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A new family of energetic salts based on oxy-bridged bis(dinitromethyl)furazan: syntheses, characterization and properties

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Abstract Energetic salts based on oxy-bridged bis(dinitromethyl)furazan (**2**) were synthesized and fully characterized by NMR (^{1}H and ^{13}C), IR spectroscopy, elemental analysis as well as differential scanning calorimetry (DSC). The crystal structures of neutral **2**, its ammonium salt (**4**), guanidinium salt (**7**) and guanidylguanidinium salt (**9**) were also determined by single-crystal X-ray diffraction. Except for hydroxylammonium salt (**5**), all the remaining salts exhibit good thermal stabilities with decomposition temperature above 180 °C. Furthermore, the densities of salts ranged from 1.65 g cm^{-3} to 1.88 g cm^{-3}. Theoretical calculations provided detonation pressures and velocities for the energetic salts within the range of 24.9-38.0 GPa and 7582.2-9072.7 m s^{-1}, respectively.

Keywords: energetic salts, oxy-bridged bis(dinitromethyl)furazan, thermal stabilities, detonation properties

Introduction

The syntheses of energetic materials with high energy and low sensitivity have attracted great interest all over the world. [1] Traditional strategy for designing energetic compound is incorporating oxidizer component and fuel component in the same molecule, such as TNT (2,4,6-trinitrotoluene) and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), whose energy relied on the combustion of the carbon backbone while consuming the oxygen provided by the nitro groups. [2] Oxygen balance (the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water) plays an important role to enhance the detonation properties of energetic compound, however the improved oxygen balance usually result in the decreased thermal and impact stability.

Unlike the traditional energetic materials, the energy of nitrogen-rich energetic materials originate from their high heat of formation due to their high N-N, C-N and N-O bonds contents. [3] Of these, energetic salts with nitrogen-rich cations are one of the special classes of materials with higher performance and good stability toward heat and stimulus which are attributed to the substantial intra- and intermolecular hydrogen bonds. [4] The syntheses of energetic salts are usually performed by the simple neutralization or metathesis reactions, thus leading to more opportunities to generate energetic material with high energy and low vulnerability characteristics. Most energetic salts consist of *N*, *O* or *C* deprotonated anions, including azolate *N*-anions, [5] nitramide *N*-anions, [6] oxide *O*-anions [7] and dinitromethyl *C*-anions [8].

Actually, the performances of energetic compounds are closely related to their density, oxygen balance and heat of formation. [1] Other than higher heat of formation, higher oxygen content is also required for a molecule to possess improved properties. The incorporation of high content of

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oxygen and nitrogen into a compound is a new strategy to develop more powerful, less sensitivity and eco-friendly energetic materials. Recently, several nitrogen-containing heterocyclic anions with high percentage of oxygen have been designed and exhibit important role to enhance the performance of energetic salts, examples including 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole, [9] 5,5'-Bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole, [9] 3,3'-Dinitroamino-4,4'-azoxyfurazan [10] and 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) [11] based salts (Figure 1).

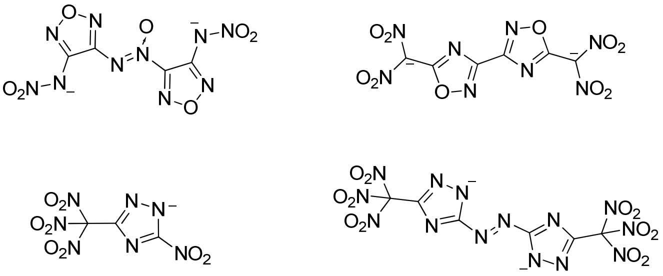


Figure 1 Examples of nitrogen-containing heterocyclic anions with high percentage of oxygen

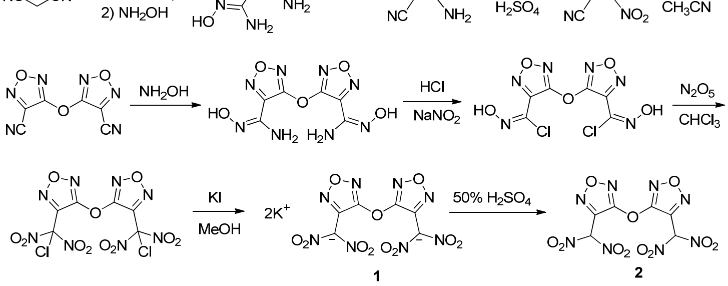
Furazan compounds in combination with dinitromethyl substituents will be of particular interest since these compounds have satisfactory oxygen content. Based on the above consideration, oxy-bridged bis(dinitromethyl)furazan anion, a new nitrogen-containing heterocyclic anion with high percentage of oxygen, was designed to generate corresponding salts. Herein, the syntheses, characterization and properties of oxy-bridged bis(dinitromethyl)furazan based salts were reported, which have potential applications in solid propellants, explosives and pyrotechnics.

Results and discussion

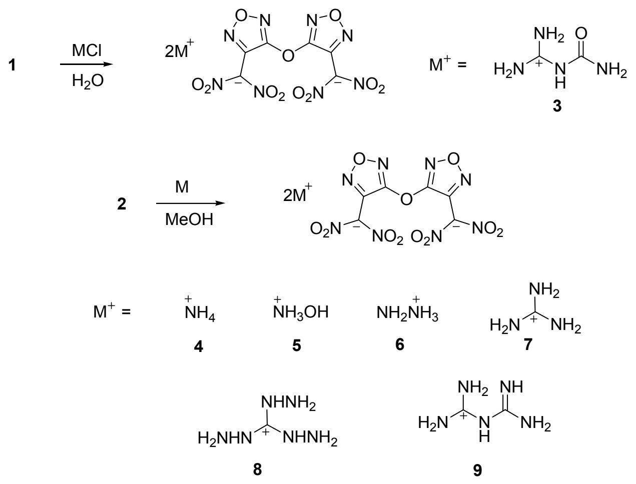
Syntheses

Dipotassium oxy-bridged bis(dinitromethyl)furazan (**1**) was synthesized through a procedure described by our group (**Scheme 1**). [12] Subsequently, oxy-bridged bis(dinitromethyl)furazan (**2**) was obtained by the treatment of **1** with 50% sulfuric acid. As for the syntheses of **3-9**, the reactions of **1** with corresponding halide salts in water were tried firstly, but the attempts failed except for **3**. Then, the neutralization of **2** with free bases in methanol solution was applied to generate **4-9** (**Scheme 2**).

All the salts were stable in air and could be stored for days. Their structures were fully investigated and confirmed by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analyses. It is notable that all the anions have similar chemical shifts in ^{13}C NMR spectra (around 161.2, 142.8 and 119.1 ppm), indicating that the anions in the salts exist isolated in the solution. The ^{13}C NMR signals of dinitromethyl group appear at higher field compared to the ones in literature (129 to 132 ppm) [8a-g], which resulted from the conjugation of negative charge throughout the aromatic rings.



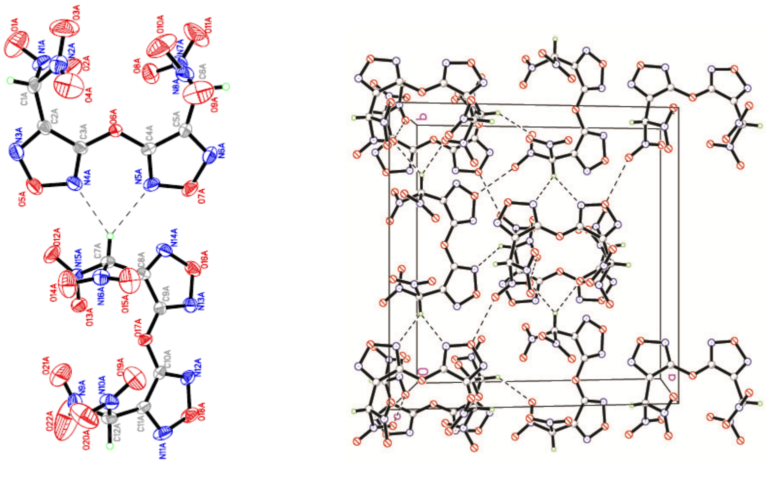
Scheme 1 Synthesis of oxy-bridged bis(dinitromethyl)furazan



Scheme 2 Syntheses of energetic salts based on oxy-bridged bis(dinitromethyl)furazan

X-ray crystallography

2 crystallizes in the monoclinic space group *C*c and has a density of 1.840 g cm^{-3}. As shown in Figure 2, there are two crystallographic independent molecules in the asymmetric unit. In each molecule, the bridged oxygen atom is nearly coplanar with each furazan ring (torsion angle O6-C4-C5-N6 179.710°, O6-C3-C2-N3 179.326°, O17-C10-C11-N11 177.170°, O17-C9-C8-N14 178.607°). The dihedral angles of the two furazan rings are 8.674° and 8.727°, respectively. The existence of non-classical intermolecular hydrogen bonds and O$\cdots$O week interactions contribute to an increase in density.

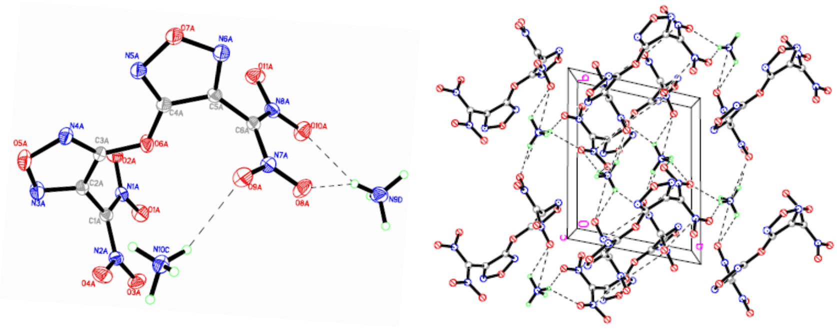


(a) (b)

Figure 2 (a) Molecular structure of **2** with thermal ellipsoids at 30% probability;

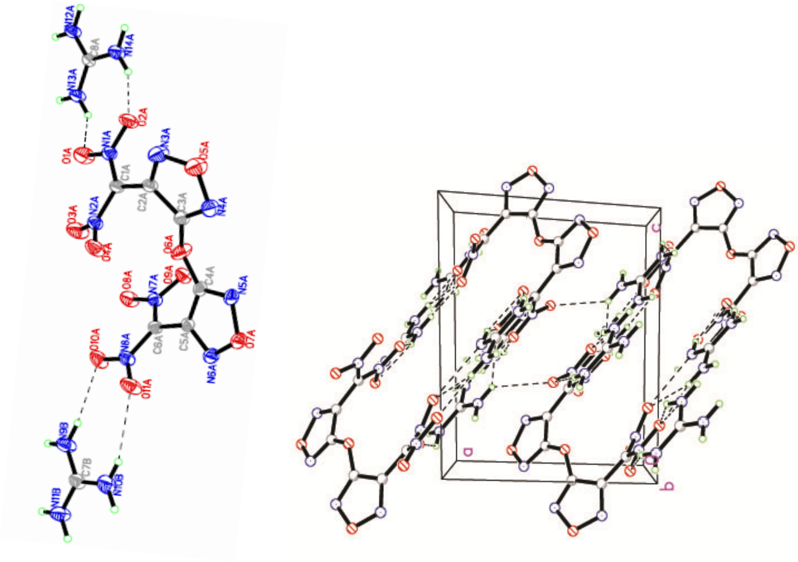
(b) Packing diagram of **2** viewed down the c axis.

4 and **7** both crystallize in the triclinic space group *P*-1, and **9** crystallizes in the orthorhombic space group *P*bcn. 4, **7** and **9** exhibit densities of 1.843, 1.765 and 1.678 g cm^{-3}, respectively. The transfer of protons from dinitromethyl groups to ammonium, guanidine and guanidylguanidine were confirmed, respectively. The structure of anions in different salts are similar with that of **2**, the dihedral angles between two furazan rings (16.25, 16.76° and 15.17°) are slightly bigger than **2**. The lengths of C-C bonds connecting dinitromethyl group and furazan ring are slightly shorter than **2**, which indicate the existing of delocalized π-electron system in the anion. In contrast to the previously reported 5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazole) anion, [11] the dinitromethyl groups and furazan rings on the same side of the bridged oxygen atom are clearly twisted rather than nearly planar, which contribute to the lower density than that of 5,5’-dinitromethyl-3,3’-bis(1,2,4-oxadiazole) based salts. As for the cations, guanidium cations in **7** crystallize in one plane, and guanidylguanidium cations in **9** have a twist at N7 with dihedral angles of 41.7° between the two guanidinium planes. The discrete cations and anions are linked into 3D network by the extensive hydrogen-bonding interactions between cations and anions (Figure 3, Figure 4 and Figure 5). The details of all hydrogen bonds are gathered in the Supporting Information.



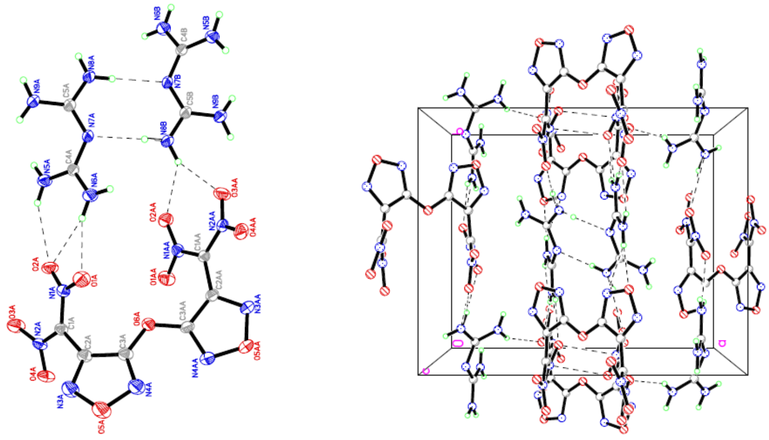
(a) (b)

Figure 3 (a) Molecular structure of **4** with thermal ellipsoids at 30% probability; (b) Packing diagram of **4** viewed down the c axis.



(a) **(b)**

Figure 4 (a) Molecular structure of **7** with thermal ellipsoids at 30% probability; (b) Packing diagram of **7** viewed down the b axis.



(a) (b)

Figure 5 (a) Molecular structure of **9** with thermal ellipsoids at 30% probability; (b) Packing diagram of **9** viewed down the c axis.

Table 1 Crystallographic data for **2**, **4**, **7** and **9**

No.	**2**	**4**	**7**	**9**
Empirical formula	$C_{12}H_4N_{16}O_{22}$	$C_6H_8N_{10}O_{11}$	$C_8H_{12}N_{14}O_{11}$	$C_{10}H_{16}N_{18}O_{11}$
Formula weight	724.30	396.22	480.32	564.12
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*Cc*	*P*-1	*P*-1	*P*bcn
a/nm	1.4974(3)	0.7691(4)	0.8882(16)	1.3873(9)
b/nm	1.4968(3)	0.9290(5)	0.1025(18)	1.1275(7)
c/nm	1.1822(2)	1.0564(5)	0.1072(19)	1.4334(10)
α/(°)	90	94.504(8)	78.079(3)	90
β/(°)	99.260(3)	104.174(7)	83.683(3)	90
γ/(°)	90	100.366(7)	71.346(2)	90
V/nm^3	2.6151(9)	0.7139(6)	0.9037(3)	2.242(3)
Z	4	2	2	8
$\rho_{calc}/(\mathrm{g{\bullet}cm^{-3}})$	1.840	1.843	1.765	1.678
μ/mm^{-1}	0.179	0.176	0.162	0.149
F(000)	1456	404	492	1168
Goodness-of-fit on F_2	1.035	1.081	1.040	1.042
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0478 *wR*2= 0.1295	*R*1 = 0.0366 *wR*2 = 0.1266	*R*1=0.0401 *wR*2=0.1108	*R*1 = 0.0638 *wR*2=0.1310
R indices (all data)	*R*1 = 0.0549 *wR*2 = 0.1364	*R*1 = 0.0410 *wR*2 = 0.1382	*R*1 = 0.0442 *wR*2=0.1153	*R*1= 0.0948 *wR*2 =0.1702
CCDC No.	1028788	1041566	1028789	1041345

Thermal stabilities and Sensitivities

The thermal stabilities of **2-9** were investigated by DSC (10 °C min^{-1}). As shown in Table 2, **2**, **8** and **9** exhibit melting point of 117.0, 116.2 and 157.6 °C, respectively. **9** exhibits the highest decomposition temperature of 221.1 °C, while **5** shows the lowest decomposition temperature of 131.5 °C. All the other salts have decomposition temperature at range of 188.3°C (**4**) to 199.4 °C (**6**).

The impact sensitivities for **2-9** were determined according to the standard BAM methods [13] and the results were displayed in Table **2**. Neutral compound (**2**) shows the highest sensitivity toward impact and is classified as “very sensitive”. All of the salts exhibit sensitivities between 4 J and

32.5 J and are classified as "sensitive". [14] Of these, **3**, **7** and **9** are less sensitive than RDX (7.5 J) [10] and **6** possesses impact sensitivity similar with RDX. Considering that the introduction of nitrogen-rich cations increase intra- and intermolecular hydrogen bonds, it is no surprise that **3-9** all are less sensitive (impact) than neutral compound (**2**).

Detonation parameters

The densities of all the salts were measured by a gas pycnometer (Table 2), falling in the range of 1.65 (**8**)-1.88 (**6**) g cm^{-3}. The heats of formation, as one of the most important characteristics for energetic salts, were computed theoretically using the Gaussian 09 program package.[15] The calculated standard enthalpy of formation for the anion was -11.3 kJ mol^{-1}, a value higher than that of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole) anion (-101.7 kJ mol^{-1}). [11] Except for **3**, the remaining salts were calculated to exhibit positive heat of formation. Among them, **8** possesses the highest heat of formation. The oxygen balances of all the salts range from -38.3% to -5.6%. Of the compounds, 4, 5 and 6 have oxygen balances of -24.0%, -12.1 and -5.6%, respectively, and thus are superior to RDX.

With the calculated heats of formation and experimental densities, detonation parameters were calculated by the Kamlet-Jacobs equation. [17] The calculated detonation pressures and velocities fall in the range of 24.9-38.0 GPa and 7582.2-9072.7 m s^{-1}, respectively. In terms of detonation velocity, **5** and **6** even exceed the benchmark explosive RDX (8748 m s^{-1}). [8] Unfortunately, **5** have unfavorable thermal stability (T_{dec} : 131.5 °C) and impact sensitivity (greater than that of RDX).

Table 2 Properties of energetic salts based on oxy-bridged bis (dinitromethyl)furazan

No.	T_m[a] (°C)	T_d[b] (°C)	ρ[c](g cm^{-3})	$\Delta_f H_{cation}$[d] (kJ mol^{-1})	$\Delta_f H_{anion}$[e] (kJ mol^{-1})	$\Delta_f H_{salt}$[f] (kJ mol^{-1})	Ω[g] (%)	P[h] (GPa)	D[i] (m s^{-1})	IS[j] (J)
2	117.0	196.0	1.83(1.84) [k]	-	-	167	-8.8	34.8	8715.3	2
3	-	189.3	1.81	350.6 [k]	-11.3	-372.9	-24.0	27.8	7828.9	15
4	-	188.3	1. 81(1.84) [k]	626.4 [k]	-11.3	30.0	-12.1	34.9	8719.7	5
5	-	131.5	1.85	669.5 [k]	-11.3	135.0	-5.6	37.8	9072.7	4.5
6	-	199.4	1.88	770.0 [k]	-11.3	327.1	-15.0	38.0	9049.6	7.5
7	-	186.6	1.74(1.77) [k]	575.9 [k]	-11.3	25.3	-28.3	29.0	8055.2	32.5
8	116.2	191.6	1.65	875.1 [k]	-11.3	715.9	-25.3	27.7	8045.8	4
9	157.6	221.1	1.69(1.68) [k]	620.9 [l]	-11.3	192.9	-38.3	24.9	7582.2	21
RDX	-	205	1.82	-	-	80.0	-21.6	34.9	8748	7.4

[a] Melting point. [b] Decomposition temperature. [c] Density measured by gas pycnometer (25 °C). [d] Calculated enthalpy of formation of cations. [e] Calculated enthalpy of formation of anions. [f] Calculated enthalpy of formation of salts. [g] Oxygen balance for $C_aH_bO_cN_d$, 1600(c-2a-b/2)/M_w; M_w = molecular weight. [h] Detonation pressure (calculated with K-J equation). [i] Detonation velocity (calculated with K-J equation). [j] Impact sensitivity. [k] Crystal densities at 298 K. [k] From ref. 17 *a*. [1] From ref. 17 *b*.

Conclusion

A series of energetic salts with acceptable oxygen balance have been synthesized in moderate to excellent yields. Based on the fact that π-electron system is delocalized in the anion, all the salts exhibit good thermal stability with the decomposition temperatures ranged from 188.3 to 221.1 °C, with the exception of **5**. Impact sensitivities of synthesized salts fall in the range from 4 to 32.5 J.

Based on the experimental densities and calculated heat of formation, detonation pressures and velocities were calculated. Most of the salts have detonation velocities higher than 8000 m s^{-1} (except for **3** and **9**), and some salts even exceed the conventional explosives RDX. Among them, hydrazidinium salt (**6**) exhibits promising comprehensive properties, such as comparable thermal stability and sensitivity with RDX, higher density and detonation property than RDX, make it a competitive secondary explosive.

Experimental Section

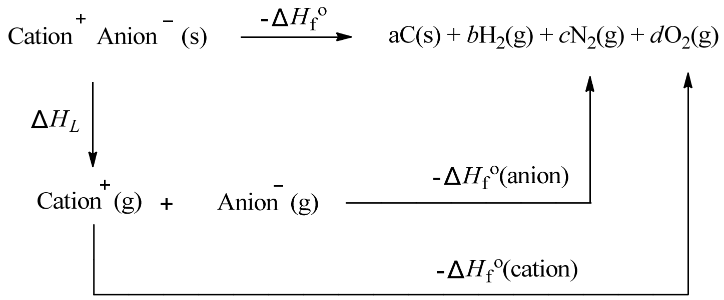
^{1}H NMR and ^{13}C NMR were obtained on a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000-400 cm^{-1}. Elemental analyses (C, H and N) were performed on a VARI-El-3 elemental analyzer. The DSC curves under a flowing nitrogen gas were obtained by a NETZSCH DSC200 F3 apparatus. Densities were measured at room temperature using a Micromeritics Accupyc II 1340 gas pycnometer. The impact sensitivities were determined on a ZBL-B impact sensitivity instrument (Nachen Co., China) with approximately 10 mg of sample.

X-ray crystallography

Crystals of **2** was obtained by slow evaporation from the solution in $CHCl_3$ at room temperature. Crystals of **4**, **7** and **9** were obtained by slow evaporation from corresponding solution in water at room temperature. For all compounds, a Bruker SMART APE II CCD X-ray diffractometer was employed for data collection using Mo Ka radiation (k = 0.71073 Å). The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL package.[16] The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on *F*2 for the non-hydrogen atoms. Crystal data and refinement results are summarized in Table 1.

Theoretical study—computational details

Computations were performed with the Gaussian 09 (Revision B. 01) suite of programs.[15] The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.



Scheme 3 Born-Harber cycle for the formation of energetic salts.

Based on a Born-Haber energy cycle (Scheme 3), the standard heats of formation of a salt can be simplified by Equation (1):

$$\Delta H_f^o\text{ (salt, 298K)} = \Delta H_f^o\text{ (cation, 298K)} + \Delta H_f^o\text{(anion, 298K)} - \Delta H_L \qquad (1)$$

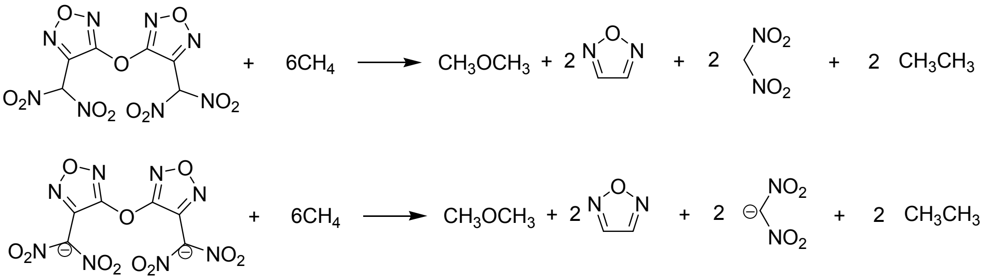
Where the calculation of the gas-phase heats of formation of oxy-bridged bis(dinitromethyl)furazan anion was carried out by the application of isodesmic reaction shown in Scheme 4. The gas-phase heats of formation of cations were taken from the literature. [17] ΔH_L is the lattice energy of the salts, which can be predicted by the formula suggested by Jenkins et al. [Eq. (2)]: [18]

$$\Delta H_L = U_{POT} + [p(n_M/2-2)+q(n_X/2-2)]RT \qquad (2)$$

where n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy (U_{POT}) has the form [Eq. (3)]:

$$U_{POT} = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

Where ρ_m is the density, M_m is the chemical formula mass of the ionic material, and values for the coefficients γ and δ are taken from the literature. [18]



Scheme 4 Isodesmic reactions of Oxy-bridged bis(dinitromethyl)furazan and its anion.

The gas-phase heat of formation for **2** was carried out by the application of isodesmic reaction shown in Scheme 4. The solid state enthalpy of formation of **2** was calculated by subtracting the enthalpy of sublimation, obtained by *Trouton*'s rule ($\Delta_{sub}H = 188 \times T_m$), from the gas-phase enthalpy. [19]

The detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet-Jacobs (K-J) equations as shown in Equations (4), (5) and (6). [20]

$$P = 1.558\,\rho^2\Phi \qquad (4)$$

$$D = 1.01\Phi^{1/2}\,(1.011+1.312\,\rho) \qquad (5)$$

$$\Phi = 0.4889N\,(MQ)^{1/2} \qquad (6)$$

D is the predicted detonation velocity (m s^{-1}), P is the detonation pressure (GPa), and ρ is the compound density (g cm^{-3}). Φ, N, M and Q are characteristic parameters of an explosive; Q is the chemical energy of detonation (kJ g^{-1}). The densities and the calculated heats of formation were used to compute the D and P values.

Dipotassium oxy-bridged bis (dinitromethyl) furazan (1)

1 was prepared in a procedure described by our group.[10] ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.8, 142.3, 118.7; IR (KBr, cm^{-1}): 1479, 1239, 1070, 1589, 1526, 997; Anal. Calc. for $C_6N_8O_{11}K_2$: C, 16.44; N, 25.57. Found: C, 16.35; N, 25.36%.

Oxy-bridged bis(dinitromethyl)furazan (2)

50% sulfuric acid (1 mL) was added to a solution of **1** (0.438 g, 1 mmol) in water (3 mL). After stirring for 10 min at room temperature, the reaction mixture was extracted with ethyl ether (3×10 mL). The extracts were washed with water and dried over magnesium sulfate. The ethyl ether solution was evaporated to obtain a white solid (0.295 g, 81.5%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 10.49 (s, 2H, CH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.2, 142.8, 119.1; IR (KBr, cm^{-1}): ν = 3004, 2983, 1481, 1366, 1623, 1322, 1239, 1148,1037, 1585, 1524, 999; Calc. for $C_6H_2N_8O_{11}$: C 19.90, H 0.56, N 30.94%; Found: C 19.84, H 0.52, N 30.78%.

Bis(N-carbamoylguanidinium) oxy-bridged bis(dinitromethyl)furazan (3)

A mixture of N-carbamoylguanidinium chloride (0.250 g, 2 mmol) and **1** (0.438 g, 1mmol) in water (10 mL) was stirred at 60 °C for 1 h. After the mixture was cooled to room temperature, the precipitate was filtered to give a yellow powder (0.363 g, 64.1%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 9.60 (s, 2H, NH), 8.03 (br, 8H, NH_2), 7.02 (br, 4H, NH_2) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.2, 155.8, 154.8, 142.8, 119.1. Elemental Anal. Calc. for $C_{10}H_{14}N_{16}O_{13}$: C, 21.21; H, 2.49; N, 39.57; Found: C, 21.15; H, 2.52; N, 39.47. IR (KBr, cm^{-1}): ν = 3428, 3199, 1745, 1693, 1594, 1536, 1485, 1339, 1246, 1141, 998, 864, 824, 746.

General procedure for synthesis of the salts 4-9

2 (1 mmol) was added to a solution of ammonia (2 mmol), hydrazine (2 mmol), hydroxylamine (2 mmol), guanidine (2 mmol), triaminoguanidine (2 mmol) and guanidylguanidine (2 mmol) in MeOH (10 mL), respectively. The resulting mixture stirred at room temperature overnight. The solution was slowly evaporated and the remaining solid was collected and washed with cool ethanol to give the desired products.

Diammonium oxy-bridged bis(dinitromethyl)furazan (4)

Light yellow solid (255 mg, 64.4%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.07 (t, J= 50.9 Hz, 8H, NH_4) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.2, 142.8, 119.1 ppm. Elemental Anal. Calc. for $C_6H_8N_{10}O_{11}$: C, 18.19; H, 2.04; N, 35.35; Found: C, 18.22; H, 2.01; N, 35.26; IR (KBr, cm^{-1}): ν = 3211, 1599, 1578, 1536, 1496, 1430, 1274, 1140, 1074, 1000, 876, 818, 750.

Dihydroxylammonium oxy-bridged bis(dinitromethyl)furazan (5)

Light yellow solid (310 mg, 72.4%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 10.09(s, 6H, NH_3), 9.91(s, 2H, OH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.7, 142.2, 118.6 ppm. Elemental Anal. Calc. for $C_6H_8N_{10}O_{13}$: C, 16.83; H, 1.88; N, 32.71; Found: C, 16.80; H, 1.92; N, 32.62. IR (KBr, cm^{-1}): ν = 3424, 3150, 1578, 1534, 1483, 1329, 1305, 1239, 1148, 1070, 1000, 875, 819, 749.

Dihydrazidinium oxy-bridged bis(dinitromethyl)furazan (6)

White solid (228 mg, 53.5%). ^{1}H NMR (CD_3OD, 500 MHz): δ = 4.95 (br, 10H, NH_2, NH_3) ppm. ^{13}C NMR (CD_3OD, 125 MHz): δ = 160.8, 142.3, 118.6 ppm. Elemental Anal. Calc. for $C_6H_{10}N_{12}O_{11}$: C, 16.91; H, 2.36; N, 39.44; Found: C, 16.96; H, 2.32; N, 39.34; IR (KBr, cm^{-1}): ν = 3443, 3329, 3148, 1582, 1536, 1481, 1384, 1324, 1238, 1144, 1072, 998, 877, 825, 743.

Bis(guanidnium) 3,3'-bis(dinitromethyl)difurazanyl ether (7)

Yellow solid (418 mg, 87.1%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.89 (s, 12H, NH_2) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.2, 158.3, 142.8, 119.1 ppm. Elemental Anal. Calc. for $C_8H_{12}N_{14}O_{11}$: C, 20.01; H, 2.52; N, 40.83; Found: C, 20.08; H, 2.49; N, 40.69. IR (KBr, cm^{-1}): ν = 3423, 3202, 1662, 1538, 1468, 1387, 1326, 1238, 1142, 1074, 997, 866, 825, 747.

Bis(triaminoguanidnium) oxy-bridged bis(dinitromethyl)furazan (8)

Yellow solid (355 mg, 62.3%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 8.59 (s, 6H, NH), 4.49 (s, 12H, NH_2) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ= 161.2, 159.5, 142.8, 119.1 ppm. Elemental Anal. Calc. for $C_8H_{18}N_{20}O_{11}$: C, 16.85; H, 3.18; N, 49.12; Found: C, 16.90; H, 3.15; N, 48.97. IR (KBr, cm^{-1}): ν=3359, 3320, 3211, 1686, 1535, 1472, 1382, 1320, 1239, 1129, 1070, 999, 948, 884, 823, 748.

Bis(guanidylguanidinium) oxy-bridged bis(dinitromethyl)furazan (9)

Yellow solid (412 mg, 89.2%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.89 (s, 9H, NH and NH_2); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.2, 159.9, 142.8, 119.1; Elemental Anal. Calc. for $C_{10}H_{16}N_{18}O_{11}$: C, 21.28; H, 2.86; N, 44.67; Found: C, 21.30; H, 2.78; N, 44.56; IR (KBr, cm^{-1}): ν = 3457, 3357, 1620, 1562, 1520, 1464, 1235, 1144, 1057, 996, 883, 745.

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