Synthesis and Properties of Methylene-bis-(nitraminofurazans)

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Methylene-bis-(3-aminofurazans) and methylene-bis-3-(nitraminofurazans) with methyl and nitro substituents at the 4- and 4'-positions have been synthesized. The thermal properties and crystal structures of the compounds have been determined. As expected, the methyl-substituted nitramino compound has better thermal stability than the nitro-substituted compound. The densities predicted for the compounds by the Holden method and those determined by X-ray crystallography are in close agreement.

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As part of our continuing study of heterocyclic nitramines [1,2], we became interested in what effect remote substituents would have on the stability of furazanonitramines. Methylene-bis-nitraminofurazans with methyl and nitro substituents at the 4- and 4'-position were selected for synthesis to determine what effect the change from an electron-donating group to an electron-withdrawing group would have on the thermal stability and other properties of the compounds.

Results.

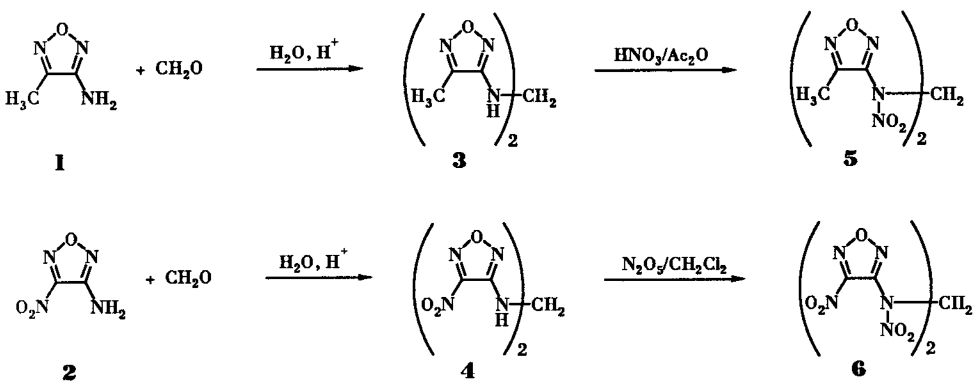
Synthesis.

The starting materials for the synthesis of the target molecules were 3-amino-4-methylfurazan [3], **1**, and 3-amino-4-nitrofurazan, **2** [4]. These were condensed with formaldehyde in water with an acid catalyst to produce excellent yields of the methylene-bis-(3-aminofurazans), **3** and **4**. Compound **3** with the methyl substituent could be easily nitrated using a standard nitric acid-acetic anhydride procedure to yield **5**. However the nitro-substituted compound, **4**, would not cleanly nitrate under these conditions. It was found that dinitrogen pentoxide in methylene chloride [5] cleanly nitrated the nitro compound, **4**, to the desired nitramino nitro compound, **6**, in essentially quantitative yield. The fact that **4** is more difficult to nitrate is consistent with the deactivation of the amino nitrogen by electron withdrawal by the nitro group. Previous results by Tselinskii *et al* have shown that the pK_a's of the conjugate acids of **1** and **2** are -2.15 and -4.46, respectively [6]. Dinitrogen pentoxide in methylene chloride has previously used a nitrating reagent by P. Golding [7].

Thermal Properties.

The thermal properties of compounds **1-6** were examined by Differential Scanning Calorimetry (DSC). These results are summarized in Table I. Based on the lower basicity of **2** as compared to **1**, it was predicted that the nitro-substituted compound **6** would be less thermally stable than the methyl-substituted compound **5**. The measured relative thermal stability of the two compounds as measured by DSC does seem to follow this prediction. Compound **5** melts at 90°, then is stable until 120° where

Scheme 1



an exothermic decomposition sets in which peaks at 146°. Compound **6** melts at 99° and a slow exothermic decomposition begins almost immediately but does not peak until 167°.

Table I

Thermal Properties of Compounds 1-6

Compound	Mp, °C	Decomposition Temperature °C		Type
		Onset	Peak	
1	74	108	189	endo [a]
2	122	160	168	exo [b]
3	198	239	241	endo
4	141	181	197	exo
5	90	120	146	exo
6	99	99	167	exo

[a] endo (endothermic); [b] exo (exothermic).

X-Ray Crystallography.

Figures 1 through 4 show thermal ellipsoid plots of compounds **3**-**6**, respectively, and Table II contains selected bond distances and angles. Complete tables of bond distances and angles are available as supplementary material.

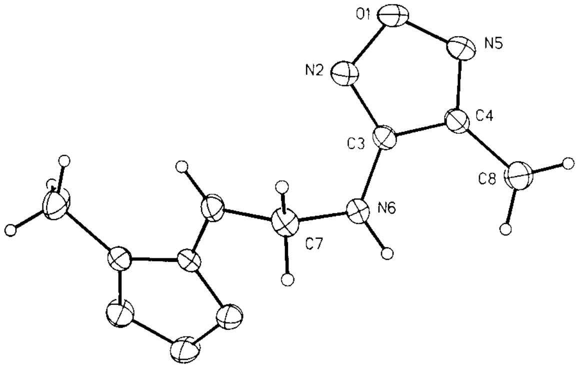


Figure 1. Molecular structure of methylene-bis-(3-amino-4-methylfurazan), 3.

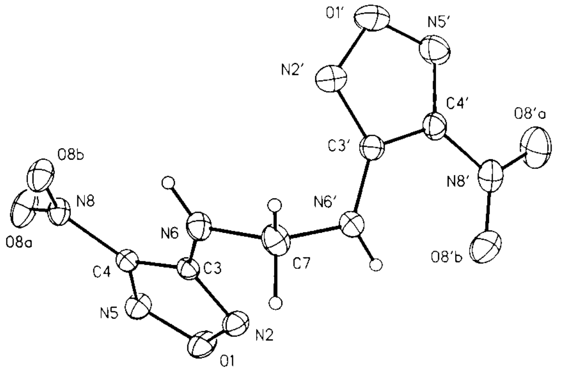


Figure 2. Molecular structure of methylene-bis-(3-amino-4-nitrofurazan), 4.

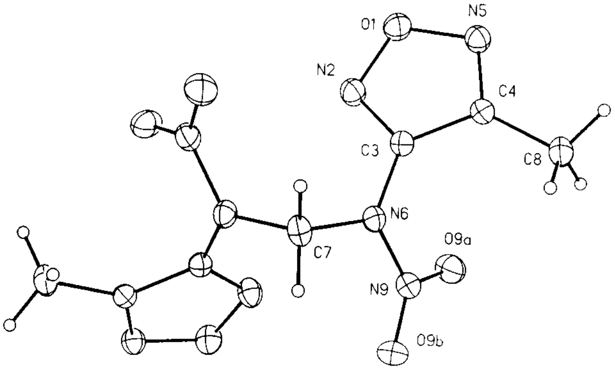


Figure 3. Molecular structure of methylene-bis-(3-nitroamino-4-methylfurazan), 5.

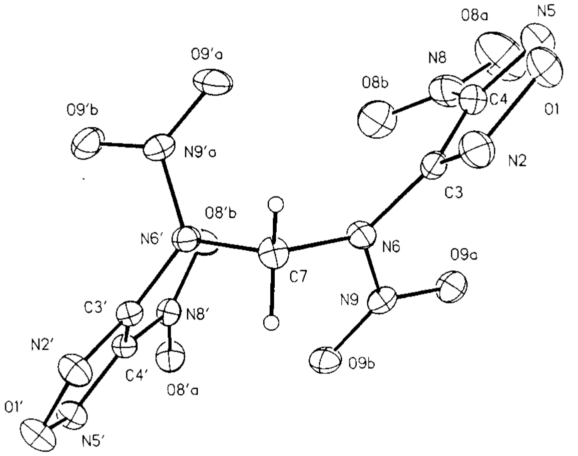


Figure 4. Molecular structure of methylene-bis-(3-nitroamino-4-nitrofurazan), 6.

Substitution of a nitro group for Me at C(4) has both electronic and steric effects and, in addition, a nitro substitution for H at N(6) precludes the intermolecular hydrogen bonding present in both **3** and **4**. In **3** through **6** the furazan rings are planar with a maximum deviation from a least-squares plane of 0.004, 0.006, 0.004, and 0.008 Å, respectively. Within the ring, the geometry of the N=C-C=N fragment shows the π delocalization common to furazans. The bond length variations are small and not much affected by the ring substituents, comparing well with the N-C = 1.300 Å, and C-C = 1.421 Å observed in furazan [8]. Examination of Table II shows the three most significant areas of variation with substituent: the endocyclic N-O distances, the C(3)-N(6) distance, and the interior N-C-C angles of the rings. In **4** where the N-O distances are most asymmetric due to the combined effects of the electron-withdrawing nitro group and weak intermolecular hydrogen bonding, the difference is O(1)-N(2) > O(1)-N(5) by 0.047 Å, while in **5** the asymmetry is 0.022 Å and opposite in direction. The carbon-amino nitrogen distances in **3** and **4** (1.342 and 1.364 Å) are considerably

Table II.

Selected Bond Lengths and Angles for Compounds **3**-**6**

	3	**4**		**5**	**6** [a]			
O(1)-N(2)	1.406(9)	1.402(3)	1.394(3)	1.372(3)	1.378(4)	1.375(4)	1.389(5)	1.382(5)
O(1)-N(5)	1.383(6)	1.355(3)	1.357(3)	1.394(3)	1.374(4)	1.377(3)	1.368(6)	1.365(5)
N(2)-C(3)	1.288(6)	1.302(3)	1.308(3)	1.293(4)	1.294(4)	1.290(4)	1.300(5)	1.284(5)
N(5)-C(4)	1.295(8)	1.287(3)	1.298(3)	1.298(3)	1.283(5)	1.289(4)	1.288(5)	1.286(4)
C(3)-C(4)	1.420(9)	1.430(3)	1.417(3)	1.421(3)	1.401(5)	1.409(4)	1.412(5)	1.420(5)
C(3)-N(6)	1.364(9)	1.342(3)	1.342(3)	1.400(3)	1.394(4)	1.396(4)	1.391(4)	1.390(4)
N(6)-C(7)	1.422(7)	1.446(3)	1.441(3)	1.453(3)	1.454(4)	1.442(4)	1.452(5)	1.453(4)
N(2)-O(1)-N(5)	109.7(4)	111.8(2)	111.7(2)	110.8(2)	111.9(2)	111.4(2)	112.4(3)	111.8(3)
O(1)-N(2)-C(3)	105.2(5)	105.2(2)	105.3(2)	104.5(2)	104.9(2)	105.5(2)	104.3(3)	105.1(3)
O(1)-N(5)-C(4)	106.2(6)	104.5(2)	104.4(2)	106.1(2)	103.4(3)	104.0(2)	103.6(3)	104.3(3)
N(2)-C(3)-C(4)	110.1(6)	107.1(2)	107.3(2)	111.3(2)	108.2(3)	108.3(3)	108.3(3)	108.5(3)
C(3)-C(4)-N(5)	108.9(4)	111.4(2)	111.3(2)	107.3(2)	111.7(3)	110.8(3)	111.4(4)	110.4(3)
N(2)-C(3)-N(6)	123.5(6)	124.6(2)	123.8(2)	120.6(2)	121.0(3)	121.5(3)	120.8(3)	120.3(3)

[a] Two molecules in the asymmetric unit cell.

shorter than a C_{sp^2}–N_{sp^3} bond (1.41 Å), while the carbon-nitramine nitrogen distances in **5** and **6** range from 1.390 to 1.400 Å. The interior N-C-C furazan ring angles are also asymmetric with differences in the range of 2.2 to 4.3°, with the sense of the difference a function of substituent. Nearly identical values are observed when comparing the corresponding N-O, C-N, and N-C-C angles in 3-amino-4-methylfurazan [9] [O(1)-N(2) = 1.404 Å, O(1)-N(5) = 1.380 Å, C(3)-N(6) = 1.344 Å, N(2)-C(3)-C(4) = 109.7°, N(5)-C(4)-C(3) = 108.2°]* [*Average values, two molecules per asymmetric unit] and the respective values in isopropyl 4-methyl-3-furazancarbamate [10] [1.392, 1.377, 1.376 Å, 110.1, 107.9°] to **3**, and additionally the respective values in 3-amino-4-nitrofurazan [11] [1.417, 1.340, 1.342 Å, 106.9°, 111.3°]* to **4**. The steric effects of the nitroamino substituents on the molecular conformation are most evidenced by the torsion angles C(4)-C(3)-N(6)-C(7) = 169.4° (**3**), -177.2 and -176.2° (**4**), -128.5° (**5**), and -132.1, -109.2, -134.0, -111.9° (**6**). The hydrogen bond parameters for **3** are N(6)--N(5) = 3.105 Å, H(6)--N(5) = 2.24 Å, and <N-H--N = 168.5°; parameters for **4** are N(6)--O(1) = 3.171 Å, H(6)--O(1) = 2.38 Å, and <N-H--O = 156.8°, and N(6)'--O(8A) = 3.159 Å, H(6)'--O(8A) = 2.42 Å, and <N-H--O = 149.4°. Intermolecular contacts in **5** and **6** are at normal van der Waals separations.

Table III

Predicted and Measured Densities of Compounds **3**-**6**

Compound	Predicted Density, g/cc [a]	Measured Density, g/cc
3	1.429	1.398
4	1.798	1.768
5	1.625	1.626
6	1.917	1.862

[a] See Ref 7.

Table III summarizes the measured and predicted densities for compounds **3**-**6**. The predicted densities were calculated by the method of Holden [12]. As one can readily see, there is close agreement between the predicted and measured values, the greatest deviation being 3%.

EXPERIMENTAL

WARNING! Compounds **5** and **6** are explosives of moderate sensitivity and should be handled accordingly.

The ^{1}H nmr spectra were recorded on a Varian EM-360A NMR spectrometer and are referenced to TMS. The ir spectra were recorded on a Nicolet 6000 FTIR spectrometer either as films (liquids) or potassium bromide pellets (solids). Melting points (decomposition points) were measured in a DuPont 910 DSC coupled to a DuPont 1090 thermal analyzer at 10°/minute. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Methylene-bis-(3-amino-4-methylfurazan), **3**.

3-Amino-4-methylfurazan (4.00 g, 40.4 mmoles), 37% formaldehyde (1.60 g, 19.7 mmoles), 1 ml concentrated hydrochloric acid, and 50 ml of water were placed in a 100 ml round bottom flask equipped with a magnetic stirring bar and a reflux condenser. A white precipitate formed almost immediately. The mixture was refluxed for 5 minutes, then cooled to 0° in an ice bath. The product was collected, washed with water, and dried. The yield was 4.03 g (19.2 mmoles, 98%). An analytical sample was recrystallized from DMF/H_2O, mp 198°; ir: 3350 (s), 1611 (s), 1563 (s), 1394 (m), 1241 (m), 1121 (w), 1063 (w) cm^{-1}; ^{1}H nmr (acetone-d_6): 2.20 (s, 6 H, CH_3), 4.65 (t, J = 5 Hz, 2 H, CH_2), 7.21 (t, J = 5 Hz, 2 H, NH) ppm.

Anal. Calcd. for $C_7H_{10}N_6O_2$: C, 40.00; H, 4.80; N, 39.97. Found: C, 39.82; H, 4.88; N, 40.36.

Methylene-bis-(3-amino-4-nitrofurazan), **4**.

In a 50-ml round bottom flask equipped with a magnetic stir-

Table IV

Crystal and Refinement Data for Compounds **3**-**6**

	3	**4**	**5**	**6**
Formula	$C_7H_{10}N_6O_2$	$C_5H_4N_8O_6$	$C_7H_8N_8O_6$	$C_5H_2N_{10}O_{10}$
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	P2nn	C2/c	C2/c	$P2_1/c$
a, Å	4.217(1)	22.371(3)	9.445(1)	11.500(1)
b, Å	10.419(2)	6.305(1)	9.028(1)	19.110(4)
c, Å	11.368(2)	14.753(2)	15.107(1)	12.004(2)
β, deg.		100.66(1)	107.80(1)	101.61(1)
V, $Å^3$	499.4(2)	2044.8(5)	1226.5(2)	2584.1 (7)
Z	2	8	4	8
Formula weight	210.2	272.2	300.2	362.2
F(000)	220	1104	616	1456
ρ(calc), g cm^{-3}	1.398	1.768	1.626	1.862
crystal dim., mm	0.02 x 0.05 x 0.51	0.08 x 0.18 x 0.42	0.03 x 0.10 x 0.15	0.30 x 0.42 x 0.56
μ, absorption coef., cm^{-1}	8.7	13.7	12.0	15.5
2θ max., deg.	115	115	115	115
ω scan speed, deg./min.	variable 3.0 to 15.0	variable 3.0 to 15.0	variable 3.0 to 15.0	variable 3.0 to 30.0
2θ scan range, deg.	2.0 + Δα1α2	2.0 + Δα1α2	2.0 + Δα1α2	2.0 + Δα1α2
data collected, h k l	-4 to 0, -11 to 0, 0 to 12	-24 to 0, -1 to 6, -15 to 16	-10 to 0, -9 to 0, -15 to 16	-12 to 12, 0 to 20, 0 to 13
unique data	403	1396	845	3530
R_{int}	NA	0.019	0.017	0.028
unique data, $F_o>3\sigma(F_o)$	371	1287	709	2983
standard reflection	1.0% random	2.1% linear decay	1.7% random	1.6% random
parameters refined	77	185	102	163
weighting funtion, g [a]	0.00023	0.00023	0.00023	0.00023
R [b], wR [c], S [d]	0.047, 0.055, 2.03	0.039, 0.052, 2.28	0.040, 0.045, 1.48	0.049, 0.052, 1.73
Fourier excursions, e $Å^{-3}$	0.20, -0.22	0.22, -0.21	0.18, -0.17	0.25, -0.25

[a] $w^{-1} = \sigma^2(F_o) + g F_o^2$. [b] $\Sigma|\Delta|\Sigma|F_o|$. [c] $\Sigma[(w\Delta^2)/\Sigma(wF_o^2)]^{1/2}$. [d] $[\Sigma w(\Delta^2)/(N_o-N_p)]^{1/2}$.

ring bar and reflux condenser was placed 1.50 g of 3-amino-4-nitrofurazan (11.5 mmoles), 0.60 g of 37% formaldehyde, 20 ml of water and 8 drops of concentrated hydrochloric acid. This mixture was refluxed for 10 minutes, cooled to 0°, and the product collected, washed with water, and dried. The yield of product was 1.50 g (5.50 mmoles, 96%). An analytical sample was recrystallized from acetone/water, mp 141°; ir (potassium bromide): 3432 (s), 1625 (sh), 1614 (vs), 1525 (s), 1449 (w), 1395 (m), 1385 (sh), 1340 (m), 1290 (w), 1197 (m), 1113 (m), 1061 (w), 1014 (m), 832 (m) cm^{-1}; ^1H nmr (acetone-d_6): 5.07 (t, J = 6 Hz, 2 H), 7.2 (bs, 2 H, NH) ppm.

Anal. Calcd. for $C_5H_4N_8O_6$: C, 22.07; H, 1.48; N, 41.17. Found: C, 22.10; H, 1.36; N, 41.14.

Methylene-bis-(3-nitramino-4-methylfurazan), **5**.

In a 25-ml round bottom flask was placed 5.0 g of 100% nitric acid. This was cooled to -5° and 3.0 g of acetic anhydride was added over 15 minutes. Methylene-bis-(3-amino-4-methylfurazan) (2.10 g, 10 mmoles) was added in small portions over 15 minutes. This mixture was stirred for 30 minutes at -5° and 30 minutes at 15°. The mixture was poured onto ice (50 g) and the product oiled out. It crystallized over several days. It was collected and washed with cold methanol. The yield was 2.85 g (9.5 mmoles, 95%). An analytical sample was recrystallized from methanol, mp 90°; ir (potassium bromide): 1595 (vs), 1507 (w), 1442 (w), 1421 (w), 1390 (w), 1093 (m), 898 (w), 768 (w), 752 (s), 734 (w), 672 (w), 632 (w) cm^{-1}; ^1H nmr (acetone-d_6): 2.42 (s, 6 H), 6.70 (s, 2 H) ppm.

Anal. Calcd. for $C_7H_8N_8O_6$: C, 28.01; H, 2.69; N, 37.32. Found: C, 28.04; H, 2.81; N, 37.14.

Methylene-bis-(3-nitramino-4-nitrofurazan), **6**.

To a 1*M* solution of nitrogen pentoxide methylene chloride (3.47 g, 3.52 mmoles) maintained at -25° was added 119 mg of methylene-bis-(3-amino-4-nitrofurazan) (0.44 mmoles) over 15 minutes. The temperature was raised to 0° and the mixture allowed to stir for 1.5 hours. The solution was stripped on a rotary evaporator without heat to give the product (150 mg, 0.42 mmole, 95%). An analytical sample was recrystallized from methanol-water, mp 99°; ir (potassium bromide): 3044 (w), 1616 (s), 1586 (s), 1547 (s), 1289 (s), 1229 (w), 1115 (m), 1081 (m), 915 (m), 836 (m); ^1H nmr (acetone-d_6): $\delta = 6.85$ (s) ppm.

Anal. Calcd. for $C_5H_2N_{10}O_{10}$: C, 16.59; H, 0.56; N, 38.67. Found: C, 16.64; H, 0.53; N, 37.75.

Crystallographic Studies.

Suitable crystals of **3**, **4**, **5**, and **6** were selected for data collection on an automated Siemens R3m/V diffractometer using CuKα radiation (λ = 1.54184 Å) and an incident beam graphite monochromator at T = 295 K. Data were corrected for Lorentz and polarization effects, but not for absorption. The space group determinations were based on extinctions present and were confirmed by the structure solution. In each case, the structures were determined by direct methods with the aid of the program SHELXTL [13] and refined using a full-matrix, least-squares program [13]. In each structure the parameters refined include the atom coordinates and anisotropic thermal parameters for all but the hydrogens. Hydrogen positions were refined isotropically with fixed thermal parameters except for ethyl hydrogens, which were placed in idealized positions (C-H = 0.96 Å) with the methyl group treated as a rigid group and allowed to rotate about the C-C bond. Table IV contains additional data collection and refinement parameters.

Acknowledgment.

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Supplementary Material Available.

Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors are available from the NRL author. Coordinates and bond lengths and angles will also be available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

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