SYNTHESIS, CHARACTERIZATION AND EXPLOSIVE PROPERTIES OF 3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE AND ITS 1-OXIDE
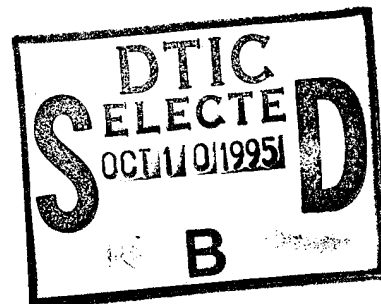
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FOREWORD

The Navy's 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). 3,5-Dinitro-2,4,6-triaminopyridine and its -1-oxide were prepared, characterized, and tested as a new class of insensitive explosives to meet this goal.

This report describes work supported by the Office of Naval Research 6.2 Explosive Block and has been reviewed for technical accuracy by William P. Norris.

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(U) 3,5-Dinitro-2,4,6-triaminopyridine was prepared by oxidative amination of 2-chloro-3,5-dinitropyridine or 2,6-diamino-3,5-dinitropyridine, or by treatment of the latter compound with hydroxylamine. 3,5-Dinitro-2,4,6-triaminopyridine-1-oxide was prepared by oxidation of the parent heterocycle with hydrogen peroxide, or by treatment of 2,6-diamino-3,5-dinitropyridine-1-oxide with hydroxylamine. This compound features intramolecular and intermolecular hydrogen bonding which results in high density, thermal stability, and insensitivity to impact.

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CONTENTS

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INTRODUCTION

As a general rule, those explosophores which contribute most to the performance of an explosive or propellant (velocity of detonation, detonation pressure, specific impulse, etc.) also include the "trigger linkage" for its initiation or ignition. As a consequence, although there is no direct correlation, powerful energetic materials tend to be relatively sensitive, while insensitive materials tend to exhibit only modest performance, which has led such ingredients as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (**1**) to be described as "wooden" explosives. There is, however, a requirement for more powerful insensitive energetic materials, both as ingredients for the Insensitive Munitions Advanced Development (IMAD) program, and as components capable of withstanding the rigors of violent impact on a hard target and yet still functioning as desired. Specific targets to satisfy this requirement include dense energetic materials which match the insensitivity (and stability) of TATB with the performance of cyclotrimethylenetrinitramine (RDX) (**2**).
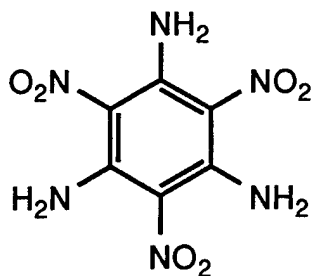
TATB

(**1**)

Density 1.78 (1.93) g/cm^3
V of D 7860 m/s
P_{CJ} 277 kbar
m.p. 350°C
$h_{50\%}$ > 200 cm
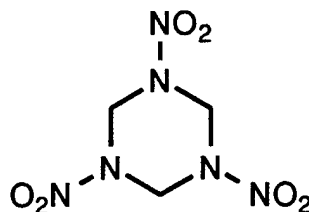
RDX

(**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

Throughout this report densities quoted are those predicted by the Holden method (Reference 1) (experimentally measured densities, where known, are presented in parentheses), while velocities of detonation and detonation pressures are those estimated by the Rothstein and Petersen method (Reference 2). Both of these procedures are empirical group additivity methods which require only the chemical structure of the ingredient. As such they are useful for prediction of the properties of an (as-yet) unknown target molecule, but

they lack the sophistication to account for the effects of isomerism, hydrogen bonding, or other group interactions. The marked discrepancy between the predicted and measured densities of TATB is attributed to extended intramolecular hydrogen bonding between the adjacent amino and nitro groups around the periphery of the molecule, and to intermolecular hydrogen bonding which facilitates assembly of the molecules in extended mica-like sheets in the crystalline structure (Reference 3). This intramolecular and intermolecular hydrogen bonding is also held responsible for the remarkable insensitivity of TATB to heat, impact, shock, and other stimuli.

The approach taken in this program was to take the intrinsic stability of an azaheterocyclic ring system (in this case the pyridine molecule), coupled with the alternating amino and nitro groups known to confer favorable stability and insensitivity in the benzenoid series, and to enhance the oxygen balance by the inclusion of the N-oxide functionality, thereby supplementing the explosive energy of the resultant molecule. Selected target compounds include 3,5-dinitro-2,4,6-triaminopyridine-1-oxide (3), whose synthesis and properties constitute the subject of this report, and 3,5-diamino-2,4,6-trinitropyridine-1-oxide (4), whose synthesis is sought in a related program (Reference 4). (Prospects for success in these endeavors was enhanced by the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (5) (References 5 and 6), which was found to have high density (1.88 grams/cubic centimeter (g/cm^3)), good stability (no melting or decomposition below 340°C), and the desired insensitivity to impact (10/10 no fires at 200 cm), friction (10/10 no fires at 1000 pounds (lbs)) and electrostatic discharge (up to 10/10 no fires at 0.25 joule (J)). Further, this compound has heat of formation, velocity of detonation (V of D), and detonation pressure (P$_{CJ}$) comparable with those of TATB (Reference 5).)
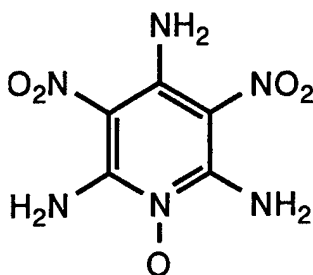
(3)

Density 1.81 g/cm^3

V of D 8010 m/s

P$_{CJ}$ 291 kbar
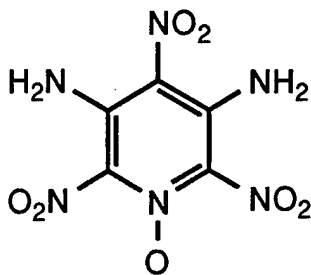
(4)

Density 1.90 g/cm^3

V of D 8650 m/s

P$_{CJ}$ 351 kbar
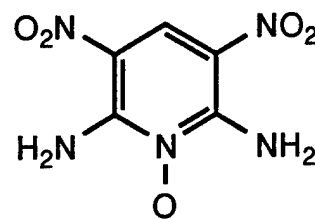
(5)

Density 1.80 (1.88) g/cm^3

V of D 7840 m/s

P$_{CJ}$ 275 kbar

m.p. >340°C

h$_{50\%}$ >200 cm

ΔH_f - 31.6 kcal/mol

RESULTS AND DISCUSSION

Two routes present themselves immediately for the synthesis of 3,5-dinitro-2,4,6-triaminopyridine-1-oxide (**3**). The first involves oxidation of 3,5-dinitro-2,4,6-triaminopyridine (**6**) using hydrogen peroxide or peracids, a method which has been used widely for the synthesis of pyridine-1-oxides (References 5 through 7). The second involves insertion of the final amino group into the 4-position of 2,6-diamino-3,5-dinitropyridine-1-oxide (**5**).
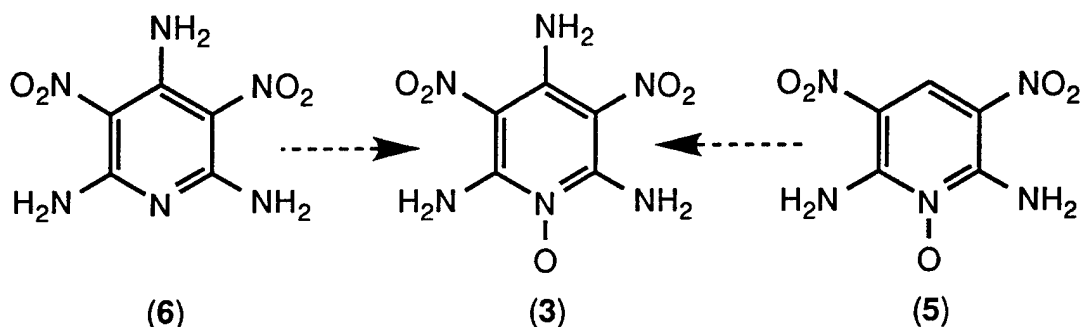
A six-step reaction sequence for the synthesis of (**6**) from pyridine-1-oxide was developed by Coburn (Reference 8), but in only 5-10% yield overall. The major problems with this sequence were with the first mercuration step, which used large quantities of mercuric acetate, and the second bromination step, which yielded mercuric salts as byproducts, and which gave a combined yield of only 10-20%. An alternative route was therefore deemed desirable.
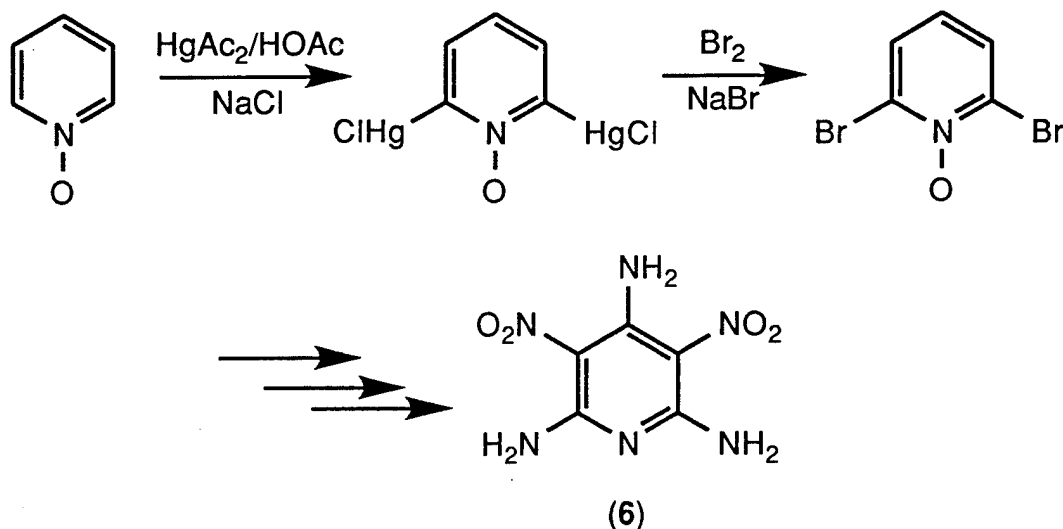
More recently van der Plas showed that, although treatment of 2-chloro-3,5-dinitropyridine (**7**) with liquid ammonia alone gave 2-amino-3,5-dinitro-pyridine (**8**), oxidative amination using potassium permanganate in liquid

ammonia afforded 2,6-diamino-3,5-dinitropyridine (9) by nucleophilic substitution in what was described as an S_N(ANRORC) mechanism (Addition of Nucleophile, Ring Opening, and Ring Closure) (References 9 and 10). Also detected in the reaction mixture were traces of the triamino derivative 6. It was subsequently shown by Wozniak that subjecting 7 to these conditions for 1 hour (h) gave 40% conversion to 9 together with 9% of 6, while extending the reaction time to 6 h gave the triamino derivative 6 as the sole product in 17% yield (Reference 11).

(7)   (8)

(7)   (9)   (6)
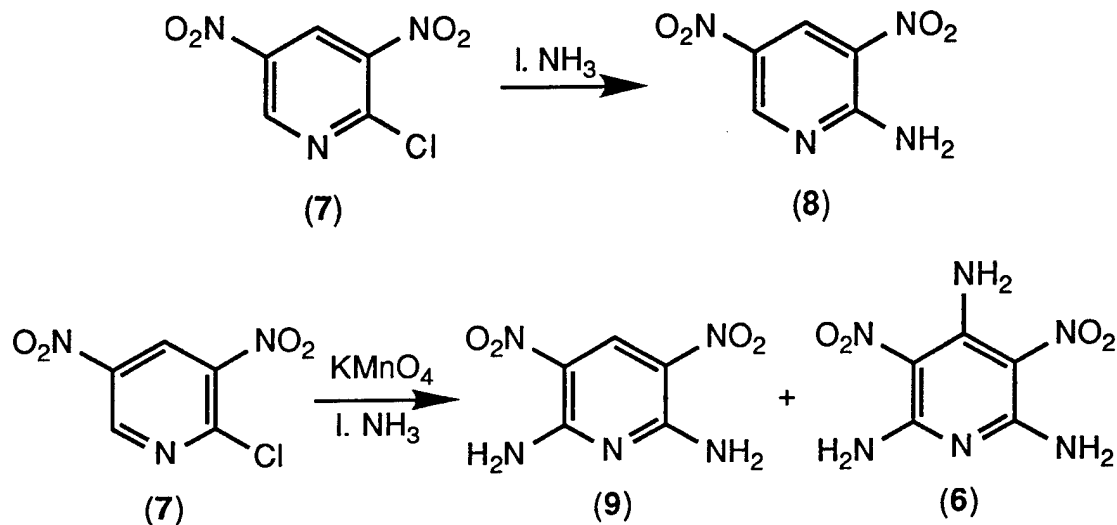
The oxidative amination procedure was repeated, and the triamino derivative 6 was obtained in somewhat variable yield. The best yield (30%) was obtained by extending the reaction time to 8 h before allowing the temperature to rise to ambient overnight, followed by continuous extraction with hot chloroform (10 days). Alternatively, treatment of 9 (prepared independently by nitration of 2,6-diaminopyridine (Reference 5)) in the same manner afforded 6 in up to 61% yield.

(9)   (6)
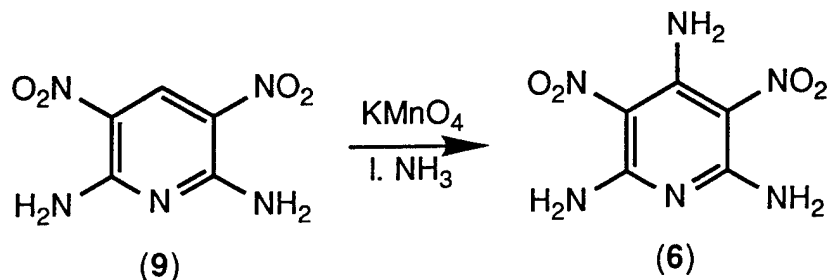
However, even this reaction scheme leaves something to be desired from an environmental standpoint, employing as it does liquid ammonia as the reaction medium, and generating substantial quantities of heavy metal residues. An approach which recommends itself is the reaction of m-dinitrobenzene with hydroxylamine under basic conditions to give 2,4-dinitrophenylene-1,3-diamine,

first described by Meisenheimer (Reference 12). This method was used successfully by Norris to prepare 7-amino-4,6-dinitrobenzofuroxan (ADNBF) by treatment of 4,6-dinitrobenzofuroxan with hydroxylamine in aqueous potassium carbonate; reaction of either of these compounds with hydroxylamine in aqueous potassium hydroxide afforded 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) (Reference 13). Katritzky developed a related method which uses 4-amino-1,2,4-triazole and potassium *tert*-butoxide in dimethylsulfoxide (DMSO) (Reference 14), and the general process has been described as "vicarious nucleophilic substitution" (References 14 and 15), since the incoming amino group is "disguised" as hydroxylamine or 4-amino-1,2,4-triazole.

Some model experiments were carried out first to evaluate the applicability of this vicarious amination process to the polynitropyridine system. Treatment of 4-amino-3,5-dinitropyridine (**10**) with hydroxylamine in aqueous potassium hydroxide gave 2,4-diamino-3,5-dinitropyridine (**11**) in about 37% yield; reaction of **10** with 4-amino-1,2,4-triazole and potassium *tert*-butoxide in DMSO gave the same product in 30% yield. In neither case was 3,5-dinitro-2,4,6-triaminopyridine (**6**) detected, and in separate experiments **11** proved inert to further reaction under each set of conditions.

(10)   (11)   (6)
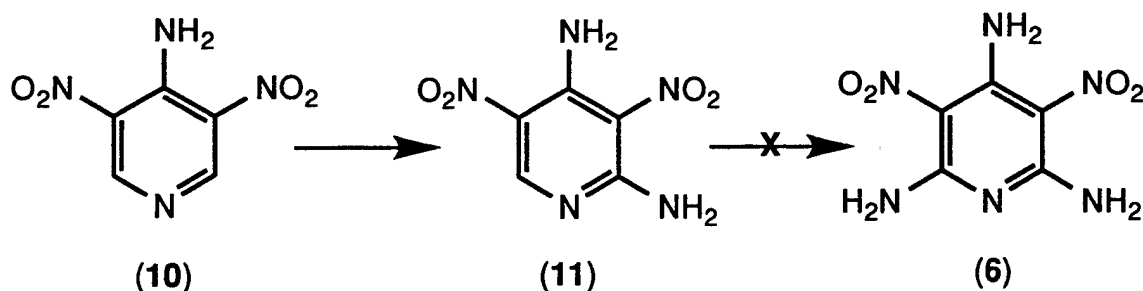
2-Amino-3,5-dinitropyridine (**8**) proved somewhat less reactive under these conditions, and was recovered largely unchanged with perhaps a trace of **9** and/or **11** being discernible in the [1]H-nuclear magnetic resonance (NMR) spectrum (but not isolated). 2,6-Diamino-3,5-dinitropyridine (**9**) was also unreactive towards 4-amino-1,2,4-triazole and potassium *tert*-butoxide in DMSO, probably due to the steric bulk of the reagents. Treatment of **9** with hydroxylamine in aqueous potassium carbonate also gave no reaction, but reaction in the presence of potassium hydroxide gave the desired 3,5-dinitro-2,4,6-triaminopyridine (**6**) in about 40% yield. The product was obtained with an approximately equimolar amount of recovered starting material, from which it was isolated (with difficulty) by fractional crystallization. Thus, **6** is certainly accessible via this more "environmentally friendly" procedure, but it is still probably more conveniently prepared from **9** by the oxidative amination method.

7

O$_2$N — NO$_2$ $\xrightarrow[\text{KOH/H}_2\text{O}]{\text{NH}_2\text{OH·HCl}}$ O$_2$N — NO$_2$

H$_2$N — N — NH$_2$ H$_2$N — N — NH$_2$

(9)   **(6)**
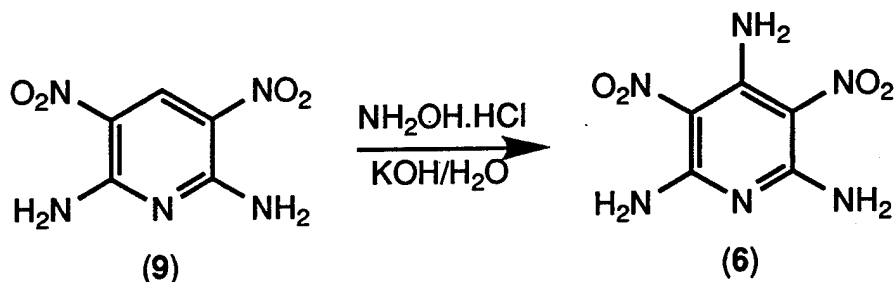
      The structure of **6** was initially assigned on the basis of its synthetic routes and its mass, infrared (IR), and ^{1}H- and ^{13}C-NMR spectra. In particular the mass spectrum showed a parent ion (and base peak) at mass 214, and the IR spectrum showed two distinct amines. While the ^{13}C-NMR spectrum also showed the expected three signals, the ^{1}H-NMR spectrum showed three distinct, but equal, signals for amine protons. (At ambient temperature the 2- and 6- amines are typically "fixed" in this class of compounds due to hydrogen bonding with the adjacent nitro groups, and the two protons thus experience different chemical environments and magnetic fields. At elevated temperatures rotation about the C-N bond overcomes the effects of hydrogen bonding, and the two signals coalesce (Reference 5).) Confirmation of this structure was provided by single crystal X-ray diffraction on crystals prepared from N-methyl-2-pyrrolidinone/dichloromethane. The amino and nitro groups of each molecule are quite coplanar, indicating extensive intramolecular hydrogen bonding of the amine protons with the oxygen atoms of the adjacent nitro groups. A centrosymmetric coplanar pair of molecules are associated as shown in Figure 1, with hydrogen bonding between one proton on the 2- (or 6-) amine of one molecule and the heterocyclic nitrogen of the other molecule. The pairs of molecules are then assembled in planar arrays, and these sheets are stacked in a manner reminiscent of TATB (Reference 3). Details of the X-ray structure determination are included as Appendix A. The resultant crystals have a density of 1.819 g/cm^3, compared with a predicted value of only 1.73 g/cm^3 (Reference mz721). This enhanced density is attributed to the extended intramolecular and intermolecular hydrogen bonding. As expected, **6** proved quite insensitive to impact in a crude laboratory hammer/anvil screening test, and its chemical stability was manifested in its melting point of 353°C (dec).
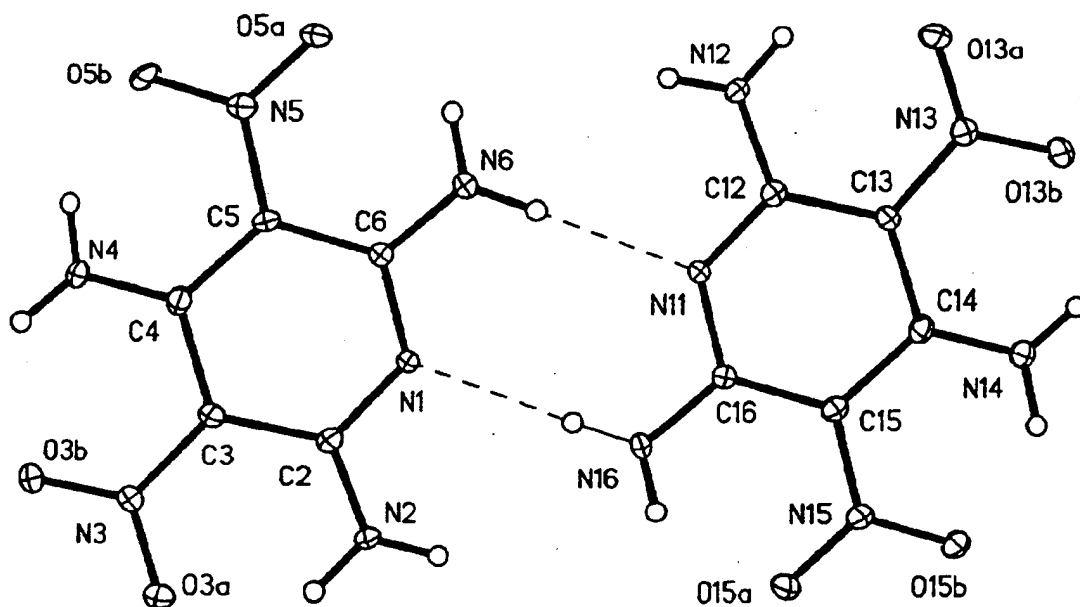
FIGURE 1. Structure of 3,5-Dinitro-2,4,6-triaminopyridine (6).

An attempt was next made to oxidize the triamino derivative **6** to 3,5-dinitro-2,4,6-triaminopyridine-1-oxide (**3**) in a manner analogous to the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (**5**) (References 5 and 6). Indeed heating **6** with 30% hydrogen peroxide in glacial acetic acid under reflux gave **3**, but only in 9-10% yield. The bulk of the starting material was recovered unchanged, but the yield of the reaction could not be improved either by increasing the concentration of hydrogen peroxide or by increasing the reaction time.

(6)   (3)
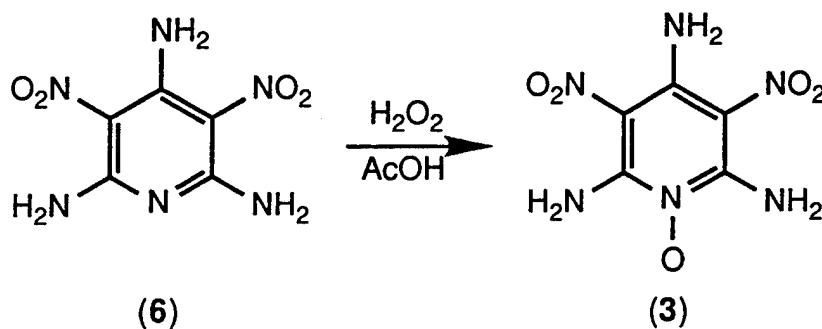
In view of the low yields in the oxidation step, and given the success in preparing **6** by the vicarious amination route, the alternate procedure to **3** by amination of 2,6-diamino-3,5-dinitropyridine-1-oxide (**5**) was considered. The latter compound proved to be unreactive to 4-amino-1,2,4-triazole and potassium

tert-butoxide in DMSO (again presumably due to the steric bulk of the reagents), and to hydroxylamine in aqueous potassium carbonate. This lack of reactivity is possibly due to the base strength, for reaction of **5** with hydroxylamine in aqueous potassium hydroxide gave a product tentatively identified as the intermediate Meisenheimer salt (**12**), which yielded the desired 3,5-dinitro-2,4,6-triaminopyridine-1-oxide (**3**) in 39% overall yield simply by washing with water. Furthermore, acidification of the original mother liquors regenerated the unconverted starting material **5** (34%), presumably from a complex formed with the hydroxide ion. Thus, the yield of **3** based on consumption of **5** was 59%. However, modification of the reaction conditions (including ingredient concentrations and reaction time and temperature) failed to improve the yield of the desired product.
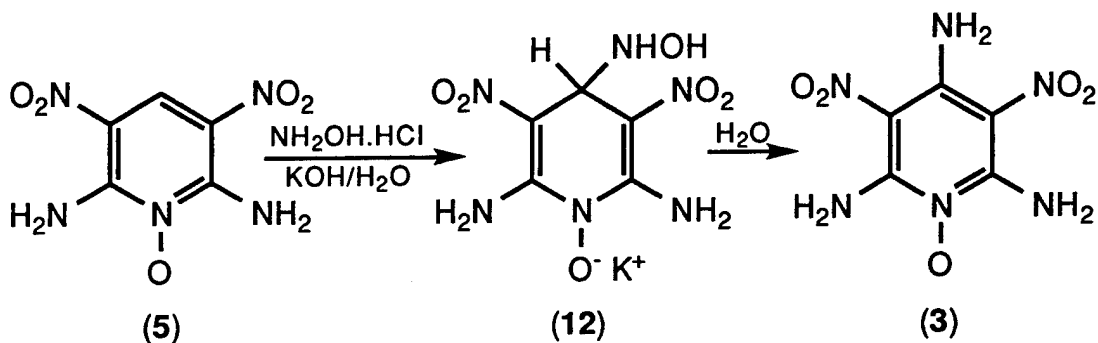
Once again, the initial structure assignment for **3** was made on the basis of its synthetic routes and its mass, IR and ^{1}H- and ^{13}C-NMR spectra. The mass spectrum showed a parent ion (and base peak) at 230, while the apparently simple IR spectrum showed the expected two distinct amines. This compound proved quite insoluble even in DMSO, and the NMR spectra had to be recorded at elevated temperature (345 K) to obtain adequate signal-to-noise ratio. Under these conditions two broad amine signals were observed in the ^{1}H-NMR spectrum in the ratio 1:2, indicating that rotation about the C-N bond was occurring, while the ^{13}C-NMR spectrum showed the expected three signals. As previously, confirmation of the assigned structure was obtained by single crystal X-ray structure determination on a crystal prepared from *N*-methyl-2-pyrrolidinone/dichloromethane, as shown in Figure 2. The details of the X-ray structure determination are included as Appendix B. The constituent atoms are essentially coplanar, and the molecular structure is essentially symmetrical; these features and the interatomic distance between the amine protons and the oxygen atoms of the adjacent nitro groups or the *N*-oxide functionality (1.9 to 2.0 Å in each case) indicate substantial intramolecular hydrogen bonding extending around the periphery of the molecule. Once again the individual molecules are assembled in planar sheets with intermolecular hydrogen bonding between amine protons and neighboring oxygen atoms, and the sheets are stacked one on top of the other to give a TATB-like structure. The resultant crystals have a density of 1.876 g/cm³, compared with the predicted value of 1.81

g/cm^3 (Reference 1). The hydrogen bonding responsible for this enhanced density is also manifested in the insensitivity and chemical stability of the material, which gave no response in a crude laboratory hammer/anvil screening test and gave 10 of 10 no fires at a drop height of 200 cm in the Bureau of Mines drop weight impact test with a 2.5 kilogram (kg) drop weight and type 12 tools, and which melted with decomposition at 308°C.
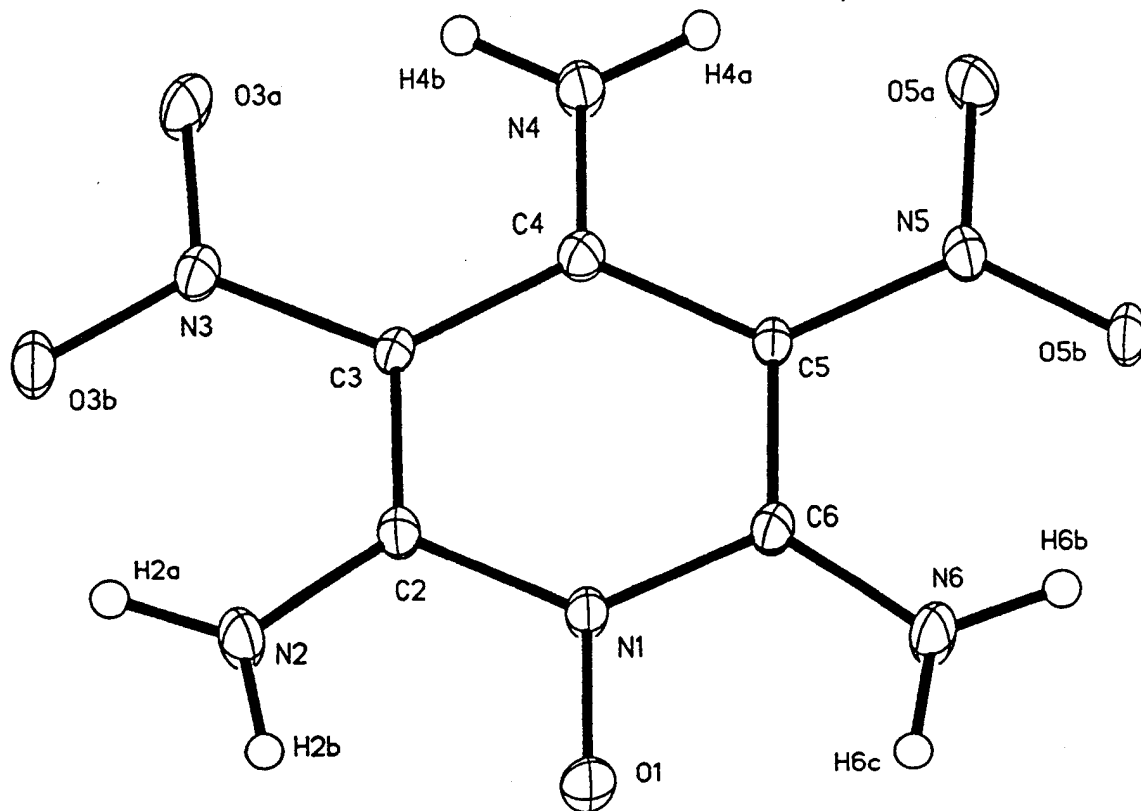
FIGURE 2. Structure of 3,5-Dinitro-2,4,6-triaminopyridine-1-oxide (3).

CONCLUSION

3,5-Dinitro-2,4,6-triaminopyridine-1-oxide has been prepared by two synthetic routes, namely oxidation of 3,5-dinitro-2,4,6-triaminopyridine using 30% aqueous hydrogen peroxide in acetic acid under reflux, and amination of 2,6-diamino-3,5-dinitropyridine-1-oxide using hydroxylamine in aqueous potassium hydroxide. Single crystal X-ray structure analysis reveals the

expected intramolecular and intermolecular hydrogen bonding, which results in a laminated planar crystal structure reminiscent of TATB and graphite. Consequences of this hydrogen bonding include high density (1.876 g/cm^3), insensitivity to impact (10/10 no fires at a drop height of 200 cm) and chemical stability manifested in a melting point of 308°C (dec). These results, together with predicted velocity of detonation of 8010 meters/second (m/s) and detonation pressure of 291 kilobars (kbar), give confidence that dense, powerful, but insensitive, energetic materials, coupling the insensitivity of TATB with the performance of RDX may be developed based on polyaminopolynitroazines and their *N*-oxides.

EXPERIMENTAL SECTION

WARNING: Compounds described in this report are potentially explosives, and 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. IR spectra were determined as KBr disks using a Perkin-Elmer Model 1330 spectrophotometer. ^{1}H-NMR spectra were determined in d$_6$-DMSO solutions (unless otherwise stated), using a Bruker AMX-400 instrument at 400 megahertz (MHz), while ^{13}C-NMR spectra were recorded on the same instrument at 100 MHz. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS).

2-AMINO-3,5-DINITROPYRIDINE (8)

2-Chloro-3,5-dinitropyridine (7) (0.25 g, 1.23 millimoles (mmol)) was added to liquid ammonia (*ca.* 30 milliliters (mL)) at -76°C, and the mixture was then stirred at reflux temperature (-33°C) for *ca.* 90 minutes (min). Methanol (30 mL) was added slowly through the condenser, and the solution was allowed to warm to ambient temperature while the ammonia evaporated. Evaporation to dryness and flash chromatography (silica/dichloromethane) gave 2-amino-3,5-dinitro-pyridine (8) (0.19 g, 84%), recrystallized from methanol as a pale yellow solid, m.p. 187-189°C (lit. 190-192°C (Reference 16)). IR: 3410, 3290, 3150, 3080, 1660, 1580, 1500, 1420, 1330, 1270 cm^{-1}. ^{1}H-NMR (d$_6$-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$_2$).

3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE (6)

(1) 2-Chloro-3,5-dinitropyridine (7) (1.0 g, 4.91 mmol) was dissolved in liquid ammonia (*ca.* 100 mL), and potassium permanganate (2.0 g, 12.66 mmol) was added. The mixture was stirred at reflux temperature (-33°C) for 8 h, and then allowed to warm to ambient temperature overnight as the ammonia evaporated. The solid residue was slurried with water (100 mL), and the slurry was subjected to continuous extraction with chloroform for *ca.* 10 days. Cooling the extract and filtration gave a pale yellow solid (0.34 g), containing (6) (80%) and (8) (20%). Extraction by refluxing twice in methanol (100 mL) removed the diamine **8**, and the residue (0.19 g; 30%) was recrystallized from *N*-methyl-2-pyrrolidinone/dichloromethane to give dark crystals of 3,5-dinitro-2,4,6-triamino-pyridine (6), m.p. 353°C (dec) (lit. 342°C (dec) (Reference 8)). IR: 3500, 3380, 3360, 3250, 1650, 1600, 1540, 1480, 1260, 1220, 1170, 1040, 790. 700, 570 cm^{-1}. ^{1}H-NMR: 10.42 (br s, -NH$_2$), 8.73 (br s, 2 -NH's), 8.20 (br s, 2 -NH's). ^{13}C-NMR: 110.02 (C$_{3,5}$), 151.20 (C$_4$), 155.80 (C$_{2,6}$). M/z: 214 (parent ion and base peak), 184, 138.

(2) 2,6-Diamino-3,5-dinitropyridine (8) (0.40 g, 2.0 mmol) was dissolved in liquid ammonia (*ca.* 30 mL), and potassium permanganate (1.00 g, 6.33 mmol) was added. The mixture was stirred at reflux temperature (-33°C) for 8 h, and then allowed to warm to ambient temperature overnight as the ammonia evaporated. The solid residue was slurried with water (50 mL), and the slurry was subjected to continuous extraction with chloroform for *ca.* 6 days. Cooling and filtration gave a yellow solid (0.26 g, 61%) identified by ^{1}H-NMR as **6** contaminated with *ca.* 2% of **8**, which was removed by refluxing in methanol (100 mL).

(3) Potassium hydroxide (2.00 g, 35.7 mmol) was dissolved in water (20 mL) and cooled in an ice bath. Hydroxylamine hydrochloride (0.20 g, 2.88 mmol) was added slowly, followed by 2,6-diamino-3,5-dinitropyridine (8) (0.20 g, 1.0 mmol). The reaction mixture was stirred at ice bath temperature for 5 h, and then filtered to yield a yellow solid identified by ^{1}H- and ^{13}C-NMR as a 2:1 mixture of **6** and unreacted **8**, which were separated by repeated fractional crystallization from methanol. The overall yield by this route is 37% (or 46% based on consumption of **8**); the procedure described in (2) is clearly superior.

SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE

C$_5$H$_6$N$_6$O$_4$, F.W. 214.2, monoclinic space group P2$_1$/c, a = 16.958(2), b = 8.934(2), c = 10.351(2) Å, ß = 94.30(2)°, V = 1563.7(5) Å^3, Z = 8, ρcalc = 1.819 g/cm^3, λ(CuKα) = 1.54178 Å, μ = 1.385 mm^{-1}, F(000) = 880, T = 293 K.

A clear pale-yellow parallelepiped 0.15 x 0.18 x 0.25 millimeter (mm) was used for data collection on an automated Siemens P4 diffractometer equipped with an incident beam monochromator. The data collection range of hkl was: $0 \leq h \leq 18$, $-9 \leq k \leq 0$, $-11 \leq l \leq 11$, with $[(\sin\theta)/\lambda]_{max} = 0.594$. Three standards, measured every 97 reflections, exhibited random variations during the data collection. A set of 2210 reflections was collected in the ω scan mode, with scan width $[\omega(K_{\alpha 1}) - 0.6]$ to $[\omega(K_{\alpha 2}) + 0.6]°$ and ω scan rate from 3.00 to 30.00°/min. There were 2046 independent reflections, and 1476 were observed with $F > 3\sigma(F)$. The structure was solved and refined with the aid of the SHELXTL system of programs (Reference 17). The full-matrix least squares refinement varied 309 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model. Final residuals were $R = 0.0465$ and $wR = 0.0526$, with goodness-of-fit of 1.55 and final Fourier excursions of 0.22 and -0.25 eÅ^{-3}. Results are detailed in Appendix A.

2,4-DIAMINO-3,5-DINITROPYRIDINE (11)

(1) Potassium hydroxide (1.00 g, 17.9 mmol) was dissolved in water (10 mL) and cooled in an ice bath. Hydroxylamine hydrochloride (0.10 g, 1.44 mmol) was added slowly, followed by 4-amino-3,5-dinitropyridine (10) (0.10 g, 0.54 mmol). The reaction mixture was stirred for *ca.* 3 h, and the resultant yellow solid (0.04 g, 37%) was filtered off. Washing twice with hot methanol gave an off-white solid identified as 2,4-diamino-3,5-dinitropyridine (11), m.p. 318°C (dec). A suitable recrystallization solvent was not found. IR: 3410, 3400, 3300, 1630, 1610, 1550, 1370, 1340, 1270, 1230, 1010, 790, 680, 640 cm^{-1}. ^{1}H-NMR: 8.90 (s, H$_6$), 9.04 (br s, -NH$_2$), 9.36, 9.41(br s (overlapping), -NH's). ^{13}C-NMR: 113.73 (C$_3$), 122.25 (C$_5$), 147.86 (C$_4$), 153.58 (C$_6$), 157.81 (C$_2$). M/z: 199 (parent ion and base peak), 182, 169, 136, 123.

(2) 4-Amino-3,5-dinitropyridine (10) (0.40 g, 2.16 mmol) and 4-amino-1,2,4-triazole (0.25 g, 2.98 mmol) were dissolved in dry DMSO (10 mL) at ambient temperature. Potassium tert.-butoxide (0.50 g, 4.46 mmol) in DMSO (10 mL) was added dropwise at ambient temperature, and the reaction mixture was stirred for *ca.* 3 h. Quenching with saturated ammonium chloride solution (50 mL) and filtration gave an off-white solid, which was washed twice with hot methanol to give 2,4-diamino-3,5-dinitropyridine (11) (0.13 g, 30%), m.p. 310-312°C.

3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE-1-OXIDE (3)

(1) 3,5-Dinitro-2,4,6-triaminopyridine (6) (0.150 g, 0.70 mmol) was suspended in glacial acetic acid (5 mL), and 30% aqueous hydrogen peroxide (0.5 mL) was added dropwise at ambient temperature. The reaction mixture was

heated under reflux for 4 h, and was then cooled and filtered to give a yellow solid (0.90 g, 60%) identified as unreacted starting material (6). The mother liquors were diluted with water (*ca.* 40 mL) and left standing at ambient temperature overnight. Filtration and washing with water and ethanol gave a yellow solid (0.017 g, 10% (or 27% based on starting material consumed)), identified by IR as 3,5-dinitro-2,4,6-triaminopyridine-1-oxide (3). Increasing the reaction time to 2 days had no effect on the yield of product or recovered starting material.

(2) Potassium hydroxide (10.00 g, 179 mmol) was dissolved in water (80 mL) and cooled in an ice bath. Hydroxylamine hydrochloride (1.00 g, 14.4 mmol) was added in portions, followed by 2,6-diamino-3,5-dinitropyridine-1-oxide (5) (1.00 g, 4.67 mmol). The reaction mixture was stirred at ice bath temperature for 1 h. Filtration gave a yellow solid (0.50 g) presumed to be an intermediate Meisenheimer complex (IR: 3390, 3280, 3200, 1600, 1580, 1400, 1300, 1230, 1190, 1150, 920, 895, 770, 700 cm^{-1}); acidification of the mother liquors with 5% hydrochloric acid gave a yellow solid (0.34 g, 34%) identified as recovered starting material (5). The product was stirred in water (40 mL) at ambient temperature overnight to give an extremely fine yellow solid (0.41 g, 39% (or 59% based on starting material consumed)). Recrystallization from *N*-methyl-2-pyrrolidinone/dichloromethane gave 3,5-dinitro-2,4,6-triamino-pyridine-1-oxide (3) as almost black crystals, m.p. 308°C (dec). IR: 3420, 3380, 3300, 3260, 1630, 1605, 1495, 1290, 1220, 1190, 1070, 1040, 770, 700, 620 cm^{-1}. ^{1}H-NMR (at 70°C): 8.82 (br s, 2 -NH$_2$'s), 9.94 (br s, -NH$_2$). ^{13}C-NMR (at 65°C): 108.52 (C$_{3,5}$), 145.81 (C$_4$), 148.66 (C$_{2,6}$). M/z: 230 (parent ion and base peak), 214, 198, 184, 166, 138.

SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE-1-OXIDE

C$_5$H$_6$N$_6$O$_5$, F.W. 2230.16, monoclinic space group P2$_1$/c, a = 8.515(2), b = 8.983(2), c = 10.731(2) Å, ß = 96.960(10)°, V = 814.8(3) Å^3, Z = 4, ρ_{calc} = 1.876 g/cm^3, λ(CuKα) = 1.54178Å, μ = 1.478 mm^{-1}, F(000) = 472, T = 293 K.

A clear orange parallelepiped 0.50 x 0.26 x 0.25 mm 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: $0 \le h \le 9$, $0 \le k \le 9$, $-11 \le l \le 11$, with [(sinθ)/λ]$_{max}$ = 0.594. Three standards, measured every 97 reflections, exhibited random variations during the data collection. A set of 1246 reflections was collected in the ω scan mode, with scan width [ω(K$_{\alpha 1}$) - 0.6] to [ω(K$_{\alpha 2}$ + 0.6]° and ω scan rate from 4.99 to 26.04°/min. There were 1116 independent 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 17). The full-matrix least squares refinement varied 172

parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model. Final residuals were $R = 0.043$ and $wR = 0.117$, with goodness-of-fit of 1.178 and final Fourier excursions of 0.295 and -0.232 eÅ^{-3}. Results are detailed in Appendix B.

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Appendix A

DETAILS OF SINGLE-CRYSTAL X-RAY STRUCTURE ANALYSIS OF 3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE (6)

TABLE A-1. Crystal Data and Structure Refinement for 6.

Identification code	wils06z
Empirical formula	$C_5H_6N_6O_4$
Formula weight	214.16
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 16.9579(7)$ Å $\quad \alpha = 90°$
	$b = 8.9339(6)$ Å $\quad \beta = 94.298(5)°$
	$c = 10.3507(8)$ Å $\quad \gamma = 90°$
Volume, Z	1563.7(2) Å^3, 8
Density (calculated)	1.819 Mg/m^3
Absorption coefficient	1.385 mm^{-1}
F(000)	880
Crystal size	0.17 x 0.2 x 0.4 mm
θ range for data collection	2.61 to 55.98°
Limiting indices	$0 \le h \le 18, -9 \le k \le 0, -11 \le l \le 11$
Reflections collected	2046
Independent reflections	2046 ($R_{int} = 0.0000$)
Absorption correction	Integration
Max. and min. transmission	0.8143 and 0.5416
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2045 / 0 / 309
Goodness-of-fit on F^2	0.986
Final R indices [I>2σ(I)]	R1 = 0.0466, wR2 = 0.1251
R indices (all data)	R1 = 0.0670, wR2 = 0.1447
Extinction coefficient	0.00016(10)
Largest diff. peak and hole	0.240 and -0.259 eÅ^{-3}

TABLE A-2. Atomic Coordinates (x10^4) and Equivalent Isotropic
Displacement Parameters (Å^2 x 10^3) for **6**. U(eq) is defined as
one-third of the trace of the orthogonalized U$_{ij}$ tensor.

	x	y	z	U(eq)
N(1)	3216(1)	2090(2)	1243(2)	28(1)
C(2)	3639(2)	2781(3)	384(2)	27(1)
N(2)	3625(2)	4254(3)	425(2)	40(1)
C(3)	4071(1)	1966(3)	-530(2)	25(1)
N(3)	4547(1)	2727(3)	-1377(2)	31(1)
O(3A)	4572(1)	4117(2)	-1377(2)	46(1)
O(3B)	4947(1)	2024(2)	-2131(2)	46(1)
C(4)	4008(1)	355(3)	-573(2)	25(1)
N(4)	4347(2)	-425(3)	-1455(2)	36(1)
C(5)	3558(2)	-335(3)	381(2)	26(1)
N(5)	3475(1)	-1902(3)	430(2)	35(1)
O(5A)	3117(1)	-2511(2)	1291(2)	49(1)
O(5B)	3764(2)	-2701(2)	-399(2)	59(1)
C(6)	3181(2)	594(3)	1298(2)	26(1)
N(6)	2762(2)	62(3)	2224(2)	37(1)
N(11)	1824(1)	2164(2)	3827(2)	28(1)
C(12)	1400(2)	1461(3)	4691(2)	28(1)
N(12)	1457(2)	-15(3)	4680(3)	47(1)
C(13)	936(2)	2270(3)	5553(2)	27(1)
N(13)	484(1)	1477(3)	6425(2)	32(1)
O(13A)	478(1)	88(2)	6425(2)	45(1)
O(13B)	86(1)	2163(2)	7193(2)	48(1)
C(14)	955(1)	3873(3)	5561(2)	27(1)
N(14)	582(2)	4659(3)	6401(2)	37(1)
C(15)	1408(2)	4573(3)	4607(2)	26(1)
N(15)	1454(1)	6144(3)	4530(2)	34(1)
O(15A)	1844(1)	6760(2)	3708(2)	46(1)
O(15B)	1101(1)	6943(2)	5289(2)	55(1)
C(16)	1828(2)	3664(3)	3753(2)	26(1)
N(16)	2261(1)	4201(3)	2839(2)	32(1)

TABLE A-3. Bond Lengths (Å) and Angles (°) for **6**.

N(1)-C(2)	1.335(3)	N(1)-C(6)	1.340(3)
C(2)-N(2)	1.316(3)	C(2)-C(3)	1.438(3)
C(3)-N(3)	1.409(3)	C(3)-C(4)	1.444(4)
N(3)-O(3A)	1.242(3)	N(3)-O(3B)	1.243(3)
C(4)-N(4)	1.314(3)	C(4)-C(5)	1.431(3)
C(5)-N(5)	1.408(3)	C(5)-C(6)	1.445(3)
N(5)-O(5A)	1.240(3)	N(5)-O(5B)	1.245(3)
C(6)-N(6)	1.323(3)	N(11)-C(16)	1.342(4)
N(11)-C(12)	1.345(3)	C(12)-N(12)	1.323(4)
C(12)-C(13)	1.429(3)	C(13)-N(13)	1.417(3)
C(13)-C(14)	1.433(4)	N(13)-O(13A)	1.241(3)
N(13)-O(13B)	1.242(3)	C(14)-N(14)	1.316(3)
C(14)-C(15)	1.439(3)	C(15)-N(15)	1.408(3)
C(15)-C(16)	1.429(3)	N(15)-O(15A)	1.244(3)
N(15)-O(15B)	1.247(3)	C(16)-N(16)	1.330(3)
C(2)-N(1)-C(6)	121.2(2)	N(2)-C(2)-N(1)	115.4(2)
N(2)-C(2)-C(3)	122.6(2)	N(1)-C(2)-C(3)	122.0(2)
N(3)-C(3)-C(2)	120.6(2)	N(3)-C(3)-C(4)	120.5(2)
C(2)-C(3)-C(4)	119.0(2)	O(3A)-N(3)-O(3B)	118.9(2)
O(3A)-N(3)-C(3)	120.3(2)	O(3B)-N(3)-C(3)	120.8(2)
N(4)-C(4)-C(5)	122.3(3)	N(4)-C(4)-C(3)	120.9(2)
C(5)-C(4)-C(3)	116.8(2)	N(5)-C(5)-C(4)	120.8(2)
N(5)-C(5)-C(6)	119.8(2)	C(4)-C(5)-C(6)	119.4(2)
O(5A)-N(5)-O(5B)	118.8(2)	O(5A)-N(5)-C(5)	121.2(2)
O(5B)-N(5)-C(5)	120.0(2)	N(6)-C(6)-N(1)	114.7(2)
N(6)-C(6)-C(5)	123.9(3)	N(1)-C(6)-C(5)	121.4(2)
C(16)-N(11)-C(12)	120.6(2)	N(12)-C(12)-N(11)	114.6(2)
N(12)-C(12)-C(13)	123.6(2)	N(11)-C(12)-C(13)	121.7(2)
N(13)-C(13)-C(12)	119.6(2)	N(13)-C(13)-C(14)	120.6(2)
C(12)-C(13)-C(14)	119.7(2)	O(13A)-N(13)-O(13B)	119.2(2)
O(13A)-N(13)-C(13)	120.3(2)	O(13B)-N(13)-C(13)	120.5(2)
N(14)-C(14)-C(13)	121.7(2)	N(14)-C(14)-C(15)	122.0(3)
C(13)-C(14)-C(15)	116.3(2)	N(15)-C(15)-C(16)	119.9(2)
N(15)-C(15)-C(14)	120.4(2)	C(16)-C(15)-C(14)	119.6(2)
O(15A)-N(15)-O(15B)	118.8(2)	O(15A)-N(15)-C(15)	120.9(2)
O(15B)-N(15)-C(15)	120.2(2)	N(16)-C(16)-N(11)	114.0(2)
N(16)-C(16)-C(15)	124.2(2)	N(11)-C(16)-C(15)	121.8(2)

TABLE A-4. Anisotropic Displacement Parameters ($Å^2$ x 10^3) for **6**.
The anisotropic displacement factor exponent takes the form:
$$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2\, hka^*b^* U_{12}].$$

	U11	U22	U33	U23	U13	U12
N(1)	37(1)	19(1)	30(1)	2(1)	17(1)	0(1)
C(2)	34(2)	22(2)	26(1)	-2(1)	7(1)	-1(1)
N(2)	61(2)	16(1)	47(2)	0(1)	31(1)	-1(1)
C(3)	30(2)	21(2)	26(1)	2(1)	10(1)	-3(1)
N(3)	35(1)	28(1)	33(1)	1(1)	14(1)	-3(1)
O(3A)	62(1)	23(1)	57(1)	3(1)	32(1)	-8(1)
O(3B)	54(1)	36(1)	52(1)	-3(1)	36(1)	-1(1)
C(4)	26(1)	27(2)	24(1)	-1(1)	7(1)	4(1)
N(4)	48(2)	25(1)	37(1)	-5(1)	23(1)	4(1)
C(5)	31(2)	16(2)	30(1)	2(1)	10(1)	2(1)
N(5)	49(2)	24(1)	36(1)	3(1)	17(1)	1(1)
O(5A)	76(2)	22(1)	54(1)	5(1)	37(1)	-4(1)
O(5B)	102(2)	19(1)	61(1)	-7(1)	48(1)	6(1)
C(6)	32(2)	22(1)	27(1)	0(1)	8(1)	0(1)
N(6)	54(2)	25(1)	37(1)	2(1)	28(1)	2(1)
N(11)	35(1)	21(1)	30(1)	0(1)	16(1)	-2(1)
C(12)	33(2)	23(2)	30(1)	0(1)	9(1)	0(1)
N(12)	69(2)	20(1)	56(2)	-2(1)	44(2)	1(1)
C(13)	31(2)	24(1)	28(1)	2(1)	13(1)	1(1)
N(13)	35(1)	29(1)	34(1)	1(1)	12(1)	1(1)
O(13A)	59(1)	26(1)	55(1)	6(1)	31(1)	-5(1)
O(13B)	61(1)	38(1)	49(1)	2(1)	38(1)	0(1)
C(14)	27(1)	29(2)	26(1)	-2(1)	6(1)	8(1)
N(14)	50(2)	27(1)	37(1)	0(1)	23(1)	7(1)
C(15)	30(2)	20(2)	28(1)	1(1)	9(1)	4(1)
N(15)	42(2)	24(1)	38(1)	-2(1)	18(1)	-1(1)
O(15A)	64(1)	24(1)	55(1)	4(1)	34(1)	-3(1)
O(15B)	83(2)	21(1)	67(2)	-5(1)	47(1)	3(1)
C(16)	29(2)	22(2)	26(1)	1(1)	6(1)	-2(1)
N(16)	43(2)	24(1)	33(1)	1(1)	23(1)	1(1)

TABLE A-5. Hydrogen Coordinates (x 10^4) and Isotropic
Displacement Parameters (Å^2 x 10^3) for **6.**

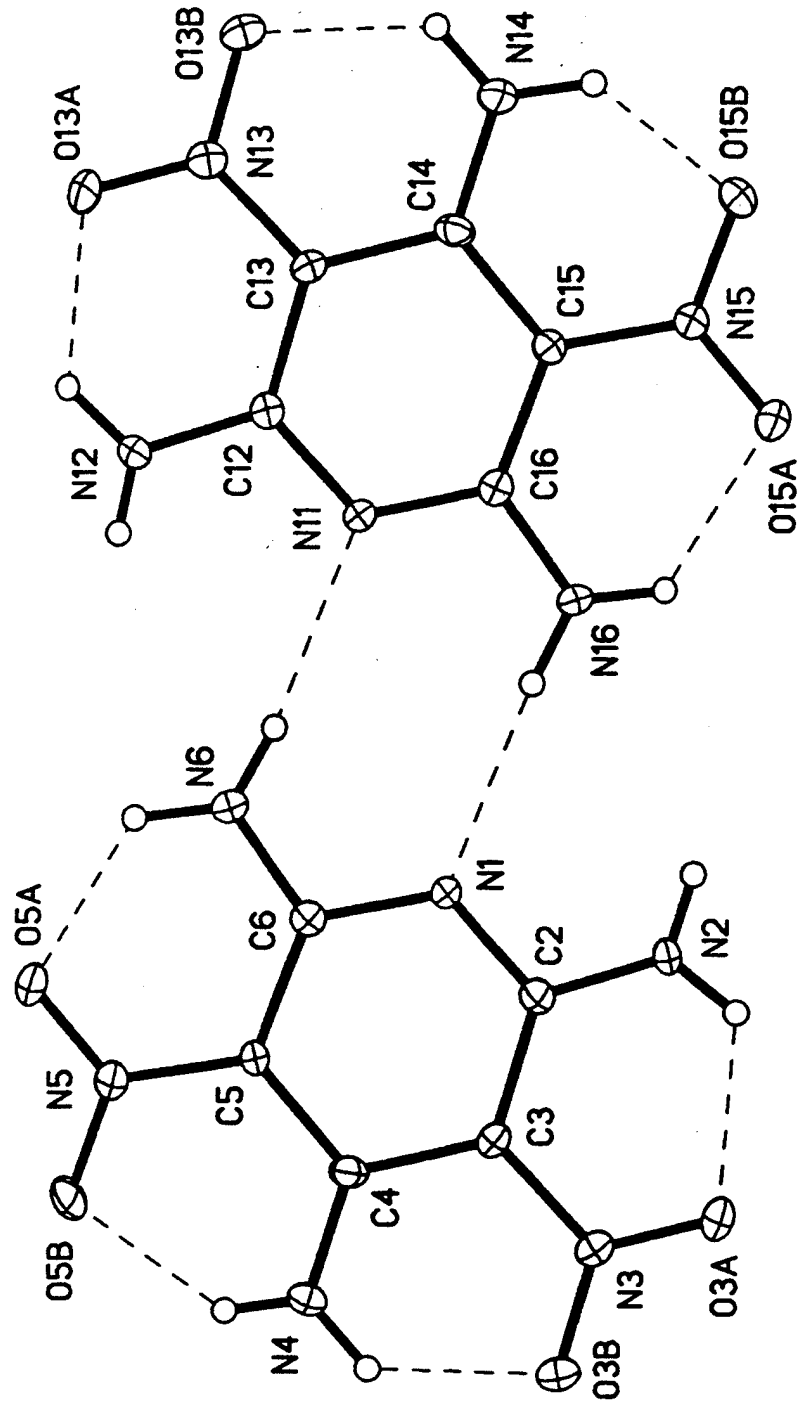|	x	y	z	U(eq)
H(2A)	3375(18)	4745(38)	928(30)	46(3)
H(2B)	3861(19)	4840(37)	-106(29)	46(3)
H(4A)	4269(17)	-1346(39)	-1461(28)	46(3)
H(4B)	4635(17)	26(34)	-2029(29)	46(3)
H(6A)	2548(18)	738(37)	2675(29)	46(3)
H(6B)	2737(17)	-942(38)	2336(28)	46(3)
H(12A)	1724(18)	-397(38)	4184(30)	46(3)
H(12B)	1166(18)	-583(37)	5223(29)	46(3)
H(14A)	640(17)	5678(39)	6336(27)	46(3)
H(14B)	309(18)	4184(36)	6973(29)	46(3)
H(16A)	2495(17)	3536(39)	2344(28)	46(3)
H(16B)	2260(17)	5187(38)	2679(28)	46(3)

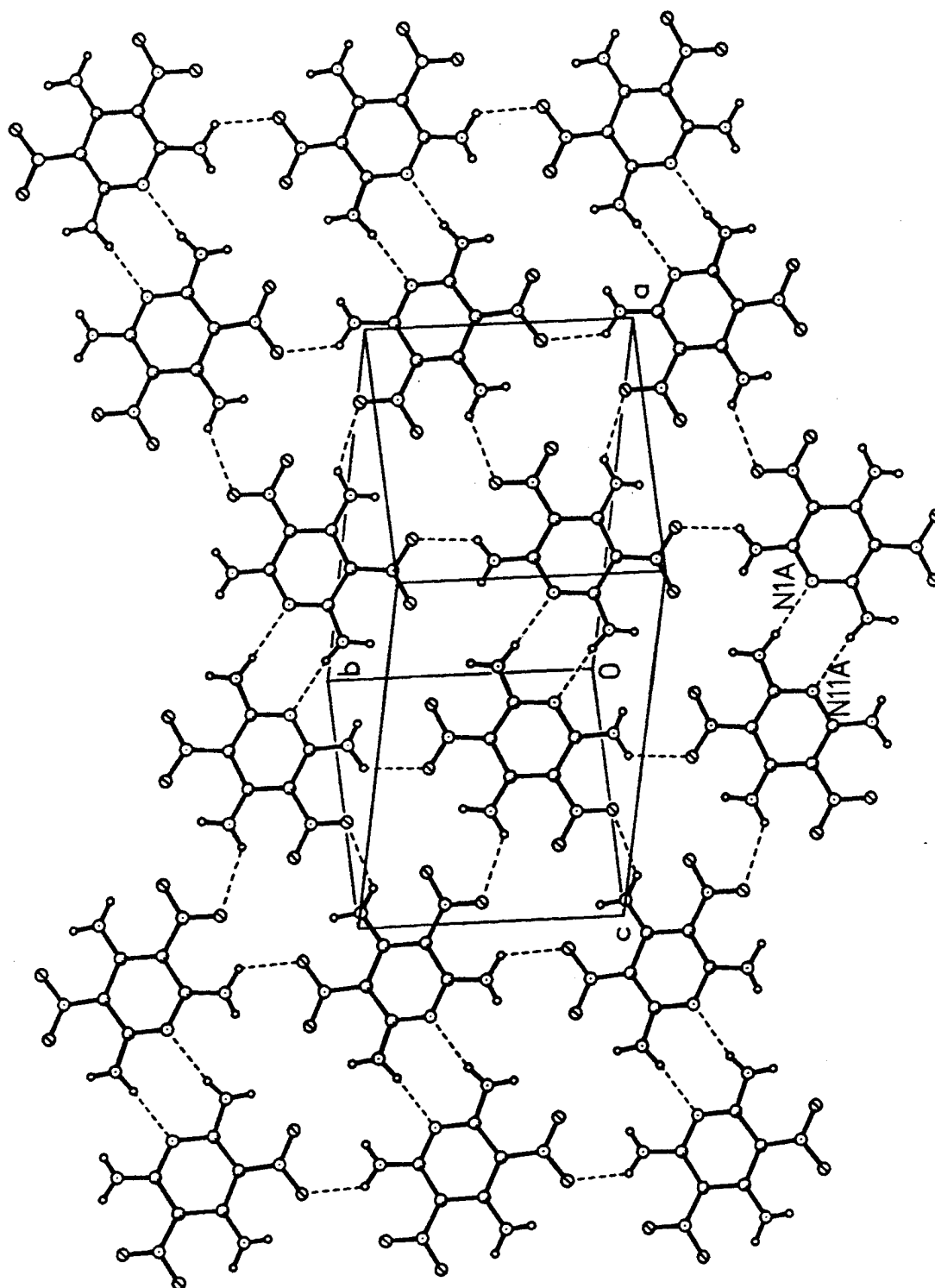FIGURE A-1. Structure of 3,5-Dinitro-2,4,6-triaminopyridine (6).

FIGURE A-2. Planar Array Showing Strong Intermolecular Hydrogen Bonding.
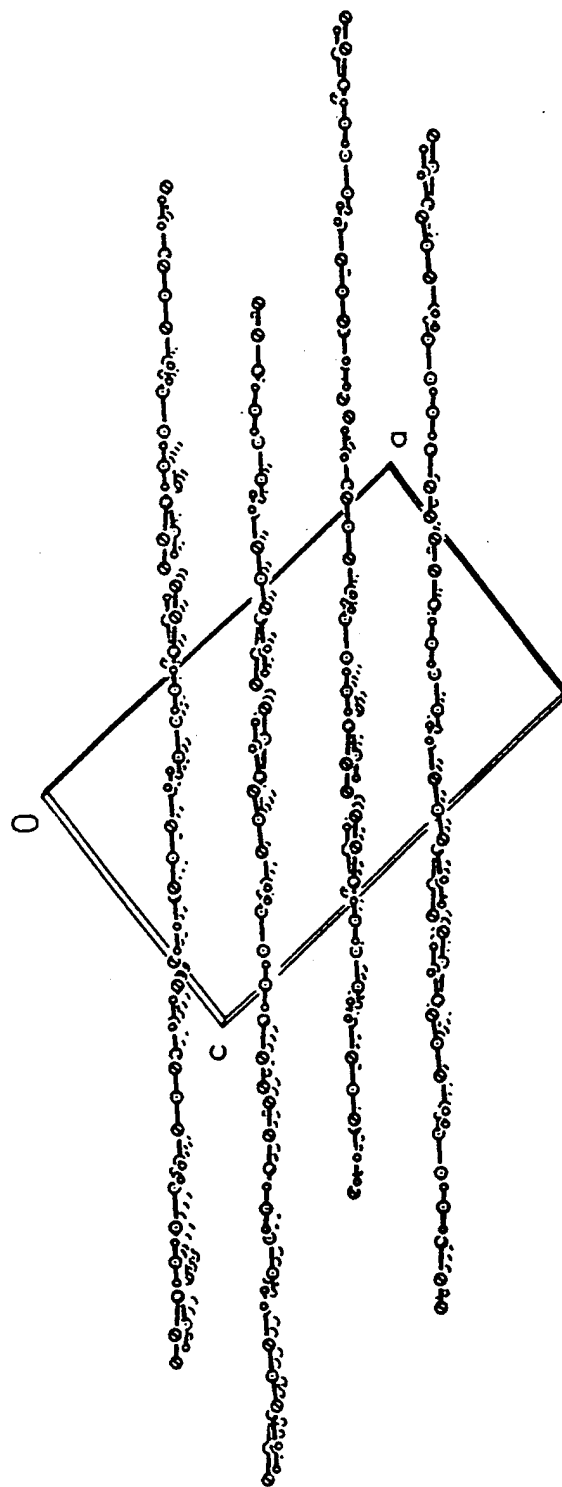
FIGURE A-3. View of Full Structure Looking in the y-Direction (b-axis), Showing Parallel Stacking.

Appendix B

DETAILS OF SINGLE CRYSTAL X-RAY STRUCTURE ANALYSIS OF 3,5-DINITRO-2,4,6-TRIAMINOPYRIDINE-1-OXIDE (3)

TABLE B-1. Crystal Data and Structure Refinement for **3.**

Identification code	wils03d
Empirical formula	$C_5H_6N_6O_5$
Formula weight	230.16
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.515(2)$ Å $\alpha = 90°$
	$b = 8.983(2)$ Å $\beta = 96.960(10)°$
	$c = 10.731(2)$ Å $\gamma = 90°$
Volume	814.8(3) $Å^3$
Z	4
Density (calculated)	1.876 Mg/m^3
Absorption coefficient	1.478 mm^{-1}
F(000)	472
Crystal size	.50 x .26 x .25 mm
θ range for data collection	5.23 to 57.46°
Index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 9$, $-11 \leq l \leq 11$
Reflections collected	1246
Independent reflections	1116 ($R_{int} = 0.0194$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1116 / 0 / 172
Goodness-of-fit on F^2	1.178
Final R indices [I>2σ(I)]	R1 = 0.0430, wR2 = 0.1174
R indices (all data)	R1 = 0.0449, wR2 = 0.1203
Extinction coefficient	0.012(2)
Largest diff. peak and hole	0.295 and -0.232 $eÅ^{-3}$

TABLE B-2. Atomic Coordinates (x10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **3**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	1574(2)	3234(2)	6027(2)	29(1)
O(1)	846(2)	2450(2)	6855(1)	44(1)
C(2)	1542(2)	4749(2)	6112(2)	25(1)
N(2)	773(2)	5230(2)	7024(2)	35(1)
C(3)	2283(2)	5592(2)	5223(2)	25(1)
N(3)	2206(2)	7162(2)	5292(2)	31(1)
O(3A)	2921(2)	7942(2)	4590(2)	47(1)
O(3B)	1432(2)	7757(2)	6067(1)	45(1)
C(4)	3089(2)	4869(2)	4295(2)	25(1)
N(4)	3744(2)	5629(2)	3444(2)	36(1)
C(5)	3151(2)	3274(2)	4329(2)	25(1)
N(5)	3989(2)	2465(2)	3500(2)	30(1)
O(5A)	4751(2)	3132(2)	2748(1)	43(1)
O(5B)	3989(2)	1084(2)	3523(1)	43(1)
C(6)	2335(2)	2463(2)	5186(2)	27(1)
N(6)	2211(2)	1010(2)	5284(2)	39(1)

TABLE B-3. Hydrogen Coordinates (x 10⁴) and Isotropic Displacement Parameters ($Å^2$ x 10^3) for **3**.

	x	y	z	U(eq)
H(2A)	608(36)	6245(40)	7233(29)	73(9)
H(2B)	462(31)	4569(33)	7407(26)	53(9)
H(4A)	4249(29)	5163(29)	2909(23)	43(7)
H(4B)	3699(29)	6594(34)	3486(22)	45(7)
H(6C)	2697(29)	339(35)	4783(24)	58(8)
H(6A)	1670(28)	739(30)	5860(24)	45(7)

TABLE B-4. Bond Lengths (Å) and Angles (°) for **3.**

N(1)-O(1)	1.344(2)	N(1)-C(6)	1.363(2)
N(1)-C(2)	1.365(3)	C(2)-N(2)	1.315(3)
C(2)-C(3)	1.423(3)	C(3)-N(3)	1.414(3)
C(3)-C(4)	1.432(3)	N(3)-O(3A)	1.242(2)
N(3)-O(3B)	1.242(2)	C(4)-N(4)	1.317(3)
C(4)-C(5)	1.434(3)	C(5)-N(5)	1.408(2)
C(5)-C(6)	1.419(3)	N(5)-O(5B)	1.241(2)
N(5)-O(5A)	1.248(2)	C(6)-N(6)	1.315(3)
O(1)-N(1)-C(6)	117.8(2)	O(1)-N(1)-C(2)	117.7(2)
C(6)-N(1)-C(2)	124.5(2)	N(2)-C(2)-N(1)	113.2(2)
N(2)-C(2)-C(3)	128.7(2)	N(1)-C(2)-C(3)	118.1(2)
N(3)-C(3)-C(2)	117.9(2)	N(3)-C(3)-C(4)	121.2(2)
C(2)-C(3)-C(4)	120.9(2)	O(3A)-N(3)-O(3B)	120.1(2)
O(3A)-N(3)-C(3)	120.1(2)	O(3B)-N(3)-C(3)	119.8(2)
N(4)-C(4)-C(3)	121.7(2)	N(4)-C(4)-C(5)	121.2(2)
C(3)-C(4)-C(5)	117.1(2)	N(5)-C(5)-C(6)	118.0(2)
N(5)-C(5)-C(4)	121.4(2)	C(6)-C(5)-C(4)	120.7(2)
O(5B)-N(5)-O(5A)	119.6(2)	O(5B)-N(5)-C(5)	120.2(2)
O(5A)-N(5)-C(5)	120.2(2)	N(6)-C(6)-N(1)	113.7(2)
N(6)-C(6)-C(5)	127.8(2)	N(1)-C(6)-C(5)	118.5(2)

TABLE B-5. Anisotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for **63**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2\ hka^*b^*U_{12}]$.

|	U11	U22	U33	U23	U13	U12
N(1)	40(1)	18(1)	32(1)	0(1)	20(1)	-1(1)
O(1)	64(1)	26(1)	48(1)	5(1)	37(1)	-6(1)
C(2)	28(1)	21(1)	28(1)	-2(1)	7(1)	3(1)
N(2)	48(1)	27(1)	35(1)	-3(1)	22(1)	4(1)
C(3)	30(1)	15(1)	31(1)	-2(1)	8(1)	1(1)
N(3)	39(1)	18(1)	38(1)	-1(1)	11(1)	2(1)
O(3A)	67(1)	17(1)	63(1)	4(1)	32(1)	-3(1)
O(3B)	64(1)	23(1)	53(1)	-7(1)	27(1)	7(1)
C(4)	27(1)	22(1)	26(1)	0(1)	6(1)	0(1)
N(4)	50(1)	22(1)	40(1)	3(1)	24(1)	0(1)
C(5)	31(1)	18(1)	29(1)	-4(1)	10(1)	1(1)
N(5)	36(1)	23(1)	35(1)	-4(1)	14(1)	2(1)
O(5A)	56(1)	33(1)	49(1)	-1(1)	36(1)	0(1)
O(5B)	59(1)	19(1)	56(1)	-7(1)	28(1)	4(1)
C(6)	33(1)	18(1)	31(1)	-1(1)	9(1)	0(1)
N(6)	60(1)	17(1)	47(1)	1(1)	28(1)	-1(1)
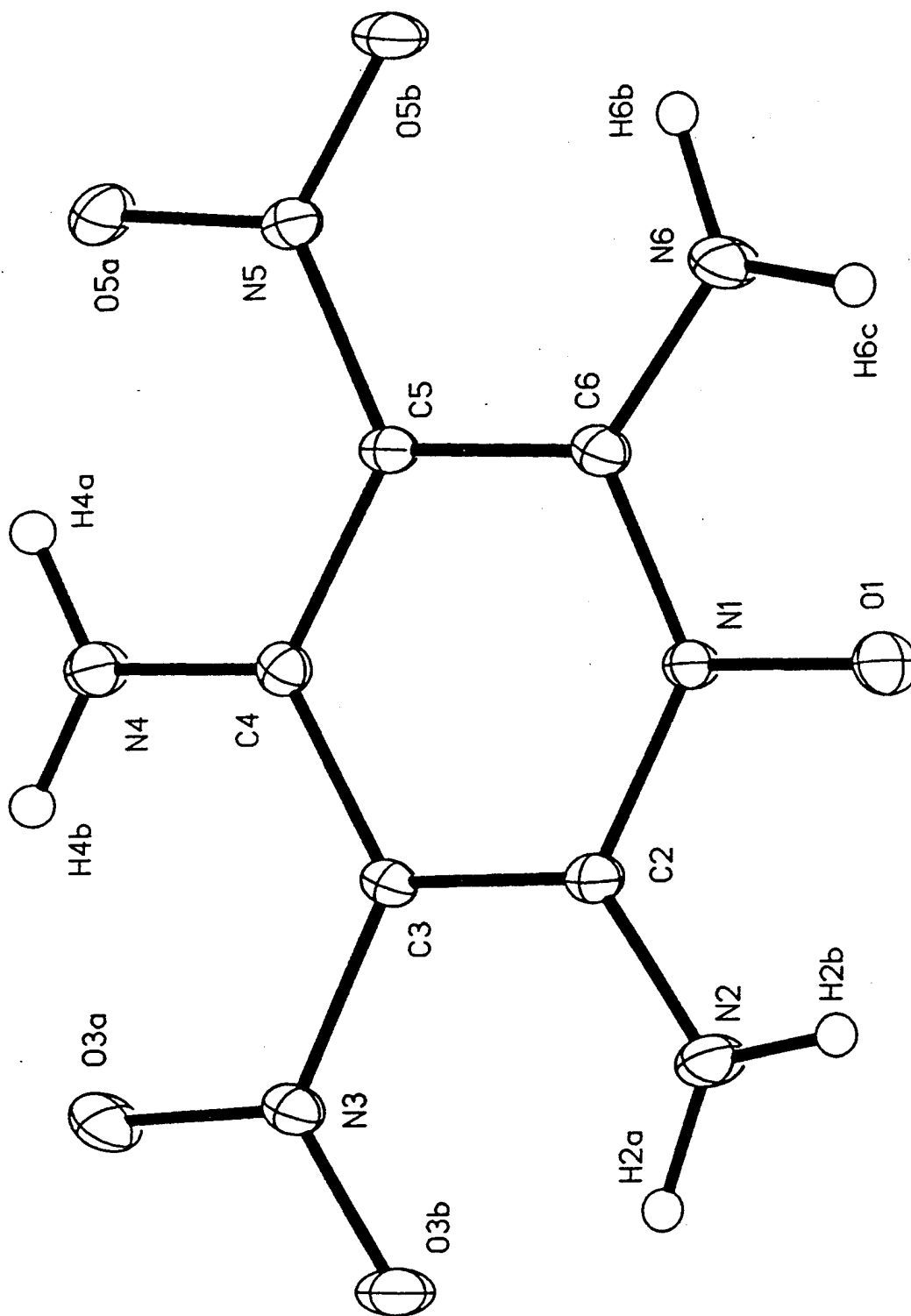
FIGURE B-1. Structure of 3,5-Dinitro-2,4,6-triaminopyridine-1-oxide (3).
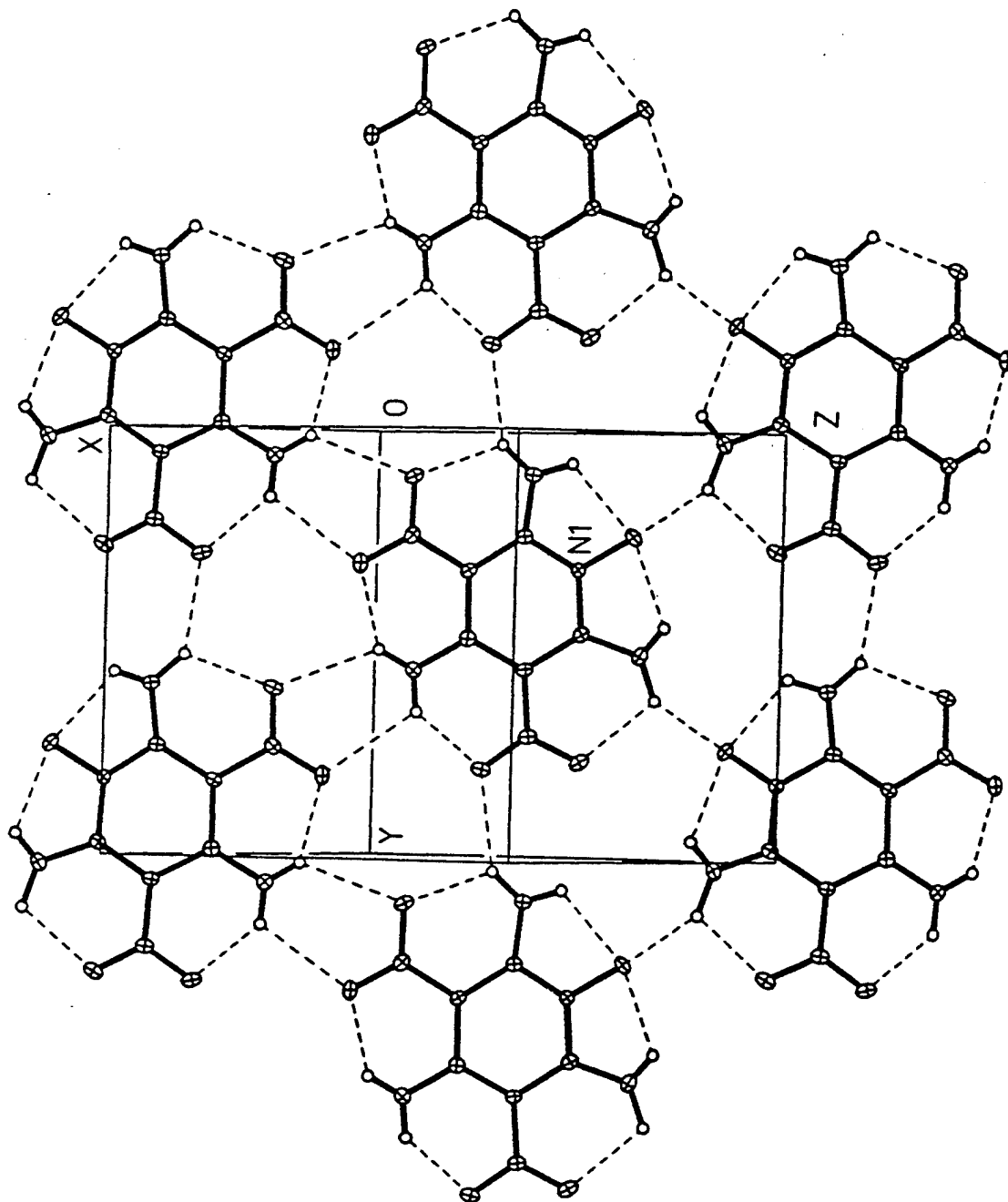
FIGURE B-2. Planar Array Showing Intramolecular and Intermolecular Hydrogen Bonding.
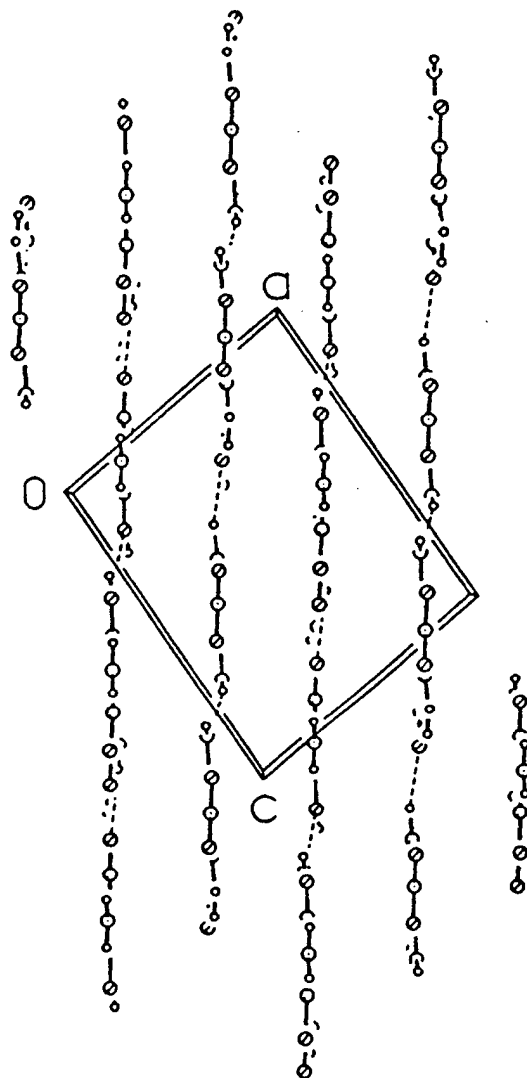
FIGURE B-3. View of Full Structure Looking in the y-Direction (b-axis), Showing Parallel Stacking.

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