

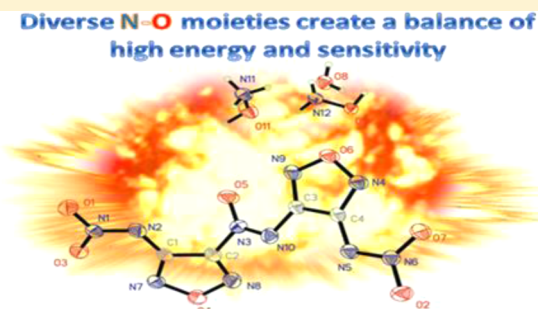
3,3'-Dinitroamino-4,4'-azoxyfuran and Its Derivatives: An Assembly of Diverse N–O Building Blocks for High-Performance Energetic Materials

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S Supporting Information

ABSTRACT: On the basis of a design strategy that results in the assembly of diverse N–O building blocks leading to energetic materials, 3,3'-dinitroamino-4,4'-azoxyfuran and its nitrogen-rich salts were obtained and fully characterized via spectral and elemental analyses. Oxone (potassium peroxomonosulfate) is an efficient oxidizing agent for introducing the azoxy N-oxide functionality into the furazan backbone, giving a straightforward and low-cost synthetic route. On the basis of heats of formation calculated with Gaussian 03 and combined with experimentally determined densities, energetic properties (detonation velocity, pressure and specific impulse) were obtained using the EXPLO v6.01 program. These new molecules exhibit high density, moderate to good thermal stability, acceptable impact and friction sensitivities, and excellent detonation properties, which suggest potential applications as energetic materials. Interestingly, 3,3'-dinitroamino-4,4'-azoxyfuran (**4**) has the highest calculated crystal density of 2.02 g cm⁻³ at 173 K (gas pycnometer measured density is 1.96 g cm⁻³ at 298 K) for N-oxide energetic compounds yet reported. Another promising compound is the hydroxylammonium salt (**6**), which has four different kinds of N–O moieties and a detonation performance superior to those of 1,3,5,7-tetranitrotetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20). Furthermore, computational results, viz., NBO charges and ESP, also support the superior qualities of the newly prepared compounds and the design strategy.



INTRODUCTION

Traditional energetic materials for civilian and military use today, such as cyclo-1,3,5-trimethylene-2,4,6-trinitamine (RDX), 2,4,6-trinitrotoluene (TNT), and lead azide, were developed in the last 2 centuries.¹ Although these explosives are effective, new research continues to promote the generation of new high-energy-density materials (HEDMs) with improved properties as well as environmental compatibility.² The desirable characteristics of modern explosives and propellants include high density, positive heat of formation, high detonation velocity and pressure, high oxygen balance, high thermal stability, and low sensitivity toward impact and friction among the most important aspects.^{3–6} However, the contradictory nature of high performance and low sensitivity usually poses interesting but challenging problems for the synthetic chemist in the development of new HEDMs.^{7,8} Therefore, suitable design strategies are necessary to guide energetic materials synthesis if the ever increasing demand for higher energy content with concomitant stability is to be realized.

One of the most acceptable strategies for the design of HEDMs is incorporating both fuel and oxidizer properties into a single molecule.⁹ Here the oxidizer part provides the oxygen needed for oxidation of the fuel portion in order to enhance combustion and therefore support release of large amounts of energy.^{10,11} This quintessential strategy can be seen in many

well-known explosives, such as RDX, 1,3,5,7-tetranitrotetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20). However, most of the other secondary explosives have lower oxygen balances, and their energy release is restricted due to incomplete redox reaction (negative oxygen balance). Recently, polynitro azoles have attracted more and more attention owing to the advantages of high oxygen content based on the presence of polynitro groups.^{12,13} Unfortunately, compounds in this category also appear to have limits, including low decomposition temperature, high impact sensitivity, and especially negative heat of formation.^{14,15} Improvement in oxygen balance accompanies the replacement of one azole nitrogen atom by an oxygen atom, which gives rise to the well-known family of energetic oxadiazoles.^{16,17} Heats of formation of potential oxadiazoles in comparison with other azole rings are given in Figure 1. On the basis of that property, 1,2,5-oxadiazole (furan, **I**) is the best choice among the possible oxadiazoles and it is slightly better than 1,2,4-triazole (**VIII**). Therefore, the combination of furazan with other energetic functional groups is favorable for maintaining a high level of heat of formation of the whole molecule.

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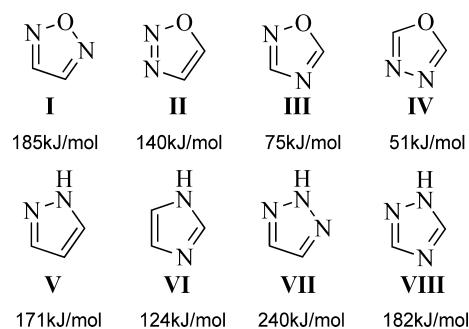


Figure 1. Calculated gas-phase heats of formation (G2 atomization method)¹⁸ for potential oxadiazoles, pyrazole, imidazole, 1,2,3-triazole, and 1,2,4-triazole.

In addition to introducing nitro groups and using oxadiazoles as backbones, the introduction of *N*-oxides is a rather recent methodology.^{19–23} The additional oxygen atom coordinated to the nitrogen system not only enhances oxygen density and performance but also tends to stabilize the entire molecule. For example, no aromatic monocyclic 1,2,3,4-tetrazine has been described and only a single compound containing this moiety is claimed to exist.²⁴ In contrast, 1,2,3,4-tetrazine-1,3-dioxide derivatives are well-known and show remarkably high stabilities.^{24–26} Calculations also provide a theoretical explanation, suggesting that the *N*-oxide moiety removes lone pair repulsion, which also increases σ – π separation and thus results in stabilization of the nitrogen system.²⁷ To date, the oxidation of tetrazole and triazole compounds has been successfully accomplished using Oxone (Figure 2) and resulted in high-

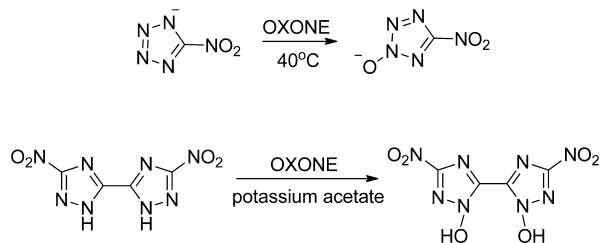


Figure 2. Oxidation of nitrotetrazolate and 3,3'-dinitro-5,5'-bis-1,2,4-triazole using oxone.

performance explosives with low sensitivity toward external stimuli.^{28,29} Among the *N*-oxide energetic materials, molecules that contain the azoxy [$-N=N(O)-$] moiety are uncommon in the literature. However, it was shown previously that the presence of the azoxy moiety imparts a high endothermic heat of formation, good detonation parameters, and especially low sensitivity to the molecule based on the limited examples explored.^{30,31}

Other than a positive oxygen balance, for a molecule or salt to be a high-performance energetic material, high-nitrogen content and high heat of formation are also required.^{32,33} Modern HEDMs can derive their energy not only from the oxidation of carbon backbone but additionally from ring strain, a large number of N–N, C–N, and N–O bonds, and high heats of formation.³⁴ Therefore, introduction of energy-rich functional groups such as nitramine ($-NHNO_2$) and azoxy groups, combined with species having high heats of formation, e. g., oxadiazoles, as backbones, is an effective way for tailoring new energetic molecules. Energetic materials based on this design strategy, which assembles multiple N–O building

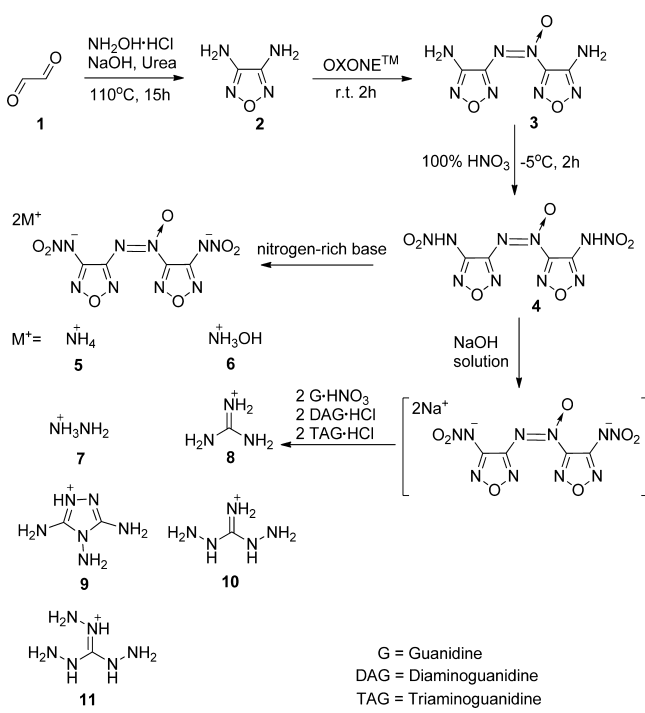
blocks, could give rise to a desirable compromise in properties with high nitrogen and oxygen content on the one hand and promising detonation properties due to high heats of formation on the other.

In a continuing effort to seek more powerful, less sensitive HEDMs, we are interested in heterocyclic compounds that contain high percentages of both nitrogen and oxygen and fulfill the requirements of the design strategies mentioned above. Herein we report the synthesis and characterization of a highly energetic nitrogen- and oxygen-rich molecule, 3,3'-dinitroamino-4,4'-azoxyfurazan (4), which consists of three N–O building blocks: nitramine, azoxy, and furazan ring. In addition, a series of 3,3'-dinitroamino-4,4'-azoxyfurazan-based energetic dicationic salts was also prepared. Among them, the hydroxylammonium salt has a fourth type of N–O building block in the cation and demonstrates the best compromise between performance and sensitivity. These compounds were characterized by X-ray diffraction, infrared, and multinuclear NMR spectroscopy, elemental analysis, and DSC. Quantum chemical investigation of target compounds assists in the understanding of their unique structures. Calculations that predict detonation properties confirm the initial hypothesis that assembly of diverse N–O building blocks is indeed an effective method to combine the benefits of each of the fragments and to improve energetic performance.

RESULTS AND DISCUSSION

Synthesis. Diaminofurazan (3,4-diamino-1,2,5-oxadiazole, 2) is a useful precursor for the preparation of new energetic materials.³⁵ The generation of 2 from the dehydraton of diaminoglyoxime which was obtained from glyoxal (1) at elevated temperatures in strong base solution and under high pressure has been known for nearly half a century.³⁶ In this study, a facile one-pot reaction is employed to safely and easily perform the dehydration reaction to furnish high purity 2. Urea can be used as a dehydrating agent and, as a consequence, helps to drive the reaction and avoid the necessity for high temperature and pressure. In our work, 3 was synthesized according to a late patent in which Oxone was used as the oxidizing agent.^{37,38} This simple, inexpensive, and straightforward method of azo *N*-oxide introduction into furazan compounds will make the synthetic route easier for industrial scale-up and practical use. 3,3'-Dinitroamino-4,4'-azoxyfurazan (4) was prepared in good yield by treatment of 3 with an excess of fuming nitric acid at -5 °C. Reaction of 3 with bases led to the formation of nitrogen-rich salts, 5–11. Due to the high solubility of 4 and the low solubility of 5–11 in ethanol, all ionic derivatives could be isolated in excellent yields and high purity (Scheme 1).

Spectroscopy. The structures of 3,3'-dinitroamino-4,4'-azoxyfurazan (4) and the new salts were determined by IR and ¹H and ¹³C NMR spectroscopy as well as elemental analysis. Additionally, ¹⁵N NMR spectra were recorded for compounds 5–8 and 10 in DMSO-*d*₆ solution, and chemical shifts are given in Figure 2 with respect to CH₃NO₂ as external standard. The IR spectra of all compounds were recorded and assigned using frequency analysis from the optimized structures (B3LYP/cc-pVDZ method based on Gaussian 03 software³⁹). Both the neutral 3,3'-dinitroamino-4,4'-azoxyfurazan and dicationic forms contain a strong, diagnostic *N*-oxide stretching frequency in the IR spectrum at ~ 1562 cm⁻¹. The calculated value for this band is 1563 and 1566 cm⁻¹ for the neutral and ionic species, respectively. The other N–NO₂ stretching bands

Scheme 1. Synthesis of 3,3'-Dinitroamino-4,4'-azoxyfuranan (4) and Its Energetic Salts (5–11)

occur in the range between 1620 and 1622, and 1315 and 1379 cm^{-1} for strong bands of high intensity (calculated at 1686–1689 and 1319–1341 cm^{-1}). Besides that, a small component of NO_2 asymmetric stretching bands was observed at 1007 cm^{-1} (calculated number is 993 cm^{-1}).

Since it is a very strong acid, the position of the resonance bands for the protons in 4 are observed at 13.62 ppm in the ^1H NMR spectrum. The ammonium anion protons appear as a sharp singlet at 7.08 ppm, differing from that in diammonium 4,4'-bis(nitramino)azofurazanate, which occurs as a broad singlet at ~ 7.25 ppm.^{40,41} In the ^{13}C NMR spectra, the asymmetric bridging azoxy group gives rise to different carbon signals between two furazan rings. The proximity of the N–O group leads to a shift from 155.2 to 148.3 ppm of the carbon atom signal for compound 4. The deprotonation of 4 with nitrogen-rich bases does not have a major effect on signal shifts in the ^{13}C NMR spectra. In most of these energetic salts, the furazan carbon atoms can be found in the 156–150 ppm range. Five well-resolved resonance bands are detected in the ^{15}N NMR spectra for 5–8 and 10.

In Figure 3, selected ^{15}N NMR spectra of 5–8 and 10 are shown. The spectrum of 5 possesses 11 signals, at -358.5 (NH_4^+), -156.5 (N9), -149.4 (N2), -6.5 (N6), -64.0 (N5), -13.1 (N1), -12.5 (N10), 6.6 (N7), 12.9 (N4), 21.4 (N8), 25.9 (N3) ppm. The signals for N6, which has oxygen as a neighbor in the azoxy linkage, appear as expected at lower field compared to N5. This is also observed in the carbon NMR, where the asymmetric bridging azoxy moiety also causes different ^{15}N signals between two furazan rings as well as the two nitroimino groups. On the basis of the values of the chemical shifts of hydroxylamine, hydrazine, guanidine, and diaminoguanidine moieties, NH , NH_2 , NH_2^+ , and NH_3^+ groups can be assigned to the resonance peaks at highest field. It is noted that these assignments are based on the literature values of the remainder of the peaks^{42,43} and compared with calculated

spectra [B3LYP/6-311+g(2d,p) with IEF-PCM continuum solvation models of the Gaussian 03 program].⁴⁴

Single Crystal X-ray Structure Analysis. Crystals of 4 and $6\cdot\text{H}_2\text{O}$, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of ethanol and water solutions at room temperature, respectively. The crystallographic data and refinement details can be found in the Supporting Information. Both of the compounds show high crystal densities (2.02 for 4 at 173 K; 1.87 for $6\cdot\text{H}_2\text{O}$ at 293 K). The structure of 4 has monoclinic (Pn) symmetry, while $6\cdot\text{H}_2\text{O}$ crystallizes in the monoclinic space group $P2_1/c$. The bond lengths of both neutral compound and anion are comparable within the limits of error, in contrast to their bond angles. The bond length of N–oxide in 4 has an average value of 1.212 Å as compared to a slightly larger value of 1.237 Å for the anion. The angles of N–N–O are 125.1° and 129.3° for 4 and $6\cdot\text{H}_2\text{O}$, respectively. For the neutral compound, it is interesting to find that two furazan rings, azoxy linkage (torsion angle C1–N5–N6–C3 , -178.7°) as well as the N-nitro moieties (torsion angle C2–N3–N4–O1 , -177.1°) are coplanar. Differently, although the N-nitro moiety is still coplanar with each furazan ring in $6\cdot\text{H}_2\text{O}$ (torsion angle C1–N2–N1–O1 , -1.4° ; C4–N5–N6–O7 , -0.8°), one of the furazan rings is bent away from the azoxy linkage and the other ring at 52.6° (torsion angle N8–C2–N3–N10). This dissimilarity may be due to the intramolecular hydrogen bond between cation and anion present in $6\cdot\text{H}_2\text{O}$. The remarkable high densities of these compounds can be rationalized in terms of considerable hydrogen bonding, especially the N-oxides being involved in multiple bonding interactions, as shown exemplarily in the molecular unit of 4 and $6\cdot\text{H}_2\text{O}$ (Figures 4 and 5).

Thermal Behavior. The phase-transition temperatures and thermal stabilities of compounds 4–11 were determined by differential scanning calorimetric (DSC) measurements scanning at 5°C min^{-1} (Table 1). None of the synthesized compounds melts prior to decomposition. Most of these compounds show sharp exothermic peaks, which indicate extremely fast decomposition. Not surprisingly, the neutral compound 4 has the lowest thermal stability, which is expected on the basis of the other nitramino derivatives.⁴⁵ While 3,3'-dinitroamino-4,4'-azoxyfuranan decomposes at 90°C , its salts are significantly more thermally stable, with decomposition temperatures ranging from 148 (5) to 246°C (8). Among these compounds, the decomposition temperatures of 8 and 9 are above 200°C , which supports their thermal stability.

Heats of Formation. All enthalpy calculations were performed with the Gaussian 03 (Revision D.01) suite of programs. The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6-31+G** basis set. Single-point energies were calculated at the MP2/6-311+G** level.⁴⁶ Atomization energies for cations were obtained by employing the G2 ab initio method.¹⁸ All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Two explicit applications of isodesmic reactions were carried out to obtain the gas-phase heats of formation of the neutral compound 4 and its anions (Supporting Information). Then the remaining task is to determine the solid-phase heats of formation for the synthesized compounds 4–11. The solid-state enthalpy of formation for neutral compounds can be estimated by subtracting the heats of sublimation from gas-phase heats of formation. On the basis of the literature,⁴⁷ the

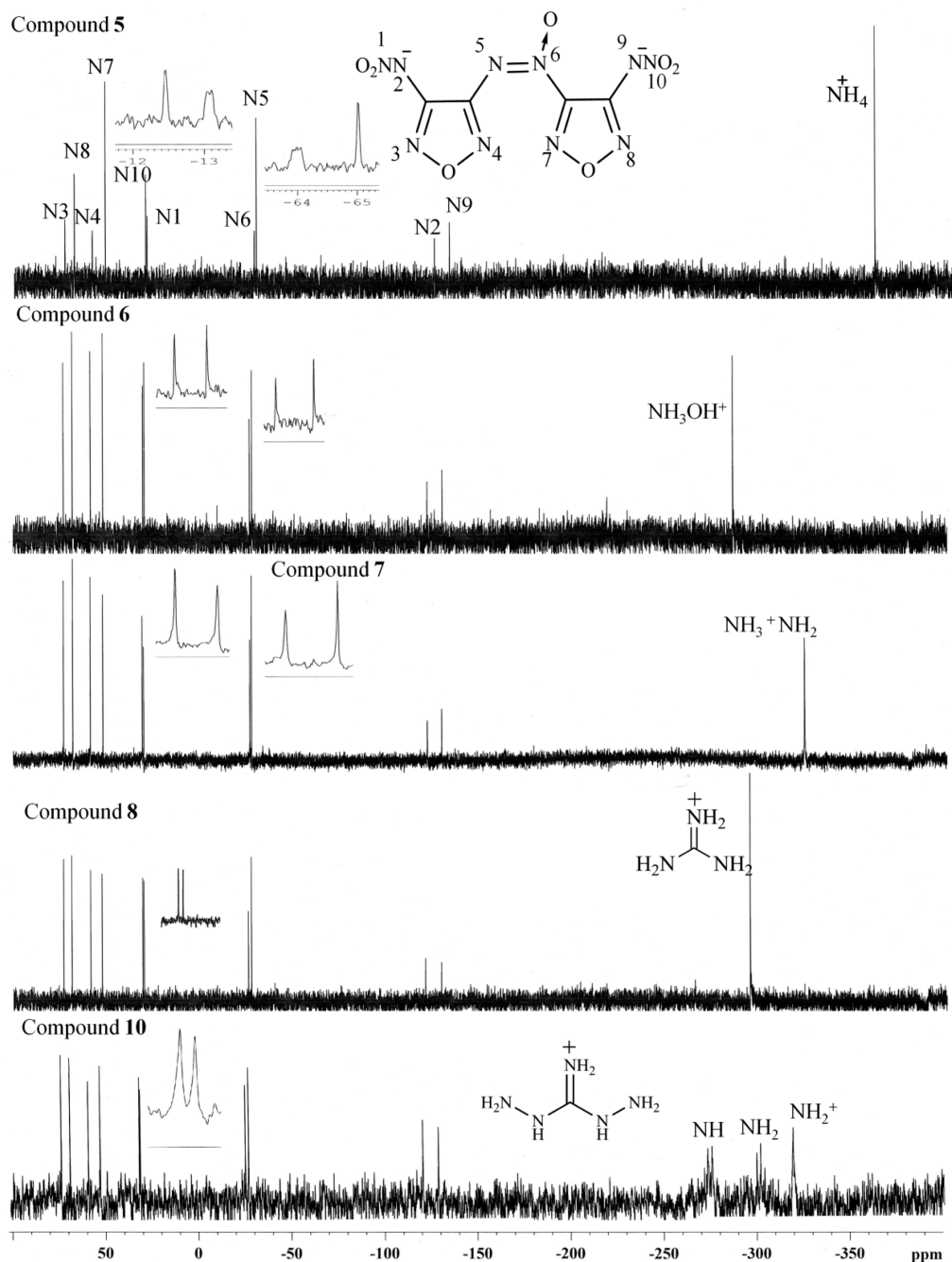


Figure 3. ^{15}N spectra of compounds 5–8 and 10 in $\text{DMSO}-d_6$.

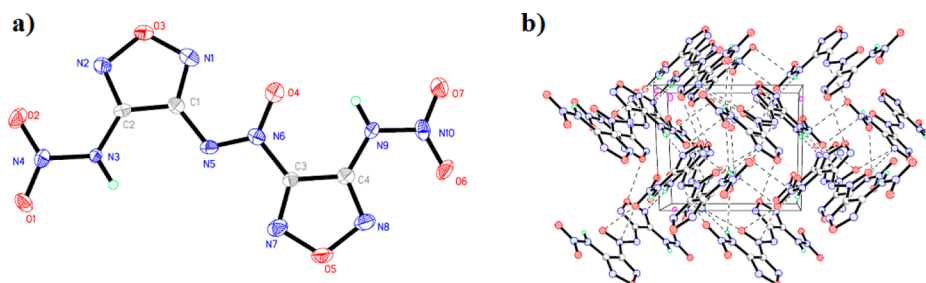


Figure 4. (a) A view of the molecular unit of 4. (b) Unit cell view along c axis; hydrogen bonds are indicated as dotted lines.

heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point

or the decomposition temperature when no melting occurs prior to decomposition:^{48,49}

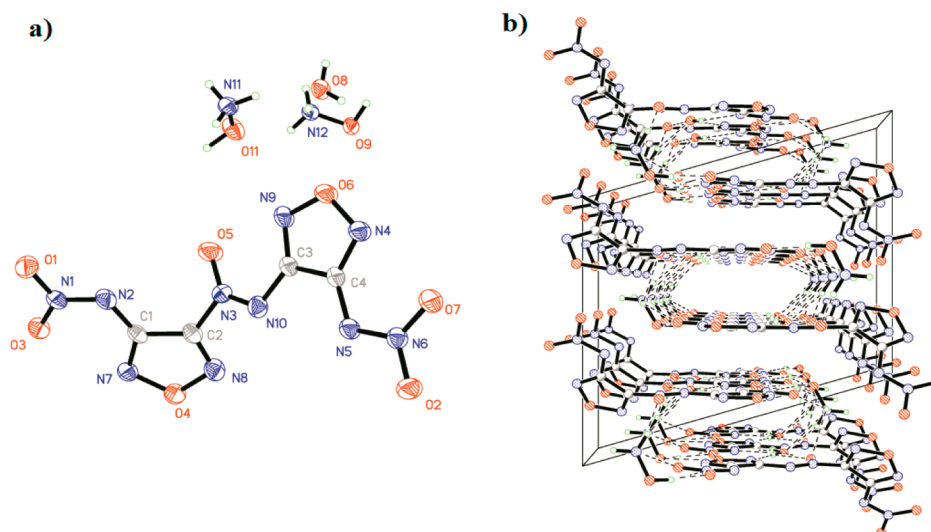


Figure 5. (a) A view of the molecular unit of 6-H₂O. (b) Unit cell view along *b* axis; hydrogen bonds are indicated as dotted lines.

Table 1. Physical Properties of 3,3'-Dinitroamino-4,4'-azoxyfurazan (4) and Its Energetic Salts (5–11) Compared with Those of RDX and HMX

compd ^a	<i>T</i> _d ^b (°C)	Ω ^c (%)	<i>d</i> ^d (g/cm ³)	Δ <i>H</i> _{Lat} ^e (kJ/mol)	Δ <i>H</i> ^f [kJ/mol (kJ/g)]	ν _D ^g (m/s)	<i>P</i> ^h (GPa)	IS ⁱ (J)	FS ^j (N)	<i>I</i> _{sp} ^k (s)
4	90	10.6	1.96		730.0 (2.42)	9746	44.1	2	10	283
5	148	−4.8	1.83 (1.88)	1315.3	523.8 (1.59)	9474	39.6	16	360	270
6	177	4.3	1.90	1273.5	651.8 (1.77)	9511	42.2	19	120	286
7	192	−8.7	1.84	1263.2	863.1 (2.36)	9459	39.3	15	60	280
8	246	−19.0	1.74	1173.5	564.6 (1.34)	8585	29.2	35	360	240
9	222	−19.7	1.75	1075.5	1265.9 (2.39)	8746	30.4	21	240	243
10	187	−23.3	1.84	1139.2	1039.1 (2.16)	9453	36.5	14	240	251
11	168	−25.1	1.76	1094.0	1259.5 (2.47)	9227	33.6	17	120	256
RDX	210	0	1.82		80.0 (0.36)	8748	34.9	7.4	120	258
HMX	280	0	1.91		104.8 (0.36)	9320	39.5	7.4	120	266
CL-20	210	11.0	2.03 (β)		397.8 (0.90)	9406	44.6	4.0	94	272

^aAll new compounds are anhydrous except compound 5, which is a monohydrate. ^bThermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). ^cOxygen balance for C_aH_bO_cN_d, 1600(*c* − *a* − *b*/2)/*M_w*; *M_w* = molecular weight. ^dGas pycnometer (25 °C), values in parentheses, were corrected by subtracting the volume of a water molecule [*V*(H₂O) = 25 Å³]. ^eCalculated lattice energy of salt. ^fCalculated heat of formation. ^gDetonation velocity. ^hDetonation pressure. ⁱImpact sensitivity. ^jFriction sensitivity. ^kSpecific impulse.

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1} \text{K}^{-1} \times T \quad (1)$$

For energetic salts, the solid-phase heat of formation can be simplified by eq 2 on the basis of Born–Haber energy cycles (Scheme 2).

$$\begin{aligned} \Delta H_f^\circ(\text{salt}, 298 \text{ K}) \\ = \Delta H_f^\circ(\text{cation}, 298 \text{ K}) + \Delta H_f^\circ(\text{anion}, 298 \text{ K}) - \Delta H_L \end{aligned} \quad (2)$$

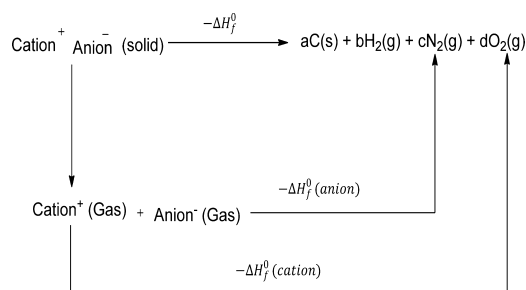
in which Δ*H_L* could be predicted by using the formula suggested by Jenkins et al. (eq 3):⁵⁰

$$\Delta H_L = U_{\text{pot}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (3)$$

In this equation, *n_M* and *n_X* depend on the nature of the ions Mp⁺ and Xq[−], 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

$$U_{\text{pot}} [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (4)$$

Scheme 2. Born–Haber Cycle for the Formation of 3,3'-Dinitroamino-4,4'-azoxyfurazan-Based Energetic Salts



in which ρ_m (g cm^{−3}) is the density, *M_m* is the chemical formula mass of the ionic material, and values for *g* and the coefficients γ (kJ mol^{−1} cm) and δ (kJ mol^{−1}) are taken from the literature.⁵⁰

Usually, oxygen-rich energetic materials such as nitro carbons have negative enthalpies of formation.⁵¹ However, in Table 1 it is shown that all of the compounds synthesized in this work are highly endothermic due to the large number of N–N bonds and two furazan backbones. Because it has the largest lattice energy, the ammonium salt 5 has the lowest calculated heat of

formation (537.1 kJ mol⁻¹, 1.59 kJ g⁻¹). The most positive value is for the triaminoguanidinium salt **11** (1269.5 kJ mol⁻¹, 2.47 kJ g⁻¹), which has the largest number of N–N single bonds, followed by the triaminotriazolium salt **9** (1265.9 kJ mol⁻¹, 2.39 kJ g⁻¹), for which the number of N–N bonds is also remarkably high. The neutral compound (**4**) shows the second highest value at 2.42 kJ g⁻¹.

Detonation Parameters. The experimentally determined densities of **4–11** range between 1.74 and 1.96 g cm⁻³, which are comparable with currently used explosives (1.6–1.8 g cm⁻³). It is noteworthy that the density of compounds **4–7** and **10** fall in the range designated for new HEDMs (1.8–2.0 g cm⁻³). Moreover, the outstanding high densities of **4** (1.96 g cm⁻³) and **6** (1.90 g cm⁻³), as a consequence of the *N*-oxide being involved in multiple intermolecular hydrogen-bonding interactions, are even comparable with those of CL-20 (1.94–2.04 g cm⁻³) and HMX (1.91 g cm⁻³). Remarkably, the crystal density of **4** (2.02 g cm⁻³) calculated at 173 K is the highest value recorded to date for the crystal density of *N*-oxide energetic compounds. It also ranks at the top of the density series (>2.00 g cm⁻³) with CHNO explosives such as CL-20, octanitrocubane, heptanitrocubane, and 5,5'-bis(trinitromethyl)-3,3'-bi(1,2,4-oxadiazole).⁵²

Using calculated values of the heats of formation and experimental densities, the detonation pressures (*P*) and velocities (*v*_D) were calculated using EXPLO5 v6.01. As can be seen in Table 1, the calculated detonation velocities lie between *v*_D = 8585 and 9746 m s⁻¹. The highest values in terms of detonation performance were observed for compounds **4** (9746 m s⁻¹), **5** (9474 m s⁻¹), **6** (9511 m s⁻¹), and also **7** (9459 m s⁻¹) and **10** (9453 m s⁻¹), all of which outperform HMX and CL-20. In comparison with other nitroamino ionic derivatives, a marked performance increase is seen and supports the advantage of introduction of the azoxy *N*-oxide group and the furazan backbone. In terms of detonation pressures, compounds **4** (44.1 GPa), **5** (39.6 GPa), and **6** (42.2 GPa) show remarkable results which are significantly greater than that of HMX (39.5 GPa). Compounds **5–7** also exhibit very promising specific impulse values (*I*_{sp} > 270 s). Oxygen balance is the index of the deficiency or excess of oxygen in a compound required to convert carbon to carbon monoxide and all hydrogen into water. Of the compounds, **4** and **6** have positive oxygen balances of 10.6% and 4.3%, respectively, and thus are superior to RDX and HMX.

The presence of the N–O building block tends to decrease the heat of formation, but it markedly contributes to the heat of detonation.⁵³ In this study, ΔH_{det} values for the new compounds and common explosives were calculated using EXPLO5 v6.01 and compared with references.^{54,55} The computed ΔH_{det} for **4–11** are 6.82, 6.07, 6.61, 6.44, 5.10, 5.48, 5.73, and 5.86 kJ/g, respectively. Plotted in Figure 6 are heats of detonation values of compounds **4–7** versus eight highly explosive materials. Two important results are seen: (1) **4** possesses comparable ΔH_{det} with octanitrocubane (ONC) and values higher than other organic explosives and (2) **6** appears to possess the highest ΔH_{det} (6.61 kJ/g) among reported ionic CHNO explosives; for comparison, the heats of explosion for ammonium dinitramide (ADN) and ammonium perchlorate (AP) are 2.67 and 1.97 kJ/g, respectively.

Sensitivities. For initial safety testing, the sensitivities of compounds **4–11** toward impact and friction were measured. The impact sensitivity (IS) was determined by using a BAM fall hammer apparatus with 10 kg drop weight on ~15 mg samples.

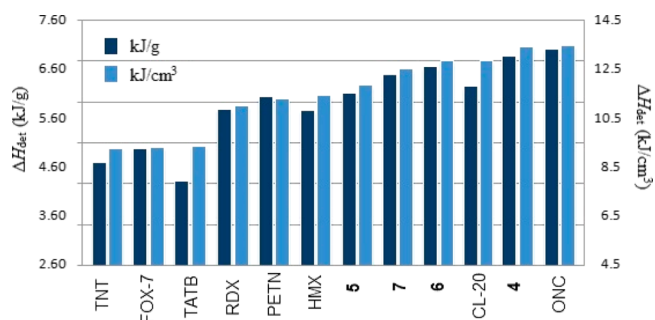


Figure 6. Bar diagram representation of the literature ΔH_{det} values for eight well-known highly explosive materials (FOX-7, 1,1-diamino-2,2-dinitroethene; TATB, triaminotrinotrobenzene; PETN, pentaerythritol tetranitrate) along with the computed ΔH_{det} for **4–7**.

Of all these new compounds, it is not surprising that neutral compound **4** is the most impact and friction sensitive explosive (IS = 2 J, FS = 10 N). Salts **5–11** are much less impact sensitive (14–35 J) than **4**, RDX, and HMX, which suggests that the guanidinium (**8**) and 3,4,5-triaminotriazolium (**9**) salts can serve as promising candidates for safe energetic materials. The friction sensitivities of **5**, **6**, and **8–11** are all higher than 120 N, which makes them less sensitive than RDX and HMX as well. In the BAM friction test, the ammonium and guanidinium salts could not be set off even with a force of 360 N, and therefore, they are classed as friction insensitive energetic materials.

Computational Structural Considerations. To gain a better understanding of structures for target compounds, natural bond orbitals (NBO) as well as electrostatic potential (ESP) calculations were based upon the B3LYP/6-311+g(2d,p) method with optimized anion structures. First, when the NBO are considered, nitroamine as well as azoxy linkages are found to form alternating positively and negatively charged chains, and in this case (as shown in Figure 7), three five-atom chains

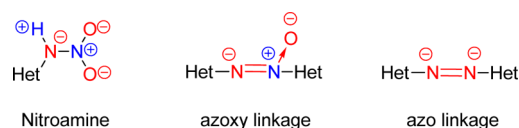


Figure 7. NBO charges on nitroamine, azoxy linkage, azo linkage, and the possible APNC systems.

with alternating charges are seen across the whole anion of **4** (computational details can be found in Figure S5 and Table S16, Supporting Information). As reported in the literature, this unique “alternating positive and negative charges” (APNC) system can be considered as the stable sign in which σ and π separation can be achieved by functionalization.^{56–59} This is also best exemplified by the stability differences between the unsaturated 1,2,3,4-tetrazine ring and 1,2,3,4-tetrazine 1-oxides.²⁴ In comparison with the 3,3'-dinitroamino-4,4'-azoxyfurazan anion, the NBO charge of the 4,4'-bis-(nitroamino)azofurazan anion was calculated using the same method as well (computational details can be found in Figure S5 and Table S17, Supporting Information). Unlike the former anion, the chain of the APNC system cannot be found on the azo linkage, since the negative charge is located on two nitrogen atoms and blocks the charge transport between furazan rings.

The ESP of **4** was computed at the B3LYP/6-311+g(2d,p) level of theory. In Figure 7 the ESP for the 0.001 electron/b³ isosurface of electron density is evaluated at the B3LYP level of

theory. It has recently been found, and is extensively used, that the computed ESP is generally related to the impact sensitivity of the bulk energetic material.^{60–62} According to this literature, the stability can be expressed as a function of the imbalance between positive and negative regions.⁶³ In most N–O systems, such as nitro (–NO₂) and nitrate (–O–NO₂), the regions of stronger positive potential are concentrated on the nitrogen atom and lead to the atypical imbalance, which causes the high impact sensitivity in theory. However, as can be seen in Figure 8, since **4** is assembled by diverse N–O building

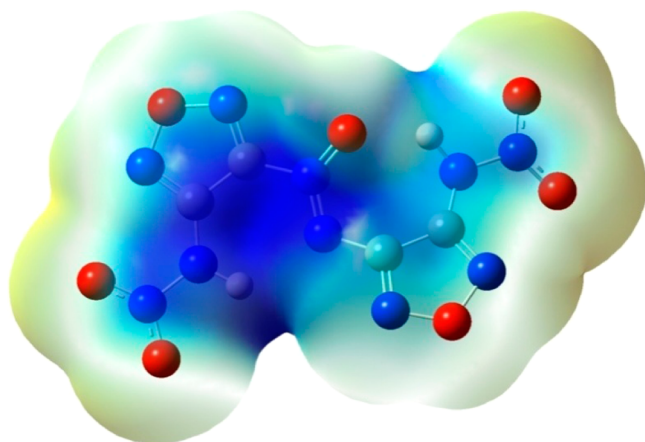


Figure 8. Electrostatic potential of compound **4** [B3LYP/6-311+g-(2d,p), 0.001 electron/b³ isosurface, energy values –0.06 to +0.06 H]. Color coding: yellow, slightly negative; green, neutral; turquoise, slightly positive; light blue, positive; dark blue, very positive.

blocks, the positive potential is dispersed over most of the area of the molecule. It also gives the theoretical explanation for the stability of such a highly energetic compound and verifies the validity of the design strategy.

CONCLUSIONS

In this work, we report the syntheses and full characterization of 3,3'-dinitroamino-4,4'-azoxyfurazan and its nitrogen-rich salts. It is found that Oxone is an efficient oxidizing agent for the introduction of azoxy *N*-oxide into the furazan backbone, which makes the synthetic route straightforward and inexpensive. On the basis of the design strategy that results in the assembly of diverse N–O building blocks leading to energetic materials, **4** is composed of three different N–O moieties, and salt **6** has four kinds. Both the neutral compound and its salts are highly energetic nitrogen- and oxygen-rich molecules, as shown by the values of their energetic properties (detonation velocity and pressure) that were calculated using the EXPLO5 6.01 program. In addition, most of these compounds show higher density (**4**–**7** and **10** in the range of 1.84–1.96 g cm³) than RDX and are comparable with HMX. In particular, **4** has the highest crystal density of 2.02 g cm^{–3} at 173 K (gas pycnometer measured density is 1.96 g cm^{–3} at 298 K) for *N*-oxide energetic compounds ever reported. All compounds were also characterized with respect to impact sensitivity, friction sensitivity, and thermal stability. Unlike their precursor, **4**, with a low decomposition temperature at 90 °C, the resulting salts are thermally stable over the range 148–246 °C. The most promising compound for industrial scale-up and practical use is the hydroxylammonium salt **6**, which has high density (1.90 g cm^{–3}), acceptable sensitivities (19 J, 120 N),

good detonation pressure (42.2 GPa), and velocity (9511 m s^{–1}). The combination of exceedingly high performance properties, which are superior to those of HMX, and its straightforward preparation highlights this compound as a new HEDM and a potential HMX replacement. Furthermore, computational results in terms of NBO charges and ESP also support the superiority of the target compounds and design strategy as well.

EXPERIMENTAL SECTION

Safety Precautions. While we have experienced no difficulties in the syntheses and characterization of these materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Face shield and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials. Mechanical actions involving scratching or scraping must be avoided, especially for **4**. All of the energetic compounds must be synthesized only in small amounts.

General Methods. Analytical grade reagents were purchased from Aldrich and Acros Organics in analytical grade and were used as received. ¹H and ¹³C spectra were recorded using a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. A 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz was used to obtain ¹⁵N spectra. DMSO-*d*₆ was employed as solvent and locking solvent unless otherwise stated. Chemical shifts in the ¹H and ¹³C spectra are reported relative to Me₄Si and ¹⁵N NMR to MeNO₂. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C min^{–1}. IR spectra were recorded using KBr pellets for solids on a Bio-Rad model 3000 FTS spectrometer. Densities were measured at room temperature using a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried out on an Exeter CE-440 elemental analyzer.

X-ray Crystallography. A colorless prism of dimensions 0.47 × 0.30 × 0.27 mm³ for **4** and a yellow prism of dimensions 0.29 × 0.29 × 0.04 mm³ for **6**·H₂O were used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Apex 2 CCD system equipped with a graphite monochromator and a Mo *K*_α fine focus tube (0.71073 Å). An Oxford Cobra low-temperature device was used to maintain the crystals **4** at a constant 173 K during data collection. The data for **6**·H₂O were collected at 298 K. The frames were integrated with the Bruker SAINT software package⁶⁴ using a narrow-frame algorithm and data were corrected for absorption effects using the multiscan method (SADABS⁶⁵). The structures were solved and refined using the Bruker SHELXTL software package.

Diaminofurazan (2).⁶⁶ A mixture of 40% glyoxal (11.5 mL, 100 mmol), hydroxylamine hydrochloride (45 g, 600 mmol), and urea (35 g, 580 mmol) in 50 mL of water was added to sodium hydroxide solution (28 g of NaOH in 60 mL) dropwise. After the addition, the mixture was refluxed for 2 h and then 35 mL of water was distilled under reduced pressure. The reaction mixture continued to reflux for another 12 h and then cooled to 5 °C. The precipitate was filtered and crystallized using 50 mL of water to give a pure product as a white solid (4.5 g, 45%). ¹H NMR: δ 5.8 (4H, NH₂) ppm. ¹³C NMR: δ 148.7 ppm. Anal. Calcd (%) for C₂H₄N₄O: C, 24.00; H, 4.03; N, 55.98. Found: C, 23.64; H, 4.00; N, 55.09.

3,3'-Diamino-4,4'-azoxyfurazan (3). Compound **3** was prepared according to the literature method.^{37,38} ¹H NMR: δ 6.7 (2H, NH₂), 6.9 (2H, NH₂) ppm. ¹³C NMR: δ 153.5, 152.1, 150.7, 147.8 ppm. Anal. Calcd (%) for C₄H₄N₈O₃: C, 22.65; H, 1.90; N, 52.82. Found: C, 22.41; H, 1.89; N, 51.99.

3,3'-Dinitroamino-4,4'-azoxyfurazan (4). To 100% nitric acid (6 mL) was added **3** (1.1g, 5.2 mmol) in small portions at –5 °C. The mixture was held at –0 °C for 2 h. The reaction mixture was poured onto ice, and the precipitate was filtered, washed with cold water, and air-dried to yield **4** (1.3 g, 86%) as an ivory solid. *T*_{dec (onset)}: 90 °C. IR (KBr): 3279, 3173, 1620, 1562, 1499, 1389, 1315, 1230, 1007, 950,

838, 751, 710 cm^{-1} . ^1H NMR: δ 13.6 (s, 2H, N–NO₂) ppm. ^{13}C NMR: δ 155.2, 153.1, 150.8, 148.3 ppm. Anal. Calcd (%) for C₄H₂N₁₀O₇: C, 15.90; H, 0.67; N, 46.36. Found: C, 15.63; H, 0.69; N, 45.47.

Diammonium 3,3'-Dinitroamino-4,4'-azoxyfurazanate Hydrate (5). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while a slight excess of aqueous ammonia (28 wt %) was added. After 1 h the precipitate was filtered and air-dried to yield **5** (0.61 g, 91%) as a yellow solid. $T_{\text{dec (onset)}}$: 148 °C. IR (KBr): 3478, 3323, 3201, 3069, 1562, 1531, 1479, 1409, 1379, 1288, 1045, 943, 816, 778, 743, 714, 561 cm^{-1} . ^1H NMR: δ 7.1 (s, 8H, NH₄⁺) ppm. ^{13}C NMR: δ 155.2, 154.9, 153.8, 151.2 ppm. ^{15}N NMR: δ 25.9 (N3, furazan), 21.4 (N8, furazan), 12.9 (N4, furazan), 6.6 (N7, furazan), -12.5 (N10, -NO₂), -13.1 (N1, -NO₂), -64.0 (N6, -N=N(O)-), -65.0 (N5, -N=N(O)-), -149.4 (N2), -156.5 (N9), -358.4 (NH₄⁺) ppm. Anal. Calcd (%) for C₄H₈N₁₂O₇: C, 13.56; H, 2.85; N, 47.45. Found: C, 13.49; H, 2.78; N, 47.10.

Dihydroxylammonium 3,3'-Dinitroamino-4,4'-azoxyfurazanate (6). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while hydroxylamine (50 wt % in water, 0.21 mL, 4.2 mmol) was added. After 1 h the precipitate was filtered and air-dried to yield **6** (0.65 g, 88%) as a pale yellow solid. $T_{\text{dec (onset)}}$: 177 °C. IR (KBr): 3496, 3163, 2941, 2728, 1530, 1478, 1409, 1309, 1164, 1047, 1012, 949, 833, 772, 714, 557 cm^{-1} . ^1H NMR: δ 9.6 (s, 6H, NH₃⁺) ppm. ^{13}C NMR: δ 155.3, 154.9, 153.9, 151.3 ppm. ^{15}N NMR: δ 25.6 (N3, furazan), 21.2 (N8, furazan), 12.7 (N4, furazan), 6.6 (N7, furazan), -12.4 (N10, -NO₂), -13.0 (N1, -NO₂), -64.2 (N6, -N=N(O)-), -65.0 (N5, -N=N(O)-), -149.6 (N2), -156.6 (N9), -331.5 (NH₃OH⁺) ppm. Anal. Calcd (%) for C₄H₆N₁₂O₉: C, 13.05; H, 2.19; N, 45.65. Found: C, 12.64; H, 2.29; N, 45.02.

Dihydrazinium 3,3'-Dinitroamino-4,4'-azoxyfurazanate (7). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while hydrazine (50 wt % in water, 0.21 mL, 4.2 mmol) was added. After 1 h the precipitate was filtered and air-dried to yield **7** (0.62 g, 85%) as a yellow solid. $T_{\text{dec (onset)}}$: 192 °C. IR (KBr): 3338, 3193, 2923, 1555, 1532, 1472, 1388, 1314, 1086, 1043, 969, 818, 775, 716, 561 cm^{-1} . ^1H NMR: δ 7.2 (br, s, 10H, NH₂NH₃⁺) ppm. ^{13}C NMR: δ 155.2, 154.9, 153.8, 151.1 ppm. ^{15}N NMR: δ 25.8 (N3, furazan), 21.5 (N8, furazan), 12.7 (N4, furazan), 6.7 (N7, furazan), -12.5 (N10, -NO₂), -13.3 (N1, -NO₂), -64.8 (N6, -N=N(O)-), -65.0 (N5, -N=N(O)-), -149.5 (N2), -156.7 (N9), -296.7 (NH₂NH₃⁺) ppm. Anal. Calcd (%) for C₄H₁₀N₁₄O₇: C, 13.12; H, 2.75; N, 53.55. Found: C, 13.03; H, 2.74; N, 53.47.

Diguanidinium 3,3'-Dinitroamino-4,4'-azoxyfurazanate (8). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while dilute sodium hydroxide solution (10 mL, 0.4 N) was added. Then guanidine nitrate (0.49 g, 4 mmol) was added to the mixture and heated to 50 °C for 30 min. After cooling to room temperature, the precipitate was collected by filtration to give **8** (0.7 g, 84%) as bright yellow solid. $T_{\text{dec (onset)}}$: 246 °C. IR (KBr): 3412, 3354, 3264, 3207, 1669, 1563, 1523, 1475, 1410, 1383, 1305, 1047, 947, 814, 776, 712, 563 cm^{-1} . ^1H NMR: δ 6.8 (br, s, 12H, NH₂) ppm. ^{13}C NMR: δ 157.9, 155.1, 154.9, 153.9, 151.2 ppm. ^{15}N NMR: δ 25.7 (N3, furazan), 21.8 (N8, furazan), 12.7 (N4, furazan), 7.1 (N7, furazan), -12.5 (N10, -NO₂), -13.1 (N1, -NO₂), -63.3 (N6, -N=N(O)-), -64.8 (N5, -N=N(O)-), -148.6 (N2), -156.3 (N9), -305.2 (NH₂⁺) ppm. Anal. Calcd (%) for C₆H₁₂N₁₆O₇: C, 17.15; H, 2.88; N, 53.33. Found: C, 16.99; H, 2.80; N, 53.10.

Di(3,4,5-triamino-triazolium) 3,3'-Dinitroamino-4,4'-azoxyfurazanate (9). 3,4,5-Triamino-triazole (0.46 g, 4 mmol) was added to a solution of **4** (0.6 g, 2 mmol) in ethanol (15 mL). The mixture was heated at 50 °C for 1 h. After cooling to room temperature, the precipitate was collected by filtration to give **9** (0.79g, 76%) as a yellow solid. $T_{\text{dec (onset)}}$: 222 °C. IR (KBr): 3384, 3269, 1669, 1663, 1564, 1528, 1487, 1420, 1389, 1276, 1019, 906, 807, 772, 708 cm^{-1} . ^1H NMR: δ 6.9 (s, 8H, NH₂), 5.5 (s, 4H, NH₂) ppm. ^{13}C NMR: δ 155.2,

155.0, 153.9, 151.3, 150.4 ppm. Anal. Calcd (%) for C₈H₁₄N₂₂O₇: C, 18.12; H, 2.66; N, 58.10. Found: C, 18.11; H, 2.72; N, 58.17.

Di(diaminoguanidinium) 3,3'-Dinitroamino-4,4'-azoxyfurazanate (10). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while dilute sodium hydroxide solution (10 mL, 0.4 N) was added. Then diaminoguanidine monohydrochloride (0.50 g, 4 mmol) was added to the mixture and heated to 50 °C for 30 min. After cooling to room temperature, the precipitate was collected by filtration to give **10** (0.72g, 75%) as a yellow solid. $T_{\text{dec (onset)}}$: 187 °C. IR (KBr): 3413, 3356, 3276, 3138, 1682, 1561, 1525, 1481, 1416, 1389, 1300, 1172, 993, 941, 805, 773, 517 cm^{-1} . ^1H NMR: δ 8.6 (br, s, 4H, NH₂⁺), 7.1 (s, 4H, NH), 4.6 (br, s, 8H, NH₂) ppm. ^{13}C NMR: δ 159.8, 155.1, 155.0, 153.8, 151.2 ppm. ^{15}N NMR: δ 25.3 (N3, furazan), 21.0 (N8, furazan), 12.2 (N4, furazan), 6.5 (N7, furazan), -12.3 (N10, -NO₂), -12.7 (N1, -NO₂), -63.3 (N6, -N=N(O)-), -64.9 (N5, -N=N(O)-), -148.8 (N2), -156.3 (N9), -286.2 (NH), -288.2 (NH), -309.8 (NH₂), -311.6 (NH₂), -313.5 (NH₂⁺), -327.3 (NH₂⁺) ppm. Anal. Calcd (%) for C₆H₁₆N₂₀O₇: C, 15.00; H, 3.36; N, 58.32. Found: C, 14.80; H, 3.23; N, 57.63.

Di(triaminoguanidinium) 3,3'-Dinitroamino-4,4'-azoxyfurazanate (11). A solution of **4** (0.6 g, 2 mmol) in a minimum amount of ethanol was stirred at room temperature while dilute sodium hydroxide solution (10 mL, 0.4 N) was added. Then triaminoguanidine monohydrochloride (0.56 g, 4 mmol) was added to the mixture and heated to 50 °C for 30 min. After cooling to room temperature, the precipitate was collected by filtration to give **11** (0.83g, 82%) as a yellow solid. $T_{\text{dec (onset)}}$: 168 °C. IR (KBr): 3546, 3346, 1688, 1524, 1476, 1416, 1387, 1337, 1302, 1132, 1005, 944, 810, 775, 712, 535 cm^{-1} . ^1H NMR: δ 8.6 (s, 6H, NH), 4.5 (s, 12H, NH₂) ppm. ^{13}C NMR: δ 159.7, 155.5, 155.3, 154.1, 151.7 ppm. Anal. Calcd (%) for C₆H₁₈N₂₂O₇: C, 14.12; H, 3.55; N, 60.38. Found: C, 13.76; H, 3.47; N, 58.85.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files in CIF format for **4** and **6**·H₂O; structure refinements; selected bond lengths, angles, dihedral angles; hydrogen-bonding details; and the methodology and details for the heats of formation and NBO calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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