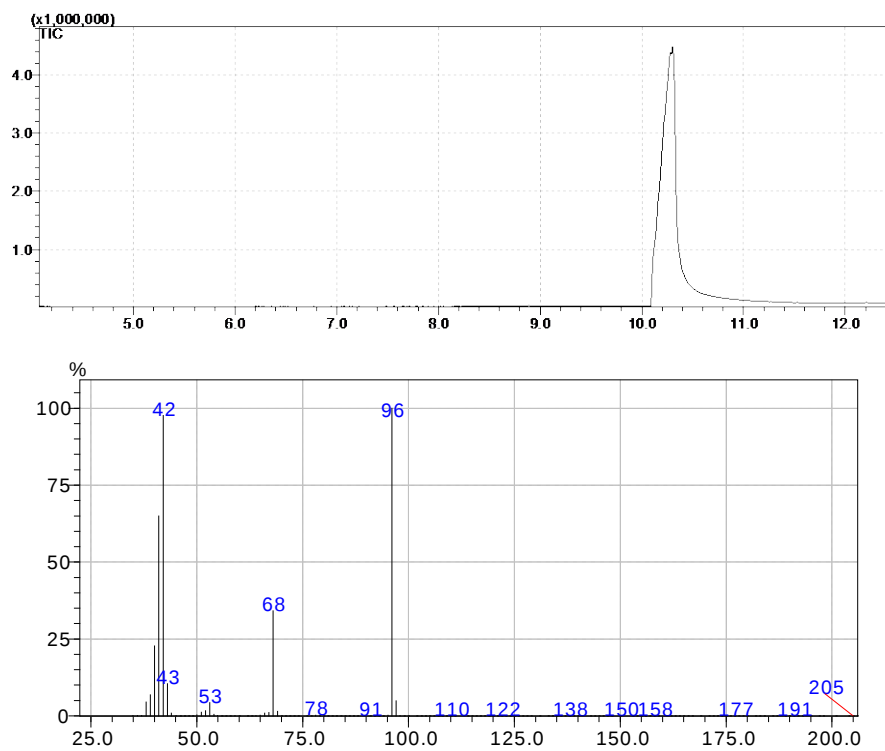
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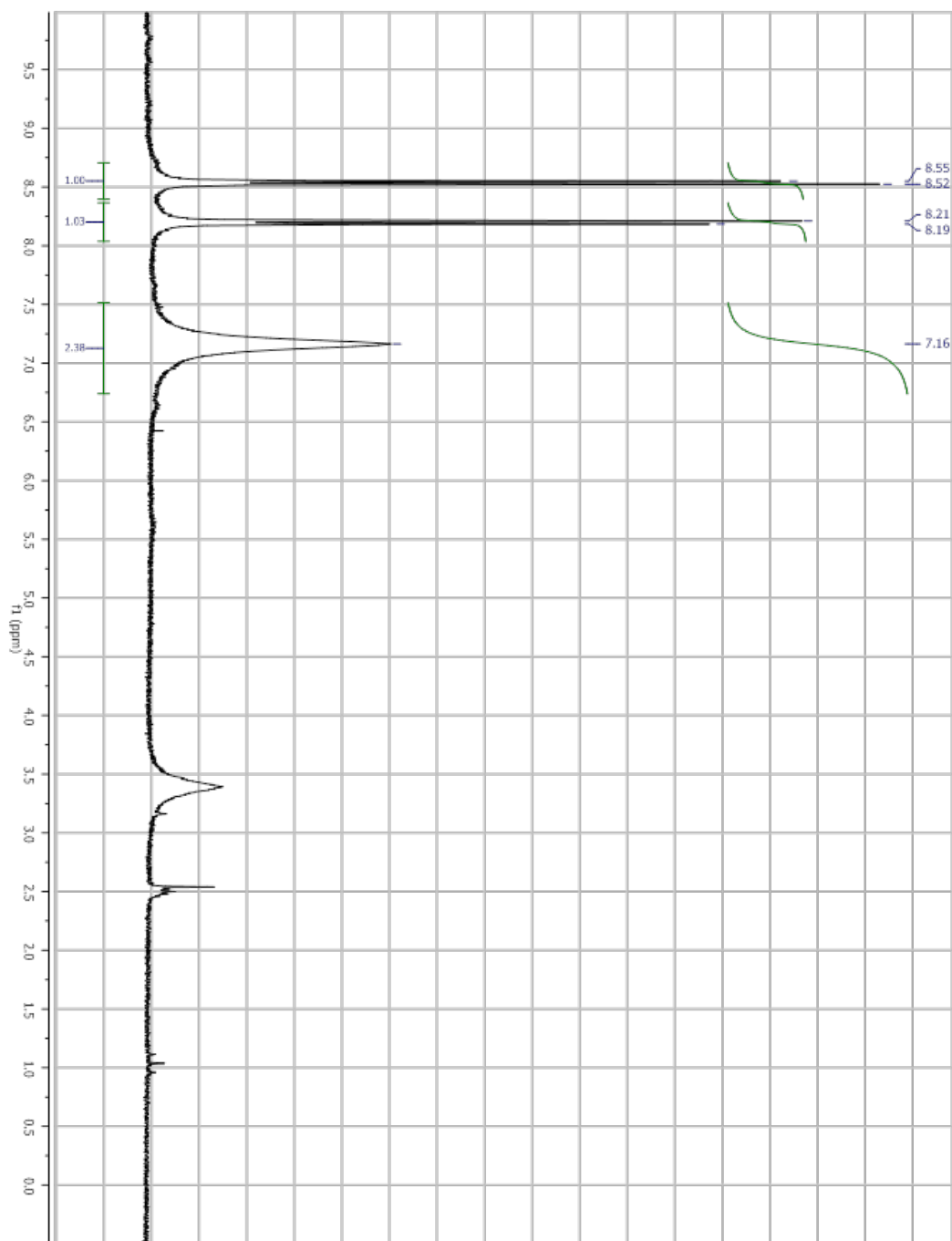
DSC of **1** at 10 °/min



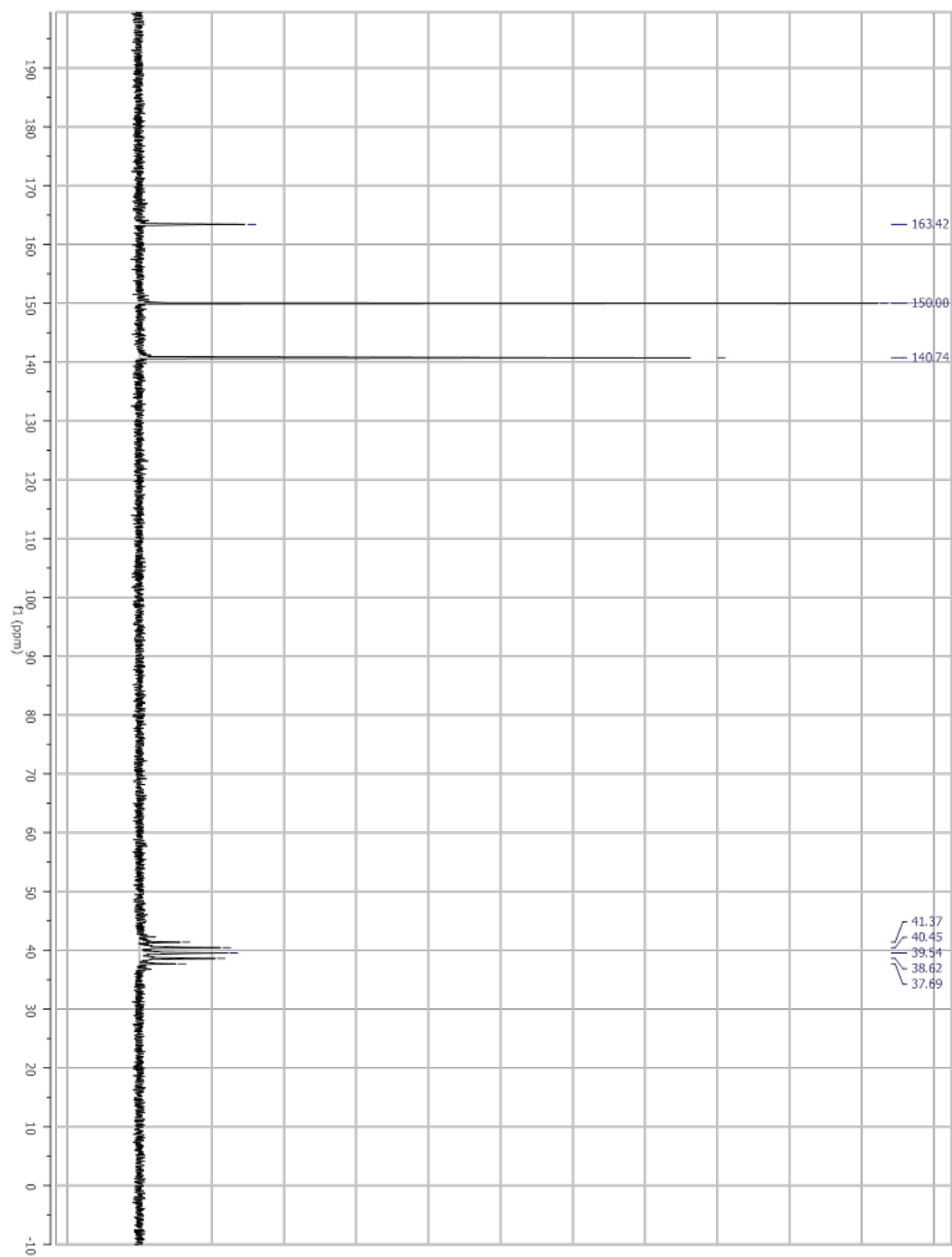
GC-MS Data of **1**



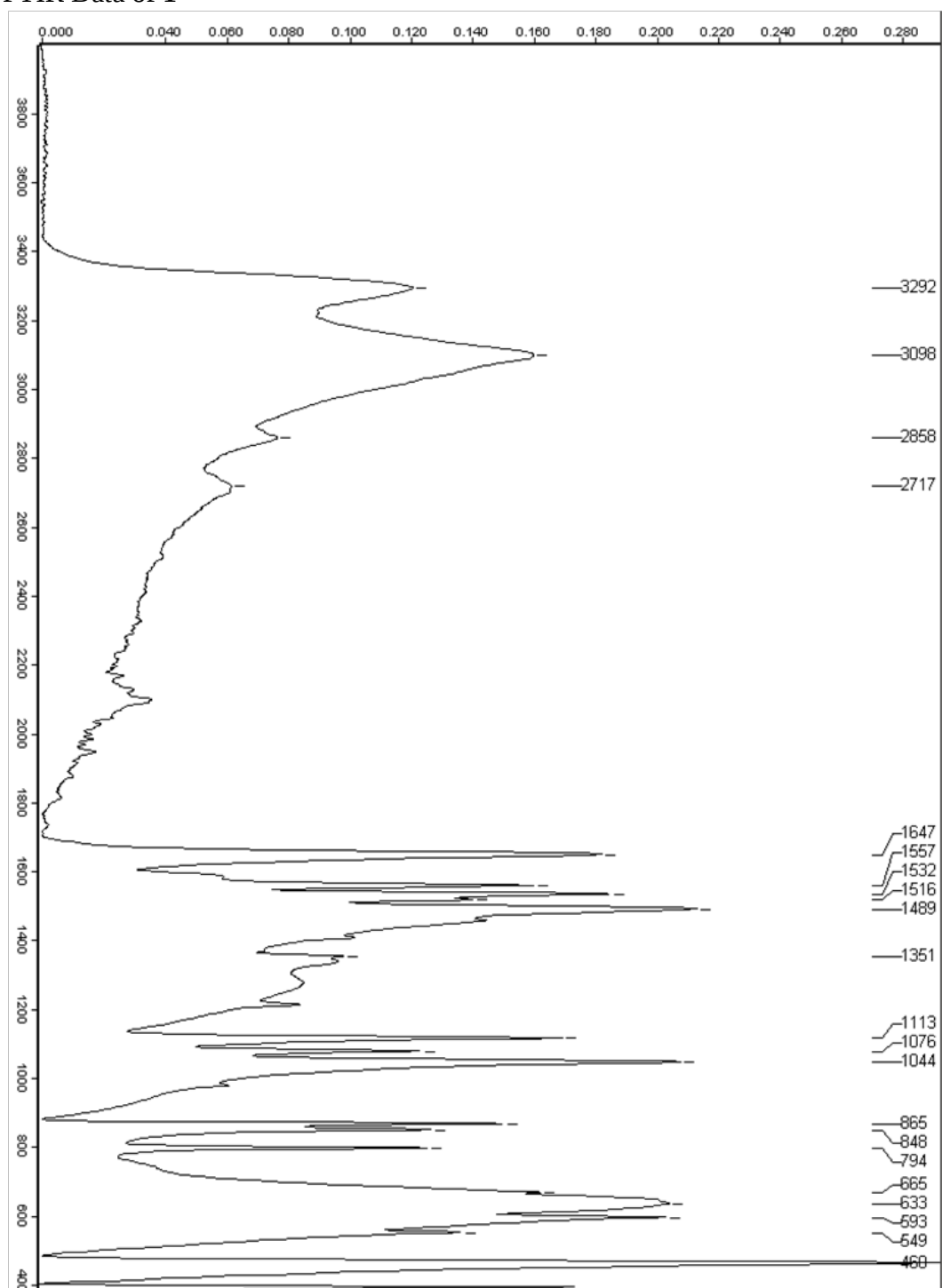
^1H NMR Data of **1**



^{13}C NMR Data of **1**



FTIR Data of 1



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List of Symbols, Abbreviations, and Acronyms

1	reference to 3-amino-1,2,4-triazine
ATR	attenuated total reflectance
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
fps	frames per second
FTIR	Fourier transform infrared
GC/MS	gas chromatograph mass spectrometer
HAN	hydroxylamine nitrate
HNO ₃	nitric acid
ISP	specific impulse
kcal/mol	kilocalorie per mole
NMR	nuclear magnetic resonance
ΔH_f	heat of formation

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