

Daryl L. Ostercamp* and Sarah Wiles

Department of Chemistry, Concordia College, Moorhead, MN 56562 USA

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The first preparation of title compound **1** is accomplished. Its heterocyclic structure was characterized spectroscopically and by X-ray structure analysis.

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We wish to report the serendipitous synthesis of title compound **1** from nitromalonaldehyde **2** and methylamine. Condensation of **2** with primary alkylamines and primary arylamines generally occurs stepwise, to form nitroenamines **3** or **4**, as desired [1-5]. A synthesis of **4** wherein R = Me has been reported [3]; our attempt to duplicate this result led instead to **1**.

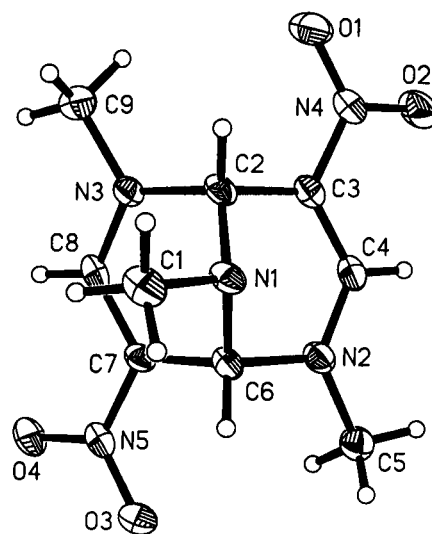
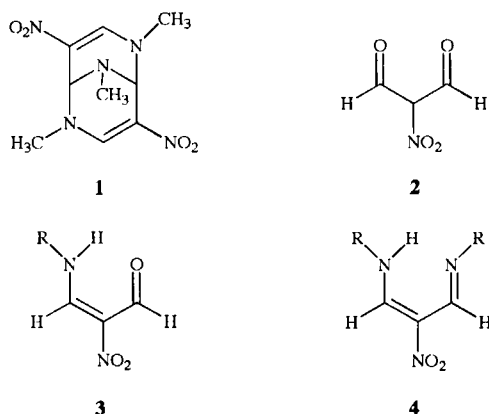


Figure 1. Molecular structure of **1** with atom numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms as small circles of arbitrary size.

Much of the three-dimensional structure of compound **1** (Figure 1) can be traced to the presence of two very nearly planar nitroenamine moieties, cojoined by tetrahedral bridgehead carbon atoms. The pyramidal nature of the single nonconjugated nitrogen (N1, Figure 1) breaks the otherwise C_2 symmetry of the molecule.

Within either of the nitroenamine enforced planes, the largest deviation from planarity of the heavy atoms is evidenced by a C6-C7-C8-N3 dihedral angle of $5.5(5)^\circ$. It is to be noted as well that twisting of either nitro group from its plane is quite minimal.

π electron delocalization and concomitant changes in bond lengths are well documented for nitroenamines. The pivotal bond lengths C3-N4 [1.409(4) Å] and C7-N5 [1.396(4) Å], C3-C4 [1.364(5) Å] and C7-C8 [1.382(4) Å], and C4-N2 [1.330(4) Å] and C8-N3 [1.331(4) Å] observed for **1** are all consistent with literature values [6-8].

Our preparation of the 2,6,9-triazabicyclo[3.3.1]nonane skeleton has two precedents. The syntheses of 2,6,9-trimethyl-2,6,9-triazabicyclo[3.3.1]nonane by Katritzky *et al.*

[9], and 1,5-dimethyl-3,7-dioxo-2,6,9-triazabicyclo[3.3.1]nonane by Shim *et al.* [10] apparently involve condensation and hetero-Michael reactions. The reaction of nitromalonaldehyde and methylamine in the presence of amine hydrochloride to form **1** can be rationalized in a similar fashion.

EXPERIMENTAL

Melting points are uncorrected and were determined using evacuated sealed capillaries inserted into a heated metal block. The nmr spectra were recorded on a Bruker ARX-300 spectrometer (^1H nmr 300 MHz, ^{13}C nmr 75 MHz), tetramethylsilane being the internal standard. Microanalysis was performed by the North Dakota State Microanalysis Laboratory.

2,6,9-Trimethyl-4,8-dinitro-2,6,9-triazabicyclo[3.3.1]nona-3,7-diene (**1**).

To a stirred solution of sodium nitromalonaldehyde monohydrate (318 mg, 2.02 mmoles) and methylamine hydrochloride

(300 mg, 4.44 mmoles) in methanol (3.5 ml) was added triethylamine (0.31 ml, 2.2 mmoles) dropwise. After 7 days at room temperature the methanolic solution was diluted with water (10 ml) to give **1** as fine yellow crystals (170 mg, 66%), mp 225–229°C. Recrystallization from 2-butanone furnished an analytical sample, mp 228–230°C; ¹H nmr (CDCl₃): δ 8.20 (s, 2H), 5.20 (s, 2H, bridgehead), 3.51 (s, 6H, NCH₃) 2.38 (s, 3H, NCH₃); ¹³C nmr (CDCl₃) δ 145.2, 121.2, 69.1 (bridgehead C' S), 43.2 (N₂CH₃ and N₆CH₃), and 37.9 (bridge NCH₃).

Anal. Calcd. for C₉H₁₃N₅O₄: C, 42.30; H, 5.13; N, 27.52. Found: C, 42.38; H, 4.98; N, 27.17.

X-Ray Structure Determination of **1** [11].

Data Collection.

A crystal of the compound was attached to a glass fiber, and mounted on a Siemens SMART Platform CCD diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from 92 reflections. Final cell constants are calculated from a set of 5687 strong reflections from the actual data collection.

The data collection technique used for this specimen is generally known as a hemisphere collection. Here a randomly oriented region of reciprocal space is surveyed to the extent of 1.0 hemispheres to a resolution of 0.84 Å. Three major swaths of frames are collected with 0.30°C steps in ω.

Table 1

Single Crystal X-ray Crystallographic Analysis of **1**

A. Crystal data	
empirical formula	C ₉ H ₁₃ N ₅ O ₄
crystal size, mm	0.28 x 0.24 x 0.04
crystal system	orthorhombic
space group	Pbca
cell dimensions	a = 8.6435(1) Å α = 90° b = 11.9464(1) Å β = 90° c = 21.8448(1) Å γ = 90°
volume	2255.6(3) Å ³
molecules/unit cell	8
density calcd.	1.503 Mg/m ³
linear absorption coefficient	0.120 mm ⁻¹
F(000)	1072
B. Refinement Parameters	
θ range for data collection	1.86 to 25.00°
index ranges	0 ≤ h ≤ 10, 0 ≤ k ≤ 14, 0 ≤ l ≤ 25
reflections collected	10063
independent reflections	1983 [R(int) = 0.04358]
solution	direct methods
refinement method	full-matrix least-squares on F ²
weighting scheme	w = [σ ² (F _o ²) + (AP) ² + (BP)] ⁻¹ , where P = (Fo ² + 2Fc ²)/3, A = 0.0469, and B = 5.8924
absorption correction	SADABS (Shelrick, 1996)
max. and min. transmission	1.000 and 0.743
data/restraints/parameters	1983/0/166
R indices [I > 2σ(I) = 1535]	R1 = 0.0674, wR2 = 0.1319
R indices (all data)	R1 = 0.0974, wR2 = 0.1464
goodness-of-fit on F ²	1.007
largest diff. peak and hole	0.223 and -0.242 e Å ⁻³

The space group Pbca was determined based on systematic absences and intensity statistics [12]. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The material was soft so one thin plate was loosened from a clump of crystals in oil. This specimen was mounted and found to diffract poorer with 10 second frames. The duration was increased to 60 seconds. The specimen appeared to diffract satisfactorily with this exposure.

Table 2

Bond Lengths (Å) and Bond Angles (°) for **1**

N1-C1	1.474(4)	N1-C6	1.464(4)
N1-C2	1.450(4)	C2-C3	1.498(5)
C2-N3	1.505(4)	C3-C4	1.364(5)
C3-N4	1.409(4)	C4-N2	1.330(4)
N2-C5	1.465(4)	N2-C6	1.478(4)
C6-C7	1.500(4)	C7-C8	1.382(4)
C7-N5	1.396(4)	C8-N3	1.331(4)
N3-C9	1.464(4)	N4-O1	1.243(4)
N4-O2	1.253(4)	N5-O4	1.243(3)
N5-O3	1.265(3)		
C2-N1-C6	109.6(2)	C2-N1-C1	113.7(3)
C6-N1-C1	112.0(3)	N1-C2-C3	105.7(3)
N1-C2-N3	111.1(3)	C3-C2-N3	112.0(3)
C4-C3-N4	119.4(3)	C4-C3-C2	121.0(3)
N4-C3-C2	119.4(3)	N2-C4-C3	121.7(3)
C4-N2-C5	122.0(3)	C4-N2-C6	118.3(3)
C5-N2-C6	118.9(3)	N1-C6-N2	107.2(2)
N1-C6-C7	109.4(3)	N2-C6-C7	112.2(3)
C8-C7-N5	118.9(3)	C8-C7-C6	120.8(3)
N5-C7-C6	119.7(3)	N3-C8-C7	121.4(3)
C8-N3-C9	122.3(3)	C8-N3-C2	118.1(3)
C9-N3-C2	119.2(3)	O1-N4-O2	121.8(3)
O1-N4-C3	118.6(3)	O2-N4-C3	119.6(3)
O4-N5-O3	121.0(3)	O4-N5-C7	121.3(3)
O3-N5-C7	117.7(3)		

Table 3

Torsion Angles for **1**

C6-N1-C2-C3	-61.2(3)	C1-N1-C2-C3	172.6(3)
C6-N1-C2-N3	60.5(3)	C1-N1-C2-N3	-65.8(3)
N1-C2-C3-C4	26.9(3)	N3-C2-C3-C4	-94.1(4)
N1-C2-C3-N4	-148.0(3)	N3-C2-C3-N4	90.9(3)
N4-C3-C4-N2	177.3(2)	C2-C3-C4-N2	2.4(5)
C3-C4-N2-C5	172.6(3)	C3-C4-N2-C6	2.2(5)
C2-N1-C6-N2	66.9(3)	C1-N1-C6-N2	-165.9(3)
C2-N1-C6-C7	-55.0(3)	C1-N1-C6-C7	72.1(3)
C4-N2-C6-N1	-35.5(4)	C5-N2-C6-N1	153.9
C4-N2-C6-C7	84.7(3)	C5-N2-C6-C7	-86.0(3)
N1-C6-C7-C8	23.1(4)	N2-C6-C7-C8	-95.8(4)
N1-C6-C7-N5	-148.3(3)	N2-C6-C7-N5	92.8(3)
N5-C7-C8-N3	177.0(3)	C6-C7-C8-N3	5.5(5)
C7-C8-N3-C9	-175.0(3)	C7-C8-N3-C2	-1.2(5)
N1-C2-N3-C8	-32.0(4)	C3-C2-N3-C8	85.9(3)
N1-C2-N3-C9	142.0(3)	C3-C2-N3-C9	-100.1(3)
C4-C3-N4-O1	-178.6(3)	C2-C3-N4-O1	-3.6(4)
C4-C3-N4-O2	2.5(5)	C2-C3-N4-O2	177.6(3)
C8-C7-N5-O4	4.5(5)	C6-C7-N5-O4	176.1(3)
C8-C7-N5-O3	-174.7(3)	C6-C7-N5-O3	-3.2(4)

Table 4

Atomic Coordinates [$\times 10^4$] and Equivalent Isotopic
Displacement Parameters [$\text{\AA}^2 \times 10^3$] for **1**

	x	y	z	U(eq) [a]
N1	-1627(3)	1986(2)	4181(1)	20(1)
C1	-3153(4)	1474(3)	4292(2)	27(1)
C2	-1510(4)	2552(3)	3596(1)	20(1)
C3	22(4)	3140(3)	3603(2)	22(1)
C4	1217(4)	2748(3)	3950(2)	22(1)
N2	1091(3)	1814(3)	4277(1)	22(1)
C5	2418(4)	1314(3)	4593(2)	28(1)
C6	-369(4)	1174(3)	4240(2)	19(1)
C7	-395(4)	391(3)	3703(1)	19(1)
C8	-1083(4)	703(3)	3158(2)	21(1)
N3	-1629(3)	1734(2)	3074(1)	20(1)
C9	-2471(5)	2057(3)	2520(2)	29(1)
N4	191(3)	4159(2)	3286(1)	24(1)
O1	-921(3)	4515(2)	2981(1)	32(1)
O2	1453(3)	4673(2)	3308(1)	36(1)
N5	90(3)	-716(2)	3776(1)	21(1)
O3	607(3)	-1002(2)	4295(1)	27(1)
O4	4(3)	-1401(2)	3350(1)	28(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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REFERENCES AND NOTES

- [1] P. D. Fanta and R. A. Stein, *Chem. Rev.*, **60**, 261 (1960).
- [2] S. M. Kvitko, Yu. V. Maksimov, T. Ya. Paperno and V. V. Perekalin, *Russ. J. Org. Chem.*, **9**, 477 (1973).
- [3] V. P. Kurbatov, S. V. Serbina and O. A. Osipov, *Russ. J. Inorg. Chem.*, **18**, 1414 (1973).
- [4] D. L. Ostercamp, L. M. Preston and K. D. Onan, *Z. Naturforsch.*, **48B**, 1138 (1993).
- [5] D. L. Ostercamp, L. M. Preston and S. Wiles, unpublished results.
- [6] E. N. Gate, M. A. Meek, C. H. Schwalbe, M. F. G. Stevens and M. D. Threadgill, *J. Chem. Soc., Perkin Trans. 2*, 251 (1985).
- [7] A. Hazell and A. Mukhopadhyay, *Acta Crystallogr.*, **B36**, 747 (1980).
- [8] J. A. Schlueter and A. G. Cook, *J. Org. Chem.*, **54**, 2255 (1985).
- [9] A. R. Katritzky, V. J. Baker, I. J. Ferguson and R. C. Patel, *J. Chem. Soc. Perkin 2*, 143 (1979).
- [10] S. C. Shim, D.-W. Kim, S.-S. Moon and Y. B. Chae, *J. Org. Chem.*, **49**, 1449 (1984).
- [11] Crystallographic data (excluding structure factors) for the structure of the title compound **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143146. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
- [12] SHELXTL-Plus V5.0, Siemens Industrial Automation, Inc., Madison, WI, USA.