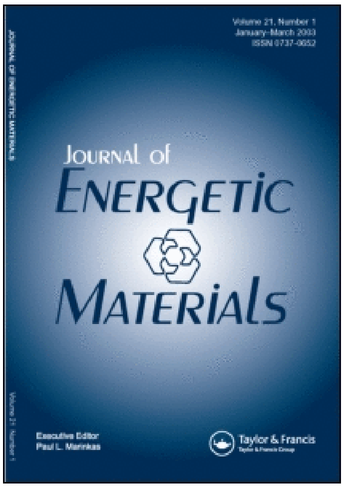

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Synthesis and properties of selected energetic organodi- and polyammonium nitrate salts

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SYNTHESIS AND PROPERTIES OF SELECTED ENERGETIC ORGANODI- AND POLYAMMONIUM NITRATE SALTS

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ABSTRACT

The objective of this investigation was to synthesize and characterize selected organodi- and polyammonium nitrate salts for use in a qualitative study of thermal and impact stability characteristics. A total of twenty-two salts were prepared and characterized. A literature search confirmed that fifteen of these materials had never been reported and, therefore, were assumed to be original. The general synthesis process is described with specific details for each compound included. Elemental analyses are provided for the new compounds as well as their nuclear magnetic resonance spectra. Other data included are

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densities (calculated and measured), heats of fusion, melting points, the temperature of the major peak associated with exothermic decomposition as measured by a differential scanning calorimeter and Fourier transform infrared spectra.

INTRODUCTION

Within the U. S. Air Force, there is an extensive, ongoing research program to develop an improved explosive fill for bombs that will, in effect, reduce the quantity-distance constraints associated with storage. One proposed new composition, EAK, was composed of a mixture of ammonium nitrate (AN), potassium nitrate (KN) and ethylenediammonium dinitrate (EDD). AN is a readily available and inexpensive oxidizer material used extensively in commercial explosives. EDD is an oxygen-deficient fuel material that forms a low melting eutectic composition with AN, as well as with many other organic and inorganic salts. It was used as an explosive ingredient as early as 1915[1] and is a principal component in a rather extensive list of explosive formulations covering the time period 1945 to present. KN was added as a solid state phase modifier for AN.

During the initial interest in the EAK mixture, the material was studied extensively with respect to its detonation characteristics; however, only minor interest was paid to gaining a basic understanding of the thermal properties of this complex salt mixture. The mixture later failed slow cookoff qualification testing. It was speculated that a comprehensive thermal property study could be accomplished rather effectively by use of a series of EDD homologues, oligomers, N-substituted species and, perhaps, other similar compounds. This prompted the synthesis of the organodi- and polyammonium nitrate salts described in this report.

A comprehensive search of the literature revealed that only a few of the nitrate salts had previously been prepared and reported. Consequently, this paper not only reports some significant properties of these materials, but also elemental analyses confirming the preparation and the nuclear magnetic resonance spectra supporting the proposed structure. All of the compounds in this report are listed in Table 1.

EXPERIMENTAL

Preparation

Typically, the nitrate salts of amines containing more than one amino functional group were prepared by reacting the base with 70 percent nitric acid in cold 95 percent ethanol or methanol. All amino functional groups within the specific molecules used in this study, whether primary, secondary or tertiary, are converted to the respective ammonium ions by this method. The acid is added dropwise to the cold alcohol solution of the respective amine with stirring. The reaction vessel should be maintained in an ice bath throughout the addition of acid to minimize formation of

TABLE 1. ORGANODI– AND POLYAMMONIUM NITRATE SALTS INCLUDED IN STUDY

	COMPOUND NAME	ACRONYM	MOLECULAR FORMULA
A.	*Homologues of EDD*		
1.	Ethylenediammonium dinitrate	EDD	$C_2H_{10}N_4O_6$
2.	1,3–Propanediammonium dinitrate	PDD	$C_3H_{12}N_4O_6$
3.	1,4–Butanediammonium dinitrate	BDD	$C_4H_{14}N_4O_6$
4.	1,6–Hexanediammonium dinitrate	HDD	$C_6H_{18}N_4O_6$
B.	*N–Substituted EDD*		
5.	N–Methylethylenediammonium dinitrate	MEDD	$C_3H_{12}N_4O_6$
6.	N–Ethylethylenediammonium dinitrate	EEDD	$C_4H_{14}N_4O_6$
7.	N–Isopropylethylenediammonium dinitrate	IPEDD	$C_5H_{16}N_4O_6$
C.	*N,N′–Substituted EDD (9=N,N–)*		
8.	N,N′–Dimethylethylenediammonium dinitrate	s–DMEDD	$C_4H_{14}N_4O_6$
9.	N,N–Dimethylethylenediammonium dinitrate	u–DMEDD	$C_4H_{14}N_4O_6$
10.	N,N′–Diethylethylenediammonium dinitrate	s–DEEDD	$C_6H_{18}N_4O_6$
D.	*N,N,N′–Substituted EDD*		
11.	N,N,N′–Trimethylethylenediammonium dinitrate	TRMEDD	$C_5H_{16}N_4O_6$
12.	N,N–Dimethyl–N′–ethylethylenediammonium dinitrate	DMEEDD	$C_6H_{18}N_4O_6$
13.	N,N,N′–Triethylethylenediammonium dinitrate	TREEDD	$C_8H_{22}N_4O_6$
E.	*N,N,N′,N′–Substituted EDD*		
14.	N,N,N′,N′–Tetramethylethylenediammonium dinitrate	TMEDD	$C_6H_{18}N_4O_6$
15.	N,N,N′,N′–Tetraethylethylenediammonium dinitrate	TEEDD	$C_{10}H_{26}N_4O_6$
F.	*Miscellaneous*		
16.	Diethylenetriammonium Trinitrate	DETN	$C_4H_{16}N_6O_9$
17.	Triethylenetetrammonium Tetranitrate	TETN	$C_6H_{22}N_8O_{12}$
18.	Tetraethylenepentammonium Pentanitrate	TEPP	$C_8H_{28}N_{10}O_{15}$
19.	Piperazinium dinitrate	PIPZD	$C_4H_{12}N_4O_6$
20.	1,4–Diaza–bicyclo[2.2.2]octane dinitrate	DABCOD	$C_6H_{14}N_4O_6$
21.	3,3′–Imino–bis–propylammonium trinitrate	IBPAT	$C_6H_{20}N_6O_9$
22.	1,1–Dimethylethylenediammonium dinitrate	TBDD	$C_4H_{14}N_4O_6$

ethyl nitrate. Since product usually forms as a whitish precipitate, it is important to ensure that enough alcohol is used to maintain free stirring. As an exception, no precipitate was formed during the preparation of 1,1-dimethylethylenediammonium dinitrate. After removal of the solvent from the reaction liquor in vacuo at approximately 70°C, acetone was added to the residual oil to effect solidification. The acetone was removed in vacuo leaving a white solid residue. Recrystallization from ethanol (95 percent) was then effected. All other samples were recrystallized from ethanol (95 percent) with just enough water added to facilitate dissolution unless stated otherwise. Elemental analyses were obtained for original compounds.

The attempted preparation of 1,5-pentanediammonium dinitrate by the method described above yielded a tan oil. Treatment of this oil with acetone produced a tan solid after removal of the latter in vacuo. Recrystallization attempts repeatedly yielded a tan oil. The FTIR spectrum of the tan solid, although showing the absorptions characteristic of nitrate ion, was of little use in helping to confirm the structure of the product. The dihydrochloride was then prepared by a method similar to that described above, m.p. 261°C[2]. This material was dissolved in water and treated with a stoichiometric amount of aqueous silver nitrate. After removal of the precipitated silver chloride by filtration, the water was removed in vacuo leaving a white solid as residue. Attempts to recrystallize this material also proved fruitless. Mass spectrometric characterization gives some support for the expected straight-chain product.

Densities

Densities were calculated for each of the salts[3] and also measured using a Quantachrome Stereopycnometer, Model Number SPY-2. The errors in the results were calculated from the standard deviations at the 95 percent Student t confidence level.

Heats of Fusion

Qualitative heats of fusion were measured for eighteen of the organodi- and polyammonium nitrate salts by the cut and weigh method and by using the Perkin-Elmer DSC-4/Thermal Analysis Data Station System. A Perkin-Elmer DSC-2 coupled with a strip-chart recorder was used to obtain the thermograms for the former method. The DSC-2 heating rate to calibrate the paper for the cut and weight method and to obtain the thermograms for each salt was 5°C/min. Each sample was run in duplicate and the melting curves were each photocopied in triplicate. The weight representing the area under the melting endotherm for each measurement is the average of the three photocopied traces. The heats of fusion determined with the DSC-4 were the result of single measurements at a heating rate of 10°C/min except for EDD and BDD, where the result is from six or more measurements. A nitrogen atmosphere and alumina reference material were used for all measurements. The DSC-4 was calibrated to the indium heat of fusion. The errors in the results were calculated from the standard deviations at the 95 percent Student t confidence level. Heat of fusion values obtained by the cut and weigh method will appear in parentheses.

Nuclear Magnetic Resonance Spectra

^{1}H NMR spectra were obtained using a Varian EM-390 90-MH$_Z$ spectrometer. D_2O was used as the solvent in all cases. The internal reference was sodium [2,2,3,3-D_4]3-(trimethylsilyl)-propionate (TSP).

Impact Sensitivity Characteristics

Impact data were obtained with a Bureau of Mines, Model No 2, Impact Device. The compounds to be tested were vacuum dried for several hours at temperatures up to 60°C. They were then ground and sieved in a low humidity box where the relative humidity was maintained in the 20 to 30 percent range. Unless otherwise noted, the sieve range used for impact testing was 80 to 325 mesh and the sample size for each test was 35 ± 3 mg. Each powdered sample was impacted on Norton coated abrasive paper of 180 grit (FSN 5350-271-7930). Twenty-five to thirty samples were used for each complete test. The $H_{50\%}$ for each compound was obtained by the Bruceton test.

Thermal Characterization

Thermal characterization was accomplished with a Perkin-Elmer DSC-4/Thermal Analysis Data Station System and a Mettler FP1 Melting and Boiling Point Apparatus. In some cases, melting points were obtained using a capillary tube in a stirred hot oil bath or a microscope equipped with a hot stage. The DSC scan rate in all cases was 10°C/min and values obtained are the result of one measurement, except for BDD where three measurements were made. Sample capsules were standard aluminum pans and covers (Perkin-Elmer part number 219-0062) with the latter perforated with a pin to a standard size hole. The sample capsule used to measure the exotherm for BDD under sealed conditions was a gold-plated, stainless steel, high pressure capsule (Perkin-Elmer part number 419-1760). The thermal results presented in this study are more extensive for BDD than for the other salts because BDD is currently the subject of a comprehensive thermal degradation investigation.

Fourier Transform Infrared Spectra

Fourier transform infrared (FTIR) spectra were obtained using a Mattson Cygnus 25 FTIR Spectrometer. All spectra were obtained as KBr pellets. Peak positions are given in cm^{-1} and have been corrected.

Mass Spectrometric Analyses

Mass spectrometric analyses were accomplished with a Finnigan MAT Mass Spectrometer Model 5100 GC/MS system operating at 70 eV.

RESULTS AND DISCUSSION

Most of the aliphatic di- and polyammonium nitrate salts reported in this paper have not previously been described. In general, they are all white crystalline solids that are soluble in water. Although no quantitative hygroscopicity studies were conducted, qualitative observations showed most to be hygroscopic to varying degrees. The preparation solvents listed below are the ones giving the highest yield. Samples of EDD and TETN were not specifically prepared for this study.

Attempts to prepare 1,5-pentanediammonium dinitrate yielded an oil, which when treated with acetone, produced a tan solid. Depending on the method of preparation, melting points of the solid varied in the range 50 to 90°C with apparent decomposition. It is possible that a cycloelimination reaction may occur during this preparation to yield piperidinium nitrate and ammonium nitrate in varying amounts. Introduction of the solid products obtained from the various preparation attempts into a mass spectrometer by the solids probe technique yielded data supportive of the expected straight chain homolog. Typically, these salts enter the mass spectrometer as the free diamine and nitric acid when flash heated to a temperature at or near their melting points. Nitric acid breaks down to yield characteristic peaks at m/e 63, 46 and 30. The diamine produces fragmentation peaks characteristic of its molecular structure. Fragmentation is similar to that observed for alcohols with the same basic structure. The tan solid previously mentioned gives a high intensity peak at m/e 56 relative to a low intensity peak at m/e 85. Whereas piperidine gives characteristic, high intensity peaks at m/e 85 and 84 relative to the peaks at m/e 56 and 55, the expected straight chain diamine gives high intensity peaks at m/e 56 and 55 versus those peaks around m/e 85. Since the salt does not appear useful relative to future thermal research, no further characterization was attempted.

Ethylenediammonium Dinitrate (EDD) is prepared by the general method described in the Experimental section: mp 188.1°C (188°C)[4]; ΔH_{fusion} = 21.21 ± 0.71 cal/g; density (g/cm^3): 1.591 (calcd), 1.603 ± 0.001 (found), 1.595[4]; NMR δ 3.4 (4H,s).

1,3-Propanediammonium Dinitrate (PDD) was prepared in ethanol and recrystallized: yield 92%; mp 126°C; ΔH_{fusion} = 21.59 cal/g (21.86 ± 1.82); density (g/cm^3): 1.509 (calcd), 1.595 ± 0.005 (found); NMR δ 2.1 (2H,m,J = 7.5Hz), 3.2 (4H,t,J = 7.5Hz). Anal. Calcd for $C_3H_{12}N_4O_6$: C,18.00; H,6.05; N,27.99. Found: C,17.91; H,6.19; N28.14.

N-Methylethylenediammonium Dinitrate (MEDD) was prepared in ethanol and recrystallized: yield 96%; mp 78°C; ΔH_{fusion} = 19.25 cal/g (23.58 ± 1.65); density (g/cm^3): 1.497 (calcd), 1.454 (found); NMR δ 2.8 (3H,s), 3.4 (4H,s). Anal. Calcd for $C_3H_{12}N_4O_6$: C,18.00; H,6.05; N,27.99. Found: C,18.04; H,6.04; N,28.27.

Piperazinium Dinitrate (PIPZD) was prepared in methanol and recrystallized: yield 91%; mp 224°C (decomp); density (g/cm^3): 1.535 (calcd), 1.577 ± 0.016 (found); NMR δ 3.6 (8H,s). Anal. Calcd for $C_4H_{12}N_4O_6$: C,22.64; H,5.71; N,26.41. Found: C,22.80; H,5.69; N,26.18.

1,4-Butanediammonium Dinitrate (BDD)^5 was prepared in ethanol and recrystallized: yield 80%; mp 139.1°C; ΔH_{fusion} = 35.80 ± 0.31 cal/g (34.88 ± 3.25); density (g/cm^3): 1.444 (calcd), 1.463 ± 0.004 (found); NMR δ 1.8 (4H,m,J = 7.5Hz), 3.1 (4H,m,J = 7.5Hz). Anal. Calcd for $C_4H_{14}N_4O_6$: C,22.43; H,6.60; N,26.16. Found: C,22.48; H,6.39; N,26.18.

1,1-Dimethylethylenediammonium Dinitrate (TBDD) was prepared in ethanol and recrystallized from 95% ethanol: yield 43%; mp 230°C; ΔH_{fusion} (see the thermal properties discussion); density (g/cm^3): 1.444 (calcd), 1.425 (found); NMR δ 1.5 (6H,s), 3.4 (2H,s). Anal. Calcd for $C_4H_{14}N_4O_6$: C,22.43; H,6.60; N,26.16. Found: C,22.47; H,6.43; N,26.12.

N,N'-Dimethylethylenediammonium Dinitrate (s-DMEDD) was prepared in methanol and recrystallized: yield 93%; mp 129°C;

ΔH_{fusion} = 23.1 cal/g (22.95 ± 2.89); density (g/cm^3): 1.424 (calcd), 1.397 ± 0.002 (found); NMR δ 2.8 (6H,s), 3.5 (4H,s). Anal. Calcd for $C_4H_{14}N_4O_6$: C,22.43; H,6.60; N,26.16. Found: C,22.63; H,6.50; N,26.17.

N,N-Dimethylethylenediammonium Dinitrate (u-DMEDD) was prepared in ethanol and not recrystallized: yield 92%; mp 52°C; density (g/cm^3): 1.424 (calcd), 1.458 (found); Not stable to long-term storage.

N-Ethylethylenediammonium Dinitrate (EEDD) was prepared in ethanol and recrystallized: yield 95%; mp 86°C; ΔH_{fusion} = 25.17 cal/g (25.10 ± 1.70); density (g/cm^3): 1.434 (calcd), 1.401 ± 0.006 (found); NMR δ 1.3 (3H,s,J = 7.5Hz), 3.2 (2H,q,J = 7.5Hz), 3.4 (4H,s). Anal. Calcd for $C_4H_{14}N_4O_6$: C,22.43; H,6.60; N,26.16. Found: C,22.86; H,6.53; N,26.03.

N-Isopropylethylenediammonium Dinitrate (IPEDD) was prepared in isopropanol and not recrystallized: yield 87%; mp 94°C; ΔH_{fusion} = 14.76 cal/g (17.88 ± 1.17); density (g/cm^3): 1.382 (calcd), 1.282 ± 0.011 (found); NMR δ 1.4 (6H,d,J = 6.8Hz), 3.47 (4H,s), 3.54 (H,m,J = 6.8Hz). Anal. Calcd for $C_5H_{16}N_4O_6$: C,26.31; H,7.07; N,24.56. Found: C,26.41; H,7.11; N,24.90.

N,N,N'-Trimethylethylenediammonium Dinitrate (TRMEDD) was prepared in and recrystallized from 95 percent ethanol: yield 90%; mp 93°C; ΔH_{fusion} = 29.04 cal/g; density (g/cm^3): 1.366

(calcd), 1.356 ± 0.005 (found); NMR δ 2.8 (3H,s), 3.0 (6H,s), 3.5 (4H,s). Anal. Calcd for $C_5H_{16}N_4O_6$: C,26.31; H,7.07; N,24.56. Found: C,26.41; H,7.12; N,24.81.

1,4-Diaza-bicyclo[2,2,2]octane Dinitrate (DABCOD) was prepared in methanol and recrystallized: yield 77%; mp 174°C (decomp); density (g/cm^3): 1.495 (calcd), 1.572 ± 0.002 (found); NMR δ 3.8 (12H,s). Anal. Calcd for $C_6H_{14}N_4O_6$: C,30.25; H,5.94; N,23.52. Found: C,30.37; H,5.88; N,23.01.

1,6-Hexanediammonium Dinitrate (HDD)[6] was prepared in methanol and recrystallized from 95% ethanol: yield 83%; mp 108°C; ΔH_{fusion} = 24.84 cal/g (24.62 ± 1.81); density (g/cm^3): 1.347 (calcd), 1.113 ± 0.001 (found).

N,N-Dimethyl-N'-ethylethylenediammonium Dinitrate (DMEEDD) was prepared in and recrystallized from 95% ethanol: yield 94%; mp 101°C; ΔH_{fusion} = 21.75 cal/g (24.38 ± 1.95); density (g/cm^3): 1.325 (calcd), 1.305 ± 0.004 (found); NMR δ 1.2 (3H,t,J = 7.1Hz), 3.0 (6H,s), 3.2 (2H,q,J = 7.1Hz), 3.5 (4H,s). Anal. Calcd for $C_6H_{18}N_4O_6$: C,29.75; H,7.49; N,23.13. Found: C,29.90; H,7.56; N,23.32.

N,N'-Diethylethylenediammonium Dinitrate (s-DEEDD) was prepared in ethanol and recrystallized: yield 96%; mp 193°C (decomp); density (g/cm^3): 1.333 (calcd), 1.32 ± 0.01 (found); NMR δ 1.3 (6H,t,J = 7.5Hz), 3.2 (4H,q,J = 7.5Hz), 3.4 (4H,s).

Anal. Calcd for $C_5H_{18}N_4O_5$: C,29.74; H,7.50; N,23.13. Found: C,29.66; H,7.37; N,22.93.

N,N,N'N'-Tetramethylethylenediammonium Dinitrate (TMEDD) was prepared in ethanol and recrystallized: yield 97%; mp 228°C (decomp); density (g/cm^3): 1.318 (calcd), 1.324 ± 0.004 (found); NMR δ 3.0 (12H,s), 3.6 (4H,s). Anal. Calcd for $C_6H_{18}N_4O_6$: C,29.75; H,7.49; N,23.13. Found: C,29.62; H,7.55; N,23.13.

N,N,N'-Triethylethylenediammonium Dinitrate (TREEDD) was prepared in and recrystallized from 95% ethanol: yield 92%; mp 86°C; ΔH_{fusion} = 18.89 cal/g; density (g/cm^3): 1.262 (calcd), 1.252 (found); NMR δ 1.3 (9H,t,J = 7.2Hz), 3.2 (2H,q,J = 7.2Hz), 3.3 (4H,q,J = 7.2Hz), 3.5 (4H,s). Anal. Calcd for $C_8H_{22}N_4O_6$: C,35.54; H,8.22; N,20.73. Found: C,35.38; H,8.22; N,20.82.

Diethylenetriammonium Trinitrate (DETN)[4] was prepared in ethanol and recrystallized from a mixture of methanol and water (80/20 by weight): yield 98%; mp 151°C; density (g/cm^3): 1.553 (calcd), 1.561 ± 0.004 (found); NMR δ 3.5 (8H,s).

N,N,N'N'-Tetraethylethylenediammonium Dinitrate (TEEDD) was prepared in and recrystallized from 95% ethanol: yield 84%; mp 140°C; ΔH_{fusion} = 17.10 cal/g (18.53 ± 1.15); density (g/cm^3): 1.210 (calcd), 1.255 ± 0.003 (found); NMR δ 1.3 (12H,t,J = 7.5Hz), 3.3 (8H,q,J = 7.5Hz), 3.6 (4H,s.). Anal. Calcd for $C_{10}H_{26}N_4O_6$: C,40.25; H,8.78; N,18.78. Found: C,40.35; H,8.58; N,18.80.

3,3'-Imino-bis-propylammonium Trinitrate (IBPAT) was prepared in ethanol and not recrystallized: yield 93%; mp 110°C; ΔH_{fusion} = 24.23 cal/g; density (g/cm^3): 1.459 (calcd), 1.459 ± 0.005 (found); NMR δ 2.1 (4H,m,J = 7.5Hz), 3.1 (4H,t,J = 7.5Hz), 3.2 (4H,t,J = 7.5Hz). Anal. Calcd for $C_6H_{20}N_6O_9$: C,22.50; H,6.31; N,26.24. Found: C,22.67; H,6.16; N,26.45.

Triethylenetetrammonium Tetranitrate (TETN)[4] is prepared by the general method described in the Experimental section: mp 228°C; density (g/cm^3): 1.536 (calcd), 1.428 ± 0.005 (found); 1.6 (1); NMR δ 3.47 (8H,s), 3.53 (4H,s).

Tetraethylenepentammonium Pentanitrate (TEPP)[7] was prepared in ethanol and not recrystallized: yield 88%; density (g/cm^3): 1.526 (calcd), 1.585 (found); NMR δ 3.2 (8H,s), 3.3 (8H,s).

^{1}H NMR spectra were obtained for twenty of the twenty-two compounds listed in Table 1. For comparative purposes, the data are compiled in Table 2 according to increasing molecular weight.

It was reported by Kamlet[8] and later by Kamlet and Adolph[9] that when the comparison of impact sensitivity data was restricted to families of energetic materials having similar trigger linkages, rough linear relationships were observed between the logarithm of the impact heights ($H_{50\%}$) and the oxidant balance (OB_{100}). Trigger linkage is defined as the weakest atom to atom linkage, the one that will most likely be cleaved under the thermal conditions generated by the impact hammer. OB_{100} is

TABLE 2. NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS

NO.	ACRONYM	MOL/WT	(PPM)
1.	EDD	186.1	3.4 (4H,s)
2.	PDD	200.2	2.1 (2H,m,J=7.5Hz), 3.2 (4H,t,J=7.5Hz)
3.	MEDD	200.2	2.8 (3H,s), 3.4 (4H,s)
4.	PIPZD	212.2	3.6 (8H,s)
5.	BDD	214.2	1.8 (4H,m,J=7.5Hz), 3.1 (4H,m,J=7.5Hz)
6.	TBDD	214.2	1.5 (6H,s), 3.4 (2H,s)
7.	s-DMEDD	214.2	2.8 (6H,s), 3.5 (4H,s)
8.	EEDD	214.2	1.3 (3H,s,J=7.5Hz), 3.2 (2H,q,J=7.5Hz), 3.4 (4H,s)
9.	IPEDD	228.2	1.4 (6H,d,J=6.8Hz), 3.47 (4H,s), 3.54 (H,m,J=6.8Hz)
10.	TRMEDD	228.2	2.8 (3H,s), 3.0 (6H,s), 3.5 (4H,s)
11.	DABCOD	238.2	3.8 (12H,s)
12.	s-DEEDD	242.2	1.3 (6H,t,J=7.5Hz), 3.2 (4H,q,J=7.5Hz), 3.4 (4H,s)
13.	DMEEDD	242.2	1.2 (3H,t,J=7.1Hz), 3.0 (6H,s), 3.2 (2H,q,J=7.1Hz), 3.5 (4H,s)
14.	TMEDD	242.2	3.0 (12H,s), 3.6 (4H,s)
15.	TREEDD	270.3	1.3 (9H,t,J=7.2Hz), 3.2 (2H,q,J=7.2Hz), 3.3 (4H,q,J=7.2Hz), 3.5 (4H,s)
16.	DETN	292.2	3.5 (8H,s)
17.	TEEDD	298.3	1.3 (12H,t,J=7.5Hz), 3.3 (8H,q,J=7.5Hz), 3.6 (4H,s)
18.	IBPAT	320.3	2.1 (4H,m,J=7.5Hz), 3.1 (4H,t,J=7.5Hz), 3.2 (4H,t,J=7.5Hz)
19.	TETN	398.3	3.47 (8H,s), 3.53 (4H,s)
20.	TEPP	504.4	3.2 (8H,s), 3.3 (8H,s)

defined as the number of equivalents of oxidant per one hundred grams of energetic material above the amount required to convert all hydrogen to water (H_2O) and all carbon to carbon monoxide (CO). In calculating OB_{100} for any given molecule, an atom of oxygen represents two equivalents of oxidant, an atom of hydrogen one equivalent of reductant and an atom of carbon two equivalents of reductant. For CHNO explosives containing no carboxyl groups (-COOH), the equation is

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C)}{\text{Mol. Wt.}}$$

where n_O, n_H and n_C represent the number of atoms of the respective elements in the molecule. For explosives balanced to carbon monoxide, $OB_{100} = 0$.

A compilation of the impact sensitivity data is presented in Table 3. The compounds are assembled into groups as follows: (1) homologous series, (2) N-substituted EDD, (3) N,N'-substituted EDD, (4) N,N,N'-substituted EDD, (5) N,N,N'N'-substituted EDD and (6) miscellaneous compounds. The limited number of data points within each group prevented more than a cursory review of the $H_{50\%}$-OB_{100} relationship. A study of the graphical representation of the 2.5 kg weight data for the homologous and N-substituted series shows a near linear sensitivity-structure trend as described by Kamlet[8]. Both series merge on EDD. It is also clear

TABLE 3. IMPACT SENSITIVITY AND OB_{100} OF SELECTED ORGANODI- AND POLYAMMONIUM NITRATE SALTS

	ACRONYM	OB_{100}	H50%	
			2.5kg (cm)	5.0kg (cm)
A. Homologous Series				
1.	EDD	−1.07	34.2	18.0
2.	PDD	−3.00	73.8a	
3.	BDD	−4.67	128.3	30.5
4.	HDD	−7.43		>200
B. N−Substituted EDD				
5.	MEDD	−3.00	41.7	
6.	EEDD	−4.67	48.9	
7.	IPEDD	−6.13	133.0	
C. N,N′−Substituted EDD (9=N,N−)				
8.	s−DMEDD	−4.67		60.5
9.	u−DMEDD	−4.67	139.7	
10.	s−DEEDD	−7.43	128.3	
D. N,N,N′−Substituted EDD				
11.	TRMEDD	−6.13		129.7
12.	DMEEDD	−7.43		>200
13.	TREEDD	−9.62		>200
E. N,N,N′,N′−Substituted EDD				
14.	TMEDD	−7.43		53.5
15.	TEEDD	−11.40		>200
F. Miscellaneous				
16.	DETN	−2.05	54.3 82(1)	
17.	TETN	−2.51	68.0 131(1)	
18.	TEPP	−2.78	113.2 >180(2)	
19.	PIPZD	−3.77	158.4	
20.	DABCOD	−5.88	101.7	
21.	IBPAT	−4.37	147.8	28.9
22.	TBDD	−4.67	162.8	

a. Sample not sieved and weight was between 35−50 mg.

from the tabulated data that the N-substituted EDD series displays a marked decrease in impact stability from that shown by the homologous series and, at the same time, shows only a minor increase with decreasing OB_{100}.

Thermal properties obtained by differential scanning calorimetry are summarized in Table 4. Also included are melting points obtained by other means and data[4,6,7,10,11] for EDD, HDD, DETN, TETN and TEPP. In general, melting points from other sources agree well with DSC endotherms. Exceptions occur with s-DMEDD, s-DEEDD, TEEDD, PIPZD, DABCOD and TBDD.

s-DEEDD begins to discolor and apparently outgas sufficiently at 193°C to cause the Mettler FP1 Melting and Boiling Point Apparatus to indicate melting, while visual inspection of the material under a microscope equipped with a hot stage reveals melting begins at 198°C with outgassing and is complete by 224°C. The endotherm at 211.2°C has not been studied, but may be associated with a solid state phase change such as occurs with EDD[10,12]. A similar explanation may account for the endotherm occurring at 115.9°C in the TEEDD thermogram. Repeated cycling through these endotherm regions and those occurring for s-DMEDD, PIPZD, DABCOD and TBDD did not reduce the area under the peaks to any significant extent, thereby lending support to the phase change theory. s-DMEDD and TBDD were analyzed more extensively. For the former, no weight loss was observed after repeated

TABLE 4. THERMAL CHARACTERIZATION DATA

NO.	ACRONYM	ENDOTHERM, °C	EXOTHERM PEAK, °C	MELTING POINT, °C[a]
1.	PDD	127.5	296.2	126
2.	BDD	140.1	308.2, 223[b]	139
3.	MEDD	75.8	292.2	78
4.	EEDD	89.2	284.8[c]	86
5.	IPEDD	95.9	265.4	94
6.	s–DMEDD	63.5, 128.9	237.3	130
7.	u–DMEDD	130.8	226.6	52[d]
8.	s–DEEDD	211.2, 228.5 (decomp)	233.2	193, 198–224[d] (decomp)
9.	TRMEDD	96.8	251.3, 271.5	93
10.	DMEEDD	102.6	248.4	101
11.	TREEDD	90.4	245.6[c], 284.2[c]	86
12.	TMEDD	229.4 (decomp)	270[e]	228
13.	TEEDD	115.9, 146.1	277.8[c]	140
14.	PIPZD	112.1	238.9	224 (decomp)
15.	DABCOD	87.5	182.2	174 (decomp)
16.	IBPAT	114.4	272.6	110
17.	TBDD	76.0, 230.0	265.0	230 (decomp)
18.	EDD	131.5, 188.1	306.0	188
19.	HDD	108.0	226.0	109
20.	DETN	151.0	302.0	150
21.	TETN	228.0	281[g]	229
22.	TEPP	f	264.0	196[d]

a. Measured with a Mettler FP1 Melting and Boiling Point Apparatus unless otherwise indicated.
b. Sealed, value is minimum obtained from five experiments (value varies with degree of seal).
c. Multiple peaks, value obtained from strongest peak.
d. Visual.
e. Multiple peaks, value obtained at approximate mid–point of exotherm range.
f. None observed.
g. Onset temperature, remainder of peak is not well defined.

recycling through the low temperature endotherm as well as through the melting point. The heat of transition associated with this apparent phase change is 9.6 cal/g. Similarly, an apparent solid state phase change occurs near 76°C for TBDD. The endothermic peak sometimes appears as a doublet which effectively lowers the onset temperature to 68°C. The energy associated with this transition is 18.8 ± 0.25 cal/g. Cycling through this transition point requires a holding period at room temperature to effect transition to the low temperature state. Melting occurs at 230°C with no apparent decomposition, however, exothermic decomposition generally follows within a few degrees. The energy associated with melting (ΔH_{fusion}) is 4.8 cal/g. All events were observed with a hot stage microscope as well as by DSC.

FTIR spectra are generally characterized by broad, poorly-defined absorptions above 1300 cm^{-1} and sharp, but less strongly absorbing, peaks in the fingerprint region between 1300 and 400 cm^{-1}. Absorptions characteristic of the inorganic nitrate ion (NO_3^-)[13,14,15,16,17], point group D_{3h}, occur at 1390 (ν_3), 1050 (ν_1), 831 (ν_2), and 720 (ν_4). Absorptions are observed for almost all of the compounds in the ranges 1385-1375 (br,vs), 826-818 (m-w) and 727-713 (w) and are tentatively assigned to the respective nitrate ion vibrations. In addition, an absorption occurs in the region 1771-1752 cm^{-1} and is tentatively assigned to the ν_1, + ν_4 combination band [14,18]. No tentative assignments for the ν_1 vibration in the 1075-1050 cm^{-1} range could be made. Absorptions thought to result from the primary ammonium ion ($-NH_3^+$)[15,16] occur near 2000, 1625-1575, 1520, 1115-1104 and 783-760 cm^{-1}. No attempt was made to assign other absorptions even though some were common to most of the spectra and are no doubt associated with the aliphatic backbone or N-substituent.

CONCLUSIONS

Eighteen organodiammonium dinitrates and four organopolyammonium polynitrate salts were successfully prepared by reacting an alcohol solution of the respective amine with concentrated nitric acid. Attempts to prepare 1,5-pentanediammonium dinitrate were not successful.

^1H nuclear magnetic resonance spectra were obtained for all but two of the materials and found to be consistent with the expected molecular configuration based on starting amine. FTIR spectra were obtained for sixteen of the salts.

Impact sensitivity data were obtained for all compounds included in this study. When data comparison was restricted to families of materials assumed to have similar trigger linkages, rough linear relationships were found between the logarithm of the impact heights ($H_{50\%}$) and the oxidant balance (OB_{100}). This relationship was found for the homologous and N-substituted series. It is readily apparent that the rate of increase of impact stability with decreasing OB_{100} is lower for the N-substituted series than for the homologous series.

While no clear cut thermal stability trends are apparent from Table 4, it is clear that the thermal chemistry associated with these salt systems is complex. At present, no further work is planned with regard to impact sensitivity, but an extensive investigation is underway to describe the thermal decomposition of some selected organodiammonium dinitrate salts.

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