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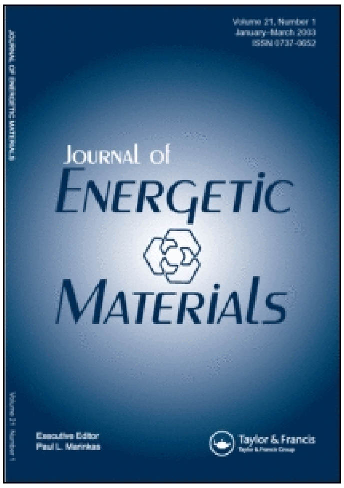

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The Properties of Ammonium Dinitramide (ADN): Part 1, Basic Properties and Spectroscopic Data

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ABSTRACT

Basic properties and spectroscopic data for the energetic oxidizer ADN (Ammonium dinitramide ($NH_4N(NO_2)_2$)) are presented. The ADN used for this work was synthesized by a new efficient and environmentally friendly method. The method is based on a direct nitration of salts of sulfamic acid by ordinary mixed acid, followed by neutralization and separation of the ADN by the use of an adsorption column. The heat of formation was measured by burning in hydrogen atmosphere in an adiabatic bomb calorimeter and was found to be 148 kJ/mole ±10 kJ/mole. The melting point was determined using DSC technique and is 93.5°C. This paper reports drop weight, friction and bullet impact sensitivity data. The friction sensitivity of ADN is much lower than that of RDX. The impact sensitivity of ADN is of the same magnitude as that of RDX but varies a great deal with the morphology of the particles, e.g. prilled ADN is nearly twice as insensitive as RDX. The bulk density measured by powder *X*-ray diffraction and was found to be 1.82 gcm^{-3}. ADN does not show any sign of phase transitions in the -150°C to +80°C temperature interval (measured by single crystal *X*-ray diffraction). FTIR and FT-Raman spectra are also presented. In the UV-VIS region, ADN is characterized by two absorption peaks at 214 and 284 nm. UV-VIS spectroscopy was also found to be the most useful method for quantitative routine analysis of ADN.

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INTRODUCTION

In the search for new energetic materials, ADN (Ammonium dinitramide ($NH_4N(NO_2)_2$))[1] has emerged as an interesting candidate for replacing AP (Ammonium Perchlorate) as a halogen-free oxidizer in composite propellants. It has also a large potential as an ingredient in gun propellants, as well as for underwater explosive applications. It could also be used as a component in melt-cast explosives as it melts at about 93 °C.

A large number of papers have been published on ADN, e.g.[2-7]. Most of these papers have been based on experiments on ADN batches from different sources. However, ADN has been shown to exhibit very different thermal behavior depending on its purity[8] and hence on its method of synthesis. It is thus very important to know the purity of ADN and preferably to use materials synthesized with the same method. This is especially important for studies of its morphology, sensitivity, thermal stability, decomposition and compatibility. ADN and Potassium Dinitramide (KDN) also exhibit several unusual decomposition behaviors[9,10](e.g. ADN decomposes faster at 60°C than at 70°C when it is very dry[9]).

This series of papers will present a comprehensive study of the properties of ADN, all performed on material synthesized with a new and simpler method[11] which produces purer ADN at a much lower price than earlier methods. This first paper will deal with the basic properties of ADN, such as heat of formation, crystal density, sensitivity (drop weight, friction and bullet impact) and spectroscopic data such as mass spectroscopy, FTIR and FT-Raman spectroscopy and UV-VIS. The next paper will deal with thermal sensitivity and stability, followed by papers on compatibility, detonation performance and shock sensitivity.

SYNTHESIS

The ADN used for this work was synthesized at the Defence Research Establishment (FOA), using the new method[11], see Figure 1. This method gives purer material and have the potential of being less expensive than the conventional (SRI) method[12] in that that it uses much cheaper starting materials and is easier to carry out. This new method is now used in production at NEXPLO Bofors AB.

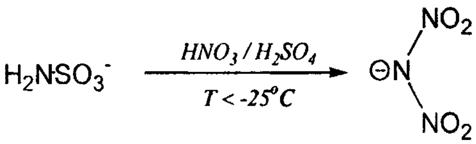

Figure 1. *Synthesis of dinitramide ion.*

The method is based on a direct nitration of salts of sulfamic acid (e.g. potassium or ammonium) by ordinary mixed acid (sulfuric and nitric acids), followed by neutralization and separation of the ADN by the use of an adsorption column. This method doesn't use any organic solvent, which is of great environmental importance. The extent of reaction was measured with UV-spectroscopy (see below), which enables the monitoring of the reaction in pseudo real time and hereby increases the yield. The purity of the ADN was measured using an HPLC technique[13], and found to be >99.5%.

The particle shape from the synthesis could best be described as fluffy flakes and needles (see Figure 2a). In order to get better particle shapes for propellant use, a melt method for prilling ADN was tested. This method produced spherical particles with a diameter of about 200 µm (see Figure 2 b).

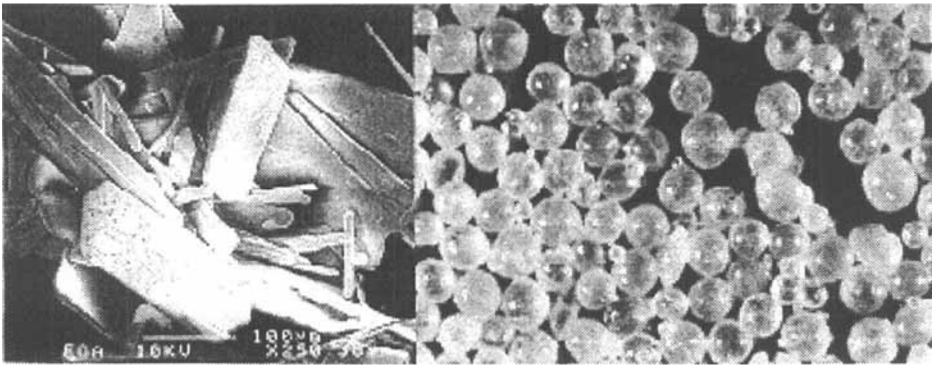

Figure 2. *ADN particle shapes: a) Electron microscope picture of re-crystallized ADN. b) Prilled ADN, about 200 µm in diameter, viewed through an ordinary optical microscope.*

The melting point of ADN was determined using DSC technique and is 93.5°C (peak value), see Figure 3. The instrument used was a Mettler 30 instrument.

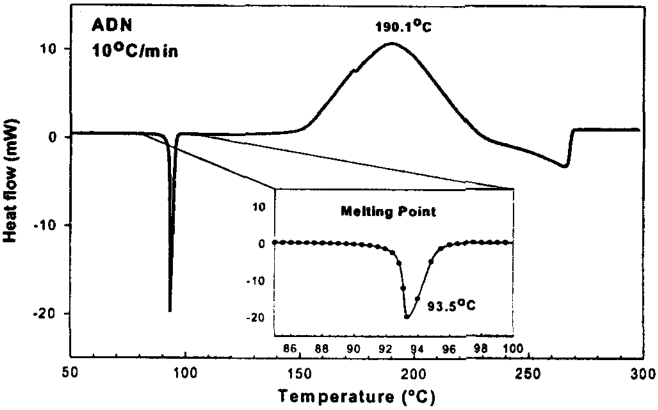

Figure 3. *DSC plot for ADN.*

SENSITIVITY

The drop-weight sensitivity and the friction sensitivity of ADN were measured. The impact sensitivity was measured with a 2 kg drop weight BAM drop-weight apparatus[14]. The results are based on tests on both sides of the 50% probability level using an up-and-down method. The friction sensitivity was measured with a BAM friction apparatus[14], using the same technique. The calculations were performed with the ML14 computer code[15]. The shock sensitivity of ADN was measured using the bullet impact test[16]. The results of these tests are given in Table 1 where data for RDX and TNT are given for comparison.

Table 1. *Sensitivity data for ADN, RDX and TNT.*

Explosive	Drop Weight (cm)	Friction Test (kp)	Bullet Impact Test (m/s)	Comments
ADN (powder)	31	> 35	309-316	See fig. 2 a
prilled ADN	59	> 35		See fig. 2 b
RDX	38	12		
TNT (powder)	>120	> 35	364-405	

The friction sensitivity of ADN is much lower than that of RDX. The impact sensitivity of ADN is of the same magnitude as that of RDX but varies a great deal with the shape of the particles. Prilled ADN for instance is nearly twice as insensitive as RDX, which indicates that sensitivity to impact is greatly dependent on the shape of the ADN particles. ADN has slightly higher shock sensitivity than TNT as measured with the bullet impact test. The reaction of ADN is less violent than that of RDX in all these tests.

DENSITY

Single-crystal *X*-ray diffraction methods have been used to investigate the temperature dependence of the cell parameters of ADN. The temperature interval in which the change in cell parameters is investigated is in the range from 123 to 353 K. The cell parameters have also been investigated at room temperature 293 K using powder *X*-ray diffraction. The bulk density of ADN using powder *X*-ray diffraction and single crystal *X*-ray diffraction density at 293 K is 1.8139(2) g·cm^{-3} and 1.8183 (10) g·cm^{-3}, respectively.

The single-crystal *X*-ray diffraction investigation of the temperature dependence of the cell parameters was performed with a selected single crystal of ADN with the shape of a plate (size 0.07·0.25·0.50 mm^3) mounted on a STOE AED2 four-circle diffractometer with a graphite monochromator isolating MoK_α radiation (λ=0.71073 Å) and with a scintillation detector. The diffractometer was equipped with a low-temperature nitrogen cryostat from Oxford Cryosystems. A total set of 22 suitable reflections in the 2θ interval 18.2°-37.1° were used, i.e. 11 independent reflections and their respective Friedel pair. For each temperature in the order 293, 273, 253, 233, 213, 193, 173, 153, 123, 163, 223, 273, 293, 313, 333, 353 K the list of reflections was centered 2 times followed by a double step-scan and a cell refinement. In this way, accurate cell parameters were determined for each temperature step in the whole temperature range. At 293 K the cell parameters were determined to be a=5.6228(5), b=11.8750(30), c=6.8954(8), β=100.17(2) and V= 453.19(11).

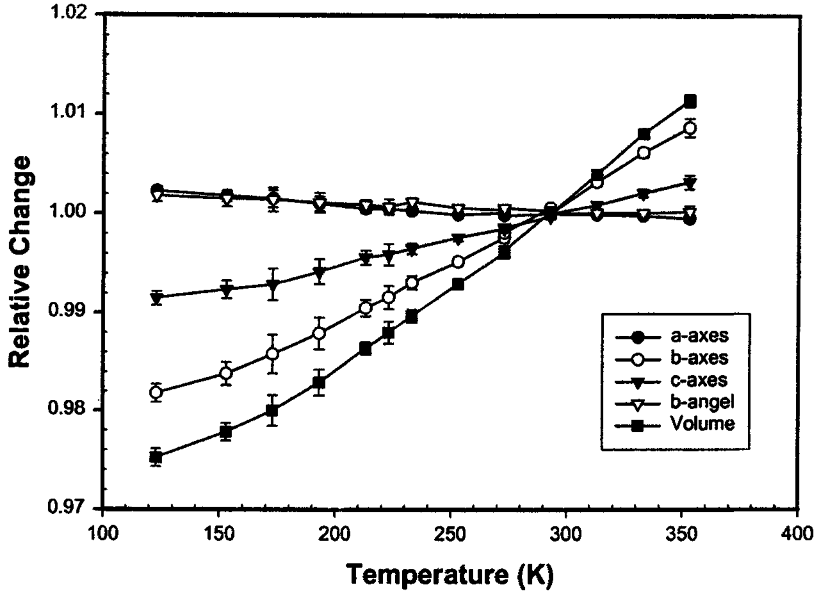

Figure 4. *Relative change of cell dimensions versus temperature*

In Figure 4 the relative change of the cell parameters a, b, c, β and V is shown, and as can be seen from Figure 4 the b- and c-axes are those which are most affected by the temperature change. The b- and c-axes decrease with decreasing temperature while the a-axis and the monoclinic β-angle increase, and moving upwards above room temperature reverses these changes and the b- and c-axes increase while the a-axis and the monoclinic β-angle decrease. The relative changes of the b- and c-axes are -1.8 % and -0.8 %, respectively, at 123 K and +0.9% and +0.3 % at 353 K. It is also seen from Figure 4 that the change in the cell parameters is reversible when temperature again increases from 123 K to 293 K. Figure 5 represents the change in density and the relative changes in the density become +2.6 % at 123 K and -1.1 % at

353K. The conclusion from these measurements it that no phase transition exists in the -150°C to +80°C temperature interval.

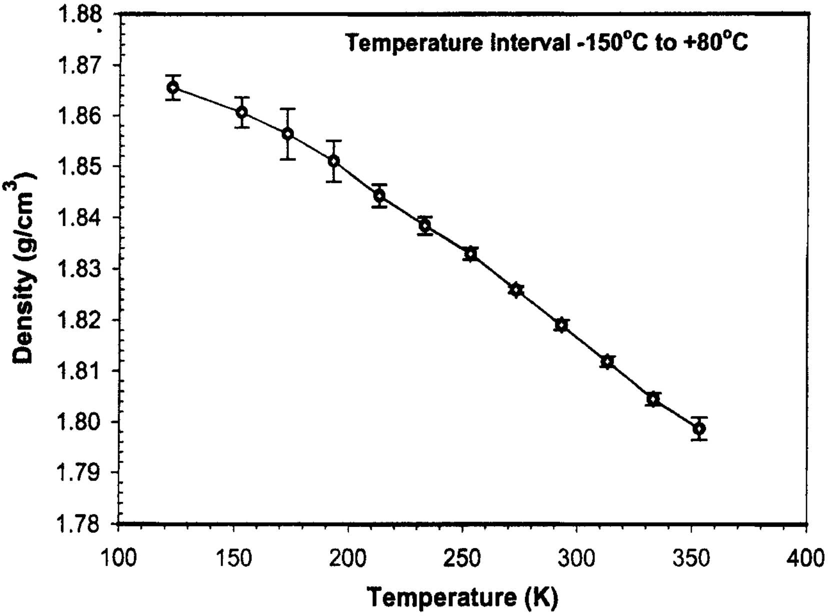

Figure 5. *Density vs. Temperature for ADN*

HEAT OF FORMATION

Generally, the determination of the heat of formation of a substance is performed by having the substance combusted in oxygen atmosphere in a bomb calorimeter. Thus, the heat of combustion is obtained, from which the heat of formation can be calculated. With a strong oxidizer like ADN, this method will cause problems. ADN has different decomposition reactions. Some of the main decomposition reactions are considered to be (1) and (2), below[4,6,7]:

$$NH_4N(NO_2)_2 \rightarrow NH_3 + HN(NO_2)_2 \rightarrow 2N_2O + 2\,H_2O \qquad (1)$$

$$2HN(NO_2)_2 \rightarrow N_2 + 3NO_2 + NO + H_2O \qquad (2)$$

The ammonia formed is oxidized by the nitrogen dioxide. Obviously, for ADN, oxygen is not the best reagent of choice. Preliminary experiments indicated that, under our reaction conditions, acidic nitrogen oxides were formed. The analysis of these reactants would be time consuming and the calculations are complex. For this reason, the reaction was instead carried out in a hydrogen atmosphere. In this way the following reaction is dominating:

$$H_4N_4O_4(s) + 2H_2(g) \rightarrow 2N_2(g) + 4H_2O(l) \qquad (3)$$

Only nitrogen and water will be formed and both the experiments and the calculation of the heat of formation is easy to carry out. The apparatus used was an adiabatic bomb calorimeter of the IKA C 4000 type.

The calibration of the calorimeter was done by combustion of certified benzoic acid in an oxygen atmosphere at a pressure of 3' MPa. The oxygen was added without displacing the original air. About one gram of the benzoic acid was added, weighed to the nearest 0.1 mg. In most experiments, 5.0 g of distilled water was added in the bomb in order to have liquid water in equilibrium with its vapor both before and after combustion. In the other cases, corrections were made for the condensation heat of that amount of water still in gas phase after the combustion reaction. The procedure was similar to the international standard ISO 1928: 1995(E).

The heat of reaction with hydrogen at constant volume of the ADN material was determined by combustion of weighed portions of the ADN sample in hydrogen at a pressure of about 0.5 MPa. Before ignition the bomb was filled and evacuated 4-5 times with hydrogen to get rid of all significant amounts of oxygen gas in the bomb. After ignition and measurement of the temperature rise, the bomb was opened and the content of the bomb was washed into a beaker with distilled water. The reaction products, which looked like pure water, were found to be alkaline, pH ≈ 11. The basicity of the reaction products indicates that to some extent at least one other reaction than (3) occur. We suggest the formation of ammonia

$$H_4N_4O_4 + 7/2H_2 \rightarrow 3/2N_2 + 4H_2O + NH_3 \qquad (4)$$

Analysis showed that small amount of ammoniac is formed (less than 5%). In comparison to the overall deviation, the correction for this reaction was considered negligible. Table 2 shows the results from the bomb calorimeter experiments with ADN.

Table 2. *Results from calorimetric experiments with ADN.*

mass ADN	Temp. rise	Heat of combustion		Heat of formation
g ADN	Δ T (K)	kJ/g	kJ/mole	$\Delta H_{f,\mathrm{const.volume}}$ kJ/mole
1.46061	1.261	7.895	979.45	-149
0.9771	0.852	7.885	977.745	-151
1.2836	1.120	7.890	978.566	-150
1.3284	1.164	7.926	982.824	-146
1.4017	1.230	7.935	984.450	-144

The mean value of the heat of formation from these experiments is thus found to be -148 kJ/mole and the estimated error is ±10 kJ/mole.

Determination of the heat of formation for ADN from combustion in hydrogen seems to be a more convenient method than by combustion in oxygen. To get good results from combustion in oxygen, mixing of the ADN sample with a combustion aid, e.g. benzoic acid, would probably make the analysis easier. In this way, however, only a small contribution of heat will be obtained from the ADN part of the sample and the deviation in the results will be large.

UV -VIS SPECTROSCOPY

Since ADN is a water-soluble salt, one of the best methods for analyzing ADN is ordinary UV-VIS spectroscopy. Figure 6 shows an UV-spectrum of ADN, or more exactly the dinitramide ion. The UV-VIS spectrum of ADN is characterized by two peaks at 214 and 284 nm. Table 3 gives the molar absorption coefficient, ε. The use of UV-VIS spectroscopy enables real-time measurements of ADN in aqueous solution. UV-VIS is also one of the best methods for routinely analyzing ADN and for concentration measurements. All measurements presented here were done on a Perkin Elmer Lambda 40.

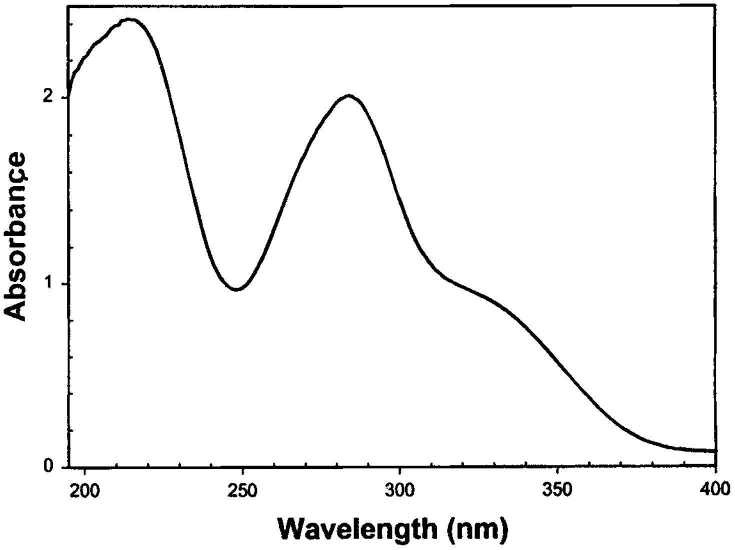

Figure 6. *UV-spectrum of dinitramide ion in water solution.*

TABLE 3. *Molar absorption coefficient, ε, of ADN*

Wavelength (nm)	ε (Lmole^{-1}cm^{-1})
214	6680
284	5500

MASS SPECTROSCOPY

The mass-spectroscopic study was conducted on a JEOL 300D double-focusing magnetic sector instrument equipped with a PC-based computer system with Technivent Vector/2 software for data analysis. All mass spectra were acquired using the solid sample inlet with a heating rate of about 50°/min. Electron Impact (EI), 20 and 70 eV, as well as Chemical Ionization (CI) spectra were acquired. The CI spectra were obtained using methane as the reagent gas. The major peaks in these spectra are given in Table 4. This data indicates that ADN has a low thermal stability because no larger mass fragment than *m/z* 46 existed even at 20 eV. This data also shows that mass spectroscopy, using EI as the ionization source, is not a viable method for analyzing or identifying ADN. Earlier measurements of the mass spectrum of ADN[17] using FAB ionizing gave more peaks and could possibly be used for analyzing ADN. A more comprehensive mass-spectroscopic study is in prep.

Table 4. *Major ADN mass peaks.*

Ionization	*m/z*
EI 20 eV	30,32,44,46
EI 70 eV	28,30,44,46

FTIR AND FT-RAMAN SPECTROSCOPY

In addition to the UV analysis of ADN, both FTIR and FT-Raman have proved useful in the identification and analysis of ADN[18]. FT-Raman spectroscopy in particular is a very good method for studying ADN. This method uses only a small amount of solid sample (a few mg of powder) and is very easy to perform. Figure 8 shows a FT-Raman spectrum of ADN. The spectrum presented here was measured with a Bruker IFS 55 equipped with a Raman attachment. The excitation wavelength was 1064 µm and the resolution used was 2 cm^{-1}. The Raman peaks are sharper than the FT/IR peaks. The major Raman peaks are given in Table 5. Earlier measurements of IR and Raman spectra have been reported[18,19]. In the paper by Fell[19], a large peak can be seen at 1040 cm^{-1} in the ADN FT-Raman spectrum. This peak is probably from ammonium nitrate impurities in the ADN. Our Raman spectrum corresponds very well with the spectrum published by Christe[18], except that the peak at 1338 cm^{-1} is stronger than the peak at 833 cm^{-1}. This could be because we used an excitation wavelength of 1064 nm instead of 488 nm, and possibly because by using FT-Raman technique instead of a scanning technique we can acquire a spectrum independent of any degradation of the sample. Our FTIR spectrum, Figure 7, shows some more structures than the spectrum by Christe, but we do not have any explanation for this. The conclusion from the FT-Raman and FTIR measurements is that FT-Raman is superior to FTIR in the study/identification of ADN, in that the peaks are sharper and more well defined, and the Raman technique is not influenced by moisture.

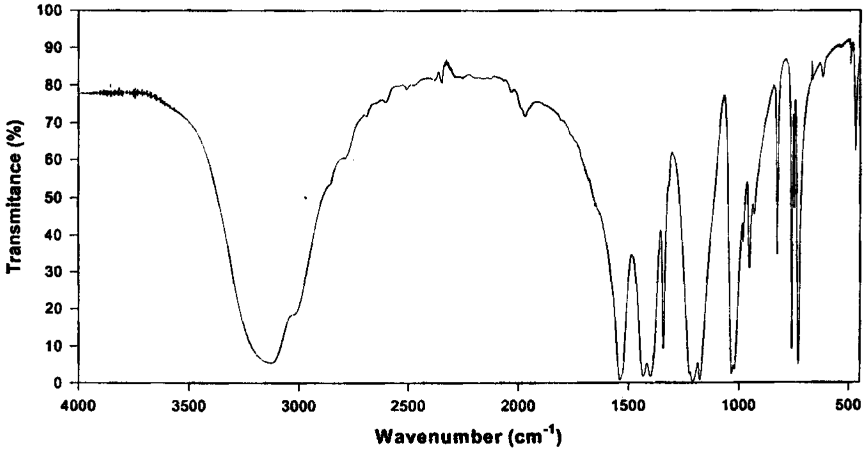

Figure 7. *FTIR Spectrum of ADN.*

Table 5. *Major Raman peaks for ADN and their assignments.*

Wavenumber (cm^{-1})	Assignment[18]	Rel. Intensity
1338	ν s NO_2 in phase	0.230 (R)
1178	ν s NO_2 out of phase	0.047 (R)
958	ν s N_3	0.051 (R)
833	δ sciss NO_2 in phase	0.183 (R)
495	δ wag NO_2 in phase	0.063 (R)
297	?	0.037 (R)

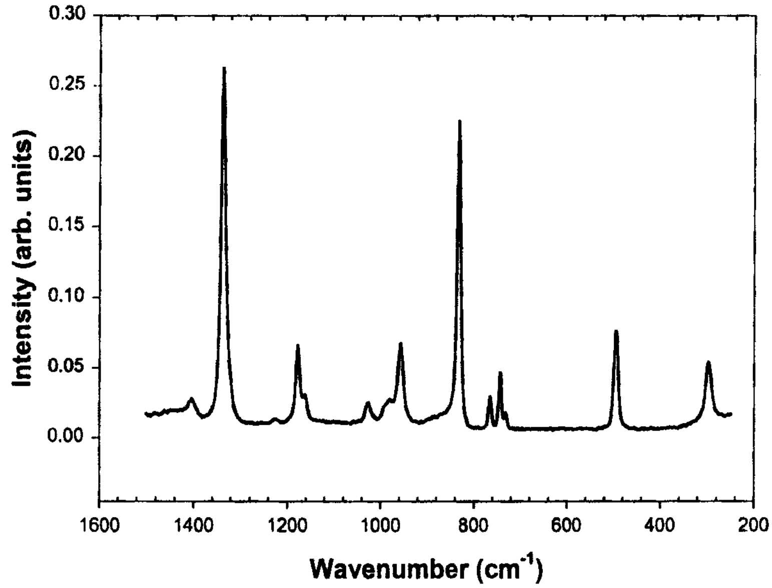

Figure 8. *FT-Raman Spectrum of ADN.*

CONCLUSIONS

As this is the first paper in a series, only conclusions based on the measurements presented here will be discussed. There is no general conclusion on the usefulness of ADN in different applications in this paper. Table 6 gives a compilation of the basic data presented in this article.

The following conclusions can be drawn:

- The impact sensitivity of ADN is of the same magnitude as that of RDX but varies a great deal with the morphology of the particles.
- The friction sensitivity is less than that of RDX.
- ADN has a high bulk density (1.82 g/cm^3) and shows no sign of phase transitions in the -150°C to +80°C temperature interval.

- UV spectroscopy is the most useful method for quantitative routine analysis of ADN.
- FT-Raman spectroscopy is superior to FTIR as the Raman lines are sharper and the method is insensitive to moisture.
- Mass spectroscopy using electron impact ionization is not a suitable method for analyzing ADN.

TABLE 6. *Compilation of basic ADN data.*

Heat of Formation, ΔH	-148 kJ/mole
Density at 293 K, by single crystal *X*-ray diffraction	1.8183 g/cm^3
by powder *X*-ray diffraction	1.8139 g/cm^3
Sensitivity, Drop Weight (RDX)	31 cm (38 cm), powder 59 cm (38 cm), prilled
Friction Test (RDX)	> 35 kp (12 kp)
Melting point (by DSC using peak value)	93.5°C
Major Raman peaks (Rel. Intensities)	495 cm^{-1} (0.063), 833 cm^{-1} (0.183), 958 cm^{-1} (0.051), 1178 cm^{-1} (0.047), 1338 cm^{-1} (0.230)
UV peaks	214 nm, 284 nm
Molar absorption coefficients	ε_{214}= 6680 Lmole^{-1}cm^{-1} ε_{284}= 5500 Lmole^{-1}cm^{-1}

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