Supporting Information

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Synthesis and Detonation Properties of 5-Amino-2,4,6-trinitro-1,3-dihydroxy-benzene

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Experimental Section

Caution: Proper safety precautions should be taken when handling these compounds. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, faceshields, and ear plugs are recommended.

General methods: All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. \(^1\)H and \(^{13}\)C NMR spectra were measured with a Bruker Avance III 300 MHz Digital NMR Spectrometer operating at 300 MHz, 75 MHz or 500M, 100Hz. All chemical shifts are quoted in ppm relative to TMS \((^1\text{H}, ^{13}\text{C})\). The decomposition point was recorded on a DSC823e at a heating rate of 5°C·min\(^{-1}\) in closed Al containers with a nitrogen flow of 30 mL·min\(^{-1}\). Sensitivity data were determined using a BAM drop- hammer and a BAM friction tester. The electrostatic sensitivity test was carried out using an Electric Spark Tester ESD JGY-50 III.

\[
\begin{array}{c}
\text{F} \\
\text{HNO}_3 \\
\text{H}_2\text{SO}_4 \\
\text{F} \\
\end{array} \quad \text{1-} \quad \begin{array}{c} \text{O}_2\text{N} \\
\text{F} \\
\text{NO}_2 \\
\text{F} \\
\end{array} \quad \text{2}
\]

In an ice-water bath and magnetic stirring, to 1 liter of three-necked flask, 225 ml sulfuric acid and 225 ml fuming nitric acid was added in order. M-difluorobenzene (114g, 1.0mol) is slowly dropped into the mixed solution at this temperature. After the m-difluorobenzene was added to the end, the mixture continue to be stirred for 2 hours, and then the temperature of the system slowly was increased to room temperature and was stirred for overnight. When the reaction is complete, the mixture is slowly poured into ice water and there is a large amount of precipitation was found. The solids were collected by
vacuum filtration with Buchner funnel and washed with water over and over to get product. (189.723g, 93%). $^1$H NMR (300M NMR, DMSO-d$_6$, TMS), δ=8.286-8.234(m, 1H), 7.539-7.465(m, 1H); $^{13}$C NMR (75Mz, DMSO-d$_6$, TMS), δ=156.605-160.439 (m, 1C), 133.705, 125.456, 110.784-110.073(m, 2C); HRMS-ESI$^+$ (m/z) calcd for C$_6$H$_2$F$_2$N$_2$NaO$_4$+ ([M + Na]$^+$) 226.99, found: 227.01.

**Compound3** Resorcinol (11.0g, 100mmol) was dissolved in 150 ml of anhydrous MDF, triethylamine (83.47ml, 60.60g, 6.0eq) and 1,5-difluoro-2,4-dinitrobenzene (20.4g, 100mmol, 1.0eq) were added sequentially at room temperature, the mixture was refluxed and stirred for 3hrs. The precipitation is filtered and washed with water three times. The solid was collected and dried to yield the product3 (pale yellow, 23.44g, 76%) $^1$H NMR (300M NMR, DMSO-d$_6$, TMS), δ=8.915(s, 2H), 7.597-7.542(m, 2H), 7.202-7.176 (m, 6H), 6.700(s, 2H); $^{13}$C NMR (75Mz, DMSO-d$_6$, TMS), δ=155.426, 154.912, 134.599, 133.006, 125.184, 118.338, 110.965, 109.255. HRMS-ESI$^+$ (m/z) calcd for C$_{24}$H$_{12}$N$_4$NaO$_{12}$$^+$ ([M + Na]$^+$) 571.035, found: 571.034.
Compound 4 In an ice-water bath and magnetic stirring, to 250ml of a three-necked flask, concentrated sulfuric acid (98%, 125ml) and raw materials 3 (10g, 18.24mmol) were added successively. Then fuming nitric acid (40ml) was dropped into the mixture slowly. After the addition of nitrate, the system slowly was heated at 65°C for 22hrs. The mixture was dumped into the ice-water slowly. Then the precipitate was filtered through Buchner funnel and washed with water over and over. The Light yellow solid was dried and collected to get compound 7 (pale yellow, 89%). $^1$H NMR (300Mz, DMSO-d$_6$, TMS), δ=8.412(s, 2H), 7.054(s, 2H); $^{13}$C NMR (75Mz, DMSO-d$_6$, TMS), δ=151.911, 136.983, 125.437, 113.433; HRMS-ESI$^+$ (m/z) calcd for C$_{24}$H$_8$N$_8$NaO$_{20}$ $^+$ ([M + Na]$^+$): 751.036, found: 751.037.
In an ice-water bath and magnetic stirring, to 250ml of an one-necked flask, 4-Amino-4H-1,2,4-triazole (ATA) (7.40g, 88mmol), DMSO(120ml), sodium methanol(10.8g, 200mmol) and compound 4(10.92g, 15mmol) were added successively. Then the mixture was heated at 65˚C for 15hrs. (TLC: ethyl acetate). After the reaction was over, it was dumped into 6M HCl (400ml) slowly at room temperature and stirred for 30minnutes. After the mixture was cooled at room temperature, the solid was filtered. The aqueous phase was extracted with ethyl acetate (3*300ml). The organic phase was combined, dried with NaSO₄ and concentrated in vacuo to get the residue. The residue and the solid were combined and purified by column chromatography (EA/PE=1/5) to get compound 6 (dark yellow solid, 5.23g, yields: 81.08%), and compound 7 (yellow solid, 4.51 g, yields: 75.16%).

**Compound 6:**

\[ \text{C}_6\text{H}_4\text{N}_3\text{O}_6^- \] (m/z) calcd for \[ \text{C}_6\text{H}_4\text{N}_3\text{O}_6^- \]: 214.08. Compounds 6: \( ^1\text{H} \) NMR (500Mz, DMSO-d₆, TMS), \( \delta = 8.61(\text{s}, 2\text{H}), 5.40(\text{s}, 1\text{H}) \); \( ^{13}\text{C} \) NMR (125Mz, DMSO-d₆, TMS), \( \delta = 170.058, 130.19, 130.036, 110.87 \). HRMS-ESI (m/z) calcd for \( \text{C}_6\text{H}_4\text{N}_3\text{O}_6^- \) ([M -H] -): 214.08.

**Compound 7:**

\[ \text{C}_6\text{H}_3\text{N}_2\text{O}_6^- \] (m/z) calcd for \[ \text{C}_6\text{H}_3\text{N}_2\text{O}_6^- \]: 199.07.

\[ \text{NH}_2 \]
\[ \text{O}_2\text{N} \]
\[ \text{HO} \]
\[ \text{NO}_2 \]

\[ \text{NH}_2 \]
\[ \text{O}_2\text{N} \]
\[ \text{HO} \]
\[ \text{NO}_2 \]

\[ \text{KNO}_3 \]
\[ \text{H}_2\text{SO}_4 \]

\[ \text{6} \]

\[ \text{8} \]

\[ \text{NH}_2 \]
\[ \text{O}_2\text{N} \]
\[ \text{HO} \]
\[ \text{NO}_2 \]

**Compound 8:** In an ice-water bath and magnetic stirring, to an one-necked flask (250ml), concentrated sulfuric acid (98%, 125ml) was added. Then KNO₃ (15g, 148 mmol) was dissolved in concentrated sulfuric acid slowly for 30minutes. Compound 6 (4.30g, 20mmol) was added into the above mixtures slowly and stirred for 30minutes.
Then the ice-water bath was moved, the system was warmed to room temperature for 10hrs (TLC: EA+1d HOAc, Rf=0.2).

When the reaction was over, the mixture was dumped into ice-water (400ml). Aqueous phase was extracted with EA (300ml*3). The organic phase was combined, dried with Na$_2$SO$_4$ and and concentrated in vacuo to get compound 8 (yellow solid: 4.13g, 79.4%).

$^1$H NMR (500Mz, DMSO-d$_6$, TMS), $\delta$=8.4659(s, 2H); $^{13}$C NMR (125Mz, DMSO-d$_6$, TMS), $\delta$=155.89, 155.80, 131.59, 123.99. HRMS-ESI$^+$ (m/z) calcd for C$_6$H$_3$N$_4$O$_8$ $^-$ ([M-H]$^-$): 259.07
Figure S1 $^1$H NMR spectrum of 2 (DMSO).

Figure S2 $^{13}$C NMR spectrum of 2 (DMSO).
Figure S3 $^1$H NMR spectrum of 3 (DMSO).

Figure S4 $^{13}$C NMR spectrum of 3 (DMSO).
Figure S5 $^1$H NMR spectrum of 4 (DMSO).
Figure S6 $^1$HNMR spectrum of 4 (DMSO).

Figure S7 1HNMR spectrum of 6 (DMSO).
Figure S8 $^{13}$CNMR spectrum of 6 (DMSO).

Figure S9 $^{13}$CNMR spectrum of 7 (DMSO).
Figure S10 $^1$H NMR spectrum of 7 (DMSO).

Figure S11 $^{13}$C NMR spectrum of 8 (DMSO).

Figure S12 $^1$H NMR spectrum of 8 (DMSO).
X-ray Structural Analysis of compound

The selected crystal was mounted with epoxy to the tip of a glass rod drawn out to a fiber. The X-ray intensity data for this colorless needle of $\text{C}_6\text{H}_{5.33}\text{N}_4\text{O}_{8.67}$ with approximate dimensions $0.25 \times 0.23 \times 0.13\ \text{mm}$ were measured with phi and omega scans at $173(2)\text{K}$ on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073\ \text{Å}$). The detector was placed at a distance of $5.00\ \text{cm}$ from the crystal. A total of 851 frames were collected (a hemisphere of data) with an exposure time of $30\ \text{sec/frame}$. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm giving a total of 3233 reflections to a maximum (angle of $25.36^\circ$ of which 851 reflections were independent. The structure was solved (direct methods) and refined using the Bruker SHELXTL version 6.1 Software Package using literature scattering factors (Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol.C.), and the orthorhombic space group Pca2(1), with $Z = 4$. No absorption correction was applied. The final anisotropic full-matrix least-squares refinement of $F_2$ converged at $R_1 = 4.60\%$, $wR_2 = 10.43\%$ and a goodness-of-fit of 1.056. All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated distances. All hydrogen atoms use a riding model, which means that the positional and thermal parameters are derived from the atom each hydrogen atom is bound to, while maintaining the calculated or determined distance and optimal angles. The largest peak and hole in the final difference map were 0.264 and -0.385e/$\text{Å}^3$, respectively. The calculated density is $1.96\ \text{g/cm}^3$ and $F(000)$ is 832 e-. Thermal ellipsoid drawings (15%) in this report were generated with the Bruker SHELXTL software.
Figure S13 (a) Dimer and (b) packing structures of compound 8
Table 1 Parameter of bond length of 8

| Atoms 1,2 | \( d_{1,2} \) [Å] | Atoms 1,2 | \( d_{1,2} \) [Å] |
|-----------|-----------------|-----------|-----------------|
| C1—O1     | 1.317(5)        | N3—O5'    | 1.223(2)        |
| C1—C2     | 1.410(3)        | N3—O5     | 1.223(2)        |
| C1—C2'    | 1.410(3)        | N1—O2     | 1.234(3)        |
| C2—C3     | 1.412(4)        | N1—O3     | 1.242(3)        |
| C2—N1     | 1.433(3)        | O1—H1A    | 0.84(2)         |
| C3—O4|N2 | 1.318(3)        | O4|N2—H4A | 0.763(18) |
| C3—C4     | 1.387(3)        | O4|N2—H2A | 0.8737 |
| C4—C3'    | 1.387(3)        | O6—H6A    | 0.85(2)         |
| C4—N3     | 1.464(5)        |           |                 |

Table 2 Angle parameters of 8

| Atoms 1,2,3 | \( \text{Angle}_{1,2,3} \) [°] | Atoms 1,2,3 | \( \text{Angle}_{1,2,3} \) [°] |
|-------------|-----------------|-------------|-----------------|
| O1—C1—C2   | 120.60(17)      | C3—C4—N3   | 118.27(18)      |
| O1—C1—C2'  | 120.60(17)      | O5'—N3—O5  | 124.5(3)        |
| C2—C1—C2'  | 118.8(3)        | O5'—N3—C4  | 117.74(17)      |
| C1—C2—C3   | 120.9(3)        | O5—N3—C4   | 117.74(17)      |
| C1—C2—N1   | 120.4(3)        | O2—N1—O3   | 120.6(2)        |
| C3—C2—N1   | 118.7(2)        | O2—N1—C2   | 120.0(2)        |
| O4|N2—C3—C4 | 116.7(3)        | O3—N1—C2     | 119.4(2)        |
| O4|N2—C3—C2 | 125.4(3)        | C1—O1—H1A    | 113.4(4)        |
| C4—C3—C2   | 117.9(3)        | C3—O4|N2—H4A | 107.2(2) |
| C3—C4—C3   | 123.5(4)        | C3—O4|N2—H2A | 125.800 |
| C3—C4—N3   | 118.28(18)      | H4A—O4|N2—H2A | 127.100 |

(i) \(-x, -x+y, 0.5-z\).

Table 3 Hydrogen bond parameter for compound 8

| Donor—Hydrogen...Acceptor | Don—Hyd [Å] | Hyd—Acc [Å] | Don—Acc [Å] | D—H—A |
|---------------------------|-------------|-------------|-------------|-------|
| O1—H1A...O6              | 0.86        | 1.86        | 2.610       | 144.8°|
| Bond      | Distance (Å) | Angle (°) | Other Bond Length (Å) | Other Angle (°) |
|-----------|--------------|-----------|-----------------------|-----------------|
| O2---H2A---O3 | 0.82         | 1.87      | 2.594                 | 148.2°          |
| O6x24---H6A---O5x28 | 0.85        | 2.43      | 3.186                 | 147.8°          |
| O6x24---H6A---O5x13 | 0.85        | 2.43      | 3.186                 | 147.8°          |
| O1x4---H1A---O2x27 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x27---H4A---O3x27 | 0.76        | 1.86      | 2.538                 | 147.0°          |
| O1x2---H1A---O2x28 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x28---H4A---O3x28 | 0.76        | 1.86      | 2.538                 | 147.0°          |
| O1x9---H1A---O2x29 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x29---H4A---O3x29 | 0.76        | 1.86      | 2.538                 | 147.0°          |
| O1x6---H1A---O2x30 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x30---H4A---O3x30 | 0.76        | 1.86      | 2.538                 | 147.0°          |
| O6x24---H6A---O5x13 | 0.85        | 2.43      | 3.186                 | 147.8°          |
| O1x4---H1A---O2x27 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x27---H4A---O3x27 | 0.76        | 1.86      | 2.538                 | 147.0°          |
| O1x2---H1A---O2x28 | 0.84        | 1.80      | 2.497                 | 139.4°          |
| O4x30---H4A---O3x30 | 0.76        | 1.86      | 2.538                 | 147.0°          |

i: 2-x,1/2+y,3/2-z; ii: 1-x,3/2+y,3/2-z; iii: x,1/2-y,-1/2+z; iv:x,-1+y,z
X-ray Crystallographic Data for 6

The selected crystal was mounted with epoxy to the tip of a glass rod drawn out to a fiber. The X-ray intensity data for this yellow needle of C$_6$H$_5$N$_3$O$_6$ with approximate dimensions 0.19 x 0.04 x 0.03 mm were measured with phi and omega scans at 173(2) K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (\(\lambda = 0.71073 \text{ Å}\)). The detector was placed at a distance of 5.00 cm from the crystal. A total of 148 frames were collected (a hemisphere of data) with an exposure time of 30 sec/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm giving a total of 2787 reflections to a maximum \(\theta\) angle of 25.39° of which 1348 reflections were independent. The structure was solved (direct methods) and refined using the Bruker SHELXTL version 6.1 Software Package using literature scattering factors (Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol.C.), and the orthorhombic space group P2(1)2(1)2(1), with \(Z = 4\). No absorption correction was applied. The final anisotropic full-matrix least-squares refinement of \(F^2\) converged at R1 = 4.89%, wR2 = 7.97% and a goodness-of-fit of 1.019. All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated distances. All hydrogen atoms use a riding model, which means that the positional and thermal parameters are derived from the atom each hydrogen atom is bound to, while maintaining the calculated or determined distance and optimal angles. The largest peak and hole in the final difference map were 0.279 and -0.321 e-/Å$^3$, respectively. The calculated density is 1.916 g/cm$^3$ and F(000) is 440 e-. Thermal ellipsoid drawings (15%) in this report were generated with the Bruker SHELXTL software.
Figure S14. (c) Dimer and (d) packing structures of compound 6
### Table 4 Parameter of bond length for compound 6

| Atoms 1,2     | \( d_{1,2} \) [Å] | Atoms 1,2     | \( d_{1,2} \) [Å] |
|---------------|---------------------|---------------|---------------------|
| C1—O1        | 1.319(5)            | C5—C6        | 1.441(5)            |
| C1—C2        | 1.382(6)            | C6—N3        | 1.416(5)            |
| C1—C6        | 1.416(6)            | N1—O4        | 1.242(4)            |
| C2—C3        | 1.372(5)            | N1—O3        | 1.266(4)            |
| C2—H2        | 0.9500              | N2—H2A       | 0.896(19)           |
| C3—O2        | 1.339(5)            | N2—H2B       | 0.861(19)           |
| C3—C4        | 1.415(6)            | N3—O5        | 1.247(4)            |
| C4—N1        | 1.419(5)            | N3—O6        | 1.253(4)            |
| C4—C5        | 1.439(6)            | O1—H1C       | 0.84(2)             |
| C5—N2        | 1.329(6)            | O2—H2C       | 0.824(19)           |

### Table 5 Angle parameters of crystal for compound 6

| Atoms 1,2,3   | Angle 1,2,3 [°] | Atoms 1,2,3   | Angle 1,2,3 [°] |
|---------------|-----------------|---------------|-----------------|
| O1—C1—C2     | 115.8(4)        | C1—C6—N3     | 119.0(4)        |
| O1—C1—C6     | 123.7(4)        | C1—C6—C5     | 120.8(4)        |
| C2—C1—C6     | 120.5(4)        | N3—C6—C5     | 120.2(4)        |
| C3—C2—C1     | 120.7(4)        | O4—N1—O3     | 119.0(3)        |
| C3—C2—H2     | 119.600         | O4—N1—C4     | 122.0(4)        |
| C1—C2—H2     | 119.600         | O3—N1—C4     | 119.0(4)        |
| O2—C3—C2     | 116.0(4)        | C5—N2—H2A    | 119.3(3)        |
| O2—C3—C4     | 123.1(4)        | C5—N2—H2B    | 113.3(3)        |
| C2—C3—C4     | 120.8(4)        | H2A—N2—H2B   | 128.4(4)        |
| C3—C4—N1     | 119.2(4)        | O5—N3—O6     | 119.3(4)        |
| C3—C4—C5     | 120.8(4)        | O5—N3—C6     | 121.2(4)        |
| N1—C4—C5     | 120.0(4)        | O6—N3—C6     | 119.5(4)        |
| Donor—Hydrogen...Acceptor | Don—Hyd [Å] | Hyd—Acc [Å] | Don—Acc [Å] | D—H—A    |
|---------------------------|--------------|-------------|-------------|---------|
| N2---H2B...O5             | 0.86         | 1.84        | 2.559       | 140.0°  |
| O1---H1C...O6             | 0.84         | 1.77        | 2.495       | 144.2°  |
| O2---H2C...O3             | 0.82         | 1.77        | 2.478       | 150.4°  |
X-ray Crystallographic Data for compound 7

The selected crystal was mounted with epoxy to the tip of a glass rod drawn out to a fiber. The X-ray intensity data for this colorless needle of C₆H₄N₂O₆ with approximate dimensions 0.21 x 0.17 x 0.14 mm were measured with phi and omega scans at 298 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (\(\lambda = 0.71073 \text{ Å}\)). The detector was placed at a distance of 5.00 cm from the crystal. A total of 1301 frames were collected (a hemisphere of data) with an exposure time of 30 sec/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm giving a total of 3929 reflections to a maximum 2\( \theta \) angle of 25.30° of which 1301 reflections were independent. The structure was solved (direct methods) and refined using the Bruker SHELXTL version 6.1 Software Package using literature scattering factors (Wilson, A. J. C., Ed. International Tables for Crystallography; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol.C.), and the orthorhombic space group Pca2(1), with Z = 4. No absorption correction was applied. The final anisotropic full-matrix least-squares refinement of F² converged at R1 = 4.54%, wR2 = 8.71% and a goodness-of-fit of 1.027. All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated distances. All hydrogen atoms use a riding model, which means that the positional and thermal parameters are derived from the atom each hydrogen atom is bound to, while maintaining the calculated or determined distance and optimal angles. The largest peak and hole in the final difference map were 0.381 and -0.242 e-/Å³, respectively. The calculated density is 1.824 g/cm³ and F(000) is 408e-. Thermal ellipsoid drawings (15%) in this report were generated with the Bruker SHELXTL software.
Figure 15 (e) Dimer and (f) packing structures of compound 7
| Atoms 1,2     | d 1,2 [Å] | Atoms 1,2     | d 1,2 [Å] |
|--------------|----------|--------------|----------|
| C1—O1        | 1.339(3) | C5—C6        | 1.380(3) |
| C1—C2        | 1.380(3) | C5—H5        | 0.9500   |
| C1—C6        | 1.417(4) | C6—N2        | 1.439(3) |
| C2—C3        | 1.375(4) | N1—O4        | 1.221(3) |
| C2—H2        | 0.9500   | N1—O3        | 1.243(3) |
| C3—O2        | 1.339(3) | N2—O5        | 1.222(3) |
| C3—C4        | 1.415(3) | N2—O6        | 1.245(3) |
| C4—C5        | 1.373(3) | O1—H1A       | 0.86(3)  |
| C4—N1        | 1.445(3) | O2—H2A       | 0.82(3)  |

| Atoms 1,2,3   | Angle 1,2,3 [°] | Atoms 1,2,3   | Angle 1,2,3 [°] |
|---------------|-----------------|---------------|-----------------|
| O1—C1—C2     | 116.9(2)        | C4—C5—H5     | 120.000         |
| O1—C1—C6     | 125.0(2)        | C6—C5—H5     | 120.000         |
| C2—C1—C6     | 118.0(2)        | C5—C6—C1     | 120.7(2)        |
| C3—C2—C1     | 122.3(2)        | C5—C6—N2     | 117.8(2)        |
| C3—C2—H2     | 118.900         | C1—C6—N2     | 121.5(2)        |
| C1—C2—H2     | 118.900         | O4—N1—O3     | 122.4(2)        |
| O2—C3—C2     | 117.3(2)        | O4—N1—C4     | 119.2(2)        |
| O2—C3—C4     | 124.2(2)        | O3—N1—C4     | 118.4(2)        |
| C2—C3—C4     | 118.5(2)        | O5—N2—O6     | 122.2(2)        |
| C5—C4—C3     | 120.5(2)        | O5—N2—C6     | 119.5(2)        |
| C5—C4—N1     | 118.0(2)        | O6—N2—C6     | 118.3(2)        |
| C3—C4—N1     | 121.5(2)        | C1—O1—H1A    | 106.3(18)        |
| Donor—Hydrogen...Acceptor | Don—Hyd [Å] | Hyd—Acc [Å] | Don—Acc [Å] | D—H———A |
|---------------------------|-------------|-------------|-------------|---------|
| O1—H1A...O6              | 0.86        | 1.86        | 2.610       | 144.8°  |
| O2—H2A...O3              | 0.82        | 1.87        | 2.594       | 148.2°  |

Table 9 Hydrogen bond parameter for compound 7
Computation details

Computations were carried out by using the Gaussian03 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies.

The gas phase heat of formation (HOF) (Table S6) was determined by using the method of isodesmic reactions. For the compounds reported here, the isodesmic reactions were carried out as Hakima Abou-Rachid did. The accuracy of the method was also proved by the HOF prediction, as shown in Table S6. According to the optimized structures, the total energy ($E_0$) and thermodynamic parameters, including zero point energy (ZPE) and thermal correction to enthalpy (HT), were obtained at the B3LYP/6-311+G** level. .298 K

$$3 \text{CH}_3\text{NO}_2 + \text{CH}_3\text{NH}_2 + 2\text{CH}_3\text{OH} \rightarrow \text{CH}_6\text{C}_6\text{N}_2\text{O}_2 + 6\text{CH}_4$$

Scheme1. Isodesmic reactions for compound 8

$A_{a}B_{b}C_{c}(g) \rightarrow aA(g) + bB(g) + cC(g)$

$$\Delta H_{298} = \sum \Delta_i H_P - \sum \Delta_i H_R$$

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

Table 10 Table Theoretical total energies, zero-point vibrational energies, thermal corrections for enthalpies and heat of formation (HOF) for 8 and the reference compounds

| compound | HF(KJ/mol) | zero-point(KJ/mol) | HT(KJ/mol) | HOF(KJ/mol) |
|----------|------------|-------------------|------------|-------------|
| 8        | -1051.83   | 335.62            | 41.76      | -285.13     |
| CH4      | -40.53     | 112.26            | 10.04      | -74.6       |
| CH3NO2   | -245.09    | 124.93            | 11.6       | -80.8       |
| CH3NH2   | -95.90     | 160.78            | 11.64      | -22.5       |
| benzene  | -232.31    | 252.53            | 14.44      | 82.93       |
| CH3OH    | -115.76    | 128.84            | 11.27      | -205.1      |
In addition, Detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet formula as

\[ P = 1.558 \rho^2 \Phi \]  \hspace{1cm} (1)

\[ D = 1.01 \Phi^{1/2} (1+1.30 \rho_0) \]  \hspace{1cm} (2)

\[ \Phi = 0.4889 N (MQ)^{1/2} \]  \hspace{1cm} (3)

Where D is the predicted detonation velocity (km/s) and P is the detonation pressure (GPa), \( \rho \) is the density of a compound (cm\(^3\)/mol). \( \Phi, N, M \) and \( Q \) are characteristic parameters of an explosive, \( Q \) is chemical energy of detonation (kJ/g). The crystal densities and the calculated heats of formation were used in computing the D and P values.

Table 11 Theoretical total energies, zero-point vibrational energies, thermal corrections for enthalpies and heat of formation 6-8

| Compound | \( E_0 \) (a.u.) | \( ZPE \) (kJ·mol\(^{-1}\)) | \( \Delta H_T \) (kJ·mol\(^{-1}\)) | \( HOF \) (kJ·mol\(^{-1}\)) |
|----------|-----------------|-----------------|-----------------|-----------------|
| 6        | -791.90         | 286.9           | 29.98           | -305.26         |
| 7        | -847.29         | 327.82          | 33.13           | -295.31         |
| 8        | -1051.83        | 335.62          | 41.76           | -285.13         |
Reference

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