Electronic Supplementary Material


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1. Spectra of 3 and 4 .................................................................3
2. X-Ray Diffraction ...............................................................7
3. Heat of formation ...............................................................8
4. Sensitivity ...........................................................................8
1. Spectra of 3 and 4

**Fig. S1** mass spectrum of 3

**Fig. S2** mass spectrum of 4
Fig. S3 1H NMR spectrum of 3 (DMSO-d6).

Fig. S4 1H NMR spectrum of 4 (acetone-d6).
Fig. S5 13C NMR spectrum of 3 (acetone-d6).

Fig. S6 13C NMR spectrum of 4 (acetone-d6).
**Fig. S7** IR spectrum of 3

**Fig. S8** IR spectrum of 4
2. X-Ray Diffraction
The single crystals of 1 and 2 were mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å). Data were collected by the ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined with theoretical calculations and refined with an isotropic vibration factor.

3. Heat of formation

\[
\text{Scheme S1 isodesmic reactions of 3 and 4.}
\]

For the isodesmic reactions, heat of reaction ($\Delta H_{298K}$) can be calculated according to the following equation:

\[
\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R}
\]

Where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the heats of formation for reactants and products at 298.15K, respectively. At the same time, $\Delta H_{298K}$ can be also obtained from the following expression:

\[
\Delta H_{298K} = \Delta E_{298K} - \Delta(PV)
\]

\[
= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta(nRT)
\]

Where $\Delta E_0$ is the change in total energy between the products and the reactants at 0 K; $\Delta ZPE$ is the difference between the zero-point energies of the products and the reactants; $\Delta H_T$ is thermal correction from 0K to 298.15K. Consequently, the heat of formation can be worked out by using $\Delta H_{298}$ and heats of formation of other reactants and products. The data in needed can be obtained from literatures and handbooks.

Table S1 The gas-phase heat of formation (HOF) of title compounds.

<table>
<thead>
<tr>
<th></th>
<th>toluene</th>
<th>TNT</th>
<th>Ph-NO=N-Ph</th>
<th>H$_2$N-NO$_2$</th>
<th>3</th>
<th>4</th>
<th>Ph</th>
<th>Ph-NO$_2$</th>
<th>Ph-NH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_0 + \Delta ZPE$</td>
<td>-271.43</td>
<td>-884.89</td>
<td>-647.73</td>
<td>-260.98</td>
<td>-1049.59</td>
<td>-1069.48</td>
<td>-232.14</td>
<td>-436.63</td>
<td>-287.47</td>
</tr>
<tr>
<td>HOF(g) /kJ mol$^{-1}$</td>
<td>50.1</td>
<td>-80.5</td>
<td>342</td>
<td>342</td>
<td>537.5</td>
<td>168.1</td>
<td>82.9</td>
<td>68.53</td>
<td>87.03</td>
</tr>
</tbody>
</table>

\[
\Delta H(\text{Solid}) = \Delta H(\text{Gas}) - \Delta H(\text{Sublimation})
\]

\[
\Delta H(\text{Sublimation}) = a(SA)^2 + b \sqrt{\sigma_{tot}^2} + c
\]
Table S2 heats of sublimation and their calculating parameters.

<table>
<thead>
<tr>
<th></th>
<th>SA/Å²</th>
<th>$\sigma^2$/(kcal•mol)$^2$</th>
<th>$\nu$</th>
<th>H(S)/kJ•mol$^{-1}$</th>
<th>HOF(S)/kJ•mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>263.39</td>
<td>99.88</td>
<td>0.2128</td>
<td>121.80</td>
<td>415.70</td>
</tr>
<tr>
<td>4</td>
<td>251.64</td>
<td>108.26</td>
<td>0.1691</td>
<td>112.74</td>
<td>55.35</td>
</tr>
</tbody>
</table>

4. 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. RDX was considered as a reference compound, the impact sensitivity of RDX is 7 J.

The friction sensitivity was tested on a FSKM 50/20K apparatus produced by OZM Research. The sample was placed between the porcelain plate and peg. The weight of leading at least one ignition in six times was recorded. Tested results for 3 and 4 are 120 N and 160 N respectively.