New Energetic Derivatives of 1-Amino-3-Nitroguanidine

Bo Wu, Hongwei Yang, Yongxing Tang, Zhixin Wang, Chunxu Lu, and Guangbin Cheng

School of Chemical Engineering, Nanjing University of Science and Technology,
Nanjing, Jiangsu, P. R. China

Two new energetic derivatives of 1-amino-3-nitroguanidine were synthesized. The furoxan moiety and 2,4,6-trinitrophenyl moiety were introduced to the nitroguanidine frame. The resulting compounds 3-methyl-4-((2-(N\text{\textsuperscript{0}})-nitrocarbamimidoyl)hydrazono)methyl)-1,2,5-oxadiazole-2-oxide (1, C\textsubscript{5}H\textsubscript{7}N\textsubscript{7}O\textsubscript{4}) and N\text{\textsuperscript{0}}-nitro-2-(2,4,6-trinitrobenzylidene)hydrazinecarboximidamide (2, C\textsubscript{8}H\textsubscript{6}N\textsubscript{8}O\textsubscript{8}) were characterized by infrared (IR) spectroscopy, multinuclear nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), as well as elemental analysis. The structure of 1 was confirmed by X-ray diffraction. Both compounds possess good thermal stability with the decomposition onset temperature above 180°C. Their sensitivity and explosive properties were investigated by experimental and theoretical methods.

Keywords: 1-amino-3-nitroguanidine, furoxan, 2,4,6-trinitrophenyl, X-ray diffraction, energetic materials

INTRODUCTION

Since the first guanidine derivative was prepared by Hofmann as early as 1866 [1], guanidine chemistry has evolved into an extremely wide-ranging field of application from bioorganic chemistry and biochemistry [2, 3] to inorganic chemistry. In recent years, the development of new high-energy-density materials has focused on environmentally high-nitrogen-content compounds [4]. The guanidine building block is an important moiety to design and synthesize novel high-nitrogen-content energetic materials. Principally, amination and nitration products of guanidine are of major interest. Various high-nitrogen-content energetic salts including full series of amination products of the guanidinium cation (amino-, diamino-, and triaminoguanidinium cation) have been investigated [5, 6]. Nitroguanidine has also been developed as an ingredient mainly used in explosive and propellant formulations [7]. As a known guanidine derivative containing both an amine and a nitro substituent, 3-amino-1-nitroguanidine has been used in the field of energetic materials. It can be used as a useful intermediate for cyclization reactions yielding bis-nitraminotriazoles [8] and for the synthesis of 5-nitriminotetrazole [9]. In addition, it has been found as a ligand for synthesis of high-energy-capacity transition metal complexes [10]. As shown in Scheme 1, some ionic energetic materials based on 3-amino-1-nitroguanidine have been also developed [11]. Unfortunately, for these ionic...
energetic materials, decomposition temperatures are significantly lower than 180°C, which is a general temperature requirement for any energetic materials prior to adaptation for practical application. The introduction of a conjugation system in explosive molecules might be useful for the improvement of the thermal stability of energetic materials. Aromatic energetic moieties such as a furoxan ring [12–15] and trinitrophenyl group [16] are promising candidates. In this article, we present two novel energetic derivatives based on 1-amino-3-nitroguanidine containing a furoxan ring and trinitrophenyl group, respectively. The resulting compounds 1 and 2 were characterized for structural aspects, thermal behavior, and explosive properties by experimental and theoretical methods.

RESULTS AND DISCUSSION

The starting materials 3-amino-1-nitroguanidine, 3-methyl-4-furoxancarbaldehyde, as well as 2,4,6-trinitrobenzaldehyde were prepared according to the literature [17–20]. It is well known that both hydrazines and amines can react with aromatic aldehyde to form Schiff bases and hydrazones. However, in 3-amino-1-nitroguanidine molecules, only the hydrazine group can readily react with the aldehyde group, and the condensation reaction of the amine group with the aldehyde group did not occur. This might be attributed to the fact that the strong electron-withdrawing inductive effect of the nitro group decreases the reactivity of amine group. 3-Amino-1-nitroguanidine reacted with 3-methyl-4-furoxancarbaldehyde and 2,4,6-trinitrobenzaldehyde to yield 3-methyl-4-((2-(N'-nitrocarbamimidoyl)hydrazono)methyl)-1,2,5-oxadiazole-2-oxide (1) and N'-nitro-2-(2,4,6-trinitrobenzylidene)hydrazinecarboximidamide (2) in yields of 95 and 90%, respectively (Scheme 2).

Single crystals of 1 suitable for X-ray crystallographic analysis were obtained by slow evaporation from its DMF/H2O solution at room temperature. Compound 1 was characterized by low-temperature (173 K) single-crystal X-ray structure determination. The crystallographic data are summarized in Table 1. Further information on the crystal structure determination is presented in Tables S1–S4 (see online Supporting Information).

Compound 1 crystallized in the monoclinic space group P2(1) with two formula units in the unit cell. The molecular structure is depicted in Fig. 1. A density of 1.653 g cm−3 was determined from the X-ray crystal structure. The molecules are in an E configuration. The furoxan moiety and C3−N3 are planar with mean deviation of 0.0164 Å. The -NH2 unit of
the aminonitroguanidine moiety sits almost inside the plane (N3-N4-C4-N6 0.7(3)°), whereas
the nitro group is slightly twisted out of the plane (N4-C4-N5-N7 171.1(2)°). The bond length
of the double bond C3\(\text{N3}\) is 1.277(6) \(\text{Å}\), which is in good agreement with that of similar fur-
oxan derivatives in the literature \[15\]. In the aminonitroguanidine moiety, the C4-N6 distances
(1.319(3) \(\text{Å}\)) are shorter than that of C4-N4 (1.344(3) \(\text{Å}\)) and C4-N5 (1.349(3) \(\text{Å}\)), which is con-
sistent with that reported for the structure of 3-amino-1-nitroguanidine \[11, 21\]. In the packing
diagram, as shown in Fig. 2, it can be seen that classical intramolecular hydrogen bonds were

| TABLE 1 |
| Crystallographic Data and Parameters |
|-------------------------------------|
| **Empirical formula** | \(\text{C}_3\text{H}_7\text{N}_7\text{O}_4\) (I) |
| Formula weight | 229.18 |
| Crystal system | Monoclinic |
| Space group | \(P2(1)\) |
| \(a\) (Å) | 6.5979(6) |
| \(b\) (Å) | 5.6829(6) |
| \(c\) (Å) | 12.3656(13) |
| \(\alpha\) (°) | 90 |
| \(\beta\) (°) | 96.806(4) |
| \(\gamma\) (°) | 90 |
| \(V\) (\(\text{Å}^3\)) | 460.38(8) |
| \(Z\) | 2 |
| \(\rho_{\text{cal}}\) (g cm\(^{-3}\)) | 1.653 |
| \(F(000)\) | 236 |
| \(\theta\) range (°) | 3.32 to 25.24 |
| Goodness-of-fit on \(F^2\) | 1.038 |
| Final \(R\) indices [I > 2\(\sigma(I)\)] | \(R_1 = 0.0373, \, wR_2 = 0.0780\) |
| \(R\) indices (all data) | \(R_1 = 0.0545, \, wR_2 = 0.0825\) |
| CCDC | 1007109 |
found in N6-H6A···N3 and N6-H6B···O3. Furthermore, N4-H4···O2i, N4-H4···N5i, and
N6-H6B···N1ii (symmetry code: i: 2 − x, −1/2 + y, 1 − z; ii: −1 + x, 1 + y, z) intermolecular
hydrogen bonds were found between the layers. These extensive hydrogen bonding interactions
form a complex 3D network, which contributes greatly to the high thermal stability of 1.

The multinuclear nuclear magnetic resonance (NMR) spectra of the compounds 1 and 2 were
recorded in [D6]DMSO (Figs. S1–S4, Supporting Information). The 1H-NMR spectrum of 1

FIGURE 1 Molecular structure of 1 and thermal ellipsoids represent 50% probability.

FIGURE 2 Ball and stick packing diagram of 1 viewed down the b axis. Dashed lines indicate strong hydrogen bonding.
exhibits four signals. The $-\text{CH}_3$ protons and the $-\text{NH}-$ protons appear as singlets at $\delta = 2.39$ and 12.24 ppm, respectively. One of the protons in the $-\text{NH}_2$ group appears as a broad singlet at $\delta = 9.00$ ppm. Another one is observed at $\delta = 8.21$ ppm, which coincides with the proton singlet of the $-\text{CH}=$-$\text{N}-$ group. In the $^{13}\text{C}$-NMR spectrum, the signals of the methyl group are observed at $\delta = 10.68$ ppm. The signals of two carbon atoms in the furoxan ring appear at $\delta = 113.1$ and 155.0 ppm. The signals of carbon atoms in the nitroguanidine moiety and $-\text{CH}=\text{N}-$ group are assigned at $\delta = 159.2$ and 137.4 ppm, respectively.

Five proton signals are observed in the $^1\text{H}$-NMR spectrum of 2. The proton signals of the 2,4,6-trinitrophenyl group appear as a sharp singlet at $\delta = 9.12$ ppm. The signals of the $-\text{CH}=\text{N}-$ and $-\text{NH}-$ groups are observed as sharp singlets at $\delta = 8.51$ and 7.64 ppm, respectively. The resonance of the $-\text{NH}_2$ group splits into two different signals appearing at $\delta = 8.98$ and 7.64 ppm, respectively. There are six signals in the $^{13}\text{C}$-NMR spectrum of 2. The signal of the nitroguanidine moiety appears at $\delta = 159.2$ ppm. The signal of the $-\text{CH}=\text{N}-$ group is observed at $\delta = 140.0$ ppm. Four signals of 2,4,6-trinitrophenyl group are assigned at $\delta = 150.4$, 148.8, 129.5, and 124.8 ppm.

The $^{15}\text{N}$-NMR spectra of compound 2 were measured in [D6]DMSO solvent, and chemical shifts are given with respect to CH$_3$NO$_2$ as an external standard. The assignments in the $^{15}\text{N}$-NMR spectra are based on the literature values of compounds with similar structures [16, 21, 22]. As shown in Fig. 3, seven resonance signals were observed. The strong signals assigned to the nitro groups appear at $\delta = -12.81$ (N8), $-15.97$ (N1/N3), and $-19.99$ (N2) ppm, respectively. The signal of the N4 atom of the $-\text{C}=\text{N}-$ group, which is directly attached to the 2,4,6-trinitrophenyl group, can be assigned to the resonances at $\delta = -56.76$ ppm due to the presence of three nitro groups in the benzene ring. The signal of the N7 atom, which is directly attached to the nitro group within the nitroguanidine moiety, can be assigned to the resonances at $\delta = -141.38$. The signals of nitrogen atoms in the $-\text{NH}-$ and $-\text{NH}_2$ groups appear at $\delta = -225.31$ ppm.
and -295.82 ppm, respectively. It should be pointed out that the $^{15}\text{N}$-NMR analysis of compound 1 is difficult to achieve, mainly due to poor solubility in most deuterated solvents (even in [D$_6$]DMSO).

The thermal stabilities of the resulting compounds 1 and 2 were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements at a heating rate of 5°C min$^{-1}$. Both compounds 1 and 2 decompose directly without a melting process. For compound 1, as shown in Fig. 4, the decomposition onset occurs at 195.7°C and the peak temperature is 217.5°C. As shown in Fig. 5, the decomposition onset and peak temperatures of compound 2 are 182.8 and 204.4°C, respectively. They are more thermally stable than other energetic derivatives of 3-amino-1-nitroguanidine, which is probably due to the existence of a large conjugation system within the structures of 1 and 2. In TG measurements, the mass loss stage occurs with a mass loss of 90% for 1 and a mass loss of 80% for 2. The temperature ranges of mass loss are consistent with the exothermic temperature ranges in the DSC measurements.

The sensitivities of compounds 1 and 2 towards impact, and friction were performed by using the standard BAM method [23]. Additionally, both compounds were tested upon the sensitivity toward electrical discharge using Electric Spark Tester ESD JGY-50 III (China North Industries Group Corporation, Beijing, China). For 1 and 2, the impact sensitivity values are 19 J and 24 J, respectively. And the friction sensitivity values of 1 and 2 are 128 N and 168 N, respectively. Based on the classification standard of sensitivities [24], both compounds 1 and 2 are sensitive. They are more sensitive than other high high-nitrogen energetic compounds with a nitroguanidine moiety [21], owing due to the introduce introduction of energetic moieties such as a furoxan ring and 2,4,6-trinitrophenyl group. But they are less sensitive than 1,3,5-trinitroperhydro-1,3,5-triazine (RDX; 7.4 J and 120 N) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX; 7.4 J and 120 N). [21]. For compounds 1 and 2, the electrostatic discharge sensitivity values are
FIGURE 5 DSC and TG plots of 2.

TABLE 2
Physicochemical Properties of 1 and 2 Compared to 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

| Compound | $T_d$ (°C) | OB$^b$ | N$^c$ (%) | $d$ (g cm$^{-3}$) | $\Delta H_m$ (kJ/mol) | $D'$ (m/s) | $P'$ (GPa) | IS$^g$ | FS$^h$ (N) | ESD$^i$ (J) |
|----------|------------|--------|-----------|-----------------|----------------------|------------|-----------|------|----------|-----------|
| 1        | 218        | -31.4  | 42.8      | 1.65$^j$        | 421.6               | 7670      | 24.8      | 19   | 128      | 0.268     |
| 2        | 204        | -14.0  | 32.8      | 1.79$^j$        | 306.2               | 7965      | 28.1      | 24   | 168      | 0.305     |
| RDX$^l$  | 205        | 0      | 37.84     | 1.80            | 92.6                | 8977      | 35.2      | 7.4  | 120      | 0.2$^{lm}$|
| HMX$^l$  | 287        | 0      | 37.84     | 1.91            | 104.8               | 9320      | 39.6      | 7.4  | 120      | —         |

$^a$Decomposition temperature.
$^b$CO oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H$_2$O. For a compound with the molecular formula of C$_a$H$_b$N$_c$O$_d$ (without crystal water), OB (%) = 1.600 [(d - a - b/2)/Mw], in which Mw is the molecular weight.
$^c$Nitrogen content.
$^d$Molar enthalpy of the formation of compound.
$^e$Detonation velocity.
$^f$Detonation pressure.
$^g$Impact sensitivity.
$^h$Friction sensitivity.
$^i$Sensitivity to the electrostatic discharge.
$^j$Density from single crystal.
$^k$Density from the theoretical calculation.
$^l$Data from Zhang et al. [21].
$^{lm}$Data from Klapötke et al. [25].
268 mJ and 305 mJ, respectively. The results indicate that they are less sensitive to electrostatic discharge than RDX (200 mJ) [25].

To investigate the energetic properties of the two new compounds, the gas-phase enthalpies of formation of compounds 1 and 2 were calculated using the Gaussian 09 suite of programs [26] by using the method of isodesmic reactions (Scheme S1, Supporting Information). As shown in Table 2, compounds 1 and 2 exhibited high positive heats of formation at 421.6 and 306.2 kJ mol\(^{-1}\), respectively. The detonation velocity (\(D\)) and detonation pressure (\(P\)), which are used to characterize the performance of a high explosive, were evaluated by the empirical Kamlet-Jacobs (K-J) equations. For compounds 1 and 2, the calculated detonation velocities are 7,670 and 7,965 ms\(^{-1}\), respectively, which are remarkably higher than that of TNT (6,881 ms\(^{-1}\)) [15] but lower than RDX (8,977 ms\(^{-1}\)). The detonation pressures are 24.8 and 28.1 GPa, which are also significantly higher than of TNT (19.5 GPa).

**CONCLUSIONS**

In summary, two new energetic derivatives from 3-amino-1-nitroguanidine were prepared by the reactions of 3-amino-1-nitroguanidine with 4-formyl-3-methyl-1,2,5-oxadiazole 2-oxide and 2,4,6-trinitrobenzaldehyde, respectively. They were well characterized by infrared (IR) spectroscopy, multinuclear NMR spectroscopy, DSC, TG analysis, as well as elemental analysis. The structure of compound 1 was confirmed by single-crystal X-ray diffraction. The resulting products 1 and 2 exhibit good thermal stabilities with decomposition temperatures above 180°C. For 1 and 2, the detonation velocities are 7,670 and 7,965 ms\(^{-1}\), respectively. The detonation pressures are 24.8 and 28.1 GPa. The results indicate that both 1 and 2 exhibit remarkably better performance than TNT.

**EXPERIMENTAL SECTION**

**Caution:** Although none of the compounds described herein exploded or detonated in the course of this research, proper safety precautions should be taken when handling these compounds. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs are recommended.

**General Methods**

All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. The multinuclear NMR spectra were recorded on a Bruker Avance 300 instrument (Bruker Corporation, Billerica, MA, USA). The measurement of \(^{15}\)N-NMR spectra for compound 2 was carried out in DMSO-\(d_6\) solution with the concentration of 1.7 mol L\(^{-1}\), and chemical shifts are given with respect to CH\(_3\)NO\(_2\) as external standard. Fourier transform infrared spectra were recorded on a BOMEM MB Series 154S FTIR spectrometer (ABB Bomem Inc., China). Elemental analysis was performed on a Vario EL III recorder (Elementar Analysensysteme GmbH, Germany). TG and DSC studies were carried out on a STD-Q600 at a heating rate of 5°C min\(^{-1}\) in closed Al containers with a nitrogen flow of 30 mL min\(^{-1}\). The electrostatic sensitivity test was carried out using an Electric Spark Tester ESD JGY-50 III (China North
Industries Group Corporation, Beijing, China). The sensitivities toward impact and friction were determined using a HGZ-1 drophammer and a BAM friction tester by using the standard BAM method. A 2.0-kg weight was dropped from a set height onto a 30-mg sample placed on 150-grit garnet sandpaper. The test was carried out at 27°C and the relative humidity was 36%.

**Synthesis of Compound 1**

3-Methyl-4-furoxancarbaldehyde (0.38 g, 3.0 mmol) was added to a suspension of 0.30 g of 3-amino-1-nitroguanidine (2.52 mmol) in 30 mL ethanol and the resultant solution was stirred and refluxed for 2 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold ethanol (50 mL), and dried; 0.55 g of 1 as a white solid was obtained in a yield of 95%. 

$^1$H-NMR (300 MHz, [D$_6$]DMSO): $\delta = 12.24$ (s, 1H, $-NH-$), 9.00 (br, 1H, $-NH_2$), 8.21 (s, 2H, $-CH=N-$ and $-NH_2$), 2.39 (s, 3H, $-CH_3$) ppm. $^{13}$C-NMR (75 MHz, [D$_6$]DMSO): $\delta = 159.2$ (C(NNO$_2$)(--$NH-$)(NH$_2$)), 155.0 (furoxan ring), 137.4 ($-CH=N-$), 113.1 (furoxan ring), 10.68 (CH$_3$) ppm. IR: $\nu = 3450$ (s), 3304 (m), 3178 (m), 3119 (m), 1618 (s), 1575 (m), 1495 (w), 1400 (vs), 1260 (s), 1164 (m), 1083 (m), 1030 (m), 945 (w), 867 (w), 816 (w), 779 (w), 638 (w), 513 (m) cm$^{-1}$. Elemental analysis for C$_5$H$_7$N$_7$O$_4$ (229.15): Calcd. C 26.21, H 3.08, N 42.79%; found: C 26.75, H 3.12, N 42.21%.

**Synthesis of Compound 2**

To a suspended solution of 0.30 g of 3-amino-1-nitroguanidine (2.52 mmol) in 30 mL of ethanol, 1 mL concentrated HCl was added. After the mixture was stirred at room temperature for 1 h, 0.72 g (3.0 mmol) of 2,4,6-trinitrobenzaldehyde was added. The suspended mixture was stirred at 60°C for 4 h and then cooled. The precipitate was filtered off and washed with ethanol. After drying, 0.78 g of 2 as a gray powder was obtained in a yield of 90%. 

$^1$H-NMR (300 MHz, [D$_6$]DMSO): $\delta = 12.42$ (s, 1H, $-NH-$), 9.12 (s, 2H, CH), 8.98 (br, 1H, $-NH_2$), 8.51 (s, 1H, $-CH=N-$), 7.64 (br, 1H, $-NH_2$) ppm. $^{13}$C-NMR (75 MHz, [D$_6$]DMSO): $\delta = 159.2$ (C(NNO$_2$)(--$NH-$)(NH$_2$)), 150.4 (CNO$_2$), 148.8 (CNO$_2$), 140.0 ($-CH=N-$), 129.5 (C$_q$), 124.8 (CH) ppm. $^{15}$N-NMR (30 MHz, [D$_6$]DMSO): $\delta = -12.81$ (NNO$_2$), $-15.97$ (CNO$_2$), $-19.99$ (CNO$_2$), $-57.76$ ($-CH=N-$), $-141.38$ (NNO$_2$), $-225.31$ ($-NH-$), $-295.82$ ($-NH_2$). IR: $\nu = 3441$ (m), 3330 (m), 3263 (m), 3082 (m), 1630 (s), 1601 (m), 1572 (vs), 1540 (vs), 1462 (w), 1432 (m), 1391 (s), 1348 (vs), 1260 (s), 1183 (m), 1154 (m), 1065 (m), 920 (w), 859 (w), 783 (w), 720 (w), 559 (w) cm$^{-1}$. Elemental analysis for C$_8$H$_6$N$_8$O$_8$ (342.03): Calcd. C 28.08, H 1.77, N 32.75%; found: C 28.54, H 1.82, N 32.18%.

**FUNDING**

This work was supported by the Natural Science Foundation of Jiangsu Province (BK2011696) and the National Natural Science Foundation of China (No. 21376121).

**SUPPLEMENTAL MATERIAL**

Supplemental data for this article can be accessed on the publisher’s website.
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[24] Impact: insensitive $>40$ J, less sensitive $>35$ J, sensitive $>4$ J, very sensitive $\leq 3$ J. Friction: insensitive $>360$ N, less sensitive $= 360$ N, sensitive $< 360$ N $> 80$ N, very sensitive $\leq 80$ N, extremely sensitive $\leq 10$ N; according to the UN Recommendations on the Transport of Dangerous Goods.

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