Supporting Information

Synthesis and thermal behavior of a fused, tricyclic pyridine-based energetic material: 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide

Congming Ma¹, Yong Pan¹*, Juncheng Jiang, Zuliang Liu², Qizheng Yao²

¹ College of Safety Science and Engineering, Nanjing Tech University, Nanjing 210009, China;
² School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

Table of Contents

Part A: Experimental
Part B: X-ray crystallography
Part C: Copies of ¹H NMR, ¹³C NMR, IR and MS
Part D: Theoretical study
Part A: Experimental

**Caution:** Some compounds are energetic materials that tend to explode under certain conditions. Proper protective measures (work with small quantities, safety glassed, face shields) should be observed.

**General:** Melting point was measured on an X-4 melting point apparatus and was uncorrected. ¹H NMR and ¹³C NMR were recorded on a Bruker Avance Spectrometer. The coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analyses were carried out on a Perkin-Elmer instrument. Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was conducted on a Q600SDT.

**Synthesis of 2.** A solution of 4-amino-2,6-dichloropyridine (0.81 g, 5 mmol) in concentrated sulfuric acid (10 mL) was stirred vigorously at room temperature and treated portionwise with potassium nitrate (1.52 g, 15 mmol). Then the mixture was heated to 50 °C for 30 min. After pouring over ice water, the precipitate solid was filtered, washed with cold water and dried. Yield: yellow solid, 0.88 g (70%). m.p. 159-161 °C; ¹H NMR (DMSO-δ6, 500 MHz): δ 8.25 (s, 2H); ¹³C NMR (DMSO-δ6, 125 MHz): δ 142.39, 141.03, 132.00; Anal. Calcd for C₆H₄Cl₂N₂O₂: C, 23.74; H, 0.80; N, 22.14; found: C, 23.65; H, 1.02; N, 22.19%; MS (ESI) m/z: 250.87: 252.86: 254.87= 9: 6: 1 (M-H).

**Synthesis of 6.** 4-amino-2,6-dichloro-3,5-dinitropyridine (1.26 g, 5 mmol) was dissolved in acetone (15 mL) and sodium azide (0.98 g, 15 mmol) was added portionwise at room temperature, then heated up to 30 °C for another 30 min. The mixture was distilled under reduced pressure, dissolved with water (15 mL), extracted with ethyl acetate (2 × 25 mL). The combined organic layers were dried over MgSO₄ and solvent evaporated. Yield: grass green solid, 1.07 g (90%). T_{dec}: 150 °C; ¹H NMR (DMSO-δ6, 400 MHz): δ 10.17 (s, 1H), 9.50 (s, 1H); ¹³C NMR (DMSO-δ6, 100 MHz): δ 148.96, 144.27, 141.87, 111.17, 105.06; Anal. Calcd for C₆H₄N₂O₄: C, 25.22; H, 0.85; N, 47.06; found: C, 25.10; H, 1.01; N, 47.22%; MS (ESI) m/z: 236.96(M-H).

**Part B: X-ray crystallography**

The grass green single crystal of title compounds was selected for X-ray diffraction analysis. The data were collected using a Nonius CAD4 detector equipped with a graphite-monochromatic MoKα radiation (λ = 0.71073 Å using a ω/2θ scan mode at 293(2) K. The structure was solved by direct methods and expanded by difference Fourier techniques with SHELXL-97 program. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added according to the theoretical models. The structure was refined by full-matrix least-squares techniques on F² with SHELXL-97.
Part C: Copies of $^1$H-NMR, $^{13}$C NMR, IR and MS

Fig. 1 $^1$H NMR spectrum of 2,6-dichloro-3,5-dinitro-4-aminopyridine(2) in DMSO-$d_6$, 500MHz

Fig. 2 $^{13}$C NMR spectrum of 2,6-dichloro-3,5-dinitro-4-aminopyridine(2) in DMSO-$d_6$, 125MHz
Fig. 3 MS of 2,6-dichloro-3,5-dinitro-4-aminopyridine(2)
Fig. 4 $^1$H NMR spectrum of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide (6) in DMSO-$d_6$, 400MHz

Fig. 5 $^{13}$C NMR spectrum of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide (6) in DMSO-$d_6$, 100MHz
Fig.6 MS of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide (6)
Part D: Theoretical study

3.1 target compound

Fig. 1 Molecular structure of ANTP (the red ball represents oxygen atom, the blue ball represents nitrogen atom, the gray ball represents carbon atom, the white ball represents hydrogen atom)

3.2 heat of formation

The heat of formation of the above isodesmic reaction at 298K was calculated with equation (1-3).

\[
\Delta H_{298} = \sum \Delta H_f (products) - \sum \Delta H_f (reactants) \quad (1)
\]

\[
\Delta H_{298} = \Delta E_{298} + \Delta (pV) \quad (2)
\]

\[
\Delta E_{298} = \Delta E_0 + \Delta E_{ZPV} + \Delta (H_{298} - H_0) \quad (3)
\]

Where \( \Delta E_0 \) and \( \Delta E_{ZPV} \) are the change in total energy and the difference between zero-point energies at 0 K of reactants and products, respectively. \( \Delta (H_{298} - H_0) \) is thermal correction of enthalpy from 0 K to 298 K. For the isodesmic reaction in this work, value of \( \Delta (pV) \) is 0.

Total energies \( (E_0) \), zero-point energies \( (ZPE) \), thermal corrections \( (H_T) \) and HOF of the title compounds among the isodesmic reaction are shown in table 2. Additional calculations were carried out for the atomization reaction \( C_{n}H_{8}O_{l}N_{d}(g) \rightarrow aC(g)+bH(g)+cO(g)+dN(g) \) using the G2 theory to get an accurate value of HOF. Besides, the experimental HOFs of C(g), H(g), O(g), N(g) are known as 716.7, 218, 249.2, 472.7 kJ·mol\(^{-1}\).
### Calculation process:

#### 3.2.1 Compound 10

Table 1 Calculated total energies ($E_0$), zero-point energies (ZPE), thermal corrections ($H_T$) for 10 ($\text{C}_5\text{H}_2\text{O}_2\text{N}_6$) using G2 method

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>$\text{C}_5\text{H}_2\text{O}_2\text{N}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$/a.u.</td>
<td>-37.78194</td>
<td>-0.497639</td>
<td>-74.979669</td>
<td>-54.515599</td>
<td>-669.483717</td>
</tr>
<tr>
<td>$E_{\text{ZPE}}$/a.u.</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.088844</td>
</tr>
<tr>
<td>$H_T$/kJ·mol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>22.93</td>
</tr>
<tr>
<td>$H$/kJ·mol</td>
<td>716.7</td>
<td>218</td>
<td>249.2</td>
<td>472.7</td>
<td>943.4976355</td>
</tr>
</tbody>
</table>

\[
\Delta H_{298} = \Sigma \Delta f H^0 - \Sigma \Delta f H^R
\]

\[
= 5\Delta f H_C + 2\Delta f H_H + 2\Delta f H_O + 6\Delta f H_N - \Delta f H
\]

\[
\Delta H_{298} = \Delta E_0 + \Delta E_{\text{ZPE}} + \Delta H_T + \Delta nRT
\]

$\Delta E_0 = -37.78194 \times 5 - 0.497639 \times 2 - 74.979669 \times 2 - 54.515599 \times 6 + 669.483717$

$\Delta E_{\text{ZPE}} = -0.088844 \ a.u. = -232.59922 \ kJ\cdot mol^{-1}$

$\Delta (H_{298} - H_0) = 22.93 \ kJ\cdot mol^{-1}$

$\Delta nRT = (5 + 2 + 2 + 6 - 1) \times 0.008314 \times 298 = 34.686008 \ kJ\cdot mol^{-1}$

$\Delta H_{298} = 716.7 \times 5 + 218 \times 2 + 249.2 \times 2 + 472.7 \times 6 - H$

$H = 943.4976355 \ kJ\cdot mol^{-1}$

#### 3.2.2 ANTP

Table 2 HOF and electronic energy of the compounds using B3LYP functional with the 6-31G** basis set

<table>
<thead>
<tr>
<th></th>
<th>$E_0$</th>
<th>ZPE</th>
<th>$H_T$</th>
<th>HOF$^a$</th>
<th>HOF$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/a.u.</td>
<td>/a.u.</td>
<td>/kJ·mol$^{-1}$</td>
<td>/kJ·mol$^{-1}$</td>
<td>/kJ·mol$^{-1}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-40.5240195</td>
<td>0.0450258</td>
<td>10.03</td>
<td>-74.60</td>
<td></td>
</tr>
<tr>
<td>CH$_3$NO$_2$</td>
<td>-245.0133754</td>
<td>0.0500041</td>
<td>14.07</td>
<td>-80.80</td>
<td></td>
</tr>
<tr>
<td>CH$_3$NH$_2$</td>
<td>-95.8636859</td>
<td>0.064199</td>
<td>11.51</td>
<td>-22.50</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_2$O$_2$N$_6$</td>
<td>-930.3312102</td>
<td>0.1086148</td>
<td>35.47</td>
<td>907.655287</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CRC book.

$^b$ Calculated using the above isodesmic reaction.

$\Delta E_0 = -670.4741631 - 245.0133754 - 95.8636859 + 40.5240195 \times 2 + 930.3312102$

$= -1011.3512244 \ kJ\cdot mol^{-1}$

$\Delta E_{\text{ZPE}} = 0.0893955$ $a.u. = 73.591124 \ kJ\cdot mol^{-1}$

$\Delta (H_{298} - H_0) = 25.19 + 14.07 + 11.51 - 10.03 \times 2 - 35.47 = -4.76 \ kJ\cdot mol^{-1}$
ΔH₂⁹⁸ = 943.4976355 - 80.80 - 22.5 + 74.6*2 - H
= 989.3976355 - H = 73.5791124 + 12.9232361 - 4.76
H = 907.655287 kJ·mol⁻¹

3.2.3 Detonation properties

The detonation velocity and pressure were estimated by the Kamlet–Jacobs equations as (4-5).

\[ D = 1.01 \left( N \sqrt[3]{M} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \]  (4)

\[ p = 1.558\rho^2 N \sqrt[3]{M} Q^{1/2} \]  (5)

where each term in the equations (4) and (5) is defined as follows: \( D \), the detonation velocity (km·s⁻¹); \( P \), the detonation pressure (GPa); \( N \), the moles of detonation gases per gram explosive; \( M \), the average molecular weight of these gases; \( Q \), the heat of detonation (kJ·g⁻¹); and \( \rho \), the loaded density of explosives (g·cm⁻³). For known explosives, their \( Q \) and \( \rho \) can be measured experimentally; thus their \( D \) and \( P \) can be calculated according to equations (4) and (5).

Table 3 Results of some parameters in the Kamlet–Jacobs equations

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( N )</td>
<td>( M )</td>
<td>( OB/% )</td>
<td>( \rho/\text{g cm}^{-3} )</td>
<td>( D/(\text{km} \cdot \text{s}^{-1}) )</td>
<td>( P/\text{GPa} )</td>
</tr>
<tr>
<td>6-31G**</td>
<td>0.027</td>
<td>30.154</td>
<td>-47.06</td>
<td>1.921</td>
<td>8.838</td>
</tr>
</tbody>
</table>