Supporting Information

Nitrogen-Rich Salts Based on 5-Hydrazinotetrazole: A New Family of High-Density Energetic Materials

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Table of Contents

S2 Optimized structures and Cartesian coordinates of 5-Hydrazinotetrazolium cation
S3 Heat of formation calculations of 5-Hydrazinotetrazolium cation
S5-S11 1H and 13C Spectra of related compounds
S11-S14 DSC thermogram of related compounds
Optimized structures of 5-Hydrazinotetrazolium cation

![Optimized structures of 5-Hydrazinotetrazolium cation](image)

**Table S1.** Cartesian coordinates of the optimized structure of 5-Hydrazinotetrazolium cation

<table>
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<th>X</th>
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Heat of formation calculations of 5-Hydrazinotetrazolium salts

Based on a Born–Haber energy cycle (Scheme 1), heats of formation of ionic salts can be simplified by Equation:
Scheme 1 Born–Haber cycle for the formation for energetic salts.

\[
\Delta H_f^o \quad \text{(ionic salts, 298K)} = \Sigma \Delta H_f^o \quad \text{(cation, 298 K)} \\
\text{ } + \Sigma \Delta H_f^o \quad \text{(anion, 298 K)} - \Delta H_L
\]  

Where \( \Delta H_f^o \) is the lattice energy of the ionic salts, the \( \Delta H_f^o \) value could be predicted by the formula suggested by Jenkins et al.

\[
\Delta H_L = U_{\text{POT}} + [p(nM / 2 - 2) + q(nX / 2 - 2)]RT
\]  

Where \( U_{\text{POT}} \) is the lattice potential energy and \( nM \) and \( nX \) depend on the nature of the ions \( M^+ \) and \( X^- \), respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy, \( U_{\text{POT}} \), takes the form of Eq. (3):

\[
U_{\text{POT}} \quad \text{(kJ mol}^{-1}) = \gamma \left( \rho_m / M_m \right)^{1/3} + \delta
\]  

Where \( \rho_m \) is density \( (\text{g} \cdot \text{cm}^{-3}) \), \( M_m \) is the chemical formula mass of the ionic material \( (\text{g}) \), and the coefficients \( \gamma \) \( (\text{kJ} \cdot \text{mol}^{-1} \cdot \text{cm}) \) and \( \delta \) \( (\text{kJ} \cdot \text{mol}^{-1}) \) are assigned literature values. The heats of formation of the cations were computed by using iso-desmic reactions. The heats of formation of the anion and the parent ions in the isodesmic reactions were calculated from protonation reactions \( (\Delta H_f^o (\text{H}^+) = 1528 \text{ kJ} \cdot \text{mol}^{-1}) \).

**Table S2.** Calculated total energy \( (E_0) \), zero-point energy \( (ZPE) \), thermal correction \( (H_T) \), and heat of formation \( (HOF) \) of 5-Hydrizinotetrazolium cation.

<table>
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<th>Compd.</th>
<th>( E_0/a.u. )</th>
<th>( ZPE/(\text{kJ} \cdot \text{mol}^{-1}) )</th>
<th>( H_T/(\text{kJ} \cdot \text{mol}^{-1}) )</th>
<th>( HOF/(\text{kJ} \cdot \text{mol}^{-1}) )</th>
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Method of calculated densities

For an ionic crystal with formula unit $M_pX_q$, its volume is simply the sum of the volumes of the ions contained in the formula unit:

$$V = pV_{M^+} + qV_{X^-} \quad (1)$$

where $M$ denotes the cation and $X$ denotes the anion. Because the volumes of individual ions are able to be evaluated using the DFT procedure, we used eq 1 to calculate formula unit volumes for ionic crystals. For those compounds that contain hydrogen atoms, a “corrected” molecular volume using a molecular structure optimized at the DFT level can be calculated using:

$$V_{\text{corrected}} = V_{\text{uncorrected}} - [0.6763 + 0.9418 \times (\text{no. of hydrogen atoms in the ion})] \quad (2)$$

Rice et al. reported that the formula unit volumes calculated using the optimized geometries at the B3LYP/6-31G** level and corrected for the number of hydrogen atoms produce average and rms deviations from experimental values of 1.3% and 5.0%, respectively, in much better agreement than the uncorrected values (5.6% and 7.3%, respectively). Therefore, we used the B3LYP/6-31G** method to calculate the molecular volumes for the energetic tetrazolium salts studied here. The volume of each ion was defined as inside a contour of 0.001 electrons bohr$^{-3}$ density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for the optimized structure of each ion to get an average volume. For the salts, the theoretical density was obtained from the molecular weight divided by the average molecular volume. This method has been successfully applied to high-nitrogen compounds.

Sensitivity

The impact sensitivity was tested on a type 12 tooling according to “up and down” method. A 2.5 kg weight was dropped from a set height onto a 20 mg sample placed on 150 grit garnet sandpaper. Each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. 50 drops were made from different heights, and an explosion or non-explosion was recorded to determine the results. An initial height was made by experiences of the testers based on the structure of the tested compound; several trials at different heights, like 40 cm, 60 cm, 50 cm, 55 cm, 60 cm, were done. For example, when tested compound 12, the weight is 5.0 kg and the initial height was set at 55 cm finally since explosion occurred when the height is 63.1 cm, while it did not happen at 40 cm. After that, each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. The test height was spaced at log 0.06 intervals. 50 drops were
made from different heights based on the method mentioned above, and an explosion or non-explosion was recorded.

$^1$H and $^{13}$C Spectra of 2-12.

**Figure S1.** $^1$H (top) spectra of 2 from DMSO-d$_6$ and $^{13}$C (bottom) spectra of 2 from D$_2$O.
**Figure S2.** $^{13}$C spectra of 3 from D$_2$O.

**Figure S3.** $^{13}$C spectra of 4 from D$_2$O.
**Figure S4.** $^{13}$C spectra of 5 from D$_2$O.

**Figure S5.** $^{13}$C (bottom) spectra of 6 from D$_2$O.
Figure S6. $^1$H (top) and $^{13}$C (bottom) spectra of 7 from D$_2$O.
**Figure S7.** $^{13}$C spectra of 8 from D$_2$O.

**Figure S8.** $^{13}$C spectra of 9 from D$_2$O.
**Figure S9.** $^{13}$C spectra of 10 from D$_2$O.

**Figure S10.** $^{13}$C spectra of 11 from D$_2$O.
**Figure S11.** $^{13}$C spectra of 12 from D$_2$O.

**DSC thermogram of the related compounds**

**Figure S12.** DSC thermogram of 2 (heating rate of 10°C·min$^{-1}$).
**Figure S13.** DSC thermogram of 5 (heating rate of 10°C·min⁻¹).

**Figure S14.** DSC thermogram of 7 (heating rate of 10°C·min⁻¹).
**Figure S15.** DSC thermogram of 8 (heating rate of 10°C·min⁻¹).

**Figure S16.** DSC thermogram of 10 (heating rate of 10°C·min⁻¹).
**Figure S17.** DSC thermogram of 11 (heating rate of 10°C·min⁻¹).

**Figure S18.** DSC thermogram of 12 (heating rate of 10°C·min⁻¹).