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SYNTHESIS AND CHARACTERIZATION OF NEW INSENSITIVE HIGH ENERGY P--ETC(U)
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Synthesis and Characterization of a New Insensitive High Energy Polynitramine Compound, 2,4,8,10-Tetranitro-2,4,8,10-Tetraazaspiro[5.5]Undecane (TNSU)

by
Rodney L. Willer
Research Department

MARCH 1982

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

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FOREWORD

The Navy has a need for new energetic compounds which are both dense and energetic and which also have high thermal stability and low sensitivity to impact. These compounds could be used as ingredients in new propellant and explosive formulations which would simultaneously optimize both the performance and safety of new weapons systems. This report describes the synthesis and preliminary characterization of one such compound, 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane (TNSU).

The work was performed under NAVSEA Project No. SR02402, under sponsorship of H. G. Adolph, Naval Surface Weapons Center (R-11).

The work was reviewed for technical accuracy by R. L. Atkins and A. T. Nielsen.

Approved by
E. B. ROYCE, *Head*
Research Department
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Under authority of
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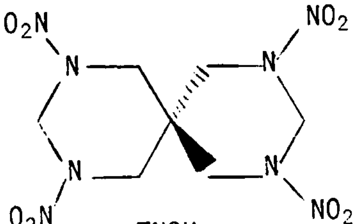
(U) *Synthesis and Characterization of a New Insensitive High Energy Polynitramine Compound, 2,4,8,10-Tetranitro-2,4,8,10-Tetraazaspiro*[5.5]*Undecane (TNSU)*, by Rodney L. Willer, China Lake, Calif., Naval Weapons Center, March 1982. 12 pp. (NWC TP 6353, publication UNCLASSIFIED.)

(U) The synthesis and preliminary characterization of a new high-energy, high-density polynitramine compound, 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane is described.

INTRODUCTION

Synthesis and characterization of a new polynitramine high energy compound which is relatively dense and energetic and has a high thermal stability is described in this paper. This compound is among the least impact sensitive of known polynitramine compounds. Such compounds are needed so that they can be evaluated as propellant and explosive ingredients for new formulations which can simultaneously optimize both the performance and safety of a weapons system. The new compound has the chemical name 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane (TNSU). TNSU was chosen as a synthetic target because it was predicted to be both relatively dense and energetic. The predicted density[1] and performance[2] of TNSU and the measured properties of trinitrotoluene (TNT) are summarized in Table 1.



TNSU

TABLE 1. Predicted Properties of TNSU and Measured Properties of TNT.

	TNSU	TNT
Density[1]	1.67 g/cc	1.65 g/cc
Detonation Velocity[2]	7.77 mm/μsec	6.900 mm/μsec
Detonation Pressure[2]	269 Kbar	205 Kbar

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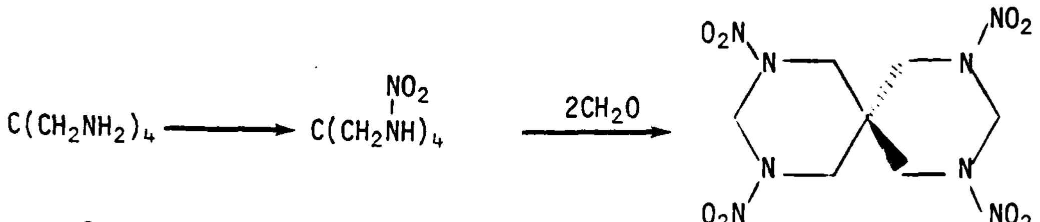
[1] Naval Surface Weapons Center. *Estimation of Normal Densities of Explosives from Empirical Atomic Volumes*, by D. A. Cichra, J. R. Holden, and C. R. Dickerson. Silver Spring, Md., NSWC, 1980. (NSWC-TR-79-273, publication UNCLASSIFIED.)

[2] L. R. Rothstein and R. Petersen. "Predicting High Explosive Detonation Velocities from their Composition and Structure," *Prop. and Explo.*, Vol. 4 (1979), pp. 56.

Two synthetic routes to TNSU were considered. The first involved the synthesis of tetrakis(nitraminomethyl)methane (1) from the known tetrakis(aminomethyl)methane (2),[3] followed by condensation of 1 with two moles of formaldehyde under acidic conditions to give the desired TNSU. This proposed synthetic route to TNSU is summarized in Scheme 1. It was based on analogy to the high-yield synthesis of 1,3-dinitro-1,3-diazacyclohexane from trimethylene dinitramine and formaldehyde.[4]

SCHEME 1. Tetrakis(nitraminomethyl)methane Route to TNSU.



2 1 TNSU

The second proposed synthetic route to TNSU involved the condensation of tetrakis(aminomethyl)methane with two moles of formaldehyde to give 2,4,8,10-tetraazaspiro[5.5]undecane. This compound was then treated with nitrous acid generating 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane. The tetranitroso compound would then be oxidized or nitrolyzed to TNSU. This proposed synthetic route is summarized in Scheme 2. This route was based upon analogy to the synthesis of 1,3-dinitroso-1,3-diazacyclohexane from trimethylene diamine by Evans[5] and the well-established conversions of nitrosamines to nitramines.[6,7]

---

[3] E. B. Fleischer and others. "Conversion of Aliphatic and Alicyclic Polyalcohols to the Corresponding Primary Polyamines," *J. Org. Chem.*, Vol. 36 (1971), pp. 3042.

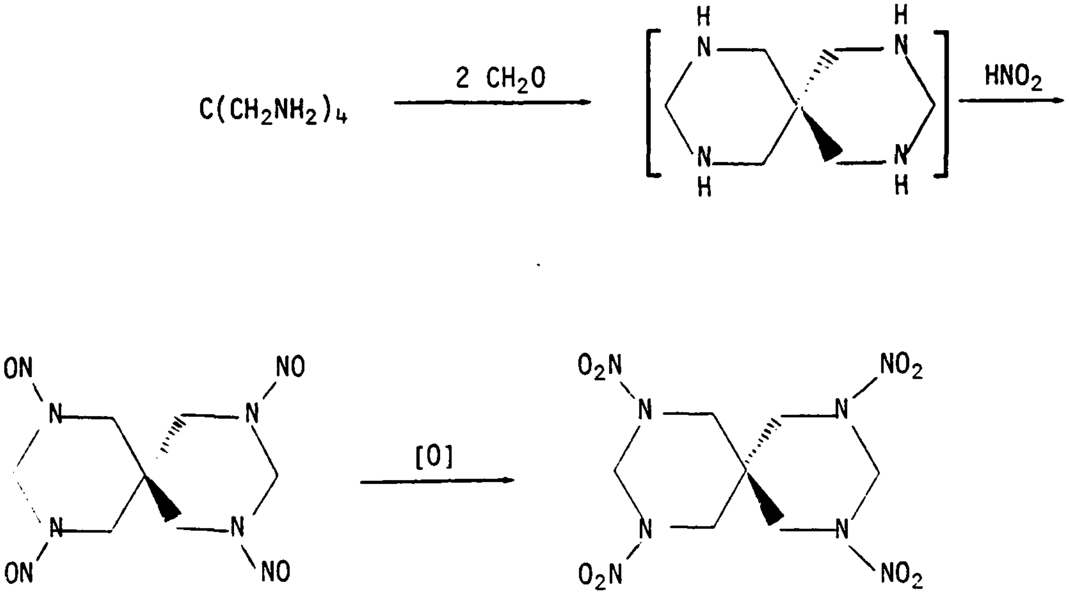
[4] J. A. Bell and I. Dunstan. "Chemistry of Nitramines. Part III. Cyclic Nitramines Derived from Trimethylene Dinitramine." *J. Chem. Soc. (C)*, 1966, pp. 870-872.

[5] R. F. Evans. "Hydropyramidines V. Hexahydropyramidines. The Reaction of Aldehydes and Ketones with 1,3-Diaminopropanes," *Aust. J. Chem.*, Vol. 20 (1967), pp. 1643-1661.

[6] F. J. Brockman, D. C. Downing, and G. F Wright. "Nitrolysis of Hexamethylenetetraamine III. Preparation of Pure Cyclonite," *Can. J. Research*, B, Vol. 27 (1949, pp. 469-474.

[7] W. D. Emmons. "Peroxytrifluoroacetic Acid. I. The Oxidation of Nitrosamines to Nitramines," *J. Amer. Chem. Soc.*, Vol. 76 (1954), pp. 3468-3470.

SCHEME 2. Nitrosamine Route to TNSU.



TNSU

RESULTS

SYNTHESIS OF TETRAKIS(AMINOMETHYL)METHANE

Both proposed synthetic routes to TNSU start with tetrakis(aminomethyl)methane, so the initial effort was directed towards developing a convenient, high-yield, laboratory synthesis of this compound. Several routes to this compound have been described in the literature, the most convenient of which appeared to be the one developed by Fleischer and others,[3] which is summarized in Scheme 3. Two slight modifications to

SCHEME 3. Literature Synthesis of Tetrakis(aminomethyl)methane[3]

$$C(CH_2OH)_4 + 4\phi\text{-}SO_2Cl \xrightarrow{\text{pyridine}} C(CH_2OSO_2\phi)_4$$

$$\xrightarrow[HOCH_2CH_2OCH_2CH_2OH]{NaN_3} C(CH_2N_3)_4 \xrightarrow{LiAlH_4} C(CH_2NH_2)_4$$

62%

this route both simplify it and raise the overall yield. The first involved using dimethylformamide as the solvent for the azide substitution reaction. This gave a somewhat higher yield and a purer product. The second modification involved reduction of the tetrakis(azidomethyl)methane by catalytic hydrogenation instead of using lithium tetrahydroaluminate. This modification resulted in a much simpler and less expensive procedure plus a higher yield of the product.[8] Our modified synthesis of tetrakis-(aminomethyl)methane is summarized in Scheme 4.

SCHEME 4. Optimized Synthesis of Tetrakis(aminomethyl)methane.

$$C(CH_2OH)_4 + 4\ \phi SO_2Cl \xrightarrow{\text{pyridine}} C(CH_2OSO_2\phi)_4$$

$$\xrightarrow[\text{DMF}]{NaN_3} C(CH_2N_3)_4 \xrightarrow[\text{EtOH}]{H_2\text{-Pd/C}^8} C(CH_2NH_2)_4$$

SYNTHESIS OF TETRAKIS(NITRAMINOMETHYL)METHANE (TNAM)

The standard methodology for the conversion of a primary amine to the corresponding primary nitramine involves a three-step procedure.[9] First, the amine is protected by conversion to the corresponding acetamide, methyl, or ethyl urethane. The protected amine is then nitrated using a mixture of nitric acid/acetic anhydride. Finally, the protecting group is removed under basic conditions and the primary nitramine is generated upon acidification of the hydrolysis mixture. Applying this methodology to tetrakis(aminomethyl)methane resulted in a reasonably high-yield synthesis of tetrakis(nitraminomethyl)methane which is summarized in Scheme 5. This compound is an interesting high-energy compound. It is the nitramine analog of pentaerythritol tetranitrate (PETN). Some of its measured and predicted physical properties are summarized in Table 2 and compared to those of ethylene dinitramine (EDNA). It appears that the compound offers no advantages over the more readily available EDNA. However, TNAM does have better predicted explosive properties.

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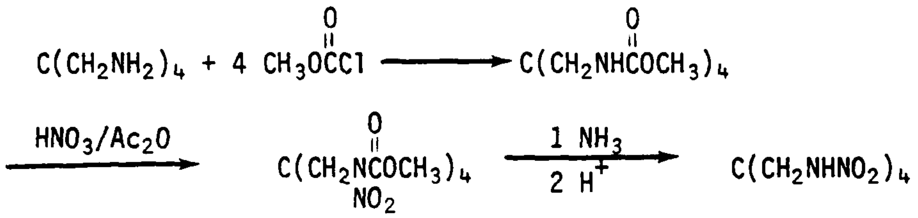
[8] P. Anselme. "Catalytic Reduction of 1,1,1-Tris(azidomethyl)ethane to 1,1,1-Tris(aminomethane)ethane," *Org. Prep. and Procedure*, Vol. 6 (1974), pp. 103.

[9] A. L. Fridman, V. P. Ivshin, and S. S. Novikov. "Progress in the Chemistry of Aliphatic Nitramines," *Russ. Chem. Rev.*, Vol. 33 (1969), pp. 640-654.

SCHEME 5. Synthesis of Tetrakis(nitraminomethyl)methane.



$$C(CH_2NH_2)_4 + 4\ CH_3O\overset{O}{\overset{\|}{C}}Cl \longrightarrow C(CH_2NH\overset{O}{\overset{\|}{C}}OCH_3)_4$$

$$\xrightarrow{HNO_3/Ac_2O} C(CH_2\underset{NO_2}{N}\overset{O}{\overset{\|}{C}}OCH_3)_4 \xrightarrow[2\ H^+]{1\ NH_3} C(CH_2NHNO_2)_4$$

TABLE 2. Physical Properties of Tetrakis-(nitraminomethyl)methane and EDNA.[10]

	TNAM	EDNA
Melting Point	164-165°C	176°C
Density	1.72 g/cc	1.71 g/cc
Detonation Velocity	8.41 mm/μsec[2]	7.75 mm/μsec

CONDENSATION OF TETRAKIS(NITRAMINOMETHYL)METHANE WITH FORMALDEHYDE

Typical procedures for the condensation of α,ω-dinitramines with formaldehyde call for the addition of the dinitramine to a 0°C solution of paraformaldehyde in 85-90% sulfuric acid[4] or the addition of the preformed mono-N-methylol derivative of the α,ω-dinitramine to a 0°C solution of 85-90% sulfuric acid.[11] Application of both of these procedures to tetrakis(nitraminomethyl)methane gave rather discouraging results. With the free nitramine, no identifiable product could be isolated. The reaction seemed to only result in the decomposition of the nitramine as evidenced by copious gas evolution. Using the N-methylol derivative procedure, a low and variable yield (0-15%) of a white powder, m.p. 242-244°C, could be isolated. This material appeared to be the desired 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane since it gave an ^1H NMR spectrum which consisted of two singlets at δ 4.25 and 6.20 in a 2:1 intensity ratio. However, sufficient material could not be accumulated for a complete characterization to be done. This synthetic route was abandoned in hopes that the other synthetic route would give a higher yield of TNSU.

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[10] R. Meyer. *Explosives.* Weinheim, Verlag Chemie, 1977.

[11] L. Goodman. "Condensation of Aliphatic Nitramines with Formaldehyde," *J. Amer. Chem. Soc.*, Vol. 75 (1953), pp. 3017-3020.

NITROSAMINE ROUTE TO TNSU

Synthesis of 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane

The literature synthesis of 1,3-dinitroso-1,3-diazacyclohexane, the model reaction sequence for the synthesis of 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane from tetrakis(aminomethyl)methane, was conducted as a two-step synthesis.[5] First trimethylene diamine was condensed with formaldehyde and the resulting 1,3-diazacyclohexane isolated. Secondly, the 1,3-diazacyclohexane was nitrosated using aqueous nitrous acid. It occurred to us that the isolation of the intermediate 1,3-diazacyclohexane was unnecessary and, in fact, probably only served to lower the overall yield of the product. Therefore, we decided to try the synthesis of 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane as a one pot reaction. First tetrakis(aminomethyl)methane was treated with two moles of formaldehyde in water generating 2,4,8,10-tetraazaspiro[5.5]undecane which was trapped by the addition of four equivalents of nitrous acid to the reaction mixture to give the desired 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane. This proved to be an exceptionally convenient synthesis giving the desired product in 50-55% yield.

Conversion of 2,4,8,10-Tetranitroso-2,4,8,10-tetraazaspiro-[5.5]undecane to TNSU

There are two well-established methods for the conversion of nitrosamine to nitramines. The first is to treat the nitrosamine with 100% nitric acid.[6] This formal oxidation is in fact a nitrolysis.[12] The second method for converting nitrosamines to nitramines is to oxidize them with peroxytrifluoroacetic acid.[7] Our previous experience with the nitric acid procedure[13] led us to try this procedure on the tetranitroso compound. A 65-70% yield of the desired TNSU could be obtained using this procedure. The complete synthesis of TNSU from tetrakis(aminomethyl)methane is summarized in Scheme 6. The TNSU could be recrystallized from dimethylformamide (DMF)/H_2O to give needles with melting point of 242-244°C.

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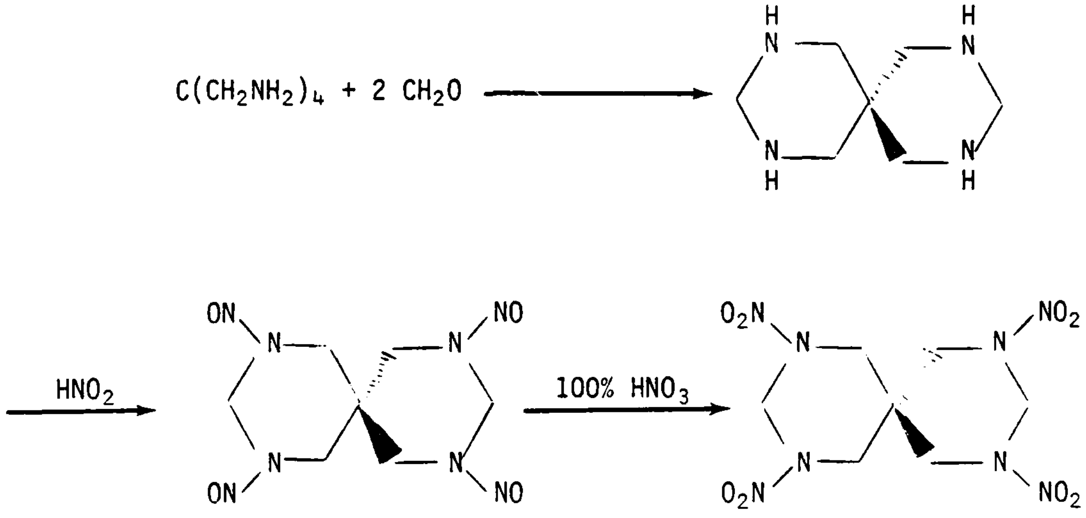
[12] R. G. Gafurov, E. M. Sogomonyan, and L. T. Eremenko. "Conversion of Nitrosomines to Nitramines," *Izv. Akad. Nauk SSSR Ser. Khim.*, 1973, p. 2826.

[13] Naval Weapons Center. *Synthesis of a New Explosive Compound, Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin*, by R. L. Willer. China Lake, Calif., NWC, August 1981, 16 pp. (NWC TP 6303, publication UNCLASSIFIED.)

SCHEME 6. Synthesis of TNSU



TNSU

Physical and Chemical Properties of TNSU

With the larger quantities of TNSU available through the nitrosamine route, a more complete determination of its physical and chemical properties was done. In Table 3 the physical and chemical properties of TNSU which have been determined are summarized and compared where possible to the predicted values.

TABLE 3. Chemical and Physical Properties of TNSU.

	Measured	Predicted
Melting Point	242-244°C	---
Density	1.72 g/cc	1.67 g/cc
Heat of Formation	5.0 Kcal/Mole	---
Detonation Velocity	8.28 mm/μsec[14]	7.77 mm/μsec[2]
Detonation Pressure	295 Kbar[14]	269 Kbar[2]
Impact Sensitivity (2.5 Kg Wt)	60 cm	---

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[14] M. J. Kamlet and S. J. Jacobs, "Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives," *J. Chem. Phys.*, Vol. 48 (1968), pp. 23-35.

EXPERIMENTAL

Densities were determined on a Systems, Science, and Software type 6102-12 gas pycnometer and are the average of three separate determinations. NMR spectra were determined on a Varian XL-100 NMR spectrometer. Impact sensitivities were measured on 35 mg samples on a Model 12 impact machine using Carborundum Co. 180-5/0 paper. Infrared spectra were recorded on a Nicolet 7000 FTIR in KBr pellets. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tennessee.

TETRAKIS(AMINOMETHYL)METHANE

The tetrabenzenesulfonyl derivative of pentaerythritol was prepared from pentaerythritol, benzenesulfonyl chloride, and pyridine in 95% yield as described.[15] The tetrabenzenesulfonate (34.8 g, 0.05 mole) was added to 200 ml of dry DMF and 16.25 g (0.25 mole) of sodium azide was added. The mixture was stirred at 120°C for 16 hours. The mixture was cooled and diluted with 300 ml of ice water. The aqueous layer was then extracted with three 100-ml portions of ether. The combined ether extracts were back extracted with water (2 x 50 ml) and dried over $MgSO_4$. The solution was filtered and the ether removed at reduced pressure to yield the crude tetrakis(*azidomethyl*)methane. This compound is a very powerful explosive. When purified it has an impact sensitivity of 2 cm (2.5 Kg wt). It should not be purified unless due precaution is taken. The crude tetraazide is dissolved in 200 ml of 95% ethanol and 1 gm of 10% Pd on C is added. The solution is hydrogenated for 12 hours with the main hydrogen tank shut off. Every 2 hours the bottle is vented to remove accumulated N_2 and fresh hydrogen is introduced. No pressure drop is observed during the hydrogenation because the reduction of each azide requires one mole of hydrogen and releases one mole of nitrogen. The reaction can be monitored by working up an aliquot and examining the IR. The product is isolated by filtering the solution to remove the catalyst and removing the solvent at reduced pressure. The crude tetrakis(aminomethyl)methane weighs 6.2 g (0.047 mole, 94%).

NMR (D_2O, tsp) $\delta = 2.50$ (s, 1H, CH), 4.70 (s, 1H, NH).

TETRAKIS(NITRAMINOMETHYL)METHANE

The tetraurethane derivative of the tetrakis(aminomethyl)methane was prepared by the simultaneous addition of equal molar amounts of aqueous sodium hydroxide and methyl chloroformate to a well-stirred

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[15] H. L. Herzog, "Pentaerythityl Tetrabromide," *Org. Syn. Coll.*, Vol. IV (1963), pp. 753.

aqueous solution of the tetraamine. The solid product was collected, washed with water, and dried. It melts at 195-196°C. An additional amount can be obtained by extracting the reaction mixture with methylene chloride. The overall yield is 70-80%.

Analysis calculated for $C_{13}H_{24}N_4O_8$: C, 42.85; H, 6.64.
Found: C, 42.60; H, 6.66.

IR 3400(m), 2950(w), 1680(vs), 1510(vs), 1440(w), 1380(w), 1300(vs), 1230(vs), 1160(m), 1130(s), 1303(s), 980(m), 890(w), 860(w), 780(w) cm^{-1}.

NMR (50:50 acetone-d_6:DMSO-d_6) δ = 3.00 (d, J = 7.5Hz, 2H, $-C\underline{H}_2NH-$), 4.03 (s, 2H, CH_3O^-), 6.50 (t, J = 7.5Hz, 1H, $-N\underline{H}CH_2-$).

A solution of 100% nitric acid in acetic anhydride was prepared by adding 5.0 ml of 100% nitric acid to 10 ml of well-stirred acetic anhydride that is maintained below 0°C. This solution was stirred for 20 minutes, then 4.20 g (10 mmoles) of the tetraurethane was added over the next 20 minutes. The cooling bath was removed and the solution stirred for 1 hour. The mixture was poured onto 40 grams of ice. After the ice had melted, the mixture was transferred to a 250-ml separating funnel with the aid of 100 ml of ether. The aqueous layer was separated. The organic phase was washed with 50 ml of water, and the ether was removed at reduced pressure. Ammonium hydroxide (20 ml) was added to the crude nitrourethane, and the mixture was stirred for 1 hour. The excess ammonia was removed at reduced pressure and the remaining solution acidified to pH 6 with concentrated HCl. Small needles of the product slowly formed. After 1 hour the product was collected and washed with water. The product weighed 2.87 g (9.2 mmoles, 92%) and decomposed at 164-165°C.

IR(KBr) 3400(s), 2980(w), 1605(vs), 1445(s), 1410(s), 1380(sh), 1345(vs), 1275(s), 1160(m), 1095(m), 865(m) cm^{-1}.

NMR (acetone-d_6) δ = 4.05 (s, 2H, $C\underline{H}_2$), 11.0 (bs, 1H, $\underline{NH}$).

Density: 1.716 g/cc

Impact sensitivity (50%): 27 cm (2.5 Kg wt)

Analysis calculated for $C_5H_{12}N_8O_8$: C, 19.23; H, 3.87; N, 35.90.
Found: C, 19.39; H, 3.95; N, 35.80.

2,4,8,10-TETRANITRO-2,4,8,10-TETRAAZASPIRO[5.5]UNDECANE

Method A

Tetrakis(nitraminomethyl)methane (0.31 g, 1 mmole) was dissolved in 0.17 g of 37% aqueous formaldehyde solution. This was added dropwise to 5 ml of well-stirred 85% H_2SO_4 which was maintained at 0°C. After the addition was complete, the mixture was stirred for 10 minutes then poured onto 20 g of ice. After the ice had melted, the crude product was collected and washed with water. It weighed 50 mg (0.15 mmole, 15%) and decomposed at 242-244°C.

IR(KBr) 2950(w), 1550(s), 1460(m), 1440(m), 1380(m), 1260(s), 1040(m), 1010(sh), 990(m), 950(m), 930(m), 890(m), 855(m), 765(m).

2,4,8,10-TETRANITROSO-2,4,8,10-TETRAAZASPIRO[5.5]UNDECANE

Tetrakis(aminomethyl)methane (6.6 g, 0.05 mole) was dissolved in 20 ml of water. Paraformaldehyde (2.8 g, 0.1 mole) was added to the mixture over 20 minutes. The paraformaldehyde dissolved slowly. The solution was stirred at room temperature for 3 hours and then cooled to 0°C. A solution of sodium nitrite (6.9 g, 0.1 mole) in water (20 ml) was then added. When the temperature of the solution was 0°C, 50 ml of ice cold 2N HCl was added over 30 seconds. Considerable foaming and gas evolution occurred during the addition. The mixture was stirred at 0°C for 1 hour and the crude product was collected by vacuum filtration and washed well with water. After drying, the product weighs 6.8-7.2 g (50-55% yield). The product melted with decomposition at 185-186°C.

Analysis Calculated for $C_7H_{12}N_8O_4$: C, 30.88; H, 4.44; N, 41.17.
Found: C, 31.14; H, 4.49; N, 41.24.

2,4,8,10-TETRANITRO-2,4,8,10-TETRAAZASPIRO[5.5]UNDECANE

Method B

Ten ml of 98% nitric acid was cooled to -30°C by means of a dichloroethane/dry ice slush and 1.0 g of the 2,4,8,10-tetranitroso-2,4,8,10-tetraazaspiro[5.5]undecane was added over 2 minutes. The dichloroethane bath was replaced with an ice/water bath and the mixture was stirred for 1 hour at 0°C. The ice water bath was removed and the mixture was stirred at room temperature for 15 minutes. The reaction was quenched by pouring onto 15 g of ice. When the ice had melted, the product was collected and washed well with water. When dry it weighed 0.80-0.85 g (65-68% yield). The product can be recrystallized from DMF to give needles, m.p. 242-244°C (dec).

IR(KBr) 3000(w), 1550(vs), 1530(vs), 1450(m), 1430(s), 1370(s), 1315(m), 1275(sh), 1250(vs), 1210(sh), 1180(w), 1155(w), 1110(w), 1030(m), 1005(sh), 985(s), 950(m), 930(m), 910(w), 890(m), 865(w), 850(m), 815(w), 770(m), 760(m).

^{1}H NMR (DMSO-d_6) δ = 4.25 (s, 2H, C-$C\underline{H}_2$N), 6.20 (s, 1H, N-$\underline{CH_2}$-N).

Analysis calculated for $C_7H_{12}N_8O_8$: C, 25.00; H, 3.60; N, 33.33.
Found: C, 25.18; H, 3.79; N, 33.20.

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1 Chief of Naval Research, Arlington (ONR-413, R. Miller)
3 Marine Corps Development and Education Command, Quantico (Marine Corps Landing Force Development Center)
1 David Taylor Naval Ship Research and Development Center, Bethesda
1 Naval Academy, Annapolis, MD (Assistant Chairman, Environmental Sciences Department, Prof. J. Williams)
1 Naval Coastal Systems Center, Panama City (Code 112.2)
2 Naval Explosive Ordnance Disposal Technology Center, Indian Head
  Code RD (1)
  Technical Library (1)
1 Naval Intelligence Support Center (NISC-60, Library)
2 Naval Ordnance Station, Indian Head
  Code F581, Kerry Wagaman (1)
  Technical Library (1)
1 Naval Special Warfare Group, Atlantic (RDT Officer)

3 Naval Special Warfare Group, Pacific
  RDT Officer (1)
  Seal Team (1)
  Underwater Demolition Team (1)
20 Naval Surface Weapons Center, Dahlgren
  G-13 (1)
  G-30 (1)
  G-34 (1)
  G-35 (1)
  G-43 (1)
  G-602 (1)
  R-10 (1)
  R-11
    H. Adolph (1)
    K. Mueller (1)
  R-12
    F. Menz (1)
    L. Roslund (1)
  R-13 (1)
  R-14 (1)
  R-15 (1)
  R-16 (1)
  R-17 (1)
  R-121 (1)
  R-122 (1)
  R-141 (1)
  Technical Library (1)
1 Naval Weapons Station, Yorktown (NEDED)
5 Naval Weapons Support Center, Crane
  Code 5042, B. E. Douda (1)
  Code 505, J. E. Short (1)
  NAPEC (1)
  R&D Library (2)
1 Office of Navy Technology, Arlington (MAT-0716, A. J. Faulstich)
1 Pacific Missile Test Center, Point Mugu (Code 2145)
1 Seal Team 2
1 Underwater Demolition Team 21
1 Naval Intelligence Support Center Liaison Officer (LNN)
3 Army Armament Materiel and Readiness Command, Rock Island
  DRSAR-IRC, G. Cowan (1)
  DRSAR-LEM, R. R. Freeman (1)
  DRSAR-SF, R. E. Young (1)
17 Army Armament Research & Development Command, Dover
  DRDAR-LCA (2)
  DRDAR-LCA-P (2)
  DRDAR-LCE (2)
  DRDAR-LCE-C, Chemistry Branch (1)
  DRDAR-LCM (2)
  DRDAR-LCM-SA, R. Westerdahl (1)

DRDAR-LCN-C, Concepts & Analysis Branch (4)
DRDAR-LCU (2)
DRDAR-LCU-E (1)
4 Army Ballistic Research Laboratories, Aberdeen Proving Ground
DRDAR-BLP, Watermeier (1)
DRDAR-BLT, Dr. Phil Howe (2)
DRDAR-TSB-S (STINFO) (1)
1 Army Medical Bioengineering Research and Development Laboratory, Fort Dietrick (J. Barkeley)
1 Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground (DRXTH-TE-D)
1 Chemical Systems Laboratory, Aberdeen Proving Ground (DRDAR-CLC-E, Charles McKnight)
3 Air Force Systems Command, Andrews Air Force Base
DLFP (1)
DLWA (1)
SDZ (1)
3 Air Force Armament Laboratory, Eglin Air Force Base
AFATL/DLDE (1)
AFATL/DLJW (1)
AFATL/DLODL (1)
12 Defense Technical Information Center
1 Department of Defense Explosives Safety Board, Alexandria (6-A-145)
1 Battelle Memorial Laboratory, Tactical Technology Information Center, Columbus, OH
1 Holston Defense Corporation, Kingsport, TN (Plant Manager)
2 Johns Hopkins University, Applied Physics Laboratory, Laurel, MD
Freeman K. Hill (1)
1 Johns Hopkins University, Applied Physics Laboratory, Chemical Propulsion Information Agency, Laurel, MD
2 Los Alamos National Laboratory, Los Alamos, NM
Harry Flaugh (1)
R. Rogers (1)
3 University of California, Lawrence Livermore National Laboratory, Livermore, CA
B. Dobratz (1)
J. Kury (1)
H. Rizzo (1)