5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole and its derivatives: from green primary to secondary explosives

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5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole (**4**) and its ammonium (**4a**), hydroxylammonium (**4b**), and hydrazinium (**4c**) salts were synthesized. Each compound was characterized by X-ray single crystal structure diffraction, infrared (IR), and ^1H and ^{13}C NMR spectroscopy, elemental analyses, thermal stability, and sensitivity to external stimulants. Crystal structures and packing coefficients were analyzed and compared with respect to π-π stacking and hydrogen bonding. Due to the presence of lattice water in compound **4**, the impact sensitivity (IS = 15 J) and friction sensitivity (FS = 120 N) are notably lower than those of the anhydrous material (IS = 3 J, FS = 20 N), which could act as a primary explosive. In this way, the primary explosive could be synthesized, transported, and stored more safely than traditional primary explosives. The detonation properties determined by EXPLO 6.02 software show that among the four compounds, **4b** has superior detonation velocity (Vd = 9201 m s^{-1}) and pressure (P = 36.0 GPa) values which are comparable to those of HMX (octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine). The impact sensitivity (10J) is less-sensitive than HMX (7.5J), which suggests compound **4b** as a potential alternative to HMX.

Introduction

Since dynamite was invented by Alfred Nobel, explosives (both primary and secondary) have played important roles in civilian industry and the military.[1] Primary explosives show a very rapid transition from deflagration to detonation and generate a shockwave that transfers the detonation to a less-sensitive secondary explosive.[2] Although $Pb(N_3)_2$, lead styphnate, and dynamite are classic primary explosives that are currently still used, the long-term use of these compounds has caused considerable heavy metal contamination of the environment. As environmental protection demands have increased, several kinds of green primary explosives have been reported which are potential alternatives to the classic primary explosives.[3] However, since these new primary explosives have extreme intrinsic sensitivities, they are very dangerous to handle during synthesis, transportation, storage, and application. A major challenge of primary explosives is to find a way to resolve this shortcoming.

The past two decades have seen the development of heterocyclic compounds as energetic materials because of their high heats of formation and nitrogen content.[4] Some of them have demonstrated tremendous potential for future applications, especially bis-heterocyclic compounds which combine two heterocyclic rings through C-C, C-N, and N-N bonds. Such compounds have increased the number of available heterocyclic energetic compounds with novel energetic character and new structure-property relationships, and they have attracted considerable attention.[5] Compounds with a C-C bridge are the most intensely studied of the bis-heterocyclic compounds because they are the most stable.[6] Tetrazole and furazan rings are two potential structures of these energetic compounds. Tetrazole rings have much higher nitrogen content and heats of formation relative to other azole rings,[7] and furazan rings have the highest heats of formation among the four kinds of oxadiazole rings (Scheme **1**) [3b,3c,8] In addition, furazan derivatives have higher densities and better oxygen balance than 1,2,4-triazole derivatives.[8c,9] While some tetrazole and furazan ring compounds bonded through C-C links have been reported,[10] there is still an insufficient amount of research about the structure-property relationships of this group of energetic compounds.

Now the synthesis and energetic characterization of 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole (**4**) and its derivatives (ammonium **4a**, hydroxylammonium **4b**, and hydrazinium 4c) have been carried out. Compound **4** is a bis-heterocyclic compound that is composed of tetrazole and furazan rings have been realized (Scheme **2**), N-O and N_3 groups were also introduced into the backbone, to enhance its nitrogen content, heat of formation, density, as well as oxygen balance. Compound **4** behaves as a new kind of green primary explosive

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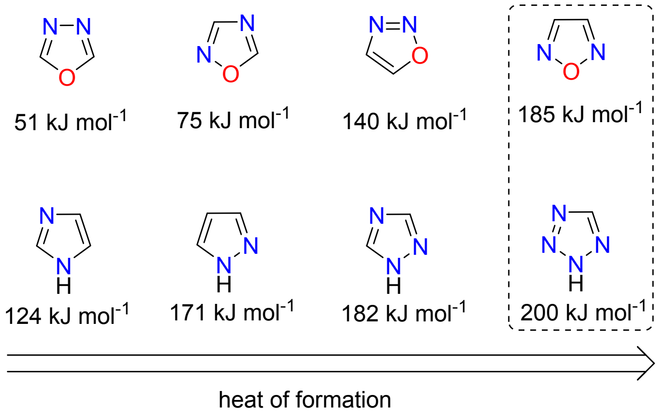


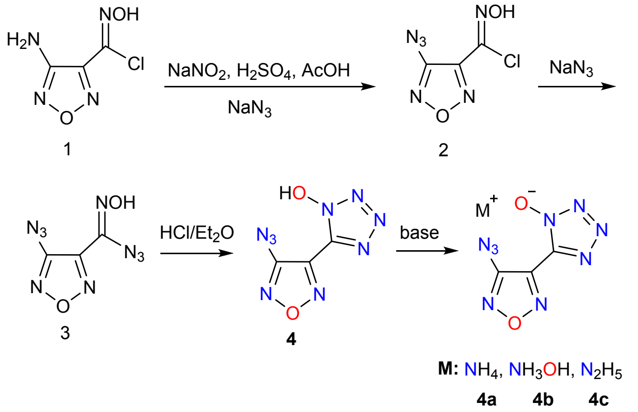
Scheme 1. Gas-phase heats of formation for various oxadiazoles and azoles.

with a controllable sensitivity since the presence of lattice water in the neutral compound can markedly increase its safety during synthesis, transportation and storage. Compounds **4a-4c** show excellent performance as secondary explosives.

Results and discussion

Synthesis and Single Crystal X-ray Structures.

4-Amino-1,2,5-oxadiazole-3-carbohydroximoyl chloride (**1**) was used as starting material. In a previous report,[11] **1** was diazotized in sulfuric and acetic acids to form the corresponding diazonium salt, which was then treated with a solution of NaN_3 to yield the azidofurazan (**2**). The halogen atom in oxadiazole 2 was easily replaced by an azido group by reacting **2** with NaN_3. The resulting carbohydroximoyl azide, **3**, readily underwent isomerization to **4** (5-(4-azidofurazan-3-yl)-1-hydroxytetrazole) upon treatment with gaseous hydrogen chloride in ether (Figure **1**). Compound **4** was reacted with aqueous ammonia (25%), hydroxylamine (50%) or hydrazine hydrate (80%) in ethanol for 30 minutes, to obtain **4a**, **4b** or **4c**, respectively. The precipitate was collected by filtration and washed with a small amount of ethanol. The solid residue was recrystallized from a mixture of methanol and water, and then dried in vacuo to obtain the product. Although the structures and partial properties of **4** and **4a** were mentioned previously,[10f] their detailed statement and detonation properties of these four crystals haven't been reported, particularly the comparison in crystal packing among these four structures haven't been studied.



Scheme 2. Synthetic route to the target compounds

Compounds **4** and **4a-4c** were characterized by X-ray single crystal diffraction. A colorless plate crystal **4** crystallizes from water in the monoclinic space group P21/n. Each unit cell contains four 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole molecules and four water molecules (Z = 4). The calculated crystal density of **4** is 1.758 g cm^{-3} at 150 K, and its density is 1.751 g cm^{-3} at room temperature, as determined with gas pycnometer. Three molecules were associated with water by forming three hydrogen bonds (H1···O1S: 1.719 Å; H2S···N5: 2.100 Å; H1S···N8: 2.35 Å (Figures **1a**, and **1b** and Table S2 - Supporting Information). In this way, the molecules were connected through hydrogen bonds to form a 2D net structure (Figure S1 – Supporting Information).

Compound **4a** was recrystallized from a mixture of water and ethanol (volume ratio: 1:1), in an orthorhombic space group ($P2_12_12_1$), with four ammonium cations and four anions in each unit cell (Z = 4). Its density is 1.746 g cm^{-3} at 150K. The ammonium cation was surrounded by four anions to form four hydrogen bonds (H1S···O1, H2S···O1, H4S···O1, and H3S···N4) whose respective lengths are 2.035, 1.909, 2.123, and 2.170 Å (Figures **1c**, and **1d** and Table S3 – Supporting Information). The crystal structure was connected by four hydrogen bonds to form a 3D network structure (Figure S2 – Supporting Information).

Compound **4b** was recrystallized from water and methanol as colorless needle crystals in a monoclinic space group $P2_1/c$. Its unit cell has four cations and four anions (Z = 4), and its calculated crystal density is 1.80 g cm^{-3} at 150K. Similar to the structure of the ammonium salt, the hydroxylammonium cation is surrounded by three anions, and hydrogen bonds are formed between H1S and O1, H2S and N5, and H4S and N4 with lengths of 1.912, 2.069, and 1.793 Å, respectively (Figures **2a**, and **2b** and Table S4 – Supporting Information). The hydroxylammonium cations and the anions were connected by three hydrogen bonds to form a 3D-net structure within the crystal (Figure S3 – Supporting Information).

Compound **4c** was recrystallized from water and methanol as a colorless plate crystal in a monoclinic space group $P2_1/c$ with four hydrazinium cations and four anions in each unit cell with a calculated crystal density of 1.66 g cm^{-3} at 150K. In contrast to the hydroxylammonium salt, the hydrogen bonds in **4c** were formed between two hydrazinium cations. Three hydrazinium

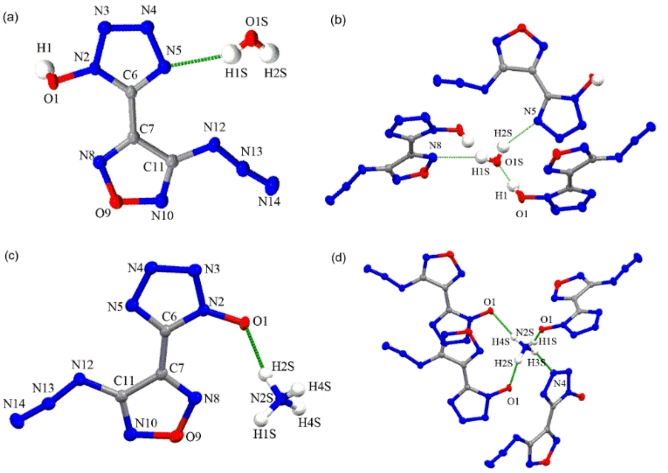


Fig 1. Single crystal structures and hydrogen bonds of 4 and 4a

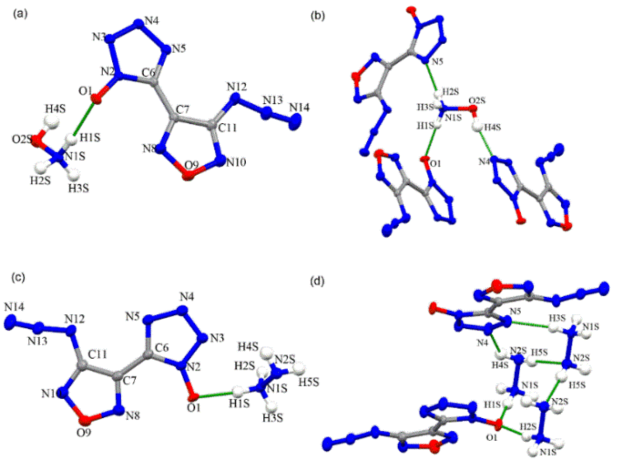


Fig 2. Single crystal structures and hydrogen bonds of 4b and 4c

cations were surrounded by six anions to form five hydrogen bonds: H1S···O1 (1.874 Å), H2S···O1 (1.857 Å), H3S···N5 (2.025 Å), H4S···N4 (2.461 Å), and H5S···N2S (2.102 Å) (Figures **2c**, and **2d** and Table S2 – Supporting Information). The cations and anions were connected by these five hydrogen bonds to form a 2D network structure along the b-axis (Figure S4 – Supporting Information).

Packing coefficient plays an important role in the density of an energetic compound with higher packing coefficients generally resulting in higher density.[12] The packing coefficients for **4** and **4a-4c** are 72.67%, 73.45%, 74.76%, and 70.20%, respectively, with a relatively large difference in the packing coefficients of **4b** and **4c**. The neutral molecule **4** and its salts **4a-4c** are nearly planar (the torsion angles N2–C6–C7–N8 in **4**, **4a-4c** are -8.99°, 3.11°, 3.19°, and -6.25°, respectively, Tables S10 and S11 – Supporting Information), and π-π stacking is observable in all four compounds. Hence, the interlayer distance and the average hydrogen bond lengths are two main factors influencing the packing coefficients. The interlayer distances of **4** and **4a-4c** are 3.038 Å, 3.062 Å, 3.054 Å, and 3.308 Å, respectively (Figure **3**), which indicates that **4c** with the greatest distance has the least compact stacking. The average hydrogen bond lengths of these compounds are 2.056 Å, 2.059 Å, 1.925 Å, and 2.054 Å, respectively. Compound **4b** has the shortest average hydrogen bond lengths and a moderate interlayer distance, which explains the highest packing coefficient and the highest density among these four crystals.

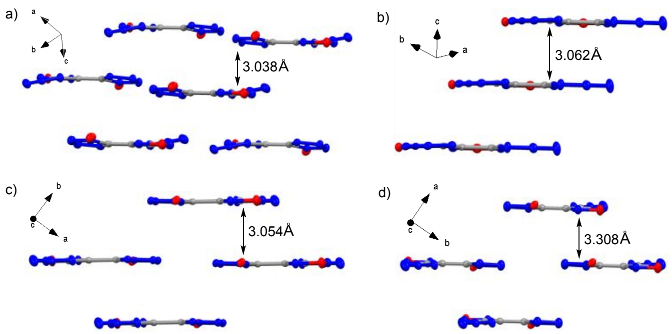


Fig 3. The interlayer distances of a) 4, b) 4a, c) 4b, d) 4c.

Thermal stability and Sensitivity

Thermal stability is an important property of energetic materials. When the decomposition temperature of an energetic compound is higher, the material can be more safely processed during transportation, use, and storage. The four compounds were measured by using differential scanning calorimetry (DSC, 5 °C min^{-1}) which showed that they had decomposition temperatures (onset) higher than 150 °C. From **4** to **4c**, they are 154 °C, 207.7 °C, 171.4 °C, and 186.4 °C (Table **1**), respectively. Compound **4a** has a decomposition temperature of 207.7 °C which is similar to that of RDX.

The sensitivity of a compound determines how likely it is to explode when stimulated by external mechanical forces, such as impact and friction which requires that extra safety precautions be taken during synthesis, use, and storage. The impact and friction sensitivities of each compound was determined according to the UN standard recommendations.[13] For **4**•H_2O, the impact and friction sensitivities are 15 J and 120 N, respectively, which are relatively low. However, when the lattice water in the crystal is removed, the impact and friction sensitivities values increase to 3 J and 20 N, respectively. Since the nitrogen content of **4** is 64.6%, and the content of nitrogen and oxygen is 81.0%, **4** can act as an green primary explosive as an alternate to replace PbN_3. Additionally, the lattice water present in **4** would increase the safety of handling the compound during the synthesis and storage compared to other primary explosives. Compounds **4a-4c** can be used as secondary explosives since their impact sensitivities are 15 J, 10 J, and 7 J, and their friction sensitivities are 120 N, 120 N, and 80 N, respectively. Compounds **4a** and 4b are less sensitive than RDX and HMX, and the sensitivity of **4c** is comparable to those of RDX and HMX.

Table 1. Physical properties of compound **4** and **4a-4c**

Compd	**Td**^{a}(°C)	**ρ**^{b} (g cm^{-3})	**N%**^{c}	**N+O%**^{d}	**HOF** (KJ mol^{-1}/ kJ g-1)^e	**IS**^{f} (J)	**FS**^{g} (N)	**V**^{h} (m s^{-1})	**P**^{i} (Gpa)
4	154	1.751	64.6	81.0	820.9/4.21	3(15)	20(120)	8784	31.8
4a	207.7	1.712	66.0	81.1	779.9/3.71	15	120	8687	29.9
4b	171.4	1.789	61.4	82.5	877.9/3.85	10	120	9201	36.0
4c	186.4	1.638	68.7	82.8	938.2/4.13	7	80	8596	28.4
RDX	210	1.80	37.84	81.08	70.3/0.32	7.5	120	8787	35.3
HMX	280	1.90	37.84	81.08	105/0.36	7	120	9221	41.5
$Pb(N_3)_2$^{j}	315	4.8	28.9	28.9	450.1/1.55	2-4	0.1-1	5877	33.4

^{a} Temperature of decomposition (onset); ^{b} Density measured by using a gas pycnometer at 25 °C; ^{C} nitrogen content (%); ^{d} nitrogen and oxygen content (%); ^{e} Calculated molar enthalpy of formation in the solid state; ^{f} Impact sensitivity; ^{g} Friction sensitivity; ^{h} Calculated detonation velocity; ^{i} Calculated detonation pressure; ^{j} reference 17

Heats of formation and detonation properties

Based on the isodesmic equations (Scheme S1 and Table S12, see Supporting Information), calculations were performed using the Gaussian03 program suite.[14] The heats of formation of the four compounds are 4.21 kJ g^{-1}, 3.71 kJ g^{-1}, 3.85 kJ g^{-1}, and 4.13 kJ g^{-1}, respectively. These values are relatively high, since only a few energetic compounds have higher heats of formation.[12a,15] Using the heats of formation, detonation performances were calculated using EXPLO 6.01 software.[16] The calculated results show that although the densities of these four compounds do not exceed 1.80 g cm^{-3}, their high nitrogen content and heats of formation give rise to detonation velocities and pressures of **4** and **4a-4c** between 8596 and 9201 m s^{-1}, and 28.4 and 36.0 GPa, respectively. Compound **4b** has a detonation velocity of 9201 m s^{-1}, which is nearly equivalent to HMX, and **4b** has a detonation pressure of 36.0 GPa which slightly exceeds that of RDX. This indicates that **4b** has energetic properties superior to RDX and are equivalent to HMX. For **4**, the detonation velocity and pressure are 8784 m s^{-1} and 31.8 GPa, respectively, which exceed those of $Pb(N_3)_2$. Compound **4** behaves as a new green primary explosive, since it has more power than traditional metal-containing primary explosives, making it a promising alternative.

Conclusions

5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole (**4**) and its ammonium (**4a**), hydroxylammonium (**4b**), and hydrazinium derivatives (**4c**) were synthesized, and their energetic performances were thoroughly characterized. It is interesting to note that while **4** (IS = 3 J, FS = 20 N) is a primary explosive, it is less sensitive (IS = 15 J, FS = 120 N) during its synthesis, transportation, and storage, due to the presence of lattice water. When **4** is to be used as a primary explosive, the lattice water can simply be removed through drying. Since **4b** has the shortest average hydrogen bond length and a moderate interlayer distance, it has the highest packing coefficient (74.76%) of the four. All four compounds have high heats of formation, and excellent detonation properties, especially **4b**. Because of good density, the detonation velocity and pressure values of 9201 m s^{-1} and 36.0 GPa for **4b** are comparable to HMX. Since its impact sensitivity is 10 J which is less sensitive than that of HMX, **4b** could be useful as an alternative to HMX. In summary, these high-nitrogen-content compounds show potential for use as next-generation green primary and secondary explosives.

Experimental

Safety Precautions.

Although we experienced no difficulties in synthesis and characterization of these materials, proper protective procedures should be followed. All the experiments were carried out in a hood behind a safety shield and face shield, and leather gloves were worn at all times. Caution was exercised at all times during the synthesis, characterization, and handling of any of these materials.

Materials and Methods.

Commercial analytical grade reagents were used without further purification. ^{1}H and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me4Si. DFT and ab initio calculations were carried out using the Gaussian 03 program package.[14] The X-ray intensity data were measured on a Bruker Apex 2 CCD system equipped with a graphite monochromator and a Mo–Kα fine focus tube (λ = 0.71073 Å). An Oxford Cobra low-temperature device was used to maintain low temperatures. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 $^{\circ}$C min^{-1}. Densities were measured at room temperature using a Micromeritics AccuPyc 1330 gas pycnometer. The impact and friction-sensitivity measurements were conducted by employing a standard BAM Fallhammer and a BAM friction tester.

X-ray Crystallography.

A colorless plate crystal of dimensions 0.228 x 0.130 x 0.047 mm^3 for 4, a colorless needle crystal of dimensions 0.518 x 0.097 x 0.078 mm^3 for 4a, a colorless needle crystal of dimensions 0.687 x 0.135 x 0.128 mm^3 for 4b, and a colorless plate crystal of dimensions 0.178 x 0.070 x 0.052 mm^3 for 4c were used for the X-ray crystallographic analysis. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm and data were corrected for absorption effects using the multiscan method (SADABS).[18]The structures were solved and refined using the Bruker SHELXTL[19]Software Package.

Syntheses

5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole (4)

Based on the literature,[11] 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole (4) was obtained in 90% yield. It was recrystallized from the mixture of water and ethanol as a colorless plate crystal. ^{1}H NMR (DMSO-d6) δ 8.53 (s, 1H) ppm. ^{13}C NMR (DMSO-d6) δ 136.0, 137.0, 153.1 ppm. IR (KBr): ṽ 3406, 3240, 2148, 1661, 1537, 1439, 1416, 1377, 1182, 999, 878 cm^{-1}; elemental analysis, Calcd (%) for $C_3HN_9O_2{\cdot}H_2O$ (213.12): C: 16.91; H: 1.42; N: 59.15; Found, C: 16.91; H: 1.28; N: 58.41; Calcd (%) for anhydrous $C_3HN_9O_2$ (195.10): C: 18.47; H: 0.52; N: 64.61; Found, C: 18.42; H: 0.46; N: 63.76.

General procedure for the preparation of salts 4a-4c.

Compound 4 (0.213g, 1 mmol) was added to ethanol (20 mL) with stirring. The free base (1 mmol) of aqueous ammonia (25%), hydroxylamine (50%) or hydrazine hydrate (80%) was added to the ethanol solution. The reaction mixture was stirred at room temperature for 30 min followed by standing for 3 h. The precipitate was collected by filtration and washed with small amounts of ethanol (5 x 2 mL) to give the product after air drying.

Ammonium 5-(4-azidofurazan-3-yl)-1-hydroxytetrazolate (4a). white solid (0.197 g, 93%); ^{1}H NMR (DMSO-d6): δ 7.29 (s, 1H) ppm; ^{13}C NMR (DMSO-d6): δ 131.67, 138.95, 152.65 ppm; IR (KBr): ṽ 3175, 3067, 2841, 2150, 1546, 1443, 1383, 1229, 1180, 988, 874, 780 cm^{-1}; elemental analysis, Calcd (%) for $C_3H_4N_{10}O_2$ (212.13): C: 16.99; H: 1.90; N: 66.03; Found, C: 17.09; H: 1.93; N: 66.09.

Hydroxylammonium 5-(4-azidofurazan-3-yl)-1-hydroxytetrazolate (4b). white solid (0.208 g, 91%); ^{1}H NMR (DMSO-d6): δ 10.19 (s, 4H) ppm; ^{13}C NMR (DMSO-d6): δ 131.92, 138.84, 152.71 ppm; IR (KBr): $\tilde{v}$ 3404, 3135, 3065, 3013, 2985, 2150, 1545, 1442, 1383, 1230, 1180, 987, 874, 780 cm^{-1}; elemental analysis, Calcd (%) for $C_3H_4N_{10}O_3$ (228.13): C: 15.79; H: 1.77; N: 61.40; Found, C: 15.72; H: 1.75; N: 62.38.

Hydrazinium 5-(4-azidofurazan-3-yl)-1-hydroxytetrazolate (4c). white solid (0.211 g, 93%); ^{1}H NMR (DMSO-d6): δ 7.09 (s, 1H) ppm; ^{13}C NMR (DMSO-d6): δ 131.76, 138.91, 152.68 ppm; IR (KBr): $\tilde{v}$ 3070, 1775, 2150, 1546, 1443, 1383, 1229, 1180, 989, 874, 780 cm^{-1}; elemental analysis, Calcd (%) for $C_3H_5N_{11}O_2$ (227.15): C: 15.86; H: 2.22; N: 67.83; Found, C: 15.81; H: 2.24; N: 67.94.

Conflicts of interest

The authors declare no conflict of interest

Acknowledgements

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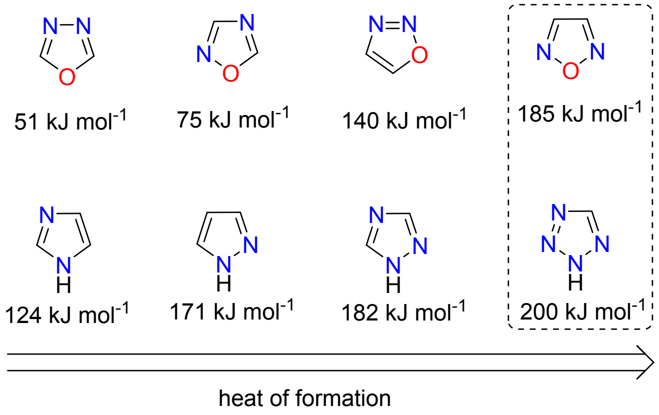

These new high-nitrogen-content azidofurazan compounds show potential for use as next-generation green primary and secondary explosives.