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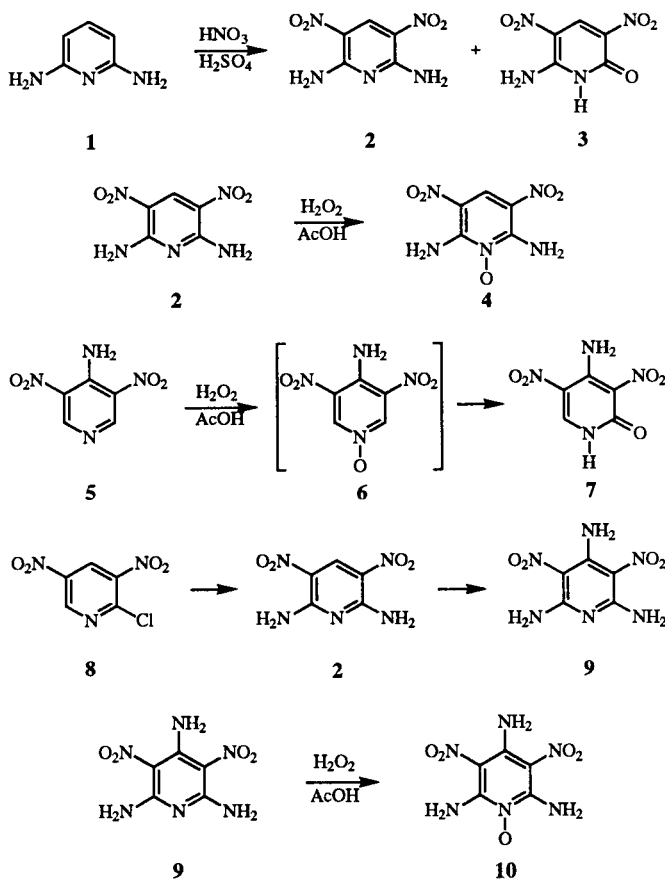
Dedicated to the memory of Professor Nicholas Alexandrou

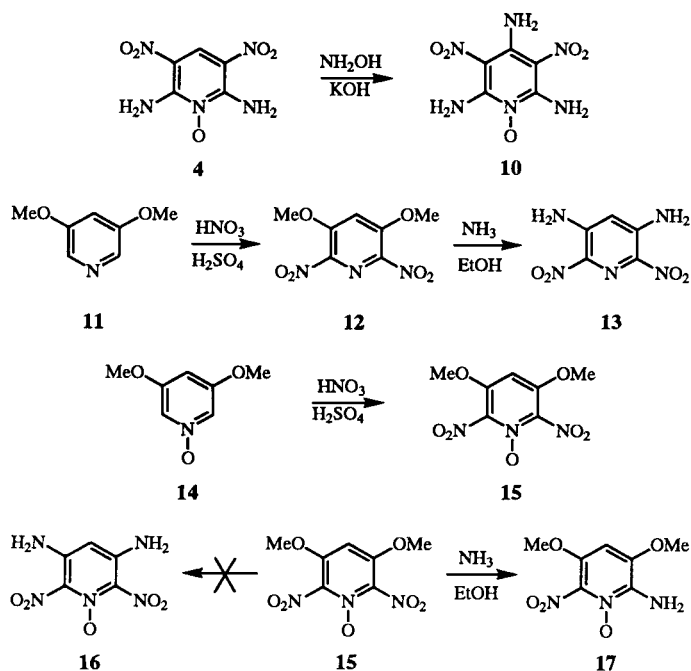
2,6-Diamino-3,5-dinitropyridine 1-oxide has been prepared by mixed acid nitration of 2,6-diaminopyridine, followed by oxidation using hydrogen peroxide in acetic acid. 3,5-Dinitro-2,4,6-triaminopyridine has been prepared by oxidative amination of 2-chloro-3,5-dinitropyridine or 2,6-diamino-3,5-dinitropyridine using potassium permanganate in liquid ammonia, or by "vicarious nucleophilic amination" of 2,6-diamino-3,5-dinitropyridine using hydroxylamine in aqueous potassium hydroxide. 3,5-Dinitro-2,4,6-triaminopyridine 1-oxide has been prepared by oxidation of 3,5-dinitro-2,4,6-triaminopyridine using hydrogen peroxide in acetic acid, and by "vicarious nucleophilic amination" of 2,6-diamino-3,5-dinitropyridine 1-oxide. Nmr spectroscopy and single crystal X-ray diffraction studies have shown that these compounds have the planar structures and intra- and inter-molecular hydrogen bonding necessary to confer on the materials the high density, the thermal and chemical stability, and the explosive insensitivity required for new insensitive energetic materials.

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As a generalization, those explosives which contribute to the performance of an energetic material also contain the "trigger linkages" at which explosive reaction is initiated [1]. As a consequence the most powerful explosives tend to be sensitive and unstable, while insensitive materials tend to be somewhat lacking in performance. There is, however, an ongoing requirement for dense and powerful but stable and insensitive materials, rugged enough to withstand the rigors of use and abuse, and yet powerful enough to accomplish the designated mission. A specific goal is the synthesis of energetic materials which match the performance of RDX (cyclotrimethylenetrinitramine) with the stability and insensitivity of TATB (2,4,6-triamino-1,3,5-trinitrobenzene). Individual molecules of TATB contain six stabilizing amino-to-nitro hydrogen bonds, which also serve to constrain the nitro groups to be essentially coplanar with the benzene ring. In the crystal, TATB is further stabilized by intermolecular hydrogen bonds which link each molecule to six neighboring molecules, thus forming infinite sheets [2]. These almost-planar sheets then stack to form dense laminar crystals reminiscent of graphite. One hypothesis to explain the insensitivity of TATB involves its lattice vibrational spectrum [3], which depends directly on this packing scheme. TATB displays a multitude of low-frequency lattice vibrations (primarily involving the bending and stretching of hydrogen bonds) which absorb energy efficiently, but this energy is transferred poorly to those higher-energy modes of motion (*e.g.* covalent bond vibrations) that can lead to bond dissociation and thus initiation of chemical reaction. Another hypothesis, not necessarily in conflict with the first, is that the presence of conjugated

electron donor and acceptor groups in TATB "buffers" the effect of local ionizing damage through electronic stabilization, rather than bond-breaking processes [4].





The approach we have taken to seek potentially superior materials is to combine the intrinsic stability of azines (pyridines, pyrimidines, *etc.*) with the alternating amino and nitro groups, and to enhance the oxygen balance and hence explosive performance by inclusion of the *N*-oxide functionality. Specific target molecules include 3,5-dinitro-2,4,6-triaminopyridine 1-oxide and 3,5-diamino-2,4,6-trinitropyridine 1-oxide.

Mixed acid nitration of 2- and 4-aminopyridines occurs smoothly to give the expected aminonitropyridines, usually through the intermediacy of the corresponding nitramine. In a like manner, treatment of 2,6-diaminopyridine (1) with 90% nitric acid in 96% sulfuric acid at 0-5° and then 60-65° gave a 60-65% yield of 2,6-diamino-3,5-dinitropyridine (2). The product was always accompanied by a trace of the pyridone 3 (in equilibrium with the corresponding 2-hydroxypyridine), generated by hydrolysis of an intermediate nitramine. It is believed that formation of 3 could probably be avoided by the use of 100% nitric

Table 1
Hydrogen Bond Parameters for 4, 9 and 10

1-2....3	R(1-2) (Å)	R(2...3) (Å)	A(1-2...3) (degrees)
4, Intramolecular:			
N(2)-H2a....O3a	0.86	2.14	120°
4, Intermolecular:			
N(2)-H2a....O3a'	0.86	2.44	121°
N(2)-H2b....O3b'	0.88	2.34	155°
C(4)-H4....O1'	0.90	2.36	180°
9, Intramolecular:			
N(2)-H2b....O3a	0.88	1.96	123°
N(4)-H4a....O5b	0.83	1.88	136°
N(4)-H4b....O3b	0.90	1.87	130°
N(6)-H6b....O5a	0.90	1.92	129°
N(12)-H12b....O13a	0.93	1.87	128°
N(14)-H14a....O15b	0.92	1.79	137°
N(14)-H14b....O13b	0.89	1.86	132°
N(16)-H16b....O15a	0.90	1.93	128°
9, Intermolecular:			
N(6)-H6a....N11	0.86	2.19	169°
N(2)-H2b....O5b'	0.88	2.22	130°
N(4)-H4b....O3a'	0.89	2.35	133°
N(16)-H16a....N1	0.90	2.16	172°
N(12)-H12b....O15b'	0.93	2.21	127°
N(14)-H14b....O13a'	0.89	2.35	131°
10, Intramolecular:			
N(2)-H2a....O3b	0.96	2.04	114°
N(2)-H2b....O1	0.79	2.03	119°
N(4)-H4a....O5a	0.87	1.88	132°
N(4)-H4b....O3a	0.87	1.87	135°
N(6)-H6a....O1	0.85	2.05	114°
N(6)-H6c....O5b	0.94	1.97	120°
10, Intermolecular:			
N(2)-H2a....O1'	0.96	1.98	139°
N(4)-H4a....O5b'	0.87	2.42	130°
N(4)-H4b....O5a'	0.87	2.42	121°
N(6)-H6c....O3a'	0.94	2.17	138°

estimated standard deviations: 0.03 Å 0.03 Å 2.0-2.5°

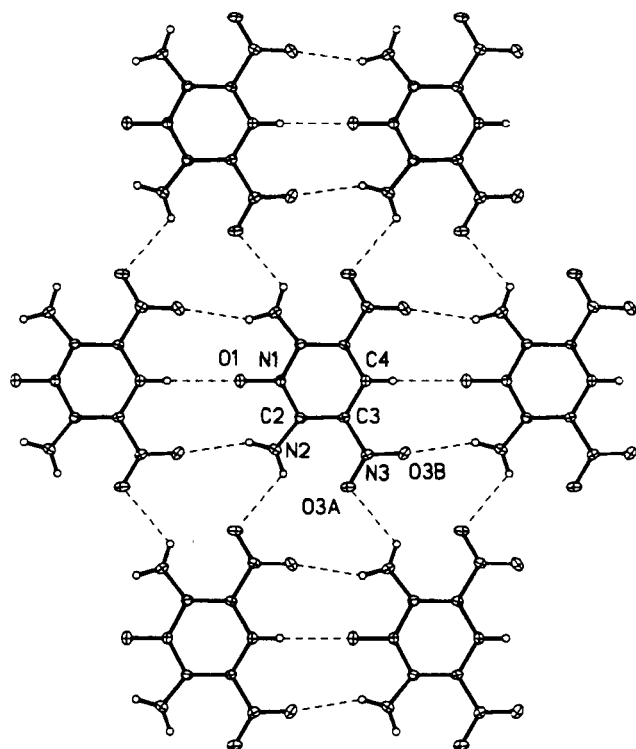


Figure 1. A thermal ellipsoid drawing showing the molecular structure of 4 and all of its hydrogen-bonded neighbors in the crystal. One half of 4 is labelled, the other is related by a 2-fold axis passing through C4 & N1. Along the 2-fold axis, which is also the b axis of the unit cell, the central molecule is linked to adjacent molecules by strong short hydrogen bonds; weaker amino-nitro hydrogen bonds extend to the molecules at the top and bottom of the figure, forming a planar sheet.

acid, but it was satisfactorily removed by washing the nitration product with aqueous alkali. Oxidation of **2** with 30% aqueous hydrogen peroxide in acetic acid under reflux afforded 2,6-diamino-3,5-dinitropyridine 1-oxide (**4**) in 80% yield. The product was always contaminated with 5% of **2**. Extended reaction times and more vigorous conditions gave the same mixture of compounds, but in reduced yield; however recrystallization from trifluoroacetic acid removed all traces of unreacted starting material.

The synthetic sequence to **4** has recently been described by Ritter and Licht [5]. Those authors also reported that oxidation of 4-amino-3,5-dinitropyridine (**5**) using 30% hydrogen peroxide in acetic acid at ambient temperature afforded the *N*-oxide **6**. In our hands, however, the reaction product was 4-amino-3,5-dinitro-2-pyridone (**7**); the infrared spectrum resembled pyridones such as **3** rather than the *N*-oxide **4**, the ^1H nmr spectrum showed a broad one-proton signal at 11.18, a sharp one-proton singlet at 8.45, and a broad two-proton signal at 8.32 ppm, and the ^{13}C nmr spectrum showed five distinct signals. Attempted oxidation of other azines lacking substitution in the 2-position to the corresponding *N*-oxide has led to the isolation of similar products [6].

The ^1H nmr spectra of **2** and **4** in DMSO at ambient temperature each show two distinct two-proton signals for the amine protons, which coalesce to single four-proton signals at elevated temperatures. This behavior has been observed in other 2-amino-3-nitropyridines, and is inter-

Table 2

Crystal Data and Structure Refinement for **4**

Identification code	holl01
Empirical formula	$\text{C}_5\text{H}_5\text{N}_5\text{O}_5$
Formula weight	215.14
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 14.864(2)$ Å $\alpha = 90^\circ$ $b = 7.3360(10)$ Å $\beta = 111.670(10)^\circ$ $c = 7.5090(10)$ Å $\gamma = 90^\circ$
Volume, Z	760.9(2) Å ³ , 4
Density (calculated)	1.878 Mg/m ³
Absorption coefficient	0.169 mm ⁻¹
$F(000)$	440
Crystal size	0.25 x 0.18 x 0.15 mm
θ range for data collection	2.95 to 25.05°
Limiting indices	$0 \leq h \leq 17, -8 \leq k \leq 4, -8 \leq l \leq 8$
Reflections collected	1030
Reflections 'observed'	542 [$I > 2\sigma(I)$]
Independent reflections	674 ($R_{\text{int}} = 0.0170$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	674/0/78
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0355, wR2 = 0.0954$
R indices (all data)	$R1 = 0.0470, wR2 = 0.1035$
Extinction coefficient	0.0027(13)
Largest diff. peak and hole	0.173 and -0.190 eÅ ⁻³

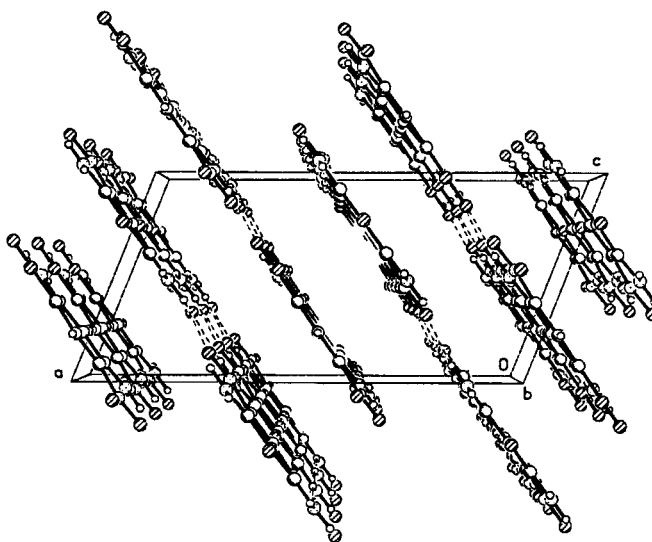


Figure 2. A view down the *b* axis of the unit cell of **4**. In this view it is apparent that all molecules are approximately planar, and the hydrogen-bonded sheets are assembled in parallel stacks. The closest sheet-to-sheet approach is 3.085 Å from nitro oxygen O3a to O3a in a molecule related by $(3/2-x, 1/2-y, 1-z)$.

preted as encouraging evidence for the desired intramolecular hydrogen bonding of the amine protons with the adjacent nitro groups (and, presumably, the *N*-oxide functionality) even in solution. Single crystal X-ray diffraction studies on **4** provide further support for this proposition. The molecular structure is planar, with the amine protons 2.14 and 2.04 Å from the adjacent nitro and *N*-oxide oxygen atoms respectively. There are two semi-linear intermolecular hydrogen bonds (with X-H...O angles $> 150^\circ$; see Table 1) which link adjacent molecules in "head-to-tail" ribbons, and weaker bent bonds which link ribbons in sheets (Figure 1). The extended sheets stack with a close perpendicular interplanar distance of 3.1 Å; all dipoles within one sheet are parallel, which is unusual, but dipoles in adjacent sheets alternate direction, and thus the overall dipole moment is zero (Figure 2). This hydrogen bonding manifests itself in a high crystal density (1.878 g/cm³), in the high stability of **4** (melts with decomposition above 340°C, but without endotherm or exotherm below that temperature) and in the desired insensitivity to impact, friction or electrostatic discharge.

Two approaches were considered for the synthesis of 3,5-dinitro-2,4,6-triaminopyridine 1-oxide, the first being oxidation of 3,5-dinitro-2,4,6-triaminopyridine (**9**). The latter compound has been prepared in 10% overall yield in a six-step sequence from pyridine 1-oxide [7], but we preferred to use an oxidative amination process employing potassium permanganate in liquid ammonia, a nucleophilic substitution designated as S_N (ANRORC) (Addition of Nucleophile, Ring Opening, and Ring Closure) [8]. Treatment of 2-chloro-3,5-dinitropyridine

(8) under these conditions led initially to a mixture of **2** (40%) and **9** (9%) [9]. Prolonged reaction gave **9** as the sole product in up to 30% yield, while treatment of **2** in the same manner gave a 61% yield of the desired **9**.

An alternative method to convert **2** to **9** is suggested by the reaction of *m*-dinitrobenzene with hydroxylamine under aqueous basic conditions to give 2,4-dinitrophenylene-1,3-diamine, a reaction first described by Meisenheimer [10]. A similar method was developed by Katritzky utilizing 4-amino-1,2,4-triazole and potassium *tert*-butoxide in DMSO [11]. These reactions have been successfully applied to the amination of a variety of aromatics, and the

Table 3

Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	5000	-384(3)	2500	29(1)
O(1)	5000	-2194(2)	2500	42(1)
C(2)	5741(1)	488(3)	3900(2)	27(1)
N(2)	6383(1)	-627(3)	5090(2)	37(1)
C(3)	5717(1)	2419(3)	3906(2)	29(1)
N(3)	6439(1)	3426(2)	5392(2)	36(1)
O(3A)	7096(1)	2592(2)	6617(2)	50(1)
O(3B)	6379(1)	5081(2)	5408(2)	61(1)
C(4)	5000	3358(4)	2500	29(1)

	x	y	z	$U(\text{iso})$
H(2A)	6885(18)	-262(33)	6025(34)	45
H(2B)	6257(17)	-1785(35)	4796(33)	45
H(4)	5000	4586(43)	2500	35

process has been described as "vicarious nucleophilic substitution," since the incoming amino group is "disguised" as hydroxylamine or 4-amino-1,2,4-triazole [12]. 2,6-Diamino-3,5-dinitropyridine (**2**) proved to be unreactive towards 4-amino-1,2,4-triazole and potassium *tert*-butoxide in DMSO, perhaps due to the steric bulk of the reagents.

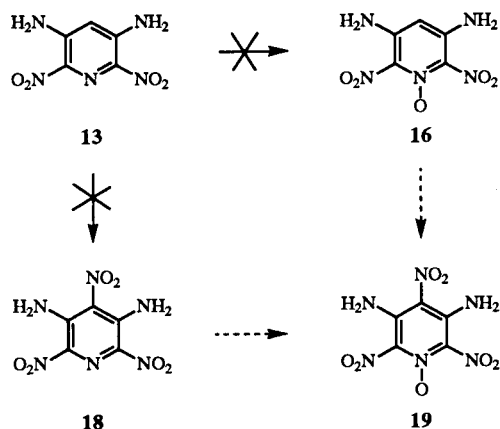


Table 4
Bond Lengths [$\text{\AA}$] and Angles [$^\circ$] for **4**

N(1)-O(1)	1.327(3)	N(1)-C(2)	1.369(2)
N(1)-C(2)#1	1.369(2)	C(2)-N(2)	1.322(2)
C(2)-C(3)	1.417(3)	C(3)-C(4)	1.376(2)
C(3)-N(3)	1.435(2)	N(3)-O(3B)	1.218(2)
N(3)-O(3A)	1.229(2)	C(4)-C(3)#1	1.376(2)

O(1)-N(1)-C(2)	117.88(11)	O(1)-N(1)-C(2)#1	117.88(11)
C(2)-N(1)-C(2)#1	124.2(2)	N(2)-C(2)-N(1)	113.9(2)
N(2)-C(2)-C(3)	129.0(2)	N(1)-C(2)-C(3)	117.1(2)
C(4)-C(3)-C(2)	120.8(2)	C(4)-C(3)-N(3)	118.9(2)
C(2)-C(3)-N(3)	120.3(2)	O(3B)-N(3)-O(3A)	121.9(2)
O(3B)-N(3)-C(3)	119.0(2)	O(3A)-N(3)-C(3)	119.1(2)
C(3)#1-C(4)-C(3)	119.9(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2

However treatment of **2** with hydroxylamine in aqueous potassium hydroxide gave the desired **9** in about 40% yield, together with an approximately equimolar amount of recovered starting material.

The ^1H nmr spectrum of **9** in DMSO at ambient temperature showed three equal signals at 10.42, 8.73 and 8.20 ppm for the amine protons. The low-field signal was essentially unaffected by temperature, and was assigned to the 4-amino group; the higher-field signals coalesced at elevated temperatures to a single signal at about 8.25 ppm, and were assigned to the different protons on the 2- and 6-amino groups. This temperature dependence was also ascribed to hydrogen bonding in **9**, even in solution. Once again single crystal X-ray diffraction studies confirmed both the structure of **9** and its hydrogen bonding in the solid state. At the molecular level, the constituent atoms are quite coplanar, consistent with extensive hydrogen bonding between the amine protons and the oxygen atoms of the adjacent nitro groups. Two molecules of **9**

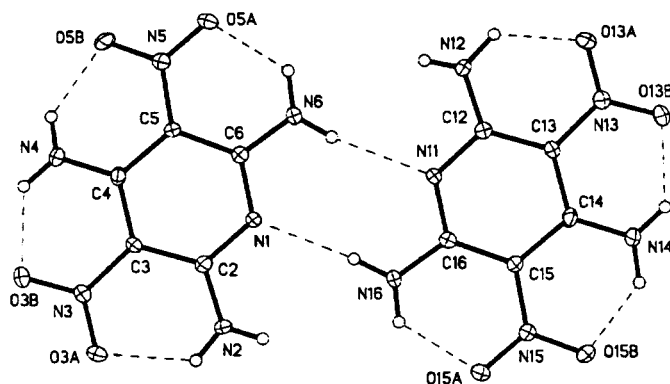


Figure 3. A drawing showing the molecular structures and numbering schemes for the two molecules of **9**, a hydrogen-bonded dimer, that comprises the asymmetric unit of its crystal. The thermal ellipsoids are drawn, here and in other figures, at the 25% probability level.

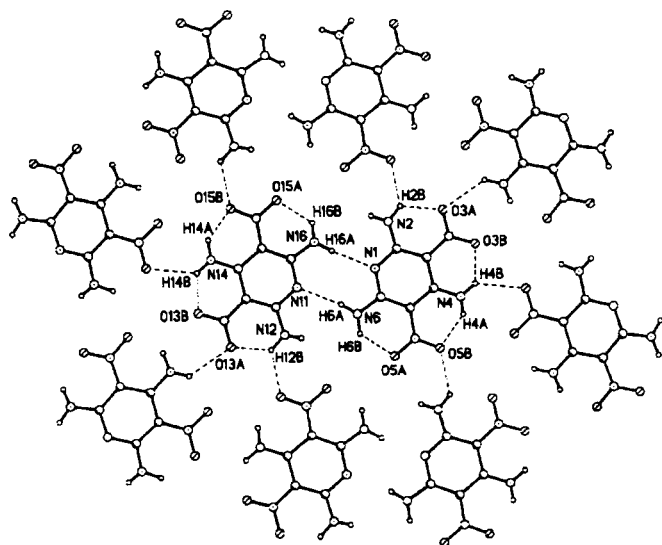


Figure 4. A drawing showing neighboring molecules that hydrogen-bond to the asymmetric unit of **9**. Repetition of such interactions produces an extended sheet, and adjacent sheets are assembled in parallel stacks, with an intersheet perpendicular distance of approximately 3.2 Å.

are linked to each other to form a dimer by almost-linear (169, 172°; see Table 1) hydrogen bonding between one proton of the 2- (or 6-) amino group of one molecule with the heterocyclic nitrogen of the other molecule (Figure 3). (This phenomenon is also responsible for the solid state CP/MAS ^{15}N nmr spectrum, which shows three distinct

signals for the amine groups [13].) This centric dimer does not lie on a crystallographic inversion center, but instead constitutes the asymmetric unit of the crystal. The two shortest ($d < 2.2$ Å) intermolecular $\text{NH}\cdots\text{N}$ hydrogen bonds are those involved in dimer formation; four slightly longer $\text{NH}\cdots\text{O}(\text{nitro})$ hydrogen bonds, repeated through the crystal symmetry operations, link the dimers in sheets. These sheets pack, like TATB, in a stacked planar sheet array (Figure 4). The extensive intramolecular and intermolecular hydrogen bonding results in high crystal density (1.819 g/cm 3), stability (mp 353° dec) and insensitivity to impact.

Table 6

Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for **9**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
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)

	x	y	z	$U(\text{iso})$
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)

Table 5

Crystal Data and Structure Refinement for **9**

Identification code	wils06z
Empirical formula	$\text{C}_5\text{H}_6\text{N}_6\text{O}_4$
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 $\alpha = 90^\circ$ $b = 8.9339(6)$ Å $\beta = 94.298(5)^\circ$ $c = 10.3507(8)$ Å $\gamma = 90^\circ$
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	0.40 x 0.2 x 0.17 mm
θ range for data collection	2.61 to 55.98°
Limiting indices	$0 \leq h \leq 18, -9 \leq k \leq 0, -11 \leq l \leq 11$
Reflections collected	2046
Reflections 'observed'	1465 [$I > 2\sigma(I)$]
Independent reflections	2046 ($R_{\text{int}} = 0.0000$)
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 [$I > 2\sigma(I)$]	$R1 = 0.0466, wR2 = 0.1251$
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 $^{-3}$

Oxidation of **9** to 3,5-dinitro-2,4,6-pyridine 1-oxide (**10**) was achieved by heating with 30% aqueous hydrogen peroxide in acetic acid, but only in 9-10% yield. The bulk of the unreacted **9** was recovered, but the yield of the reaction could not be improved either by more vigorous reaction conditions or by extended reaction times.

However our success in applying the vicarious amination process to the synthesis of 3,5-dinitro-2,4,6-triaminopyridine (**9**) from **2** prompted us to consider the same process for **10**. Indeed, although 2,6-diamino-3,5-dinitropyridine 1-oxide (**4**) proved unreactive towards 4-amino-1,2,4-triazole and potassium *tert*-butoxide in DMSO, treatment with hydroxylamine in aqueous potassium hydroxide afforded **10** in 39% yield. Since 34% **4** was regenerated on acidification of the mother liquors, the effective conversion to **10** was a respectable 59%. Modification of the reaction conditions led to no improvement in the yield.

Insolubility of **10** even in DMSO prevented measurement of its ^1H nmr spectrum at ambient temperature, and the spectrum 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 ratio 2:1, indicating that rotation about the C-N bonds of the 2- and 6-amino groups was occurring and that any hydrogen bonding with the adjacent oxygen atoms was disrupted. The ^{13}C nmr spectrum showed the anticipated

three signals. Single crystal X-ray diffraction studies on **10** confirmed the molecular structure, and again provided corroboration of extensive intra- and inter-molecular hydrogen bonding. All three of the molecules (**4**, **9** and **10**) studied by X-ray diffraction show the close stacking seen in TATB and graphite. Within one sheet, **10** more nearly resembles TATB than either of the other two, for it is linked to six near neighbors with bent bifurcated hydrogen bonds (Figure 5), as is TATB. The *N*-oxide atom, O1, participates in a particularly short (1.98 Å; see Table 1) inter-molecular hydrogen bond with the amino nitrogen, N2. In all three structures, the sheets are close to planar (experimental average atomic deviations from a plane are 0.08 to 0.09 Å for **4**, **9** and **10**, and 0.05 Å for TATB). The perpendicular intersheet distances are 3.09 Å for **4**, 3.19 Å for **9**, 3.15 Å for **10**, 3.13 Å for TATB, and, for comparison, 3.35 Å for graphite. Again the hydrogen bonding in **10** manifests itself in high crystal density (1.876 g/cm³), stability (mp 308° dec) and insensitivity to initiation by impact.

Aminonitropyridines are not accessible by nitration of 3-aminopyridines, probably due to hydrolytic instability

Table 7

Bond Lengths [Å] and Angles [°] for **9**

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)

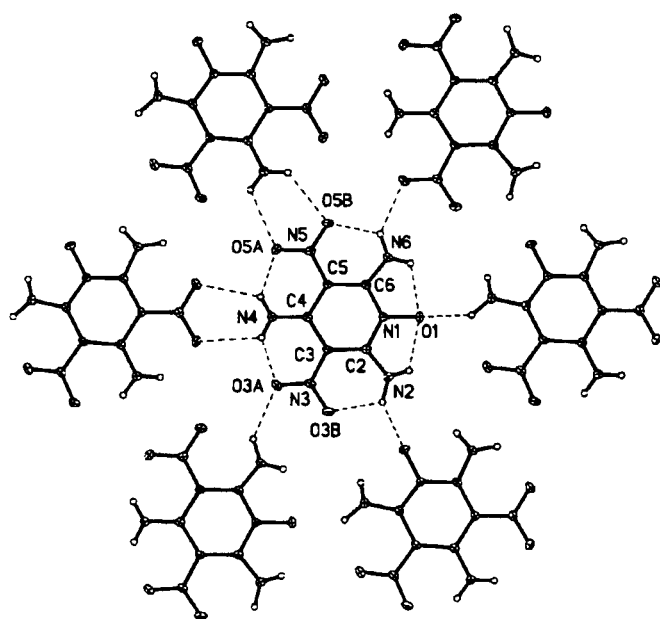


Figure 5. A thermal ellipsoid drawing showing the molecular structure and numbering scheme for **10**, embedded in a portion of an extended hydrogen-bonded planar sheet. Similar parallel sheets stack in the crystal, with an intersheet perpendicular distance (between idealized least squares planes) of 3.15 Å, but, because the sheets are not perfectly planar (ave. atomic dev. 0.08 Å), one of the inter-sheet nitro-nitro contacts is only 3.02 Å.

Table 8
Crystal Data and Structure Refinement for **10**

Identification code	wils03d
Empirical formula	C ₅ H ₆ N ₆ O 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 = 96.963(14)° c = 10.731(2) Å gamma = 90°
Volume, Z	814.8(3) Å ³ , 4
Density (calculated)	1.876 Mg/m ³
Absorption coefficient	1.478 mm ⁻¹
F(000)	472
Crystal size	0.25 x 0.26 x 0.50 mm
θ range for data collection	5.23 to 57.46°
Limiting indices	0 ≤ h ≤ 9, 0 ≤ k ≤ 9, -11 ≤ l ≤ 11
Reflections collected	1246
Reflections 'observed'	1035 [I > 2σ(I)]
Independent reflections	1116 (R _{int} = 0.0232)
Absorption correction	Integration
Max. and min. transmission	0.7535 and 0.6733
Refinement method	Full matrix least-squares on F ²
Data/restraints/parameters	1116/0/170
Goodness-of-fit on F ²	1.183
Final R indices [I > 2σ(I)]	R1 = 0.0431, wR2 = 0.1177
R indices (all data)	R1 = 0.0451, wR2 = 0.1204
Extinction coefficient	0.012(2)
Largest diff. peak and hole	0.302 and -0.239 e Å ⁻³

of the initially formed 3-nitraminopyridines, but mixed acid nitration of 3,5-dimethoxypyridine (**11**) gives a modest yield of 3,5-dimethoxy-2,6-dinitropyridine (**12**) [14], which was converted to 3,5-diamino-2,6-dinitropyridine (**13**) in 75% yield by heating in a Carius tube at 100° with ethanolic ammonia. Crystals of **13** suitable for single crystal X-ray diffraction studies have not been obtained. However ¹H nmr spectra of this material in DMSO at room temperature reveal only a single four-proton signal for the amine protons, suggesting that there is little intramolecular hydrogen bonding in this compound, at least in solution.

Mixed acid nitration of the *N*-oxide **14** also gave 3,5-dimethoxy-2,6-dinitropyridine 1-oxide (**15**) [15]. However ammonolysis of **15** gave not the desired 3,5-diamino-2,6-dinitropyridine 1-oxide (**16**), but rather 2-amino-6-nitro-3,5-dimethoxypyridine 1-oxide (**17**). Clearly the presence of the *N*-oxide functionality activates the adjacent nitro group to nucleophilic displacement; we have encountered such unexpected activation of nitro groups to nucleophilic displacement in a number of aromatic and heteroaromatic compounds [16].

Attempts at oxidation of **13** to the *N*-oxide **16**, and at nitration of **13** (or the other 2,6-dinitropyridine derivatives **12** and **15**) in the 4-position to give 3,5-diamino-2,4,6-trinitropyridine (**18**), have proven unsuccessful, resulting either in reclamation of unreacted starting material or in

Table 9
Atomic Coordinates [x 10⁴] and Equivalent Isotropic Displacement Parameters [Å² x 10³] for **10**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	1574(2)	3234(2)	6027(2)	28(1)
O(1)	846(2)	2450(2)	6855(1)	43(1)
C(2)	1542(2)	4750(2)	6112(2)	24(1)
N(2)	773(2)	5230(2)	7024(2)	35(1)
C(3)	2283(2)	5592(2)	5223(2)	24(1)
N(3)	2206(2)	7162(2)	5292(2)	31(1)
O(3A)	2920(2)	7942(2)	4590(2)	46(1)
O(3B)	1432(2)	7757(2)	6067(1)	44(1)
C(4)	3089(2)	4869(2)	4295(2)	24(1)
N(4)	3744(2)	5629(2)	3445(2)	35(1)
C(5)	3151(2)	3274(2)	4329(2)	24(1)
N(5)	3989(2)	2465(2)	3500(2)	30(1)
O(5A)	4751(2)	3132(2)	2748(1)	43(1)
O(5B)	3988(2)	1084(2)	3523(1)	42(1)
C(6)	2336(2)	2463(2)	5185(2)	26(1)
N(6)	2211(2)	1010(2)	5284(2)	39(1)

	x	y	z	U(iso)
H(2A)	605(36)	6246(40)	7240(30)	74(9)
H(2B)	463(31)	4571(33)	7409(26)	51(8)
H(4A)	4249(29)	5159(29)	2908(23)	43(7)
H(4B)	3696(29)	6594(34)	3487(22)	45(7)
H(6C)	2692(29)	335(36)	4785(24)	58(8)
H(6A)	1671(28)	735(30)	5863(24)	44(7)

Table 10
Bond Lengths [Å] and Angles [°] for **10**

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)	1.241(2)
N(3)-O(3B)	1.243(2)	C(4)-N(4)	1.317(3)
C(4)-C(5)	1.434(3)	C(5)-N(5)	1.407(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)

fragmentation of the heterocyclic ring system. Thus approaches to the synthesis of 3,5-diamino-2,4,6-trinitropyridine 1-oxide (**19**) have been thwarted. Current efforts are directed towards vicarious amination of 2,4,6-trinitropyridine and its *N*-oxide, accessible *via* an alternative route, and towards investigation of aminonitropyrimidine 1,3-dioxides.

EXPERIMENTAL

WARNING: Compounds described in this report are potentially explosive, 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 potassium bromide disks using a Perkin-Elmer Model 1330 spectrophotometer. The ^1H nmr spectra were determined in d_6 -DMSO solutions (unless otherwise stated), using a Bruker AMX-400 instrument at 400 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).

2,6-Diamino-3,5-dinitropyridine (2).

2,6-Diaminopyridine (1) (21.8 g, 200 mmoles) was dissolved in 96% sulfuric acid cooled in an ice/salt bath and stirred with an overhead stirrer. Over a period of *ca.* 3 hours, 90% nitric acid (22 ml) was added dropwise at such a rate that the temperature did not exceed 5° . The reaction mixture was allowed to warm to ambient temperature, and was then warmed to 60 – 65° and held at that temperature for 1 hour. 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 hours in 2*N* sodium hydroxide solution (250 ml), filtered, boiled in water (1 l) for 1 hour 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 (2) as a yellow-ochre solid, mp 345 – 347° dec (lit 348 – 350° dec [17]); ir: 3470, 3350, 1610, 1450, 1390, 1370, 1320, 1280, 1225, 1040, 770 cm^{-1} ; ^1H nmr: 8.99 (s, 1H, H_4), 8.35 (br s, 2H, $-\text{NH}'\text{s}$), 8.24 (br s, 2H, $-\text{NH}'\text{s}$); ^{13}C nmr: 120.8 ($\text{C}_{3,5}$), 136.0 (C_4), 155.2 ($\text{C}_{2,6}$); ms: *m/z* 199 (parent ion and base peak), 183, 169, 123, 107, 95, 80. 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 (3) as yellow crystals, mp 305 – 310° dec; ir: 3380, 3220, 1700, 1640, 1570, 1500, 1390, 1330, 1250 cm^{-1} ; ^1H nmr: 11.75 (br s, 1H, $-\text{NH}$), 9.04 (s, 1H, H_4), 9.03 (br s, 1H, $-\text{NH}$), 8.00 (br s, 1H, $-\text{NH}$); ^{13}C nmr: 113.9 (C_5), 125.1 (C_3), 137.4 (C_4), 151.8 (C_2), 153.6 (C_6); ms: *m/z* 200 (parent ion and base peak), 170, 142, 108, 96, 80.

2,6-Diamino-3,5-dinitropyridine 1-Oxide (4).

2,6-Diamino-3,5-dinitropyridine (2) (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 hours, 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 ^1H 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 (4) as a yellow powder (16.0 g), mp $>340^\circ$ dec (lit 340° dec [5]); ir: 3430, 3260, 1630, 1610, 1480, 1440, 1340, 1320, 1275, 1230, 1030, 800 cm^{-1} ; ^1H nmr: 9.18 (br s, 2H, $-\text{NH}'\text{s}$), 8.84 (br s, 2H, $-\text{NH}'\text{s}$),

8.80 (s, 1H, H_4); ^{13}C nmr: 118.6 ($\text{C}_{3,5}$), 123.3 (C_4), 147.7 ($\text{C}_{2,6}$); ms: *m/z* 215 (parent ion and base peak), 199, 151, 107, 93, 79.

4-Amino-3,5-dinitro-2-pyridone (7).

4-Amino-3,5-dinitropyridine (5) (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 (7) as yellow needles, mp 201 – 205°C dec; ir: 3450, 3330, 1610, 1570, 1540, 1450, 1355, 1210, 825 cm^{-1} ; ^1H nmr: 11.18 (br s, 1H, $-\text{NH}$), 8.45 (s, 1H, H_6), 8.32 (br s, 2H, $-\text{NH}_2$); ^{13}C nmr: 128.1 (C_4), 135.5 (C_6), 139.8 (C_5), 142.1 (C_3), 147.2 (C_2); ms: *m/z* 200 (parent ion and base peak), 170, 142, 108, 85, 79.

3,5-Dinitro-2,4,6-triaminopyridine (9).

(1) 2-Chloro-3,5-dinitropyridine (8) (1.0 g, 4.91 mmoles) was dissolved in liquid ammonia (*ca.* 100 ml), and potassium permanganate (2.0 g, 12.66 mmoles) was added. The mixture was stirred at reflux temperature (-33°) for 8 hours, 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 9 (80%) and 2 (20%). Extraction by refluxing twice in methanol (100 ml) removed the diamine 2, 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-triaminopyridine (9), mp 353° dec (lit 342° dec [7]); ir: 3500, 3380, 3360, 3250, 1650, 1600, 1540, 1480, 1260, 1220, 1170, 1040, 790, 700, 570 cm^{-1} ; ^1H nmr: 10.42 (br s, $-\text{NH}_2$), 8.73 (br s, 2 $-\text{NH}'\text{s}$), 8.20 (br s, 2 $-\text{NH}'\text{s}$); ^{13}C nmr: 110.0 ($\text{C}_{3,5}$), 151.2 (C_4), 155.8 ($\text{C}_{2,6}$); ms: *m/z* 214 (parent ion and base peak), 184, 138.

(2) 2,6-Diamino-3,5-dinitropyridine (2) (0.40 g, 2.0 mmoles) was dissolved in liquid ammonia (*ca.* 30 ml), and potassium permanganate (1.00 g, 6.33 mmoles) was added. The mixture was stirred at reflux temperature (-33°) for 8 hours, 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 ^1H nmr as 3,5-dinitro-2,4,6-triaminopyridine (9) contaminated with *ca.* 2% of (2), which was removed by refluxing in methanol (100 ml).

(3) Potassium hydroxide (2.00 g, 35.7 mmoles) was dissolved in water (20 ml) and cooled in an ice bath. Hydroxylamine hydrochloride (0.20 g, 2.88 mmoles) was added slowly, followed by 2,6-diamino-3,5-dinitropyridine (2) (0.20 g, 1.0 mmoles). The reaction mixture was stirred at ice bath temperature for 5 hours, and then filtered to yield a yellow solid identified by ^1H and ^{13}C nmr as a 2:1 mixture of 3,5-dinitro-2,4,6-triaminopyridine (9) and unreacted 2, which were separated by repeated fractional crystallization from methanol. The overall yield by this route is 37% (or 46% based on consumption of (2)); the procedure described in (2) is clearly superior.

3,5-Dinitro-2,4,6-triaminopyridine 1-Oxide (10).

(1) 3,5-Dinitro-2,4,6-triaminopyridine (9) (0.150 g, 0.70 mmole) 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 hours, and was then cooled and filtered to give a yellow solid (0.90 g, 60%) identified as unreacted starting material **9**. 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 (**10**). 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 mmoles) was dissolved in water (80 ml) and cooled in an ice bath. Hydroxylamine hydrochloride (1.00 g, 14.4 mmoles) was added in portions, followed by 2,6-diamino-3,5-dinitropyridine 1-oxide (**4**) (1.00 g, 4.67 mmoles). The reaction mixture was stirred at ice bath temperature for 1 hour. 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 **4**. 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-triaminopyridine 1-oxide (**10**) as almost black crystals, mp 308° dec; ir: 3420, 3380, 3300, 3260, 1630, 1605, 1495, 1290, 1220, 1190, 1070, 1040, 770, 700, 620 cm^{-1} ; ^1H nmr (at 70°): 8.82 (br s, 2 $-\text{NH}_2$'s), 9.94 (br s, $-\text{NH}_2$); ^{13}C nmr (at 65°): 108.5 ($\text{C}_{3,5}$), 145.8 (C_4), 148.7 ($\text{C}_{2,6}$); ms: *m/z* 230 (parent ion and base peak), 214, 198, 184, 166, 138.

Anal. Calcd. for $\text{C}_5\text{H}_6\text{N}_6\text{O}_5$: C, 26.09; H, 2.63; N, 36.52. Found: C, 26.02; H, 2.53; N, 36.41.

3,5-Dimethoxy-2,6-dinitropyridine (**12**).

3,5-Dimethoxypyridine (**11**) (1.5 g, 10.8 mmoles) was dissolved in 96% sulfuric acid (50 ml) and 70% nitric acid (10 ml) was added dropwise and with stirring at ambient temperature. The solution was heated to 40° for 22 hours, quenched on ice and the precipitate filtered and washed with cold water to give a yellow powder (0.65 g, 36%). Recrystallization from ethanol gave 3,5-dimethoxy-2,6-dinitropyridine (**12**) as very pale yellow needles (0.55 g, 22%), mp 178–180° (lit 181–182° [14]); ir: 1600, 1580, 1480, 1460, 1430, 1380, 1320, 1290, 1230, 1150, 1100, 1000, 870, 860, 840, 710, 690 cm^{-1} ; ^1H nmr (acetone): 7.86 (s, H_4), 4.21 (s, OCH_3); ^{13}C nmr (acetone): 154.3 ($\text{C}_{3,5}$), 137.3 ($\text{C}_{2,6}$), 111.4 (C_4), 58.7 (OCH_3); ms: *m/z* 229 (parent ion), 213, 199, 183, 169, 153, 111, 107 (base peak).

3,5-Diamino-2,6-dinitropyridine (**13**).

3,5-Dimethoxy-2,6-dinitropyridine (**12**) (1.15 g, 5.5 mmoles) was added to ethanol (100 ml), and the solvent saturated with ammonia gas. The mixture was heated under reflux for 3 days, and the solvent was removed under vacuum. The residue was placed in a Carius tube with ethanol (25 ml) saturated with ammonia, and the tube was sealed and heated in an oven at 100° for a week. The solid was filtered off to give **16** as a brown solid (0.75 g, 75%), recrystallized from *N*-methylpyrrolidinone/dichloromethane as 3,5-diamino-2,6-dinitropyridine (**13**) (0.15 g, 65%), mp >350° (chars from 300°); ir: 3480, 3380, 3340, 1660, 1560, 1490, 1320, 1240, 890 cm^{-1} ; ^1H nmr: 7.53 (br s, NH_2), 6.70 (s, H_4); ^{13}C nmr: 145.0 ($\text{C}_{3,5}$), 129.4 ($\text{C}_{2,6}$), 108.2

(C_4); ms: *m/z* 199 (parent ion and base peak), 169, 153, 94, 80.

Anal. Calcd. for $\text{C}_5\text{H}_5\text{N}_5\text{O}_4$: C, 30.16; H, 2.53; N, 35.17. Found: C, 30.05; H, 2.64; N, 35.09.

3,5-Dimethoxy-2,6-dinitropyridine 1-Oxide (**15**).

3,5-Dimethoxypyridine 1-oxide (**14**) (1.0 g, 6.5 mmoles) was dissolved in 96% sulfuric acid at ambient temperature, and 70% nitric acid (1.5 ml) was added dropwise and with stirring. The solution was warmed to 90° and maintained at that temperature for 4 hours. Quenching in ice/water (250 ml) and filtration gave a pale yellow/off-white solid (0.66 g, 42%). Recrystallization from ethanol/acetone gave 3,5-dimethoxy-2,6-dinitropyridine 1-oxide (**15**) as a pale yellow solid (0.36 g, 23%), mp 265–267° dec (lit 260–261° [15]); ir: 3090, 1580, 1550, 1480, 1440, 1410, 1360, 1220, 1200, 1130, 970, 830, 820, 690 cm^{-1} ; ^1H nmr (acetone): 7.55 (s, H_4), 4.19 (s, OCH_3); ^{13}C nmr (acetone): 151.6 ($\text{C}_{3,5}$), 139.7 ($\text{C}_{2,6}$), 99.7 (C_4), 59.2 (OCH_3); ms: *m/z* 245 (parent ion), 215, 185, 169, 153, 127, 126, 110 (base peak).

2-Amino-3,5-dimethoxy-6-nitropyridine 1-Oxide (**17**).

3,5-Dimethoxy-2,6-dinitropyridine 1-oxide (**15**) (0.35 g, 1.4 mmoles) was added to ethanol (50 ml), and ammonia gas was bubbled in until saturation. The flask was sealed, and the reaction mixture was stirred at ambient temperature for 2 weeks. Filtration gave an orange powder (0.24 g, 78%). Recrystallization from ethanol gave 2-amino-3,5-dimethoxy-6-nitropyridine 1-oxide (**17**) as orange crystals, mp 177–179°; ir: 3440, 3220, 3180, 1600, 1580, 1550, 1530, 1230, 1180, 1130, 1080, 820 cm^{-1} ; ^1H nmr: 7.19 (s, H_4), 6.10 (br s, NH_2), 3.94 (s, OCH_3), 3.87 (s, OCH_3); ^{13}C nmr: 147.0 (C_3), 143.1 (C_2), 141.8 (C_5), 137.1 (C_6), 106.4 (C_4), 57.9, (OCH_3), 56.6, (OCH_3); ms: *m/z* 215 (parent ion), 198, 168, 151, 137, 123, 110 (base peak), 69. The same product was obtained if the reaction was carried out under reflux, or in a Carius tube at 100°.

Anal. Calcd. for $\text{C}_7\text{H}_9\text{N}_3\text{O}_5$: C, 39.07; H, 4.22; N, 19.53. Found: C, 38.95; H, 4.18; N, 19.41.

X-ray Diffraction Analyses of **4**, **9** and **10**.

For all three compounds, data collection was carried out on an automated Siemens diffractometer equipped with an incident beam monochromator at $T = 294\text{K}$. Space groups were based on extinctions present in the diffraction patterns, and were confirmed by the structure solutions. All structures were initially determined by direct methods, aided by the program XS, and refined with the full-matrix least squares program XLS, contained in the SHELXTL collection of computer programs [18]. Bond lengths and bond angles all fell within the expected range. All hydrogen atoms on **4**, **9** and **10** were found in difference Fourier maps. Their coordinates were refined, but primarily to establish their existence and to improve indirectly the C, N and O results; hydrogen nuclear locations are not found accurately in X-ray analyses because of the strong polarization of the electron density in C-, N- and O-H bonds.

Crystal Data (**4**): $\text{C}_5\text{H}_5\text{N}_5\text{O}_5$, F.W. = 215.1, crystallizes in monoclinic space group $\text{C}2/c$, with $a = 14.864(2)$, $b = 7.336(1)$, $c = 7.509(1)$ Å, $\beta = 111.67(1)^\circ$, Vol = 760.9(2) Å³, $Z = 4$, and Dens(X-ray) = 1.878 g/cc. A clear yellow 0.15 x 0.18 x 0.25 mm crystal, in the shape of a flattened octahedron, was used, with MoK α radiation, $\lambda = 0.71073$ Å. The refinement agreement factors were $R = 0.0470$, $wR2 = 0.1035$ for all (none considered unobserved) 1727 unique reflections. Hydrogen atoms were assigned isotropic thermal factors 20% higher than those of the

bonded neighbor atoms. Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, and bond lengths and bond angles for **4** are presented in Tables 2, 3 and 4.

Crystal Data (**9**): $C_5H_6N_6O_4$, F.W. = 214.2, crystallizes in monoclinic space group $P2_1/c$, with $a = 16.9579(7)$, $b = 8.9339(6)$, $c = 10.3507(8)$ Å, $\beta = 94.298(5)^\circ$, Vol = $1563.7(2)$ Å³, $Z = 8$, and Dens(X-ray) = 1.819 g/cc. A clear pale-yellow parallelepiped crystal, $0.17 \times 0.20 \times 0.40$ mm, was used, with $CuK\alpha$ radiation, $\lambda = 1.54178$ Å. Intensity data were corrected for appreciable absorption by indexing the crystal faces and integrating, $T_{min} = 0.542$, $T_{max} = 0.814$. The refinement agreement factors were $R = 0.0670$, $wR2 = 0.1447$ for all (none considered unobserved) 2045 unique reflections. All hydrogen atoms were assigned a common refined isotropic thermal factor. Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, and bond lengths and bond angles for **9** are presented in Tables 5, 6 and 7.

Crystal Data (**10**): $C_5H_6N_6O_5$, F.W. = 230.2, crystallizes in monoclinic space group $P2_1/c$, with $a = 8.515(2)$, $b = 8.983(2)$, $c = 10.731(2)$ Å, $\beta = 96.96(1)^\circ$, Vol = $814.8(3)$ Å³, $Z = 4$, and Dens(X-ray) = 1.876 g/cc. A clear orange $0.25 \times 0.26 \times 0.50$ mm crystal, in the shape of a multifaceted bipyramid, was used, with $CuK\alpha$ radiation, $\lambda = 1.54178$ Å. Intensity data were corrected for absorption by indexing the crystal faces and integrating, $T_{min} = 0.673$, $T_{max} = 0.754$. The refinement agreement factors were $R = 0.0451$, $wR2 = 0.1204$ for all (none considered unobserved) 1116 unique reflections. Hydrogen atoms were assigned isotropic thermal factors which were individually refined. Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, and bond lengths and bond angles for **10** are presented in Tables 8, 9 and 10.

Further details have been deposited with the Cambridge Crystal Structure Database, and are available from author (RG).

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