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ARTICLE

New thermal stable energetic materials: synthesis and characterization of guanylhydrazone substituted furoxan energetic derivatives

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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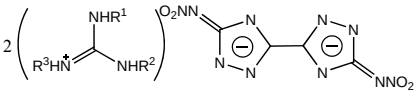
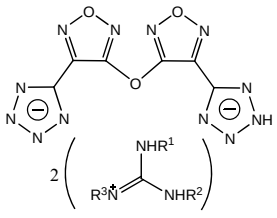
New guanylhydrazone substituted furoxan energetic derivatives were synthesized via the condensation reactions of 3-methyl-4-furoxancarbaldehyde with aminoguanidine derivatives. The resulting compounds **1**-**5** were well characterized by IR spectroscopy, multinuclear NMR spectroscopy, differential scanning calorimetry, thermogravimetry analysis as well as elemental analysis. Additionally, the structures of compounds **1**, **2** and **5** were confirmed by single crystal X-ray diffraction. Except for the compounds **1** and **2**, all the remaining products exhibit good thermal stabilities with decomposition temperatures above 200 °C. The detonation pressure values calculated for these compounds range from 17.0 to 28.3 GPa, and the detonation velocities range from 6906 to 8210 m s^{-1}. These values suggest that the guanylhydrazone substituted furoxan energetic derivatives could be potential candidates for thermally stable energetic materials.

Introduction

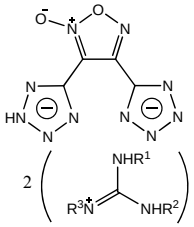
In recent years, a new class of energetic compounds containing a large fraction of nitrogen has attracted considerable interest.[1] In contrast to conventional energetic materials, the energy of these high nitrogen content energetic compounds is derived from their very high positive heat of formation directly attributed to a large number of inherently energetic N—N and C—N bonds.[2] Moreover, their high level of environmental compatibility is another advantage over the traditional energetic materials.[3] Nitrogen-rich building blocks such as guanidine,[4] furazan,[5] 1,2,4,5-tetrazine,[6] tetrazole,[7] or triazole[8] are essential units to design and synthesize high nitrogen energetic materials. Among them, furoxan (1,2,5-oxadiazole-2-oxide) is a *N*-oxide derivative of furazan. It is also a highly energetic heterocycle used in the field of energetic materials. The combination of *N*-oxide and "latent" nitro group structure could enhance the detonation performances of the energetic furoxan derivatives.[9] Additionally, guanidine-containing compounds such as guanidine, aminoguanidine, diaminoguanidine, and triaminoguanidine are important starting materials of energetic organic salts. Generally, they pair with the energetic anions to form new energetic salts. These energetic salts oftentimes possess high positive heats of formation and high thermal stabilities. Typical highly thermal stable guanidine-containing energetic salts[5c,8d,9a] are shown in Scheme 1.



$R^1 = R^2 = R^3 = H$ (T_{dec} = 265 °C)
$R^1 = NH_2$; $R^2 = R^3 = H$ (T_{dec} = 248 °C)
$R^1 = R^2 = NH_2$; $R^3 = H$ (T_{dec} = 235 °C)
$R^1 = R^2 = R^3 = NH_2$ (T_{dec} = 244 °C)



$R^1 = R^2 = R^3 = H$ (T_{dec} = 287 °C)
$R^1 = NH_2$; $R^2 = R^3 = H$ (T_{dec} = 289 °C)
$R^1 = R^2 = NH_2$; $R^3 = H$ (T_{dec} = 213 °C)
$R^1 = R^2 = R^3 = NH_2$ (T_{dec} = 237 °C)



$R^1 = R^2 = R^3 = H$ (T_{dec} = 264 °C)
$R^1 = NH_2$; $R^2 = R^3 = H$ (T_{dec} = 241 °C)
$R^1 = R^2 = NH_2$; $R^3 = H$ (T_{dec} = 290 °C)
$R^1 = R^2 = R^3 = NH_2$ (T_{dec} = 220 °C)

Scheme 1. Highly thermal stable energetic salts containing

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†Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

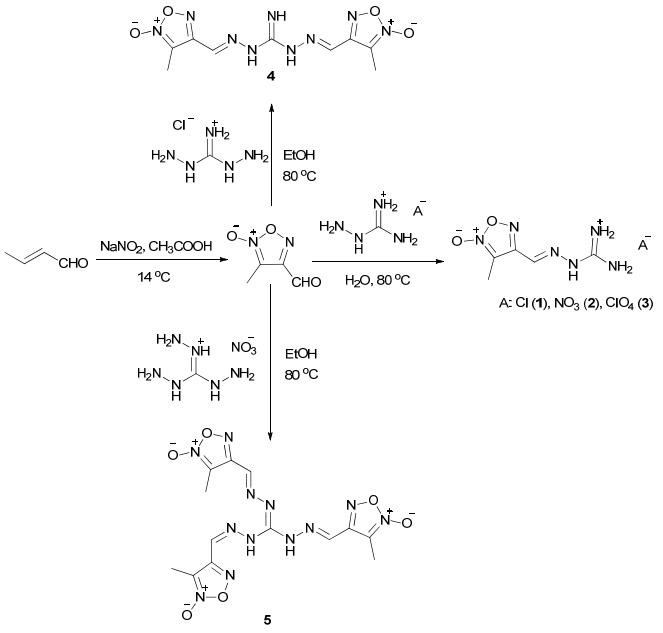
guanidine moiety

Guanylhydrazone derivatives have been widely used in medicine field. They can be used as antibacterial, antihypertensive, antitumor agents and so on.[10] However, few guanylhydrazones have been reported in the field of energetic materials. In our previous study,[9d] the condensation reaction of amino group in 1,5-diaminotetrazole with aldehyde group in 3-methyl-4-furoxancarbaldehyde has been investigated. Herein, the reactions of hydrazine groups in aminoguanidine derivatives with 3-methyl-4-furoxancarbaldehyde are further studied. The resulting new guanylhydrazone substituted furoxan derivatives are characterized for structural aspects, thermal behaviour and explosive properties by experimental and theoretical methods.

Results and discussion

Synthesis

As shown in Scheme 2, 3-methyl-4-furoxancarbaldehyde was synthesized according to the literature.[11] Starting with a 1.2-fold excess of 3-methyl-4-furoxancarbaldehyde, treatment of aminoguanidine salts such as aminoguanidine hydrochloride, aminoguanidium nitrate and aminoguanidinium perchlorate led to mono-guanylhydrazone furoxan derivatives in high yield (above 90%). After synthesis of these mono-guanylhydrazone furoxan derivatives, the preparation of bisguanylhydrazones and trisguanylhydrazones was also investigated. The desired 1,3-bis-(3-methylfuroxan-4-methyleneamino)guanidine (**4**) and 1,2,3-tris-(3-methylfuroxan-4-methyleneamino)guanidine (**5**) were obtained via the reactions of 4-fold excess and 6-fold excess of 3-methyl-4-furoxancarbaldehyde with 1,3-diaminoguanidine monohydrochloride and triaminoguanidine nitrate in the yield of 55% and 85%, respectively.



Scheme 2. Synthesis of compounds **1-5**

NMR Spectroscopy

All compounds were investigated using ^{1}H, ^{13}C spectroscopy. Additionally, the ^{15}N NMR spectra were recorded for compounds **1**, **2** and **3**. The multinuclear NMR spectra were measured in DMSO-d_6 and the chemical shifts are given with respect to DMSO or CH_3NO_2 as external standard. The ^{1}H and ^{13}C NMR spectra of all compounds are given in the Electronic Supplementary Information (Figures S1-S10, ESI†).

In the ^{1}H NMR spectra, for all compounds, proton signals of the methyl group are found at δ = 2.37–2.43 ppm. One singlet for the hydrogen atom of -CH=N- can be found at chemical shifts of 8.29 to 8.66 ppm. The hydrogen signals -NH- for all compounds appear between δ = 11.20 and 12.87 ppm. The carbon atoms in the methylfuroxan moiety occur as four singlets, and the assignments agree with values of similar compounds reported in the literature.[9d, 11] In compounds **1-3**, the carbon atoms of the aminoguanidine-containing moiety are identified at δ = 156.8, 156.4 and 156.4 ppm. The carbon atom in triaminoguanidine structure occurs at δ = 153.9 ppm in compound **5**. For compound **4**, the carbon atom of diaminoguanidine moiety appears at δ = 154.9 ppm, which is identical with that of the carbon atom bonded with N-oxide nitrogen atom in the furoxan ring. The value agrees with that reported in the literature for similar compounds.[4c, 5f, 6e, 9a, 9c]

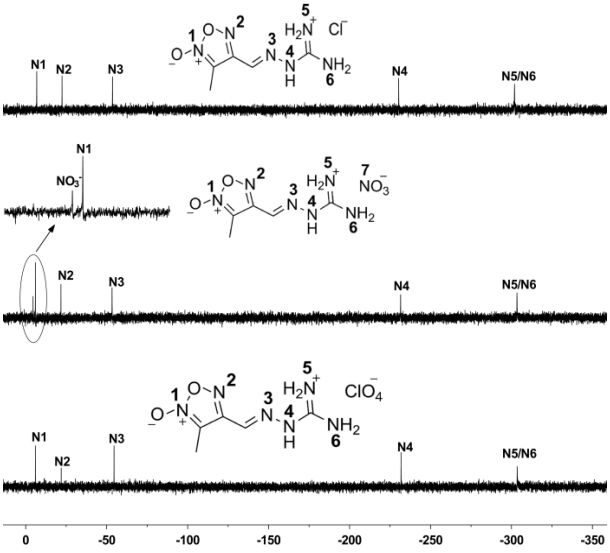


Figure 1. ^{15}N NMR spectra of compounds **1-3**

The ^{15}N NMR spectra for compound **1** and **3** show five singlet resonances. And six well-resolved resonances are detected in the ^{15}N NMR of compound **2**. ^{15}N signal assignments are based on the theoretical and experimental data in the literature.[4a, 12] Within their similar guanylhydrazone structures, three ^{15}N signals are observed at the high field with ranging from -52.93 to -54.55 ppm. The signals of –NH- group of compounds **1-3** are found at δ = -229.67 (**1**), -231.45 (**2**), and -231.78 (**3**), respectively. The signals of –C=N- group bonded with the furoxan ring appear at δ = -52.93 (**1**), -53.23 (**2**), and -54.55 (**3**). Within the furoxan ring, the *N*-oxide (N1) resonates downfield

appearing around -6 ppm while another nitrogen atom appears around -21 ppm due to the electron-withdrawing inductive effect of oxygen atom. In the spectra of **2**, signals at lowest field are assigned to nitrate anion appearing at δ = -4.46 ppm.

Single-Crystal X-ray Analysis

Compounds **1**, **2** and **5**•DMF were characterized by low temperature (173 K) single crystal X-ray structure determination. The crystallographic data are summarized in Table 1.

Table 1. Crystallographic data for **1**, **2**, and **5**•DMF.

	1	**2**	**5**•DMF
Formula	$C_5H_9N_6O_2Cl$	$C_5H_9N_7O_5$	$C_{16}H_{21}N_{13}O_7$
Formula weight	220.63	247.19	507.46
Temperature	173(2) K	173(2) K	173(2) K
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1/c$	P-1
ρ/ g cm^{-3}	1.526	1.587	1.475
a/ Å	5.8923(5)	12.6945(11)	8.8526(11)
b/ Å	11.4413(9)	7.5903(8)	11.6239(14)
c/ Å	7.6951(7)	11.6510(11)	12.4741(15)
α/°	90	90	109.894(4)
β/°	112.239(3)	112.837(3)	101.069(4)
γ/°	90	90	100.231(4)
Goodness-of-fit on F^2	1.006	0.993	1.005
Final R indexes [$I>2\sigma(I)$]	R_1 = 0.0507, wR_2 = 0.1002	R_1 = 0.0480, wR_2 = 0.1031	R_1 = 0.0581, wR_2 = 0.0641
Final R indexes (all data)	R_1 = 0.0785, wR_2 = 0.1137	R_1 = 0.0921, wR_2 = 0.1163	R_1 = 0.1629, wR_2 = 0.0807
CCDC	996724	996725	996726

3-Methyl-4-furoxancarbaldehyde guanylhydrazone•HCl (**1**) crystallizes in the monoclinic space group $P2_1$ with a cell volume of 480.18(7) Å^3. A density of 1.526 g cm^{-3} was determined from the X-ray crystal structure. As shown in Figure 2, the molecules are in an *E* configuration. The furoxan ring and C=N bonds are in a plane with mean deviation of 0.0143 Å resulting from the large π-conjugation system. The protonated guanidine moiety shows a completely planar assembly due to the electron delocalization in the moiety. The dihedral angle between them is 8.4°. The C4-N3 bond length, 1.277(6) Å, shows typical C-N double bond values. Owing to the electron delocalization effect, the C-N bond lengths of the protonated guanidine moiety are longer than that of C–N double bonds (1.277(6) Å) but shorter than that of C–N single bond (1.460(2) Å). They differ in a range of 1.317(6) Å to 1.337(6) Å, which are closed to that of C-N bond within the furoxan ring. In the packing diagram, as shown in Figure 3, the discrete chloride ion and protonated guanidine moiety are linked into a 3D network by the extensive classical interactions between cations and anions.

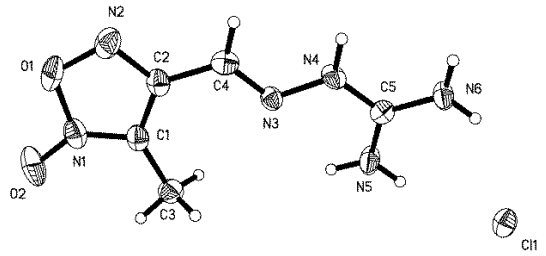


Figure 2. Molecular structure of **1**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

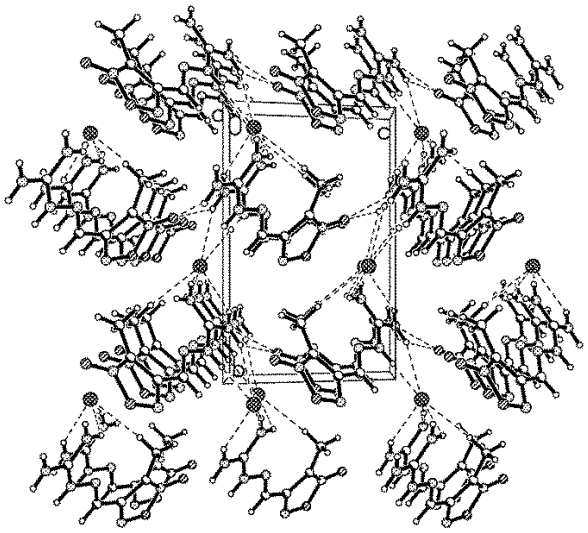


Figure 3. Ball and stick packing diagram of **1** viewed down the *a*-axis. Unit cell is indicated and dashed lines represent hydrogen bonding. N(4)–H(4A)•••Cl(1)^{i} 3.048(4) Å; N(5)–H(5A)•••Cl(1)^{i} 3.196(4) Å; N(6)–H(6B)•••Cl(1)^{i} 3.495(4) Å; N(5)–H(5B)•••Cl(1)^{ii} 2.7638(13) Å; N(6)–H(6A)•••Cl(1)^{iii} 3.303(4) Å. Symmetry code: i: 1-x, 1/2+y, -z; ii: -1+x, y, z; iii: -x, -1/2+y, 1-z.

3-Methyl-4-furoxancarbaldehyde guanylhydrazone•HNO_3 (**2**) crystallizes in the monoclinic $P2_1$/c with a cell volume of 1034.64(17) Å^3 and four molecules in the unit cell. The density is 1.587 g cm^{-3}. The molecular structure is shown in Figure 4. The molecules are also in an *E* configuration. The protonated guanidine moiety is planar with mean deviation of 0.0031 Å. The furoxan ring and C=N bonds are in a plane with mean deviation from ring plane of 0.0399 Å. The dihedral angle between them is 5.0°, which indicates that the planarity of 2 is

superior to that of **1**. In the packing diagram of **2** (Figure 5), layers that run parallel to the *b* axes are formed. The π-π stacking interactions exist between the layers. The perpendicular distance between adjacent sheets is only 3.3 Å, which is even shorter than the interplanar spacing in graphite (3.4 Å).

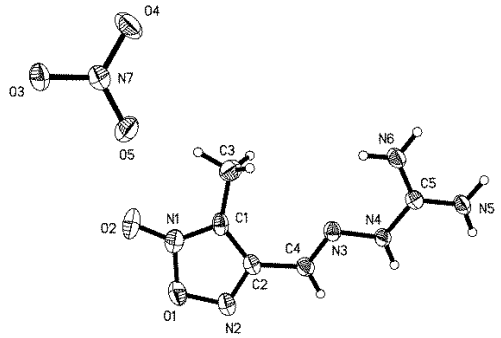


Figure 4. Molecular structure of **2**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

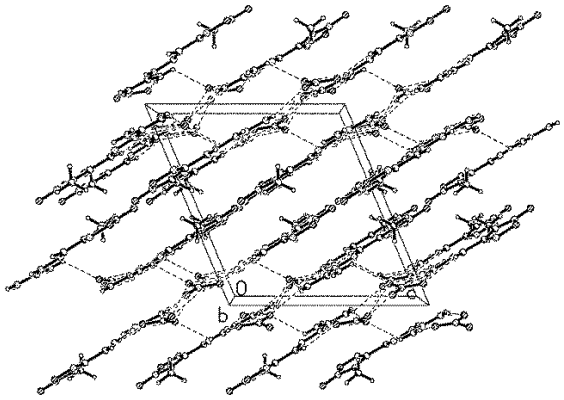


Figure 5. Ball and stick packing diagram of **2** viewed down the *b*-axis. Unit cell is indicated and dashed lines represent hydrogen bonding.

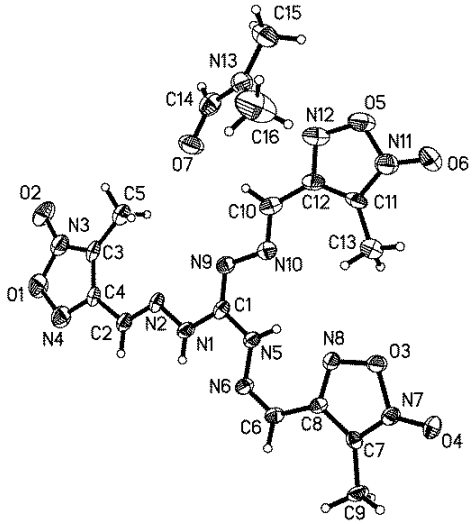


Figure 6. Molecular structure of **5**•DMF. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

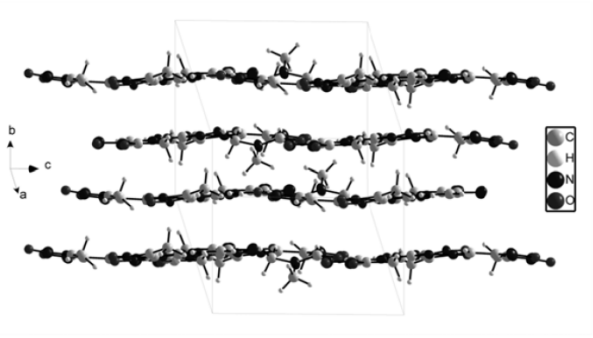


Figure 7. A view of **5**•DMF showing the stacking of layers.

The structure of compound **5** was confirmed by X-ray crystal structure analysis of **5**•DMF. The 5•DMF crystallizes in the triclinic, *P*-1 with a cell volume of 1142.8(2) Å^3 and two molecules in the unit cell. A density of 1.475 g cm^{-3} was determined from the X-ray crystal structure. In contrast to mono-guanylhydrazone furoxan derivatives **1** and **2**, the protonated guanidine structure was not observed within the trisguanylhydrazones derivative **5**. It can be attributed to decreasing the imine basicity of the guanidine moiety resulting from the electron-withdrawing inductive effect of the three furoxan rings in the structure of **5**. As showed in Figure 6, the molecules of **5** contain three hydrazone structures. Among them, two hydrazone structures are in an *E* configuration and another one is in a *Z* configuration. In the structure of **5**, the C1-N9 double bond (1.301(3) Å) of the guanidine moiety is longer than that of the hydrazone moiety (C2-N2 (1.275(3) Å), C6-N6 (1.287(4) Å) and C10-N10 (1.285(3) Å)). But it is shorter than C-N double bond in the furoxan ring whose values differ in the range from 1.315(4) Å to 1.324(4) Å. It indicates that the conjugation was also found in the guanidine structure, which is weaker than that of the furoxan ring. The atoms of the guanidine moiety and three furoxan rings are planar with mean deviation from ring plane of 0.0895 Å. The wave-like layer structure can be observed despite of the presence of DMF molecules in the crystal, showed in Figure 7. The weak π-π stacking interactions exist between the layers with the centroid-to-centroid distance of 3.623(2) Å.

Thermal Behavior and Sensitivities

The thermal stabilities of compounds **1**–**5** were determined by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) at a heating rate of 10 ^{o}C min^{-1} (Electronic Supplementary Information, Figures S11-S15). For all compounds, the decomposition temperatures are determined by the decomposition onset temperatures. As shown in Table 2, Compounds **1** and **3** have a melting process, whereas the other compounds decompose directly. Except for the compounds **1** ($T_{d,\ \text{onset}}$ = 199.5 °C) and **2** ($T_{d,\ \text{onset}}$ = 179.0 °C), the

decomposition temperature ($T_{d,\ onset}$) of all other guanylhydrazone substituted furoxan energetic compounds is higher than 200 °C, thus indicating that these compounds are promising energetic materials that exhibit good thermal stability. Of these, compound **4** has the highest thermal stability, $T_{d,\ onset}$ = 231.7 °C, which is much higher than that of RDX (205 °C), but lower than that of TNT (295 °C). For all compounds, the exothermic temperature range agrees with that of weight loss. A least mass loss with the value of 40% can be observed at the exothermic temperature range of compound **1**. It would be caused by its lowest nitrogen and oxygen content in all products. A mass loss of 70% can be observed within the decomposing process of compound **2**, which is nearly identical with that of compound **4**. In all compounds, compound **5** possesses the highest mass loss of 98% within its decomposing process, which indicates that the products of thermal decomposition are almost all gases.

Impact sensitivity measurements were performed by using the standard BAM method.[13] Additionally, all compounds were tested upon the sensitivity toward electrical discharge using Electric Spark Tester ESD JGY-50 III. As shown in Table 2, the IS values of **1**-**3** are 6.8 J, 4.2 J and 3.1 J, respectively. It shows that they are more sensitive than RDX (7.4 J). However, the IS values of **4** and **5** are 22 J and 18 J, which are much higher than that of RDX. For all compounds, similar trends are observed in the results of electrostatic discharge sensitivity. Compounds **1**-**3** are less sensitive to electrostatic discharge, wherein, **3** (103 mJ) is more sensitive than **1** (194 mJ) and **2** (132 mJ). Compounds **4** (425 mJ) and **5** (353 mJ) are significantly less sensitive to electrostatic discharge.

Heats of Formation and Detonation Parameters

The heat of formation is an important parameter to evaluate the performance of these new energetic compounds. The heats of formation were calculated by using the Gaussian 09 suite of program[14] by using the method of isodesmic reactions (Supporting Information, Scheme S1). The lattice energy of the ionic compounds **1**-**3** were predicted by using the formula suggested by Jenkins et al.[15] As listed in Table 2, the resulting heats of formation of these compounds are in the range of 160 kJ mol^{-1} (**3**) to 1214 kJ mol^{-1} (**5**). The detonation velocity (D) and detonation pressure (P), which are used to characterize the performance of a high explosive, were calculated by using the EXPLO v6.01 program. For these new compounds, because of the low density of the all compounds, the calculated detonation velocities lie in the range between 6906 and 8210 m s^{-1}, which are lower than that of RDX (8983 m s^{-1}), but higher than that of TNT (6881 m s^{-1}). Among them, compound **2** exhibits the highest detonation velocity (8210 m s^{-1}) which is comparable to that of TATB (8114 m s^{-1}). The detonation pressures range between 17.0 and 28.3 GPa, in which the highest P value of **3** (28.3 GPa) is much higher than that of TNT (19.5 GPa).

Table 2. The physicochemical properties of **1**–**5** compared with trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

Compd	**1**	**2**	**3**	**4**	**5**	TNT[16]	RDX[17]
T_m[a]	199.5	-	186.6	-	-	80.4	-
T_d[b]	199.5	179.0	200.0	231.7	215.3	295	205
OB[c]	-90.6	61.50	-47.78	-100.89	-99.46	-73.97	-21.61
N %[d]	38.1	39.7	29.5	40.8	38.7	18.5	37.8
ρ [g cm^{-3}]	1.526[e] /1.584[f]	1.587[e] /1.681[f]	1.788[f]	1.557[f]	1.570[f]	1.654	1.816
Q[g] (J/g)	3970	5292	5336	5646	5964	4271	-
$\Delta_f H_m$[h] [kJ/mol]	240	163	160	766	1214	-295	176.2
D[i] [m/s]	6906	8210	8175	7532	7528	6881	8983
P[j] [GPa]	17.0	25.8	28.3	20.2	20.8	19.5	35.2
IS[k] [J]	6.8	4.2	3.1	22	18	15	7.5
ESD[l] [J]	0.194	0.132	0.103	0.425	0.353	-	0.1-0.2

[a] Melting point. [b] Thermal decomposition temperature under nitrogen gas (determined by the DSC exothermal peak, 10 °C min^{-1}). [c] Oxygen balance (%) for CaHbNcOd: OB (%) =1600 × (d-2a-b/2)/ Mw (based on carbon dioxide). [d] Nitrogen content. [e] Density from X-ray structure. [f] Density from theoretical calculation. [g] Heat of explosion. [h] Molar enthalpy of the formation. [i] Detonation velocity. [j] Detonation pressure. [k] Impact sensitivity. [l] Electrostatic discharge sensitivity.

Conclusions

The reactions of 3-methyl-4-furoxancarbaldehyde with aminoguanidine derivatives generate the previously unknown guanylhydrazone substituted furoxan energetic derivatives. All compounds have been well characterized by IR spectroscopy, multinuclear NMR spectroscopy, differential scanning calorimetry, thermogravimetry analysis and elemental analysis. Single crystal X-ray measurements were accomplished for compounds **1**, **2** and **5**•DMF and provide insight into structural characteristics as well as inter and intramolecular interactions. Except for the compounds **1** and **2**, all the remaining products exhibit good thermal stabilities with decomposition onset temperatures above 200 °C. All resulting compounds reveal positive heats of formation in the range of 160 kJ mol^{-1} (**3**) to

1214 kJ mol^{-1} (**5**). The detonation pressure values calculated for these compounds range from 17.0 to 28.3 GPa, and the detonation velocities range from 6906 to 8210 m s^{-1}. The most interesting compound regarding the thermal and energetic properties is **3**. It exhibits decomposition temperatures at 200 °C. Its detonation pressure and detonation velocities values are 28.3 GPa and 8175 m s^{-1}, which are significantly higher than that of TNT. In conclusion, the introduction of aminoguanidine moiety into energetic heterocycles through C=N bonds enriches the methodology for synthesizing aminoguanidine-containing energetic materials.

Experimental

Caution: *Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged*.

General

All chemical reagents and solvents were obtained by purchase and were used as supplied without further purification. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker Avance III 300 instrument at 25 °C. The chemical shifts are given relative to dimethyl sulfoxide (^{1}H, ^{13}C) or nitromethane (^{15}N) as external standards. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m),"weak" (w) and "very weak" (vw). TG and DSC studies were performed at a heating rate of 10 °C min^{-1} in closed Al containers with a nitrogen flow of 30 mL min^{-1} with an STD-Q600 instrument. Analyses of C/H/N were performed with a Vario EL III Analyzer. The electrostatic sensitivity test was carried out using an Electric Spark Tester ESD JGY-50 III. The impact sensitivity tests were carried out using a HGZ-1 drop hammer. Test specimens were kept between two hardened anvils and a 2.0 kg drop weight was allowed to fall freely from different heights. Twenty-five tests were conducted for each compound.

X-ray Crystallography

The data for **1**, **2** and **5**•DMF were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement was performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

General procedures for the preparation of energetic compounds 1-3

3-Methyl-4-furoxancarbaldehyde[11] and aminoguanidinium perchlorate[4a] were synthesized according to the literature.

A solution of aminoguanidium salts (5.0 mmol) and 3-methyl-4-furoxancarbaldehyde (0.77g, 6.0 mmol) in 30 mL ethanol was refluxed for 24 h. Then, the reaction mixture was cooled to room temperature and the precipitate of target product was collected by filtration. The filtrate was separated by column chromatography on silica gel using 10:1 ethyl acetate: methanol as eluent to give the remaining target product.

3-Methyl-4-furoxancarbaldehyde guanylhydrazone.HCl (1)

0.85 g of **1** was obtained as white solid in a yield of 92%. ^{1}H NMR (300MHz, DMSO): δ (ppm): 12.87 (s, 1H, -NH-), 8.39(s, 1H, -CH=N-), 8.03 (s, 4H, -NH_2), 2.37(s, 3H, -CH_3); ^{13}C NMR (75MHz, DMSO): δ (ppm): 156.8, 154.8, 137.8, 113.2, 10.7. IR (KBr): 3421 (s), 3166 (m), 2953 (w), 2840 (m) 1682 (s), 1616 (vs), 1538 (m), 1501 (w), 1460 (s), 1156 (m), 1038 (w), 1013 (w), 804 (w), 678 (w), 608 (m), 516 (w). Elemental analysis.: $C_5H_9ClN_6O_2$ (220.62): calcd. C 27.22, H 4.11, N 38.09; foud C 27.11, H 4.09, N 37.91.

3-Methyl-4-furoxancarbaldehyde guanylhydrazone.HNO_3 (2)

1.14 g of **2** was obtained as white solid in a yield of 92%. ^{1}H NMR (300MHz, DMSO): δ (ppm): 12.08 (s, 1H, -NH-), 8.29 (s, 1H, -CH=N-), 7.89 (s, 4H, -NH_2), 2.37 (s, 3H, -CH_3); ^{13}C NMR (75MHz, DMSO): δ (ppm): 156.4, 154.8, 138.2, 113.2, 10.6. IR (KBr): 3390 (s), 3308 (s), 3212 (s), 3163 (s), 3012 (m), 2903 (w), 1698 (s), 1633 (s), 1608 (vs), 1565 (w), 1503 (w), 1457 (m), 1385 (vs), 1329 (m), 1316 (m), 1302 (m), 1149 (w), 1039 (m), 1011 (w), 924 (w), 798 (w), 702 (w), 599 (m), 512 (w). Elemental analysis.: $C_5H_9N_7O_5$ (247.17): calcd. C 24.30, H 3.67, N 39.67; foud C 23.90, H 3.73, N 39.31.

3-Methyl-4-furoxancarbaldehyde guanylhydrazone.$HClO_4$ (3)

1.30 g of **3** was obtained as white solid in a yield of 91%. ^{1}H NMR (300MHz, DMSO): δ (ppm): 11.96 (s, 1H, –NH–), 8.29 (s, 1H, –CH=N–), 7.81 (s, 4H, –NH_2), 2.37 (s, 3H, –CH_3); ^{13}C NMR (75MHz, DMSO): δ (ppm): 156.4, 154.8, 138.3, 113.1, 10.6. IR (KBr): 3407 (s), 3316 (s), 3224 (m), 3168 (m), 3006 (w), 2925 (w), 2857 (w), 2361 (m), 2337 (m), 1684 (vs), 1611 (vs), 1540 (m), 1501 (m), 1464 (s), 1402 (m), 1380 (w), 1332 (w), 1310 (w), 1147 (s), 1091 (vs), 1067 (m), 1046 (s), 970 (w), 924 (w), 875 (w), 807 (m), 672 (m), 629 (s), 512 (m). Elemental analysis: $C_5H_9ClN_6O_6$ (284.61): calcd. C 21.10, H 3.19, N 29.53; found C 21.19, H 3.14, N 29.44.

1, 3-Bis-(3-methylfuroxan-4-methyleneamino)guanidine (4)

A solution of 1, 3-diaminoguanidine monohydrochloride (0.628 g, 5.0 mmol) and 3-methyl-4-furoxancarbaldehyde (2.56 g, 20.0 mmol) in 30 mL ethanol was refluxed for 24 h. Then, the reaction mixture was cooled to room temperature and the precipitate of target product was collected by filtration. The filtrate was separated by column chromatography on silica gel

to afford the remaining target product. 0.85 g white solid was obtained in a yield of 55%.

^{1}H NMR (300MHz, DMSO): δ (ppm): 12.63 (br, –NH–), 8.66 (s, 2H, –CH=N–), 8.62 (s, 2H, –NH_2), 2.43 (s, 6H, –CH_3); ^{13}C NMR (75MHz, DMSO): δ (ppm): 154.9, 140.0, 113.3, 10.7. IR (KBr): 3453 (s), 3210 (s), 2812 (s), 2361 (m), 1669 (vs), 1611 (vs), 1465 (s), 1433 (s), 1378 (s), 1346 (m),1314 (w), 1280 (w), 1189 (w), 1118 (s), 1033 (m), 954 (w), 927 (w), 826 (m), 798 (w), 739 (w), 678 (m), 625 (m), 600 (w), 486 (s). Elemental analysis: $C_9H_{11}N_9O_4$ (309.24): calcd. C 34.96, H 3.59, N 40.76; found C 34.90, H 3.56, N 39.98.

1, 2, 3-Tris-(3-methylfuroxan-4-methyleneamino)guanidine (5)

A solution of triaminoguanidium nitrate (0.835 g, 5.0 mmol) and 3-methyl-4-furoxancarbaldehyde (3.84 g, 30.0 mmol) in 30 mL ethanol was refluxed for 24 h. Then, the reaction mixture was cooled to room temperature and the precipitate of target product was collected by filtration. 1.84 g of yellow solid was obtained in a yield of 85%.

^{1}H NMR (300MHz, DMSO): δ (ppm): 11.20 (s, 2H, –NH–), 8.38 (s, 3H, –CH=N–), 2.41 (s, 9H, –CH_3); ^{13}C NMR (75MHz, DMSO): δ (ppm): 155.6, 153.7, 134.6, 113.4, 10.7 ppm. IR (KBr): 3422 (w), 3330 (m), 2361 (m), 1638 (m), 1604 (vs), 1576 (s), 1544 (s), 1489 (m), 1457 (s), 1409 (m), 1377 (m), 1303 (m), 1284 (w), 1152 (s), 1102 (m), 1033 (m), 963 (w), 929 (w), 869 (w), 820 (m), 728 (vw), 666 (w), 611 (w), 496 (w). $C_{13}H_{14}N_{12}O_6$ (434.33): calcd. C 35.95, H 3.25, N 38.70; found C 36.39, H 3.29, N 38.65.

Acknowledgements

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

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