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Synthesis and Properties of Selected Energetic Organodi- and Polyammonium Nitrate Salts

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MUNITIONS DIVISION

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The objective of this program 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 synthetic 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 densities (calculated and measured), heats of fusion, melting points and the temperature of the major peak associated with exothermic decomposition as measured by a differential scanning calorimeter.

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PREFACE

This report describes an in-house program conducted by personnel of the Energetic Materials Branch (DLJE), Munitions Division (DLJ), Air Force Armament Laboratory (AFATL), Armament Division (AD), Eglin Air Force Base, Florida, under Project 2502, "Conventional Ordnance Technology," Task 10, "Advanced Explosives," Work Unit 12, "Explosive Response to Thermal and Shock Stimuli."

The work reported herein was performed under the direction of Maj Robert A. Hildreth for the period 1 January 1983 to 31 May 1984 and the author, Dr Robert L. McKenney Jr (AFATL/DLJE), project scientist, for the period 1 June 1984 to 31 October 1985. The report was released by the author in December 1985.

The author wishes to thank Dr Paul R. Bolduc and Mr Stephen A. Aubert, Energetic Materials Branch, for their helpful discussions and their assistance in interpreting nuclear magnetic resonance spectra.

This report is one of several planned reports that will describe the synthesis and complete thermal characterization of specific organodi- and polyammonium nitrate salts. Other reports will follow at appropriate times during the progress of this effort.

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SECTION I
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). The former ingredient is a readily available and inexpensive oxidizer material used extensively in commercial explosives. The latter compound 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 (Reference 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 the slow cookoff IHE qualification test. 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. Hence, 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 the elemental analysis confirming the preparation and the nuclear magnetic resonance spectra supporting the proposed structure. All of the compounds in this report are compiled in Table 1.

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	$C_4H_{12}N_4O_6$

TABLE 1. ORGANODI- AND POLYAMMONIUM NITRATE SALTS INCLUDED IN STUDY (CONCLUDED)

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	$C_4H_{14}N_4O_6$

SECTION II
EXPERIMENTAL

1. 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 specific molecules of molecular weight 504 or below, 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 ethyl nitrate. Since product usually forms as a whitish precipitate, it is important to ensure that enough alcohol is used to maintain free stirring. Elemental analyses were obtained for original compounds.

Attempts to prepare 1,5-pentanediammonium dinitrate by the method described above yielded a yellow to orange oil that would not solidify. No attempt was made to characterize the oil.

2. DENSITIES

Densities were calculated for each of the salts by the method described in Reference 2 and measured using a Quantachrome Stereopycnometer, Model Number SPY-2. Eight to ten pressure measurements were made for each salt and the densities calculated according to the equation

$$\rho = \frac{Mp}{V_C + \dfrac{V_A}{1 - P_2/P_3}}$$

where ρ = density (g/cm^3), Mp = sample mass (g), V_C = volume of sample cell holder (cm^3), V_A = added volume (cm^3), P_2 = pressure reading after pressurizing the cell and P_3 = pressure reading after the added V_A. All standard deviations were calculated at the 95 percent Student t confidence level.

3. 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 obtain the gram per calorie constant and 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. All standard deviations were calculated at the 95 percent Student t confidence level. Heat of fusion values obtained by the cut and weigh method will appear in parentheses.

4. NUCLEAR MAGNETIC RESONANCE SPECTRA

^1H 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 $^2H_4$]3-(trimethylsilyl)proprionate (TSP).

5. 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.

6. 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^{0}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).

SECTION III

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.

Ethylenediammonium Dinitrate (EDD) is prepared by the general method described in Section II: mp 188.1°C (188°C) (Reference 3); $\Delta H_{fusion} = 21.21 \pm 0.71$ cal/g; density (g/cm^3): 1.591 (calcd), 1.603 ± 0.001 (found), 1.595 (Reference 3); NMR δ 3.4 (4H,s).

1,3-Propanediammonium Dinitrate (PDD) was prepared in ethanol and recrystallized from hot ethanol with just enough water added to facilitate dissolution: yield 92%; mp 126°C; $\Delta H_{fusion} = 21.59$ 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 from ethanol/DMSO (5 w/w): yield 96%; mp 78°C; $\Delta H_{fusion} = 19.25$ 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 not 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) (Reference 4) was prepared in ethanol and recrystallized from hot ethanol with just enough water added to facilitate dissolution: yield 80%; mp 140.1°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 a mixture of methanol and methylene chloride: yield (not measured); mp 230°C (decomp); 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 not recrystallized: yield 93%; mp 130°C; ΔH_{fusion} = 23.90 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 not 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 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 not 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) (Reference 5) was prepared in methanol and recrystallized from 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 ethanol and not recrystallized: 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 not 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 $C_6H_{18}N_4O_6$: 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 not 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 ethanol and recrystallized from hot ethanol with just enough water added to facilitate dissolution: 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) (Reference 3) 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 ethanol and not recrystallized: 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) (Reference 3) is prepared by the general method described in Section II: 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) (Reference 6) 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 and coupling constants were measured for nine of them. For comparative purposes, the data are compiled in Table 2 according to increasing molecular weight.

It was reported by Kamlet (Reference 7) and later by Kamlet and Adolph (Reference 8) 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 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, $OB_{100} = 0$.

TABLE 2. NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS

NO.	ACRONYM	MOL	δ (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)

A compilation of the impact sensitivity data are presented in Table 3. The compounds are assembled into groups as follows: (1) homologues of EDD, (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 overall $H_{50\%}$ data for the 2.5kg weight are shown graphically in Figure 1 where the logarithm of the $H_{50\%}$ is plotted versus OB_{100}. Each class of compounds for which there were at least three data points was analyzed by the least squares regression method and an equation derived. The equation for the EDD homologue series is

$$\log H_{50\%} = 1.37 - 0.160\ OB_{100}$$

where the number of data points (n) = 3, the correlation coefficient = 0.999 and the standard deviation = 0.015 logarithmic units, corresponding to a standard deviation of 3.5 percent in 50% impact height. It is readily seen that the linear sensitivity-structure trend described by Kamlet (Reference 7) holds for this structurally similar, albeit small, series. The $H_{50\%}$ for HDD, shown to be greater than 200cm with both the 2.5 and 5.0kg weights, is predicted by the equation to be 362cm for the former. The BDD isomer (TBDD) is included in Figure 1, but not in the regression analysis. It has a slightly higher $H_{50\%}$ than the linear isomer, perhaps indicating some apparent stability imparted by the branched structure.

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

		ACRONYM	OB_{100}	$H_{50\%}$	
				2.5kg (cm)	5.0kg (cm)
A.	Homologues of EDD				
	1.	EDD	-1.07	34.2	18.0
	2.	PDD	-3.00	73.8[a]	
	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	-10.73		>200
E.	N,N,N',N'-Substituted EDD				
	14.	TMEDD	-7.43		53.5
	15.	TEEDD	-12.06		>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.A

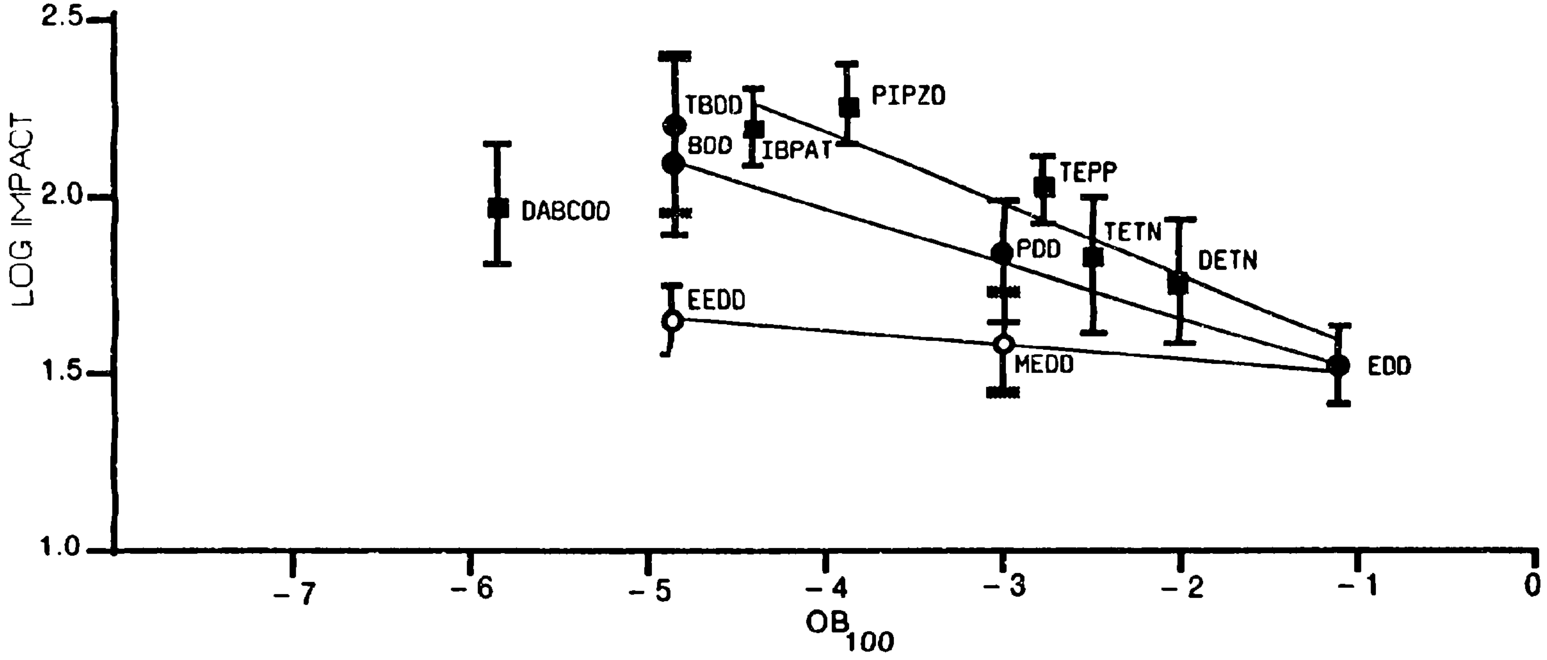

Figure 1. Impact Sensitivities of Some Selected Organodi- and Ployammonium Nitrate Salts Plotted Versus OB_{100}.

The N-substituted EDD series displays a marked decrease in impact stability from that shown by the homologue series and, at the same time, shows only minor improvement with decreasing OB_{100}. The equation for this series is

$$\log H_{50\%} = 1.49 - 0.0432\ OB_{100}$$

where n=3, the correlation coefficient = 0.9998 and the standard deviation = 0.0016 logarithmic units, corresponding to a standard deviation of 0.6 percent in 50% impact height. This relationship is shown in Figure 1. The data point for IPEDD, which deviates from the above relationship, is included in the graphical display but not in the regression analysis. This derivative shows significant impact height (133cm) stability over that which would be predicted for the n-propyl derivative (57cm) based on the above curve. It is clear from the comparison of these two series that mono-N-substitution destabilizes a given molecule toward impact.

N-substitution in the form of repeating units (oligomers of EDD and IBPAT), however, appears to impart significant impact stability to a given molecule with decreasing OB_{100} over that of simple N-substituted compounds. In fact, the rate of stability increase is greater than that of the homologue series. The equation for the curve, which is also displayed in Figure 1, is

$$\log H_{50\%} = 1.332 - 0.213\ OB_{100}$$

where n=6, the correlation coefficient = 0.952 and the standard deviation - 0.081 logarithmic units, corresponding to a standard deviation of 19 percent in 50% impact height. This regression analysis also includes data for the ring compound, PIPZD, and the PDD oligomer, IBPAT. The cage compound, DABCOD, has a considerably lower impact $H_{50\%}$ than would be predicted for a linear compound with a similar OB_{100}. Although the cage structure is probably not strained to any significant degree, the degree of overall rotational freedom is reduced and this is probably reflected in its lower impact value. DABCOD was not included in the regression analysis. PIPZD, on the other hand, has a higher impact value which may result simply from its higher degree of overall rotational freedom.

Thermal properties obtained by differential scanning calorimetry are summarized in Table 4. Also included are melting points obtained by other means and data (References 3,5,6,9,10) for EDD, HDD, DETN, TETN and TEPP. In general, melting points from other sources agree well with DSC endotherms. Exceptions occur with s-DEEDD, TEEDD, PIPZD, DABCOD, and TBDD.

s-DEEDD begins to discolor and outgas sufficiently to trigger the FPl at 193°C, 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 (References 9 and 11). 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 PIPZD, DABCOD and TBDD did not reduce the area under the peaks to any significant extent, thereby lending some support to the phase change theory.

For the series of eight compounds that includes the EDD homologues and the mono-N-substituted EDD salts, there is a linear relationship between the exothermic peak temperature (T_{ex}) and the molecular weight (MW). The two compounds that deviate from this relationship are BDD, which is more stable than predicted, and HDD, which is less stable than predicted. T_{ex}/MW trends also exist for the mono, di, tri, and tetra-N-methyl- and N-ethyl-substituted EDDs. The mono-N-substituted derivatives are the most thermally stable in each series and the disubstituted compounds are the least stable. Thermal stability then increases in a somewhat linear fashion with increasing N-substitution, thus forming a check-shaped curve. These trends are shown graphically in Figure 2.

It was also observed that thermal stability decreased through the oligomer series EDD, DETN, TETN and TEPP. Increasing the carbon chain lengths by one methylene group each in DETN to form IBPAT, also decreased thermal stability. Ring and cage formation (PIPZD and DABCOD) decreased thermal stability rather drastically when compared to linear compounds with a similar number of carbon chains, e.g. DETN and TETN. The rationalization of these trends was not attempted during this cursory study.

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	130.8	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	76.4, 233.7	273.1	230 (decomp)
18.	EDD	131.5, 188.1	306	188
19.	HDD	108	226	104
20.	DETN	151	302	150
21.	TETN	228	281[g]	229
22.	TEPP	[f]	264	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.

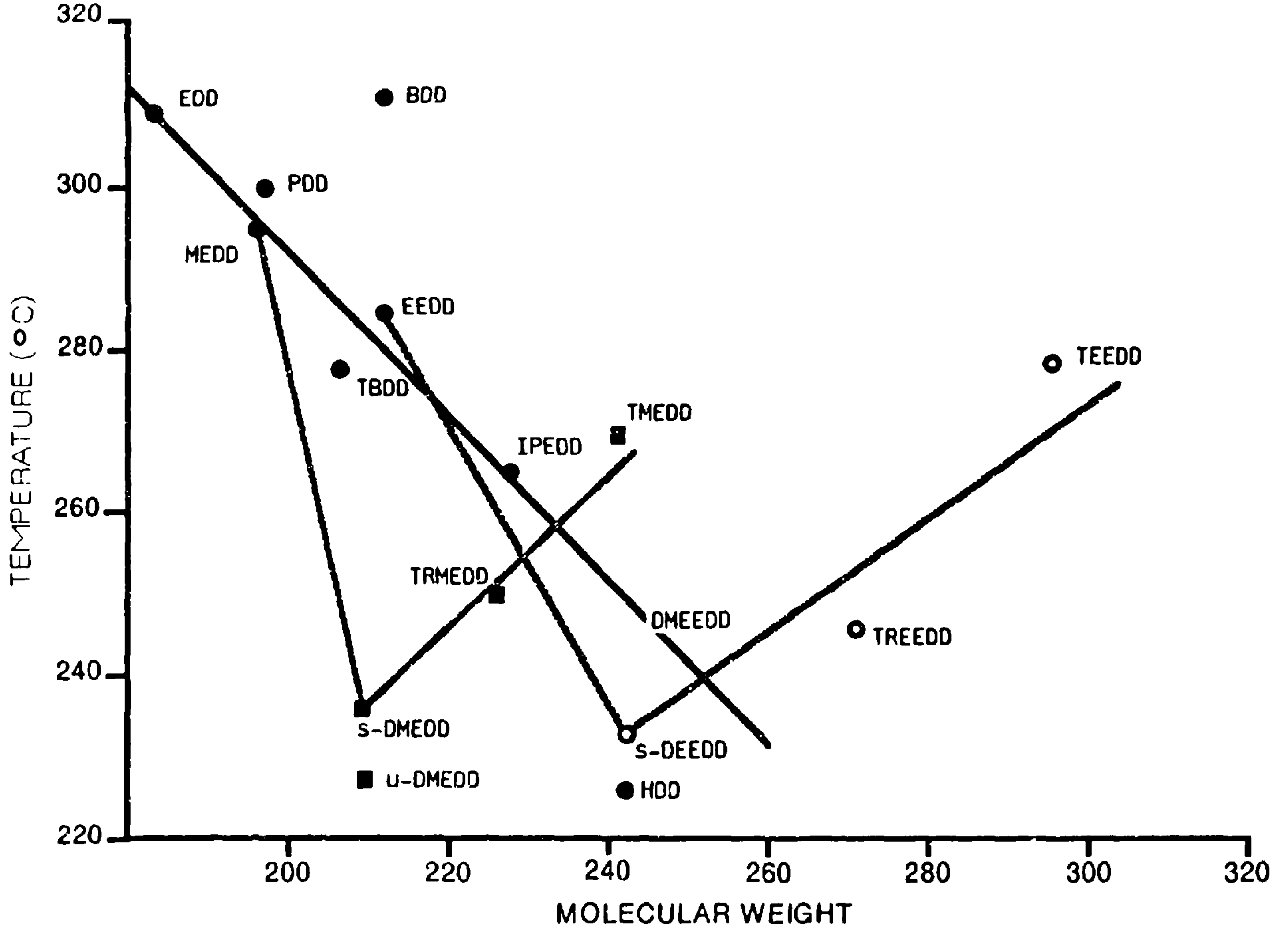

Figure 2. Exothermic Decomposition Temperature of Selected End-Terminated Aliphatic Diammonium Dinitrate Salts Plotted Versus Molecular Weight. EDD Homologue and N-substituted Salts (●), *Methyl Substituted Salts* (■), *Ethyl Substitued* Salts (○).

SECTION IV
CONCLUSIONS AND RECOMMENDATIONS

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 yielded an oil in all cases. Attempts to purify the oil by recrystallization proved fruitless. It is speculated that cyclization may have occurred during the preparation, thus forming a mixture of piperidinium nitrate and ammonium nitrate. No characterization of the oil was attempted. ^{1}H 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.

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 to hold for the EDD homologue series and the N-substituted series and the mixed series including the oligomers of EDD and PIPZD and IBPAT. It was readily shown that the rate of increase of impact stability with decreasing OB_{100} was least for the N-substituted series and most for the oligomer/PIPZD/IBPAT series.

Thermal stability, as determined by the position of the DSC exotherm peak, has been shown to exhibit trends with respect to molecular weight, which also generally holds for OB_{100}. With few exceptions for compounds of the combined EDD homologue and N-substituted EDD series, those with the lowest molecular weight or least negative OB_{100} had their exothermic decomposition peak occur at the highest temperature.

This is opposite that observed for impact stability for the same two series where stability increased for those materials with a more negative OB_{100}. Furthermore, the two series displayed completely different rates of stability increase with the N-substituted EDD series showing the least increase with decreasing OB_{100}. The other interesting trend is exhibited by the series with increasing N-ethyl substitution. EEDD has the greatest thermal stability and s-DEEDD the least. Thermal stability then increases from s-DEEDD through TEEDD. Impact stability for this series increases from EEDD through TEEDD. This thermal trend is also followed by the N-methyl substituted series, but TMEDD does not fall into place in the impact stability trend.

It is clear that considerable work is required to explain these trends and the complex processes that cause them. At present, no further work is planned with regard to impact sensitivity, but work is underway to investigate the thermal decomposition of some selected organodiammonium dinitrate salts.

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