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# 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

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**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. $^1$H NMR and $^{13}$C 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 ℃ 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 ℃; $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 8.25 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz): $\delta$ 142.39, 141.03, 132.00; Anal. Calcd. for $C_5H_2Cl_2N_4O_4$: 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 ℃ 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 $MgSO_4$ and solvent evaporated. Yield: grass green solid, 1.07 g (90%). $T_{\mathrm{dec}}$: 150 ℃; $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 10.17 (s, 1H), 9.50 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 148.96, 144.27, 141.87, 111.17, 105.06; Anal. Calcd. for $C_5H_2N_8O_4$: 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 Mo$K\alpha$ radiation ($\lambda$ = 0.71073 Å using a $\omega/2\theta$ 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 $F^2$ with SHELXL-97.

## **Part C:** Copies of $^{1}$H-NMR, $^{13}$C NMR, IR and MS

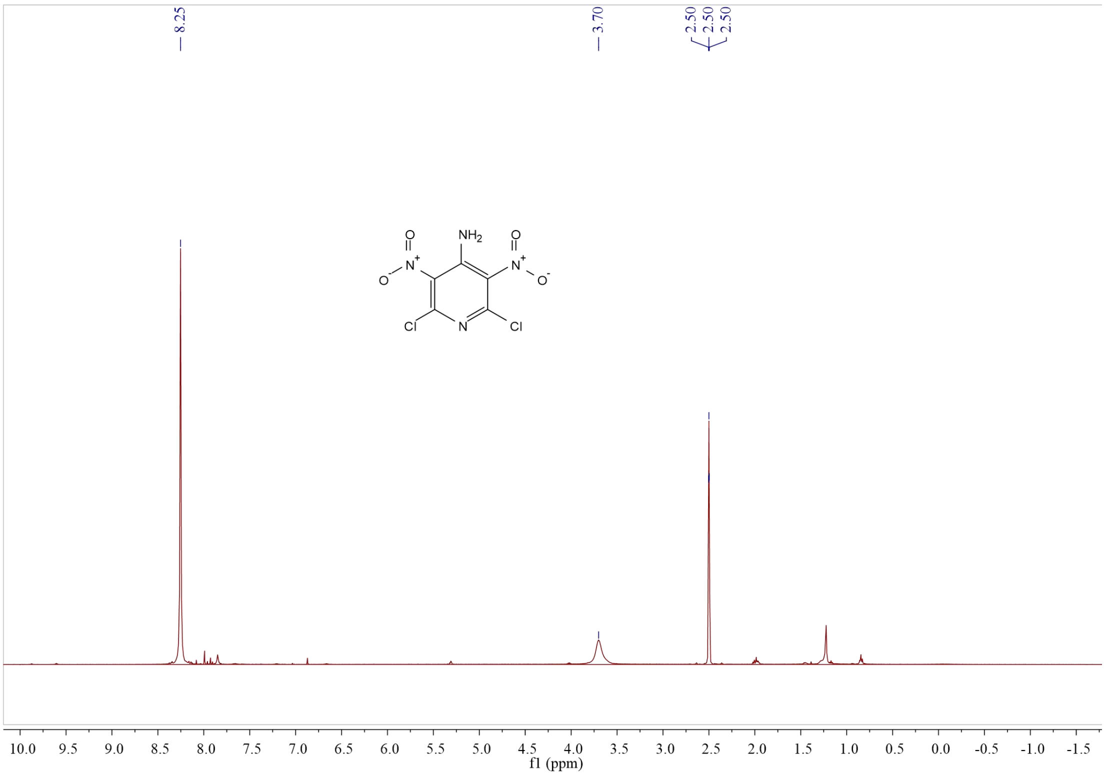


Fig.1 $^{1}$H NMR spectrum of 2,6-dichloro-3,5-dinitro-4-aminopyridine(**2**) in DMSO-$d_6$, 500MHz

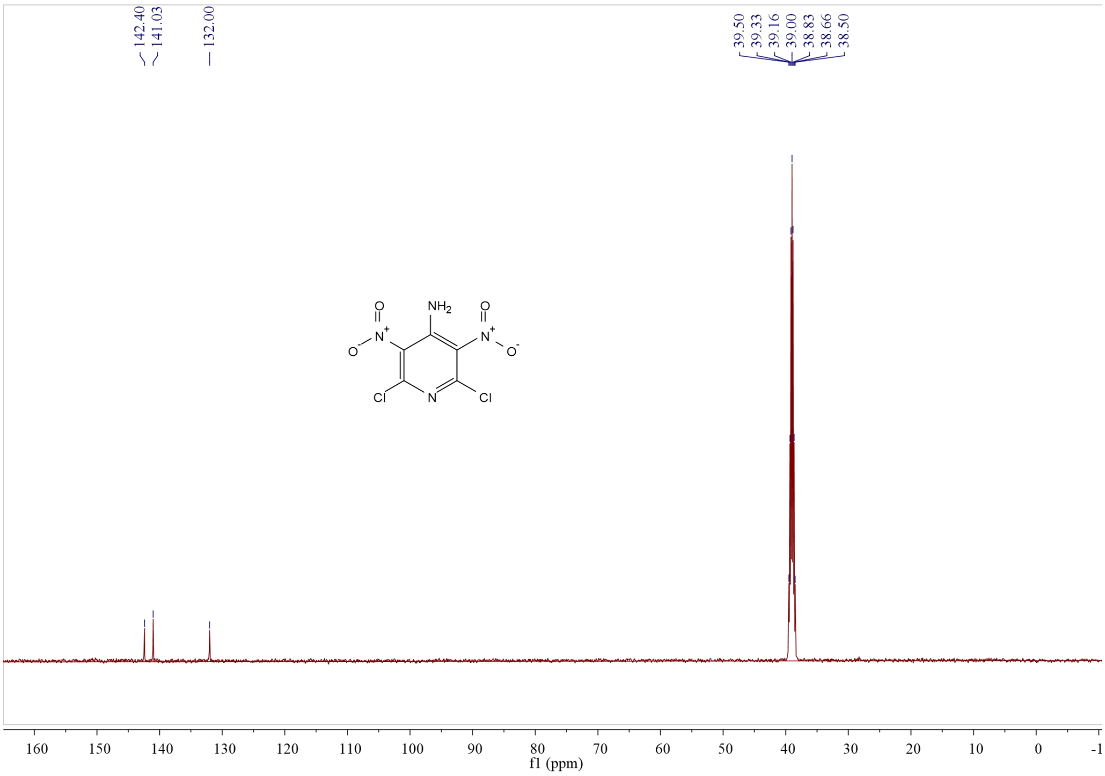


Fig.2 $^{13}$C NMR spectrum of 2,6-dichloro-3,5-dinitro-4-aminopyridine(**2**) in DMSO-$d_6$, 125MHz

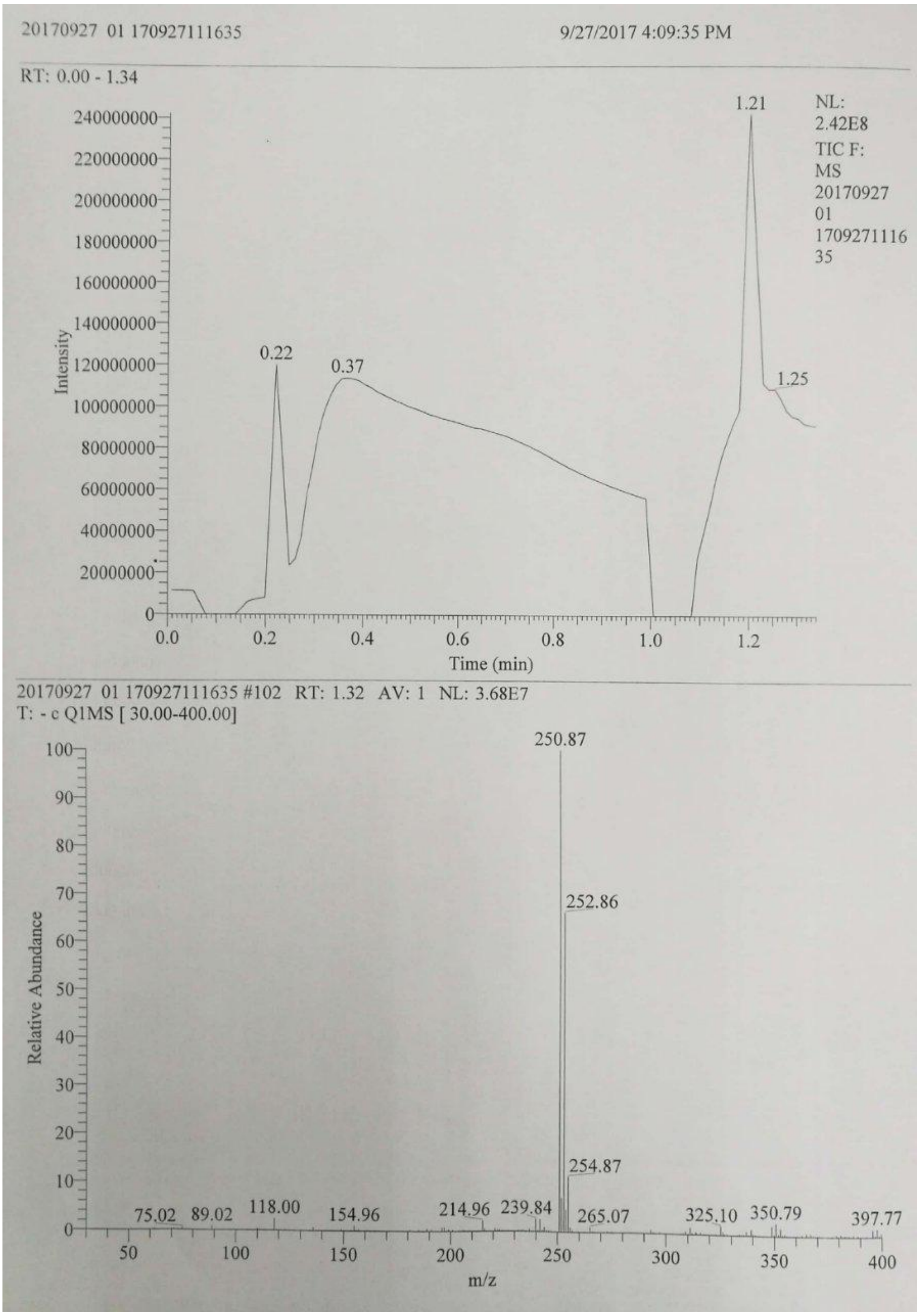


Fig.3 MS of 2,6-dichloro-3,5-dinitro-4-aminopyridine(**2**)

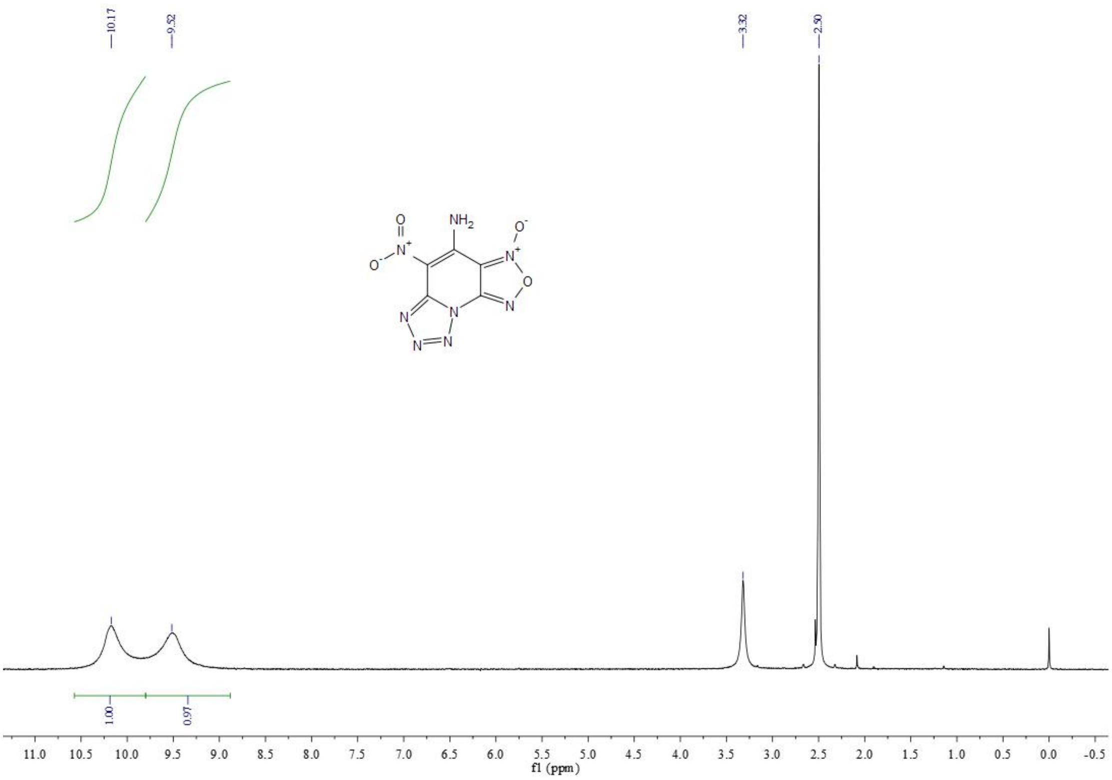


Fig.4 $^{1}$H NMR spectrum of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide (**6**) in DMSO-$d_6$, 400MHz

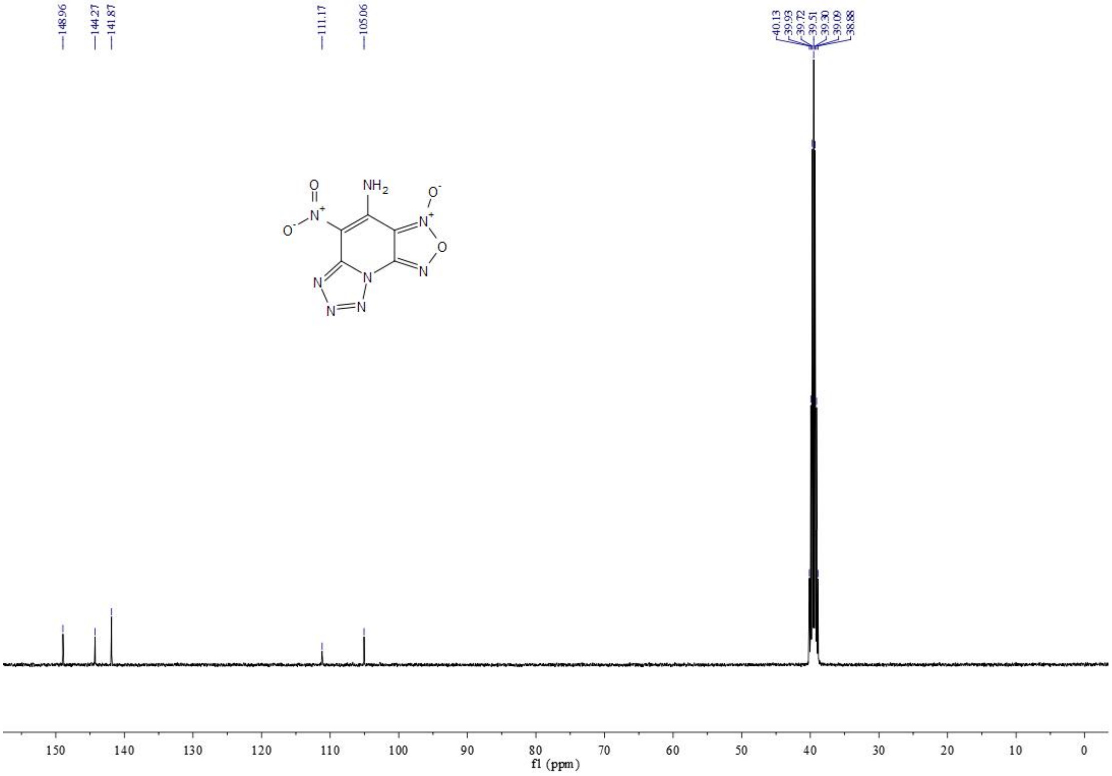


Fig.5 $^{13}$C NMR spectrum of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-*e*]tetrazolo[1,5-*a*]pyridine-3-oxide (**6**) in DMSO-$d_6$, 100MHz

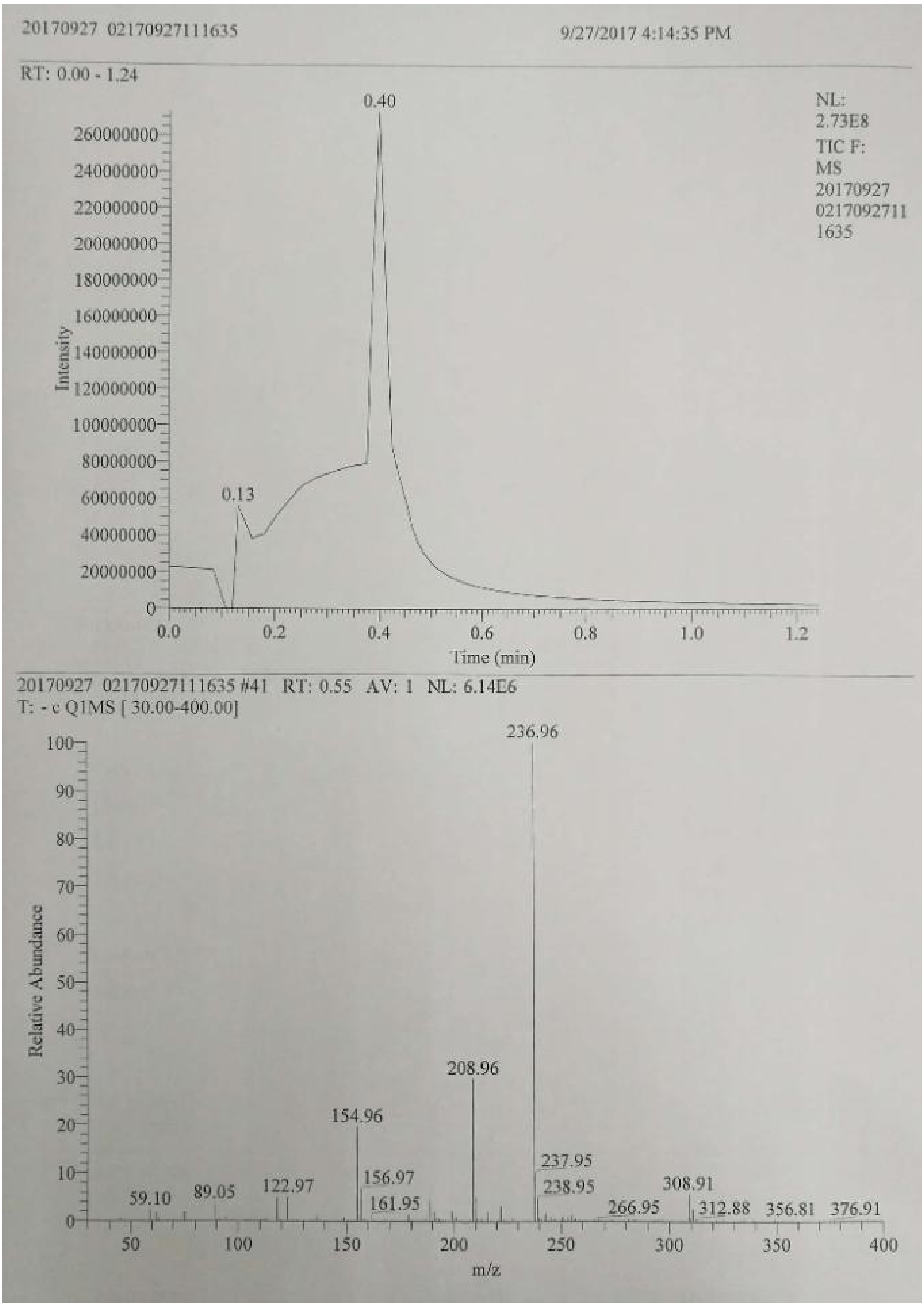


Fig.6 MS of 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-*e*]tetrazolo[1,5-*a*]pyridine- 3-oxide (**6**)

## **Part D:** Theoretical study

### 3.1 target compound

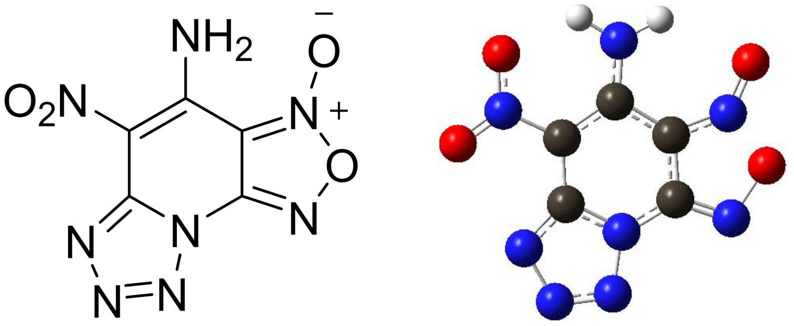
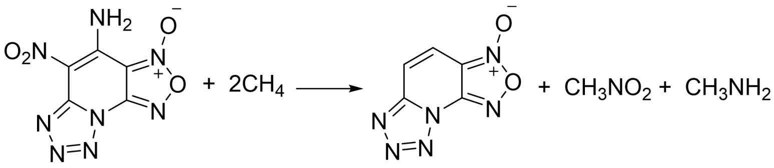


Fig. 1 Molecular structure of ANTP (the red ball represents oxygen atom, the blue ball represents nitrogen atom, the gray ball represents carbon atom, the white ball represents hydrogen atom)

### 3.2 heat of formation



**6, ANTP** **10**

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

$$\Delta H_{298} = \sum \Delta H_{\mathrm{f}}(\text{products}) - \sum \Delta H_{\mathrm{f}}(\text{reactants}) \tag{1}$$

$$\Delta H_{298} = \Delta E_{298} + \Delta(pV) \tag{2}$$

$$\Delta E_{298} = \Delta E_0 + \Delta E_{\mathrm{ZPV}} + \Delta(H_{298} - H_0) \tag{3}$$

Where $\Delta E_0$和$\Delta E_{\mathrm{ZPV}}$ 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 $C_aH_bO_cN_d(g) \rightarrow aC(g)+bH(g)+cO(g)+dN(g)$ 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** ($C_5H_2O_2N_6$) using G2 method

| | | C | H | O | N | $C_5H_2O_2N_6$ |
|---|---|---|---|---|---|---|
| G2 | $E$/a.u. | -37.78194 | -0.497639 | -74.979669 | -54.515599 | -669.483717 |
| | $E_{ZPE}$/a.u. | 0 | 0 | 0 | 0 | 0.088844 |
| | $H_T$/kJ·mol | 0 | 0 | 0 | 0 | 22.93 |
| | $H$/ kJ·mol | 716.7 | 218 | 249.2 | 472.7 | **943.4976355** |

$$\Delta H_{298}=\Sigma\Delta_f H_P-\Sigma\Delta_f H_R$$

$$=5\Delta_f H_C+2\Delta_f H_H+2\Delta_f H_O+6\Delta_f H_N-\Delta_f H$$

$$\Delta H_{298}=\Delta E_0+\Delta E_{ZPE}+\Delta H_T+\Delta nRT$$

$\Delta E_0$=-37.78194*5-0.497639*2-74.79669*2-54.515599*6+669.483717
=-188.9097-0.995278-149.959338-327.093594+669.483717
=-666.95791+669.483717=**2.525807** *a.u.*=**6631.5062785** kJ·mol$^{-1}$
$\Delta E_{ZPV}$=**-0.088844** *a.u.*=**-232.259922** kJ·mol$^{-1}$
$\Delta(H_{298}-H_0)$=**-22.93** kJ·mol$^{-1}$
$\Delta nRT=(5+2+2+6-1)*0.008314*298$=**34.686008** kJ·mol$^{-1}$
$\Delta H_{298}$=716.7*5+218*2+249.2*2+472.7*6-H
=7354.5-H=6631.5062785-232.259922-22.93+34.686008
$H$=**943.4976355** kJ·mol$^{-1}$

### 3.2.2 ANTP

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

| | $E_0$ /a.u. | ZPE /a.u. | $H_T$ / kJ·mol$^{-1}$ | HOF[a] / kJ·mol$^{-1}$ | HOF[b] / kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $CH_4$ | -40.5240195 | 0.0450258 | 10.03 | -74.60 | |
| $CH_3NO_2$ | -245.0133754 | 0.0500041 | 14.07 | -80.80 | |
| $CH_3NH_2$ | -95.8636859 | 0.064199 | 11.51 | -22.50 | |
| $C_5H_2O_4N_8$ | -930.3312102 | 0.1086148 | 35.47 | | 907.655287 |

[a] CRC book.

[b] Calculated using the above isodesmic reaction.

$\Delta E_0$=-670.4741631-245.0133754-95.8636859+40.5240195*2+930.3312102
=-1011.3512244+1011.3792492
=**0.0280248** *a.u.*=**73.5791124** kJ·mol$^{-1}$
$\Delta E_{ZPV}$=0.0893955+0.0500041+0.064199-0.0450258*2-0.1086148
**=0.0049222** *a.u.*=**12.9232361** kJ·mol$^{-1}$
$\Delta(H_{298}-H_0)$=25.19+14.07+11.51-10.03*2-35.47=**-4.76** kJ·mol$^{-1}$

$\Delta H_{298}$=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).

$$\mathrm{D} = 1.01\left(N\bar{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho) \qquad (4)$$

$$\mathrm{p} = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \qquad (5)$$

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

| | *N* | *M* | *OB*/% | $\rho$/(g·cm$^{-3}$) | *D*/(km·s$^{-1}$) | *P*/GPa |
|---|---|---|---|---|---|---|
| 6-31G** | 0.027 | 30.154 | -47.06 | 1.921 | 8.838 | 36.012 |