Synthesis of 2,3,4,5-Tetranitropyrrole

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Dealkylation of 1-*tert*-butyl-2,3,4-trinitropyrrole in boiling trifluroacetic acid gave 2,3,4-trinitropyrrole, the structure of which was confirmed by X-ray crystallography. Treatment of this trinitropyrrole with nitric acid/oleum briefly at 60° gave 2,3,4,5-tetranitropyrrole.

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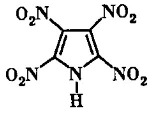
There is current attention directed toward the synthesis of polynitroaromatic species for possible propellant and explosive applications. Furthermore, there is fundamental interest in the effects of multiple nitro group substitutions on the chemical/physical properties of aromatic and heteroaromatic systems. In contrast to energetic materials derived from polynitrobenzenes [1-5], relatively little is known regarding nitrogen unsubstituted polynitropyrrole derivatives [6].

Whereas dinitropyrroles are readily produced upon nitration of pyrrole, successful attempts to force further nitration of pyrrole have not been reported [6]. Accordingly, trinitropyrroles and the tetranitropyrrole **1** have heretofore not been available for chemical studies and evaluation as high energy ingredients.

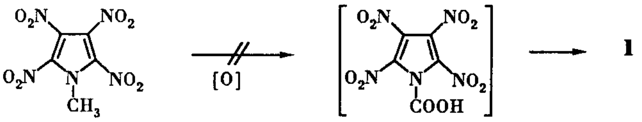


1

We now report the synthesis of 2,3,4-trinitropyrrole and its direct nitration to **1**.

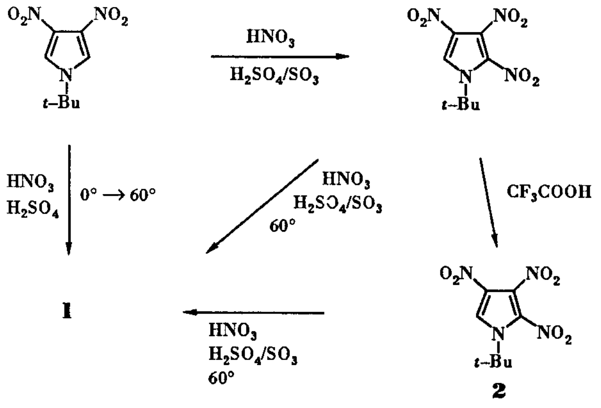
Reports of the successful polynitration of dinitro-*N*-methylpyrroles [7,8] prompted us to examine routes to **1** involving nitration of suitably *N*-protected pyrroles followed by removal of the protecting functionality.

Several attempts (chromium trioxide/acetic acid, chromium trioxide/sulfuric acid, sodium dichromate/sulfuric acid, nitronium tetrofluoroborate) to remove the presumably activated methyl group from the known [8] *N*-methyltetranitropyrrole, perhaps *via* an intermediate *N*-carboxyl species, were unsuccessful. In all cases, either starting material was recovered or extensive decomposition was observed.



On the other hand, 1-*tert*-butyl-2,3,4-trinitropyrrole [8] was found to dealkylate readily in boiling trifluoroacetic acid giving 2,3,4-trinitropyrrole **2** in 50% yield. This is the first example of a nitrogen unsubstituted trinitropyrrole. Brief treatment of **2** with 100% nitric acid in fuming sulfuric acid at 60° degrees gives tetranitropyrrole **1** in low yield. Alternately, **1** is produced upon nitration, with concomitant dealkylation, of 1-*tert*-butyl-2,3,4-trinitropyrrole with nitric acid/oleum at 60°. Also, treatment of 1-*tert*-butyl-3,4-dinitropyrrole [8] with nitric acid/sulfuric acid initially at 0°, [9] followed by brief heating of the reaction mixture at 60°, leads directly to **1** (Scheme 1).

Scheme 1



The structure of trinitropyrrole **2** follows from spectral data (see Experimental) and is confirmed by single crystal X-ray structure determination (*vide infra*).

For tetranitropyrrole, the expected $C_4HN_5O_8$ molecular formula is confirmed by high resolution mass spectroscopy (see Experimental), while the symmetrical structure of **1** is indicated, at least in solution, by the ^{13}C nmr spectrum which shows resonances for only two tertiary carbons [10,11] with reasonable chemical shifts (132.2, 123.6 ppm) compared with those of **2**. Compound **1** is rather unstable, the solid material or acetone solutions discoloring under ambient conditions. This behavior has frustrated attempts to accurately study many chemical and physical properties of **1**. For example, crystals of **1** decomposed rapidly in the X-ray beam upon attempted structural analysis.

X-ray Crystallographic Study of **2**.

The results of the X-ray study are illustrated in Figure 1 in which only one of the two crystallographically unique molecules in the asymmetric unit is shown.

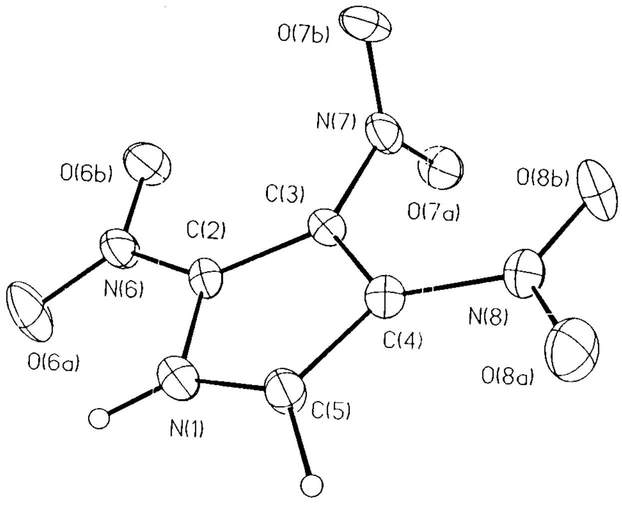


Figure 1. Thermal ellipsoid plot of 2 drawn at the 20% probability level; only one of the two crystallographically independent molecules is shown

The two molecules share the same configuration with the largest differences between the molecules being the torsion angles of the nitro groups in the ring plane with differences of 9.2° to 12.8°. The ring nitrogen positions could not be located with confidence on the basis of the molecular geometry or packing contacts but were assigned on the basis of electron density alone. The molecules pack with the ring planes near parallel to the c axis and within 8° of lying either in or perpendicular to the [110] plane. In this arrangement, there are several intermolecular approaches at or near van der Waals separations (2.46 Å to 2.66 Å) between the hydrogens in each molecule and the nitro oxygens. Measured bond lengths and angles are summarized in Tables 1-3.

EXPERIMENTAL

Caution: All polynitropyrroles should be considered potentially explosive and therefore should be handled only in small quantities with appropriate safety shielding.

Melting points are uncorrected. The nmr spectra were recorded in dimethyl sulfoxide-d_6 at 299.94 MHz (^{1}H) and 75.43 MHz (^{13}C) using a Varian XL-300 instrument. Chemical shifts are

Table 1

Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^{2}x10^3) For 2,3,4-Trinitropyrrole (2)

	x	y	z	U (eq)*
N(1)	7950(8)	2969(8)	633	44(3)
C(2)	8827(8)	3958(8)	865(7)	33(3)
C(3)	8888(7)	4049(8)	1790(8)	32(2)
C(4)	8014(8)	3077(8)	2122(9)	37(3)
C(5)	7365(11)	2464(10)	1397(8)	51(4)
N(6)	9503(9)	4682(7)	197(7)	52(3)
O(6A)	9409(9)	4346(8)	-588(7)	84(3)
O(6B)	10201(9)	5622(7)	460(8)	69(3)
N(7)	9733(8)	4943(7)	2292(7)	49(3)
O(7A)	10907(6)	4585(6)	2490(8)	58(2)
O(7B)	9298(8)	6028(6)	2463(8)	66(3)
N(8)	7706(8)	2822(7)	3049(7)	49(3)
O(8A)	6895(8)	1961(7)	3222(7)	71(3)
O(8B)	8320(7)	3428(7)	3625(7)	64(3)
N(1')	2232(8)	1999(8)	3122(8)	46(3)
C(2')	1127(10)	1168(8)	3301(8)	45(3)
C(3')	912(9)	1121(7)	4221(8)	36(3)
C(4')	1933(11)	1964(8)	4589(7)	45(3)
C(5')	2653(9)	2528(10)	3899(9)	44(4)
N(6')	363(7)	505(8)	2609(7)	48(3)
O(6A')	783(8)	606(8)	1835(7)	84(3)
O(6B')	-612(7)	-112(8)	2845(7)	70(3)
N(7')	-71(6)	288(7)	4700(7)	38(2)
O(7A')	-1151(6)	827(6)	4887(8)	61(2)
O(7B')	244(7)	-829(6)	4868(8)	65(3)
N(8')	2146(8)	2272(7)	5534(8)	53(3)
O(8A')	3018(8)	3098(7)	5724(8)	77(3)
O(8B')	1441(7)	1641(6)	6076(7)	60(2)
H(1)	7902(89)	2842(83)	34(16)	50
H(5)	7090(89)	1550(31)	1421(65)	60
H(1')	2498(89)	2258(83)	2565(29)	50
H(5')	3498(50)	3037(70)	3928(61)	50

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Bond Lenghts (Å) for 2,3,4-Trinitropyrrole (2)

N(1)-C(2)	1.36(1)	N(1')-C(2')	1.39(1)
N(1)-C(5)	1.36(1)	N(1')-C(5')	1.33(1)
C(2)-C(3)	1.37(1)	C(2')-C(3')	1.37(1)
C(2)-N(6)	1.39(1)	C(2)-N(6')	1.43(1)
C(3)-C(4)	1.39(1)	C(3')-C(4')	1.41(1)
C(3)-N(7)	1.43(1)	C(3')-N(7')	1.45(1)
C(4)-C(5)	1.39(1)	C(4')-C(5')	1.36(1)
C(4)-N(8)	1.42(1)	C(4')-N(8')	1.44(1)
N(6)-O(6A)	1.21(1)	N(6')-O(6A')	1.22(1)
N(6)-O(6B)	1.23(1)	N(6')-O(6B')	1.18(1)
N(7)-O(7A)	1.23(1)	N(7')-O(7A')	1.21(1)
N(7)-O(7B)	1.20(1)	N(7')-O(7B')	1.20(1)
N(8)-O(8A)	1.20(1)	N(8')-O(8A)	1.22(1)
N(8)-O(8B)	1.21(1)	N(8')-O(8B')	1.23(1)

Table 3

Bond Angles (deg) for 2,2,4-Trinotropyrrole (2)

C(2)-N(1)-C(5)	109.2(7)	C(2')-N(1')-C(5')	108.4(10)
N(1)-C(2)-C(3)	109.1(7)	N(1')-C(2')-C(3')	109.0(9)
N(1)-C(2)-N(6)	120.3(9)	N(1')-C(2')-N(6')	123.2(10)
C(3)-C(2)-N(6)	130.5(8)	C(3')-C(2')-N(6')	127.7(8)
C(2)-C(3)-C(4)	106.2(8)	C(2')-C(3')-C(4')	104.6(8)
C(2)-C(3)-N(7)	125.8(8)	C(2')-C(3')-N(7')	126.9(9)
C(4)-C(3)-N(7)	128.0(11)	C(4')-C(3')-N(7')	128.3(10)
C(3)-C(4)-C(5)	108.8(11)	C(3')-C(4')-C(5')	108.9(9)
C(3)-C(4)-N(8)	126.6(9)	C(3')-C(4')-N(8')	126.9(9)
C(5)-C(4)-N(8)	124.4(8)	C(5')-C(4')-N(8')	124.0(9)
N(1)-C(5)-C(4)	106.3(9)	N(1')-C(5')-C(4')	108.6(9)
C(2)-N(6)-O(6A)	119.5(8)	C(2')-N(6')-O(6A')	117.3(8)
C(2)-N(6)-O(6B)	116.2(10)	C(2')-N(6')-O(6B')	116.8(10)
C(6A)-N(6)-O(6B)	124.3(10)	C(6A')-N(6')-O(6B')	125.9(10)
C(3)-N(7)-O(7A)	117.9(7)	C(3')-N(7')-O(7A')	114.5(7)
C(3)-N(7)-O(7B)	119.1(8)	C(3')-N(7')-O(7B')	118.7(7)
O(7A)-N(7)-O(7B)	122.9(9)	O(7A')-N(7')-O(7B')	126.8(9)
C(4)-N(8)-O(8A)	118.2(9)	C(4')-N(8')-O(8A')	117.9(10)
C(4)-N(8)-O(8B)	118.9(8)	C(4')-N(8')-O(8B')	115.9(8)
O(8A)-N(8)-O(8B)	122.8(11)	O(8A')-N(8')-O(8B')	126.2(11)

reported in ppm (δ) using residual protiosolvent as an internal standard. High resolution mass spectra were obtained using a VG Micromass 7050E Double Focusing Instrument with VG Data System 2000 at 70 ev at the Department of Chemistry, University of Utah.

2,3,4-Trinitropyrrole (**2**).

A mixture of 1-*tert*-butyl-2,3,4-trinitropyrrole [8] (6.0 g, 0.023 mole) and 60 ml of trifluoroacetic acid was refluxed overnight with protection from moisture. After this period, the precipitate was collected, washed with trifluoroacetic acid, and dried under vacuum at 35° yielding **2** (2.9 g, 50% yield) as pale yellow crystals, mp 161-162°; ^{1}H nmr: 11.7 (br s, 1H), 8.1 (s, 1H); ^{13}C nmr: 131.5 (s), 127.6 (s), 125.3 (s), 124.1 (d); exact mass m/z 201.9993 (calculated for $C_4H_2N_4O_6$ 201.9974).

Anal. Calcd. for $C_4H_2N_4O_6$: C, 23.8; H, 1.0; N, 27.7. Found: C, 23.5; H, 1.1; N, 25.2. We and others [1,4] have observed problems with low nitrogen analyses from polynitro compounds.

2,3,4,5-Tetranitropyrrole (**1**).

A solution of 1-*tert*-butyl-3,4-dinitropyrrole [8] (2.0 g, 0.078 mole) in 30 ml of concentrated sulfuric acid was cooled to 0°. With stirring, 15 ml of 90% nitric acid was added dropwise slowly. The reaction was allowed to warm to room temperature then heated carefully to 55° (note: delayed exotherm; ice bath cooling may be necessary to hold at <60°) and held at this temperature for 15 minutes. The reaction was then cooled to 0° and poured carefully over about 100 g of crushed ice. The resulting mixture was extracted with ethyl acetate (3 x 15 ml), and the combined ethyl acetate extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was dissolved in 10 ml of trifluoroacetic acid without heating. Upon standing, the solution deposited a solid which was collected, washed with trifluoroacetic acid, and immediately transferred to a vacuum oven and dried at room temperature under reduced pressure. The product (**1**) (0.4 g, 21% yield) was obtained as a yellow solid mp 156-158° dec which discolored and softened on standing in the open laboratory atmosphere; ^{1}H nmr: 10.2 (br s); ^{13}C nmr: [12] 132.2 (s), 123.6 (s); exact mass m/z 246.9812 (calculated for $C_4HN_5O_8$ 246.9825).

Due to the instability of **1**, an acceptable combustion analysis could not be obtained.

Nitration of 2,3,4-Trinitropyrrole and 1-*tert*-Butyl-2,3,4-trinitropyrrole.

Treatment of these polynitropyrroles with excess nitric acid in sulfuric acid or oleum as above also gave **1** in low yield. Variations in nitration time and/or temperature have not yet resulted in significant improvements in yield, perhaps due to the inherent instability of **1** under the reaction conditions.

Single-crystal X-ray Structured Analysis of **2**.

$C_4H_2N_4O_6$, molecular weight 202.1, orthohombic space group $Pca2_1$, $a = 9.686(2)$ Å, $b = 10.113(3)$ Å, $c = 14.767(3)$ Å, $D_{calc} = 1.856$ g cm^{-3}, $\mu = 0.17$ mm^{-1}, $F(000) = 816$, $Z = 8$ (two molecules per asymmetric unit). A total of 2982 reflections were measured, 1334 unique, to a 2θmax = 50° with a Nicolet R3m automated diffractometer. The instrument used MoKα radiation (= 0.71069 Å), and an incident beam graphite monochromator was used to obtain intensity data. The space group $Pca2_1$ was chosen based on E value statistics and the structure solution. Data were collected by the θ-2θ scan method. The scan width was $[2\theta(K_{\alpha 1})-0.8]$ to $[2\theta(K_{\alpha 2})+0.8]$° and the 2θ scan rate was a function of count rate with a minimum speed of 3.0°/minute and 30.0°/minute maximum. The data were corrected for Lorentz and polarization, but not for absorption effects.

The structure was solved with direct methods as implemented in the SHELXTL [13] system of programs, and all atoms were located in Fourier difference maps. The full matrix least-squares refinement minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w = 1/[\sigma^2(|F_o|) + g.(F_o)^2]$ and $g = 0.0003$. There were a total of 265 parameters refined. These include atom coordinates and anisotropic thermal parameters for all but the hydrogen atoms, which were refined isotropically with fixed thermal parameters. The final R factors for the 1120 reflections observed with $F_o \geq 3\sigma(F_o)$ were $R = 0.063$ and $wR = 0.069$, and the error in an observation of unit weight, S, was 2.22. Atomic scattering factors are from the International Tables for X-ray Crystallography (1974) [14].

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[9] Under these conditions, 1-*tert*-butyl-2,3,4-trinitropyrrole is formed initially [8].

[10] Confirmed by comparison of spectra with and without proton decoupling.

[11] The simplicity of the ^{13}C nmr spectrum supports **1** as opposed to alternative α or β pyrrolenine structures.

[12] The similarity of this spectrum taken in dimethyl sulfoxide-d$_6$ with one obtained in acetonitrile-d$_3$ [130.3 (s), 124.7 (s) ppm] as well as the spectral simplicity suggests that little reaction occurs between **1** and the weakly nucleophilic dimethyl sulfoxide solvent at least during acquisition of data.

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