Electronic Supplementary Information

Energetic salts based on 1-methoxy-5-nitroiminotetrazole

Young-Hyuk Joo,*† Jin Hyuk Chung,‡ Soo Gyeong Cho,‡ Eun Mee Goh‡

† Department of Energetic Materials & Pyrotechnics, Hanwha Corporation Defence R&D Center, Daejeon, 305-156 (Korea)
E-mail: joo2011@hanwha.co.kr

‡ Defense Advanced R&D Center, Agency for Defense Development, Daejeon, 305-600 (Korea)

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DSC, IR, $^1$H NMR, $^{13}$C NMR, $^{15}$N NMR Spectra

$^1$H NMR

NN
N=O

2

$^1$H NMR

$^{13}$C NMR

NN
N=O

2
$^1$H NMR

$^{13}$C NMR
DSC

Sample: GU-MNIT, 0.500 mg
Method: DSC, 100/10 K, AM01, Ar50
at 1.00 K
[1] 25.0-400.0 °C, 10.00 K/min, Ar 50.0 ml/min
synchronization enabled

Integral 800.07 mJ
Onset 176.92 °C
Peak 193.28 °C

5

H2N
NH2

H2N
NH2

\[ \begin{align*}
\text{Integral: } & -55.68 \text{ mJ} \\
\text{Onset: } & 174.51 ^\circ \text{C} \\
\text{Peak: } & 179.19 ^\circ \text{C}
\end{align*} \]

Hanwha: METTLER

IR

STAR+ SW 10.00
$^{1}H$ NMR

$^{13}C$ NMR
$^{15}\text{N} \text{ NMR}$

Sample Name:
Sample directory:
PrepRun: R15_ban_NMR
Pulse Sequence: zqfp
Spectra collected on: May 30 2012

**DSC**
IR

$^1$H NMR
**$^{13}$C NMR**

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**15N NMR**

Sample Name:  
Sample Directory:  
Pulse Sequence: apul  
Date collected: May 30 2012

**DSC**

Sample: DAG-MNIT, 1.5000 mg  
Method: D 25.0-400/10K, AMOx, 5x50  
dt 1.00 s  
1.25.0-400.0 °C, 10.00 K/min, Ar 50.0 ml/min  
Synchronization enabled  
Integral normalized  
Peak: 3441.95 MJmol⁻¹  
Onset: 183.60 °C  
Integral normalized  
Peak: -219.46 MJmol⁻¹  
Onset: 114.68 °C  

Hanwha: METTLER  
STAR® SW 10.00
15N NMR

DSC

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IR

\[ \text{IR spectrum image} \]

$^1$H NMR

\[ \text{NMR spectrum image} \]

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$^{13}$C NMR

Trisunquinodimine 1-methyl-2-nitroisothiazolate

$^{15}$N NMR

Agilent Technologies
DSC

Integral: 327.24 mJ
Normalized: 604.48 J/g
Onset: 151.28 °C
Peak: 155.87 °C

Sample: CH-MNIT, 0.5000 mg
Method: U CL-408/12K, A=MIX, A+MIX
dt 1.00 s
(I) 25.0, 400.0 °C, 10.00 K/min, At 50.0 mJ/min
Synchronization enabled

07.05.2012 19:00:10
CH-MNIT, 0.5000 mg

Hanwha: METTLER
STAR® SW 10.00

IR
15N NMR

DSC
IR

$^1$H NMR
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DSC

exo

D-4AT-MNIT

02.05.2012 16:15:29

Hanwha: METTLER

STAR® SW 10.00

1H NMR

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Electronic Supplementary Material (ESI) for New Journal of Chemistry
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DSC

- exo

Method: D 25-400/10K, AHDL, Ar<50
- d1.20 s
- 15.0.40K.0 °C, 10.00°K/min, Ar 55.0 mL/min
- Synchronization enabled
Sample: 3.5-OAT-MNT, 1.6000 mg
- 3.5-OAT-MNT, 07/05/2012 16:02:47
- 3.5-OAT-MNT, 1.6000 mg

Integral normalized
- 673.62 mJ
- 421.20 Jg⁻¹
Onset
- 160.80 °C
Peak
- 162.11 °C

Hanwha: METTLER

IR

[Graph showing IR spectroscopy data]
**1H NMR**

![1H NMR Spectrum]

**13C NMR**

![13C NMR Spectrum]
$^{15}$N NMR

Sample Name:

Data Collected on:

Agilent Technologies

Sample Concentration:

Matrix: DMSO

Pulse Sequence: aliph

Data collected on: May 31, 2013

![NMR Spectrum](image-url)
X-ray information

**Compound 5** (thermal displacement set at 50% probability)

**Compound 6** (thermal displacement set at 50% probability)
**Compound** (thermal displacement set at 50% probability)

![Diagram of Compound]

**Compound 9** (thermal displacement set at 50% probability)

![Diagram of Compound 9]

**Compound 10** (thermal displacement set at 50% probability)

![Diagram of Compound 10]
Compound 11 (thermal displacement set at 50% probability)
Computation information

Theoretical study. Calculations were carried out by using the Gaussian 03 (Revision D.01) suite of programs. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without having imaginary frequencies.

\[
\Delta H_f^\circ (\text{ionic salt, 298 K}) = \Delta H_f^\circ (\text{cation, 298 K}) + \Delta H_f^\circ (\text{anion, 298 K}) - \Delta H_L
\]

(1)

where \( \Delta H_L \) is the lattice energy of the ionic salt. The \( \Delta H_L \) value could be predicted by the formula suggested by Jenkins et al. [Equation (2)], where \( U_{\text{POT}} \) is the lattice potential energy and \( n_M \) and \( n_X \) depend on the nature of the ions \( M_p^+ \) and \( X_q^- \), respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

(2)

The equation for the lattice potential energy, \( U_{\text{POT}} \), takes the form of Equation (3),

Figure S1. Born-Haber cycle for the formation of 1-methoxy-5-nitroiminotetrazole salts.

Based on Born-Haber energy cycles, heats of formation of ionic salts can be simplified by the formula [Eq. (1)]:

\[
\Delta H_f^\circ (\text{ionic salt, 298 K}) = \Delta H_f^\circ (\text{cation, 298 K}) + \Delta H_f^\circ (\text{anion, 298 K}) - \Delta H_L
\]

(1)
\[ U_{\text{POT}} \text{ (kJ mol}^{-1} \text{)} = \gamma (\rho_{m}/M_{m})^{1/3} + \delta \]

(3)

where \( \rho_{m} \) is the density (g cm\(^{-3} \)), \( M_{m} \) is the chemical formula mass of the ionic material (g), and the coefficients \( \gamma \) (kJ mol\(^{-1} \) cm) and \( \delta \) (kJ mol\(^{-1} \)) are assigned literature values.\(^{[15]} \)

\[ \begin{array}{c}
\text{O} \quad \text{N} \quad \text{N}^+ \quad \text{NO}_2 \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\end{array} \]

\[ + \quad 2 \text{NH}_3 \quad \longrightarrow \quad \begin{array}{c}
\text{HN} \quad \text{N}^+ \quad \text{NH} \\
\text{N} = \text{N}
\end{array} \quad + \quad \text{H}_3\text{C} = \text{O} \quad \text{NH}_2 \quad + \quad \text{H}_2\text{N} \quad \text{NO}_2
\]

Scheme S1. Isodesmic reaction of 1-methoxy-nitroiminotetrazolate anion

Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E\(_0\)), Zero Point Energy (ZPE), Values of Thermal correction (H\(_T\)), and Heats of Formation (HoF) [kJ/mol] of the compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E(_0) (kJ/mol)</th>
<th>ZPE (kJ/mol)</th>
<th>H(_T) (kJ/mol)</th>
<th>HoF (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O} \quad \text{N} \quad \text{N}^+ \quad \text{NO}_2 )</td>
<td>-630.6396716</td>
<td>0.01035</td>
<td>0.01260</td>
<td>315.92</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} \quad \text{NH}_2 )</td>
<td>-204.8735031</td>
<td>0.075945</td>
<td>0.005496</td>
<td>26.0</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} \quad \text{NH} )</td>
<td>-260.5457263</td>
<td>0.114876</td>
<td>0.006227</td>
<td>566.7</td>
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<tr>
<td>( \text{H}_2\text{N} \quad \text{N}^+ \quad \text{NH} )</td>
<td>-315.7583524</td>
<td>0.13361</td>
<td>0.007123</td>
<td>769.0176204</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} \quad \text{N}^+ \quad \text{NH}_2 )</td>
<td>-370.9707208</td>
<td>0.152308</td>
<td>0.008131</td>
<td>871.4723014</td>
</tr>
</tbody>
</table>
References
