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Synthesis of a New Explosive Compound, *trans*-1,4,5,8-Tetranitro- 1,4,5,8-Tetraazadecalin

by
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Research Department

AUGUST 1981

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555



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FOREWORD

New explosives and propellants for naval weapons applications which combine increased performance in combat and enhanced safety in handling, are required for the new generation of weapons systems now under development. A new energetic material with potential explosive and propellant applications, *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin, has been synthesized. The new compound has several physical properties which are superior to RDX and HMX.

The work was performed under NAVSEA Project No. SR02403, under sponsorship of L. A. Roslund, Naval Surface Weapons Center (WR-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
J. J. LAHR
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(U) *Synthesis of a New Explosive Compound, trans-1,4,5,8-Tetranitro-1,4,5,8-Tetraazadecalin*, by Rodney L. Willer. China Lake, Calif., Naval Weapons Center, August 1981. 16 pp.
(NWC TP 6303, publication UNCLASSIFIED.)

(U) The synthesis of a new explosive compound, *trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin*, is described. The compound has several physical properties which are superior to those of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and RDX (1,3,5-trinitro-1,3,5-hexahydrotriazine). These superior physical properties include heat stability and insensitivity to impact.

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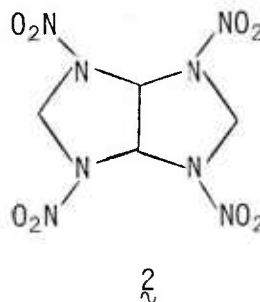
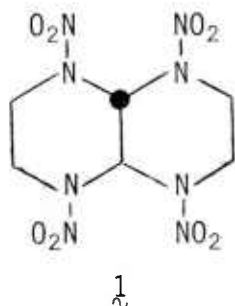
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INTRODUCTION

This paper describes the synthesis of a new explosive compound, *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin, **1** (TNAD). This molecule was chosen as a synthetic target for two reasons. First, it has both a good predicted density^{1,2} and good predicted detonation velocity.³ The predicted density and predicted detonation velocity are summarized below the structure. Secondly, TNAD is structurally related to the highly sought after "Bicyclo-HMX (2,4,6,8-tetranitro-2,4,6,8-tetraaza-bicyclo[3.3.0]cyclooctane)," **2**, and it was hoped a successful synthesis of TNAD would shed some light on how to synthesize **2**.



Calculated Density^{1,2} 1.77 g/cm³, 1.73 g/cm³

Calculated Detonation Velocity³ 8.21 mm/μs

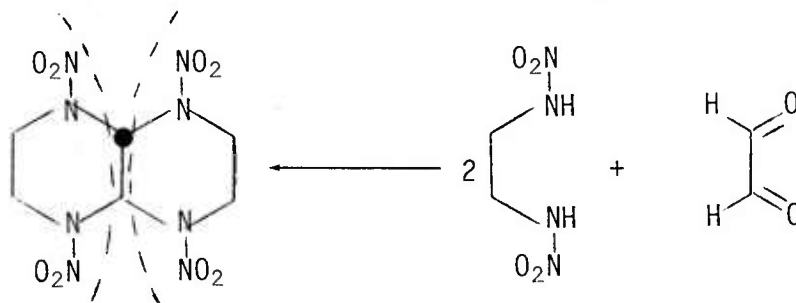
¹Naval Weapons Center. *Calculation of Densities of Fuels and Explosives from Molar Volume Additive Increments*, by A. T. Nielsen. China Lake, Calif., NWC, February 1973, 20 pp. (NWC TP 5452, publication UNCLASSIFIED.)

²Naval Surface Weapons Center. *Estimation of Normal Densities of Explosives from Empirical Atomic Volumes*, by D. A. Cichra, J. R. Holden, and C. R. Dickerson. White Oak, Maryland, NSWC, 1980, 47 pp. (NSWC-TR-79-273, publication UNCLASSIFIED.)

³L. R. Rothstein and R. Petersen. "Predicting High Explosive Detonation Velocities from their Composition and Structure," *Prop. and Explo.*, Vol. 4 (1979), p. 56-59.

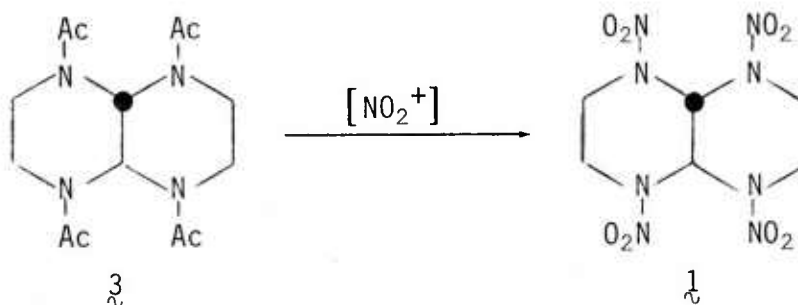
Three synthetic routes to TNAD were considered. The first route was based on a retro-synthetic analysis of TNAD into two molecules of ethylene dinitramine and a molecule of glyoxal as diagrammed in Scheme 1. It is known that dinitramines can be condensed with formaldehyde to give 1,3-dinitramines.^{4,5} It was hoped that glyoxal would react similarly to formaldehyde.

SCHEME 1. Retro-Synthetic Analysis of TNAD.



The second route considered for the synthesis of TNAD was the nitrolysis of the known *trans*-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin, **3**,⁶ as outlined in Scheme 2. The nitrolysis of N-acyl compounds is a well-established synthetic method for making secondary nitramines.^{7,8}

SCHEME 2. Nitrolysis Route to TNAD.



⁴L. Goodman. "Condensation of Aliphatic Nitramines with Formaldehyde," *J. Amer. Chem. Soc.*, Vol. 75 (1953), p. 3017-3020.

⁵J. A. Bell and I. Dunstan. "Chemistry of Nitramines. Part III. Cyclic Nitramines Derived from Trimethylene Dinitramine," *J. Chem. Soc. (C)*, (1966), p. 870-872.

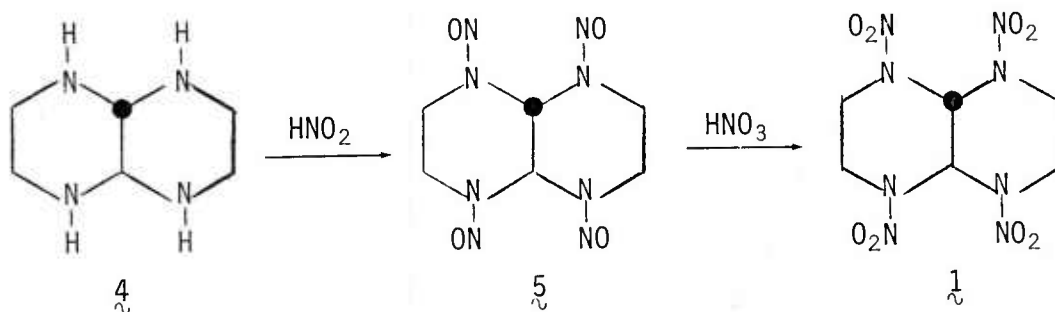
⁶H. Baganz, L. Domaschke, and G. Kirchner. "Di- α -halogenäther. V Ringschlussreaktionen des 1,2-Dichloro-1,2-diäthoxy-äthans mit Diaminen," *Chem. Ber.*, Vol. 94 (1961), p. 2676-2680.

⁷J. H. Robson and J. Reinhart. "The Synthesis of Secondary Nitramines by the Nitrolysis of N,N-disubstituted Amides," *J. Amer. Chem. Soc.*, Vol. 77 (1955), p. 2453-2457.

⁸J. H. Robson. "The Nitrolysis of N,N-Dialkylformamides," *J. Amer. Chem. Soc.*, Vol. 77 (1955), p. 107-108.

The third synthetic route considered for the synthesis of TNAD was the conversion of the known *trans*-1,4,5,8-tetraazadecalin (TAD), 4 ,^{6,9-11} into its tetranitroso derivative, 5 , and nitrolysis of this to TNAD. This route is summarized in Scheme 3. This route is based on analogy to the synthesis of pure 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX) from 1,3,5-trinitroso-1,3,5-hexahydrotriazine (R-salt) by G. F Wright and co-workers.¹²

SCHEME 3. Nitrosation-Nitrolysis Route to TNAD.



RESULTS

ETHYLENE DINITRAMINE/GLYOXAL CONDENSATION ROUTE TO TNAD

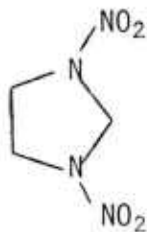
The direct condensation of ethylene dinitramine and glyoxal to give TNAD was tried under a variety of conditions similar to those used by Goodman⁴ to synthesize 1,3-dinitro-1,3-diazacyclopentane, 6 , from ethylene dinitramine and formaldehyde. None of the reactions produced identifiable products. Normally, copious gas evolution occurred indicating that the nitramine was undergoing decomposition.

⁹H. C. Chitwood and R. W. McNamee. Piperazino-piperazines. March 1944. (U.S. Patent 2,345,237, UNCLASSIFIED.)

¹⁰L. A. Cort and N. R. Francis. "Halogeno-1,4-dioxanes and their Derivatives. Part III. Interaction of Trans-2,3-dichloro-1,4-dioxan and Amines," *J. Chem. Soc.*, (1964), p. 2799-2801.

¹¹B. Fuchs and A. Elleneweig. "Structure and Conformation of Heterocycles. X. on 1,4,5,8-Tetraazadecalins," *Recueil*, Vol. 98 (1979), p. 326-333.

¹²F. J. Brockman, D. C. Downing, and G. F Wright. "Nitrolysis of Hexamethylenetetraamine III. Preparation of Pure Cyclonite," *Can. J. Research, B*, Vol. 27 (1949), p. 469-474.

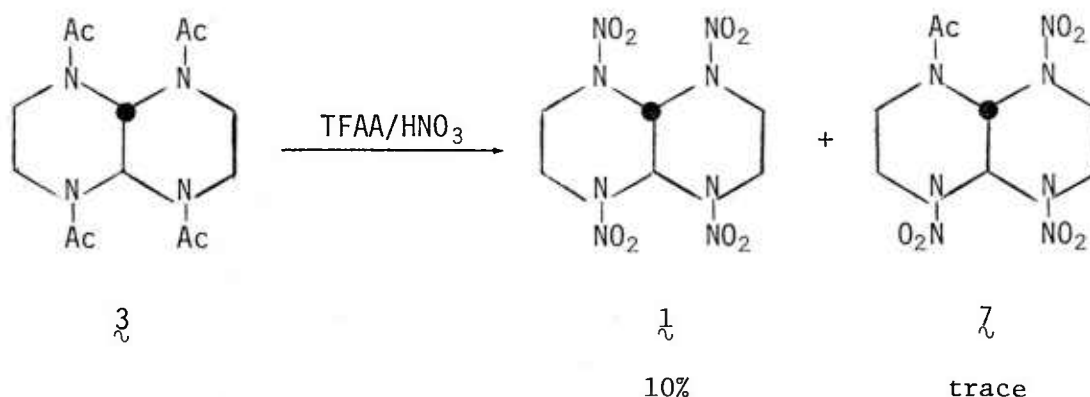


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NITROLYSIS ROUTE TO TNAD

The second synthetic route to TNAD explored was the nitrolysis of *trans*-1,4,5,8-tetraacetyl-1,4,5,8-tetraazadecalin, **3**. Several procedures were tried with the best being one developed by Gilbert and co-workers¹³ for the conversion of 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN) to HMX. This procedure uses a mixture of trifluoroacetic anhydride (TFAA) and 100% nitric acid to generate N_2O_5 . With the best conditions developed, only a low yield of the desired TNAD could be obtained. In addition, the product seemed to contain small amounts of the impurity, 1,4,5-trinitro-8-acetyl-1,4,5,8-tetraazadecalin, **7**, since a small carbonyl peak was observed in the infrared spectrum of the product and a singlet at 2.2 ppm was observed in the 1H NMR spectrum of the product. These results are summarized in Scheme 4.

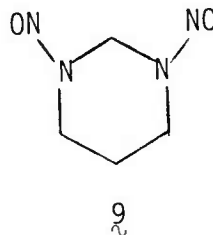
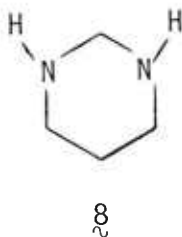
SCHEME 4. Reaction Product of the Nitrolysis of 1,4,5,8-Tetraacetyl-1,4,5,8-tetraazadecalin.



¹³U.S. Army Research and Development Command. *Alternative Processes for HMX Manufacture*, by Victor I. Siele and others. Dover, New Jersey, ARRADCOM, October 1979, 119 pp. (ARI,CD-TR-78008, publication UNCLASSIFIED.)

NITROSATION-NITROLYSIS ROUTE TO TNAD

The third synthetic route (see Scheme 3) proved to be more fruitful. The conversion of the *trans*-1,4,5,8-tetraazadecalin, 4, to *trans*-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin, 5, was accomplished in over 90% yield using a procedure developed by Evans for the conversion of hexahydropyrimidine, 8, to N,N-dinitrosohexahydropyrimidine, 9.¹⁴ This procedure

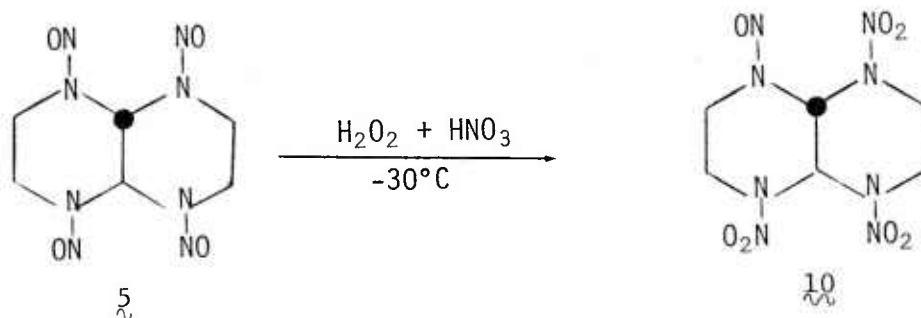


involves adding 1.25 equivalents of dilute hydrochloric acid to an aqueous solution of one equivalent of the amine and 1.25 equivalents of sodium nitrite. This procedure is superior to the normal procedure of adding a solution of sodium nitrite to an aqueous solution of the amine hydrochloride because 1,4,5,8-tetraazadecalin undergoes rapid reversion to ethylene diamine and glyoxal in aqueous acid. The tetranitroso compound, 5, gave a satisfactory elemental analysis and was fully characterized spectroscopically.

The conversion of the tetranitroso compound to TNAD was initially attempted using the same conditions which Wright and co-workers used to convert R-salt to RDX.¹² This involves adding 3-5% hydrogen peroxide to 100% nitric acid, then cooling this mixture to -30°C for the addition of the nitrosoamine. Using this procedure, a good yield of a white solid was obtained. The ¹H NMR spectrum clearly indicated that it was not the desired TNAD because the bridgehead proton appeared as an AB quartet. Considerable N-NO₂ stretching was apparent in the IR spectrum of the product and it was concluded that this material was *trans*-8-nitroso-1,4,5-trinitro-1,4,5,8-tetraazadecalin, 10. This reaction is summarized in Scheme 5. Wright and co-workers observed a similar occurrence in the conversion of R-salt to RDX. At short reaction times at low temperature the product obtained was the 1,3-dinitro-5-nitroso-1,3,5-hexahydrotriazine. This product was, however, readily converted to RDX when the final reaction temperature was raised to 0°C or the reaction time at the lower temperature was increased. Applying these modifications to the reaction of compound 5, however, did not lead to a conversion of 10 into 1. In fact, the only result was to lower the yield of 10. There is good evidence

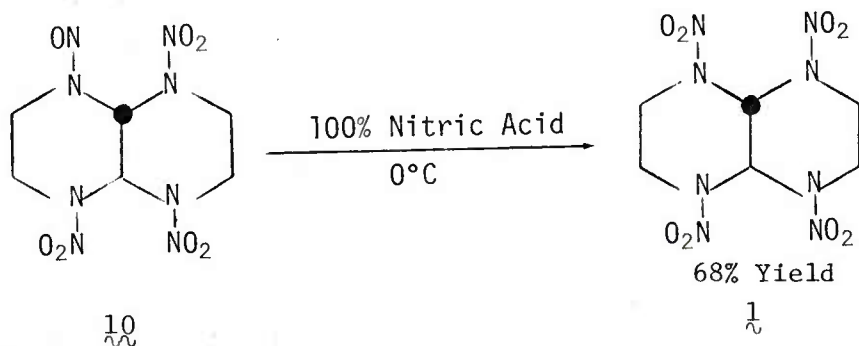
¹⁴R. F. Evans. "Hydropyrimidines V. Hexahydropyrimidines. The Reaction of Aldehydes and Ketones with 1,3-Diaminopropanes," *Aust. J. Chem.*, Vol. 20 (1967), p. 1643-1661.

SCHEME 5. Reaction of 1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecalin with $\text{H}_2\text{O}_2/\text{HNO}_3$.



that these reactions are nitrolysis reactions and not oxidations.¹⁵ It appeared then that an equilibrium condition is reached where the NO^+ ions build up in solution to a point where they begin to compete for the ring nitrogen atoms, thus preventing the reaction from going to completion. If this was the case, the solution for converting **10** to **1** appeared to be to reintroduce the trinitro-nitroso compound, **10**, to fresh 100% nitric acid. Indeed, when this was done a good yield of the desired TNAD was obtained as summarized in Scheme 6.

SCHEME 6. Reaction of *trans*-8-Nitroso-1,4,5-trinitro-1,4,5,8-tetraazadecalin with Nitric Acid.



In Scheme 7 the complete synthesis of TNAD from ethylene diamine and glyoxal is outlined. The overall yield for the four-step synthesis is 47%.

Several of the physical properties of TNAD have now been determined. These are summarized in Table 1 and are compared, where possible, to the predicted values. TNAD has several rather interesting physical properties.

¹⁵R. G. Gafurov, E. M. Sogomonyan and L. T. Eremenko. "Conversion of Nitrosamines to Nitramines," *Izv. Akad. Nauk SSSR Ser. Khim.* (1973), p. 2826.

It is more heat stable than RDX and is less sensitive to impact than both RDX or HMX. It has essentially the same density as RDX and only a slightly lower calculated detonation velocity. TNAD will probably find use as both a propellant and an explosive.

SCHEME 7. Synthesis of TNAD from Ethylene Diamine and Glyoxal.

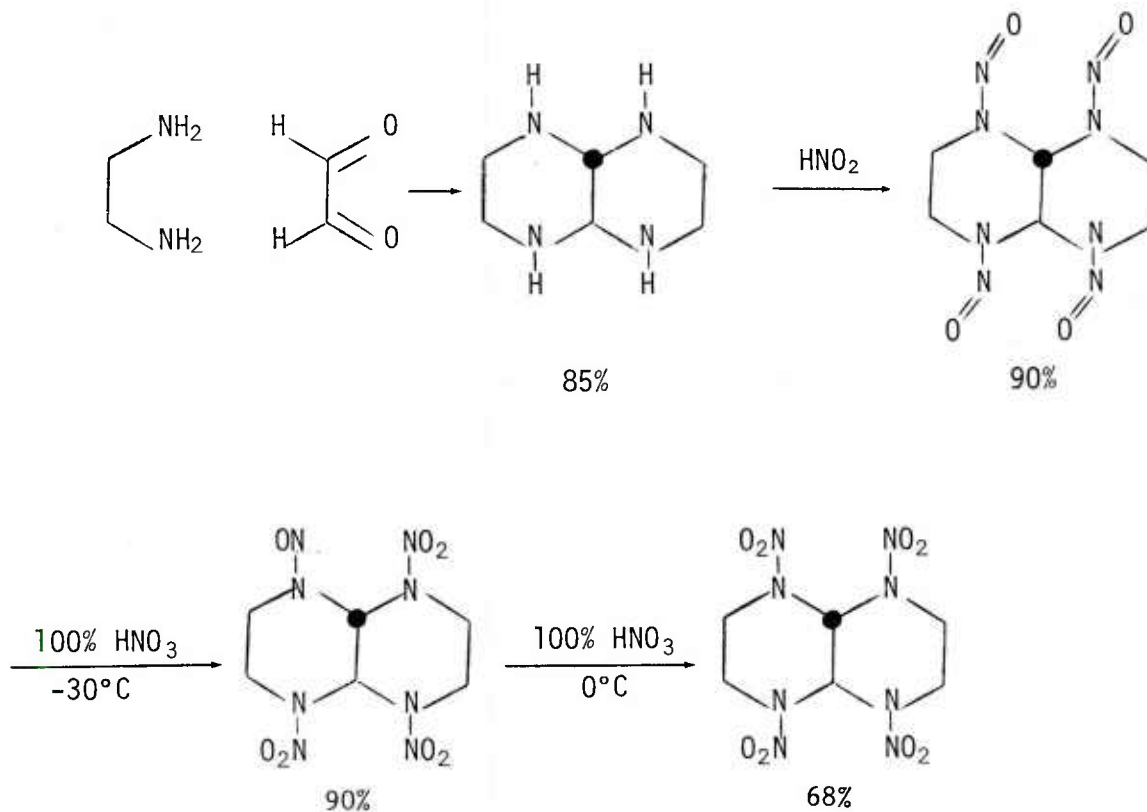


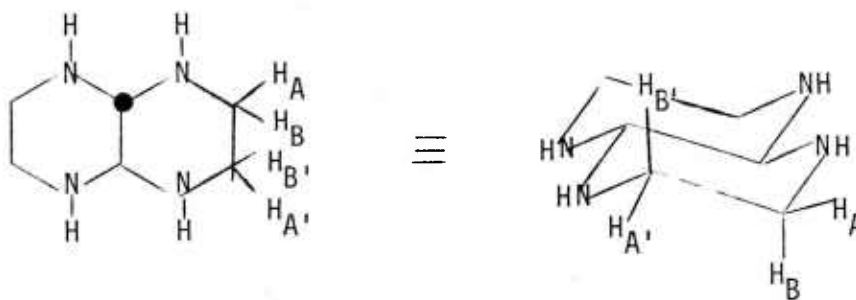
TABLE 1. Physical Properties of TNAD.

	Calculated	Measured
Density (g/cm^3)	1.77 (1^1), 1.74 (1^2)	1.80
Detonation Velocity ($\text{mm}/\mu\text{s}$)	8.21 ³	----
Impact Sensitivity (2.5 kg wt)	----	40 cm
Melting Point	----	232-234°C

STEREOCHEMISTRY OF TAD AND TNAD

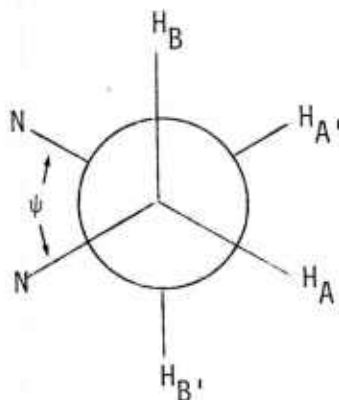
The stereochemistry of 1,4,5,8-tetraazadecalin was recently established by Fuchs and Elleneweig¹¹ as *trans*. The assignment was based on establishing that the ethylene fragment is an AA'BB' spin system with coupling constants typical for a staggered ethylene configuration. The coupling constants and chemical shift values are summarized in Scheme 8. From the coupling constants one can calculate the R value for the ethylene fragment from Equation 1 and in turn calculate the dihedral angle, ψ , for the ethylene fragment from Equation 2.¹⁶

SCHEME 8. Chemical Shifts and Coupling Constants for *trans*-1,4,5,8-Tetraazadecalin.



$\nu_A = 2.94$ ppm	$J_{AB} = J_{A'B'} = -13.0$ Hz
$\nu_B = 2.79$ ppm	$J_{AB'} = J_{A'B} = 3.6$ Hz
	$J_{AA'} = 1.5$ Hz
	$J_{BB'} = 12.3$ Hz

¹⁶J. B. Lambert. "Structural Chemistry in Solution. R Value," *Accounts of Chemical Research*, Vol. 4 (1971), p. 87-94.



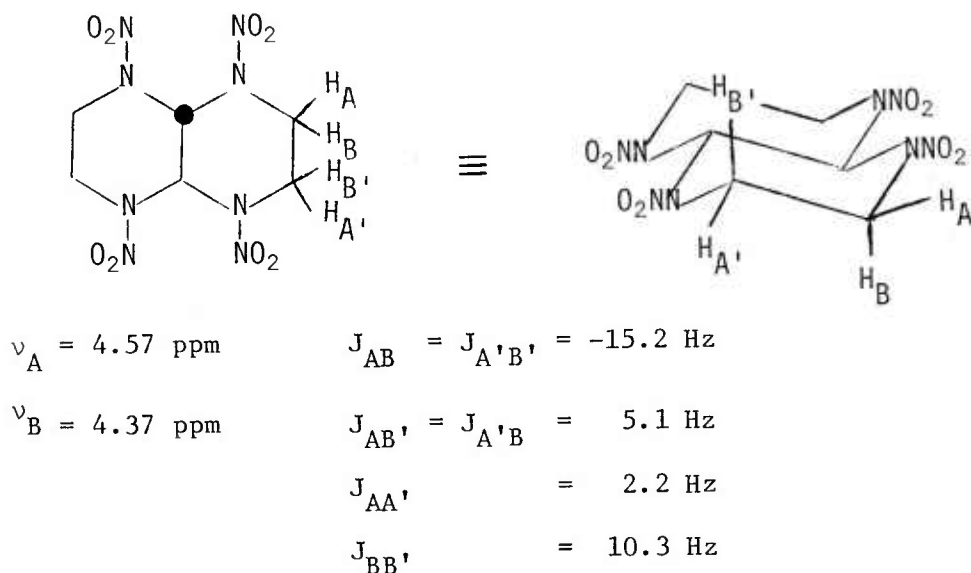
$$R = \frac{J_{\text{trans}}}{J_{\text{cis}}} = \frac{(J_{AA'} + J_{BB'})/2}{J_{AB'}} \quad (1)$$

$$\cos \psi = \left(\frac{3}{2 + 4R} \right)^{1/2} \quad (2)$$

Values of 2.13 for R and 58° for ψ are calculated from Fuchs and Ellenewieg's¹¹ values for the coupling constants. These values fall in the range typical for a puckered six-membered ring.¹⁶

Since several steps occur in the conversion of TAD to TNAD where the possibility exists for epimerization of the bridgehead protons, we felt that it was necessary to clearly establish the stereochemistry of the ring fusion. The method chosen was to analyze the ^1H NMR spectrum of the ethylene fragment. In Scheme 8 the coupling constants and chemical shifts obtained from the analysis of the 200 MHz spectrum of TNAD are summarized. The spectrum was easily analyzed as an $AA'BB'$ spectrum which clearly established the stereochemistry of the ring fusion as *trans*. In addition, they allow the R value and ψ to be calculated, which gives some information on the shape of the six-membered ring in TNAD. The R value and ψ calculated for TNAD are 1.23 and 49° , respectively. These values indicate that the six-membered ring has flattened, which is consistent with a change in hybridization of the ring nitrogens from sp^3 in the amine to sp^2 in the nitraamine.

SCHEME 9. Coupling Constants and Chemical Shifts for TNAD.

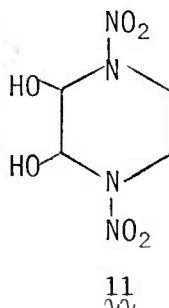


EXPERIMENTAL

ATTEMPTED CONDENSATION OF ETHYLENE DINITRAMINE AND GLYOXAL

After cooling 20 ml of 87% sulfuric acid to 0°C, 0.70 g of glyoxal trimer (10 mmoles of glyoxal) was added. This mixture was stirred for 10 minutes then 3.0 g (20 mmoles) of ethylene dinitramine was slowly added over 10 minutes. The resulting mixture was stirred at 0°C for 20 minutes then quenched on 20 g of ice. During the stirring, gas evolution occurred. The white solid product was collected by vacuum filtration, washed with water, and dried. It proved to be ethylene dinitramine (NMR).

In a modification of the above procedure 1.45 g of 40% aqueous glyoxal (10 mmoles) was substituted for the glyoxal trimer since it appeared that the trimer was insoluble in 87% sulfuric acid. The reaction was run identically to that described above. The product in this case was mainly ethylene dinitramine but it seems to contain some (10%) of diol 11. This diol, 5,6-dihydroxy-1,4-dinitro-1,4-diazacyclohexane, is the addition product of glyoxal and ethylene dinitramine.

1,4,5,8-Tetraazadecalin (4)

In a 250-ml round-bottom flask was placed 24.0 g of ethylene diamine (0.40 mole). This was cooled to 0°C by a salt/ice bath and 14.5 g of 40% aqueous glyoxal solution (0.10 mole) was added dropwise during the next 30 minutes. This solution was then heated at 80°C for 5 hours. During the heating period crystals formed in the solution. The solution was allowed to slowly cool to room temperature, then cooled to 0°C. The product was then collected by vacuum filtration and washed with cold 50% ethanol. The yield of product m.p. 162-170°C (dec) (Lit⁶ 162-187°C (dec)) is 12.0 g (0.085 mole, 85%).

1,4,5,8-Tetraacetyl-1,4,5,8-tetraazadecalin (3)

A 1.42 g portion of 4 (10 mmoles) was slowly added to 30 ml of well-stirred acetic anhydride. The solution was stirred for 2 hours, then the acetic acid and excess acetic anhydride were removed at reduced pressure. The resulting thick mixture was treated with 20 ml of acetone. The product crystallized and was collected. The product with m.p. 201-203°C (Lit⁶ 201-203°C) weighed 3.02 g (9.7 mmoles, 97%).

1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecalin (5)

A solution of 3.45 g (50 mmoles) sodium nitrite and 1.42 g (10 mmoles) of 1,4,5,8-tetraazadecalin was prepared in a 125-ml erlenmeyer flask. The temperature was not allowed to exceed 5°C. It was cooled to -2°C and 50 ml of 1N hydrochloric acid was added during the next 60 seconds. A white precipitate formed immediately. The mixture was stirred at 0°C for 30 minutes, then at room temperature for 1 hour. The product was collected by vacuum filtration and washed well with water. It was dried overnight in a vacuum oven to give an off-white powder, which was suitable for further synthetic uses. It weighed 2.35 g (9.1 mmoles, 91%) and decomposed at 211-212°C. It could be recrystallized from DMF/H₂O to yield fine light-yellow needles.

IR (KBr) 2900(w), 1475(m), 1450(sh), 1410(m), 1370(m), 1310(m), 1300(m), 1275(m), 1260(m), 1210(m), 1190(m), 1110(m), 1050(m), 975(m), 935(m), 895(w), 830(w), 735(m).

^1H NMR ($\text{DMSO}-d_6$ - -80°C): δ 3.90 (ABCD , $J_{\text{AD}} = 1.0$ Hz, $J_{\text{BD}} = 4.0$ Hz, $J_{\text{CD}} = -14.6$ Hz, 2H), 3.95 (ABCD , $J_{\text{AC}} = 5.8$ Hz, $J_{\text{BC}} = 13.3$ Hz, $J_{\text{CD}} = -14.6$ Hz, 2H), δ 4.92 (ABCD , $J_{\text{AB}} = -14.70$ Hz, $J_{\text{BC}} = 13.3$ Hz, $J_{\text{BD}} = 4.0$ Hz, 2H), δ 5.52 (ABCD , $J_{\text{AD}} = -14.7$ Hz, $J_{\text{AC}} = 5.8$ Hz, $J_{\text{AD}} = 1.0$ Hz, 2H) δ 6.76 (s, 2H, $\text{H}_{9,10}$).

Analysis calcd. for $\text{C}_6\text{H}_{10}\text{N}_8\text{O}_4$: C, 27.90; H, 3.91; N, 43.40;

Found: C, 27.92; H, 3.91; N, 43.53.

8-Nitroso-1,4,5-trinitro-1,4,5,8-tetraazadecalin (9)

Ten ml 100% nitric acid and a magnetic stirring bar were placed in a 50-ml erlenmeyer flask. This was cooled to -30°C by a dichloroethane/dry ice slush. The 1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin (1.00 g, 3.87 mmoles) was added over 30 minutes. The dichloroethane/dry ice bath was removed and replaced by an ice bath. The mixture was stirred for an additional hour, then poured onto 50 g of ice. A fine white precipitate formed. The crude product was collected and washed well with water. After drying in vacuum, it weighed 1.07 g (3.52 mmoles, 90%) and decomposed at 210 – 212°C . This compound contained small amounts of the tetranitro compound as evidenced by a small singlet in the NMR at 6.50 ppm.

IR (KBr) 2950(w), 1550(vs), 1440(m), 1400(w), 1350(m), 1275(vs), 1205(m), 1195(m), 1080(m), 1030(m), 980(w), 960(w), 890(w), 865(m), 840(w), 770(w), 755(m).

^1H NMR ($\text{DMSO}-d_6$): δ 3.80–5.20 (cm, 8H, $\text{H}_{2,3,6,7}$), 6.52 (AB , 1H, $J_{\text{AB}} = 10.0$ Hz), 6.81 (AB , 1H, $J_{\text{AB}} = 10$ Hz) ppm.

1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin (1)

A portion of 8-nitroso-1,4,5-trinitro-1,4,5,8-tetraazadecalin (1.0 g, 3.3 mmoles) was slowly added to 10 ml of well-stirred 100% nitric acid maintained at 0°C over a 15-minute time period. The solution developed a light-yellow color. It was stirred for 5 additional minutes at 0°C , then the cooling bath was removed. The stirring was continued for 5 more minutes. The reaction mixture was quenched by pouring onto 20 g of ice. A white precipitate formed and was collected by vacuum filtration. It was washed well with water and dried. It weighed 0.72 g (2.2 mmoles, 68%) and decomposed at 236°C , but darkened above 200°C . It could be recrystallized to fine crystals by dissolving in hot cyclohexanone (≈ 1 g/10 ml) and adding an equal volume of ethanol.

IR (KBr) 2980(w), 2950(w), 1555(vs), 1460(m), 1420(w), 1360(m), 1300(sh), 1280(vs), 1245(w), 1210(w), 1175(m), 1130(m), 1065(m), 1015(m), 960(w), 885(w), 860(w), 855(w), 755(m).

^1H NMR (DMSO- d_6): δ 4.29-4.65 (AA'BB', 8H, H_{2,3,6,7}), 6.50 (s, 2H, H_{9,10}).

Analysis calcd. for C₆H₁₀N₈O₈: C, 22.36; H, 3.13; N, 34.78;
 Found: C, 22.52; H, 3.18; N, 34.72.
 Density: 1.796 $\pm$ 0.001 g/cm³.

Nitrolysis of 1,4,5,8-Tetraacetyl-1,4,5,8-tetraazadecalin (3)

Twenty ml of trifluoroacetic anhydride were placed in a 100-ml r.b. flask. This was cooled to -5°C, and 10 ml of absolute nitric acid was added by drops over 20 minutes. This mixture was stirred for 20 additional minutes, then 1.0 g (3.2 mmoles) of 3 was added during the next 15 minutes. The cooling bath was removed and the mixture stirred at room temperature for 3 hours. The volatile materials were removed at reduced pressure (0°C, 30 mm) and the residue poured onto 20 g of ice. A fine white precipitate formed which was collected and washed with water and dried. It weighed 0.12 g (0.37 mmole, 11%). This product was reasonably pure 1 contaminated with a little of the trinitroacetyl compound, as evidenced by a small peak in the IR at 1670 cm⁻¹ and a small peak in the NMR at 2.2 ppm.

CONCLUSIONS AND FUTURE PLANS

A high-yield four-step synthesis of a new, potentially useful explosive compound (TNAD) has been developed. This compound has several desirable physical properties such as high density, high melting point, and low-impact sensitivity. The compound may find use in both explosive and propellant applications. Future plans include attempts to reduce the synthesis to a three-step process by combining the last two steps. An X-ray crystallographic study of both TNAD and its precursor, *trans*-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin, are planned. The crystal structure of TNAD will yield valuable information on the shape of the rings, the peri-interaction of the nitro groups, and on the crystal packing of the molecule.

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