
Synthesis of New High Energy Density Matter (HEDM): Extra High Energy Oxidizers and Fuels

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14. ABSTRACT This program focused on the discovery and synthesis of new, extra-high energy oxidizers and fuels for the High Energy Density Matter (HEDM) program. The goals included the preparation of new compounds having unusual bonding to yield high energy, dense materials for propellant applications. The specific objectives for this program were (1) to develop new fuels and oxidizers for propellant applications. The materials must be simple to make (cubane is difficult); be storable and usable; have significantly improved performance over conventional materials; develop burn rate accelerators to improve and accelerate combustion. (2) Invent new compositions of matter to meet needs of the program. The requirements for the new materials included simplicity of synthesis and good long-term stability to make these material candidates for propellant applications. The work was directed primarily toward the synthesis of highly energetic fuels and fuel additives because this area has been relatively unexplored, although this report discusses a new oxidizer family with great promise. A new concept of combinatorial type synthesis for energetic materials is also discussed in this report.					
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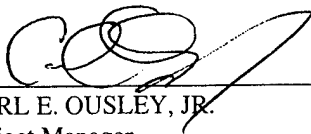
FOREWORD

This final technical report, entitled "Synthesis of New High Energy Density Matter (HEDM): Extra High Energy Oxidizers and Fuels," was prepared by SRI International, Menlo Park, CA, under contract F04611-96-K-0013, for the Air Force Research Laboratory (AFRL), Edwards AFB CA. The Project Manager(s) for the Air Force Research Laboratory were E.J. Wucherer and Carl E. Ousley, Jr..

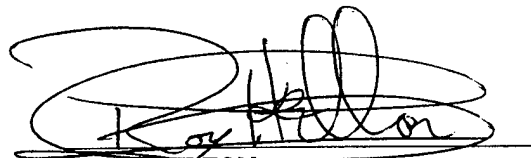
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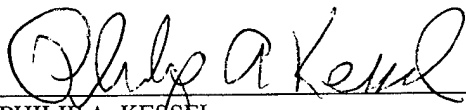
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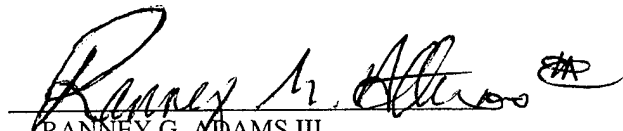
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1.0 INTRODUCTION

SRI International's program for the U.S. Air Force focused on the discovery and synthesis of new, extra-high energy oxidizers and fuels for the High Energy Density Matter (HEDM) program. The goals included the preparation of new compounds having unusual bonding to yield high energy, dense materials for propellant applications.

The specific objectives for this program were

- Develop new fuels and oxidizers for propellant applications. The materials must
 - be simple to make (cubane is difficult)
 - be storable and usable
 - have significantly improved performance over conventional materials
 - develop burn rate accelerators to improve and accelerate combustion (better fuel efficiency)
- Invent new compositions of matter to meet needs of the program. The existing materials are incapable of meeting the energy, density, and performance requirements for propellant systems. New compositions of matter are required and using new materials break the unsuccessful paradigm of using existing materials in new combinations.

The requirements for the new materials included simplicity of synthesis and good long-term stability to make these materials candidates for propellant applications. The work was directed primarily toward the synthesis of highly energetic fuels and fuel additives because this area has been relatively unexplored, although this report discusses a new oxidizer family with great promise.

The focus in energetic fuels has been on the synthesis of acetylene-based materials. Acetylenes have the highest heat of formation per gram of a hydrocarbon compound and a higher heat of formation per gram than cubane or quadracyclane. Acetylenes are vastly simpler to prepare in bulk than strained ring compounds. A new concept of combinatorial type synthesis for energetic materials is also discussed in this report.

2.0 BACKGROUND

In deciding what to synthesize, it is important to remember what makes an excellent propellant material. The energy density of the propellant is the difference between the heat of formation (ΔH_f) of the starting materials and the products on a per gram basis. It is critical to distinguish between the energy density of a single ingredient and the energy density of a propellant because the propellant involves many ingredients in combination. It is the high combustion energy density of the propellant mixture that makes a good propellant, not the energy of the individual ingredient. The specific impulse (I_{sp}) is then proportional to the square root of the heat of reaction divided by the average molecular weight of the products (Eq. 1).

$$I_{sp} \propto \sqrt{\frac{\Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}}{\text{Average Molecular Weight}}} \quad I_{sp} \propto \sqrt{\frac{\Delta H_{\text{Products}} - \Delta H_{\text{Starting}}}{\text{Average Molecular Weight}}} \quad (1)$$

The density of the propellant ingredients then play a role in determining the efficiency of the system as does having low molecular weight products. Rocket makers use as a figure of merit the I_{sp} times the density to a power, where the exponent varies with the application (Eq. 2).

$$\text{Density } I_{sp} = I_{sp} * \text{Density}^n \quad (2)$$

This is called a density I_{sp} . Ultimately, the energy density then relates to the obtainable I_{sp} per unit of volume.

For fuels, functional groups such as acetylenes and strained cyclic rings increase the ΔH_f of the starting materials generally without diluting energy density. Carbon and hydrogen content improve the energy density as a result of their combustion to CO , CO_2 , and H_2O , which have a negative $\Delta H_{f,\text{product}}$, but compounds having a high nitrogen content (amines, azo, aza, or polyaza compounds) contribute less than one would expect. This is due to the production of N_2 , which has a $\Delta H_{f,\text{product}}$ of 0 kcal/mol.

Metals such as aluminum are added to increase the combustion energy on a per gram basis because the combustion to the oxides is highly exothermic. Metals such as boron, silicon, and tungsten are sometimes used for their density and high heat of combustion.

The situation for oxidizers is different. Oxidizers must burn fuel to be useful, so a positive heat of formation and especially a high oxygen content are desired. Oxidizing anions are common (e.g., nitrate, perchlorate, dinitramide) due to the stabilizing effect of the negative charge. An improved oxidizer would have an oxidizing cationic group, but such functionality is usually unstable. Other factors also contribute, such as two-phase flow losses and tradeoffs of the ΔH_f of starting materials versus their $\Delta H_{\text{combustion}}$.

The work in this program was of immediate, practical value to the U.S. Air Force and to the development of improved space launch. Some of the compounds prepared in this program were suggested to NASA as fuel additives to increase performance of hydrocarbon-based liquid rocket engines and are proposed for scale-up and testing. These suggestions resulted in a development program at the Air Force Research Laboratory, Edwards AFB to study such compounds.

3.0 DISCUSSION AND RESULTS

3.1 New Fuels

Several potential new fuels for hydrocarbon-based propulsion applications were considered. The current and potential fuels are summarized in Tables 1, 2, and 3. These tables compare the performance obtained from the combustion of various fuels with oxygen (simulation of a hydrocarbon/LOX rocket engine). Table 1 focuses on the current standard materials in use and under consideration. RP-1 is a standard kerosene type rocket fuel. Quadracyclane, cubane, and acetylene were considered as fuels because of their high energy density.

Table 1. Specific Impulse (I_{sp}) and Flame Temperatures of Standard Hydrocarbons Used in Propellant Applications (calculated with oxygen, NASA-Lewis Code)

Compound	I_{sp} sec	Flame Temperature K	ΔH_f kcal/mol	ΔH_f cal/g
RP-1	300	3670	-4.93	-350
Quadracyclane (C ₇ H ₈)	308	3906	+60.5	658
Cubane (C ₈ H ₈)	317	4039	+139	1,336
Acetylene (C ₂ H ₂)	327	4116	+54.2	2,084

Quadracyclane and cubane have problems associated with their synthesis. The synthesis of both is costly and in the case of cubane extremely long for a material expected to be used in large quantities. Quadracyclane requires a photochemical ring closure. As shown in Table 1, quadracyclane, cubane, and acetylene all significantly improve on the specific impulse (I_{sp}) obtained from RP-1. However, both cubane and quadracyclane are difficult to prepare in bulk and are likely to be prohibitively expensive. Further, pure acetylene is an explosion hazard.

Table 2. Specific Impulse (I_{sp}) and Flame Temperatures of Potential Fuels Prepared under this Contract (calculated with oxygen, NASA-Lewis Code)

Compound	I_{sp} sec	Flame Temperature K	ΔH_f kcal/mol	ΔH_f cal/g
C ₆ H ₆ O	314	3958	+75 ^a	798
C ₂₄ H ₂₄ NB	316	3967	+440 ^a	1,306
C ₂₈ H ₃₂ NB	313	4023	+400 ^a	1,017
C ₉ H ₉ N	316	4050	+168 ^a	1,282
C ₂₀ H ₁₆ NB	322	4198	+480 ^a	1,708
HC≡CCH ₂ NH ₂	316	---	130 ^a	2,363
HC≡CCH ₂ OH	305	---	10.7 ^a	191
(HC≡CCH ₂) ₂ O	330	---	145 ^a	1,543
CH ₃ C≡C-C≡CCH ₃	318	---	104 ^a	1,333
C ₆ H ₇ N	316	3947	111	1,196
C ₂₁ H ₁₈ N ₆	303	3986	331	936
C ₃ H ₂ (polymer)	312	4107	50	1,321

^aCalculated using Benson Additivity

**Table 3. Proposed New Materials Combustion with Oxygen,
NASA-Lewis Code**

Compound	I_{sp}	Flame Temperature	ΔH_f	ΔH_f
	sec	K	kcal/mol	cal/gram
C (Polycarbon)	334	6150	+30 ^c	2,500
C ₁₂ H ₈ N ₄	295	---	+43 ^a	688
C ₄ H ₄ N ₄	304	3993	+130 ^a	1,204
C ₉ H ₆ N ₂	301	3027	134 ^a	944
C ₇ H ₅ (polymer)	308	4082	98	1,099
C ₁₆ H ₁₆ N ₂	315	3986	292	1,238
C ₁₈ H ₁₆ N ₂	315	4096	347	1,335
C ₅ H ₂ (polymer)	315	4377	105	1,697
C ₁₁ H ₆ (polymer)	312	4192	206	1,490
C ₁₂ Al ₂ (polymer)	306	4823	349	1,837
C ₁₅ H ₆ Al ₂ C ₁₅ H ₆ Al ₂ (polymer)	311	4385	334	1,441
C ₂ HN ₄ O ₂ Fb	263	3761	32 ^{bb}	242

^aCalculated using Benson Additivity.

^bMonopropellant.

^cPer carbon.

Several alternatives to cubane and quadracyclane were considered. These are summarized in Table 2, which lists the new materials prepared in this program. Table 3 lists materials were because this program was terminated early due to a lack of funding.

The compounds in Tables 1 through 3 are calculated using the NASA-Lewis code and thus can be compared directly with each other. The calculations are done as a pure substance, and no consideration was given to whether the materials could profit from the presence of a low molecular weight working fluid to increase the performance to a higher value. Table 4 provides a key to relate the molecular formula to the structure of the compound.

In most cases, the proposed materials have significantly improved performance as measured on an I_{sp} basis over RP-1. The compounds in Tables 2 and 3 will have significantly higher density due to the inclusion of heteroatoms that are known to significantly enhance density, resulting in an improved energy density even for the compounds that have a calculated I_{sp} near that of RP-1. The materials in Table 2 are generally easier to synthesize than cubane and quadracyclane and more stable than pure acetylene.

Table 4. Molecular Formula and Molecular Structure Key

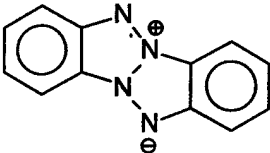
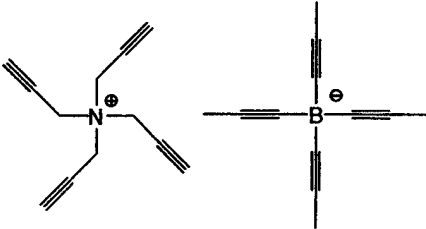
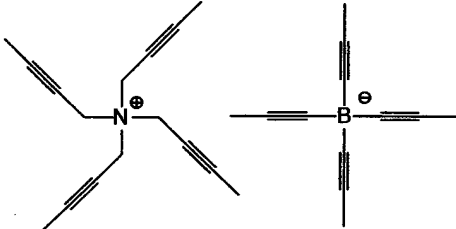
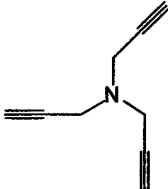
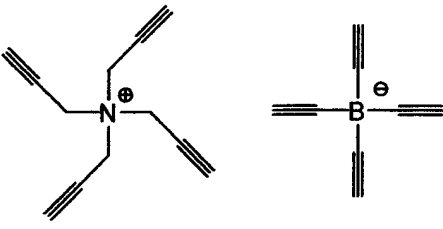
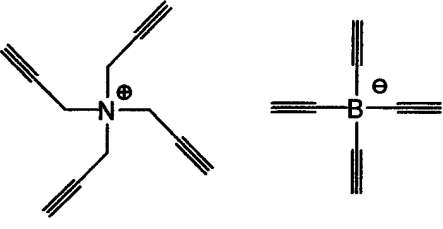
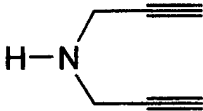
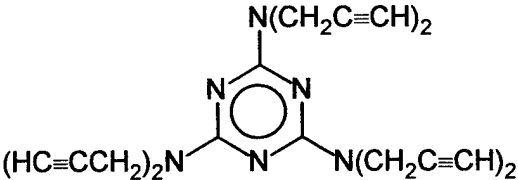
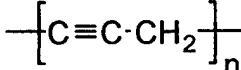
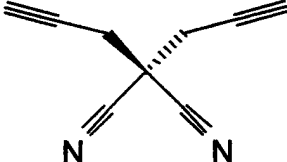


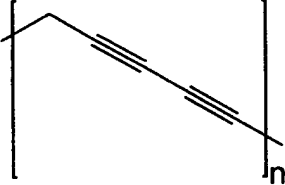
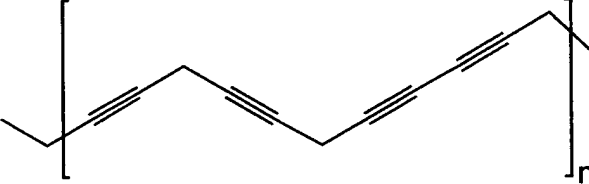
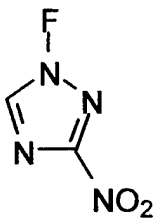
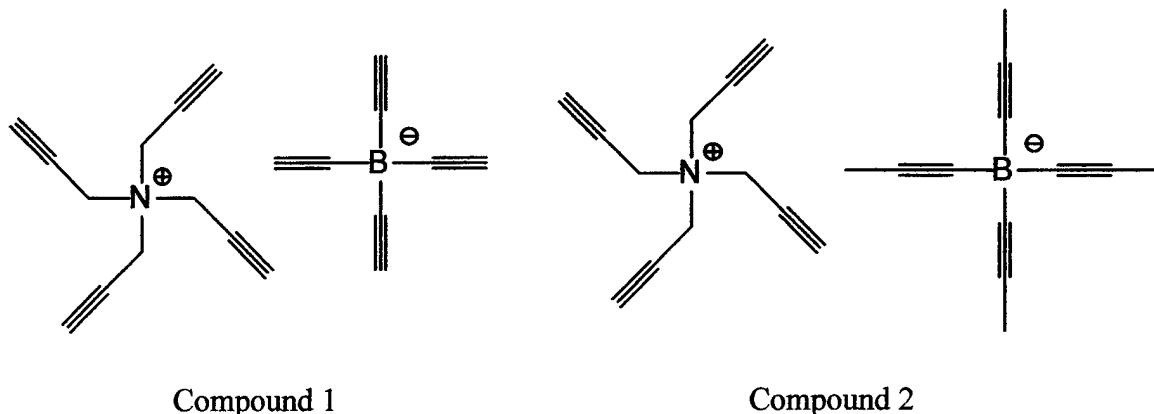
Compound	Structure
C ₁₂ H ₈ N ₄	
C ₂₄ H ₂₄ NB	
C ₂₈ H ₃₂ NB	
C ₉ H ₉ N	
C ₂₀ H ₁₆ NB	
C ₂₀ H ₁₆ NB	
C ₃ H ₅ N	<p data-bbox="906 1839 1081 1869">HC≡CCH₂NH₂</p>

Table 4. (Cont.) Molecular Formula and Molecular Structure Key

Compound	Structure
C ₆ H ₇ N	
C ₂₁ H ₁₈ N ₆	
C ₃ H ₂ (polymer)	
C ₉ H ₆ N ₂	
C ₁₆ H ₁₆ N ₂	
C ₁₈ H ₁₆ N ₂	
C ₅ H ₂ (polymer)	
C ₁₁ H ₆ (polymer)	
C ₂ HN ₄ O ₂ F	

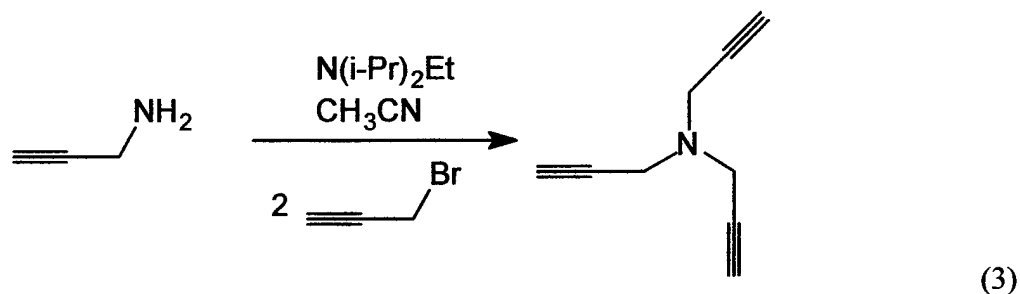
An example of what one can do to create new energetic fuels is shown by the ionic salts prepared based on tetrapropargyl ammonium ion (as an energetic fuel cation) and two different borate anions having acetylide and propyne units attached to the boron. These are the $C_{24}H_{24}NB$ (Compound 1) and $C_{28}H_{32}NB$ (Compound 2) derivatives. The structure of these compounds are shown below.

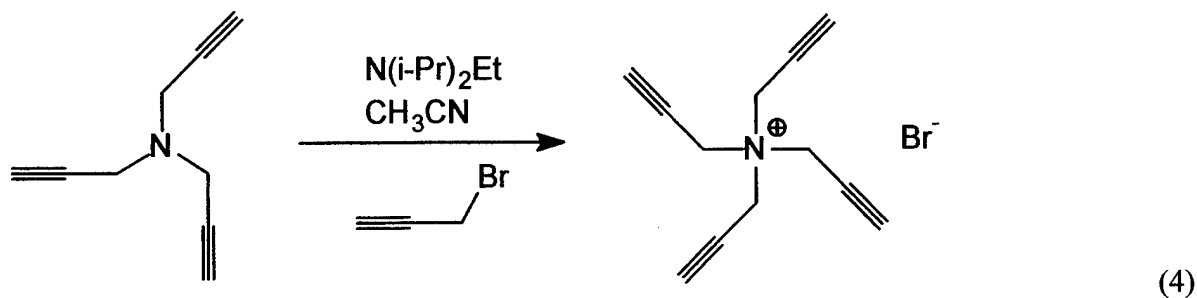


3.2 New Fuels Based on Acetylene Derivatives

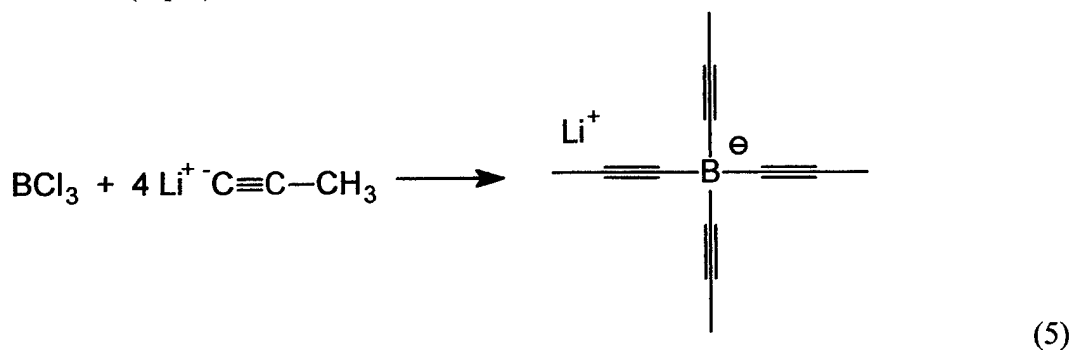
Initial work focused on the synthesis of the propargyl derivatives of ammonia. Propyne, the precursor to propargyl compounds, has a high positive heat of formation and is a potential fuel for rocket propulsion, but propyne itself is a low density, highly volatile material. To address these issues, new derivatives of propyne that address the energy density problem and volatility problems were created. The first compounds synthesized were the tetrapropargylammonium ion and tripropargylamine. Simultaneously, the new borate derivatives, tetraethynylborate, having acetylide functional groups were synthesized. These boroacetylides have exceptionally high positive heats of formation and should have exceptional combustion energies. This is a new form of boron and should be evaluated in an engine to determine its effectiveness. The positively charged tetrapropargylammonium ion and the negatively charged tetraethynylborate were then combined by ion exchange to create new, exceptionally energy-dense fuels and fuel additives. Because these derivatives are ionic, they can be combined with a range of counterions to create a range of new materials for propulsion applications. The synthesis of these salts is described next.

Tripropargyl amine, tetrapropargyl ammonium tetrapropynylborate, and tetrapropargyl ammonium tetraethynylborate were synthesized on this program. Tripropargylamine is synthesized by the addition of 2 equivalents of propargylbromide to propargylamine (Eq. 3).

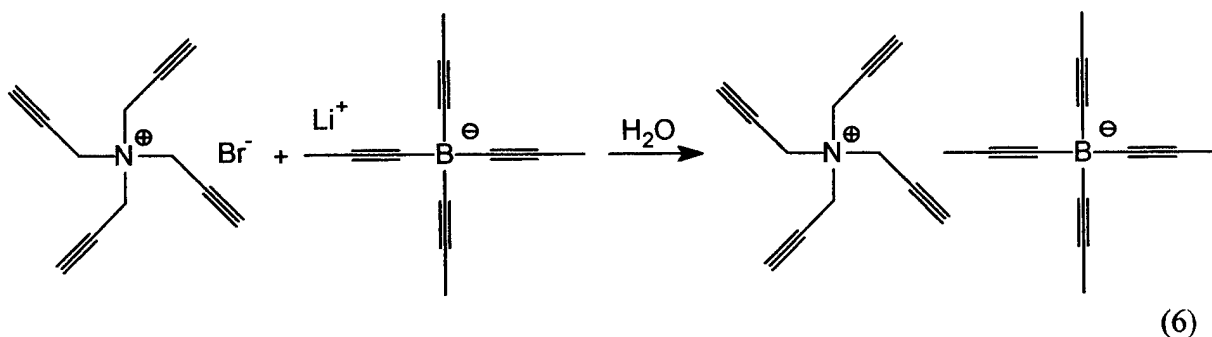




Tetrapropynylborate is prepared by the reaction of four equivalents of 1-lithium propyne to boron trichloride (Eq. 5).



Tetraethynylborate is prepared in a method analogous to tetrapropynyl borate, but substituting lithium ethyne for lithium propyne. The tetrapropargylamine tetrapropynylborate and tetrapropargylamine tetraethynylborate salts are prepared by combination of the precursors in deionized water, followed by immediate precipitation of the desired products (Equations 6 and 7). The complete sequence of the synthesis is shown in Equations 3 through 7.



Examples of SRI's highly energy dense compounds prepared under this contract are the tripropargyl amine, tetrapropargylammonium ion, tetrapropynylborate, tetraethynylborate, tetrapropargylammonium tetraethynylborate and tetrapropargylammonium tetrapropynylborate. We obtained a crystal structure of tetrapropargylammonium tetrapropynylborate from Dr. Richard Gilardi of the Naval Research Laboratory (Fig. 1 and 2). These results have not been published elsewhere and were performed as part of the project. He confirmed the structure and assigned a density of 1.02 g/cc for tetrapropargylammonium tetrapropynylborate. A differential scanning calorimetry (DSC) analysis gave a decomposition onset of tetrapropargylammonium tetrapropynylborate at 165°C (Fig. 3), so this material is thermally stable for most potential applications. A heat of formation of +440 kcal/mol based on Benson group additivity was calculated, as shown in Table 1.

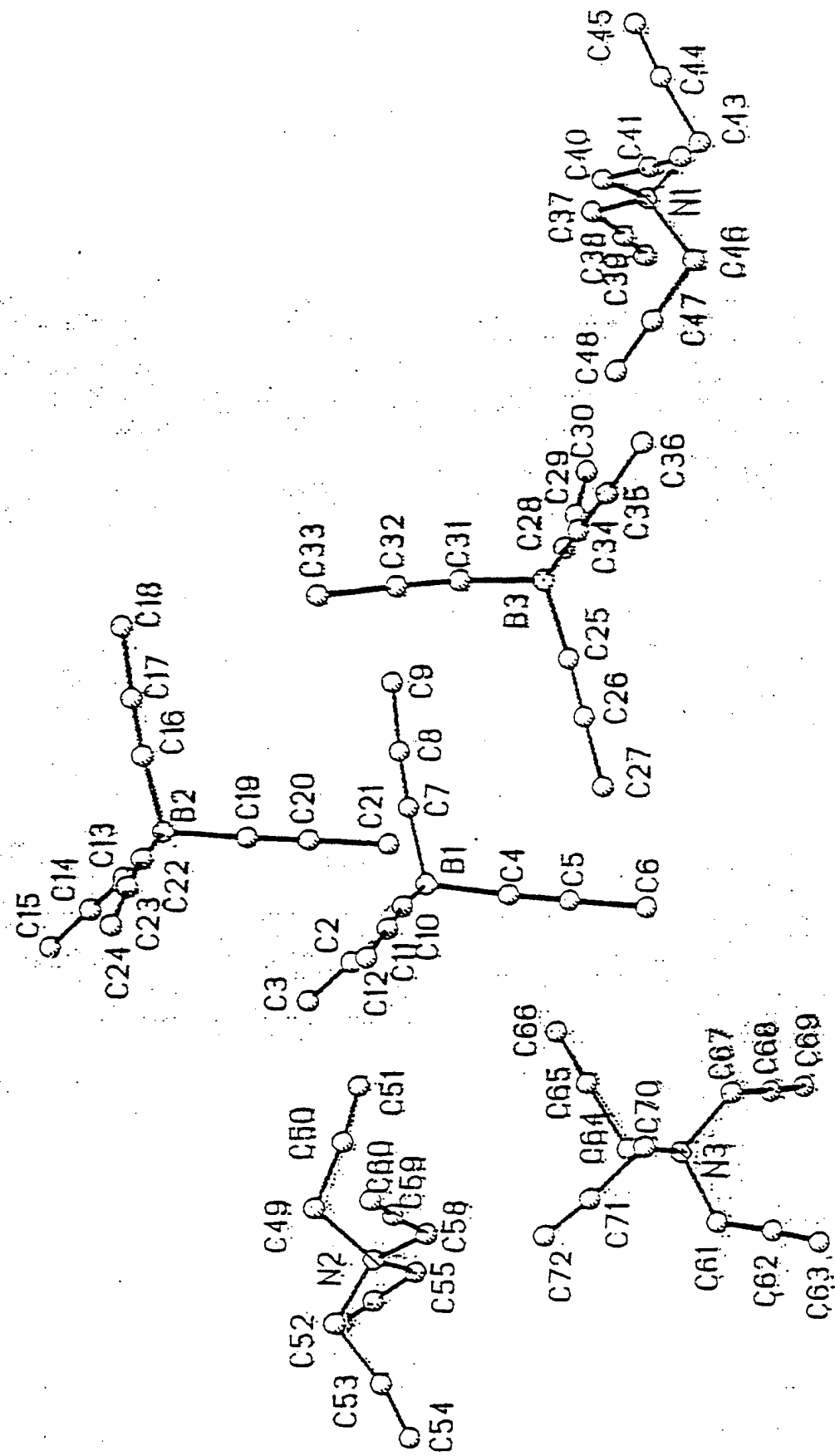


Figure 1. Crystal structure of tetrapropylammonium tetrapropynylborate.
 (Courtesy of R. Gilardi, NRL)

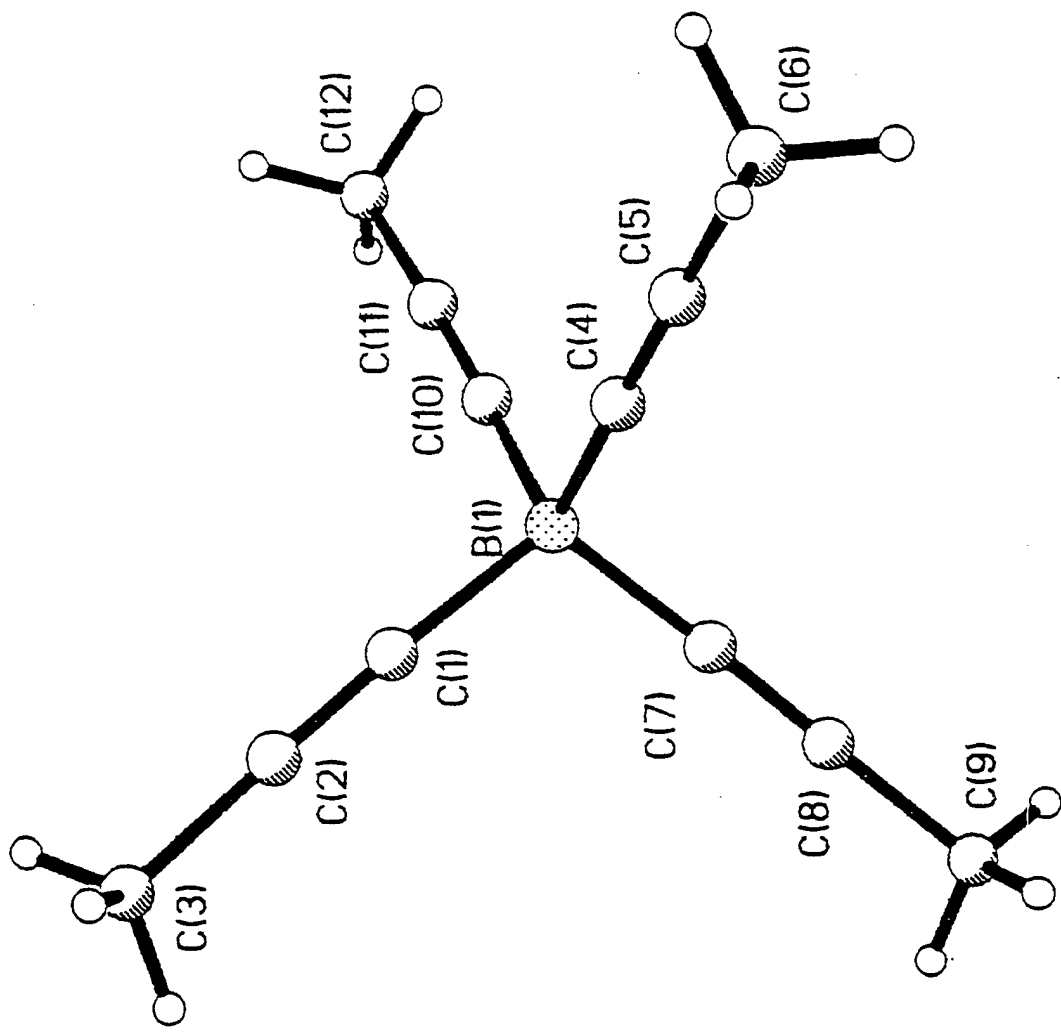


Figure 2. Crystal structure of tetrapropylborate showing hydrogens.
(Courtesy of R. Gilardi, NRL)

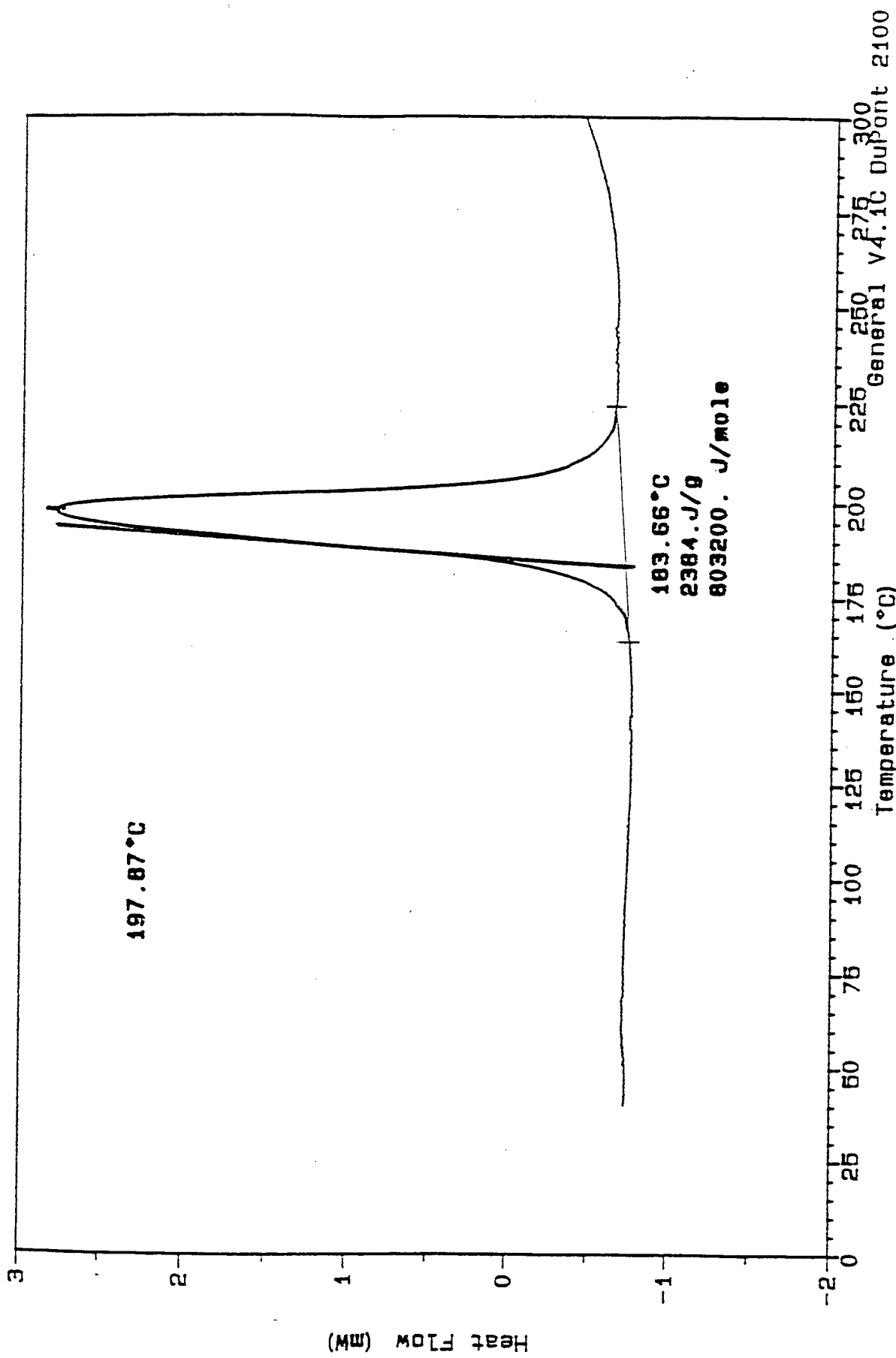
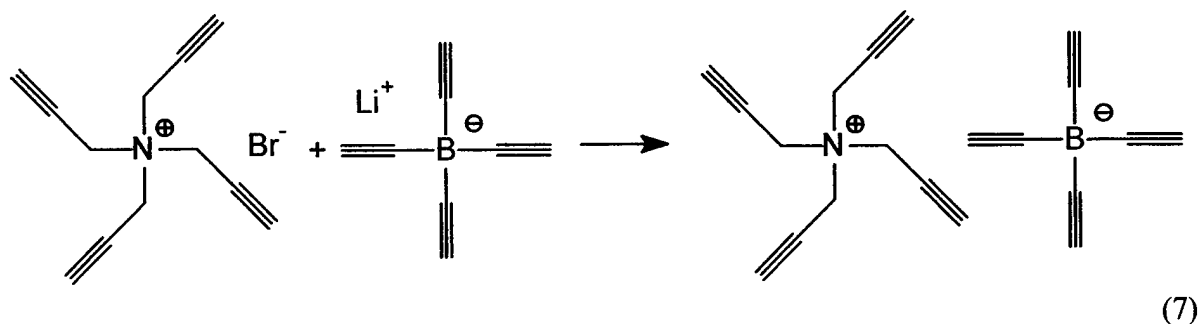


Figure 3. DSC of tetrapropylammonium tetrapropargylborate.

Tripropynylamine shows similar thermal stability decomposing at $>160^{\circ}\text{C}$ (Fig. 4). Tripropargyl amine has a calculated heat of formation of $+168$ kcal/mole and an energy density of $+1,292$ cal/gram. The per gram energy density compares favorably with cubane and exceeds that of quadracyclane (see Table 1).

Tetrapropargylammonium tetraethynylborate was synthesized by the route shown in Equation 7.



The DSC of tetrapropargylammonium tetraethynylborate is given in Figure 5. This compound shows a thermal onset for decomposition at 175°C . Tetrapropargylammonium tetraethynylborate has exceptional energy density of $1,708$ cal/gram, with a calculated heat of formation of $+480$ kcal/mol. For a thermally stable compound, these values are the highest the authors have seen, exceeding the values of quadracyclane and cubane (see Table 1) by a large amount while being much easier to synthesize.

It is believed that tetrapropargylammonium tetrapropynylborate and the other compounds shown in Tables 1 through 4 offer realistic alternatives to cubane and quadracyclane. The synthetic complexity of cubane and quadracyclane will limit their usability, but the decomposition values are very good. Such materials meet the thermal requirements of any hydrocarbon based fuels. The calculated performance values and their ease of synthesis makes them candidates replacements for either cubane or quadracyclane, and they should be considered for scale-up and testing in an engine.

It is suggested that two other acetylene compounds should be considered for application as fuel additives for hydrocarbon based fuels. These are the propargyl alcohol and propargyl ether listed in Table 1.

Following the synthesis of these boron derivatives, there were also prepared several new compounds using only CHN in the molecule. These compounds again have acetylene or in some cases nitrile functional groups present in the molecule to contribute to the heat of formation and energy density. The absence of a metal center means that there will be no metal oxides in the exhaust from such compounds. The synthesis and structure of the final product for some the compounds are shown below, and the calculated properties can be found in Table 2.

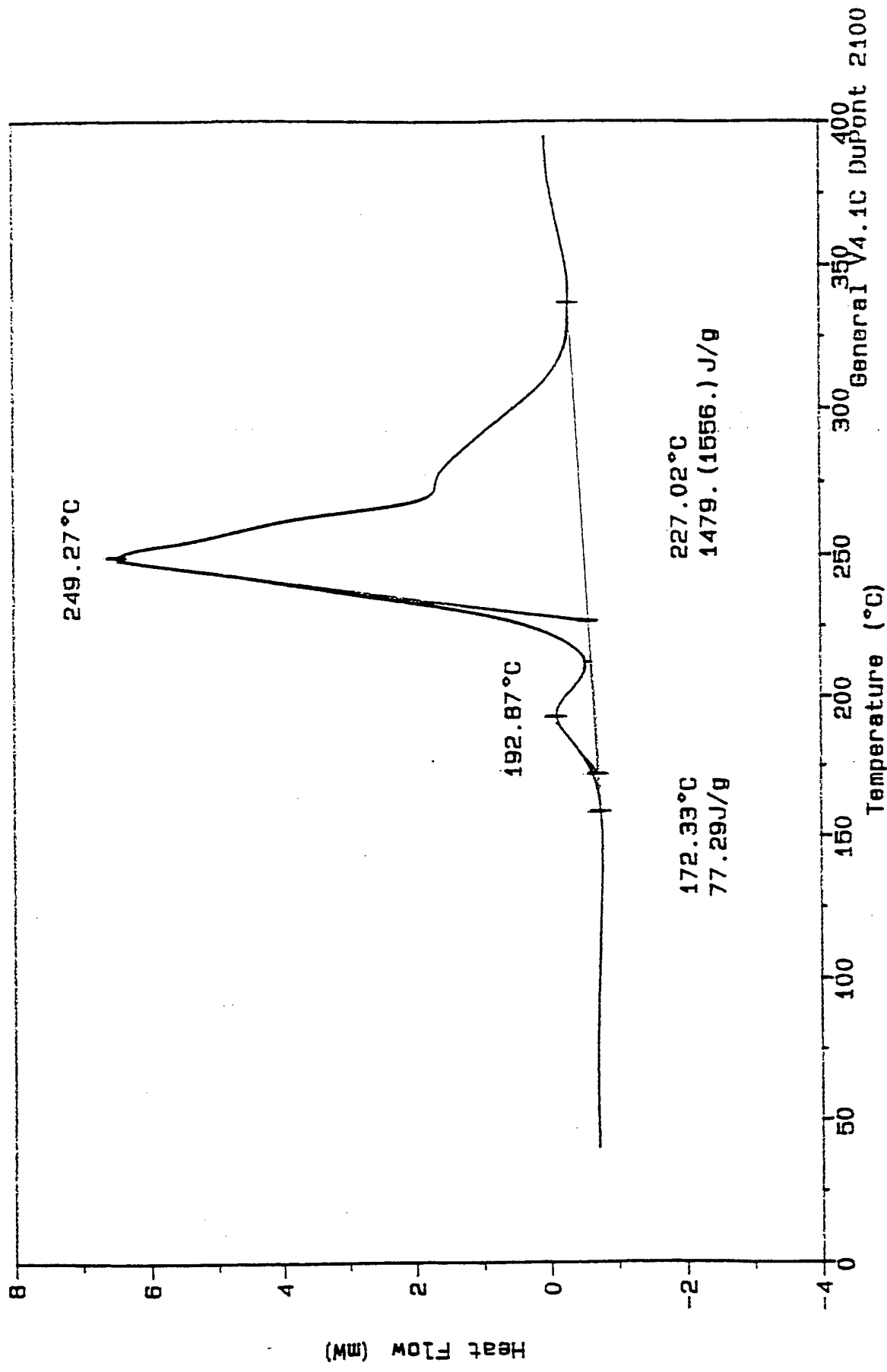


Figure 4. DSC of tri(1-propynyl)amine.

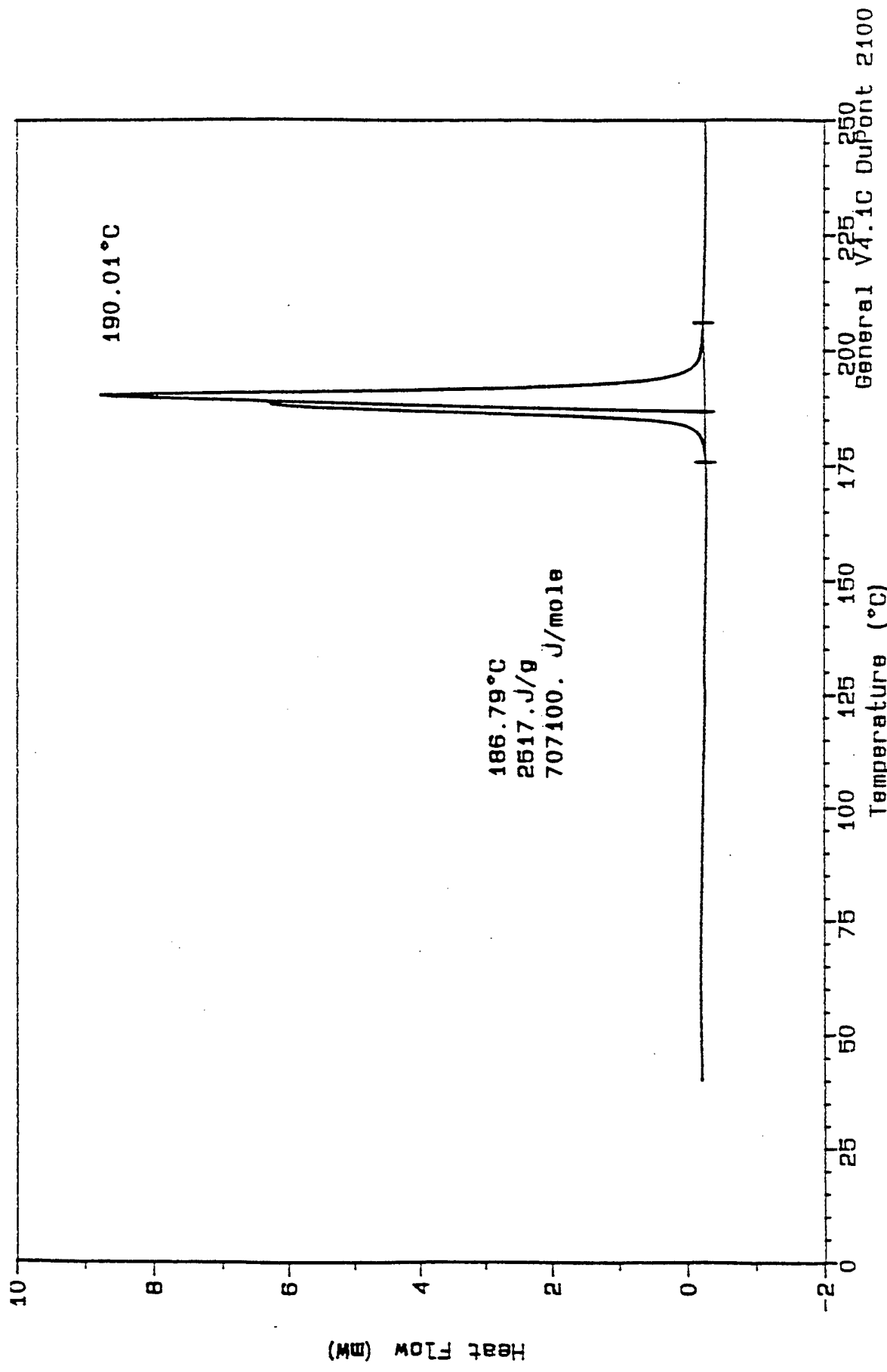
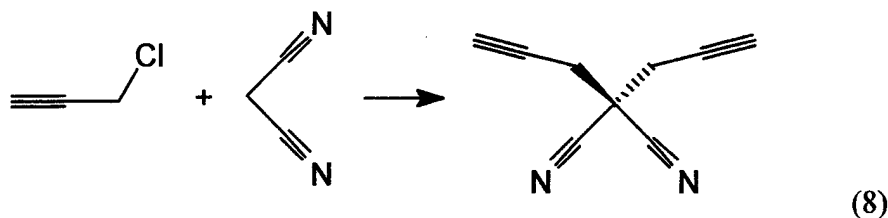


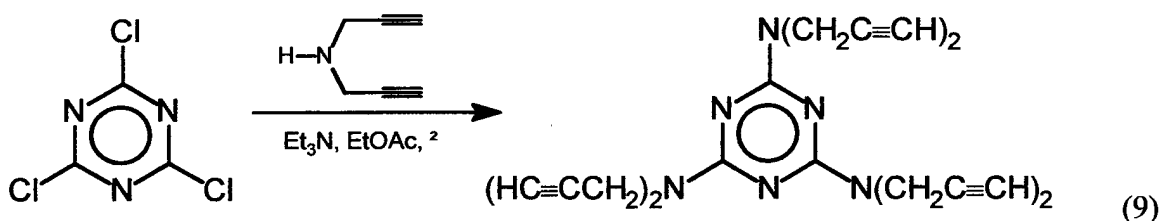
Figure 5. DSC of tetrapropylammonium tetraethynylborate.

We prepared 4,4-dicyano-hepta-1,4-diyne by the condensation of cyanamide and propargyl chloride. The synthesis is shown in Equation 8.



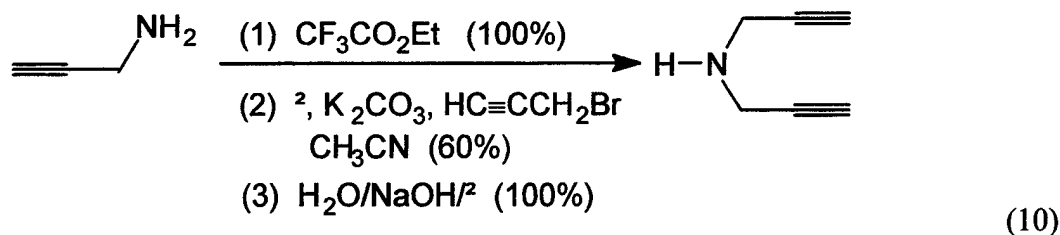
4,4-Dicyano-hepata-1,4-diyne is highly stable thermally. The DSC is shown in Figure 6. It melts at 72°C and does not thermally decompose until over 200°C. This compound should have solubility in hydrocarbon systems and can be further functionalized to change its solubility or thermal properties by replacement of the acetylinic protons. The density is good and it is a candidate for propellant applications.

The synthesis of 2,4,6-tris(dipropargylamino)-1,3,5-triazene is shown in Equation 9.



This compound was synthesized to demonstrate an aromatic center for our proposed energy dense fuels. Unfortunately, the calculations do not support this material as being a significant improvement of performance unless density is taken into consideration. Calculations give a heat of formation of +331 kcal/mol and a likely I_{sp} value of only 303 sec^{-1} versus RP-1 (combusting with oxygen) at 300 sec^{-1} . This is an example of where simply having a high heat of formation does not yield high performance. The modest performance is probably due to a combination of the lack of hydrogen, and the high nitrogen density in the system. The system would perform better with a benzene ring or cyclohexane center due to the higher hydrogen content and combustible hydrogen versus the triazene ring prepared in this program prepared. Still, the density is higher than that of RP-1, and an overall improvement in fuel performance will be achieved by use of such materials.

A much simpler compound is dipropargylamine, whose synthesis is shown in Equation (10).



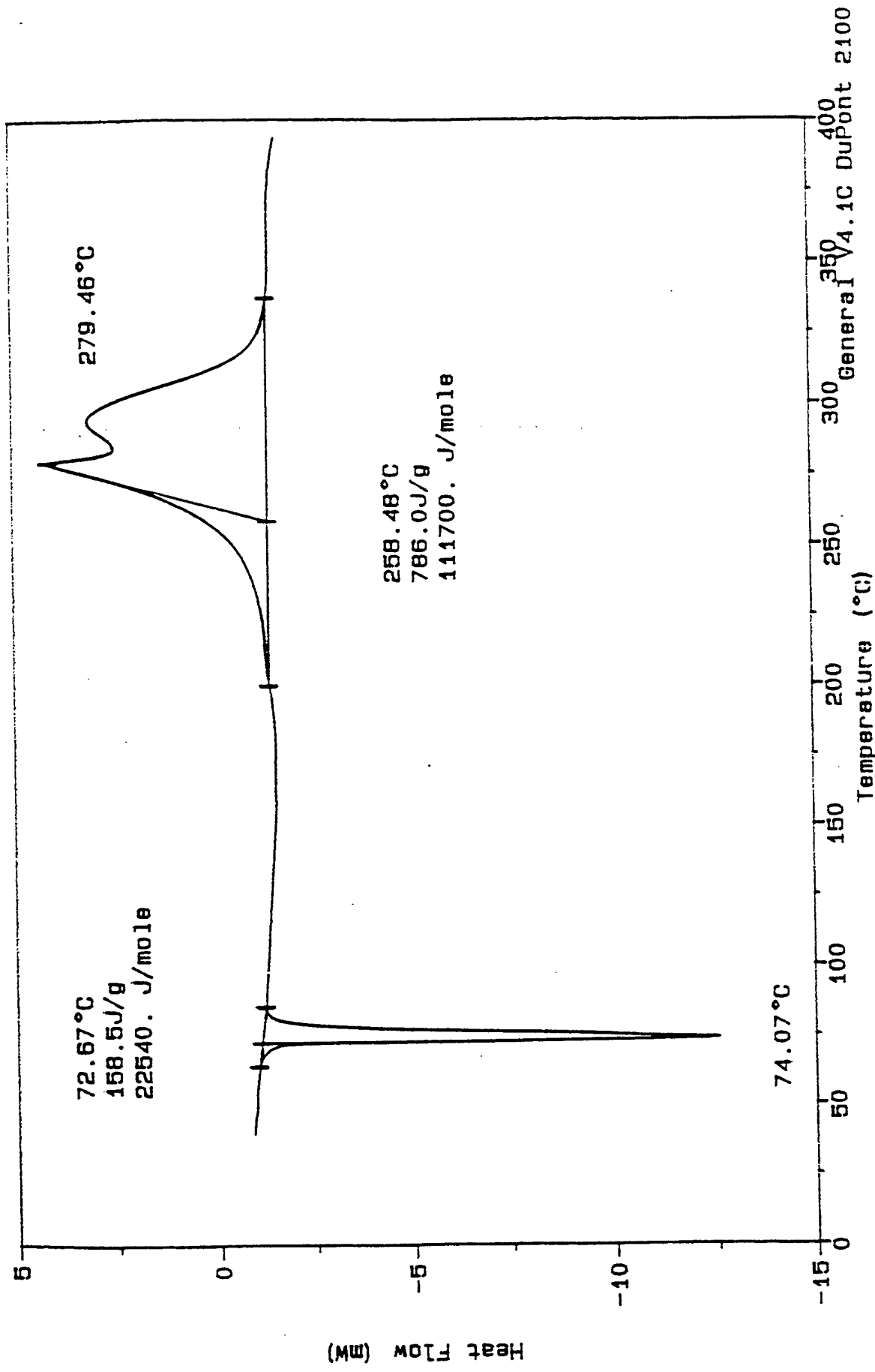


Figure 6. DSC of dipropargylmalonitrile.

Dipropargylamine has a calculated heat of formation of +111 kcal/mole. Here the system has a calculated performance of 316 sec^{-1} and an energy density of +1,196 cal/gram. This compound should be an exceptional additive to hydrocarbon-based propellant systems because it is readily prepared, has a good density, and shows excellent calculated performance. The simplicity of such compounds should make them attractive for propellant applications.

A preliminary synthesis of a polymer based on a propargyl group as the repeat unit, poly(propyne) was accomplished. The proposed structure for the material is shown in Equation (11).



Though the preliminary characterization indicated success, it was not determined whether the synthesis resulted in the desired material, but a preliminary characterization of the materials indicated success. This is a simple material, yet it calculates to have a heat of formation of +50 kcal/mol and an energy density of +1,321 cal/gram, which is on the order of cubane (+1,336 cal/gram) and would be higher than tetramethylcubane. This heat of formation results in a calculated performance of 312 sec^{-1} , an exceptionally high value for such a simple material that can be prepared in bulk. Figure 7 shows the DSC for this compound. This compound can be used in hydrocarbon-based systems or as a fuel for hybrid type rocket systems.

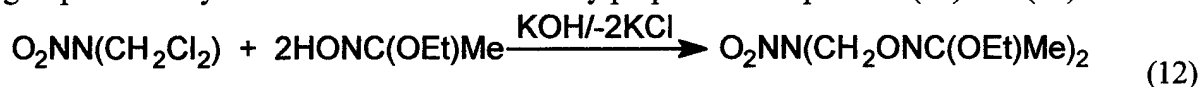
3.3 New Oxidizers

SRI investigated new beyond-the-state-of-the-art oxidizers for use in propellant systems. These studies addressed the need for more energetic oxidizers having reasonable stability. The oxidizers chosen to investigate are based on the methylene bisoxamine [MBO or $\text{CH}_2(\text{ONH}_2)_2$] type of functionalities.¹

The R-O-NH₂ group appears to address some of the problems associated with instability in hydroxyl ammonium salts while retaining the excess and having reactive oxygen. The primary problem observed with MBO salts is that they are highly hygroscopic. Hygroscopicity causes immense problems when a propellant is being formulated and MBO-based salts are probably not candidate materials for propellants for that reason.

The MBO technology was combined with other observations. Also discovered in the 1970s, the methylene bridged nitramine organic azides, $\text{N}_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}_3$ and $\text{N}_3\text{CH}_2(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}_3$, were prepared for use as energetic plasticizers.¹ These nitramine derivatives are not hygroscopic, but they are not oxidizers.

SRI combined the MBO technology with observations on the methylene bridged nitramine organic azides. It was discovered that a new class of oxidizers can be prepared by combining the best of the MBO salts with the nitramine center from the methylene bridged nitramine organic azides. The precursors to the methylene bridged nitramine organic azides, $\text{ClCH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{Cl}$ and $\text{ClCH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{Cl}$, are susceptible to nucleophilic substitution by many weak nucleophiles due to the electron withdrawing nature of the nitramine groups. The oxyamine derivatives were readily prepared via Equations (12) and (13).



¹ C. S. McDowell, C. I. Merrill, and M. W. Barnes, Synthesis of a New High-Energy Solid Propellant Oxidizer, Technical Report AFRPL-TR-69-274, September, 1969. Dr. Petrie was investigating MBO salts (originally discovered in the 1970s by Mr. Claude Merrill at AFRL) at Edwards AFB before coming to SRI. When he arrived at SRI, further investigations were done to solve some of the problems associated with the MBO salts.

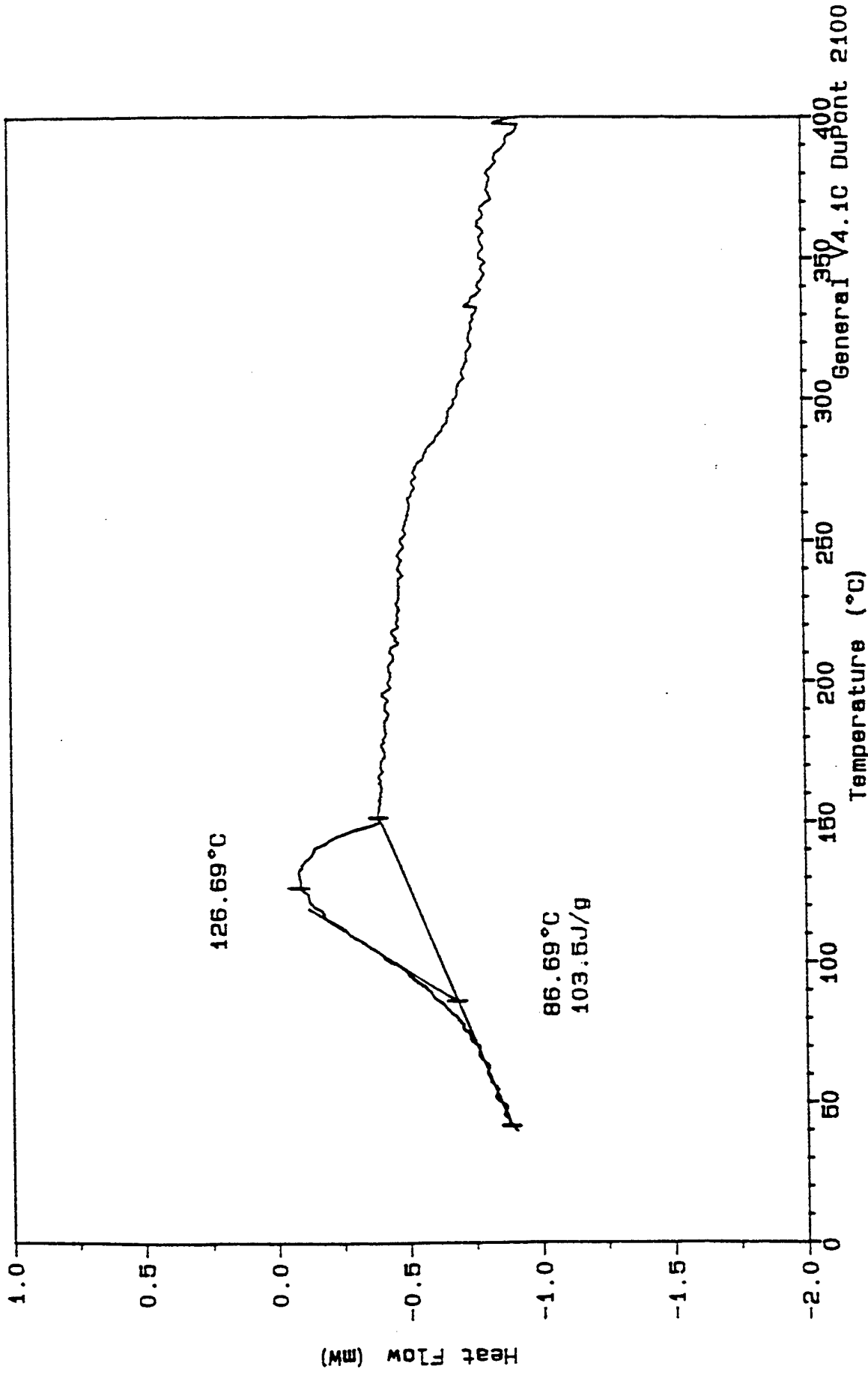
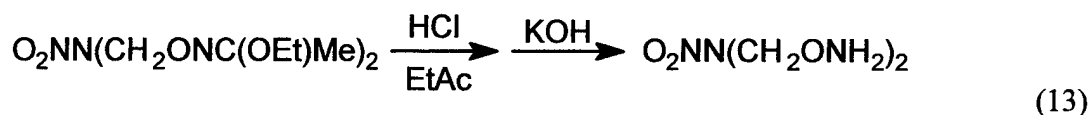
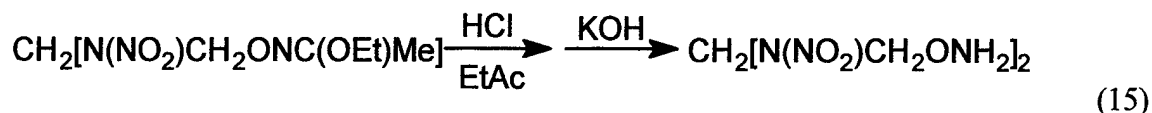
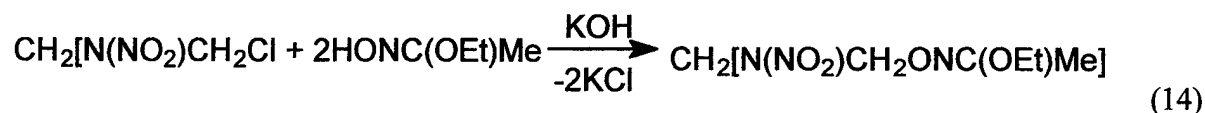


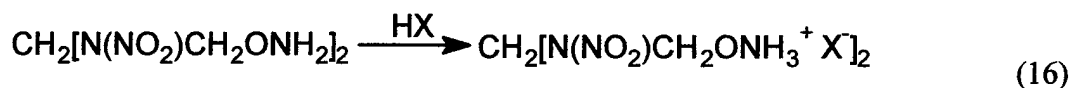
Figure 7. DSC of poly(propyne).



The dioxyamines, $\text{N}(\text{NO}_2)[\text{CH}_2\text{ONH}_2]_2$ and $\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2\text{ONH}_2]_2$ were isolated in good yield as crystalline solids using the routes shown in Equations (12) and (13) and Equations (14) and (15), respectively and Figures 8 and 9, respectively.



The diperchlorate salt of 1,3-dioxyamine-2-nitrazapropene, $\text{N}(\text{NO}_2)[\text{CH}_2\text{ONH}_3^+ \text{ClO}_4^-]_2$, was prepared by reaction with perchloric acid and the free base (the DSC, as shown in Fig. 10). $\text{N}(\text{NO}_2)[\text{CH}_2\text{ONH}_3^+ \text{ClO}_4^-]_2$ is sensitive to impact as tested in a mortar and pedestal and melts at $\sim 150^\circ\text{C}$ by DSC followed by decomposition after melting. The properties of $\text{N}(\text{NO}_2)[\text{CH}_2\text{ONH}_3^+ \text{ClO}_4^-]_2$ (Eq. 16) are interesting; however due to a program funding cut, no further investigation of these perchlorate salts and the corresponding $\text{C}(\text{NO}_2)_2^-$, NO_3^- and $\text{N}(\text{NO}_2)_2^-$ salts was undertaken.



No salts were prepared of the 2,4-dinitraazapentane.

3.4 Combinatorial Approach to Energetic Materials

During this program, a combinatorial strategy for the synthesis of new energetic materials for propellant applications was considered. This work is only in the most primitive of stages, but the thought processes in this area are discussed here. The current synthesis strategy for energetic materials is to conceive of a new material, develop a route, and then synthesize the compound. This neglects the possibility of serendipity (synthesis of a compound that wasn't predicted or planned on, such as the synthesis of the CL-20 cage structure). This one-at-a-time, custom synthesis method has been highly effective in the development of energetic materials. Dinitramide and its salts are an example of this approach.

However, the strategy for synthesis in the pharmaceutical and biotherapeutics industry has undergone a paradigm shift by the use of combinatorial methods for the synthesis of new compounds. A combinatorial approach allows the preparation of many derivatives of a desired molecular structure for fast screening. A combinatorial approach has not been used for the synthesis of basic new ring structures, but complex structures can be built up using known functional parts.

Combinatorial approaches are hardly new. In reality, at a certain level, this approach has been used when the conditions of a reaction (e.g., solvent, pH, temperature, time) are varied to optimize the yield of reaction. When different anion/cation pairings are combined, combinatorial work is done. Neither of these are formally described as combinatorial, nor is the approach optimized to address the synthetic needs.

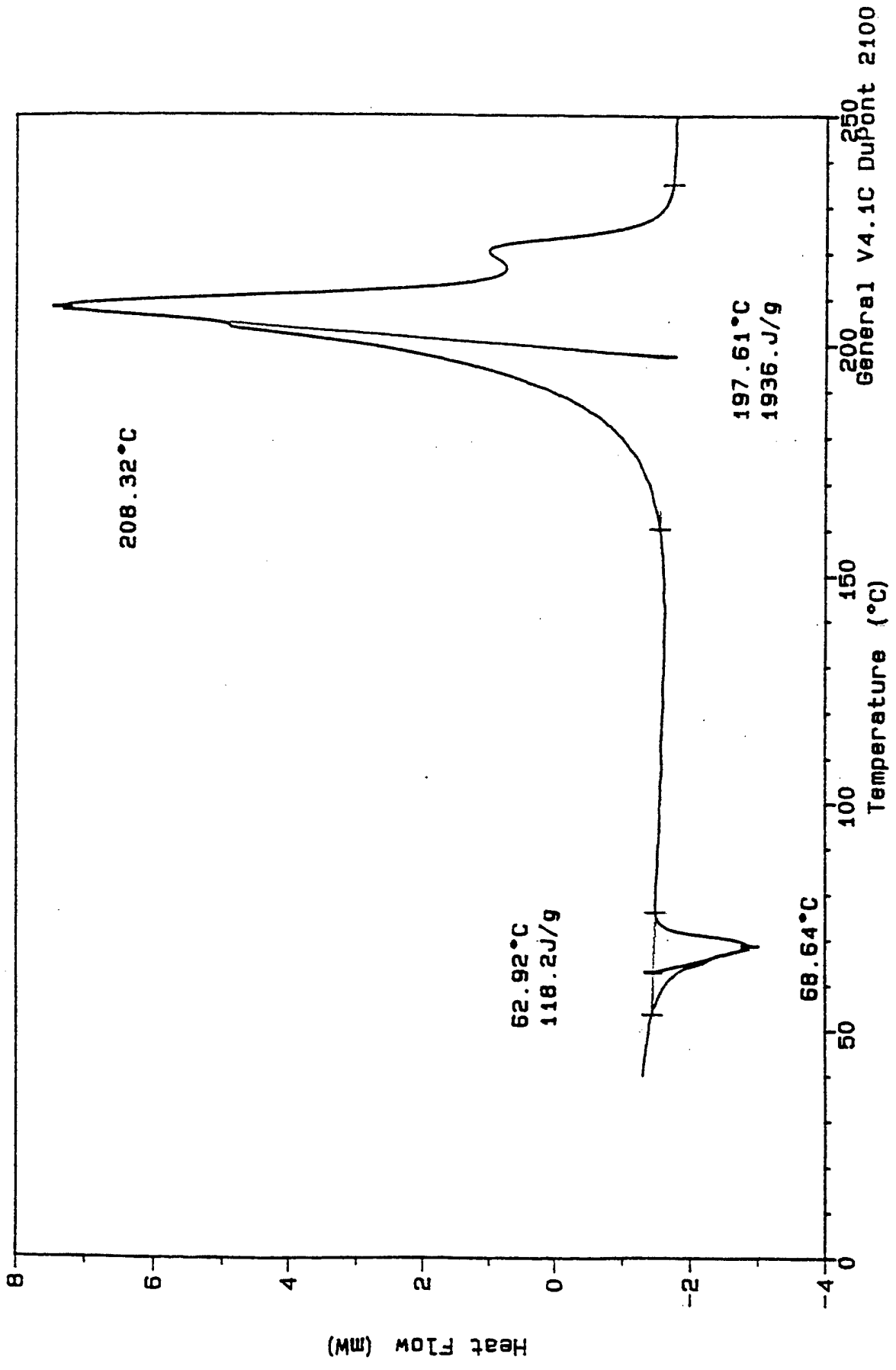


Figure 8. DSC of N-nitro-N,N-bis(methylene oxyamine)amine.

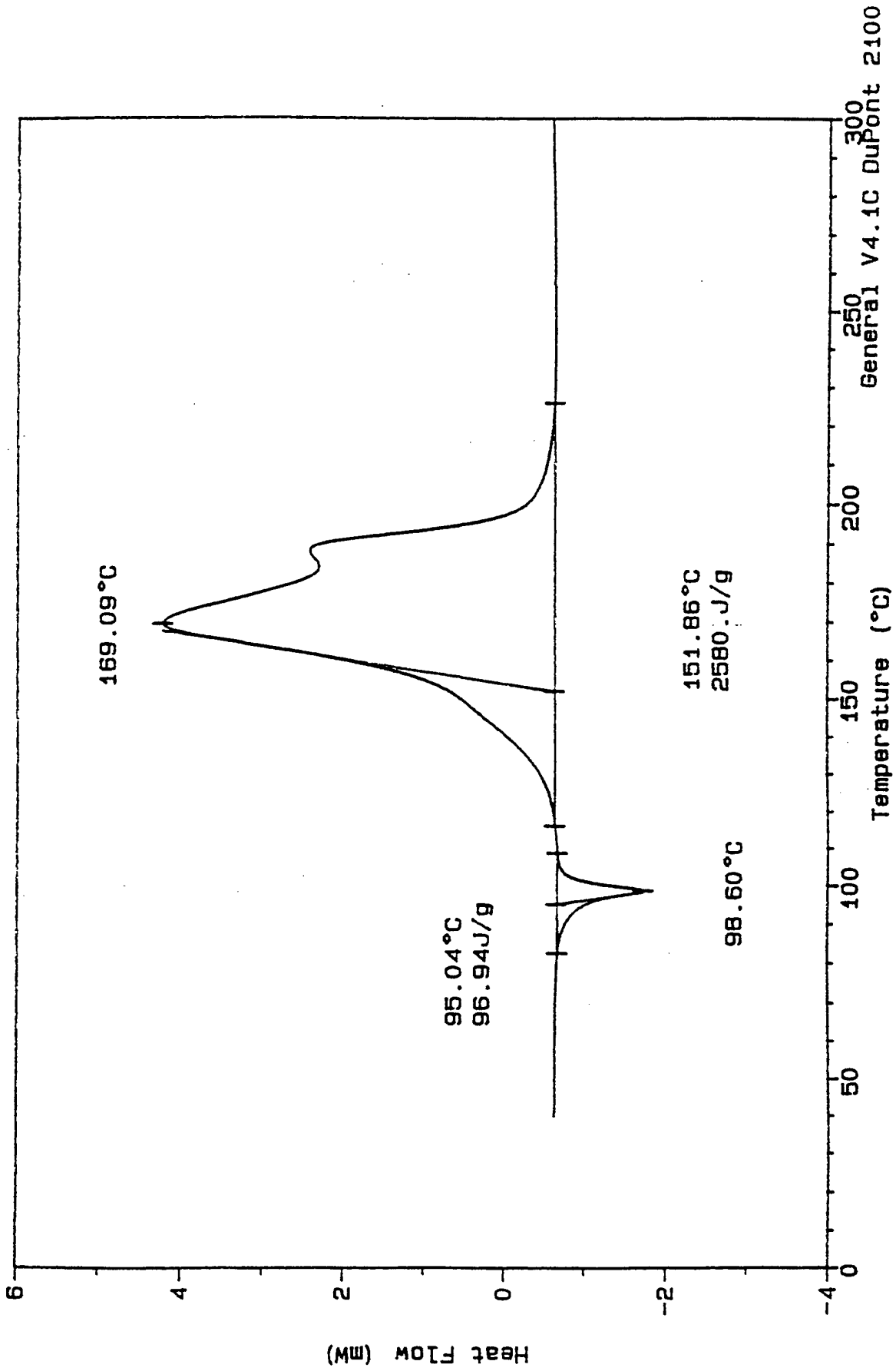


Figure 9. DSC of $\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2\text{ONH}_2]_2$

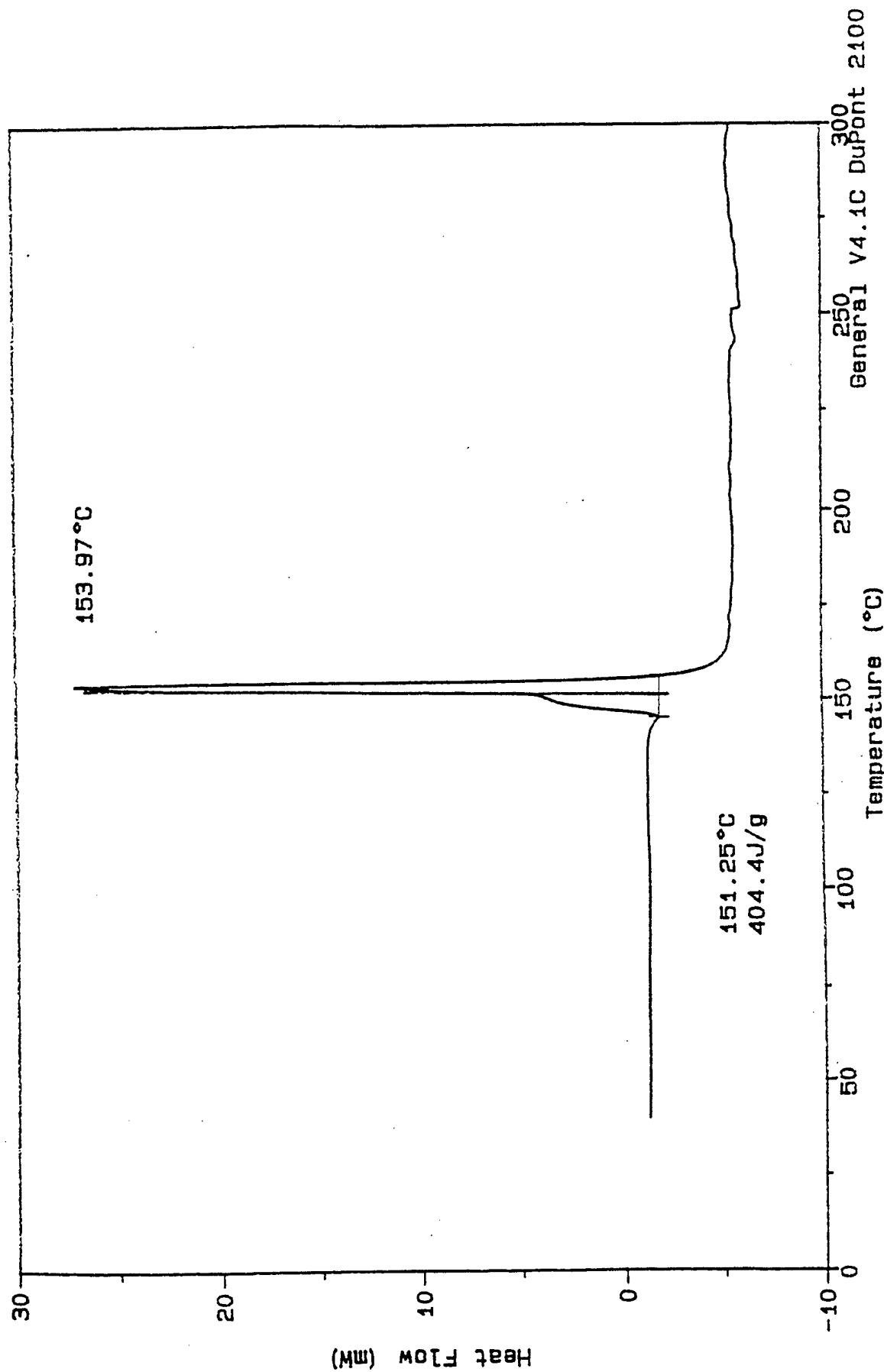


Figure 10. DSC of $O_2NN[CH_2ONH_3^+ClO_4]_2$.

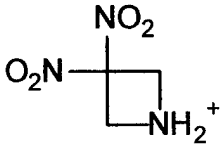
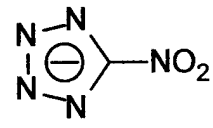
It is believed that combinatorial approaches can be used for the synthesis of new energetic materials. Energetic fuels and oxidizers can be prepared this way. To build up a molecular structure based on known materials, one could

- Pick “interesting” energy dense functional groups
 - use as building blocks
- Choose energetic functional groups that allow simple synthesis
- Use combinatorial approach to make molecules
 - many different functional groups
 - many different combinations
- Determine most desirable materials
 - physical properties
 - energy density
 - oxidizer or fuel or combination of both
- Explore methods especially useful for salts or polymers (block or random)
 - ion-exchange of anions and cations easy
 - many good anions available
 - energetic borates are good anions
 - energetic groups in polymer backbones and side-chains
- Use acetylide is an energy-dense moiety
 - acidic hydrogen on acetylene provides convenient handle for synthetic modification
 - acetylide is a convenient nucleophile for attack on metal-halides and on substituted organic halides
- Amines are good nucleophiles
 - propargyl is easily substituted onto amines
 - energetic cations can be prepared

Examples of energetic anions and cations are shown in Table 5. This is a short set of charged moieties, but illustrates the types of systems currently used in the energetics field for combinatorial type synthesis. This list can be expanded, and similar lists can be made for energetic functional groups for fuels or oxidizers and for densiphores. As new reactions for novel combinations of energetic functionalities are developed, the cardinality of our combinatorial basis set can be expanded.

The combinatorial approach presented here is not yet completely thought out, but it offers a way of thinking about and categorizing the synthesis of new materials. Ultimately, it could result in more choices of energetic materials if correctly applied.

Table 5. Anions and Cations Used in Energetic Materials

Cations	Anions
$N_2H_6^{+2}$	NO_3^-
NO^+	NO_2^-
M^{+n}	$N(NO_2)_2^-$
$N_2H_5^+$	ClO_4^-
NO_2^+	$C(NO_2)_3^-$
NH_3OH^+	
	

4.0 EXPERIMENTAL PROCEDURES

4.1 Synthesis of 1,3 -dioxyamine-2-nitraazapropane, $O_2NN[CH_2ONH_2]_2$

$O_2NN[CH_2ONC(OCH_2CH_3)CH_3]_2$: Ethyl-N-hydroxyacetamidate (3.89 g, 38 mmol) was dissolved in MeCN (150-ml) in a three-neck 200-mL flask. KOH (85%, 2.49 g, 38 mmol), ground to a fine powder, was then added to the solution which was warmed to 68°C for 30 min. The solution was cooled to ambient temperature and added via large bore cannulae to $O_2NN[CH_2Cl]_2$ in MeCN (75 mL). The color of the resulting solution was yellow-orange, and a fine white precipitate was observed. The mixture was heated at 65°C for 1 hr, cooled to ambient temperature over 30 min and filtered. Removal of solvent in vacuo produced a yellow oil that dissolved in Et₂O (30-ml) and was washed with water (3 x 20-ml). After drying the Et₂O layer over Na₂SO₄, all solvent was removed in vacuo. The oily residue was distilled and the product collected at 120°C (10-2 torr). The yield was 3.42 g, 62%, having a melting point of 63°C. The ¹H NMR gave (CDCl₃, 30°C) 5.6 (s, 4H), 4.05 (q, 4H), 1.97 (s, 6H), 1.3 (t, 6H).

$O_2NN[CH_2ONH_2]_2$: $O_2NN[CH_2ONC(OCH_2CH_3)CH_3]_2$ (1.96 g, 6.7 mmol) was dissolved in absolute EtOH (40-ml). HCl (37%, 1.44 g, 14.7 mmol) was added to this solution after stirring for 2 hrs all volatiles were removed, leaving a solid residue. This dihydrochloride salt of $O_2NN[CH_2ONH_2]_2$ was washed with Et₂O (2 x 20-ml) and dried in vacuo. The yield was assumed quantitative. The solid was transferred to a flask, suspended in absolute EtOH (30-ml) and neutralized to a pH of 8 with a premade KOH solution (1.0 g, 85% KOH in 20-ml of EtOH). The KCl was removed by filtration and the mother liquor concentrated in vacuo to give a waxy solid product (0.92 g, 90%). The $O_2NN[CH_2ONH_2]_2$ may be recrystallized from EtOH with significant losses. The melting point was 63°C and ¹H NMR (DMSO, 30°C) gave 6.45 (s, 4H), 5.27 (s, 4H).

4.2 Synthesis of $O_2NN[CH_2ONH_3^+]_2 [ClO_4^-]_2$

$O_2NN[CH_2ONH_2]_2$ (0.52 g, 3.42 mmol) was dissolved in absolute EtOH (20-ml) and cooled to 0°C. Perchloric acid (70%, 0.98 g, 6.84 mmol) was then added dropwise and the solution was stirred at ambient temperature for 20 min. Drierite (3 g, presaturated with EtOH) was added and the slurry was stirred for 20 min and filtered. The filtrate was then concentrated to 2 mL and Et₂O (5 mL) was layered carefully on top of the solution. After 48 h crystals appeared and were isolated by filtration, washed with Et₂O (20-ml), and dried in vacuo. The yield was 0.4 g, 33%, having a melting point of 150°C, and a ¹H NMR (DMSO, 30°C) of 5.4 (s, 4H), 3.5 (brs).

4.3 Synthesis of 1,5 -dioxyamine-2, 4-dinitraazapentane, $CH_2[N(NO_2)CH_2ONH_2]_2$

$CH_2[N(NO_2)CH_2ONC(OCH_2CH_3)CH_3]_2$: Ethyl-N-hydroxyacetamidate (4.05 g, 39 mmol) was combined with MeCN (175 mL) in a three-neck 250-mL flask. One equivalent of KOH (85%, 2.49 g, 39 mmol), ground to a fine powder, was then added to the solution that was warmed to 68°C for 30 min. Then $CH_2[N(NO_2)CH_2Cl]_2$ (4.0 g, 19.5 mmol) dissolved in MeCN (20-ml) was added to this mixture over a period of 10 min. After addition and stirring at 68°C for 30 min. The slurry was cooled to ambient temperature and filtered over a medium glass frit. The filtered solid was dissolved in water (30-ml/0-ml) and extracted with Et₂O (3 x 100-ml). Removal of the solvent from the filtrate in vacuo produced a yellow-brown oil that was dissolved in Et₂O (140-ml) and washed with water (3 x 30-ml). All Et₂O fractions were combined and dried over Na₂SO₄. Concentration and cooling to -20°C produced 1.27 g of crystalline product. Repeat of this procedure produced 0.75 g more product giving a combined yield of 2.02 g, 31%. The melting point was 71-74°C. The ¹H NMR (DMSO, 30°C) gave 5.85 (s, 2H), 5.6 (s, 4H), 3.92 (q, 4H), 1.9 (s, 6H), 1.2 (t, 6H).

$\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2\text{ONH}_2]_2$: $\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2\text{ONC}(\text{OCH}_2\text{CH}_3)\text{CH}_3]_2$ (1.00 g, 2.96 mmol) was suspended in absolute EtOH (30-ml). HCl (37%, 0.58 g, 14.7 mmol) was added to this solution at 25°C. The reaction was slow until the mixture was warmed to 50°C and the dihydrochloride salt of $\text{CH}_2[\text{N}(\text{NO}_2)\text{CH}_2\text{ONH}_2]_2$ precipitated. After stirring for 1 hr the solid was isolated by filtration and rinsed with EtOH and then Et₂O. The yield was 0.71 g, 80%. The salt (0.6 g, 2.0 mmol) was suspended in absolute EtOH (40-ml), and KOH solution (0.5 g of 85% KOH in 30-ml of EtOH) was used to neutralize to a pH of 8. The KCl was removed by filtration and the solvent was removed from the filtrate to give 0.25 g of product. Further rinsing of the KCl solid gave more product, 0.15 g. The combined yield was 0.35 g, 77% and the melting point was 90-95°C. ¹H NMR (DMSO, 30°C) gave 6.6 (s, 4H), 5.88 (s, 2H), 5.3 (s, 4H).

4.4 Synthesis of Tetrapropargyl Ammonium Tetrapropynyl Borate

Tetrapropargyl ammonium bromide. Tripropargyl amine (2.6 g, 2 mmol, obtained from Aldrich) was mixed neat with propargyl bromide (2.4 g, 2 mmol) and allowed to stand at room temperature, for 48 hr, at which point the mixture was completely solid. The solid was dissolved in 20-ml H₂O, decanting away from insolubles.

Lithium tetrapropynyl borate. Propyne (60 mmol, 2.4 g) was dissolved in 100-ml THF, cooled to 0°C under argon and treated with 50 mmol of n-butyllithium (2 m solution in hexanes). A white precipitate resulted, and this was treated with a solution of 10 mmol of BCl₃ in 25 mL of toluene.

The resulting suspension was stirred 30 min at 0°C, warmed to 50°C for 5 min, cooled, treated with 50-ml of EtOH, and purged with CO₂ until neutral. The mixture was then concentrated in vacuo, digested in 25 ml of 1:1 EtOAc/CH₃CN, and passed through a 1-in x 2 in silica column, eluting with 1:1 CH₃CN/EtOAc, collecting the R_f = 0.6 peak.

The effluent was concentrated, giving 1 g of waxy solid.

Tetrapropargyl ammonium tetrapropynyl borate. The aqueous solution from tetrapropargylammonium bromide along with the aqueous solution of 500 mg of the solid of lithium tetrapropynyl borate in 20-ml H₂O were combined, resulting in a precipitate of fine needles, collected by filtration, yielding 100 mg (20%) of the desired product. The ¹H NMR (CD₃CN/CDCl₃/TMS) gave δ 1.7 (m, 12 H); δ 3.35 (m, 4 H); δ 4.6 (d, 8 H), the IR (KBr) gave r = 2120 (s), 1440 cm⁻¹. X-ray crystal analysis confirmed structure.

4.5 Synthesis of Tetrapropargylammonium Tetraethynylborate

The procedure was identical to that for the tetrapropynyl borate salt, except that a four-fold excess of acetylene was dissolved in the THF to prevent Li₂C₂ formation. The yield was also ~20%. ¹H NMR (CD₃CN/CDCl₃/TMS) gave δ 2.0 (s, 4 H); δ 3.3 (m, 4 H); δ 4.5 (d, 8 H). IR (KBr) gave r = 3250 (s), 2130 cm⁻¹.

4.6 Synthesis of Poly(propyne-1,3-diyl) or (-C-C-CH₂-)_n

Diisopropylamine (11 g, 110 mmol) was dissolved in 150-ml THF, cooled to 0°C under argon, and treated with 100 mmol of n-BuLi (as a 2 m solution in hexane). Next, the mixture was cooled to -18°C and treated with 100 mmol of HC≡C-CH₂Br in one aliquot. The reaction was stirred overnight and allowed to warm to room temperature. It was a deep amber color at this point and was worked up. The reaction was concentrated in vacuo, digested in 250-ml CH₃OH, and filtered, collecting 1.7 g of brick-red powder.

The IR (KBr) gave r = 2130 (weak) cm⁻¹. The polymer deflagrated upon strong abrasion, exploded on heating to > 100°C in air.

4.7 Synthesis of Dipropargyl Malonitrile

Malonitrile (6.6 g, 100 mmol) and K_2CO_3 (40 g, 300 mmol) were mixed in 100-ml of DMF, stirred in an ice-bath under argon and treated with 30 g (250 mmol) of propargyl bromide over 30 min. The reaction was stirred 1 h at $0^\circ C$ and 4 hr at room temperature, and was worked up, by pouring the mixture into 500-ml H_2O and extracting 1 x 200-ml toluene. The toluene layer was extracted 2 x 500-ml H_2O , dried, passed through a 2 in x 1 in plug of SiO_2 , concentrated, and crystallized from heptane/ $CHCl_3$ to give 11.5 g (~70%) of needles, with a melting point of $73^\circ C$. The 1H NMR ($CDCl_3/TMS$) gave δ 2.5 (f, 2 H, $j = 2$ Hz); δ 3.2 (d, 4 H, $j = 2$ Hz).

5.0 CONCLUSIONS AND RECOMMENDATIONS

A number of new highly energetic fuels and fuel additives have been invented for use in hydrocarbon based systems. These can be used as fuels or as fuel additives in hydrocarbon/LOX-based systems. It is recommended that these compounds be scaled-up and tested and evaluated for use in liquid systems. The compounds of interest include the acetylene polymers monopropargylamine, dipropargylamine, and tripropargylamine, the tetraalkylammonium tetraethynylborate salts, and 2,4-hexadiyne. The ability to efficiently burn the acetylide group to obtain its energy along with long-term storage and handling concerns, have not yet been determined.

It is also recommended that the new oxidizers discovered under this contract be scaled up and tested for use as perchlorate replacements. Their energy density and oxidizing power are in excess of ammonium perchlorate and they should be considered for use. These compounds show excellent thermal properties, are energy dense, and are not hygroscopic as are other oxyamine derivatives.

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333 Ravenswood Avenue
Menlo Park CA 94025

AFRL/PR Technical Library (3)
6 Draco Drive
Edwards AFB CA 93524-7130

Air University Library (1)
AUL/SE
600 Chennault Circle
Maxwell AFB AL 36112-6424

Chemical Propulsion Information Agcy (1)
Attn: Tech Lib (Dottie Becker)
10630 Little Patuxent Parkway, Suite 202
Columbia MD 21044-3200

Defense Technical Information Center (Orig + 1)
Attn: DTIC-ACQS (Acquisitions)
8725 John J. Kingman Road, Suite 94
Ft. Belvoir VA 22060-6218