

Alexander K. Zelenin and Mark L. Trudell*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Richard D. Gilardi

Naval Research Laboratory, Code 6030, 4555 Overlook Avenue, SW, Washington, D.C. 20375-5000

Received July 29, 1997

The synthesis of dinitroazofurazan (**3**) was achieved from readily available diaminofurazan (**6**) in two steps and 20% overall yield. The structure of the energetic material **3** was unequivocally confirmed by X-ray crystallography and found to have a crystal density of 1.742 g/cm³.

J. Heterocyclic Chem., **35**, 151 (1998).

The furazan ring system has long been recognized as a useful substructure for the design and synthesis of high density energetic compounds [1,2]. Recently a number of energetic furazan derivatives have been reported in the literature [3-10]. Of these, dinitroazoxyfurazan (**1**) [4] has been shown to have high crystal density and excellent calculated energetic properties of detonation velocity (*D*) and detonation pressure (*P*_{CJ}, Table 1). However, the sensitivity of **1** toward impact and friction has been found to be greater than that of RDX and HMX, thus limiting the potential usefulness of **1** as an explosive, propellant or composite ingredient [10].

Table 1

Calculated Density and Energetic Properties of **1**, **2** and **3** [11]

Compound	<i>d</i> (g/cm ³)	<i>D</i> (mm/μsec)	<i>P</i> _{CJ} (kbar)
1	1.91 1.856 [a]	9.8	456
2	1.87 1.856 [b]	9.4	420
3	1.84 1.742 [c]	9.7	449

[a] X-ray crystal density, lit [3]; [b] X-ray crystal density of 2·EtOH·1/2H₂O, lit [10]; [c] X-ray crystal density.

As an attempt to reduce the sensitivity of **1**, the synthesis of aminonitroazoxyfurazan (**2**) was recently completed in our laboratories [10]. The amino derivative **2** was found to be qualitatively less sensitive than **1** in a hammer/anvil test. Presumably, this is due to the formation of intramolecular and intermolecular hydrogen bonds within the crystal lattice by the amino group [10].

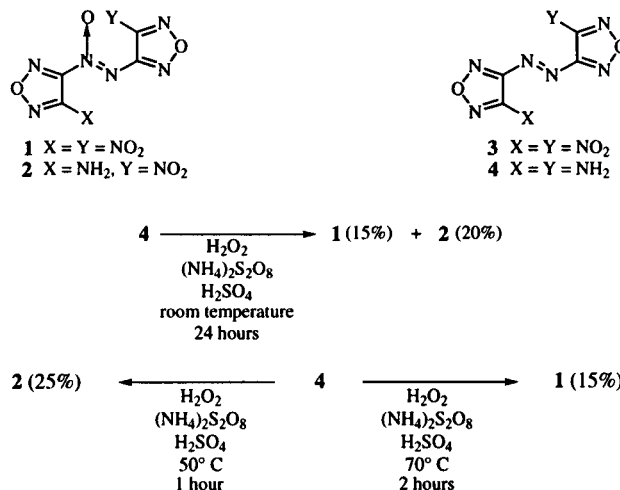
As part of a continuing effort focused on the synthesis of insensitive energetic materials, it was of interest to explore the effect of replacing the azoxy linkage of **1** with an azo linkage. Based on computational results, the dinitroazofurazan (**3**) was found to possess slightly lower

energetic properties (Table 1) and would therefore be expected to be slightly less sensitive [11]. In light of these results, **3** was envisaged as a potentially less sensitive substitute for **1**. Herein we wish to describe an efficient synthesis of **3** and present the first X-ray crystal structure of this compound.

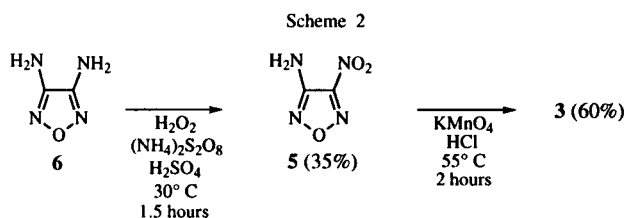
To investigate the potential usefulness of **3** as an energetic material, it was necessary to employ a synthetic sequence which could potentially provide gram quantities of material for initial characterization as well as advanced study. Initial attempts to prepare **3** from aminoazofurazan (**4**) according to methods described in the literature failed [4]. Attempted ammonium persulfate/hydrogen peroxide oxidation of the amino groups of **4** in sulfuric acid media under a variety of conditions only afforded the azoxy derivatives **1** and **2** or mixtures of the azoxy derivatives (Scheme 1). Attempts to modify the concentrations of reagents and the reaction temperature were also unsuccessful and this approach was abandoned.

It had been reported that potassium permanganate oxidative coupling of higher order aminofurazan derivatives with 3-amino-4-nitrofurazan (**5**) [1,12] resulted in

Scheme 1



the formation of **3** as a side-product of the reaction [5]. Based on this result it was of interest to further develop this methodology for the synthesis of **3**. As illustrated in Scheme 2, readily available diaminofurazan (**6**) [9,13] was oxidized by a modified procedure with ammonium persulfate/hydrogen peroxide in sulfuric acid to afford **5** in 35% yield [12]. Treatment of **5** with potassium permanganate at 40° to 55° afforded the azo derivative **3** in 60% isolated yield as an oil. The oil was found to be pure by nmr; however, further purification by column chromatography and crystallization from dichloromethane/pentane furnished **3** as a yellow crystalline material.



The structure of the azofurazan was unequivocally confirmed by X-ray crystallography (Figure 1 and Tables 2-5). As expected the azo linkage possessed a *trans* geometry. The nitrogen-nitrogen double bond length (1.243 Å, Table 3) was comparable to the nitrogen-nitrogen double bond length of azobenzene (1.24 Å) [14] and was slightly shorter than the azoxy nitrogen-nitrogen double bond length of **1** (1.30 Å) [3] and **2** (1.31 Å) [10]. In addition, the carbon-carbon bond lengths in the furazan rings of **1** (A: 1.402 Å; B: 1.409 Å; C: 1.409 Å; D: 1.403 Å) were shorter than those observed in other furazan derivatives (1.413 to 1.446 Å) reported in the Cambridge Crystal Structure Database, including **5** (1.428 Å) and **6** (1.446 Å) [15].

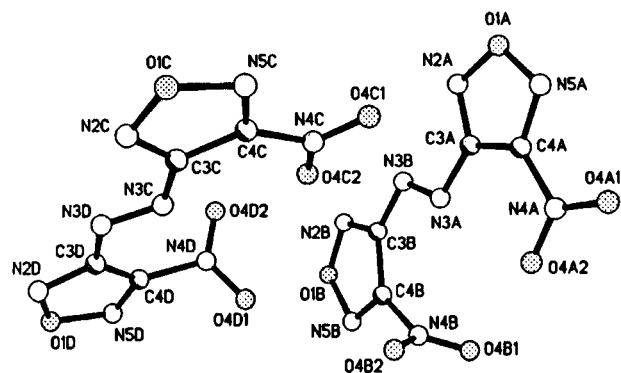


Figure 1. A drawing showing the molecular structures and labeling schemes for two neighboring molecules **3** that comprise the asymmetric unit in the crystal form reported herein. The conformations of the two molecules differ slightly but are quite similar; in each case, rotations about the single bonds of the azo bridge cause both nitro groups to project to the same side of the azofurazan system, and one nitro group is almost perpendicular to the azofurazan plane.

Table 2
Crystal Data and Structure Refinement **3**

Formula	C ₄ N ₈ O ₆
Formula Weight	256.12
Temperature	294(2) K
Wavelength	1.54178 Å
Crystal System	Triclinic
Space Group	P1
Unit Cell Dimensions	<i>a</i> = 10.3166(9) Å <i>b</i> = 10.3904(6) Å <i>c</i> = 10.4314(12) Å α = 67.957(5)° β = 70.399(7)° γ = 83.106(5)°
Volume, Z	976.4(2) Å ³ , 4
Density (Calculated)	1.742 Mg/m ³
Absorption Coefficient	1.462 mm ⁻¹
F(000)	512
Crystal Size	0.16 x 0.56 x 0.54 mm
Θ Range for Data Collection	4.55 to 55.99°
Limiting Indices	-11 ≤ <i>h</i> ≤ 1, -10 ≤ <i>k</i> ≤ 10, -11 ≤ <i>l</i> ≤ 10
Reflections Collected	2739
Reflections "Observed"	2045 [<i>I</i> > 2σ(<i>I</i>)]
Independent Reflections	2484 (<i>R</i> _{int} = 0.0421)
Absorption Correction	Integration
Max. and Min. Transmission	0.8140 and 0.4123
Refinement Method	Full-Matrix Least-Squares on F ²
Data/Restrains/Parameters	2483/0/326
Goodness-of-Fit on F ²	1.060
Final R Indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0570, <i>wR</i> 2 = 0.1473
R Indices (All Data)	<i>R</i> 1 = 0.0669, <i>wR</i> 2 = 0.1616
Extinction Coefficient	0.0113(13)
Largest Diff. Peak and Hole	0.263 and -0.262 eÅ ⁻³

It is noteworthy that within the crystal lattice, **3** is not symmetric. The two furazan rings, which could have been related by a center of symmetry or by a two-fold axis, are not related. For example, the C3A-C4A bond is *trans* to the N3A-N3B azo bond, but the C3B-C4B bond is *cis* to the azo bond (see Figure 1). The situation is the same in the other molecule of **3** found in the asymmetric unit of this crystal form. This pattern of ring placement serves to bring both nitro groups to the same side of the molecule.

Molecules of **3** are planar (to within ±0.05 Å) throughout their azofurazan systems, but display various out-of-plane rotations for the nitro substituents. The nitro groups on rings A and B make dihedral angles of 4.8° and 85.4° with the azofurazan plane. In the other molecule, the dihedrals in rings C and D are 8.1° and 81.9°. Thus in each case, there is one nitro group which is essentially perpendicular to the azofurazan π-system; this orientation is one way to minimize the electrostatic repulsion between the close electron-rich oxygen atoms of the two nitro groups.

Perhaps because of the protruding perpendicular nitro groups, the two molecules in the asymmetric unit do not nestle closely together, but are almost orthogonal. The

Table 3

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

	x	y	z	U(eq)
O(1A)	250(3)	7039(4)	8807(3)	92(1)
N(2A)	409(3)	7380(4)	7359(4)	74(1)
C(3A)	1725(3)	7523(3)	6717(4)	50(1)
N(3A)	2386(3)	7861(3)	5210(3)	51(1)
C(4A)	2358(3)	7276(4)	7785(4)	57(1)
N(4A)	3799(3)	7325(4)	7625(4)	79(1)
O(4A1)	4134(3)	7170(4)	8658(4)	103(1)
O(4A2)	4575(4)	7511(7)	6452(5)	181(3)
N(5A)	1471(4)	6974(4)	9067(4)	77(1)
O(1B)	2608(3)	8872(3)	773(3)	76(1)
N(2B)	1638(3)	8619(3)	2099(4)	68(1)
C(3B)	2310(3)	8346(3)	3021(4)	52(1)
N(3B)	1585(3)	8047(3)	4499(3)	60(1)
C(4B)	3725(3)	8443(3)	2230(4)	53(1)
N(4B)	4914(3)	8242(4)	2740(3)	69(1)
O(4B1)	5382(4)	9240(4)	2730(5)	131(2)
O(4B2)	5304(4)	7074(4)	3189(4)	115(1)
N(5B)	3913(3)	8761(3)	871(3)	69(1)
O(1C)	1250(3)	360(3)	8372(3)	76(1)
N(2C)	1562(3)	496(3)	6945(3)	68(1)
C(3C)	1763(3)	1818(3)	6203(4)	51(1)
N(3C)	2112(3)	2459(3)	4680(3)	52(1)
C(4C)	1569(3)	2487(3)	7205(4)	53(1)
N(4C)	1710(3)	3949(3)	6926(4)	67(1)
O(4C1)	1635(4)	4282(3)	7932(4)	98(1)
O(4C2)	1900(4)	4720(3)	5703(4)	114(1)
N(5C)	1264(3)	1614(3)	8527(3)	69(1)
O(1D)	3161(3)	2632(3)	286(3)	79(1)
N(2D)	2874(3)	1666(3)	1650(4)	72(1)
C(3D)	2615(3)	2353(3)	2524(4)	54(1)
N(3D)	2276(3)	1641(3)	4024(3)	60(1)
C(4D)	2746(3)	3771(4)	1661(4)	55(1)
N(4D)	2529(4)	4983(3)	2117(3)	69(1)
O(4D1)	3531(4)	5483(4)	2069(4)	120(1)
O(4D2)	1372(4)	5345(3)	2519(4)	107(1)
N(5D)	3079(3)	3966(3)	303(4)	74(1)

azofurazan system of one molecule makes a dihedral angle of 93.4° with the azofurazan system of the other. This leads to a crystal structure that partitions space into a number of almost orthogonal boxes. Figure 2 shows this packing from a viewpoint perpendicular to **a** and **b** of the unit cell. Molecule 1 (ring atoms labelled A and B) and all of its symmetry mates are perpendicular to **b**, while molecule 2 (ring atoms labelled C and D) and its mates are perpendicular to **a**, and thus approximately orthogonal to the first set. Only two intermolecular approaches are less than usual van der Waals contact distances [16] by more than 0.1 Å; they are N2A' to C3D, at 3.06 Å (vdW is 3.25 Å), and O4C1 to C3A, at 3.12 Å (vdW is 3.22 Å). All of the dashed lines shown in Figure 2, relating orthogonal neighboring molecules, are symmetrically equivalent to these two contacts.

As would be expected, these shortest contacts are between electronegative peripheral atoms and the ring

Table 4

Bond Lengths [Å] and Angles [°] for 3

O(1A)-N(5A)	1.364(4)	O(1A)-N(2A)	1.371(4)
N(2A)-C(3A)	1.296(4)	C(3A)-C(4A)	1.402(5)
C(3A)-N(3A)	1.408(4)	N(3A)-N(3B)	1.240(4)
C(4A)-N(5A)	1.287(5)	C(4A)-N(4A)	1.445(5)
N(4A)-O(4A2)	1.174(5)	N(4A)-O(4A1)	1.189(4)
O(1B)-N(2B)	1.359(4)	O(1B)-N(5B)	1.372(4)
N(2B)-C(3B)	1.297(4)	C(3B)-N(3B)	1.398(4)
C(3B)-C(4B)	1.409(5)	C(4B)-N(5B)	1.278(4)
C(4B)-N(4B)	1.459(4)	N(4B)-O(4B1)	1.190(4)
N(4B)-O(4B2)	1.199(4)	O(1C)-N(2C)	1.367(4)
O(1C)-N(5C)	1.375(4)	N(2C)-C(3C)	1.300(4)
C(3C)-N(3C)	1.406(4)	C(3C)-C(4C)	1.409(5)
N(3C)-N(3D)	1.243(4)	C(4C)-N(5C)	1.290(4)
C(4C)-N(4C)	1.452(5)	N(4C)-O(4C2)	1.188(4)
N(4C)-O(4C1)	1.199(4)	O(1D)-N(2D)	1.355(4)
O(1D)-N(5D)	1.385(4)	N(2D)-C(3D)	1.301(4)
C(3D)-N(3D)	1.394(4)	C(3D)-C(4D)	1.403(5)
C(4D)-N(5D)	1.281(5)	C(4D)-N(4D)	1.474(5)
N(4D)-O(4D1)	1.189(4)	N(4D)-O(4D2)	1.191(4)
N(5A)-O(1A)-N(2A)	112.8(2)	C(3A)-N(2A)-O(1A)	104.7(3)
N(2A)-C(3A)-C(4A)	107.9(3)	N(2A)-C(3A)-N(3A)	125.4(3)
C(4A)-C(3A)-N(3A)	126.7(3)	N(3B)-N(3A)-C(3A)	113.8(3)
N(5A)-C(4A)-C(3A)	111.7(3)	N(5A)-C(4A)-N(4A)	118.9(3)
C(3A)-C(4A)-N(4A)	129.4(3)	O(4A2)-N(4A)-O(4A1)	124.0(4)
O(4A2)-N(4A)-C(4A)	116.4(4)	O(4A1)-N(4A)-C(4A)	119.6(4)
C(4A)-N(5A)-O(1A)	103.0(3)	N(2B)-O(1B)-N(5B)	111.5(2)
C(3B)-N(2B)-O(1B)	105.8(3)	N(2B)-C(3B)-N(3B)	119.5(3)
N(2B)-C(3B)-C(4B)	107.5(3)	N(3B)-C(3B)-C(4B)	133.0(3)
N(3A)-N(3B)-C(3B)	110.8(3)	N(5B)-C(4B)-C(3B)	110.9(3)
N(5B)-C(4B)-N(4B)	119.3(3)	C(3B)-C(4B)-N(4B)	129.7(3)
O(4B1)-N(4B)-O(4B2)	125.5(4)	O(4B1)-N(4B)-C(4B)	117.5(4)
O(4B2)-N(4B)-C(4B)	116.9(4)	C(4B)-N(5B)-O(1B)	104.2(3)
N(2C)-O(1C)-N(5C)	112.2(2)	C(3C)-N(2C)-O(1C)	105.5(3)
N(2C)-C(3C)-N(3C)	126.2(3)	N(2C)-C(3C)-C(4C)	107.5(3)
N(3C)-C(3C)-C(4C)	126.3(3)	N(3D)-N(3C)-C(3C)	114.4(3)
N(5C)-C(4C)-C(3C)	111.6(3)	N(5C)-C(4C)-N(4C)	119.2(3)
C(3C)-C(4C)-N(4C)	129.1(3)	O(4C2)-N(4C)-O(4C1)	125.4(3)
O(4C2)-N(4C)-C(4C)	116.5(3)	O(4C1)-N(4C)-C(4C)	118.1(3)
C(4C)-N(5C)-O(1C)	103.2(3)	N(2D)-O(1D)-N(5D)	111.5(3)
C(3D)-N(2D)-O(1D)	106.0(3)	N(2D)-C(3D)-N(3D)	119.9(3)
N(2D)-C(3D)-C(4D)	107.3(3)	N(3D)-C(3D)-C(4D)	132.7(3)
N(3C)-N(3D)-C(3D)	111.0(3)	N(5D)-C(4D)-C(3D)	111.7(3)
N(5D)-C(4D)-N(4D)	119.2(3)	C(3D)-C(4D)-N(4D)	129.1(3)
O(4D1)-N(4D)-O(4D2)	126.7(4)	O(4D1)-N(4D)-C(4D)	116.4(4)
O(4D2)-N(4D)-C(4D)	116.9(3)	C(4D)-N(5D)-O(1D)	103.4(3)

carbon atoms, which are positively charged by electron delocalization. However, there are also spaces at the middle of the orthogonal cavities seen in Figure 2; for example, test atoms placed at the inversion centers (0.0, 0.0, 0.5 or 0.5, 0.0, 0.5) approach no atoms closer than 2.46 Å. This is much greater than the van der Waals radii of atoms in this structure (1.70 Å, C; 1.55 Å, N; 1.52 Å, O). Unfortunately (from an energetic materials viewpoint), this mode of packing leads to a density considerably less than that expected from a volume-additivity algorithm (Table 1) [11]. Attempts to crystallize the compound as a higher density polymorph are currently under investigation.

Table 5

Anisotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for **3**.
The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [(h a^*)^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1A)	56(2)	140(3)	78(2)	-51(2)	-1(1)	-12(2)
N(2A)	49(2)	103(3)	72(2)	-40(2)	-9(2)	-7(2)
C(3A)	41(2)	50(2)	64(2)	-27(2)	-13(2)	-1(1)
N(3A)	45(2)	48(2)	66(2)	-25(1)	-19(1)	-2(1)
C(4A)	52(2)	57(2)	66(2)	-26(2)	-17(2)	-2(2)
N(4A)	62(2)	103(3)	75(2)	-31(2)	-25(2)	0(2)
O(4A1)	95(2)	130(3)	110(3)	-50(2)	-58(2)	-4(2)
O(4A2)	55(2)	383(8)	96(3)	-78(4)	-19(2)	-11(3)
N(5A)	72(2)	92(2)	70(2)	-35(2)	-15(2)	-8(2)
O(1B)	79(2)	88(2)	73(2)	-27(2)	-37(2)	-3(1)
N(2B)	61(2)	70(2)	80(2)	-25(2)	-31(2)	-4(2)
C(3B)	48(2)	49(2)	64(2)	-20(2)	-24(2)	-2(1)
N(3B)	46(2)	63(2)	69(2)	-21(2)	-19(2)	-5(1)
C(4B)	50(2)	55(2)	62(2)	-24(2)	-23(2)	-2(2)
N(4B)	55(2)	86(2)	65(2)	-24(2)	-19(2)	-6(2)
O(4B1)	126(3)	120(3)	165(4)	-23(3)	-85(3)	-47(2)
O(4B2)	98(2)	126(3)	148(3)	-63(3)	-72(2)	43(2)
N(5B)	68(2)	79(2)	67(2)	-29(2)	-24(2)	-5(2)
O(1C)	91(2)	56(2)	73(2)	-4(1)	-34(1)	-15(1)
N(2C)	81(2)	49(2)	71(2)	-12(2)	-28(2)	-10(2)
C(3C)	46(2)	43(2)	64(2)	-15(2)	-20(2)	-6(1)
N(3C)	52(2)	44(2)	64(2)	-23(1)	-19(1)	-2(1)
C(4C)	48(2)	49(2)	62(2)	-18(2)	-21(2)	-2(2)
N(4C)	76(2)	57(2)	74(2)	-28(2)	-27(2)	2(2)
O(4C1)	141(3)	83(2)	105(2)	-57(2)	-59(2)	9(2)
O(4C2)	207(4)	50(2)	79(2)	-23(2)	-34(2)	-11(2)
N(5C)	72(2)	67(2)	70(2)	-19(2)	-30(2)	-7(2)
O(1D)	88(2)	85(2)	78(2)	-48(2)	-22(2)	4(2)
N(2D)	73(2)	69(2)	84(2)	-46(2)	-19(2)	2(2)
C(3D)	45(2)	53(2)	70(2)	-31(2)	-14(2)	-2(2)
N(3D)	59(2)	48(2)	74(2)	-29(2)	-16(2)	-2(1)
C(4D)	53(2)	58(2)	58(2)	-26(2)	-16(2)	-5(2)
N(4D)	98(3)	50(2)	63(2)	-19(2)	-27(2)	-10(2)
O(4D1)	141(3)	99(3)	139(3)	-58(2)	-33(2)	-46(2)
O(4D2)	123(3)	91(2)	126(3)	-64(2)	-46(2)	39(2)
N(5D)	84(2)	71(2)	74(2)	-33(2)	-24(2)	-3(2)

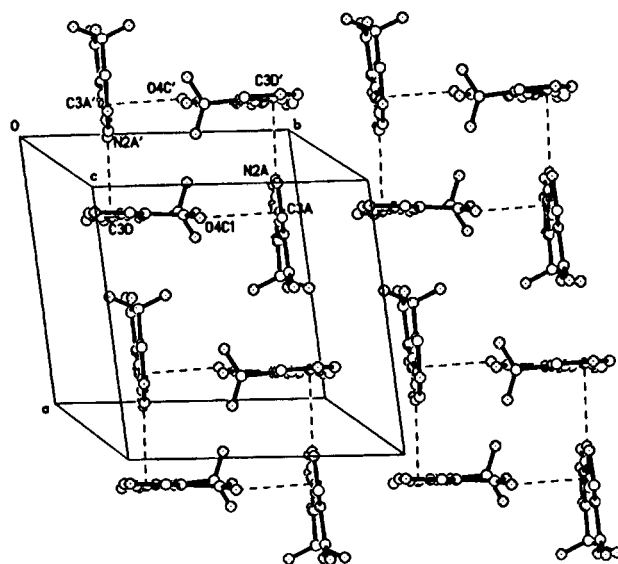


Figure 2. A drawing of a layer of molecules in the crystal of **3**, viewed down a vector perpendicular to *a* and *b* of the unit cell. Vertical molecules are related to one another by crystallographic symmetry, as are also the horizontal molecules. The two sets are independent.

EXPERIMENTAL

All chemicals and reagents not otherwise noted were purchased from Aldrich Chemical Co. The ^{13}C nmr spectra were obtained on a Varian-Gemini Multiprobe 300 MHz nmr spectrometer and mass spectra were recorded on a Hewlett-Packard 5655 GCMS spectrometer. Melting points were determined on a Mel-Temp II and are reported uncorrected. Elemental analyses were obtained from Atlantic Microlab, Inc., Norcross, GA. **Caution:** Compounds **3** and **5** should be handled as dangerously explosive materials.

3-Amino-4-nitrofurazan (**5**).

A solution of diaminofurazan (4.0 g, 0.040 mole) in concentrated sulfuric acid (90 g) was added dropwise over a period of 30 minutes at $5\text{--}10^\circ$ to a stirred suspension of ammonium persulfate (50 g) in hydrogen peroxide (30%, 60 g). The resulting mixture was allowed to warm to 30° and stirring was continued at 30° for 1.5 hours. After cooling the reaction mixture in an ice bath the precipitate was filtered off and the filtrate was poured into cold water (250 ml). The water solution was extracted with dichloromethane (5 x 200 ml), washed with water (100 ml) and dried (sodium sulfate). Evaporation of the solvent under vacuum gave an orange oil which was purified by crystallization from water to give light yellow crystals 1.8 g (35%), mp 120° , lit [12] mp 122.5° .

Dinitroazofurazan (**3**).

To a stirred suspension of **4** (200 mg, 1.50 mmoles) in concentrated hydrochloric acid (8 ml), a solution of potassium permanganate (474 mg, 3.00 mmoles) in water (53 ml) was added dropwise over a period of 1 hour at 40° . The resulting mixture was stirred for 2 hours at 55° . After cooling the solution was extracted with dichloromethane (3 x 50 ml). The combined organic fractions were washed with water (50 ml), dried (sodium

Similar to the azoxy compounds **1** and **2**, the dinitroazofurazan (**3**) was readily detonated by a hammer blow (hammer/anvil test). However, unlike **1**, no flame was observed during the detonation of **3**. Based on this result, **3** should be considered to be a sensitive explosive comparable to pentaerythol tetranitrate (PETN) [17]. Quantitative analysis of the sensitivity of **3** to impact and friction will be the subject of future investigations and reported elsewhere.

In summary, dinitroazofurazan (**3**) was found to be a highly explosive material comparable to the azoxyfurazans **1** and **2**. The azo linkage did not seem to offer any advantage toward the reduction of sensitivity. However, the short moderate yielding and relatively safe synthesis of **3** makes it an attractive energetic material worthy of further investigation.

sulfate) and the solvent was removed under vacuum to give **3** as an orange oil, 120 mg (60%). A crystalline sample was obtained by column chromatography (silica gel-pentane:dichloromethane, 1:2) followed by crystallization from a mixture of dichloromethane/pentane (1:1) mp 51-53°; lit [7] mp 56°; ¹³C nmr (deuteriochloroform): δ 155.7, 153.2; ms: (CI) m/z 257 (MH⁺).

Anal. Calcd. for C₄N₈O₆: C, 18.75; N, 43.76. Found: C, 18.98; N, 43.62.

X-ray Diffraction Analysis of Dinitroazofurazan (**3**).

Data collection was carried out on an automated Siemens P4S diffractometer equipped with an incident beam monochromator. The space group assignment was based on intensity statistics and was confirmed by the structure solution. The structure was initially determined by direct methods, using the program XS, and refined on F² values with the full-matrix least squares program XL, contained in the SHELXTL collection of computer programs [18]. The observed F² data were corrected for appreciable absorption by indexing the crystal faces and integrating over the actual paths of the X-rays through the crystal. Numerical set-up parameters and the results are listed in Table 3. Further details have been deposited with the Cambridge Crystal Structure database and are available from the author (RG).

Acknowledgments.

We are grateful for the financial support of this research provided by the Ballistic Missile Defense Organization and the Office of Naval Research through contract N00014-95-1339; Program Officers: Dr. Leonard H. Caveny (BMDO) and Dr. Richard S. Miller (ONR). In addition, this work was supported by the Office of Naval Research, Mechanics Division.

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