2,6-Diamino-3,5-dinitropyridine-1-oxide— A New Insensitive Explosive

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FOREWORD

The Navy need for new dense insensitive but powerful energetic materials continues, both as Insensitive Munitions Advanced Development (IMAD) ingredients to minimize risks to personnel and material and as components in munitions to defeat hard structures. The goal is the development of an explosive to match the insensitivity of 3,5-triamino-2,4,6-trinitrobenzene (TATB) with the performance of cyclotrimethylenetrinitramine (RDX). 2,6-Diamino-3,5-dinitropyridine-1-oxide was prepared, characterized, and tested to evaluate a new class of insensitive energetic materials with the potential to attain this goal.

This report describes work supported by the Office of Naval Research and has been reviewed for technical accuracy by William P. Norris.

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(U) The synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide from 2,6-diaminopyridine by nitration using a mixture of nitric and sulfuric acids followed by oxidation with hydrogen peroxide in acetic acid is described. This dense, stable high melting explosive is insensitive to impact, friction and electrostatic discharge. An explosive formulation containing 5% by weight ethylene vinyl acetate copolymer (EVA) binder and pressed to 97% theoretical maximum density (TMD) has a velocity of detonation of 7060 meters/second and a detonation pressure of 181 kilobars, indicating that 2,6-diamino-3,5-dinitropyridine-1-oxide is comparable in performance to TATB.

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CONTENTS

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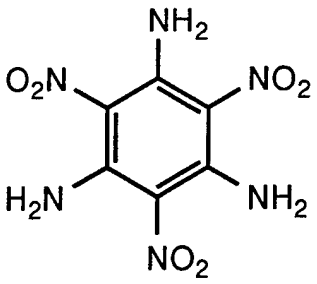
INTRODUCTION

The ongoing requirement of the Navy, and indeed the other Services, for ever more powerful energetic materials has been well documented (Reference 1). Materials such as hexanitrohexaazaisowurtzitane (CL-20), 1,3,3-trinitroazetidine (TNAZ), and ammonium dinitramide (ADN) are needed as explosive ingredients for more powerful warheads and as oxidizers in rocket motors of longer range to enable a weapon system to defeat otherwise inaccessible and/or invulnerable targets. There is a parallel but less glamorous requirement for less sensitive energetic materials. One facet of this requirement is to reduce the hazards to personnel and materiel of accidental initiation of a weapon due to environmental stimuli such as rough handling, fragment impact, and particularly thermal cook-off; this problem has been addressed by the Insensitive Munitions Advanced Development (IMAD) program, which has concentrated largely on engineering solutions to ensure that the weapon "fails safe." However, a need also exists for hardware such as penetration warheads, follow-through warheads, and aimable or deformable warheads for explosive ingredients, which can accept extreme abuse, but still function as intended at the target.

There is therefore a requirement for new insensitive energetic materials. This requirement is not for materials more insensitive than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), currently the benchmark for insensitive explosives; indeed current tests would probably not permit us to recognize such a material, since TATB marks the most insensitive limit of these tests. Rather, the requirement is for a material which matches the insensitivity and stability of TATB (**1**), as represented by its impact insensitivity and high melting point, with the power of cyclotrimethylenetrinitramine (RDX) (**2**), as represented by high velocity of detonation and detonation pressure, yet which retains a high density. This material should also be amenable to production by an economically viable process, and should be sufficiently tractable to allow recrystallization and thence modification of crystal size and shape to satisfy the demands of explosive formulation. (That such materials have not yet been developed is itself testament to the fact that this is no trivial task!) It should be noted that, unless otherwise stated, the densities quoted in this paper are calculated by the method of Holden (Reference 2), and the velocities of detonation and detonation pressures are calculated by the Rothstein and Petersen method (Reference 3). Both are simple empirical "group additivity" methods, and take no account of polymorphism, isomerism, or group interactions. The marked difference between the calculated density of TATB (1.79 g/cm^3) and the experimentally determined value (1.93 g/cm^3) is attributed to intramolecular and intermolecular hydrogen bonding, which

are also held responsible for the insensitivity and stability of the material. We hope that other explosives that show this discrepancy between calculated and experimentally determined densities might exhibit similarly enhanced insensitivity and stability.



TATB

(**1**)

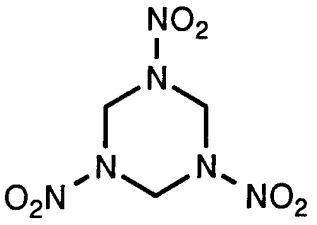
Density 1.78 (1.93) g/cm^3

V of D 7860 m/s

P_{CJ} 277 kbar

m.p. 350°C

10/10 NF @ 200 cm



RDX

(**2**)

Density 1.80 (1.83) g/cm^3

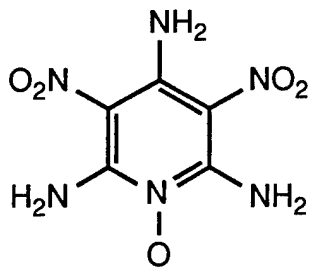
V of D 8940 m/s

P_{CJ} 378 kbar

m.p. 205°C

$h_{50\%}$ 22-24 cm

Several classes of heterocyclic compounds have been investigated as potential new insensitive explosives, including azoles (imidazoles and 1,2,4-triazoles), benzazoles (benzimidazoles and benzotriazoles), derivatives of TACOT (tetranitrodibenzotetraazapentalenes), and benzotetrazines. However, this report is concerned with polyaminopolynitropyridine-1-oxides, which take the inherent stability of the aromatic heterocyclic ring system and combine it with the insensitivity and stability associated with alternating amino and nitro groups, and supplement the performance with an energy contribution from the *N*-oxide functionality. Selected insensitive targets include 2,4,6-triamino-3,5-dinitro-pyridine-1-oxide (**3**) (which should feature extended intramolecular hydrogen bonding around the periphery of the molecule, including both the nitro groups and the *N*-oxide functionality, but which should show only modest improvement in performance over TATB) and 3,5-diamino-2,4,6-trinitropyridine-1-oxide (**4**) (in which the intramolecular hydrogen bonding would not involve the *N*-oxide functionality, but which should show markedly improved performance). If these materials realize expectations, attention will be turned to 2,5-diamino-4,6-dinitro-pyrimidine-1,3-dioxide (**5**), in which intramolecular hydrogen bonding would be localized at the two ends of the molecule, but which should have an explosive performance that truly matches that of RDX.

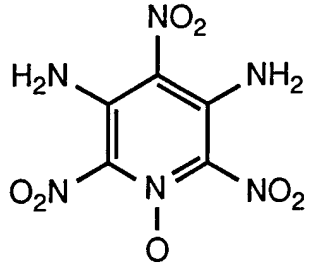


(3)

Density 1.81 g/cm^3

V of D 8010 m/s

P_{CJ} 291 kbar

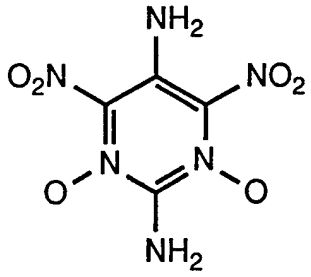


(4)

Density 1.90 g/cm^3

V of D 8650 m/s

P_{CJ} 351 kbar



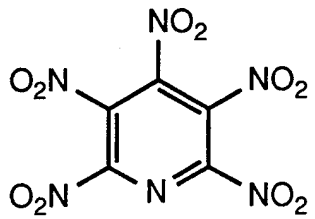
(5)

Density 1.92 g/cm^3

V of D 8930 m/s

P_{CJ} 377 kbar

These polyaminopolynitropyridines should also be recognized as potential precursors for very energetic materials such as pentanitropyridine (**6**) and the corresponding *N*-oxide (**7**), which have detonation properties which match those of hexanitrobenzene and CL-20. Note that (**7**) is in fact "over-oxidized," and should have even better performance in a formulated explosive where it can react with the binder as a fuel.

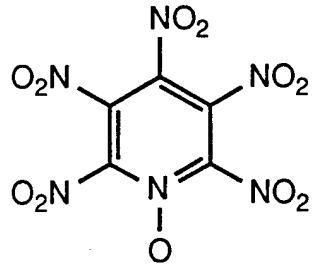


(6)

Density 1.95 g/cm^3

V of D 9290 m/s

P_{CJ} 411 kbar



(7)

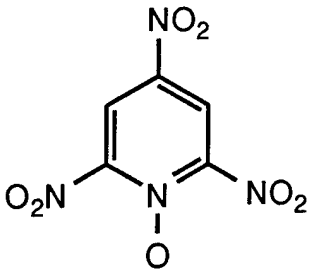
Density 2.07 g/cm^3

V of D 9050 m/s

P_{CJ} 388 kbar

There is some precedent for the incorporation of the *N*-oxide functionality in energetic materials. Ritter and Licht prepared 2,4,6-trinitropyridine-1-oxide (**8**), which is quite energetic but resembles pentaerythritol tetranitrate (PETN) in its sensitivity (Reference 4). Pagoria prepared 2,6-diamino-3,5-dinitropyrazine-1-oxide (**9**), which also had excellent performance, but was more sensitive than desired. This compound also had a higher than calculated density, which was attributed to strong hydrogen bonding (Reference 5). Coburn prepared 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (**10**), which he designated LAX-112.

This unusual explosive, which contains no nitro groups, is quite dense and quite insensitive. However, although it is more powerful than TATB and 3-nitro-1,2,4-triazole-5-one (NTO), it does not match predictions, and is not RDX-like (Reference 6).

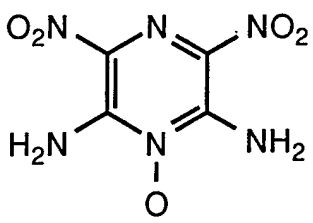


(8)

Density 1.86 (1.86) g/cm^3

V of D 8370 m/s

PETN-like

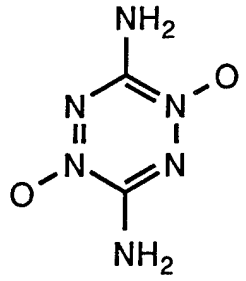


(9)

Density 1.84 (1.91) g/cm^3

V of D 8730 m/s

$h_{50\%}$ 70 cm



LAX-112

(10)

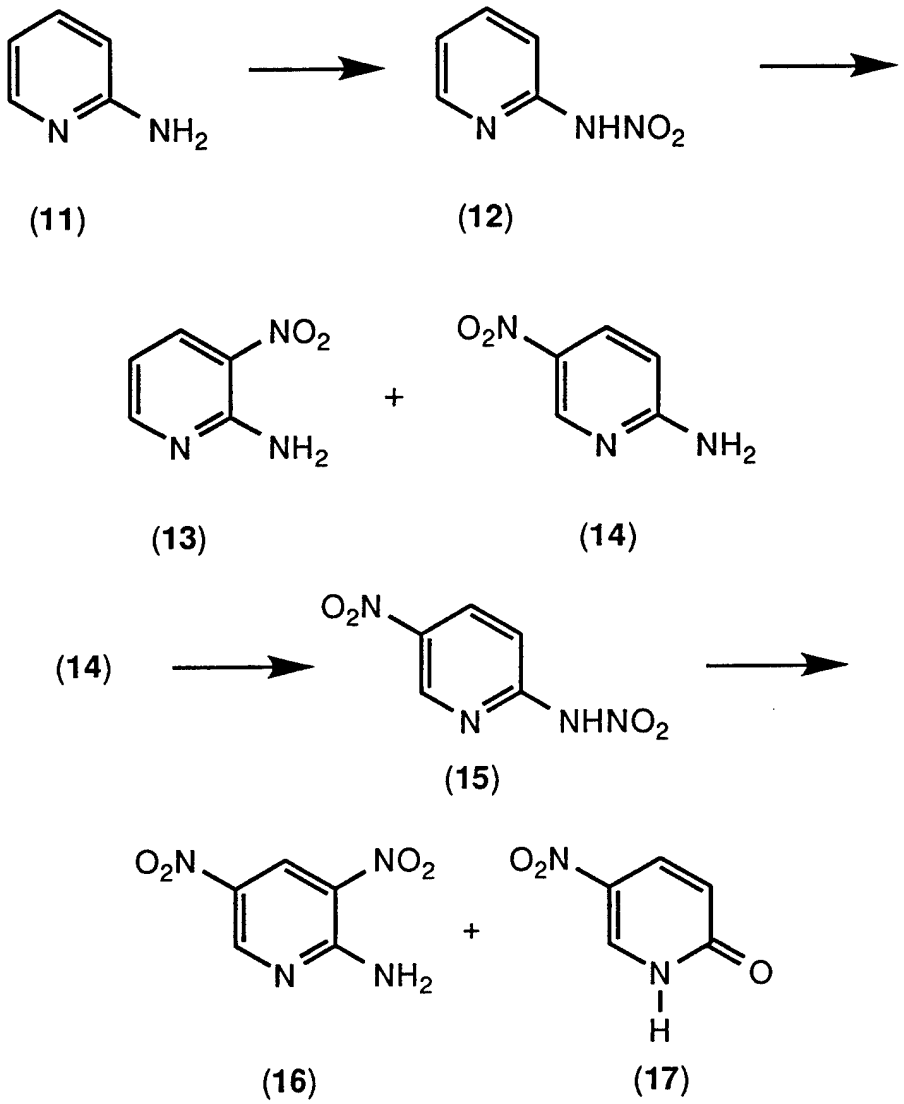
Density 1.81 (1.86) g/cm^3

V of D 8780 m/s

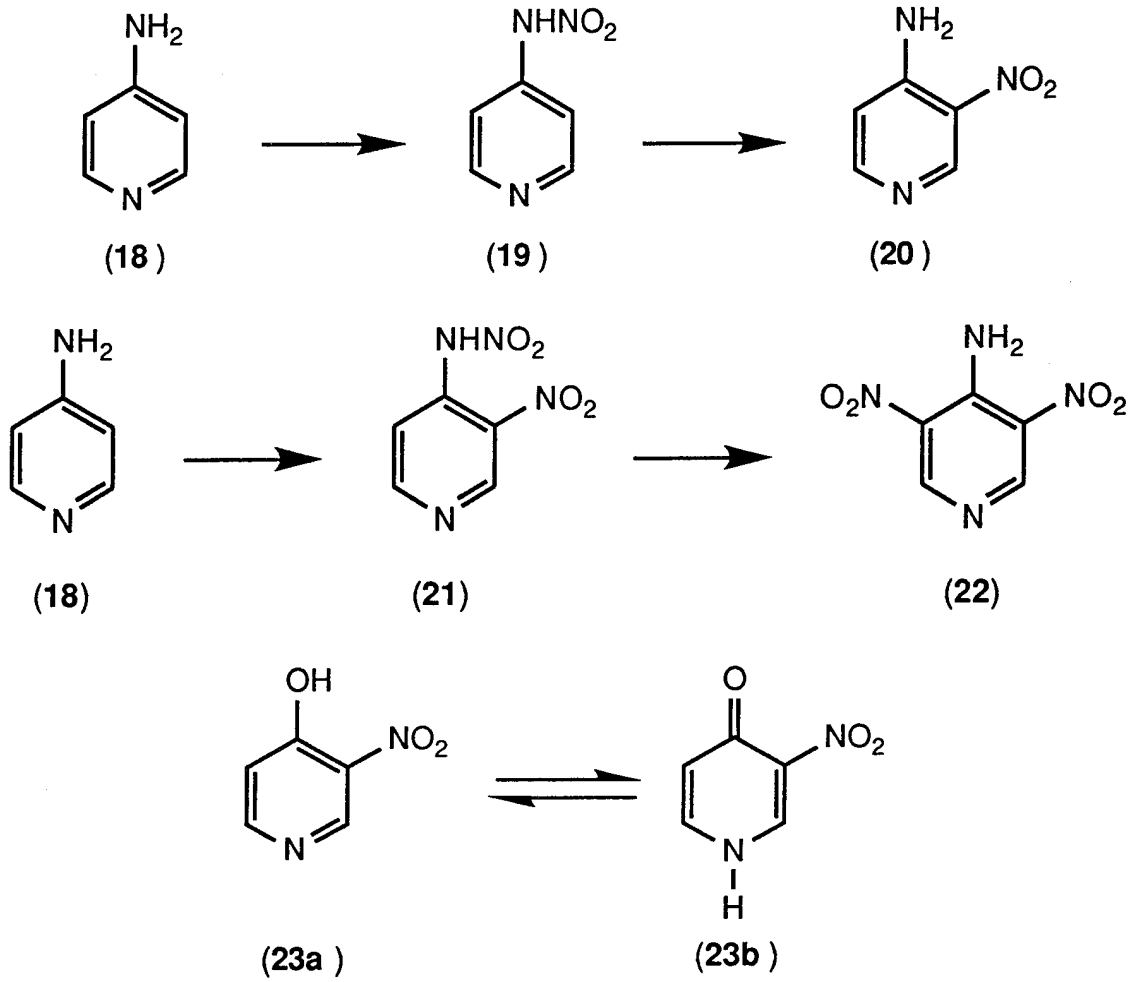
$h_{50\%}$ 179 cm

RESULTS AND DISCUSSION

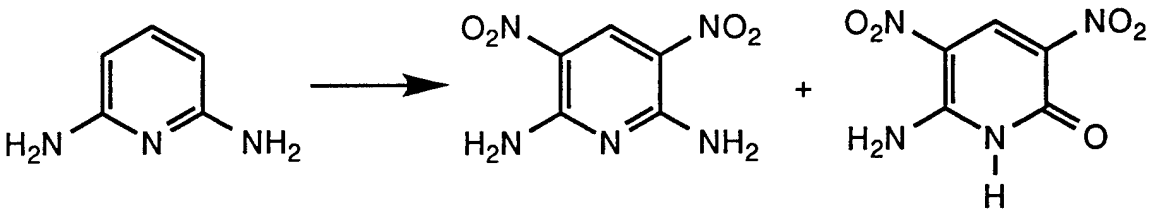
2-Aminopyridine (**11**) was readily nitrated using mixed acid at or below ambient temperature. The initial product was 2-nitraminopyridine (**12**), which could either be isolated or rearranged by warming the reaction mixture to 50°C, yielding a mixture of 2-amino-3-nitropyridine (**13**) and 2-amino-5-nitropyridine (**14**) in which the latter predominated. (The same reaction may be carried out by stirring the isolated **12** in concentrated sulfuric acid at ambient temperature.) Nitration of **14** in mixed acid at ice bath temperatures afforded 2-nitramino-5-nitropyridine (**15**), which rearranged to 2-amino-3,5-dinitropyridine (**16**); if the rearrangement was carried out at elevated temperatures, **16** was formed only as a minor product, with the major product 5-nitro-2-pyridone (**17**) believed to be formed via acid hydrolysis of **15**. Nitration of the minor isomer **13** followed by rearrangement in sulfuric acid also afforded **16** (References 7 through 10).



4-Aminopyridine (**18**) also underwent ready nitration with mixed acid. Careful nitration at ice-bath temperatures gave 4-nitraminopyridine (**19**), which (presumably) rearranges in sulfuric acid at ambient temperature to give 4-amino-3-nitropyridine (**20**). If the nitration mixture was carefully warmed to 80°C, a mixture of 4-nitramino-3-nitropyridine (**21**) and 4-amino-3,5-dinitropyridine (**22**) was obtained. Again **21** rearranged to **22** on treatment with sulfuric acid at ambient temperature. If sufficient care was not taken to control the temperature of the nitration reaction, 4-hydroxy-3-nitropyridine (**23a**) or 3-nitro-4-pyridone (**23b**) was formed, presumably from **19** or **21** (References 11 and 12).



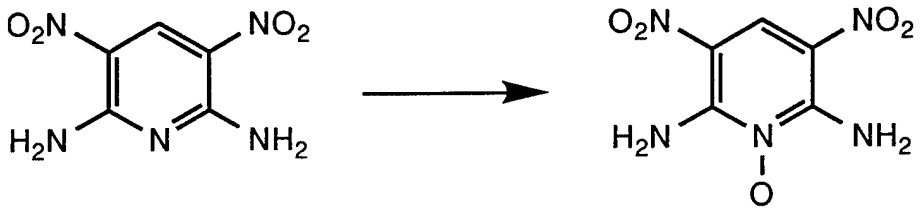
In a similar fashion, 2,6-diaminopyridine (**24**) also underwent nitration in a mixture of 96% sulfuric acid and 90% nitric acid, first at 5°C and then at 60-70°C (Reference 13). In our hands the major product was the desired 2,6-diamino-3,5-dinitropyridine (**25**) (up to 65% yield), but it was always contaminated with 6-amino-3,5-dinitro-2-pyridone (**26**). We believe that **26** was derived by acid hydrolysis of an intermediate nitramine, and its formation was minimized by using the minimum amount of concentrated nitric acid, and controlling the reaction temperature in the early stages. Production of **26** could probably be avoided completely by using 100% nitric acid, but it is readily removed from the product by basification and then extraction with boiling water.



(24) (25) (26)

Encouraging support for the desired intramolecular hydrogen bonding of the amine protons to the adjacent nitro groups was garnered from the ^{1}H-nuclear magnetic resonance (NMR) spectra of **16**, **25,** and even **26** in d_6-acetone or d_6-dimethylsulfoxide (DMSO) solution. In each case the amine protons showed two distinct signals, reflecting restricted rotation even in solution and markedly different chemical environments for the two protons. In each case the two signals coalesced at elevated temperatures to a single peak.

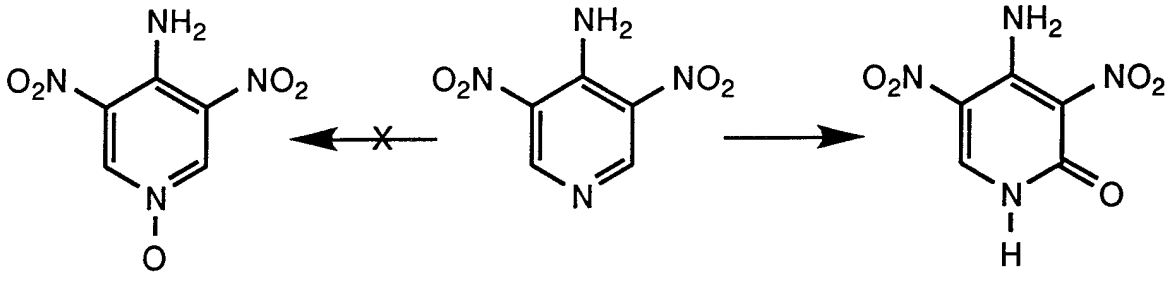
Oxidation of **25** to 2,6-diamino-3,5-dinitropyridine-1-oxide (**27**) was achieved using the general procedure described by Ochiai for preparation of pyridine-1-oxides (Reference 14). Thus, suspension of **25** in acetic acid containing 30% aqueous hydrogen peroxide and heating for 4 hours (h) at 70°C (Reference 15) or under reflux afforded **27** in up to 85% yield. The product always contained about 5% of unreacted starting material; prolonged reaction resulted in reduced yields without elimination of the unreacted starting material, while alternative oxidation procedures were either ineffective or resulted in destructive oxidation of the pyridine ring. However, recrystallization of the product first from trifluoroacetic acid and then from *p*-dioxane or dimethylformamide (DMF) gave pure *N*-oxide (**27**), without any trace of the precursor.



(25) (27)

(Licht and Wanders also report (Reference 15) that oxidation of 4-amino-3,5-dinitropyridine (**22**) using 30% aqueous hydrogen peroxide in acetic acid gave the corresponding *N*-oxide (**28**). The reaction was repeated in these laboratories to give a product which matched that described by Licht and Wanders. However, the infrared spectrum was reminiscent of **26** rather than **27**, while the ^{1}H-NMR spectrum in DMSO showed a broad one-proton signal at 11.18 parts per million (ppm), a sharp one-proton signal at 8.45 ppm and a broad two-proton signal at 8.32 ppm. Finally, the ^{13}C-NMR spectrum showed five

distinct signals, and the product was identified as 4-amino-3,5-dinitro-2-pyridone (**29**).)



(**28**) (**22**) (**29**)

2,6-Diamino-3,5-dinitropyridine-1-oxide (**27**) is not a specific target molecule; its molecular formula is $C_5H_5N_5O_5$ (that of TATB is $C_6H_6N_6O_6$) and its oxygen balance ($OB_{100} = 100(2n_O-n_H-2n_C-2n_{COO})/MW$) is -2.33, and it has a predicted density of only 1.80 grams/cubic centimeter (g/cm^3), velocity of detonation of 7840 meters/second (m/s) and detonation pressure of 275 kilobars (kbar). However, Licht and Wanders noted the thermal stability of **27** (melting point (m.p.) > 340°C), reported a density of 1.84 g/cm^3 and found the impact sensitivity to be comparable with 2,4,6-trinitrotoluene (TNT) (Reference 15). We confirmed the thermal stability (differential scanning calorimetry (DSC) showed no exotherm or endotherm below 340°C), obtained a measured density (gas pycnometry) of 1.90 g/cm^3 and were unable to initiate the material in a crude hammer/anvil laboratory screening test, indicating impact sensitivity *less* than that of TNT. These results, together with the ^{1}H-NMR spectrum in DMSO, which showed two similar but distinct signals for the amine protons, seemed evidence of the desired extended intramolecular hydrogen bonding between the amine groups and both the adjacent nitro groups and the *N*-oxide functionality. Other attractive features were the straightforward synthetic procedure that promised suitability of the process for scale-up, and the fact that the product can indeed be recrystallized, giving promise for modification of particle size and shape. We considered that evaluation of **27** and its material and explosive properties would provide "proof-of-principle" for the concept of polyaminopolynitroheterocyclic *N*-oxides as more energetic insensitive explosives. We also felt that such evaluation would also give valuable insight into this new class of materials.

Crystallization of **27** by transfusion of dichloromethane into a solution in *N*-methyl-2-pyrrolidinone provided clear yellow flattened octrahedra, suitable for the single crystal X-ray structure determination carried out at the Laboratory for the Structure of Matter, Naval Research Laboratory (NRL), Washington, DC, and included in the Appendix. This study confirmed the density of **27** (1.878 g/cm^3); it also confirmed the presence of both intramolecular and intermolecular hydrogen bonding. On the molecular level the structure is planar, with the amine

protons 2.02 and 2.18 Å from the adjacent nitro and *N*-oxide oxygen atoms respectively. The asymmetry of bond lengths and of bond angles are consistent with intramolecular hydrogen bonding. The molecules assemble head-to-tail in "ribbons," with the amine protons and nitro group oxygens separated by 2.27 Å; the ribbons align parallel in sheets with -O...H- separation of 2.50 Å, with individual atoms all within *ca.* 0.1 Å of "their sheet." Finally, the sheets assemble separated by 3.13 Å, with dipoles reversed, in a manner strongly reminiscent of TATB (Reference 16).

(A procedure has been developed to include in the prediction of density contributions from interactions between non-bonded atoms (Reference 17). This procedure includes determination of the molecular structure and probable conformation by an appropriate molecular model, determination of trial crystal structure models, minimization of the energy of these trial models with respect to unit cell parameters, etc., and calculation of the crystal density from the resulting unit cell volume. Application of the *ab initio* Gaussian 92 program (3-21g basis set) led to prediction of a density of 1.860 g/cm^3 for 2,6-diamino-3,5-dinitro-pyridine-1-oxide (**27**), within 1% of the value calculated from the X-ray structure (Reference 18).)

These results prompted us to examine further the explosive properties of **27**, starting first with explosive sensitivity. This compound proved to be quite insensitive to impact, with 10 out of 10 no-fires using a 2.5 kilogram (kg) drop weight with type-12 tools (the sample being placed on garnet paper) and using a drop height of 200 cm, and insensitive to friction, with 10 out of 10 no-fires at 1000 lb in the Allegheny Ballistics Laboratory (ABL) sliding friction test. Fine material purified by recrystallization from trifluoroacetic acid had an electrostatic sensitivity as low as 0.16 Joule (J), but material prepared by careful recrystallization from *N*-methyl-2-pyrrolidinone was insensitive, with 10 out of 10 no-fires at 0.25 J; we believed that the extremely small particle size was responsible for the initial sensitivity to electrostatic discharge.

Next, the heat of combustion of **27** was measured (the material was very easily pressed into pellets for this analysis, indicating the material may well be suitable for pressing into explosive charges without the need for any binder) by calorimetry, giving a value of -2842 calorie/gram (cal/g) (-611 kilocalorie/mole (kcal/mol)), from which was calculated a heat of formation of -31.6 kcal/mol. This latter value compares with a heat of formation of -35.1 kcal/mol for TATB.

Finally, a formulation composed of 95% by weight of **27** with 5% by weight of ethylene vinyl acetate copolymer (EVA) as binder was prepared to gain a first indication of the explosive performance of this new material. As indicated above, **27** appears to press quite well neat (i.e., without binder). However, there is a body of experience with explosive formulations based on the EVA binder system at China Lake, and it was decided to take advantage of that technology. A

lacquer of EVA in dichloromethane was prepared, to which was added the requisite amount of **27** recrystallized from *N*-methyl-2-pyrrolidinone and dichloromethane. The mixture was stirred to ensure efficient coating of the crystalline explosive, and the solvent was removed by evaporation to leave a free-flowing molding powder. This molding powder was insensitive to both friction and electrostatic discharge (10 out of 10 no-fires at 1000 lb and 0.25 J, respectively), but it was, surprisingly, more sensitive to initiation by impact, with a drop height of 49 cm. No indication of chemical change to **27** could be discerned by ^{1}H-NMR or by DSC, but the increased sensitivity must be regarded as evidence of some chemical incompatibility, and the system should be carefully examined before it is used further.

The observed impact sensitivity of the molding powder did not preclude pressing, however, and a 20-ton press and a 0.5-inch die set were used with a pressure of 30,000 pounds per square inch (psi), a pressing temperature of 76°C and a dwell time of 3 minutes (min) to press the explosive into pellets 0.5- by 0.5-inch in diameter. The mean density of the pellets was 1.744 g/cm^3, or 97.01% of the theoretical maximum. The pellets were fitted into a steel tube 6 inches long and with an inside diameter of 0.5 inch. The steel tube was fitted with four piezoelectric pins for measurement of velocity of detonation, and was placed on a 6- by 6- by 2-inch mild steel witness plate with a Rockwell hardness of B-83. The charge was initiated by a RP-501 detonator and 0.5- by 0.5-inch RDX booster charge. The velocity of detonation measured was 7060 m/s, while the dent in the witness plate was 0.114 inch. Comparison with the dents left by explosives of known detonation pressures, including PBXN-5, Tetryl, PBXN-7, HMX and RDX allowed estimation of the detonation pressure of the experimental formulation as 191 kbar. If allowance is made for both voidage and the presence of binder, these experimental values are probably comparable with those predicted for **27** (and for TATB); unfortunately, there is no unanticipated bonus in performance.

CONCLUSION

2,6-Diamino-3,5-dinitropyridine-1-oxide is a new insensitive explosive. The placement of the amine groups between the nitro groups and *N*-oxide functionality allows for extensive hydrogen bonding, both intramolecular and intermolecular, which enables efficient molecular packing in the crystal lattice and a higher than predicted crystal density of 1.88 g/cm^3. This hydrogen bonding also confers on the compound both thermal and chemical stability and explosive insensitivity; the material melts above 340°C without sign of earlier decomposition, and is insensitive to initiation in the drop weight impact test. There are indications of chemical incompatibility with EVA binder, but explosive

formulations press readily. Explosive performance appears to match those predicted, and to be comparable with those of TATB. The indications are that related polyaminopolynitroheterocyclic *N*-oxides will provide the desired new powerful but insensitive explosive ingredients.

EXPERIMENTAL SECTION

WARNING: Many of the compounds described in this report are potentially explosives, which may be subject to accidental initiation by such environmental stimuli as impact, friction, heat, or electrostatic discharge. Appropriate precautions should therefore be taken in their handling and/or use. Melting points were determined in capillary tubes using a Mel-Temp II melting point apparatus. Infrared (IR) spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer. ^{1}H-NMR spectra were determined in d_6-acetone or -DMSO solutions, using an IBM NR-80 instrument at 80 megahertz (MHz) or a Bruker AMX-400 instrument at 400 MHz; ^{13}C-NMR spectra were recorded on the latter instrument at 100 MHz, while the various two-dimensional NMR experiments were carried out on the same instrument. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS).

2-NITRAMINOPYRIDINE (12)

2-Aminopyridine (**11**) (10.0 g, 107 millimoles (mmoles)) was added carefully to 96% sulfuric acid (20 milliliter (mL)) in an ice bath, and the solution was cooled to 10°C. A mixture of 70% nitric acid (8 mL) and 96% sulfuric acid (8 mL) was added dropwise, and the mixture was stirred at 10°C for 1 h. The reaction mixture was quenched on ice-water (*ca.* 400 mL) to give a nearly white solid which was filtered off and dried at the pump overnight. Recrystallization from water gave 2-nitraminopyridine (**12**) as white needles (13.23 g, 89%), m.p. 186-188°C (dec) (lit. 185-189°C (dec) (Reference 9)). IR: 2800, 1610, 1590, 1530, 1430, 1400, 1360, 1320, 1300, 1250, 1220, 1150, 770 cm^{-1}. ^{1}H-NMR (acetone): 8.25 (ddd, J = 5.72, 1.88, 0.82 Hz), 8.02 (ddd, J = 8.72, 7.07, 1.88 Hz), 7.55 (ddd, 8.72, 1.30, 0.82 Hz), 7.18 (ddd, J = 7.07, 5.72, 1.30 Hz). ^{13}C-NMR: 118.16 (C_3), 118.90 (C_5), 139.04 (C_6), 143.93 (C_4), 153.96 (C_2).

2-AMINO-5-NITROPYRIDINE (14)

2-Nitraminopyridine (**12**) (6.7 g, 48 mmoles) was added with stirring to 96% sulfuric acid (15 mL) at ambient temperature. The solution was stirred at

ambient temperature for 3 h, and then quenched on ice-water (100 mL) and neutralized with sodium carbonate. Filtration and drying at the pump gave a virtually quantitative yield of tan-yellow solid, which was recrystallized from ethanol/water 2-amino-5-nitropyridine (**14**) as tan platelets (4.40 g, 63%), m.p. 187.5-188.5°C (dec) (lit. 188°C (Reference 9)). IR: 3400, 3300, 1620, 1590, 1560, 1490, 1460, 1320, 1280, 1125, 840, 765 cm^{-1}. ^{1}H-NMR (acetone): 8.86 (d, J = 2.75 Hz, H_6), 8.15 (dd, J = 9.20, 2.75 Hz, H_4), 6.70 (br s, $-NH_2$), 6.63 (d, J = 9.20 Hz, H_3). ^{13}C-NMR: 107.75 (C_3) ,133.09 (C_4), 134.94 (C_5), 147.29 (C_6), 163.53 (C_2).

2-NITRAMINO-5-NITROPYRIDINE (15)

2-Amino-5-nitropyridine (**14**) (7.5 g, 54 mmoles) was dissolved in 96% sulfuric acid (15 mL) and cooled in an ice-bath. A mixture of 70% nitric acid (6 mL) and 96% sulfuric acid (6 mL) was added dropwise and with stirring, and the mixture was stirred at ice-bath temperature for 3 h. Quenching on ice-water (600 mL) and filtration gave an off-white solid, which was recrystallized from water (*ca.* 1300 mL) and gave 2-nitramino-5-nitropyridine (**15**) as white needles (7.6 g, 77%), m.p. 156-158°C (dec) (lit. 158-159°C (Reference 8)). IR: 3420, 1605, 1520, 1480, 1420, 1350, 1270, 1200, 1110, 920, 840, 750 cm^{-1}. ^{1}H-NMR (acetone): 9.20 (dd, J = 2.72, 0.61 Hz, H_6), 8.71 (dd, J = 9.28, 2.72 Hz, H_4), 8.05 (dd, J = 9.28, 0.61 Hz, H_3). ^{13}C-NMR: 115.22 (C_3), 135.40 (C_4), 140.49 (C_5), 143.41 (C_6), 154.66 (C_2).

2-AMINO-3,5-DINITROPYRIDINE (16)

(1) 2-Nitramino-5-nitropyridine (**15**) (2.0 g, 10.9 mmoles) was added to 100% sulfuric acid (20 mL) and stirred at ambient temperature for 3 days. Quenching in ice-water (400 mL) gave a yellow solid (0.72 g, 36%), recrystallized from methanol to give 2-amino-3,5-dinitropyridine (**16**) as lemon-colored needles, m.p. 187-189°C (lit. 190-192°C (Reference 8)). IR: 3410, 3290, 3150, 3080, 1660, 1580, 1500, 1420, 1330, 1270 cm^{-1}. ^{1}H-NMR (acetone): 9.17 (d, J = 1.05 Hz, 1H), 9.10 (d, J = 1.05 Hz, 1H), 8.35 (br s, $-NH_2$). ^{13}C-NMR: 125.66 (C_3), 131.60 (C_4), 134.11 (C_5), 151.64 (C_6), 155.95 (C_2).

(2) 2-Nitramino-5-nitropyridine (4.5 g, 24.4 mmoles) was added slowly to 96% sulfuric acid (10 mL) and stirred at ambient temperature for 2 h. The temperature was raised to 80°C over 3 h, and the solution was quenched in ice-water (200 mL). Filtration and recrystallization from ethanol gave a pale yellow solid (1.6 g). Flash chromatography (silica/dichloromethane, then methanol) gave first 2-amino-3,5-dinitropyridine (**16**) (0.54 g, 12%) recrystallized from methanol as lemon needles, m.p. 187-189°C (lit. 190-192°C (Reference 8), and then 5-nitro-2-pyridone (**17**) (1.16 g, 26%) recrystallized from ethanol as white

crystals, m.p. 185-187°C. IR: 3400, 3080, 3020, 1650, 1500, 1360, 1240, 1120, 830, 630 cm^{-1}. ^{1}H-NMR (acetone): 8.70 (dd, J = 3.14, 0.48 Hz, H_6), 8.14 (dd, J = 10.12, 3.14 Hz, H_4), 6.46 (dd, J = 10.12, 0.48 Hz, H_3). ^{13}C-NMR: 119.26 (C_3), 130.60 (C_5), 134.57 (C_4), 138.82 (C_6), 162.70 (C_2).

4-NITRAMINOPYRIDINE (19)

4-Aminopyridine (**18**) (5.0 g, 53.3 mmoles) was added in portions to 96% sulfuric acid (10 mL) stirred in an ice-bath. A mixture of 90% nitric acid (4 mL) and 96% sulfuric acid (4 mL) was added dropwise, taking care to prevent any temperature rise. The mixture was allowed to warm slowly to ambient temperature, and was stirred overnight. Quenching in ice-water (300 mL) gave an off-white solid (3.55 g, 48%). Recrystallization from water gave 4-nitramino-pyridine (**19**) as pale yellow needles, m.p. 224-225°C (dec) (lit. 243-244°C (Reference 11)). IR: 2600, 1630, 1610, 1480, 1450, 1390, 1290, 1225, 1180, 1100, 1010, 825, 770 cm^{-1}. ^{1}H-NMR (DMSO): 13.27 (br s, $-NHNO_2$), 8.23 (d, J = 7.45 Hz, 2H), 7.46 (d, 7.45 Hz, 2H). ^{13}C-NMR: 114.41 ($C_{3,5}$), 140.06 ($C_{2,6}$), 161.34 (C_4).

4-NITRAMINO-3-NITROPYRIDINE (21)

4-Aminopyridine (**18**) (10 g, 106.5 mmoles) was added in portions and with stirring to 96% sulfuric acid (20 mL) cooled in an ice-bath, forming a solid white mass. A mixture of 90% nitric acid (10 mL) in 96% sulfuric acid (10 mL) was added dropwise, without allowing the temperature to rise. The reaction mixture was then allowed to warm to ambient temperature, and was warmed slowly to 85°C and held at that temperature for 30 min. The solution was cooled and quenched in ice-water (600 mL), and the resultant white solid (5.2 g, 27%) was filtered off, washed with cold water and dried. Recrystallization from water gave 4-nitramino-5-nitropyridine (**21**) as elongated yellow plates, m.p. 195-198°C (dec) (lit. 202°C (dec) (Reference 12)). IR: 3200, 3050, 2900, 1640, 1600, 1540, 1470, 1425, 1290, 1220, 830, 760 cm^{-1}. ^{1}H-NMR (DMSO): 10.16 (br s, $-NHNO_2$), 9.01 (d, J = 1.11 Hz, H_2), 8.23 (dd, J = 7.20, 1.11 Hz, H_6), 7.60 (d, J = 7.20 Hz, H_5). ^{13}C-NMR: 114.82 (C_5), 135.35 (C_3), 138.96 (C_2), 141.55 (C_6), 152.21 (C_4). The filtrate was continuously extracted with dichloromethane to give 4-amino-3,5-dinitropyridine (1.5 g, 8%), recrystallized from methanol as yellow needles, m.p. 164-166°C.

4-AMINO-3,5-DINITROPYRIDINE (22)

4-Nitramino-3-nitropyridine (**21**) (5.0 g, 27.2 mmoles) was added slowly to 96% sulfuric acid (35 mL) cooled in an ice bath. The solution was allowed to

warm slowly to ambient temperature, and was stirred for 3 days. Quenching in ice-water (500 mL) and continuous extraction with dichloromethane for a week gave 4-amino-3,5-dinitropyridine (3.10 g, 62%), recrystallized from methanol as yellow needles, m.p. 164-166°C. IR : 3400, 3240, 1620, 1520, 1350, 1300, 1280, 1240, 1180, 1120, 900, 870, 730 cm^{-1}. ^{1}H-NMR (DMSO): 9.21 (s, $H_{2,6}$), 8.70 (br s, $-NH_2$). ^{13}C-NMR: 132.36 ($C_{3,5}$), 143.97 (C_4), 152.10 ($C_{2,6}$).

3-NITRO-4-PYRIDONE (23)

4-Aminopyridine (**18**) (5.0 g, 53.3 mmoles) was added in portions to 96% sulfuric acid (10 mL) cooled in an ice-bath, forming a mass of white solid. A mixture of 90% nitric acid (5 mL) and 96% sulfuric acid (5 mL) was added without much caution, and the reaction "took off" to give a brown solution. The reaction mixture was set aside at ambient temperature for several days, and was then slowly warmed to 85°C for 30 min. The solution was then cooled and quenched in ice-water (300 mL) to give a cream/white solid (1.5 g, 20%), recrystallized from water to give 3-nitro-4-pyridone (**23**) as pale yellow needles, m.p. 278-282°C (dec). IR: 2740, 1630, 1600, 1540, 1490, 1330, 1240, 1160, 840 cm^{-1}. ^{1}H-NMR (DMSO): 12.09 (br s, -OH), 8.76 (d, J = 1.64 Hz, H_2), 7.75 (dd, J = 7.46, 1.64 Hz, H_6), 6.46 (d, J = 7.47 Hz, H_5). ^{13}C-NMR: 122.53 (C_5), 138.13 (C_6), 138.52 (C_3), 139.82 (C_2), 168.78 (C_4).

2,6-DIAMINO-3,5-DINITROPYRIDINE (25)

2,6-Diaminopyridine (**24**) (21.8 g, 200 mmoles) was dissolved in 96% sulfuric acid (220 mL) cooled in an ice/salt bath and stirred with an overhead stirrer. Over a period of *ca.* 3 h, 90% nitric acid (22 mL) was added dropwise at such a rate that the temperature did not exceed 5°C. The reaction mixture was allowed to warm to ambient temperature, and was then warmed to 60-65°C and held at that temperature for 1 h. The hot solution was poured over ice (1500 mL), and filtered, washed with water and dried to give an ochre solid (29.0 g). The solid was stirred for 2 h in 2N sodium hydroxide solution (250 mL), filtered, boiled in water (1 L) for 1 h and then washed with water to give an ochre solid (27.4 g, 69%), recrystallized from *p*-dioxane to give 2,6-diamino-3,5-dinitropyridine (**25**) as a yellow-ochre solid, m.p. 345-347°C (dec) (lit. 348-350°C (dec) (Reference 13)). IR: 3470, 3350, 1610, 1450, 1390, 1370, 1320, 1280, 1225, 1040, 770 cm^{-1}. ^{1}H-NMR (DMSO): 8.99 (s, 1H, H_4), 8.35 (br s, 2H, -NH's), 8.24 (br s, 2H, -NH's). ^{13}C-NMR: 120.81 ($C_{3,5}$), 136.04 (C_4), 155.20 ($C_{2,6}$). Acidification of the combined washings gave an orange solid (up to 1.6 g, 4%) recrystallized from *p*-dioxane to give 6-amino-3,5-dinitro-2-pyridone (**26**) as yellow crystals, m.p. 305-310°C (dec). IR: 3380, 3220, 1700, 1640, 1570, 1500, 1390, 1330, 1250 cm^{-1}. ^{1}H-NMR (DMSO): 11.75 (br s, 1H, -NH), 9.04 (s, 1H,

H_4), 9.03 (br s, 1H, -NH), 8.00 (br s, 1H, -NH). ^{13}C-NMR: 113.92 (C_5), 125.12 (C_3), 137.42 (C_4), 151.83 (C_2), 153.58 (C_6).

2,6-DIAMINO-3,5-DINITROPYRIDINE-1-OXIDE (27)

2,6-Diamino-3,5-dinitropyridine (**25**) (25 g, 125.6 mmoles) was suspended in glacial acetic acid (600 mL), and 30% aqueous hydrogen peroxide (80 mL) was added. The reaction mixture was heated under reflux with stirring for 7 h, and then cooled overnight to ambient temperature. Filtration, washing first with acetic acid and then with dichloromethane, and drying at the pump gave a bright yellow solid (22.6 g, 84%), shown by ^{1}H-NMR to include about 5% unreacted starting material. Recrystallization from trifluoroacetic acid, filtration, washing with a mixture of trifluoroacetic acid and dichloromethane (1:1) and then dichloromethane and finally drying at the pump gave pure 2,6-diamino-3,5-dinitropyridine-1-oxide (**27**) as a yellow powder (16.0 g), m.p. >340°C (dec). IR: 3430, 3260, 1630, 1610, 1480, 1440, 1340, 1320, 1275, 1230, 1030, 800 cm^{-1}. ^{1}H-NMR (DMSO): 9.18 (br s, 2H, -NH's), 8.84 (br s, 2H, -NH's), 8.80 (s, 1H, H_4). ^{13}C-NMR: 118.55 ($C_{3,5}$), 123.33 (C_4), 147.73 ($C_{2,6}$).

SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 2,6-DIAMINO-3,5-DINITROPYRIDINE-1-OXIDE

$C_5H_5N_5O_5$ F.W. 215.1, monoclinic space group C2/c, a = 14.864(2), b = 7.336(2), c = 7.509(2) Å, ß = 111.67(2)°, V = 760.9(2) Å^3, Z = 4, ρcalc = 1.878 g/cm^3, λ(MoKα) = 0.71073 Å, μ = 0.169 mm^{-1}, F(000) = 440, T = 294 K.

A clear yellow 0.15 x 0.18 x 0.25 mm crystal, in the shape of a flattened octahedron, was used for data collection on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator. The data collection range of hkl was: $0 \le h \le 17$, $-8 \le k \le 4$, $-8 \le l \le 8$, with $[(\sin\theta)/\lambda]_{max}$ = 0.594. Three standards, measured every 97 reflections, exhibited random variations during the data collection. A set of 1030 reflections was collected in the ω scan mode, with scan width [$\omega(K_{\alpha1})$ - 0.6] to [$\omega(K_{\alpha2}$ + 0.6]° and ω scan rate from 4.99 to 26.04°/min. There were 674 unique reflections, and 551 were observed with $F > 3\sigma(F)$. The structure was solved and refined with the aid of the SHELXTL system of programs (Reference 19). The full-matrix least squares refinement varied 73 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model. Atoms N(1), O(1), C(4), and H(4) were observed to lie on a two-fold axis of symmetry that exactly relates the two halves of the molecule to each other. Final residuals were R = 0.059 and wR = 0.076, with goodness-of-fit of 2.75 and final Fourier excursions of 0.35 and -0.46 eÅ^{-3}. Results are detailed in the Appendix.

4-AMINO-3,5-DINITRO-2-PYRIDONE (29)

4-Amino-3,5-dinitropyridine (**22**) (1.08 g, 5.9 mmoles) was dissolved in glacial acetic acid (25 mL), and 30% aqueous hydrogen peroxide (4.6 mL) was added. The solution was stirred at ambient temperature, and the resultant crystalline solid (0.63 g, 54%) was filtered off and recrystallized from methanol to give 4-amino-3,5-dinitro-2-pyridone (**29**) as yellow needles, m.p. 201-205 (dec). IR: 3450, 3330, 1610, 1570, 1540, 1450, 1355, 1210, 825 cm^{-1}. ^{1}H-NMR (DMSO): 11.18 (br s, 1H, -NH), 8.45 (s, 1H, H_6), 8.32 (br s, 2H, $-NH_2$). ^{13}C-NMR: 128.12 (C_4), 135.51 (C_6), 139.84 (C_5), 142.14 (C_3), 147.15(C_2).

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Appendix

DETAILS OF SINGLE-CRYSTAL X-RAY STRUCTURE ANALYSIS OF 2,6-DIAMINO-3,5-DINITROPYRIDINE-1-OXIDE

STRUCTURE DETERMINATION SUMMARY

CRYSTAL DATA

Empirical Formula	$C_5 H_5 N_5 O_5$
Color; Habit	Clear yellow flattened octahedra
Crystal Size (mm)	0.15 x 0.18 x 0.25
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	$\underline{a}$ = 14.864(2) Å
	$\underline{b}$ = 7.336(2) Å
	$\underline{c}$ = 7.509(2) Å
	β = 111.67(2)°
Volume	760.9(2) $Å^3$
Z	4
Formula Weight	215.1
Density(calc.)	1.878 Mg/m^3
Absorption Coefficient	0.169 mm^{-1}
F(000)	440

DATA COLLECTION

Diffractometer Used	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	294
Monochromator	Highly oriented graphite crystal
2θ Range	3.4 to 50.0°
Scan Type	ω
Scan Speed	Variable; 4.99 to 26.04°/min. in ω
Scan Range (ω)	1.10°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$0 \leq h \leq 17$, $-8 \leq k \leq 4$ $-8 \leq \ell \leq 8$
Reflections Collected	1030
Independent Reflections	674 (R_{int} = 1.02%)
Observed Reflections	551 ($F > 3.0\sigma(F)$)
Absorption Correction	N/A

SOLUTION AND REFINEMENT

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Number of Parameters Refined	73
Final R Indices (obs. data)	R = 5.93 %, wR = 7.59 %
R Indices (all data)	R = 7.34 %, wR = 7.90 %
Goodness-of-Fit	2.75
Largest and Mean Δ/σ	0.005, 0.001
Data-to-Parameter Ratio	7.5:1
Largest Difference Peak	0.35 $eÅ^{-3}$
Largest Difference Hole	-0.46 $eÅ^{-3}$

TABLE A-1. Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2x10^3$).[a]

	x	y	z	U(eq)
N(1)	5000	-357(5)	2500	27(1)
O(1)	5000	-2184(5)	2500	44(1)
C(2)	5737(2)	455(4)	3896(4)	23(1)
N(2)	6388(2)	-609(5)	5095(4)	37(1)
C(3)	5712(2)	2379(5)	3902(4)	29(1)
N(3)	6439(2)	3469(4)	5395(4)	35(1)
O(3A)	7093(2)	2580(4)	6615(3)	53(1)
O(3B)	6381(2)	5108(4)	5407(4)	59(1)
C(4)	5000	3411(7)	2500	30(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE A-2. H-Atom Coordinates ($x10^4$) and Isotropic Displacement Coefficients ($Å^2x10^3$).

	x	y	z	U
H(2A)	6891	-112	6052	54(13)
H(2B)	6337	-1828	4968	80(17)
H(4)	5000	4720	2500	128(34)

TABLE A-3. Anisotropic Displacement Coefficients ($Å^2 x 10^3$).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	29(2)	20(2)	28(2)	0	5(2)	0
O(1)	55(2)	22(2)	48(2)	0	10(2)	0
C(2)	25(2)	17(2)	24(2)	1(1)	5(1)	0(1)
N(2)	31(2)	37(2)	34(2)	8(1)	0(1)	9(1)
C(3)	30(2)	27(2)	27(2)	-3(2)	6(1)	-6(1)
N(3)	30(2)	35(2)	32(2)	-4(1)	0(1)	-2(1)
O(3A)	42(2)	55(2)	40(2)	1(2)	-8(1)	-7(1)
O(3B)	54(2)	28(2)	65(2)	-5(1)	-13(1)	-10(1)
C(4)	30(2)	30(3)	28(2)	0	7(2)	0

[a] The anisotropic displacement factor exponent takes the form:
$-2\pi^2 (h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

TABLE A-4. Bond Lengths (Å) and Angles (°).

N(1)-O(1)	1.340 (5)	N(1)-C(2)	1.344 (3)
N(1)-C(2A)	1.344 (3)	C(2)-N(2)	1.309 (4)
C(2)-C(3)	1.412 (5)	C(3)-N(3)	1.473 (4)
C(3)-C(4)	1.407 (4)	N(3)-O(3A)	1.246 (3)
N(3)-O(3B)	1.205 (4)	C(4)-C(3A)	1.407 (4)

O(1)-N(1)-C(2)	116.3(2)	O(1)-N(1)-C(2A)	116.3(2)
C(2)-N(1)-C(2A)	127.3(4)	N(1)-C(2)-N(2)	117.1(3)
N(1)-C(2)-C(3)	115.6(3)	N(2)-C(2)-C(3)	127.4(3)
C(2)-C(3)-N(3)	122.2(3)	C(2)-C(3)-C(4)	123.3(3)
N(3)-C(3)-C(4)	114.6(3)	C(3)-N(3)-O(3A)	115.4(3)
C(3)-N(3)-O(3B)	120.8(3)	O(3A)-N(3)-O(3B)	123.7(3)
C(3)-C(4)-C(3A)	114.9(5)		

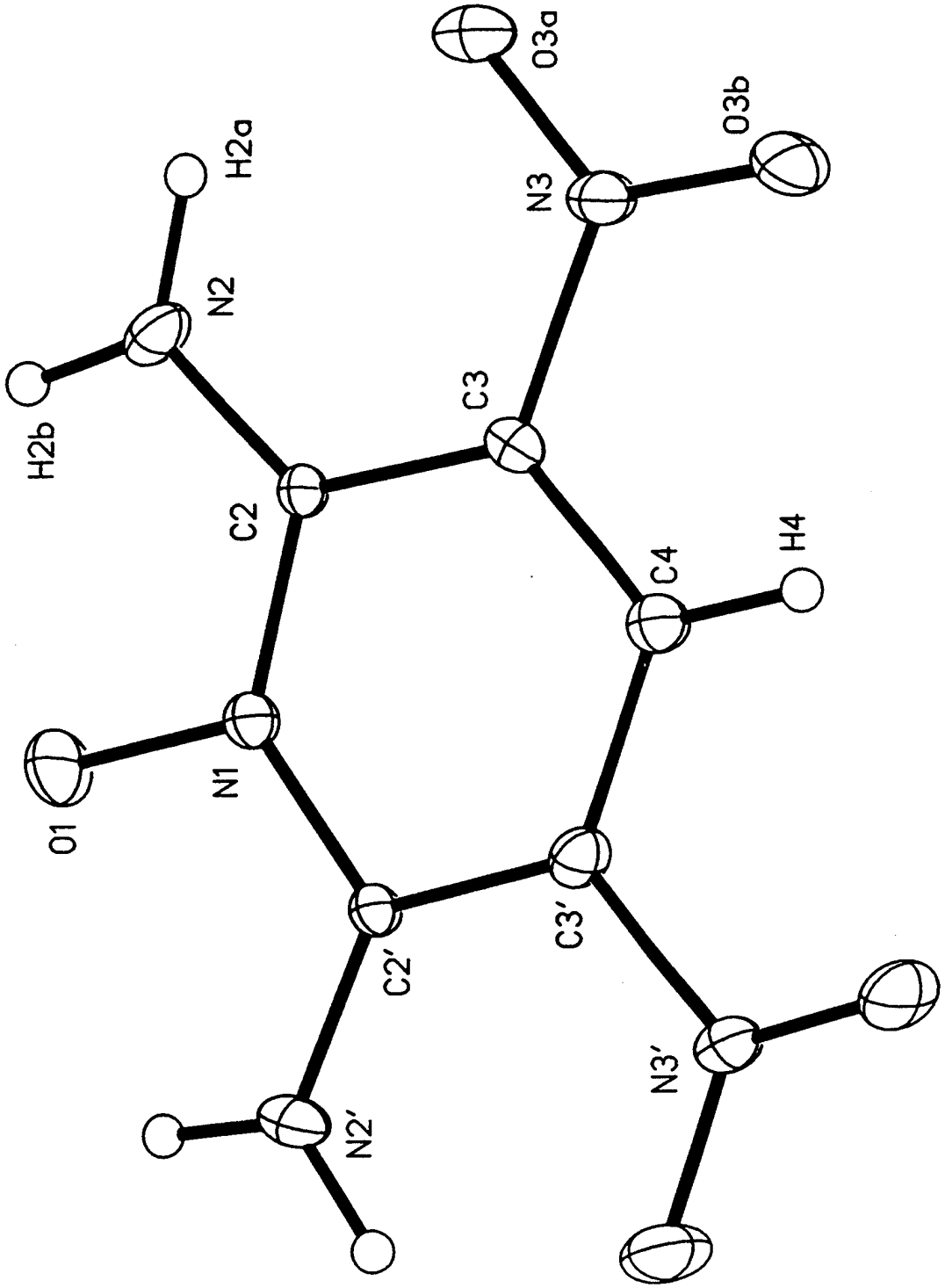

FIGURE A-1. Structure of 2,6-Diamino-3,5-dinitropyridine-1-oxide .

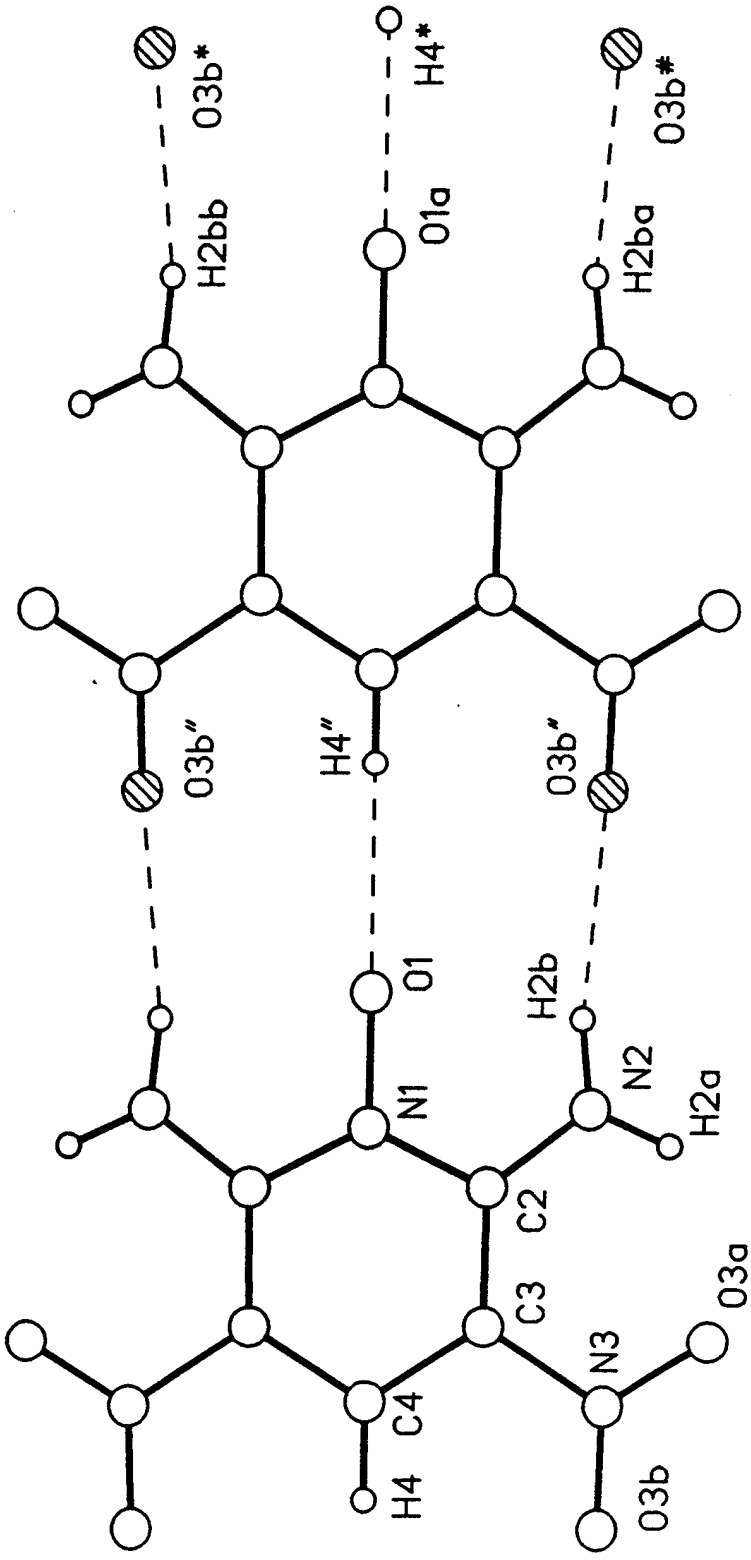

FIGURE A-2. Segment of Polar Ribbon Formed by Strong Hydrogen Bonds.

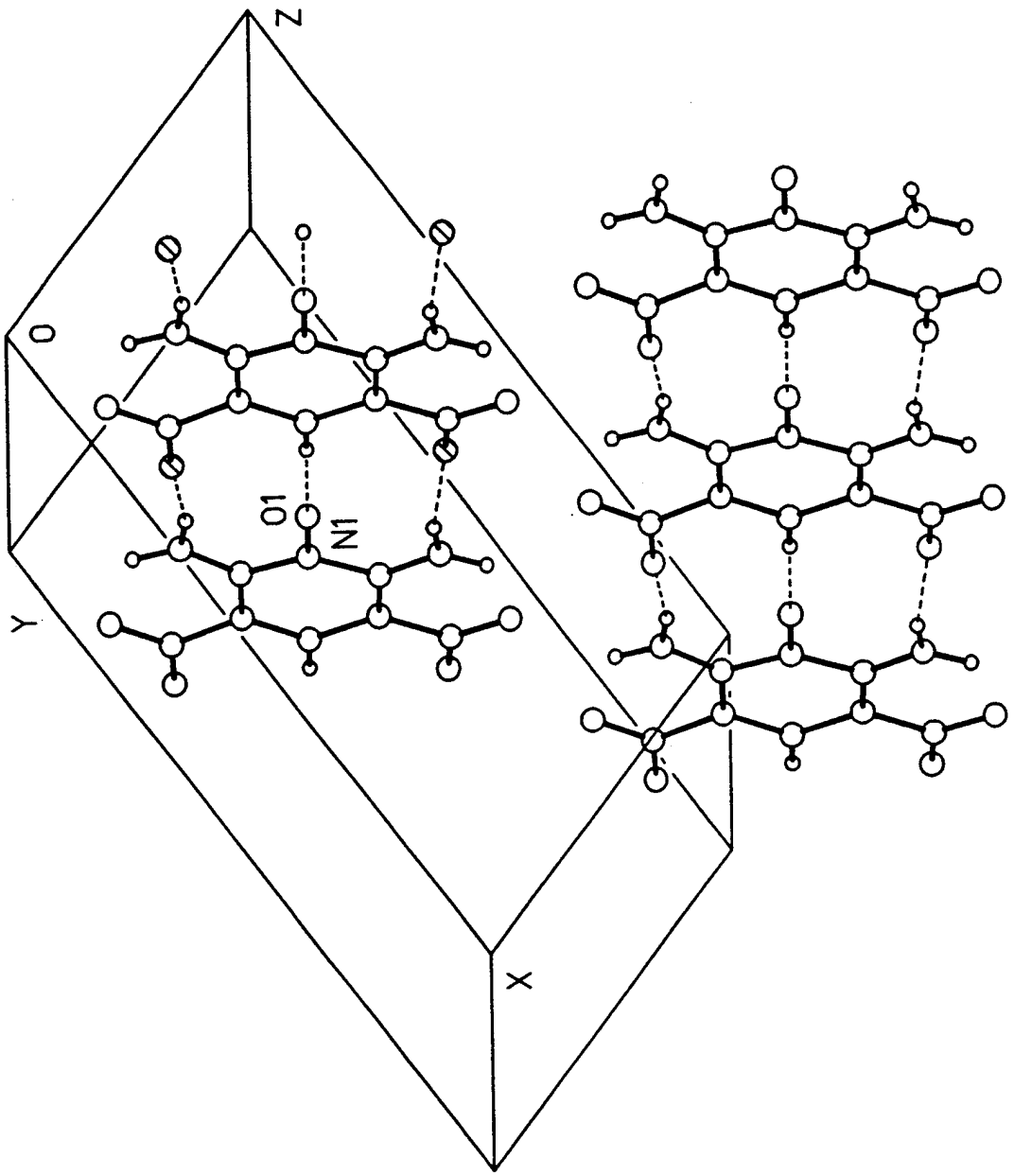

FIGURE A-3. Two Polar Ribbons, Side-by-Side, Having a Net Dipole in the y-Direction. Weak hydrogen bonds linking the ribbons are not shown.

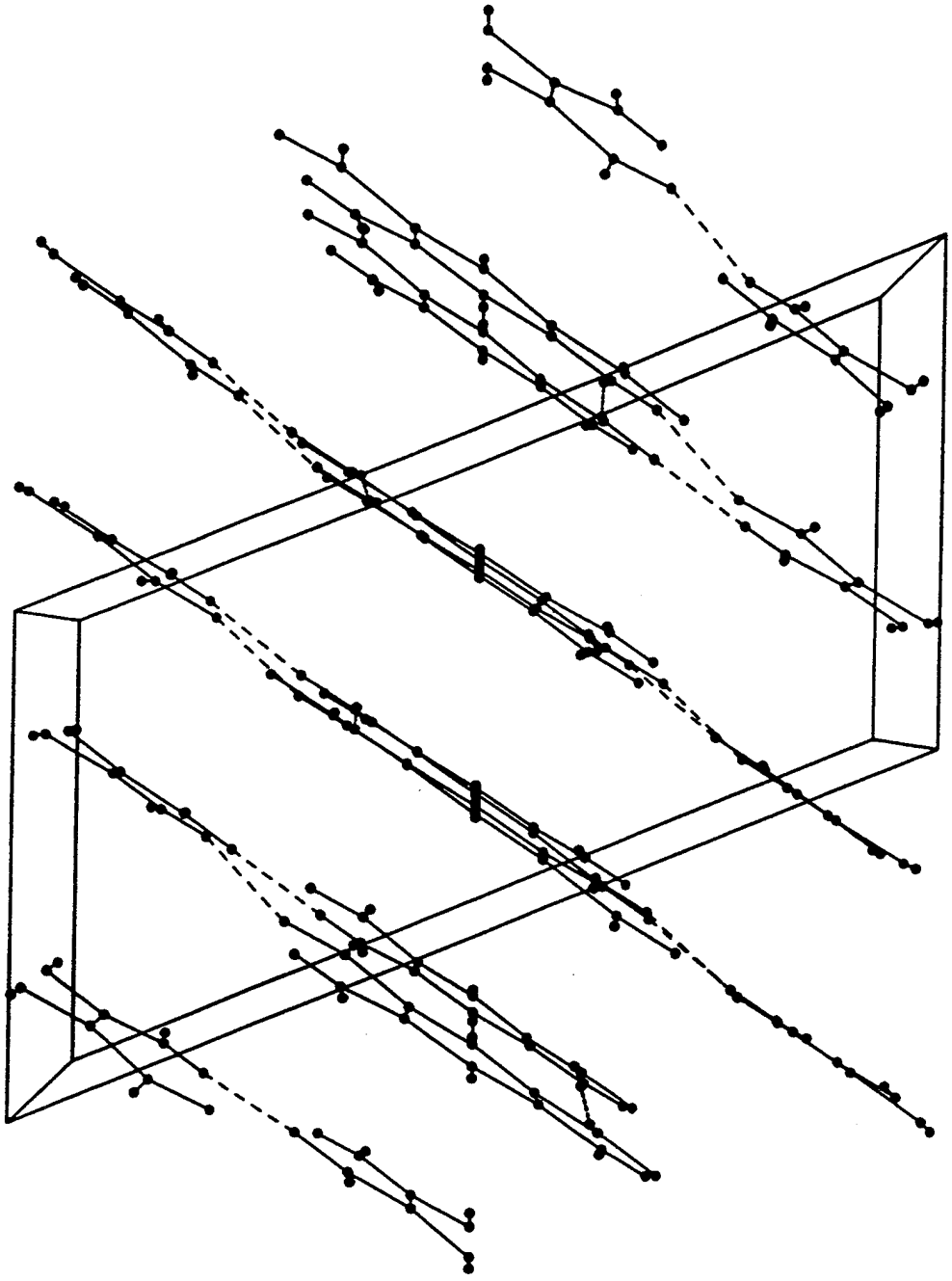

FIGURE A-4. View of Full Structure Looking in the y-Direction (b-axis). The dipole of each ribbon is headed directly into or out of the plane of the paper. Alternate sheets are reversed and the dipoles cancel one another.

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