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SYNTHESIS OF CUBANE BASED ENERGETIC MOLECULES

Final Report

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The need to pack more power with less weight into less space in tomorrow's weapons drove this program for the synthesis of super energetic materials. Our original impetus was a program based solely on the energetic properties of cubane. However, as a course of our studies here and in a parallel ONR sponsored program (SRI project number 6654, ONR contract No. N00014-88-C-0537), we discovered and developed an alternative oxidizer to cubyl based systems, the dinitramide salts. We will report on our developments in the synthesis of new oxidizers based on cubane and dinitramide.

In this research, we developed new methods for the functionalization of the cubane nucleus and synthesized new energetic cubanes. We developed several new routes for the synthesis of the dinitramino group, $(N(NO_2)_2)$. Our work on the preparation of the dinitramide group led to the synthesis of the dinitramide ion, and as a consequence ammonium dinitramide. We have in turn used this synthesis to prepare cubane ammonium dinitramide salts. We synthesized cubane-1,4-bis-(ammonium dinitramide) and cubane-1,2,4,7-tetrakis(ammonium dinitramide) as well as several other dinitramide salts.

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SUMMARY

The need to pack more power with less weight into less space in tomorrow's weapons drove this program for the synthesis of new generations of superenergetic materials. Our original impetus was a program based solely on the energetic properties of cubane. However, in the course of our studies here and in a parallel program also under Office of Naval Research (ONR) sponsorship (SRI Project No. 6654, ONR Contract No. N00014-88-C-0537), we discovered and developed an alternative oxidizer to cubyl based systems, the dinitramide salts. We report here on our developments in the synthesis of new oxidizers based on cubane and dinitramide for propellant applications.

A driving force for the use of cubane is cubane's high positive heat of formation (+161 kcal/mol), density (1.29 g/cm^3), and strain energy (+159 kcal/mol). These values are extraordinarily high, a combination not exceeded by any other stable hydrocarbon that is available in reasonable quantities. The addition of energy-rich and/or oxidizing groups creates exceptionally dense and powerful explosives, propellants, and fuels.

The cubane system is geometrically very different from ordinary compounds, and thus innovative methods have had to be developed to prepare substituted cubanes. To do this in sensible ways requires a keen appreciation of the effects of distorted geometry on reactivity, the subject of much speculation and hypothesis for the past two decades. This SDI/IST project provides for the first time extended testing of the theories of organic chemistry regarding highly strained compounds. We have already made tremendous progress turning theory into practice. The first energetic cubanes were synthesized, including the synthesis of the only cubanes that are sufficiently oxidized to be considered as explosives or propellants.

In this research, we developed new methods for the functionalization of the cubane nucleus and synthesized new energetic cubanes. Synthetic achievements under this program include development of new methods of cubane functionalization that have resulted in a more efficient, environmentally sound method for the synthesis of the important intermediate cubane-1,2,4,7-tetracarboxylic acid, the synthesis of the first fully oxidized cubane compounds, and an improved synthesis of 1,4-cubane diol. We have also achieved the first preparation of energetic polynitrocubanes: cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester), cubane-1,4-bis(ß,ß,ß-trinitroethylester), cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitroethylester), N,N'-bis-(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane,

N-nitro-N'-nitroso-bis-N,N'-(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane, and N,N'-dinitro-bis-N,N'-(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane. Synthesis of the highly energetic 1,4-dicyanocubane and cubane-1,4-diisocyanide provided examples of highly energy dense fuels. Our most recent work has involved the synthesis of 1,2,4,7-tetracyanocubane, an important precursor to several other energetic cubanes. We have prepared the cubane-1,2,4,7-tetrakis(ammonium perchlorate) salt. This compound has the correct energy balance for use as either a propellant or explosive; however, it is much too impact sensitive for actual application.

We developed several new routes for the synthesis of the dinitramino group, $N(NO_2)_2$ in other investigations related to this program. This work resulted in new, more efficient, and flexible routes to the dinitramino group. We applied these results to the attempted synthesis of dinitramino cubanes. However, our work on the preparation of the dinitramide group led to the synthesis of the dinitramide ion and, as a consequence, ammonium dinitramide (SRI-12). We have in turn used this synthesis to prepare cubane ammonium dinitramide salts. We synthesized cubane-1,4-bis-(ammonium dinitramide) and cubane-1,2,4,7-tetrakis(ammonium dinitramide) as wel' as several other dinitramide salts. The synthetic efforts described in this report are divided into the following categories:

- Polynitroderivatives of amino cubane

- Cubane esters of trinitroethanol and fluorodinitroethanol

- Cubane-1,2,4,7-tetrakis(ammonium perchlorate)

- New cubane based fuels

- Development of new methods to substitute cubane (New synthesis of cubane-1,2,4,7-tetracarboxylic Acid,)

- Synthesis of alkyldinitramine compounds

- Synthesis of dnitramide salts.

- Gas phase properties of the dinitramide ion.

ACKNOWLEDGMENTS

INTRODUCTION

This program was directed toward the exploration of innovative concepts in molecular structures. Such concepts must be explored to achieve the goal of generating more propulsion power with less weight and in less space. The energetic materials now available do not have enough energy density for advanced propellant applications such as those required for the Strategic Defense Initiative (SDI).

All energetic propellants are metastable by nature, so the trick is to find kinetically stable molecular structures, compounds that can withstand long-term storage. The ultimate goal is to find compounds that are kinetically rocks but thermodynamically powerhouses. As a consequence, we have explored class of materials that have exceptional material and energetic properties: the cubanes. Cubane's heat of formation (+161 kcal/mol), density (1.29 g/cm^3), and strain energy (+159 kcal/mol) are extraordinarily high, and this combination is not exceeded by any other stable hydrocarbon available in reasonable quantities. The addition of energy-rich and/or oxidizing groups to cubanes will create exceptionally dense and powerful explosives, propellants, and fuels.

The cubane system is geometrically very different from ordinary compounds. This program's goal was to prepare substituted cubanes. To do this in sensible ways requires a keen appreciation of the effects of distorted geometry on reactivity, the subject of much speculation and hypothesis for the past two decades. This SDI/IST project provided for the first time extended testing of the propellant properties regarding highly strained compounds such as cubane. We made tremendous progress turning these theories into practice. The first energetic cubanes were synthesized under this program, including the only cubanes sufficiently oxidized to be considered as explosives or propellants.

Our studies on the cubane system led to the invention of a new composition of matter, the dinitramide ion (these compounds were invented and developed in cooperation with SRI Project No. 6654, ONR contract No. N00014-88-C-0537). Dinitramide salts, particularly the ammonium derivative, have the potential of being better oxidizers than the cubanes. As a consequence, the final two years of this project were primarily devoted to the development of dinitramide chemistries. The current best synthesis of the dinitramide ion is classified and will not be presented here, but instead will appear in a classified report later. We will comment that the synthesis of ammonium dinitramide (SRI-12 or ADN) has

progressed to the level that it is now practical to prepare multipound quantities and we do not see any restraints in scaling up the synthesis to larger levels.

RESULTS

CUBANE BASED OXIDIZERS AND EXPLOSIVES

Polynitro Derivatives of Aminocubane

We have succeeded in synthesizing the first polynitro cubane compounds under this program. The first derivatives prepared have nitro groups substituted onto the amino group of a cubane. These compounds are only intermediate targets along the pathway to the synthesis of cubanes that are nitrated on the cage. The first amino cubane substituted with energetic groups was N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane (Scheme 1). This compound was further nitrated to give N-nitro-N'-nitroso-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane, the second amino substituted energetic cubane (Scheme 2).
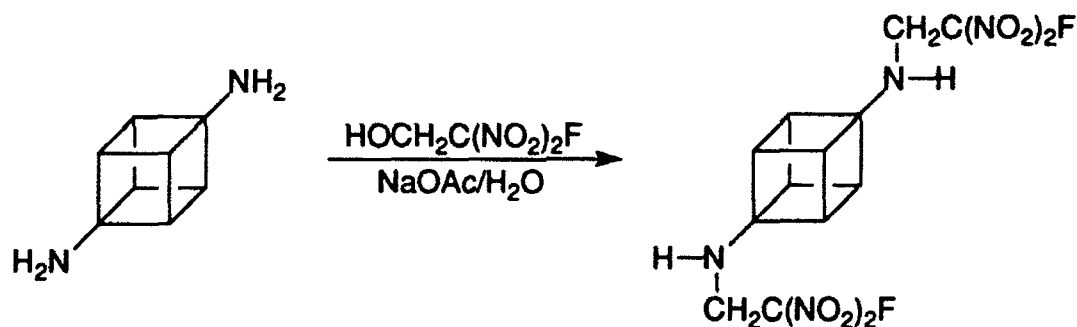
Scheme 1: Synthesis of N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane
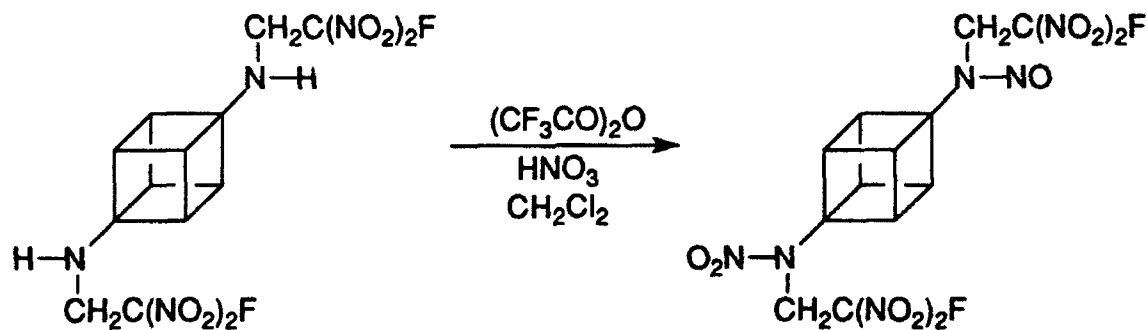
Scheme 2: Synthesis of N-nitro-N'-nitroso-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane

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The density of N-nitro-N'-nitroso-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane is 1.827 g/cm^3. This is a good value for a β,β-dinitro-β-fluoroethyl subtituted compound. The x-ray crystal structure of N-nitro-N'-nitroso-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane is presented in Figure 1.
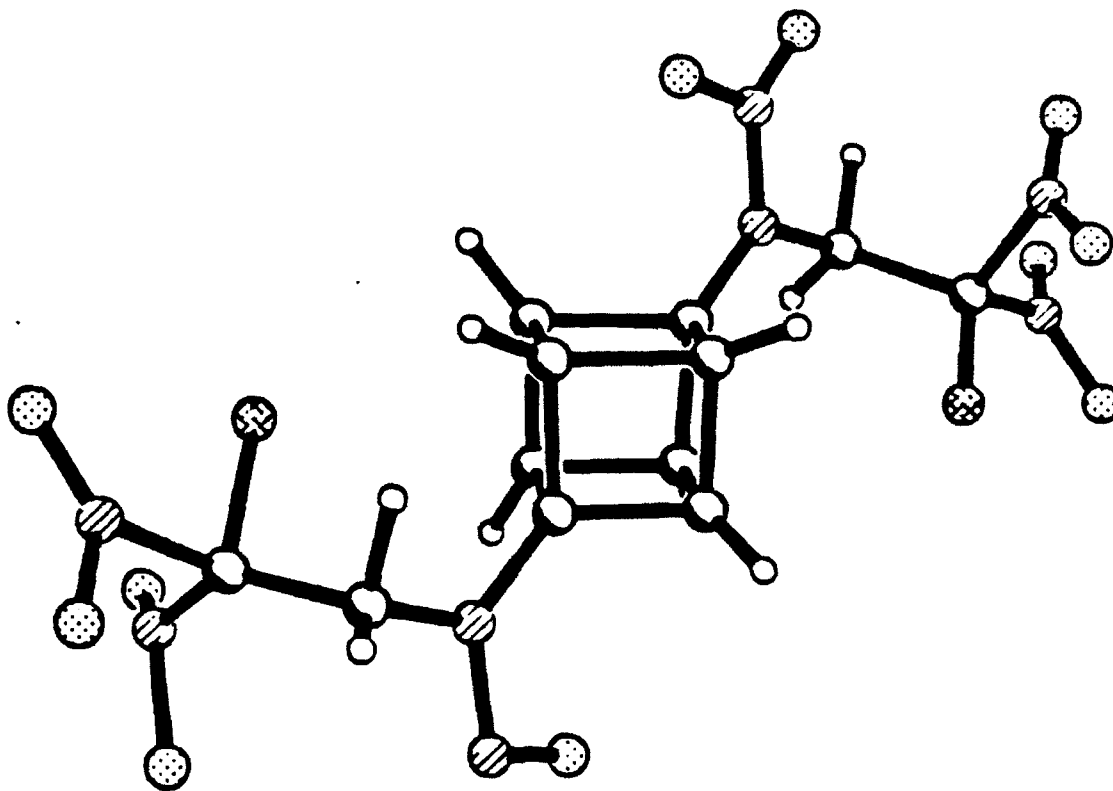
Figure 1.   X-ray crystal structure of N-nitro-N'-nitroso-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane.

Our simple KJSM[1-3] calculations indicate that N-nitro-N'-nitroso-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane has a detonation pressure (P$_{CJ}$) of 351 kbar and a detonation velocity (D$_{vel}$) of 8.9 mm/μs. These values compare favorably to those of HMX, the best oxidizer currently used. HMX has a P$_{CJ}$ of 371 kbar and a D$_{vel}$ of 9.0 mm/μs, as calculated by the KJSM method. The calculated detonation properties of N-nitro-N'-nitroso-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane are surprisingly good when one considers that the molecule does not contain enough oxygen to completely oxidize all the carbon and hydrogen to CO and water upon combustion. These excellent

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detonation properties are an example of the effect of adding a cubane nucleus into the molecule: both the density and the heat of formation are markedly increased, and these increases result in the high P_{CJ} and D_{vel}.

We succeeded in synthesizing the fully oxidized derivative, N,N'-dinitro-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane, by oxidation of the initially formed product as shown in Scheme 3.
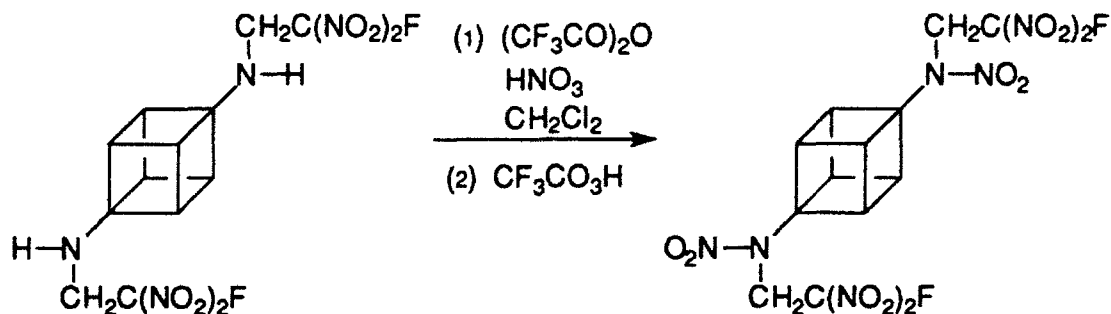
Scheme 3: Synthesis of N,N'-dinitro-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane

The results of differential scanning calorimetry (DSC) for N,N'-dinitro-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane are shown in Figure 2. This compound is a good example of the use of the cubane nucleus to enhance energetic properties through simple chemistry.

A remarkable aspect of these compounds is that both N,N'-dinitro-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane and N-nitro-N'-nitroso-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane are more stable than either 1,4-diaminocubane or N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane. The initial step in the diaminocubane system is itself unstable and eventually decomposes upon standing. The decomposition pathway is believed to be opening of the cubane ring. This step is driven by the donation of the amino free electron pair to the N-C bond, catalyzing the breaking of a cubyl C-C bond. The N-nitro groups stabilize the aminocubane system by withdrawing electron density from the amino group; this withdrawal prevents the lone pair of electrons on the amino group from being donated into the cage and catalyzing its decomposition. This observation supports the prediction that N-nitro-aminocubanes or aminocubanes with strongly electron withdrawing groups on the amino group will in general be stable.
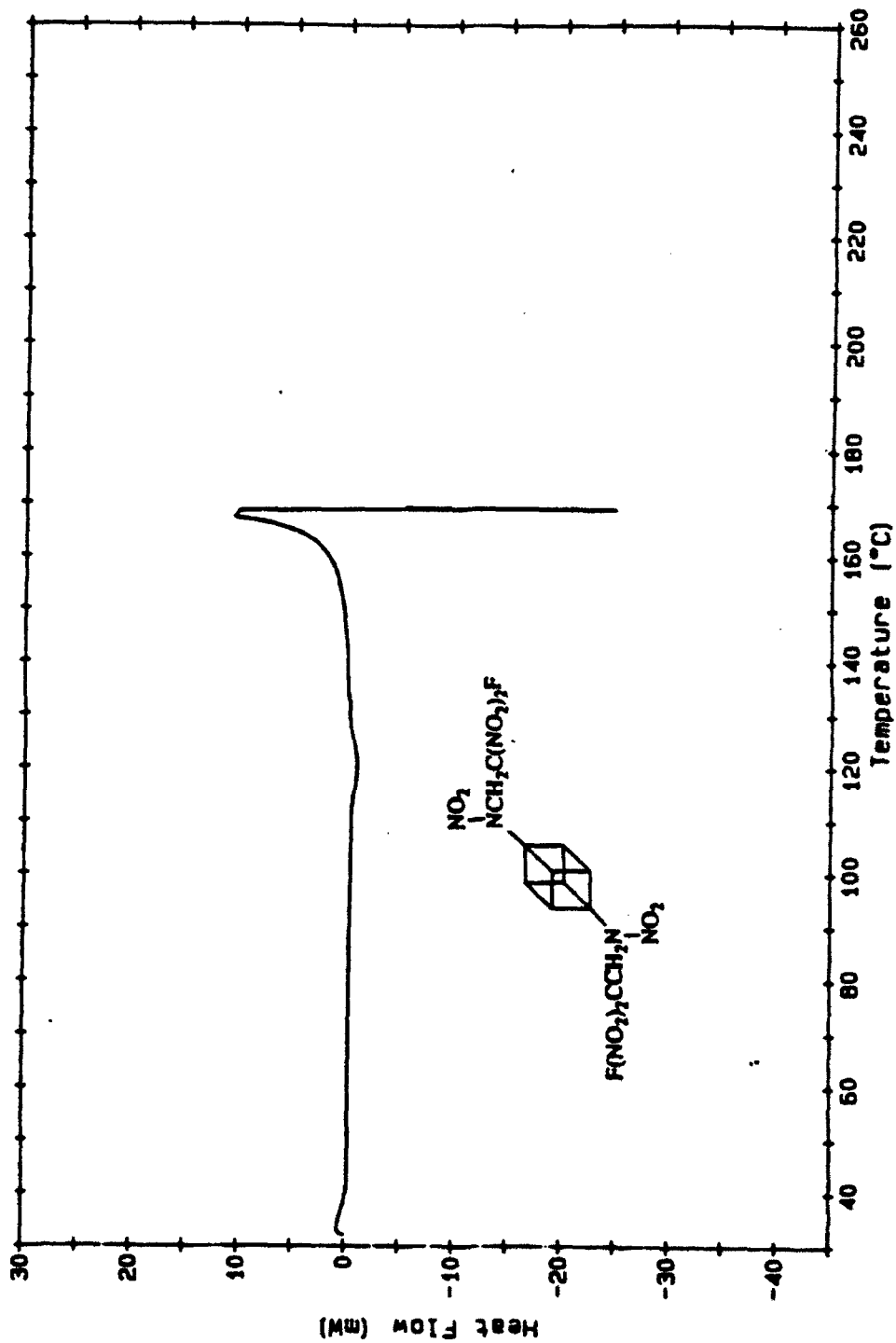
Figure 2. DSC for N,N'-dinitro-N,N'-bis(β,β-dinitro-β-fluoroethyl)-1,4-diaminocubane.

Cubane Esters of Trinitroethanol and Fluorodinitroethanol

We have prepared cubane esters substituted with 2,2,2-trinitroethanol (TNE) and 2,2-dinitro-2-fluoroethanol (FDNE). These compounds give immediate access into very highly nitrated cubanes oxidized to $CO/H_2O/N_2$ and beyond. These compounds represent the first examples of fully oxidized cubanes (Scheme 4).

$$\text{(cube)}-(CO_2Cl)_n$$

$$HOCH_2C(NO_2)_2F \qquad\qquad HOCH_2C(NO_2)_3$$

$$\text{(cube)}-(CO_2CH_2C(NO_2)_2F)_n \qquad\qquad \text{(cube)}-(CO_2CH_2C(NO_2)_3)_n$$
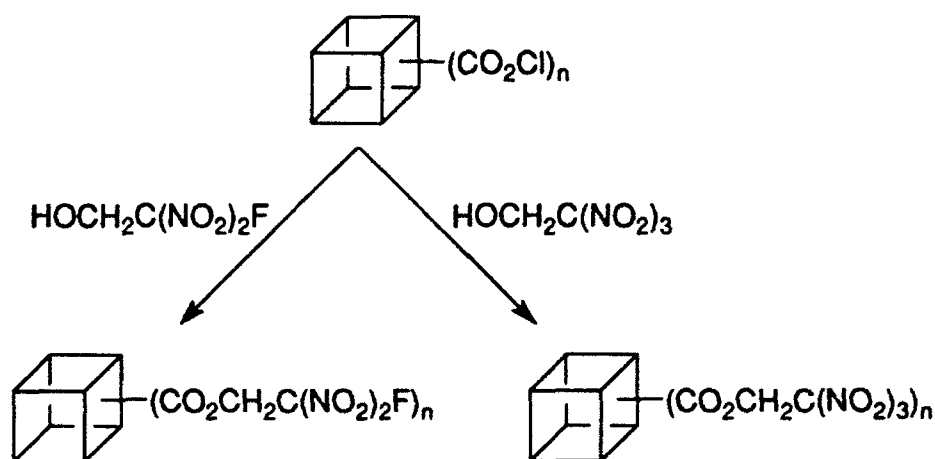
Where n = 2 or 4.

Scheme 4: Synthesis of energetic esters of cubane

We have thus far synthesized three of the possible polynitro esters: cubane-1,4-bis(ß,ß,ß-trinitroethylester), cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitroethylester) and cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester). The structures are shown below.
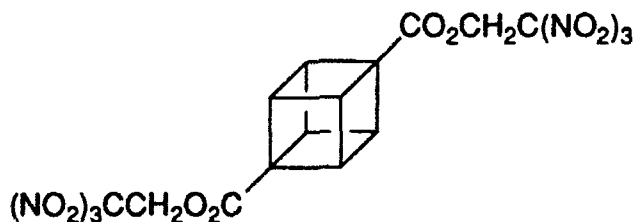
$$CO_2CH_2C(NO_2)_3$$
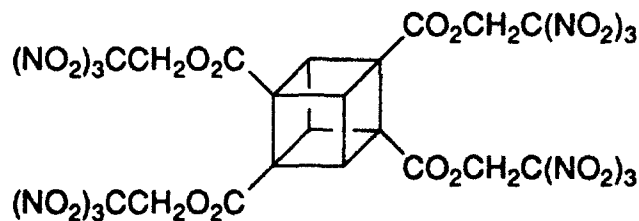
$$(NO_2)_3CCH_2O_2C-\text{(cube)}$$

Cubane-1,4-bis(ß,ß,ß-trinitroethylester)

Cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitroethylester)
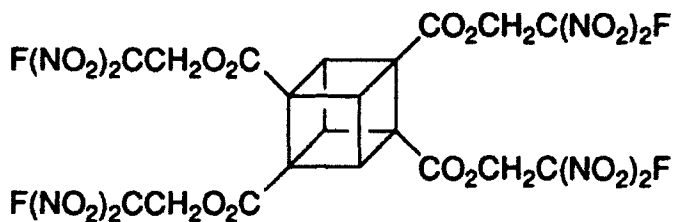
Cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester)
Density = 1.762 g/cm^3

Cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester) and cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitro-ethylester) represent the first examples of potentially useful energetic materials made from a cubane nucleus. Cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitroethylester) is over-oxidized and is an energetic powerhouse. Figure 3 shows the x-ray crystal structure of cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester), done by Dr. Richard Gilardi of the Naval Research Laboratory, which confirms our structure for the molecule and gives a crystal structure density of 1.762 g/cm^3. Figure 4 shows the DSC for this compound.

Cubane-1,2,4,7-tetrakis(ammonium perchlorate)

The first synthesis of cubane-1,2,4,7-tetrakis(ammonium perchlorate) was done at Thiokol by R. Willer. This was followed later by SRI's synthesis of cubane-1,2,4,7-tetrakis(ammonium perchlorate) using a different route. In our synthesis, we began with the conversion of cubane-1,2,4,7-tetraisocyanate to the carbamate followed by reaction with perchloric acid. A fine white solid material was isolated in approximately 40% yield. Upon further attempts at generating x-ray quality crystals, this material decomposed. We have observed that this material, suspected to be cubane-1,2,4,7-tetrakis(ammonium perchlorate), is extremely shock sensitive, detonating readily upon impact. Both SRI and
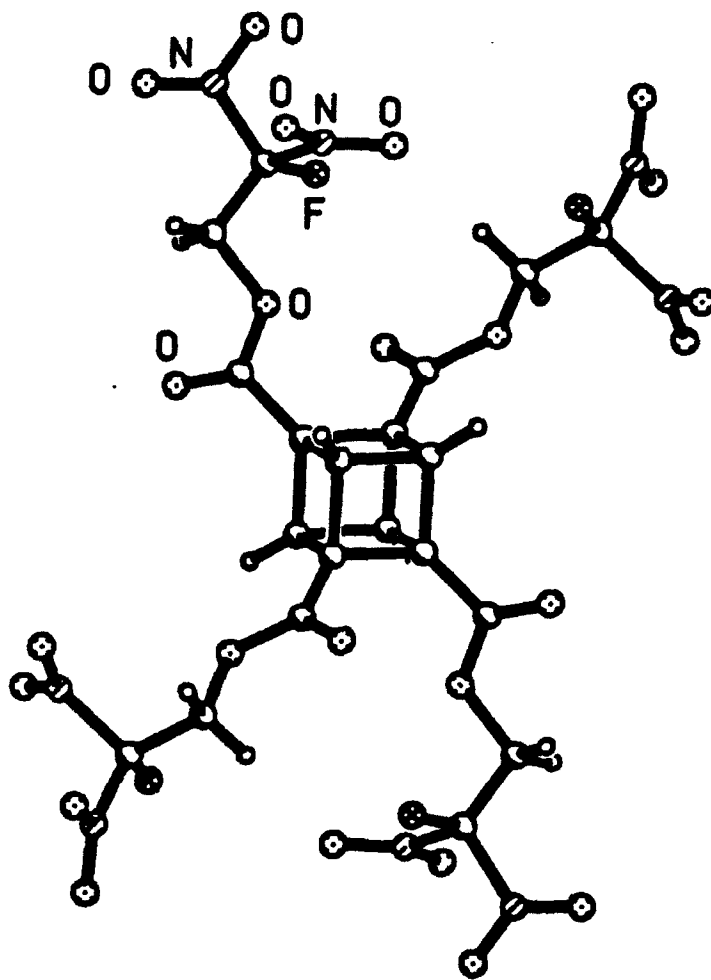
Figure 3.   Cubane-1,2,4,7-tetrakis((β,β-dinitro-β-dinitro-β-fluoroethylester).
Density = 1.762 g/cm^3

Figure 4. DSC of cubane-1,2,4,7-tetrakis(β,β-dinitro-β-dinitro-β-fluoroethylester).

Thiokol will be undertaking further studies on this compound to confirm the structure and decrease the sensitivity.
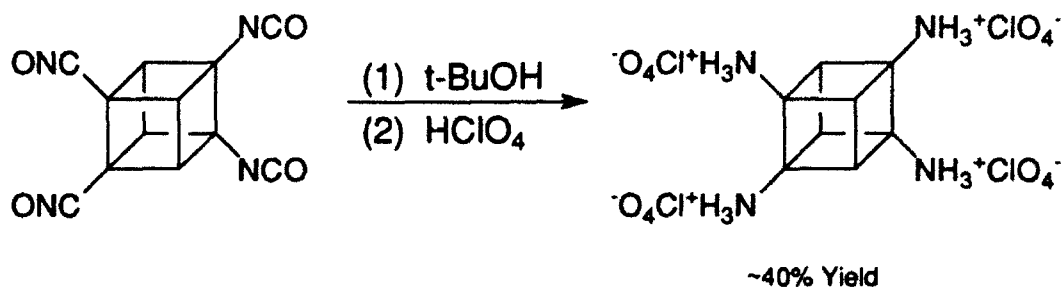
Scheme 5: Synthesis of cubane-1,2,4,7-tetrakis(ammonium perchlorate)

Figure 5 shows the DSC of the cubane-1,2,4,7-tetrakis(ammonium perchlorate) isolated on this project. The reaction is extremely exothermic; in fact, the exotherm was so strong we damaged the DSC equipment during the analysis.

NEW CUBANE BASED FUELS

Polycyanocubanes

We have started work on the synthesis of polycyanocubanes for use as dense, high energy rocket fuels. For example, calculations give octacyanocubane a heat of formation (ΔH_f) of +395 kcal/mol and a density greater than 1.5 g/cm^3. Each cyano group contributes 30.9 kcal/mol to the ΔH_f of the molecule. Thus, the cyanocubanes would be ideal energy dense fuels for volume limited applications. We have synthesized 1,4-dicyanocubane (the DSC for which is shown in Figure 6) and 1,2,4,7-tetracyanocubane (the DSC and TGA for which are shown in Figure 7 and 8). The structure and calculated ΔH_f of these two compounds are shown below.
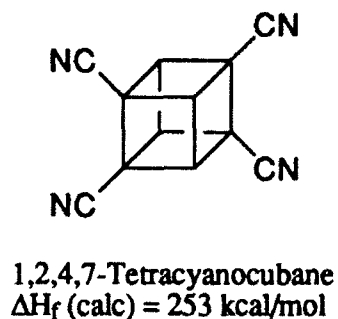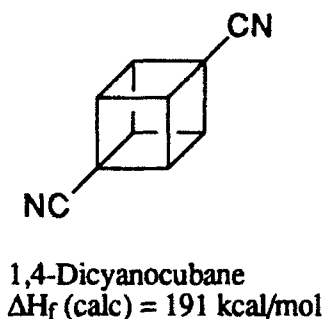
1,4-Dicyanocubane
ΔH_f (calc) = 191 kcal/mol

1,2,4,7-Tetracyanocubane
ΔH_f (calc) = 253 kcal/mol

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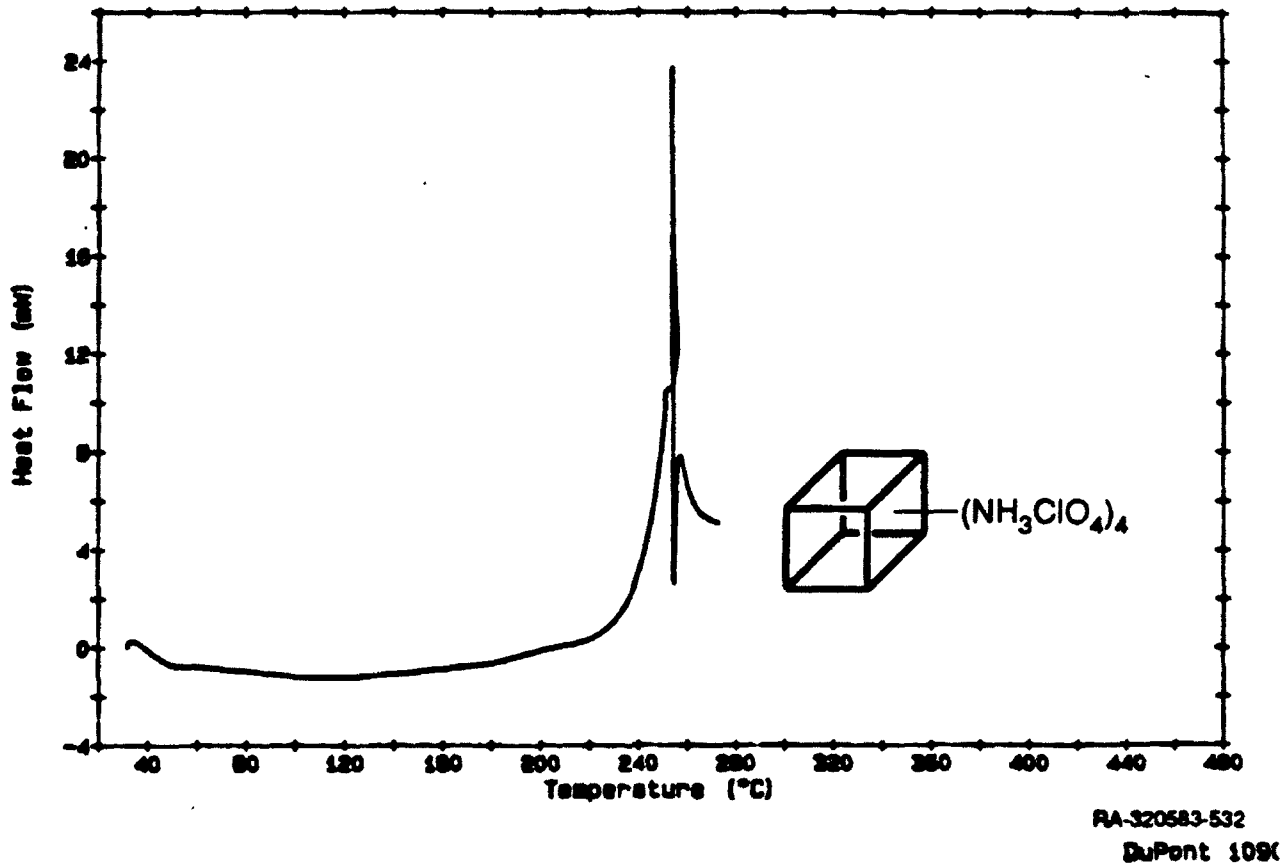
Figure 5.   DSC of cubane-1,2,4,7-tetrakis(ammonium perchlorate).

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PERKIN-ELMER

7 Series Thermal Analysis System

DSC Data File: decc01
Sample Weight: 0.000 mg
Mon Jul 27 13:04:51 1987
dicyanocubane
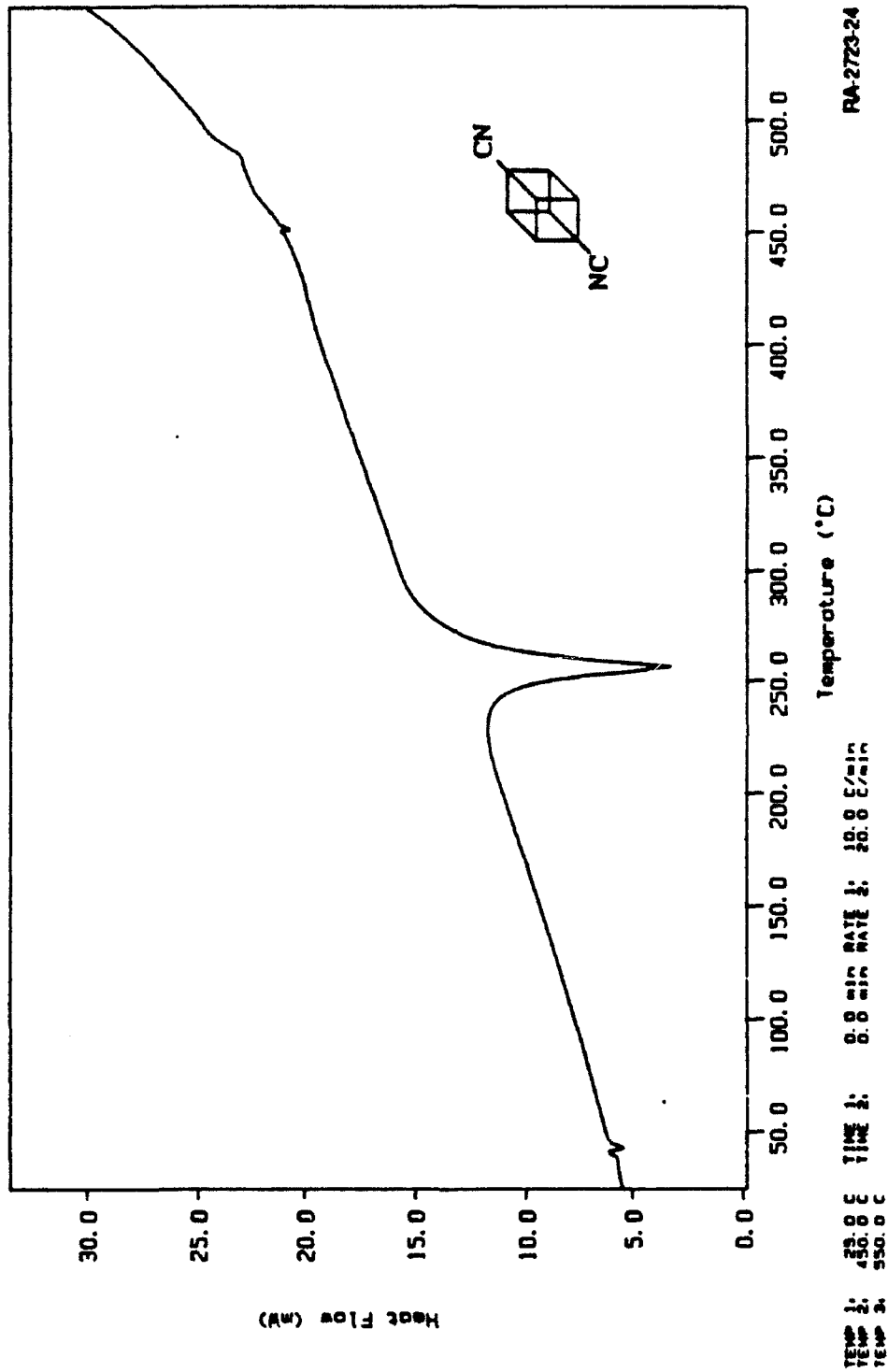
Figure 6. DSC of 1,4-dicyanocubane.

Sample: 1247TETRACNCUBANE
Size: 2.11 MG
Rate: 10 DEG/MIN
Program: Interactive DSC V3.0

DSC

Date: 30-Jun-89   Time: 17:36:00
File: BOTTARO.07 SERVICE # 11
Operator: PEP
Plotted: 3-Jul-89   7:56:06
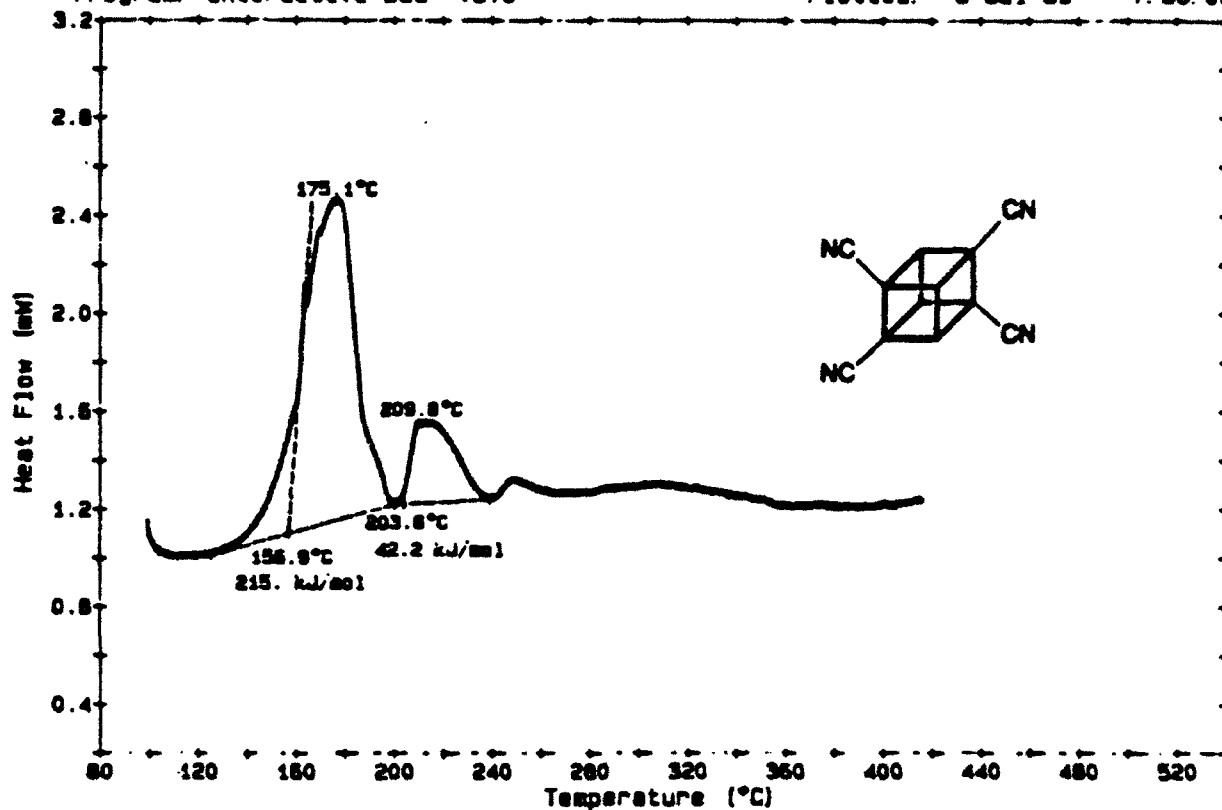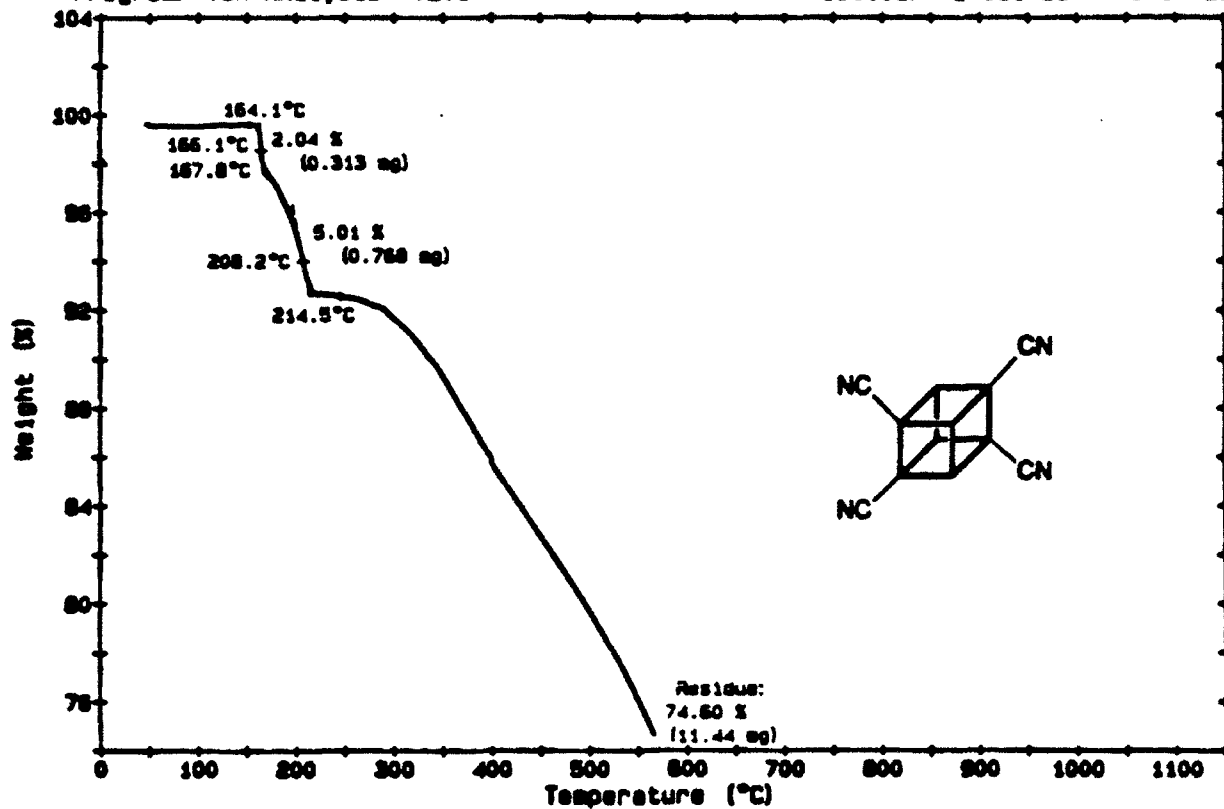
Figure 7.   DSC of 1,2,4,7-tetracyanocubane.

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Figure 8.   Thermogravimetric analysis (TGA) of 1,2,4,7-tetracyanocubane.

The DSC for the decomposition of 1,2,4,7-tetracyanocubane is especially interesting because it displays several sequential decomposition steps as shown by the various exotherms. We will not speculate on the possible mechanism of decomposition.

Cubane-1,4-diisocyanide

The isocyanides are especially interesting as energy increasing groups. Isocyanocubanes, like the polycyanocubanes, should make extremely good fuels or fuel additives for propellant applications because of their very high positive ΔH_f. The isocyanide group is even more energy dense than the cyano group, and thus even more energy is obtained for the same weight of compound. Each isocyanide group contributes +45.8 kcal/mol to the ΔH_f, a very dramatic increment.

We synthesized cubane-1,4-diisocyanide by reacting cubane-1,4-diisocyanate with Cl₃SiH in Et₃N as shown in Scheme 6. This was the only isocyanide that we attempted to prepare under this program.
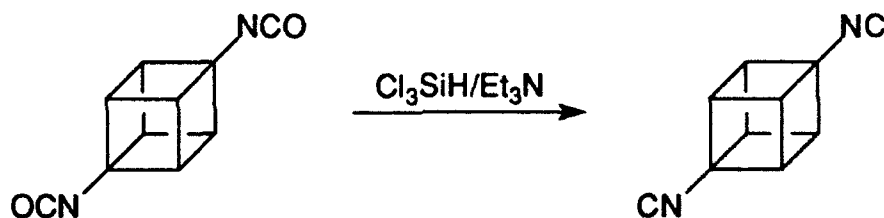
Scheme 6: Synthesis of cubane-1,4-diisocyanate

Cubane-1,4-diisocyanide is calculated to have a ΔH_f of +221 kcal/mol, an extremely high value for a compound containing only C, H, and N. In our hands, milligram quantities of this material detonated violently upon strong heating.

DEVELOPMENT OF NEW METHODS TO SUBSTITUTE CUBANE

New Synthesis of Cubane-1,2,4,7-Tetracarboxylic Acid

The original synthesis of cubane-1,2,4,7-tetracarboxylic acid required a large number of steps in the route developed by P. Eaton and coworkers.[4] The number of steps severely limited the ability both to scale up its synthesis and to develop other cubanes based on substitution using amides as directing groups. Finding amide directing groups that were

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more easily removable than diisopropylamide appeared to be a good approach for simplifying the synthesis.

In response to this need, we developed a simpler synthesis for cubane-1,2,4,7-tetracarboxylic acid (see Appendix A for a copy of a journal article describing this work). The two synthetic routes are shown in Figures 9 and 10. The crucial factor in our synthetic route is the discovery that a different amide, ethyl-t-butylamide, can successfully be used in place of diisopropylamide in the ortho lithiation of the cubane nucleus. Not only does this new cubyl amide give a higher yield than the diisopropylamide for the lithiation step, but we can remove the ethyl-t-butylamide nearly quantitatively in one step and thus easily isolate the cubane-1,2,4,7-tetracarboxylic acid from the reaction mixture. This improved synthesis eliminates the need for the oxidation, reduction, methylation, and demethylation sequence previously required to isolate the cubane-1,2,4,7-tetracarboxylic acid from the cubane-1,4-diisopropylamide-2,7-diacid. We have observed, that following this work, the Eaton group used similar amide functional groups to allow their synthesis of highly substituted cubyl derivatives.
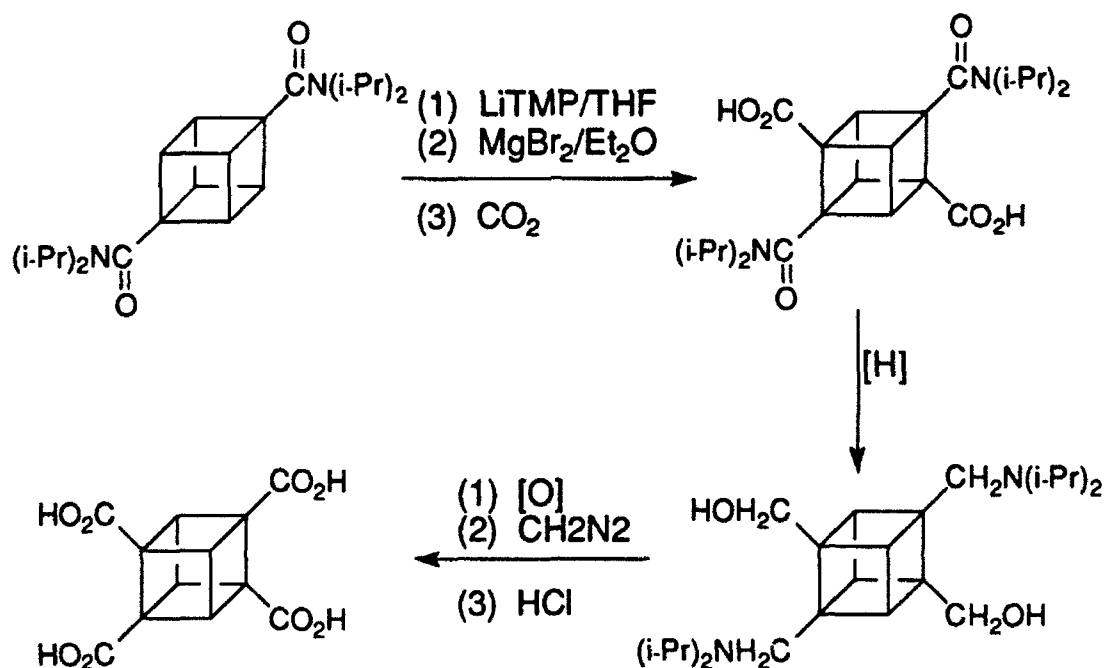
Figure 9. Current synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by P. Eaton.
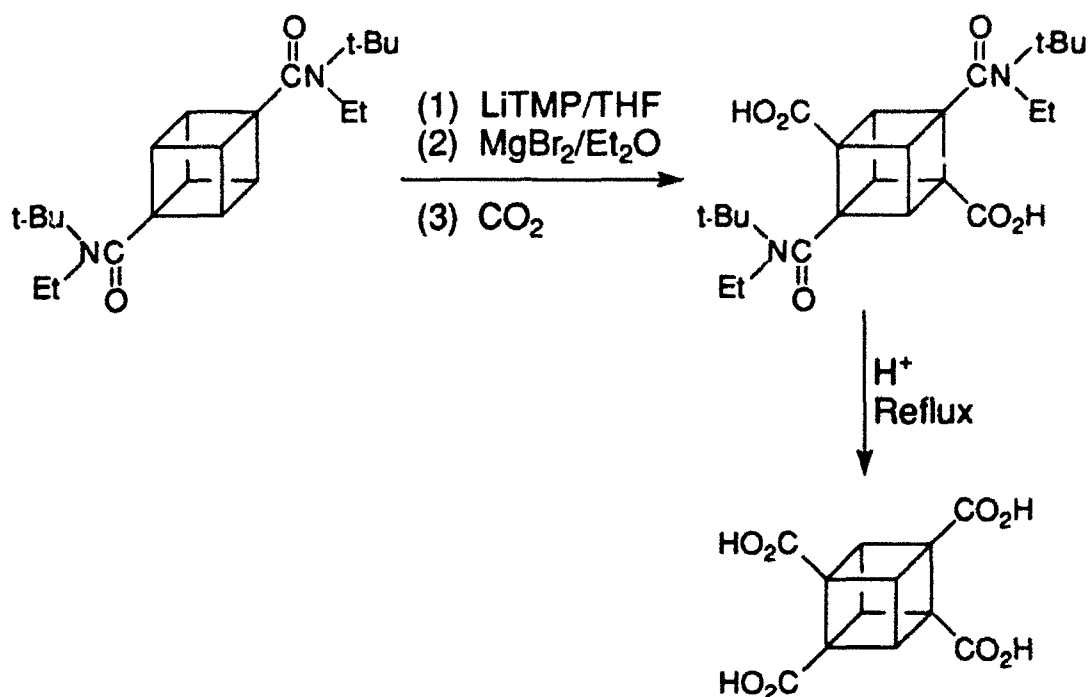
Figure 10. Improved synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by
SRI International

The ramifications of using this new procedure for the synthesis of cubane-1,2,4,7-
tetracarboxylic acid were not explored in detail in this program. Consequently, we cannot
report on the effect of this new cubyldiamide on the synthesis of substituted cubyl
derivatives.

A range of amide functionalities were explored prior to the finding that the N-ethyl-
N-t-butyl derivative is easily removed. Following the discovery that the N-ethyl-N-t-butyl
derivative meets that need for a removable amide directing group, we moved onto other
studies. We summarize in Table 1 the different amides that were explored in this program
as possible replacements for diisopropylamide before discovery of the N-ethyl-N-t-butyl
derivative that served us so well.

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Table 1

ATTEMPTED METALLATIONS OF CUBANE

(1) LiTMP/THF
(2) MgBr$_2$/Et$_2$O
(3) CO$_2$
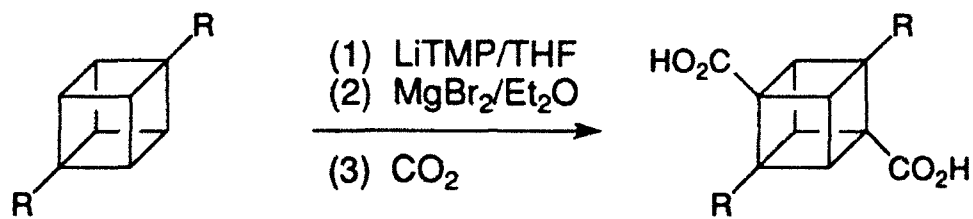
R	Carboxylation Observed (Yield)
	None
	None
	None
	25%
	75%

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Attempted Synthesis of Cubylnitrates

The recent synthesis of cubane-1,4-diol by Eaton has led us to attempt the synthesis of cubane-1,4-dinitrate from the diol. We were initially encouraged by our success in synthesizing 1,4-bis(trimethylsiloxy)cubane from the diol (Scheme 7) under conditions similar to those required for the synthesis of the nitrate.
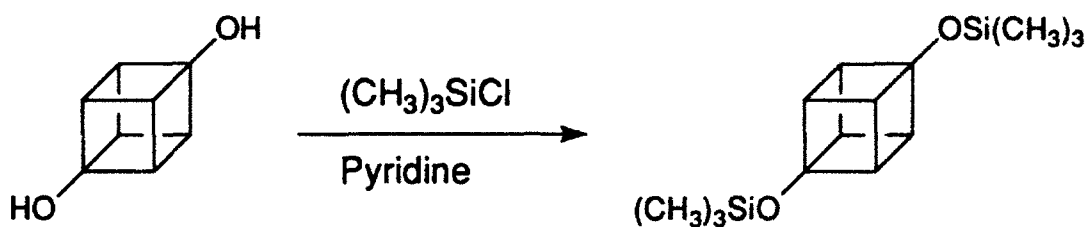
Scheme 7. Synthesis of 1,4-bis(trimethylsiloxy)cubane
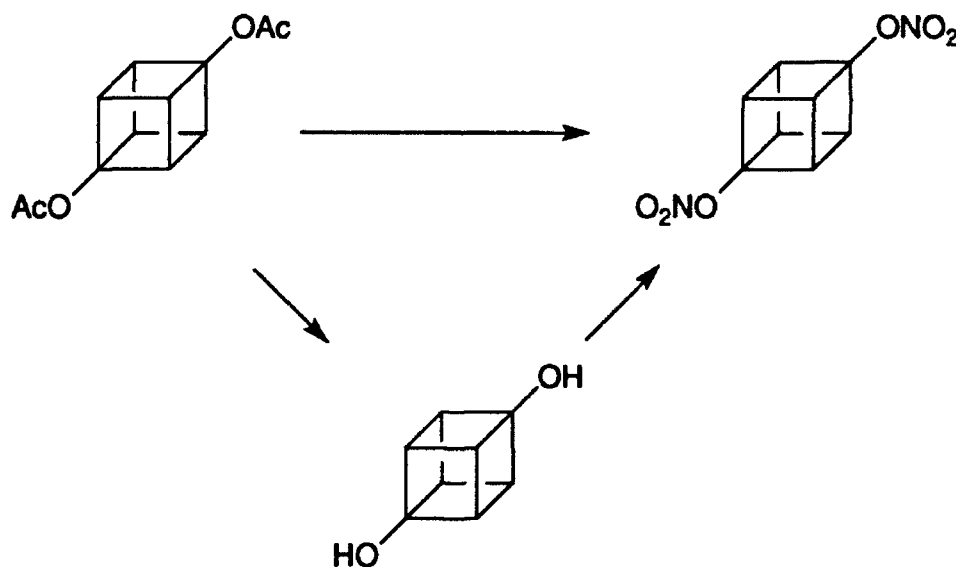
Scheme 8: Attempted synthesis of cubane-1,4-dinitrate

However, we were not able to synthesize the cubane-1,4-dinitrate as expected. Our initial results from the reaction of the 1,4-cubanediol with KF/N_2O_5 in CH_2Cl_2 (Schemes 8 and 9) indicate that we have indeed synthesized the dinitrate. This is demonstrated by a shift of the cubyl protons from 3.8 δ (s) for the diol to 4.3 δ (s) for the suspected dinitrate. The

infrared (IR) spectrum shows the presence of both of the expected peaks for nitrate at 1680 and 1450 cm^{-1}, exactly as expected for the dinitrate. However, these samples were impure, and we were not able develop a purification procedure in which the presumed dinitrate survives.
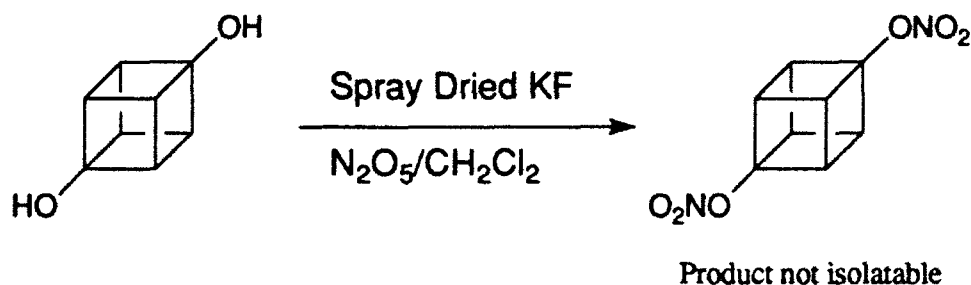
Scheme 9: Attempted synthesis of cubane-1,4-dinitrate.

SYNTHESIS OF ALKYLDINITRAMINE COMPOUNDS

During our work on the synthesis of energetic cubane derivatives, an interest developed in preparing cubyl-N,N-dinitramino compounds[5,6] (see Appendix C for a copy of the paper resulting from this work).[7] Our investigations of the available methodologies for the synthesis of this functional group led us to develop a better synthetic route for N,N-dinitramines. We were unable to prepare the cubyl derivatives of interest using this method, and we will discuss the reasons below.

The established method[2] takes four steps and involves the preparation of an alkyl nitramine via the N-nitromethylcarbamate followed by nitration with nitronium ion as shown in Scheme 10.
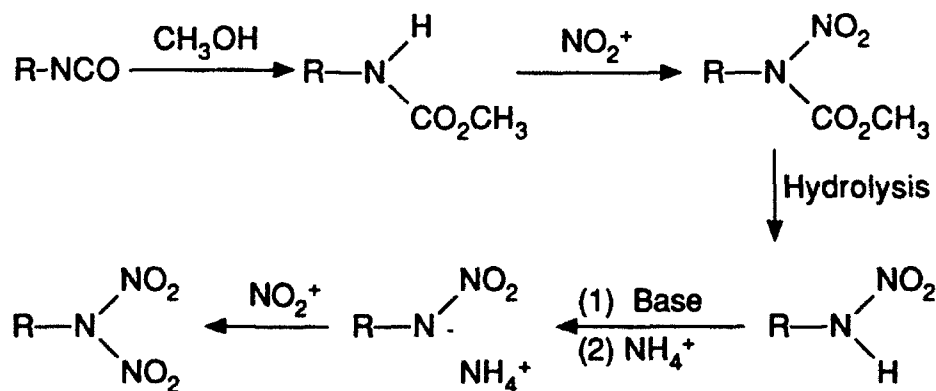
Scheme 10: Original synthesis of N,N-dinitramine compounds.

Our one-step synthesis of N,N-dinitramines from aliphatic isocyanates uses stoichiometric quantities of nitronium tetrafluoroborate and nitric acid in acetonitrile as the nitrating system (Scheme 11).

$$R\text{—}NCO \xrightarrow[\text{CH}_3\text{CN}]{\text{NO}_2\text{BF}_4 / \text{HNO}_3} R\text{—}N\begin{array}{l} \nearrow \text{NO}_2 \\ \searrow \text{NO}_2 \end{array}$$
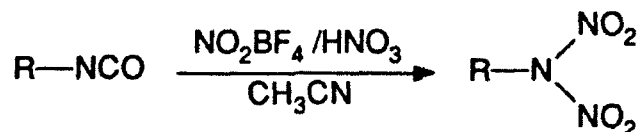
Scheme 11: New synthesis of N,N-dinitramino compounds

This route differs from the previous work in that it involves only one step instead of four and requires the presence of both nitric acid and high quality nitronium tetrafluoroborate in the reaction medium. If either reagent is absent, no N,N-dinitramine is formed.

We proposed the simple mechanism shown in Scheme 12, in accordance with the observation of Ledebev et al.,[6] who reacted isocyanates with nitronium ions in the absence of nitric acid to give monoalkyl-mononitramino compound via intermediate 2. Adding an aliphatic isocyanate to a preformed, ice-cooled mixture of acetonitrile, nitric acid, and nitronium tetrafluoroborate results in the initial formation of the corresponding acylium ion 2 to which HNO$_3$ is added, resulting in loss of a proton and CO$_2$, to give the corresponding aliphatic N,N-dinitramine 4. Consistent with this mechanism is our observation that no N,N-dinitramines are formed when the reaction is run in the absence of free nitric acid, which presumably acts as a nucleophile toward acylium ion 2. An alternative to the proposed mechanism below is the direct addition of N$_2$O$_5$ (formed by the reaction of NO$_2$BF$_4$ with HNO$_3$) across the alkyl isocyanate giving the same reactive intermediate shown below and also giving 4.
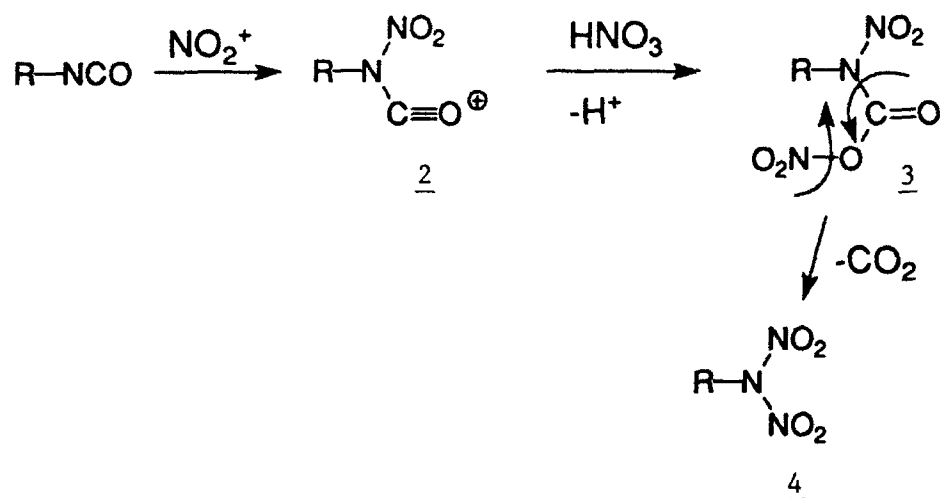
Scheme 12: Proposed mechanism for N,N-dinitramine synthesis

This reaction is most successful with primary alkyl isocyanates. For example, hexamethylene-1,6-diisocyanate is converted in 10% yield (Scheme 13), the square of the yield obtained for monofunctional substrates, indicating that the two distant functional groups are not interacting in this case.
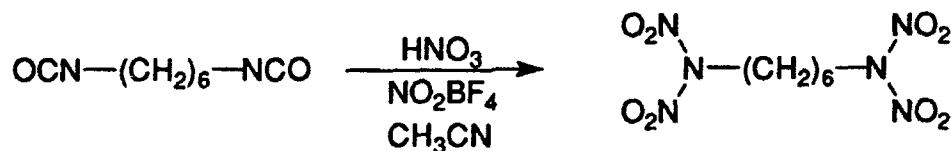
Scheme 13: Synthesis of 1,6-bis(N,N-dinitramino)hexane (10% yield)

When 1-adamantyl isocyanate was subjected to the conditions of this procedure, only a trace at best (<1%) of the desired N,N-dinitramine was formed, with the remainder of the substrate transformed into a complex mixture (Scheme 14). This result indicates a high sensitivity either to steric hindrance or to the stability of the ternary carbonium ion or radical formed if the dinitramine group leaves and then rearranges. We would expect that the dinitramide group is an excellent leaving group and obviously quite labile when attached to a ternary position such as the 1-position of adamantane. This lability would be exaggerated in the case of cubanes and hence explains why we were unable to prepare cubyl derivatives.

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$$R-NCO \xrightarrow[\substack{NO_2BF_4 \\ CH_3CN}]{HNO_3} R-N\begin{smallmatrix} NO_2 \\ NO_2 \end{smallmatrix}$$
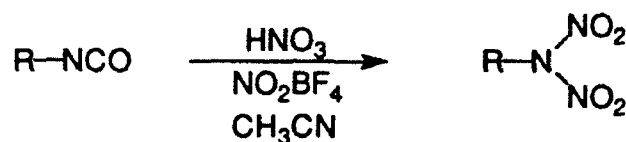
Scheme 14: New synthesis of N,N-dinitroamines (R = butyl, 35%; adamantyl, 1%)

The substrates investigated are shown in Table 2, along with the yields. The overall yields from this route are no better than those of previous syntheses, but the transformation is accomplished in one rather than four steps.

Table 2

Synthesis of N,N-Dinitramines

Substrate	Product	Yield
n-Butyl isocyanate	1-(N,N-Dinitramino) butane	35%
Methyl isocyanate	N,N-Dinitramino-methane	30%
1-Adamantyl isocyanate	1-(N,N-Dinitramino) adamantane	<<1%
Hexamethylene diisocyanate	1,6-bis(N,N-Dinitramino)hexane	10%
Ethane-1,2-diisocyanate	1,2-bis(N,N-Dinitramino)ethane	-0-
2-(Trimethylsilyl-ethyl)-1-isocyanate	1-(N,N-Dinitramino)-2-trimethylsilyl-ethane	25%

DINITRAMIDE SALTS

We invented a completely new, stable class of inorganic oxidizers that will have both fundamental scientific interest and practical application to rocket propulsion (this work was done in cooperation with another ONR project, SRI Project No. 6654, Contract No. N00014-88-C-0537). These oxidizers are based on a newly discovered inorganic anion known as the dinitramide anion, which has the formula $N(NO_2)_2^-$. The dinitramide anion is a uniquely stable, high oxygen density grouping that can be prepared in many different combinations, including the ammonium salt (SRI-12), the compound expected to be of most interest for rocket propulsion. Since the dinitramide anion has never been observed before, there is fundamental interest in its properties and structure, and much work needs to be performed to improve its synthesis and better understand its full impact. Since the

dinitramide salts and the parent compound dinitraminic acid are a new composition of matter, we provide in Table 3 below a set of nomenclature for nitro-amino compounds to clarify the naming of these compounds

Table 3

NOMENCLATURE OF THE DINITRAMIDES

Example	Example
N,N-Dinitraminomethane	$CH_3N(NO_2)_2$
Nitramide	NH_2NO_2
Dinitraminic Acid	$HN(NO_2)_2$
Ammonium Dinitramide	$NH_4N(NO_2)_2$

As part of this study, we have prepared many different dinitramide salts, including the lithium, cesium, ammonium, hydrazinium, hydroxylammonium, and guanidinium salts as well as other derivatives. The compounds prepared are summarized in Table 4.

Table 4

PROPERTIES OF DINITRAMIDE SALTS

Code Name	Formula	Density[a] (g/cm^3)	ΔH_f[b] (kcal/mol)	
	LiN(NO$_2$)$_2$			
SRI-11	CsN(NO$_2$)$_2$	3.05 (x-ray)		
SRI-12	NH$_4$N(NO$_2$)$_2$	1.80 (x-ray)	-35.8[b]	(Measured)
SRI-13	N$_2$H$_5$N(NO$_2$)$_2$	1.83 (x-ray)	-8	(Estimated)
SRI-14	(NH$_2$OH)$_2$HN(NO$_2$)$_2$			
SRI-17	Cubane-1,4-(NH$_3$N(NO$_2$)$_2$)	1.77 (x-ray)		
SRI-19	Cubane-1,2,4,7-(NH$_3$N(NO$_2$)$_2$)	1.85 (x-ray)		
SRI-21	C(NH$_2$)$_3$N(NO$_2$)$_2$	1.67 (x-ray)	-40.7± 1.5[b]	(Measured)
	NH$_3$OHN(NO$_2$)$_2$		-32	(Estimated)
For Comparison				
	LiClO$_4$	2.42	-91	
KP	KClO$_4$	2.53	-102.8	
	CsClO$_4$	3.33	-103.9	
AP	NH$_4$ClO$_4$	1.95	-70.7	
HAP	NH$_3$OHClO$_4$	~2	-66.5	

[a]Crystal structures determined by R. Gilardi, J. Flippin-Anderson, and C. George, Structure of Matter Laboratory, NRL.

[b]Heat of formation for SRI-12 determined at Naval Warfare Center (NWC), China Lake; that for SRI-21 determined at Los Alamos National Laboratory (LANL).

Cesium Dinitramide

Cesium dinitramide is synthesized by a β-elimination reaction with cesium fluoride ion and 1-(N,N-dinitramino)-2-trimethylsilylethane to give a fluoride-ion-catalyzed elimination of trimethylsilylfluoride, ethylene, and the desired cesium dinitramide (SRI-11). Scheme 15 shows the reaction.

$$Cs^+ \left[N \genfrac{}{}{0pt}{}{NO_2}{NO_2} \right]^- + C_2H_2 + Me_3SiF \tag{1}$$
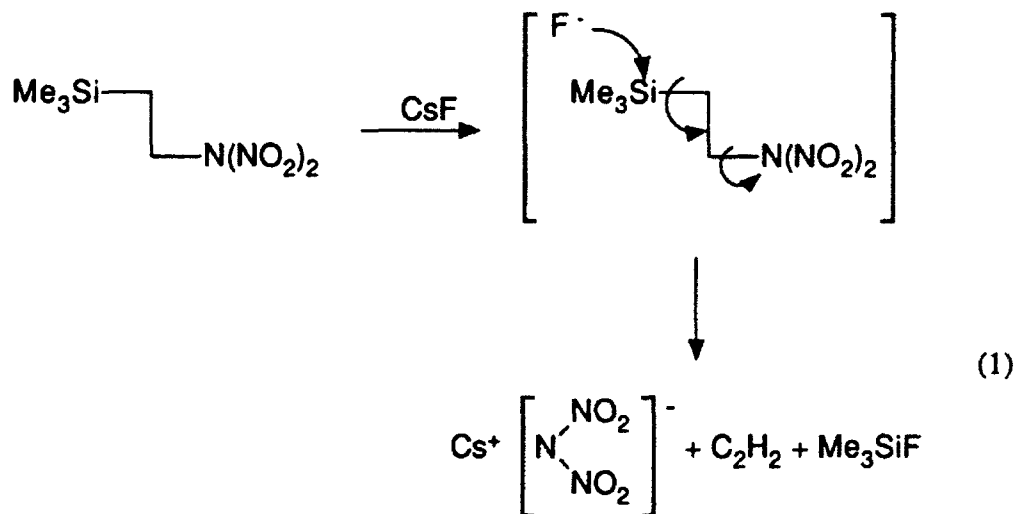
Scheme 15: Synthesis of cesium dinitramide.

1-(N,N-Dinitramino)-2-trimethylsilylethane is synthesized by either of two methods. The most direct route is through a recently discovered reaction between an isocyanate and a mixture of nitric acid and nitronium tetrafluoroborate (Scheme 16).[7] The publication describing this synthesis is attached as Appendix C.

$$Me_3Si \text{—} CO_2H \xrightarrow[\substack{(2)\ NaN_3 \\ (3)\ \Delta,\ -N_2}]{(1)\ SOCl_2} Me_3Si \text{—} NCO \xrightarrow{HNO_3/NO_2BF_4} Me_3Si \text{—} N(NO_2)_2 \tag{3}$$
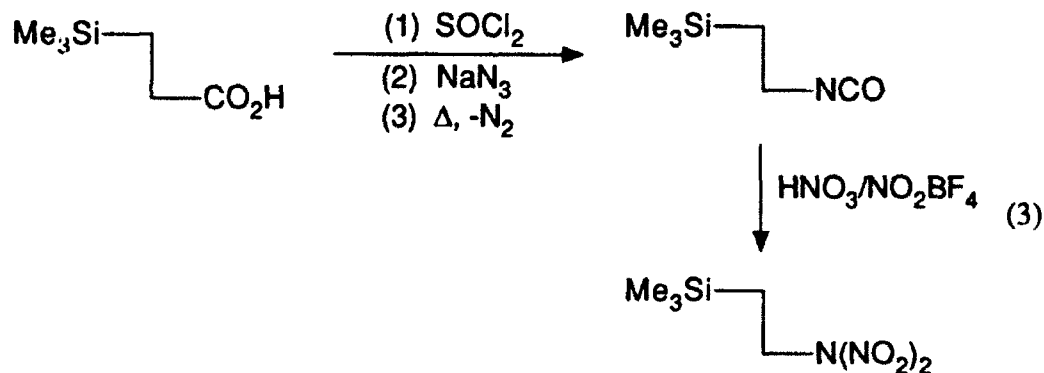
Scheme 16: Synthesis of 1-(N,N-dinitramino)-2-trimethylsilylethane.

The x-ray crystal structure of cesium dinitramide (determined by Gilardi and co-workers at NRL) is shown in Figure 11. The crystal structure presents two cesium dinitramide molecules, with the ionic interaction between cesium and the oxygen of the dinitramide shown by dashed lines. Note that the closest approach of the cesium ion to the dinitramide ion is through the oxygens of the nitro groups and not through the central nitrogen of the dinitramide. This packing behavior of the cation is seen in all dinitramide crystal structures, which implies that the highest charge density is found on the nitro oxygens in the crystal lattice rather than on the central amide group.
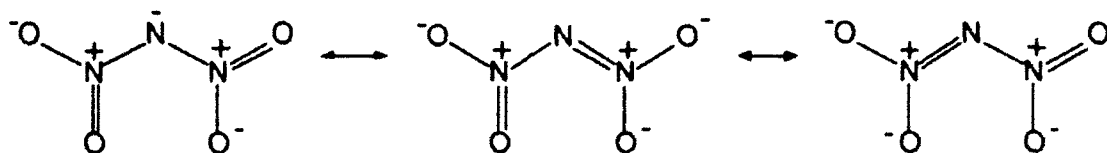
Cesium dinitramide has a melting point of 87°C followed by the onset of exothermic decomposition at 175°C (DSC, Figure 12). Its density is 3.05 g/cm^3. The dinitramide ion is stable to base. Cesium dinitramide has a UV maximum at 284 nm [ϵ (H$_2$O) = 4.24 x 10^3 l mol^{-1} cm^{-1}]. Further studies of the thermal and solution properties of this anion are under way.

Other counterions can be substituted for cesium either by using alternative fluoride ion sources or by passing the cesium dinitramide through an ion-exchange column (Scheme 17). Several other salts that have been prepared using these methods are shown in Table 4.

$$CsN(NO_2)_2 \xrightarrow[\text{Ion Exchange}]{M^+} M^+ N(NO_2)_2^-$$

Scheme 17: Ion exchange of cesium dinitramide to give other dinitramide salts

The crystal structures of dinitramides show N-N bond distances between those of a single bond and a double bond, indicating resonance stabilization of the charge and a

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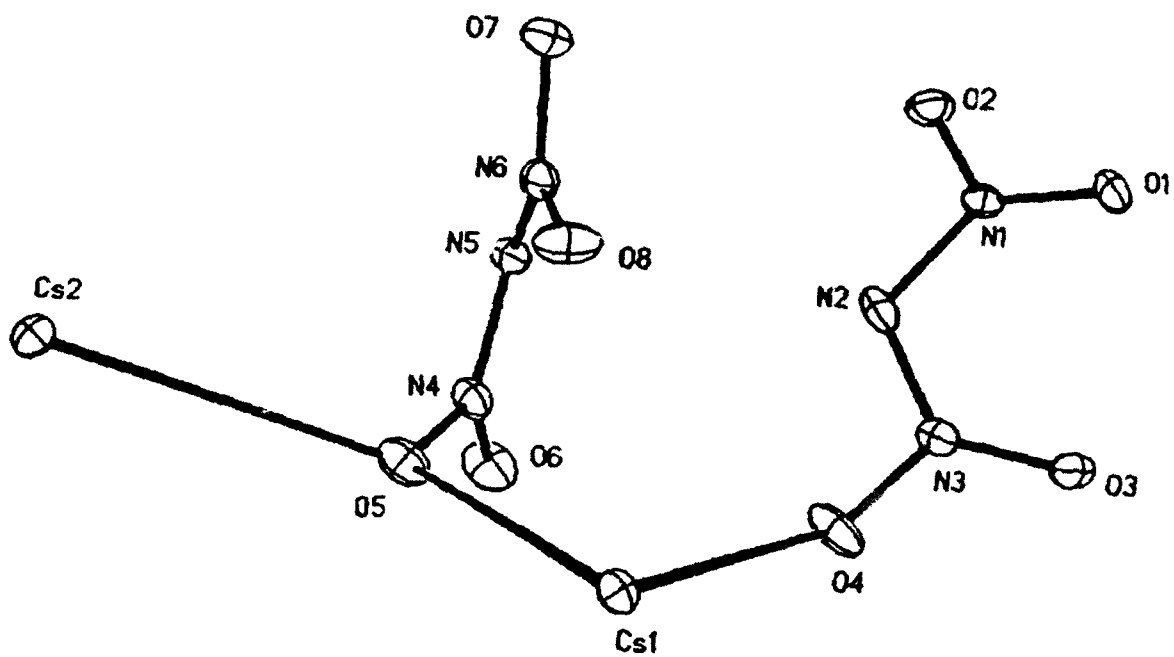
Figure 11. Crystal structure of $CsN(NO_2)_2$ (SRI-11).
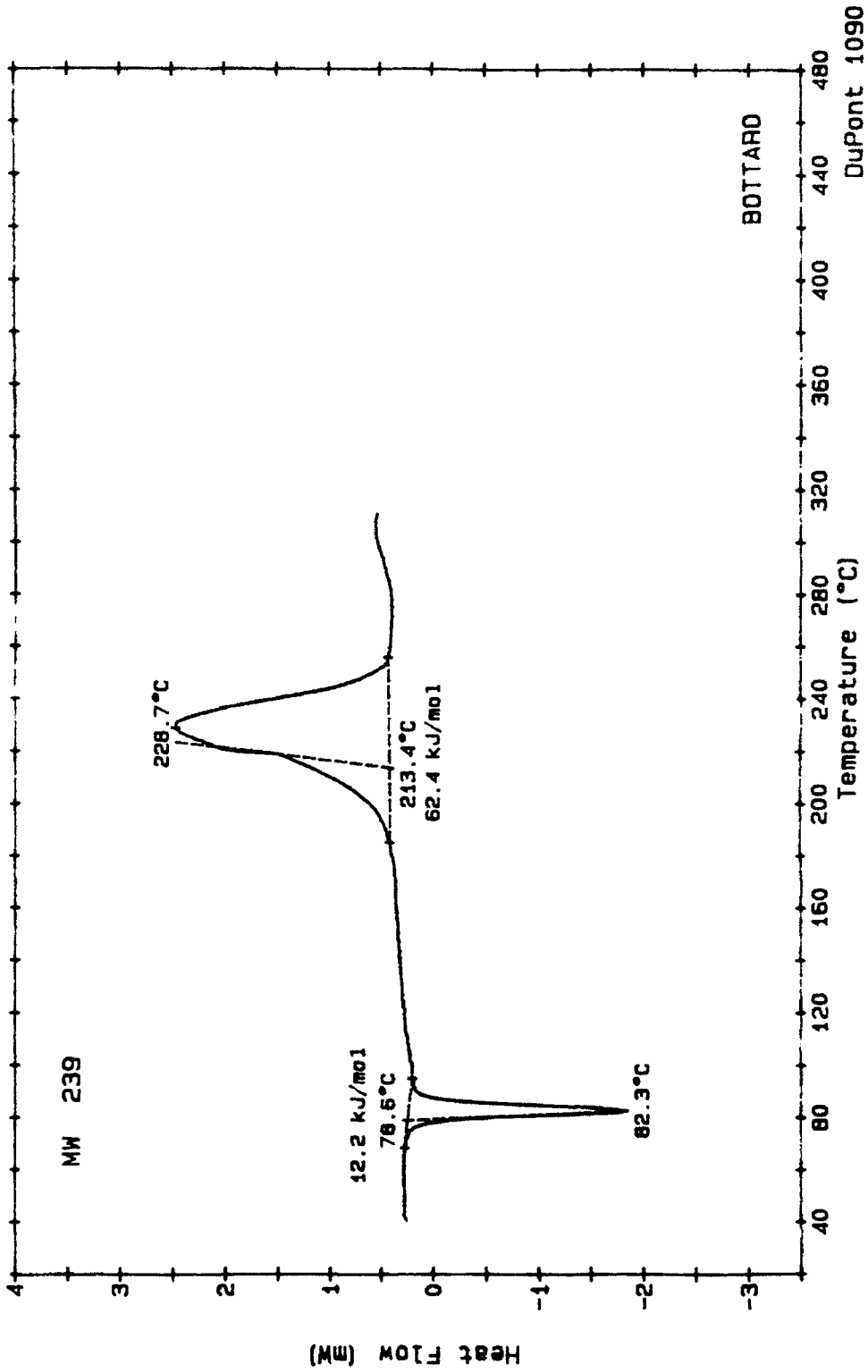
Figure 12. DSC of CsN(NO₂)₂ (SRI-11).

significantly stronger N-N bond than is found in conventional nitramines or dinitramines. Some of the resonance forms of the dinitramide ion are shown on the previous page, with the negative charge localized on the central nitrogen or delocalized out on either of the two nitro groups. In crystal packing, it appears that the negative charge is predominantly on the oxygen.

The bond angles and distances in dinitramide salts are summarized in the two structures below, and typical bond distances and angles are given in Table 5. These structures give the average bond distances and angles for nine different dinitramide salts. As can be seen from these averages, the N-N bond distance is almost exactly halfway between a single and a double N-N bonding distance. The N-O bond distances for the nitro groups are close to those observed in other nitro compounds. The N-N-N bond angle is less than that for sp^2 hybridization and greater than that observed for sp^3 hybridization.
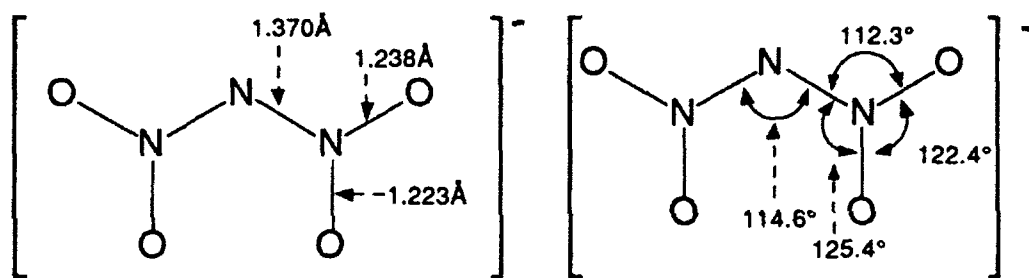
Table 5

TYPICAL BOND DISTANCES FOR NITROGEN CONTAINING COMPOUNDS

Bond	Typical Length
N-N	1.451 Å (substituted hydrazine
N=N	1.25 Å
N=O	1.22 Å (nitro)
O-N-O bond angle	124° (aromatic)

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Ammonium Dinitramide (ADN, SRI-12)

The original synthesis of SRI-12 (also referred to as ADN), as was reported in our international patent applications,[8,9] is shown in Scheme 18. The patent application that resulted is attached as Appendix D.

$$Me_3Si\text{—}N(NO_2)_2 \xrightarrow{CsF} \left[Me_3Si\text{—}N(NO_2)_2 \right] $$

$$NH_4^+N(NO_2)_2^- \xleftarrow{\text{Ion Exchange}} Cs^+N(NO_2)_2^- + C_2H_2 + Me_3SiF$$
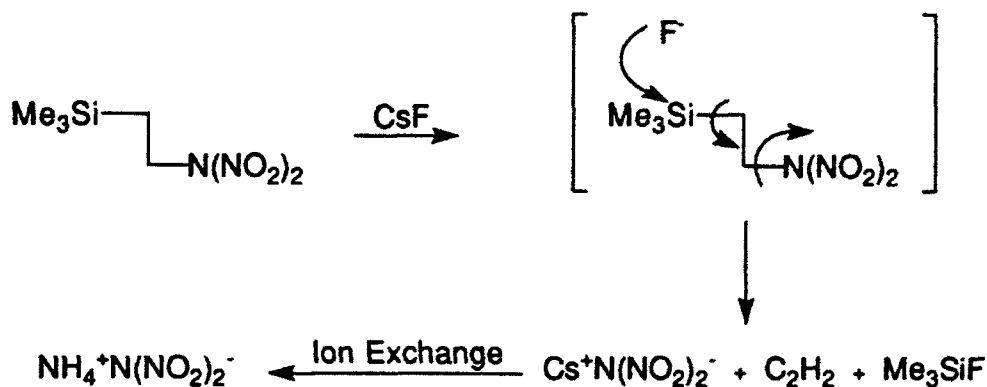
Scheme 18: Original synthesis of SRI-12 (ADN) by silyl elimination

We obtain approximately 25% overall yield from this route based on 3-trimethylsilylpropionic acid. We will not discuss in this document the current route for the synthesis of SRI-12, but it will be reported in a classified document. The new routes are a significant improvement over the route shown above.

The crystal structure for SRI-12 is shown in Figure 13. The crystal structure again shows that the closest approaches are between the cation and the oxygens of the dinitramide anion. This is illustrated much more clearly in Figures 14 and 15. In Figure 14, one ammonium cation is shown in the presence of the four closest dinitramide anions. The dotted lines illustrate the closest approaches (H-bonding) between the anion and cation. Figure 15 shows the opposite case, one dinitramide anion surrounded by the four nearest ammonium ions.

Figure 16 shows a view of the dinitramide ion down the plane of the molecule. The two nitro groups in all the dinitramide salts are out of plane with respect to each other, probably the result of nonbonded repulsion. This is an excellent demonstration of the steric effects that the nitro groups have on each other. We predict that the dinitramide ion would be planar were there not a steric penalty imposed by the nitro groups.

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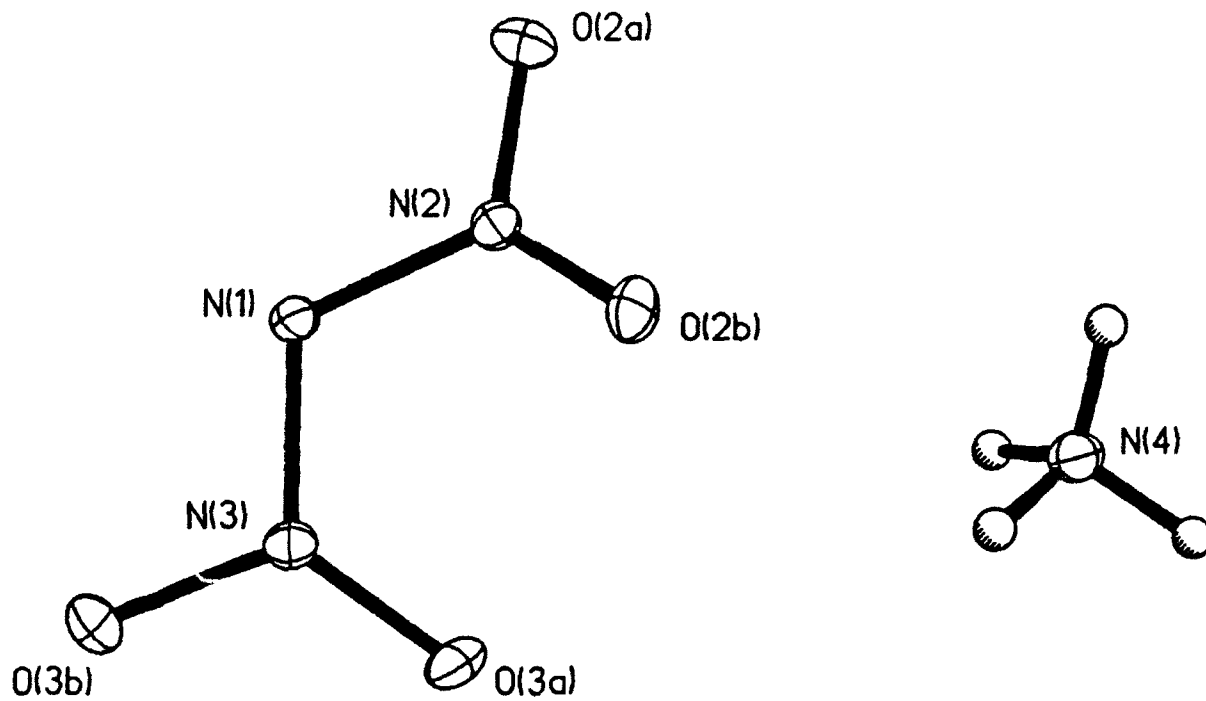
Figure 13.   Crystal structure of ammonium dinitramide (SRI-12).
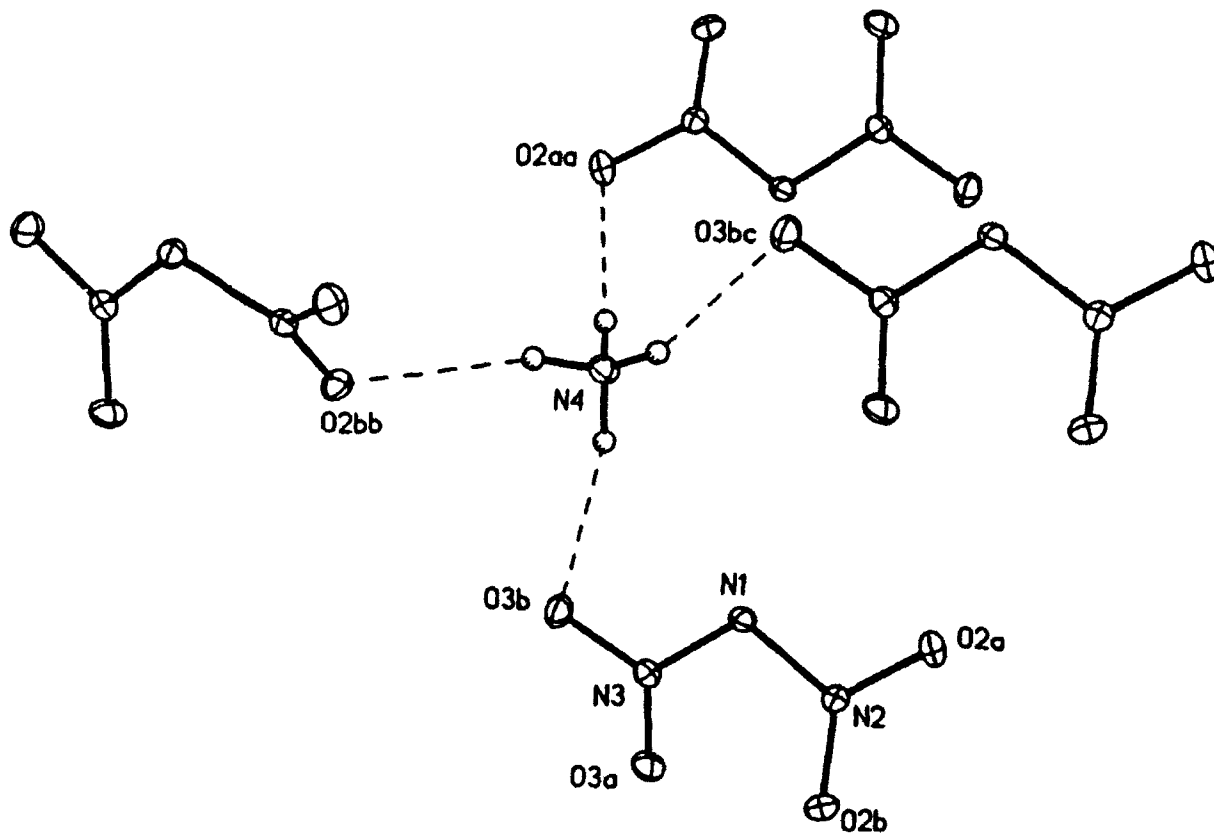
Figure 14.   Partial crystal lattice view showing closest approach of 4 dinitramide anions
to the ammonium ion.
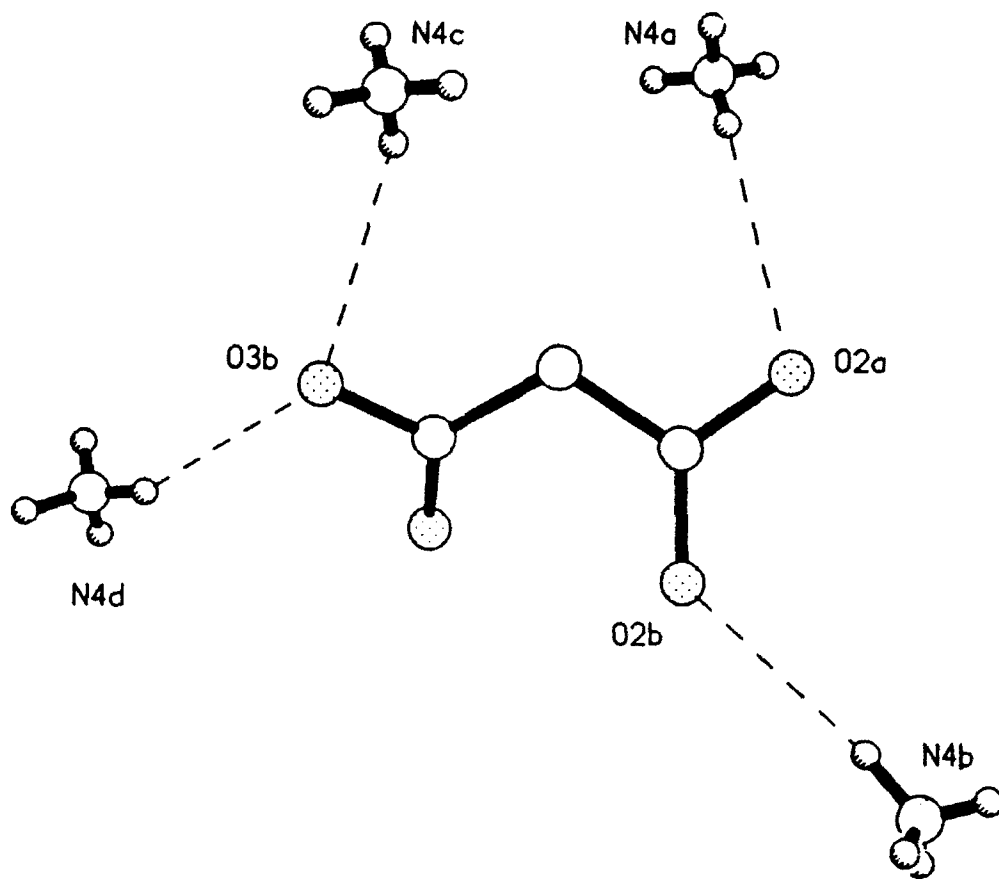
Figure 15.   Partial crystal lattice view showing closest approach of 4-ammonium ions
to one dinitramide anion.
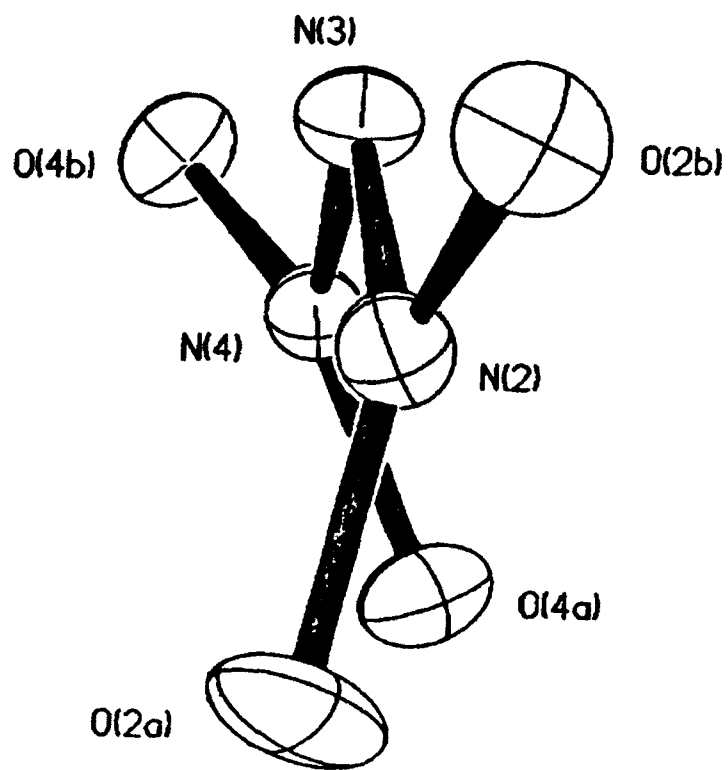
Figure 16.   View of dinitramide ion down the plane of the ion.

SRI-12 has good thermal properties. Its DSC and TGA are shown in Figures 17 and 18, respectively. The DSC of SRI-12 shows the melting point onset at approximately 88°C and the onset of decomposition at 145°C. The TGA shows no weight loss until above 160°C, with complete weight loss by 240°C The heat of formation of SRI-12 was measured at NWC, China Lake. The value obtained is -35.8 kcal/mol.

Hydrazinium Dinitramide (SRI-13)

The crystal structure of hydrazinium dinitramide and its DSC are shown in Figures 19 and 20, respectively. This compound was prepared to take advantage of the heat of formation that is obtained from the use of hydrazinium derivatives, which is higher than that of ammonium derivatives. Unfortunately, hydrazinium dinitramide is highly shock (impact) sensitive and thus has no practical value. Additionally, as observed in the DSC, the melting point is slightly lower than that of the ammonium derivative, further reducing the possibility of this compound having practical value.

Hydroxylammonium Dinitramide and Hydroxylammonium-hydroxylamine Dinitramide (SRI-14)

We attempted to prepare the hydroxylammonium dinitramide salt because of the interest in obtaining a material having increased oxygen density. This compound would be comparable to hydroxylammonium perchlorate or nitrate. Unfortunately, studies in this laboratory have shown hydroxylammonium dinitramide to be a liquid.

However, we were able to isolate the hydroxylammonium-hydroxylamine dinitramide derivative as a crystalline solid. The x-ray crystal structure of this compound is shown in Figure 21. The crystal lattice contains both a hydroxylammonium and a hydroxylamine for each dinitramide anion present. We have been informed by R. Gilardi at NRL that the crystal structure has another unusual feature: there is hydrogen bonding to both the oxygen and nitrogen of the hydroxylamine. This feature can be seen in Figure 21.

The DSC of hydroxylammonium-hydroxylamine dinitramide (not shown) indicates that the onset for melting of this derivative is near 75°C and the thermal onset for decomposition is around 150°C. The melting point is slightly lower than that of the ammonium derivative, but the decomposition onset is near that of the ammonium salt. Qualitative determination of the impact (shock) sensitivity showed this compound to be considerably more sensitive than the corresponding ammonium derivative. This derivative is stable in base and may find application as a liquid gun propellant.
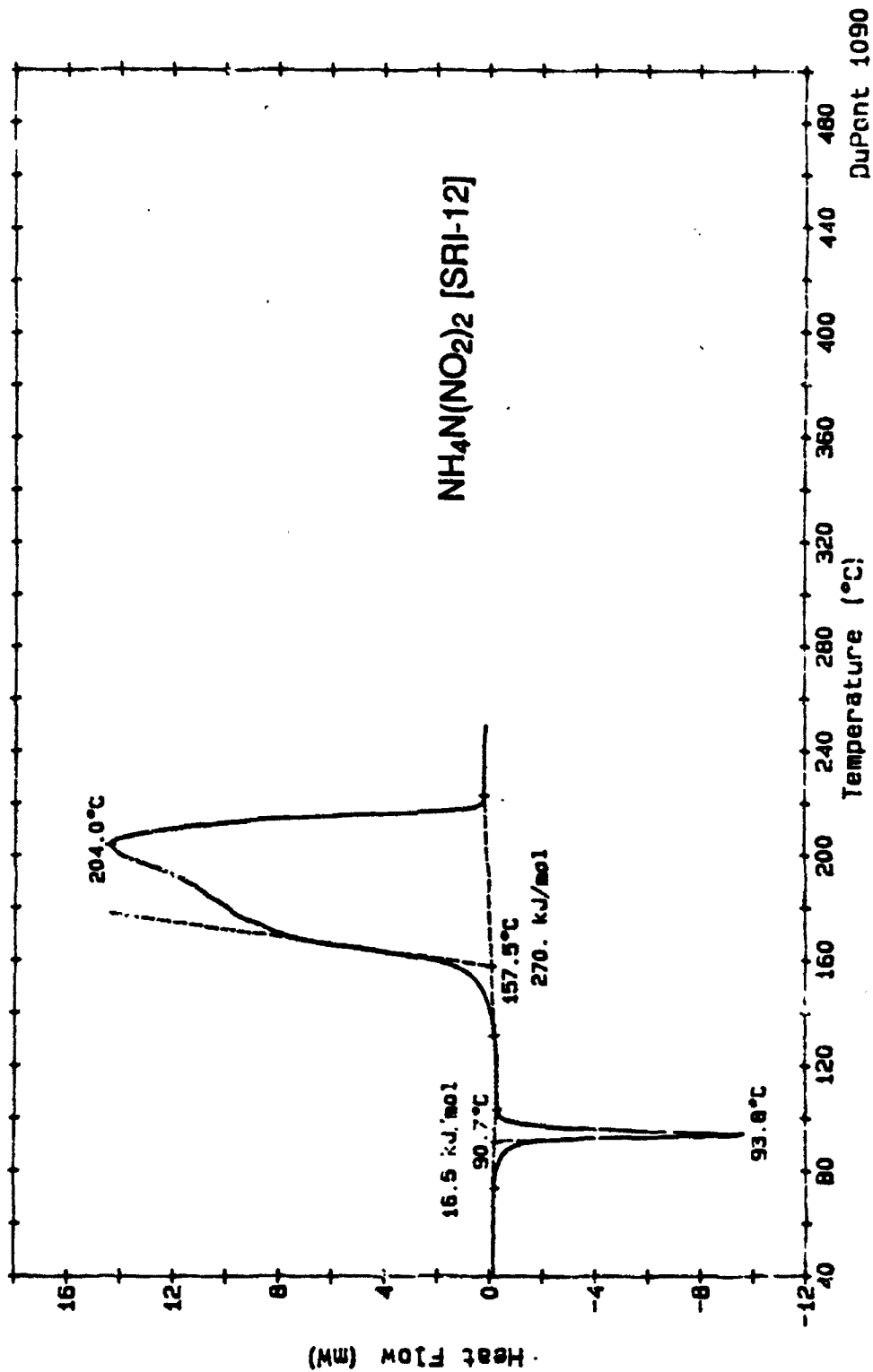
Figure 17.   DSC of ammonium dinitramide.
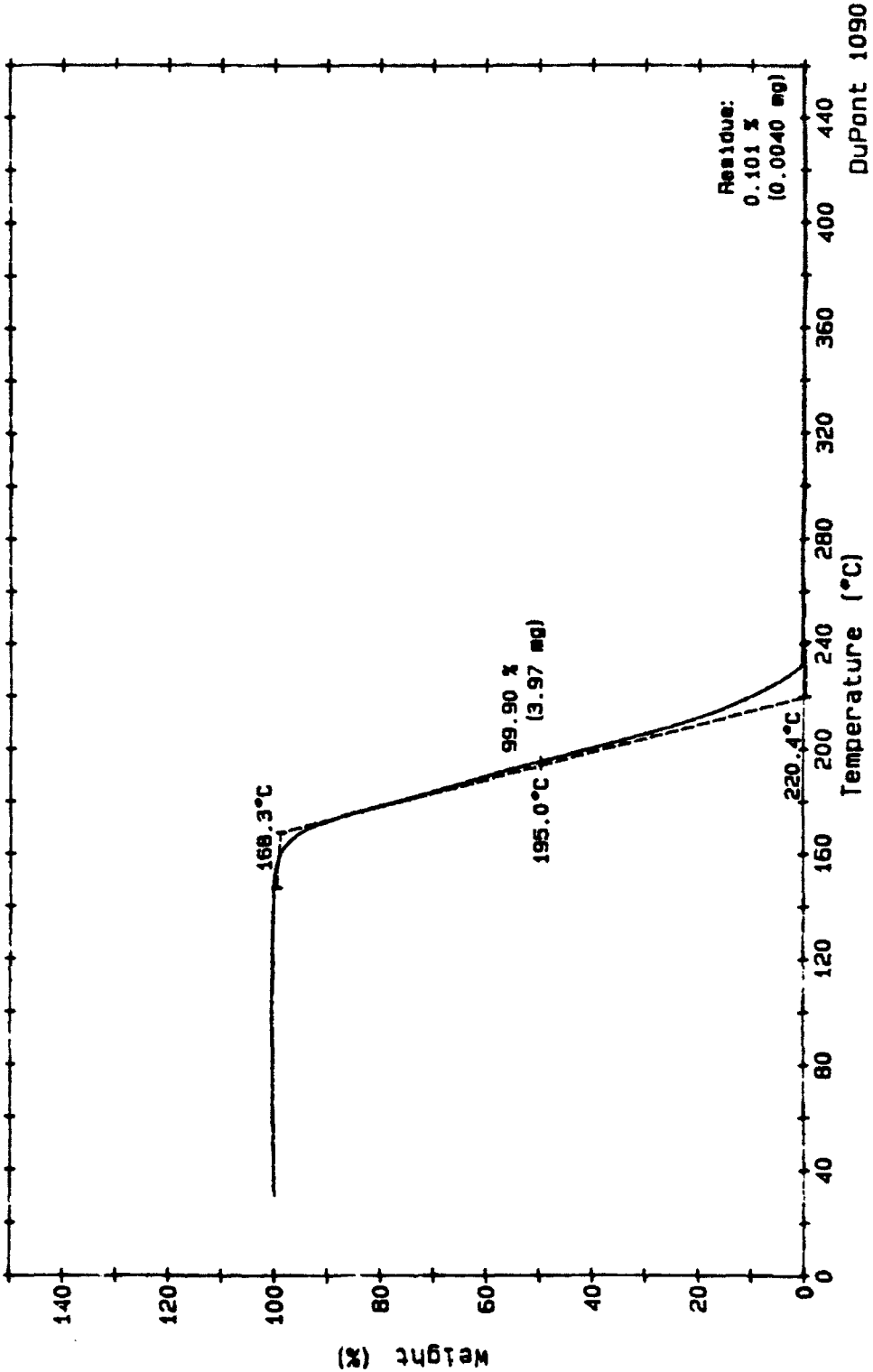
Figure 18.   TGA of ammonium dinitramide.

39
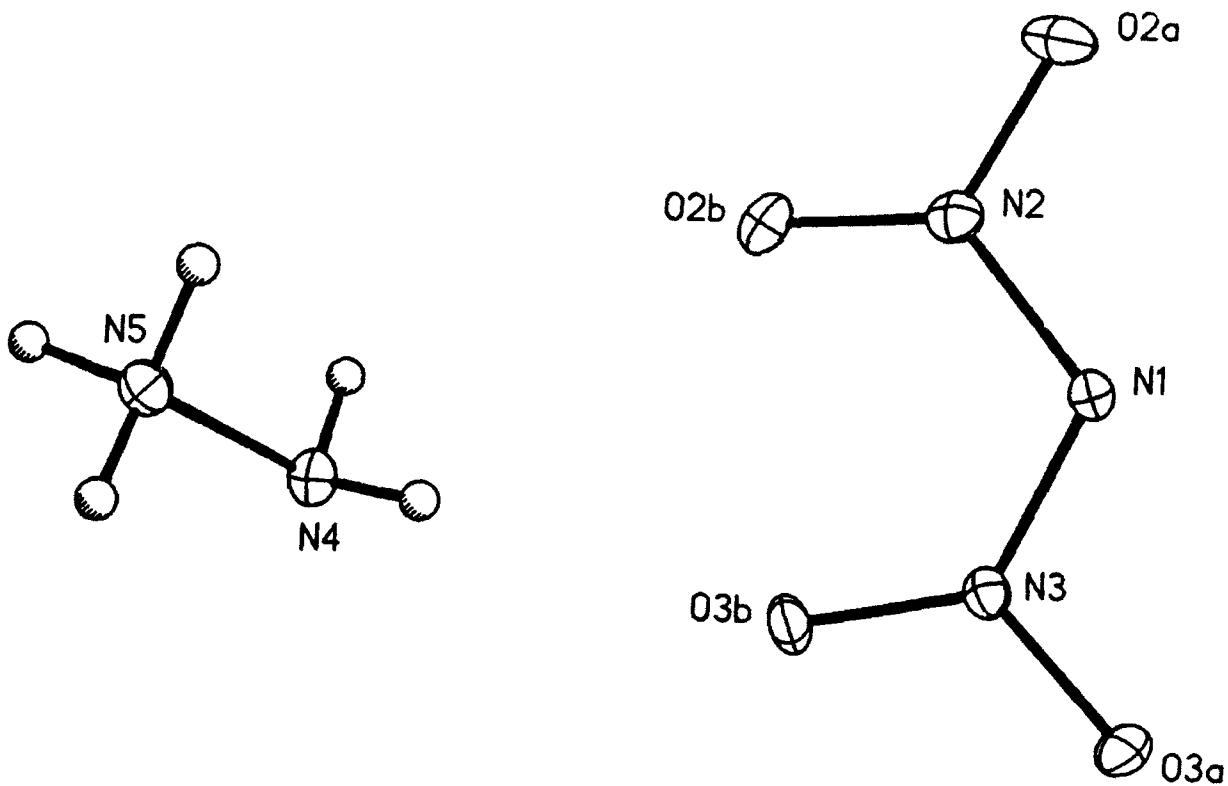
Figure 19.   Crystal structure of hydrazinium dinitramide (SRI-13).
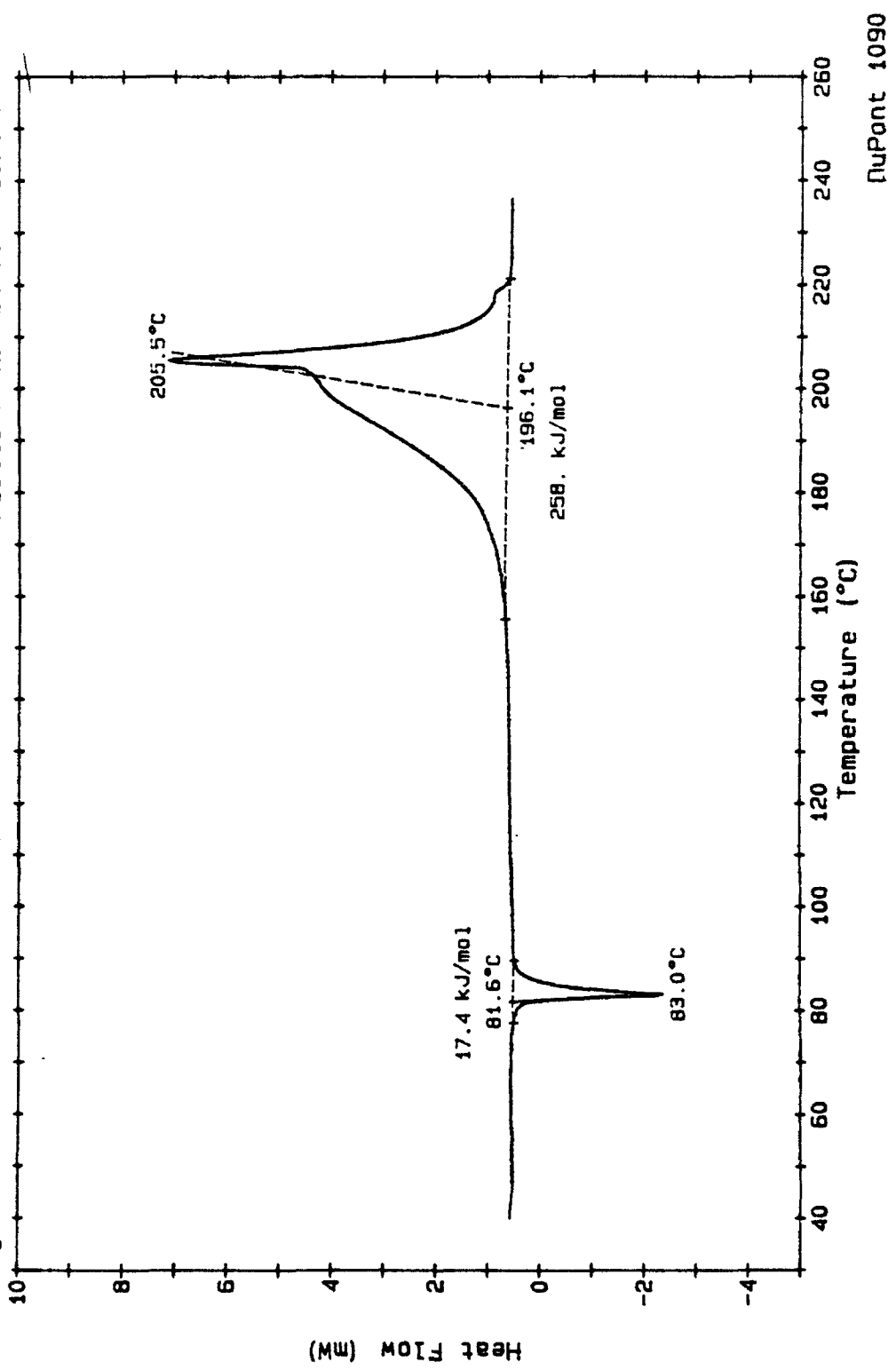
Figure 20.   DSC of hydrazinium dinitramide (SRI-13).

41
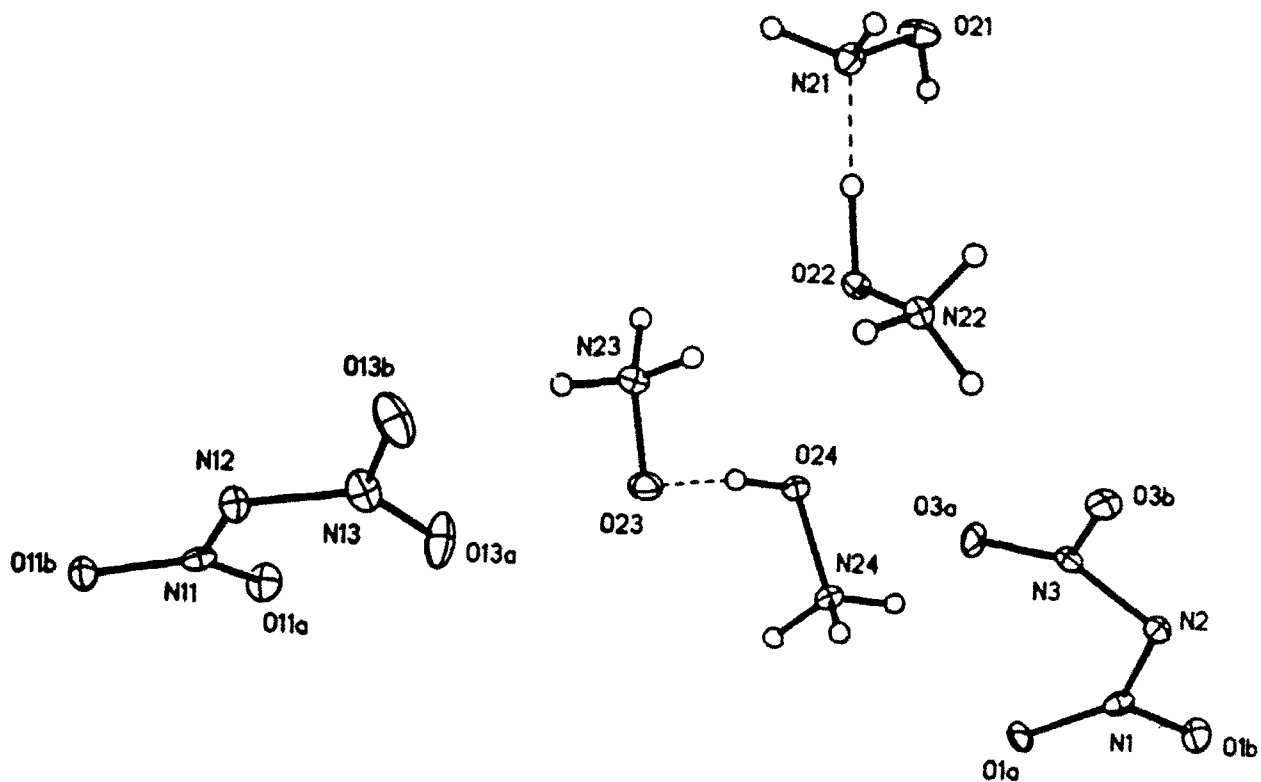
Figure 21.   Crystal structure of SRI-14.

Guanidinium Dinitramide (SRI-21)

Guanidinium dinitramide was prepared because we believed that it would have reduced shock and thermal sensitivity as compared to other insensitive materials, but initial measurement of its impact sensitivity indicates that this is not the case. The impact sensitivity is approximately equal to that of the ammonium derivative. These tests, along with a measurement of the heat of formation of the guanidinium derivative, were performed at Los Alamos National Laboratory (LANL) through the courtesy of Dr. Michael Coburn.

The heat of formation measured for this salt at LANL is -40.7 ± 1.5 kcal/mol. Thus, the guanidinium derivative has a fairly high heat of formation as compared to the perchlorate (-74.1 kcal/mol) or nitrate derivatives (-93 kcal/mol).

The x-ray crystal structure of guanidinium dinitramide is shown in Figure 22. In this crystal structure, two guanidinium dinitramide salt molecules are shown, with the proposed hydrogen bonding between the anions and cations being indicated by dashed lines. A high degree of hydrogen bonding is inherent in this salt. Figure 23 presents a more comprehensive view of the crystal lattice, showing just how extensive the hydrogen bonding is. One item of note in Figure 23 is the large holes or gaps that are observed in the crystal lattice. The presence of these gaps may explain why the density of the guanidinium derivative is so unexpectedly low, only 1.67 g/cm^3. This low density is probably the factor that most limits the usefulness of guanidinium dinitramide as a potential energetic material.

The thermal properties of guanidinium dinitramide are interesting. The DSC shown in Figure 24 indicates what appears to be a phase change at around 110°C, with the melting point onset near 140°C. This melting point is surprisingly high for a dinitramide salt and is only matched or exceeded in the cubane derivatives (see below). Further investigations need to be done to determine if a true phase change occurs or whether it is due to the presence of trace impurities in the crystals. The onset for decomposition is again near 150°C, as is seen in most other dinitramide salts and appears to be characteristic of dinitramide derivatives in general.

Cubane-1,4-bis(ammonium dinitramide) (SRI-17)

Cubane-1,4-bis(ammonium dinitramide) was the first of two cubane compounds prepared under this program and our SDI/ONR project, Contract No. N00014-88-C-0537. Its x-ray crystal structure is shown in Figure 25. One unique aspect of this crystal is the
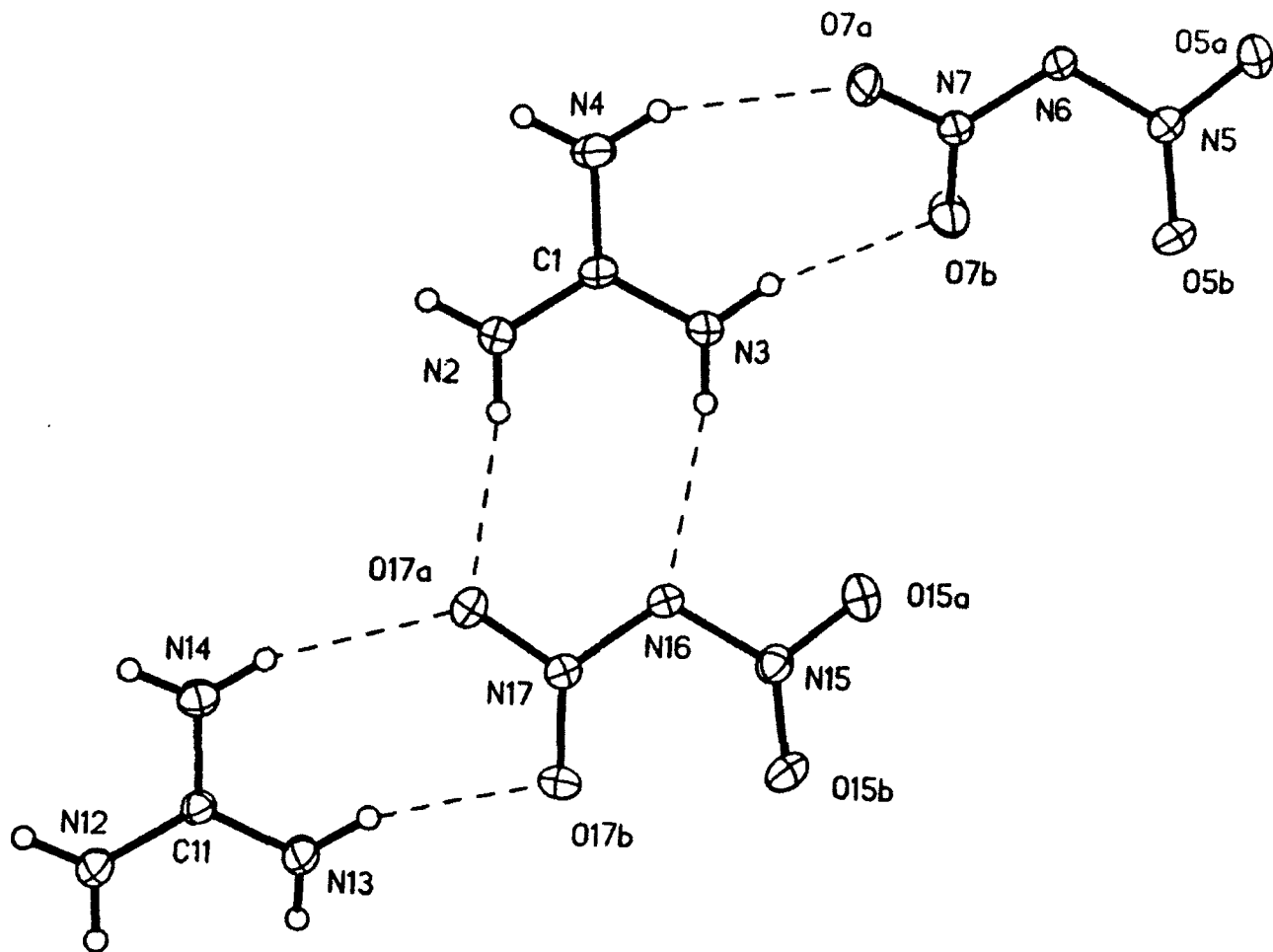
Figure 22. Crystal structure of guanidinium dinitramide (SRI-12) showing 2 molecules in view.
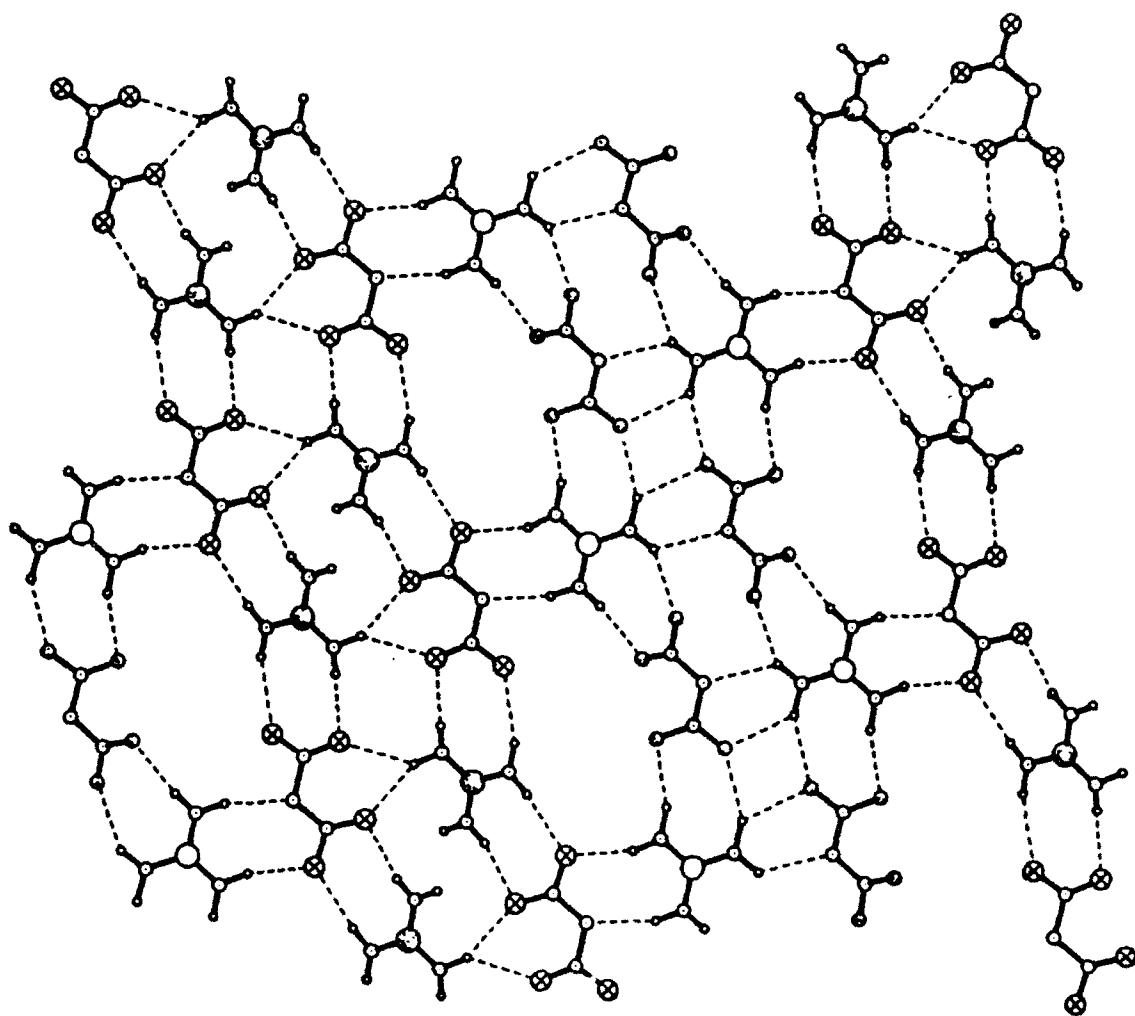
Figure 23.   View of crystal lattice of guanidinium dinitramide.

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Sample: SAI-21 GUAN DN Date: 18-Jul-90 Time: 14:21:14
Size: 0.49 MG File: BOTTARO.02 PROJECTS #4 PEP
Rate: 10 DEG/MIN Operator: PEP
Program: Interactive DSC V3.0 Plotted: 18-Jul-90 14:56:09

DSC

203.8°C

27.1 kJ/mol
144.9°C

173.1°C
193. kJ/mol

146.4°C

NH_2^+
C
H_2N NH_2
$N(NO_2)_2^-$

Heat Flow (mW)

Temperature (°C)

DuPont 1090
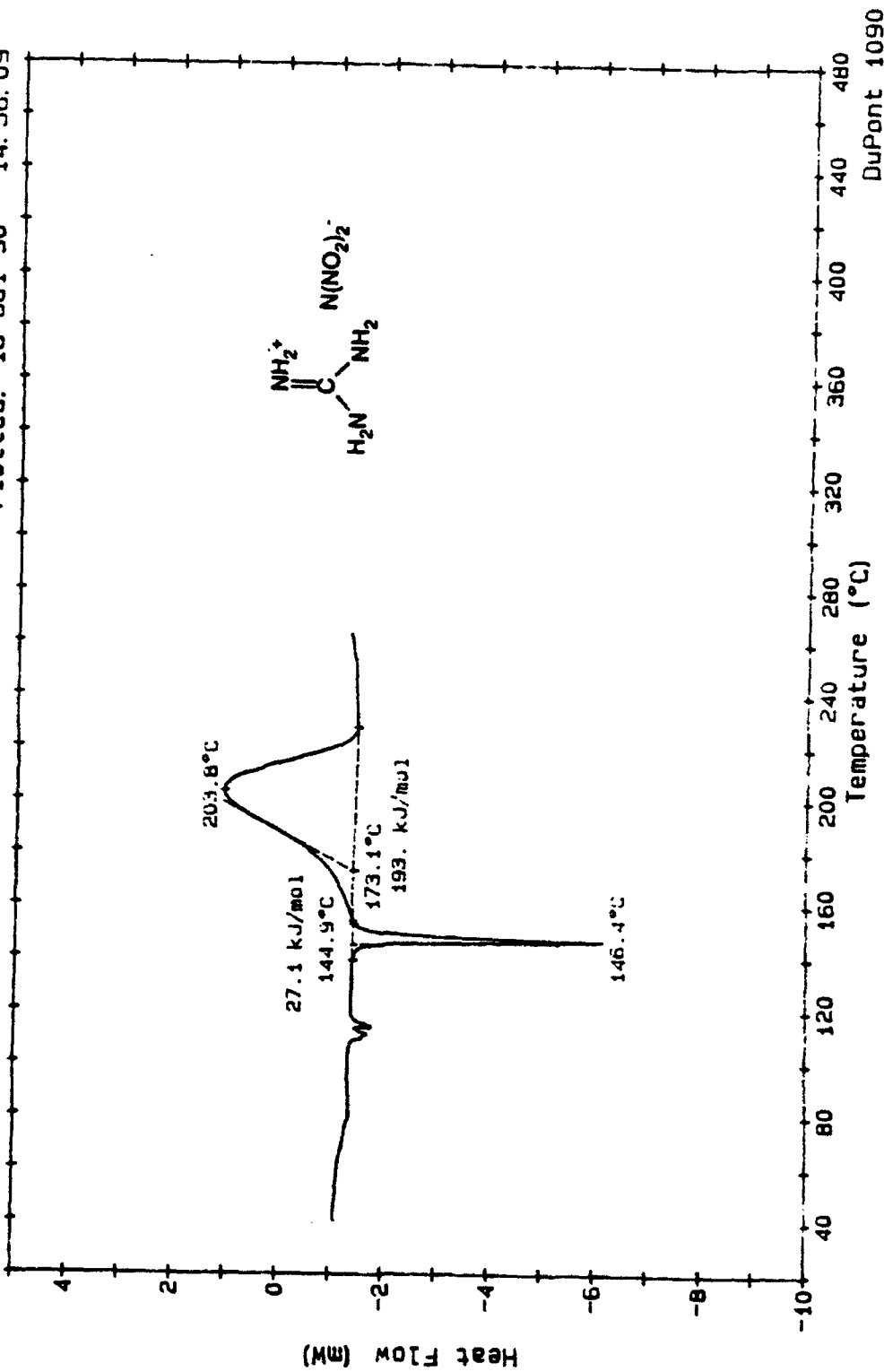
Figure 24. DSC of guanidinium dinitramide.

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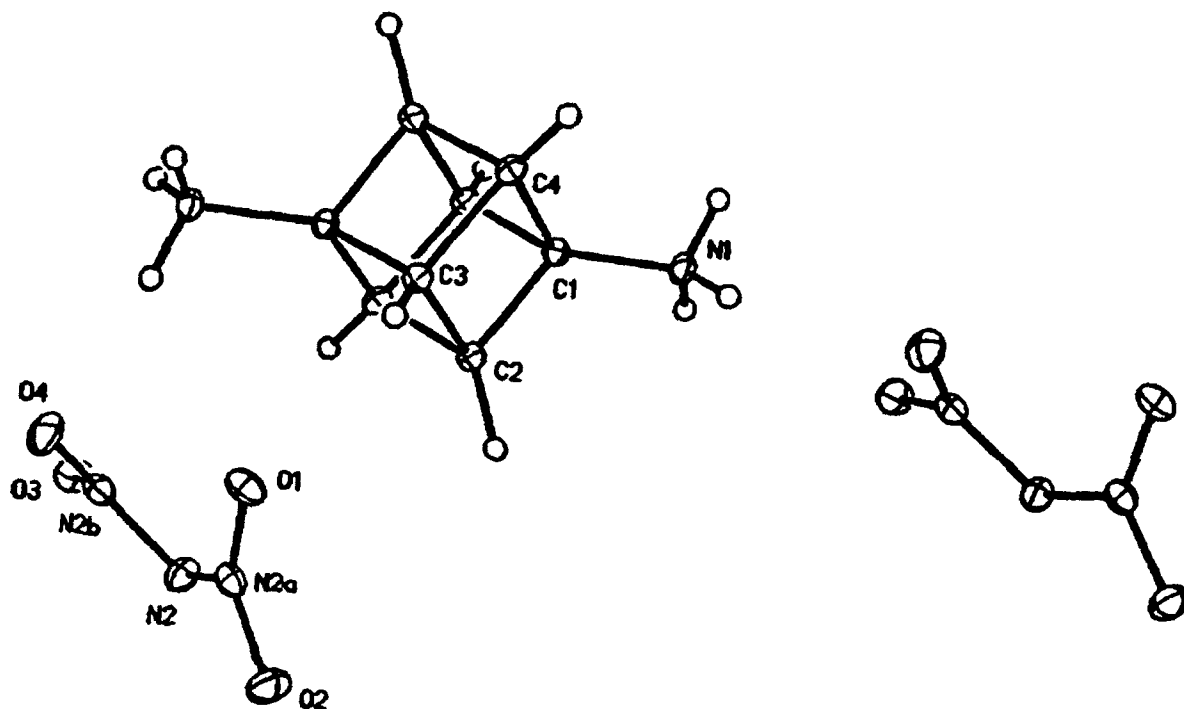
Figure 25.   Crystal structure of cubane-1,4-bis(ammonium dinitramide).

high degree of twist observed in the dinitramide anions, as can be seen in the crystal structure. This twist causes the two nitro groups in the dinitramide anions to be rotated out of plane with respect to each other to a high degree. Surprisingly, this twist in the dinitramide anions does not appear to create any special instability in the thermal properties of this compound. In the DSC (Figure 26), there is no melting point for this compound and the onset for decomposition is moved up to approximately 170°C. The combination of the absence of a melting point and this very high decomposition onset is unique among dinitramide salts.

Unfortunately, the observed density for this compound, 1.77 g/cm^3, is not high, nor is the compound particularly well oxidized. The presence of the cubane should give it a positive heat of formation (no heat of formation has been measured), but this is not enough to make it a desirable explosive derivative.

Cubane-1,2,4,7-tetrakis(ammonium dinitramide) (SRI-19)

Cubane-1,2,4,7-tetrakis(ammonium dinitramide) was the second of the two cubane compounds prepared under this program and our SDI/ONR project, Contract No. N00014-88-C-0537. The x-ray crystal structure is shown in Figure 27. The hydrogen bonding in this compound is of interest. The oxygens of one dinitramide anion interact with two ammonium ions on one face of the cubane. This hydrogen bonding pattern is repeated for all four dinitramide ions. A comprehensive view of the crystal lattice is shown in Figure 28. In this view of the crystal lattice, it is easy to see how each of the cubane-1,2,4,7-tetrakis(ammonium dinitramide)s interacts with its neighbor. Each successive cubane-1,2,4,7-tetrakis(ammonium dinitramide) appears to be just slightly offset to allow the dinitramide ions to slip between each other, thus allowing for good packing in the crystal lattice. The overall density of this compound is low, only 1.85 g/cm^3, and the compound is quite sensitive to shock, which limits its value. The overall heat of formation should be positive because of the presence of the cubane, but no heat of formation has been measured to date. The synthesis of cubane-1,2,4,7-tetrakis(ammonium dinitramide) is shown in the equation below.
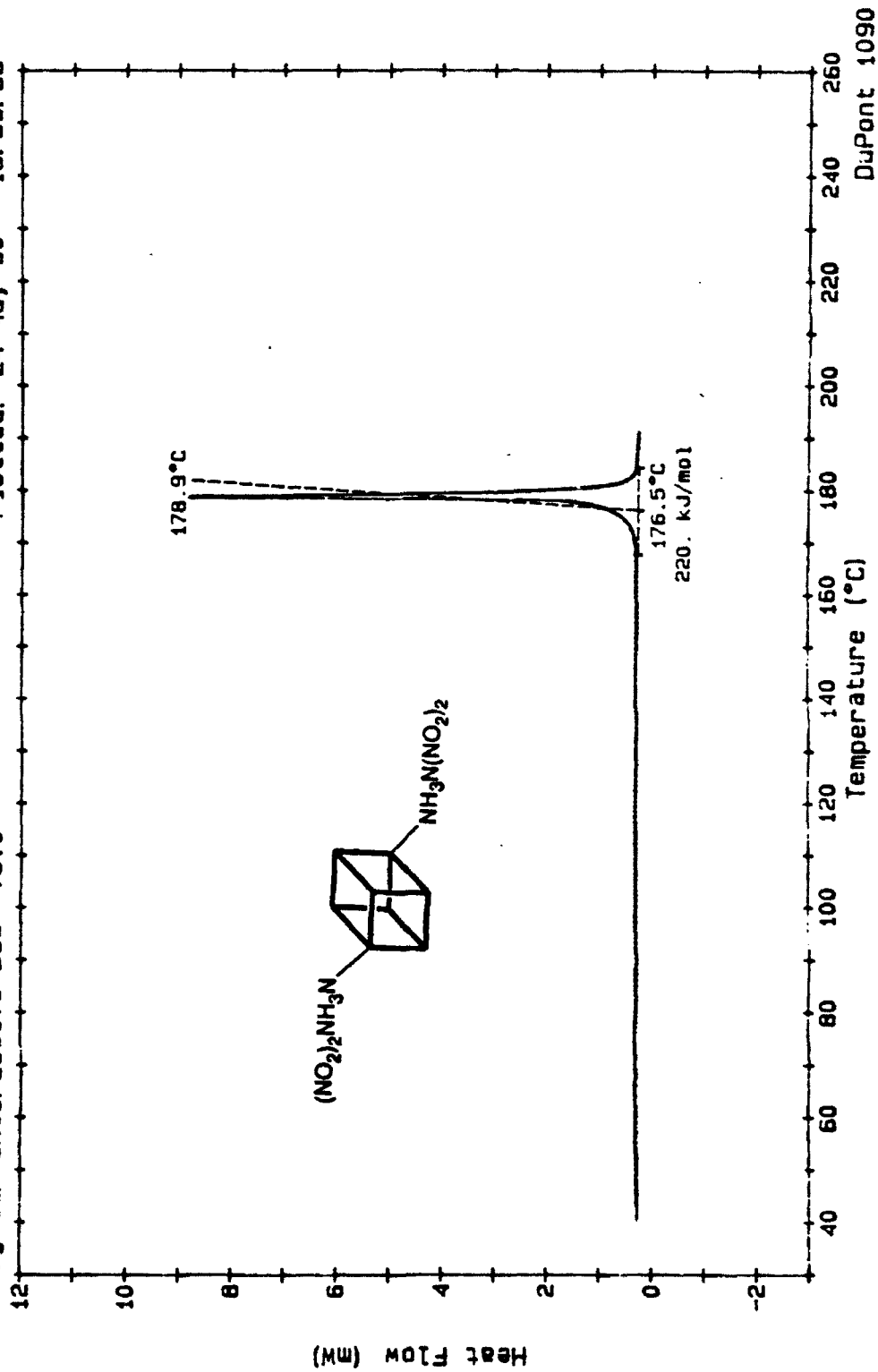
Figure 26.   DSC of cubane-1,4-bis(ammonium dinitramide).

49
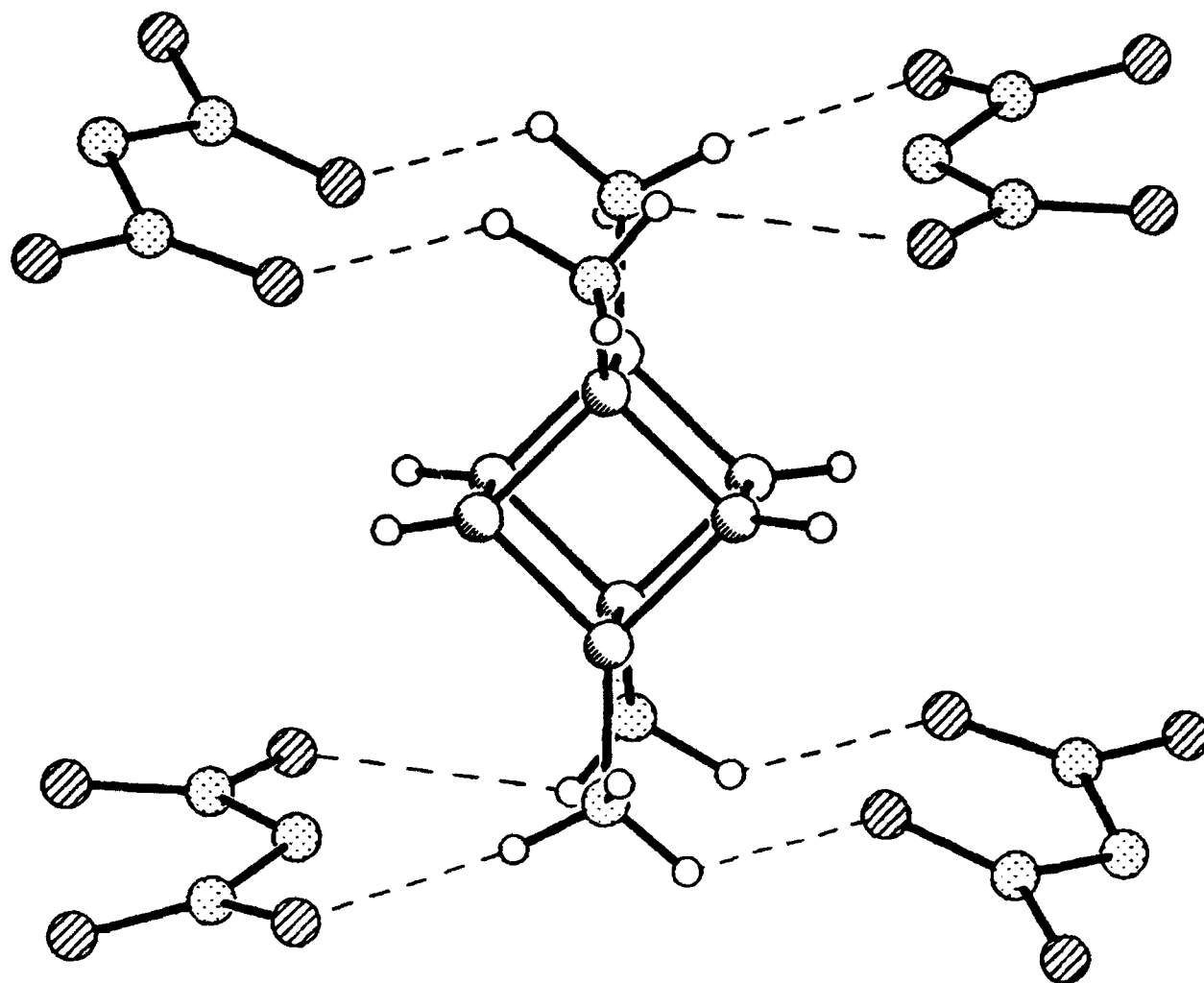
Figure 27. Crystal structure of cubane-1,2,4,7-tetrakis(ammonium dinitramide).
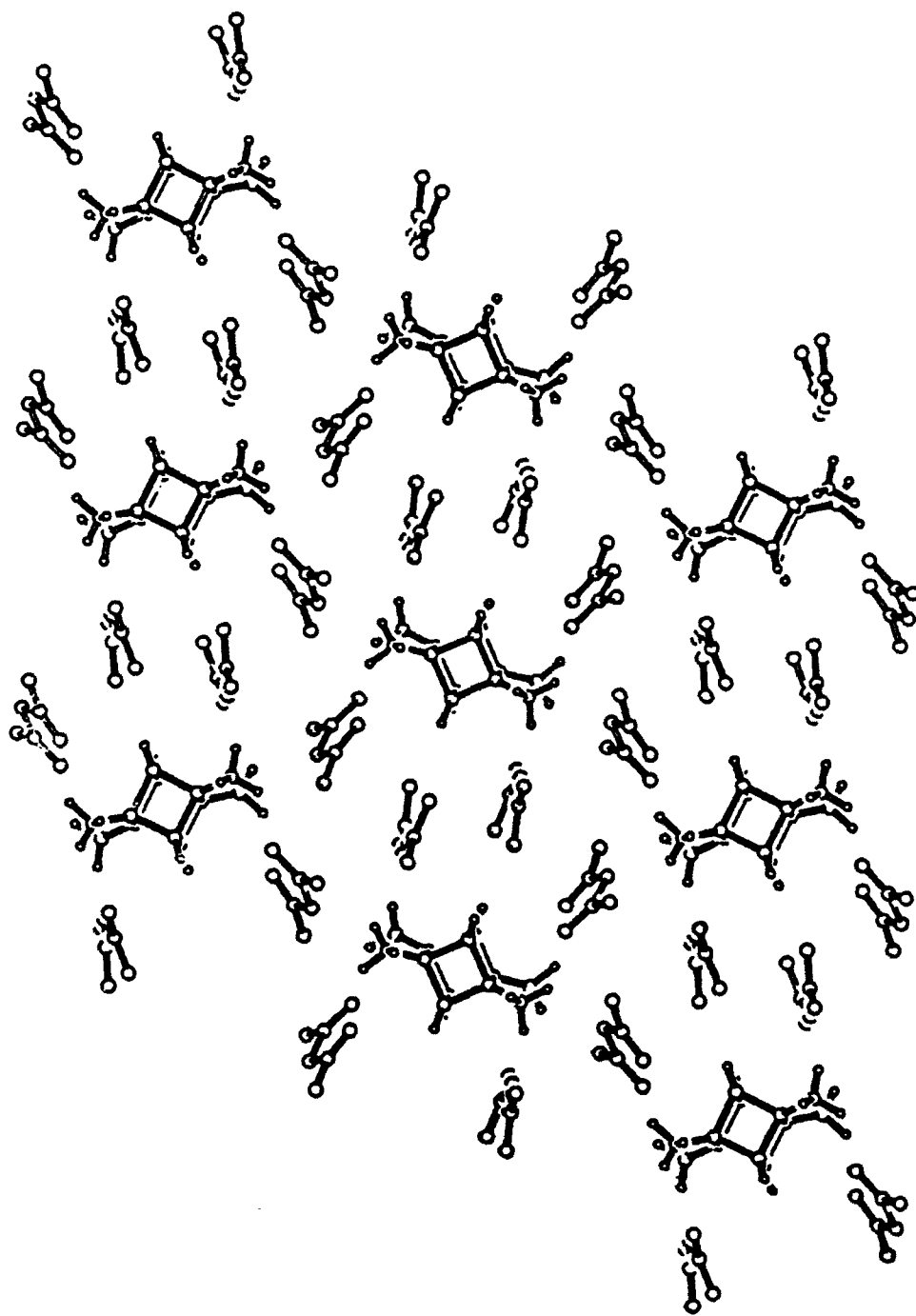
Figure 28.   View of crystal lattice of cubane-1,2,4,7-tetrakis(ammonium dinitramide).
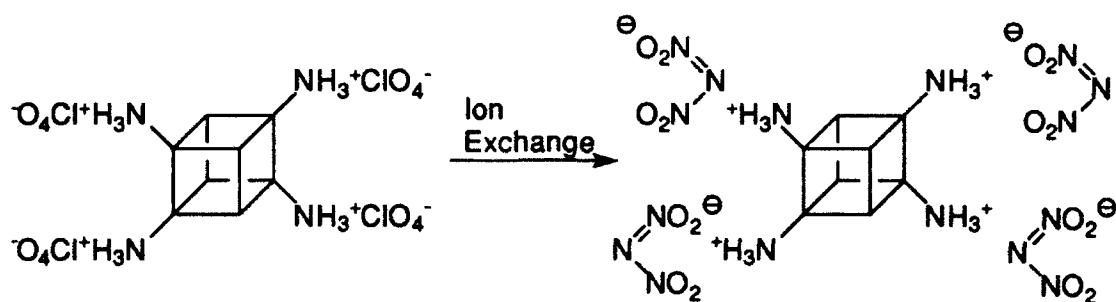
The thermal properties of cubane-1,2,4,7-tetrakis(ammonium dinitramide) are again unusual, as seen in Figure 29. The compound shows no melting point, but the onset for thermal decomposition is now around 135°C and thus appears to be dominated by the presence of the dinitramide ions in the crystal lattice.

Acid and Base Stability of Dinitramide Salts

Under this program, we have been able to make several preliminary observations on the acid/base stability of dinitramide salts. We have not performed extensive studies of the acid/base properties of dinitramides, but we report here our preliminary observations on their stability. The proposed mechanisms are speculative, based on the products observed.

In general, we have found dinitramides to be stable to concentrated base. For example, cesium dinitramide is stable to decomposition in 12 M NH_4OH at room temperature. We have not had time to investigate its stability at higher temperatures or with other bases.

The situation in acids, however, is considerably different. We have observed that even traces of acid will catalyze the decomposition of dinitramide salts over time. The primary decomposition products are nitrate and presumably N_2O (not determined spectroscopically, but rather inferred from the likely decomposition pathways shown in Scheme 19 below). The rate of acid catalyzed decomposition increases directly with acidity. In sulfuric acid, decomposition is quite rapid in 18 M (concentrated) H_2SO_4 and slower at lower acid concentrations. Spectral changes are observed in the UV/vis spectrum between 10 M and 12 M H_2SO_4. Between 10 M and 12 M H_2SO_4, the dinitramide absorption at 284 nm is significantly reduced. We interpret this finding as indicating that a protonation of the dinitramide ion is occurring over this acid range, giving $HN(NO_2)_2$. At lower concentrations, the compound exists as the separated ion pair $M^+/N(NO_2)_2^-$ in
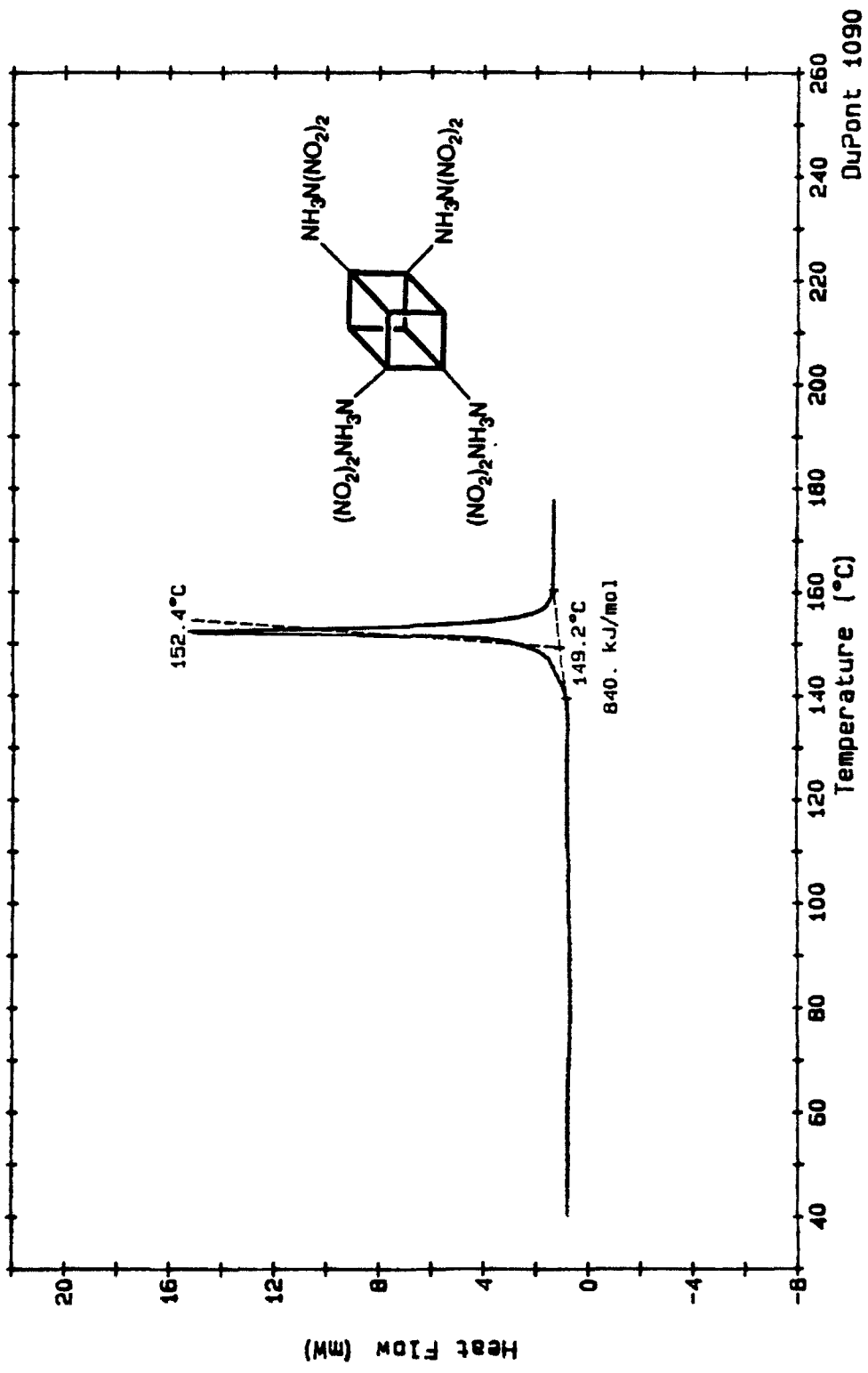
Figure 29.   DSC of cubane-1,2,4,7-tetrakis(ammonium dinitramide).

solution. Dilution of these concentrated acid solutions returns the UV/vis spectrum to its original form, by converting the acid form to the separated ion pair (when we allow for the dilution effects and some decomposition of the dinitramide caused by the acid). Table 6 lists our preliminary measurements on the rate of decomposition of dinitramide ions in sulfuric acid over the range 11 to 13 M.

Table 6

PRELIMINARY MEASUREMENTS OF THE DECOMPOSITION OF $CsN(NO_2)_2$ IN H_2SO_4 AT ROOM TEMPERATURE

Sulfuric Acid Concentration (Molarity)	$k(min^{-1})$	$t_{1/2}$ (min)
11.0	0.00742	93
12.0	0.0252	28
13.0	0.335	2.1

As one would expect for an acid catalyzed reaction, the rate of decomposition increases with the acidity. The plots of the decomposition of dinitramide show a first-order decomposition. The rate of decomposition increases with increasing acid concentration.

In our proposed mechanism, the decomposition of dinitramide occurs upon the second protonation of the anion, as shown in the mechanisms in Scheme 19. Protonation can occur at either the oxygens or the central nitrogen. Protonation on the oxygen should follow the mechanism below with initial elimination of nitrous oxide, nitronium ion, and water. This mechanism is consistent with the observed products of decomposition. We cannot distinguish the first route from the second proposed decomposition pathway, where the protonation occurs at the central nitrogen. We favor the first route (with protonation at oxygen), since the electron densities on the nitro groups would tend to indicate that this route would be favored. The decomposition products in either case should be the same, and further studies are required to distinguish these routes.

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$$N_2O + NO_2^+ + H_2O$$

$$N_2O + HNO_3 + H^+$$

$$+ H^+ \longrightarrow \qquad \longrightarrow N_2O + NO_2^+ + H_2O$$

$$N_2O + HNO_3 + H^+$$
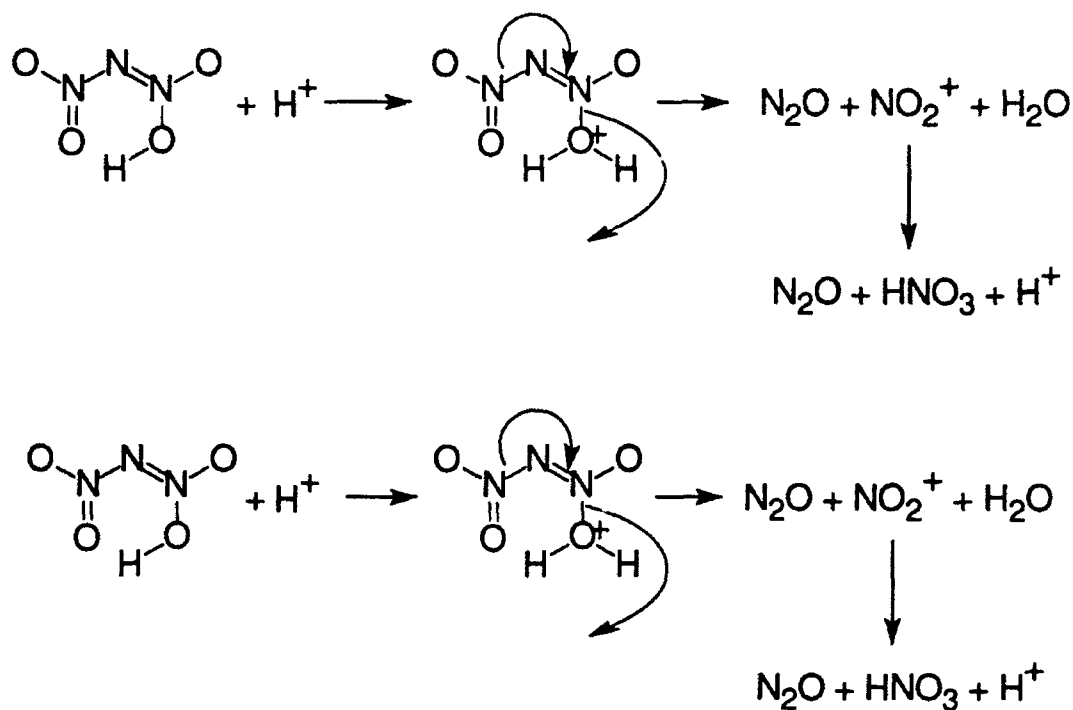
Scheme 19: Proposed routes for the acid catalyzed decomposition of dinitramide ion

The mechanisms proposed above do not explain the production of a small quantity of nitrite ion as an observed decomposition product of dinitramide. To date, there is no good mechanistic explanation for nitrite production. We speculate that nitrite is formed by a nitro-nitrite rearrangement that then cleaves to give NO^+, which then reacts with water to give nitrous acid (a source of nitrite ion) and a proton.

Preliminary measurements show that the rate of decomposition of the dinitramide ion in nitric acid is dependent on the purity of the nitric acid (the absence of NO_x species). Cesium dinitramide in a solution of 70% nitric acid without purification has a $t_{1/2} = 3$ hours, but the $t_{1/2}$ increases to 14 hours when a small amount of urea[10] is added to the nitric acid solution. Thus, the rate of decomposition of dinitramide in nitric acid is significantly slowed by removal of NO^+ or NO_x species from nitric acid solutions, which indicates that the primary decomposition route in nitric acid is via a one-electron oxidation route rather than an acid catalyzed decomposition. The results of this preliminary study are summarized in Table 7 below.

Table 7

PRELIMINARY MEASUREMENTS OF THE DECOMPOSITION OF $CsN(NO_2)_2$ IN HNO_3 AT ROOM TEMPERATURE

Nitric Acid Concentration (%)	$k(h^{-1})$	$t_{1/2}$ (h)
70	0.228	3.04
70*	0.048	14.4
90	1.81	0.38

*Urea added to eliminate NO_x.

As can be seen from these measurements, the rate of reaction is significantly reduced when urea is added to decompose the lower oxides of nitrogen. The lifetime of dinitramide under these conditions is about 4.8 times as long as in the samples where the lower oxides were still present. The results with 90% nitric acid show the dramatic enhancement of the rate of decomposition of dinitramides as the acid concentration is increased.

GAS PHASE PROPERTIES OF THE DINITRAMIDE ION

As an aspect of this study, we undertook a study to measure the fundamental properties of the dinitramide ion. These studies were done using a tandem flowing afterglow-selected ion flow tube located at the University of Colorado, Boulder.[11] The full paper that was published on these studies is attached as Appendix E.

Figure 30 gives a overview of the tandem flowing afterglow-selected ion flow tube used in these experiments. On the upstream end of the instrument, ions are created in the ionizer region. These ions are then mass selected to obtain the specific ion of interest in the selected ion flow tube (SIFT) quadrupole mass filter. The mass selected ions are then injected into the flow tube at the SIFT injection orifice and allowed to react with neutral species to give the mass selected ion-molecule reaction. The products of this reaction are then analyzed in the detection quadrupole mass filter and ion counted by the electron multiplier. This system was used to bracket the acidity and electron affinity of dinitraminic acid and dinitramide ion, respectively. We were also able to investigate the gas-phase ion-molecule chemistry of both the dinitramide ion and dinitraminic acid. These studies are only preliminary because the error bars on both the acidity and electron affinity need to be

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Source Flow Tube Ionic species generated by electron impact

Selection Region Single ionic species selected by quadrupole mass filter
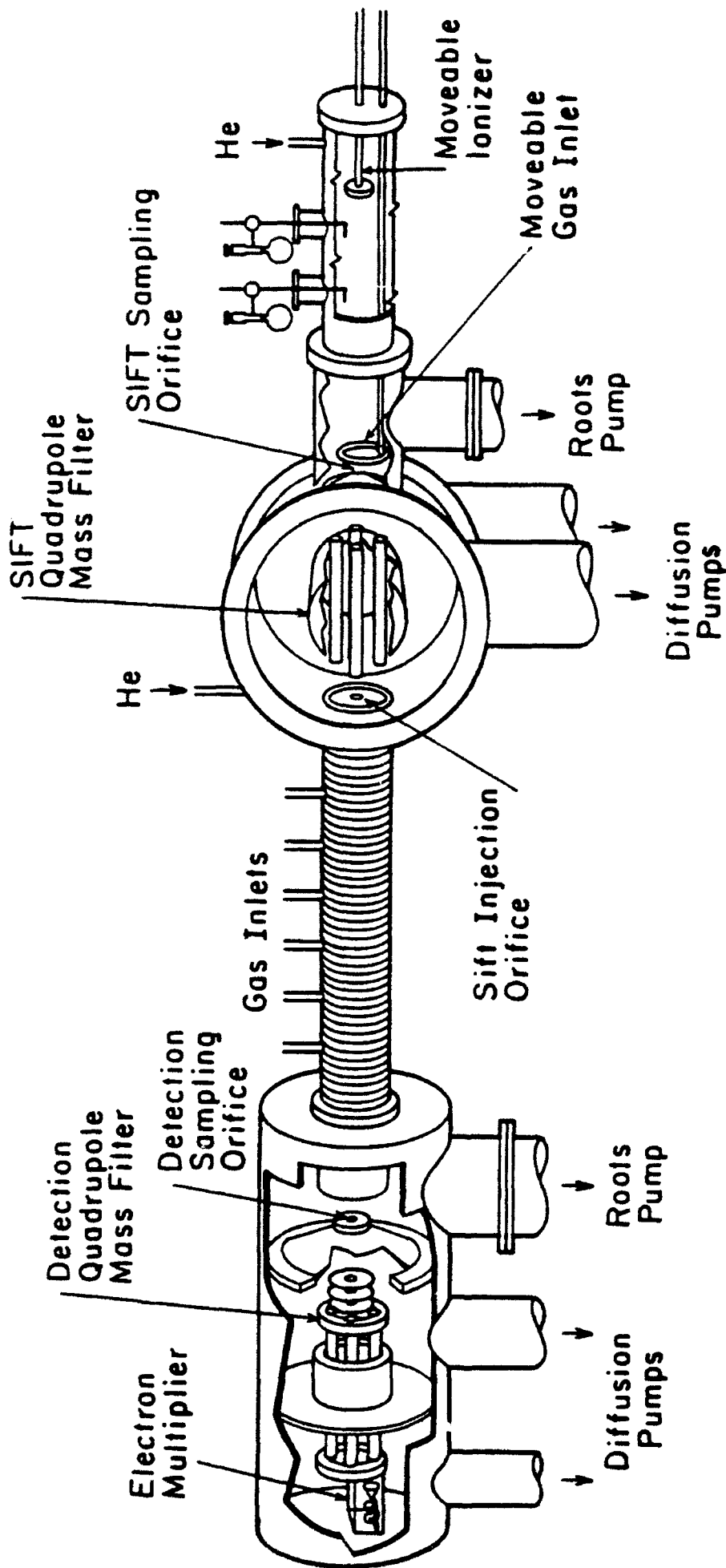
Reaction Flow Tube Chemical reactions of the selected ionic species

Detection Region Ionic products detected by quadrupole mass filter

Figure 30. Tandem flowing after glow-selected Ion flow tube.

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minimized and further investigations of the gas phase ion-molecule chemistry should be undertaken.

Acidity of $HN(NO_2)_2$

The gas phase acidity of dinitraminic acid is the enthalpy of heterolytic bond dissociation:

$$HN_3O_4 \longrightarrow H^+ + N(NO_2)_2^- \quad \Delta H^0_{acid}(HN_3O_4)$$

Scheme 20: Enthalpy of heterolytic bond dissociation

This value can be measured by comparing the proton-transfer ability of dinitraminic acid and of dinitramide anion with species [HB] of known gas-phase acidity (Scheme 21).[12]

$$B^- + HN_3O_4 \rightleftharpoons HB + N(NO_2)_2^-$$

Scheme 21: Proton transfer equilibrium

Thus the occurrence of proton abstraction in the reaction of $N(NO_2)_2^- + HB$ would indicate that HB is more acidic than HN_3O_4, whereas proton abstraction in the reverse reaction would indicate that HN_3O_4 is more acidic than HB. The absence of proton transfer suggests that the reaction of interest is endoergic, although kinetic barriers can sometimes diminish reactivity.

The dinitramide anion does not react with the following molecules, which are listed in order of increasing acid strength (ΔH^0_{acid} in kcal/mol) [13]: H_2O (390.8), $CH_3C(O)CH_3$ (369.0), HCl (333.4), and HBr (323.6). With HI (314.3), the cluster ion $[N(NO_2)_2^- \cdot HI]$ is formed and only a minute trace of I^- is detected. These studies suggest that the dinitramide anion is extremely stable and dinitraminic acid is highly acidic in the gas phase. Therefore, bases on the extreme end of the known acidity scale were allowed to interact with dinitraminic acid (ΔH^0_{acid} of the conjugate acids listed in parentheses): NO_3^- (324.6), I^- (314.3) and HSO_4^- (309.5). [4] These anions initiate facile proton abstraction indicating that $\Delta H^0_{acid}(HN_3O_4) \leq 310$ kcal/mol. In an attempt to further characterize the acidity, we

examined the reaction of dinitraminic acid with $NO_3^- \cdot HNO_3$. The ΔH^0_{acid} for this cluster ion is 308 kcal/mol to generate the dimer $HNO_3 \cdot HNO_3$ and 299 kcal/mol to generate $2HNO_3$. Reaction occurs by ligand switching (Scheme 22):

$$NO_3^- \cdot HNO_3 + HN_3O_4 \longrightarrow NO_3^- \cdot HN(NO_2)_2 + HNO_3$$

Scheme 22: Ligand exchange

A small amount of $N(NO_2)_2^-$ is also observed, but this ion appears to be generated by the NO_3^- that is initially present and that is formed by collision-induced dissociation of the injected $NO_3^- \cdot HNO_3$ cluster. The apparent lack of proton abstraction by $NO_3^- \cdot HNO_3$ suggests that ΔH^0_{acid} $(HN_3O_4) > 299$ kcal/mol, but further experiments are required to confirm this result. In any event, dinitraminic acid is among the most acidic of known gas phase acids.

Dinitramide is extremely unreactive in the gas phase and is a very poor nucleophile. The reaction of dinitramide with $(CH_3)_3SiCl$ gives only a trace of cluster, and no nucleophilic displacement is observed.[15,16] Dinitramide does not react with O_2, CO_2, CS_2, or SO_2 and yields only a trace of cluster ion product in reaction with BrCN.

Similarly, dinitramide does not undergo electron transfer with several species with moderately high electron affinities (EA):[17] NO_2 (EA = 2.27 eV), Cl_2 (EA = 2.38 eV), and Br_2 (EA = 2.55 eV). The reaction of dinitramide with Cl_2 does yield a trace of Cl^- and $O_2N=N-Cl^-$. Since electron transfer is usually facile when exoergic, these results suggest that EA $[N(NO_2)_2] > 2.55$ eV.

Possible Sites of Protonation on Dinitraminic Acid

There are three likely locations of the proton in dinitraminic acid: on the central nitrogen **5** or on one of the oxygens, where it can either be in an endo position and form a hydrogen bond with the oxygen from the other nitro group **6**, or be in either of the two exo positions **7** and **8**. There exists another possibility where the proton is hydrogen bound to the lone pair of the central nitrogen (an endo form of structure **8**), but we consider this unlikely because of the strain associated with the required four-member ring.

5

6

7

8
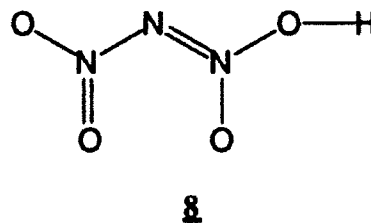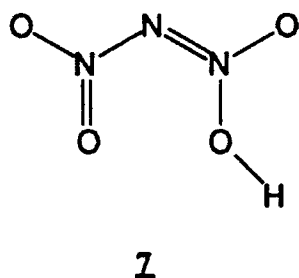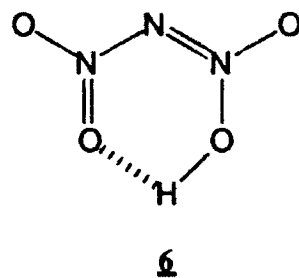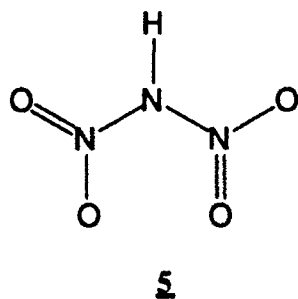
The reaction of dinitraminic acid with SO_3^- suggests the presence of form **6**. This reaction generates two products, HSO_4^- by OH abstraction and $N(NO_2)_2^-$ by proton abstraction (Scheme 23). HSO_4^- probably results from a direct hydroxyl abstraction from structure **6** rather than by a two-step process with sequential oxygen atom and hydrogen atom abstraction from structure **5**.

$$HN(NO_2)_2 + SO_3^- \longrightarrow \begin{cases} HSO_4^- + N_3O_3 \\ N(NO_2)_2^- + HSO_3 \end{cases}$$
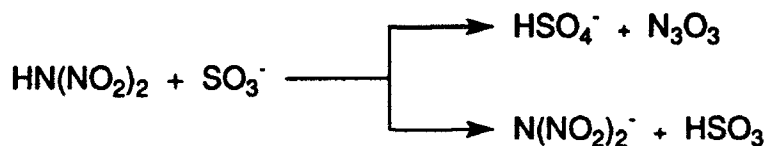
Scheme 23: Reaction of dinitraminic acid with SO_3^-

Collision-Induced Dissociation of the Dinitraminic Acid

For the studies of the acidity and reactivity of dinitramide, the anion is injected into the reaction flow tube at low energies to avoid dissociation or excitation of this species. However, the potential difference between the ion source and the venturi inlet can be increased so that the injected ions undergo higher energy collisions with helium and thus suffer some collision-induced dissociation (CID). CID of $N(NO_2)_2^-$ produces $N_2O_2^-$ at m/z 60 as the major product as well as a trace of NO_2^- at m/z 46 (Scheme 22).

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$$\text{N(NO}_2\text{)}_2^- \xrightarrow{\text{CID}} \begin{cases} [\text{N}_2\text{O}_2]^- + \text{NO}_2 \quad \text{major} \\ \\ \text{NO}_2^- + \text{N}_2\text{O}_2 \quad \text{trace} \end{cases}$$
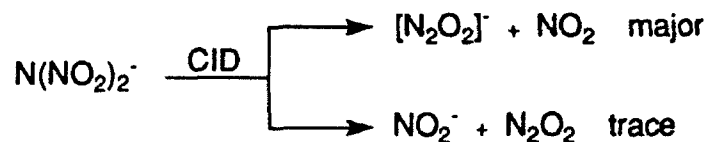
Scheme 24: Collision induced dissociation of the dinitramide ion

We believe that the likely product structures are those shown below. The most likely product is the first one, where an NO_2 group has been ripped from the molecule. This is consistent with the original structure of the dinitramide ion and with the proposed resonance stabilization (see above) where a double bond is initially present when the negative charge is stabilized out on one of the nitro groups, leaving a noncharged nitro group present in the anion. The simple rupture of the $N\text{-}NO_2$ single bond would give the first proposed product shown below.

$$O_2N\!=\!N^- \quad \text{or} \quad \underset{N=N-O^-}{\overset{O}{\diagdown}}$$
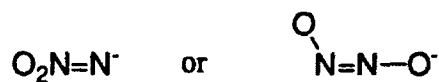
EXPERIMENTAL PROCEDURES

Cubane-1,4-bis(N-ethyl, N-t-butylamide). Cubane-1,4-dicarboxylic acid (30.00 g, 0.156 mol) was added to 500 mL dry chlorobenzene in a 1-L flask equipped with mechanical stirrer and argon purge. Phosphorus pentachloride (97.53 g, 0.468 mol, 50% excess) was added to the diacid in two portions. The reaction stirred for 2 h at ambient temperature, and then excess pentachloride was destroyed by stirring with acetic anhydride (14.7 mL, 0.156 mol) for 15 min. The solution was concentrated to dryness at 50°C using aspirator pressure at first and then higher vacuum. To remove residual acetic anhydride, a cycle of dissolving the cubane-1,4-bis(acid chloride) in dry, ethanol free chloroform was followed by concentrating to dryness at 50° C at reduced pressure. This step was repeated two or three times until no anhydride was present. Finally, the pale yellow crystals were dried under high vacuum for approximately 2 h at 50°C. The cubane-1,4-bis(acid chloride) was dissolved in 500 mL dry chloroform and transferred to a 1-L flask with mechanical stirrer, argon purge, 50-mL addition funnel, and cold water bath (5-10°C). Triethylamine (31.59 g, 0.312 mol) was added slowly over 5 min and then N-ethyl-N-t-butylamine (31.59 g., 0.312 mol) was added dropwise over 20 min while maintaining the cold water bath. After the addition, the reaction was stirred for 2 h at ambient temperature and washed with 3 X 100 mL 5% HCl, 2 X 100 mL 5% KOH, and 1 X 100 mL sat. NaCl. The yellow chloroform layer was treated with activated carbon, dried over $MgSO_4$, and filtered over Celite to give a less colored solution which was concentrated to dryness, leaving a pale yellow solid. This solid was slurried in 400 mL dry ethyl acetate at 40°-50°C, cooled in ice, filtered, washed with cold ethyl acetate, and dried under high vacuum to yield 41.02 g (73%) of the title compound as pure white crystals. NMR (^{1}H, $CDCl_3$, TMS standard) δ 1.3 (triplet, 3 H, J = 7 Hz, CH_3), δ 1.4 (s, 9H, t-butyl), δ 3.8 (quartet, 2H, J = 7 Hz, CH_2), δ 4.55 (S, 6H); IR (KBr) 2970, 1610, 1390, 1205 cm^{-1}; mp = 185-88°C.

Cubane-1,4-dicarboxylic acid-2,7-bis(N-ethyl-N-t-butylamide). 2,2,6,6-Tetramethylpiperidine (107.37 g, 0.760 mol, 10 eq) and tetramethylethylenediamine (12.6 mL, 1.1 eq) were added to 600 mL dry tetrahydrofuran (THF) (distilled over CaH) in a 2-L flask with mechanical stirrer, 500-mL addition funnel, cooling bath, and argon purge. The reaction was cooled in dry ice/acetone, and 2.5 M n-butyllithium in hexane (304 mL, 0.760 mol, 10 eq) was added dropwise with stirring over 2 h at -78°C and then the mixture was stirred a 0°C for 1 h. The reaction mixture was

again cooled in the dry ice acetone bath. Magnesium bromide etherate (98.14 g, 0.380 mol, 5 eq) and the cubanediamide (27.25 g, 0.076 mol, 1 eq) were added all at once to the reaction, which was then placed in the bath and stirred for 8 h. To effect the carboxylation, the reaction was cooled in dry ice acetone and Coleman grade CO_2 (< 10 ppm H_2O) was introduced via a fritted glass tube connected with a swagelock type fitting to a copper supply tube from the gas tank. Before introduction of the gas, the copper and glass tubes were purged with CO_2 while heating with a hot air gun to remove moisture. The CO_2 was bubbled through the stirring reaction for 12 h at dry ice acetone temperature to yield a light tan suspension that was concentrated to dryness on the rotovap first using aspirator pressure then higher vacuum for about 2 h. The light tan solid was vigorously stirred with 1500 mL H_2O for 1 h and the resulting suspension transferred to a 2-L flask and then cooled to 0°C. Ice-cold 19% HCl was added slowly with stirring to bring the pH to 1 (about 250 ml, there was some foaming). The suspension was filtered to give a light brown paste,which was dissolved in 600 mL boiling dichloromethane, cooled in the freezer overnight, filtered, and washed with cold dichloromethane to give 20.0 g of colorless plates. The mother liquor was concentrated to one-third volume and cooled to give a second crop of 5.5 g, for a total yield of 25.5 g (75%) of cubane-1,4-dicarboxylic acid-2,7-bis(ethyl, t-butylamide). Elemental analysis: calc. % C, 64.56; H, 7.67; N, 6.27; O, 21.50, found % C, 64.54; H, 7.55; N, 6.27; O, 21.18.

Cubane-1,2,4,7-tetracarboxylic acid. Cubane-1,4-dicarboxylic acid-2,7-bis(ethyl, t-butylamide) (5.82 g, 0.013 mol) was added to 125 mL stirring 70% HNO_3 in a 250-mL flask with heating mantle, condenser, thermometer, and magnetic stirrer. Heating was started, and at 58°C the reaction instantly turned dark red as copious amounts of NO_2 came off and the temperature went rapidly to 75°C. Mild reflux was continued for 4 h at which time the reaction was pale yellow. The reaction was cooled in the freezer overnight, filtered; washed with cold 70% HNO_3 and then, after changing the filter flask, in 100% ethanol; and dried to give 3.44 g of the product (95%) as a pure white powder. ^{1}H NMR (CD_3OD) δ 4.3 (s). Elemental analysis: calc. % C, 51.44; H, 2.88; O, 45.68, found % C, 51.21; H, 2.88; O, 43.25

N-Ethyl-N-t-butylamine. Ethyl bromide (109 g, 1.0 mol) was mixed with t-butylamine (220 g, 3 mol) and stirred with cooling in a large ice bath, the reaction temperature being allowed to rise slowly over a period of approximately 5 to room temperature. The reaction mixture, that contained a large amount of crystalline precipitate, was stirred for an additional 24 h and worked up. The workup consisted of extraction with 1 x 500 mL of 10 M NaOH, followed by distillation at atmospheric pressure and collection of the 85-93°C fraction (yield ~100 g). This fraction was then

distilled off of calcium hydride to give pure, dry N-ethyl-N-t-butylamine, bp 89°C, in a yield of 85 g (85%).

Cubane-1,2,4,7-tetrakis(ß,ß,ß-trinitroethylester). Cubane-1,2,4,7-tetracarboxylic acid (15 mg, 0.05 mmol) was stirred with 0.5 g PCl_5 in 4 mL of 1,2-dichloroethane for 24 h under argon. The resulting solution was treated with 250 mg Ac_2O and then freed of volatile materials by careful distillation under high vacuum. At the end of the distillation, the residue was heated to 75°C for 5 min. The crude tetraacid chloride, which was a yellow oil, was combined with 100 mg (0.6 mmol) of rigorously dried 2,2,2-trinitroethanol and 2 mL of 1:1 EtOAc/$CHCl_3$. Pyridine (50 mg, 0.6 mmol) was added, and the entire mixture was sealed under argon and stirred for 3 days. The reaction mixture was dissolved in 50 mL EtOAc and extracted with 50 mL 10% Na_2CO_3, concentrated, and chromatographed over 20 g SiO_2, being eluted with 1:1 EtOAc/$CHCl_3$. The $R_f = 0.7$ material was collected and found to be crystalline, with a mass of 4.0 mg. This material was crystallized from EtOAc/$CHCl_3$ to give 2 mg of crystals (~5% yield). ^1H NMR (D_6-acetone, TMS standard, 400 MHz) δ 5.9 (s, 8 H, CH_2), δ 4.6 (s, 4H, C-H); ^{13}C NMR (D_6-acetone) δ 48.7, δ 56.2, δ 61.8, δ 165.2. IR (KBr) 2995, 1730, 1600, 1300, 1200, 1185, 1065 cm^{-1}.

Cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester). The procedure used for the synthesis of the ß,ß,ß-trinitroethylester was followed on double the scale, with fluorodinitro-ethanol substituted for the trinitroethanol. Cubane-1,2,4,7-tetrakis(ß,ß-dinitro-ß-fluoroethylester), 1 mg (8%), isolated as needles. ^1H NMR (D_6-acetone, TMS standard, 60 MHz) δ 4.7 (s, 4 H, C-H), δ 5.65 (d, j = 15 Hz, 2 H, CH_2). The x-ray crystal structure determined by R. Gilardi of NRL gave a density of 1.827 g/cm^3.

N,N'-Bis(ß,ß-dinitro-ß-fluoroethyl)diaminocubane. 1,4-Diamino-cubane hydrochloride (200 mg, 0.95 mmol), prepared by the method of Eaton, was dissolved in 10 mL H_2O and treated with purified 2-fluoro-2,2-dinitroethanol (900 mg, 6 mmol) followed by sodium acetate (700 mg, 8 mmol) for 12 h at room temperature. An orange precipitate was isolated by filtration, dissolved in EtOAc and filtered through a 2 x 1/2-inch plug of silica gel, concentrated, and crystallized from $CHCl_3$/EtOAc to give 180 mg (45%) of needles of N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane. ^1H NMR (D_6-acetone TMS standard, 60 MHz) δ 3.7 (s, 6 H, C-H), δ 4.0-4.5 (m, 6 H, CH_2 + NH); IR (KBr) 3375, 3000, 1630, 1600, 1585, 1330 cm^{-1}.

N-Nitro-N'-nitroso-N,N'-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane. N,N'-Bis(ß,ß-dinitro-ß-fluoroethyl)diaminocubane (60 mg, 0.15 mmol) was dissolved in 5 mL $CHCl_3$ and added to a preformed solution prepared by combining

trifluoroacetic anhydride (400 mg, 2 mmol) with 100% HNO_3 (180 mg, 3 mmol) at 0°C, stirring for 10 min, and then diluting with 5 mL $CHCl_3$. The resulting mixture was stirred at 0°C for 15 min, warmed to 20°C, diluted with 50 mL $CHCl_3$, and concentrated *in vacuo*. The residue was chromatographed, using ethyl acetate over SiO_2 for elution, and the fastest effluent was collected. The resulting material was crystallized from ethyl acetate/$CHCl_3$ to give 30 mg of crystals. ^1H NMR (D_6-acetone, TMS standard, 90 MHz) δ 4.1-4.8 (m, 6 H), δ 5.2-6.2 (m, 4 H, CH_2); IR (KBr) 3040, 1630, 1560, 1460, 1415, 1310, 1290, 1170 cm^{-1}. The x-ray crystal structure determined by R. Gilardi of NRL gave a density of 1.827 g/cm^3.

N,N'-Dinitro-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diamino-cubane. The N-nitro-N'-nitroso-bis(ß,ß-dinitro-ß-fluoroethyl)-1,4-diaminocubane described above (50 mg, 0.11 mmol) was dissolved in 5 mL of a 0.5 M solution of CF_3CO_3H in 1:1 $CHCl_3$/EtOAc and stirred for 36 h. The reaction mixture was diluted to 100 mL with high performance liquid chromatography (HPLC) grade ethyl acetate, extracted with 50 mL of 1 M Na_2SO_3, dried, and concentrated *in vacuo* to give 50 mg (95%) of pure dinitramine as white plates. ^1H NMR (D_6-acetone, TMS standard 90 MHz) δ 4.4 (s, 6 H, C-H), δ 5.65 (d, J = 14 Hz, 4 H, CH_2), IR (KBr) 3000, 1625. 1555, 170ºC 1280 cm^{-1}, mp = 170ºC (explodes).

Cubane-1,4-diol. Cubane-1,4-diacetate (100 mg, 0.4 mmol) was dissolved in 25 mL of HPLC grade $CHCl_3$ and cooled to 0°C under an argon blanket. Diisobutyl aluminum hydride (2 mmol of a 1.5 M solution in toluene) was added and the resulting mixture was stirred for 30 min. Ethyl acetate (50 mL) was added, and 4 mL of 2 M NaH_2PO_4 was then added to destroy all organoaluminum species. The mixture was stirred until all organoaluminum species had precipitated out (~2 h). The organic layer was decanted, the inorganic paste that remained was washed and stirred with 50 mL of EtOAc, and both organic layers were concentrated *in vacuo* to give a white powder that was titurated with $CHCl_3$ to give 50 mg (80%) cubane-1,4-diol. mp = 150°C (decomposition); IR (KBr) 3200, 2960, 1330, 1140, 1000, 930 cm^{-1}; ^1H NMR (CD$_3$OD, 60 MHz) δ 3.2 (s, C-H).

1,4-Bis(trimethylsiloxy)cubane. Cubane-1,4-diol (15 mg, 0.1 mmol) was suspended in 2 mL hexamethyldisilazane. Chlorotrimethylsilane (0.2 mL) was added, and the resulting mixture was stirred for 24 h. Diethylamine (0.5 mL) was added to quench excess chlorotrimethylsilane. The mixture was evaporated to dryness *in vacuo*, redissolved in EtOAc, filtered to remove $Et_2NH_2^+Cl^-$, and concentrated to give 25 mg (100%) 1,4-bis(trimethylsiloxy)cubane, a waxy solid. ^1H NMR (CDCl$_3$) δ 3.85 (s, 6 H, C-H), δ 0.25 (s, 16 H, CH$_3$-Si).

1,4-Dicyanocubane. Cubane-1,4-diacid chloride (2.3 g, 10 mmol) was dissolved in 100 mL $CHCl_3$ and treated with excess NH_3 gas until the exotherm subsided. The NH_3-saturated $CHCl_3$ suspension was stirred for 2 h at room temperature and concentrated *in vacuo*. A white solid product remained. The white solid was suspended in 100 mL of CH_2Cl_2 and treated with 10 mL of Et_3N plus 10 mL $POCl_3$. This mixture was stirred for 3 days, concentrated *in vacuo*, freed of $POCl_3$ by chasing with chlorobenzene on a rotary evaporator, and partitioned between 200 mL $CHCl_3$ and 100 mL 10% Na_2CO_3. The $CHCl_3$ layer was kept. The crude product was chromatographed using 80% $CHCl_3$/20% EtOAc over silica gel for elution. The $R_f = 0.5$ material was collected as white prisms in a yield of 400 mg (25%). IR (KBr) 3060, 2260, 1290, 1230, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS standard, 60 MHz) δ 4.5 (s, C-H), mp = 225°C (explodes).

Cubane-1,4-diisocyanide. Trichlorosilane (1.7 g, 13 mmol) was dissolved in 15 mL of CH_2Cl_2, cooled to 0°C under argon, and treated with 3.7 g (30 mmol) diisopropyl-ethylamine, followed by 1 g (5.5 mmol) cubane-1,4-diisocyanate. The reaction mixture was stirred for 2 h at 0°C, treated with excess ammonia gas to destroy the acidic chlorosilanes, and partitioned between 400 mL of $CHCl_3$ and 400 mL of 1 M NaOH. The chloroform layer was dried, concentrated, and flash-chromatographed, eluting 1:1 EtOAc/$CHCl_3$ over a 3 x 1/2-inch plug of silica gel. The fastest effluent ($R_f = 0.5$) was collected and crystallized from hexane to give 20 mg (2%) of cubane-1,4-diisocyanide crystals. Decomposition > 125°C, detonating on rapid heating. IR (KBr) 3000, 2100, 1330 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS standard, 60 MHz) δ 4.3 (s).

General Procedure for Conversion of Isocyanates to N,N-Dinitramines. To an ice-cooled mixture of 1.45 g (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO_3 (under argon) was added 10 mmol of aliphatic isocyanate, with fume-off avoided by controlling the rate of addition as appropriate. The reaction mixture was then stirred for 15 min at 0°C, diluted to 25 mL with $CHCl_3$, filtered rapidly through a 1 x 3-in. plug of SiO_2, and eluted with 100 mL of $CHCl_3$. Chromatography of the crude product, elution with $CHCl_3$ over SiO_2, and collection of the fastest moving UV-active material ($R_f = 0.5$) yielded the desired dinitramines in fair quantity. N,N-Dinitro-1-butylamine and N,N-dinitromethylamine show spectral properties identical to those of known samples synthesized by established methods.[5,6]

1-Adamantyl-N,N-dinitramine: IR (Neat) 2900, 1610 (s), 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2-2.5 (m); thin layer chromatography (TLC): $R_f = 0.7$ ($CHCl_3$/SiO_2) bleaches I_2.

1,6-bis(N,N-dinitramino)hexane: IR (Neat 2940, 2860, 1640 (s), 1600 (s), 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.1 (t, 4H, J = 6 Hz, CH$_2$-N) δ 1.2-1.9 (m, 6H, CH$_2$); TLC: R$_f$ = 0.5 (CHCl$_3$/SiO$_2$) bleaches I$_2$.

Synthesis of 1-(N,N-dinitramino)-2-trimethylsilylethane

To form a 2-(trimethylsilylethyl)-N,N-dinitramine precursor, an ice-cooled mixture of 1.45 (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO$_3$ (under argon) was formed, and then 10 mmol of 2-(trimethylsilylethyl)isocyanate was added, with fume-off avoided by controlling the rate of addition as appropriate. The reaction was stirred for 15 min at O°C, diluted to 25 mL with CHCl$_3$, and filtered rapidly through a 1 x 3-inch plug of SiO$_2$, eluting with 100 mL of CHCl$_3$. Chromatography of the crude product, by eluting CHCl$_3$ over SiO$_2$ and collecting the fastest-moving, UV-active material (R$_f$ = 0.5), resulted in collection of 500 mg of the desired 2-(trimethylsilylethyl)-N,N-dinitramine precursor, about a 25% yield.

Synthesis of Cesium Dinitramide (SRI-11)

About 2.5 mL of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed above, was dissolved in 20 mL of acetonitrile and maintained at 20° C. To this solution was added 1 g of cesium fluoride. The solution was stirred for about 120 minutes. The cesium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate and acetonitrile. The product yield was 900 mg, or about a 50% yield.

Synthesis of Tetramethylammonium Dinitramide

About 2.5 mL of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed above, was dissolved in 20 mL of acetonitrile and maintained at 20°C. To this solution was added 1 g of tetramethylammonium fluoride. The solution was stirred for about 120 min. The tetramethylammonium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate. The product yield was 900 mg, or about a 50% yield.

Synthesis of Other Dinitramide Salts by Ion Exchange

All desired dinitramide salts can be prepared by ion exchange starting from cesium dinitramide and using AMBERLYST 15 Sulfonic Acid Resin charged with the appropriate cation: Elution is performed using a methanolic solution of cesium dinitramide over a large excess of the charged resin.

In a typical example, 10 g of AMBERLYST 15 (sulfonic acid resin) was suspended in 100 mL of CH_3OH, treated with 5 mL of 95% hydrazine, filtered, and washed with 100 mL of CH_3OH. This 10 g of material was then placed into a 4 x 0.5-inch column and eluted with a solution of 200 mg of cesium dinitramide in 5 mL of CH_3OH, followed by washing with an additional 20 mL of CH_3OH. Concentration of the effluent gave approximately 100 mg of pure hydrazinium dinitramide (SRI-13) after crystallization from CH_3CN. **This material is shock sensitive and one should exercise caution in handling it.**

CONCLUSIONS

We have synthesized several new energetic cubanes, developed new methodologies for the polyfunctionalization of cubane, and prepared several members of a new class of energetic, high density fuels. We have found that the N-nitraminocubanes are more stable than the aminocubane system itself. Perhaps most importantly, we have developed a new composition of matter, the dinitramide ion. Dinitramide may find great importance as an oxidizer replacement for ammonium perchlorate in future space missions.

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Improved Synthesis of
Cubane-1,2,4,7-tetracarboxylic Acid

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We report here a simplification in the synthesis of cubane-1,2,4,7-tetracarboxylic acid (3), a key intermediate from which other cubane derivatives are synthesized. Limitations in the synthetic routes to this compound have prevented the preparation of other, interesting cubane compounds.

The original breakthrough in the synthesis of functionalized cubanes was made by Eaton and co-workers[1] with the discovery that *N*,*N*-diisopropylamide groups could be

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Scheme I
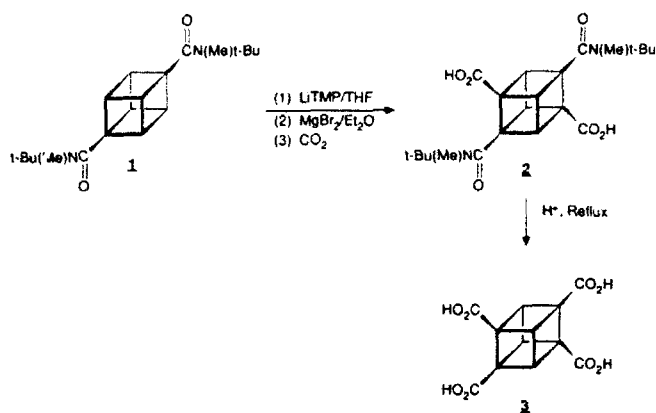
used as activating/directing groups to make ortho lithiation[2] of cubane possible (eq 1).

$$(1)$$
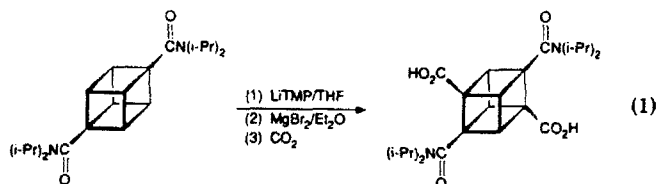
The cubyl anion was originally trapped in this route by the exchange of lithium for mercury. Bashir-Hashemi and Eaton developed the necessary methodology for hydrolysis of the N,N-diisopropylamide groups to give the tetraacid. This route was significantly improved by Bashir-Hashemi with the discovery that $MgBr_2$ etherate could be substituted for $HgCl_2$.[3,4] The synthesis of the cubane tetraacid is a multistep process involving the lithiation of $N,N,-N',N'$-tetraisopropylcubane-1,4-dicarboxamide using lithium tetramethylpiperidine (LiTMP) as the base, trapping of the carbanion as the magnesium salt, carboxylation with CO_2, and then a reduction, an oxidation, methylation, and finally acid hydrolysis of the N,N-diisopropylamides to give 3. The reduction and oxidation step are necessary because the N,N-diisopropylamide groups proved resistant to hydrolysis with very strong acids, bases, and oxidants. This group was even resistant to refluxing red fuming nitric acid, returning only unchanged starting material. The number of steps required limits the availability of 3.

We have improved the synthesis of 3 by a subtle variation in the amide group, which results in a significantly shorter route that substitutes a simple hydrolysis step for the oxidation and reduction steps (Scheme I). The crucial improvement results from our discovery that a different amide, bis(N-tert-butyl-N-ethyl)amide 1, cannot only be used in place of the N,N-diisopropylamide for the ortho lithiation of the cubane nucleus but also can be removed through direct acid hydrolysis, thereby significantly reducing the number of steps required. We explored several other amides before discovering one capable of replacing the diisopropylamide (Table I). The metalations listed in Table I were done by the method of Bashir-Hashemi.[3,4] The hydrolysis of 2 to 3 was done with 70% nitric acid, because this method allows ready isolation of 3 as a filterable solid precipitate while the other byproducts are

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Table I. Attempted Metalation–Carboxylations of Cubane-1,4-dicarboxamides

R	carboxylation observed (% yield)
CON⟨t-Bu⟩⟨t-Bu⟩	none
CON⟨t-Bu⟩⟨cyclohexyl⟩	none
CON⟨t-Bu⟩⟨piperidine⟩	none
CON⟨pyrrolidine⟩	25
CON⟨t-Bu⟩⟨Et⟩	75

oxidized or dissolved by the acid. Dilute hydrochloric or other dilute acids are also effective for the hydrolysis reaction.

The advantages of the N-tert-butyl-N-ethylamide over the N,N-diisopropylamide are the former's greater ease of removal by acid hydrolysis and higher yield in the carboxylation. The N-tert-butyl-N-ethylamide can be removed nearly quantitatively by acid hydrolysis in one step, eliminating several steps from the long sequence previously required.

This hydrolysis step illustrates the oxidative and protic stability of the cubane nucleus when substituted with electron-withdrawing groups. Despite the fact that cubane is not normally considered to be stable under extreme conditions, we have refluxed 2 in dilute HCl or red fuming HNO_3 and obtained a high yield of 3. Under the same conditions, the corresponding N,N-diisopropylamide is recovered (unchanged) nearly quantitatively, with no decomposition or hydolysis.

Experimental Section

Materials. ^{1}H NMR spectra were recorded at 90 MHz. Cubane-1,4-dicarboxylic acid dimethyl ester was purchased from Fluorochem (Azusa, CA) or EniChem Sintesi (Milan, Italy) and converted to the free acid by refluxing in dilute HCl. Aldrich Chemical Co. was the major supplier of the remaining chemicals.

N-Ethyl-1,1-dimethylethanamine. Ethyl bromide (109 g, 1.0 mol) was mixed with tert-butylamine (220 g, 3 mol) and stirred with cooling in a large ice bath, allowing the reaction temperature to rise slowly over a period of approximately 5 h to room temperature. The reaction mixture, which contained a large amount of crystalline precipitate, was stirred for an additional 24 h and worked up. The workup consists of extraction with 1 × 500 mL of 10 M NaOH, followed by distillation at atmospheric pressure and collection of the 85–93 °C fraction (yield ~100 g). This fraction was redistilled from calcium hydride to give pure, dry N-ethyl-1,1-dimethylethanamine: bp 89 °C; 85 g (85%); ^{1}H NMR (CHCl₃) δ 1.1 (s, 9 H, tert-butyl), 1.1 (t, *J* = obscured by tert-butyl, 3 H, CH₃), 2.6 (q, *J* = 8 Hz, 2 H, CH₂).

N,N'-Di-tert-butyl-N,N'-diethylcubane-1,4-dicarboxamide (1). Cubane-1,4-dicarboxylic acid (30.0 g, 0.156 mol) was added to 500 mL of dry chlorobenzene under an argon purge. PCl₅ (97.5 g, 0.468 mol, 50% excess) was added to the diacid in two portions.

The reaction was stirred for 2 h at room temperature, and then excess PCl₅ was destroyed by stirring with acetic anhydride (14.7 mL, 0.156 mol) for 15 min. The solution was concentrated to dryness at 50 °C by using aspirator pressure at first and then higher vacuum. To remove residual acetic anhydride, the cubane-1,4-bis(carbonyl chloride) was dissolved in dry, ethanol-free CHCl₃, followed by concentrating to dryness at 50 °C at reduced pressure. This step was repeated two or three times, until no anhydride was present. Finally, the pale yellow crystals were dried under high vacuum for ~2 h at 50 °C. The cubane-1,4-bis(acid chloride) was dissolved in 500 mL of dry CHCl₃ and transferred to a 1-L flask with mechanical stirrer, argon purge, 50-mL addition funnel, and cold water bath (5–10 °C). Triethylamine (31.6 g, 0.312 mol) was added slowly over 5 min and then N-tert-butyl-N-ethylamine (31.6 g, 0.312 mol) was added dropwise over 20 min while the cold water bath was maintained. After the addition, the reaction mixture was stirred for 2 h at room temperature and washed with 5% HCl (3 × 100 mL), 5% KOH (2 × 100 mL), and saturated NaCl (1 × 100 mL). The yellow CHCl₃ layer was treated with activated carbon, dried (MgSO₄), and filtered over Celite to give a less colored solution, which when concentrated to dryness left a pale yellow solid. This solid was slurried in 400 mL of dry ethyl acetate at 40–50 °C, cooled in ice, filtered, washed with cold ethyl acetate, and dried under high vacuum to yield 41.0 g (73%) of the title compound as pure white crystals: mp 185–188 °C; ¹H NMR (¹H, CDCl₃, TMS standard) δ 1.3 (t, 3 H, J = 7 Hz, CH₃), 1.4 (s, 9 H, tert-butyl), 3.8 (q, 2 H, J = 7 Hz, CH₂), 4.55 (s, 6 H); IR (KBr) 2970, 1610, 1390, 1205 cm⁻¹.

N,N'-Di-tert-butyl-N,N'-diethyl-2,7-dicarbamoylcubane-1,4-dicarboxylic Acid (2). 2,2,6,6-Tetramethylpiperidine (107 g, 0.760 mol, 10 equiv) and tetramethylethylenediamine (12.6 mL, 1.1 equiv) were added to 600 mL of dry THF (distilled over CaH) in a 2-L flask equipped with an argon purge. The reaction mixture was cooled in dry ice/acetone, and 2.5 M n-butyllithium in hexane (304 mL, 0.760 mol, 10 equiv) was added dropwise with stirring over 2 h at −78 °C. and then the reaction was stirred at 0 °C for 1 h. The reaction mixture was cooled in a dry ice/acetone bath. MgBr₂ etherate (98.1 g, 0.380 mol, 5 equiv) and 1 (27.2 g, 0.076 mol, 1 equiv) were added all at once, and the mixture was then

placed in the bath and stirred for 8 h. The reaction mixture was cooled in dry ice/acetone, and CO₂ was bubbled through the stirring reaction for 12 h at dry ice/acetone temperature to yield a light tan suspension, which was concentrated to dryness on the rotovap, first using aspirator pressure and then higher vacuum for about 2 h. The light tan solid was vigorously stirred with 1500 mL of H₂O for 1 h, and the resulting suspension was transferred to a 2-L flask and then cooled to 0 °C. Ice-cold 19% HCl was added slowly with stirring to bring the pH to 1 (about 250 mL; there was some foaming). The suspension was filtered to give a light brown paste, which was dissolved in 600 mL of boiling CH₂Cl₂, cooled in the freezer overnight, filtered, and washed with cold CH₂Cl₂ to give 20.0 g of diacid 2 as colorless plates which decompose exothermically without melting at 239.3 °C. The mother liquor was concentrated to one-third volume and cooled to give a second crop of 5.5 g for a total yield of 25.5 g (75%): ¹H NMR (CD₃OD) δ 1.25 (t, J = 6 Hz, 6 H), 1.5 (s, 9 H), 3.75 (q, J = 6 Hz, 4 H), 4.6 (s, 4 H), failed to observe carboxylic acid proton. Anal. Calcd C, 64.56; H, 7.67; N, 6.27. Found: C, 64.54; H, 7.55; N, 6.27.

Cubane-1,2,4,7-tetracarboxylic Acid (3). Compound 2 (5.82 g, 0.013 mol) was added to 125 mL of 70% HNO₃. The mixture was heated and at 58 °C the reaction instantly turned dark red, evolving NO₂, and the temperature went rapidly to 75 °C. Mild reflux was continued for 4 h, at which time the reaction was pale yellow. The reaction was cooled in the freezer overnight, filtered, washed with cold 70% HNO₃ and then, after changing the filter flask, with 100% ethanol, and dried to give 3.44 g of the product (95%) as a pure white powder which decomposes quite exothermically at 267 °C. Dilute HCl at reflux can be substituted for nitric acid; however, the isolation of the product is more difficult. Identification was based on comparison with the known material.[5] ¹H NMR (CD₃OD) δ 4.3 (s). Anal. Calcd: C, 51.44; H, 2.88. Found: C, 51.21; H, 2.88.

(5) Eaton, P. E., private communication.

APPENDIX B

A NEW SYNTHESIS OF ALKYL-N,N-DINITRAMINES BY DIRECT NITRATION OF ISOCYANATES

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ABSTRACT

A facile conversion of aliphatic isocyanates to N,N-dinitramines has been developed. An aliphatic isocyanate is treated with a mixture of nitronium fluoroborate and nitric acid in acetonitrile giving fair yields and simplifing the existing synthesis.

The N,N-dinitramine function is a highly labile functional group accessible only by difficult preparative procedures. Recently, renewed interest has developed in preparing N,N-dinitramines as possible energetic groups for propellant applications. The established method,[1] takes four steps and involves the preparation of an alkyl nitramine via the N-nitromethylcarbamate followed by nitration with nitronium ion, according to Equation 1.

(1)

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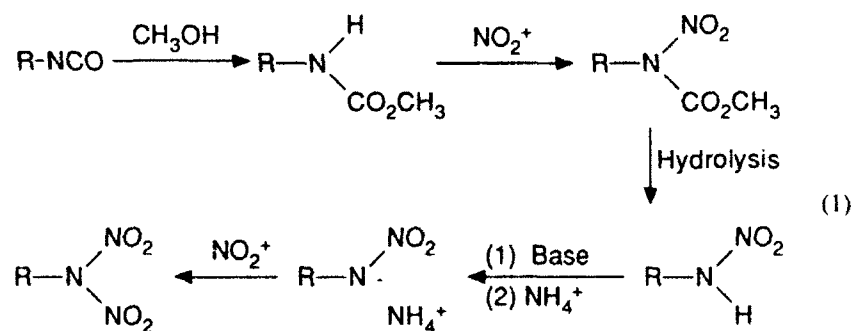
[*] To whom correspondence should be addressed

We report here a new, simple, one-step synthesis of N,N-dinitramines from aliphatic isocyanates, using stoichiometric quantities of nitronium tetrafluoroborate and nitric acid in acetonitrile as the nitrating system, according to Equation 2.

$$R\!-\!NCO \xrightarrow[\text{CH}_3\text{CN}]{\text{NO}_2\text{BF}_4\,/\text{HNO}_3} R\!-\!N\!\!\begin{array}{c}\nearrow NO_2 \\ \searrow NO_2\end{array} \quad (2)$$
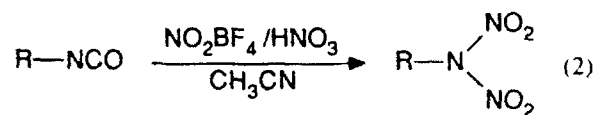
This route differs from the previous work in that it is only one step instead of four, and requires the presence of both nitric acid and high quality nitronium tetrafluoroborate in the reaction medium. If either reagent is absent, no N,N-dinitramine is formed.

We propose the simple mechanism shown in Scheme I, in accordance with the observation of Ledebev et al (Scheme I) who reacted isocyanates with nitronium ions in the absence of nitric acid to give *monoalkyl-mononitramino compound* via intermediate 2.[2] Adding an aliphatic isocyanate to a preformed, ice-cooled mixture of acetonitrile, nitric acid, and nitronium tetrafluoroborate results in the initial formation of the corresponding acylium ion 2 to which HNO_3 is added, then losing a proton and CO_2, to give the corresponding aliphatic N,N-dinitramine 4. Consistent with this mechanism is our observation that no N,N-dinitramines are formed when the reaction is run in the absence of free nitric acid which presumably acts as a nucleophile toward acylium ion 2. An alternative to the proposed mechanism below is the direct addition of N_2O_5 (formed by the reaction of NO_2BF_4 with HNO_3) across the alkyl isocyanate giving the same reactive intermediate shown below also giving 4.

This reaction is most successful with primary alkyl isocyanates. When 1-adamantyl isocyanate was subjected to the conditions of this procedure, only a trace (<1%) of the desired N,N-dinitramine was formed, with the remainder of the substrate transformed into a complex mixture. This result indicates a high sensitivity either to steric hindrance or to the stability of the ternary carbonium ion or radical formed if the dinitramine group leaves and then rearranges. We would expect that the dinitramide groups is an excellent leaving group and obviously quite
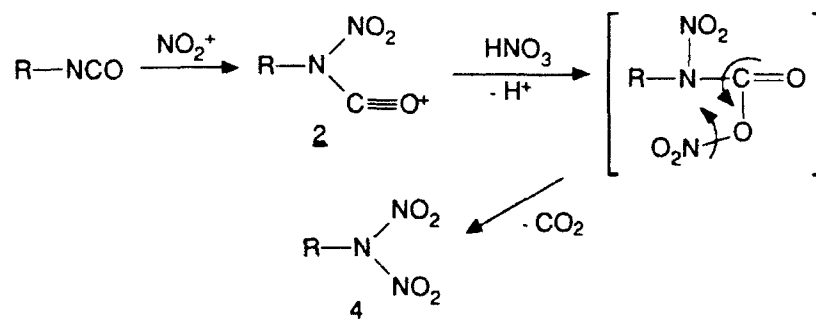
Scheme 1: Proposed Mechanism for N,N-Dinitramine Synthesis

Table I

Substrate	Product	Yield
n-Butyl isocyanate	1-(N,N-Dinitramino) butane	35%
Methyl isocyanate	N,N-Dinitramino-methane	30%
1-Adamantyl isocyanate	1-(N,N-Dinitramino) adamantane	<1%
Hexamethylene diisocyanate	1,6-bis(N,N-Dinitramino)hexane	10%
Ethane-1,2-diisocyanate	1,2-bis(N,N-Dinitramino)ethane	-0-
2-(Trimethylsilyl-ethyl)-1-isocyanate	1-(N,N-Dinitramino)-2-trimethylsilyl-ethane	25

labile when attached to a ternary position such as the 1-position of adamantane. Hexamethylene diisocyanate is converted in 10% yield, the square of the yield obtained for monofunctional substrates, indicating that the two distant functional groups are not interacting in this case.

The substrates investigated are shown in Table I, along with the yields. The overall yields from this route are no better than those of previous syntheses, but the transformation is accomplished in one rather than four steps.

EXPERIMENTAL

CAUTION: All the products described in this paper are potentially explosive and should be handled in 0.5-g quantities and stored at 0°C. All NMR spectra were obtained on a Varian EM-360 spectrometer. IR spectra were obtained on a Perkin-Elmer 1420 Infrared spectrophotometer. Elemental analysis could not be obtained because of the marked instability of the products. All thin-layer chromatography was run by elution of $CHCl_3$ over silica gel.

General Procedure for Conversion of Isocyanates to N,N-Dinitramines. To an ice-cooled mixture of 1.45 g (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO_3 (under argon) was added 10 mmol of aliphatic isocyanate, avoiding fume-off by controlling the rate of addition as appropriate. The reaction mixture was then stirred for 15 min at 0°C, diluted to 25 mL with $CHCl_3$, filtered rapidly through a 1 x 3-in. plug of SiO_2, and eluted with 100 mL of $CHCl_3$. Chromatography of the crude product, elution $CHCl_3$ over SiO_2, and collection of the fastest moving UV-active material ($R_f = 0.5$) yielded the desired dinitramines in fair quantity. N,N-Dinitro-1-butylamine id N,N-dinitromethylamine show spectral properties identical to those of known samples synthesized by established methods.[1]

1-Adamantyl-N,N-dinitramine: IR (Neat) 2900, 1610 (s), 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2-2.5 (m) TLC: $R_f = 0.7$ ($CHCl_3/SiO_2$) bleaches I_2.

1,6-bis(N,N-dinitramino)hexane: IR (Neat 2940, 2860, 1640 (s), 1600 (s), 1340 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.1 (t, 4H, J = 6 Hz, CH_2-N) δ 1.2-1.9 (m, 6H, CH_2) TLC: $R_f = 0.5$ ($CHCl_3/SiO_2$) bleaches I_2.

REFERENCES

1.   a. Aerojet-General Corp., Brit. 1,126,591 05 Sept 1968. U.S. 3,428,667 (1969); C.A. 70 67584g (1969). b. E. E. Hammel, C. Heights, and R. E. Olsen, British Patent No. 1,126,591 (1968); Chem. Abstr. 70, 67584g (1969).
2.   L. V. Cherednichenko, B. A. Ledebev, and B. V. Gidaspov, Zh. Org. Khim 14(4) 735-7 (1978).

APPENDIX C

PATENT COOPERATION TREATY

| INTERNATIONAL PUBLICATION No. WO91/19669 |
| INTERNATIONAL APPLICATION No.   PCT/US91/04268 |

NOTICE
INFORMING THE APPLICANT OF
THE COMMUNICATION OF THE
INTERNATIONAL APPLICATION
TO THE DESIGNATED OFFICES
issued under PCT RULE 47.1(c),
first sentence

To:

LANGE, Richard, P.
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025-3493
ÉTATS-UNIS D'AMÉRIQUE

DATE OF MAILING OF THIS NOTICE
26 December 1991 (26.12.91)

APPLICANT'S OR AGENT'S
FILE REFERENCE
   P-2744

From:
The International Bureau of WIPO
1211 Geneva 20
Switzerland

Notice is hereby given that the International Bureau has communicated, as provided
in PCT Article 20, the international application referred to above to the following
designated Offices on the date indicated above as the date of mailing of this
Notice:
to the national Offices of CA,JP, and to EP

The applicant is reminded that he must enter the "national phase" before each
designated Office by performing, within the time limit applicable under PCT Article
22 or 39(1), the acts referred to therein.

In accordance with PCT Rule 47.1(c), third sentence, each designated Office has
been informed, separately from the communication of the international application,
of the sending and the date of mailing of the present notice.

Form PCT/IB/308 (January 1988)

J. Zahra
(Authorized Officer)

C-1

(54) Title: DINITRAMIDE SALTS AND METHOD OF MAKING SAME

(57) Abstract

A N,N-dinitramide salt is disclosed having the formula $MN(NO_2)_2$ where M is a cation selected from the class consisting of a metal ion and a nitrogen-containing ion. The dinitramide salt exhibits high temperature stability, high energy density, and an absence of smoke generating halogens, rendering it useful as an oxidizer in rocket fuels. The dinitramide salts are meltable and pumpable oxidizers which may be used in start-stop rocket engines instead of other less stable oxidizers.

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DINITRAMIDE SALTS AND METHOD OF MAKING SAME

GOVERNMENT RIGHTS

This invention was made under government contracts
N00014-86-C-0699 and N00014-88-C-0537 of the Office
5   of Naval Research; and the government of the United
States, therefore, has rights in this invention.

BACKGROUND OF THE INVENTION

1.   **Field of the Invention**
This invention relates to dinitramide salts and a
10   method of making same from alkyl-N,N-dinitramines.

2.   **Description of the Related Art**
Solid oxidizers, such as ammonium perchlorate or
potassium perchlorate, have been used in the past in
rocket propellant formulation because of their
15   greater stability than liquid oxidizers. However,
the presence of a halogen in the solid oxidant
produces a smoke trail which is observable on radar
and sometimes visually as well. Also, chlorine
poses a serious atmospheric environmental hazard of
20   ozone depletion.

Because of such shortcomings in the use of perchlor-
ate solid fuel oxidizers, other materials, including
nitrate (NO_3^-) compounds, have been investigated in
the search for oxidizers which would provide the
25   desired energy density and stability, without the
drawbacks of the perchlorate oxidants.

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Hamel et al. U.S Patent 3,428,667 describes the
reaction of an ionic nitronium salt with a primary
organic nitramine to form N,N-dinitramines having
the general formula R-N((NO_2)_2), where n is 1-2 and
R is a monovalent or divalent organic radical.
These compounds are said to be highly energetic and
useful as ingredients in propellant, explosive, and
pyrotechnic compositions.

Willer et al. U.S. Patent 4,878,968 describes the
formation of gun and rocket propellants which
include substituted cubanes such as cubane-1,4-
bis(ammonium nitrate), or 1,4-bis(ammonium)pentacy-
clo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane dinitrate; and cubane
ammonium nitrate, or pentacyclo-[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]-
octylammonium nitrate.

Leroy et al., in "A Theoretical Investigation of the
Structure and Reactivity of Nitrogen-Centered
Radicals", published in the Journal of Molecular
Structure (Theochem), 153 (1987) on pages 249-267,
by Elsevier Science Publishers B.V. Amsterdam, The
Netherlands, discusses the structure, stability, and
reactivity of nitrogen-centered radicals. Listed in
Table 6 are various reactions of N-centered radi-
cals, including reactions of $N(NO_2)_2$ with NH_2 to form
$2NHNO_2$, and with CH_3NHNO_2 to form CH_3NNO_2 and $NH(NO_2)$.

In the Third Quarterly Report on Basic Research in
Solid Oxygen Oxidizers of Government Contract AF
04(611)-8549 dated December 1963, on pages 6 and 7,
the reaction of nitronium tetrafluoroborate with the
dianion of methylenedinitramine to form an interme-
diate anion is hypothesized and it is speculated

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that the intermediate anion may either react with a
second equivalent of nitronium tetrafluoroborate to
form N,N,N',N'-tetranitromethylenediamine or undergo
fragmentation to form an anion which has the formula
5    $N(NO_2)_2$.

It would, however, be desirable to provide a stable
solid ionic nitro compound useful as a rocket
propellant fuel which would have the clear advantage
over perchlorates of being free of chlorine, but
10   would be as stable as presently used perchlorate
compounds and be much more stable and cheaper than
prior art dinitramine compounds.

SUMMARY OF THE INVENTION

It is, therefore an object of this invention to
15   provide novel N,N-dinitramide salts having the
formula M^+ $N(NO_2)_2$, where M is selected from the
class consisting of a metal cation and a nitrogen-
containing cation.

It is another object of this invention to provide
20   novel N,N-dinitramide salts having the formula
M^+ $N(NO_2)_2$, where M is selected from the class
consisting of a metal cation and a nitrogen-contain-
ing cation having from 1 to 8 nitrogen atoms.

It is yet another object of this invention to
25   provide novel N,N-dinitramide salts having the
formula M^+ $N(NO_2)_2$, where M^+ is a metal ion, the salt
of which is capable of reacting with a nitrogen-
containing compound to form the N,N-dinitramide
salt.

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It is still another object of this invention to
provide novel N,N-dinitramide salts having the
formula $M^+ \, N(NO_2)_2$, where M^+ is a 1-8 nitrogen-
containing ion.

5   It is a further object of this invention to provide
novel N,N-dinitramide salts having the formula
$M^+ \, N(NO_2)_2$, where M^+ is a 1-8 nitrogen-containing ion
having the formula $(R_k H_m N_z)^{+z}$, wherein n = 1 to 8, z
= 1 to n, k = 0 to n+2+z, m = n+2+z-k, and each R is
10   the same or different 1-6 carbon alkyl.

It is still a further object of this invention to
provide novel N,N-dinitramide salts having the
formula $M^+ \, N(NO_2)_2$, where M is selected from the
class consisting of a nitrogen-containing cation
15   having from 1 to 2 nitrogen atoms, such as a substi-
tuted ammonium ion, an ammonium ion, a substituted
hydrazinium ion, and a hydrazinium ion.

It is yet a further object of this invention to
provide a method of making N,N-dinitramide salts
20   having the formula $M^+ \, N(NO_2)_2$, where M^+ is selected
from the class consisting of a metal cation and a
nitrogen-containing cation such as a substituted
ammonium ion, an ammonium ion, a substituted hydra-
zinium ion, and a hydrazinium ion.

25   It is still another object of this invention to
provide a method of making N,N-dinitramide salts
having the formula $M^+ \, N(NO_2)_2$ by reacting a nitro-
amine having the formula $R_k H_m N(NO_2)_2$ with either a

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metal-containing compound or a nitrogen-containing
compound.

It is still another object of this invention to
provide a method of making N,N-dinitramide salts
5   having the formula $M^+ N(NO_2)_2$ by reacting a nitro-
amine having the formula $L_nZR'N(NO_2)_2$ with a salt
having the formula MX, where n is 1 to 3, depending
upon the valence of Z; L is the same or different 1-
6 carbon alkyl, aryl, hydrogen, halogen, amine, or
10   ether group; Z is an element selected from the class
consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg;
and R' is a 1 to 6 carbon alkylene group; the M^+ ion
is selected from the class consisting of a metal
cation, a substituted ammonium cation, an ammonium
15   cation, a substituted hydrazinium cation, and a
hydrazinium cation; and the X anion is an ion
selected from the class consisting of fluoride,
chloride, carbonate, hydroxyl, alkoxide, and carbox-
ylate ions.

20   These and other objects of the invention will be
apparent from the following description and accom-
panying flowsheet.

BRIEF DESCRIPTION OF THE DRAWING

The sole drawing is a flowsheet illustrating one
25   embodiment of the process of the invention.

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DETAILED DESCRIPTION OF THE INVENTION

The invention comprises novel dinitramide salts
having the formula $M^+ N(NO_2)_2$ which comprise stable
high density, meltable, pumpable oxidizers useful as
5   propellants in rocket engines, including stop-start
rocket engines. The salts are stable up to tempera-
tures as high as 140°C and, unlike prior art per-
chlorate oxidizers, do not leave smoke trails
detectable visually or by radar.

10   In the formula for the novel dinitramide salts,
$M^+ N(NO_2)_2$, the M^+ cation may be a mono, di, or
trivalent metal cation, or a nitrogen-containing
cation, such as a 1-8 nitrogen-containing cation
having the formula $M^+ N(NO_2)_2$, where M^+ is an ion
15   containing 1-8 nitrogen atoms and having the formula
$(R_k H_m N_n)^{+z}$, wherein n = 1 to 8, z = 1 to n, k = 0 to
n+2+z, m = n+2+z-k, and each R is the same or
different 1-6 carbon alkyl.

As will be discussed in more detail with respect to
20   the method of making the claimed dinitramide salts,
metal ions which may comprise M^+ include metal ions
which form soluble salts with either fluoride or
chloride.   Typical metals which may comprise M
include alkali metals Li, Na, K, Rb, and Cs; alka-
25   line earth metals Ca, Ba, Sr, and Mg; Group Ib
metals Cu, Ag, and Au; Group IIb metals Zn, Cd, and
Hg; Group III metals Al, Sc, Y, Ga, In, and the
Lanthanide elements (57-71); Group IV metals Ti, Zr,
Hf, Ge, and Sn; Group V metals V, Nb, and Ta; Group
30   VI metals Cr, Mo, and W; Group VIIa metals Mn, Tc,
and Re; and Group VIII metals Fe, Co, Ni, Ru, Rh,

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Pd, Os, Ir, and Pt. Of the foregoing metal ions,
Li, Na, K, Be, and Mg are preferred metal ions for
the dinitramide salts of the invention.

5   When the M^+ ion is a 1-2 nitrogen-containing cation,
it may have the formula $R_kH_mN_n^+$, wherein n = 1 to 2,
k = 0 to 3+n, m = 3+n-k, and each R is the same or
different 1-6 carbon straight chain or branched
alkyl. Examples of such ions include NH_4^+, $CH_3NH_3^+$,
10   $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$, $C_2H_5NH_3^+$, $(C_2H_5)_2NH_2^+$,
$(C_2H_5)_3NH^+$, $(C_2H_5)_4N^+$, $(C_2H_5)(CH_3)NH_2^+$, $(C_2H_5)(CH_3)_2NH^+$,
$(C_2H_5)_2(CH_3)_2N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $N_2H_5^+$, $CH_3N_2H_4^+$,
$(CH_3)_2N_2H_3^+$, $(CH_3)_3N_2H_2^+$, $(CH_3)_4N_2H^+$, $(CH_3)_5N_2^+$, etc.

The M^+ ion may also comprise a cubane-1,4-bis
15   ammonium ion, such as described in the aforemen-
tioned Willer et al. U.S. Patent 4,878,968, cross-
reference to which is hereby made; a cubane-1,2,4,7-
tetra ammonium ion; a cubane-1,3,5,7-tetra ammonium
ion; a cubane-1,2,3,4,-tetra ammonium ion; a cubane-
20   1,2,3,4,7-penta ammonium ion; or a cubane-1,2,4,6,8-
penta ammonium ion.

Other nitrogen-containing cations which may comprise
M^+ include guanidium $(C(NH_2)_3^+)$; triaminoguanidinium
$(C(N_2H_3)_3^+)$; nitronium $(O=N=O^+)$; nitrosonium $(N\equiv O^+)$;
25   and a 1-10,000 nitrogen polymer of ethyleneimine.

a.   <u>First Method of Preparing Dinitramide Salts</u>

The dinitramide salts of the invention may be
formed, in one embodiment, by a reaction of a
dinitramine having the formula $L_kZR'N(NO_2)_2$ with a

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metal-containing compound or a nitrogen-containing
compound such as ammonia, hydrazine, or a salt
having the formula MX, where n is 1 to 3, L is the
same or different 1-6 carbon alkyl, aryl, hydrogen,
5   halogen, amine, or ether group, Z is an element
selected from the class consisting of Si, Sn, Ge,
As, B, Sb, Bi, Pb, and Hg; and R' is a 1 to 6 carbon
alkylene group; the M^+ ion is selected from the
class consisting of a metal cation, a substituted
10   ammonium cation, an ammonium cation, a substituted
hydrazinium cation, and a hydrazinium cation; and
the X anion is an ion selected from the class
consisting of fluoride, chloride, alkoxide, carbox-
ylate, hydroxyl, and carbonate ions. The reaction,
15   when a salt is reacted with the dinitramine, is
shown in the following equation:

$$L_nZR'N(NO_2)_2 + MX \quad \text{-------->} \quad MN(NO_2)_2 + L_nZX + R$$

An example of such a dinitramine precursor is
2-trimethylsilylethyl-N,N-dinitramine having the
20   formula $(CH_3)_3Si(CH_2)_2-N(NO_2)_2$.

The dinitroamine precursor may be formed by known
prior art methods such as described in Hamel et al.
U.S. Patent 3,428,667, cross-reference to which is
hereby made; or as described in the aforementioned
25   Third Quarterly Report of AF Contract 04(611)-8549,
cross-reference to which is also made.

Alternatively, in accordance with one aspect of the
invention, the dinitramine precursor may be formed
directly from an aliphatic isocyanate using stoi-
30   chiometric quantities of nitronium tetrafluoroborate

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and nitric acid in acetonitrile as the nitrating
system as shown in the equation below:

$$R-N=C=O \quad \xrightarrow[\substack{NO_2^+BF_4^- \\ CH_3CN}]{HNO_3} \quad R-N(NO_2)_2$$

5
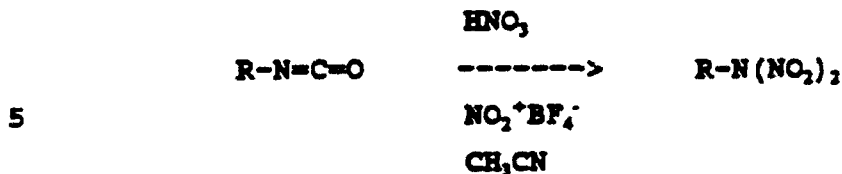
The degradation reaction of the $RN(NO_2)_2$ dinitramine
with the MX salt takes places in an inorganic or
organic solvent which preferably will be a polar

10   solvent, such as water, alcohols, or acetone, at any
pH compatible with the starting materials, but
usually within a range of from about 3 to about 10.

The temperature of the degradation reaction may
range from -40°C to 150°C, preferably from about 0°C

15   to about 20°C. The degradation reaction may be
carried out at ambient pressure for a time period
which may range from as short as 1 minute to as long
as one week, depending upon the reactivity of the
starting materials, the temperature selected, and

20   the desired yield. Usually the reaction will be
carried out for a period of from about 1 to about 2
hours.

b.   Second Method of Preparing Dinitramide Salts

The dinitramide salts of the invention may also be

25   prepared by the initial reaction of nitramide
(having the formula NH_2NO_2) with a nitrating agent
such as nitronium tetrafluoroborate having the

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formula NO_2BF_4 to form the free acid $HN(NO_2)_2$ as shown
in the following equation:

$$NH_2NO_2 + NO_2BF_4 \text{ --------> } HN(NO_2)_2 + HBF_4$$

Other nitrating agents which may be reacted with
5   nitramine instead of nitronium tetrafluoroborate
include $(NO_2^+)_2(S_2O_7^{-2})$, $NO_2^+ AlCl_4^-$, N_2O_5, NO_2F, $NO_2^+ PF_6^-$,
$NO_2^+ AsF_6^-$, $NO_2^+ SbF_6^-$, acetylnitrate, trifluoroacetyl-
nitrate, trifluoroacetylnitrate in combination with
catalytic BF_3, acetonecyanohydrin nitrate in combi-
10 nation with catalytic BF_3, and any one of these in
combination with nitric acid.

This intermediate product is then reacted with the
previously described metal-containing compound or
nitrogen-containing compound, such as ammonia,
15 hydrazine, and the previously described MX salt to
form the dinitramide salt of the invention, which,
in the case of the MX salt, is illustrated in the
following equation:

$$HN(NO_2)_2 + MX \text{ --------> } MN(NO_2)_2 + HX$$

20 If hydrazine is used as the neutralizing agent,
extreme care should be exercised when handling the
resultant product due to its possible shock sensi-
tivity.

It should be noted that the above reaction works
25 well in the absence of NO^+, NO, and NO_2, i.e. when
less than about 5 wt.% total of any or all of the
above oxides of nitrogen are present. Therefore, in

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accordance with a preferred embodiment of the
invention, the reagents used in this reaction should
be made or purified to provide a content of NO^+, NO,
and/or NO_2 less than about 5 wt.%.

5   The following examples will serve to further illus-
trate the invention.

Example I

To form a 2-(trimethylsilylethyl)-N,N-dinitramine
precursor, an ice-cooled mixture of 1.45 grams (11
10   millimoles) of nitronium tetrafluoroborate, 10 ml of
acetonitrile, and 700 milligrams (11 millimoles) of
99+% HNO_3 (under argon) was formed, and then 10
millimoles of 2-(trimethylsilylethyl)isocyanate was
added, avoiding fume-off by controlling the rate of
15   addition as appropriate. The reaction was stirred
for 15 minutes at 0°C, diluted to 25 ml with $CHCl_3$,
and filtered rapidly through a 1" x 3" plug of SiO_2,
eluting with 100 ml of $CHCl_3$. Chromatography of the
crude product, eluting $CHCl_3$ over SiO_2 and collecting
20   the fastest-moving, UV active material (R_f=0.5),
resulted in collection of 500 milligrams of the
desired   2-(trimethylsilylethyl)-N,N-dinitramine
precursor, about a 25% yield.

A 1-adamantyl-N,N-dinitramine compound was formed
25   from 1-adamantylisocyanate; and a 1,6-bis(N,N-
dinitramino)hexane compound was formed from 1,6-
hexane isocyanate using the same procedure as
described above.

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Example II

To about 2.5 milliliters of 2-(trimethylsilylethyl)-
N,N-dinitramine, such as formed in Example I,
dissolved in 20 ml of acetonitrile and maintained at
5   20°C was added 1 gram of tetramethylammonium fluo-
ride.   The solution was stirred for about 120
minutes.   The tetramethylammonium N,N-dinitramide
salt product was then recovered by crystallization
from ethyl acetate.   The product yield was 900
10 milligrams or about a 50% yield.

The same procedure was repeated by reacting tetra-
butylammonium fluoride and cesium fluoride respec-
tively with 2-(trimethylsilylethyl)-N,N-dinitramine
to form the corresponding tetrabutyl ammonium
15 dinitramide and cesium dinitramide salts.

Example III

2 millimoles of nitramide was dissolved in 4 ml of
anhydrous acetonitrile cooled under argon to a
temperature of -10°C, and then treated with 300 mg
20 (2.3 millimoles) of nitronium tetrafluoroborate.
The reaction mixture was stirred for 10 minutes and
was then added to a stirred mixture of 8 ml of 1
molar NH$_3$/2-propanol in 100 ml of ethyl ether. The
mixture was stirred for 5 minutes. The mixture was
25 evaporated to dryness, triturated with 10 ml of 1:1
acetone/ethyl acetate, filtered, evaporated to
dryness, and 0.15 grams of ammonium dinitramide was
crystallized from 2 ml of butanol.

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Example IV

2 millimoles of nitramide was dissolved in 4 ml of
anhydrous acetonitrile cooled under argon to a
temperature of -10°C, and then treated with 300 mg
5   (2.3 millimoles) of nitronium tetrafluoroborate.
The reaction mixture was stirred for 10 minutes and
was then added to 8 ml of 1 molar aqueous potassium
carbonate. The mixture was stirred for 5 minutes.
The mixture was evaporated to dryness, triturated
10   with 10 ml of 1:1 acetone/ethyl acetate, filtered,
evaporated to dryness, and 0.15 grams of potassium
dinitramide was crystallized from 2 ml of butanol.

Example V

To show the stability and utility of the dinitramide
15   salts of the invention, Differential Scanning
Calorimetry (DSC) and Thermogravimetric Analysis
(TGA) tests were carried out to determine the
thermal stability of the compounds as well as the
energy derived from each compound. Acid and base
20   stability tests were also carried out to determine
the pH range at which the compounds were stable.
The results are shown in the following table:

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Table I

Dinitramide Salt	Cs^+ $N(NO_2)_2$	NH_4^+ $N(NO_2)_2$	$N_2H_5^+$ $N(NO_2)_2$
5 Onset of Decomposition	190°C	140°C	150°C
pH Stability	0-14	0-14*	0-10
Melting Point	83°C	92°C	83°C
10 Energy of Decomposition	62.4 KJ Mole	270 KJ Mole	258 KJ Mole

* loss of NH_3 above 10

Thus, the invention provides novel dinitramide salts
useful as oxidizers in rocket fuels and which
exhibit high temperature stability, high energy
15   density, and an absence of smoke generating halo-
gens. The dinitramide salts of the invention are
meltable and pumpable oxidizers which may be used in
start-stop rocket engines instead of other less
stable oxidizers.

20   Having thus described the invention what is claimed
is:

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1.   A N,N-dinitramide salt having the formula
MN(NO$_2$)$_2$ where M is a cation selected from the class
consisting of a metal ion and a nitrogen-containing
ion.

2.   The N,N-dinitramide salt of claim 1 wherein M is
a mono, di, or trivalent metal cation selected from
the class consisting of Li, Na, K, Rb, Cs, Ca, Ba,
Sr, Mg, Cu, Ag, Au, Zn, Cd, Hg, Al, Sc, Y, Ga, In,
5   Lanthanide elements (57-71), Ti, Zr, Hf, Ge, Sn, V,
Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Co, Ni, Ru, Rh,
Pd, Os, Ir, and Pt.

3.   The N,N-dinitramide salt of claim 2 wherein M is
a metal cation selected from the class consisting of
Li, Na, K, Be, and Mg.

4.   The N,N-dinitramide salt of claim 1 wherein M is
a 1-8 nitrogen-containing cation.

5.   The N,N-dinitramide salt of claim 1 wherein M is
a 1-8 nitrogen-containing cation having the formula
$R_k H_m N_z^{+z}$, wherein n = 1 to 8, k = 0 to 2+n, z = 1 to
n, m = n+2+z-k, and each R is the same or different
5   1-6 carbon straight chain or branched alkyl.

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6. The N,N-dinitramide salt of claim 1 wherein M is
a nitrogen-containing cation selected from the class
consisting of guanidinium; triaminoguanidinium;
nitronium; nitrosonium; a 1-10,000 nitrogen polymer
5   of ethyleneimine; cubane-1,4-bis ammonium ion;
cubane-1,2,4,7-tetra ammonium ion; cubane-1,2,3,4-
tetra ammonium ion; cubane-1,3,5,7-tetra ammonium
ion; cubane-1,2,3,4,7-penta ammonium ion; and
cubane-1,2,4,6,8-penta ammonium ion.

7. The N,N-dinitramide salt of claim 1 wherein said
salt is the reaction product of a nitramine compound
with a compound selected from the class consisting
of ammonia, hydrazine, and a salt having the formula
5   MX wherein X is an ion selected from the class
consisting of fluoride, chloride, hydroxyl, carbon-
ate, alkoxide, and carboxylate.

8. The N,N-dinitramide salt of claim 7 wherein said
salt is the reaction product of a dinitramine having
the formula $L_nZR'N(NO_2)_2$ with said MX compound,
wherein n is 1 to 3; L is the same or different 1-6
5   carbon alkyl, aryl, hydrogen, halogen, amine, or
ether group; Z is an element selected from the class
consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg;
and R' is a 1 to 6 carbon alkylene group; the M^+ ion
is selected from the class consisting of a metal
10 cation, a substituted ammonium cation, an ammonium
cation, a substituted hydrazinium cation, and a
hydrazinium cation; and the X anion is a halogen
ion selected from the class consisting of fluoride
and chloride ions.

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9. The N,N-dinitramide salt of claim 7 wherein said dinitramide salt is the reaction product of a nitr-amine compound having the formula NH_2NO_2 with a nitrating agent selected from the class consisting

5   of nitronium tetrafluoroborate, $(NO_2^+)_2(S_2O_7^{-2})$, NO_2^+ $AlCl_4^-$, N_2O_5, NO_2F, NO_2^+ PF_6^-, NO_2^+ AsF_6^-, NO_2^+ SbF_6^-, acetylnitrate, trifluoroacetylnitrate, trifluoro-acetylnitrate in combination with catalytic BF_3, acetonecyanohydrin nitrate in combination with

10   catalytic BF_3, and any one of these in combination with nitric acid, and to form an acid having the formula $HN(NO_2)_2$ which is then reacted with a com-pound selected from the class consisting of a metal-containing compound and a nitrogen-containing

15   compound to form said dinitramide salt having the formula $MN(NO_2)_2$.

10.   The N,N-dinitramide salt of claim 1 wherein said salt is the reaction product of a nitramine compound having the formula NH_2NO_2 with nitronium tetrafluoroborate to form an acid having the formula

5   $HN(NO_2)_2$, which is then reacted with a compound selected from the class consisting of a metal-containing compound and a nitrogen-containing compound to form said dinitramide salt having the formula $MN(NO_2)_2$.

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11.   A N,N-dinitramide salt having the formula
MN(NO$_2$)$_2$ where M is a cation selected from the class
consisting of:

5   a)   mono, di, and trivalent metal ions elected
         from the class consisting of Li, Na, K, Rb,
         Cs, Ca, Ba, Sr, Mg, Cu, Ag, and Au, Zn, Cd,
         Hg, Al, Sc, Y, Ga, In, Lanthanide elements
         (57-71), Ti, Zr, Hf, Ge, Sn, V, Nb, Ta, Cr,
         Mo, W, Mn, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, Os,
10   Ir, and Pt;

         b)   a 1-8 nitrogen-containing cation having
         the formula $R_kH_mN_n^{+z}$, wherein n = 1 to 8, k = 0
         to 2+n, z = 1 to n, m = n+2+z-k, and each R is
         the same or different 1-6 carbon straight
15   chain or branched alkyl; and

         c)   a nitrogen-containing cation selected from
         the class consisting of guanidinium; triamino-
         guanidinium; nitronium; nitrosonium; a 1-
         10,000 nitrogen polymer of ethyleneimine;
20   cubane-1,4-bis ammonium ion; cubane-1,2,4,7-
         tetra ammonium ion; cubane-1,2,3,4-tetra
         ammonium ion; cubane-1,3,5,7-tetra ammonium
         ion; cubane-1,2,3,4,7-penta ammonium ion; and
         cubane-1,2,4,6,8-penta ammonium ion.

12.   A method of making a N,N-dinitramide salt
having the formula MN(NO$_2$)$_2$ wherein M is a cation
selected from the class consisting of a metal cation
and a nitrogen-containing cation which comprises
5   reacting a dinitramine compound with a compound
selected from the class consisting of a metal-
containing compound and a nitrogen-containing
compound.

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13.   A method of making a N,N-dinitramide salt
having the formula $MN(NO_2)_2$ wherein M is a cation
selected from the class consisting of a metal cation
and a nitrogen-containing cation which comprises
5   reacting a dinitramine compound with a compound
selected from the class consisting of ammonia,
hydrazine, and a salt having the formula MX wherein
X is a halogen anion selected from the class con-
sisting of fluoride and chloride.

14.   The method of claim 13 which includes reacting
a dinitramine having the formula $L_4ZR'N_e(NO_2)_2$ with
said ammonia, hydrazine, or MX salt wherein n is 1
to 3; L is the same or different 1-6 carbon alkyl,
5   aryl, hydrogen, halogen, amine, or ether group; Z is
an element selected from the class consisting of Si,
Sn, Ge, As, B, Sb, Bi, Pb, and Hg; R' is a 1 to 6
carbon alkylene group; the M^+ ion is selected from
the class consisting of a metal cation, a substitut-
10   ed ammonium cation, an ammonium cation, a substitut-
ed hydrazinium cation, and a hydrazinium cation; and
the X anion is an ion selected from the class
consisting of fluoride, hydroxyl, carbonate, alkox-
ide, carboxyl, and chloride ions.

15.   The method of claim 14 wherein said dinitramine
having the formula $RN(NO_2)_2$ is formed from an ali-
phatic isocyanate having the formula R-N=C=O using
stoichiometric amounts of nitronium tetrafluoro-
5   borate and nitric acid in acetonitrile.

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16.   A method of making a N,N-dinitramide salt
having the formula $MN(NO_2)_2$ wherein M is a cation
selected from the class consisting of a metal cation
and a nitrogen-containing cation which comprises:
5   a)   reacting nitramide having the formula
         NH_2NO_2 with a nitrating agent to form an acid
         having the formula $HN(NO_2)_2$; and
         b)   reacting said acid with a compound select-
         ed from the class consisting of ammonia,
10   hydrazine, and a salt having the formula MX
         wherein X is a halogen anion selected from the
         class consisting of fluoride, hydroxyl, car-
         bonate, alkoxide, carboxyl, and chloride ions.

17.   The method of claim 16 wherein said step of
reacting nitramide with said nitrating agent further
comprises reacting said nitramide with a nitrating
agent selected from the class consisting of nitron-
5   ium tetrafluoroborate, $(NO_2^+)_2(S_2O_7^{-2})$, $NO_2^+ AlCl_4^-$, N_2O_5,
     NO_2F, $NO_2^+ PF_6^-$, $NO_2^+ AsF_6^-$, $NO_2^+ SbF_6^-$, acetylnitrate,
     trifluoroacetylnitrate, trifluoroacetylnitrate in
     combination with catalytic BF_3, acetonecyanohydrin
     nitrate in combination with catalytic BF_3, and any
10   one of these in combination with nitric acid, to
     form said acid having the formula $HN(NO_2)_2$.

18.   The method of making a N,N-dinitramide salt of
claim 16 which comprises:
         a)   reacting nitramide having the formula
         NH_2NO_2 with nitronium tetrafluoroborate to form
5   an acid having formula $HN(NO_2)_2$; and
         b)   reacting said acid with said salt having
         the formula MX.

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19.   The method of claim 16 wherein said step of
reacting said acid with a compound selected from the
class consisting of ammonia, hydrazine, and a salt
having the formula MX is carried out at a tempera-
5   ture of from about -40°C to about 150°C at ambient
pressure for a time period ranging from about 1
minute to about 168 hours.

20.   The method of claim 16 wherein said step of
reacting said acid with a compound selected from the
class consisting of ammonia, hydrazine, and a salt
having the formula MX is carried out at a tempera-
5   ture of from about 0°C to about 20°C at ambient
pressure for a time period ranging from about 1 hour
to about 2 hours.

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┌─────────────────────────────────────────┐
│       FORMING A DINITROAMINE HAVING      │
│    THE FORMULA RN(NO₂)₂ BY REACTING      │
│    AN ALIPHATIC ISOCYANATE HAVING A      │
│   FORMULA R-C=N=O WITH STOICHIOMETRIC    │
│        QUANTITIES OF NITRONIUM           │
│          TETRAFLUOROBORATE AND           │
│       NITRIC ACID IN ACETONITRILE        │
└─────────────────────────────────────────┘
                     │
                     │
┌─────────────────────────────────────────┐
│   REACTING EITHER A DINITRAMINE HAVING   │
│     THE FORMULA RN(NO₂)₂ OR AN ACID      │
│     HAVING THE FORMULA HN(NO₂)₂ WITH     │
│   AMMONIA, HYDRAZINE, OR A SALT HAVING   │
│        THE FORMULA MX TO FORM A          │
│        DINITROAMIDE SALT HAVING THE      │
│     FORMULA MN(NO₂)₂ WHERE M IS A        │
│      METAL CATION OR A NITROGEN-         │
│      CONTAINING CATION AND X IS A        │
│     FLUORIDE, CHLORIDE, HYDROXYL,        │
│ CARBONATE, ALKOXIDE, OR CARBOXYL ANION   │
└─────────────────────────────────────────┘
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I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5   C01B21/082 ; C06B41/00 ; C06B25/00 ; C06B25/10

II. FIELDS SEARCHED

Minimum Documentation Searched[7]	
Classification System	Classification Symbols
Int.Cl. 5	C01B ; C06B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	GB,A,1 126 591 (AEROJET-GENERAL CORP.) December 5, 1968 see the whole document	1,4
A	see page 1, line 44 - line 63	7,9,10, 12,13, 16-20
	& US,A,3 428 667 (HAMEL ET AL.) February 18, 1969 cited in the application ---	
A	EP,A,324 609 (MORTON THIOKOL) July 19, 1989 cited in the application see the whole document ---	6,11

* Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 OCTOBER 1991	24 OCT 1991

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	WIM E. ZALM

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US   9104268
SA   48808

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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14/10/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-1126591		US-A- 3428667	18-02-69
EP-A-324609	19-07-89	US-A- 4878968	07-11-89
		AU-A- 2841189	13-07-89
		JP-A- 2000741	05-01-90

APPENDIX D

A NEW OXIDE OF NITROGEN:
THE DINITRAMIDE ANION AND ITS SALTS

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ABSTRACT

We have synthesized a completely new, stable class of inorganic salts that will have both fundamental scientific interest and practical applications. These salts are based on a newly discovered inorganic anion known as the dinitramide anion, $N(NO_2)_2^-$. The dinitramide anion is a uniquely stable, high oxygen density grouping that can be prepared in many different salt combinations including the ammonium or hydrazinium salts.
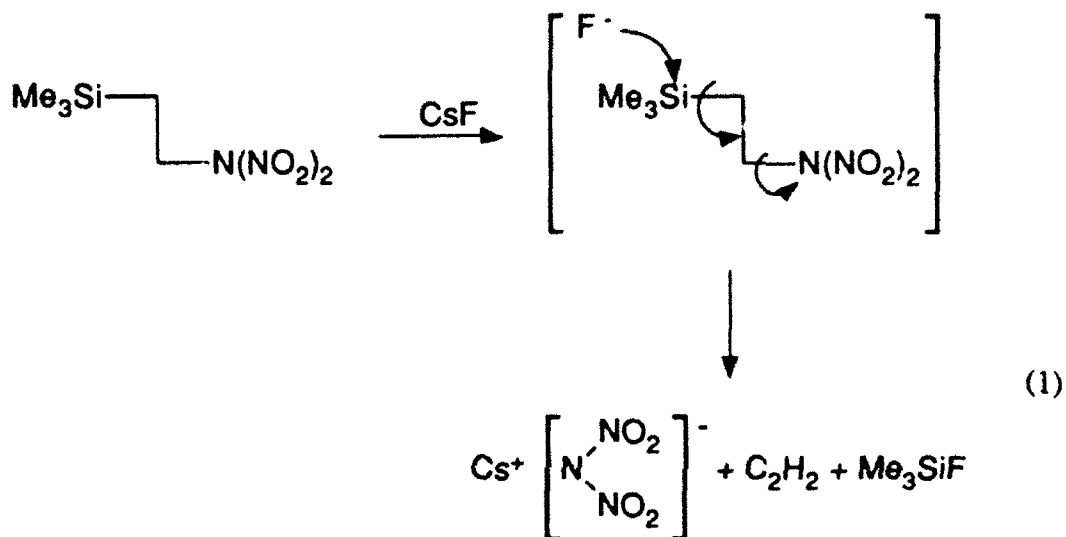
SUMMARY

We have synthesized a completely new, stable class of inorganic salts based on a newly discovered inorganic anion known as the dinitramide anion, $N(NO_2)_2^-$ that will have both fundamental scientific interest and practical applications.


The field of nitrogen oxide chemistry is considered a mature,[1] well-developed area where it is not expected that any breakthroughs will occur.[2,3] We report here the synthesis of a completely new, stable class of nitrogen oxide salts that will have both fundamental scientific interest and as well as potential practical applications. These salts are based on a newly discovered inorganic anion we have named the dinitramide anion, $N(NO_2)_2^-$.[4] Dinitramide is a uniquely stable, high oxygen density grouping has been prepared with many different counterions including the cesium, ammonium, or hydrazinium salts. The dinitramide ion is less thermally and shock stable than ammonium nitrate, but considerably more stable than the related alkyldinitramines $(R-N(NO_2)_2)$[5,6] or nitramide.[7,8,9] A

potential practical use for this compound is as a replacement for oxidizers such as ammonium perchlorate to give an environmentally clean propellant system, eliminating the emission of chloride from rocket motors or as a gas generating species for air bag applications.
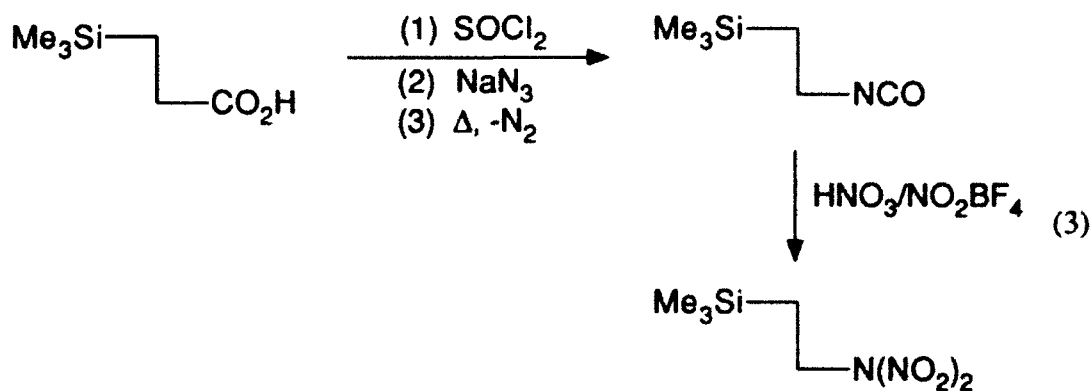
Dinitramide salts are synthesized by a β-elimination reaction with cesium fluoride ion and 1-(N,N-dinitramino)-2-trimethylsilylethane. The fluoride ion catalyzes an elimination of trimethylsilylfluoride, ethylene, and the desired cesium dinitramide (eq. 1).

$$Me_3Si-\!\!\!-N(NO_2)_2 \xrightarrow{\text{CsF}} \left[F^- \curvearrowright Me_3Si\!\!\!-\!\!\!-N(NO_2)_2 \right] \qquad (1)$$

$$\downarrow$$

$$Cs^+ \left[N \begin{array}{c} NO_2 \\ NO_2 \end{array} \right]^- + C_2H_2 + Me_3SiF$$

Substitution of cesium by other cations is done by either using alternative fluoride salts (M^+F^-) in the elimination reaction or by ion-exchange (eq. 2). Several other salts have been prepared using these methods including the ammonium, hydrazinium, sodium, and potassium. The structure of dinitramide salts has been determined by x-ray crystallography and will be discussed separately.[10]

$$CsN(NO_2)_2 \xrightarrow[\text{Ion Exchange}]{M^+} M^+ N(NO_2)_2^- \qquad (2)$$
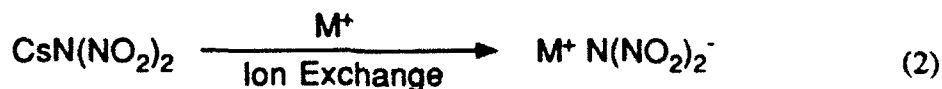
1-(N,N-Dinitramino)-2-trimethylsilylethane is synthesized by recently discovered reaction between an isocyanate and a mixture of nitric acid and nitronium tetrafluoroborate (eq. 3).[11]

$$\text{Me}_3\text{Si}-\text{CO}_2\text{H} \quad \xrightarrow[\substack{(2)\ \text{NaN}_3 \\ (3)\ \Delta,\ \text{-N}_2}]{(1)\ \text{SOCl}_2} \quad \text{Me}_3\text{Si}-\text{NCO}$$

$$\Big\downarrow \text{HNO}_3/\text{NO}_2\text{BF}_4 \qquad (3)$$

$$\text{Me}_3\text{Si}-\text{N(NO}_2)_2$$

Dinitramide has improved acid, base, oxidative, thermal and shock stability when compared to alkyl-dinitramines, nitramide, or primary nitramines, but is less stable than the nitrate or nitrite ions. We believe that the observed stability is due to the presence of an overall negative charge that is distributed by resonance over the entire molecular system, thus strengthening those N-NO$_2$ bonds most susceptible to rupture. Some of the resonance forms are shown below (figure 1).
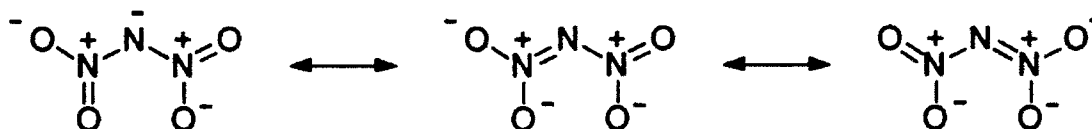

Figure 1. Representative Resonance Structures of the Dinitramide Ion

We have begun initial investigations of the chemical reactions of the dinitramide anion.[12] The reaction of cesium dinitramide with methyl triflate gives a 40% yield of methyl dinitramine, identified by comparison with a known sample. We see that to a large extent the dinitramide anion reacts at the central nitrogen, demonstrating a significant electron density at this site. The other products have not yet been analyzed in detail but are likely to result from reaction via attack at the oxygens.

$$\text{CsN(NO}_2)_2 \ + \ \text{CH}_3\text{OSO}_2\text{CF}_3 \quad \longrightarrow \quad \text{CH}_3-\text{N(NO}_2)_2 \qquad (4)$$
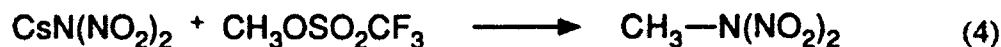
Cesium dinitramide has a melting point of 87°C followed by an onset of an exothermic decomposition at 175°C (DSC). Its density is 3.05 g/cm^3 (x-ray). Cesium dinitramide has a UV maximum at 284 nm (ε (H$_2$O) = 4.24 x 10^3 l mol^{-1} cm^{-1}). The dinitramide ion is stable to base and only begins to decompose in acid slowly acid 12 M H$_2$SO$_4$ at room temperature. Preliminary measurements show that the rate of decomposition of the dinitramide ion in nitric acid is dependent on the purity of the nitric acid. A solution of ammonium dinitramide in 70% nitric acid has a half life of about 3 hrs. Purification of the nitric acid by addition of a small amount of urea[13] increases the $t_{1/2}$ to 14 hours. Thus, the rate of decomposition of dinitramide in nitric acid is significantly slowed by removal of NO$^+$ or NO$_x$ species from nitric acid solutions. This result indicates a greater susceptibility to a one-electron oxidation rather than an acid catalyzed decomposition in nitric acid. Further studies of the thermal and solution properties of this anion are underway.

Caution: All dinitramide salts and alkyl dinitramines are potentially hazardous materials that are both thermally and shock sensitive. These compounds are strong oxidizers and can be explosive under certain conditions. Use extreme care when handling these materials.

SUPPLEMENTARY MATERIALS
EXPERIMENTAL PROCEDURES

Caution: All dinitramide salts and alkyl dinitramines are potentially hazardous materials that are both thermally and shock sensitive. These compounds are strong oxidizers and can be explosive under certain conditions. Use extreme care when handling these materials.

Synthesis of 2-(trimethylsilylethyl)-N,N-dinitramine

To form the 2-(trimethylsilylethyl)-N,N-dinitramine precursor, an ice-cooled mixture of 1.45 grams (11 millimoles) of nitronium tetrafluoroborate, 10 ml of acetonitrile, and 700 milligrams (11 millimoles) of 99+% HNO_3 (under argon) was formed, and then 10 millimoles of 2-(trimethylsilylethyl)isocyanate was added, avoiding fume-off by controlling the rate of addition as appropriate. The reaction was stirred for 15 minutes at O°C, diluted to 25 ml with $CHCl_3$, and filtered rapidly through a 1" x 3" plug of SiO_2, eluting with 100 ml of $CHCl_3$. Chromatography of the crude product, eluting $CHCl_3$ over SiO_2 and collecting the fastest-moving, UV active material ($R_f = 0.5$), resulted in collection of 500 milligrams of the desired 2-(trimethylsilylethyl)-N,N-dinitramine precursor, about a 25% yield.

Synthesis of Cesium Dinitramide

To about 2.5 milliliters of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed in Example I, dissolved in 20 ml of acetonitrile and maintained at 20 C was added 1 gram of cesium fluoride. The solution was stirred for about 120 minutes. The cesium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate. The product yield was 900 milligrams or about a 50% yield.

Synthesis of Other Dinitramide Salts by Ion Exchange

All desired dinitramide salts can be prepared by ion exchange starting from cesium dinitramide and using AMBERLYST 15 Sulfonic Acid Resin charged with the appropriate cation: Elution is performed using a methanolic solution of cesium dinitramide over a large excess of the charged resin.

In a typical example, 10 g of AMBERLYST 15 (sulfonic acid resin) was suspended in 100 mL of CH_3OH, treated with 5 mL of 95% hydrazine, filtered, and washed with 100 mL of CH_3OH. This 10 g of material was then placed into a 4 x 0.5 inch column and eluted with at solution of 200 mg of cesium dinitramide in 5 mL of CH_3OH, followed by washing with an additional 20 mL of CH_3OH. Concentration of the effluent gave approximately 100 mg of pure hydrazinium dinitramide (SRI-13) after crystallization from CH_3CN. **These materials are shock sensitive and one should exercise caution in handling.**

APPENDIX E

Gas phase chemistry of dinitramide and nitroacetylide ions*

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ABSTRACT

Using the tandem flowing afterglow-selected-ion flow tube, we have examined the basicity, reactivity, electron binding energy and collision-induced dissociation of two novel nitro species. the dinitramide ion ($N(NO_2)_2^-$) and the nitroacetylide ion ($O_2NC\equiv C^-$). Dinitraminic acid is among the strongest known gas phase acids with $\Delta H^\circ_{acid} \leqslant 310\,\text{kcal mol}^{-1}$. The conjugate base, dinitramide anion, has a high electron binding energy. is extremely unreactive and is a very poor nucleophile. Collision-induced dissociation of dinitramide anion generates the $O_2N=N^-$ anion. Nitroacetylene is a moderately strong acid with $\Delta H^\circ_{acid} = 354 \pm 4\,\text{kcal mol}^{-1}$; this value is similar to those of other nitro compounds and substituted acetylenes. The nitroacetylide ion is generally unreactive but exhibits a rich chemistry upon reaction with hydrogen sulfide. The anion has a high electron binding energy and generates four ions upon collision-induced dissociation, ONC^-, C_2^-, C_2O^-, and CN^-.

Keywords: dinitramide ion; nitroacetylide ion; gas phase chemistry; flowing afterglow; SIFT.

INTRODUCTION

There has been considerable theoretical and experimental interest in the chemistry and stability of nitro compounds, owing to their importance as explosives and propellants. In this paper we report gas phase studies of the basicity, electron binding energy and chemistry of two new nitro species, the dinitramide and nitroacetylide ions. The first synthesis of the dinitramide ion [1] and a practical synthesis of the nitroacetylide ion [2] were recently introduced by Schmitt and co-workers. However, no fundamental properties have been reported for either of these species.

The dinitramide ion is a new oxide of nitrogen [3]. This species exhibits surprising stability (acid–base, oxidative, thermal and shock) when compared
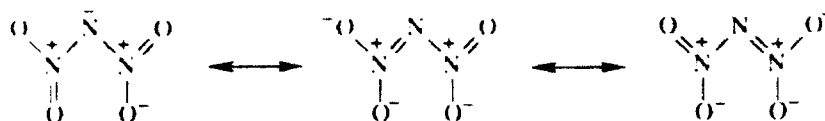
Fig. 1. Representative resonance structures of the dinitramide ion.

with alkyl dinitramines, nitramide, or primary nitramines, but is less stable than the nitrate or nitrite ions. The high stability is attributed to the resonance delocalization of the net negative charge over the molecular system which strengthens those $N-NO_2$ bonds that are most susceptible to rupture. Some of the resonance forms are shown in Fig. 1 which illustrates the conjugation between the nitro groups and the central nitrogen. This study explores and characterizes the stability and chemistry of this species in the gas phase.

Nitroacetylenes [4] are the least stable and least characterized of the nitro-carbons. Until our recent synthetic work, there were no nitroacetylenes known with sufficient stability to allow an investigation of their properties. This study of the thermochemistry and reactivity of the nitroacetylide ion (Fig. 2) in the gas phase allows comparison with the properties of other acetylenes and nitro-substituted compounds.

EXPERIMENTAL

These studies were carried out in a tandem flowing afterglow-selected-ion flow tube (FA-SIFT), which has been described in detail previously [5]. The experiments were conducted at room temperature and at a helium buffer gas pressure of 0.5 Torr. Dinitramide ion was formed by electron impact of dinitraminic acid. The acid was obtained by displacement of the ammonium salt by p-toluenesulfonic acid from a solution of $NH_4N(NO_2)_2$ in ethanol. These reagents were combined in a glass flask which was connected to the flowing afterglow ion source and the dinitraminic acid was distilled directly into the flow tube.

$$HN_3O_4 \xrightarrow{\epsilon} N(NO_2)_2^- + H^+$$
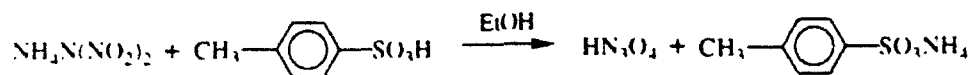
Nitroacetylide ion was prepared by the gas phase ion/molecule reaction [6] of
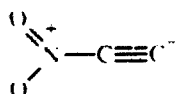
Fig. 2. The nitroacetylide ion.

E-2

F^- with 1-tri(isopropylsilyl)-2-nitroacetylene:

$$[(CH_3)_2CH]_3Si - C\equiv C - NO_2 + F^- \longrightarrow [(CH_3)_2CH]_3SiF + {}^-C\equiv C - NO_2$$
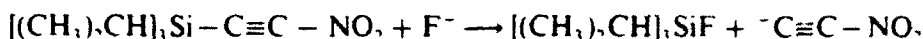
Caution: All dinitramide salts, nitroacetylenes, and alkyldinitramines are potentially hazardous materials that are both thermally and shock sensitive. These compounds are strong oxidizers and can be explosive under certain conditions. Extreme care must be used when handling these materials.

The HSO_4^- ion was generated by electron impact of sulfuric acid which had been deposited on the accelerating grid of the ionizer. All other reactant ions were formed by standard procedures. The reactant ions were then mass-selected and injected into the reaction flow tube, in the absence of other ionic and neutral species.

Gases were obtained from commercial sources and were of the following purities: He, 99.995%; NF_3, 99.5%; CO_2, 99.5%; SO_2, 99.9%; NO_2, 99.99%; H_2S, 99.5%; HCl, 99.0%; HBr, 99.8%; HI, 98.0% min; Cl_2, 99.5%; Br_2, 99.5%; O_2, 99.98%; CH_3SH, 99.5%; and HCCH, 99.6%. The other reagents were obtained from commercial sources and were purified as necessary before use. The helium buffer gas was passed through a liquid nitrogen-cooled molecular sieve trap before entering the flow tubes.
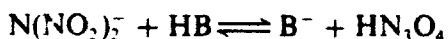
RESULTS AND DISCUSSION

Dinitramide anion

Acidity

The gas phase acidity of dinitraminic acid is the enthalpy of heterolytic bond dissociation:

$$HN_3O_4 \longrightarrow H^+ + N(NO_2)_2^- \qquad \Delta H^\circ_{acid} (HN_3O_4)$$
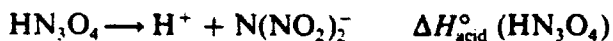
This value can be measured by comparing the proton transfer abilities of dinitraminic acid and dinitramide anion with species [HB] of known gas phase acidity [7]:

$$N(NO_2)_2^- + HB \rightleftharpoons B^- + HN_3O_4$$

Thus the occurrence of proton abstraction in the reaction $N(NO_2)_2^- + HB$ would indicate that HB is more acidic than HN_3O_4 whereas proton abstraction in the reverse reaction would indicate that HN_3O_4 is more acidic than HB. The absence of proton transfer suggests that the reaction of interest is endoergic although kinetic barriers can sometimes diminish reactivity.

The dinitramide anion does not react with the following molecules listed in order of increasing acid strength (ΔH°_{acid} in kcal mol^{-1}) [Reference 8 is the

source of all thermochemical values used in this paper, unless otherwise noted]: H_2O (390.8); $CH_3C(O)CH_3$ (369.0); HCl (333.4); and HBr (323.6). With HI (314.3), the cluster ion $N(NO_2)_2^- \cdot HI$ is formed in a relatively slow reaction and only a minute trace of I^- is detected. These studies suggest that the dinitramide anion is extremely stable and that dinitraminic acid is highly acidic in the gas phase. Therefore, bases on the extreme end of the known acidity scale [8] were allowed to interact with dinitraminic acid (ΔH°_{acid} of the conjugate acids listed in parentheses): NO_3^- (324.6); I^- (314.3); and HSO_4^- (309.5) [9]. These anions initiate facile proton abstraction indicating that ΔH°_{acid} $(HN_3O_4) \leqslant 310$ kcal mol^{-1}. In an attempt to further characterize the acidity, we examined the reaction of dinitraminic acid with $NO_3^- \cdot HNO_3$. The ΔH°_{acid} value [9] for this cluster ion is 308 kcal mol^{-1} to generate the dimer $HNO_3 \cdot HNO_3$ and 299 kcal mol^{-1} to generate $2HNO_3$. Reaction occurs by ligand switching:

$$NO_3^- \cdot HNO_3 + HN_3O_4 \longrightarrow NO_3^- \cdot HN_3O_4 + HNO_3$$
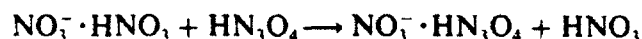
A small amount of $N(NO_2)_2^-$ is also observed but this ion appears to be generated by the NO_3^- which is initially present and which is formed by collision-induced dissociation of the injected $NO_3^- \cdot HNO_3$ cluster. The apparent lack of proton abstraction by $NO_3^- \cdot HNO_3$ suggests that ΔH°_{acid} $(HN_3O_4) > 299$ kcal mol^{-1} but further experiments are required to confirm this result. In any event, dinitraminic acid is among the most acidic of known gas phase acids.

There are two possible locations of the hydrogen in dinitraminic acid: on the central nitrogen (1); or on one of the oxygens (2). While there is only one stable nitro form, there are several stable conformers of the aci form (2) [10].

(1)   (2)
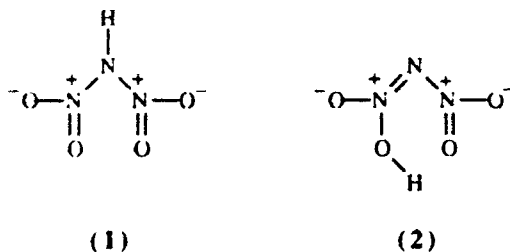
Recent ab initio calculations of Michels and Montgomery [10] indicate that structure 1 is the more stable form, lying 9.4 kcal mol^{-1} lower in energy than structure 2. They determined the gas phase acidities of isomers 1 and 2 as 312.0 (± 2) and 302.6 (± 2) kcal mol^{-1} respectively. Both these values are sufficiently close to our experimental determination that it is not possible to unambiguously identify the structure of HN_3O_4 that is generated and studied in our experiments. However, the reaction of dinitraminic acid with SO_2

suggests the presence of form **2**. This reaction generates two products, HSO_4^- by OH abstraction and $N(NO_2)_2^-$ by proton abstraction:

$$SO_3^- + HN_3O_4 \begin{cases} \longrightarrow HSO_4^- + N_3O_3 \\ \\ \longrightarrow N(NO_2)_2^- + HSO_3 \end{cases}$$
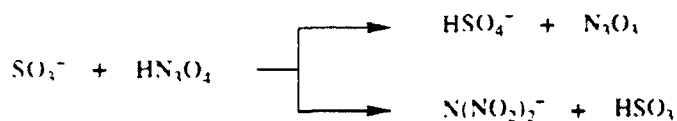
HSO_4^- probably results from a direct hydroxy abstraction from structure **2** rather than by a two-step process with sequential oxygen atom and hydrogen atom abstraction from structure **1**.
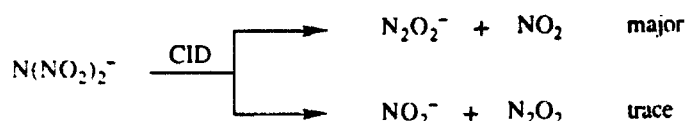
Reactivity

Dinitramide is extremely unreactive in the gas phase and is a very poor nucleophile. The reaction of dinitramide with $(CH_3)_3SiCl$ [11] gives only a trace of cluster and no nucleophilic displacement is observed. Dinitramide does not react with O_2, CO_2, CS_2, or SO_2 and yields only a trace of cluster ion product in reaction with BrCN.

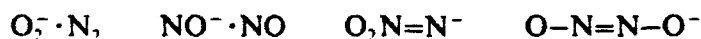Similarly, dinitramide does not undergo electron transfer with several species with moderately high electron affinities (EAs) [8]: NO_2 (EA = 2.27 eV); Cl_2 (EA = 2.38 eV); and Br_2 (EA = 2.55 eV). The reaction of dinitramide with Cl_2 does yield a trace of Cl^- and $O_2N=N-Cl^-$. Since electron transfer is usually facile when exoergic, these results suggest EA $[N(NO_2)_2] > 2.55$ eV. Indeed, Michels and Montgomery [10] estimate that the electron affinity of the $N(NO_2)_2$ radical is 5.0 (± 0.5) eV.

Collision-induced dissociation

For the studies of the acidity and reactivity of dinitramide, the anion is injected into the reaction flow tube at low energies to avoid dissociation or excitation of this species. However, the potential difference between the ion source and the venturi inlet can be increased so that the injected ions undergo higher energy collisions with helium and thus suffer some collision-induced dissociation (CID). CID of $N(NO_2)_2^-$ produces $N_2O_2^-$ at m/z 60 as the major product as well as a trace of NO_2^- at m/z 46:

$$N(NO_2)_2^- \xrightarrow{\text{CID}} \begin{cases} \longrightarrow N_2O_2^- + NO_2 \quad \text{major} \\ \\ \longrightarrow NO_2^- + N_2O_2 \quad \text{trace} \end{cases}$$

There are four possible structures of the $N_2O_2^-$ anion:

$$O_2^- \cdot N_2 \qquad NO^- \cdot NO \qquad O_2N=N^- \qquad O-N=N-O^-$$

Posey and Johnson [12] have identified the first three forms in their study of the photoelectron spectroscopy of negative cluster ions. The latter two structures have been implicated [13,14] as intermediates in the gas phase

reaction O^- + N_2O and have also been identified in matrix isolation studies of $N_2O_2^-$ [15]. The $O_2N=N^-$ isomer is the most likely product of the CID of $N(NO_2)_2^-$ as it can arise from simple bond cleavage without rearrangement. Moreover, the $O_2N=N^-$ isomer is presumably the most thermodynamically stable form; the nitro group provides charge stabilization and this species resembles the isoelectronic, highly stable CO_2^- structure.
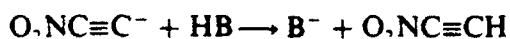
Nitroacetylide anion

Acidity

The gas phase acidity of nitroacetylene

$$O_2NC\equiv CH \longrightarrow H^+ + O_2NC\equiv C^- \qquad \Delta H^\circ_{acid} (O_2NC_2H)$$

was bracketed by studying the proton transfer reactions of nitroacetylide anion with a series of known acids [8]:

$$O_2NC\equiv C^- + HB \longrightarrow B^- + O_2NC\equiv CH$$

The reverse reactions cannot be examined since the parent acid $O_2NC\equiv CH$ is unknown and will probably exist only at low temperatures if at all. There was a clear cut-off in the ability of nitroacetylide to proton abstract. It fails to abstract a proton from $HC\equiv CH$ (377.8) [16], CCl_3H (357.1), CH_3SH (356.8), and CH_3NO_2 (356.4) but it does proton abstract from $(CH_3)_3CSH$ (352.5), H_2S (351.1), CH_3CO_2H (348.7), HCO_2H (345.1) $CH_3C(O)CH_2$ $C(O)CH_3$ (343.7), HCl (333.4), and HI (314.3). These results allow us to assign ΔH°_{acid} ($O_2NC\equiv CH$) as 354 ± 4 kcal mol^{-1}. The rather large error bars reflect both the uncertainty in the acidities of the bracketing acids as well as our inability to examine proton transfer in both directions. Nitroacetylene is thus 24 kcal mol^{-1} more acidic than acetylene but its acidity is very similar to those of other nitro compounds [CH_3NO_2 (356.4), $(CH_3)_2CHNO_2$ (356.1), CH_3 CH_2NO_2 (356.0), and $(CH_3)_3CCH_2NO_2$ (355.2)] and other substituted acetylenes [$CF_3C\equiv CH$ (355.2) and $NCC\equiv CH$ (350.8)].
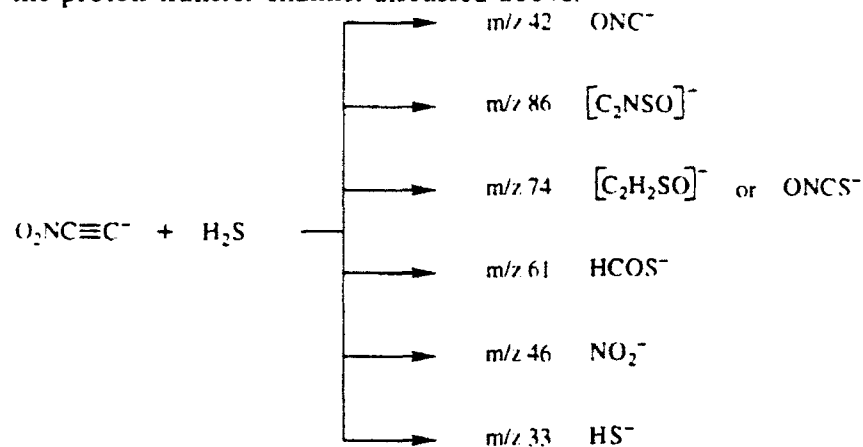
In the course of these studies we also examined the reactions of nitroacetylide anion with three fluorine-containing acids: $(CF_3)_2CHOH$ (344.9); CF_3HCO_2H (330.8); and CF_3CO_2H (322.9). Although proton transfer is exoergic in each case, little or no proton abstraction was observed. Instead, there was a decrease in the total ion signal, suggesting that some form of electron detachment is occurring.

Reactivity

Although nitroacetylide is moderately basic, it is relatively unreactive in the gas phase. Thus it undergoes slow nucleophilic displacement reactions with CH_3I and $(CH_3)_3SiCl$ and is completely unreactive with O_2, CO_2, $C^{34}S_2$, and

C_6F_6. With SO_2, adduct formation is observed. The reaction of nitroacetylide anion with Br_2 generates Br^- but yields no electron transfer product, suggesting that EA ($O_2NC\equiv C$) > 2.55 eV.

Quite surprisingly nitroacetylide reacts extensively with H_2S, in addition to the proton transfer channel discussed above:
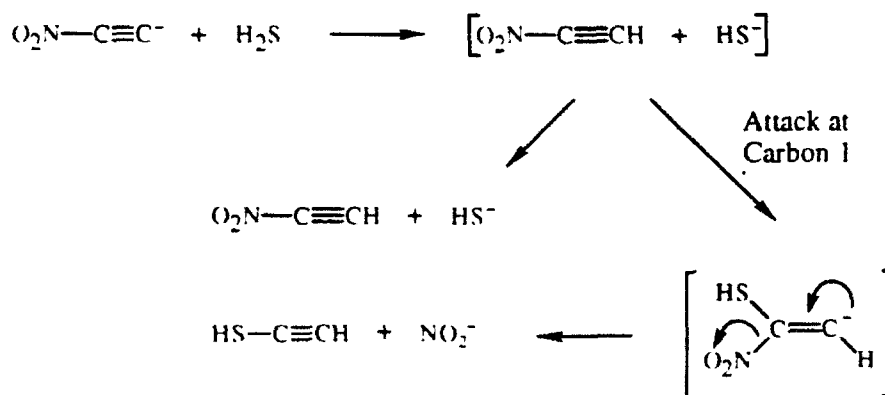
$$O_2NC\equiv C^- + H_2S \longrightarrow$$

m/z 42	ONC^-	
m/z 86	$[C_2NSO]^-$	
m/z 74	$[C_2H_2SO]^-$	or $ONCS^-$
m/z 61	$HCOS^-$	
m/z 46	NO_2^-	
m/z 33	HS^-	

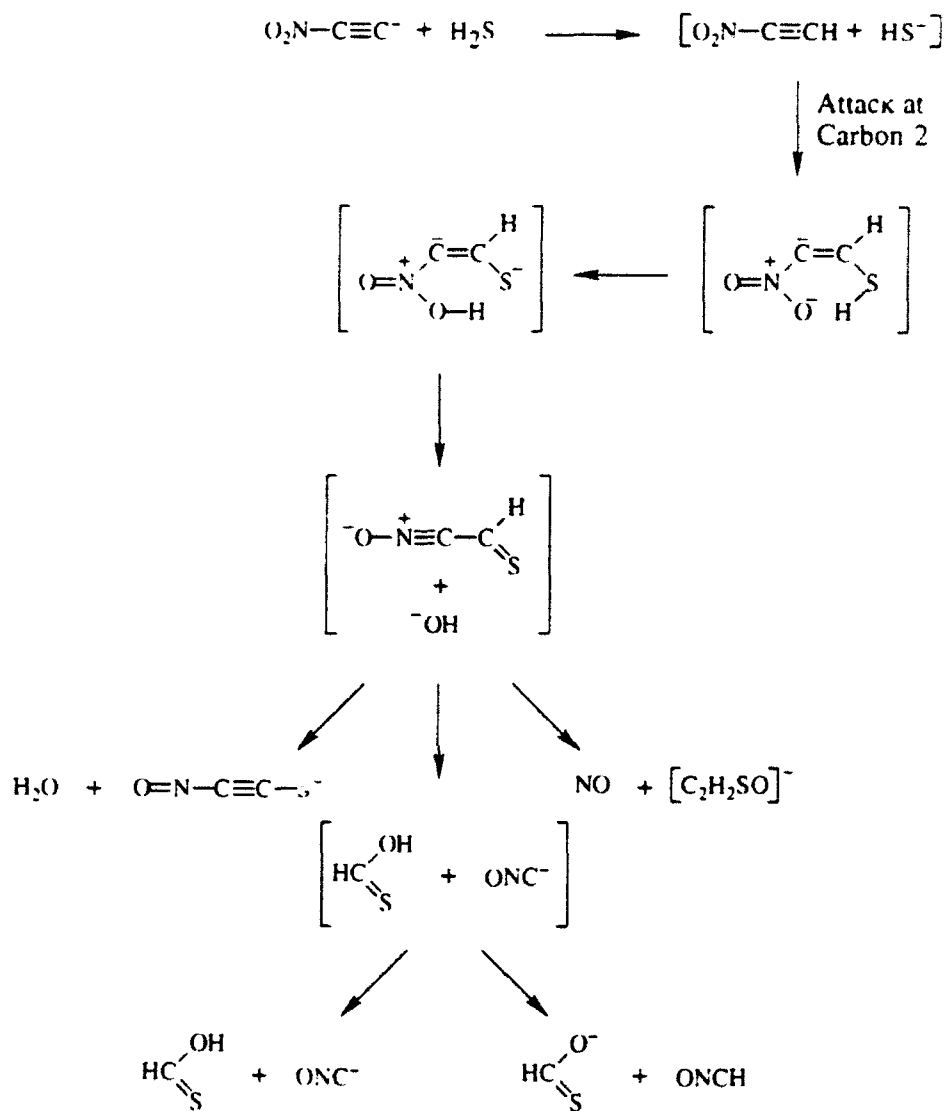The product channels are listed in decreasing order of their importance.

Nitroacetylene is only 3 kcal mol^{-1} less acidic than hydrogen sulfide. We propose that the first step in this reaction is the deprotonation of H_2S to generate HS^- which can be lost from the reaction complex. Alternatively, HS^- can attack any of three electrophilic centers in nitroacetylene: carbon 1 (α to the nitro group); carbon 2; or the nitrogen of the nitro group.

Attack at carbon 1 by HS^- gives an initial addition complex, which then rearranges to generate NO_2^- and $HSC\equiv CH$ as shown in Scheme 1.

Attack by HS^- at carbon 2 (Scheme 2) initiates a more complicated mechanism which yields four products, ONC^-, $HCOS^-$, $[ONCCS]^-$, and
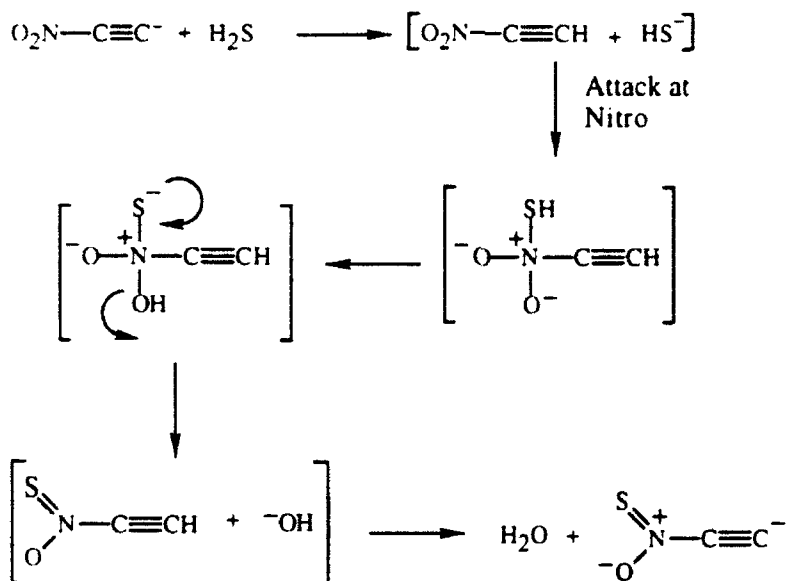
$$O_2N-C\equiv C^- + H_2S \longrightarrow [O_2N-C\equiv CH + HS^-]$$

Attack at Carbon 1

$$O_2N-C\equiv CH + HS^-$$

$$HS-C\equiv CH + NO_2^- \longleftarrow \left[\begin{array}{c} HS \\ O_2N \end{array} C=C \begin{array}{c} \\ H \end{array} \right]$$

Scheme 1. Reaction at carbon 1 by HS^-.

$$O_2N-C\equiv C^- + H_2S \longrightarrow \left[O_2N-C\equiv CH + HS^-\right]$$

Attack at
Carbon 2

Scheme 2. Reaction at carbon 2 by HS⁻.

$[C_2H_2SO]^-$. The initial attack at carbon 2 gives an addition complex which first undergoes proton transfer to oxygen and then loses OH^-. The hydroxy group can then either proton abstract to generate $ONCCS^-$, attack at carbon 2 leading to either ONC^- or $HC(S)O^-$, or attack at carbon 1 leading to $[C_2H_2SO]^-$.

Since only the mass-to-charge ratios of the product ions are determined, their compositions and structures can not be unambiguously identified. For

$$O_2N—C≡C^- + H_2S \longrightarrow [O_2N—C≡CH + HS^-]$$

Attack at
Nitro

$$\left[\begin{array}{c} ^-O—\overset{+}{N}—C≡CH \\ \end{array}\right] \longleftarrow \left[\begin{array}{c} ^-O—\overset{+}{N}—C≡CH \\ | \\ O^- \end{array}\right]$$

$$\left[\begin{array}{c} S \\ \diagdown \\ N—C≡CH \ + \ ^-OH \\ O \diagup \end{array}\right] \longrightarrow H_2O + \begin{array}{c} S \\ \diagdown \overset{+}{N}—C≡C^- \\ ^-O \diagup \end{array}$$

Scheme 3. Attack at nitro group by HS⁻.

example, ONC⁻ may be NCO⁻ and the product ion at m/z 74 may have the structure ONCS⁻ rather than that given in Scheme 2. However, there are no obvious mechanisms for generating these latter species.

Scheme 3 presents an alternative route to m/z 86, giving a second possible isomer. HS⁻ can attack at the nitro group to form an intermediate complex that rearranges to lose OH⁻. Hydroxide then proton abstracts from the thionitroacetylene to give O(S)NCC⁻ and water.

The proposed mechanism is complicated but accounts for all of the observed products.

Collision-induced dissociation

CID of nitroacetylide anion yields four ionic products, listed in order of decreasing abundance:

$$O_2N—C≡C^- \xrightarrow{CID} \begin{cases} ONC^- + CO \\ C_2^- + NO_2 \\ C_2O^- + NO \\ CN^- + CO_2 \end{cases}$$
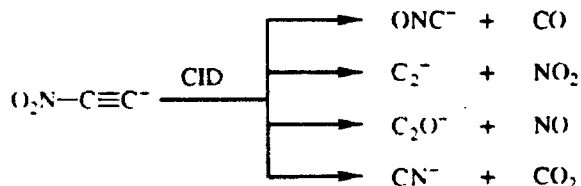
In each case, stable neutral species are generated. With the exception of the second channel, and in contrast to the CID of dinitramide, rearrangements must occur during the dissociation process. A proposed mechanism for decomposition is shown in Scheme 4.
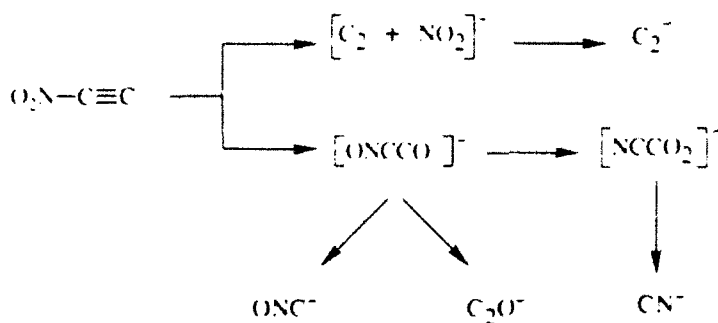
Scheme 4. CID of nitroacetylide.

It is interesting to note that in the simple bond cleavage which generates C_2^- + NO_2, the electron exclusively leaves with the species of higher electron affinity (EA (C_2) = 3.39 eV, EA (NO_2) = 2.27 eV [8]).

We also carried out CID of the m/z 86 product of the reaction of nitroacetylide with hydrogen sulfide, in an attempt to distinguish between the two possible isomeric structures for this species coming from attack of HS⁻ either at carbon 2 or at the nitro group:

$$O=N-C\equiv C-S^-$$

$$\begin{array}{c} ^-O \\ \diagdown \\ /N-C\equiv C^- \\ S \end{array}$$

This ion was therefore generated in the flowing afterglow ion source by the reaction $O_2NC\equiv C^-$ + H_2S, mass-selected, and injected into the second flow tube. In contrast to the decomposition of $O_2NC\equiv C^-$, CID cleanly generates only one product ion, ONC⁻. The absence of C_2^-, which could form by simple bond cleavage of the second structure, in analogy with CID of nitroacetylide, argues in favor of $O=N-C\equiv C-S^-$ as the structure of the m/z 86 product (attack by HS⁻ at carbon 2).

CONCLUSIONS

We have characterized the basicity, reactivity, electron binding energy and CID of the dinitramide ion ($N(NO_2)_2^-$) and the nitroacetylide ion ($O_2NC\equiv C^-$) using the tandem FA-SIFT instrument. The dinitramide anion is an exceptionally stable, resonance-delocalized species. Thus it is extremely unreactive toward a wide variety of reagents, possesses a high electron binding energy and a very low basicity (ΔH^0_{acid} (HN$_3$O$_4$) < 310 kcal mol⁻¹). CID proceeds by simple nitrogen–nitrogen bond cleavage to generate the $O_2N=N^-$ ion. The nitroacetylide ion is slightly more reactive and exhibits a wide array

of product channels with H_2S. This anion possesses a high electron binding energy and a moderate basicity (ΔH^o_{acid} ($O_2NC{\equiv}CH$) = 354 ± 4 kcal mol^{-1}) which is remarkably similar to that of other acetylide and nitro anions. In contrast to $N(NO_2)_2^-$, $O_2NC{\equiv}C^-$ undergoes considerable rearrangement in the CID process and generates four ionic products, ONC^-, C_2^-, C_2O^-, and CN^-. These studies provide the first experimental characterization of the properties of these novel nitro anions.

ACKNOWLEDGMENTS

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