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SYNTHESIS OF CUBANE BASED ENERGETIC MOLECULES

Final Report

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December 1989

By: Robert J. Schmitt, Jeffrey C. Botaro,
and Paul E. Penwell
Organic Chemistry Program

Prepared for:

OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, VA 22217-5000

Attention: Dr. Richard Miller
Code 1132P

Contract No. N00014-86-C-0699
SRI Project PYU-2723

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Approved by:

David M. Golden, Laboratory Director
Chemistry Laboratory

G. R. Abrahamson
Senior Vice President
Sciences Group

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<p>The need to pack more power with less weight into less space in tomorrow's weapons drives this program for the synthesis of new generations of super energetic materials based on cubane. Cubane's heat of formation (+161 kcal/mol), density (1.29 g/cm³), and strain energy (+159 kcal/mol) make a combination not exceeded by any other stable hydrocarbon available in reasonable quantities. The addition of energy-rich and/or oxidizing groups will create exceptionally dense and powerful explosives, propellants, and fuels.</p> <p>The cubane system is geometrically very different from ordinary compounds and thus requires the development of innovative methods to prepare substituted cubanes. This SDI/IST project provides the first extended testing of the theories of organic chemistry regarding highly strained compounds. The first energetic cubanes have been synthesized including the only cubanes sufficiently oxidized to be considered as explosives or propellants. The objective has been to develop new methods for the functionalization of the cubane nucleus and to synthesize energetic cubanes for the SDI/IST program. This program has developed new methods of cubane functionalization that have resulted in a more efficient, environmentally sound method for the synthesis.</p>					
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of the important intermediate cubane-1,2,4,7-tetracarboxylic acid and an improved synthesis of 1,4-cubane diol. The first preparation of several energetic polynitrocubanes has also been achieved: cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester), cubane-1,4-bis(β,β,β -trinitro-ethylester), cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester), N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, and N,N'-dinitro-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The highly energetic 1,4-dicyanocubane and cubane-1,4-diisocyanide have been synthesized as examples of highly energy dense fuels. The most recent work has involved the synthesis of 1,2,4,7-tetracyanocubane, an important precursor to several other energetic cubanes. Several new routes have been developed for the synthesis of the powerhouse dinitramino group, $N(NO_2)_2$. This work has resulted in new, more efficient and flexible routes to the dinitramino group. These results are being applied to the synthesis of dinitramino cubanes.

CONTENTS

EXECUTIVE SUMMARY	iii
Energetic Cubanes Synthesized.....	v
PREFACE	vii
INTRODUCTION.....	1
RESULTS	2
New Oxidizers and Explosives	2
Polynitro Derivatives of Aminocubane.....	2
Cubane Esters of Trinitroethanol and Fluorodinitroethanol.....	7
Cubane-1,2,4,7-Tetrakis(Ammonium Perchlorate).....	8
Synthesis of Geminal Dinitramines.....	11
New Fuels and Syntheses.....	13
Polycyanocubanes	13
Cubane-1,4-Diisocyanide.....	17
New Synthesis of Cubane-1,2,4,7-Tetracarboxylic Acid.....	18
Propellancubane Nitration.....	21
Attempted Synthesis of Cubylnitrates.....	22
EXPERIMENTAL PROCEDURES.....	24
CONCLUSIONS.....	29
REFERENCES	30
APPENDIX: IMPROVED SYNTHESIS OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID.....	A-1

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EXECUTIVE SUMMARY

The need to pack more power with less weight into less space in tomorrow's weapons drives this program for the synthesis of new generations of super energetic materials based on cubane. Cubane's heat of formation (+161 kcal/mol), density (1.29 g/cm³), and strain energy (+159 kcal/mol) are extraordinarily high, a combination not exceeded by any other stable hydrocarbon available in reasonable quantities. The addition of energy-rich and/or oxidizing groups will create exceptionally dense and powerful explosives, propellants, and fuels.

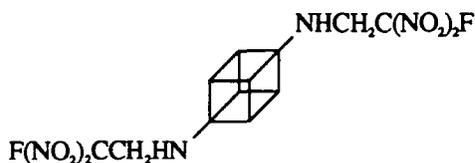
The cubane system is geometrically very different from ordinary compounds and thus requires the development of innovative methods to prepare substituted cubanes. To do this in sensible ways requires a keen appreciation of the effects of distorted geometry on reactivity, the subject of much speculation and hypothesis for the past two decades. This SDI/IST project provides the first 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 have been synthesized, including the only cubanes sufficiently oxidized to be considered as explosives or propellants.

The objective of our research has been to develop new methods for the functionalization of the cubane nucleus and to synthesize energetic cubanes for the SDI/IST program. Achievements in previous years of this program of cubane research 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 and an improved synthesis of 1,4-cubane diol. We have also done the first preparation of several energetic polynitrocubanes: cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester), cubane-1,4-bis(β,β,β -trinitroethylester), cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester), N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, and N,N'-dinitro-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The highly energetic 1,4-dicyanocubane and cubane-1,4-diisocyanide have been synthesized as 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. In other investigations, we have developed several new routes for the synthesis of the

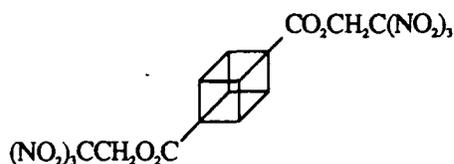
powerhouse dinitramino group, $N(NO_2)_2$. This work has resulted in new, more efficient and flexible routes to the dinitramino group. These results are being applied to the synthesis of dinitramino cubanes. A summary of the synthetic efforts is included on the next two pages.

Energetic Cubanes Synthesized

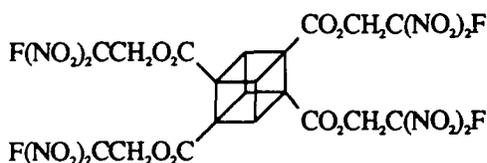
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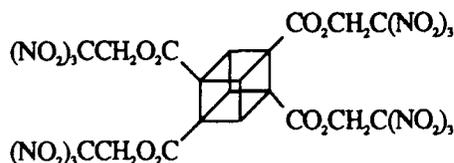
July 1986. N,N' -bis-(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The first energetic cubane derivative, precursor to other, more energetic cubanes.



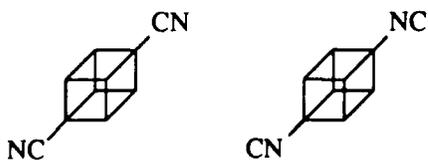
January 1987. Cubane-1,4-bis-(β,β,β -trinitroethylester). Model for other, more highly functionalized energetic cubyl esters.



October 1987. Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester). The first fully oxidized cubane.



October 1987. Cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester). The first over-oxidized cubane derivative.

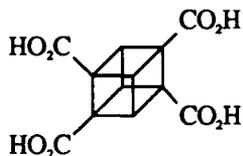


January 1987. 1,4-Dicyanocubane. April 1988. 1,4-Diisocyanocubane. First examples of new cubane fuels using cyano and isocyanato groups to increase the heat of formation. Calculated heats of formation +191 kcal/mol and +221 kcal/mol, respectively.

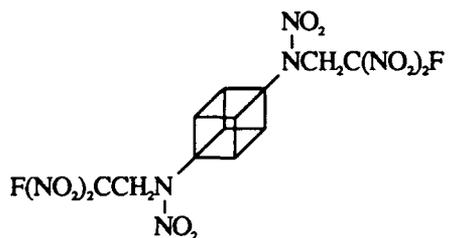
Energetic Cubanes Synthesized

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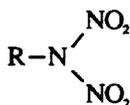
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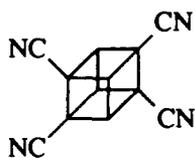
July 1988. Cubane-1,2,4,7-tetraacid. New, significantly shorter, and more efficient synthesis of this important intermediate.



August 1988. N,N'-dinitro-N,N'-bis(beta,beta-dinitro-beta-fluoroethyl)-1,4-diaminocubane. Model compound for the tetrasubstituted derivative.



May 1989. Development of new methods for the preparation of dinitramino groups.



June 1989. 1,2,4,7-Tetracyanocubane, a key intermediate for the synthesis of 1,2,4,7-tetrakis(dinitromethyl)cubane.

PREFACE

We thank Dr. Richard Miller and Dr. William Koppes of the Office of Naval Research (Contract No. N00014-86-C-0699), the Strategic Defense Research Initiative, Office of Science and Technology, for support of this work and Dr. Philip Eaton for the many long and stimulating discussions. We thank Dr. Richard Gilardi of the Naval Research Laboratory Structure of Matter Laboratory for the x-ray crystal structure determinations, which made it possible to progress much faster than would otherwise have been possible.

INTRODUCTION

Innovative concepts in molecular structures must be explored to achieve the goal of generating more propulsion power with less weight and in less space because the materials now available do not have enough energy density for advanced applications such as those in the SDI/IST project. All energetic propellants are metastable by nature, so the trick is to find kinetically stable molecular structures, compounds that can undergo long term storage. The ultimate goal is to find compounds that are kinetically rocks but thermodynamically powerhouses. A class of materials that have exceptional material and energetic properties but have until now been unexplored for propellant applications are the cubanes. Cubane's heat of formation (+161 kcal/mol), density (1.29 g/cm³), 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.

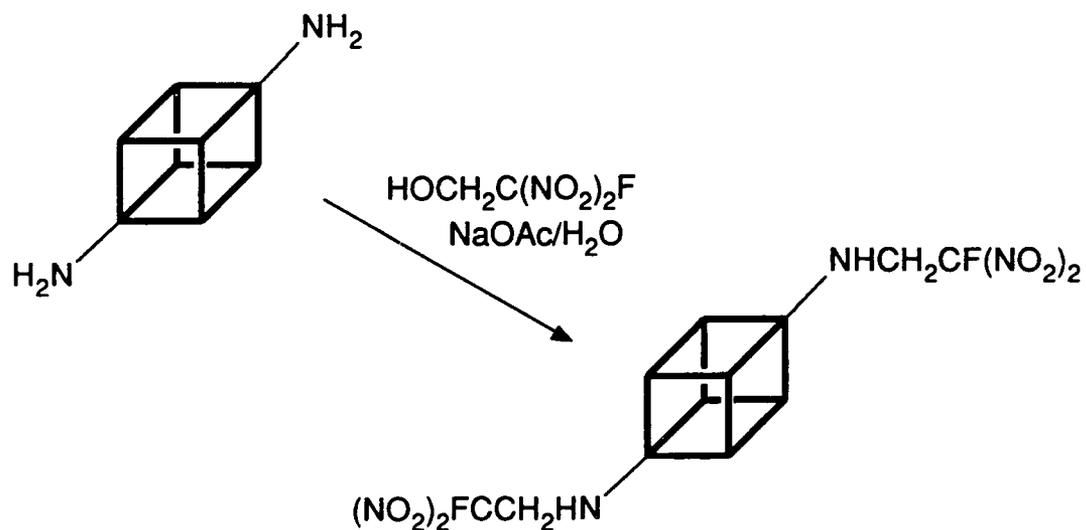
The cubane system is geometrically very different from ordinary compounds, so innovative methods must be developed to prepare substituted cubanes. To do this in sensible ways requires a keen appreciation of the effects of distorted geometry on reactivity, the subject of much speculation and hypothesis for the past two decades. This SDI/IST project provides the first extended testing of the theories of organic chemistry regarding highly strained compounds. Under the sponsorship of the Office of Naval Research (ONR Contract No. N00014-86-C-0699), this program has already made tremendous progress turning theory into practice. Novel methodology has been developed for the systematic substitutions and functional group transformations on the cubane nucleus. The first energetic cubanes have been synthesized, including the only cubanes sufficiently oxidized to be considered as propellants or explosives.

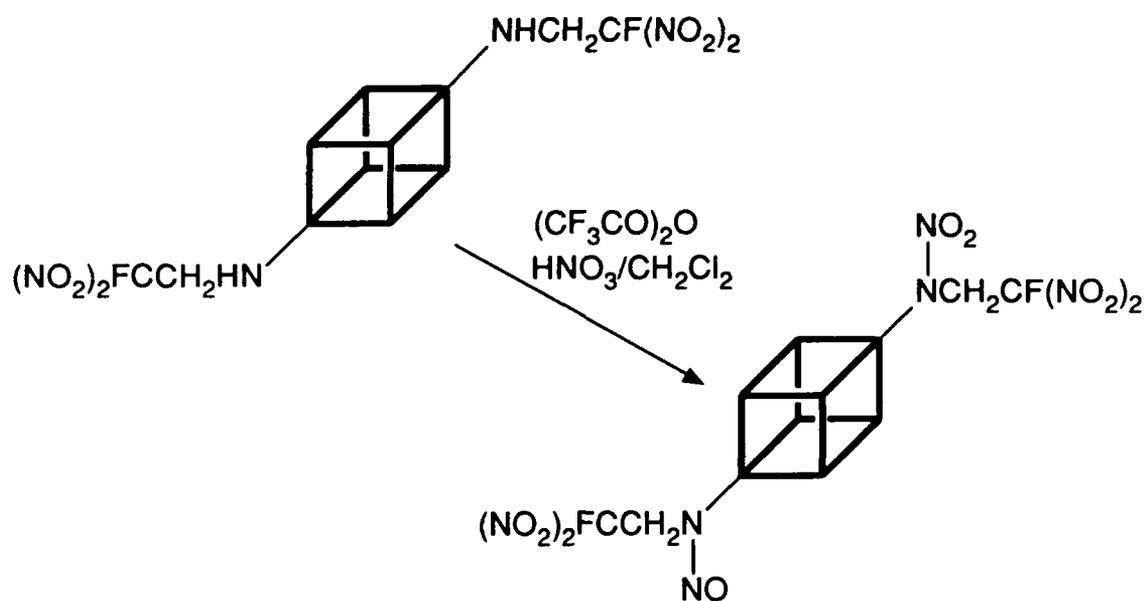
RESULTS

NEW OXIDIZERS AND EXPLOSIVES

Polynitro Derivatives of Aminocubane

We have succeeded in synthesizing the first polynitro cubane compounds. The derivatives we prepared have nitro groups substituted at the amino group of a cubane. Clearly, these compounds are only intermediate targets along the pathway to the synthesis of cubanes that are nitrated on the cage. The first amino substituted cubane we prepared was *N,N'*-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, which was then further nitrated to give the second, *N*-nitro-*N'*-nitroso-*N,N'*-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, as shown below.

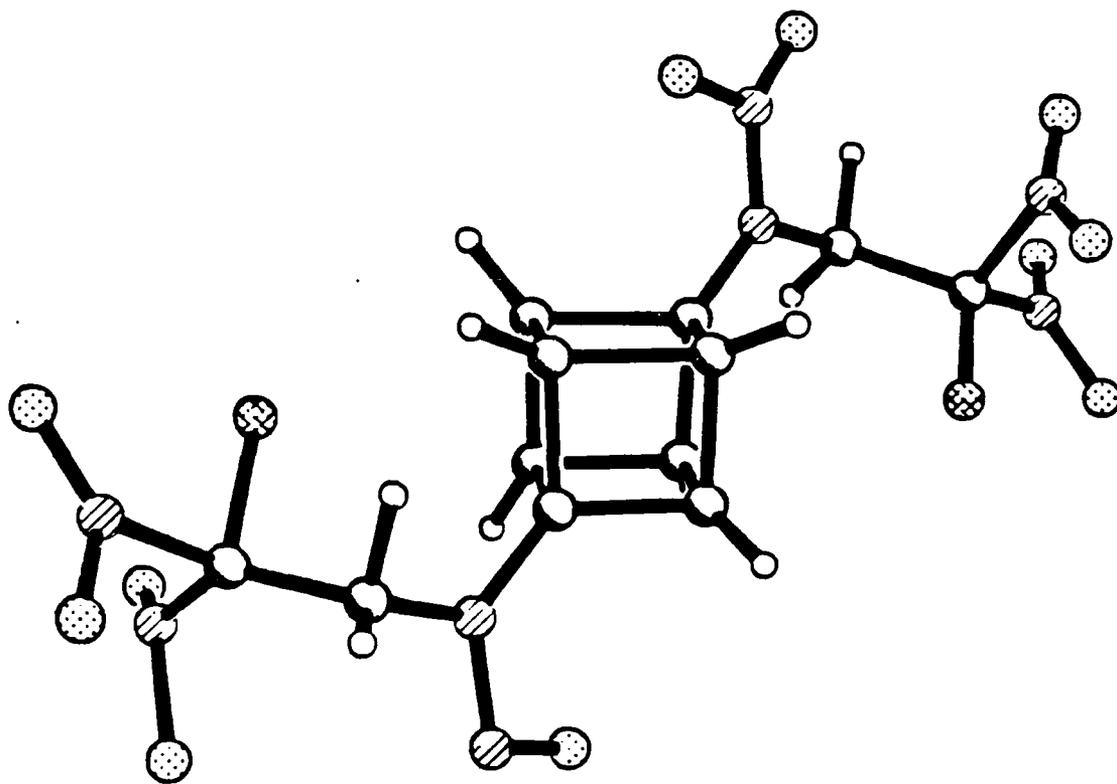




The density of N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane is 1.827 g/cm³. Its x-ray crystal structure is shown in Figure 1.

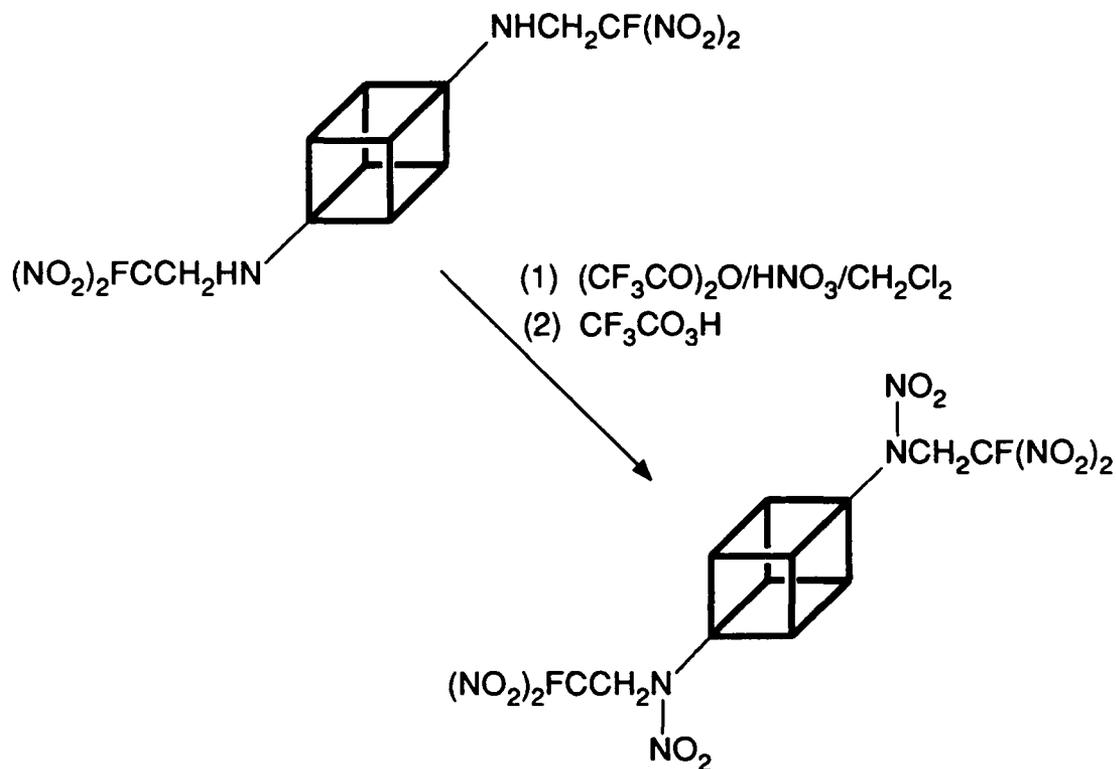
Our simple KJSM^{1,2,3} calculations indicate that N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane has a detonation pressure (P_{CJ}) of 351 kbar and a detonation velocity (D_{vel}) of 8.9 mm/ μs . These values compare favorably to those of HMX, the best oxidizer currently 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 of the carbon and hydrogen to CO and water upon combustion. These excellent 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} .

In recent work, we succeeded in synthesizing the fully oxidized derivative, N,N'-dinitro-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane, by oxidation of the initially formed product as shown below.



RA-2723-18

Figure 1. X-ray crystal structure of N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -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 what can be done with the cubane nucleus to enhance its energetic properties by 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(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane are more stable than *N,N'*-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The aminocubane system is itself unstable and eventually decomposes via opening of the cubane ring system through donation of the free electron pair of the amino group into the cubyl cage. 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 is important because it indicates that *N*-nitro-aminocubanes or aminocubanes with strongly electron withdrawing groups on the amino group will be stable.

Sample: 1 4 NO2 AMINE CUBANE
Size: 3.72 MG
Rate: 10 DEG/MIN

DSC

Date: 23-Aug-88 Time: 12:56:25
File: 082388.04 SERVICE DISK #5
Operator: PEP

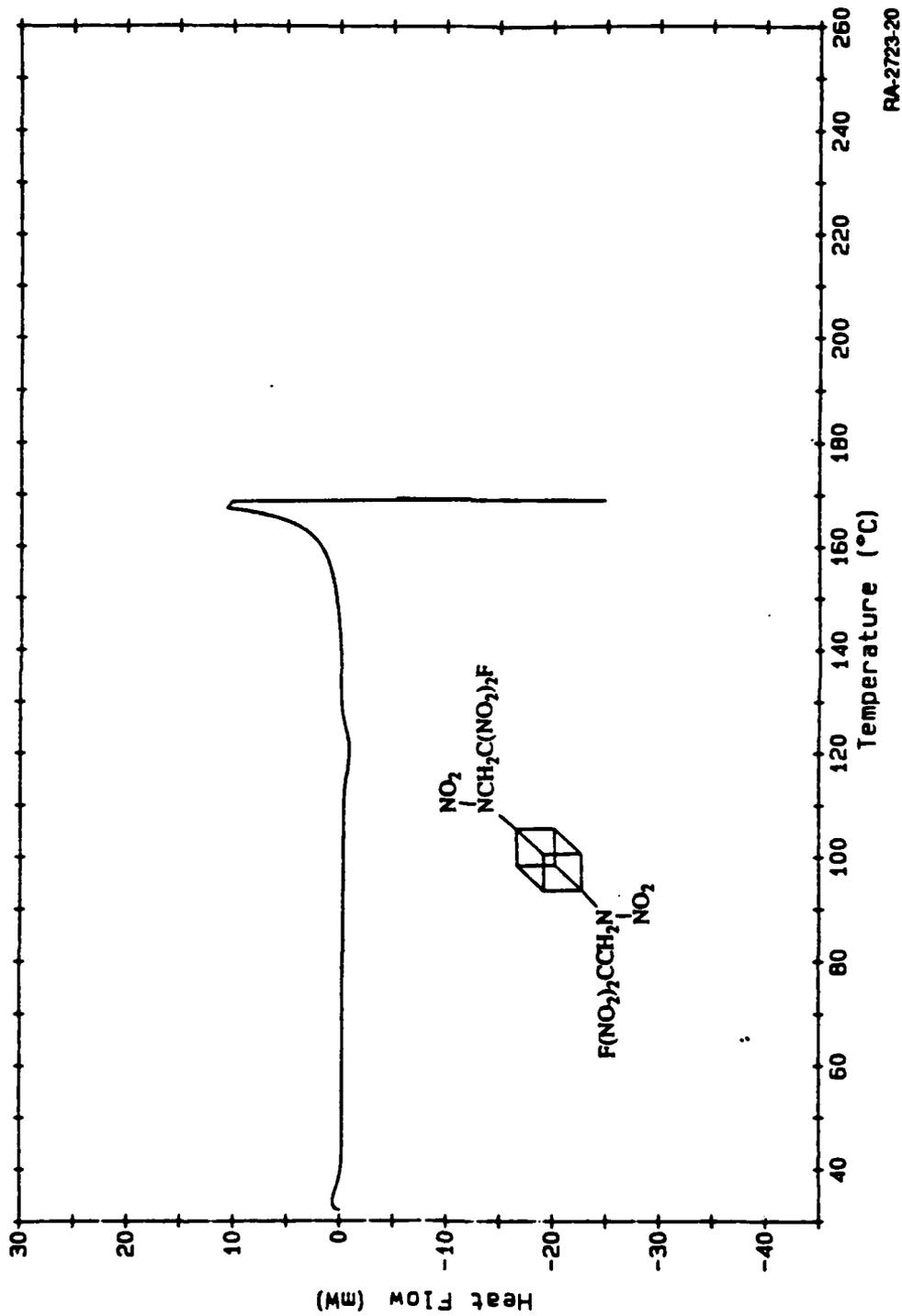
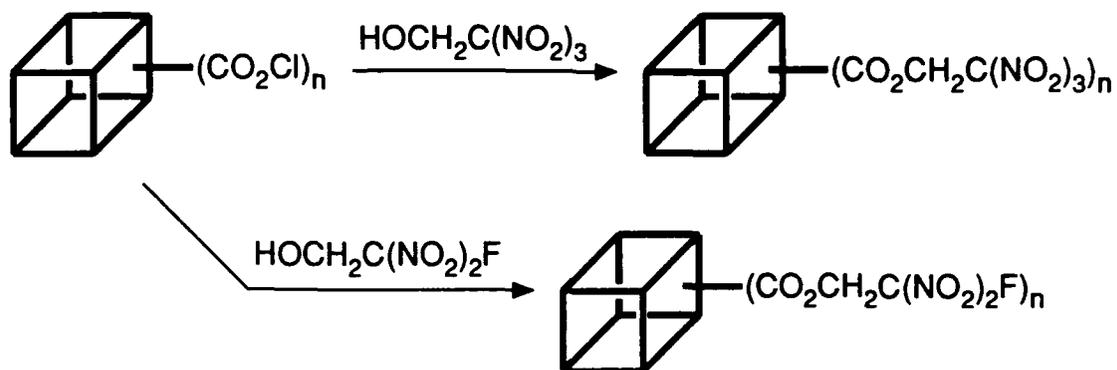


Figure 2. DSC for N,N'-dinitro-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane.

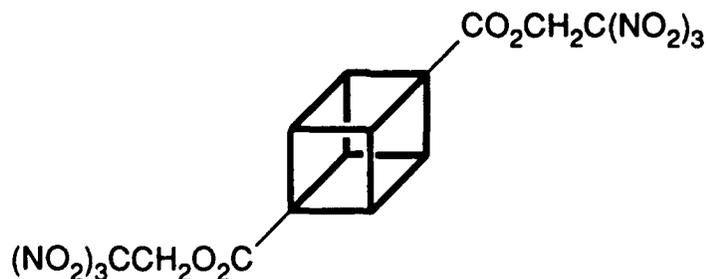
Cubane Esters of Trinitroethanol and Fluorodinitroethanol

We have also prepared cubane esters substituted with 2,2,2-trinitroethanol (TNE) and 2,2-dinitro-2-fluoroethanol (FDNE). These compounds give immediate access to very highly nitrated cubanes that are oxidized to $\text{CO}/\text{H}_2\text{O}/\text{N}_2$ and beyond. These compounds represent the first examples of fully oxidized cubanes.

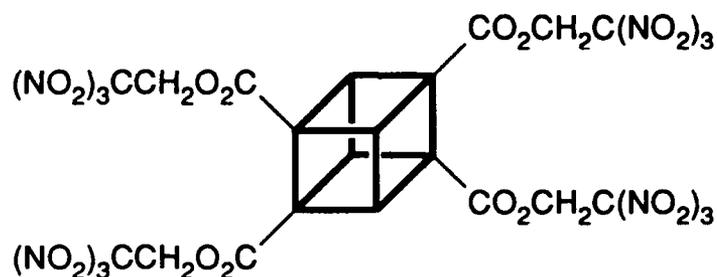


where $n = 2$ or 4 .

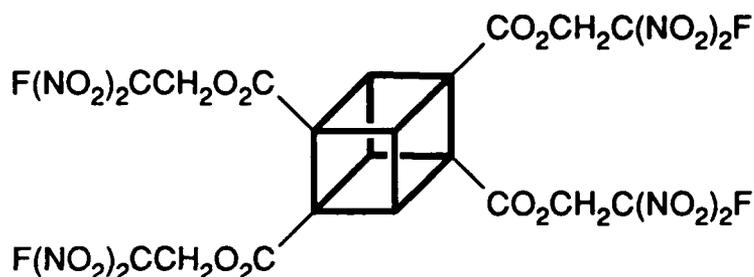
We have thus far synthesized three of the possible polynitro esters: cubane-1,4-bis(β,β,β -trinitroethylester), cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester), and cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester). Structures of these compounds are shown below.



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



Cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester)



Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester)

Density = 1.762 g/cm³

Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester) and cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester) represent the first examples of potentially useful energetic materials made from a cubane nucleus. Cubane-1,2,4,7-tetrakis(β,β,β -trinitroethylester) is over-oxidized and is an energetic powerhouse. Figure 3 shows the x-ray crystal structure of cubane-1,2,4,7-tetrakis(β,β -dinitro- β -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/cm³. Figure 4 shows the DSC for this compound.

Cubane-1,2,4,7-Tetrakis(Ammonium Perchlorate)

The first synthesis of a compound believed to be cubane-1,2,4,7-tetrakis(ammonium perchlorate) was done at Thiokol by Rod Willer and later by a different method at SRI. In our synthesis, we began with the conversion of cubane-1,2,4,7-tetraiscyanate 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.

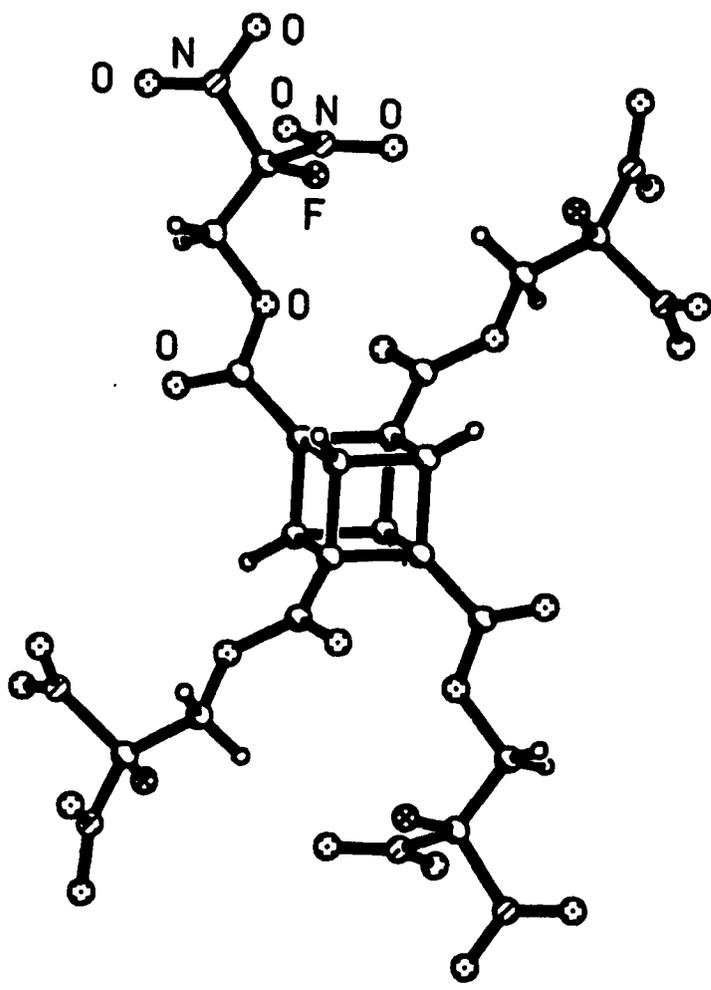


Figure 3. Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -fluoroethylester).

Density = 1.762 g/cm³

DSC Data File: gph10
 Sample Weight: 0.000 mg
 Fri Jul 31 16:38:44 1987
 cubane(CO2FDNE) 4

PERKIN-ELMER
 7 Series Thermal Analysis System

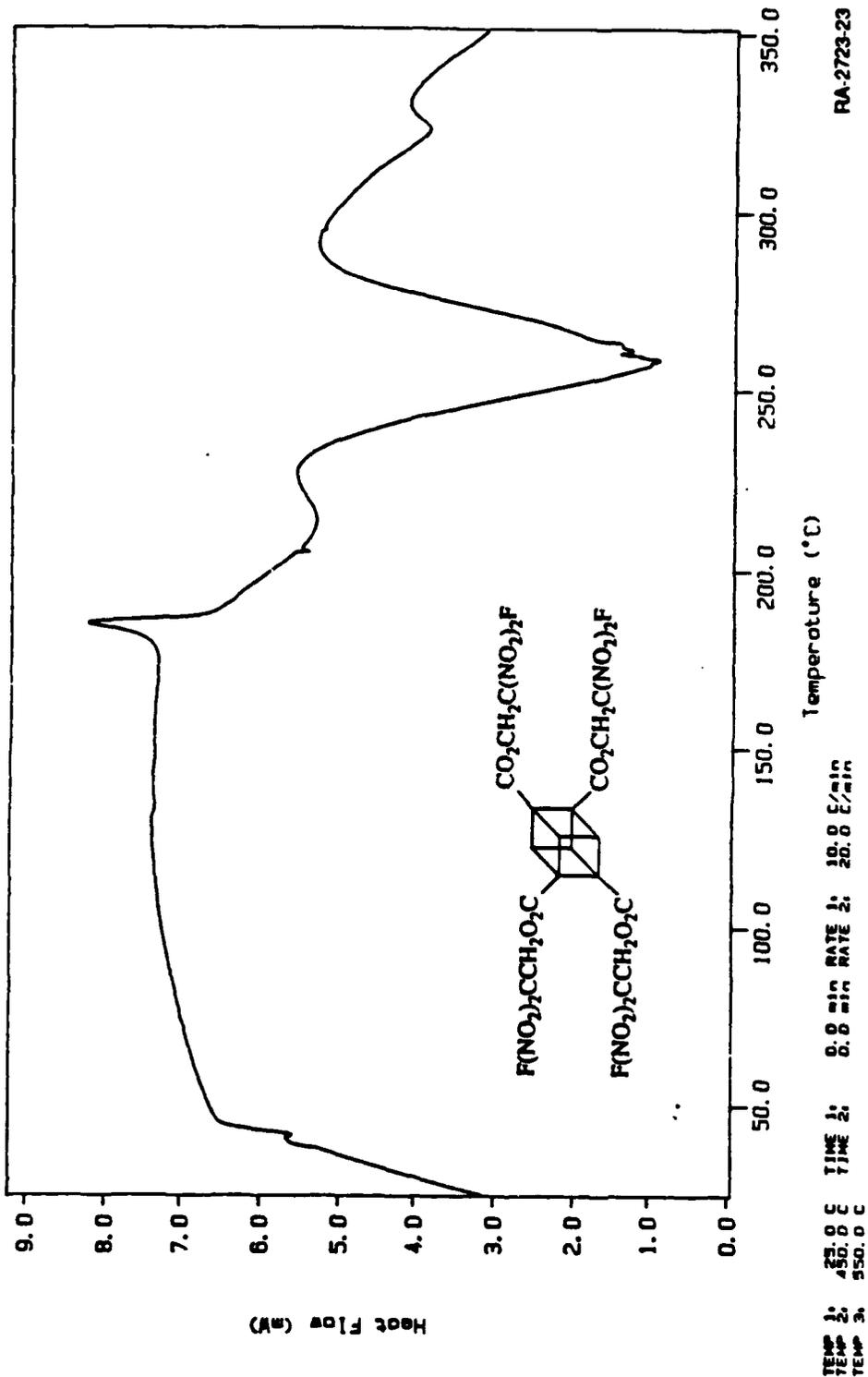


Figure 4. X-ray crystal structure of cubane-1,2,4,7-tetrakis(β,β-dinitro-β-fluoroethyl ester).

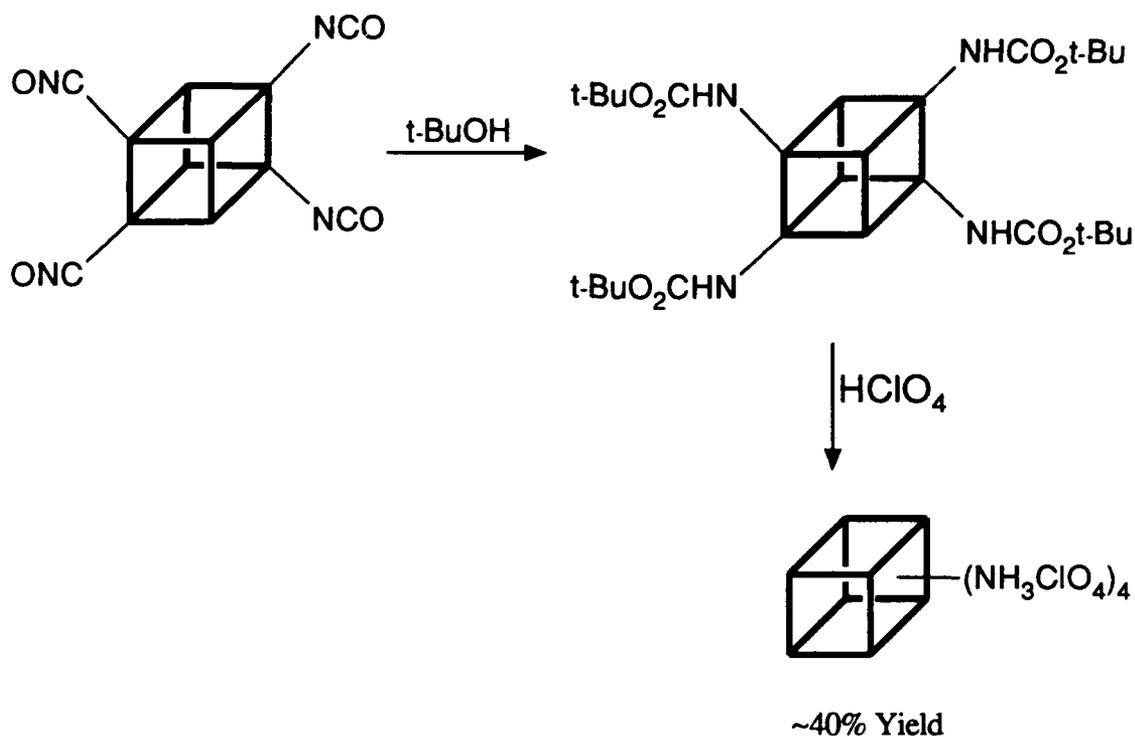


Figure 5 shows the DSC of the cubane-1,2,4,7-tetrakis(ammonium perchlorate) isolated on this project. The reaction is extremely exothermic; in fact, the exotherm was so strong we damaged the DSC equipment during the analysis.

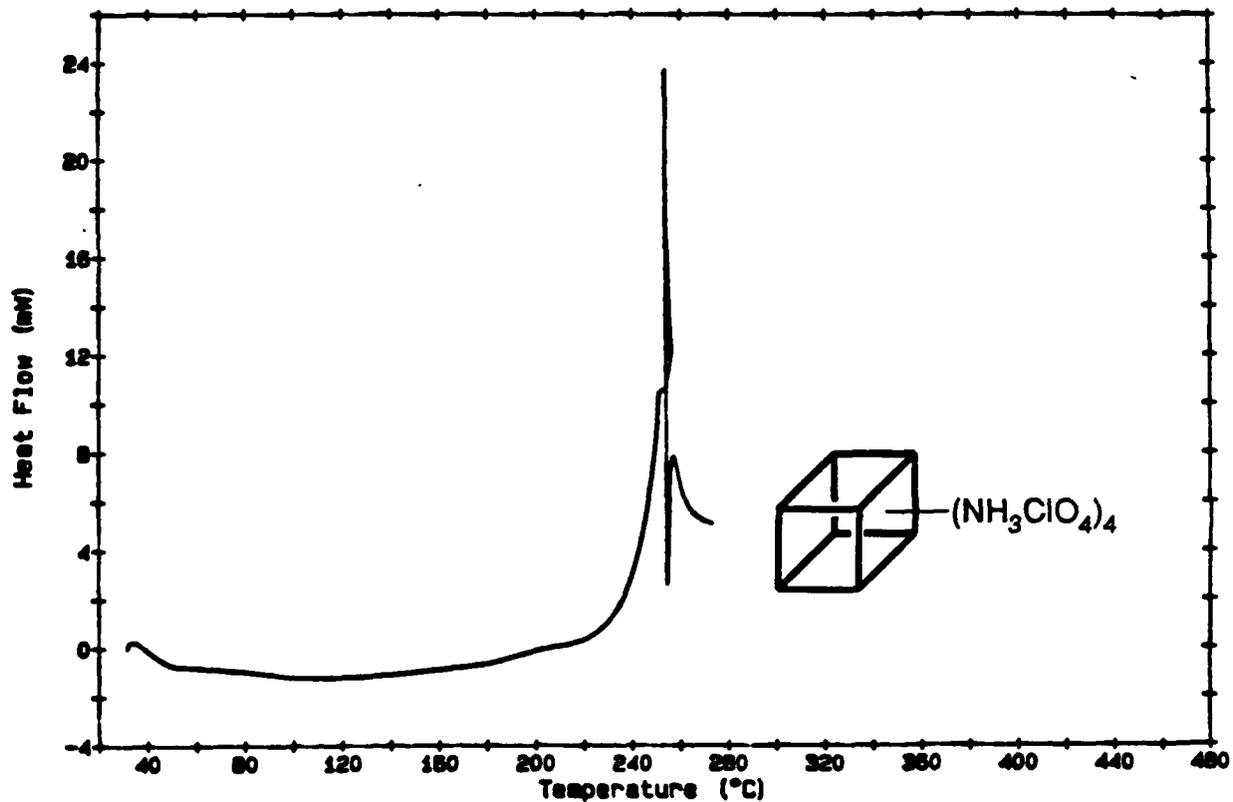
Synthesis of Geminal Dinitramines

Rod Willer of Thiokol has demonstrated that the dinitramino group on cubane decomposes with ring opening. However, in the course of this work, we developed several new routes to the synthesis of geminal dinitramino compounds that are not applicable to the synthesis of cubyl dinitramino compounds but nevertheless have resulted in an advancement in the state of the art. The best results were obtained in the synthesis of N,N -dinitramines from isocyanates. We were able to obtain the dinitramino derivative in up to 35% yield when the isocyanate was attached to a primary carbon, but only a 1% yield was obtained from the tertiary carbon of adamantane-1-isocyanate. We obtained no yield of cubane dinitramine from the same reaction. A further demonstration of the utility of this reaction is the synthesis of 1,6-bis(N,N -dinitramino)hexane and 1- N,N -dinitraminobutane in one step in reasonable yield.

Sample: CUBANE TETRA-NH4 ClO4
Size: 0.53 MG
Rate: 25 DEG/MIN

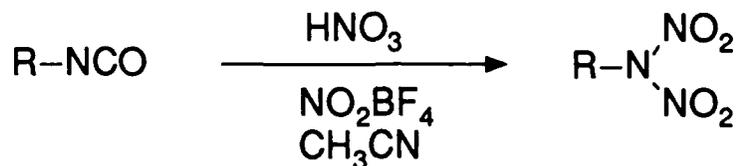
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Date: 24-Jan-89 Time: 8:30:06
File: BOTTARO.01 SERVICE #7
Operator: PEP

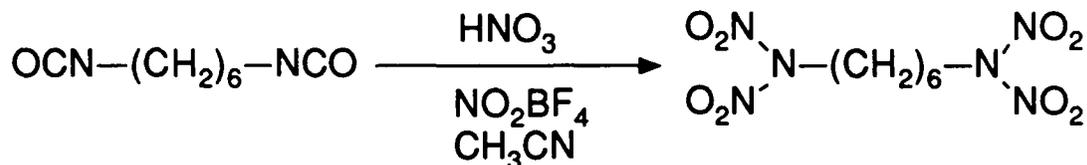


RA-320583-532
DuPont 109C

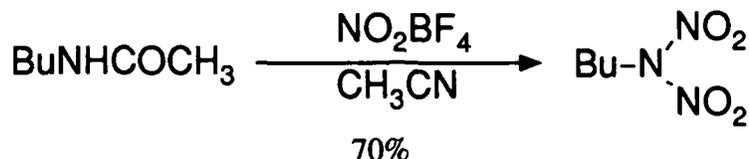
Figure 5. DSC of cubane-1,2,4,7-tetrakis(ammonium perchlorate).



R = Butyl, 35%
R = Adamantyl, 1%



10%



70%

These new synthetic reactions give a higher yield of geminal dinitramine and provide greater synthetic flexibility than was previously available.

NEW FUELS AND SYNTHESSES

Polycyanocubanes

We synthesized several of polycyanocubanes for use as dense, high energy rocket fuels. For example, octacyanocubane is calculated to have a heat of formation (ΔH_f) of +395 kcal/mol and a density greater than 1.5 g/cm³. 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 thermogravimetric analysis for which are shown in Figure 7 and 8). The structure and ΔH_f of these two compounds are shown below.

DSC Data File: dcc01
 Sample Weight: 0.000 mg
 Mon Jul 27 13:04:51 1987
 dicyanocubane

PERKIN-ELMER
 7 Series Thermal Analysis System

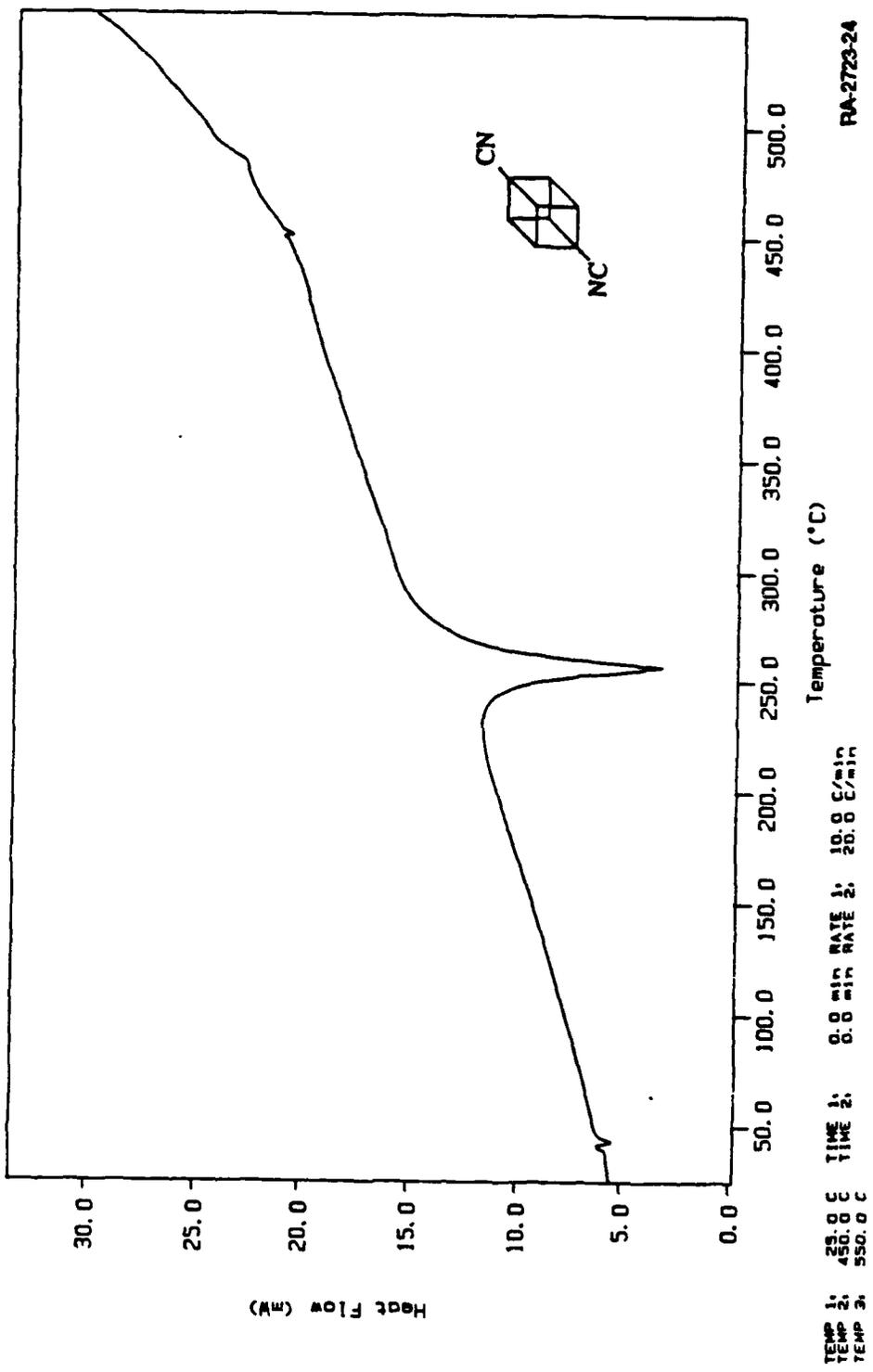
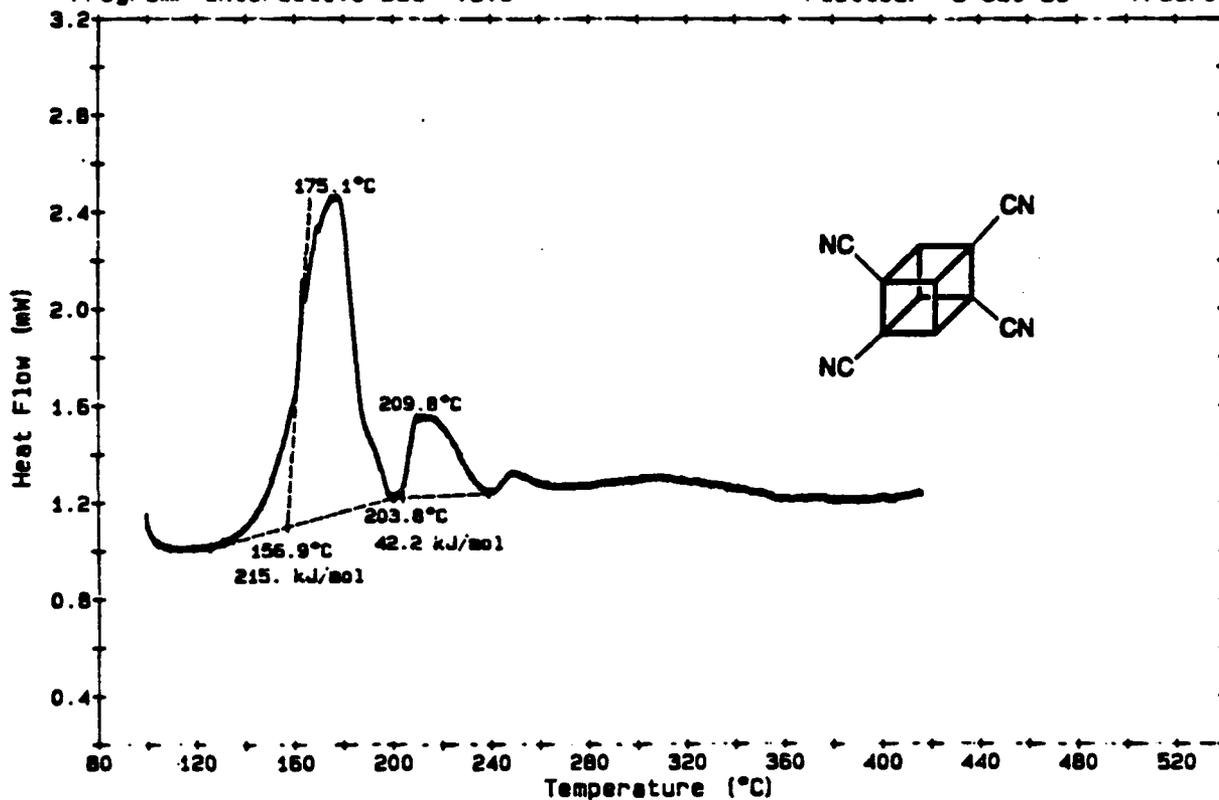


Figure 6. DSC of 1,4-dicyanocubane.

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



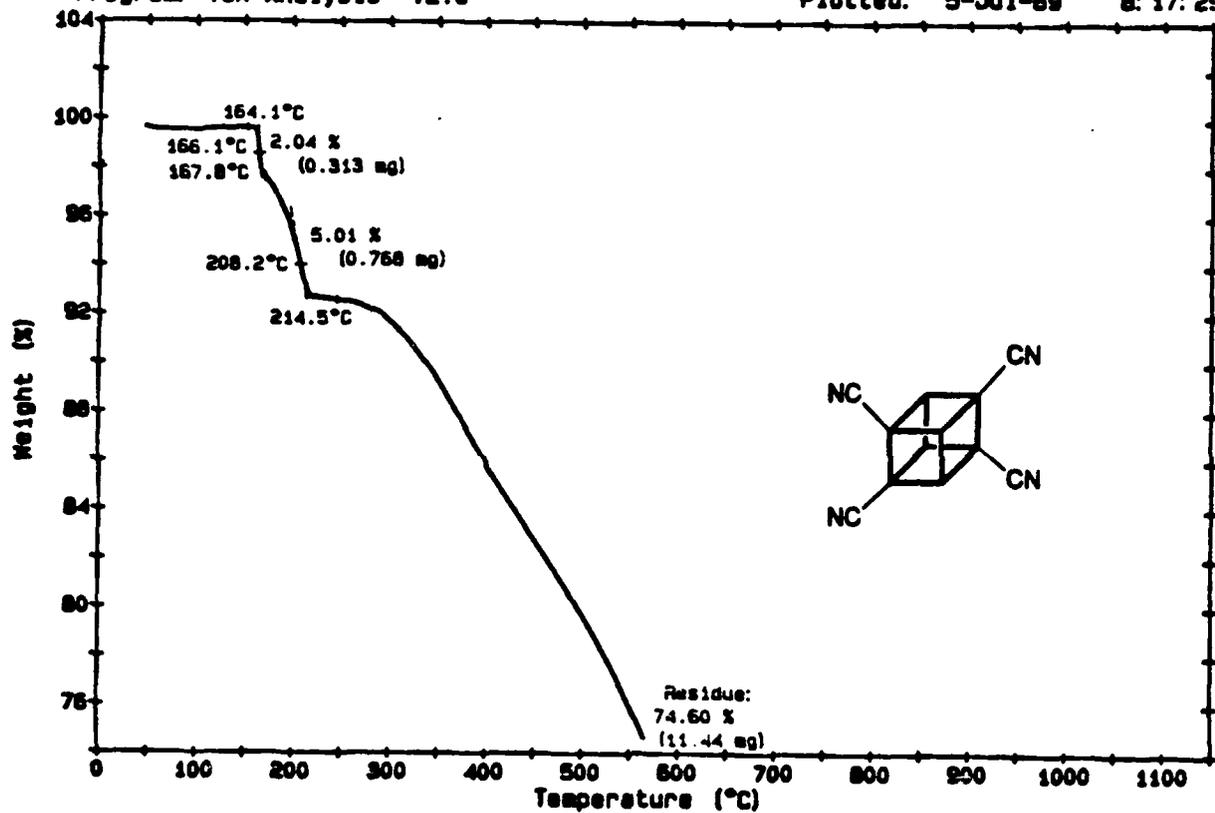
DuPont 1090
RA-320583-533

Figure 7. DSC of 1,2,4,7-tetracyanocubane.

Sample: 1247TETRACNCUBANE
Size: 15.33 mg
Rate: 1.0 DEG/MIN
Program: TGA Analysis V2.0

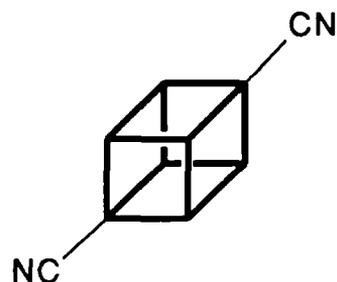
TGA

Date: 3-Jul-89 Time: 9:28:44
File: BOTTARO.09 SERVICE # 11
Operator: PEP
Plotted: 5-Jul-89 8:17:29

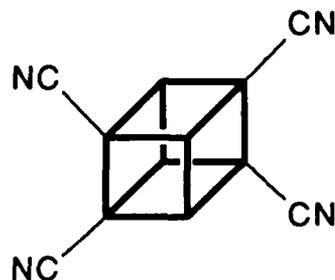


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RA-320583-534

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



1,4-Dicyanocubane
 ΔH_f (calc) = 191 kcal/mol

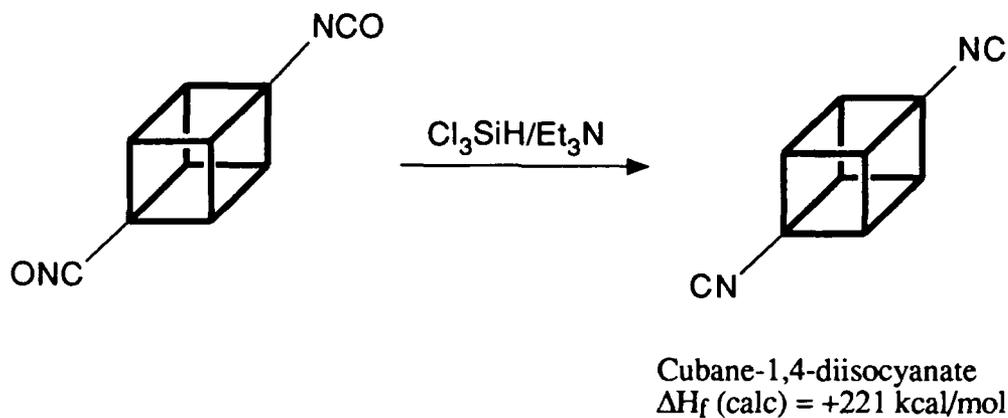


1,2,4,7-Tetracyanocubane
 ΔH_f (calc) = 253 kcal/mol

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 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.

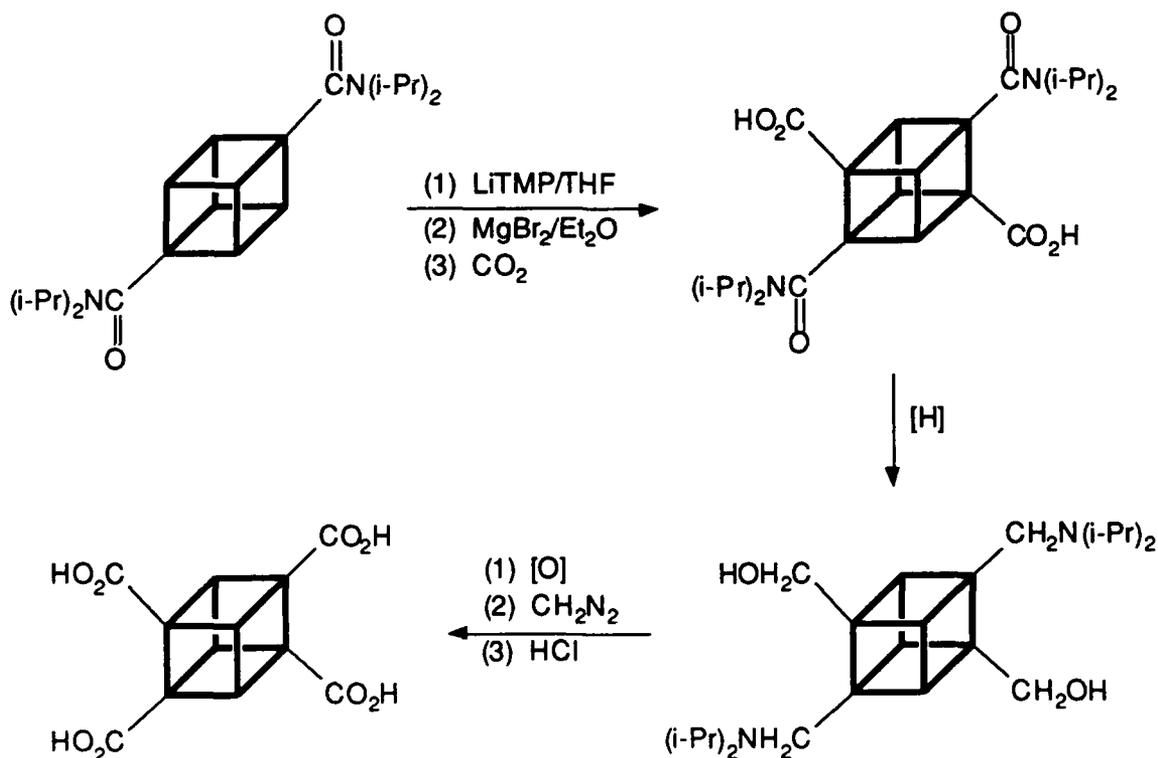
We recently synthesized cubane-1,4-diisocyanide by reacting cubane-1,4-diisocyanate with Cl_3SiH in Et_3N as shown below.



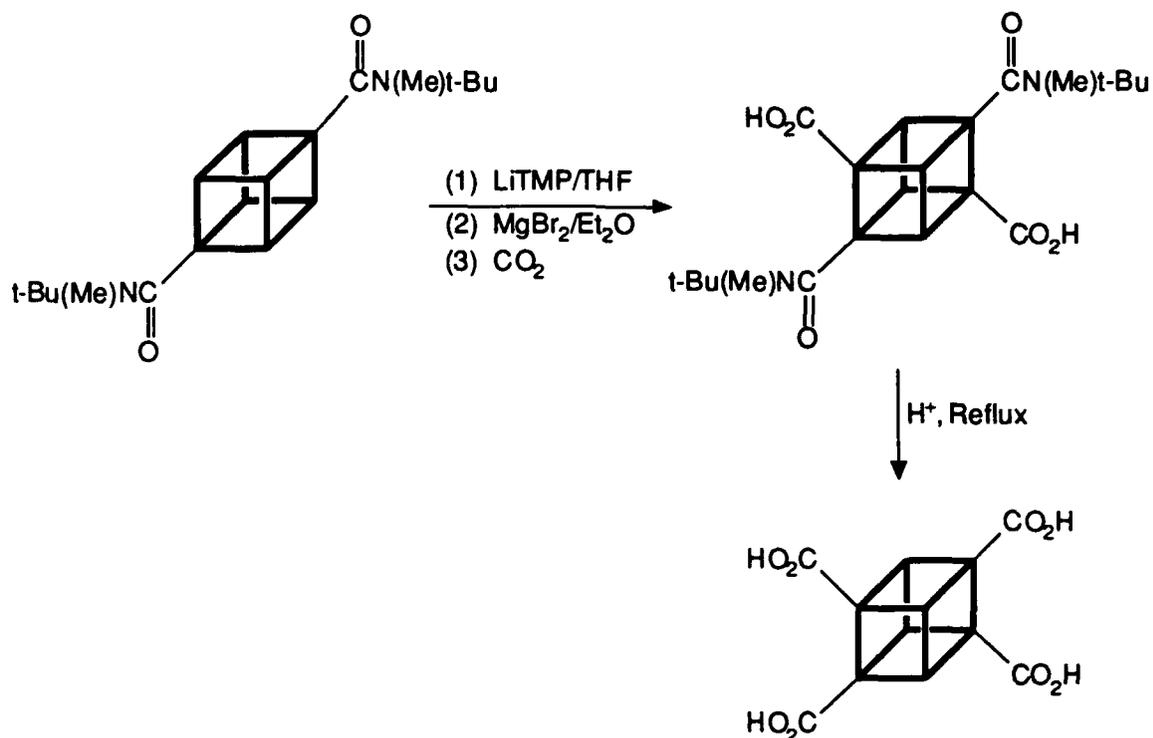
Cubane-1,4-diisocyanide is calculated to have a ΔH_f of +221 kcal/mol, an extremely high value for a compound containing only C, H, and N.

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

The large number of steps in the current synthesis of cubane-1,2,4,7-tetracarboxylic acid, a route initially developed by P. Eaton,⁴ limits the ability to scale up its synthesis. We have developed a new, simpler synthesis for this intermediate. Both syntheses are shown below. 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 isolate the cubane-1,2,4,7-tetracarboxylic acid from the reaction mixture as a solid. This improvement 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.



(a) Current synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by P. Eaton.

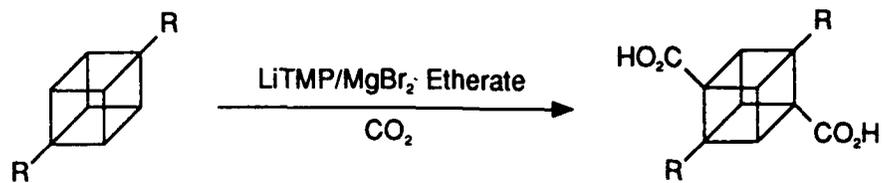


(b) Improved synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by SRI International

We have not yet explored all the ramifications of this change in the overall procedure for the synthesis of cubane-1,2,4,7-tetracarboxylic acid, so we do not yet know whether the use of this new cubyl diamide will allow the use of less expensive materials than tetramethylpiperidine (TMP) in the lithiation step as well as for other, equally complicated transformations. Table 1 shows several different amides we explored as replacements for diisopropylamide before discovering the one that is serving us so well.

Table 1

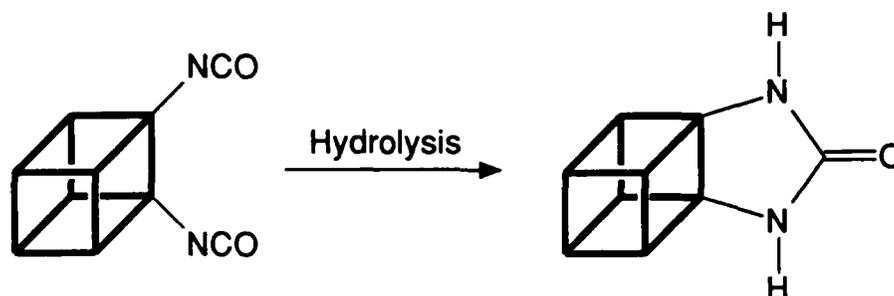
ATTEMPTED METALLATIONS OF CUBANE



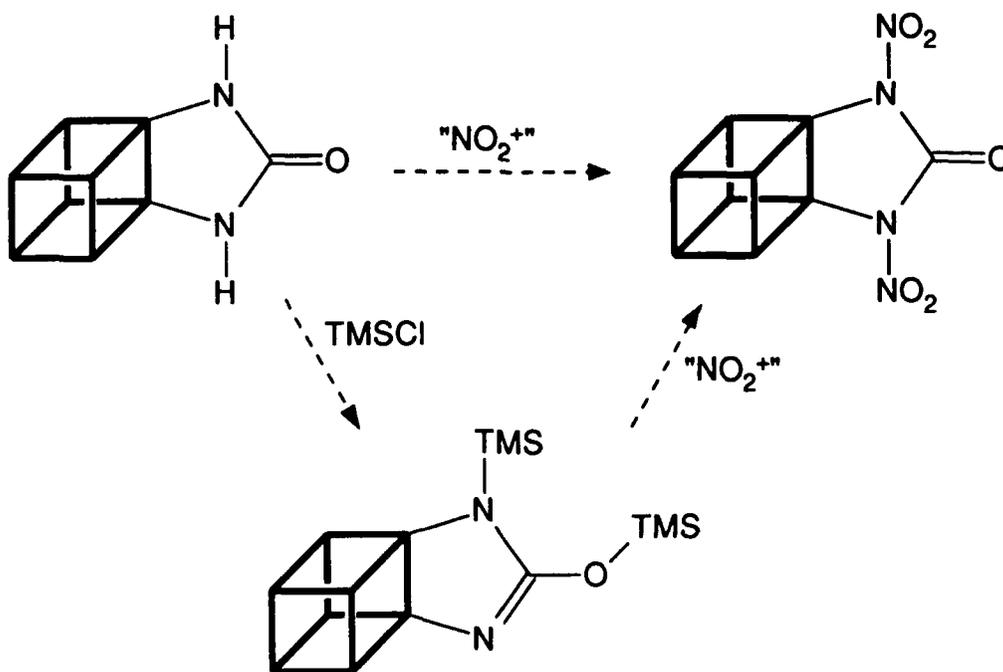
R	Carboxylation Observed (Yield)
	None
	None
	None
	25%
	75%

Propellanocubane Nitration

A synthesis of the propellanocubane below has recently been worked out in Professor Eaton's laboratory.

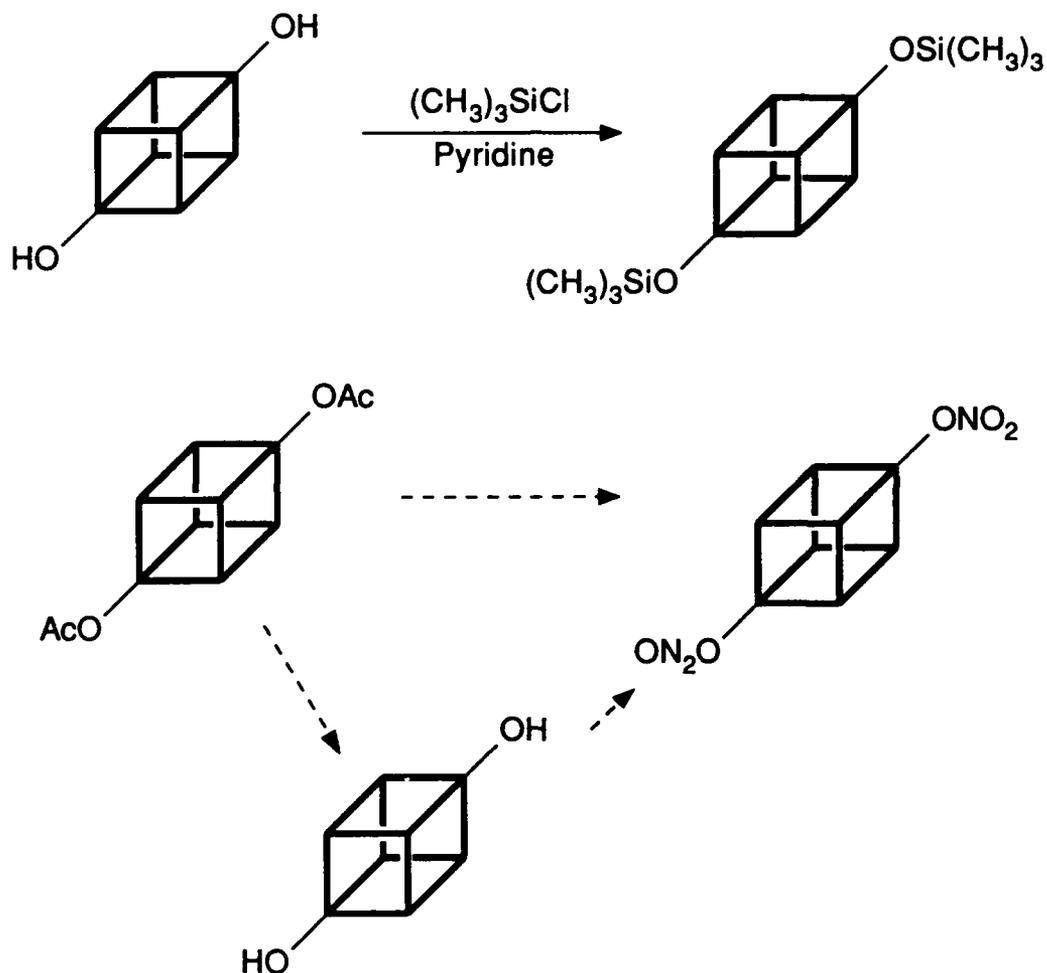


We have been studying the nitration of this interesting intermediate with the goal of synthesizing the tetra-N-nitro derivative of the bis-propellanocubane, a cubane equivalent of TNGU. Initially, we synthesized the bis-trimethylsiloxy (TMS) derivative by reacting TMS-Cl/base with propellanocubane. The goal here was to prepare a protected version of the propellanocubane with improved solubility. All attempts at nitration of this intermediate and direct nitration of propellanocubane have thus far failed to result in the bis-N-nitro-propellanocubane we seek.



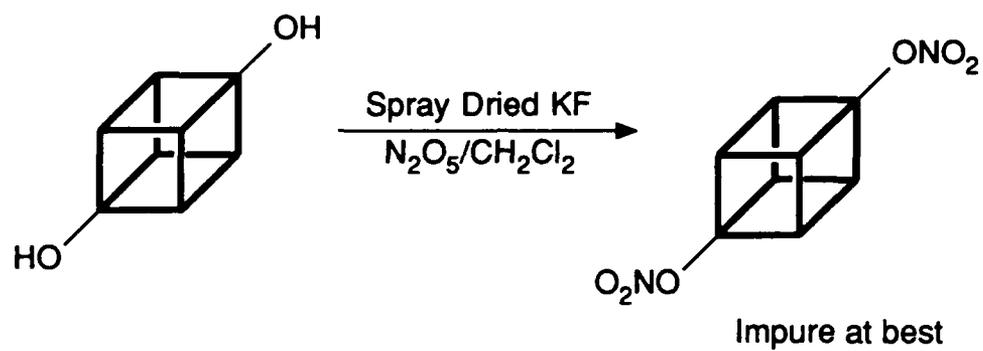
Attempted Synthesis of Cubylnitrates

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 (as shown below) under conditions similar to those required for the synthesis of the nitrate.



However, we have not yet been able to synthesize the cubane-1,4-dinitrate as expected. Our initial results from the reaction of the 1,4-cubanediol with $\text{KF}/\text{N}_2\text{O}_5$ in CH_2Cl_2 indicate that we have indeed synthesized the dinitrate as 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 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 have not yet been able to develop a purification procedure in which the presumed dinitrate survives.



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 was stirred for 2 hours at ambient temperature and then excess pentachloride was destroyed by stirring with acetic anhydride (14.7 mL, 0.156 mol) for 15 minutes. The solution was concentrated to dryness at 50°C by using a aspirator pressure at first and then higher vacuum. Residual acetic anhydride was removed by a cycle of dissolving the cubane-1,4-bis(acid chloride) in dry, ethanol free chloroform 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 hours 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 minutes and then N-ethyl-N-*t*-butylamine (31.59 g, 0.312 mol.) was added dropwise over 20 minutes while the cold water bath was maintained. After the addition, the reaction was stirred for 2 hours 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 MgSO₄, 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 of dry ethyl acetate at 40-50°C, cooled in ice, filtered, washed with cold ethyl acetate, and dried under high vacuum to yield 41.02 g (73%) of the title compound as pure white crystals. NMR (¹H, CDCl₃, TMS standard) δ 1.3 (triplet, 3 H, J = 7 Hz, CH₃), δ 1.4 (s, 9H, *t*-butyl), δ 3.8 (quartet, 2H, J = 7 Hz, CH₂), δ 4.55 (s, 6H); IR (KBr) 2970, 1610, 1390, 1205 cm⁻¹; mp = 185-188°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 tetramethylethylene-diamine (12.6 mL, 1.1 eq) were added to 600 mL dry 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 2.5M *n*-butyl,lithium in hexane (304 mL, 0.760 mol, 10 eq)

was added dropwise with stirring over 2 hours. at -78°C and then was stirred at 0°C for 1 hour. 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 hours. 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 being heated with a hot air gun to remove moisture. The CO_2 was bubbled through the stirring reaction for 12 hours at dry ice-acetone temperature to yield a light tan suspension, which was concentrated to dryness on the rotovap by first using aspirator pressure and then higher vacuum for about 2 hours. The light tan solid was vigorously stirred with 1500 mL H_2O for 1 hour, 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 boiling dichloromethane, cooled in a 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; the temperature went rapidly to 75°C . Mild reflux was continued for 4 hours, 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 the filter flask was changed in 100% ethanol. The suspension was then dried to give 3.44 g of the product (95%) as a pure white powder. ^1H 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 was allowed to rise slowly over a period of approximately 5 hours to room temperature. The reaction mixture, which contained a large amount of crystalline precipitate, was stirred for an additional 24 hours and worked up. The workup consists of

extraction with 1 x 500 mL of 10 M NaOH, followed by distillation at atmospheric pressure and collection of 85-93°C fraction (yield ~100 g). This fraction was then distilled off 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(β,β,β -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 hours under argon. The resulting solution was treated with 250 mg of 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 minutes. 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 of EtOAc and extracted with 50 mL of 10% Na_2CO_3 , concentrated, and chromatographed over 20 g of 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(β,β -dinitro- β -fluoroethylester). The procedure used for the the synthesis of the β,β,β -trinitroethylester was followed on double the scale, with fluorodinitro-ethanol substituted for the trinitroethanol. Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -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(β,β -dinitro- β -fluoroethyl)diaminocubane.** 1,4-Diamino-cubane hydrochloride (200 mg, 0.95 mmol), prepared by the method of Eaton,^{6b} was dissolved in 10 mL of 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 hours at room temperature. An orange precipitate was isolated by filtration, dissolved in EtOAc, and filtered through a 2-inch by 1/2-inch plug of silica gel, concentrated, and crystallized from $\text{CHCl}_3/\text{EtOAc}$ to give 180 mg (45%) of needles of *N,N'*-bis(β,β -dinitro- β -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, $\text{CH}_2 + \text{NH}$); IR (KBr) 3375, 3000, 1630, 1600, 1585, 1330 cm^{-1} .

N-Nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. N,N'-bis(β,β -dinitro- β -fluoroethyl)diaminocubane (60 mg, 0.15 mmol) was dissolved in 5 mL of 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 minutes, and then diluting with 5 mL CHCl_3 . The resulting mixture was stirred at 0°C for 15 minutes, warmed to 20°C , diluted with 50 mL of 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(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane described above (50 mg, 0.11 mmol) was dissolved in 5 mL of a 0.5 M solution of $\text{CF}_3\text{CO}_3\text{H}$ in 1:1 $\text{CHCl}_3/\text{EtOAc}$ and stirred for 36 hours. The reaction mixture was diluted to 100 mL with 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, 1280 cm^{-1} ; mp = 170°C (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 minutes. 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 hours). 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 titrated with CHCl_3 to give 50 mg (80%) of cubane-1,4-diol. ^1H NMR (CD_3OD , 60 MHz) δ 3.2 (s, C-H); IR (KBr) 3200, 2960, 1330, 1140, 1000, 930 cm^{-1} ; mp = 150°C (decomposition).

1,4-Bis(trimethylsiloxy)cubane. Cubane-1,4-diol (15 mg, 0.1 mmol) was suspended in 2 mL of hexamethyldisilazane. Chlorotrimethylsilane (0.2 mL) was added, and the resulting mixture was stirred for 24 hours. Diethylamine (0.5 mL) was added to

quench excess chlorotrimethylsilane. The mixture was evaporated to dryness *in vacuo*, redissolved in EtOAc, filtered to remove $\text{Et}_2\text{NH}_2^+\text{Cl}^-$, and concentrated to give 25 mg (100%) of 1,4-bis(trimethylsiloxy)cubane, a waxy solid. $^1\text{H NMR}$ (CDCl_3) δ 3.85 (s, 6 H, C-H), δ 0.25 (s, 16 H, $\text{CH}_3\text{-Si}$).

1,4-Dicyanocubane. Cubane-1,4-diacid chloride (2.3 g, 10 mmol) was dissolved in 100 mL of CHCl_3 and treated with excess NH_3 gas until the exotherm subsided. The NH_3 -saturated CHCl_3 was stirred for 2 hours 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 of 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 of CHCl_3 and 100 mL of 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%). $^1\text{H NMR}$ (CDCl_3 , TMS standard, 60 MHz) δ 4.5 (s, C-H); IR (KBr) 3060, 2260, 1290, 1230, 1220 cm^{-1} ; 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) of diisopropyl-ethylamine, followed by 1 g (5.5 mmol) of cubane-1,4-diisocyanate. The reaction mixture was stirred for 2 hours 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 with 1:1 EtOAc/ CHCl_3 over a 3-inch by 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. $^1\text{H NMR}$ (CDCl_3 , TMS standard, 60 MHz) δ 4.3 (s); IR (KBr) 3000, 2100, 1330 cm^{-1} .

CONCLUSIONS

We have developed a new, simpler method for functionalizing the cubane nucleus and have synthesized several polysubstituted cubanes as well as 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. We have also determined that the polycyanocubanes should make extremely good fuels or fuel additives because of their high positive heats of formation, and the isocyanocubanes, with even higher heats of formation, should be even better for this use.

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4. For reviews, see (a) H. W. Gschwend and H. R. Rodriguez, *Org. React.* (N. Y.), 1979, **26**, 1; (b) P. Beak and V. Snieckus, *Acc. Chem. Res.*, 1982, **15**, 306; (c) V. Snieckus, *Heterocycles*, 1980, **14**, 1649; (d) N. S. Narasimhan and R. S. Mali, *Synthesis*, 1983, 957; (e) P. Beak and A. I. , *Acc. Chem. Res.*, 1986, **19**, 356.

Appendix

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

IMPROVED SYNTHESIS OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID

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(415)-859-5579

We report here an improvement in the synthesis of cubane-1,2,4,7-tetracarboxylic acid. The original breakthrough in the synthesis of functionalized cubanes was made by Eaton.¹

with the discovery that N,N-diisopropylamide groups could be used as activators to make ortho-lithiation² of cubane possible and that the cubyl anion could be trapped by exchange of lithium for mercury. Eaton then developed the necessary methodology to remove the the N,N-diisopropylamide groups to give the tetraacid. This synthesis was improved by Hashimi³ with the substitution of MgBr₂-etherate for HgCl₂. Eaton's current route for the synthesis of cubane-1,2,4,7-tetracarboxylic acid is shown in Scheme 1. The synthesis of the cubane tetraacid involves the lithiation of cubane-1,4-bis(N,N-diisopropylamide) by using lithium tetramethylpiperidine as the base, trapping carbanion as the magnesium salt, carboxylating with CO₂, and using subsequent reduction and oxidation steps to remove the N,N-diisopropylamide group. The reduction and oxidation steps are required because the N,N-diisopropylamide group has proved resistant to all attempts for direct removal, including hydrolysis with strong acids, bases, or oxidants. The number of steps required in this synthesis limits the availability of cubane-1,2,4,7-tetracarboxylic acid.

We have developed an improved synthesis for cubane-1,2,4,7-tetracarboxylic acid. The crucial improvement in our synthetic route is the discovery that a different amide, N-ethyl, N-t-butylamide, not only can be used in place of N,N-diisopropylamide for the ortho-lithiation of the cubane nucleus but can be removed successfully through direct acid hydrolysis which significantly reduces the number of steps required. We explored several other amides before discovering one capable of replacing diisopropylamide, which has

served us so well (Table 1). The metallations listed in Table 1 were done with the metallation of Hashimi.³ The utility of this amide is not limited to cubane ortho-lithiation chemistry; it can be used for ortho-lithiation of other aromatic or aliphatic compounds where a readily removable amide group is of interest. The hydrolysis of cubane-1,4-dicarboxylic acid-2,7-bis(N-ethyl-N-*t*-butylamide) was done with nitric acid because this method allowed ready isolation of cubane-1,2,4,7-tetracarboxylic acid as a filterable solid precipitate while the other by-products were oxidized or solubilized by the nitric acid. Other acids will surely be effective for the hydrolysis reaction but were not explored.

The advantages of N-ethyl, N-*t*-butylamide over N,N-diisopropylamide are the former's immensely greater ease of removal by acid hydrolysis and higher yield in the carboxylation. N-Ethyl, N-*t*-butylamide can be removed nearly quantitatively by acid hydrolysis in one step, eliminating several steps from the long sequence of amination, carboxylation, oxidation, and reduction previously required to synthesize cubane-1,2,4,7-tetracarboxylic acid from the cubane-1,4-diacid. This acid hydrolysis allows the isolation of nearly pure cubane-1,2,4,7-tetracarboxylic acid from the reaction mixture as a solid. The synthetic pathway is shown in Scheme 2.

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 cubane-1,4-dicarboxylic acid-2,7-bis(N-ethyl-N-*t*-butylamide) in 90% red fuming nitric acid and obtained high yields of the tetraacid. Under the same conditions, cubane 1,4-dicarboxylic acid-2,7-bis(N,N-diisopropylamide) is recovered (unchanged) nearly quantitatively with no decomposition or hydrolysis.

We have not yet explored whether N-ethyl, N-*t*-butylamide has general use for ortho-lithiation, particularly for lithiation of aromatic compounds. We do know that use of this new procedure provides a much more convenient route for the synthesis of substituted cubanes. We are currently studying whether N-ethyl-N-*t*-butylamine is generally effective for ortho-lithiation of other compounds.

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 was stirred for 2 hours at ambient temperature and then excess pentachloride was destroyed by stirring with acetic anhydride (14.7 mL, 0.156 mol) for 15 minutes. The solution was concentrated to dryness at 50°C by using a aspirator pressure at first and then higher vacuum. Residual acetic anhydride was removed by a cycle of dissolving the cubane-1,4-bis(acid chloride) in dry, ethanol free chloroform 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 hours 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 minutes and then N-ethyl-N-*t*-butylamine (31.59 g, 0.312 mol.) was added dropwise over 20 minutes while the cold water bath was maintained. After the addition, the reaction was stirred for 2 hours 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 MgSO₄, 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 of dry ethyl acetate at 40-50°C, cooled in ice, filtered, washed with cold ethyl acetate, and dried under high vacuum to yield 41.02 g (73%) of the title compound as pure white crystals. NMR (¹H, CDCl₃, TMS standard) δ 1.3 (triplet, 3 H, J = 7 Hz, CH₃), δ 1.4 (s, 9H, *t*-butyl), δ 3.8 (quartet, 2H, J = 7 Hz, CH₂), δ 4.55 (s, 6H); IR (KBr) 2970, 1610, 1390, 1205 cm⁻¹; mp = 185-188°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 tetramethylethylene-diamine (12.6 mL, 1.1 eq) were added to 600 mL dry 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 2.5M *n*-butyl,lithium in hexane (304 mL, 0.760 mol, 10 eq)

was added dropwise with stirring over 2 hours. at -78°C and then was stirred at 0°C for 1 hour. 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 hours. 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 being heated with a hot air gun to remove moisture. The CO_2 was bubbled through the stirring reaction for 12 hours at dry ice-acetone temperature to yield a light tan suspension, which was concentrated to dryness on the rotovap by first using aspirator pressure and then higher vacuum for about 2 hours. The light tan solid was vigorously stirred with 1500 mL H_2O for 1 hour, 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 boiling dichloromethane, cooled in a 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; the temperature went rapidly to 75°C . Mild reflux was continued for 4 hours, 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 the filter flask was changed in 100% ethanol. The suspension was then dried to give 3.44 g of the product (95%) as a pure white powder. ^1H 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 was allowed to rise slowly over a period of approximately 5 hours to room temperature. The reaction mixture, which contained a large amount of crystalline precipitate, was stirred for an additional 24 hours and worked up. The workup consists of

extraction with 1 x 500 mL of 10 M NaOH, followed by distillation at atmospheric pressure and collection of 85-93°C fraction (yield ~100 g). This fraction was then distilled off 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(β,β,β -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 hours under argon. The resulting solution was treated with 250 mg of 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 minutes. 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 of EtOAc and extracted with 50 mL of 10% Na_2CO_3 , concentrated, and chromatographed over 20 g of 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(β,β -dinitro- β -fluoroethylester). The procedure used for the the synthesis of the β,β,β -trinitroethylester was followed on double the scale, with fluorodinitro-ethanol substituted for the trinitroethanol. Cubane-1,2,4,7-tetrakis(β,β -dinitro- β -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(β,β -dinitro- β -fluoroethyl)diaminocubane. 1,4-Diamino-cubane hydrochloride (200 mg, 0.95 mmol), prepared by the method of Eaton,^{6b} was dissolved in 10 mL of 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 hours at room temperature. An orange precipitate was isolated by filtration, dissolved in EtOAc, and filtered through a 2-inch by 1/2-inch plug of silica gel, concentrated, and crystallized from $\text{CHCl}_3/\text{EtOAc}$ to give 180 mg (45%) of needles of N,N'-bis(β,β -dinitro- β -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, $\text{CH}_2 + \text{NH}$); IR (KBr) 3375, 3000, 1630, 1600, 1585, 1330 cm^{-1} .

N-Nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. N,N'-bis(β,β -dinitro- β -fluoroethyl)diaminocubane (60 mg, 0.15 mmol) was dissolved in 5 mL of 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 minutes, and then diluting with 5 mL CHCl_3 . The resulting mixture was stirred at 0°C for 15 minutes, warmed to 20°C , diluted with 50 mL of 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} ; mp = $__^\circ\text{C}$. The x-ray crystal structure determined by R. Gilardi of NRL gave a density of 1.827 g/cm^3 .

N,N'-Dinitro-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane. The N-nitro-N'-nitroso-N,N'-bis(β,β -dinitro- β -fluoroethyl)-1,4-diaminocubane described above (50 mg, 0.11 mmol) was dissolved in 5 mL of a 0.5 M solution of $\text{CF}_3\text{CO}_3\text{H}$ in 1:1 $\text{CHCl}_3/\text{EtOAc}$ and stirred for 36 hours. The reaction mixture was diluted to 100 mL with 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, 1280 cm^{-1} ; mp = 170°C (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 minutes. 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 hours). 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 titrated with CHCl_3 to give 50 mg (80%) of cubane-1,4-diol. ^1H NMR (CD_3OD , 60 MHz) δ 3.2 (s, C-H); IR (KBr) 3200, 2960, 1330, 1140, 1000, 930 cm^{-1} ; mp = 150°C (decomposition).

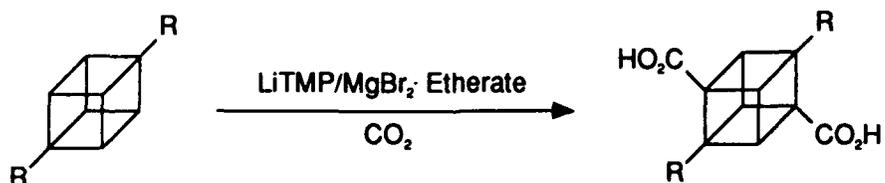
1,4-Bis(trimethylsiloxy)cubane. Cubane-1,4-diol (15 mg, 0.1 mmol) was suspended in 2 mL of hexamethyldisilazane. Chlorotrimethylsilane (0.2 mL) was added, and the resulting mixture was stirred for 24 hours. Diethylamine (0.5 mL) was added to

quench excess chlorotrimethylsilane. The mixture was evaporated to dryness *in vacuo*, redissolved in EtOAc, filtered to remove $\text{Et}_2\text{NH}_2^+\text{Cl}^-$, and concentrated to give 25 mg (100%) of 1,4-bis(trimethylsiloxy)cubane, a waxy solid. $^1\text{H NMR}$ (CDCl_3) δ 3.85 (s, 6 H, C-H), δ 0.25 (s, 16 H, $\text{CH}_3\text{-Si}$).

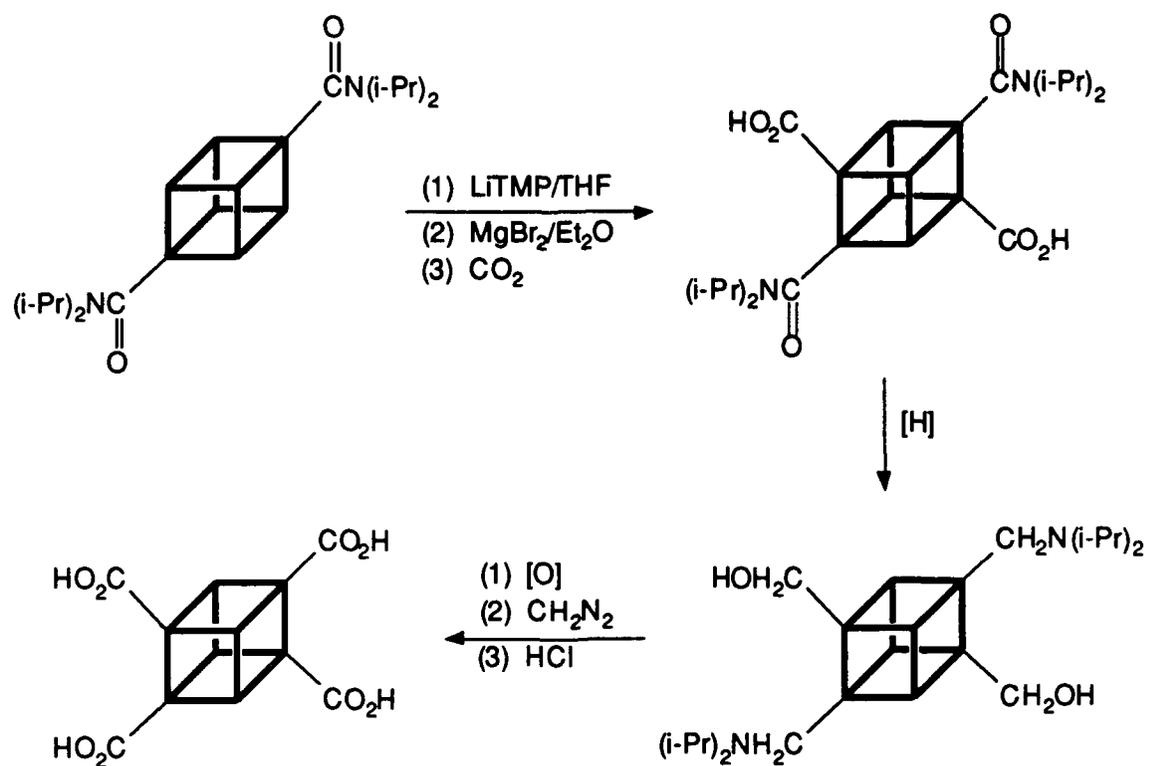
1,4-Dicyanocubane. Cubane-1,4-diacid chloride (2.3 g, 10 mmol) was dissolved in 100 mL of CHCl_3 and treated with excess NH_3 gas until the exotherm subsided. The NH_3 -saturated CHCl_3 was stirred for 2 hours at room temperature and concentrated *in vacuo*. A white solid product remained. The white solid was suspended in 100 mL of CH_2Cl_2 and treated with 10 mL of Et_3N plus 10 mL of 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 of CHCl_3 and 100 mL of 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%). $^1\text{H NMR}$ (CDCl_3 , TMS standard, 60 MHz) δ 4.5 (s, C-H); IR (KBr) 3060, 2260, 1290, 1230, 1220 cm^{-1} ; 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) of diisopropyl-ethylamine, followed by 1 g (5.5 mmol) of cubane-1,4-diisocyanate. The reaction mixture was stirred for 2 hours 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 with 1:1 EtOAc/ CHCl_3 over a 3-inch by 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. $^1\text{H NMR}$ (CDCl_3 , TMS standard, 60 MHz) δ 4.3 (s); IR (KBr) 3000, 2100, 1330 cm^{-1} .

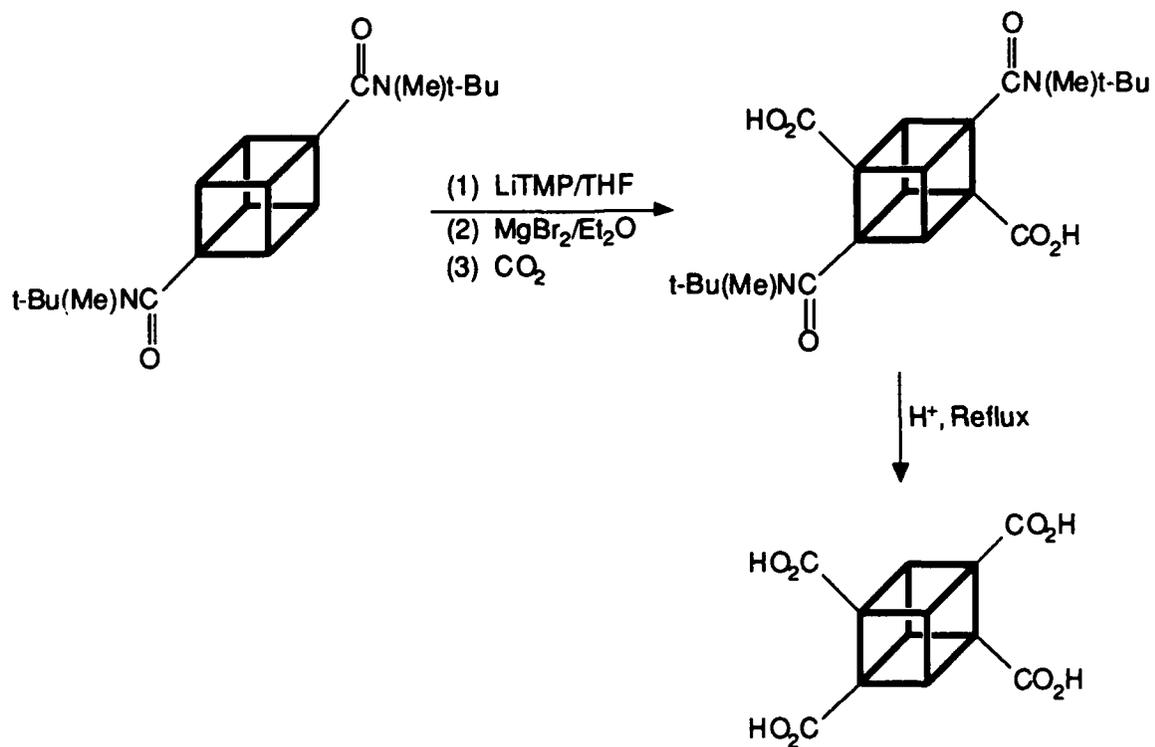
Table 1: Attempted Metallations of Cubane



<u>R</u>	<u>Carboxylation Observed (% Yield)</u>
	None
	None
	None
	25
	75



Scheme 1. Current synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by P. Eaton.



Scheme 2. Improved synthesis of cubane-1,2,4,7-tetracarboxylic acid developed by S & I International.

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