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Process studies for converting cubane-1,4-dicarboxylic acid to cubane-1,2,4,7-tetracarboxylic acid were carried out. The diacid was converted to the diacid chloride which was reacted with *t*-butylethylamine to give cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide). This bisamide was reacted with lithium 2,2,6,6-tetramethylpiperidide and magnesium bromide etherate to give dimetallated intermediate which was carbonated with carbon dioxide. The resulting diacid bisamide was the hydrolyzed with 70% nitric acid to give the tetraacid in 60% yield based on the diacid. The tetraacid was converted to the tetraacid chloride and to the tetramethyl and tetraethyl esters. Routes to the preparation of *t*-butylethylamine and 2,2,6,6-tetramethylpiperidine were developed.

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T. G. Archibald, D. M. Farnia, and K. Baum

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I. INTRODUCTION

Propellant formulations with improved performance are required for Strategic Defense Initiative applications. There is a particular need for non-metal containing propellants with increased specific impulse (Isp) for rocket-propelled kinetic energy weapons as higher Isp would reduce the minimum effective mass of the projectiles. An approach that has been taken to meet the Isp-intensive needs of SDI applications is based on the intrinsic energy that would be released during combustion of energetic cubane derivatives. These advanced materials rely on the high thermodynamic strain energy¹ and inherent high density² of cubane (known to be greater than 166 Kcal/mole and 1.3 g/cm³ for the unsubstituted hydrocarbon). In addition, cubane derivatives have excellent thermal stability making them ideal candidates for incorporation into advanced propellant and explosive formulations. The strain energy is expected to add significantly to the performance of cubane derivatives containing either ring or side-chain energetic functional groups.

The most readily accessible starting material for the synthesis of energetic cubanes is cubane-1,4-dicarboxylic acid. Functional group transformations have yielded energetic derivatives, such as 1,4-dinitrocubane² and 1,4-bis(N,N-dinitroamino)cubane³, demonstrating the feasibility of synthesizing stable, energetic cubane compounds. The dinitraminocubane is stable above 200°C as indicated by DSC. However, to realize improved performance for SDI applications requires oxygen balance at least to the CO level. Cubane-1,2,4,7-tetracarboxylic acid is available through metallation chemistry of cubane-1,4-dicarboxylic acid derivatives and provides an attractive source of oxygen-balanced propellant ingredients.

The development of a facile synthesis of the tetrafunctional derivatives is needed to allow rapid preparation of significant quantities of propellants based on an energetic cubane derivative for performance testing in a demonstration motor. In addition, ready availability of tetrafunctional cubane derivatives will encourage commercial applications in polymers and pharmaceuticals.⁴

In 1987, a consortium of investigators at the University of Chicago, SRI, and Morton Thiokol, Inc. was formed to extend the practical synthesis of energetic cubane derivatives. Based on theoretical calculations, a number of targets was identified, of which cubane-1,2,4,7-tetraammonium tetraperchlorate was selected as the most accessible for initial C* testing. Other tetrafunctional cubane oxidizers with energetic groups were also predicted to have improved performance. These groups are N,N-dinitroamino, perchlorate esters, nitrate esters, N,N-difluoramino, N-fluoro-N-nitroamino and N-(2,2,2-trinitroethyl)-N-nitroamino. Calculations of the densities and energetic properties of these materials are found in Figures 19-23.³

All of these advanced materials potentially can be prepared from a common precursor, cubane-1,2,4,7-tetracarboxylic acid. The objective of the present Phase I program was development of a route suitable for kilogram scale preparations of cubane-1,2,4,7-tetracarboxylic acid.

II. RESULTS AND DISCUSSION

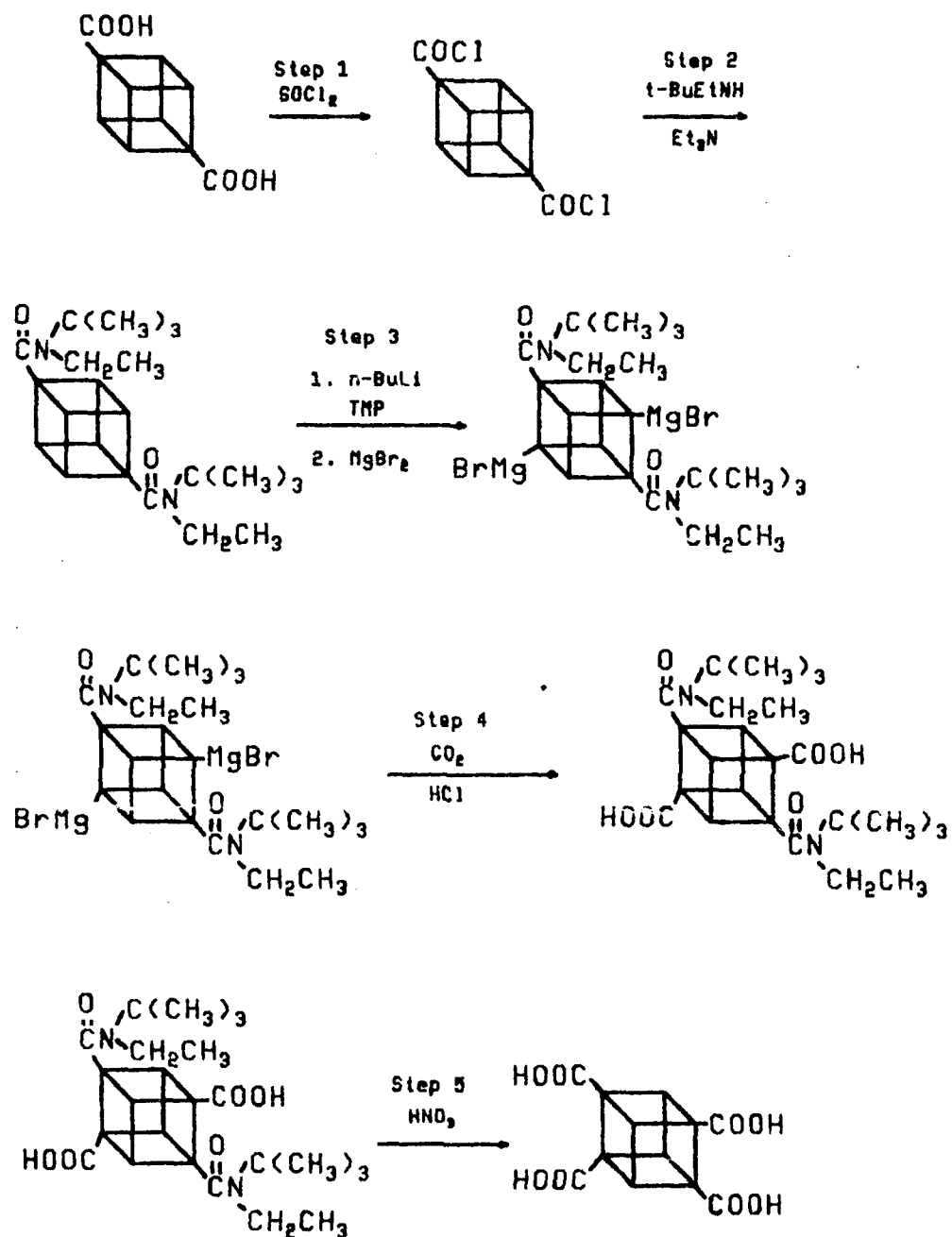
Cubane-1,4-diacid⁵ was first prepared by Eaton as a key intermediate in his synthesis of the parent hydrocarbon, cubane. This diacid is actively being investigated in many laboratories as the synthetic starting point for the application of cubane technology to fuels, energetic

materials, binders, and liquid gun propellants. Fluorochem, Inc. has been involved in a program of process development of the multi-step synthesis required to make this starting material.⁶

During the present program, the conversion of cubane-1,4-diacid to cubane-1,2,4,7-tetraacid was explored. All known methods⁷ for this transformation require conversion of the diacid to a diamide, "ortho" lithiation with lithium tetramethylpiperidine (LiTMP), trapping the anions by metal-metal interchange, carbonation with carbon dioxide, and removal of the amide groups. Earlier routes involved two barriers to scale up: first environmentally hazardous mercury or zinc salts were used in the metal-metal interchange reaction, and second, amide removal was carried out by reduction with lithium aluminum hydride and subsequent oxidation with potassium permanganate.

The first problem was overcome by the use of magnesium bromide⁸ in the exchange reaction. Although Grignard reagents alone will not "ortho" metallate the cubyl amides, a mixture of excess LiTMP and magnesium bromide dimetallates the cubane ring in high yield. Unlike the mercury or zinc procedures, this reaction can be scaled up to 10 g without significant loss in yield. The use of magnesium salts provides no environmental problems.

The second problem was overcome by replacing the previously used di-*i*-propylamino groups in the amide with *t*-butylethylamino groups.⁹ It is known that *t*-butyl groups may be removed easily by acid catalysis, and this method has proven successful in the cubane system. After metallation and carboxylation of cubane-1,4-bis(*N-t*-butyl-*N*-ethylcarboxamide), the amide groups from the intermediate diamide diacid could



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

SCHEME I

be hydrolyzed by nitric acid. The 5 step preparation of tetraacid from diacid is summarized in Scheme I.

Step 1. Synthesis of Cubane-1,4-dicarboxylic Acid Chloride from cubane-1,4-dicarboxylic acid. Cubane-1,4-dicarboxylic acid chloride is unstable thermally and above 100°C can decompose explosively. It is moisture sensitive and its low solubility makes purification by recrystallization difficult. Therefore it was necessary to use high purity cubane-1,4-diacid. Prior to this study, cubane-1,4-dicarboxylic acid was converted to the dimethyl ester for purification. The diester was recrystallized and then hydrolyzed with base to regenerate the diacid. Since both the esterification and the hydrolysis steps gave yields of 60 to 80%, this transformation resulted in substantial losses of starting materials. Subsequently, a method was sought to isolate the pure diacid from its crude preparation mixture without esterification. The solubility of cubane-1,4-dicarboxylic acid in common solvents was investigated and is shown in Table I.

TABLE I. SOLUBILITY OF CUBANE 1,4 DICARBOXYLIC ACID

Solvent	Solubility g/L	Comments
THF	>14	a
Acetone	4	a
Ethyl Acetate	1.3	a
Acetonitrile	0.95	a
Diethyl Ether	0.90	b
Dichloromethane	0.30	c

Solubility at 25°C of a Saturated Solution

- a. Dissolves impurities
- b. Partially dissolves impurities
- c. Does not dissolve impurities.

It was found that the crude diacid could be purified by washing with cold acetone or ethyl acetate. Cubane-1,4-diacid has a low solubility in these solvents, but the organic impurities are readily extracted leaving essentially pure diacid. In some cases, the crude reaction product contained sodium bromide or sodium chloride. These inorganic salts were removed by dissolving the diacid in aqueous base, filtering, and precipitating with hydrochloric acid. Diacid purified in this manner was suitable for conversion to the diacid chloride.

Reaction of cubane diacid with phosphorus pentachloride in dichlorobenzene or with neat thionyl chloride gives the cubane diacid chloride. The low solubility of the diacid in dichlorobenzene resulted in long reaction times and poor yields. Thus, the thionyl chloride method was used for this program. Freshly distilled thionyl chloride was required to avoid incomplete reaction and colored products. Optimum reaction times of 14 hours of reflux in excess thionyl chloride were found to give nearly quantitative yields. The excess thionyl chloride was removed by vacuum distillation to avoid subjecting the product to excessive heat.

The diacid chloride is moisture sensitive, and reconverts on standing in air to the diacid. No purification appears feasible but the crude diacid chloride could be used directly in the preparation of the bisamide. Analysis by ^1H NMR (Figure 1) was used to differentiate the diacid chloride (singlet at δ 4.48) from the starting diacid (singlet at δ 4.10). The preparation of the diacid is summarized in Table II.

TABLE II. PREPARATION OF DIACID CHLORIDE FROM DIACID.

Run #	I g (mol)	ml Thionyl Chloride	Time h	Temp °C	Yield g (%)
1	100 (0.51)	a	13	rt	25 (38)
2	24 (0.125)	50	4	90	25.5 (90)
3	22 (0.114)	60	5	80-90	22.5 (84)
4	22 (0.114)	70	5	80-90	18 (82)
5	95 (0.49)	200	4	80-90	90 (80)
6	200 (1.04)	250	12	80-90	190 (80)
7	100 (0.51)	200	14	95	116 (97)

a. 180 g of PCl_5 in 500 ml of o-dichlorobenzene

Step 2. Preparation of cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide). Cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide) was prepared by reaction of cubane-1,4-acid chloride with t-butylethylamine and triethylamine. t-Butylethylamine is not commercially available, and has been prepared previously in 50% yield from t-butylamine and ethyl bromide.¹⁰ We found that material prepared in this manner was contaminated with t-butylamine and t-butyldiethylamine which could not be removed by distillation. The presence of unreacted t-butylamine led to the formation of t-butylamides thus lowering the yield of the bis(t-butylethylamide). We developed an alternative high yield preparation of t-butylethylamine by the reaction of t-butylamine with diethyl sulfate in aqueous sodium hydroxide. The crude amine was stirred over solid potassium hydroxide for 24 hours and then distilled. This procedure gave pure amine from inexpensive materials and was scaled up to 1.4 kg during this program (Table III). The purity of the material was determined by NMR and glc analysis (Figures 2-4).

TABLE III. PREPARATION OF T-BUTYLETHYLAMINE.

Run #	$t\text{-BuNH}_2$ g (mol)	EtBr g (mol)	Et ₃ SO g (mol)	Time h	Yield g (%)
1	154 (2.1)	149 (1.3)		12	60 (58) ^a
2	580 (8)	610 (6.6)		15	245 (60) ^a
3	430 (5.8)		1 kg (6.4)	1	390 (65)
4	1.9 kg (26)		4 kg (26)	4	1400 (53)

Isolated yield distilled from KOH
a. 98% by glc; contained 2% t -butylamine.

The reaction of t -butylethylamine with cubane diacid chloride in gave the bisamide in 56-98% yield (Table IV). Two moles of triethylamine was used to remove the hydrogen chloride formed. Reactions run in methylene chloride gave higher yields than those run in chloroform. The bisamide was purified by recrystallization from ethyl acetate. Several batches of 175-200 g were prepared. Highest yields were obtained with reaction times of over 50 hours. Analytical techniques using NMR, and melting point by DSC were developed to monitor the purity of the material.

TABLE IV. CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE).

Run #	Diacid Chloride g (mol)	$t\text{-BuEtNH}_2$ g (mol)	Et ₃ N g (mol)	Solvent mL	Time h	Yield g (%)
1	60 (0.28)	57 (0.57)	58 (5.7)	500a	48	20 (21)
2	25 (0.11)	40 (0.4)	40 (0.4)	250a	3	29 (72)
3	11 (0.05)	10.6 (0.1)	10.6 (0.1)	300b	3	10 (70)
4	155 (0.65)	146 (1.4)	146 (1.4)	1000b	12	175 (62)
5	118 (0.5)	115 (1.1)	115 (1.1)	500b	12	200 (56)
6	114 (0.49)	121 (1.2)	121 (1.2)	1000b	54	178 (98)

Reactions run at 25°C

a. CHCl_3
b. CH_2Cl_2

Step 3. Lithiation of the Bisamide. Unlike other metal salts previously investigated for the transmetallation reactions of lithiated cubane derivatives, the magnesium salts do not precipitate from solution. Difficulties from heterogeneity, often encountered in scale up of organometallic reactions, will therefore be minimized. However, other typical problems associated with the handling of air and moisture sensitive materials are not avoided.

The metal transfer reagent used in the metallation reaction in large excess is 2,2,6,6-tetramethylpiperidine (TMP). TMP was reacted with butyl lithium in THF at low temperature (-78°C) to give the lithium salt (LiTMP). Although this reaction was quantitative and trouble-free in the small scale reactions of this program, mixing and temperature control in this exothermic reaction is critical and may be difficult on scale up.

Deuterium exchange studies by ^1H NMR (Figure 5) showed that when LiTMP and the bisamide were allowed to react for several hours before the addition of the magnesium salts no significant reaction occurs prior to the addition of the magnesium salts. As a result, the amide and these salts are now added together in bulk. An excess of LiTMP was required for dilithiation. In reactions containing a 10 mole excess, the dilithiation reaction was complete after 2 hours; a 7 mole excess required 24 hours and, with less than 5 mole excess, only mono-lithiation occurred.

The magnesium bromide salts for the transmetallation reaction also were required in excess and a 5 mole excess was found to give the highest yields. Previously tetramethylethylene diamine (TMEDA) was used to chelate the magnesium salts into solution. We have found that this material is not needed with the t-butylethylamide.

The use of other bases to replace LiTMP was studied briefly. The lithium salt of *t*-butylethylamine did not appear to deprotonate the bisamide as indicated by lack of deuterium incorporation upon quenching with deuterium oxide. Lithium di-*i*-propylamide effectively deprotonated the cubane ring, but at a substantially slower rate with 36 hours required for complete dilithiation. The longer reaction times may be justified by the reduced reagent cost.

Although TMP is commercially available from Aldrich Chemical Co., it is expensive. As part of Phase I, procedures were developed to synthesize TMP. Ammonia and acetone were reacted using calcium chloride as a dehydrating agent to give triacetone amine which was converted to TMP in 30% yield on a 3 kg scale by Wolff-Kischner reduction with hydrazine.¹¹

Step 4. Carboxylation of the Dilithiated Cubane Intermediate. The carboxylation reaction of the metallated bisamide with carbon dioxide gas was quite slow usually requiring 3-12 hours (see Table V.) Attempts to react the dilithiated intermediate with ethyl chloroformate were unsuccessful. Isolation of the diamide diacid presented some difficulty since the *t*-butyl group could be easily cleaved in acid to give an oily product which was difficult to isolate. A procedure was developed to separate this intermediate product from solvent, residual TMP and inorganic salts. First the solvents and excess amines were removed under vacuum (0.1 torr) at a maximum temperature of 40°C. The residue was dissolved in a minimum amount of water and carefully acidified and the product was isolated by filtration. The IR, ¹H and ¹³C NMR spectra of the bisacid bisamide are shown in Figures 6-8. In some runs, monoacid bisamide and starting bisamide were observed, possibly due to incomplete reaction or the

presence of water in the carbon dioxide. These impurities did not survive the acid hydrolysis in the next step. The yield of this step was 50-60%, but in most reactions this intermediate was not isolated, and the crude carbonated materials were taken directly through the acid hydrolysis to the final tetraacid.

TABLE V. CUBANE-1,4-BISACID-2,7-BISAMIDE

Run #	Bisamide g (mol)	LiTMP mol	MgBr ₂ mol	THF mL	CO ₂ h	Yield g (%)
1	10 (0.28)	0.28	0.14	600	3	6.5 (52)
2	9.3 (0.026)	0.28	0.14	500	5	7.5 (60)
3	10 (0.28)	0.33	0.19	700	3	0.0 (0) a
4	10 (0.28)	0.33	0.19	800	3	11.0 b
5	10 (0.028)	0.28	0.14	600	24	3.0 (39)c
6	10 (0.028)	0.28	0.14	600	3	4.0 (51)c
7	10 (0.028)	0.28	0.14	800	3	3.0 (39)c
8	9.3 (0.026)	0.28	0.14	700	3	5.0 (64)c
9	50 (0.138)	1.03	0.57	1.6 L	3	17.5 (46)c
10	32 (0.088)	0.88	0.44	1.5 L	12	10.0 (42)c

a. Oxidized TMP from old bottle was used

b. Contained 10-15% monoacid.

c. yield of Tetraacid after oxidation

Step 5. Hydrolysis of the bisacid bisamide. Acid hydrolysis of the bisacid bisamide gave pure cubane-1,2,4,7-tetracarboxylic acid. Presumably, impurities are destroyed by the acid. Although 100% nitric acid was used initially, 70% nitric acid was found to be satisfactory and was used in most reactions. Reaction times of 4-12 hours were necessary for complete reaction. The acid hydrolysis in 70% nitric acid resulted in 50-60% yields (Table VI). Neither dilute or concentrated hydrochloric acid was effective in catalyzing the hydrolysis. The tetraacid was isolated directly upon cooling and was essentially pure after drying (Figure 9). If

further purification is necessary, the tetraacid can be converted to the tetramethyl or tetraethyl ester (Figures 11-14). The tetraester can then be recrystallized and hydrolyzed back to the tetraacid.

TABLE VI. CUBANE-1,2,4,7-TETRACARBOXYLIC ACID.

Run #	Bisamide g (mmol)	HNO ₃ mL (%)	Time h	yield g (%)
1	10 (28)	240 (90)	5	3.0 (39) ^a
2	10 (28)	100 (70)	5	4.0 (51.2) ^a
3	10 (28)	30 (90)	12	3.0 (39) ^a
4	9.3 (26)	20 (90)	4	5.0 (64) ^a
5	50 (138)	120 (70)	5	17.5 (46) ^a
6	32 (88)	110 (50)	12	10.0 (42) ^a
7	1.4 (3.1) ^b	30 (70)	12	0.6 (68.5) ^c

a. Isolated yield based on Bisamide

b. Bisamide Bisacid

c. Yield of Hydrolysis step only

Based on the Phase I results, it appears the tetraacid prepared by the current method will be pure enough for direct conversion to the tetraamine. The isolated tetraacid showed no impurities by ¹³C and ¹H NMR analysis (Figure 9). The DSC of the tetraacid (Figure 16) showed a sharp decomposition point at 258°C and a small exothermic transition at 206°C. The DSC of cubane-1,4-diacid (Figure 15) shows a similar sharp decomposition exotherm at 246°C and a smaller unexplained exotherm at 220°C. TGA analysis revealed that the diacid is stable in air up to 200°C with an onset of decomposition of 226°C (Figure 17). However, the TGA of the tetraacid shows slow decomposition above room temperature, 2% weight loss at 100°C, 5% at 200°C and the onset of major decomposition above 250°C (Figure 18).

The tetraacid was converted with thionyl chloride to the tetraacid chloride in 95% yield. Esterification of the tetraacid in acidic methanol gave the tetramethyl ester in 66% yield (Figures 11, 12). The tetraethyl ester was similarly isolated in 98% yield (Figures 13, 14).

III. EXPERIMENTAL¹²

Cubane-1,4-dicarboxylic Acid from the Favorskii Mixture. A mixture of crude cubane-1,4-diacid and salt (800 g) (obtained from the filtration of an acidified Favorskii reaction mixture resulting from 1 kg of cage' dione) was stirred with 10% aqueous NaOH (600 mL) for 0.5 h and filtered. The filtrate was acidified by dropwise addition of conc HCl. The solid was filtered, and washed with cold water (3 x 50 mL) and cold acetone (3 x 50 mL), and dried at ambient temperature in vacuo (0.5 torr) to give 175 g (30% based on cage dione) of 95% pure cubane-1,4-dicarboxylic acid (by titration with standard NaOH) as a white powder, mp 225°C: ¹H NMR (DMSO-d₆) δ 4.09 (s).

Cubane-1,4-diacid Chloride. A mixture of cubane-1,4-dicarboxylic acid (100 g, 0.52 mol) and freshly distilled SOCl₂ (326 g, 2.7 mol) was refluxed under N₂ for 14 h to give a homogeneous solution. The excess thionyl chloride was removed under reduced pressure. The residue was extracted sequentially with toluene (50 mL) and CCl₄ (50 mL), filtered and dried to give 116 g (97%) of cubane-1,4-diacid chloride, as a white solid, mp 135°C: δ ¹H NMR (CDCl₃) 4.48.

Cubane-1,4-bis(N-t-butyl-N-ethylcarboxamide) (Bisamide). A solution of cubane-1,4-dicarboxylic acid chloride (114 g, 0.49 mol) in dichloromethane (1000 mL) was cooled to 0°C and a mixture of triethylamine (121 g,

1.3 mol) and *t*-butylethylamine (121 g, 1.2 mol) was added dropwise. This mixture was stirred at room temperature for 48 h and the solvent was removed in vacuo. The residue was extracted with water (3 x 100 mL) and acetone (3 x 80 mL) and dried to give 178 g (98%) of cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide), as a white solid, mp 185°C: IR (KBr) 3050, 1620, 1400, 1220 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.27 (s), 3.14 (q), 1.55 (s), 1.22 (t); ^{13}C NMR δ 171, 59.7, 56.6, 40.7, 30.1, 20.09, 18.7. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_2$: C, 73.7; H, 9.49. Found: C, 73.39; H, 9.48.

Cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide)-2,7-dicarboxylic acid (Bisacid Bisamide). A solution of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was prepared by the dropwise addition under N_2 of *n*-butyl lithium in hexane (111 mL, 0.26 mol) to a stirred solution of 2,2,6,6-tetramethylpiperidine (39 g, 0.277 mol) in THF (500 mL, freshly distilled from sodium benzophenone ketal) at a rate such that the internal temperature did not exceed -50°C. This solution was warmed to 0°C and was stirred for 3 h with cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide) (9.5 g, 26.5 mmol) and magnesium bromide etherate (35 g, 139 mmol) and then allowed to stand at -15°C for 48 h. Carbon dioxide gas was passed through the cooled solution for 5 h during which time the temperature rose to ambient. The solvent was evaporated in vacuo at 40°C and the residue was suspended in water (500 mL) at 0°C and conc. HCl (100 mL) was added in 5 portions resulting in a pH of 3. The precipitate was removed by filtration, washed with water (2 x 10 mL), and dried at ambient temperature (0.1 torr) to give 7.5 g (60%) of cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide)-2,7-dicarboxylic acid as an off-white solid, mp 241°C: IR (KBr) 3050, 1725, 1550, 1490, 1200, 1020 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.57 (s, 4 H), 3.7 (q, $J = 7$ Hz,

4 H), 1.48 (s, 18 H), 1.28 (t, $J = 7$ Hz, 6 H); ^{13}C NMR (CDCl_3) δ 172.0, 171.0, 61.2, 59.1, 56.7, 51.1, 39.8, 28.2, 18.4. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_6$: C, 64.59; H, 7.16; N, 6.28. Found: C, 64.28; H, 7.47; N, 6.21.

Cubane-1,2,4,7-tetracarboxylic Acid from Bisamide. A solution of LiTMP (1.05 mol) in THF (1.6 L) (prepared as described above), cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide) (50 g, 138 mmol) and magnesium bromide etherate (143 g, 570 mmol) was stirred under N_2 at 0°C for 2 h. Carbon dioxide was passed through the solution for 3 h and the temperature was allowed to rise to ambient. The solvent was evaporated, the residue suspended in an ice-water mixture (1.5 kg), and a pH of 3 attained by addition of conc HCl (160 mL). The mixture was filtered and the crude solid dissolved in cold conc HNO_3 (120 mL, 70%). The acid solution was refluxed for 5 h, cooled and filtered. The solid was washed with acetonitrile (3 x 10 mL) to give 17.5 g (46%) of cubane-1,2,4,7-tetracarboxylic acid as a white solid, mp 265°C (dec): IR (KBr) 3200 (br), 1740, 1600, 1460, 1300, 1230, 1205, 1120, 880 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 4.27 (s) ^{13}C NMR (acetone- d_6 , D_2O) δ 173, 56.13, 47.78.

Cubane-1,2,4,7-tetracarboxylic Acid from Bisacid Bisamide. Solid cubane-1,4-bis(*N*-*t*-butyl-*N*-ethylcarboxamide)-2,7-dicarboxylic acid (1.4 g, 3.14 mmol) was added to conc HNO_3 (30 mL, 70%) at 0°C and the solution was then heated at reflux for 12 h. The resulting mixture was cooled, filtered and the solids washed with acetonitrile (2 x 10 mL) to give 0.6 g (68%) of cubane-1,2,4,7-tetracarboxylic acid as a white solid, mp 265°C (dec) identical to that prepared above.

Cubane-1,2,4,7-tetracarboxylic Acid Chloride. A mixture of cubane-1,2,4,7-tetracarboxylic acid (1.0 g, 3.6 μmoles) and freshly distilled thionyl

chloride (25 mL) was stirred and refluxed for 6 h to give a homogeneous solution. The thionyl chloride was removed in vacuo (0.5 torr) and the residue was recrystallized from dry toluene to give 1.2 g (95%) of cubane-1,2,4,7-tetracarboxylic acid chloride, mp 132°C (DSC): ^1H NMR (CDCl_3) δ 4.8. Anal. Calcd for $\text{C}_{16}\text{H}_4\text{Cl}_4\text{O}_4$: C, 40.7; H, 1.13; Cl, 40.06. Found: C, 49.79; H, 1.31; Cl, 38.84.

Tetramethyl Cubane-1,2,4,7-tetracarboxylate. A suspension of cubane-1,2,4,7-tetracarboxylic acid (7.6 g, 27 mmol) in methanol (150 mL) and trifluoromethanesulfonic acid (1.0 g, 6.7 mmol) was refluxed for 4 h until a homogenous solution formed. The cooled solution was diluted with a saturated NaHCO_3 solution (150 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried (Na_2SO_4), evaporated and the residue recrystallized from CH_2Cl_2 /hexane (1:4.5) to give 6.0 g (68%) of tetramethyl cubane-1,2,4,7-tetracarboxylate as a white solid, mp 180°C: IR (KBr) 3050, 1720, 1450, 1320, 1220, 1020 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.47 (s, 4 H), 3.8 (s, 12 H); ^{13}C NMR (CDCl_3) δ 168.45, 55.89, 51.97, 47.39.

Tetraethyl Cubane-1,2,4,7-tetracarboxylate. A suspension of cubane-1,2,4,7-tetracarboxylic acid (0.7 g, 2.5 mmol) in ethanol (20 mL) and trifluoromethanesulfonic acid (1 drop) was refluxed for 5 h. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (20 mL), and washed with water (2 x 15 mL). The organic layer was dried (Na_2SO_4) and the solvent was evaporated to give 1.0 g (98%) of tetraethyl cubane-1,2,4,7-tetracarboxylate as a white solid, mp 86°C: IR (KBr) 3050, 1720, 1320, 1220, 1040 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.45 (s, 4 H), 4.18 (q, $J = 7$ Hz, 8 H), 1.27 (t, $J = 7$ Hz, 12 H).

***t*-Butylethylamine.** A mixture of 50% KOH (475 mL), water (200 mL)

and *t*-butylamine (431 g, 5.89 moles) was cooled to 0°C and diethyl sulfate (1000 g, 6.48 moles) was added with rapid stirring over 1 h. The organic layer was separated, stirred over solid KOH for 16 h, filtered and distilled from CaH_2 to give 390 g (66%) of *t*-butylethylamine, b.p. 81–85°C, ^1H NMR: 2.6 (q, $J = 7$ Hz, 2 H); 1.1 (s, 9 H); 1.15 (t, $J = 7$ Hz, 3 H).

2,2,6,6-Tetramethylpiperidine. Ammonia gas (1400 g, 82 mol) was added to a stirred suspension of acetone (12.5 kg, 215 mol) and calcium chloride (4 kg) over 48 hours at a rate such that the temperature was maintained below 40°C. The solvent was removed at 30–40°C (30 torr) and a 10% aqueous NaOH solution (5 L) was added. The organic layer was decanted and the water extracted with CH_2Cl_2 (3 x 2 L). The organic materials were combined and solvent evaporated to give 8.5 kg of crude triacetone amine.

A solution of the crude triacetone amine (8.5 kg), hydrazine hydrate (10 kg), KOH (9.3 kg) in polyethylene glycol (carbowax 400, 80 L) was heated at 135°C for two hours and then the temperature was slowly increased to 180°C. The two-phased distillate was extracted with CH_2Cl_2 (2 x 2 L), separated, and the organic layer was dried (Na_2SO_4). This solution contained 3.4 kg (31%) of essentially pure 2,2,6,6-tetramethylpiperidine, by nmr assay, and was stored in solution. The solvent was evaporated from a 200 mL aliquot and the crude product stirred for 24 h over solid KOH, filtered and distilled to give 2,2,6,6-tetramethylpiperidine, bp 151–152°C.

IV. REFERENCES

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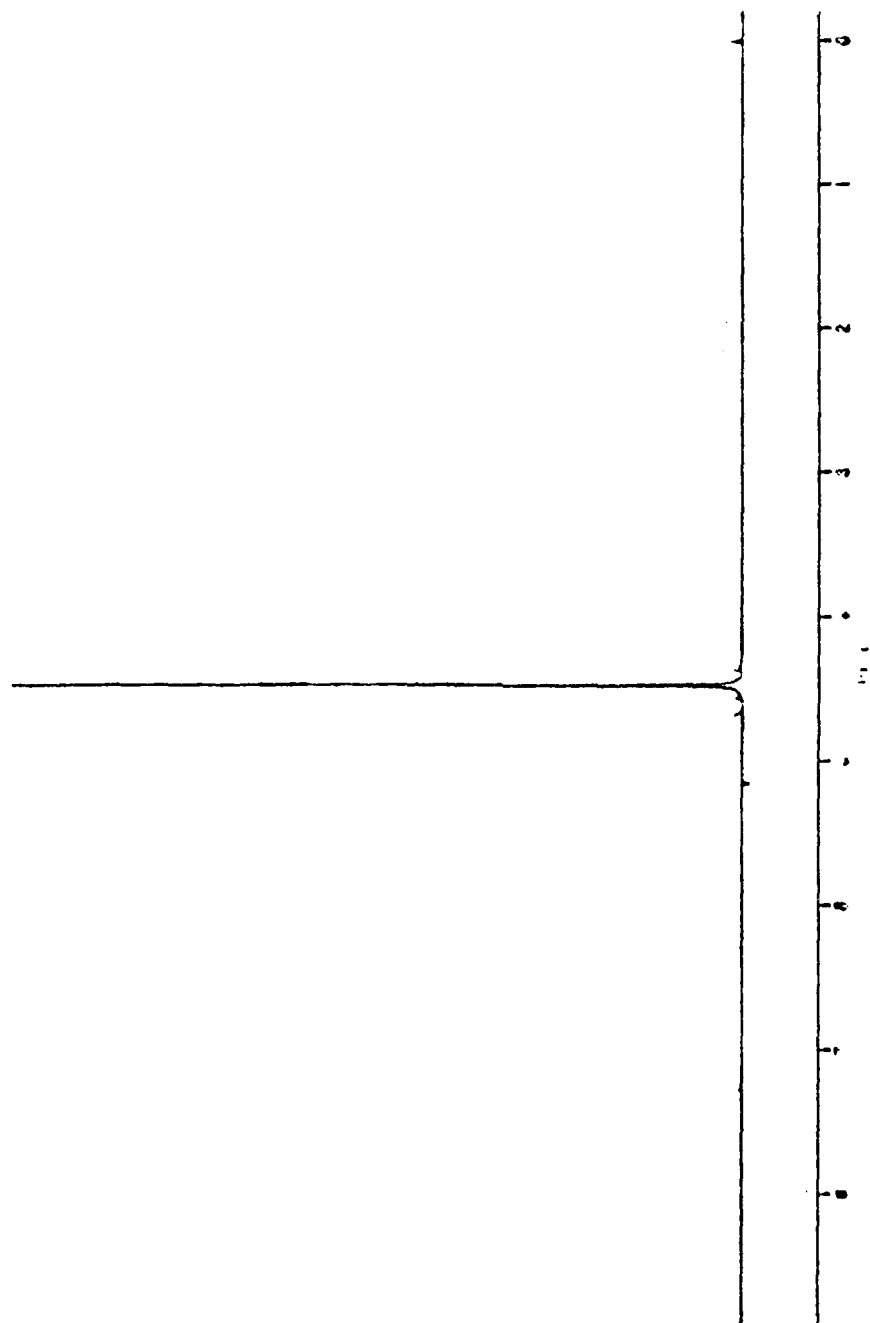


FIGURE 1. ^1H NMR of CUBANE-1,4-DIACID CHLORIDE

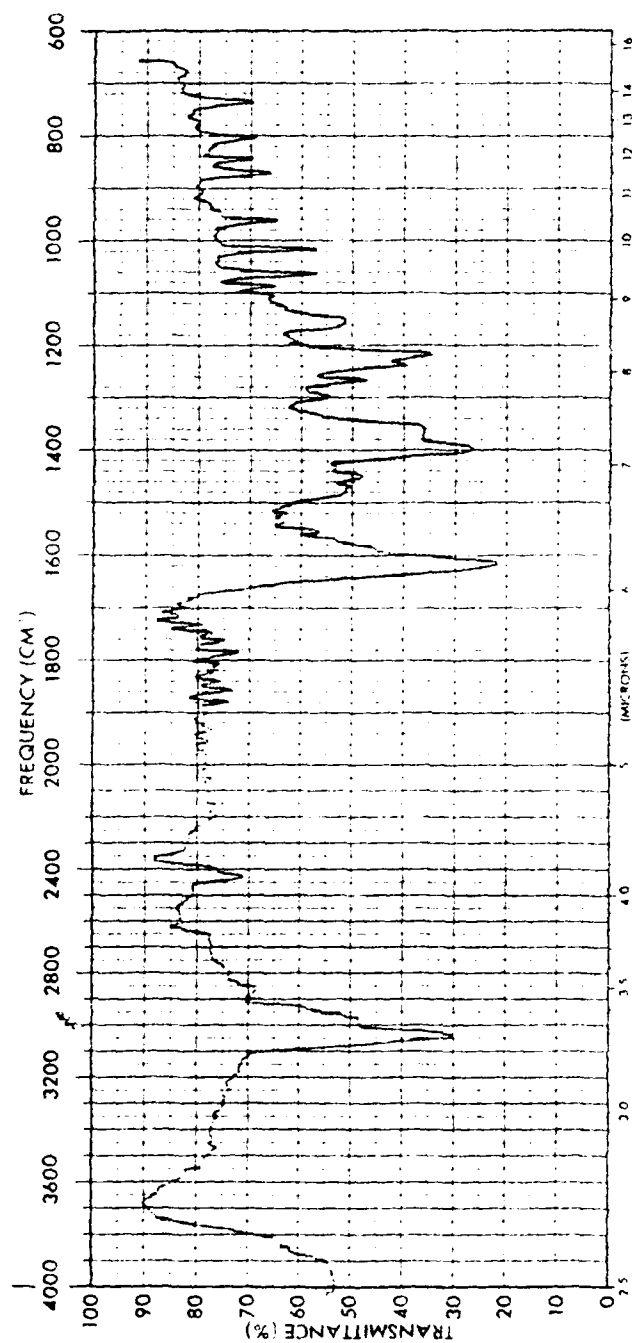


FIGURE 2. IR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYL-CARBOXYAMIDE)

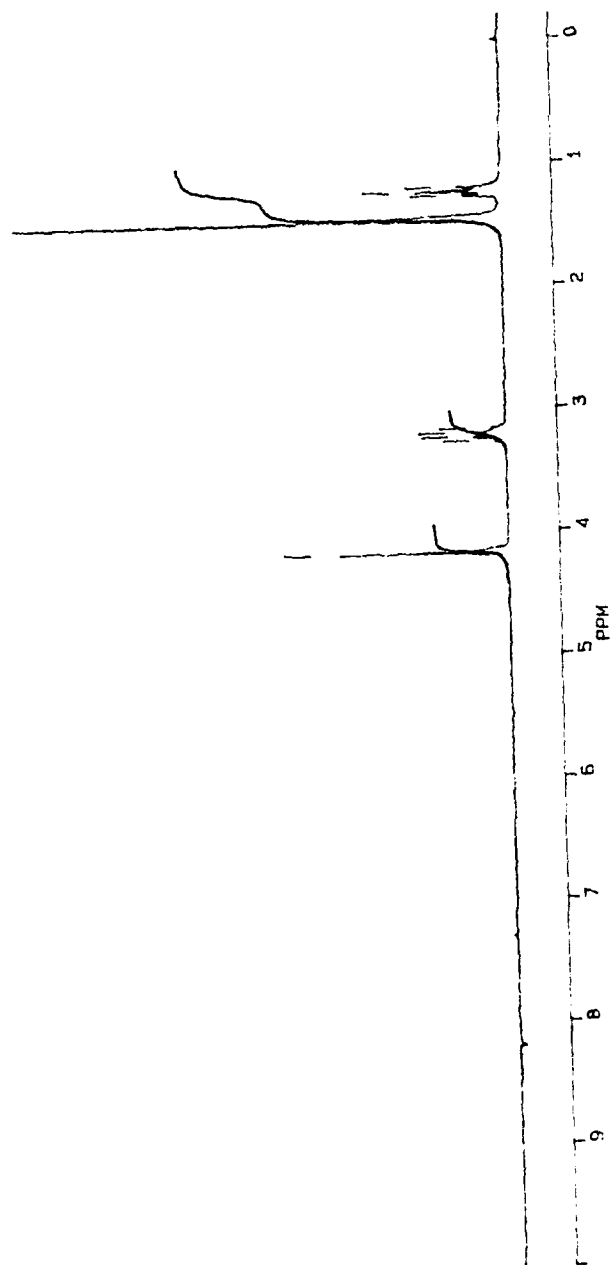


FIGURE 3. ^1H NMR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE)

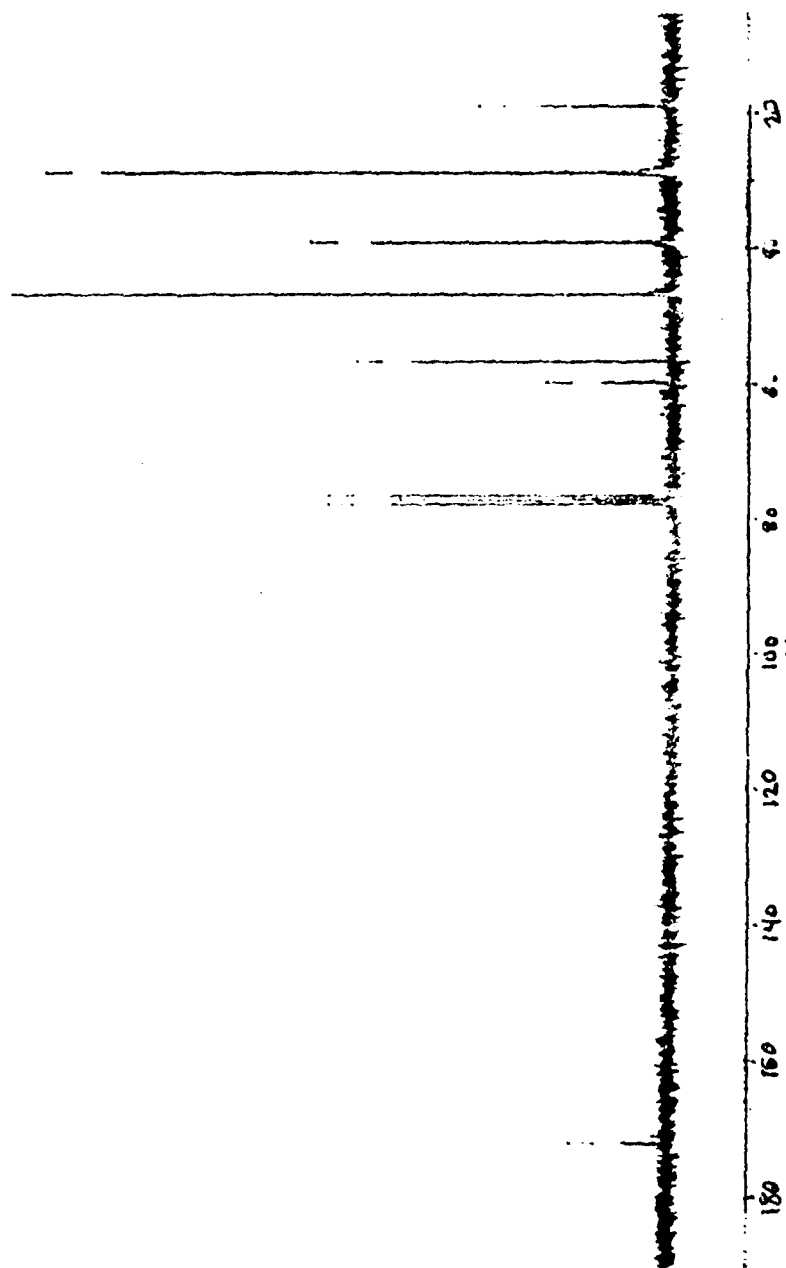


FIGURE 4. ^{13}C NMR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE)

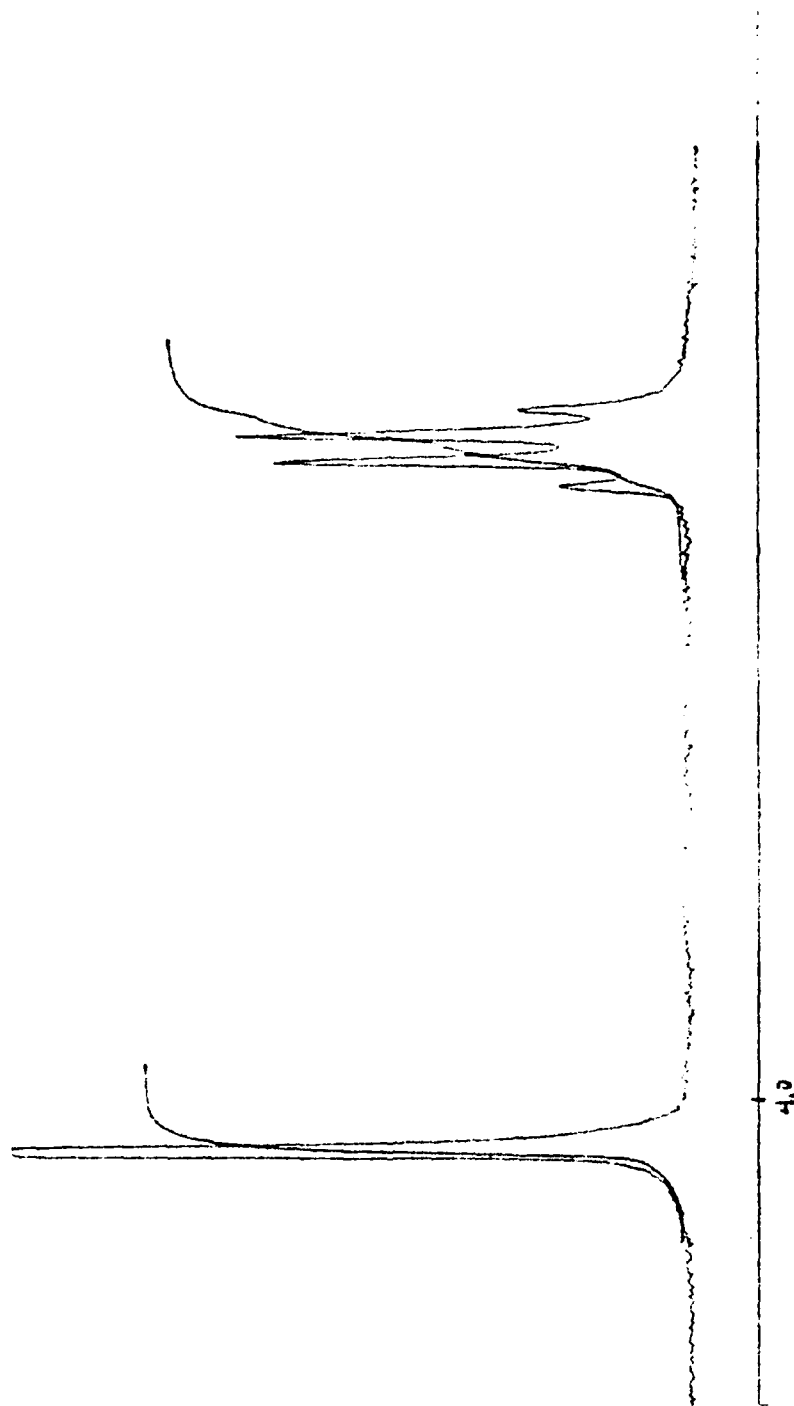


FIGURE 5. ^1H NMR OF DILITHIATED BISAMIDE QUENCHED WITH D_2O
 δ 3.0-4.2.

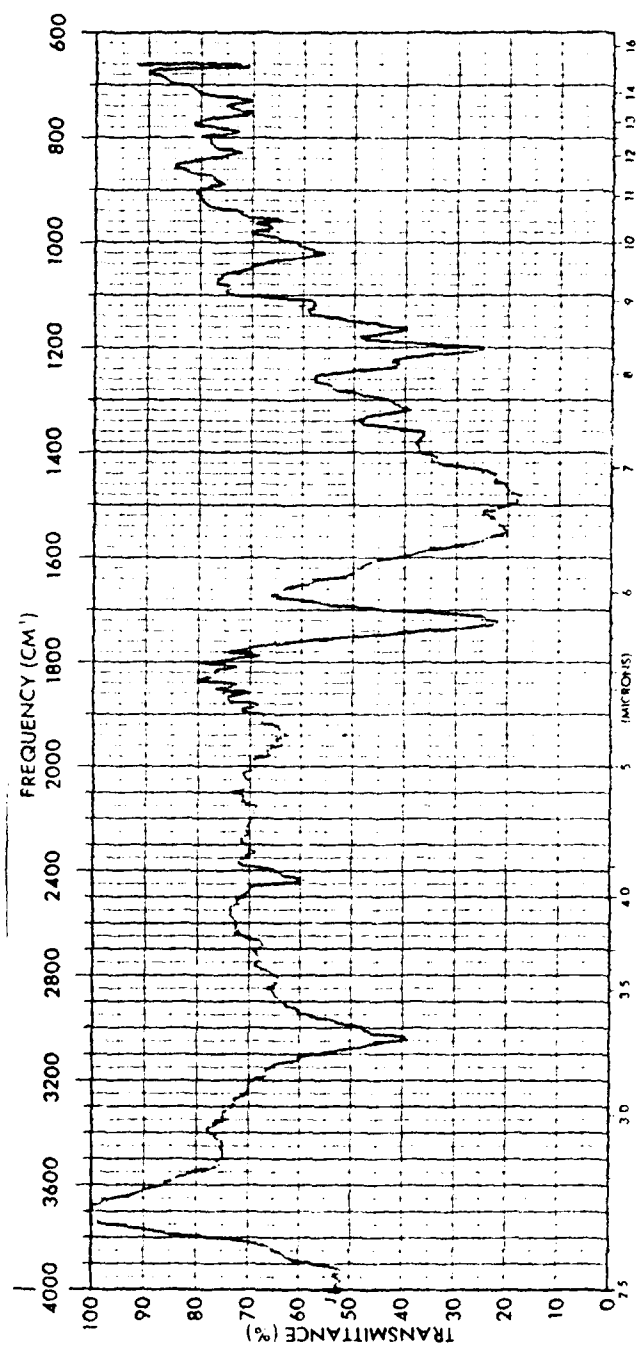


FIGURE 6. IR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE)-2,7-DICARBOXYLIC ACID

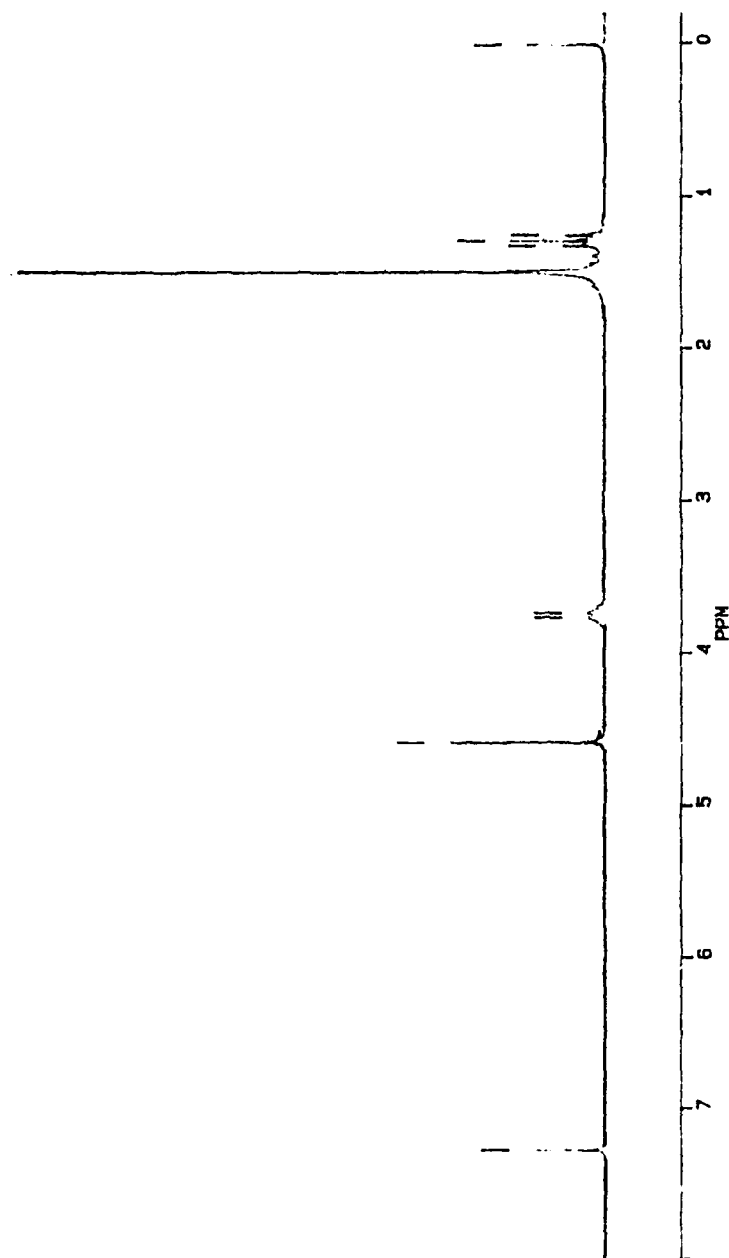


FIGURE 7. ^1H NMR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE)-2,7-DICARBOXYLIC ACID

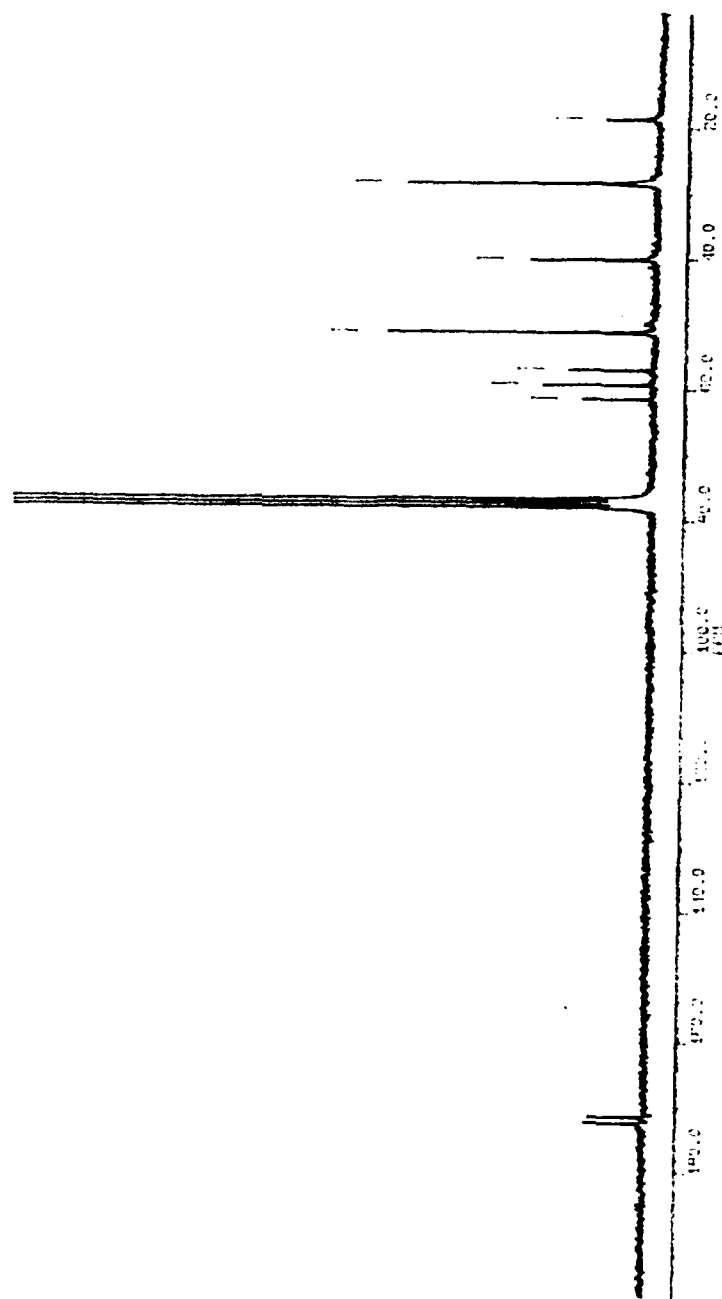


FIGURE 8. ^{13}C NMR OF CUBANE-1,4-BIS(N-T-BUTYL-N-ETHYLCARBOXAMIDE)-2,7-DICARBOXYLIC ACID.

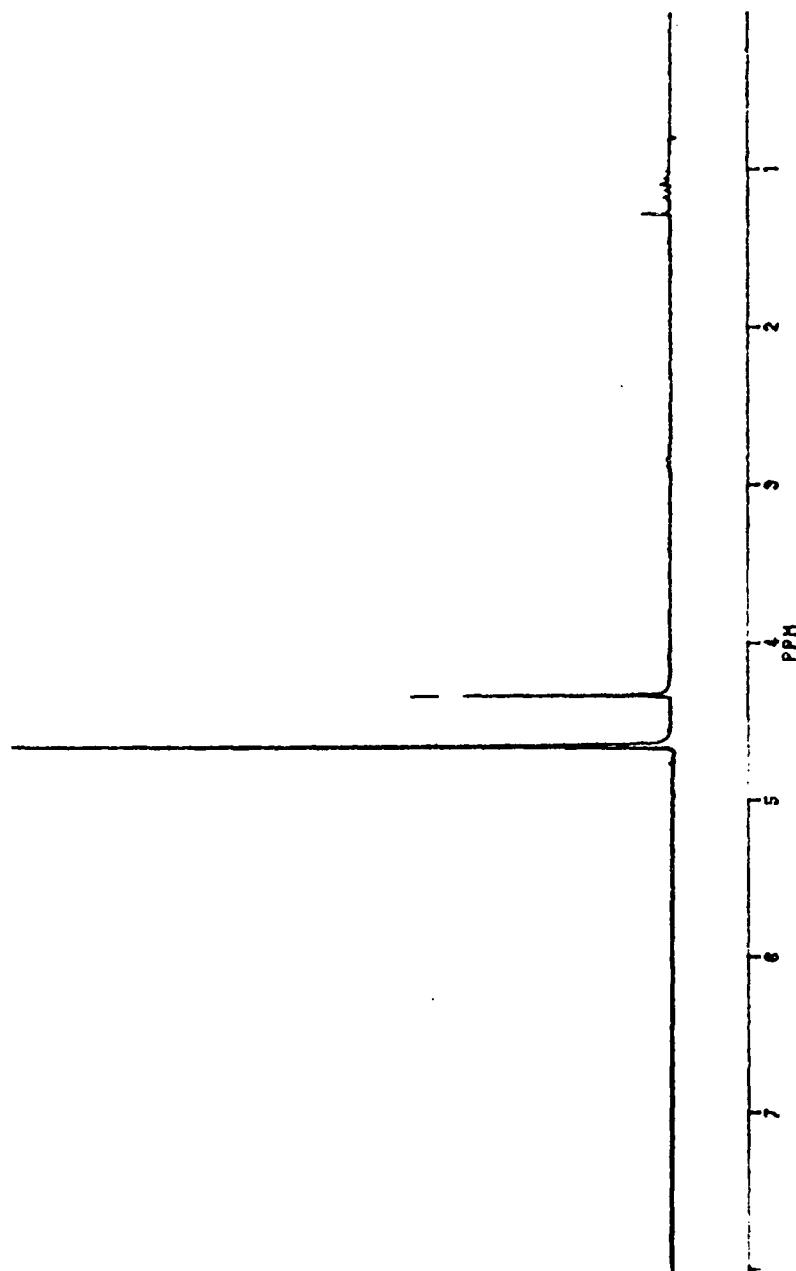


FIGURE 9. ^1H NMR OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID
IN D_2O

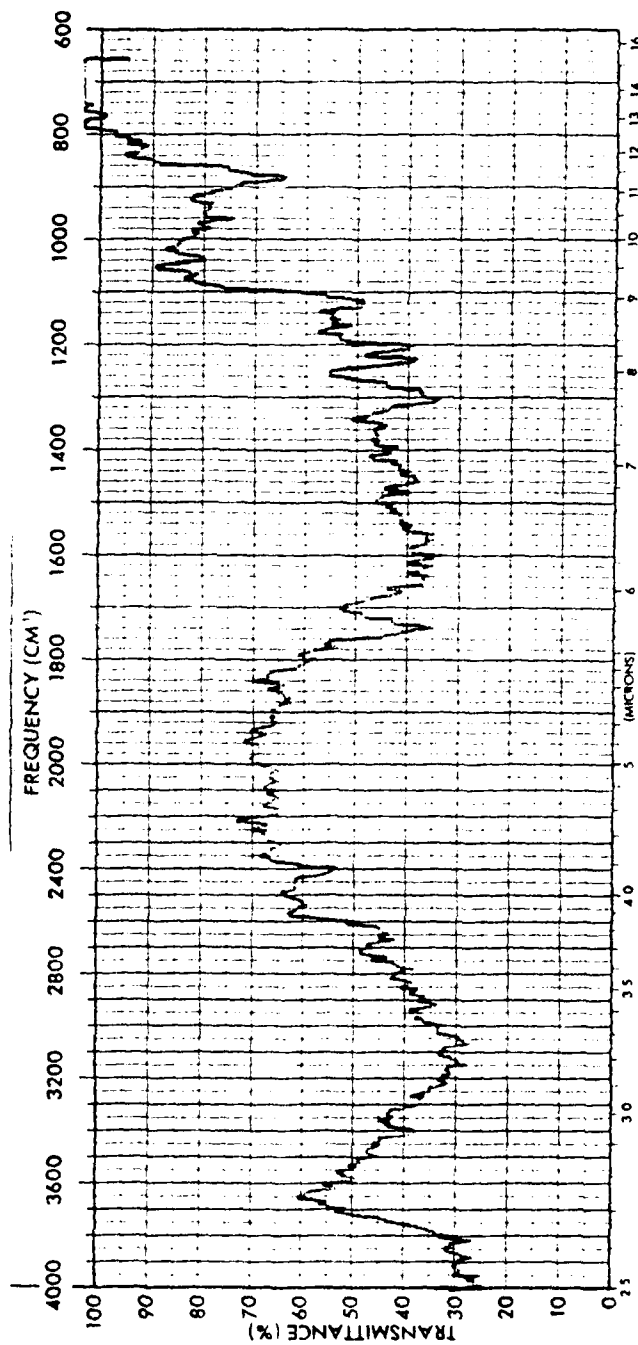


FIGURE 10. IR OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID

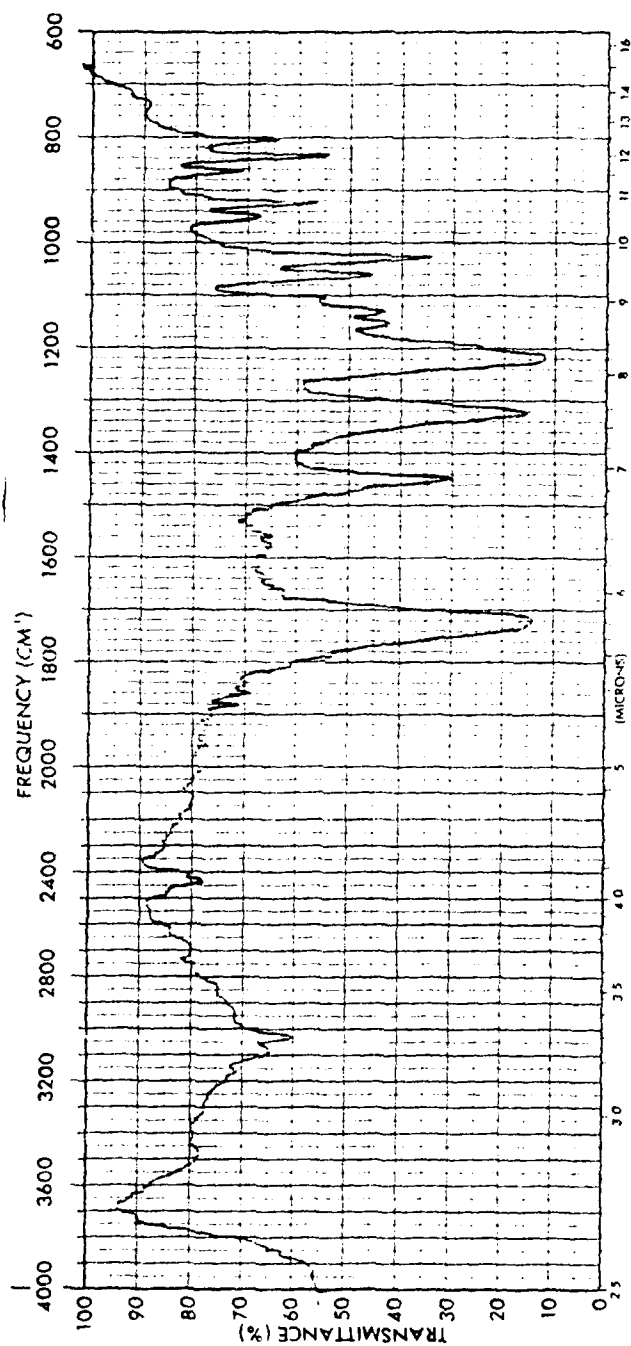


FIGURE 11. IR OF TETRAMETHYL CUBANE-1,2,4,7-TETRACARBOXYLATE

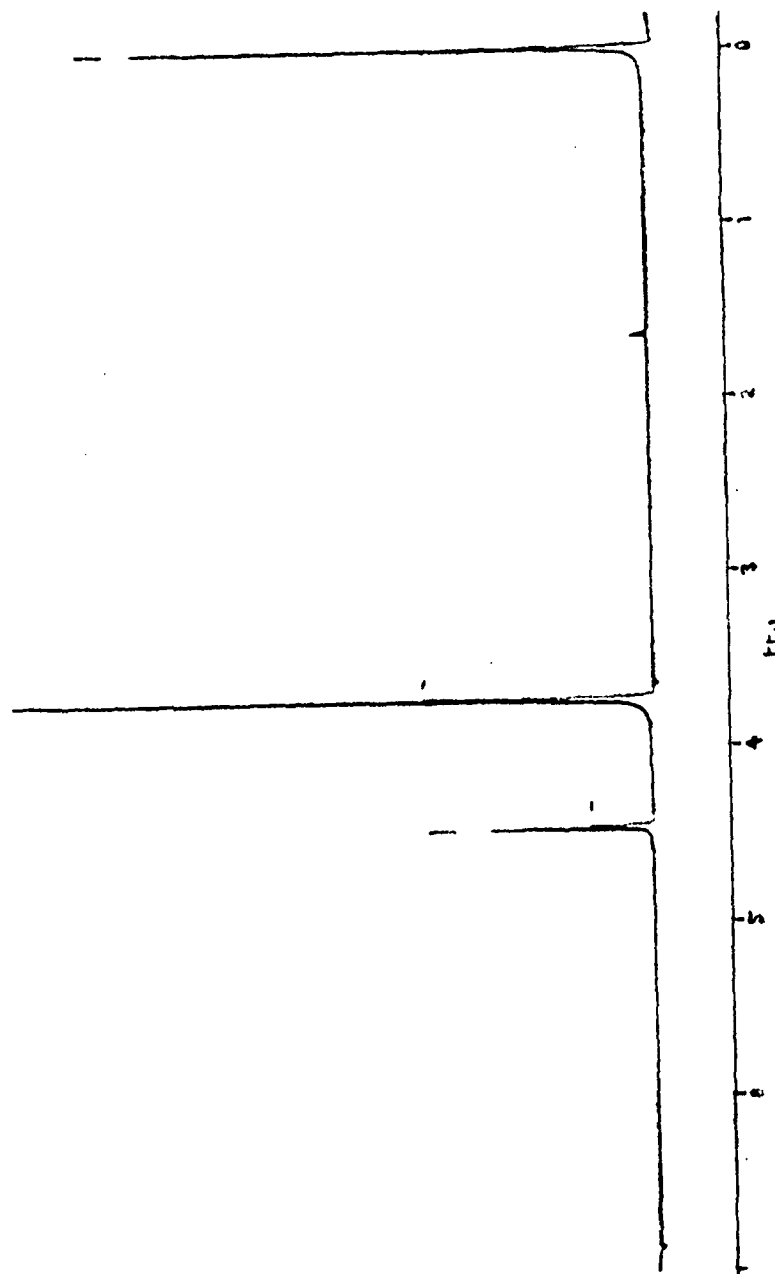


FIGURE 12. ^1H NMR OF TETRAMETHYL CUBANE-1,2,4,7-TETRACARBOXYLATE

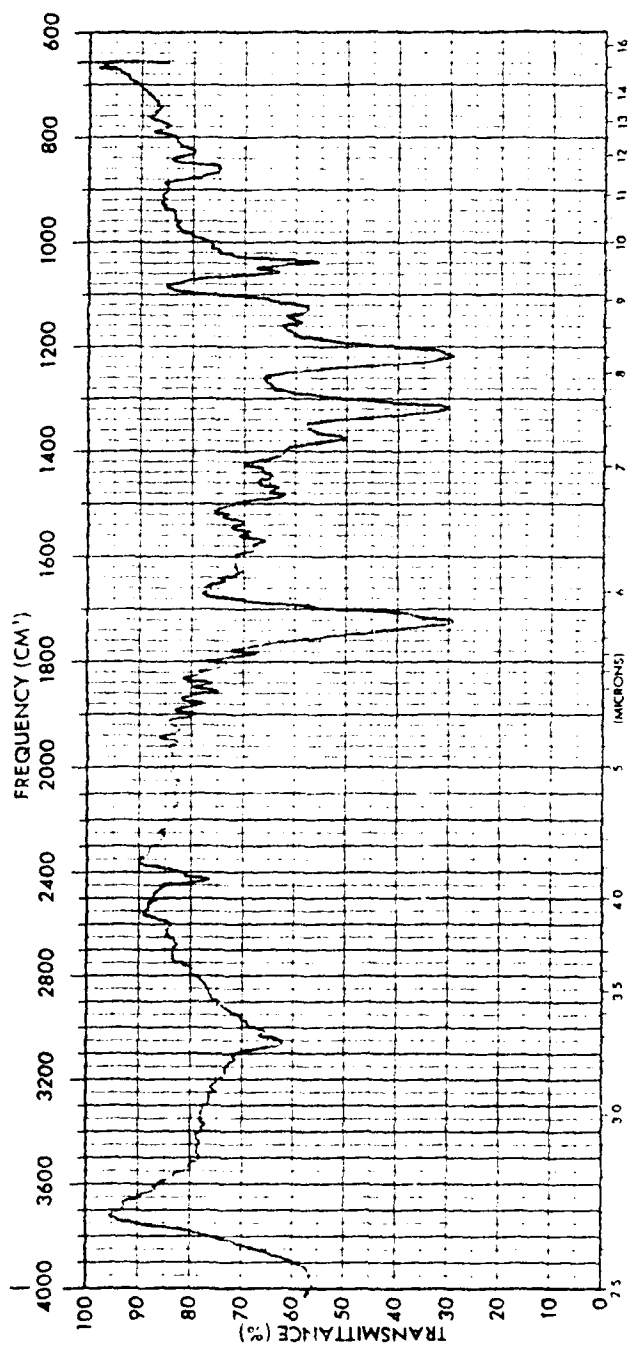


FIGURE 13. IR OF TETRAETHYL CUBANE-1,2,4,7-TETRACARBOXYLATE

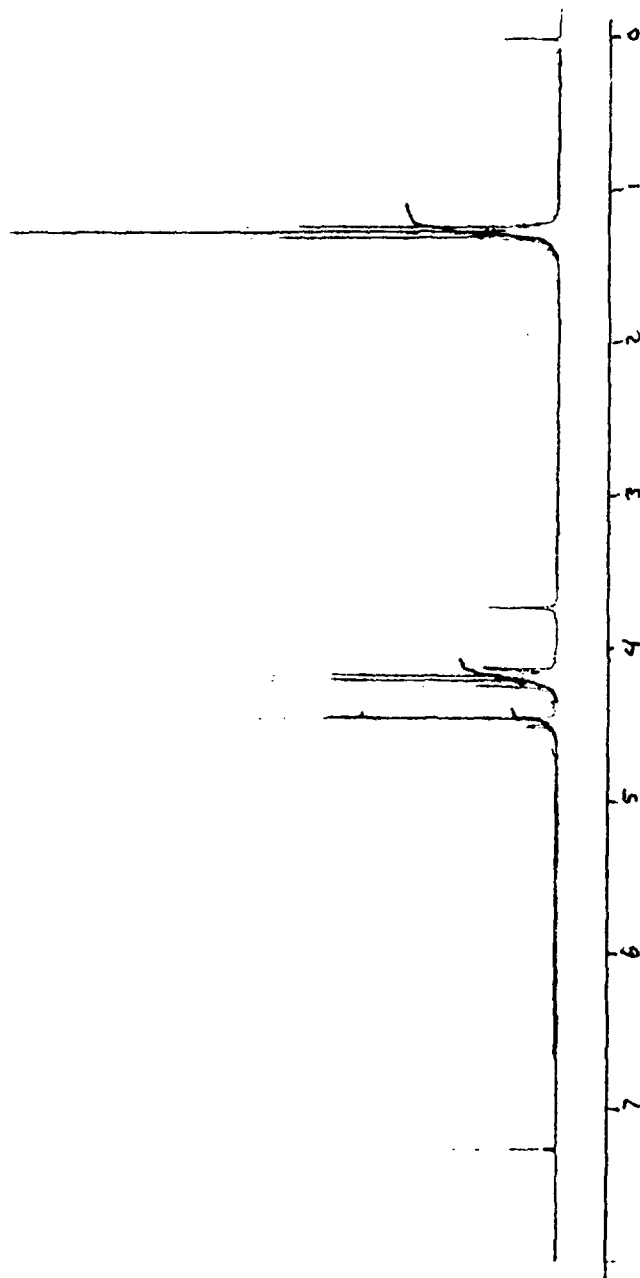


FIGURE 14. ^1H NMR OF TETRAETHYL CUBANE-1,2,4,7-TETRACARBOXYLATE

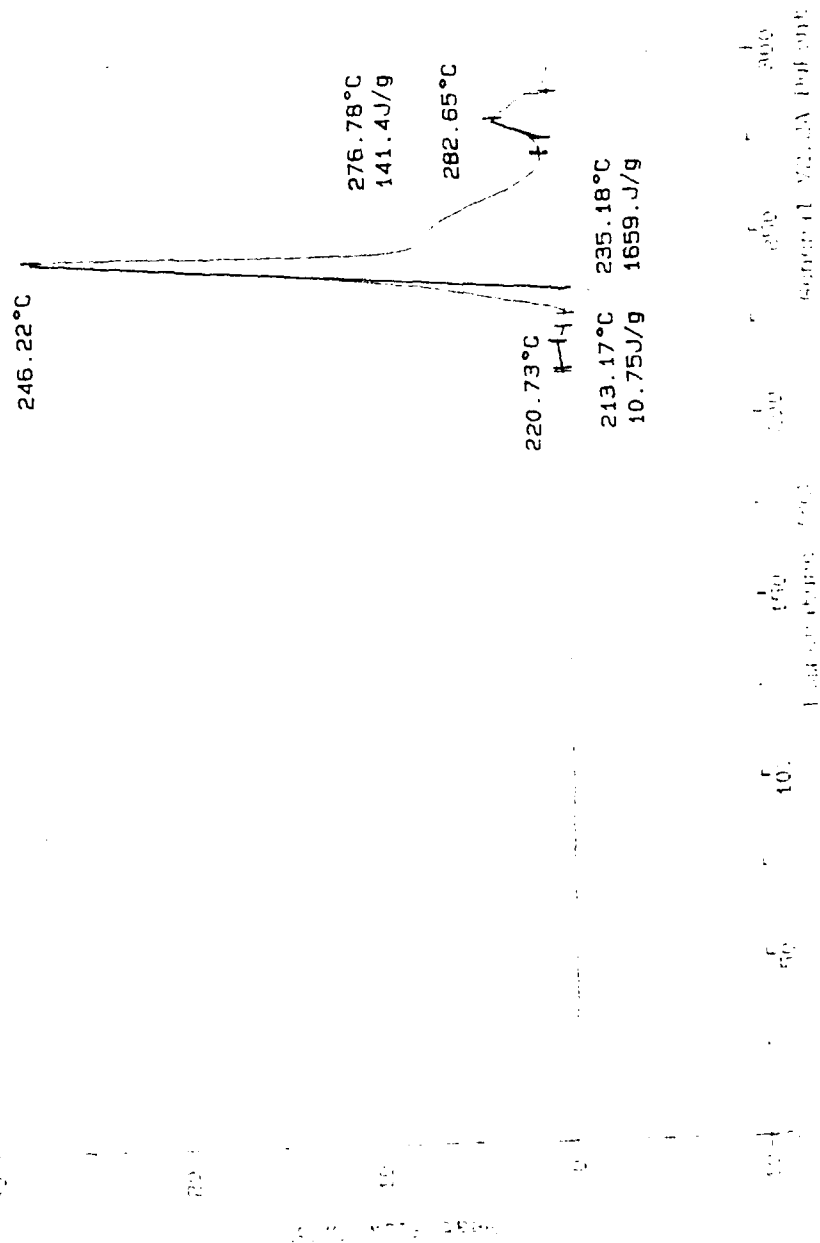
[illegible]

FIGURE 15. DSC OF CUBANE-1,4-DICARBOXYLIC ACID

Date: 10/10/94
 Time: 10:00 AM
 Operator: A. J. HALL
 Method: DSC
 Comment: 25 to 300 °C, at 10 °C/min

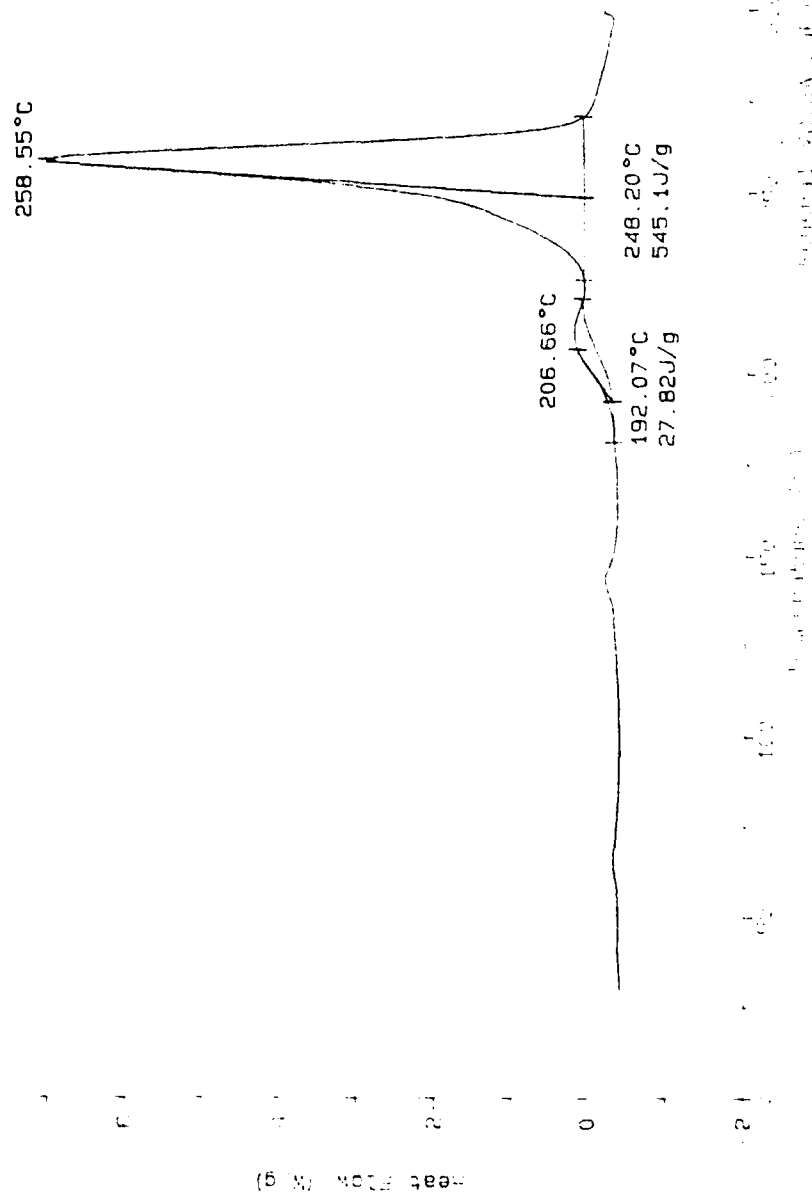


FIGURE 16. DSC OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID

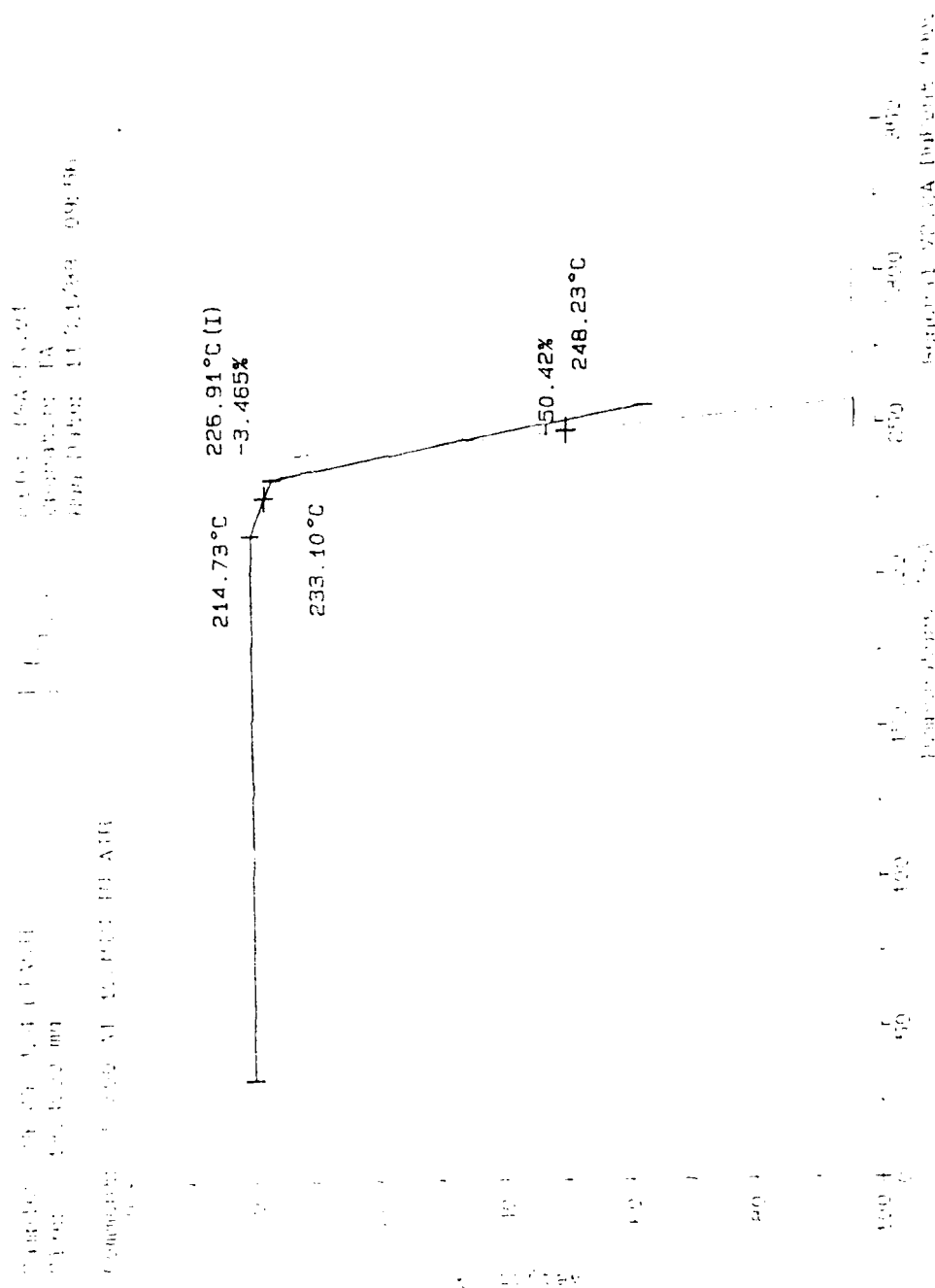


FIGURE 17. TGA OF CUBANE 1,4-DICARBOXYLIC ACID

Sample: CUBANE-1,2,4,7-TETRACARBOXYLIC
 Weight: 0.0030 mg
 Method: TGA
 Temperature: 25-300 AT 10 MIN AT 100

File: 117000
 Date: 11/11/88 11:17
 Operator: J.A.

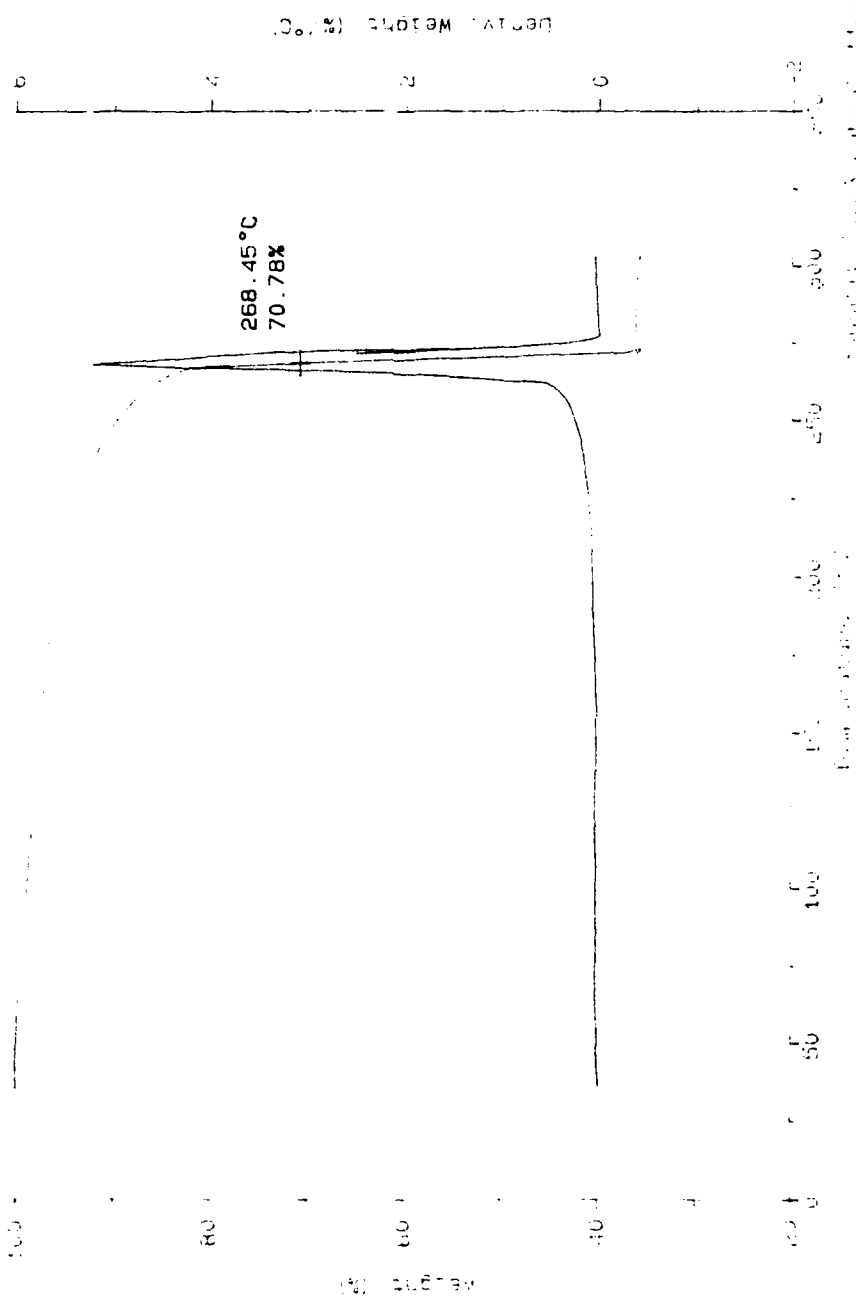
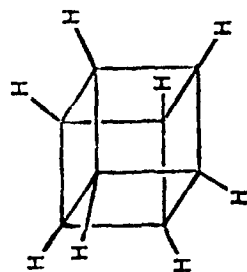


FIGURE 18. TGA OF CUBANE-1,2,4,7-TETRACARBOXYLIC ACID



CUBANE

melting point
stability
decomposition
density
heat of formation(gas)
strain energy

130-131°C (easily lowered)
inert to light, water, air
>220° (very slow)
1.29 g/cm³
+144 kcal/mole
+166 kcal/mole

CUBANE HAS THE HIGHEST ENERGY CONTENT OF ANY AVAILABLE STABLE HYDROCARBON BY WEIGHT OR VOLUME
PREDICTION: CUBANE DERIVATIVES WILL BE EXCEPTIONAL EXPLOSIVES, FUELS, PROPELLANTS, ETC.

ILLUSTRATIONS:

AS A FUEL

Density	I_{sp}/O_2	wt-%	I_{sp}/HNO_3	wt-%	BTU/gal
1.29	316	36	274	22	204,450
0.81	304	28	262	16	120,400

Cubane
versus
JP-5

AS AN EXPLOSIVE

Density	Det. Vel.	P_{cl}
2.02	10.0	470
2.10	9.82	467
1.89	9.12	382

$C_8H_4[N(NO_2)_2]_4$
&
Octanitrocubane
versus
HMX

AS AN SDI PROPELLANT

Density	ΔH_f	I_{sp}	(binder)
2.02	+250	286	(15% BAMO/NMNO)
1.95	-71	245	(15% HTPB)
2.07	-66	263	(15% HTPB)

$C_8H_4[N(NO_2)_2]_4$
versus
AP
HAP

GOALS

AT THE RESEARCH LEVEL:

1. FIND METHODS FOR MAKING HIGH ENERGY CUBANES
2. EVALUATE THESE CUBANES FOR SDI MISSIONS

AT THE ENGINEERING LEVEL:

1. SYNTHESIS OF CUBANES AT PILOT PLANT SCALE
2. FORMULATION AND PERFORMANCE TESTING

ESTIMATED PARAMETERS FOR PROPELLANTS BASED ON TETRASUBSTITUTED CUBANES

ENERGETIC SUBSTITUENT	MOLECULAR FORMULA	DENSITY (g/cm ³)	ΔH_f (solid) (kcal/mole)	I_{sp} (sec)		
				MONOPROPELLANT	15%HTPB	15%BAMO/NMMO
-NO ₂	C ₈ H ₄ N ₄ O ₈	1.87	+71	250	229	242
-ONO ₂	C ₈ H ₄ N ₄ O ₁₂	1.94	+33	274	239	263
-NHNO ₂	C ₈ H ₈ N ₈ O ₈	1.86	+160	261	239	251
-N(NO ₂) ₂	C ₈ H ₄ N ₁₂ O ₁₆	2.02	+250	283	269	286
-N(NO ₂)CH ₂ C(NO ₂)F	C ₁₆ H ₁₂ N ₁₆ O ₂₄ F ₄	1.86	-77	264	229	251
-N(NO ₂)CH ₂ C(NO ₂) ₃	C ₁₆ H ₁₂ N ₂₀ O ₃₂	1.89	+70	270	240	265
-N(NO ₂)C(O)N(NO ₂)-	C ₁₀ H ₄ N ₈ O ₁₀	2.01	+108	243	223	236
-CO ₂ CH ₂ C(NO ₂) ₃	C ₂₀ H ₁₂ N ₁₂ O ₃₂	1.82	-308	242	205	230
-CO ₂ CH ₂ C(NO ₂) ₂ F	C ₂₀ H ₁₂ N ₈ O ₂₄ F ₄	1.77	-454	213	195	205
-C(NO ₂) ₃	C ₁₂ H ₄ N ₁₂ O ₂₄	1.96	+40	264	246	267
-OCIO ₃	C ₈ H ₄ Cl ₄ O ₁₆	>2.0	+100	262	263	274
-NF ₂	C ₈ H ₄ N ₄ F ₈	1.92	+103	246	-	269
-NH ₂ ·HClO ₄	C ₈ H ₁₆ Cl ₄ O ₁₆	>2.2(?)	-100	267	231	258
REFERENCE COMPOUNDS						
. HMX	C ₄ H ₈ N ₈ O ₈	1.90	+17.9	265	226	251
XX	C ₆ H ₆ N ₁₂ O ₁₂	1.98	+101	272	238	264
AP	NH ₄ ClO ₄	1.95	-71	-	245	235
HAP	NH ₄ ClO ₅	2.07	-66	-	263	234

Eaton, U. of Chicago

ESTIMATED PARAMETERS FOR VARIOUS TETRASUBSTITUTED CUBANES AND REFERENCE COMPOUNDS

Energetic Substituent	Molecular Formula	Density, g / cm ³	ΔH_f (solid), Kcal / mole	I_{sp}		
				Monopropellant	15% R45M	15% BAMO / NMMO
-NO ₂	C ₈ H ₄ N ₄ O ₈	1.87	+71	249.8	229.1	242.1
-ONO ₂	C ₈ H ₄ N ₄ O ₁₂	1.94	+33	274.1	238.6	263.2
-NHNO ₂	C ₈ H ₈ N ₈ O ₈	1.86	+100	260.9	239.1	251.3
-N(NO ₂) ₂	C ₈ H ₄ N ₁₂ O ₁₆	2.02	+250	282.7	269.0	285.7
-C(NO ₂) ₃	C ₁₂ H ₄ N ₁₂ O ₂₄	1.96	+40	263.7	245.5	267.1
-NF ₂	C ₈ H ₄ N ₄ F ₈	1.92	+103	246.1		268.9
-NNO ₂ CONNO ₂	C ₁₀ H ₄ N ₈ O ₁₀	2.01	+108	243.0	223.0	235.72
-NH ₃ ClO ₄	C ₈ H ₁₆ Cl ₄ O ₁₆	> 2.20(?)	-100	267.0	230.5	257.6
-OCIO ₃	C ₈ H ₄ Cl ₄ O ₁₆	> 2.00	+100	262.1	263.2	273.6
-N(NO ₂)CH ₂ C(NO ₂) ₃	C ₁₆ H ₁₂ N ₂₀ O ₃₂	1.89	+70	269.6	239.9	264.6

MORTON THIOKOL, INC.

Elkton Division

Y868158 (1) (23)

ESTIMATED PARAMETERS FOR VARIOUS TETRASUBSTITUTED CUBANES AND REFERENCE COMPOUNDS (CONTINUED)

Energetic Substituent	Molecular Formula	Density, g / cm ³	ΔH_f (solid), Kcal / mole	I_{sp}		
				Monopropellant	15% R45M	15% BAMO / NMMO
-N(NO ₂)CH ₂ C(NO ₂) ₂ F	C ₁₆ H ₁₂ N ₁₆ O ₂₄ F ₄	1.86	-77	264.5	229.0	250.7
-CO ₂ CH ₂ C(NO ₂) ₃	C ₂₀ H ₁₂ N ₁₂ O ₃₂	1.82	-308	242.0	205.0	229.6
-CO ₂ CH ₂ C(NO ₂) ₂ F	C ₂₀ H ₁₂ N ₈ O ₂₄ F ₄	1.77	-454	213.0	195.0	204.8
AP	NH ₄ ClO ₄	1.95	-71		245.1	235.03
HAP	NH ₄ ClO ₅	2.07	-66		262.5	234.0
HMX	C ₄ H ₈ N ₈ O ₈	1.90	+17.9	265.1	225.7	251.3
XX	C ₆ H ₆ N ₁₂ O ₁₂	1.98	101.0	272.4	237.6	263.5

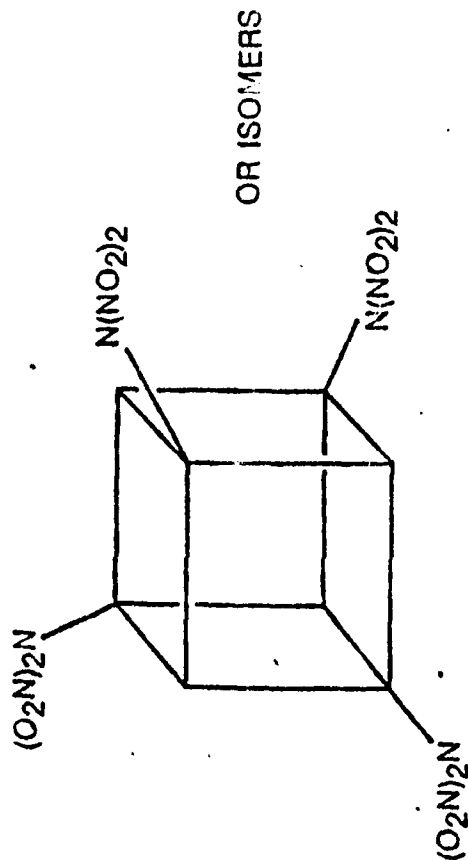
MORTON THIOKOL, INC.

Elkton Division

Y888158 (2) [23]

CONSORTIUM ACCOMPLISHMENTS: 1987-1988
UNIVERSITY OF CHICAGO / SRI INTERNATIONAL / MORTON THIOKOL, INC.

THE ULTIMATE SOLID PROPELLANT OXIDIZER?



	ΔH_f	I_{sp} , lb-sec/lb		Detonation	
		Neat	15% HTPB	Pressure, kbars	Velocity, mm/ μ sec
$d = 2.02$ g/cc	220	279.9	264.3	462	9.88
$\Delta H_f = 240 - 263.4$ kcal/mole	240	281.7	267.4	467	9.93
$C_8H_4N_{12}O_{16}$	260	283.6	270.6	472	9.98

Eaton, U. of Chicago